Second Coordination Sphere Effect of Benzothiophene Groups Enhancing Chain Transfer in Ethylene (Co)Oligomerization

Huijun Fan† [a, b], Guanru Chang† [b, c], Hui Wang *[d], Shengyu Dai*[a,b]

[a]*School of Chemical and Environmental Engineering, Anhui Polytechnic University, Wuhu, Anhui 241000, China.*
[b]*Institutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Anhui University, Hefei, Anhui, 230601, China.*
[c]*School of Chemistry and Chemical Engineering, Key Laboratory of Inorganic Functional Material, Huangshan University, Huangshan, Anhui 245041, China*
[d]*School of Chemistry and Chemical Engineering, Hefei Normal University, Hefei, Anhui 230061, China*

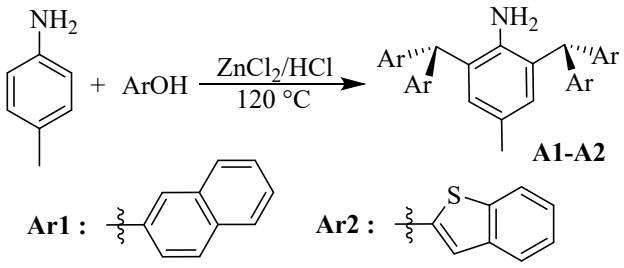
†The first two authors are equal first authors.

1. Experimental Sections

1.1 General Considerations

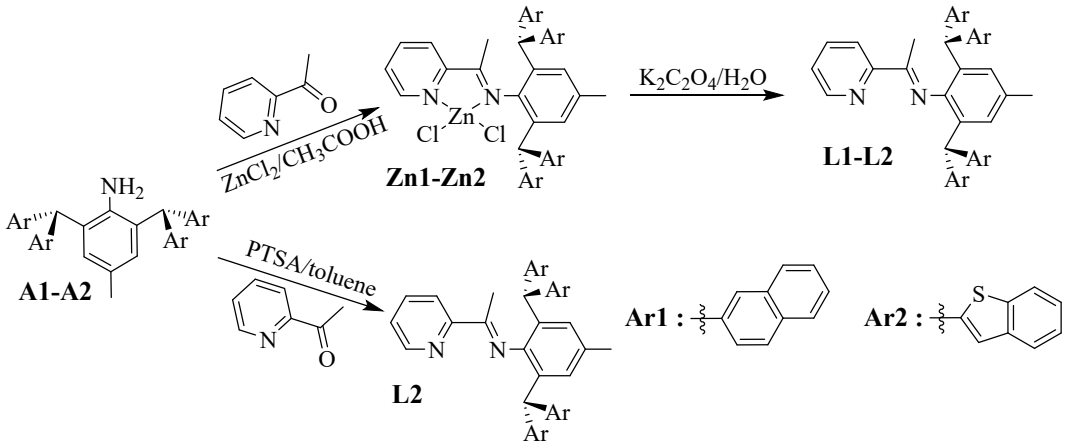
All chemicals were commercially sourced, except those whose synthesis is described. All experiments were carried out under a dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded by a JEOL JNM-ECZ600R 600 or 400 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 and Elemental analysis were performed by the Analytical Center of the Anhui University.

1.2 Procedure for the Synthesis of Arylamines A1-A2.

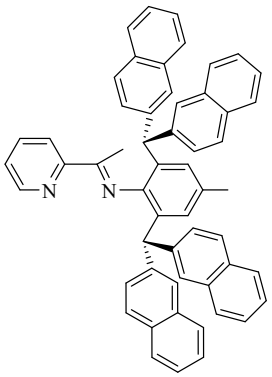


The arylamines were synthesized according to the literature procedure.[1]

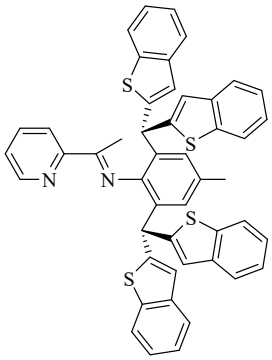
1.3 Procedure for the Synthesis of Ligands L1-L2.



The ligands **L1-L2** were prepared as follows: $ZnCl_2$ (0.34 g, 2.5 mmol) and 2-acetylpyridine (2.0 mmol), were suspended in glacial acetic acid (5 mL). Anilines (2 mmol) was added, and the reaction mixture was refluxed under stirring for 4 h. The solution was allowed to cool to room temperature, and a bright yellow solid precipitated. The solid was separated by filtration and washed with acetic acid (3 × 5 mL) and diethyl ether (5 × 5 mL), to remove remaining acetic acid. Drying under vacuum gave bright yellow, poorly soluble solid. Then the zinc was removed from the zinc diimine complex. The product of the previous step was suspended in methylene chloride (30 mL), and a solution of potassium oxalate (0.41 g, 2.2 mmol) in water (5 mL) was added. The reaction mixture was stirred vigorously for 1 h. The two phases were separated, and the organic layer was washed with water (3 × 20 mL) and dried with $MgSO_4$. After filtration, the solvent was removed under vacuum, **L1-L2** afforded the product as a yellow powder, and dried under high vacuum. Whereas ligand **L2** was also prepared from the condensation of 2-acetylpyridine and **A2** catalyzed by acid in toluene due to the low yield of the above template preparation method for **L2**. 2-Acetylpyridine (0.73 g, 6 mmol) and the aniline **A2** (0.74 g, 2 mmol) were dissolved in anhydrous toluene. Subsequently, a catalytic amount of *p*-methylbenzenesulfonic acid (0.02 g) was added in the solution, and the reaction mixture was refluxed under stirring. After 12 h, the reaction mixture was concentrated and 20 ml ethanol was added. The yellow solid precipitated and was separated by filtration. The pure product can be obtained by layering their CH_2Cl_2 solution with ethanol at room temperature.

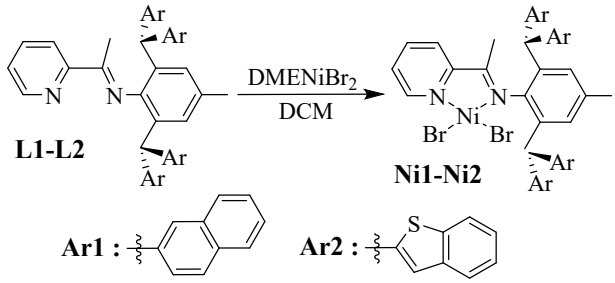


L1: (1.08 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.4 Hz, 1H, Ar-*H*), 7.96 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.87 – 7.70 (m, 8H, Ar-*H*), 7.64 (t, *J* = 6.5 Hz, 3H, Ar-*H*), 7.57 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.50 – 7.39 (m, 12H, Ar-*H*), 7.34 (d, *J* = 8.8 Hz, 3H, Ar-*H*), 7.30 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 6.84 (s, 2H, Ar-*H*), 5.62 (s, 2H, C*H*Ar_2), 2.19 (s, 3H, CH_3), 1.09 (s, 3H, Ar-C(CH_3)=N). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.47 (*C*=N), 155.91, 148.46, 146.48, 141.18, 139.99, 136.09, 133.46, 133.35, 132.16, 132.14, 131.94, 129.08, 128.51, 128.32, 127.96, 127.94, 127.85, 127.81, 127.61, 127.58, 127.52, 125.87, 125.77, 125.59, 125.46, 124.67, 121.49, 52.43 (*C*HAr_2), 21.36 (*C*H_3), 17.21 (Ar-C(*C*H_3)=N). APCI-MS (m/z): calcd for $C_{56}H_{43}N_2$: 743.3421, Found, 743.3430, $[M+H]^+$.

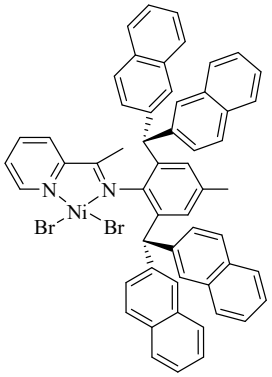


L2: (1.06 g, 69%). The solubility of **L2** is too poor to obtain the corresponding ^{1}H and ^{13}C NMR spectra. APCI-MS (m/z): calcd for $C_{48}H_{35}N_2S_4$: 767.1678, Found, 767.1685, $[M+H]^+$.

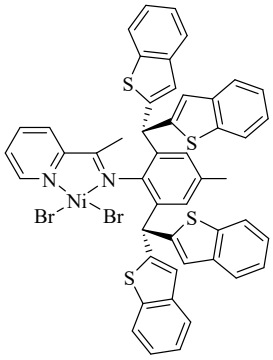
1.4 Procedure for the Synthesis of Nickel Complexes Ni1-Ni2.



Complexes **Ni1-Ni2** were synthesized by the reaction of 1 equiv. of (DME)$NiBr_2$ with the corresponding ligands in methylene chloride. The corresponding ligand (0.2 mmol) was added in 5 mL of methylene chloride in a Schlenk tube under a nitrogen atmosphere. (DME)$NiBr_2$ (0.2 mmol, 62 mg) was added to the above solution. The resulting mixture was stirred at room temperature overnight. The solvent was evaporated under reduced pressure to afford a solid. The product was washed with 4 × 5 mL hexane and dried under vacuum.

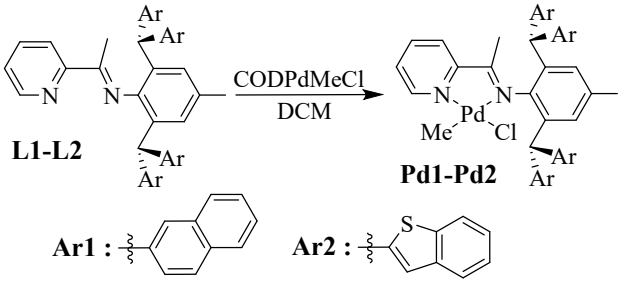


Ni1: (160 mg, 83%). Elemental analysis: calc. for $C_{56}H_{42}Br_2N_2Ni$: C, 69.96; H, 4.40; N, 2.91. Found: C, 69.87; H, 4.31; N, 2.84.

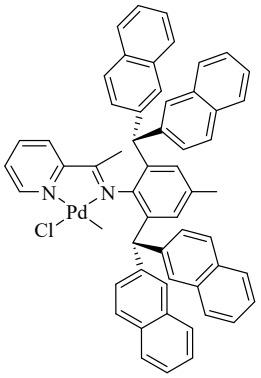


Ni2: (152 mg, 77%). Elemental analysis: calc. for $C_{48}H_{34}Br_2N_2NiS_4$: C, 58.50; H, 3.48; N, 2.84. Found: C, 58.31; H, 3.29; N, 2.71.

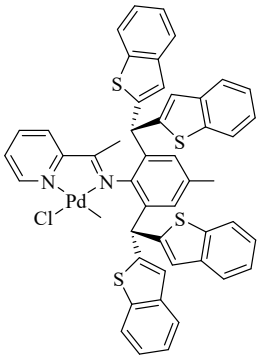
1.5 Procedure for the Synthesis of Palladium Complexes Pd1-Pd2.



A mixture of the ligand (0.5 mmol), (COD)PdMeCl (133 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) was stirred for 24 h at room temperature. During stirring, the color of the solution was deepening. At the end of the reaction, the solvent was partially evaporated under reduced pressure. The remaining mixture was diluted with Et_2O (20 mL). The resulting yellow solid was collected by filtration, dried in vacuum.



