Supporting Information

Rare-Earth Metal Hydrides Supported by Silicon-Bridged Boratabenzene Fluorenyl Ligands: Synthesis, Structure and Reactivity

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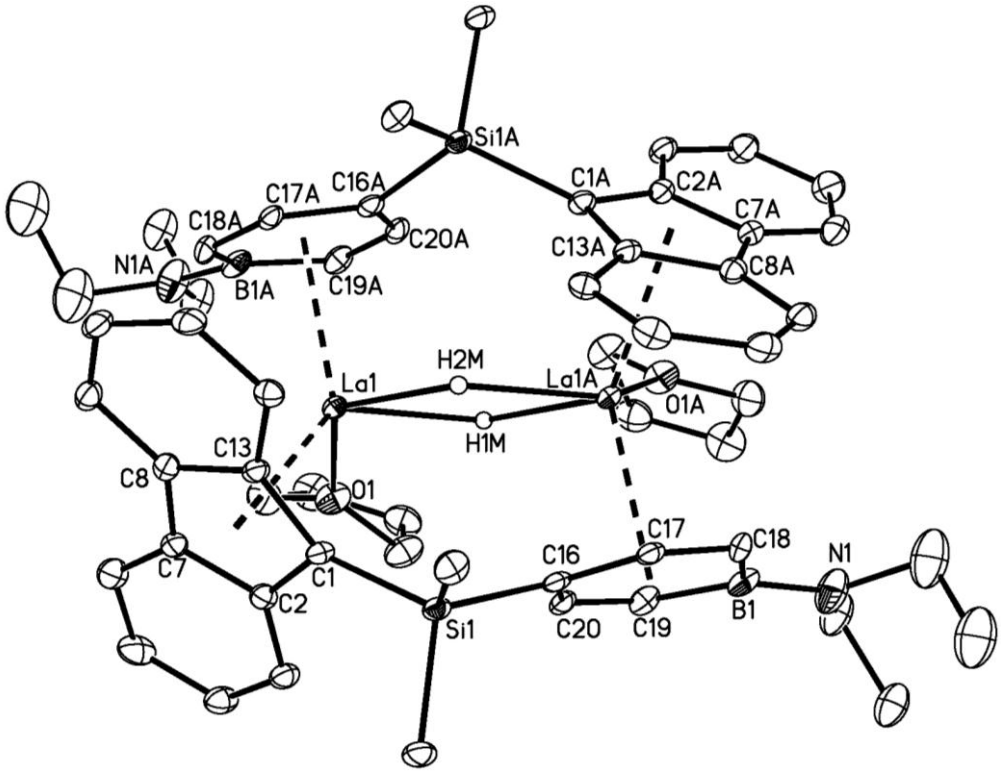


Fig. S1 Molecular structure of **3-La** with thermal ellipsoids set at 30% probability. Hydrogen atoms (except H1M and H2M) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): La1-H1M 2.198(5), La1-H2M 2.248(5), La1-C1 2.809(5), La1-C2 2.930(5), La1-C7 2.989(5), La1-C8 2.934(5), La1-C13 2.811(5), La1-Cent1 2.625, La1-C16A 2.866(5), La1-C17A 2.820(4), La1-C18A 2.909(4), La1-C19A 3.026(5), La1-C20A 2.913(5), La1-B1A 3.173(5), La1-Cent2 2.578, La1 ··La1A 3.868(5), La1-O1 2.542(4), B1A-N1A 1.450(8), ΣN1A 359.2, La1-H1M-La1A 118.7(2), La1-H2M-La1A 123.3(2), H1M-La1-H2M 59.0(2), C1-Si1-C16 116.3(2), Cent1-La1-Cent2 131.8. Cent1 represents the centroid of the fluorenyl ring. Cent2 represents the centroid of the boratabenzene ring.

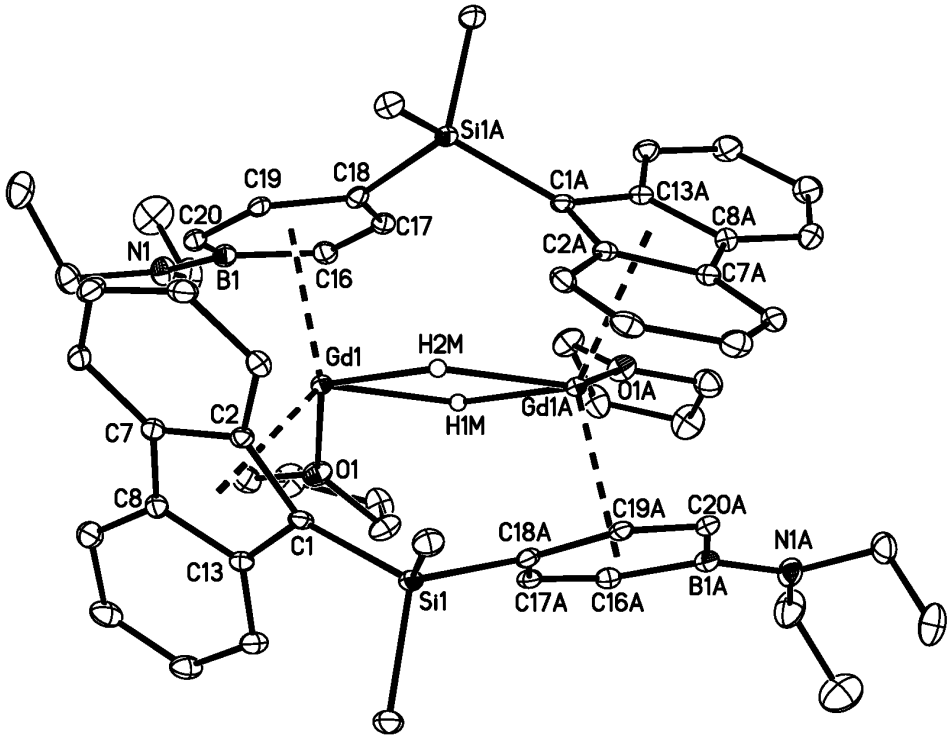


Fig. S2 Molecular structure of **3-Gd** with thermal ellipsoids set at 30% probability. Hydrogen atoms (except H1M and H2M) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Gd1-H1M 2.12(2), Gd1-H2M 2.09(3), Gd1-C1 2.675(3), Gd1-C2 2.713(3), Gd1-C7 2.893(3), Gd1-C8 2.951(3), Gd1-C13 2.857(3), Gd1-Cent1 2.540, Gd1-C16 2.960(3), Gd1-C17 2.801(3), Gd1-C18 2.722(3), Gd1-C19 2.695(3), Gd1-C20 2.807(3), Gd1-B1 3.122(3), Gd1-Cent2 2.460, Gd1-O1 2.438(3), Gd1 ··Gd1A 3.658(1), B1-N1 1.431(5), ΣN1 360.0, Gd1-H1M-Gd1A 119.4(3), Gd1-H2M-Gd1A 122.3(3), H1M-Gd1-H2M 59.2(19), C1-Si1-C18A 114.3(2), Cent1-Gd1-Cent2 129.6. Cent1 represents the centroid of the fluorenyl ring. Cent2 represents the centroid of the boratabenzene ring.

