

Direct Synthesis of Chain-end Toluene Functionalized Hyperbranched Ethylene Oligomers

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1. Spectra Data

1.1 ¹H and ¹³C NMR of the Synthetic Compounds.

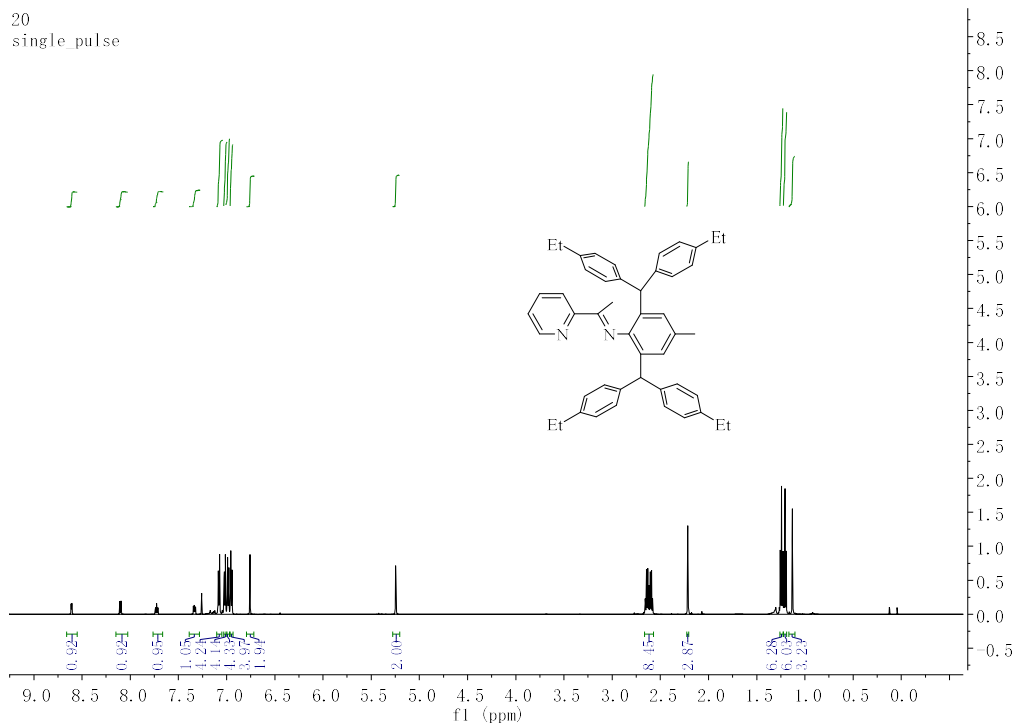


Figure S1. ^1H NMR spectrum of **L1** in CDCl_3 .

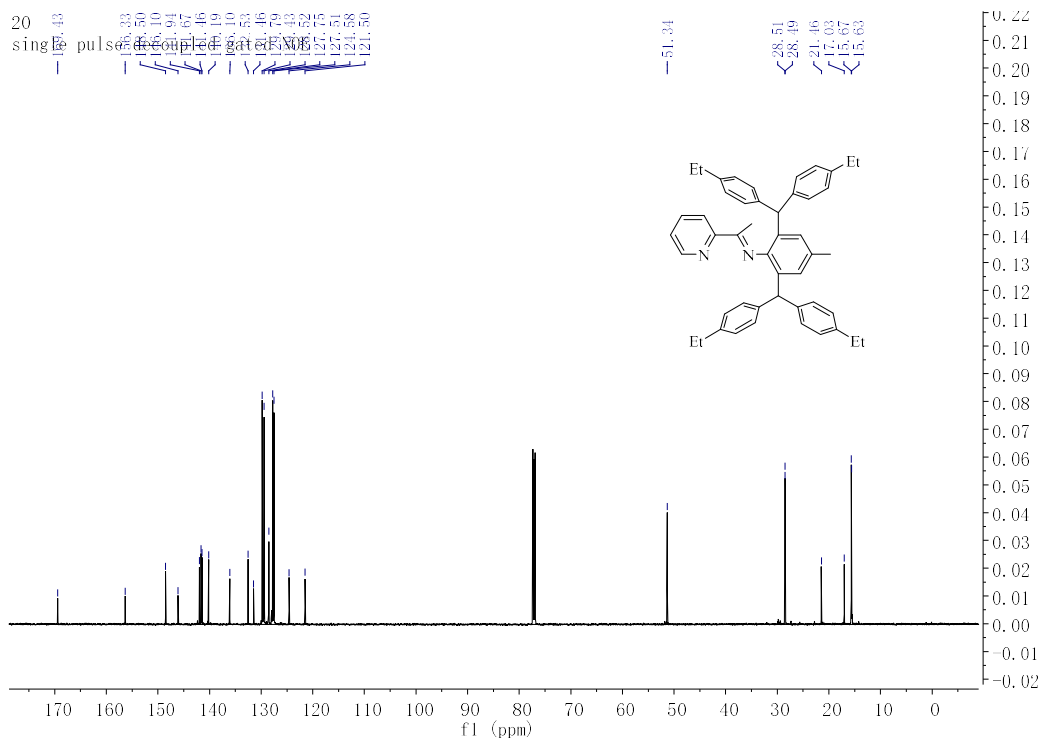


Figure S2. ^{13}C NMR spectrum of **L1** in CDCl_3 .

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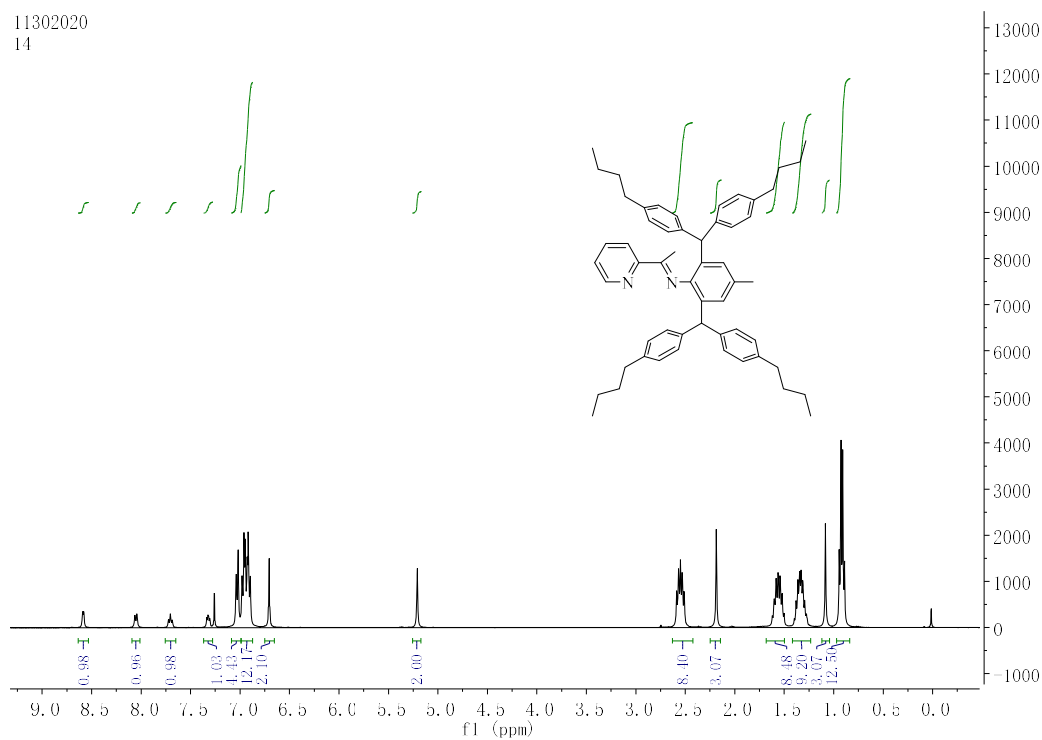


Figure S3. ^1H NMR spectrum of **L2** in CDCl_3 .

