Cover Page for Supporting Information

Title:

Half-sandwich Bis(propiolamidinate) Rare-earth Metal Complexes: Synthesis, Structure and Dissociation of Cyclopentadienyl Ligand via Competition with an Amidinate

Authors:

Ling Xu, [a] Yu-Chen Wang,[a] Wen-Xiong Zhang,*[,a,b] Zhenfeng Xi[a]

Affiliations:

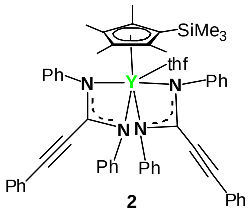
[a] Beijing National Laboratory for Molecular Sciences, MOE Key Laboratory of Bioorganic Chemistry and Molecular Engineering, College of Chemistry, Peking University, Beijing 100871, China.
[b] State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, China

Fax: +86-10-62751708; Tel: +86-10-62758294;
E-mail: wx_zhang@pku.edu.cn

Contents:

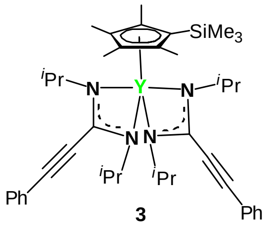
1) Experimental Section

General Methods: All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques or under a nitrogen atmosphere in a Vigor (SG 1200/750TS-F) glovebox. The nitrogen in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-500 (FT, 500 MHz for ^{1}H; 125 MHz for ^{13}C), Bruker-400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) or a JEOL-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C) at room temperature, unless otherwise noted.



2

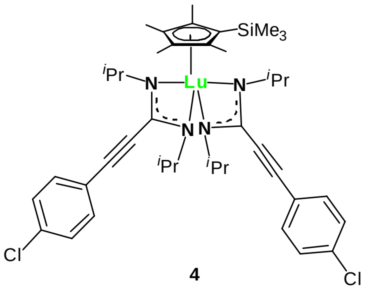
Preparation of 2: In a 25 mL flask, **1-Y** (105.5 mg, 0.20 mmol) in benzene (5 mL) was mixed with PhC≡CH (40.8 mg, 0.40 mmol). The mixture was stirred for 2 minutes at room temperature and a benzene solution (1 mL) of PhN=C=NPh (77.7 mg, 0.40 mmol) was added to this mixture and the color of the solution turned to yellow immediately. After stirring for 6 h at room temperature, the solvent was removed under reduced pressure and the residue **2** was given as yellow solid (174.0 mg, 0.184 mmol, 92% yield). This yellow solid is pure enough for NMR experiment without further purification. The crystal suitable for X-ray analysis could be grown from benzene/hexane solution of **2** at –20 °C for one week. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.36$ (s, 9H; Me_3Si), 1.34–1.37 (m, 4H; β-CH_2, thf), 2.07 (s, 6H; Cp*Me*), 2.23 (s, 6H; Cp*Me*), 3.68 (t, $J = 6.4$ Hz, 4H; α-CH_2), 6.72–6.76 (m, 4H; Ph), 6.78–6.82 (m, 2H; Ph), 6.96–7.03 (m, 8H; Ph), 7.20–7.24 (m, 8H; Ph), 7.29–7.31 (m, 8H; Ph). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 2.6$, 11.7, 14.6, 25.5, 68.9, 80.7 (d, $J_{(\mathrm{C,\,CNY})} = 3.4$ Hz), 98.5, 115.3, 121.7, 123.5, 124.7, 125.6, 128.4, 128.5, 128.6, 129.6, 132.6, 149.1, 157.2 (d, $J_{(\mathrm{C,\,NY})} = 2.4$ Hz).



3

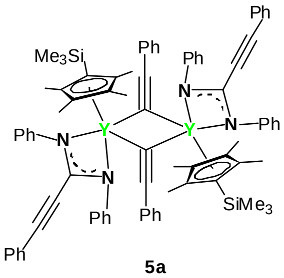
Preparation of 3: After a solution of PhC≡CH (61.2 mg, 0.60 mmol) in C_6H_6 (1 mL) was added to a solution of **1-Y** (158.6 mg, 0.30 mmol) in C_6H_6 (3 mL), the color of the mixture turned dark gradually. During this process a solution of ^{i}PrN=C=N^{i}Pr (DIC, 75.7 mg, 0.60 mmol) in C_6H_6 (1 mL) was added to this mixture and the color of the solution turned to yellow immediately. After having been stirred for 0.5 h at room temperature, the solvent was removed under reduced pressure and the residue **3** was given as yellow oil (221.6 mg, 0.30 mmol, >99% yield). This yellow oil is pure enough for NMR experiment without further purification. ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): $\delta = 0.54$ (s, 9H; Me_3Si), 1.47 (d, $J = 6.6$ Hz, 24H; CH*Me*$_2$), 2.23 (s, 6H; Cp*Me*), 2.51 (s, 6H;

Cp*Me*), 4.08–4.17 (m, 4H; C*H*Me$_2$), 6.94–6.96 (m, 6H; Ph), 7.35–7.37 (m, 4H; Ph).^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 2.9, 12.1, 15.8, 25.6, 50.0, 80.5 (d, $J_{(C, CNY)}$ = 4.0 Hz), 98.5, 113.8, 122.3, 123.6, 128.2, 128.7, 129.4, 132.0, 160.2 (d, $J_{(C, NY)}$ = 1.9 Hz).



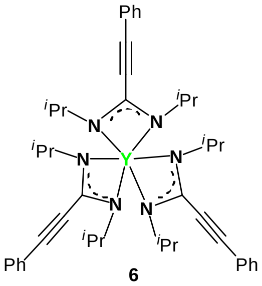
4

Preparation of 4: Starting from **1-Lu** (184.5 mg, 0.30 mmol), 4-ClC$_6$H$_4$C≡CH (81.9 mg, 0.60 mmol) and ^{i}PrN=C=N^{i}Pr (75.7 mg, 0.60 mmol), **4** was obtained as yellow oil (257.4 mg, 0.289 mmol, 96% yield). ^{1}H NMR (500 MHz, C_6D_6, Me_4Si): δ = 0.49 (s, 9H; SiMe$_3$), 1.45 (d, *J* = 6.7 Hz, 24H; CH*Me*$_2$), 2.19 (s, 6H; Cp*Me*), 2.48 (s, 6H; Cp*Me*), 4.02–4.10 (m, 4H; C*H*Me$_2$), 6.91 (d, *J* = 8.4 Hz, 4H; C$_6$H$_4$), 7.04 (d, *J* = 8.4 Hz, 4H; C$_6$H$_4$). ^{13}C NMR (125 MHz, C_6D_6, Me_4Si): δ = 2.8, 12.0, 15.6, 25.2, 49.6, 81.9, 97.7, 112.9, 120.5, 122.5, 127.6, 129.0, 133.0, 135.7, 158.9.



