

# **Efficient Incorporation of Polar Comonomer for Direct Synthesis of Hyperbranched Polar Functional Ethylene Oligomers**

Shuaikang Li<sup>†</sup>, Zhou Lu<sup>†</sup>, Weigang Fan\*, Shengyu Dai\*

*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*

<sup>†</sup>These authors contributed equally to this work.

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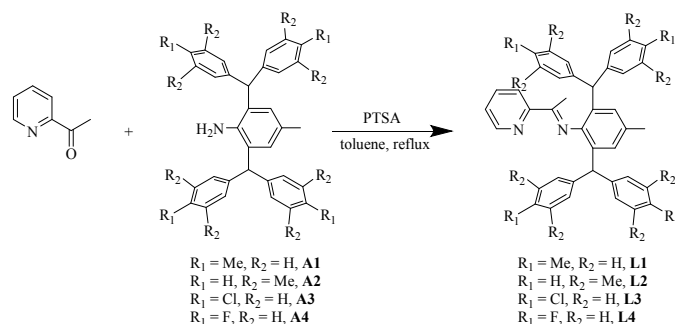
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## 1. Experimental sections

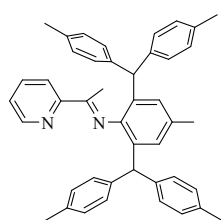
### 1.1 General Considerations

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.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded by a JNM-ECZ600R or JNM-ECZ400R spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Mass spectra were obtained by the Analytical Center of Anhui University. Elemental analysis was performed by the Analytical Center of Anhui University. X-ray Diffraction data were collected at 293(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ).

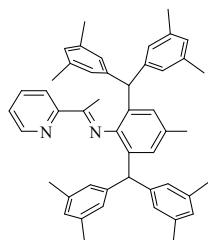
### 1.2 Procedure for the Synthesis of Ligands L1-L4.



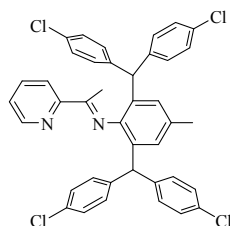
A mixture of 2-acetylpyridine (20.0 mmol, 2.42 g), arylamines (2.0 mmol, **A1** 0.99 g; **A2** 1.10 g; **A3** 1.15 g; **A4** 1.02 g) and *p*-toluenesulfonic acid (15 mg) in toluene (20 mL) were refluxed for 24 h. The solvent was partially evaporated under reduced pressure until the formation of a light yellow solid. The remaining mixture was diluted with methanol (100 mL). The resulting yellow solid was collected by filtration and recrystallized from  $\text{CH}_2\text{Cl}_2$  and hexanes to afford the desired product.



**L1** (0.67 g, 56%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 293K)  $\delta$  8.62 (d,  $^3J = 4.4$  Hz, 1H, Ar-*H*), 8.08 (t,  $^3J = 8.5$  Hz, 1H, Ar-*H*), 7.72 (td,  $^3J = 7.7$ ,  $^4J = 1.7$  Hz, 1H, Ar-*H*), 7.36 – 7.31 (m, 1H, Ar-*H*), 7.03 (d,  $^3J = 8.0$  Hz, 4H, Ar-*H*), 6.97 (d,  $^3J = 7.9$  Hz, 4H, Ar-*H*), 6.92 (d,  $^3J = 7.9$  Hz, 4H, Ar-*H*), 6.88 (d,  $^3J = 7.9$  Hz, 4H, Ar-*H*), 6.70 (s, 2H, Ar-*H*), 5.19 (s, 2H,  $\text{CHAr}_2$ ), 2.31 (s, 6H, Ar- $\text{CH}_3$ ), 2.27 (s, 6H, Ar- $\text{CH}_3$ ), 2.18 (s, 3H,  $\text{CH}_3$ ), 1.10 (s, 3H, Ar- $\text{C}(\text{CH}_3)=\text{N}$ ).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ , 293K)  $\delta$  169.44 ( $\text{C}=\text{N}$ ), 156.25, 148.47, 145.98, 141.18, 139.90, 136.18, 135.52, 135.31, 132.46, 131.49, 129.70, 129.37, 129.22, 128.98, 128.73, 128.48, 124.62, 121.50, 51.24 ( $\text{CHAr}_2$ ), 29.79 (Ar- $\text{CH}_3$ ), 21.41 (Ar- $\text{CH}_3$ ), 21.10 ( $\text{CH}_3$ ), 17.06 (Ar- $\text{C}(\text{CH}_3)=\text{N}$ ). MS (*m/z*): calcd for  $\text{C}_{44}\text{H}_{43}\text{N}_2$ : 599.3426, Found, 599.3413,  $[\text{M}+\text{H}]^+$ .

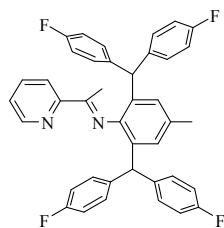


**L2** (0.80 g, 61%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 293K)  $\delta$  8.99 (d,  $^3J = 4.3$  Hz, 1H, Ar-*H*), 8.11 (dt,  $^3J = 7.8$ , 3.9 Hz, 1H, Ar-*H*), 7.83 (dt,  $^3J = 9.2$ ,  $^4J = 4.6$  Hz, 1H, Ar-*H*), 7.22 (d,  $^3J = 7.9$  Hz, 1H, Ar-*H*), 6.98 (s, 4H, Ar-*H*), 6.80 (s, 2H, Ar-*H*), 6.78 (s, 2H, Ar-*H*), 6.66 (s, 2H, Ar-*H*), 6.58 (s, 4H, Ar-*H*), 5.90 (s, 2H,  $\text{CHAr}_2$ ), 2.25 (s, 12H, Ar( $\text{CH}_3$ ) $_2$ ), 2.22 (s, 3H,  $\text{CH}_3$ ), 2.21 (s, 3H, Ar- $\text{C}(\text{CH}_3)=\text{N}$ ), 1.96 (s, 12H, Ar( $\text{CH}_3$ ) $_2$ ).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ , 293K)  $\delta$  174.89 ( $\text{C}=\text{N}$ ), 149.54, 147.76, 142.14, 140.96, 140.35, 137.98, 137.85, 137.40, 136.13, 135.80, 129.26, 128.84, 128.34, 128.09, 127.83, 127.79, 127.44, 124.17, 51.24 ( $\text{CHAr}_2$ ), 21.56(Ar( $\text{CH}_3$ ) $_2$ ), 21.45( $\text{CH}_3$ ), 21.20 (Ar( $\text{CH}_3$ ) $_2$ ), 16.15 (Ar- $\text{C}(\text{CH}_3)=\text{N}$ ). MS (*m/z*): calcd for  $\text{C}_{48}\text{H}_{51}\text{N}_2$ : 655.4052, Found, 655.4044,  $[\text{M}+\text{H}]^+$ .



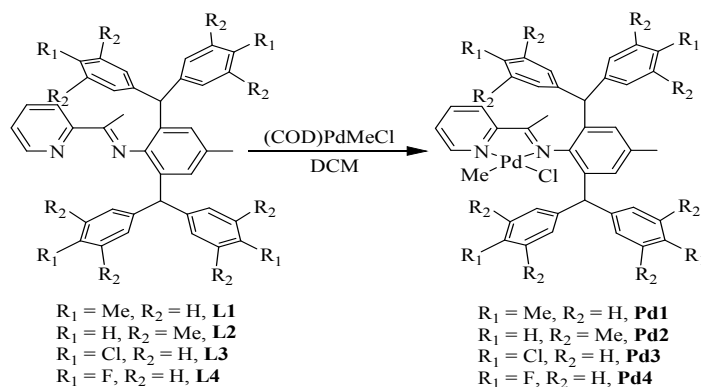
**L3** (0.79 g, 58%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 293K)  $\delta$  8.61 (d,  $^3J = 4.3$  Hz, 1H, Ar-*H*),

7.94 (d,  $^3J = 7.9$  Hz, 1H, Ar-*H*), 7.73 (td,  $^3J = 7.8$ ,  $^4J = 1.6$  Hz, 1H, Ar-*H*), 7.45 – 7.33 (m, 1H, Ar-*H*), 7.23 – 7.13 (m, 8H, Ar-*H*), 6.96 – 6.84 (m, 8H, Ar-*H*), 6.62 (s, 2H, Ar-*H*), 5.18 (s, 2H,  $CHAr_2$ ), 2.20 (s, 3H,  $CH_3$ ), 1.25 (s, 3H, Ar- $C(CH_3)=N$ ).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ , 293K)  $\delta$  169.65 ( $C=N$ ), 155.60, 148.80, 145.83, 141.69, 140.65, 136.36, 132.45, 132.27, 132.17, 131.56, 131.01, 130.68, 128.79, 128.70, 128.36, 125.05, 121.22, 50.84 ( $CHAr_2$ ), 21.35 ( $CH_3$ ), 17.31 (Ar- $C(CH_3)=N$ ). MS (m/z): calcd for  $C_{40}H_{31}Cl_4N_2$ : 681.1212, Found, 681.1202,  $[M+H]^+$ .



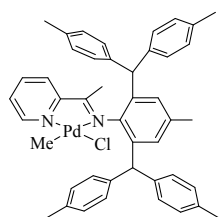
**L4** (1.08 g, 88%).  $^1H$  NMR (600 MHz,  $CDCl_3$ , 293K)  $\delta$  8.60 (d,  $^3J = 4.4$  Hz, 1H, Ar-*H*), 7.97 (d,  $^3J = 8.0$  Hz, 1H, Ar-*H*), 7.81 – 7.65 (m, 1H, Ar-*H*), 7.46 – 7.32 (m, 1H, Ar-*H*), 7.01 – 6.84 (m, 16H, Ar-*H*), 6.63 (s, 2H, Ar-*H*), 5.22 (s, 2H,  $CHAr_2$ ), 2.19 (s, 3H,  $CH_3$ ), 1.21 (s, 3H, Ar- $C(CH_3)=N$ ).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ , 293K)  $\delta$  169.53 ( $C=N$ ), 162.31, 162.24, 160.68, 160.62, 155.75, 148.75, 145.84, 139.20, 138.20, 138.19, 136.30, 132.11, 132.07, 131.16, 131.11, 130.79, 130.74, 128.64, 124.95, 121.21, 115.41, 115.27, 115.02, 114.88, 50.56 ( $CHAr_2$ ), 21.36 ( $CH_3$ ), 17.15 (Ar- $C(CH_3)=N$ ).  $^{19}F$  NMR (565 MHz,  $CDCl_3$ , 293K)  $\delta$  -116.15 (d,  $J = 6.0$  Hz), -116.47 – -118.80 (m). MS (m/z): calcd for  $C_{40}H_{31}F_4N_2$ : 615.2423, Found, 615.2404,  $[M+H]^+$ .

### 1.3 Procedure for the Synthesis of Palladium Complexes Pd1-Pd4.

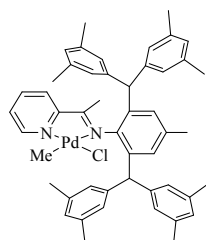


A mixture of the ligand (0.5 mmol, **L1** 0.30 g; **L2** 0.33 g; **L3** 0.34 g; **L4** 0.31 g),

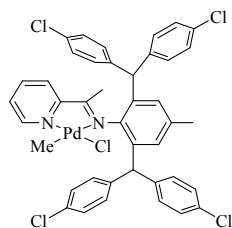
Pd(COD)MeCl (133 mg, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was stirred for 24 h at room temperature. During stirring, the color of the solution was deepening. At the end of the reaction, the solvent was partially evaporated under reduced pressure. The remaining mixture was diluted with Et<sub>2</sub>O (20 mL). The resulting yellow solid was collected by filtration, dried in vacuum.



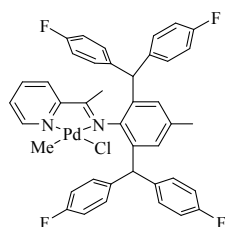
**Pd1** (0.33 g, 87%). a-isomer: b-isomer = 20:1 <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 293K) δ 9.34 (dd, <sup>3</sup>J = 5.0, 0.9 Hz, 1H, Ar-H), 7.91 (td, <sup>3</sup>J = 7.8, <sup>4</sup>J = 1.7 Hz, 1H, Ar-H), 7.73 – 7.65 (m, 1H, Ar-H), 7.19 (dd, <sup>3</sup>J = 11.6, 8.0 Hz, 1H, Ar-H), 7.00 (dt, <sup>3</sup>J = 15.3, 8.1 Hz, 10H, Ar-H), 6.91 – 6.82 (m, 10H, Ar-H), 6.05, 5.83 (d, <sup>3</sup>J = 7.2 Hz, s, 2H, CHAr<sub>2</sub>), 2.30 – 2.20, 2.16 (m, d, J = 4.9 Hz, , 12H, Ar-CH<sub>3</sub>), 1.61 (d, J = 15.6 Hz, 3H, CH<sub>3</sub>), 0.92 (s, 3H, Ar-C(CH<sub>3</sub>)=N), -0.00, -0.10 (s, 3H, Pd-CH<sub>3</sub>). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 293K) δ 178.18 (C=N), 152.66, 149.36, 141.02, 139.84, 138.51, 138.42, 136.08, 135.95, 135.89, 130.03, 129.63, 129.32, 129.20, 129.03, 128.88, 128.13, 123.92, 51.14 (CHAr<sub>2</sub>), 21.57 (CH<sub>3</sub>), 21.06 (Ar-CH<sub>3</sub>), 17.77 (Ar-C(CH<sub>3</sub>)=N), 2.63 (Pd-CH<sub>3</sub>). MS (m/z): calcd for C<sub>45</sub>H<sub>45</sub>N<sub>2</sub>Pd: 719.26, Found, 719.42, [M-Cl]<sup>+</sup>. Anal. Calcd for C<sub>45</sub>H<sub>45</sub>ClN<sub>2</sub>Pd: C, 71.52; H, 6.00; N, 3.71; Found, C, 71.26; H, 5.84; N, 3.52.



**Pd2** (0.35 g, 86%). Poor solubility is not suitable for NMR. MS (m/z): calcd for C<sub>49</sub>H<sub>53</sub>N<sub>2</sub>Pd: 775.32, Found, 775.50, [M-Cl]<sup>+</sup>. Anal. Calcd for C<sub>49</sub>H<sub>53</sub>ClN<sub>2</sub>Pd: C, 72.49; H, 6.58; N, 3.45; Found, C, 72.36; H, 6.84; N, 3.67.



**Pd3** (0.39 g, 93%). Poor solubility is not suitable for NMR. MS (m/z): calcd for  $C_{41}H_{33}Cl_4N_2Pd$ : 801.04, Found, 801.42,  $[M-Cl]^+$ . Anal. Calcd for  $C_{41}H_{33}Cl_5N_2Pd$ : C, 58.81; H, 3.97; N, 3.35; Found, C, 58.65; H, 4.21; N, 3.17.



**Pd4** (0.35 g, 91%). a-isomer: b-isomer = 3:1  $^1H$  NMR (600 MHz,  $CDCl_3$ , 293K)  $\delta$  9.64, 9.34 (dd,  $^3J = 5.4, 1.0$  Hz, 1H, Ar-H), 8.09, 7.94 (td,  $^3J = 7.9, ^4J = 1.3$  Hz, 1H, Ar-H), 7.83 – 7.79, 7.75 – 7.73 (m, 1H, Ar-H), 7.22, 7.71 (d,  $^3J = 3.3$  Hz, 1H, Ar-H), 7.09 (d,  $^3J = 7.9$  Hz, 2H, Ar-H), 7.05 (dd,  $^3J = 8.5, 5.3$  Hz, 2H, Ar-H), 7.01 – 6.95 (m, 8H, Ar-H), 6.94 – 6.89 (m, 6H, Ar-H), 6.84 – 6.76 (m, 6H, Ar-H), 6.11, 5.89 (s, 2H,  $CHAr_2$ ), 2.22, 2.17 (s, 3H,  $CH_3$ ), 0.88 (s, 3H, Ar-C( $CH_3$ )=N), 0.08, 0.03 (s, 3H, Pd- $CH_3$ ).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ , 293K)  $\delta$  178.06 (C=N), 162.47, 160.84, 160.80, 155.59, 152.15, 152.00, 149.65, 140.89, 140.40, 140.02, 138.84, 137.97, 137.81, 136.90, 136.74, 136.62, 135.59, 131.50, 131.45, 131.19, 131.14, 130.83, 130.78, 129.32, 128.67, 125.52, 124.13, 115.96, 115.81, 115.67, 115.27, 115.13, 115.01, 50.83 ( $CHAr_2$ ), 50.30 ( $CHAr_2$ ), 21.72 ( $CH_3$ ), 21.55 ( $CH_3$ ), 18.06 (Ar-C( $CH_3$ )=N), 17.72 (Ar-C( $CH_3$ )=N), 2.60 (Pd- $CH_3$ ).  $^{19}F$  NMR (565 MHz,  $CDCl_3$ , 293K)  $\delta$  -114.12 (q,  $J = 9.8$  Hz), -114.52 (t,  $J = 9.4$  Hz), -114.78 (d,  $J = 18.6$  Hz), -115.15 – -115.25 (m), -116.00 (t,  $J = 9.3$  Hz), -116.13 (t,  $J = 9.3$  Hz), -116.43 (d,  $J = 16.6$  Hz), -116.81 – -116.91 (m). MS (m/z): calcd for  $C_{41}H_{33}F_4N_2Pd$ : 735.16, Found, 735.33,  $[M-Cl]^+$ . Anal. Calcd for  $C_{41}H_{33}ClF_4N_2Pd$ : C, 63.82; H, 4.31; N, 3.63; Found, C, 63.64; H, 4.41; N, 3.54.

