Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Bis(phenolate) N-Heterocyclic Carbene Rare Earth Metal Complexes: Synthesis, characterization and Applications in the Polymerization of n-Hexyl Isocyanate

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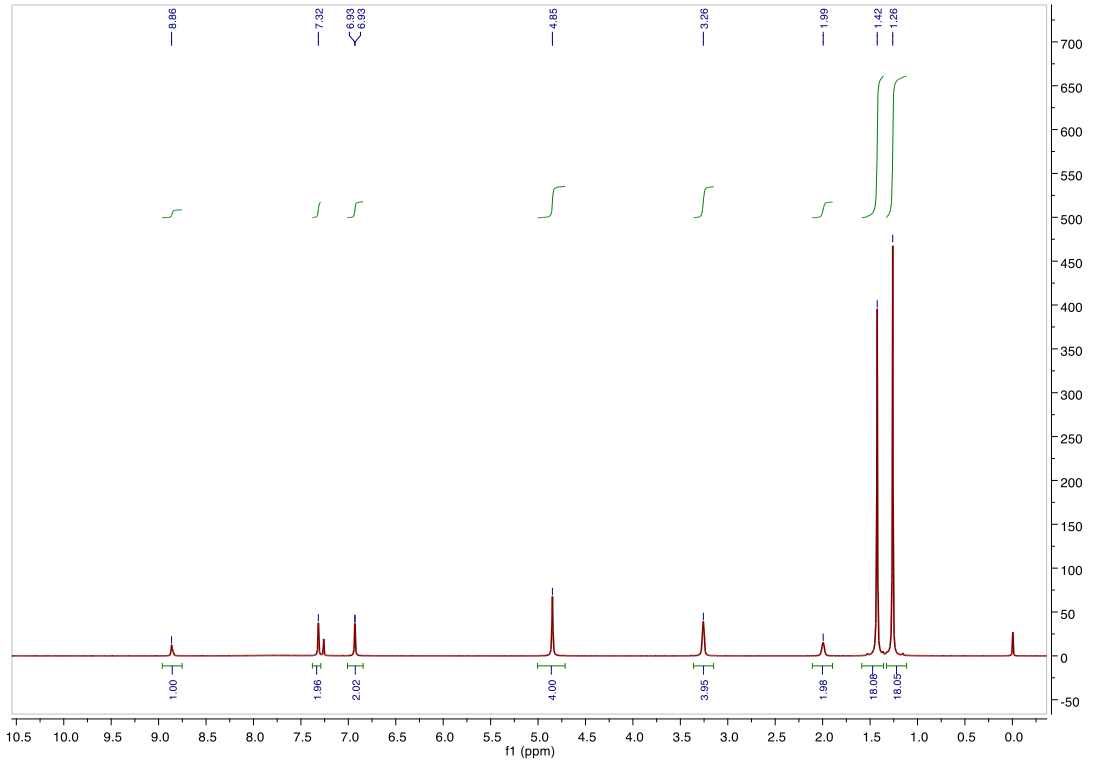

