

SUPPORTING INFORMATION

**Polymerization of Isoprene and Butadiene with  
Unparallel Stereoselectivity Catalysed by Rare-earth Metal  
Cationic Species Bearing a Novel Tridentate Ligand**

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**Figure S1**  $^1\text{H}$  NMR spectrum of **L1-H** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  
**Figure S2**  $^{13}\text{C}$  NMR spectrum of **L1-H** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  
**Figure S3**  $^1\text{H}$  NMR spectrum of **1-Sc** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  
**Figure S4**  $^{13}\text{C}$  NMR spectrum of **1-Sc** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  
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**Figure S8**  $^{13}\text{C}$  NMR spectrum of **1-Lu** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  
**Figure S9** (a) Polymerization of isoprene with **1-Y** /  $[(\text{Ph}_3\text{C})(\text{B}(\text{C}_6\text{F}_5)_4)]$  as a precursor: molecular weight vs conversion. (b) Polymerization of isoprene with **1-Y** /  $[(\text{Ph}_3\text{C})(\text{B}(\text{C}_6\text{F}_5)_4)]$  as a precursor: molecular weight vs isoprene-to-**[1-Y]** ratio.  
**Figure S10**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polyisoprene catalyzed by **1-Sc** (Entry 1 in Table 1)  
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**Figure S16**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polyisoprene catalyzed by **1-Y**/ $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$  (Entry 6 in Table 1)  
**Figure S17**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polyisoprene catalyzed by **1-Y**/ $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$  (Entry 6 in Table 1)  
**Figure S18**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polybutadiene catalyzed by **1-Y** (Entry 14 in Table 1)  
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**Figure S25**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polyisoprene catalyzed by **1-Tm** (Entry 21 in Table 1)

**Figure S26**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polybutadiene catalyzed by **1-Tm** (Entry 23 in Table 1)

**Figure S27**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polybutadiene catalyzed by **1-Tm** (Entry 23 in Table 1)

**Figure S28**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polyisoprene catalyzed by **1-Er** (Entry 25 in Table 1)

**Figure S29**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polyisoprene catalyzed by **1-Er** (Entry 25 in Table 1)

**Figure S30**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polybutadiene catalyzed by **1-Er** (Entry 27 in Table 1)

**Figure S31**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polybutadiene catalyzed by **1-Er** (Entry 27 in Table 1)

**Figure S32**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polyisoprene catalyzed by **1-Ho** (Entry 29 in Table 1)

**Figure S33**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polyisoprene catalyzed by **1-Ho** (Entry 29 in Table 1)

**Figure S34**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polybutadiene catalyzed by **1-Ho** (Entry 31 in Table 1)

**Figure S35**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of polybutadiene catalyzed by **1-Ho** (Entry 31 in Table 1)

**Figure S36**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-1** catalyzed by **1-Y** (Entry 1 in Table 2)

**Figure S37**  $^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-1** catalyzed by **1-Y** (Entry 1 in Table 2)

**Figure S38**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-2** catalyzed by **1-Y** (Entry 2 in Table 2)

**Figure S39**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-2** catalyzed by **1-Y** (Entry 2 in Table 2)

**Figure S40**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-3** catalyzed by **1-Y** (Entry 3 in Table 2)

**Figure S41**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-3** catalyzed by **1-Y** (Entry 3 in Table 2)

**Figure S42**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-4** catalyzed by **1-Y** (Entry 4 in Table 2)

**Figure S43**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-4** catalyzed by **1-Y** (Entry 4 in Table 2)

**Figure S44**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-5** catalyzed by **1-Y** (Entry 5 in Table 2)

**Figure S45**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-5** catalyzed by **1-Y** (Entry 5 in Table 2)

**Figure S46**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-6** catalyzed by **1-Y** (Entry 6 in Table 2)

**Figure S47**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-6** catalyzed by **1-Y** (Entry 6 in Table 2)

**Figure S48**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-7** catalyzed by **1-Y** (Entry 7 in Table 2)

**Figure S49**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-7** catalyzed by **1-Y** (Entry 7 in Table 2)

**Table S1** The data for Fineman-Ross diagram

**Table S2** The data for content of isoprene and butadiene in the copolymers versus the conversions

**Figure S50** DSC curves of highly *trans*-1,4-PBD

**Figure S51** DSC curves of copolymers after hydrogenation

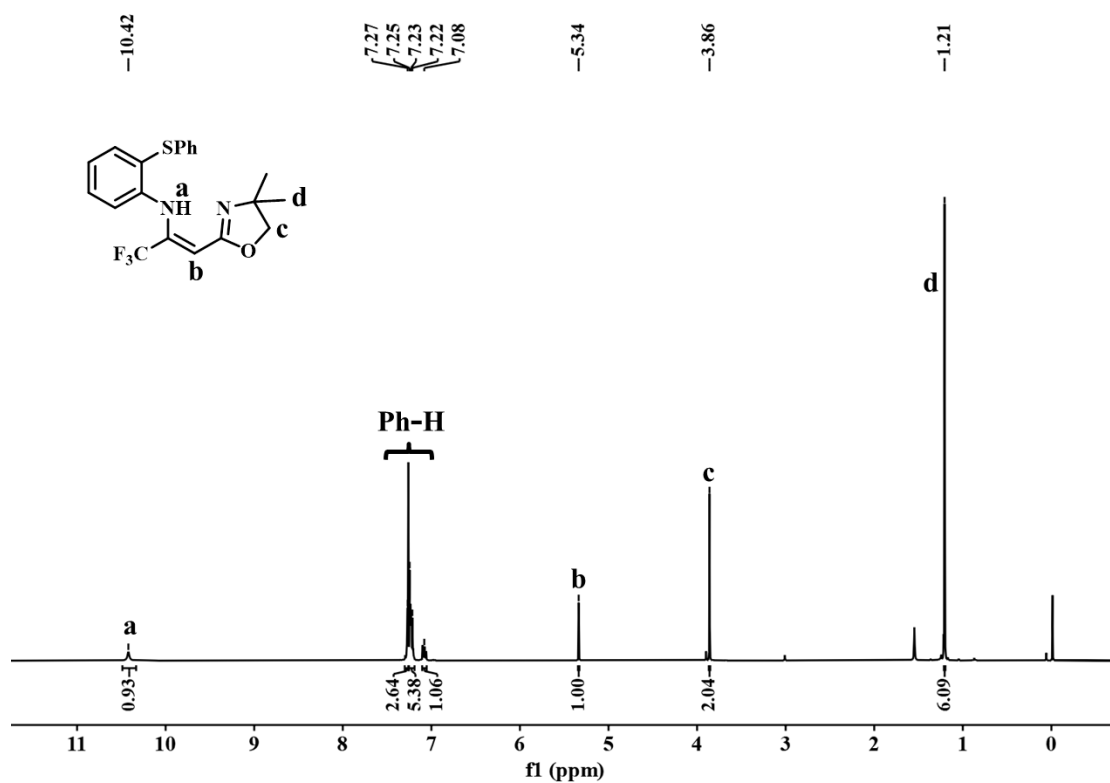


Figure S1 <sup>1</sup>H NMR spectrum of L1-H (400 MHz, CDCl<sub>3</sub>, 25 °C)

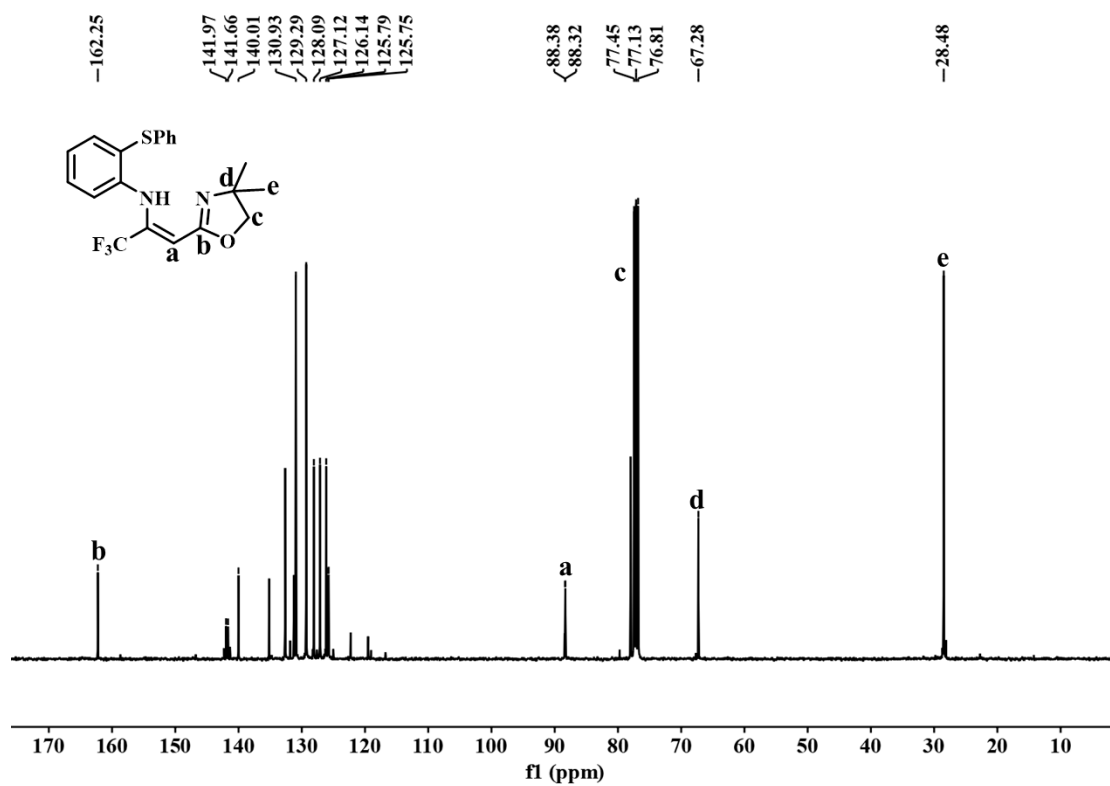
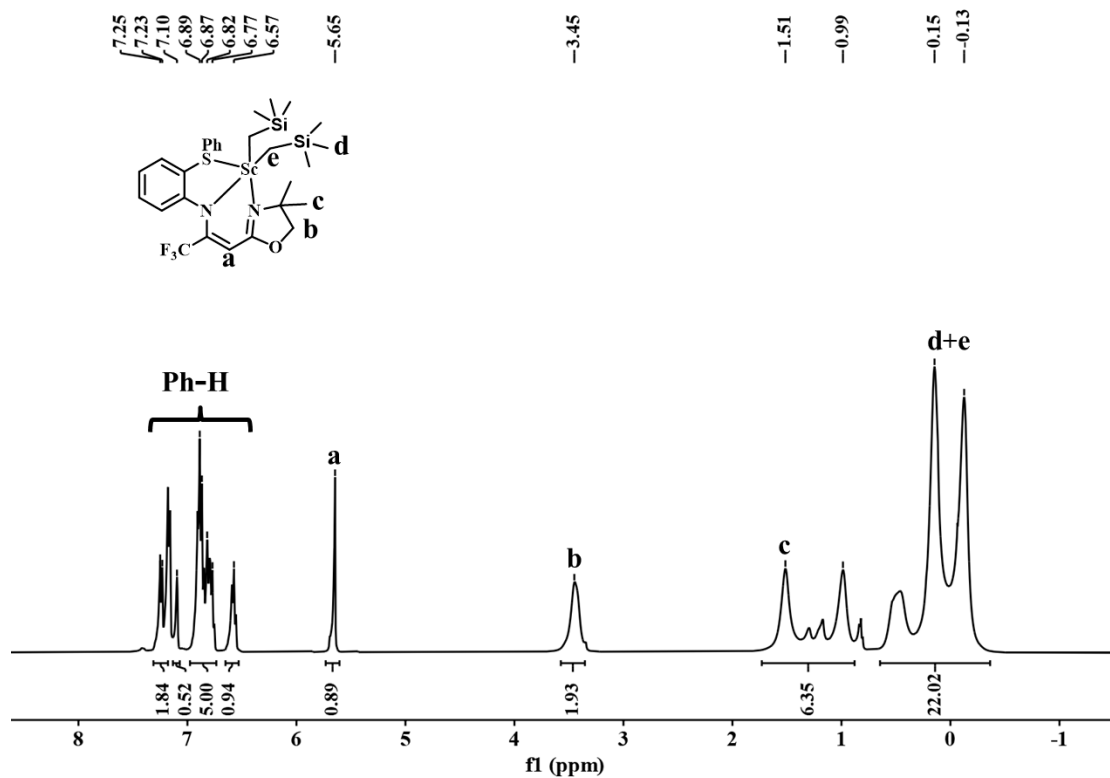
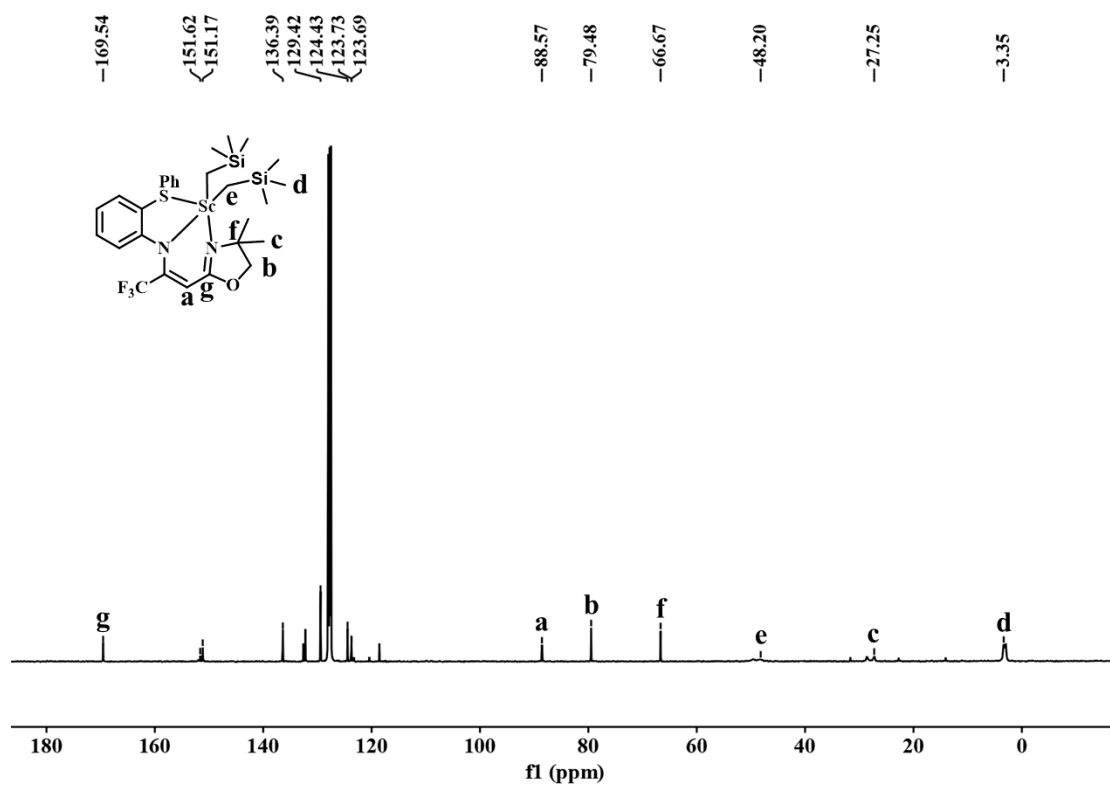


Figure S2 <sup>13</sup>C NMR spectrum of L1-H (400 MHz, CDCl<sub>3</sub>, 25 °C)



**Figure S3** <sup>1</sup>H NMR spectrum of **1-Sc** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)



**Figure S4** <sup>13</sup>C NMR spectrum of **1-Sc** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)

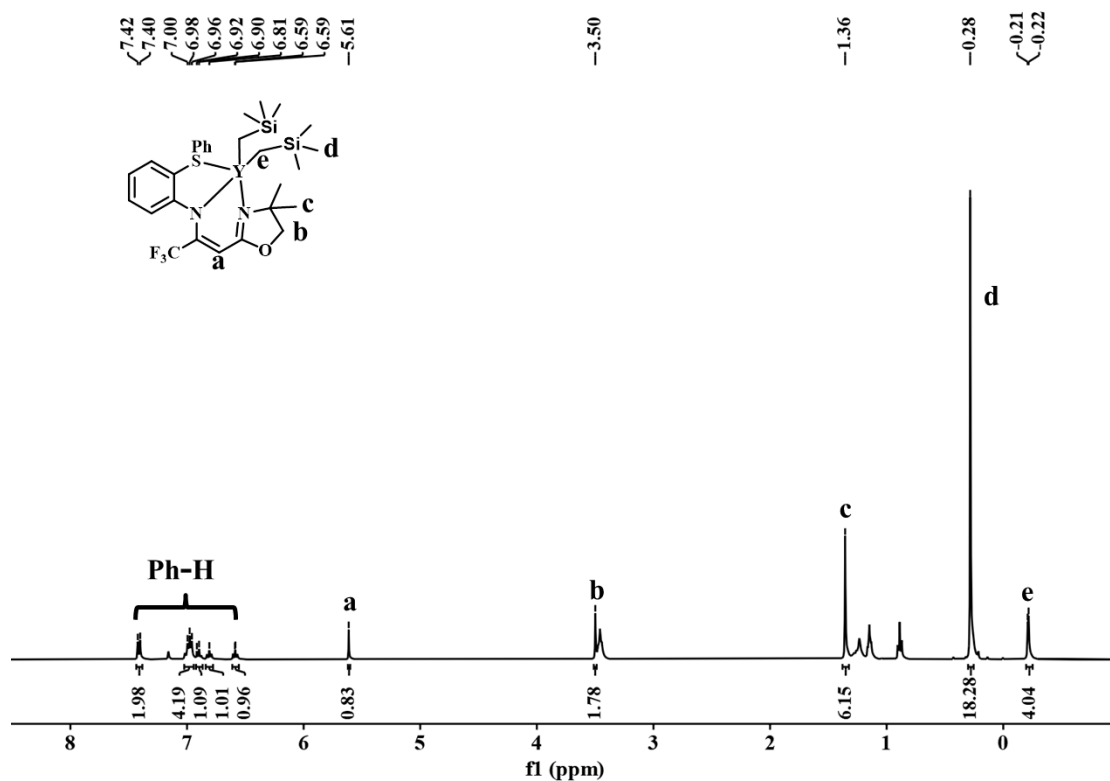


Figure S5 <sup>1</sup>H NMR spectrum of **1-Lu** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)