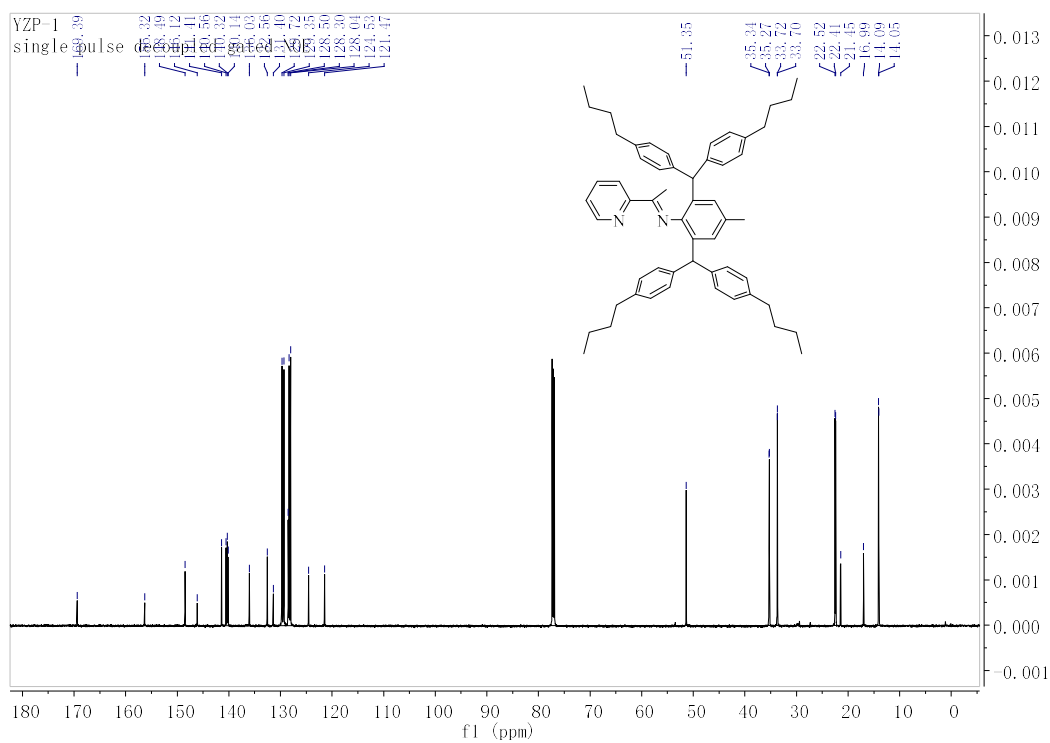


Figure S4. ^{13}C NMR spectrum of **L2** in CDCl_3 .

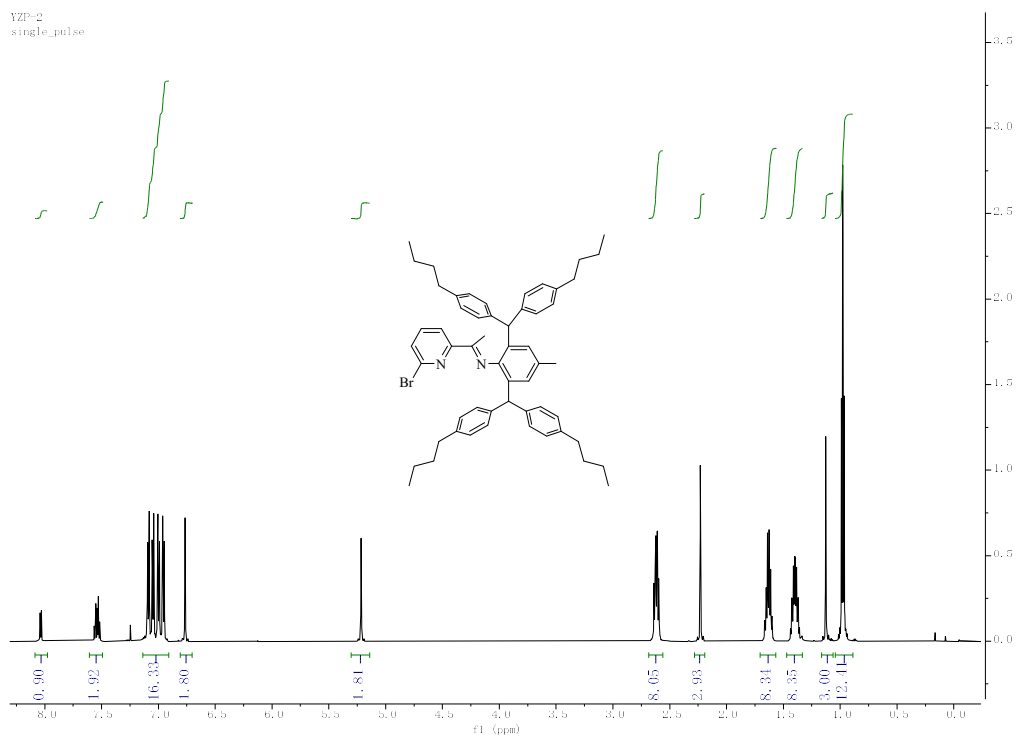


Figure S7. ¹H NMR spectrum of L4 in CDCl₃.