Fig. s1 ^{1}H NMR spectrum of **L1** in $CDCl_3$

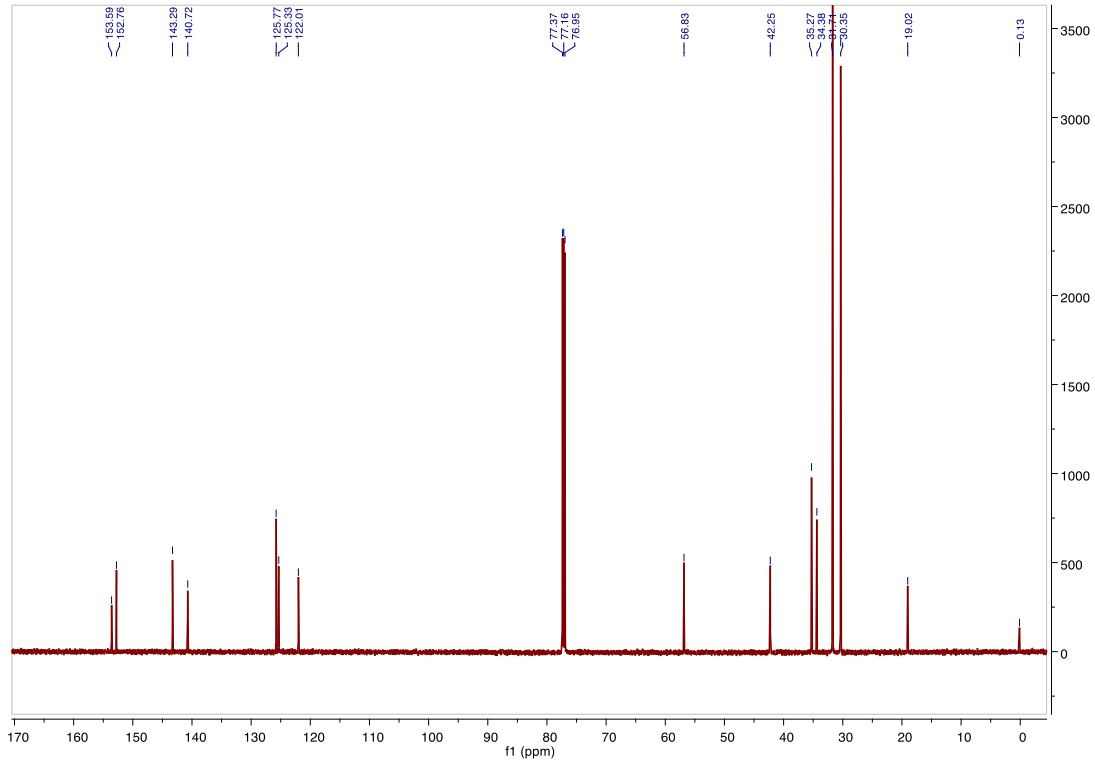

Fig. s2 ^{13}C NMR spectrum of **L1** in $CDCl_3$

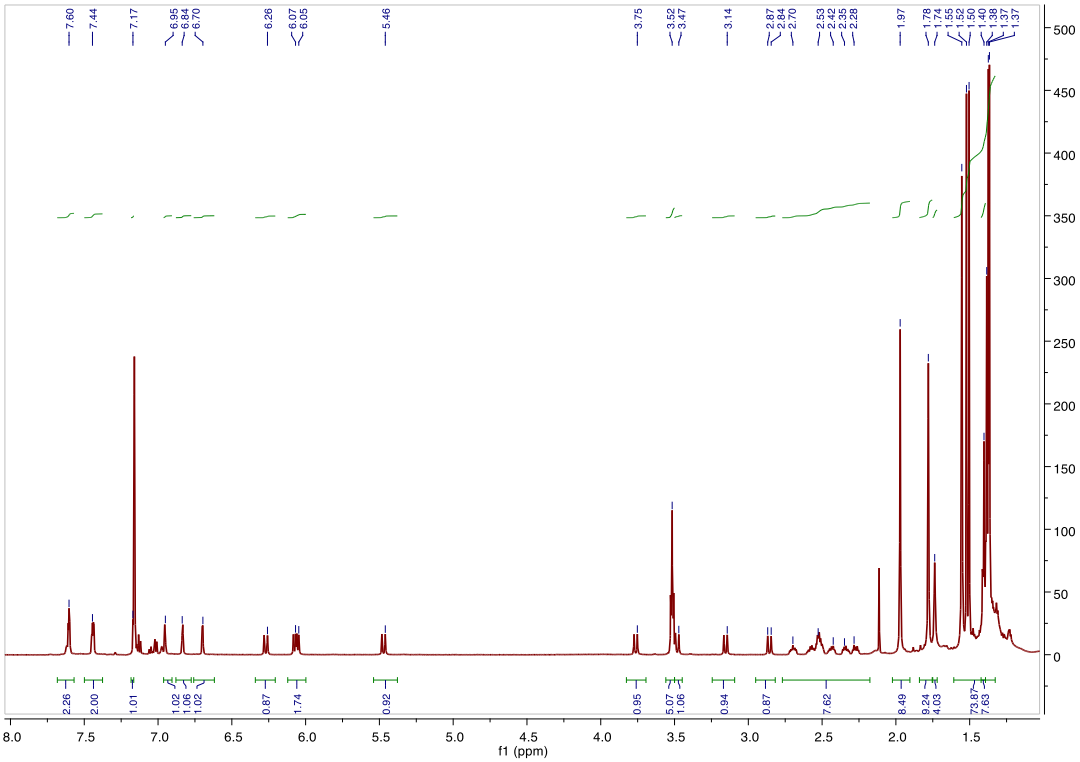

Fig. s3 ^{1}H NMR spectrum of complex **2** in C_6D_6

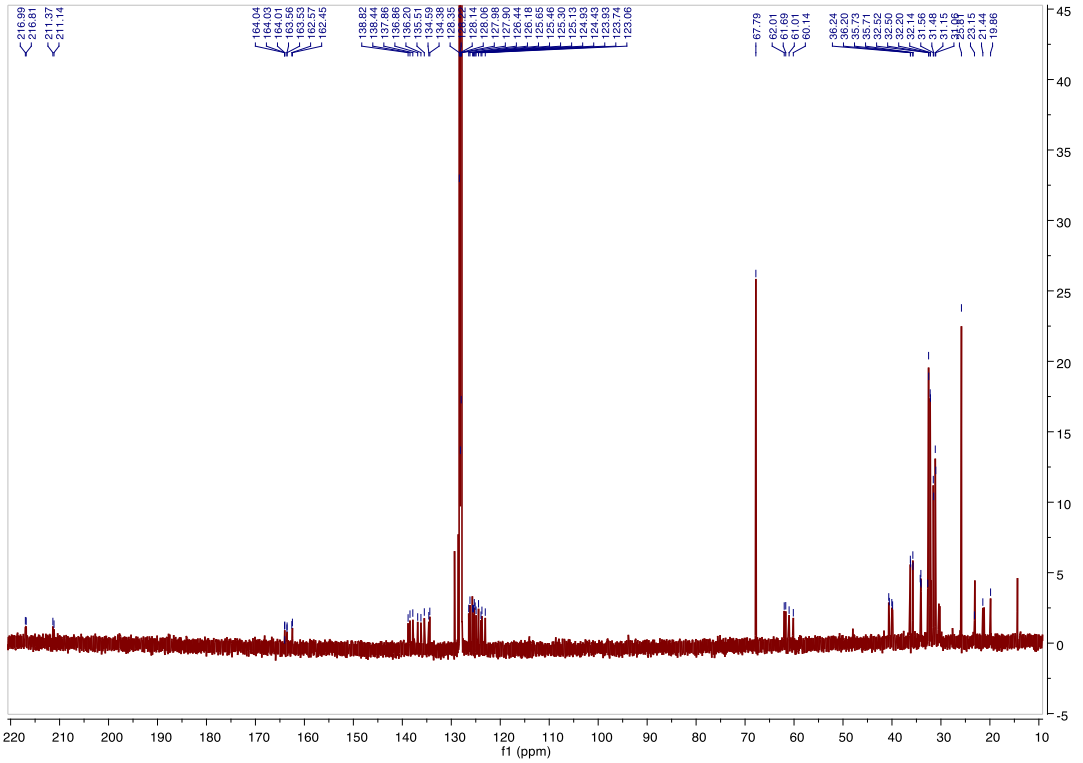

