Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Displacement Type Fluorescent Probe Reveals Active Species in Coordinative Polymerization of Olefin

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Experimental Section

Materials

All catalysts and the polymerization process were carried out in a nitrogen-filled MBraun glovebox. $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were purchased from Tosoh Finechem Corporation and used as received. $LiCH_2SiMe_3$ (1.0 M solution in pentane), Al^iBu_3 (1.1 M solution in hexane), $AlMe_3$ (1.0 M solution in Toluene) $AlEt_3$ (0.6 M solution in heptane) and $LnCl_3$ were purchased from Aldrich and Stream. 2,4,6-trimethybenzaldehyde, 2,4-dimethylpyrrole, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), trifuoroacetic acid (TFA), CaH_2, dichloromethane, petroleum ether and methanol were purchased from Energy Chemistry and used as received. The Dipyrromethene (DPM)[1] and $Ln(CH_2SiMe_3)_3(THF)_2$[2] were synthesized according to the literature. Isoprene were purchased form Aldrich and TCI, and dried through CaH_2. Toluene,

[1] Fu, L.; Jiang, F.; Fortin, D.; Harvey, P. D.; Liu, Y. *Chem. Commun.,* **2011**, 47, 5503–5505.

[2] Li, X.; Nishiura, M.; Hu, L.; Mori, K.; Hou, Z. *J. Am. Chem. Soc.* **2009***, 131*, 13870–13882.

hexane and THF were purified by a solvent purification system (SPS-800, Mbraun), and dried through Na in the glovebox. The deuterated solvents C_6D_6 (99.6 atom% D) and $CDCl_3$-d (99.8 atom% D) were obtained from Cambridge Isotope.

General Methods

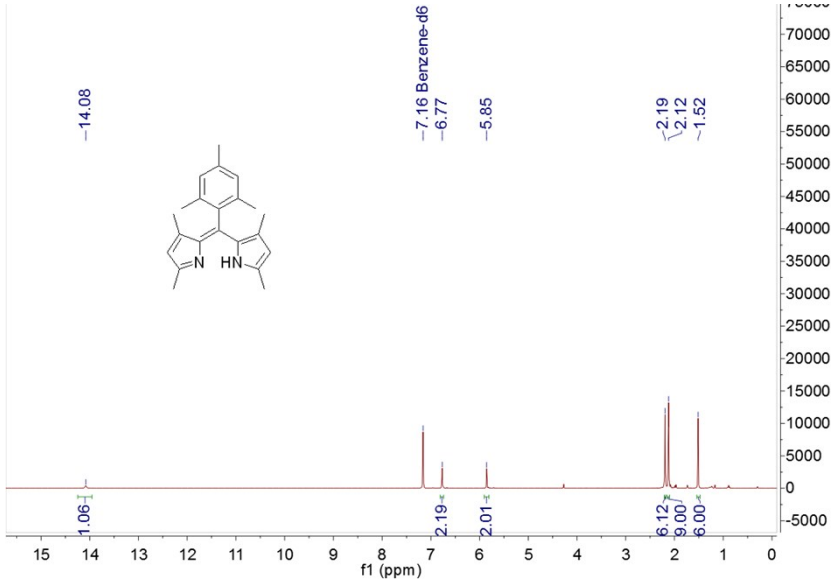
Samples of rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. The NMR (^1H, ^{13}C) spectra of catalyst precursors were recorded on an AVANCE 400 spectrometer at room temperature with C_6D_6 as a solvent. ^1H, ^{13}C NMR spectra of polyisoprene samples obtained in this paper were recorded on an AVANCE 400 spectrometer in $CDCl_3$ at room temperature. Elemental analyses were performed on an Elementary Vario MICRO CUBE (Germany). The molecular weights and the molecular weight distributions of the polyisoprene samples were determined at 40 °C by gel permeation chromatography (GPC) on a WATERS 1515 apparatus. THF was employed as the eluent at a flow rate of 1 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). The DSC measurements were performed on a TA 60 (TA Co.) at a rate of 10 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 100 °C, cooling at 10 °C/min to -100 °C, and then recording the second DSC scan.

X-ray Crystallographic Analysis

A crystal was sealed in oil under a microscope in the glove box. Data collections were performed at –100 °C on a Bruker Smart-Apex CCD diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL-97 program. Refinements were performed on F2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1543893 (**1**), 1543892 (**2**), 1552494 (**3**), and 1552495 (**4**) contain the

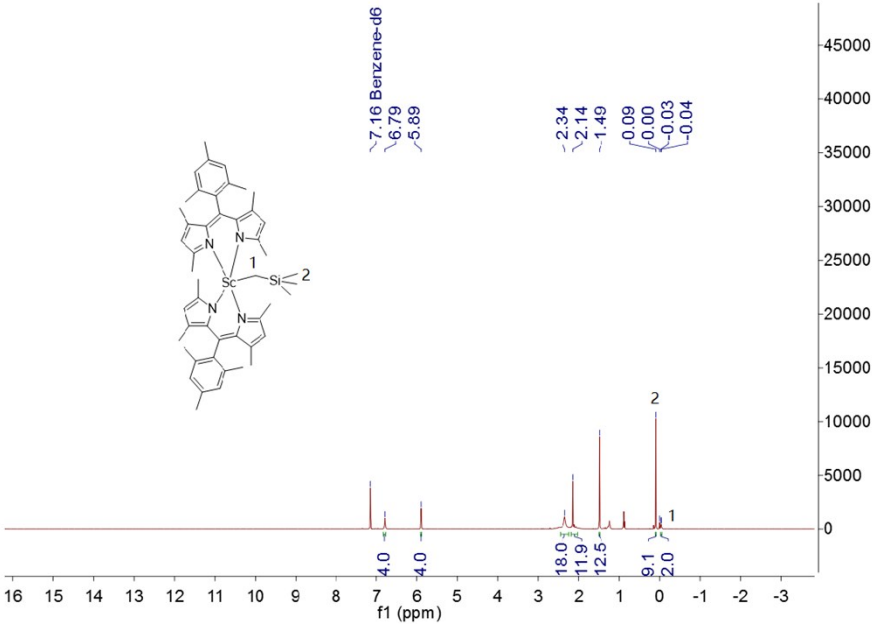
supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Dipyrromethene (DPM). A 500mL round-bottom flask equipped with a magnetic stirring bar, dry argon inlet and septum was successively charged with 2,4,6-trimethybenzaldehyde (508 μL, 5 mmol), dichloromethane (250 mL), and 2,4-dimethylpyrrole (1.03 mL, 10 mmol). The reaction mixture was stirred 10 min and TFA (3 drops) was added. The resulted dark red solution was stirred at 20 °C overnight. TLC monitoring showed then complete consumption of benzaldehyde (silica; EtOAc/cyclohexane 1:4). A suspension of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.2 g, 5.3 mmol) in dichloromethane (60 mL) was added and stirring was continued for 30 min. The reaction mixture was washed with water (100 mL), the organic phase was dried over Na_2SO_4, filtered and the volatiles were evaporated under reduced pressure. The black crude material was purified by chromatography over aluminum oxide (CH_2Cl_2 to CH_2Cl_2/MeOH 99:1) to give a khaki powder-- DPM (720 mg, yield 52%). ^{1}H NMR (400 MHz, C_6D_6) δ 14.08 (s, 1H), 6.77 (s, 2H), 5.85 (s, 2H), 2.19 (s, 6H), 2.12 (s, 9H), 1.52 (s, 6H).

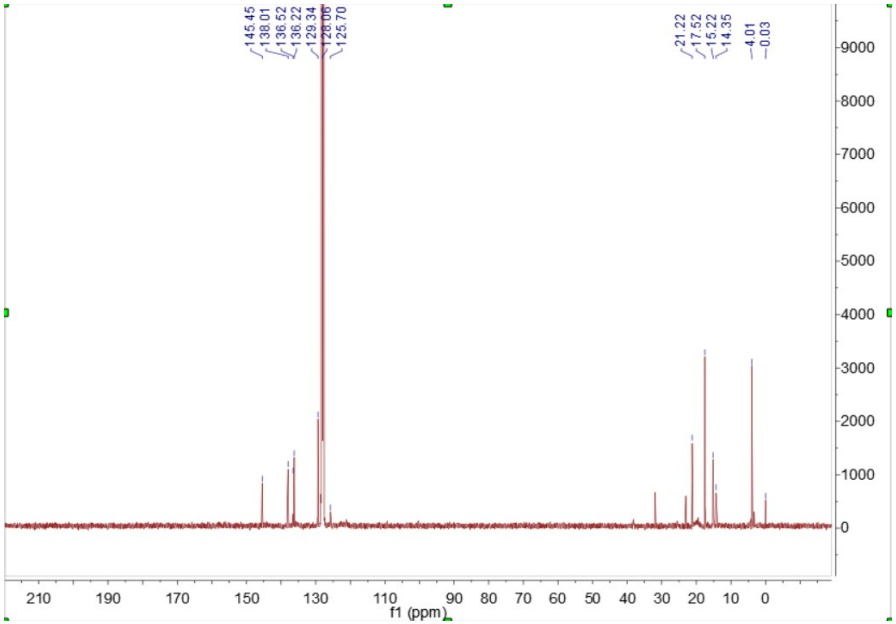


SFigure 1. ^{1}H NMR spectrum of **DPM**.

Synthesis of Rare Earth Scandium Monoalkyl Complex 1 - $(DPM)_2ScCH_2SiMe_3$. To a colorless toluene solution (5 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.283 g, 0.628 mmol) was added a solution of DPM (0.2 g, 0.628 mmol) in toluene (5.0mL) at room temperature. The mixture was stirred at room temperature for 4 h. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at −30 °C to give complex **1** as red powder (0.14 g, yield 30%). Quantum Yield: 0.14. ^{1}H NMR (400 MHz, C_6D_6) δ 6.79 (s, 4H), 5.89 (s, 4H), 2.34 (s, 18H), 2.14 (s, 12H), 1.49 (s, 12H), 0.09 (s, 9H), -0.04 (s, 2H). ^{13}C NMR(100MHz, C_6D_6) δ 145.45, 138.01, 136.52, 136.22, 129.34, 21.22, 17.52, 15.22, 14.35, 4.01, 0.03. Anal. Calcd (%) for $C_{48}H_{61}N_4ScSi$: C, 75.16; H, 8.02; N, 7.30. Found: C, 74.79; H, 7.65; N, 6.92.



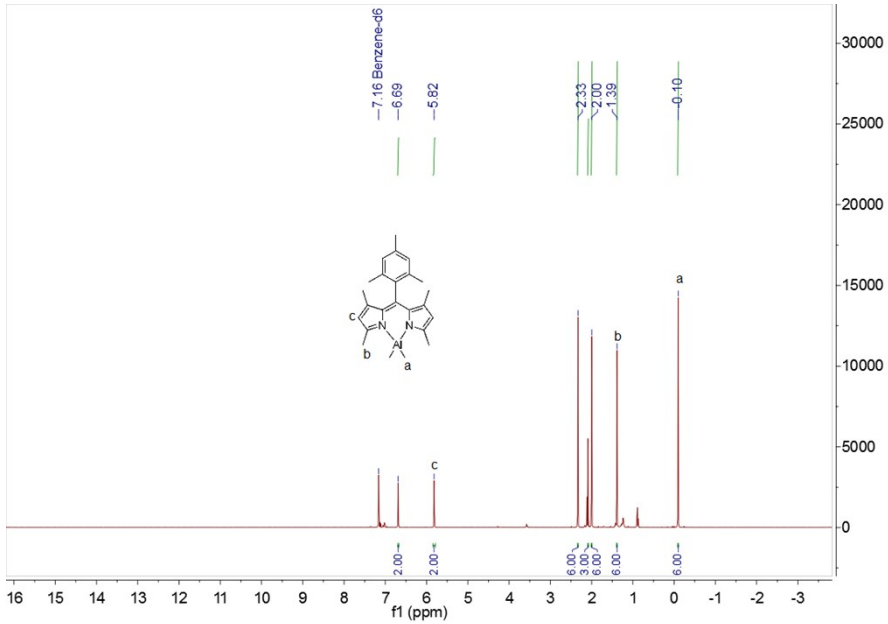
SFigure 2. ^{1}H NMR spectrum of the complex of **$(DPM)_2Sc(CH_2SiMe_3)$**.



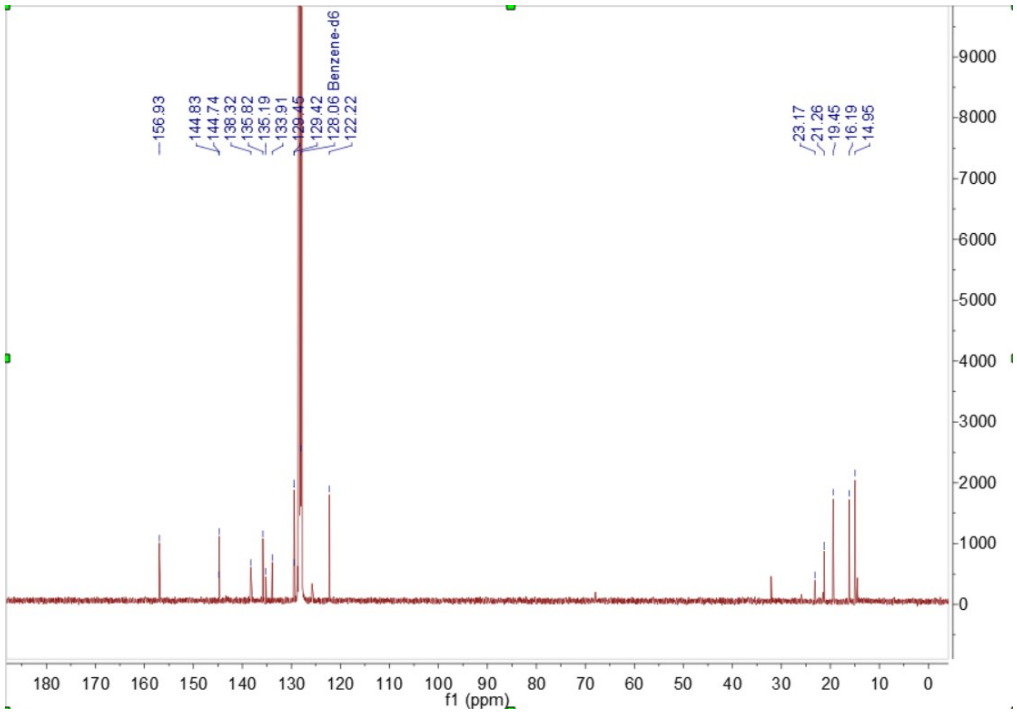
SFigure 3. ^{13}C NMR spectrum of the complex of **$(DPM)_2Sc(CH_2SiMe_3)$**.

