Support Information

Nickel-Catalyzed Direct Synthesis of Hyperbranched Liquid Oligoethylene

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1. Experimental section

1.1 General Considerations

All chemicals were commercially sourced, except those whose synthesis is described. All experiments were carried out under a dry nitrogen atmosphere in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded by a JNM-ECZ600R or JNM-ECZ400R spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Mass spectra were obtained by the Analytical Center of Dalian University of Technology using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (Bruker autoflex max). Elemental analysis and ESI-MS were performed by the Analytical Center of Anhui University. Molecular weight of the polymers was determined by ^{1}H and ^{13}C NMR spectra. Crystal data were collected on a XtaLAB Synergy diffractometer with the new generation of high-resolution X-ray detector HyPix6000HE, using Cu Kα radiation (λ= 1.54184) at 296.93 (10)K. GC Test (Yuke-GC-7860): Set the initial temperature to 50℃, ramp to 150℃ at 10℃/min, then to 300℃ at 3℃/min, and hold for 60 minutes using a HP-POMA column.

2.1 ^{1}H and ^{13}C NMR of the Synthetic Compounds.

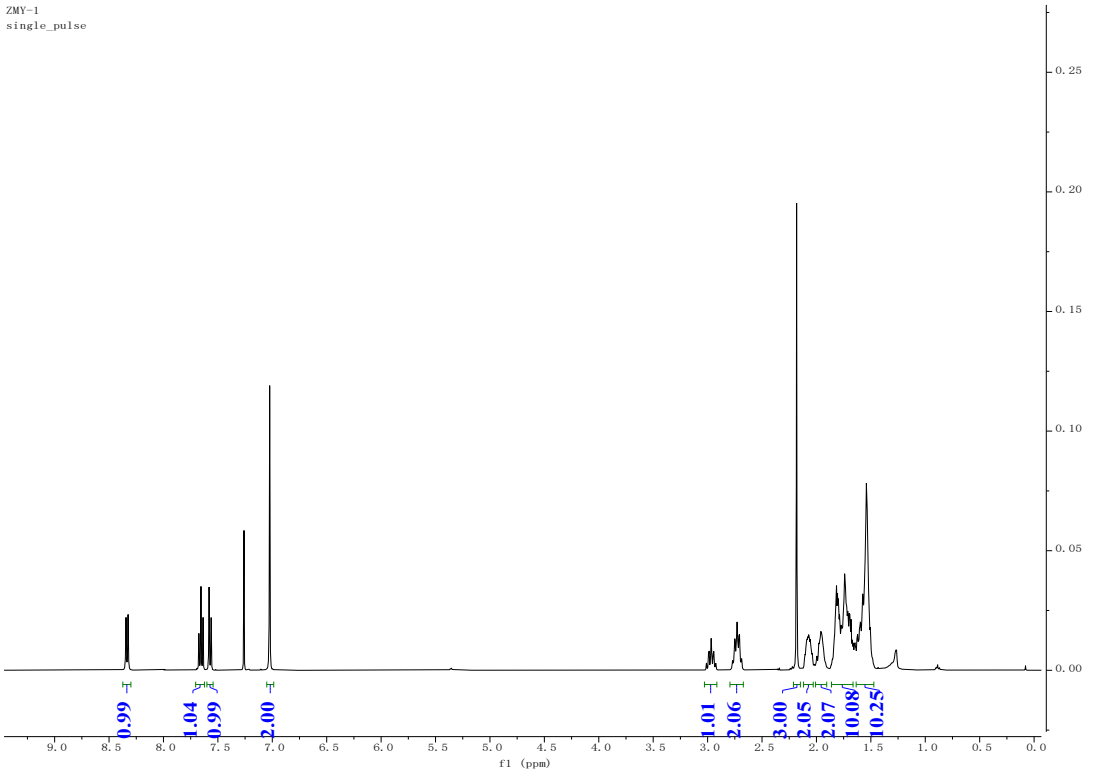

Figure S1. ^{1}H NMR spectrum of **L1** in $CDCl_3$ (400 MHz, 20 ℃).

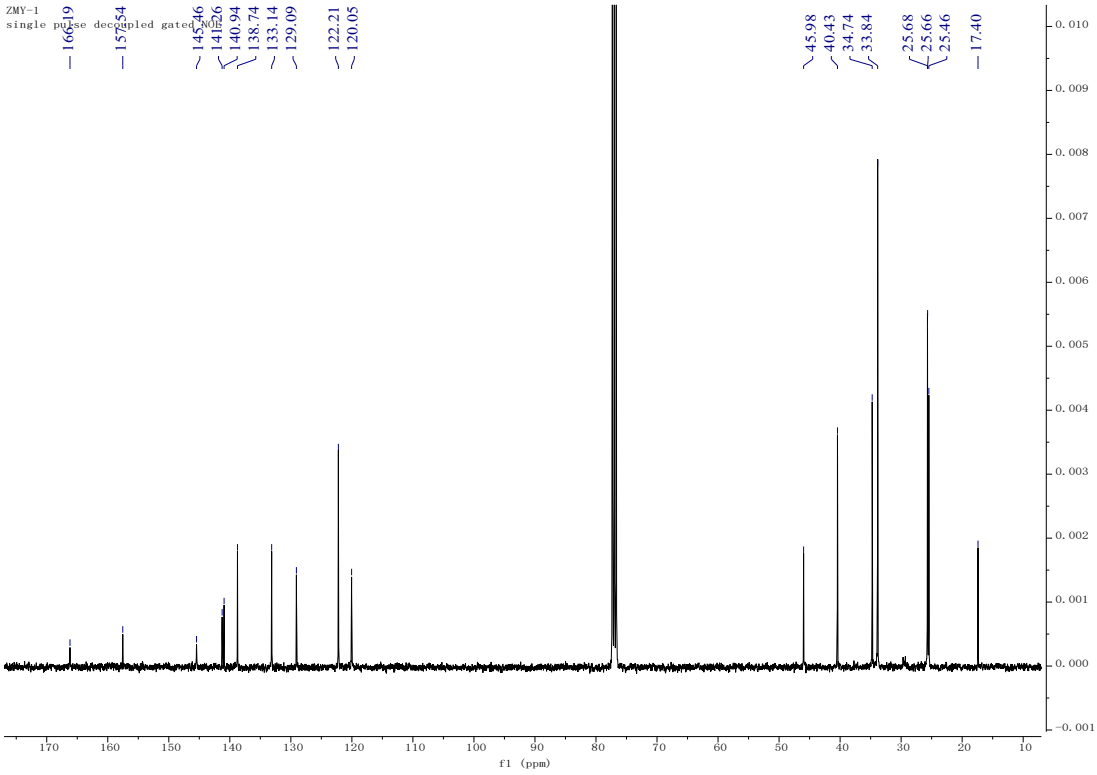

Figure S2. ^{13}C NMR spectrum of **L1** in $CDCl_3$ (400 MHz, 20 ℃).

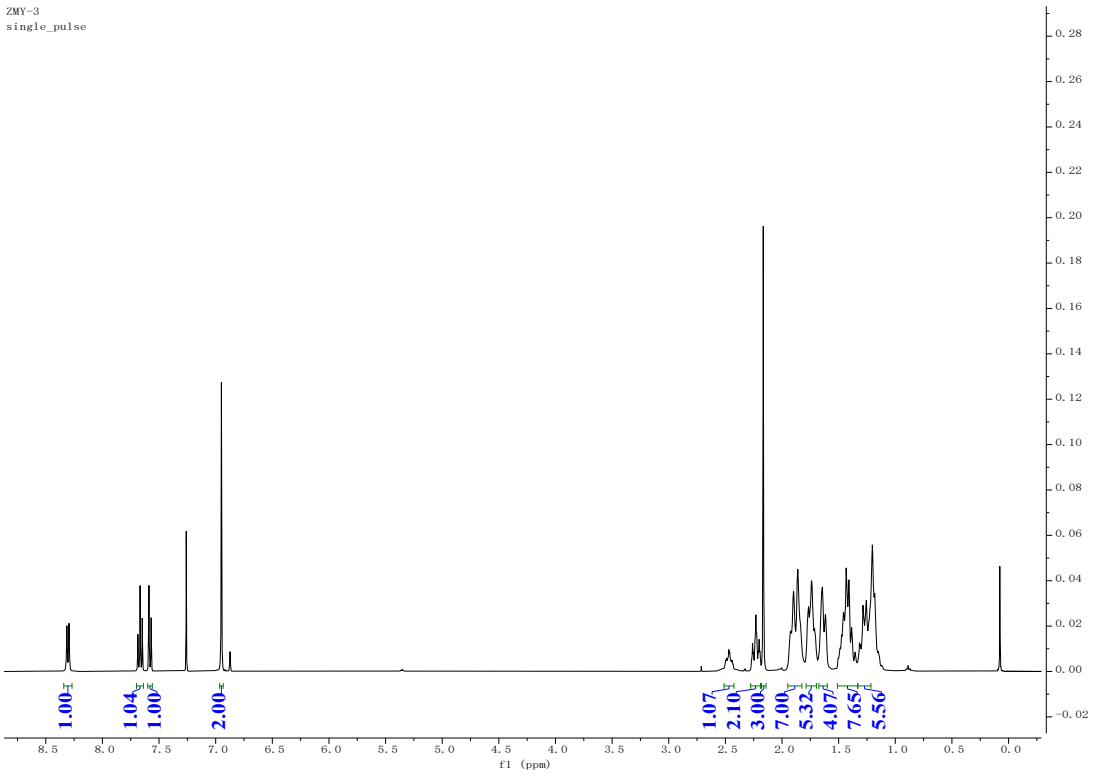

Figure S3. ^{1}H NMR spectrum of **L2** in $CDCl_3$ (400 MHz, 20 ℃).

