Electronic Supplementary Information

Yttrium Dialkyl Supported by a Silaamidinate Ligand: Synthesis, Structure and Catalysis on Cyclotrimerization of Isocyanates

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General Experimental

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon by using modified Schlenk line and glovebox techniques. The ^{1}H, ^{13}C and ^{29}Si NMR spectroscopic data were recorded on a Bruker AV400 spectrometer. Elemental analyses were carried out on an Elementar Vario EL analyzer. High resolution ESI mass experiments were operated on an IonSpec FT-ICR mass spectrometer with ESI resource. IR spectra were recorded in the range of 400−4000 cm^{-1} on a Bruker Alpha II spectrophotometer in glove box filled with Ar gas.

The solvents (THF, toluene, Et_2O and *n*-hexane) were freshly distilled from sodium and degassed prior to use. Chlorosilylene $PhC(N\textit{t}Bu)_2SiCl$ (**1**)[S1] and $Y(CH_2SiMe_3)_3(THF)_2$[S2] were synthesized according to the published procedures. $PhC(NtBu)_2Si(2,6\text{-}\textit{i}Pr_2C_6H_3N)Cl$ (**2**) was prepared via the reaction between **1** and N_3Ar ($Ar = 2,6\text{-}\textit{i}Pr_2C_6H_3$) in 80.0 % yield [S3]. The spectra of **2** were consistent with literature.[S4] Other chemicals were of analytical grade and were used as received.

Synthesis of [PhC(N*t*Bu)$_2$Si(NAr)$_2$]H (3): *n*BuLi (2.4 M in *n*-hexane, 15 mmol) was added to a solution of $2,6\text{-}\textit{i}Pr_2C_6H_3NH_2$ (2.66 g, 15 mmol) in 30 mL THF dropwisely. The solution was stirred at room temperature for 4 hours. Then the pale yellow solution was added to **2** in Et_2O at –78 °C. The mixture was warmed to room temperature slowly and stirred 12 hours. After removing the solvent under reduced pressure, the residue was washed by *n*-hexane. Removal of solvent yielded a light powder (6.11 g, 66.7 %). **Mp:** 191 °C. Anal. Calcd for $C_{39}H_{58}N_4Si$ (611.01): C, 76.67; H, 9.57; N, 9.17; Found: C, 76.03; H, 9.31; N, 9.01. **^{1}H NMR** (400 MHz, C_6D_6, 23 °C) δ 7.38 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar-*H*), 7.33 (d, $^3J_{HH}$ = 6.8 Hz, 1H, Ar-*H*), 7.23–7.17 (m, 3H, Ar-*H*), 7.13 (dd, $^3J_{HH}$ = 8.8, 6.2 Hz, 1H, Ar-*H*), 7.07 (t, $^3J_{HH}$ = 7.4 Hz, 1H, Ar-*H*), 6.94–6.85 (m, 3H, Ar-*H*), 4.04 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 3.97 (s, 1H, N*H*), 3.92 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 1.52 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$), 0.95 (s, 18H, C*Me*$_3$). **^{13}C NMR** (101 MHz, C_6D_6, 23 °C) δ 176.53 (N*C*N), 147.82, 143.48, 139.29, 130.22, 124.11, 122.86, 122.18, 115.15 (Ar-

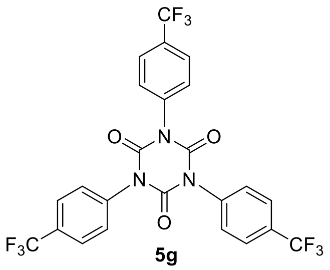
C), 53.73 (*C*Me$_3$), 30.41 (*C*HMe$_2$), 28.43 (C*Me*$_3$), 24.02, 23.25 (CH*Me*$_2$). **^{29}Si NMR** (101 MHz, C$_6$D$_6$, 23 °C) *δ* –85.70 (N*Si*N). **IR** (cm^{-1}): $\tilde{\nu}$ (s, N–H) 3421, (s, Si=N) 1493, (s, C=N) 1406.

