Supporting Information

Nature of the Entire Range of Rare-Earth Metal Based Cationic Catalysts for Highly Active and Syndioselective Styrene Polymerization

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Content

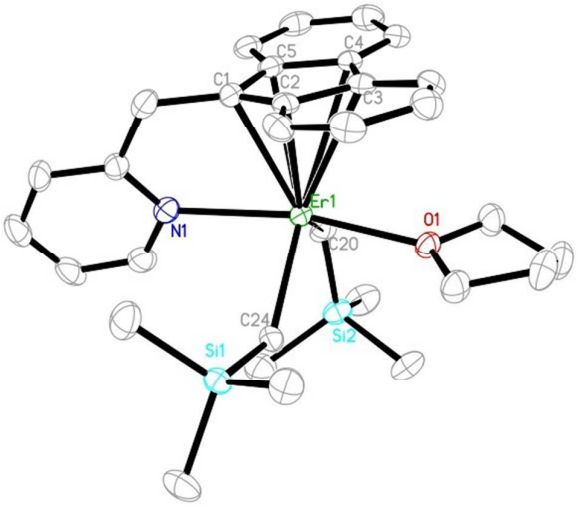


Figure S1. X-ray structure of complex **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

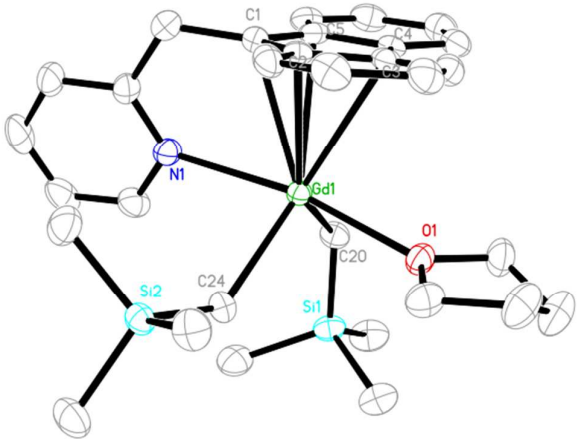


Figure S2. X-ray structure of complex **9** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

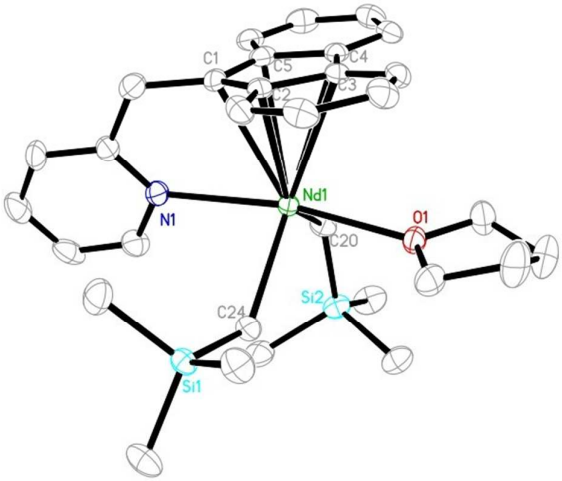


Figure S3. X-ray structure of complex **10** with thermal ellipsoids drawn at the 30%

probability level. Hydrogens are omitted for clarity.