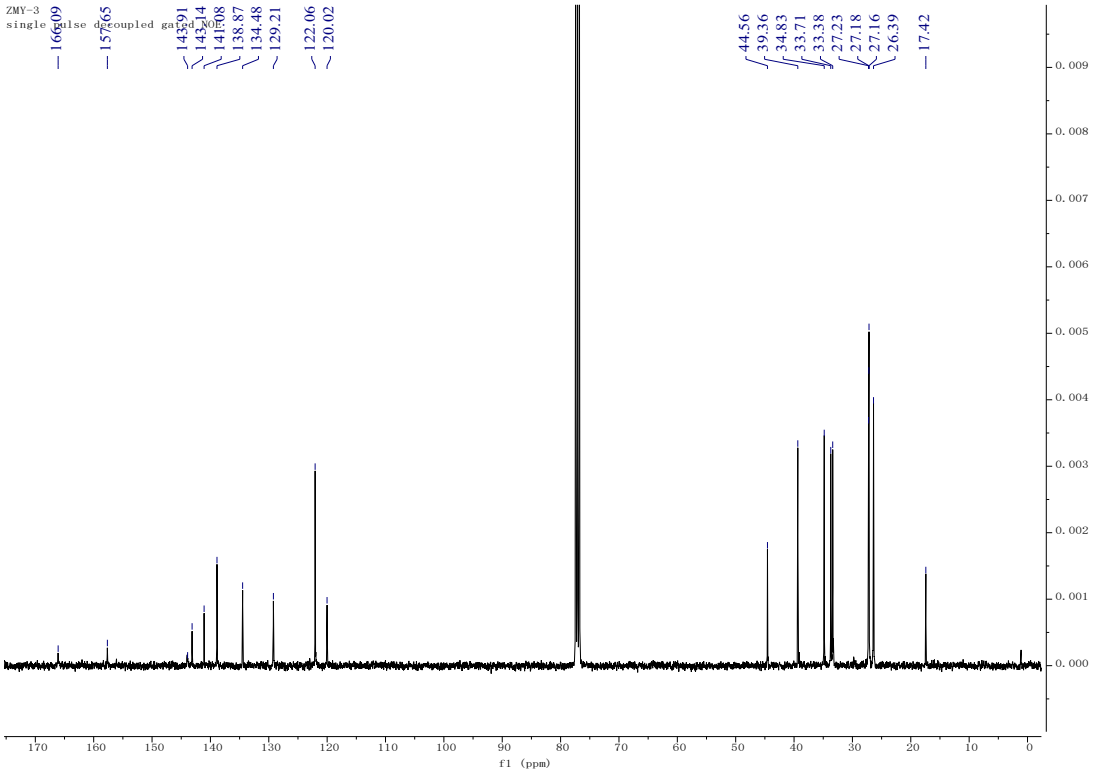

Figure S4. ^{13}C NMR spectrum of **L2** in $CDCl_3$ (400 MHz, 20 ℃).

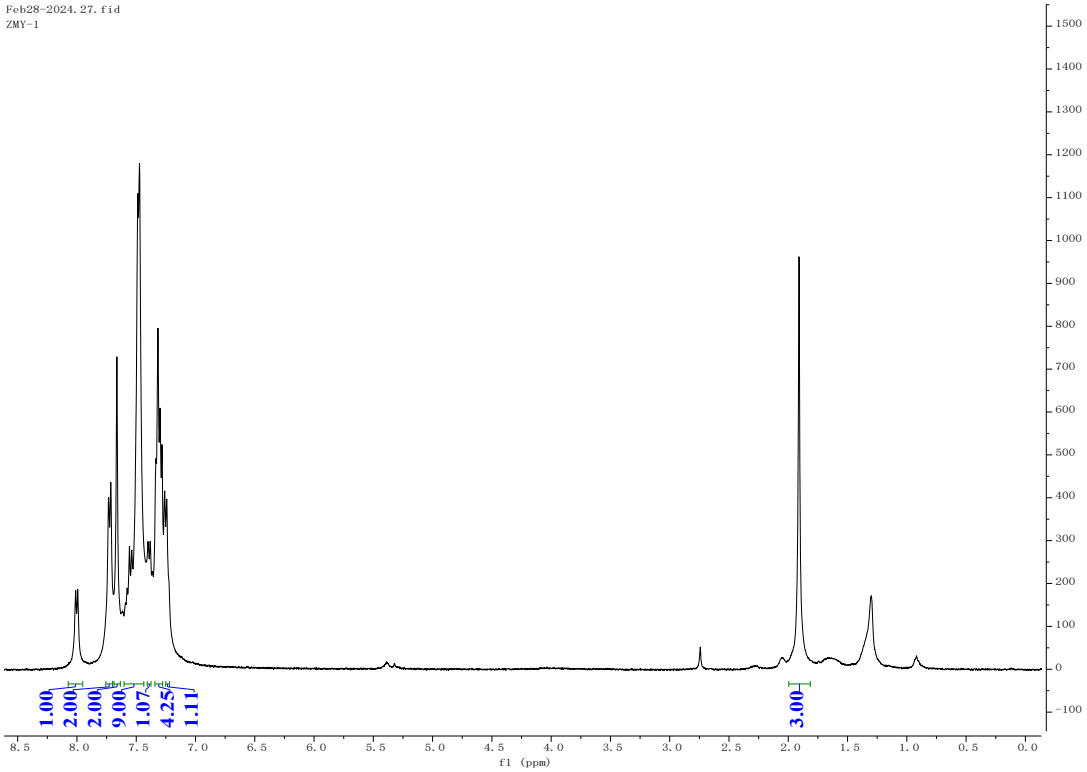

Figure S5. ^{1}H NMR spectrum of **L3** in $CDCl_3$ (400 MHz, 20 ℃).

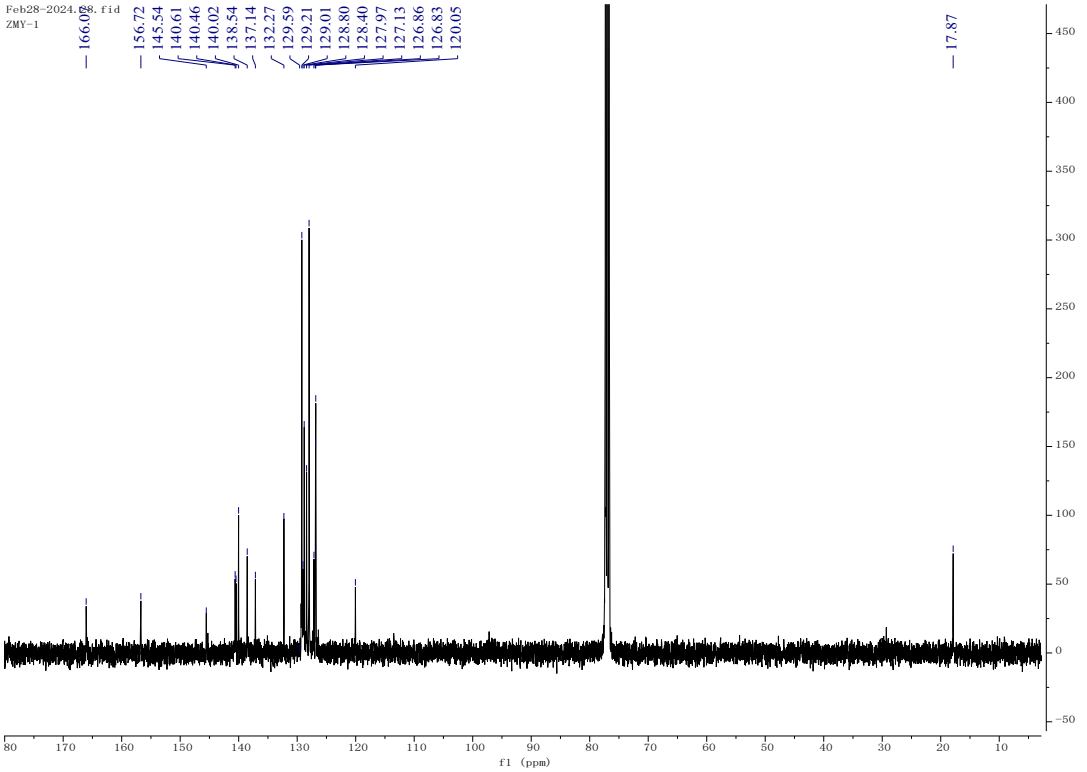

Figure S6. ^{13}C NMR spectrum of **L3** in $CDCl_3$ (400 MHz, 20 ℃).

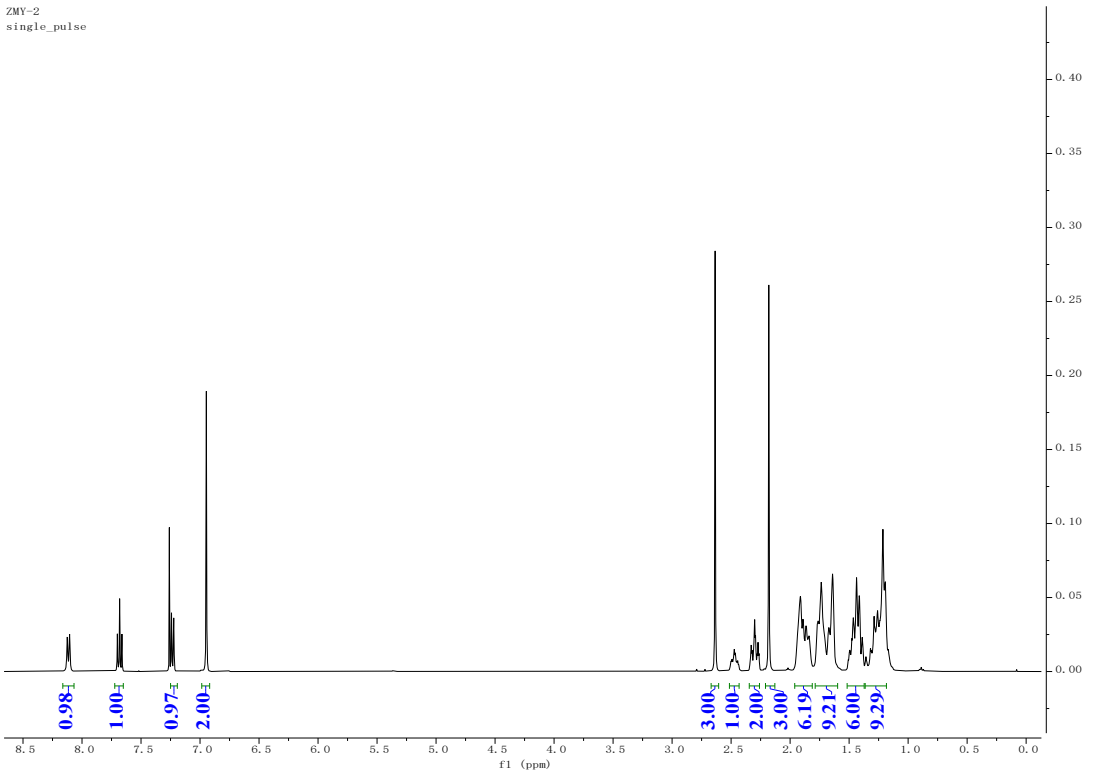

Figure S7. ^{1}H NMR spectrum of **L4** in $CDCl_3$ (400 MHz, 20 ℃).

