Supporting Information for

Sulfur-containing stable five-membered "cycloallene" complexes: 1-thia-2-zircona- and 1-thia-2-titanacyclopenta-3,4-dienes

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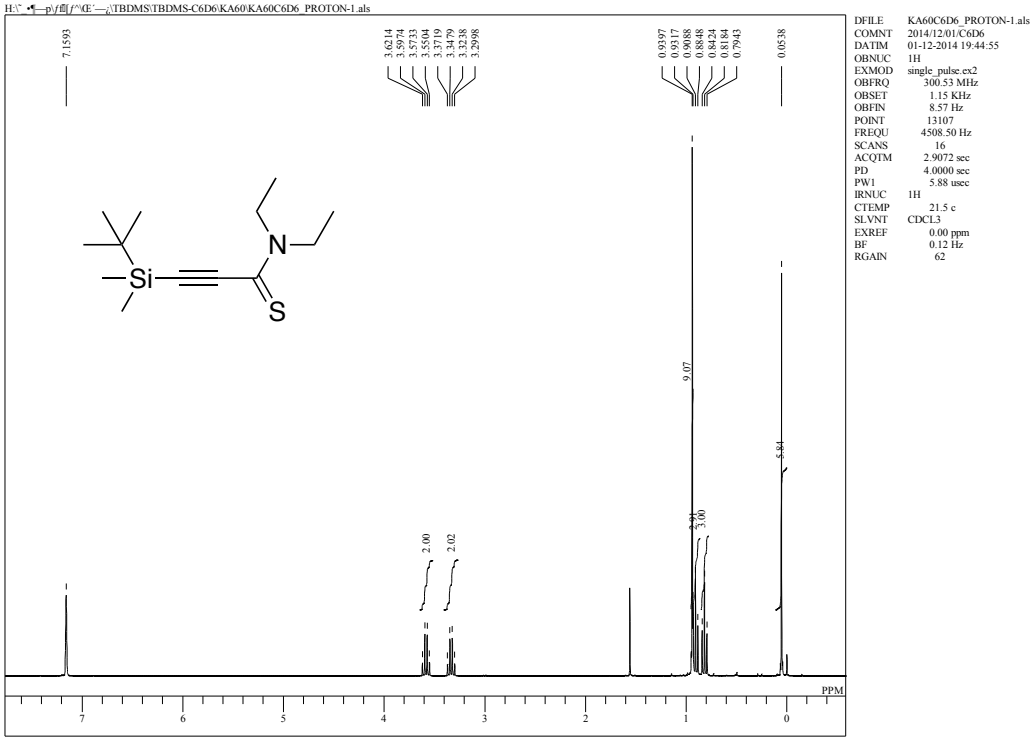
3-(*tert*-Butyldimethylsilyl)-*N*,*N*-diethylprop-2-ynethioamide (**4b**).

^{1}H NMR

2014/12/01/C6D6



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PD 4.0000 sec
PW1 5.88 usec
IRNUC 1H
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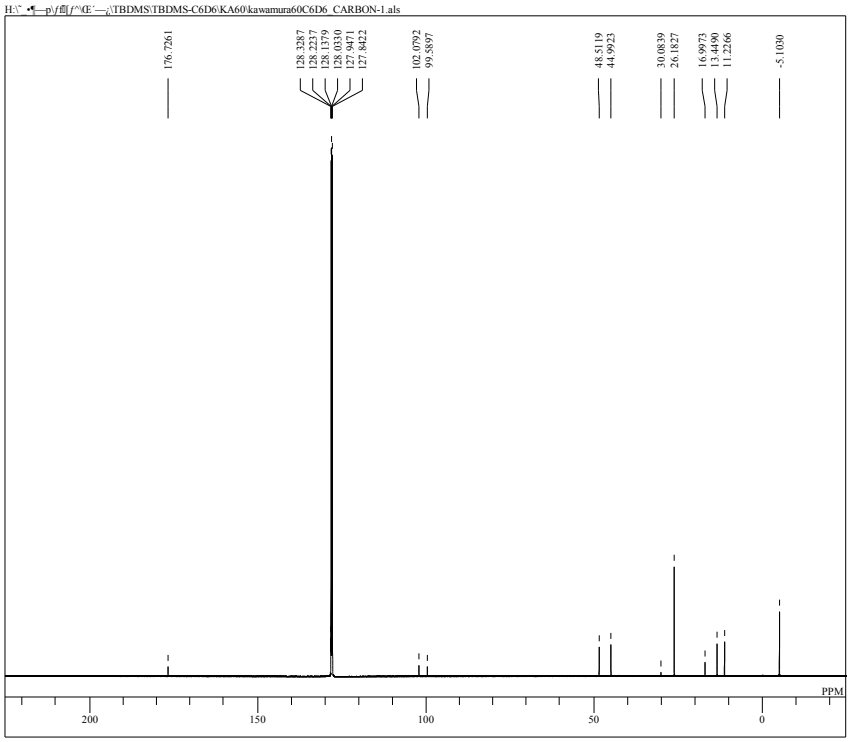
BF 0.12 Hz
RGAIN 62

^{13}C NMR

36/kawamura60C6D6



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POINT 26214
FREQU 31446.06 Hz
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PW1 3.67 usec
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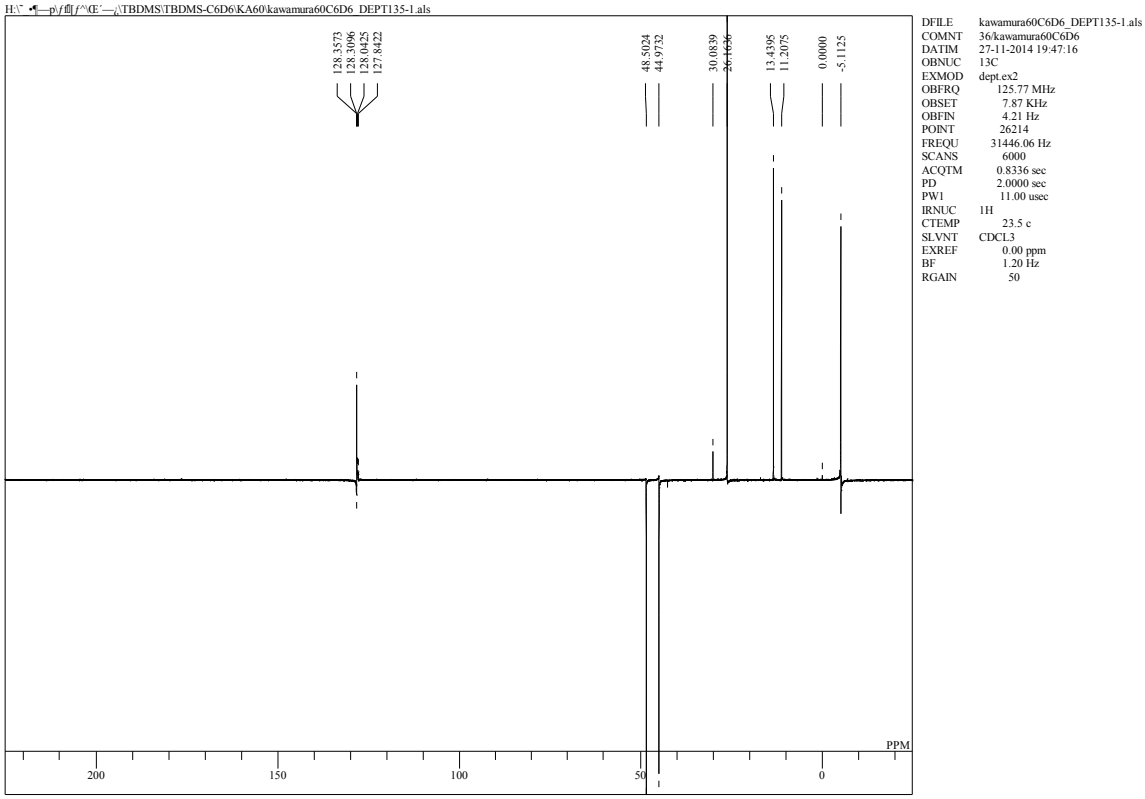
DEPT

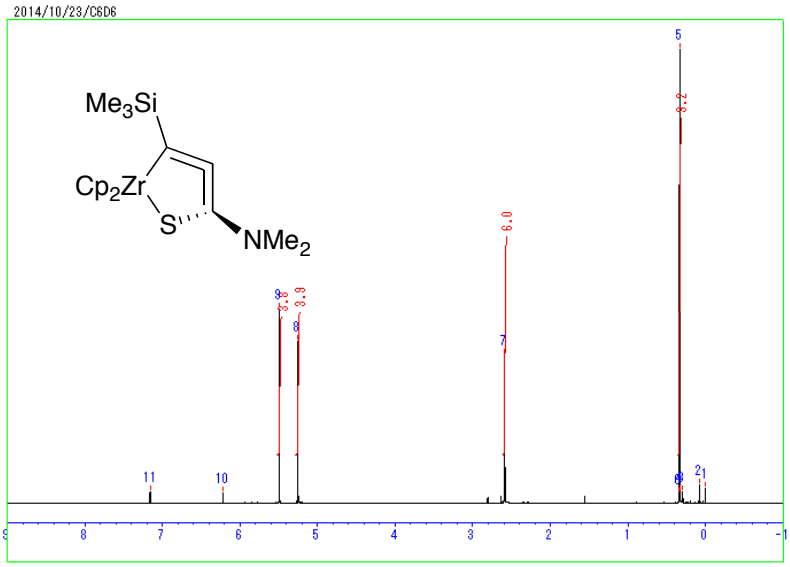
36/kawamura60C6D6



2,2-Bis(η^5-cyclopentadienyl)-3-trimethylsilyl-5-dimethylamino-1-thia-2-zirconacyclopenta-3,4-diene (5a).

