

Supporting Information

Homo- and copolymerization of norbornene with tridentate nickel complexes bearing *o*-aryloxy-N-heterocyclic carbene ligands

Dandan Yang,[†] Jie Dong,[†] and Baiquan Wang^{*,†,‡,§}

[†]State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry,

[‡]Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, People's Republic of China

[§]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

*To whom correspondence should be addressed.

Tel and fax: +86-22-23504781. E-mail: bqwang@nankai.edu.cn.

Figures S1–2. ^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of **L1**.

Figures S3–4. ^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of **L2**.

Figures S5–6. ^1H NMR (400 MHz, DMSO) and ^{13}C NMR (100 MHz, DMSO) spectra of **L3**.

Figures S7–8. ^1H NMR (400 MHz, DMSO) and ^{13}C NMR (100 MHz, DMSO) spectra of **Ni1**.

Figures S9–10. ^1H NMR (400 MHz, CD_3CN) and ^{13}C NMR (100 MHz, CD_3CN) spectra of **Ni2**.

Figures S11–12. ^1H NMR (400 MHz, DMSO) and ^{13}C NMR (100 MHz, DMSO) spectra of **Ni3**.

Figures S13–14. ^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of **Ni4**.

Figure S15. ^1H NMR spectra of poly(NB-co-1-octene)s: (a) 12%, (b) 15%, (c) 17%, (d) 9%, (e) 12% of 1-octene molar ratio obtained by **Ni1–Ni3**/ $\text{B}(\text{C}_6\text{F}_5)_3$ systems.

Figure S16. ^{13}C NMR spectra of poly(NB-co-1-octene)s: (a) 12%, (b) 15%, (c) 17%, (d) 9%, (e) 12% of 1-octene molar ratio obtained by **Ni1–Ni3**/ $\text{B}(\text{C}_6\text{F}_5)_3$ systems.

Figures S17–27. GPC curve of poly(NBE) of the polymer obtained by Table 1.

Figures S28–38. GPC curve of poly(NBE) of the polymer obtained by Table 2.

Figures S39–43. GPC curve of poly(NB-co-1-octene)s of the polymer obtained by Table 3.

Figures S44–49. GPC curve of poly(NBE) of the polymer obtained by Table 4.

Figure S50. IR spectrum of PNB activated by Et_2AlCl (Table 1 entry 6).

Figure S51. IR spectrum of PNB activated by Me_2AlCl (Table 1 entry 11).

Figure S52. IR spectrum of PNB activated by $\text{B}(\text{C}_6\text{F}_5)_3$ (Table 2 entry 11).

Figures S53–55. IR spectra of poly(NB-co-1-octene)s (Table 3).

Figure S56. DSC thermograms of PNB obtained by **Ni1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ system (Table 2 entry 11).

Figures S57–59. DSC thermograms of poly(NB-co-1-octene)s obtained by **Ni1–Ni3**/ $\text{B}(\text{C}_6\text{F}_5)_3$ system.

Figure S60. TGA of PNB.

Figure S61. TGA of poly(NB-co-1-octene)s.

Figures S62–63. ^1H NMR and ^1F NMR spectra of a mixture of nickel complex **Ni1** with 1 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ reacted at 80 °C for 20 min.

Figures S64–65. ^1H NMR and ^{19}F NMR spectra of a mixture of nickel complex **Ni1** with 5 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ reacted at 80 °C for 20 min.

Figures S66–67. ^1H NMR and ^{19}F NMR spectra of a mixture of nickel complex **Ni1** with 5 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ reacted at room temperature for 20 min.

Figure S68. ^{19}F NMR spectra of poly(NB-co-1-octene)s obtained by **Ni1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ system (Table 3 entry 4).

Table S1. Catalytic optimization with **Ni1–Ni4**/ Me_2AlCl .

Table S2. Time dependence studies at high temperature with **Ni1–Ni3**/ $\text{B}(\text{C}_6\text{F}_5)_3$.

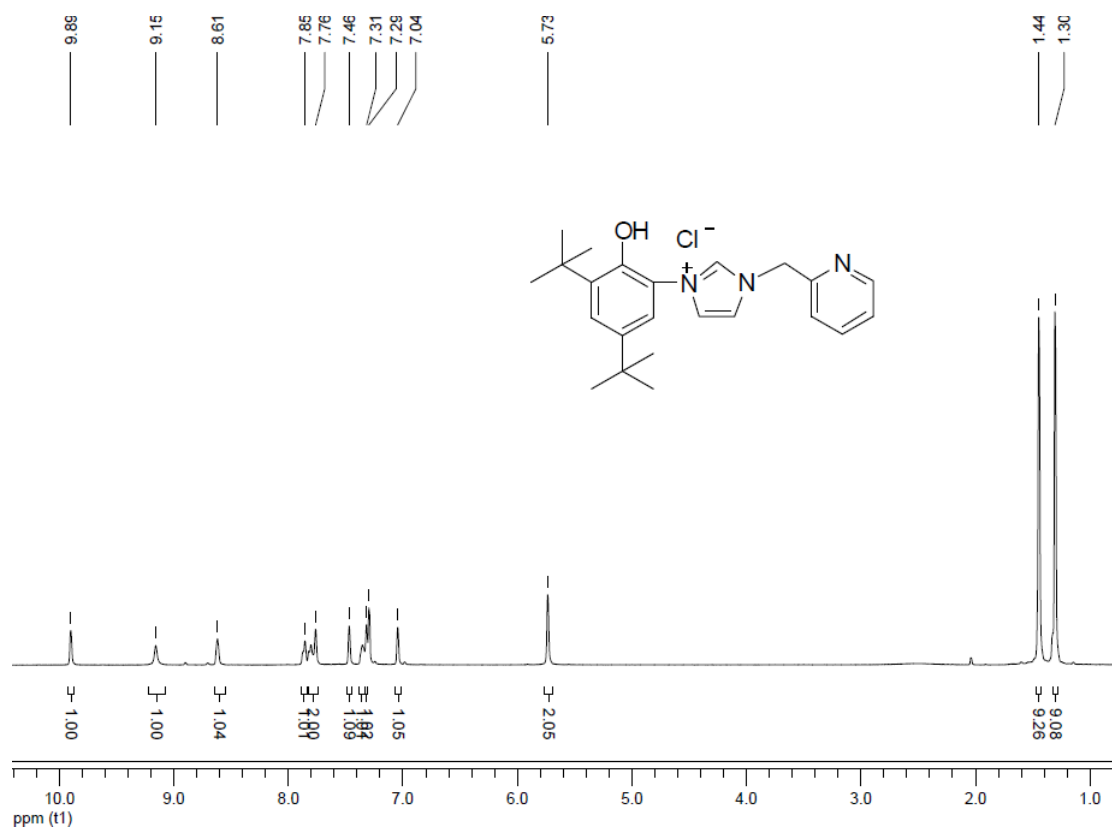


Figure S1. ¹H NMR (400 MHz, CDCl₃) spectrum of L1.

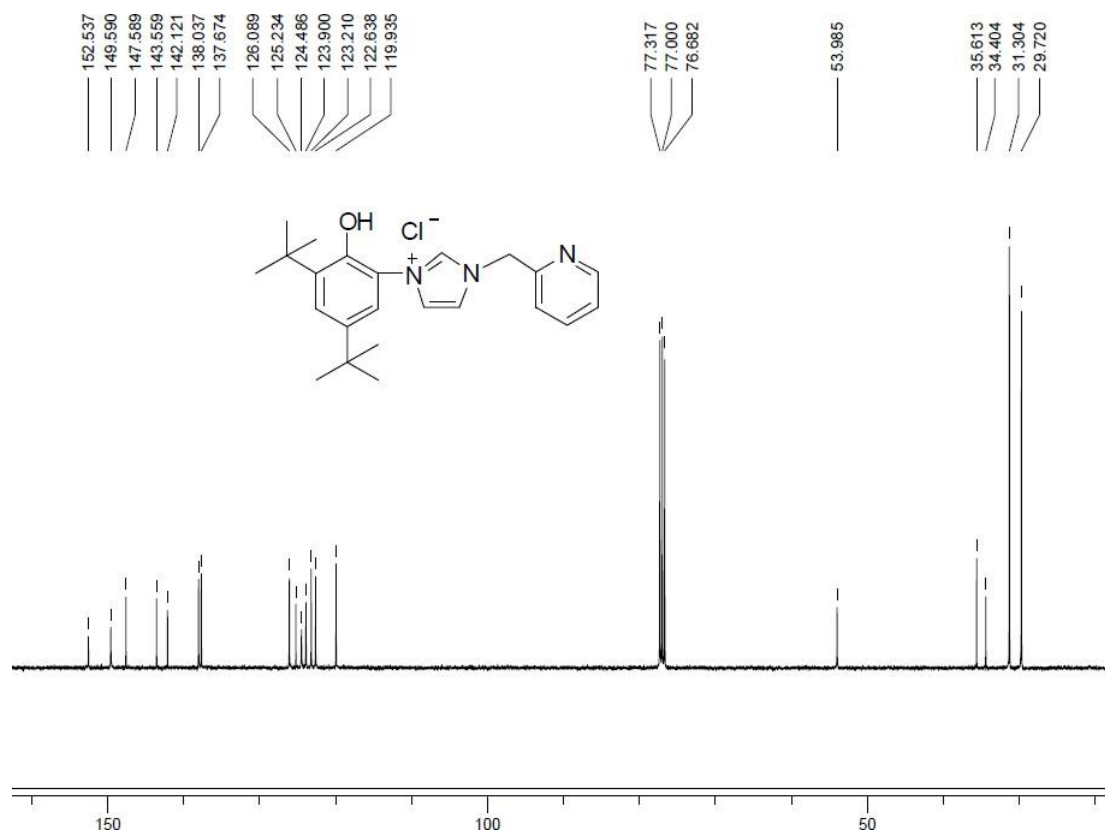


Figure S2. ¹³C NMR (100 MHz, CDCl₃) spectrum of L1.

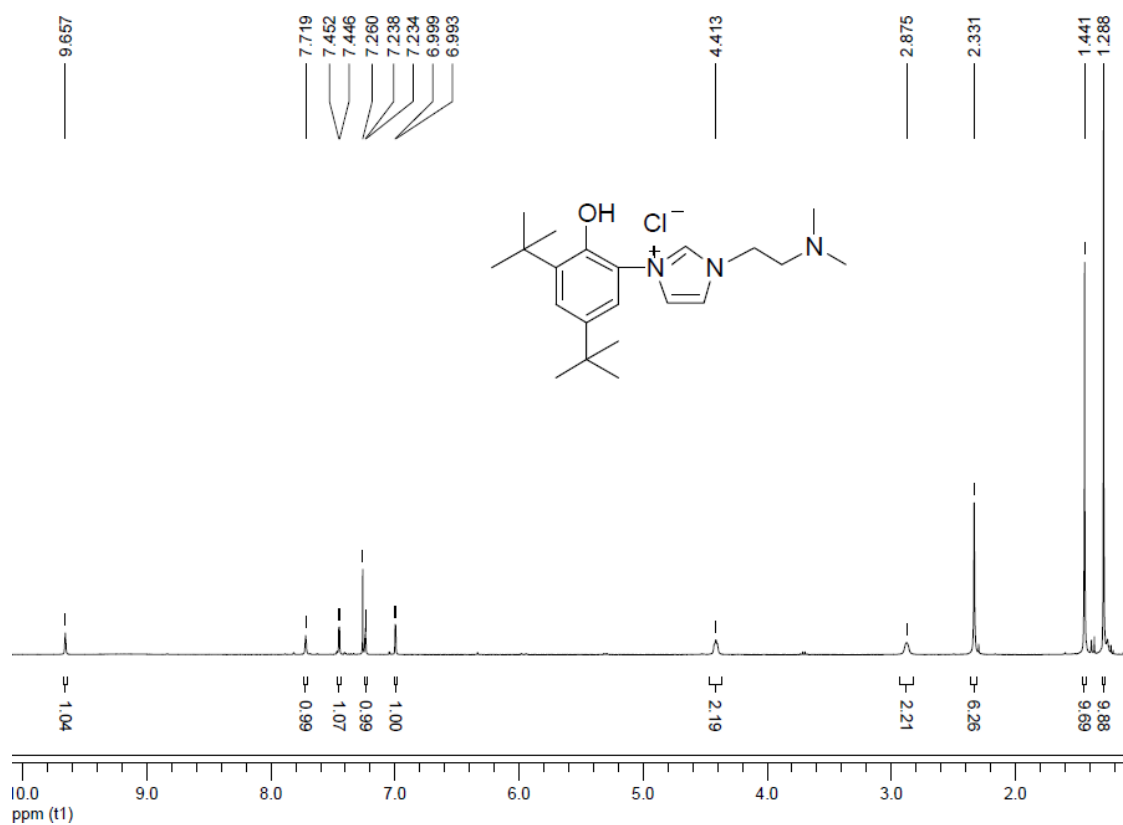


Figure S3. ¹H NMR (400 MHz, CDCl₃) spectrum of L2.

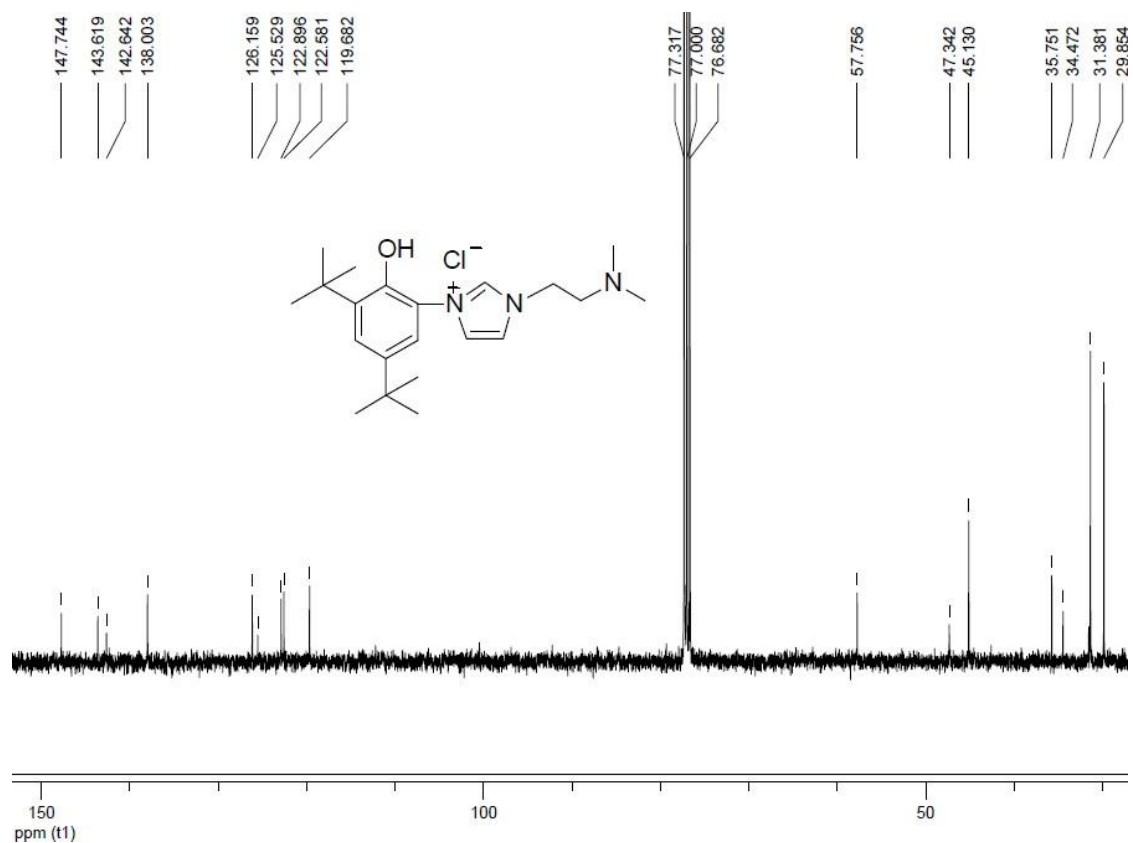


Figure S4. ¹³C NMR (100 MHz, CDCl₃) spectrum of L2.

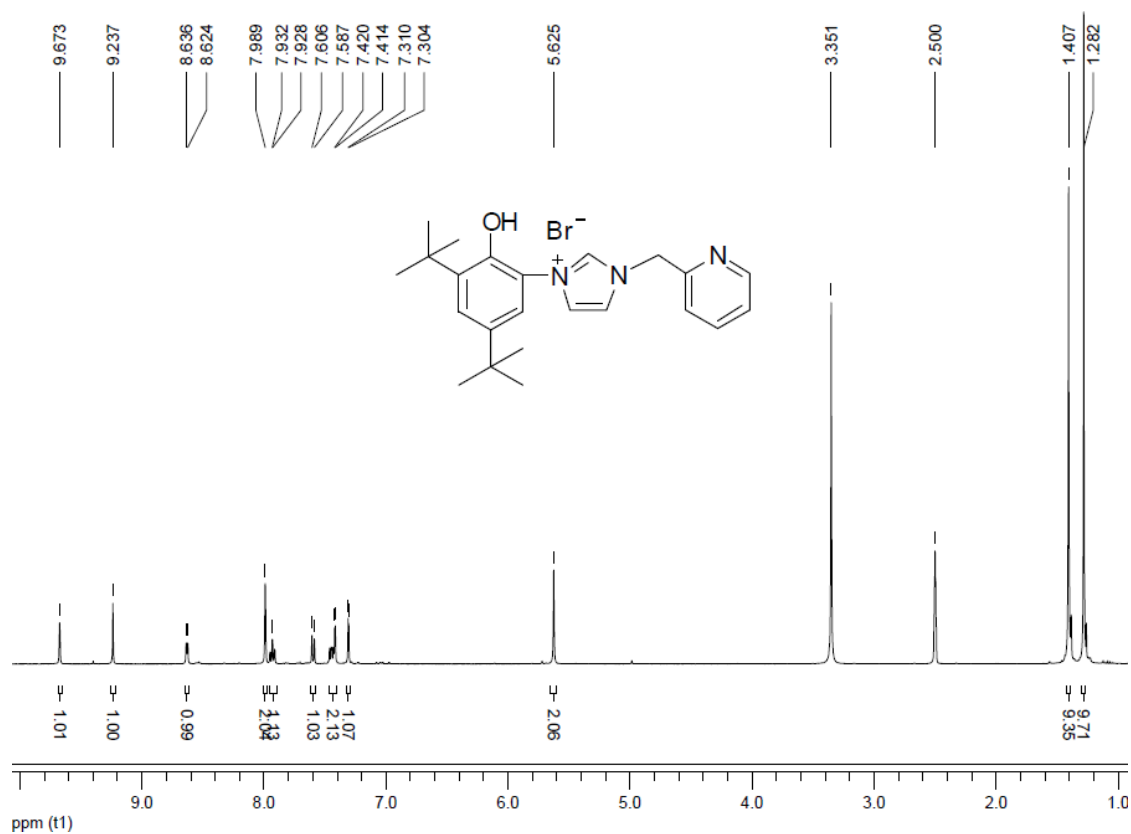


Figure S5. ¹H NMR (400 MHz, DMSO) spectrum of L3.

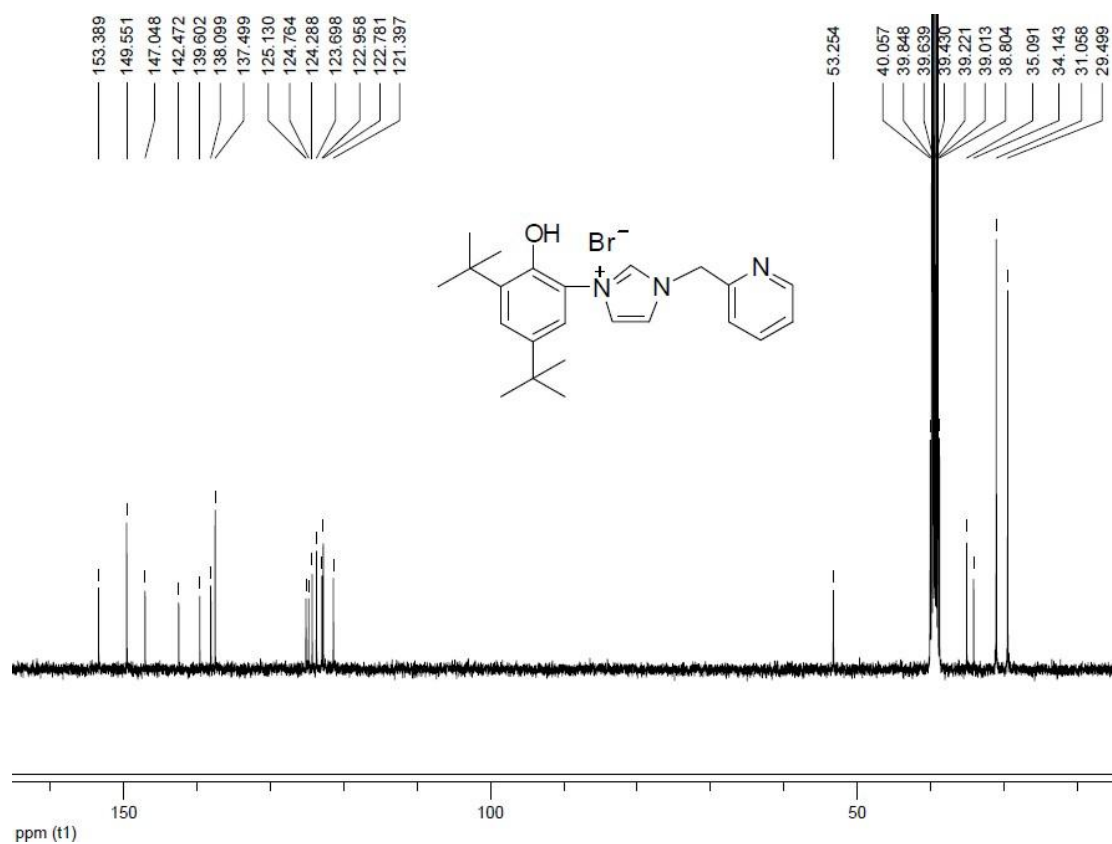


Figure S6. ¹³C NMR (100 MHz, DMSO) spectrum of L3.