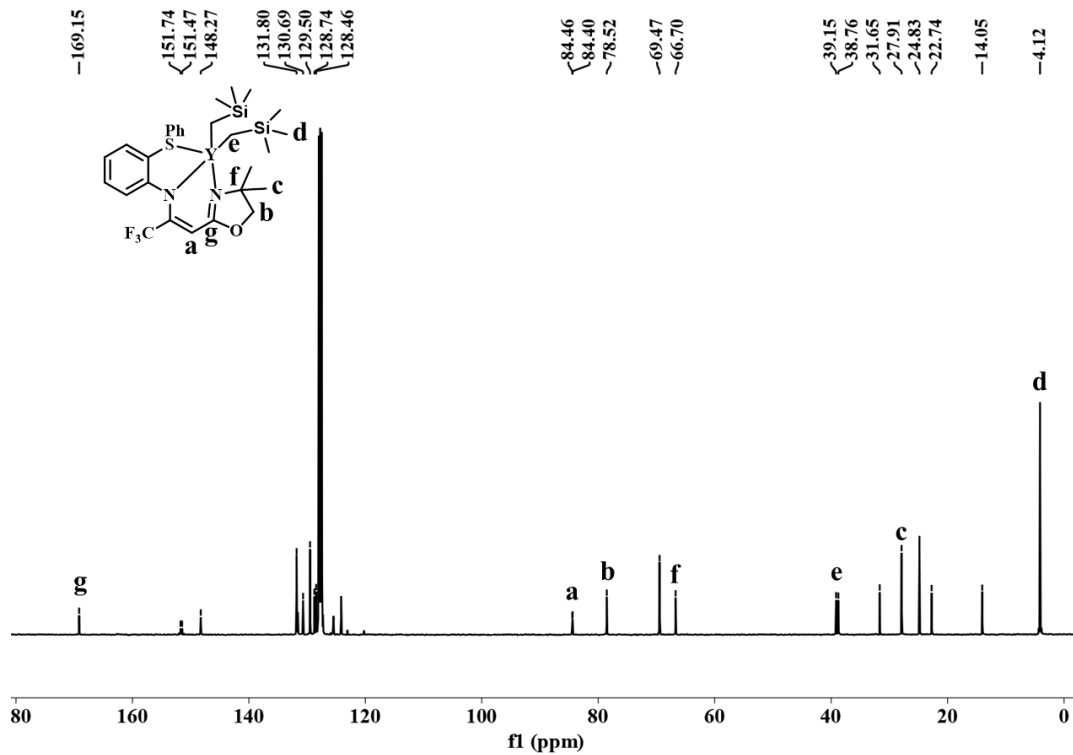
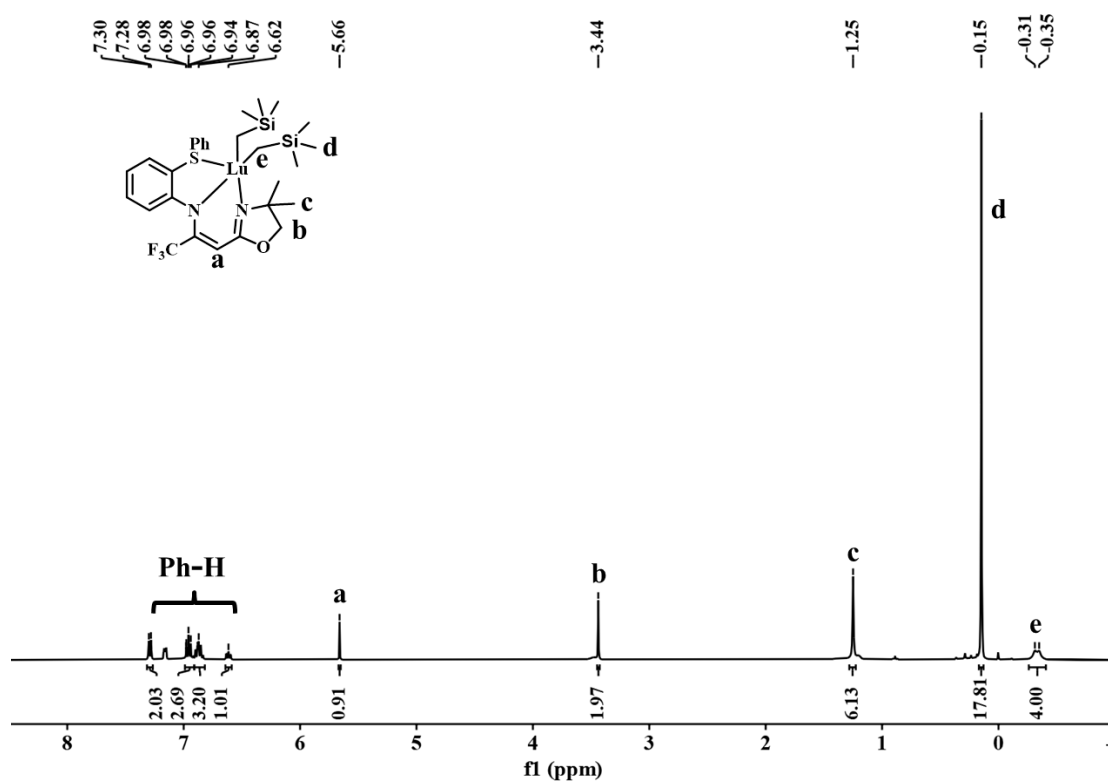
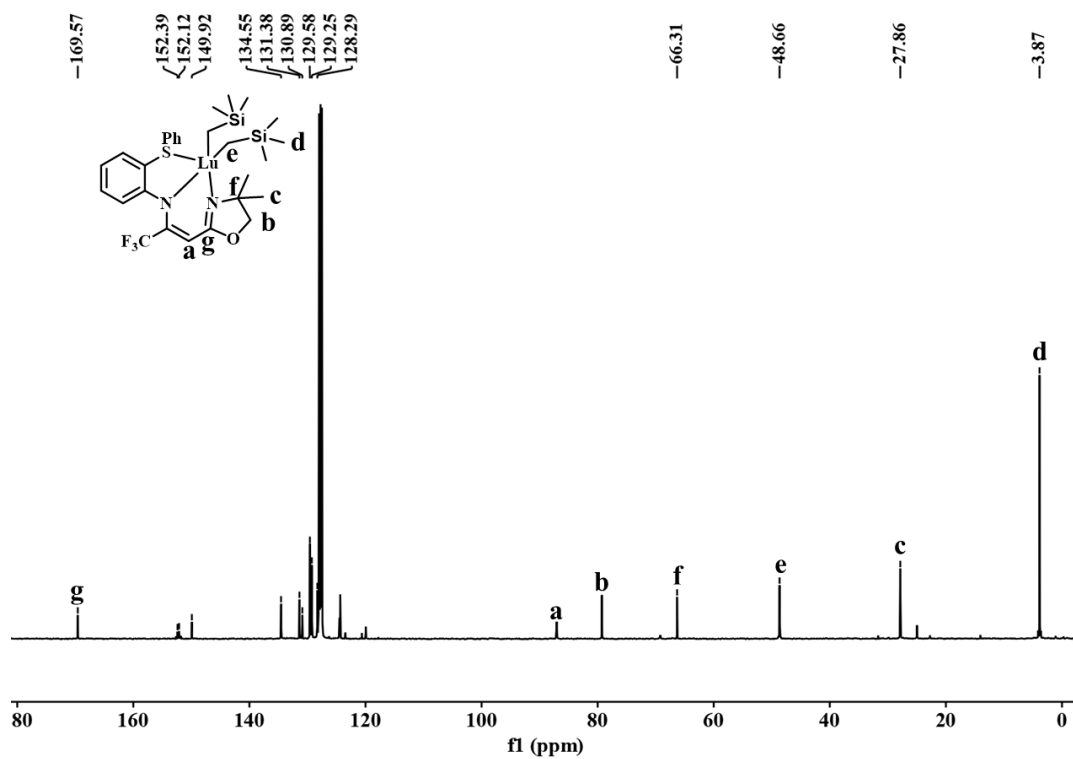


Figure S6 <sup>13</sup>C NMR spectrum of **1-Lu** (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)

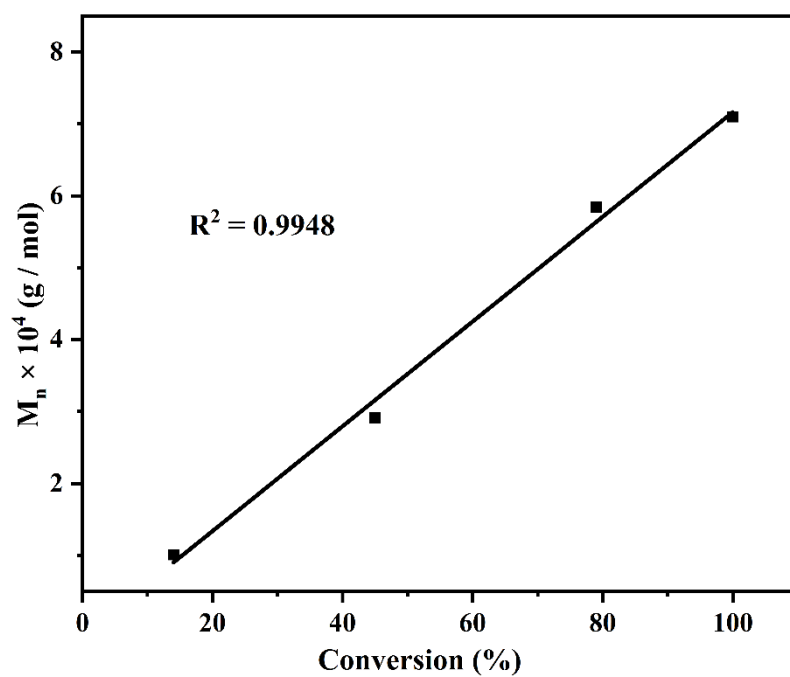


**Figure S7**  $^1\text{H}$  NMR spectrum of **1-Lu** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)

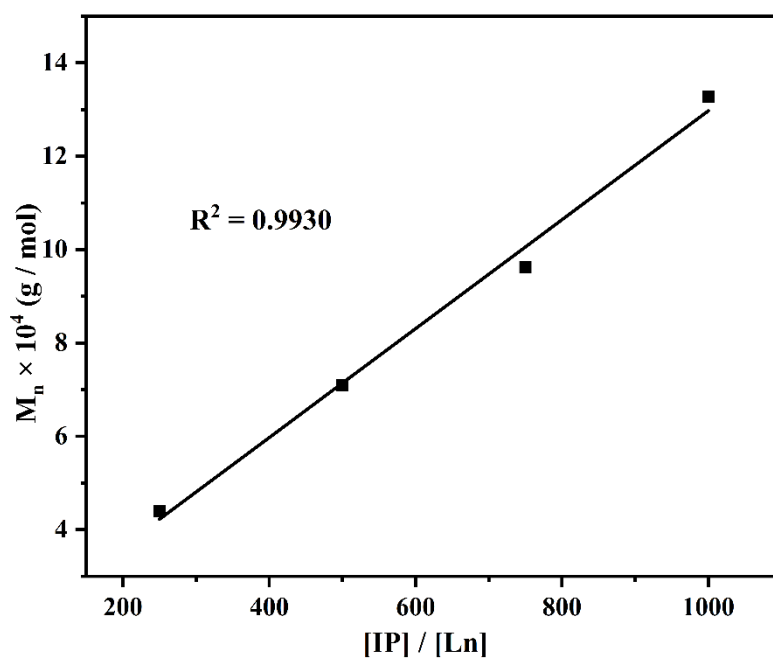


**Figure S8**  $^{13}\text{C}$  NMR spectrum of **1-Lu** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)



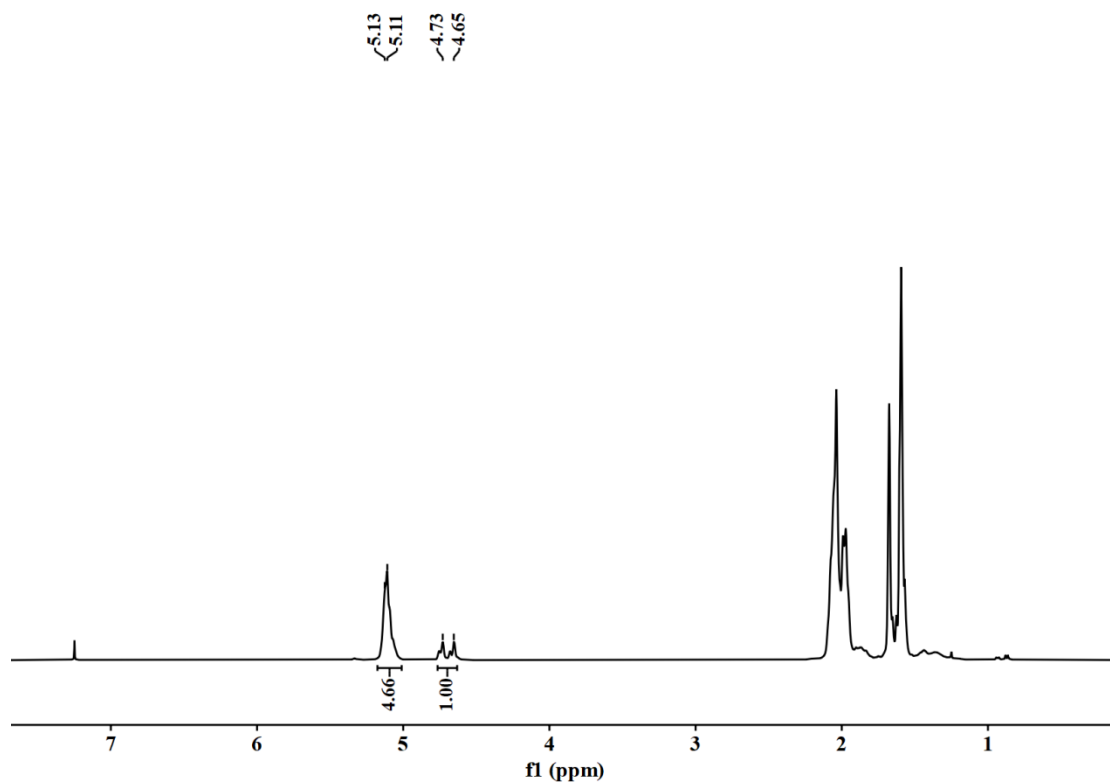


(a)

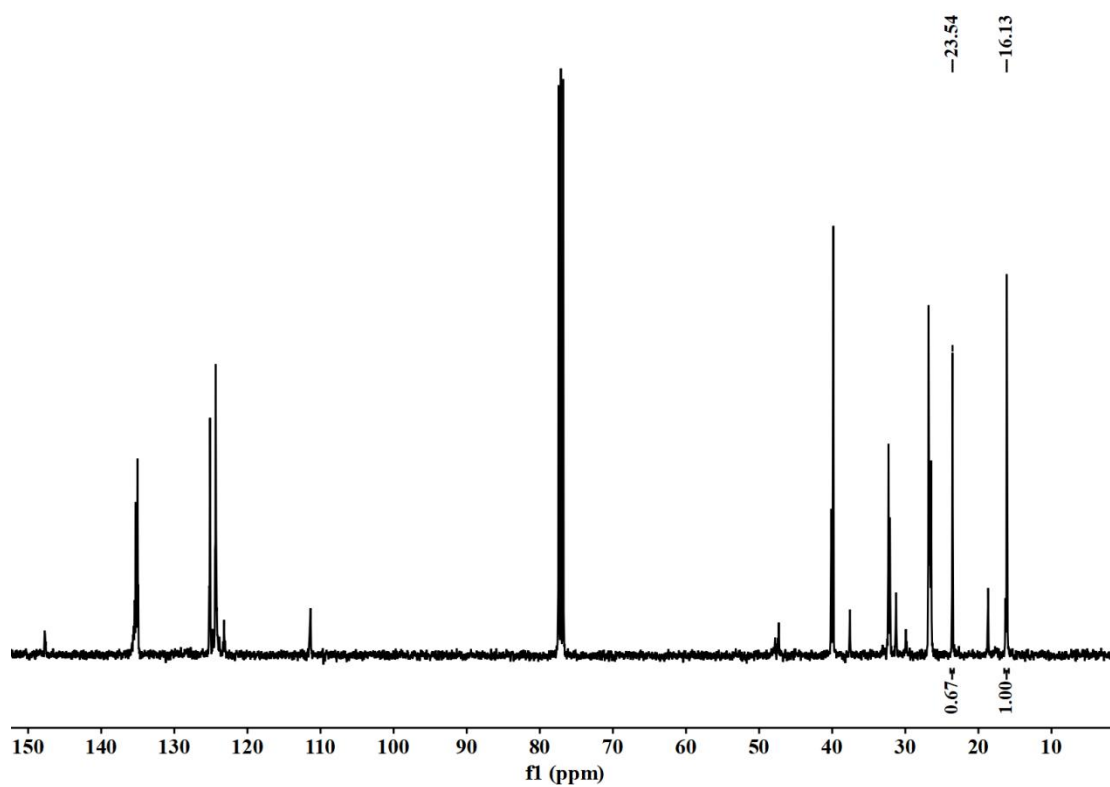


(b)

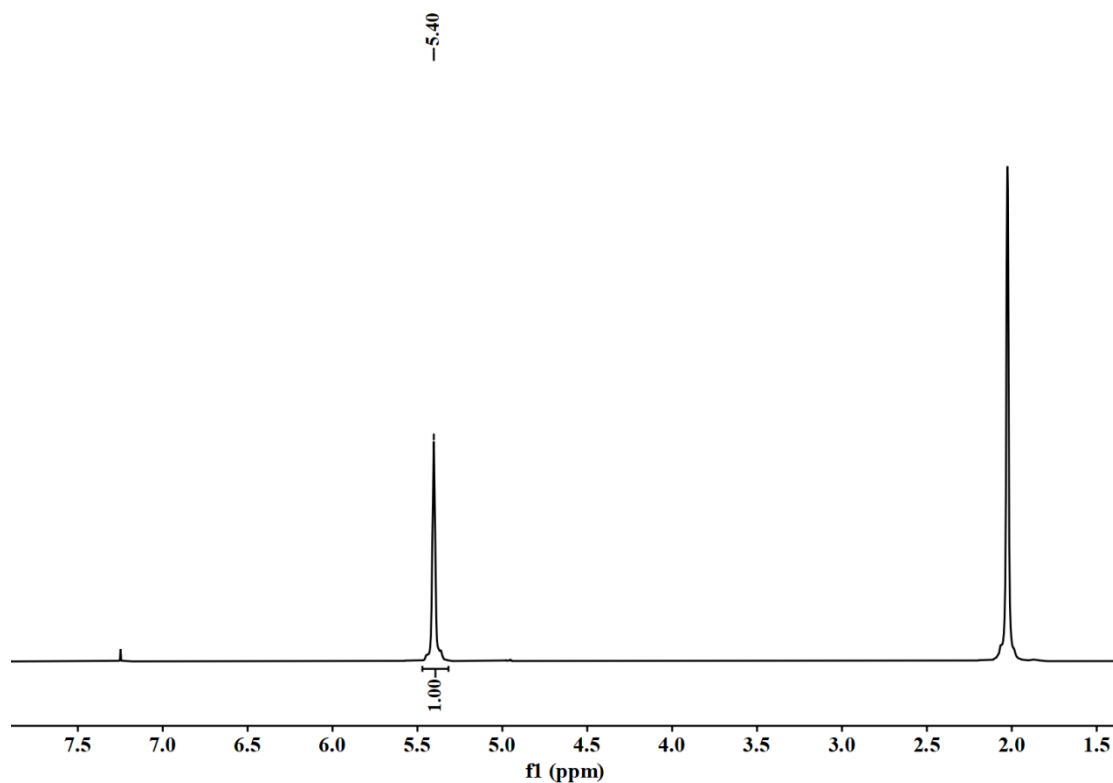
**Figure S9** (a) Polymerization of isoprene with **1-Y** /  $[(Ph_3C)(B(C_6F_5)_4)]$  as a precursor: molecular weight vs conversion. (b) Polymerization of isoprene with **1-Y** /  $[(Ph_3C)(B(C_6F_5)_4)]$  as a precursor: molecular weight vs isoprene-to-[**1-Y**] ratio.