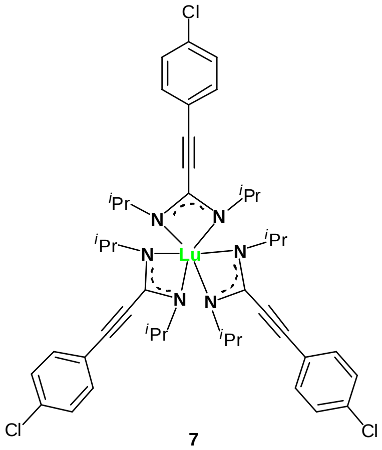
5a

Isolation of 5a: In a 25 mL flask, **1-Y** (105.5 mg, 0.20 mmol) in benzene (5 mL) was mixed with PhC≡CH (40.8 mg, 0.40 mmol). The mixture was stirred for 2 minutes at room temperature and a benzene solution (1 mL) of PhN=C=NPh (38.8 mg, 0.20 mmol) was added to this mixture. After stirring for 1 h at room temperature, the yellow powder precipitated from the yellow solution. The mother liquid was moved and the yellow powder was dried up under vacuum to give **5a** (118.7 mg, 0.087 mmol, 87% yield). The yellow crystal suitable for X-ray analysis could be grown from dilute benzene solution of **5a** at room temperature for several days. Poorly soluble in benzene and THF, partly dedimerization in benzene. ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.35 (s, 9H; SiMe$_3$), 0.42 (s, 6H; SiMe$_3$), 2.33 (s, 4H; Me), 2.34 (s, 6H; Me), 2.35 (s, 6H; Me), 2.41 (s, 4H; Me), 6.51 (t, *J* = 7.7 Hz, 2H; Ph), 6.64–6.82 (m, 5H; Ph), 6.90–6.98 (m, 4H; Ph), 7.00–7.08 (m, 12H; Ph), 7.20 (d, *J* = 7.6 Hz, 3H; Ph), 7.50 (d, *J* = 7.3 Hz, 4H; Ph), 7.67 (d, *J* = 7.4 Hz, 3H; Ph).



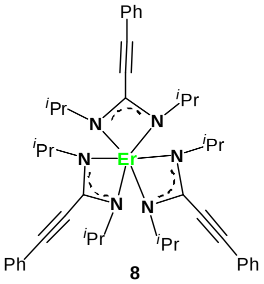
6

Preparation of 6: Method A. In a 25 mL Schlenk tube, in-situ generated **3** from **1-Y** (105.6 mg, 0.20 mmol), PhC≡CH (40.8 mg, 0.40 mmol) and DIC (50.4 mg, 0.40 mmol) was mixed with PhC≡CH (20.4 mg, 0.20 mmol) and DIC (25.2 mg, 0.20 mmol) solved in C$_6$H$_6$ (5 mL). Then the tube was taken outside the glovebox and the mixture was stirred at 80 °C for 3 h. After the solvent was removed under reduced pressure, hexane (0.5 mL) was added to the residue. **6** was obtained as colorless solid (136.2 mg, 0.177 mmol, 88% yield) by recrystallization at –20 °C in glovebox. **Method B.** In a 25 mL Schlenk tube in-situ generated **3** from **1-Y** (158.6 mg, 0.30 mmol), PhC≡CH (61.2 mg, 0.6 mmol) and DIC (75.7 mg, 0.6 mmol) were mixed with PhCCC(=N^{i}Pr)NH^{i}Pr (68.5 mg, 0.30 mmol) solved in C$_6$H$_6$ (5 mL). Then the tube was taken outside the glovebox and the mixture was stirred at 80 °C for 12 h. After the solvent was removed under reduced pressure, hexane (0.5 mL) was added to the residue. **6** was obtained as colorless solid (231.6 mg, 0.30 mmol, > 99% yield). **Method C.** In a 25 mL Schlenk tube, **1-Y** (105.6 mg, 0.20 mmol), PhC≡CH (61.2 mg, 0.60 mmol) and DIC (75.7 mg, 0.60 mmol) were mixed. Then the tube was taken outside the glovebox and the mixture was stirred at 80 °C for 3 h. After the solvent was removed under reduced pressure, hexane (0.5 mL) was added to the residue. **6** was obtained as colorless solid (136.0 mg, 0.176 mmol, 88% yield) by recrystallization at –20 °C in glovebox. Single crystal suitable for X-ray analysis could be grown from Et_2O/hexane for 1 day at room temperature. ^1H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.48 (d, J = 6.3 Hz, 36H; CH*Me*$_2$), 4.18–4.27 (m, 6H; C*H*Me$_2$), 6.90–6.97 (m, 9H; Ph), 7.35–7.38 (m, 6H; Ph). ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 26.6, 50.1, 78.9 (d, $J_{(C, CNY)}$ = 3.4 Hz), 97.7, 122.4, 128.6, 129.3, 132.4, 160.8 (d, $J_{(C, NY)}$ = 1.8 Hz).



7

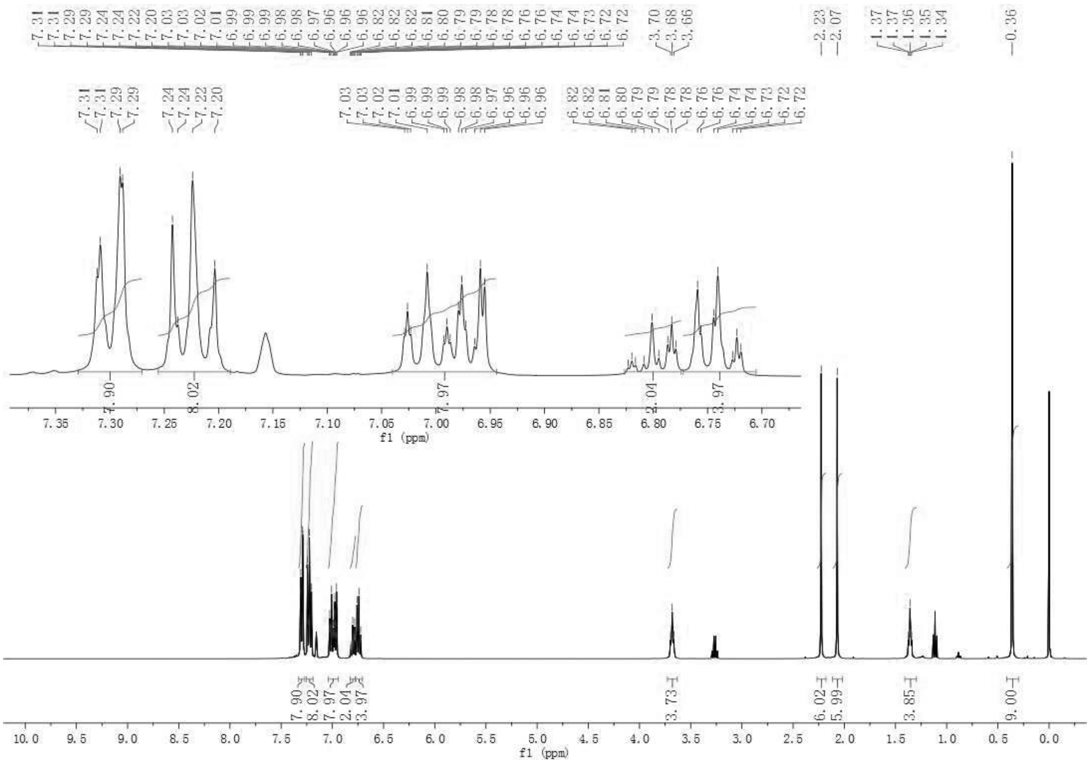
Preparation of 7: Similar to method **C**, starting from **1-Lu** (123.0 mg, 0.2 mmol), 4-ClC$_6$H$_4$C≡CH (81.9 mg, 0.60 mmol) and DIC (75.7 mg, 0.60 mmol), **7** was obtained as pale yellow solid (192.3 mg, 0.166 mmol, 83% yield). ^1H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.47 (d, J = 6.4 Hz, 36H; CH*Me*$_2$), 4.20–4.29 (m, 6H; C*H*Me$_2$), 6.90 (d, J = 8.5 Hz, 6H; C$_6$*H*$_4$), 7.04 (d, J = 8.5 Hz, 6H; C$_6$*H*$_4$). ^{13}C NMR (100 MHz, C_6D_6): δ = 26.5, 50.2, 79.9, 96.8, 120.5, 129.0, 133.5, 135.6, 160.0.