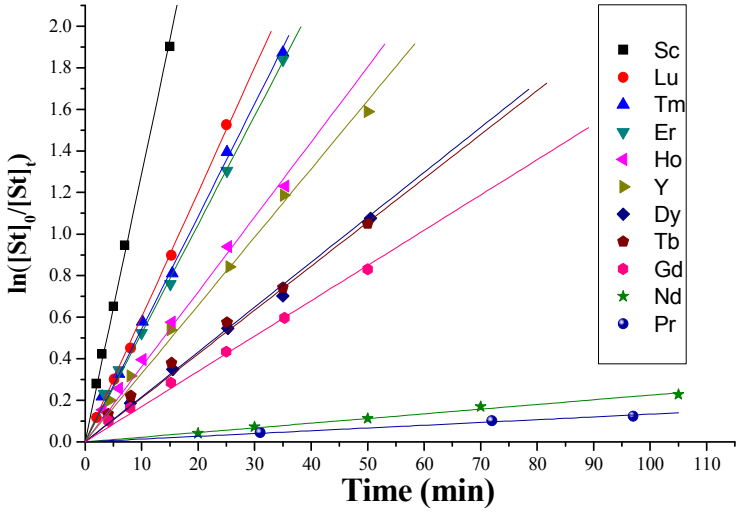


Figure S4. Plot of $\ln([St]_0/[St]_t)$ vs. time catalyzed by complex **1-11**. (Ln (10μmol), [Ln]/[Al^{i}Bu$_3$]/[Ph$_3$C][B(C$_6$F$_5$)$_4$]/[St] = 1/5/1/2000 (mol/mol/mol), toluene/monomer = 30/1 (v/v), T_p = 15 °C.)

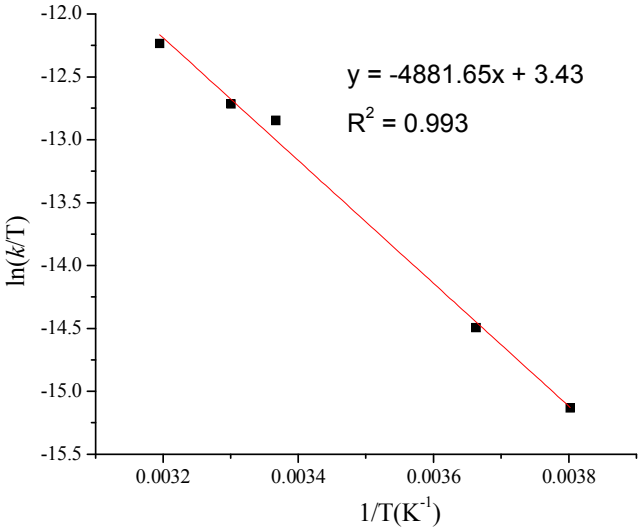


Figure S5. Eyring-plot for Sc(**1**)-catalyzed St polymerization in toluene ($\Delta H^{\ddagger}$ = 40.59 kJ mol^{-1}, $\Delta S^{\ddagger}$ = -169.01 J (mol K)$^{-1}$).

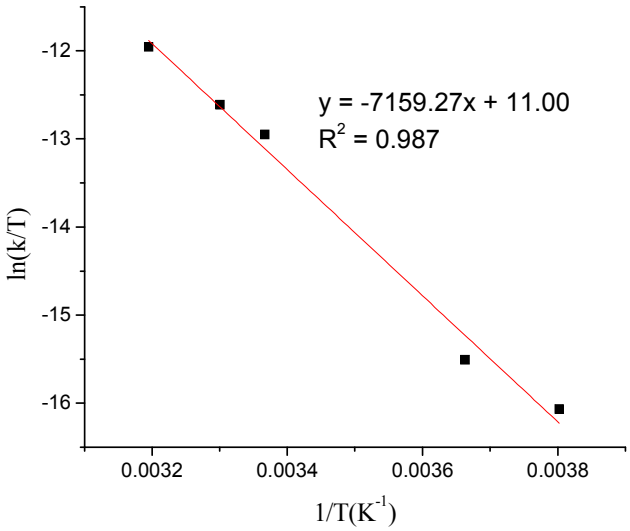


Figure S6. Eyring-plot for Lu(**2**)-catalyzed St polymerization in toluene ($\Delta H^{\ddagger}$ = 59.53 kJ mol^{-1}, $\Delta S^{\ddagger}$ = -106.09 J (mol K)$^{-1}$).

