Formation of spiro compound *via* coupling of cyclopentadienyl ligand with diene moiety of titanacyclopentadiene

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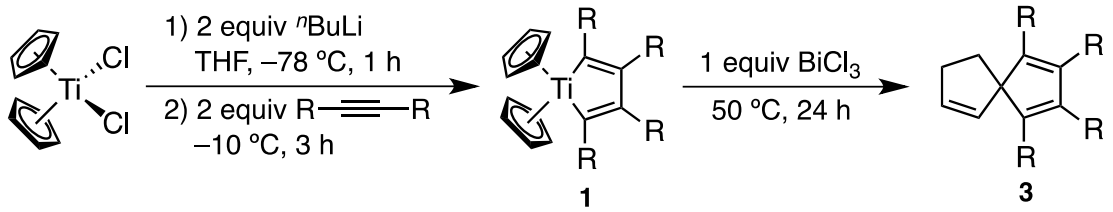
Supporting Information

Table of Contents

General.

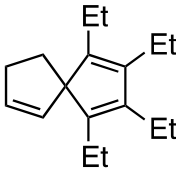
All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. Tetrahydrofuran (THF), hexane and benzene were distilled from benzophenone-ketyl under nitrogen prior to use. Toluene was distilled from Na under nitrogen prior to use. All chemicals were obtained from commercial sources unless otherwise noted. All commercially available chemicals were used without further purification. NMR spectra were recorded on a ECX-400. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 101 MHz) chemical shifts δ are reported in ppm downfield of internal tetramethlysilane or given relative to the respective residual solvent peaks (^{1}H: $CHCl_3$ at 7.26, ^{13}C: $CHCl_3$ at 77.0). NMR yields were determined using dichloromethane as internal standard. For X-ray crystal structure analyses, data sets were collected with a Rigaku R-RAXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods (SHELXS-2013/1) and refined on F^2 using SHELXL-2017/1. All calculations were performed using the CrystalStructure crystallographic software package.

Typicial Procedures for Synthesis of Spiro Compound 3.



A typical procedure is given for the synthesis of **3a**. A solution of Cp_2TiCl_2 (156 mg, 0.625 mmol) in THF (2.5 mL) was cooled to –78 ºC, and ^{n}BuLi (1.55 M in hexane, 0.80 mL, 1.25 mmol) was added dropwise. After stirring for 1 h at the same temperature, 3-hexyne (0.11 ml, 1 mmol) was added, and the reaction mixture was warmed up to –10 ºC. After stirring for 3 h at –10 ºC, bis(cyclopentadienyl)titanacyclopentadiene **1a** was formed in a dark green solution. $BiCl_3$ (158 mg, 0.5 mmol) was added to the solution, and the mixture was heated to 50 ºC. After vigorous stirring for 24 h, the mixture was quenched with 3 N HCl aq and extracted with hexane. The organic layer was washed with water, saturated $NaHCO_3$ aq and brine, and then dried over Na_2SO_4. After solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: hexane) and GPC to give **3a** as a colorless oil.

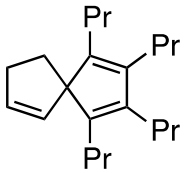
1,2,3,4-tetraethylspiro[4.4]nona-1,3,6-triene (3a).



Colorless oil. NMR yield: 70%. Isolated yield: 40%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (t, *J* = 7.6 Hz, 6H), 1.07 (t, *J* = 7.6 Hz, 6H), 1.91-1.96 (m, 2H), 2.05-2.20 (m, 4H), 2.24 (q, *J* = 7.6 Hz, 4H), 2.55-2.60 (m, 2H), 5.10 (dt, *J* = 5.5 Hz, 2.1 Hz, 1H), 5.89 (dt, *J* = 5.5 Hz, 2.3 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, CDCl3): δ 15.1, 15.7, 18.8, 18.9, 28.2, 33.9, 71.1, 131.3, 136.1, 140.0, 146.5. HRMS(EI) Calcd for $C_{17}H_{26}$: 230.2035. Found: 230.2028.

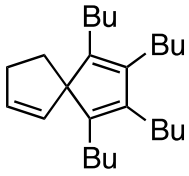
1,2,3,4-tetrapropylspiro[4.4]nona-1,3,6-triene (3b).



Colorless oil. NMR yield: 55%. Isolated yield: 35%

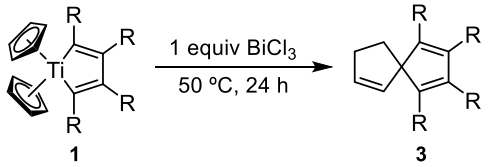
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.3 Hz, 6H), 0.94 (t, *J* = 7.3 Hz, 6H), 1.32-1.47 (m, 8H), 1.88-1.92 (m, 2H), 1.97-2.12 (m, 4H), 2.13-2.17 (m, 4H), 2.53-2.57 (m, 2H), 5.06 (dt, *J* = 5.5 Hz, 2.0 Hz, 1H), 5.85 (dt, *J* = 5.4 Hz, 2.3 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$): δ 14.5, 14.9, 23.6, 24.0, 28.4, 28.6, 33.8, 71.0, 131.1, 136.3, 138.9, 145.5. HRMS(EI) Calcd for $C_{21}H_{34}$: 286.2661. Found: 286.2652.

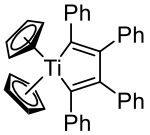
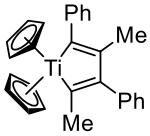
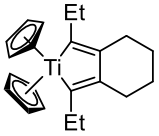
1,2,3,4-tetrabutylspiro[4.4]nona-1,3,6-triene (3c)



Colorless oil. NMR yield: 66%. Isolated yield: 41%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88-0.96 (m, 12H), 1.26-1.43 (m, 16H), 1.89-1.92 (m, 2H), 1.99-2.14 (m, 4H), 2.16-2.20 (m, 4H), 2.53-2.58 (m, 2H), 5.06 (dt, *J* = 5.3 Hz, 2.2 Hz, 1H), 5.86 (dt, *J* = 5.4 Hz, 2.3 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$): δ 14.0, 14.1, 23.2, 23.5, 25.9, 28.5, 32.7, 33.1, 33.8, 71.0, 131.0, 136.4, 138.9, 145.3. HRMS(EI) Calcd for $C_{25}H_{42}$: 342.3287. Found: 342.3274.

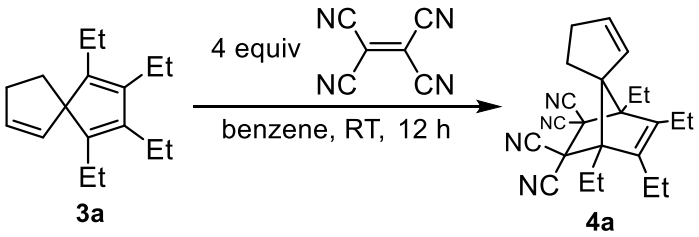


entry	complex **1**	spiro compound **3**
1		not obtained
2		not obtained
3		24% (inseparable)

NMR yields

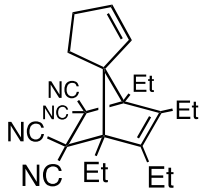
Table S3 Reactions of titanacyclopentadiene **1** with $BiCl_3$

Synthesis of Diels-Alder adduct 4.