#### **1.4 A General Procedure for the Homopolymerization of Ethylene using Pd Complexes.**

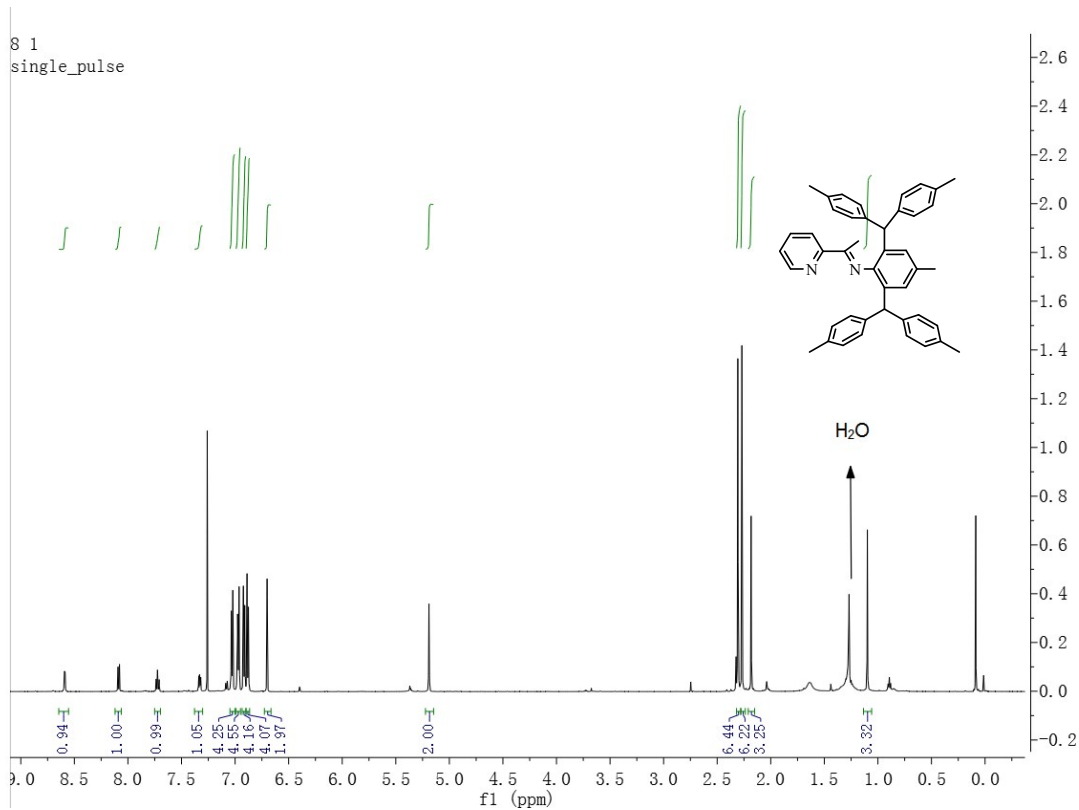
In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 38 mL of DCM and the desired amount NaBARF was added to the reactor under N<sub>2</sub> atmosphere, then the desired amount of catalyst in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was injected into the polymerization 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 polymer was dried under vacuum by rotary evaporator.

#### **1.5 A General Procedure for the Copolymerization of Methyl Acrylate with Ethylene using Pd Complexes.**

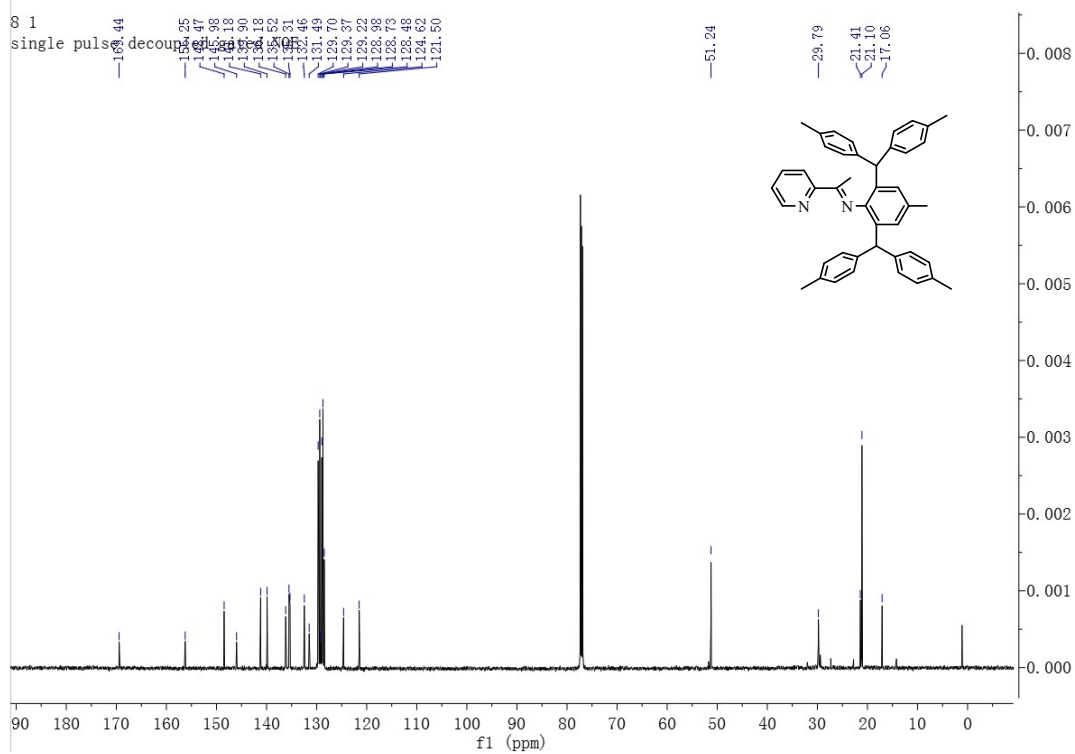
In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 18 mL of DCM and desired methyl acrylate with the desired amount NaBARF was added to the reactor under N<sub>2</sub> atmosphere, then the Pd catalyst in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> 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 12 h, the pressure reactor was vented and the copolymer was dried under vacuum by rotary evaporator.

## **2. Spectra Data**

### **2.1 <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR of the Synthetic Compounds.**

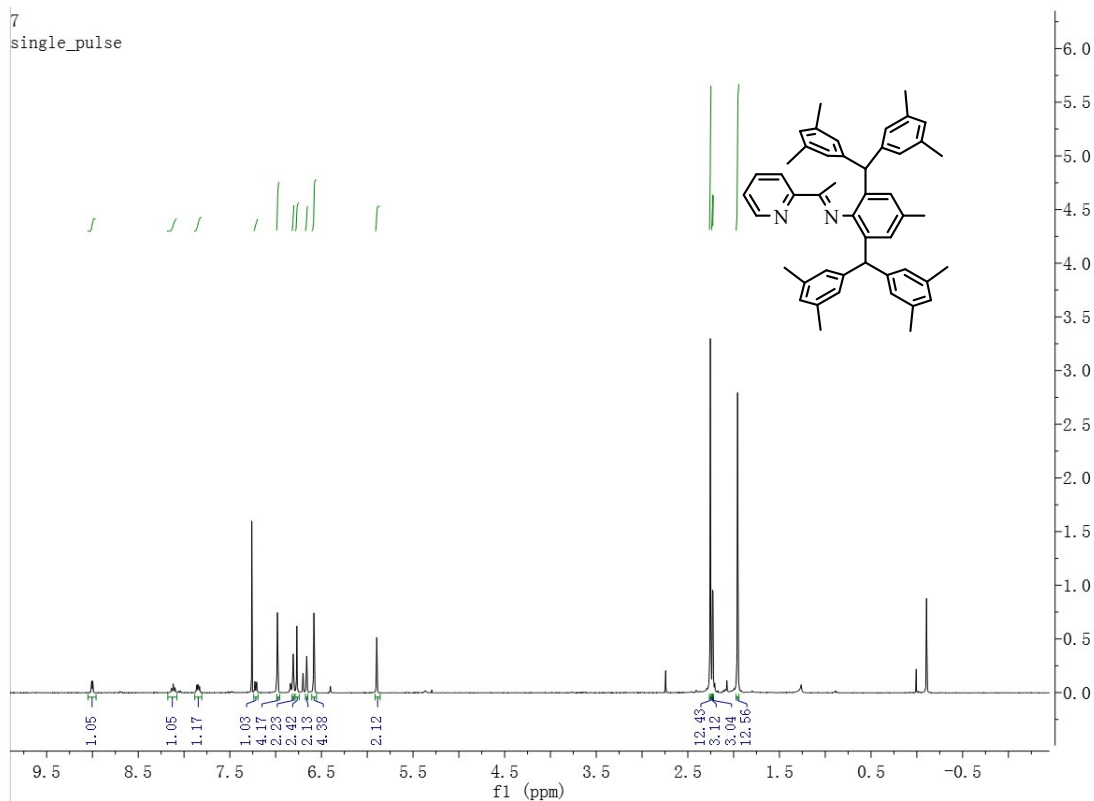


**Figure S1.** <sup>1</sup>H NMR spectrum of L1 in CDCl<sub>3</sub> (600 MHz, 293K).

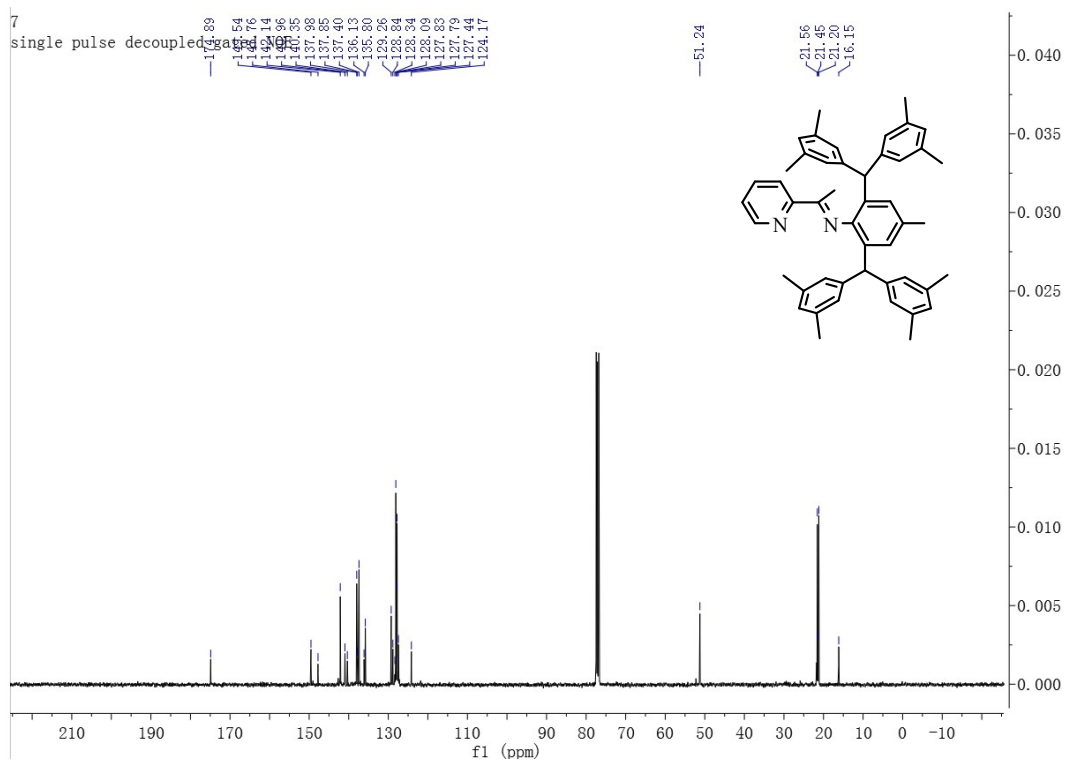


**Figure S2.** <sup>13</sup>C NMR spectrum of L1 in CDCl<sub>3</sub> (151 MHz, 293K).





**Figure S3.**  $^1\text{H}$  NMR spectrum of **L2** in  $\text{CDCl}_3$  (600 MHz, 293K).



**Figure S4.**  $^{13}\text{C}$  NMR spectrum of **L2** in  $\text{CDCl}_3$  (151 MHz, 293K).

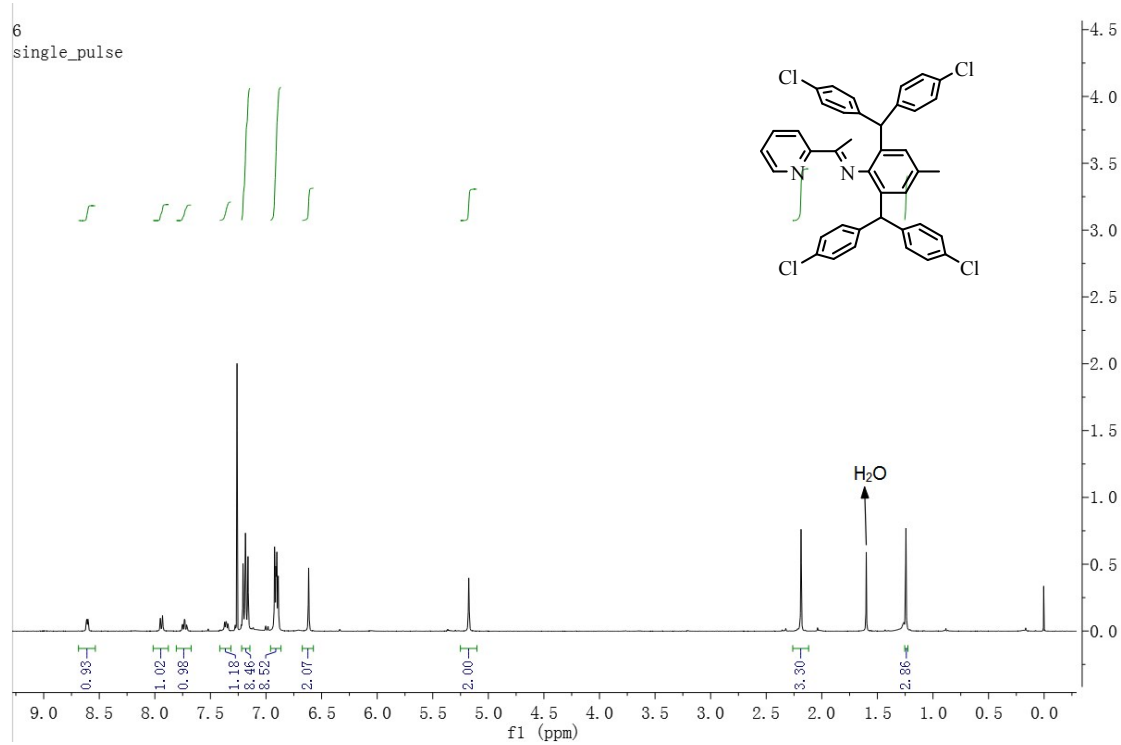


Figure S5.  $^1\text{H}$  NMR spectrum of L3 in  $\text{CDCl}_3$  (600 MHz, 293K).

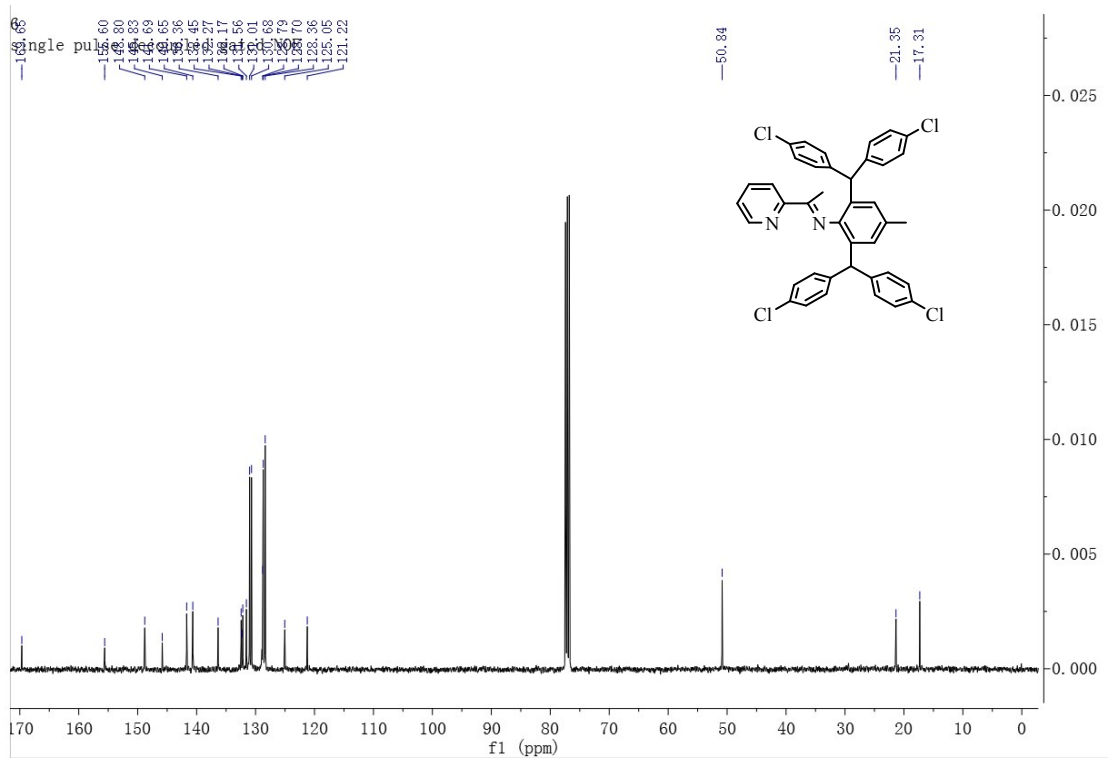
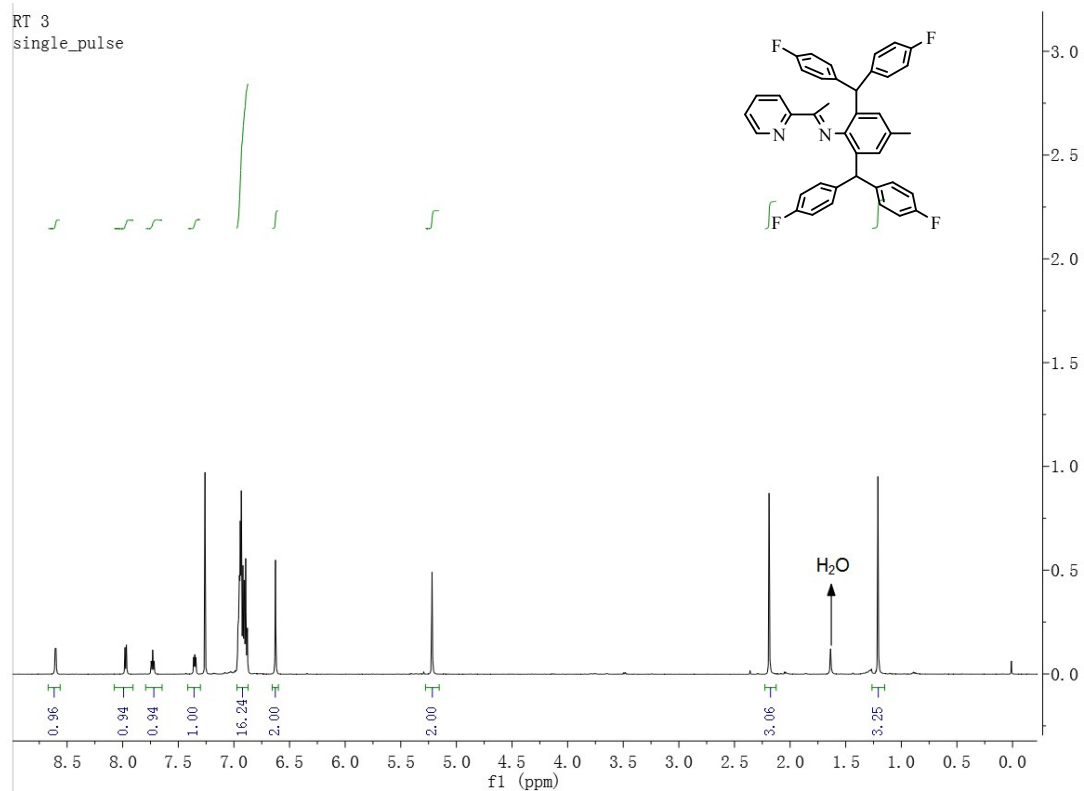
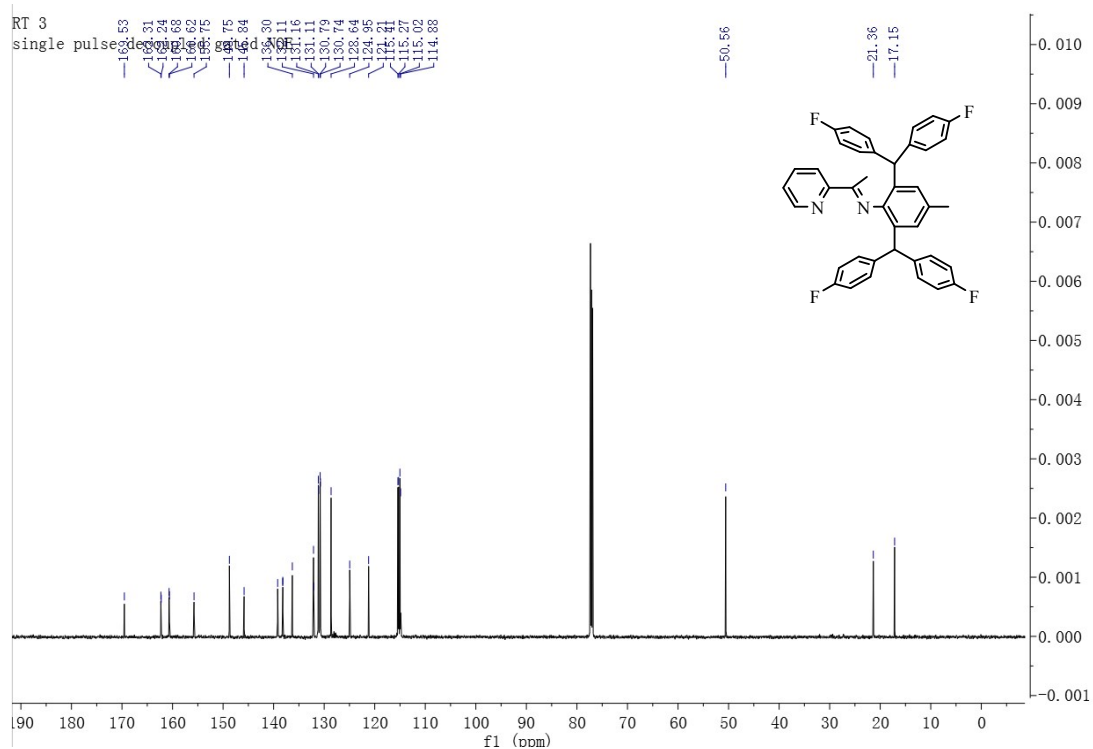


