Supplementary Information for

Organocatalyzed Photoredox Radical Cyclopolymerization of Methacrylate- and Acrylamide-Crotonate Hybrid Monomers

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1. Materials and Methods

1.1 Materials

All Chemicals were purchased from TCI, J&K, Energy Chemical, and Adamas-beta, and were used as received without further purification.

Deuterated chloroform was purchased from Cambridge Isotope Laboratories.

All anhydrous solvents were purchased from J&K and were used as received.

1.2 Methods

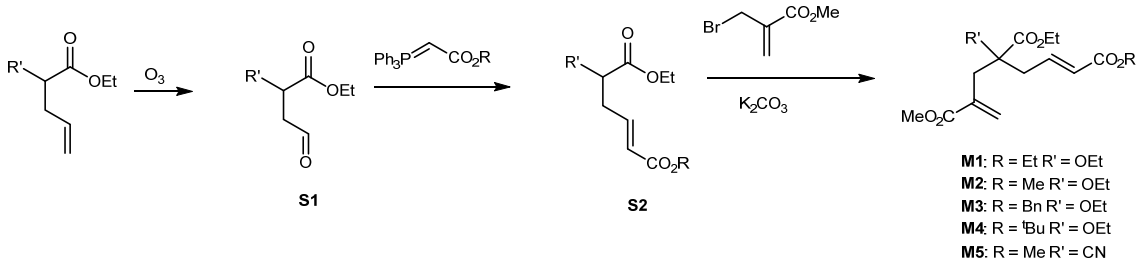
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 Hz (100 Hz for ^{13}C) spectrometer at ambient temperature. Chemical shifts (δ) for both ^{1}H and ^{13}C NMR spectra were given in ppm relative to tetramethylsilane. All NMR spectra were referenced to the residual solvent ($CHCl_3$) signal (δ = 7.26 ppm for ^{1}H NMR and δ = 77.00 ppm for ^{13}H NMR).

Analysis of polymer's number-average molecular weight (M_n) and dispersity ($Đ$) was performed using a Waters e2695 system (with one guard column and two Styragel columns) coupled with Waters 2414 refractive index detector (calibrated with 10 polystyrene standards). The analysis was performed at 40 °C using THF as the eluent at a flow rate of 1.0 mL/minute.

Decomposition temperatures ($T_d^{5\%}$) at 5% of weight loss and maximum rate decomposition temperatures (T_{max}) of the obtained polymers were measured by thermal gravimetric analysis (TGA) on a TA Q50 analyzer, TA instruments. Polymer samples were measured by heating the polymer samples from 25 °C to 700 °C at the rate of 10 °C/min. Glass transition temperatures (T_g) of obtained polymers were measured by differential scanning calorimetry (DSC) on a TA Q20 analyzer, at a rate of 10 °C/min. All T_g values were obtained from a second scan.

White-light LED beakers were made according to our previous procedure.[1] White LED strips (Yifaguang, item no. 5050, 14.4 W/meter) was wrapped around the inside of a 400 mL beaker, and powered by a 12VDC power Supply (Yifaguang, item no. 12V8A96W).

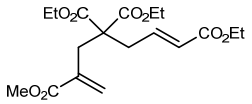
2. Synthesis of Monomers



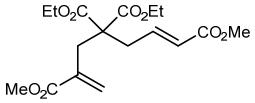
According to the literature's procedure,[1] in situ-generated ozone was bubbled through a 100 mL round-bottomed flask with diethyl allylmalonate (5.9 mL, 30 mmol, 1.0 equiv.) and CH_2Cl_2 (50 mL) at -78 ℃ until it turned a deep blue color. Then oxygen was bubbled through the resulting solution until the color dissipated. Triphenylphosphine (11.80 g, 45 mmol, 1.50 equiv.) was added and the mixture was stirred at room temperature for 12 hours. The mixture was concentrated under reduced pressure, and purified by flash column chromatography (EtOAc/hexanes) to give **S1**.

S1 (2.02 g, 10 mmol, 1.00 equiv.) was added in one portion to a solution of ethyl 2-(triphenylphosphoranylidene)acetate (3.85 g, 11 mmol, 1.10 equiv.) in anhydrous CH_2Cl_2 (60 mL). The resulting mixture was stirred at room temperature until full conversion of **S1**. The mixture was concentrated, and the residue was purified by flash column chromatography (EtOAc/hexanes) to give **S2**.

To a 100 mL oven-dried flask, **S2** (1.36 g, 5 mmol, 1.0 equiv.), 20 mL of anhydrous DMF, methyl 2-(bromomethyl)acrylate (1.38 g, 7.7 mmol, 1.5 equiv.) and K_2CO_3 (1.38 g, 10 mmol, 2.00 equiv.) were sequentially added. The resulting mixture was rigorously stirred at room temperature for 12 hours. The reaction was quenched with water, then extracted with EtOAc (3 × 30 mL). The combined organic phase was washed three times with H_2O and brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography (hexane/ EtOAc) to give the pure diene monomer.

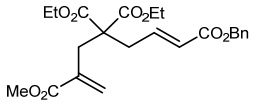


1,4,4-triethyl 6-methyl (E)-hepta-1,6-diene-1,4,4,6-tetracarboxylate (M1)
Colorless oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.87 – 6.79 (m, 1H), 6.28 (s, 1H), 5.88 – 5.81 (m, 1H), 5.66 (s, 1H), 4.23 – 4.09 (m, 6H), 3.72 (s, 3H), 2.99 (s, 2H), 2.71 (d, *J* = 7.6 Hz, 2H), 1.25 (dt, *J* = 14.3, 7.1 Hz, 9H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.0, 167.2, 165.8, 142.6, 135.6, 129.6, 125.1, 61.6, 60.3, 57.3, 52.0, 35.6, 34.2, 14.2, 13.9.

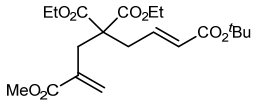


4,4-diethyl 1,6-dimethyl (E)-hepta-1,6-diene-1,4,4,6-tetracarboxylate (M2)
Colorless oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.85 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.28 (d, *J* = 1.3 Hz, 1H), 5.85 (dd, *J* = 15.6, 1.5 Hz, 1H), 5.66 (d, *J* = 1.3 Hz, 1H), 4.23 – 4.08 (m, 4H), 3.71 (d, *J* = 2.4 Hz, 6H), 2.98 (s, 2H), 2.71 (dd, *J* = 7.6, 1.5 Hz,

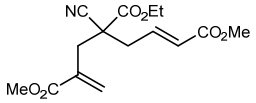
2H), 1.23 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.0, 167.2, 166.2, 143.0, 135.6, 129.6, 124.6, 61.6, 57.3, 52.0, 51.5, 35.6, 34.1, 13.9.



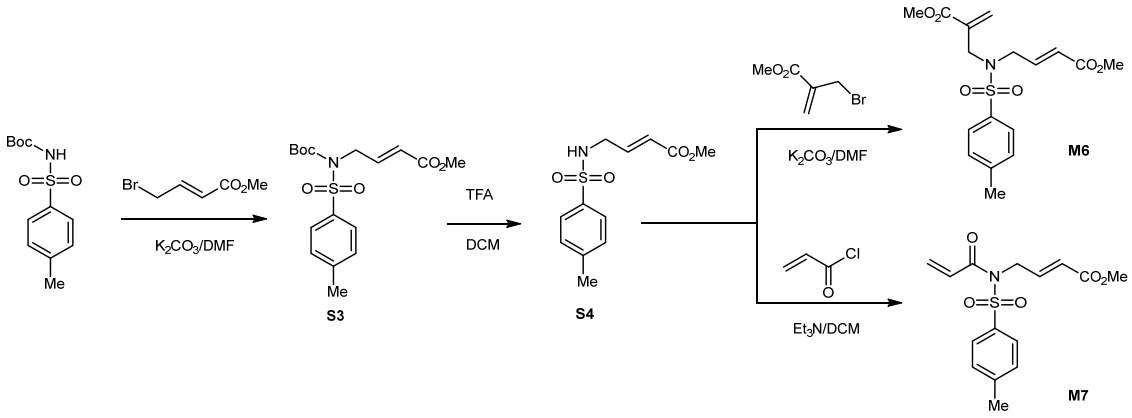
1-benzyl 4,4-diethyl 6-methyl (E)-hepta-1,6-diene-1,4,4,6-tetracarboxylate (M3)
Colorless oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.41 – 7.27 (m, 5H), 6.90 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.28 (d, *J* = 1.3 Hz, 1H), 5.90 (dt, *J* = 15.5, 1.4 Hz, 1H), 5.66 (d, *J* = 1.4 Hz, 1H), 5.16 (s, 2H), 4.24 – 4.08 (m, 4H), 3.70 (s, 3H), 2.99 (s, 2H), 2.72 (dd, *J* = 7.6, 1.5 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 6H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.0, 167.2, 165.6, 143.5, 136.0, 135.6, 129.6, 128.5, 128.1, 124.6, 66.1, 61.6, 57.3, 52.0, 35.7, 34.2, 13.9.



1-(tert-butyl)4,4-diethyl6-methyl(E)-hepta-1,6-diene-1,4,4,6-tetracarboxylate(M4)
Colorless oil.**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 6.71 (dt, *J* = 15.4, 7.6 Hz, 1H), 6.28 (d, *J* = 1.3 Hz, 1H), 5.76 (dt, *J* = 15.5, 1.5 Hz, 1H), 5.66 (d, *J* = 1.3 Hz, 1H), 4.22 – 4.15 (m, 2H), 4.15 – 4.09 (m, 2H), 3.71 (s, 3H), 3.00 – 2.95 (m, 2H), 2.68 (dd, *J* = 7.6, 1.5 Hz, 2H), 1.45 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.0, 167.2, 165.2, 141.3, 135.6, 129.5, 126.8, 80.3, 61.5, 57.3, 51.9, 35.5, 34.2, 28.1, 13.9.



4-ethyl 1,6-dimethyl (E)-4-cyanohepta-1,6-diene-1,4,6-tricarboxylate(M5)
Colorless oil.**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.87 (dt, *J* = 15.3, 7.5 Hz, 1H), 6.44 (d, *J* = 0.7 Hz, 1H), 5.99 (dt, *J* = 15.6, 1.4 Hz, 1H), 5.86 (q, *J* = 1.0 Hz, 1H), 4.32 – 4.15 (m, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 2.97 (dd, *J* = 14.0, 1.0 Hz, 1H), 2.92 – 2.80 (m, 2H), 2.66 (ddd, *J* = 14.2, 7.6, 1.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.0, 166.4, 165.7, 139.6, 133.8, 130.8, 126.4, 117.4, 63.2, 52.3, 51.7, 48.7, 39.0, 37.6, 13.9.



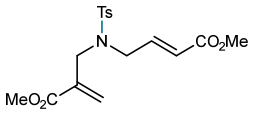
According to the literature's procedure,[2] to a 100 mL oven-dried flask, TsNHBoc (4.77 g, 17.6 mmol, 1.00 equiv.), methyl 4-bromobut-2-enoate (2.2 mL, 18.5 mmol, 1.05 equiv.), 30 mL of anhydrous DMF, NaI (527 mg, 3.5 mmol, 0.17 equiv.) and K_2CO_3 (4.86 g, 35.2 mmol, 2.00 equiv.) were sequentially added. The mixture was

vigorously stirred at 60 °C for 3 hours. The reaction was quenched with H_2O, extracted with EtOAc (3 × 30 mL). The combined organic phase was washed three times with H_2O and brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by recrystallization (hexane/ DCM) to give **S3** as a white solid. 5.41 g, 83 % yield.

To a 100 mL oven-dried flask containing **S3** (2.44 g, 6.6 mmol, 1.00 equiv.) in 20 mL of anhydrous CH_2Cl_2 at 0 °C, TFA (3.1 mL, 39.6 mmol, 6.00 equiv.) was slowly added. The mixture was stirred at room temperature for 16 hours. Then the reaction was quenched with saturate aq. $NaHCO_3$, extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was washed with H_2O and brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by recrystallization (hexane/DCM) to give **S4** as a white solid. 1.59 g, 89% yield.

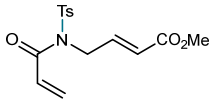
To a solution of **S4** (539 mg, 2.0 mmol, 1.00 equiv.) in 15 mL of anhydrous DMF, methyl 2-(bromomethyl)acrylate (430 mg, 2.4 mmol, 1.20 equiv.) and K_2CO_3 (553 mg, 4.0 mmol, 2.00 equiv.) were added. The resulting suspension was vigorously stirred at room temperature for 15 hours. The reaction was quenched with 50 mL H_2O, and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by flash column chromatography to give **M6** as a white solid. 526 mg, 72% yield.

To a 100 mL oven-dried flask containing a solution of **S4** (1.0 g, 3.7 mmol, 1.00 equiv.) and triethylamine (1.6 mL, 11.1 mmol, 3.00 equiv.) in 20 mL of anhydrous CH_2Cl_2 at 0 °C, acryloyl chloride (0.9 mL, 11.1 mmol. 3.00 equiv.) was added dropwise. The mixture was stirred at room temperature for 12 h. The reaction was quenched with 1 M aq. $NaHCO_3$, extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was washed with H_2O and brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography to give **M7** as a white solid (0.67 g, 56% yield).



methyl(E)-4-((N-(2-(methoxycarbonyl)allyl)-4-methylphenyl)sulfonamido)but-2-enoate(M6)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 – 7.65 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.66 (dt, *J* = 15.6, 6.0 Hz, 1H), 6.35 (s, 1H), 5.91 – 5.79 (m, 2H), 4.02 (s, 2H), 3.96 (dd, *J* = 6.0, 1.7 Hz, 2H), 3.71 (d, *J* = 4.2 Hz, 6H), 2.43 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.2, 165.9, 143.8, 142.1, 136.5, 135.1, 129.8, 128.1, 127.2, 123.8, 52.0, 51.7, 49.0, 48.0, 21.5.



methyl (E)-4-(N-tosylacrylamido)but-2-enoate(M7)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.85 (m, 2H), 6.40 (dd, *J* = 16.7, 1.6 Hz, 1H), 5.97 (dt, *J* = 15.7, 1.8 Hz, 1H), 5.80 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.60 (dd, *J* = 5.2, 1.8 Hz, 2H), 3.73 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.1, 165.2, 145.3, 142.0, 136.2, 132.2, 130.0, 127.9, 127.6, 123.2, 51.7, 46.7, 21.6.

3.#Visible-light-Promoted Radical cyclopolymerization of divinyl monomer

3.1 General Polymerization Procedure

An oven-dried 20 mL vial equipped with a small magnetic stir bar was transferred into a N_2-filled glove box. To this vial, monomer (0.5 mmol), anhydrous PhCl or EtOAc, and the alkyl bromide solution were sequentially added. The vial was then tightly capped and placed under white LED irradiation while stirring in the glovebox with a cooling fan to maintain the temperature at ~30 °C. For the progress analysis, an aliquot of the reaction mixture was taken via syringe and immediately quenched by injecting into a 1.5 mL vial containing ~0.6 mL of $CDCl_3$. This aliquot was analyzed via ^1H NMR for monomer conversion, then dried under vacuum for direct GPC analysis to obtain the M_n and $Đ$. For further purification, the reaction mixture was slowly added into 20.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane (5.0 mL × 2) and dried overnight under vacuum at 50 °C to a constant weight.

3.2 Optimization for the Polymerization

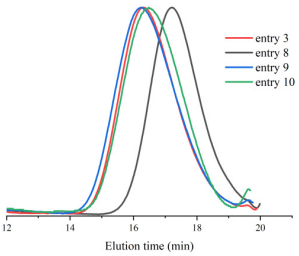


Fig. S1 Overlay of GPC traces corresponding to **PM1** in Table 1.

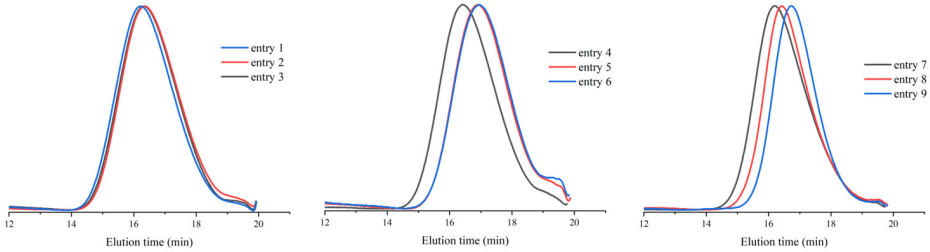


Fig. S2 Overlay of GPC traces for corresponding to **PM1** in Table 2.

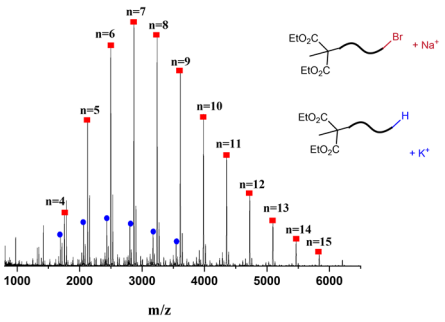


Fig. S3 MALDI-TOF MS spectrum of low-MW **PM1** synthesized with TBAB

3.3 Kinetic Study

Table S1. Progress analysis for polymerization of **M1** under 10.8 W white LED irradiation[a]

entry	Time	Conv.% [b]	$M_{n,theo}$(kDa) [c]	M_n(kDa)[d]	$Đ$ [d]
1	0	0	-	-	
2	0.5	17	3.4	-	
3	1	34	6.5	9.2	1.72
4	2	59	11.2	13.3	1.72
5	3	72	13.6	14.6	1.77
6	4	81	15.3	15.4	1.75
7	5	86	16.2	14.6	1.83

[a]Polymerizations performed using 0.5 mmol of **M1**, 0.01 mmol of DBMM, 0.001 mmol of PC, 0.5 mL of PhCl, and irradiated by white LEDs (10.8 W) for 12 h. A cooling fan was used to maintain the temperature ~30 °C. [b]Measured by crude ^{1}H-NMR. [c]$M_{n,theo}$ = MW(initiator) + MW(**M1**) × conversion × ([**M1**]/[initiator]). [d]Determined by gel permeation chromatography (GPC) in THF (1.0 mL/min, 40 °C) and calibrated with polystyrene standards.

