Supporting information

Alkaline earth metal complexes stabilized by amidine and guanidine ligands: synthesis, structure and their catalytic activity towards polymerization of rac-lactide

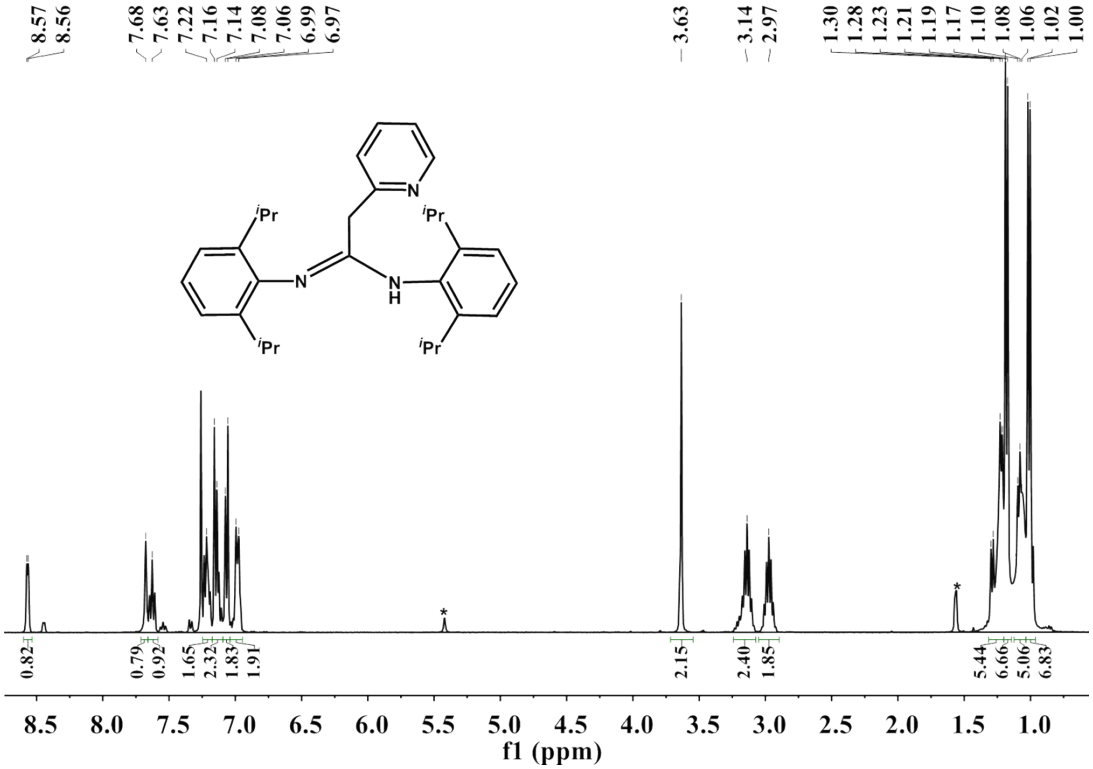

Fig. S1. ^{1}H NMR spectrum of HL^{1} ($CDCl_3$, 400 MHz, 25 ^{o}C)

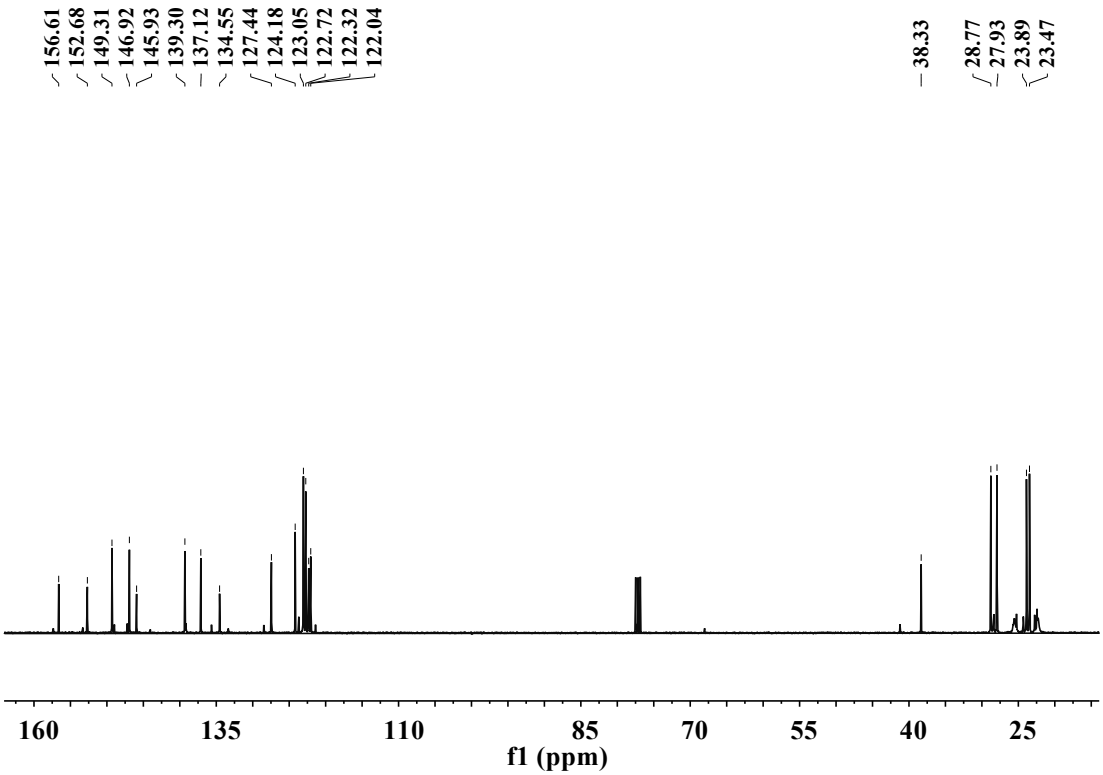

Fig. S2. ^{13}C NMR spectrum of HL^1 ($CDCl_3$, 100 MHz, 25 °C)

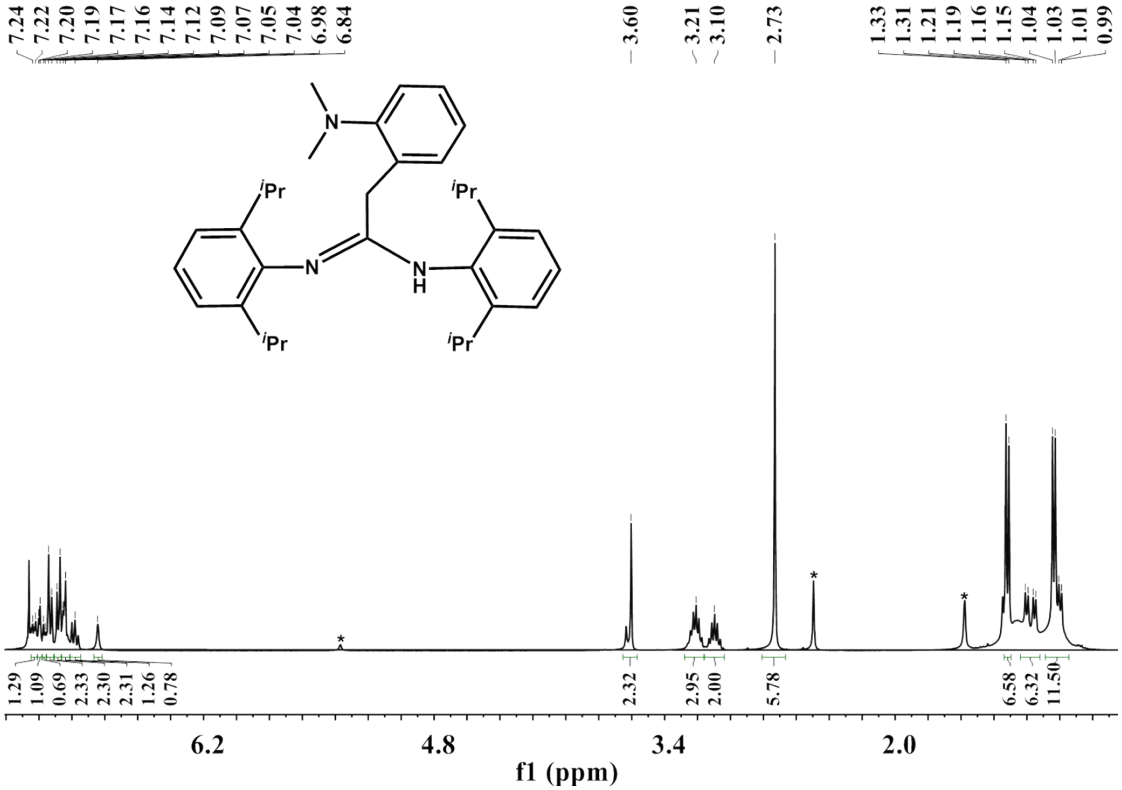

Fig. S3. ^{1}H NMR spectrum of HL^2 ($CDCl_3$, 400 MHz, 25 °C)