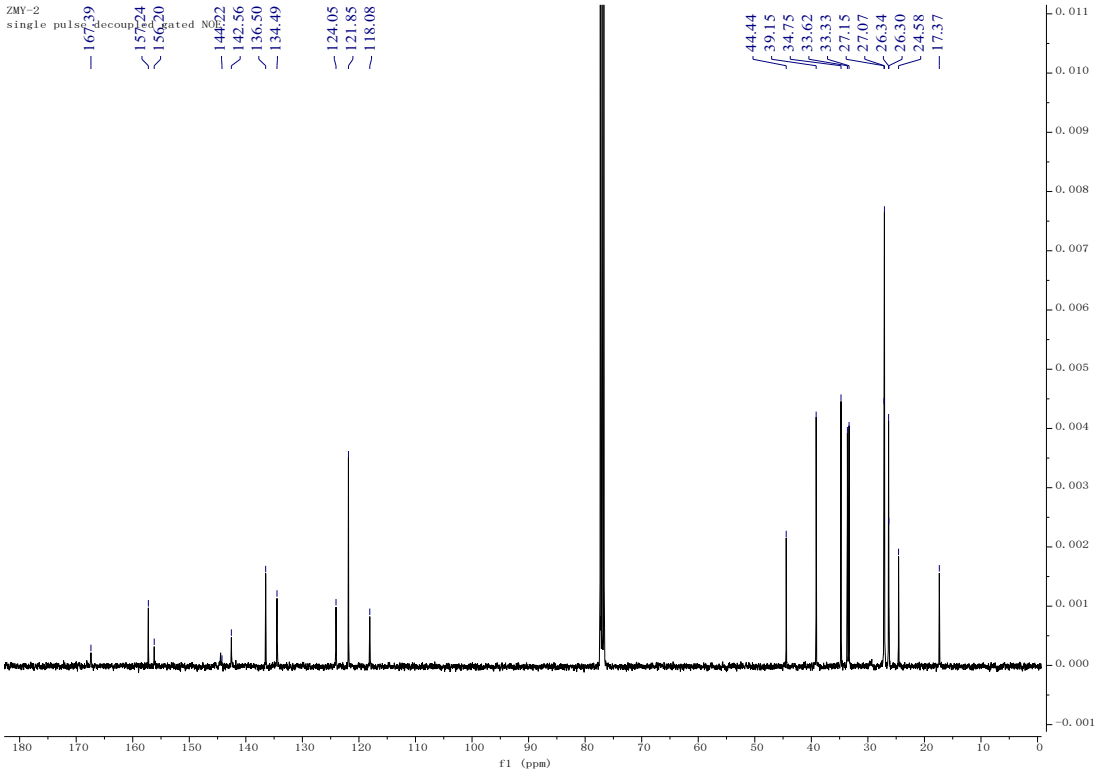

Figure S8. ^{13}C NMR spectrum of **L4** in $CDCl_3$ (400 MHz, 20 ℃).

2.2 MS of L1-L4 and Ni1-Ni4.

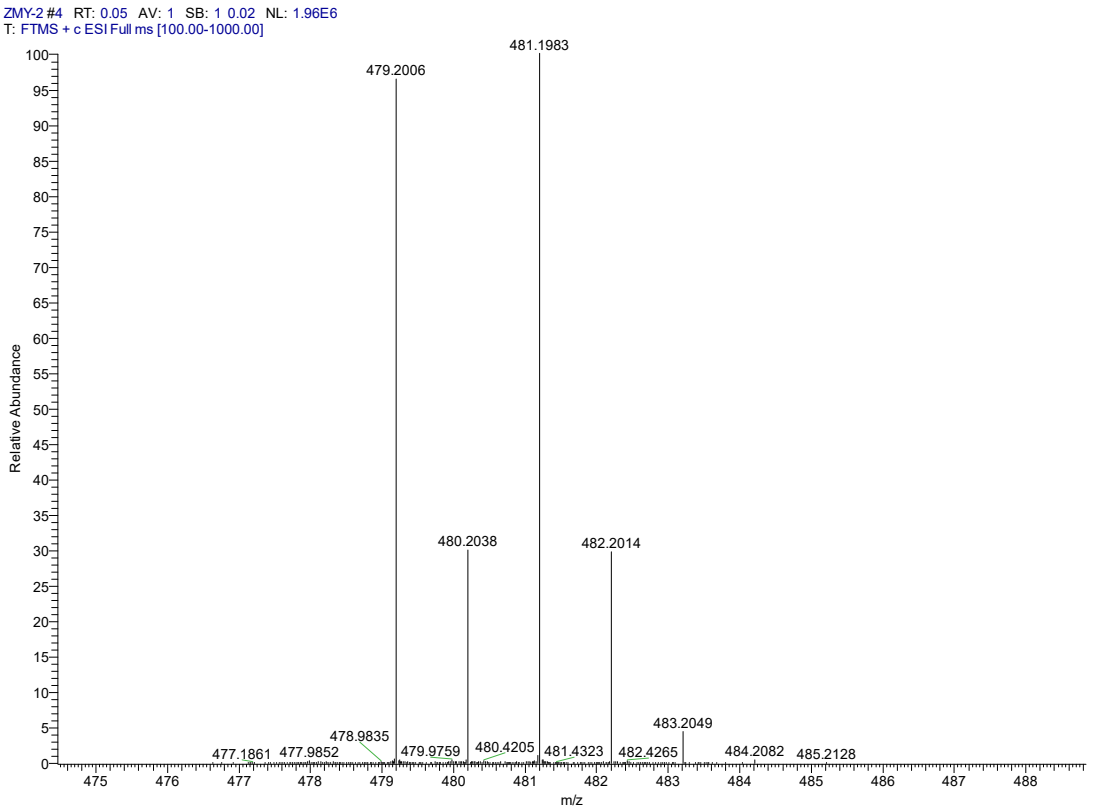

Figure S9. ESI-MS of **L1**.

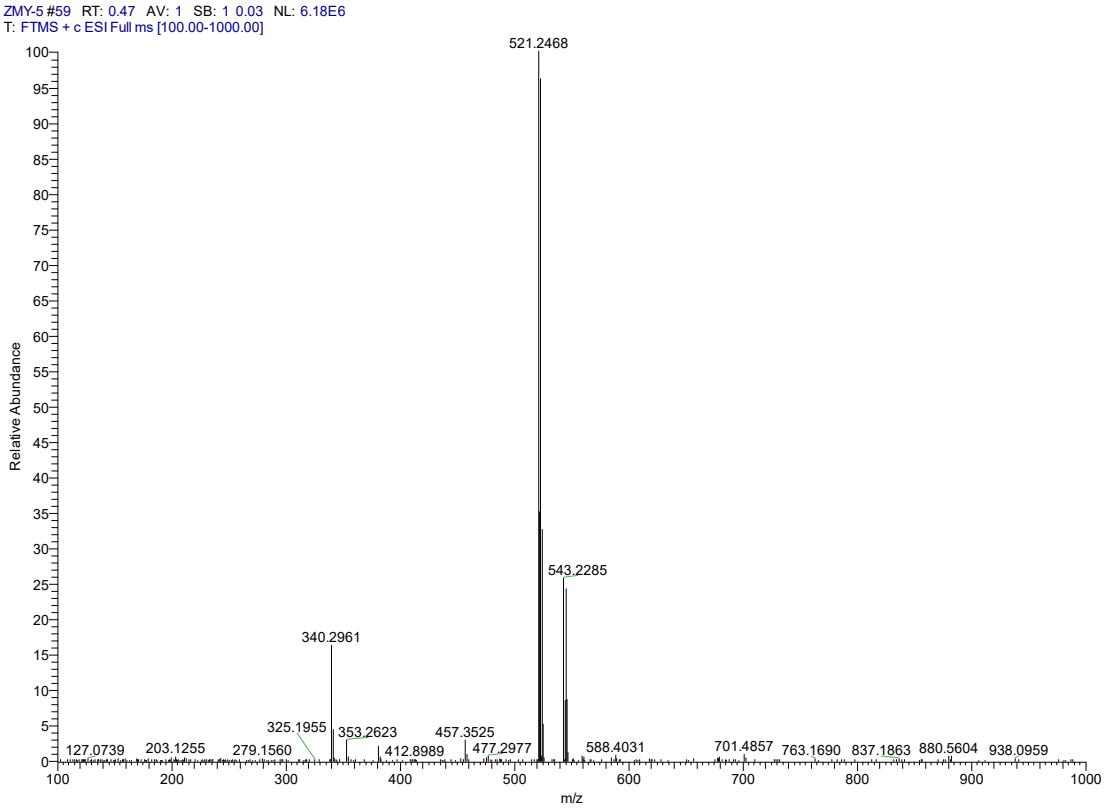

Figure S10. ESI-MS of **L2**.