^{1}H NMR

No.	δ/ppm	Height	No.	δ/ppm	Height
1	0.00	3.20	8	5.25	35.37
2	0.08	4.10	9	5.49	42.36
3	0.29	2.59	10	6.22	2.34
4	0.32	2.48	11	7.16	2.38
5	0.33	98.76			
6	0.35	2.08			
7	2.59	32.28			

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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                 16
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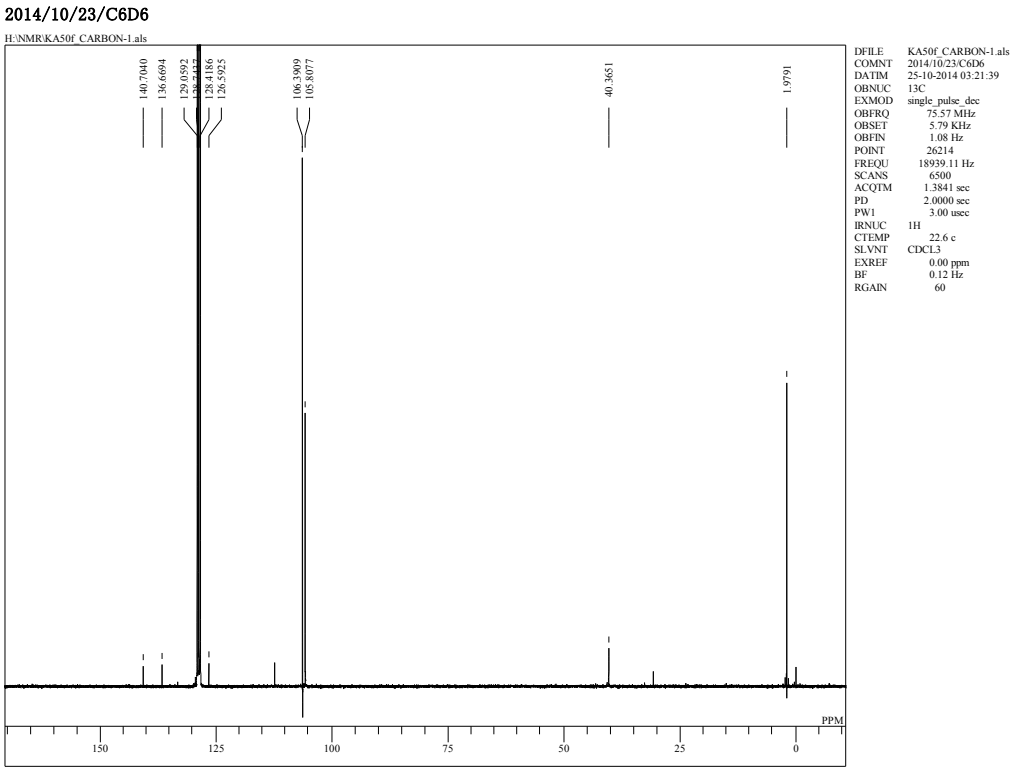
^{13}C NMR

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PD         2.0000 sec
PW1         3.00 usec
IRNUC     1H
CTEMP       22.6 c
SLVNT     CDCL3
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BF          0.12 Hz
RGAIN         60
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DEPT

2014/10/23/C6D6

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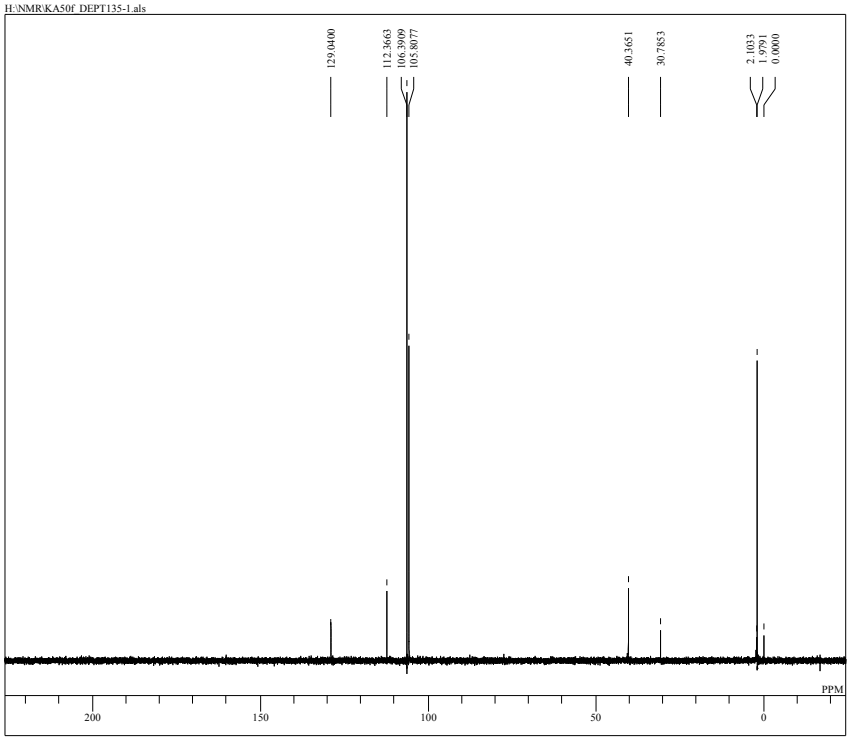


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SCANS        4500
ACQTM     1.3841 sec
PD        2.0000 sec
PW1          9.00 usec
IRNUC     1H
CTEMP       22.5 c
SLVNT     CDCL3
EXREF        0.00 ppm
BF           0.12 Hz
RGAIN        60
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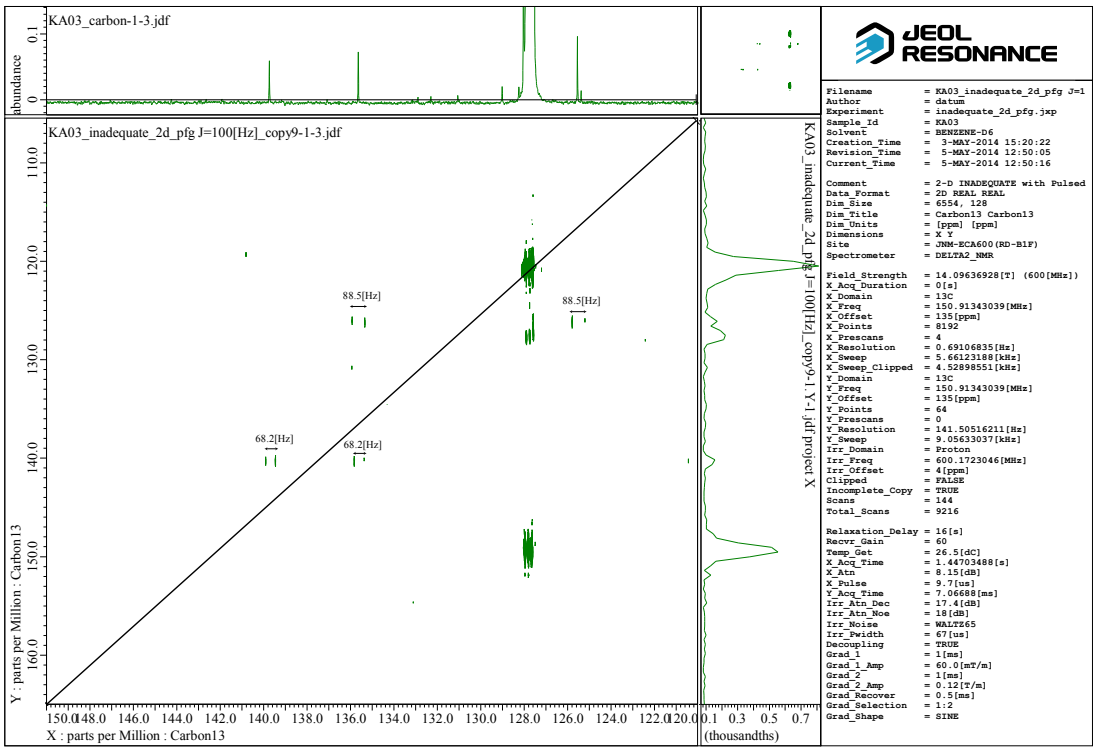
INADEQUATE

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Spectrometer      = DELTA2_NMR