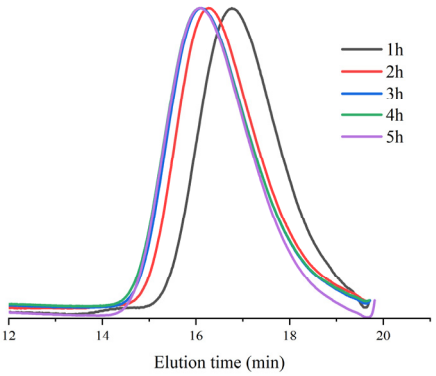


Fig. S4 Overlay of GPC traces corresponding to **PM1** in Table S1.

Table S2. Results of progress analysis for polymerization of **M1** under 7.2 W white LED irradiation[a]

entry	Time	Conv.% [b]	$M_{n,theo}$(kDa) [c]	M_n(kDa)[d]	$Đ$ [d]
1	0	0	-	-	-
2	0.5	18	3.6	6.7	1.67
3	1	33	6.4	12.2	1.66
4	2	53	10.1	14	1.68
5	3	66	12.5	16	1.73
6	4	75	14.1	16.1	1.78

[a]Polymerizations performed using 0.5 mmol of **M1**, 0.01 mmol of DBMM, 0.001 mmol of PC, 0.5 mL of PhCl, and irradiated by white LEDs (7.2 W) for 12 h. A cooling fan was used to maintain the temperature ~30 °C. [b]Measured by crude ^{1}H-NMR. [c]$M_{n,theo}$ = MW(initiator) + MW(**M1**) × conversion × ([**M1**]/[initiator]). [d]Determined by gel permeation chromatography (GPC) in THF (1.0 mL/min, 40 °C) and calibrated with polystyrene standards.

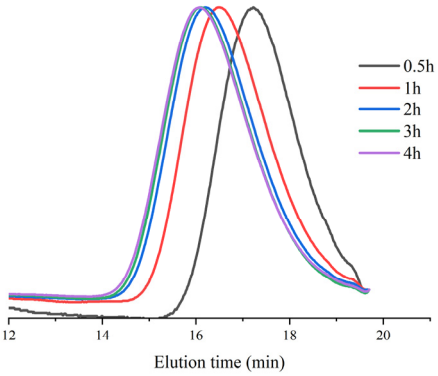


Fig. S5 Overlay of GPC traces corresponding to **PM1** in Table S2.

Table S3. Results of progress analysis for polymerization of **M1** under 3.6 W white LED irradiation[a]

entry	Time	Conv.% [b]	$M_{n,theo}$(kDa) [c]	M_n(kDa)[d]	$Đ$ [d]
1	0	0	-	-	-
2	0.5	17	3.4	4.8	1.63
3	1	31	6.0	8.9	1.7
4	2	49	9.3	12.8	1.78
5	3	62	11.7	14.2	1.79
6	4	70	13.2	15.3	1.74

[a]Polymerizations performed using 0.5 mmol of **M1**, 0.01 mmol of DBMM, 0.001 mmol of PC, 0.5 mL of PhCl, and irradiated by white LEDs (3.6 W) for 12 h. A cooling fan was used to maintain the temperature ~30 °C. [b]Measured by crude ^{1}H-NMR. [c]$M_{n,theo}$ = MW(initiator) + MW(**M1**) × conversion × ([**M1**]/[initiator]). [d]Determined by gel permeation chromatography (GPC) in THF (1.0 mL/min, 40 °C) and calibrated with polystyrene standards.

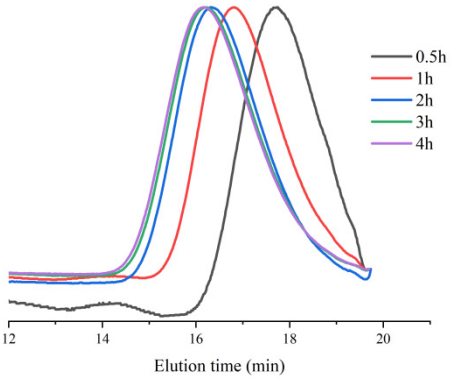


Fig. S6 Overlay of GPC traces for **PM1** in Table S3.

Table S4. Results of progress analysis for polymerization of **M1** under 1.4 W white LED irradiation[a]

entry	Time	Conv.% [b]	$M_{n,theo}$(kDa) [c]	M_n(kDa)[d]	$Đ$ [d]
1	0	0	-	-	-
2	0.5	7	-	-	-
3	1	15	-	-	-
4	2	26	5.1	5.4	1.78
5	3	36	6.9	6.7	1.8
6	4	45	8.6	7.8	1.83
7	5	52	9.9	9.5	1.78

[a]Polymerizations performed using 0.5 mmol of **M1**, 0.01 mmol of DBMM, 0.001 mmol of PC, 0.5 mL of PhCl, and irradiated by white LEDs (1.4 W) for 12 h. A cooling fan was used to maintain the temperature ~30 °C. [b]Measured by crude ^{1}H-NMR. [c]$M_{n,theo}$ = MW(initiator) + MW(**M1**) × conversion × ([**M1**]/[initiator]). [d]Determined by gel permeation chromatography (GPC) in THF (1.0 mL/min, 40 °C) and calibrated with polystyrene standards.

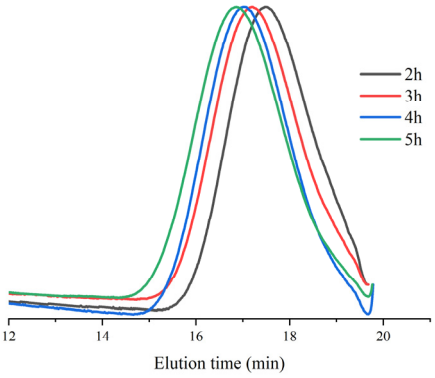


Fig. S7 Overlay of GPC traces corresponding to **PM1** in Table S4.

3.4 Pusled-Irradiation Experiment

Table S5. Results of pusled-irradiation experiment of **PM1** at ~30 °C[a]

entry	Time	Conv.% [b]	$M_{n,theo}$(kDa) [c]	M_n(kDa)[d]	$Đ$ [d]
1	0	0	-	-	-
2	2	24	4.7	4.8	1.81
3	4	24	4.7	4.8	1.82
4	6	42	8.0	7.5	1.87
5	12	42	8.0	7.5	1.83
6	13	51	9.7	8.7	1.87

[a]Polymerizations performed using 0.5 mmol of **M1**, 0.01 mmol of DBMM, 0.001 mmol of PC, 0.5 mL of PhCl, and irradiated by white LEDs (1.4 W) for 12 h. A cooling fan was used to maintain the temperature ~30 °C. [b]Measured by crude ^{1}H-NMR. [c]$M_{n,theo}$ = MW(initiator) + MW(**M1**) × conversion × ([**M1**]/[initiator]). [d]Determined by gel permeation chromatography (GPC) in THF (1.0 mL/min, 40 °C) and calibrated with polystyrene standards.

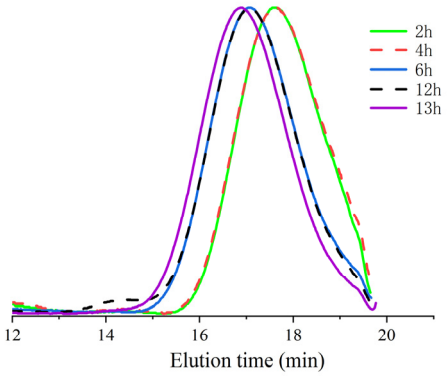


Fig. S8 Overlay of GPC traces corresponding to **PM1** in Table S5.

3.5 Chain-Extension Experiment

*Synthesis of **PM1** macroinitiator.* An oven-dried 20 mL vial equipped with a small magnetic stir bar was transferred into a N_2-filled glove box. To this vial, **M1** (0.5 mmol) and 0.20 mL of the stock solution of DBMM in PhCl (0.05 M) were added. The vial was then tightly capped and placed in the beaker wrapped with white LED strips while stirring in the glovebox with a cooling fan to maintain the temperature at ~30 °C. For purification, the reaction mixture was slowly added into 50.0 mL of hexane while stirring at room temperature. The precipitated polymer was collected by vacuum filtration, washed with hexane (5.0 mL ×2) and dried overnight under vacuum at 50 °C to a constant weight.

Chain-Extension Experiment. An oven-dried 20 mL charged with a magnetic stir bar and **PM1** macroinitiator (M_n = 5.3 kDa, $Đ$ = 1.71, 50 mg, 0.01 mmol) was transferred into a N_2-filled glovebox. To this vial, **M6** monomer (0.50 mmol) and 1.0 mL of anhydrous solvent were quickly added. The vial was then tightly capped and irradiated in the beaker equipped with white LED strips while stirring in the glove box. A cooling fan was used to keep the temperature at ~30 °C. After 12 h, an aliquot was taken for ^{1}H NMR analysis. The aliquot was then dried under vacuum for direct GPC analysis.

An oven-dried 20 mL charged with a magnetic stir bar and **PM1** macroinitiator (M_n = 4.9 kDa, $Đ$ = 1.60, 230 mg, 0.047 mmol) was transferred into a N_2-filled glovebox. To this vial, MMA monomer (0.50 ml, 4.7mmol) and 1 mL of anhydrous solvent were quickly added. The vial was then tightly capped and irradiated in the beaker equipped with white LED strips while stirring in the glove box. A cooling fan was used to keep the temperature at ~30 °C. After 32h, an aliquot was taken for ^{1}H NMR analysis. The aliquot was then dried under vacuum for direct GPC analysis.

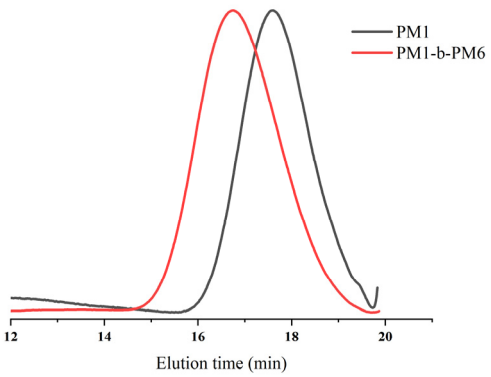
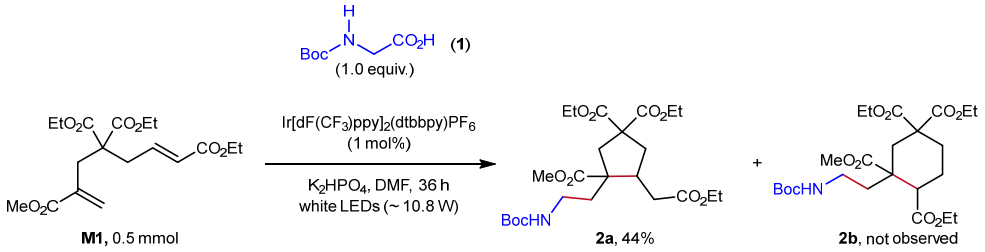
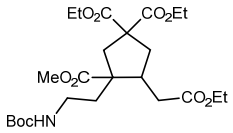


Fig. S9 Overlay of GPC traces before and after chain extension of **PM1** with **M6**.

4. Small-Molecule Model Reaction of M1



According to the literature procedure,[4] an oven-dried 20 mL vial equipped with a small magnetic stir bar was charged with Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (5.6 mg, 5 μmol, 0.01 equiv), Boc-Gly-OH **1** (87.6 mg, 0.5 mmol, 1.0 equiv.), **M1** (185.2 mg, 0.5 mmol, 1.0 equiv.), K_2HPO_4 (104.5 mg, 0.6 mmol, 1.2 equiv.), and 1.3 mL of DMF. The reaction mixture was degassed by bubbling nitrogen stream for 15min, then irradiated with a 10.8 W white LED irradiation. After 36h, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution, extracted with EtOAc (3 × 50 mL). The combined organic phase was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **2a** as a colorless oil (110 mg, 44% yield). Product **2b** was not observed.



1,1-diethyl 3-methyl 3-(2-((tert-butoxycarbonyl)amino)ethyl)-4-(2-ethoxy-2-oxoethyl)cyclopentane-1,1,3-tricarboxylate

^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.53 (s, 1H), 4.20 – 4.12 (m, 4H), 4.08 (dd, *J* = 7.2, 3.0 Hz, 2H), 3.63 (d, *J* = 16.7 Hz, 3H), 3.10 (d, *J* = 41.3 Hz, 2H), 2.86 (d, *J* = 14.5 Hz, 1H), 2.77 – 2.56 (m, 1H), 2.50 (d, *J* = 3.6 Hz, 1H), 2.40 – 2.32 (m, 2H), 2.17 (d, *J* = 15.2 Hz, 2H), 2.07 – 1.75 (m, 2H), 1.39 (s, 9H), 1.21 (dd, *J* = 9.2, 7.2 Hz, 9H). **^{13}C NMR for major** (126 MHz, Chloroform-*d*) δ 174.6, 172.7, 172.0, 171.4, 155.6, 61.8, 61.5, 60.6, 58.2, 51.8, 45.7, 41.0, 38.6, 35.2, 28.4, 14.2, 14.0, 14.0.**^{13}C NMR for minor** (126 MHz, Chloroform-*d*) δ 175.6, 172.1, 172.1, 171.6, 79.1, 61.7, 60.5, 57.7, 54.8, 52.3, 43.2, 39.6, 38.2, 37.7, 37.3, 34.6.

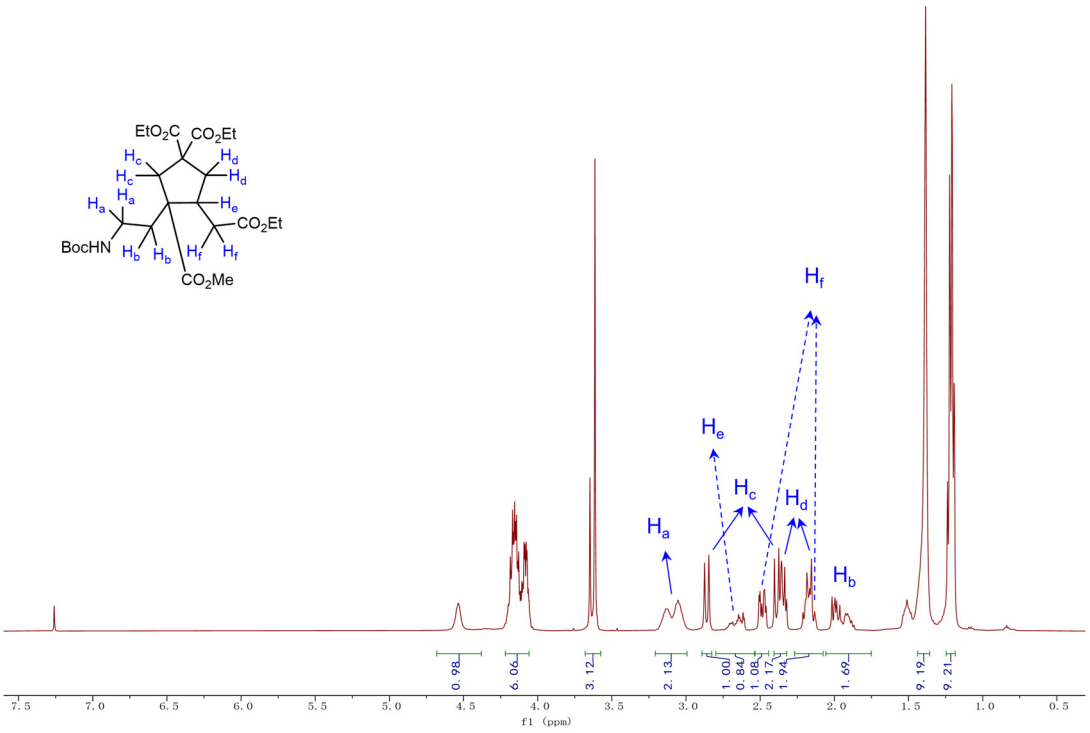


Fig. S10 ^{1}H NMR spectrum of **2a** in $CDCl_3$

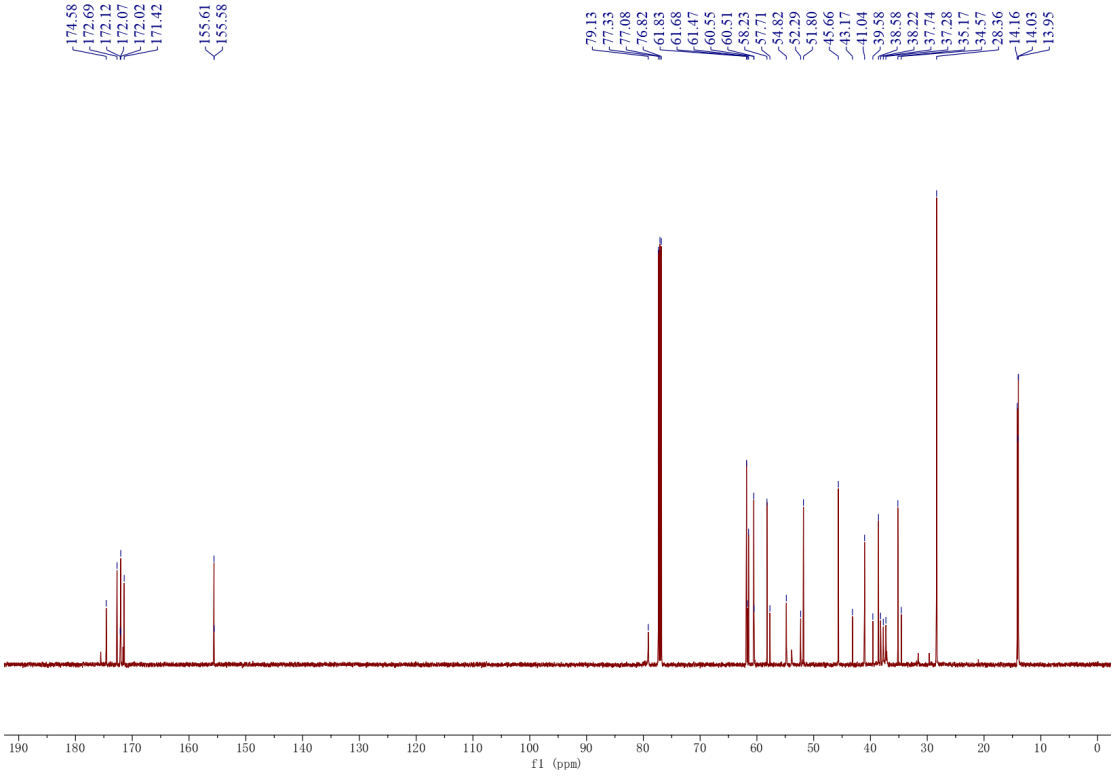


Fig. S11 ^{13}C NMR spectrum of **2a** in $CDCl_3$

5. Thermal Analysis

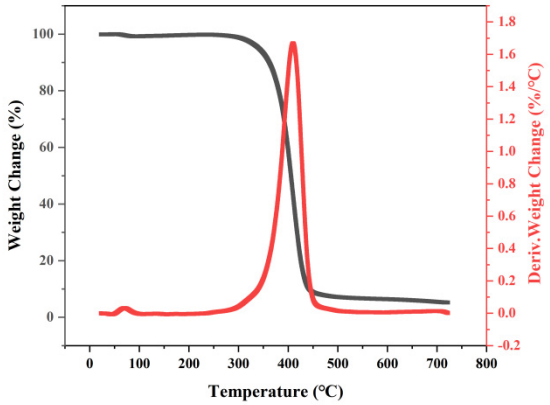


Fig. S12 TGA and DTG curves of **PM1** (168.4 kDa, $Đ$ = 1.49). $T_d^{5\%}$ = 341 °C, T_{max} = 410 °C.

