Supporting Information

α-Diimine Catalyzed Propylene-Diene Copolymerization: Toward a Potential Sulfur-crosslinked Elastomeric Alternative to EPDM

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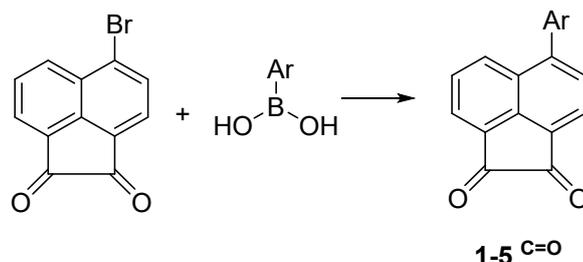wpzhao@qust.edu.cn (W. Zhao); hengliu@qust.edu.cn (H. Liu);

Contents

1. Experimental section

1.2 Procedure for the ligand precursors

1.2.1 Synthesis of ketone 1-5$^{C=O}$

1-5 $^{C=O}$

For diketone **1$^{C=O}$**: in a glovebox, into a 250 mL Schlenk flask were sequentially charged with Pd(PPh$_3$)$_4$ (0.022 g, 0.28 mmol), 5-bromoacenaphthylene-1,2-dione (1.5 g, 5.74 mmol), naphthalene boronic acid (0.988 g, 8.61 mmol), and sodium carbonate (0.421 g, 3.97 mmol). Subsequently, 120 ml mixture of toluene/water/ethanol (5:1:1 v/v/v) was added, which was degassed via freeze-pump-thaw. Afterwards, the reaction mixture was heated to 130 °C and left being reflux for 12 h. Upon completion, the reaction was quenched by adding a small amount of hydrochloric acid with stirring for 3-5 min. The mixture was washed three times with water, and the organic phase was extracted with chloroform. The combined organic layers were dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure to afford an orange-red powder. The crude product was dissolved in a minimal amount of dichloromethane (DCM) and precipitated by adding a large excess of hexane. The resulting solid was collected by filtration and further purified by further recrystallization from DCM, yielding compound **1$^{C=O}$** as an orange-yellow powder. Yield: 82% (1.45 g, 4.71 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.25 (d, J = 7.2 Hz, 1H), 8.13 (d, J = 7.7 Hz, 1H), 8.06–7.99 (m, 2H), 7.90 (d, J = 7.2 Hz, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.72-7.63 (m, 2H), 7.57-7.52 (m, 2H), 7.44-7.35 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 188.50, 188.00, 146.15, 145.26, 135.69, 133.80, 132.10, 131.90, 130.90, 130.28, 129.39, 128.89, 128.71, 128.55, 128.32, 127.80, 126.84, 126.48, 125.63, 125.51, 122.24, 122.03, 77.48,

76.84.

Ketone **2****C=O** was prepared in a similar method to **1****C=O**. Yield: 85% (1.50 g , 4.88 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.29-8.23 (m, 2H), 8.14 (d, J = 6.9 Hz, 1H), 7.88 (d, J = 7.1 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.74-7.68 (m, 1H), 7.62 (t, J = 6.5 Hz, 1H), 7.49 (dd, J = 7.8, 5.3 Hz, 1H), 7.43 (d, J = 7.5 Hz, 2H), 7.33 (dd, J = 10.1, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 188.39, 187.94, 160.60, 158.08, 146.11, 144.44, 133.32, 133.27, 131.91, 131.74, 131.67, 130.96, 130.51, 128.92, 128.69, 128.41, 127.81, 127.77, 127.69, 126.83, 126.81, 125.69, 125.66, 124.10, 123.94, 122.32, 122.04, 121.28, 121.23, 109.41, 109.20, 77.48, 76.84.

Ketone **3****C=O** was prepared in a similar method to **1****C=O**. Yield: 79% (1.62 g, 4.54 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.43 (d, J = 10.6 Hz, 1H), 8.24 (d, J = 7.2 Hz, 1H), 8.11 (d, J = 7.0 Hz, 1H), 7.90-7.86 (m, 2H), 7.71-7.66 (m, 1H), 7.58-7.50 (m, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 2.5 Hz, 2H), 6.99 (d, J = 7.9 Hz, 1H), 4.12 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 188.70, 187.60, 156.37, 146.33, 145.63, 135.34, 135.28, 135.18, 132.81, 132.30, 131.17, 130.55, 130.50, 128.87, 128.39, 128.14, 128.09, 128.06, 127.99, 127.94, 127.91, 127.30, 125.80, 125.78, 125.41, 122.71, 122.16, 122.14, 103.51, 77.48, 76.84, 55.87.

Ketone **4****C=O** was prepared in a similar method to **1****C=O**. Yield: 86% (1.61 g, 4.94 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.41 (d, J = 8.1 Hz, 1H), 8.18 (d, J = 7.2 Hz, 1H), 8.12 (d, J = 6.9 Hz, 1H), 8.09-8.01 (m, 2H), 7.95 (s, 2H), 7.90 (d, J = 7.2 Hz, 1H), 7.83-7.78 (m, 1H), 7.71 (d, J = 6.6 Hz, 1H), 7.63-7.57 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 188.68, 187.93, 135.66, 133.46, 133.34, 131.76, 129.72, 129.42, 129.03, 128.97, 128.84, 128.74, 128.44, 128.02, 127.18, 127.09, 122.25, 122.22, 77.48, 76.84.

Ketone **5****C=O** was prepared in a similar method to **1****C=O**. Yield: 84% (1.63 g, 4.82 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.68 (s, 1H), 8.35 (d, J = 7.1 Hz, 1H), 8.14 (dd, J = 7.7, 4.4 Hz, 3H), 7.94 (d, J = 7.1 Hz, 1H), 7.63-7.57 (m, 1H), 7.53-7.46 (m, 3H), 7.32 (d, J = 5.6 Hz, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 188.51, 188.15, 145.84, 143.63, 132.12, 131.58, 131.48, 130.53, 129.13, 128.94, 128.86, 128.67, 128.46, 126.57, 125.65, 122.49, 122.11.

2 Crystallographic details

Table S1. Crystallographic data for complexes **Ni5**

	Ni5
Formula	$C_{103}H_{102}Br_4Cl_6N_4Ni_2$
CCDC number	2488915
Formula weight	2045.64
Temperature	296.15K
Crystal system	monoclinic
space group	P21/c
a (Å)	16.5580(14)
b (Å)	22.4207(17)
c (Å)	13.3943(12)
α (deg)	90
β (deg)	94.097(3)
γ (deg)	90
Volume($Å^3$)	4959.8(7)
Z	2
Calculated density (g/cm^3)	1.370
Absorption coefficient (mm^{-1})	2.199
F(000)	2092.0
Crystal size (mm)	$0.1 \times 0.1 \times 0.1$
2θ range (deg)	4.744 to 52.736
Limiting indices	$-20 \leq h \leq 20$ $-28 \leq k \leq 23$ $-16 \leq l \leq 16$
Reflections collected	35829
Independent reflections	10122 [R_{int} = 0.0560, R_{sigma} = 0.0568]
Data / restraints / parameters	10122/5328/558
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1= 0.0655, wR2= 0.1782
R indices (all data)	R1= 0.1000, wR2= 0.2024
Largest diff. peak and hole (e./Å^{-3})	1.04/-1.05

3. NMR spectra of the ligands
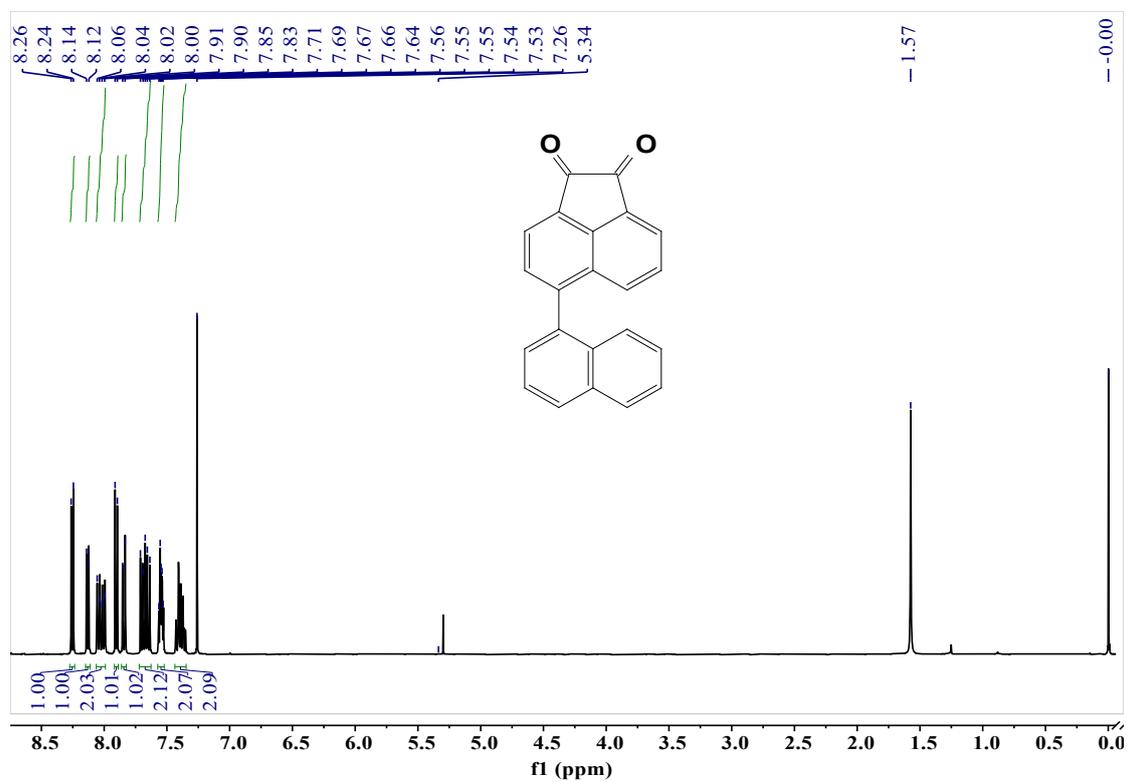
Figure S1. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **1$^{C=O}$**.
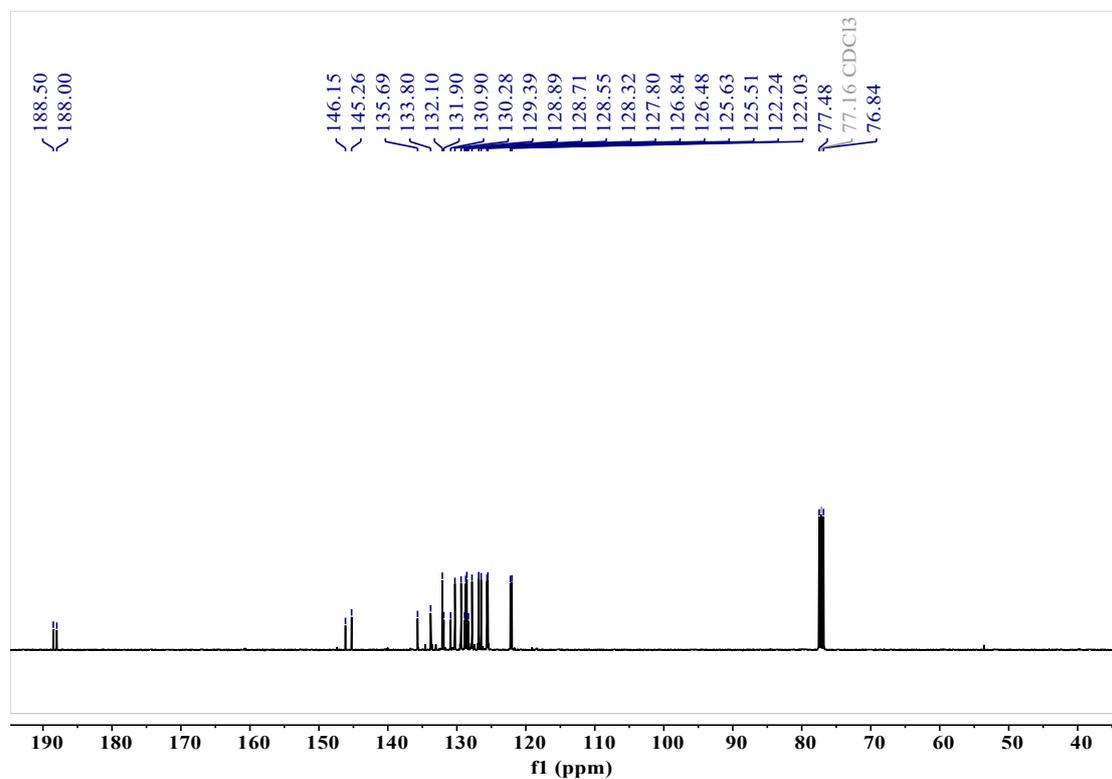
Figure S2. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of **1$^{C=O}$** .
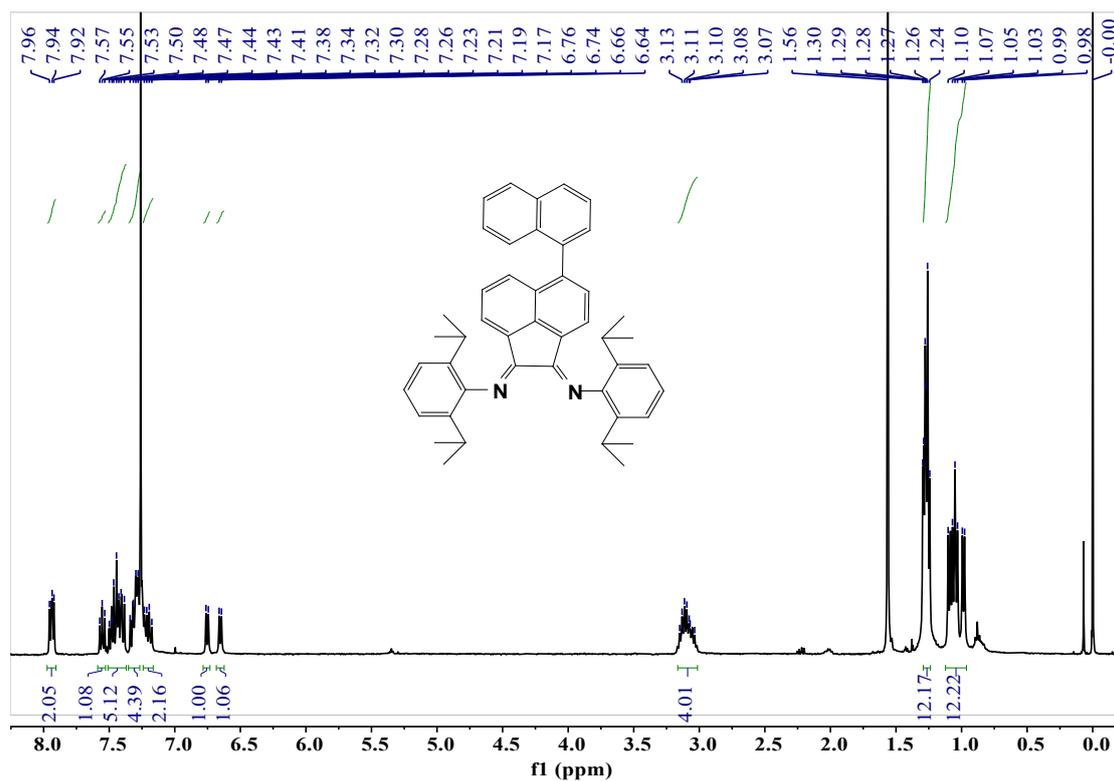
Figure S3. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **L1.**
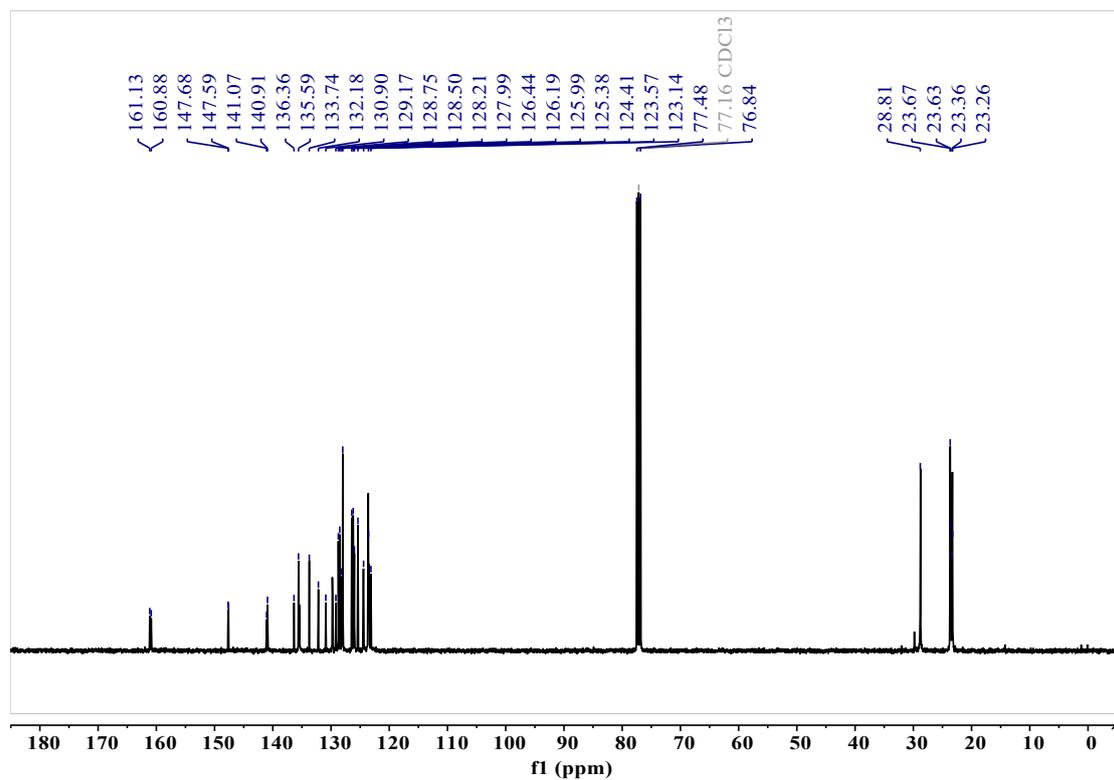
Figure S4. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of **L1**.
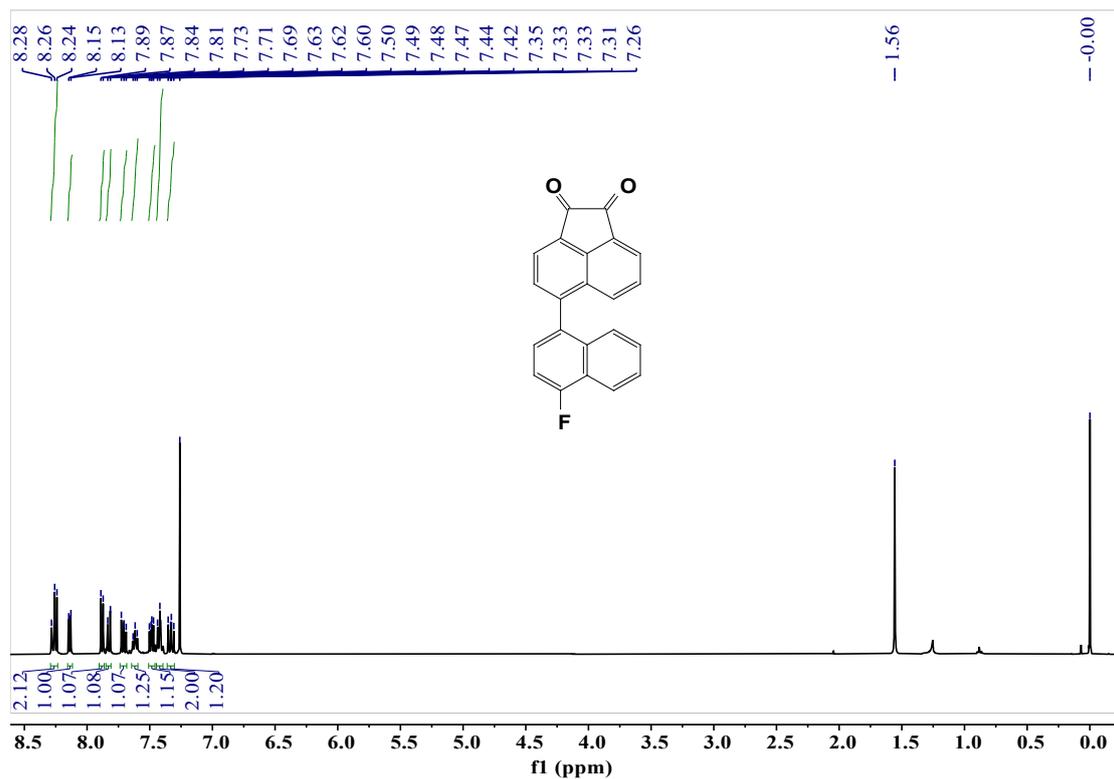
Figure S5. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of $\mathbf{2^{C=O}}$.
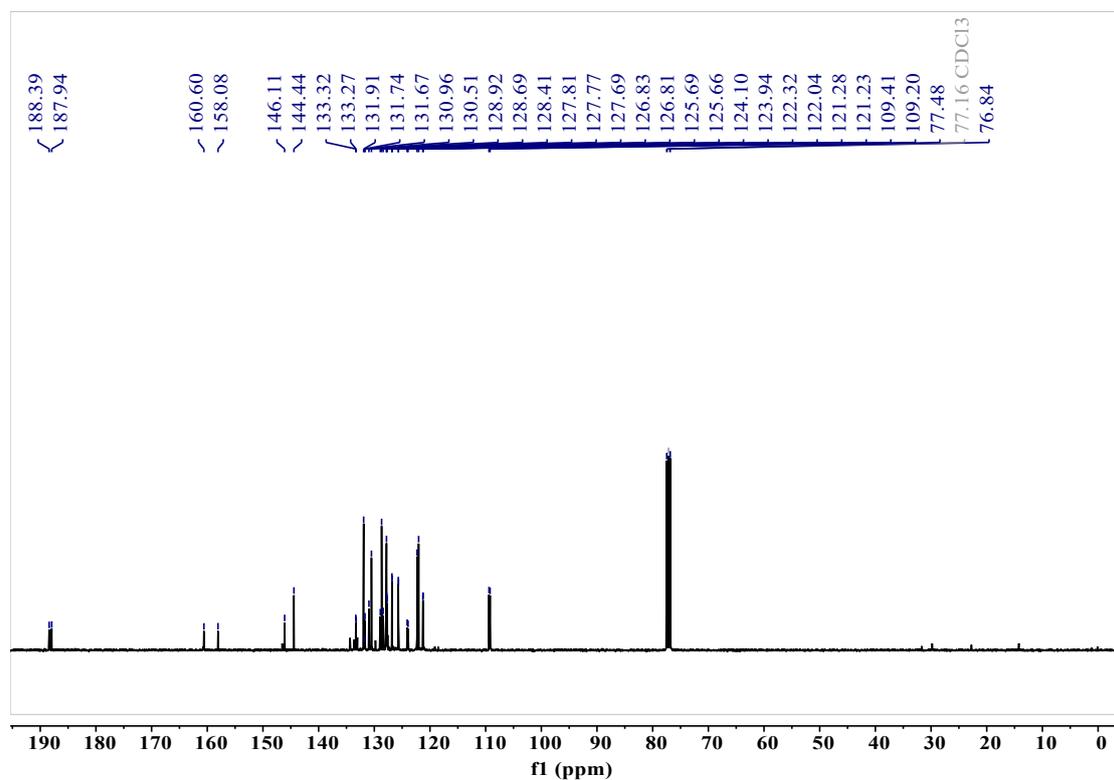
Figure S6. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of $\mathbf{2^{C=O}}$.
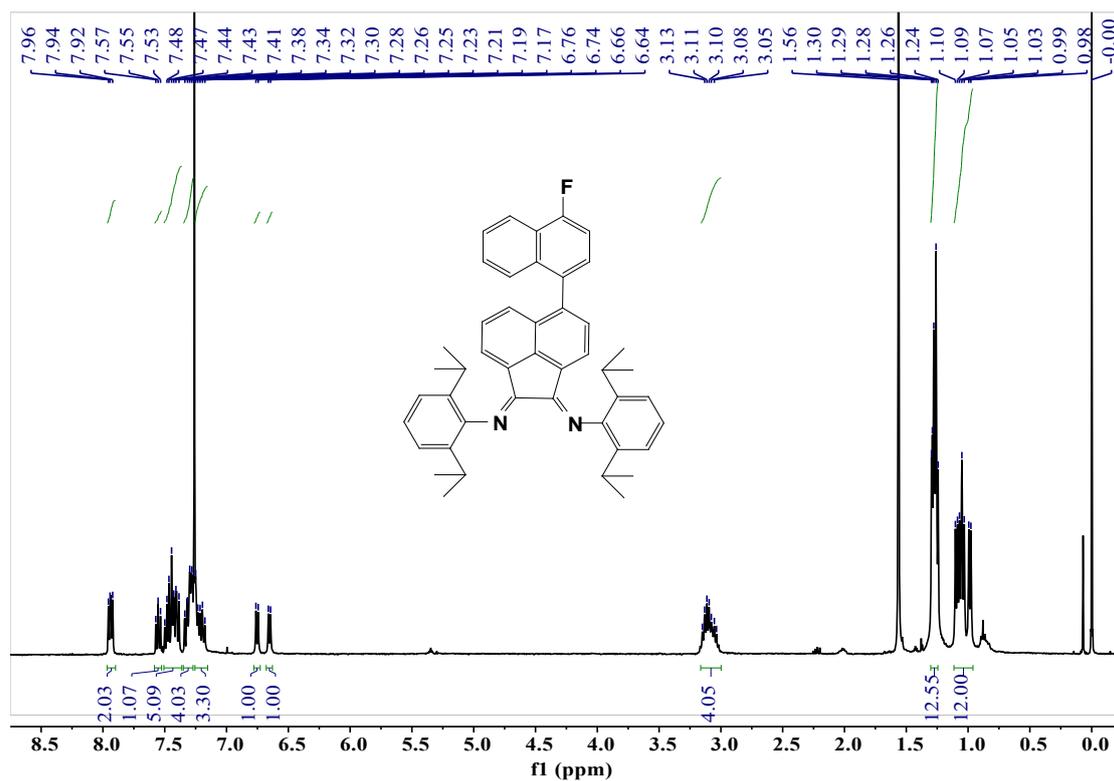
Figure S7. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **L2.**
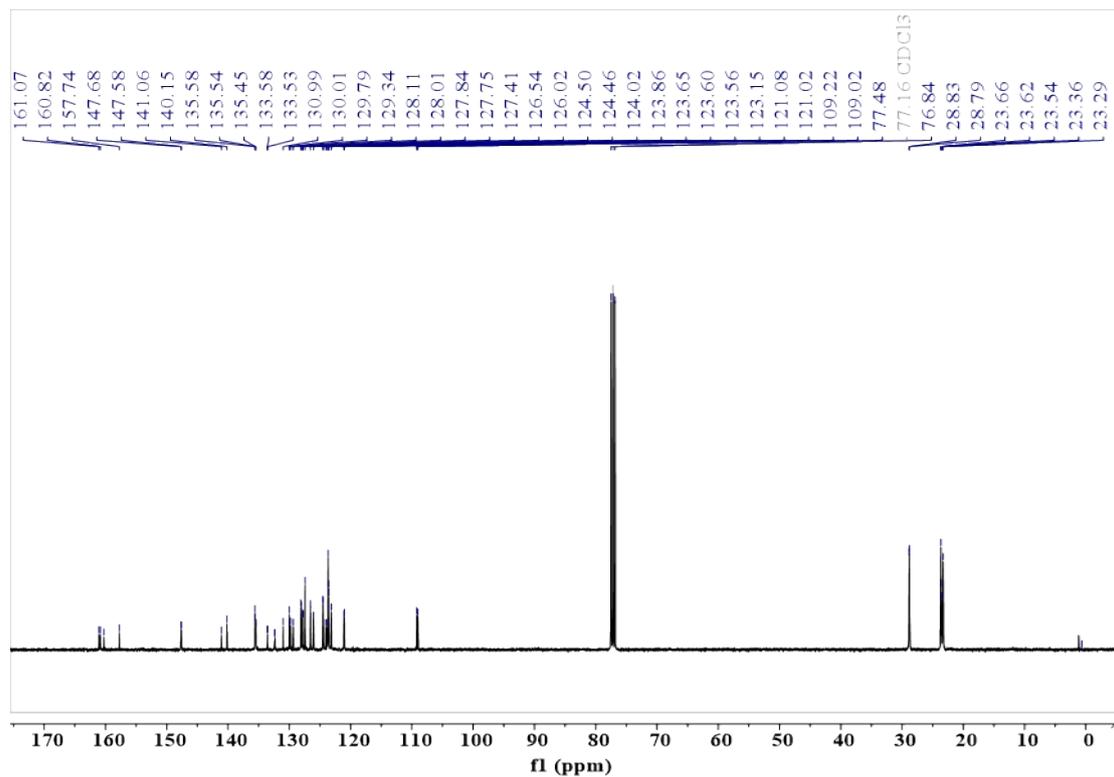
Figure S8. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of **L2**
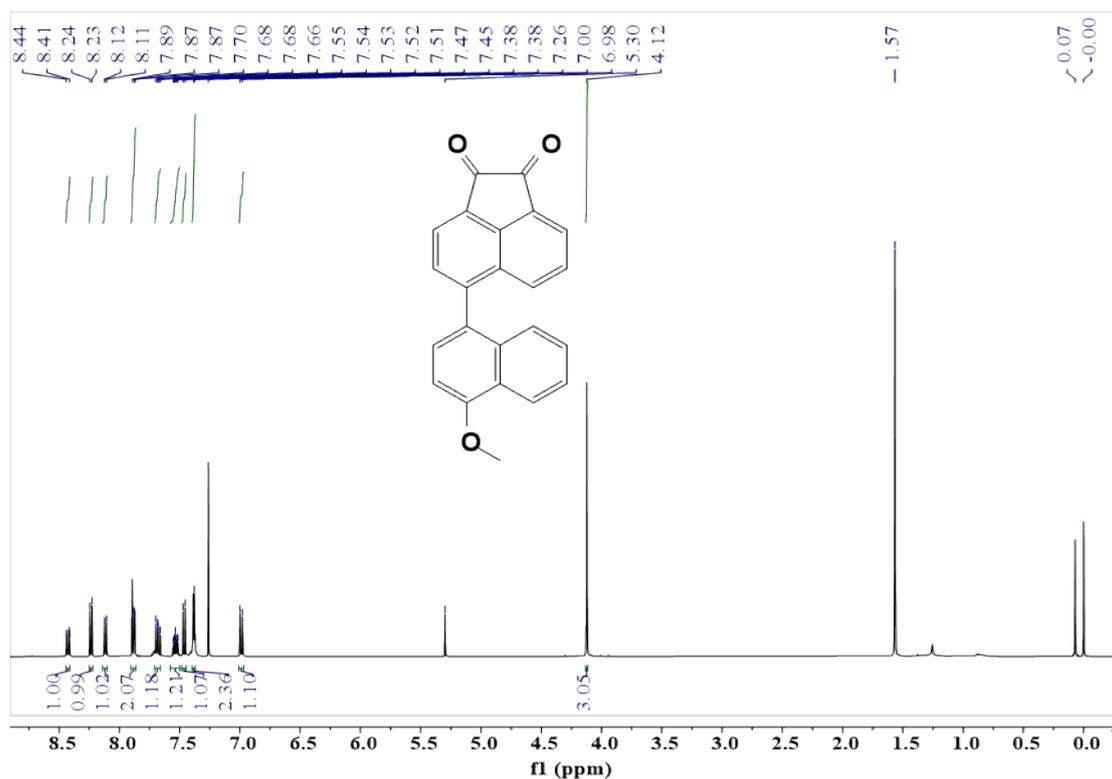
Figure S9. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **3$^{C=O}$** .
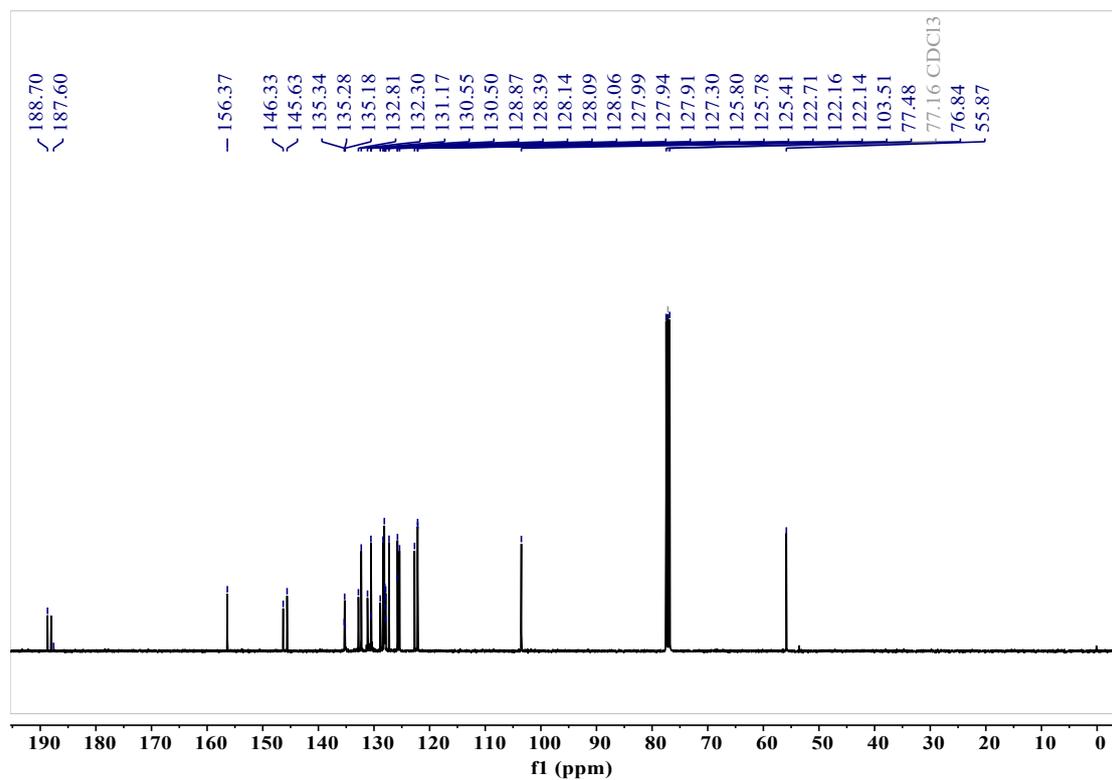
Figure S10. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of **3$^{C=O}$** .
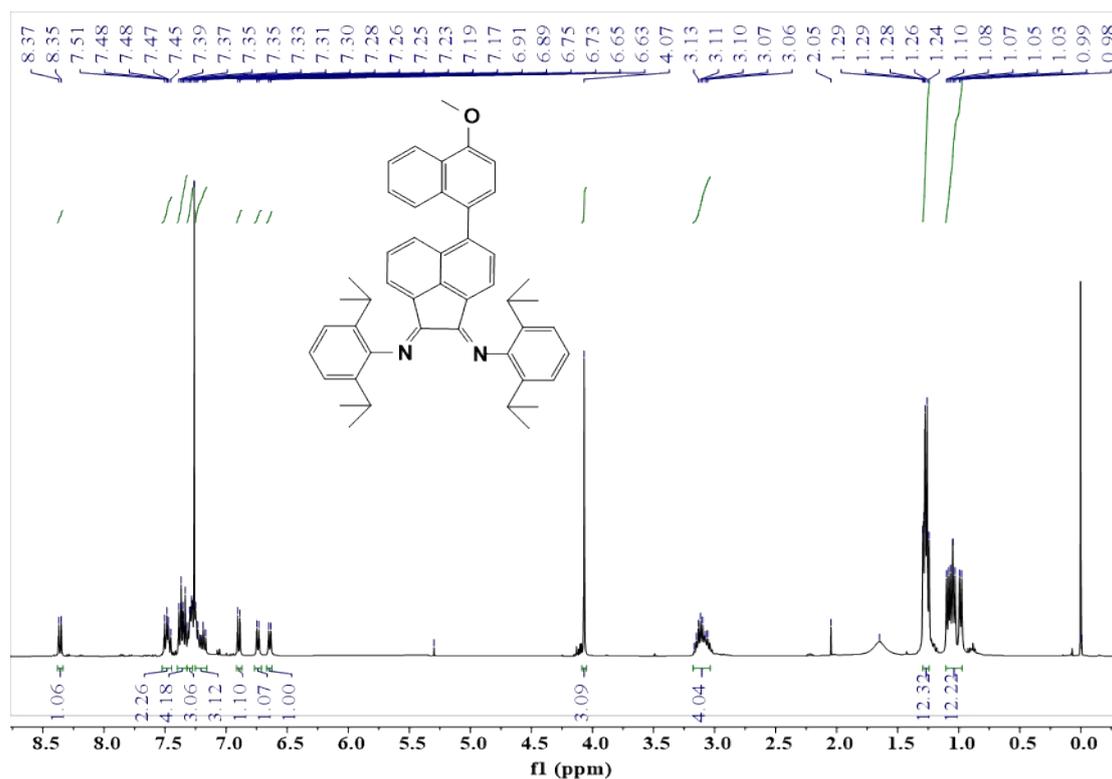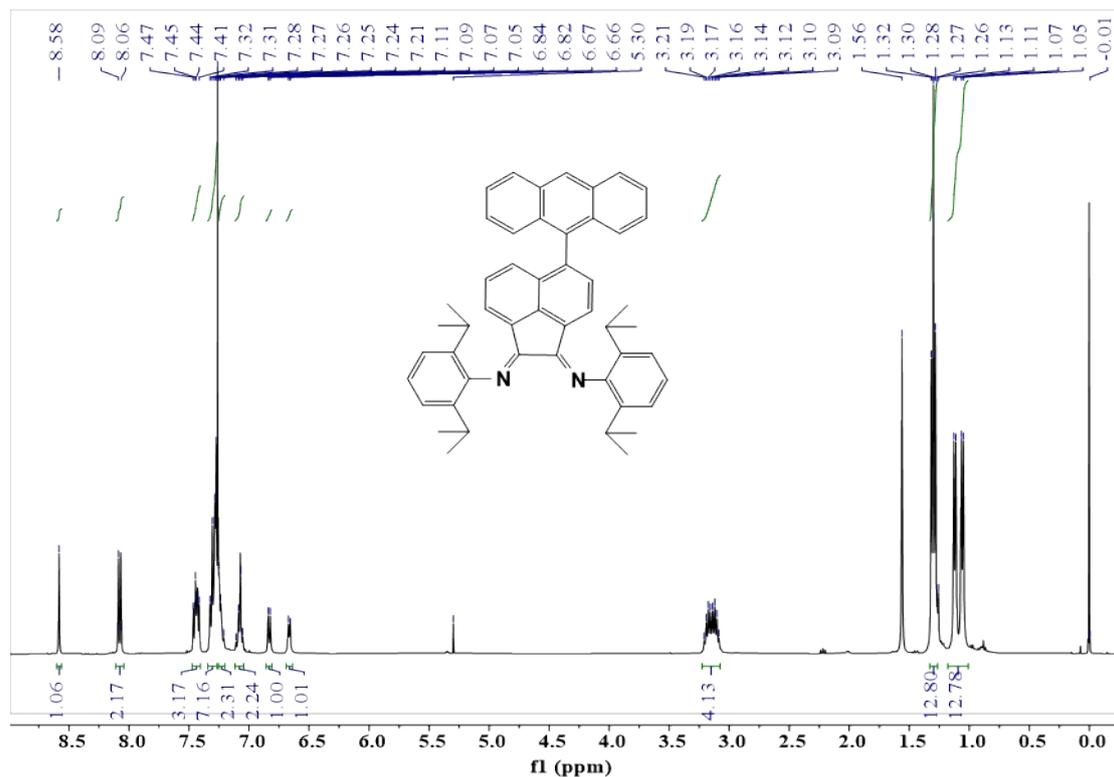
Figure S11. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **L3**.
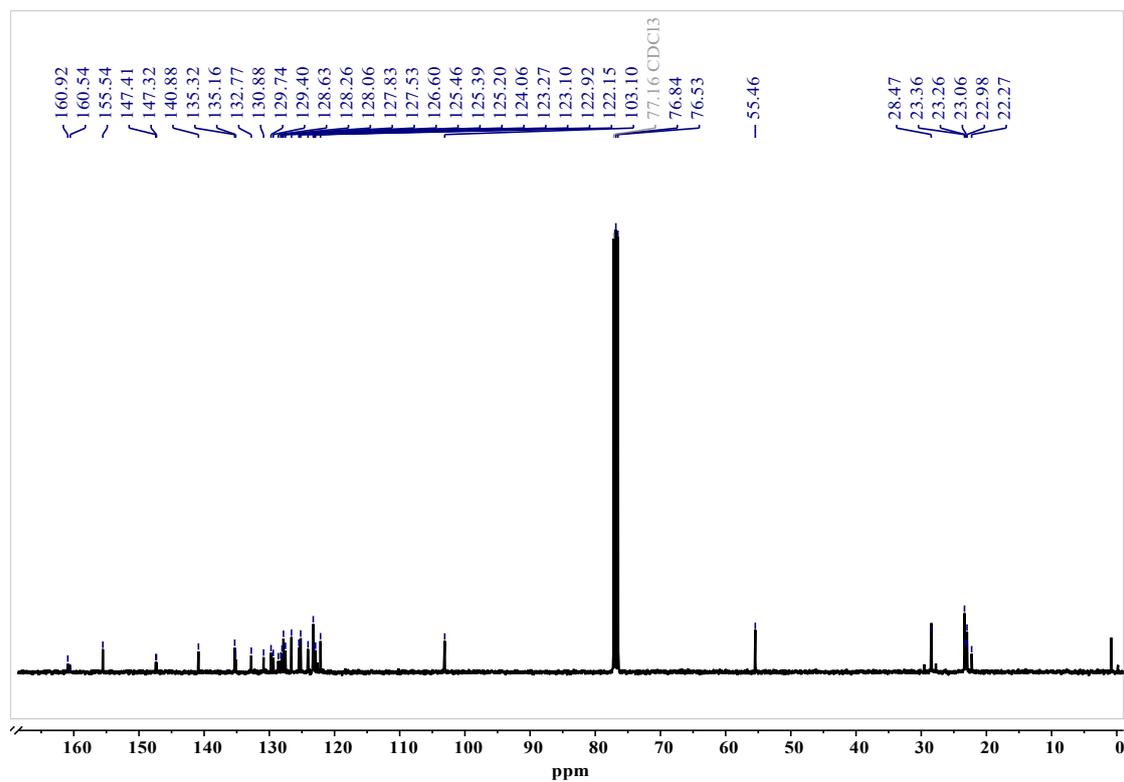
Figure S12. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of **L3**.
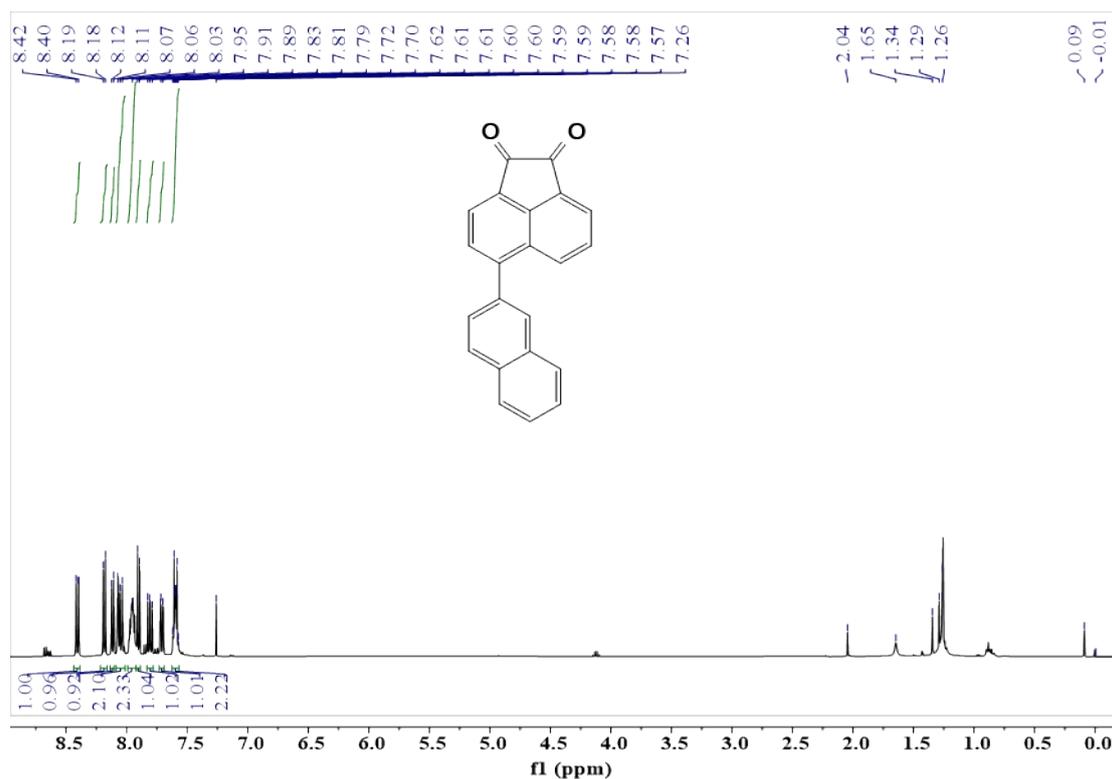
Figure S13. ^1H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **4$^{C=O}$**
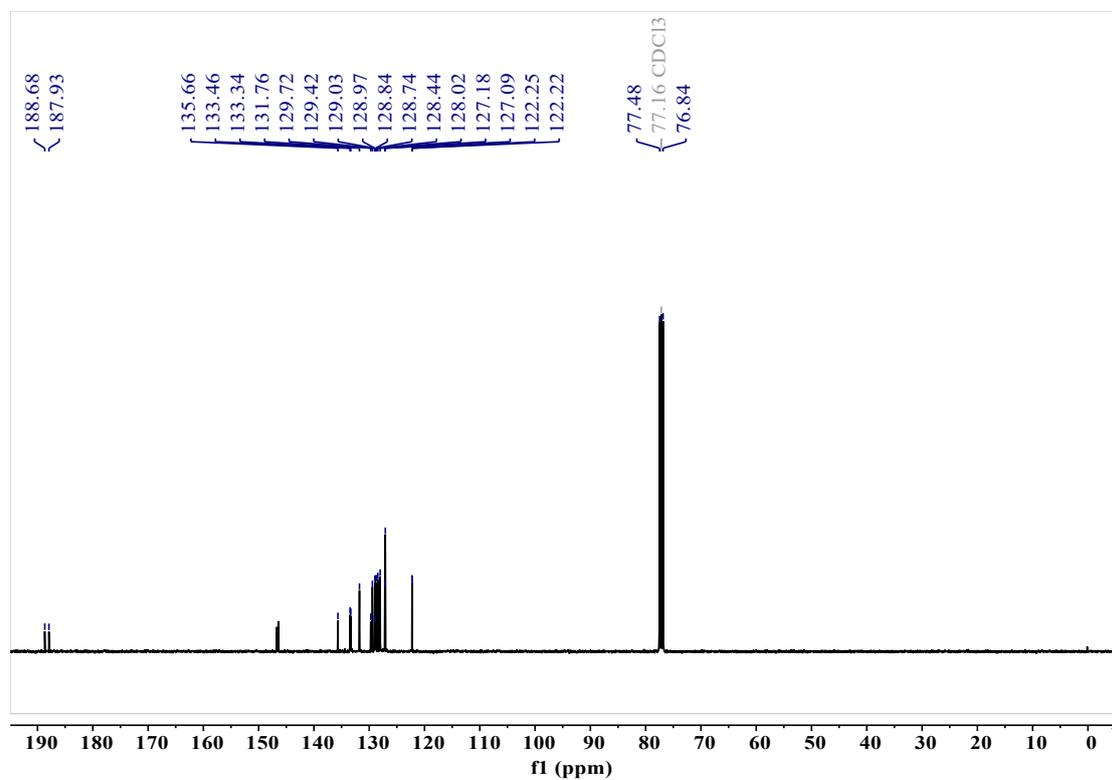
Figure S14. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of **4$^{C=O}$** .