Pd1: (364 mg, 81%). a-isomer: b-isomer = 10:1 ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 –9.72, 9.49 – 9.43 (m, 1H, Ar-*H*), 7.79 (dd, *J* = 15.2, 8.3 Hz, 4H, Ar-*H*), 7.72 (d, *J* = 5.0 Hz, 1H, Ar-*H*), 7.68 (d, *J* = 8.2 Hz, 3H, Ar-*H*), 7.61 (t, *J* = 7.5 Hz, 4H, Ar-*H*), 7.47 – 7.42 (m, 5H, Ar-*H*), 7.40 (dd, *J* = 3.8, 1.4 Hz, 2H, Ar-*H*), 7.39 – 7.33 (m, 6H, Ar-*H*), 7.30 (dd, *J* = 9.2, 4.7 Hz, 3H, Ar-*H*), 7.19 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 6.92 (s, 2H, Ar-*H*), 6.37 6.31 (s, 2H, C*H*Ar_2), 6.23 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 2.20, 2.17 (s, 3H, CH_3), 1.27, 1.22 (s, 3H, Pd-CH_3), -0.60, -0.55 (s, 3H, Ar-C(CH_3)=N). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.59 (*C*=N), 152.33, 149.35, 141.78, 140.15, 138.39, 138.25, 136.47, 135.34, 133.31, 133.08, 132.21, 131.92, 129.64, 128.93, 128.29, 128.19, 128.13, 127.97, 127.95, 127.84, 127.55, 127.35, 126.19, 126.07, 125.92, 125.77, 124.10, 52.18 (*C*HAr_2), 21.49 (*C*H_3), 17.54 (Ar-C(*C*H_3)=N), 2.83 (Pd-*C*H_3). Elemental analysis: calc. for $C_{57}H_{45}ClN_2Pd$: C, 76.08; H, 5.04; N, 3.11. Found: C, 76.21; H, 5.12; N, 3.21.



Pd2: (370 mg, 80%). a-isomer: b-isomer = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66, 9.39 (d, *J* = 4.8 Hz, 1H, Ar-*H*), 7.86 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.78 – 7.74 (m, 1H, Ar-*H*), 7.69 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.59 (t, *J* = 8.6 Hz, 4H, Ar-*H*), 7.42 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.23 (d, *J* = 7.5 Hz, 4H, Ar-*H*), 7.20 (dd, *J* = 6.8, 3.8 Hz, 4H, Ar-*H*), 7.04 (s, 2H, Ar-*H*), 6.93 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 6.87 (s, 2H, Ar-*H*), 6.41 (s, 2H, Ar-*H*), 5.32, 5.26 (s, 2H, C*H*Ar_2), 2.29, 2.22 (s, 3H, C*H*$_3$), 1.23, 0.99 (s, 3H, Pd-C*H*$_3$), 0.41, 0.37 (s, 3H, Ar-C(C*H*$_3$)=N). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.18 (*C*=N), 152.14, 149.60, 145.85, 145.16, 140.18, 139.96, 139.50, 139.31, 139.06, 138.67, 137.69, 134.33, 128.89, 128.76, 124.71, 124.66, 124.27, 124.23, 124.17, 123.95, 123.52, 123.46, 123.42, 122.40, 122.21, 53.46 (*C*HAr_2), 43.37 (*C*HAr_2), 21.59 (*C*H$_3$), 17.39 (Ar-C(*C*H$_3$)=N), 2.73 (Pd-*C*H$_3$). Elemental analysis: calc. for $C_{49}H_{37}ClN_2PdS_4$: C, 63.70; H, 4.04; N, 3.03. Found: C, 63.59; H, 4.21; N, 3.19.

1.6 A General Procedure for the Ethylene Oligomerization Using Ni Complexes.

In a typical experiment, a 350 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 20 mL of toluene and the desired amount Et_2AlCl was added to the reactor under N_2 atmosphere, then the desired amount of catalyst in 1 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 6 atm of ethylene. After 10 min, the pressure reactor was vented and the oligomer was precipitated in ethanol, filtered and dried at 50 °C for at least 24 h under vacuum.

1.7 A General Procedure for the Ethylene Oligomerization Using Pd Complexes.

In a typical experiment, a 350 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted

to the desired polymerization temperature. 38 mL of DCM and the desired amount NaBArF was added to the reactor, then the Pd catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at 4 atm of Ethylene. After 1 h, the pressure reactor was vented and the oligomer was dried under vacuum by rotary evaporator.

1.8 A General Procedure for the Co-oligomerization of Methyl Acrylate with Ethylene using Pd Complexes.

In a typical experiment, a 350 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 18 mL of DCM with the desired amount NaBArF and MA was added to the reactor, then the Pd catalyst in 2 mL of CH_2Cl_2 was injected into the co-oligomerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 4 atm of Ethylene. After 3 h, the pressure reactor was vented and the co-oligomer was dried under vacuum by rotary evaporator.

2. Spectra Data

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

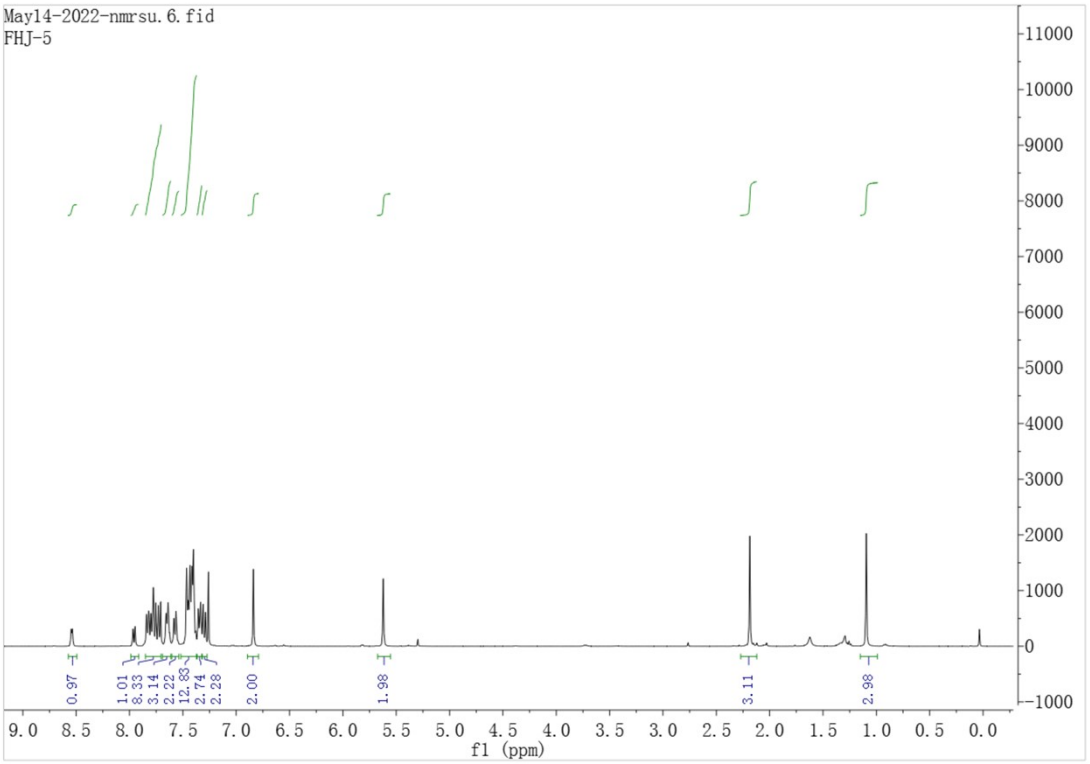


Figure S1. ^{1}H NMR spectrum of **L1** in $CDCl_3$.

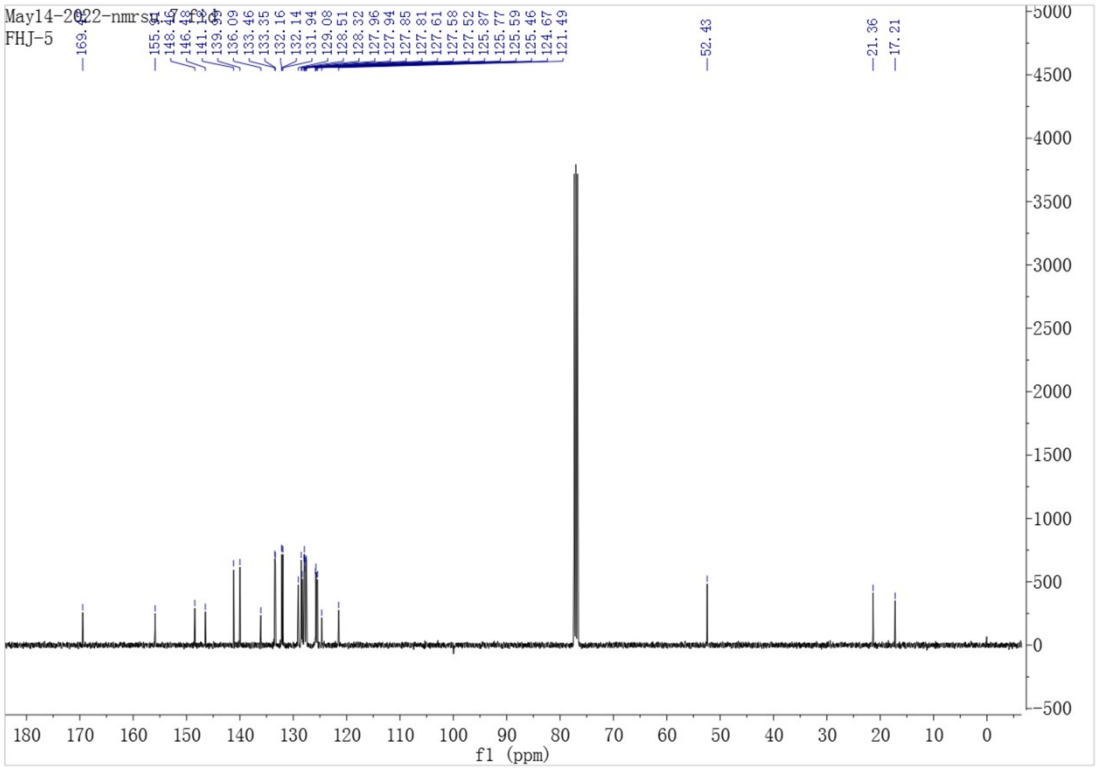


Figure S2. ^{13}C NMR spectrum of **L1** in $CDCl_3$.

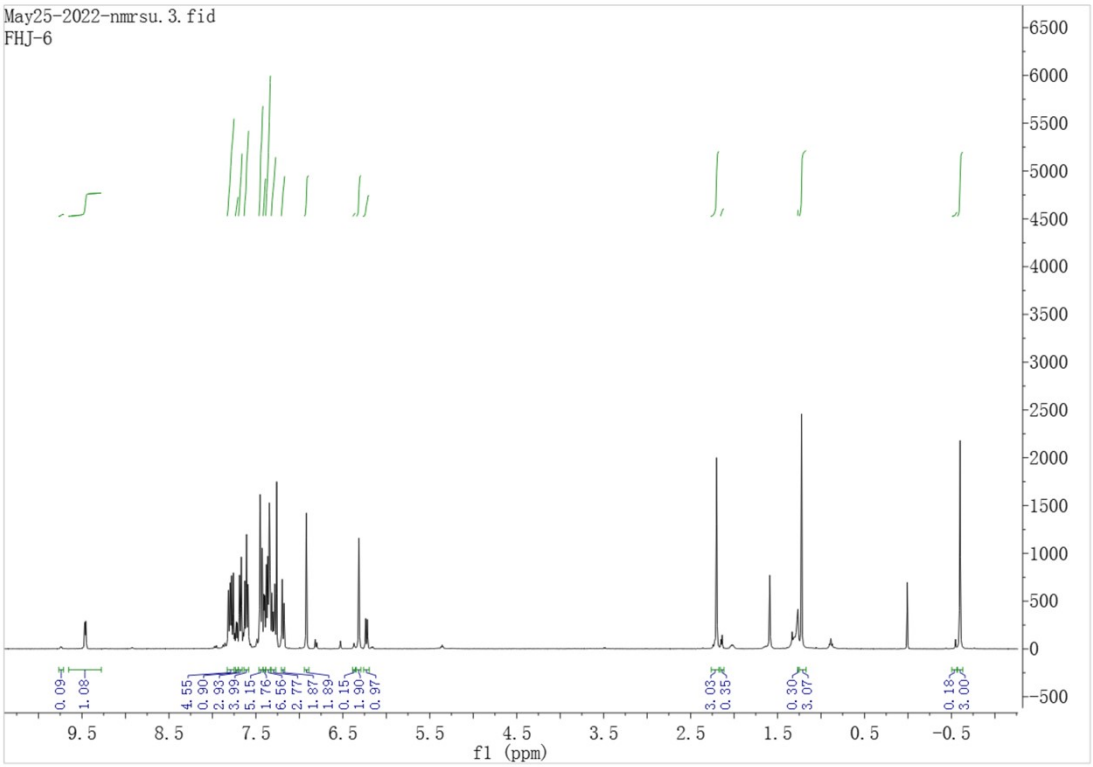


Figure S3. ^{1}H NMR spectrum of **Pd1** in $CDCl_3$.