Fig. s4 ^{13}C NMR spectrum of complex **2** in C_6D_6

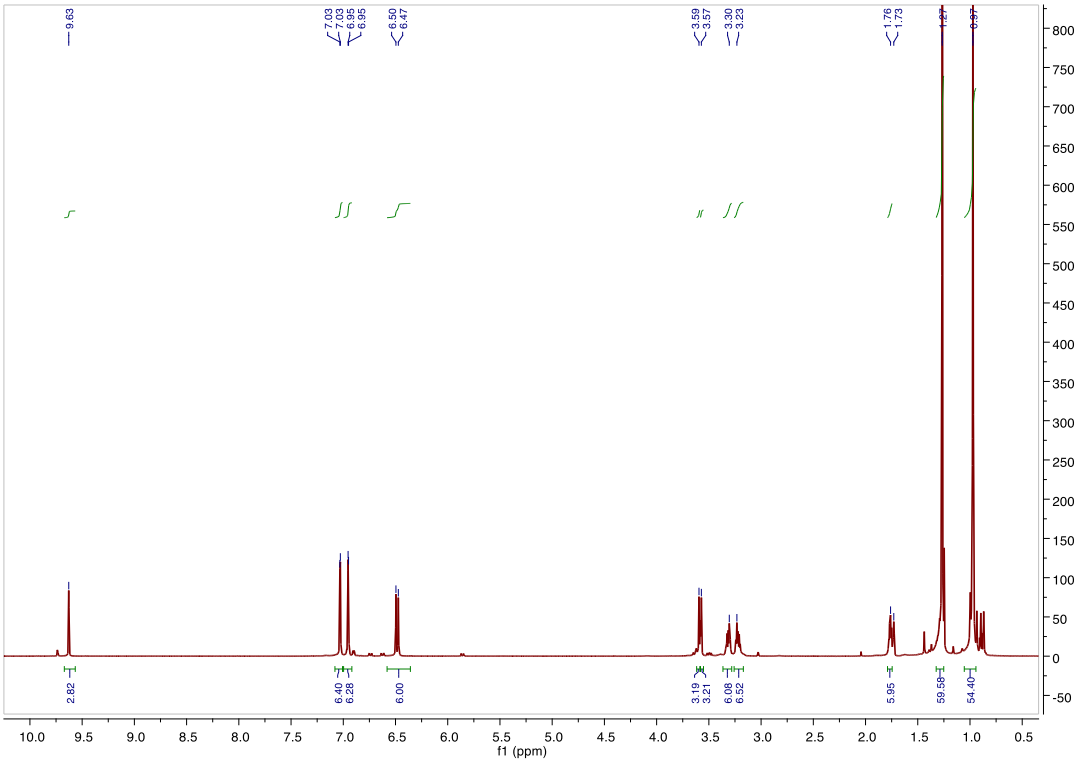

Fig. s5 ^{1}H NMR spectrum of complex **4** in THF-d_8

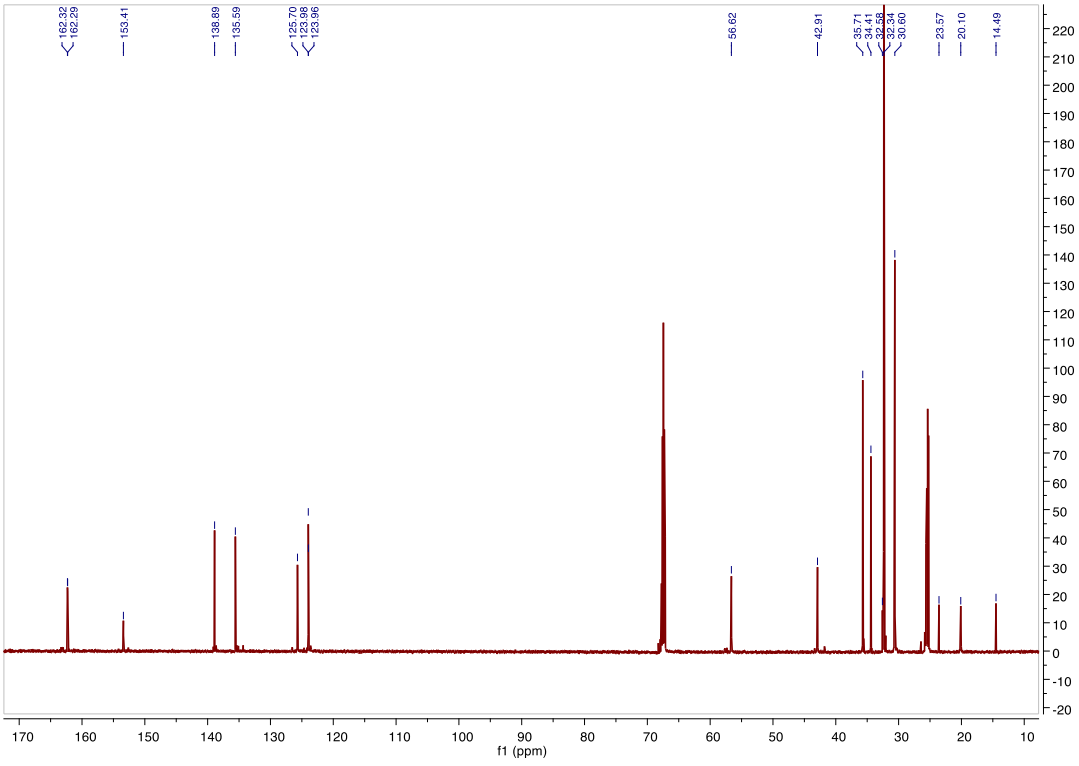

Fig. s6 ^{13}C NMR spectrum of complex **4** in THF-d_8