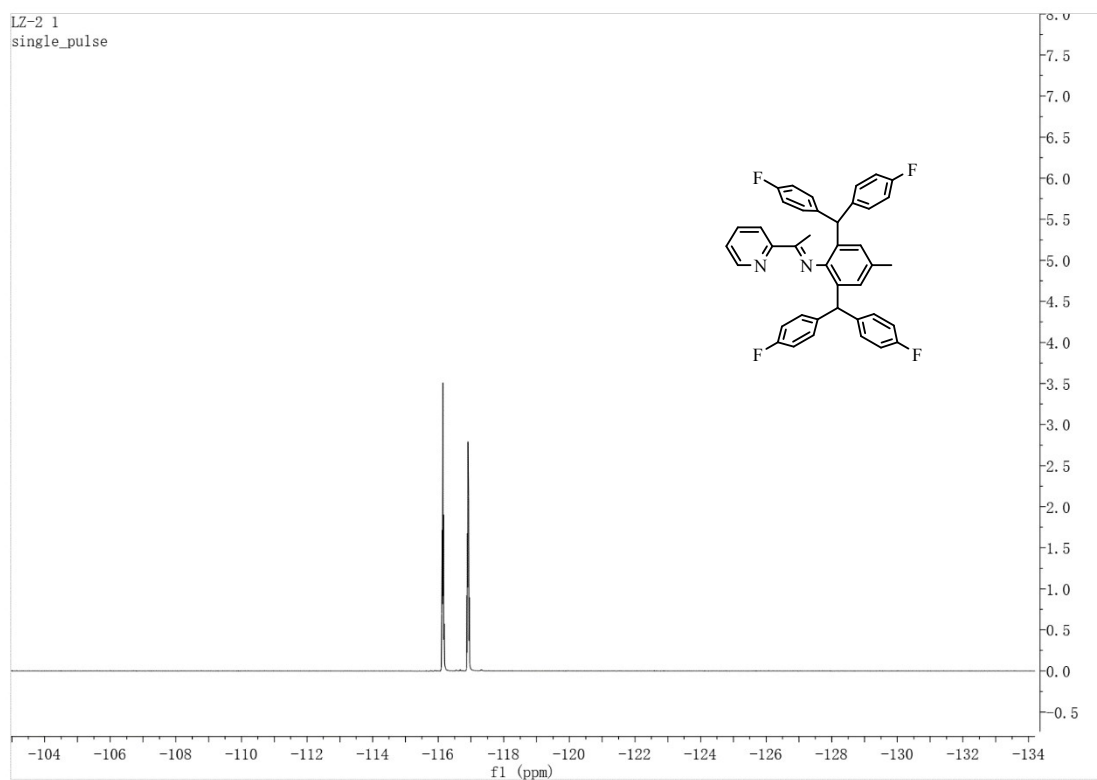
Figure S6.  $^{13}\text{C}$  NMR spectrum of L3 in  $\text{CDCl}_3$  (151 MHz, 293K).



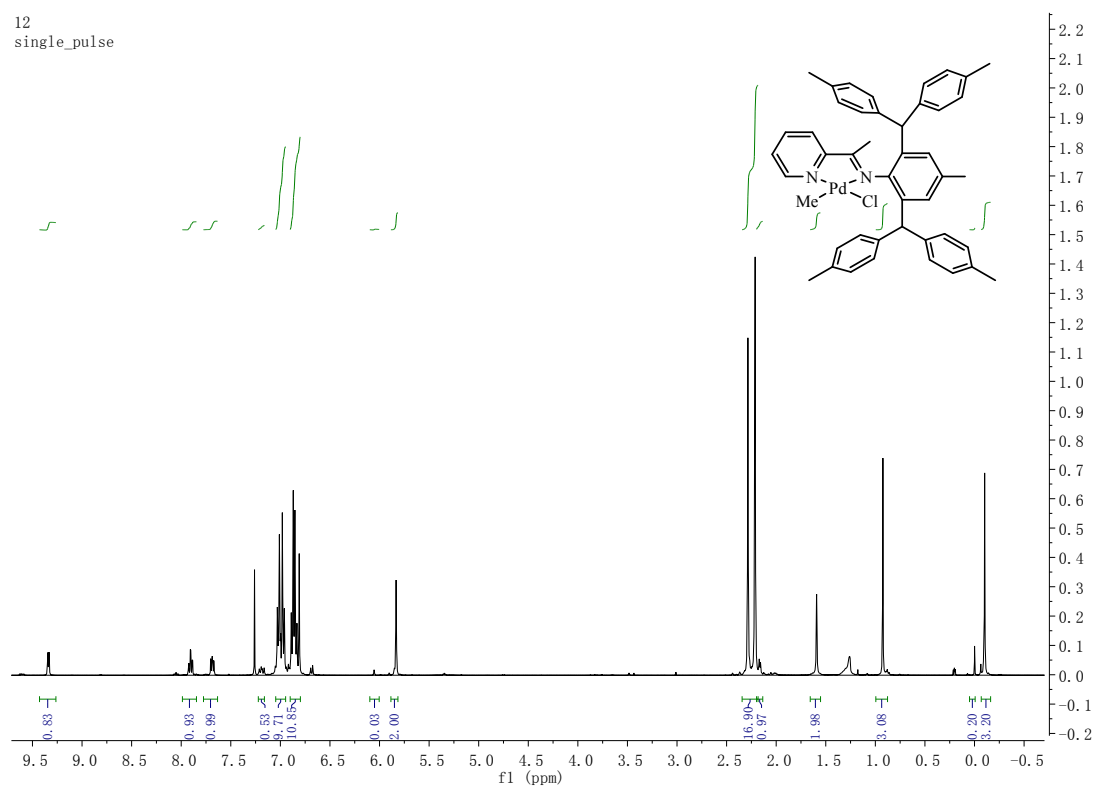
**Figure S7.** <sup>1</sup>H NMR spectrum of L4 in CDCl<sub>3</sub> (600 MHz, 293K).



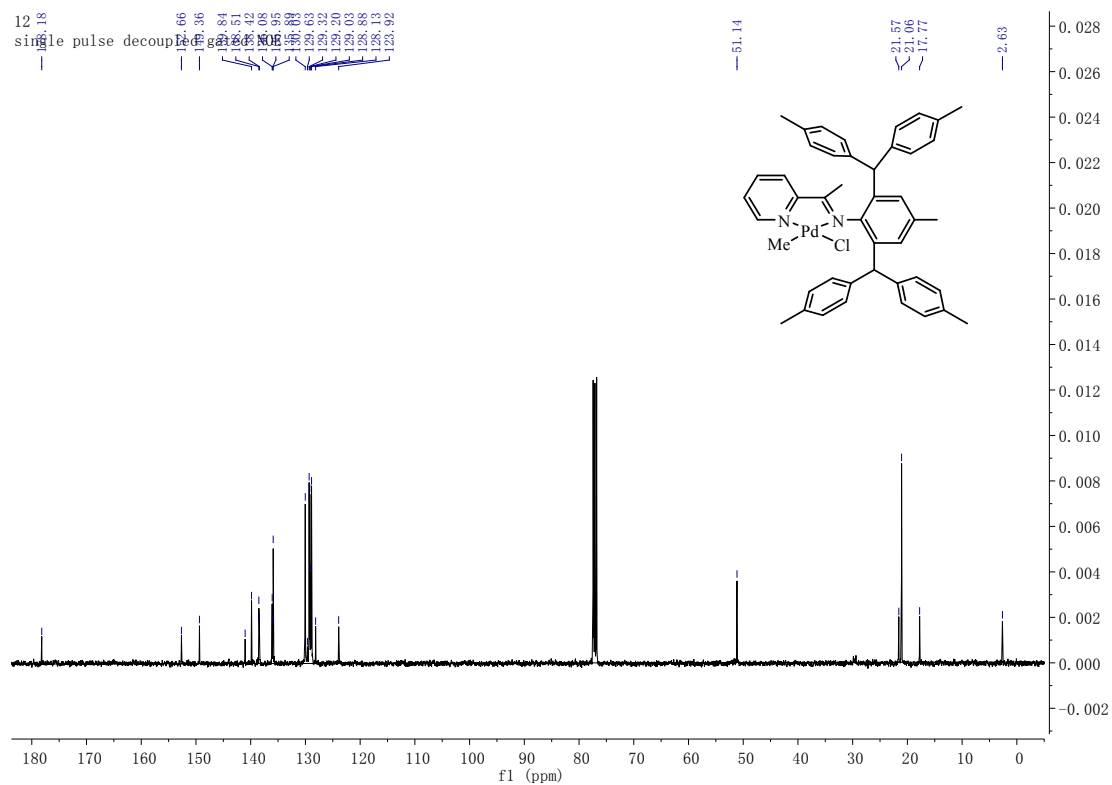
**Figure S8.** <sup>13</sup>C NMR spectrum of L4 in CDCl<sub>3</sub> (151 MHz, 293K).



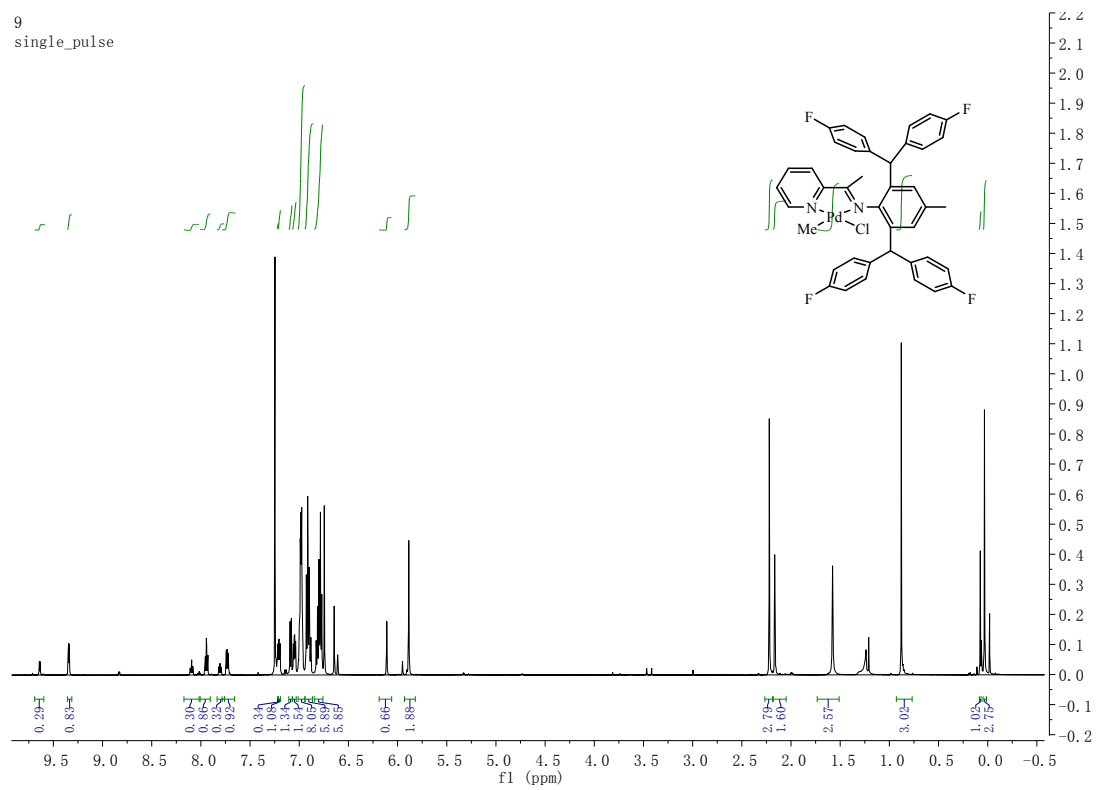
**Figure S9.**  $^{19}\text{F}$  NMR spectrum of **L4** in  $\text{CDCl}_3$  (565 MHz, 293K).



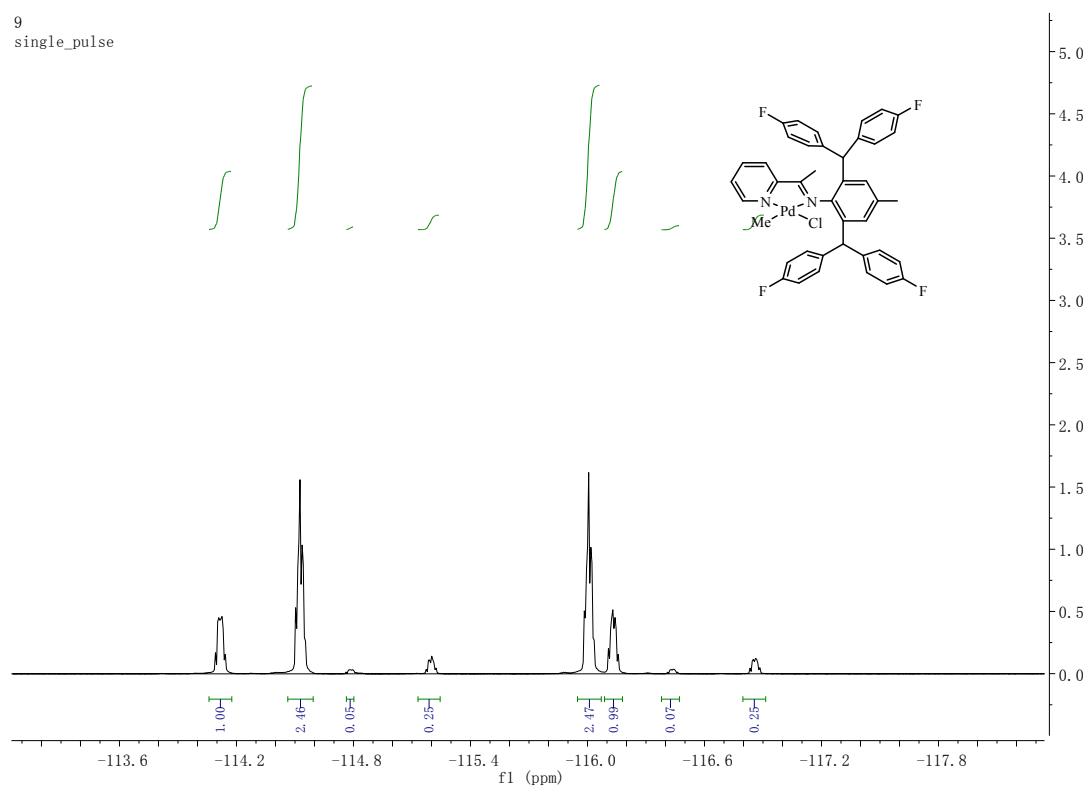
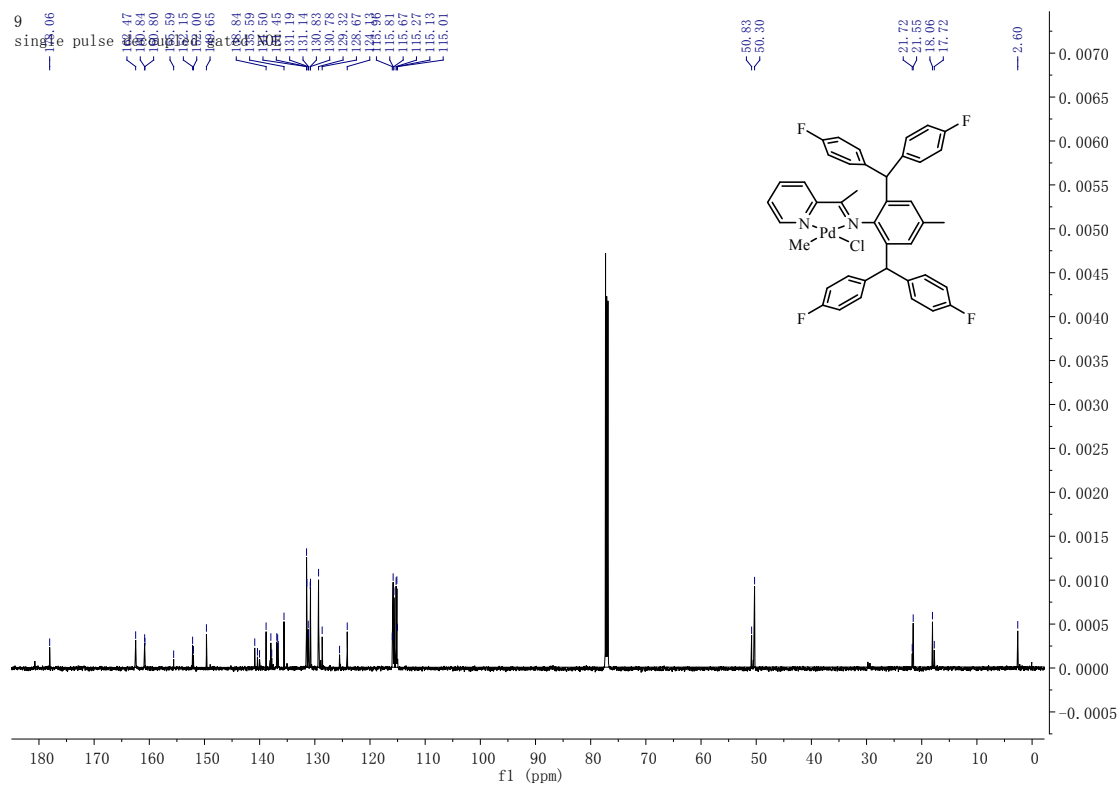
**Figure S10.**  $^1\text{H}$  NMR spectrum of **Pd1** in  $\text{CDCl}_3$  (600 MHz, 293K).