Figure S15. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **L4**.

Figure S16. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of **L4**.
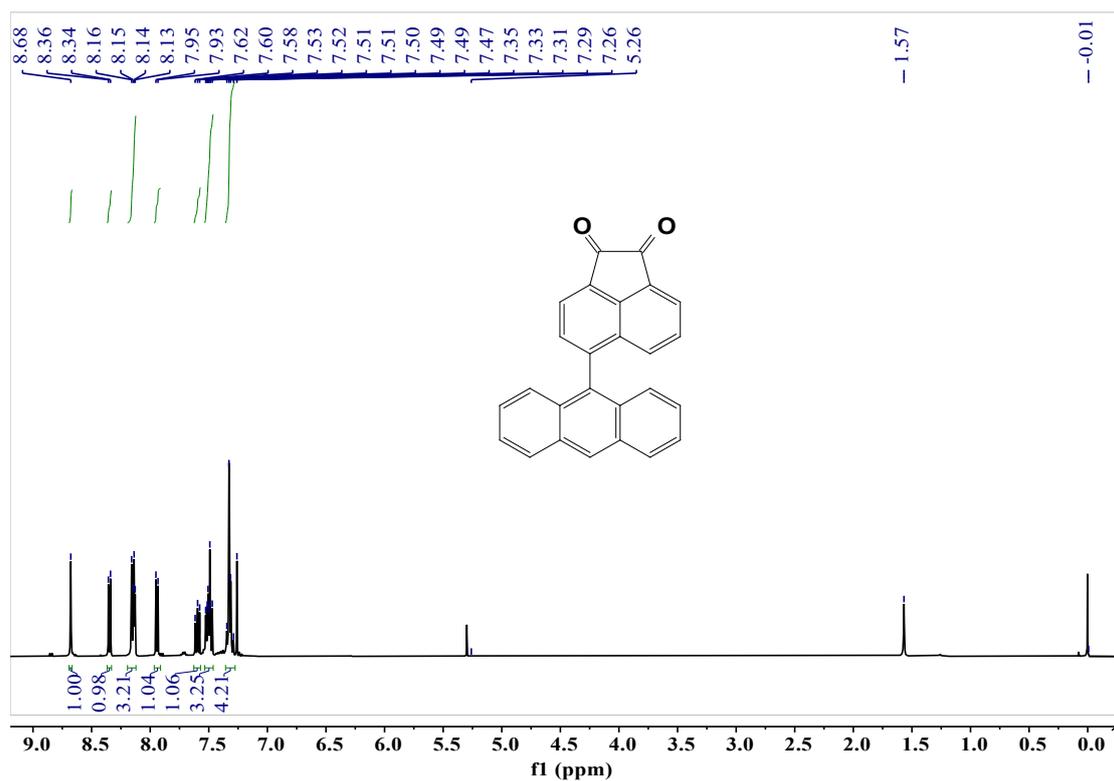
Figure S17. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **5$^{C=O}$** .
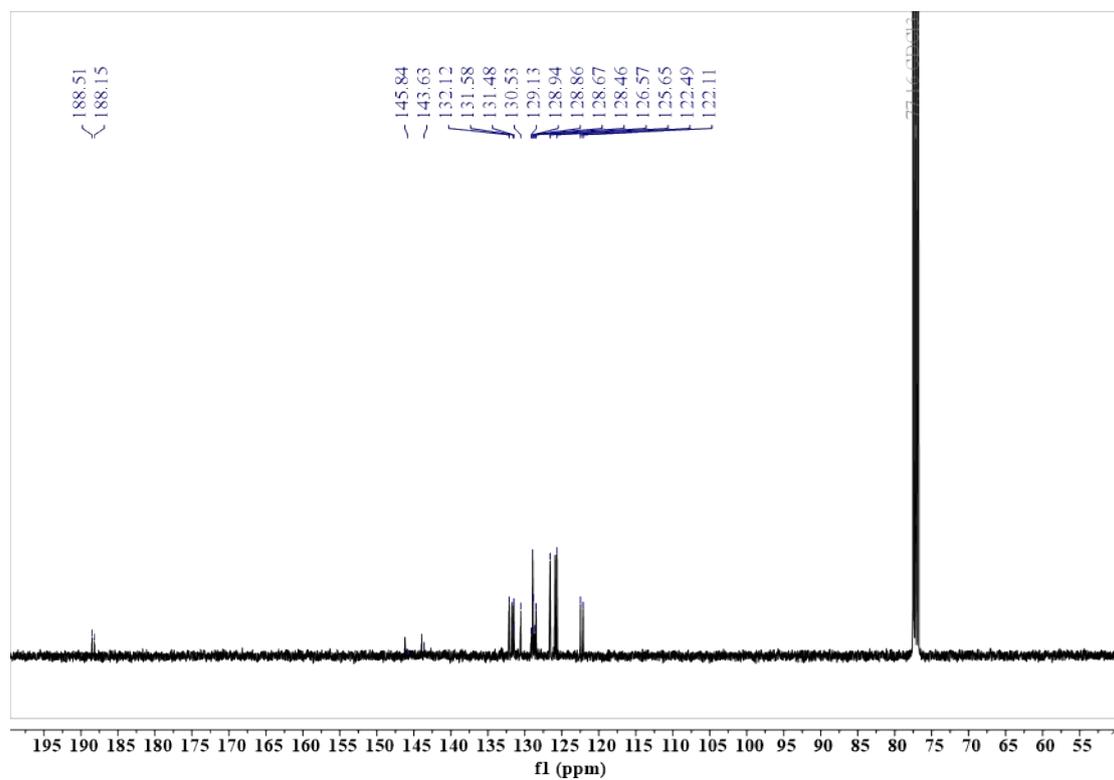
Figure S18. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of **5$^{C=O}$** .

Figure S19. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of **L5**.
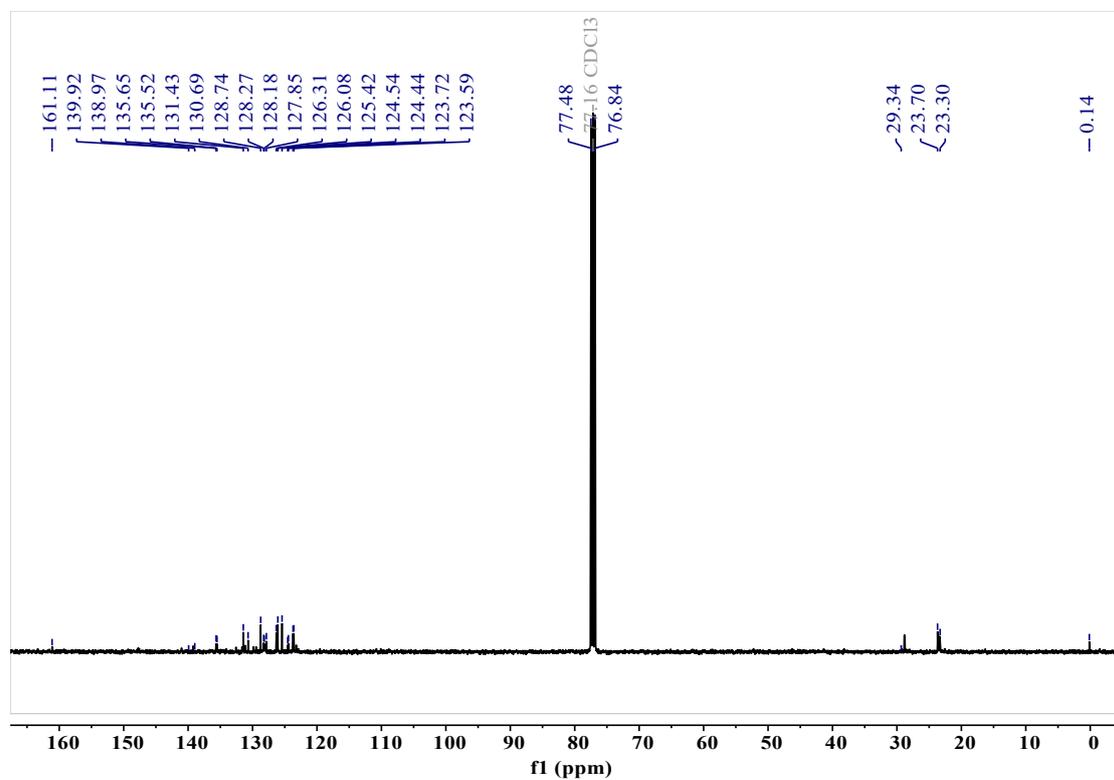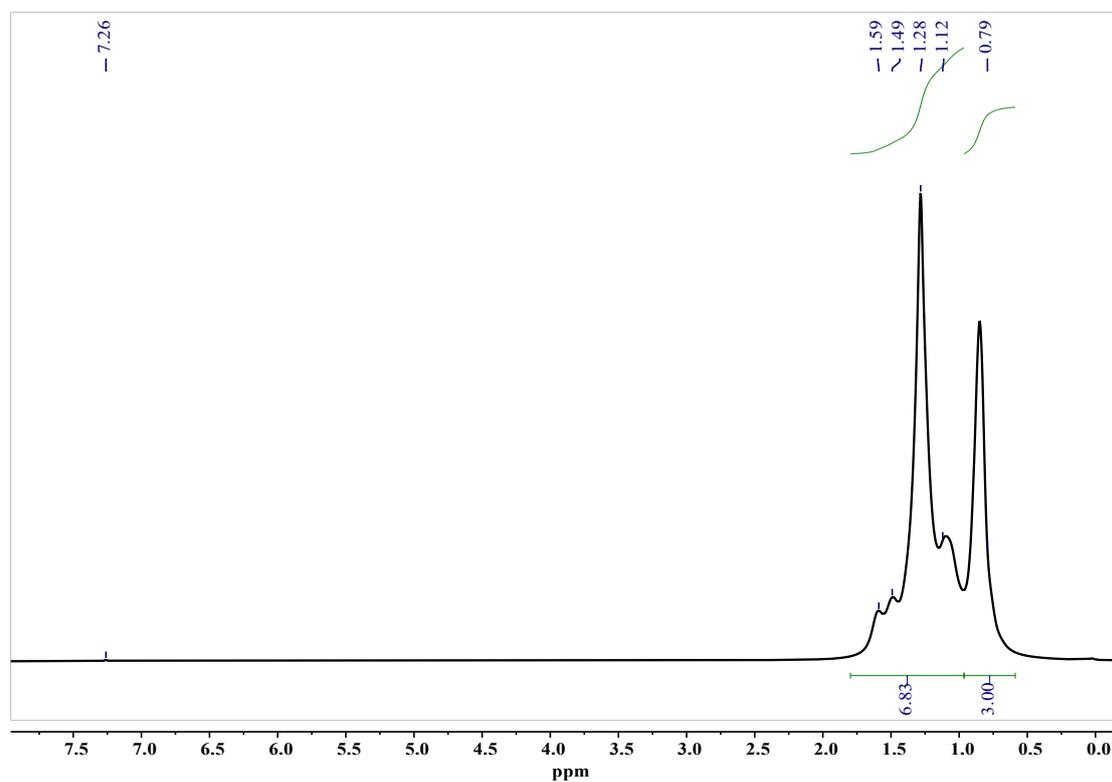

