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Supplementary Materials for

Reactions of Five-Membered Zirconacycloalkynes And Zirconacycloallenes with $Cp_2Zr(H)Cl$; Formal Hydrogenation by Metal Hydrides.

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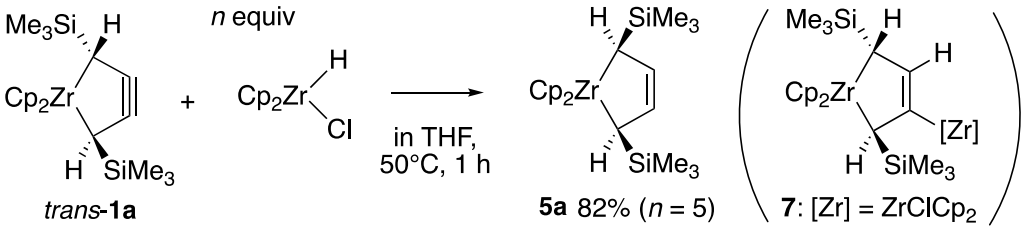
1. General

All manipulations involving organometallic compounds were conducted under argon using standard Schlenk technique or under nitrogen in a glove box. Anhydrous tetrahydrofuran was purchased from Kanto Chemical Co., Inc. and purified with Glass Contour Solvent System™ (SG Water, USA) prior to use. 9-Borabicyclo[3.3.1]nonane (9-BBN) dimer, *n*-butyllithium (1.6 M hexane solution) and diisobutylaluminium hydride (1.0 M toluene solution) were purchased from Kanto Chemical Co., Inc. and used as received. Bis(η^5-cyclopentadienyl)zirconium chloride hydride was purchased from Tokyo Chemical Industry Co., Ltd. and stored under nitrogen in a glove box. Dichlorobis(η^5-cyclopentadienyl)zirconium and deuterium chloride 35% in D_2O were purchased from Sigma-Aldrich Co. LLC. 1-Zirconacyclopent-3-yne compounds **1a-c** were prepared according to the previously reported method.[1, 2] (*Z*)-1,4-Bis(trimethylsilyl)buta-1,2,3-triene-1,4-d_2 and **1a-*d*$_2$** was prepared as previously reported.[3] 1-Zirconacyclopenta-2,3-diene complexes **2** were synthesized as previously reported, [4, 5] and the molecular structure of **2e** was newly characterized by X-ray diffraction analysis in this study, although the results of analysis was not fully satisfactory. The dideuterated complex **2a-*d*$_2$** was prepared from (*E*)-(but-1-en-3-yne-1,4-diyl-d_2)bis(trimethylsilane) **4a-*d*$_2$**, that was synthesized using trimethylsilylacetylene-d_1 (see the supporting information). Butatrienes **3a** and **3b** were prepared according to the literature. [6, 7] 1,4-Disilylbut-1-en-3-ynes **4** were prepared by Ir-catalyzed dimerization of silylacetylenes described in the literature. [8, 9] $[Cp_2ZrCl]_2O$ was prepared according to the literature.[10] NMR spectra were recorded on JEOL ECA 500 and Bruker Avance III HD400 spectrometers. Fast atom bombardment (FAB) mass spectrometry was measured on a JEOL JMS-700 instrument. Electrospray ionization-mass spectrometry (ESI-MS) with time-of-flight (TOF) detection for high resolution measurements were recorded on a JEOL JMS-T100LC. All manipulations involving organometallic compounds were conducted under argon using standard Schlenk technique or under nitrogen in a glove box. Anhydrous tetrahydrofuran was purchased from Kanto Chemical Co., Inc. and purified with Glass Contour Solvent System™ (SG Water, USA) prior to use.

2. Syntheses and Reactions

2.1. Reaction of 1-zirconacyclopent-3-yne ***1a*** *and* $Cp_2Zr(H)Cl$ *(Schwartz reagent); formation of 1-zirconacyclopent-3-ene* ***5a****.*



In a thoroughly dried Schlenk tube filled with argon, complex **1a** (82.9 mg, 0.2 mmol) was dissolved in THF (1 mL) and $Cp_2Zr(H)Cl$ (257 mg, 1.0 mmol) was added. The solution was stirred at 50 °C for 1 h. Observation of the dark brown solution by ^{1}H NMR spectroscopy showed the formation of **5a** (82%) accompanied with the dinuclear μ-oxo complex (41 %) at 6.1 ppm. Signals assignable to **7** were not found. Oxygen gas might have been included during the preparation of the NMR sample, where the solution was moved from the Schlenk tube to a NMR tube via a syringe.

^{1}H NMR (THF/C_6D_6, C_6D_5H = 7.16, 500 MHz): δ –1.18 (m, 2H, C*H*), 0.20 (s, 18H, SiCH_3), 4.83 (m, 2H, C*H*), 5.03 (s, Cp), 5.57 (s, Cp).

^{13}C NMR (THF/C_6D_6, C_6D_6 = 128, 125.8 MHz): δ 1.53 (Si*C*H_3), 58.70 (Si*C*H), 100.77 (Cp), 104.25 (Cp), 115.49 (=*C*H).

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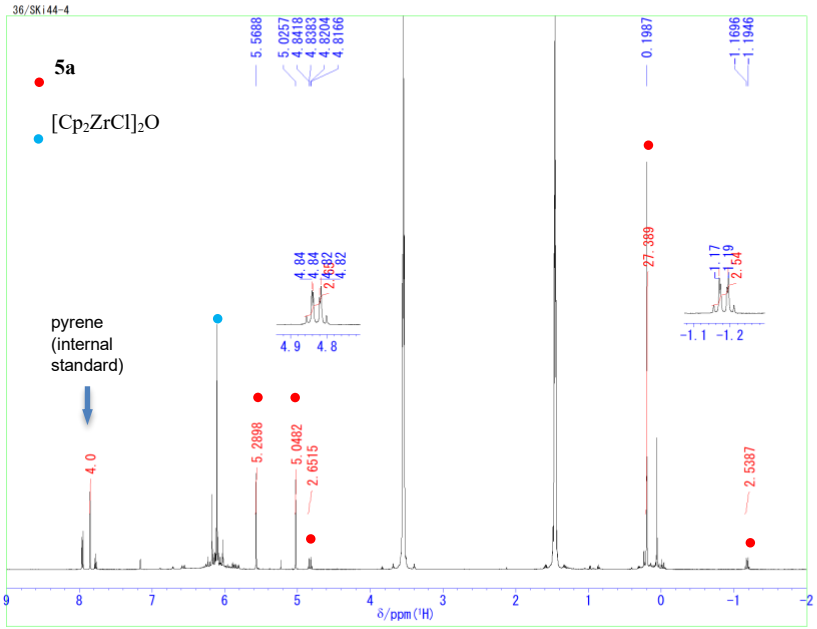
^{1}H NMR



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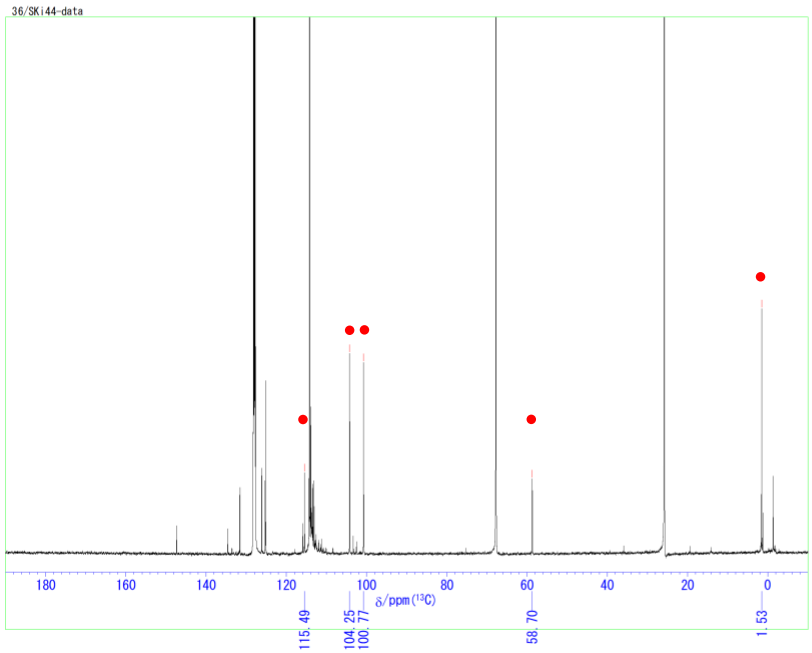


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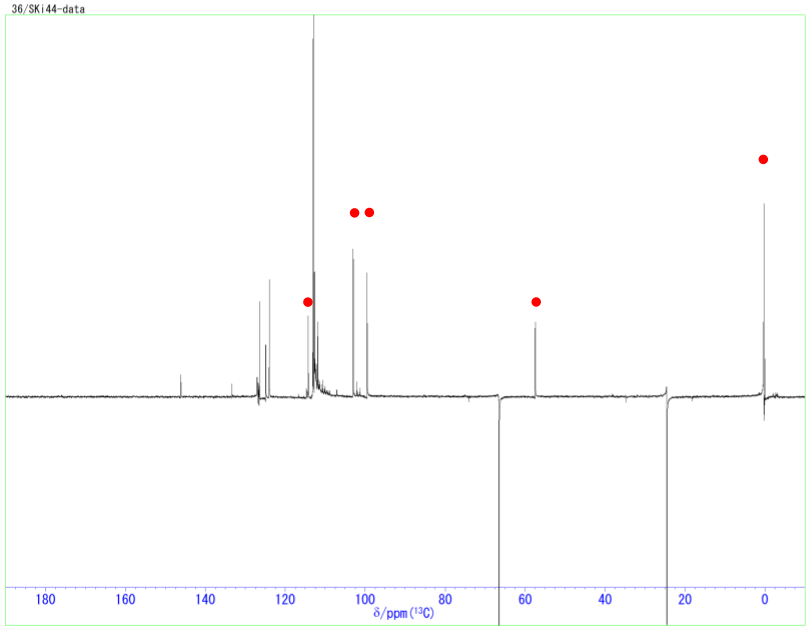


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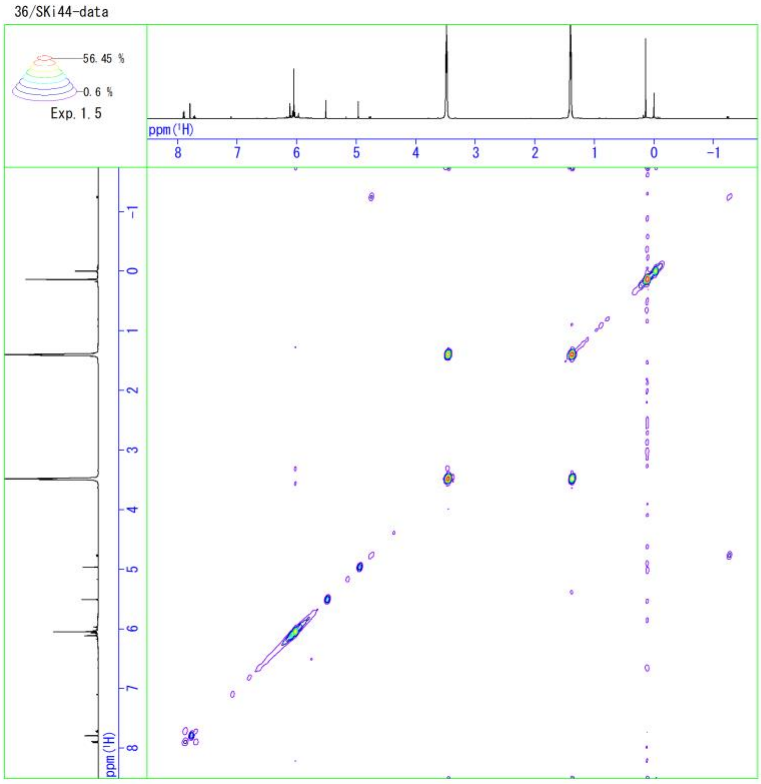

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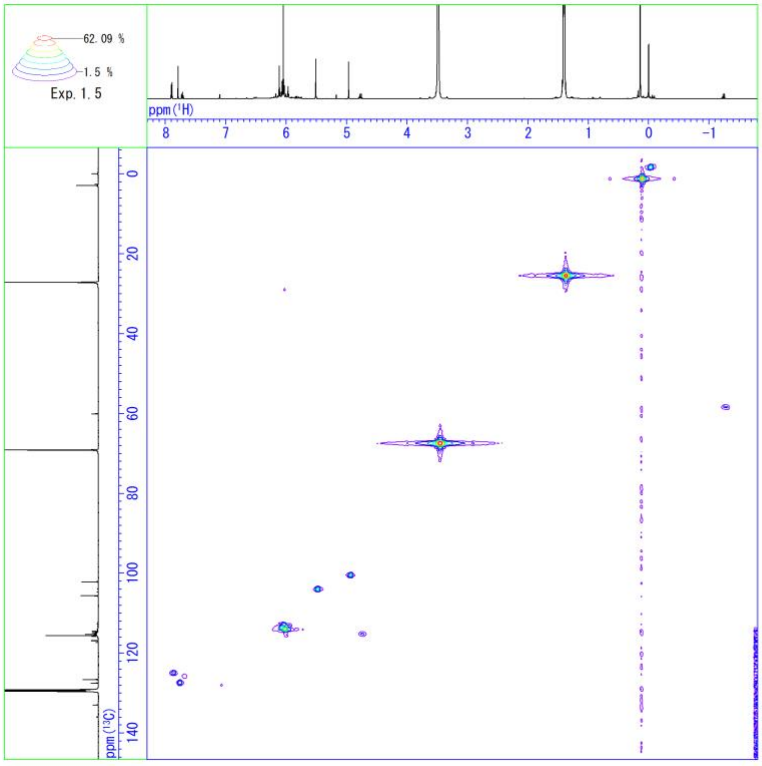

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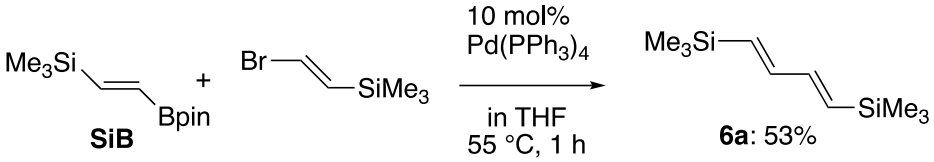
*2.2. Synthesis of 1,4-bistrimethylsilylbuta-1,3-diene (**6a**)* [11]



(*E*)-Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**SiB**) was prepared from trimethylacetylene and pinacol borane according to the literature. [12] Obtained **SiB** (973 mg, 4.30 mmol) and (2-bromovinyl)trimethylsilane (1.00 mg, 5.60 mmol) were dissolved in THF (50 mL) and $Pd(PPh_3)_4$ (497 mg, 0.430 mmol) and an aqueous solution of Cs_2CO_3 (1.4 M, 15 mL) were added. The mixture was stirred at 55 °C for 1 h. Water was added to the reaction mixture and extracted with diethyl ether. The combined organic layer was washed with brine and water, and then dried over $MgSO_4$. The volatiles were removed in vacuo and the residue was purified by column chromatograph on silica gel (hexane/diethyl ether = 10/1) to afford **6a** as yellow oil (449 mg, 53% isolated). [13]

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ -0.01 (s, 18H, SiC*H*$_3$), 5.81 (m, 2H, C*H*), 6.43 (m, 2H, C*H*).

^{13}C NMR ($CDCl_3$, Me_4Si, 126 MHz): δ -1.6 (SiC*H*$_3$), 134.5 ($J_{C\text{-}Si}$ = 65 Hz, SiC*H*), 146.4 (C*H*).

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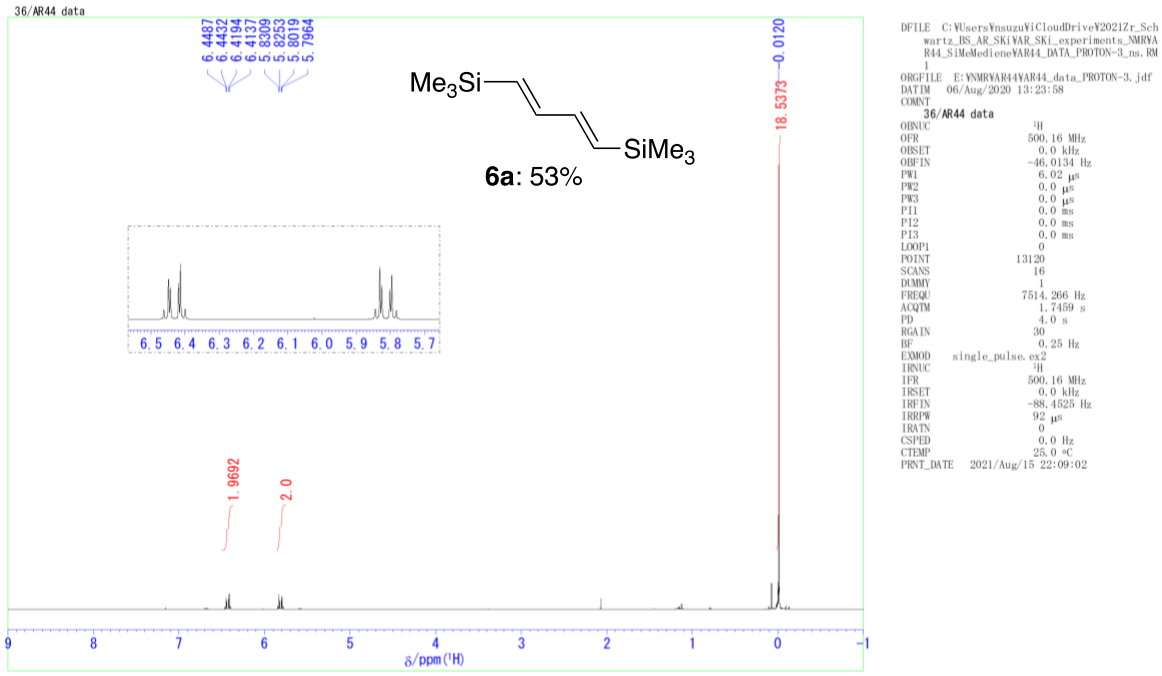

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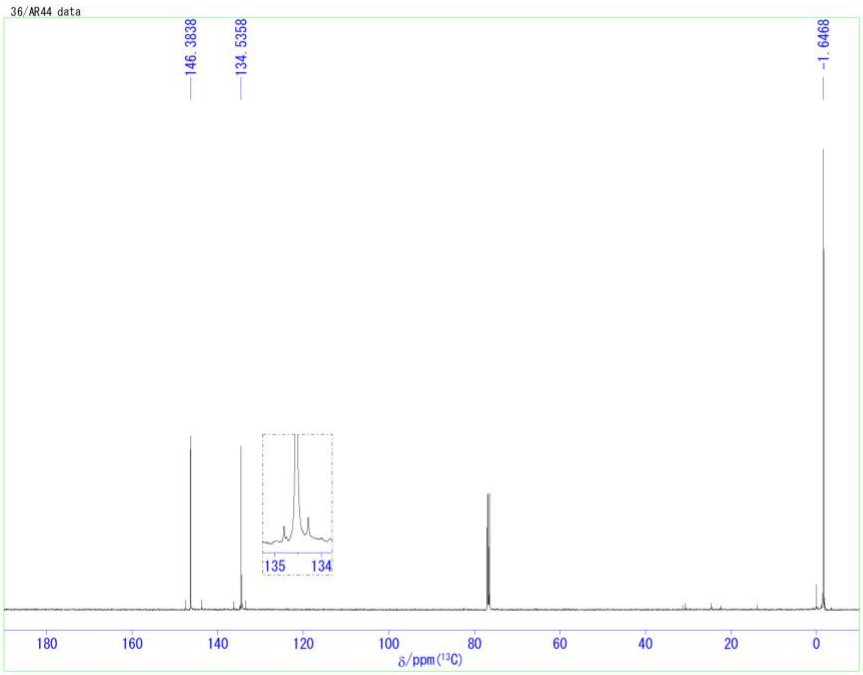