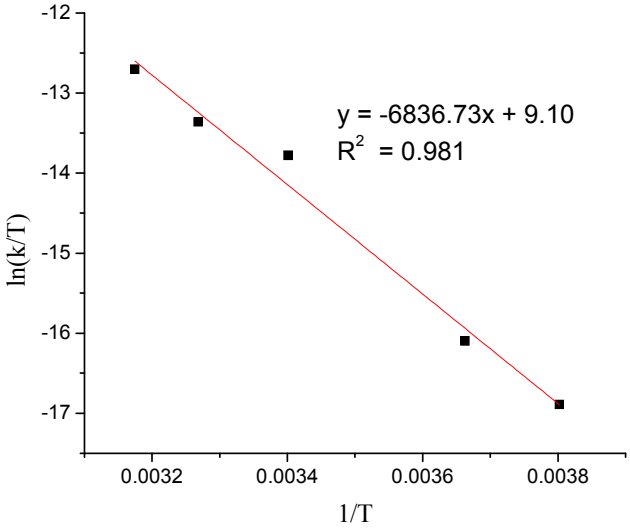


Figure S7. Eyring-plot for Ho(**5**)-catalyzed St polymerization in toluene ($\Delta H^{\ddagger}$ = 56.84 kJ mol^{-1}, $\Delta S^{\ddagger}$ = -121.89 J (mol K)$^{-1}$).

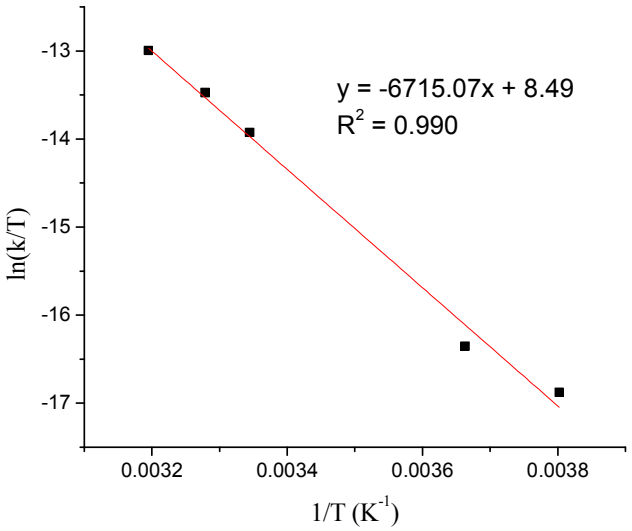


Figure S8. Eyring-plot for Gd(**9**)-catalyzed St polymerization in toluene ($\Delta H^{\ddagger}$ = 55.83 kJ mol^{-1}, $\Delta S^{\ddagger}$ = -126.96 J (mol K)$^{-1}$).

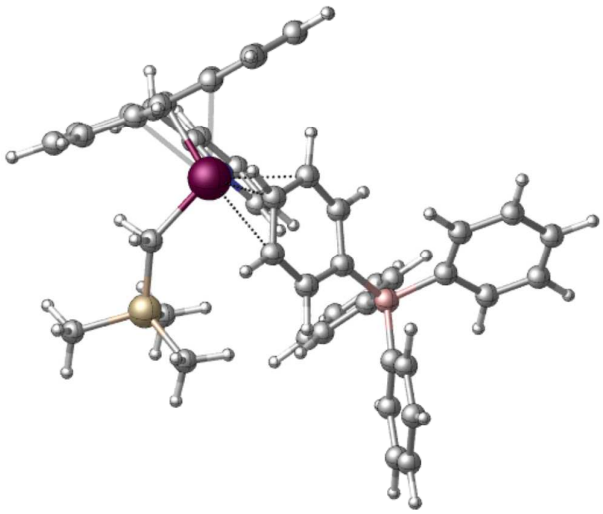
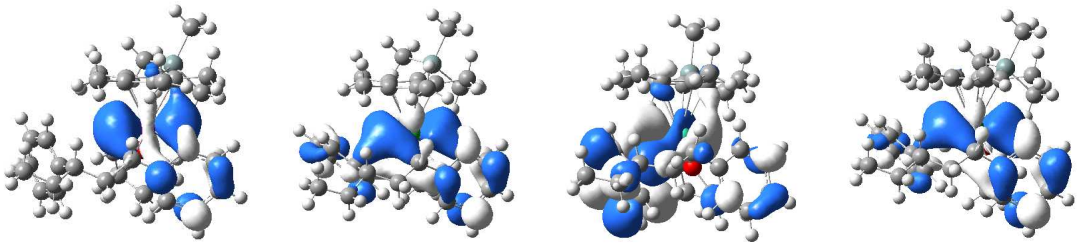


Figure S9. The molecular structure of the ion pair of [(Flu−CH_2−Py)Sc(CH_2SiMe_3)]$^+$[$B(C_6H_6)_4$]$^-$ simulated by DFT calculation.