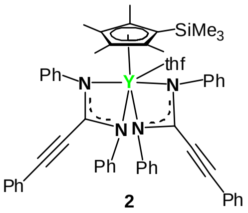


8

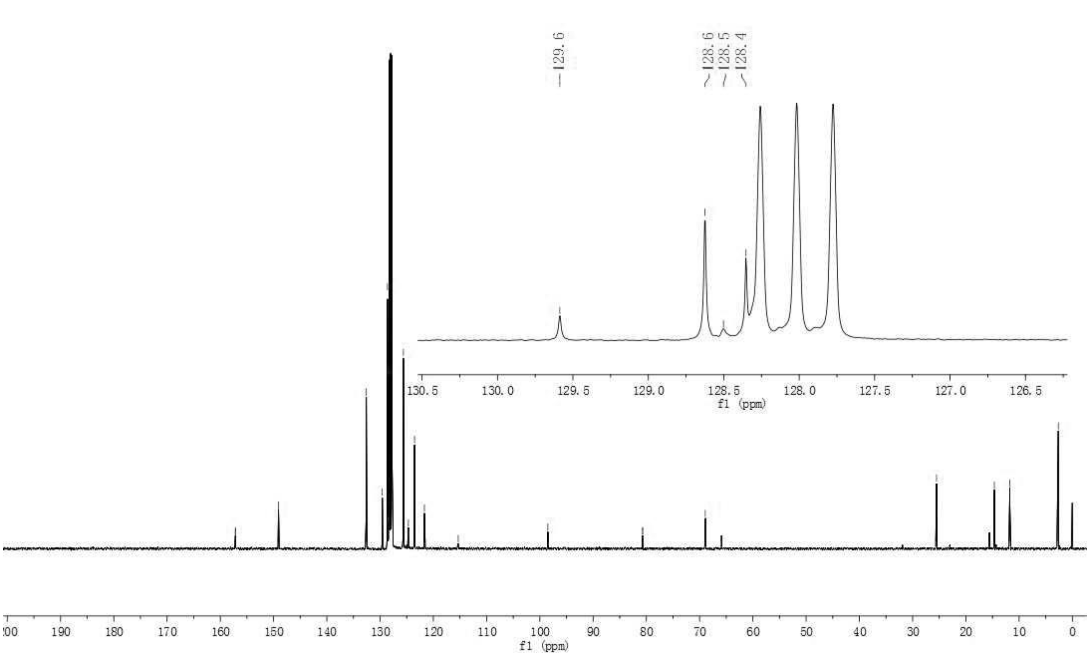
Preparation of 8: Similar to method **C**, starting from **1-Er** (182.1 mg, 0.3 mmol), **8** was obtained as pink solid (252.4 mg, 0.297 mmol, 99% yield). Single crystal suitable for X-ray analysis could be grown from Et_2O/hexane for 1 day at room temperature. Anal. Calcd for $C_{45}H_{57}ErN_6$: C, 63.64; H, 6.77; N, 9.90; Found: C, 63.59; H, 6.77; N, 9.82.

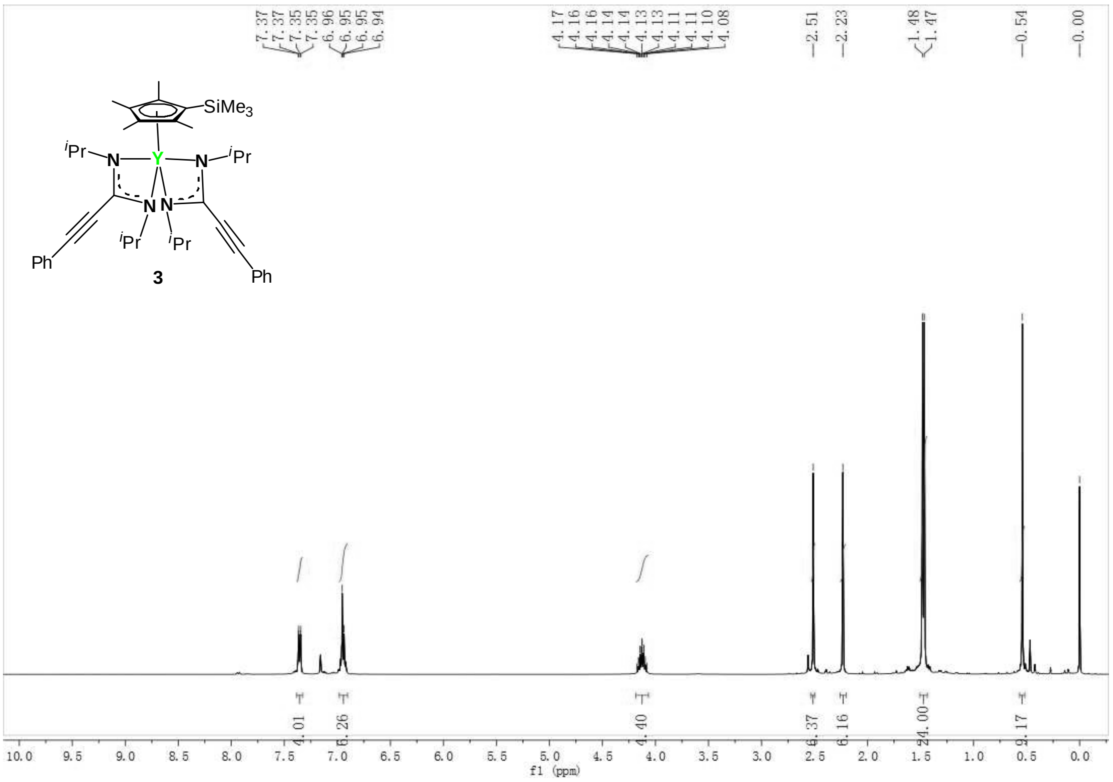
2) Copies of ^{1}H NMR and ^{13}C NMR Spectra of All New Compounds