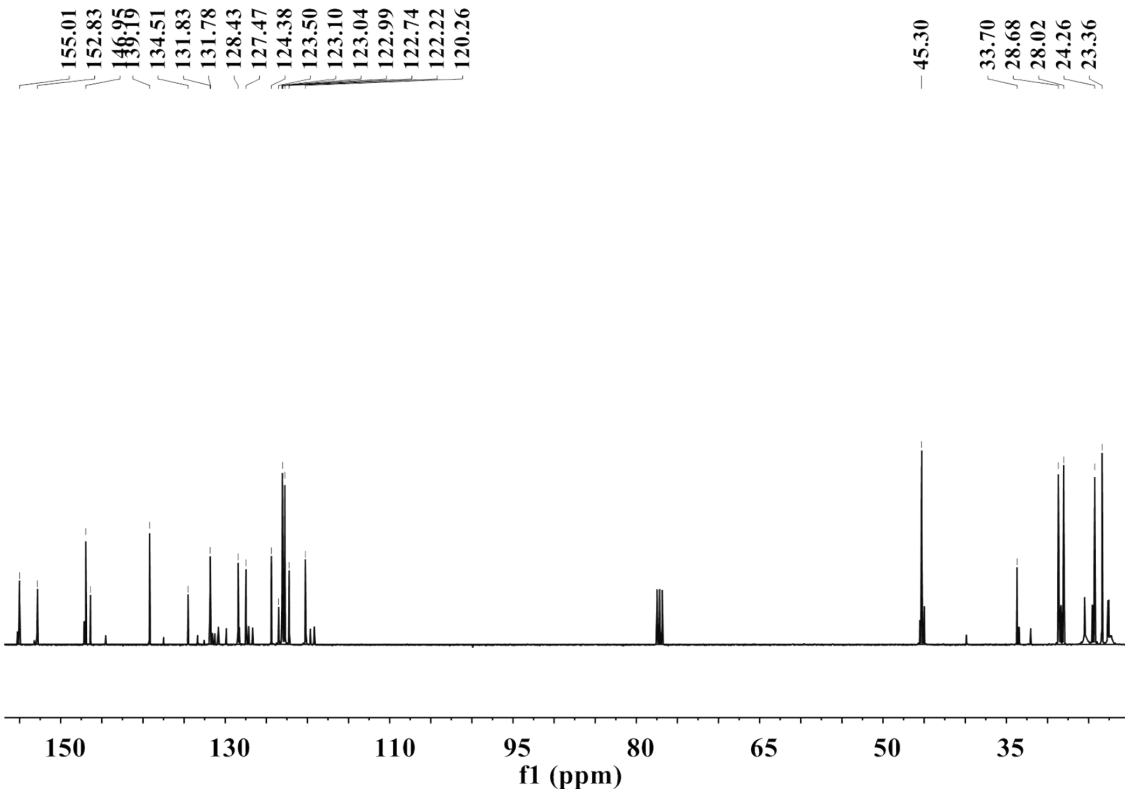

Fig. S4. ^{13}C NMR spectrum of HL^2 ($CDCl_3$, 100 MHz, 25 °C)

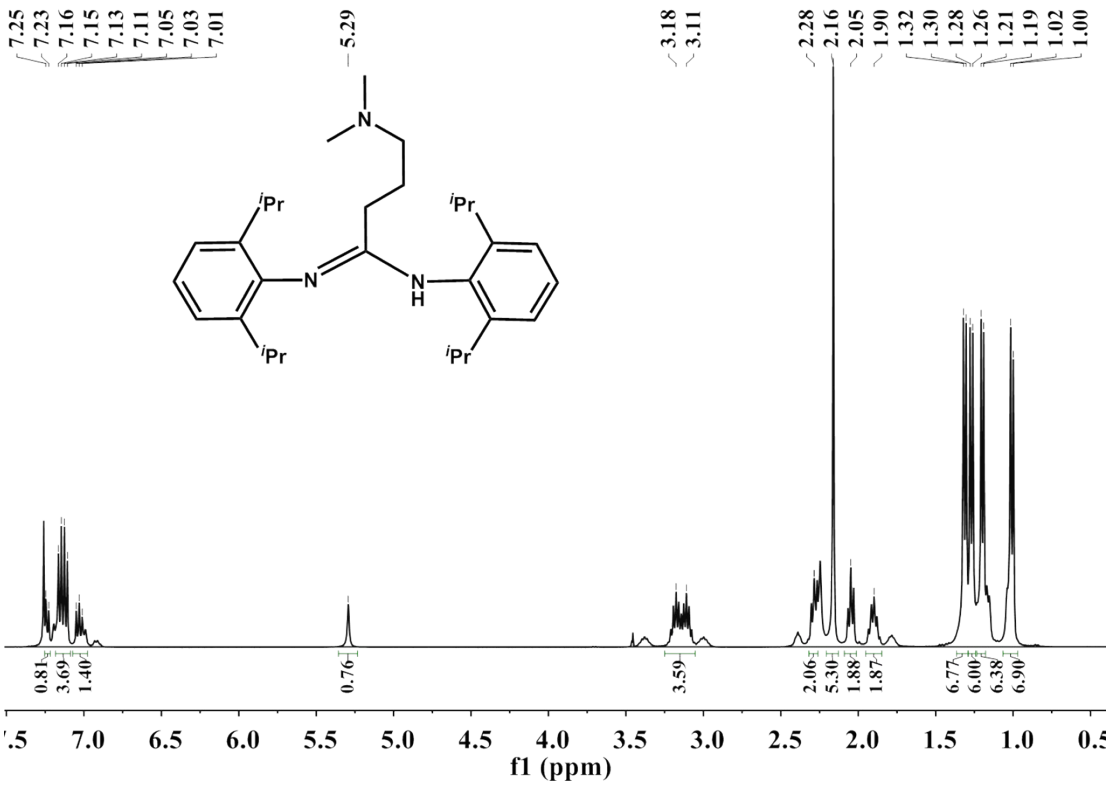

Fig. S5. ^{1}H NMR spectrum of HL^{3} ($CDCl_3$, 400 MHz, 25 ^{o}C)

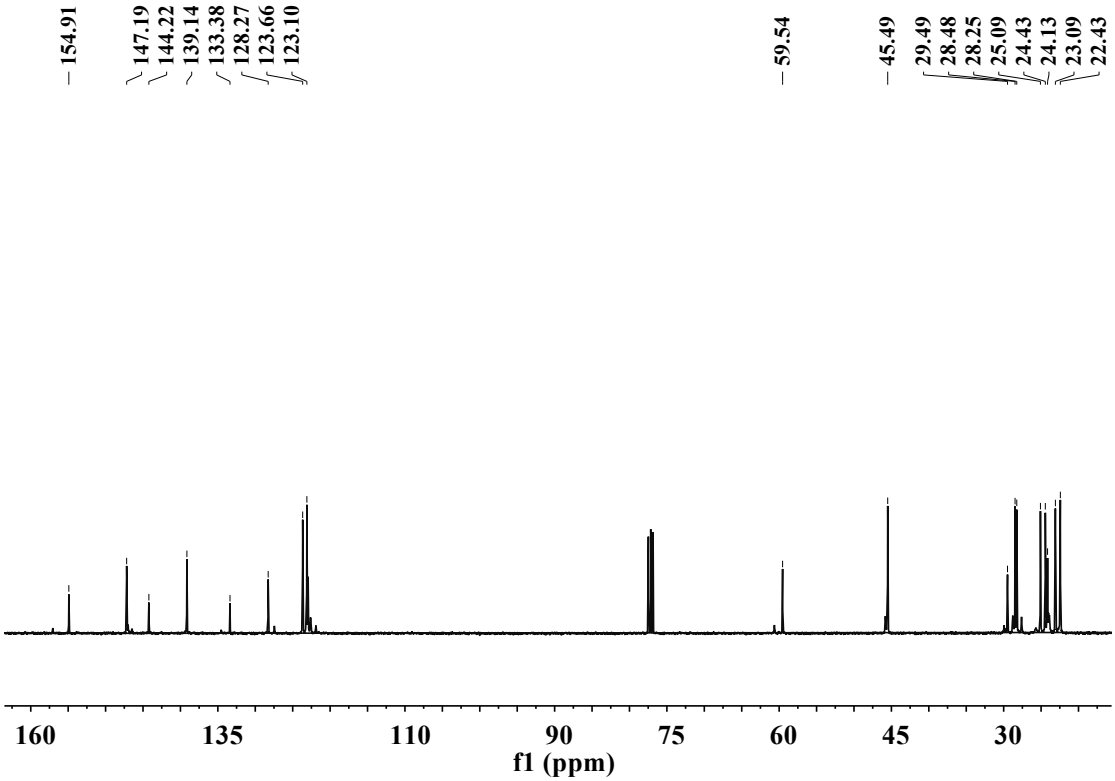

Fig. S6. ^{13}C NMR spectrum of HL^{3} ($CDCl_3$, 100 MHz, 25 ^{o}C)

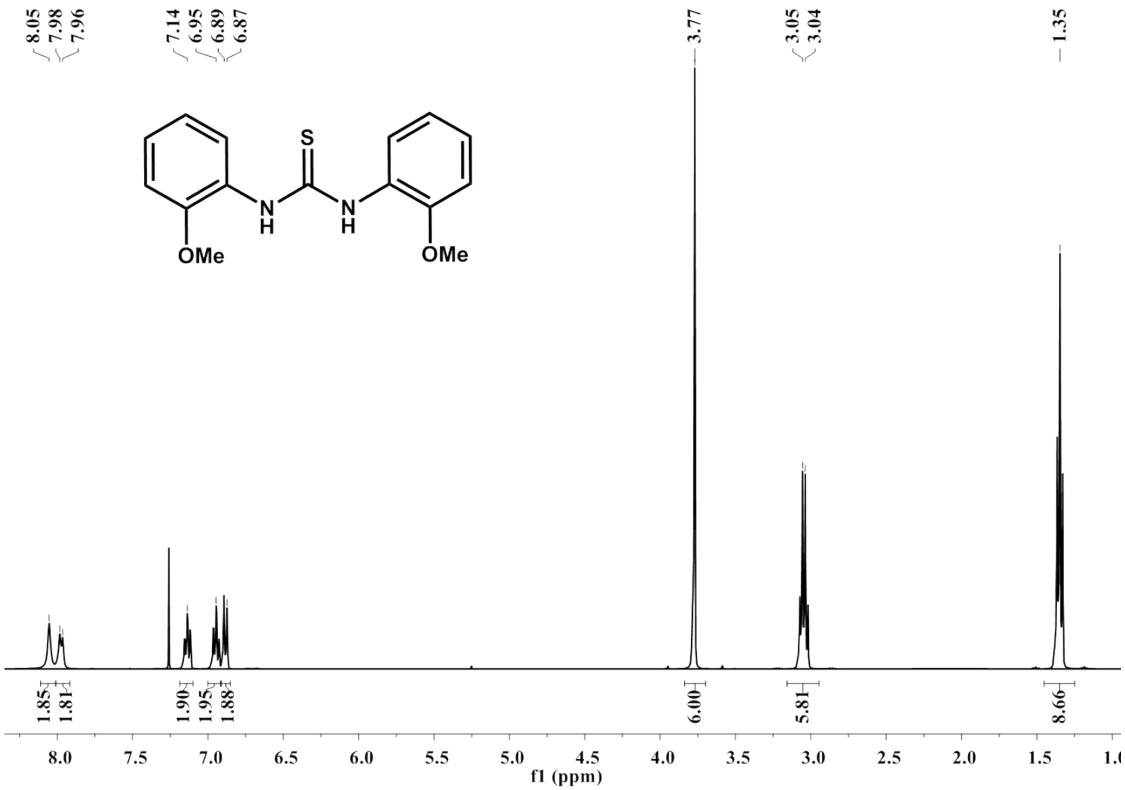

Fig. S7. ^{1}H NMR spectrum of thiourea (**I**) ($CDCl_3$, 400 MHz, 25 ^{o}C)

