Electronic Supplementary Information for:

Di- and trinuclear rare-earth metal complexes supported by 3-amido appended indolyl ligands: Synthesis, characterization and catalytic activity towards isoprene 1,4-*cis* polymerization

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1. Table S1. Crystallographic Data for Complexes 1 – 12

	1	**2**	**3**	**4**	**5**
Formula	$C_{27}H_{47}YbN_2O_2Si_2$	$C_{54}H_{94}Er_2N_4O_2Si_4$	$C_{54}H_{94}Y_2N_4O_2Si_4$	$C_{62}H_{110}N_4O_4Si_4Yb_2$	$C_{62}H_{110}N_4O_4Si_4Er_2$
FW	644.89	1278.21	1121.51	1433.98	1278.21
Space group	*P-1*	*P-1*	*P1*	*P2(1)/n*	*P 1 21/n 1*
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	monoclinic
a (Å)	10.4517(14)	10.4376(7)	10.408(3)	16.9930(8)	30.625(3)
b (Å)	11.3563(15)	11.4218(7)	11.353(4)	15.1128(7)	15.0990(16)
c (Å)	14.994(2)	15.0140(9)	14.924(5)	28.0534(14)	33.700(4)
α (deg)	78.823(2)	78.6510(10)	78.753(4)	90	90
β (deg)	76.843(2)	76.9410(10)	77.074(4)	97.2400(10)	115.6740(10)
γ(deg)	83.550(2)	83.5880(10)	83.801(4)	90	90
Z	2	1	1	4	8
V ($Å^3$)	1695.8(4)	1705.29(19)	1681.9(10)	7147.0(6)	1705.29(19)
Dc (Mgm^{-3})	1.263	1.245	1.107	1.333	1.345
μ (mm^{-1})	2.846	2.549	1.823	2.711	2.486
F (000)	658	654	596	2952	5856
Reflns collected	14366	14945	14326	61467	28645
Unique reflns	7541	7740	7614	16417	22015
Parameters	304	304	304	863	1442
Goodness of fit	0.998	1.056	0.912	1.020	1.056
θ range (deg)	1.42 to 27.46	1.82 to 27.65	1.83 to 27.74	1.49 to 27.56	2.26 to 27.60
R_1 ($I > 2\sigma(I)$)	0.0525	0.0551	0.0722	0.0500	0.0392
wR_2 ($I > 2\sigma(I)$)	0.1114	0.1311	0.1800	0.0695	0.0989
Largest diff.peak and hole (e. $Å^{-3}$)	1.298 / -1.308	1.697 / -0.933	1.056 / -0.694	0.740 / -1.095	2.198 / -2.028

	6	**7**	**8**	**9**	**10**	**11**	**12**
Formula	$C_{62}H_{110}N_4O_4Si_4Y_2$	$C_{62}H_{110}Gd_2N_4O_4Si_4$	$C_{76}H_{115}Er_3N_8O_5Si$	$C_{76}H_{115}N_8O_5SiY_3$	$C_{76}H_{115}Dy_3N_8O_5Si$	$C_{80}H_{110}N_8OEr_2$	$C_{80}H_{110}N_8OY_2$
FW	1265.72	1402.40	1750.63	1515.58	1736.35	1534.28	1377.58
Space group	*P 1 21/c 1*	*P21/c*	*P2(1)/c*	*P 21/c*	*P2(1)/c*	*P-1*	*P-1*
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
a (Å)	16.873(3)	17.006(3)	15.8978(10)	15.8890(16)	15.9167(11)	12.0912(4)	12.0907(5)
b (Å)	15.102(2)	15.194(3)	23.9240(15)	23.917(3)	23.9395(17)	14.9505(6)	14.9826(7)
c (Å)	30.748(5)	31.049(5)	24.6951(15)	24.683(3)	24.7080(17)	24.4254(10)	24.4211(11)
α (deg)	90	90	90	90	90	104.891(2)	104.563(2)
β (deg)	115.655(11)	115.666(8)	95.6670(10)	95.663(2)	95.6220(10)	98.886(2)	98.834(2)
γ(deg)	90	90	90	90	90	93.187(2)	93.354(2)
Z	4	4	4	4	4	2	2
V ($Å^3$)	7063(2)	7231(2)	9346.6(10)	9333.9(17)	9369.4(11)	4194.8(3)	4209.1(3)
Dc (Mgm^{-3})	1.187	1.288	1.244	1.079	1.231	1.215	1.087
μ (mm^{-1})	1.747	1.927	2.725	1.906	2.424	2.030	1.415
F (000)	2680	2904	3540	3192	3516	1580	1464
Reflns collected	52781	80089	66372	80005	66454	82369	60301
Unique reflns	13377	16101	16457	21379	16486	19292	14346
Parameters	805	870	853	841	853	879	879
Goodness of fit	1.032	1.147	0.970	1.009	0.964	1.050	0.997
θ range (deg)	1.50 to 25.00	1.33 to 27.37	1.54 to 25.00	1.54 to 27.52	1.54 to 25.00	2.88 to 27.57	2.96 to 25.00
R_1 ($I > 2\sigma(I)$)	0.0830	0.0467	0.0379	0.0367	0.0367	0.0838	0.0876
wR_2 ($I > 2\sigma(I)$)	0.1881	0.1161	0.0853	0.0897	0.0837	0.1465	0.2099
Largest diff.peak and hole (e. $Å^{-3}$)	1.261 -0.984	0.956 -0.946	0.867 -0.746	0.45 -0.24	0.935 -0.653	2.373 -2.620	0.613 -0.745

Molecular structure of the complexes

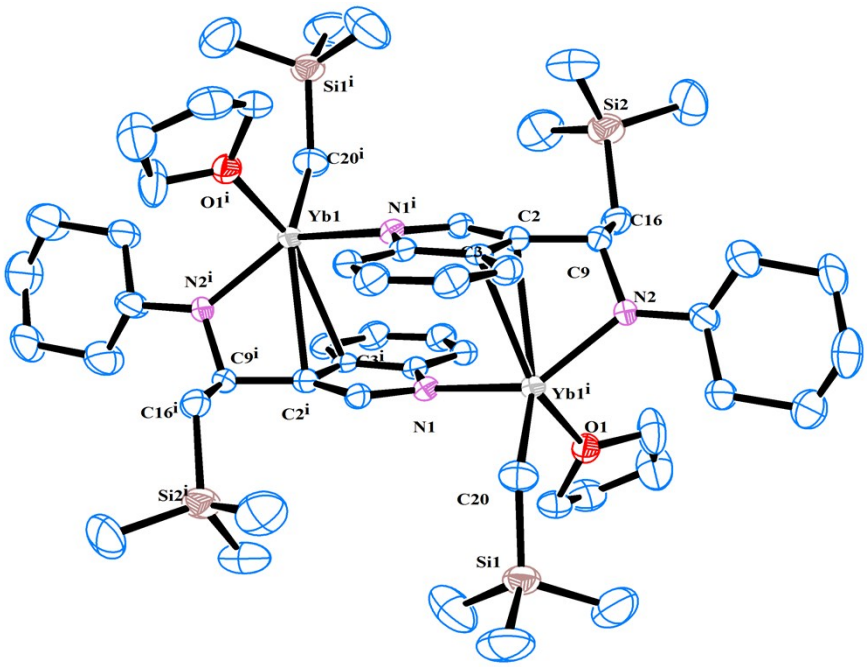

Figure S1. Molecular structure of complex **1**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

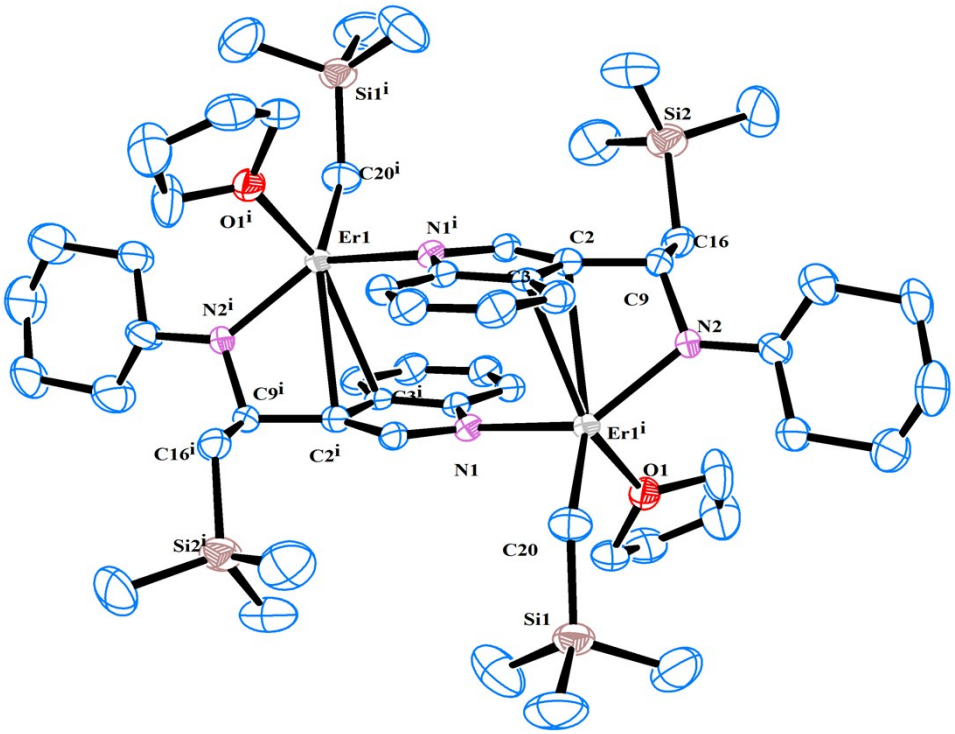

Figure S2. Molecular structure of complex **2**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

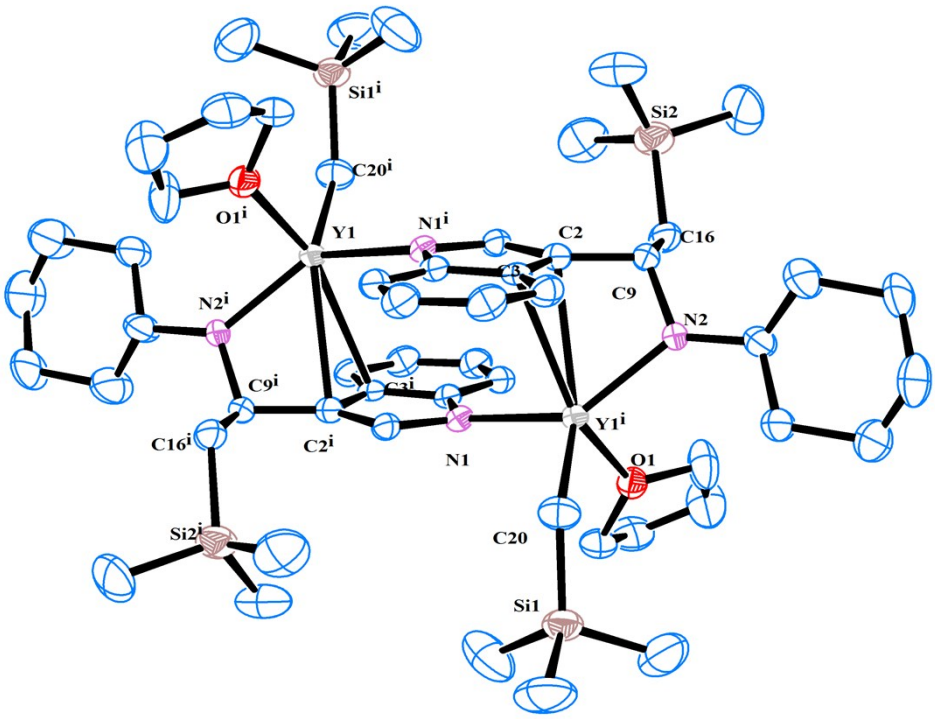

Figure S3. Molecular structure of complex **3**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

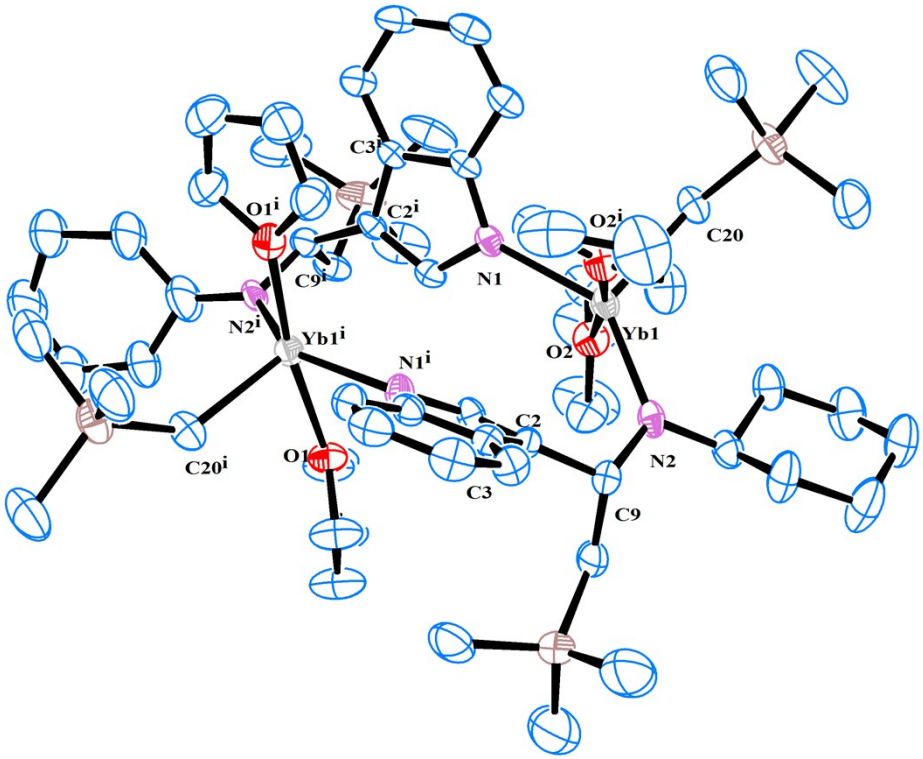

Figure S4. Molecular structure of complex **4**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

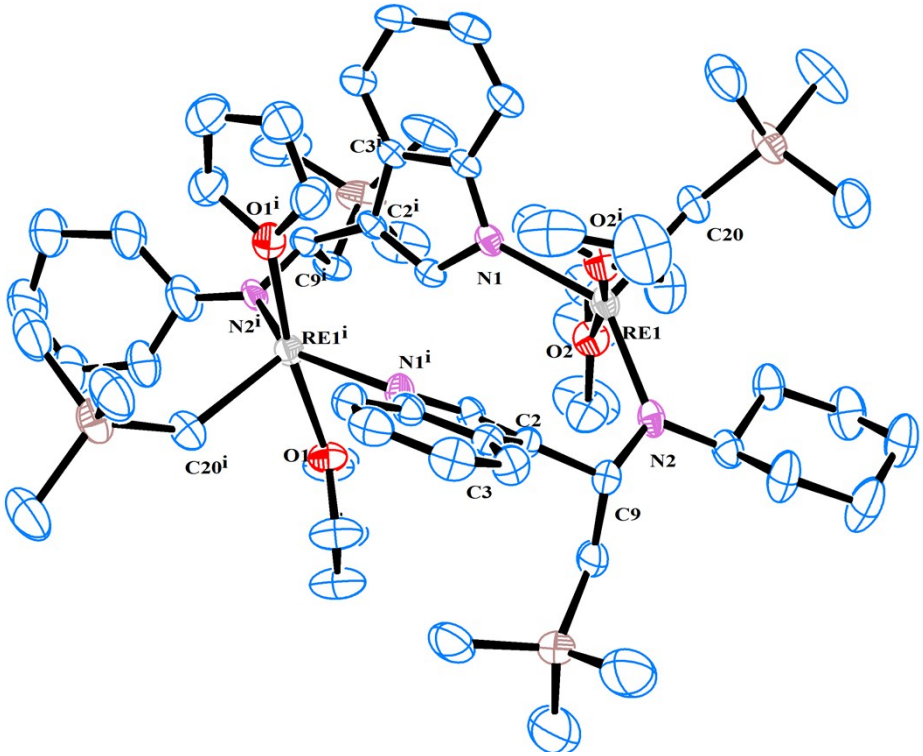

Figure S5. Molecular structure of complex **5**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

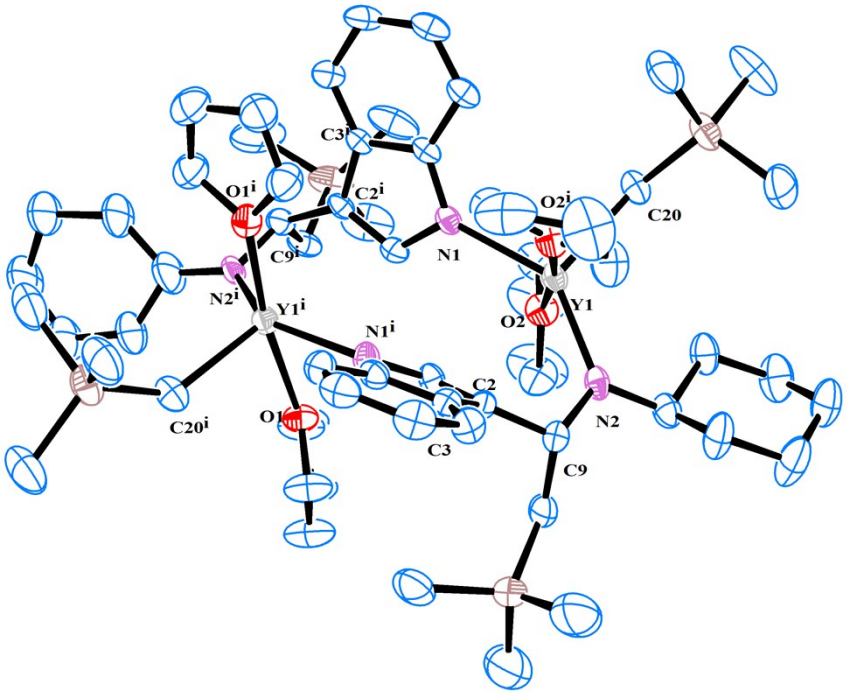

Figure S6. Molecular structure of complex **6**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

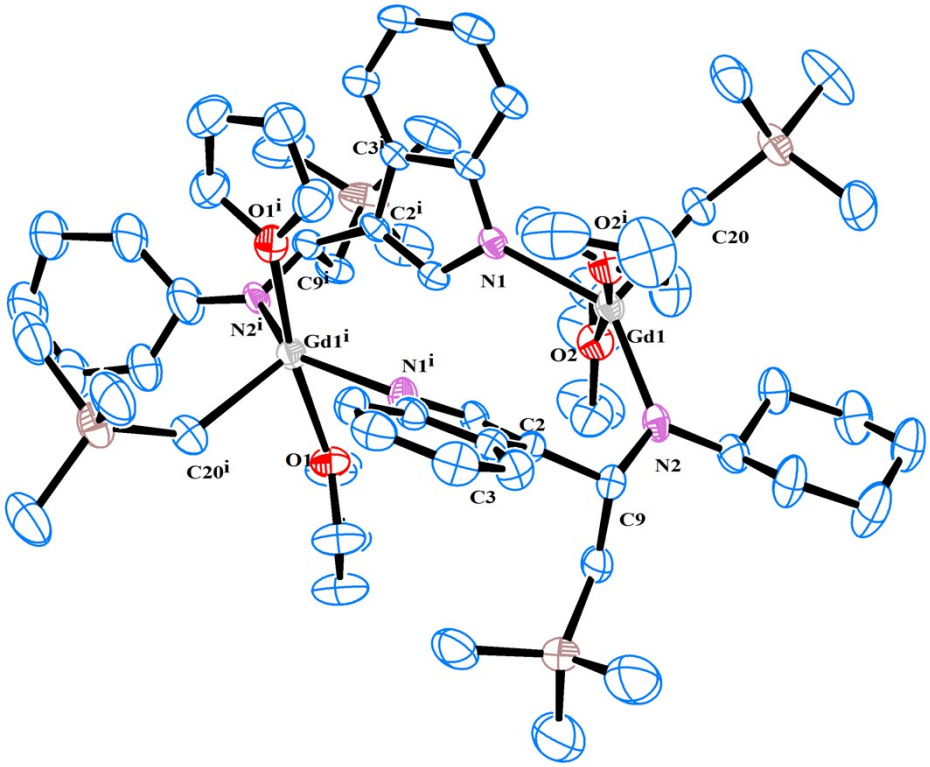

Figure S7. Molecular structure of complex **7**. Thermal ellipsoids are set at at 30% probability. Hydrogen atoms are omitted for clarity.