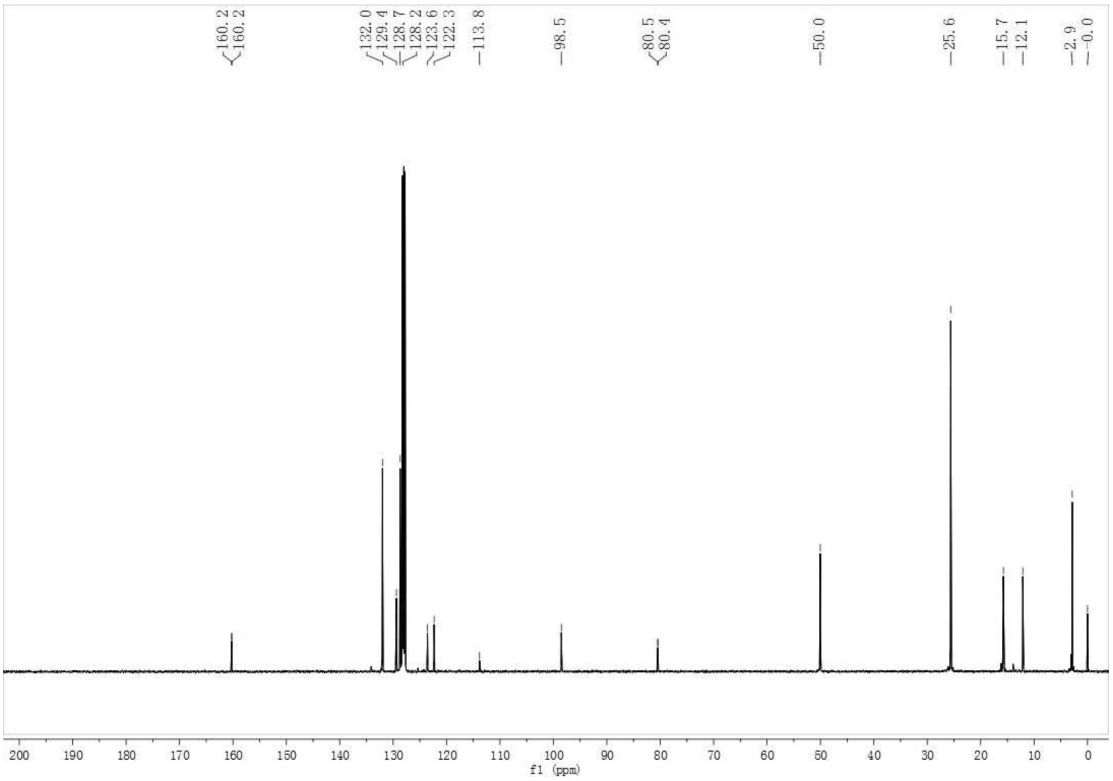


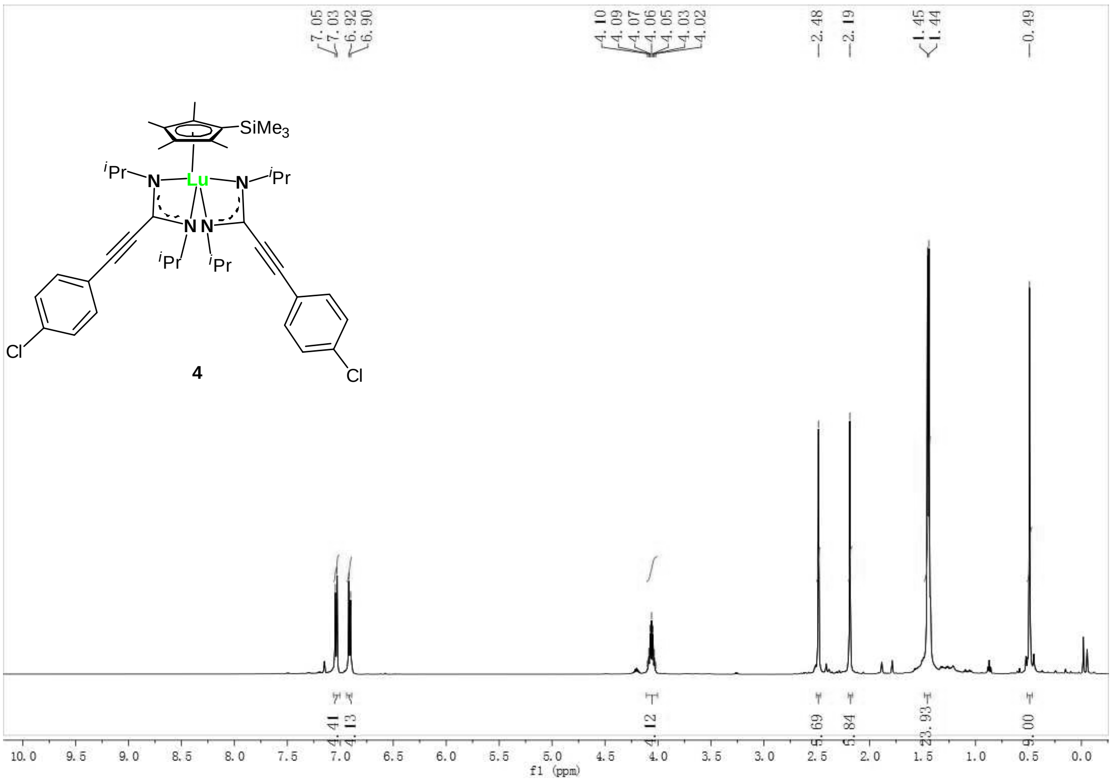


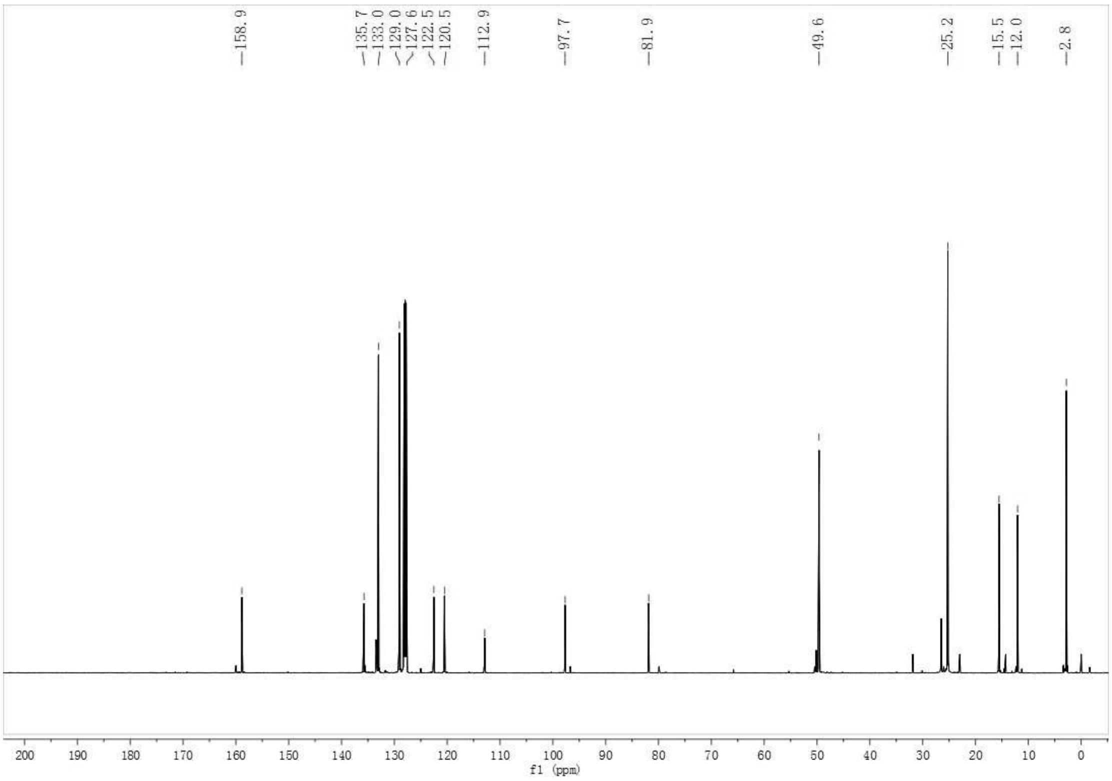
2

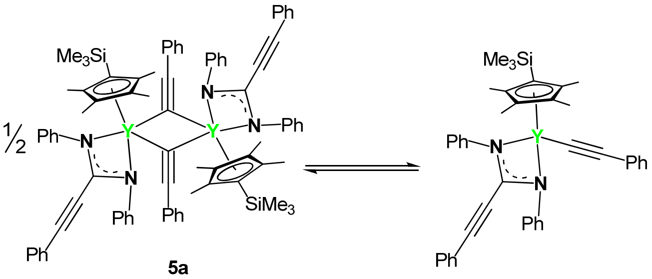



7.37
7.37
7.35
7.35
6.96
6.95
6.95
6.94
4.17
4.16
4.16
4.14
4.14
4.13
4.13
4.11
4.11
4.10
4.08
2.51
2.23
1.48
1.47
0.54
0.00
SiMe3
iPr