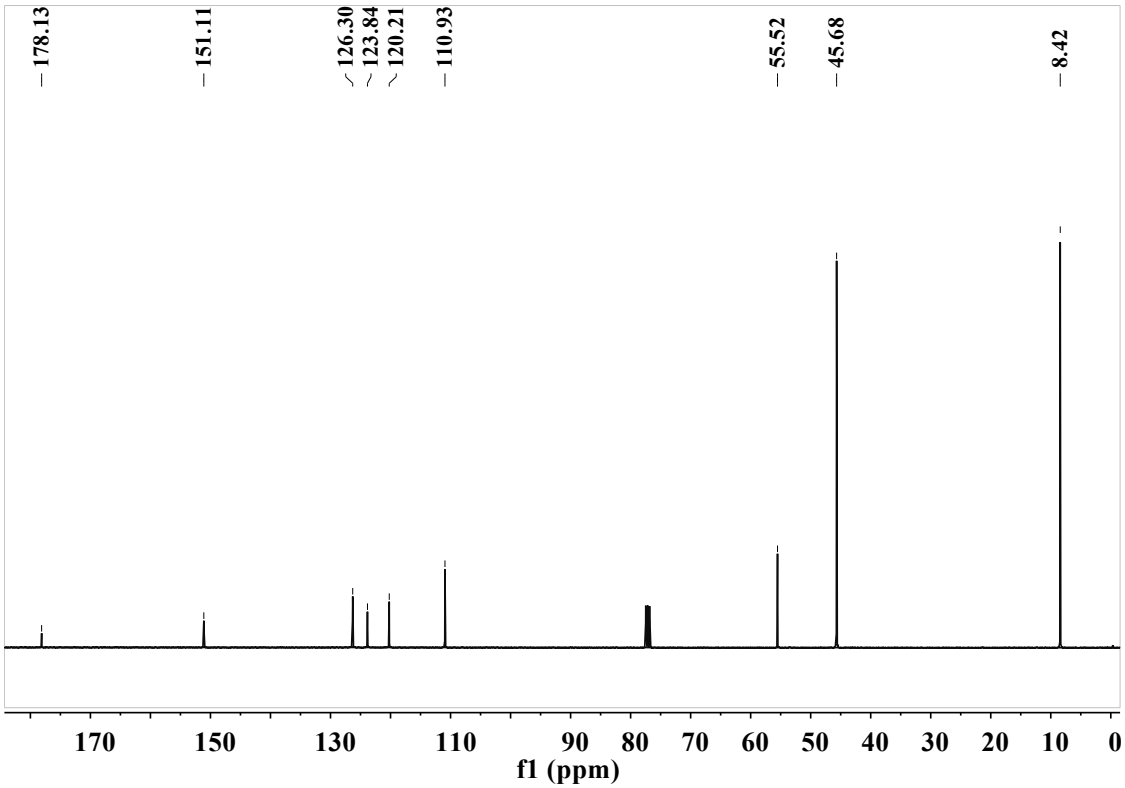

Fig. S8. ^{13}C NMR spectrum of thiourea (**I**) ($CDCl_3$, 100 MHz, 25 ^{o}C)

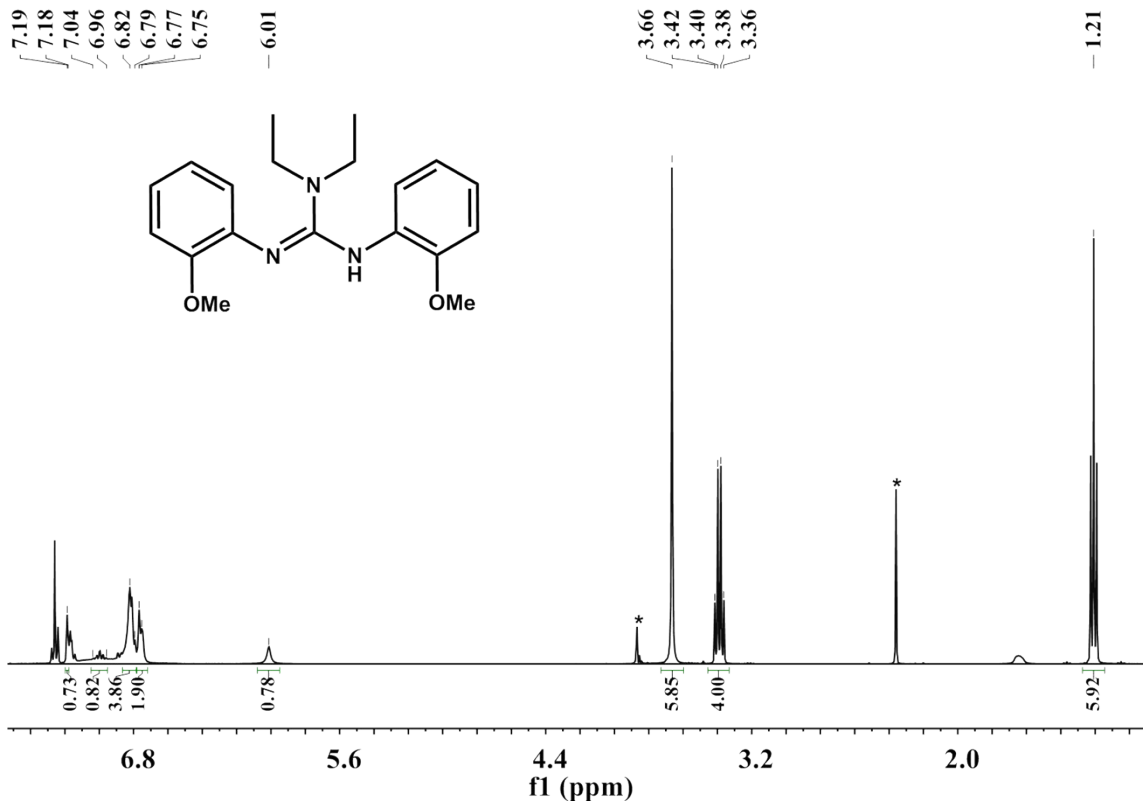

Fig. S9. ^{1}H NMR spectrum of HL^4 ($CDCl_3$, 400 MHz, 25 °C)

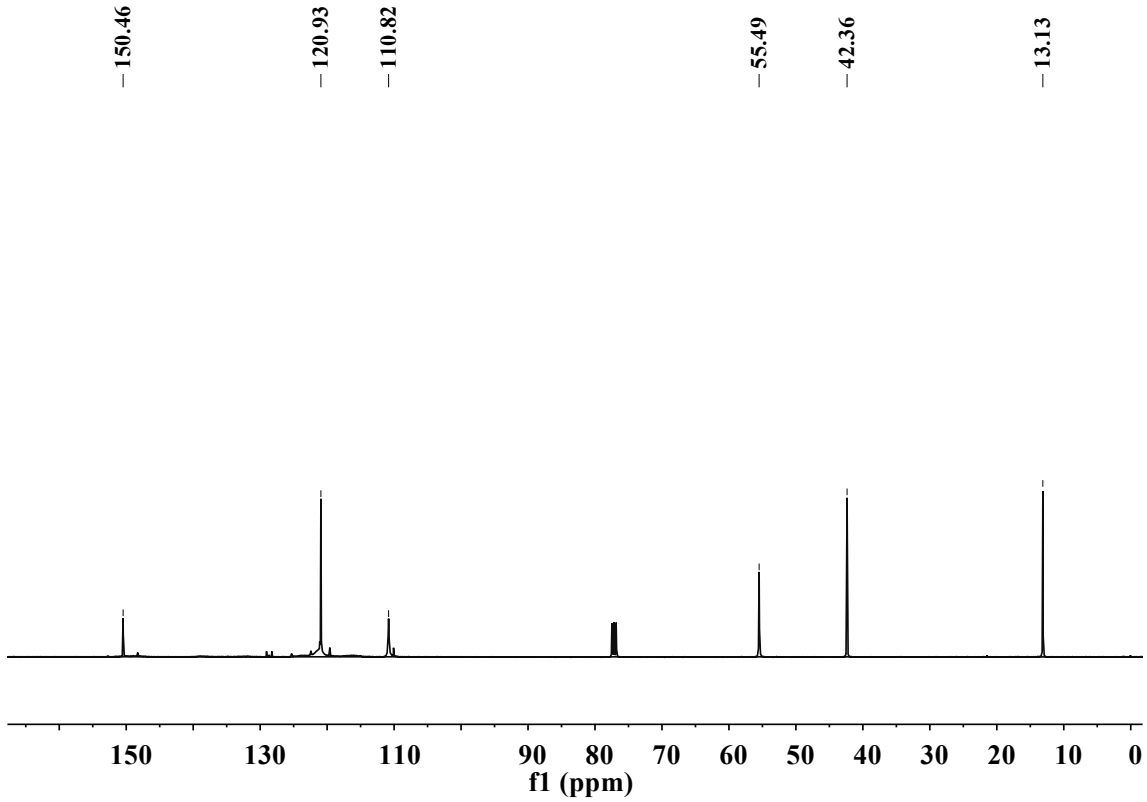

Fig. S10. ^{13}C NMR spectrum of HL^4 ($CDCl_3$, 100 MHz, 25 °C)

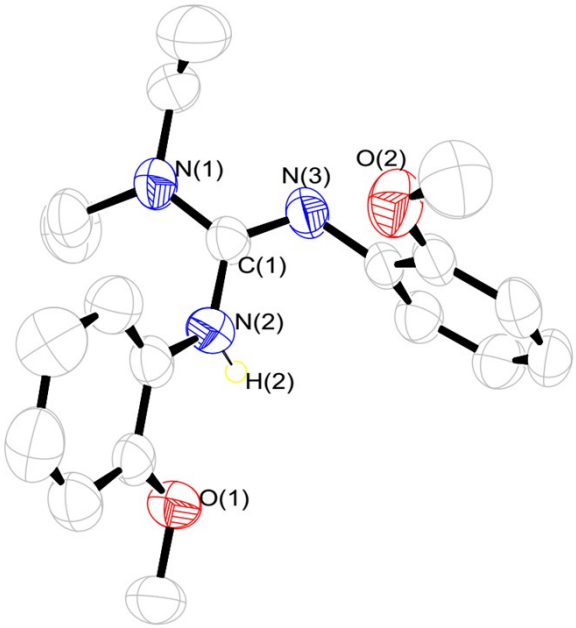

Fig. S11. Crystal structures of guanidine ligand **HL[4]**. Thermal ellipsoids are drawn at the 35% probability level. Hydrogen atoms except N-H are omitted for clarity. Selected bond lengths (Å) and angles (deg): N(3)-C(1) 1.273, N(2)-C(1) 1.391, N(1)-C(1) 1.359, N(2)-H(2) 0.860, N(3)-C(1)-N(1) 120.38, N(2)-C(1)-N(1) 116.84, H(2)-N(2)-C(1) 116.78.