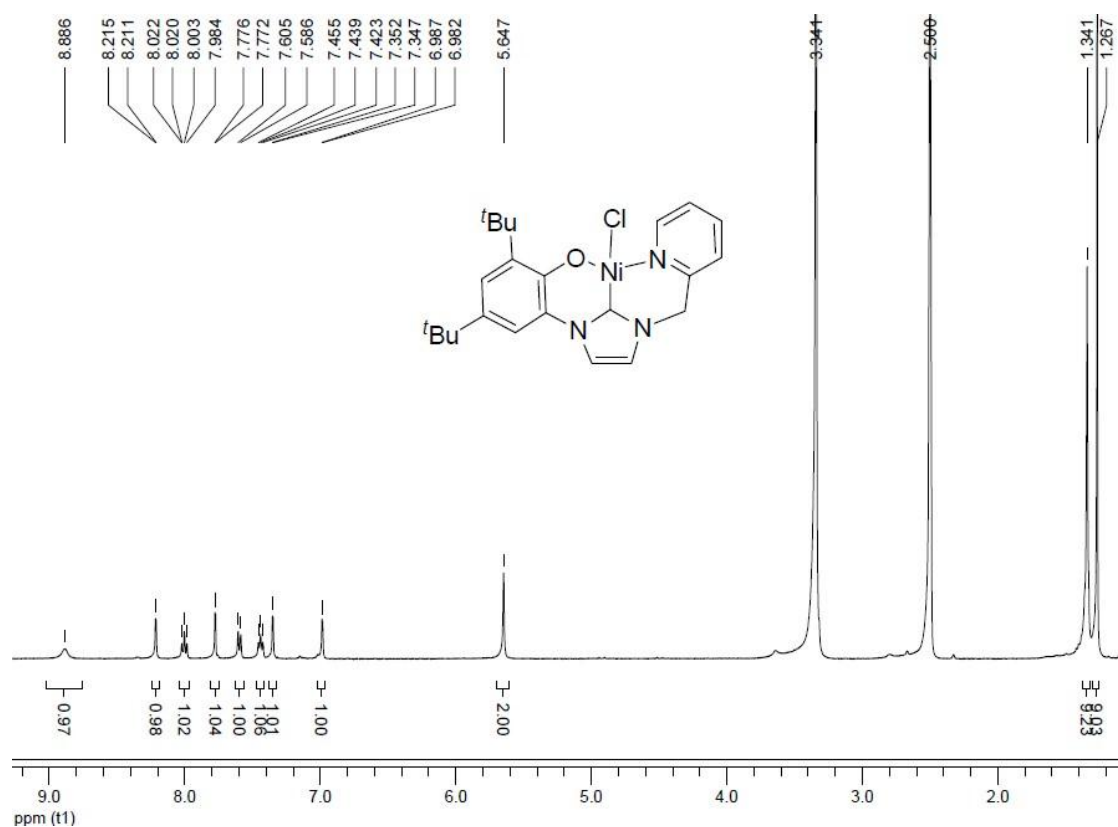


Figure S7. ¹H NMR (400 MHz, DMSO) spectrum of Ni1.

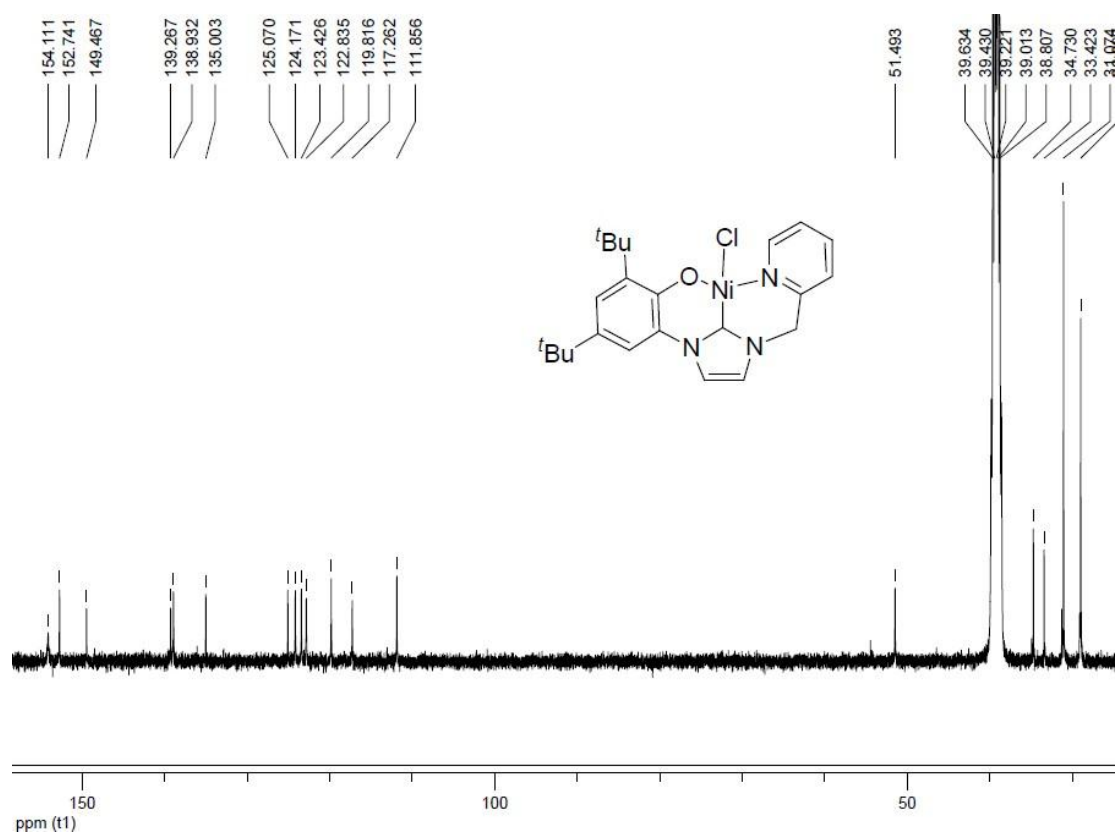


Figure S8. ¹³C NMR (100 MHz, DMSO) spectrum of Ni1.

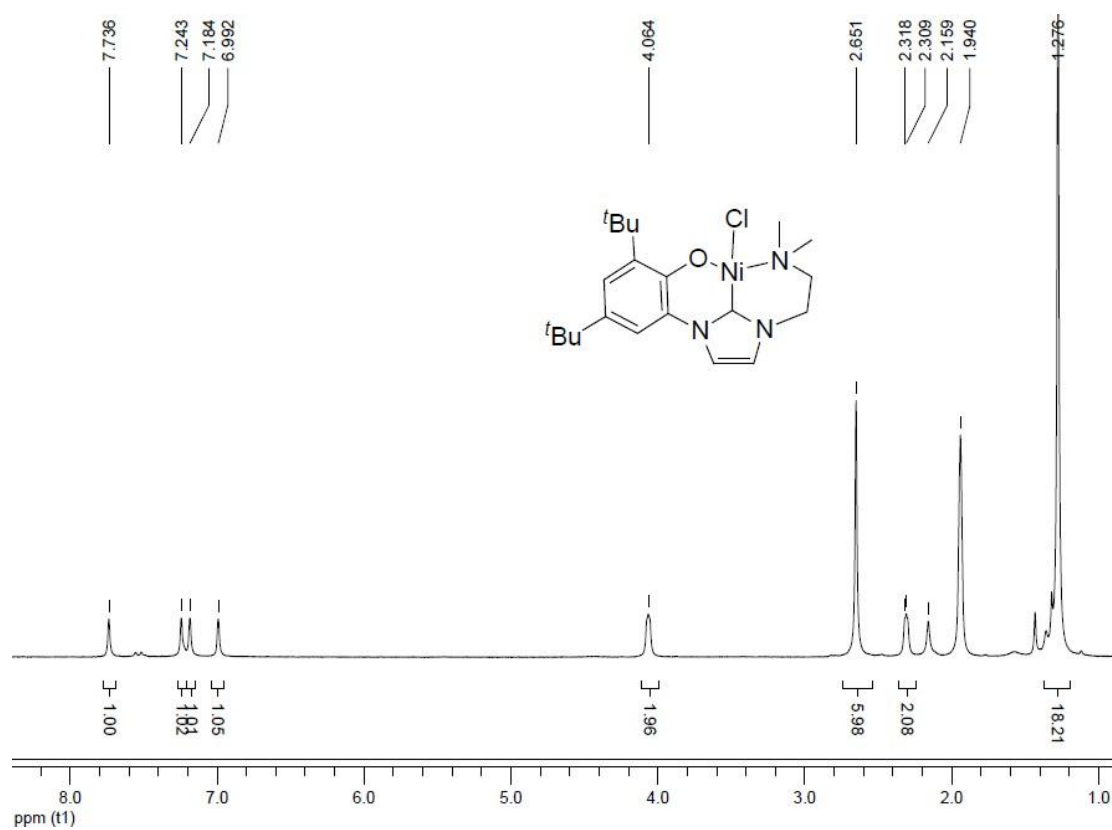


Figure S9. ¹H NMR (400 MHz, CD₃CN) spectrum of Ni2.

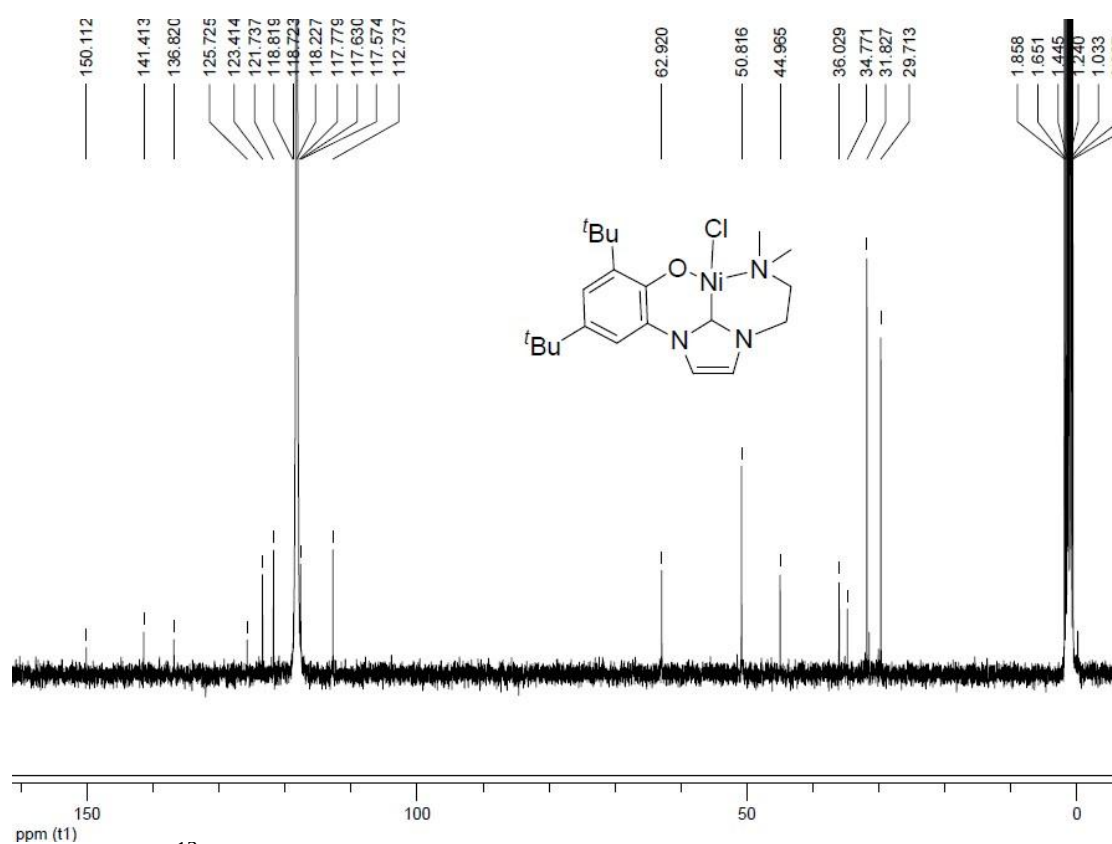


Figure S10. ¹³C NMR (100 MHz, CD₃CN) spectrum of Ni2.

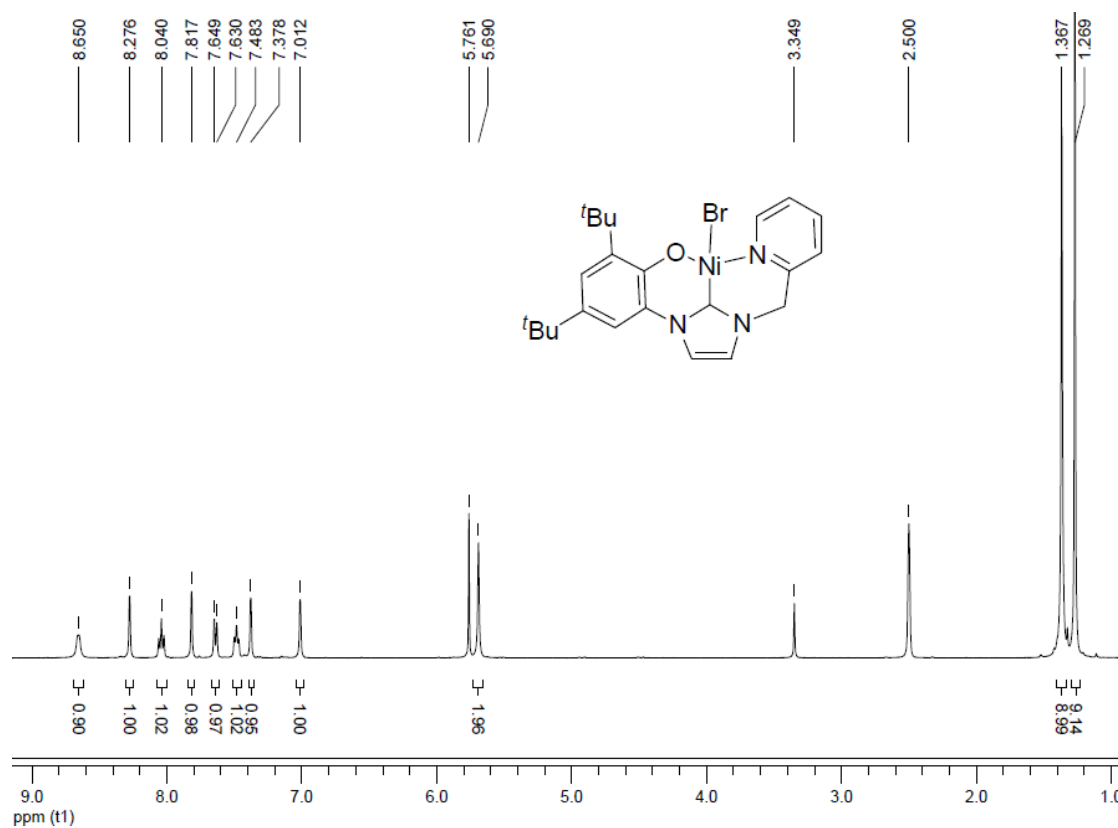


Figure S11. ¹H NMR (400 MHz, DMSO) spectrum of Ni3.

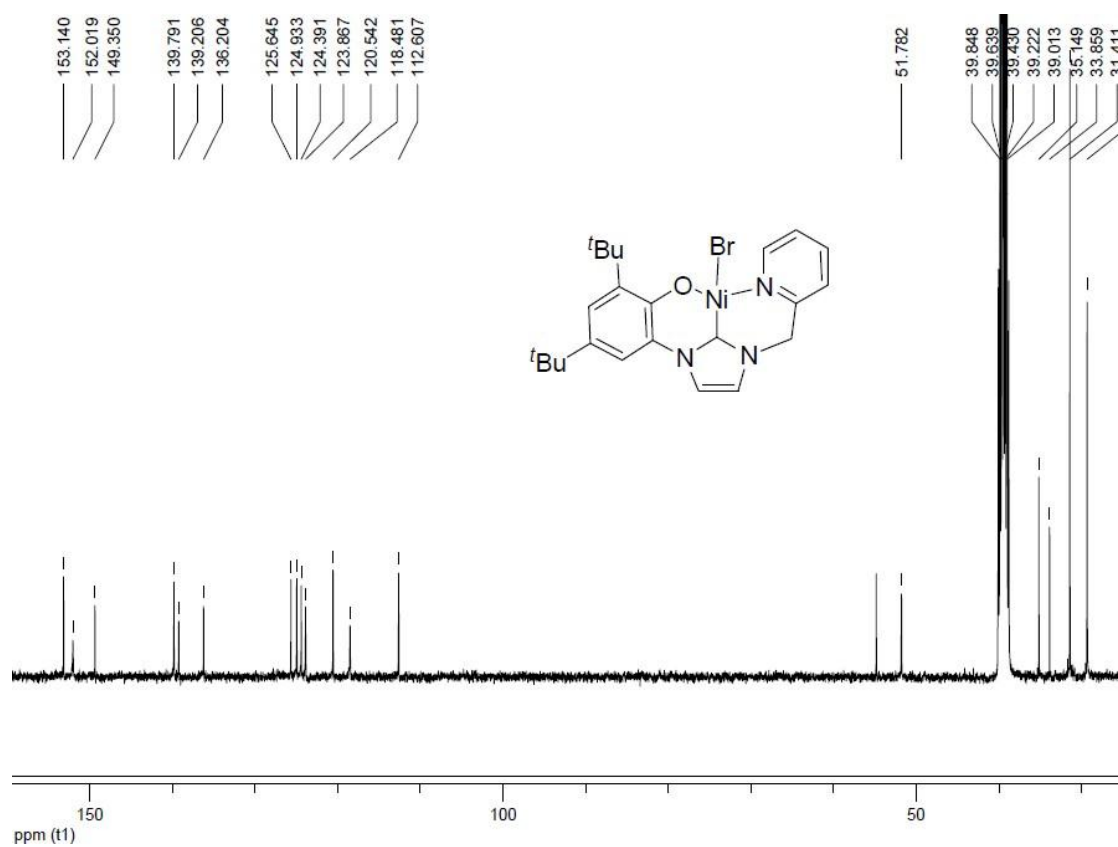


Figure S12. ¹³C NMR (100 MHz, DMSO) spectrum of Ni3.

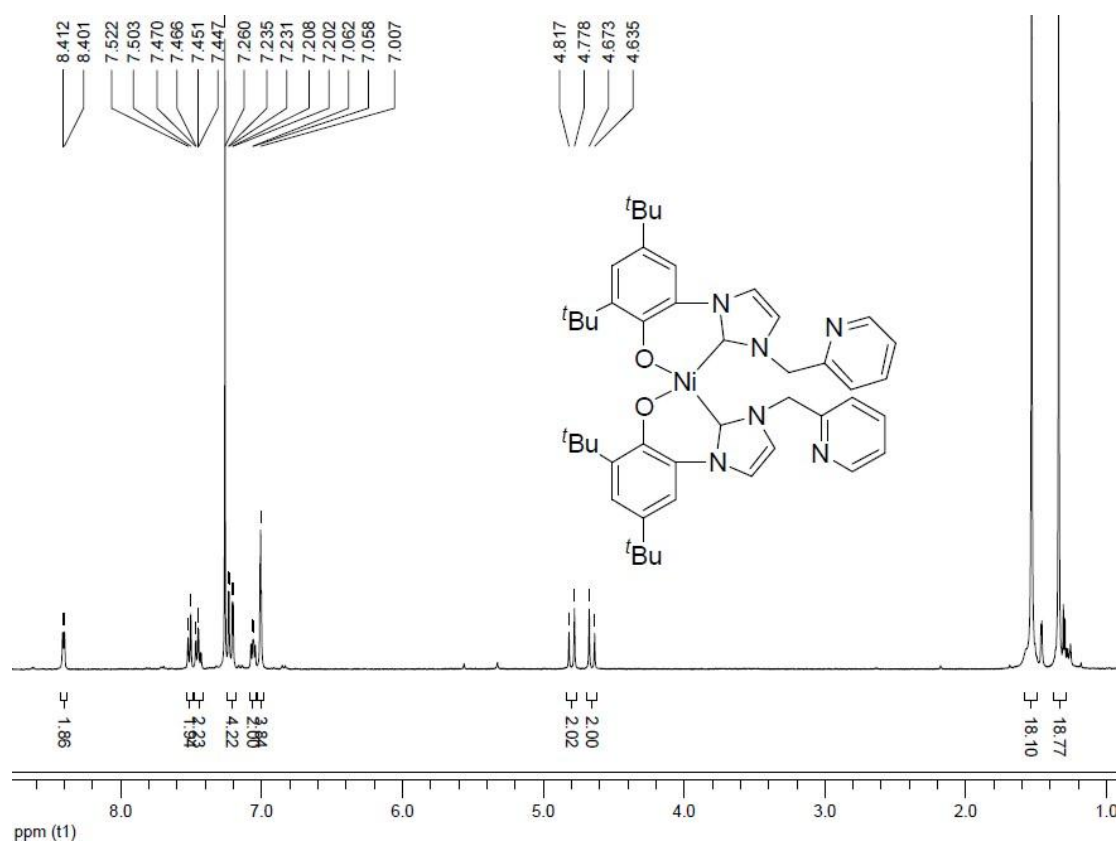


Figure S13. ¹H NMR (400 MHz, CDCl₃) spectrum of Ni4.

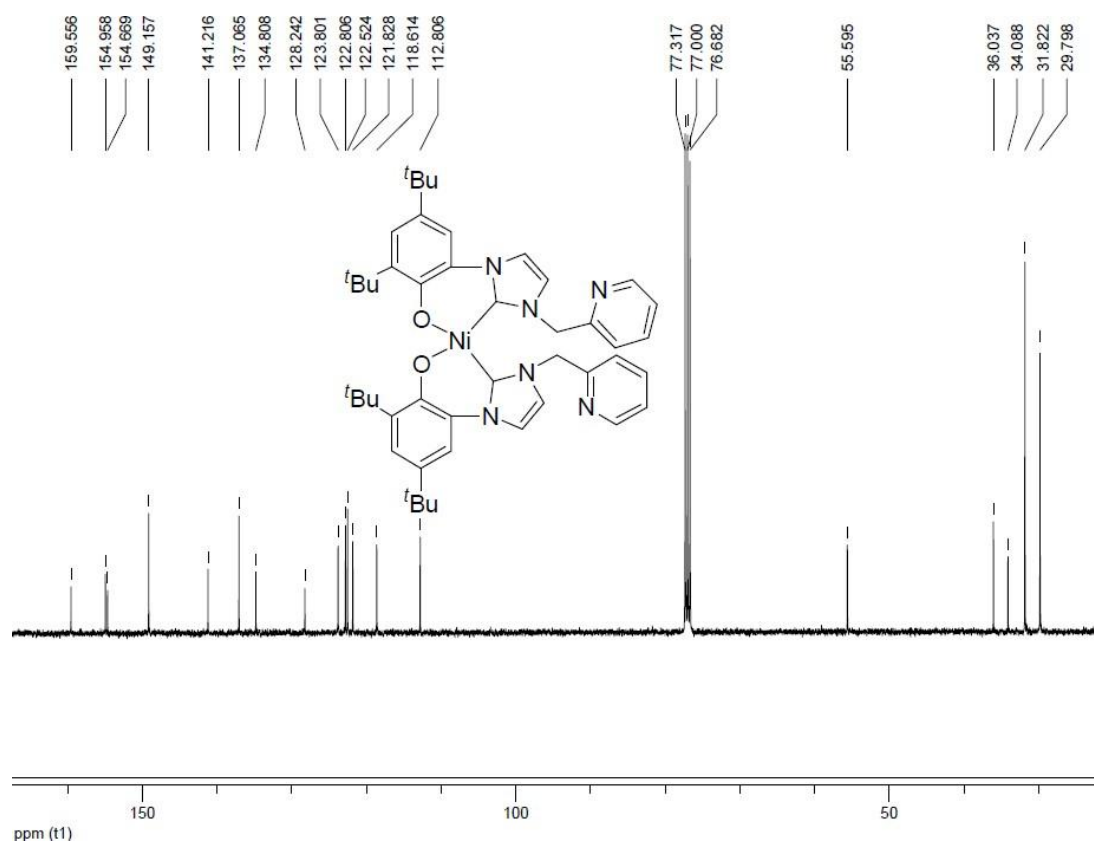


Figure S14. ¹³C NMR (100 MHz, CDCl₃) spectrum of Ni4.