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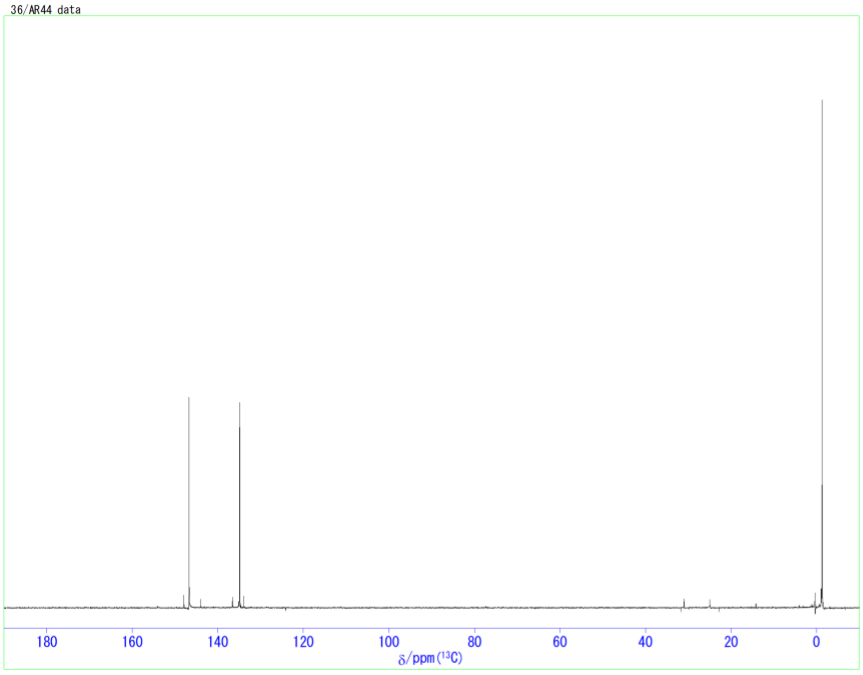


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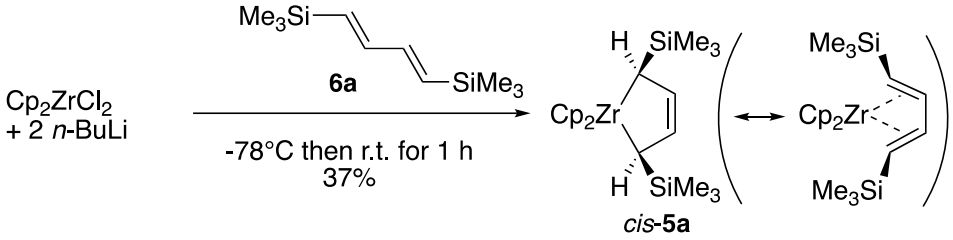
2.3. Preparation of zirconocene-diene complex ***5a*** *from* ***6a****; 1,1-bis(η^5-cyclopentadienyl)-cis-2,5-bis(trimethylsilyl)-1-zirconacyclopent-3-ene*

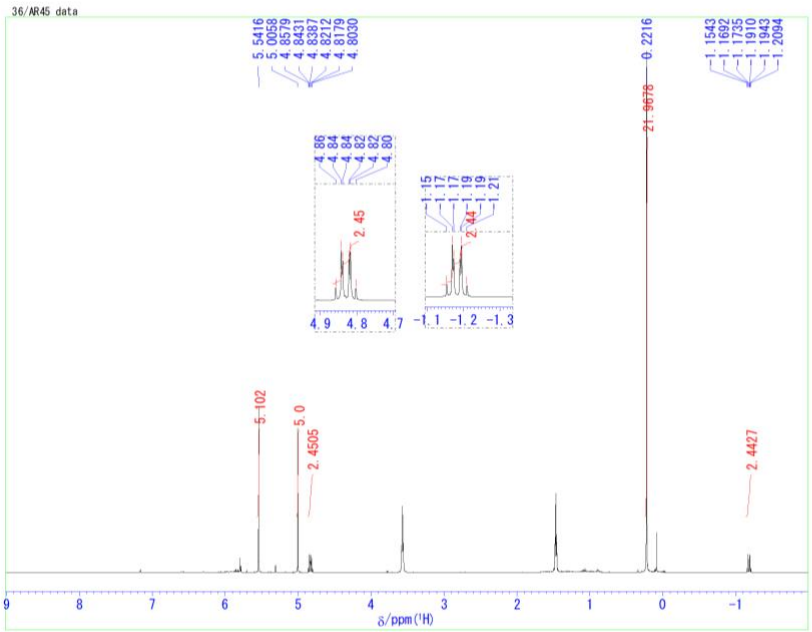


In a dried Schlenk tube (20 mL), dichlorobis(η^5-cyclopentadienyl)zirconium (146 mg, 0.500 mmol) was dissolved in THF (2.5 mL) and the solution was cooled at –78 °C. *n*-Buryllithium (1.55 M in hexane, 0.645 mL, 1.00 mmol） was added dropwise to this solution and the mixture was stirred at –78 C for 1 h. To this solution was added (*E*),(*E*)-1,4-bis(trimethylsilyl)buta-1,3-diene (**6a**) (99.0 mg, 0.500 mmol) and the mixture was allowed to warm up to room temperature. The mixture was stirred at rt for 1 h and pyrene was added to the orange solution as an internal standard, and it was observed by NMR. The NMR spectra showed the formation of *cis*-**5a** in 48% yield. The volatiles were removed in vacuo, and the residue was dissolved in C_6D_6 and analyzed by NMR spectroscopy. Recrystallization from hexane solution gave orange crystals of **5a** (174 mg, 41% isol.).

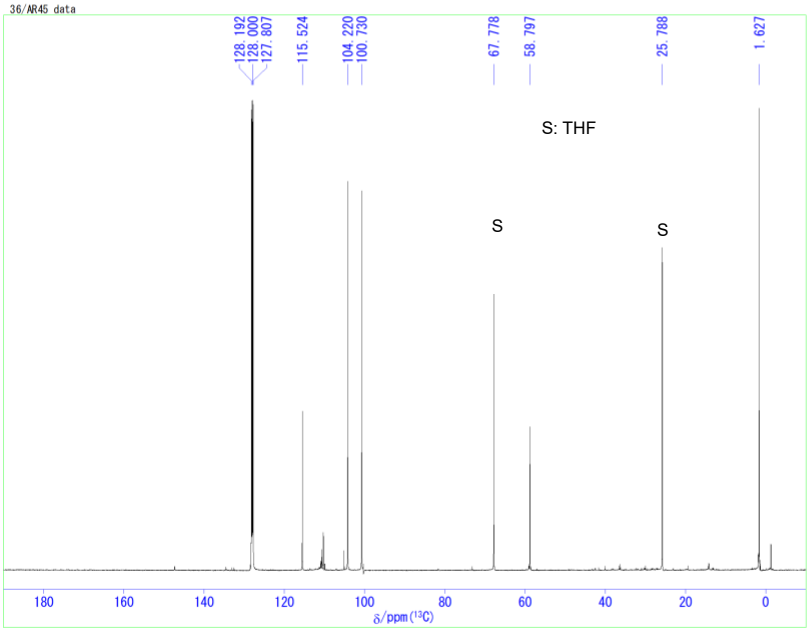
^{1}H NMR (C_6D_6, C_6D_5H = 7.16, 500 MHz): δ –1.18 (m, 2H, C*H*), 0.22 (s, 18H, SiCH_3), 4.83 (m, 2H, C*H*), 5.01 (s, 5H, Cp), 5.54 (s, 5H, Cp).

^{13}C NMR (C_6D_6, C_6D_6 = 128.0, 126 MHz): δ 1.6 (Si*C*H$_3$), 58.8 ($J_{C\text{-}Si}$ = 68 Hz, Si*C*H), 100.7 (Cp), 104.2 (Cp), 115.5 (*C*H).

^{1}H NMR



^{13}C NMR

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PI3                  0.0 ms
LOOP1                   0
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SCANS                1024
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PD                   2.0 s
RGAIN                  52
BF                   0.25 Hz
EXMOD       single_pulse_dec
IRNUC                   1H
IFR                 500.16 MHz
IRSET                0.0 kHz
IRFIN               -88.4525 Hz
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CTEMP                26.2 °C
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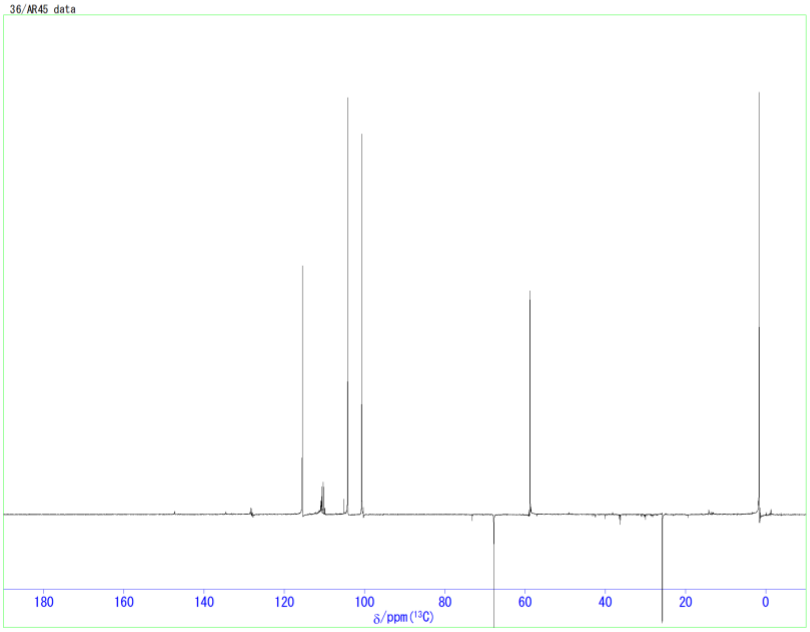


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ORGFILE G:¥2021Zr_Schwartz_BS_AR_SKi¥AR45¥A
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DATIM   21/Aug/2020 14:58:33
COMNT
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OBSET                -5.0 kHz
OBFIN               301.0403 Hz
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PW3                  0.0 µs
PI1                  0.0 ms
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PI3                  0.0 ms
LOOP1                   0
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SCANS                1024
DUMMY                   4
FREQU               31456.86 Hz
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RGAIN                  54
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EXMOD           dept.ex2
IRNUC                   1H
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PRNT_DATE   2021/Aug/01 21:21:01
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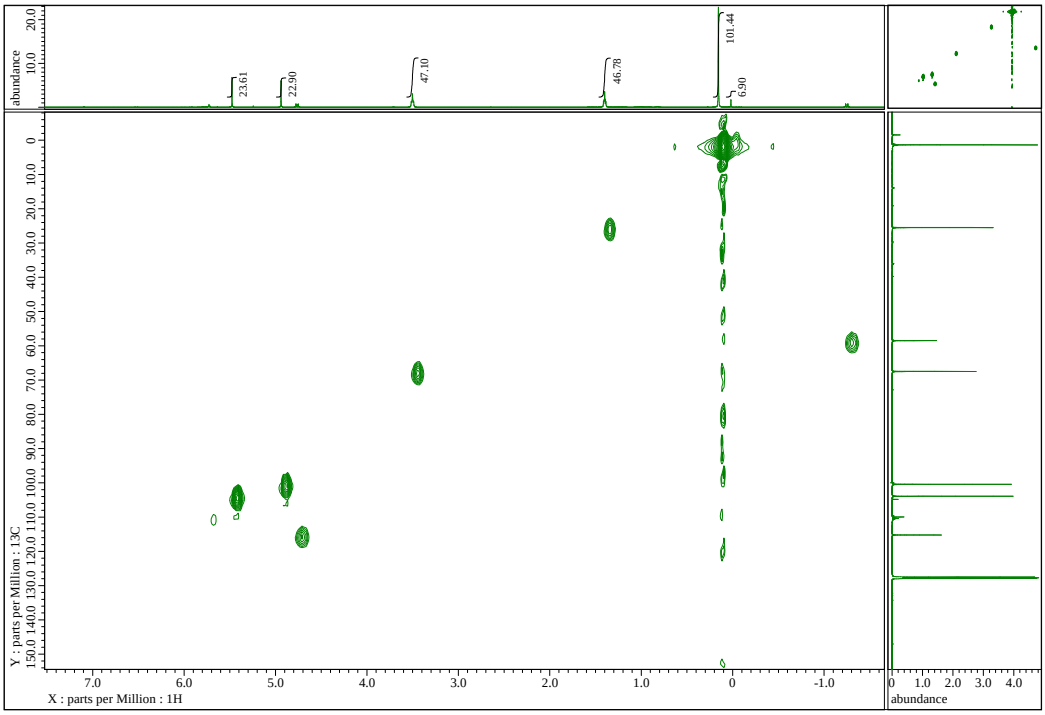
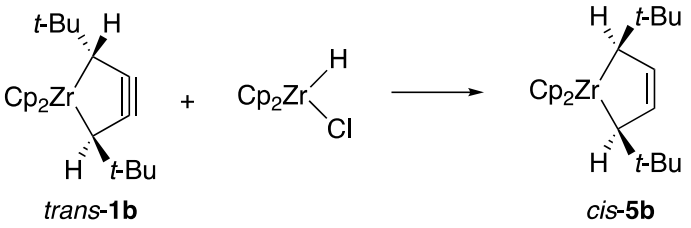
HMQC


abundance
23.61
22.90
47.10
46.78
101.44
6.90
Y : parts per Million : 13C
X : parts per Million : 1H
abundance

2.4. The reaction of trans-1,1-bis(η^5-cyclopentadienyl)-2,5-di-tert-butyl-1-zirconacyclopent-3-yne ***1b*** *with $Cp_2Zr(H)Cl$; formation of* ***5b****.*

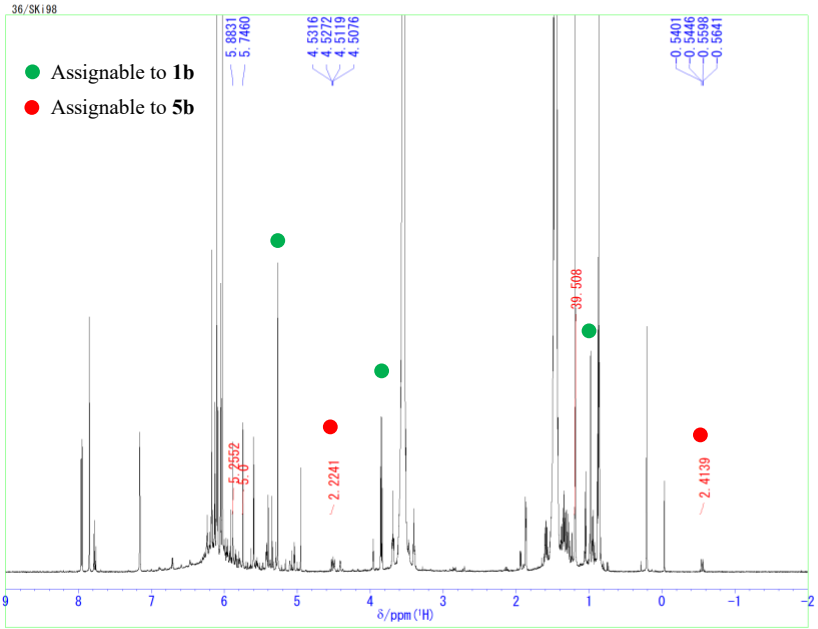


trans-**1b** *cis*-**5b**

In a dry Schlenk tube, **1b** (76.0 mg, 0.2 mmol) was dissolved in THF (1 mL), and $Cp_2Zr(H)Cl$ (258 mg, 1.0 mmol) was added. The mixture was stirred at 50 °C for 24 h, and the dark reddish solution was observed by NMR using pyrene (20.2 mg, 0.1 mmol) as an internal standard. ^{1}H NMR spectroscopy suggested the formation of **5b** in 27% yield, while a part of **1b** remained unchanged (22%).

^{1}H NMR (THF/C_6D_6, Me_4Si, 500 MHz): δ -0.55 (m, 2H, C*H*), 1.19 (s, 18H, *t*-Bu), 4.52 (m, 2H, C*H*), 5.75 (s, Cp), 5.88 (s, Cp).

^{1}H NMR



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OBSET 0.0 kHz
OBFIN -88.4525 Hz
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PW2 0.0 µs
PW3 0.0 µs
PI1 0.0 ms
PI2 0.0 ms
PI3 0.0 ms
LOOP1 0
POINT 13120
SCANS 16
DUMMY 1
FREQU 7514.266 Hz
ACQTM 1.7459 s
PD 4.0 s
RGAIN 20
BF 0.25 Hz
EXMOD single_pulse.ex2
IRNUC ¹H
IFR 500.16 MHz
IRSET 0.0 kHz
IRFIN -88.4525 Hz
IRBPW 118 µs
IRATN 0
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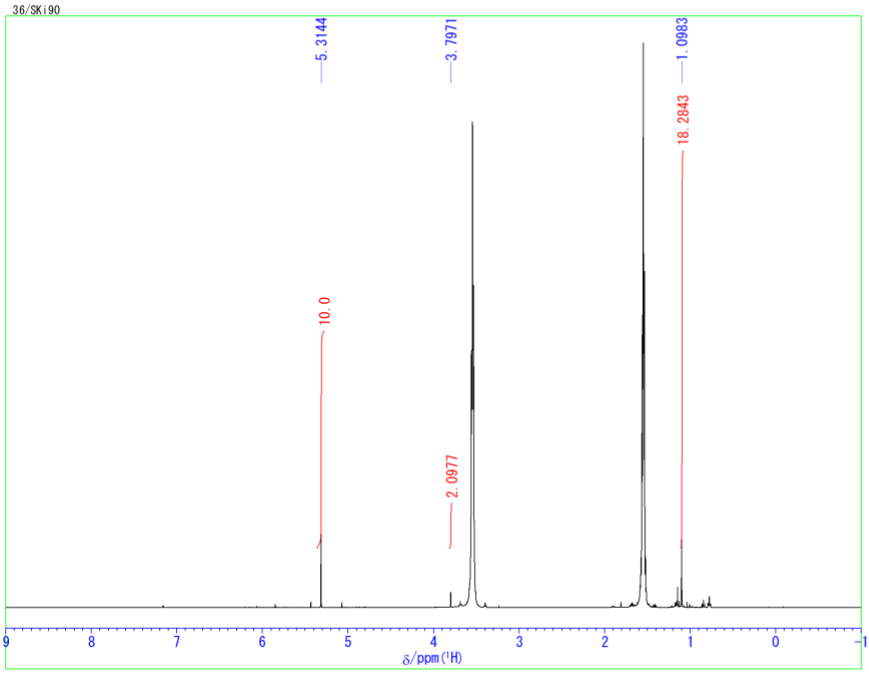
CTEMP 21.5 °C
PRNT_DATE 2021/Jul/23 16:44:30

For reference; ^{1}H NMR of *trans*- **1b** in THF.