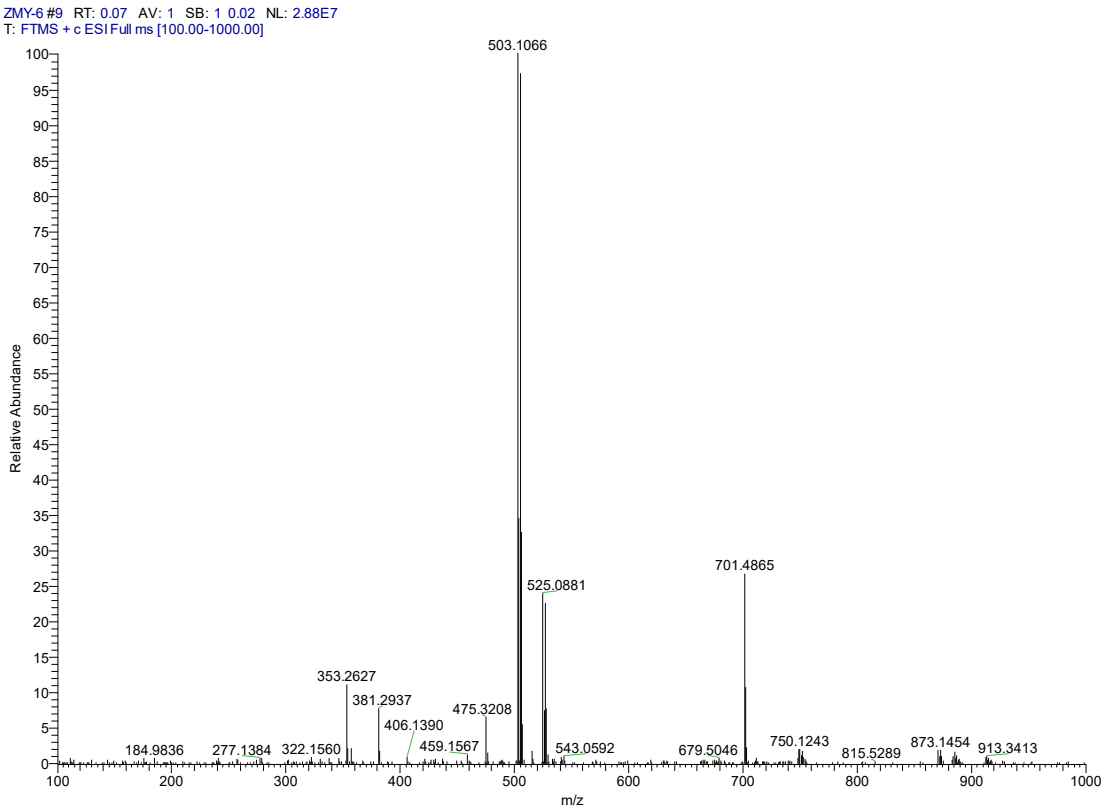

Figure S11. ESI-MS of **L3**.

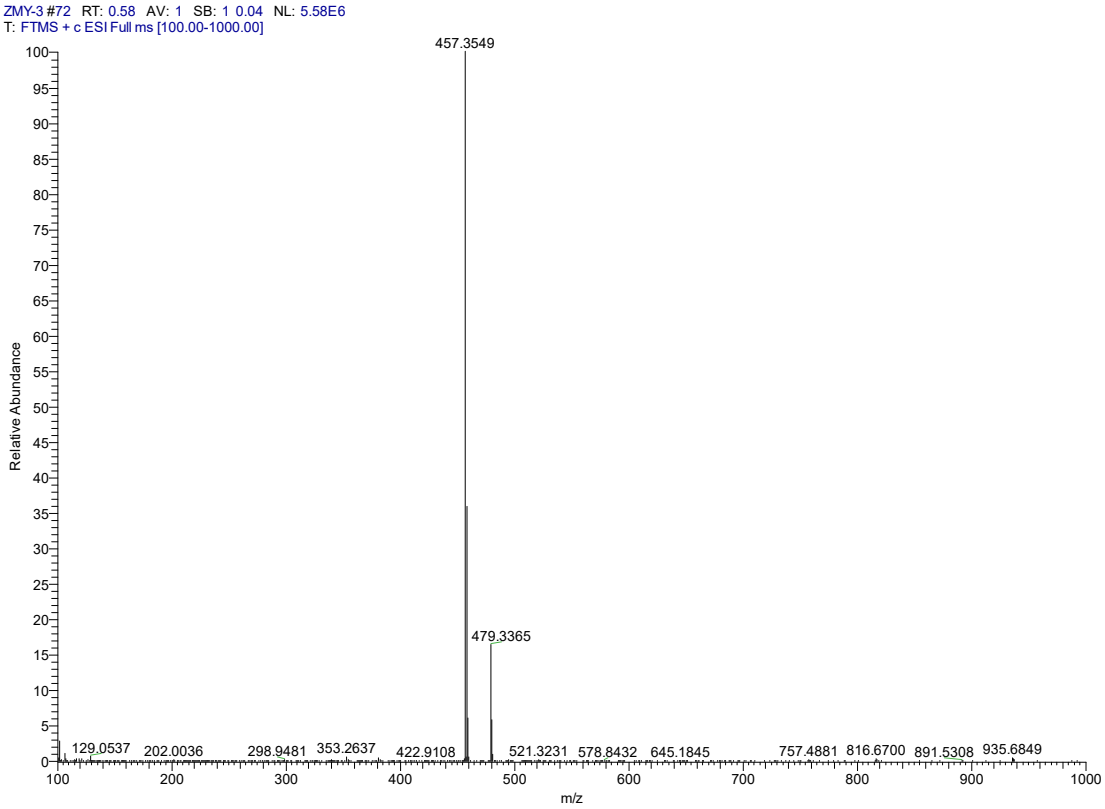

Figure S12. ESI-MS of **L4**.

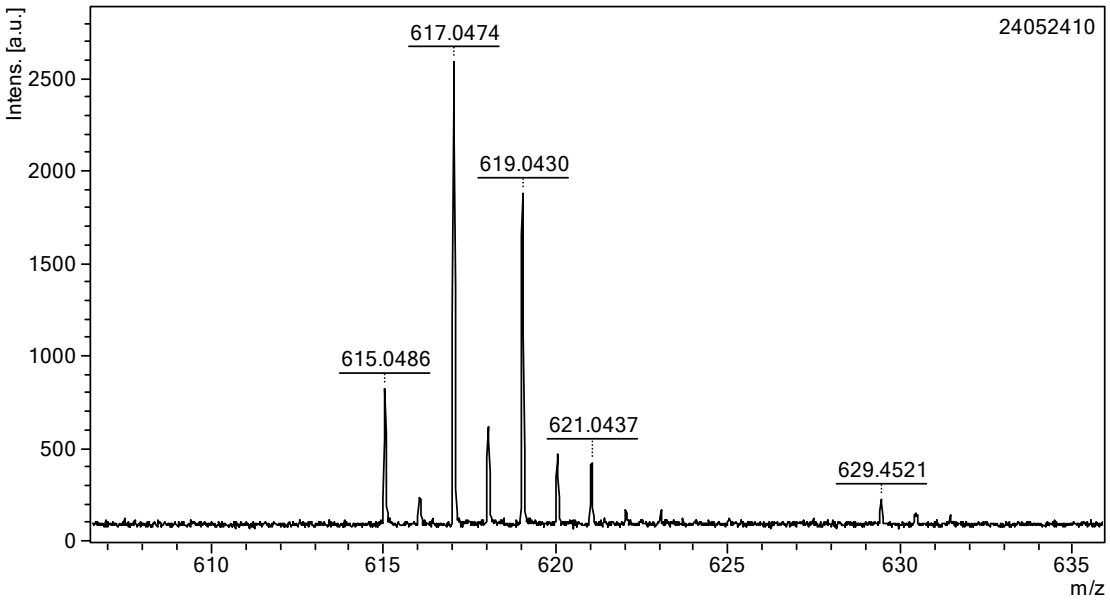

Figure S13. MALDI-TOF-MS of **Ni1**.

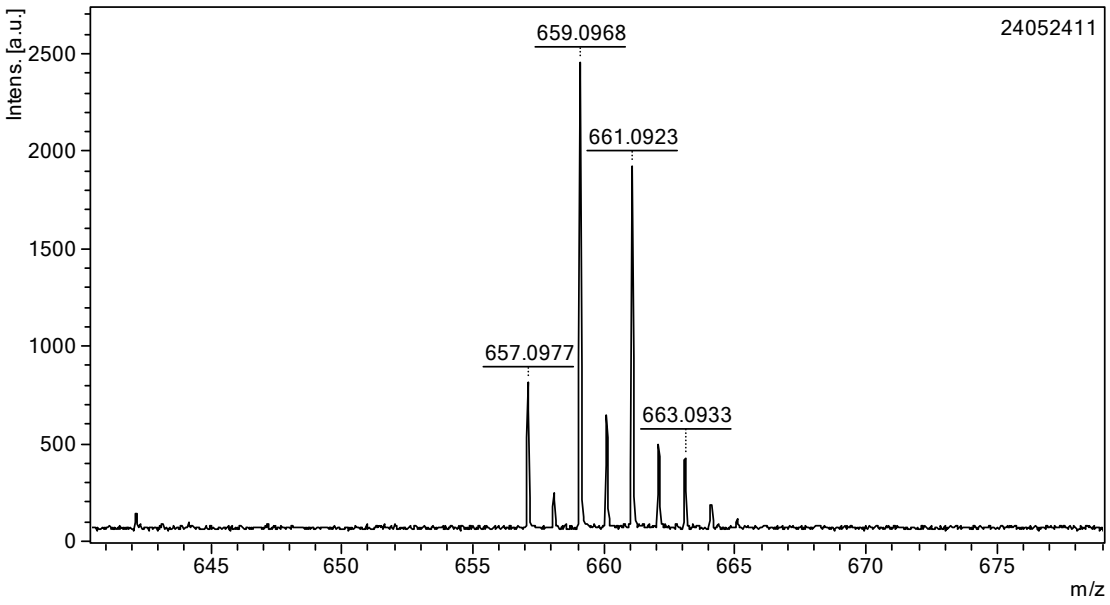

Figure S14. MALDI-TOF-MS of **Ni2**.