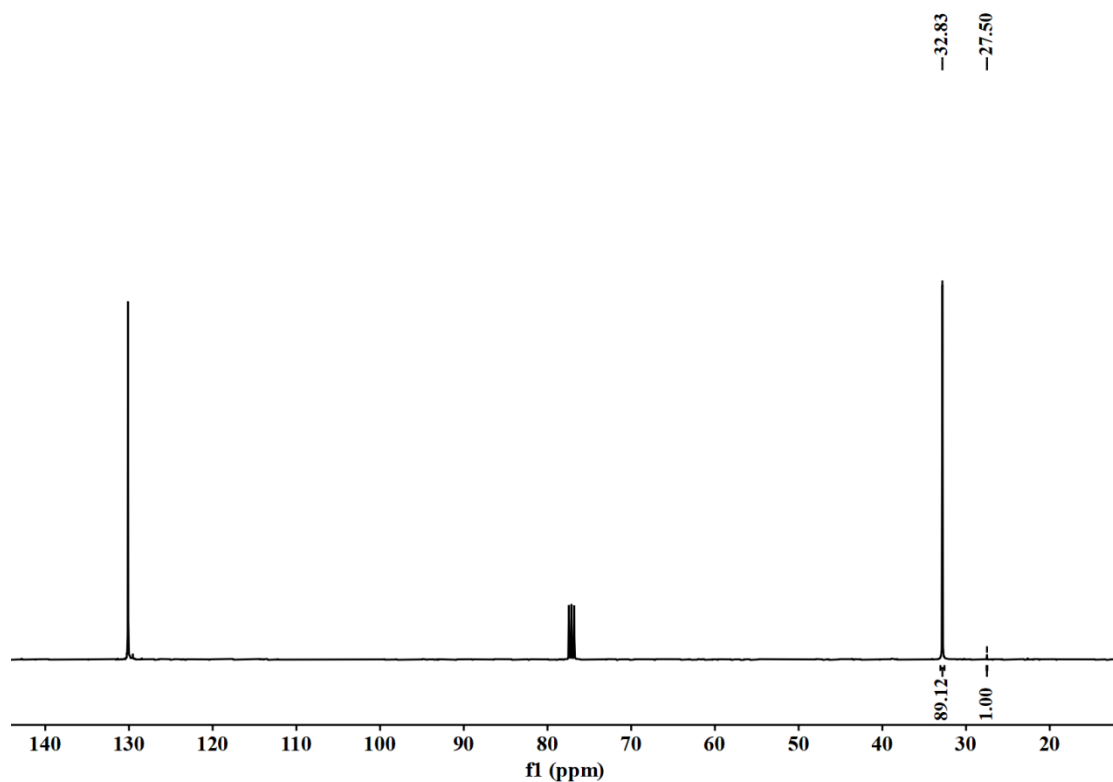
**Figure S10**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Sc** (Entry 1 in Table 1)



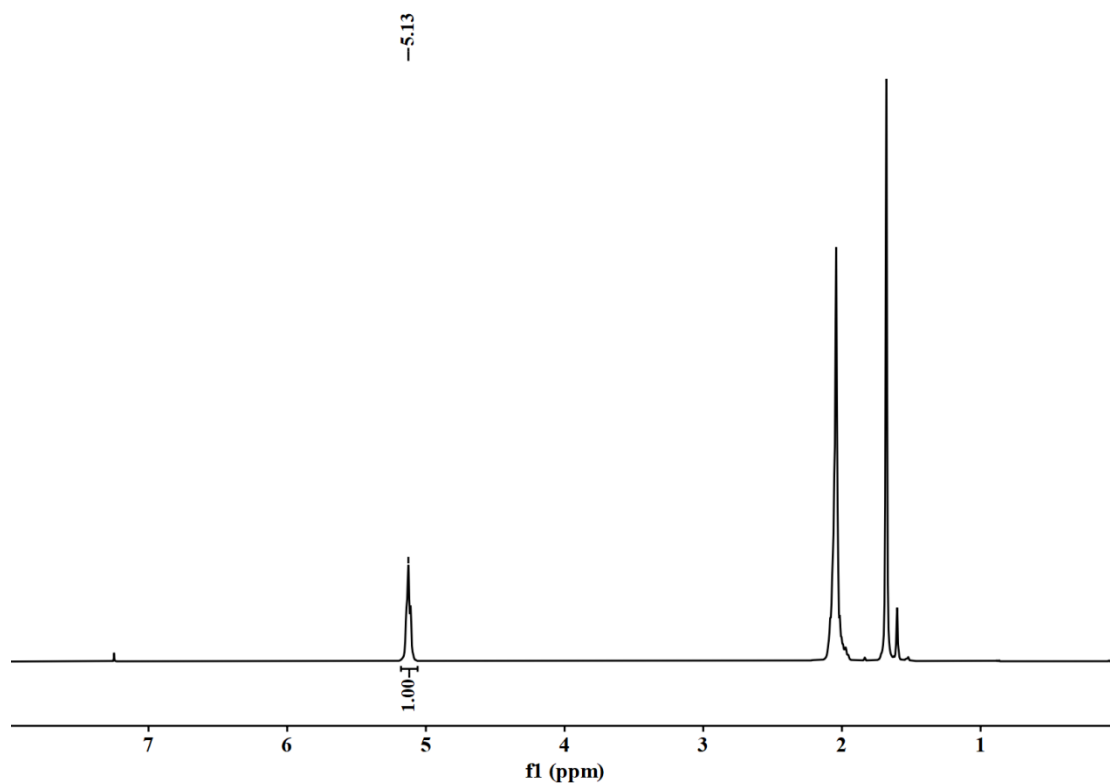
**Figure S11**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Sc** (Entry 1 in Table 1)



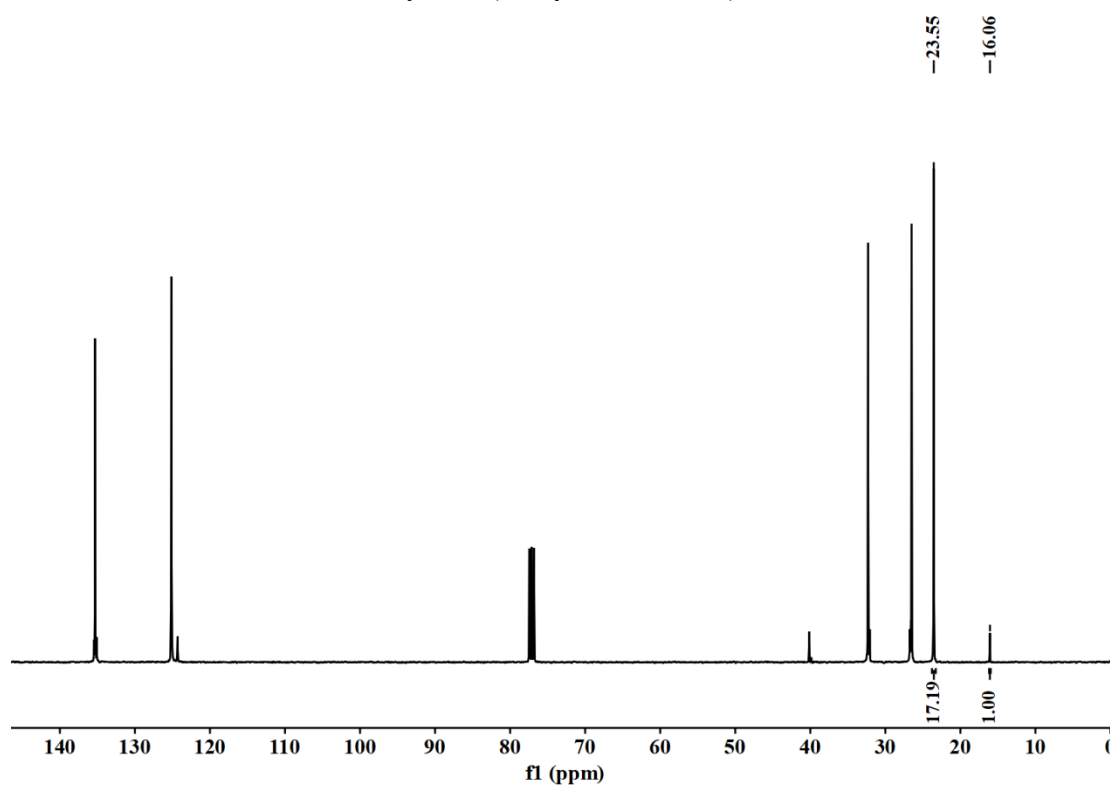
**Figure S12**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Sc** (Entry 3 in Table 1)



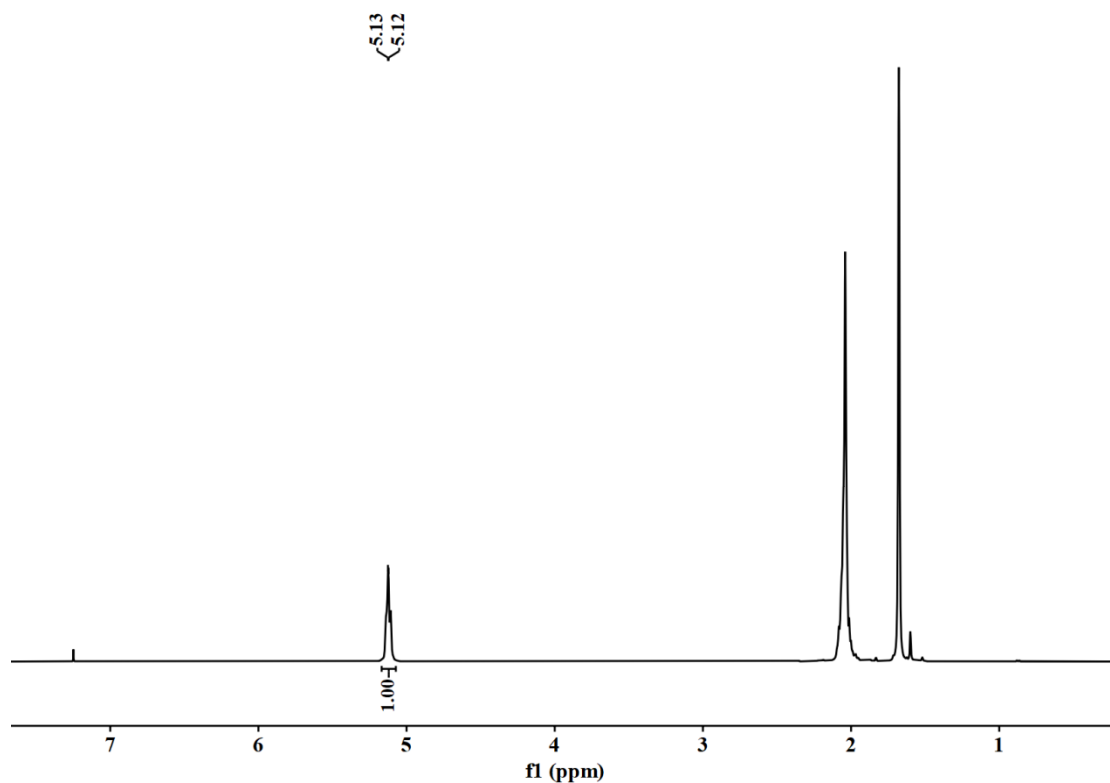
**Figure S13**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Sc** (Entry 3 in Table 1)



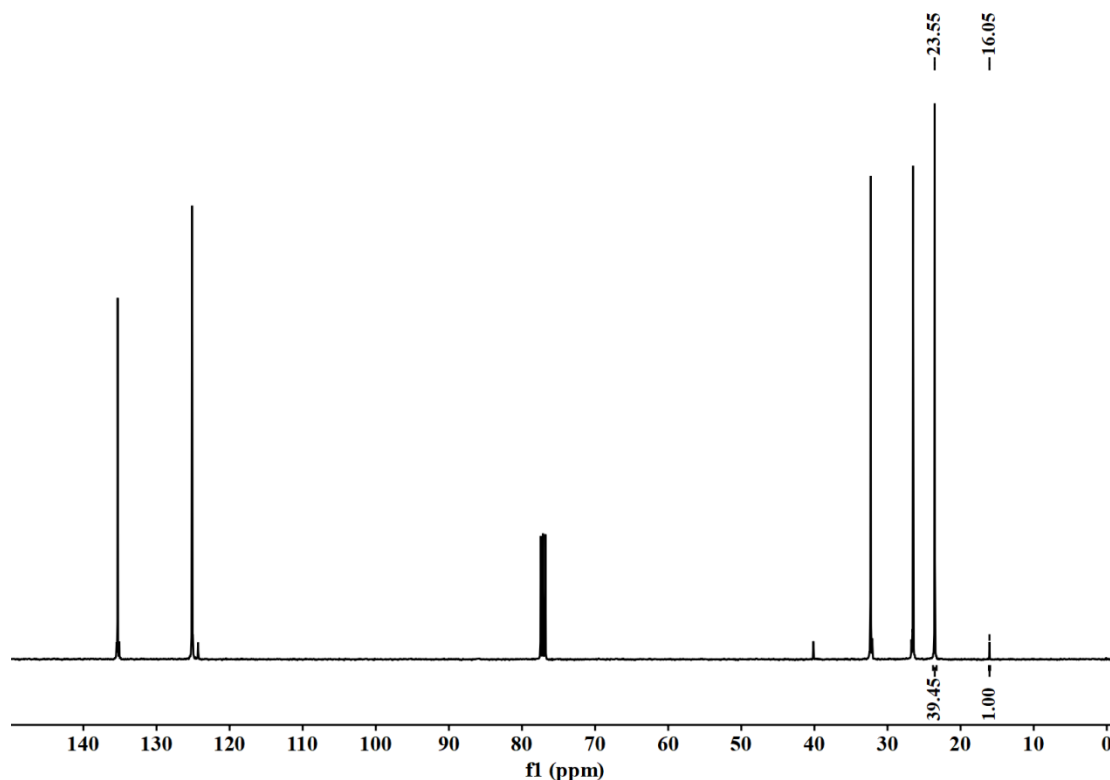
**Figure S14**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Y** (Entry 5 in Table 1)



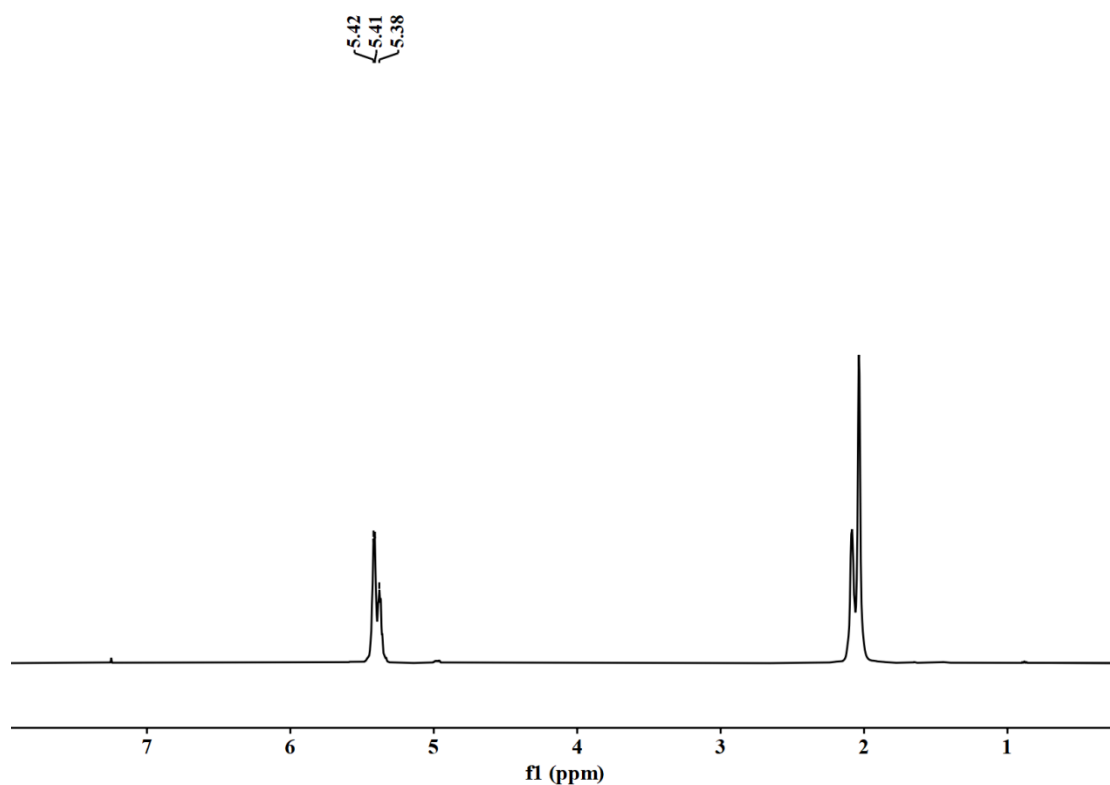
**Figure S15**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Y** (Entry 5 in Table 1)