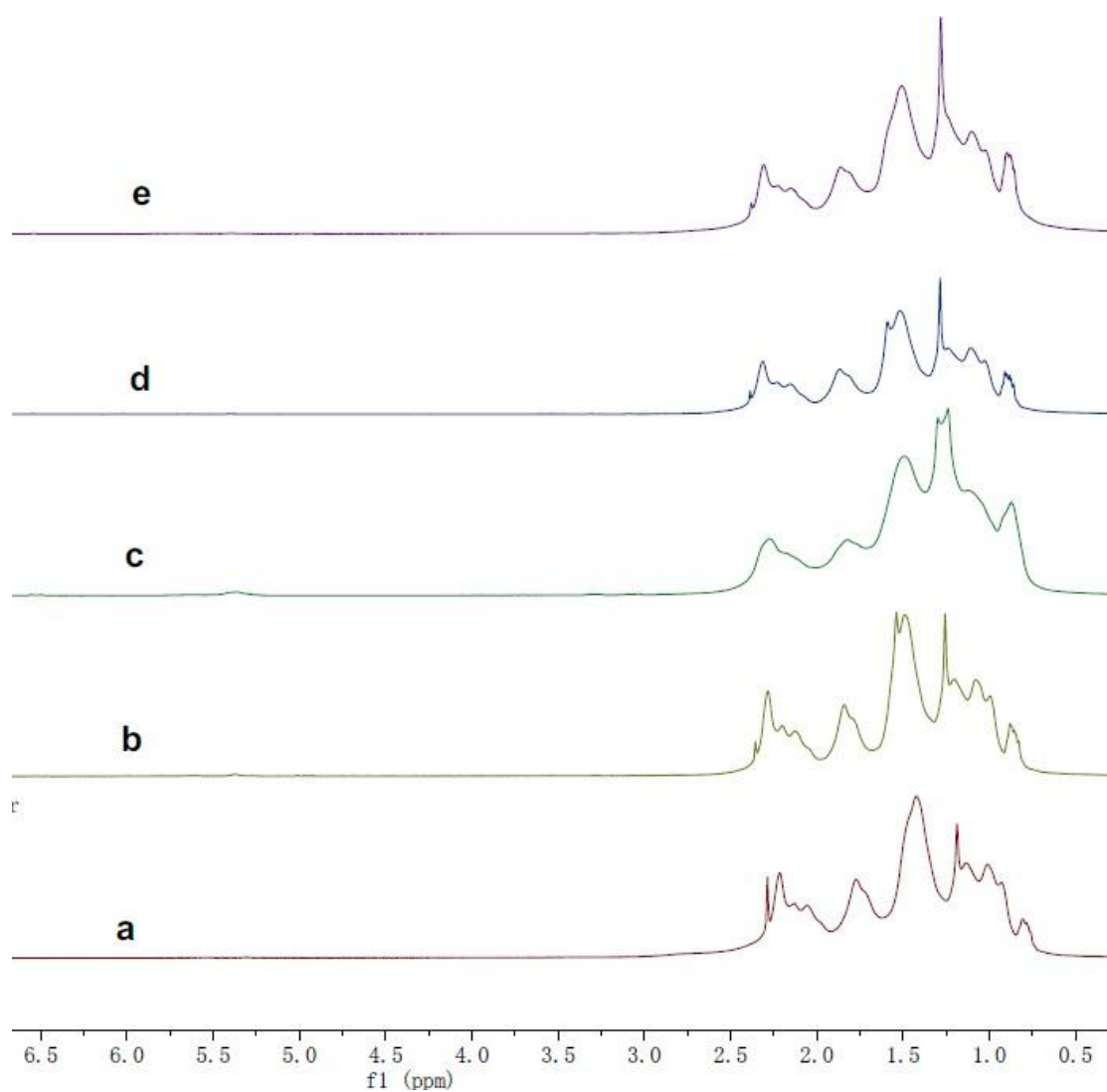


Figure S15. ^1H NMR spectra of poly(NB-co-1-octene)s: (a) 12% (Table 3 entry 3), (b) 15% (Table 3 entry 4), (c) 17% (Table 3 entry 8), (d) 9% (Table 3 entry 10), (e) 12% (Table 3 entry 11) of 1-octene molar ratio obtained by **Ni1–Ni3**/ $\text{B}(\text{C}_6\text{F}_5)_3$ systems.

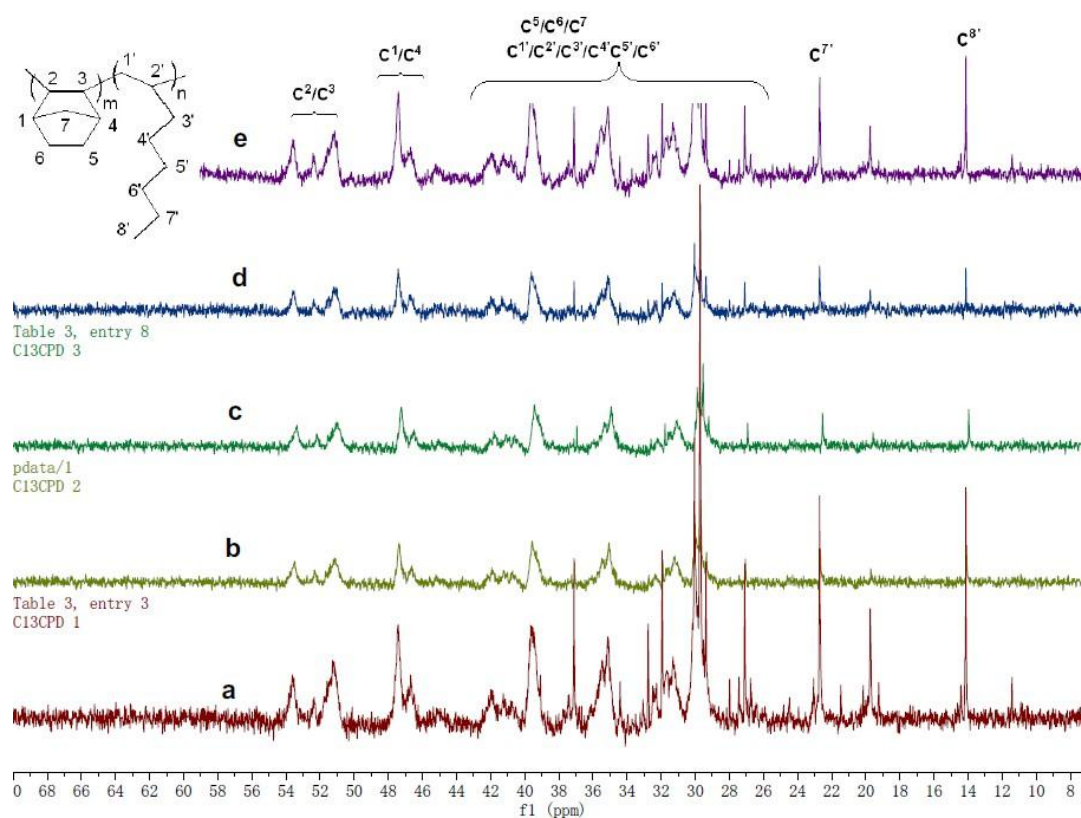
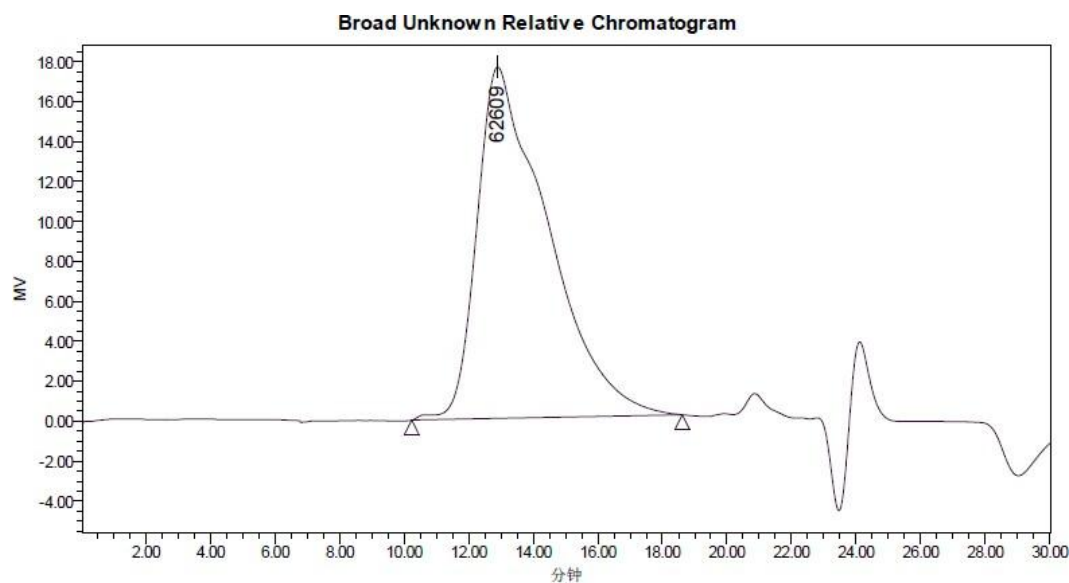


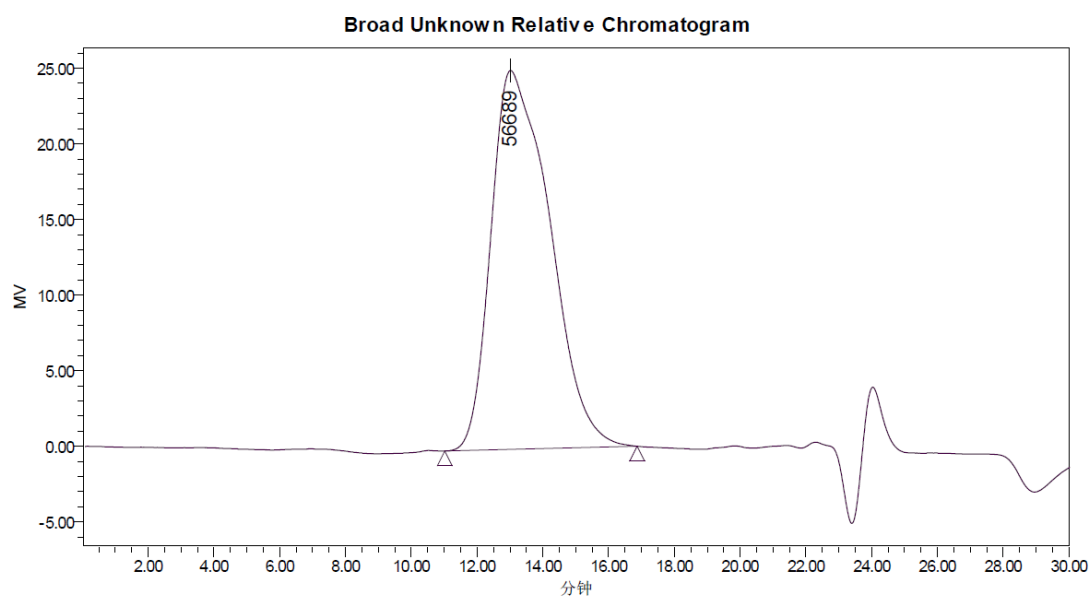
Figure S16. ¹³C NMR spectra of poly(NB-co-1-octene)s: (a) 12% (Table 3 entry 3), (b) 15% (Table 3 entry 4), (c) 17% (Table 3 entry 8), (d) 9% (Table 3 entry 10), (e) 12% (Table 3 entry 11) of 1-octene molar ratio obtained by **Ni1–Ni3**/B(C₆F₅)₃ systems.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		26727	51974	62609	92915	170709	1.944607	1.787703	3.284483

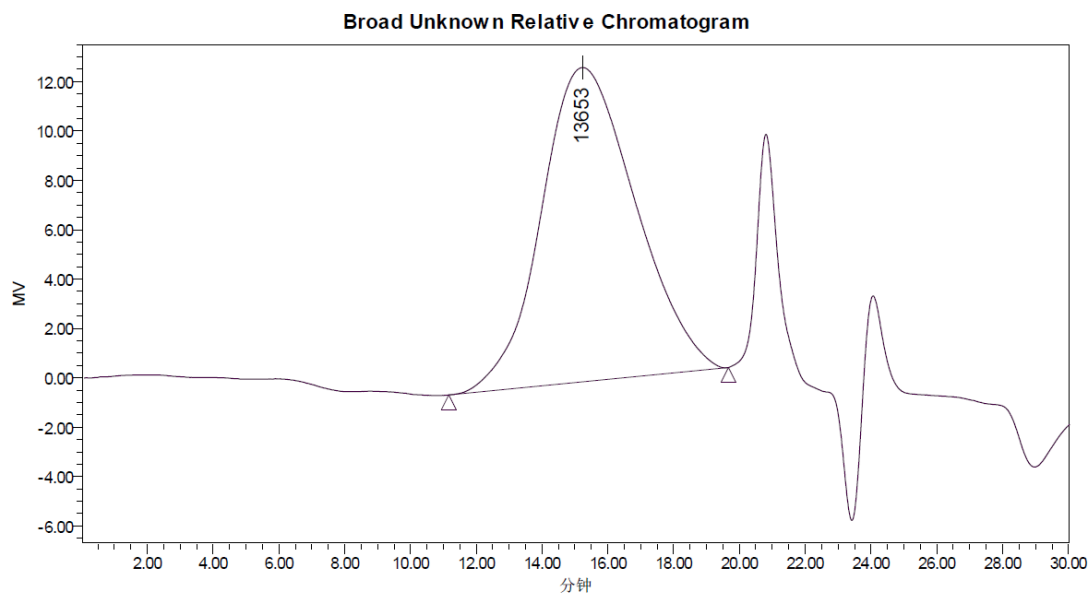
Figure S17. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 1.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		36153	50929	56689	70236	93233	1.408701	1.379092	1.830639

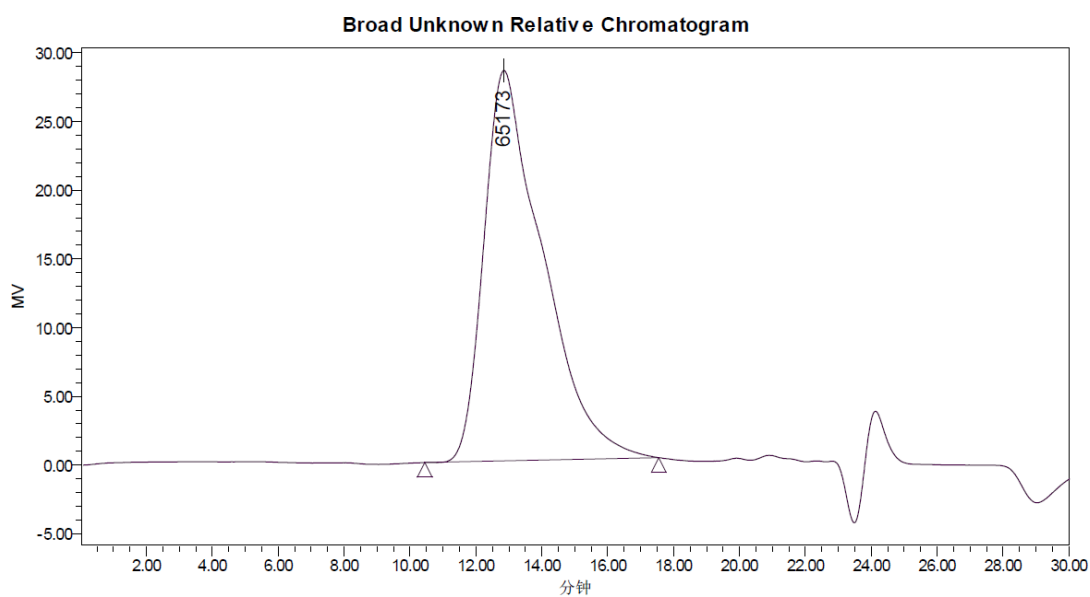
Figure S18. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 2.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		8513	16140	13653	31300	61732	1.895800	1.939288	3.824846

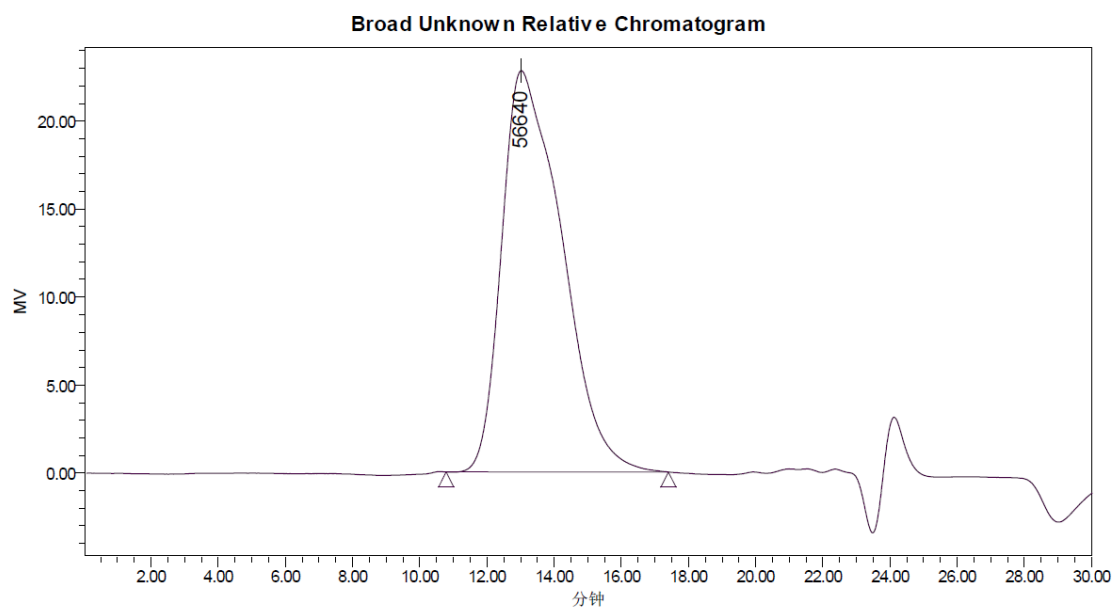
Figure S19. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 3.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		35801	57566	65173	83421	111345	1.607938	1.449136	1.934220

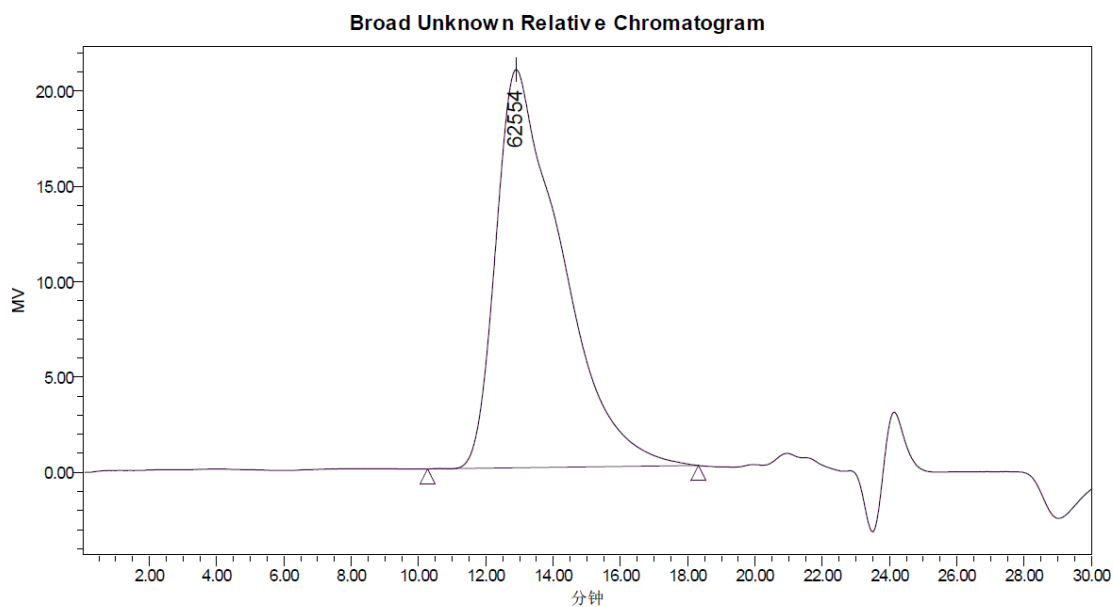
Figure S20. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 6.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		34710	49916	56640	69047	91351	1.438085	1.383263	1.830094

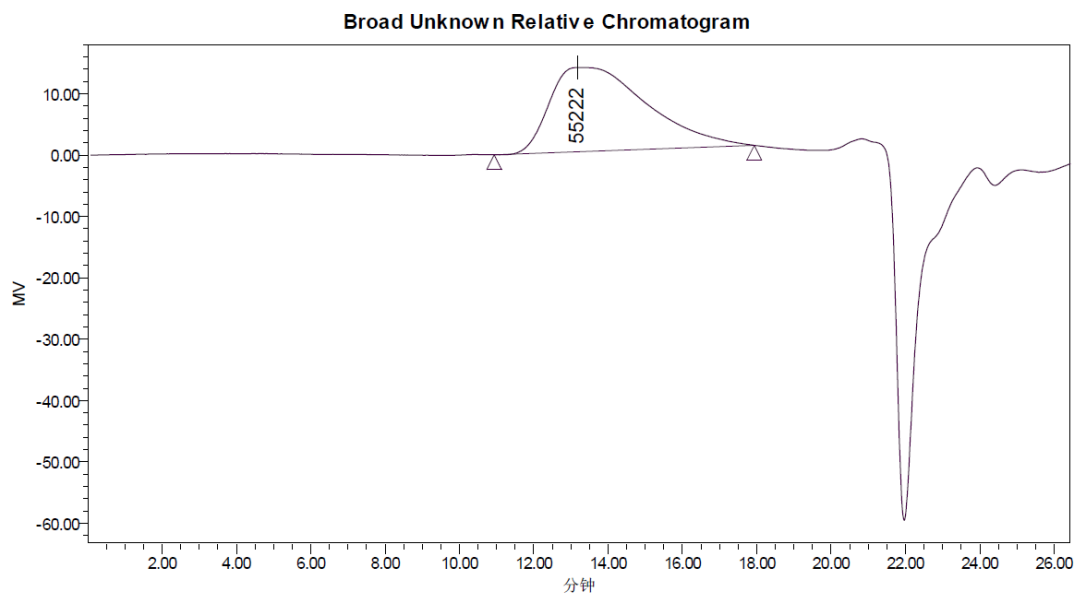
Figure S21. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 7.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		30180	51885	62554	77148	103989	1.719216	1.486899	2.004207