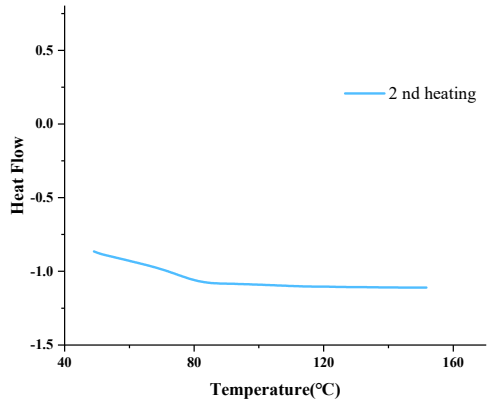


Fig. S13 DSC curves of **PM1** (16.1 kDa, $Đ$ = 1.57). T_g = 75 °C (2nd heating scan)

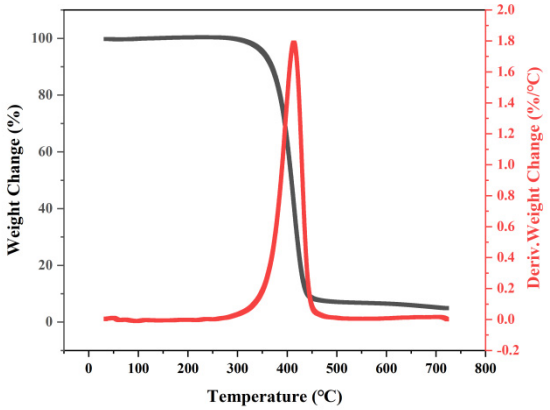


Fig. S14 TGA and DTG curves of **PM2** (17.2 kDa, $Đ$ = 1.51). $T_d^{5\%}$ = 351 °C, T_{max} = 414 °C.

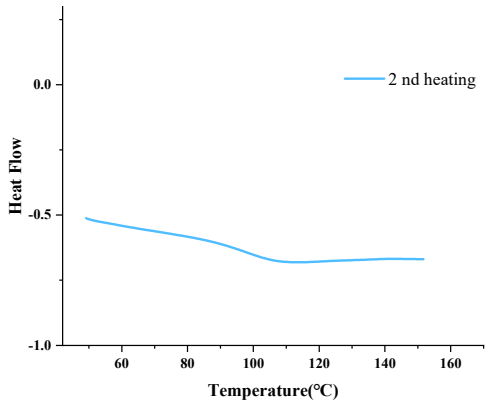


Fig. S15 DSC curves of **PM2** (17.2 kDa, $Đ$ = 1.51). T_g = 99 °C (2nd heating scan)

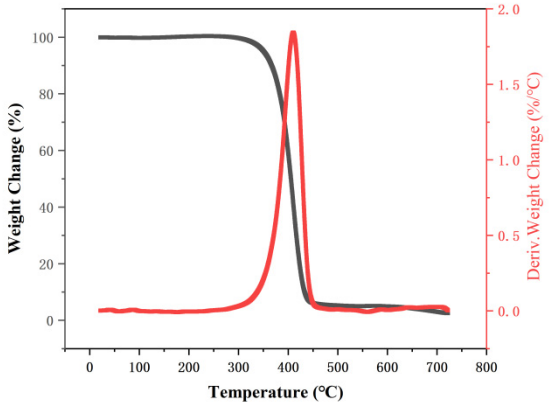


Fig. S16 TGA and DTG curves of **PM3** (14.4 kDa, $Đ$ = 1.56). $T_d^{5\%}$ = 351 °C, T_{max} = 409 °C.

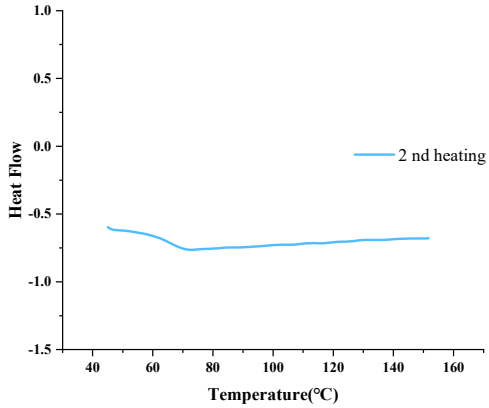


Fig. S17 DSC curves of **PM3** (14.4 kDa, $Đ$ = 1.56). T_g = 65 °C (2nd heating scan)

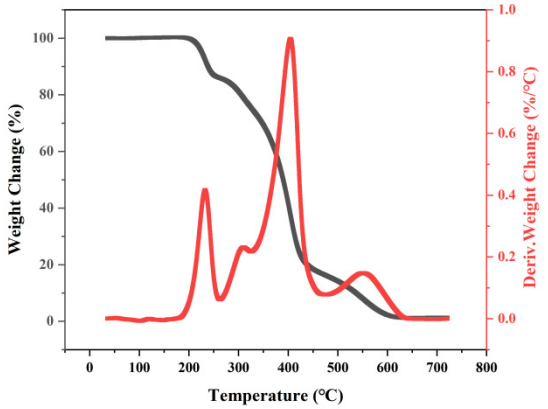


Fig. S18 TGA and DTG curves of **PM4** (10.3 kDa, $Đ$ = 1.53). $Td^{5\%}$ = 226 °C, T_{max1} = 231 °C, T_{max2} = 405 °C, T_{max3} = 539 °C.

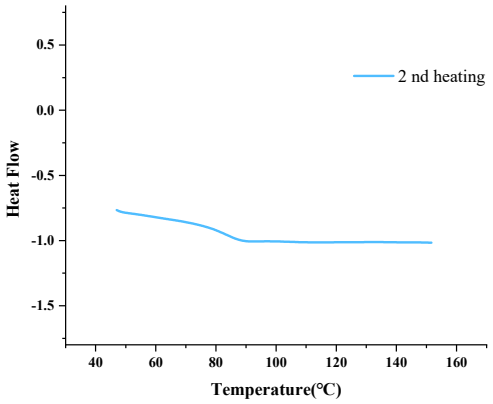


Fig. S19 DSC curves of **PM4** (10.3 kDa, $Đ$ = 1.53). T_g = 82 °C (2nd heating scan).

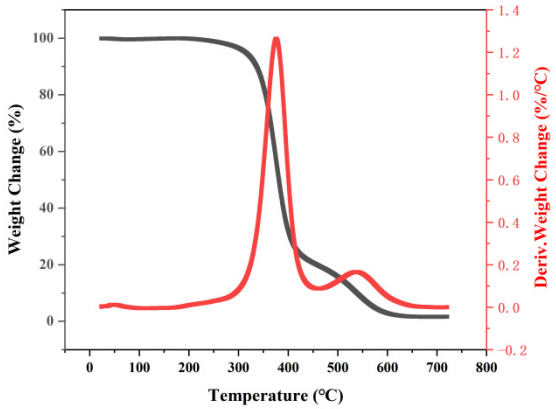


Fig. S20 TGA and DTG curves of **PM5** (4.5 kDa, $Đ$ = 1.58). $Td^{5\%}$ = 313 °C, T_{max1} = 375 °C, T_{max2} = 524 °C.

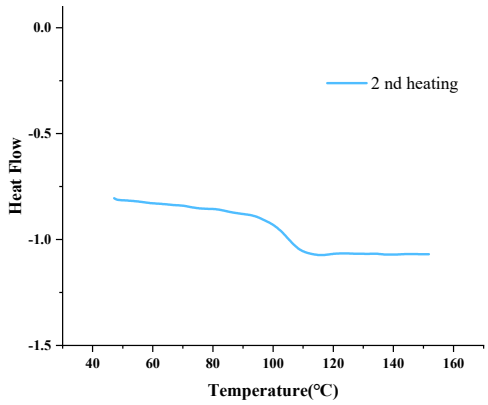


Fig. S21 DSC curves of **PM5** (4.5 kDa, $Đ$ = 1.58). T_g = 104 °C (2nd heating scan)

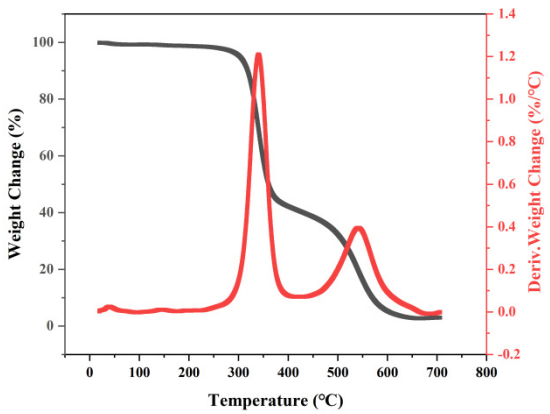


Fig. S22 TGA and DTG curves of **PM6** (7.1 kDa, $Đ$ = 1.66). $T_d^{5\%}$ = 302 °C, T_{max1} = 340 °C, T_{max2} = 538 °C.

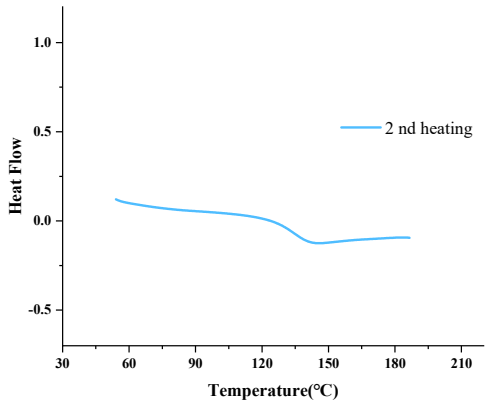


Fig. S23 DSC curves of **PM6** (7.1 kDa, $Đ$ = 1.66). T_g = 138 °C (2nd heating scan)

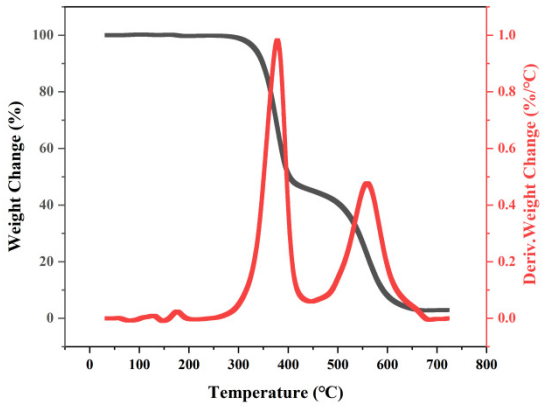


Fig. S24 TGA and DTG curves of **PM7** (22.2 kDa, $Đ$ = 1.80). $T_d^{5\%}$ = 333 °C, T_{max1} = 378 °C, T_{max1} = 556 °C.

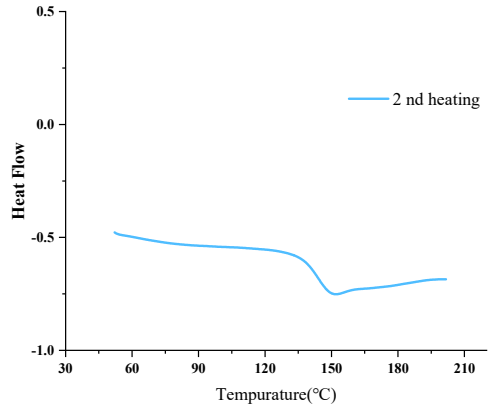


Fig. S25 DSC curves of **PM7** (22.2 kDa, $Đ$ = 1.80). T_g = 142 °C (2nd heating scan)

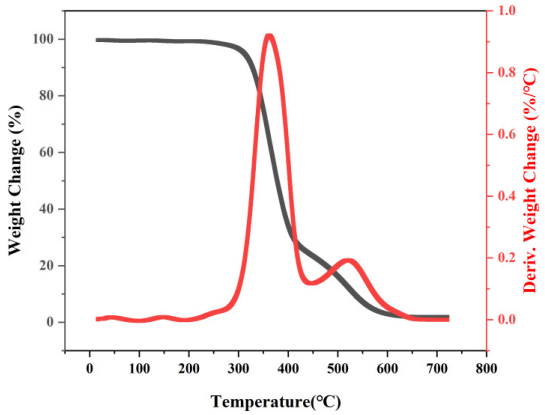


Fig. S26 TGA and DTG curves of **PM1-b-PM6** (10.3 kDa, $Đ$ = 1.65). $T_d^{5\%}$ = 312 °C, T_{max1} = 361 °C, T_{max2} = 520 °C.

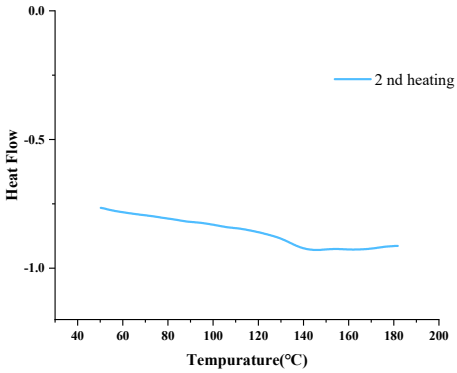


Fig. S27 DSC curves of **PM1-*b*-PM6** (10.3 kDa, $Đ$ = 1.65). T_g = 133 °C (2nd heating scan)

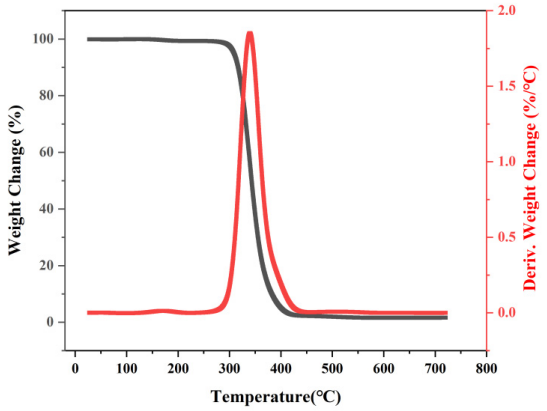


Fig. S28 TGA and DTG curves of **PM1-b-PMMA** (18.4 kDa, $Đ$ = 1.49). $T_d^{5\%}$ = 308 °C, T_{max} = 340 °C.