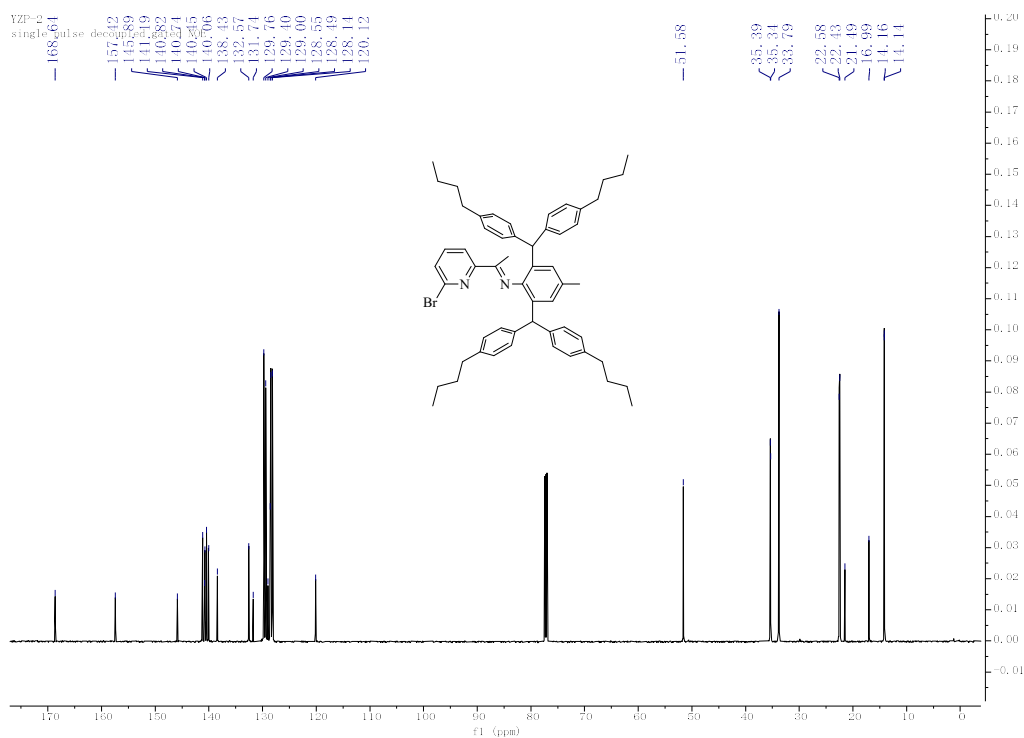


Figure S8. ¹³C NMR spectrum of L4 in CDCl₃.

1.2 MS of L1-L4.

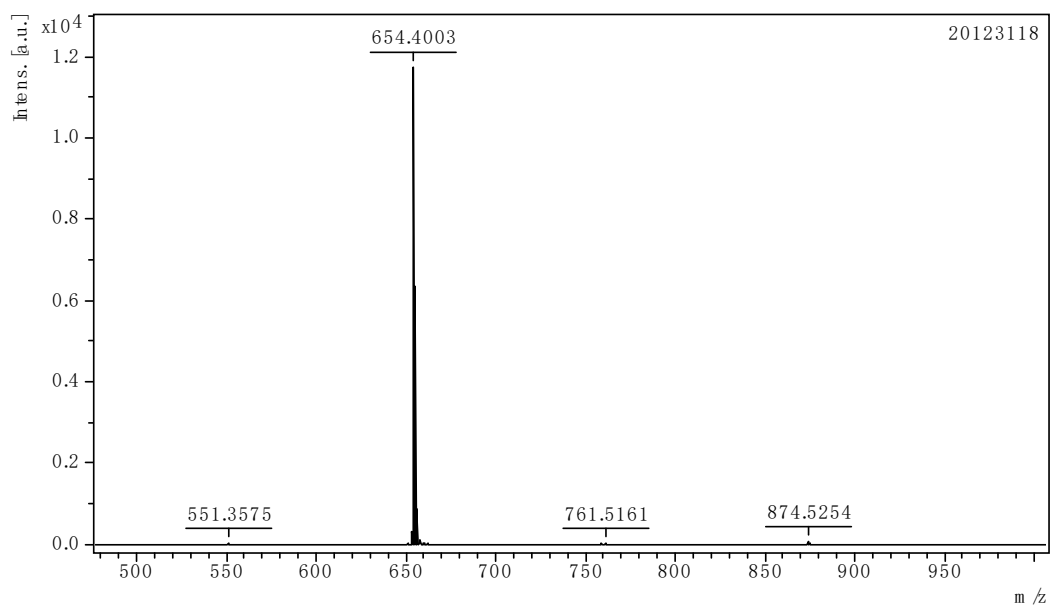


Figure S9. MALDI-TOF-MS of L1.

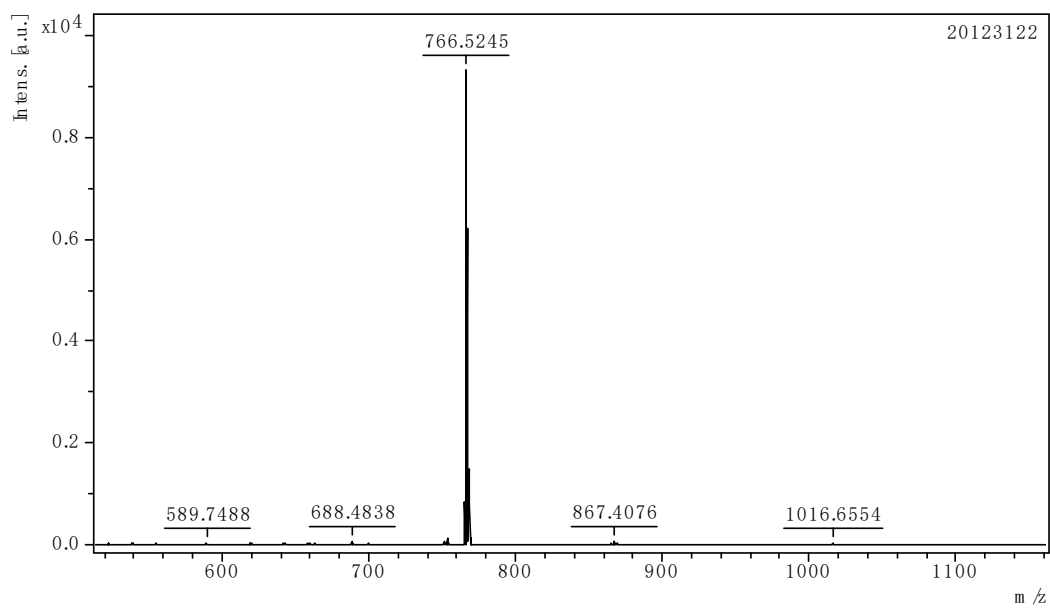


Figure S10. MALDI-TOF-MS of L2.

YZP-1 #20 RT: 0.16 AV: 1 SB: 1 0.02 NL: 2.01E8
T: FTMS + c APCI corona Full ms [100.00-1000.00]