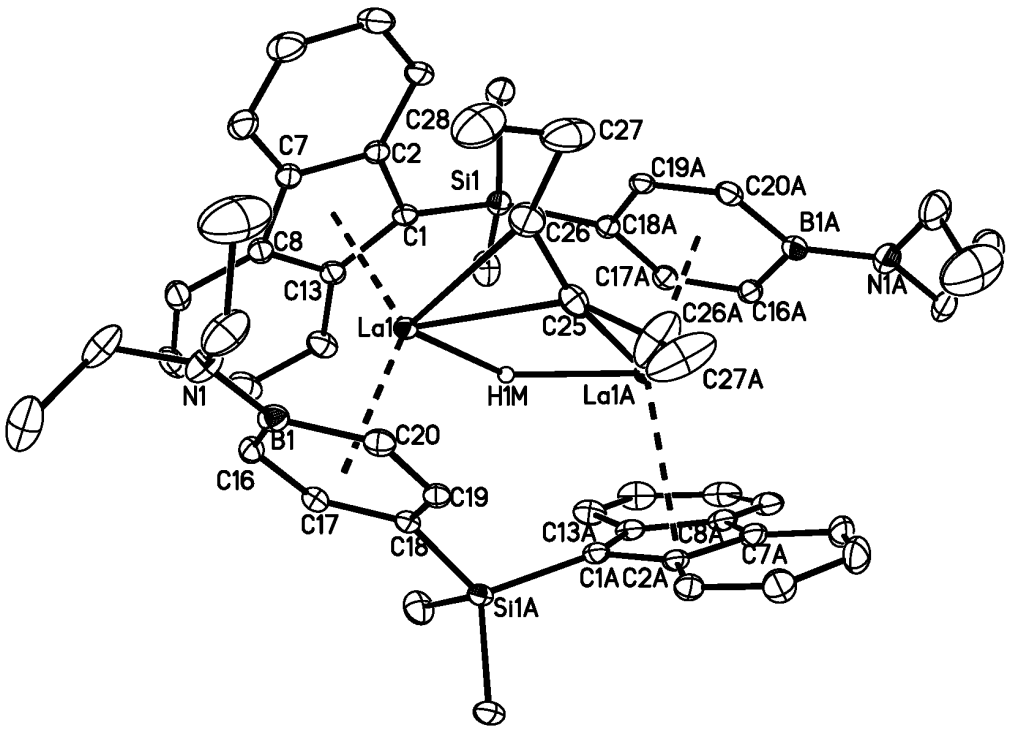


Fig. S3 Molecular structure of **5-La** with thermal ellipsoids set at 30% probability. Hydrogen atoms (except H1M) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): La1-H1M 2.12(2), La1-C1 2.802(3), La1-C2 2.897(3), La1-C7 2.902(3), La1-C8 2.885(3), La1-C13 2.789(3), La1-Cent1 2.579, La1-C16 2.894(3), La1-C17 2.816(3), La1-C18 2.815(3), La1-C19 2.888(3), La1-C20 2.954(3), La1-B1 3.063(3), La1-Cent2 2.521, La1···La1A 3.765(3), La1-C25 2.703(3), La1-C26 2.910(5), C25-C26 1.433(5), B1-N1 1.428(4), ΣN1 359.5, La1-H1M-La1A 125.4(1), La1-C25-La1A 88.3(1), H1M-La1-C25 73.2(13), C1-Si1-C18 115.7(1), Cent1-La1-Cent2 133.4. Cent1 represents the centroid of the fluorenyl ring. Cent2 represents the centroid of the boratabenzene ring.

Table S1. Crystallographic data and refinement patameters for complexes 3-Ln (Ln =La, Nd, Gd)

	3-La	**3-Nd**	**3-Gd**
formula	$C_{28}H_{37}BNOSiLa$	$C_{28}H_{37}BNOSiNd$	$C_{56}H_{74}B_2N_2O_2Si_2Gd_2$
fw	581.39	586.73	1199.47
temperature (K)	140(2)	140(2)	140(2)
color	yellow	yellow	yellow
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/c	*C*2/c	*C*2/c
a, Å	17.463(3)	17.262(1)	17.238(2)
b, Å	17.602(3)	17.704(1)	17.577(2)
c, Å	19.082(3)	19.087(2)	19.014(2)
α, deg	90	90	90
β, deg	113.818(3)	114.271(1)	114.300(2)
γ, deg	90	90	90
V, Å^3	5366.1(16)	5317.4(7)	5250.4(10)
Z	8	8	4
D_{calcd}, mg/m^3	1.439	1.466	1.517
F(000)	2368	2392	2424
θ range, deg	1.72 to 30.51	1.73 to 30.70	1.74 to 30.60
no. of reflns collected	26126	26066	25567
no. of independent reflns	8162	8186	8020
no. of obsd reflns ($I>2\sigma(I)$)	4831	6899	6089
no. of params	319	305	306
final R_1, wR ($I>2\sigma(I)$)	0.056, 0.091	0.032, 0.084	0.034, 0.084
goodness of fit on F^2	0.978	1.085	1.010
$\Delta\rho_{max,min}$, eÅ^{-3}	1.433, -2.001	2.552 , -1.269	1.948, -1.539

Table S2. Crystallographic data and refinement patameters for complexes 4-Nd, 5-La and 5-Nd

	4-Nd	**5-La**	**5-Nd**
formula	$C_{64}H_{66}B_2N_2Si_2Nd_2$	$C_{60}H_{81}B_2N_2Si_2La_2$	$C_{60}H_{81}B_2N_2Si_2Nd_2$
fw	1229.46	1185.89	1196.55
temperature (K)	140(2)	140(2)	140(2)
color	orange	yellow	yellow
crystal system	orthorhombic	monoclinic	monoclinic
space group	*Pna*2$_1$	*C*2/c	*C*2/c
a, Å	23.504(2)	16.458(2)	16.481(2)
b, Å	10.787(1)	20.025(2)	20.015(2)
c, Å	27.740(2)	18.863(3)	18.556(2)
α, deg	90	90	90
β, deg	90	113.130(2)	112.625(2)
γ, deg	90	90	90
V, Å^3	7032.9(9)	5716.8(12)	5649.7(9)
Z	4	4	4
D_{calcd}, mg/m^3	1.161	1.378	1.407
F(000)	2488	2428	2452
θ range, deg	1.47 to 29.62	1.69 to 30.62	1.68 to 30.60
no. of reflns collected	62875	28183	28026
no. of independent reflns	19092	8796	8665
no. of obsd reflns ($I>2\sigma(I)$)	14406	6648	6509
no. of params	650	320	320
final R_1, wR ($I>2\sigma(I)$)	0.064, 0.151	0.037, 0.090	0.036, 0.094
goodness of fit on F^2	1.065	1.020	1.007
$\Delta\rho_{max,min}$, eÅ^{-3}	2.734, -3.858	1.154, -1.450	1.178, -1.162

Table S3. Crystallographic data and refinement patameters for complexes 6-La, 7-La and 8-La

	6-La ∃C_6H_6	**7-La 0.75C_7H_8**	**8-La 0.5C_6H_6**
formula	$C_{80}H_{86}B_2N_4Si_2La_2$	$C_{126.5}H_{164}B_4N_8Si_4La$	$C_{58}H_{74}B_2N_4Si_2La_2$
fw	1459.14	2507.89	1182.83
temperature (K)	140(2)	140(2)	140(2)
color	yellow	yellow	yellow
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	10.710(2)	18.717(1)	12.671(2)
b, Å	11.678(2)	19.518(1)	19.773(2)
c, Å	14.604(3)	21.789(2)	23.209(3)
α, deg	73.746(3)	64.072(1)	90
β, deg	85.409(3)	67.221(1)	104.069(2)
γ, deg	89.834(3)	86.825(1)	90
V, Å^3	1747.5(5)	6537.9(8)	5640.6(12)
Z	1	2	4
D_{calcd}, mg/m^3	1.387	1.274	1.393
F(000)	746	2566	2408
θ range, deg	1.46 to 25.50	1.14 to 26.00	1.37 to 30.56
no. of reflns collected	11432	46821	55824
no. of independent reflns	6397	25418	17225
no. of obsd reflns ($I>2\sigma(I)$)	5425	18662	9607
no. of params	433	1347	628
final R_1, *wR* ($I>2\sigma(I)$)	0.044, 0.115	0.047, 0.129	0.053, 0.094
goodness of fit on F^2	1.080	0.988	0.992
$\Delta\rho_{max,min}$, eÅ^{-3}	1.53, -1.25	2.26 , -0.98	1.41, -1.73

Table S4. Crystallographic data and refinement patameters for complexes 9-La

	9-La
formula	$C_{31}H_{43}BN_3SiLa$
fw	635.49
temperature (K)	140(2)
color	yellow
crystal system	monoclinic
space group	*C*2/c
a, Å	20.586(4)
b, Å	9.252(2)
c, Å	33.235(6)
α, deg	90
β, deg	103.612(3)
γ, deg	90
V, Å^3	6152.2(19)
Z	8
D_{calcd}, mg/m^3	1.372
F(000)	2608
θ range, deg	1.26 to 25.50
no. of reflns collected	20164
no. of independent reflns	5726
no. of obsd reflns ($I>2\sigma(I)$)	5223
no. of params	341
final R_1, *wR* ($I>2\sigma(I)$)	0.069, 0.135
goodness of fit on F^2	1.263
$\Delta\rho_{max,min}$, eÅ^{-3}	1.79, -3.30