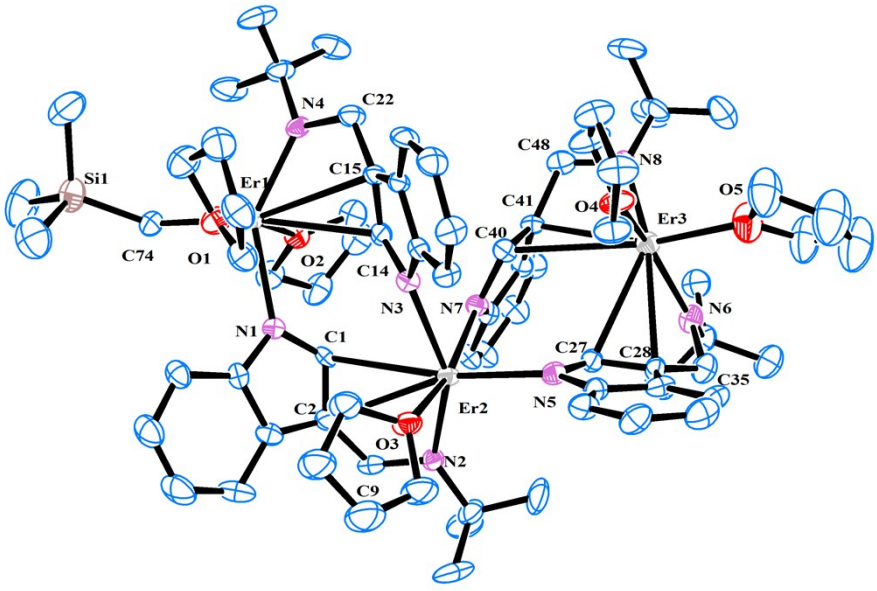

Figure S8. Molecular structure of complex **8**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms and the tertiary butyl groups on N2, N4, N6, N8 atoms are omitted for clarity.

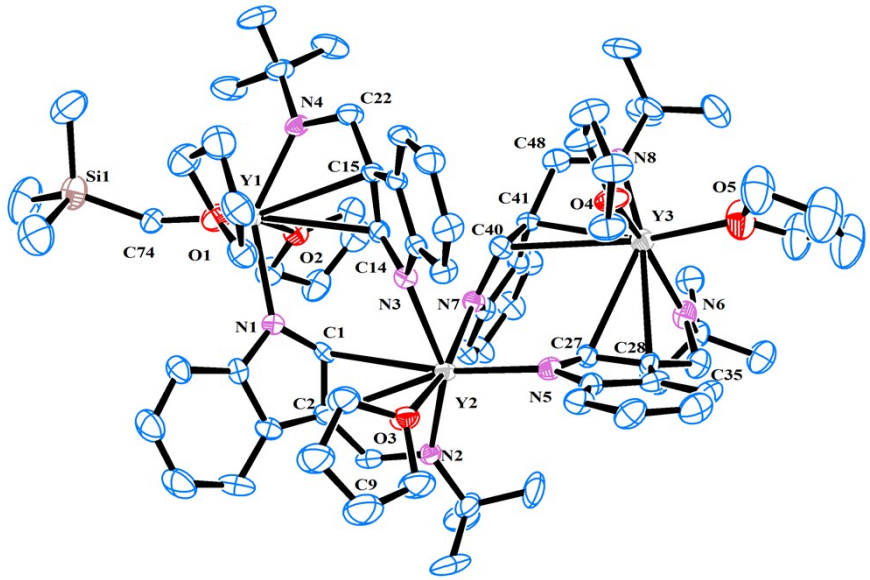

Figure S9. Molecular structure of complex **9**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms and the tertiary butyl groups on N2, N4, N6, N8 atoms are omitted for clarity.

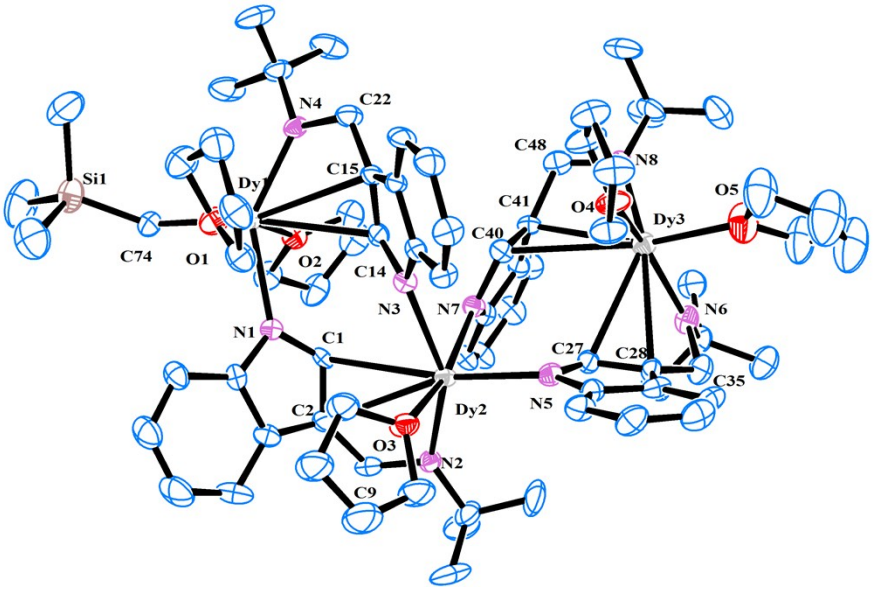

Figure S10. Molecular structure of complex **10**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms and the tertiary butyl groups on N2, N4, N6, N8 atoms are omitted for clarity.

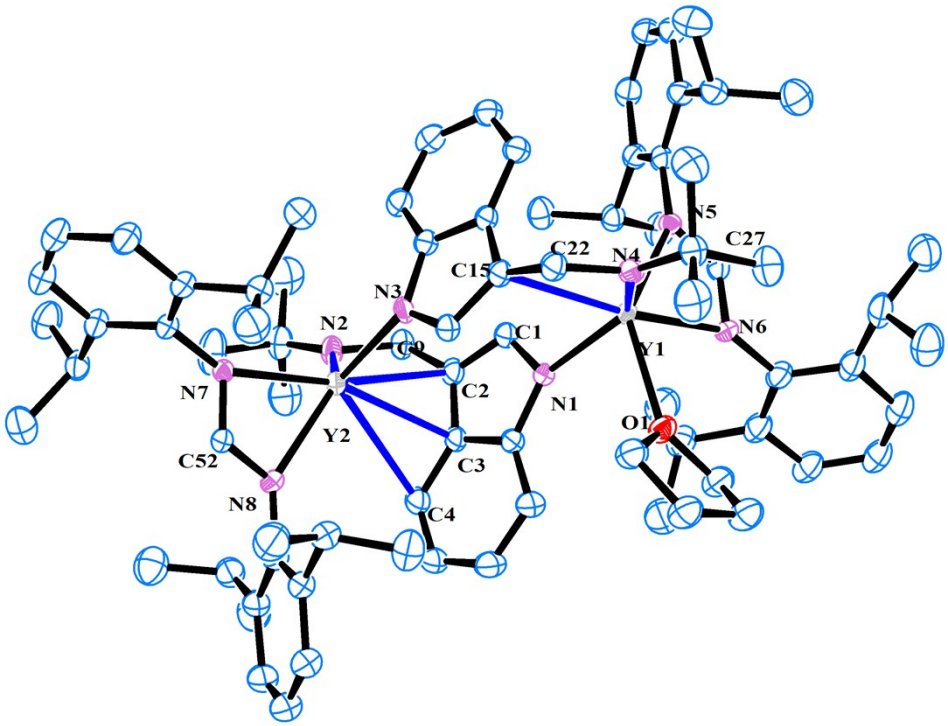

Figure S11. Molecular structure of complex **11**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

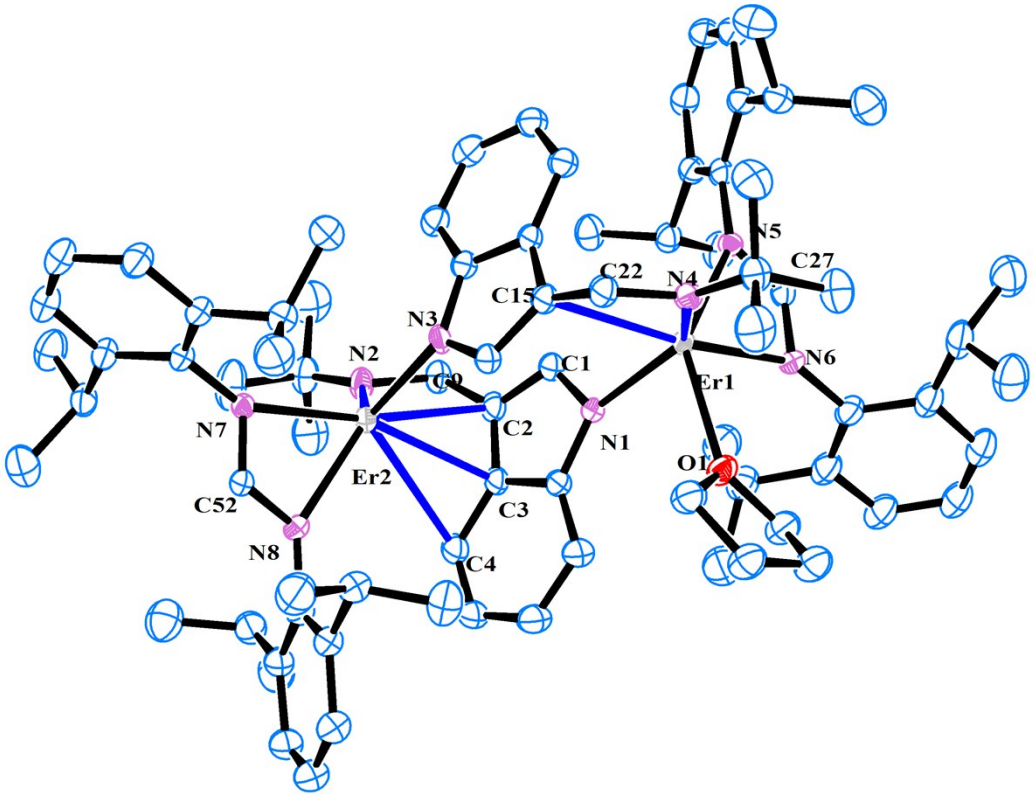

Figure S12. Molecular structure of complex **12**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

^{1}H NMR and ^{13}C NMR spectra of complex 3, 6 and 9

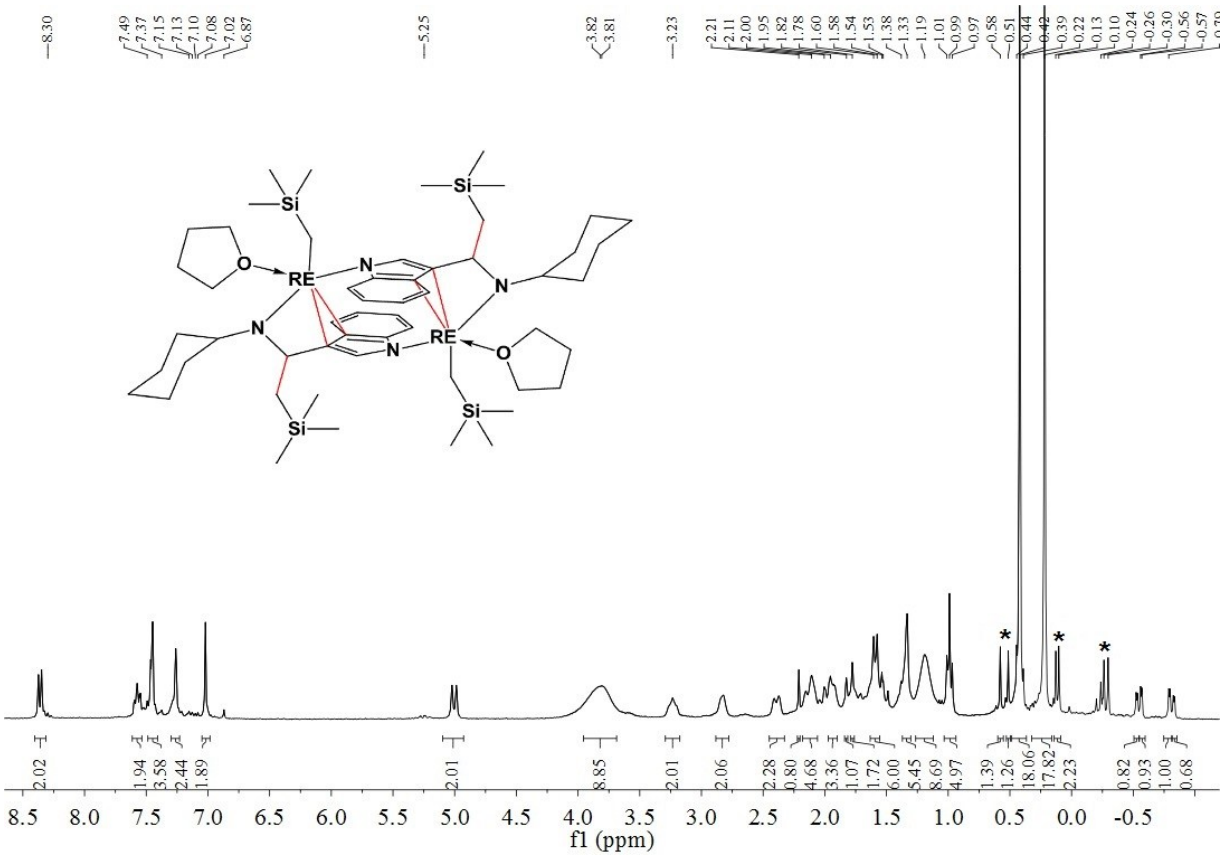

Figure S13. ^{1}H NMR spectrum of complex **3** (300 MHz, C_6D_6, 25 °C, * indicates impurities)

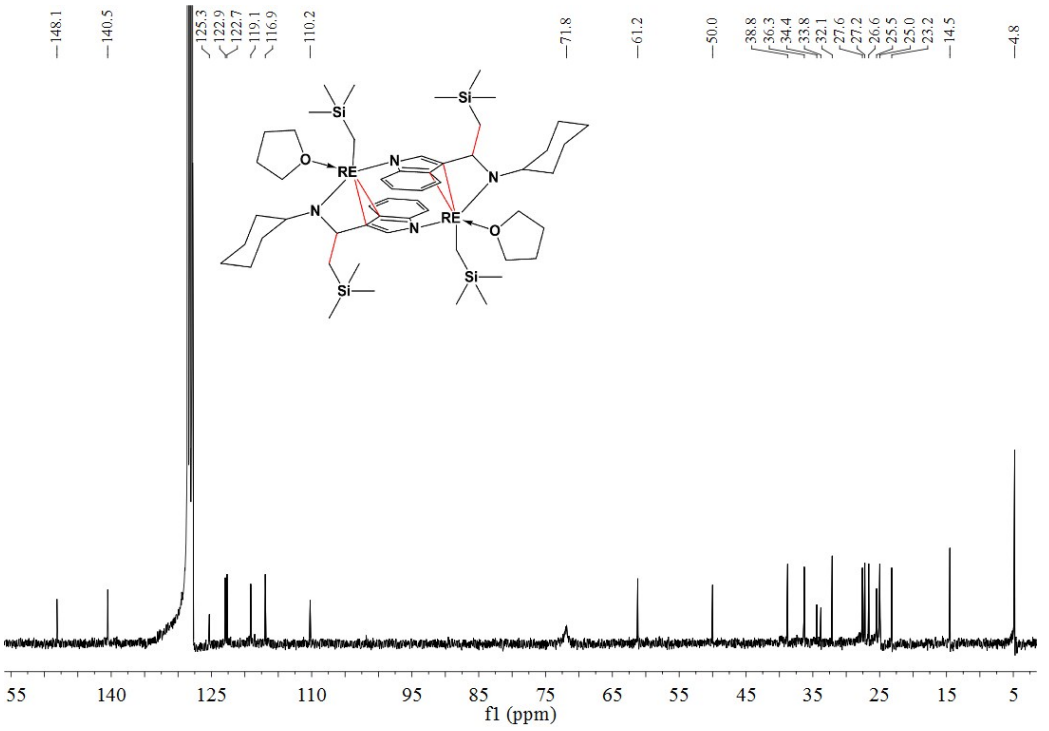

Figure S14. ^{13}C NMR spectrum of complex **3** (75 MHz, C_6D_6, 25 °C)