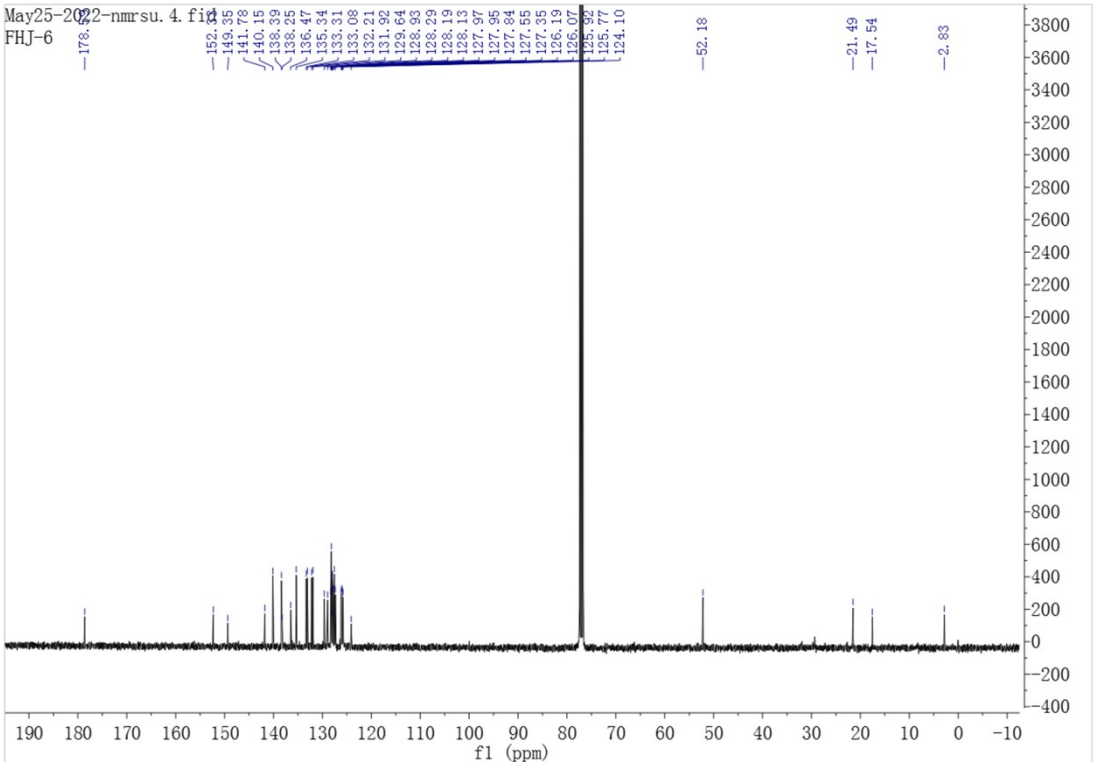


Figure S4. ^{13}C NMR spectrum of **Pd1** in $CDCl_3$.

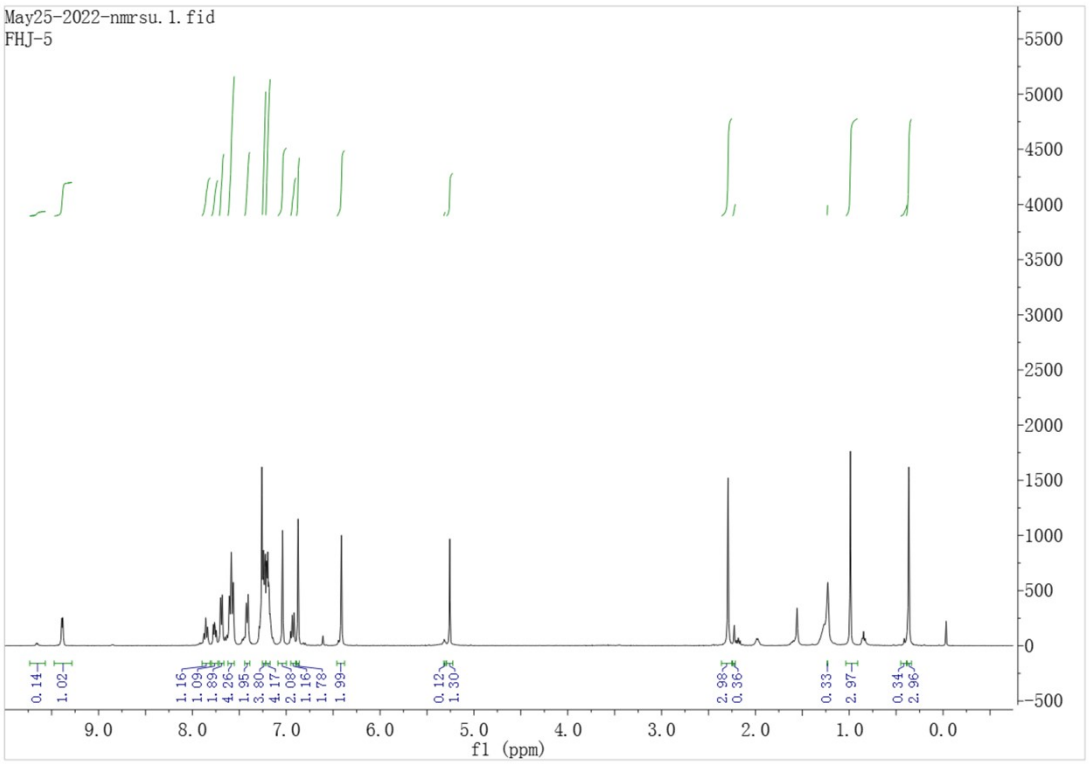


Figure S5. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

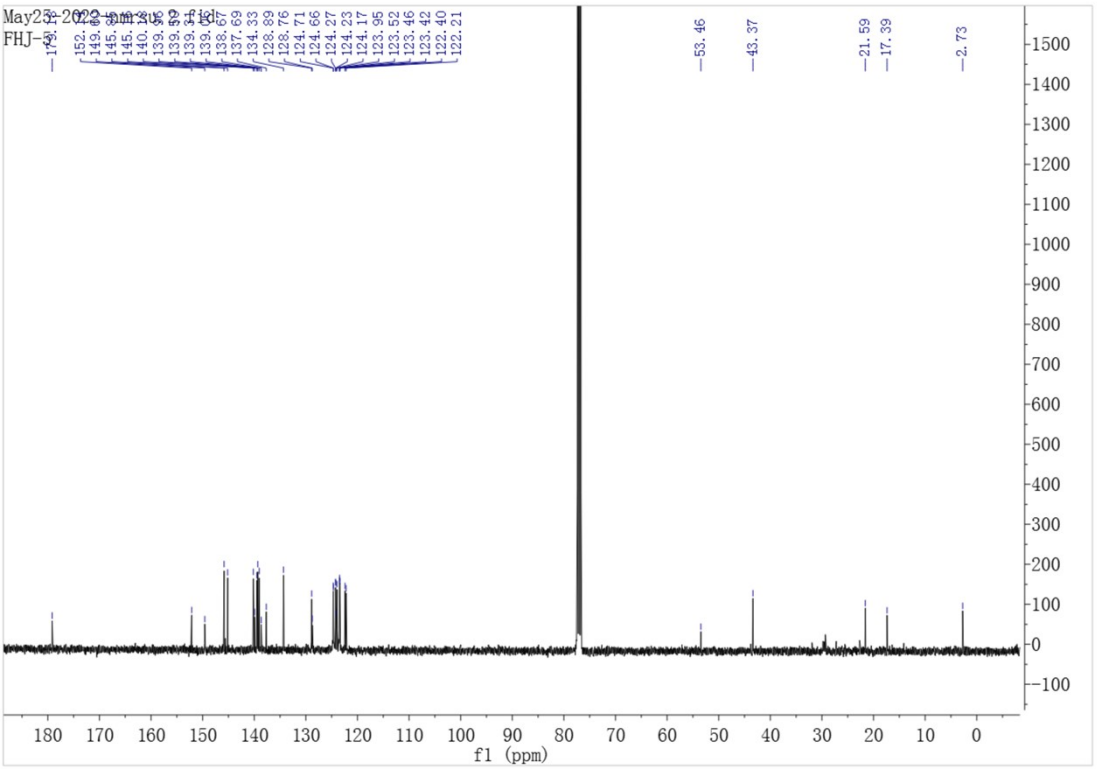


Figure S6. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

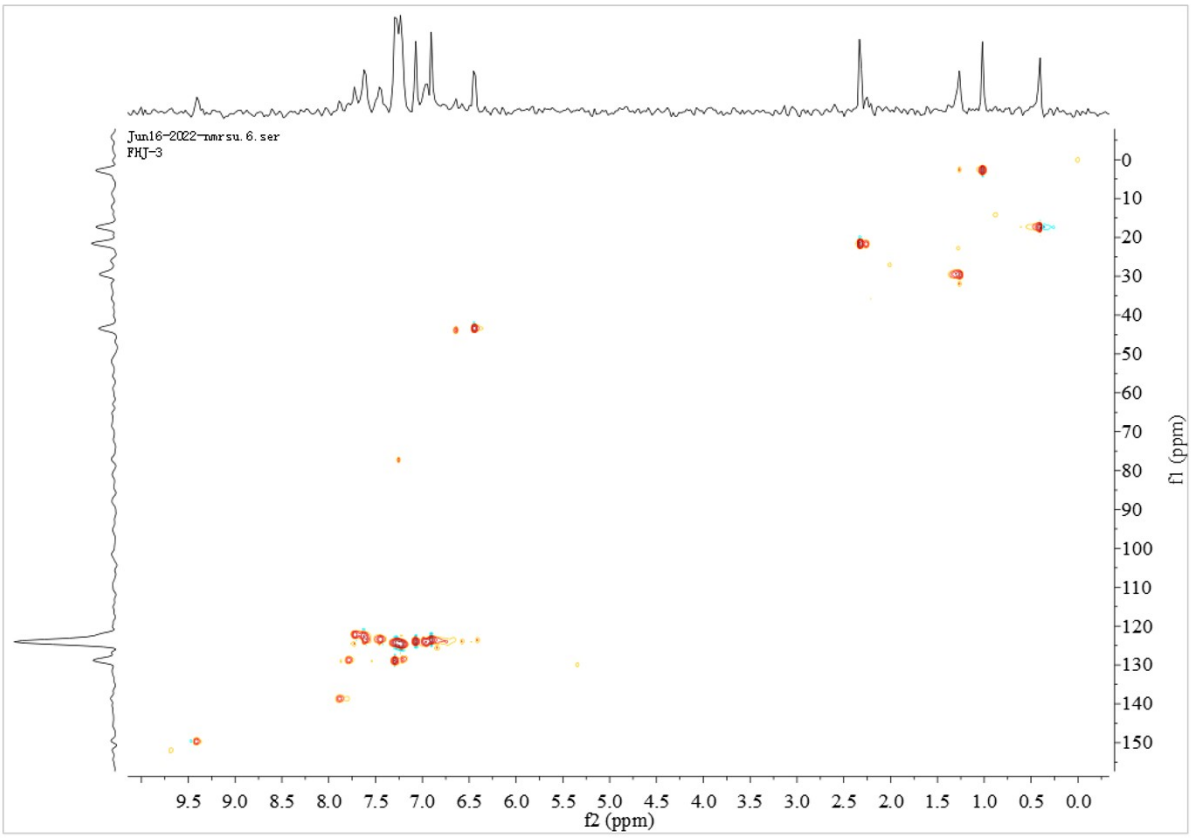


Figure S7. ^{1}H-^{13}C HSQC NMR spectrum of **Pd2** in $CDCl_3$.

