Supplemental Information for

Mono-telechelic Polymers by Catalytic Living Ring-Opening Metathesis Polymerization with Second-Generation Hoveyda–Grubbs Catalyst

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General information

Materials

Celite, ethyl vinyl ether, Hoveyda-Grubbs 2nd generation catalyst, chlorotriisopropylsilane, imidazole, triethyl amine, CuI and *N*-Boc-ethanolamine were purchased from Sigma-Aldrich and used without further purification. DIBAL-H in hexane, *N*-Bromosuccinimide, cyclohexene, cyclopentene, cyclopropylacetylene, 2-methylfuran, 3-chloropyridine, *N*-methylmaleimide and *endo*-5-norbornene-2,3-dicarboxylic anhydride were purchased from Acros Organics and used without further purification. *trans*-3-Hexenedioic acid were purchased from TCI. *cis*-4-Octene was purchased from Alfa Aesar. Solvents of analytical grade were purchased from Honeywell, Acros Organics, Sigma Aldrich, Fischer Scientific and were used without further purification. Dichloromethane for reactions was dried in P_2O_5 overnight and purified by distillation under Ar and degassed under Ar. Deuterated solvents (CD_2Cl_2, $CDCl_3$) were purchased from Cambridge Isotope Laboratories Inc. Grubbs 3rd generation catalyst was prepared from Grubbs 2nd generation catalyst which was dissolved in a large excess of 3-bromopyridine, precipitated in n-pentane and then dried under high vacuum. All monomers (**MNI**, **PNI**, **OMNI**, **MOMNI**, **NBSM**), **CTAs** (**CTA 1** and **CTA2**) and **SCTAs** (**SCTA 1**, **SCTA 2, SCTA 3** and **SCTA 4**) were synthesized according to the literature[1,2,3].

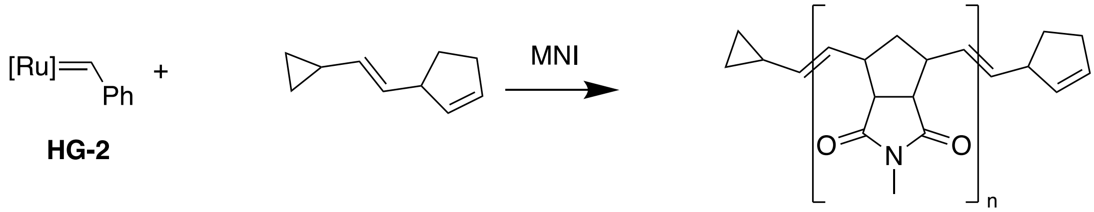
Instrumentation

ESI-MS analysis for synthesized compounds was carried out on a Bruker 4.7T BioAPEX II. GC-MS analysis for synthesized compounds was carried out on a Thermo Scientific Trace GC Ultra DSQ II system with Zebron capillary GC column (ZB-5MS 0.25 µm, 30m×0.25mm). MALDI-ToF MS analysis of the polymers was carried out on a Bruker ultrafleXtreme™ using 2-(*2E*)-3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix and silver trifluoroacetate or sodium trifluoroacetate as the added salt. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) with an Agilent Technologies 1260 Infinity II GPC system (pump, autosample, RI detector) and two MZ-Gel SDplus Linear columns (5 µm, 300×8.0mm), a MZ-Gel SDplus Linear precolumn (5 µm, 50×8.0mm) at a flow rate of 1mL/min for samples measured in $CHCl_3$. Calibrations were carried out using PSS-polymer polystyrene standards. NMR spectra were recorded on a Bruker Avance III 300 MHz NMR spectrometer (^{1}H NMR 300 MHz, ^{13}C-NMR 75 MHz) or Bruker Avance III 400 MHz NMR spectrometer (^{1}H NMR 400 MHz, ^{13}C-NMR 101 MHz). Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/DSC

1 STAR system under nitrogen up to 700°C with a heating rate of 10 °C/min. The reported degradation temperature (T_d) was taken at the degradation onset. Differential scanning calorimetry (DSC) was conducted on a Mettler Toledo DSC 2 STAR system under nitrogen up to 300°C with a heating and cooling rate of 20 °C/min. The data was taken from the second heating cycle and the glass transition temperature (T_g) was taken from the middle point of the tangent onset.

Polymerisations

Different Mn



HG2 (1.2mg, 0.001875mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA 1** which was dissolved in degassed DCM (1.0ml). To this solution, **MNI** (266mg, 1.5mmol, 800eq) which was dissolved in degassed DCM (0.3mmol/ml) was added at a speed of 0.83 ml/h by syringe pump (the needle, Ø = 0.5mm, was inserted into reaction solution). After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The reaction solution was precipitated into cold hexane (50ml) to give the polymer.

Table S1 Catalytic Living ROMP of Different Molecular Weight

Entry	Eq. CTA	Eq. MNI	Conc. of MNI mmol/ml	Speed ml/h	Mn Ther. g/mol	Mn Exp. g/mol	Đ	Yield%
1	20 (5.0mg)	800	0.3	1.0	7214	24000	1.25	96
2[a]	20 (5.0mg)	800	0.3	1.0	7214	12400	1.36	95
3	10 (2.5mg)	800	0.3	0.83	14294	15300	1.36	95
4	20 (5.0mg)	800	0.3	0.83	7214	7500	1.39	93
5	40 (10.1mg)	800	0.3	0.83	3674	4000	1.43	90
6	60 (15.1mg)	800	0.3	0.83	2494	3000	1.44	92
7	100 (25.2mg)	800	0.3	0.83	1550	2000	1.47	90

[a] 3-chloropyridine (1.2mg, 0.0105mmol, 5eq.) was added in the reaction solution.

Polymer 1 (Table S1, Entry 1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.69-5.75 (m), 5.43-5.55 (m), 5.04-5.16 (m), 2.63-3.43 (m), 1.96-2.26 (m), 1.38-1.70 (m), 0.63-0.72 (m), 0.34-0.40 (m). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.37, 133.45, 132.68, 131.93, 52.99, 52.60, 51.11, 50.99, 45.63, 40.85, 34.12, 24.85, 24.78, 22.33, 14.07. The molecular weight is too high to be detected in MALDI-ToF mass.

Polymer 2 (Table S1, Entry 2)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.69-5.75 (m), 5.43-5.55 (m), 5.05-5.16 (m), 2.63-3.43 (m), 1.96-2.26 (m), 1.38-1.70 (m), 0.63-0.73 (m), 0.33-0.39 (m). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.38, 133.57, 133.48, 132.64, 131.88, 131.68, 52.99, 52.62, 51.12, 50.98, 45.64, 41.46, 40.86, 34.12, 24.90, 24.85, 24.79, 22.34, 14.07. The molecular weight is too high to be detected in MALDI-ToF.

Polymer 3 (Table S1, Entry 3)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.69-5.76 (m), 5.44-5.54 (m), 5.07-5.14 (m), 2.66-3.35 (m), 1.96-2.29 (m), 1.56-1.77 (m), 0.61-0.73 (m), 0.32-0.39 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.36, 133.47, 132.68, 131.88, 131.84, 131.62, 53.44, 53.00, 52.64, 51.85, 51.12, 50.99, 46.20, 45.99, 45.82, 45.63, 43.01, 42.50, 42.02, 41.46, 40.86, 24.89, 24.84, 24.77, 13.62. The molecular weight is too high to be detected in MALDI-ToF.

Polymer 4 (Table S1, Entry 4)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.68-5.78 (m), 5.44-5.58 (m), 5.07-5.15 (m), 2.62-3.33 (m), 1.98-2.35 (m), 1.42-1.71 (m), 0.67-0.73 (m), 0.33-0.40 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.35, 133.52, 131.85, 131.69,53.02, 52.68, 51.12, 51.00, 46.06, 45.69, 42.78, 42.01, 41.46, 40.87, 24.89, 24.77, 13.63. MALDI-ToF MS calcd. For $C_{200}H_{223}N_{19}O_{38}Ag^+$ [M+Ag$^+$]: 3605.51; Found: 3605.52

Polymer 5 (Table S1, Entry 5)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.67-5.78 (m), 5.44-5.63 (m), 5.08-5.15 (m), 2.63-3.34 (m), 1.97-2.33 (m), 1.44-1.74 (m), 0.68-0.70 (m), 0.33-0.38 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.34, 135.57, 133.49, 132.05, 53.01, 52.65, 51.85, 51.01, 48.24, 46.25, 46.05, 45.61, 42.47, 41.98, 41.47, 41.22, 40.86, 32.09, 30.64, 24.84, 24.77, 13.62. MALDI-ToF MS calcd. For $C_{140}H_{157}N_{13}O_{26}Na^+$ [M+Ag$^+$]: 2459.13; Found: 2459.18

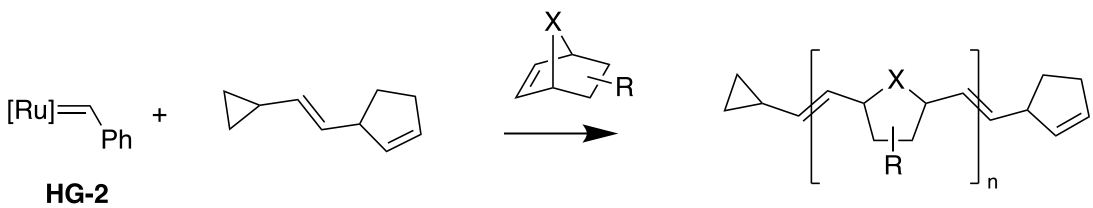
Polymer 6 (Table S1, Entry 6)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.68-5.78 (m), 5.44-5.63 (m), 5.08-5.15 (m), 2.59-3.33 (m), 1.98-2.36 (m), 1.34-1.71 (m), 0.69-0.71 (m), 0.36-0.38 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.34, 178.28, 135.57, 133.51, 132.74, 131.92, 131.46, 53.02, 52.67, 51.86, 51.15, 48.24, 46.25, 45.68, 42.41, 40.86, 32.11, 30.65, 24.84, 13.63. MALDI-ToF MS calcd. For $C_{120}H_{135}N_{11}O_{22}Ag^+$ [M+Ag$^+$]: 2188.88; Found: 2188.87

Polymer 7 (Table S1, Entry 7)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.68-5.79 (m), 5.44-5.64 (m), 5.08-5.15 (m), 2.60-3.31 (m), 1.98-2.37 (m), 1.45-1.69 (m), 0.69-0.71 (m), 0.36-0.38 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.34, 135.57, 133.52, 131.70, 53.00, 52.67, 51.02, 48.26, 46.05, 45.61, 42.48, 40.83, 32.11, 30.65, 24.77, 24.73, 13.63. MALDI-ToF MS calcd. For $C_{190}H_{212}N_{18}O_{36}Ag^+$ [M+Ag$^+$]: 3428.44; Found: 3428.45

Different Monomers



HG-2 (3.2mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1ml) was added, followed by addition of **CTA 1** (6.7mg, 0.05mmol, 10eq) which was dissolved in degassed DCM (1.0ml). To this solution monomer, which was dissolved in degassed DCM (0.3mmol/ml) was added at a speed of 0.83ml/h by syringe pump (the needle, Ø = 0.5mm, was inserted into reaction solution). After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The reaction solution obtained was precipitated into cold hexane (50ml) to give the polymer.

Table S2 Catalytic Living ROMP of Different Monomers

Entry	Monomer	Eq. CTA	Eq. Monomer	Mn Ther. g/mol	Mn Exp. g/mol	Đ	Speed ml/h	Yield%
1	**MNI** (266mg)	10	300	5444	7300	1.33	0.83	93
2	**PNI** (359mg)	10	300	7314	11000	1.25	0.83	97
3	**OMNI** (269mg)	10	300	5504	9900	1.73	0.83	90
4[a]	**NBSM** (280mg)	10	120	5734	3800	1.75	0.83	85
5[b]	**NBSM** (280mg)	10	120	5734	3300	1.74	0.83	83
6[c]	**MOMNI** (290mg)	10	300	5924	5100	1.80	One-pot	85

[a] The polymer was precipitated in 50ml cold methanol. [b] 3-chloropyridine (5.7mg, 0.05mmol, 10eq.) was added in the reaction solution. The polymer was precipitated in 50ml cold methanol. [c] **HG2** and **CTA 1** were mixed together in 2ml degassed DCM, then **MOMNI** (in 5ml degassed DCM) was added in one shot under Ar. The solution was kept stirring overnight.

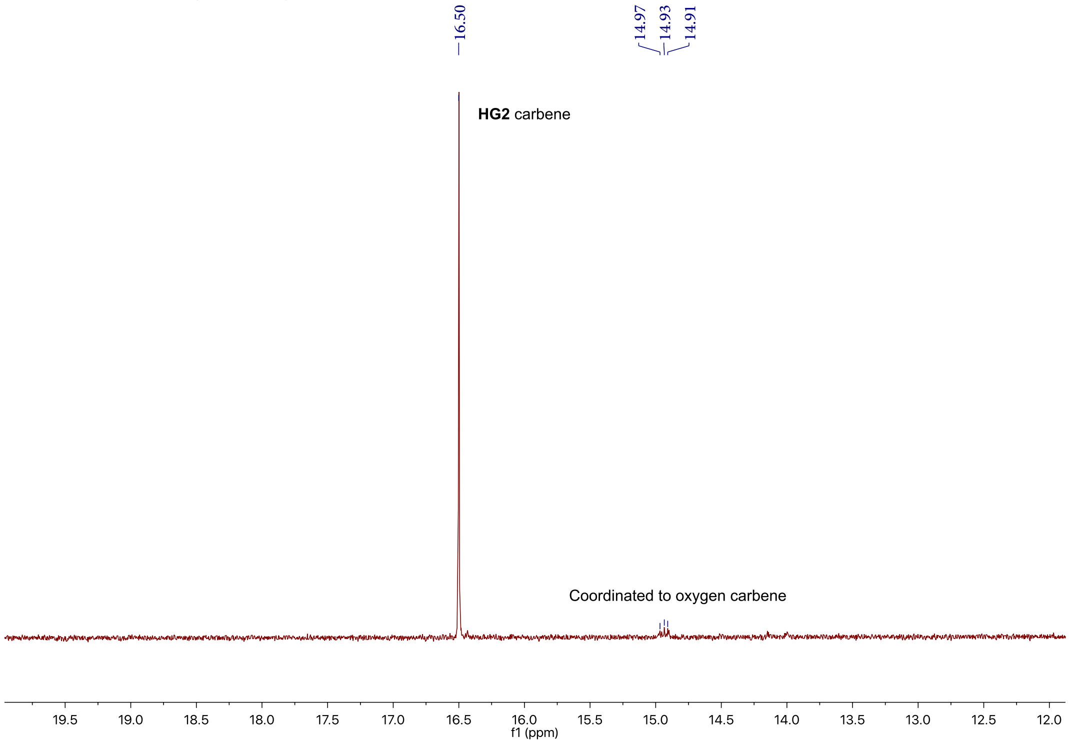


Fig. S1. ^{1}H NMR reaction of **HG2** and **MOMNI**. **HG2** (3.2mg, 0.005mmol, 1.0eq.) was dissolved in 0.75ml degassed CD_2Cl_2 under Ar, then **MOMNI** (54mg, 0.28mmol, 56eq.) was added into the solution. The ^{1}H NMR was measured in 10min.

Polymer 8 (Table S2, Entry 1)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.68-5.78 (m), 5.44-5.62 (m), 5.08-5.15 (m), 2.64-3.31 (m), 1.99-2.29 (m), 1.48-1.76 (m), 0.69-0.71 (m), 0.35-0.38 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.35, 135.57, 133.49, 132.04, 131.87, 53.03, 52.67, 51.00, 45.72, 45.69, 42.48, 41.23, 40.87, 24.84, 24.77, 13.63. MALDI-ToF MS calcd. For $C_{220}H_{245}N_{21}O_{42}Ag^{+}$ [M+Ag^{+}]: 3959.67; Found: 3959.68

Polymer 9 (Table S2, Entry 2)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17-7.46 (m), 5.70-5.83 (m), 5.47-5.65 (m), 5.10-5.18 (m), 2.78-3.53 (m), 2.09-2.36 (m), 1.38-1.73 (m), 0.69-0.71 (m), 0.36-0.38 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.26, 177.15, 133.91, 132.00, 129.07, 128.93, 128.35, 126.71, 126.43, 99.99, 53.06, 52.81, 51.95, 51.11, 46.16, 43.64, 42.82, 42.47, 41.58, 41.01, 13.65. The molecular weight is too high to be detected in MALDI-ToF mass.

Polymer 10 (Table S2, Entry 3)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.00-6.10 (m), 5.59-5.81 (m), 5.32-5.41 (m), 4.92-5.03 (m), 4.29-4.56 (m), 3.23-3.39 (m), 2.79-3.01 (m), 1.53-1.74 (m), 0.74-0.76 (m), 0.43-0.45 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.84, 175.65, 131.99, 131.45, 130.99, 81.00, 80.89, 53.49, 52.44, 52.21, 25.12, 25.09. MALDI-ToF MS calcd. For $C_{100}H_{104}N_{10}O_{30}Ag^{+}$ [M+Ag^{+}]: 2031.60; Found: 2031.62

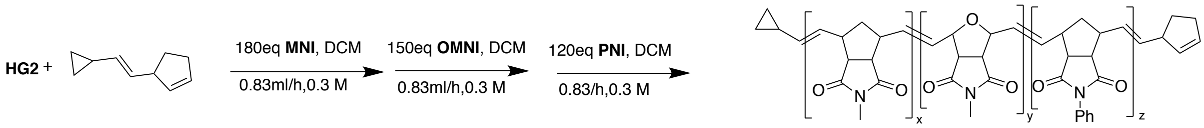
Polymer 11 (Table S1, Entry 4)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.27-5.75 (m), 4.87-4.96 (m), 3.72-3.88 (m), 2.94-3.00 (m), 2.61-2.69 (m), 2.10-2.39 (m), 1.83-1.93 (m), 1.46-1.63 (m), 0.88-1.08 (m), 0.61-0.63 (m), 0.27-0.29 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.35, 132.16, 131.63, 130.70, 63.43, 61.99, 61.83, 50.89, 49.04, 48.78, 48.06, 45.56, 44.59, 38.60, 30.93, 18.16, 18.06, 12.10. MALDI-ToF MS calcd. For $C_{172}H_{338}O_{22}Si_{12}Ag^{+}$ [M+Ag^{+}]: 3039.21; Found: 3039.20

Polymer 12 (Table S1, Entry 6)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.89-6.11 (m), 5.46-5.80 (m), 5.23-5.29 (m), 4.48-4.71 (m), 3.26-3.54 (m), 2.94-2.98 (m), 1.63-1.70 (m), 1.25-1.39 (m), 0.70-0.73 (m), 0.37-0.40 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.41, 175.15, 140.52, 138.14, 136.91, 128.03, 83.97, 80.59, 79.14, 54.71, 52.96, 50.69, 49.49, 24.99, 22.33, 15.63. MALDI-ToF MS calcd. For $C_{100}H_{113}N_9O_{27}Ag^+$ [M+Ag$^+$]: 1978.68; Found: 1978.70

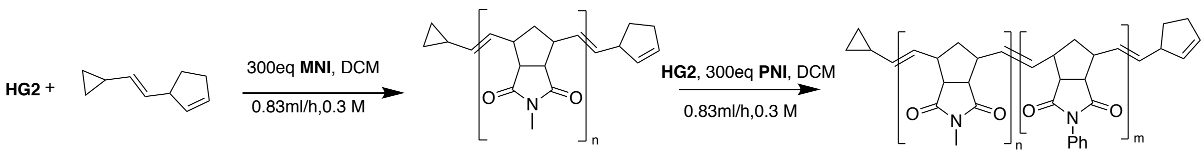
Synthesis of block copolymers



HG2 (3.2mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1.0ml) was added, followed by addition of **CTA 1** (6.7mg, 0.05mmol, 10eq) which was dissolved in degassed DCM (1.0ml). To this solution **MNI** (160 mg, 0.9mmol, 180eq.) which was dissolved in degassed DCM (3ml, 0.3mmol/ml) was added at a speed of 0.83ml/h by syringe pump. After complete addition, **OMNI** (135 mg, 0.75mmol, 150eq.) which was dissolved in degassed DCM (2.5ml, 0.3mmol/ml) was added at a speed of 0.83ml/h by syringe pump. After complete addition, **PNI** (144 mg, 0.6mmol, 120eq.) which was dissolved in degassed DCM (2ml, 0.3mmol/ml) was added at a speed of 0.83ml/h by syringe pump. After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The reaction solution obtained was precipitated into cold hexane (50ml) to give 421 mg of **polymer 13** (PolyMNI-*b*-PolyOMNI-*b*-PolyPNI). Yield: 96%.

Polymer 13

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.19-7.47 (m), 5.97-6.10 (m), 5.68-5.82 (m), 5.45-5.64 (m), 5.06-5.16 (m), 4.93-5.02 (m), 1.37-4.56 (m), 2.65-3.54 (m), 1.98-2.31 (m), 1.47-1.72 (m), 0.68-0.72 (m), 0.35-0.38 (m). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.37, 177.18, 175.74, 133.53, 131.82, 129.08, 128.94, 126.71, 126.39, 81.01, 77.46, 53.47, 52.66, 51.12, 46.20, 45.59, 42.76, 42.48, 41.93, 41.48, 25.17, 25.13, 24.86. MALDI-ToF MS can not be detected due to the too high molecular weight. PolyMNI: $M_{n\ GPC}$ ($CHCl_3$) = 3500 g mol^{-1}, Đ = 1.33, PolyMNI-*b*-PolyOMNI: $M_{n\ GPC}$ ($CHCl_3$) = 7500 g mol^{-1}, Đ = 1.56, PolyMNI-*b*-PolyOMNI-*b*-PolyPNI: $M_{n\ GPC}$ ($CHCl_3$) = 13000 g mol^{-1}, Đ = 1.52. T_d = 336 °C*,* T_g = 204 °C.



HG2 (3.2mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1.0ml) was added, followed by addition of **CTA 1** (6.7mg, 0.05mmol, 10eq) which was

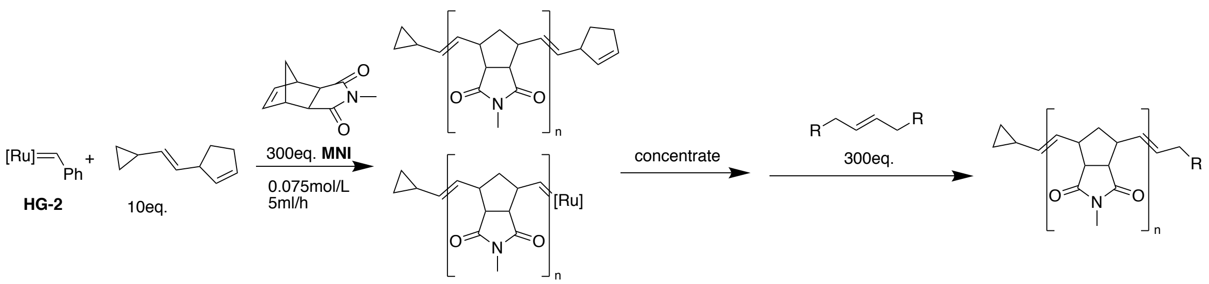
dissolved in degassed DCM (1.0ml) was added under Ar. To this solution **MNI** (266 mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (5ml, 0.3mmol/ml) was added at a speed of 0.83ml/h by syringe pump. After complete addition, the reaction solution obtained was precipitated into cold hexane (50ml) to give **polymer 8**.

HG2 (3.2mg, 0.005mmol,1.0eq) and **polymer 8** (all from last step, except 20mg was taken for analysis) were dissolved in degassed DCM (2ml) under Ar. To this solution, **PNI** (360 mg, 1.5mmol, 300eq) which was dissolved in degassed DCM (5ml, 0.3mmol/ml) was added at a speed of 0.83ml/h by syringe pump. After complete addition, vinyl ether (0.5ml) was added to terminate the reaction. The reaction solution obtained was precipitated into cold hexane (50ml) to give 614mg of **polymer 14** (PolyMNI-*b*-PolyPNI). Yield: 98%.

Polymer 14

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18-7.47 (m), 5.70-5.80 (m), 5.45-5.59 (m), 5.06-5.16 (m), 2.66-3.52 (m), 2.01-2.32 (m), 1.47-1.82 (m), 0.68-0.71 (m), 0.35-0.38 (m).^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.38, 177.59, 177.14, 176.90, 135.71, 133.91, 133.54, 132.05, 131.81, 128.94, 128.31, 126.71, 126.43, 53.04, 53.00, 52.61, 51.10, 46.64, 46.18, 45.68, 45.61, 42.80, 42.53, 40.88, 24.92, 24.80, 14.09. MALDI-ToF MS cannot be detected due to the too high molecular weight. $M_{n\ GPC}$ ($CHCl_3$) = 21000 g mol^{-1}, Đ = 1.47. T_d = 370 °C, T_g = 210 °C.