Synthesis of [PhC(N*t*Bu)$_2$Si(NAr)$_2$]Y(CH$_2$SiMe$_3$)$_2$ (4): A mixture of **3** (0.92 g, 1.5 mmol) and Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.74 g, 1.5 mmol) was added 30 mL toluene. The solution was stirred at room temperature for 3 hours. After removing the solvent under reduced pressure, the residue was washed by *n*-hexane. The colorless crystals of **4** (0.79 g 60.3 %) were afforded in Et$_2$O at −35 ℃ overnight. **Mp:** 241 °C. Anal. Calcd for C$_{47}$H$_{79}$N$_4$Si$_3$Y (873.34): C, 64.64; H, 9.12; N, 6.42; Found: C, 64.24; H, 9.04; N, 6.12. **^{1}H NMR** (400 MHz, C$_6$D$_6$, 23 °C) *δ* 7.23 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 4H, Ar-*H*), 7.03 (m, 4H, Ar-*H*), 6.83 (t, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 1H, Ar-*H*), 6.75 (t, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 2H Ar-*H*), 3.78 (sept, $^3J_{\mathrm{HH}}$ = 6.4 Hz, 2H, C*H*Me$_2$), 3.62 (sept, $^3J_{\mathrm{HH}}$ = 6.7 Hz, 2H, C*H*Me$_2$), 1.89 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 6H, CH*Me*$_2$), 1.54 (d, $^3J_{\mathrm{HH}}$ = 6.2 Hz, 6H, CH*Me*$_2$), 1.39 (d, $^3J_{\mathrm{HH}}$ = 6.7 Hz, 6H, CH*Me*$_2$), 1.36 (d, $^3J_{\mathrm{HH}}$ = 7.0 Hz, 6H, CH*Me*$_2$), 0.64 (s, 18H, C*Me*$_3$), 0.32 (s, 18H, YCH$_2$Si*Me*$_3$), –0.12 (dd, $^2J_{\mathrm{HH}}$ = 11.3 Hz, $^2J_{\mathrm{YH}}$ = 1.7 Hz, 2H,YC*H*HSiMe$_3$), –0.26 (dd, $^2J_{\mathrm{HH}}$ = 11.4 Hz, $^2J_{\mathrm{YH}}$ = 2.3 Hz, 2H, YCH*H*SiMe$_3$). **^{13}C NMR** (101 MHz, C$_6$D$_6$, 23 °C) *δ* 178.35 (N*C*N), 147.33, 140.48, 140.13, 130.84, 129.43, 123.46, 123.15, 120.51 (Ar-*C*), 54.83 (*C*Me$_3$), 32.46 (d, $^1J_{\mathrm{YC}}$ = 38.7 Hz, Y*C*H$_2$SiMe$_3$), 29.94 (*C*HMe$_2$), 29.87 (C*Me*$_3$), 28.37, 25.43, 23.00, 21.54 (CH*Me*$_2$), 4.65 (Si*Me*$_3$). **^{29}Si NMR** (79 MHz, C$_6$D$_6$, 23 °C) *δ* –2.78 (CH$_2$*Si*Me$_3$), –62.82 (N*Si*N). **IR** (cm^{-1}): $\tilde{\nu}$ (s, Si=N) 1421, (s, C=N) 1395.

Synthesis of [PhC(N*t*Bu)$_2$Si(NAr)$_2$]Y[OC(CH$_2$SiMe$_3$)N(3-MeC$_6$H$_4$)]$_2$ (6): (3-MeC$_6$H$_4$)NCO (0.266 g, 2 mmol) was added to a solution of **4** (0.87 g, 1 mmol) in 20 mL toluene. The solution was stirred at room temperature for 12 hours. The colorless crystals of **6** (0.57 g 58.7 %) were afforded in toluene at −35 ℃ overnight. **Mp:** 198 °C. Anal. Calcd for C$_{51}$H$_{69}$N$_6$O$_2$Si$_3$Y (971.31): C, 63.07; H, 7.16; N, 8.65; Found: C, 62.66; H, 6.69; N, 8.61. **^{1}H NMR** (400 MHz, C$_6$D$_6$, 23 °C) *δ* 7.31 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 4H, Ar-*H*), 7.12–7.02 (m, 7H, Ar-*H*), 6.86–6.72 (m, 5H, Ar-*H*), 6.34–6.29 (m, 3H, Ar-*H*), 4.20 (br, 4H, C*H*Me$_2$), 2.22 (s, 6H, 3-*Me*C$_6$H$_4$), 1.85 (s, 4H, C*H*$_2$SiMe$_3$), 1.58 (dd, $^3J_{\mathrm{HH}}$ = 6.7

Hz, 12H, CH*Me*$_2$), 1.53 (dd, $^3J_{HH}$ = 6.6 Hz, 12H, CH*Me*$_2$), 0.93 (s, 18H, C*Me*$_3$), 0.05 (s, 18H, CH$_2$Si*Me*$_3$). **^{13}C NMR** (101 MHz, C$_6$D$_6$, 23 °C) δ 182.29 (O*C*N), 178.07 (N*C*N), 149.25, 147.76, 137.76, 130.44, 129.27, 128.00, 126.30, 123.80, 122.81, 120.01 (Ar-*C*), 54.86 (*C*Me$_3$), 30.65 (*C*H$_2$SiMe$_3$), 28.41 (C*Me*$_3$), 24.09 (*C*HMe$_2$), 23.78, 21.60 (CH*Me*$_2$), –0.43 (Si*Me*$_3$). **^{29}Si NMR** (79 MHz, C$_6$D6) δ 0.86 (CH$_2$*Si*Me$_3$), –63.42 (N*Si*N). **IR** (cm^{-1}): $\tilde{\nu}$ (s, O-C-N) 1521, (s, Si=N) 1421, (s, C=N) 1394.

General Procedure for the Cyclotrimerization of Isocyanate: In an Ar glove box, a Schlenk tube was charged with catalyst **4** (0.017 g, 0.02 mmol, 0.25 mol %), isocyanate (8 mmol) and 5 mL THF. The Schlenk tube was quickly removed from the glovebox. The reaction mixture was stirred at room temperature. After the reaction was complete, the product was washed with *n*-hexane and further purified by recrystallization from THF to yield colorless crystals. The spectra of cyclotrimerization of isocyanate products 5a,[S5] 5b,[S6] 5c,[S7] 5d,[S8] 5e,[S8] 5f,[S5] 5h,[S8] 5i,[S6] 5j[S9] and 5k[S10] were consistent with literature.



5g

Following the general procedure with 4-(trifluoromethyl)phenyl isocyanate (8 mmol), catalyst **4** (0.02 mmol), and 5 mL THF. **^{1}H NMR** (400 MHz, CDCl$_3$, 23 °C) δ 7.80 (d, $^3J_{HH}$ = 8.3 Hz, 6H), 7.55 (d, $^3J_{HH}$ = 8.2 Hz, 6H). **^{13}C NMR** (101 MHz, CDCl$_3$, 23 °C) δ 147.74, 136.08, 131.68, 129.06, 124.79, 122.08. Anal. Calcd for $C_{24}H_{12}F_9N_3O_3$ (561.36) C, 51.35; H, 2.15; N, 7.49; Found: C, 51.39; H, 2.66; N, 7.59.