A typical procedure is given for the synthesis of **4a**. To a solution of spiro compound **3a** (46 mg, 0.20 mmol) in benzene (2.0 mL) was added tetracyanoethylene (102 mg, 0.80 mmol) and the mixture was stirred at room temperature for 12 h. The solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel (eluent: hexane:ethyl acetate = 3:1) to give **4** as a colorless solid.

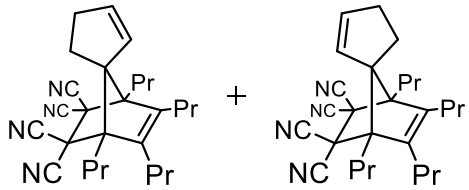
(1*R*,4*R*)-1,2,3,4-tetraethylspiro[bicyclo[2.2.1]hept[2]ene-7,1'-cyclopent[2]ene]-5,5,6,6-tetracarbonitrile (4a).



Colorless solid. NMR yield: 79%. Isolated yield: 62%

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (t, *J* = 7.7 Hz, 6H), 1.31 (t, *J* = 7.7 Hz, 6H), 1.96-2.12 (m, 4H), 2.14-2.18 (m, 2H), 2.30-2.40 (m, 2H), 2.48-2.58 (m, 4H), 5.32 (dt, *J* = 5.9 Hz, 2.1 Hz, 1H), 5.97 (dt, *J* = 5.9 Hz, 2.2 Hz, 1H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$): δ 9.6, 13.4, 19.9, 20.4, 25.1, 34.0, 50.8, 70.7, 81.6, 111.1, 112.2, 131.4, 136.5, 148.0. Anal. Calcd for $C_{23}H_{26}N_4$: C, 77.06; H, 7.31; N, 15.62. Found: C, 76.66; H, 7.30; N, 15.52.

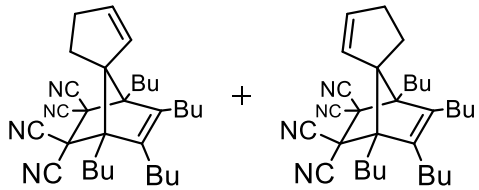
(1*R*,4*R*)-1,2,3,4-tetrapropylspiro[bicyclo[2.2.1]hept[2]ene-7,1'-cyclopent[2]ene]-5,5,6,6-tetracarbonitrile (4b).



Colorless solid. Isolated yield: 59% The ratio of two isomers: Major: Minor = 3:1.

^{1}H NMR (600 MHz, $CDCl_3$): δ 1.02-1.07 (m, Major - 12 H, Minor - 12 H), 1.34-1.45 (m, Major - 2 H, Minor - 2 H), 1.50-1.60 (m, Major - 2 H, Minor - 2 H, overlapped with peak of water), 1.63-1.69 (m, Major - 2 H), 1.73-1.80 (m, Major - 2 H, Minor - 2 H), 1.81-1.89 (m, Major - 2 H, Minor - 6 H), 1.90-1.96 (m, Major - 2 H, Minor - 2 H), 2.14-2.17 (m, Major - 2 H), 2.20-2.30 (m, Major - 2 H, Minor - 4 H), 2.37-2.43 (m, Major - 2 H, Minor - 2 H), 2.50-2.52 (m, Major - 2 H), 5.25-5.26 (m, Major - 1 H), 5.94-5.95 (m, Major - 1 H), 5.97-5.98 (m, Minor - 1 H), 6.24-6.25 (m, Minor - 1 H). ^{13}C{^{1}H} NMR(151 MHz, $CDCl_3$): δ 14.8, 14.9, 15.3, 15.4, 18.3 (2 C), 22.5, 22.6, 25.1, 29.4, 29.7 (2 C), 29.8 (2 C), 30.0, 33.9, 50.4, 50.8, 70.3, 70.8, 81.6, 81.8, 111.1, 111.4, 112.1, 112.3, 126.7, 131.2, 136.6, 141.5, 147.0, 147.1. Anal. Calcd for $C_{27}H_{34}N_4$: C, 78.22; H, 8.27; N, 13.51. Found: C, 78.08; H, 8.28; N, 13.52.

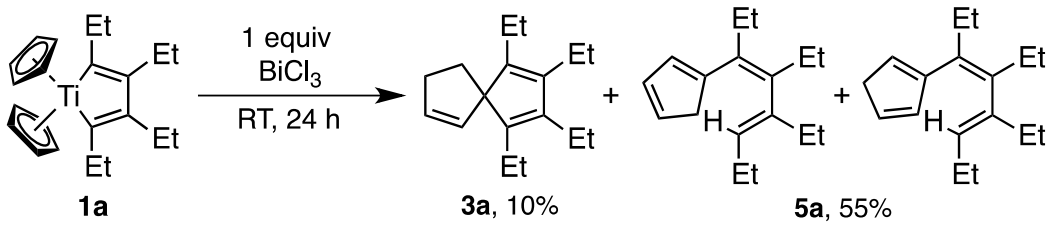
(1*R*,4*R*)-1,2,3,4-tetrabutylspiro[bicyclo[2.2.1]hept[2]ene-7,1'-cyclopent[2]ene]-5,5,6,6-tetracarbonitrile (4c).



Colorless solid. Isolated yield: 65% The ratio of two isomers: Major: Minor = 6.4:1.

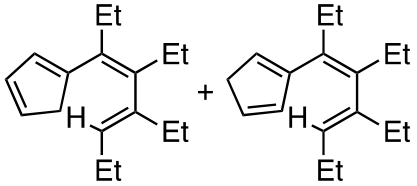
^{1}H NMR (600 MHz, $CDCl_3$): δ 0.95-1.00 (m, Major - 12 H, Minor - 12 H), 1.30-1.53 (m, Major - 12 H, Minor - 12 H), 1.58-1.65 (m, Major - 2 H), 1.68-1.76 (m, Major - 2 H, Minor - 2 H), 1.81-1.88 (m, Major - 2 H, Minor - 6 H), 1.93-1.99 (m, Major - 2 H, Minor - 2 H), 2.14-2.16 (m, Major - 2 H), 2.22-2.32 (m, Major - 2 H, Minor - 4 H), 2.40-2.46 (m, Major - 2 H, Minor - 2 H), 2.49-2.52 (m, Major - 2 H), 5.26-5.28 (m, Major - 1 H), 5.96-5.98 (m, Major - 1 H, Minor - 1 H), 6.24-6.26 (m, Minor - 1 H). ^{13}C{^{1}H} NMR(151 MHz, $CDCl_3$): δ 13.7 (4 C), 23.3 (2 C), 23.9, 24.0, 25.1, 26.7, 26.8, 26.9, 27.2 (2 C), 27.5, 29.7, 29.8, 31.1, 31.3, 34.0, 50.4, 50.9, 70.3, 70.7, 81.8, 81.9, 111.1, 111.4, 112.2, 112.3, 126.8, 131.3, 136.6, 141.5, 147.0 (2 C). Anal. Calcd for $C_{31}H_{42}N_4$: C, 79.10; H, 8.99; N, 11.90. Found: C, 79.17; H, 9.05; N, 11.93.