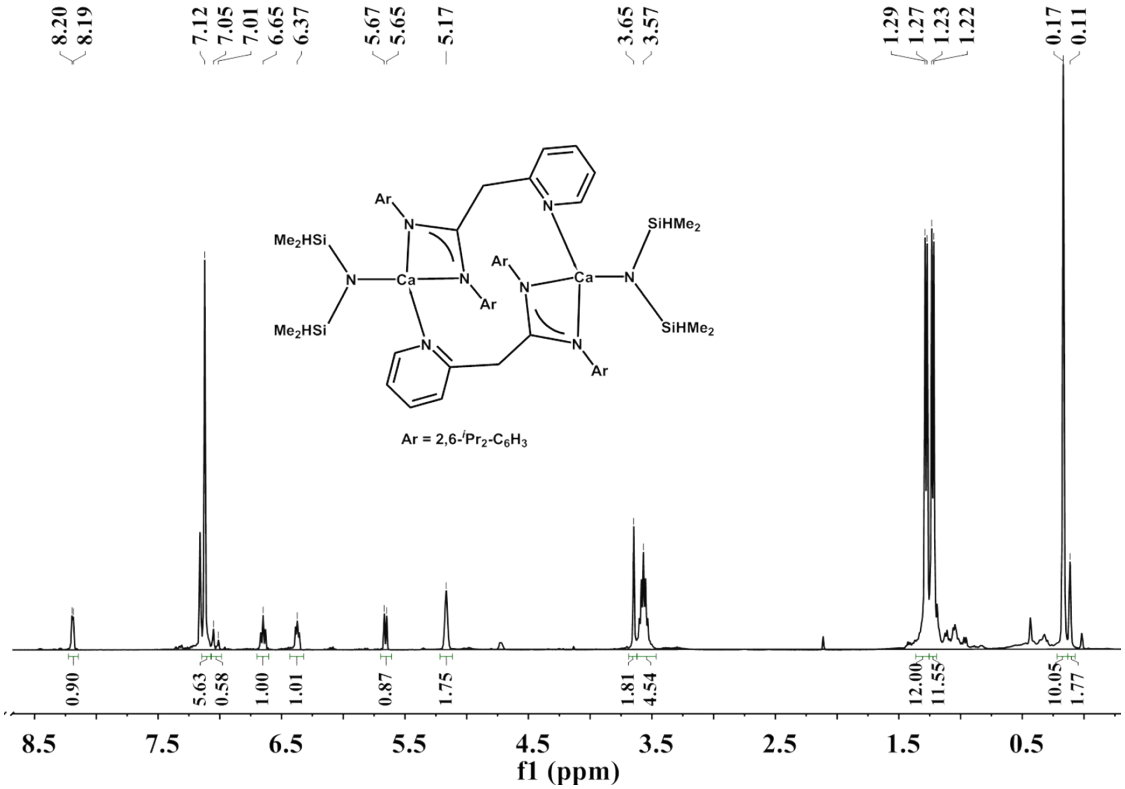

Fig. S12. ^{1}H NMR spectrum of complex **1** (C_6D_6, 400 MHz, 25 °C)

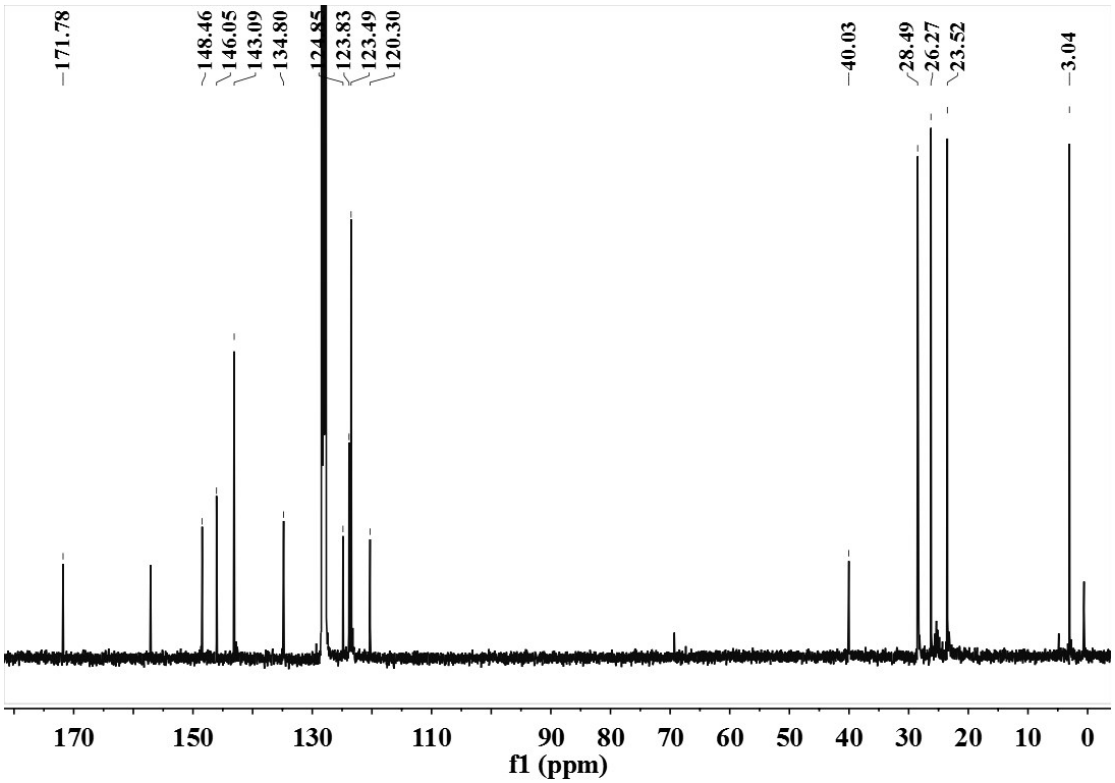

Fig. S13. ^{13}C NMR spectrum of complex **1** (C_6D_6, 100 MHz, 25 °C)

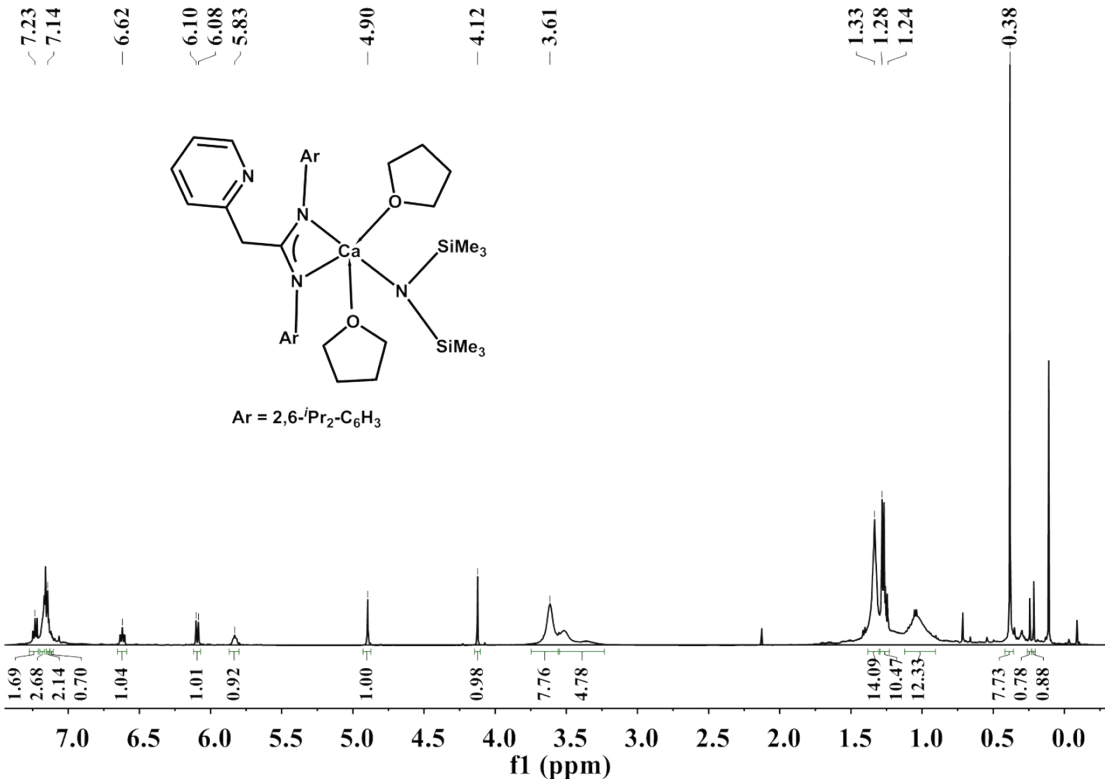

Fig. S14. ^{1}H NMR spectrum of complex **2** (C_6D_6, 500 MHz, 25 °C)