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Irr_Offset        = 4[ppm]
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Grad_1_Amp        = 60.0[mT/m]
Grad_2            = 1[ms]
Grad_2_Amp        = 0.12[T/m]
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Grad_Shape        = SINE
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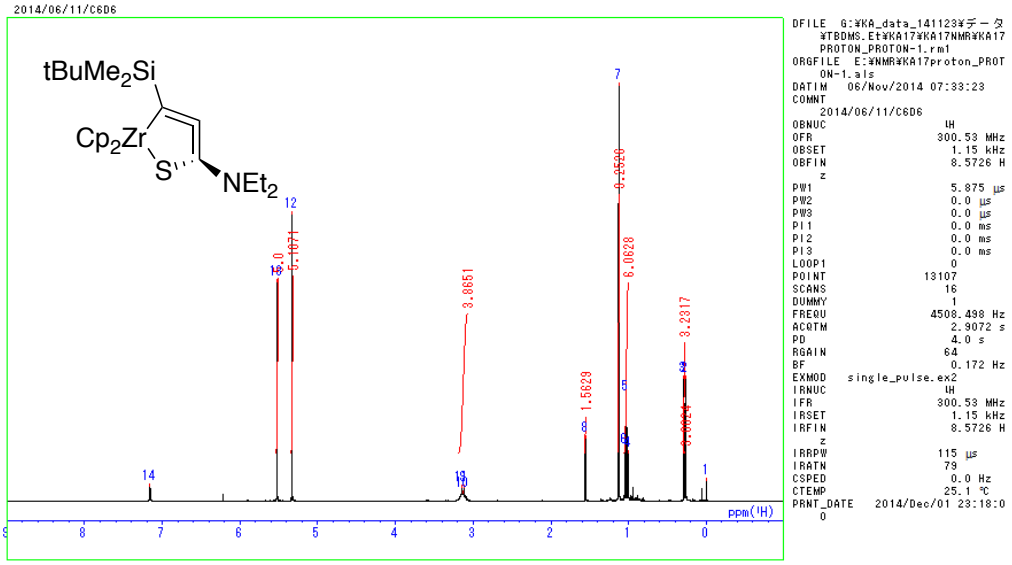
2,2-bis(η^5-cyclopentadienyl)-3-*tert*-butyldimethylsilyl-5-diethylamino-1-thia-2-zirconacyclo-penta-3,4-diene (5b)

^{1}H NMR

No.	δ/ppm	Height	No.	δ/ppm	Height
1	0.00	4.74	8	1.56	14.77
2	0.27	29.17	9	3.12	3.14
3	0.29	29.28	10	3.13	1.66
4	1.00	11.16	11	3.14	3.09
5	1.03	24.67	12	5.33	68.37
6	1.05	12.10	13	5.52	52.22
7	1.13	99.34	14	7.16	3.34

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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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PD                      4.0 s
RGAIN                   64
BF                      0.172 Hz
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IRSET                   1.15 kHz
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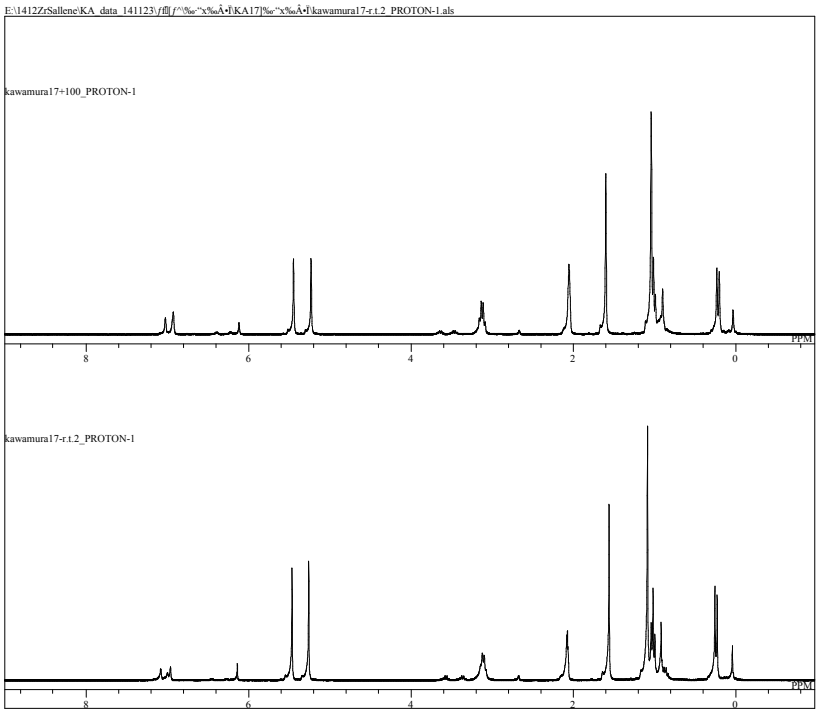
^{1}H NMR Spectra measured at 100 °C (top) and rt (bottom) in toluene-d_8.

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OBFIN     8.57 Hz
POINT     13107
FREQU     4508.50 Hz
SCANS     16
ACQTM     2.9072 sec
PD        4.0000 sec
PW1       5.88 usec
IRNUC     1H
CTEMP     24.1 c
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RGAIN     66
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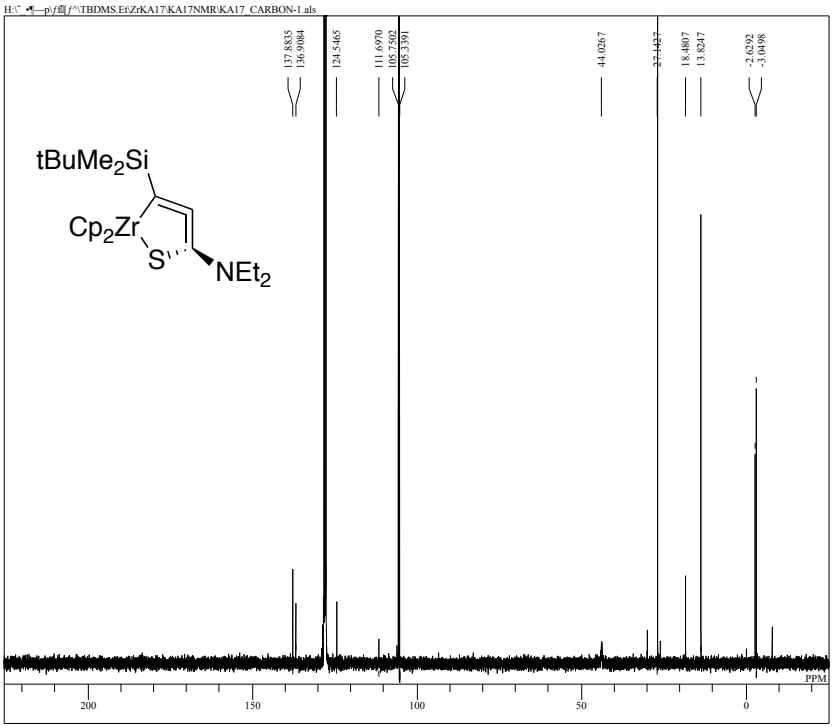
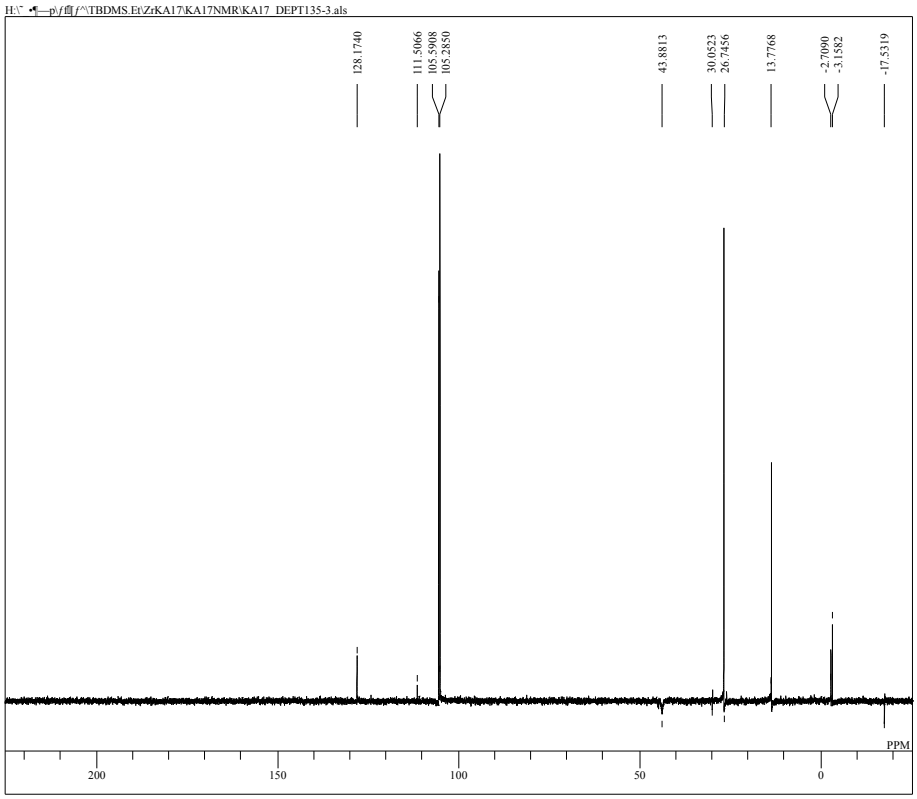
^{13}C NMR