Synthesis of Aluminum Dialkyl Complex 2 - $(DPM)AlMe_2$. In the glovebox, to a round-bottom flask equipped with a magnetic stirring bar was added to DPM (300 mg, 942 mmol) in Toluene (10 mL), then $AlMe_3$ (0.95 ml, 945 mmol, 1.0M in Toluene) was then slowly added to provide a dark green solution .After 4h, the volatiles were evaporated under reduced pressure. The brown crude material was purified by recrystallization from hexane to provide brown powder ($DPMAlMe_2$) (254 mg, yield 90%). Quantum Yield: 0.066. ^1H NMR (400 MHz, C_6D_6) δ 6.69 (s, 2H), 5.82 (s, 2H), 2.33 (s, 6H), 2.00 (s, 3H), 1.39 (s, 6H), -0.10 (s, 6H). ^{13}C NMR(100MHz, C_6D_6) δ 156.93, 144.7, 138.32, 135.82, 135.19, 133.91, 129.42, 122.22, ,

23.17, 21.26, 19.45, 16.19, 14.95,. Anal. Calcd (%) for $C_{24}H_{31}AlN_2$: C, 76.97; H, 8.34; N, 7.48. Found: C, 76.88; H, 8.14; N, 7.14.

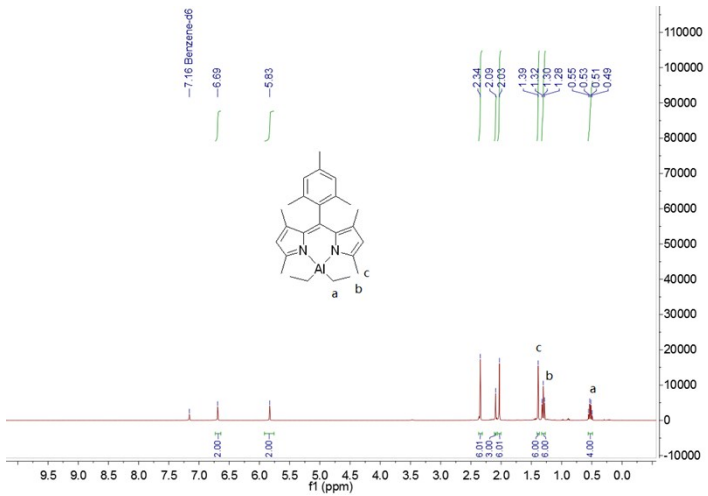


SFigure 4. ^{1}H NMR spectrum of the complex of **(DPM)AlMe$_2$**.

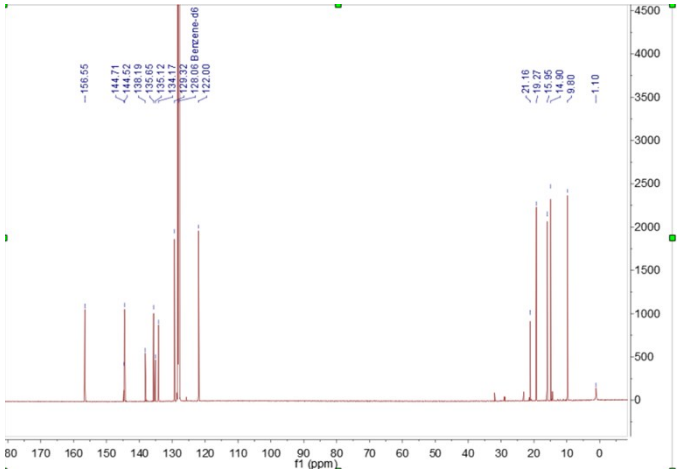


SFigure 5. ^{13}C NMR spectrum of the complex of (**DPM)AlMe$_2$**.

Synthesis of Aluminum Dialkyl Complex 3 - (DPM)AlEt$_2$ The synthesis procedure is similar to (DPM)AlMe$_2$, yield: 89%.^{1}H NMR (400 MHz, C_6D_6) δ 6.69 (s, 2H), 5.83 (s, 2H), 2.34 (s, 6H), 2.09 (s, 3H), 2.03 (s, 6H), 1.39 (s, 6H), 1.32-1.28 (t, J = 8 Hz, 6H), 0.55-0.49 (q, J = 8 Hz, 4H); ^{13}C NMR (100MHz, C_6D_6) δ 156.55,144.71, 144.52, 138.19, 135.65, 135.12, 134.17, 129.3, 122.00, 23.06, 21.16, 19.27, 15.95, 14.90, 9.80. Anal. Calcd (%) for $C_{26}H_{35}AlN_2$: C, 77.57; H, 8.76; N, 6.96. Found: C, 77.67; H, 8.86; N, 7.06.

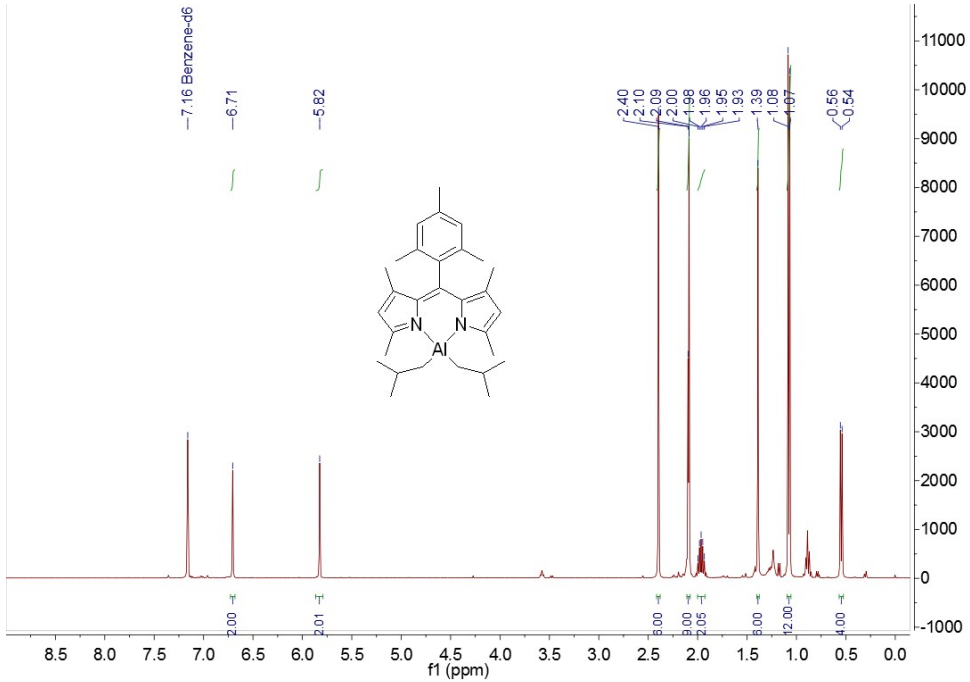


SFigure 6. ^{1}H NMR spectrum of the complex of (**DPM)AlEt$_2$**.

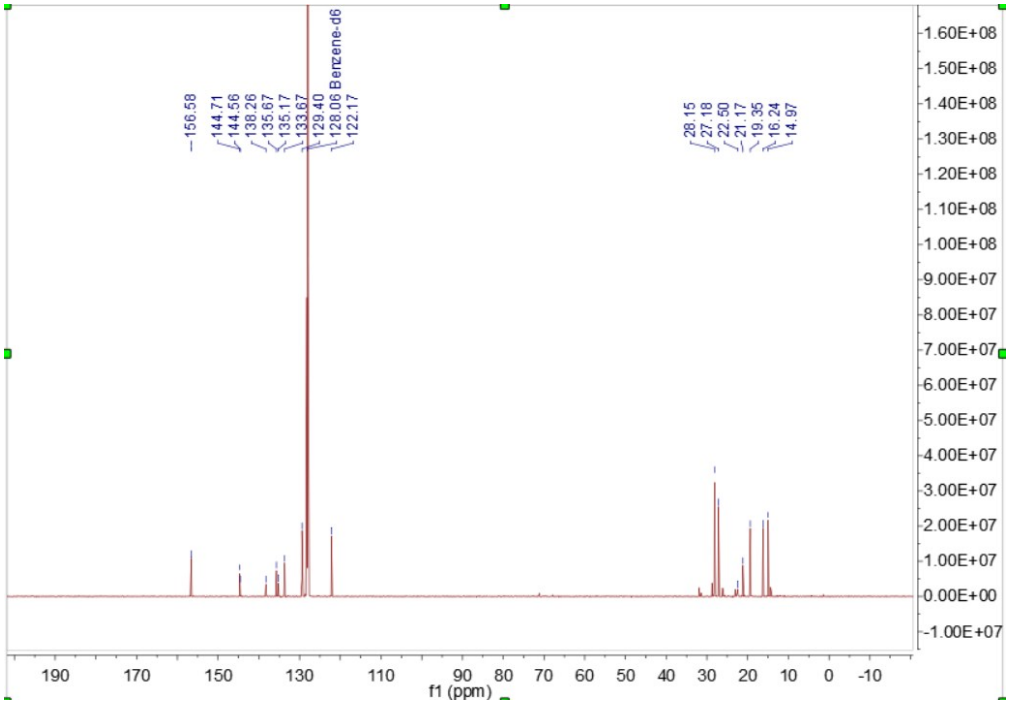


SFigure 7. ^{13}C NMR spectrum of the complex of (**DPM)AlEt$_2$**.

Synthesis Aluminum Dialkyl Complex 4 - (DPM)Al^{i}Bu$_2$ The synthesis procedure is similar to (DPM)AlMe$_2$,yield: 85%. ^{1}H NMR (400 MHz, C_6D_6) δ 6.71 (s, 2H), 5.82 (s, 2H), 2.40 (s, 6H), 2.34 (s, 6H), 2.10 (s, 3H), 2.09 (s, 6H), 2.0-1.93 (m, 2H), 1.39 (s, 6H), 1.08-1.07 (d, J = 4 Hz, 12H), 0.56-0.54 (d, J = 8 Hz, 4H); ^{13}C NMR (100MHz, C_6D_6) δ 156.58, 144.71, 144.56, 138.26, 135.67, 133.67, 129.40, 122.17, 28.15, 27.18, 21.17, 19.35, 16.24, 14.97. Anal. Calcd (%) for $C_{30}H_{43}AlN_2$: C, 78.56; H, 9.45; N, 6.11. Found: C, 78.36; H, 9.28; N, 5.85.



SFigure 8. ^{1}H NMR spectrum of the complex of (**DPM)Al^{i}Bu$_2$.**



SFigure 9. ^{1}H NMR spectrum of the complex of **(DPM)Al^{i}Bu$_2$.**

A Typical Procedure for the Polymerization of Isoprene by complexes 1/Activator/AlR$_3$ systems

In a glovebox, to a toluene solution (10 ml) was slowly added to $AlMe_3$ (1M Tol) (0.2 mL, 0.02 mmol) under magnetic stirring in a flask , then $(DPM)_2Sc(CH_2SiMe_3)$ (15.34mg, 0.02 mmol) was added. After the mixture was stirred for 5 min, a toluene solution (1.0 mL) of Borate (0.02 mmol) was slowly added to the resulting solution, and isoprene (0.39 g, 4 mmol) were added. The polymerization was quenched by addition of ethanol (30 mL, containing 5% butylhydroxytoluene (BHT) as

a stabilizing agent). Then the mixture was poured into methanol (100 mL) to precipitate the polymer product. The precipitated polymer was dried under vacuum at 40 °C to a constant weight.