X–ray Diffraction Parameters and Data

All intensity data were collected with a Bruker SMART CCD diffractometer, using graphite–monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were resolved by direct methods and refined by full matrix least squares on F^2.[S11] Hydrogen atoms were considered in calculated positions. All non-hydrogen atoms were refined anisotropically. The Ortep-3 program was utilized to draw the molecules.[S12] Crystal data and data collection details are collected in Tables S1. CCDC 1906987 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic detail for **4**.

	4
formula	$C_{47}H_{79}N_4Si_3Y$
Fw	873.32
T (K)	113
Space group	*P -1*
a (Å)	11.665(2)
b (Å)	12.804(3)
c (Å)	19.310(4)
α (°)	77.91(3)
β (°)	72.79(3)
γ (°)	87.15(3)
V (Å^3)	2693.6(11)
Z	2
d_{calcd} (g/cm^3)	1.077
F(000)	940
GOF	1.006
R_1, wR_2 ($I>2\sigma(I)$)	0.0694, 0.1646
R_1, wR_2 (all data)	0.0960, 0.1780
CCDC	1906987

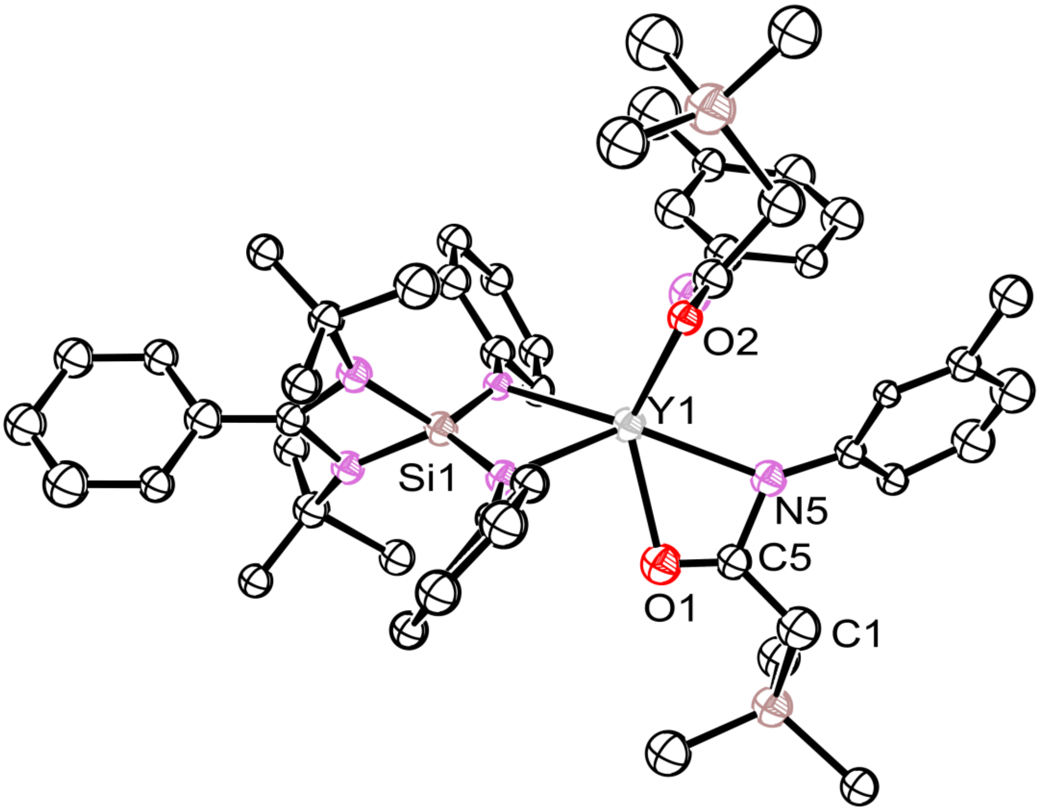


Figure S1 Molecular structure of complex **6**. Hydrogen atoms and *i*Pr groups have been omitted for clarity. The single crystallinity of **6** was of low quality, and repeated attempts to grow higher quality crystals of this complex were unsuccessful. The connectivity of the structure can be unambiguously established. However, no meaningful comments on the metrical parameters can be made at this time.