2014/06/10/C6D6



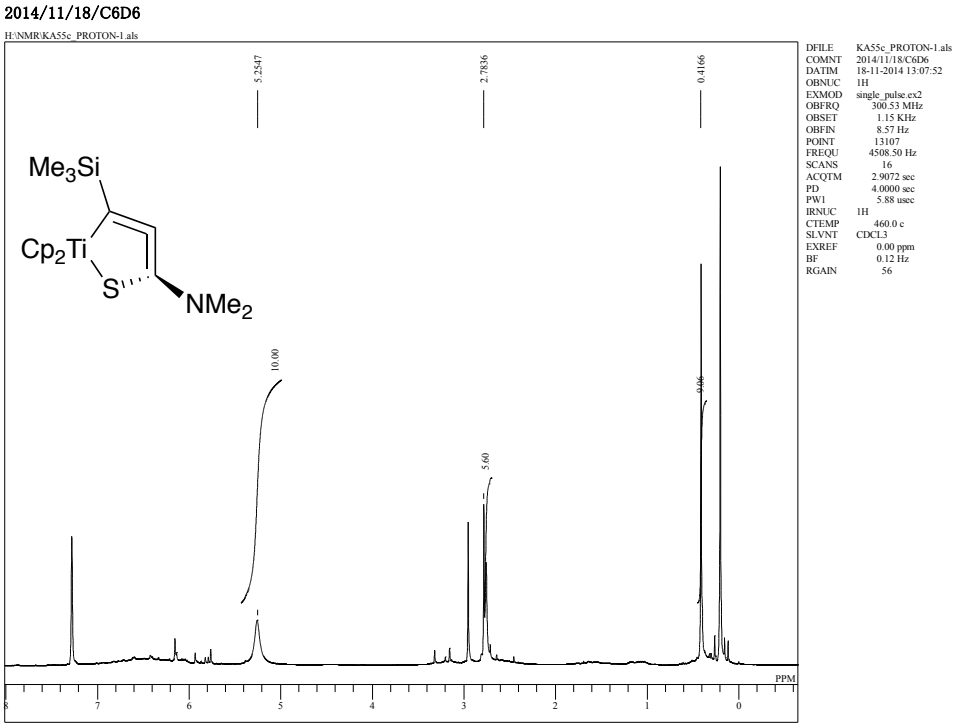
DEPT

2014/06/10/C6D6



2,2-Bis(η^5-cyclopentadienyl)-3-trimethylsilyl-5-dimethylamino-1-thia-2-titanacyclopenta-3,4-diene (6a).

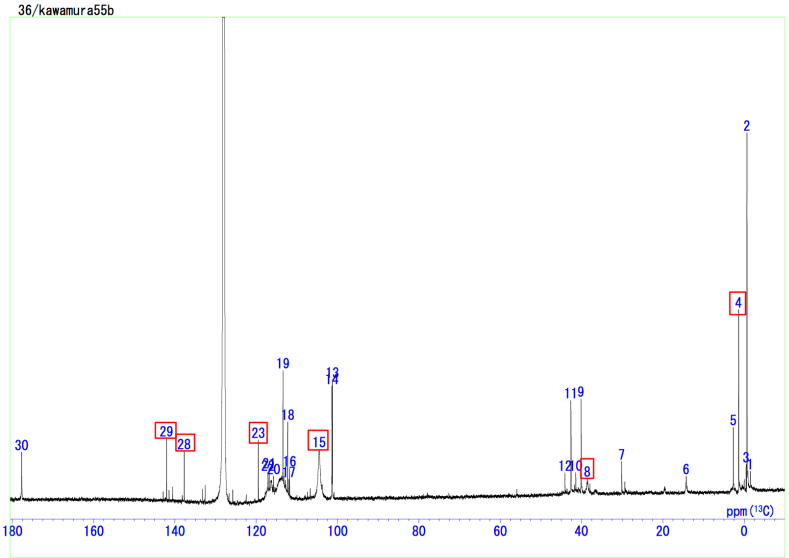
^{1}H NMR (rt)



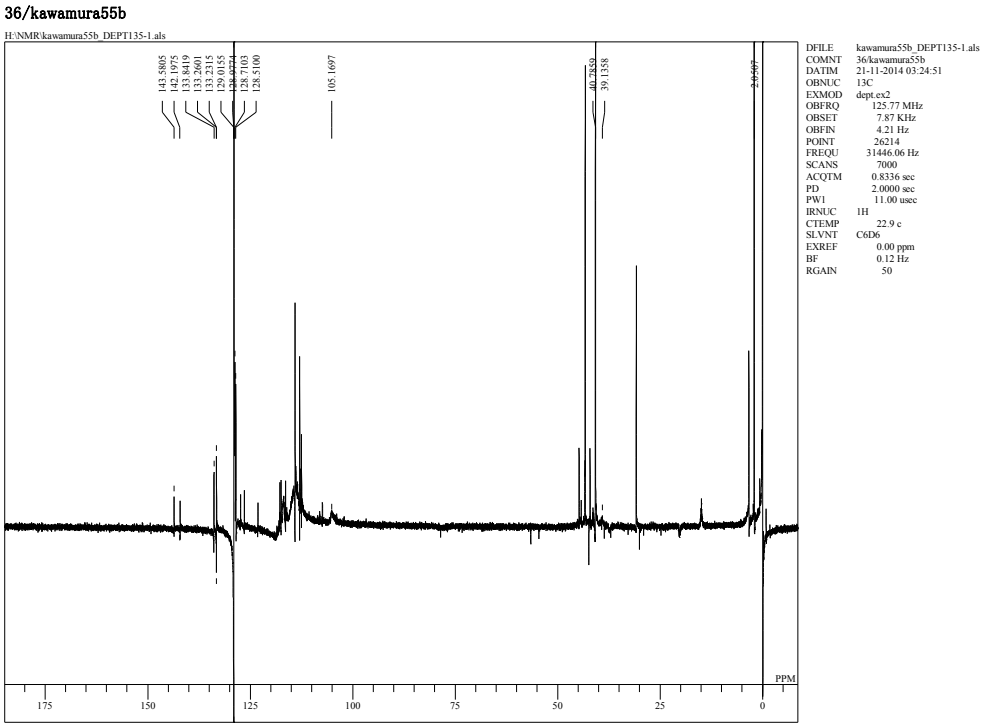
^{13}C NMR

The mixture contained unreacted starting materials (**4a**) and unidentified impurities. The signals for **6a** are indicated with red frames.

No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height	No.	δ/ppm	Height
1	-1.54	0.17	8	38.61	0.12	15	104.54	0.30	22	117.11	0.16	29	142.07	0.36
2	-0.67	2.20	9	40.13	0.80	16	111.82	0.19	23	119.49	0.35	30	177.69	0.28
3	-0.47	0.21	10	41.42	0.16	17	111.98	0.12	24	127.83	96.63			
4	1.37	1.14	11	42.63	0.59	18	112.27	0.46	25	128.03	97.68			
5	2.67	0.43	12	44.09	0.16	19	113.43	0.77	26	128.22	96.77			
6	14.26	0.14	13	101.27	0.72	20	115.74	0.14	27	128.31	4.85			
7	30.12	0.23	14	101.40	0.68	21	116.82	0.17	28	137.71	0.29			