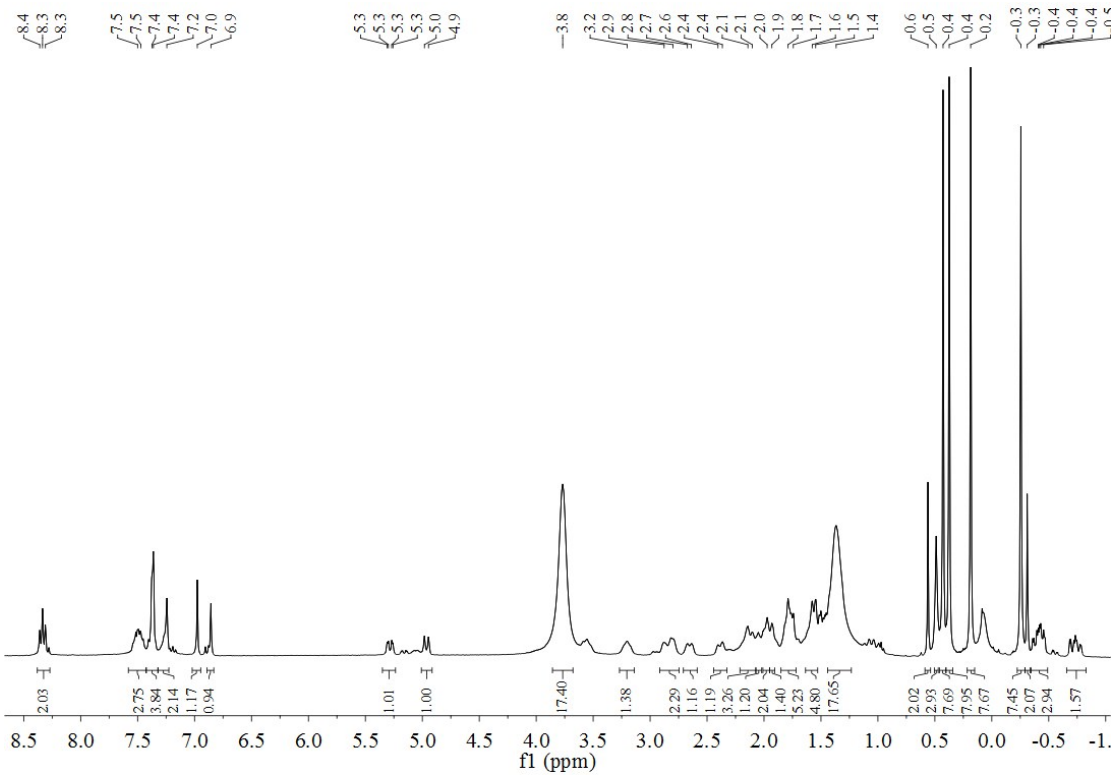

Figure S15. ^{1}H NMR spectrum of complex **6** (300 MHz, C_6D_6, 25 °C)

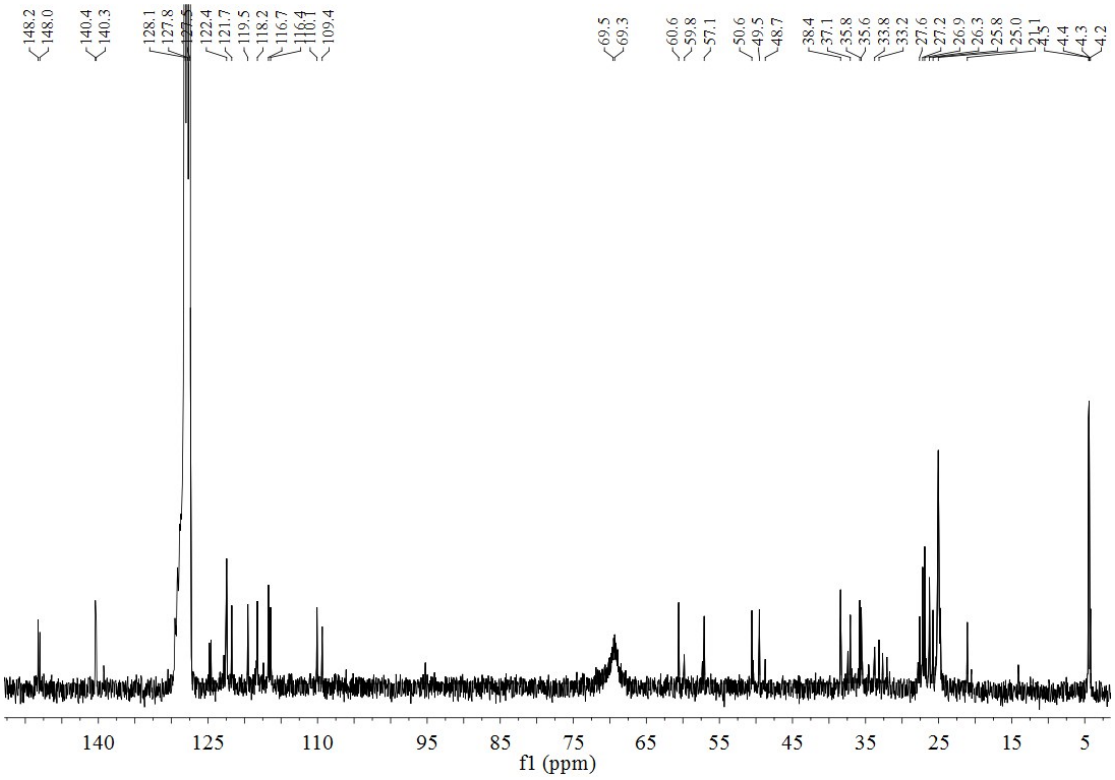

Figure S16. ^{13}C NMR spectrum of complex **6** (75 MHz, C_6D_6, 25 °C)

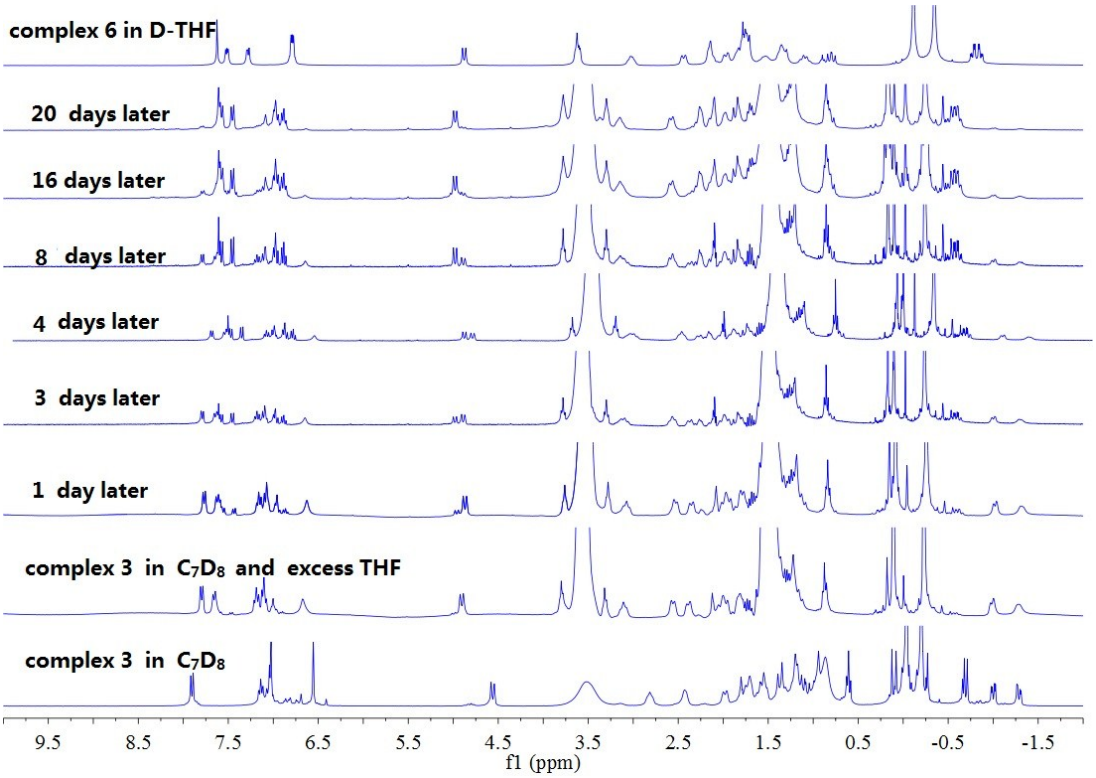

Figure S17. The reaction of complex **3** with THF at the NMR scale (300 MHz, 25 °C)

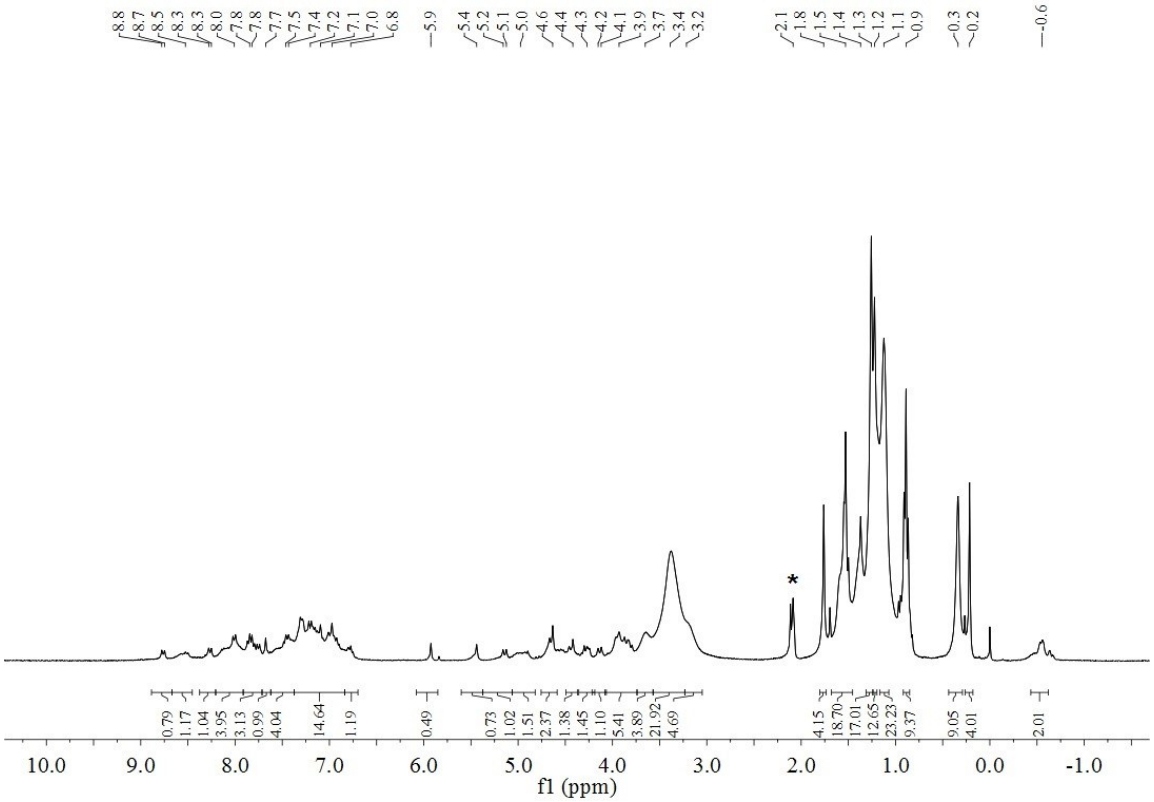

Figure S18. ^{1}H NMR spectrum of complex **9** (300 MHz, C_7D_8, TMS, 25 °C, * indicates solvent residual peak)

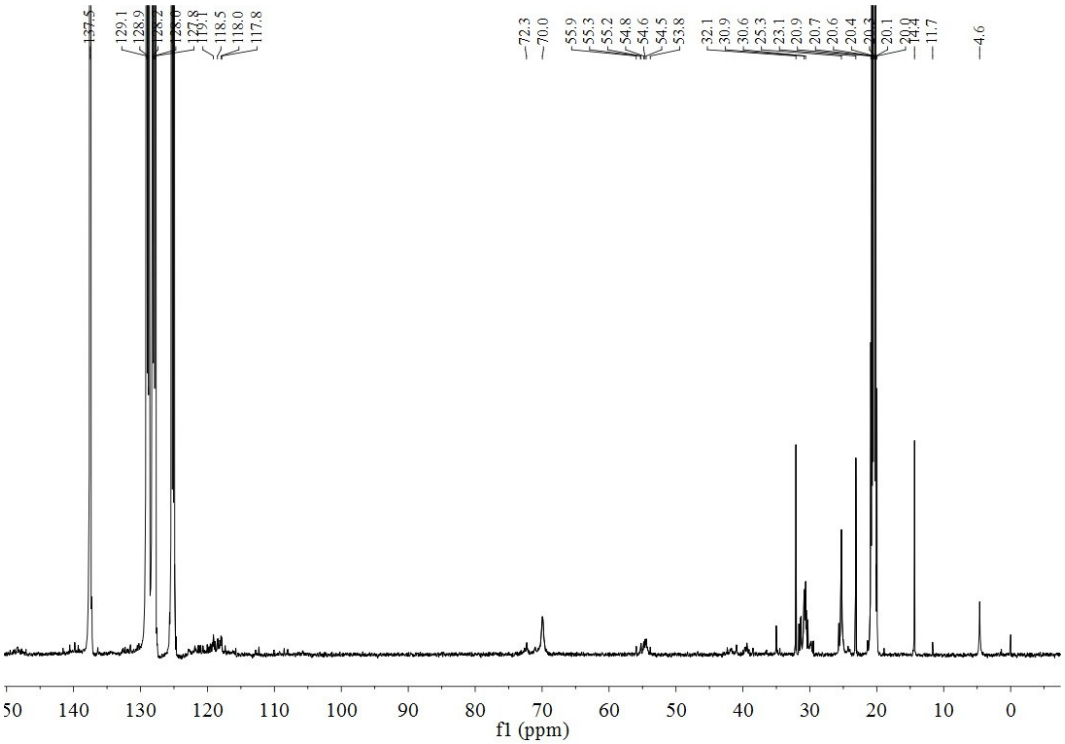

Figure S19. ^{13}C NMR spectrum of complex **9** (75 MHz, C_7D_8, TMS, 25 °C)

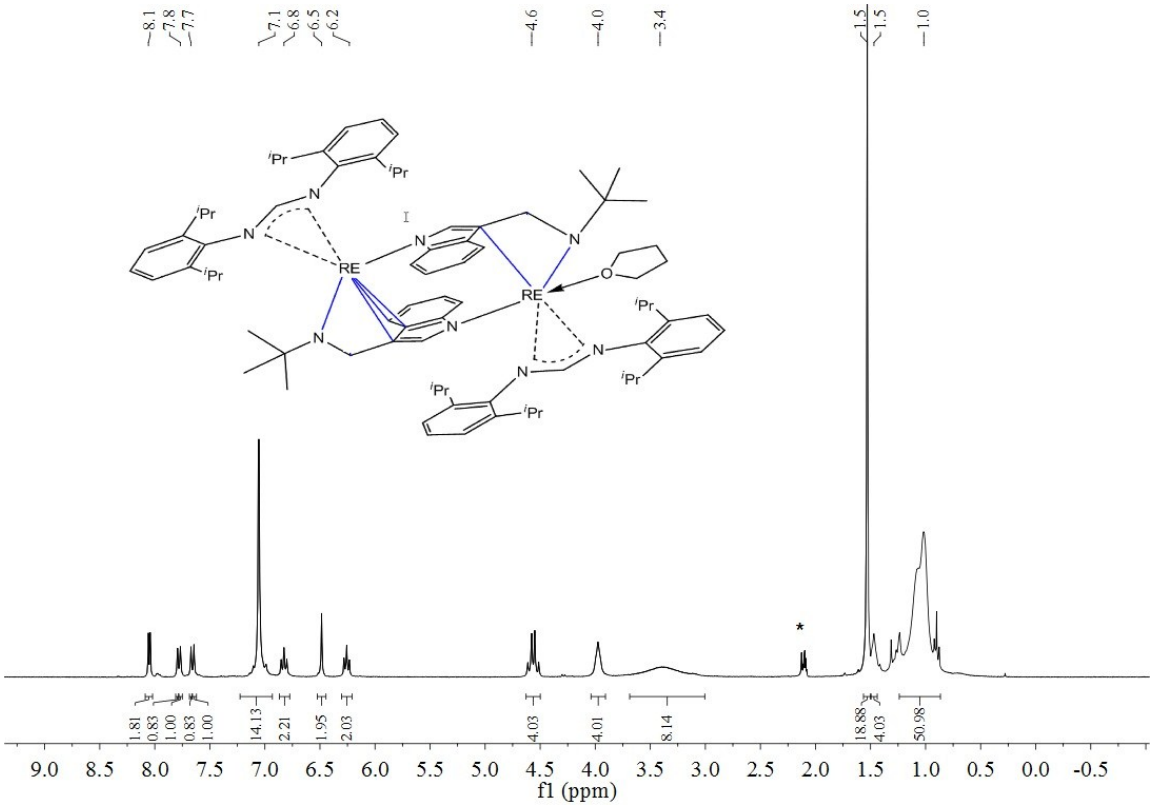

Figure S20. ^{1}H NMR spectrum of complex **12** (300 MHz, C_7D_8, 25 °C, * indicates solvent residual peak)