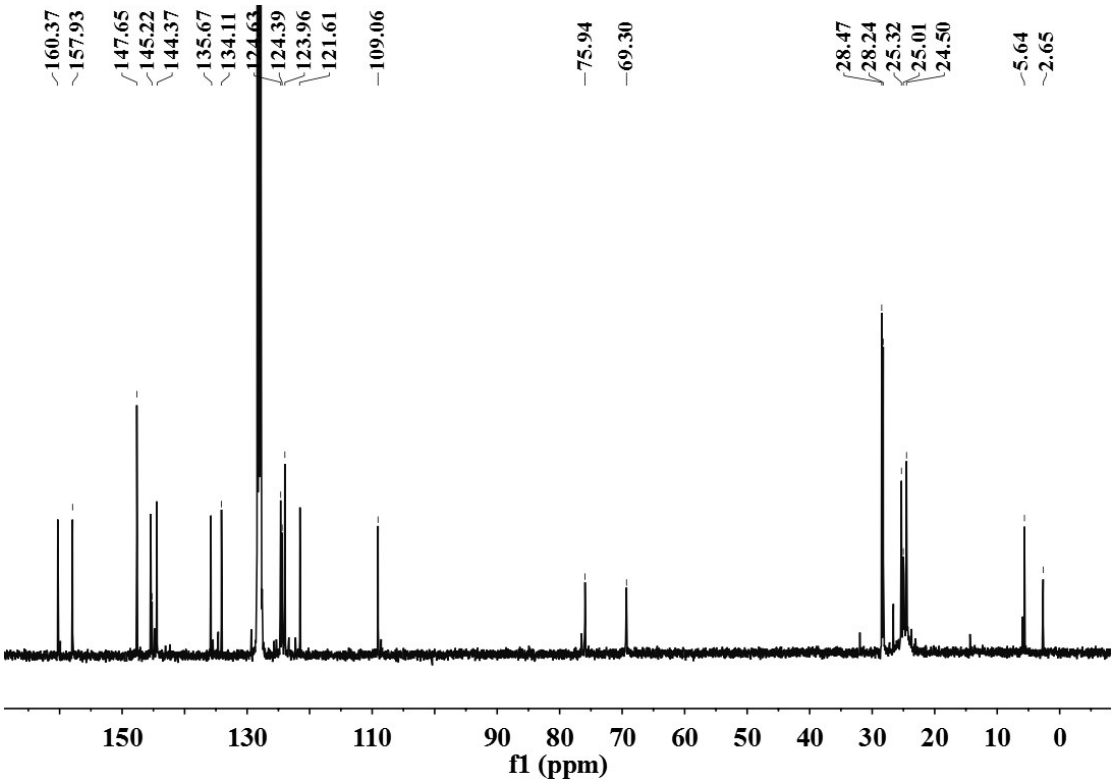

Fig. S15. ^{13}C NMR spectrum of complex **2** (C_6D_6, 126 MHz, 25 °C)

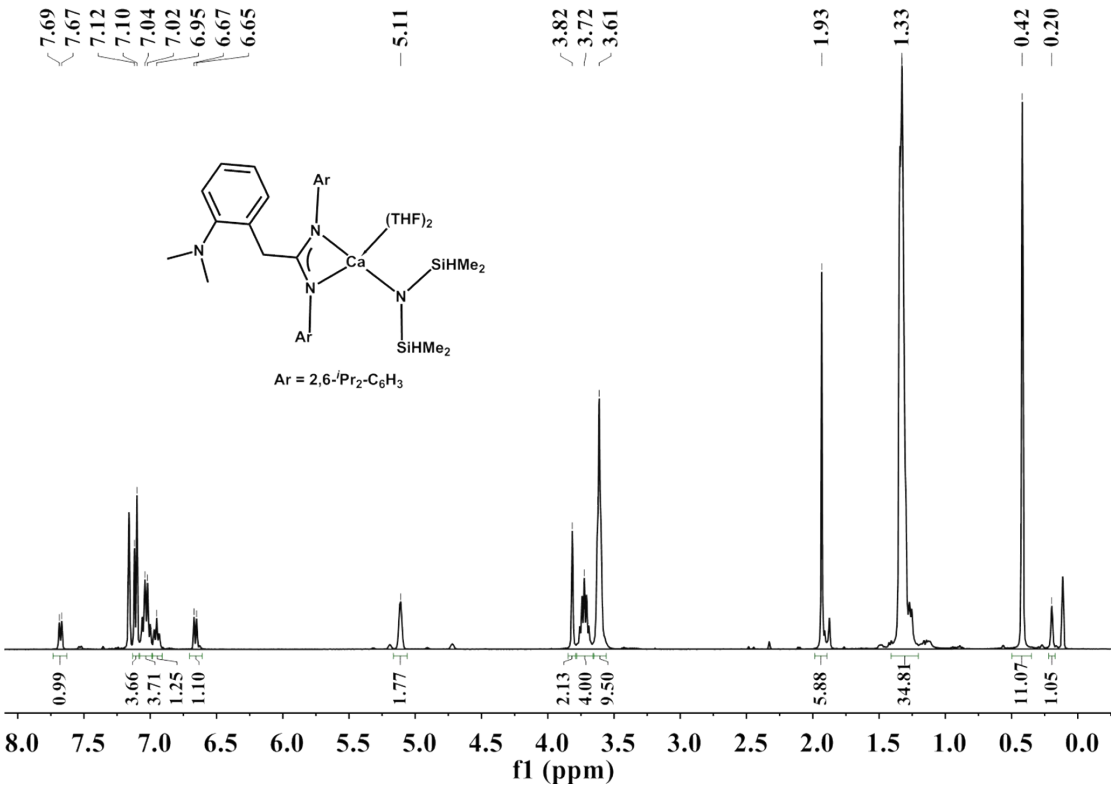

Fig. S16. ^{1}H NMR spectrum of complex **3** (C_6D_6, 400 MHz, 25 °C)

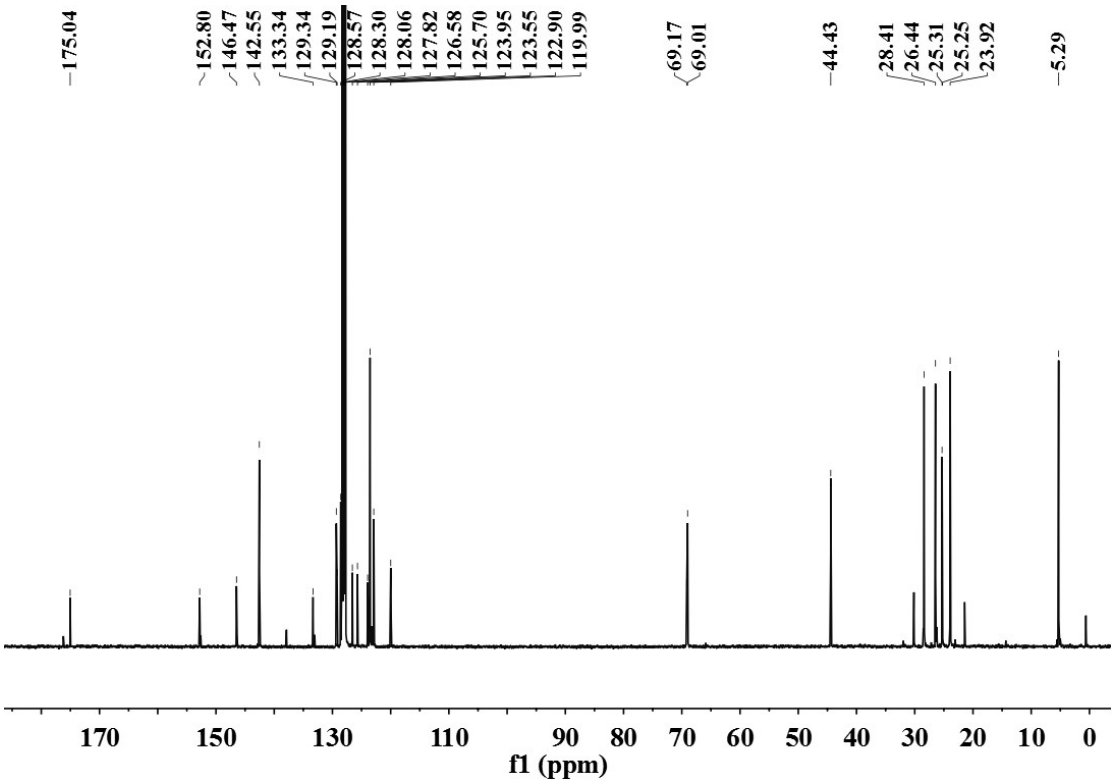

Fig. S17. ^{13}C NMR spectrum of complex **3** (C_6D_6, 100 MHz, 25 °C)

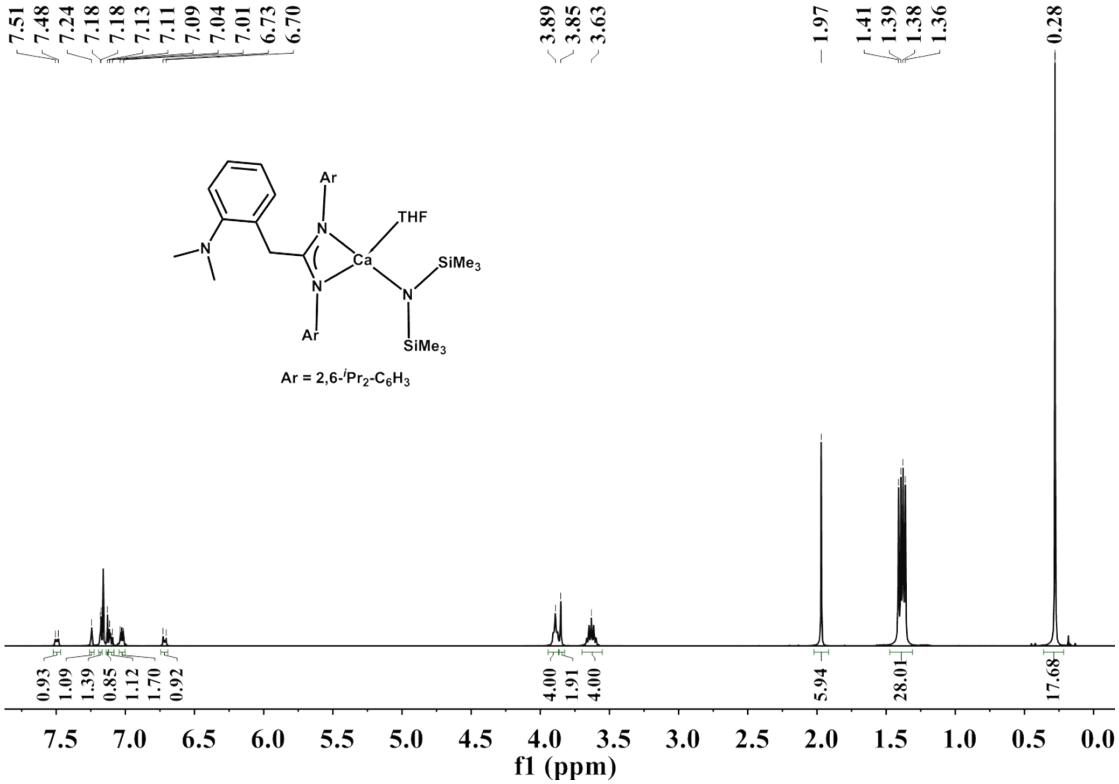

Fig. S18. ^{1}H NMR spectrum of complex **4** (C_6D_6, 400 MHz, 25 °C)