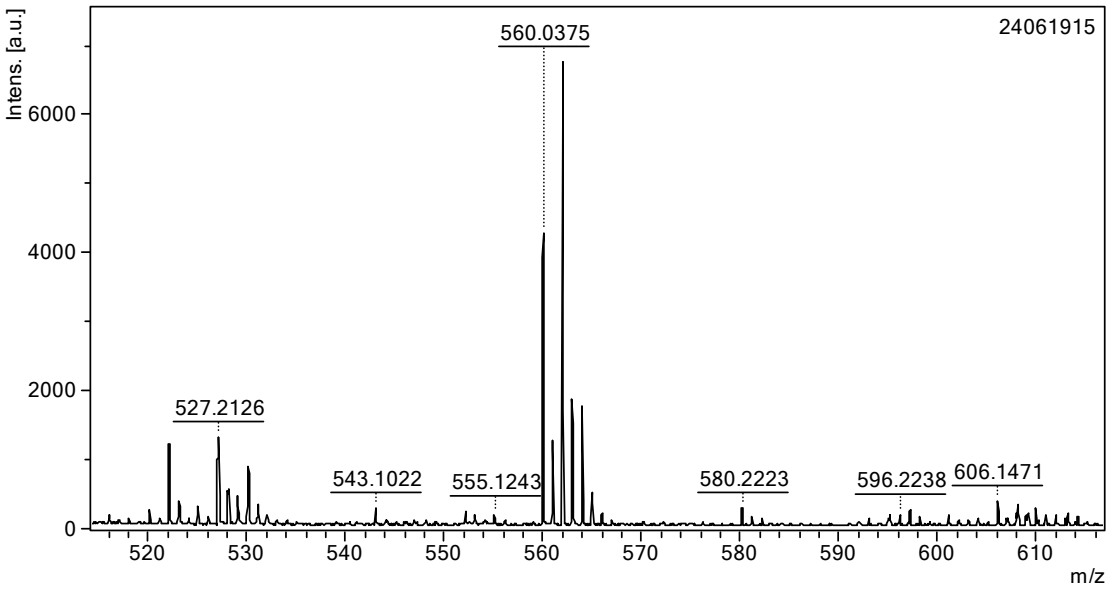

Figure S15. MALDI-TOF-MS of **Ni3**.

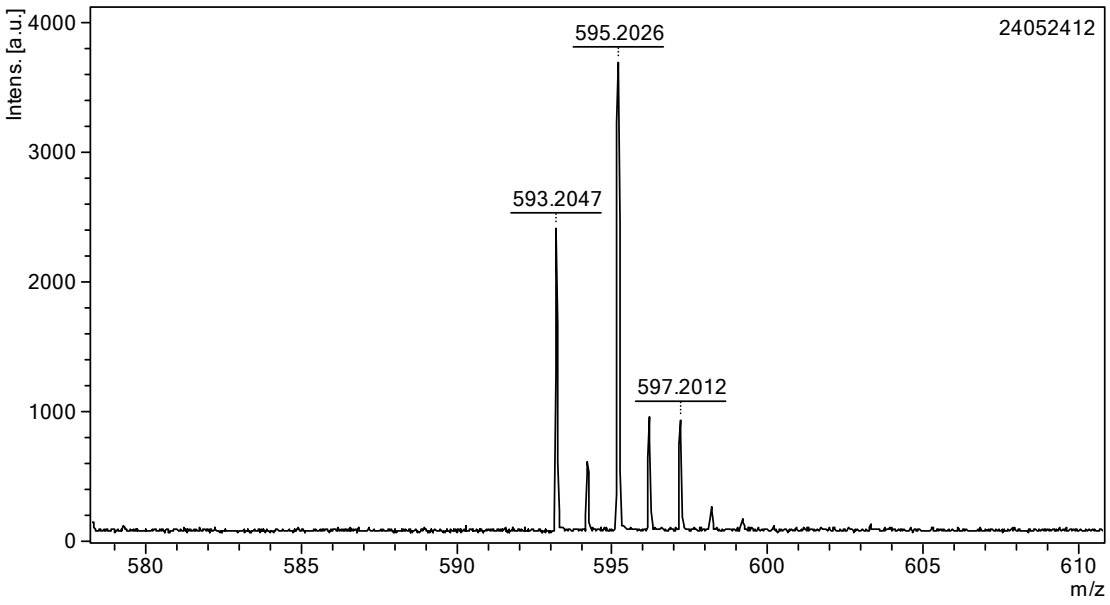

Figure S16. MALDI-TOF-MS of **Ni4**.

2.3 ^{1}H and ^{13}C NMR and GC of Representative HBOEOs.

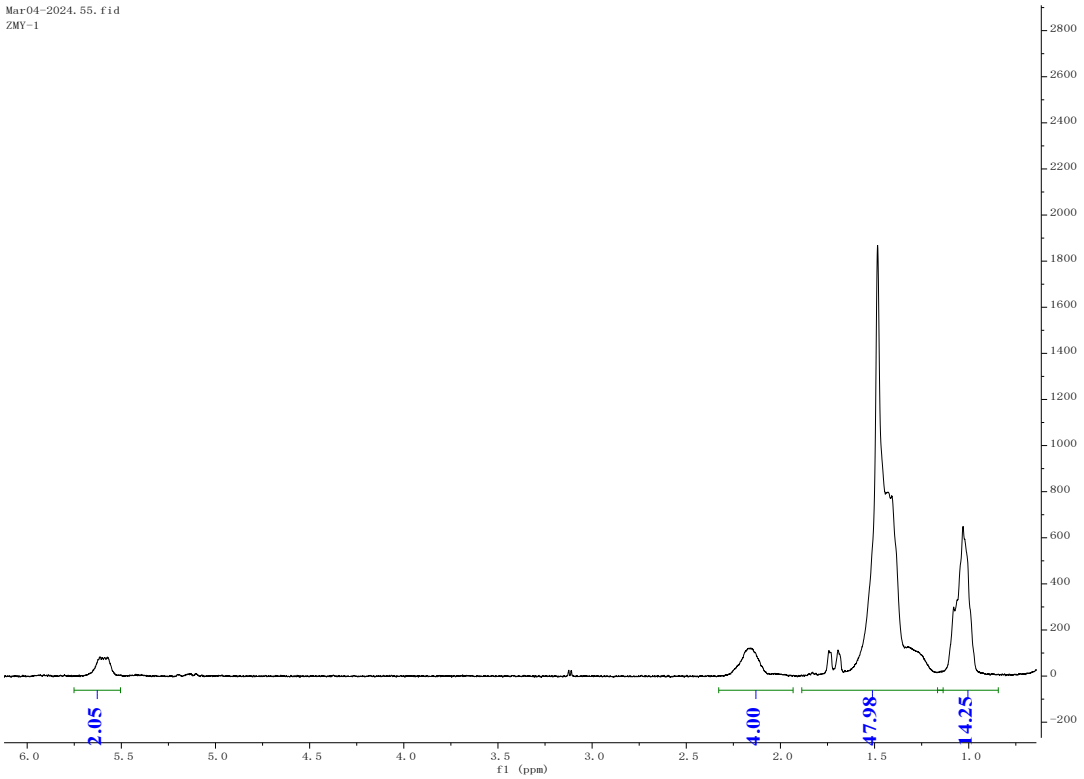

Figure S17. ^{1}H NMR spectrum of the HBOEO from table 1, entry 1 ($CDCl_3$, 20 ^{o}C).

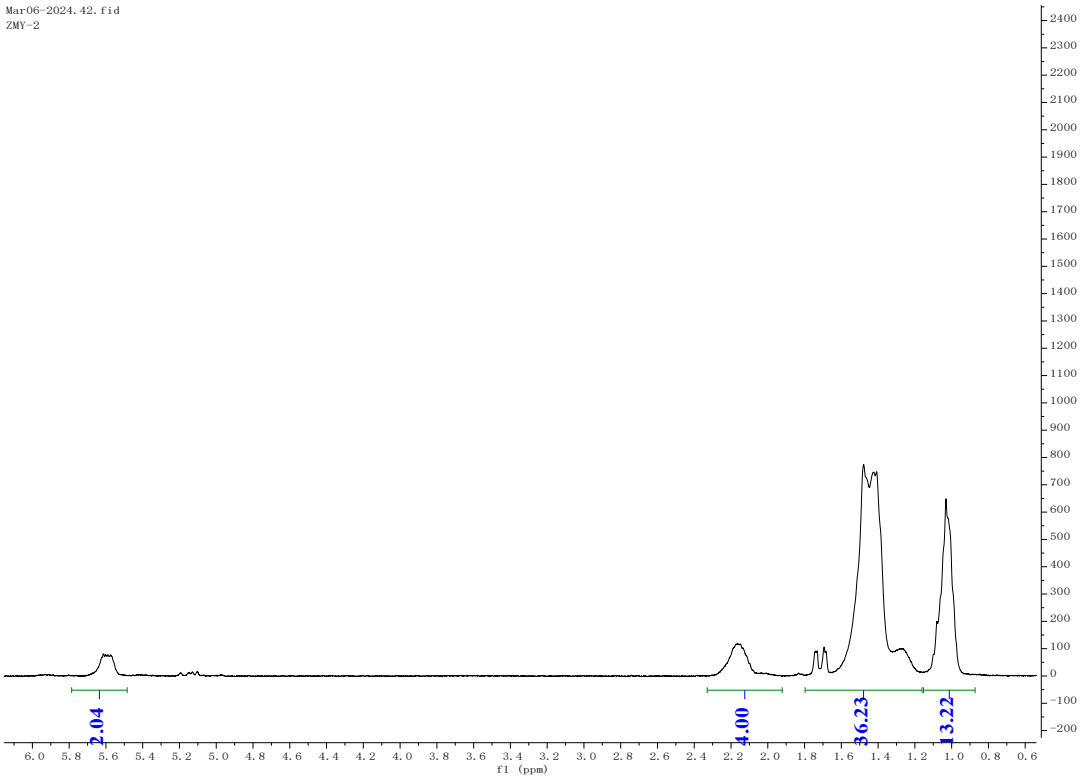

Figure S18. ^{1}H NMR spectrum of the HBOEO from table 1, entry 2 ($CDCl_3$, 20 ^{o}C).