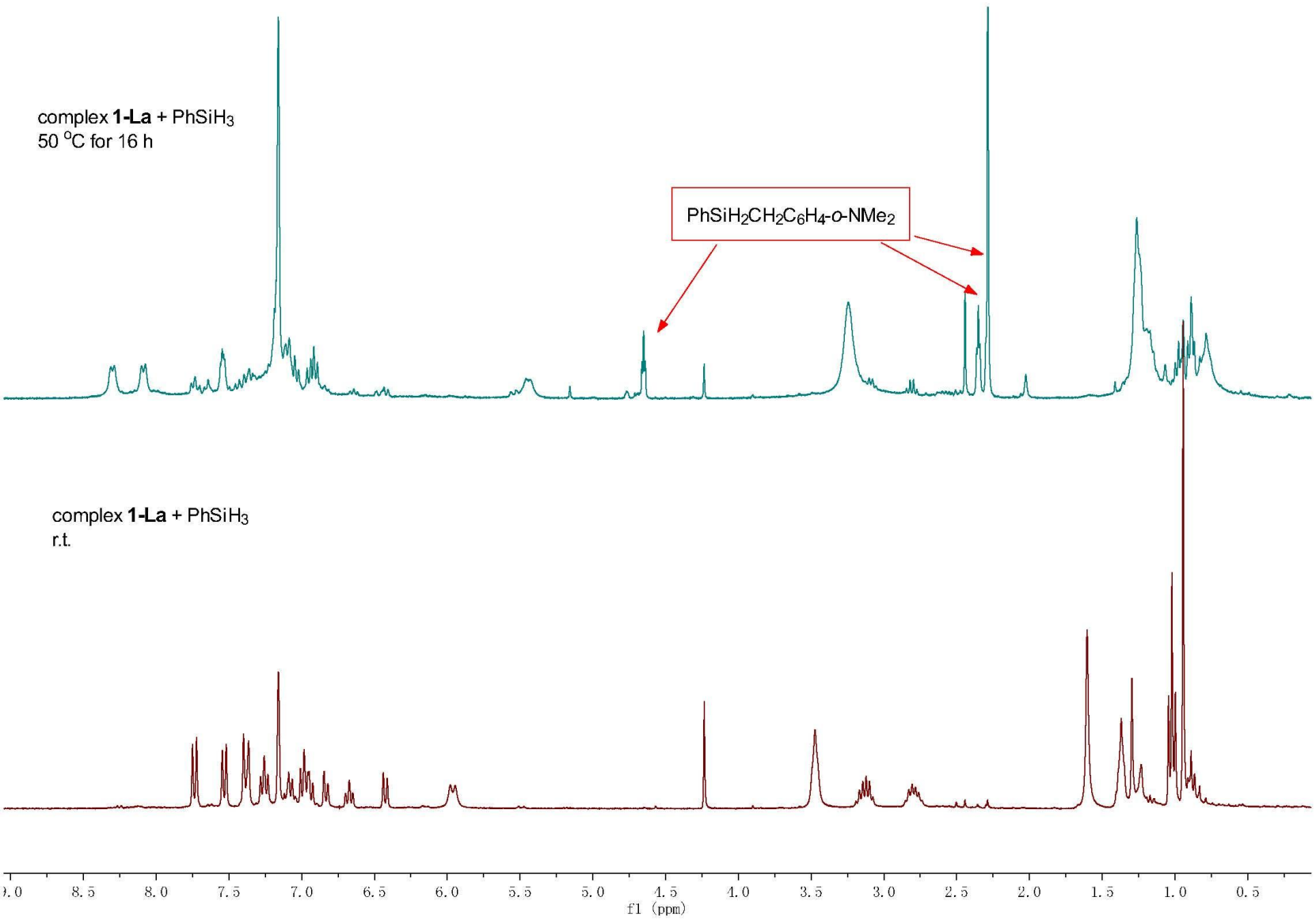


Fig. S4 ^{1}H NMR spectra of the reaction solution of **1-La** with $PhSiH_3$ (300 MHz, C_6D_6, 25 ^{o}C).

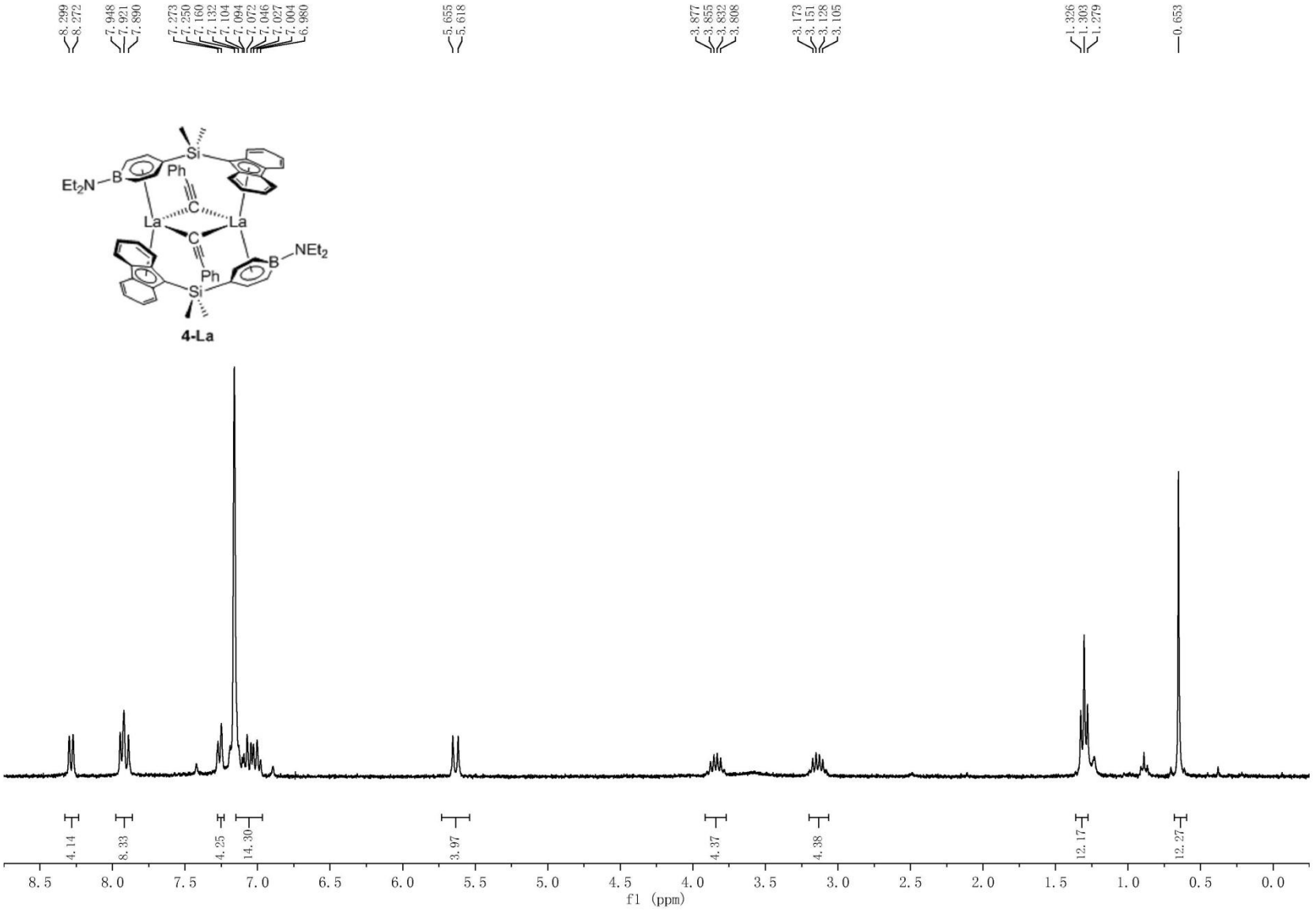


Fig. S5 ^{1}H NMR spectrum of **4-La** (300 MHz, C_6D_6, 25 ^{o}C).