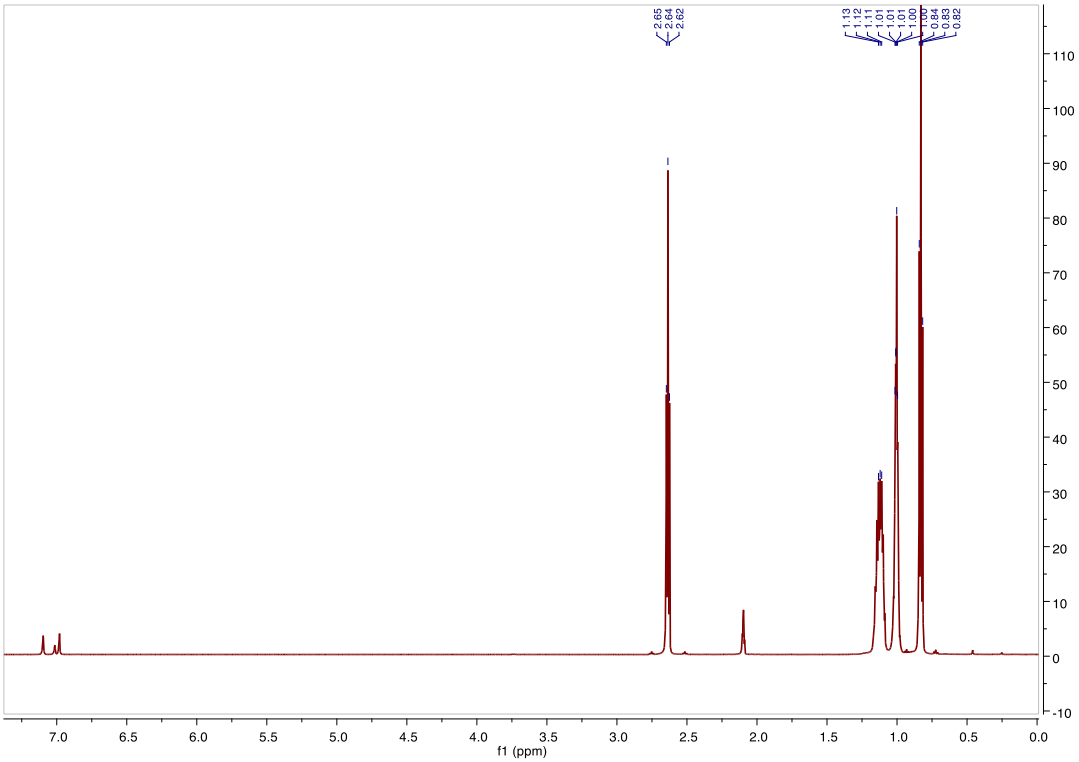

Fig. s7 ^{1}H NMR spectrum of *n*-hexyl isocyanate in toluene-d_8

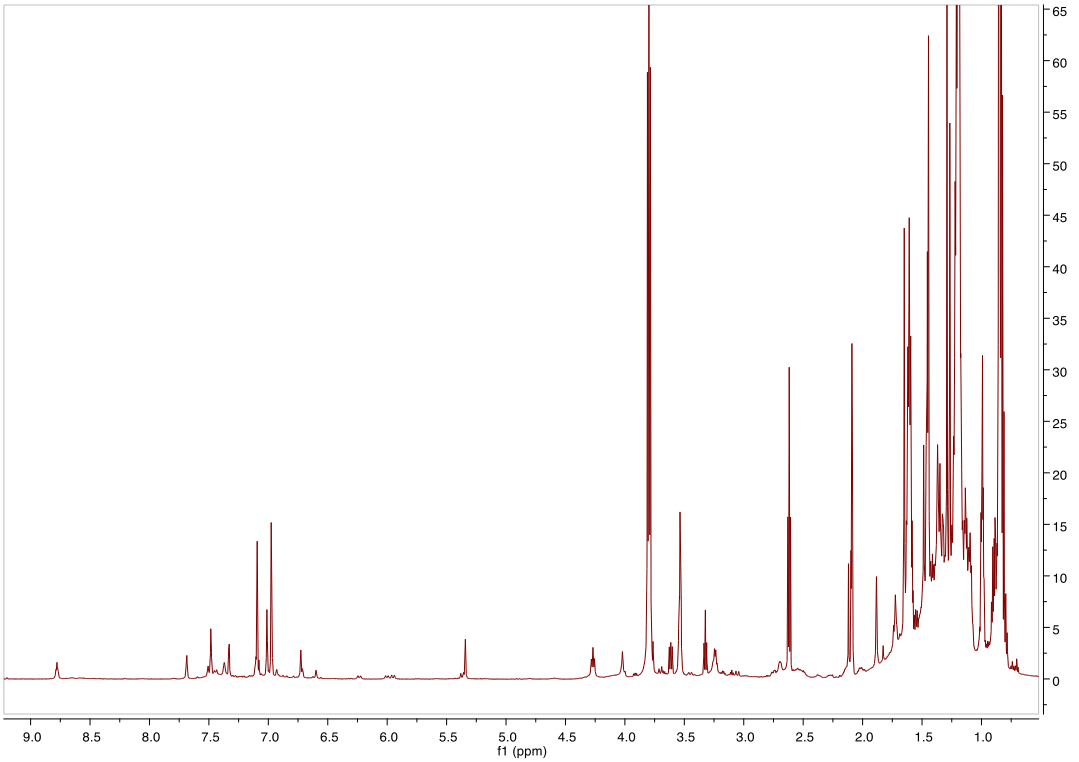

Fig. s8 ^{1}H NMR spectrum of in situ polymerization in toluene-d_8 with complex **2** nearly all participated in the initiation