The isomer contents of the polyisoprene products were calculated from the ^{1}H and ^{13}C NMR spectra according to the following formula (1–5):

(1) Mol 1,4-IP%=$\{I_{H1}/(I_{H1}+0.5I_{H2})\}*100$

(2) Mol 3,4-IP%=$\{0.5I_{H2}/(I_{H1}+0.5I_{H2})\}*100$

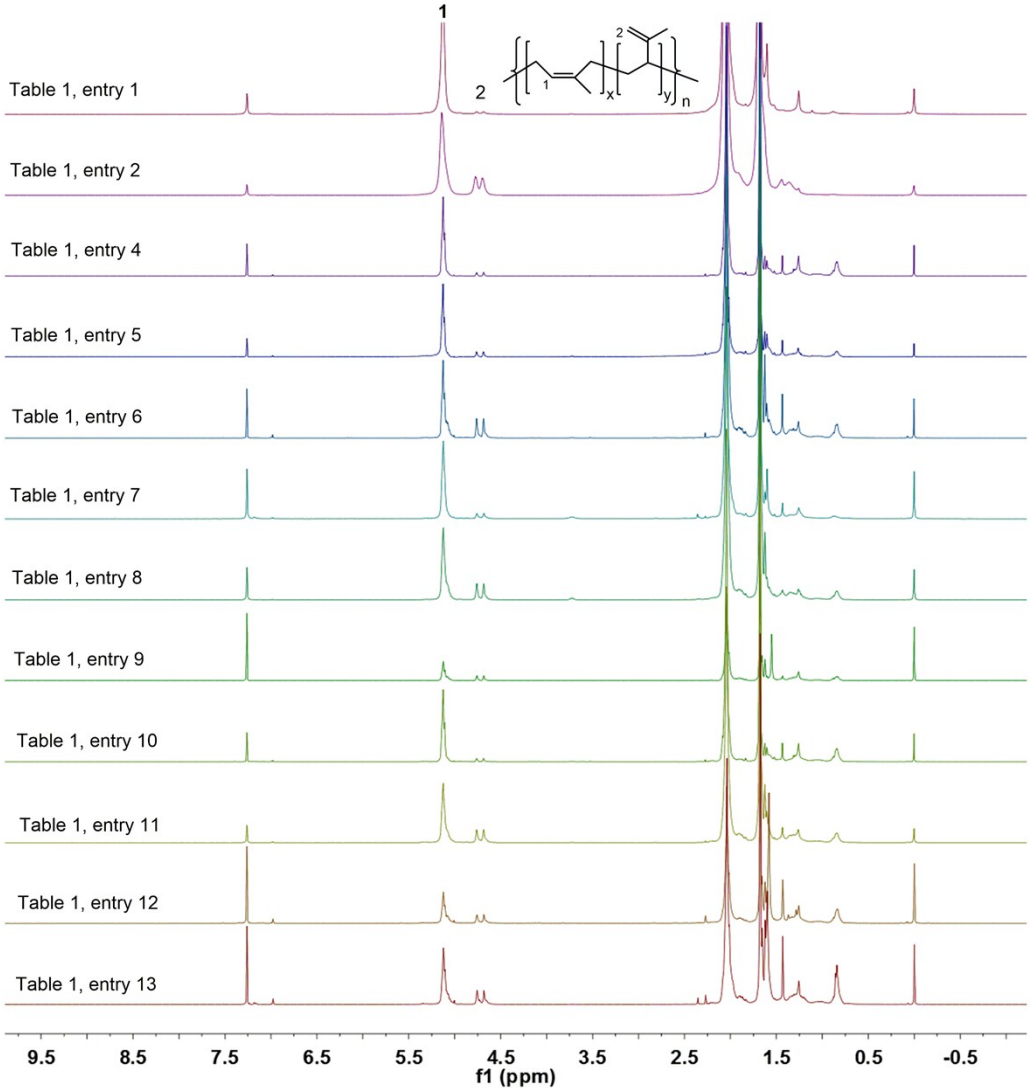
in which I_{H1} is the integration of the resonance at 5.13 ppm (one vinyl proton of the 1,4-isoprene unit), and I_{H2} is the integration of the resonance at 4.72 ppm (two vinyl protons of the 3,4-isoprene unit) in the ^{1}H NMR spectrum.

(3) Mol *cis*-1,4-IP%=$\{I_{C1}/(I_{C1}+I_{C2}+I_{C3})\}*100$

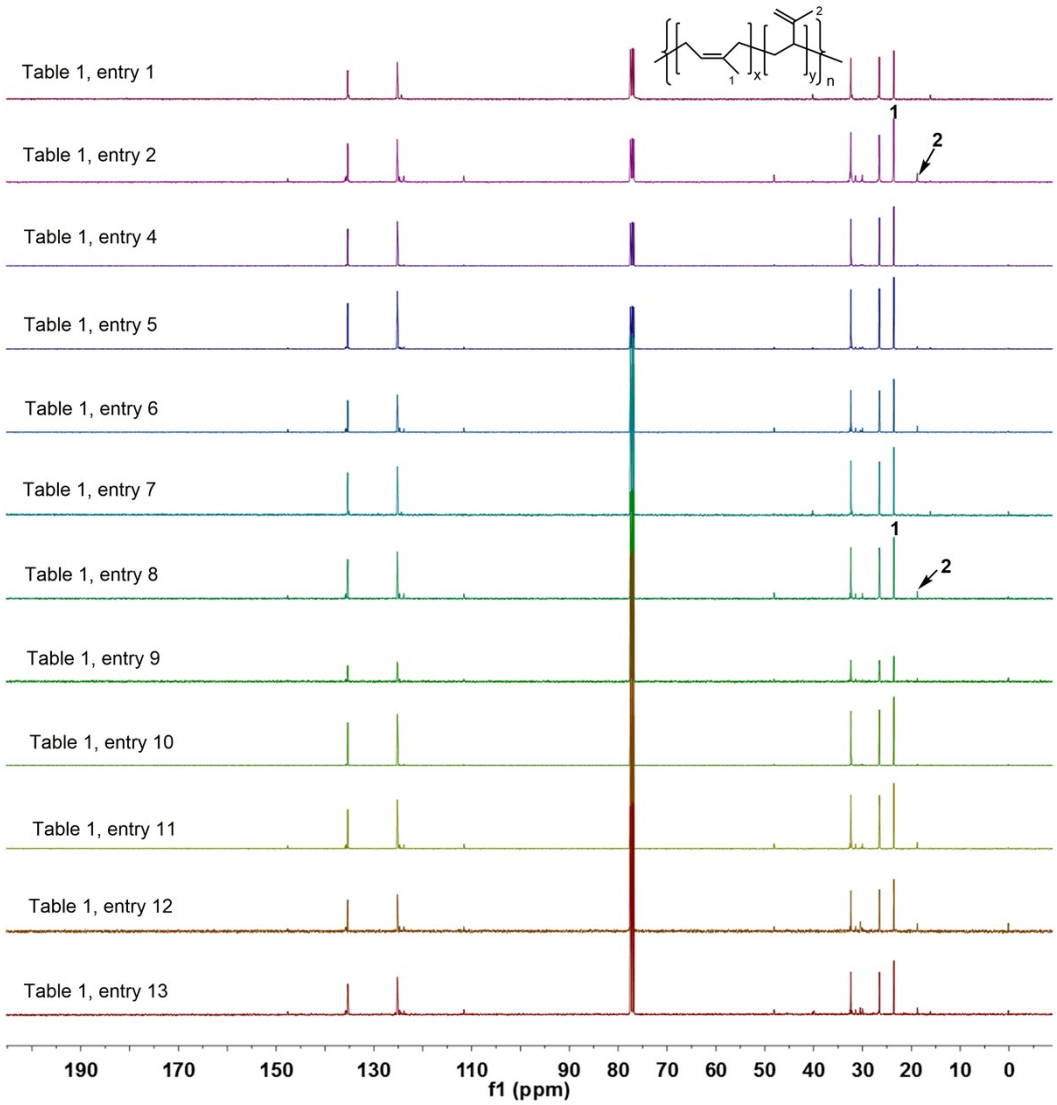
(4) Mol *trans*-1,4-IP%=$\{I_{C3}/(I_{C1}+I_{C2}+I_{C3})\}*100$

(5) Mol 3,4-IP%=$\{I_{C2}/(I_{C1}+I_{C2}+I_{C3})\}*100$

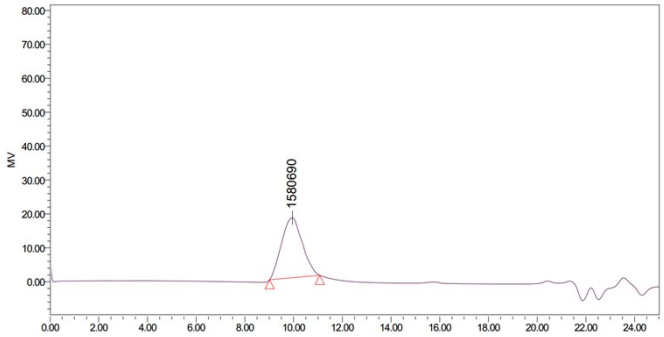
in which I_{C1} is the integration of the signals at 23.2 ppm assigned as the methyl carbon of the *cis*-1,4-isoprene unit, and I_{C2} is the integration of the signals at 18.5 ppm assigned as the methyl carbon of the 3,4-isoprene unit, while I_{C3} is the integration of the signals at 15.9 ppm assigned as the methyl carbon of the *trans*-1,4-isoprene unit in the ^{13}C NMR spectrum.



SFigure 10. ^{1}H NMR spectra of the polyisoprenes by complexes **1**/AlR_3/Borate systems in Table 1.



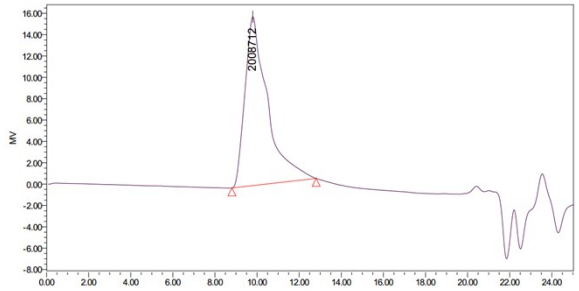
SFigure 11. ^{13}C NMR spectra of the polyisoprenes by complexes **1**/ AlR_3/ Borate systems in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.952	9.952	9.952	1376828	1923729	1580690	2634128	3400809	1.369282

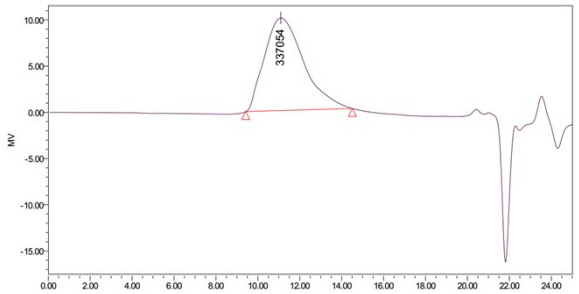
SFigure 12. GPC profiles of the polyisoprenes by complexes **1**/Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.800	9.800	9.800	757427	1781311	2008712	2904021	3951558	1.630271

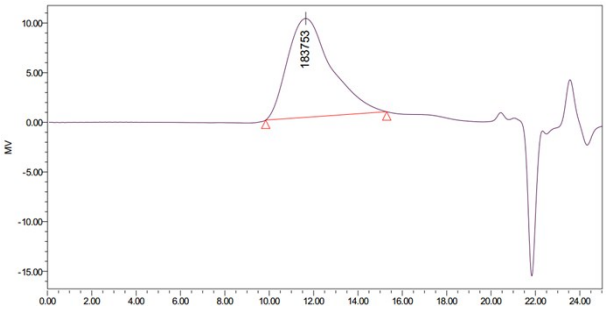
SFigure 13. GPC profiles of the polyisoprenes by complexes **1**/ Al^{i}Bu$_3$/[PhMe$_2$NH][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.095	11.095	11.095	171726	410806	337054	837126	1312224	2.037763

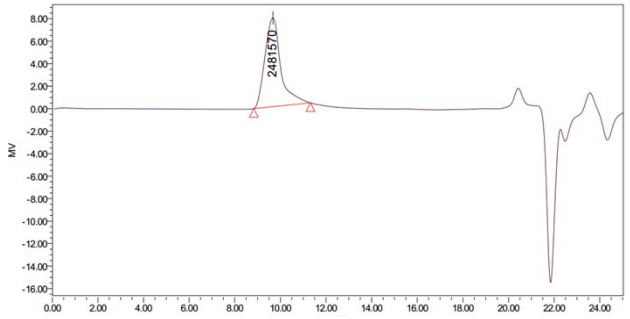
SFigure 14. GPC profiles of the polyisoprenes by complexes **1**/$AlMe_3$/$[Ph_3C][B(C_6F_5)_4]$ systems in Table 1, entry 4.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.647	11.647	11.647	98041	213433	183753	409603	643564	1.919114

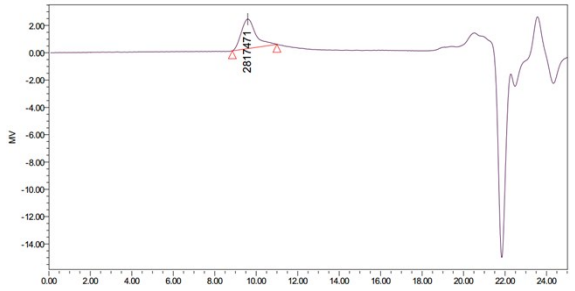
SFigure 15. GPC profiles of the polyisoprenes by complexes **1**/$AlMe_3$/$[PhMe_2NH][B(C_6F_5)_4]$ systems in Table 1, entry 5.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.670	9.670	9.670	1851001	2721874	2481570	3576070	4418169	1.313827

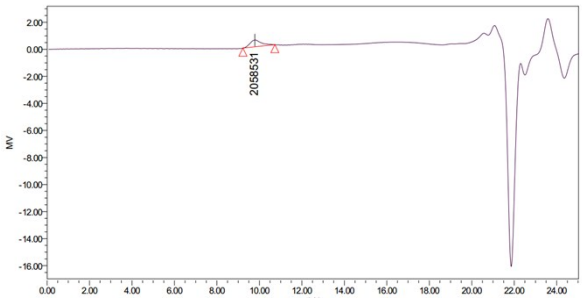
SFigure 16. GPC profiles of the polyisoprenes by complexes **1**/Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 7.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.594	9.594	9.594	1998640	2868556	2817471	3742573	4578301	1.304689

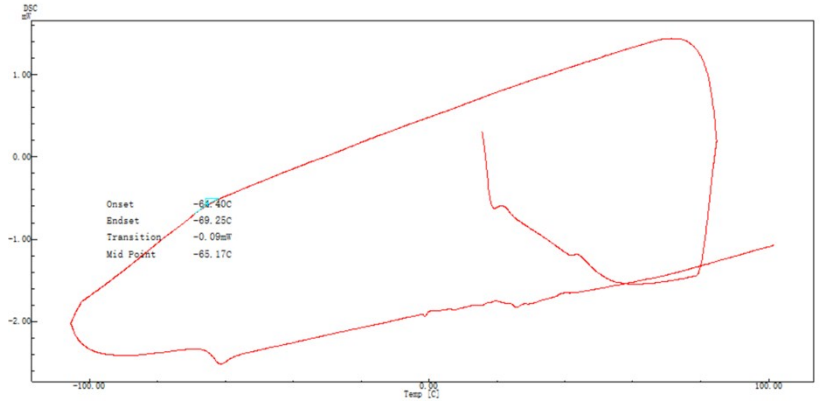
SFigure 17. GPC profiles of the polyisoprenes by complexes **1**/Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 8.