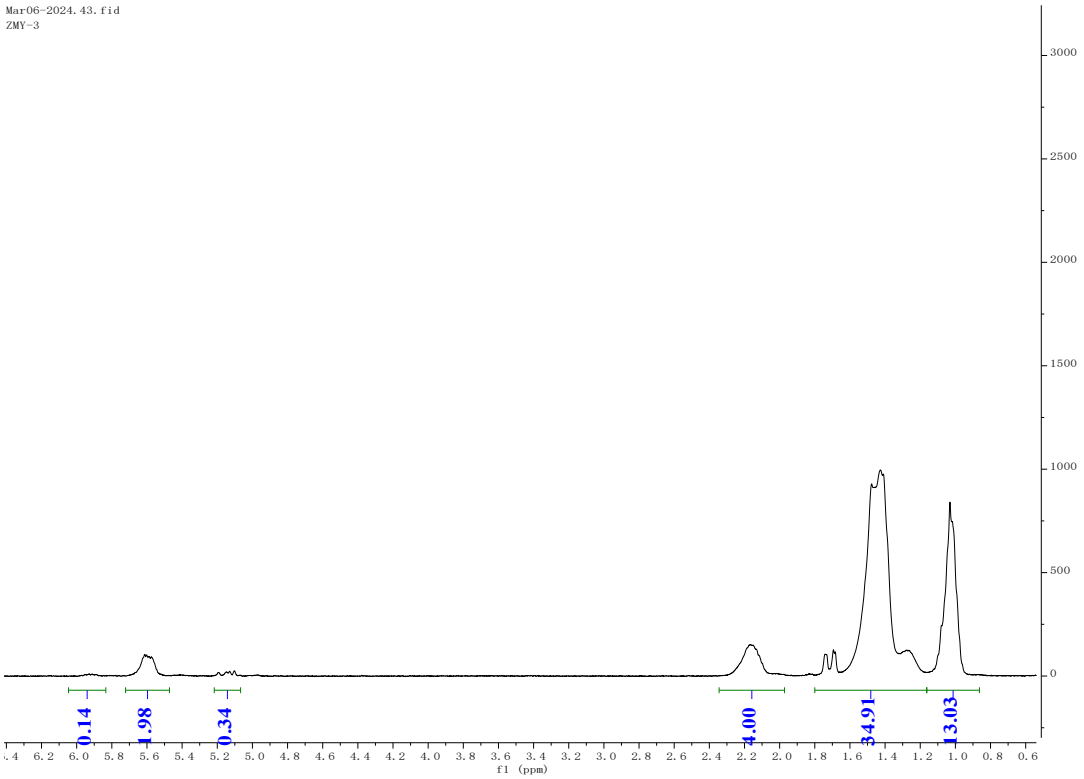

Figure S19. ^{1}H NMR spectrum of the HBOEO from table 1, entry 3 ($CDCl_3$, 20 ^{o}C).

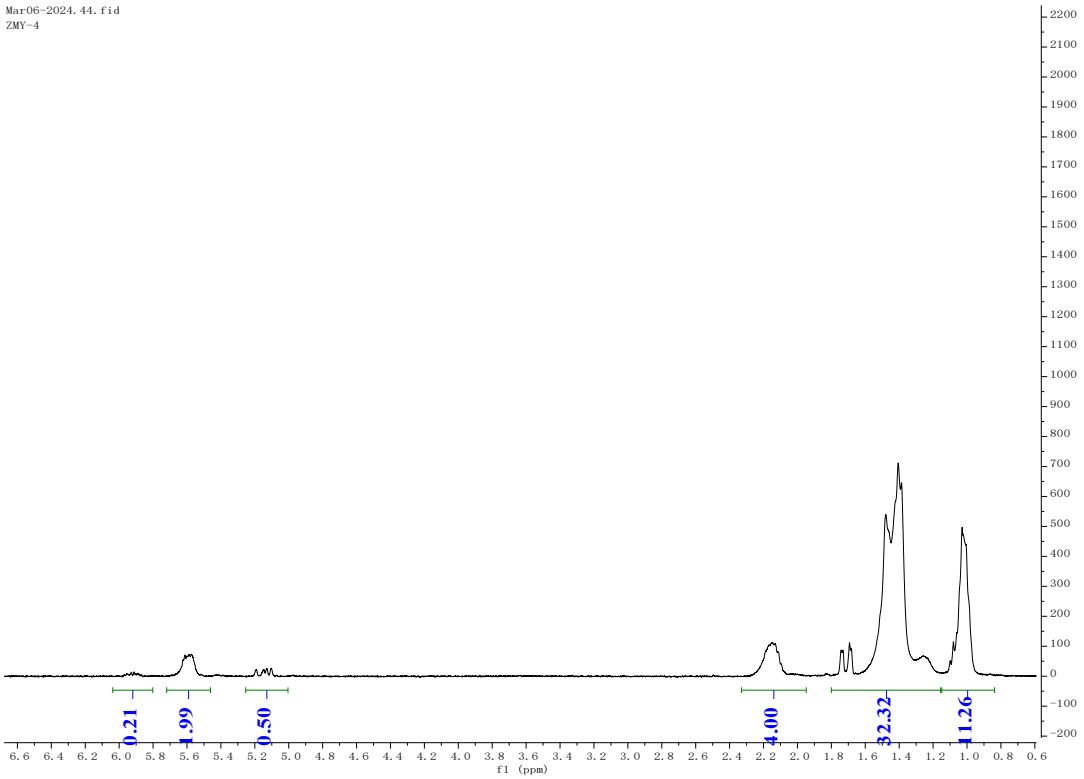

Figure S20. ^{1}H NMR spectrum of the HBOEO from table 1, entry 4 ($CDCl_3$, 20 ^{o}C).

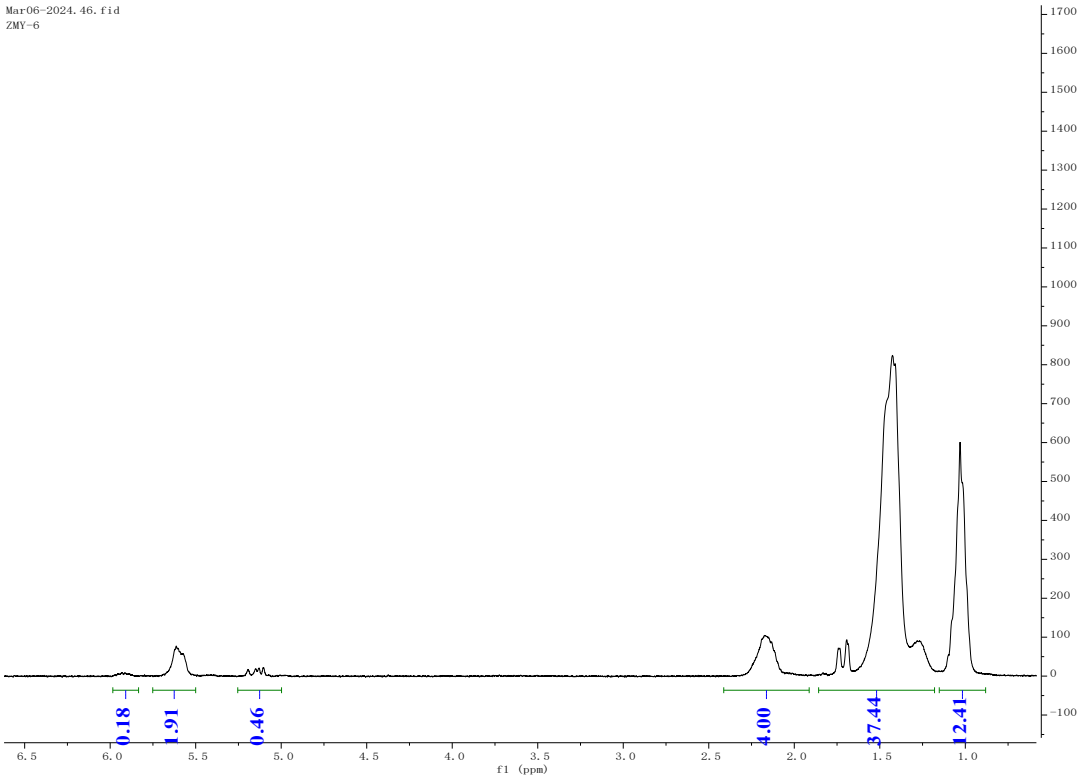

Figure S21. ^{1}H NMR spectrum of the HBOEO from table 1, entry 6 ($CDCl_3$, 20 ^{o}C).

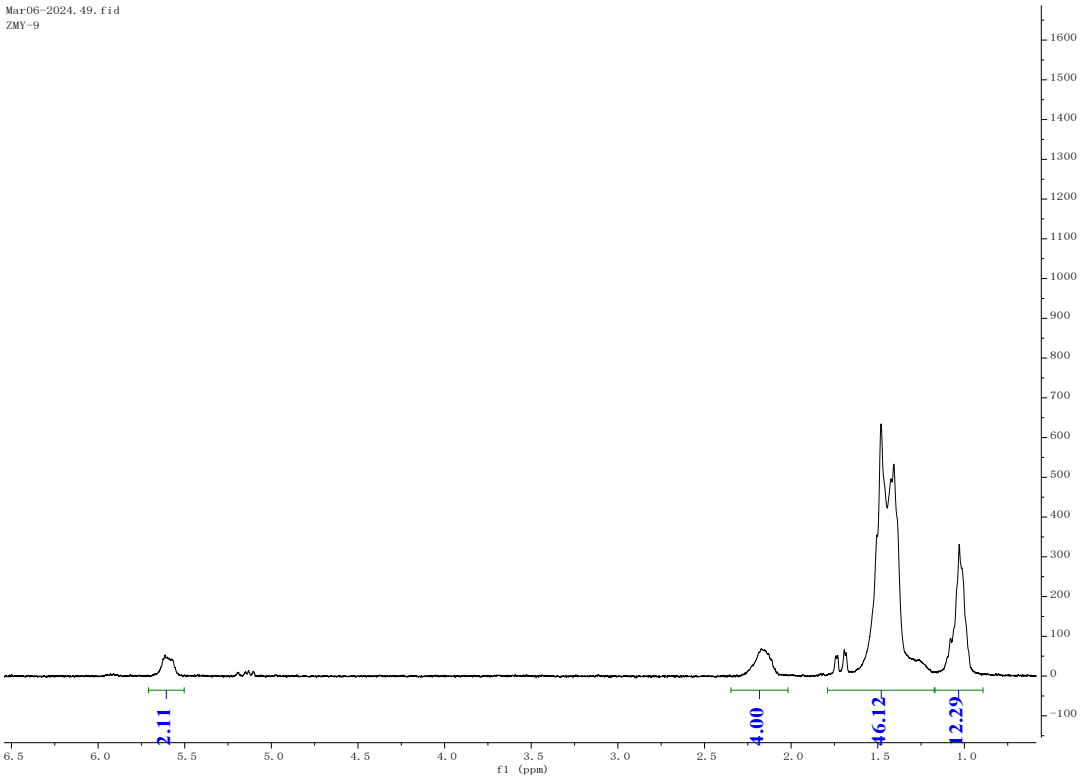

Figure S22. ^{1}H NMR spectrum of the HBOEO from table 1, entry 9 ($CDCl_3$, 20 ^{o}C).