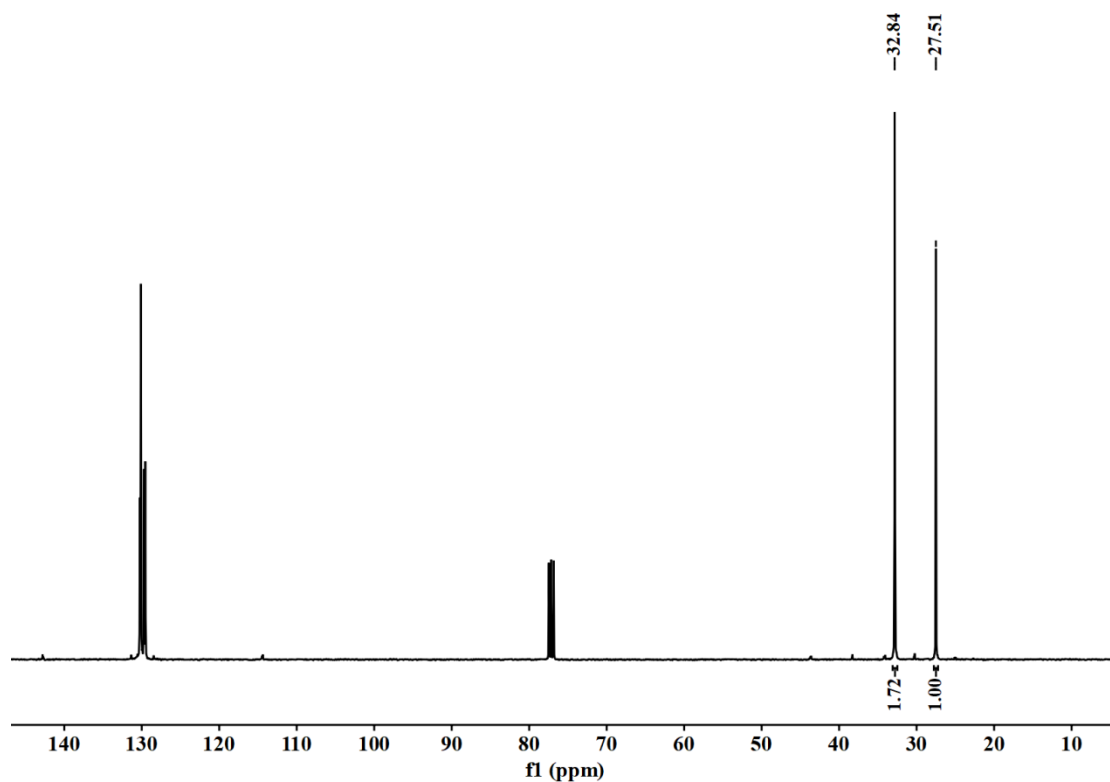
**Figure S16** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of polyisoprene catalyzed by **1-Y**/[PhMe<sub>2</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Entry 6 in Table 1)



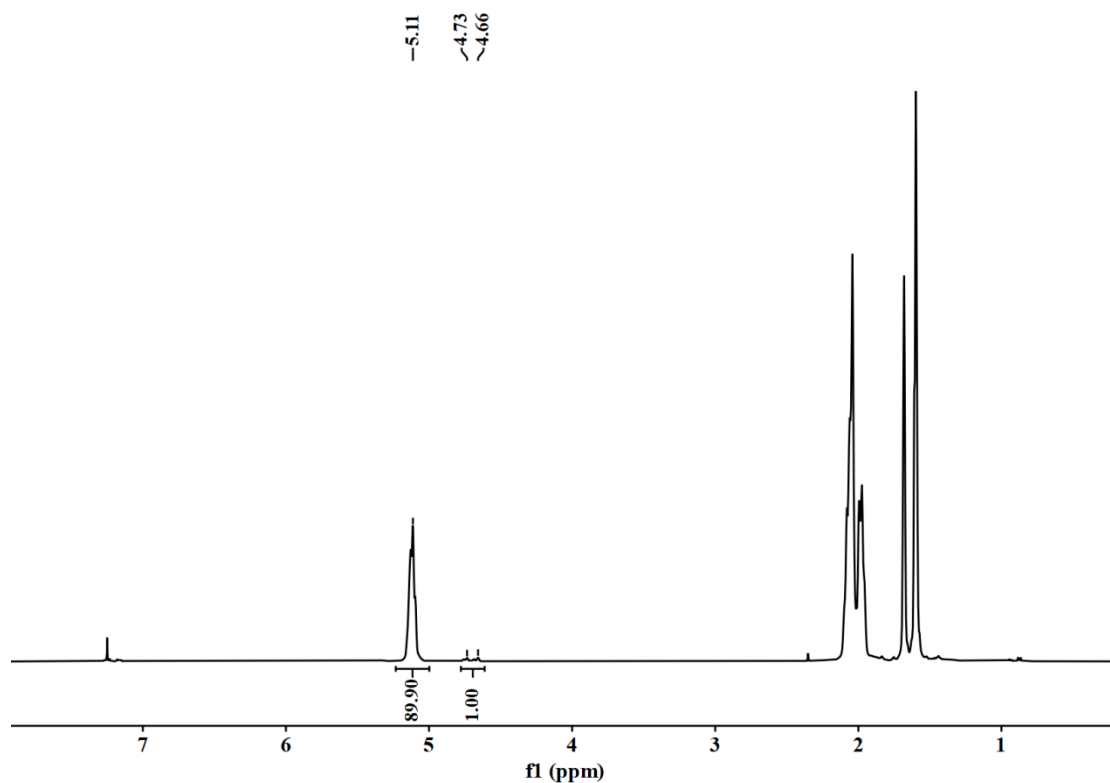
**Figure S17** <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of polyisoprene catalyzed by **1-Y**/[PhMe<sub>2</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Entry 6 in Table 1)



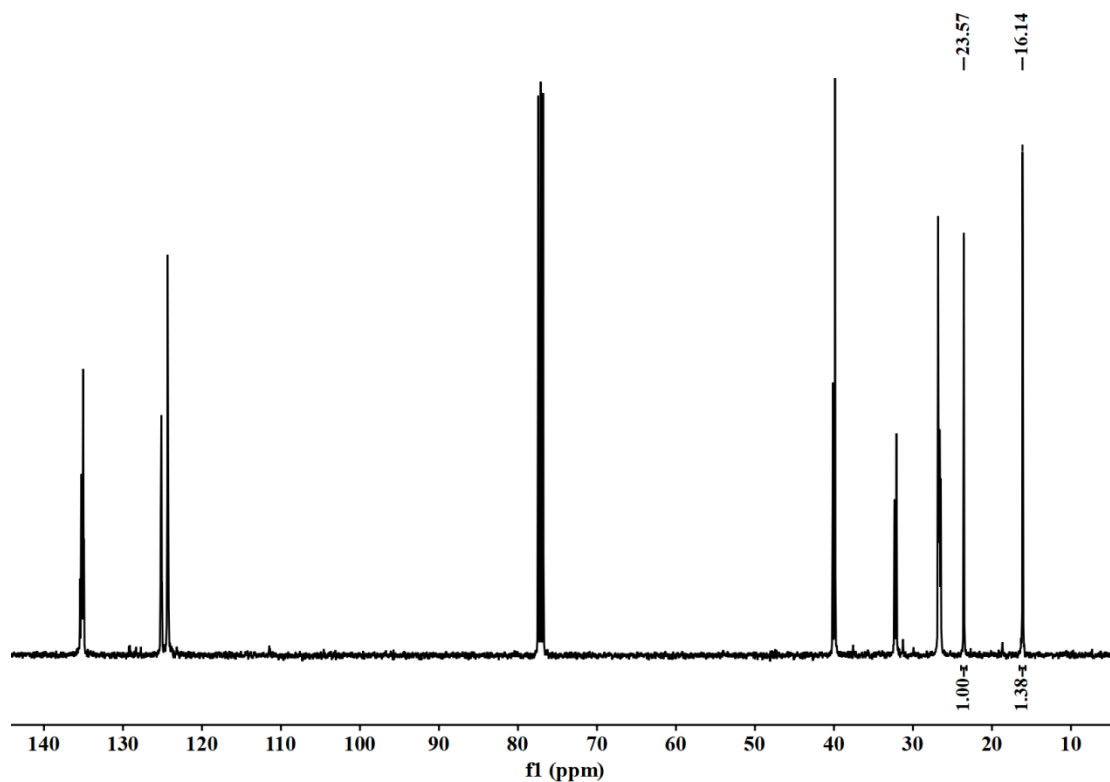
**Figure S18**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Y** (Entry 14 in Table 1)



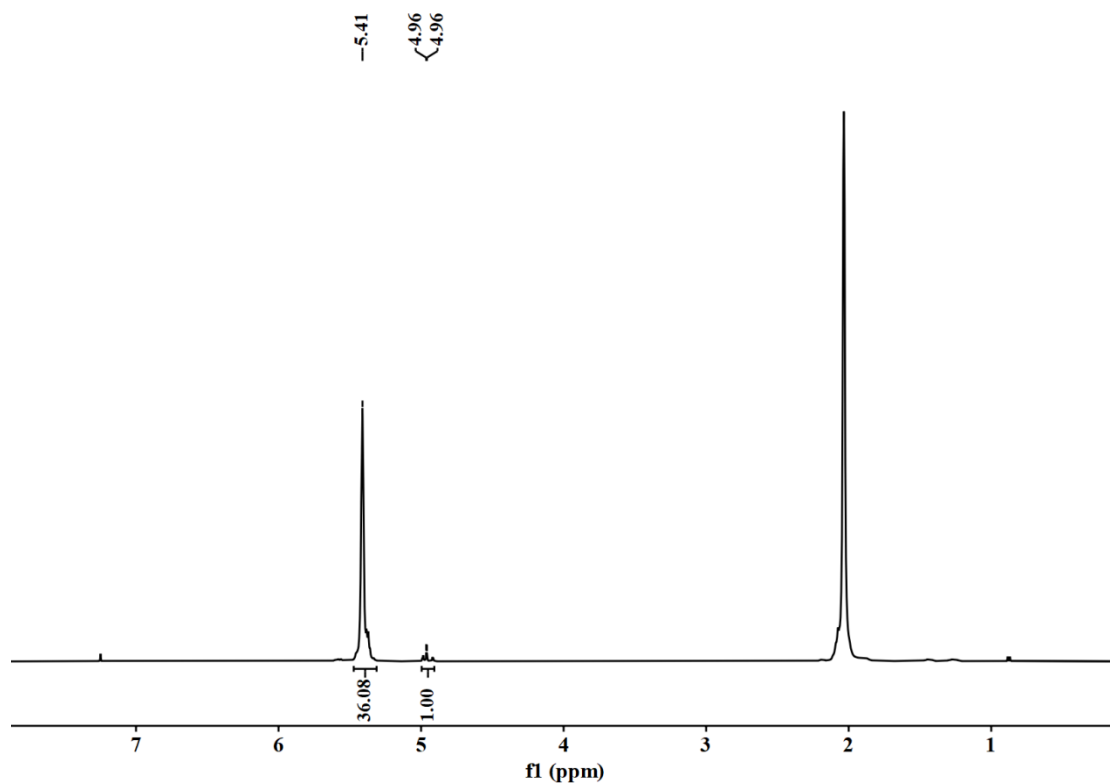
**Figure S19**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Y** (Entry 14 in Table 1)



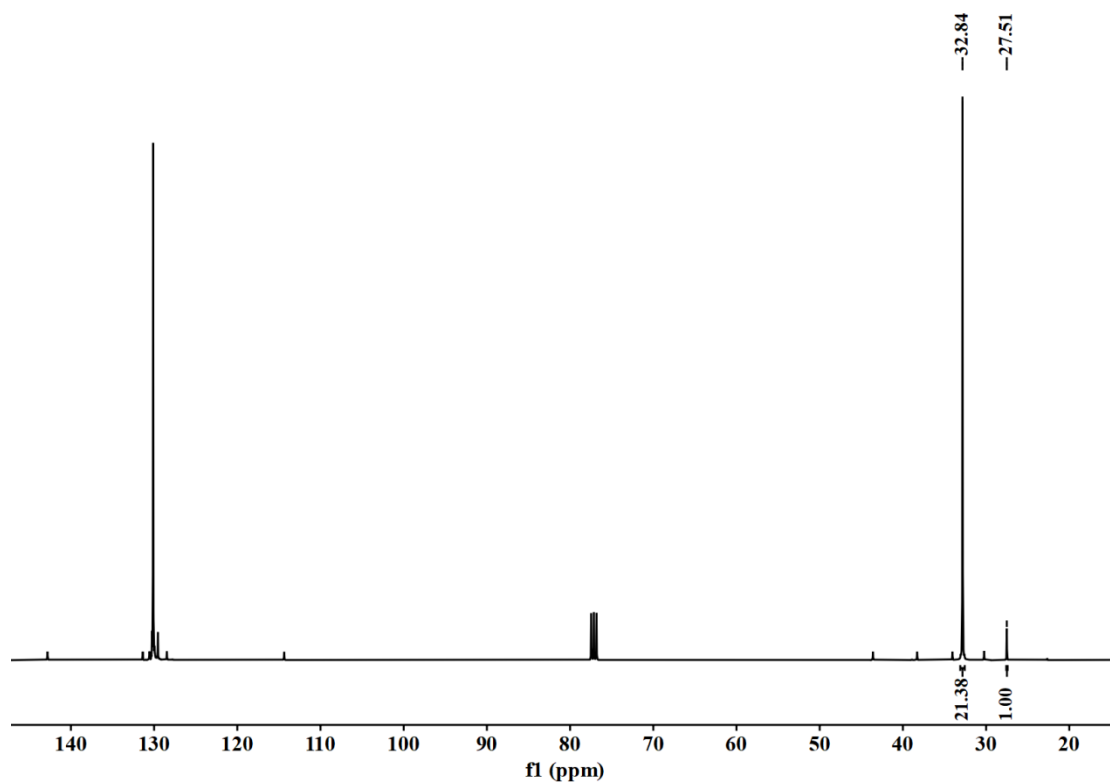
**Figure S20**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Lu** (Entry 17 in Table 1)