**Figure S11.**  $^{13}\text{C}$  NMR spectrum of **Pd1** in  $\text{CDCl}_3$  (151 MHz, 293K).



**Figure S12.**  $^1\text{H}$  NMR spectrum of **Pd4** in  $\text{CDCl}_3$  (600 MHz, 293K).



## 2.2 MS of L1-L4.

LZ-L-Me #21 RT: 0.16 AV: 1 NL: 7.02E8  
T: FTMS + c APCI corona Full ms [150.00-1000.00]

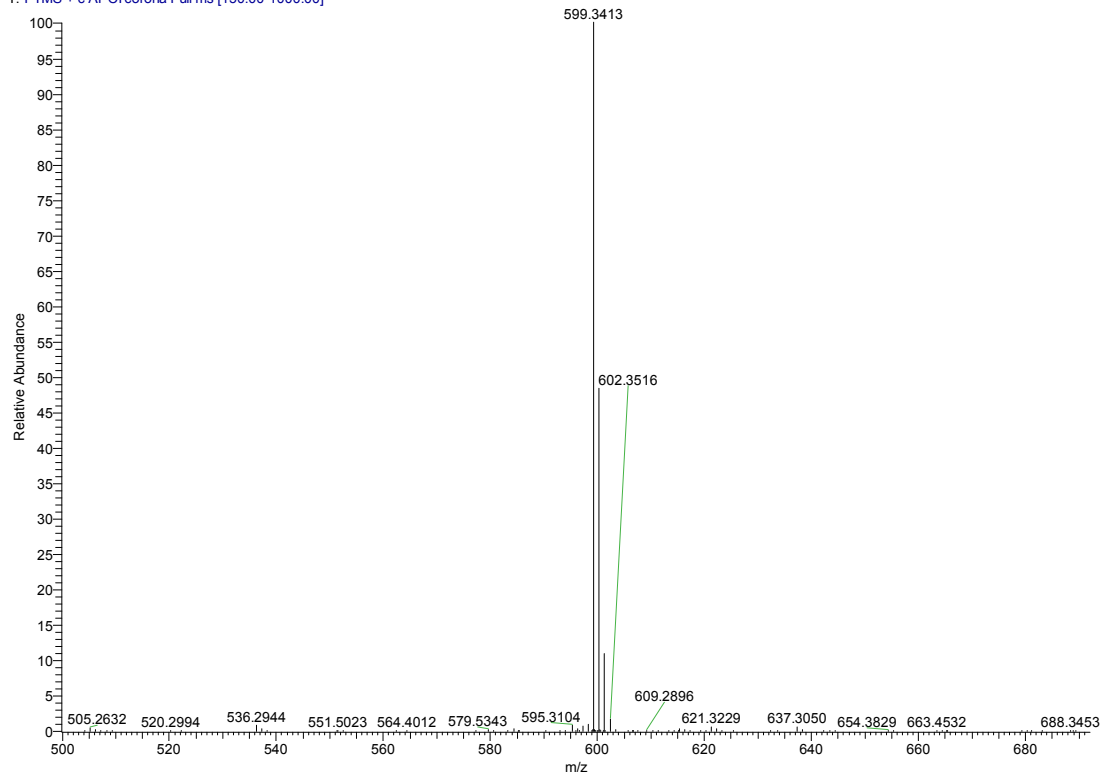


Figure S15. MS of L1.

LZ-L-DMe #21 RT: 0.16 AV: 1 NL: 1.87E8  
T: FTMS + c APCI corona Full ms [150.00-1000.00]

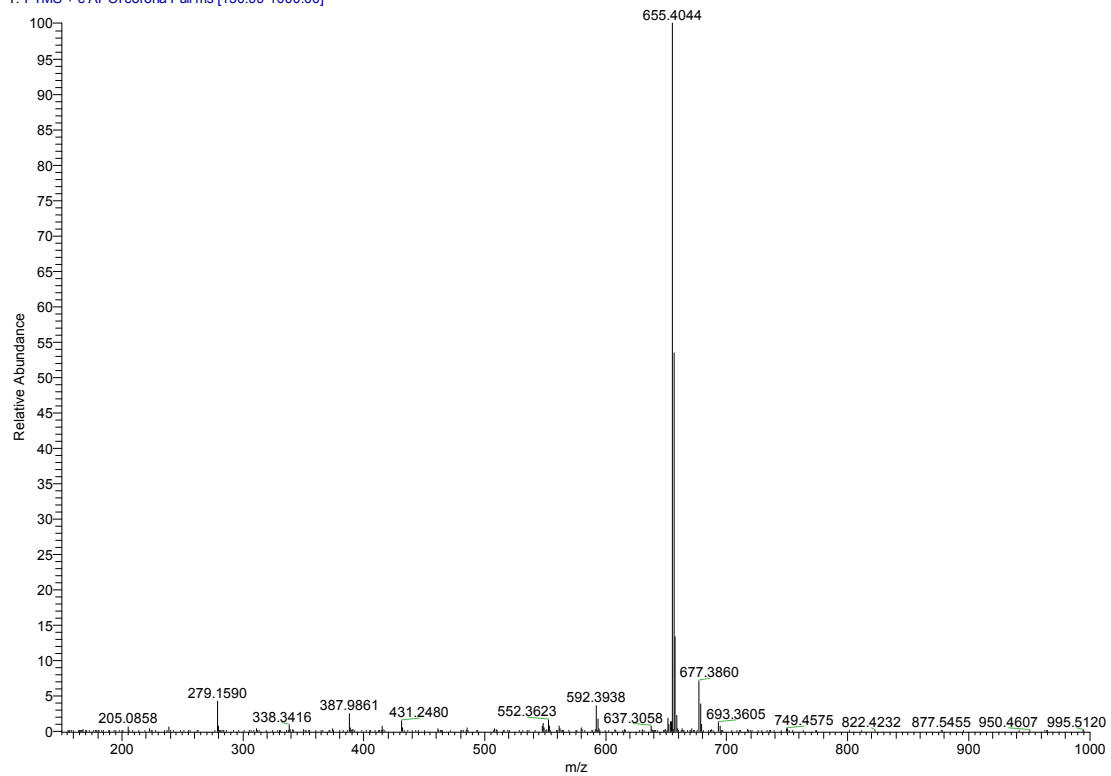


Figure S16. MS of L2.

LZ-L-CL #22 RT: 0.17 AV: 1 NL: 1.74E8  
T: FTMS + c APCI corona Full ms [150.00-1000.00]

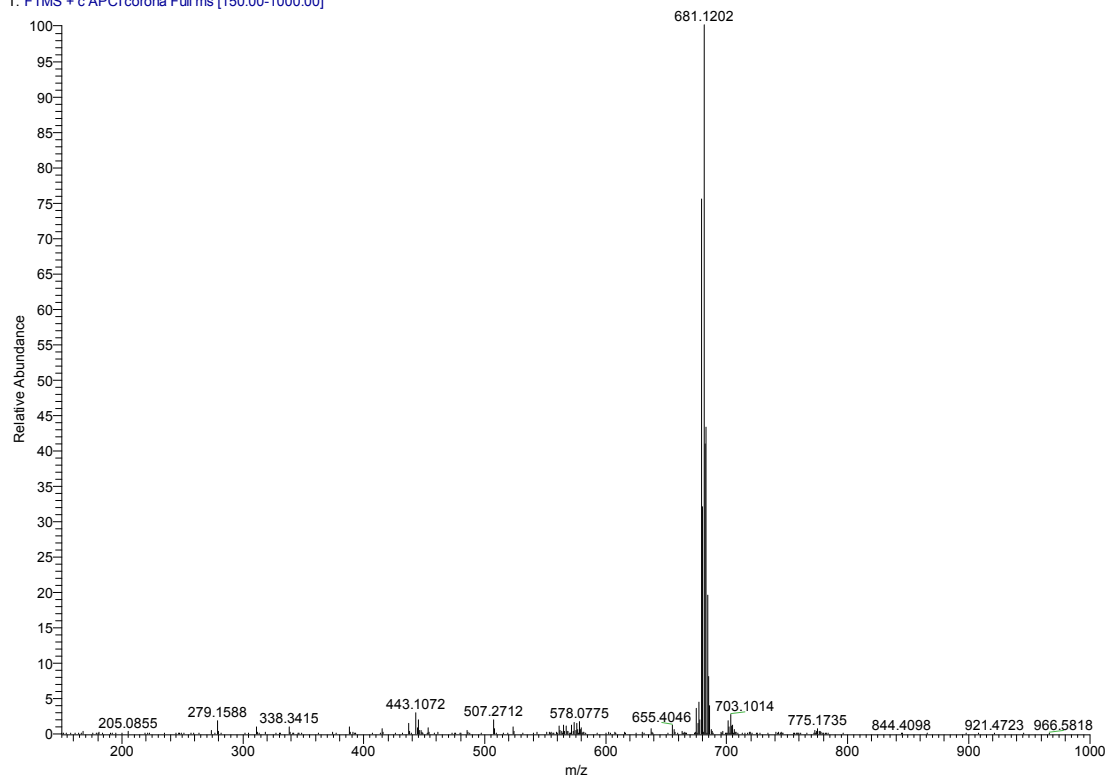


Figure S17. MS of L3.

LZ-L-F #21 RT: 0.16 AV: 1 NL: 4.78E8  
T: FTMS + c APCI corona Full ms [150.00-1000.00]

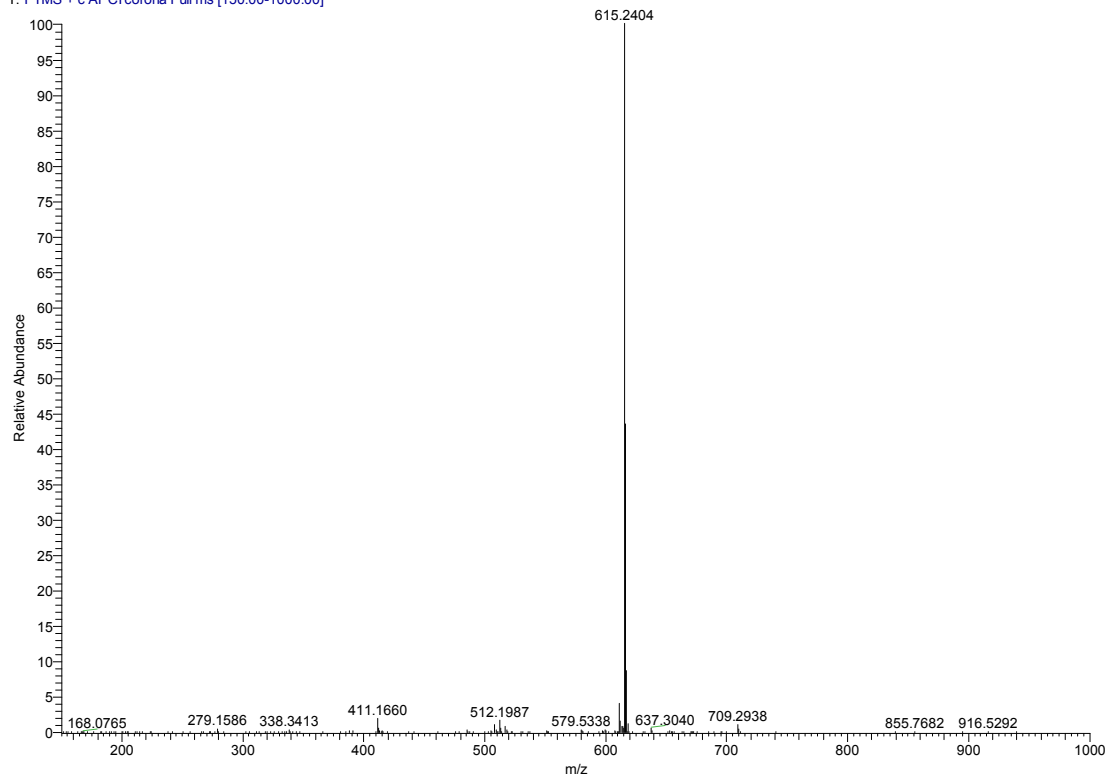


Figure S18. MS of L4.



### 2.3 MS of Complexes Pd1-Pd4.

LZ-Pd-Me #38 RT: 0.18 AV: 1 NL: 1.47E5  
T: ITMS + p ESI Full ms [200.00-1400.00]

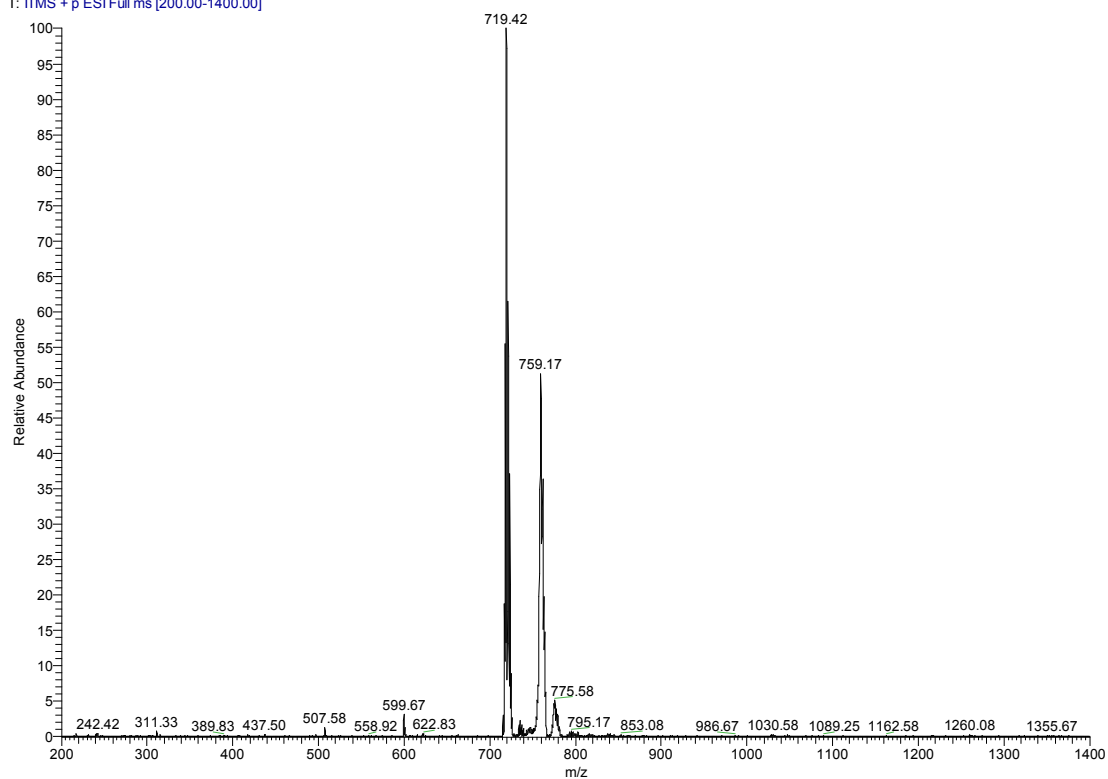


Figure S19. MS of complex Pd1.

LZ-Pd-DMe #44 RT: 0.20 AV: 1 NL: 4.75E4  
T: ITMS + p ESI Full ms [200.00-1400.00]

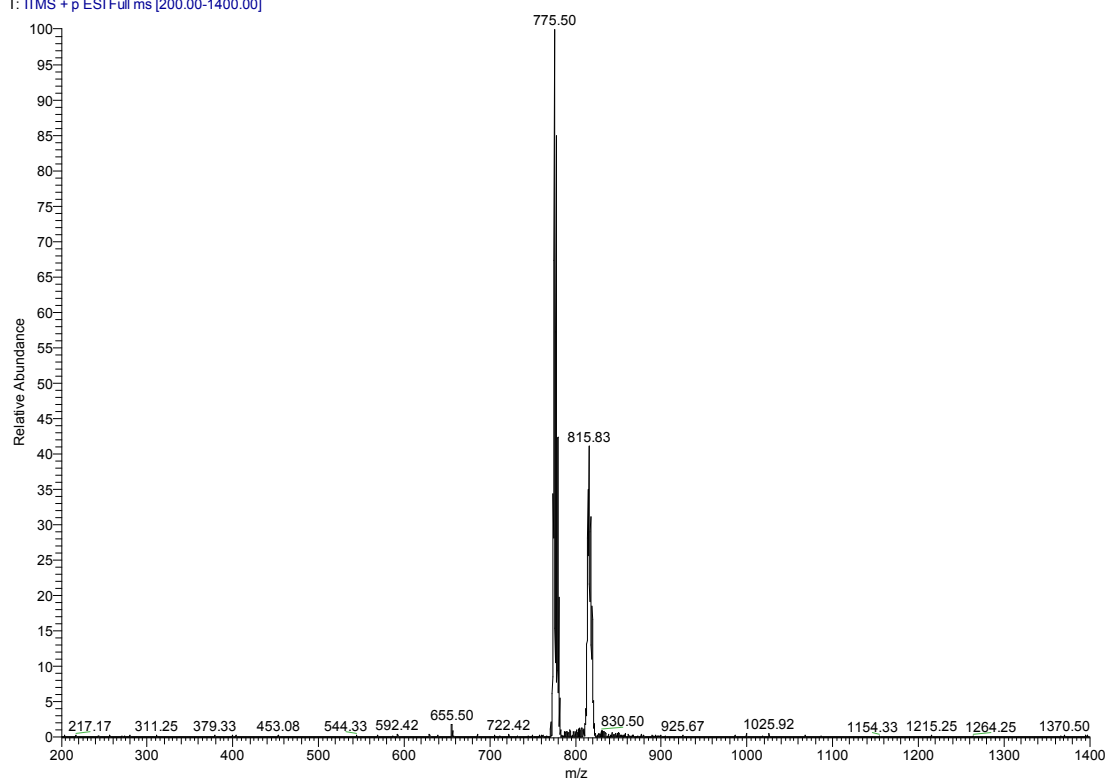


Figure S20. MS of complex Pd2.