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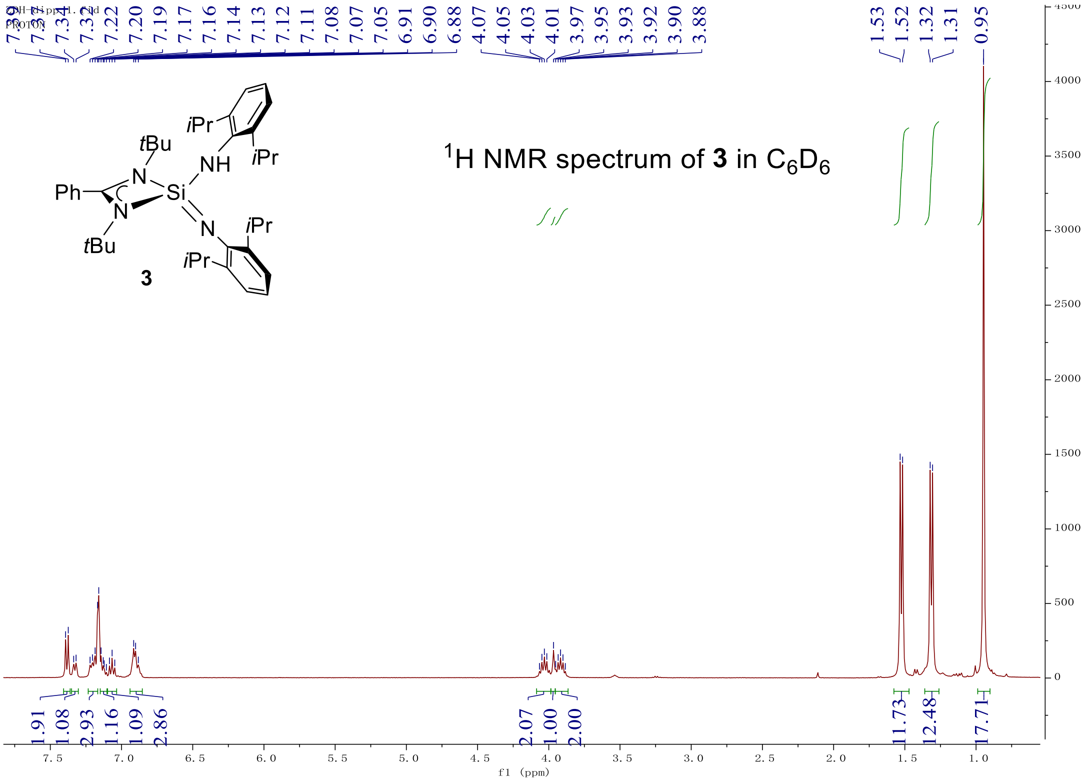
NMR Spectra