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OBFIN              -88.4525 Hz
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PW2                    0.0 µs
PW3                    0.0 µs
PI1                    0.0 ms
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SCANS                    16
DUMMY                    1
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ACQTM                1.7459 s
PD                     4.0 s
RGAIN                   10
BF                    0.25 Hz
EXMOD    single_pulse.ex2
IRNUC                    ¹H
IFR                 500.16 MHz
IRSET                 0.0 kHz
IRFIN              -88.4525 Hz
IRRPW                  92 µs
IRATN                    0
CSPED                 0.0 Hz
CTEMP                21.8 ℃
PRNT_DATE   2021/Oct/18 22:45:48
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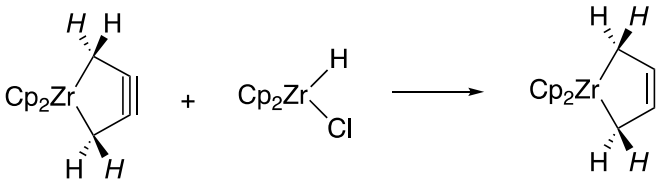
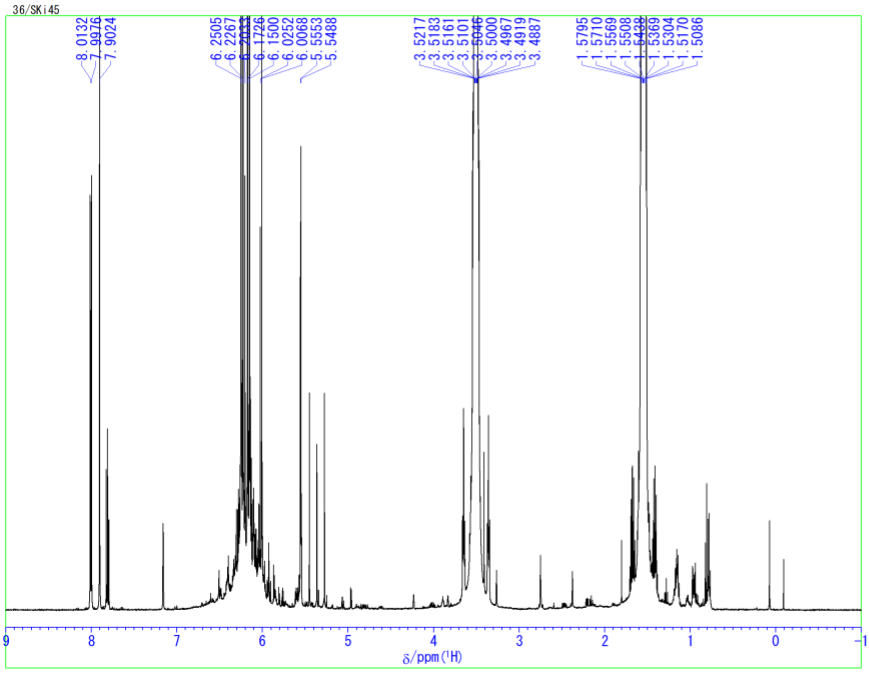
2.5. The reaction of 1,1-bis(η^5-cyclopentadienyl)-1-zirconacyclopent-3-yne ***1c*** *with $Cp_2Zr(H)Cl$.*



1c **5c**: ~0%

In a dry Schlenk tube, **1c** (54.0 mg, 0.2 mmol) was dissolved in THF (1 mL), and $Cp_2Zr(H)Cl$ (258 mg, 1.0 mmol) was added. The solution immediately turned to dark orange, and was stirred at r.t. for 1 h. Pyrene (0.1 mmol, 20.2 mg) was added to the solution as an internal standard, and the solution was observed by NMR. No signals assignable to **5c** were observed judging from the ^{1}H NMR spectroscopy, although most of **1c** was consumed.

^{1}H NMR of the reaction solution.



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DATIM 11/Dec/2020 18:24:05
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36/SKi45

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PW2	0.0 μs
PW3	0.0 μs
PI1	0.0 ms
PI2	0.0 ms
PI3	0.0 ms
LOOP1	0
POINT	13120
SCANS	16
DUMMY	1
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ACQTM	1.7459 s
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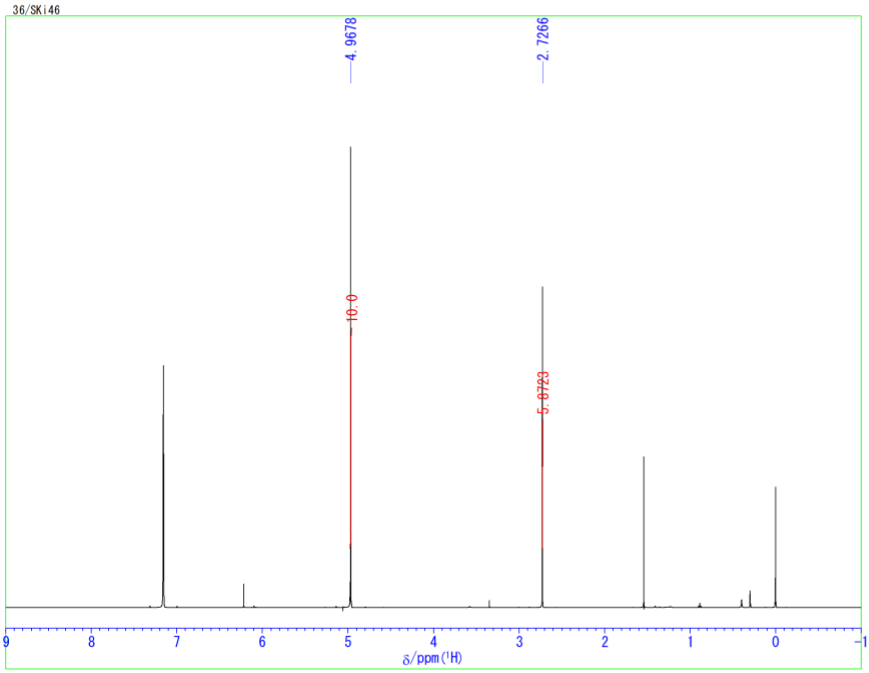
PRNT_DATE	2021/Oct/18 22:50:42

For reference, ^{1}H NMR of **1c** in C_6D_6.

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PI3                       0.0 ms
LOOP1                       0
POINT                   13120
SCANS                      16
DUMMY                       1
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ACQTM                  1.7459 s
PD                       4.0 s
RGAIN                      54
BF                      0.25 Hz
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IRNUC                       ¹H
IFR                    500.16 MHz
IRSET                    0.0 kHz
IRFIN                 -88.4525 Hz
IRRPW                    92 μs
IRATN                       0
CSPED                    0.0 Hz
CTEMP                   17.1 ℃
PRNT_DATE    2021/Oct/18 22:48:55
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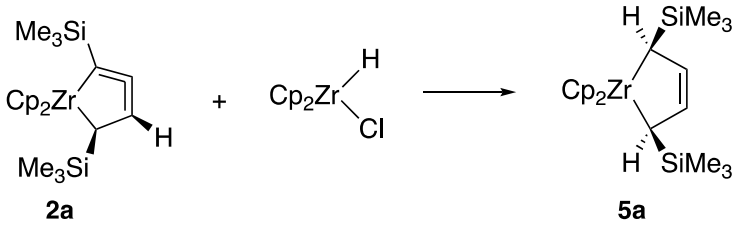
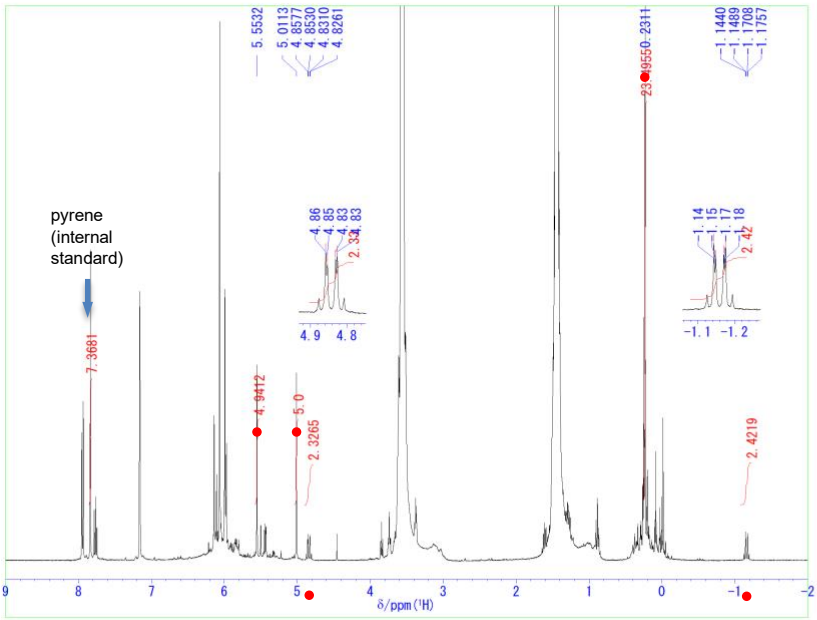
2.6. The reaction of trans-1,1-bis(η^5-cyclopentadienyl)-2,5-bis(trimethyhlsilyl)1-zirconacyclopenta-2,3-diene ***2a*** *with $Cp_2Zr(H)Cl$.*



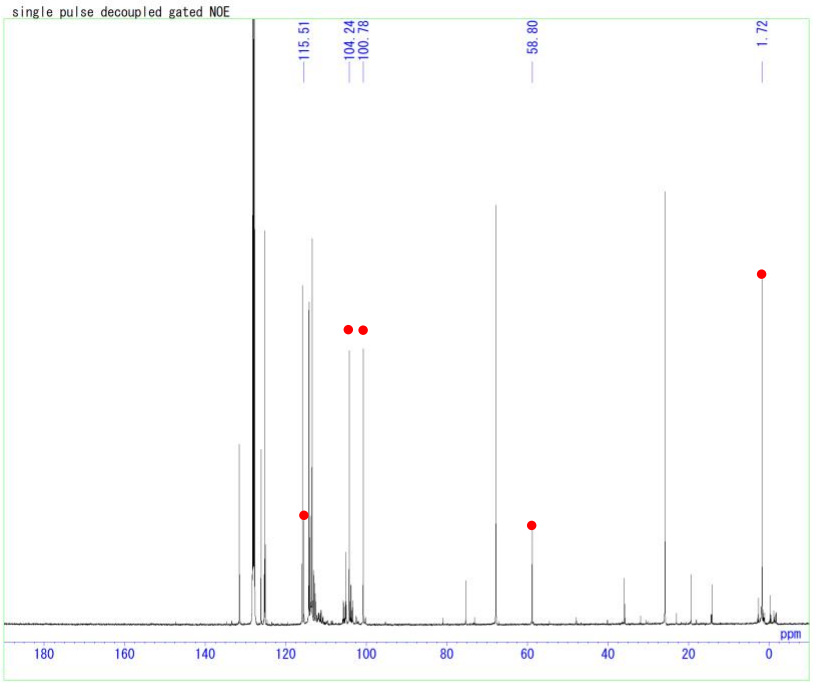
In a thoroughly dried Schlenk tube, **2a** (135 mg, 0.323 mmol) was dissolved in THF (2.0 mL) and $Cp_2Zr(H)Cl$ (333 mg, 1.29 mmol) was added. The mixture was stirred at 50 °C for 24 h. To this clear orange solution was added C_6D_6, and the mixture was observed by NMR. The ^{1}H NMR spectra indicated the formation of **5a** in 58%. The signal at 6.1 ppm can be assigned to $[Cp_2ZrCl]_2O$ (**8**) (44%).
Mass spectrometry (ESI, *m/z*): 437 ($C_{20}H_{32}Si_2Zr+H_3O^+$).

^{1}H NMR (THF/C_6D_6, C_6D_5H = 7.16, 400.1 MHz): δ –1.16 (m, 2H, C*H*), 0.23 (s, 18H, SiCH_3), 4.84 (m, 2H, C*H*), 5.01 (s, Cp), 5.55 (s, Cp).
^{13}C NMR (THF/C_6D_6, C_6D_6 = 128, 126 MHz): δ 1.7 (Si*C*H$_3$), 58.8 (Si*C*H), 100.8 (Cp), 104.2 (Cp), 115.5 (=*C*H).

^{1}H NMR



^{13}C NMR

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RGAIN                      54
BF                      0.25 Hz
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IFR                   500.16 MHz
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IRFIN                 -88.4525 H
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IRRPW                     92 µs
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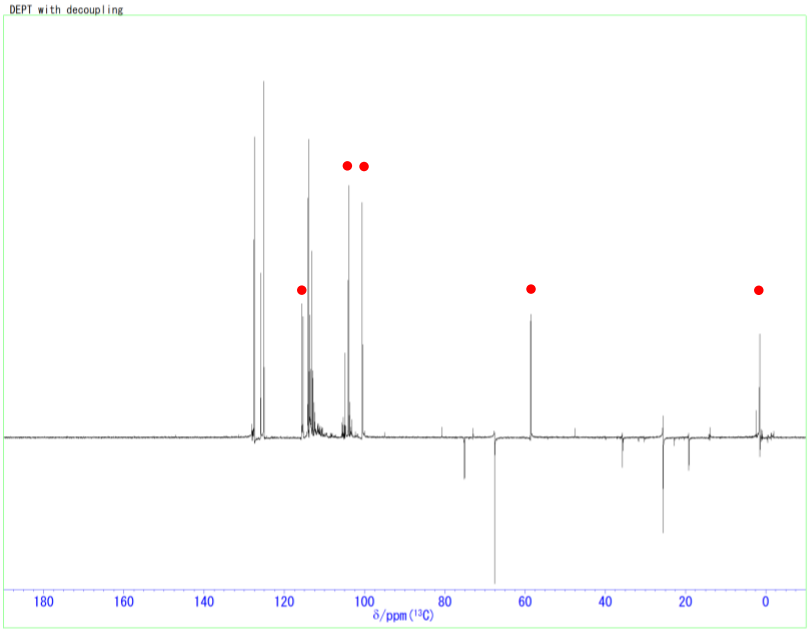


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ORGFILE   F:¥NMR¥AR101-150¥AR130¥AR130DEPT-
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PW3                      0.0 µs
PI1                      0.0 ms
PI2                      0.0 ms
PI3                      0.0 ms
LOOP1                       0
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SCANS                     500
DUMMY                       4
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PD                       2.0 s
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PRNT_DATE   2021/Jul/23 14:07:00
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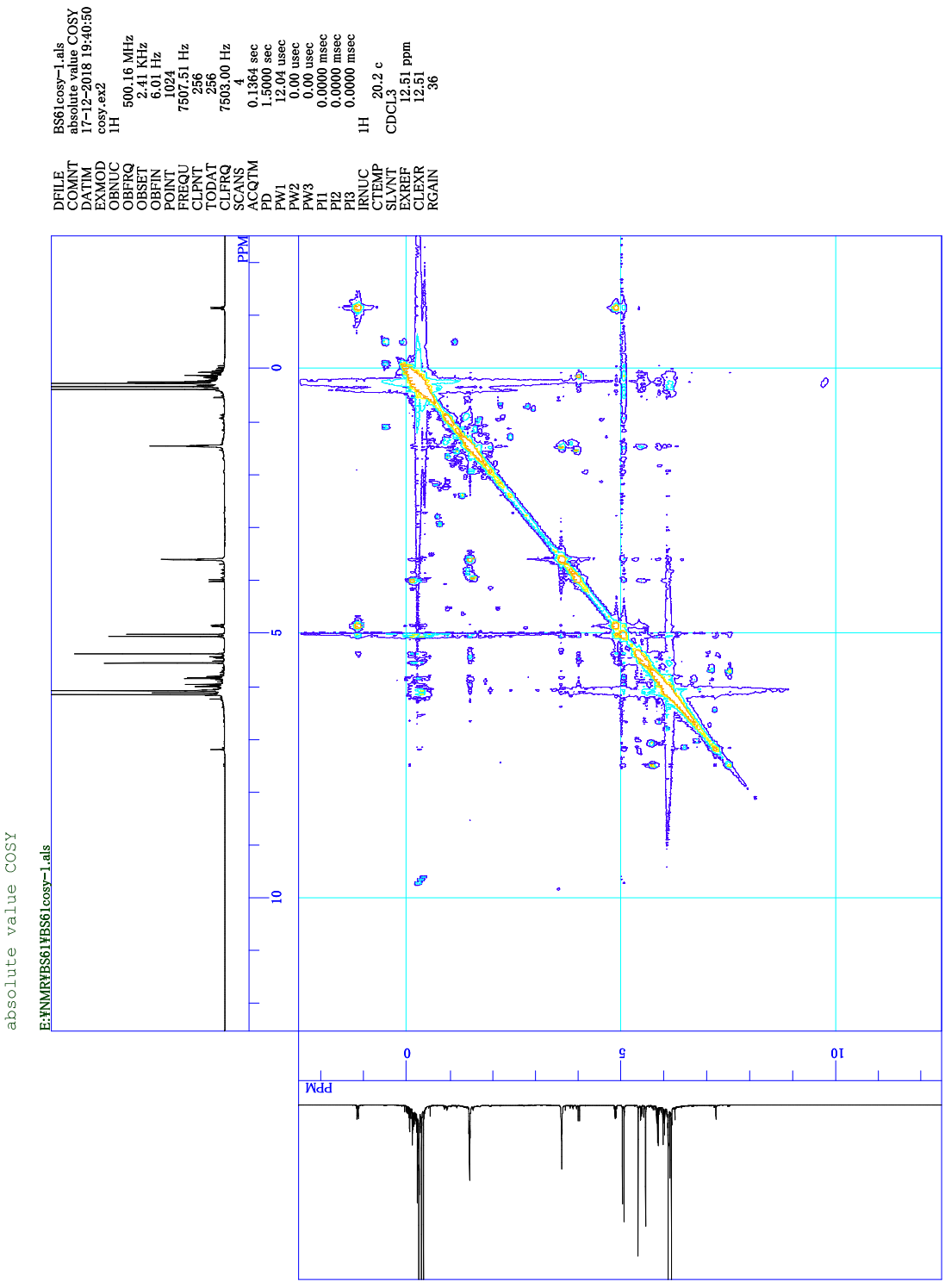
COSY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6.01 Hz
1024
7507.51 Hz
256
256
7503.00 Hz
4
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1.5000 sec
12.04 usec
0.00 usec
0.00 usec
0.0000 msec
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0.0000 msec
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CDCL3
12.51 ppm
12.51
36
DFILE
COMNT
DATIM
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PI2
PI3
IRNUC
CTEMP
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PPM
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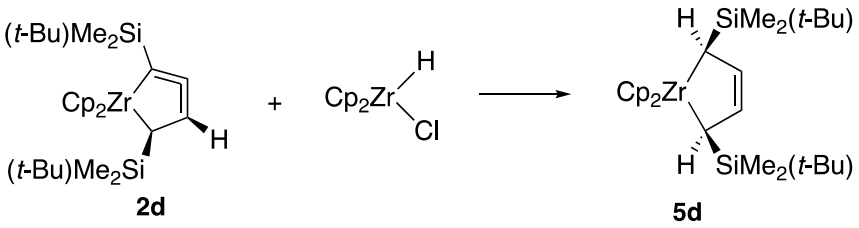
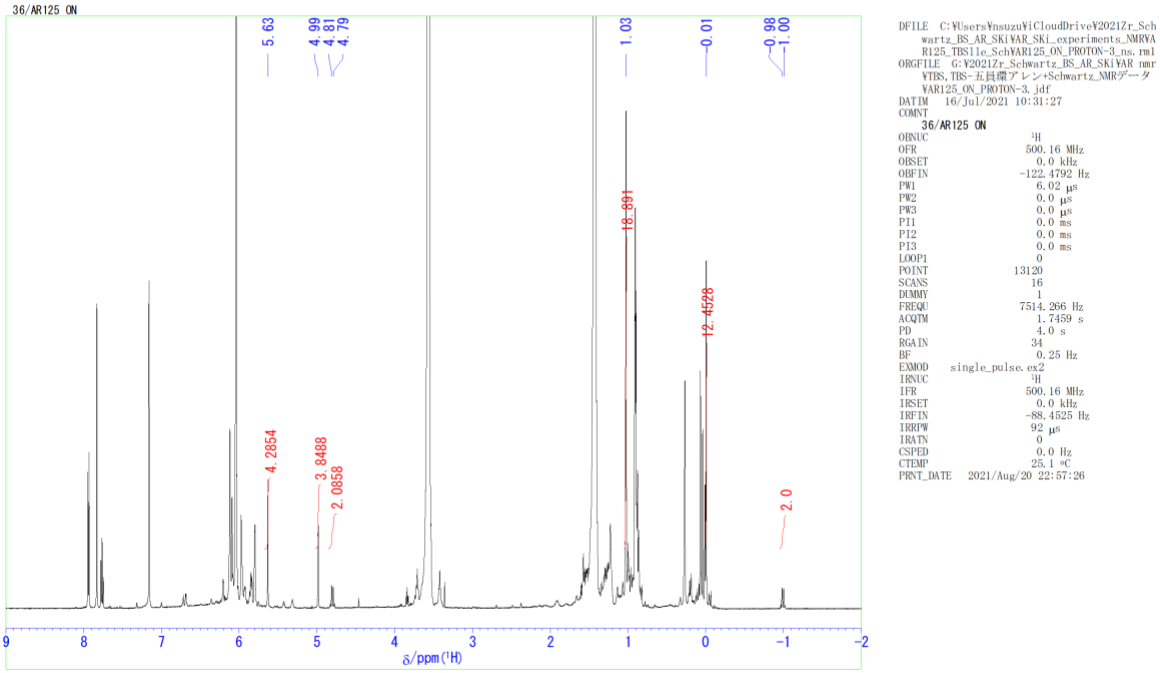
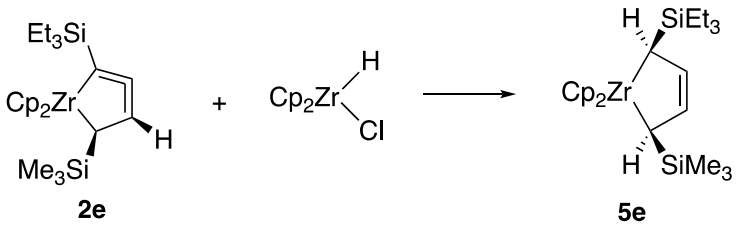
2.7. The reaction of trans-1,1-bis(η^5-cyclopentadienyl)-2,5-bis(tert-butyldimethyhlsilyl)-1-zirconacyclopenta-2,3-diene ***2a*** *with Cp$_2$Zr(H)Cl; formation of* ***5c****.*