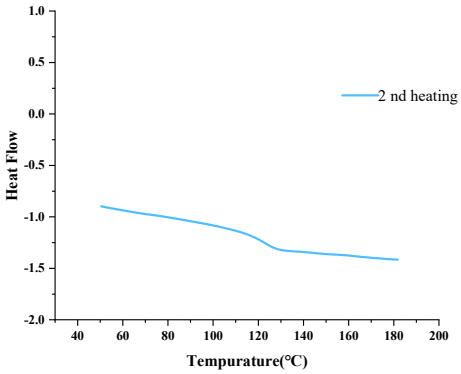


Fig. S29 DSC curves of **PM1-b-PMMA** (18.4 kDa, $Đ$ = 1.49). T_g = 121 °C (2nd heating scan)

6. NMR Spectra of M1–M7

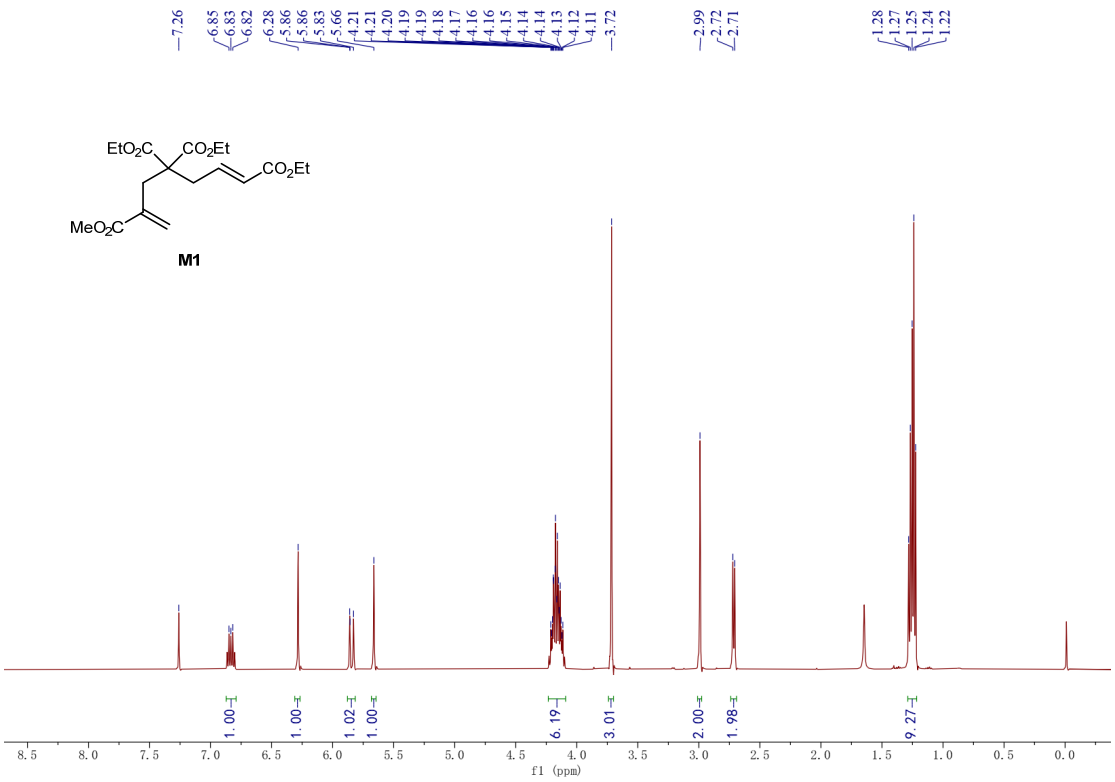


Fig. S30 ^{1}H NMR spectrum of **M1** in $CDCl_3$

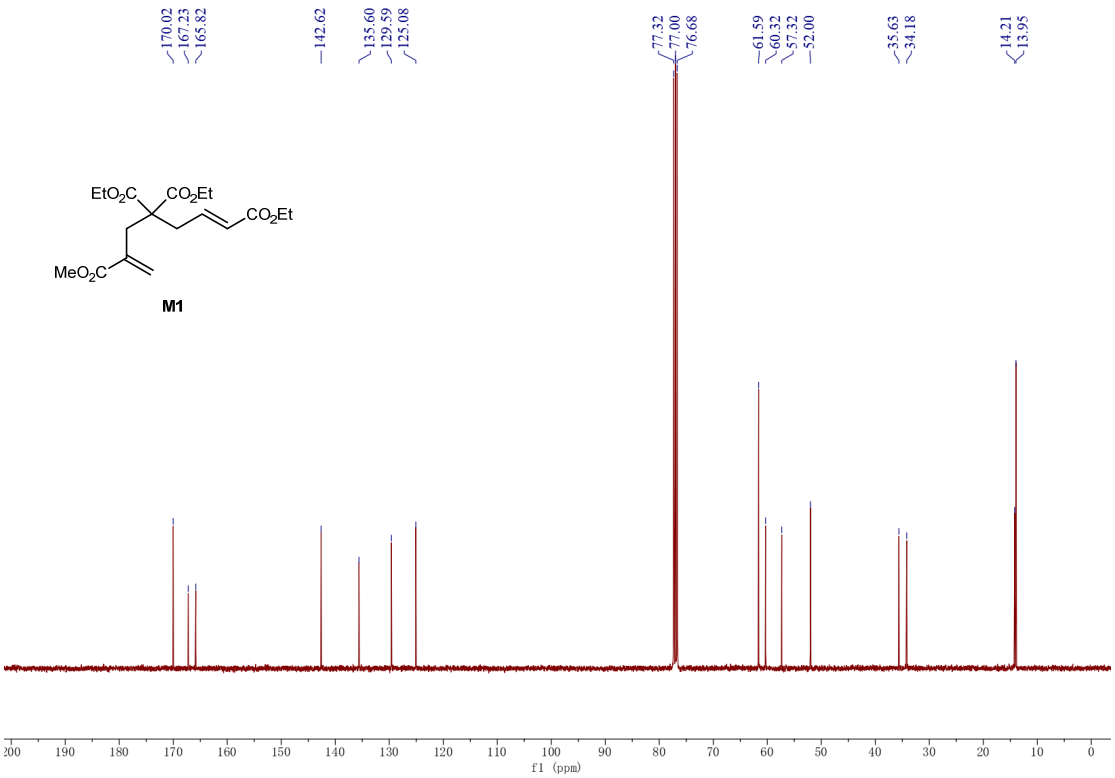


Fig. S31 ^{13}C NMR spectrum of **M1** in $CDCl_3$

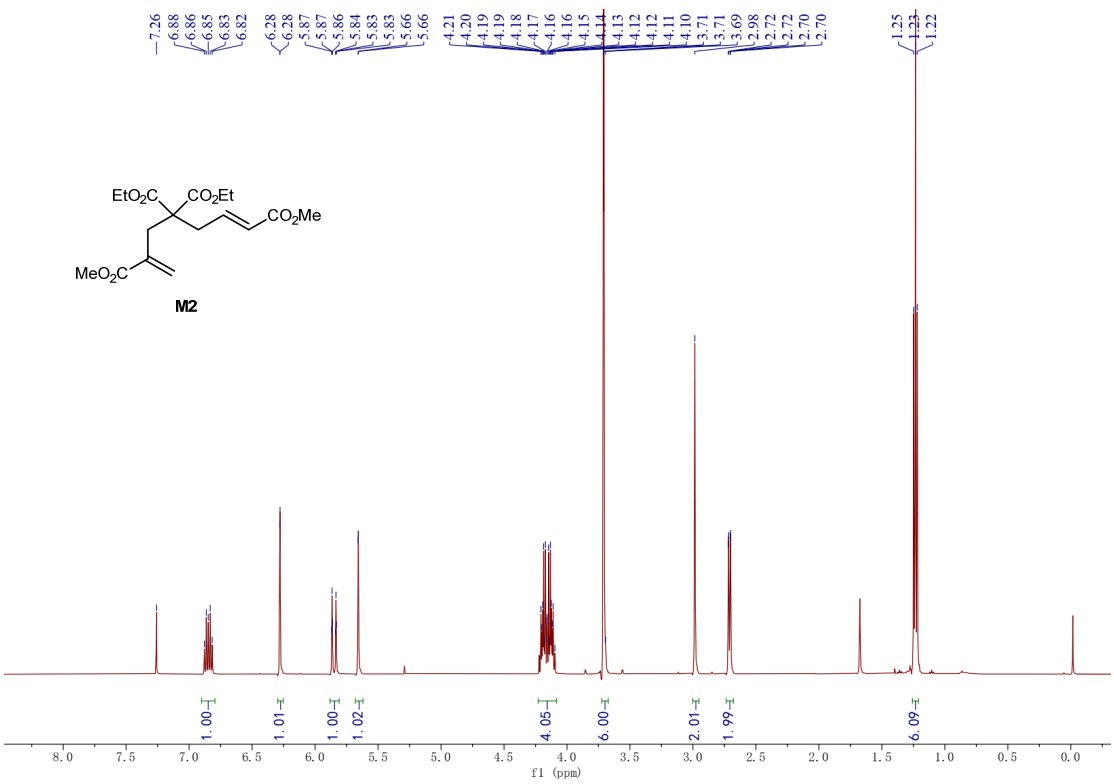


Fig. S32 ^{1}H NMR spectrum of **M2** in $CDCl_3$

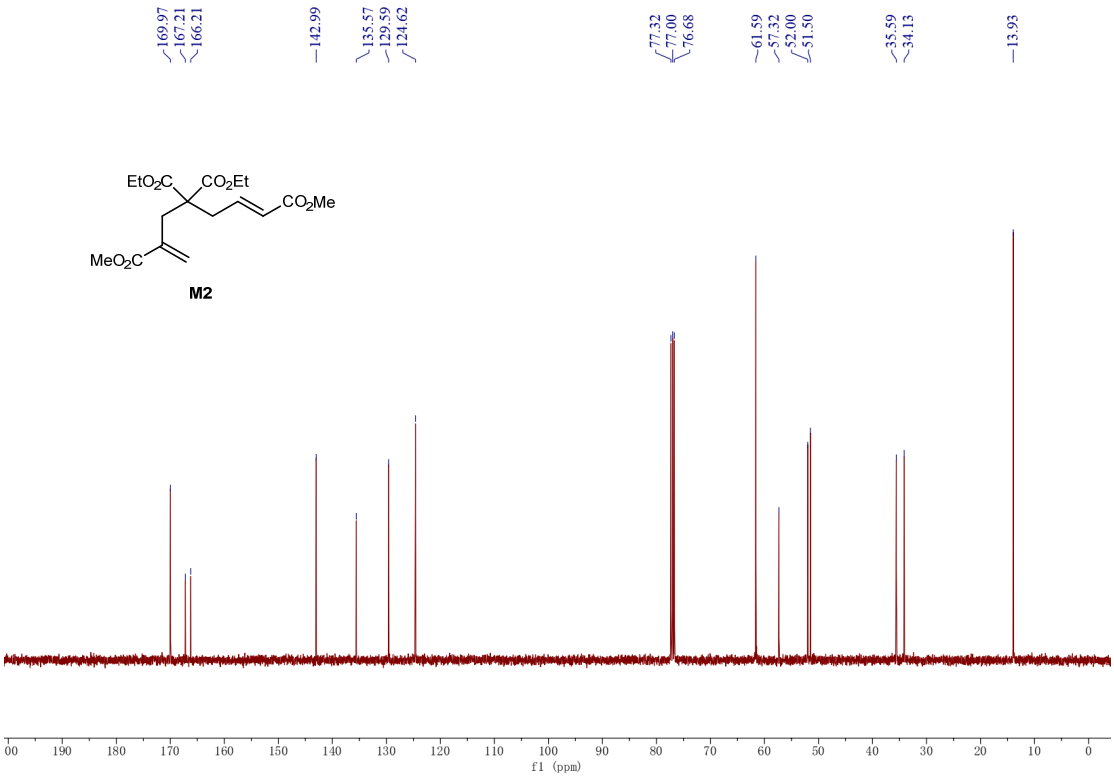


Fig. S33 ^{13}C NMR spectrum of **M2** in $CDCl_3$

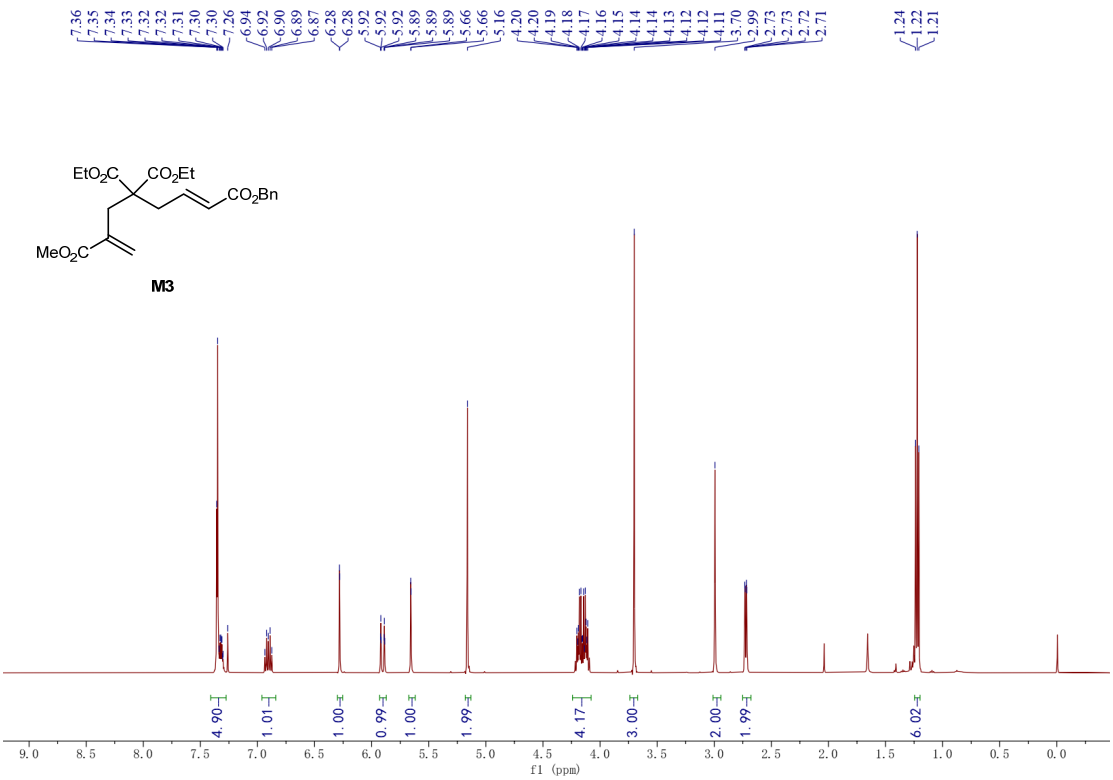


Fig. S34 ^{1}H NMR spectrum of **M3** in $CDCl_3$

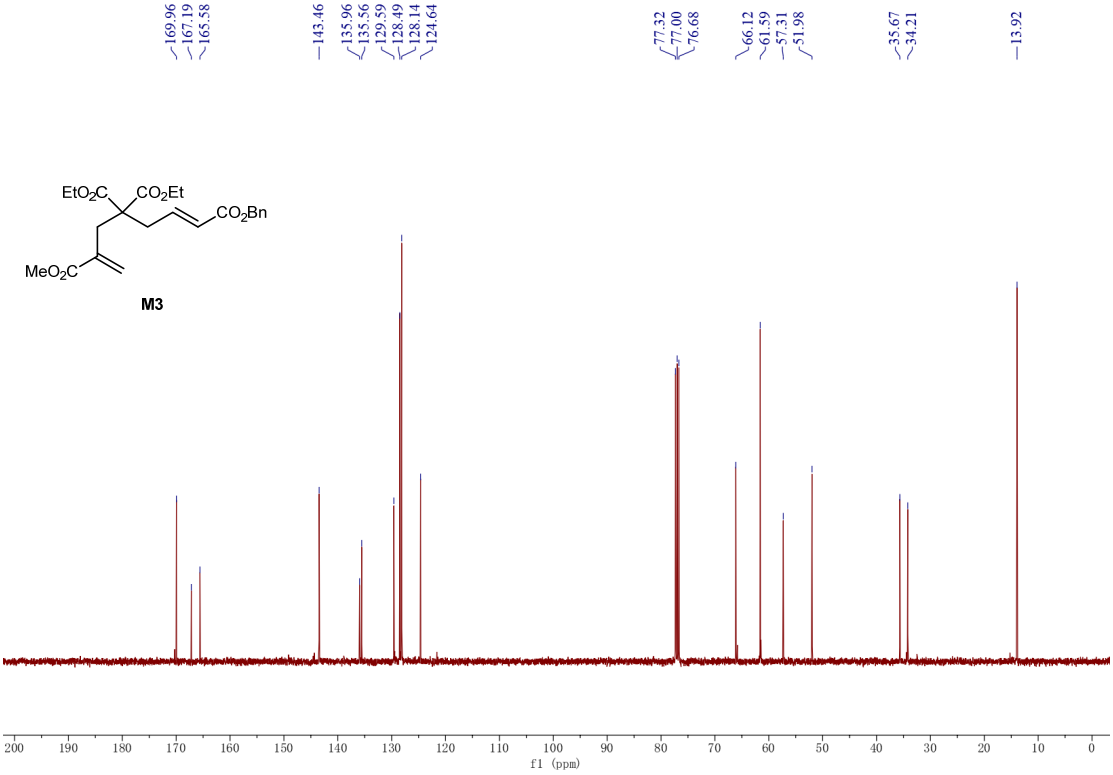