N
Y
N
iPr
N
N
iPr
iPr
Ph
Ph
3
4.01
6.26
4.40
6.37
6.16
24.00
9.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

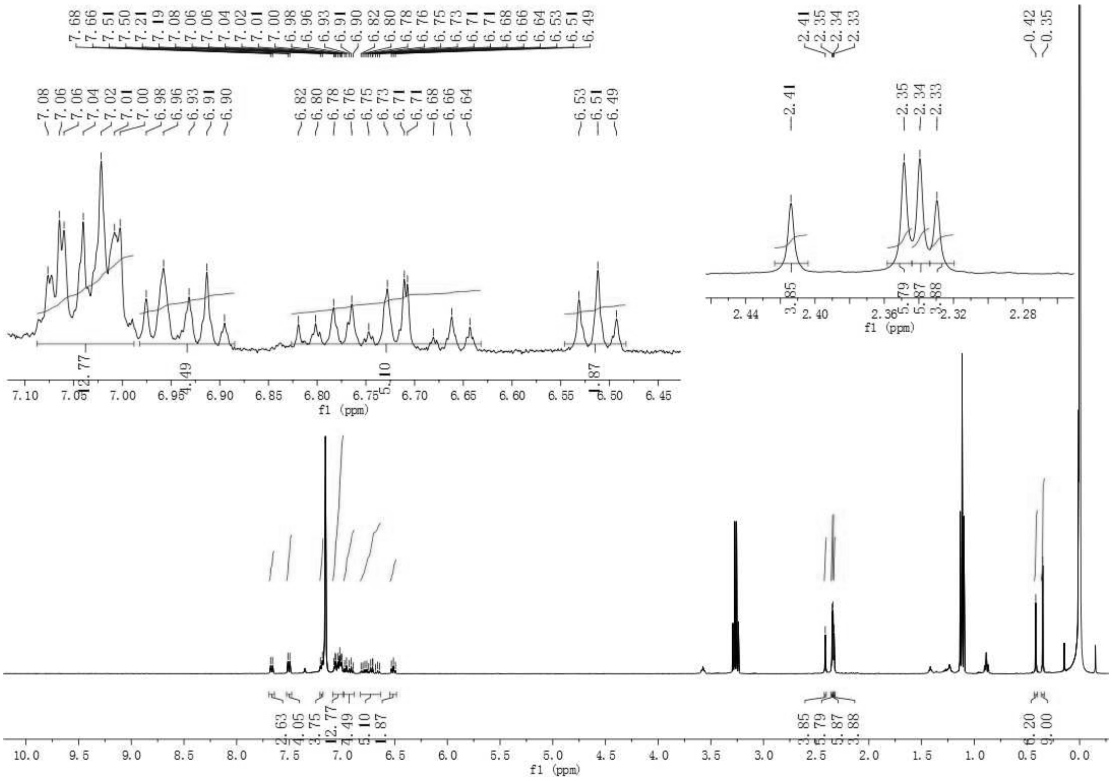

160.2
160.2
132.0
129.4
128.7
128.2
123.6
122.3
113.8
98.5
80.5
80.4
50.0
25.6
15.7
12.1
2.9
-0.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