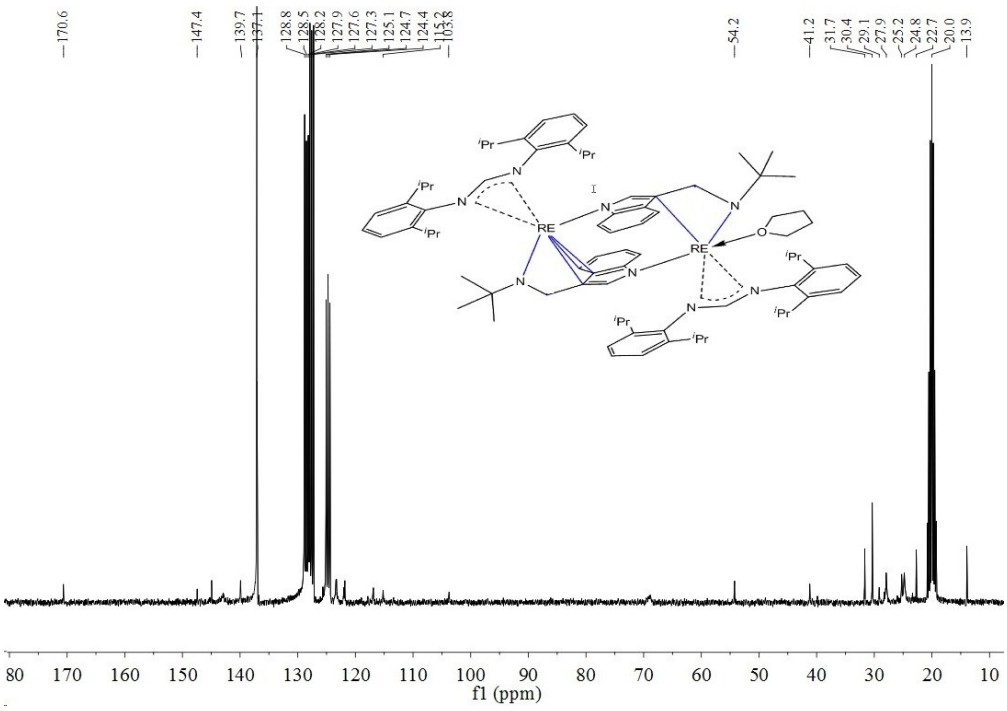

Figure S21. ^{13}C NMR spectrum of complex **12** (75 MHz, C_7D_8, 25 °C)

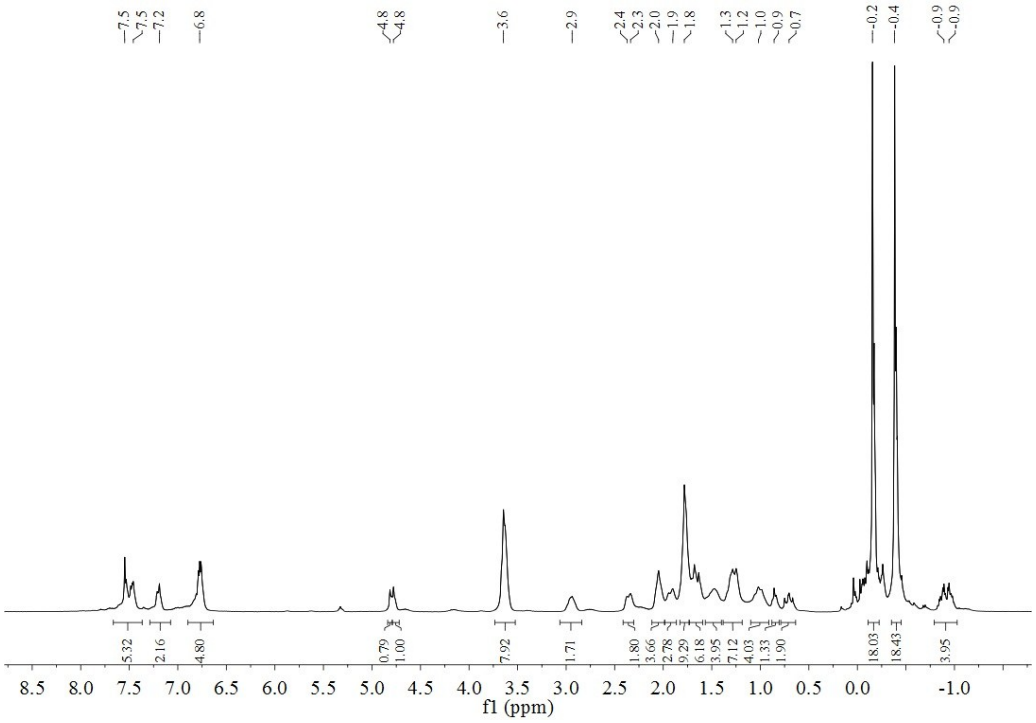

Figure S22. ^{1}H NMR spectrum of complex 6 (300 MHz, CD_2Cl_2, 25 °C)

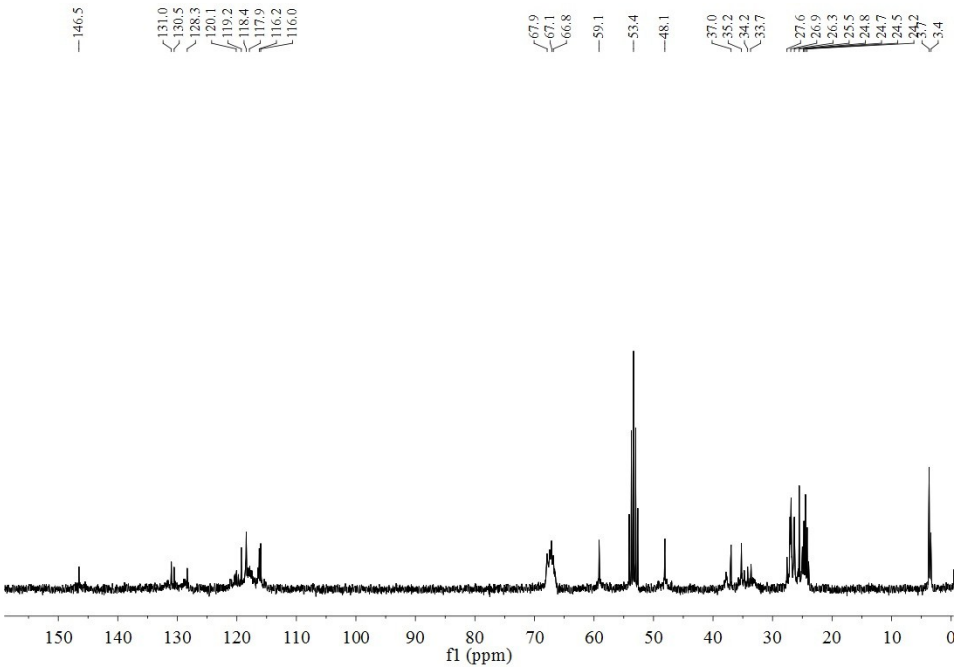

Figure S23. ^{13}C NMR spectrum of complex 6 (75 MHz, CD_2Cl_2, 25 °C)

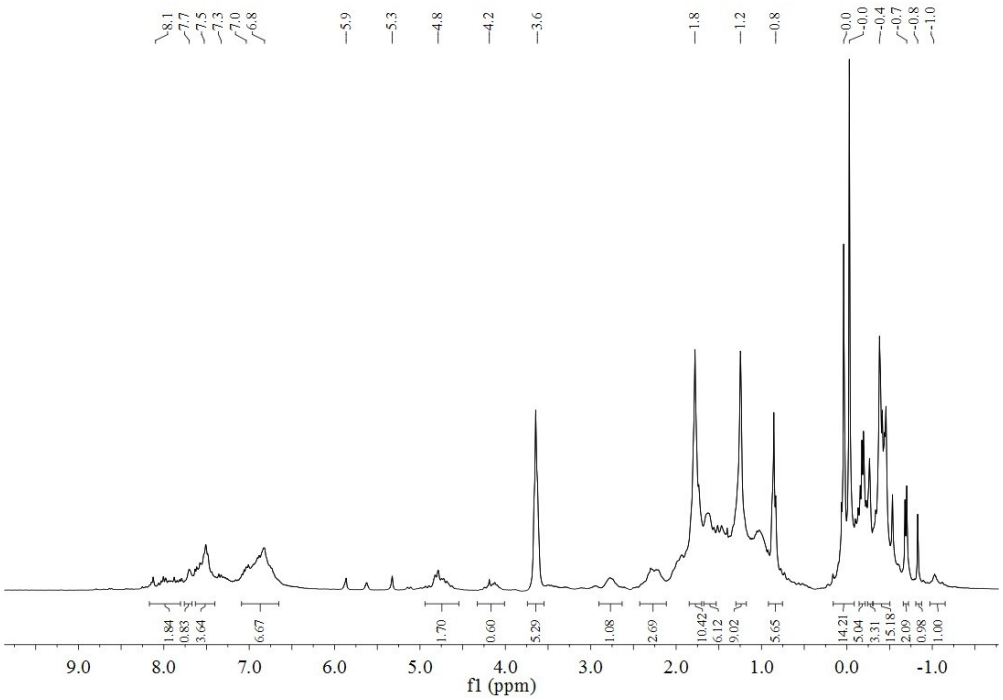

Figure S24. ^{1}H NMR spectrum of complex 3 (300 MHz, CD_2Cl_2, 25 °C)

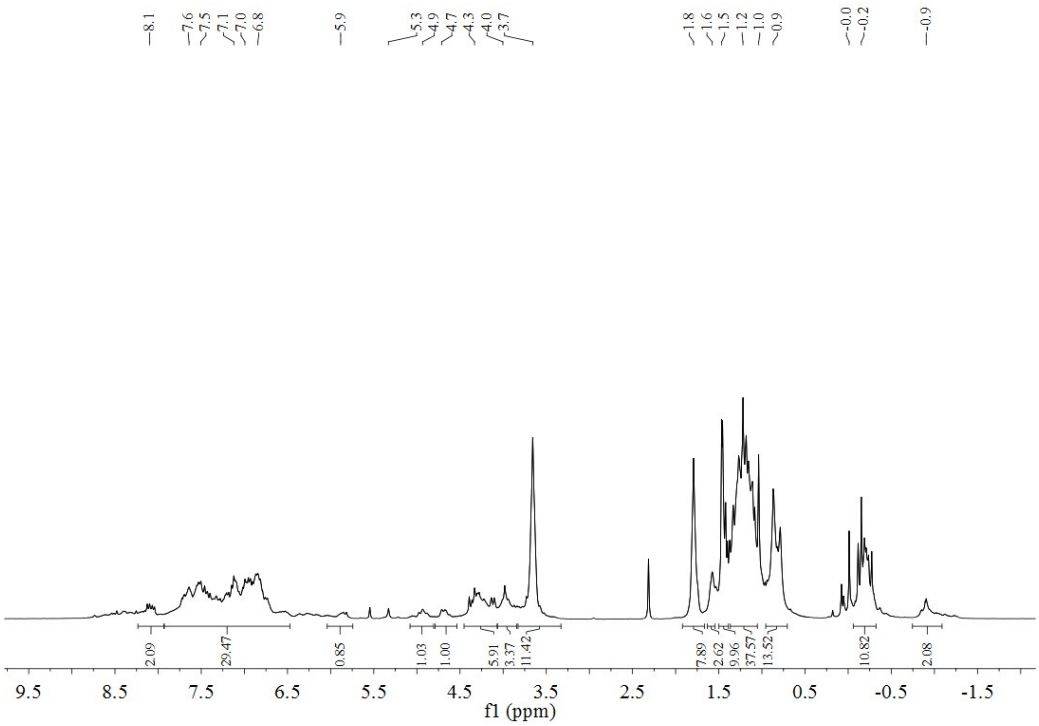

Figure S25. ^{1}H NMR spectrum of complex 9 (300 MHz, CD_2Cl_2, 25 °C)

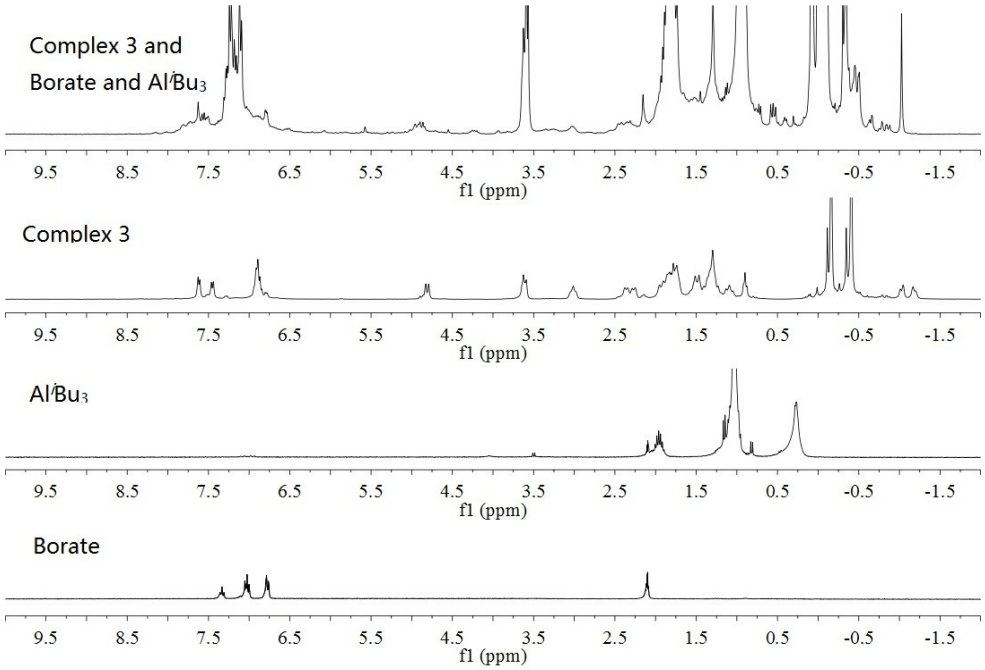

Figure S26. ^{1}H NMR spectra of Borate, Al^{i}Bu$_3$ and (complex **3** after Borate and Al^{i}Bu$_3$ treatment) (300 MHz, d_8-THF, 25 °C)

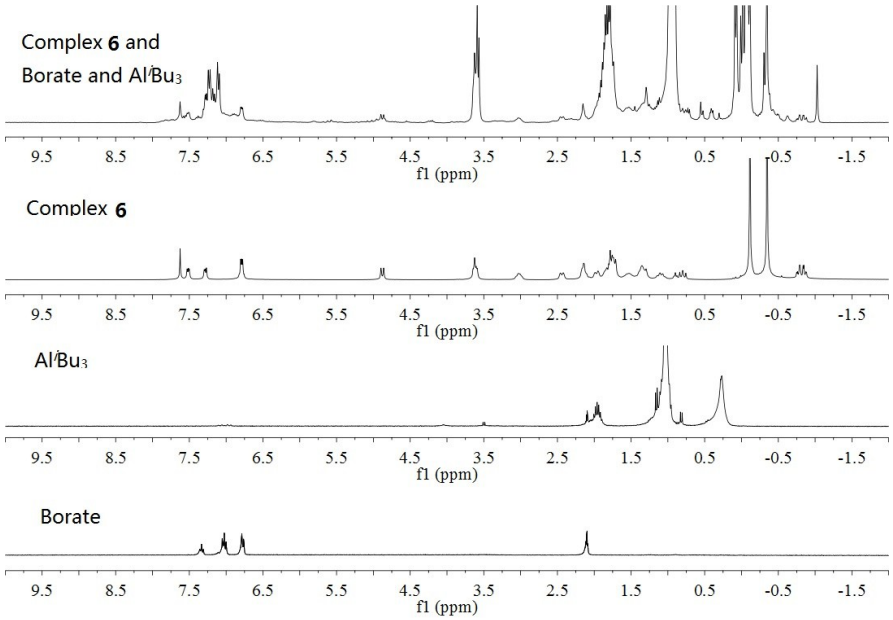

Figure S27. ^{1}H NMR spectra of Borate, Al^{i}Bu$_3$ and (complex **6** after Borate and Al^{i}Bu$_3$ treatment) (300 MHz, d_8-THF, 25 °C)

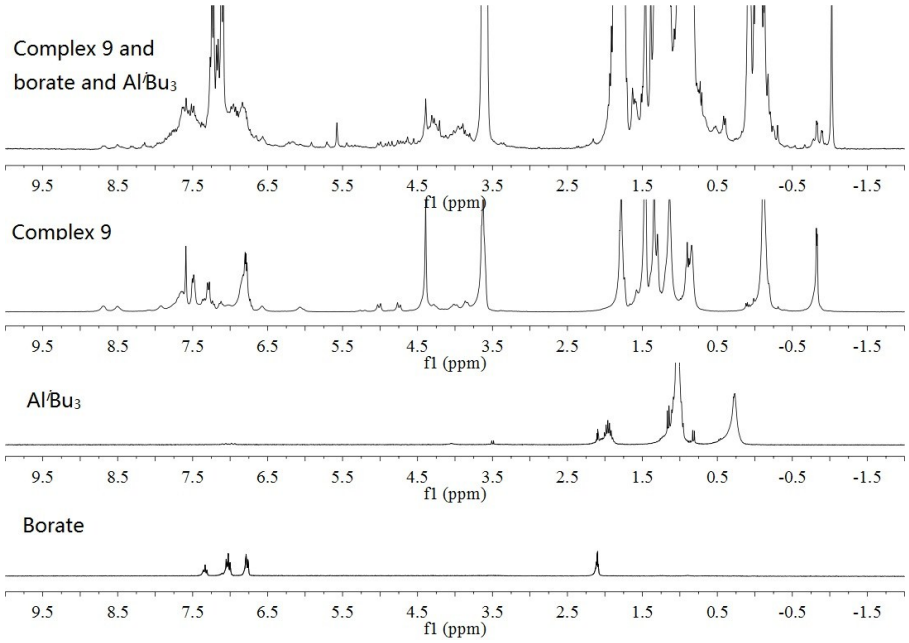

Figure S28. ^{1}H NMR spectra of Borate, Al^{i}Bu$_3$ and (complex **9** after Borate and Al^{i}Bu$_3$ treatment) (300 MHz, d_8-THF, 25 °C)