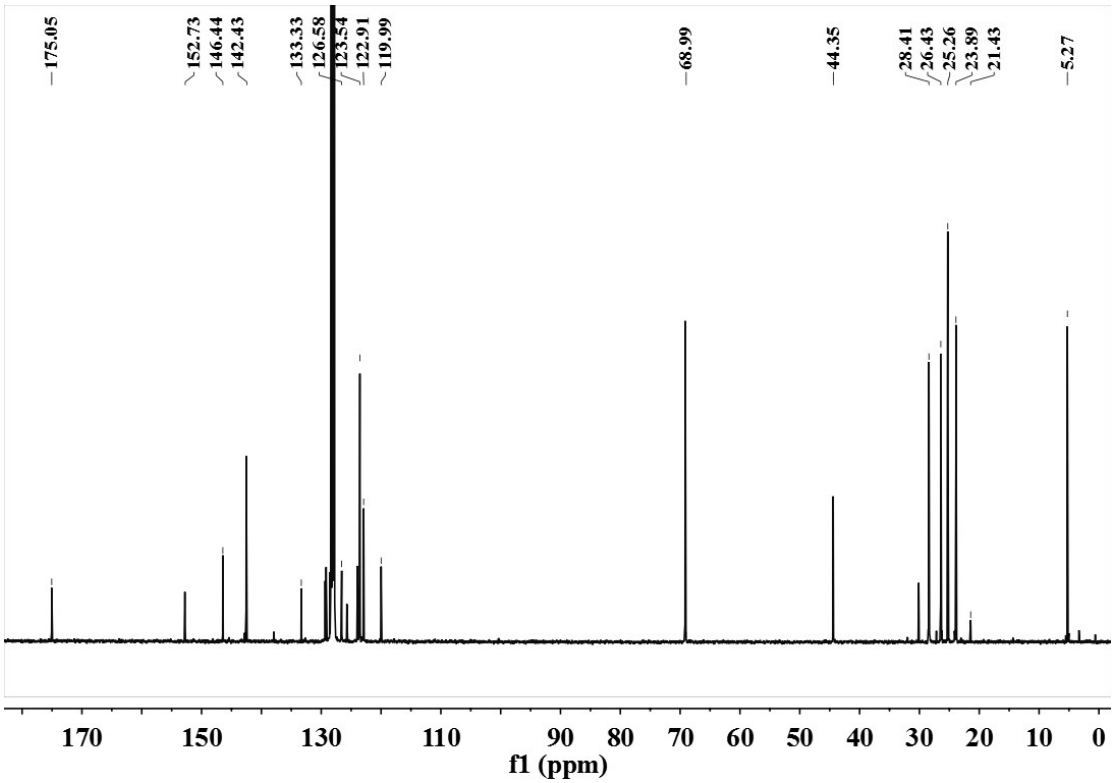

Fig. S19. ^{13}C NMR spectrum of complex **4** (C_6D_6, 100 MHz, 25 °C)

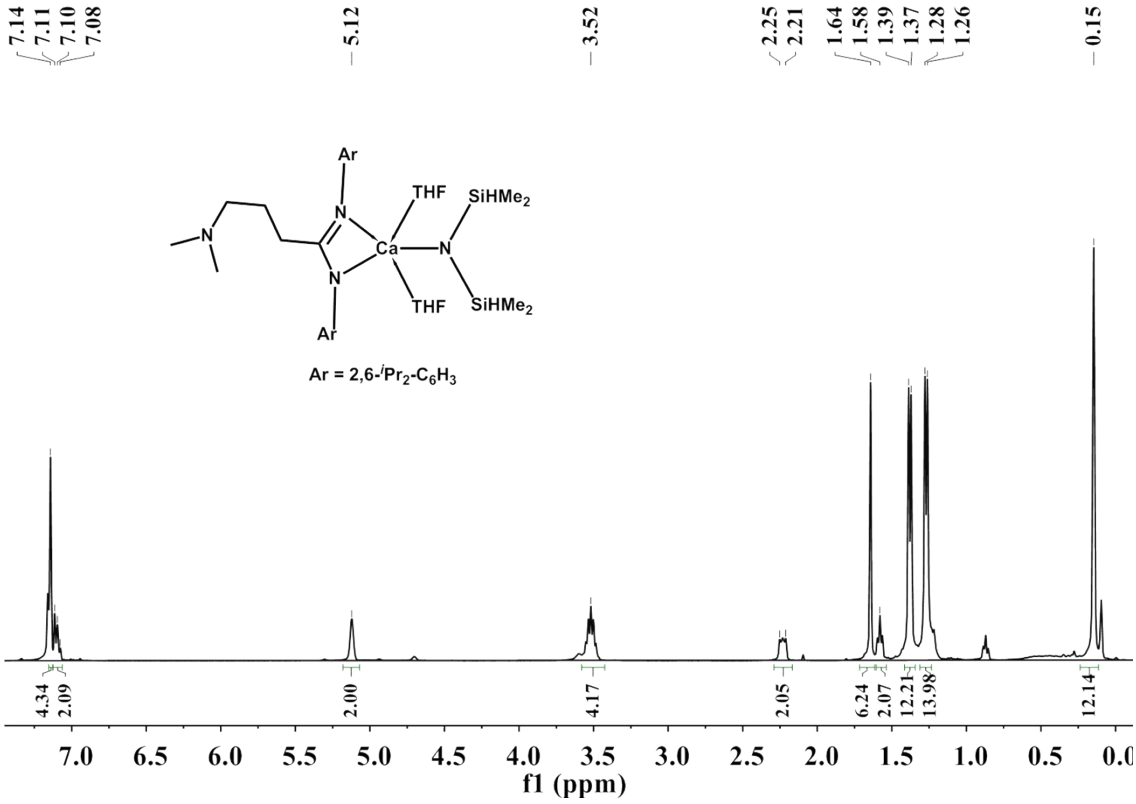

Fig. S20. ^{1}H NMR spectrum of complex **5** (C_6D_6, 400 MHz, 25 °C)

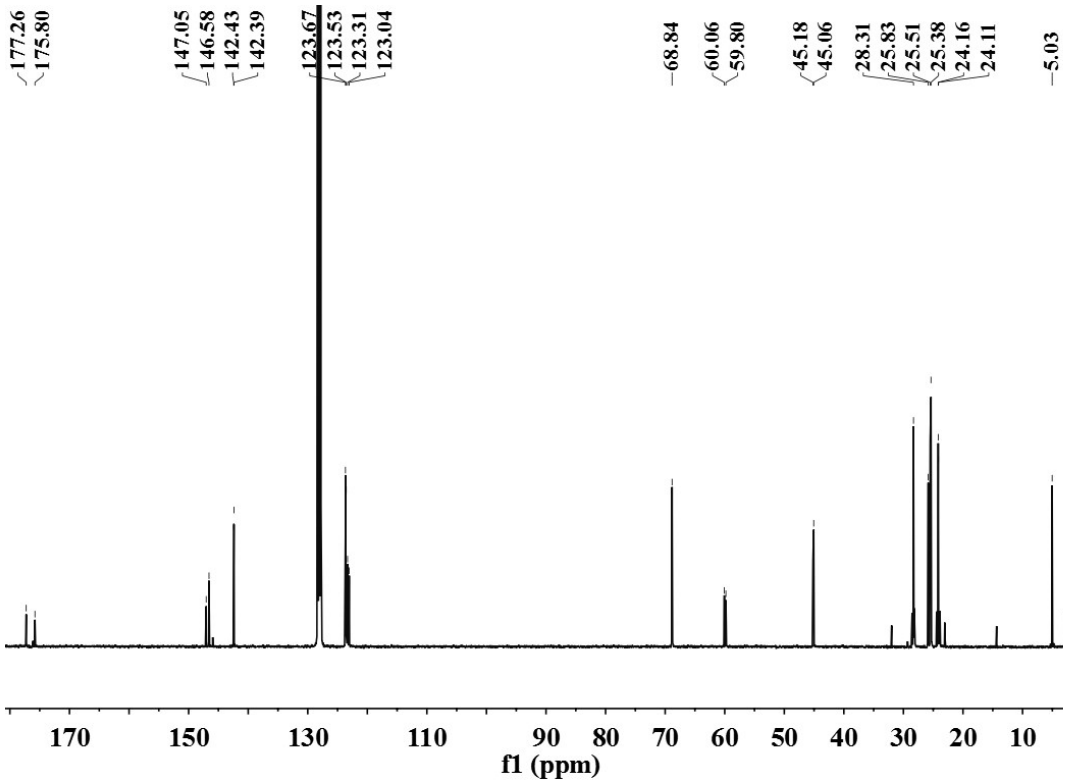

Fig. S21. ^{13}C NMR spectrum of complex **5** (C_6D_6, 100 MHz, 25 °C)

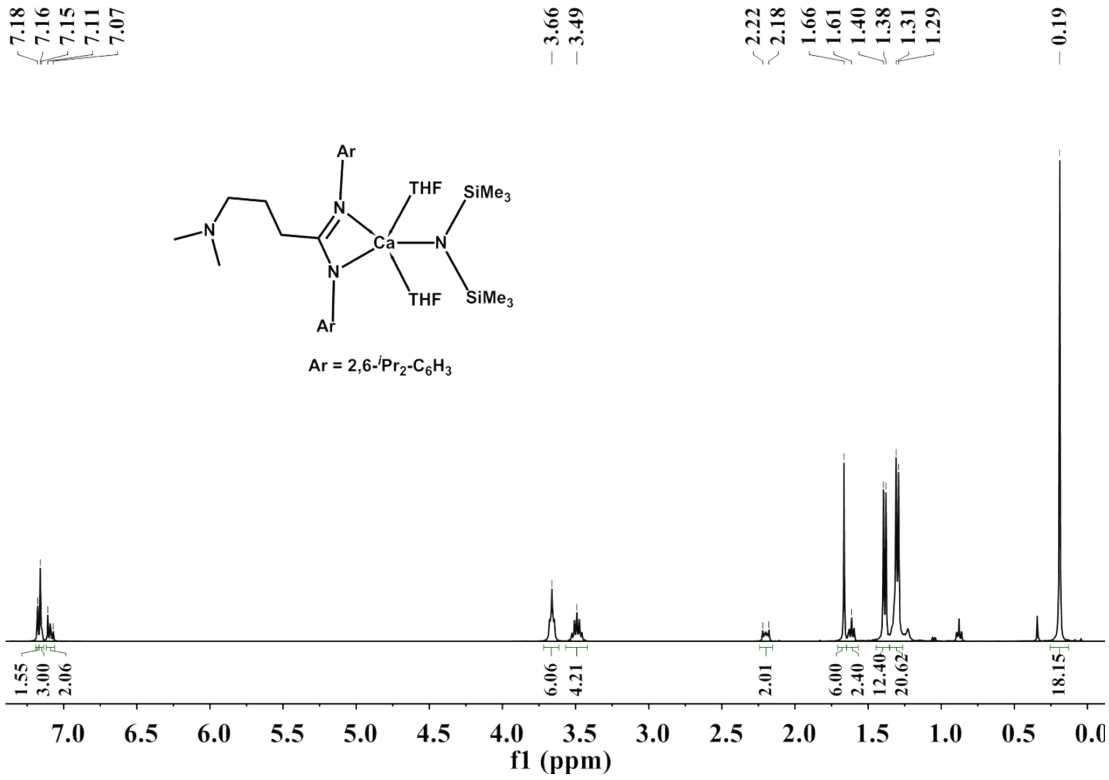

Fig. S22. ^{1}H NMR spectrum of complex **6** (C_6D_6, 400 MHz, 25 °C)