Metal	Sc	Gd	Y	Lu
E_{LUMO} [a] (au)	-0.17276	-0.16068	-0.15312	-0.14955
ΔE [b] (au)	0.05312	0.06520	0.07276	0.07633
Activity [c] kg/(mol$_{(Ln)}$•h)	13618	15	13	6

[a] The LUMO energy of $[C_5Me_4SiMe_3)Ln–(C_{17}H_{19})]^+$ was analyzed on the basis of its optimized geometry afforded via using small core RECPs basic sets; [b] $\Delta E = E_{LUMO(active\ species)} - E_{HOMO(Styrene)}$ ($E_{HOMO(Styrene)}$ = –0.22588 au); [c] The values come from reference 3

Figure S10. LUMOs of $[(C_5Me_4SiMe_3)Ln(C_{17}H_{19})(THF)]^+$ complexes. The isosurface value of the MOs is set to be 0.03 au.

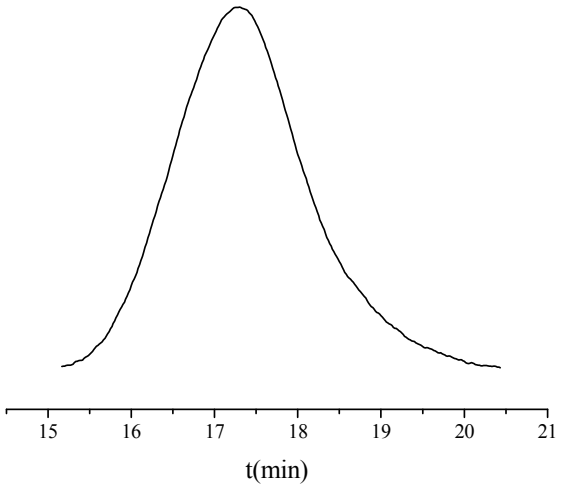


Figure S11. GPC curve of sPS (entry 1, Table 1).

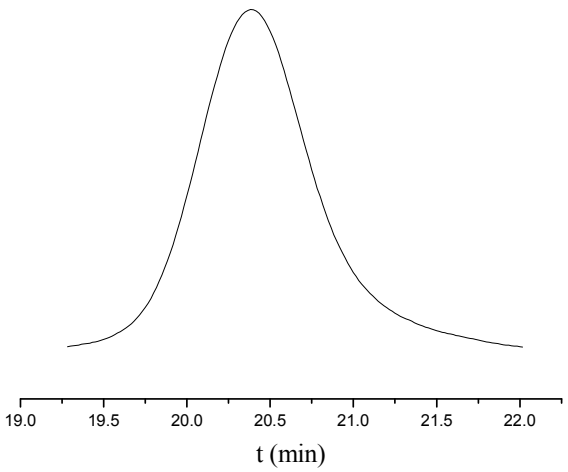


Figure S12. GPC curve of sPS (entry 5, Table 1).

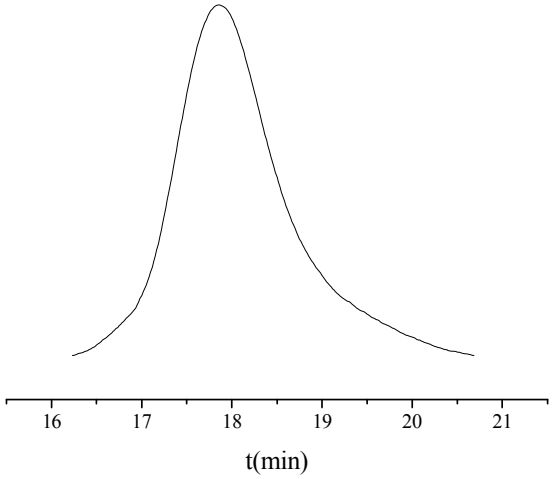


Figure S13. GPC curve of sPS (entry 9, Table 1).