Polymerization of Isoprene

^{1}H NMR and ^{13}C NMR spectra of PIP

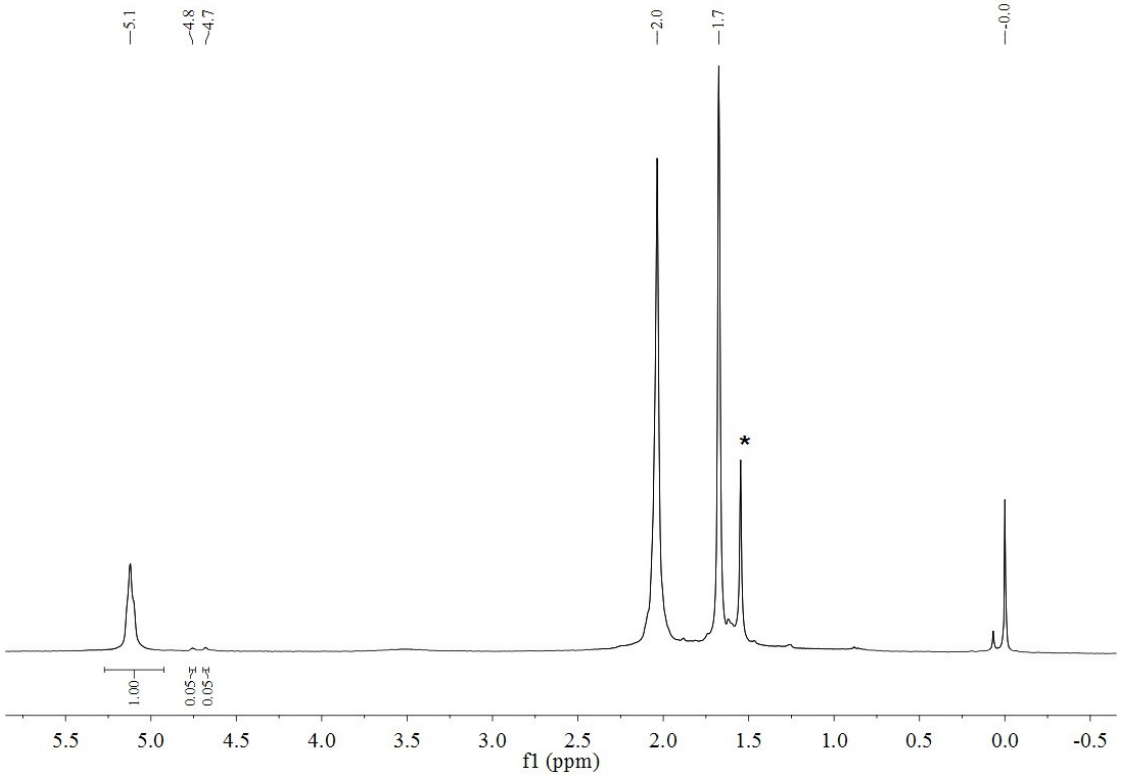

Figure S29. [1]H NMR spectrum of polyisoprene for Entry 3 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, * is water peak)

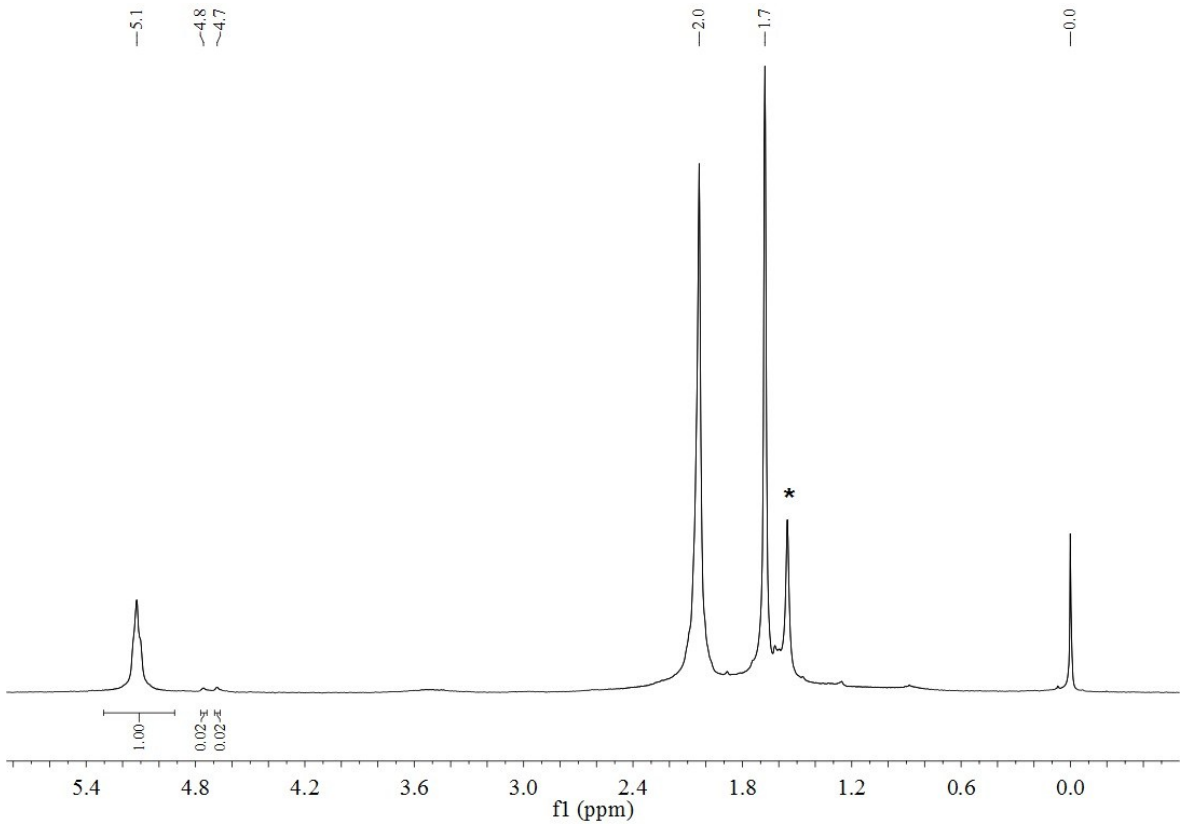

Figure S30. [1]H NMR spectrum of polyisoprene for Entry 4 (Table 3, 300 MHz, $CDCl_3$, TMS,

25 °C, * is water peak)

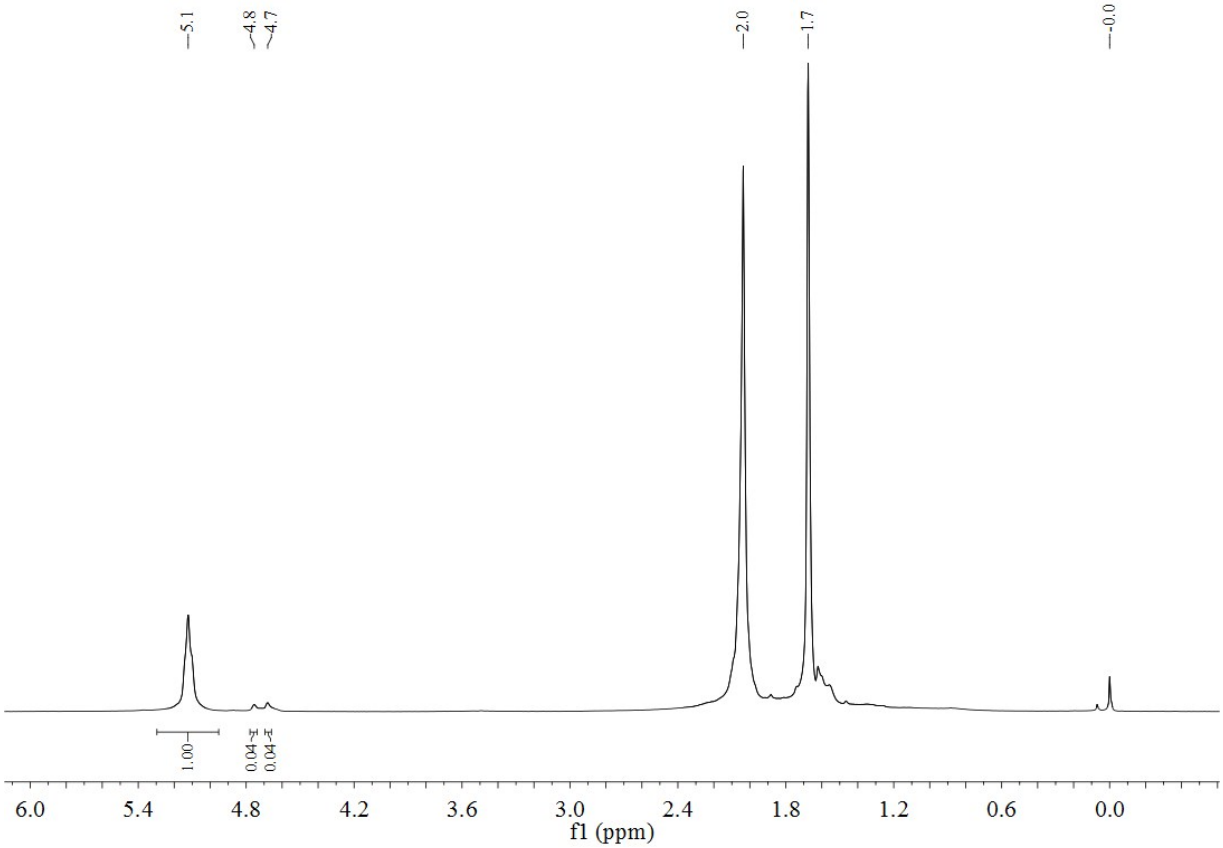

Figure S31. [1]H NMR spectrum of polyisoprene for Entry 5 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C)

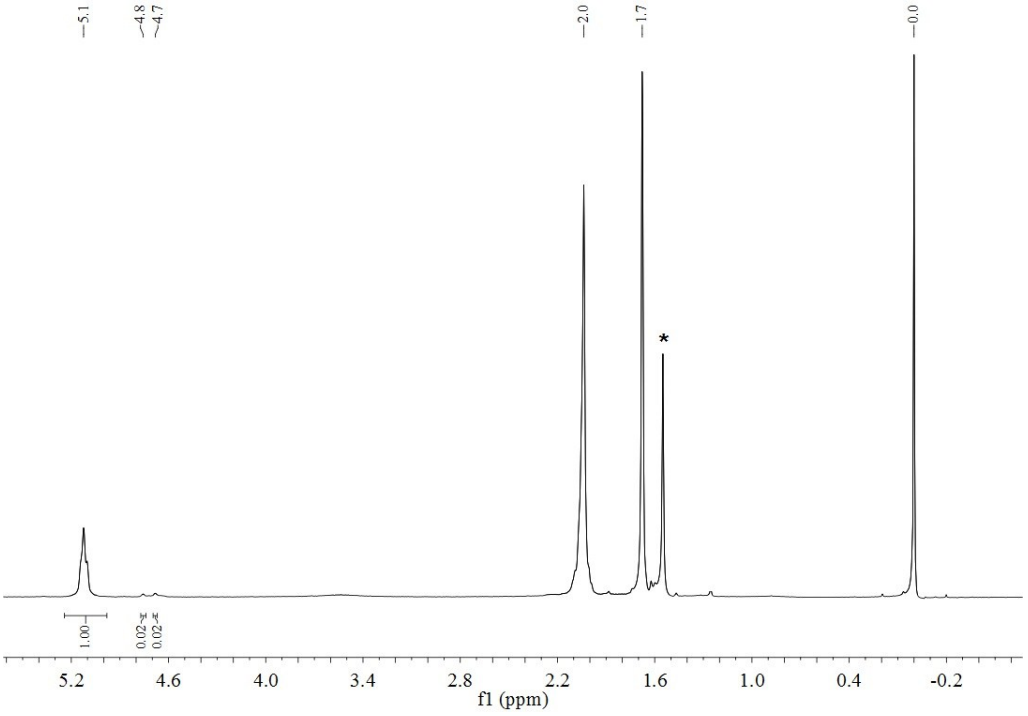

Figure S32. [1]H NMR spectrum of polyisoprene for Entry 8 (Table 3, 300 MHz, $CDCl_3$, TMS,

25 °C, * is water peak)

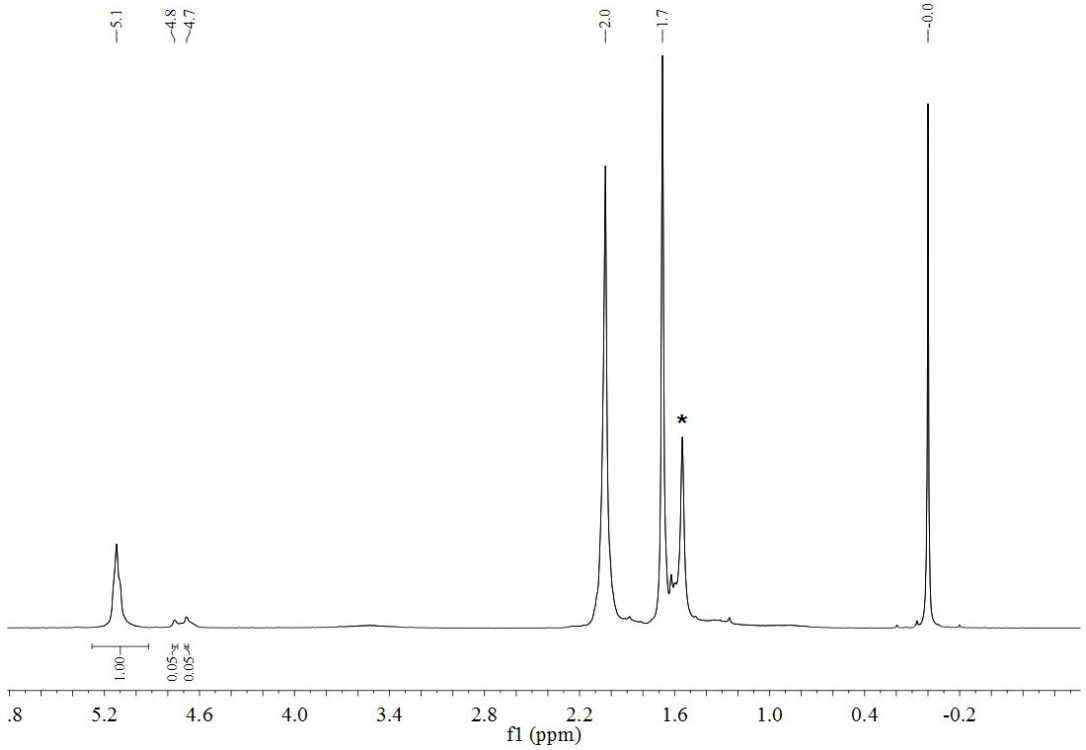

Figure S33. [1]H NMR spectrum of polyisoprene for Entry 9 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, * is water peak)

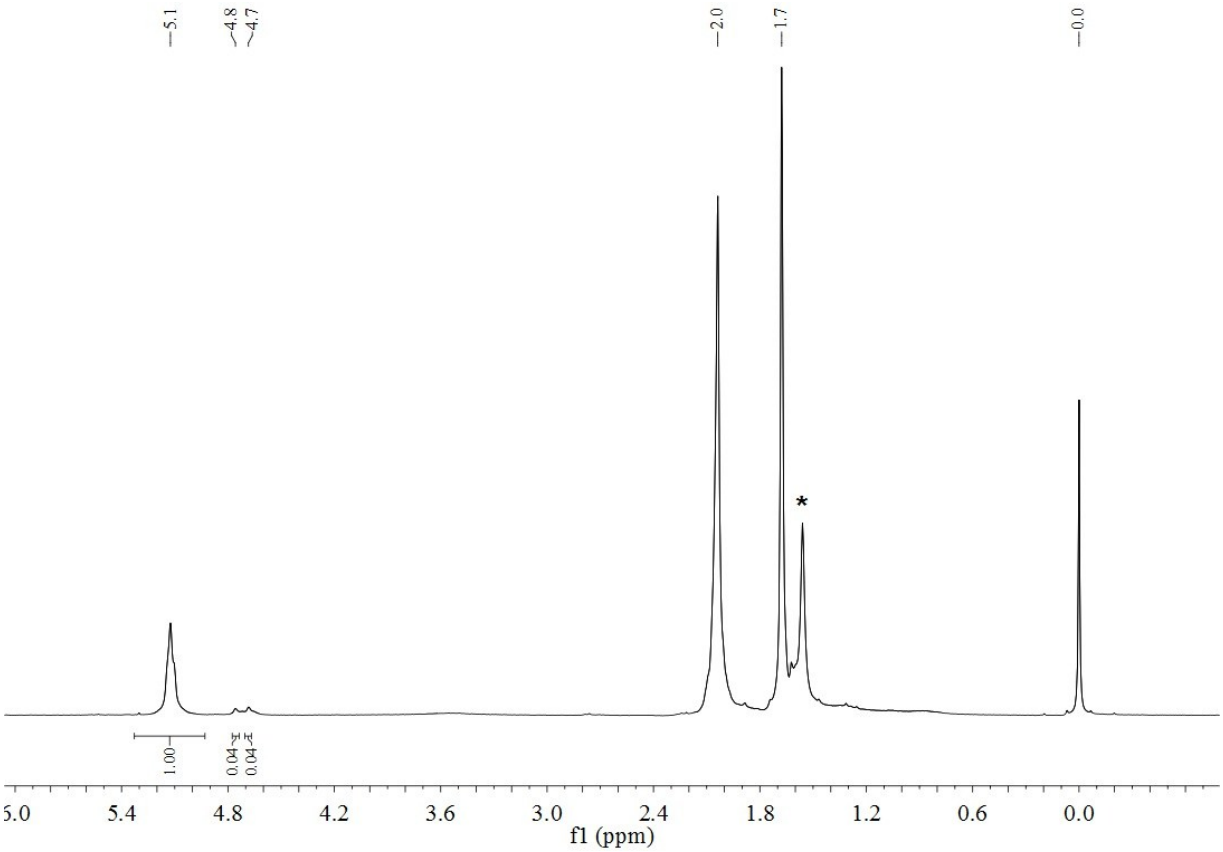

Figure S34. [1]H NMR spectrum of polyisoprene for Entry 12 (Table 3, 300 MHz, $CDCl_3$, TMS,

25 °C, * is water peak)

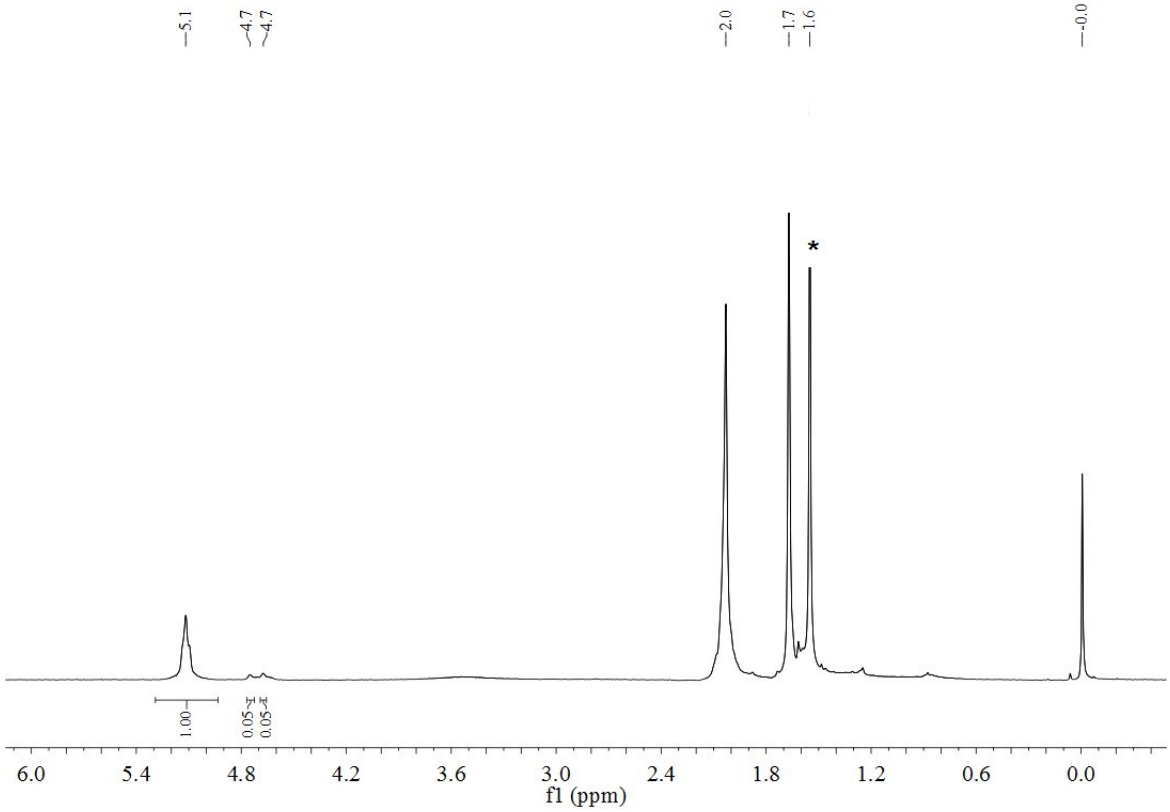

Figure S35. [1]H NMR spectrum of polyisoprene for Entry 13 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, * is water peak)