Fig. S35 ^{13}C NMR spectrum of **M3** in $CDCl_3$

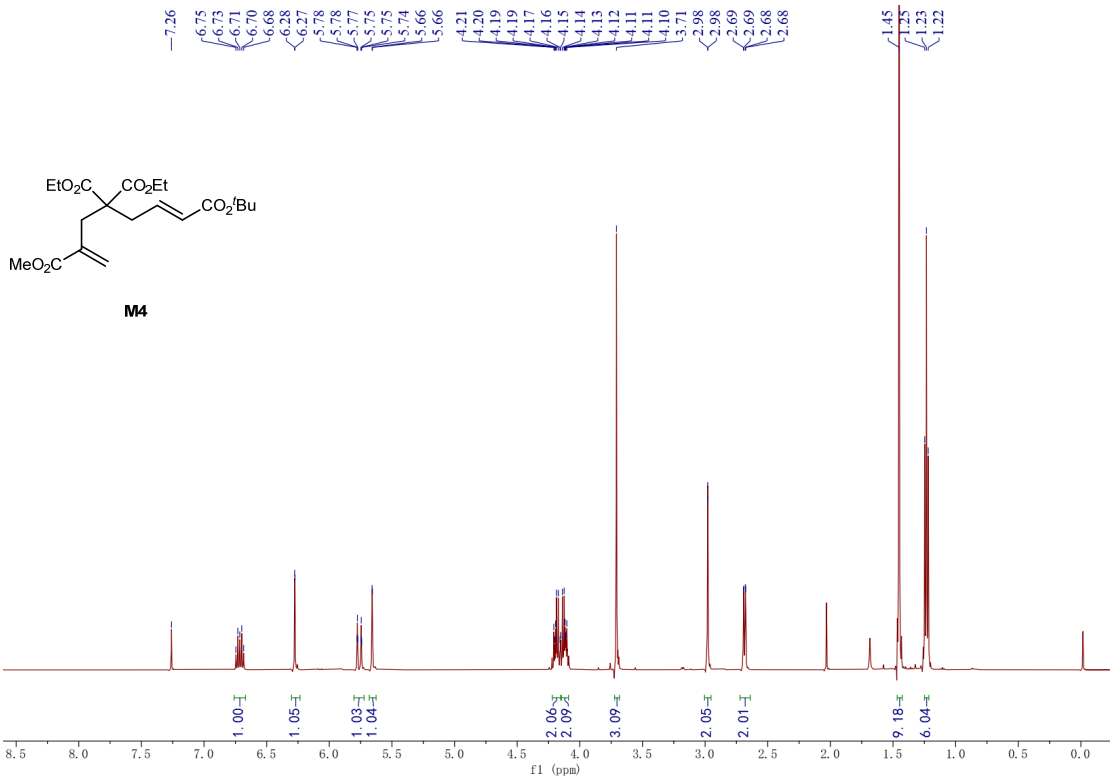


Fig. S36 ^{1}H NMR spectrum of **M4** in $CDCl_3$

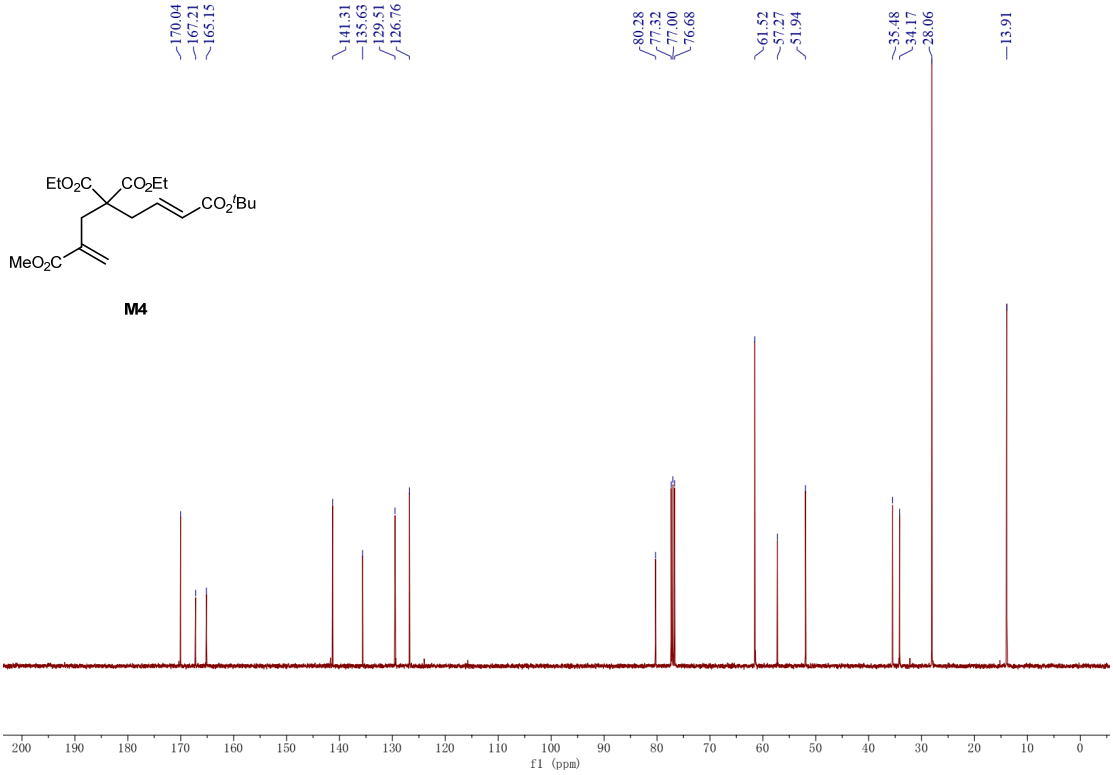


Fig. S37 ^{13}C NMR spectrum of **M4** in $CDCl_3$

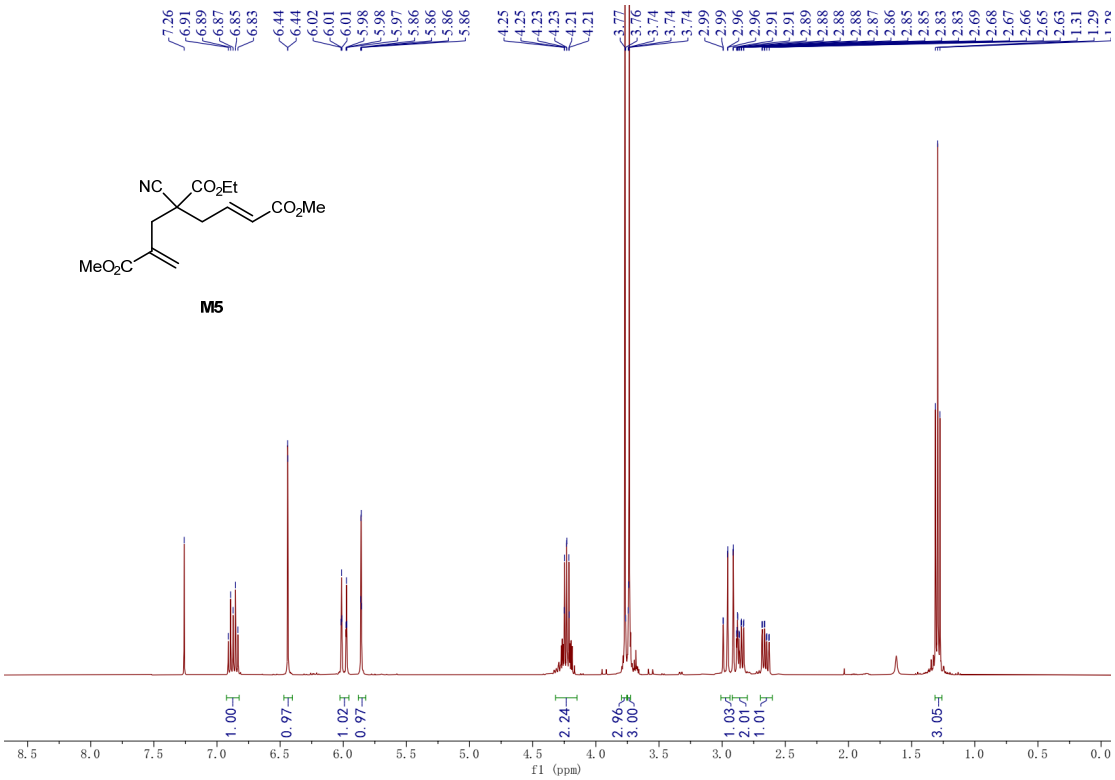


Fig. S38 ^{1}H NMR spectrum of **M5** in $CDCl_3$

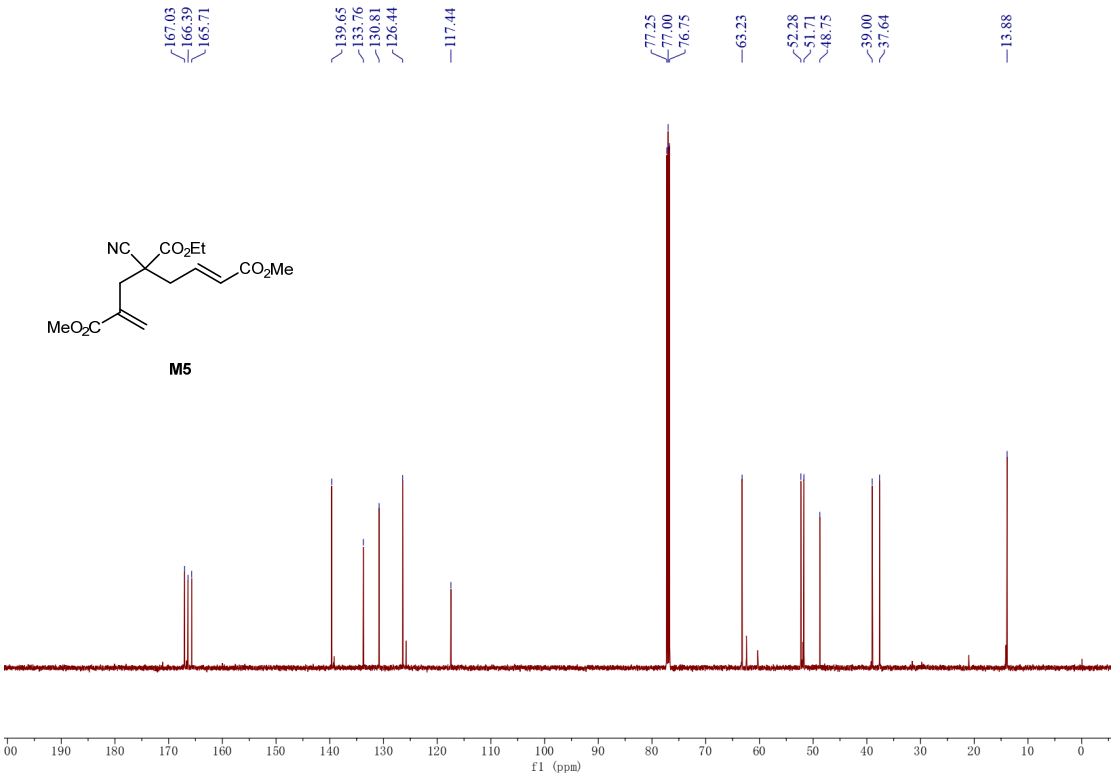


Fig. S39 ^{13}C NMR spectrum of **M5** in $CDCl_3$

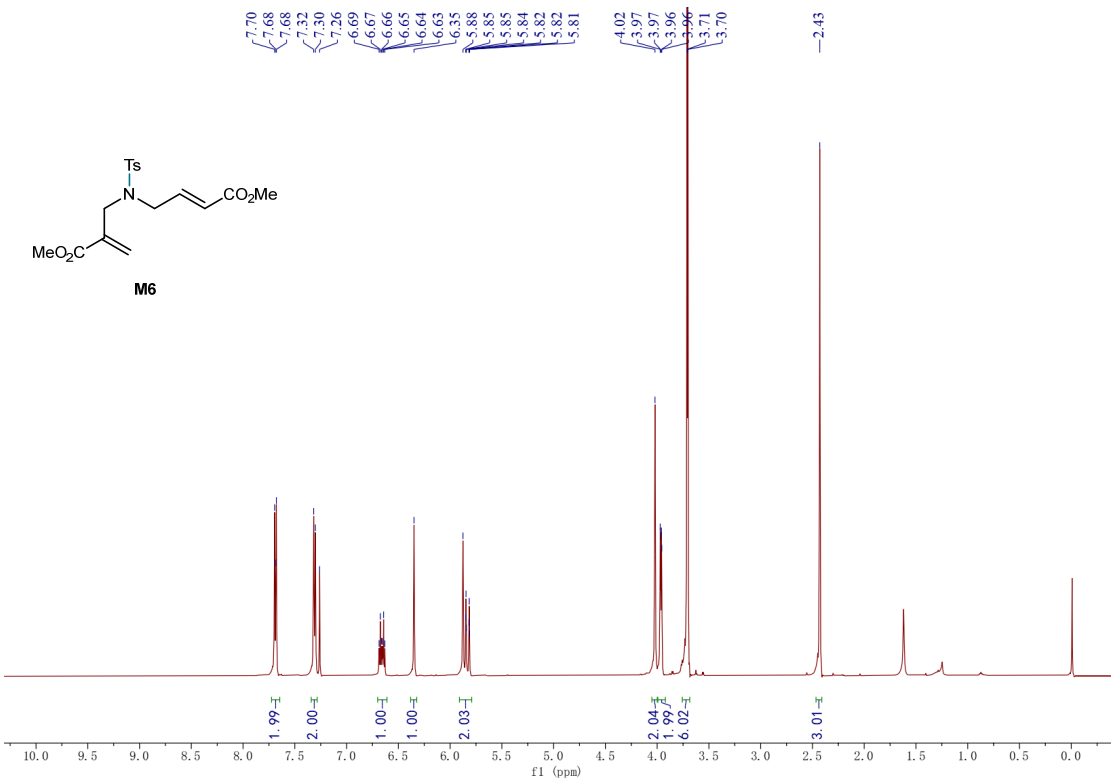


Fig. S40 ^{1}H NMR spectrum of **M6** in $CDCl_3$

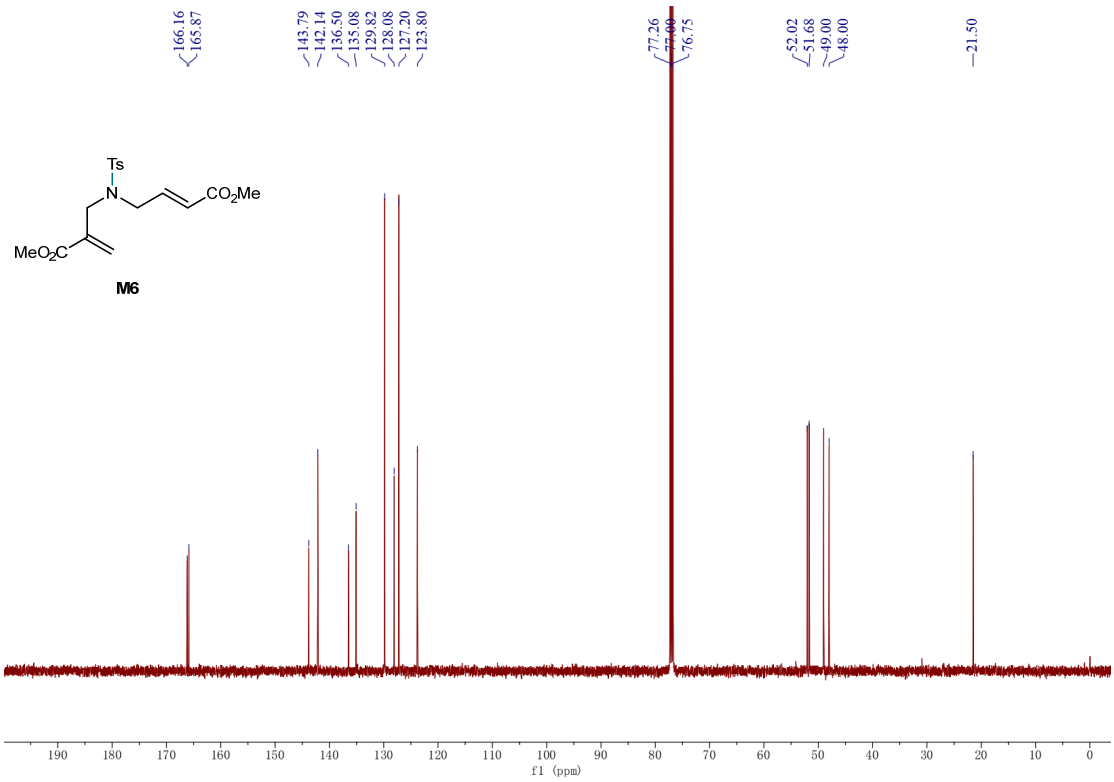


Fig. S41 ^{13}C NMR spectrum of **M6** in $CDCl_3$

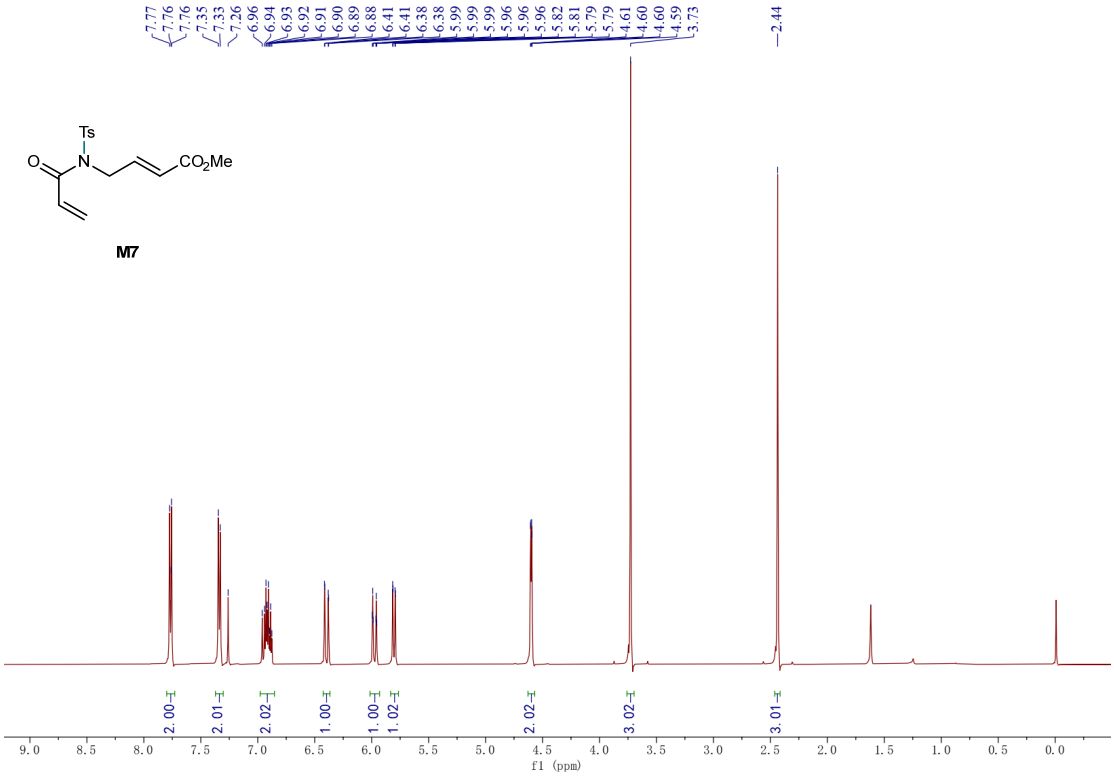