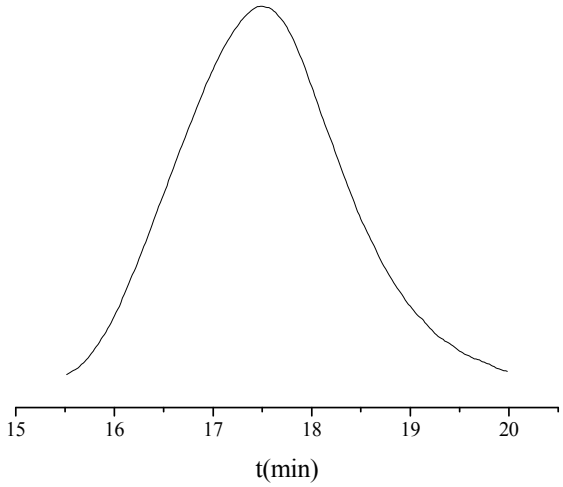


Figure S14. GPC curve of sPS (entry 10, Table 1).

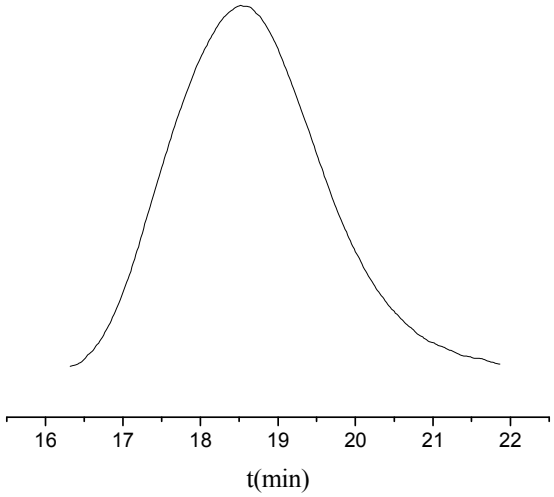


Figure S15. GPC curve of sPS (entry 16, Table 1).

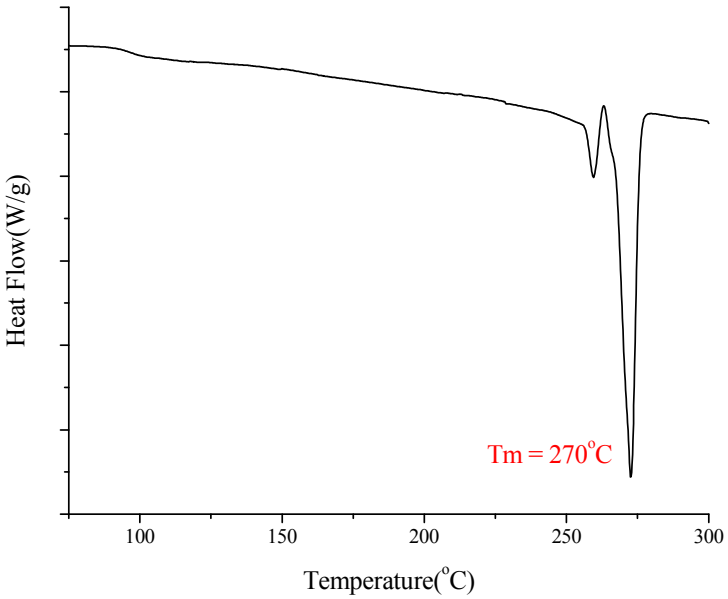


Figure S16. DSC curve of sPS (entry 1, Table 1).