Reaction of Titanacyclopentadiene 1 with $BiCl_3$ at room temperature.



$BiCl_3$ (158 mg, 0.5 mmol) was added to the solution of titanacyclopentadiene **1a**, and the mixture was stirred for 24 h at room temperature. The mixture was quenched with 3 N HCl aq and extracted with hexane. The organic layer was washed with water, saturated $NaHCO_3$ aq and brine, and then dried over Na_2SO_4, then evaporated. ^{1}H NMR analysis revealed that dienylcyclopentadiene **5a** was obtained in 55% yield as a mixture of double bond positional isomers, along with the formation of spiro compound **3a** in 10% NMR yield. ^{1}H and ^{13}C NMR data of **5a** were consistent with the published data.[S1]

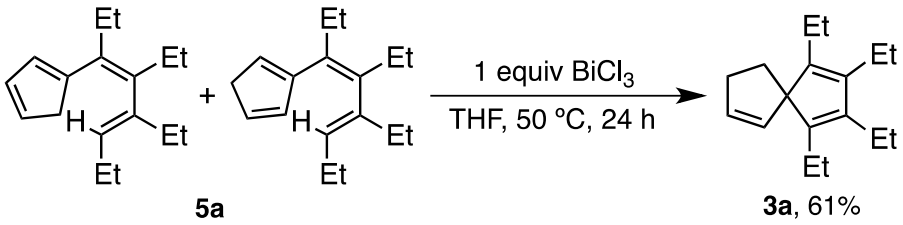
(3*Z*,5*E*)-3-(Cyclopentadienyl)-4,5-diethylocta-3,5-diene (5a)



The ratio of two isomers: Major: Minor = 6.4:1.

^{1}H NMR (400 MHz, C_6D_6): δ 0.86 (t, *J* = 7.5 Hz, Minor - 3 H), 0.87 (t, *J* = 7.5 Hz, Major - 3 H), 0.94 (t, *J* = 7.7 Hz, Major - 3 H), 0.98 (t, *J* = 7.7 Hz, Minor - 3 H), 1.01-1.10 (m, Major - 6 H, Minor - 6 H), 1.89-2.02 (m, Major - 2 H, Minor - 2 H), 2.04-2.27 (m, Major - 4 H, Minor - 4 H), 2.33 (q, *J* = 7.5 Hz, Major - 2 H), 2.39 (q, *J* = 7.5 Hz, Minor - 2 H), 2.82 (q, *J* = 1.5 Hz, Minor - 2 H), 3.06 (br q, *J* = 1.5 Hz, Major - 2 H), 5.17 (br t, *J* = 7.2 Hz, Major - 1 H), 5.21 (br t, *J* = 7.2 Hz, Minor - 1 H), 6.07-6.11 (m, Minor - 1 H), 6.21-6.26 (m, Major - 1 H, Minor - 1 H), 6.42 (m, Major - 1 H), 6.48 (ddt, *J* = 5.4, 2.2, 1.6 Hz, Major - 1 H), 6.64 (dq, *J* = 5.3 Hz, 1.5 Hz, Minor - 1 H). ^{13}C{^{1}H} NMR(101 MHz, C_6D_6): δ 13.3, 13.4 (2 C), 13.6, 14.1 (2 C), 14.2, 14.3, 21.4, 21.5, 23.2, 23.6, 24.9, 25.9, 26.3, 26.4, 41.1, 44.8, 127.9, 129.8, 130.4, 131.1, 131.2, 131.6, 132.6, 132.9, 133.1, 136.8, 140.7 (2 C), 141.2, 141.6, 148.3, 149.3.

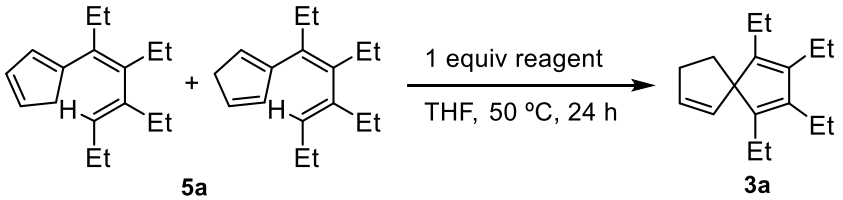
Reaction of dienylcyclopentadiene 5a with $BiCl_3$.



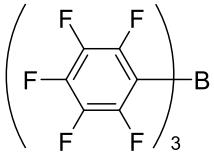
5a **3a**, 61%

To a solution of dienylcyclopentadiene **5a** (69 mg, 0.30 mmol) in THF (1.5 mL) was added $BiCl_3$ (95 mg, 0.30 mmol) and the mixture was stirred at 50 °C for 24 h. The mixture was quenched with 3 N HCl aq and extracted with hexane. The organic layer was washed with water, saturated $NaHCO_3$ aq and brine, and then dried over Na_2SO_4, then evaporated. ^1H NMR analysis revealed that spiro compound **3a** was obtained in 61% yield. The formation of uncharacterized byproducts was also observed. This is the major reason of the rather low yield of **3a** from **5a**.

Reactions of dienylcyclopentadiene **5a** with Lewis acids were carried out as shown in table S6. BCF was even better at transforming 5a into 3a than $BiCl_3$.



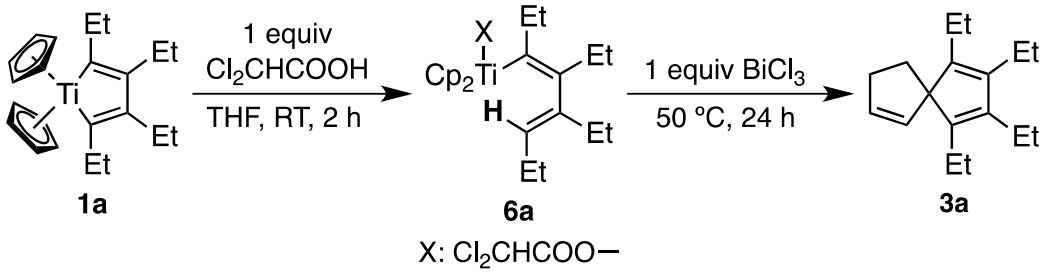
5a **3a**

entry	reagent	3a(%)[1]	5a(%)[1]
1	$BiCl_3$	61	0
2	$InCl_3$	21	62
3	$AlCl_3$	61	0
4	$FeCl_3$	27	0
5	$TiCl_4$	42	0
6		73	0
7[2]	$BiCl_3$	18	73

[1] NMR yields
[2] The reaction was carried out in the presence of 1.25 equivalent of PMe_3.