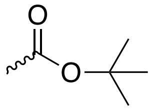
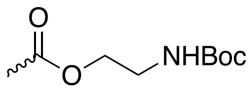
Different End-groups



HG2 (3.2mg, 0.005mmol,1.0eq) was added into a Schlenk flask under Ar, then degassed DCM (1.0ml) was added, followed by addition of **CTA** (0.05mmol, 10eq) which was dissolved in degassed DCM (1.0ml). To this solution, **MNI** (266mg, 1.5mmol, 300eq) which was dissolved in 20ml degassed DCM (0.075mmol/ml) was added at a speed of 5 ml/h by syringe pump. After complete addition, the **SCTA** was added in 2ml degassed DCM under Ar. Then the solvent was evaporated to around 2ml and kept stirring overnight. Vinyl ether (0.5ml) was added to terminate the reaction. The solution obtained was precipitated into cold hexane(50ml) to give the polymer. The polymers were dialyzed against DMSO using dialysis membrane

(MWCO:3500D) overnight to remove the excess **SCTAs**. The final polymer was obtained by precipitation in cold hexane.

Table S3 Catalytic Living ROMP of end-groups

Entry	R	Eq. CTA	Mn Ther. g/mol	Mn Exp. g/mol	Đ	Speed ml/h	Yield%
1	-Ethyl	10	5420	7600	1.44	5.0	90
2		10	5492	6900	1.35	5.0	93
3[a]		10	5578	5500	1.29	5.0	95
4[a]		10	5579	6800	1.27	5.0	97

[a] (*E*)-3-(2-cyclopentylvinyl)cyclopent-1-ene (**CTA2**) was used as CTA instead of (*E*)-3-(2-cyclopropylvinyl)cyclopent-1-ene (**CTA1**) to increase the steric hindrance to avoid the formation of homo-telechelic polymers.

Polymer 15 (Table S3, Entry 1)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.68-5.82 (m), 5.37-5.62 (m), 5.06-5.16 (m), 2.64-3.31 (m), 1.94-2.30 (m), 1.48-1.72 (m), 1.18-1.43 (m), 0.82-0.85 (m), 0.68-0.71 (m), 0.35-0.38 (m). ^{13}C NMR (75 MHz, Chloroform-*d*) δ178.33, 133.19, 132.20, 130.21, 52.99, 52.65, 51.11, 51.00, 45.67, 41.92, 40.97, 24.85, 24.78, 13.65. MALDI-ToF MS calcd. For $C_{208}H_{234}N_{20}O_{40}Ag^+$ [M+Ag$^+$]: 3758.59; Found: 3758.28

Polymer 16 (Table S3, Entry 2)

^{1}H NMR (400 MHz, Chloroform-d) δ 5.67-5.77 (m), 5.61-5.65 (m), 5.46-5.55 (m), 5.05-5.17 (m), 2.62-3.30 (m), 1.98-2.29 (m), 1.38-1.70 (m), 1.22-1.79 (m), 0.68-0.71 (m), 0.35-0.39 (m). ^{13}C NMR (75 MHz, Chloroform-d) δ 178.34, 171.05, 133.46, 131.85, 126.05, 53.01, 52.65, 51.84, 51.12, 51.00, 45.64, 40.87, 39.14, 28.08, 24.85, 24.78. MALDI-ToF MS calcd. For $C_{157}H_{175}N_{15}O_{32}Ag^+$ [M-C_4H_9+H+Ag$^+$]: 2889.16; Found: 2889.05

Polymer 17 (Table S3, Entry 3)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.66-5.76 (m), 5.40-5.59 (m), 5.19-5.29 (m), 3.57-3.70 (m), 2.61-3.29 (m), 1.97-2.30 (m), 1.68-1.46 (m), 0.95-1.06 (m), 0.80-0.82 (m). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.36, 136.42, 133.46, 132.02, 131.86, 130.57, 128.59, 127.91, 63.45, 63.17, 52.97, 52.62, 51.82, 50.98, 16.17, 45.61, 43.08, 42.47, 41.46, 40.85, 36.51. 33.03, 24.83, 18.00, 17.71, 12.29, 11.99. MALDI-ToF MS calcd. For $C_{208}H_{245}N_{19}O_{39}SiAg^{+}$ [M+Ag⁺]: 3767.66; Found: 3767.68

Polymer 18 (Table S3, Entry 4)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.69-5.76 (m), 5.45-5.55 (m), 4.13-4.16 (m), 2.88-3.39 (m), 2.61-2.78 (m), 2.036-2.29 (m), 1.44-1.72 (m). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.36, 171.43, 133.48, 132.69, 131.83, 131.71, 64.01, 52.66, 51.78, 51.15, 46.29, 45.62, 40.98, 37.62, 33.20, 33.05, 28.38, 24.89. MALDI-ToF MS cannot be detected.