Figure S20. ^{13}C NMR spectrum (101 MHz, CDCl$_3$, 298 K) of **L5**.
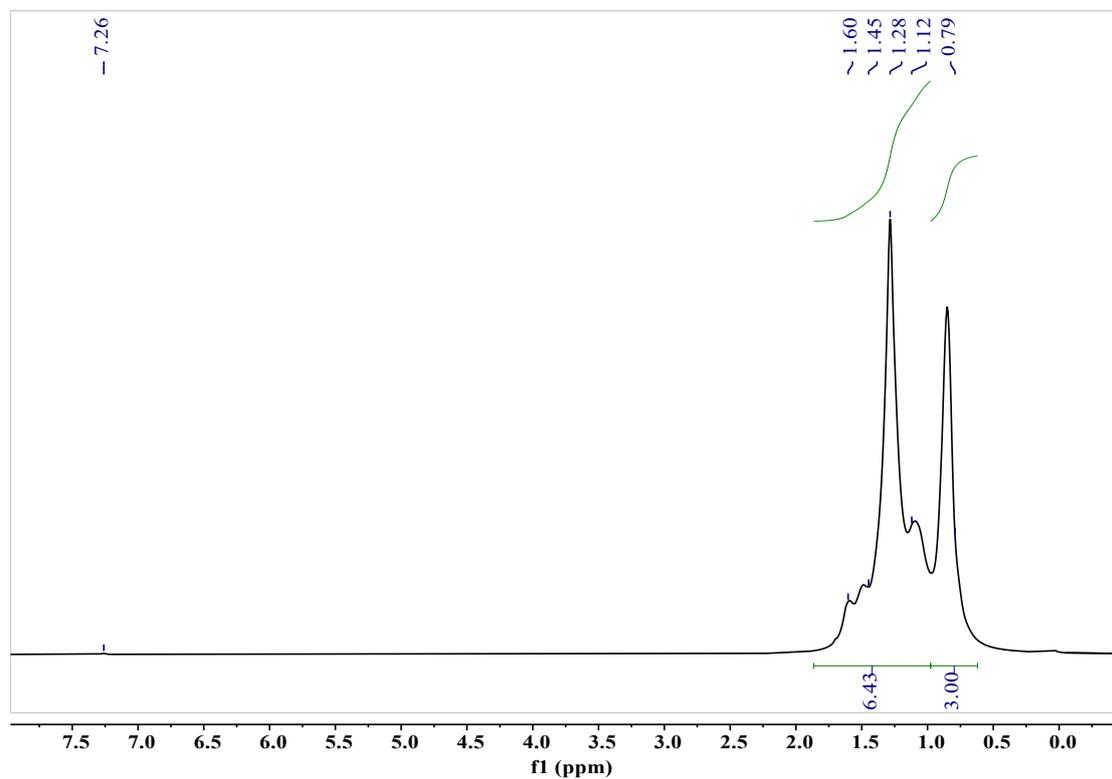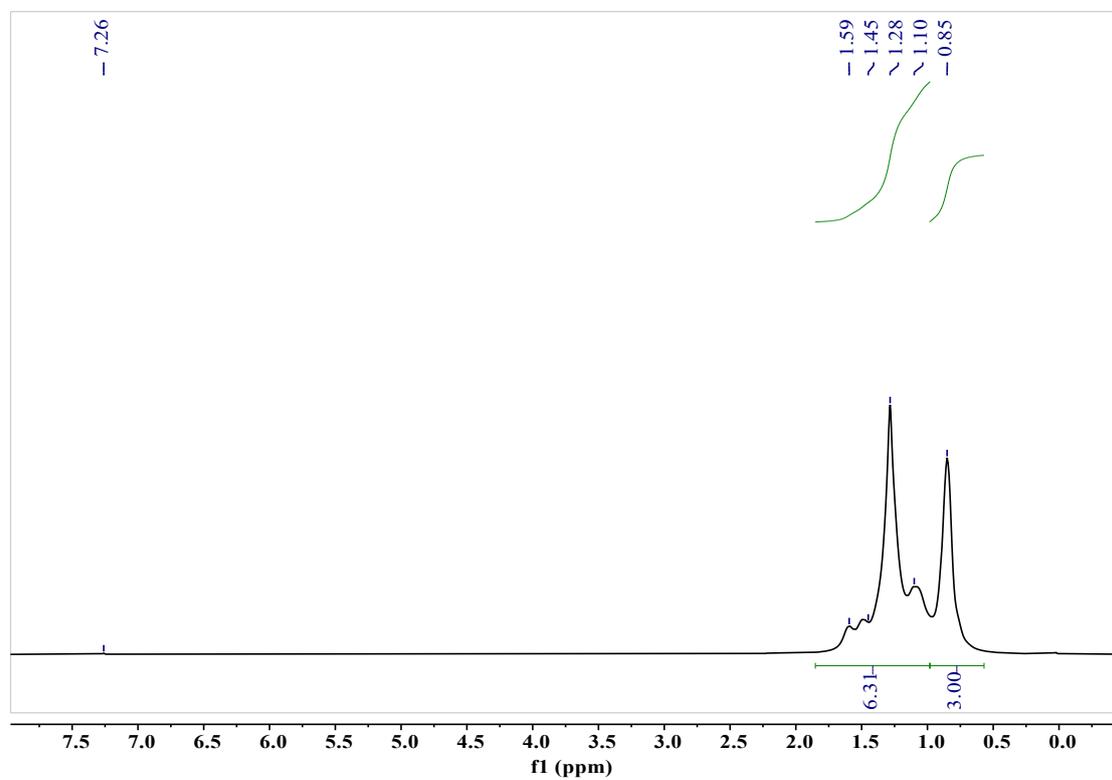
4. NMR spectra of the polymers
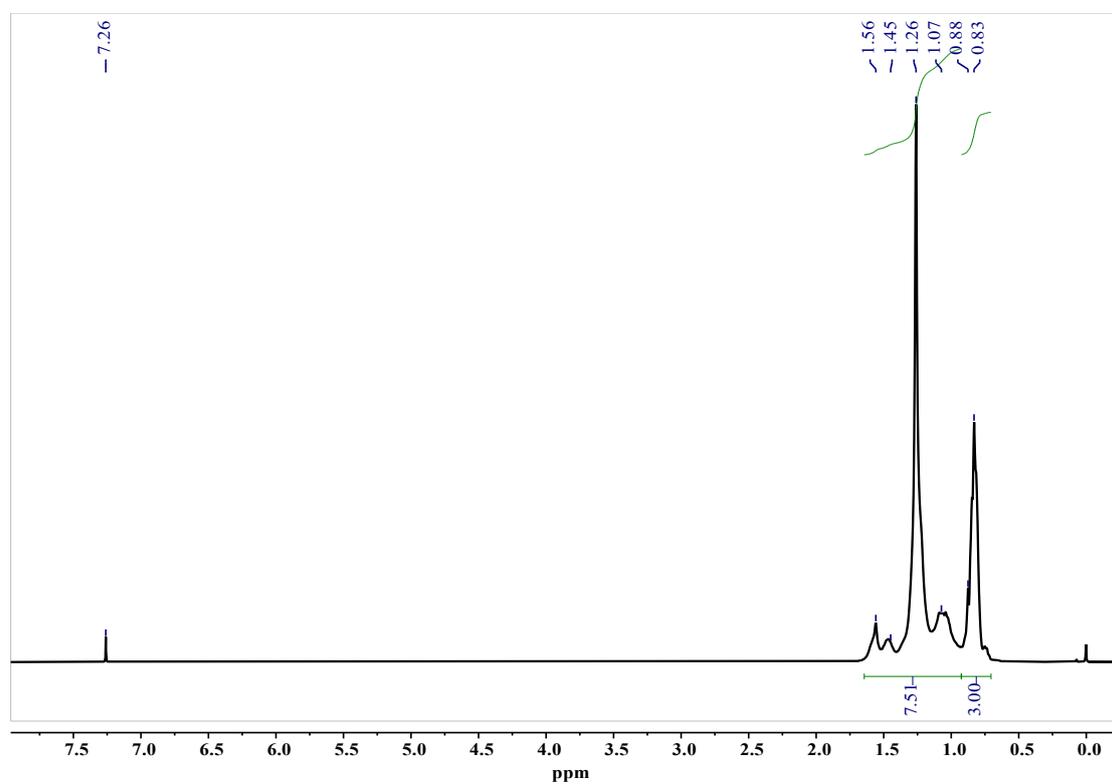
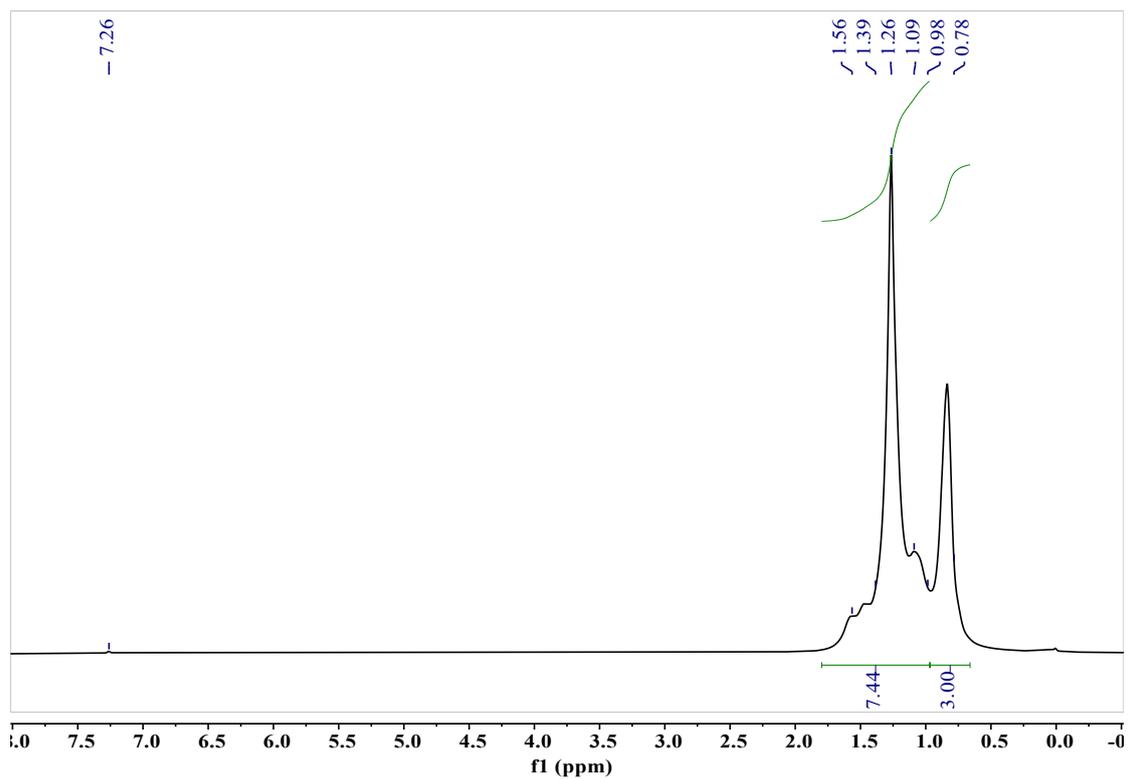**Figure S21.** ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 1.

Figure S22. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 2.

Figure S23. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 3.

Figure S24. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 4.

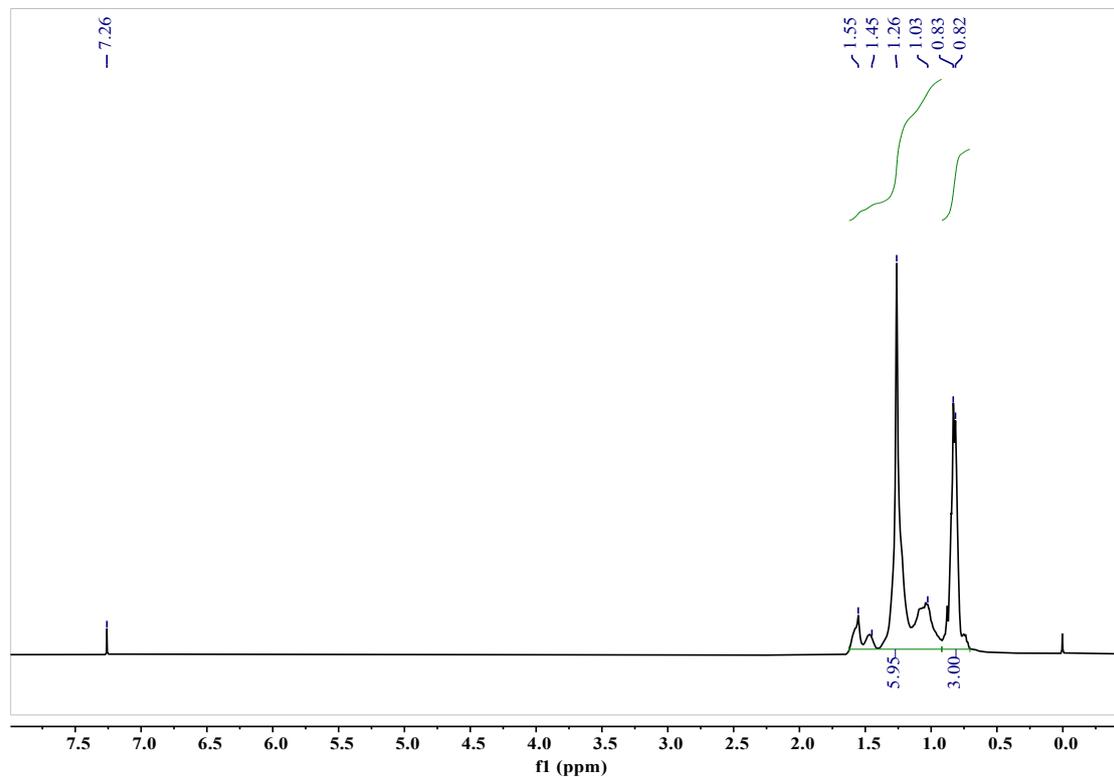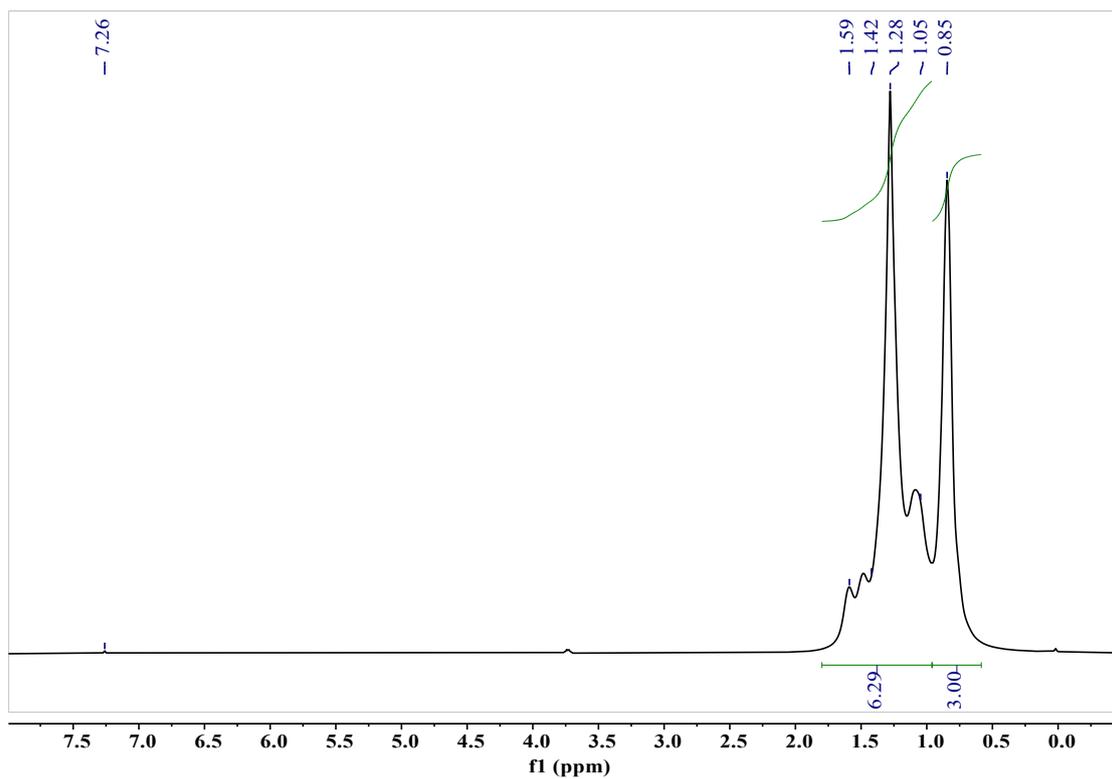**Figure S25.** ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 5.

Figure S26. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 6.
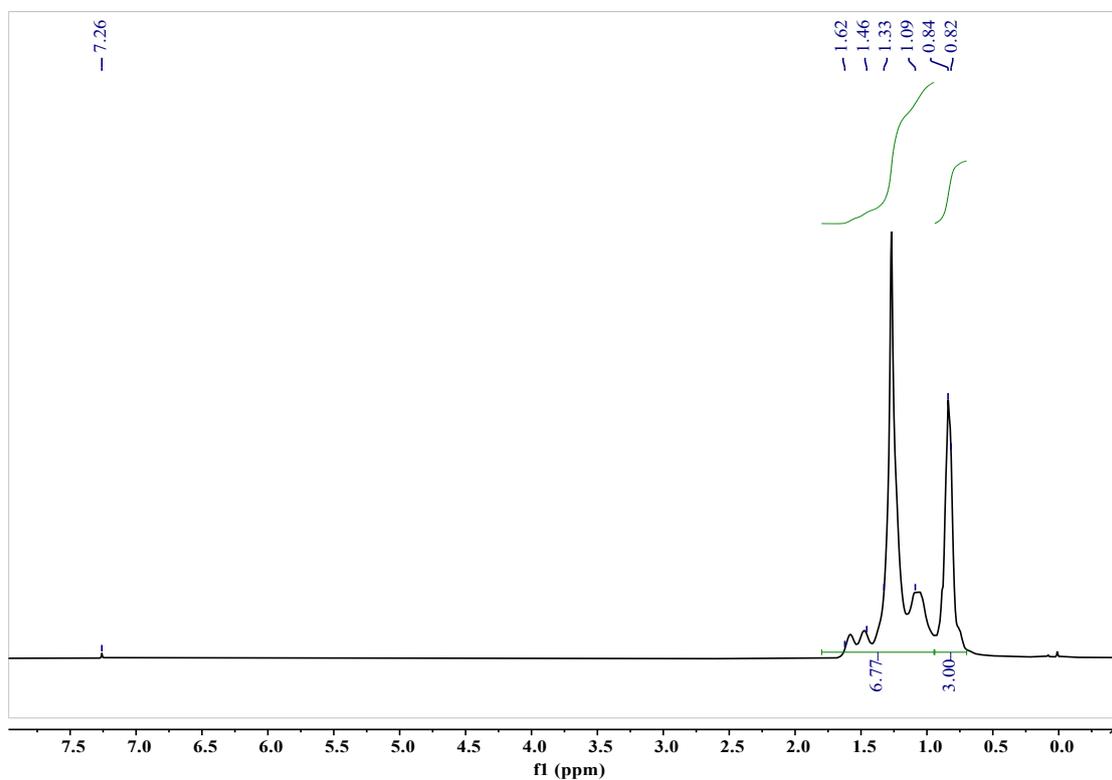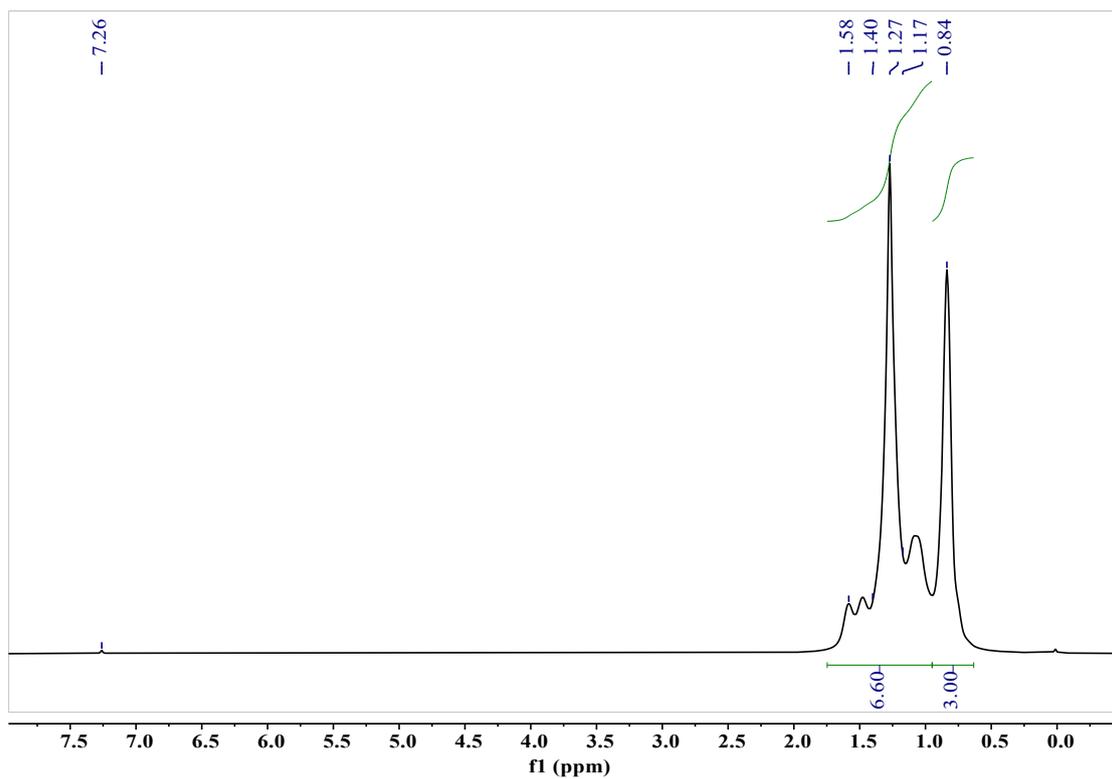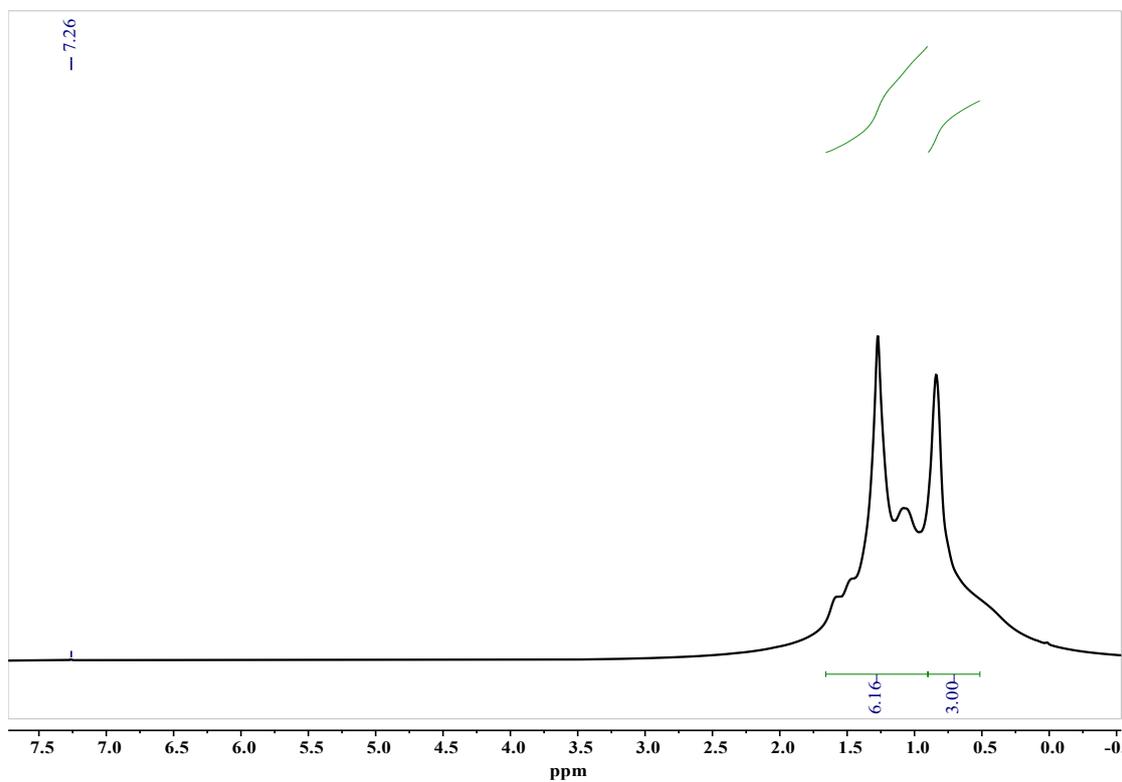
Figure S27. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 8.
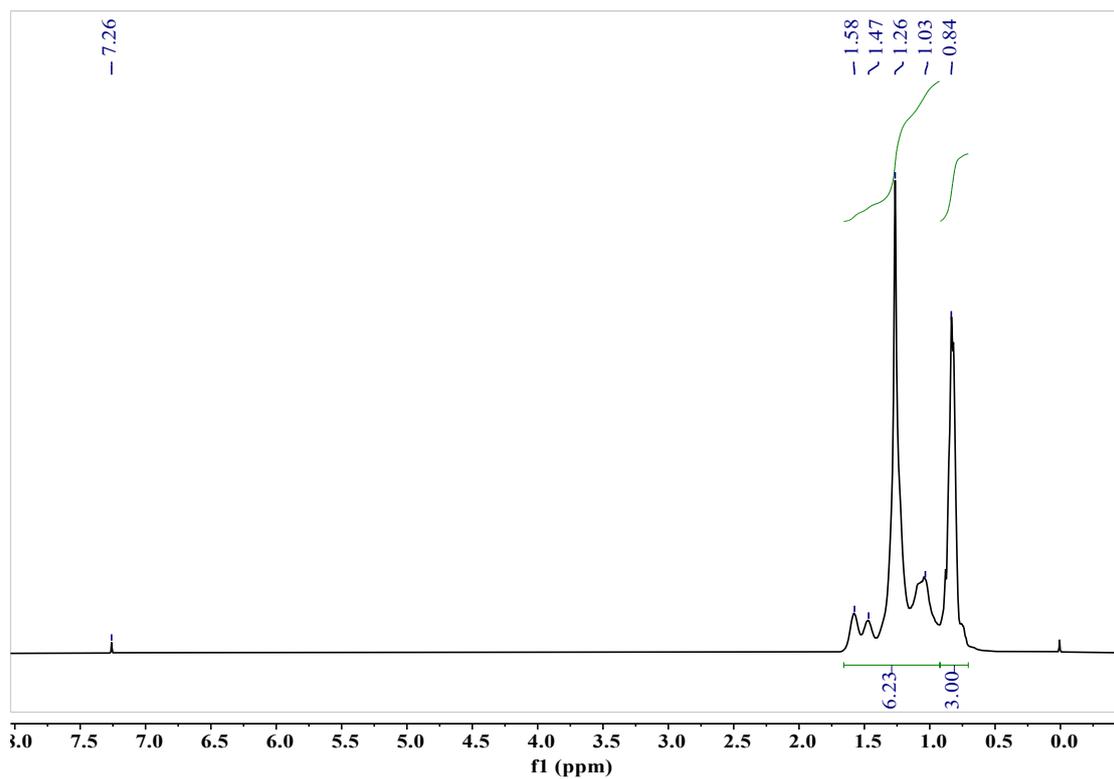

Figure S28. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 9.

Figure S29. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 10.

Figure S30. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 11.

Figure S31. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 12.

Figure S32. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 13.

Figure S33. ¹H NMR spectrum (400 MHz, 298 K) of table 1, run 14.

Figure S34. ¹H NMR spectrum (400 MHz, 298 K) of table 1, run 15.

Figure S35. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 16.

Figure S36. ^{1}H NMR spectrum (400 MHz, 298 K) of table 1, run 17.

Figure S37. ^{1}H NMR spectrum (400 MHz, 298 K) of table 2, run 2.

Figure S38. ^{1}H NMR spectrum (400 MHz, 298 K) of table 2, run 4.
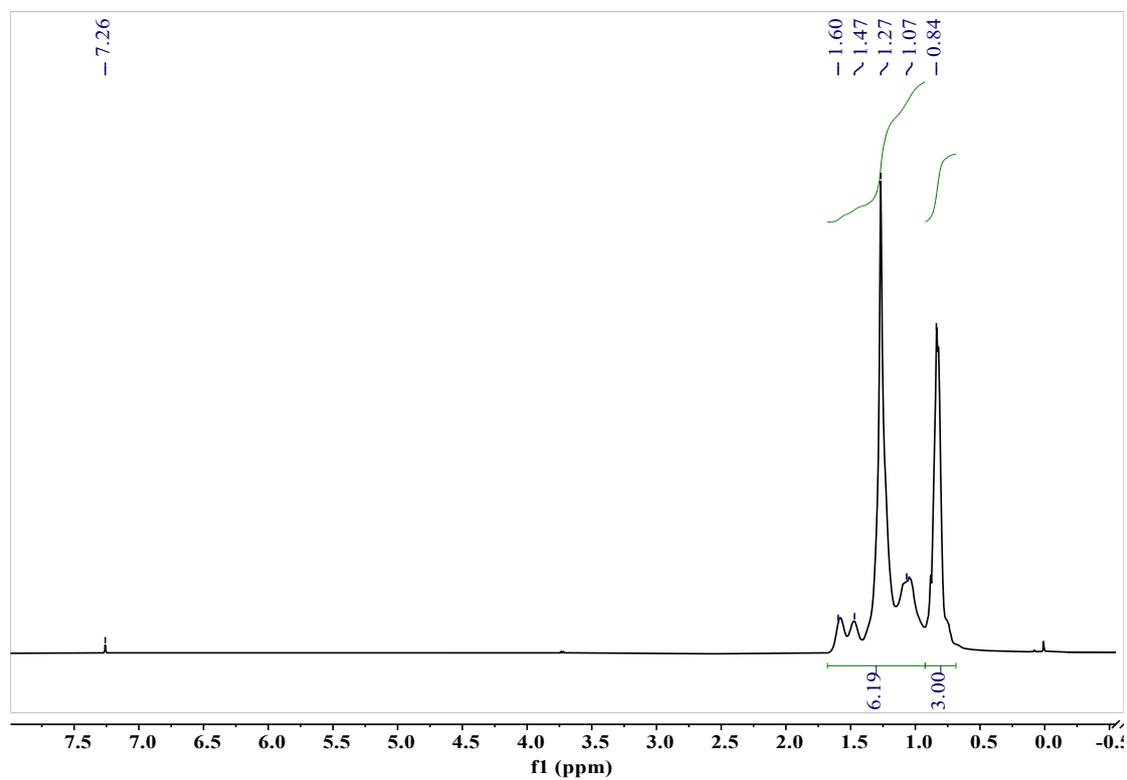
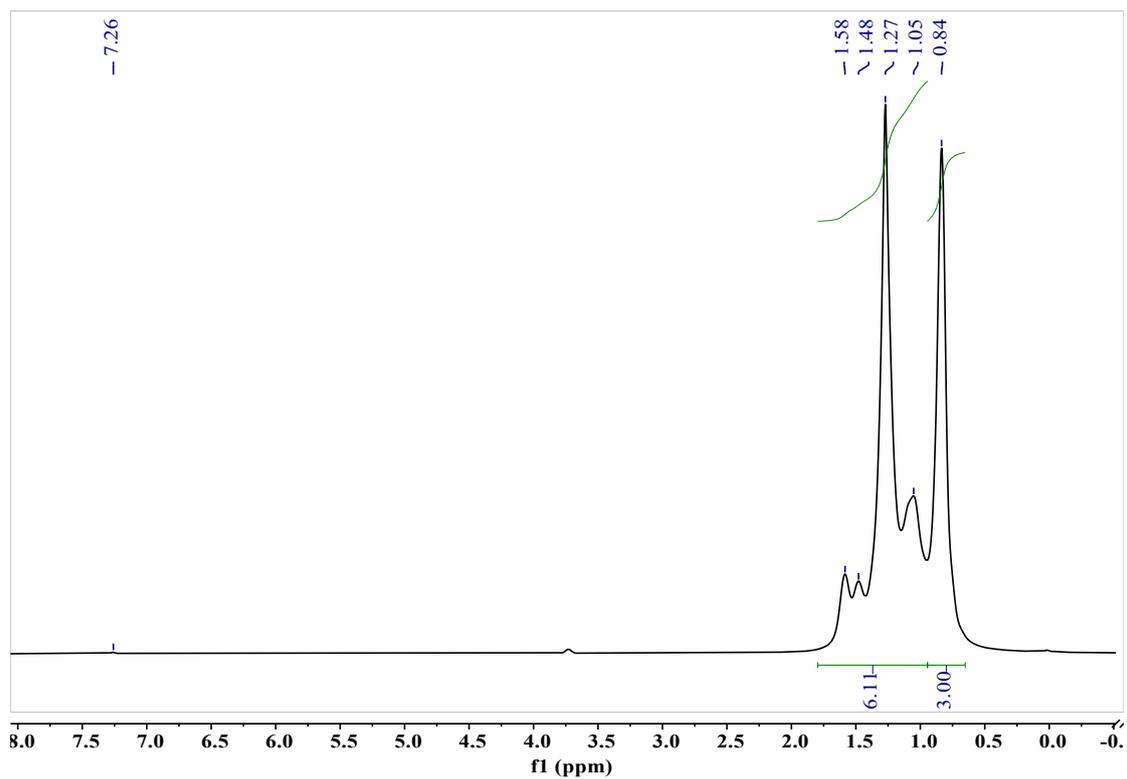**Figure S39.** ^{1}H NMR spectrum (400 MHz, 298 K) of table 2, run 5.