Complex **2d** (165 mg, 0.329 mmol) was dissolved in THF (2 mL) in a dry Schlenk tube. To this solution was added Cp$_2$Zr(H)Cl (339 mg, 1.32 mmol), and the solution was stirred at 50 °C for 24 h. 1H NMR spectra of the solution indicated the formation of **5d** (39%).
^{1}H NMR (THF/C_6D_6, C_6D_5H = 7.16, 500 MHz): δ –0.99 (m, 2H, C*H*), –0.01 (s, 12H, SiCH_3), 1.03 (s, 18H, SiCCH_3), 4.80 (m, 2H, C*H*), 4.99 (s, Cp), 5.63 (s, Cp).

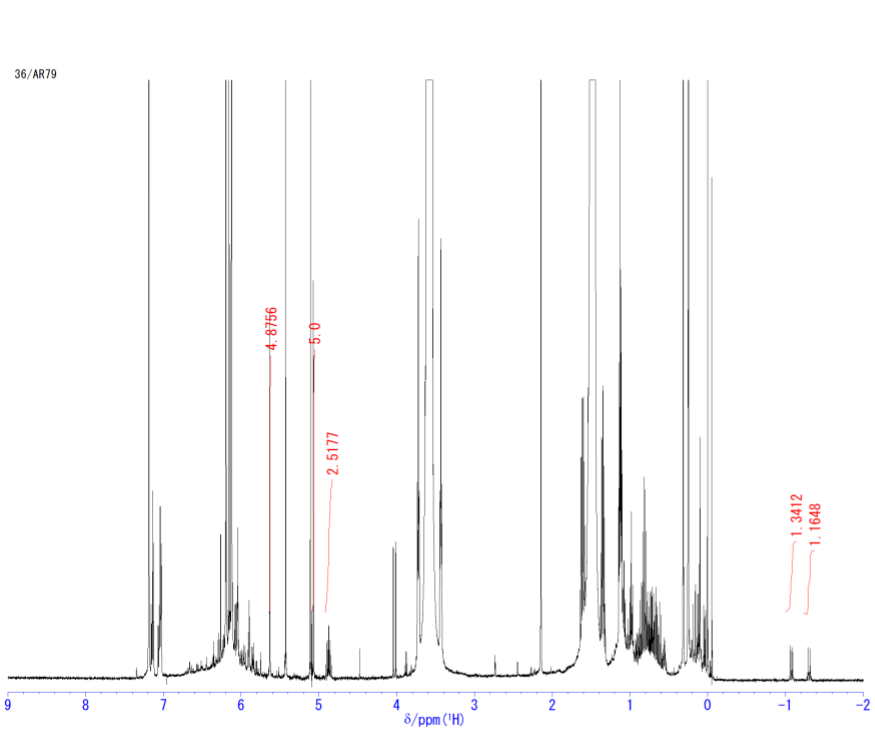


2.8. The reaction of trans-1,1-bis(η^5-cyclopentadienyl)-2-trimethyhlsily-5-triethylsilyl-1-zirconacyclopent-3-yne ***2e*** *with* $Cp_2Zr(H)Cl$.



In a thoroughly dried Schlenk tube, **2c** (125 mg, 0.3 mmol) was dissolved in THF (6 mL) and $Cp_2Zr(H)Cl$ (155 mg, 0.6 mmol) was added. The mixture was stirred at 50 °C for 1 h. To this pale orange solution was added C_6D_6, and the mixture was observed by NMR. The ^{1}H NMR spectra indicated the formation of **5c** in 22%.

^{1}H NMR (THF/C_6D_6, Me_4Si, 500 MHz): δ –1.34 (m, 1H, C*H*), –1.11 (m, 1H, C*H*), -0.03 (s, 9H, SiC*H*$_3$), 0.6–0.7 (m, 6H, SiC*H*$_2$), 1.06 (m, 9H, C*H*$_3$), , 4.85 (m, 2H, C*H*), 5.04 (s, Cp), 5.60 (s, Cp).

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IFR                 500.16 MHz
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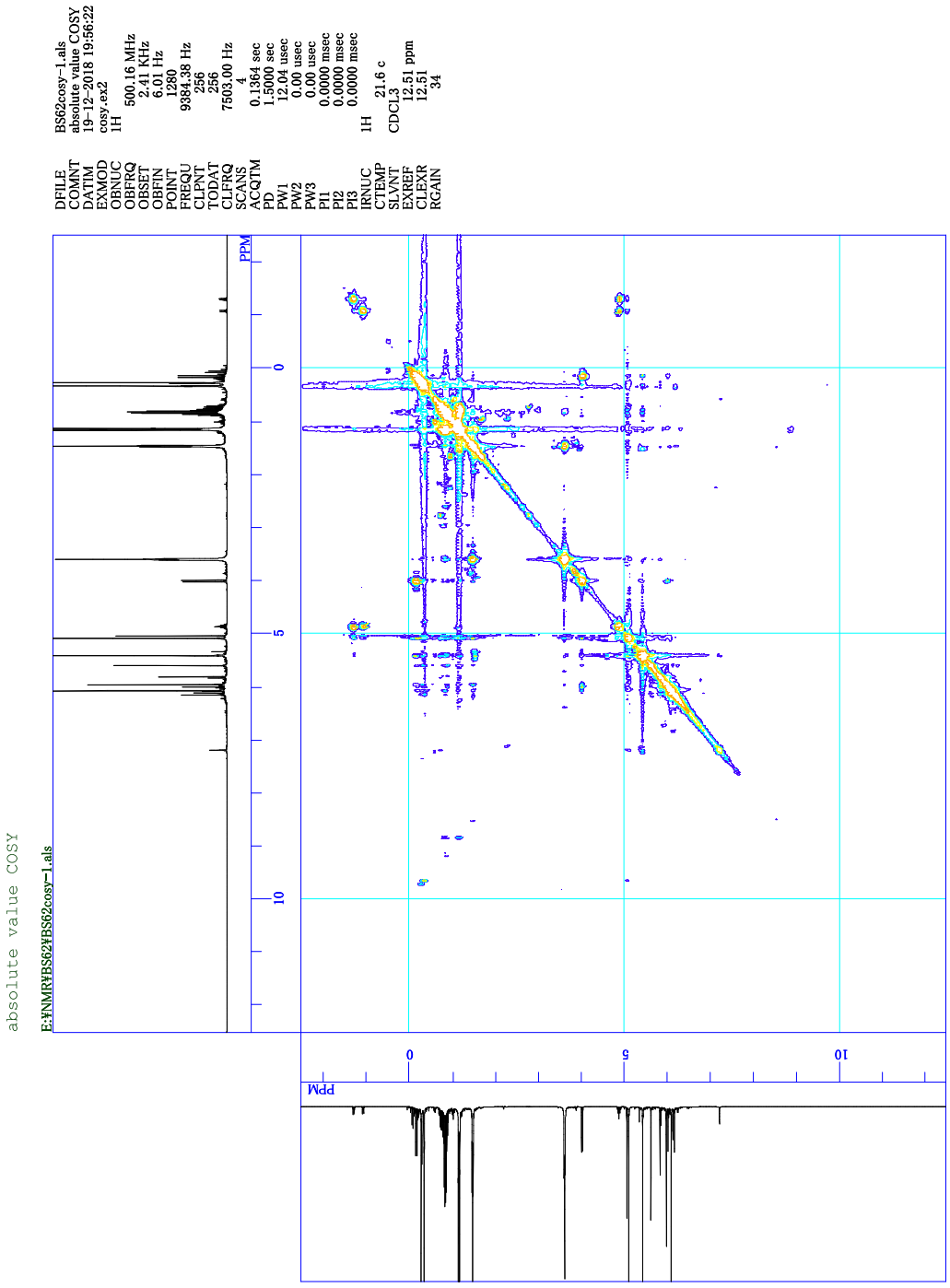
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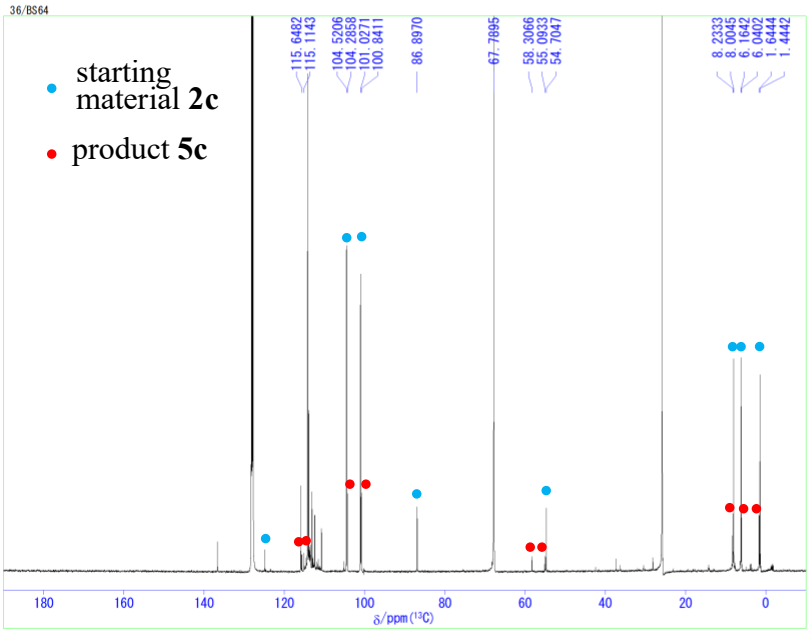
13C NMR



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PW3 0.0 µs
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PI2 0.0 ms
PI3 0.0 ms
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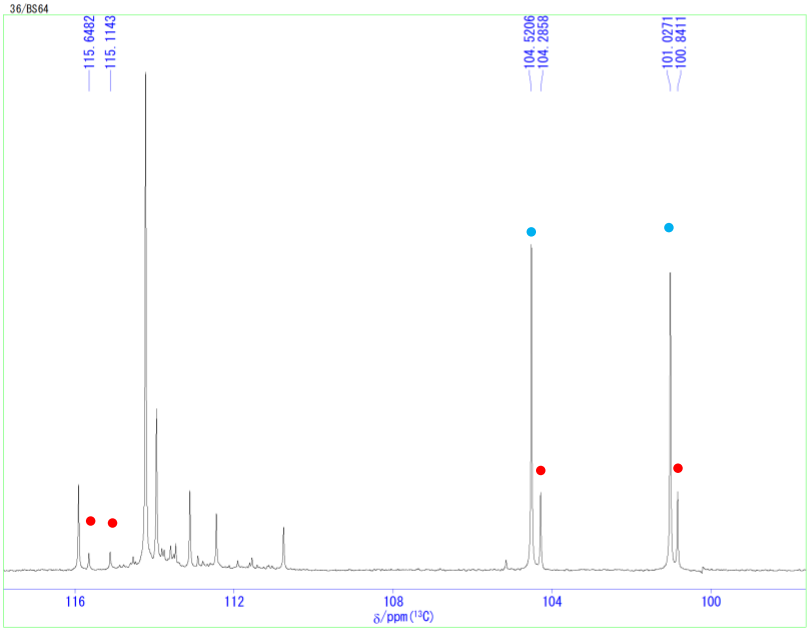

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PW2 0.0 µs
PW3 0.0 µs
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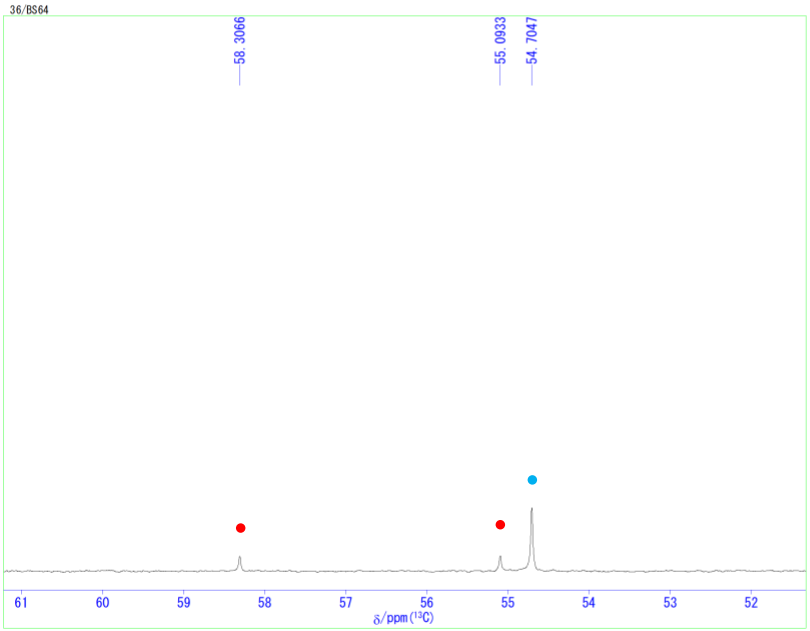


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PI3                     0.0 ms
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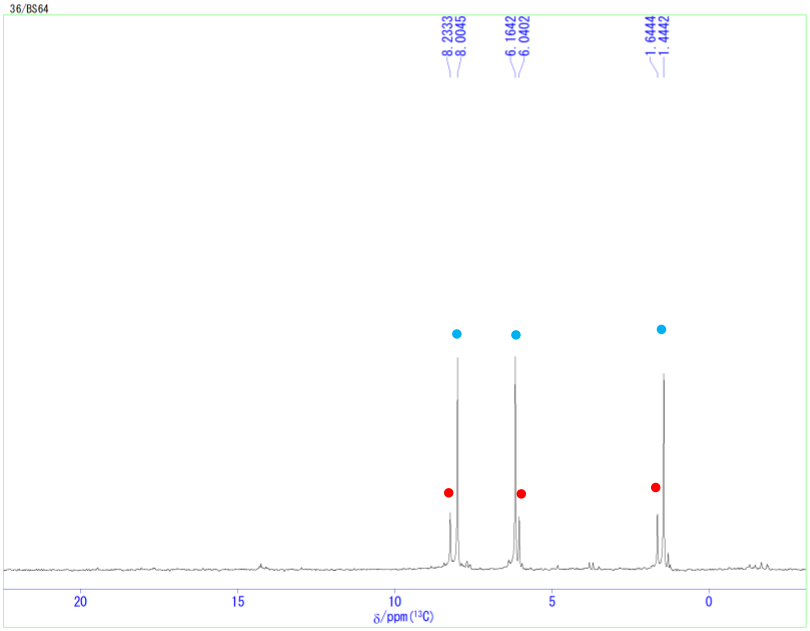


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PW3                     0.0 μs
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PI2                     0.0 ms
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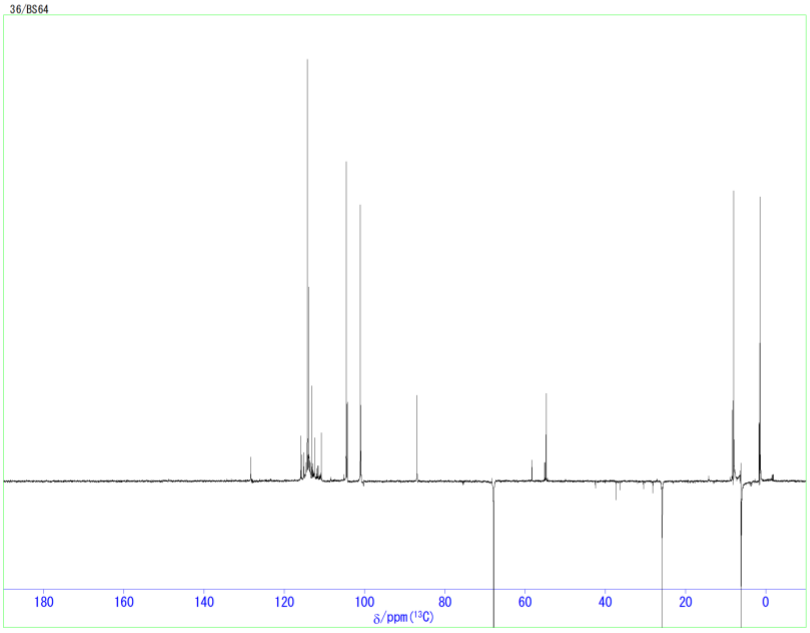