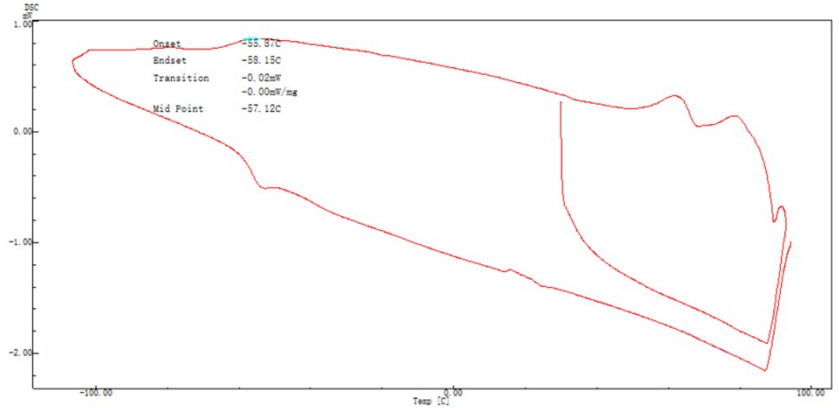
GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		9.785	9.785	9.785	1679489	1994521	2058531	2306195	2602445	1.156265

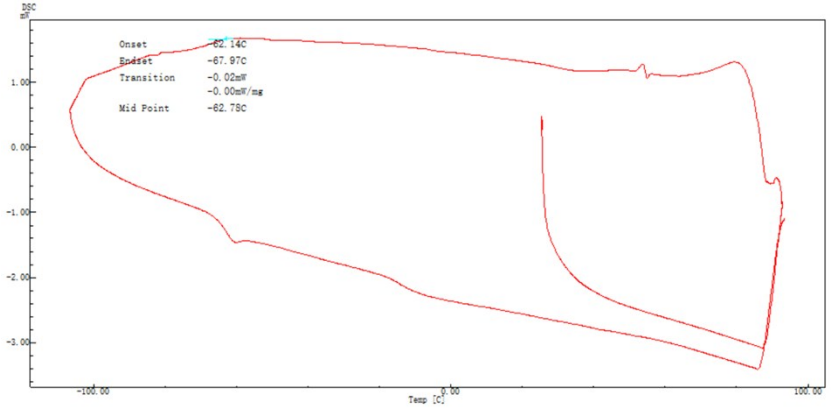
SFigure 18. GPC profiles of the polyisoprenes by complexes **1**/Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 10.



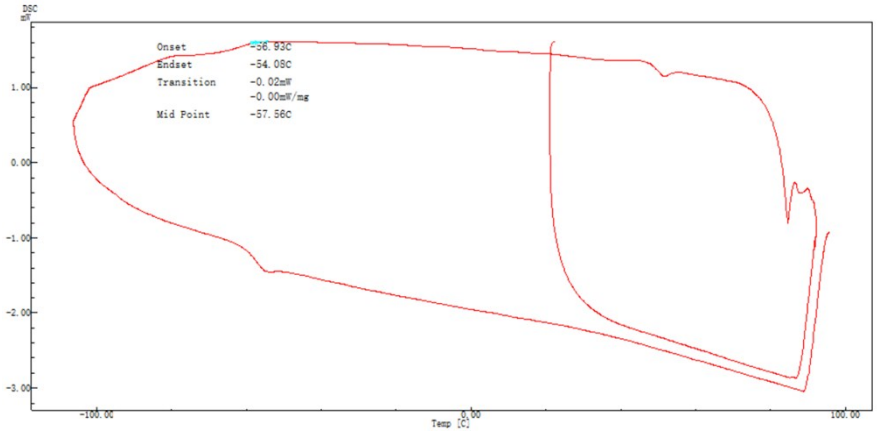
SFigure 19. DSC charts of the polyisoprenes by complexes **1**/Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 1.



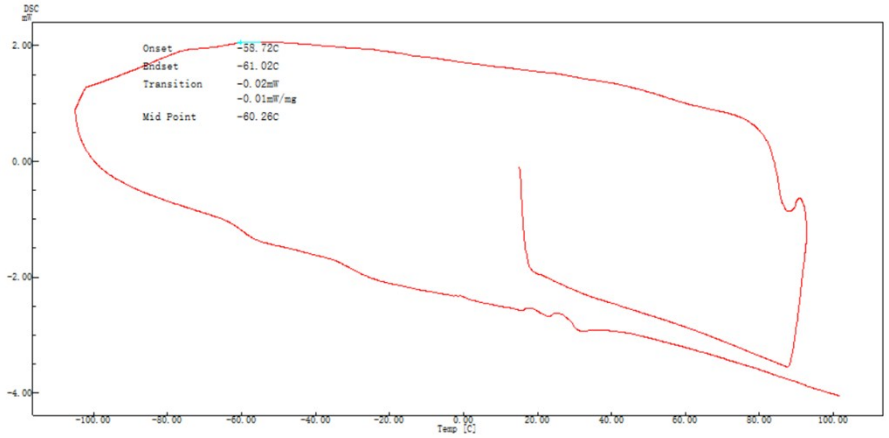
SFigure 20. DSC charts of the polyisoprenes by complexes **1**/ Al^{i}Bu$_3$/[PhMe$_2$NH][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 2.



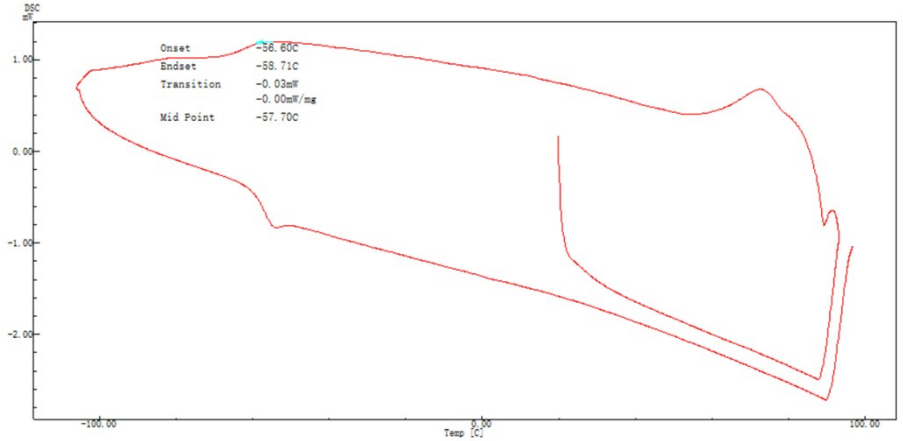
SFigure 21. DSC charts of the polyisoprenes by the **1**/AlMe$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 4.



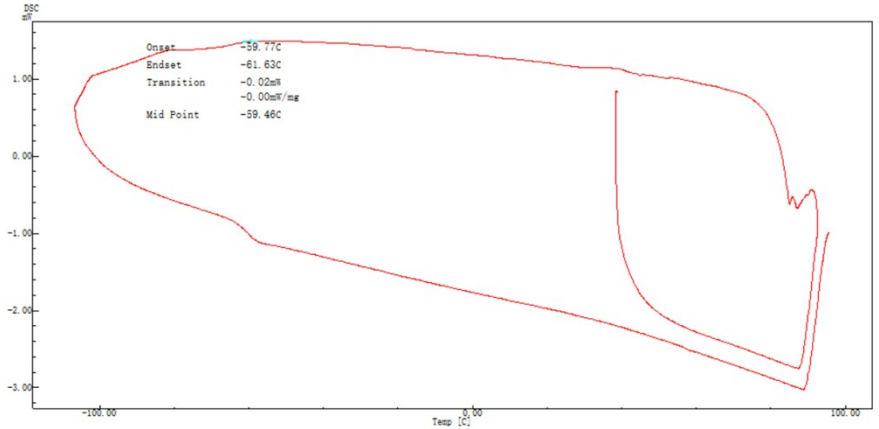
SFigure 22. DSC charts of the polyisoprenes by the **1**/$AlEt_3$/$[Ph_3C][B(C_6F_5)_4]$ systems in Table 1, entry 6.



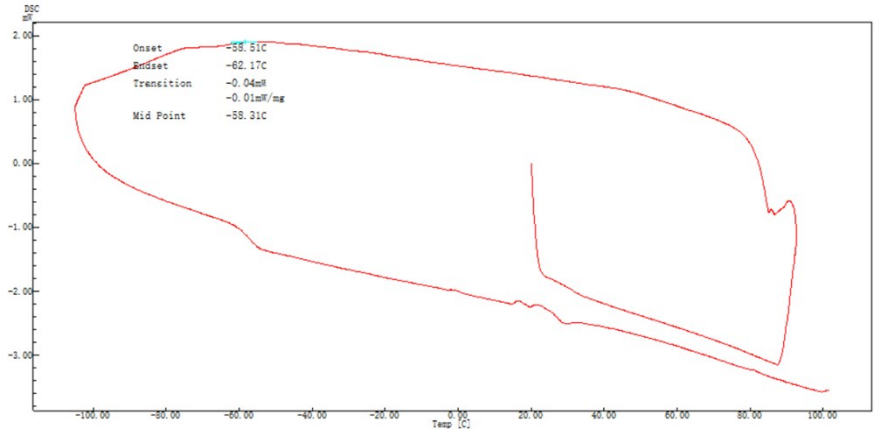
SFigure 23. DSC charts of the polyisoprenes by the **1**/ Al^iBu_3/$[Ph_3C][B(C_6F_5)_4]$ systems in Table 1, entry 7.



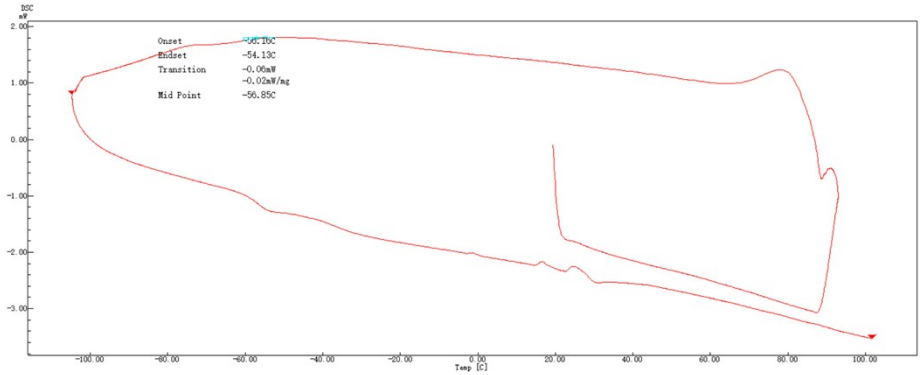
SFigure 24. DSC charts of the polyisoprenes by the **1**/ Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 9.



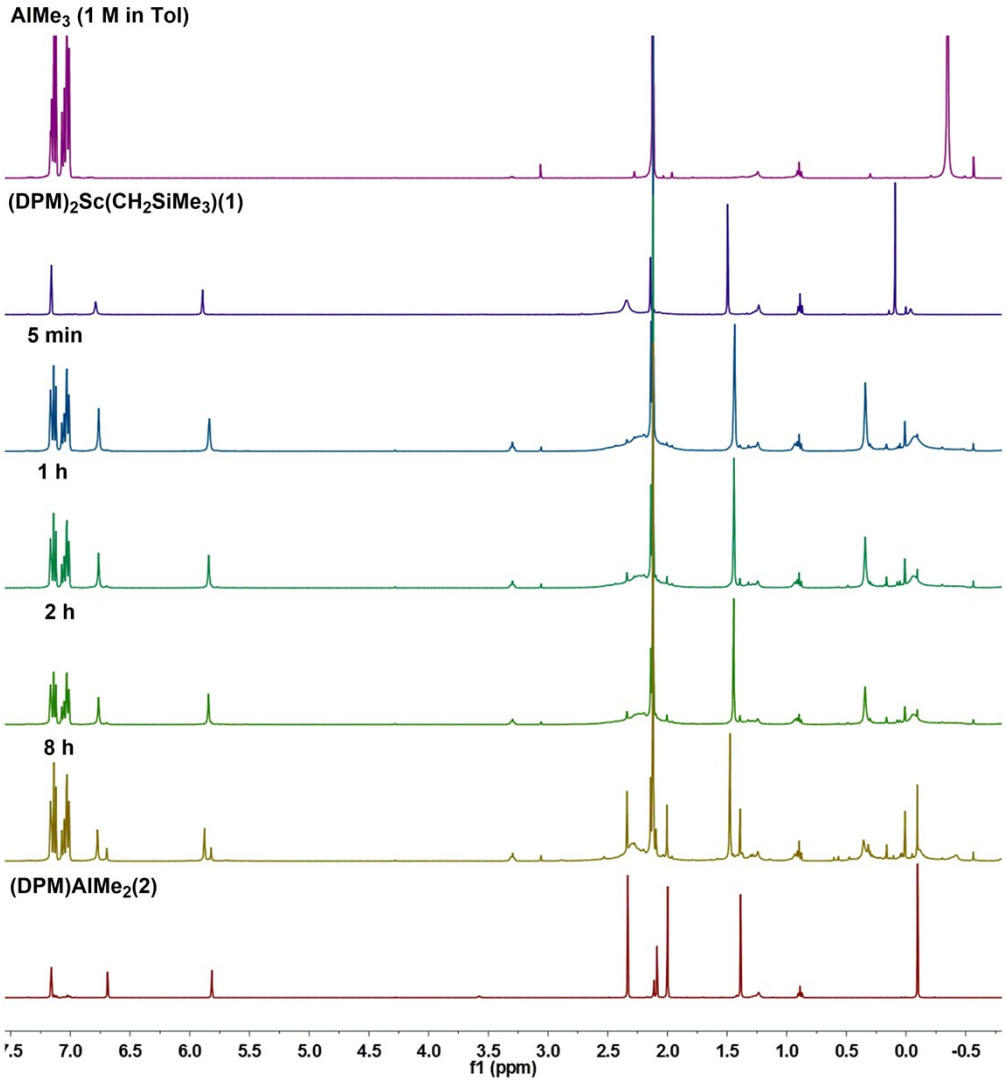
SFigure 25. DSC charts of the polyisoprenes by the **1**/ Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 11.