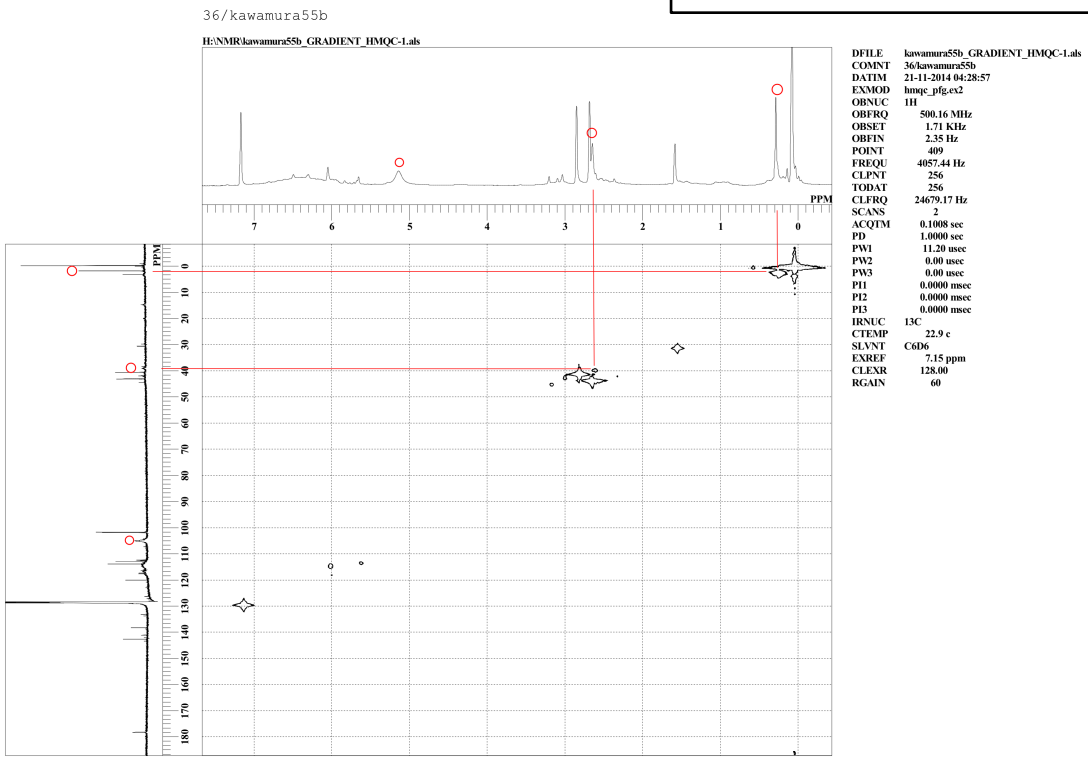


DEPT135



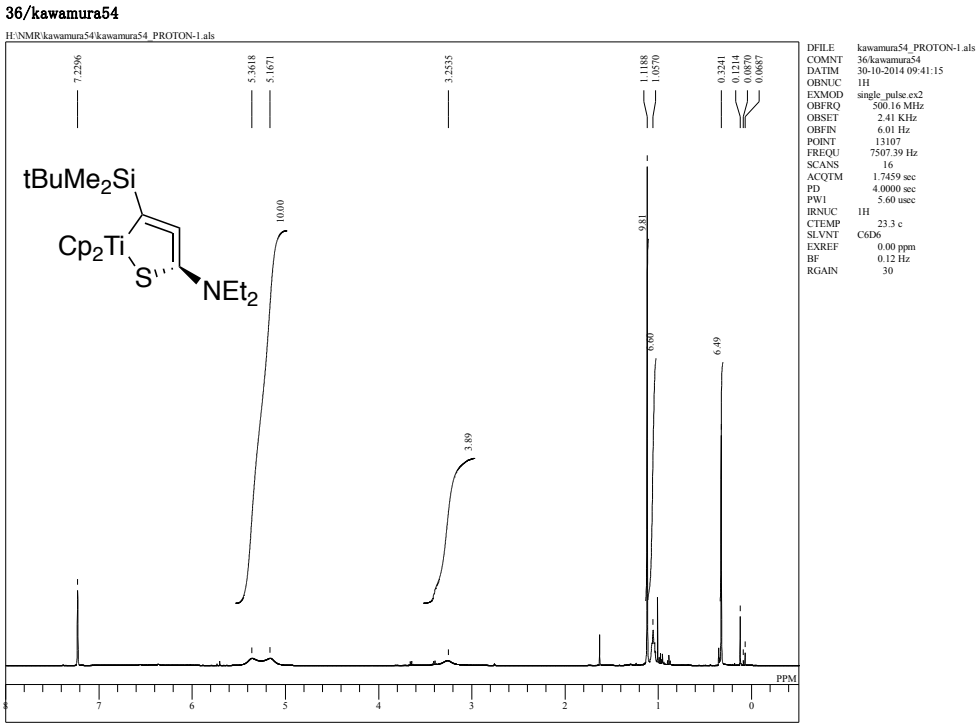
HMQC

The Correlation between ^{1}H and ^{13}C in Cp rings were not observed because of the broad signals by fast flipping movement of **6a**.



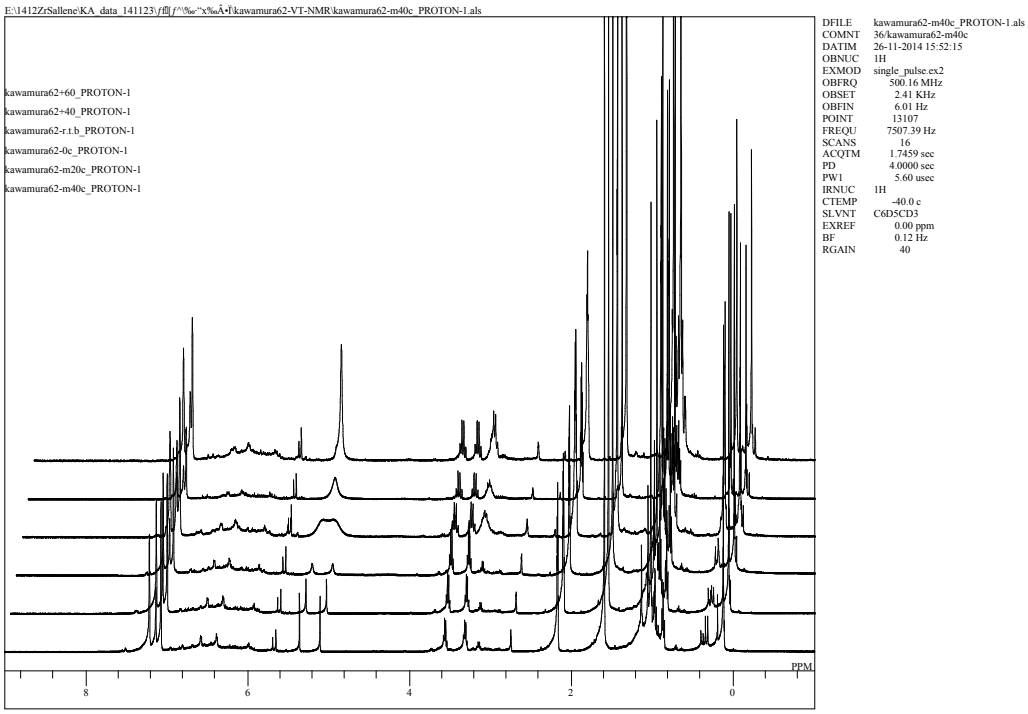
2,2-Bis(η^5-cyclopentadienyl)-3-*tert*-butyldimethylsilyl-5-diethylamino-1-thia-2-titanacyclopenta-3,4-diene (6b)

^{1}H NMR (room temperature)



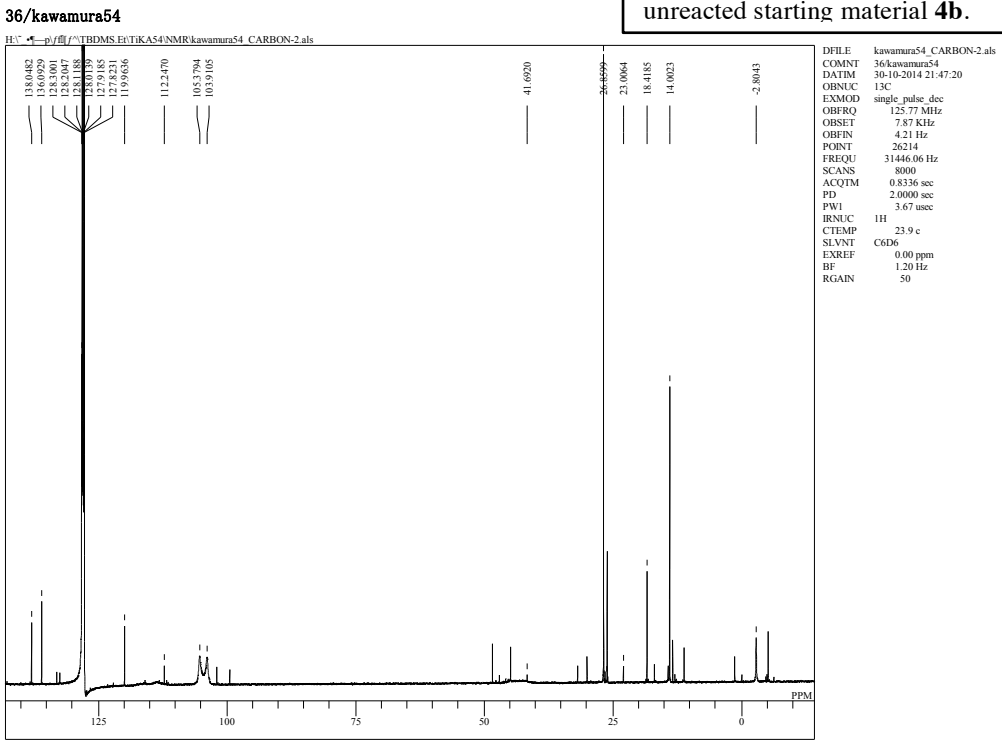
^{1}H NMR at variable temperature (–40 to 60 °C)

This sample contains considerable amount of unreacted starting material **4b**.

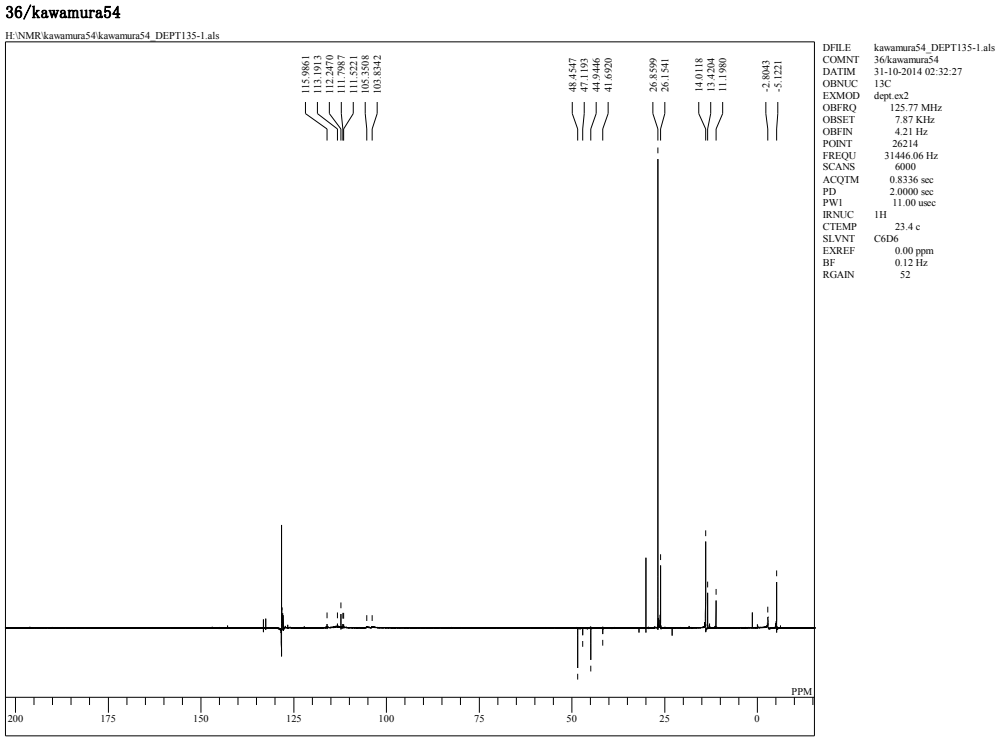


^{13}C NMR

This sample contains considerable amount of unreacted starting material **4b**.