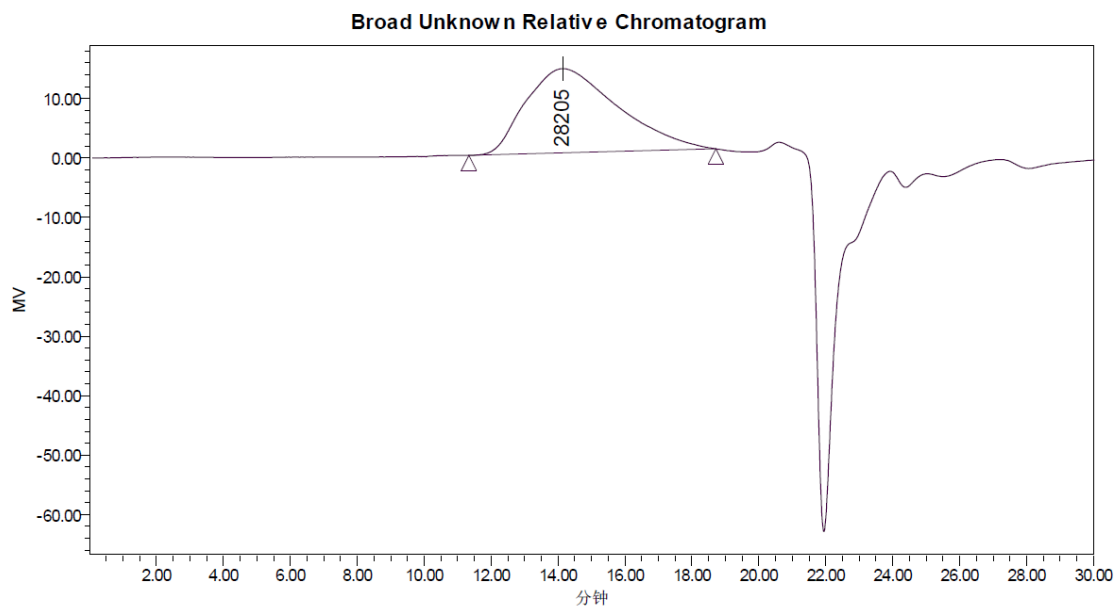
Figure S22. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 8.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		23607	44222	55222	69956	95795	1.873228	1.581934	2.166231

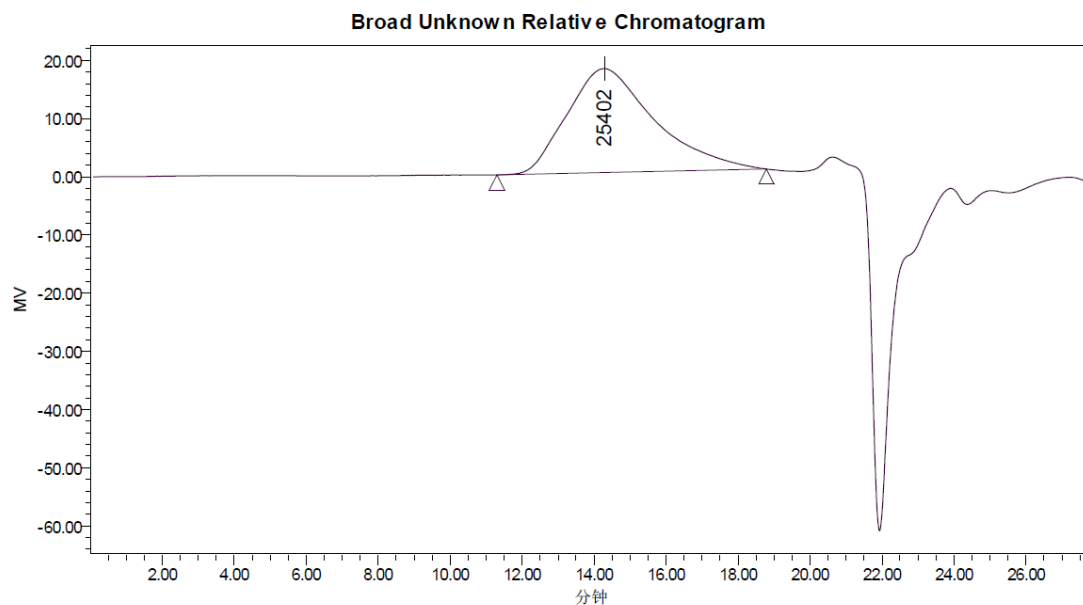
Figure S23. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 9.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		14952	29563	28205	48964	70219	1.977174	1.656256	2.375211

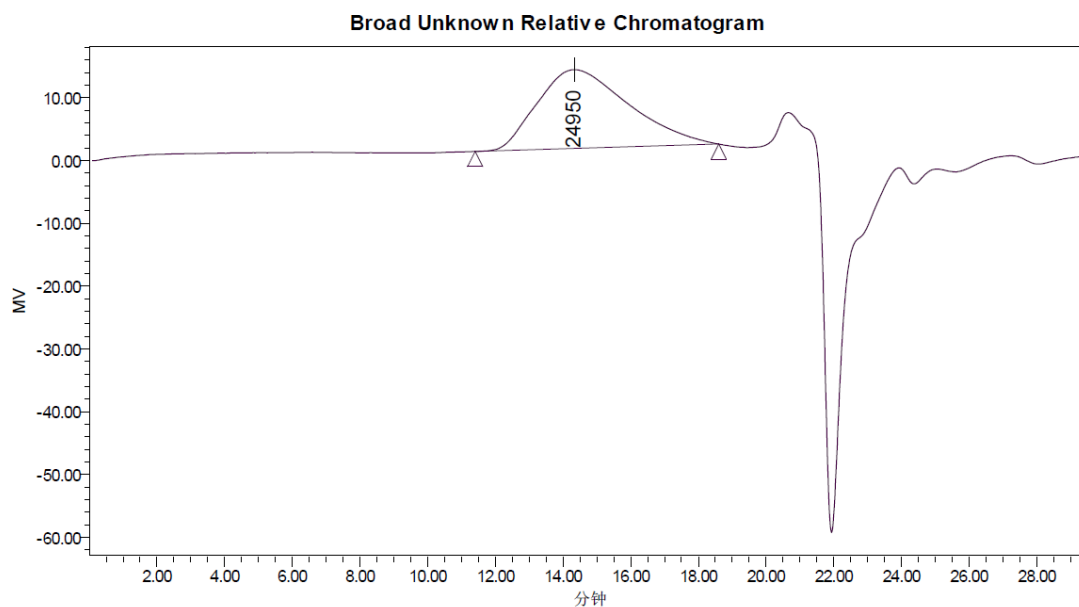
Figure S24. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 11.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	15035	27598	25402	43510	62095	1.835561	1.576578	2.249960

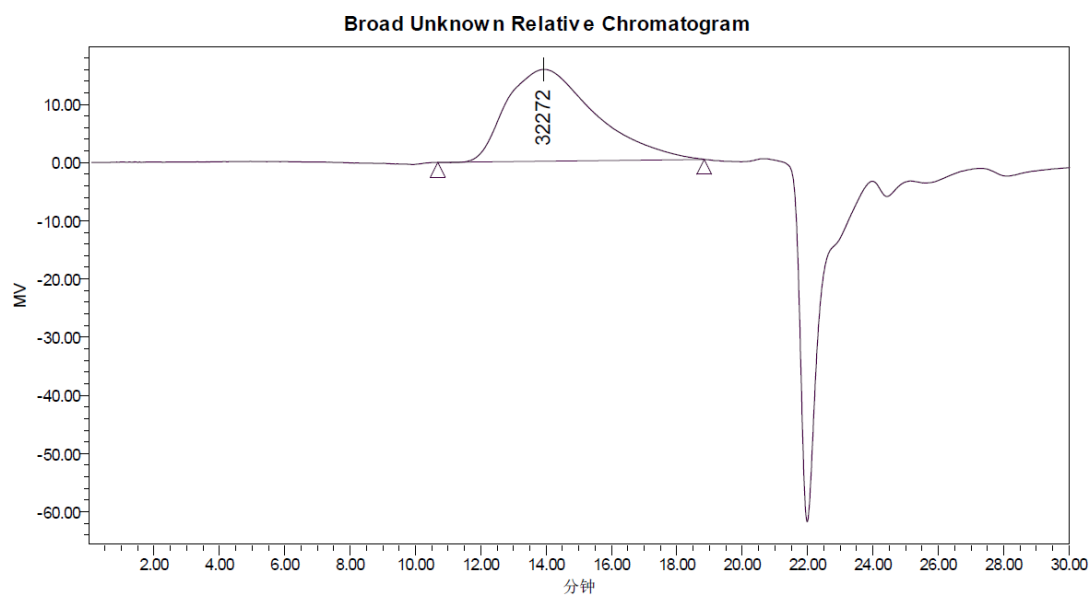
Figure S25. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 12.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	14014	26284	24950	42868	62012	1.875456	1.630990	2.359352

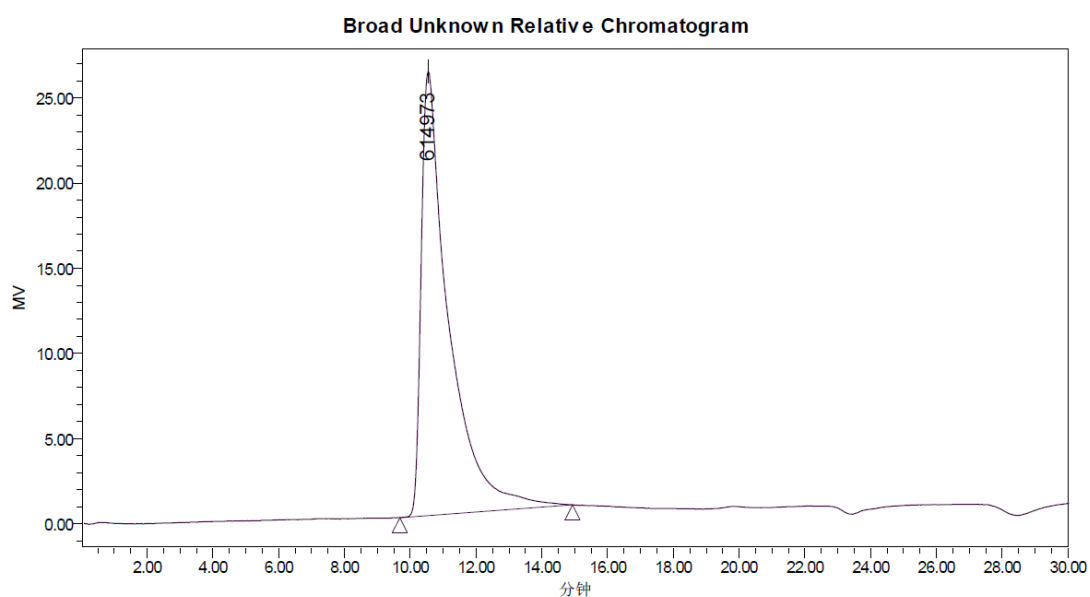
Figure S26. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 13.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		17063	35214	32272	58657	83777	2.063815	1.665733	2.379084

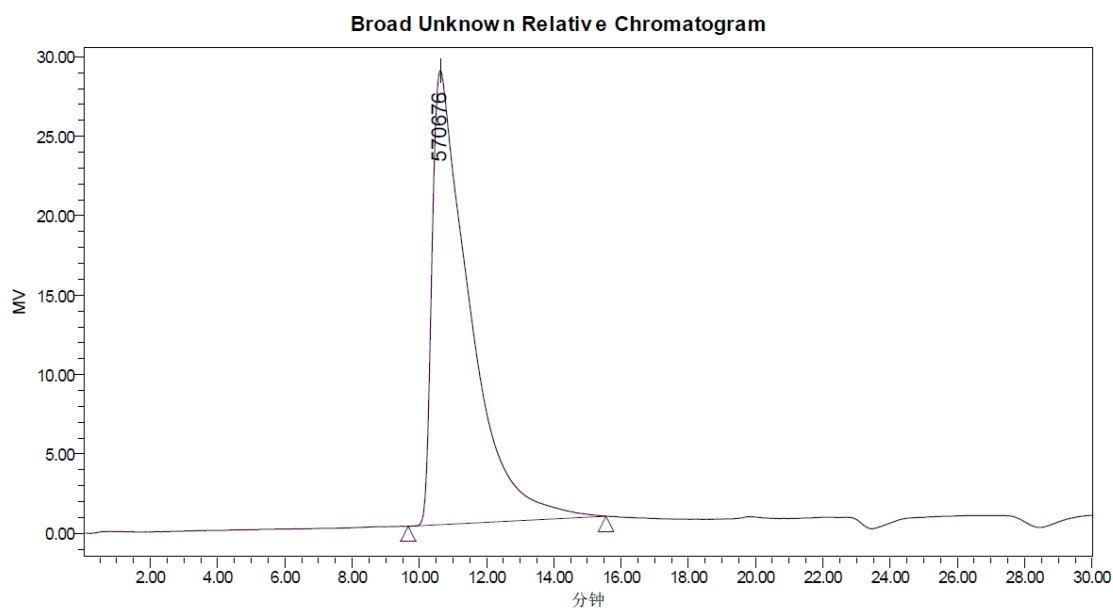
Figure S27. GPC curve of poly(NBE) of the polymer obtained by Table 1 entry 14.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		225466	366888	614973	441482	481673	1.627246	1.203314	1.312860

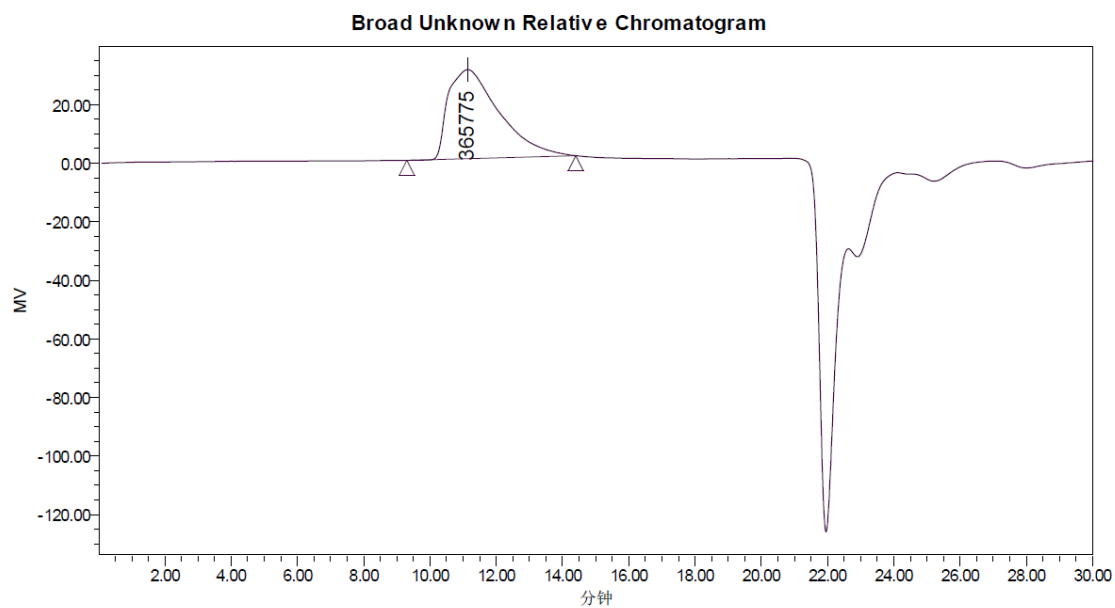
Figure S28. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 1.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		183280	325872	570676	411365	460136	1.777995	1.262352	1.412015

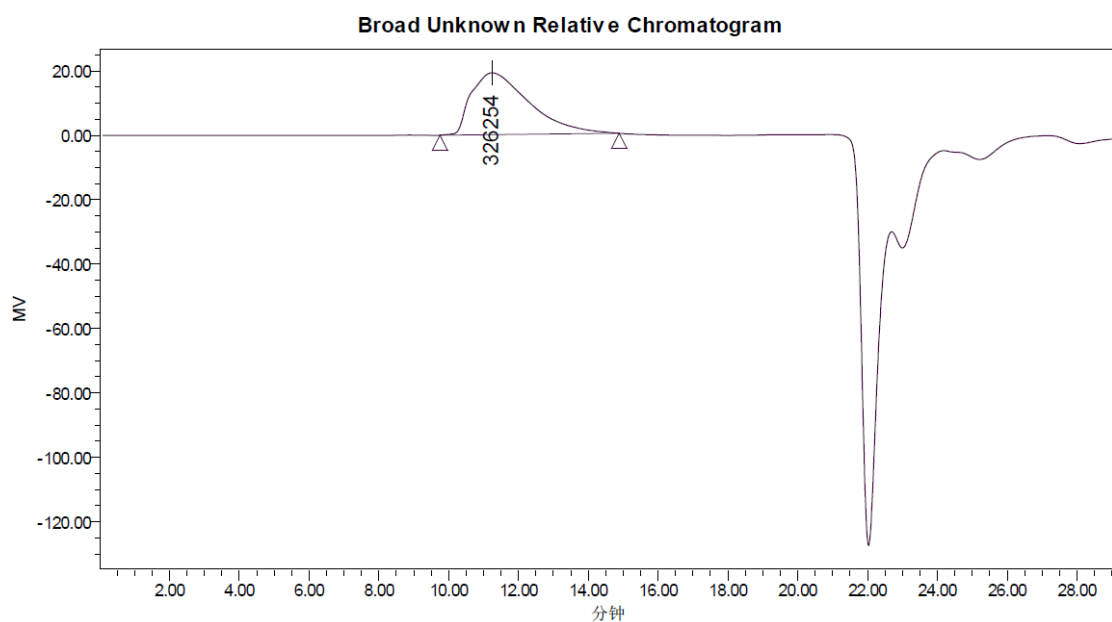
Figure S29. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 2.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		171322	272495	365775	358624	417715	1.590549	1.316074	1.532927

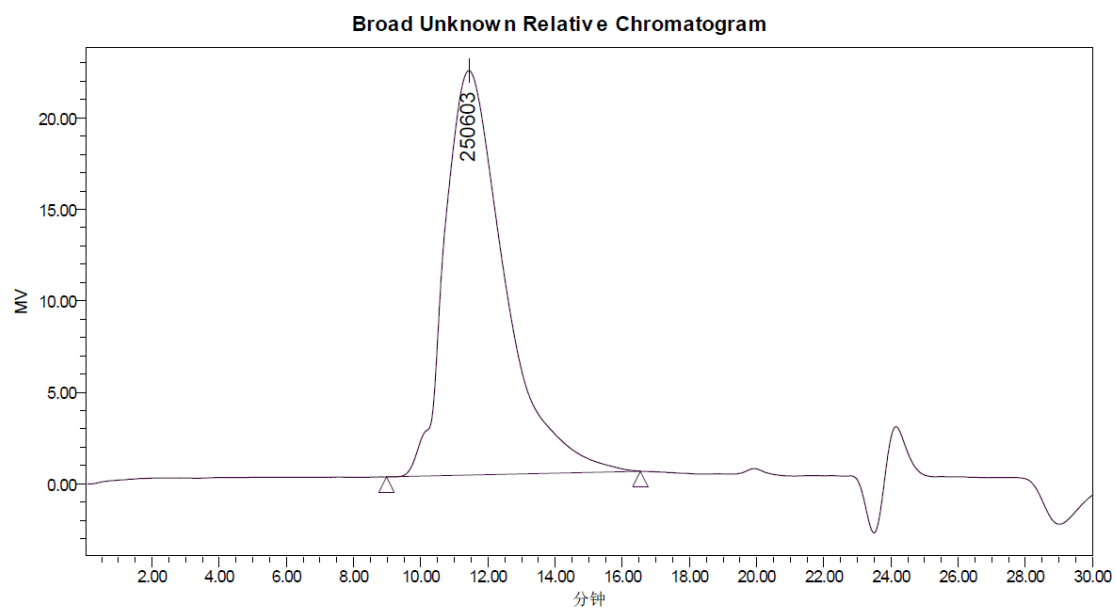
Figure S30. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 3.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		144921	247498	326254	339358	403810	1.707811	1.371155	1.631567

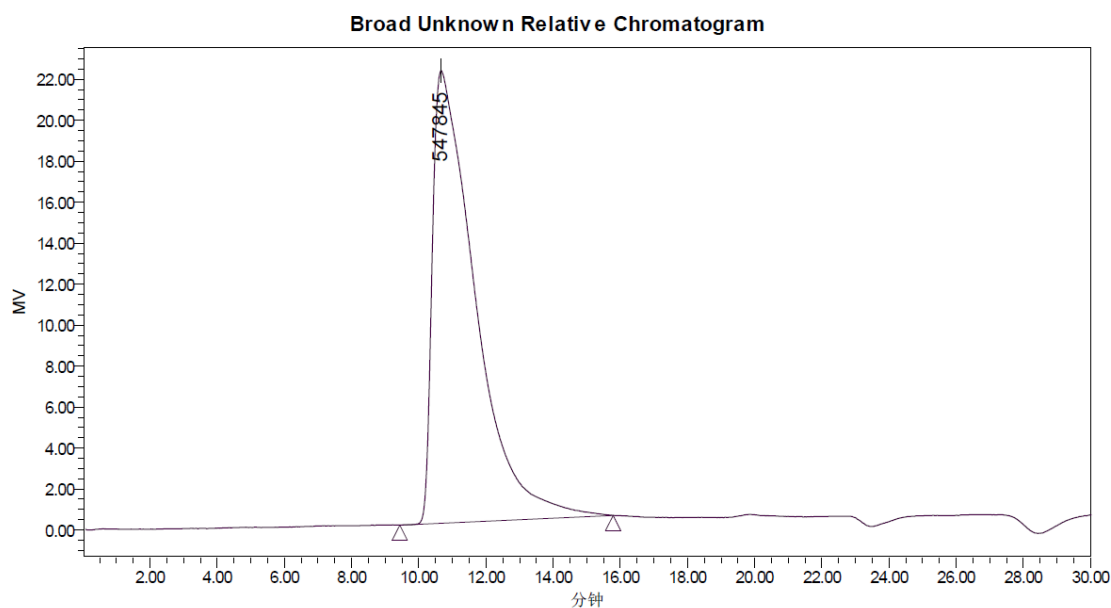
Figure S31. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 4.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		106895	219407	250603	319053	389787	2.052537	1.454163	1.776552