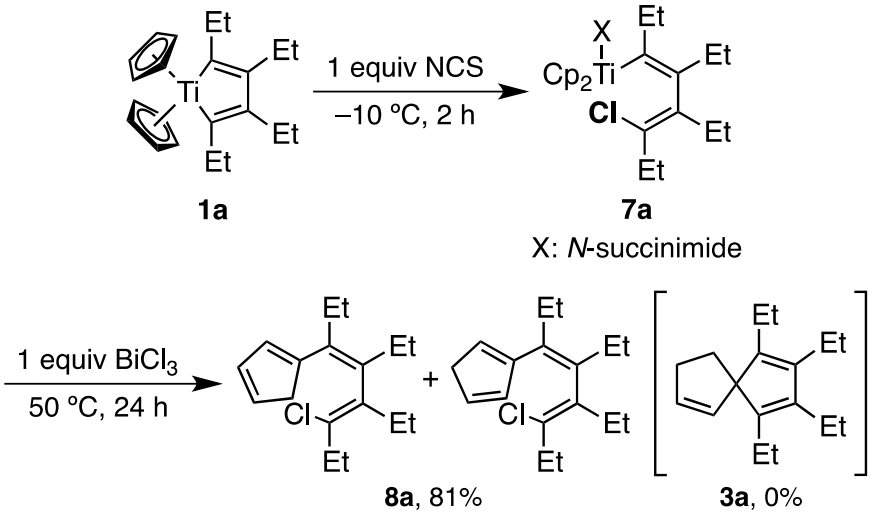
Table S6 Reactions of dienylcyclopentadiene **5a** with Lewis acids

Reaction of dienyltitanocene 6a with $BiCl_3$.



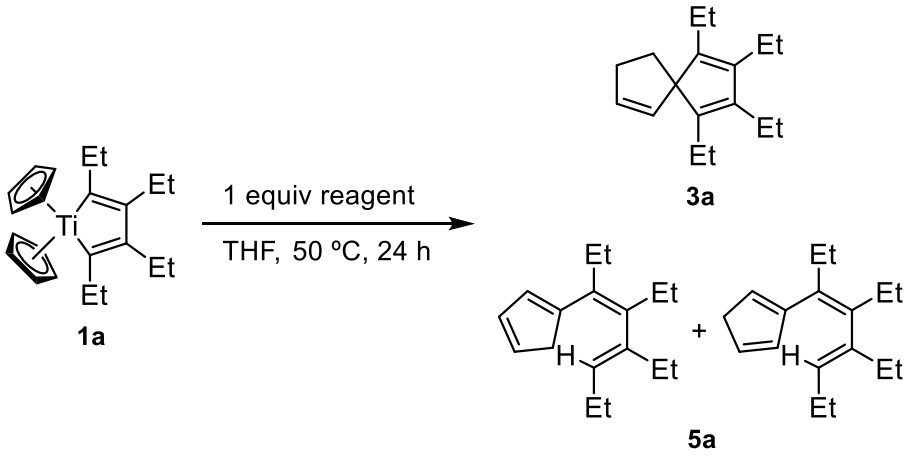
Synthesis of **1a** and its transformation to **6a** were followed by literature procedure.[S2] A solution of Cp_2TiCl_2 (156 mg, 0.625 mmol) in THF (2.5 mL) was cooled to –78 ºC, and ^{n}BuLi (1.55 M in hexane, 0.80 mL, 1.25 mmol) was added dropwise. After stirring for 1 h at the same temperature, 3-hexyne (0.11 ml, 1 mmol) was added, and the reaction mixture was warmed up to –10 ºC. After stirring for 3 h at –10 ºC, bis(cyclopentadienyl)titanacyclopentadiene **1a** was formed in a dark green solution. $Cl_2CHCOOH$ (41 µl, 0.5 mmol) was added to the reaction mixture, and then the mixture was stirred for 1 h at room temperature to generate complex **6a**. $BiCl_3$ (158 mg, 0.5 mmol) was added to the solution, and the mixture was heated to 50 ºC. After vigorous stirring for 24 h, the mixture was quenched with 3 N HCl aq and extracted with hexane. The organic layer was washed with water, saturated $NaHCO_3$ aq and brine, dried over Na_2SO_4, then evaporated. ^{1}H NMR analysis revealed that spiro compound **3a** was formed in 44% NMR yield.

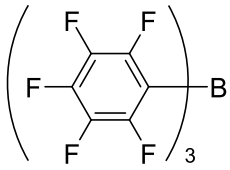
Reaction of chlorodienyltitanocene 7a with $BiCl_3$.



Synthesis of **1a** and its transformation to **7a** were followed by literature procedure.[S2] A solution of Cp_2TiCl_2 (156 mg, 0.625 mmol) in THF (2.5 mL) was cooled to –78 ºC, and ^{n}BuLi (1.55 M in hexane, 0.80 mL, 1.25 mmol) was added dropwise. After stirring for 1 h at the same temperature, 3-hexyne (0.11 ml, 1 mmol) was added, and the reaction mixture was warmed up to –10 ºC. After stirring for 3 h at –10 ºC, bis(cyclopentadienyl)titanacyclopentadiene **1a** was formed in a dark green solution. *N*-Chlorosuccinimide (83 mg, 0.625 mmol) was added to the reaction mixture, and then the mixture was stirred for 2 h at the same temperature to generate complex **7a**. $BiCl_3$ (158 mg, 0.5 mmol) was added to the solution, and the mixture was heated to 50 ºC. After vigorous stirring for 24 h, the mixture was quenched with 3 N HCl aq and extracted with hexane. The organic layer was washed with water, saturated $NaHCO_3$ aq and brine, dried over Na_2SO_4, then evaporated. ^{1}H NMR analysis revealed that compound **8a** was formed in 81% NMR yield and no compound **3a** was observed.

Reactions of titanacyclopentadiene **1a** with other reagents were carried out as shown in table S9.

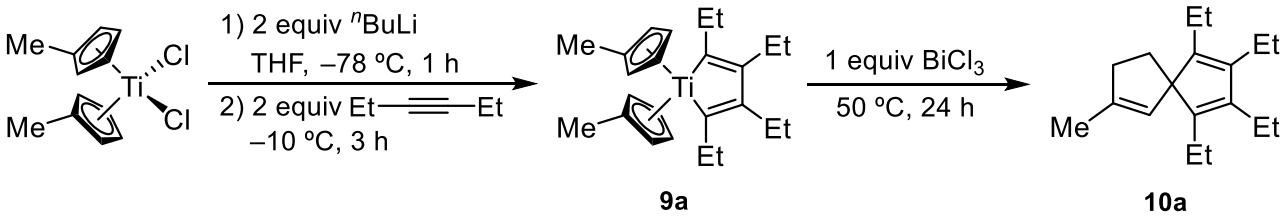


entry	reagent	3a	5a
1	$BiCl_3$	70	trace
2	$SnCl_2$	2	24
3	$FeCl_3$	4	41
4	$AlCl_3$	0	0
5	$InCl_3$	0	30
6		0	0
7	TBACl	0	0

NMR yields

Table S9 Reactions of titanacyclopentadiene **1a** with other reagents

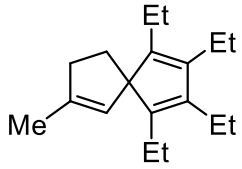
Synthesis of spiro compound 10a.