LZ-Pd-CL #30 RT: 0.16 AV: 1 SB: 1 0.06 NL: 3.62E4  
T: ITMS + p ESI Full ms [200.00-1400.00]

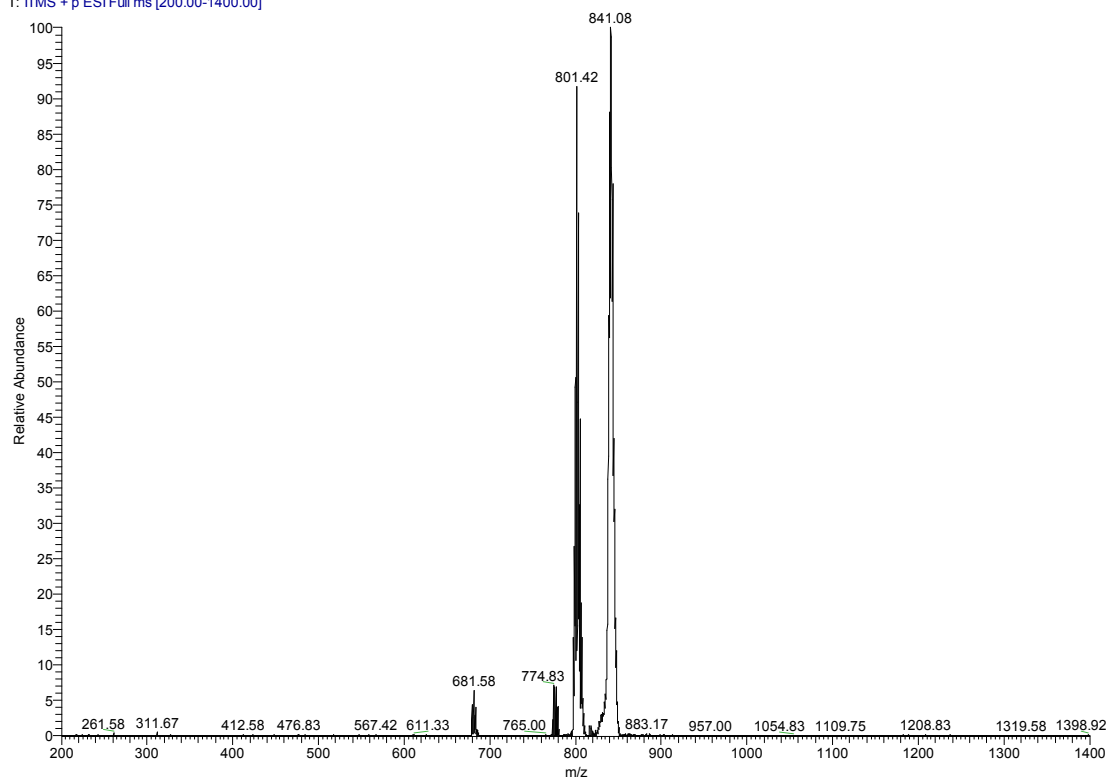


Figure S21. MS of complex Pd3.

LZ-Pd-F #37 RT: 0.17 AV: 1 NL: 1.86E5  
T: ITMS + p ESI Full ms [200.00-1400.00]

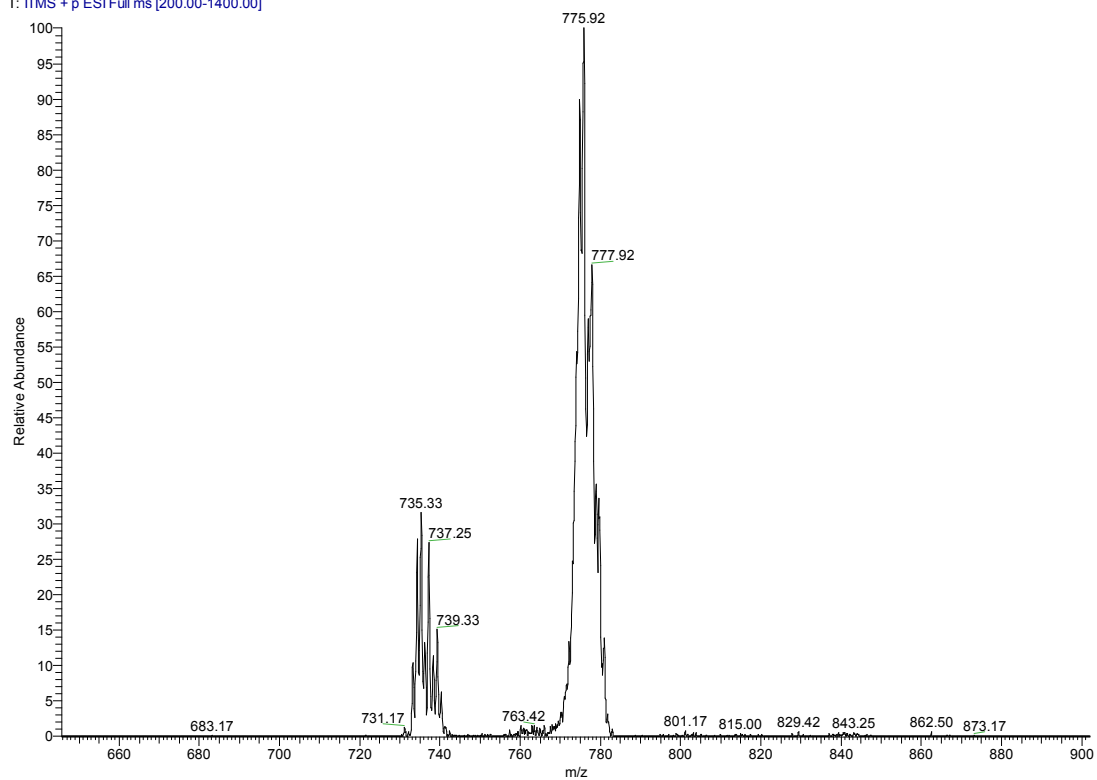
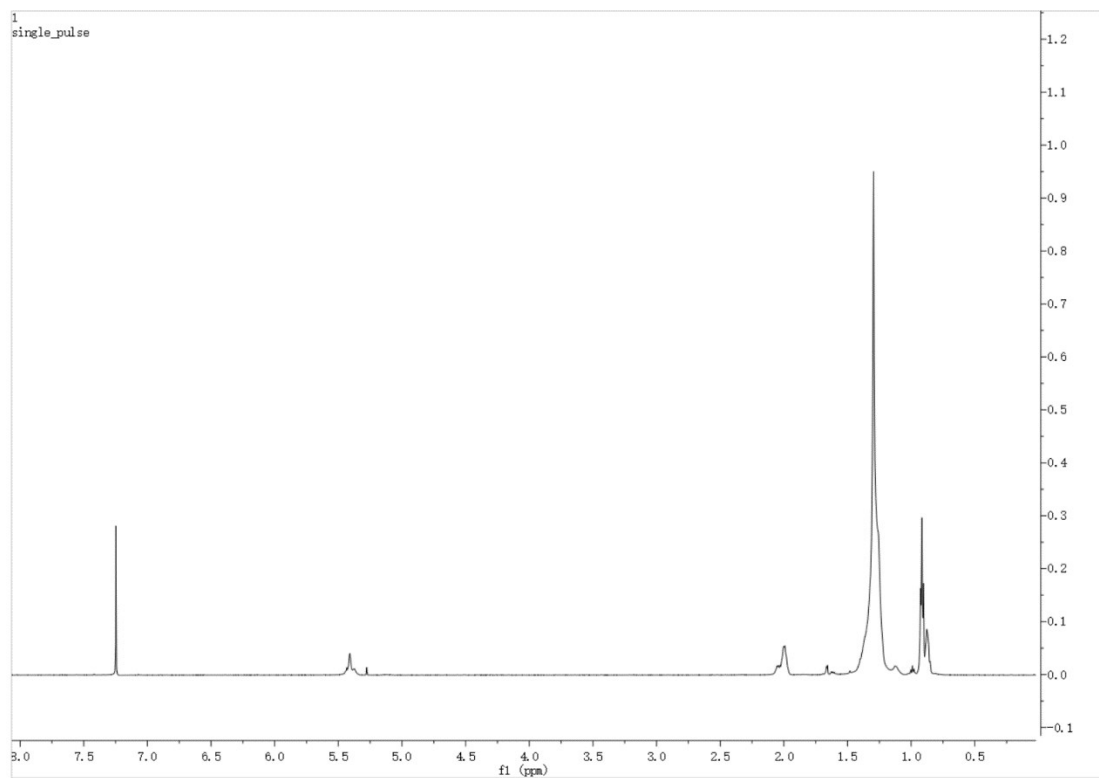
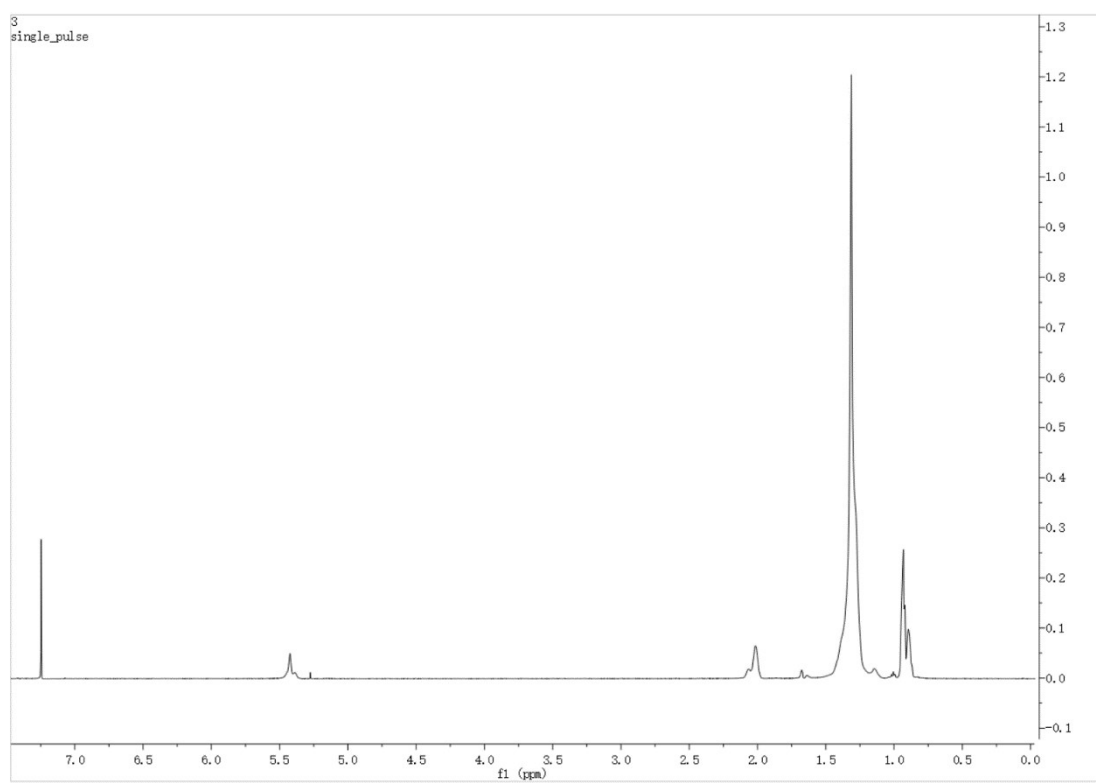


Figure S22. MS of complex Pd4.

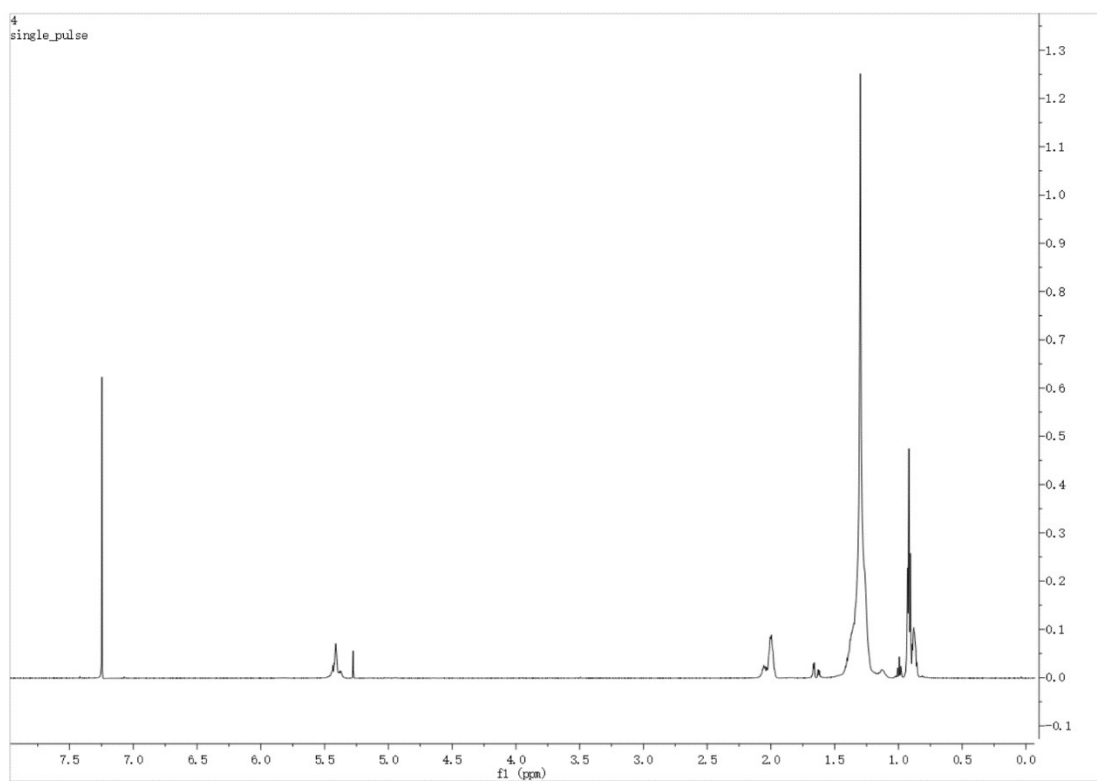
## 2.4 $^1\text{H}$ and $^{13}\text{C}$ NMR of polymers and copolymers.



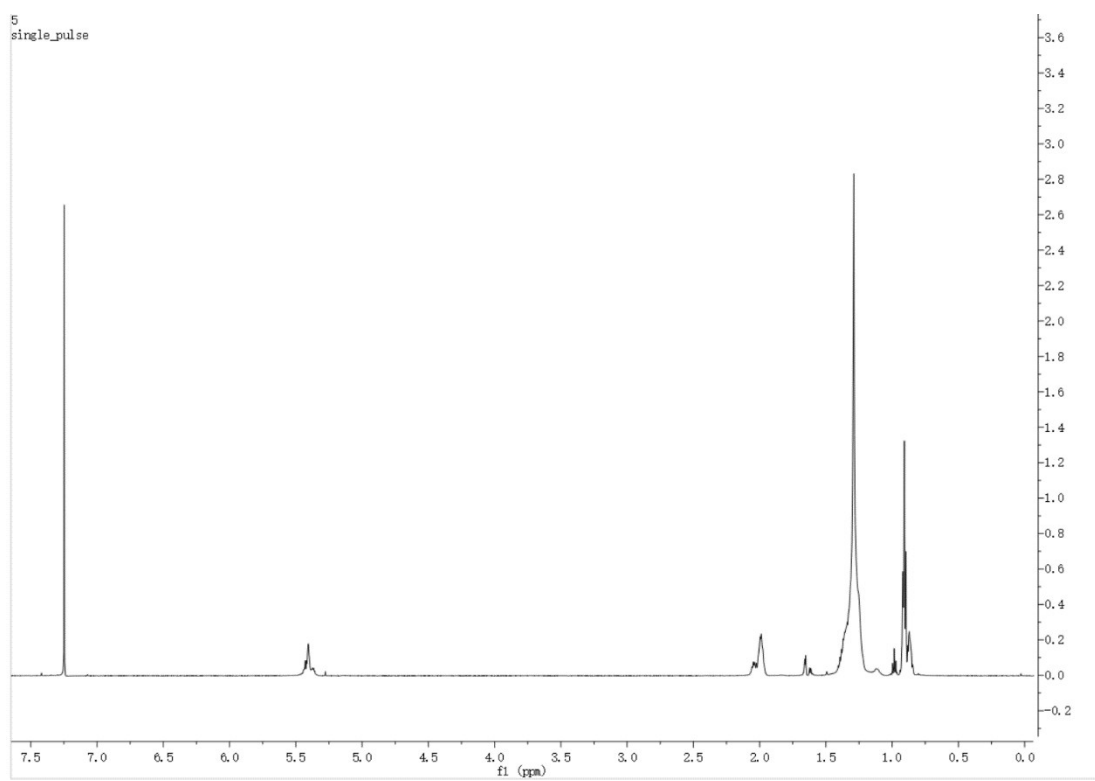
**Figure S23.**  $^1\text{H}$  NMR spectrum of the polymer from table 1, entry 1 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).