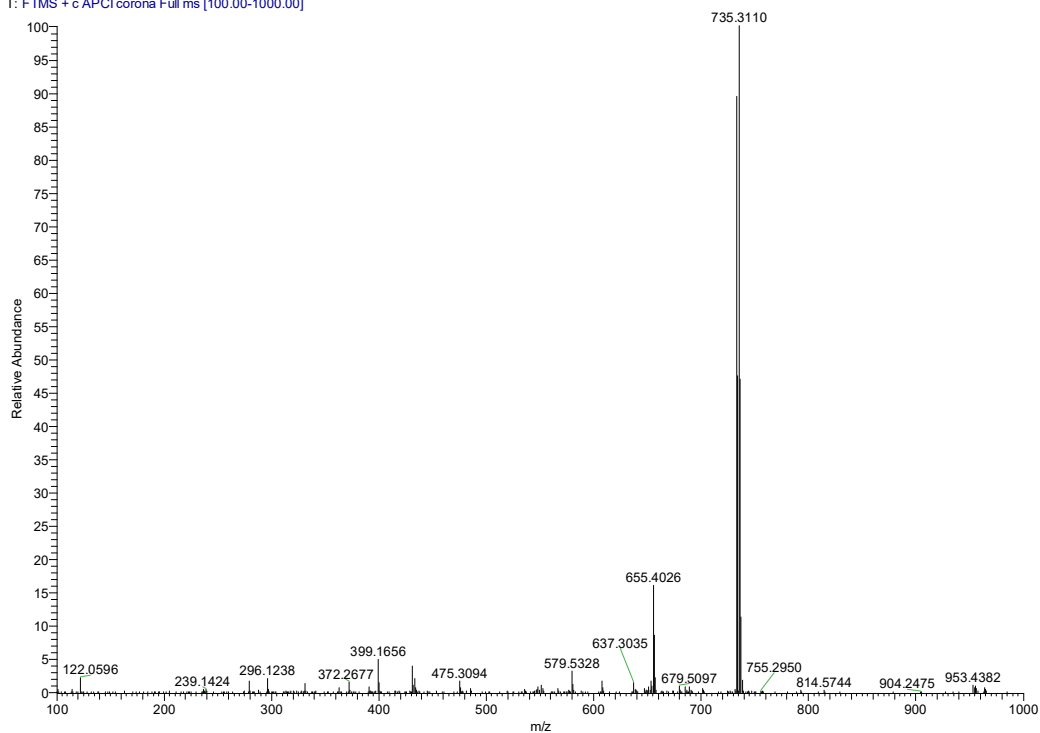


Figure S11. APCI-MS of L3.

YZP-2 #16 RT: 0.13 AV: 1 SB: 1 0.03 NL: 6.75E8
T: FTMS + c APCI corona Full ms [100.00-1000.00]

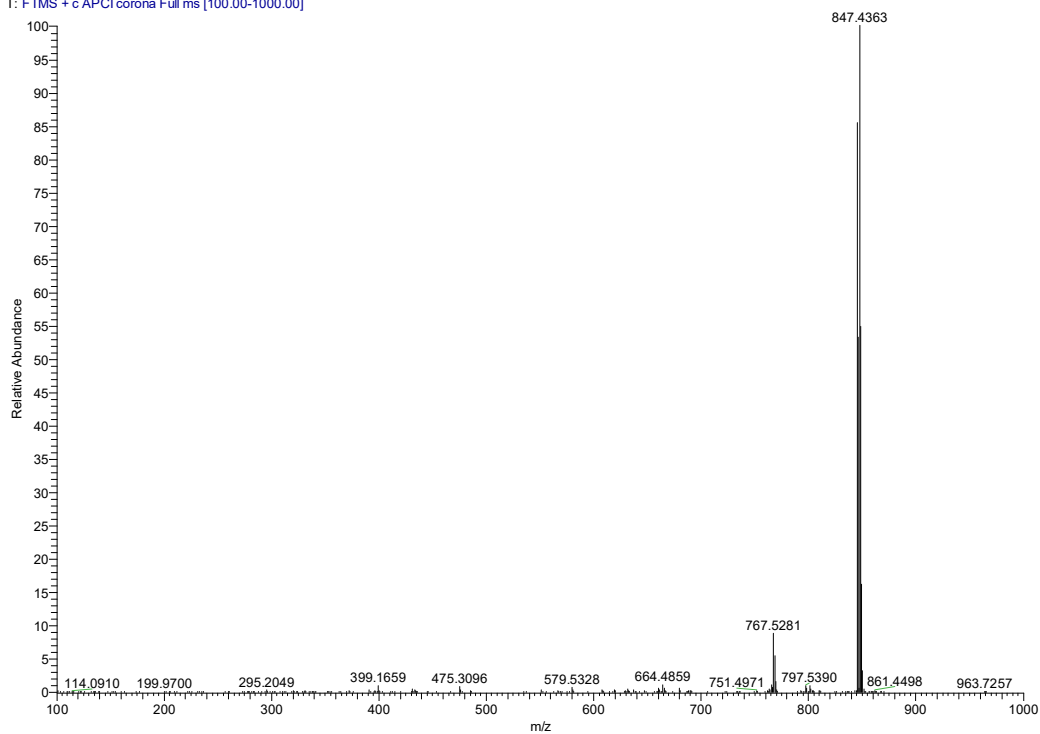


Figure S12. APCI-MS of L4.

1.3 MS of Complexes Ni1-Ni4

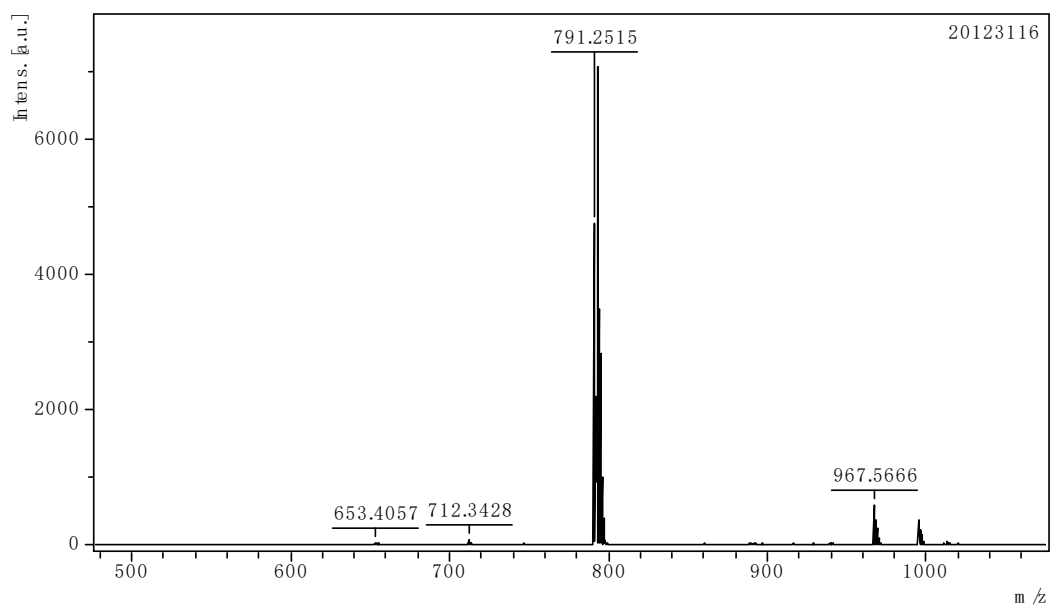


Figure S13. MALDI-TOF-MS of Ni1.