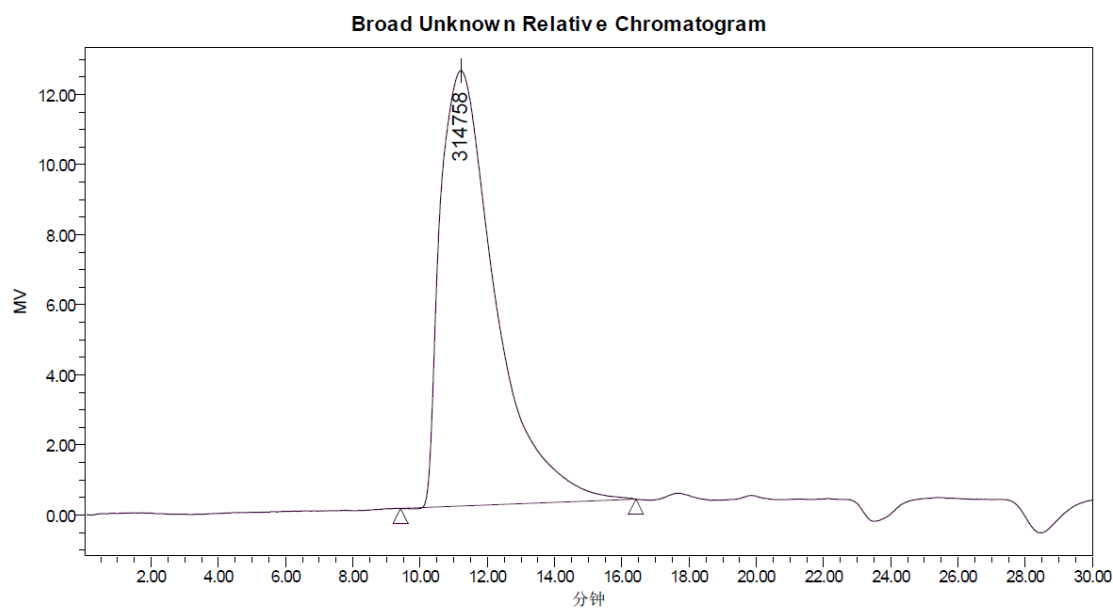
Figure S32. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 5.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		169836	308781	547845	396925	449297	1.818112	1.285456	1.455065

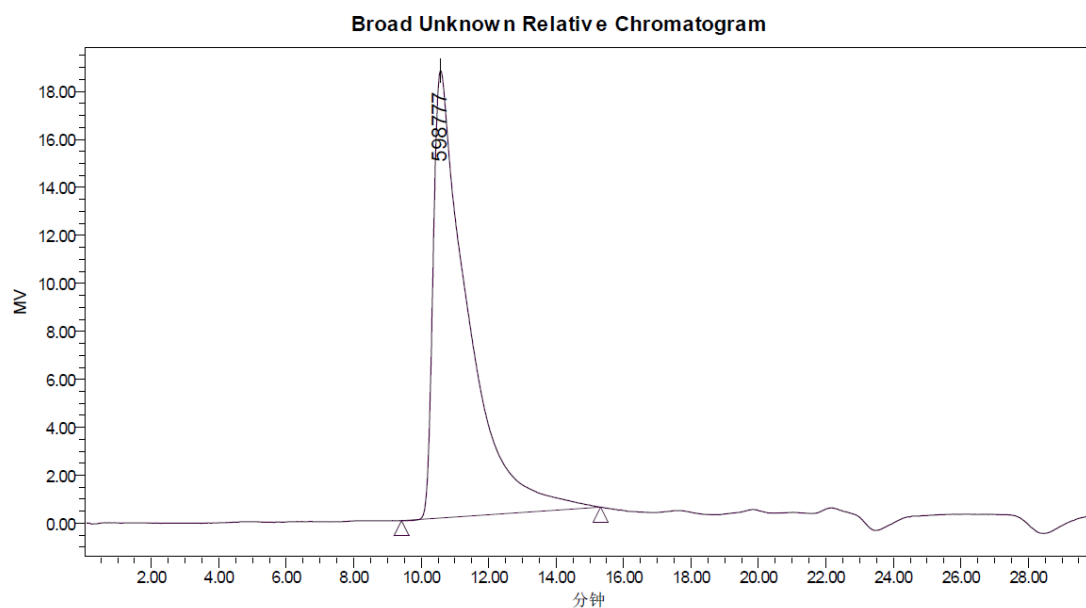
Figure S33. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 6.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		123025	250186	314758	349427	413712	2.033616	1.396669	1.653616

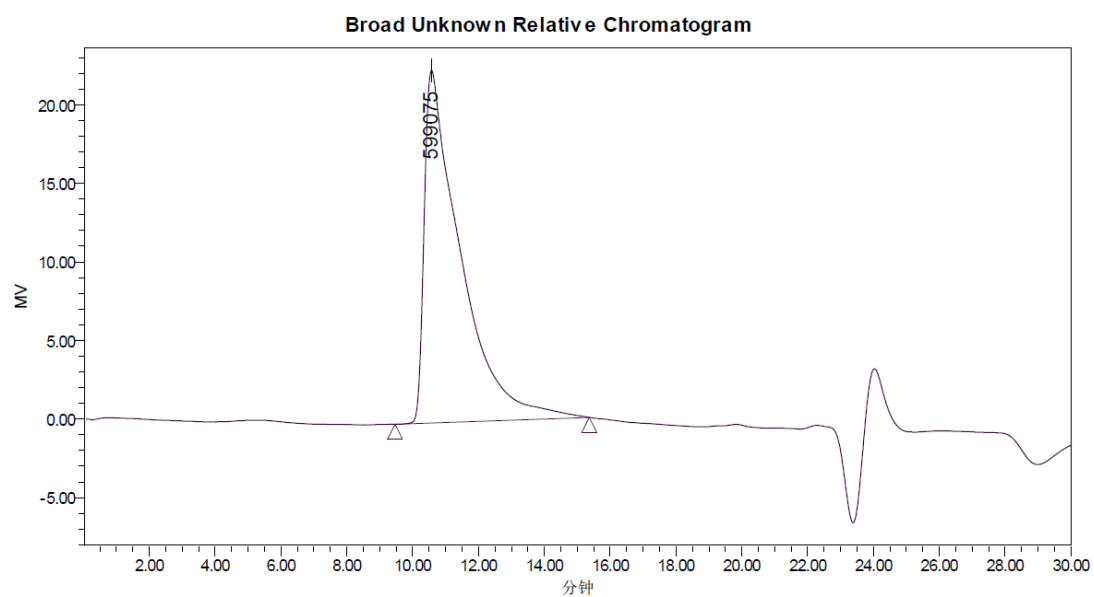
Figure S34. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 7.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		177871	330882	598777	419548	467443	1.860238	1.267969	1.412720

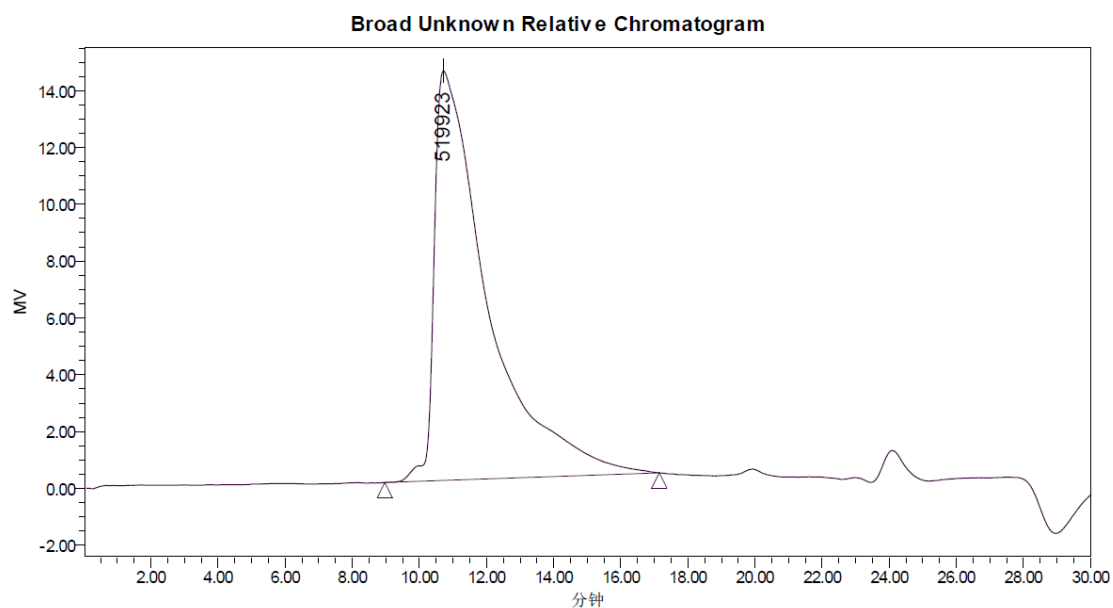
Figure S35. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 11.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		175972	323033	599075	412116	462130	1.835706	1.275771	1.430599

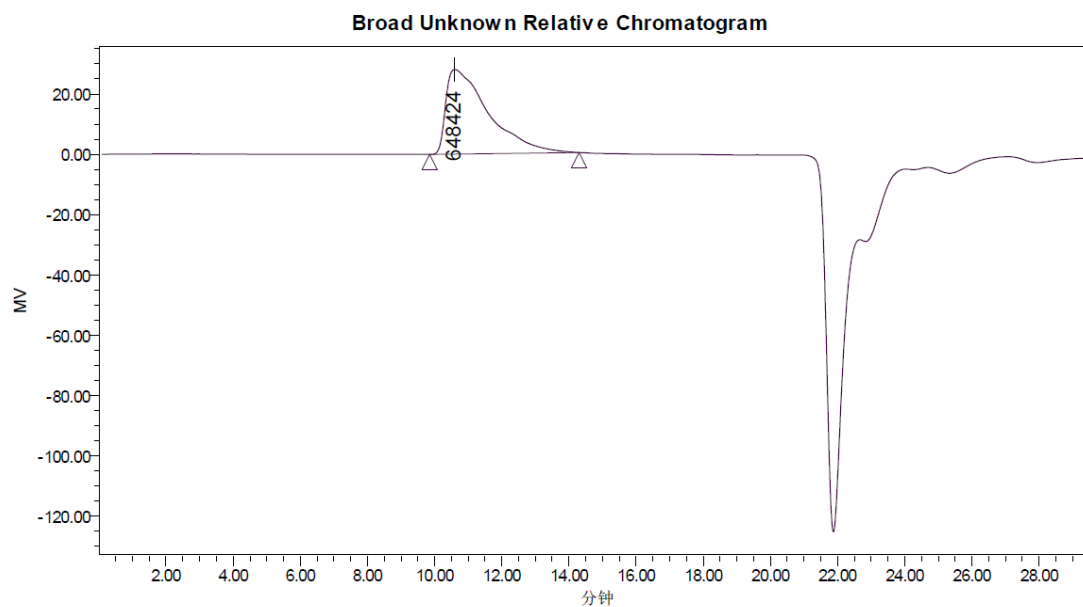
Figure S36. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 12.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		92437	258927	519923	377657	439580	2.801114	1.458544	1.697695

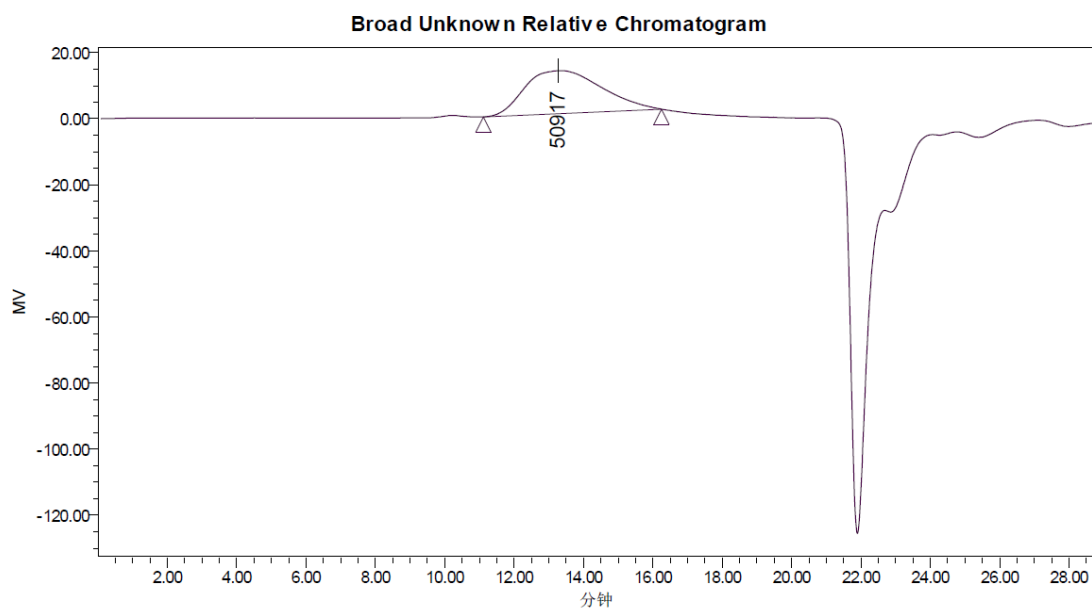
Figure S37. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 14.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		211747	331414	648424	420174	475511	1.565144	1.267822	1.434794

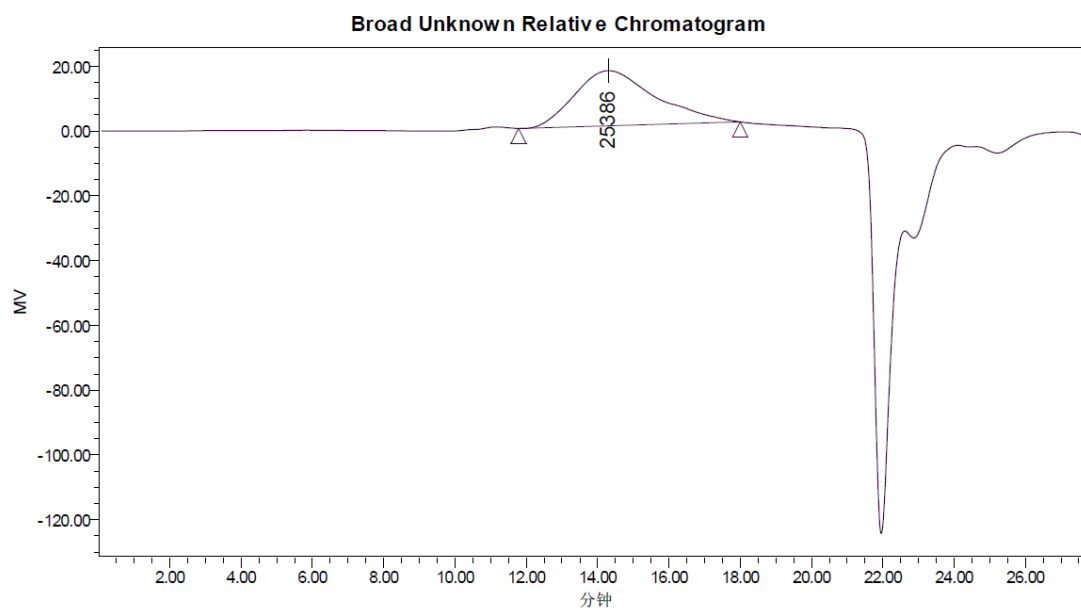
Figure S38. GPC curve of poly(NBE) of the polymer obtained by Table 2 entry 16.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		36454	57241	50917	86491	119383	1.570243	1.511000	2.085626

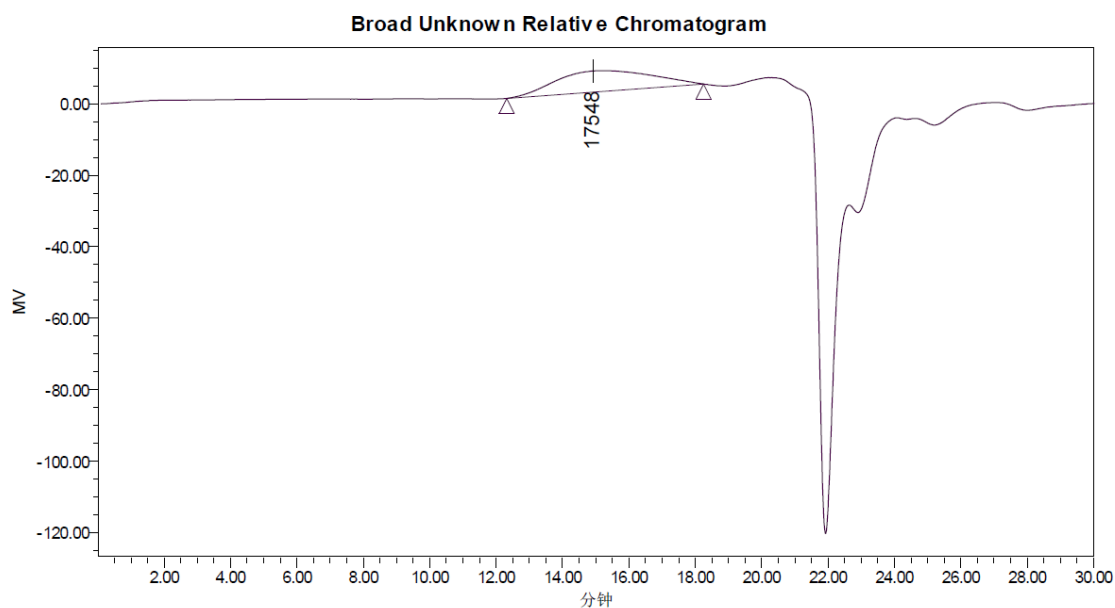
Figure S39. GPC curve of poly(NB-co-1-octene)s of the polymer obtained by Table 3 entry 3.



Broad Unknown Relative Peak Table

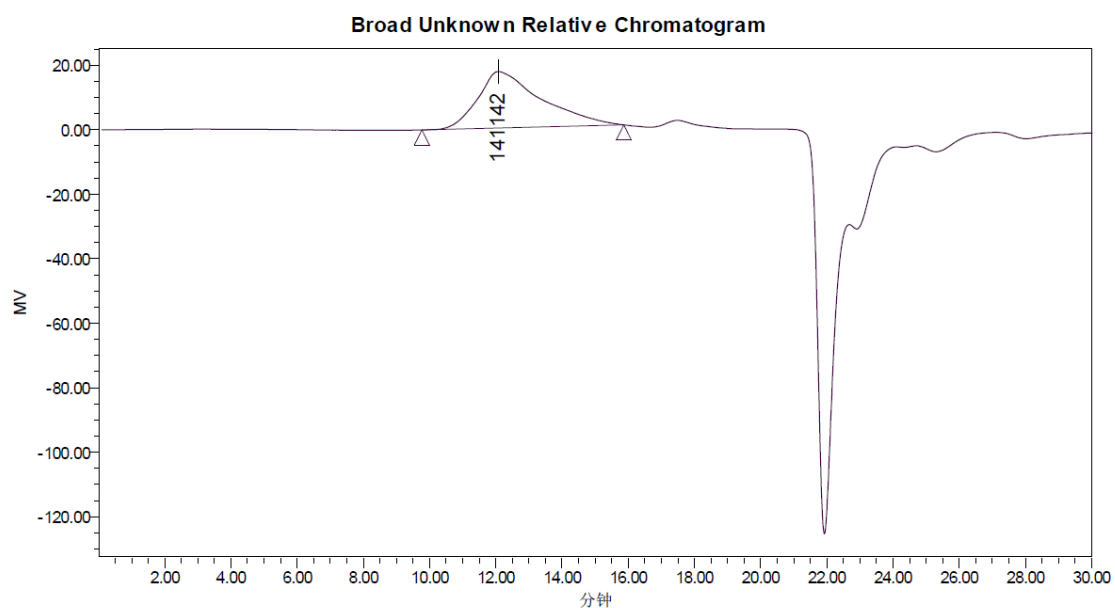
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		16326	26224	25386	38153	51014	1.606240	1.454889	1.945324

Figure S40. GPC curve of poly(NB-co-1-octene)s of the polymer obtained by Table 3 entry 4.



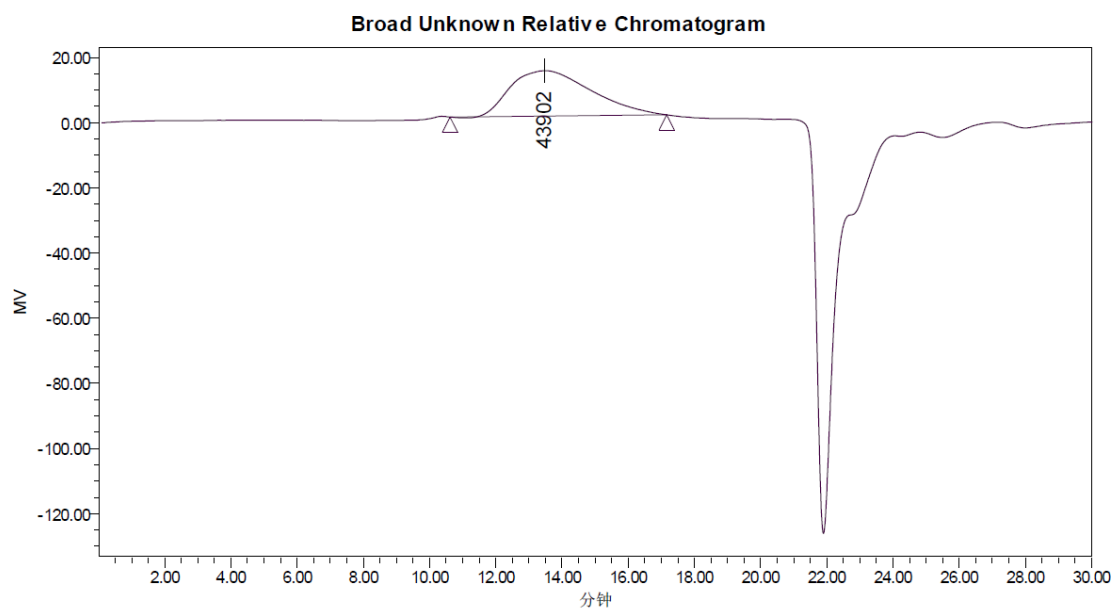
Broad Unknown Relative Peak Table									
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		10798	18611	17548	29267	40805	1.723541	1.572566	2.192517

Figure S41. GPC curve of poly(NB-co-1-octene)s of the polymer obtained by Table 3 entry 8.