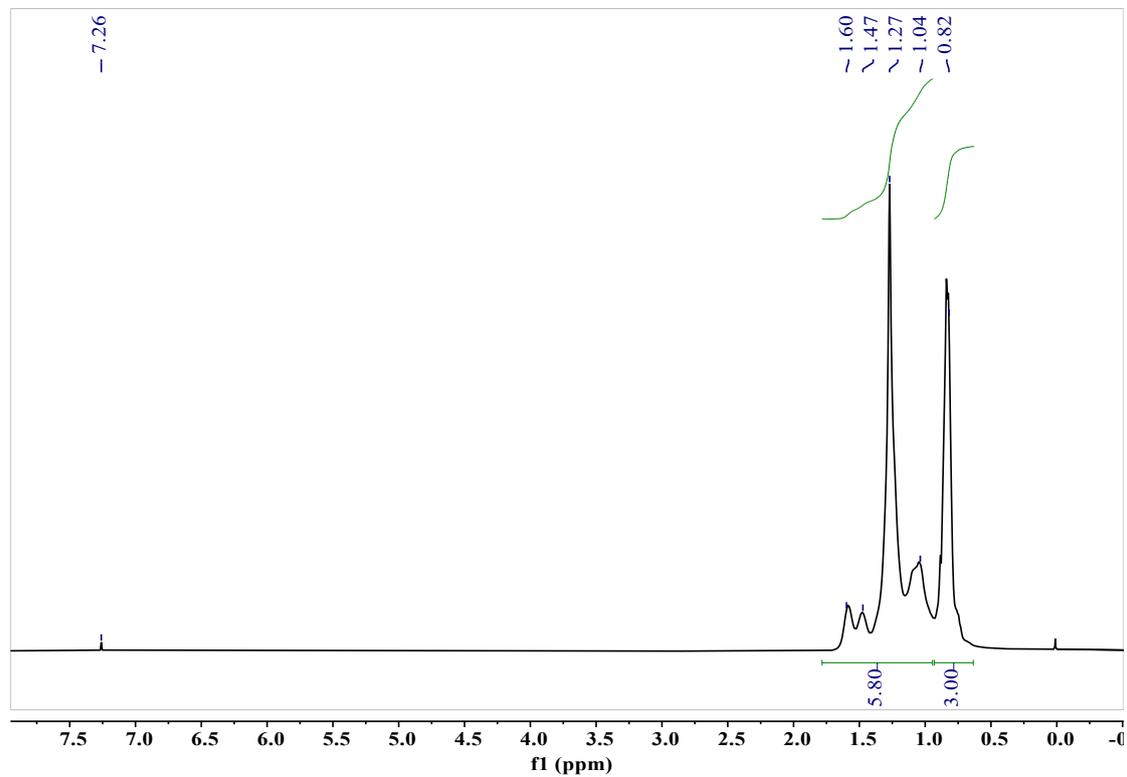**Figure S40.** ^{1}H NMR spectrum (400 MHz, 298 K) of table 3, run 1.
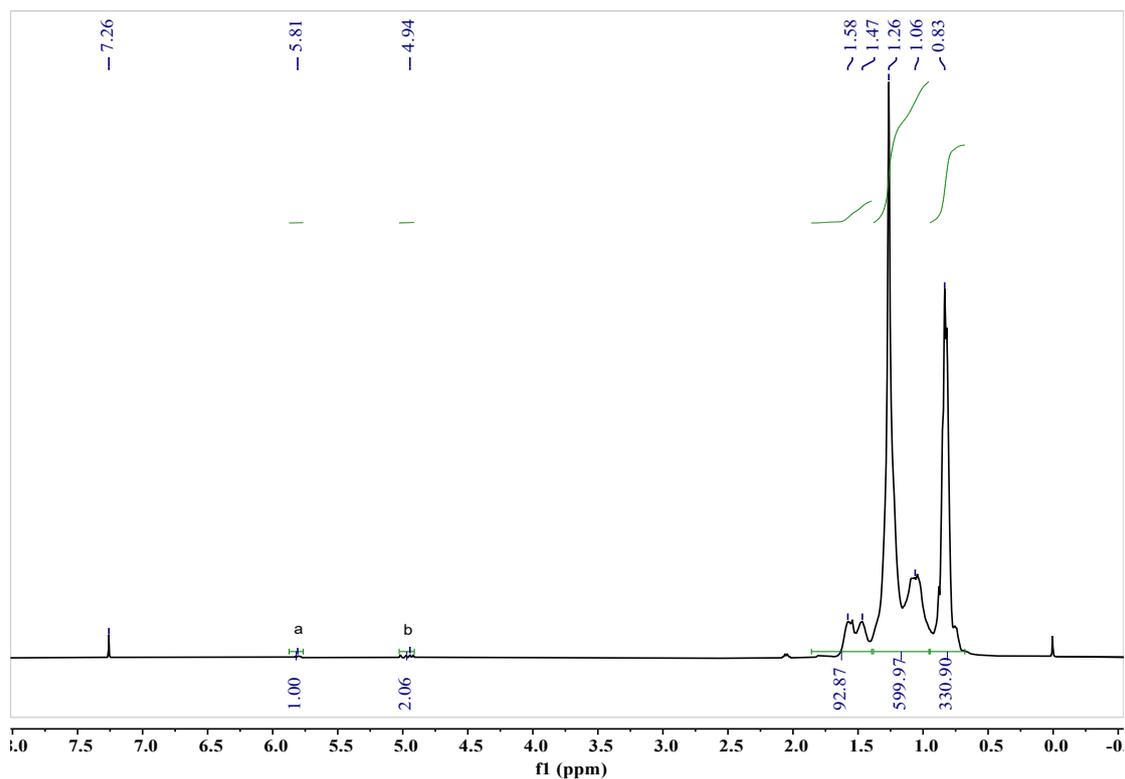
Figure S41. ^{1}H NMR spectrum (400 MHz, 298 K) of table 3, run 2.
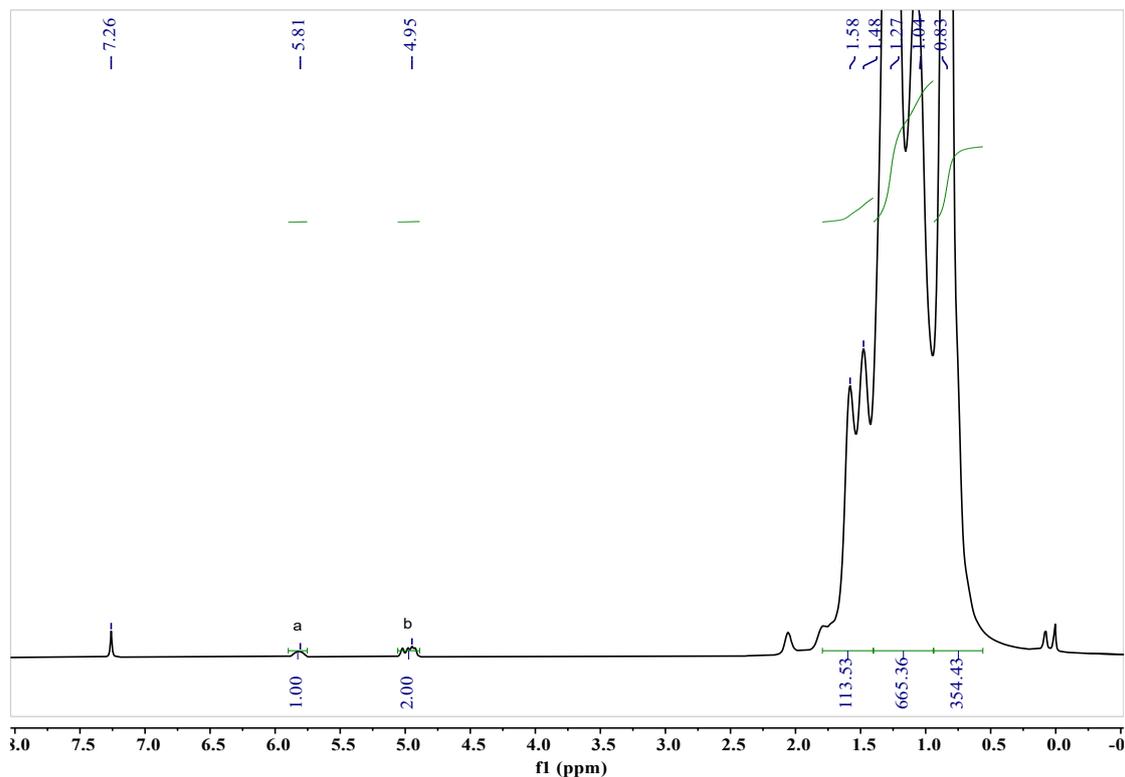
Figure S42. ^{1}H NMR spectrum (400 MHz, 298 K) of table 3, run 3.
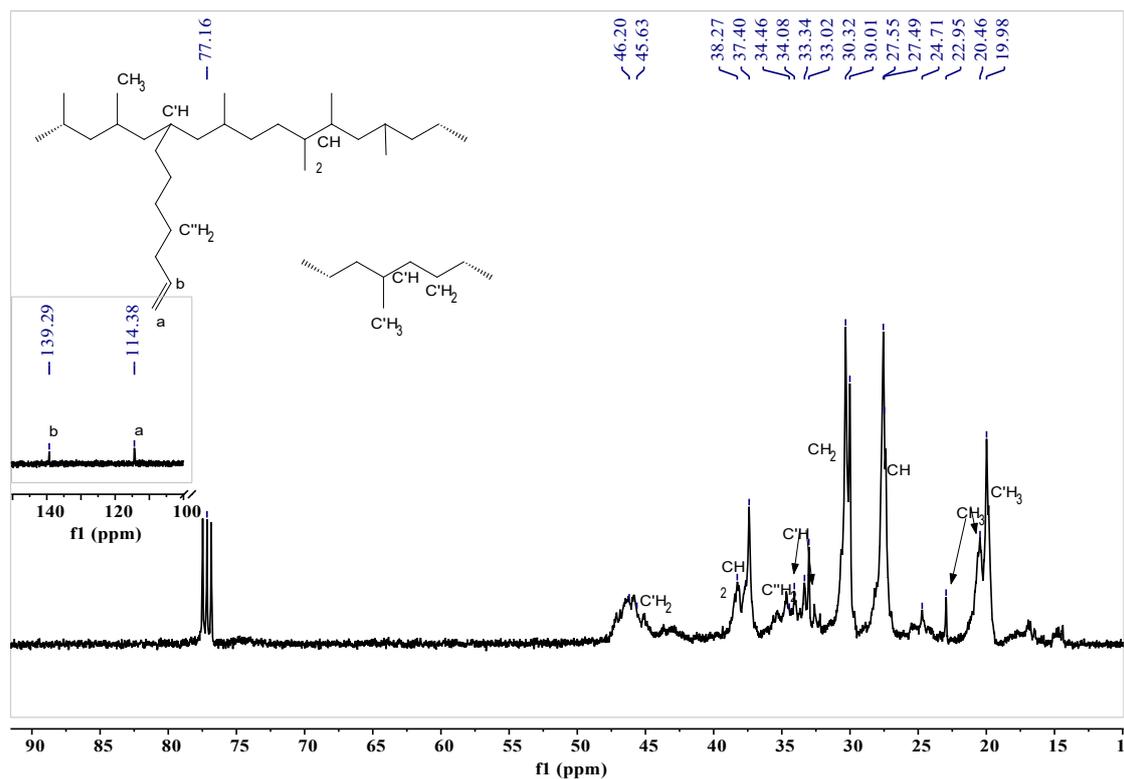
Figure S43. ^{13}C NMR spectrum (101 MHz, 298 K) of table 3, run3.
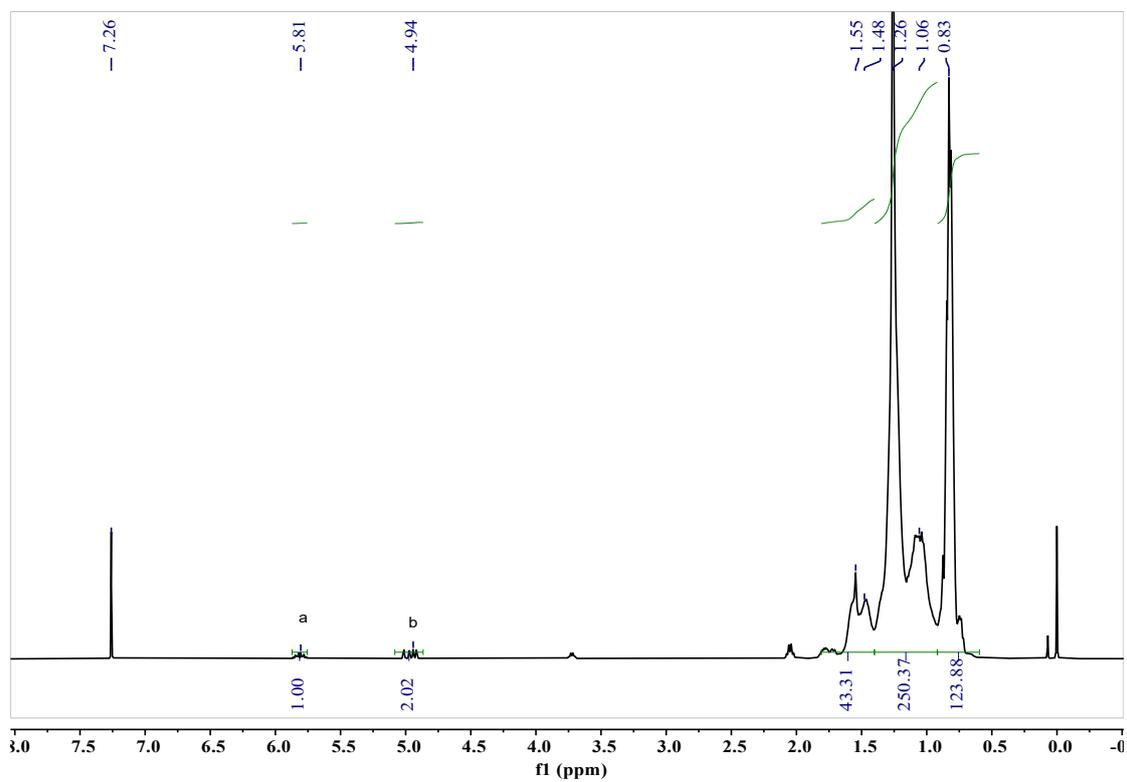
Figure S44. ^1H NMR spectrum (400 MHz, 298 K) of table 3, run 4.
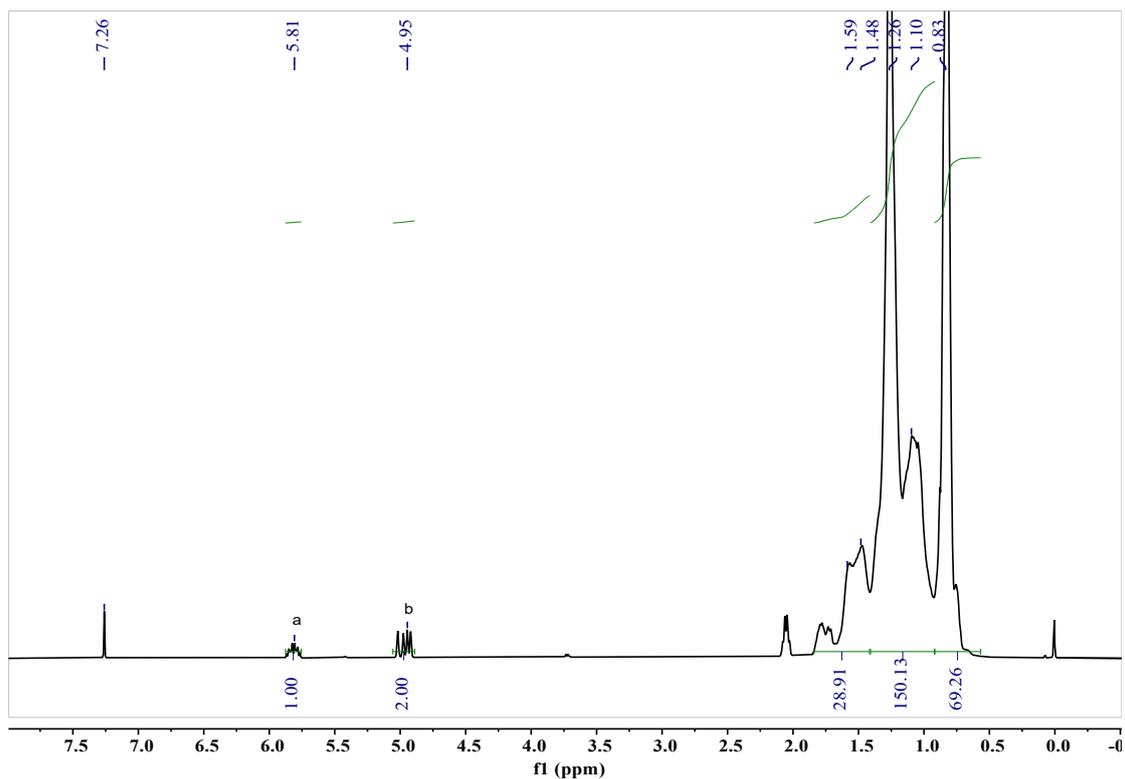
Figure S45. ^{1}H NMR spectrum (400 MHz, 298 K) of table 3, run 5.
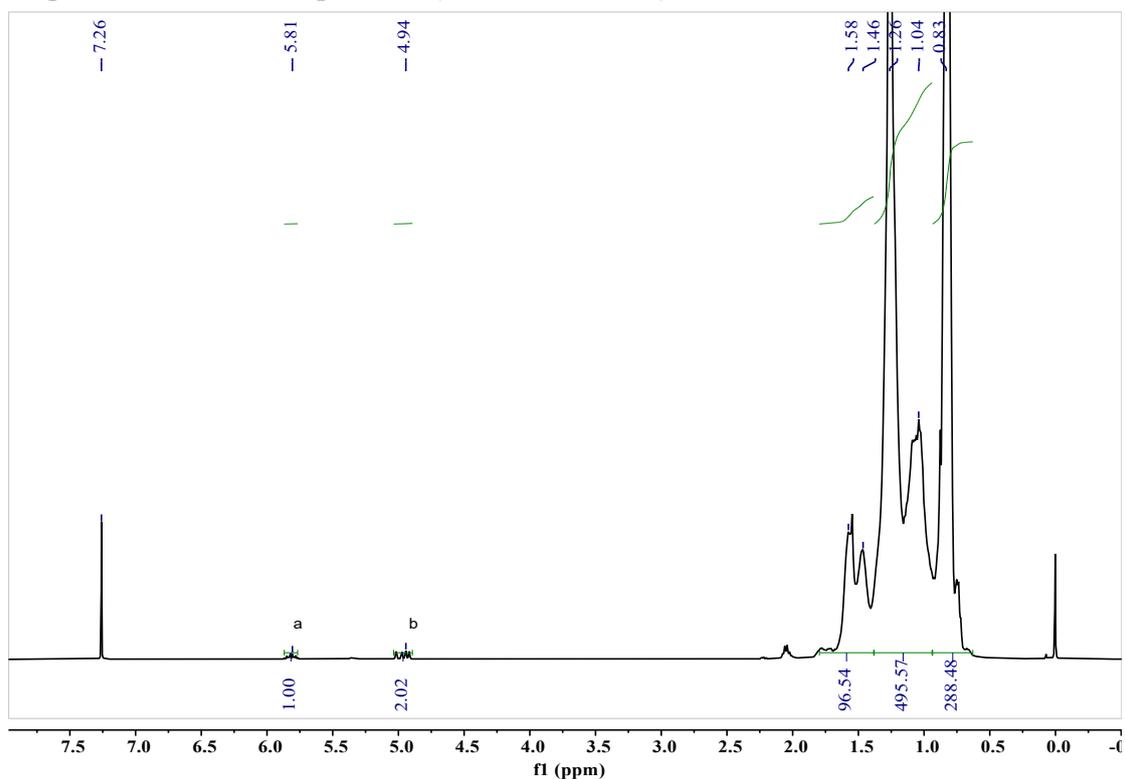
Figure S46. ^{1}H NMR spectrum (400 MHz, 298 K) of table 3, run 6.
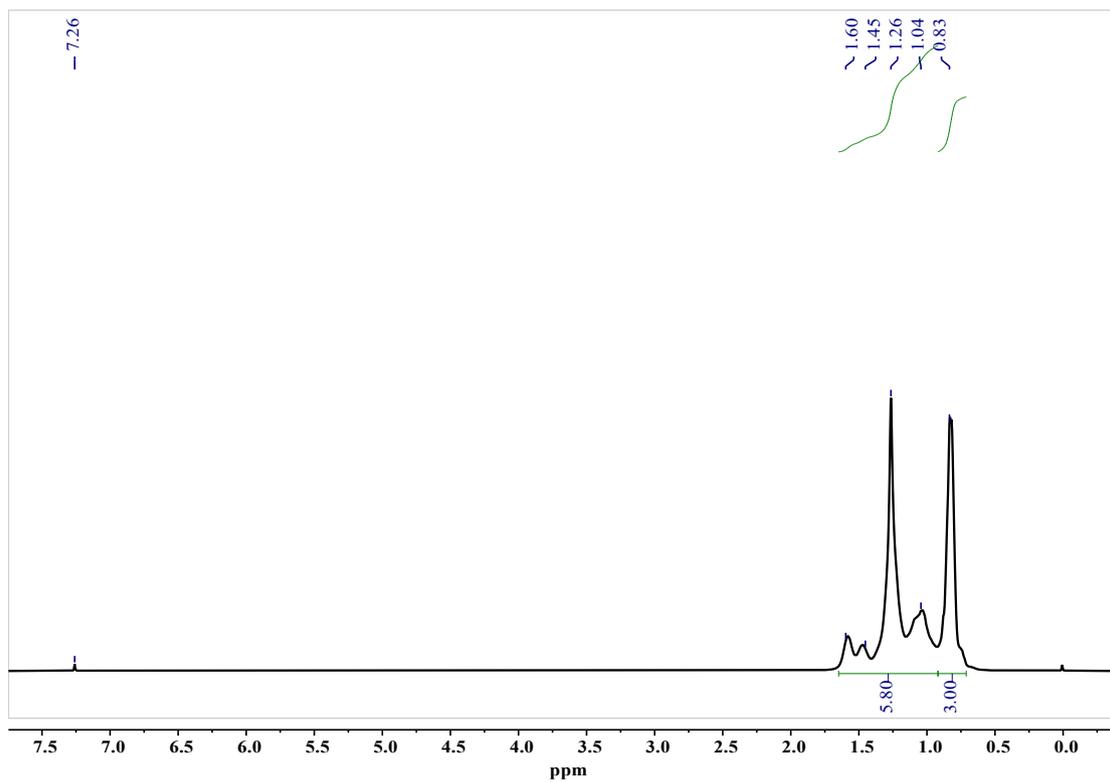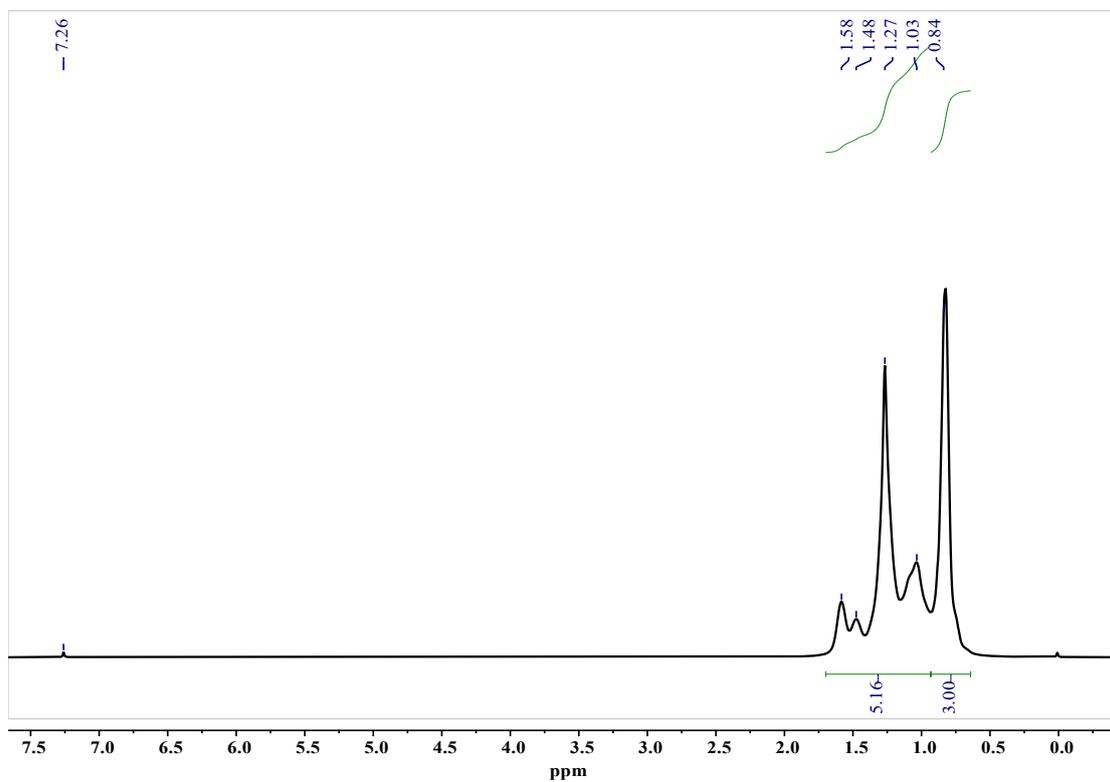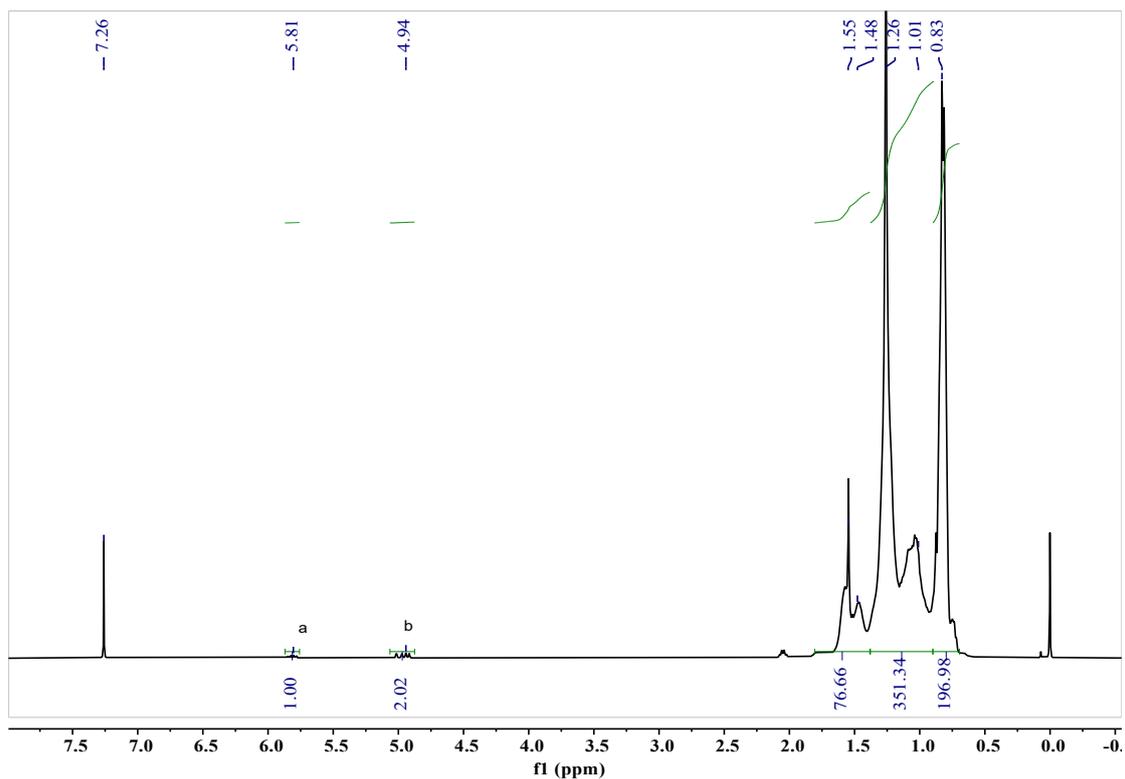
Figure S47. ^{1}H NMR spectrum (400 MHz, 298 K) of table 3, run 7.
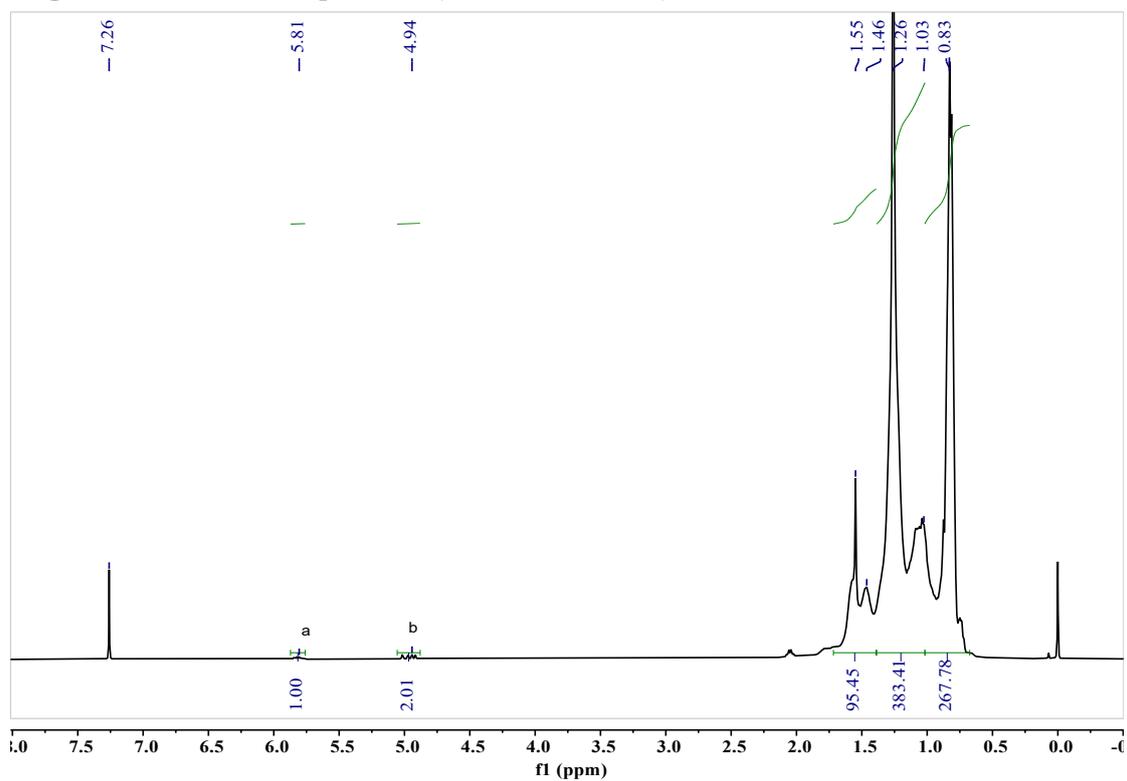
Figure S48. ^{1}H NMR spectrum (400 MHz, 298 K) of table 3, run 8.
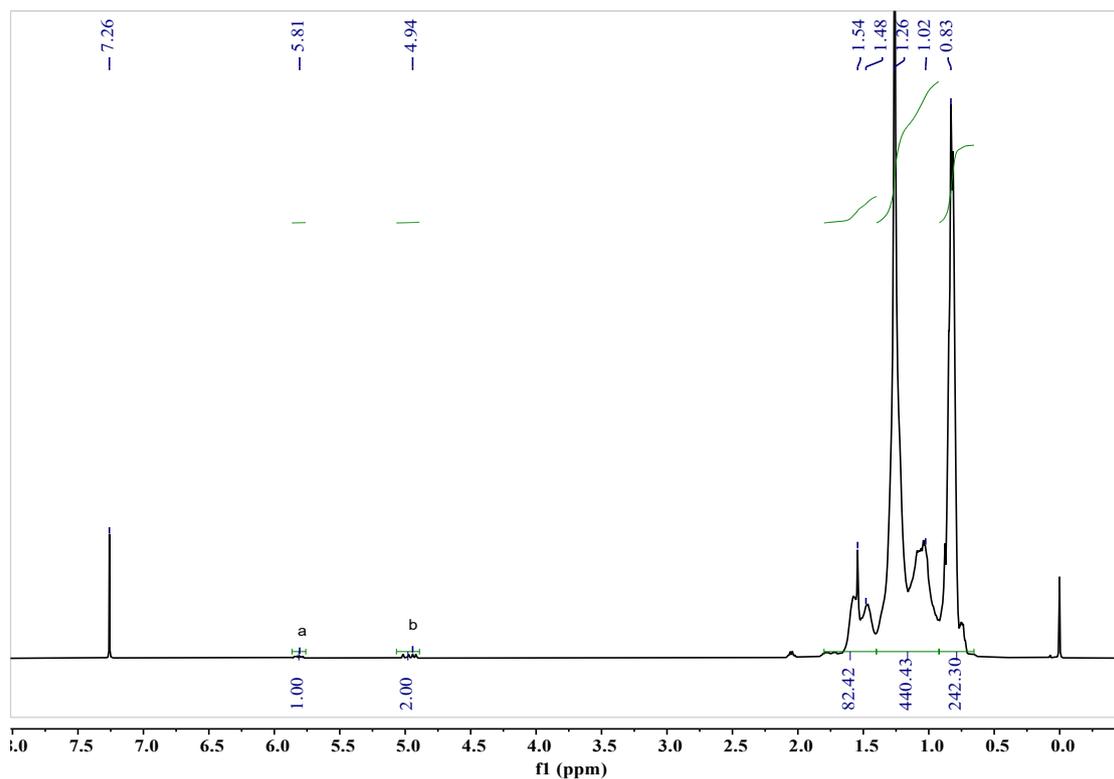
Figure S49. ^{1}H NMR spectrum (400 MHz, 298 K) of table 4, run 9.
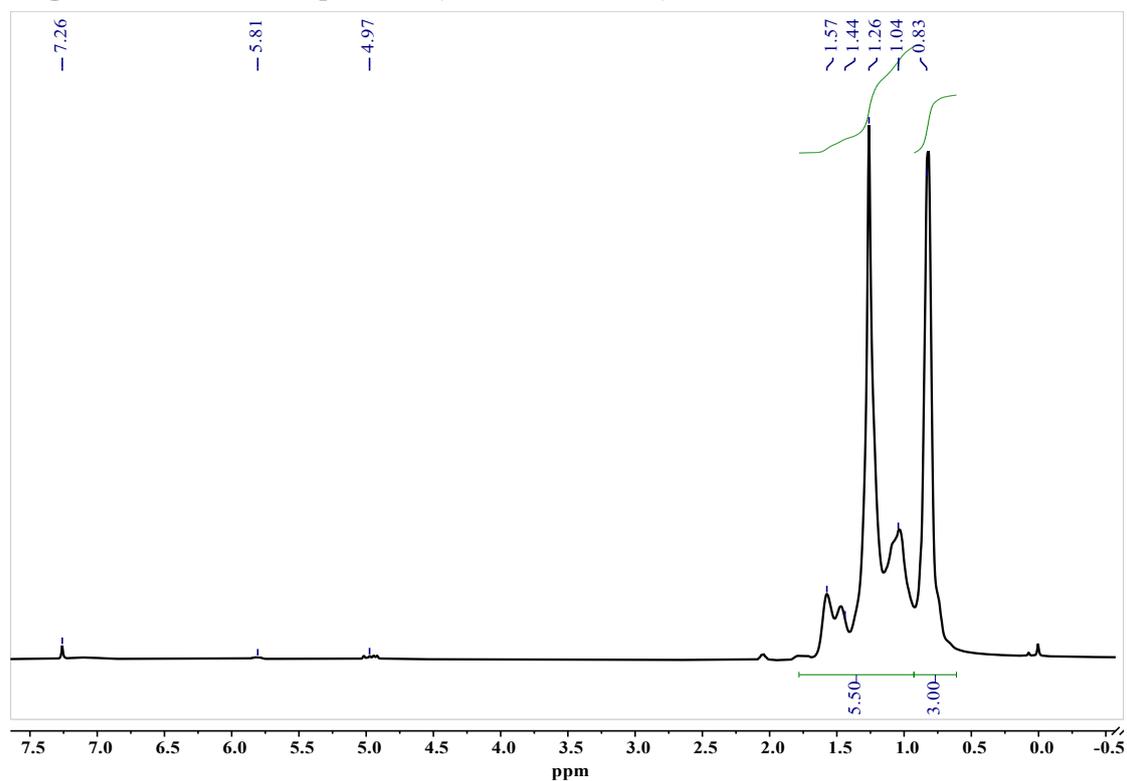
Figure S50. ^{1}H NMR spectrum (400 MHz, 298 K) of table 4, run 10.
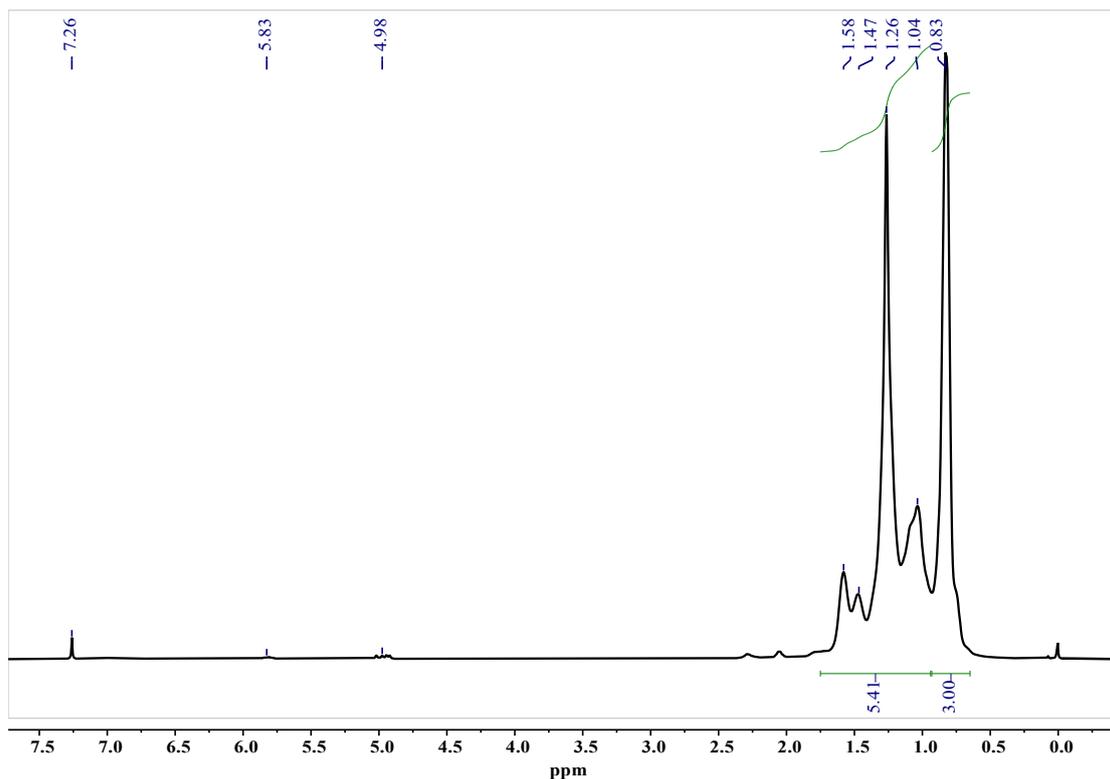
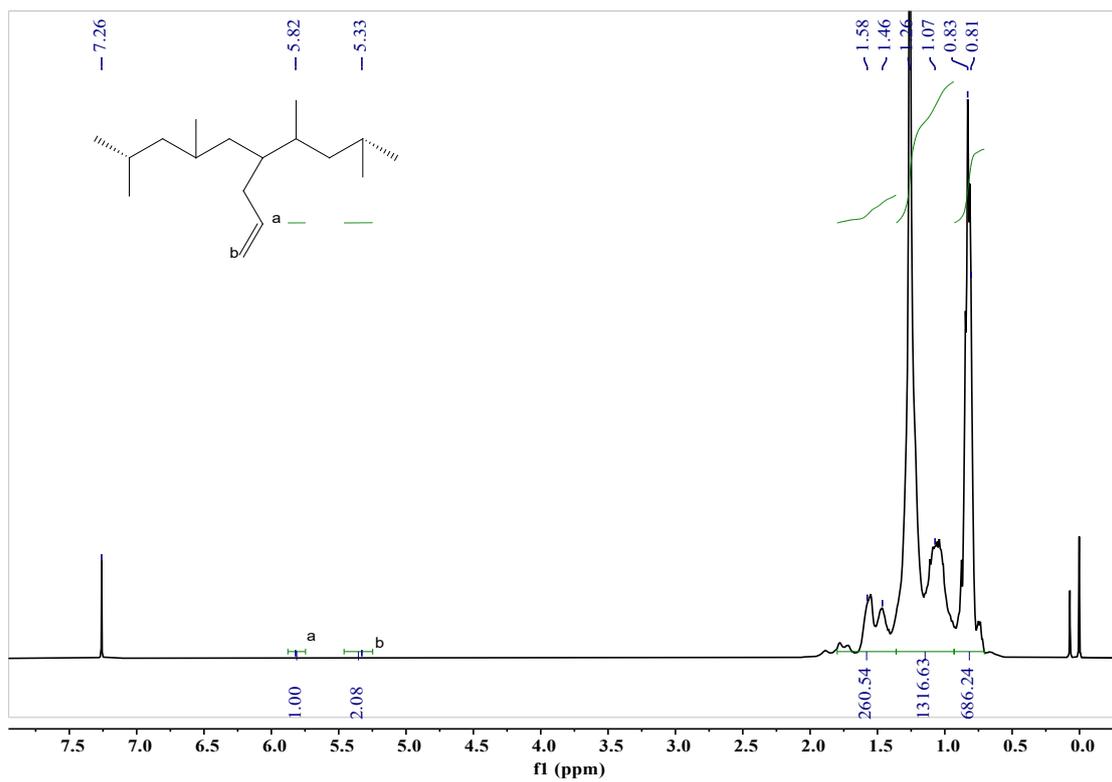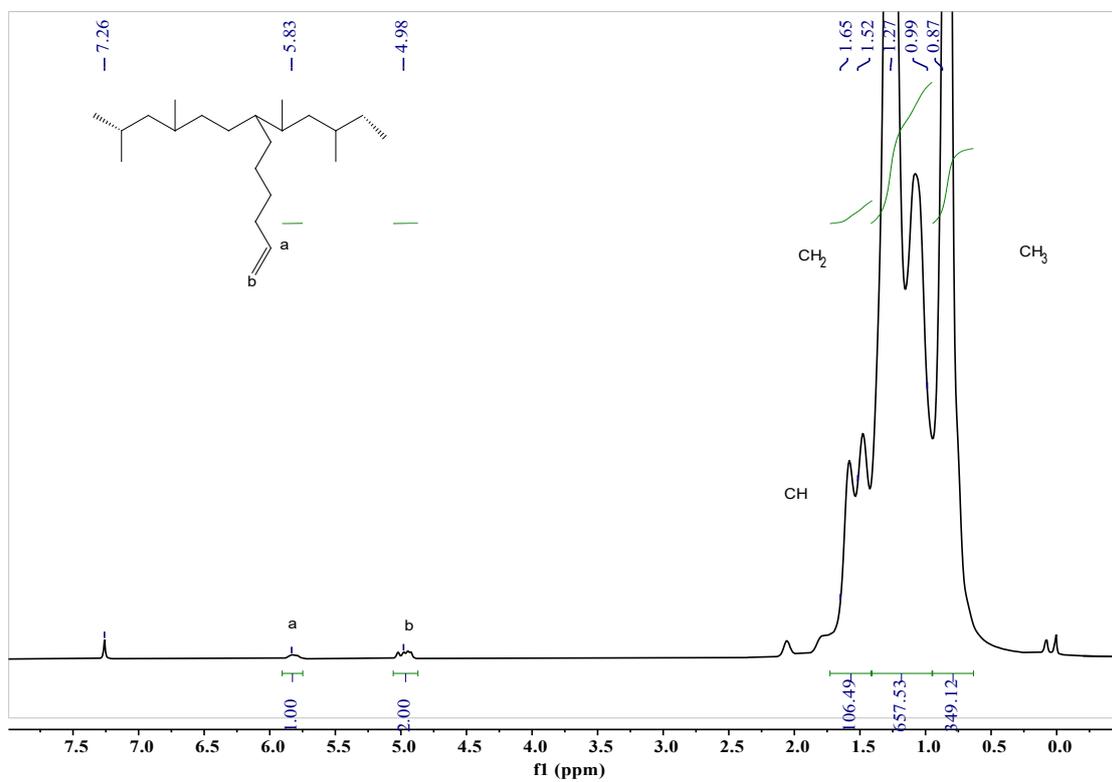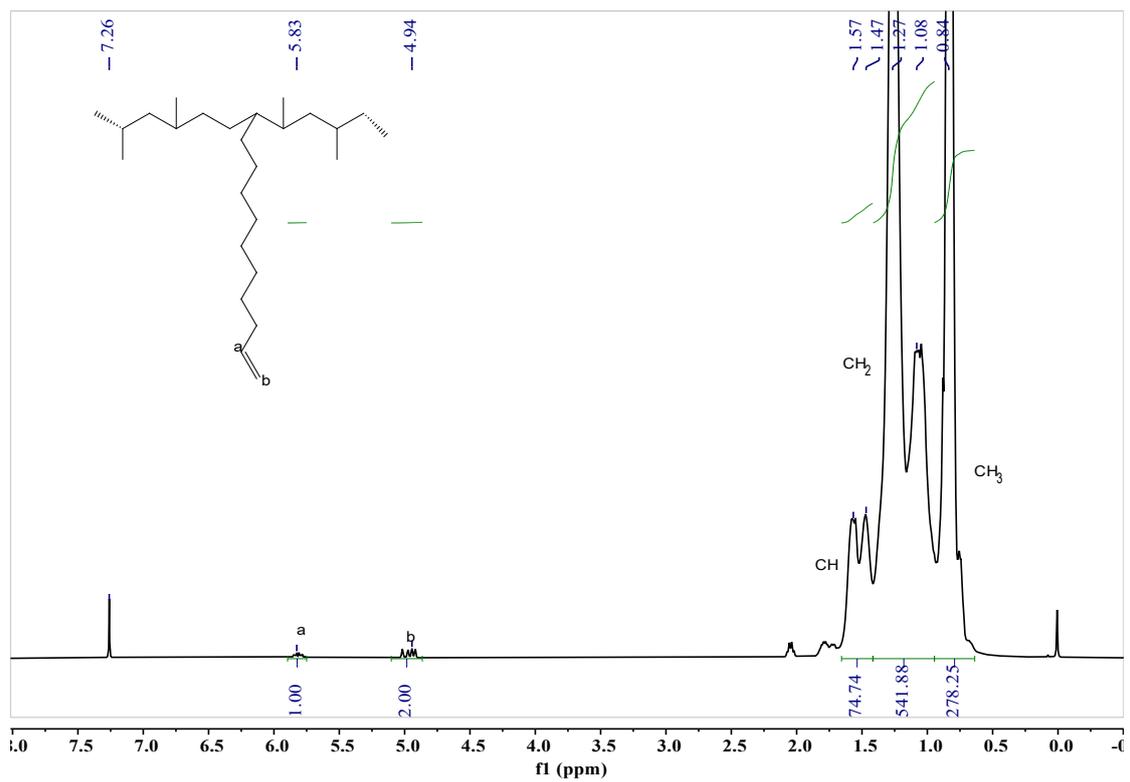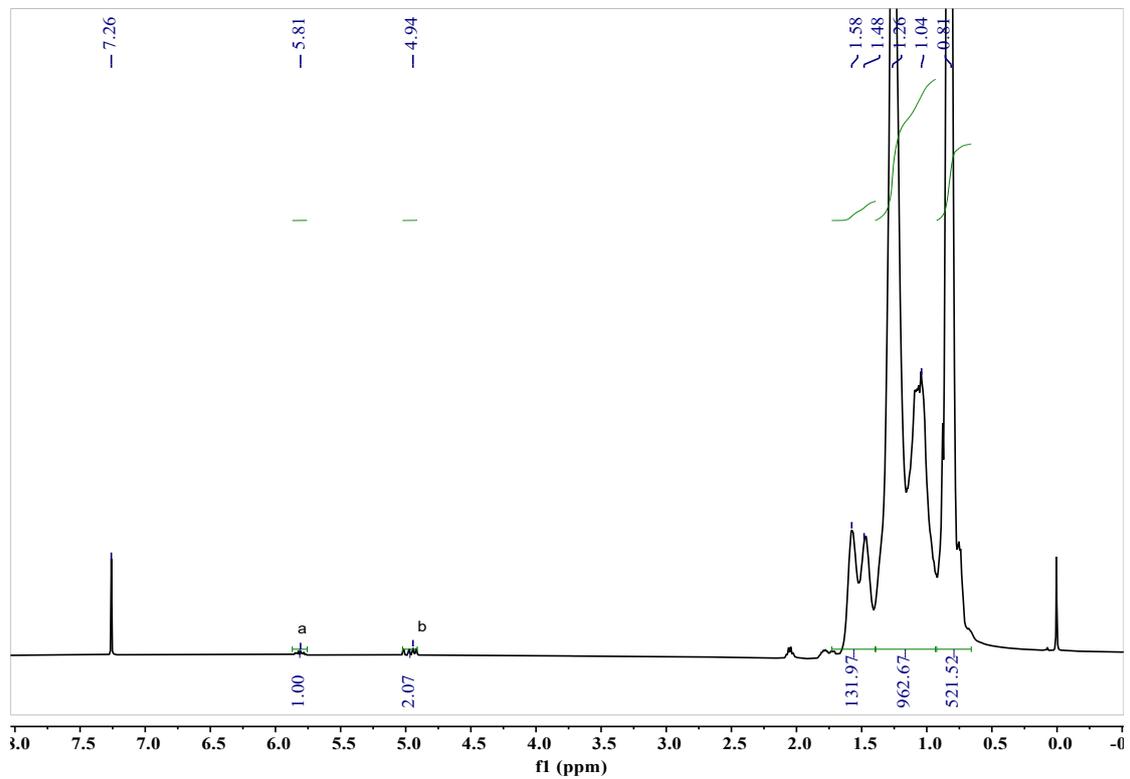**Figure S51.** ^{1}H NMR spectrum (400 MHz, 298 K) of table 4, run 11.