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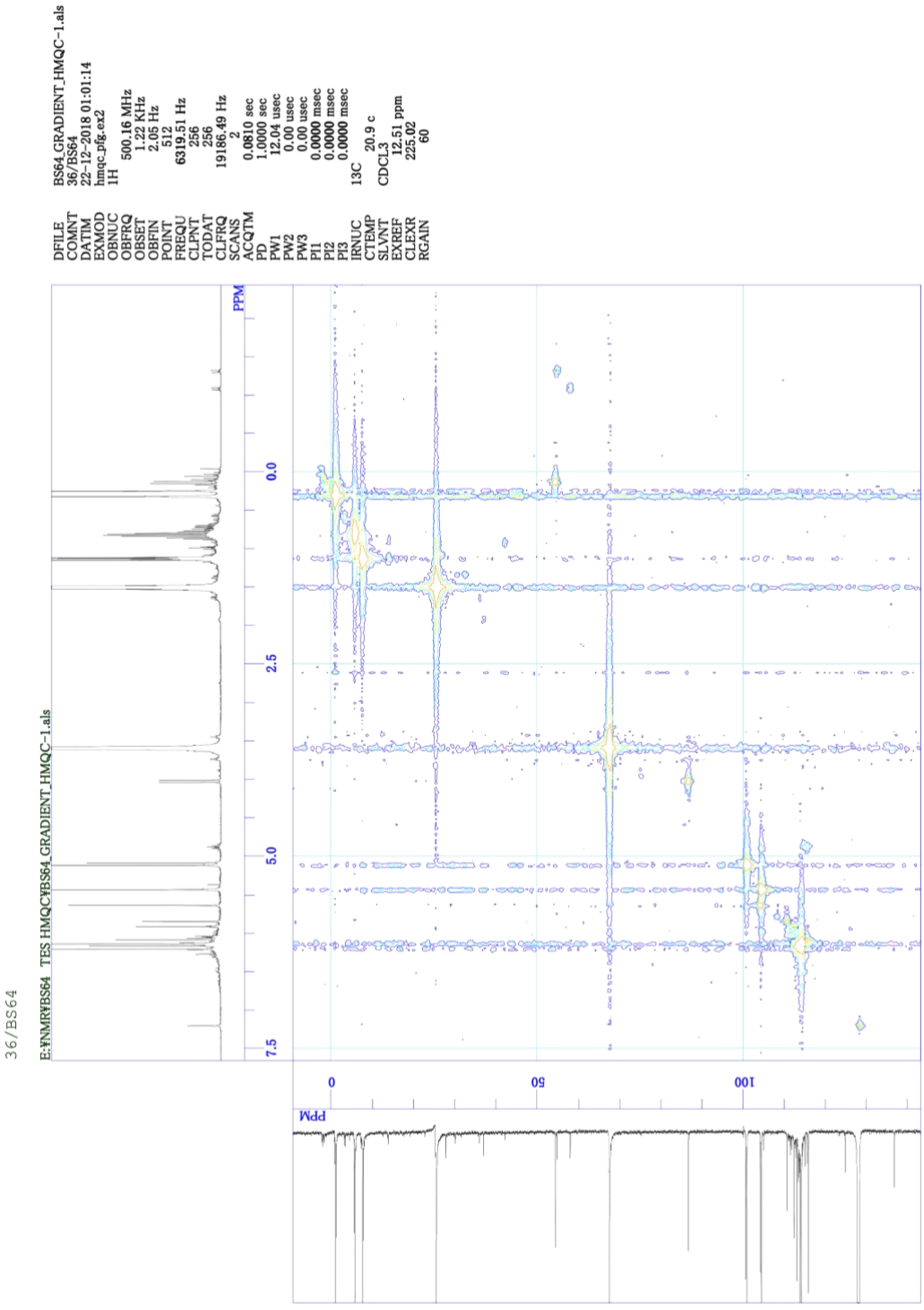
HMQC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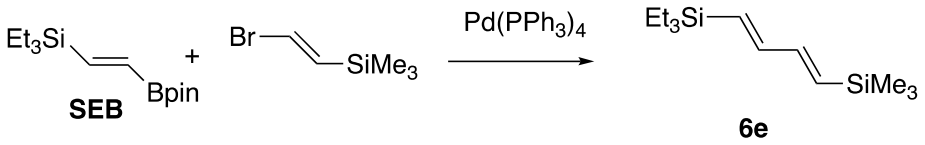
2.5
5.0
7.5
0
50
100
PPM

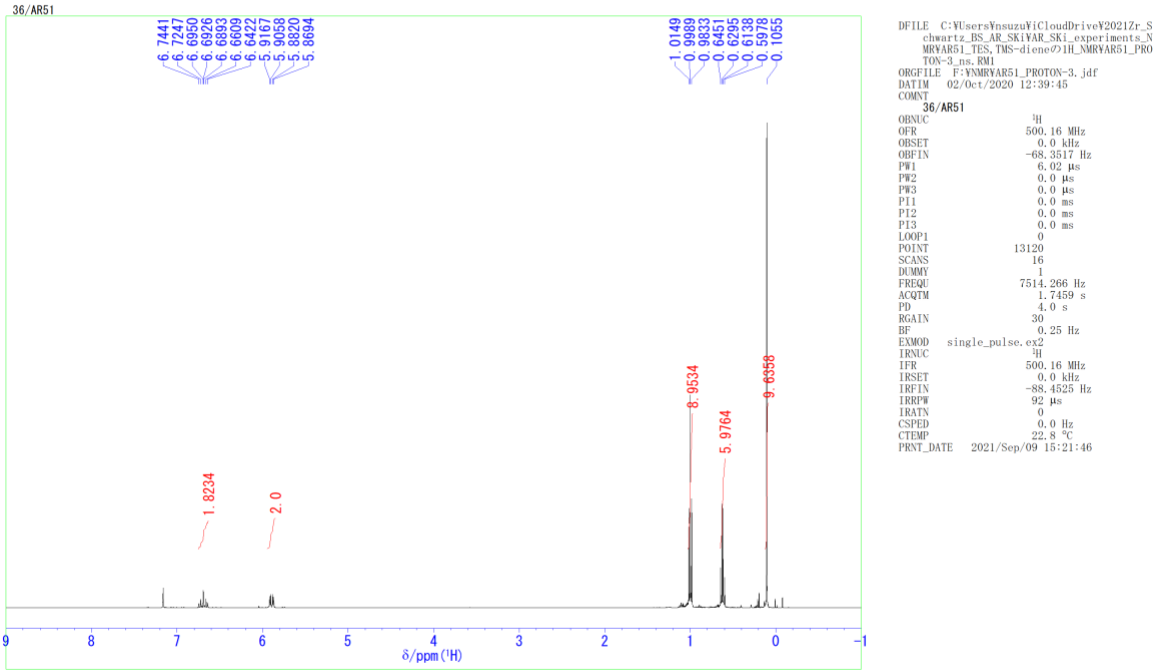
*2.9. Preparation of (1E,3E)-1-triethylsilyl-4-trimethylsilylbuta-1,3-diene (**6e**).* [14]



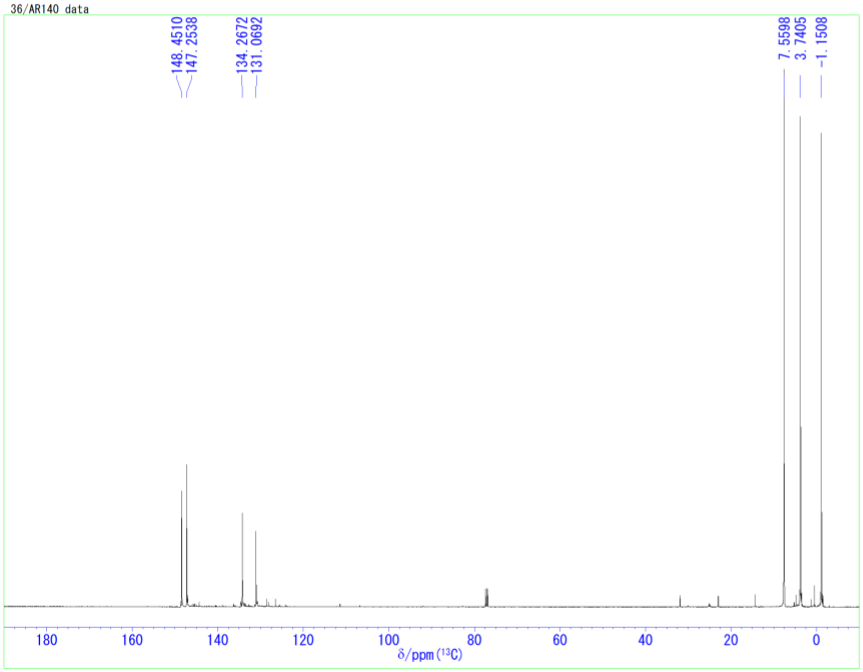
(*E*)-Triethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**SEB**) was prepared from triethylacetylene and pinacol borane according to the literature. [12] **SEB** (1.15 g, 4.30 mmol) and (2-bromovinyl)trimethylsilane (1.00 mg, 5.60 mmol) were dissolved in THF (50 mL) and $Pd(PPh_3)_4$ (497 mg, 0.430 mmol) and an aqueous solution of Cs_2CO_3 (1.4 M, 15 mL) were added. The mixture was stirred at 55 °C for 3 h. Water was added to the reaction mixture and extracted with diethyl ether. The combined organic layer was washed with brine and water, and then dried over $MgSO_4$. The volatiles were removed in vacuo and the residue was purified by column chromatograph on silica gel (hexane/diethyl ether = 10/1) to afford **6e** as yellowish brown oil (830 mg, 80% isolated). [13]

^{1}H NMR (C_6D_6, C_6D_6MH = 7.16, 500 MHz): δ 0.11 (s, 9H, SiC*H*$_3$), 0.62 (q, *J* = 8 Hz, 6H, C*H*$_2$), 1.00 (t, *J* = 8 Hz, 9H, C*H*$_3$), 5.89 (dd, *J* = 17, 6 Hz, 2H, C*H*), 6.69 (m, 2H, C*H*).
^{13}C NMR ($CDCl_3$, $CDCl_3$ = 77.16, 126 MHz): δ -1.15 (Si*C*H$_3$), 3.74 (Si*C*H$_2$CH$_3$), 7.56 (SiCH$_2$*C*H$_3$), 131.07 (*C*H), 134.27 (*C*H), 147.25 (*C*H), 148.45 (*C*H).

^{1}H NMR



^{13}C NMR

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PW3                       0.0 µs
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PI2                       0.0 ms
PI3                       0.0 ms
LOOP1                       0
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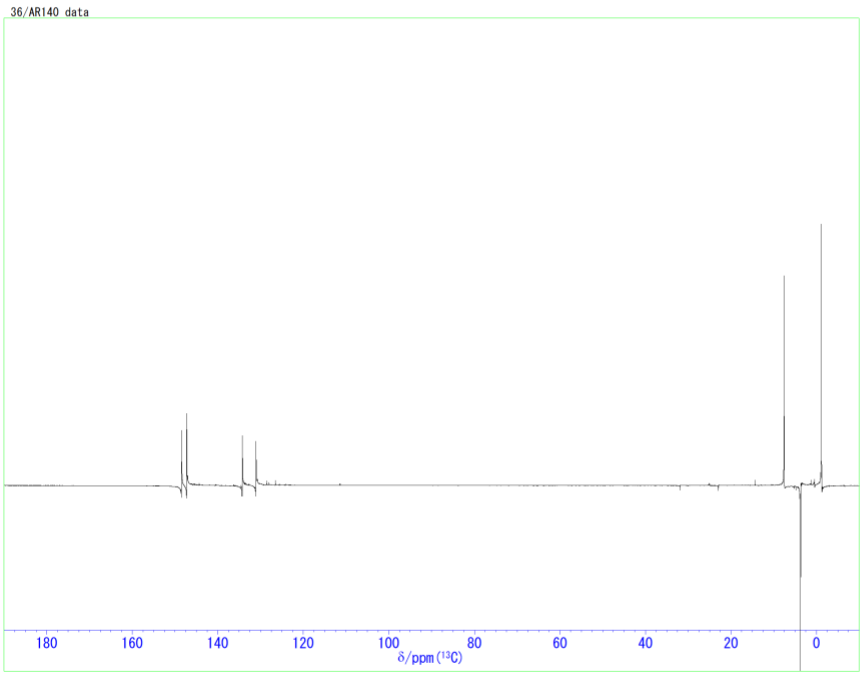
DEPT135

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PW3                       0.0 µs
PI1                       0.0 ms
PI2                       0.0 ms
PI3                       0.0 ms
LOOP1                       0
POINT                   26224
SCANS                    1024
DUMMY                       4
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PD                        2.0 s
RGAIN                      50
BF                      0.25 Hz
EXMOD          dept.ex2
IRNUC                      ¹H
IFR                    500.16 MHz
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IRFIN                 -88.4525 Hz
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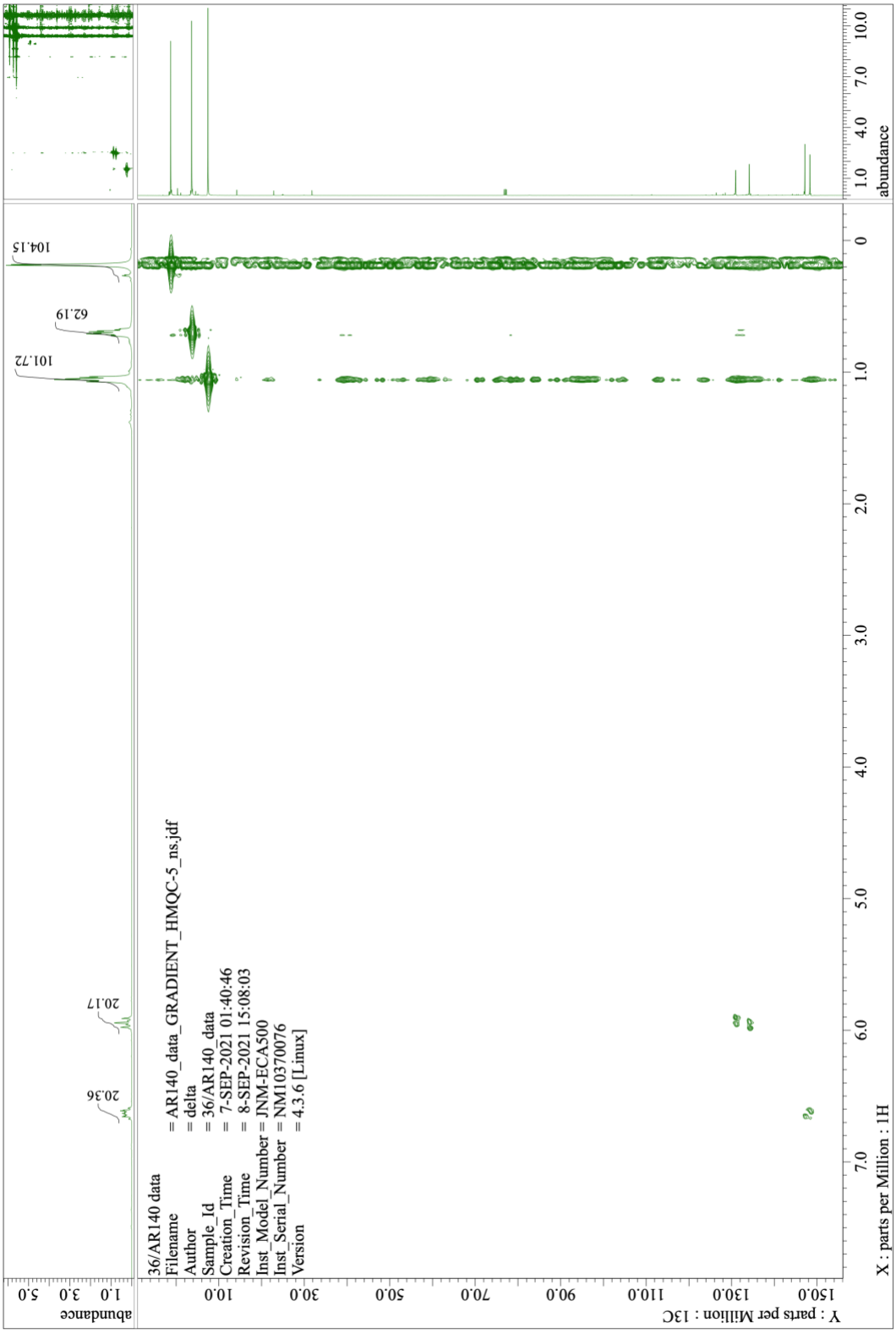
HMQC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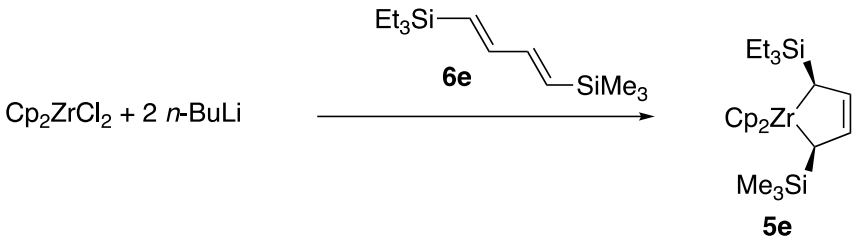
Inst_Serial_Number = NM10370076
Version = 4.3.6 [Linux]
Y : parts per Million : 13C
X : parts per Million : 1H
abundance
abundance

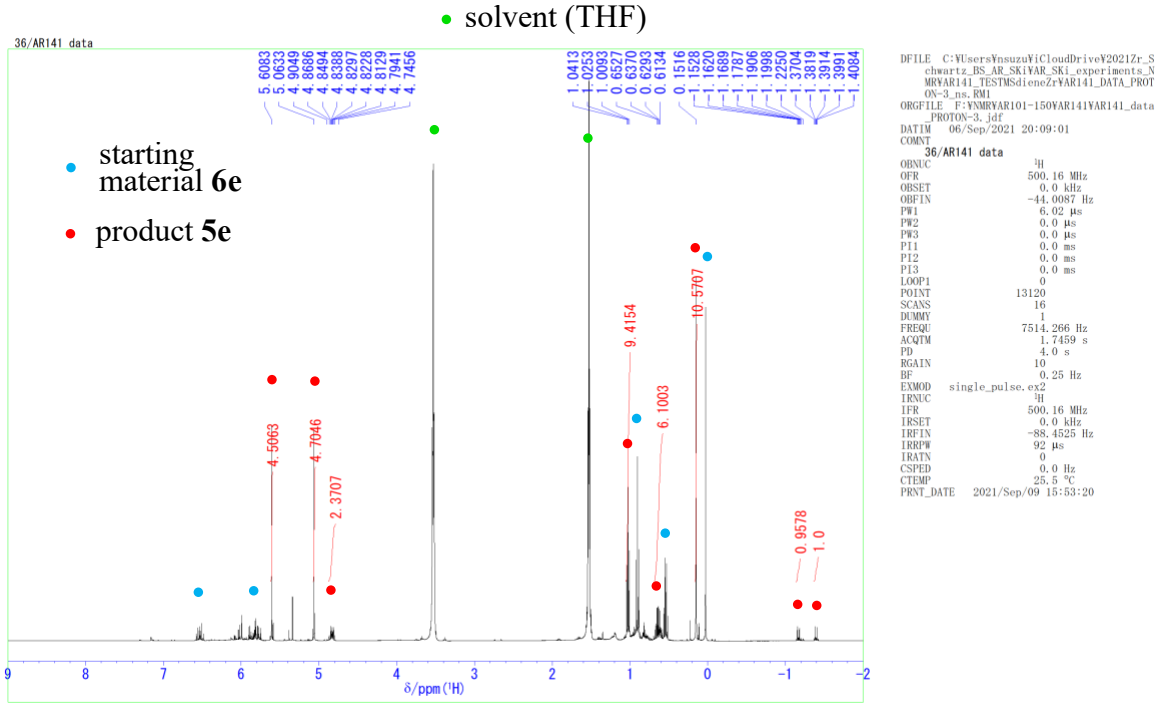
*2.10. Preparation of zirconocene-diene complex; 1,1-bis(η^5-cyclopentadienyl)-cis-2-triethylsilyl-5-trimethylsilyl-1-zirconacyclopent-3-ene (**5e**)*



The diene complex **5e** was prepared in a similar manner to **5a** using **6e** instead of **6a** (32% by ^{1}H NMR).