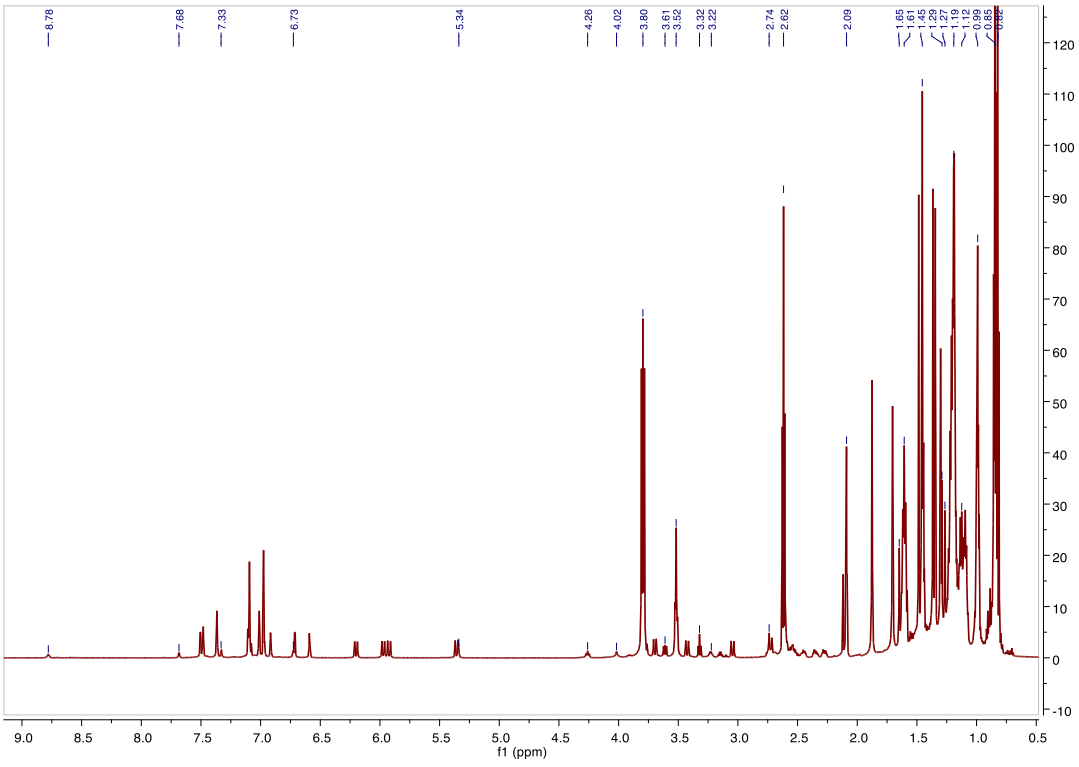

Fig. s9 ^{1}H NMR spectrum of in situ polymerization in toluene-d_8 with complex **2** a small amount participated in the initiation

The peak picked are the same with the peak shown in **Fig. s8**, and the remaining peaks represent the unreacted hydrogens of complex **2**, which can be identified by comparison with **Fig. s3**.

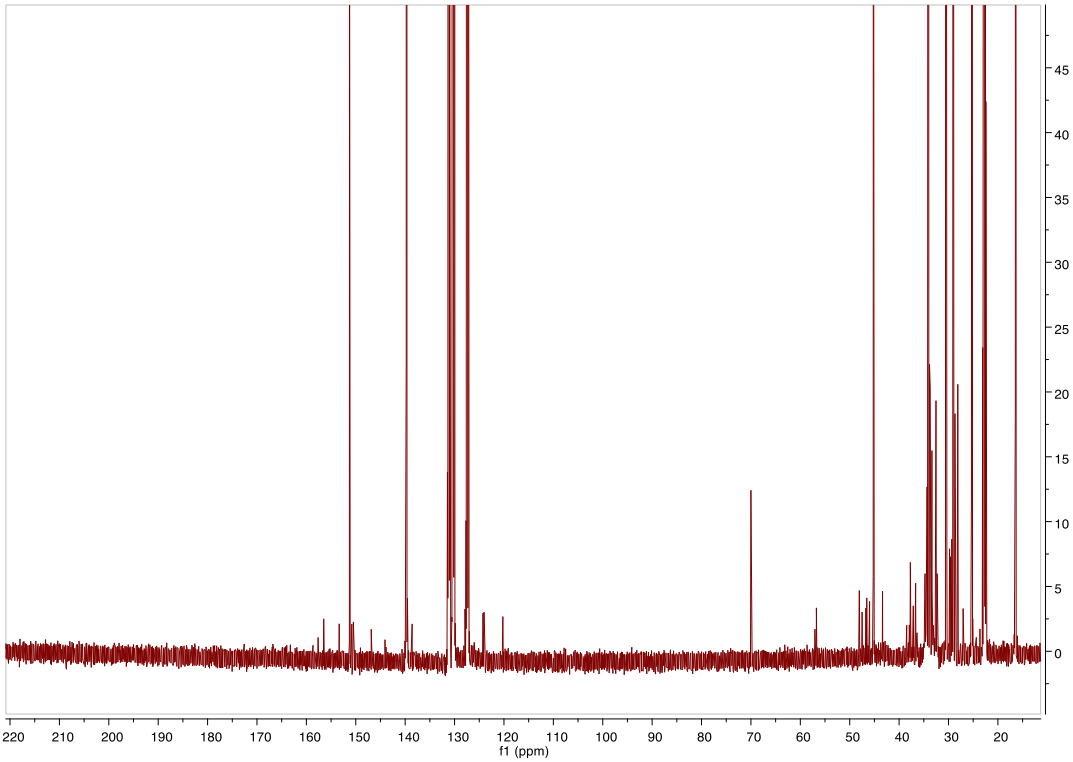

Fig. s10 ^{13}C NMR spectrum of in situ polymerization in toluene-d_8 with complex **2** nearly all participated in the initiation