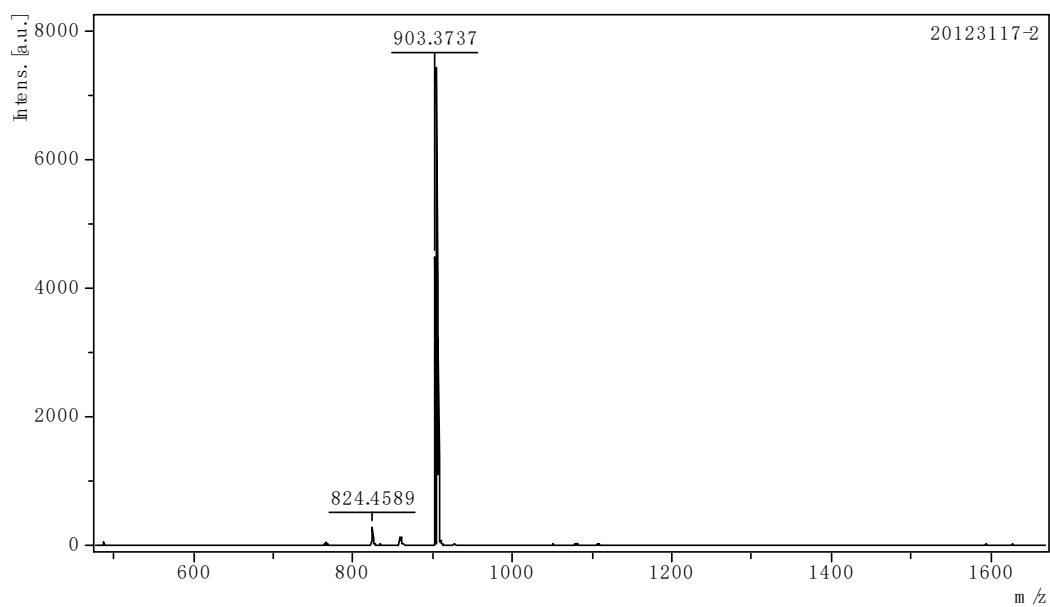


Figure S14. MALDI-TOF-MS of Ni2.

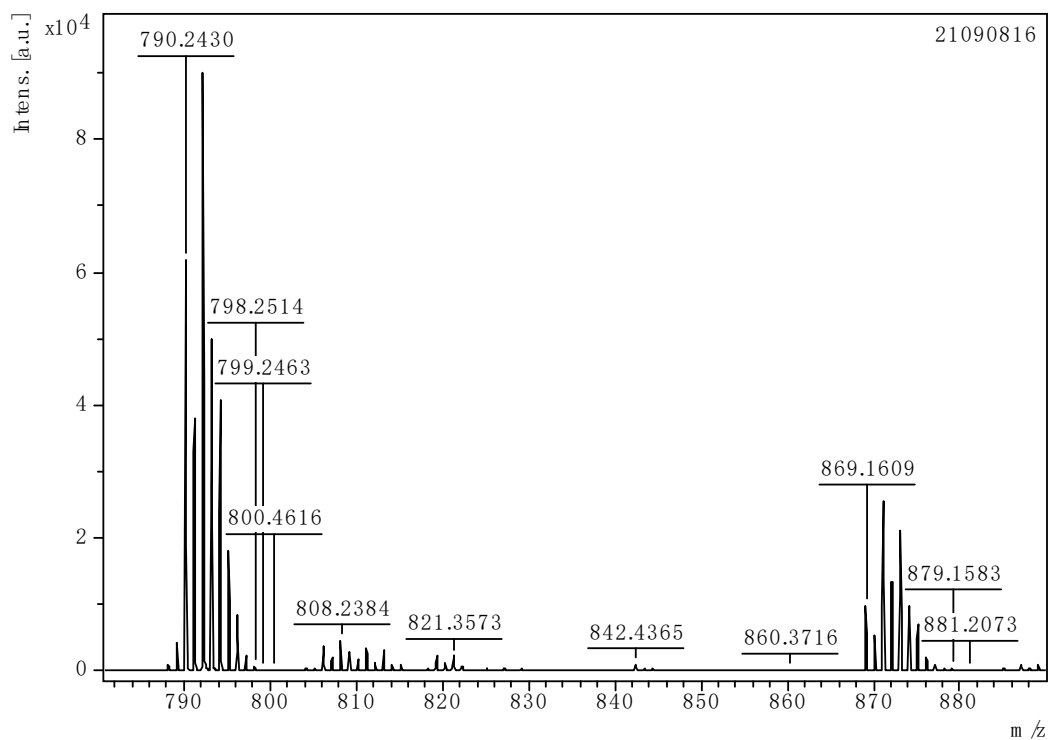


Figure S15. MALDI-TOF-MS of Ni₃.

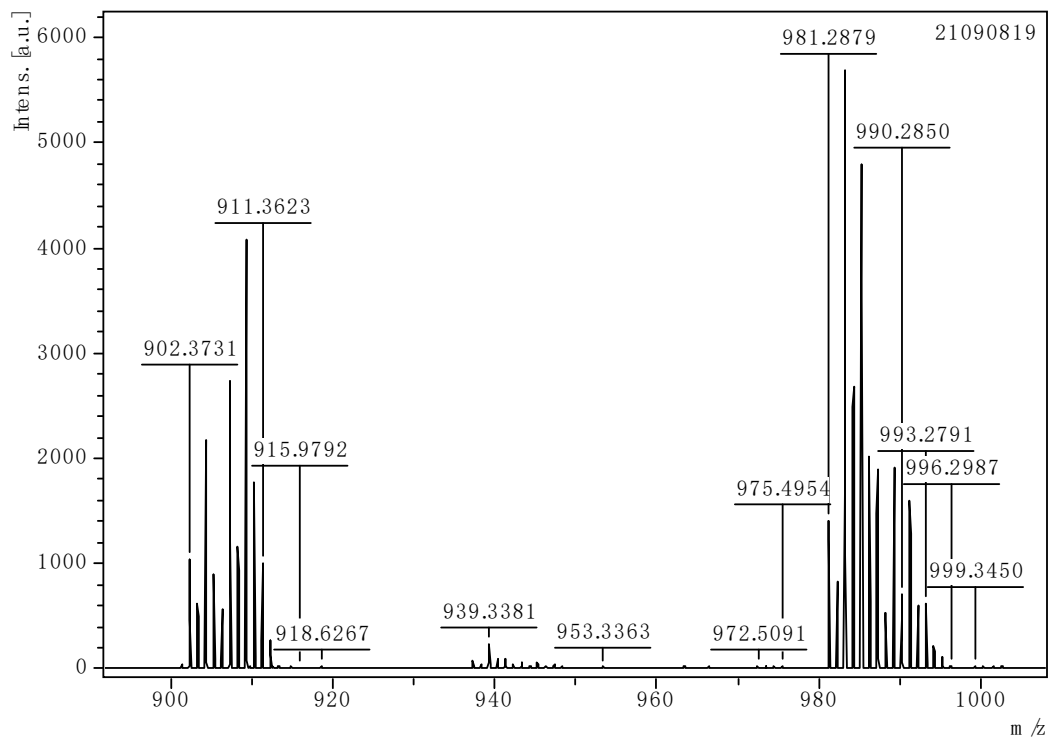


Figure S16. MALDI-TOF-MS of Ni₄.

1.4 ^1H and ^{13}C NMR of Representative Ethylene Oligomers.