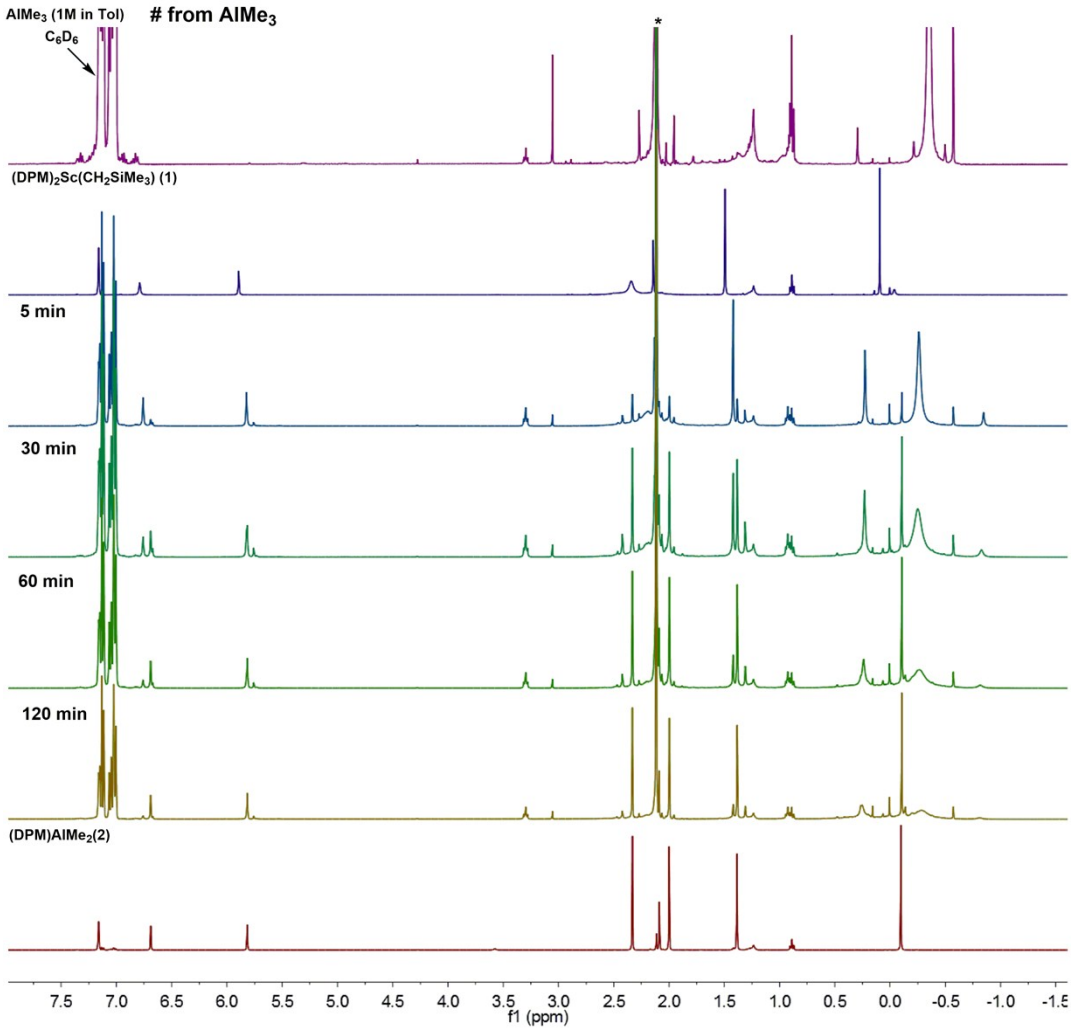
SFigure 26. DSC charts of the polyisoprenes by the **1**/ Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 12.



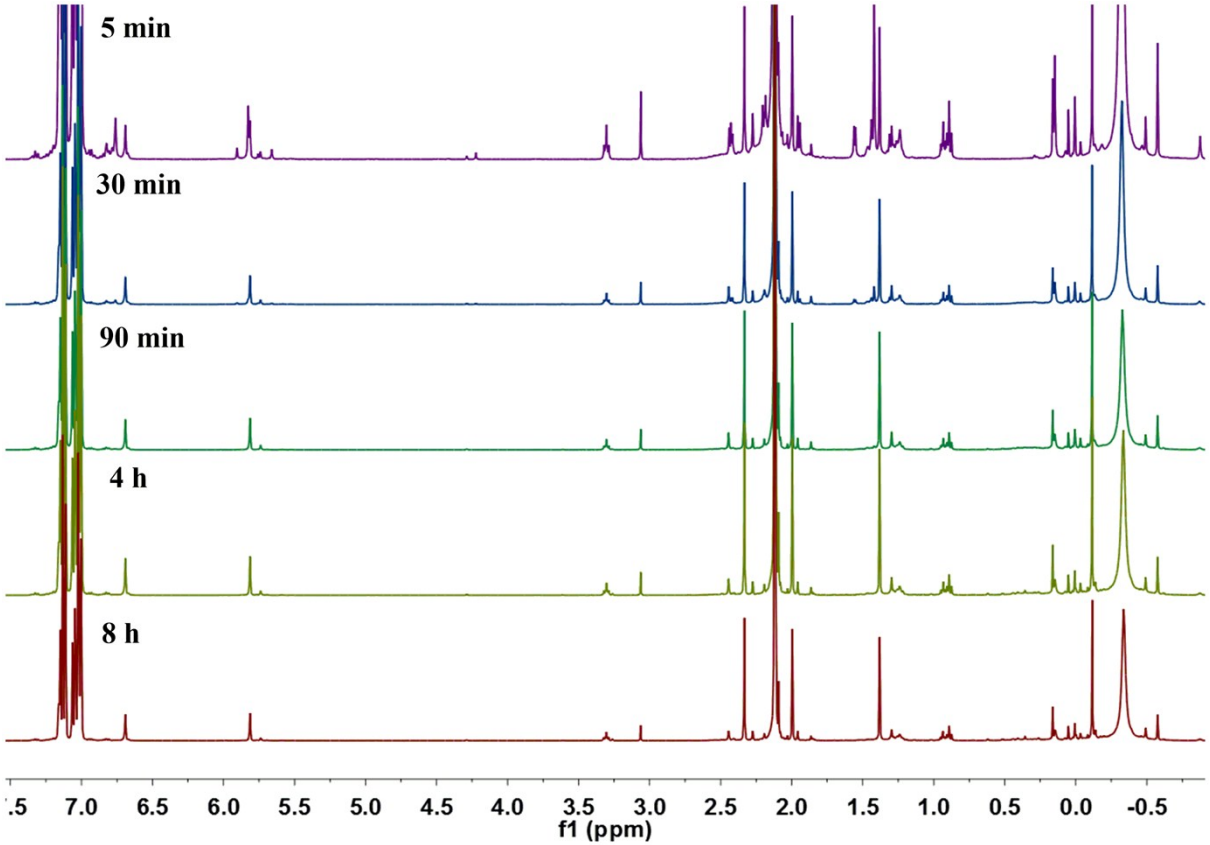
SFigure 27. DSC charts of the polyisoprenes by the **1**/ Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] systems in Table 1, entry 13.



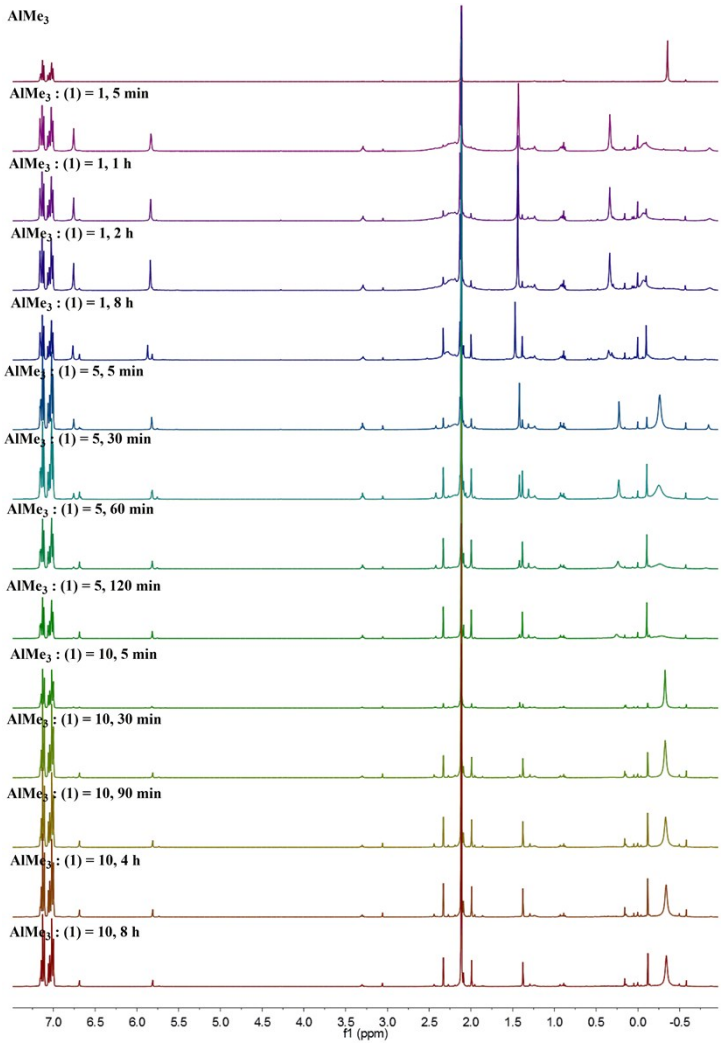
SFigure 28.*In-situ* ^{1}H NMR spectra for the reaction of the complex **1** with $AlMe_3$ (1 M in toluene) under the molar ratio of [$AlMe_3$]/[Sc] as 1/1 at different time in C_6D_6 at 25 ℃.



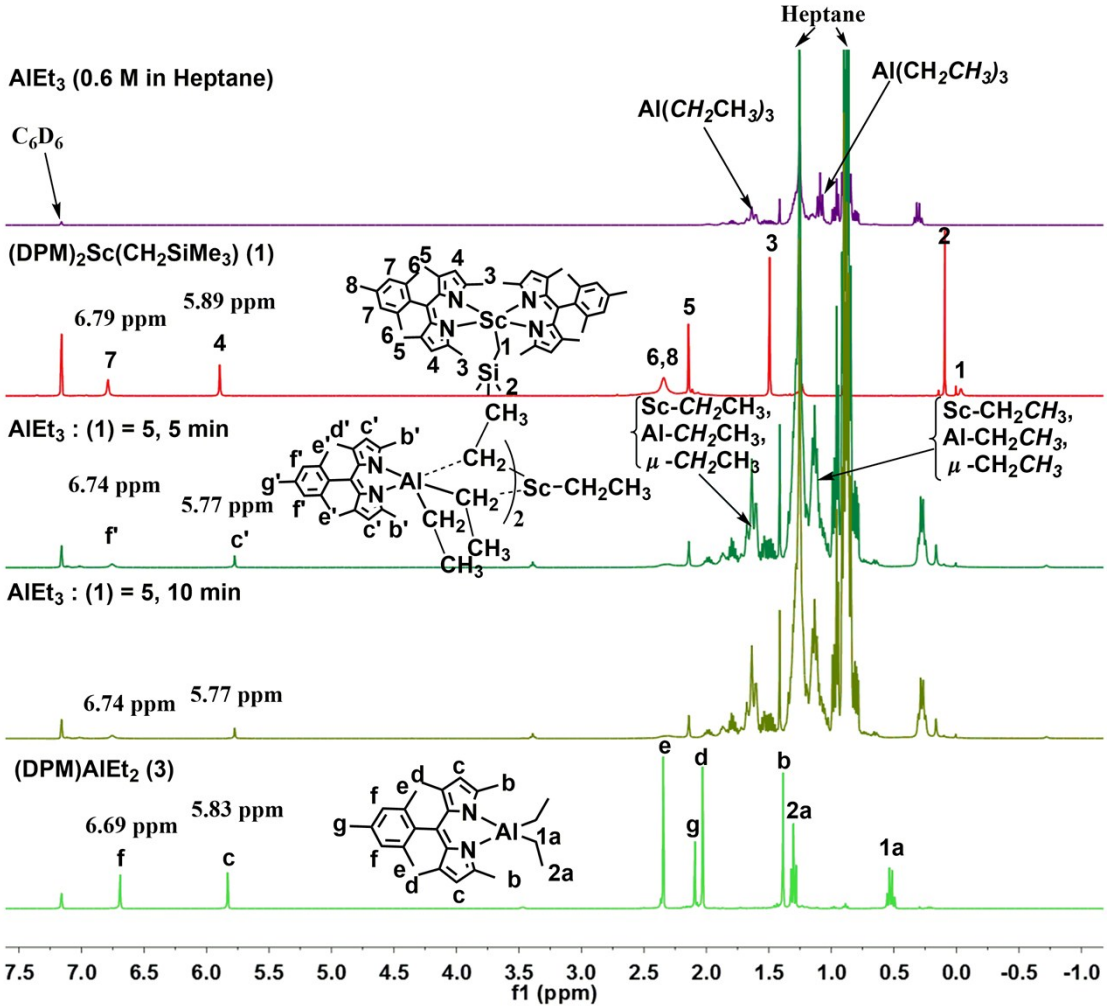
SFigure 29.*In-situ* ^{1}H NMR spectra for the reaction of the complex **1** with $AlMe_3$ (1 M in toluene) under the molar ratio of $[AlMe_3]/[Sc]$ as 5/1 at different time in C_6D_6 at 25 ℃.