^{1}H NMR (C_6D_6, C_6D_6H = 7.16, 500 MHz): δ -1.39 (m, 1H, C*H*), -1.16 (m, 1H, C*H*), 0.15 (s, 9H, SiCH_3), 0.63 (m, 6H, CH_2), 1.03 (t, *J* = 8 Hz, 9H, CH_3), 4.83 (m, 2H, C*H*), 5.06 (s, 5H, Cp), 5.61 (s, 5H, Cp).
^{13}C NMR (C_6D_6, C_6D_6 = 128.06, 126 MHz): δ 1.59 (Si*C*H$_3$), 6.05 (Si*C*H$_2$CH$_3$), 8.18 (SiCH$_2$*C*H$_3$), 55.04 (*C*H), 58.28 (*C*H), 100.94 (Cp), 104.39 (Cp), 115.21 (*C*H), 115.72 (*C*H).

^{1}H NMR



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PI2 0.0 ms
PI3 0.0 ms
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PD 4.0 s
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IRSET 0.0 kHz
IRFIN -88.4525 Hz
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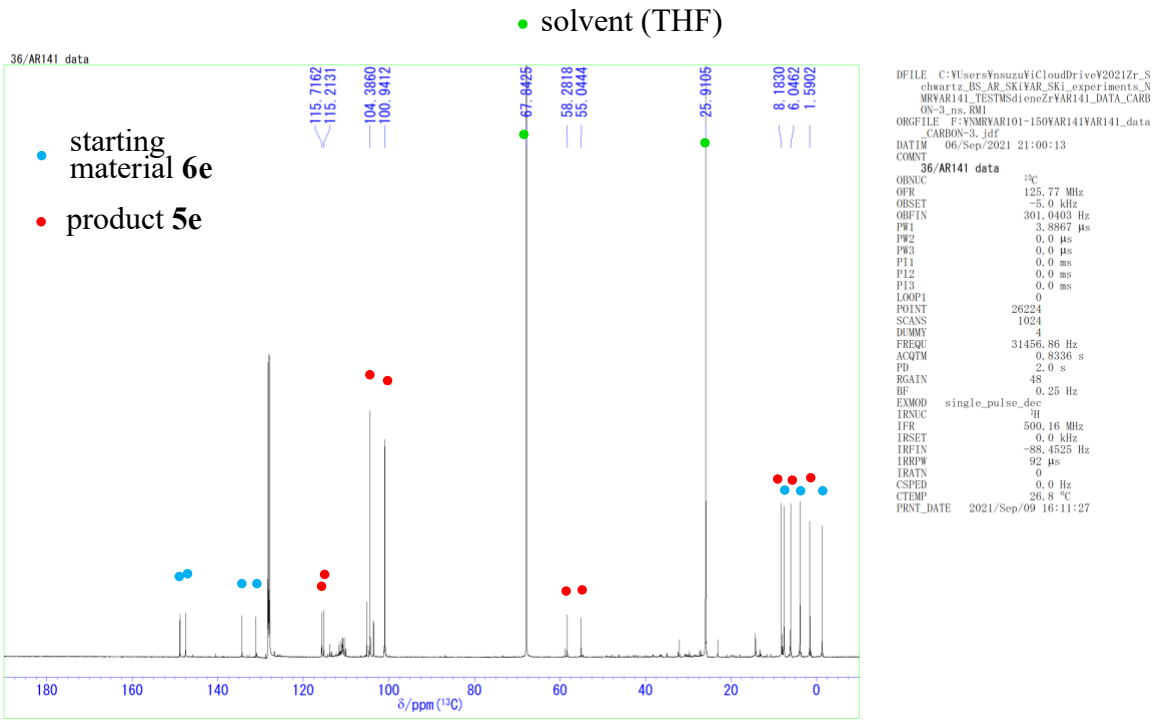
CTEMP 25.5 °C
PRNT_DATE 2021/Sep/09 15:53:20

^{13}C NMR



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PRNT_DATE 2021/Sep/09 16:11:27

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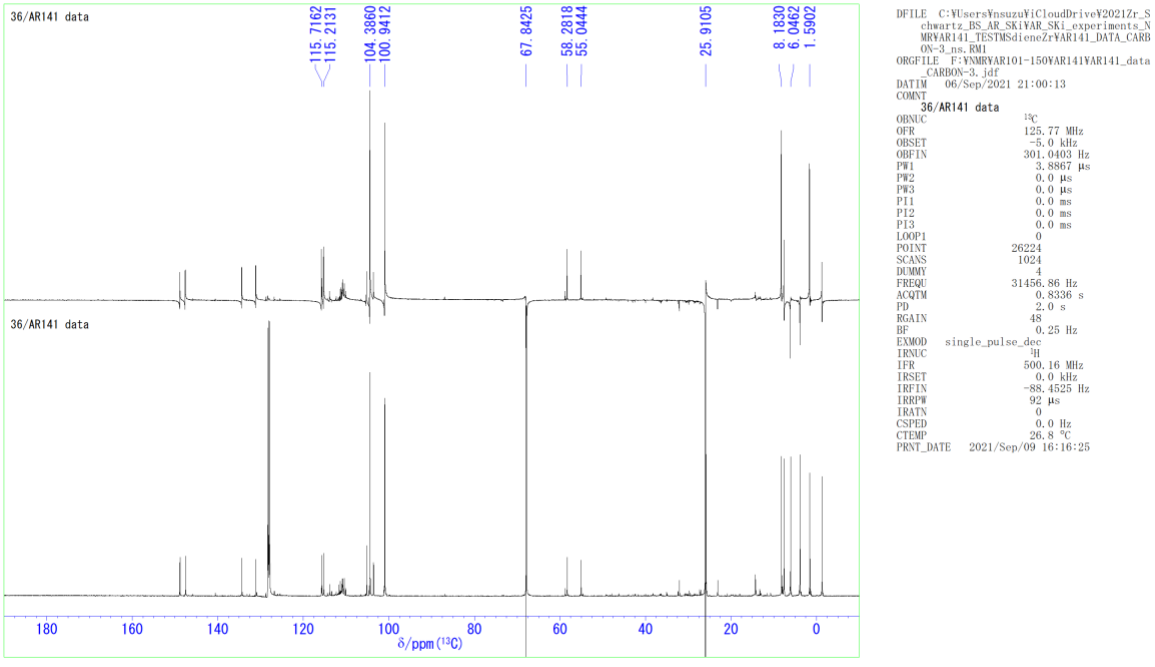

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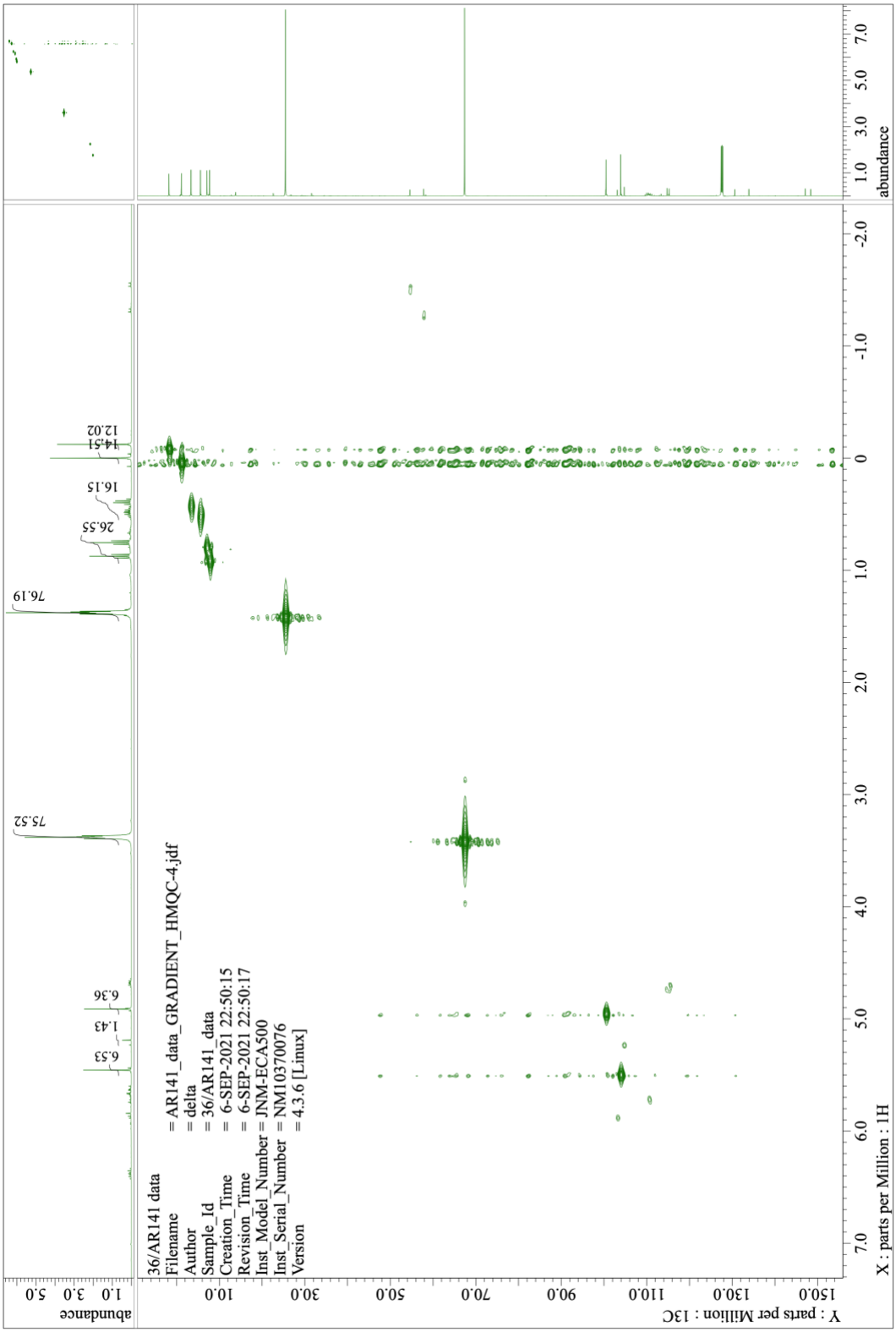
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Y : parts per Million : 13C
abundance
76.19
75.52
26.55
16.15
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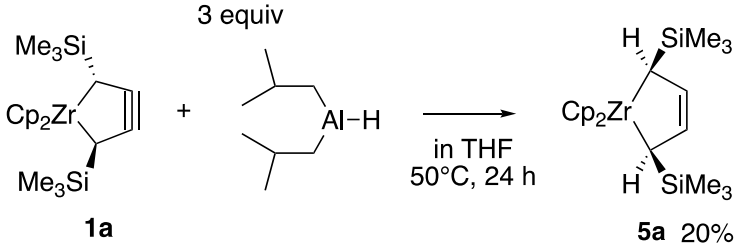
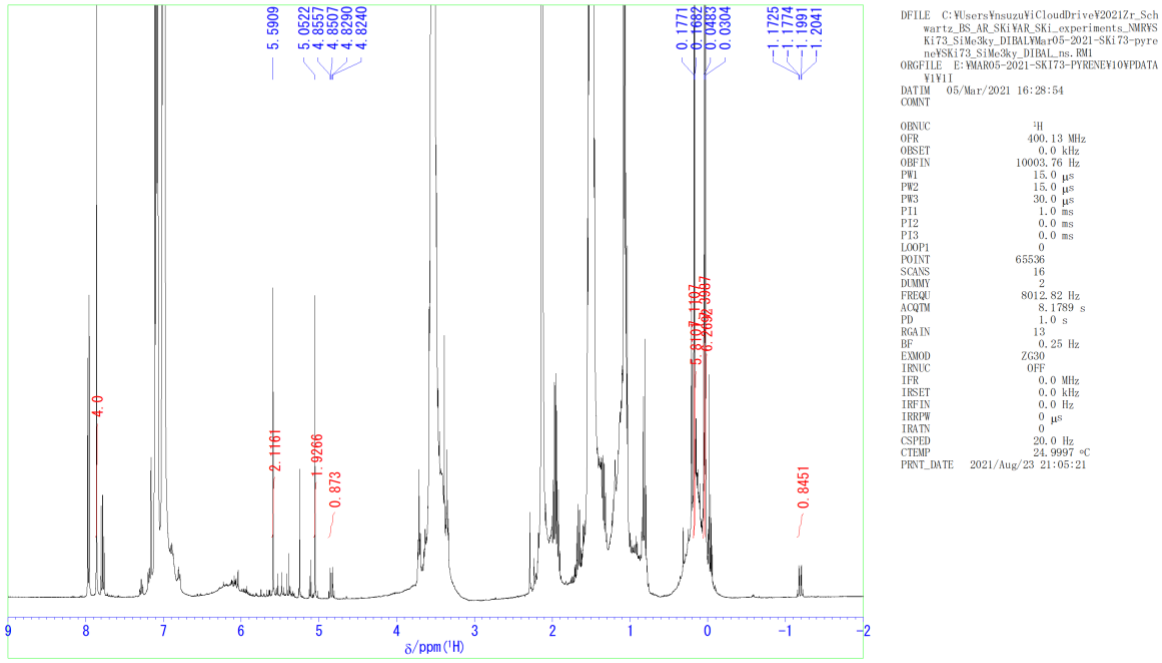
12.02
6.53
1.43
6.36

*2.11. The reaction of **1a** with diisobutylaluminum hydride (DIBAL-H).*

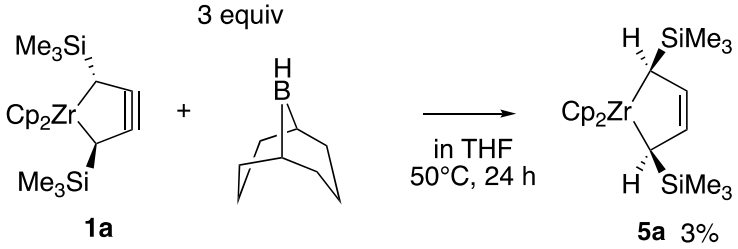


In a dry Schlenk tube, **1a** (82.6 mg, 0.2 mmol) was dissolved in THF (1 mL) and diisobutylaluminum hydride (1.0 M toluene solution, 0.6 mL, 0.6 mmol) was added. The solution was stirred at 50 °C for 24 h, and the brown solution was observed by 1H NMR to confirm the formation of **5a** (20%).

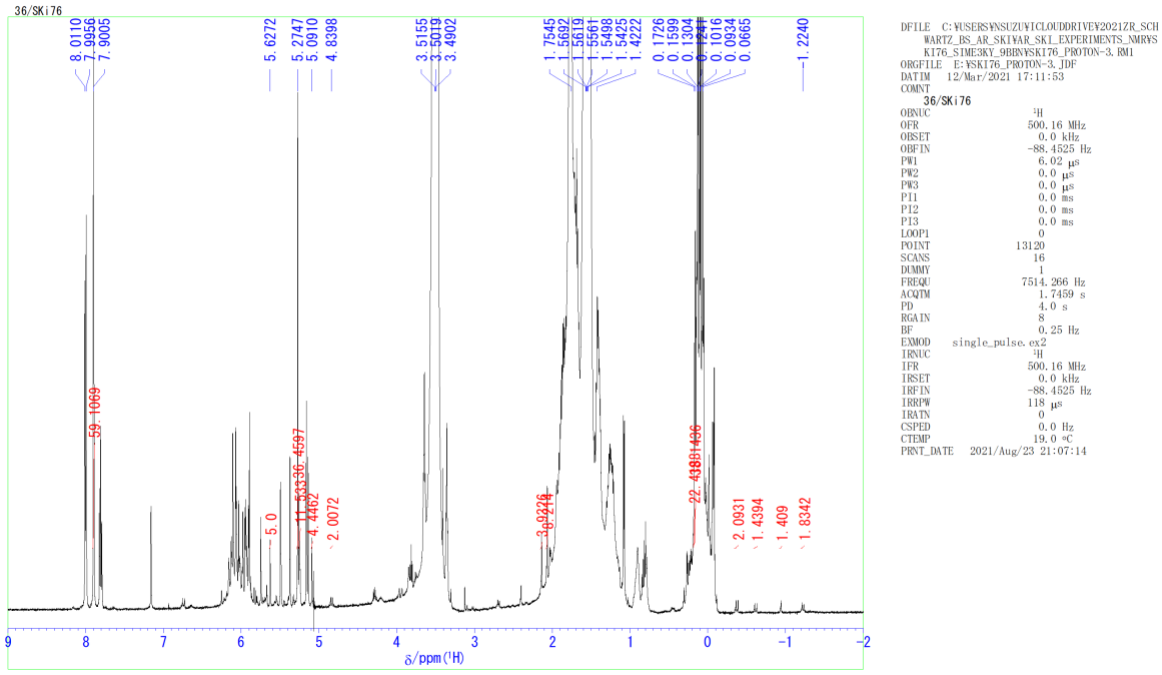
^{1}H NMR



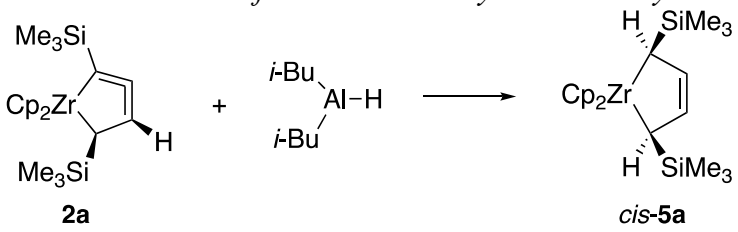
*2.12. The reaction of **1a** with 9-Borabicyclo[3.3.1]nonane (9-BBN).*



In a dry Schlenk tube, **1a** (82.6 mg, 0.2 mmol) was dissolved in THF (1 mL) and 9-Borabicyclo[3.3.1]nonane dimer (74 mg, 0.3 mmol) was added. The solution was stirred at 50 °C for 24 h, and the brown solution was observed by ^{1}H NMR to confirm the formation of **5a** (≤3%).