5. GPC profiles for the polymer products
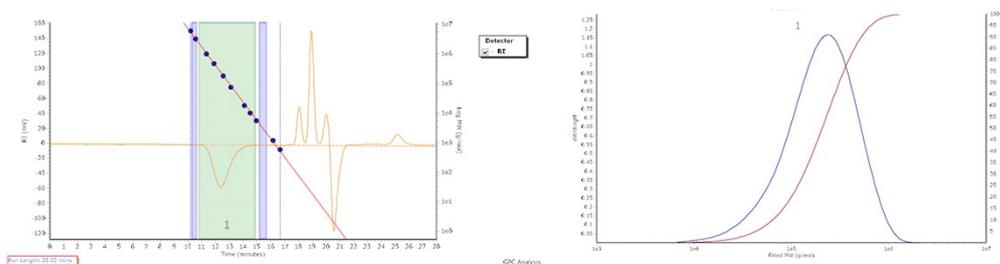
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	231660	131549	262146	415330	574521	241846	1.992763

Peaks	Start(mins)	End (mins)			
Peak 1	10.83333	14.88333			
	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)	
	RI	12.38333	4651.657	-56.218	

Figure S52. GPC trace of the polymer from table 1, run 1.
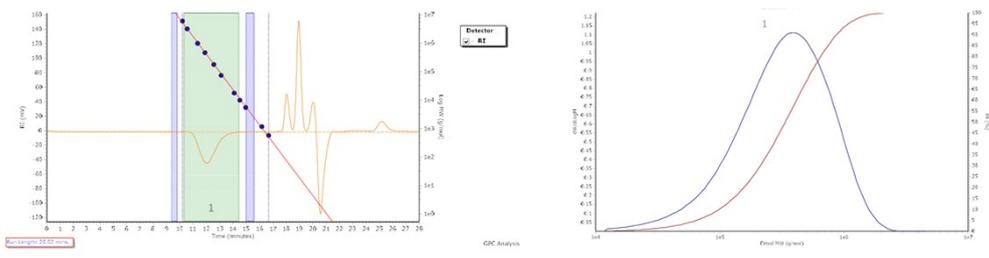
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	373273	202132	429508	689813	947236	394564	2.124889

Peaks	Start(mins)	End (mins)
Peak 1	10.3	14.46667

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.05	3752.73	-43.208

Figure S53. GPC trace of the polymer from table 1, run 2.
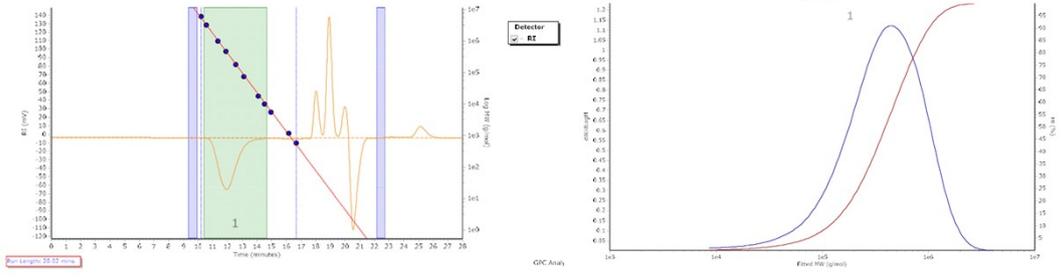
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	441101	221748	503567	817977	1155583	462114	2.270898

Peaks	Start(mins)	End (mins)
Peak 1	10.38333	14.7

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	11.93333	5183.6	-60.2288

Figure S54. GPC trace of the polymer from table 1, run 3.
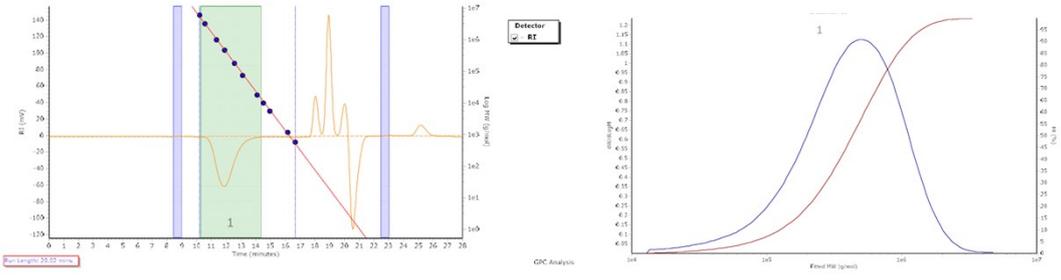
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak\1	496971	247122	551711	910204	1334680	505619	2.232545

Peaks	Start(mins)	End (mins)
Peak 1	10.26667	14.4

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	11.85	5197.449	-60.5324

Figure S55. GPC trace of the polymer from table 1, run 4.
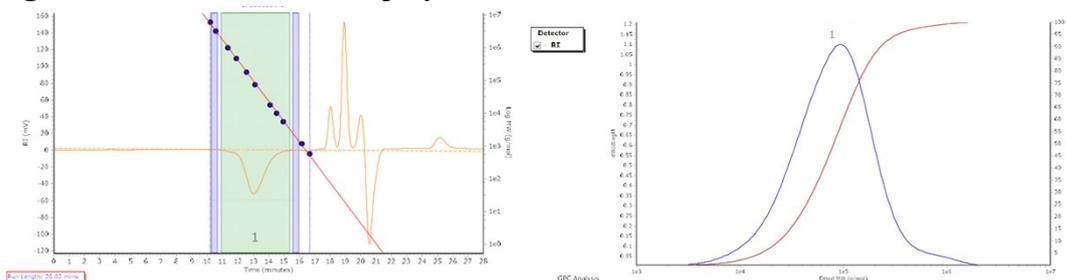
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	93588	50108	121697	320550	746260	106291	2.428694

Peaks	Start(mins)	End (mins)
Peak 1	10.88333	15.4

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	13.01667	4586.205	-52.2826

Figure S56. GPC trace of the polymer from table 1, run 5.
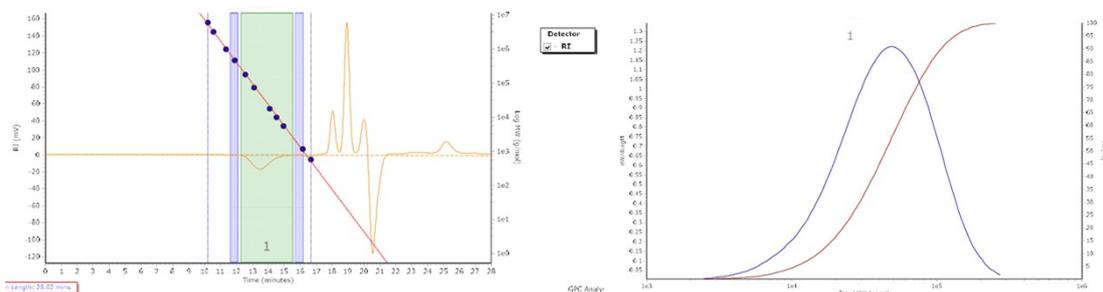
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	49151	30699	55150	84407	114885	51270	1.796475

Peaks	Start(mins)	End (mins)
Peak 1	12.26667	15.58333

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	13.46667	1320.908	-16.7234

Figure S57. GPC trace of the polymer from table 1, entry 6.
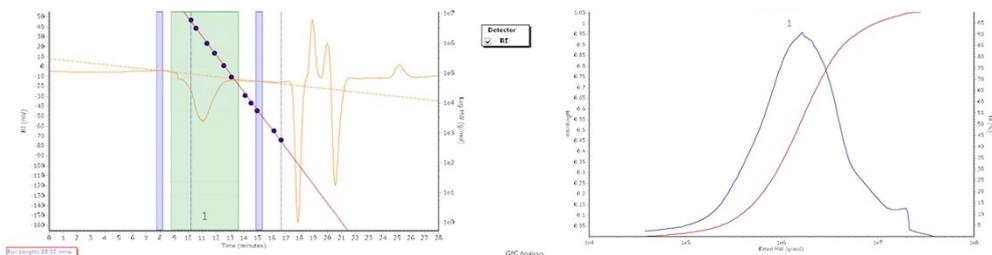
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	1599227	781944	2705062	7396116	13722856	2288586	3.459406

Peaks	Start(mins)	End (mins)		
Peak 1	8.783333	13.66667		
	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
	RI	11.03333	4709.94	-47.014

Figure S58. GPC trace of the polymer from table 1, run 8.
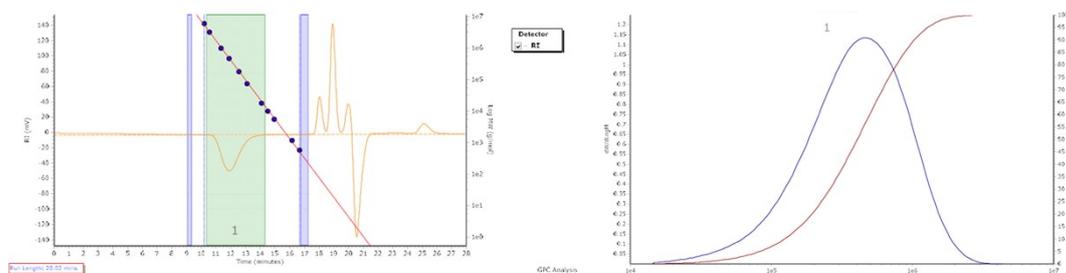
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	462653	252642	514748	821239	1139749	474116	2.03746

Peaks	Start(mins)	End (mins)		
Peak 1	10.33333	14.33333		
	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
	RI	11.9	4024.524	-47.3367

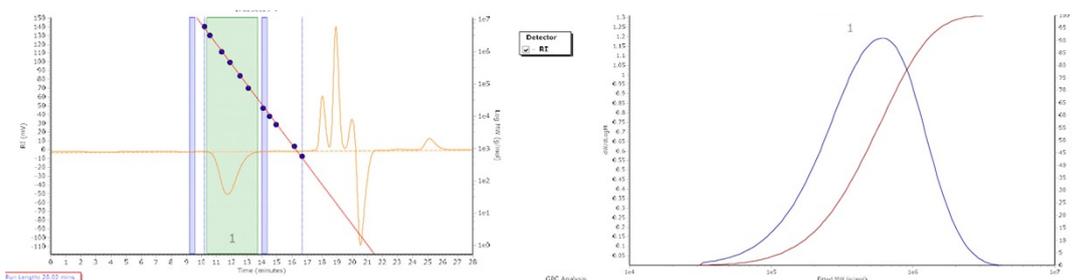**Figure S59**. GPC trace of the polymer from table 1, run 9.
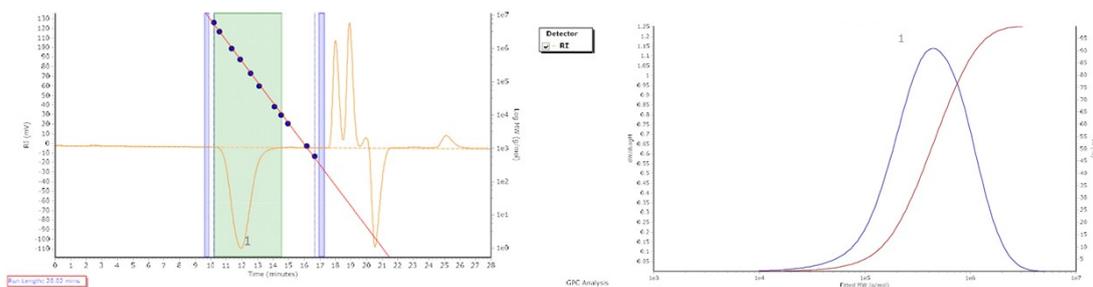
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
							1.983711
Peak1	441101	279999	555437	910405	1321182	510952	

Peaks	Start(mins)	End (mins)
Peak 1	10.21667	14.6

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	11.93333	8941.476	-105.497

Figure S60. GPC trace of the polymer from table 1, run 10.

MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	601453	350287	640497	989012	1356306	594324	1.828492

Peaks	Start(mins)	End (mins)
Peak 1	10.35	13.78333

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	11.71667	3927.228	-48.5071

Figure S61. GPC trace of the polymer from table 1, run 11.
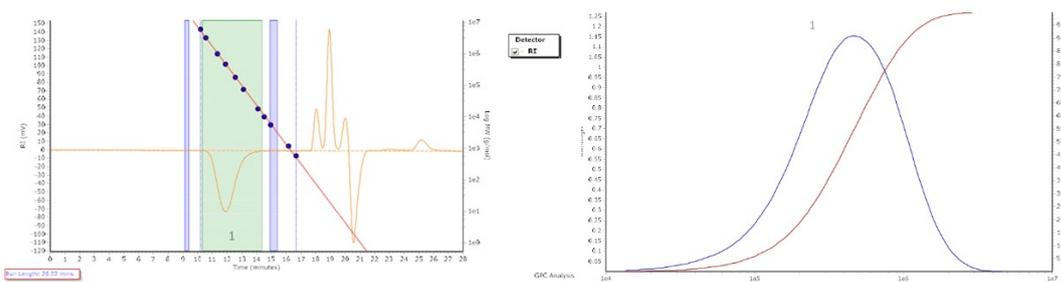
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	462653	270186	540292	866058	1222999	498053	1.999704

Peaks	Start(mins)	End (mins)
Peak 1	10.3	14.38333

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	11.9	6063.213	-72.4973

Figure S62. GPC trace of the polymer from table 1, run 12.
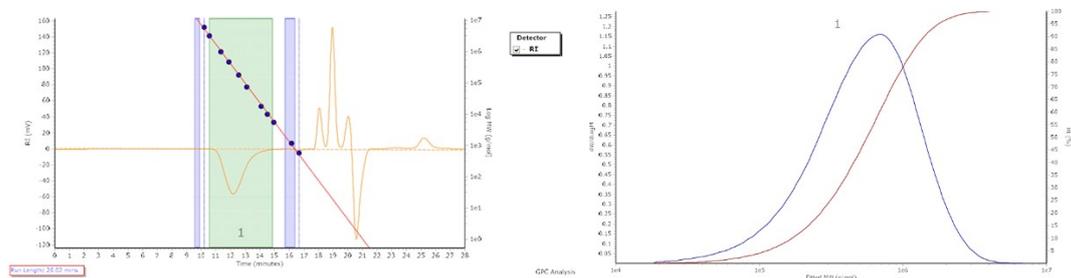
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	308430	143869	347716	591151	852137	316157	2.416893

Peaks	Start(mins)	End (mins)
Peak 1	10.56667	14.91667

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.18333	5090.096	-56.2219

Figure S63. GPC trace of the polymer from table 1, run 13.
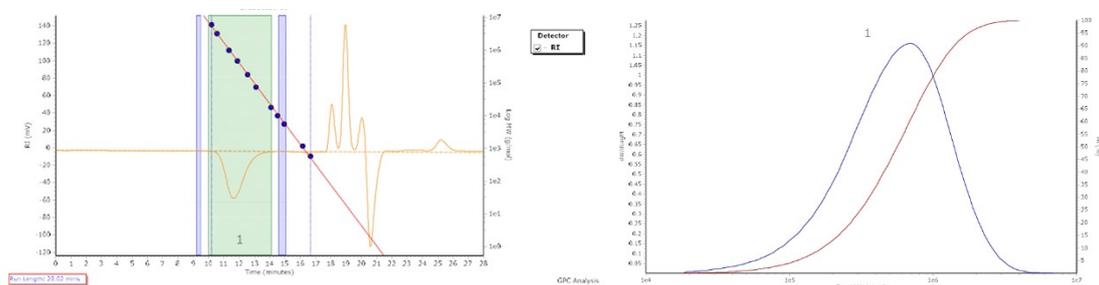
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	677634	344767	711228	1154320	1670165	654205	2.062924

Peaks	Start(mins)	End (mins)
Peak 1	10.01667	14.16667

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	11.63333	4522.652	-54.3958

Figure S64. GPC trace of the polymer from table 1, run 14.
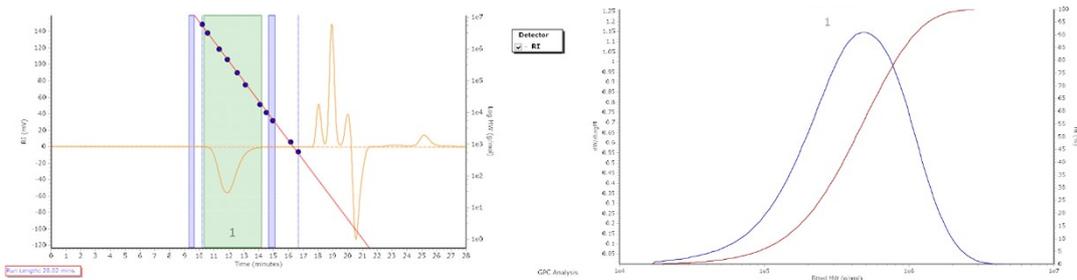
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	496971	272254	546659	872842	1222217	503873	2.007901

Peaks	Start(mins)	End (mins)		
Peak 1	10.31667	14.21667		
	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
	RI	11.85	4713.3	-55.9354

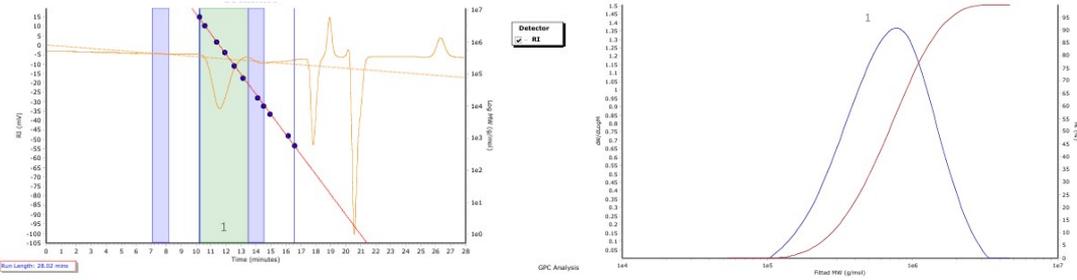**Figure S65.** GPC trace of the polymer from table 1, run 15.
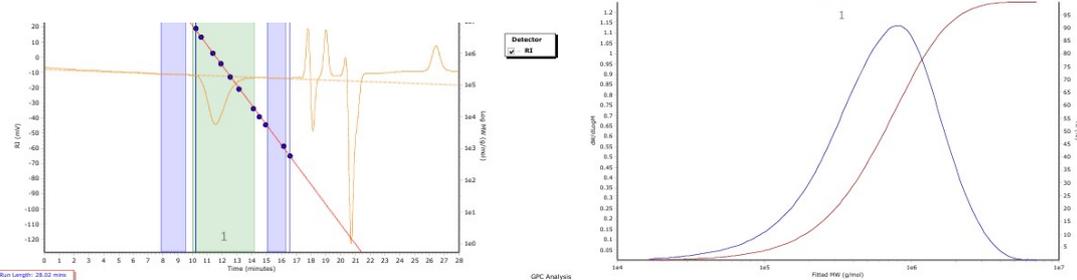
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	789428	379554	838763	1378641	1963381	768457	2.209865

Peaks	Start(mins)	End (mins)		
Peak 1	10.03333	14.25		
	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
	RI	11.55	2681.536	-31.8314

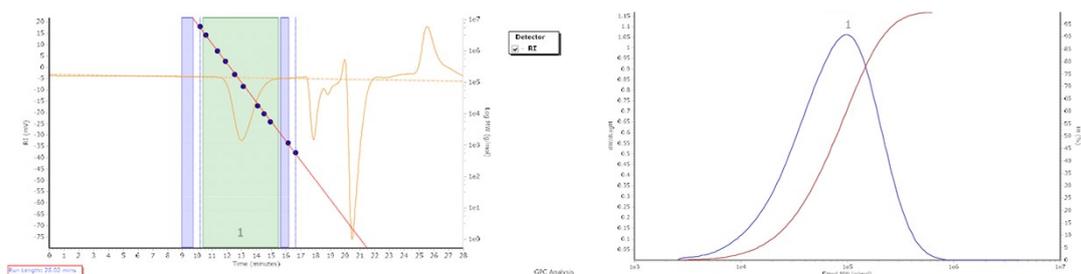**Figure S66.** GPC trace of the polymer from table 1, run 16.

MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD

Peak 1	770669	544120	817032	1142775	1467338	772560	1.501566

Peaks	Start (mins)	End (mins)
Peak 1	10.31667	13.43333

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	11.56667	1868.422	-26.7289

Figure S67. GPC trace of the polymer from table 1, run 17.

MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	98160	46408	104232	179733	265017	94739	2.245992

Peaks	Start(mins)	End (mins)
Peak 1	10.36667	15.53333

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.98333	2530.94	-27.8544

Figure S68. GPC trace of the polymer from table 2, run 2.
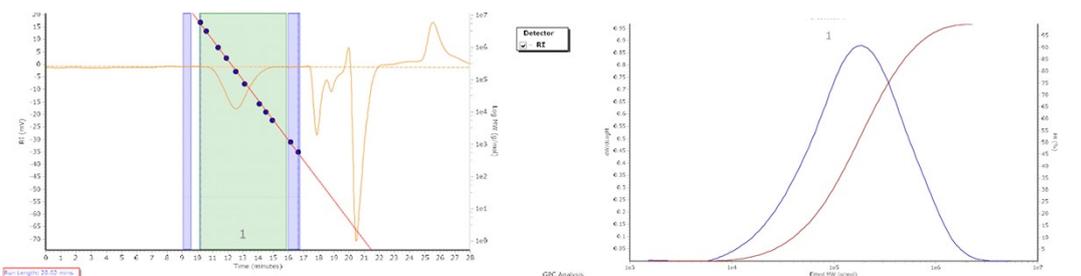
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	182500	91067	272800	601291	1010057	237412	2.995597

Peaks	Start(mins)	End (mins)
Peak 1	10.16667	15.91667

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.55	1847.395	-16.8648

Figure S69. GPC trace of the polymer from table 2, run 4.
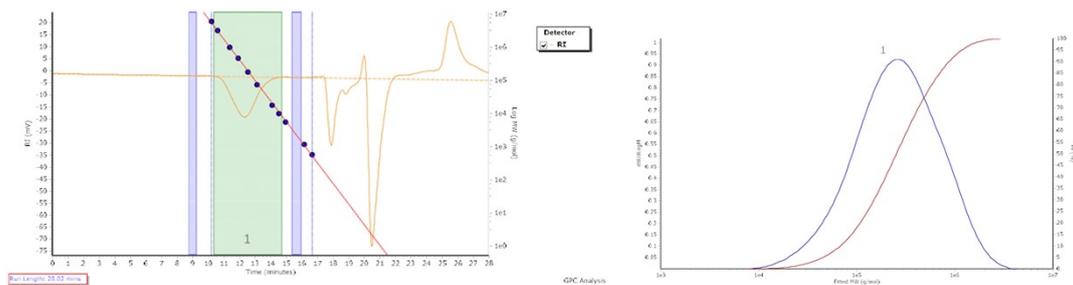
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	267303	151444	389855	793118	1261173	344372	2.574252

Peaks	Start(mins)	End (mins)
Peak 1	10.33333	14.73333

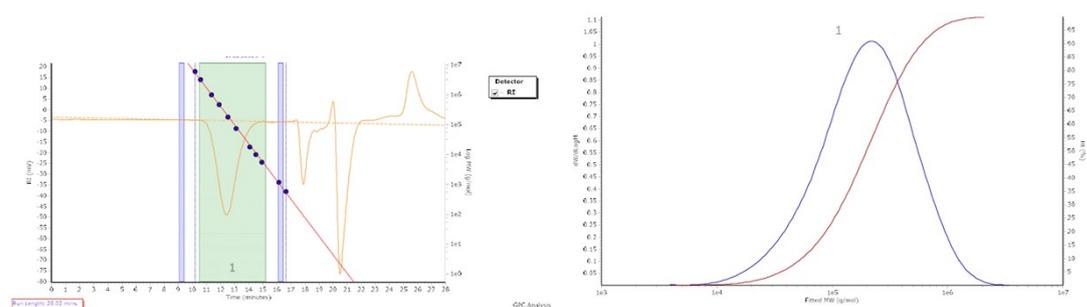| Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.28333	1755.031	-16.8284

Figure S70. GPC trace of the polymer from table 2 run 5.
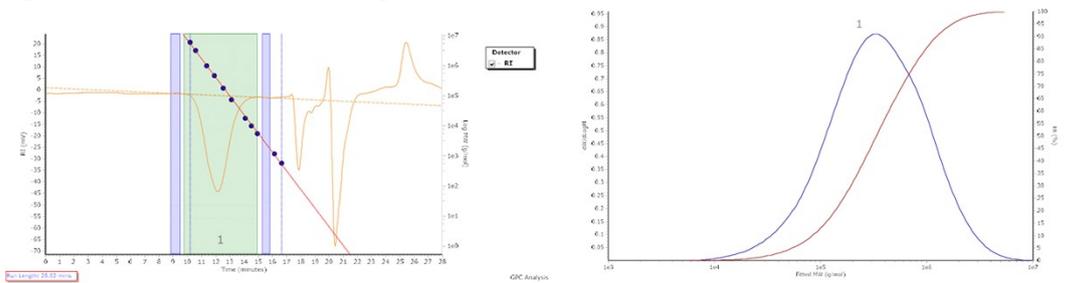
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	323500	183987	550990	1286657	2333518	476943	2.994722

Peaks	Start(mins)	End (mins)
Peak 1	9.766667	14.98333

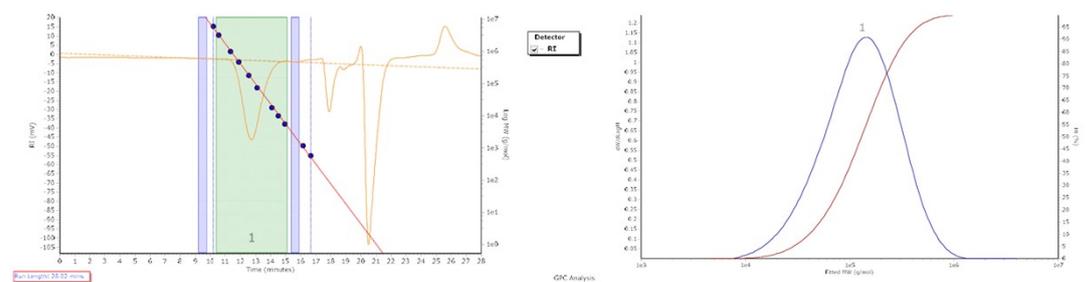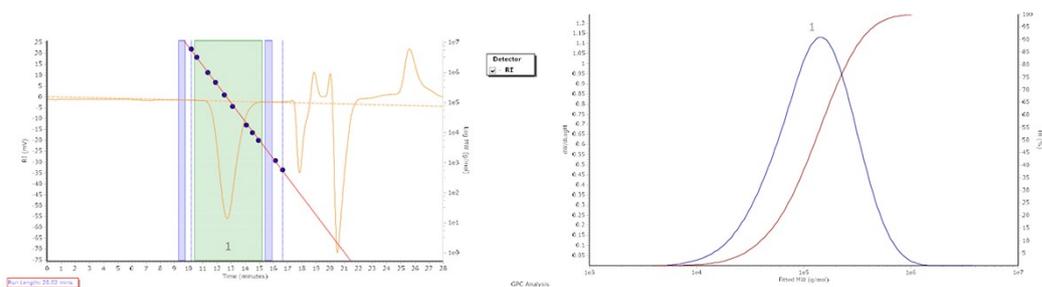| Trace	Peak Max RT (mins)	Peak Area(mV.s)	Peak Height (mV)
RI	12.15	4637.259	-41.8759

Figure S71. GPC trace of the polymer from table 3, run 1.
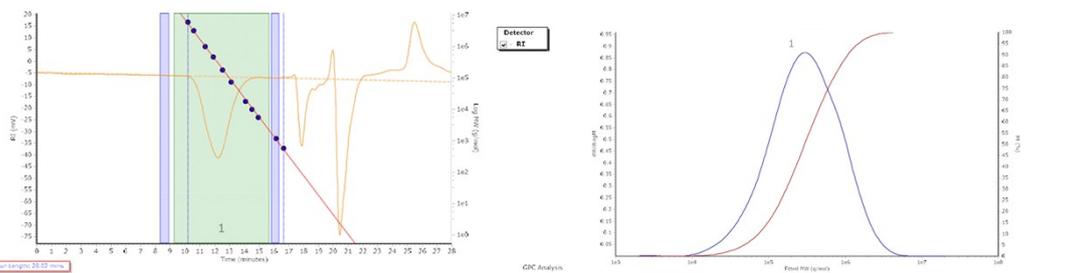
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	287131	160779	478661	1078488	2003946	416279	2.977136

Peaks	Start(mins)	End (mins)
Peak 1	9.266667	15.7

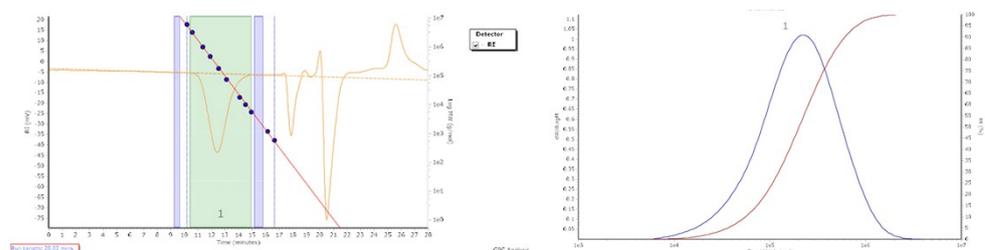| Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.23333	3832.908	-34.6706

Figure S72. GPC trace of the polymer from table 3, run 2.

MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	182500	91067	272800	601291	1010057	237412	2.995597
Peaks	Start(mins)	End (mins)					
Peak 1	10.16667	15.91667					

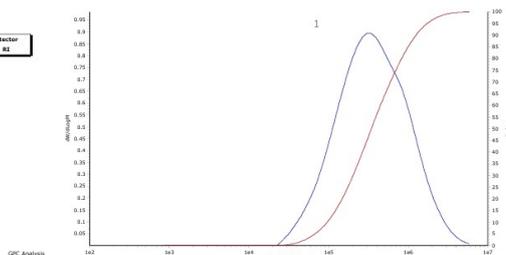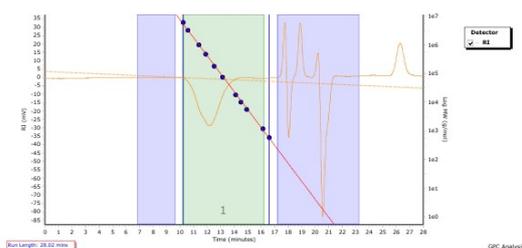| Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.55	1847.395	-16.8648

Figure S73. GPC trace of the polymer from table 3, run 3.
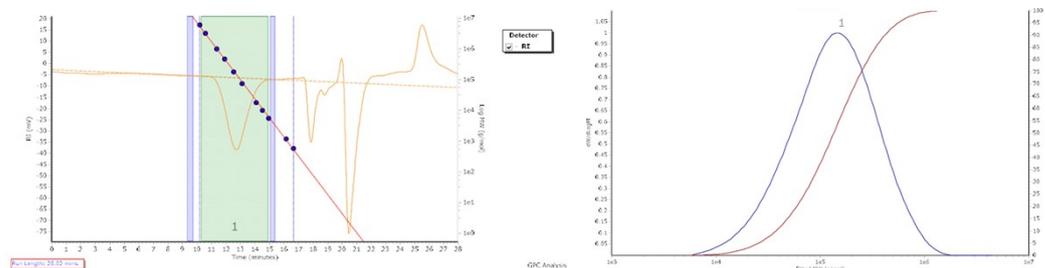
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	143773	83217	194142	370719	580330	173760	2.332961
Peaks	Start (mins)	End (mins)					
Peak 1	10.31667	14.95					

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.71667	3092.735	-32.0028

Figure S74. GPC trace of the polymer from table 3, run 4.
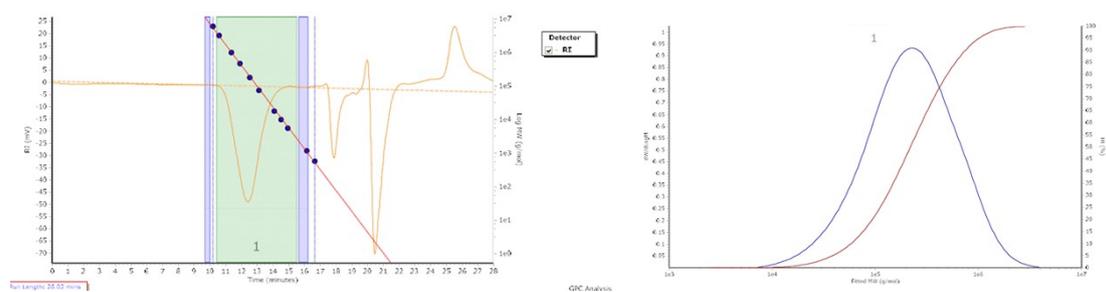
MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	226200	128827	336729	706185	1185675	296687	2.613808

Peaks	Start (mins)	End (mins)
Peak 1	10.41667	15.55

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.4	4912.515	-47.5173

Figure S75. GPC trace of the polymer from table 3, run 5.

MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	220869	117403	282131	542528	888286	252623	2.403099

Peaks	Start (mins)	End (mins)
Peak 1	10.5	15.25

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.41667	4185.228	-43.93

Figure S76. GPC trace of the polymer from table 3, run 6.

MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	143773	87535	171132	287973	422590	156722	1.955012

Peaks	Start (mins)	End (mins)
Peak 1	10.4	15.13333

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.71667	3711.464	-43.3349

Figure S77. GPC trace of the polymer from table 3, run 7.

MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	140384	84595	170683	290503	434501	156057	2.017649

Peaks	Start(mins)	End (mins)
Peak 1	10.43333	15.25

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.73333	4624.131	-54.2057

Figure S78. GPC trace of the polymer from table 3, run 8.

MW Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak1	220869	119174	285808	539312	856551	256437	2.398241

Peaks	Start(mins)	End (mins)
Peak 1	10.43333	14.96667

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.41667	3557.343	-37.6319

Figure S79. GPC trace of the polymer from table 3, run 9.

MW
Averages

Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	324245	220266	558428	1227324	2086059	488458	2.535244

Peaks	Start (mins)	End (mins)
Peak 1	10.16667	16.26667

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.16667	2989.03	-27.9385

Figure S80. GPC trace of the polymer from table 3, run 10.

MW
Averages
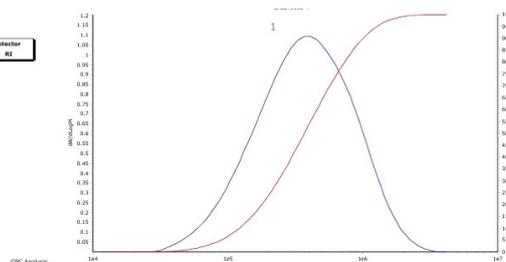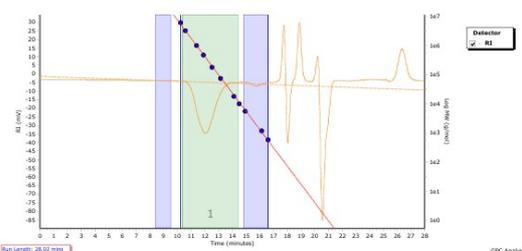
Peaks	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	383693	260026	492250	818293	1179506	451578	1.89308