Broad Unknown Relative Peak Table									
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		65108	124201	141142	204056	284942	1.907622	1.642951	2.294199

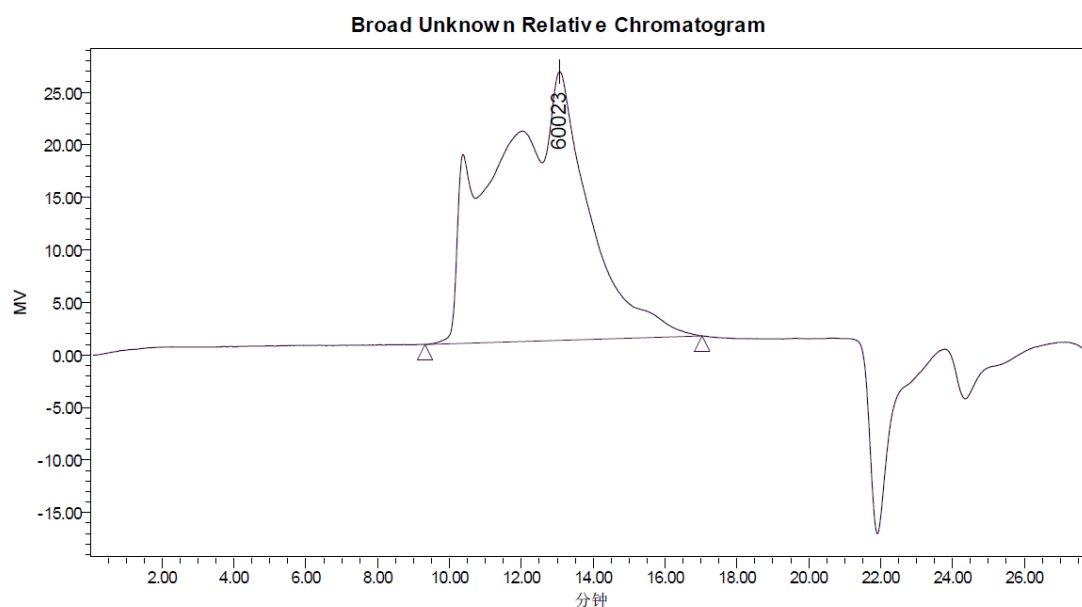
Figure S42. GPC curve of poly(NB-co-1-octene)s of the polymer obtained by Table 3 entry 10.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		27937	48099	43902	75373	103734	1.721693	1.567035	2.156664

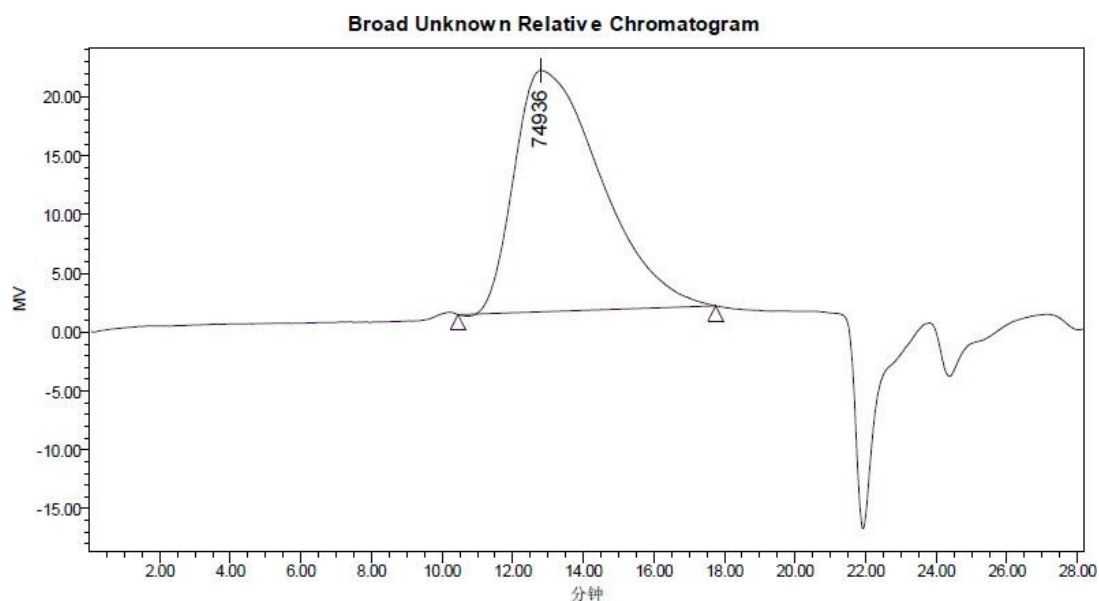
Figure S43. GPC curve of poly(NB-co-1-octene)s of the polymer obtained by Table 3 entry 11.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		56655	143064	60023	278435	383117	2.525183	1.946227	2.677936

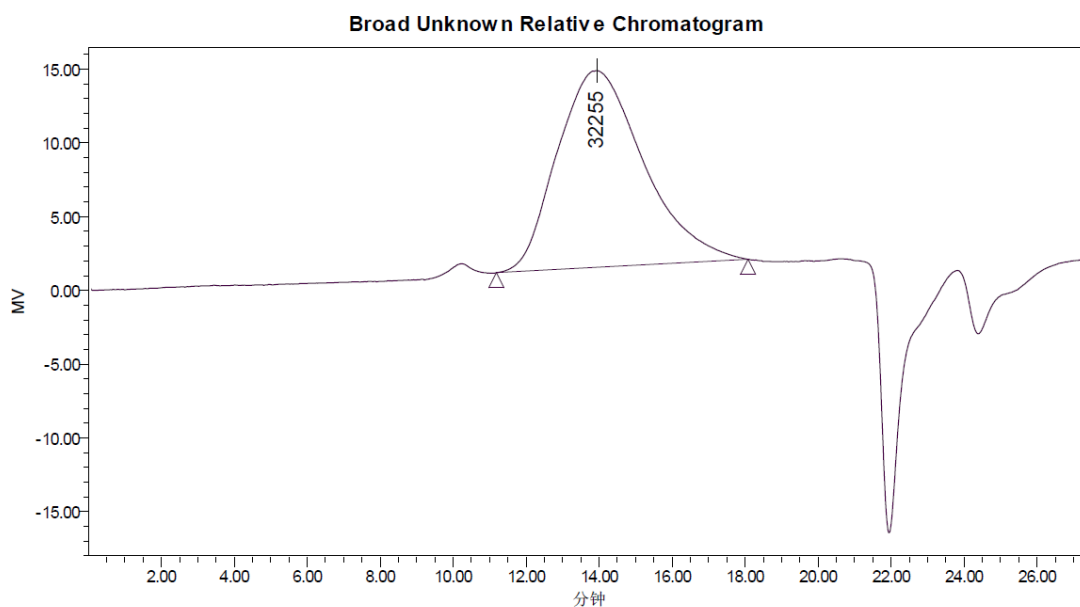
Figure S44. GPC curve of poly(NBE) of the polymer obtained by Table 4 entry 1.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	32293	63549	74936	106765	153321	1.967869	1.680045	2.412657

Figure S45. GPC curve of poly(NBE) of the polymer obtained by Table 4 entry 5.



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	21676	37676	32255	60905	91045	1.738127	1.616545	2.416507

Figure S46. GPC curve of poly(NBE) of the polymer obtained by Table 4 entry 6.

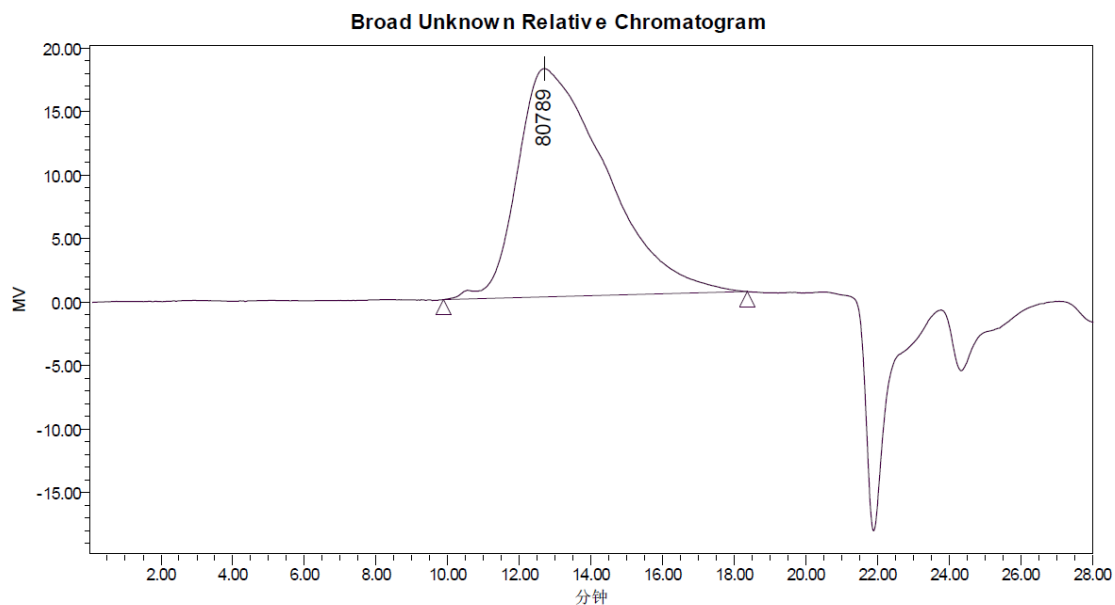


Figure S47. GPC curve of poly(NBE) of the polymer obtained by Table 4 entry 8.

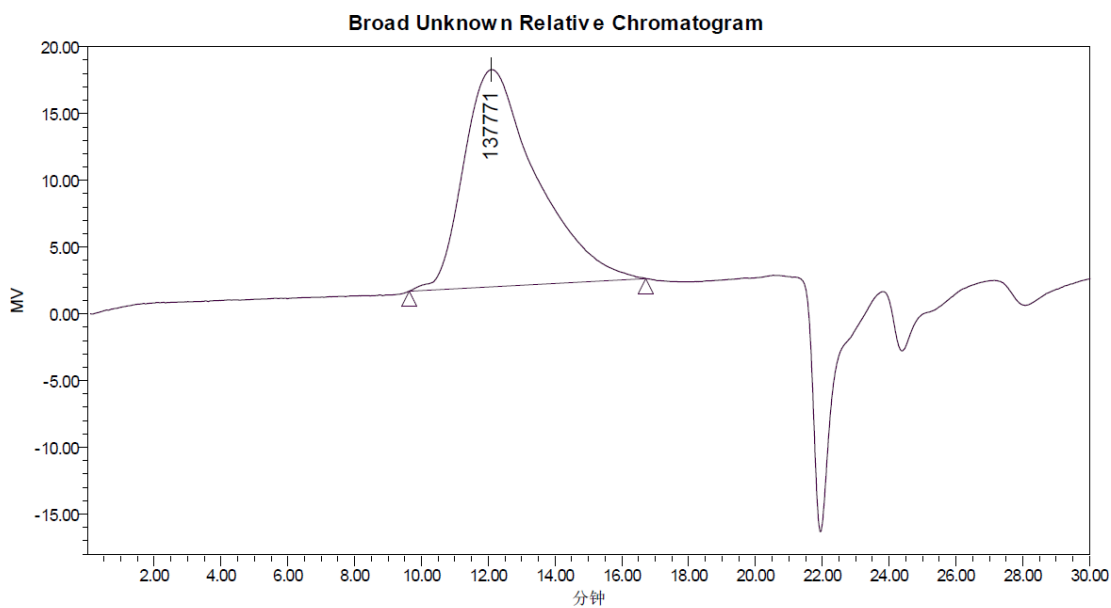
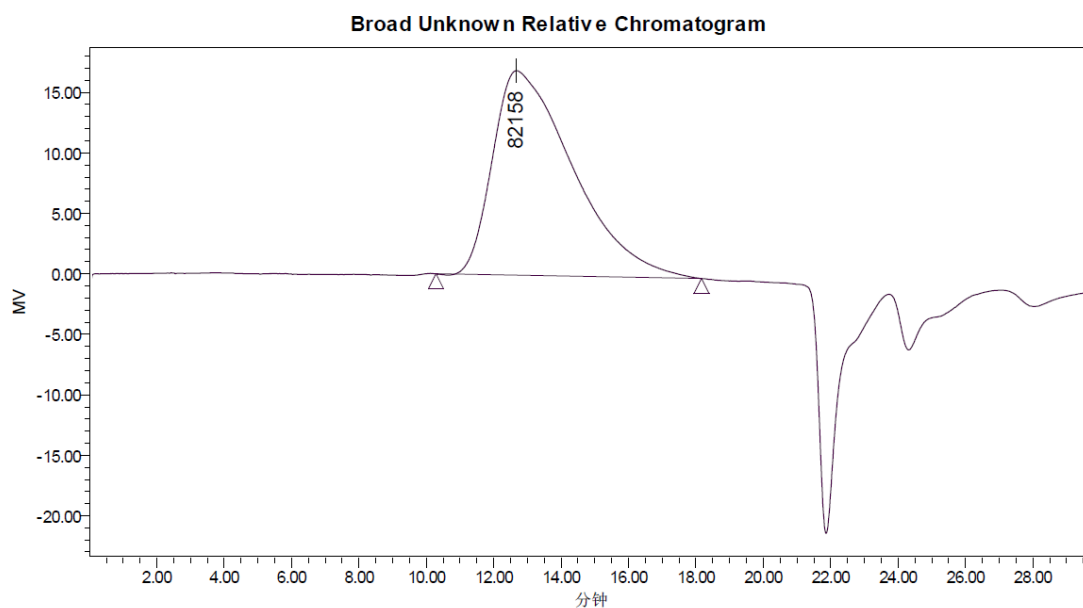


Figure S48. GPC curve of poly(NBE) of the polymer obtained by Table 4 entry 10.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		32893	68279	82158	115213	165263	2.075755	1.687395	2.420421

Figure S49. GPC curve of poly(NBE) of the polymer obtained by Table 4 entry 11.

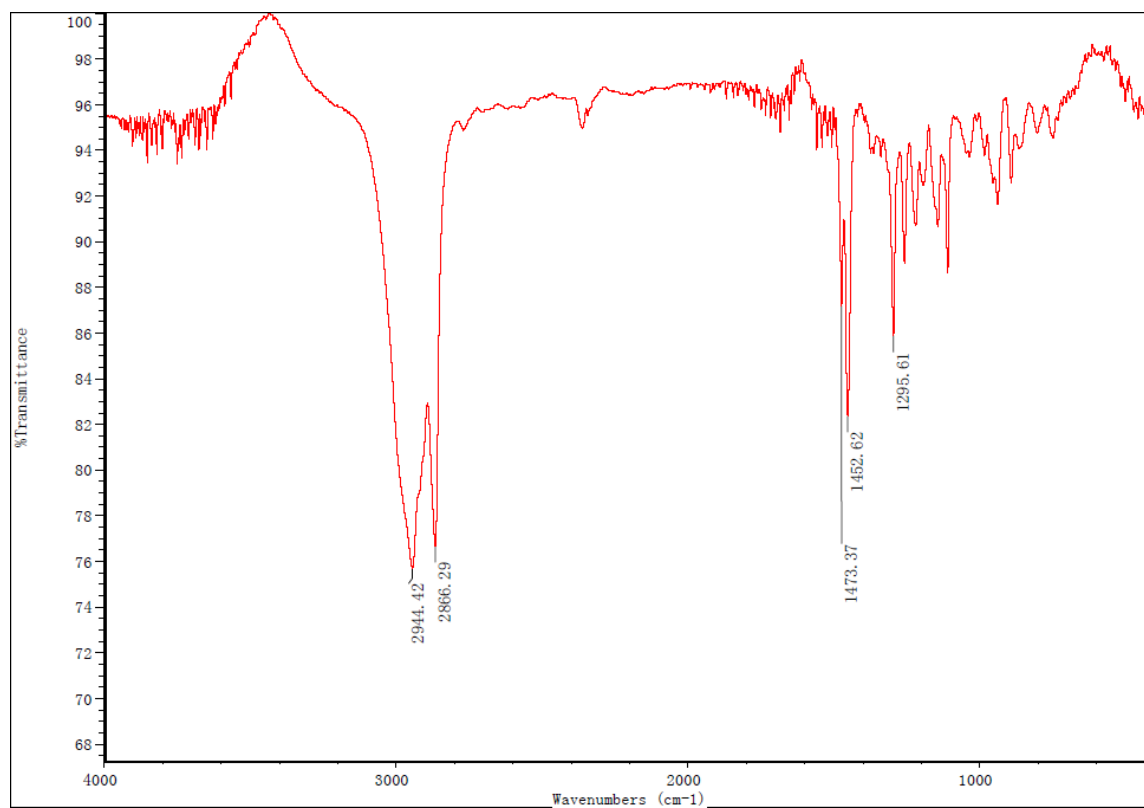


Figure S50. IR spectrum of PNB activated by Et_2AlCl (Table 1 entry 6).

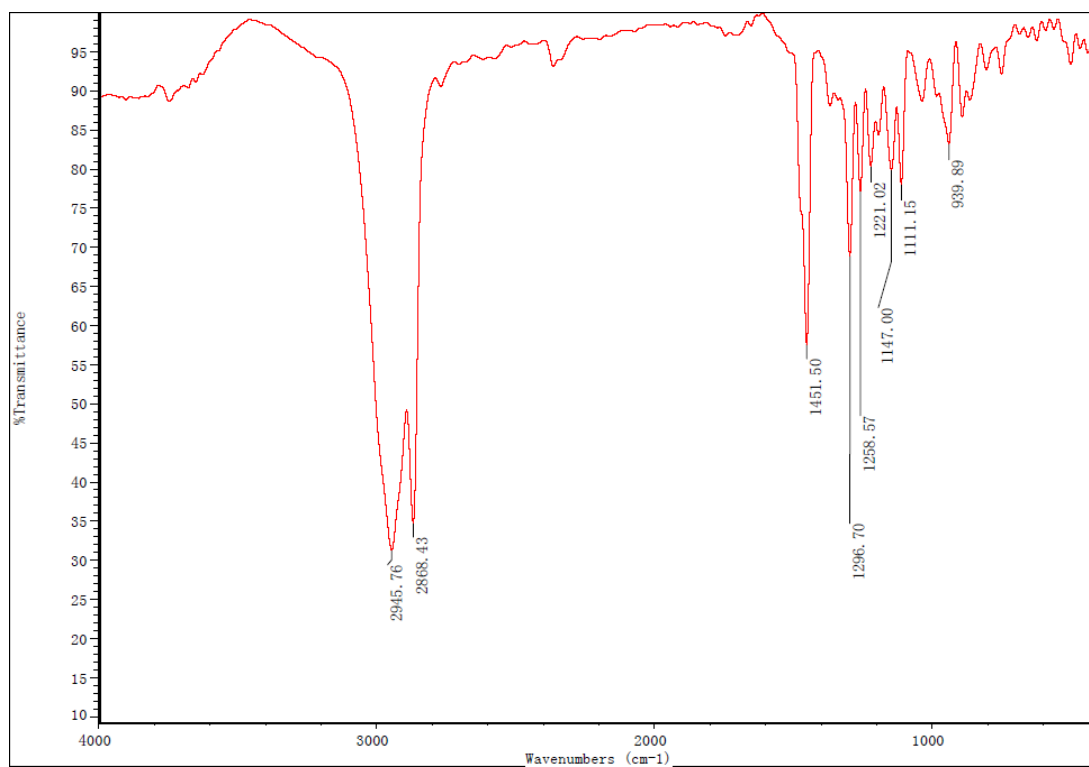


Figure S51. IR spectrum of PNB activated by Me_2AlCl (Table 1 entry 11).

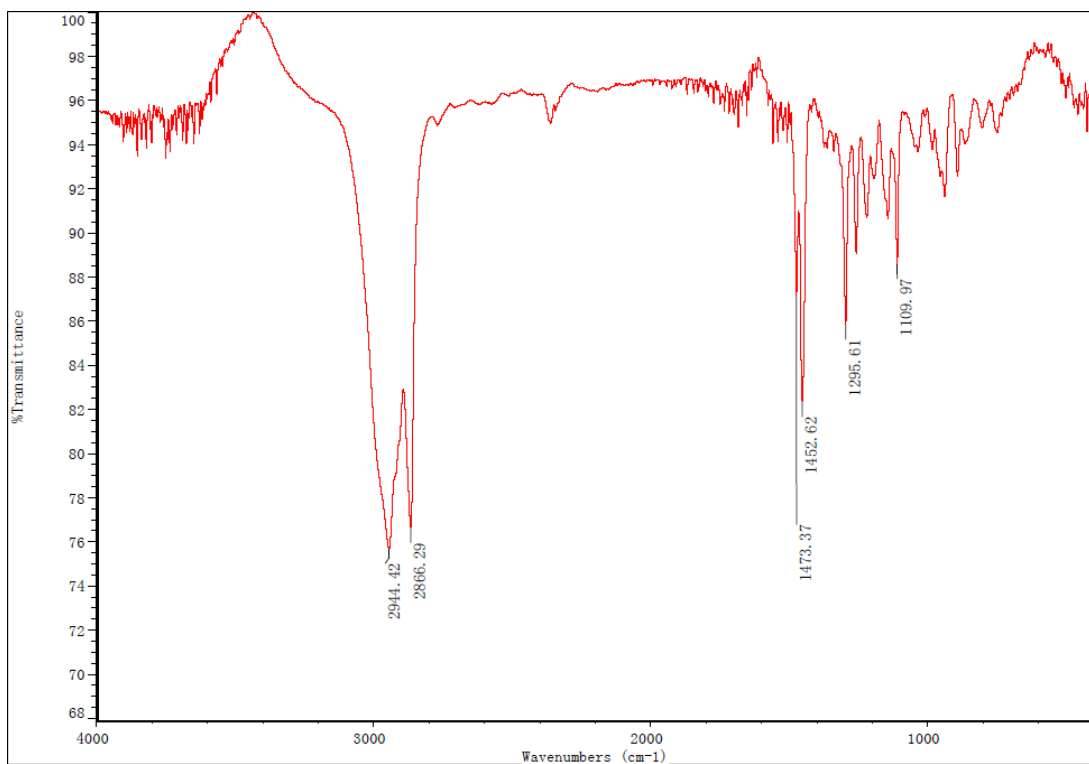


Figure S52. IR spectrum of PNB activated by $\text{B}(\text{C}_6\text{F}_5)_3$ (Table 2 entry 11).