A solution of $(MeCp)_2TiCl_2$ (173 mg, 0.625 mmol) in THF (2.5 mL) was cooled to –78 ºC, and ^{n}BuLi (1.55 M in hexane, 0.80 mL, 1.25 mmol) was added dropwise. After stirring for 1 h at the same temperature, 3-hexyne (0.11 ml, 1 mmol) was added, and the reaction mixture was warmed up to –10 ºC. After stirring for 3 h at –10 ºC, bis(cyclopentadienyl)titanacyclopentadiene **9a** was formed in a dark green solution. $BiCl_3$ (158 mg, 0.5 mmol) was added to the solution, and the mixture was heated to 50 ºC. After vigorous stirring for 24 h, the mixture was quenched with 3 N HCl aq and extracted with hexane. The organic layer was washed with water, saturated $NaHCO_3$ aq and brine, and then dried over Na_2SO_4. After solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: hexane) to give **10a** as a colorless oil.

Measurement of ^{13}C-NMR spectrum was not successful due to decomposition of compound **10a**.

(10a)



Colorless oil. NMR yield: 19%. Isolated yield: 6%.

^{1}H NMR (400 MHz, $CDCl_3$): d 1.00 (t, *J* = 7.6 Hz, 6H), 1.05 (t, *J* = 7.6 Hz, 6H), 1.78 (d, *J* = 1.2 Hz, 3H), 1.93-1.96 (m, 2H), 2.05-2.19 (m, 4H), 2.22 (q, *J* = 7.6 Hz, 4H), 2.44-2.48 (m, 2H), 4.68 (q, *J* = 1.6 Hz, 1H).

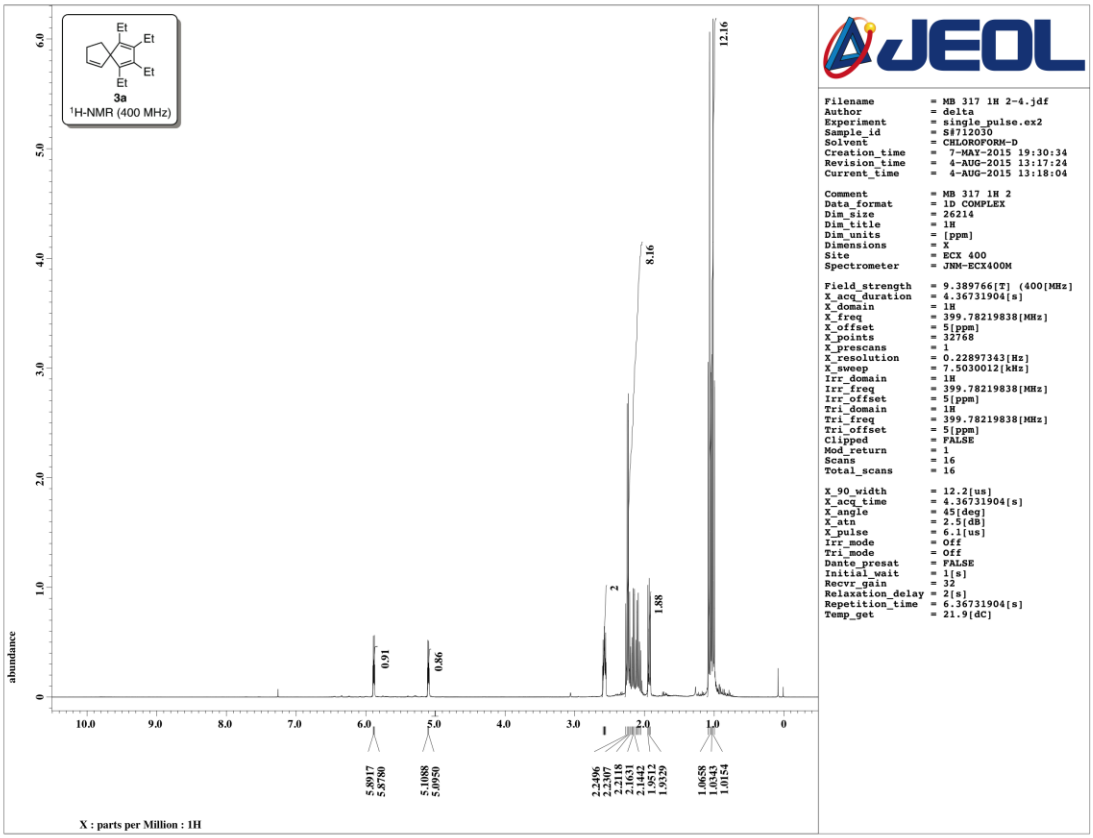
HRMS(EI) Calcd for $C_{18}H_{28}$: 244.2191. Found: 244.2195.

Reference.

[S1] Z.Song, Y.-F. Hsieh, K.Nakajima, K. Kanno and T. Takahashi, *Organometallics*, 2011, **30**, 844.

Discussion on the fate of “CpTi” fragment

After workup of the reaction shown in Scheme 2, spiro compound and Cp_2TiCl_2 were formed in 60% and 43% NMR yields respectively. And, we also observed three singlet peaks at 6.68, 6.62 and 6.54 ppm which were assignable to Cp protons of "CpTi" fragments (mono-Cp titanium species). NMR yields of the "CpTi" species were 15%, 14% and 30% respectively (total yield was 59%). This result was consistent with 60% NMR yield of spiro compound and indicated that the "CpTi" species were generated along with the formation of spiro compound. We also confirmed that the "CpTi" species were different from $(CpTiCl_2)_2O$, the fate of "CpTi" fragment in previously reported our reactions (Please see a ref for detail. Y. Mizukami, H. Li, K. Nakajima, Z. Song and T. Takahashi, *Angew. Chem. Int. Ed.*, 2014, **53**, 8899). Separation of the "CpTi" species by column chromatography and recrystallization was not successful.