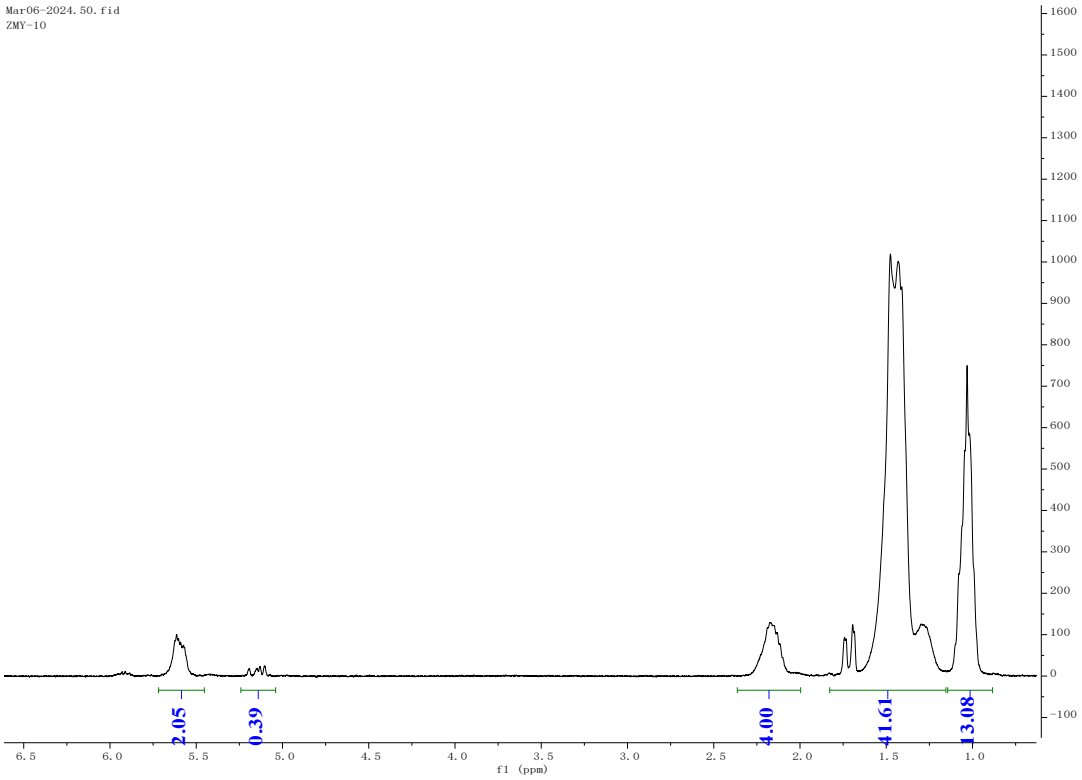

Figure S23. ^{1}H NMR spectrum of the HBOEO from table 1, entry 10 ($CDCl_3$, 20 ^{o}C).

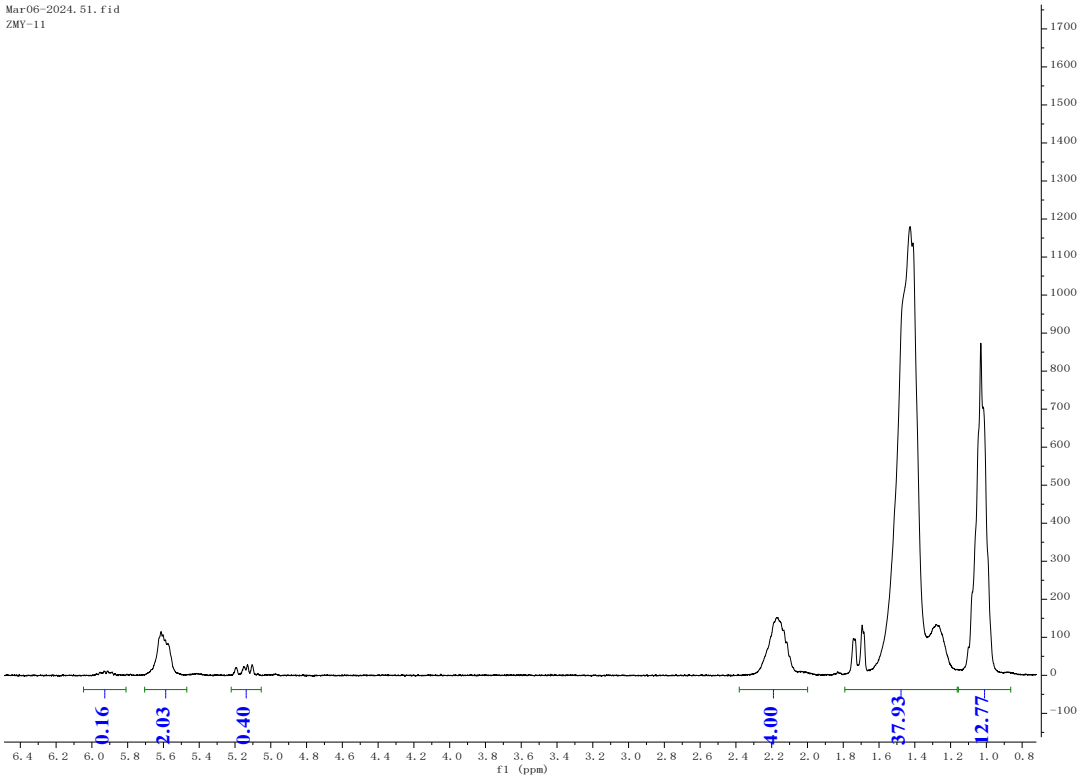

Figure S24. ^{1}H NMR spectrum of the HBOEO from table 1, entry 11 ($CDCl_3$, 20 ^{o}C).

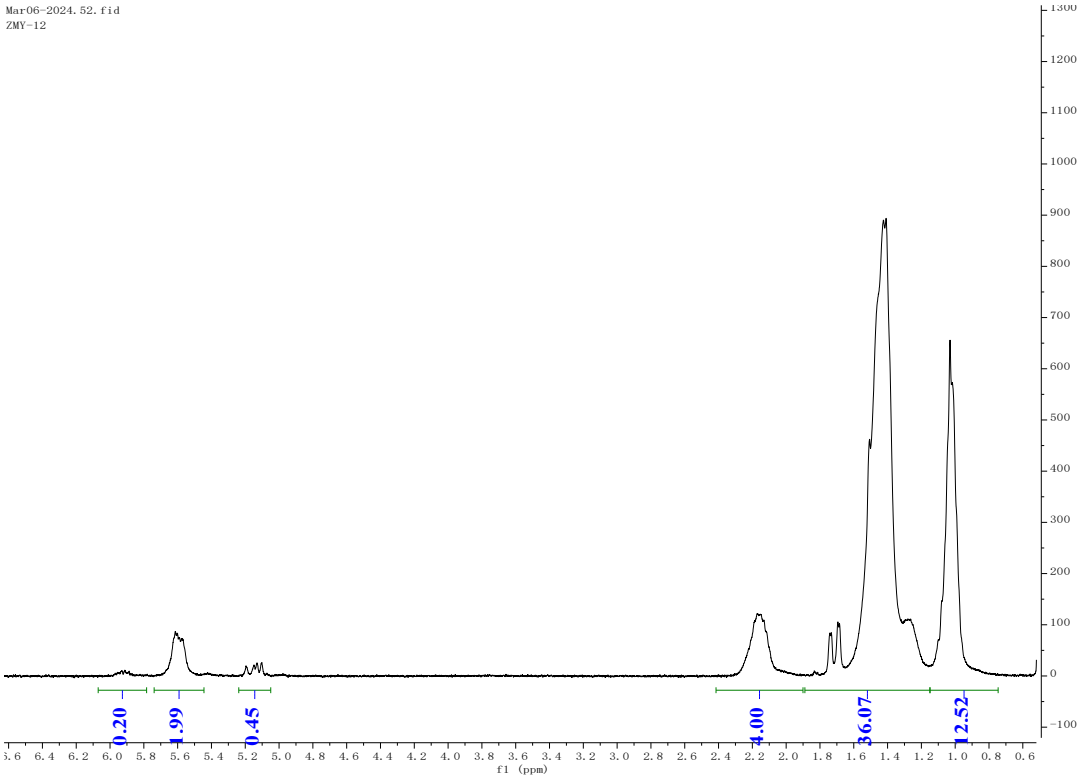

Figure S25. ^{1}H NMR spectrum of the HBOEO from table 1, entry 12 ($CDCl_3$, 20 ^{o}C).

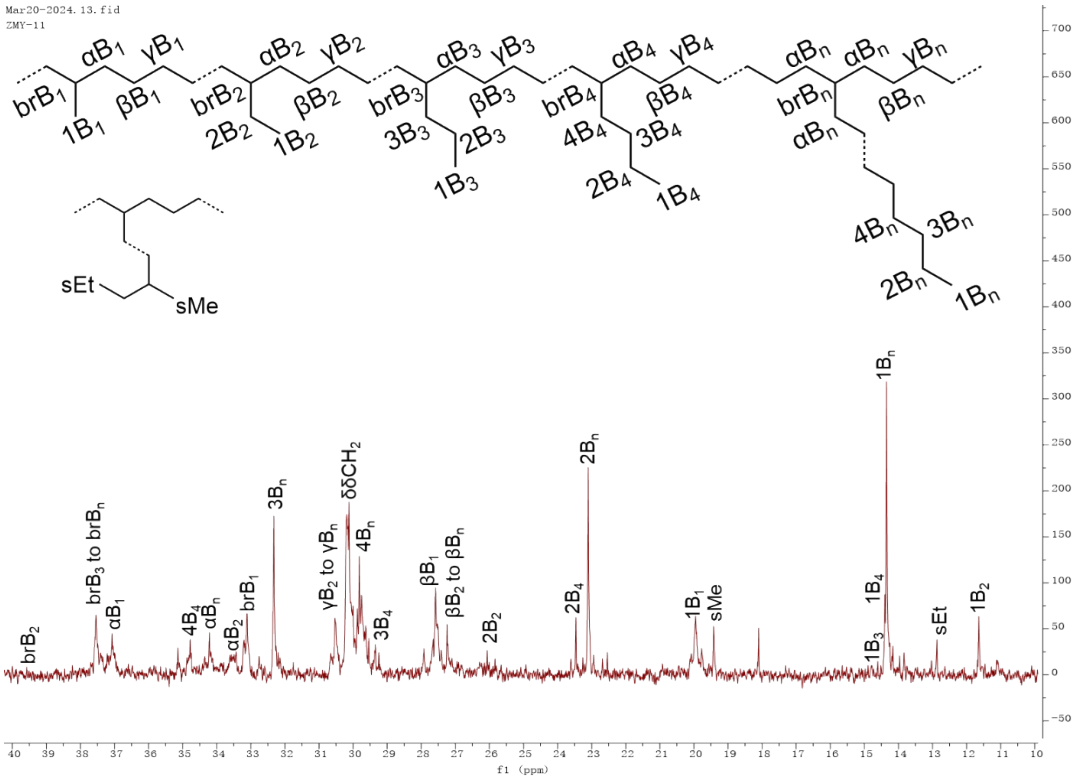

Figure S26. ^{13}C NMR spectrum assignment of HBOEO from table 1, entry 11 ($CDCl_3$, 20 ^{o}C).