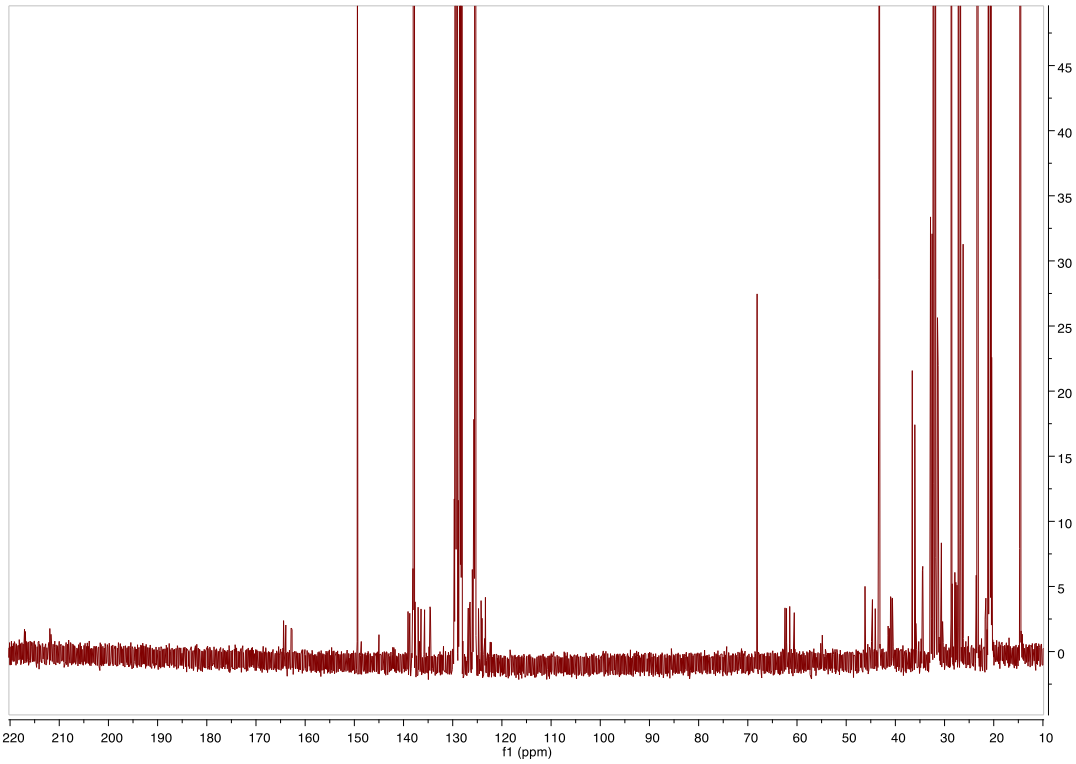

Fig. s11 ^{13}C NMR spectrum of in situ polymerization in toluene-d_8 with complex **2** a small amount participated in the initiation

It can be seen that after initiation, the signals of carbon on methane Ar*C*H$_2$N move up field (from δ 62.41, 62.13, 61.47, 60.56 to 55.17, 54.87). the signals of carbon on the NHC ring N*C*H$_2$C*H*$_2$*C*H$_2$N move upfield (from δ 40.96, 40.84, 40.59, 40.48 to 36.05, 35.84, 35.76, 35.25). The enhanced intensity of the signals at δ 45.62, 44.87 represent the chiral carbon on the deprotonated monomer. The high resonance $C_{carbene}$ at δ 211.93, 216.94 disappear in **Fig. s10**. And this further confirms the bond breakage of NHC and yttrium.