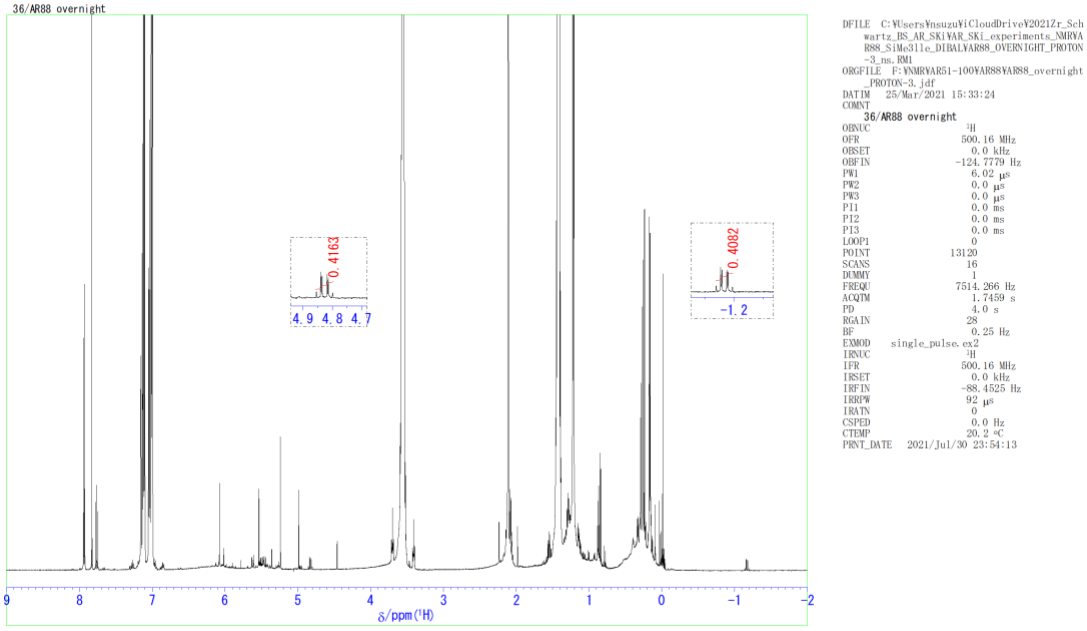


*2.13. The reaction of **2a** with diisobutylaluminum hydride (DIBAL-H).*

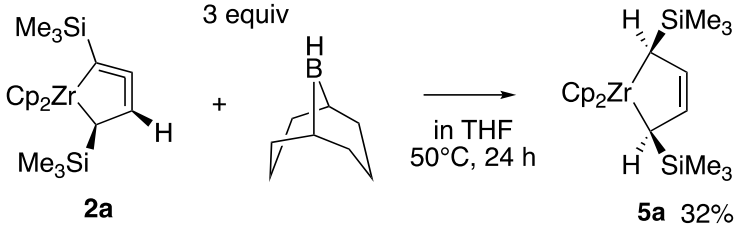


(AR88)

In a dry Schlenk tube, **2a** (125 mg, 0.3 mmol) was dissolved in THF (2 mL) and diisobutylaluminum hydride (1.0 M hexane solution, 0.9 mL, 0.9 mmol) was added. The solution was stirred at 50 °C for 24 h, and the brown solution was observed by ^{1}H NMR to confirm the formation of **5a** (15%).

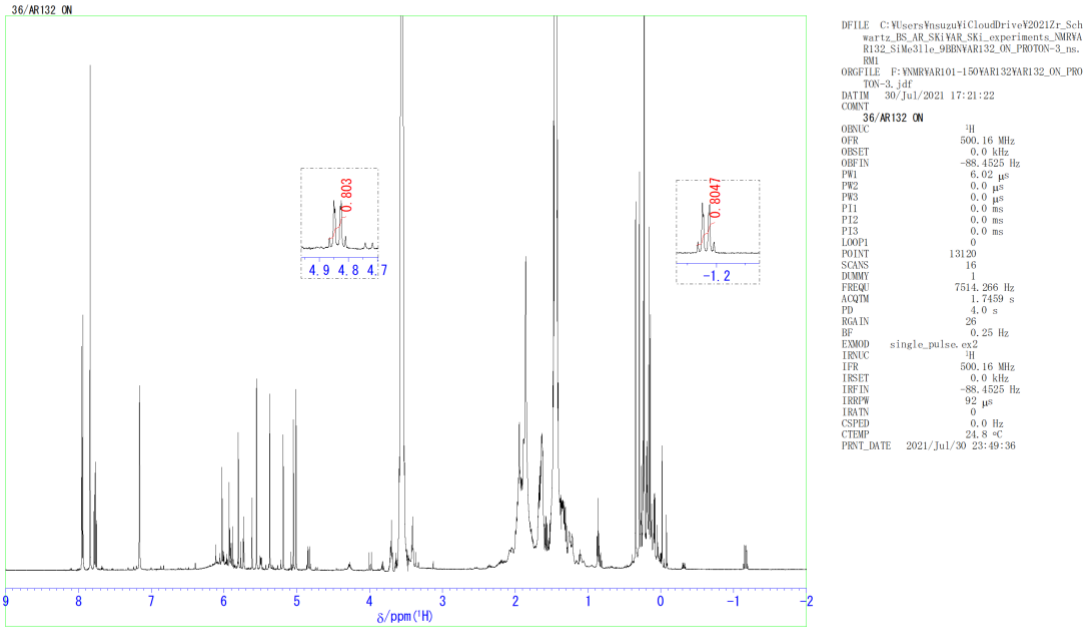


*2.14. The reaction of **2a** with 9-Borabicyclo[3.3.1]nonane (9-BBN).*

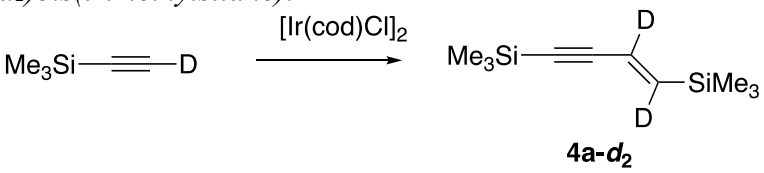


(AR132)

In a dry Schlenk tube, **2a** (135 mg, 0.323 mmol) was dissolved in THF (2 mL), and 9-borabicyclo[3. 3. 1]nonane dimer (118 mg, 0.485 mmol) was added. The mixture was stirred at 50 °C for 24 h. The orange solution was observed by ^{1}H NMR. Complex **5a** was produced in 32% yield.



2.15. Preparation of dideuterated enyne ***4a-d₂****; (E)-(but-1-en-3-yne-1,4-diyl-d₂)bis(trimethylsilane).*



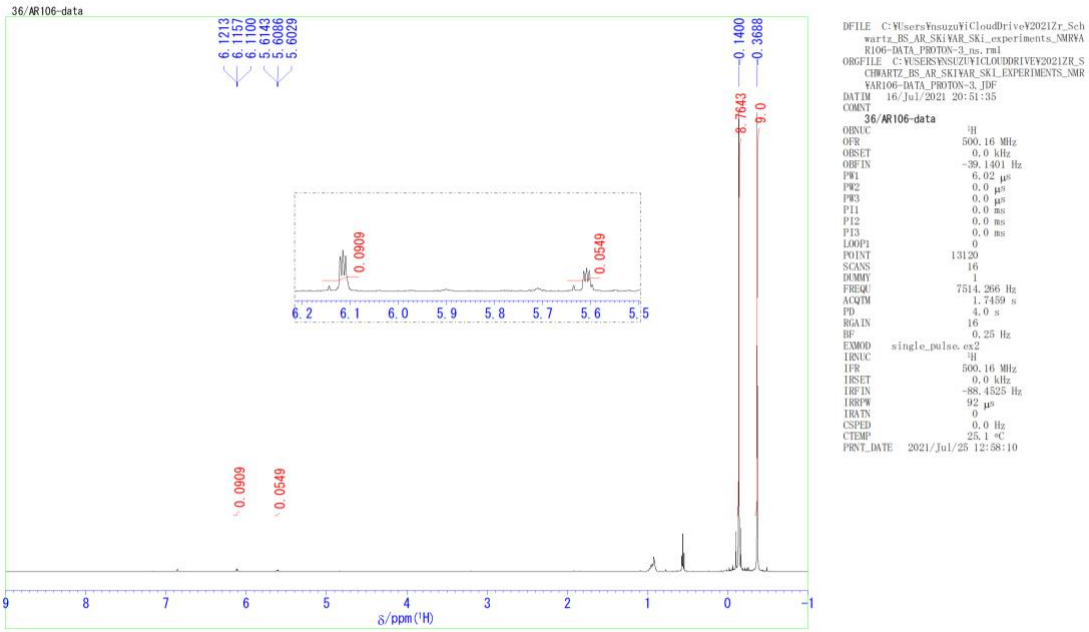
4a-*d*₂

A Schlenk tube was dried by heating under vacuum and filled with argon. In this tube trimehylsilylacetylene (1.96 g, 20.0 mmol) was dissolved in dry hexane (2.83 mL) and the solution was cooled at –78 °C. To this mixture, *n*-buryllithium (1.60 M in hexane, 13.8 mL, 22.0 mmol) was added dropwise over 20 min. The mixture was warmed to 0 °C and stirred at 0 °C for 30 min. The reaction mixture was again cooled at –78 °C and D_2O (4.0 g, 200 mmol) was added. The mixture was allowed to warm up to r.t., and stirred for 1 h. The reaction mixture was quenched with $_{dil}$HCl and the organic layer was dried over magnesium sulfate. The solution was filtered with glass filter and the obtained filtrate (12.8 mL) was used for the next reaction. The hexane solution of trimethylsilylacetylene-*d* was mixed with dry hexane (7 mL). To this solution was added $[Ir(cod)Cl]_2$ (48.4 mg, 0.072 mmol), triphenylphosphine (76 mg, 0.290 mmol) and triethylamine (1.21 g, 12.0 mmol), and the mixture was stirred at 50 °C for 6 h. [9] And then the volatiles were removed in vacuo and the residue was purified by column chromatograph on silica gel with hexane as an eluent. The title compound was obtained as brownish oil (1.00 g, 51% isolated, based on trimethylsilyl acetylene). Deuterium incorporation was determined by ^{1}H NMR (95%D at 1-position and 91%D at 2-position).

^{1}H NMR (C_6D_6, C_6D_5H = 7.16, 500 MHz): δ –0.37 (s, 9H, SiC*H*$_3$), –0.14 (s, 9H, SiC*H*$_3$), 5.61 (J_{DH} = 2.9 Hz, 0.05H, =C*H*C≡CSiMe$_3$), 6.12 (J_{DH} = 2.8 Hz, 0.09H, =C*H*SiMe$_3$).

^{13}C NMR (C_6D_6, C_6D_6 =128, 126 MHz): δ –1.73 (Si*C*H$_3$), 0.06 (Si*C*H$_3$), 94.78 (J_{CSi} = 84 Hz, =CDC≡*C*SiMe$_3$), 105.99 (=CD*C*≡CSiMe$_3$), 124.09 (J_{CD} = 25 Hz, =*C*DC≡CSiMe$_3$), 145.61 (J_{CD} = 21 Hz, =*C*HSiMe$_3$).

$_1$H NMR



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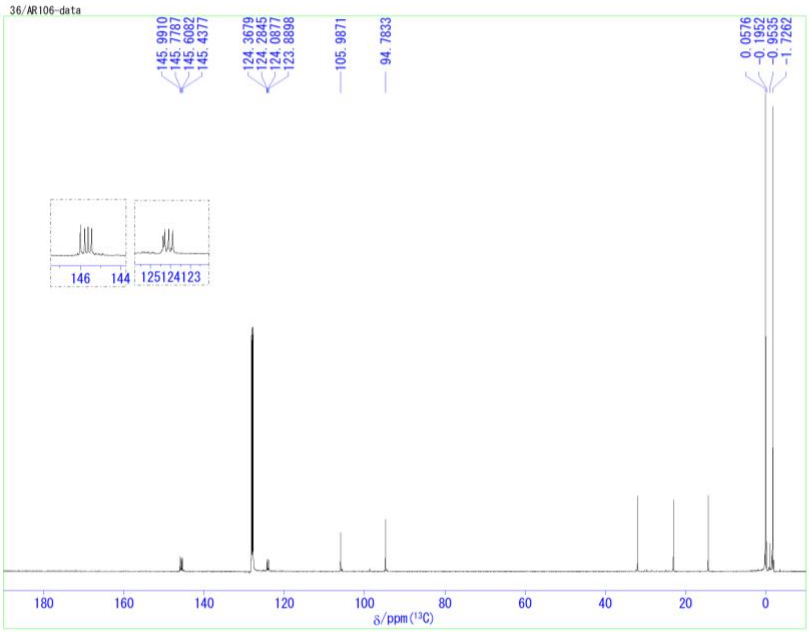
^{13}C NMR

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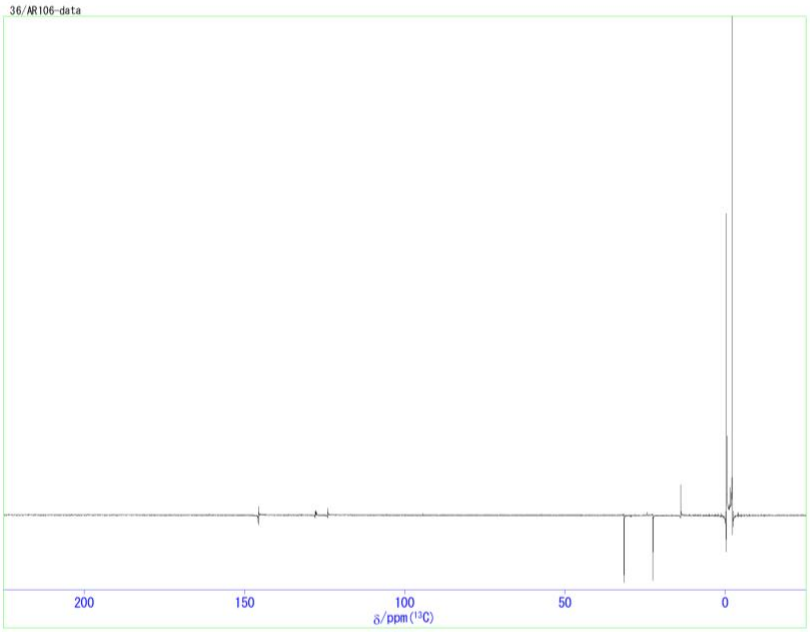
DEPT135

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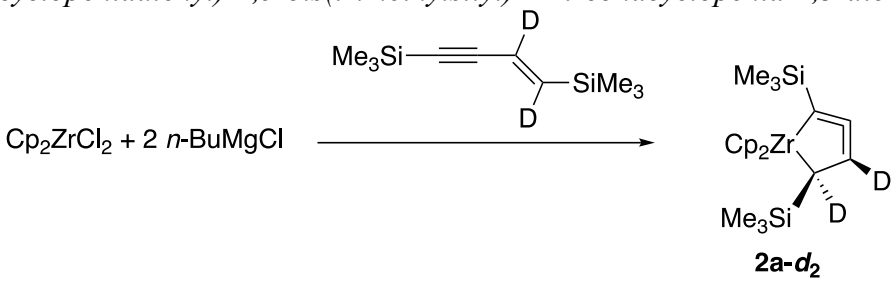
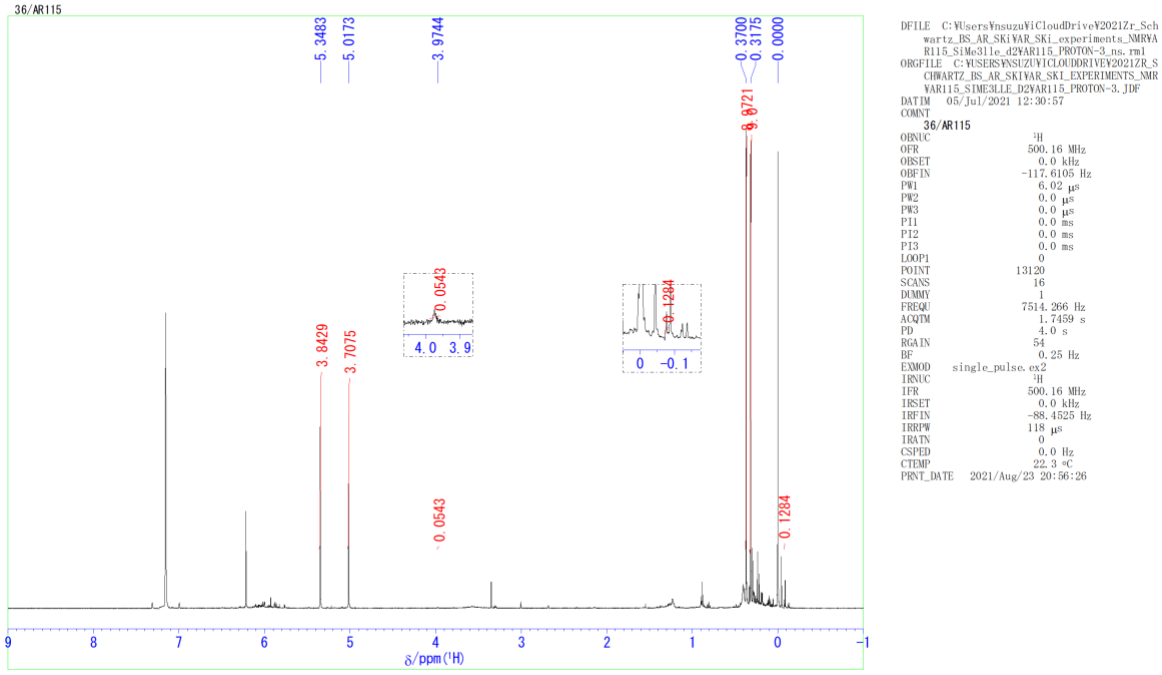
2.16. Preparation of deuterated cyclic allene complex with $SiMe_3$ ***2a-d₂****; 1,1-bis(η^5-cyclopentadienyl)-2,5-bis(trimethylsilyl)-1-zirconacyclopenta-2,3-diene-3,4-d₂.*



2a-*d*₂

The dideuterated **2a-*d*₂** was prepared according to the previously reported method for **2a** using **4a-*d*₂**.[4]



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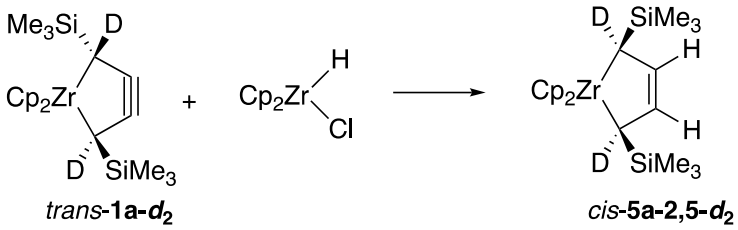
2.17. The reaction of trans-1,1-bis(η^5-cyclopentadienyl)-2,5-bis(trimethyhlsilyl)1-zirconacyclopent-3-yne-d_2 ***1a-d₂*** *with $Cp_2Zr(H)Cl$.*

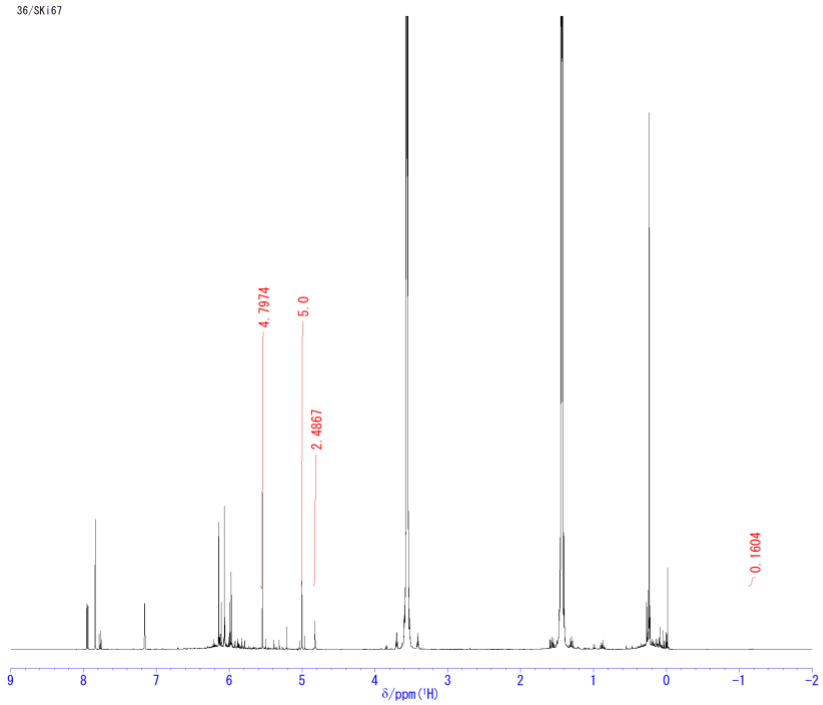


trans-**1a-d_2** *cis*-**5a-2,5-d_2**

In a thoroughly dried Schlenk tube, **1a-*d*₂** (84.2 mg, 0.2 mmol) was dissolved in THF (1 mL) and $Cp_2Zr(H)Cl$ (254 mg, 1.0 mmol) was added. The solution was stirred at 50 °C for 1 h, and C_6D_6 and pyrene (internal standard) were added to the dark brown solution. The solution was observed by NMR to confirm the formation of **5a-*d*₂** (56%). Deuterium incorporation at the 2,5-position was 93%, and the 3,4-position was ≤7%.