Copies of NMR Spectra

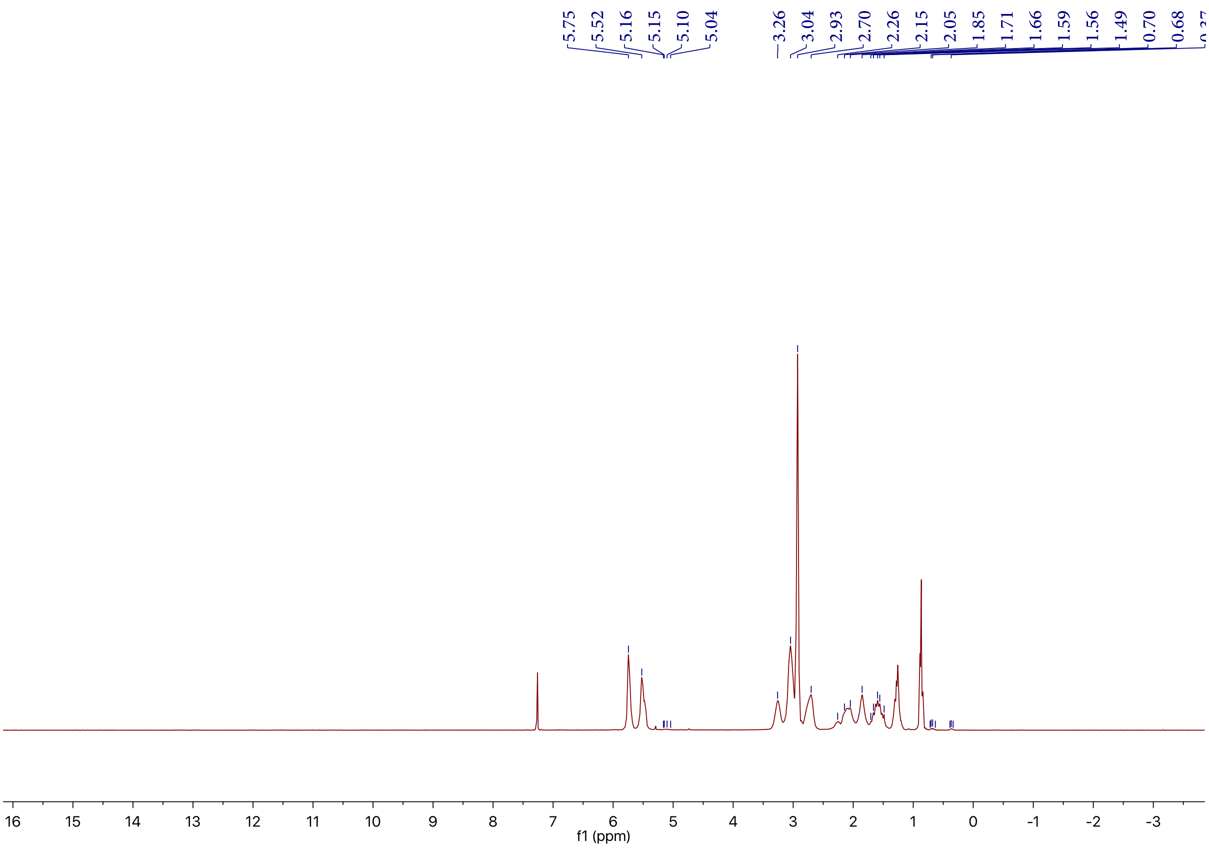


Figure S2 ^{1}H NMR spectrum (300MHz, $CDCl_3$) of Polymer 1

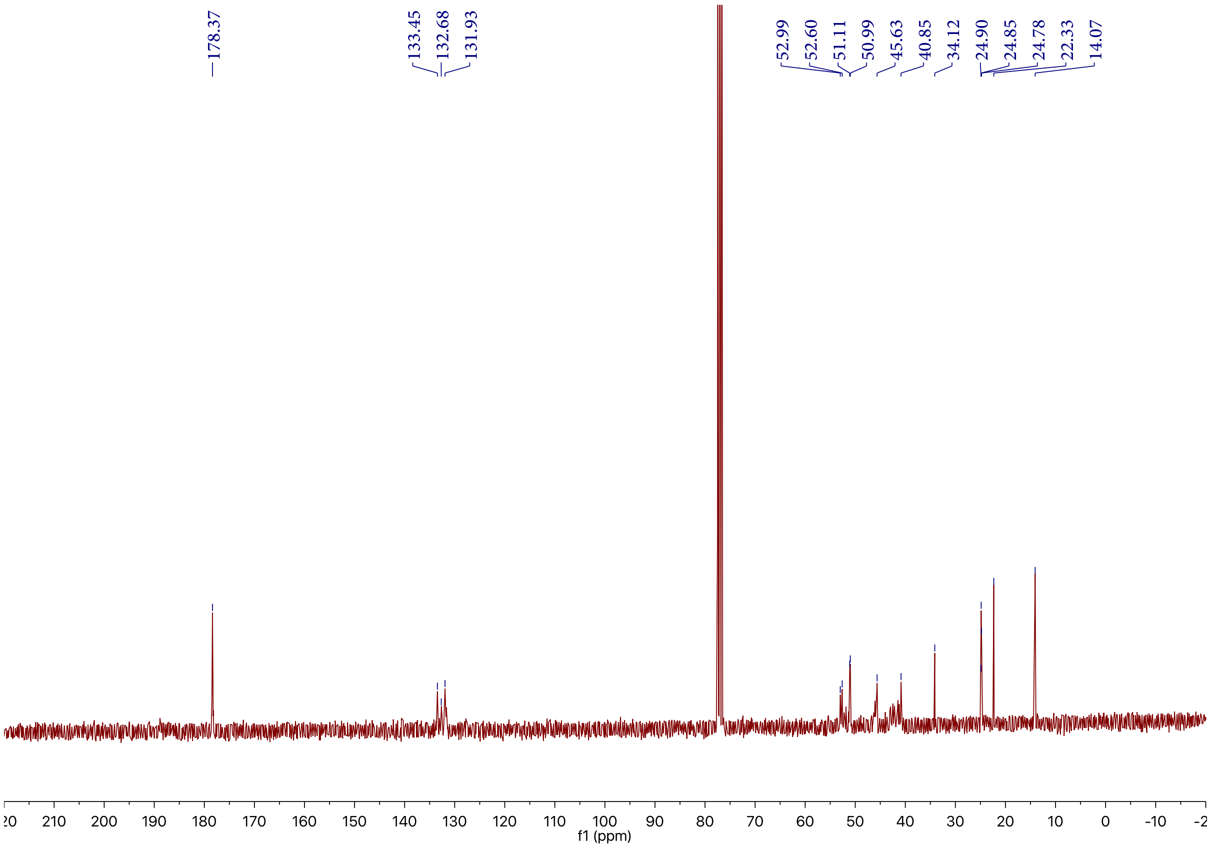


Figure S3 ^{13}C NMR spectrum (75MHz, $CDCl_3$) of Polymer 1

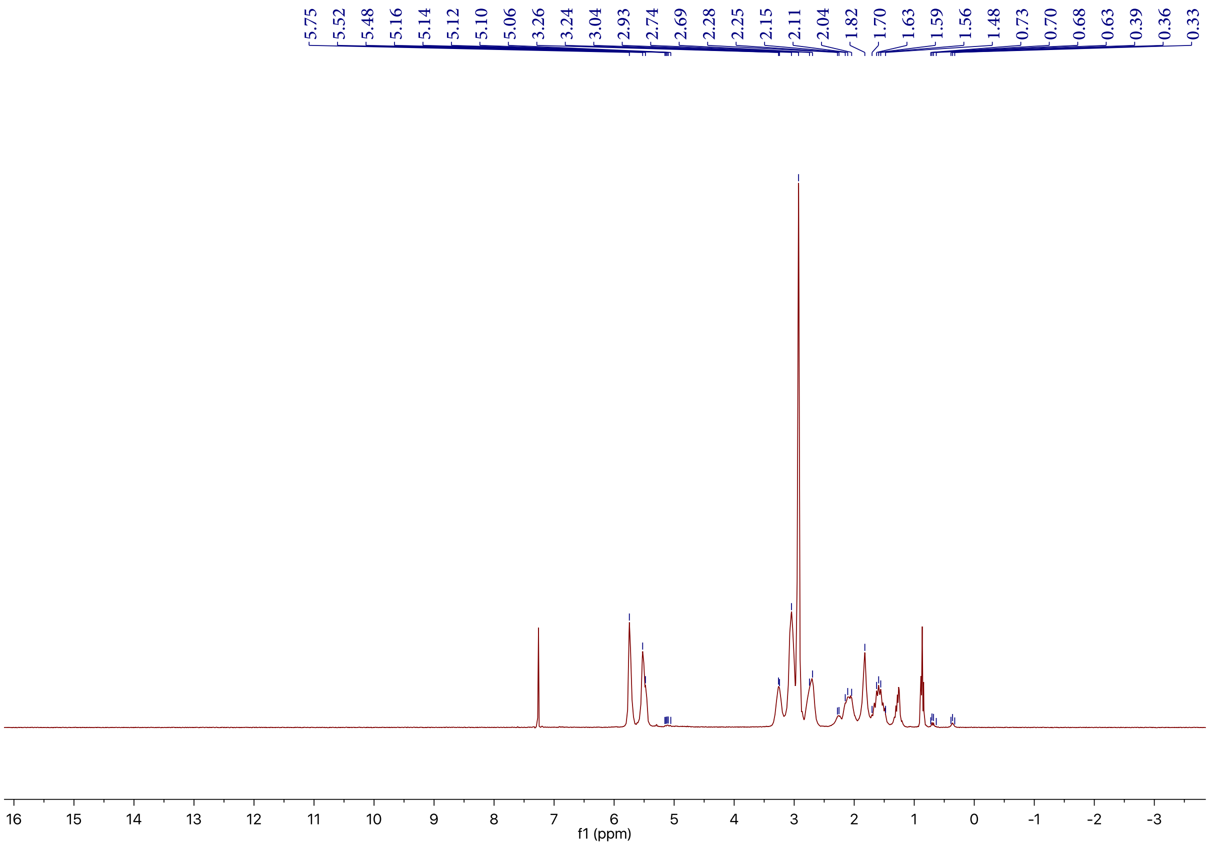


Figure S4 ^{1}H NMR spectrum (300MHz, $CDCl_3$) of Polymer 2

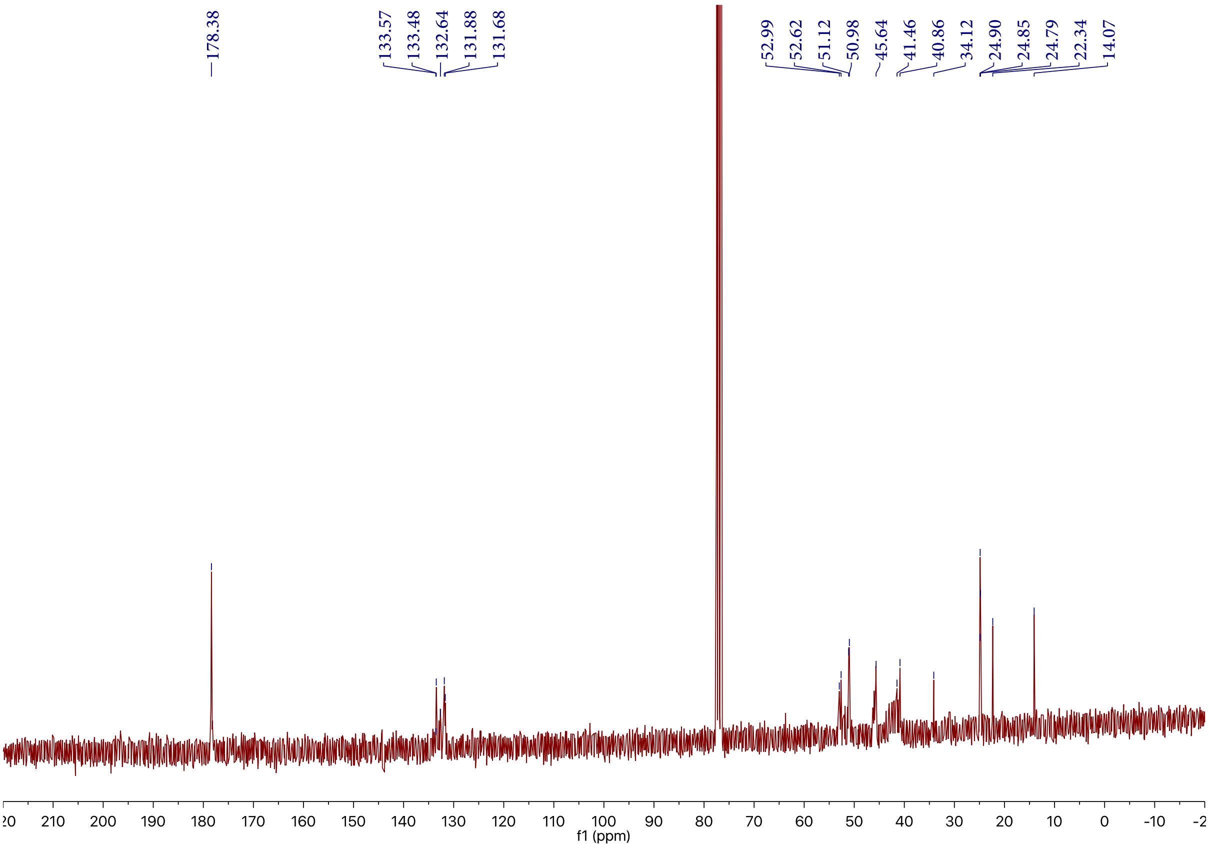


Figure S5 ^{13}C NMR spectrum (75MHz, $CDCl_3$) of Polymer 2

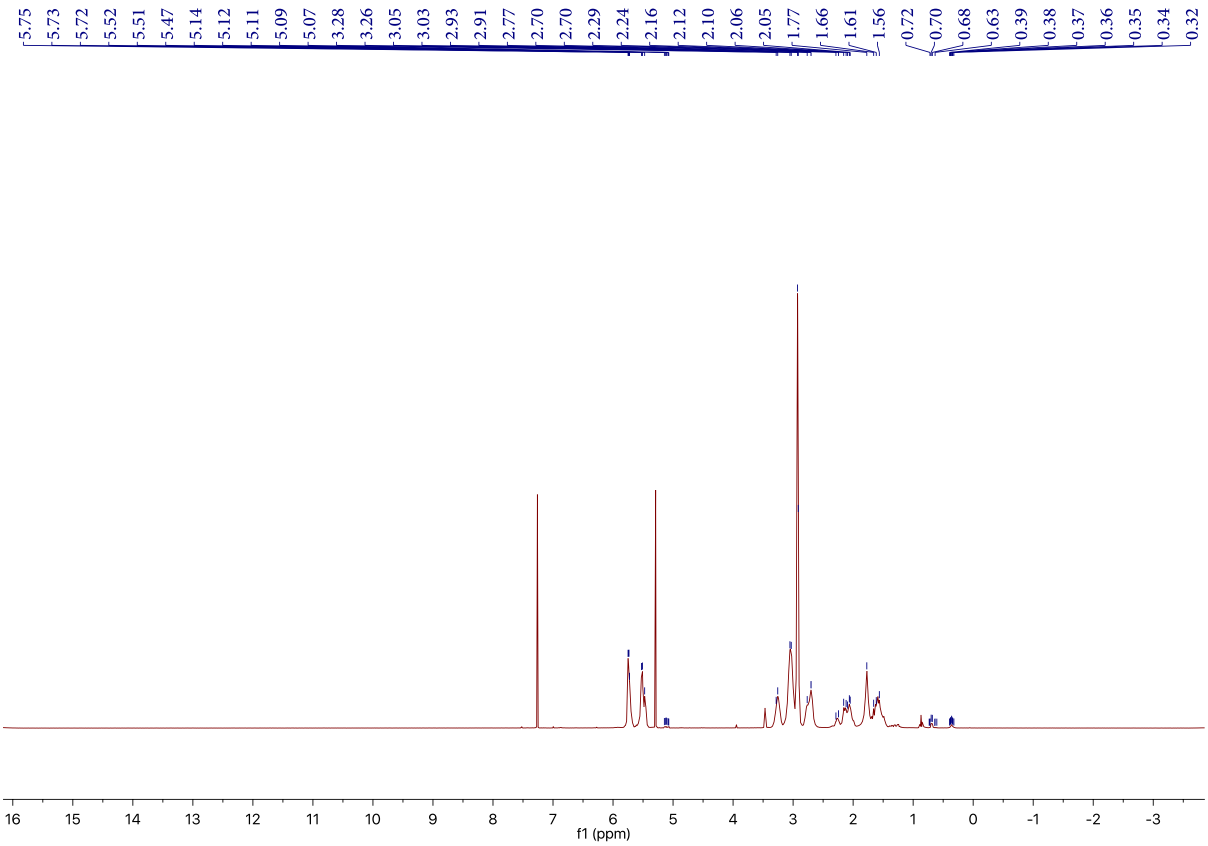


Figure S6 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 3

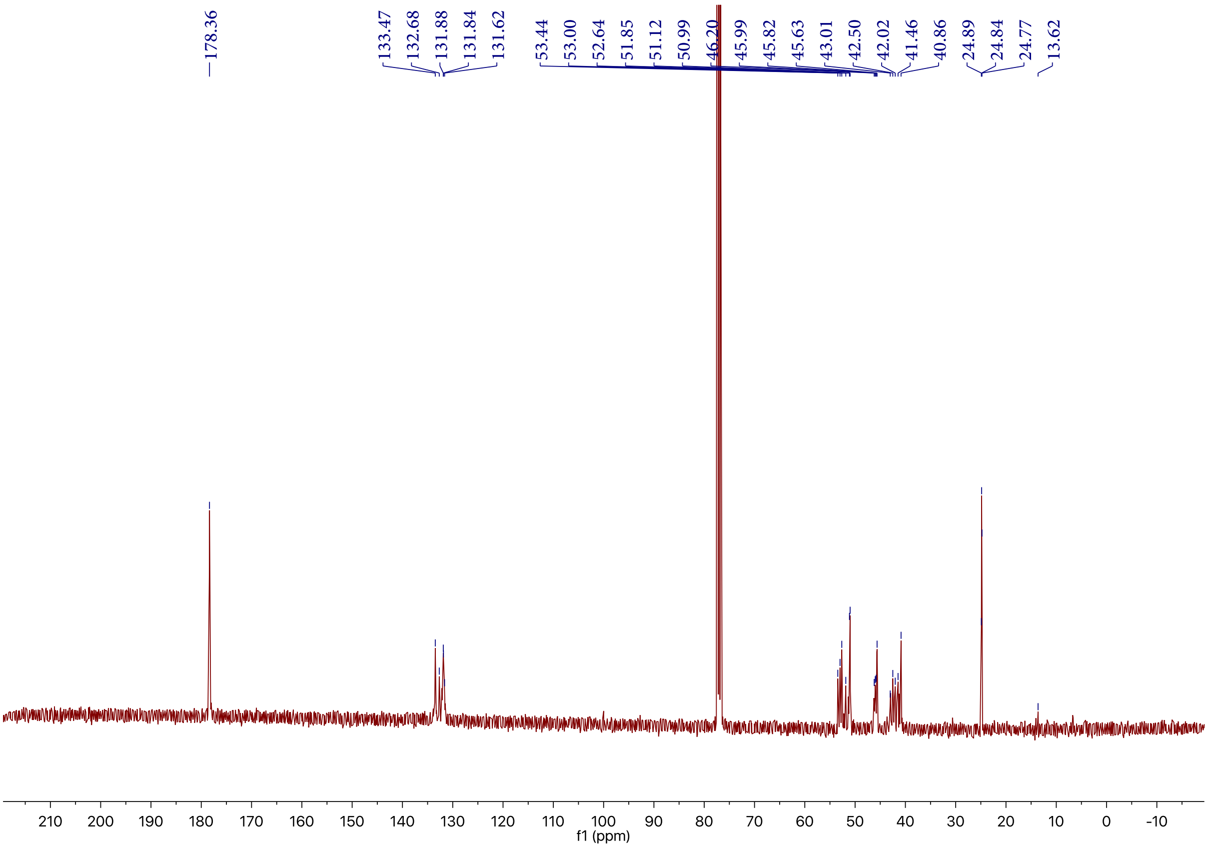


Figure S7 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 3

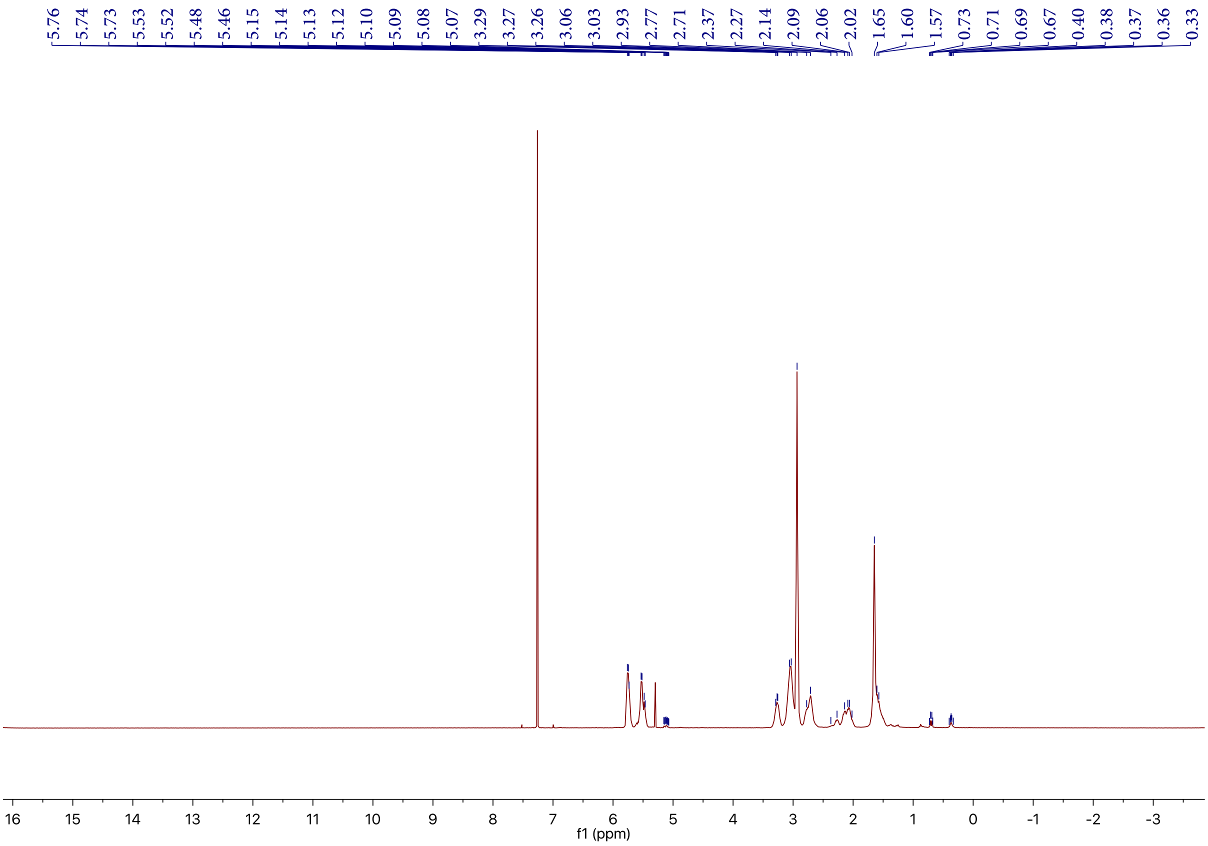


Figure S8 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 4

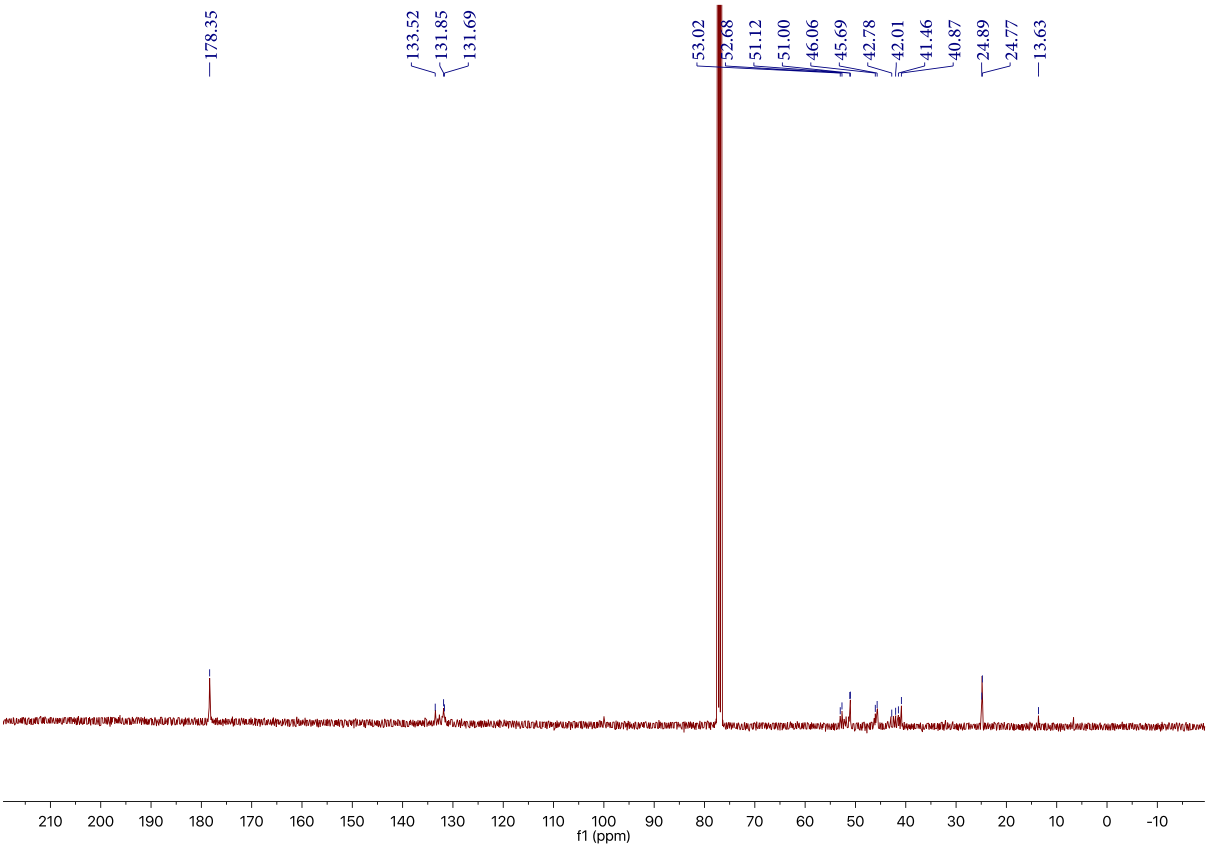


Figure S9 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 4

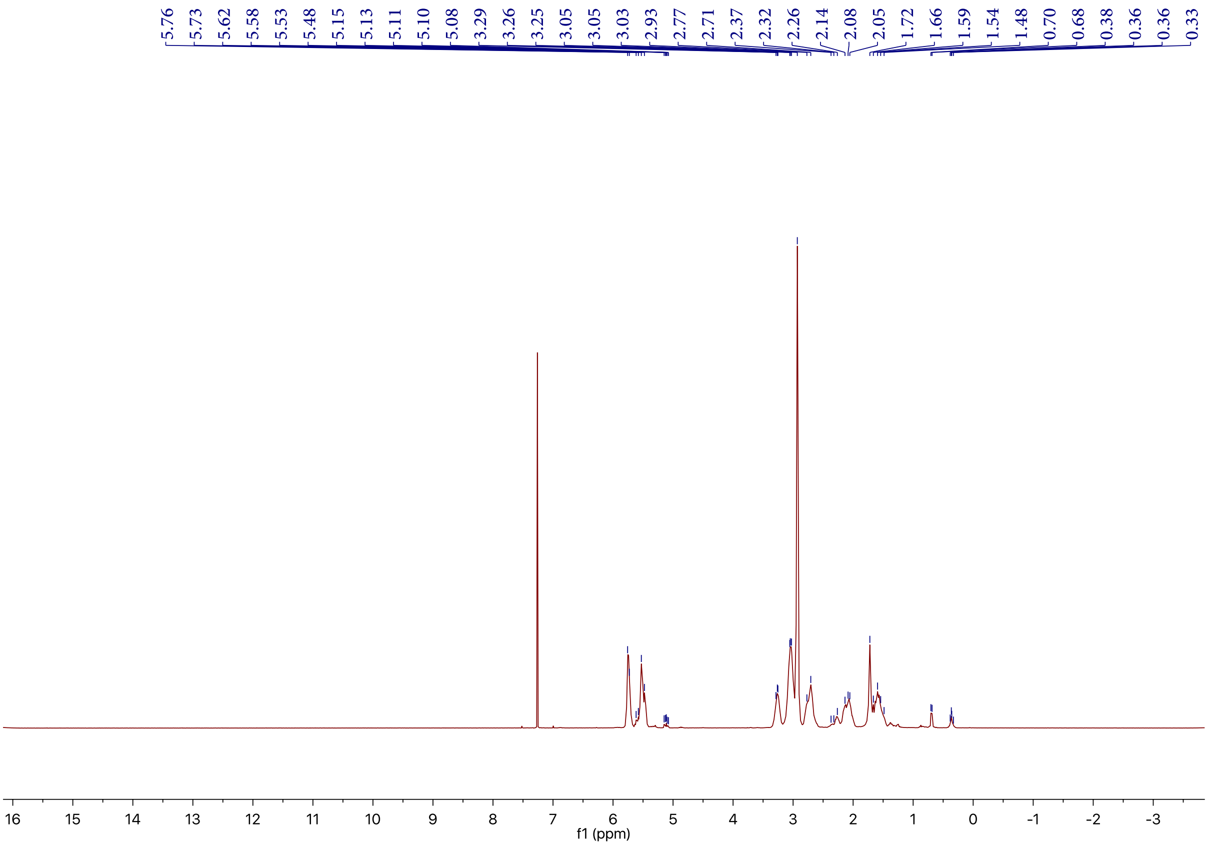


Figure S10 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 5

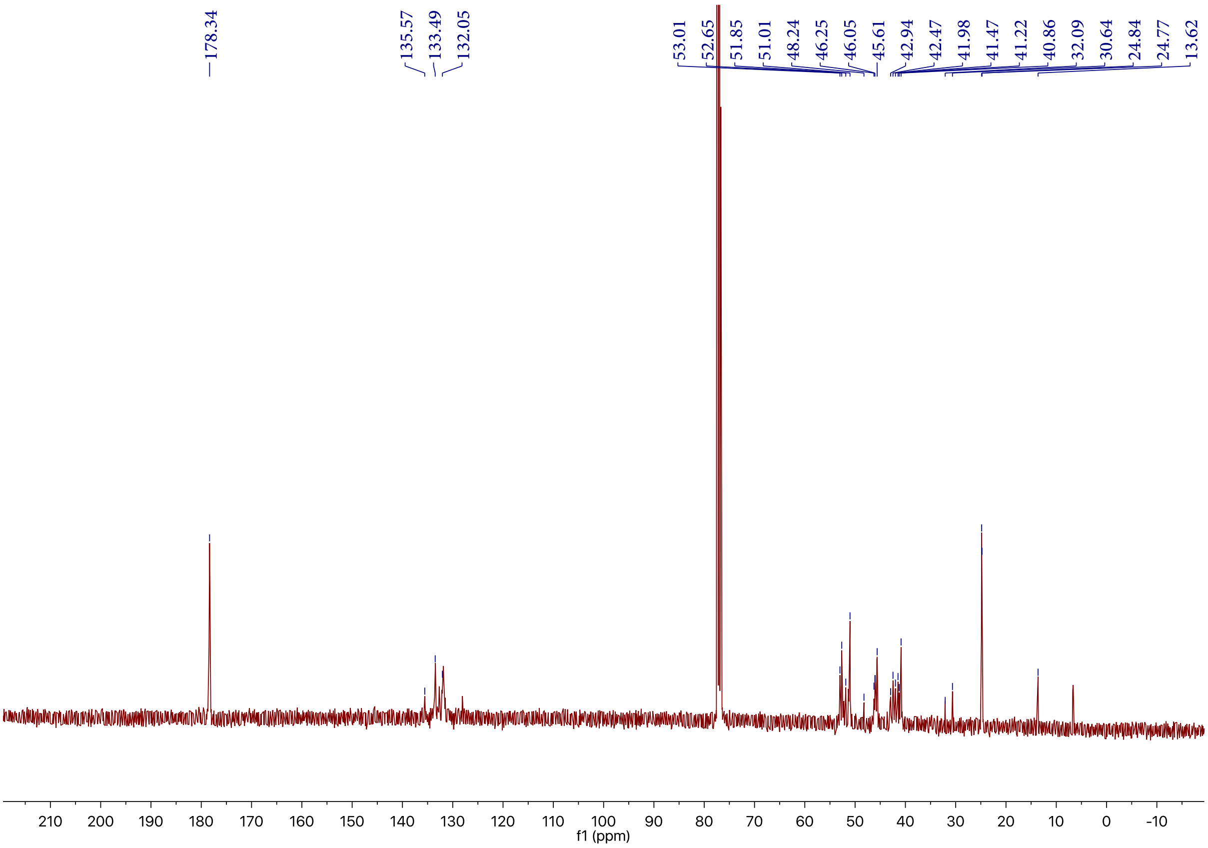


Figure S11 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 5