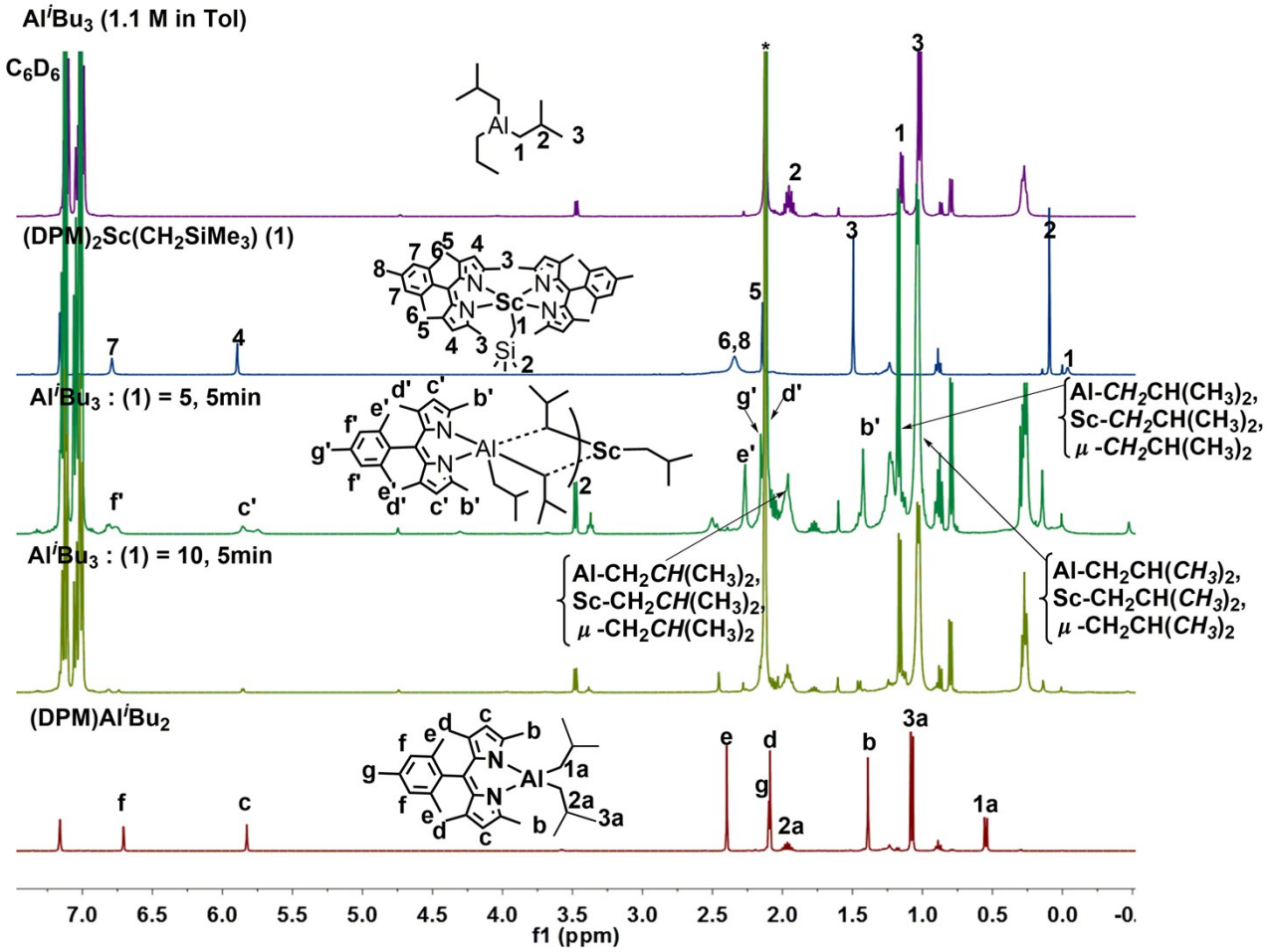
SFigure 30.*In-situ* ^{1}H NMR spectra for the reaction of the complex **1** with $AlMe_3$ (1 M in toluene) under the molar ratio of [$AlMe_3$]/[Sc] as 10/1 at different time in C_6D_6 at 25 ℃.



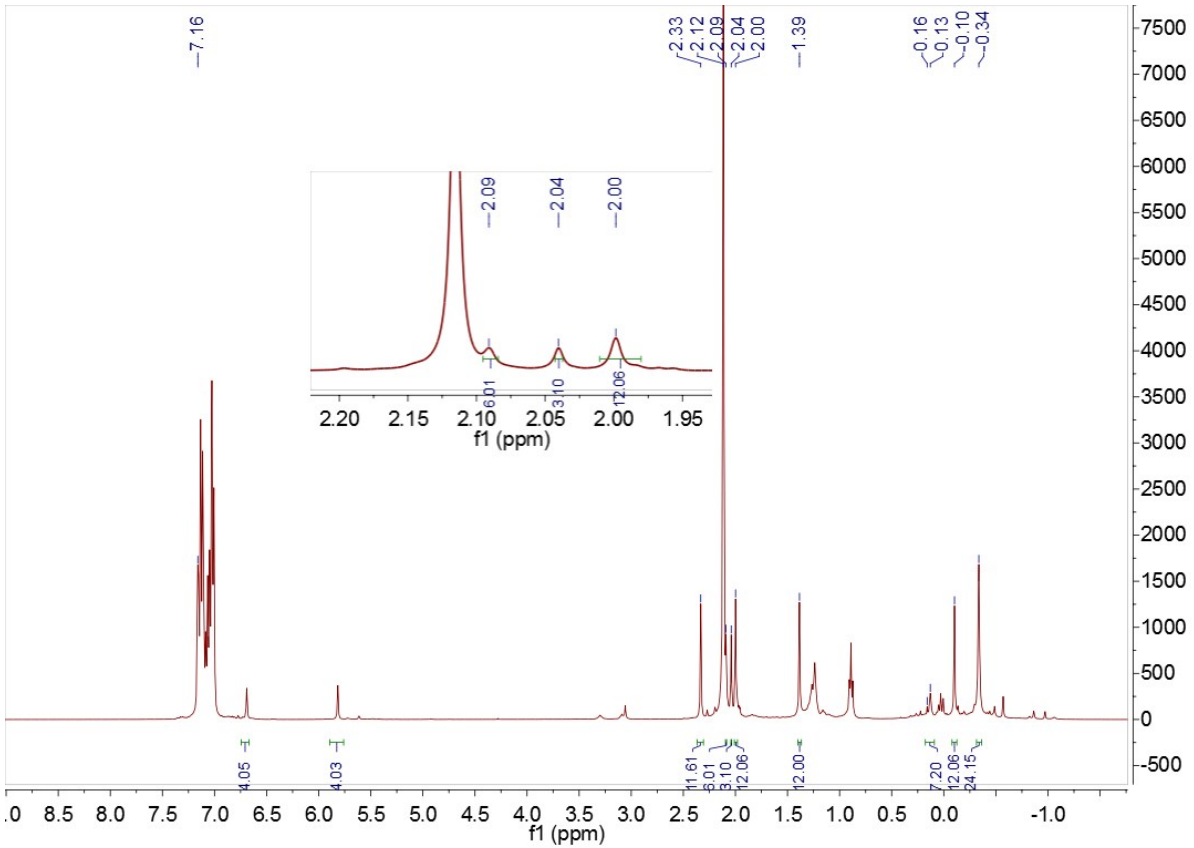
SFigure 31. *In-situ* ^{1}H NMR spectra for the reaction of the complex **1** with $AlMe_3$ (1 M in toluene) at different the molar ratio at different time in C_6D_6 at 25 ℃.



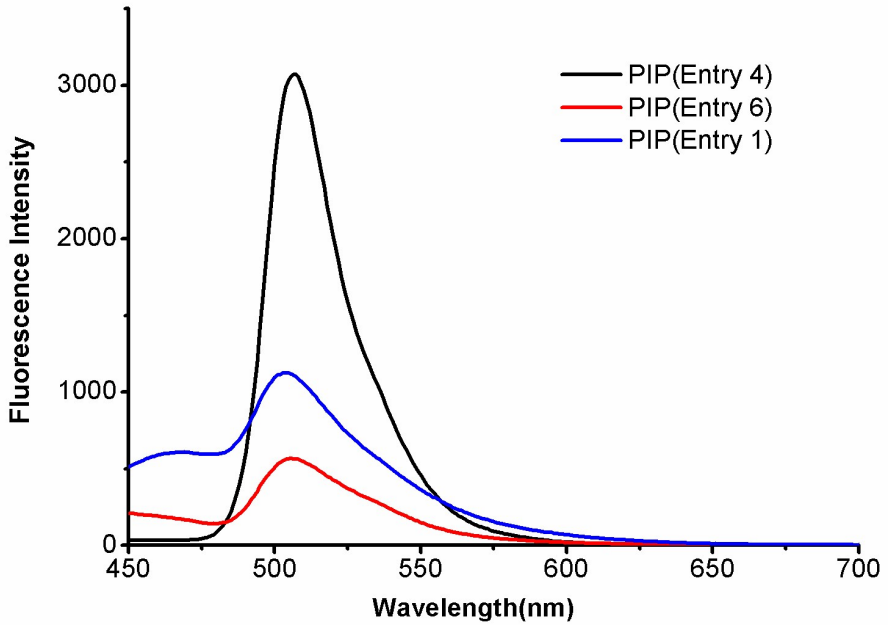
SFigure 32.*In-situ* ^{1}H NMR spectra for the reaction of the complex **1** with $AlEt_3$ (0.6 M in heptane) under the molar ratio of [$AlEt_3$]/[Sc] as 5/1 at different time in C_6D_6 at 25 ℃. (The spectra show that no free (DPM)$AlEt_2$ were found in the solution , suggesting that the (DPM)$AlEt_2$ is a part of the resulting active species.)



SFigure 33.*In-situ* ^{1}H NMR spectra for the reaction of the complex **1** with Al^{i}Bu$_3$ (1.1 M in toluene) under the molar ratio of [Al^{i}Bu$_3$]/[Sc] as 5/1 and 10/1 at different time in C_6D_6 at 25 ℃. (The spectra show that no free (DPM)Al^{i}Bu$_2$ were found in the solution , suggesting that the (DPM)Al^{i}Bu$_2$ is a part of the resulting active species.)



SFigure 34. *In-situ* ^{1}H NMR spectrum for the reaction of the complex **1** with $AlMe_3$ (1 M in toluene) under the molar ratio of [$AlMe_3$]/[Sc] as 5/1 after adding borate A in C_6D_6 at 25 ℃.



SFigure 35. Fluorescence spectrum of the polyisoprenes by the **1**/AlR_3/$[Ph_3C][B(C_6F_5)_4]$ systems in Table 1, entry 1, 4, 6.

Table 1. Crystal data, data collection and processing parameters for complexes **1 - 4**.