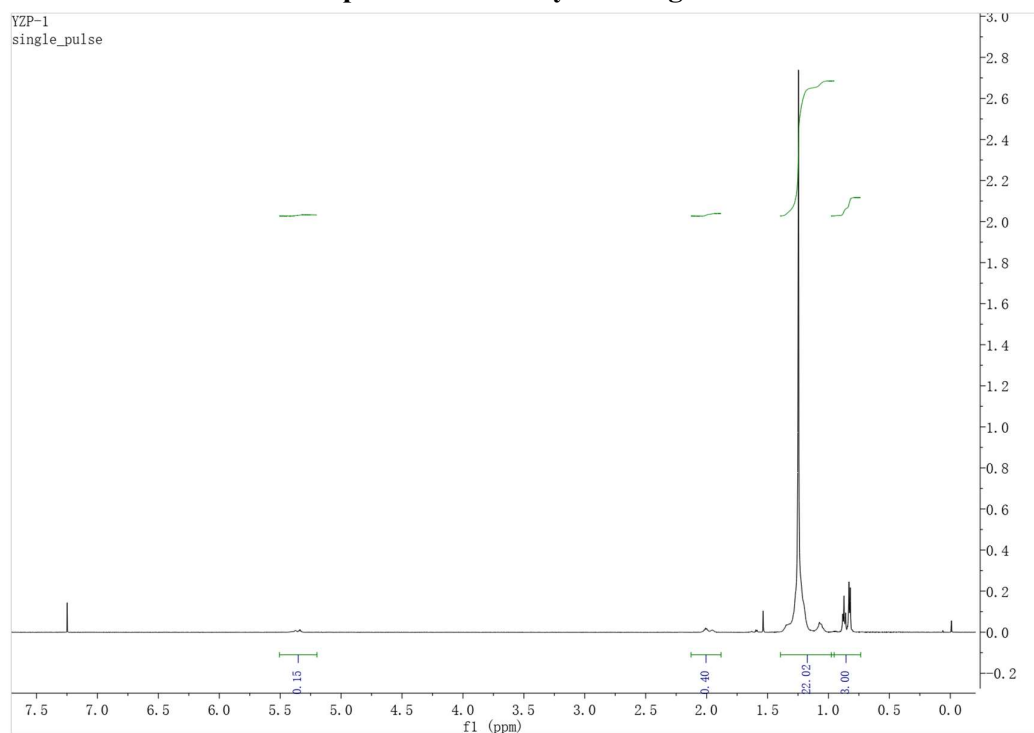


Figure S17. ^1H NMR spectrum of the polymer from table 1, entry 1 (CDCl_3 , 20 $^\circ\text{C}$).

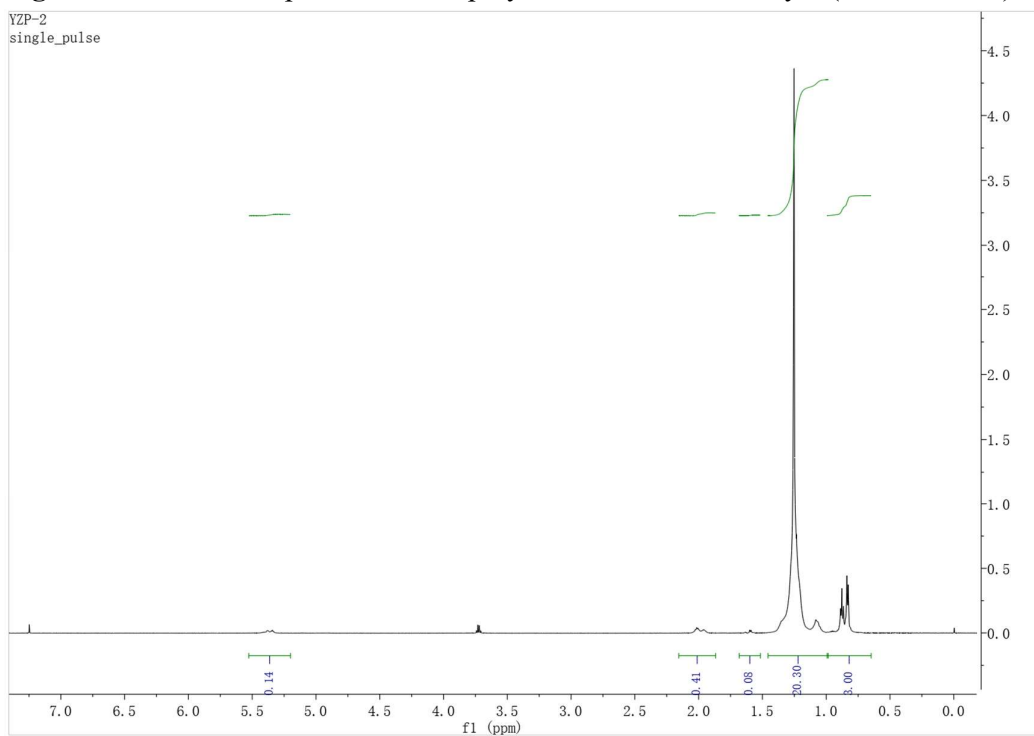


Figure S18. ^1H NMR spectrum of the polymer from table 1, entry 2 (CDCl_3 , 20 $^\circ\text{C}$).

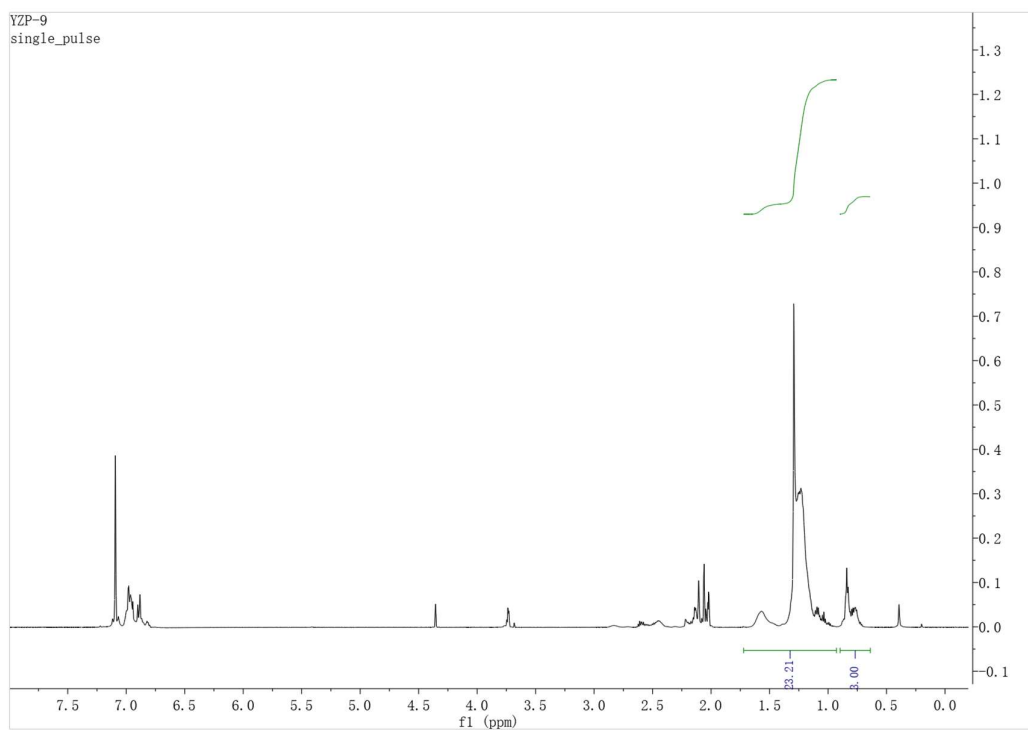


Figure S19. ^1H NMR spectrum of the polymer from table 1, entry 8 (CDCl_3 , 20 $^\circ\text{C}$).