2.2 APCI-MS of Ligands L1-L2.

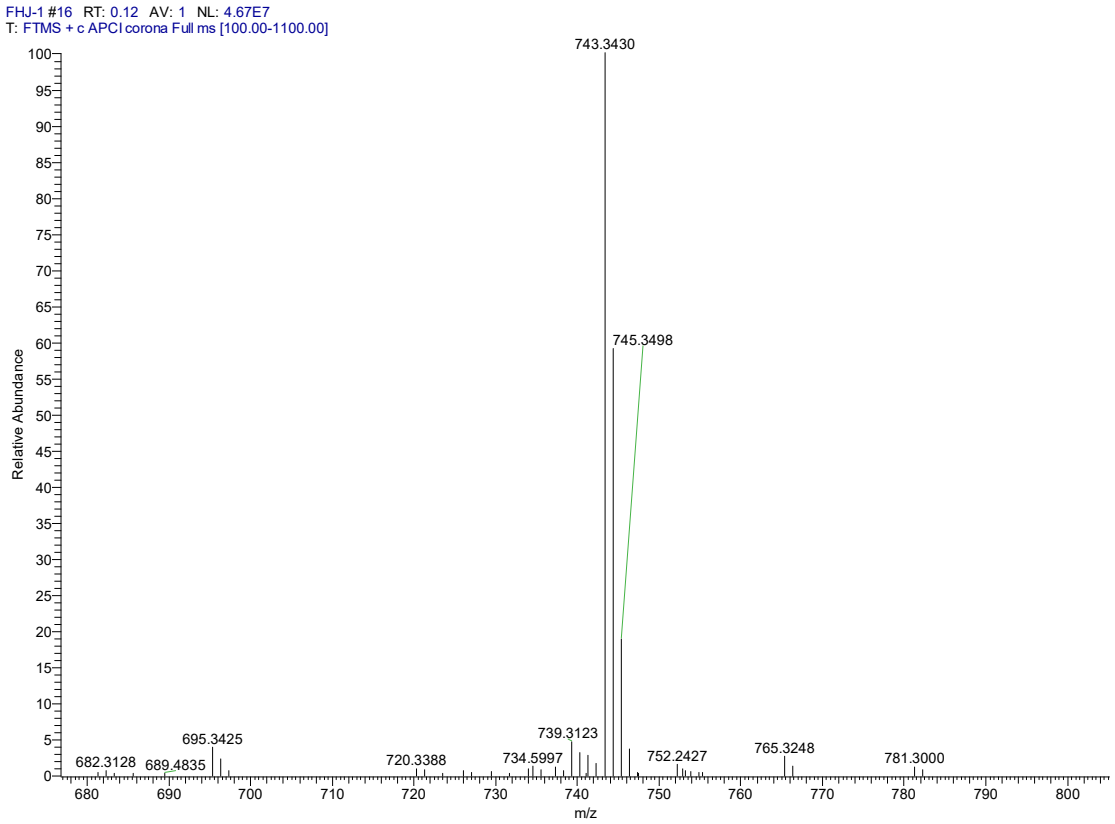


Figure S8. APCI-MS of Ligand **L1**.

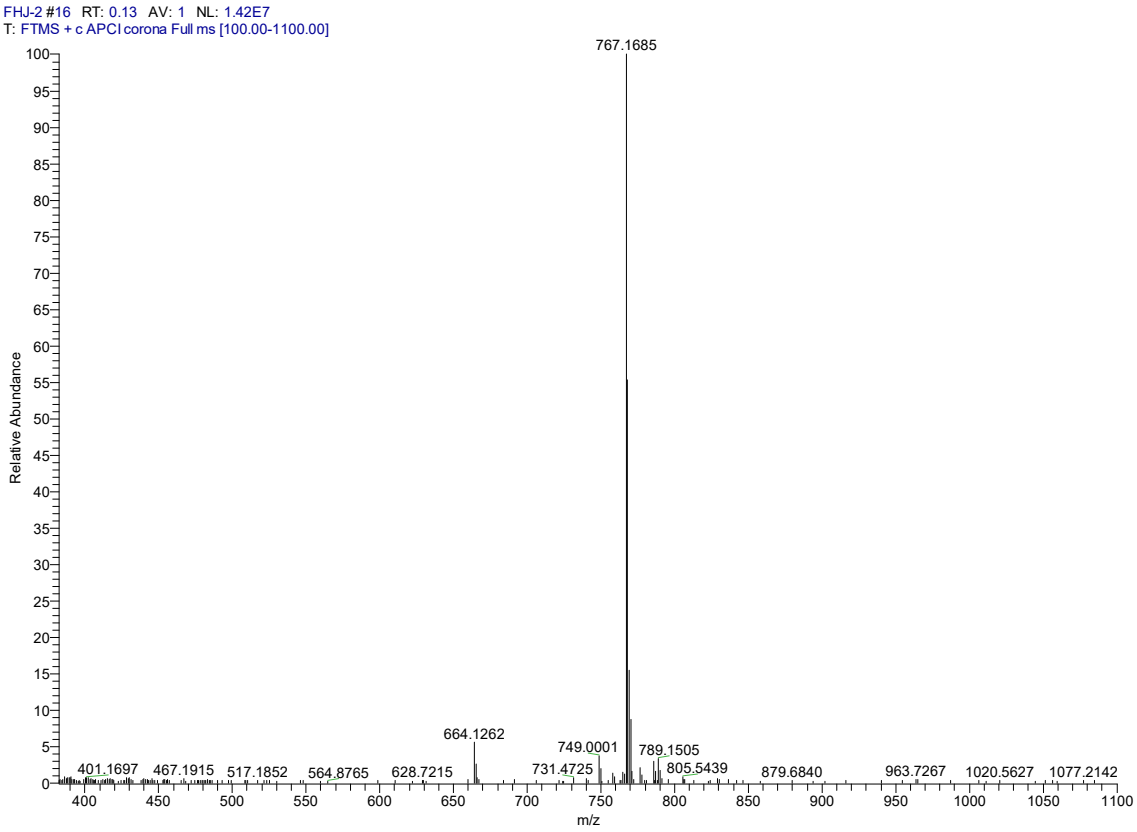


Figure S9. APCI-MS of Ligand **L2**.

2.3 ^{1}H and ^{13}C NMR of Typical Ethylene Oligomers and E-MA Co-oligomers.

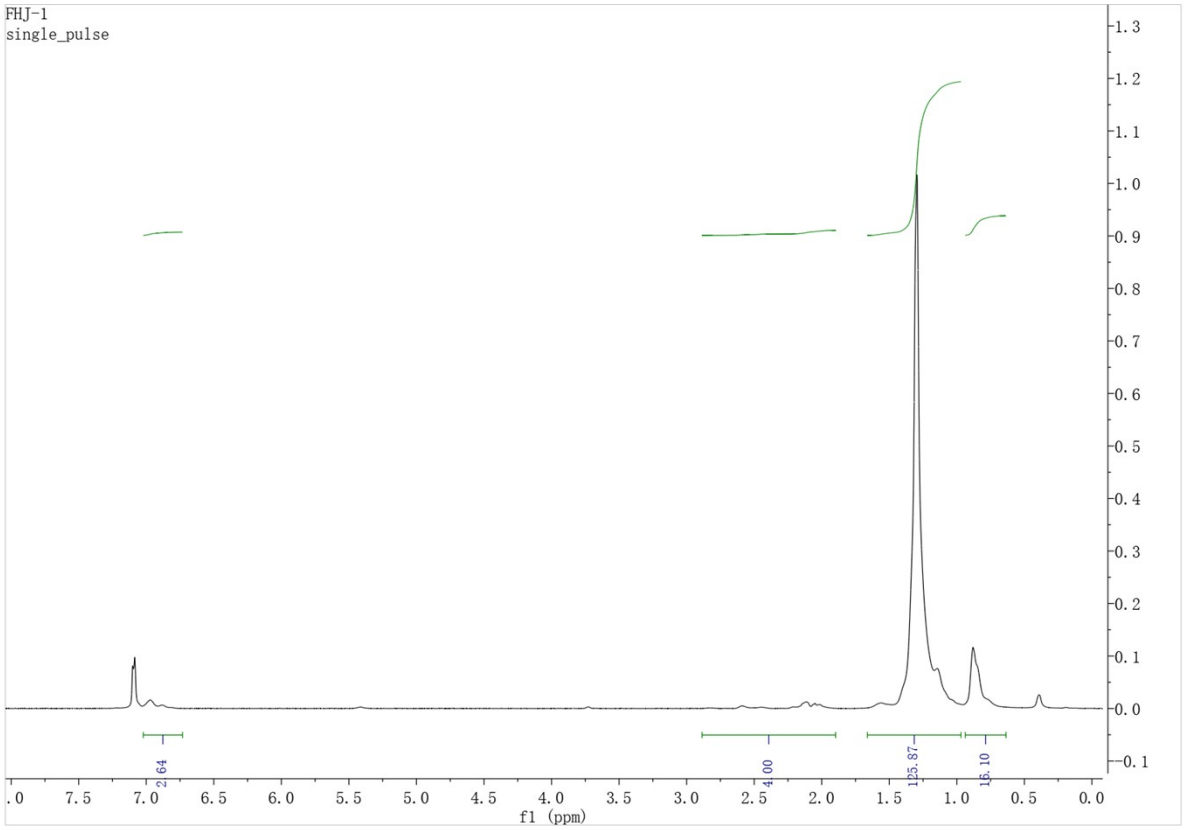


Figure S10. ^{1}H NMR spectrum of the ethylene oligomer from table 1, entry 1.

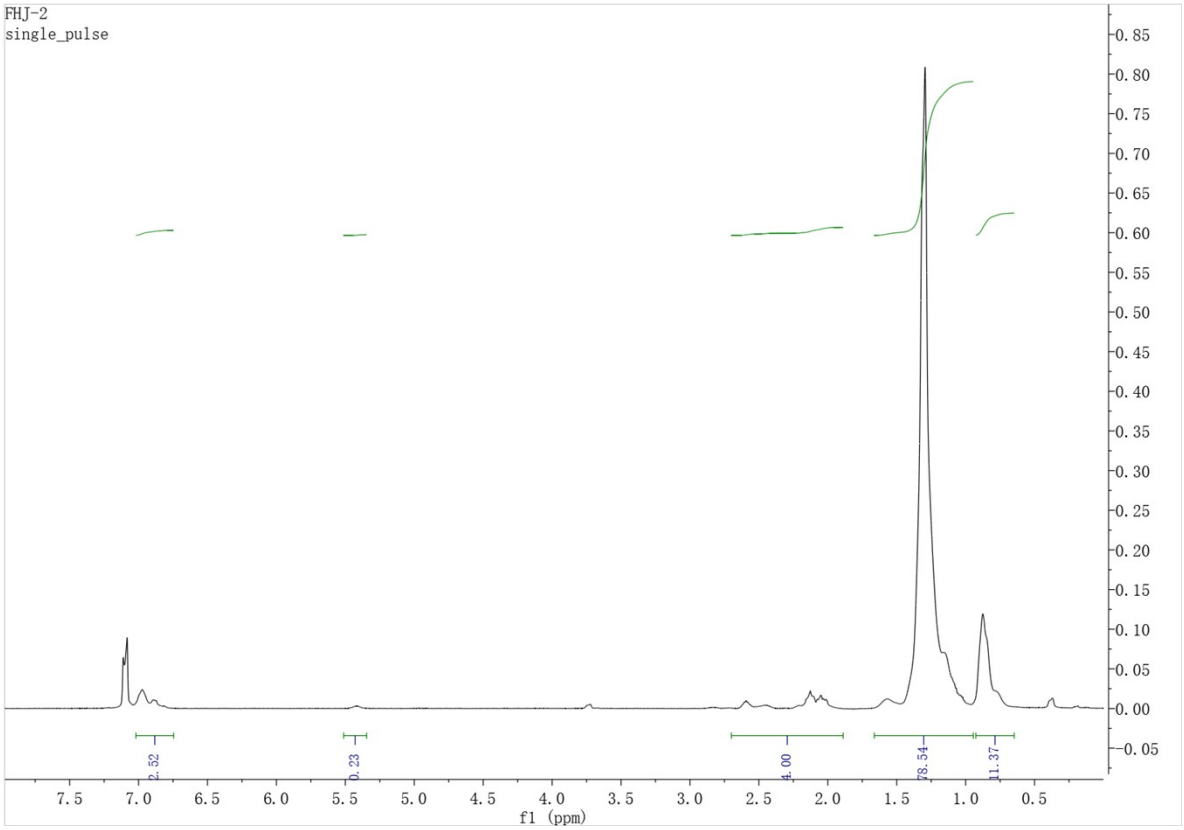


Figure S11. ^{1}H NMR spectrum of the ethylene oligomer from table 1, entry 2.