	1	2	3	4
Formula	$C_{48}H_{61}N_4SiSc$	$C_{24}H_{31}N_2Al$	$C_{26}H_{35}N_2Al$	$C_{30}H_{43}N_2Al$
Mw	767.05	374.49	402.54	458.64
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$
a [Å]	15.263(3)	7.0719(14)	7.8769(16)	8.6985(17)
b [Å]	11.695(2)	11.897(2)	28.840(6)	11.354(2)
c [Å]	25.821(5)	15.148(3)	10.921(2)	28.622(6)

α [°]	90	76.92(3)	90	90
β [°]	106.57(3)	86.12(3)	106.63(3)	94.73(3)
γ [°]	90	85.20(3)	90	90
V [Å^3]	4417.8(17)	1235.5(5)	2377.1(9)	2817.1(10)
Z	4	2	4	4
ρ_{calcd} [gcm^{-3}]	1.153	1.007	1.125	1.081
μ [mm^{-1}]	0.230	0.091	0.099	0.091
F (000)	1648.0	404.0	872.0	1000.0
θ range [°]	4.47 to 62.982	3.966 to 63.014	5.58 to 63.012	4.586 to 63.002
no of reflns collected	65886	15469	23487	41434
no of indep reflns	14652[R_{int}=0.0578, R_{sigma} = 0.0676]	7995[R_{int}=0.0311, R_{sigma}= 0.0672]	7873[R_{int}=0.0383, R_{sigma}= 0.0490]	9322[R_{int}=0.0254, R_{sigma}= 0.0224]
no of date / restraints / params	14652/0/504	7995/0/253	7873/0/271	9322/0/308
GOF	1.114	0.951	1.105	1.078
Final R indexes [I>2σ (I)]	R_1=0.0603,wR_2=0.1467	R_1=0.0478,wR_2=0.1236	R_1=0.0581,wR_2=0.1509	R_1=0.0509,wR_2=0.1359
Final R indexes(all data)	R_1=0.0748,wR_2=0.1564	R_1=0.0737,wR_2=0.1336	R_1=0.0683,wR_2=0.1597	R_1=0.0564,wR_2=0.1411
Largest diff. peak/hole / e Å^{-3}	0.33/-0.48	0.32/-0.17	0.34/-0.40	0.38/-0.30

Crystal Data

Bond length of Complex **1**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Sc1	N1	2.1883(14)	C12	C15	1.501(2)
Sc1	N2	2.1495(14)	C13	C14	1.410(2)
Sc1	N3	2.1919(14)	C14	C16	1.497(2)
Sc1	N4	2.1943(14)	C17	C18	1.435(2)
Sc1	C45	2.2605(18)	C18	C19	1.384(2)
Si1	C45	1.8396(19)	C18	C21	1.504(2)
Si1	C46	1.885(2)	C19	C20	1.401(2)
Si1	C47	1.876(2)	C20	C22	1.495(2)
Si1	C48	1.876(2)	C23	C24	1.505(2)
N1	C11	1.408(2)	C24	C25	1.405(2)
N1	C14	1.336(2)	C25	C26	1.376(2)
N2	C17	1.4122(19)	C26	C27	1.445(2)
N2	C20	1.358(2)	C26	C44	1.505(2)
N3	C29	1.4158(19)	C27	C28	1.411(2)
N3	C32	1.358(2)	C28	C29	1.414(2)
N4	C24	1.342(2)	C28	C35	1.499(2)
N4	C27	1.411(2)	C29	C30	1.438(2)
C1	C2	1.509(2)	C30	C31	1.382(2)

C2	C3	1.387(3)	C30	C34	1.503(2)
C2	C7	1.389(3)	C31	C32	1.391(2)
C3	C4	1.393(2)	C32	C33	1.499(2)
C4	C5	1.403(2)	C35	C36	1.404(2)
C4	C8	1.510(2)	C35	C40	1.405(2)
C5	C6	1.401(2)	C36	C37	1.394(2)
C5	C10	1.499(2)	C36	C42	1.510(2)
C6	C7	1.396(2)	C37	C38	1.392(3)
C6	C9	1.508(3)	C38	C39	1.393(3)
C10	C11	1.405(2)	C38	C43	1.512(3)
C10	C17	1.414(2)	C39	C40	1.395(2)
C11	C12	1.448(2)	C40	C41	1.505(2)
C12	C13	1.378(2)			

Angel of Complex **1**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Sc1	N3	93.73(6)	N1	C14	C13	111.18(14)
N1	Sc1	N4	170.27(5)	N1	C14	C16	122.54(15)
N1	Sc1	C45	86.36(6)	C13	C14	C16	126.27(15)
N2	Sc1	N1	83.61(5)	N2	C17	C10	123.11(13)

N2	Sc1	N3	104.08(5)	N2	C17	C18	108.28(13)
N2	Sc1	N4	105.45(5)	C10	C17	C18	128.24(14)
N2	Sc1	C45	115.43(6)	C17	C18	C21	131.05(15)
N3	Sc1	N4	80.74(6)	C19	C18	C17	106.16(14)
N3	Sc1	C45	140.20(6)	C19	C18	C21	122.79(15)
N4	Sc1	C45	92.76(6)	C18	C19	C20	108.38(14)
C45	Si1	C46	113.48(10)	N2	C20	C19	110.23(14)
C45	Si1	C47	111.40(10)	N2	C20	C22	123.50(14)
C45	Si1	C48	112.11(9)	C19	C20	C22	126.27(15)
C47	Si1	C46	105.63(11)	N4	C24	C23	123.31(15)
C48	Si1	C46	105.96(10)	N4	C24	C25	110.81(15)
C48	Si1	C47	107.82(11)	C25	C24	C23	125.88(16)
C11	N1	Sc1	122.05(10)	C26	C25	C24	108.31(15)
C14	N1	Sc1	124.68(11)	C25	C26	C27	105.75(14)
C14	N1	C11	106.92(13)	C25	C26	C44	123.66(15)
C17	N2	Sc1	124.45(10)	C27	C26	C44	130.59(16)
C20	N2	Sc1	126.79(10)	N4	C27	C26	108.31(13)
C20	N2	C17	106.90(13)	N4	C27	C28	123.08(13)
C29	N3	Sc1	124.45(10)	C28	C27	C26	128.52(14)

C32	N3	Sc1	125.02(11)	C27	C28	C29	126.61(14)
C32	N3	C29	106.30(13)	C27	C28	C35	116.60(13)
C24	N4	Sc1	124.41(11)	C29	C28	C35	116.75(13)
C24	N4	C27	106.80(13)	N3	C29	C30	108.49(13)
C27	N4	Sc1	126.99(10)	C28	C29	N3	122.82(13)
C3	C2	C1	120.3(2)	C28	C29	C30	128.10(14)
C3	C2	C7	118.34(16)	C29	C30	C34	131.98(15)
C7	C2	C1	121.3(2)	C31	C30	C29	105.68(14)
C2	C3	C4	121.99(17)	C31	C30	C34	122.30(15)
C3	C4	C5	118.72(16)	C30	C31	C32	108.80(15)
C3	C4	C8	119.66(15)	N3	C32	C31	110.65(14)
C5	C4	C8	121.61(14)	N3	C32	C33	124.40(16)
C4	C5	C10	119.30(14)	C31	C32	C33	124.90(15)
C6	C5	C4	120.39(14)	C36	C35	C28	120.41(14)
C6	C5	C10	120.30(14)	C36	C35	C40	120.18(14)
C5	C6	C9	120.41(16)	C40	C35	C28	119.41(13)
C7	C6	C5	118.83(17)	C35	C36	C42	120.92(15)
C7	C6	C9	120.76(17)	C37	C36	C35	118.93(16)
C2	C7	C6	121.71(17)	C37	C36	C42	120.14(15)

C11	C10	C5	116.10(13)	C38	C37	C36	121.95(16)
C11	C10	C17	127.90(14)	C37	C38	C39	118.13(16)
C17	C10	C5	115.86(13)	C37	C38	C43	121.94(18)
N1	C11	C12	108.26(13)	C39	C38	C43	119.93(18)
C10	C11	N1	123.55(13)	C38	C39	C40	121.83(16)
C10	C11	C12	128.13(14)	C35	C40	C41	121.23(14)
C11	C12	C15	131.09(14)	C39	C40	C35	118.97(15)
C13	C12	C11	105.85(13)	C39	C40	C41	119.79(15)
C13	C12	C15	122.92(14)	Si1	C45	Sc1	132.76(9)
C12	C13	C14	107.77(14)				

Bond length of Complex **2**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Al1	N1	1.9055(13)	C7	C17	1.4027(17)
Al1	N2	1.9058(13)	C8	C9	1.3976(18)
Al1	C23	1.9710(15)	C8	C13	1.4021(17)
Al1	C24	1.9681(15)	C9	C10	1.3908(18)
N1	C2	1.3511(16)	C9	C14	1.5089(19)
N1	C6	1.4040(16)	C10	C11	1.386(2)
N2	C17	1.4085(16)	C11	C12	1.390(2)

N2	C21	1.3471(16)	C11	C15	1.506(2)
C1	C2	1.4890(18)	C12	C13	1.3924(18)
C2	C3	1.3989(18)	C13	C16	1.5076(19)
C3	C4	1.3808(18)	C17	C18	1.4390(18)
C4	C5	1.5029(18)	C18	C19	1.504(2)
C4	C6	1.4376(17)	C18	C20	1.3776(19)
C6	C7	1.4068(17)	C20	C21	1.404(2)
C7	C8	1.4939(17)	C21	C22	1.4849(19)

Angel of Complex **2**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Al1	N2	94.12(5)	C9	C8	C7	119.35(11)
N1	Al1	C23	110.03(6)	C9	C8	C13	120.35(11)
N1	Al1	C24	111.10(6)	C13	C8	C7	120.28(11)
N2	Al1	C23	111.98(6)	C8	C9	C14	121.04(12)
N2	Al1	C24	109.24(6)	C10	C9	C8	118.83(12)
C24	Al1	C23	117.85(7)	C10	C9	C14	120.12(12)
C2	N1	Al1	125.18(9)	C11	C10	C9	122.11(13)
C2	N1	C6	107.69(11)	C10	C11	C12	117.99(12)
C6	N1	Al1	127.06(9)	C10	C11	C15	121.47(14)

C17	N2	Al1	126.99(8)	C12	C11	C15	120.54(13)
C21	N2	Al1	125.80(9)	C11	C12	C13	121.91(12)
C21	N2	C17	107.17(11)	C8	C13	C16	121.14(12)
N1	C2	C1	122.38(12)	C12	C13	C8	118.76(12)
N1	C2	C3	109.92(12)	C12	C13	C16	120.10(12)
C3	C2	C1	127.69(13)	N2	C17	C18	108.20(11)
C4	C3	C2	108.40(11)	C7	C17	N2	122.82(11)
C3	C4	C5	122.95(12)	C7	C17	C18	128.97(12)
C3	C4	C6	106.22(11)	C17	C18	C19	130.70(12)
C6	C4	C5	130.81(12)	C20	C18	C17	105.92(12)
N1	C6	C4	107.76(11)	C20	C18	C19	123.37(13)
N1	C6	C7	122.76(11)	C18	C20	C21	108.47(12)
C7	C6	C4	129.46(11)	N2	C21	C20	110.24(12)
C6	C7	C8	116.31(11)	N2	C21	C22	122.84(13)
C17	C7	C6	126.05(11)	C20	C21	C22	126.91(13)
C17	C7	C8	117.60(11)				

Bond length of Complex **3**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Al1	N1	1.9134(13)	C6	C7	1.3890(18)

Al1	N2	1.9067(12)	C6	C9	1.5061(19)
Al1	C23	1.9768(17)	C10	C11	1.497(2)
Al1	C25	1.9725(15)	C11	C12	1.399(2)
N1	C11	1.3458(17)	C12	C13	1.3776(19)
N1	C15	1.4092(16)	C13	C14	1.4984(19)
N2	C17	1.4056(15)	C13	C15	1.4393(18)
N2	C21	1.3475(17)	C15	C16	1.4040(17)
C1	C2	1.509(2)	C16	C17	1.4052(17)
C2	C3	1.388(2)	C17	C18	1.4384(17)
C2	C7	1.391(2)	C18	C19	1.4988(19)
C3	C4	1.3933(19)	C18	C20	1.3780(19)
C4	C5	1.3985(17)	C20	C21	1.3986(19)
C4	C8	1.506(2)	C21	C22	1.4935(19)
C5	C6	1.4045(17)	C23	C24	1.518(3)
C5	C16	1.4990(16)	C25	C26	1.529(2)

Angel of Complex **3**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Al1	C23	112.83(7)	N1	C11	C10	122.37(13)
N1	Al1	C25	108.31(6)	N1	C11	C12	110.34(12)

N2	Al1	N1	94.44(5)	C12	C11	C10	127.23(13)
N2	Al1	C23	108.59(7)	C13	C12	C11	108.50(12)
N2	Al1	C25	109.27(6)	C12	C13	C14	123.59(13)
C25	Al1	C23	120.29(7)	C12	C13	C15	105.96(12)
C11	N1	Al1	125.69(10)	C15	C13	C14	130.43(12)
C11	N1	C15	107.20(11)	N1	C15	C13	108.00(11)
C15	N1	Al1	126.32(9)	C16	C15	N1	122.81(11)
C17	N2	Al1	126.77(9)	C16	C15	C13	129.17(12)
C21	N2	Al1	125.90(9)	C15	C16	C5	117.13(11)
C21	N2	C17	107.33(11)	C15	C16	C17	126.31(11)
C3	C2	C1	121.33(15)	C17	C16	C5	116.49(10)
C3	C2	C7	118.28(12)	N2	C17	C18	107.94(11)
C7	C2	C1	120.39(15)	C16	C17	N2	122.85(11)
C2	C3	C4	121.81(13)	C16	C17	C18	129.18(11)
C3	C4	C5	118.81(12)	C17	C18	C19	130.31(12)
C3	C4	C8	120.31(13)	C20	C18	C17	106.09(11)
C5	C4	C8	120.88(12)	C20	C18	C19	123.59(12)
C4	C5	C6	120.48(11)	C18	C20	C21	108.37(12)
C4	C5	C16	121.03(11)	N2	C21	C20	110.27(12)

C6	C5	C16	118.48(11)	N2	C21	C22	122.52(13)
C5	C6	C9	121.03(12)	C20	C21	C22	127.21(13)
C7	C6	C5	118.73(12)	C24	C23	Al1	114.00(13)
C7	C6	C9	120.25(12)	C26	C25	Al1	113.42(11)
C6	C7	C2	121.89(13)				