Fig. S42 ^{1}H NMR spectrum of **M7** in $CDCl_3$

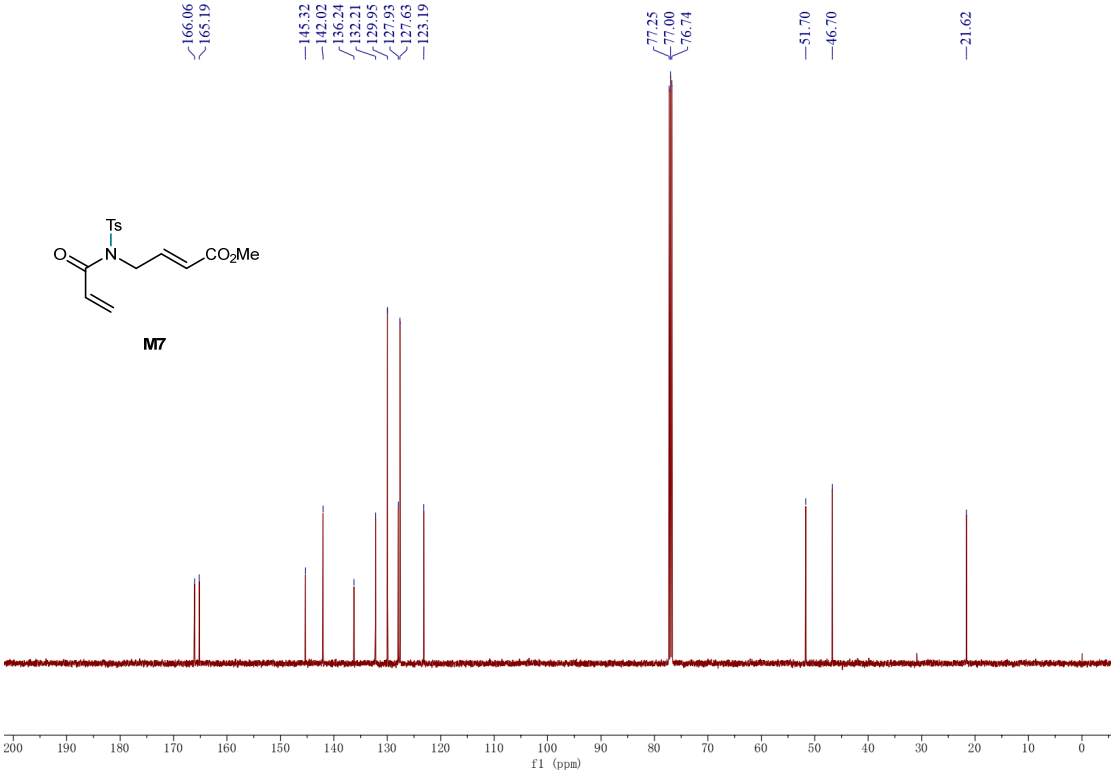


Fig. S43 ^{13}C NMR spectrum of **M7** in $CDCl_3$

7. NMR Spectra of PM1-PM7

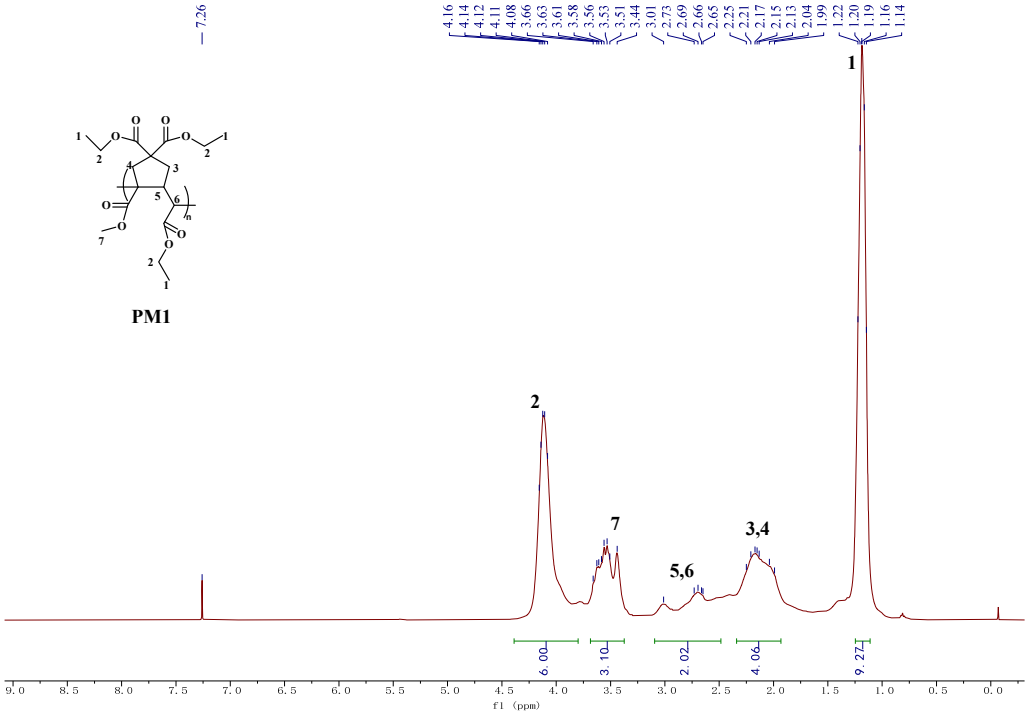


Fig. S44 ^{1}H NMR spectrum of **PM1** in $CDCl_3$

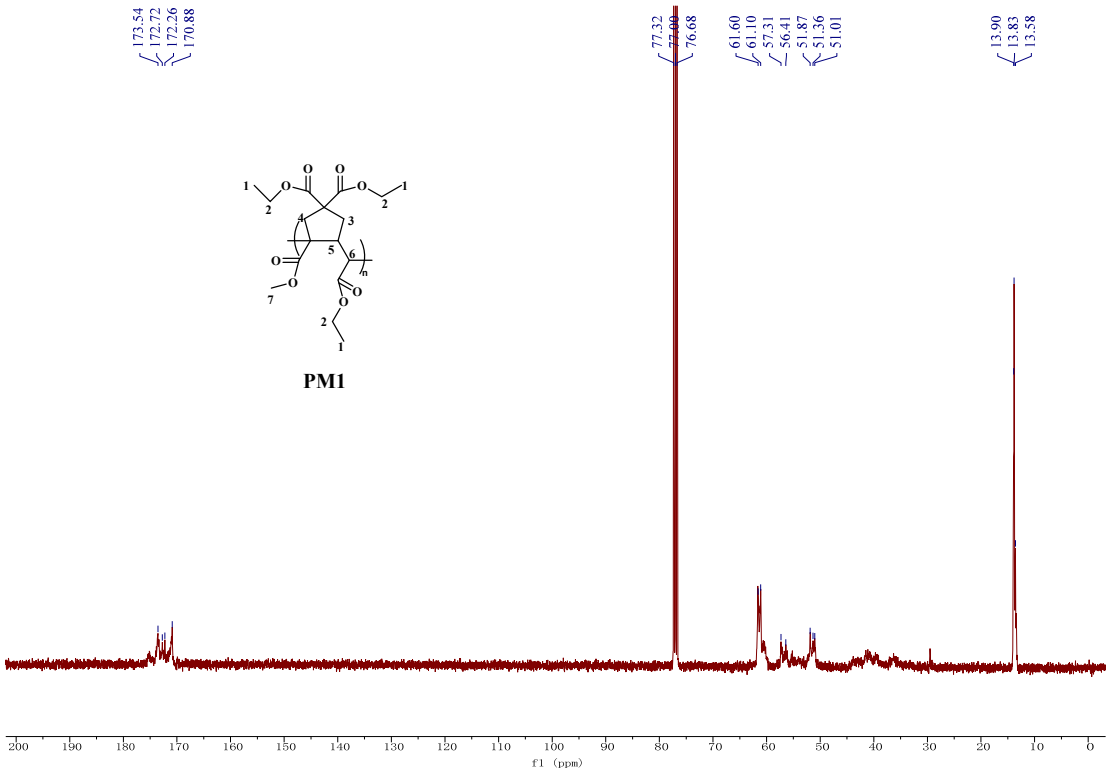


Fig. S45 ^{13}C NMR spectrum of **PM1** in $CDCl_3$

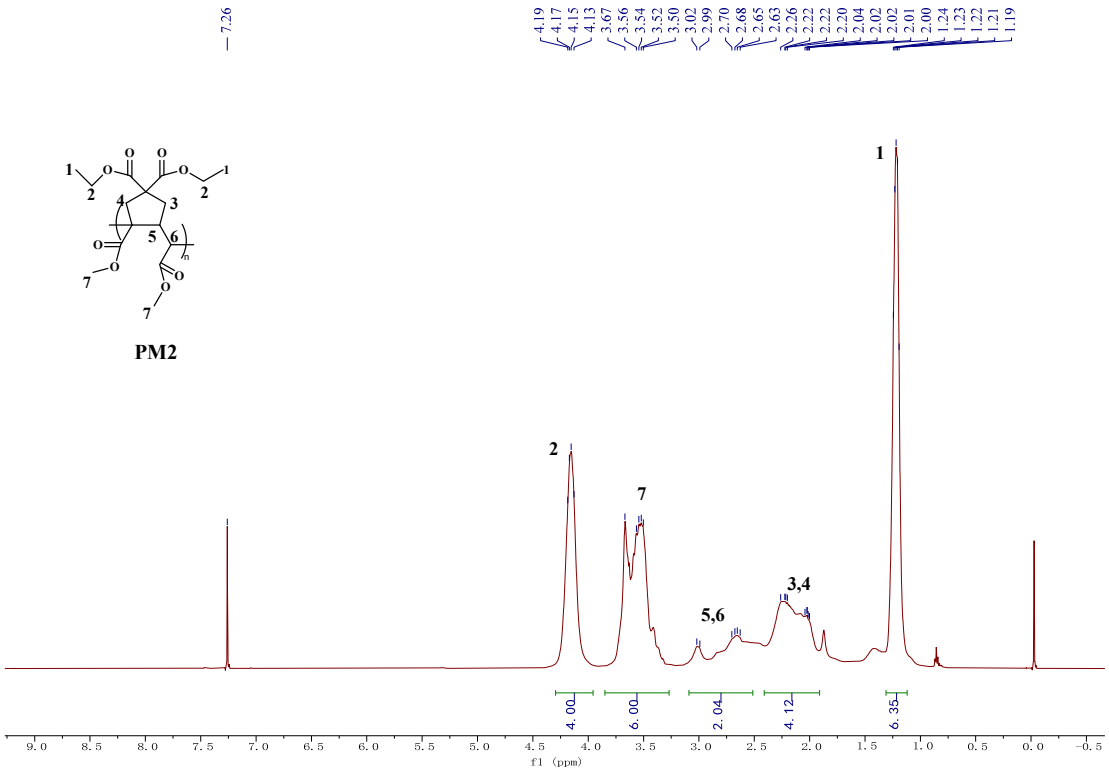


Fig. S46 ^{1}H NMR spectrum of **PM2** in $CDCl_3$

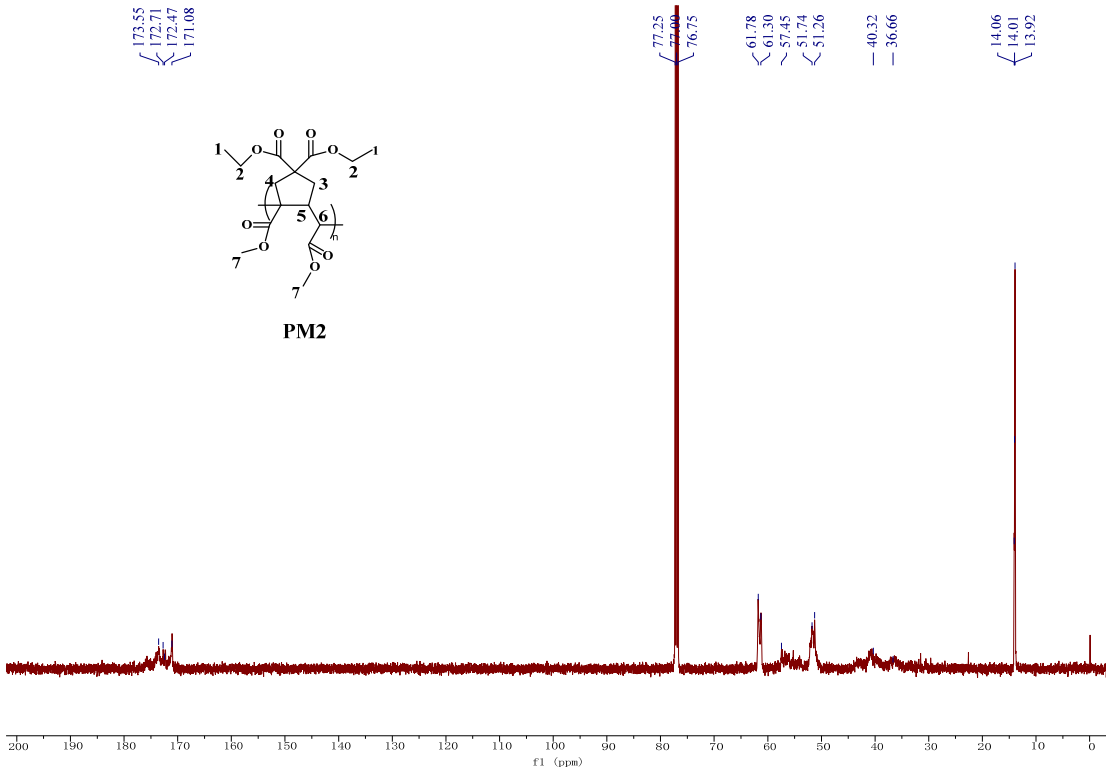


Fig. S47 ^{13}C NMR spectrum of **PM2** in $CDCl_3$

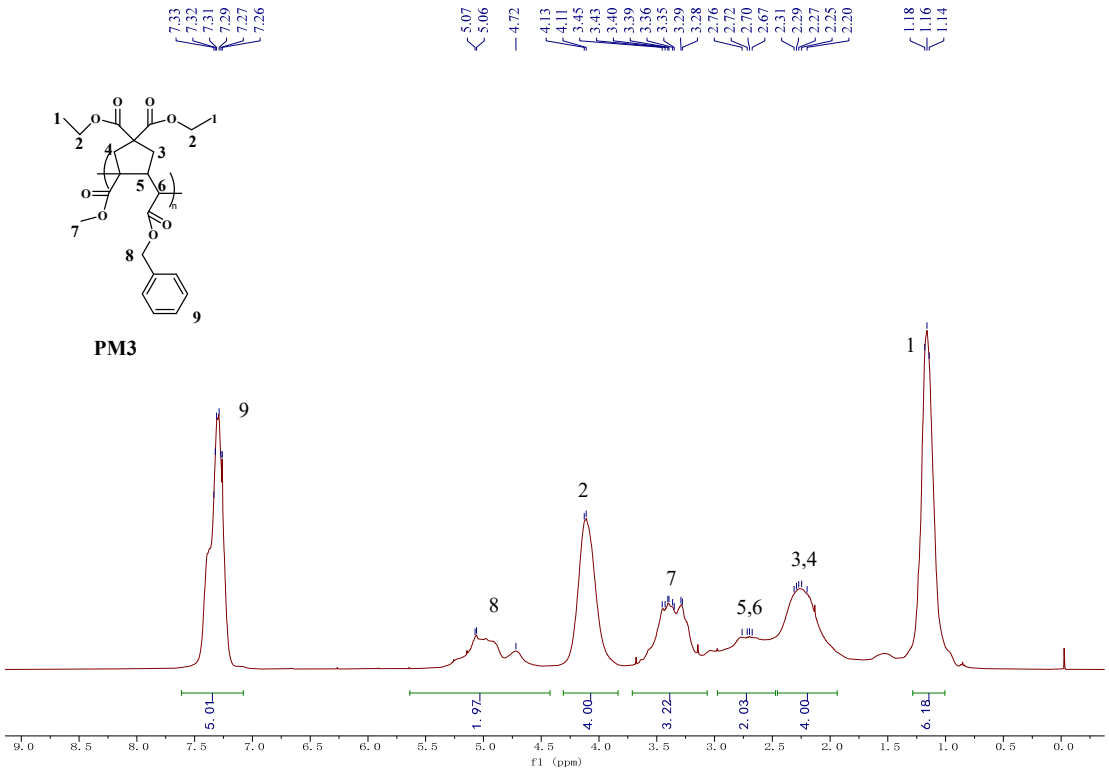


Fig. S48 ^{1}H NMR spectrum of **PM3** in $CDCl_3$

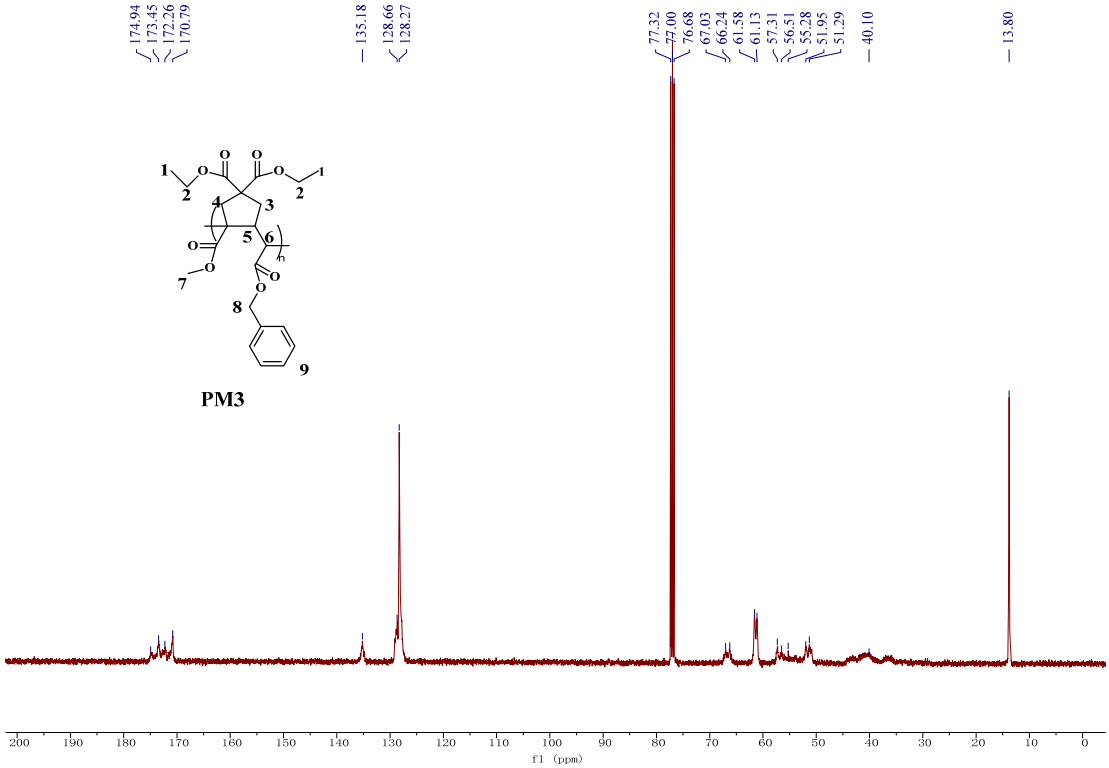