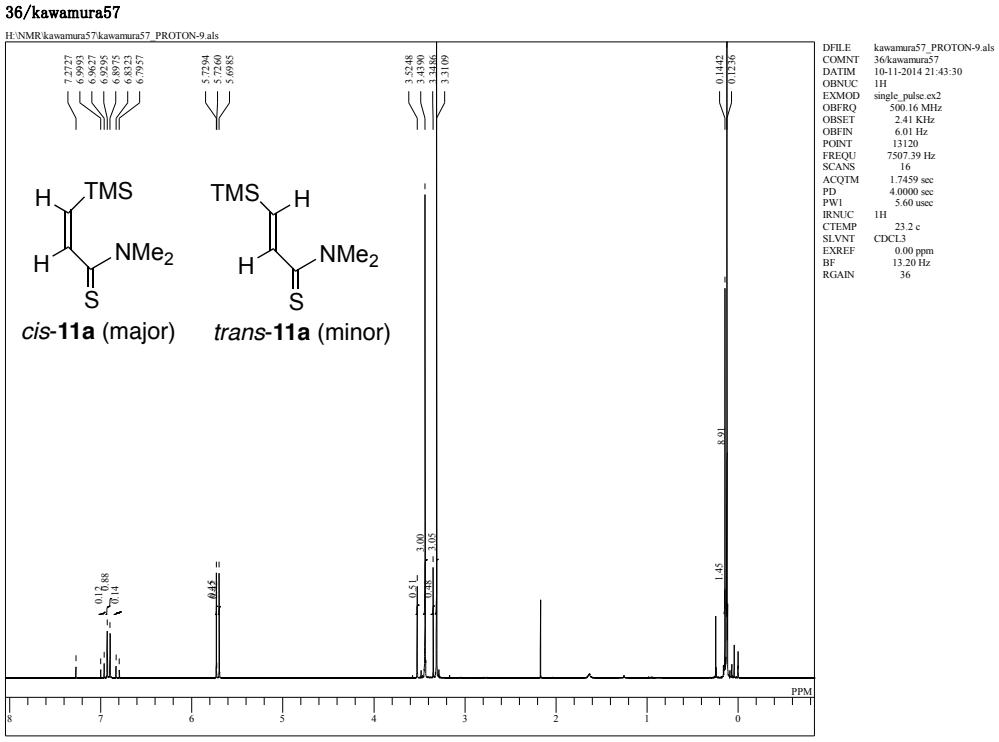


DEPT135



(*Z*)- and (*E*)-*N*,*N*-dimethyl-3-(trimethylsilyl)prop-2-enethioamide (11a) (a mixture)

^{1}H NMR



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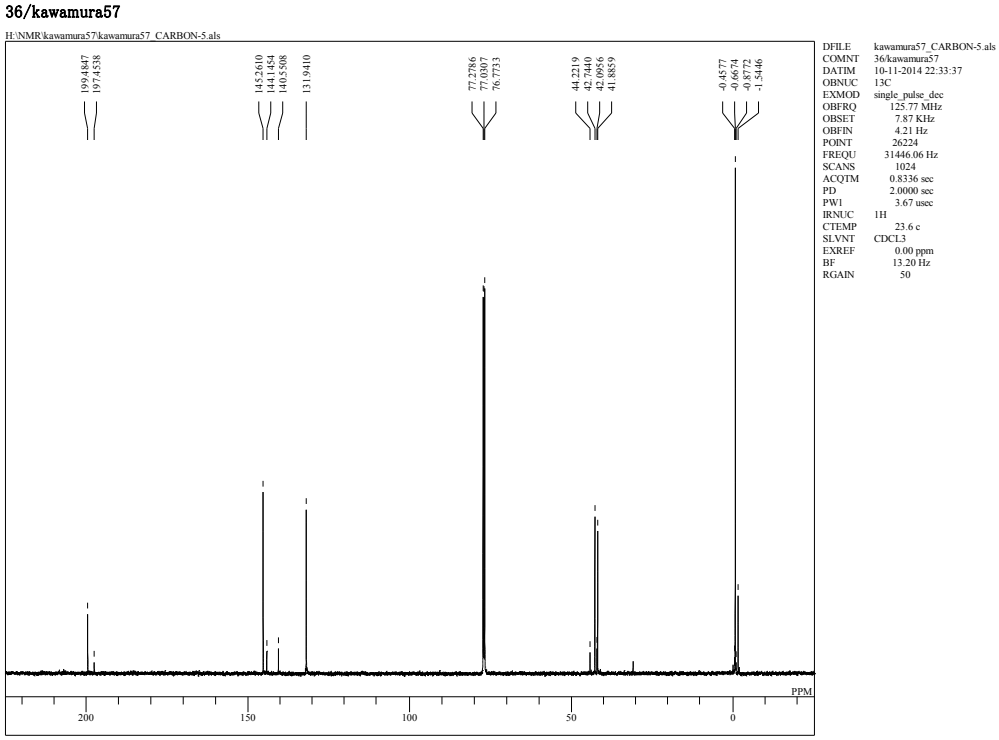
ACQTM 1.7459 sec
PD 4.0000 sec
PW1 5.60 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 13.20 Hz
RGAIN 36

^{13}C NMR



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OBFIN 4.21 Hz
POINT 26224
FREQU 31446.06 Hz
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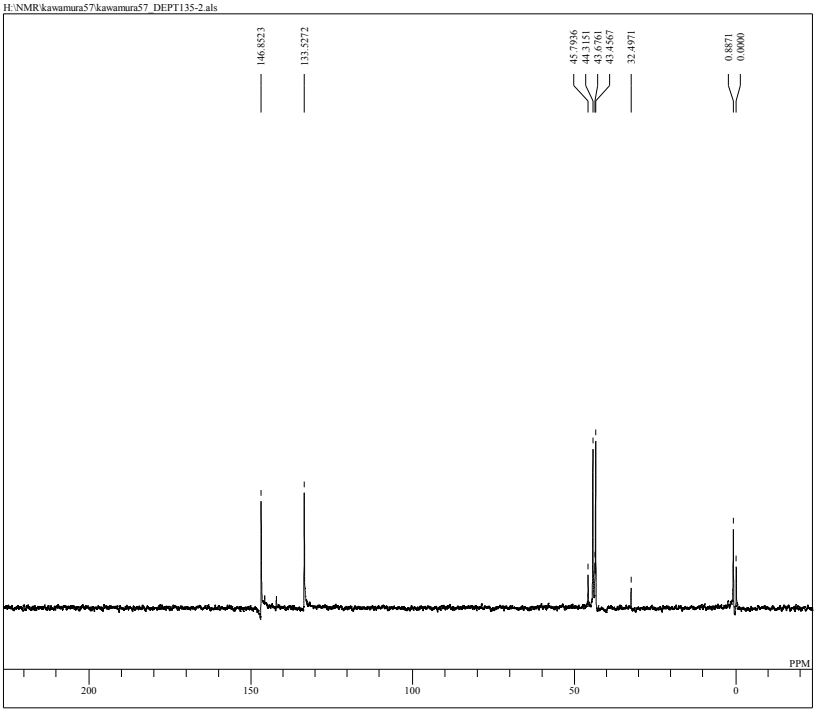
PD 2.0000 sec
PW1 3.67 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 13.20 Hz
RGAIN 50

DEPT135

36/kawamura57

H:\NMR\kawamura57\kawamura57_DEPT135-2.als



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OBFIN	4.21 Hz
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CTEMP	23.2 c
SLVNT	CDCL3
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RGAIN	54

HMQC

36/kawamura57

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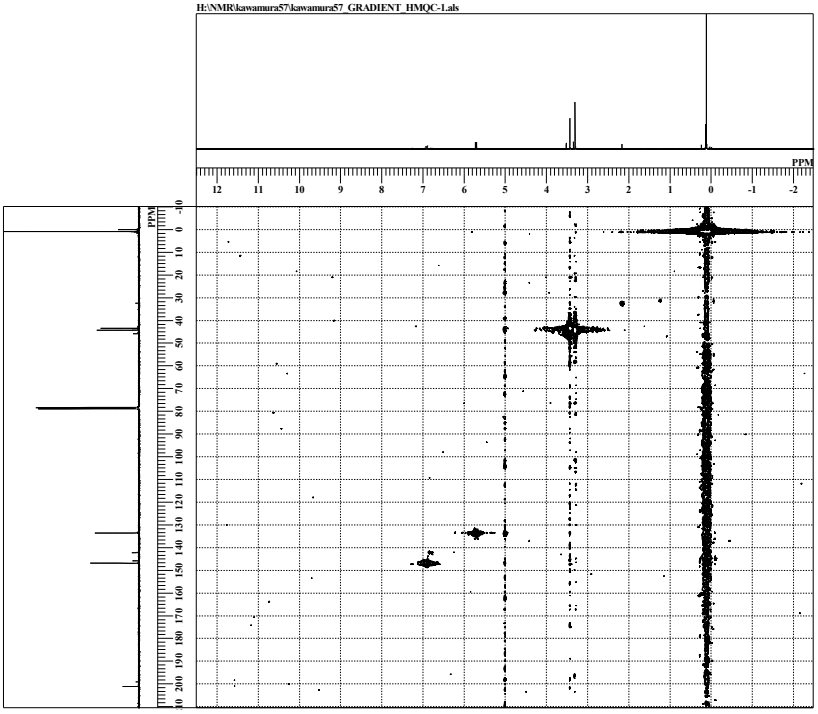