Bond length of Complex **4**

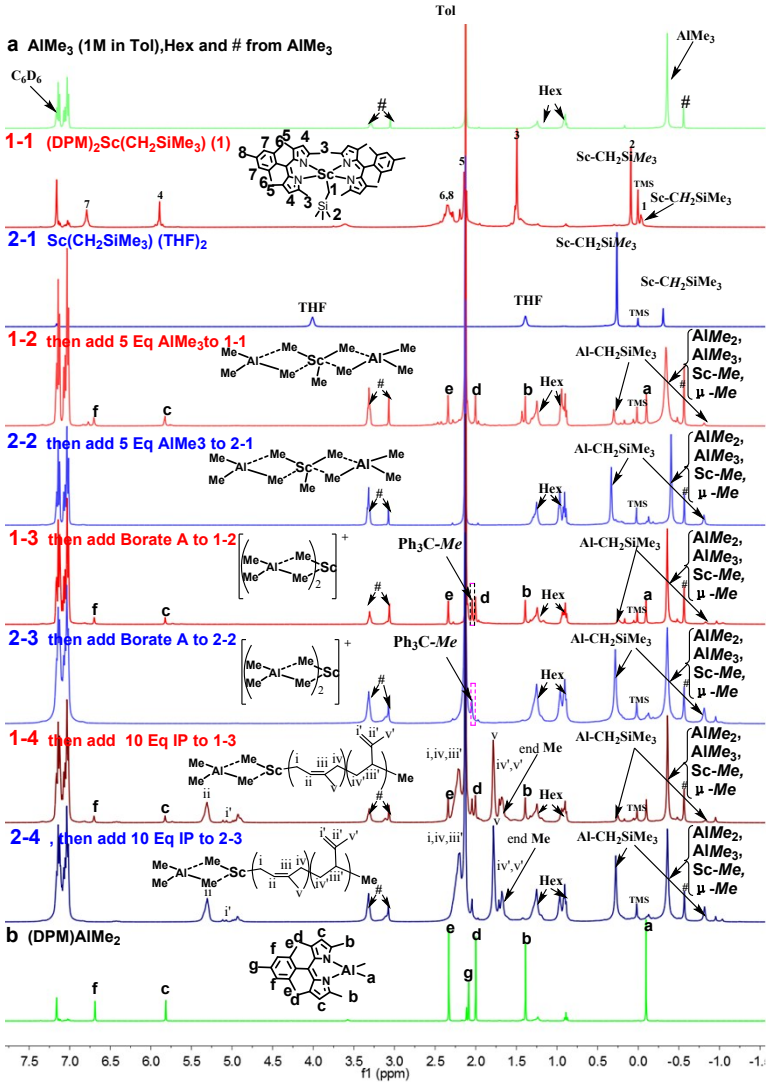
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Al1	N1	1.9098(9)	C10	C11	1.4995(15)
Al1	N2	1.9091(10)	C11	C12	1.3807(15)
Al1	C23	1.9835(11)	C11	C15	1.4420(14)
Al1	C27	1.9779(12)	C12	C13	1.4051(15)
N1	C13	1.3443(14)	C13	C14	1.4948(15)
N1	C15	1.4076(12)	C15	C16	1.4023(14)
N2	C17	1.4068(13)	C16	C17	1.4099(14)
N2	C20	1.3445(14)	C17	C18	1.4375(15)
C1	C2	1.3931(16)	C18	C19	1.3824(17)
C1	C6	1.3915(16)	C18	C21	1.4992(16)
C1	C7	1.5081(16)	C19	C20	1.4000(17)
C2	C3	1.3920(14)	C20	C22	1.4958(17)

C3	C4	1.4023(14)	C23	C25	1.5265(16)
C3	C8	1.5057(15)	C24	C25	1.520(2)
C4	C5	1.4034(14)	C25	C26	1.5289(17)
C4	C16	1.4971(13)	C27	C29	1.5354(15)
C5	C6	1.3928(14)	C28	C29	1.5259(18)
C5	C9	1.5082(15)	C29	C30	1.5291(16)

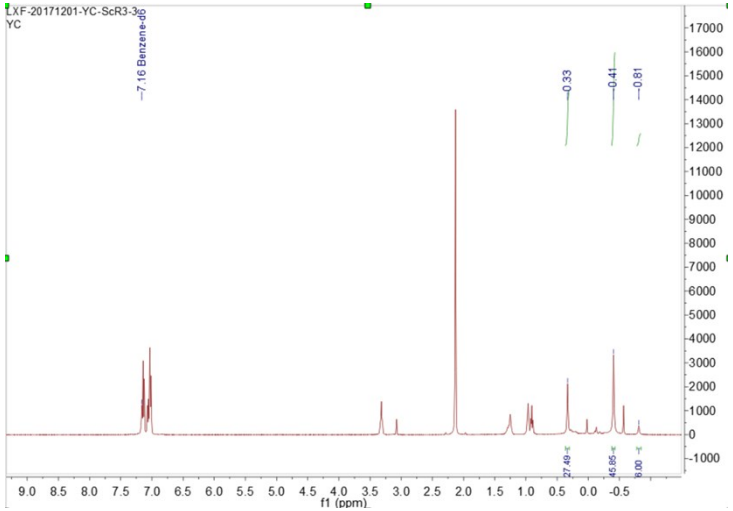
Angel of Complex **4**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Al1	C23	110.18(4)	C11	C12	C13	108.27(10)
N1	Al1	C27	112.30(5)	N1	C13	C12	110.22(9)
N2	Al1	N1	93.85(4)	N1	C13	C14	122.67(10)
N2	Al1	C23	112.74(5)	C12	C13	C14	127.11(10)
N2	Al1	C27	111.04(5)	N1	C15	C11	107.85(9)
C27	Al1	C23	114.89(5)	C16	C15	N1	122.80(9)
C13	N1	Al1	125.11(7)	C16	C15	C11	129.34(9)
C13	N1	C15	107.59(8)	C15	C16	C4	117.78(9)
C15	N1	Al1	127.25(7)	C15	C16	C17	125.86(9)
C17	N2	Al1	126.95(7)	C17	C16	C4	116.37(9)
C20	N2	Al1	125.30(8)	N2	C17	C16	122.79(9)

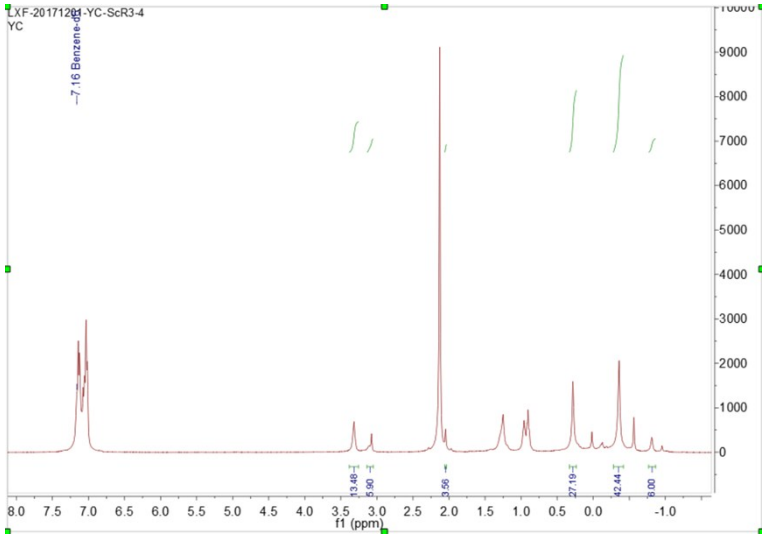
C20	N2	C17	107.46(9)	N2	C17	C18	107.93(9)
C2	C1	C7	120.78(11)	C16	C17	C18	129.25(10)
C6	C1	C2	118.03(10)	C17	C18	C21	130.99(11)
C6	C1	C7	121.18(11)	C19	C18	C17	106.03(10)
C3	C2	C1	121.98(10)	C19	C18	C21	122.93(10)
C2	C3	C4	118.95(9)	C18	C19	C20	108.25(10)
C2	C3	C8	120.29(9)	N2	C20	C19	110.31(10)
C4	C3	C8	120.75(9)	N2	C20	C22	122.90(11)
C3	C4	C5	120.12(9)	C19	C20	C22	126.79(11)
C3	C4	C16	119.59(9)	C25	C23	Al1	117.57(7)
C5	C4	C16	120.28(8)	C23	C25	C26	112.66(10)
C4	C5	C9	120.86(9)	C24	C25	C23	110.56(12)
C6	C5	C4	119.10(9)	C24	C25	C26	109.41(11)
C6	C5	C9	120.04(9)	C29	C27	Al1	118.18(7)
C1	C6	C5	121.80(10)	C28	C29	C27	111.72(9)
C12	C11	C10	123.34(10)	C28	C29	C30	110.11(10)
C12	C11	C15	106.06(9)	C30	C29	C27	111.48(10)
C15	C11	C10	130.60(10)				



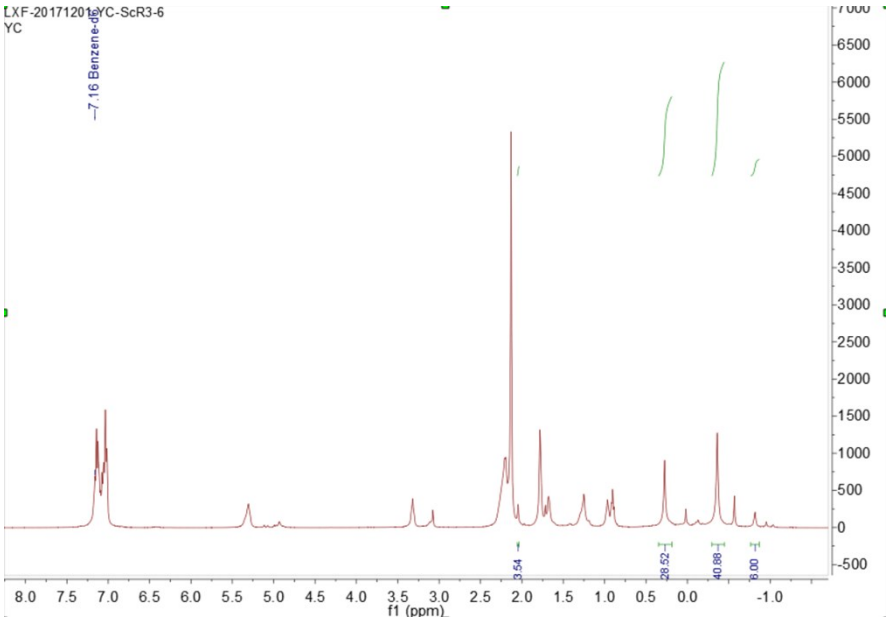
SFigure 36. *In-situ* ^{1}H NMR spectrum under different catalyst system at 25 °C in C_6D_6.



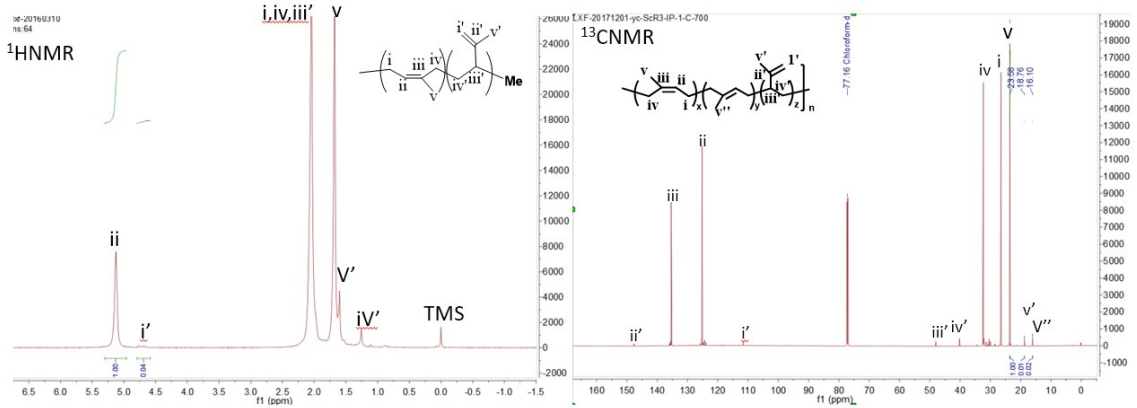
SFigure 37. The original *in-situ* ^{1}H NMR spectrum of SFigure 36 : 2-2.



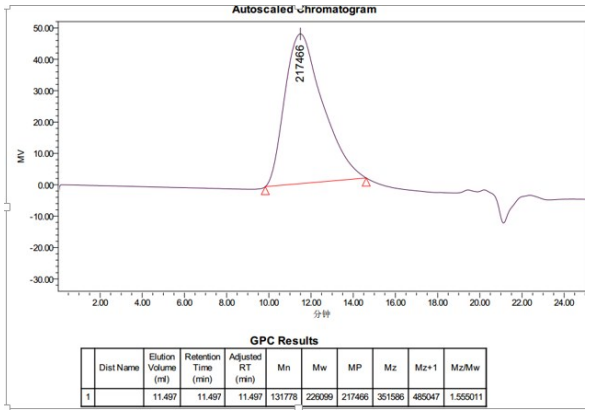
SFigure 38. The original *in-situ* ^{1}H NMR spectrum of SFigure 36 : 2-3.



SFigure 39. The original *in-situ* ^{1}H NMR spectrum of SFigure 36 : 2-4.



SFigure 40. ^{1}H NMR and ^{13}CNMR spectra of the polyisoprenes by $Sc(CH_2SiMe_3)_3(THF)_2/AlR_3$/Borate A systems in $CDCl_3$ in Table 1, entry 14.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.497	11.497	11.497	131778	228099	217466	351586	485047	1.555011

SFigure 41. GPC profiles of the polyisoprenes by $Sc(CH_2SiMe_3)_3(THF)_2/AlMe_3/[Ph_3C][B(C_6F_5)_4]$ systems in Table 1, entry 14.