PROTON
7.34
7.32
7.22
7.20
7.19
7.17
7.16
7.14
7.13
7.12
7.11
7.08
7.07
7.05
6.91
6.90
6.88
4.07
4.05
4.03
4.01
3.97
3.95
3.93
3.92
3.90
3.88
1.53
1.52
1.32
1.31
0.95
iPr
tBu
NH
iPr
Ph
N
Si
N
N
iPr
tBu
iPr
3
1H NMR spectrum of 3 in C6D6
1.91
1.08
2.93
1.16
1.09
2.86
2.07
1.00
2.00
11.73
12.48
17.71
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1000
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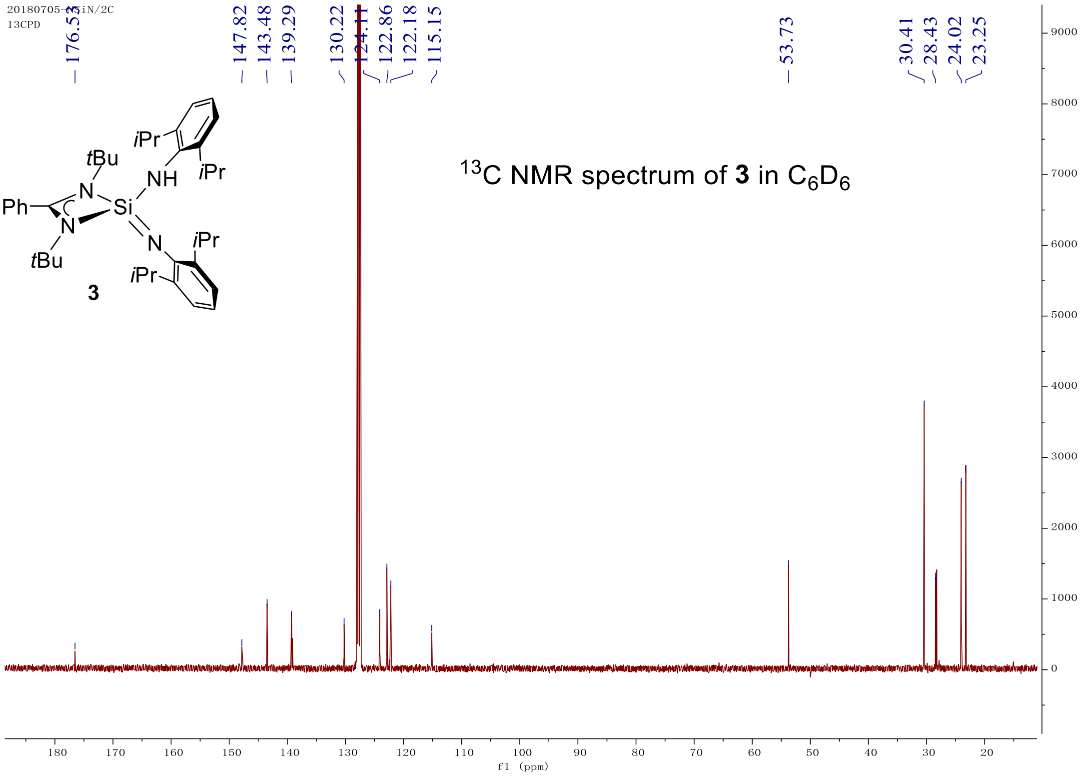
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28.43
24.02
23.25
iPr
tBu
NH
iPr
Ph
N
Si
N
N
iPr
tBu
iPr
3
13C NMR spectrum of 3 in C6D6
180
170
160
150
140
130
120
110
100
90
80
70
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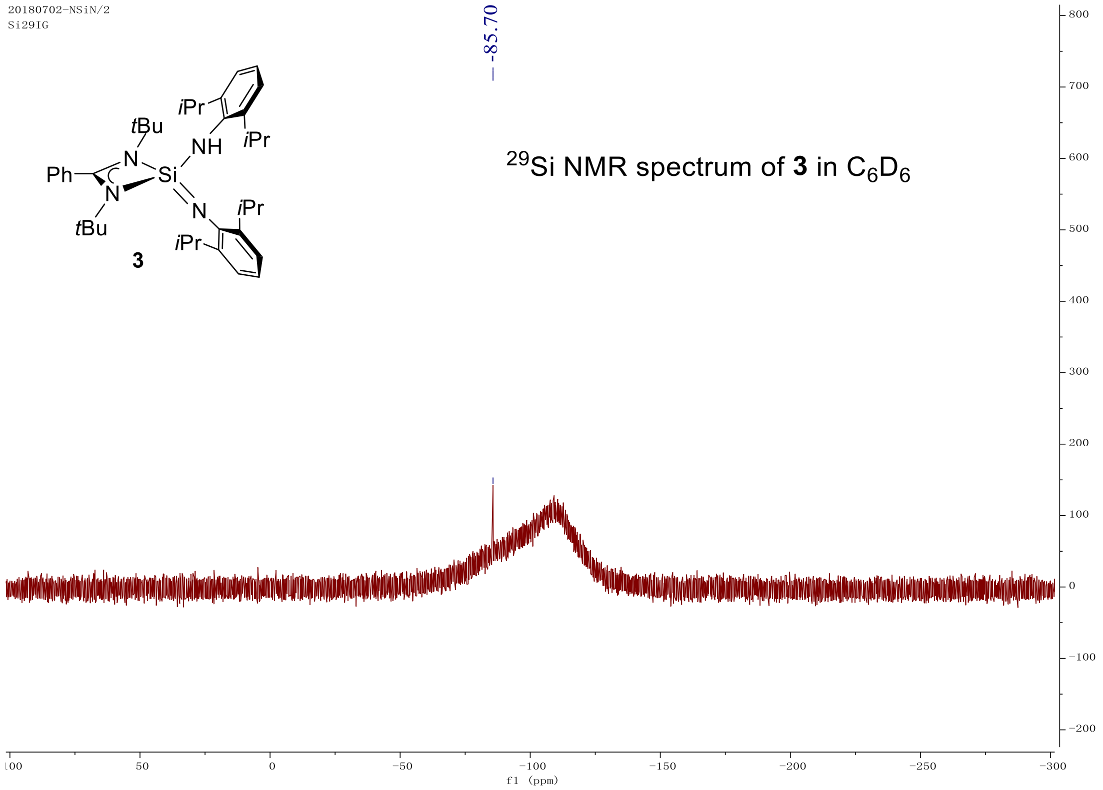
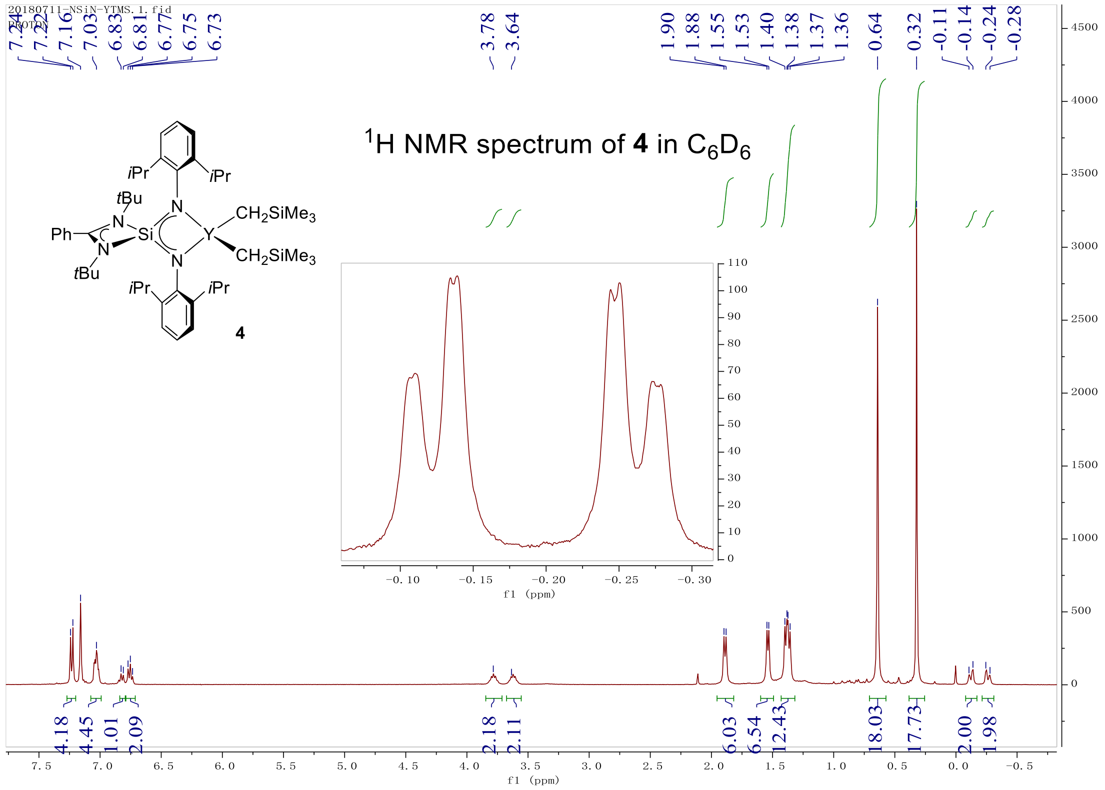