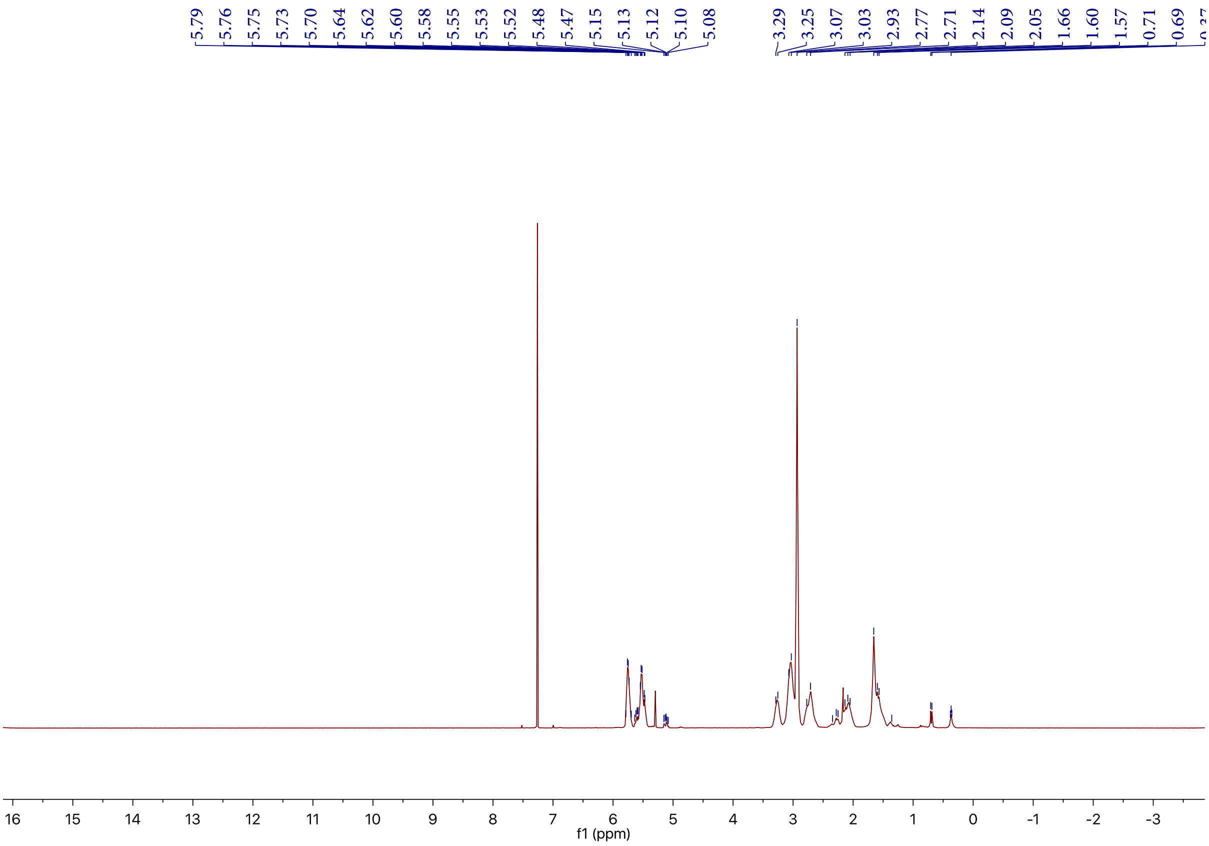


Figure S12 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 6

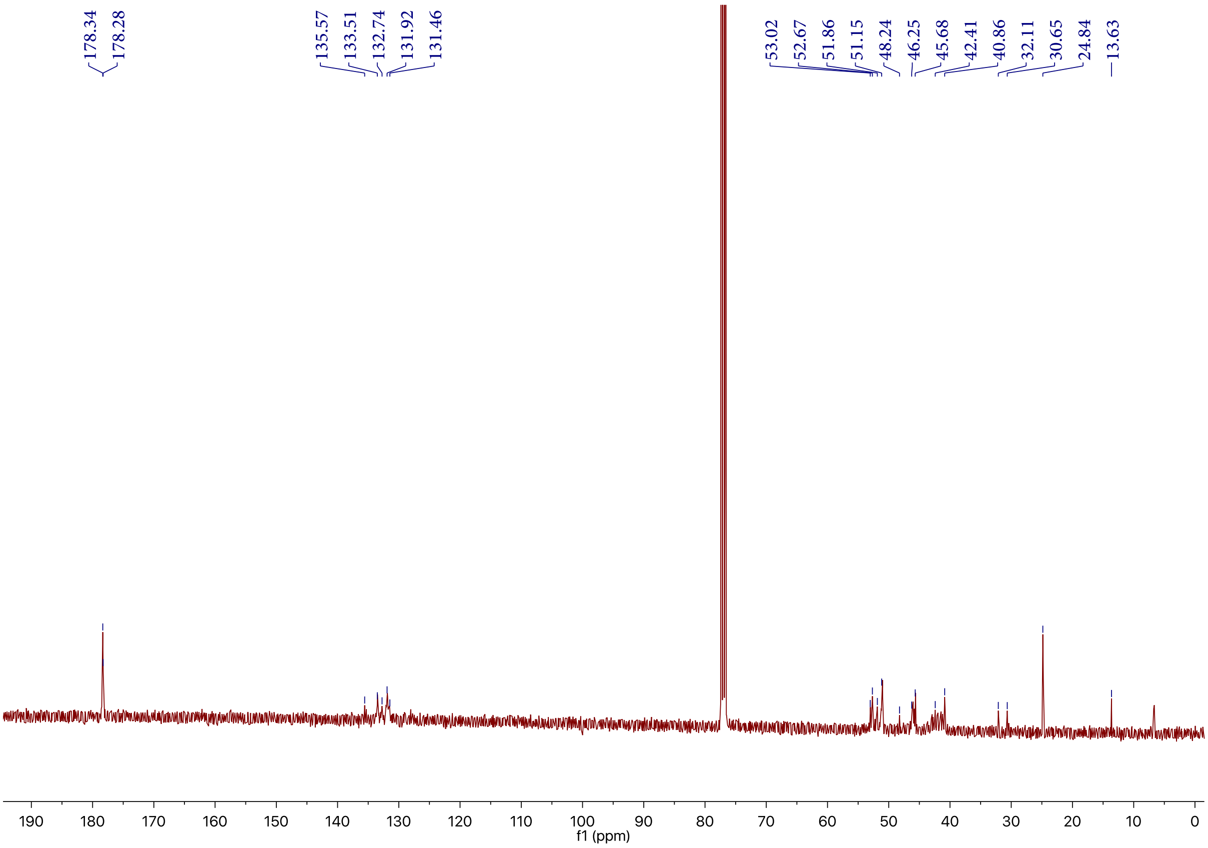


Figure S13 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 6

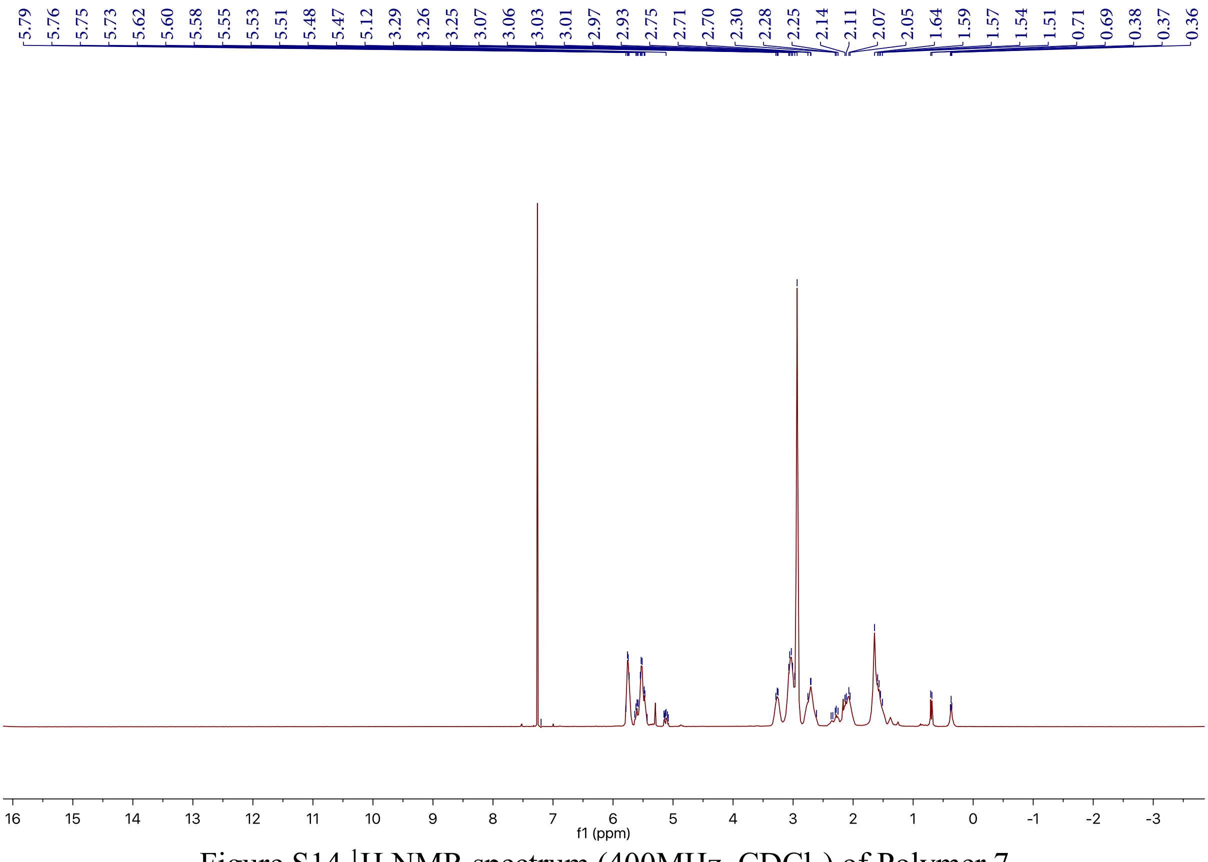


Figure S14 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 7

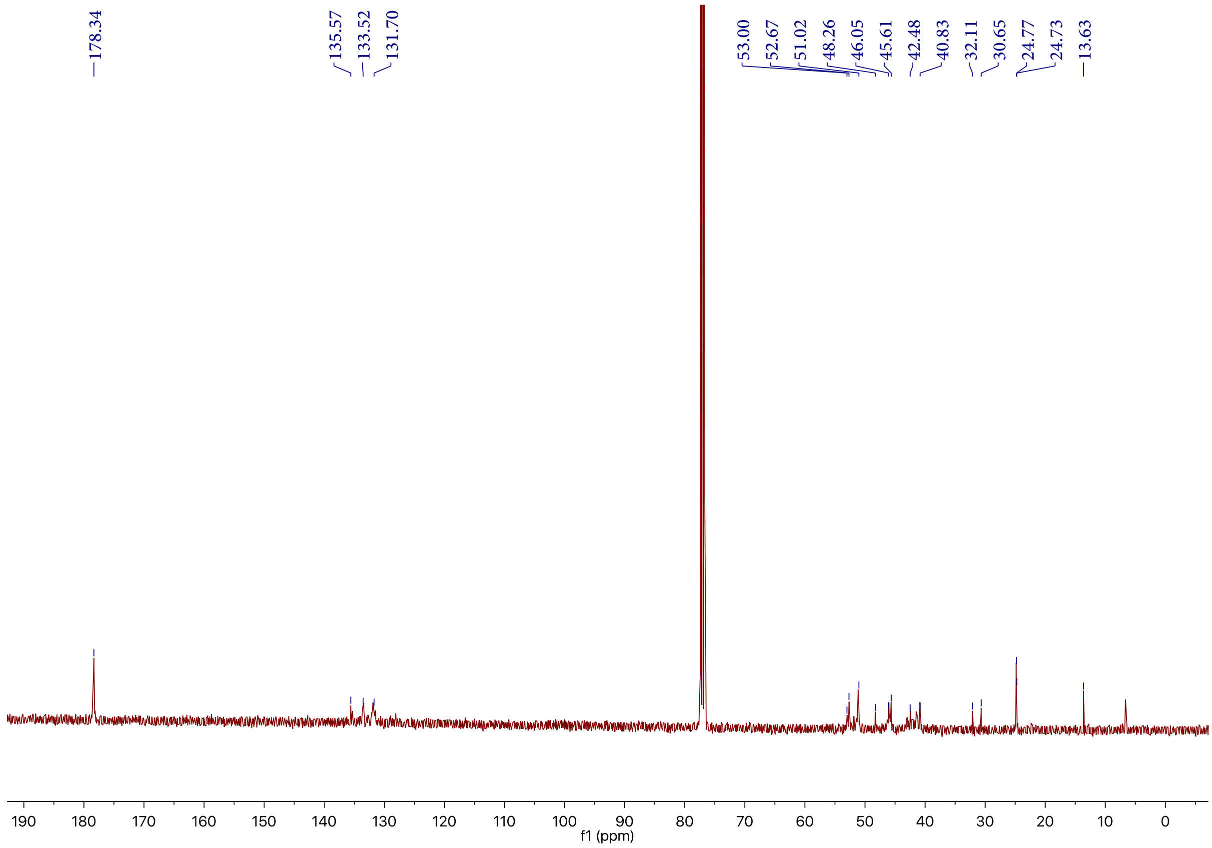


Figure S15 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 7

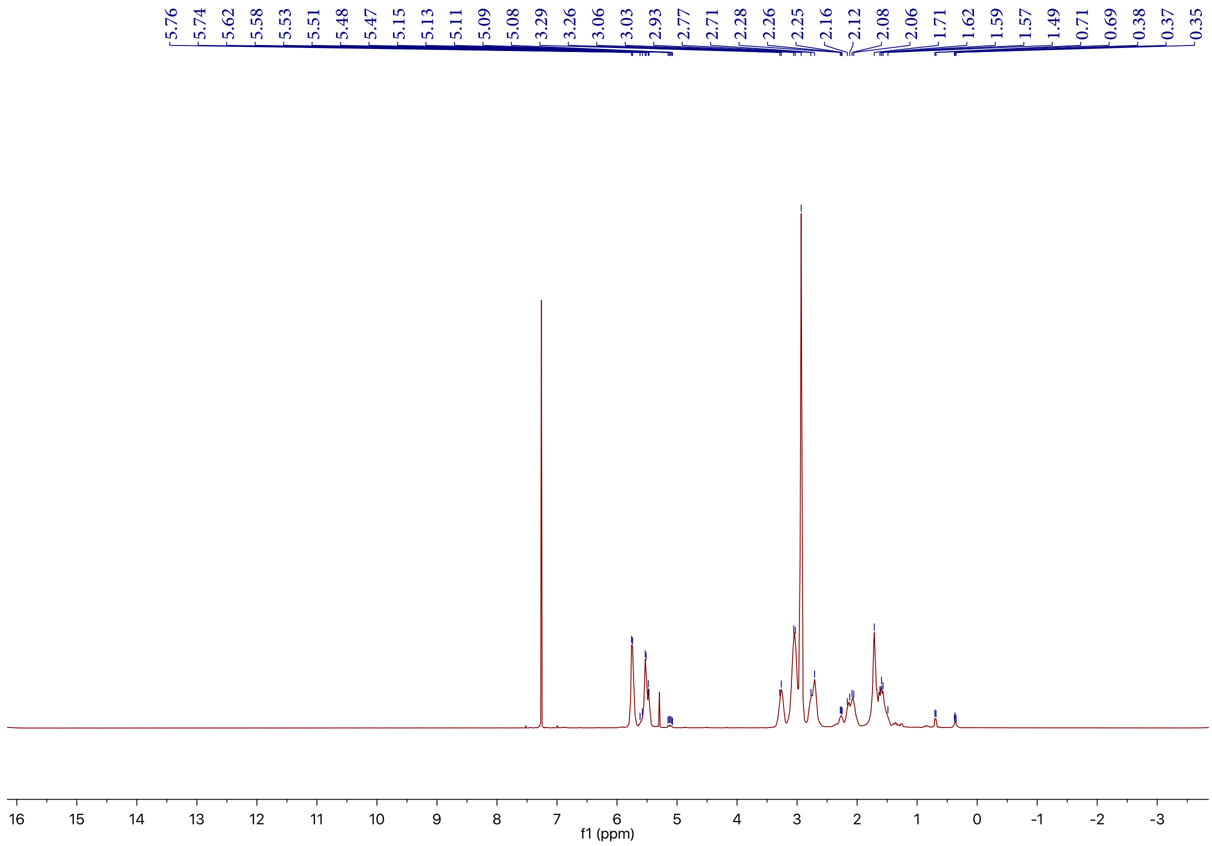


Figure S16 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 8

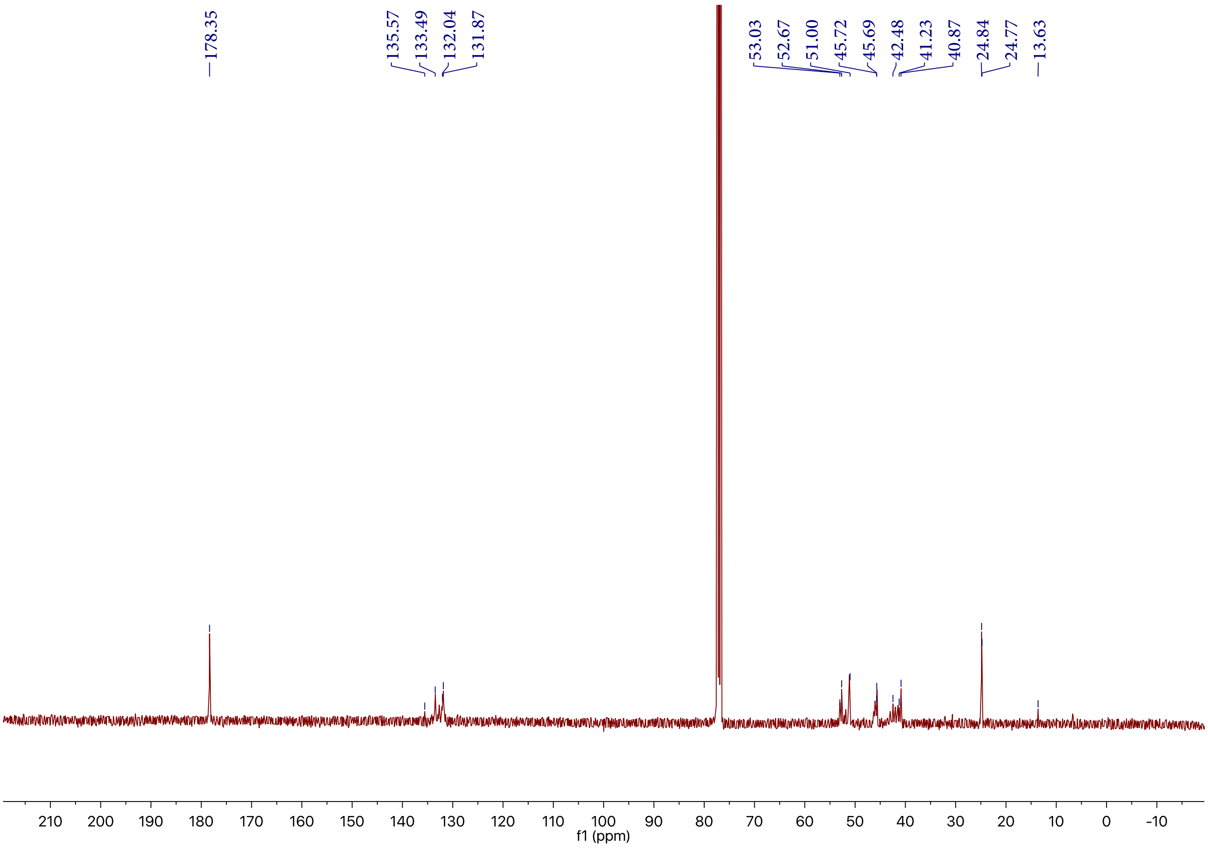


Figure S17 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 8

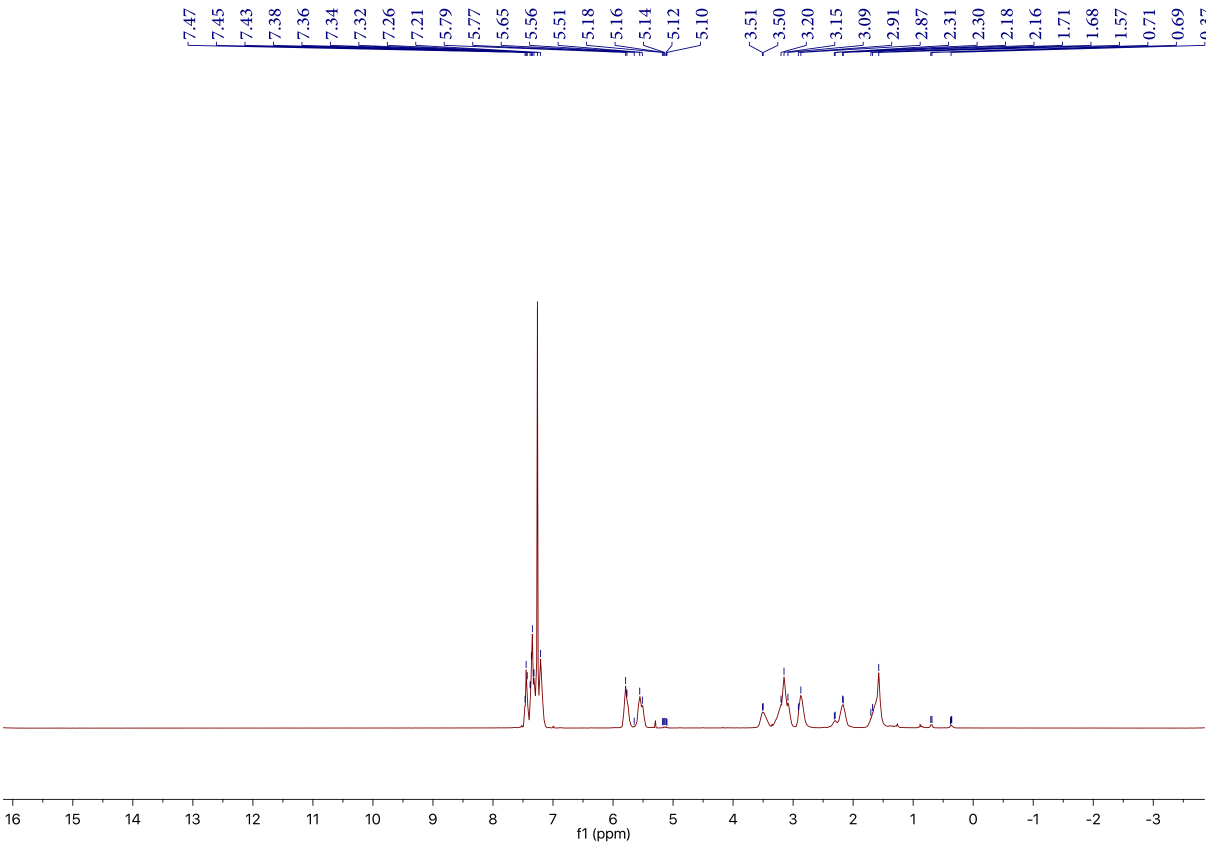


Figure S18 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 9

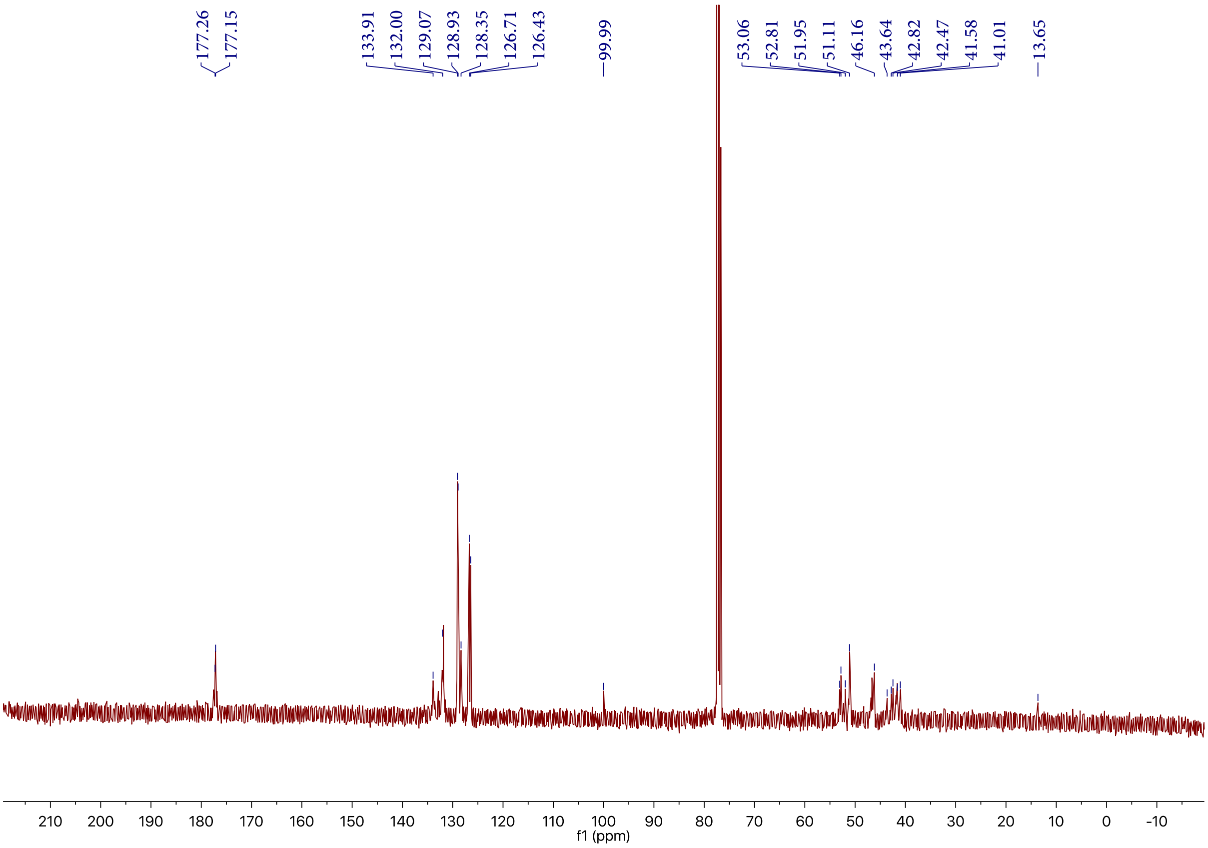


Figure S19 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 9

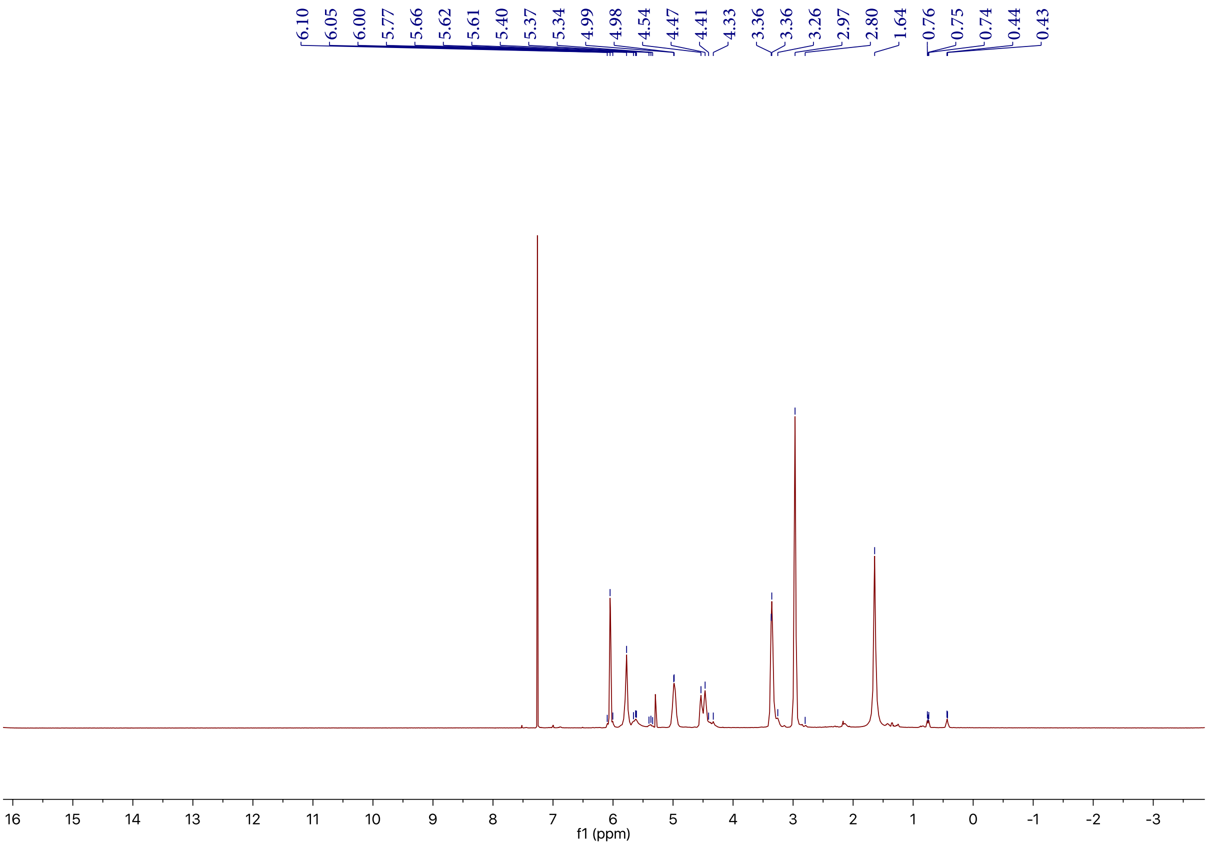


Figure S20 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 10

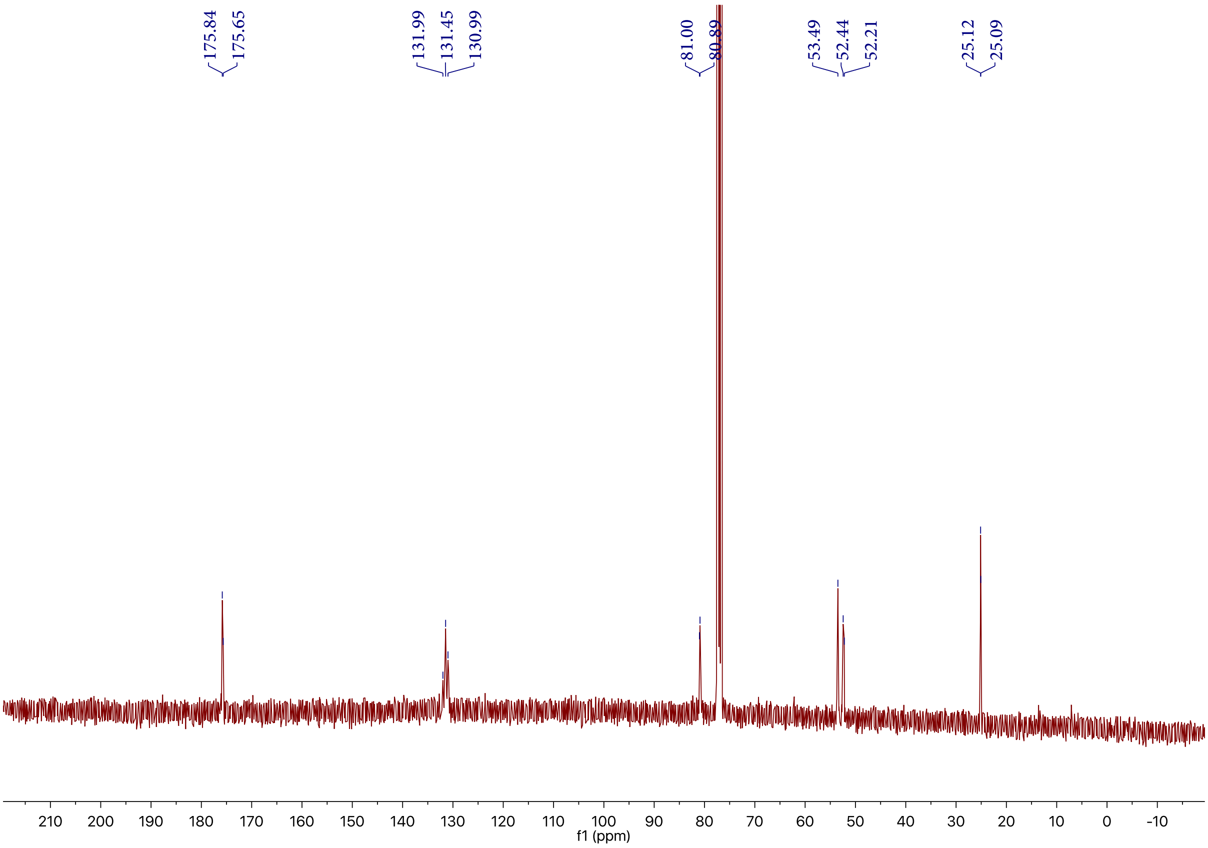


Figure S21 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 10