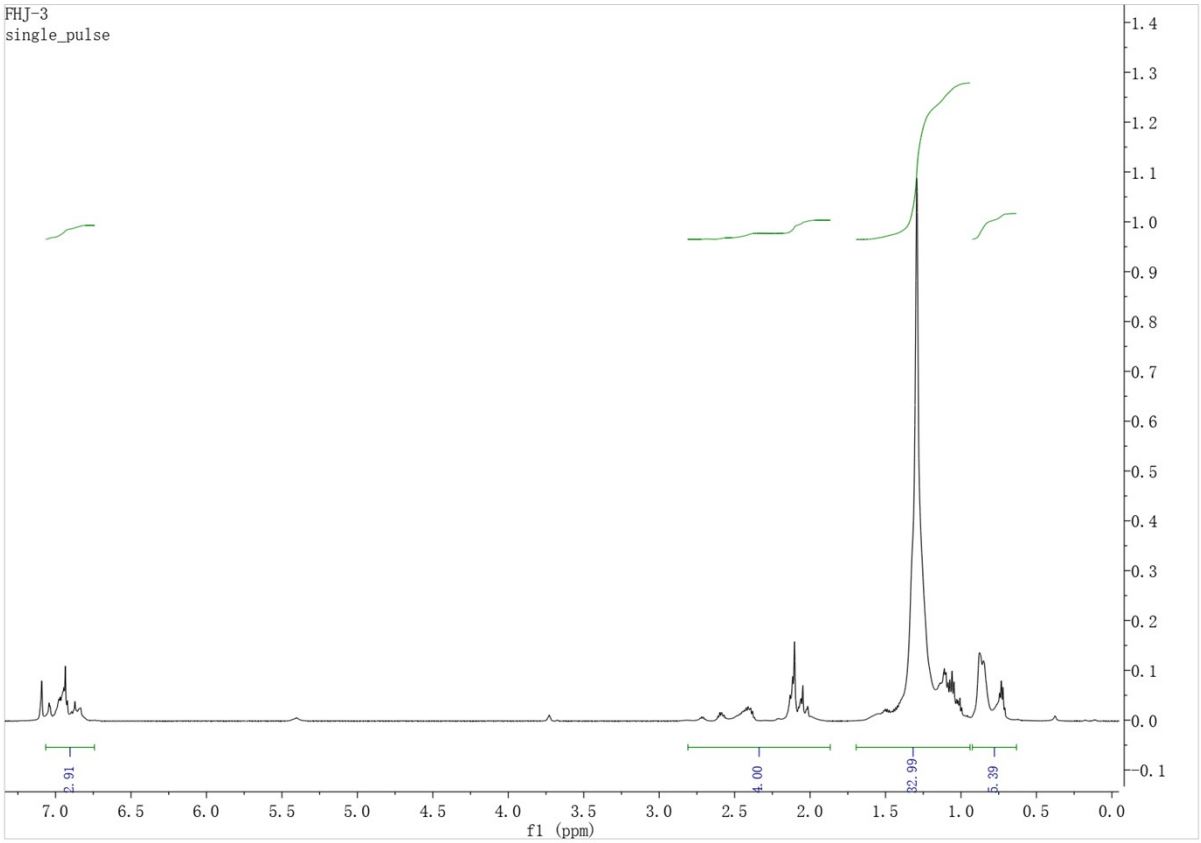


Figure S12. ^{1}H NMR spectrum of the ethylene oligomer from table 1, entry 3.

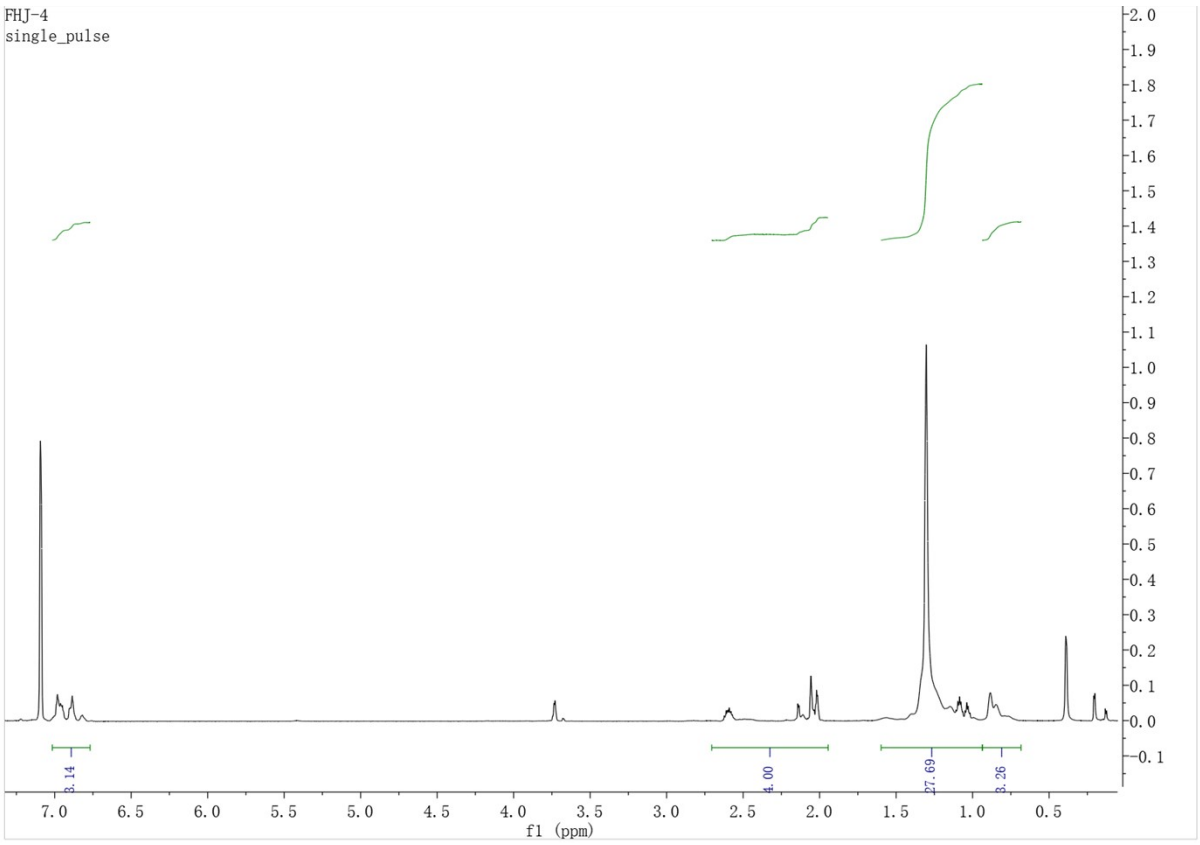


Figure S13. ^{1}H NMR spectrum of the ethylene oligomer from table 1, entry 4.

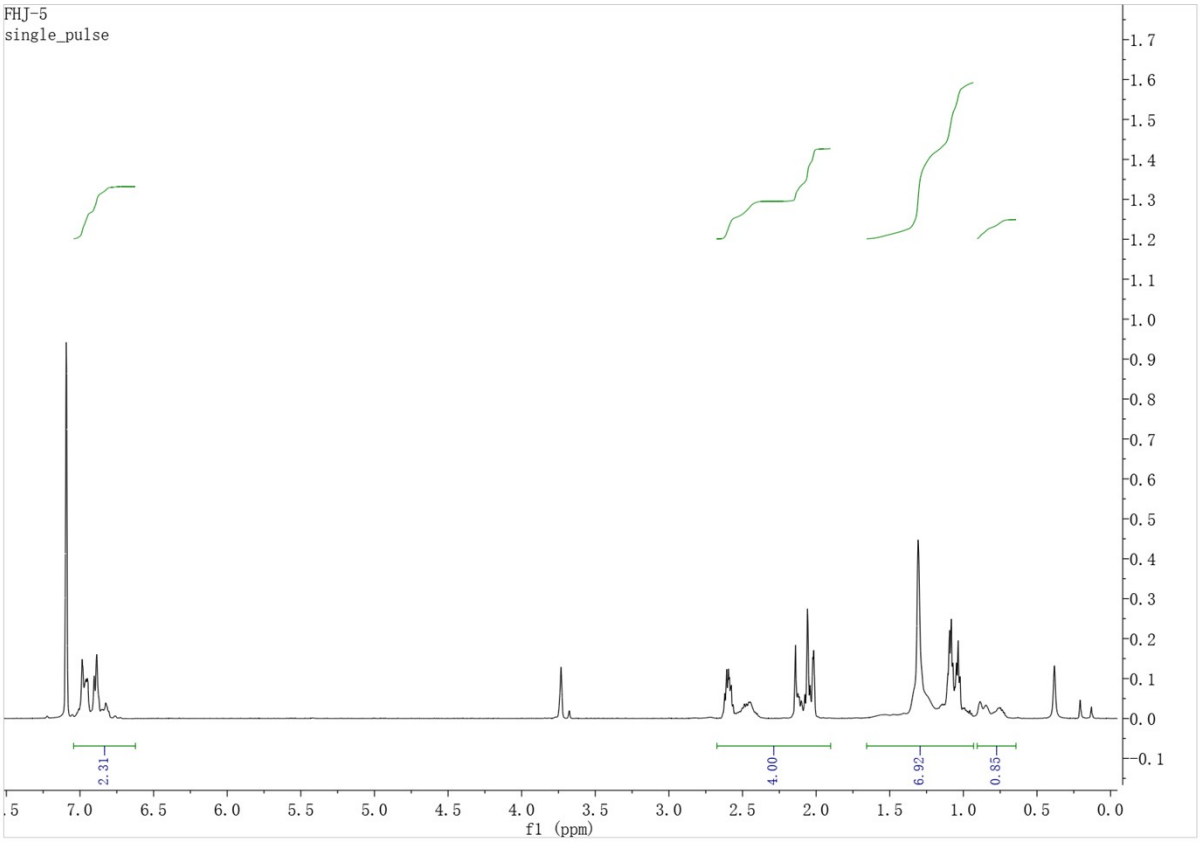


Figure S14. ^{1}H NMR spectrum of the ethylene oligomer from table 1, entry 5.