Peaks	Start (mins)	End (mins)
Peak 1	10.4	14.48333

Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
RI	12.05	2599.881	-29.752

6. DSC curves for the polymer products
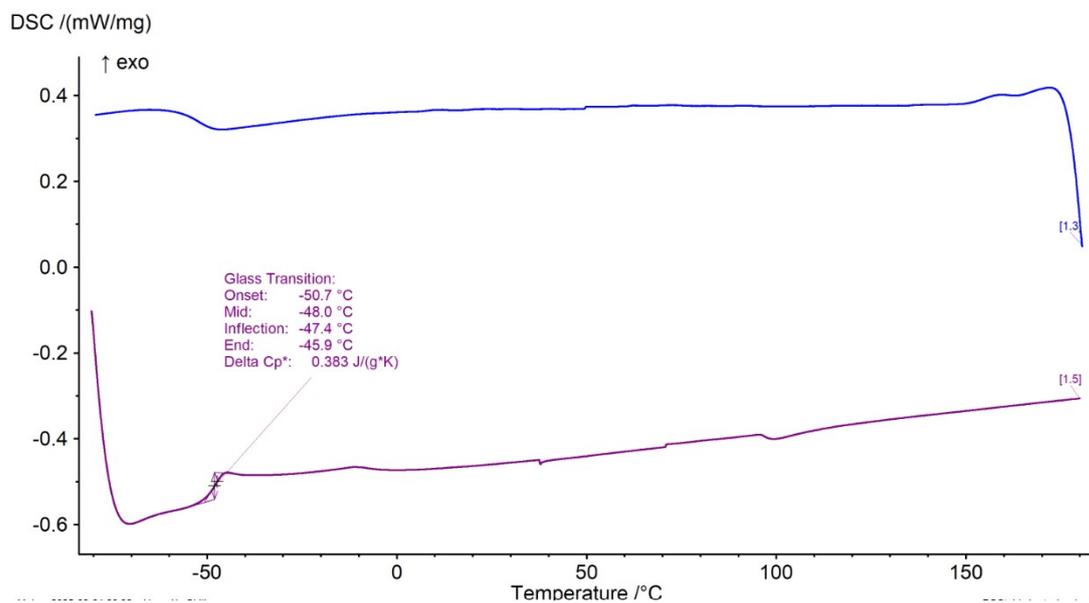
Figure S81. DSC curve of the polymer from table 1, run 1.
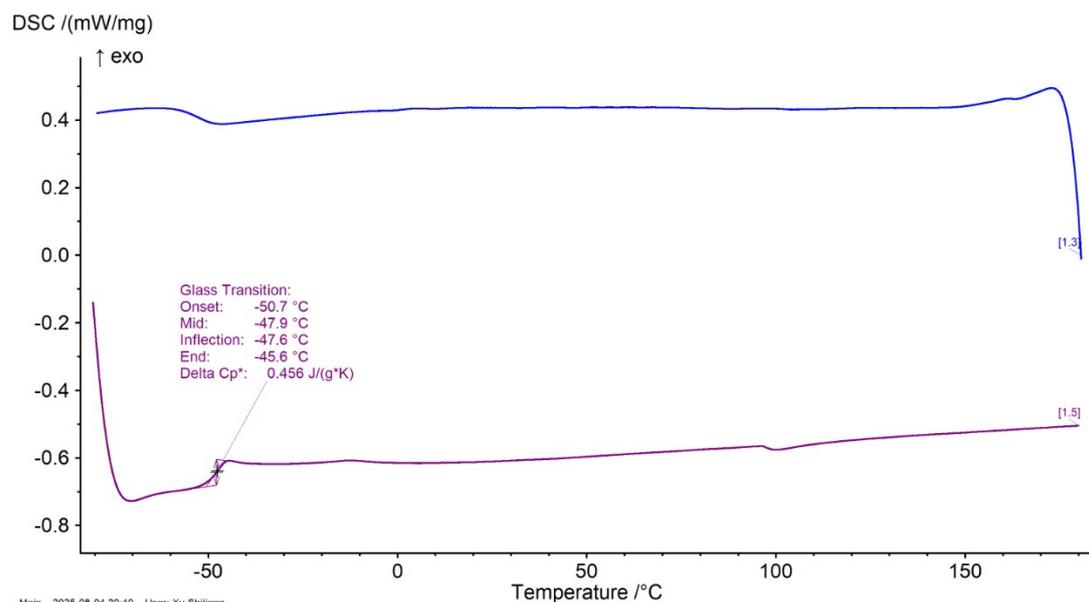
Figure S82. DSC curve of the polymer from table 1, run 2.
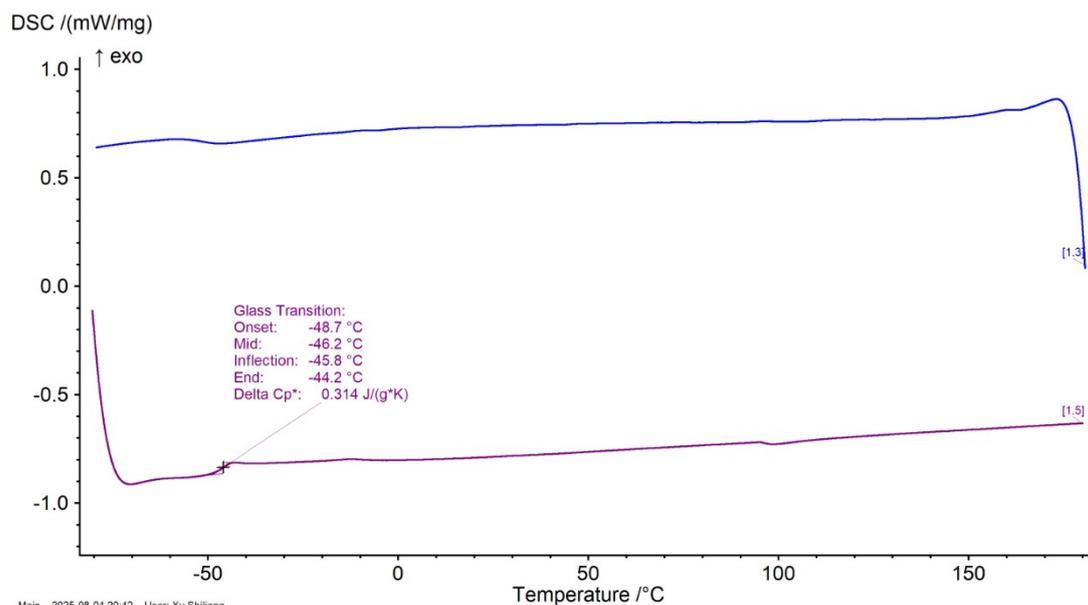
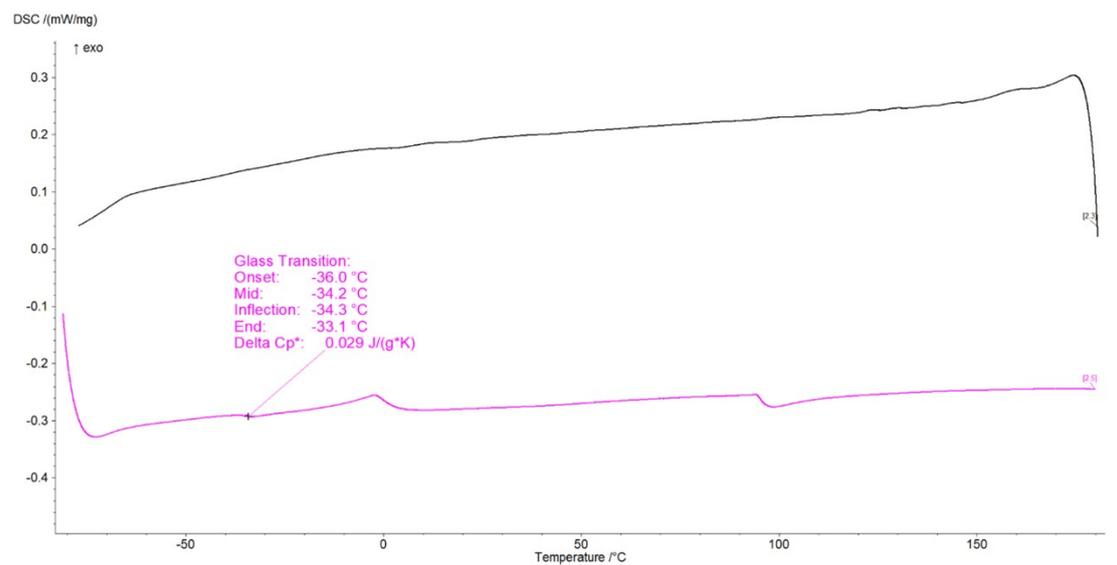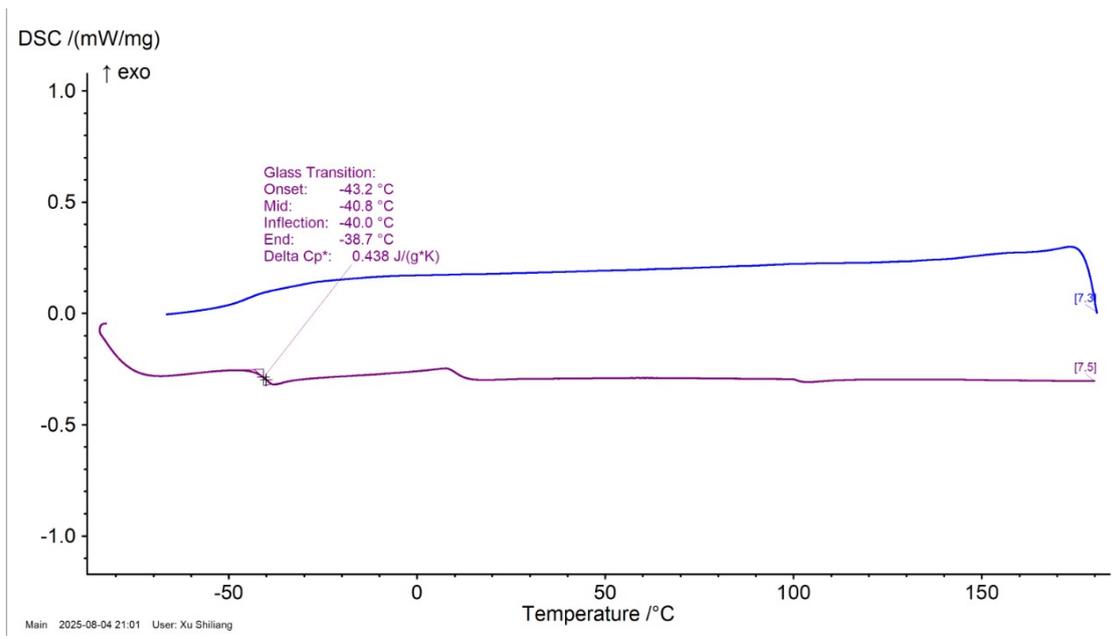**Figure S83**. DSC curve of the polymer from table 1, run 3.
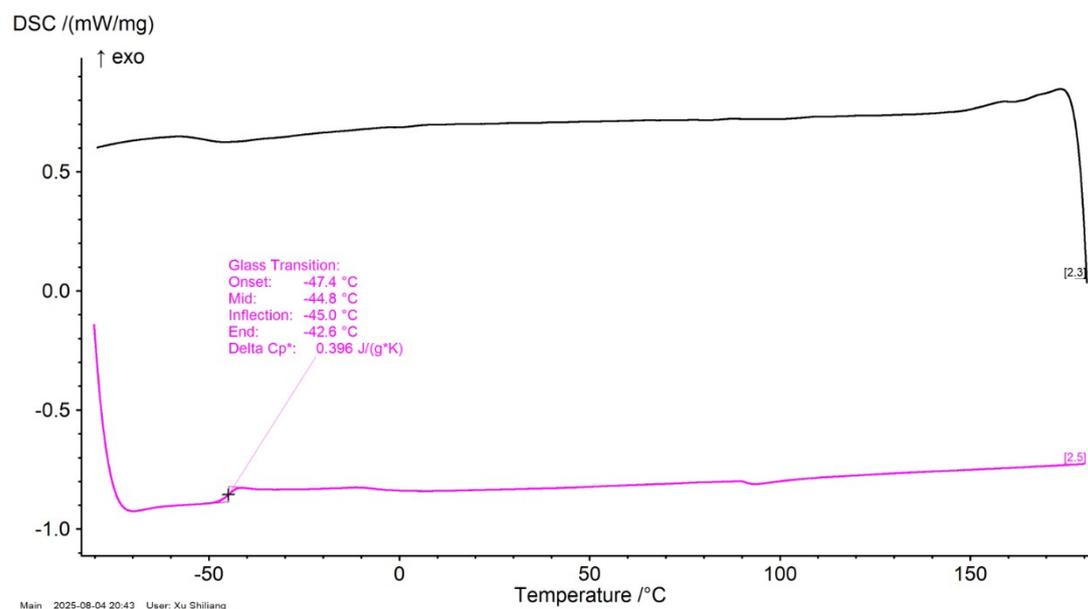
Figure S84. DSC curve of the polymer from table 1, run 4.
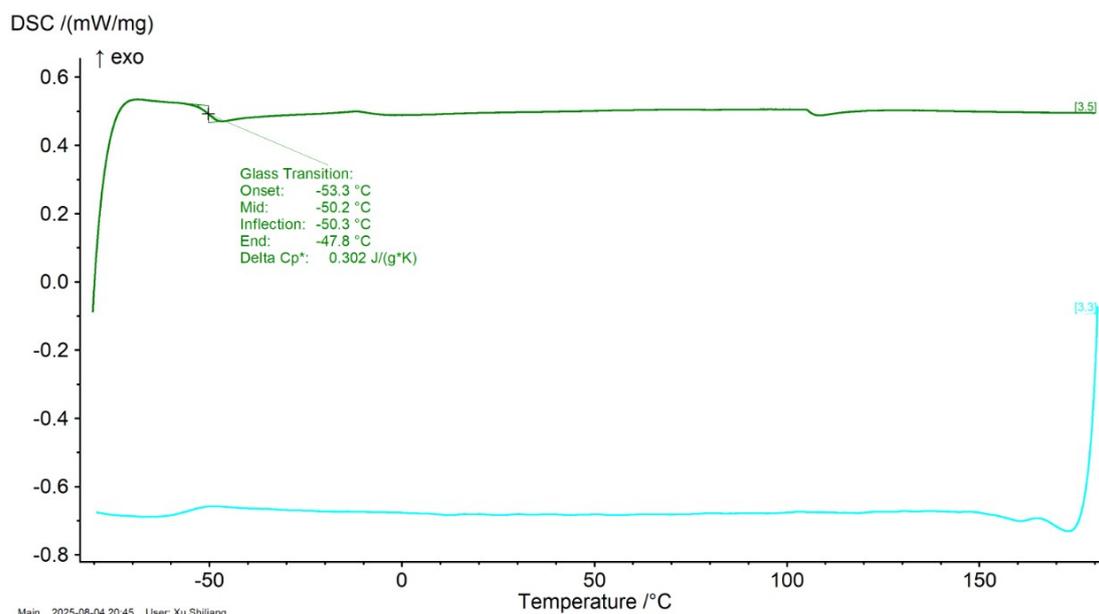
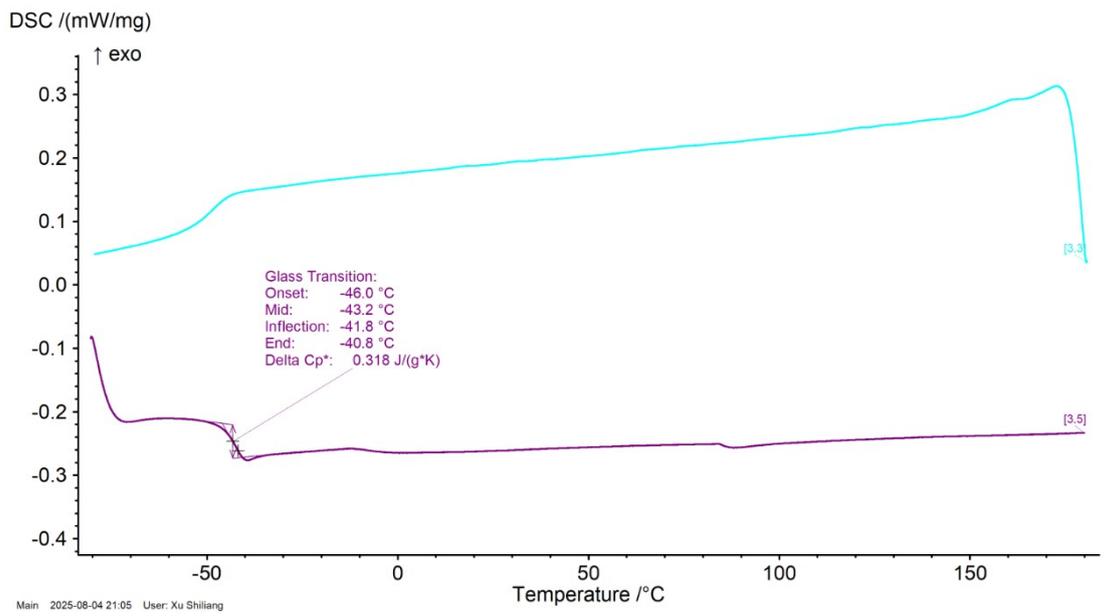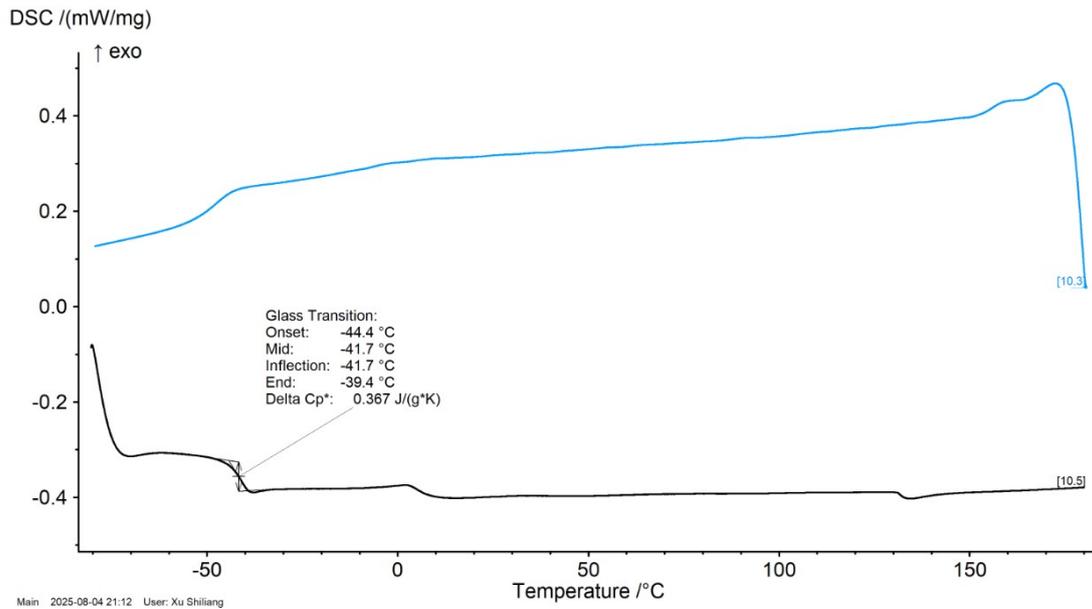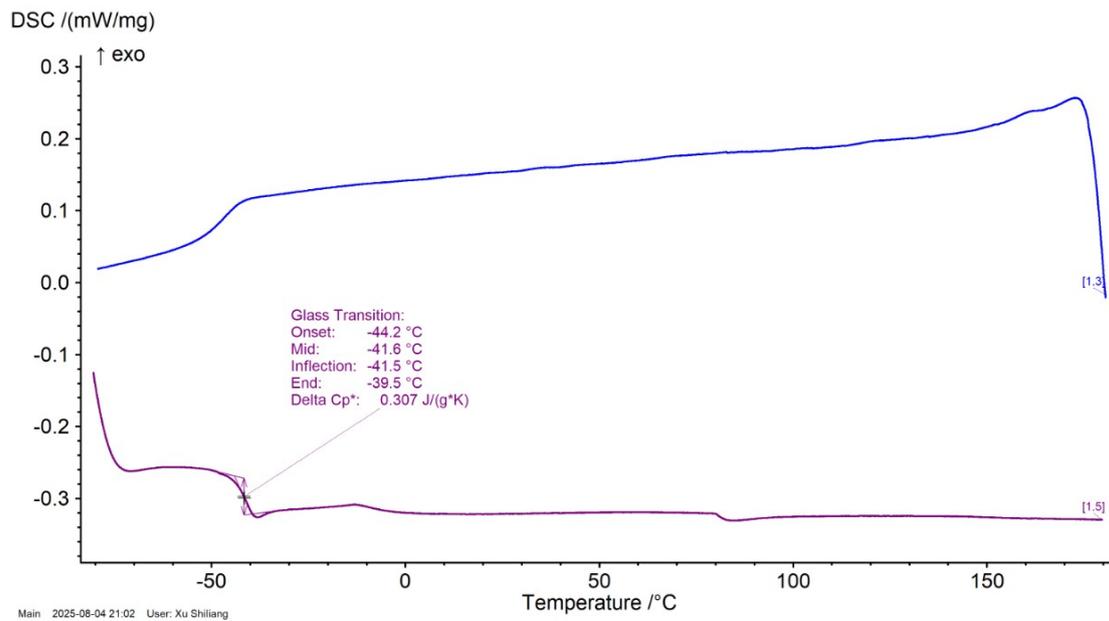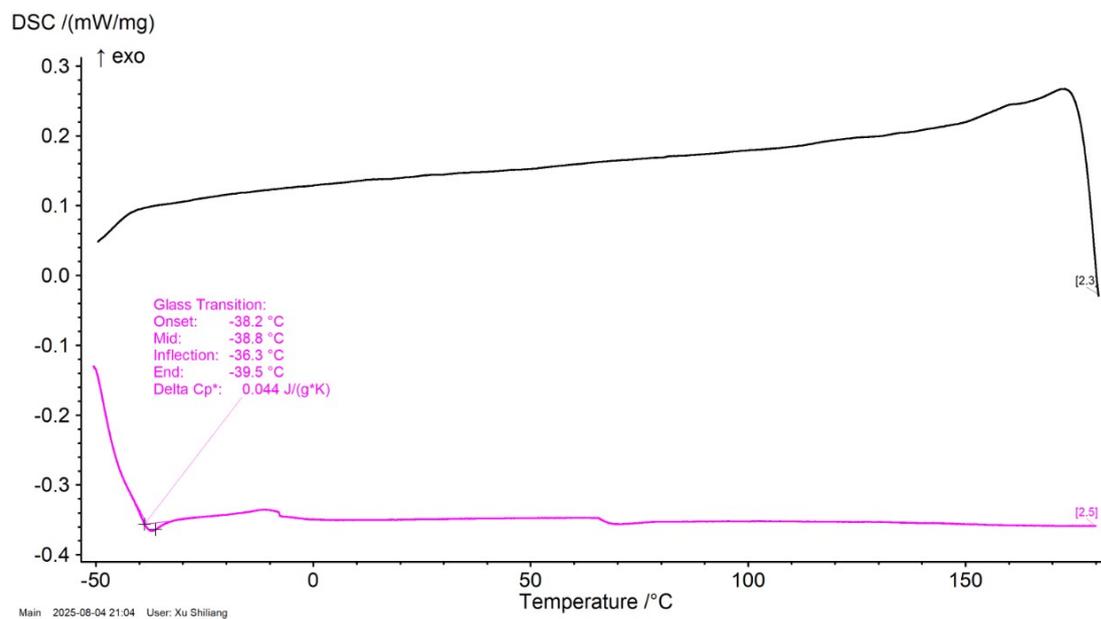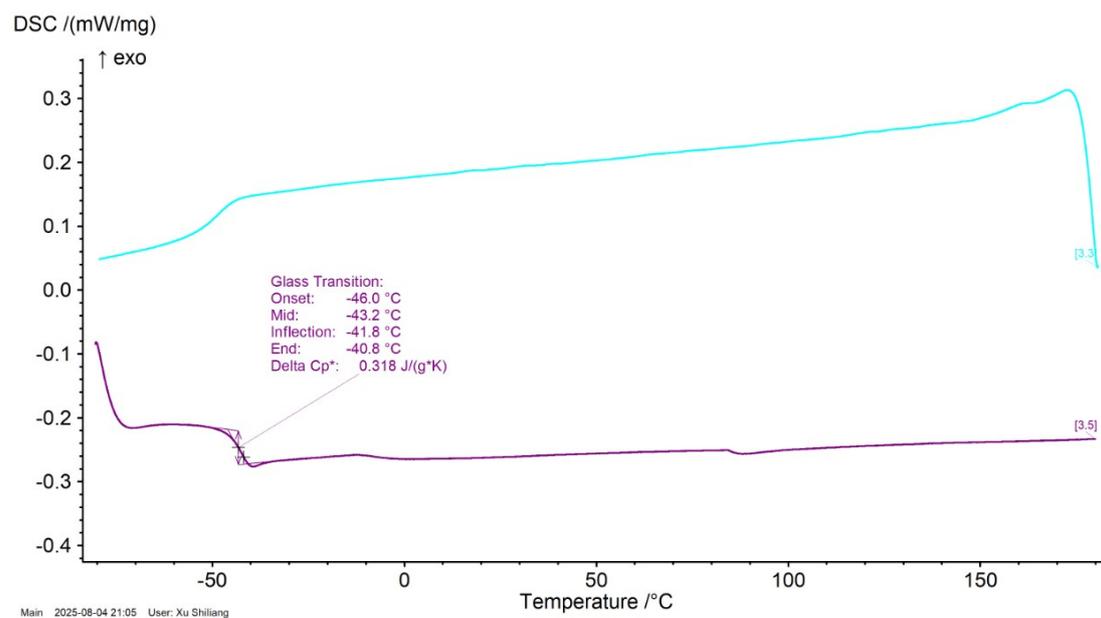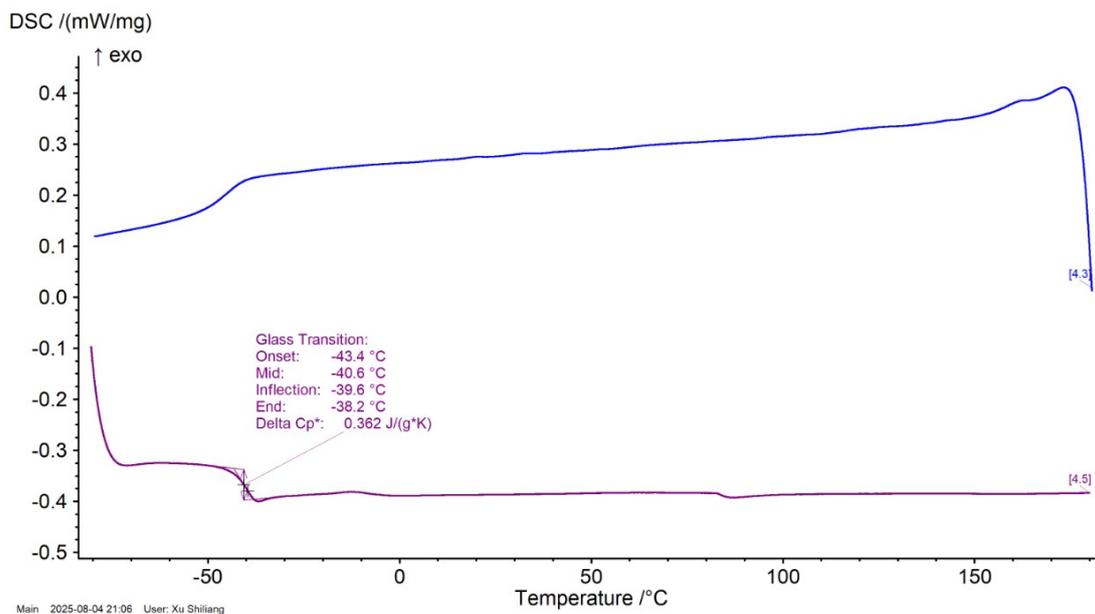**Figure S85**. DSC curve of the polymer from table 1, run 5.
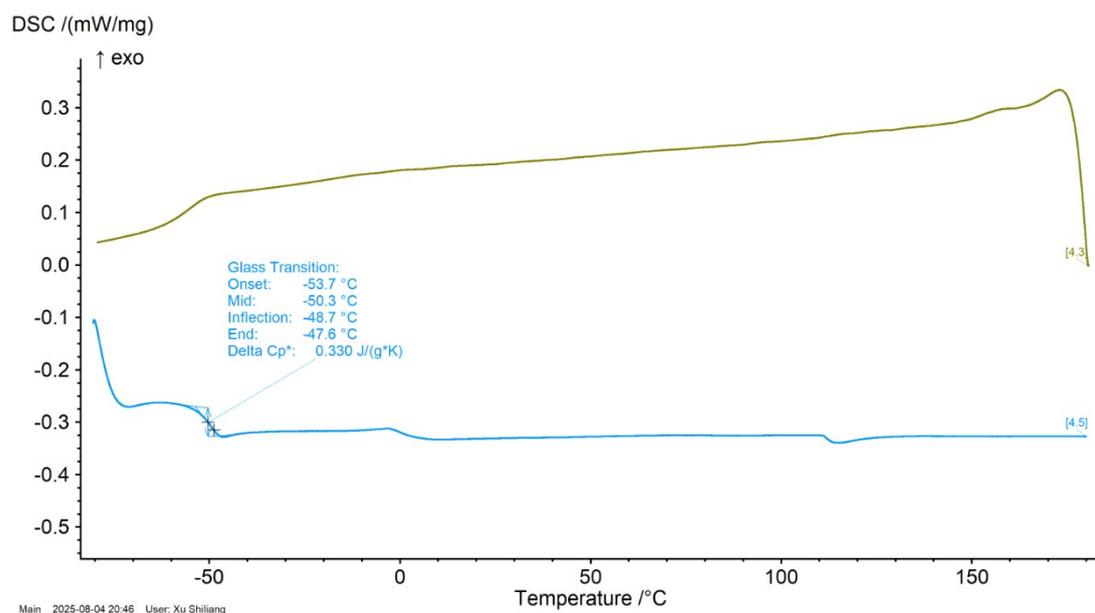
Figure S86. DSC curve of the polymer from table 1, run 6.
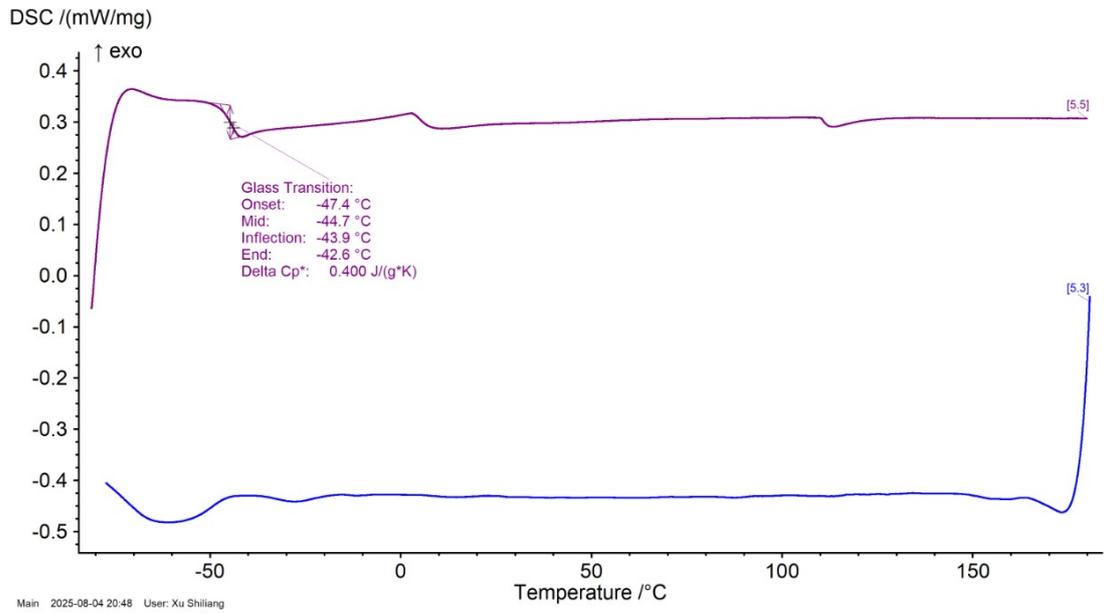
Figure S87. DSC curve of the polymer from table 1, run 8.
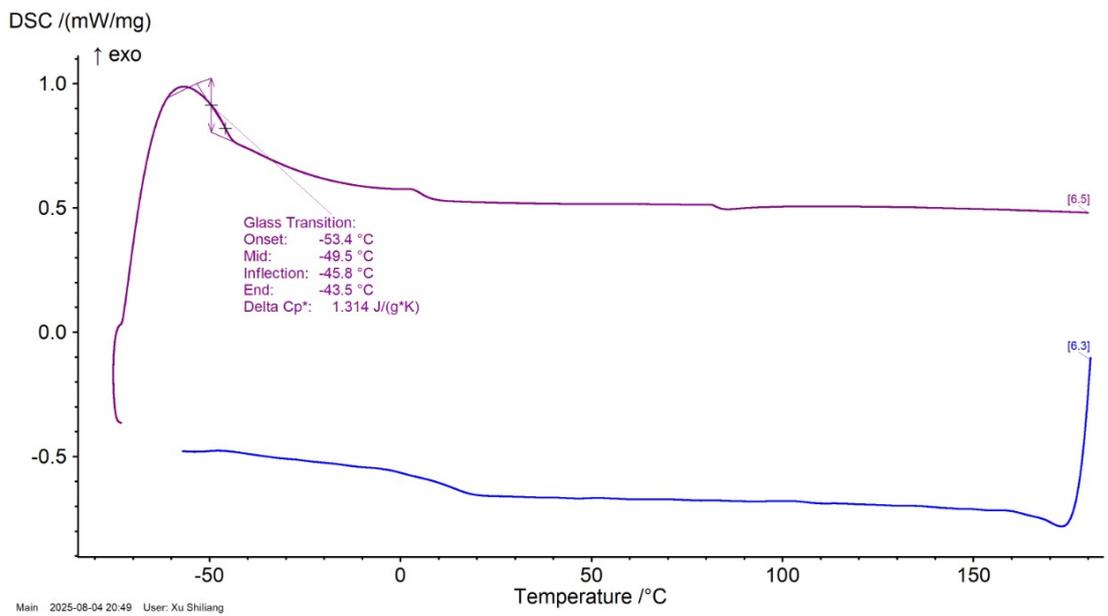
Figure S88. DSC curve of the polymer from table 1, run 9.
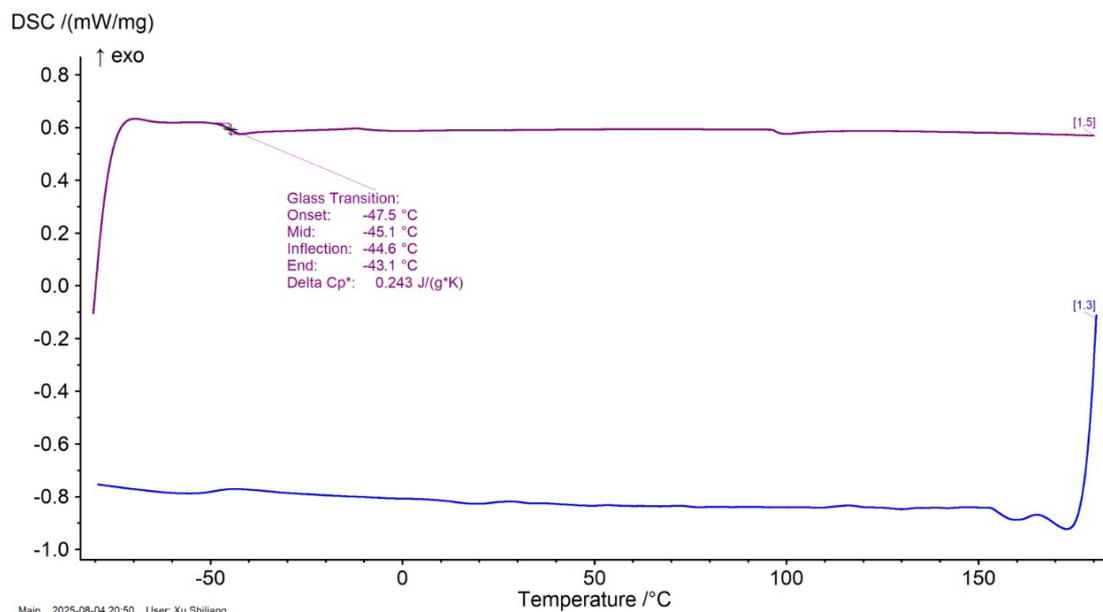
Figure S89. DSC curve of the polymer from table 1, run 10.
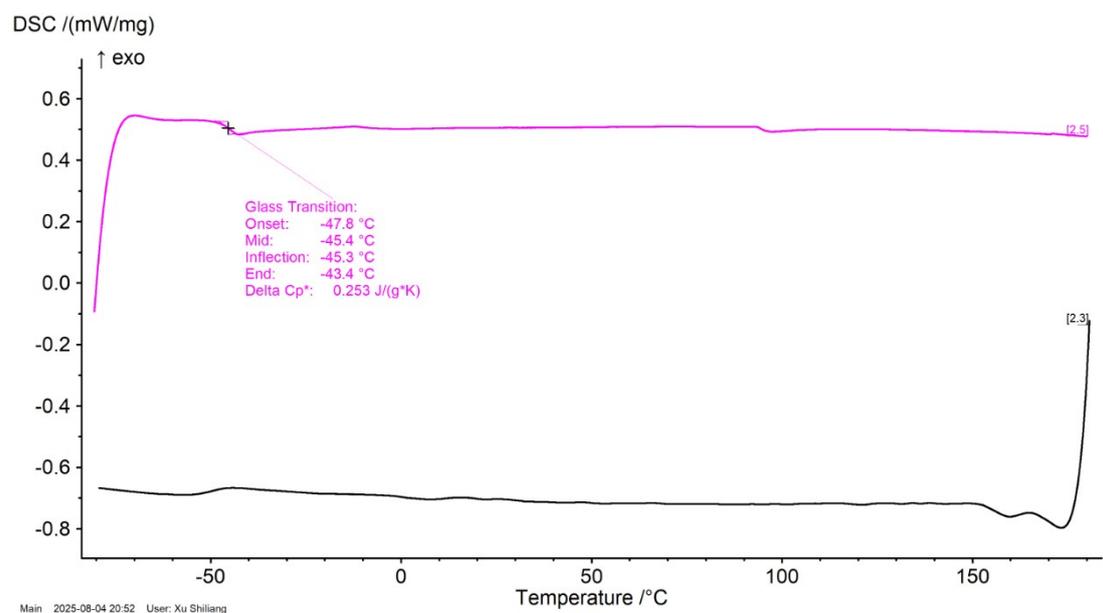
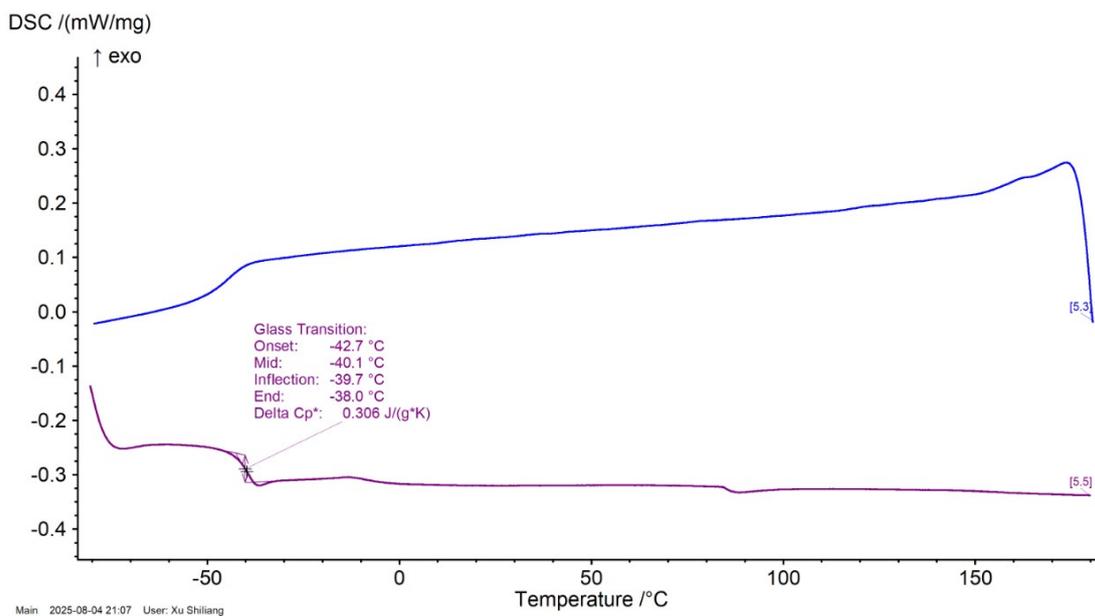**Figure S90**. DSC curve of the polymer from table 1, run 11.
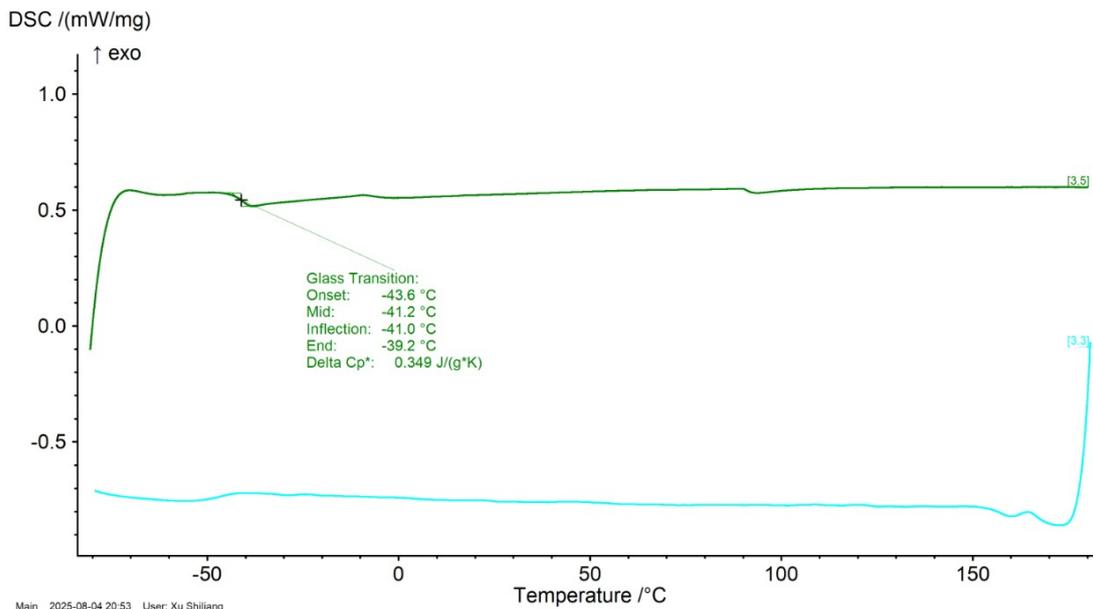
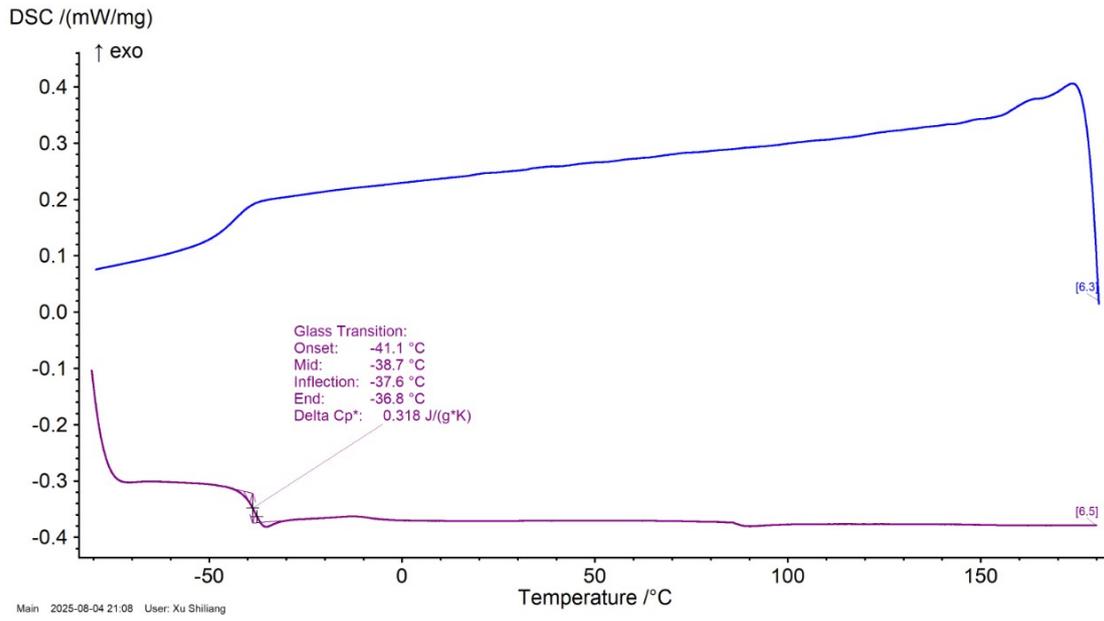**Figure S91**. DSC curve of the polymer from table 1, run 12.
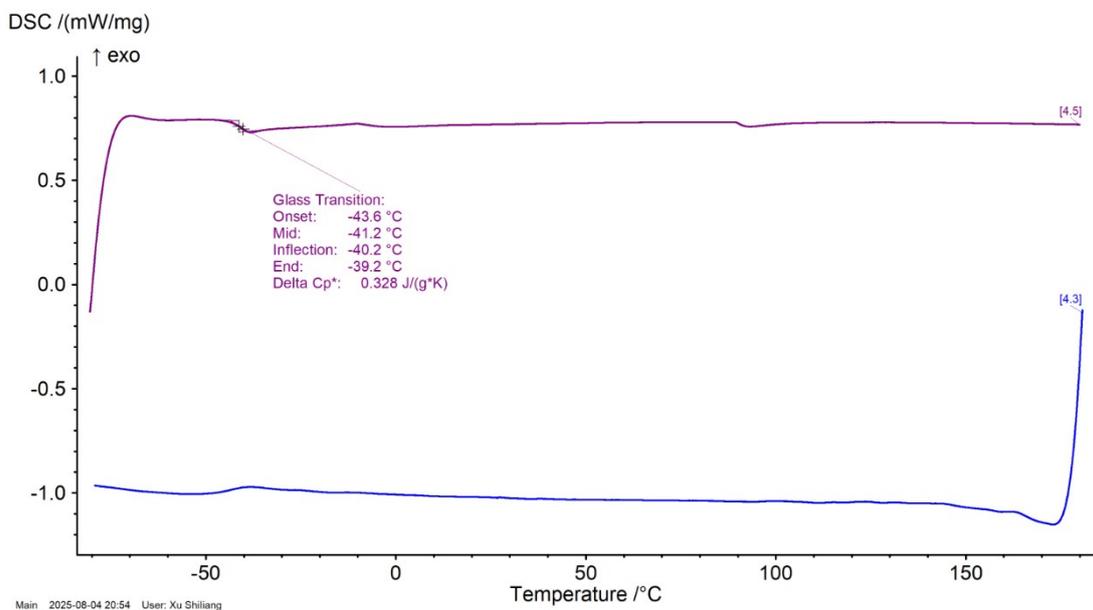
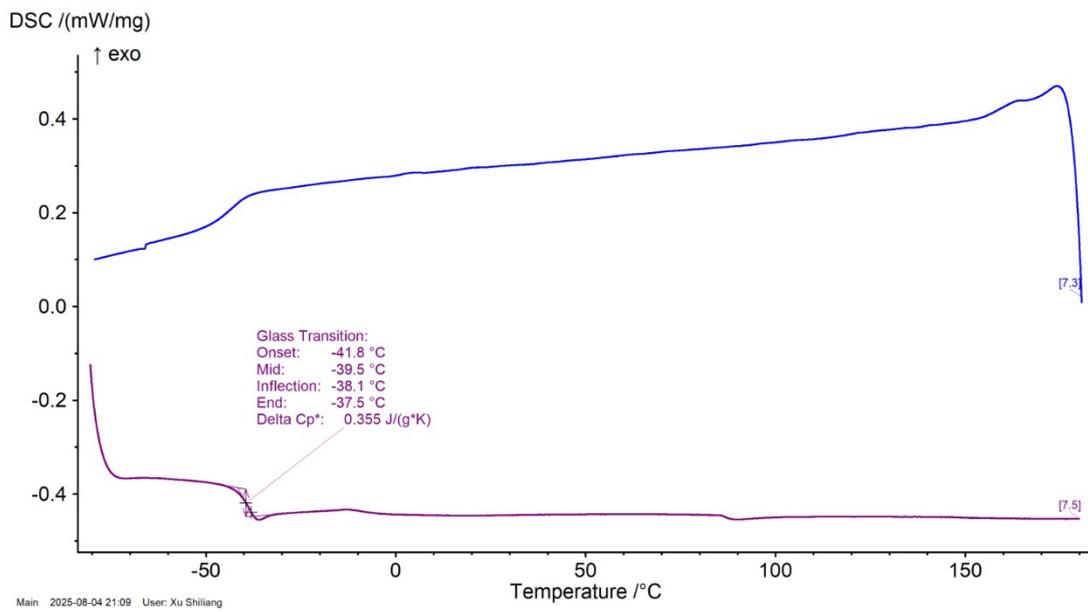**Figure S92**. DSC curve of the polymer from table 1, run 13.
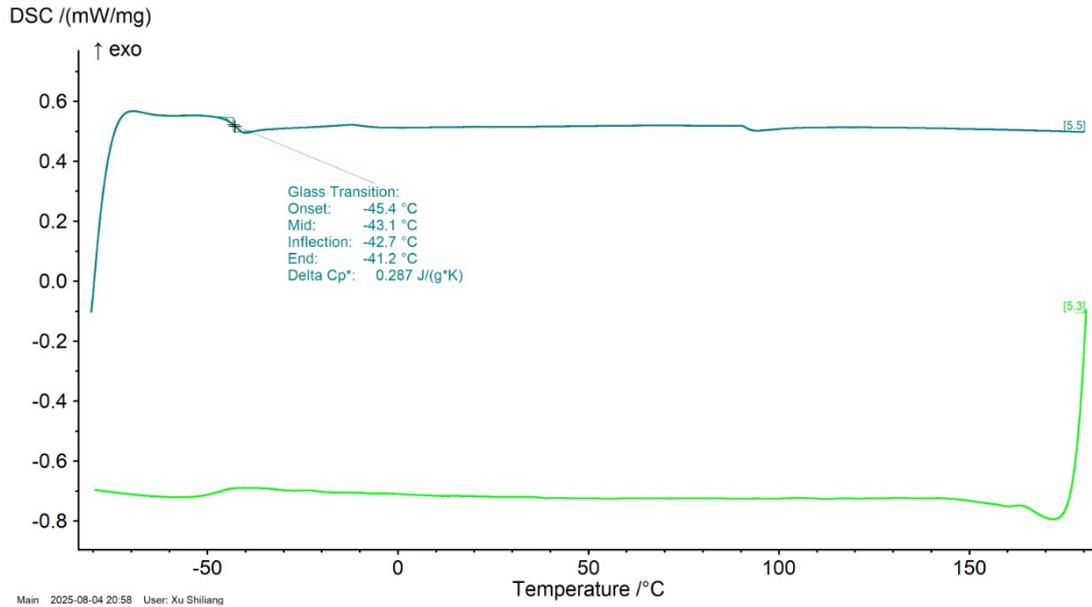
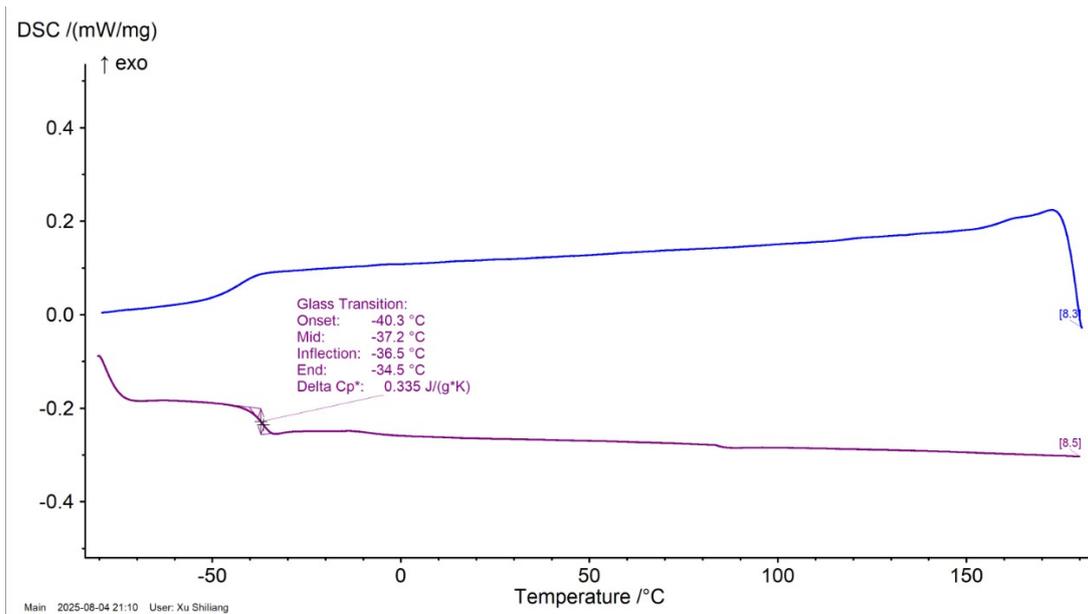**Figure S93**. DSC curve of the polymer from table 1, run 14.
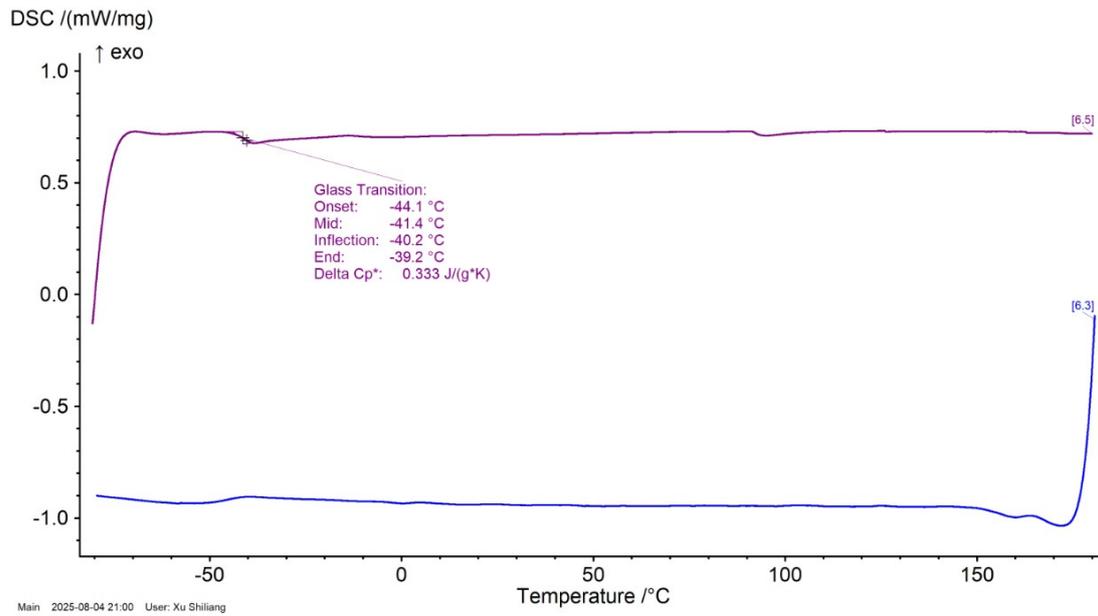
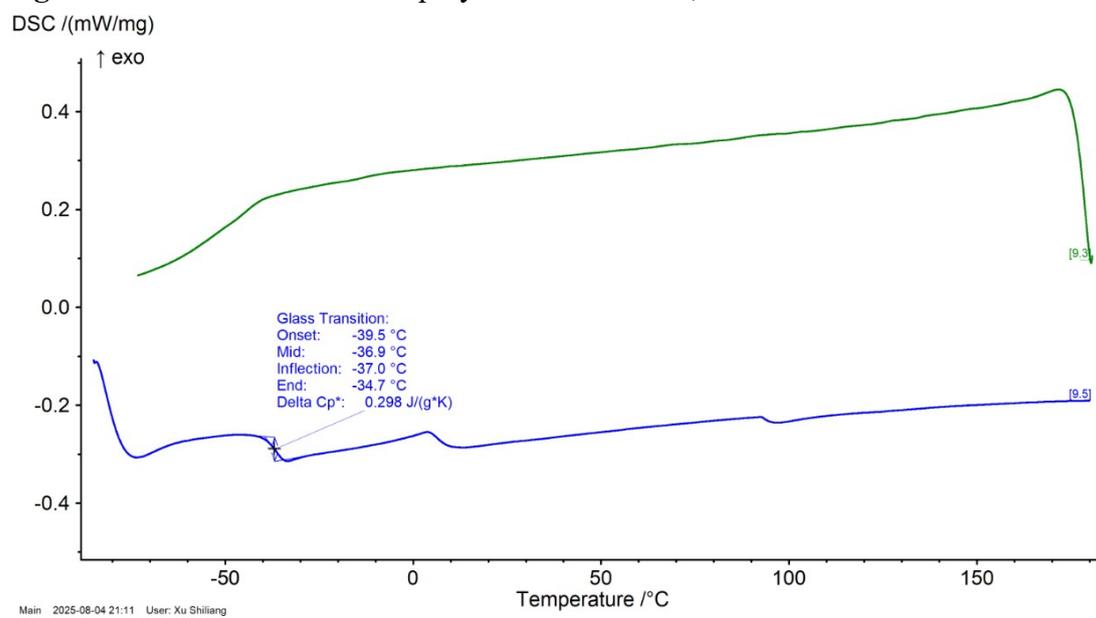**Figure S94**. DSC curve of the polymer from table 1, run 15.
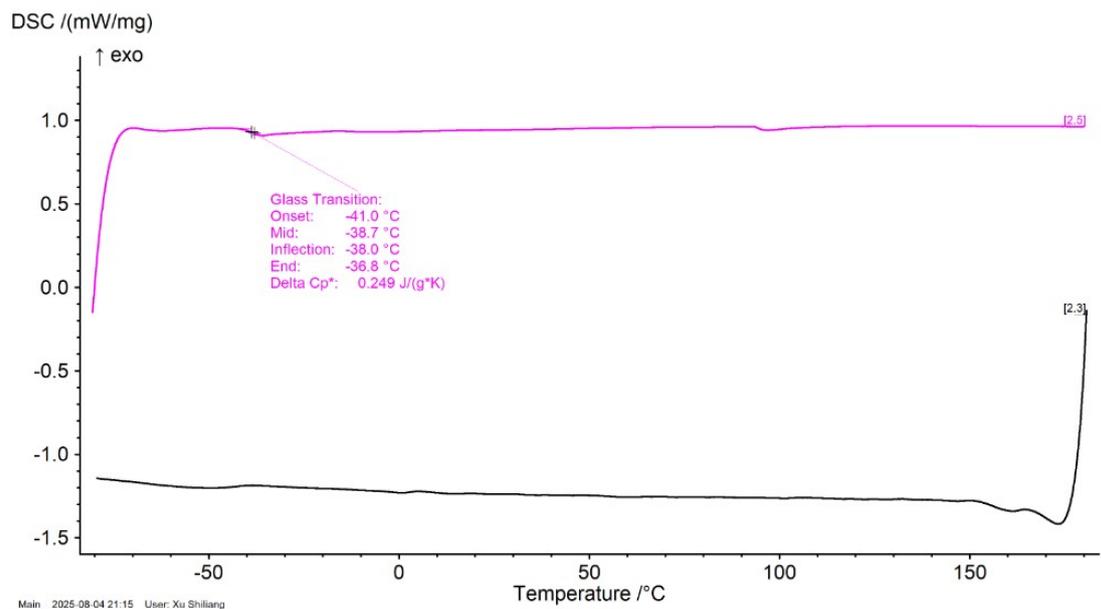
Figure S95. DSC curve of the polymer from table 1, run 16.