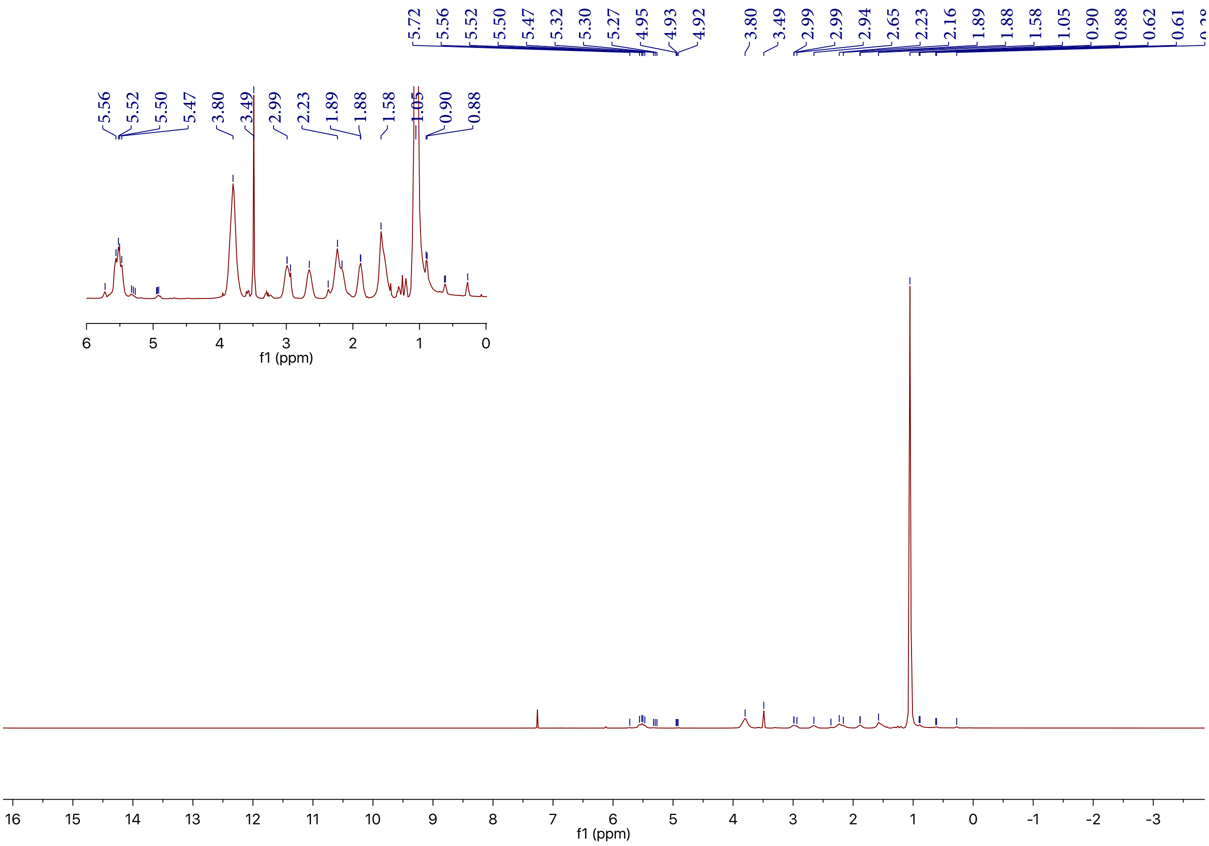


Figure S22 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 11

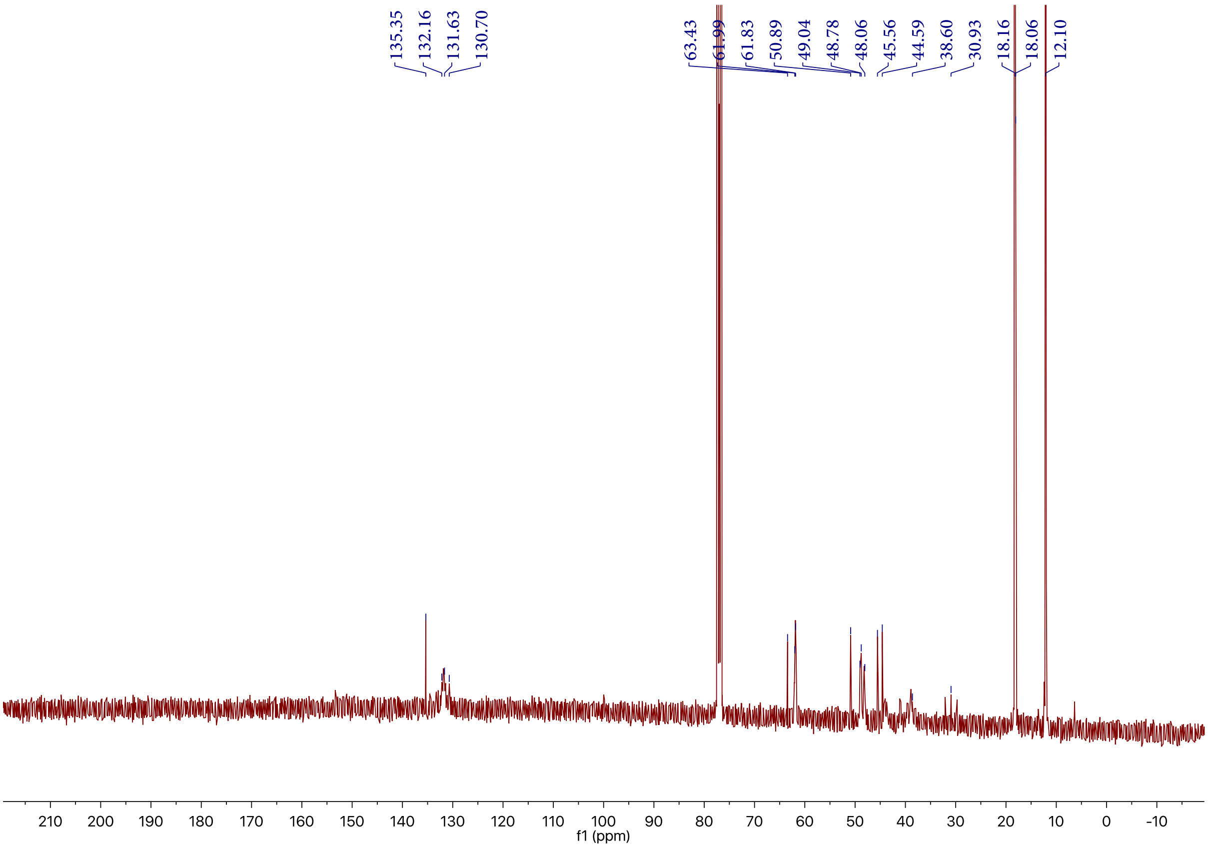


Figure S23 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 11

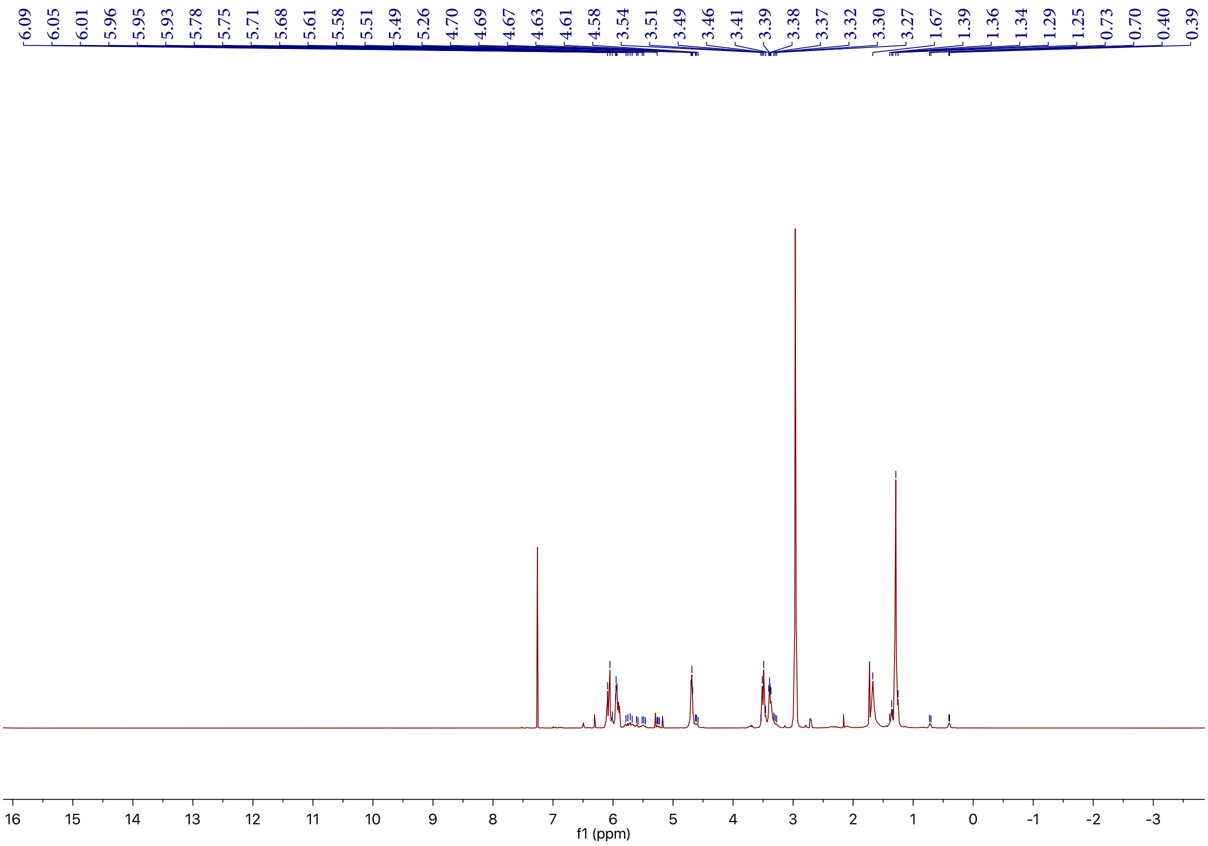


Figure S24 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 12

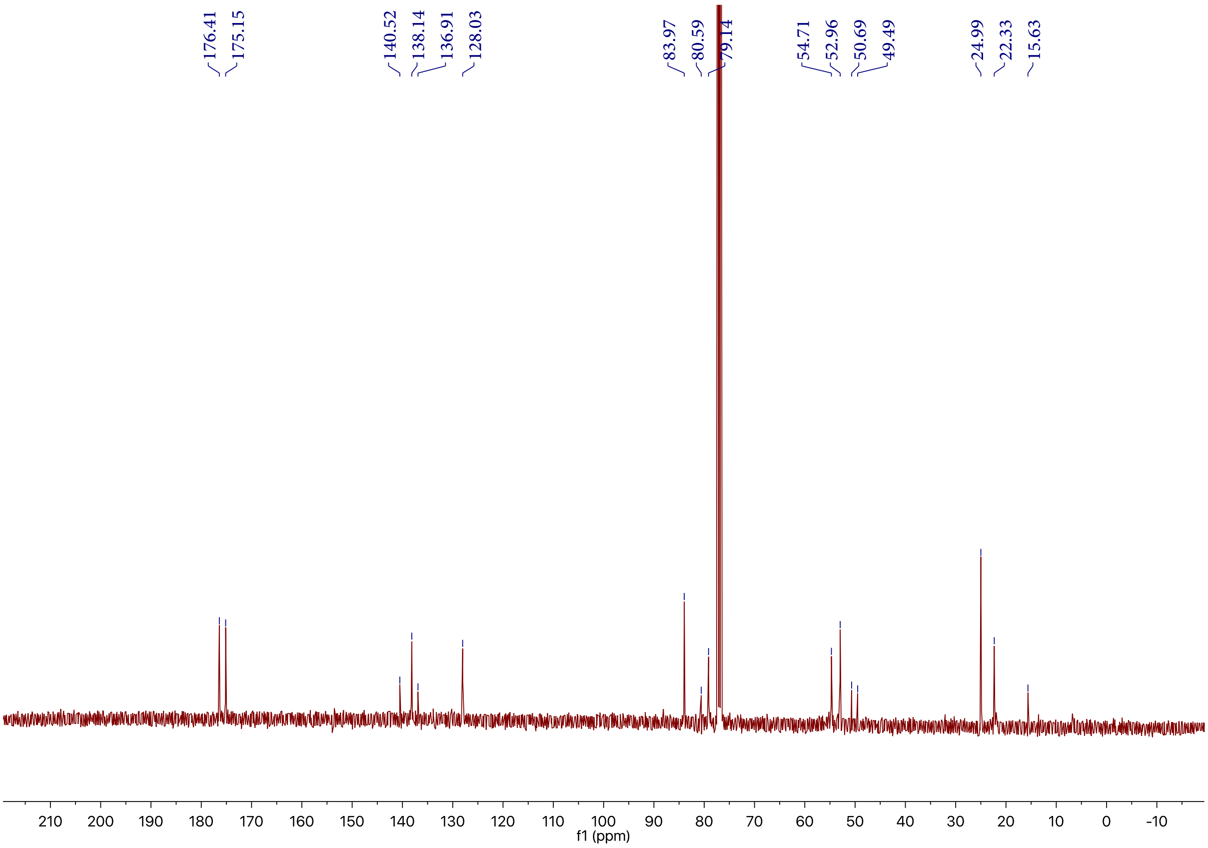


Figure S25 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 12

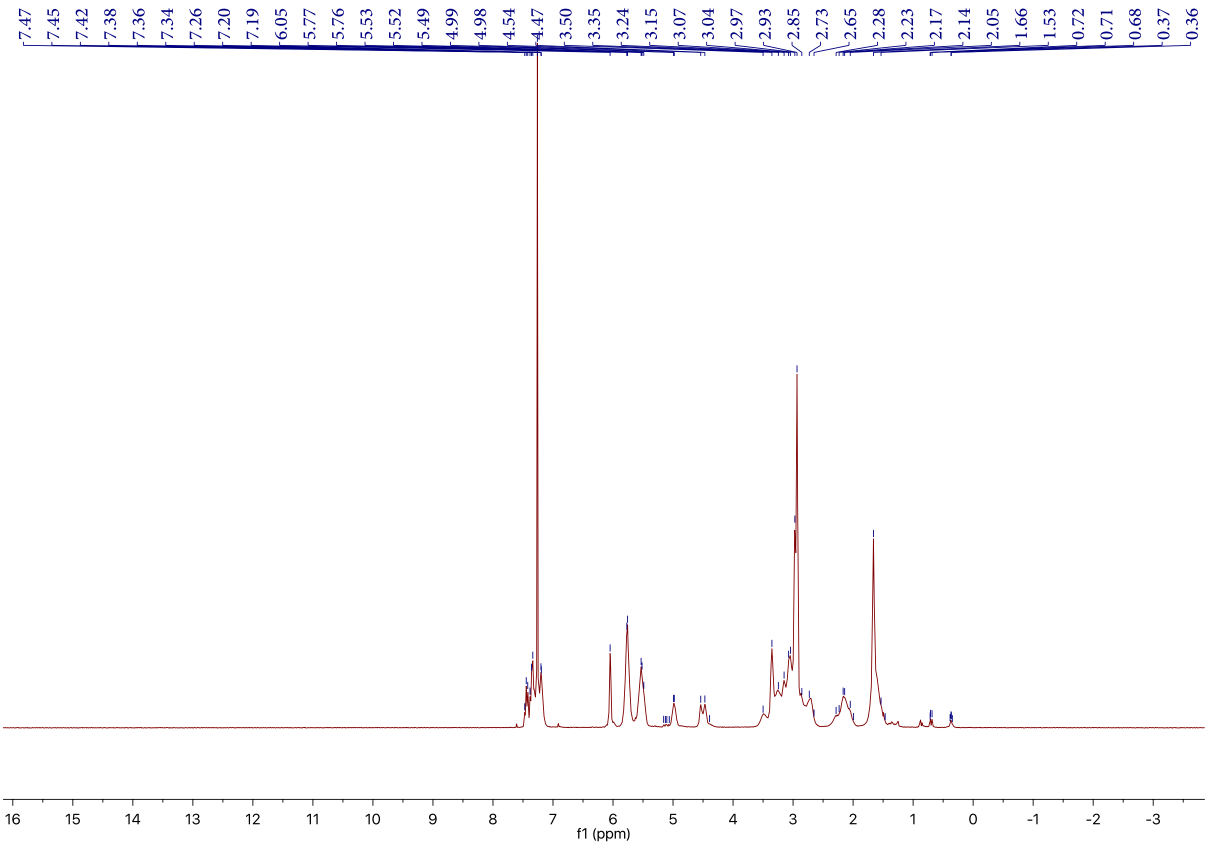


Figure S26 ^{1}H NMR spectrum (300MHz, $CDCl_3$) of Polymer 13

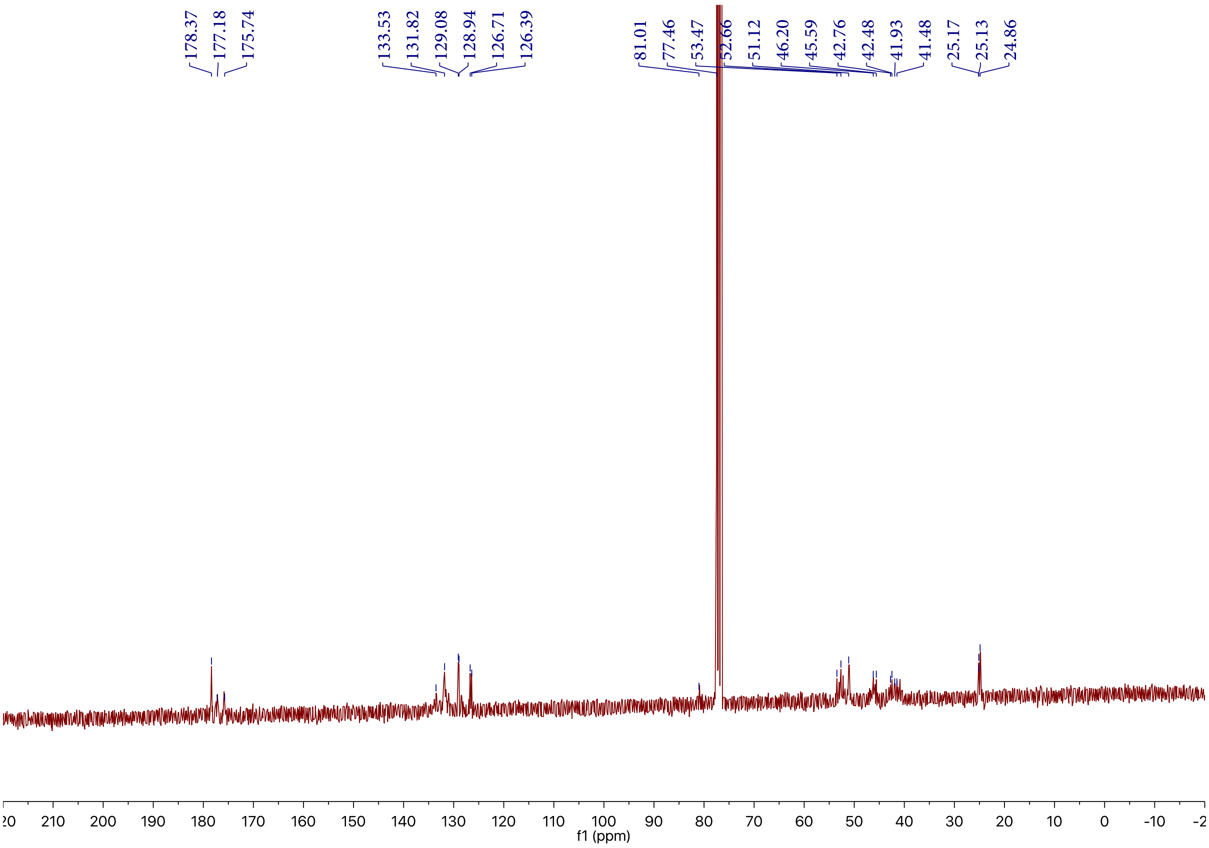


Figure S27 ^{13}C NMR spectrum (75MHz, $CDCl_3$) of Polymer 13

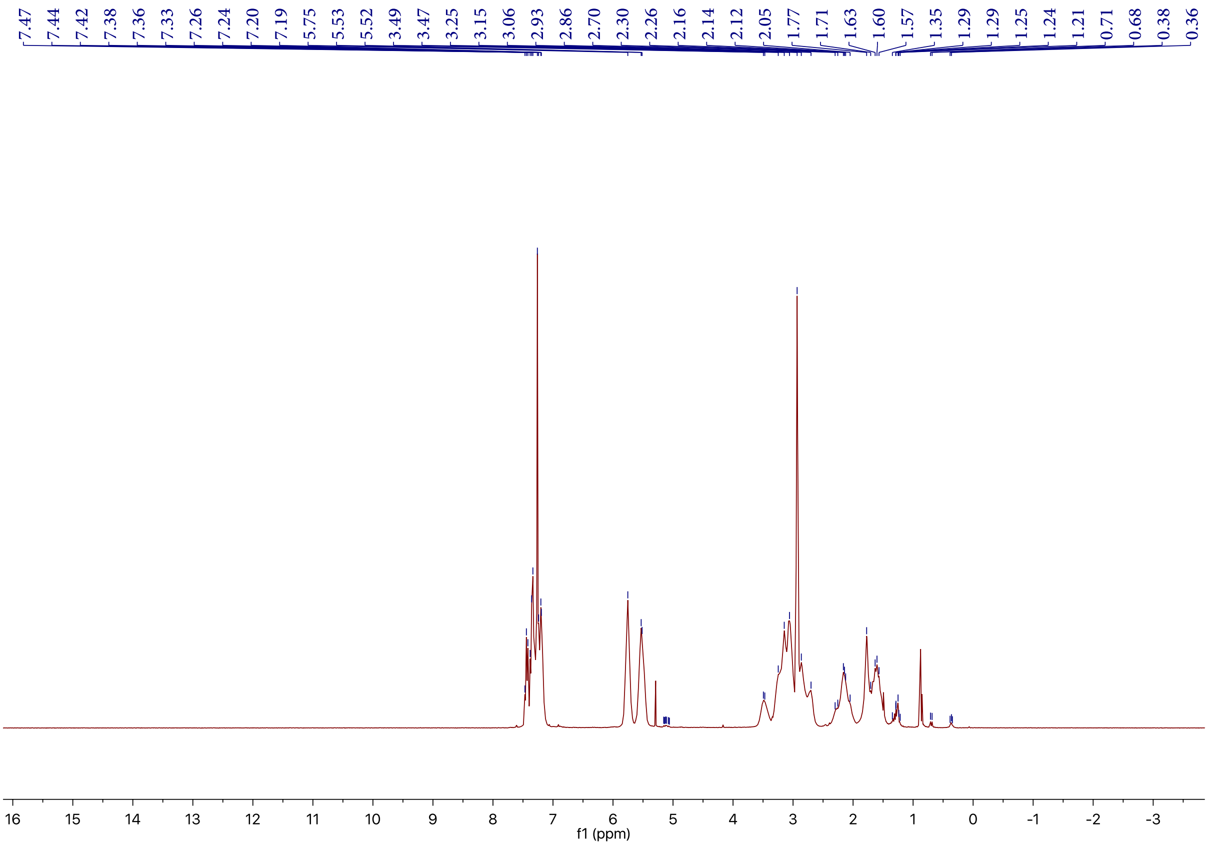


Figure S28 ^{1}H NMR spectrum (300MHz, $CDCl_3$) of Polymer 14

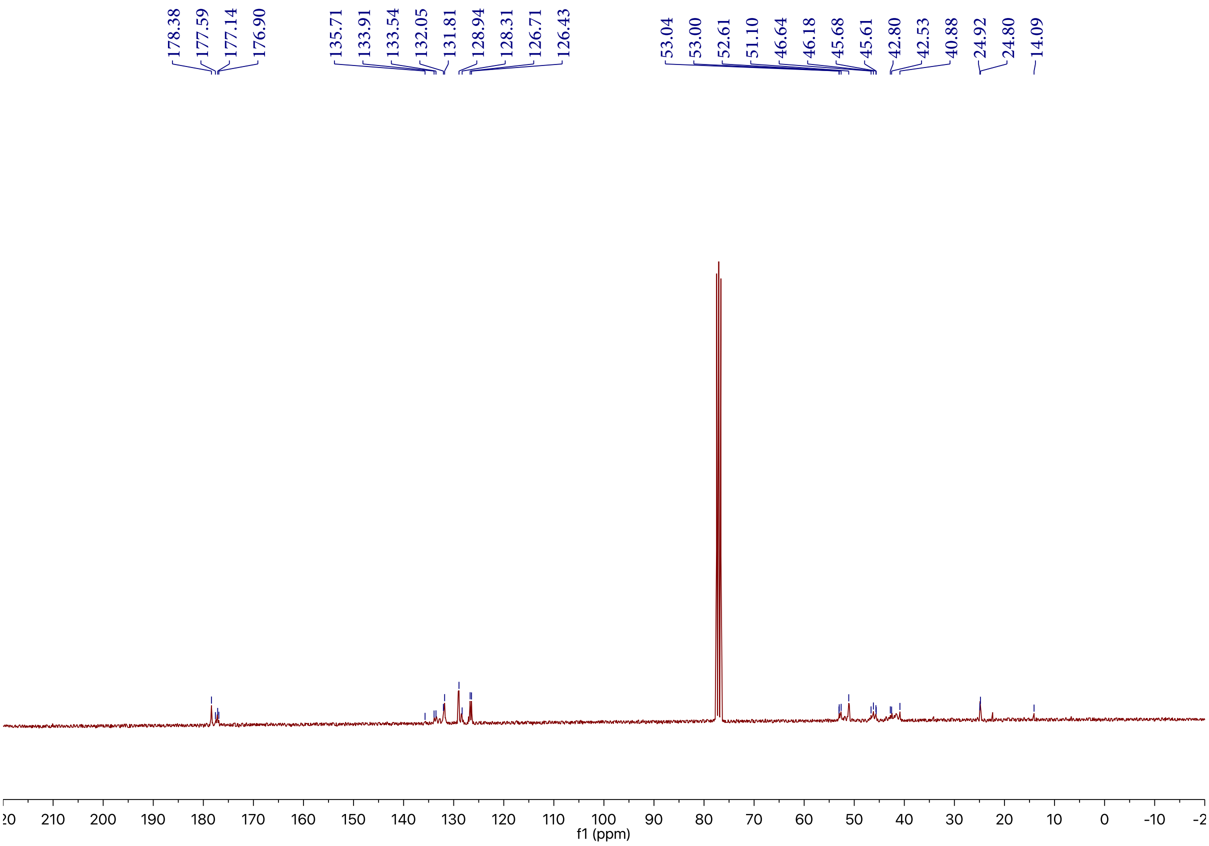


Figure S29 ^{13}C NMR spectrum (75MHz, $CDCl_3$) of Polymer 14

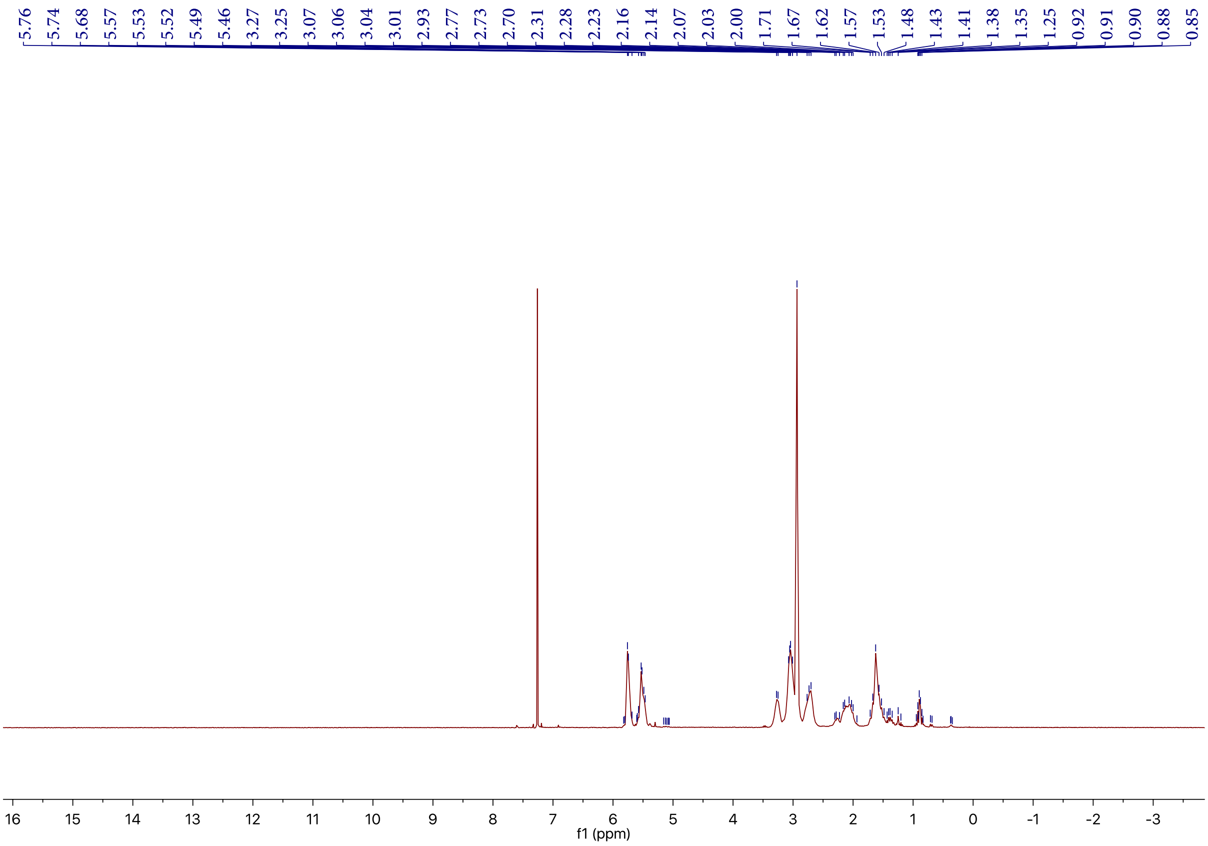


Figure S30 ^{1}H NMR spectrum (300MHz, $CDCl_3$) of Polymer 15

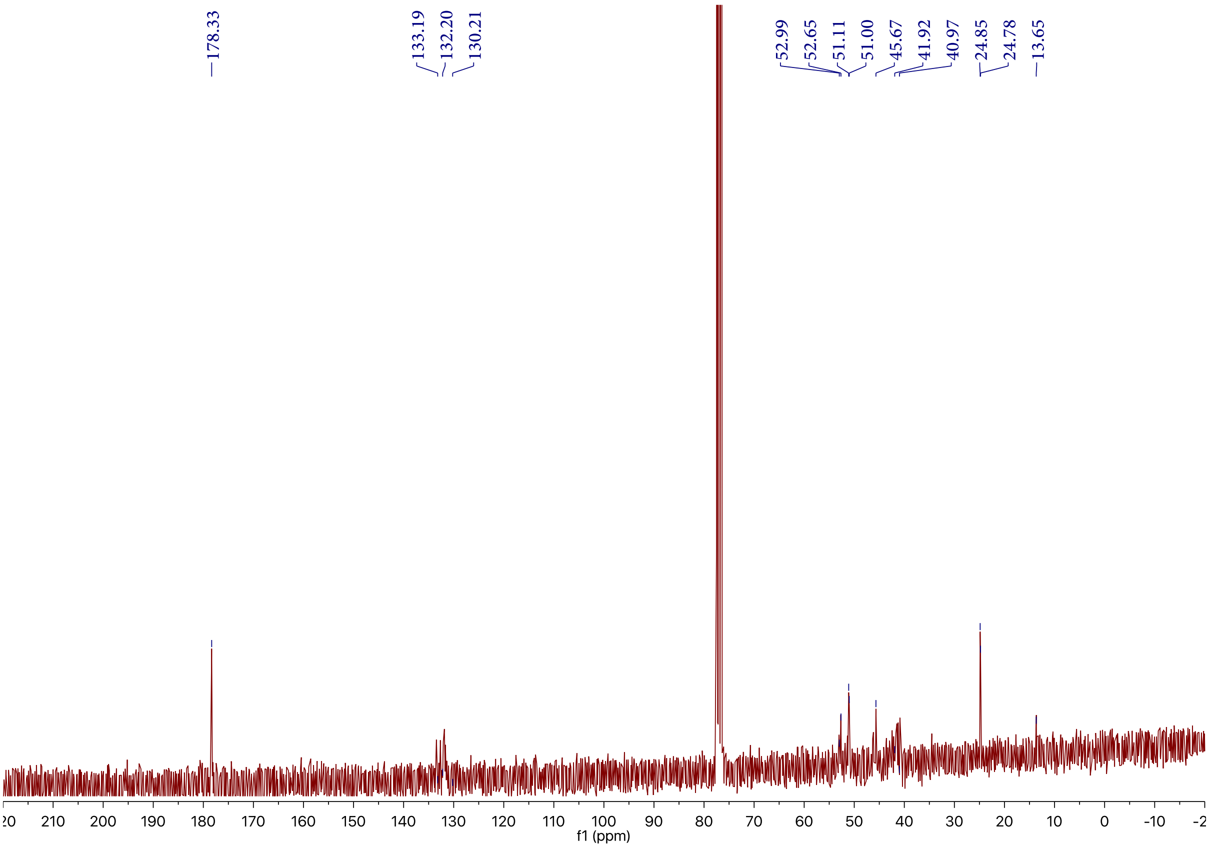


Figure S31 ^{13}C NMR spectrum (75MHz, $CDCl_3$) of Polymer 15

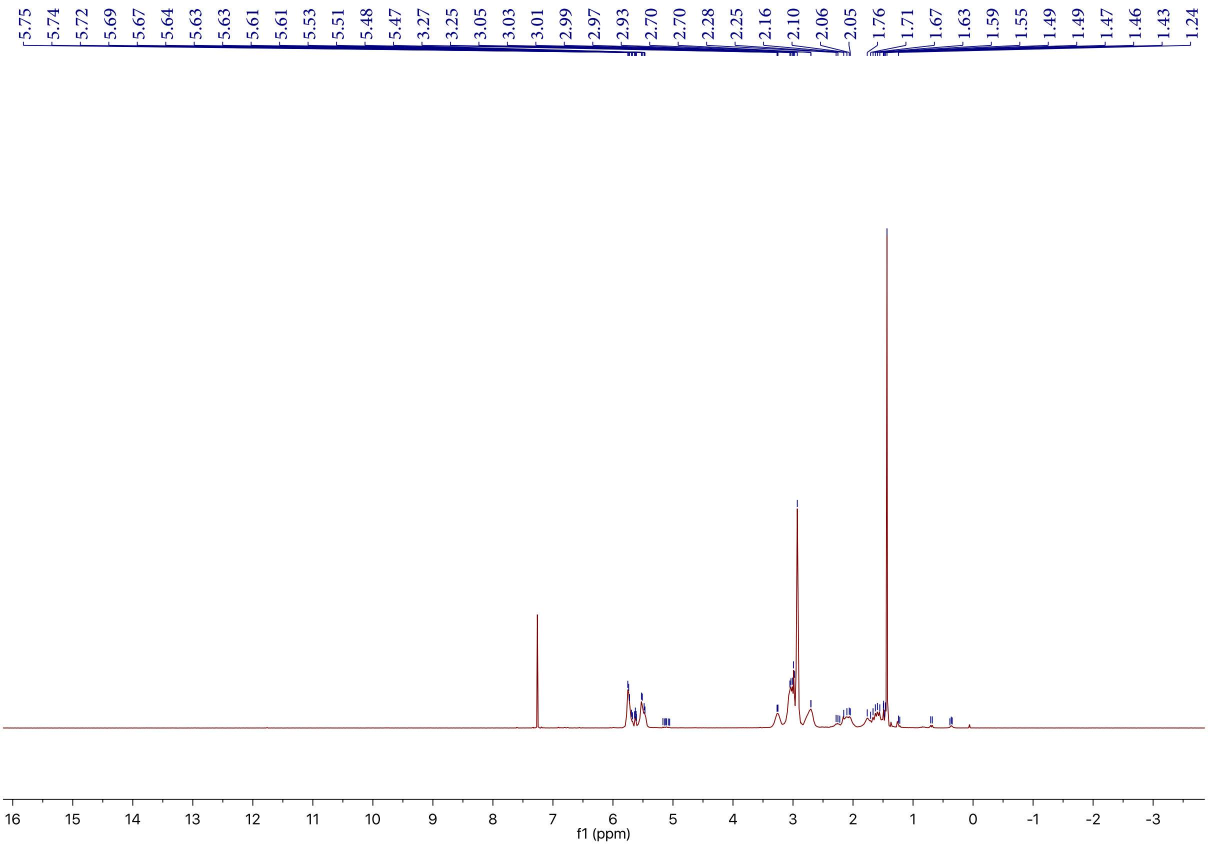