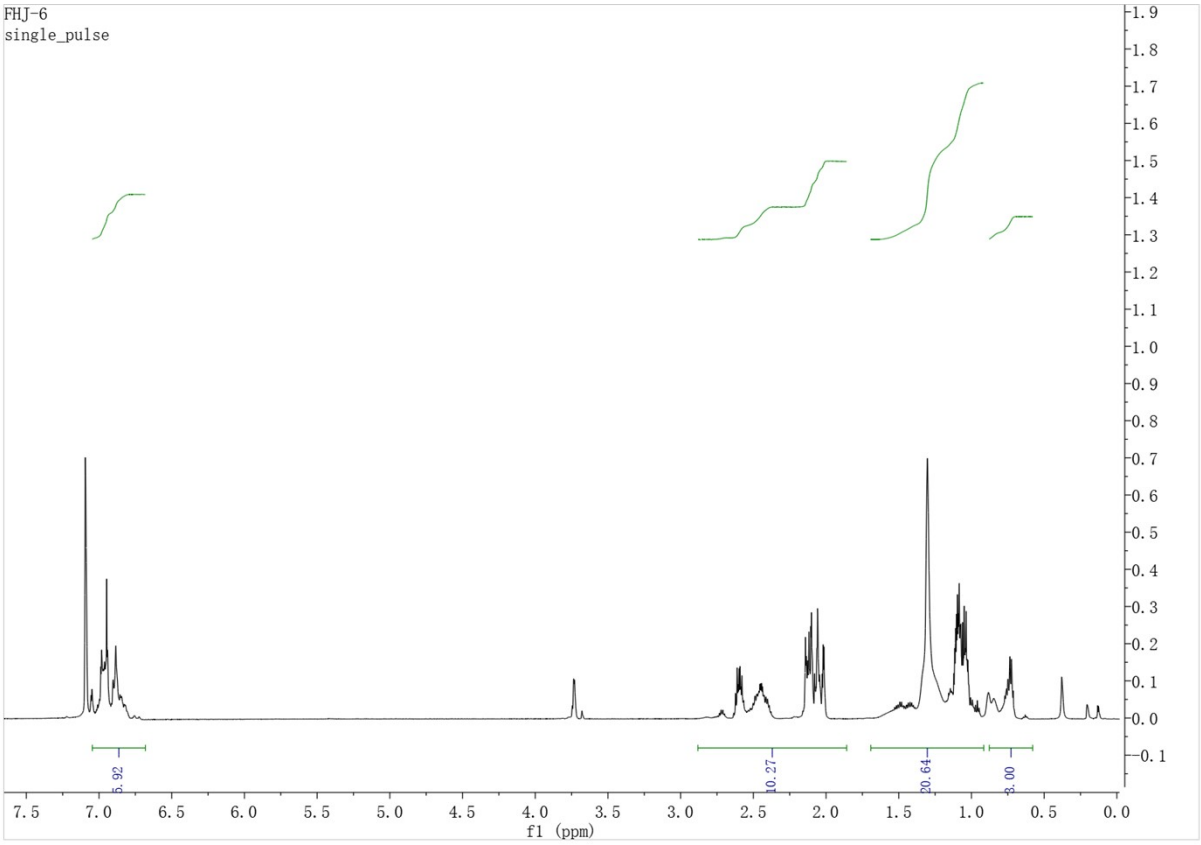


Figure S15. ^{1}H NMR spectrum of the ethylene oligomer from table 1, entry 6.

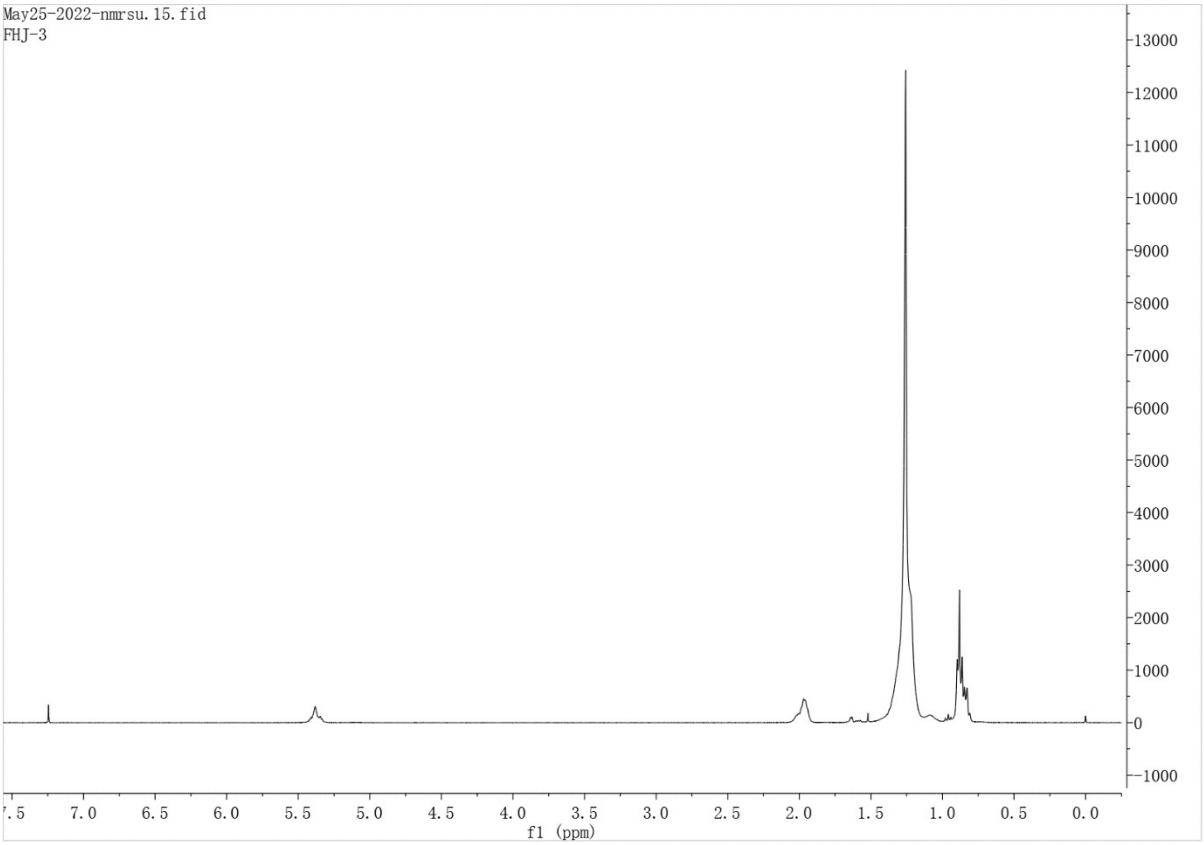


Figure S16. ^{1}H NMR spectrum of the ethylene oligomer from table 2, entry 1.

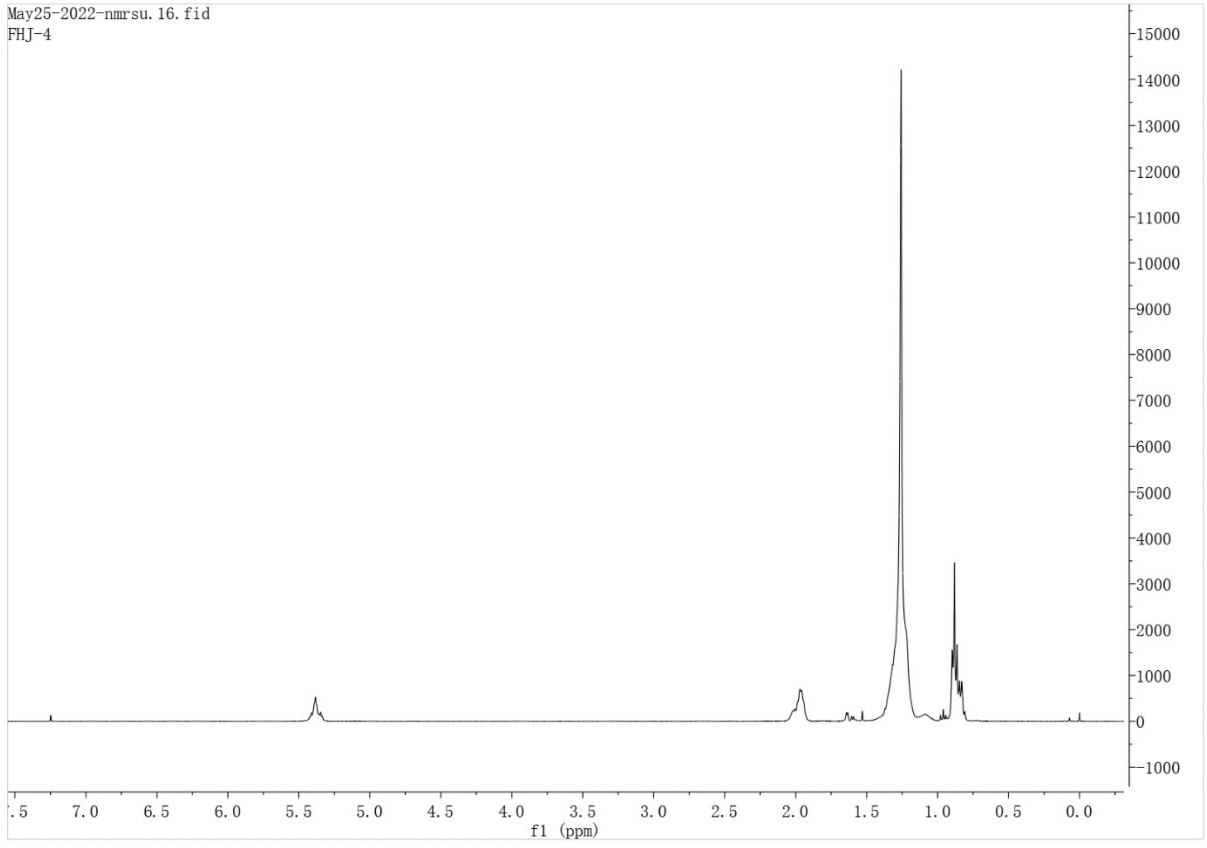


Figure S17. ^{1}H NMR spectrum of the ethylene oligomer from table 2, entry 2.

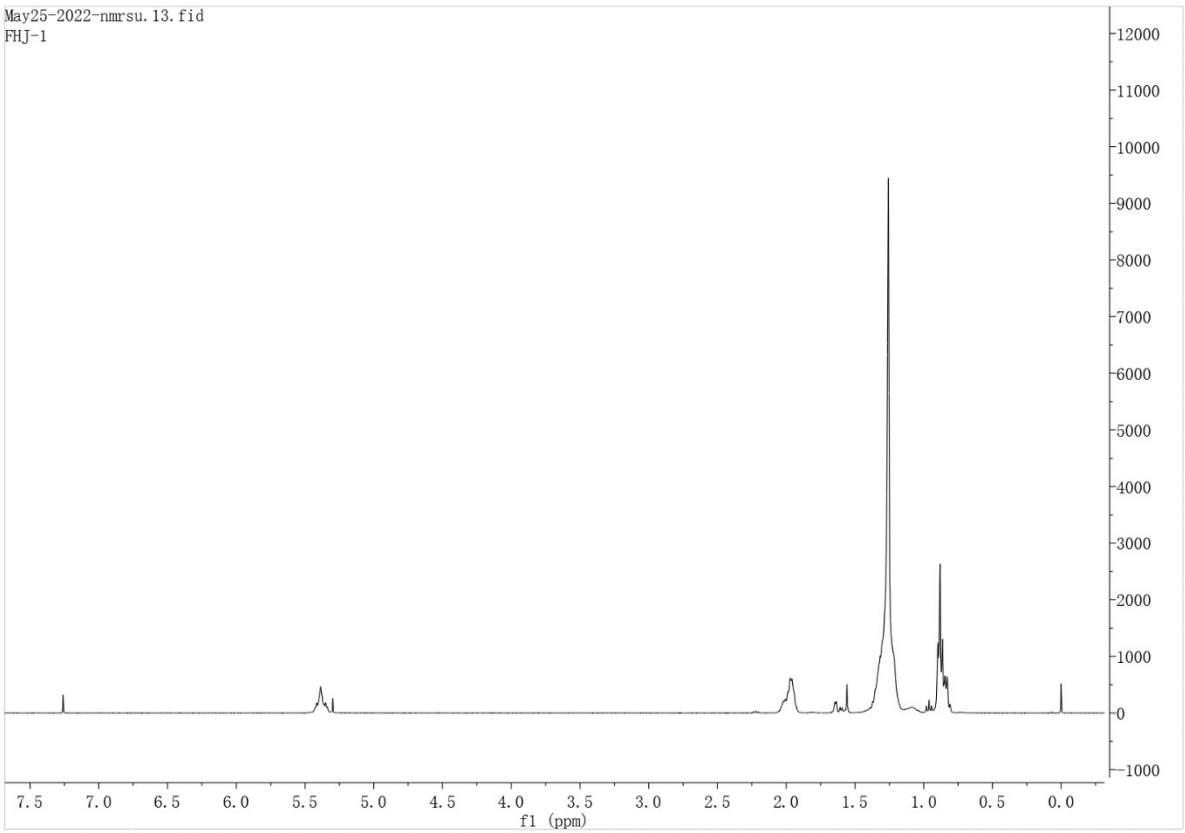


Figure S18. ^{1}H NMR spectrum of the ethylene oligomer from table 2, entry 3.