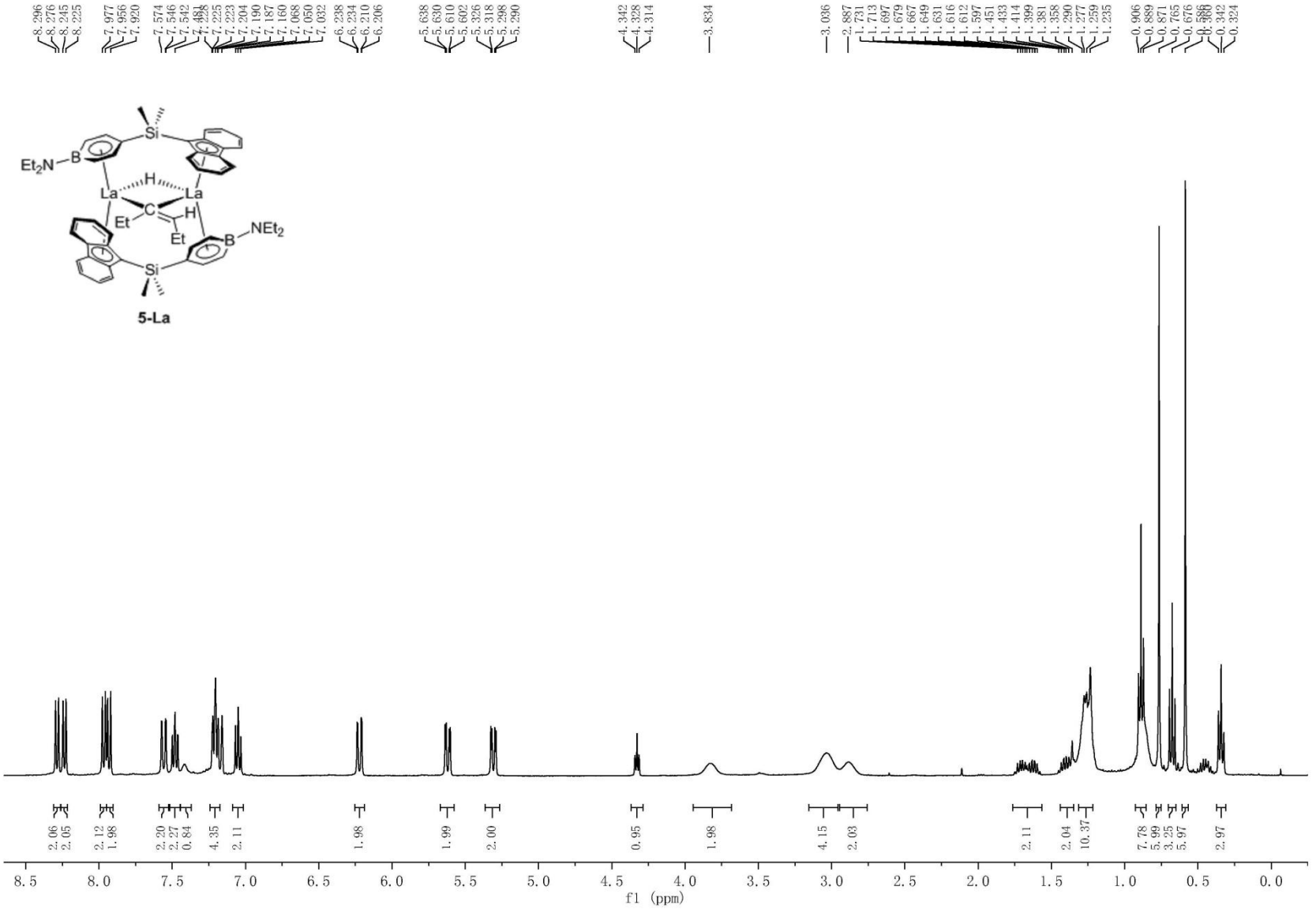


Fig. S6 ^{1}H NMR spectrum of **5-La** (400 MHz, C_6D_6, 25 ^{o}C).

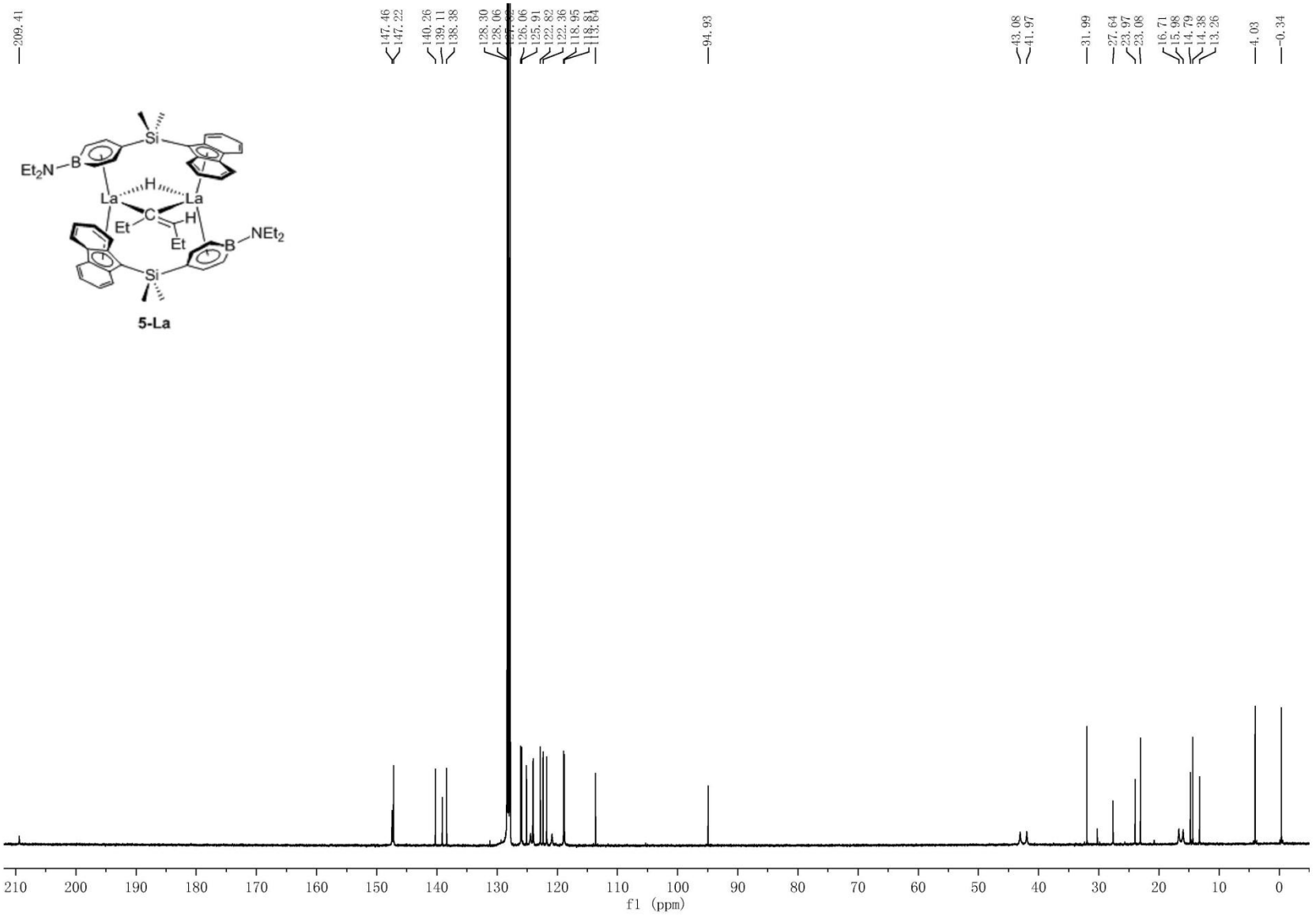


Fig. S7 ^{13}C NMR spectrum of **5-La** (100 MHz, C_6D_6, 25 ^{o}C).