^{29}Si NMR spectrum of **3** in C_6D_6



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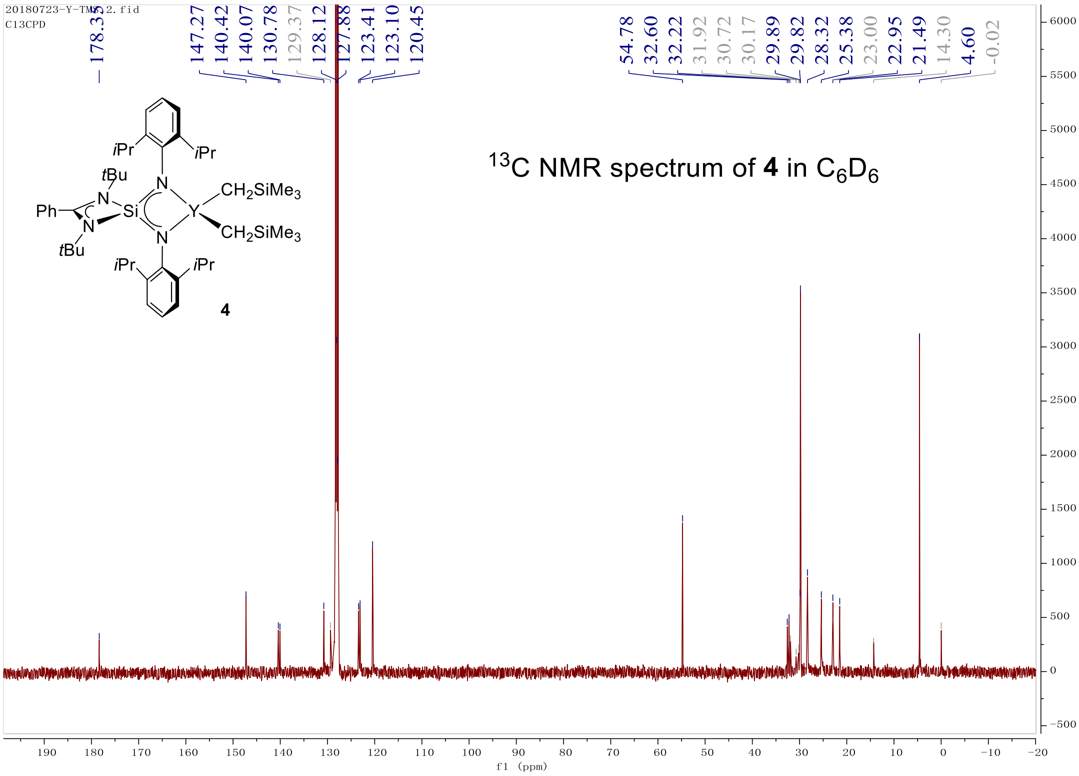

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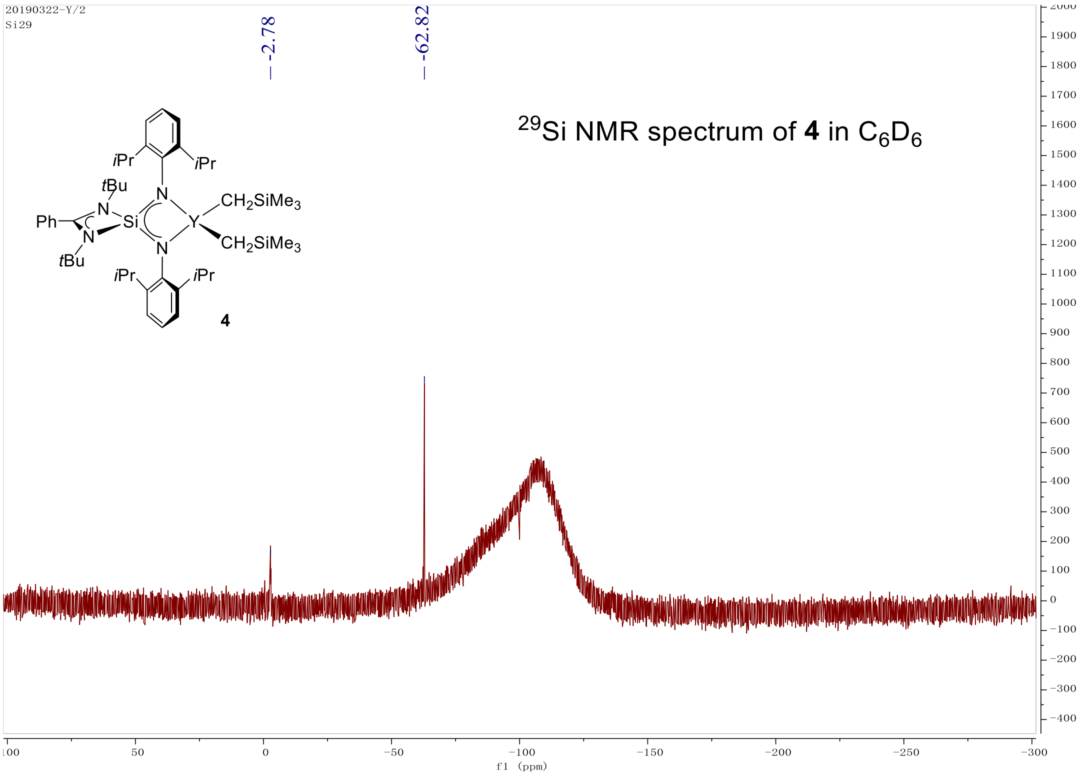