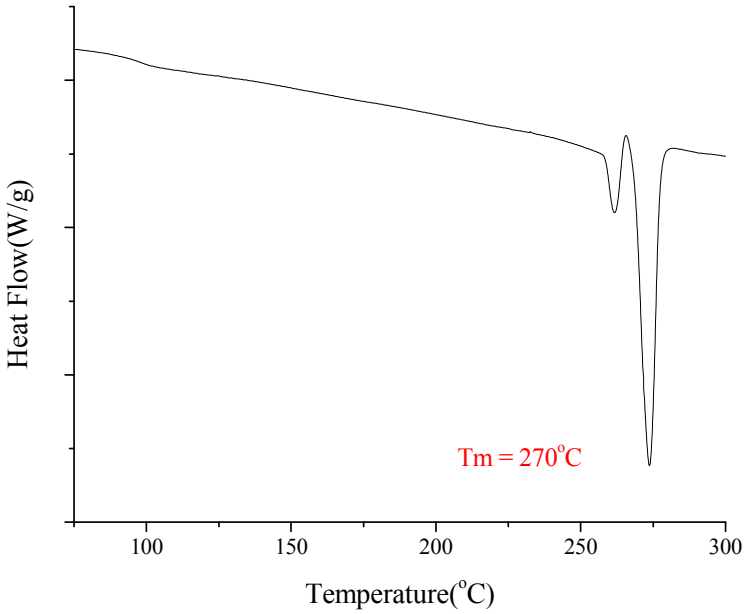


Figure S17. DSC curve of sPS (entry 12, Table 1).

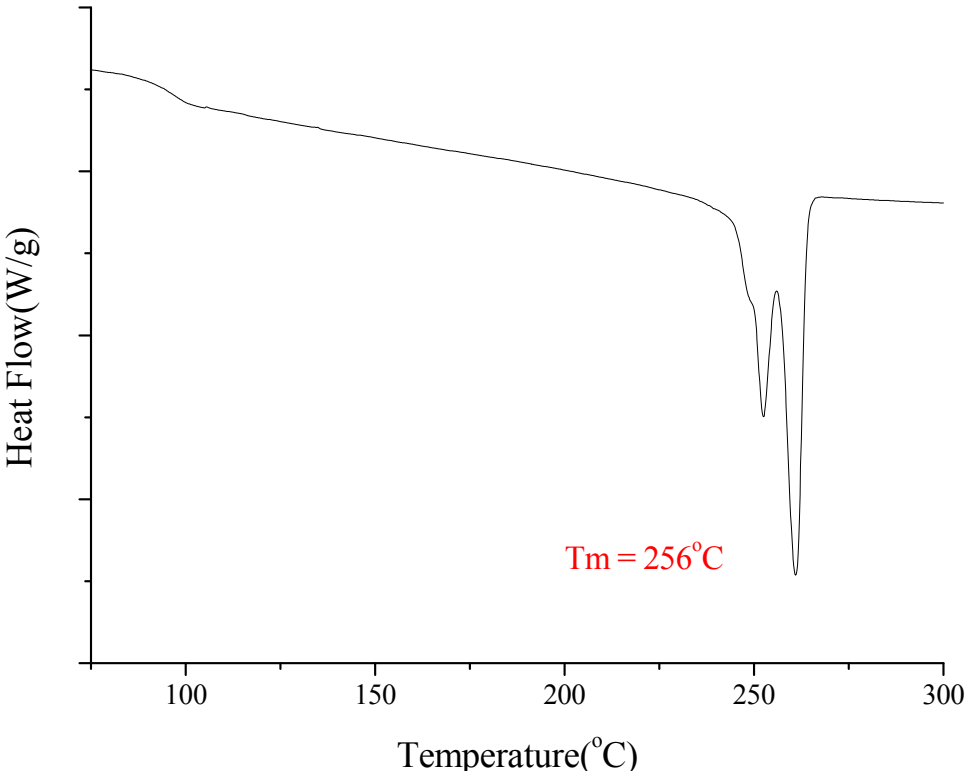


Figure S18. DSC curve of sPS (entry 13, Table 1).