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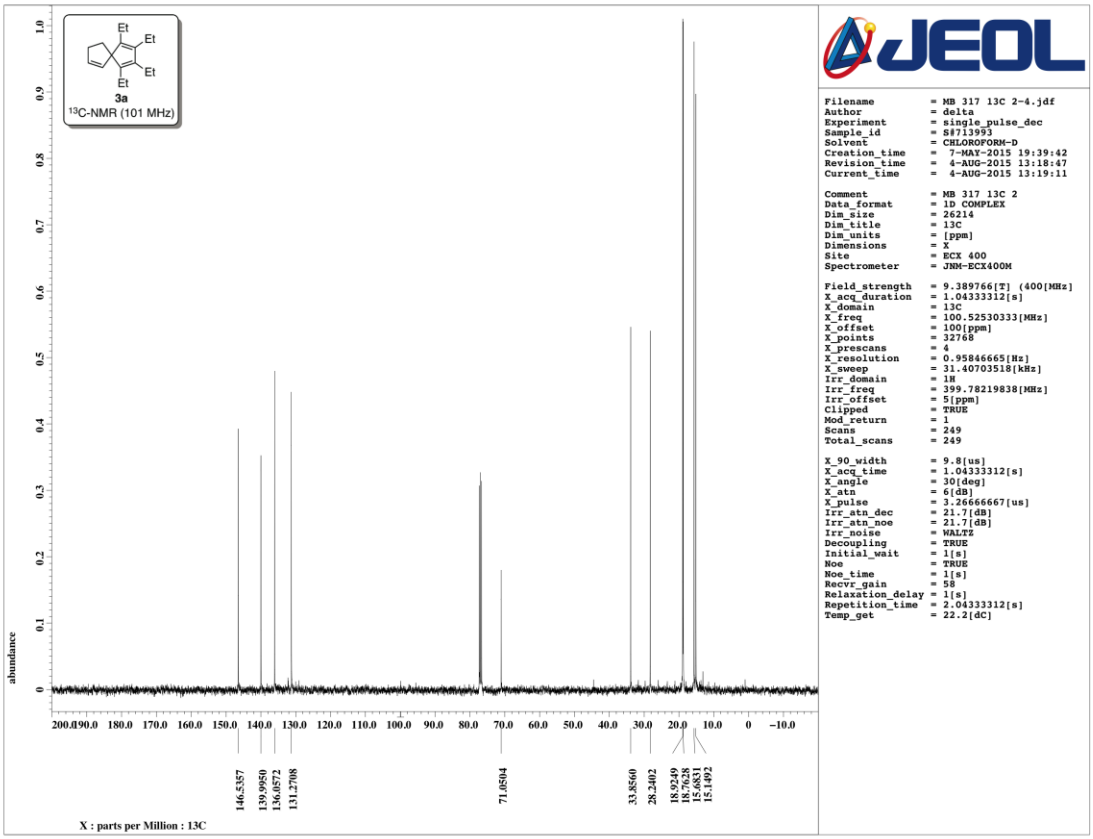
Filename          = MB 317 1H 2-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#712030
Solvent           = CHLOROFORM-D
Creation_time     =  7-MAY-2015 19:30:34
Revision_time     =  4-AUG-2015 13:17:24
Current_time      =  4-AUG-2015 13:18:04

Comment           = MB 317 1H 2
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400M

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 12.2[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 2.5[dB]
X_pulse           = 6.1[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 32
Relaxation_delay  = 2[s]
Repetition_time   = 6.36731904[s]
Temp_get          = 21.9[dC]
```

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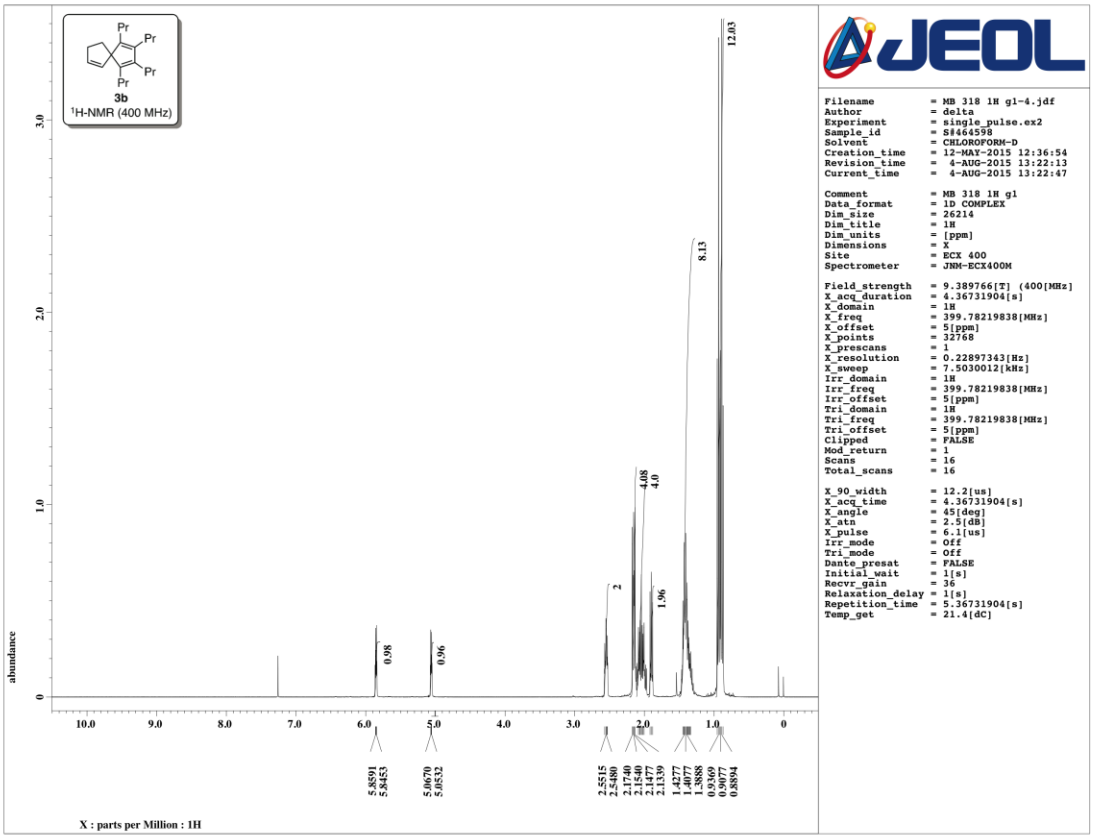
Filename          = MB 317 13C 2-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#713993
Solvent           = CHLOROFORM-D
Creation_time     =  7-MAY-2015 19:39:42
Revision_time     =  4-AUG-2015 13:18:47
Current_time      =  4-AUG-2015 13:19:11

Comment           = MB 317 13C 2
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400M

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 249
Total_scans       = 249

X_90_width        = 9.8[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 6[dB]
X_pulse           = 3.26666667[us]
Irr_atn_dec       = 21.7[dB]
Irr_atn_noe       = 21.7[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 58
Relaxation_delay  = 1[s]
Repetition_time   = 2.04333312[s]
Temp_get          = 22.2[dC]
```