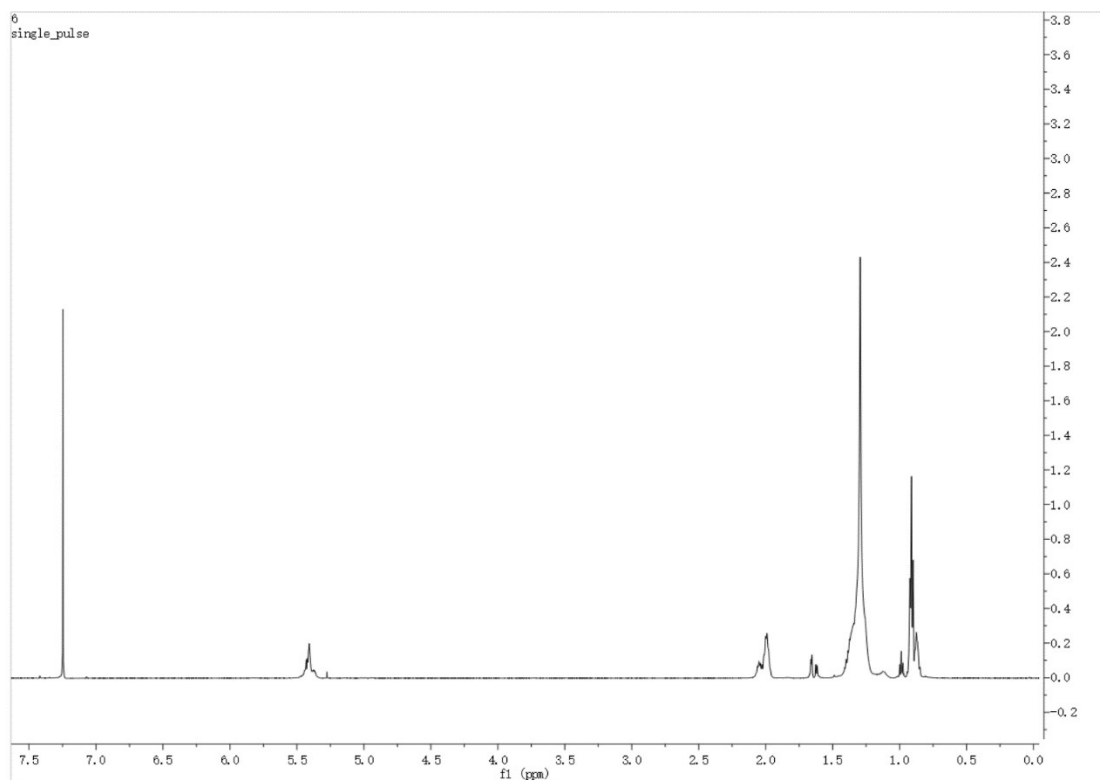
**Figure S24.**  $^1\text{H}$  NMR spectrum of the polymer from table 1, entry 3 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).



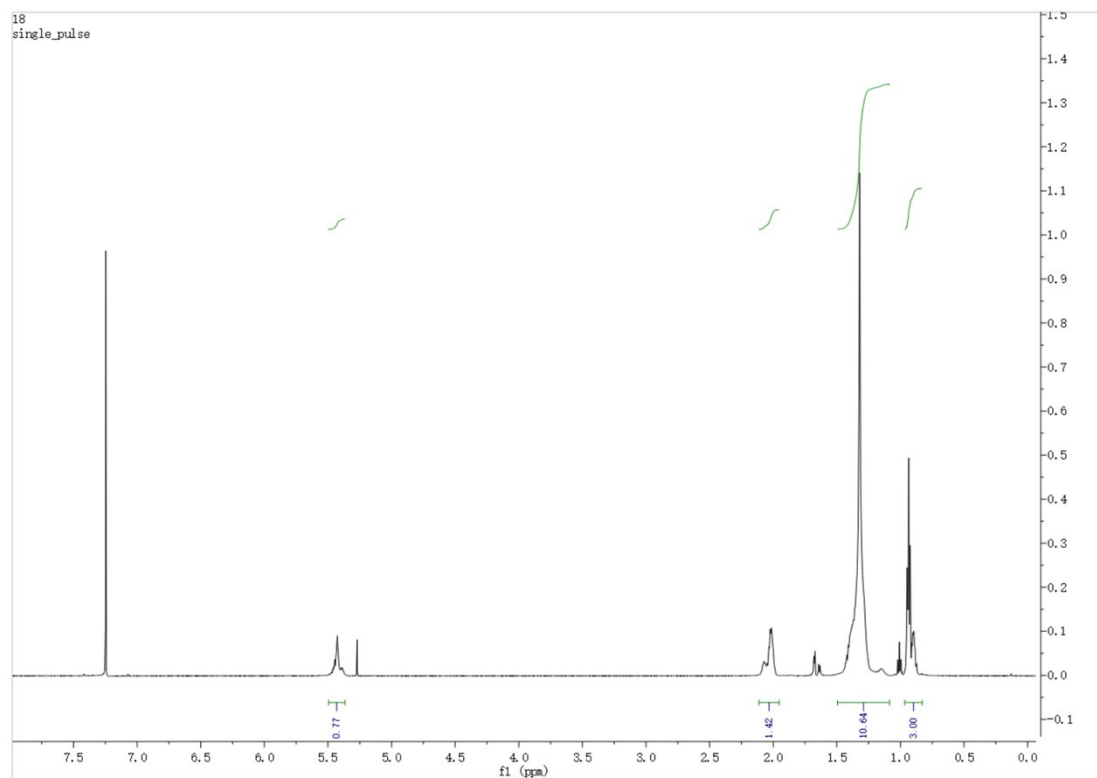
**Figure S25.** <sup>1</sup>H NMR spectrum of the polymer from table 1, entry 4 (CDCl<sub>3</sub>, 20 °C).



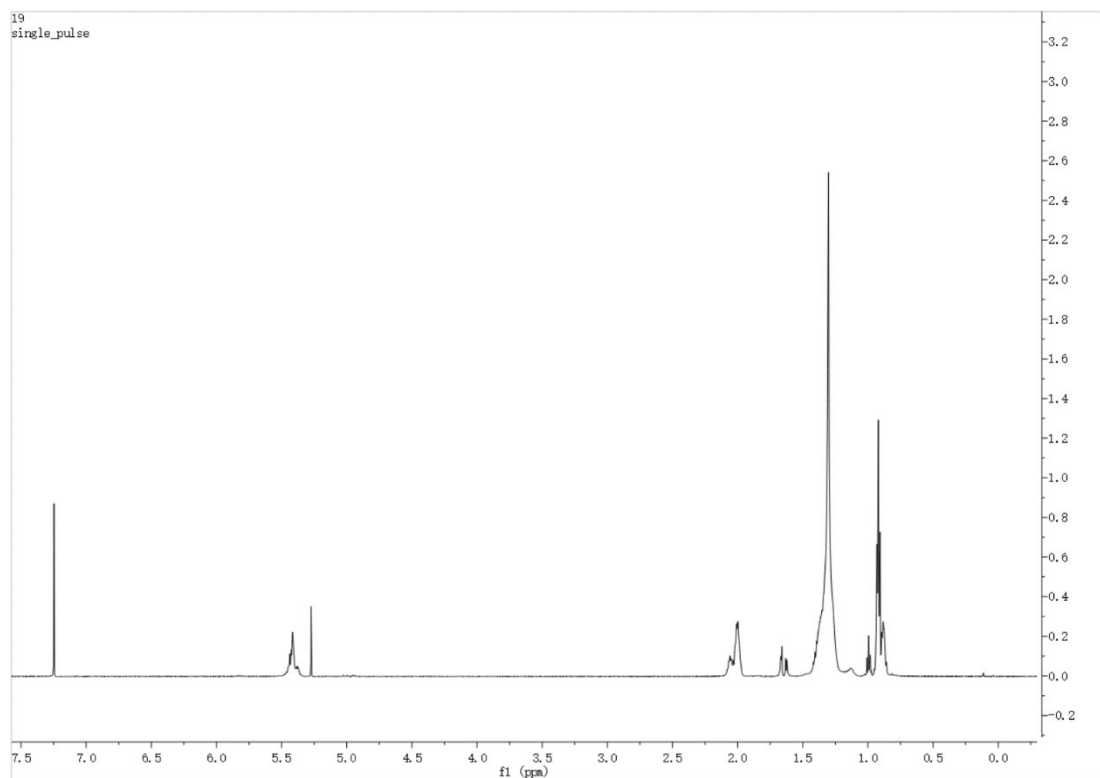
**Figure S26.** <sup>1</sup>H NMR spectrum of the polymer from table 1, entry 5 (CDCl<sub>3</sub>, 20 °C).



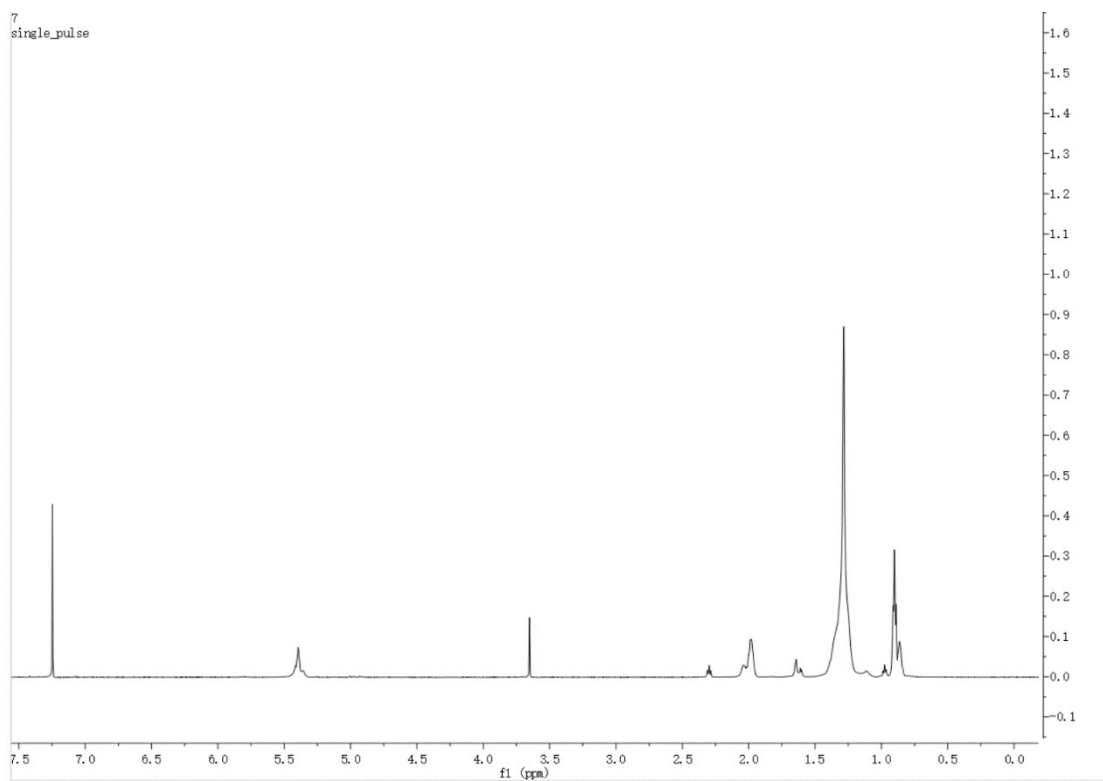
**Figure S27.**  $^1\text{H}$  NMR spectrum of the polymer from table 1, entry 6 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).



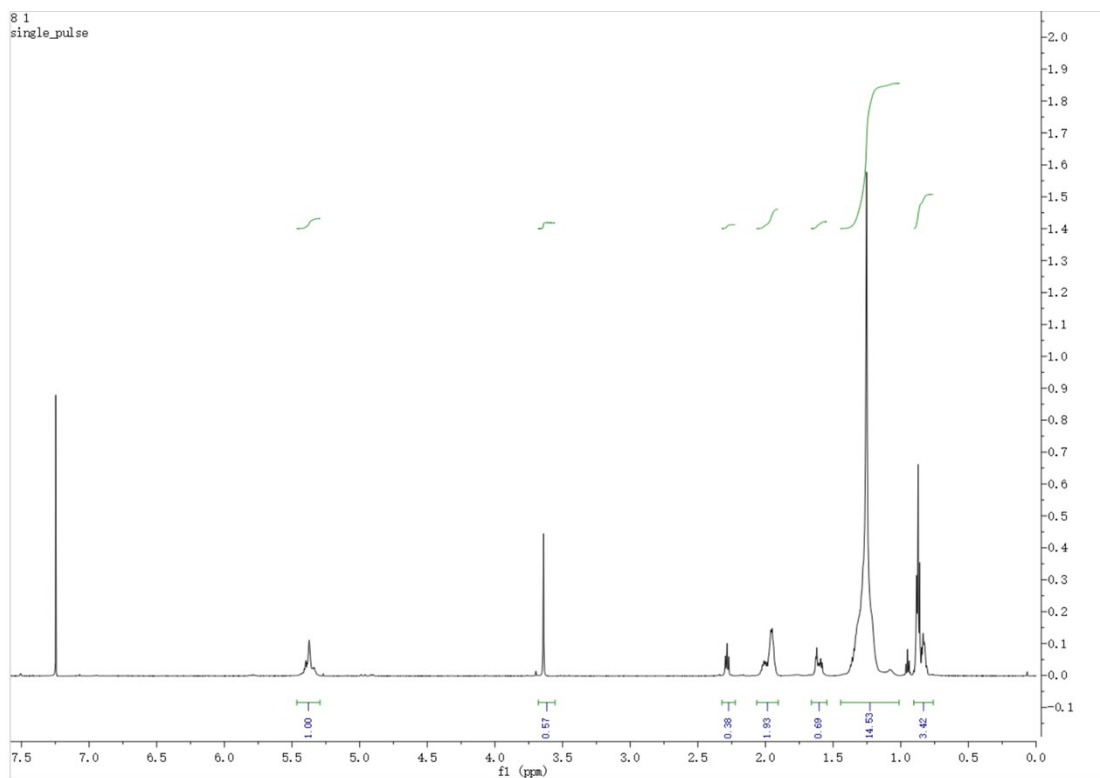
**Figure S28.**  $^1\text{H}$  NMR spectrum of the polymer from table 1, entry 7 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).



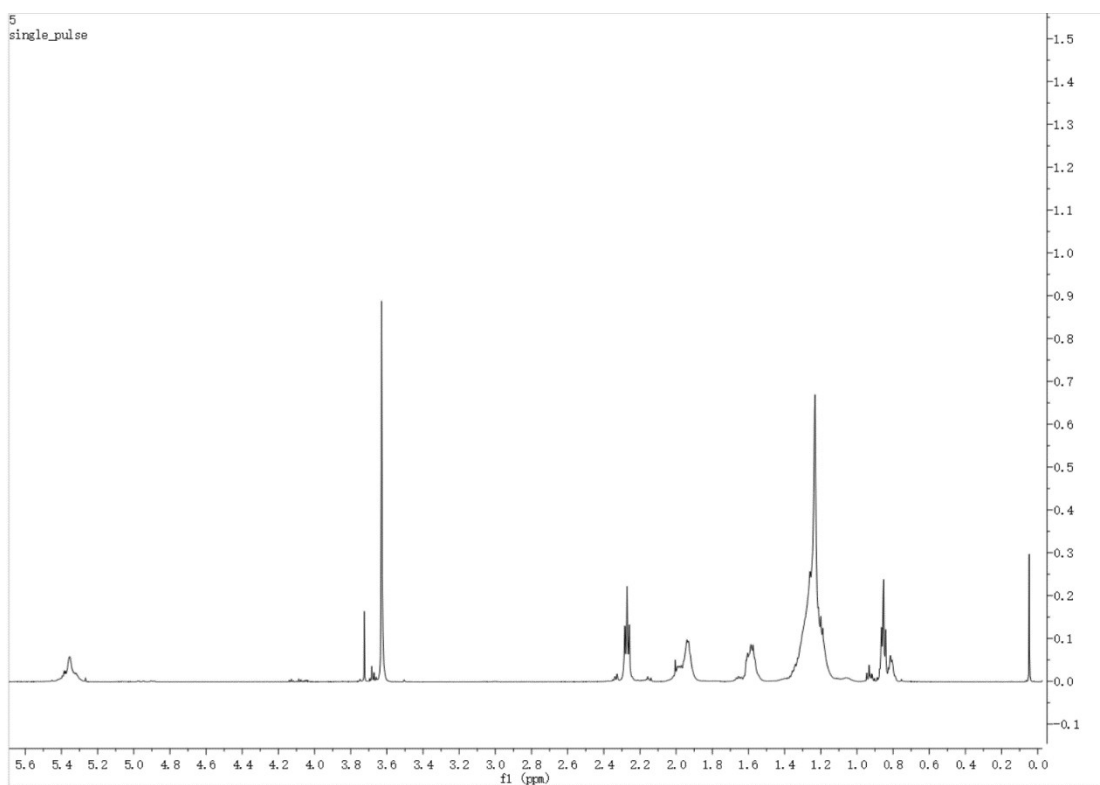
**Figure S29.** <sup>1</sup>H NMR spectrum of the polymer from table 1, entry 8 (CDCl<sub>3</sub>, 20 °C).



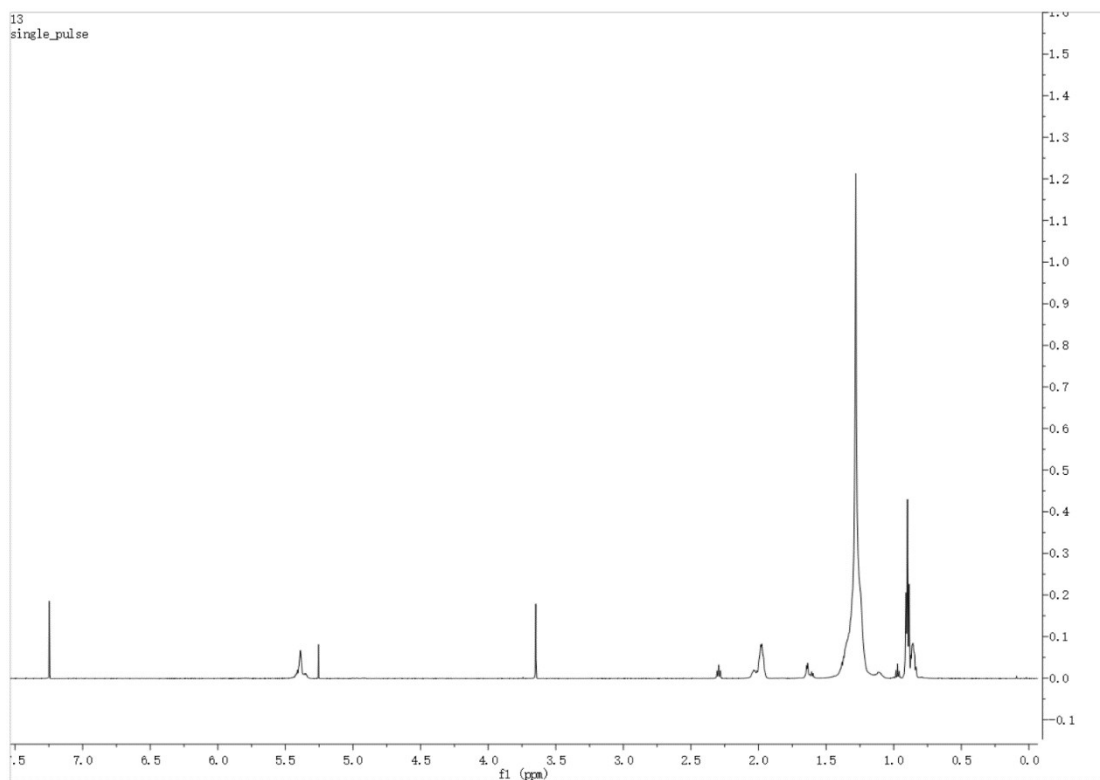
**Figure S30.** <sup>1</sup>H NMR spectrum of the polymer from table 2, entry 1 (CDCl<sub>3</sub>, 20 °C).