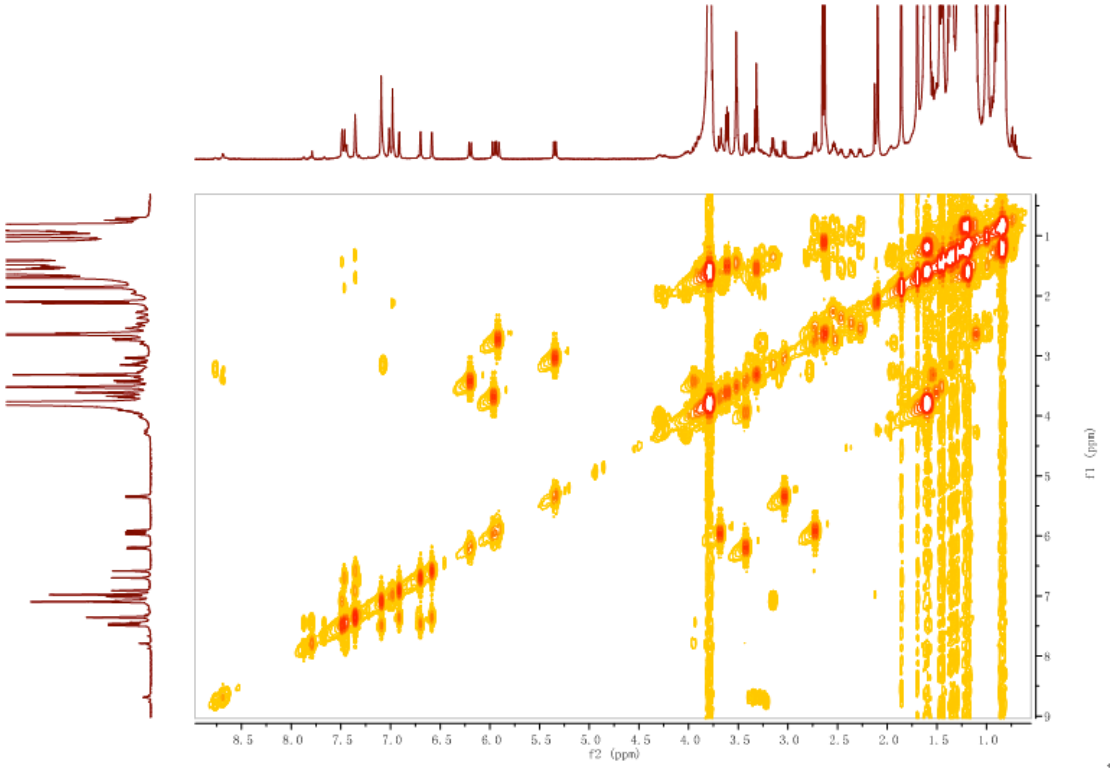

Fig. s12 ^{1}H-^{1}H COSY spectrum of in situ polymerization in toluene-d_8 with complex **2** a small amount participated in the initiation (overview).

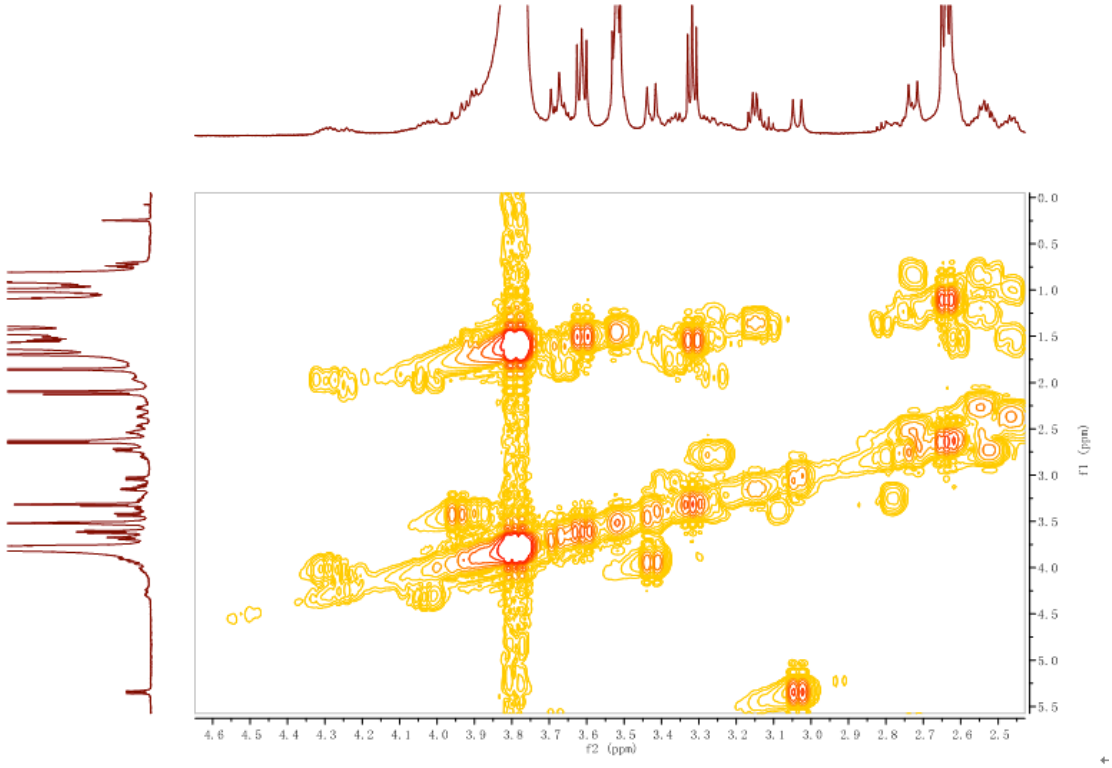

Fig. s13 ^{1}H-^{1}H COSY spectrum of in situ polymerization in toluene-d_8 with complex **2** a small amount participated in the initiation (part).

After hydrogen-abstraction, the hydrogen left H^{i} on the chiral carbon occurred at δ 4.26, 4.02 and the methene signals were coupled with protons H^{j} on adjacent carbon. The signal at δ 3.22 H^{k} was coupled with H^{t} and H^{j} on the ^{1}H-^{1}H COSY spectrum.