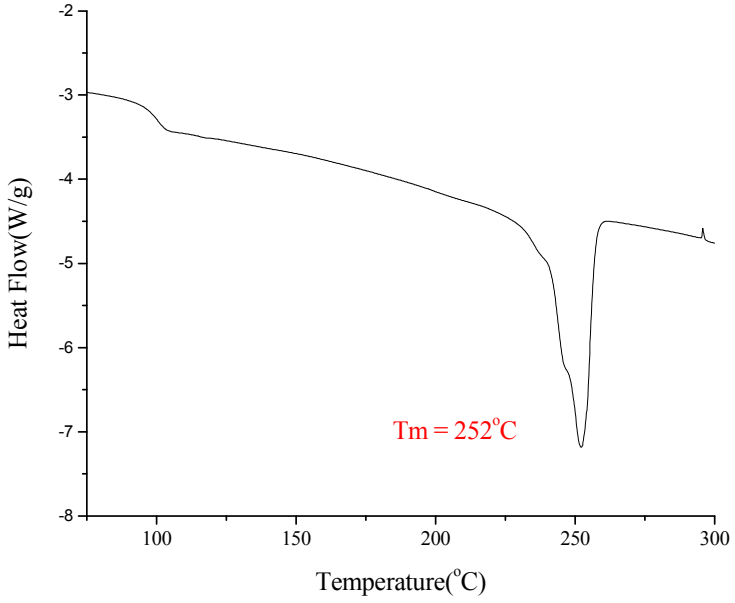


Figure S19. DSC curve of sPS (entry 14, Table 1).

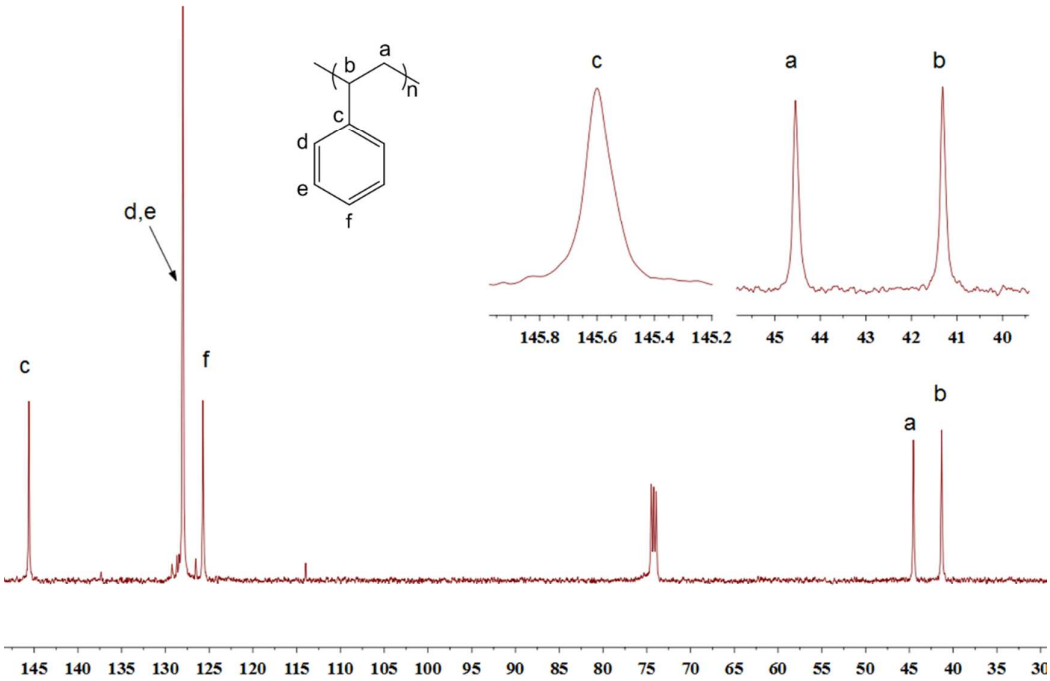


Figure S20. ^{13}C NMR spectrum of sPS in *d*-$C_2D_2Cl_4$, *rrrr*＞99% at 125°C (75.5 MHz).

Table S1. Selected bond distances (Å) and angles (deg) of complexes **2, 4**, **9**, **10** and **11**

	Ln-Flu_{cent} distance(Å)	Ln-N distance(Å)	Ln-C distance[a](Å)	Bite angles(deg)
2(Lu)	2.502(3)	2.460(3)	2.340(4)	92.23(7)
4(Er)	2.507(4)	2.490(4)	2.366(5)	91.53(10)
9(Gd)	2.551(4)	2.552(4)	2.421(4)	89.75(8)
10(Nd)	2.595(4)	2.605(4)	2.462(4)	88.20(8)
11(Pr)	2.582(11)	2.630(11)	2.472(15)	88.58(25)

[a] an average distance of Ln-C_{alkyl}.