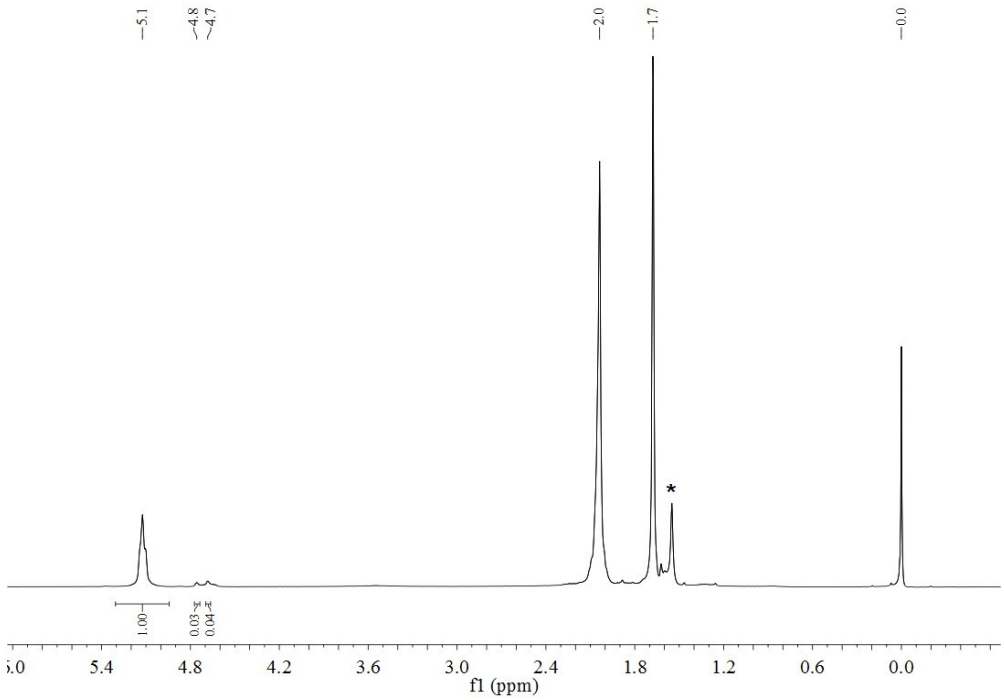

Figure S36. [1]H NMR spectrum of polyisoprene for Entry 14 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, * is water peak)

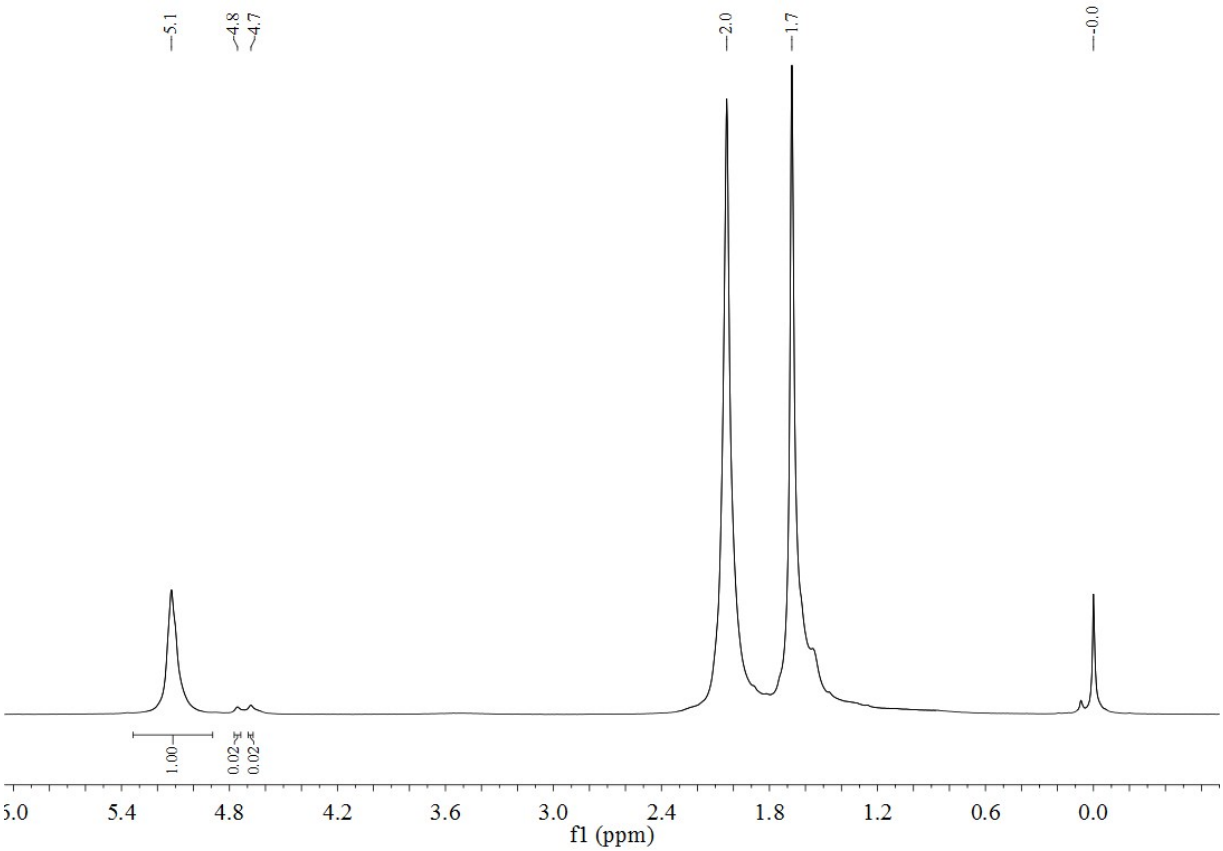

Figure S37. ^{1}H NMR spectrum of polyisoprene for Entry 15 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C)

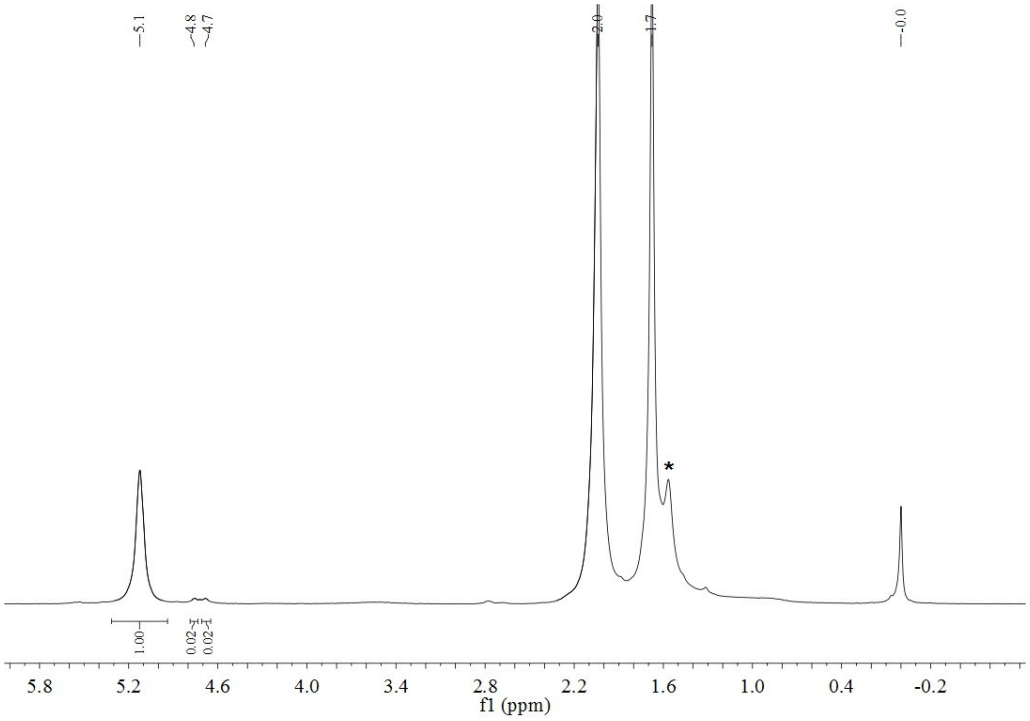

Figure S38. ^{1}H NMR spectrum of polyisoprene for Entry 16 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, * is water peak)

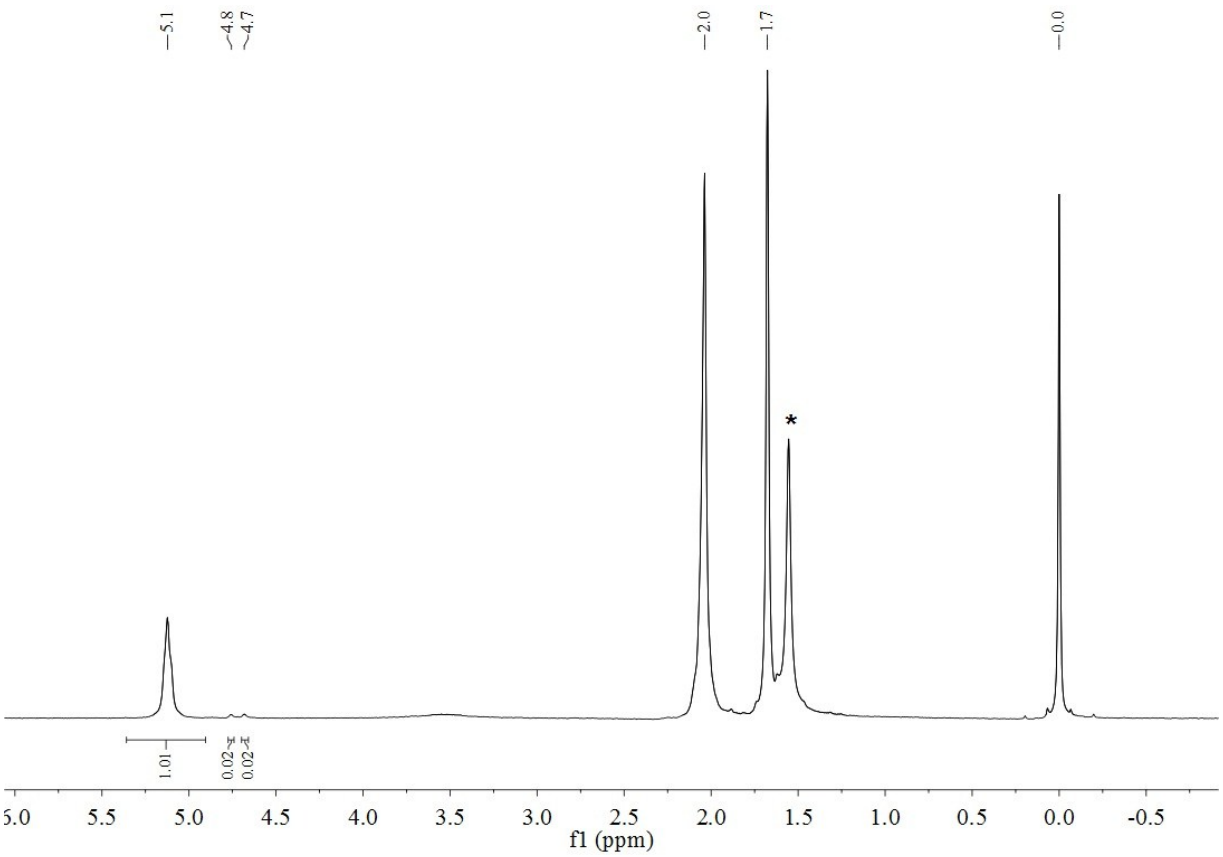

Figure S39. ^{1}H NMR spectrum of polyisoprene for Entry 17 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, * is water peak)

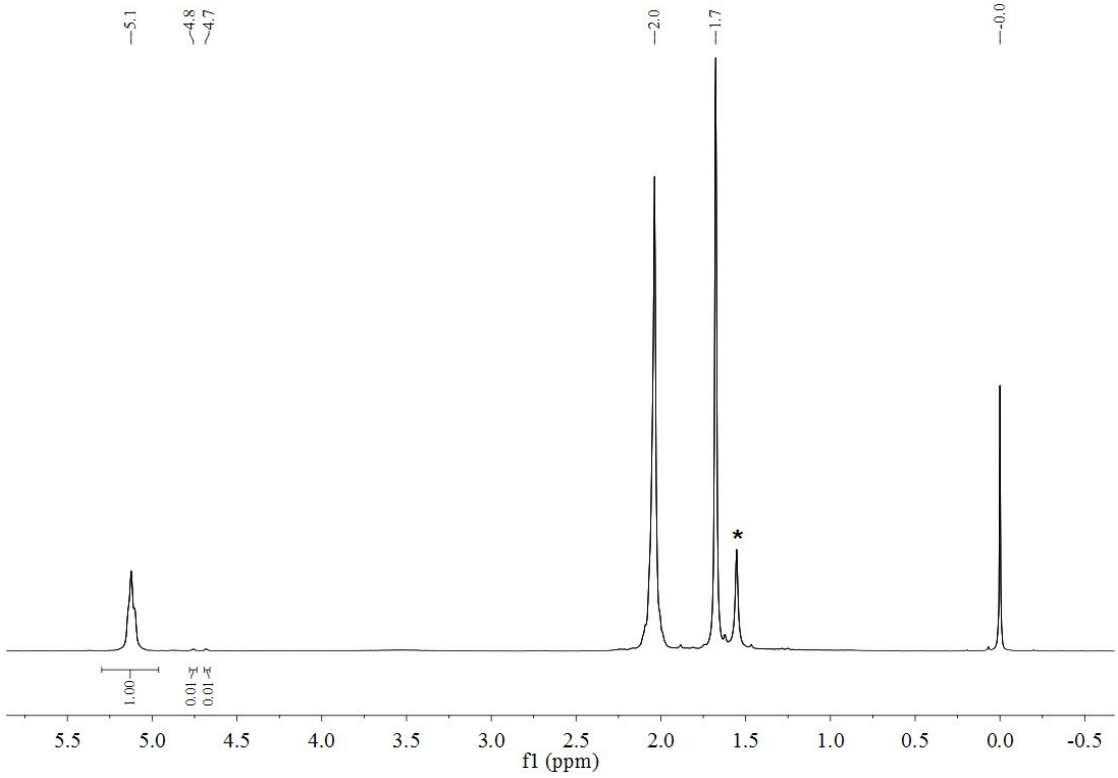

Figure S40. ^{1}H NMR spectrum of polyisoprene for Entry 18 (Table 3, 300 MHz, $CDCl_3$, TMS, TMS, 25 °C, * is water peak)

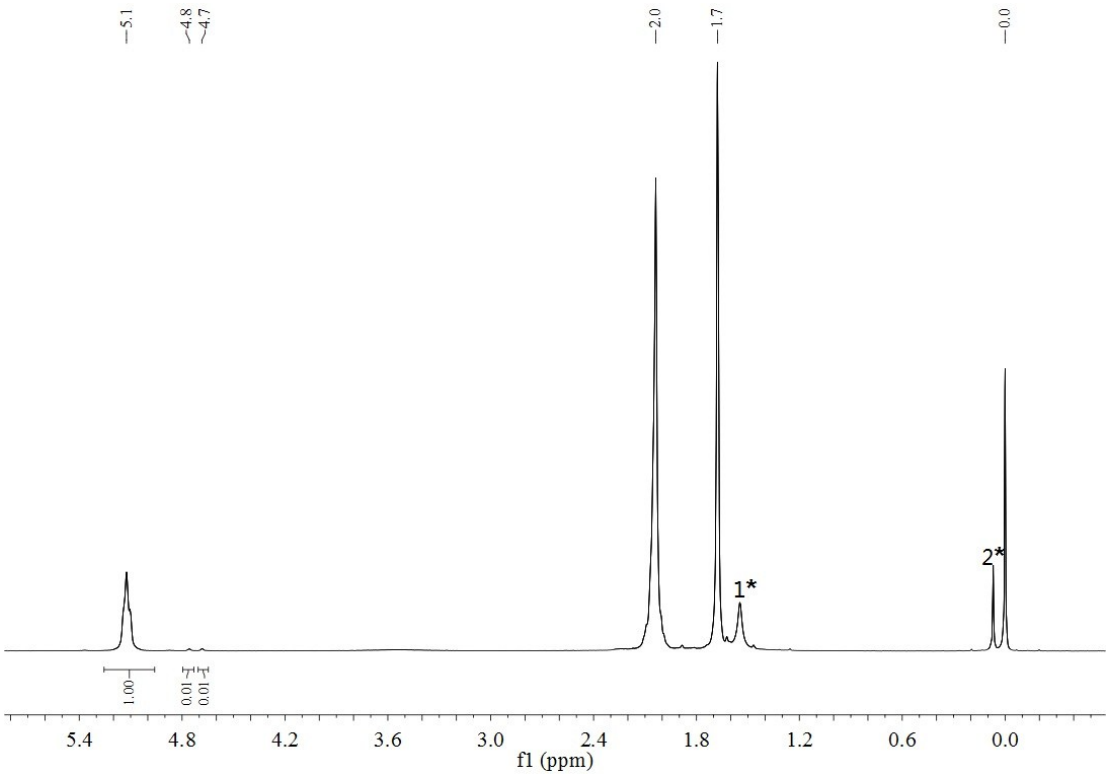

Figure S41. [1]H NMR spectrum of polyisoprene for Entry 19 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, 1* is water peak, 2* is impurity of silicone grease)