**Figure S21**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Lu** (Entry 17 in Table 1)

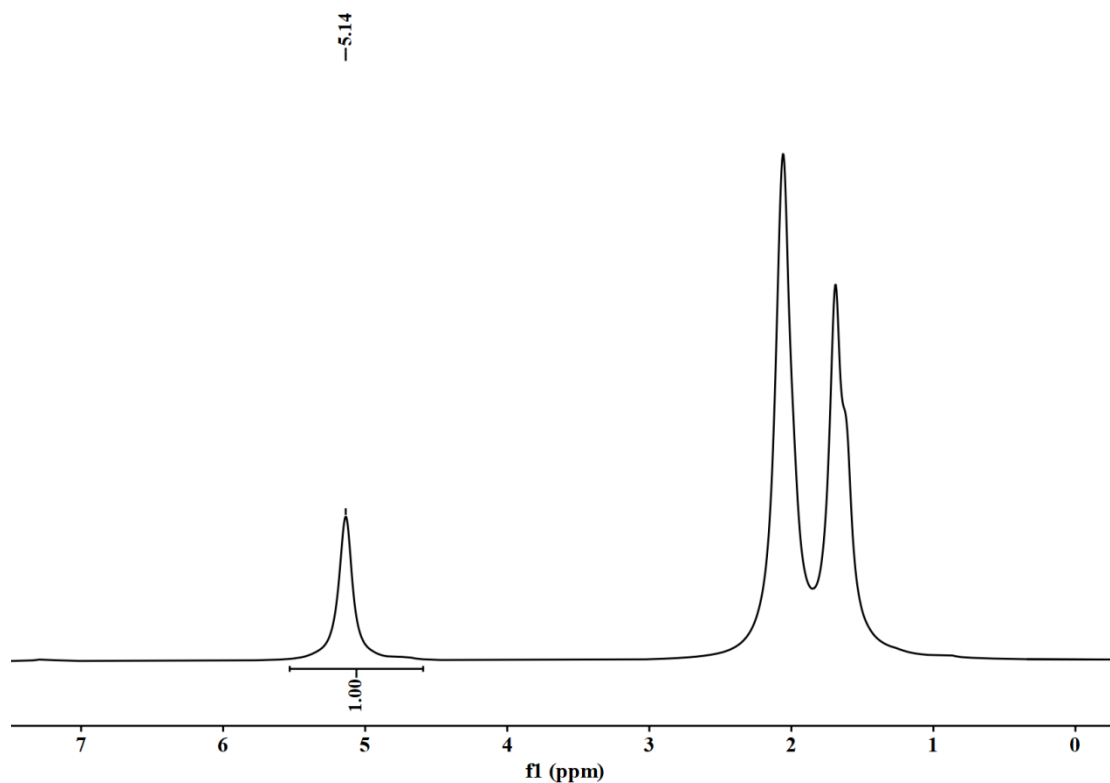


**Figure S22**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Lu** (Entry 19 in Table 1)

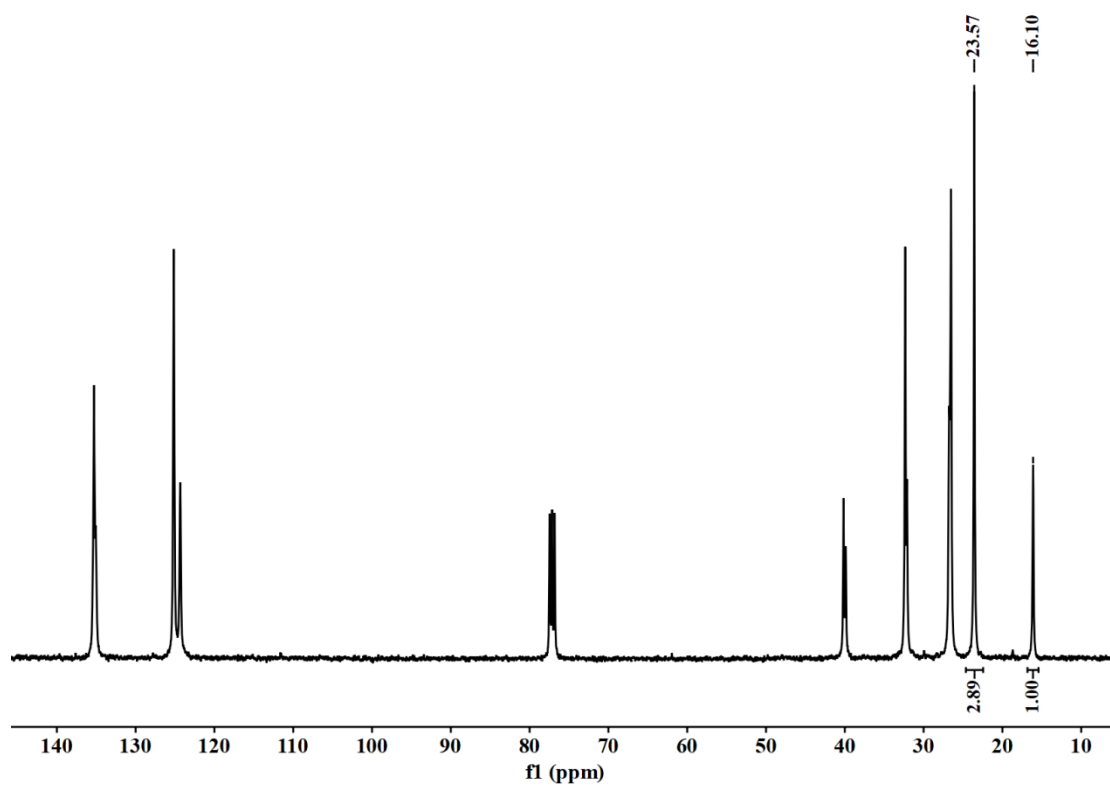


**Figure S23**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Lu** (Entry 19 in Table 1)

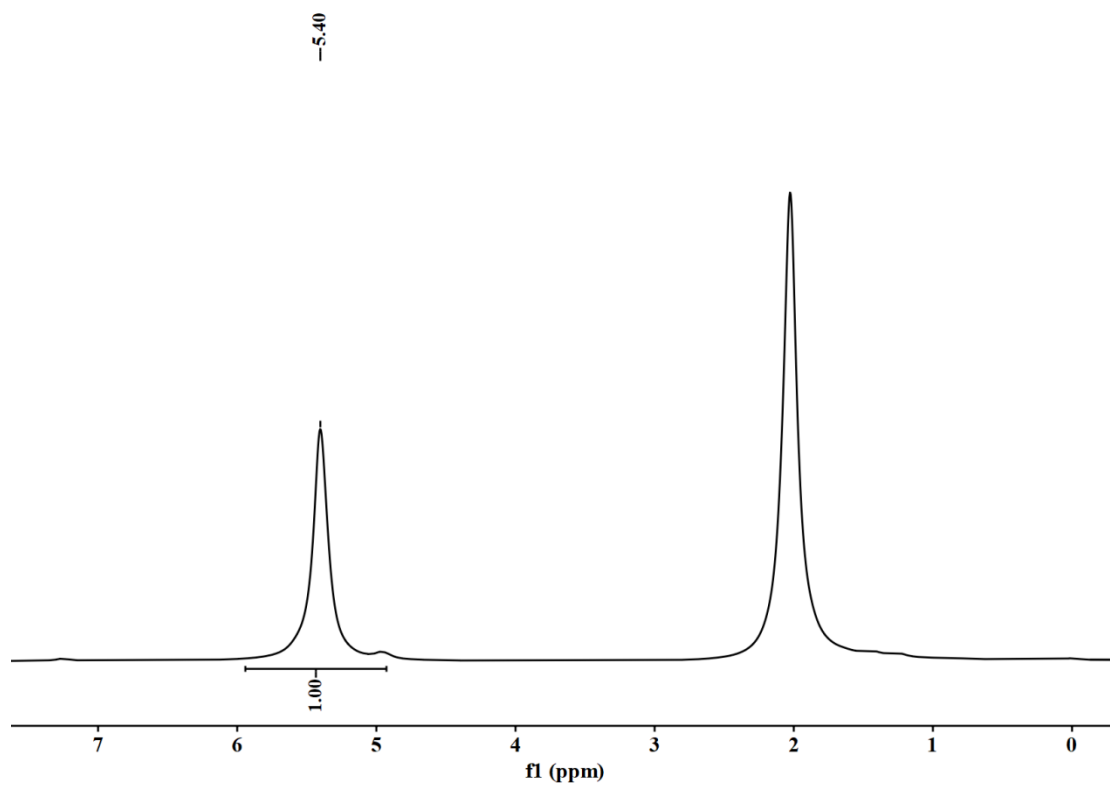




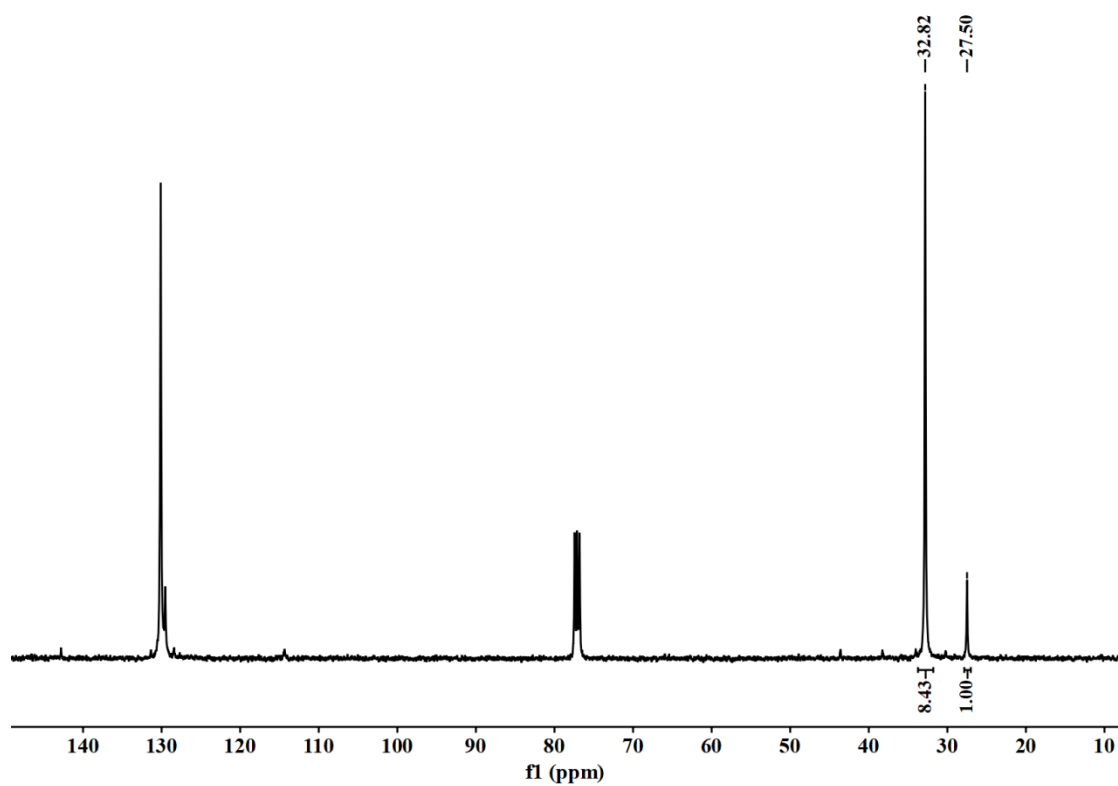
**Figure S24**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Tm** (Entry 21 in Table 1)



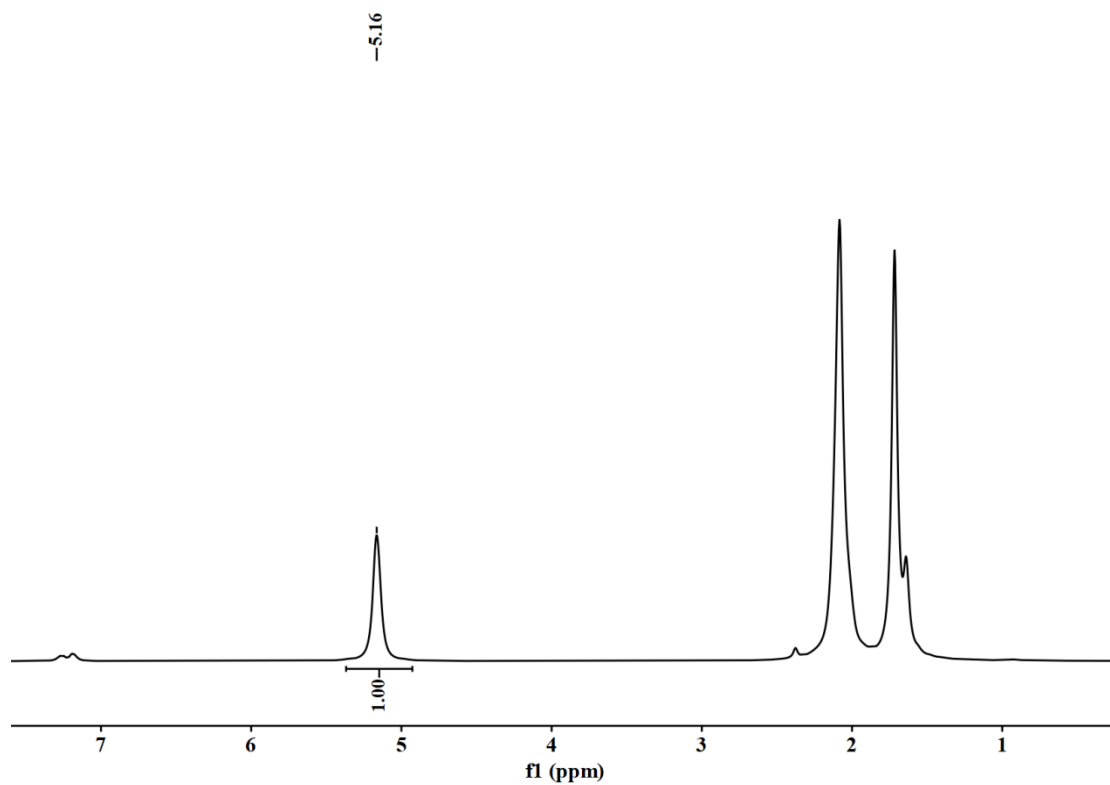
**Figure S25**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Tm** (Entry 21 in Table 1)



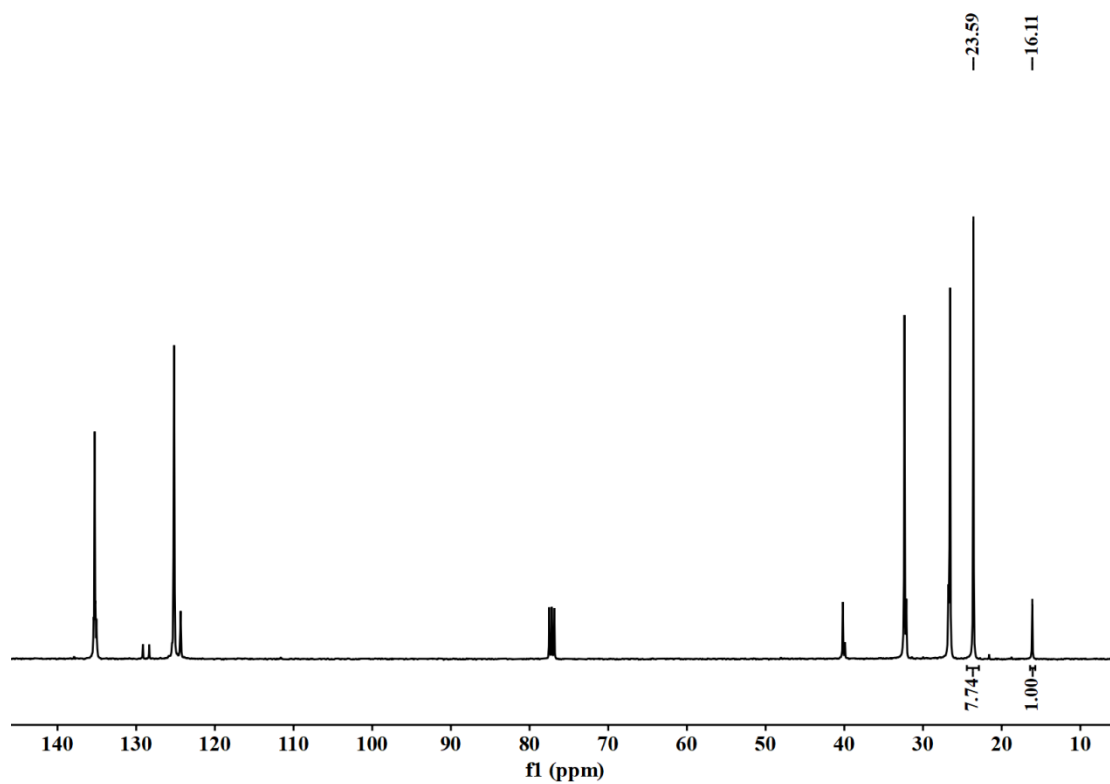
**Figure S26**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Tm** (Entry 23 in Table 1)



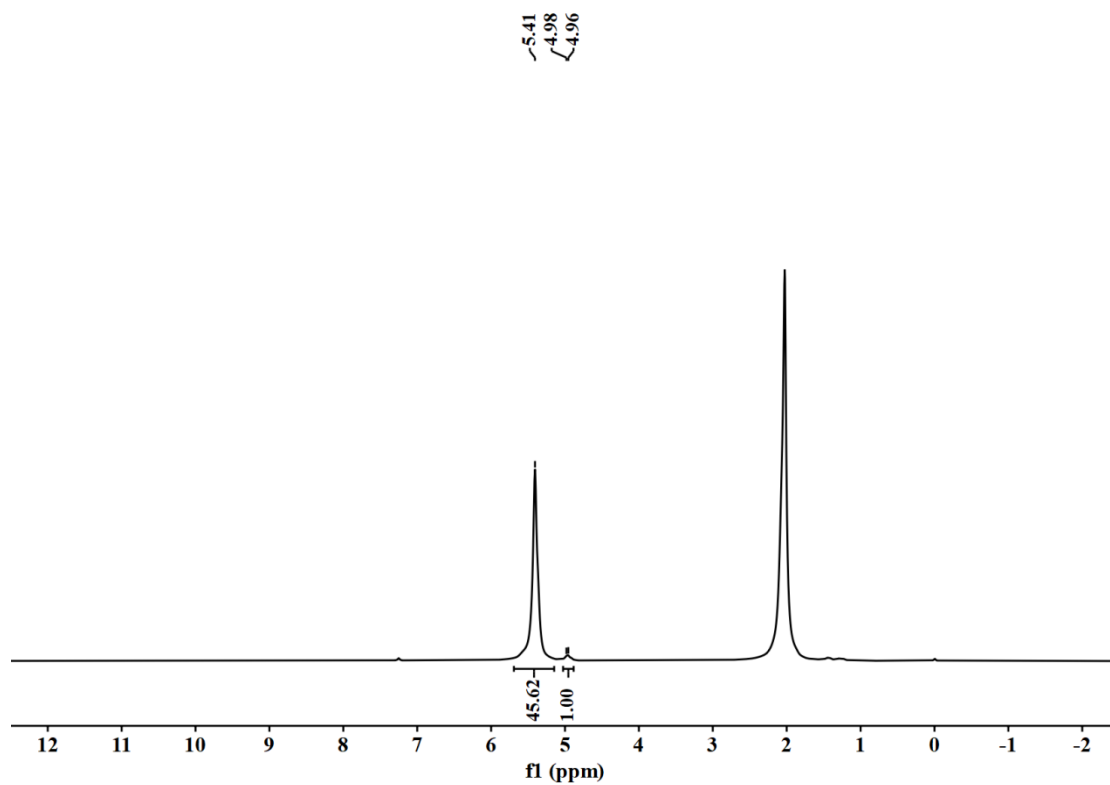
**Figure S27**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Tm** (Entry 23 in Table 1)



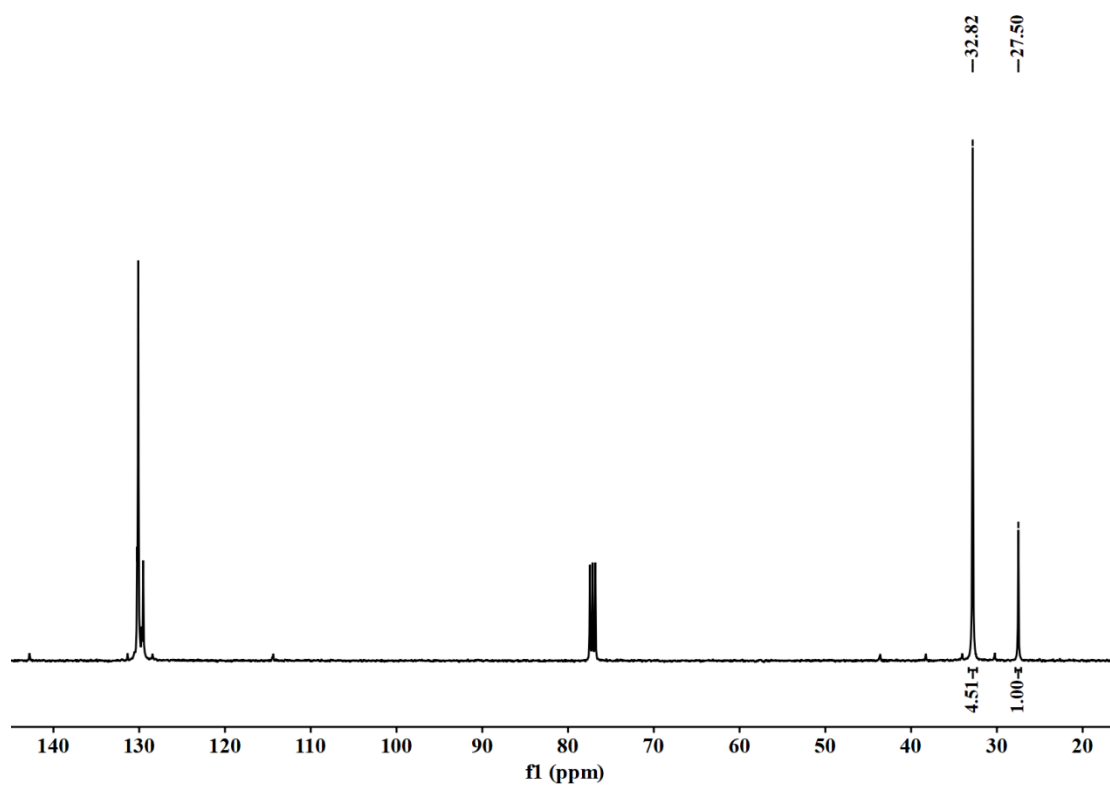
**Figure S28**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Er** (Entry 25 in Table 1)