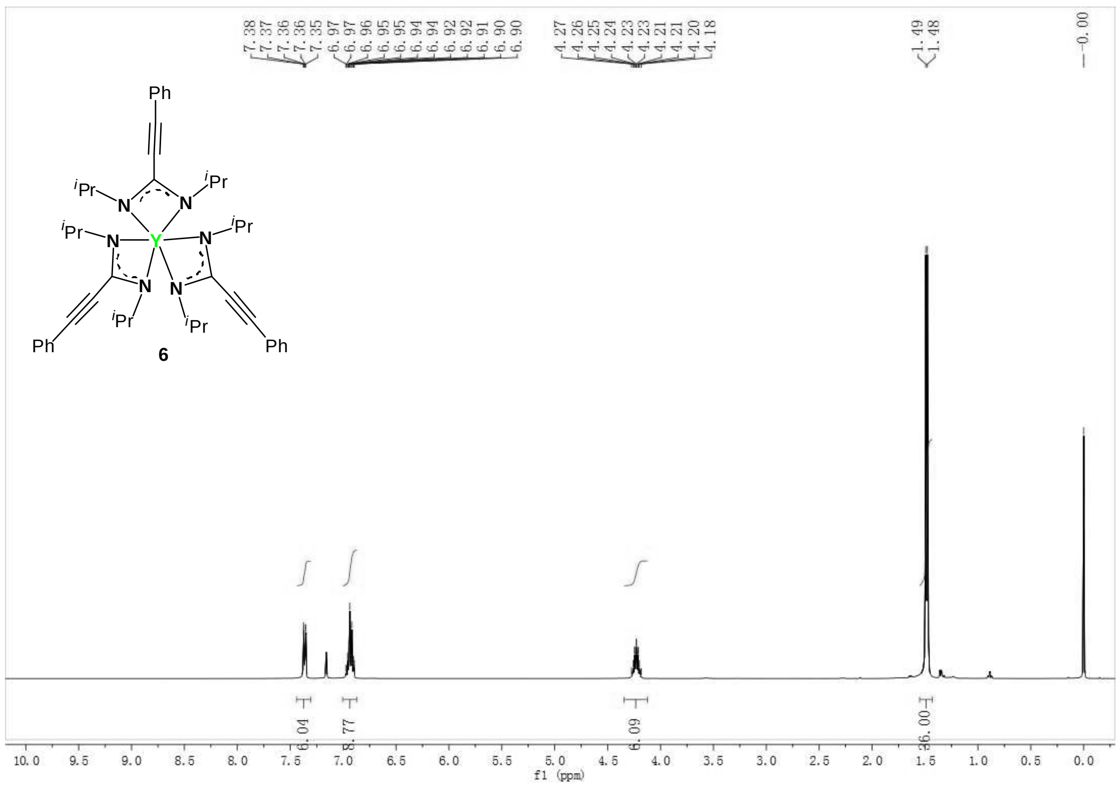

7.05
7.03
6.92
6.90
4.10
4.09
4.07
4.06
4.05
4.03
4.02
2.48
2.19
1.45
1.44
0.49
SiMe3
iPr
N
Lu
N
iPr
N
N
iPr
iPr
Cl
4
Cl
4.41
4.13
4.12
5.69
5.84
23.93
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

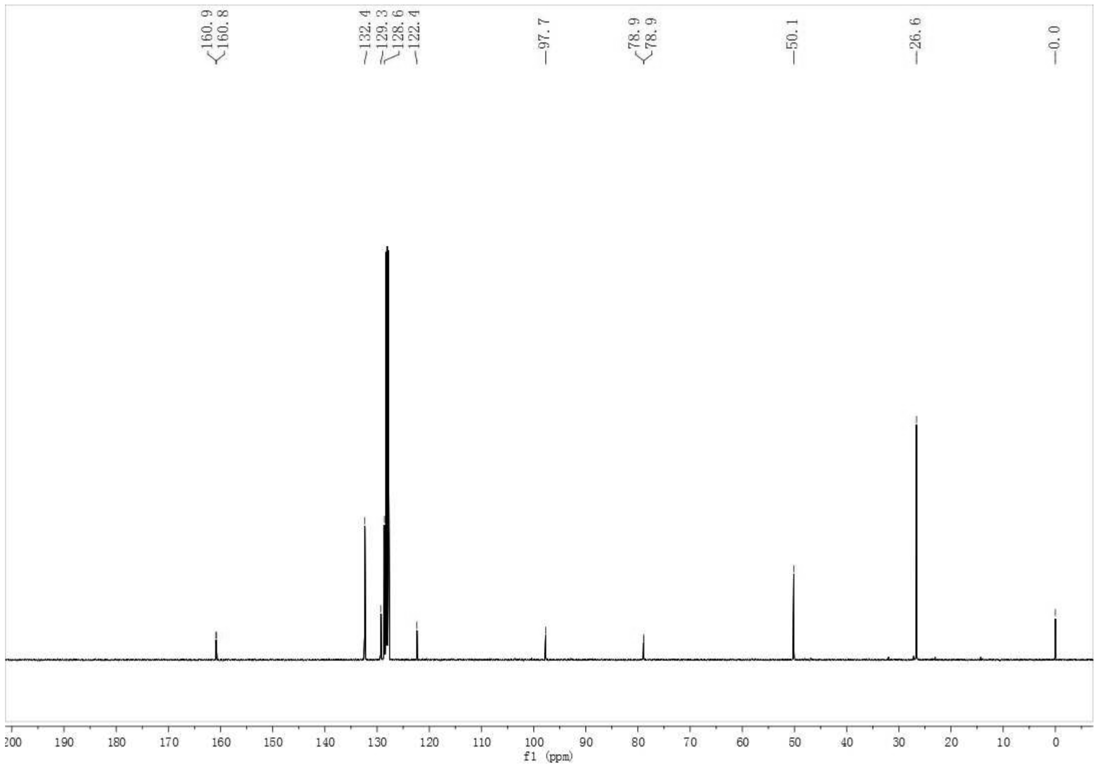

158.9
135.7
133.0
129.0
127.6
122.5
120.5
112.9
97.7
81.9
49.6
25.2
15.5
12.0
2.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