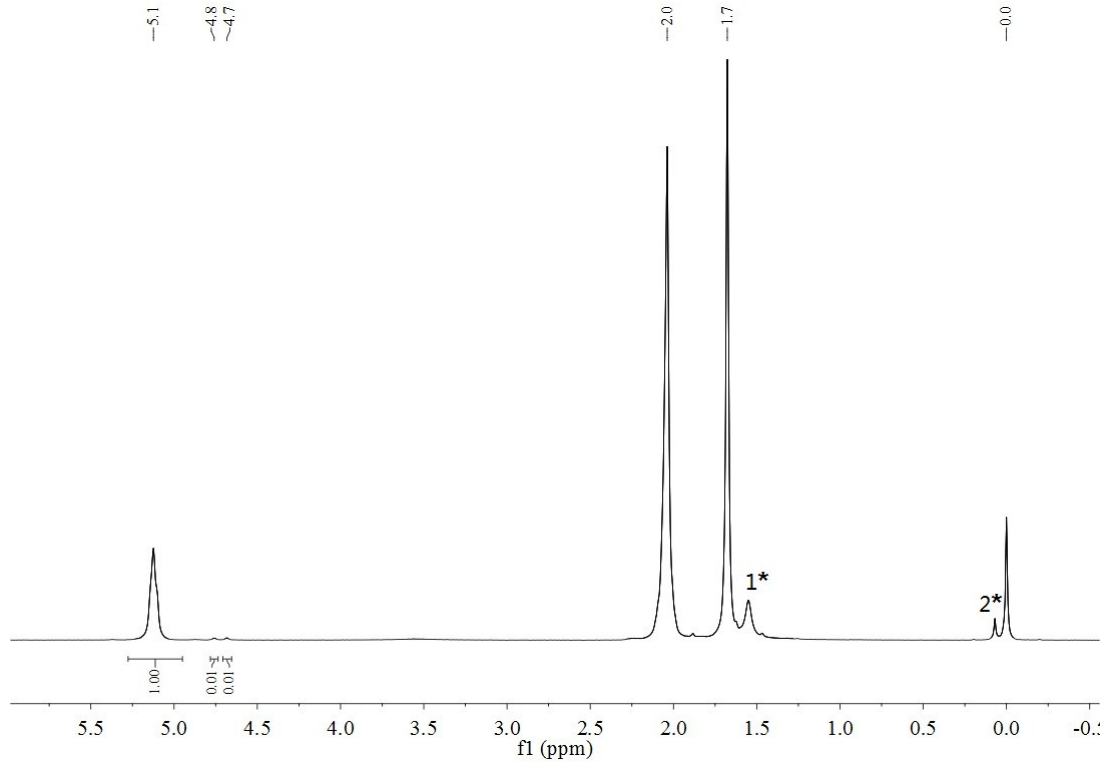

Figure S42. [1]H NMR spectrum of polyisoprene for Entry 20 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, 1* is water peak, 2* is impurity(silicone grease)

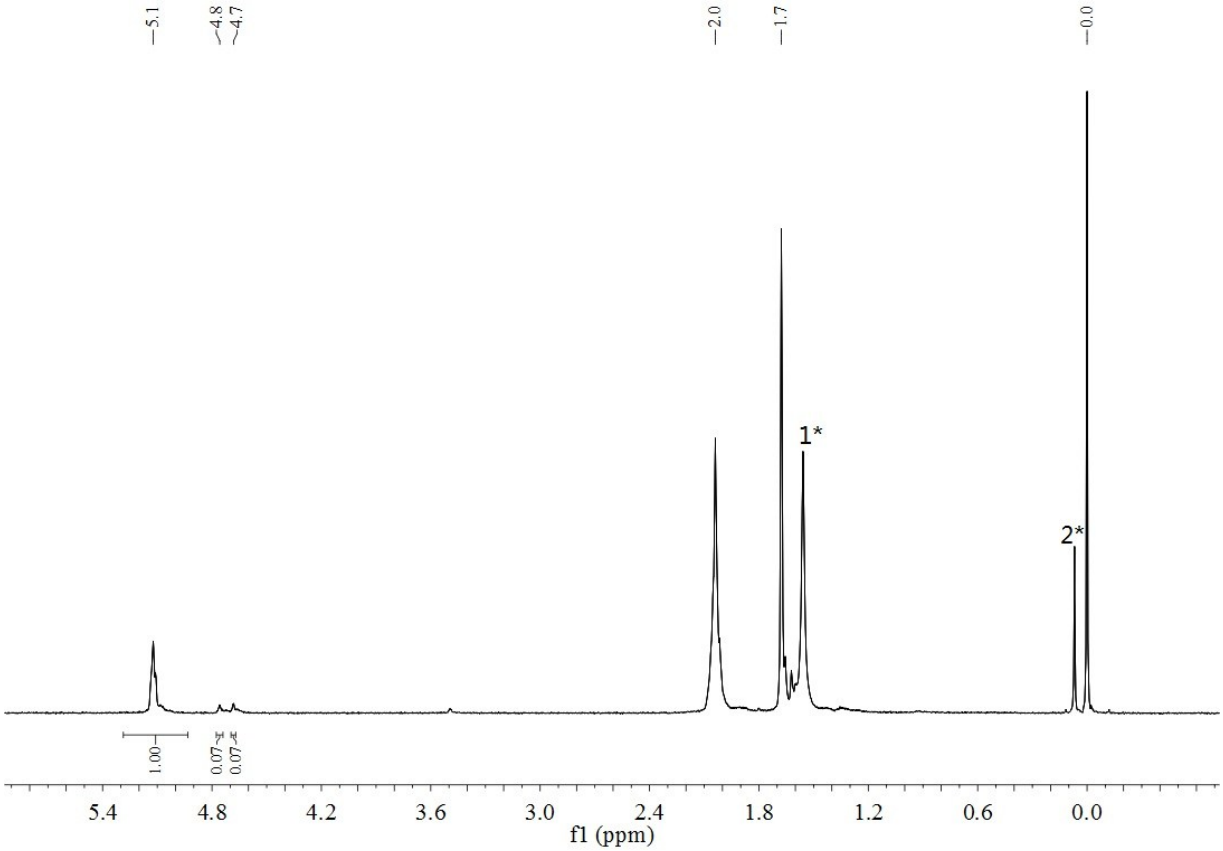

Figure S43. [1]H NMR spectrum of polyisoprene for Entry 21 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, 1* is water peak, 2* is impurity(silicone grease)

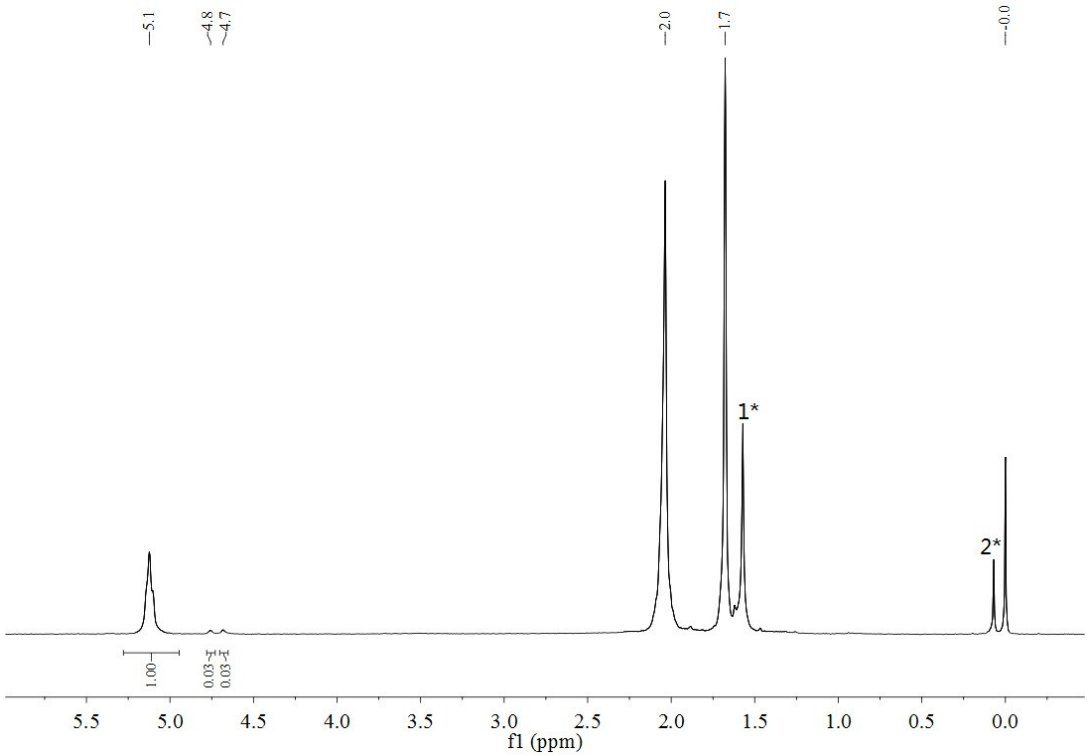

Figure S44. [1]H NMR spectrum of polyisoprene for Entry 22 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, 1* is water peak, 2* is impurity of silicone grease)

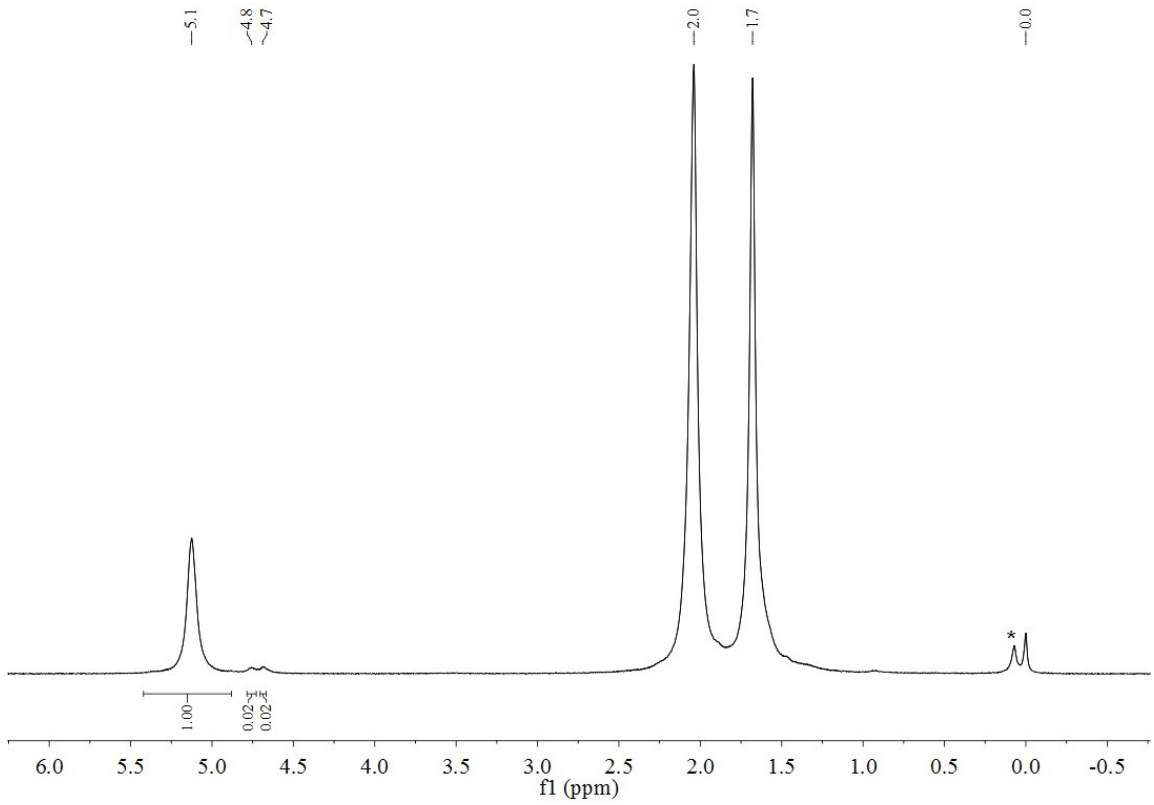

Figure S45. ^{1}H NMR spectrum of polyisoprene for Entry 23 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, * is impurity of silicone grease)

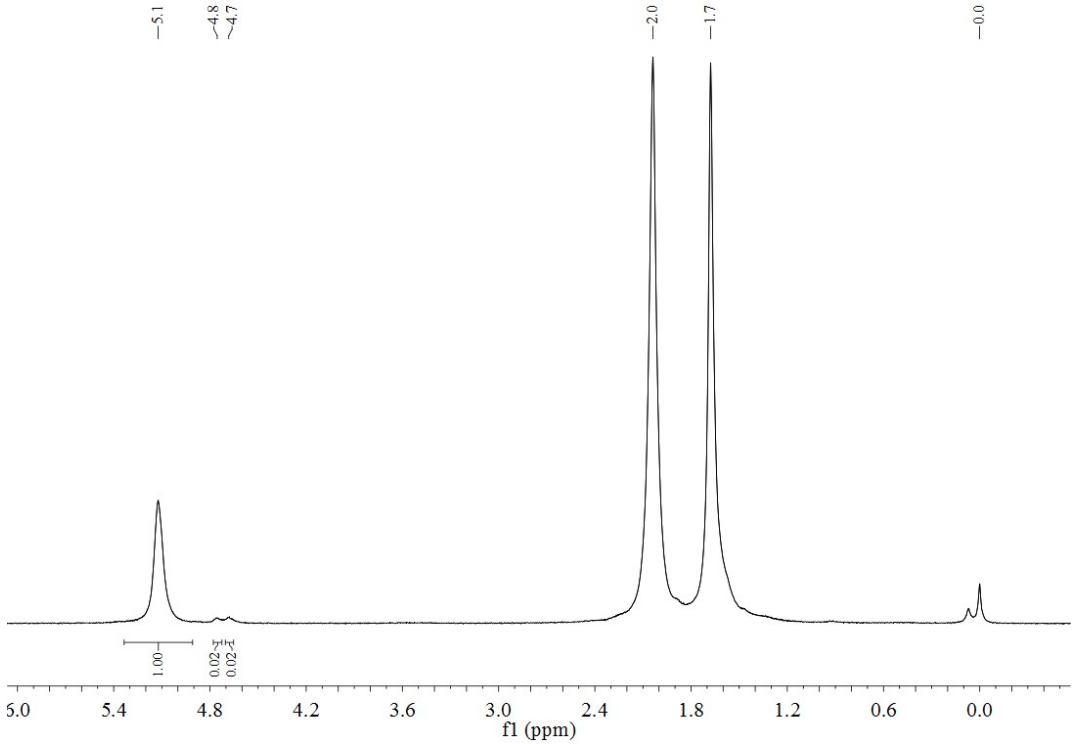

Figure S46. ^{1}H NMR spectrum of polyisoprene for Entry 24 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C)

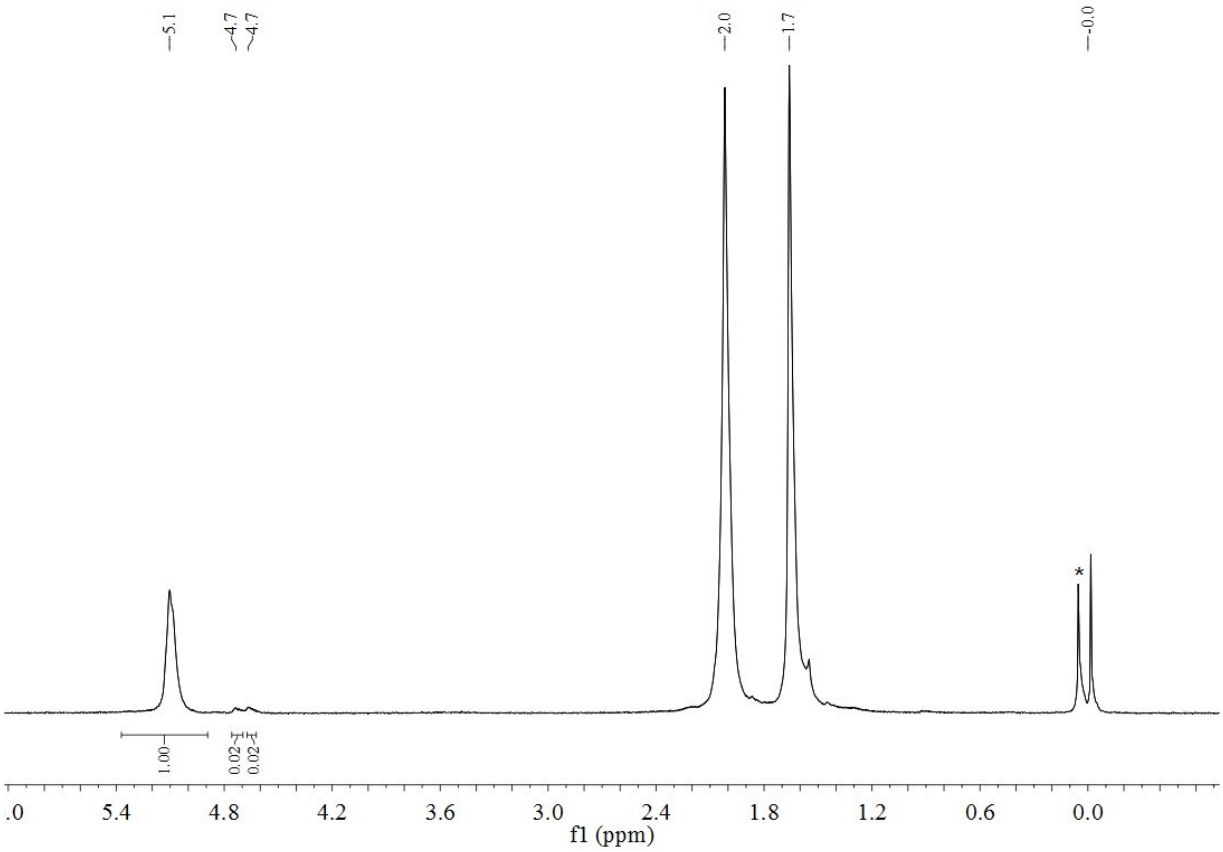

Figure S47. ^{1}H NMR spectrum of polyisoprene for Entry 25 (Table 3, 300 MHz, $CDCl_3$, TMS, 25 °C, * is impurity(silicone grease)