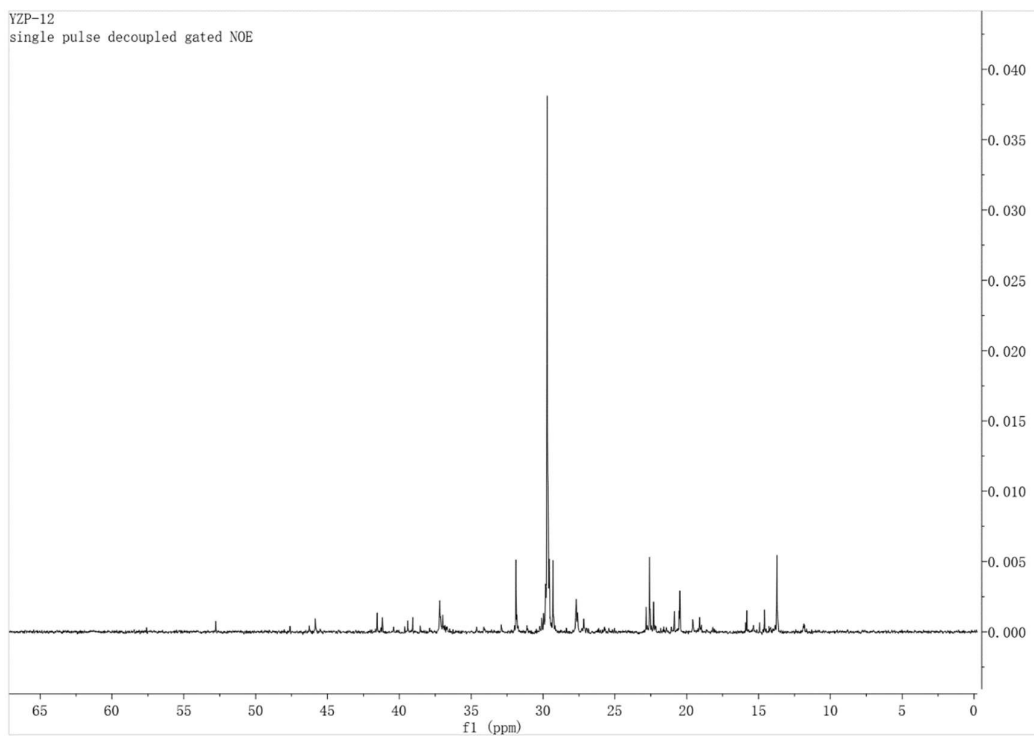
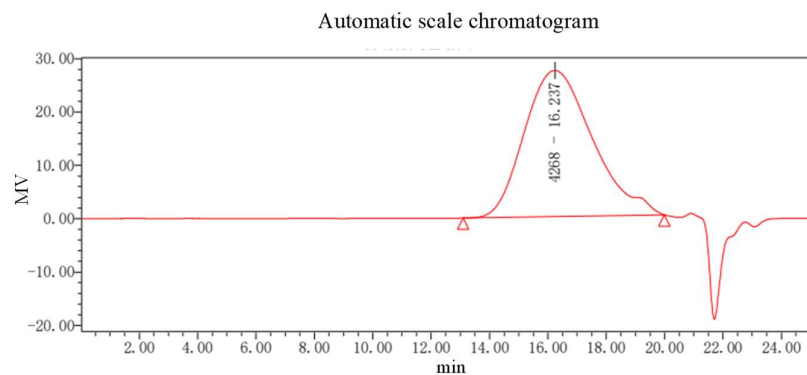


Figure S20. ^{13}C NMR spectrum of the polymer from table 1, entry 11 (CDCl_3 , 20 $^\circ\text{C}$).

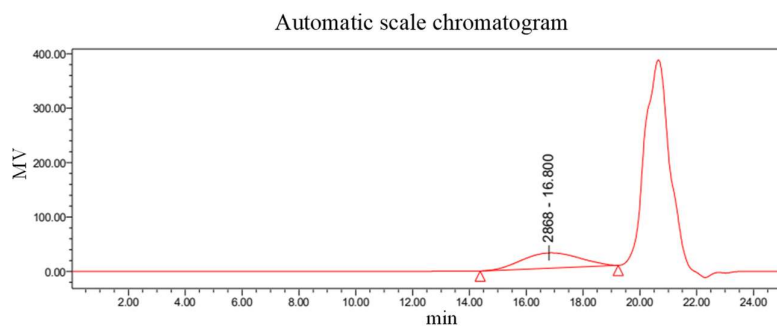
1.5 GPC and GC-MS of Representative Ethylene Oligomers.



GPC Results

	Distribution name	Mn (Dalton)	Mw (Dalton)	MP	Mz (Dalton)	Mz+1 (Dalton)	Mv	PDI	Mw Mark1	Mw Mark2
1		3574	5058	4268	7039	9278		1.415168		

Figure S21. GPC of the oligomer from table 1, entry 1.



GPC Results

	Distribution name	Mn (Dalton)	Mw (Dalton)	MP	Mz (Dalton)	Mz+1 (Dalton)	Mv	PDI	Mw Mark1	Mw Mark2
1		2797	3575	2868	4584	5685		1.278126		

Figure S22. GPC of the oligomer from table 1, entry 3.

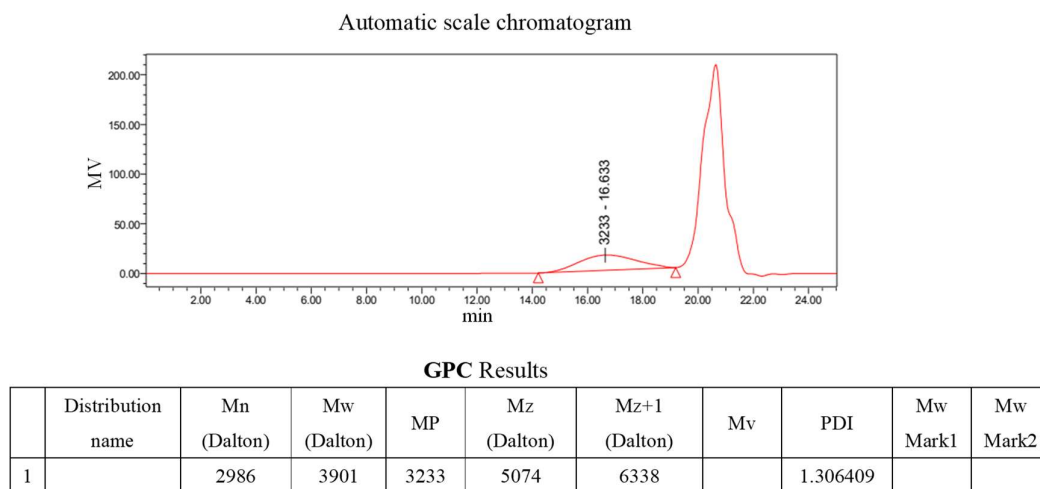


Figure S23. GPC of the polymer from table 1, entry 6.