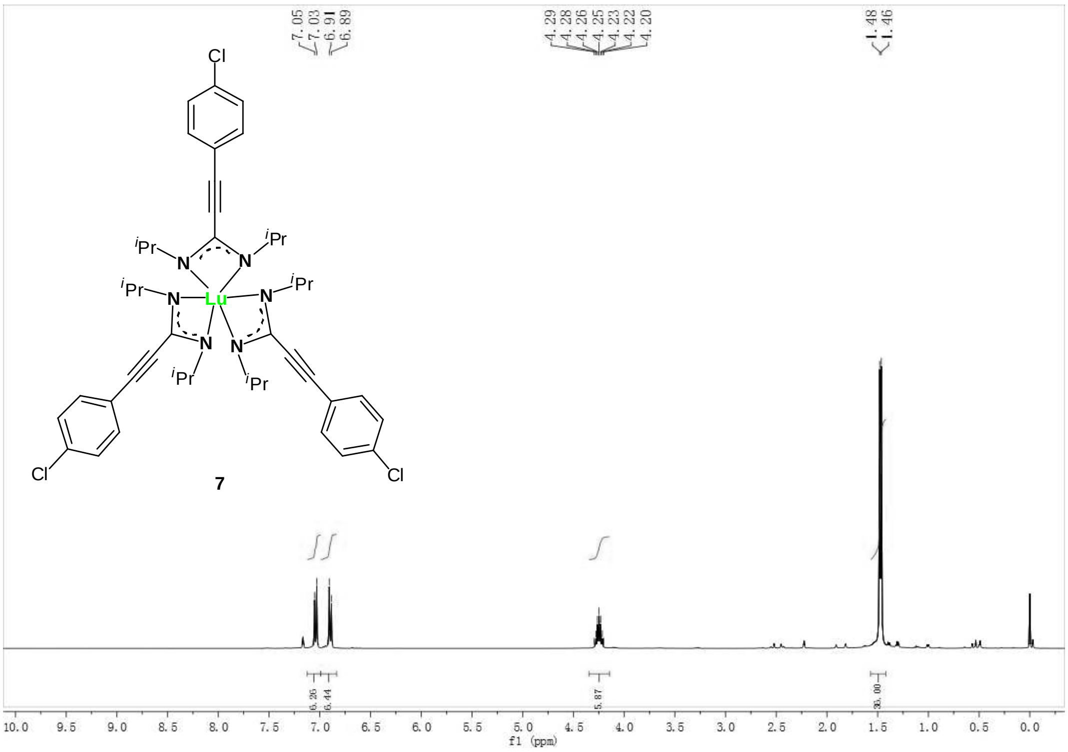

Ph
Me3Si
Ph
Ph
½
Ph
N
Y
Y
N
Ph
N
N
Ph
Ph
SiMe3
Ph
Me3Si
Ph
N
Y
Ph
N
Ph
Ph

5a

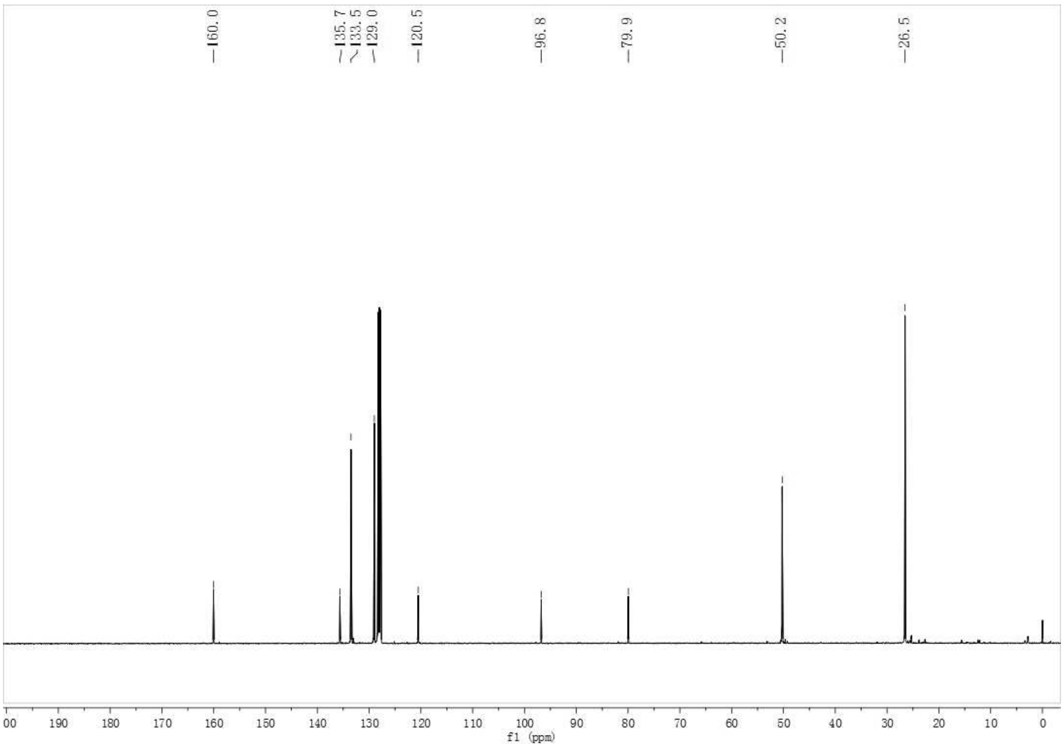

7.68 7.66 7.51 7.50 7.21 7.19 7.08 7.06 7.06 7.04 7.02 7.01 7.00 6.98 6.96 6.93 6.91 6.90 6.82 6.80 6.78 6.76 6.75 6.73 6.71 6.71 6.68 6.66 6.64 6.53 6.51 6.49
2.41 2.35 2.34 2.33
0.42 0.35
12.77
4.49
5.10
1.87
7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60 6.55 6.50 6.45
f1 (ppm)
3.85 5.79 5.87 3.88
2.44 2.40 2.36 2.32 2.28
f1 (ppm)
2.63 4.05 3.75 12.77 4.49 5.10 1.87
3.85 5.79 5.87 3.88
6.20 9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.38
7.37
7.36
7.36
7.35
6.97
6.97
6.96
6.95
6.95
6.94
6.94
6.92
6.92
6.91
6.90
6.90
4.27
4.26
4.25
4.24
4.23
4.23
4.21
4.21
4.20
4.18
1.49
1.48
-0.00
Ph
^{i}Pr
N
Y
6
6.04
8.77
6.09
36.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.9
160.8
132.4
129.3
128.6
122.4
97.7
78.9
78.9
50.1
26.6
-0.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

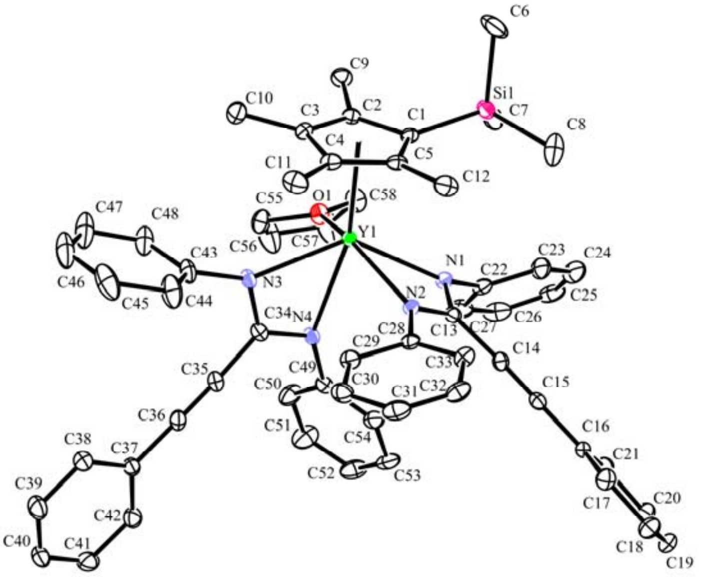

7.05
7.03
6.91
6.89
4.29
4.28
4.26
4.25
4.23
4.22
4.20
1.48
1.46
Cl
iPr
N
Lu
6.26
6.44
5.87
36.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

7

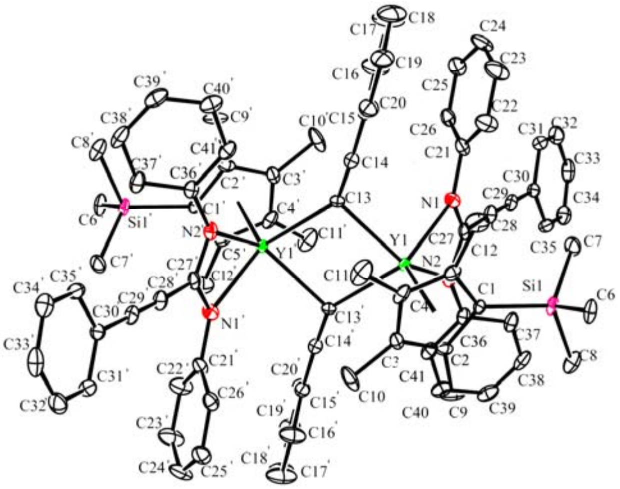

160.0
135.7
133.5
129.0
120.5
96.8
79.9
50.2
26.5
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3) X-ray Crystallographic Studies for 2, 5a, 6 and 8.