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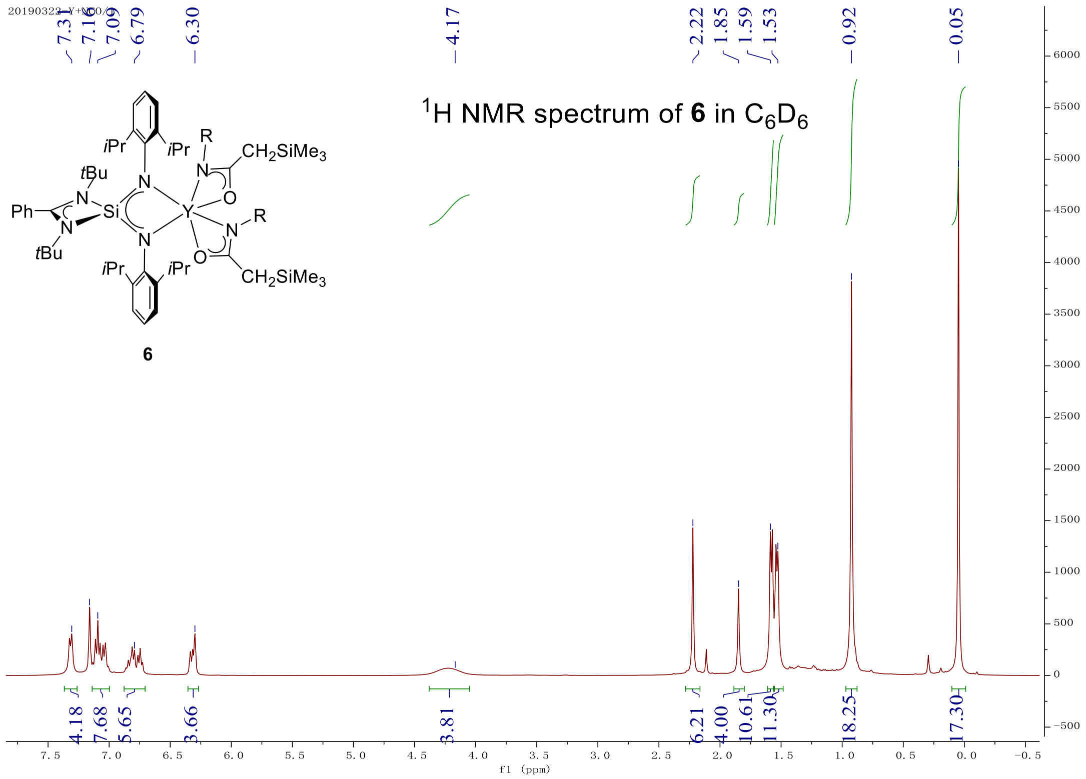
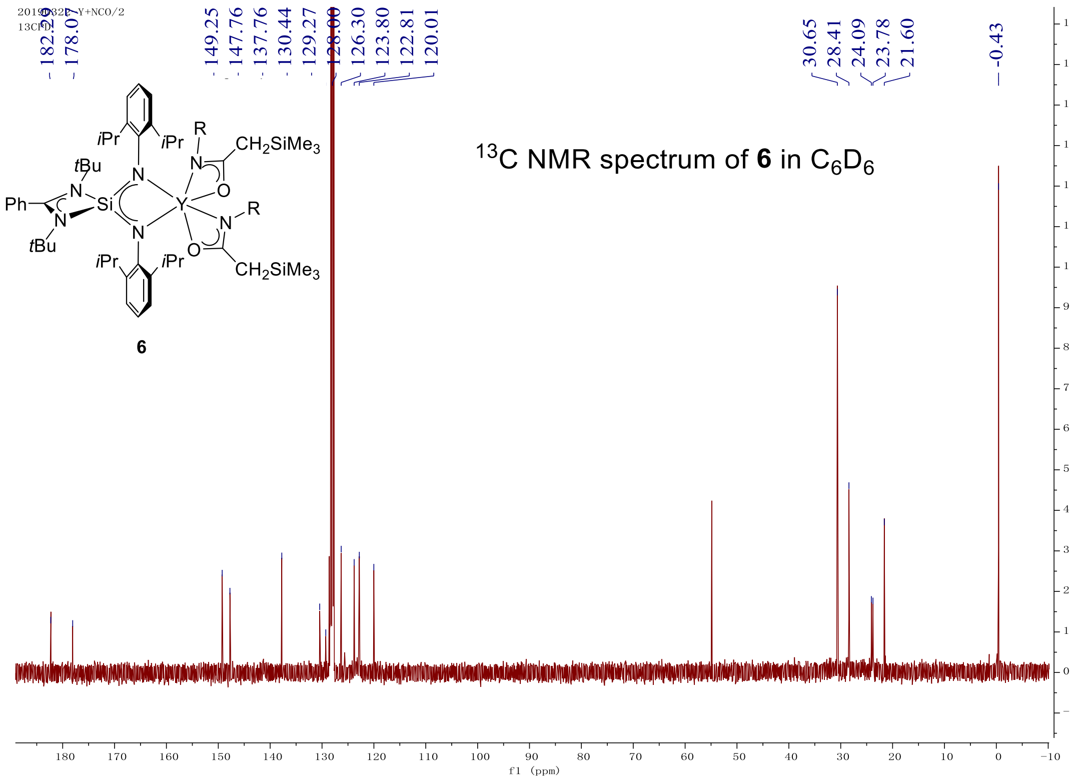