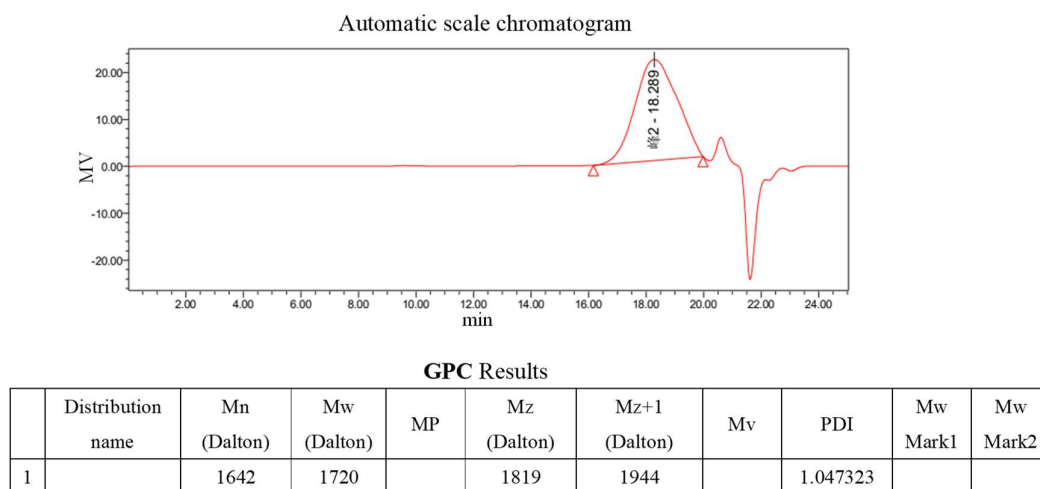


Figure S24. GPC of the polymer from table 1, entry 10.

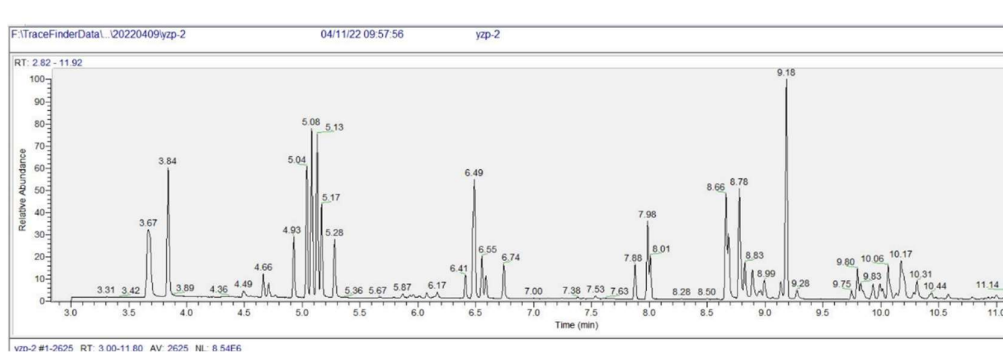


Figure S25. GC-MS of the polymer from table 1, entry 12.

2. References

[1] Yan, Z.; Li, S.; Dai, S. Synthesis and characterization of hyperbranched polar functionalized olefin oligomers. *Chin. J. Synth. Chem.* **2021**, *29*, 1033–1044.

3. X-ray Crystallography.

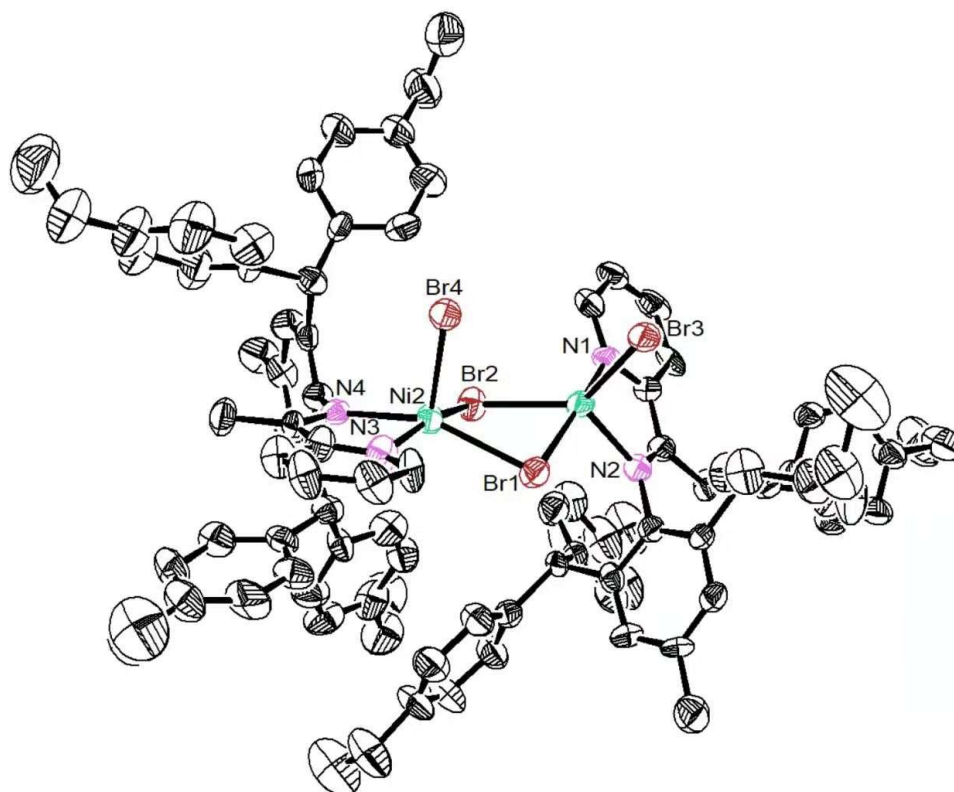


Table S1 Crystal data and structure refinement for Ni1.

Identification code	Ni1
Empirical formula	C _{97.5} H ₁₀₃ Br ₄ N ₄ Ni ₂
Formula weight	1874.25
Temperature/K	298(2)
Crystal system	Triclinic
Space group	P-1
a/Å	16.0191(14)
b/Å	18.2202(15)
c/Å	19.2910(17)
α /°	98.562(3)
β /°	91.765(2)
γ /°	111.897(5)
Volume/Å ³	5143.1(8)

Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.210
μ/mm^{-1}	2.039
F(000)	1926
Crystal size/ mm^3	0.34 x 0.21 x 0.17
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	1.82 to 25.02
Index ranges	-19 $\leq h \leq$ 12, -21 $\leq k \leq$ 21, -22 $\leq l \leq$ 22
Reflections collected	25536
Independent reflections	17798 [R(int) = 0.0751]
Data/restraints/parameters	17798 / 745 / 1032
Goodness-of-fit on F^2	1.093
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.1009, wR2 = 0.2391
Final R indexes [all data]	R1 = 0.2156, wR2 = 0.2732
Largest diff. peak/hole / e \AA^{-3}	1.206 and -1.626