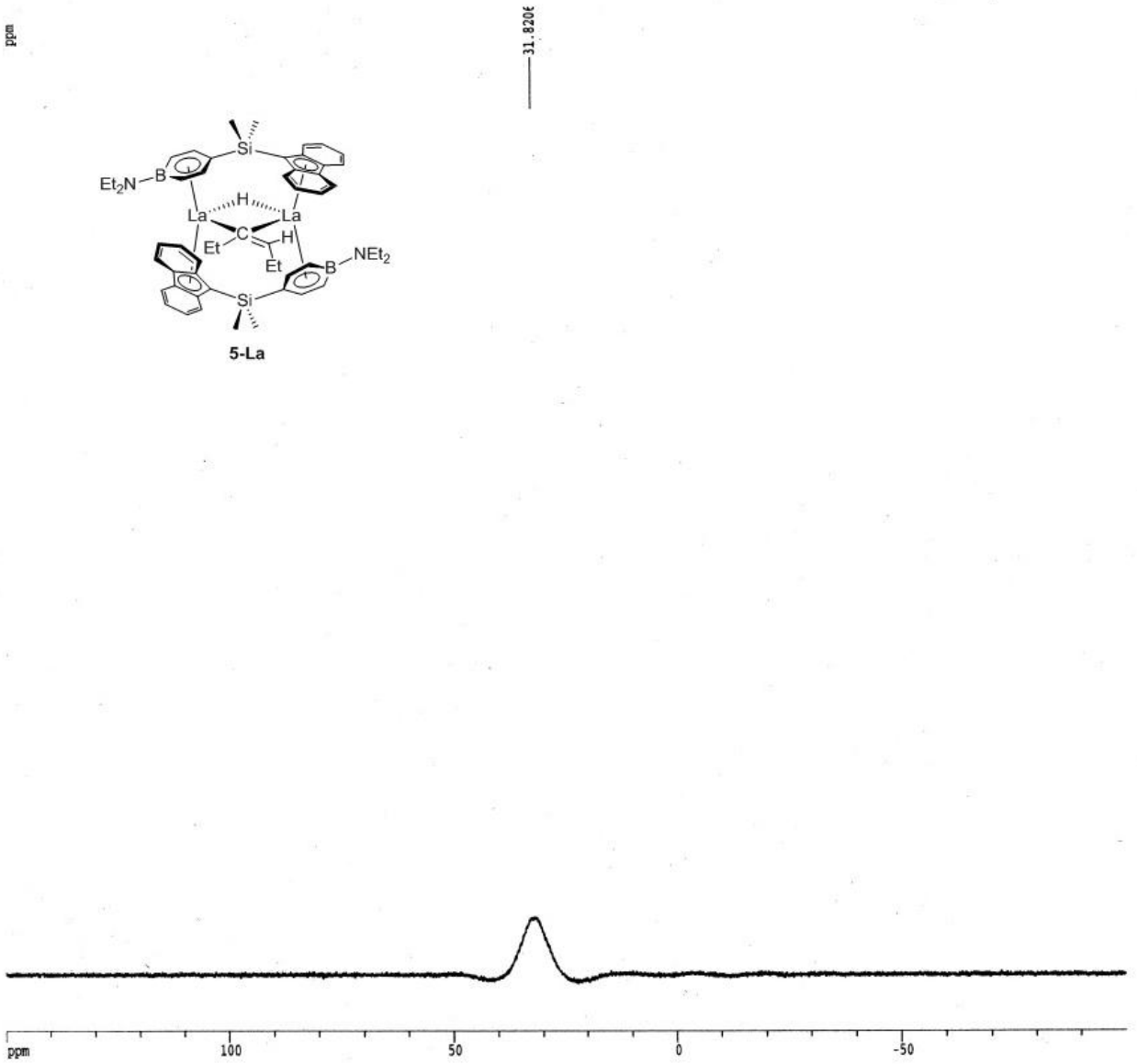


Fig. S8 ^{11}B NMR spectrum of **5-La** (128 MHz, C_6D_6, 25 ^{o}C).

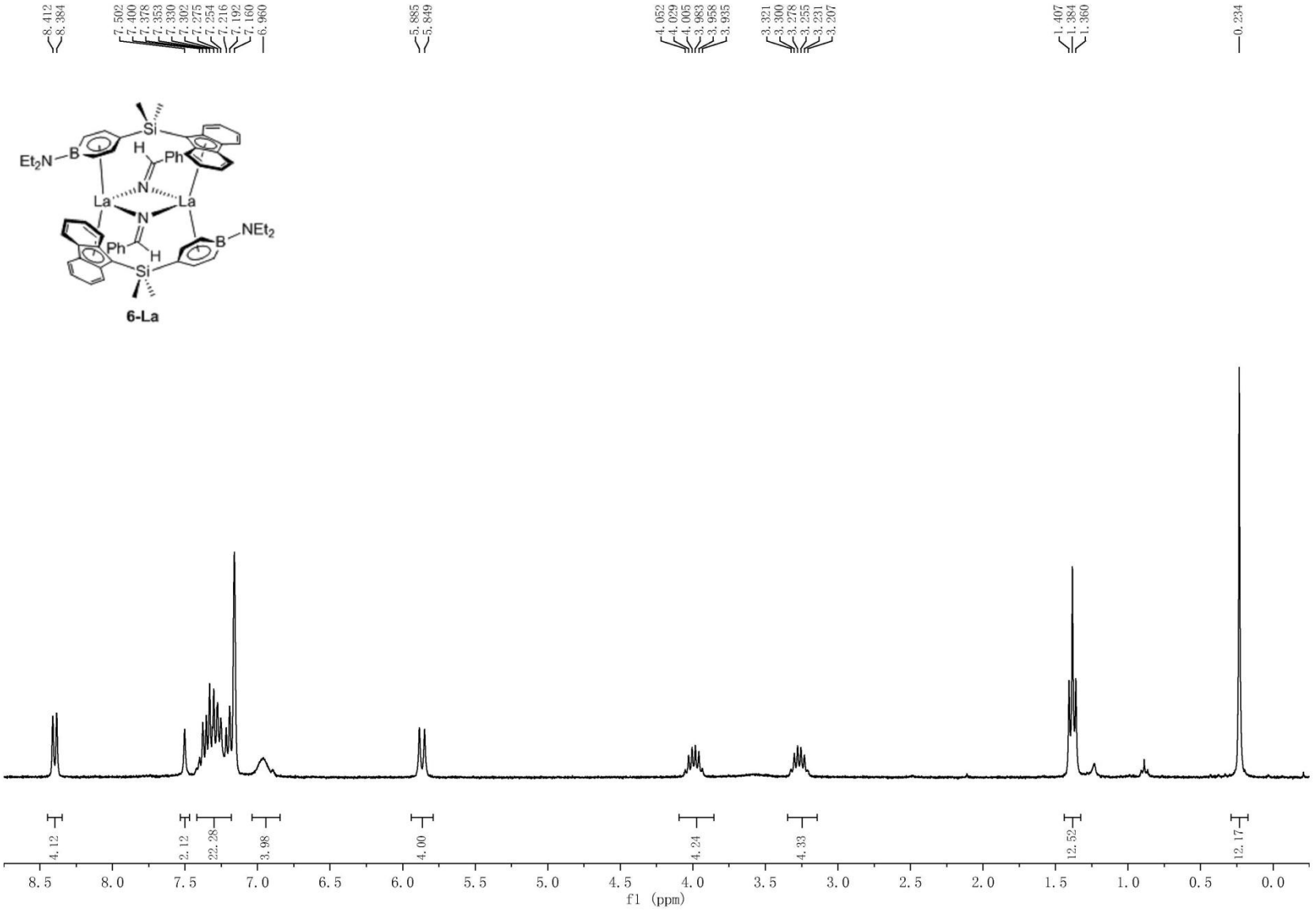


Fig. S9 ^{1}H NMR spectrum of **6-La** (300 MHz, C_6D_6, 25 ^{o}C).