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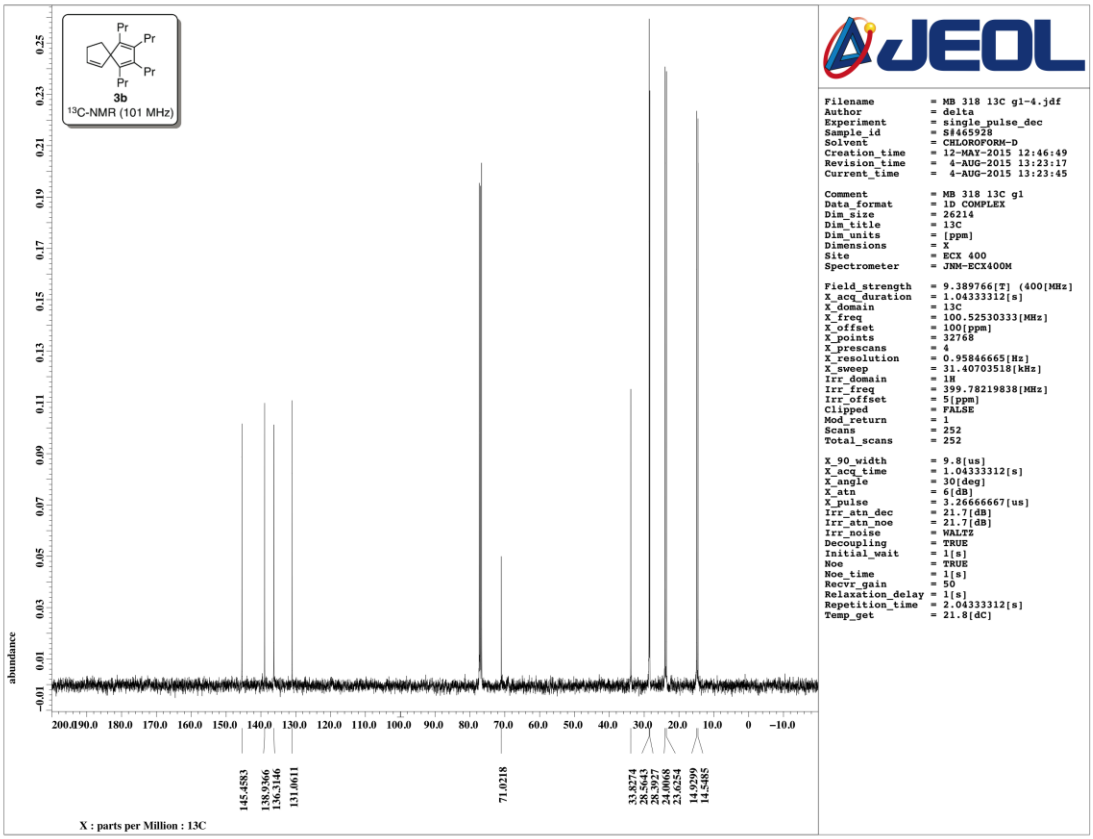
Filename          = MB 318 1H g1-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#464598
Solvent           = CHLOROFORM-D
Creation_time     = 12-MAY-2015 12:36:54
Revision_time     =  4-AUG-2015 13:22:13
Current_time      =  4-AUG-2015 13:22:47

Comment           = MB 318 1H g1
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400M

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 12.2[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 2.5[dB]
X_pulse           = 6.1[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 36
Relaxation_delay  = 1[s]
Repetition_time   = 5.36731904[s]
Temp_get          = 21.4[dC]
```




```
Filename          = MB 318 13C g1-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#465928
Solvent           = CHLOROFORM-D
Creation_time     = 12-MAY-2015 12:46:49
Revision_time     =  4-AUG-2015 13:23:17
Current_time      =  4-AUG-2015 13:23:45

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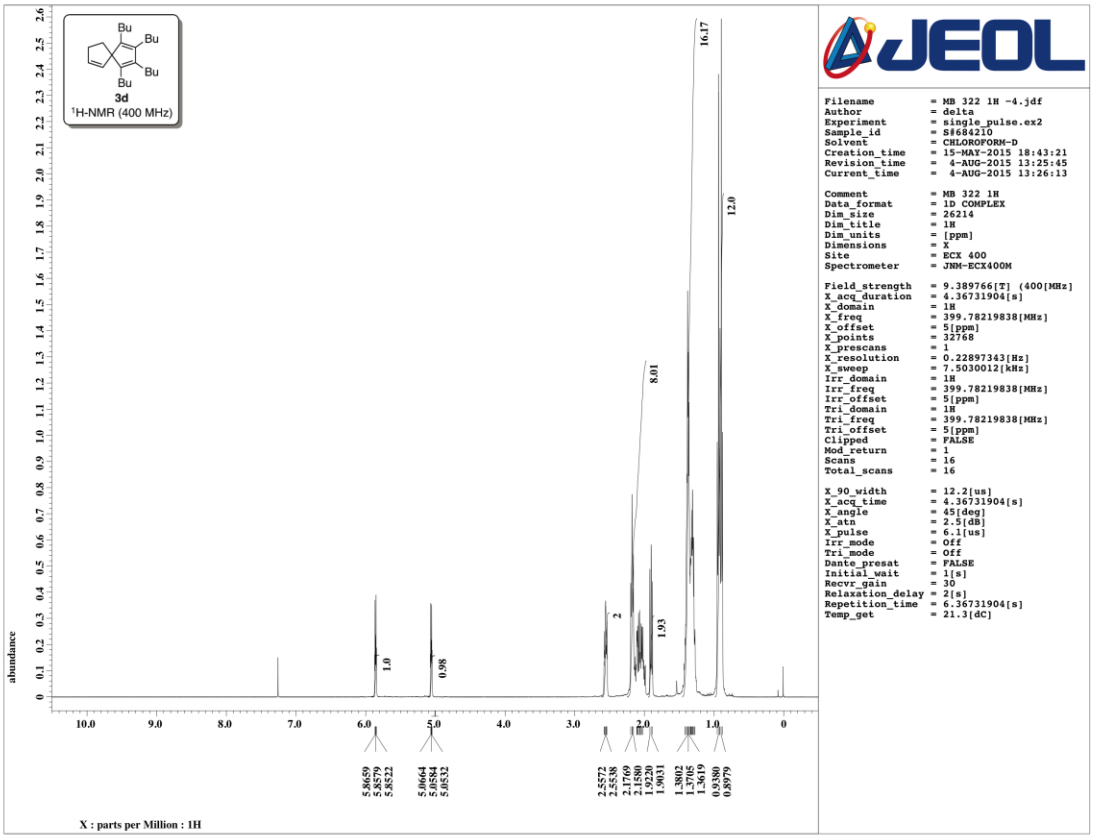
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400M

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 252
Total_scans       = 252

X_90_width        = 9.8[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 6[dB]
X_pulse           = 3.26666667[us]
Irr_atn_dec       = 21.7[dB]
Irr_atn_noe       = 21.7[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 50
Relaxation_delay  = 1[s]
Repetition_time   = 2.04333312[s]
Temp_get          = 21.8[dC]
```