Fig. S49 ^{13}C NMR spectrum of **PM3** in $CDCl_3$

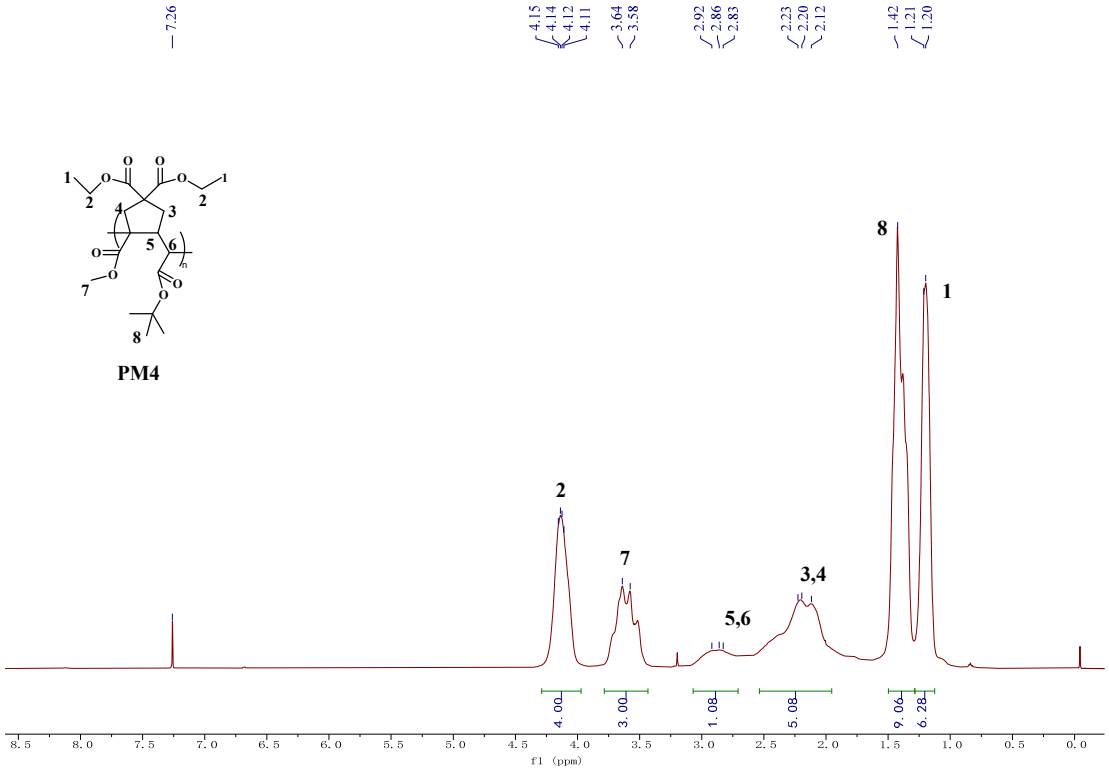


Fig. S50 ^{1}H NMR spectrum of **PM4** in $CDCl_3$

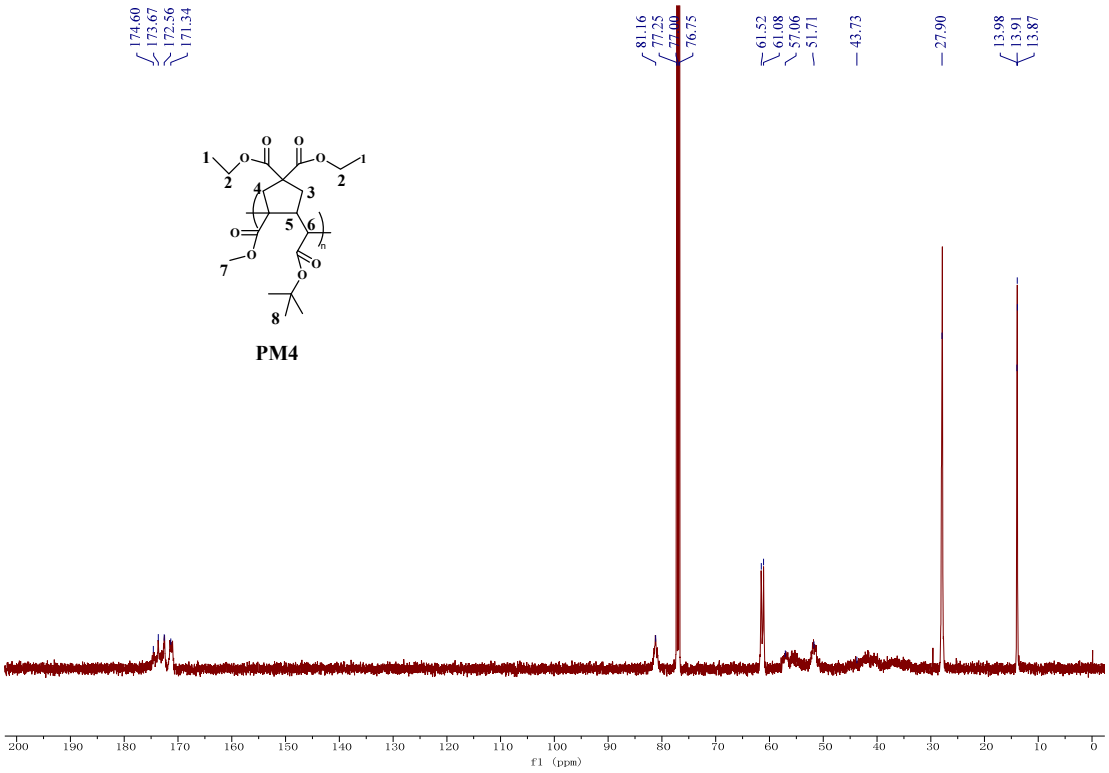


Fig. S51 ^{13}C NMR spectrum of **PM4** in $CDCl_3$

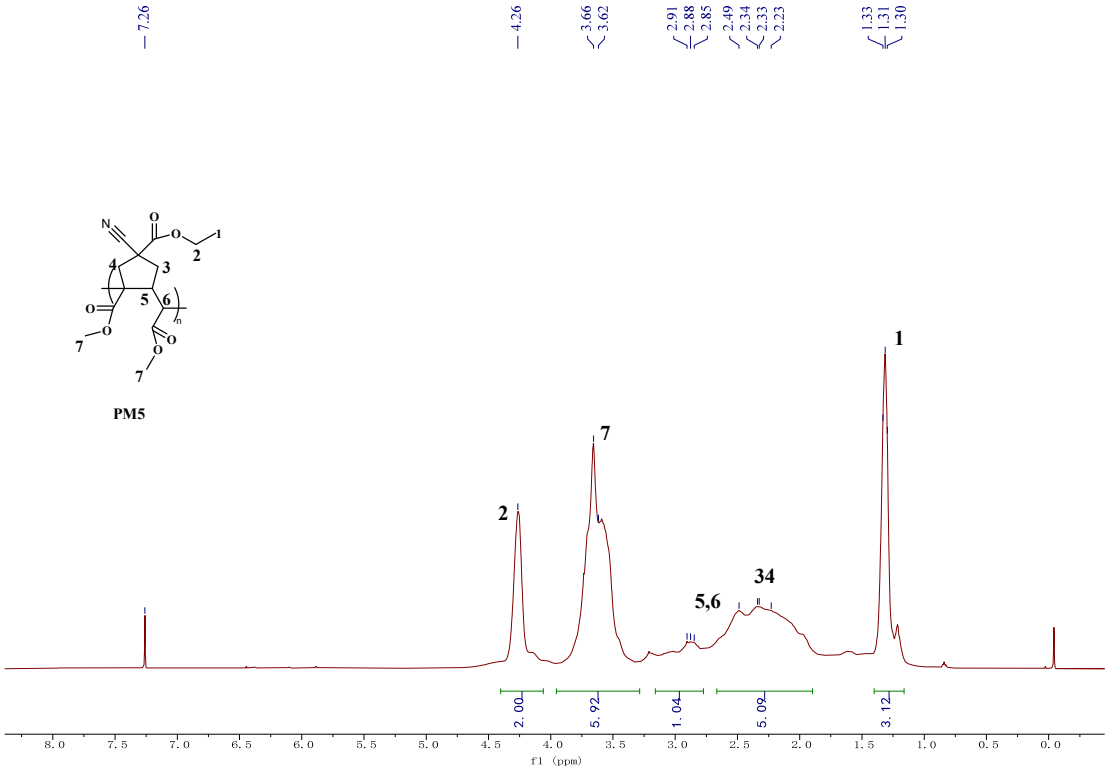


Fig. S52 ^{1}H NMR spectrum of **PM5** in $CDCl_3$

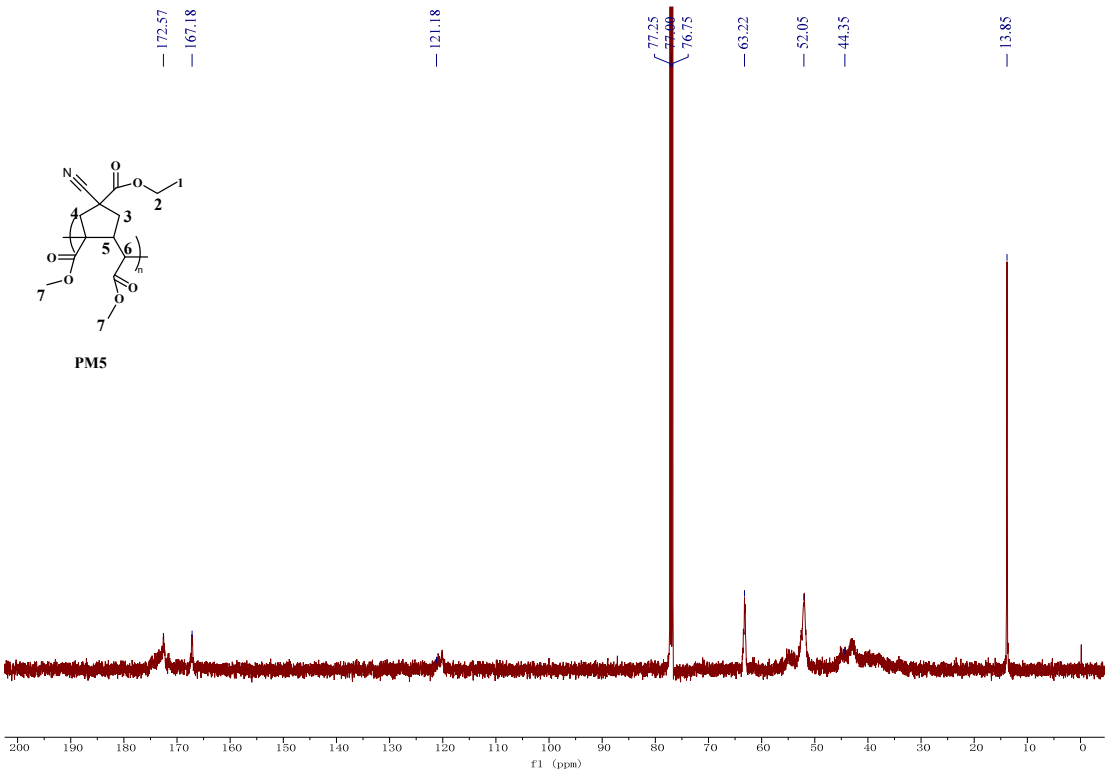


Fig. S53 ^{13}C NMR spectrum of **PM5** in $CDCl_3$

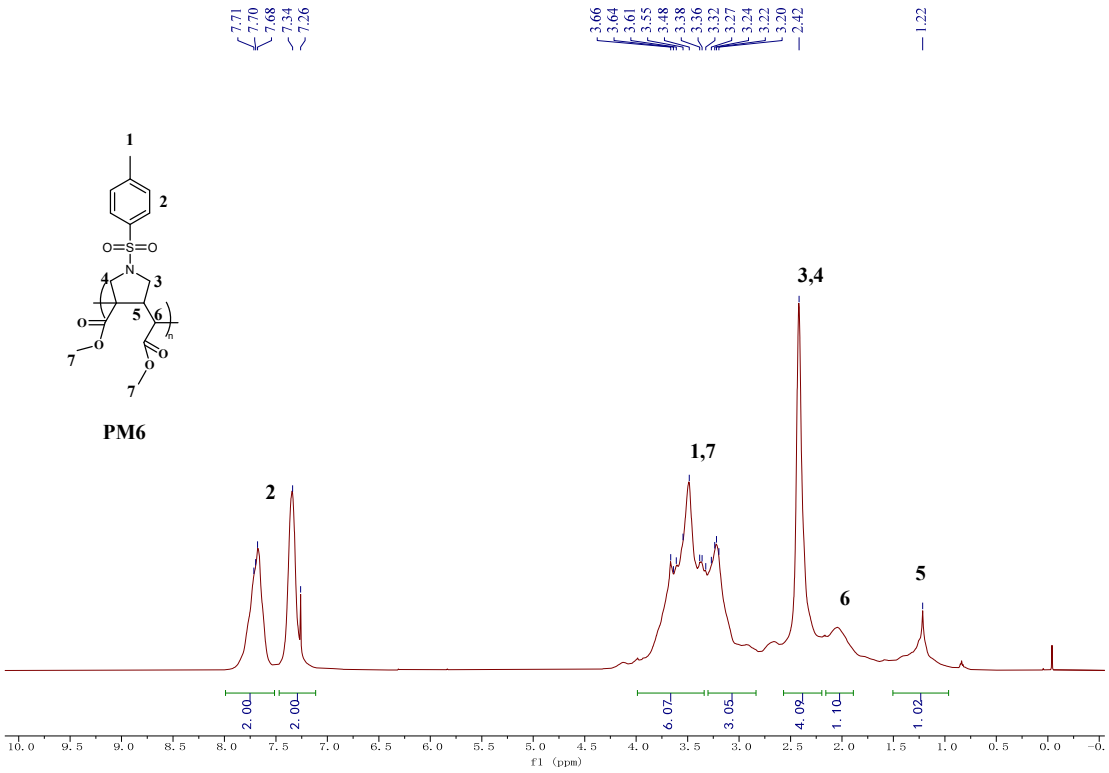


Fig. S54 ^{1}H NMR spectrum of **PM6** in $CDCl_3$

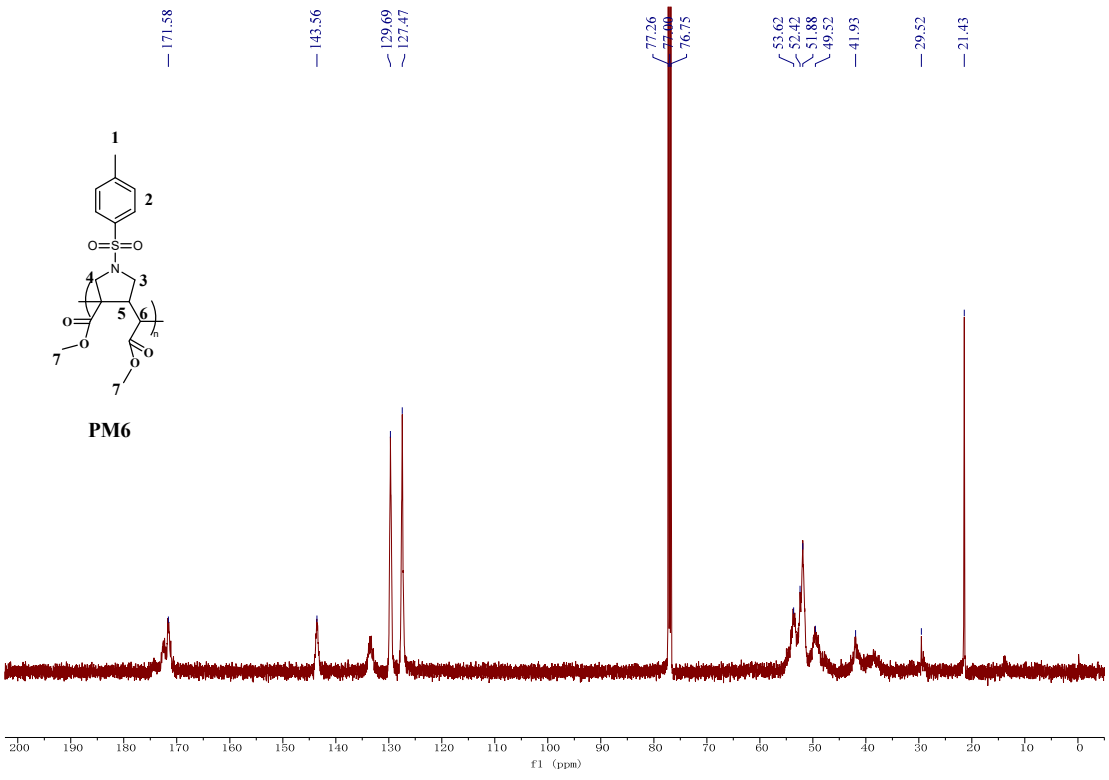


Fig. S55 ^{13}C NMR spectrum of **PM6** in CDCl

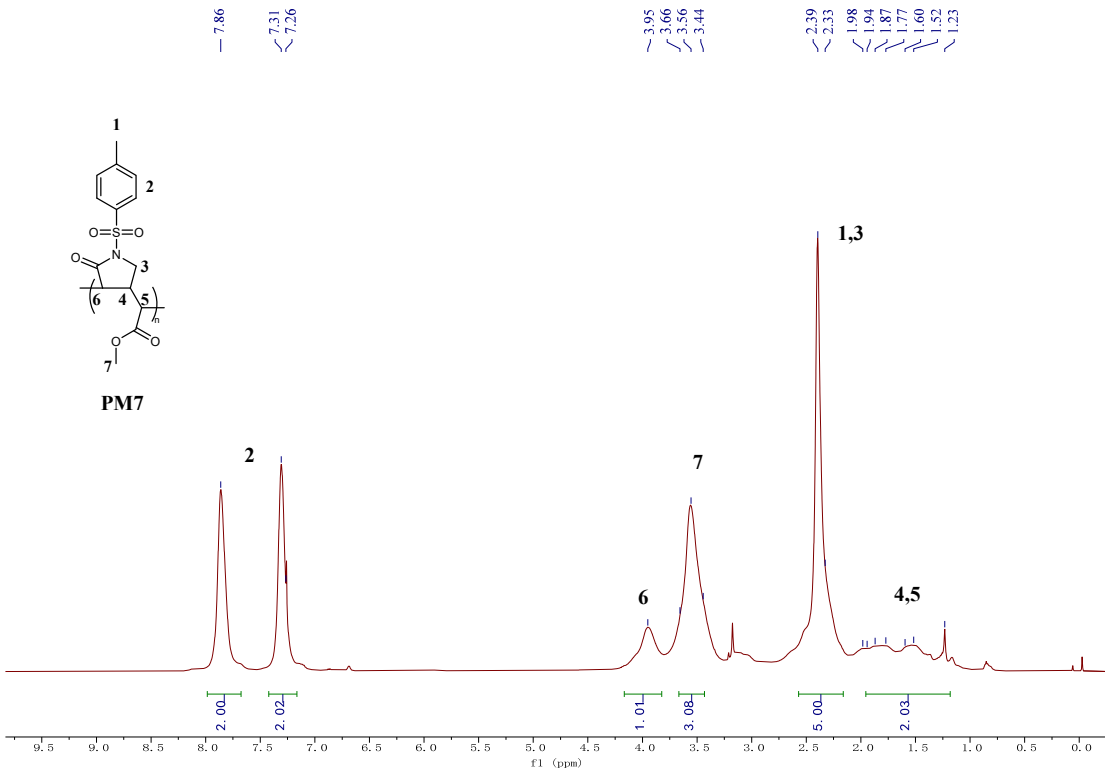