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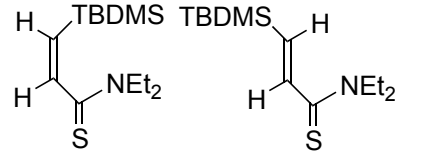
PW2	0.00 usec
PW3	0.00 usec
PI1	0.0000 msec
PI2	0.0000 msec
PI3	0.0000 msec
IRNUC	13C
CTEMP	23.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
CLEXR	0.00
RGAIN	60

(*Z*)- and (*E*)-*N*,*N*-diethyl-3-(*tert*-butylditrimethylsilyl)prop-2-enethioamide (11b) (a mixture)

^{1}H NMR



cis-**11b** (major) *trans*-**11b** (minor)

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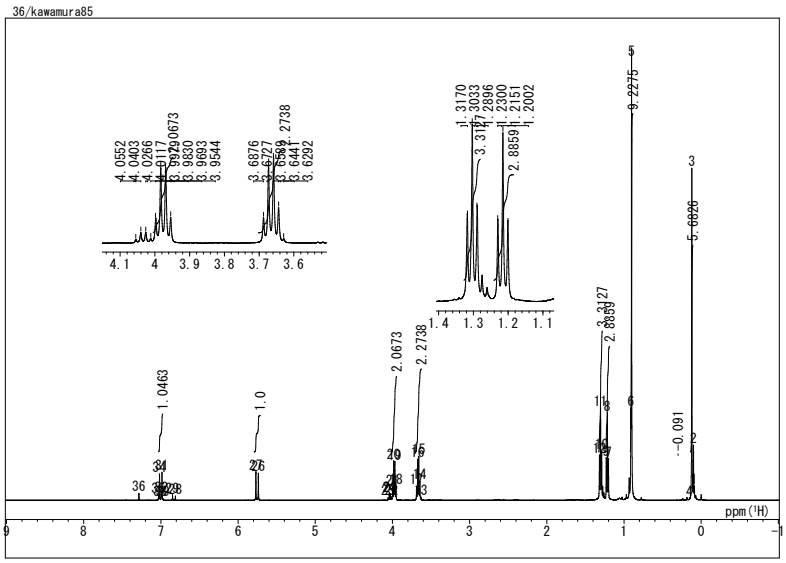
1	0.09	2.89	8	1.22	18.88	15	3.66	9.33	22	4.01	0.49	29	6.85	0.99	36	7.28	1.30
2	0.10	11.78	9	1.23	9.04	16	3.67	8.74	23	4.03	1.20	30	6.97	0.23			
3	0.12	72.26	10	1.29	10.44	17	3.69	2.82	24	4.04	1.17	31	6.99	5.87			
4	0.15	0.33	11	1.30	19.85	18	3.95	2.87	25	4.06	0.38	32	6.99	1.20			
5	0.90	96.27	12	1.32	9.57	19	3.97	8.19	26	5.74	5.66	33	7.01	0.30			
6	0.91	19.92	13	3.63	0.48	20	3.98	8.36	27	5.77	5.99	34	7.02	5.53			
7	1.20	8.74	14	3.64	3.96	21	4.00	2.71	28	6.81	0.66	35	7.03	0.83			

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^{13}C NMR with DEPT135

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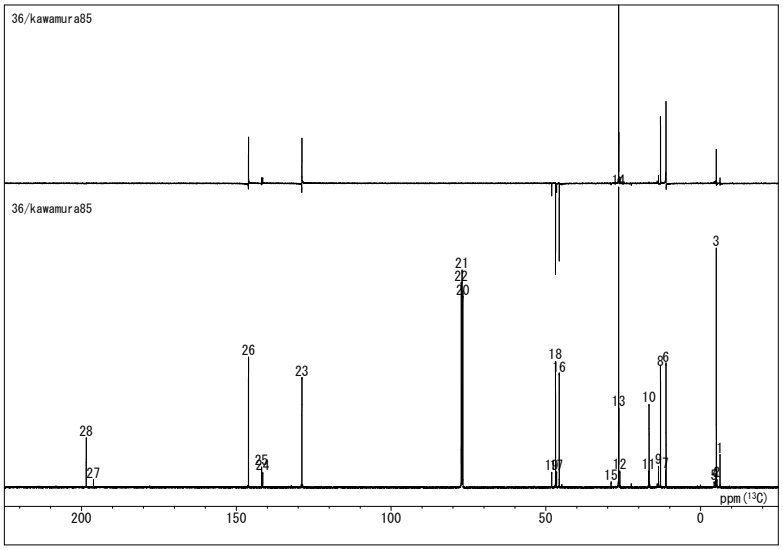
1	-6.27	6.86	8	12.97	25.87	15	28.94	0.93	22	77.34	44.37
2	-5.27	1.45	9	13.61	4.31	16	45.68	24.47	23	128.82	23.56
3	-5.06	51.93	10	16.66	17.82	17	46.54	3.13	24	141.47	2.97
4	-4.86	1.33	11	16.77	3.23	18	46.88	27.23	25	141.84	4.14
5	-4.38	0.94	12	26.10	3.28	19	48.12	2.98	26	146.07	28.13
6	11.18	26.56	13	26.45	17.01	20	76.82	41.35	27	196.14	1.38
7	11.35	3.44	14	26.50	88.07	21	77.08	47.16	28	198.48	10.54

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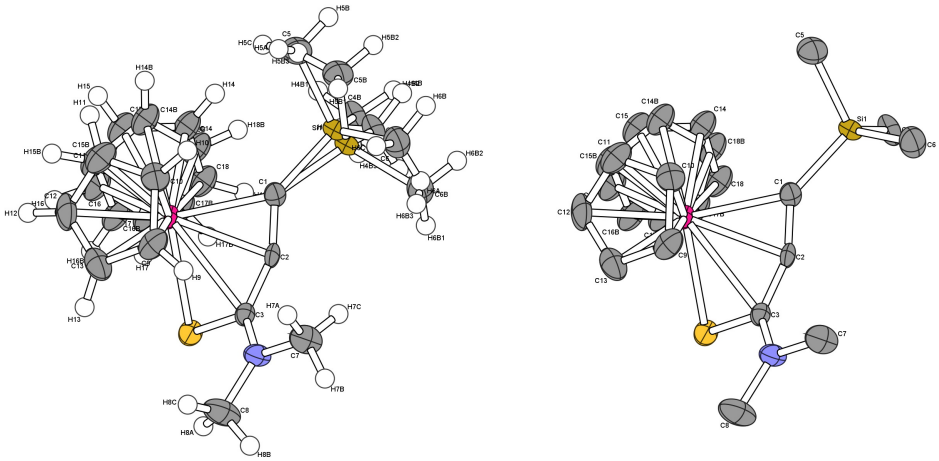
X-ray diffraction analyses of 2,2-bis(η^5-cyclopentadienyl)-3-trimethylsilyl-5-dimethylamino-1-thia-2-zirconacyclopenta-3,4-diene (5a).

Crystals were obtained from a hexane solution. An orange platelet crystal (0.3 × 0.2 × 0.05 mm) was mounted on a polyamide film (MicroMounts™, MiTegen), and coated with paraffin. All data were collected on a Rigaku Mercury 70 CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 153K. The structure was solved by direct methods[1] and expanded using Fourier techniques. Most non-hydrogen atoms were refined anisotropically, while two carbon atoms in the trimethylsilyl groups were refined isotropically without placing hydrogen atoms. The trimethylsilyl group was disordered over two positions with relative occupancy 0.503/0.497. One of the cyclopentadienyl groups was disordered over tow positions with relative occupancy 0.530/0.470. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 4167 observed reflections and 200 variable parameters. All calculations were performed using the CrystalStructure[2] crystallographic software package except for refinement, which was performed using SHELXL97.[3] Crystallographic data are summarized in table S. CIF data were deposited in Cambridge Structural Database (CCDC-1023319).

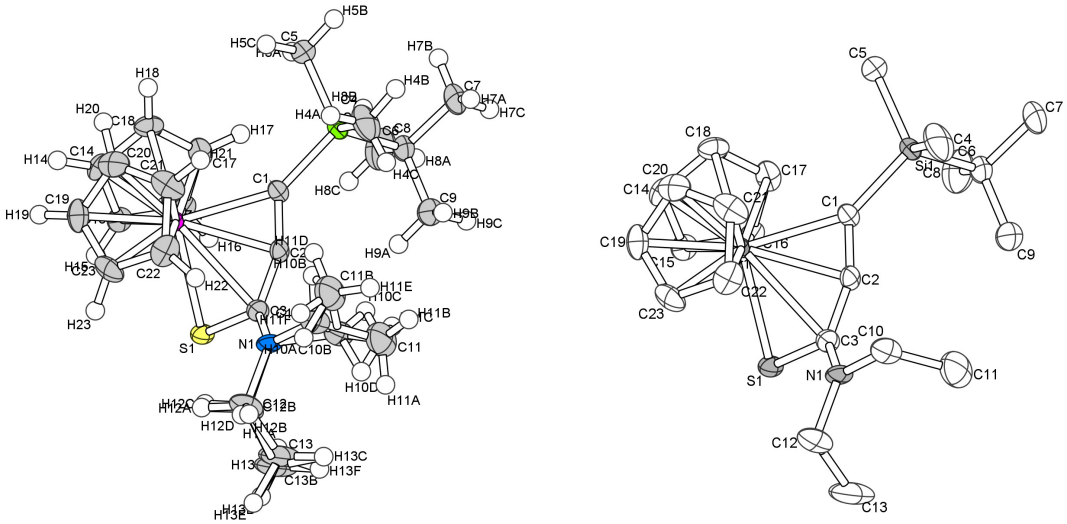


The molecular structure of **5a** (Left).