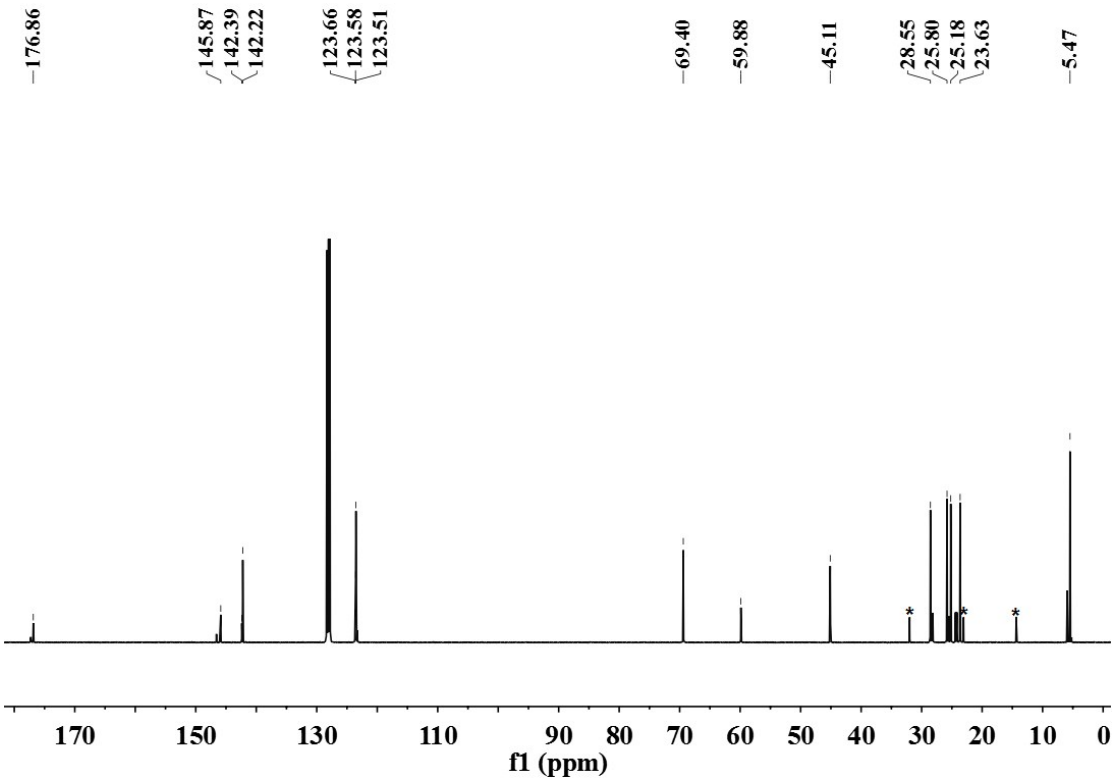

Fig. S23. ^{13}C NMR spectrum of complex **6** (C_6D_6, 100 MHz, 25 °C)

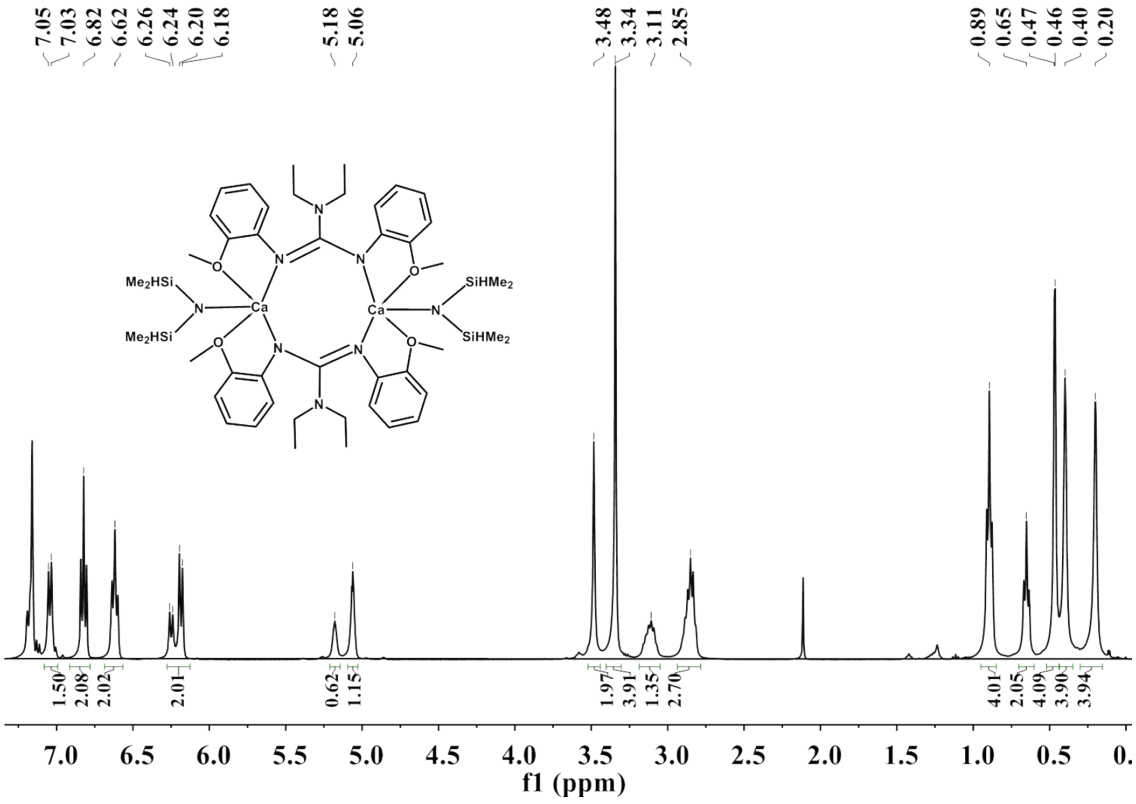

Fig. S24. ^{1}H NMR spectrum of complex **7** (C_6D_6, 400 MHz, 25 °C)

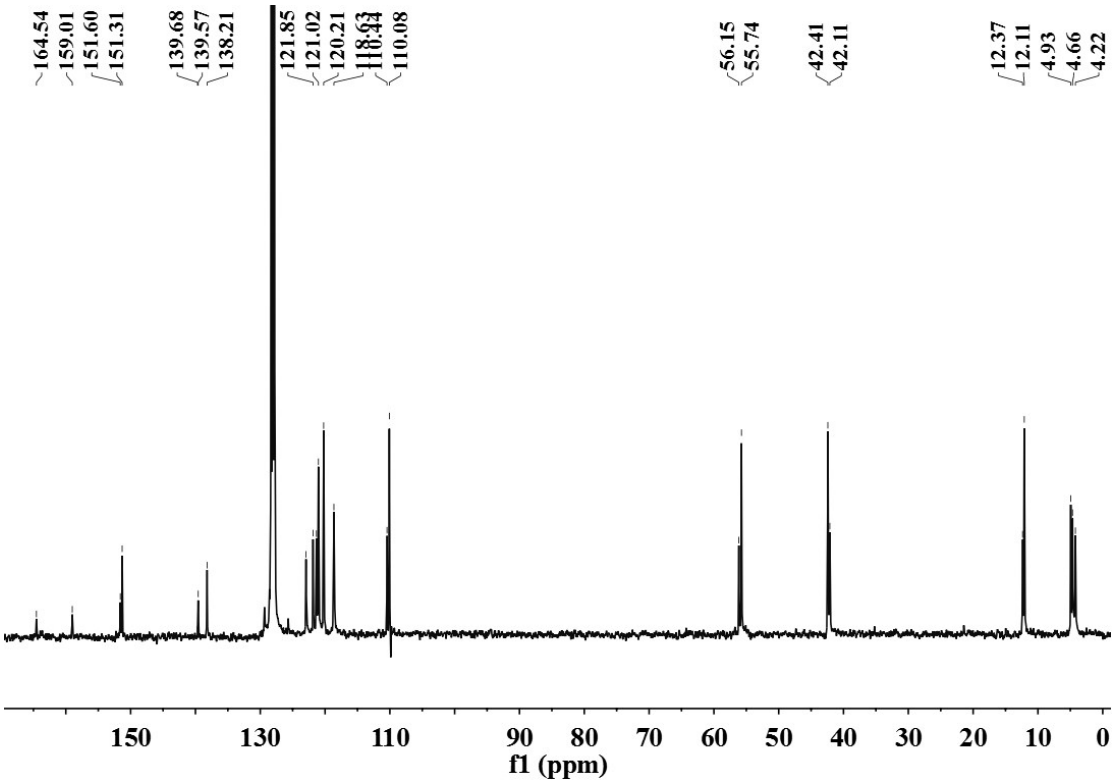

Fig. S25. ^{13}C NMR spectrum of complex **7** (C_6D_6, 100 MHz, 25 °C)