^{1}H NMR spectrum of **6** in C_6D_6

6



^{13}C NMR spectrum of **6** in C_6D_6

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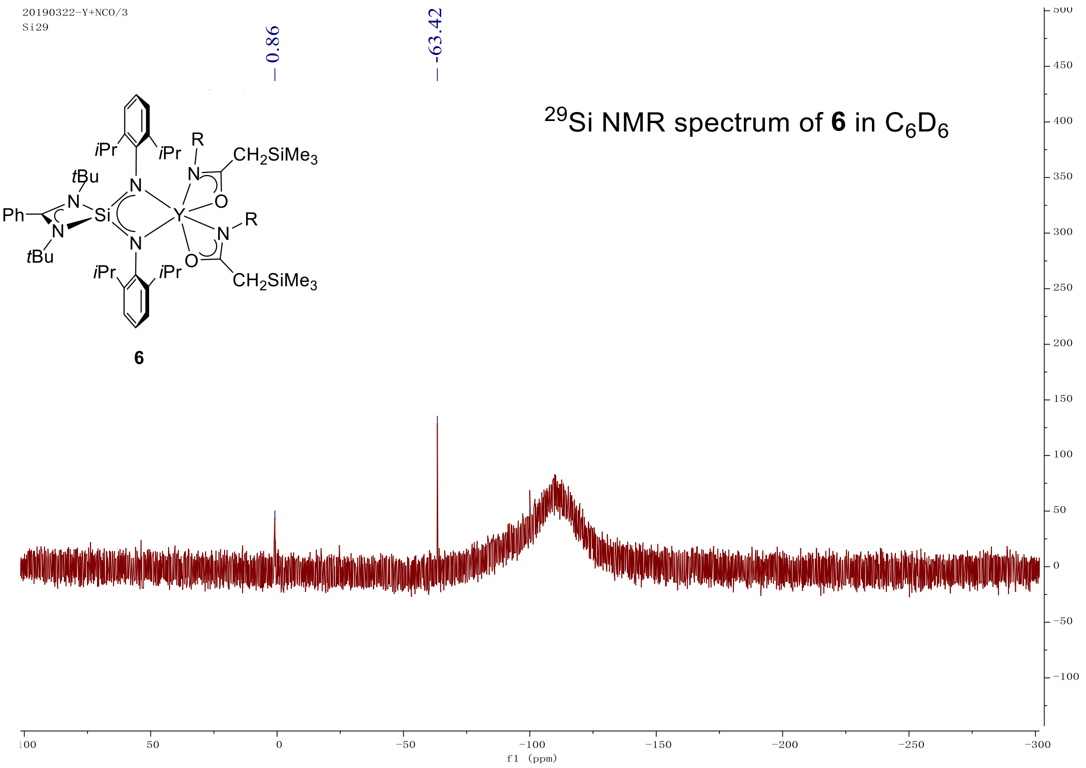
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-63.42
^{29}Si NMR spectrum of **6** in C_6D_6
iPr
iPr
R
CH$_2$SiMe$_3$
tBu
Ph
N
Si
Y
O
tBu
6
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450
400
350
300
250
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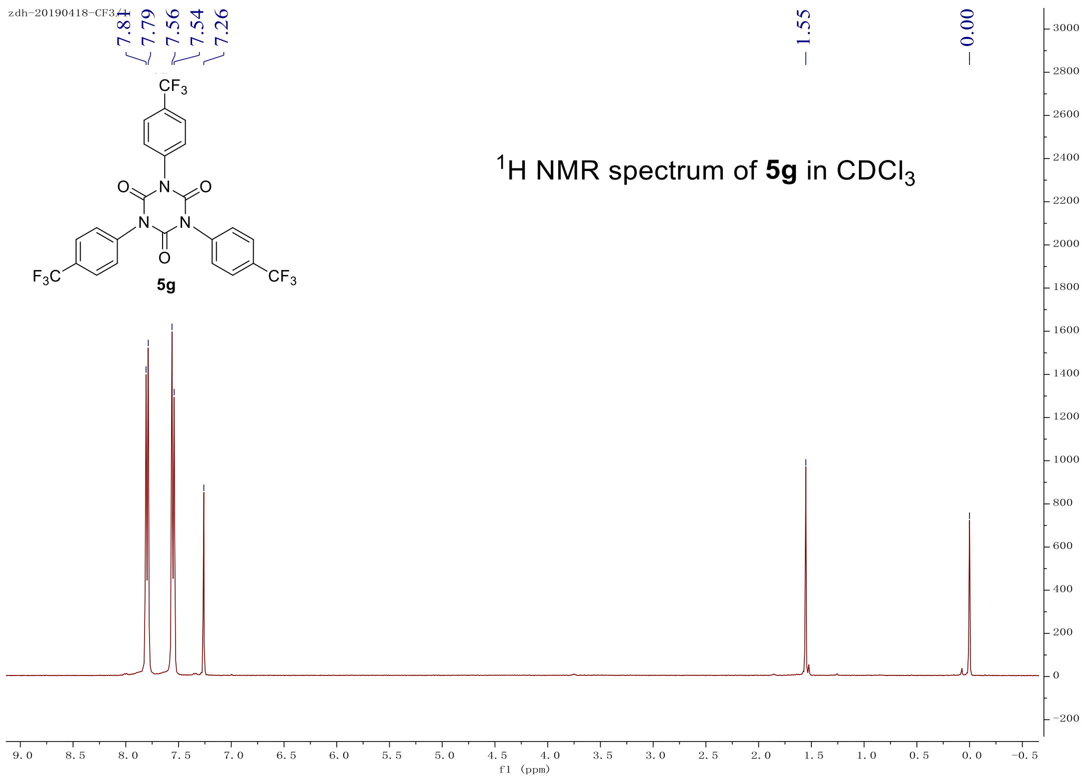
-300
f1 (ppm)


zdh-20190418-CF3/1
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7.79
7.56
7.54
7.26
1.55
0.00
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CF$_3$
F$_3$C
N
O
5g
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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
-0.5
f1 (ppm)