Fig. S56 ^{1}H NMR spectrum of **PM7** in $CDCl_3$

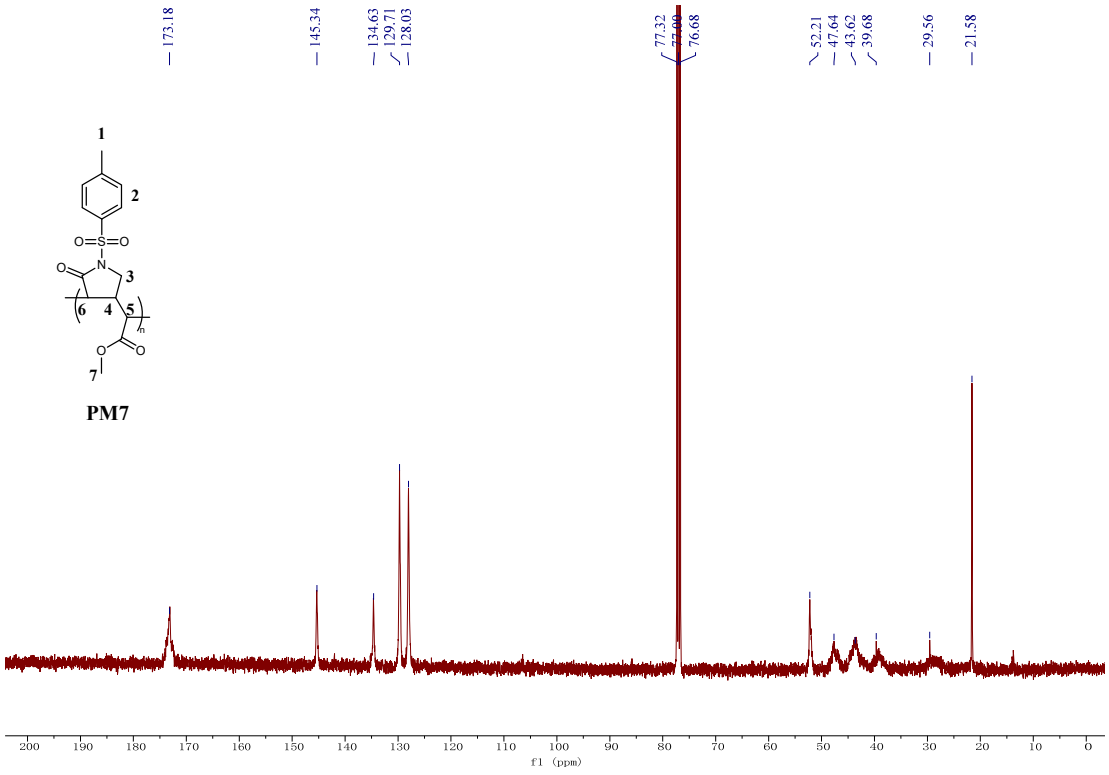


Fig. S57 ^{13}C NMR spectrum of **PM7** in $CDCl_3$

8.NMR Spectra of block copolymers

PM1-b-PM6

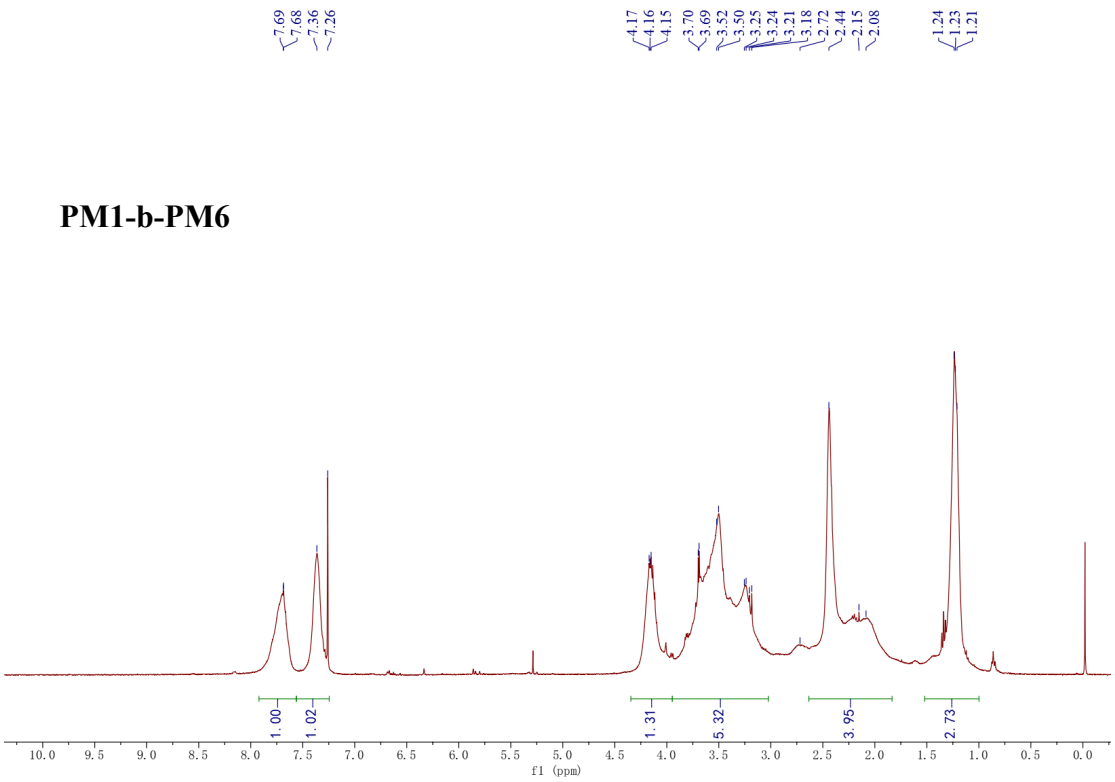


Fig. S58 ^{1}H NMR spectrum of **PM1-b-PM6** in $CDCl_3$

PM1-b-PM6

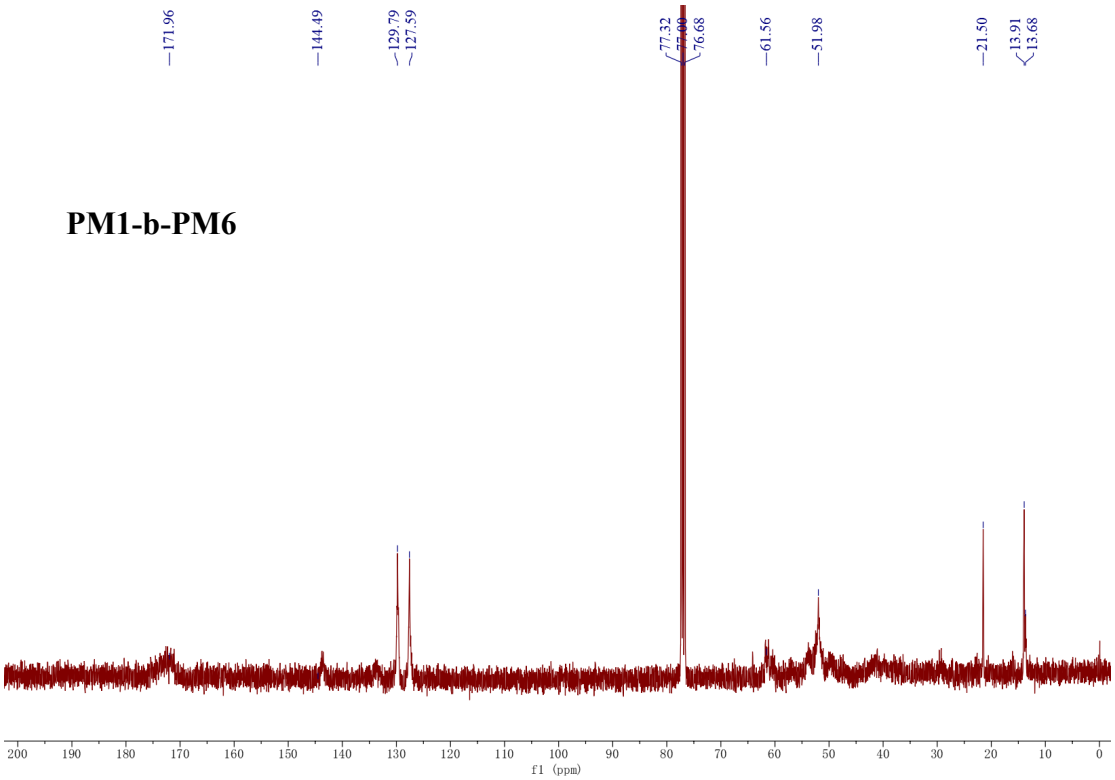


Fig. S59 ^{13}C NMR spectrum of **PM1-b-PM6** in $CDCl_3$

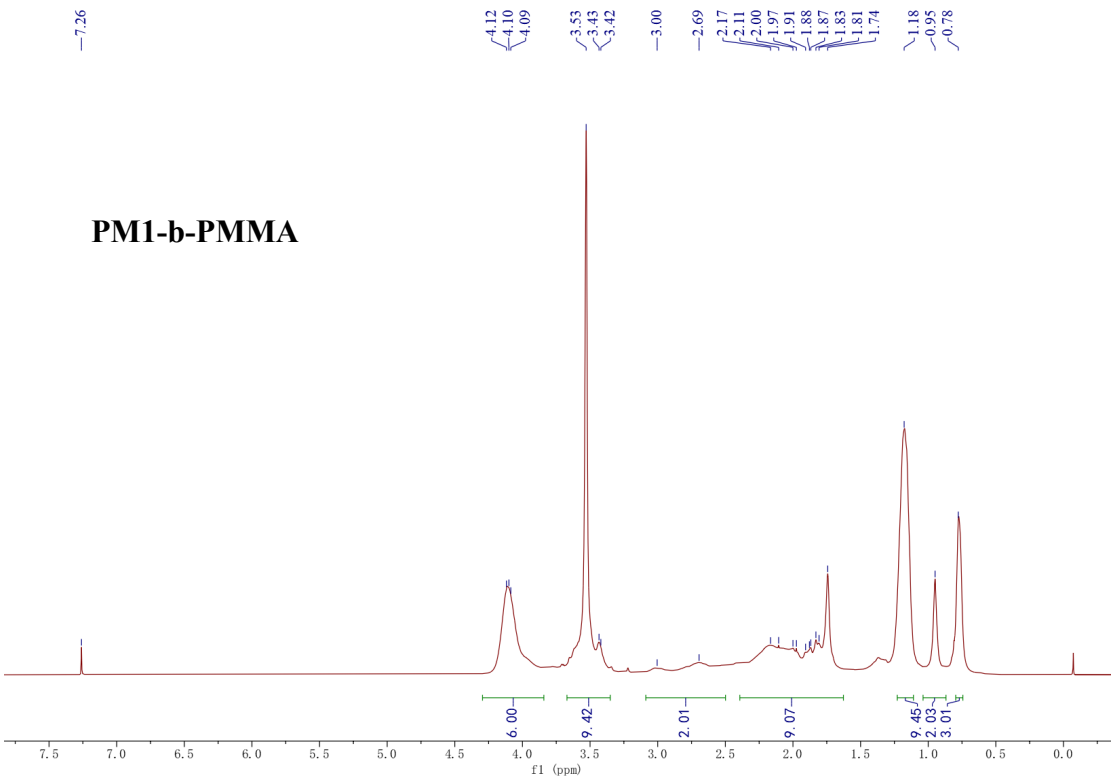


Fig. S60 ^{1}H NMR spectrum of **PM1-b-PMMA** in $CDCl_3$

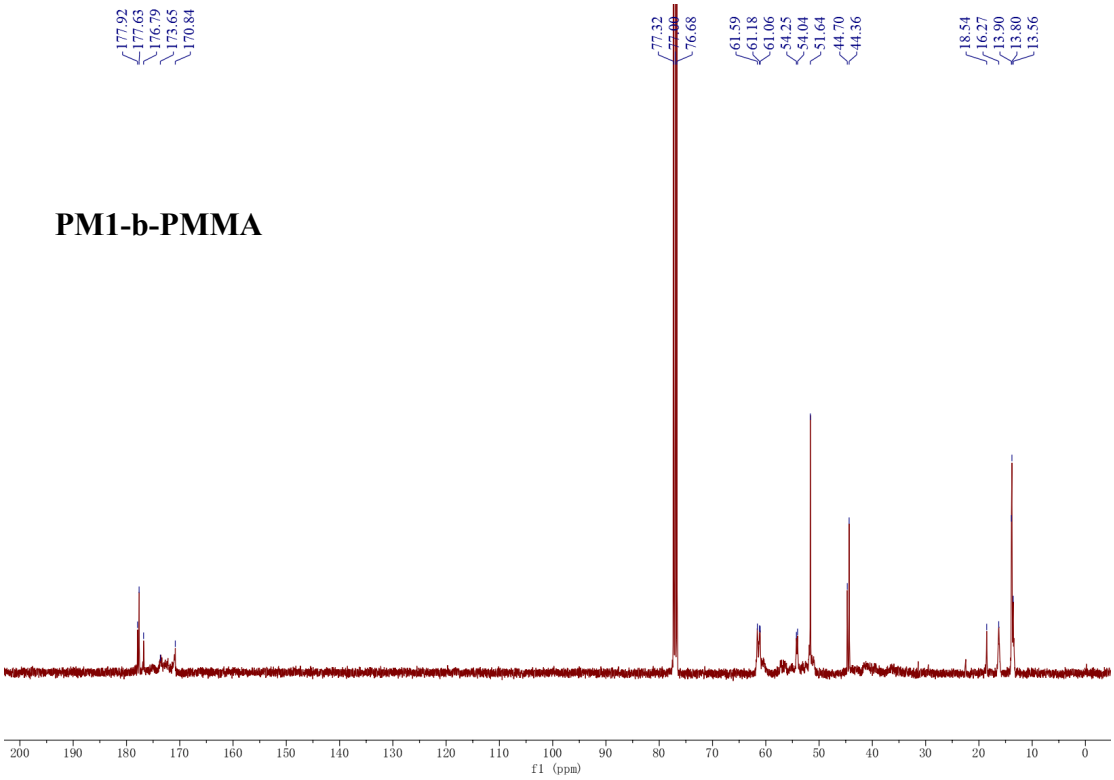


Fig. S61 ^{13}C NMR spectrum of **PM1-b-PMMA** in $CDCl_3$

9. Reference

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