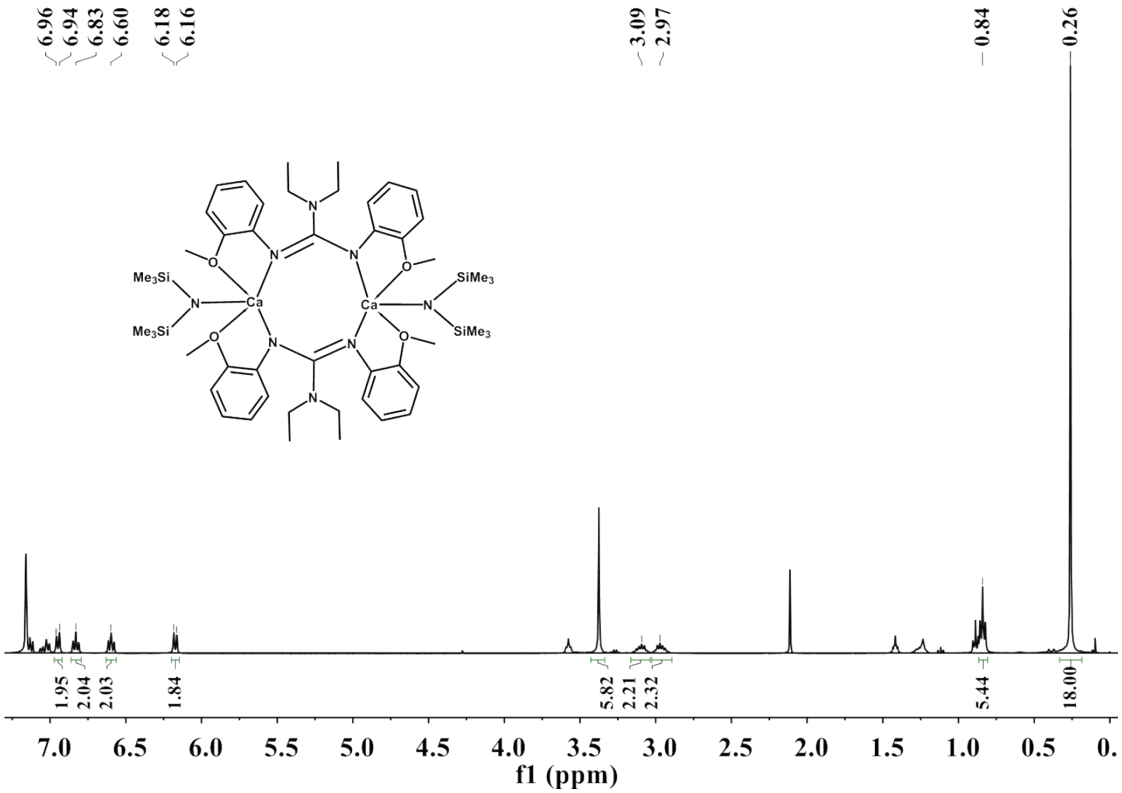

Fig. S26. ^{1}H NMR spectrum of complex **8** (C_6D_6, 400 MHz, 25 °C)

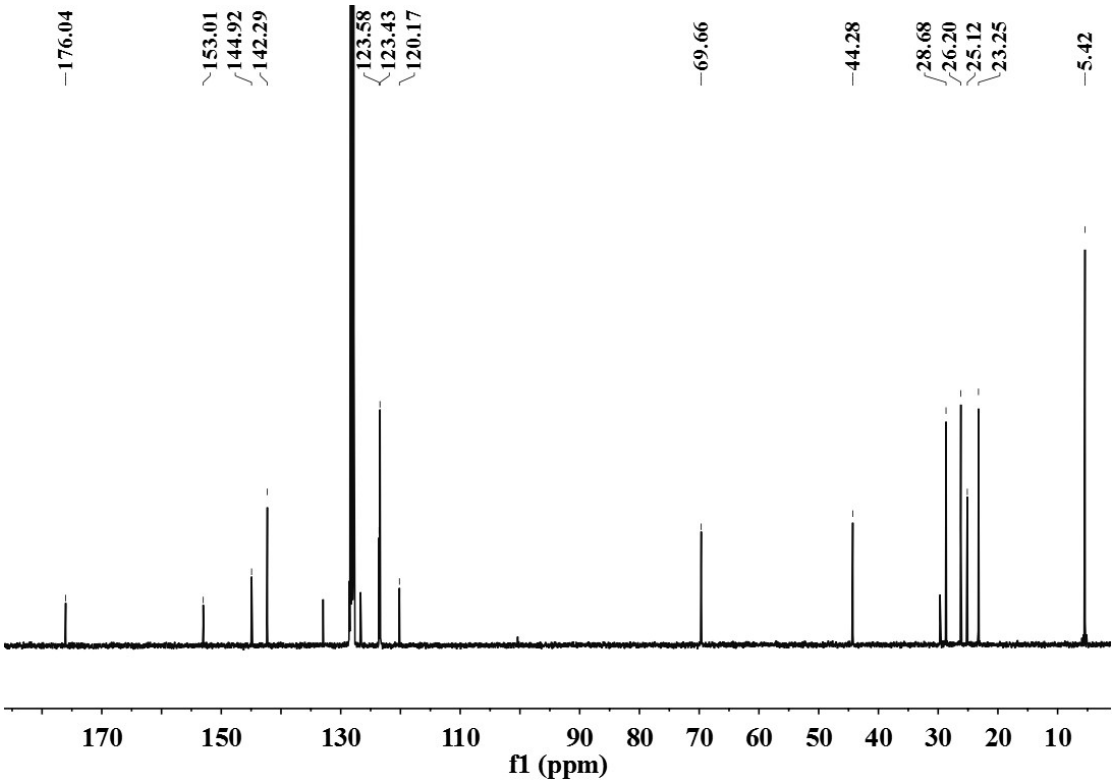

Fig. S27. ^{13}C NMR spectrum of complex **8** (C_6D_6, 100 MHz, 25 °C)

Table S1. Crystallographic data and structure refinement details for **HL⁴**

Parameter	**HL⁴**
Empirical formula	$C_{19}H_{25}N_3O_2$
Formula weight	387.47
Temperature/K	296(2)
Wavelength/ Å	0.71073
Crystal system	Triclinic
space group	P-1
a (Å)	8.965(5)
b (Å)	8.972(5)
c (Å)	13.985(5)
α(deg)	93.281(5)
β (deg)	102.433(5)
γ (deg)	106.766(5)
V (Å^3)	1043.2(9)
Z	2
D_{calcd} [g cm^{-3}]	1.234
μ [mm^{-1}]	0.080
F [000]	412
$2\theta_{max}$ [deg]	50.00
Reflections collected	6049
Independent reflections	3658 [R(int) = 0.0346]

GOF	1.079
Final *R* indices[$I>2\sigma(I)$]	R_1 = 0.0555, wR_2 = 0.1665

Table S2. Crystallographic data and structure refinement details for amidinate complexes **3**, **5-6**

Parameter	**3**	**5**	**6**
Empirical formula	$C_{53}H_{84}CaN_4O_2Si_2$	$C_{42}H_{76}CaN_4O_2Si_2$	$C_{44}H_{80}CaN_4O_2Si_2$
Formula weight	905.50	765.32	793.38
Temperature/K	184.5(2)	184.5(2)	184.5(2)
Wavelength/ Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Orthorhombic
space group	P-1	P2(1)/n	Pbca
a (Å)	10.9102(10)	11.670(5)	20.9710(11)
b (Å)	13.5063(13)	20.804(5)	19.1804(10)
c (Å)	19.3671(19)	20.145(5)	24.3516(12)
α(deg)	92.792(2)	90.000(5)	90.00
β (deg)	102.919(2)	103.268(5)	90.00
γ (deg)	91.739(2)	90.000(5)	90.00
V (Å^3)	2775.8(5)	4760.0(3)	9795.0(9)
Z	2	4	8
D_{calcd} [g cm^{-3}]	1.082	1.068	1.076
μ [mm^{-1}]	0.196	0.217	0.213
F [000]	986	1680	3488
$2\theta_{max}$ [deg]	52.20	50.24	50.08
Reflections collected	14670	27710	55853
Independent reflections	10692 [R(int) = 0.0894]	17804 [R(int) = 0.0802]	8642 [R(int) = 0.1163]
GOF	1.026	1.037	1.019
Final *R* indices[$I>2\sigma(I)$]	R_1 = 0.0789, wR_2 = 0.2577	R_1 = 0.0753, wR_2 = 0.2162	R_1 = 0.0706, wR_2 = 0.1734

Table S3 Crystallographic data and structure refinement details for guanidinate complexes **7-8**

Parameter	**7**	**8**
Empirical formula	$C_{23}H_{38}CaN_4O_2Si_2$	$C_{32}H_{50}CaN_4O_2Si_2$
Formula weight	498.83	619.02
Temperature/K	184.5(2)	184.5(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
space group	Pccn	Pccn
a (Å)	14.8204(14)	14.9714(12)
b (Å)	15.7062(15)	16.1922(13)

c (Å)	29.189(3)	29.027(2)
α(deg)	90.00	90.00
β (deg)	90.00	90.00
γ (deg)	90.00	90.00
V (Å^3)	6794.3(11)	7036.8(10)
Z	8	8
D_{calcd} [g cm^{-3}]	0.975	1.169
μ [mm^{-1}]	0.276	0.279
F [000]	2144	2672
$2\theta_{max}$ [deg]	52.80	50.08
Reflections collected	35714	39332
Independent reflections	6960 [R(int) = 0.0580]	6229 [R(int) = 0.0784]
GOF	1.029	1.014
Final R indices[$I>2\sigma(I)$]	R_1 = 0.0645, wR_2 = 0.2047	R_1 = 0.0535, wR_2 = 0.1413

Table S4 ROP of *rac*-LA catalyzed by calcium complexes **1-8**[a]

entry	Cat.	$[M]_0/[cat]_0/[CTA]_0$	Conv.[b] (%)	$M_{n,calcd}$[c] (10^4)	$M_{n,exp}$[d] (10^4)	M_w/M_n[d]
1	**1**	200/1/0	63	1.82	1.68	1.92
2	**2**	200/1/0	51	1.47	1.20	1.31
3	**3**	200/1/0	78	2.25	2.49	1.60
4	**4**	200/1/0	54	1.56	1.37	1.80
5	**5**	200/1/0	76	2.19	1.94	2.11
6	**6**	200/1/0	66	1.90	1.89	1.98
7[e]	**7**	200/1/0	62	0.96	1.78	1.40
8[e]	**8**	200/1/0	64	1.09	1.84	1.64

[a] Conditions：Cat., 10 μmol, $[rac\text{-LA}]_0$ = 0.5 M, THF as solvent, 25 °C. Polymerization time was 12 h and not optimized. [b] Determined by ^{1}H NMR spectrum. [c] $M_{n,calcd} = [LA]_0/[Cat]_0 \times 144.13 \times$ conv. (%). [d] Determined by GPC against polystyrene standard, M_n using a correcting factor for polylactides (0.58). [e]cat., 5 μmol.