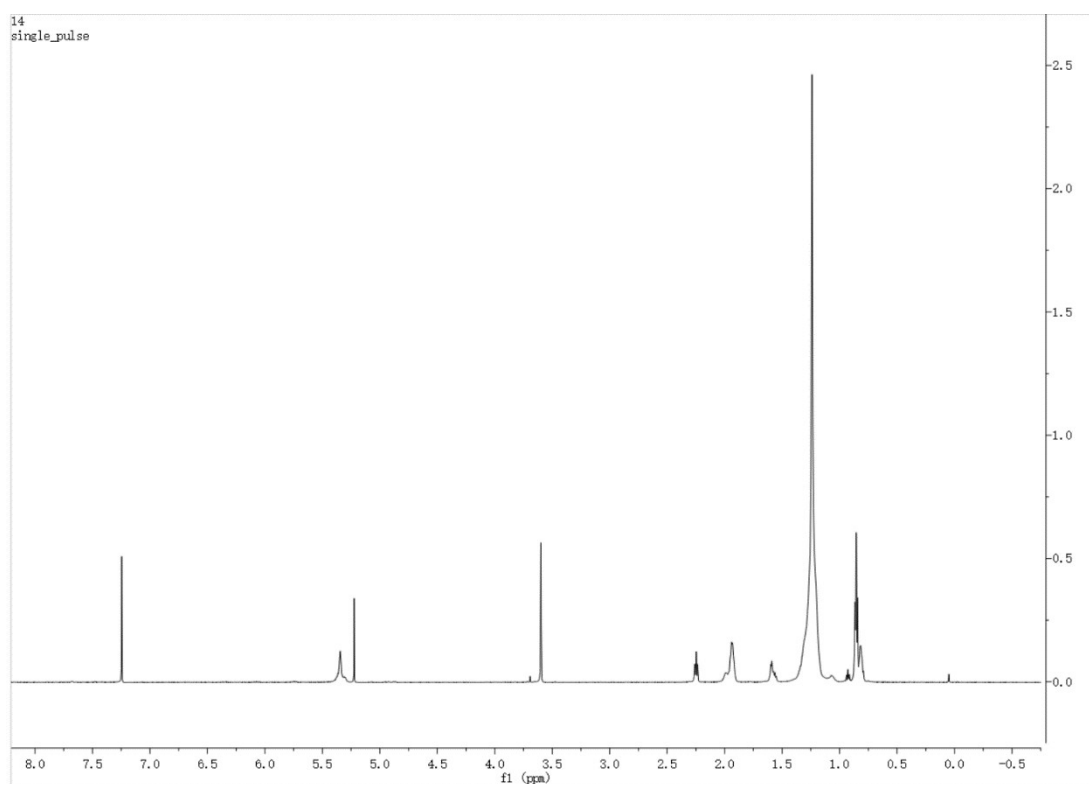
**Figure S31.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 2 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).



**Figure S32.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 4 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).

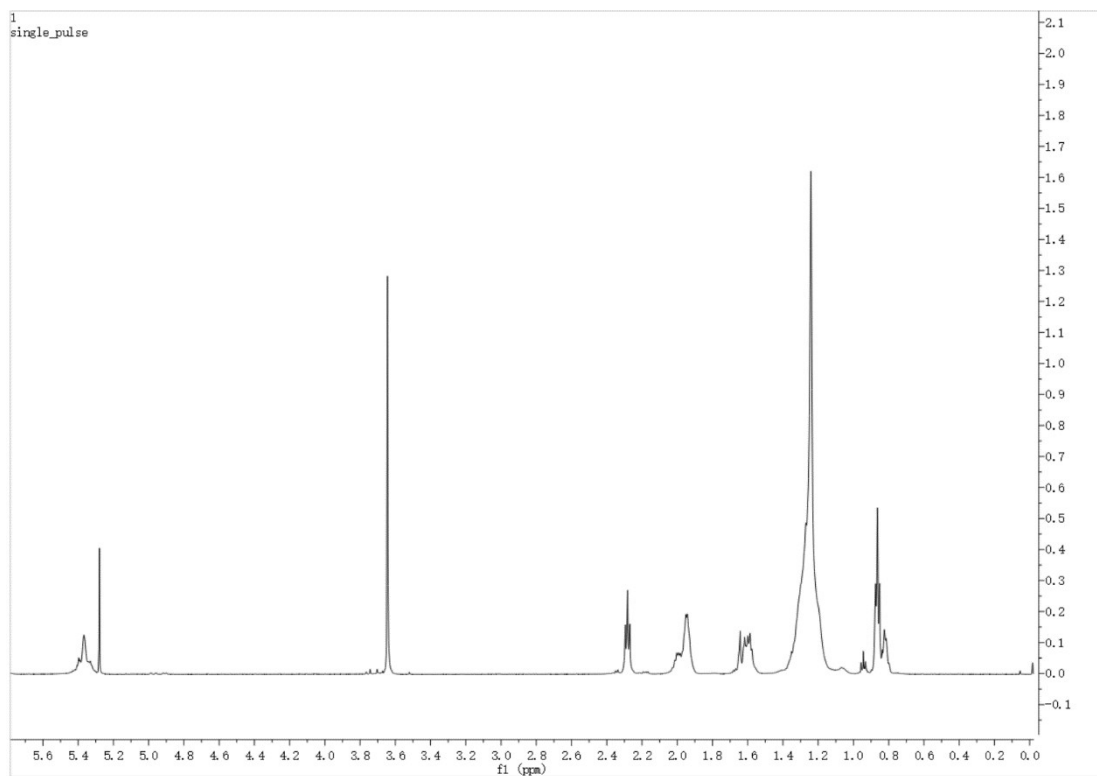


**Figure S33.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 5 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).

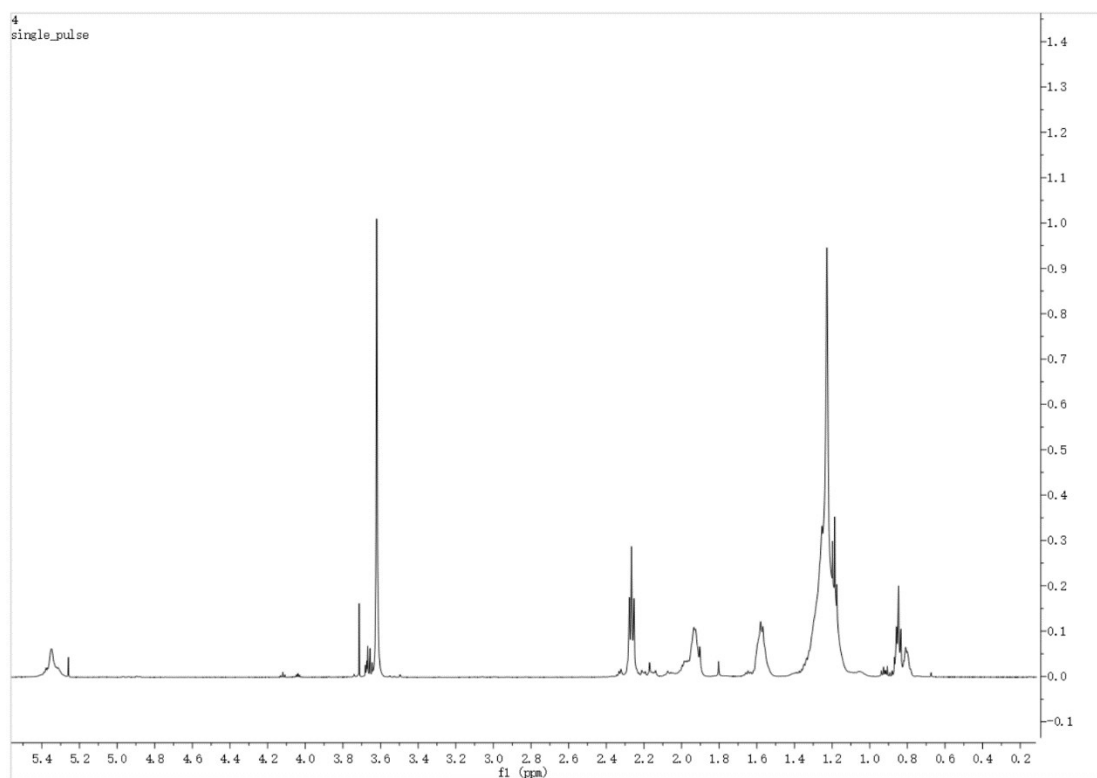


**Figure S34.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 6 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).

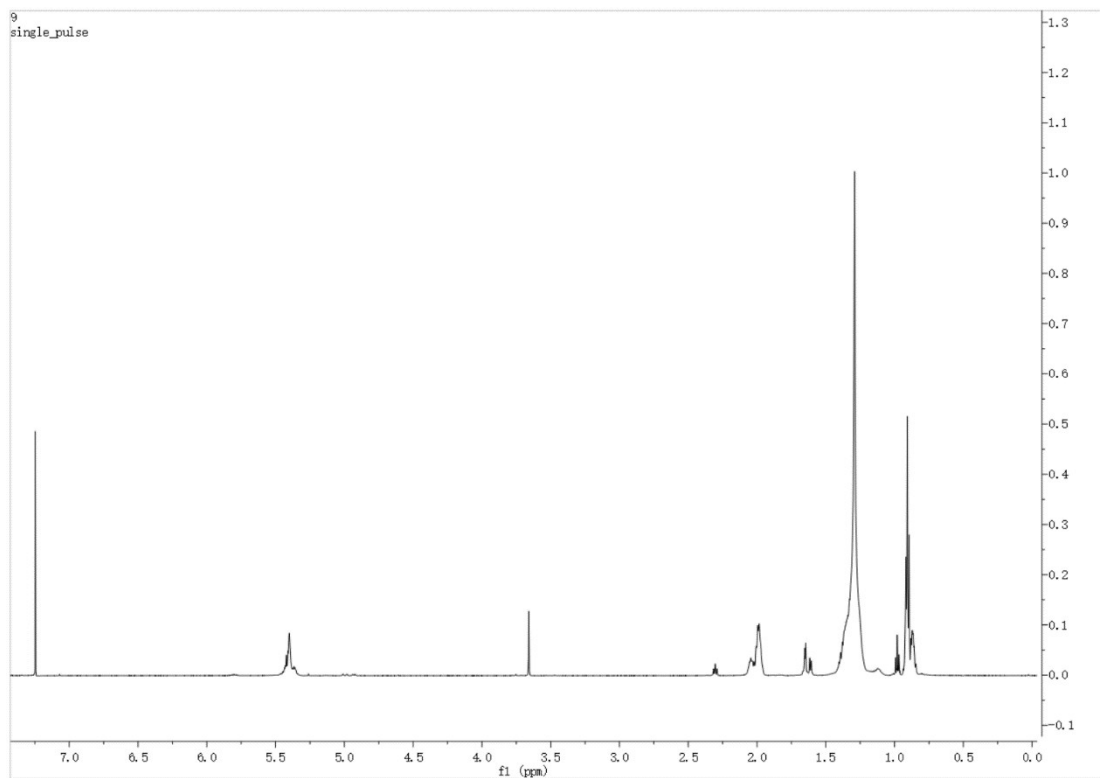




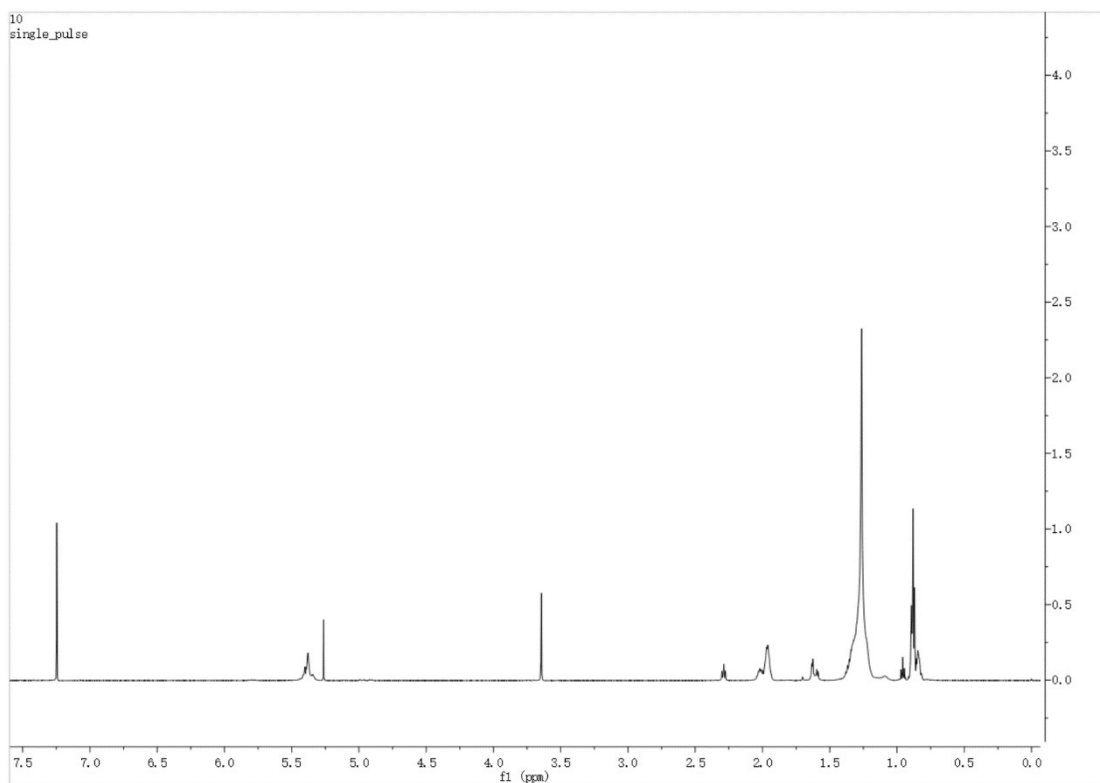
**Figure S35.** <sup>1</sup>H NMR spectrum of the polymer from table 2, entry 7 (CDCl<sub>3</sub>, 20 °C).



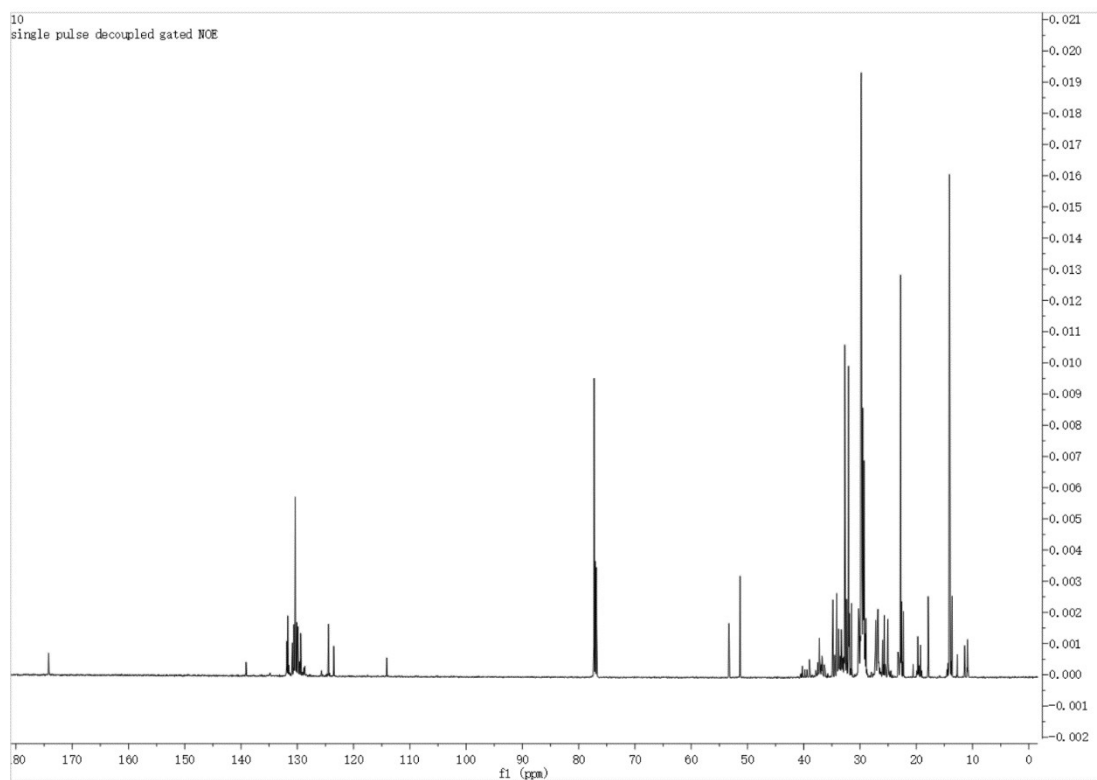
**Figure S36.** <sup>1</sup>H NMR spectrum of the polymer from table 2, entry 8 (CDCl<sub>3</sub>, 20 °C).