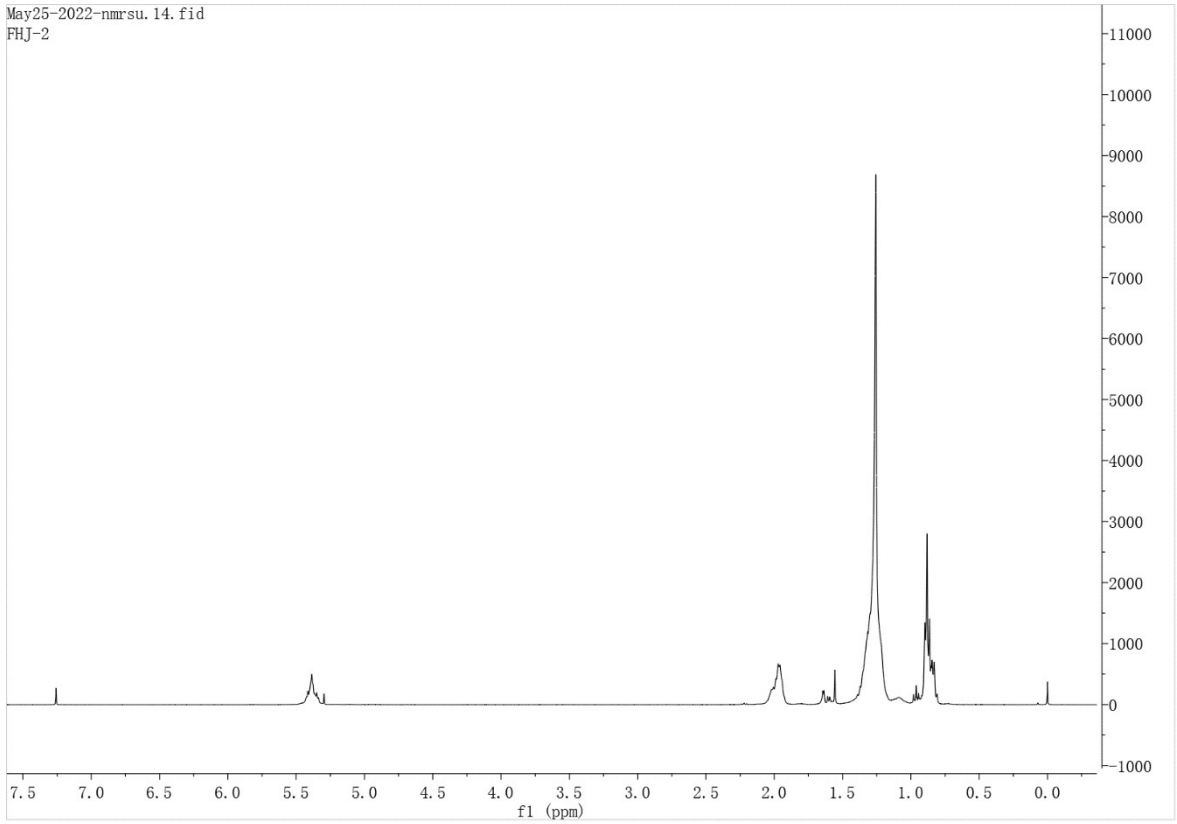


Figure S19. ^{1}H NMR spectrum of the ethylene oligomer from table 2, entry 4.

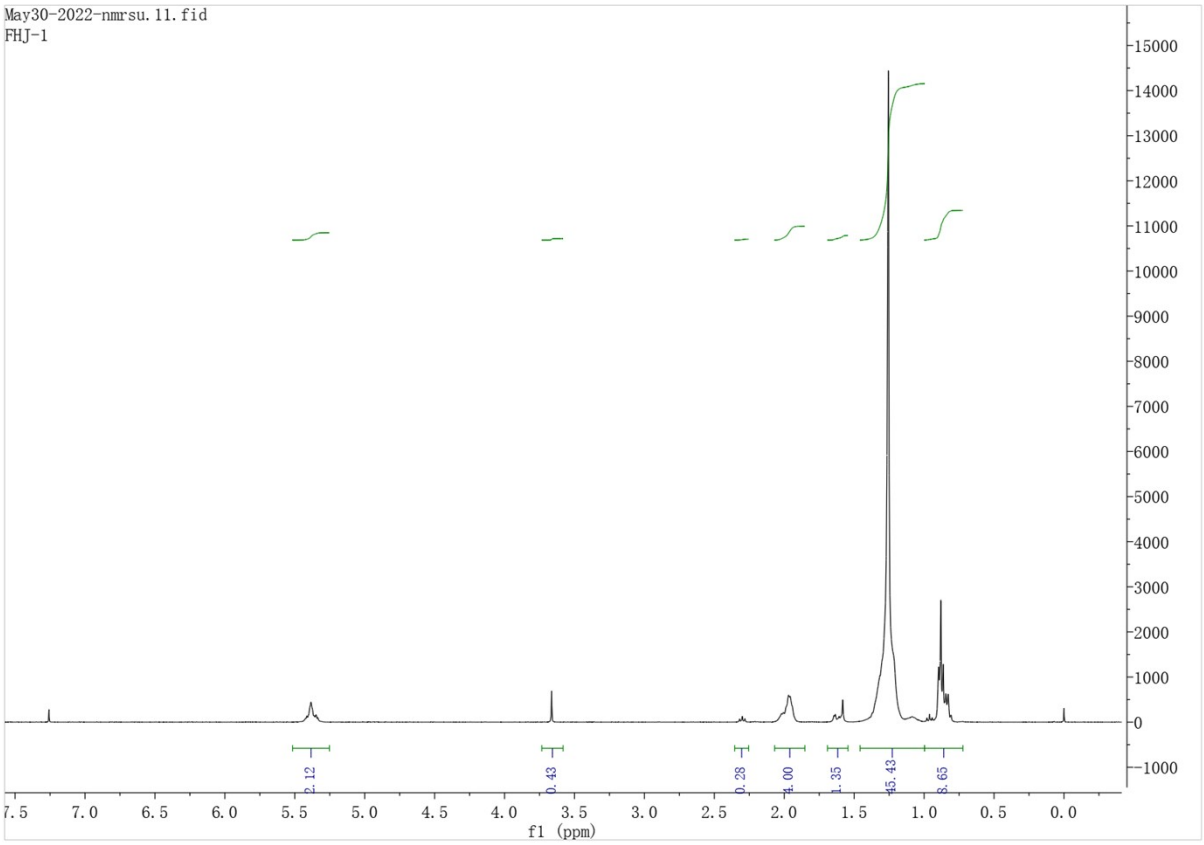


Figure S20. [1]H NMR spectrum of the ethylene-MA co-oligomer from table 3, entry 1.

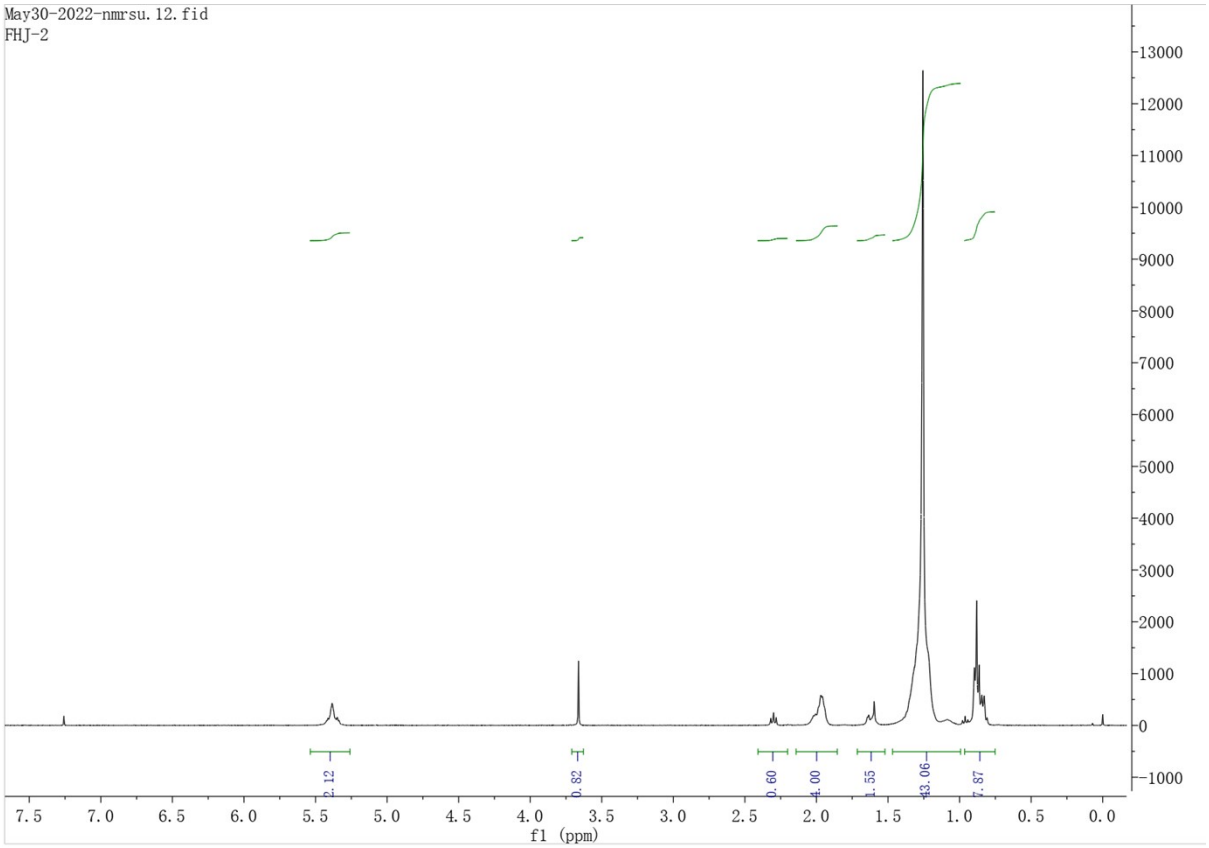


Figure S21. [1]H NMR spectrum of the ethylene-MA co-oligomer from table 3, entry 2.

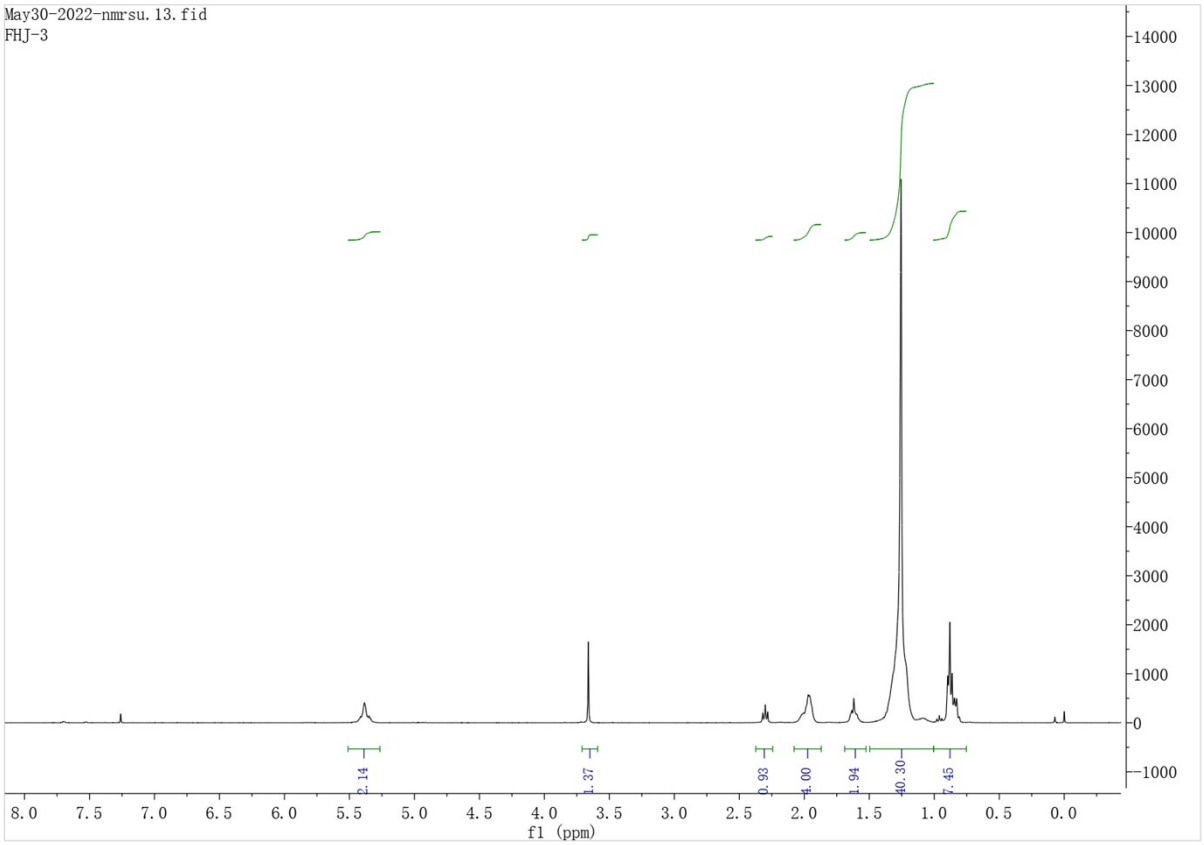


Figure S22. [1]H NMR spectrum of the ethylene-MA co-oligomer from table 3, entry 3.