Hydrogen atoms and one position of disordered trimethylsilyl groups are omitted (Right).

X-ray diffraction analyses of 2,2-bis(η^5-cyclopentadienyl)-3-*tert*-butyldimethylsilyl-5-diethylamino-1-thia-2-zirconacyclopenta-3,4-diene (5b)

Crystals were obtained from a toluene solution. An orange platelet crystal (0.4 × 0.3 × 0.02 mm) was mounted on a polyamide film, MicroMounts™ (MiTegen), and coated with paraffin. All data were collected on a Rigaku Mercury 70 CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 153 K. The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The diethylamino group was disordered over two positions with relative occupancy 0.625/0.375. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 5501 observed reflections and 251 variable parameters. All calculations were performed using the CrystalStructure[2] crystallographic software except for refinement, which was performed using SHELXL97.[3] Crystallographic data are summarized in table S. CIF data were deposited in Cambridge Structural Database (CCDC-1023317).

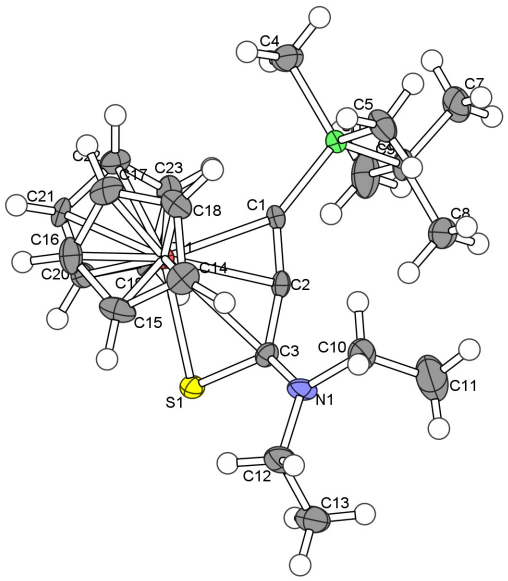


Molecular structure of **5b** (Left).

Hydrogen atoms and one position of disordered trimethylsilyl groups are omitted (Right).

X-ray diffraction analyses of 2,2-bis(η^5-cyclopentadienyl)-3-*tert*-butyldimethylsilyl-5-diethylamino-1-thia-2-titanacyclopenta-3,4-diene (6b).

Crystals were obtained by recrystallization from a toluene solution. A red platelet crystal (0.15 × 0.07 × 0.02 mm) was mounted on a polyamide film (MicroMounts™, MiTegen), and coated with paraffin. All data were collected on a Rigaku Mercury 70 CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 153 K. The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 4105 observed reflections and 251 variable parameters. All calculations were performed using the CrystalStructure[2] crystallographic software package except for refinement, which was performed using SHELXL97.[3] Crystallographic data are summarized in table S. CIF data were deposited in Cambridge Structural Database (CCDC-1023315).



Molecular structure of **6b**

X-ray diffraction analyses of (*Z*)-3-(trimethylsilyl)-*N*,*N*-dimethylprop-2-enethioamide (11a).

Crystals were obtained by recrystallization from a hexane solution. A colorless platelet crystal (0.20 × 0.10 × 0.03 mm) was mounted on a polyamide film (MicroMounts™, MiTegen), and coated with paraffin. All data were collected on a Rigaku Mercury 70 CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 93 K. The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 1994 observed reflections and 105 variable parameters. A maximum/minimum residual density was found (3.51) with maximum (positive) residual density 1.53 eA^{-3}. Although the reason for this is unclear yet, several residual peaks were found along with the molecular plane. All calculations were performed using the CrystalStructure[2] crystallographic software package except for refinement, which was performed using SHELXL97.[3] Crystallographic data are summarized in table S. CIF data were deposited in Cambridge Structural Database (CCDC-1051704).

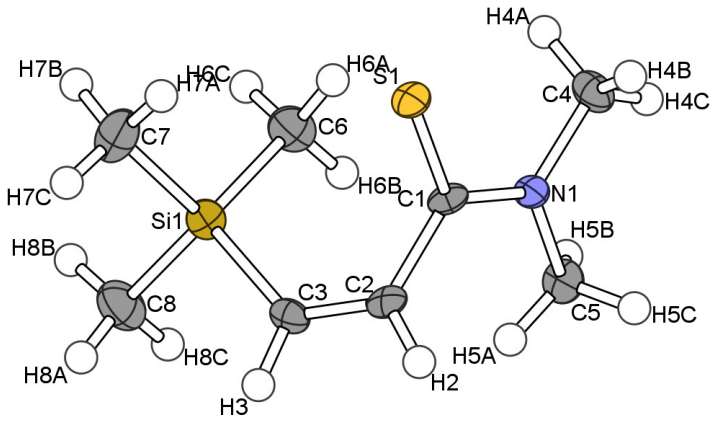


Table S. Crystal data and structure refinement for **5a**, **5b**, **6b** and **11a**

Complex	**5a**	**5b**	**6b**	**11a**
Empirical Formula	$C_{18}H_{25}NSSiZr$	$C_{23}H_{35}NSSiZr$	$C_{23}H_{35}NSSiTi$	$C_8H_{27}NSSi$
Formula Weight	406.77	476.90	545.96	187.37
Crystal Color, Habit	orange, platelet	orange, platelet	red, platelet	Colorless, platelet
Crystal Dimensions	0.30 × 0.20 × 0.05 mm	0.40 × 0.30 × 0.02 mm	0.15 × 0.07 × 0.02 mm	0.20 × 0.10 × 0.03 mm
Crystal System	monoclinic	monoclinic	monoclinic	triclinic
Lattice Type	Primitive	Primitive	Primitive	Primitive
Space Group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	P-1(#2)
Lattice Parameters	a = 15.471(8) Å	a = 18.125(5) Å	a = 18.029(8) Å	a = 6.260(4) Å
	b = 9.164(4) Å	b = 9.870(2) Å	b = 9.695(4) Å	b = 6.930(5) Å
	c = 14.060(7) Å	c = 14.346(4) Å	c = 14.246(7) Å	c = 14.430(10) Å
				α = 92.03(3)
	β = 108.281(5) °	β = 110.562(3) °	β = 110.517(8)	β = 99.07(3)
				γ = 112.21(3)
	V = 1892.8(16) Å^3	V = 2763.4(12) Å^3	V= 2332.1(18) Å^3	V= 569.3(7) Å^3
Z value	4	4	4	2
Absorption coefficient	7.507 cm^{-1}	6.019 cm^{-1}	5.160 cm^{-1}	3.385 cm^{-1}
Radiation	MoKα (λ = 0.71073 Å) graphite monochromated	MoKα (λ = 0.71073 Å) graphite monochromated	MoKα (λ = 0.71073 Å) graphite monochromated	MoKα (λ = 0.71073 Å) graphite monochromated
Temperature	153 K	153 K	153 K	93 K
No. of Reflections Measured	Total: 6976 Unique: 4168 (R_{int} = 0.0244)	Total: 26600 Unique: 5501 (R_{int} = 0.0195)	Total: 14591 Unique: 4105 (R_{int} = 0.0724)	Total: 5433 Unique: 1994 (R_{int} = 0.0374)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.824 - 0.963)	Lorentz-polarization Absorption (trans. factors: 0.871 - 0.988)	Lorentz-polarization Absorption (trans. factors: 0.856 - 0.990)	Lorentz-polarization Absorption (trans. factors: 0.903 - 0.990)
No. of Reflections	4167	5501	4105	1994
No. Variables	212	269	251	105
Reflection/Parameter Ratio	19.66	20.45	16.35	18.99
Residuals: R; wR (All data)	0.0606; 0.0939	0.0367; 0.0750	0.0952; 0.1420	0.0906; 0.2447
Residuals: R_1	0.0448	0.0321	0.0619	0.0737
No. of Reflections to calc R_1	3344	4883	2873	1549
Goodness of Fit Indicator	1.098	1.124	1.067	1.096
Max Shift/Error in Final Cycle	0.000	0.000	0.002	0.002
Maximum peak in Final Diff. Map (e Å^3)	0.85	0.904	0.79	1.51
Minimum peak in Final Diff. Map (e Å^3)	–0.63	-0.367	-0.36	-0.43
CCDC#	1023319	1023317	1023315	1051704

References

1. *SIR 2008*: M.C. Burla, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna (2007).
2. *CrystalStructure 4.1*: Crystal Structure Analysis Package, Rigaku Corporation (2000-2014). Tokyo 196-8666, Japan.
3. *SHELX97*: G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112-122.