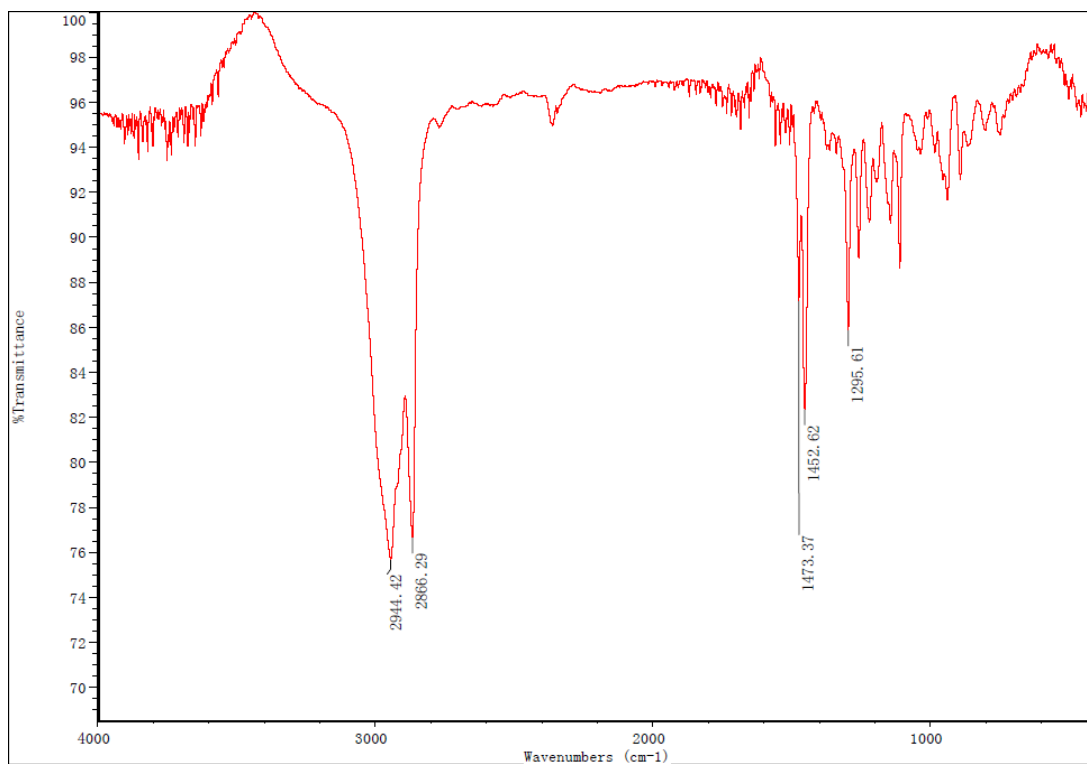


Figure S53. IR spectrum of poly(NB-co-1-octene)s (Table 3 entry 3).

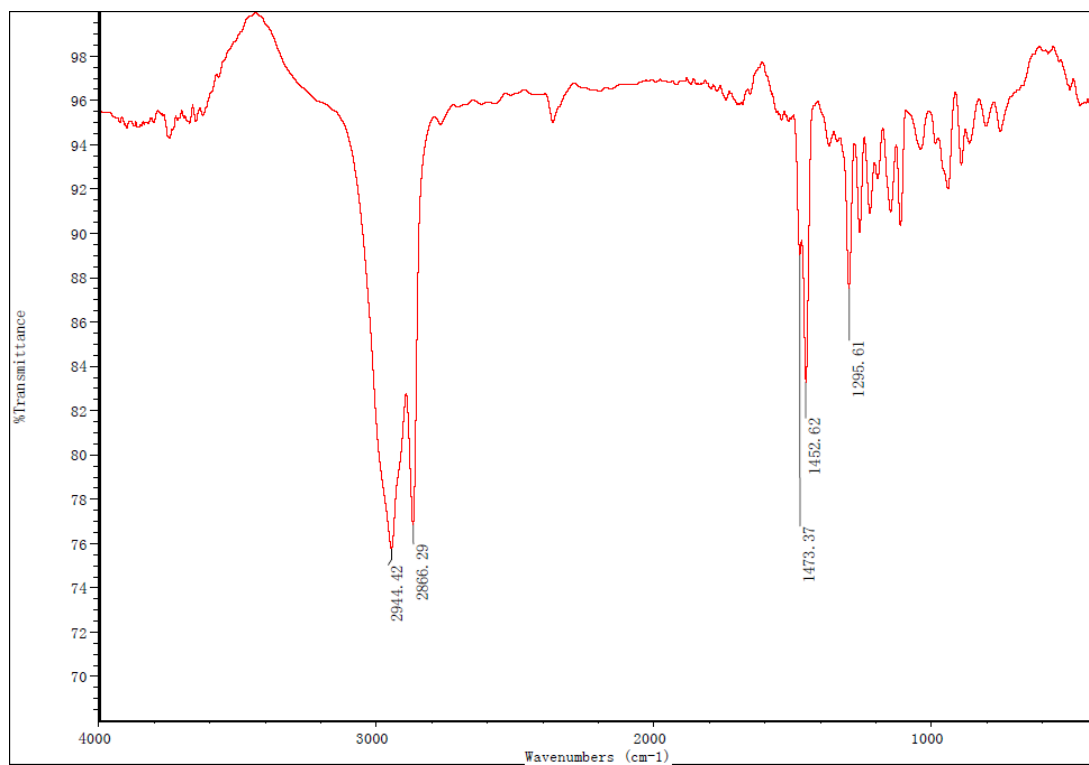


Figure S54. IR spectrum of poly(NB-co-1-octene)s (Table 3 entry 7).

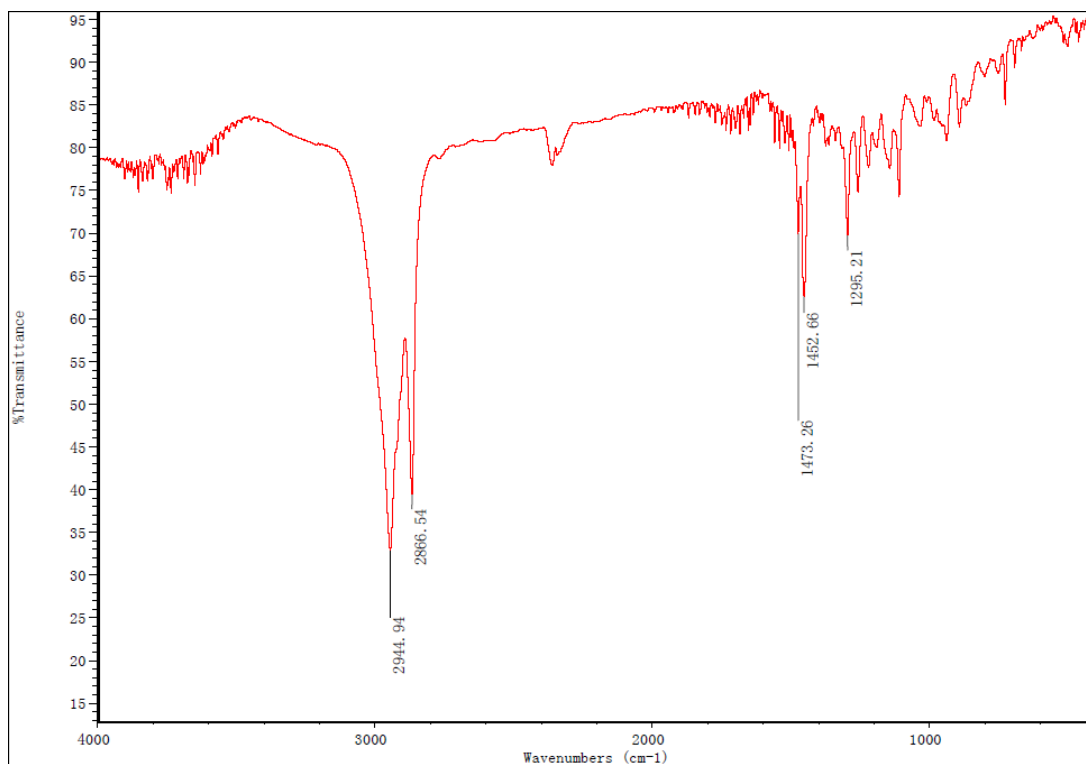


Figure S55. IR spectrum of poly(NB-co-1-octene)s (Table 3 entry 11).

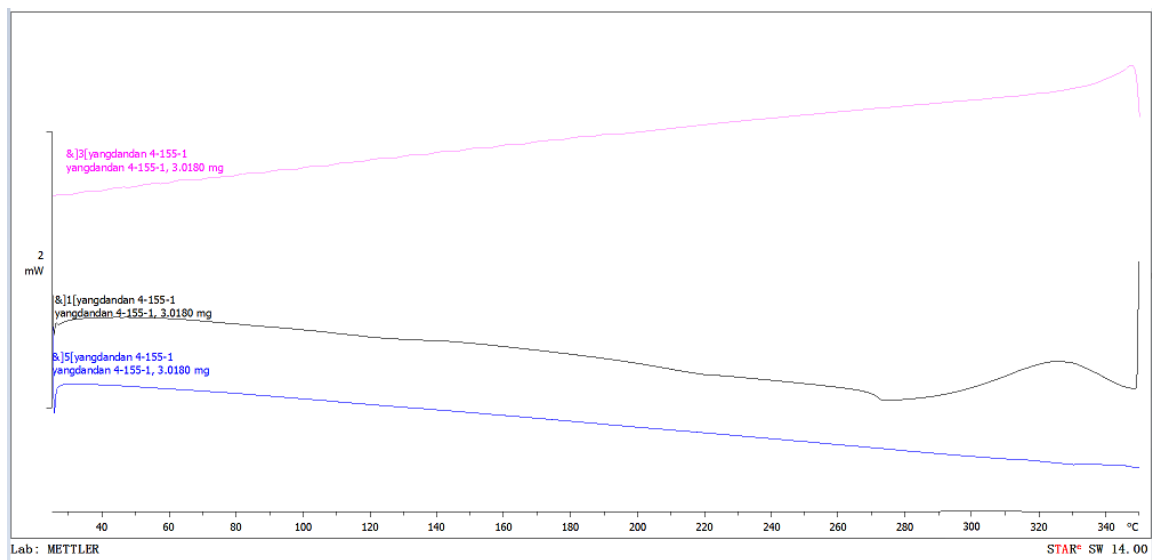


Figure S56. DSC thermograms of PNB obtained by $\text{Ni1/B(C}_6\text{F}_5)_3$ system (Table 2 entry 11).

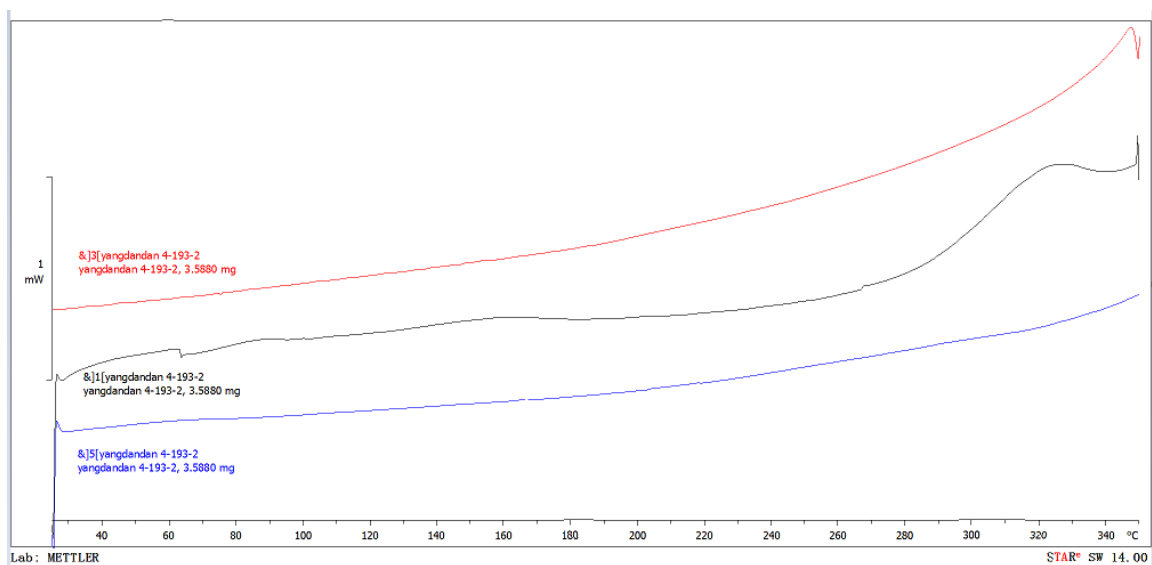


Figure S57. DSC thermograms of poly(NB-co-1-octene)s obtained by **Ni1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ system (Table 3 entry 3).

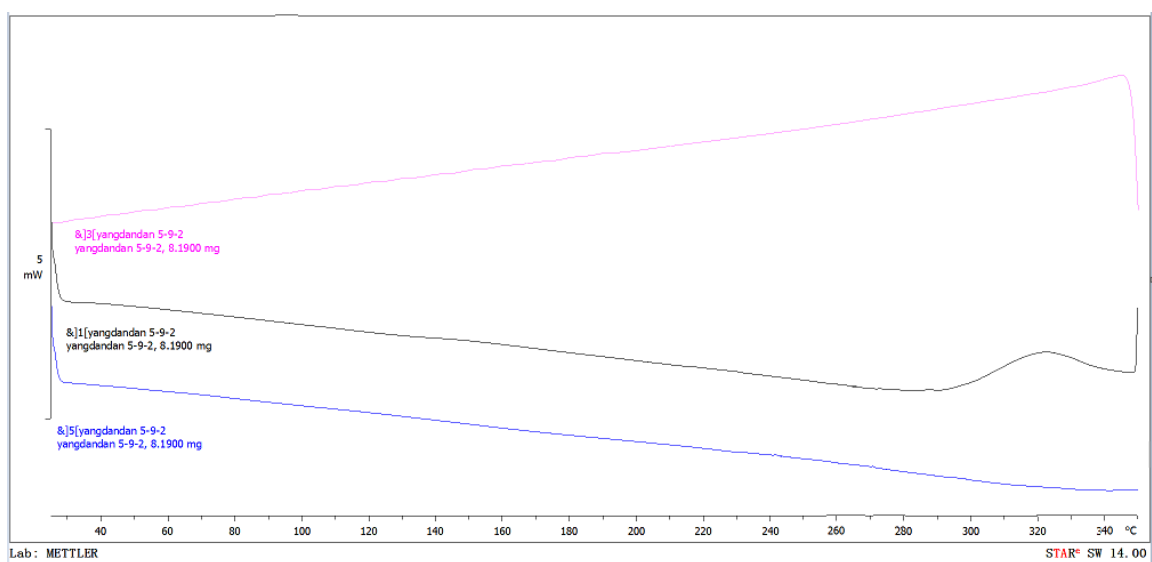


Figure S58. DSC thermograms of poly(NB-co-1-octene)s obtained by **Ni2**/ $\text{B}(\text{C}_6\text{F}_5)_3$ system (Table 3 entry 7).

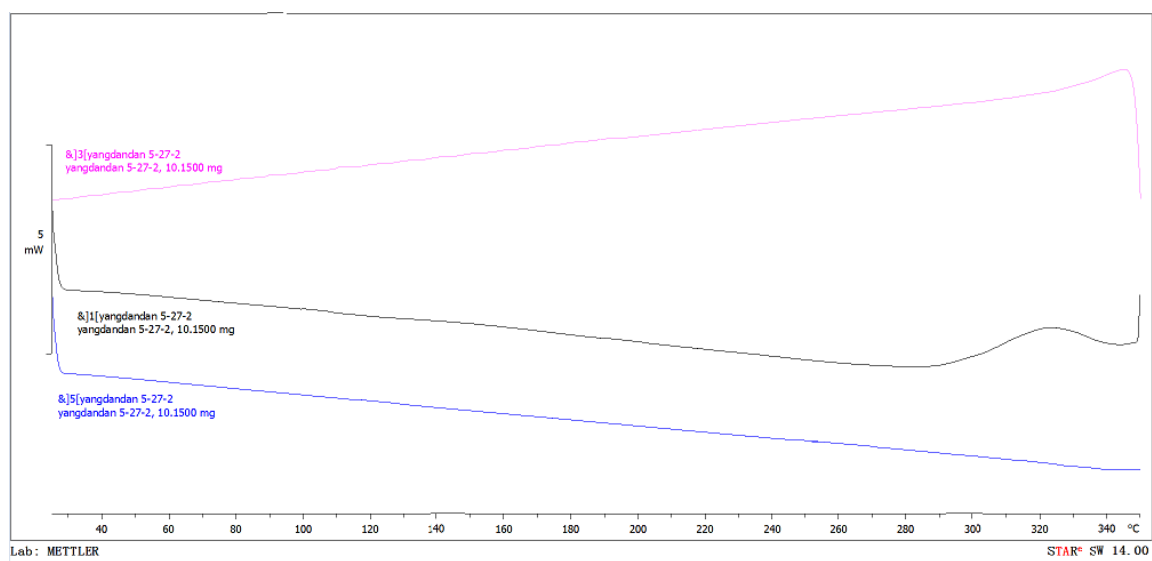


Figure S59. DSC thermograms of poly(NB-co-1-octene)s obtained by $\text{Ni}_3/\text{B}(\text{C}_6\text{F}_5)_3$ system (Table 3 entry 11).

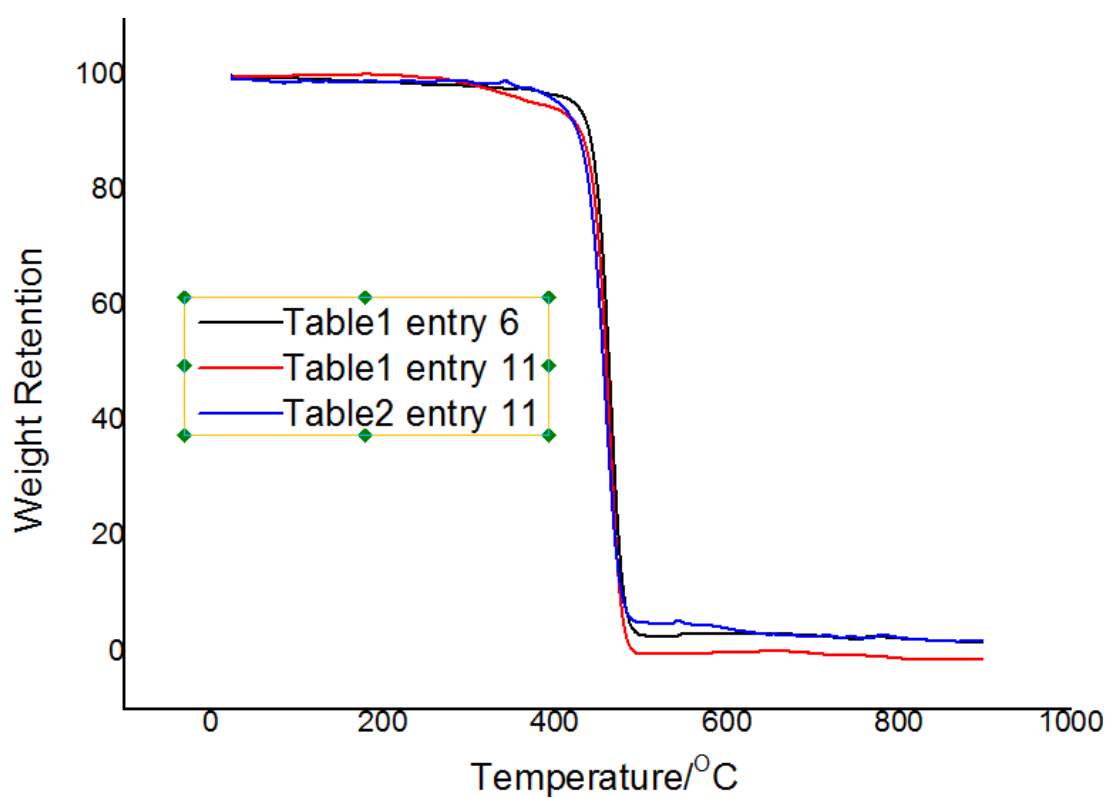


Figure S60. TGA of PNB.

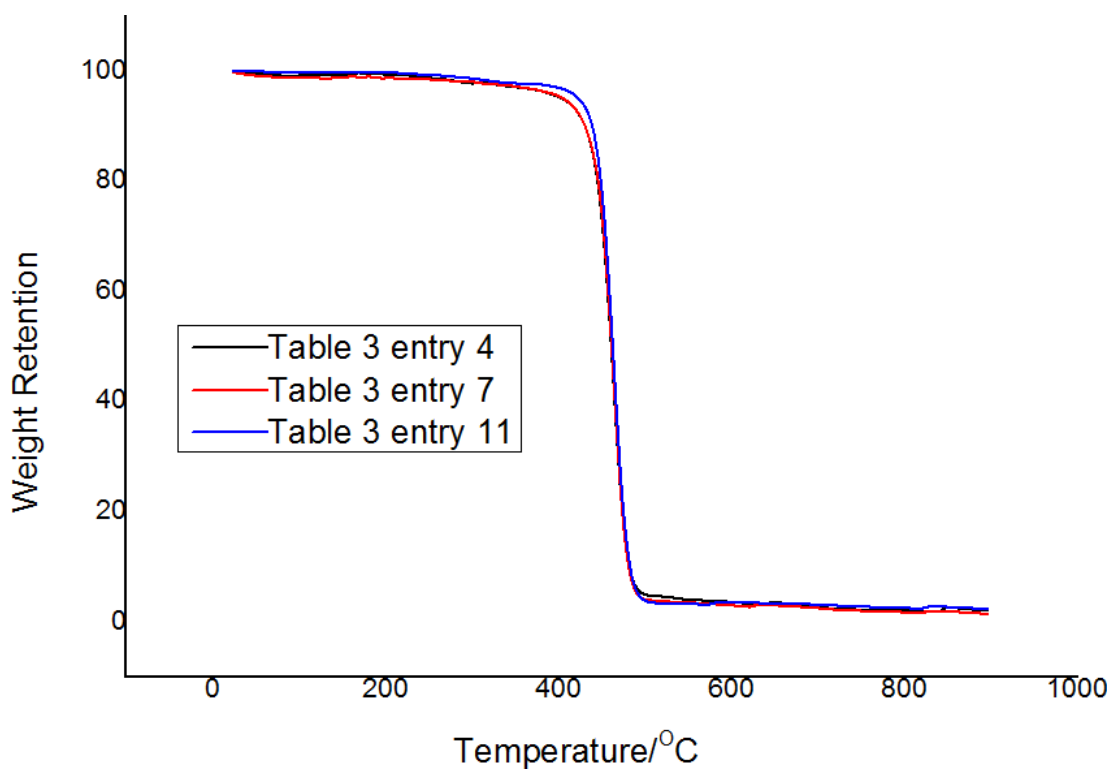


Figure S61. TGA of poly(NB-co-1-octene)s.