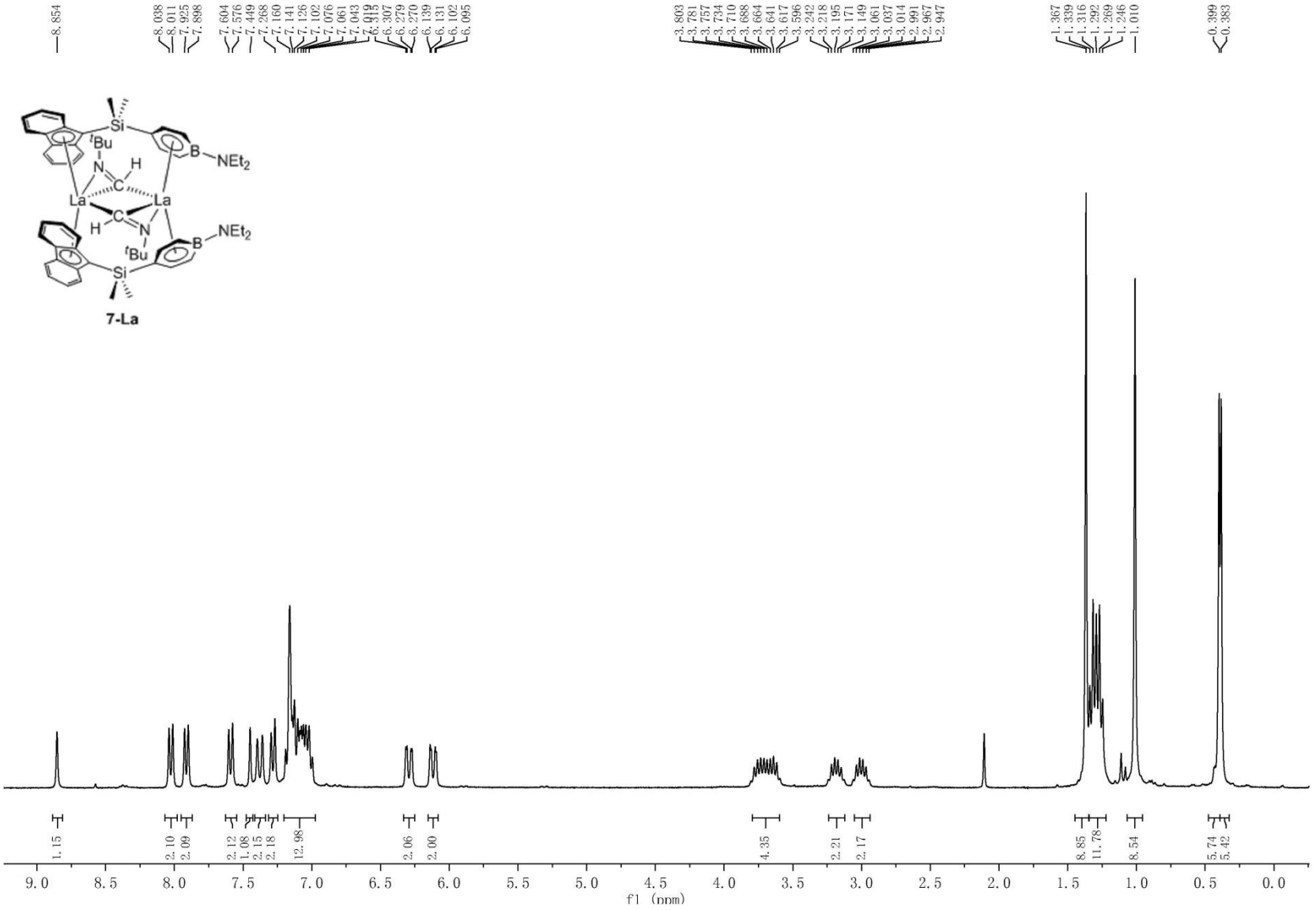


Fig. S10 ^{1}H NMR spectrum of **7-La** (300 MHz, C_6D_6, 25 ^{o}C).

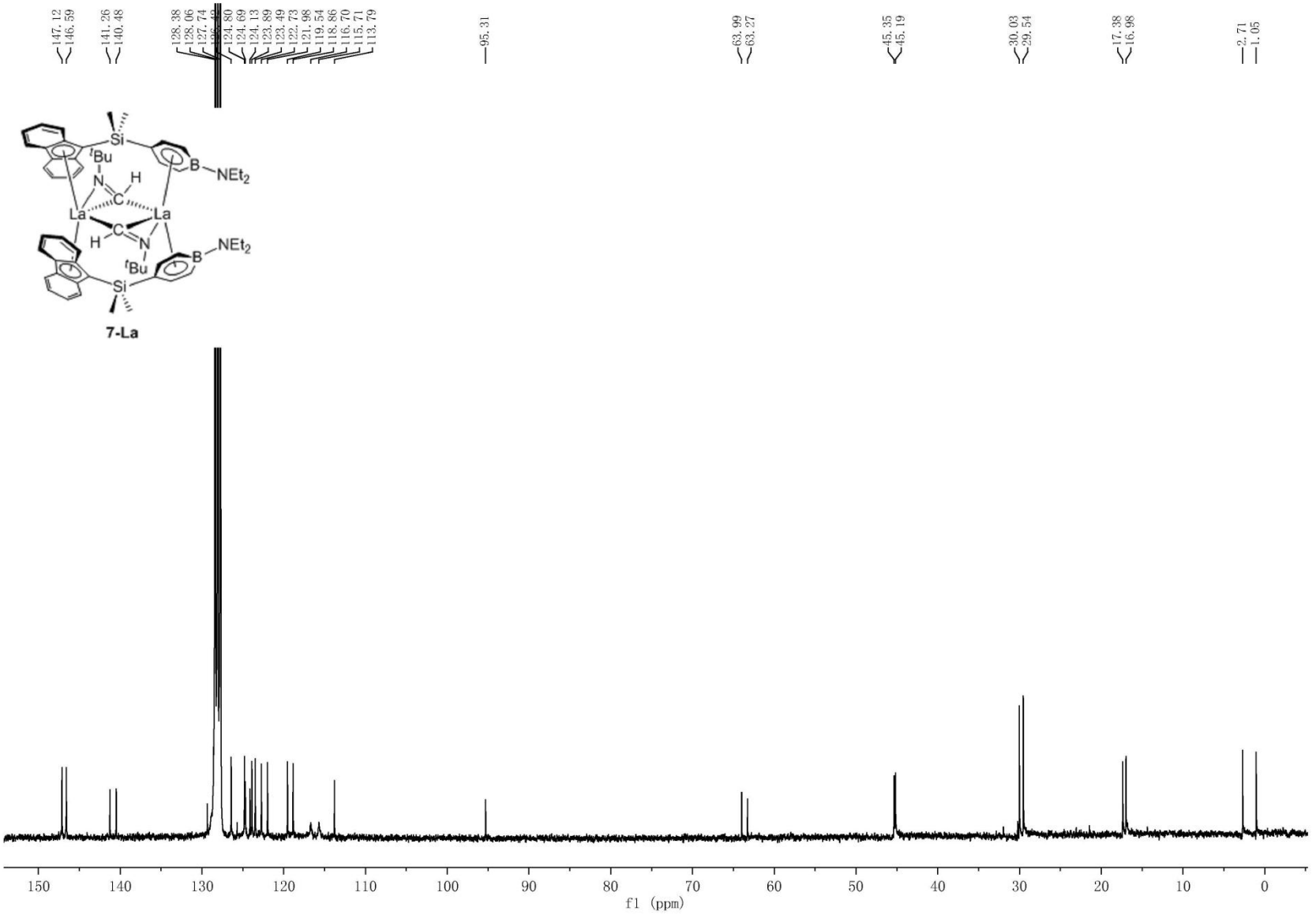


Fig. S11 ^{13}C NMR spectrum of **7-La** (75 MHz, C_6D_6, 25 ^{o}C).

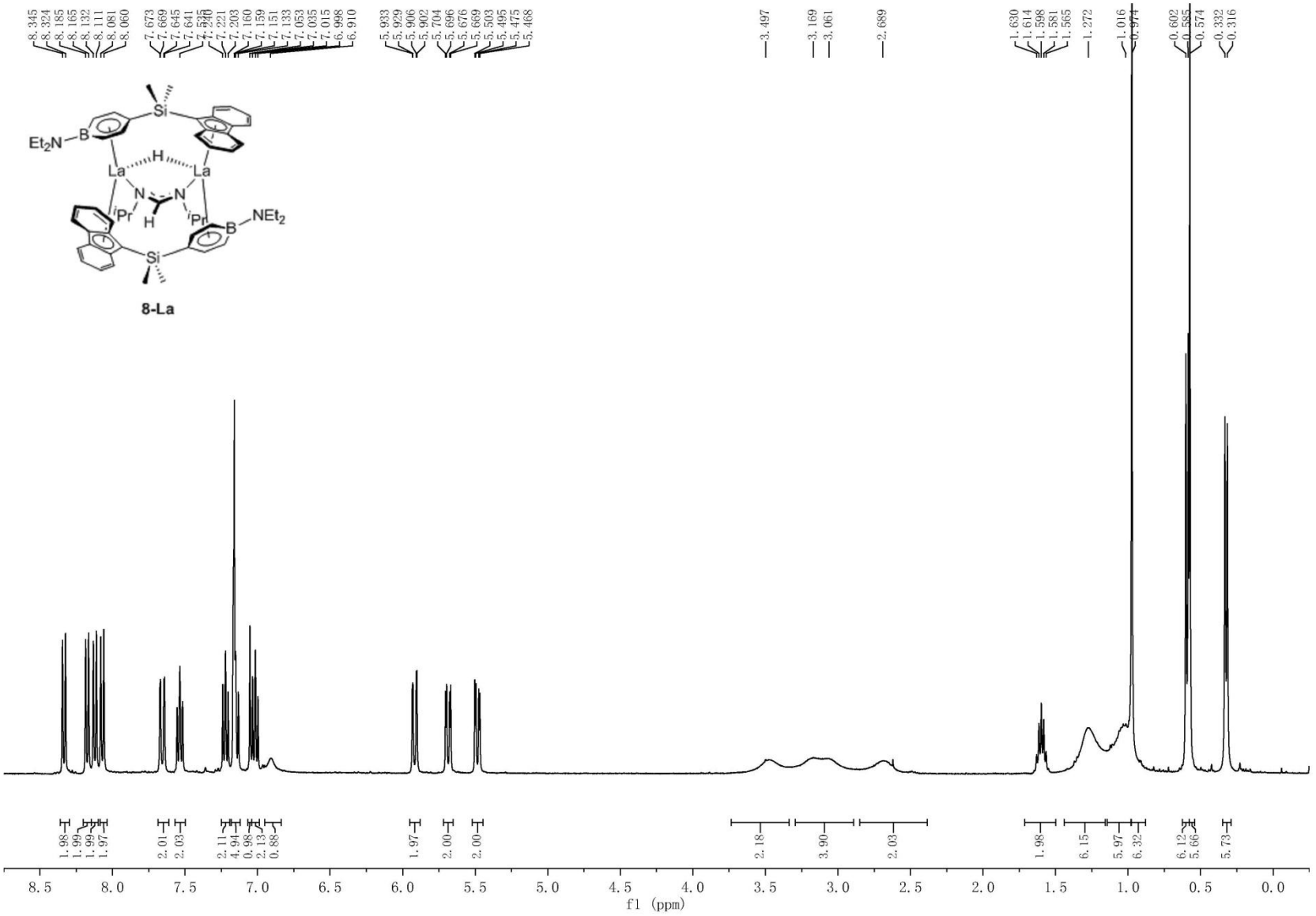


Fig. S12 ^{1}H NMR spectrum of **8-La** (400 MHz, C_6D_6, 25 ^{o}C).