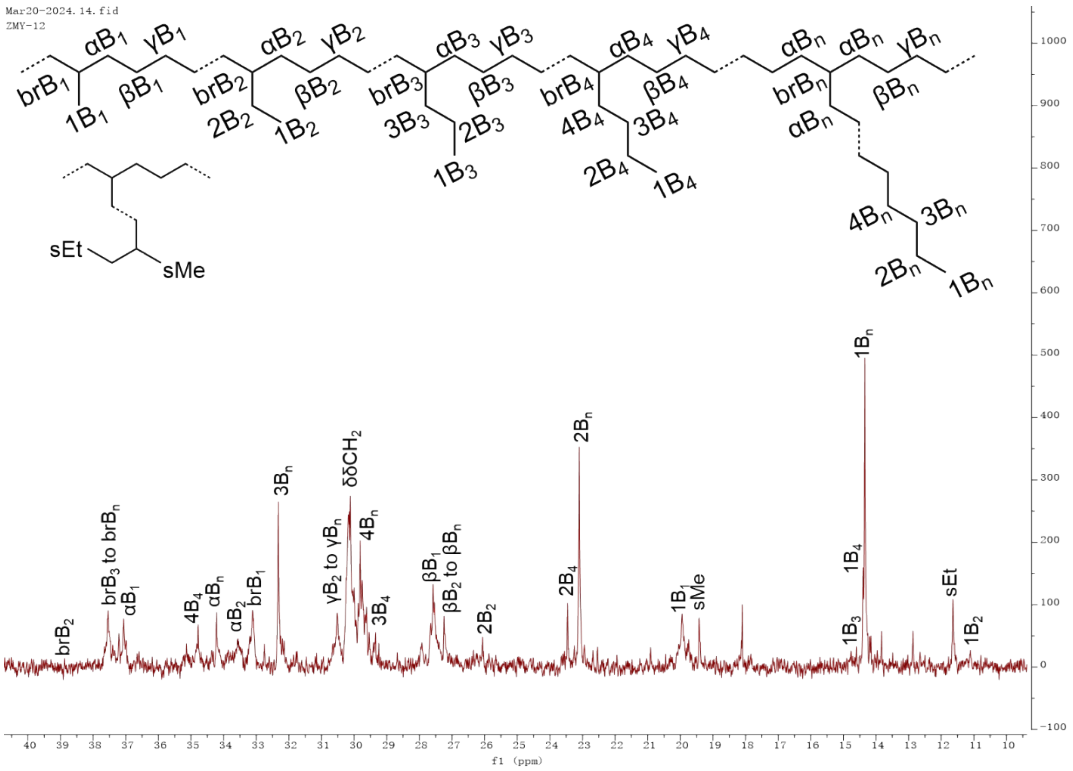

Figure S27. ^{13}C NMR spectrum assignment of HBOEO from table 1, entry 12 ($CDCl_3$, 20 °C).

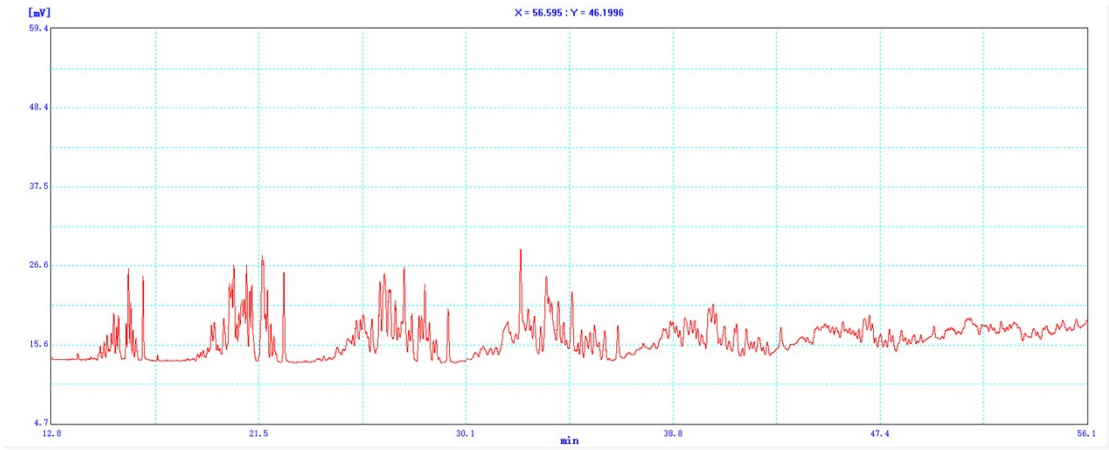

Figure S28. GC of the HBOEO from table 1, entry 1.

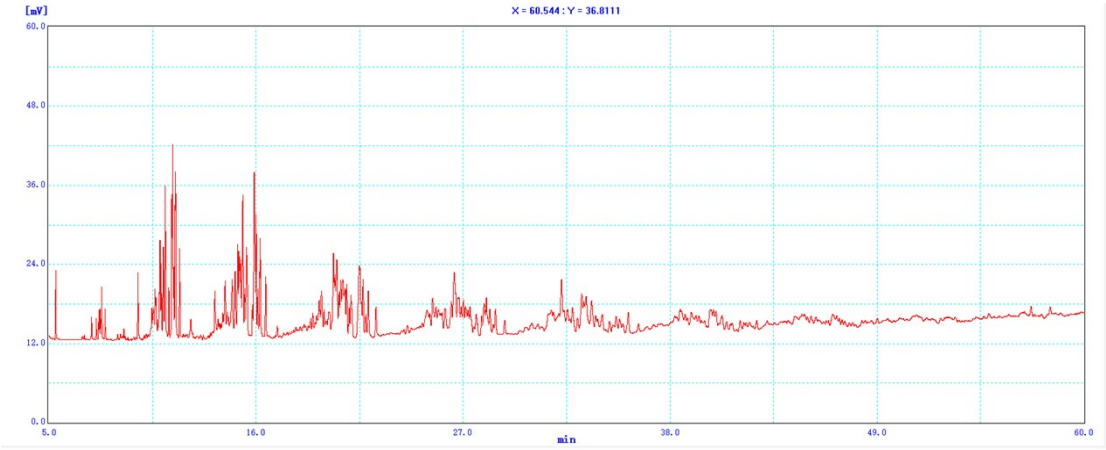

Figure S29. GC of the HBOEO from table 1, entry 2.

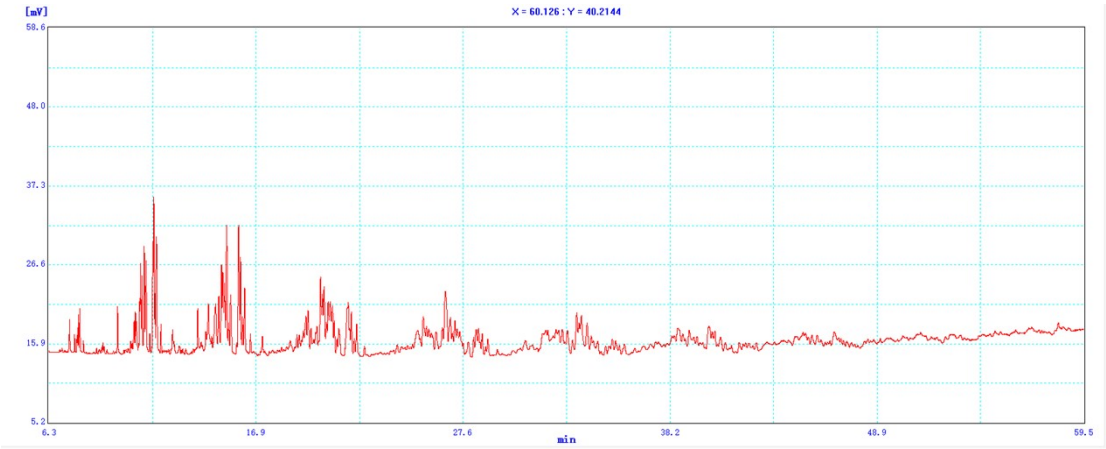

Figure S30. GC of the HBOEO from table 1, entry 3.

3. X-ray Crystallography

Table S1 Crystal data and structure refinement for Ni2.	
Identification code	**Ni2**
Empirical formula	$C_{31}H_{41}Br_3N_2NiO_2$
Formula weight	772.10
Temperature/K	296.93(10)
Crystal system	monoclinic
Space group	-C 2yc
a/Å	18.9221(2)
b/Å	18.1077(2)
c/Å	21.0075(3)
α/°	90
β/°	105.8140(10)
γ/°	90
Volume/Å^3	6925.49(15)
Z	8

ρ_{calc}g/cm^3	1.481
μ/mm^{-1}	5.074
F(000)	3120
Crystal size/mm^3	0.12 × 0.11 × 0.10
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.42 to 156.2
Index ranges	-23 ≤ h ≤ 18, -22 ≤ k ≤ 22, -26 ≤ l ≤ 26
Reflections collected	27825
Independent reflections	6573 [Rint = 0.0392, Rsigma = 0.0455]
Data/restraints/parameters	6573/0/353
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R1 = 0.0508, wR2 = 0.1505
Final R indexes [all data]	R1 = 0.0486, wR2 = 0.1530
Largest diff. peak/hole / e Å^{-3}	-0.6/1.4