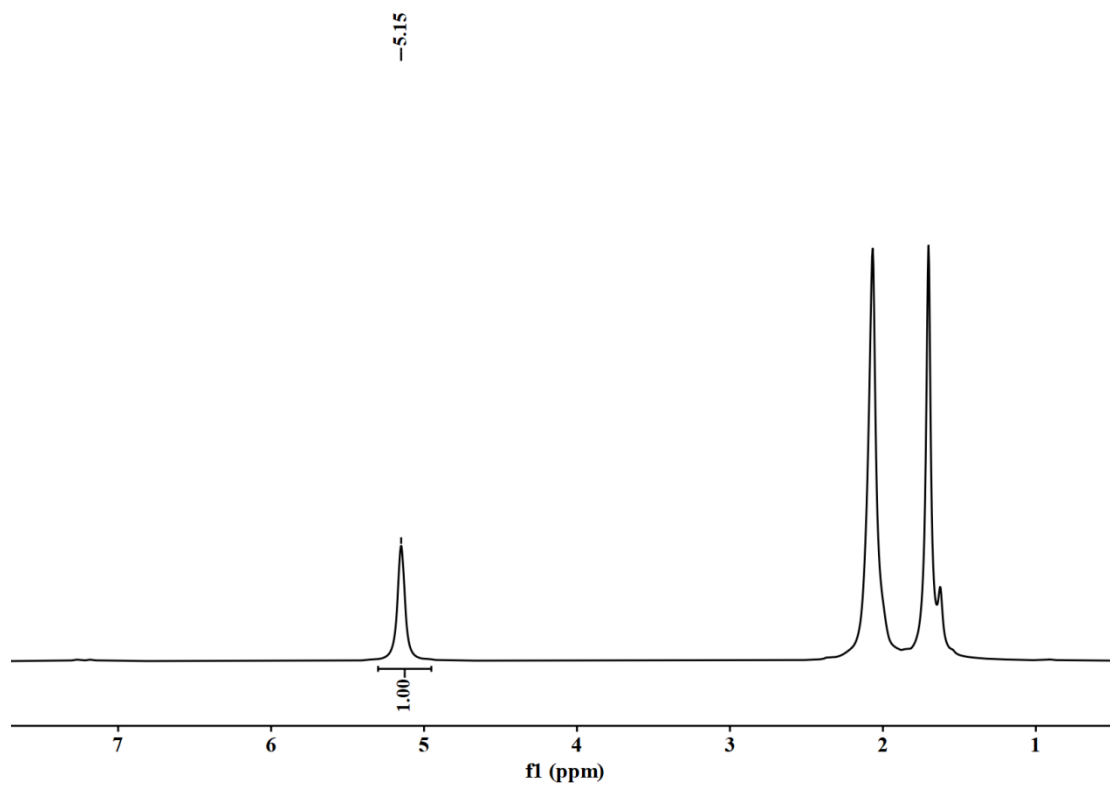
**Figure S29**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Er** (Entry 25 in Table 1)



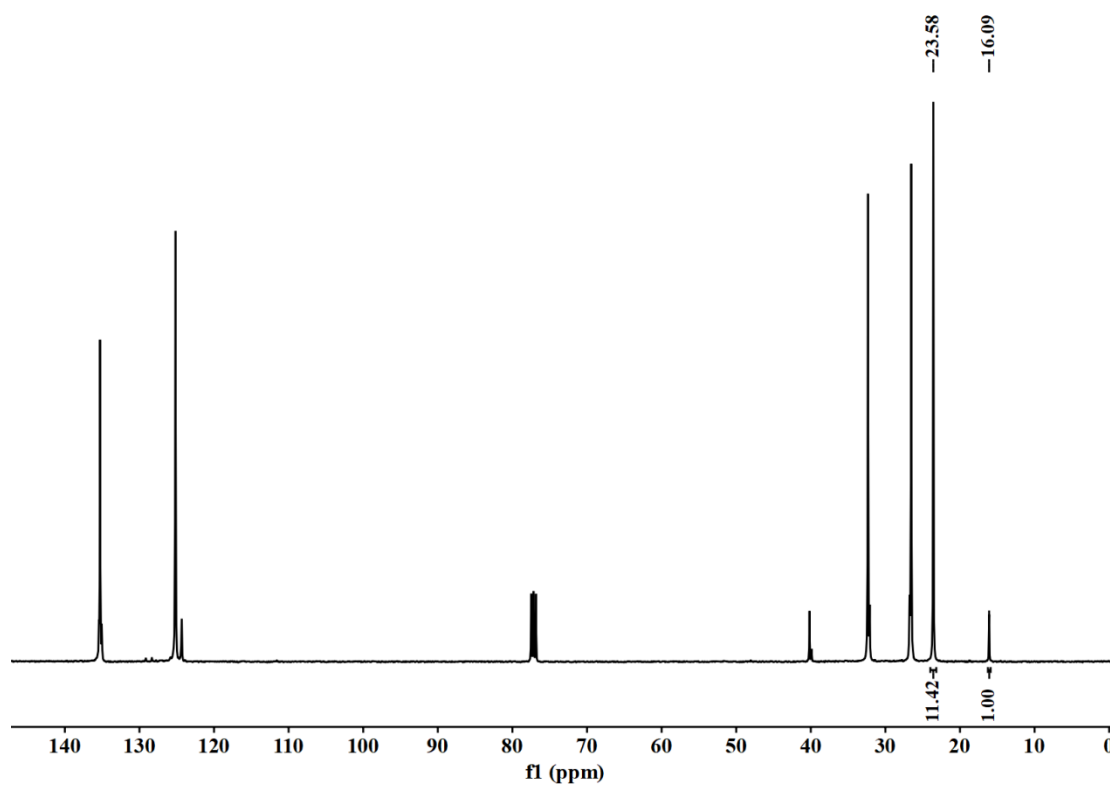
**Figure S30**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Er** (Entry 27 in Table 1)



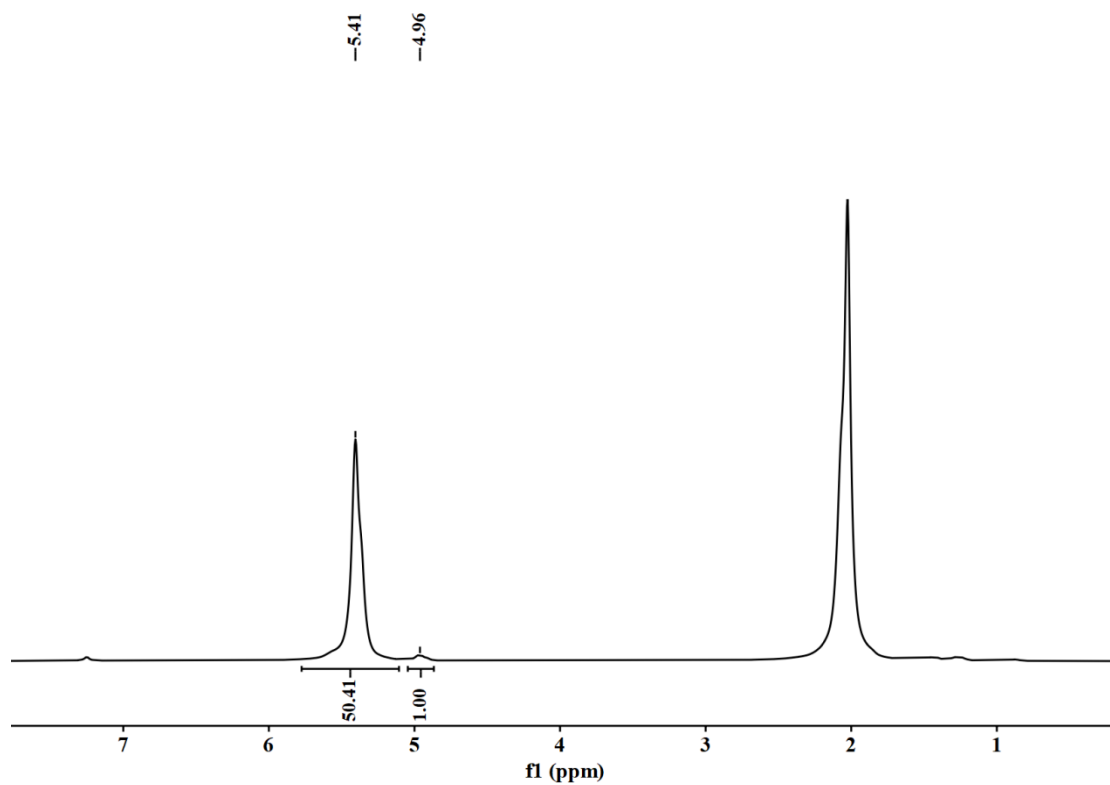
**Figure S31**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Er** (Entry 27 in Table 1)



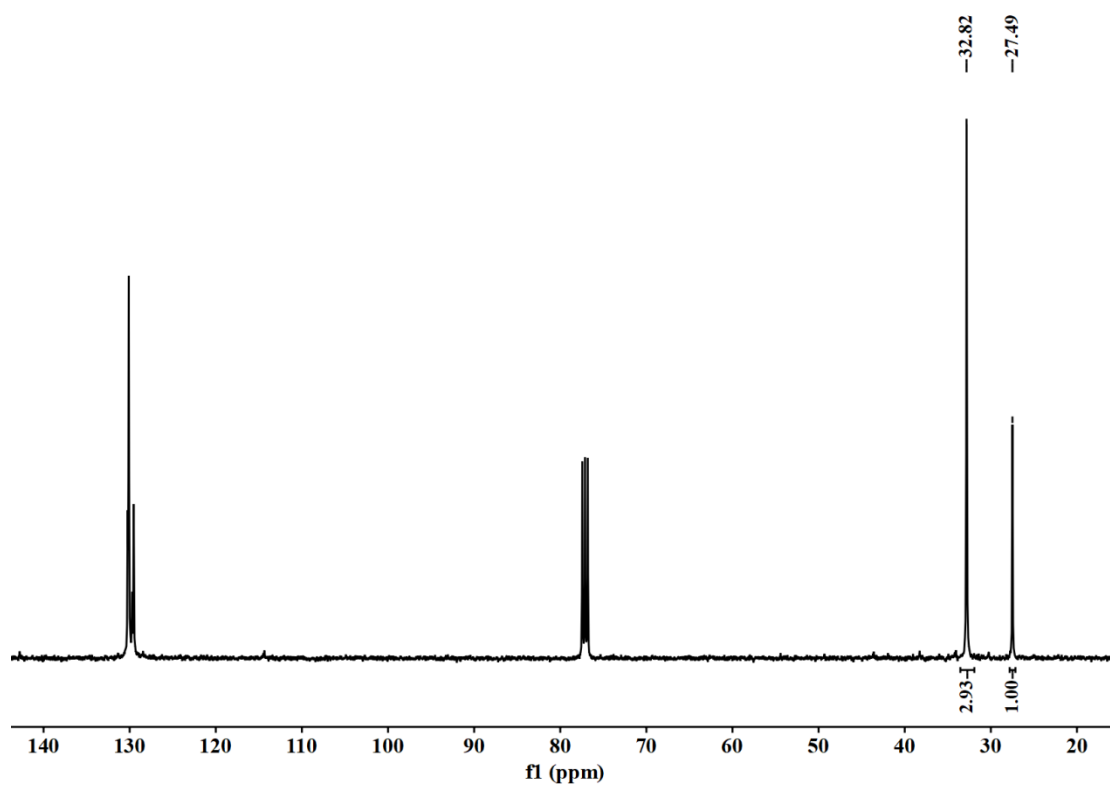
**Figure S32**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Ho** (Entry 29 in Table 1)



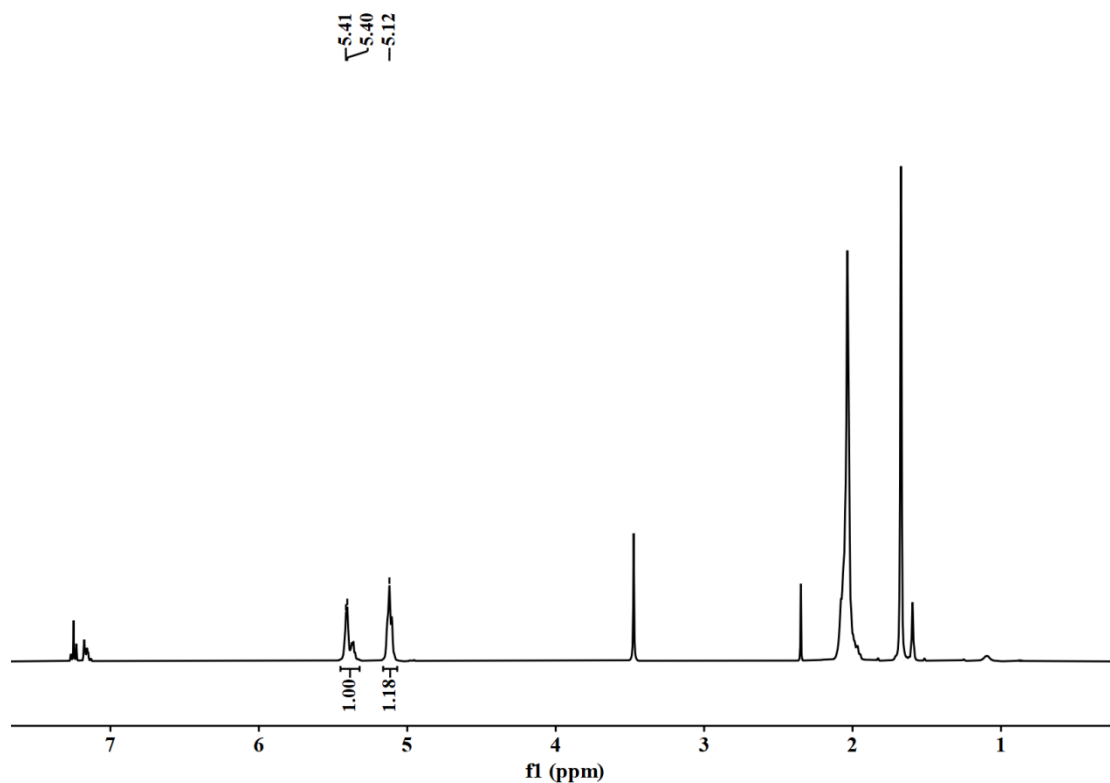
**Figure S33**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polyisoprene catalyzed by **1-Ho** (Entry 29 in Table 1)



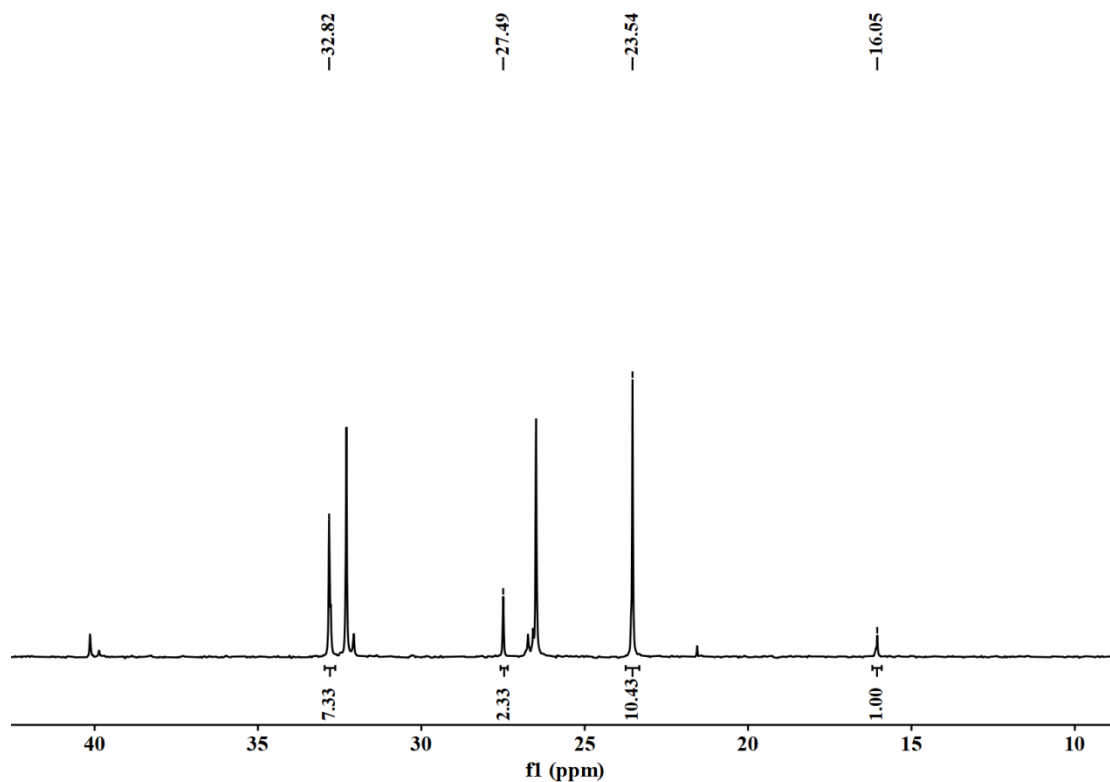
**Figure S34**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Ho** (Entry 31 in Table 1)



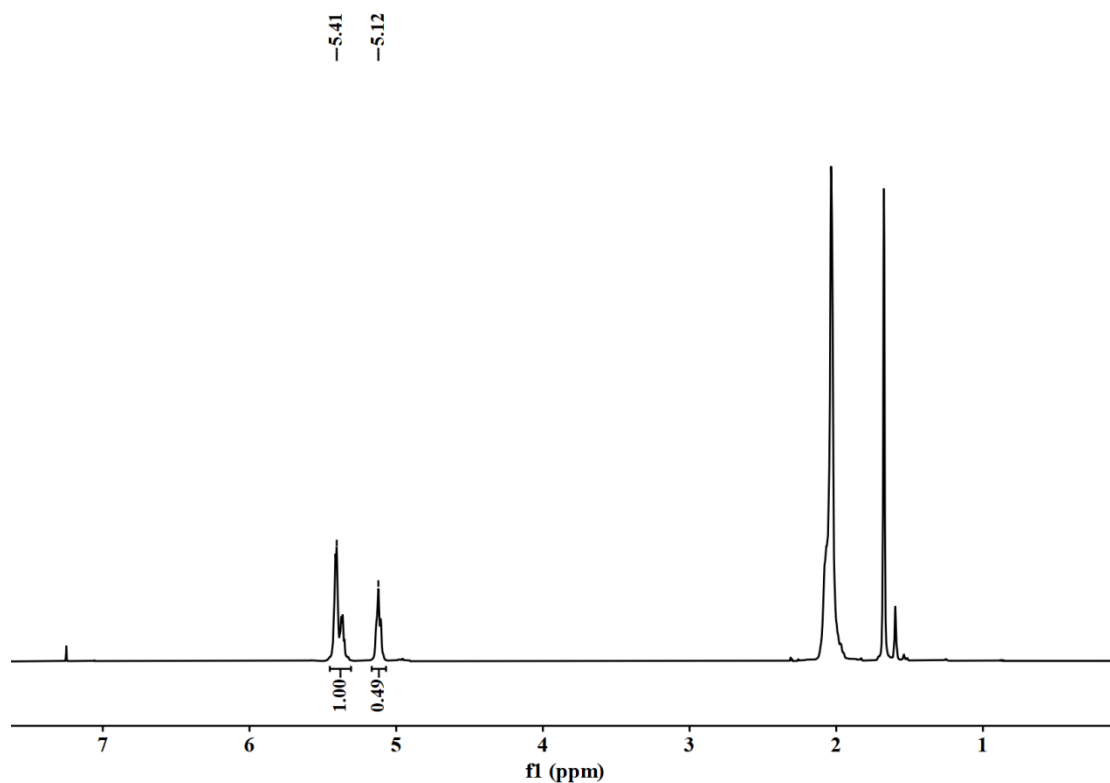
**Figure S35**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of polybutadiene catalyzed by **1-Ho** (Entry 31 in Table 1)