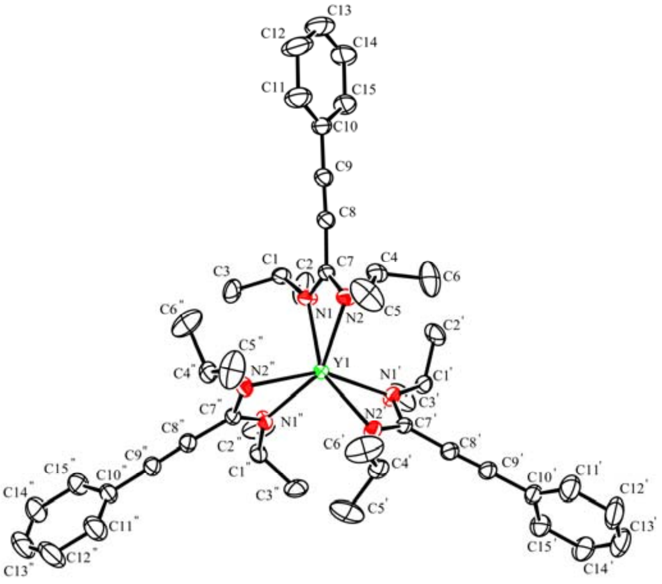
Crystals of **2, 5a, 6** and **8** suitable for X-ray analysis were grown as shown in experimental section. Data collections for **2** and **5a** were performed at 180 K and 100 K on a SuperNova diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collections for **6** was performed at 173 K on a RIGAKU CCD SATURN724 diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collections for **8** was performed at 293 K on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Using Olex2, the structure of **2**, **5a** and **6** were solved with the Superflip structure solution program using Charge Flipping and refined with the XL refinement package using Least Squares minimisation. The determination of crystal class and unit cell parameters for **6** was carried out by CrystalClear (Rigaku Inc., 2007). The raw frame data were processed using CrystalClear (Rigaku Inc., 2007) for **6** to yield the reflection data file. The structure of **8** was solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 949450 (**2**), CCDC 949451 (**5a**), CCDC 949454 (**6**), and CCDC 949453 (**8**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



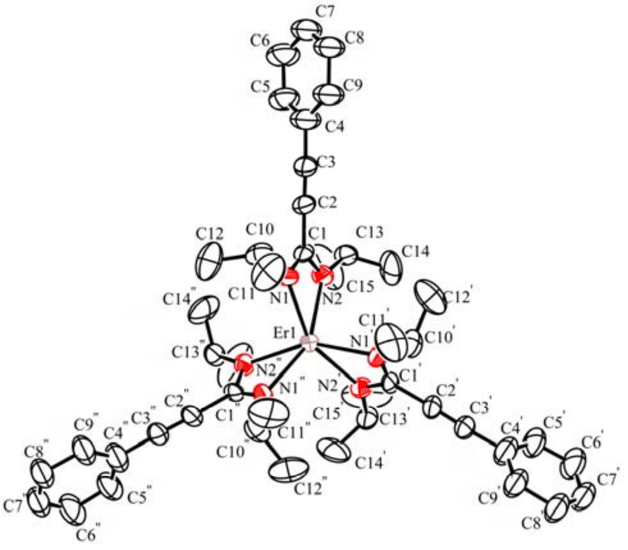
SFigure 1 ORTEP drawing of **2**.



SFigure 2 ORTEP drawing of **5a**.



SFigure 3 ORTEP drawing of **6**.



SFigure 4 ORTEP drawing of **8**.

STable 1 Crystal data and structure refinement for **2, 5a, 6** and **8.**

Identification code	**2**	**5a**	**6**	**8**
Empirical formula	$C_{58}H_{59}N_4SiOY$	$C_{82}H_{82}N_4Si_2Y_2$	$C_{45}H_{57}N_6Y$	$C_{45}H_{57}N_6Er$
Formula weight	945.09	1357.51	770.88	849.23
Temperature/K	180.00(10)	100.00(10)	173(2)	293(2)
Crystal system	monoclinic	triclinic	hexagonal	hexagonal
Space group	$P2_1/c$	P-1	$P6_3$	$P6_3$
a/Å	13.1931(9)	13.1259(3)	16.124(2)	16.263(2)
b/Å	19.6695(15)	16.2231(5)	16.124(2)	16.263(2)
c/Å	20.343(2)	16.4294(5)	9.945(2)	10.028(2)
α/°	90	90.497(2)	90.00	90.00
β/°	106.481(9)	90.033(2)	90.00	90.00
γ/°	90	93.204(2)	120.00	120.00
Volume/Å^3	5062.2(8)	3492.93(16)	2239.1(6)	2297.0(6)
Z	4	2	2	2
ρ_{calc}mg/mm^3	1.240	1.291	1.143	1.228
m/mm^{-1}	1.219	1.735	1.337	1.861
F(000)	1984.0	1416.0	816.0	874.0
Crystal size/mm^3	0.2×0.2×0.2	0.1×0.1×0.1	0.21×0.2×0.17	0.2×0.1×0.1
2Θ range for data collection	6.52 to 52.04°	5.85 to 52.04°	5.05 to 52.04°	2.9 to 55°
Index ranges	$-13 \le h \le 16$, $-24 \le k \le 19$, $-25 \le l \le 18$	$-16 \le h \le 16$, $-20 \le k \le 20$, $-20 \le l \le 20$	$-19 \le h \le 19$, $-19 \le k \le 19$, $-12 \le l \le 12$	$-21 \le h \le 21$, $-21 \le k \le 21$, $-13 \le l \le 13$
Reflections collected	19286	52519	14012	15646
Independent reflections	9934[R(int) = 0.0715]	13686[R(int) = 0.0715]	2910[R(int) = 0.0760]	3523[R(int) = 0.0771]
Data/restraints/parameters	9934/0/587	13686/12/863	2910/1/162	3523/5/144
Goodness-of-fit on F^2	1.013	1.144	1.130	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0640, wR_2 = 0.1057	R_1 = 0.0848, wR_2 = 0.1825	R_1 = 0.0536, wR_2 = 0.1123	R_1 = 0.0551, wR_2 = 0.1219
Final R indexes [all data]	R_1 = 0.1444, wR_2 = 0.1344	R_1 = 0.0989, wR_2 = 0.1888	R_1 = 0.0575, wR_2 = 0.1142	R_1 = 0.0878, wR_2 = 0.1305
Largest diff. peak/hole / e Å^{-3}	0.63/-0.72	0.94/-1.04	0.39/-0.22	1.19/-0.68