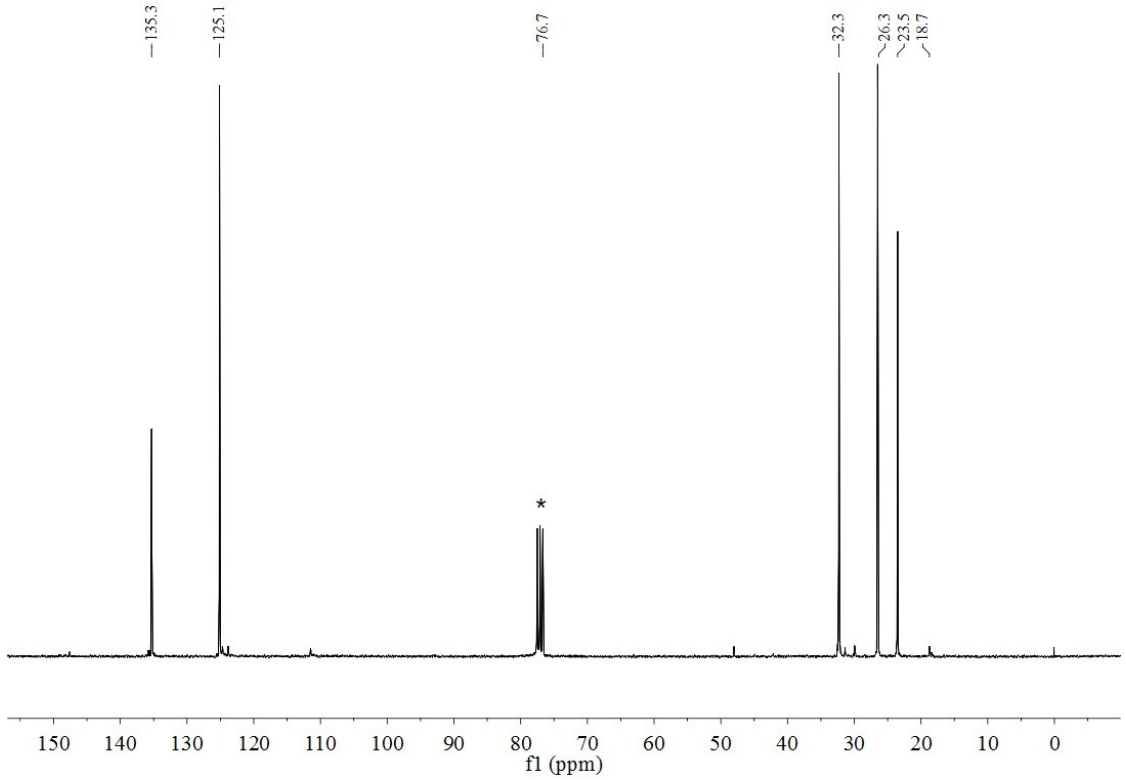

Figure S48. ^{13}C NMR spectrum of polyisoprene for Entry 8 (Table 3) scan 8000 times (500 MHz, $CDCl_3$, TMS, 25 °C, * indicates solvent peak). No 1,4-trans-polymer

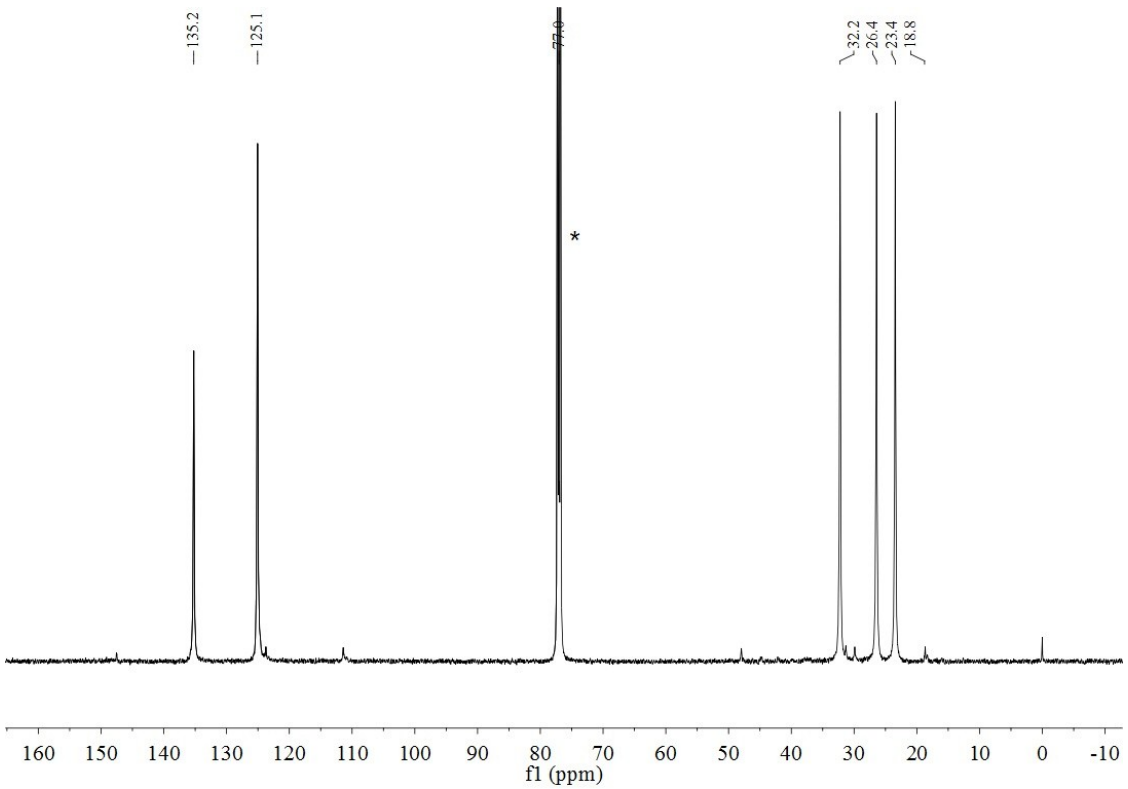

Figure S49. ^{13}C NMR spectrum of polyisoprene for Entry 9 (Table 3) scan 10240 times (500 MHz, $CDCl_3$, TMS, 25 °C, * indicates solvent peak). No 1,4-trans-polymer

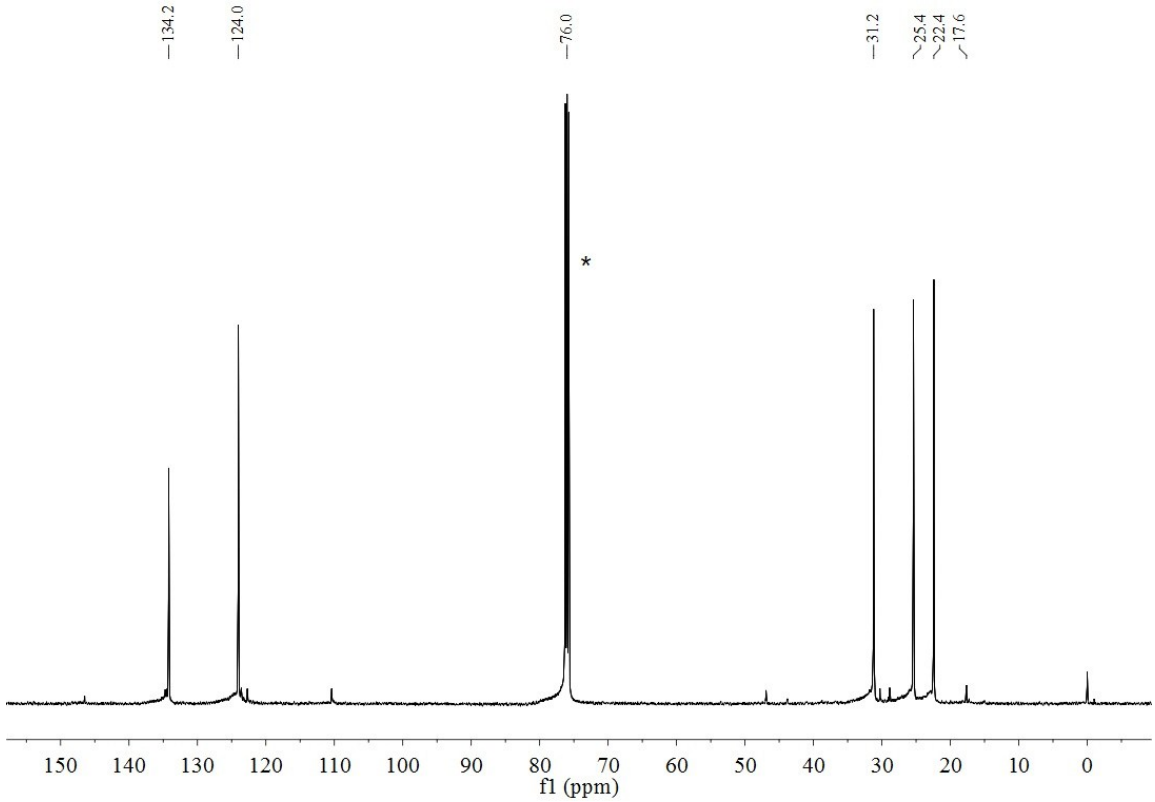

Figure S50. ^{13}C NMR spectrum of polyisoprene for Entry 14 (Table 3) scan 10000 times (500 MHz, $CDCl_3$, TMS, 25 °C, * indicates solvent peak). No 1,4-trans-polymer

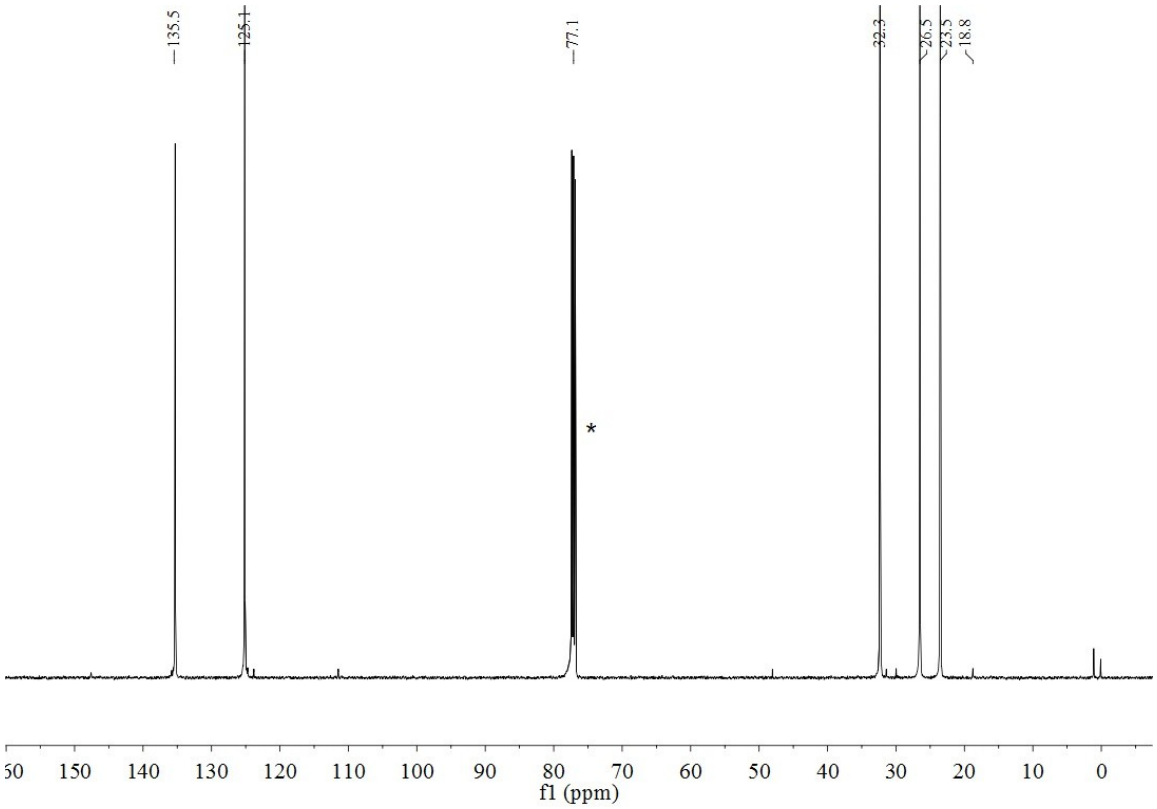

Figure S51. ^{13}C NMR spectrum of polyisoprene for Entry 17 (Table 3) scan 10240 times (500 MHz, $CDCl_3$, TMS, 25 °C, * indicates solvent peak). No 1,4-trans-polymer

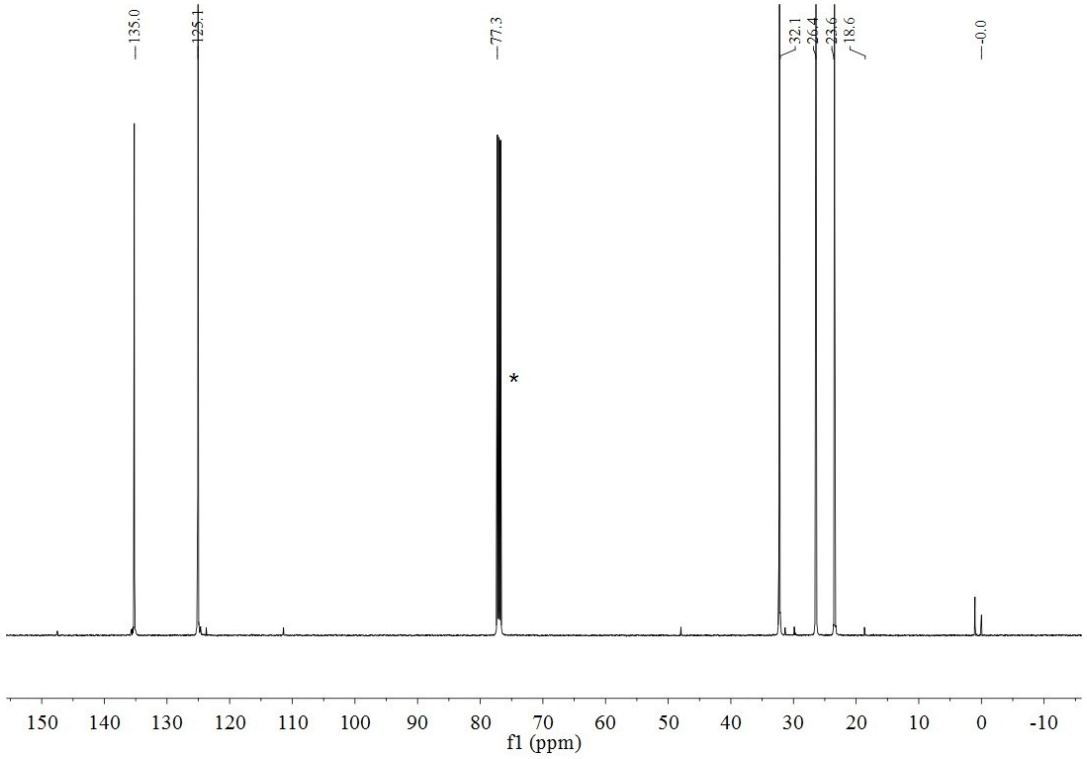

Figure S52. ^{13}C NMR spectrum of polyisoprene for Entry 20 (Table 3) scan 10240 times (500 MHz, $CDCl_3$, TMS, 25 °C, * indicates solvent peak). No 1,4-trans-polymer

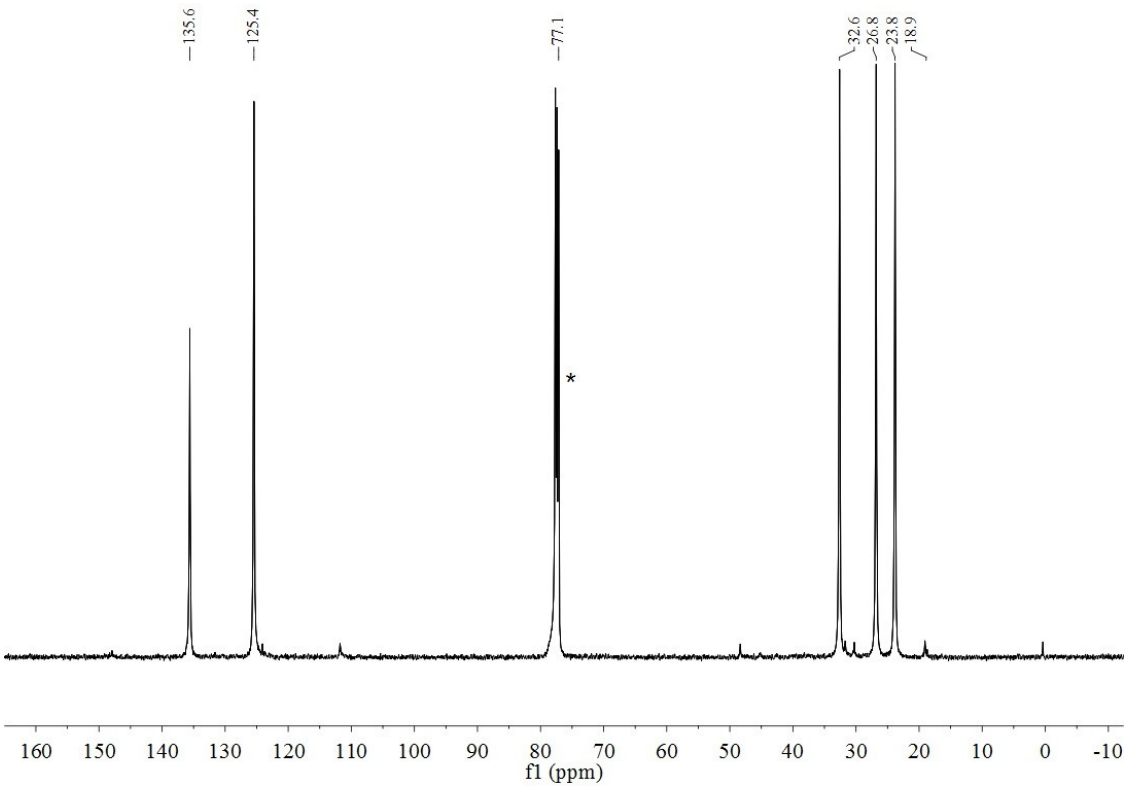

Figure S53. ^{13}C NMR spectrum of polyisoprene for Entry 25 (Table 3) scan 10240 times (500 MHz, $CDCl_3$, TMS, 25 °C, * indicates solvent peak). No 1,4-trans-polymer