Figure S96. DSC curve of the polymer from table 1, run 17.

Figure S97. DSC curve of the polymer from table 2, run 2.

Figure S98. DSC curve of the polymer from table 2, run 4.

Figure S99. DSC curve of the polymer from table 2, run 5.

Figure S100. DSC curve of the polymer from table 3, run 1.

Figure S101. DSC curve of the polymer from table 3, run 2.

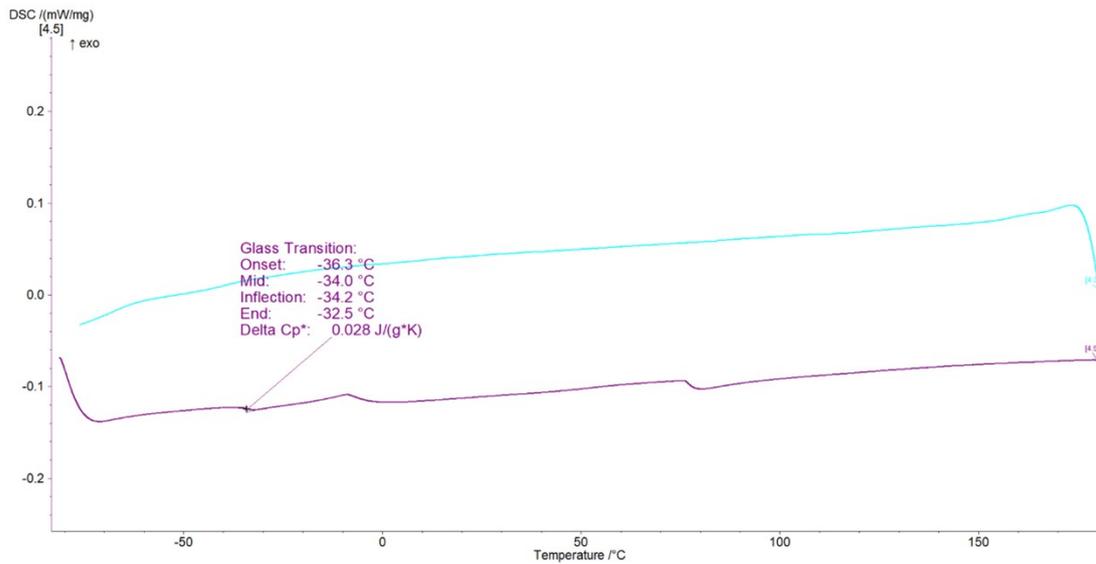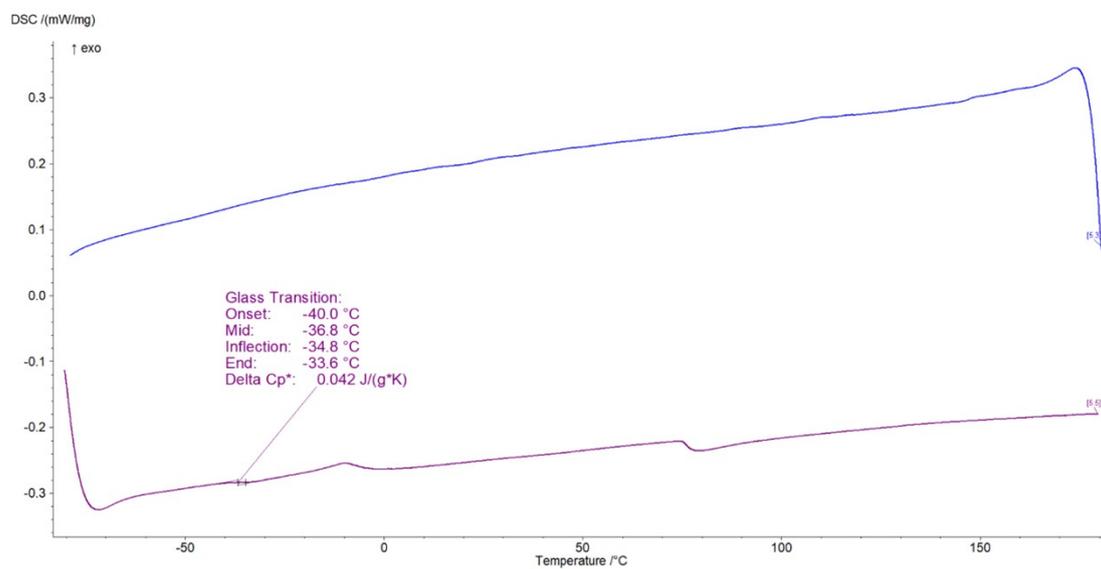**Figure S102**. DSC curve of the polymer from table 3, run 3.

Figure S103. DSC curve of the polymer from table 3, run 4.

Figure S104. DSC curve of the polymer from table 3, run 5.

Figure S105. DSC curve of the polymer from table 3, run 6.

Figure S106. DSC curve of the polymer from table 3, run 7.

Figure S107. DSC curve of the polymer from table 3, run 8.

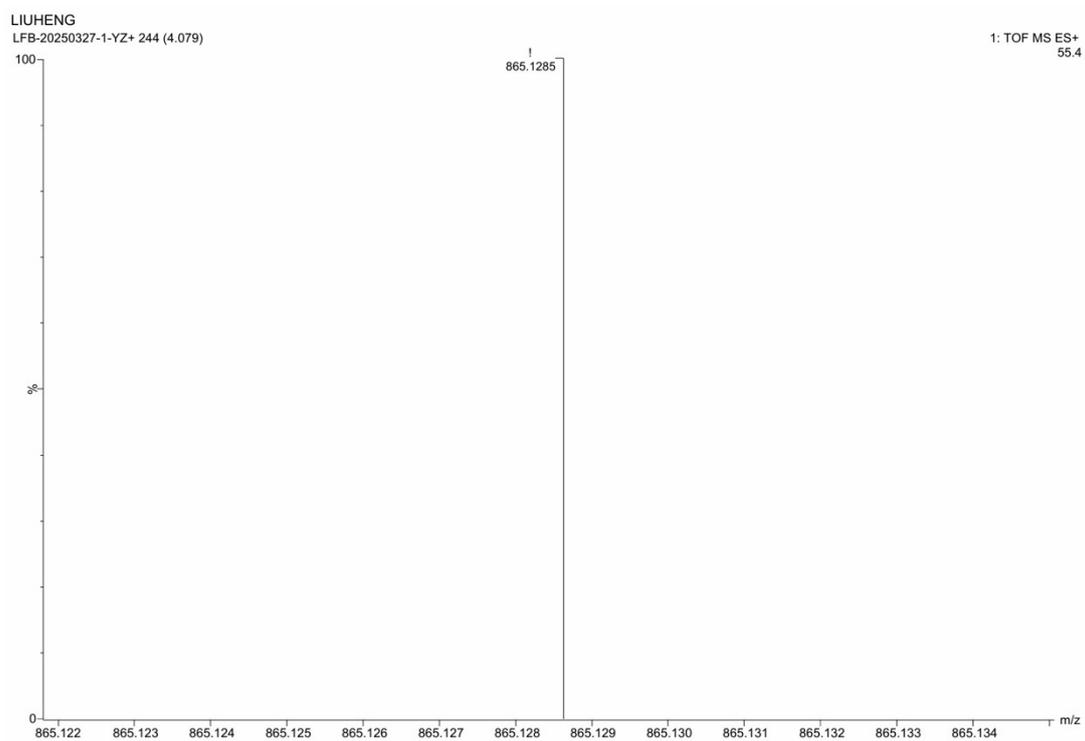**Figure S108**. DSC curve of the polymer from table 3, run 9.

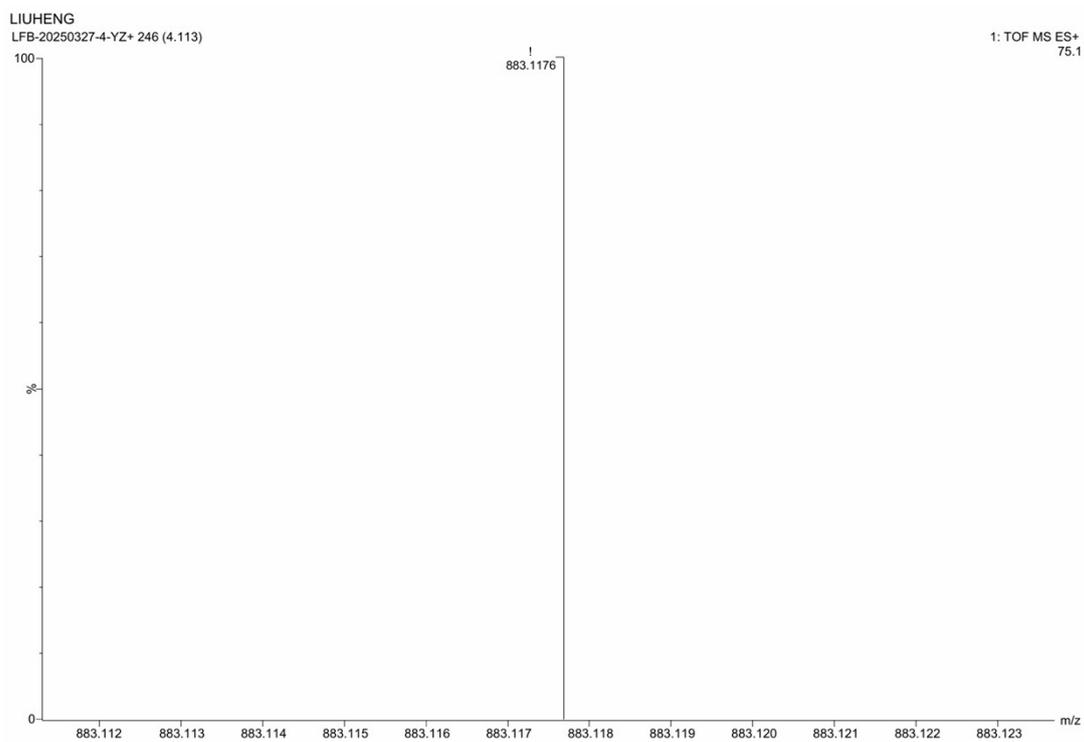**Figure S109**. DSC curve of the polymer from table 3, run 10.

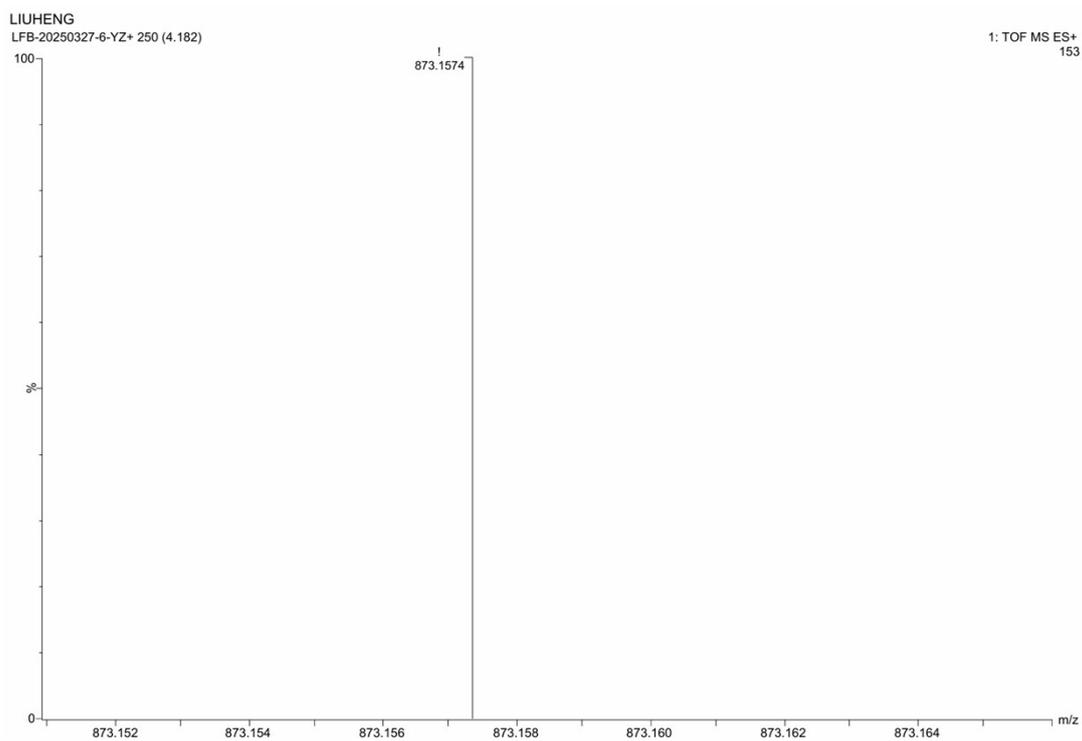**Figure S110**. DSC curve of the polymer from table 3, run 11.
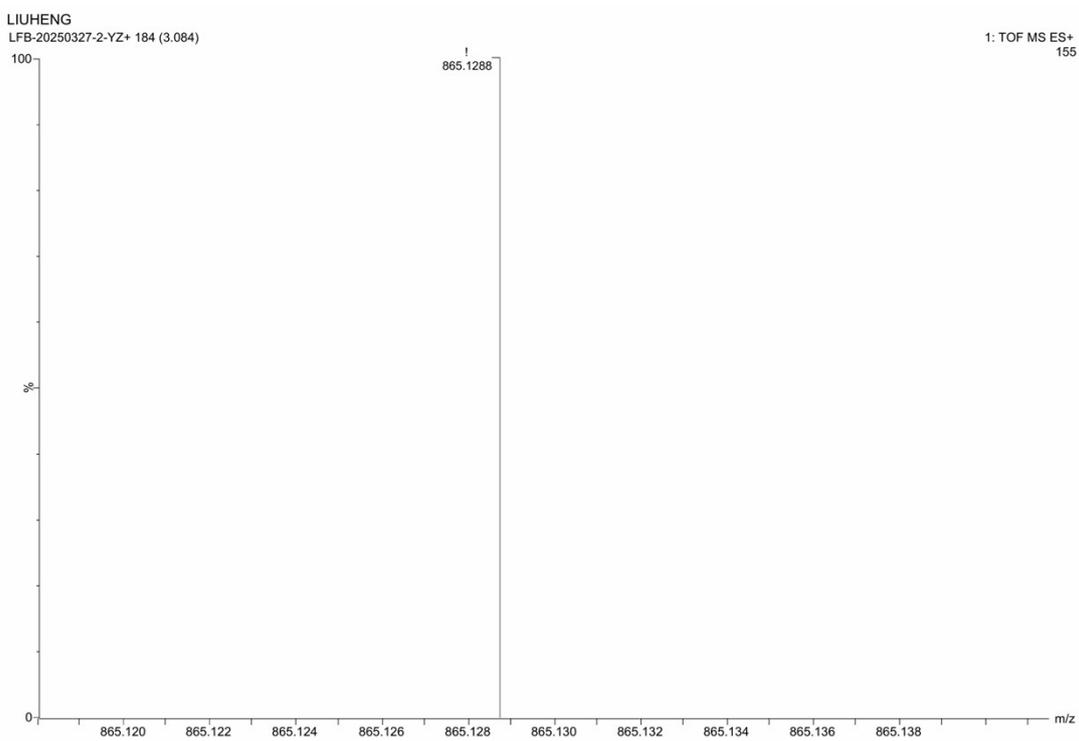
7.HR-LCMS characterization of Ni1-Ni5

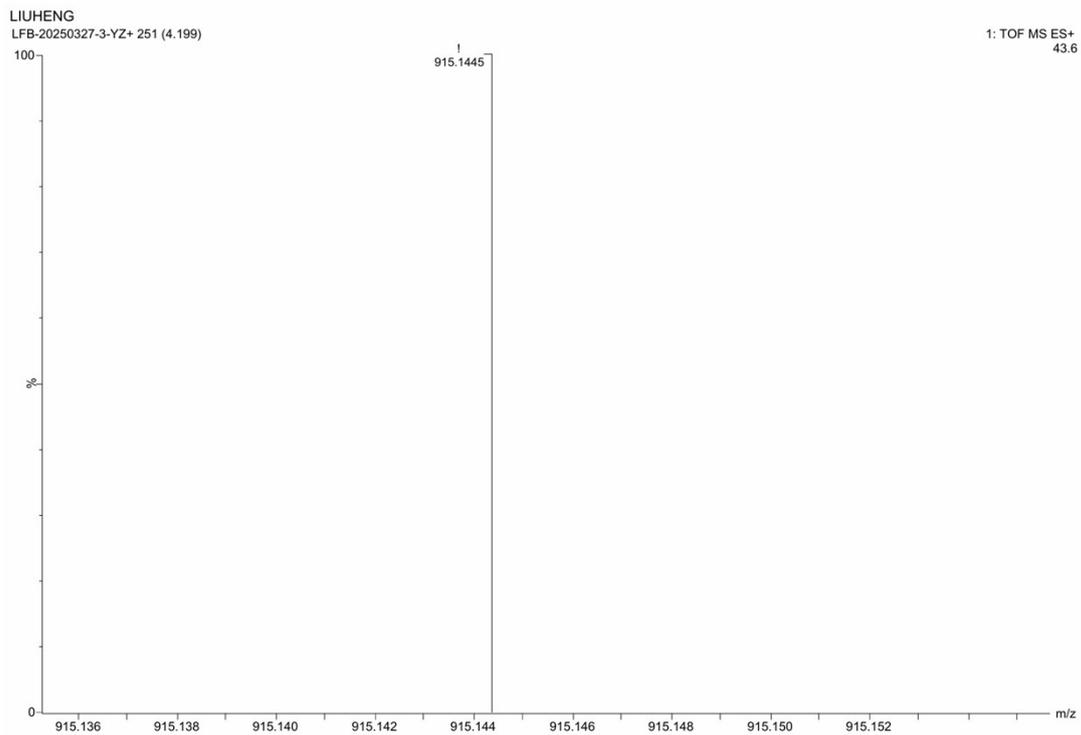**Figure S111**. ESI-MS spectrum of the molecular **Ni1**.

Figure S112. ESI-MS spectrum of the molecular **Ni2**.

Figure S113. ESI-MS spectrum of the molecular **Ni3**.

Figure S114. ESI-MS spectrum of the molecular **Ni4**.

Figure S115. ESI-MS spectrum of the molecular **Ni5**.