Figure S32 ^{1}H NMR spectrum (300MHz, $CDCl_3$) of Polymer 16

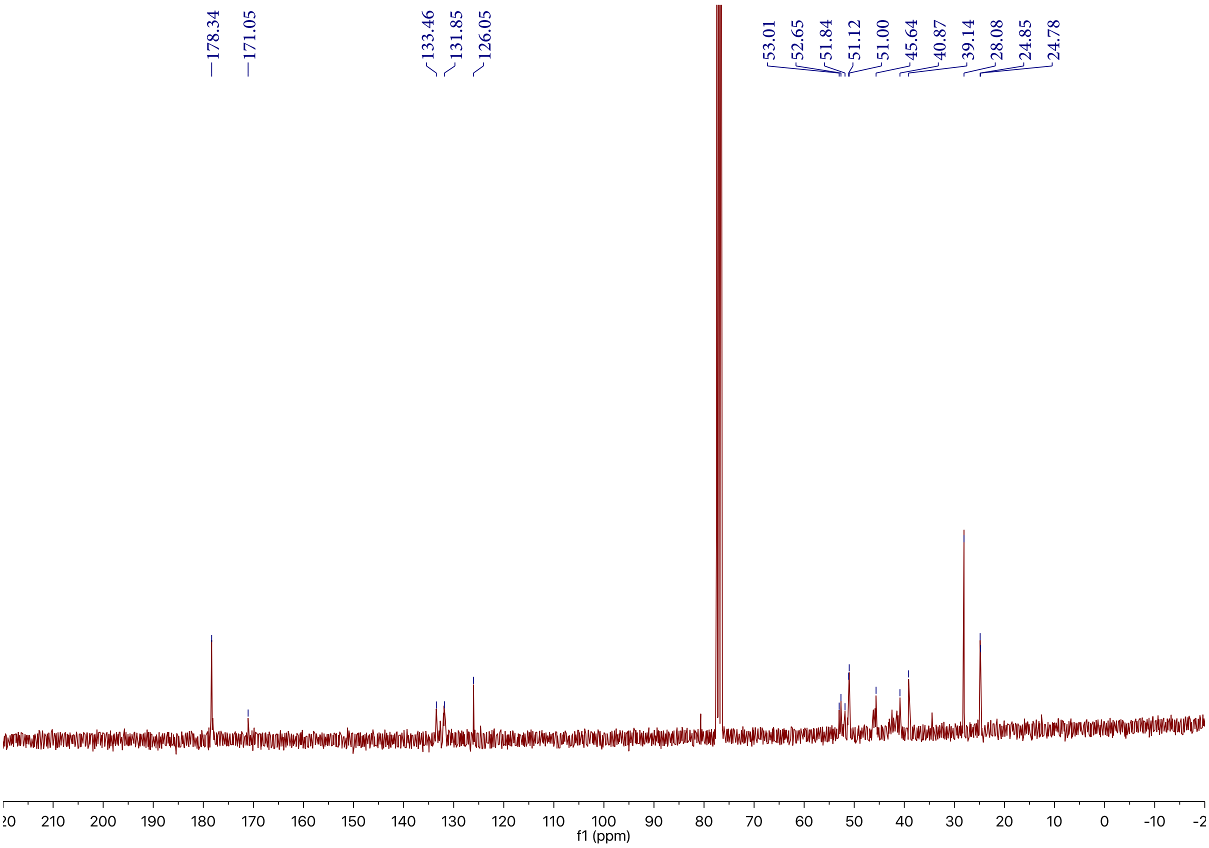


Figure S33 ^{13}C NMR spectrum (75MHz, $CDCl_3$) of Polymer 16

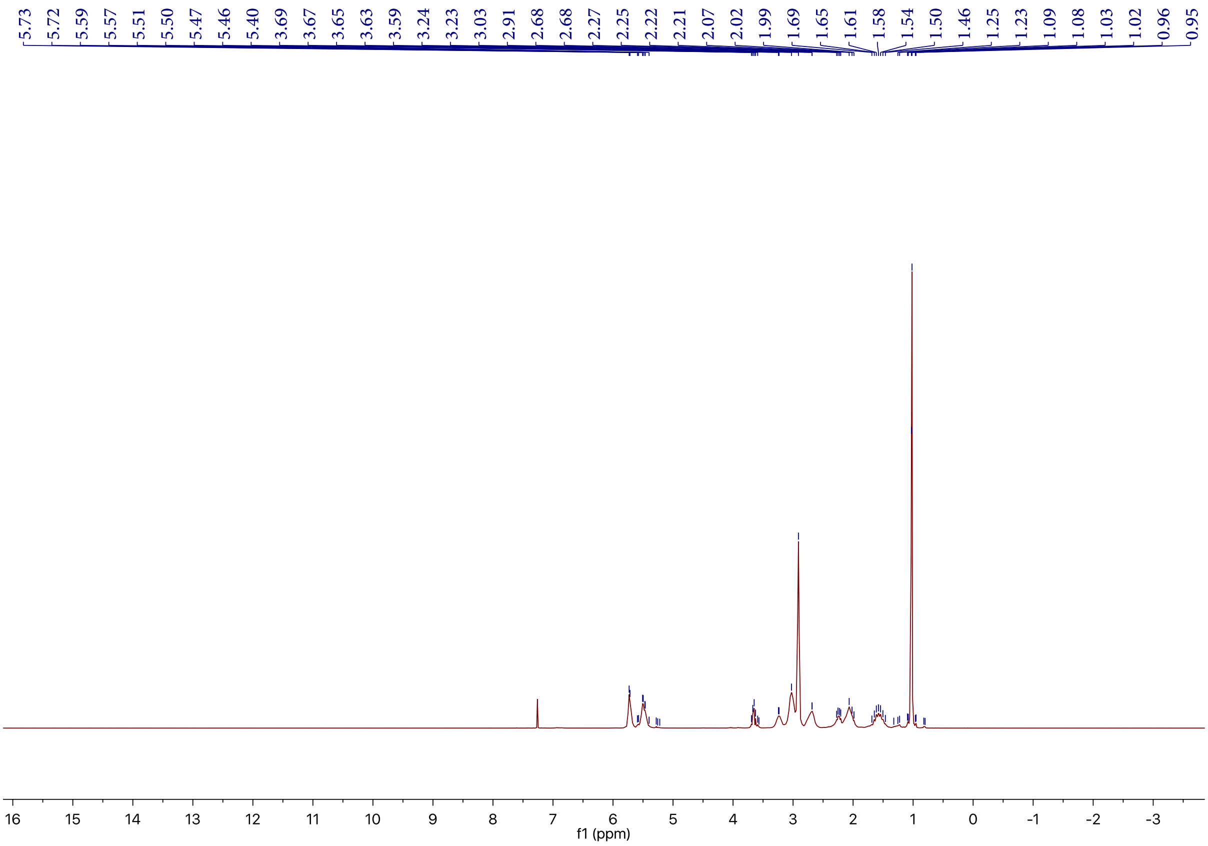


Figure S34 ^{1}H NMR spectrum (300MHz, $CDCl_3$) of Polymer 17

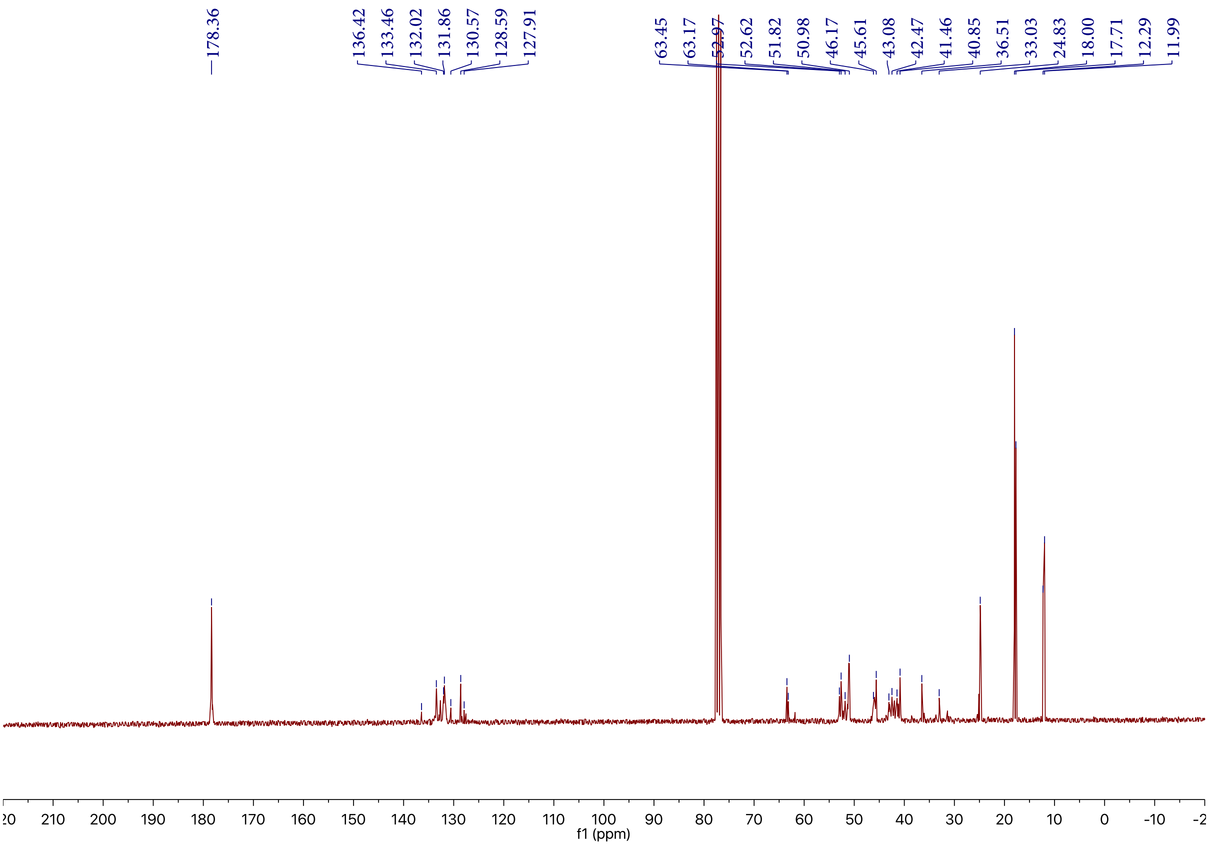


Figure S35 ^{13}C NMR spectrum (75MHz, $CDCl_3$) of Polymer 17

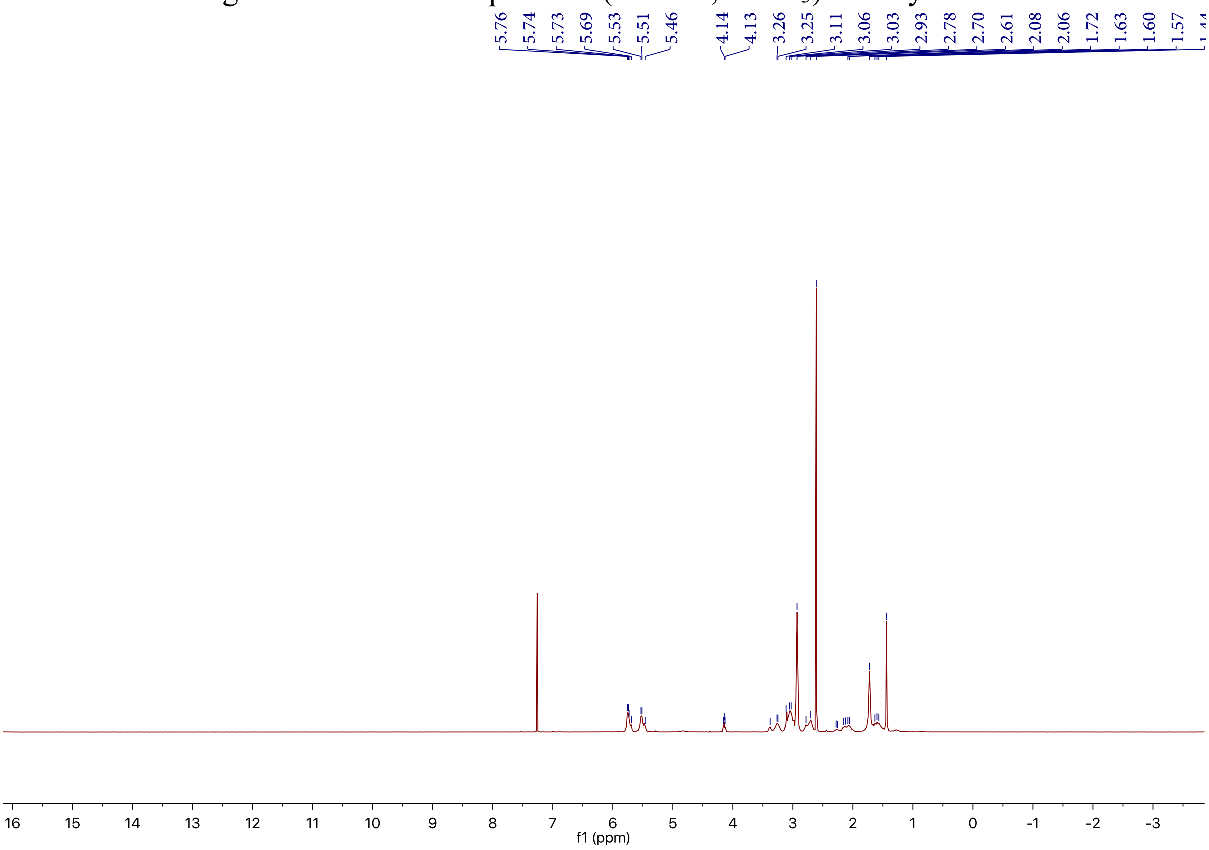


Figure S36 ^{1}H NMR spectrum (400MHz, $CDCl_3$) of Polymer 18

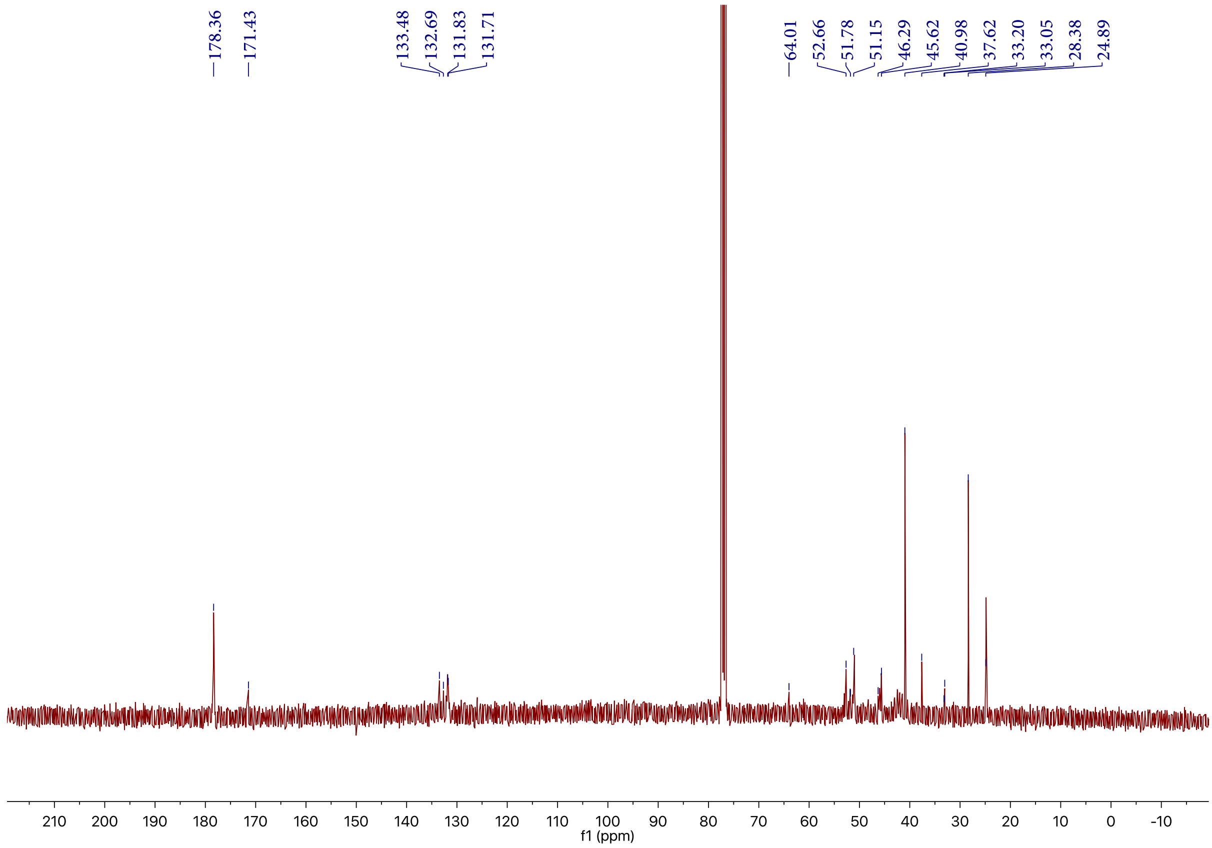


Figure S37 ^{13}C NMR spectrum (101MHz, $CDCl_3$) of Polymer 18

Copies of MALDI-ToF Mass Spectra

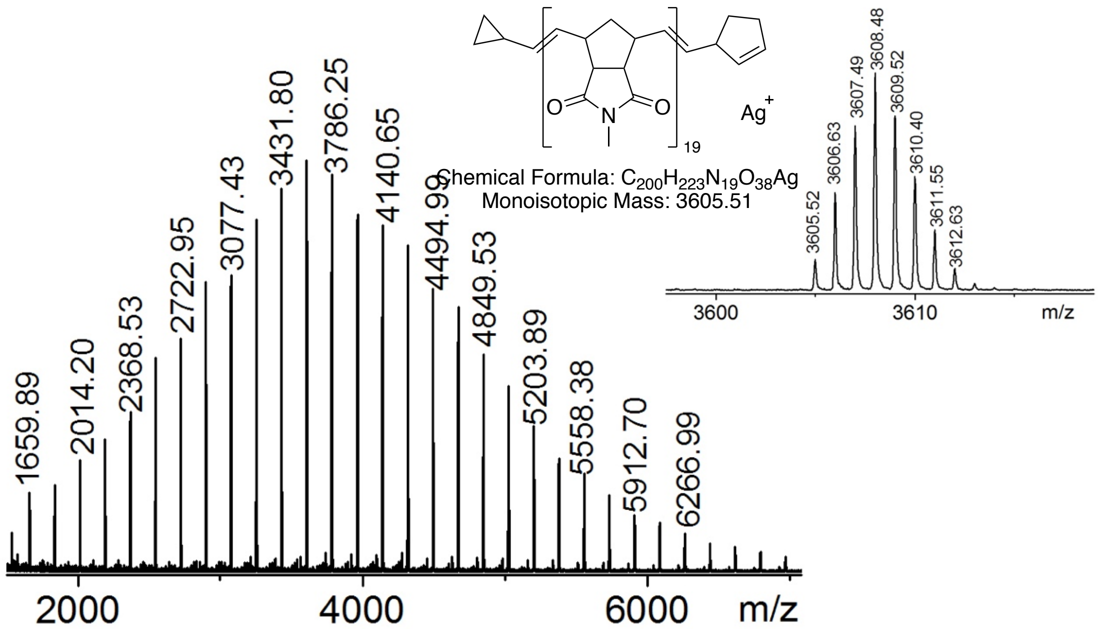


Figure S38 MALDI-ToF of Polymer 4

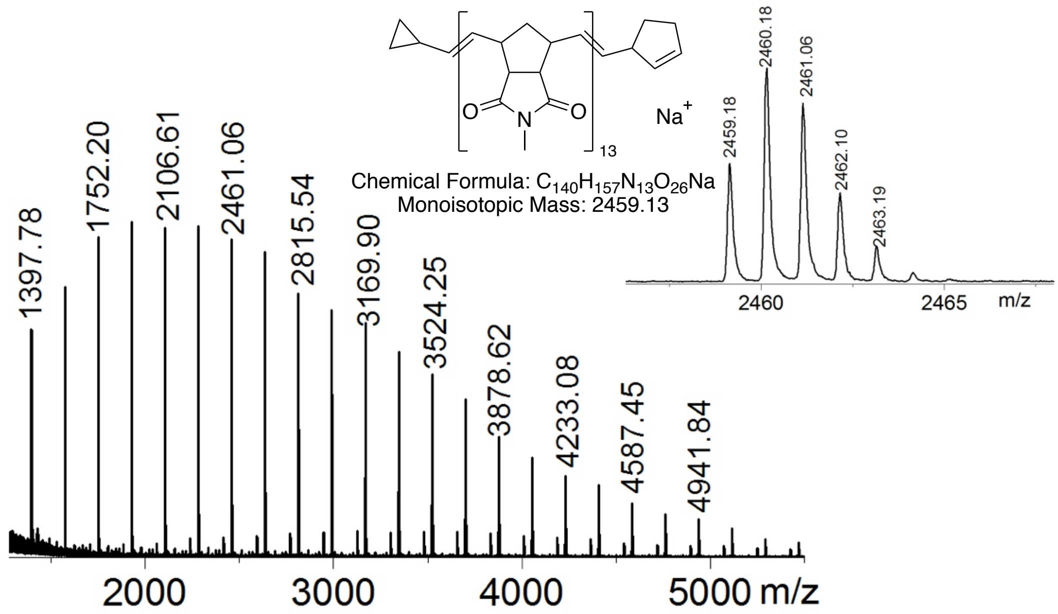


Figure S38 MALDI-ToF of Polymer 5

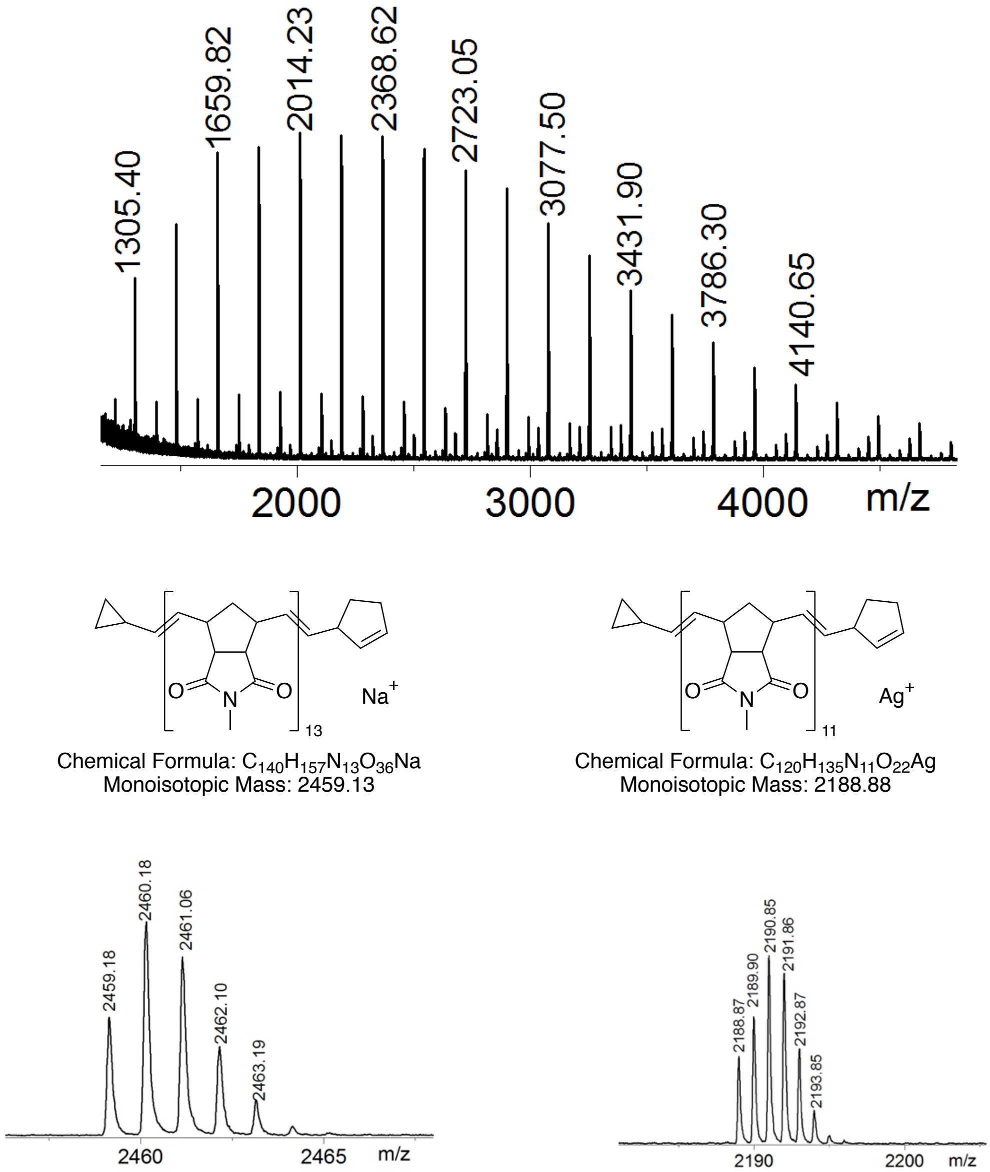


Figure S39 MALDI-ToF of Polymer 6

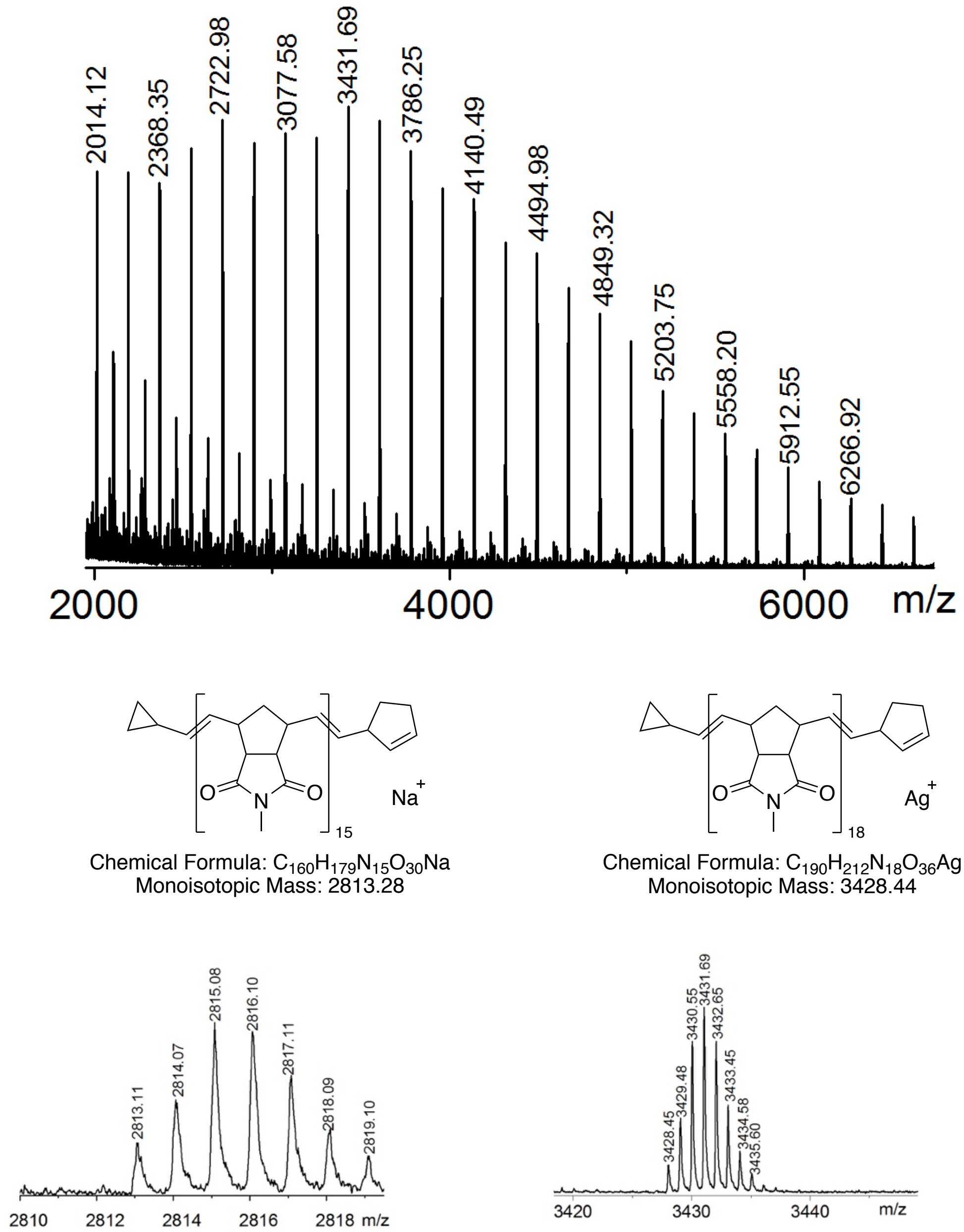


Figure S40 MALDI-ToF of Polymer 7

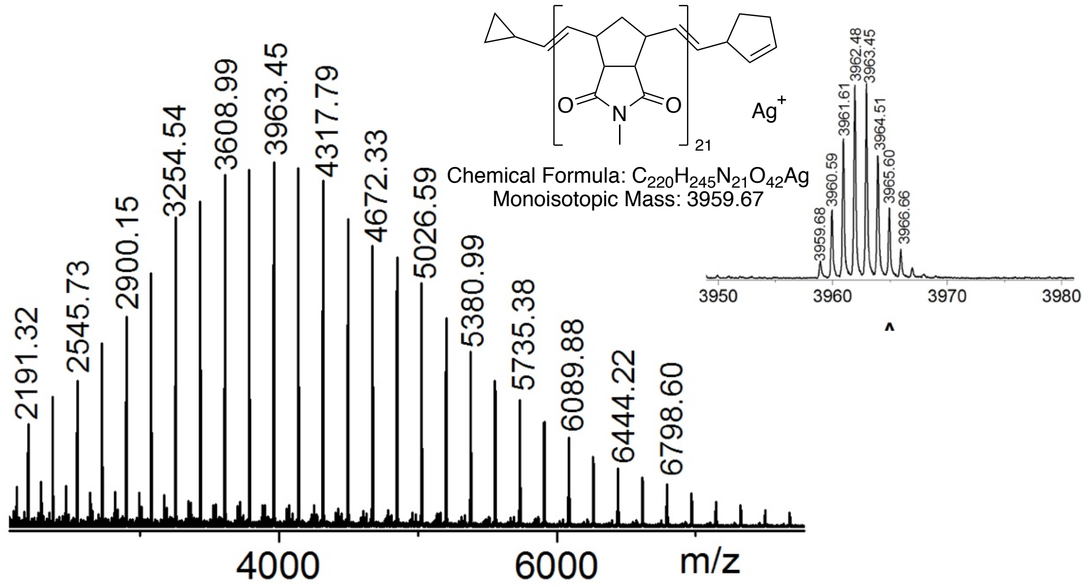


Figure S41 MALDI-ToF of Polymer 8

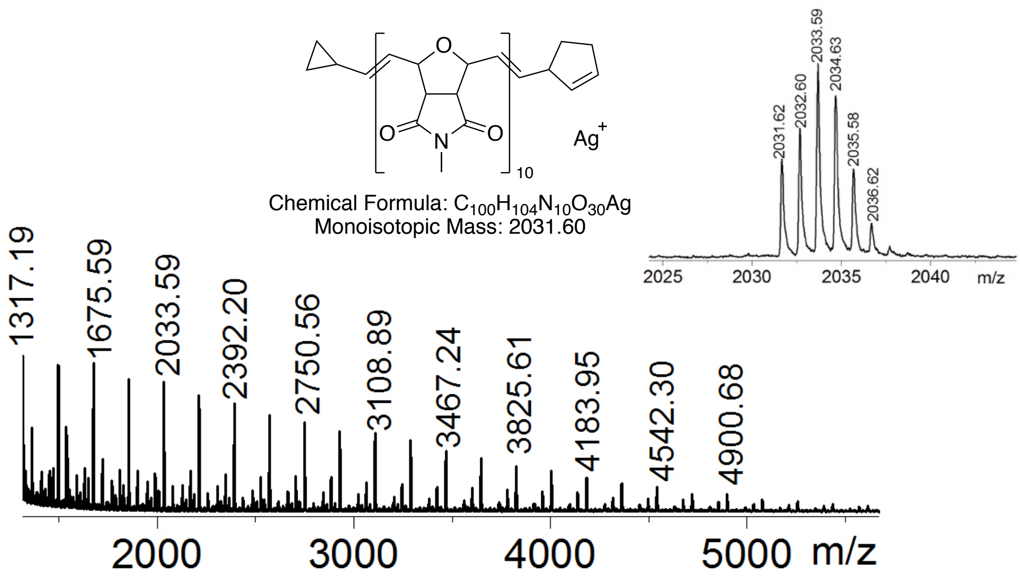


Figure S42 MALDI-ToF of Polymer 10