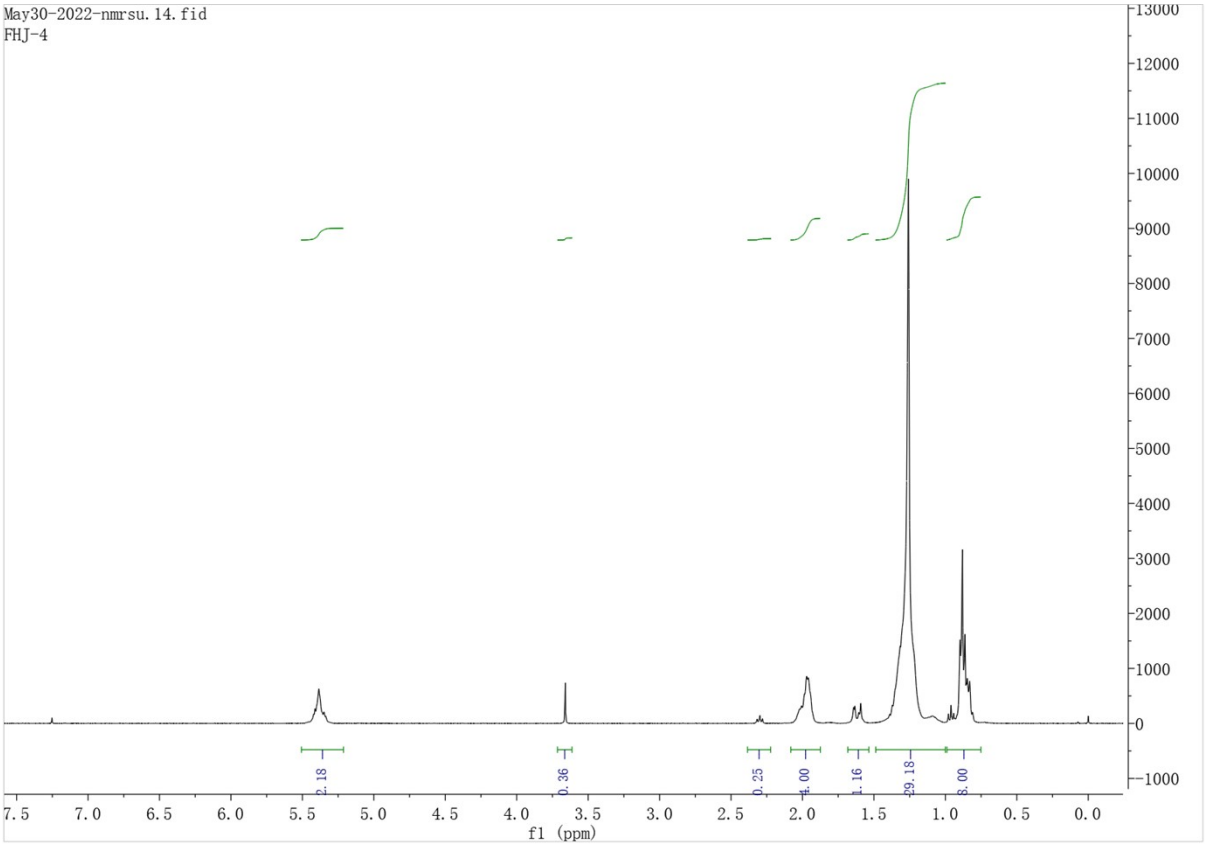


Figure S23. [1]H NMR spectrum of the ethylene-MA co-oligomer from table 3, entry 4.

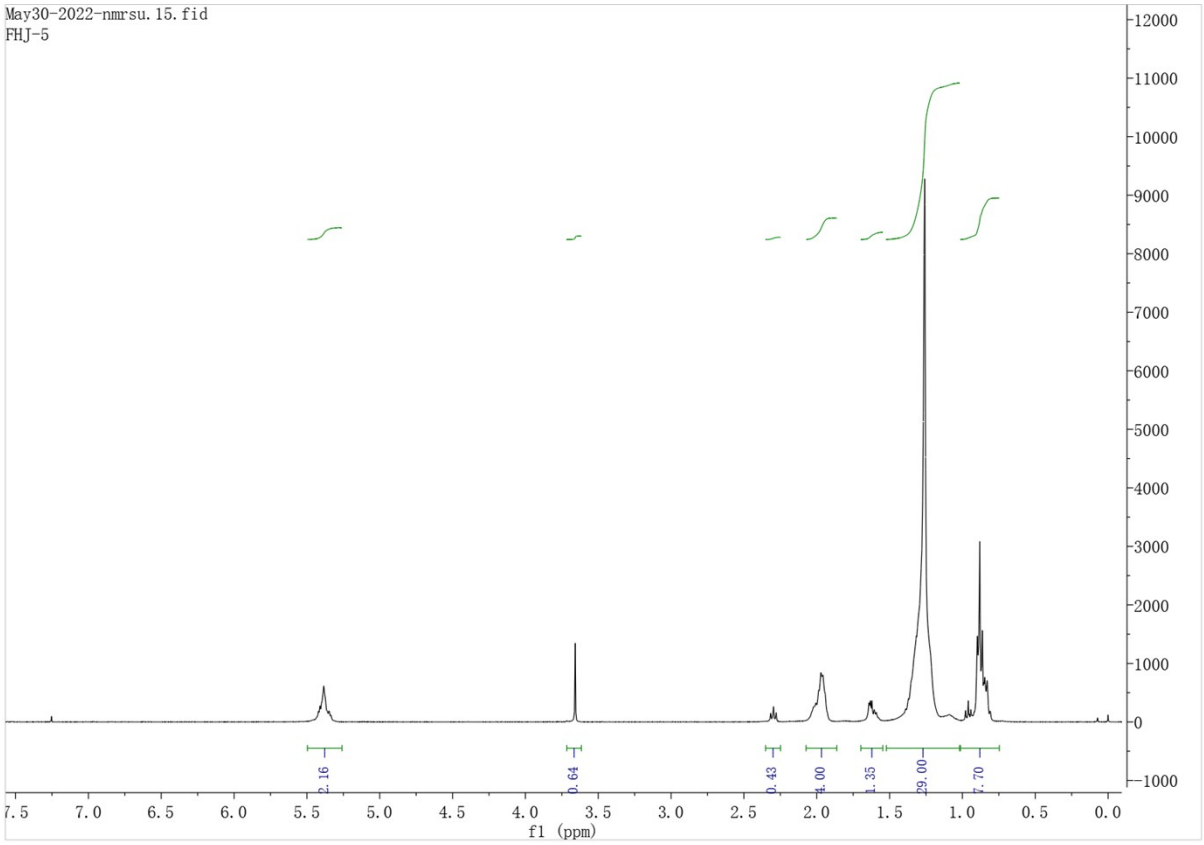


Figure S24. [1]H NMR spectrum of the ethylene-MA co-oligomer from table 3, entry 5.

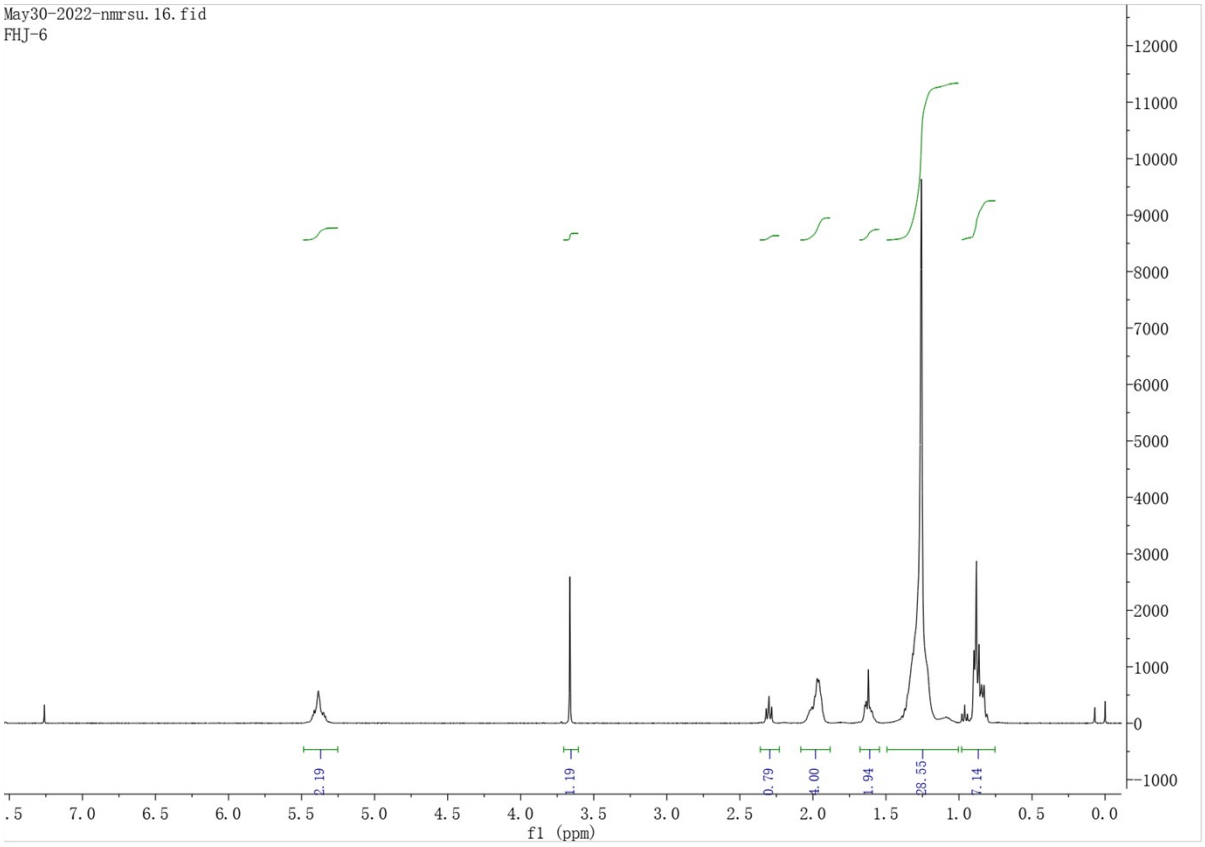


Figure S25. [1]H NMR spectrum of the ethylene-MA co-oligomer from table 3, entry 6.

3. References

[1] S. Dai and C. Chen, Direct synthesis of functionalized high-molecular-weight polyethylene by copolymerization of ethylene with polar monomers, *Angew. Chem. Int. Ed.*, 2016, **55**, 13281-13285.