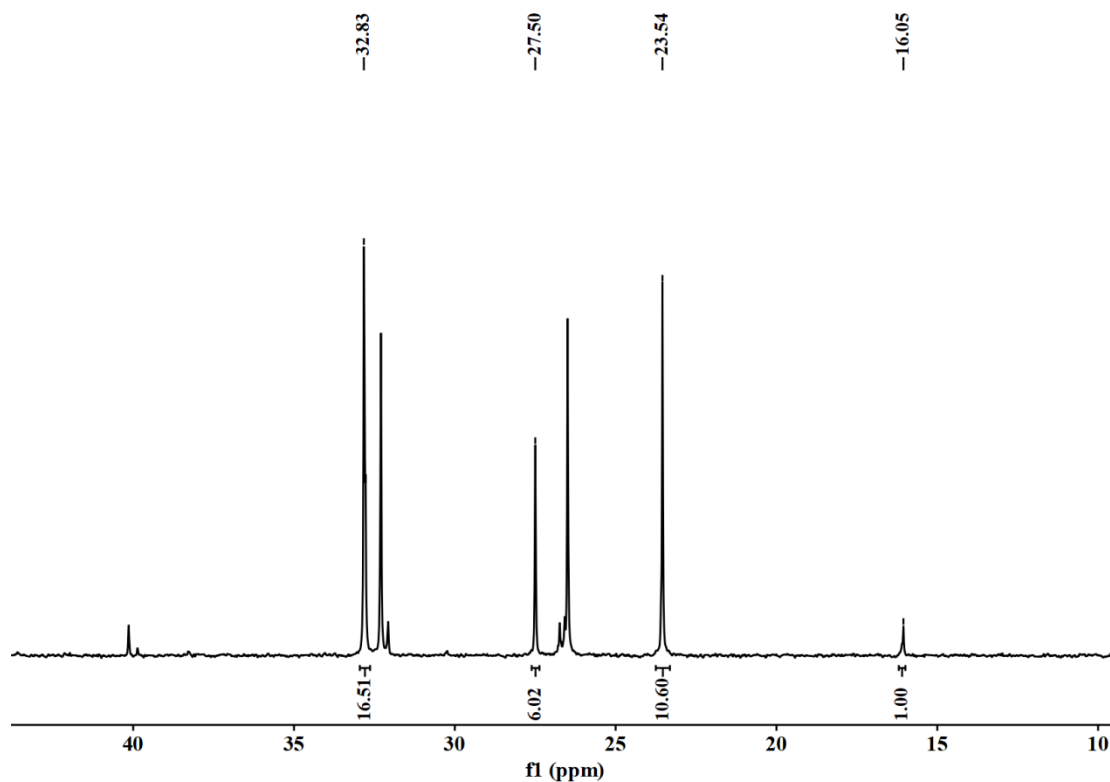
**Figure S36**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-1** catalyzed by **1-Y** (Entry 1 in Table 2)



**Figure S37**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-1** catalyzed by **1-Y** (Entry 1 in Table 2)

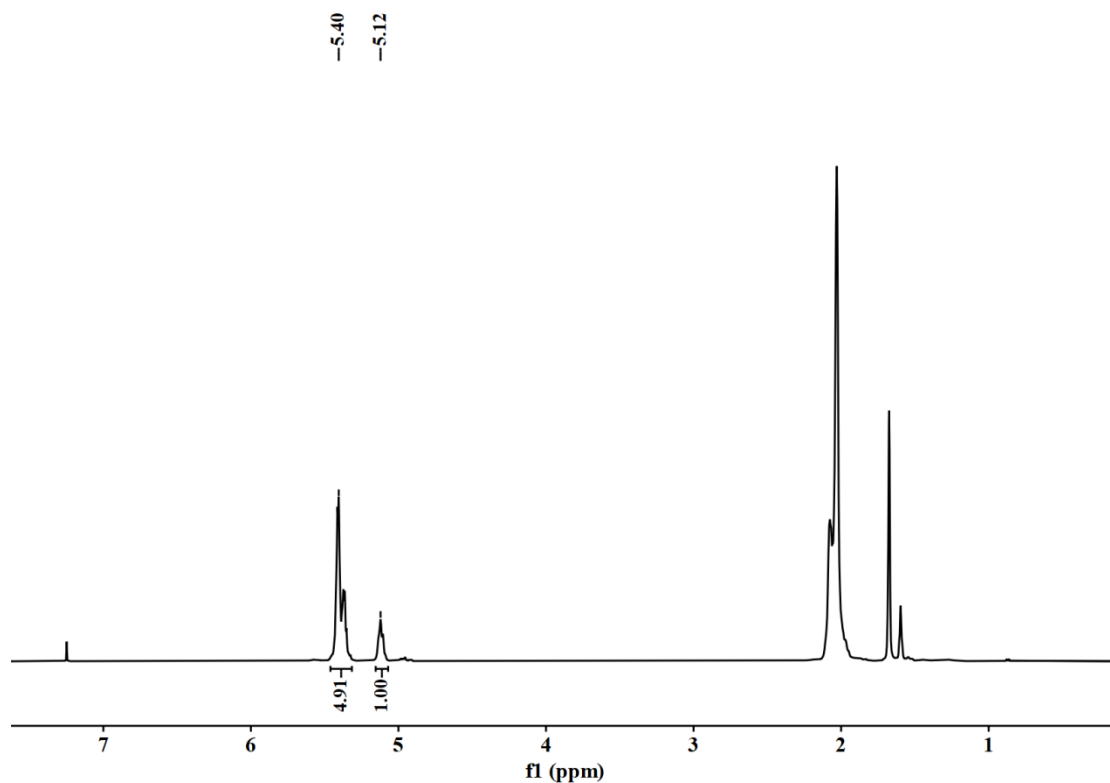


**Figure S38**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-2** catalyzed by **1-Y** (Entry 2 in Table 2)

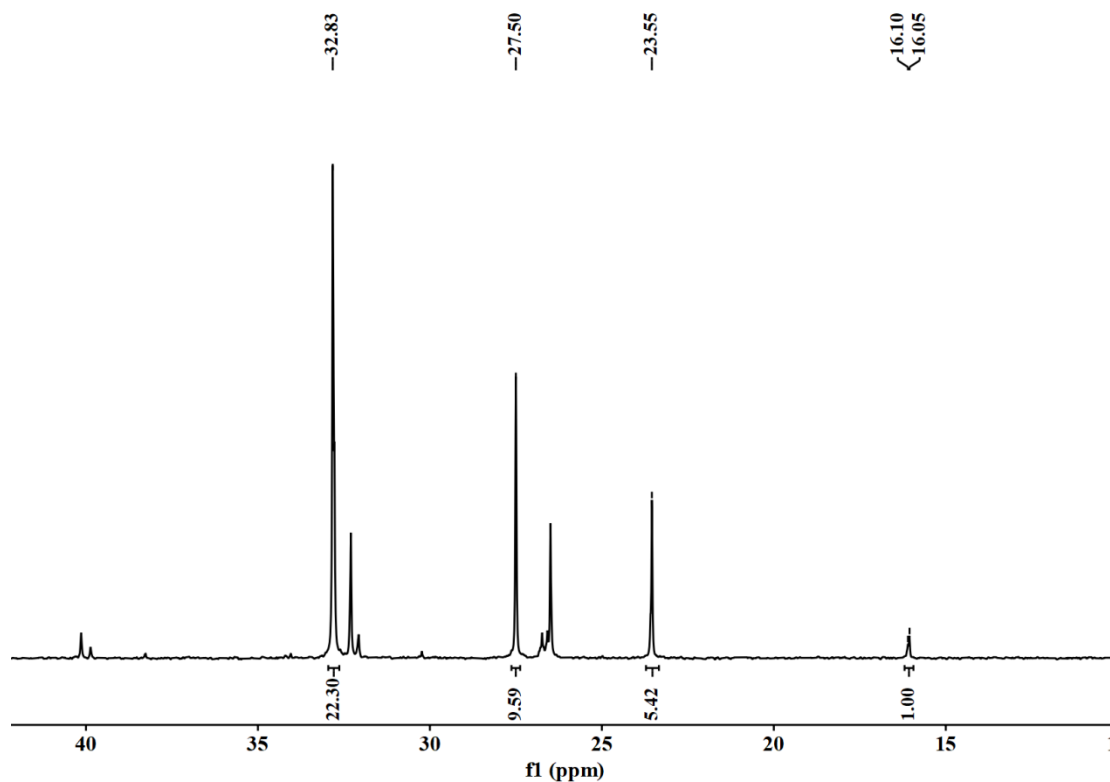


**Figure S39**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-2** catalyzed by **1-Y** (Entry 2 in Table 2)

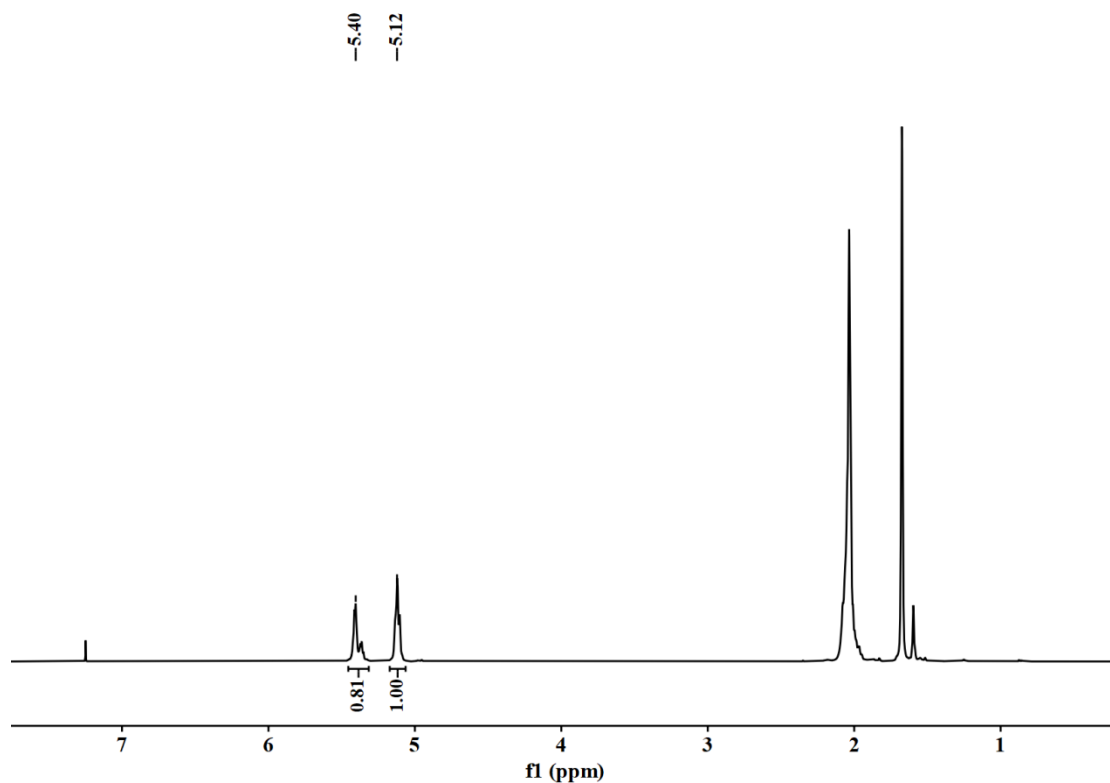




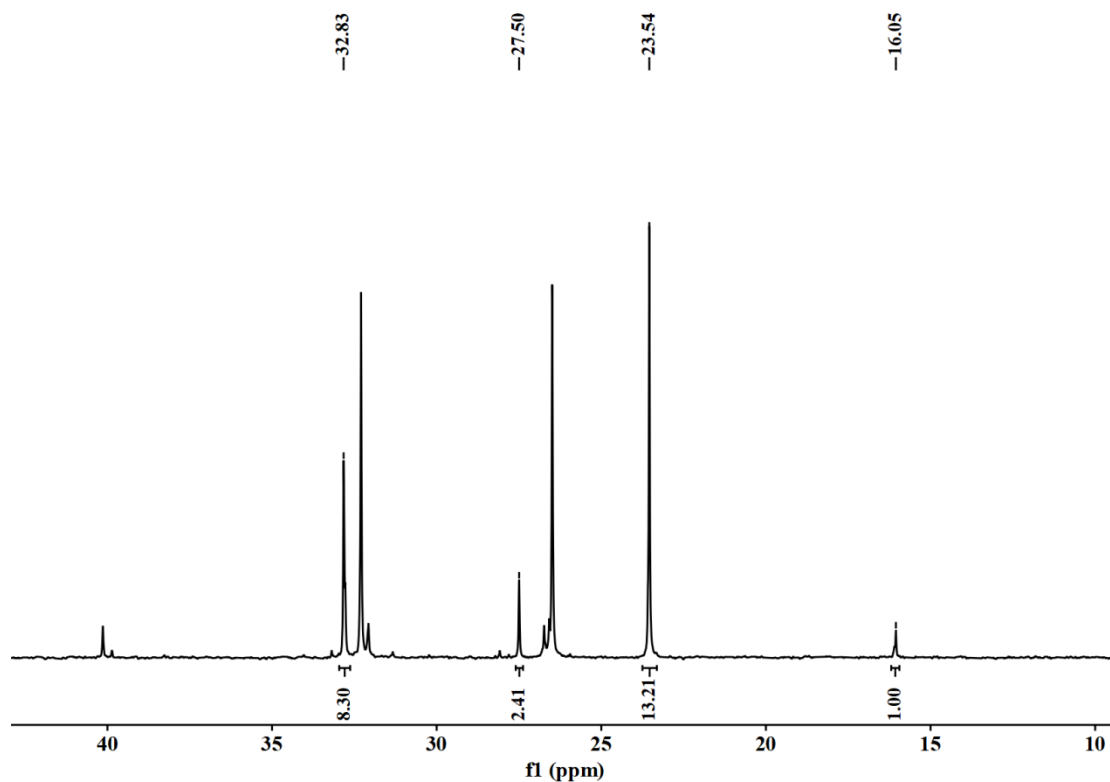
**Figure S40**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-3** catalyzed by **1-Y** (Entry 3 in Table 2)



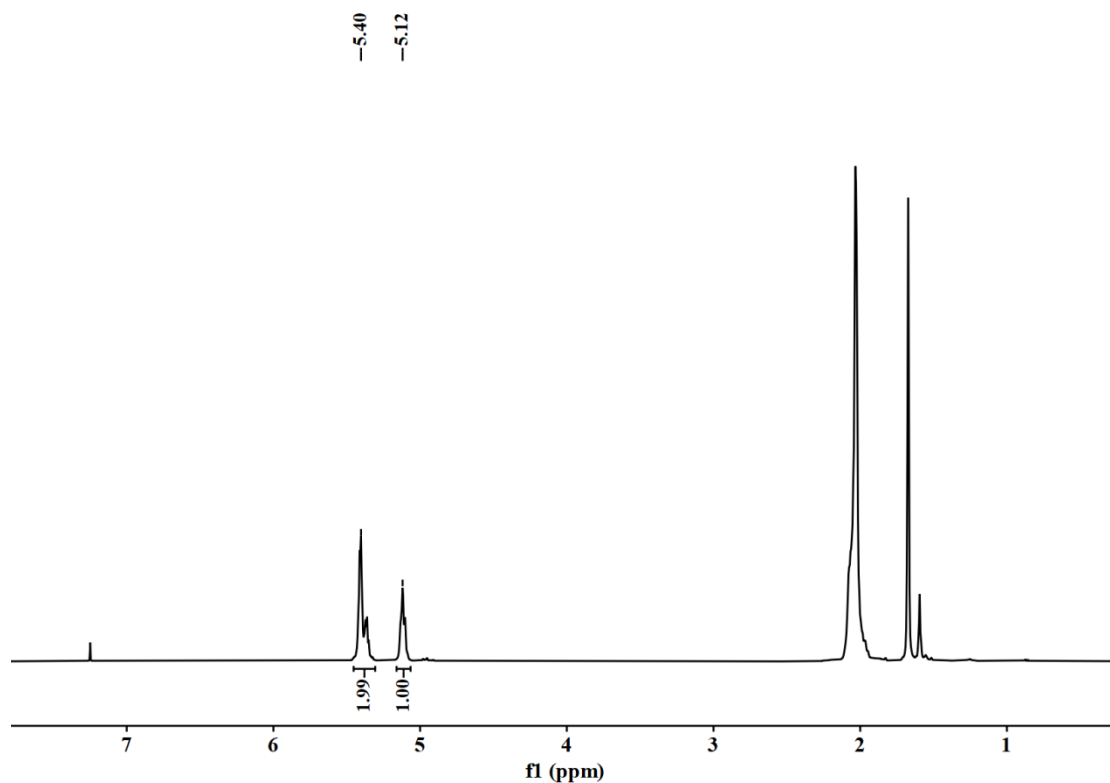
**Figure S41**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-3** catalyzed by **1-Y** (Entry 3 in Table 2)



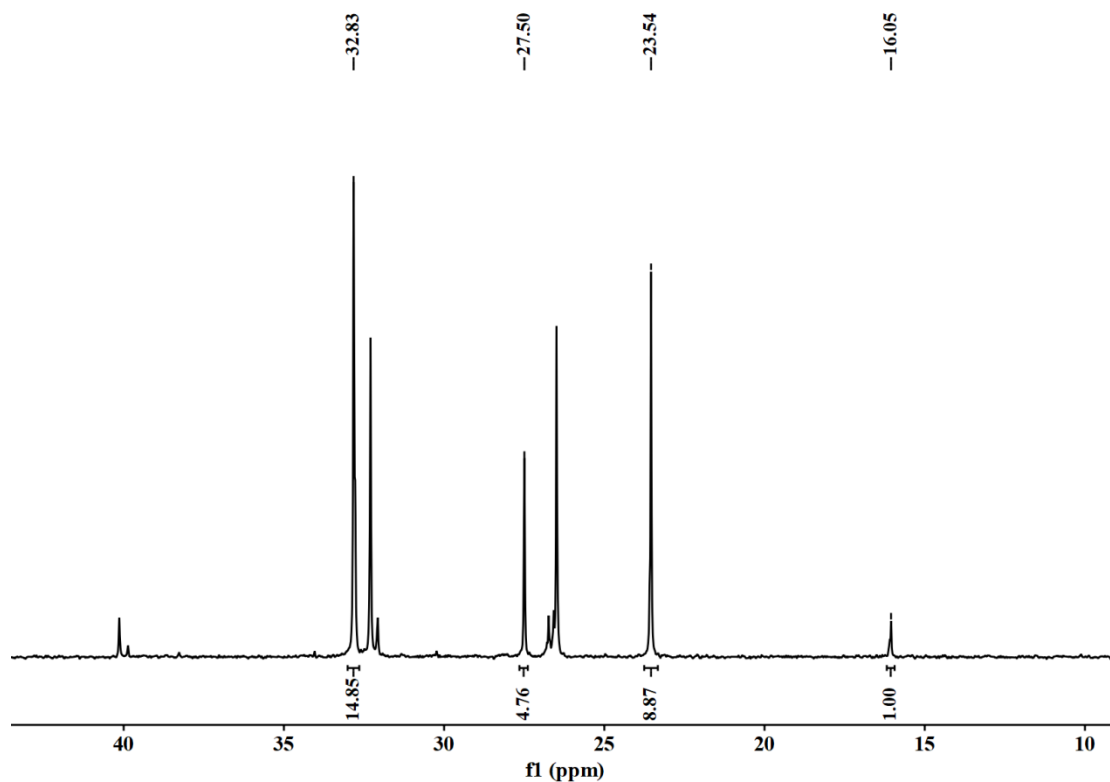
**Figure S42**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-4** catalyzed by **1-Y** (Entry 4 in Table 2)