^{1}H NMR (THF/C_6D_6, Me_4Si, 500 MHz): δ –1.17 (m, 2H, C*H*, D = 93%), 0.24 (s, 18H, SiC*H*$_3$), 4.82 (m, 2H, C*H*, D ≤ 7%), 5.00 (s, Cp), 5.54 (s, Cp).

^{1}H NMR

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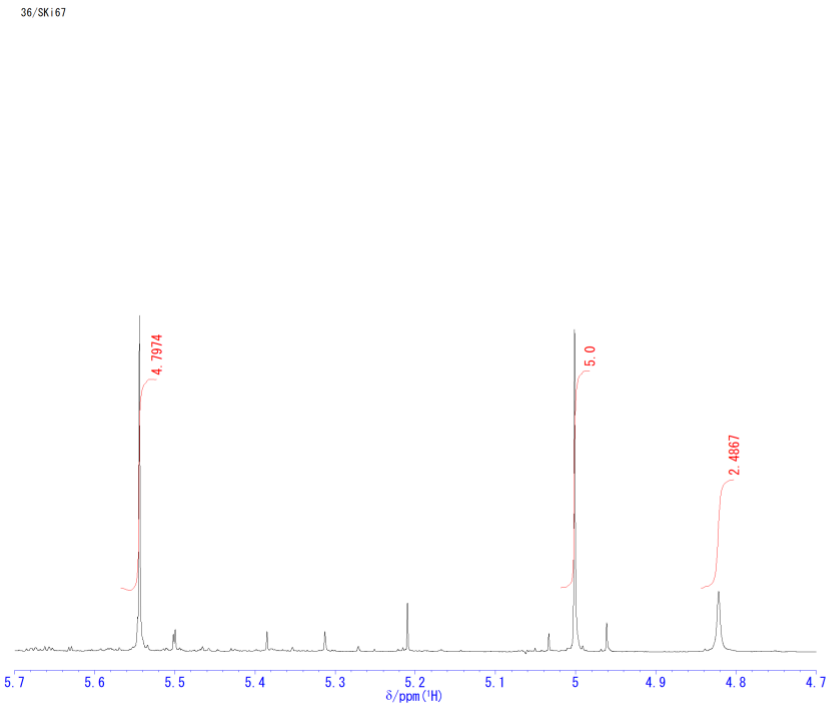
^{1}H NMR (enlarged)

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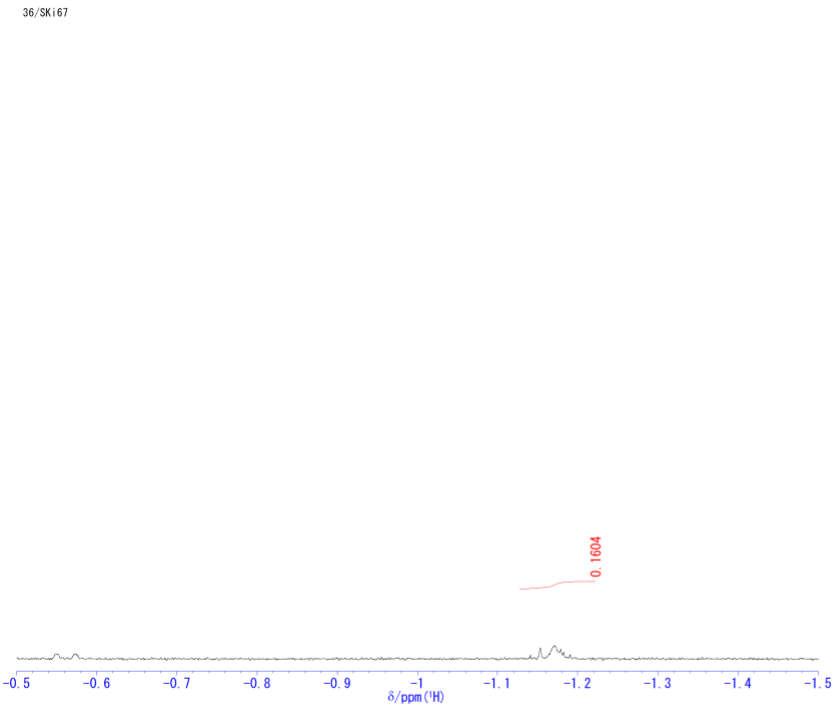
^{1}H NMR (enlarged)

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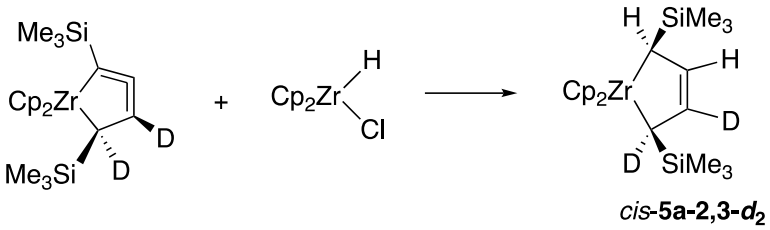
2.18. The reaction of trans-1,1-bis(η^5-cyclopentadienyl)-2,5-bis(trimethyhlsilyl)1-zirconacyclopenta-2,3-diene ***2a*** *with $Cp_2Zr(H)Cl$.*

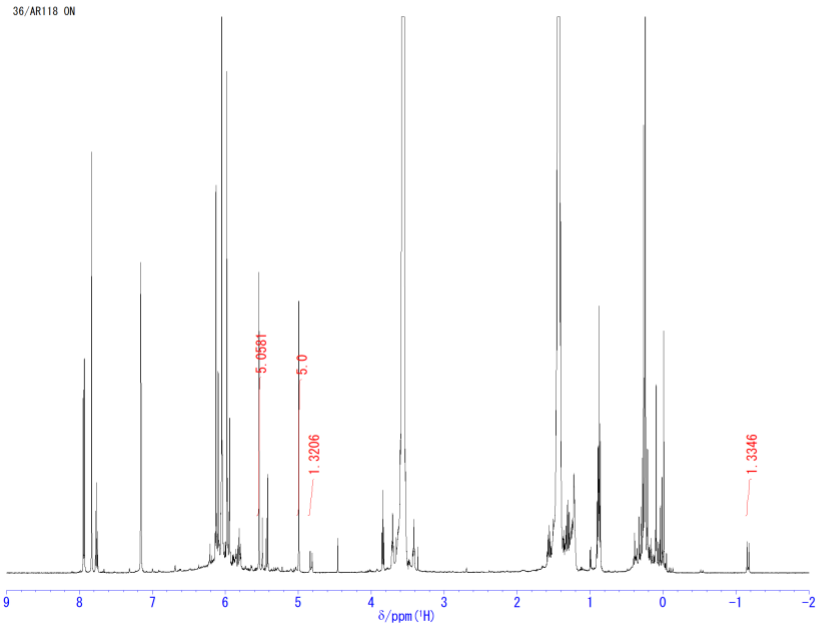


cis-**5a-2,3-d_2**

In a dry Schlenk tube, compound **2a-d_2** (135 mg, 0.321 mmol) was dissolved in THF (2 mL) and $Cp_2Zr(H)Cl$ (331 mg, 1.28 mmol) was added to this solution. The solution was stirred at 50°C for 24 h and the solution was observed by ^{1}H NMR. C_6D_6 and pyrene as internal standard were added to the solution and the mixture was observed by ^{1}H NMR. Formation of **5a-d_2** was confirmed (83%). Deuterium incorporation at the 2,5-position was 42%, and the 3,4-position was 44%.

^{1}H NMR (THF/C_6D_6, Me_4Si, 500 MHz): δ –1.16 (d, *J* = 14 Hz, 2H, C*H*, D = 42%), 0.24 (s, 18H, SiCH_3), 4.81 (d, *J* = 14 Hz, 2H, C*H*, D = 44%), 4.99 (s, Cp), 5.53 (s, Cp).

^{1}H NMR



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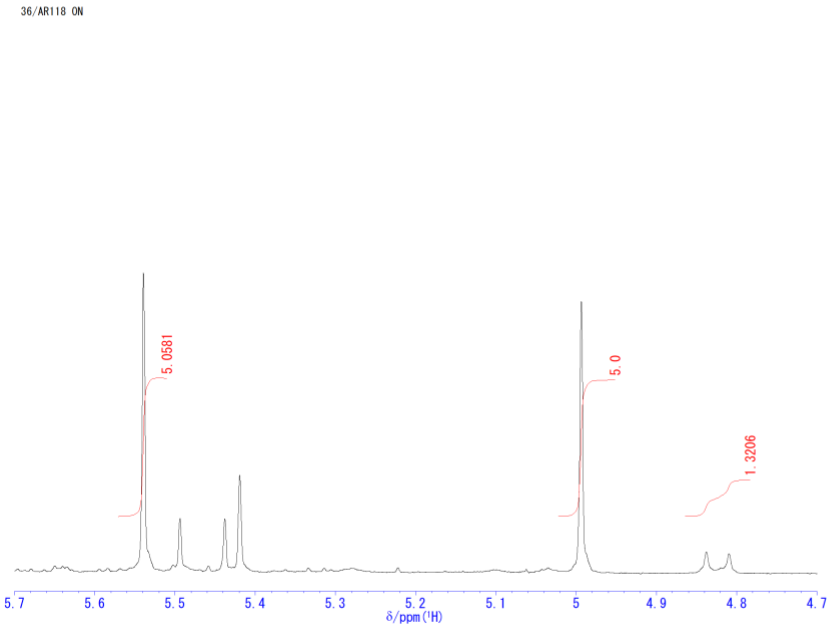
PRNT_DATE 2021/Jul/16 16:52:42

^{1}H NMR (enlarged)

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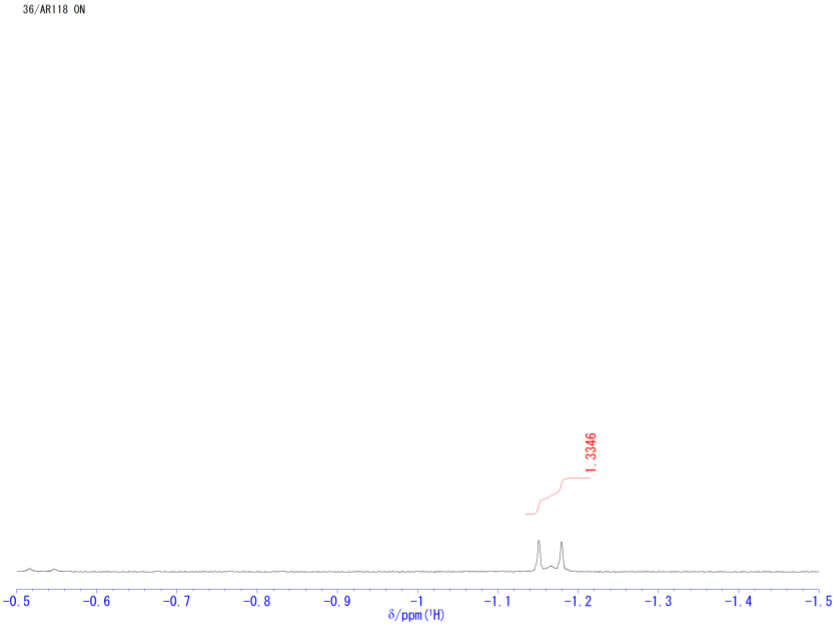
^{1}H NMR (enlarged)

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PRNT_DATE   2021/Jul/16 16:53:38
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2.19. X-ray diffraction analysis of 1,1-bis(η^5-cyclopentadienyl)-2-triethylsilyl-5-trimethylsilyl-1-zirconacyclopenta-2,3-diene ***2e***

Crystals were obtained from a hexane solution by cooling at -30 °C. A yellow platelet crystal (0.13 × 0.06 × 0.03 mm) was mounted on a polyimide film, MicroMounts™ (MiTegen), and coated with paraffin. All measurements were made on a Rigaku XtaLAB Synergy-S diffractometer using multi-layer mirror monochromated Cu-*Kα* radiation at 213K. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction). [15] The structure was solved by direct methods[16] and expanded using Fourier techniques. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 4554 observed reflections and 235 variable parameters. The analysis results were not very satisfactory because of disordered triethyl groups, although it was good enough to identify the molecule. All calculations were performed using the CrystalStructure[17] crystallographic software package except for refinement, which was performed using SHELXL97.[18] Crystallographic data are summarized in table S1. CIF data were deposited in Cambridge Structural Database (CCDC- 2104685).

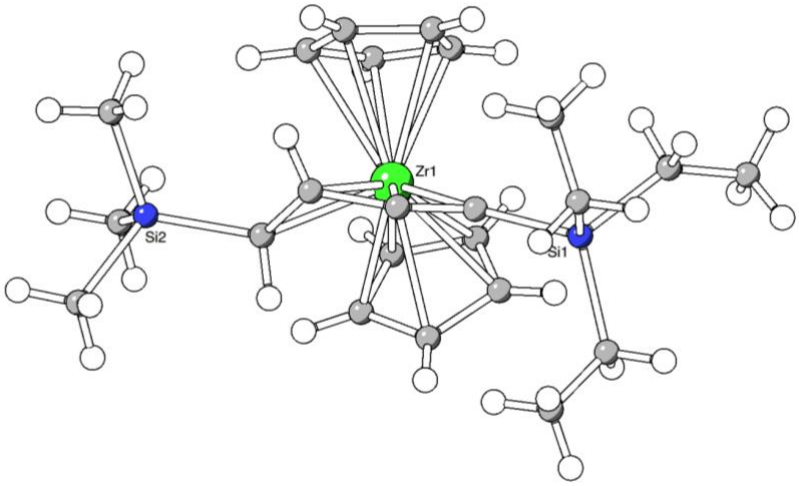

Figure S1. Molecular structure of **2e**.

2.20. X-ray diffraction analysis of 1,1-bis(η^5-cyclopentadienyl)-2,5-bis(trimethylsilyl)-1-zirconacyclopent-3-ene ***5a***

Crystals were obtained from a hexane solution by cooling at -80 °C. An orange platelet crystal (0.07 × 0.03 × 0.02 mm) was mounted on a polyimide film, MicroMounts^{TM} (MiTegen), and coated with perfluoropolyalkylether. All measurements were made on a Rigaku XtaLAB Synergy-S diffractometer using multi-layer mirror monochromated Cu-*Kα* radiation at 123K. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction). [15] The structure was solved by direct methods[16] and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the carbon atoms in the disordered cyclopentadienyl group and the hexane solvent were refined isotropically. Hydrogen atoms were refined using the riding model, and some hydrogen atoms on the disordered carbon atoms were omitted. The final cycle of full-matrix least-squares refinement on F^2 was based on 4279 observed reflections and 260 variable parameters. The unit cell contained two crystallographically independent molecules and one hexane molecule. Each molecule of **5e** was analyzed as a half molecule and expanded. One of the cyclopentadienyl groups was disordered. Analysis results were not very satisfactory because of the disordered cyclopentadienyl groups, although it was good enough to identify the molecule. CheckCIF raised Alert A and B, and most of them were ascribed to the disordered structure. All calculations were performed using the CrystalStructure[17] crystallographic software package except for refinement, which was performed using SHELXL97.[18] Crystallographic data are summarized in table S1. CIF data were deposited in Cambridge Structural Database (CCDC- 2110240).

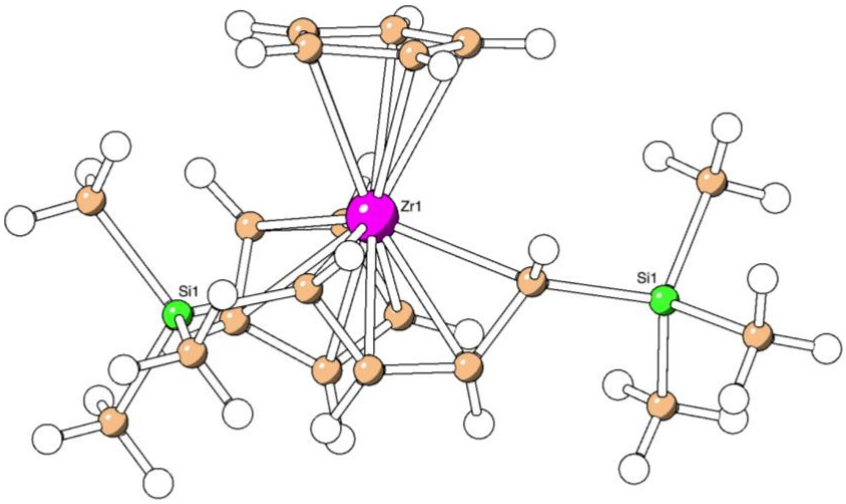

Figure S1. Molecular structure of **5a**.

Table S1. Crystal data and structure refinement for **2e** and **5a**.

	2e	**5a**
Empirical Formula	$C_{23}H_{36}Si_2Zr$	$C_{20}H_{32}Si_2Zr \bullet 0.5C_6H_{14}$
Formula Weight	459.93	462.96
Crystal Color, Habit	yellow, platelet	orange, platelet
Crystal Dimensions	0.13 × 0.06 × 0.03 mm	0.07 × 0.03 × 0.02 mm
Crystal System	monoclinic	orthorhombic
Lattice Type	Primitive	Primitive
Space Group	$P2_1/n$ (#14)	Pbcm (#57)
Lattice Parameters	a = 7.55776(9) Å b = 23.9500(6) Å c = 13.75372(17) Å V = 2488.59(8) Å^3	a = 13.37714(16) Å b = 15.7203(2) Å c = 23.1966(4) Å V = 4878.07(12) Å^3
Z value	4	8
Absorption coefficient	46.752 cm^{-1}	47.696 cm^{-1}
Radiation	CuKα (λ = 1.54187 Å) multi-layer mirror monochromated	CuKα (λ = 1.54187 Å) multi-layer mirror monochromated
Temperature	213 K	123 K
No. of Reflections Measured	Total: 33855 Unique: 4571 (R_{int} = 0.0585)	Total: 59269 Unique: 4279 (R_{int} = 0.0563)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.358 – 0.869)	Lorentz-polarization Absorption (trans. factors: 0.601 – 0.909)
No. of Reflections	4571	4279
No. Variables	229	260
Reflection/Parameter Ratio	19.96	16.46
Residuals: R; wR (All data)	0.0833; 0.2341	0.0766; 0.1669
Residuals: R_1	0.0789	0.0707
No. of Reflections to calc R_1	4135	3847
Goodness of Fit Indicator	1.064	1.046
Max Shift/Error in Final Cycle	0.022	0.003
Maximum peak in Final Diff. Map (e Å^3)	1.51	2.21
Minimum peak in Final Diff. Map (e Å^3)	–0.79	–1.13
CCDC#	2104685	2110240

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