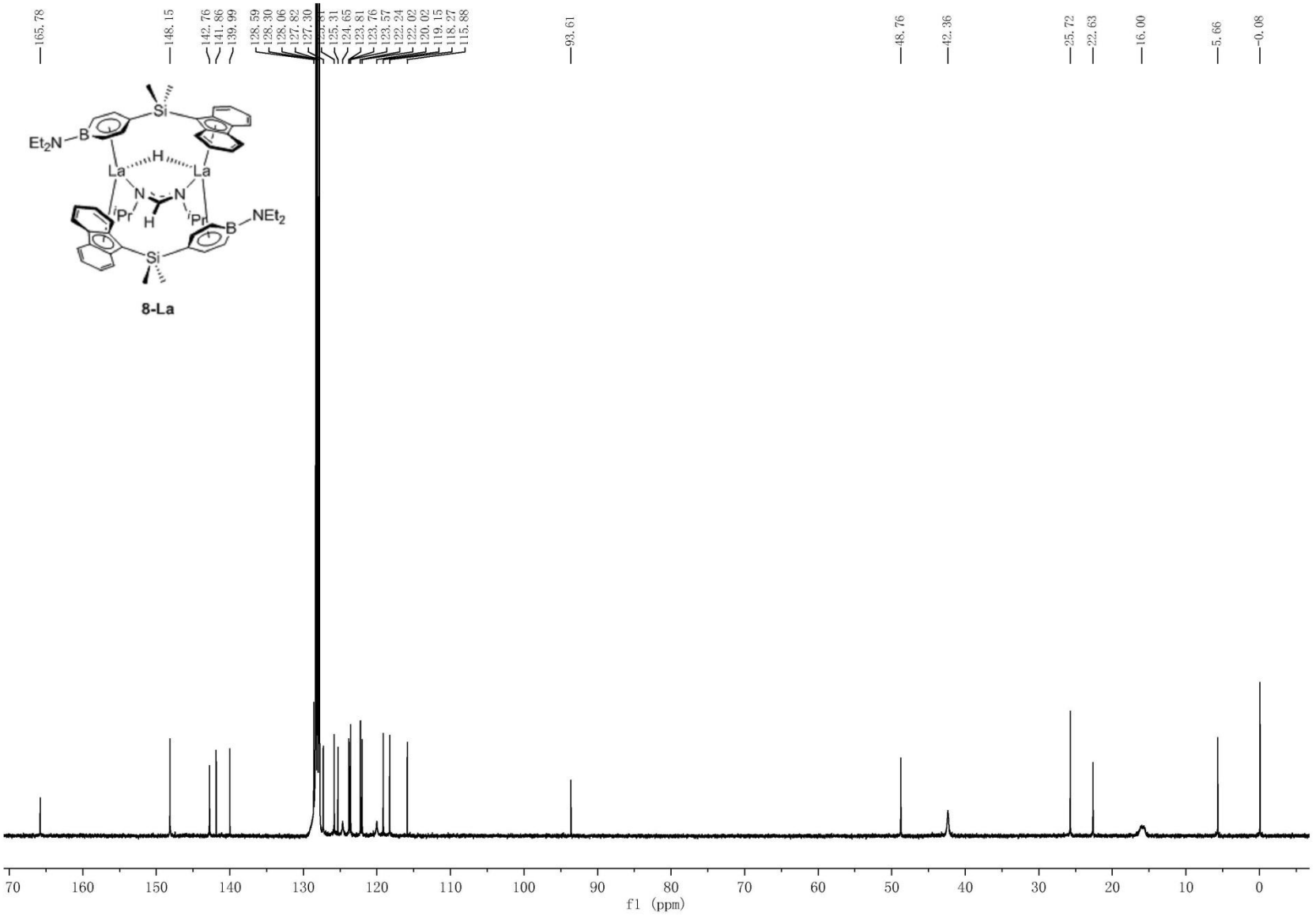
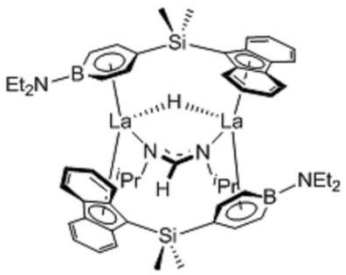


Fig. S13 ^{13}C NMR spectrum of **8-La** (100 MHz, C_6D_6, 25 ^{o}C).



8-La

Fig. S14 ^{11}B NMR spectrum of **8-La** (193 MHz, C_6D_6, 25 ^{o}C)..

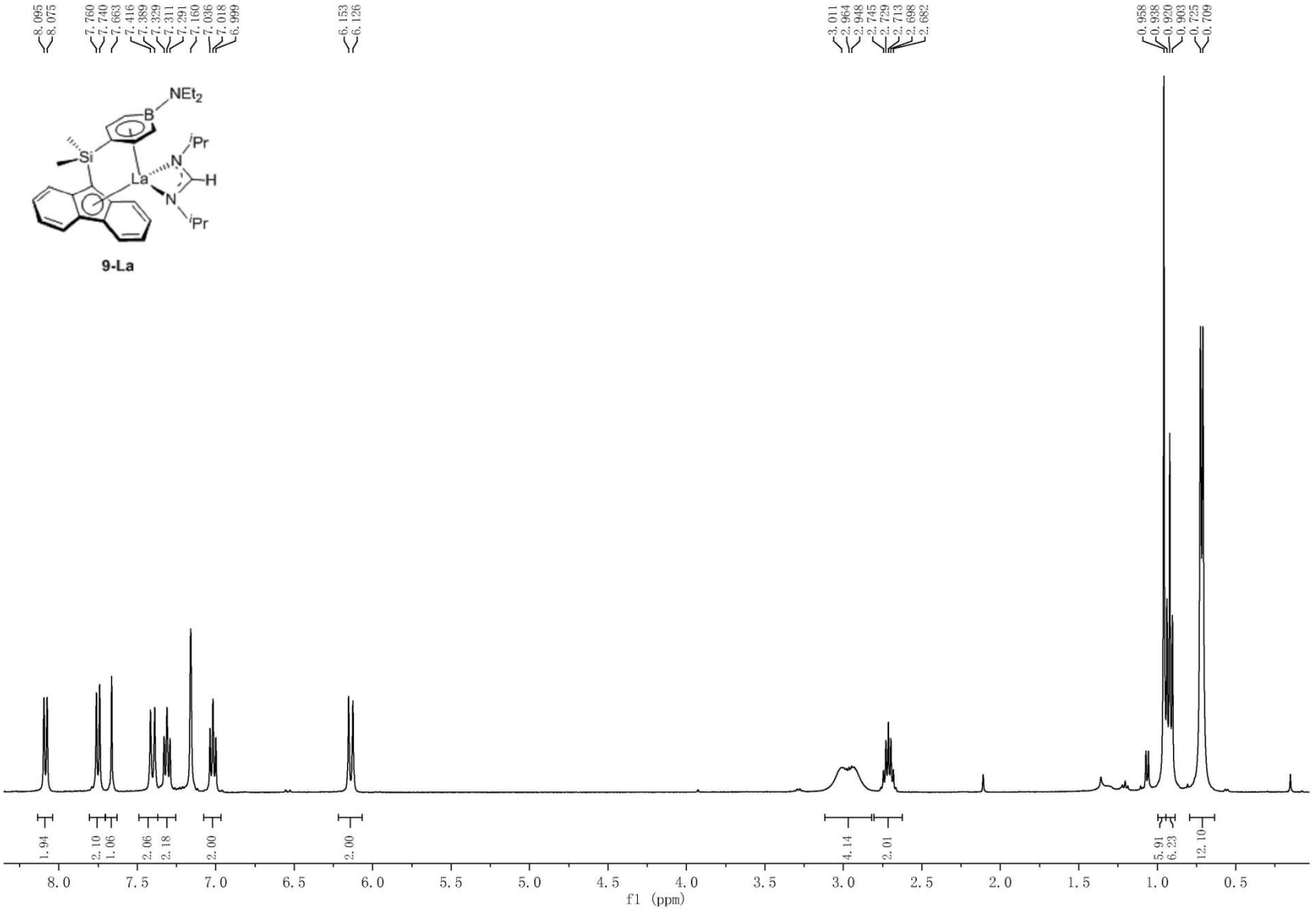


Fig. S15 ^{1}H NMR spectrum of **9-La** (400 MHz, C_6D_6, 25 ^{o}C).