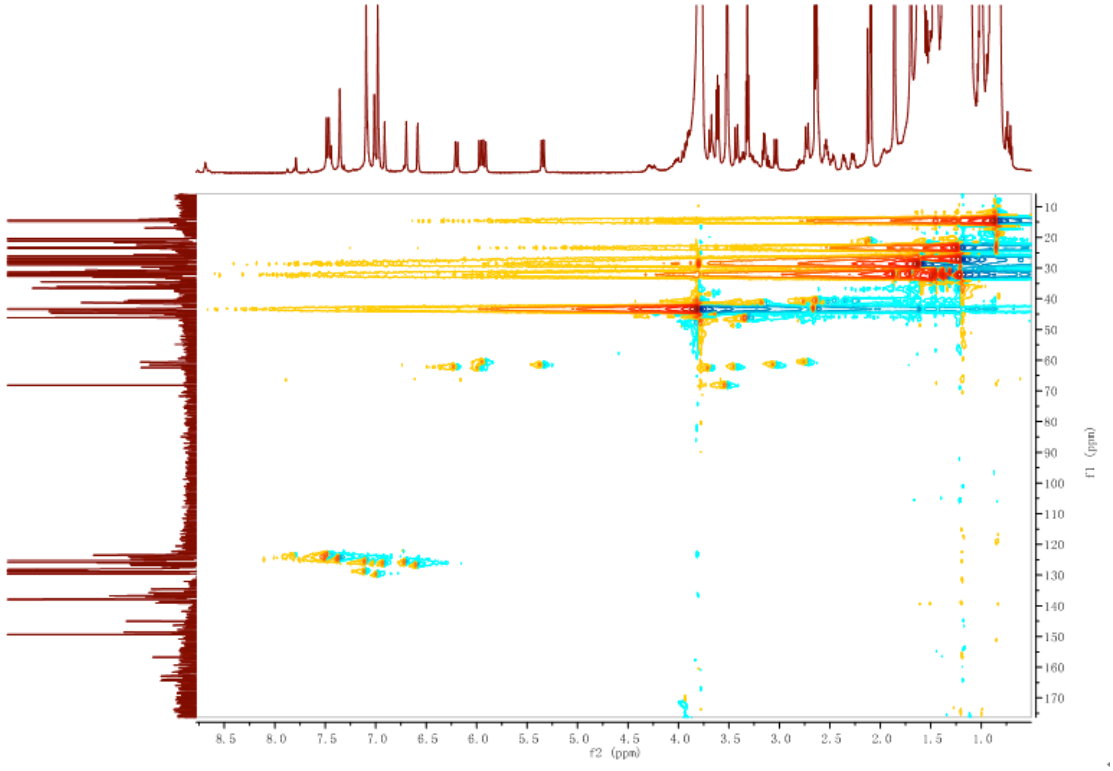

Fig. s14 ^{1}H-^{13}C HSQC spectrum of in situ polymerization in toluene-d_8 with complex **2** a small amount participated in the initiation (overview).

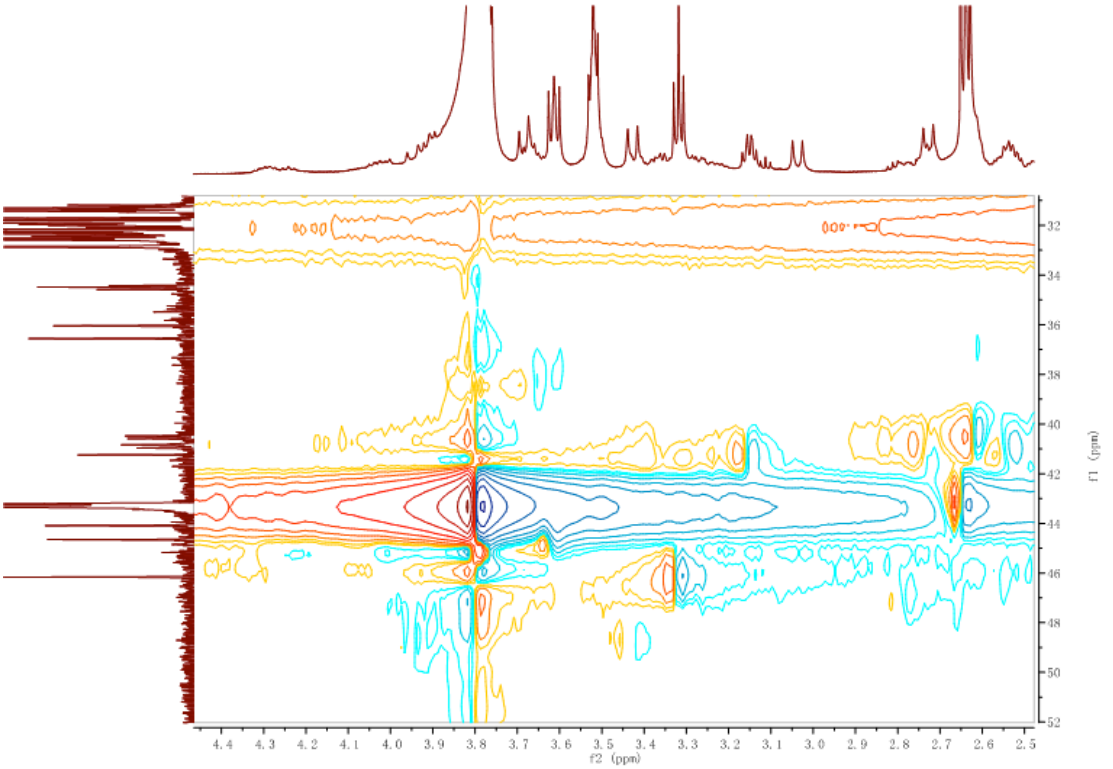

Fig. s14 ^{1}H-^{13}C HSQC spectrum of in situ polymerization in toluene-d_8 with complex **2** a small amount participated in the initiation (part).

The siganls of the chiral carbon can be assigned to δ 45.62, 44.87. The H^{i} was coupled with the chiral carbon.

Table s1 Crystallographic data for complexes **1**, **3**

Compound reference	**1**	**3**
Chemical formula	$C_{72}H_{108}N_4KNdO_5$	$C_{102}H_{153}O_6N_6Cl_3Sm_2$
Formula Mass	1292.96	1966.38
Crystal system	Monoclinic	triclinic
a/Å	15.5124(5)	18.2347(5)
b/ Å	18.0557(6)	18.5751(4)
c/ Å	26.2035(9)	21.1019(5)
α/°	90.00	75.4933(18)
β/°	100.873(3)	65.628(2)
γ/°	90.00	76.527(2)
Unit cell volume/Å^3	7207.5(4)	6234.5(3)
Temperature/K	170	170
Space group	*P*21/*n*	P -1
No. of formula units per unit cell, *Z*	4	2
Absorption coefficient, μ/mm^{-1}	0.826	1.040
No. of reflections measured	31743	40518
R_{int}	0.0456	0.0374
Final R_1 values ($I > 2\sigma(I)$)	0.0414	0.0465
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0834	0.1240
Final R_1 values (all data)	0.0703	0.0673
Final $wR(F^2)$ values (all data)	0.0953	0.1355
Goodness of fit on F2	1.051	1.078
CCDC number	1407874	994627