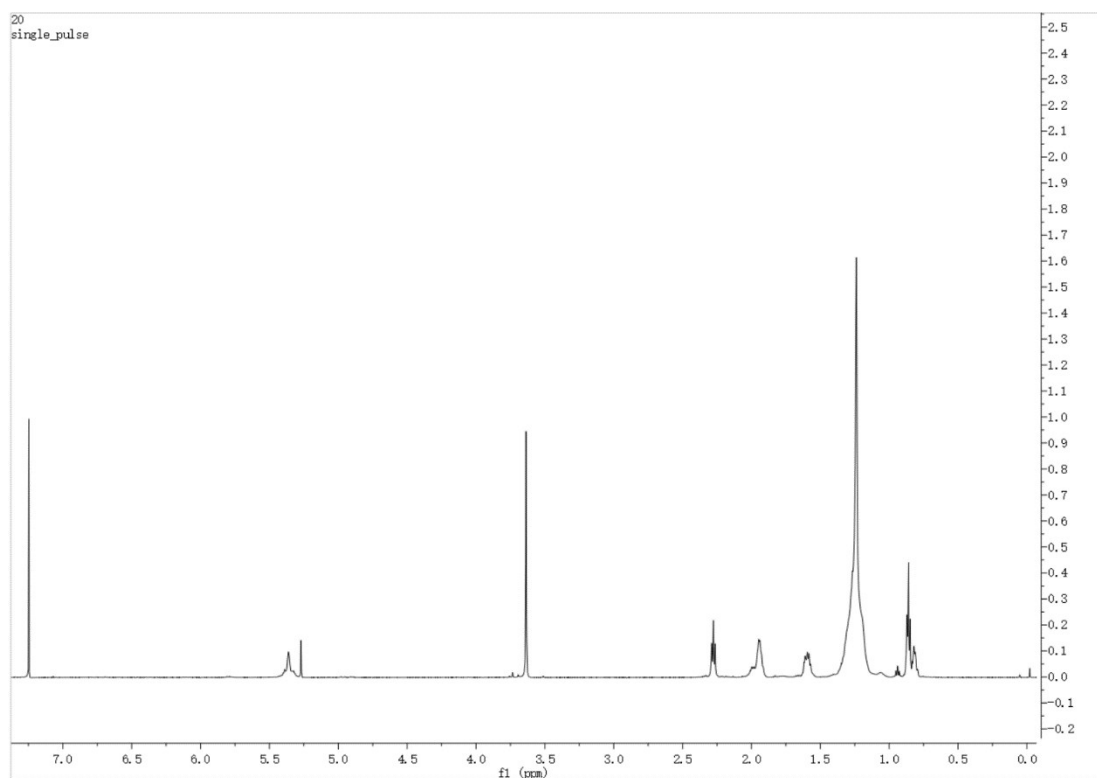
**Figure S37.** <sup>1</sup>H NMR spectrum of the polymer from table 2, entry 9 (CDCl<sub>3</sub>, 20 °C).



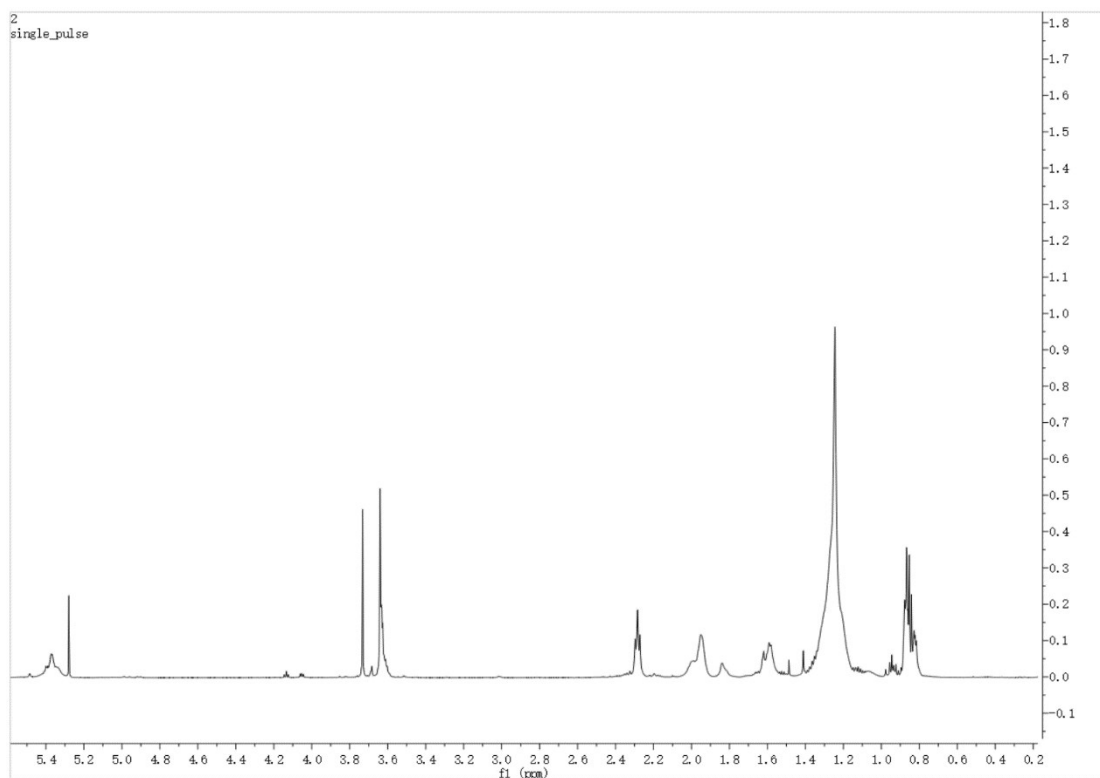
**Figure S38.** <sup>1</sup>H NMR spectrum of the polymer from table 2, entry 10 (CDCl<sub>3</sub>, 20 °C).



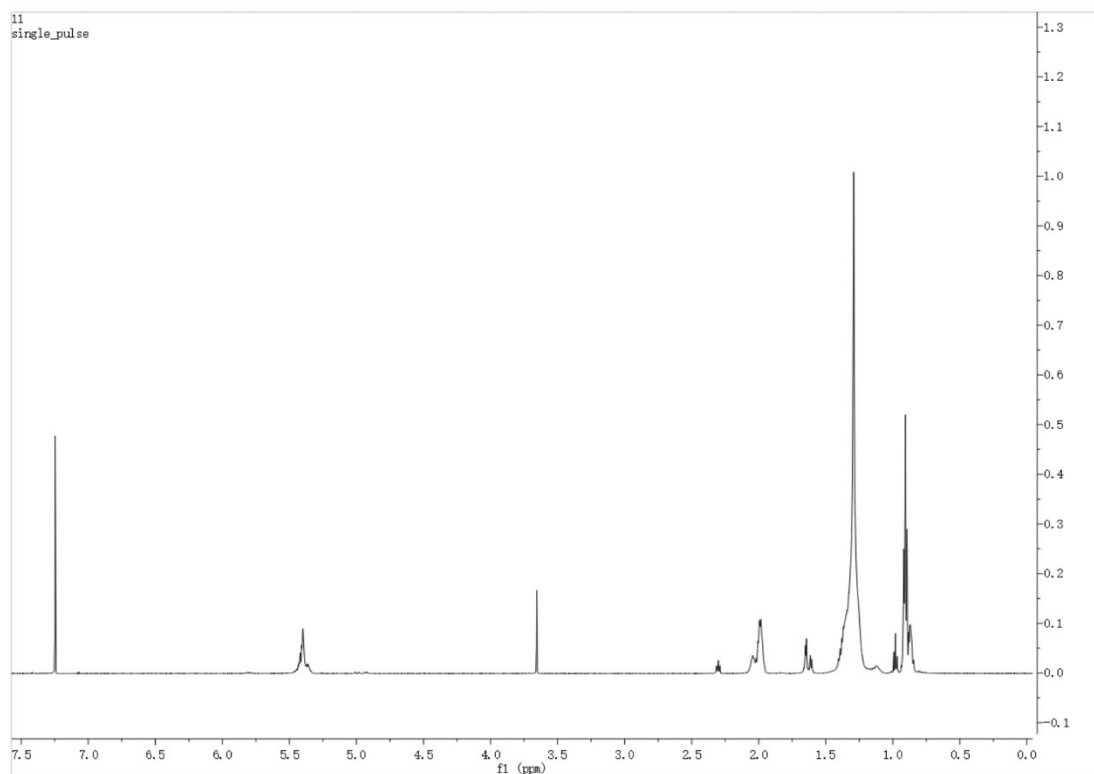
**Figure S39.**  $^{13}\text{C}$  NMR spectrum of the polymer from table 2, entry 10 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).



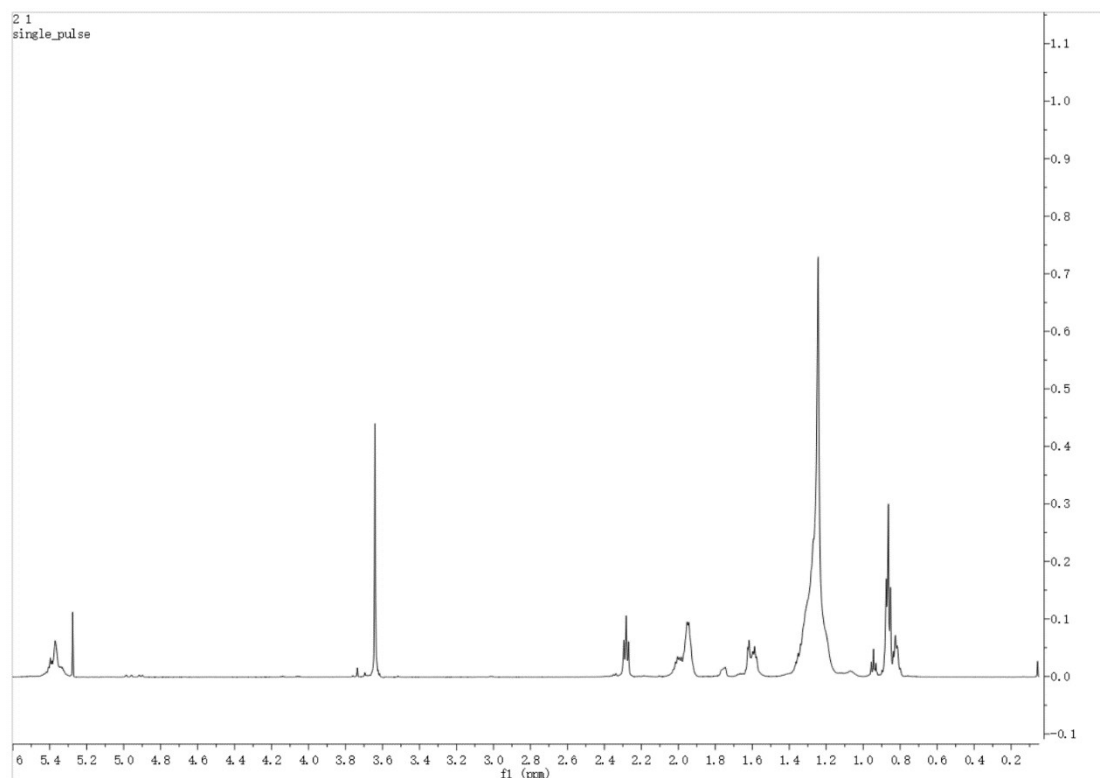
**Figure S40.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 11 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).



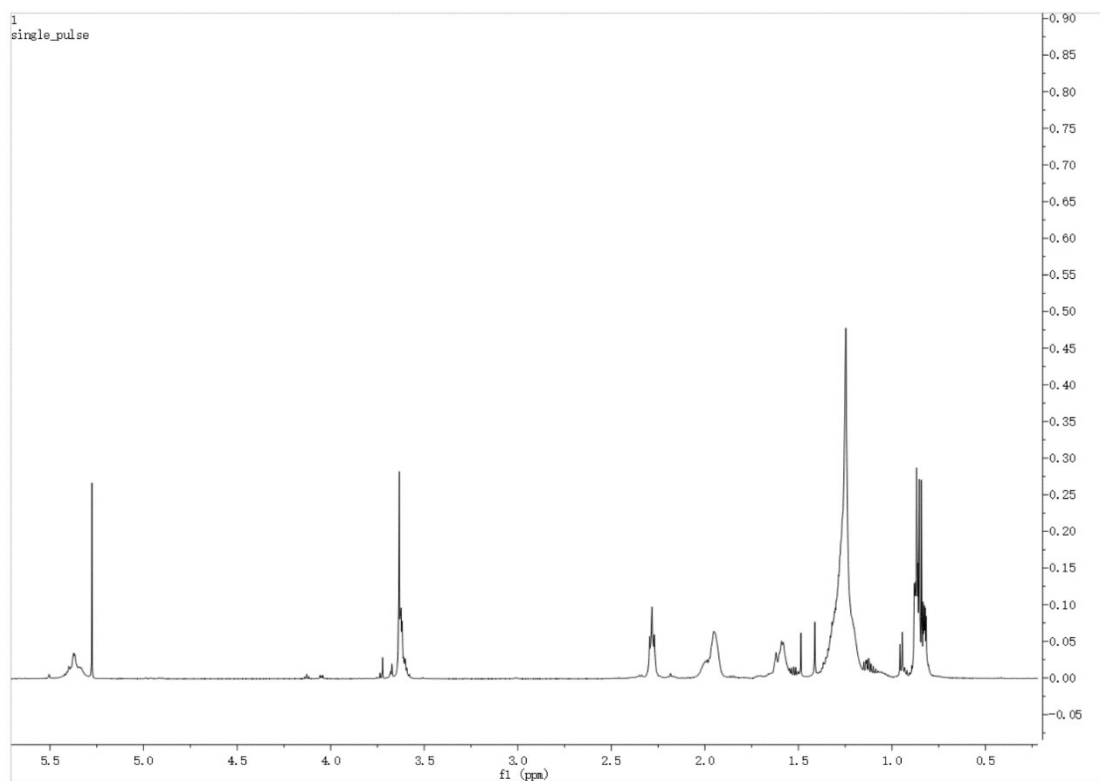
**Figure S41.** <sup>1</sup>H NMR spectrum of the polymer from table 2, entry 12 (CDCl<sub>3</sub>, 20 °C).



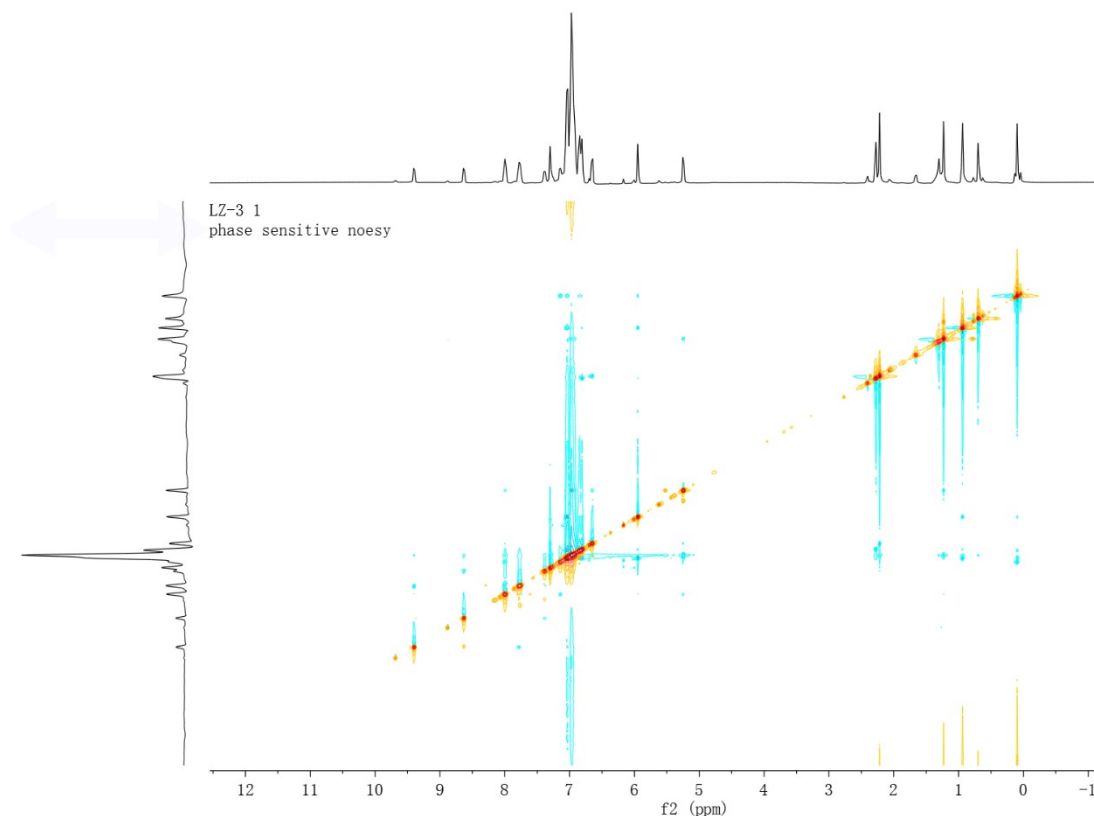
**Figure S42.** <sup>1</sup>H NMR spectrum of the polymer from table 2, entry 13 (CDCl<sub>3</sub>, 20 °C).



**Figure S43.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 15 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).



**Figure S44.**  $^1\text{H}$  NMR spectrum of the polymer from table 2, entry 16 ( $\text{CDCl}_3$ , 20  $^\circ\text{C}$ ).



**Figure S45.**  $^1\text{H}$ - $^1\text{H}$  NOESY NMR spectrum of **Pd4** in  $\text{CDCl}_3$  (600 MHz, 293K).

### 3. X-ray Crystallography.

CCDC numbers of **Pd3** is 2043771. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

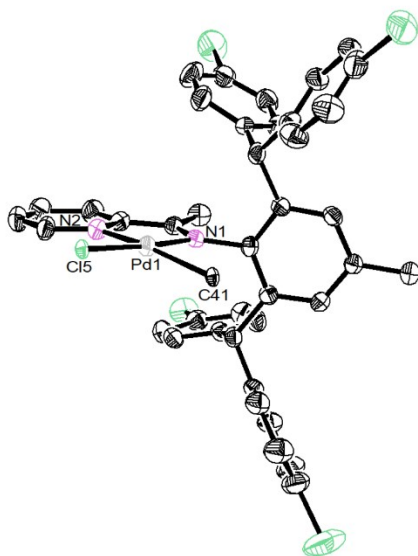


Table S1 Crystal data and structure refinement for **Pd3**.

Identification code	<b>Pd3</b>
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Empirical formula	C42.25 H35.50 C17.50 N2 Pd
Formula weight	943.50
Temperature/K	293(2) K
Crystal system	Triclinic
Space group	P-1
a/Å	9.9796(7)
b/Å	14.2509(14)
c/Å	17.1337(17)
$\alpha$ /°	111.363(4)
$\beta$ /°	93.366(2)
$\gamma$ /°	94.829(2)
Volume/Å <sup>3</sup>	2250.7(3)
Z	2
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.392
$\mu$ /mm <sup>-1</sup>	0.888
F(000)	953
Crystal size/mm <sup>3</sup>	0.36 x 0.24 x 0.16
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	2.35 to 25.01
Index ranges	-10 $\leq$ h $\leq$ 11, -16 $\leq$ k $\leq$ 16, -20 $\leq$ l $\leq$ 20
Reflections collected	11323
Independent reflections	7738 [R(int) = 0.0466]
Data/restraints/parameters	7738 / 23 / 502
Goodness-of-fit on F <sup>2</sup>	1.159
Final R indexes [I] $\geq$ 2 $\sigma$ (I)]	R1 = 0.0754, wR2 = 0.1956
Final R indexes [all data]	R1 = 0.1030, wR2 = 0.2098
Largest diff. peak/hole / e Å <sup>-3</sup>	1.506 and -0.879