Table S2. Syndiospecific polymerization of styrene with rare-earth metal bisalkyl complexes **1-12** activated by Al^iBu_3 and $[Ph_3C][B(C_6F_5)_4]$ with low conversion.[a]

Entry	Cat.	t(min)	Conv.(%)	M_n[b]×10^{-4}	M_w/M_n[b]
1	Sc(**1**)	5	69.7	20.1	1.34
2	Lu(**2**)	5	48.2	17.2	1.22
3	Tm(**3**)	5	46.9	16.5	1.21
4	Er(**4**)	5	34.9	12.5	1.17
5	Ho(**5**)	5	34.7	13.2	1.22
6	Y(**6**)	5	32.5	10.2	1.14

7	Dy(**7**)	5	23.6	8.9	1.23
8	Tb(**8**)	5	20.2	8.6	1.16
9	Gd(**9**)	5	18.6	8.3	1.25
10	Nd(**10**)	30	10.4	8.6	1.34
11	Pr(**11**)	60	9.9	7.9	1.49
12	La(**12**)	120	0	--	--

[a] Polymerization conditions: Ln (10 μmol), [Cat]/Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$]/St = 1/10/1/2500 (mol/mol/mol/mol), toluene/monomer = 10/1 (v/v), T_p = 20 °C. [b] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against polystyrene standard.

Table S3 Temperature-dependent kinetics for Sc(**1**)-catalyzed St polymerization (0.1389 mmol L^{-1} Sc(**1**), 0.1389 mmol L^{-1} [Ph$_3$C][B(C$_6$F$_5$)$_4$], 1.3889 mmol L^{-1} Al^{i}Bu$_3$, 0.2778 mol L^{-1} St, toluene)

Entry	T/K	k(s^{-1})	ln(k/T)	1/T
1	263	7.04823E-05	-15.13230298	0.003802281
2	273	0.000138477	-14.49427811	0.003663004
3	297	0.00078302	-12.84608446	0.003367003
4	303	0.0009091	-12.71678826	0.00330033
5	313	0.00152	-12.23524813	0.003194888

Table S4 Temperature-dependent kinetics for Lu(**2**)-catalyzed St polymerization (0.1389 mmol L^{-1} Lu(**2**), 0.1389 mmol L^{-1} [Ph$_3$C][B(C$_6$F$_5$)$_4$], 1.3889 mmol L^{-1} Al^{i}Bu$_3$, 0.2778 mol L^{-1} St, toluene)

Entry	T/K	k(s^{-1})	ln(k/T)	1/T
1	263	2.76537E-5	-16.06790506	0.003802281
2	273	5.02225E-5	-15.50851922	0.003663004
3	297	7.05931E-4	-12.9497252	0.003367003
4	303	0.00101	-12.61153775	0.00330033
5	313	0.00201	-11.95582375	0.003194888

Table S5. Temperature-dependent kinetics for Ho(**5**)-catalyzed St polymerization (0.1389 mmol L^{-1} Ho(**5**), 0.1389 mmol L^{-1} [Ph$_3$C][B(C$_6$F$_5$)$_4$], 1.3889 mmol L^{-1} Al^{i}Bu$_3$, 0.2778 mol L^{-1} St, toluene)

Entry	T/K	k(s^{-1})	ln(k/T)	1/T
1	263	1.21691E-05	-16.8888	0.003802281
2	273	2.78936E-05	-16.0966	0.003663004
3	294	0.000305311	-13.7778	0.003401361
4	306	0.000482293	-13.3605	0.003267974
5	315	0.000957917	-12.7033	0.003174603

Table S6. Temperature-dependent kinetics for Gd(**9**)-catalyzed St polymerization (0.1389 mmol L^{-1} Gd(**9**), 0.1389 mmol L^{-1} $[Ph_3C][B(C_6F_5)_4]$, 1.3889 mmol L^{-1} Al^iBu_3, 0.2778 mol L^{-1} St, toluene)

Entry	T/K	k(s^{-1})	ln(k/T)	1/T
1	263	1.23051E-5	-16.87765078	0.003802281
2	273	2.15671E-5	-16.35381335	0.003663004
3	299	2.68019E-4	-13.92489626	0.003344482
4	305	4.29448E-4	-13.47332167	0.003278689
5	313	7.10801E-4	-12.99532125	0.003194888