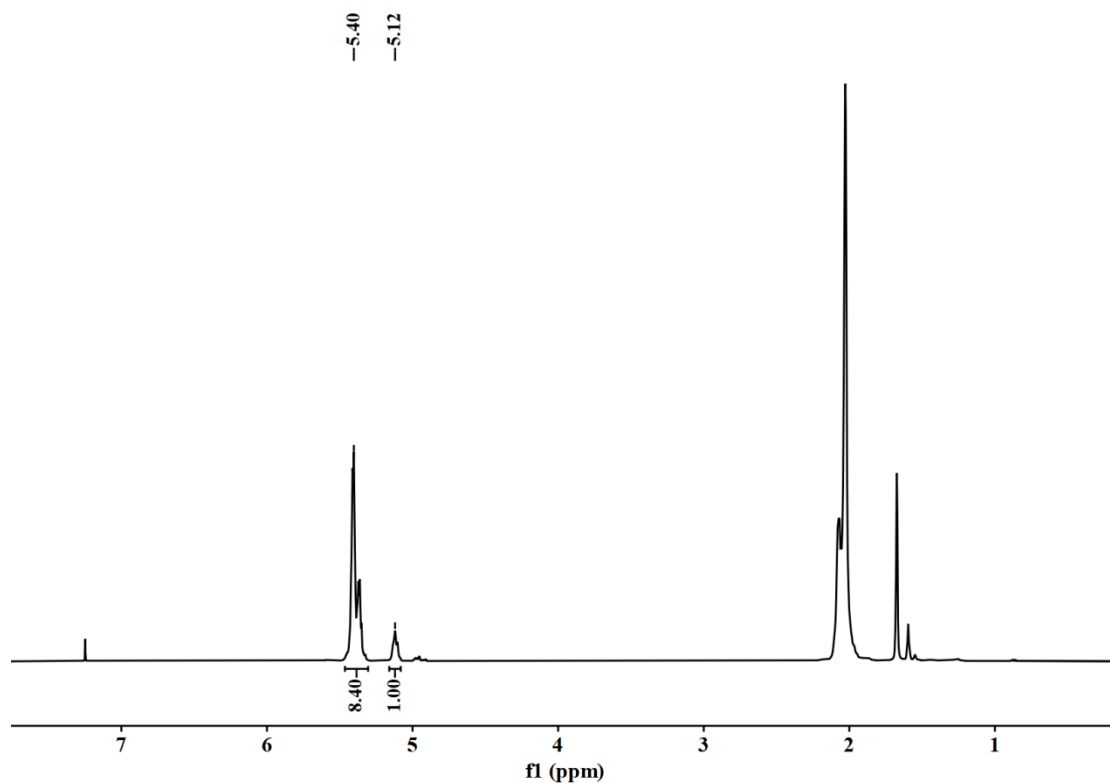
**Figure S43**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of copolymer **P-4** catalyzed by **1-Y** (Entry 4 in Table 2)



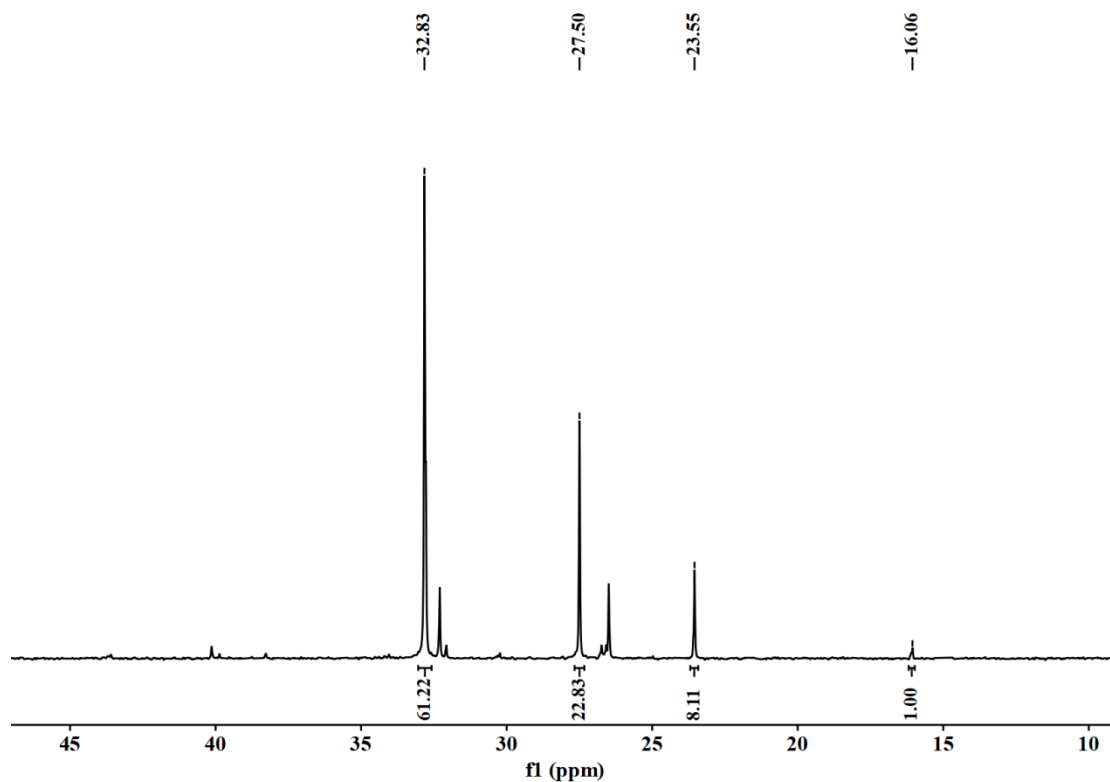
**Figure S44**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-5** catalyzed by **1-Y** (Entry 5 in Table 2)



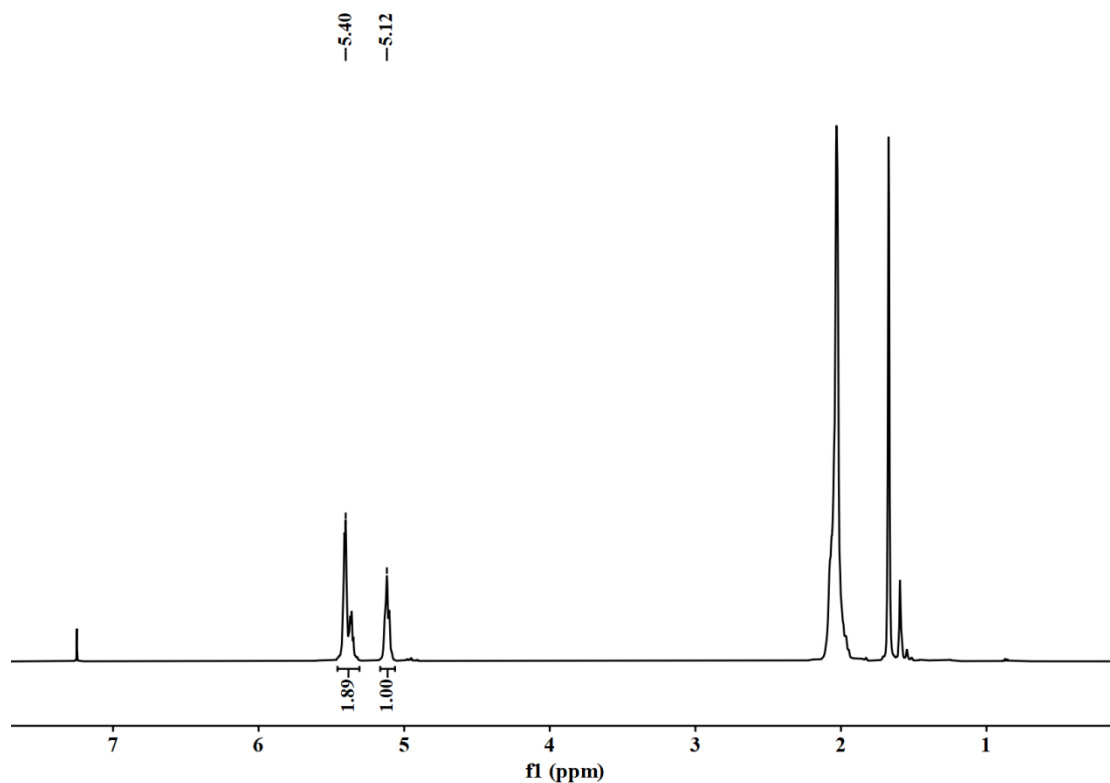
**Figure S45**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-5** catalyzed by **1-Y** (Entry 5 in Table 2)



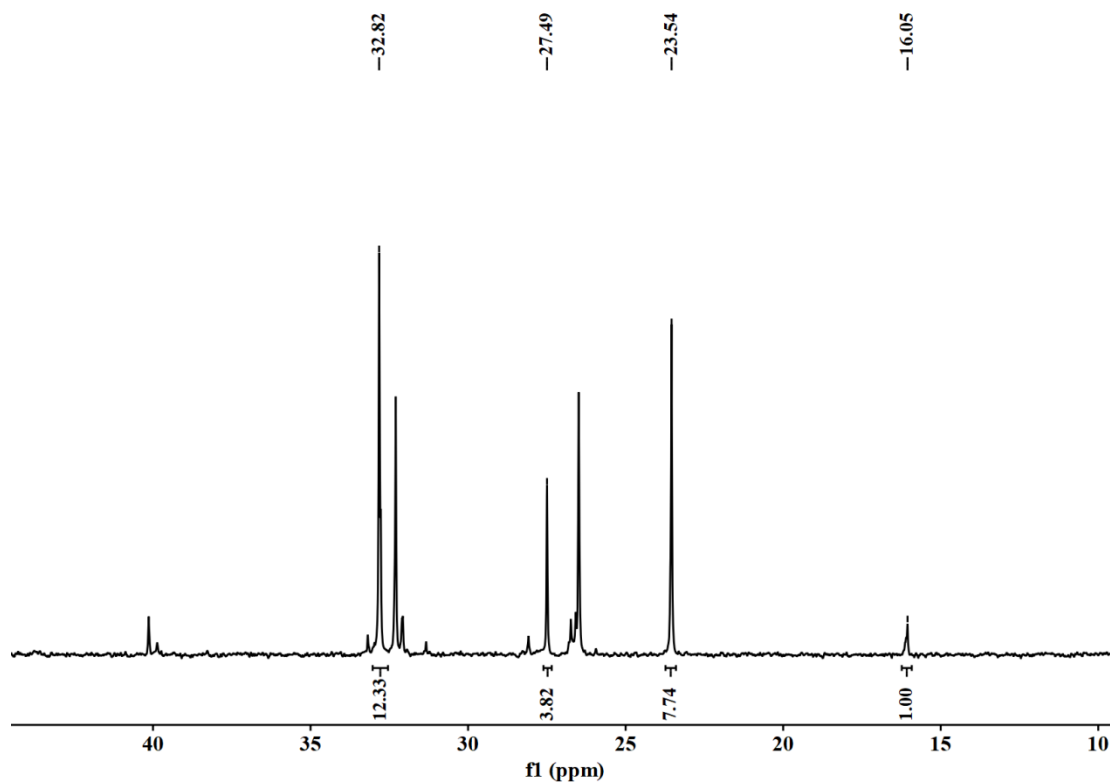
**Figure S46**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-6** catalyzed by **1-Y** (Entry 6 in Table 2)



**Figure S47**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-6** catalyzed by **1-Y** (Entry 6 in Table 2)



**Figure S48**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-7** catalyzed by **1-Y** (Entry 7 in Table 2)



**Figure S49**  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ) spectrum of copolymer **P-7** catalyzed by **1-Y** (Entry 7 in Table 2)

**Table S1** The data for Fineman-Ross diagram

$F=(M_1/M_2)$	$F=(m_1/m_2)$	$F^2/f$	$F(f-1)/f$
0.25	0.55	0.11	-0.20
0.67	1.49	0.30	0.22
1.00	2.20	0.46	0.55
1.50	3.45	0.65	1.07
2.33	5.88	0.93	1.94

**Table S2** The data for content of isoprene and butadiene in the copolymers versus the conversions

<b>Entry</b>	<b>Conversion (%)</b>	<b>Content of PIP sequence in the polymer</b>	<b>Content of PBD sequence in the polymer</b>
<b>1</b>	15.9	66.7	33.3
<b>2</b>	27.8	66.4	33.6
<b>3</b>	42.2	64.4	35.6
<b>4</b>	54.3	63.1	36.9
<b>5</b>	68.9	61.3	38.7
<b>6</b>	73.8	59.7	40.3
<b>7</b>	82.4	57.5	42.5
<b>8</b>	90.9	54.3	45.7
<b>9</b>	92.8	53.5	46.5
<b>10</b>	100.0	50.7	49.3

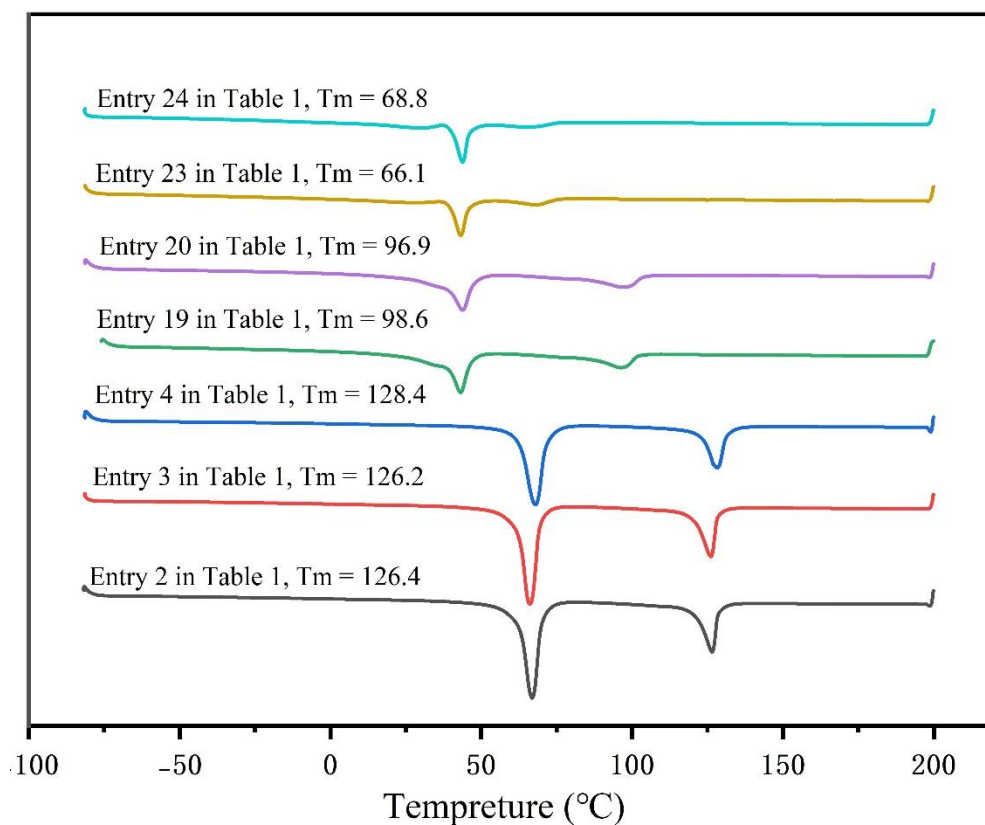


Figure S50 DSC curves of highly *trans*-1,4-PBD

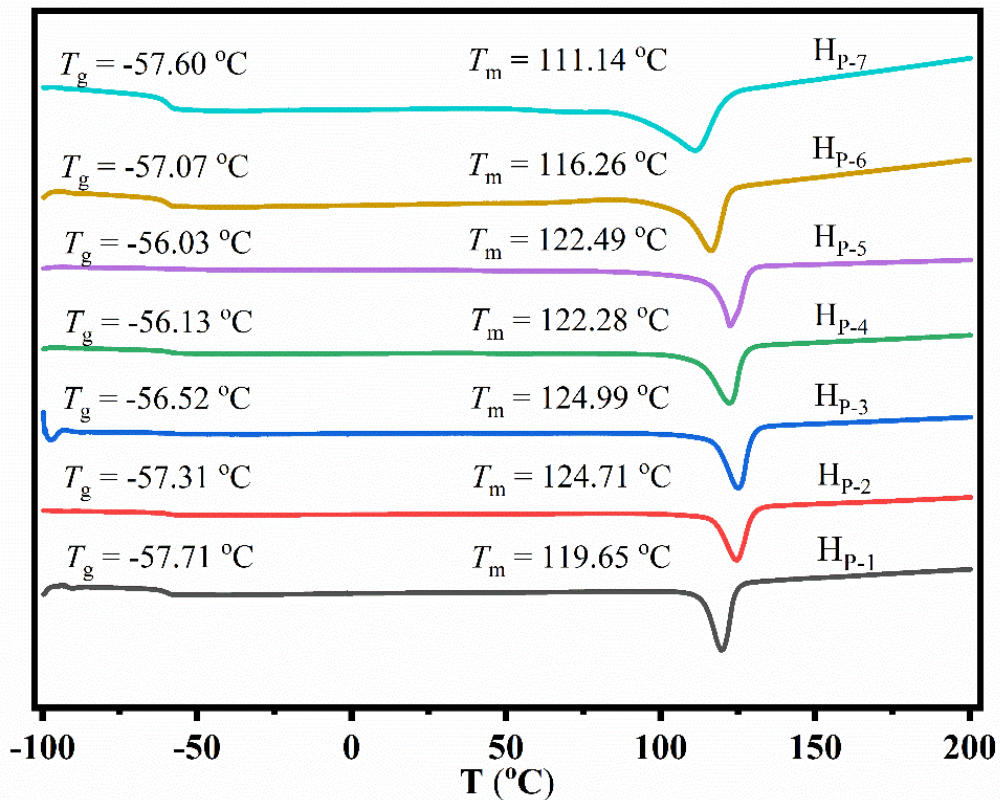


Figure S51 DSC curves of copolymers after hydrogenation