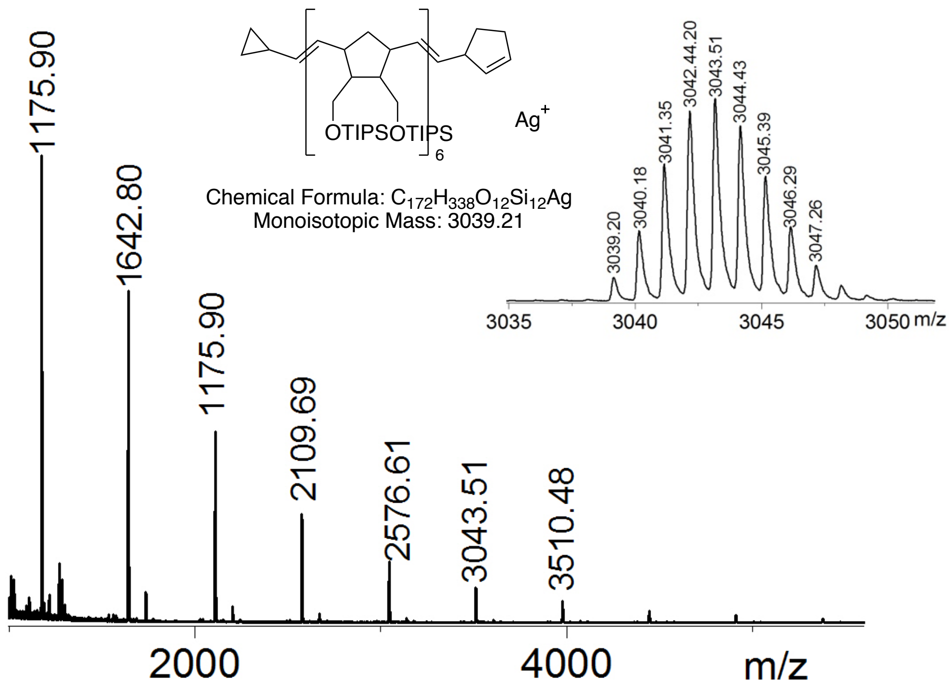


Figure S43 MALDI-ToF of Polymer 11

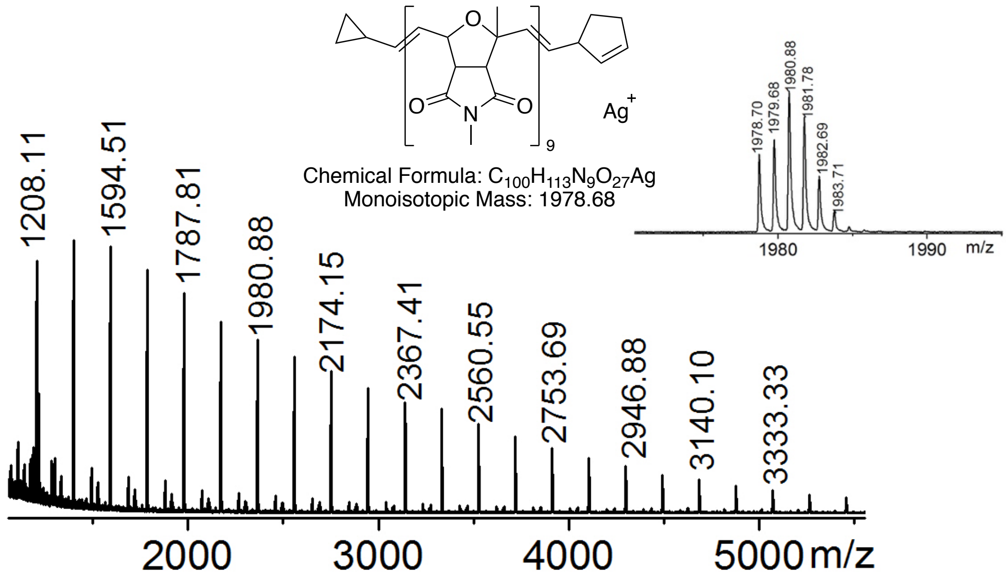


Figure S44 MALDI-ToF of Polymer 12

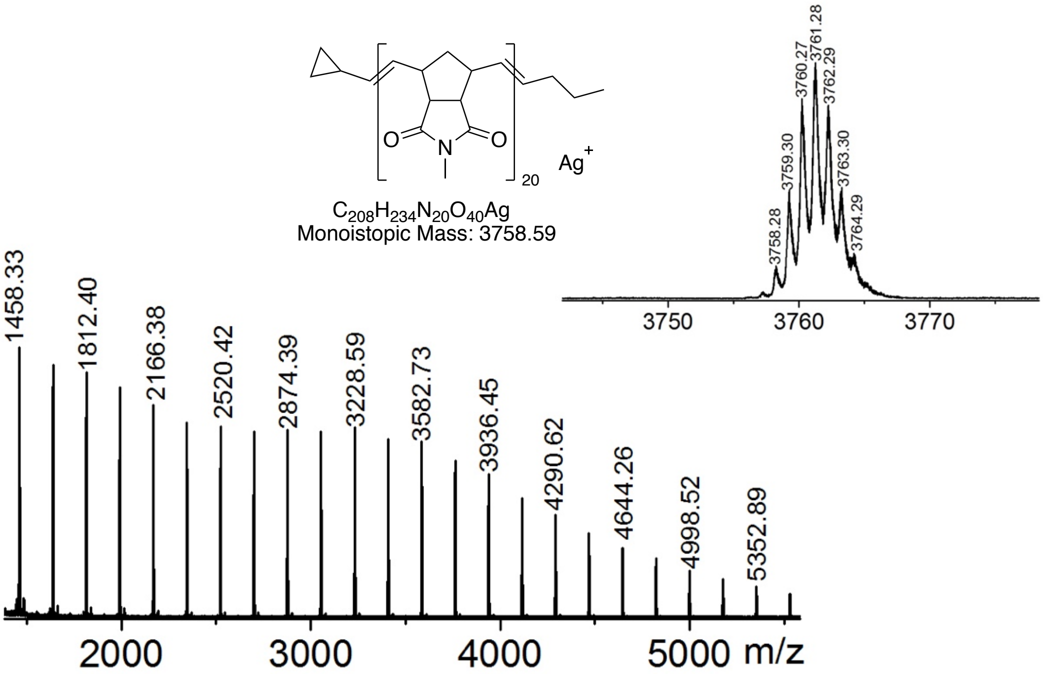


Figure S45 MALDI-ToF of Polymer 15

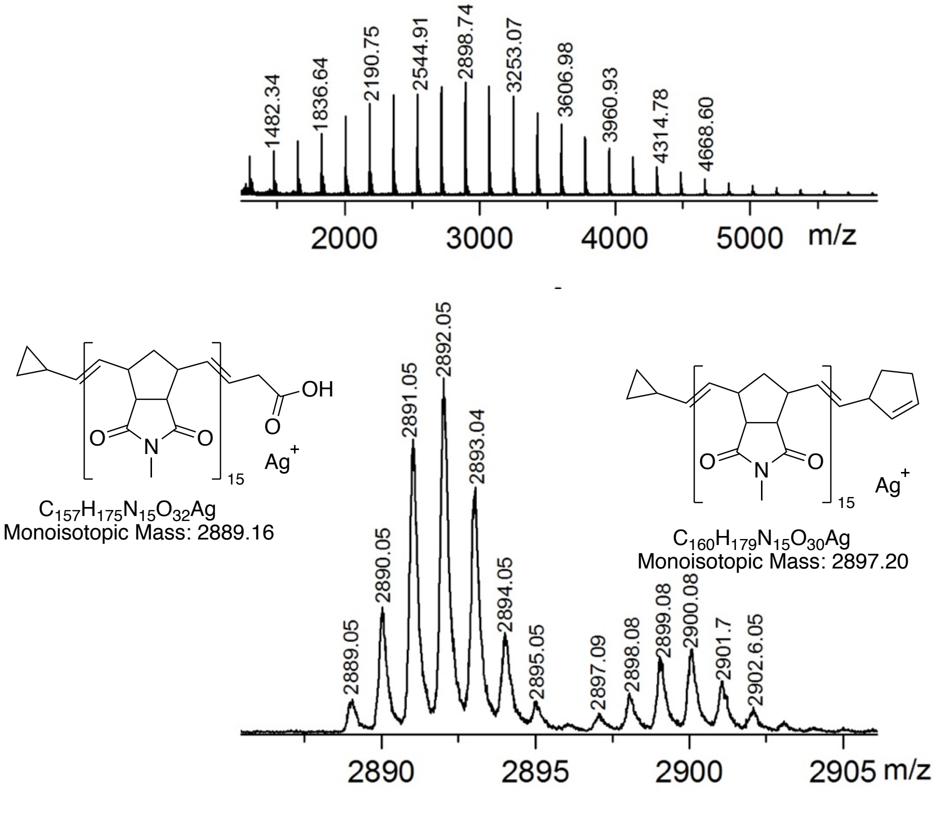


Figure S46 MALDI-ToF of Polymer 16

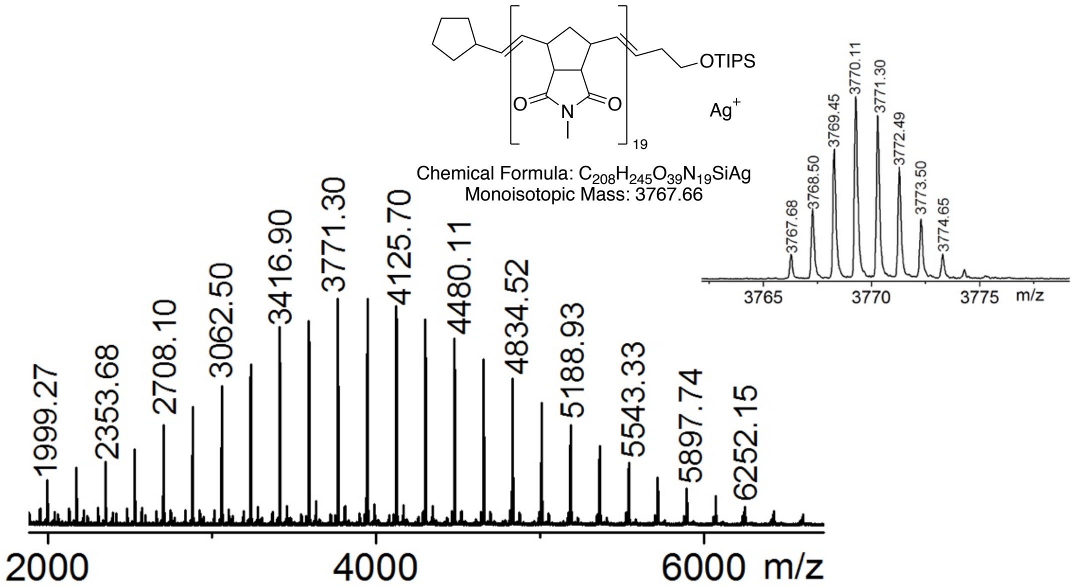


Figure S47 MALDI-ToF of Polymer 17

Copies of GPC Elugrams

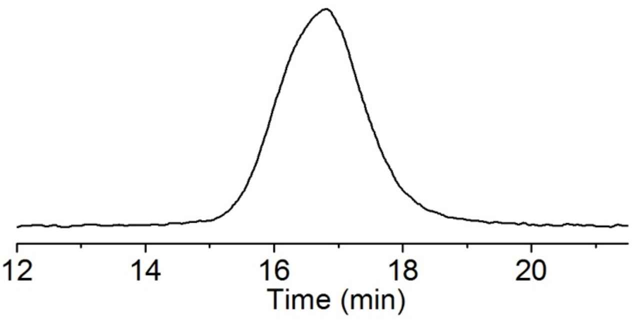


Figure S48 GPC trace of Polymer 1

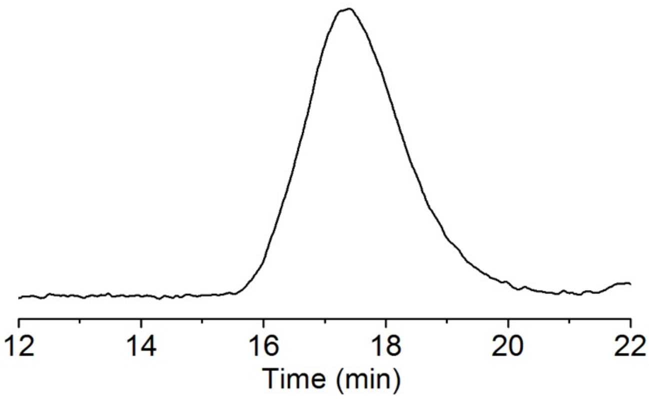


Figure S49 GPC trace of Polymer 2

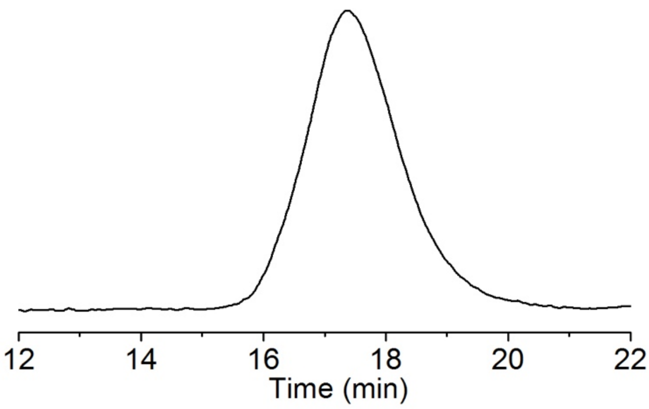


Figure S50 GPC trace of Polymer 3

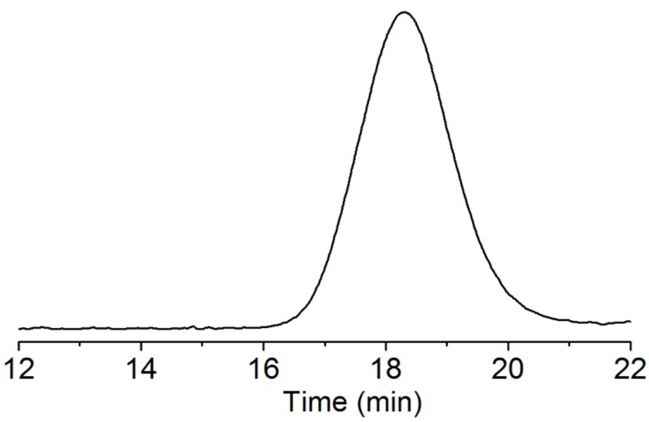


Figure S51 GPC trace of Polymer 4

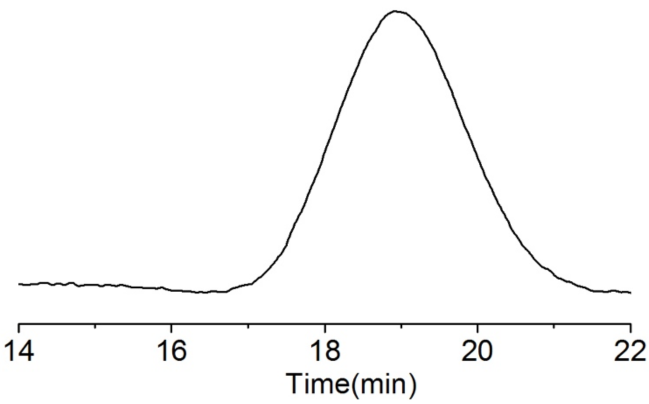


Figure S52 GPC trace of Polymer 5

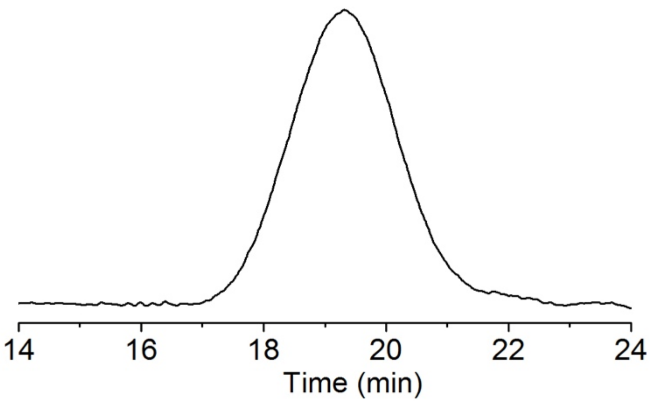


Figure S53 GPC trace of Polymer 6

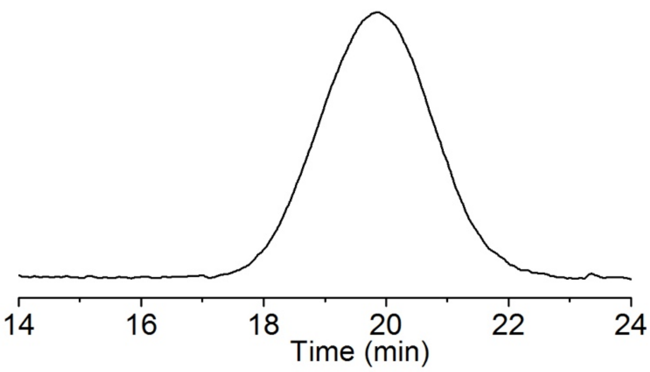


Figure S54 GPC trace of Polymer 7

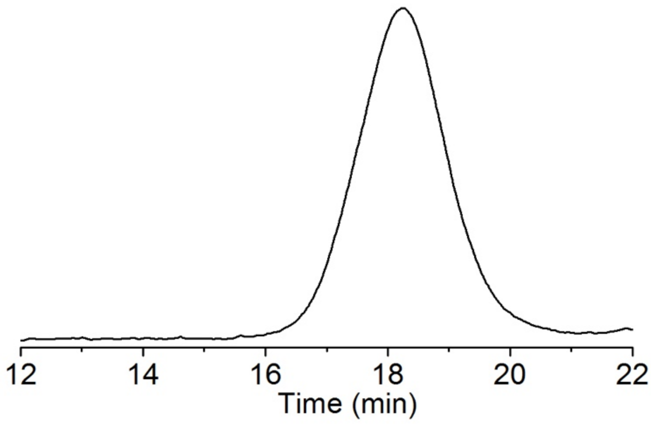


Figure S55 GPC trace of Polymer 8

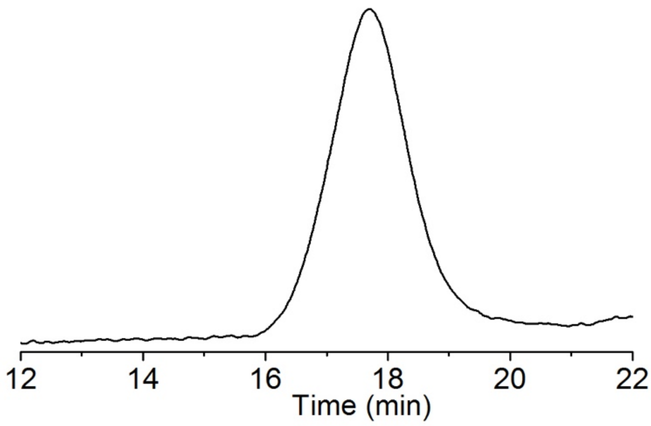


Figure S56 GPC trace of Polymer 9