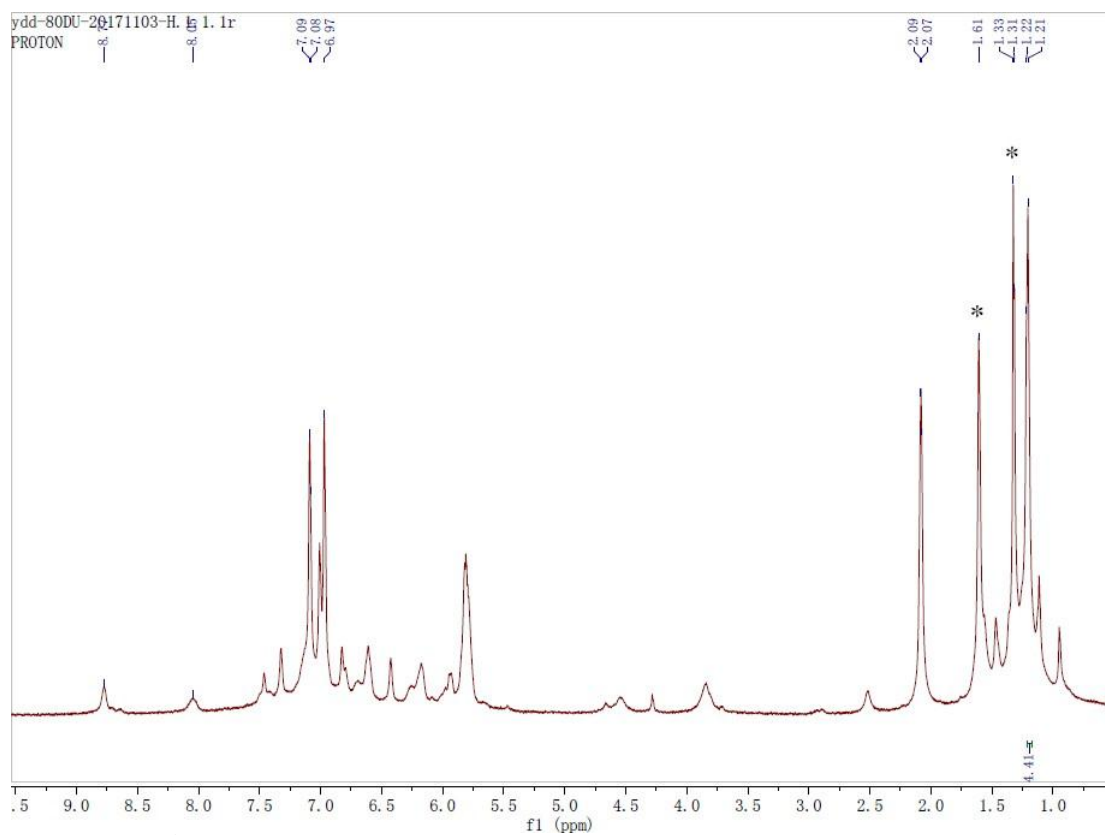


Figure S62. ^1H NMR spectra of a mixture of nickel complex **Ni1** with 1 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ reacted at 80 °C for 20 min.

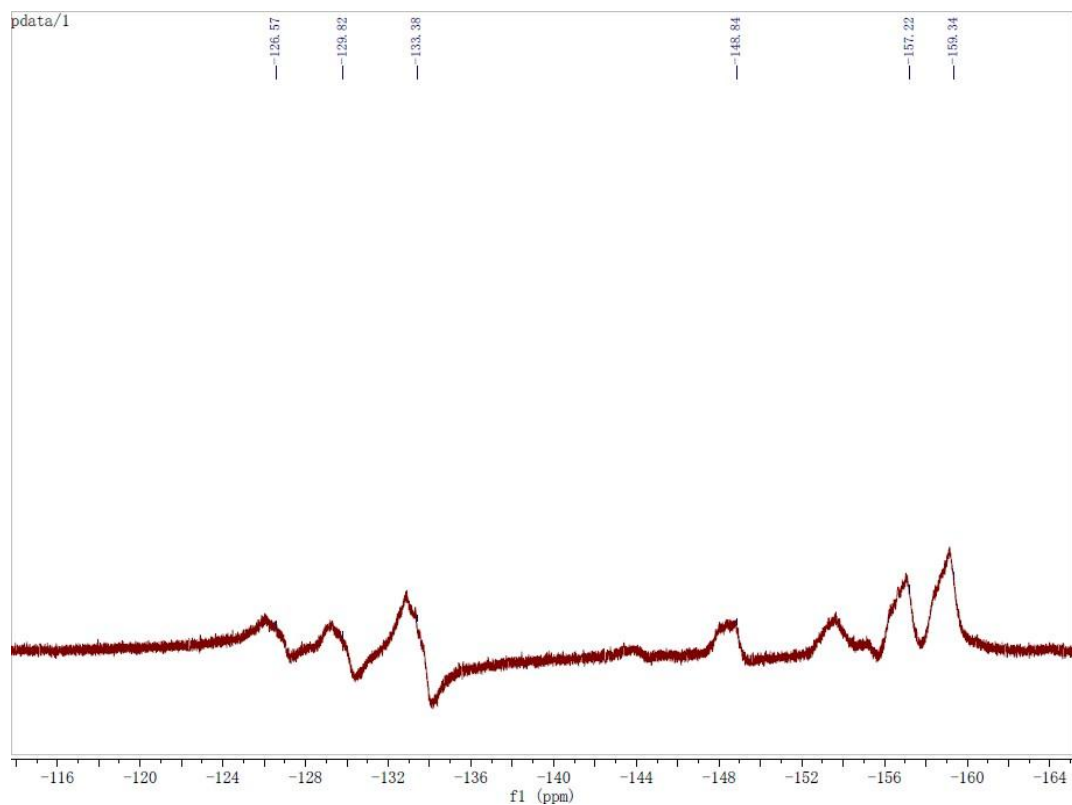


Figure S63. ^{19}F NMR spectrum a mixture of nickel complex **Ni1** with 1 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ reacted at 80 °C for 20 min.

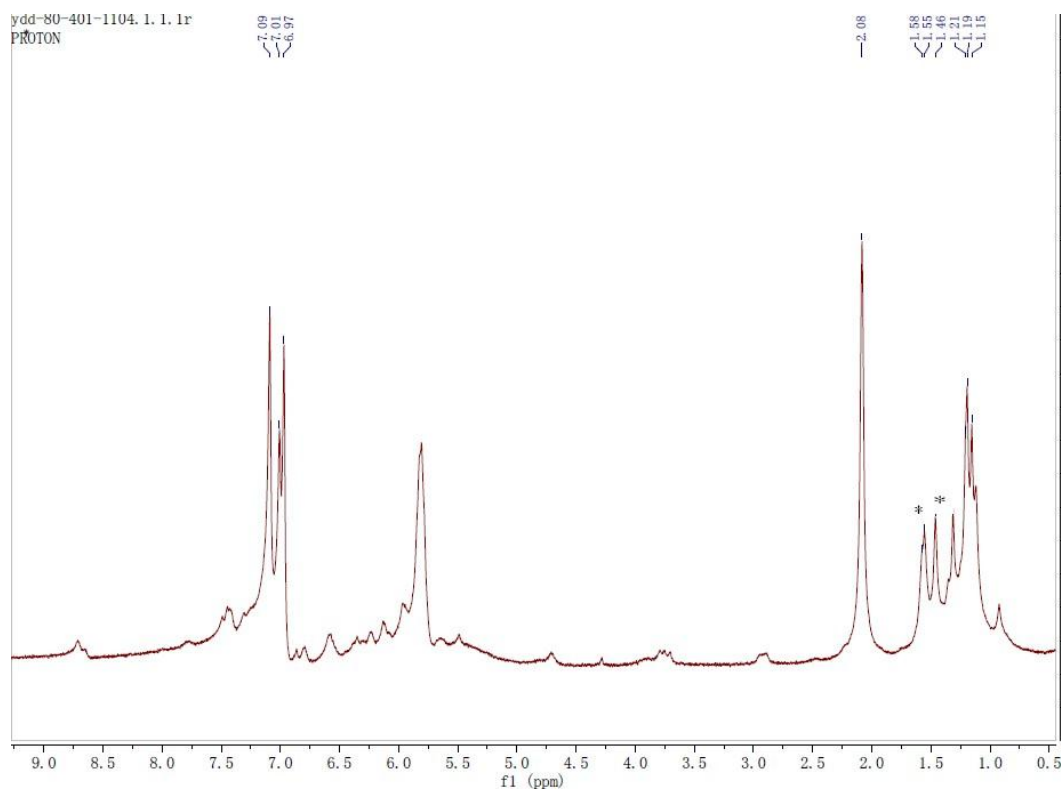


Figure S64. ^1H NMR spectra of a mixture of nickel complex **Ni1** with 5 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ reacted at 80 °C for 20 min. and heated (a) at 60 oC room temperature for 5 min (b).

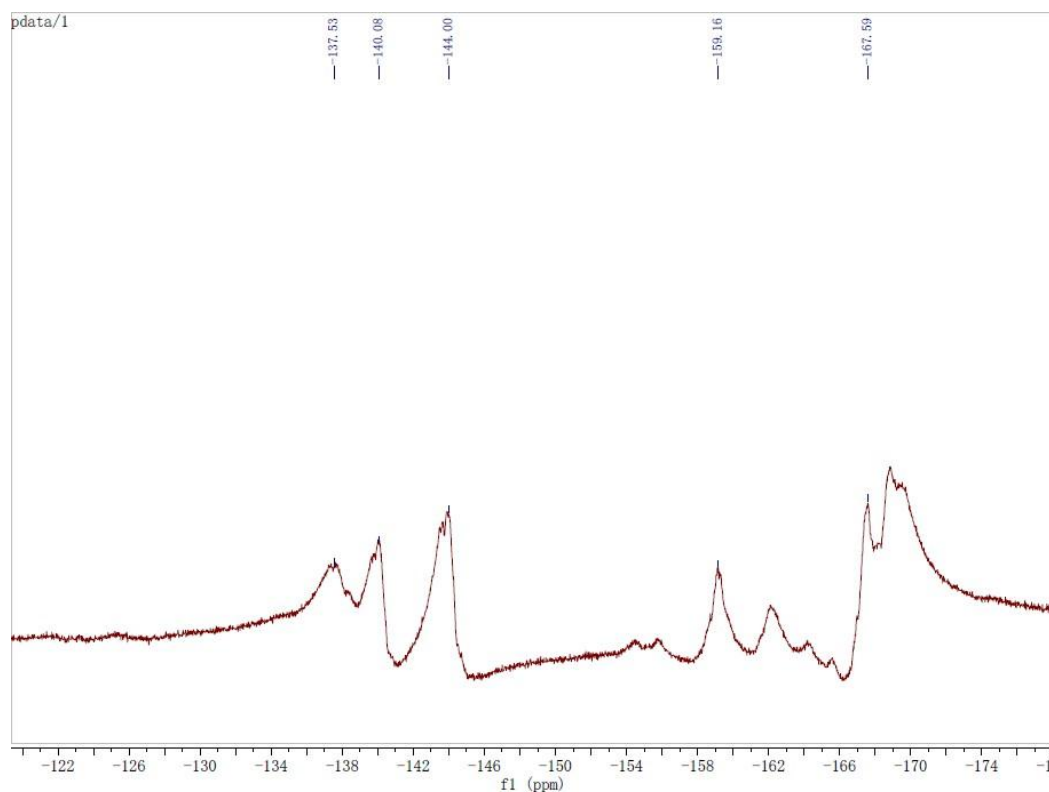


Figure S65. ^{19}F NMR spectra of a mixture of nickel complex **Ni1** with 5 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ reacted at 80 °C for 20 min.

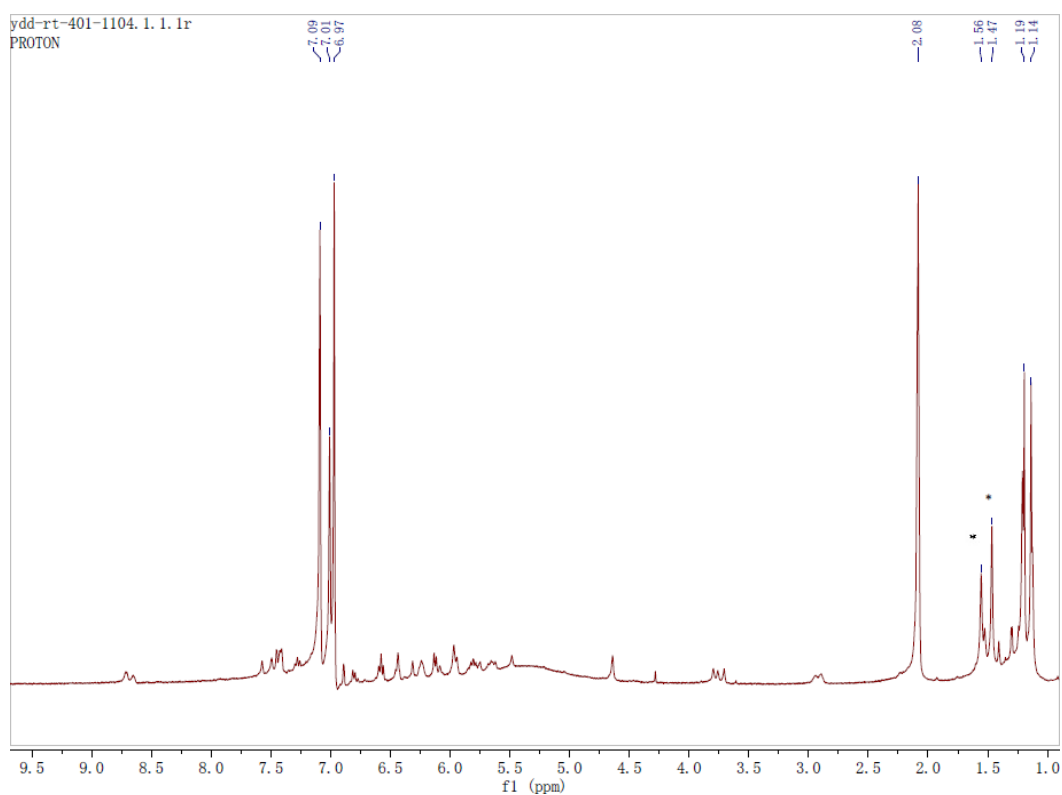


Figure S66. ^1H NMR spectra of a mixture of nickel complex **Ni1** with 5 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ reacted at room temperature for 20 min.

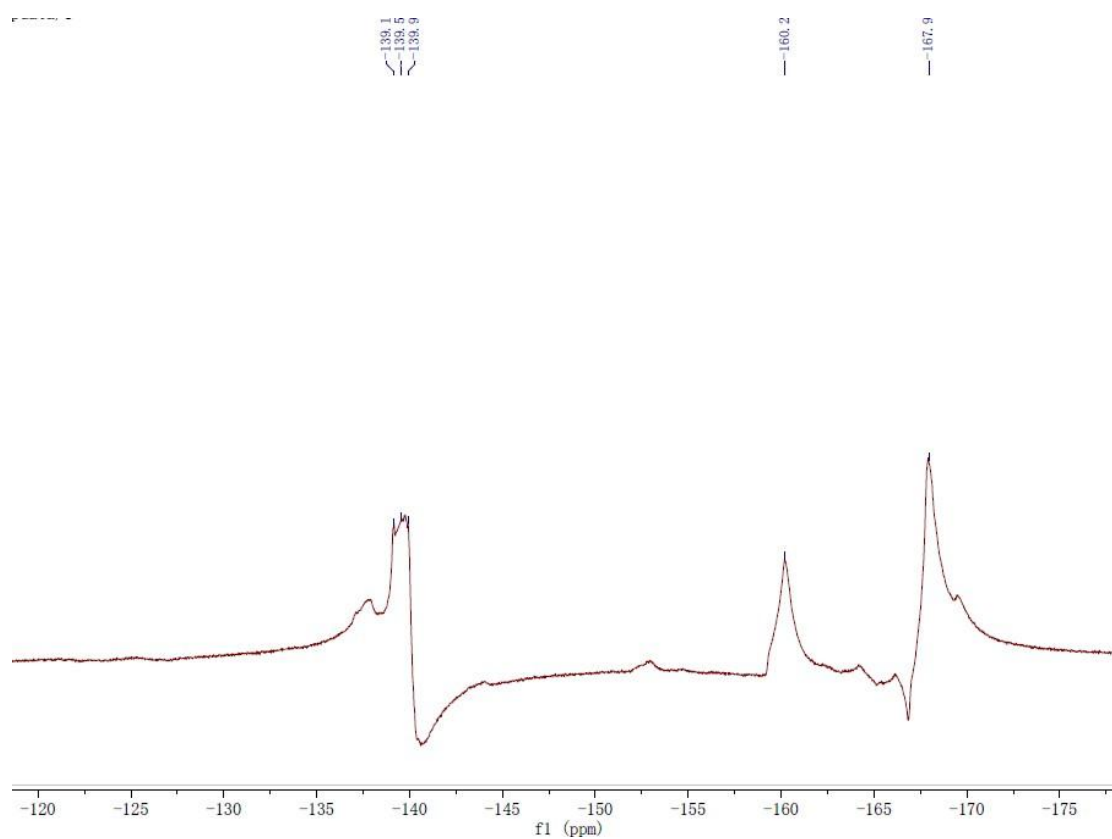


Figure S67. ^{19}F NMR spectra of a mixture of nickel complex **Ni1** with 5 equiv $\text{B}(\text{C}_6\text{F}_5)_3$ reacted at room temperature for 20 min.

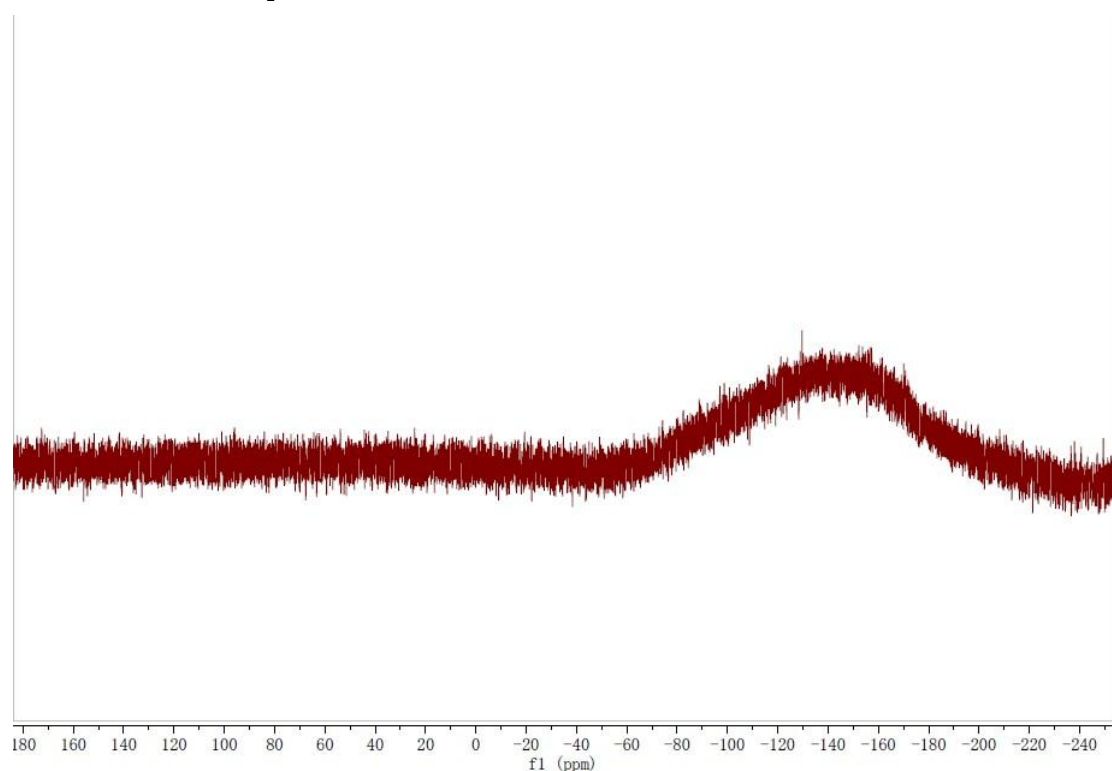


Figure S68. ^{19}F NMR spectra of poly(NB-co-1-octene)s obtained by **Ni1**/ $\text{B}(\text{C}_6\text{F}_5)_3$ system (Table 3 entry 4).

Table S1. Catalytic optimization with **Ni1–Ni4**/Me₂AlCl^a

entry	cotalalyst	Cat.	<i>T</i> (°C)	<i>t</i>	(Al/Ni)	PNB(g)	conv.(%)	activity ^b
1	Me ₂ AlCl	Ni1	0	12 h	200	0.3006	32.0	5.01
2	Me ₂ AlCl	Ni1	20	12 h	200	0.3221	34.3	5.37
3	Me ₂ AlCl	Ni1	40	12 h	200	0.3285	34.9	5.48
4	Me ₂ AlCl	Ni1	60	12 h	200	0.2396	25.5	3.99
5	Me ₂ AlCl	Ni1	20	12 h	50	0.2293	24.4	3.82
6	Me ₂ AlCl	Ni1	20	12 h	100	0.3190	33.9	5.32
7	Me ₂ AlCl	Ni1	20	12 h	500	0.2985	31.8	4.98
8	Me ₂ AlCl	Ni1	20	12 h	1000	0.2490	26.5	4.15
9	Me ₂ AlCl	Ni2	20	12 h	100	0.3694	39.3	6.16
10	Me ₂ AlCl	Ni3	20	12 h	100	0.3513	37.4	5.86
11	Me ₂ AlCl	Ni4	20	12 h	100	0.2282	24.3	3.80

^aPolymerization conditions: solvent, toluene; *V*_{total}, 10 mL; *n*[Ni] = 5.0 μmol; norbornene, 1.0 g; Me₂AlCl, 0.9 M in heptane. ^bIn units of 10³ g of PNB (mol of Ni)^{−1}h^{−1}.

Table S2. Time dependence studies at high temperature with **Ni1–Ni3**/B(C₆F₅)₃.

entry	cotalalyst	Cat.	<i>T</i> (°C)	<i>t</i> (min)	(B/Ni)	PNB(g)	conv.(%)	activity ^b
1	B(C ₆ F ₅) ₃	Ni1	100	10	100	0.1137	11.4	0.273
2	B(C ₆ F ₅) ₃	Ni1	100	20	100	0.1250	12.5	0.150
3	B(C ₆ F ₅) ₃	Ni1	100	30	100	0.3483	34.8	0.279
4	B(C ₆ F ₅) ₃	Ni1	100	40	100	0.6138	61.4	0.368
5	B(C ₆ F ₅) ₃	Ni2	100	10	100	0.8021	80.2	1.925
6	B(C ₆ F ₅) ₃	Ni2	100	20	100	0.8583	85.8	1.030
7	B(C ₆ F ₅) ₃	Ni2	100	30	100	0.9004	90.0	0.720
8	B(C ₆ F ₅) ₃	Ni2	100	40	100	0.9108	91.1	0.546
9	B(C ₆ F ₅) ₃	Ni3	100	10	100	0.1960	19.6	0.470
10	B(C ₆ F ₅) ₃	Ni3	100	20	100	0.3166	31.7	0.380
11	B(C ₆ F ₅) ₃	Ni3	100	30	100	0.4163	41.6	0.333
12	B(C ₆ F ₅) ₃	Ni3	100	40	100	0.4530	45.3	0.272

^aPolymerization conditions: solvent, toluene; *V*_{total}, 40 mL; *n*[Ni] = 2.5 μmol; norbornene, 1.0 g; ^bIn units of 10⁶ g of PNB (mol of Ni)^{−1} h^{−1}.