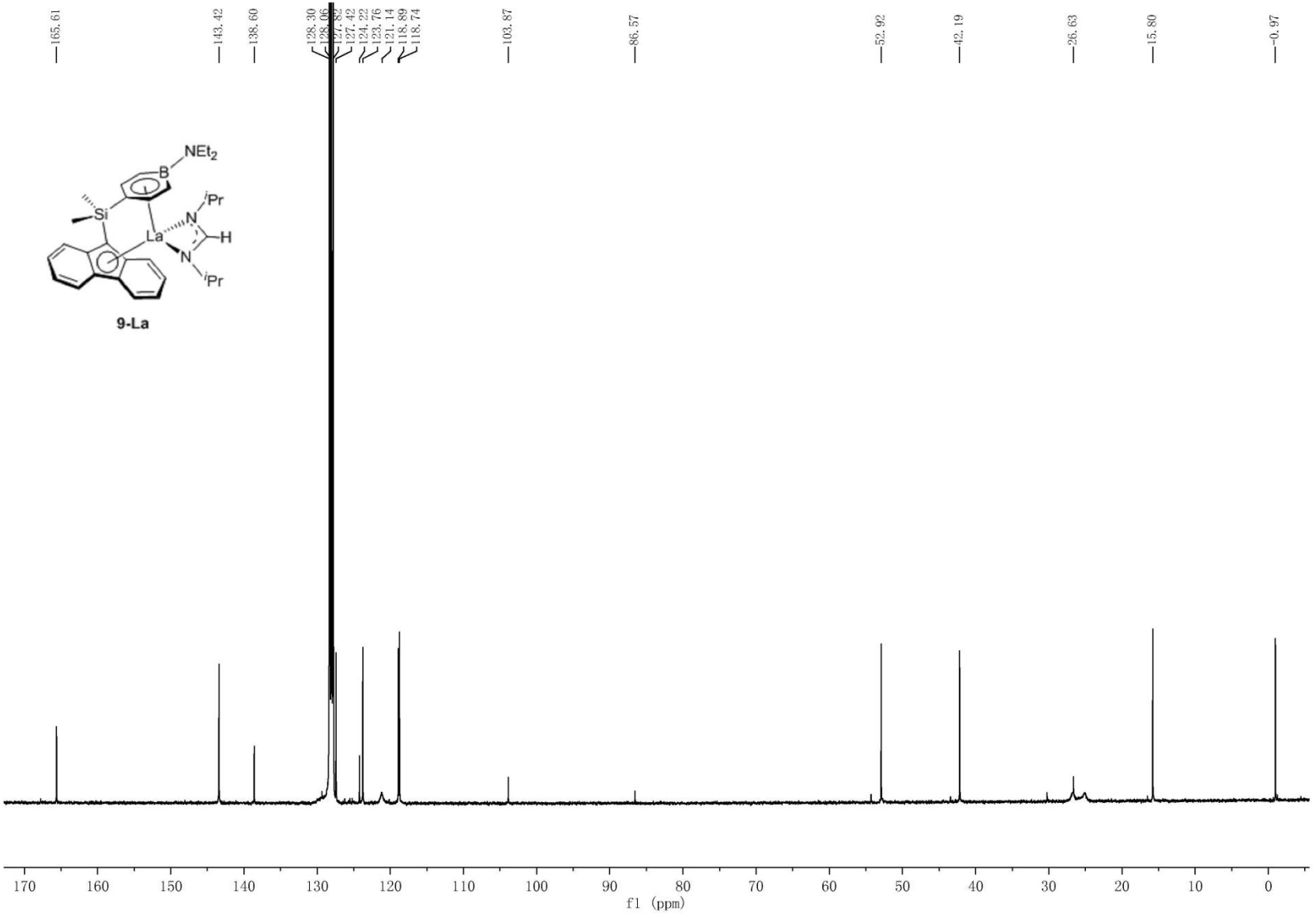


Fig. S16 ^{13}C NMR spectrum of **9-La** (100 MHz, C_6D_6, 25 ^{o}C).

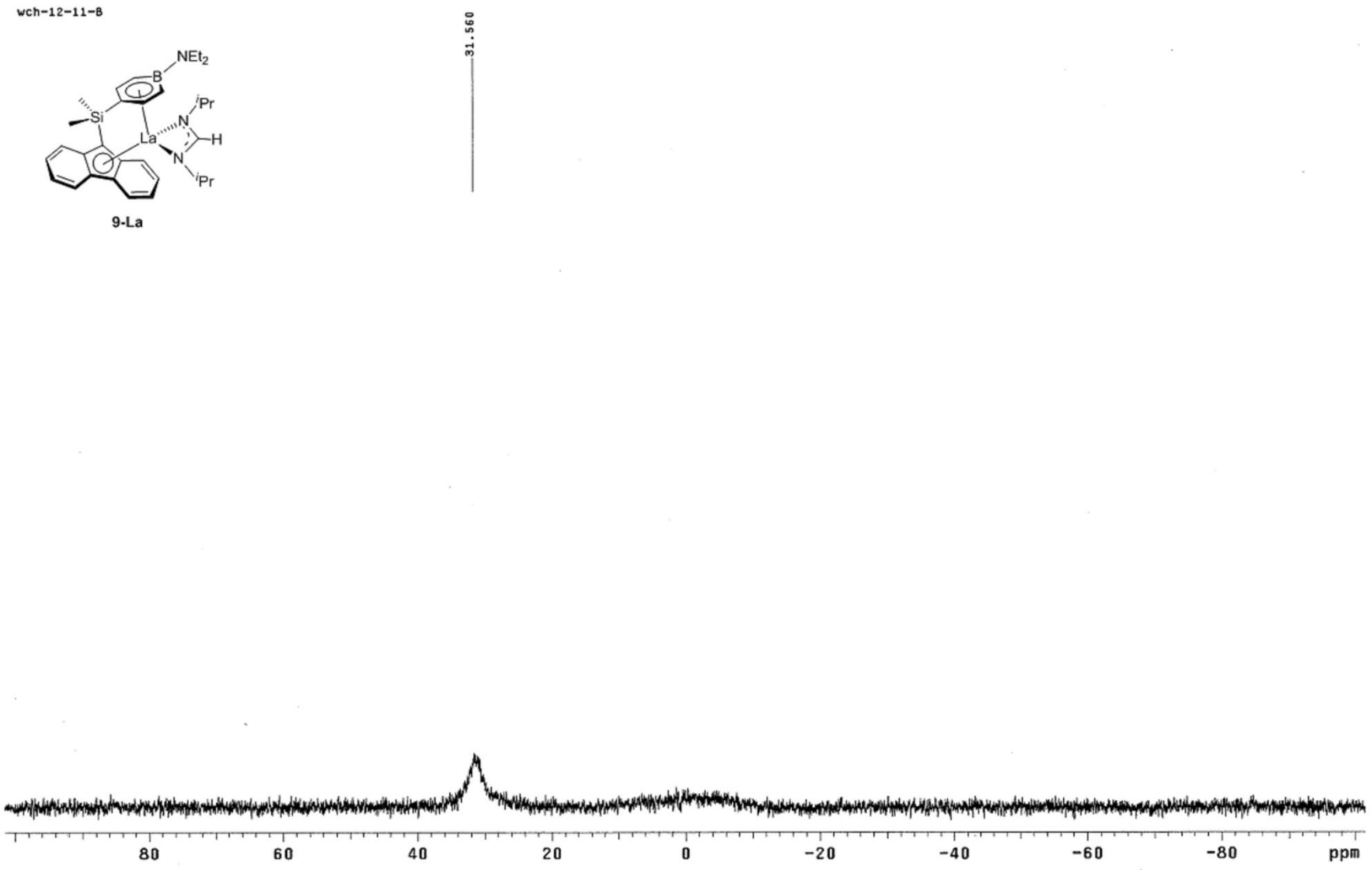


Fig. S17 ^{11}B NMR spectrum of **9-La** (193 MHz, C_6D_6, 25 ^{o}C).