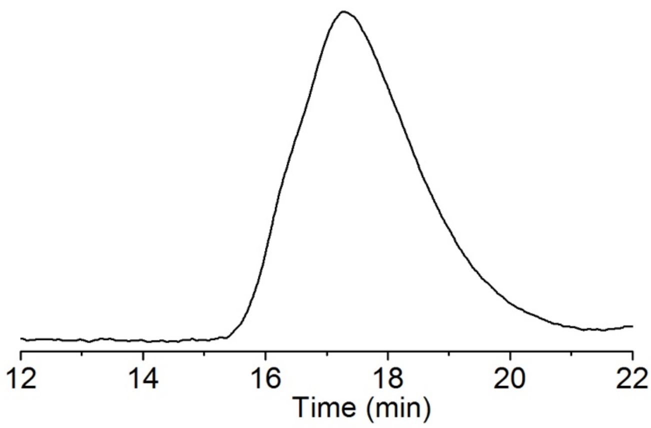


Figure S57 GPC trace of Polymer 10

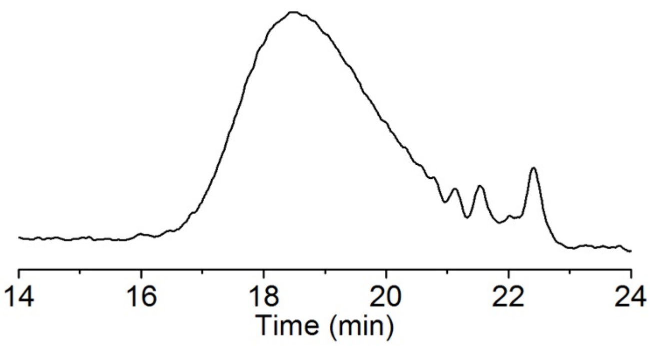


Figure S58 GPC trace of Polymer 11

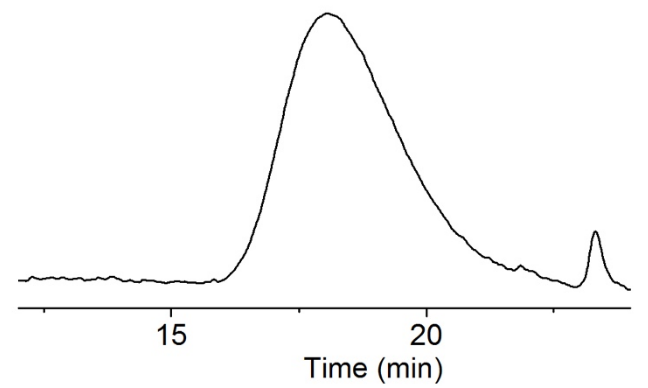


Figure S59 GPC trace of Polymer 12

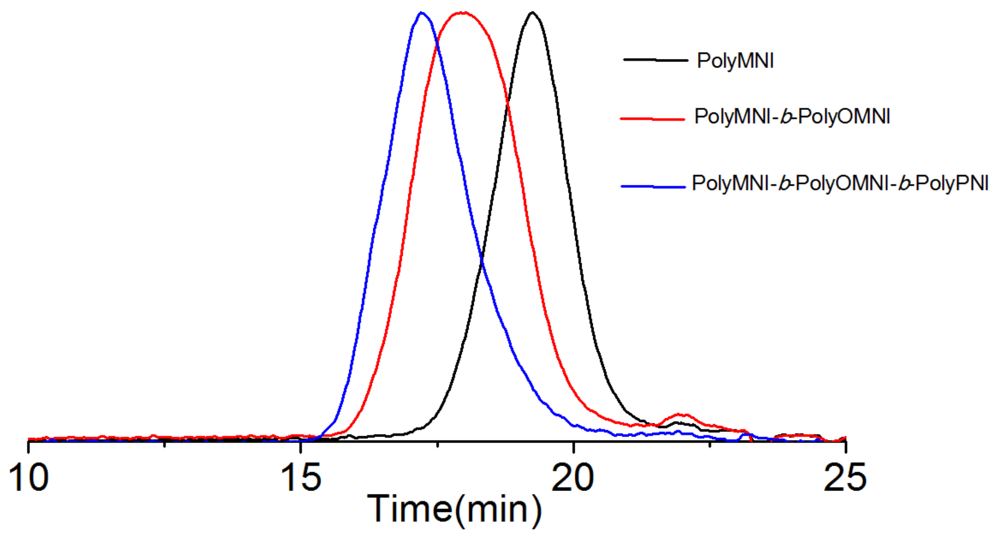


Figure S60 GPC trace of Polymer 13 (PolyMNI-*b*-PolyOMNI-*b*-PolyPNI)

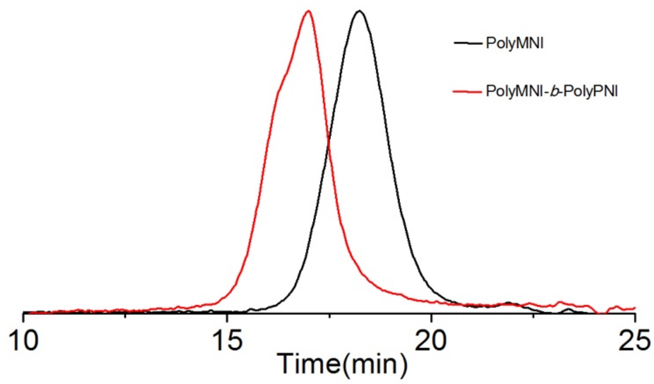


Figure S61 GPC trace of Polymer 14 (PolyMNI-*b*- PolyPNI)

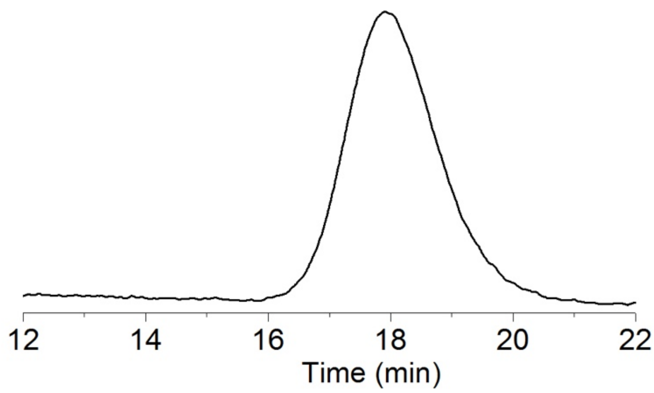


Figure S62 GPC trace of Polymer 15

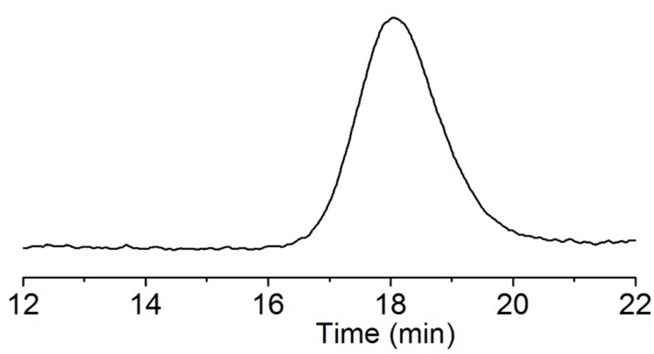


Figure S63 GPC trace of Polymer 16

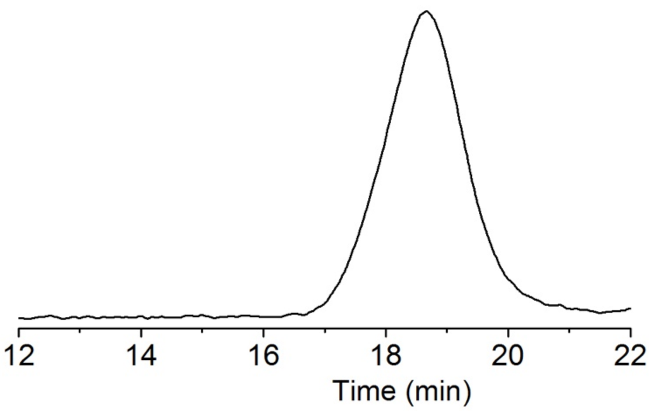


Figure S64 GPC trace of Polymer 17

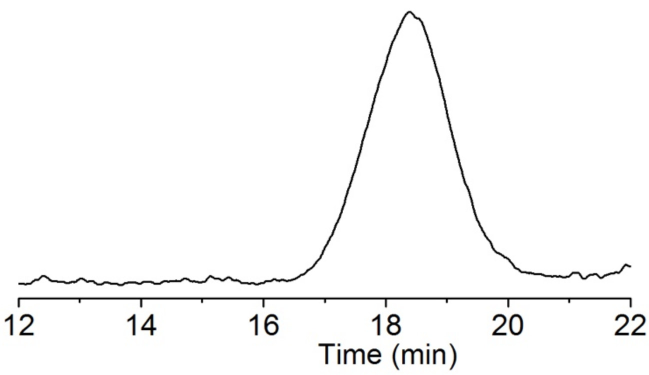


Figure S65 GPC trace of Polymer 18

Copies of TGA and DSC

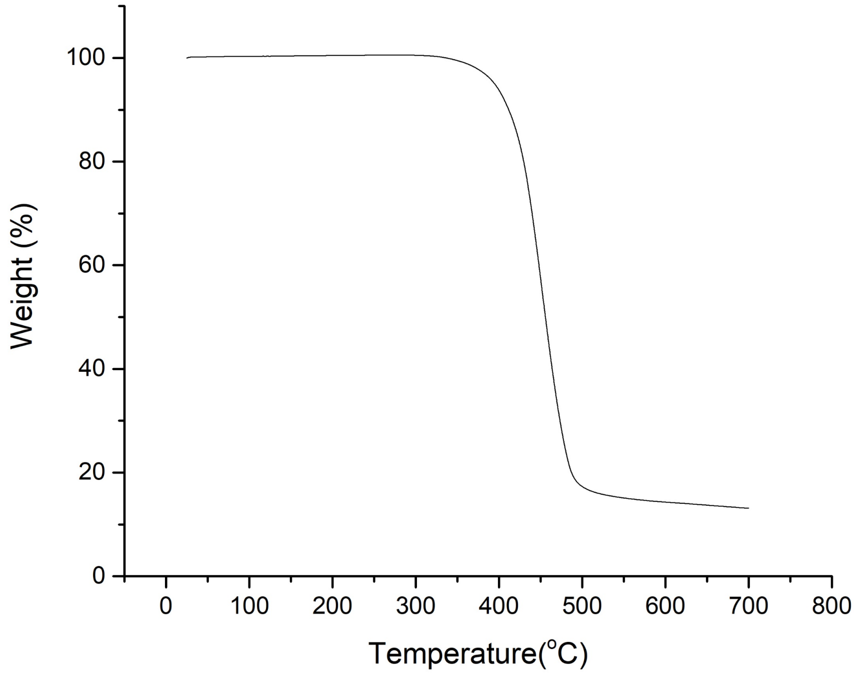


Figure S66 TGA of Polymer 13

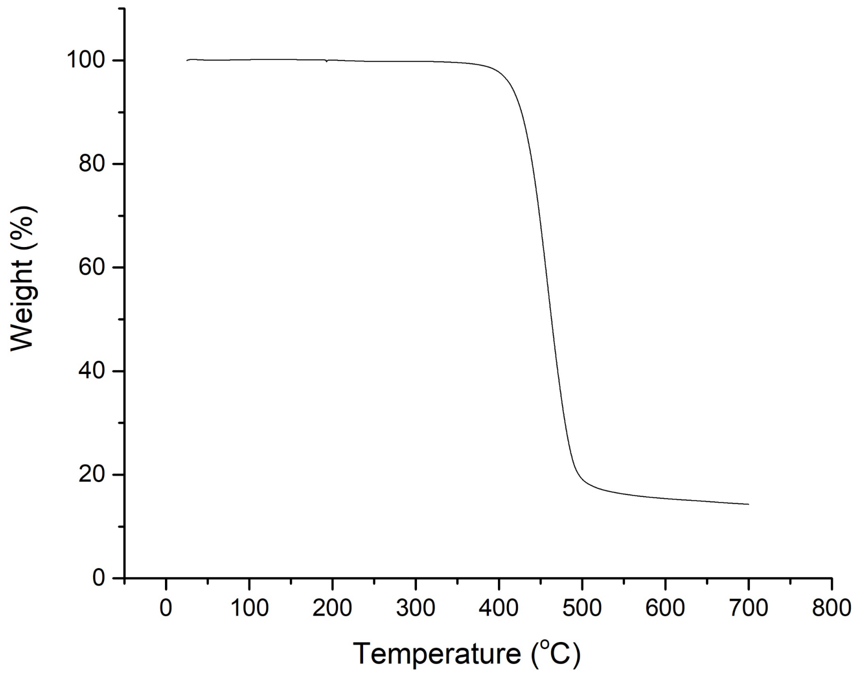


Figure S67 TGA of Polymer 14

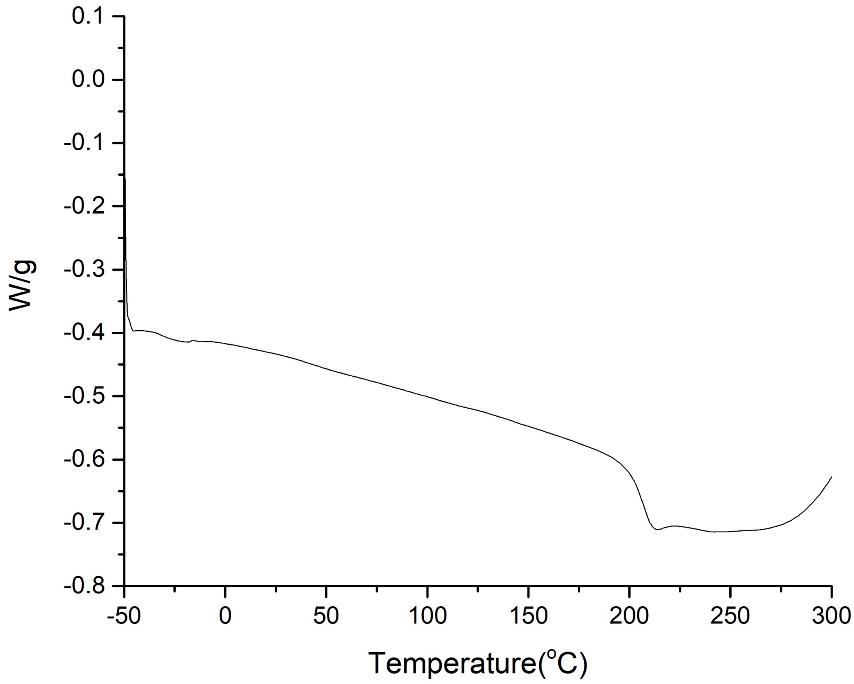


Figure S68 DSC of Polymer 13

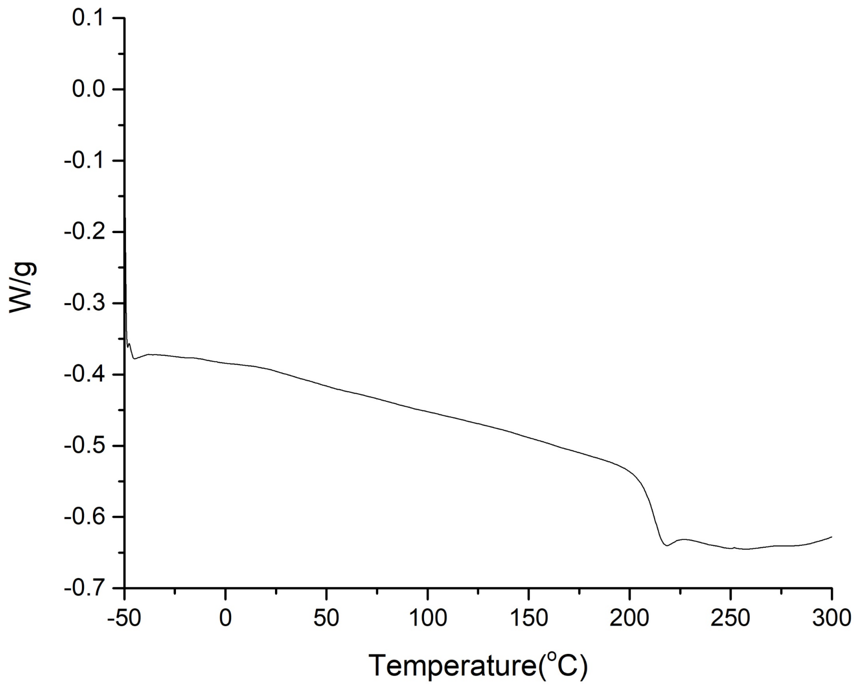


Figure S69 DSC of Polymer 14

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