```
Filename          = MB 322 1H -4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#684210
Solvent           = CHLOROFORM-D
Creation_time     = 15-MAY-2015 18:43:21
Revision_time     =  4-AUG-2015 13:25:45
Current_time      =  4-AUG-2015 13:26:13

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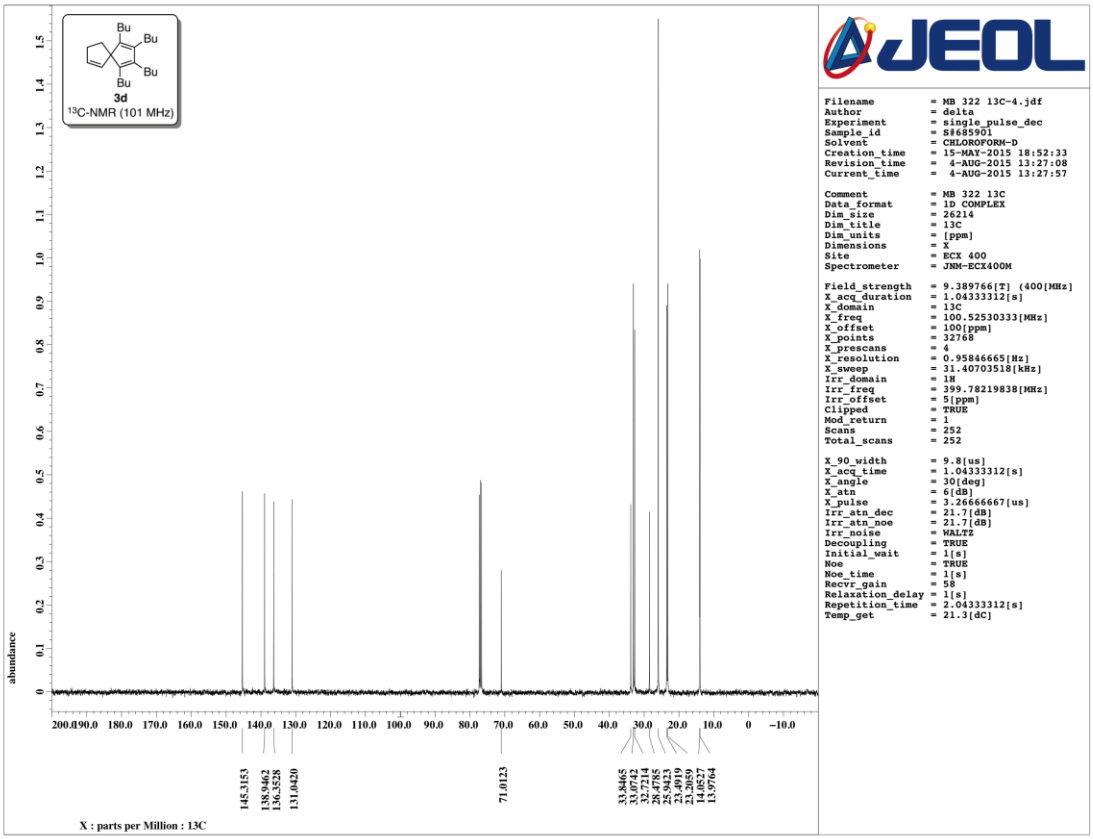
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400M

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 12.2[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 2.5[dB]
X_pulse           = 6.1[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Repetition_time   = 6.36731904[s]
Temp_get          = 21.3[dC]
```

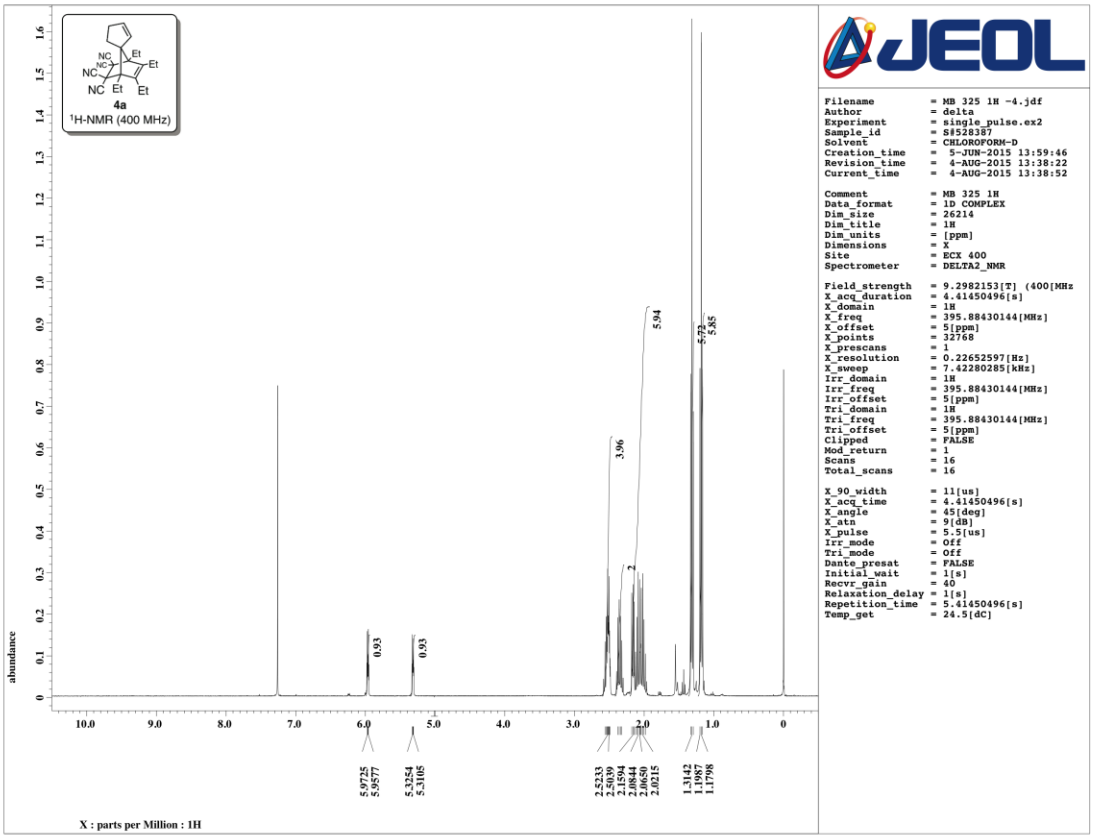



```
Filename          = MB 322 13C-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#685901
Solvent           = CHLOROFORM-D
Creation_time     = 15-MAY-2015 18:52:33
Revision_time     =  4-AUG-2015 13:27:08
Current_time      =  4-AUG-2015 13:27:57

Comment           = MB 322 13C
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400M

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 252
Total_scans       = 252

X_90_width        = 9.8[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 6[dB]
X_pulse           = 3.26666667[us]
Irr_atn_dec       = 21.7[dB]
Irr_atn_noe       = 21.7[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 58
Relaxation_delay  = 1[s]
Repetition_time   = 2.04333312[s]
Temp_get          = 21.3[dC]
```

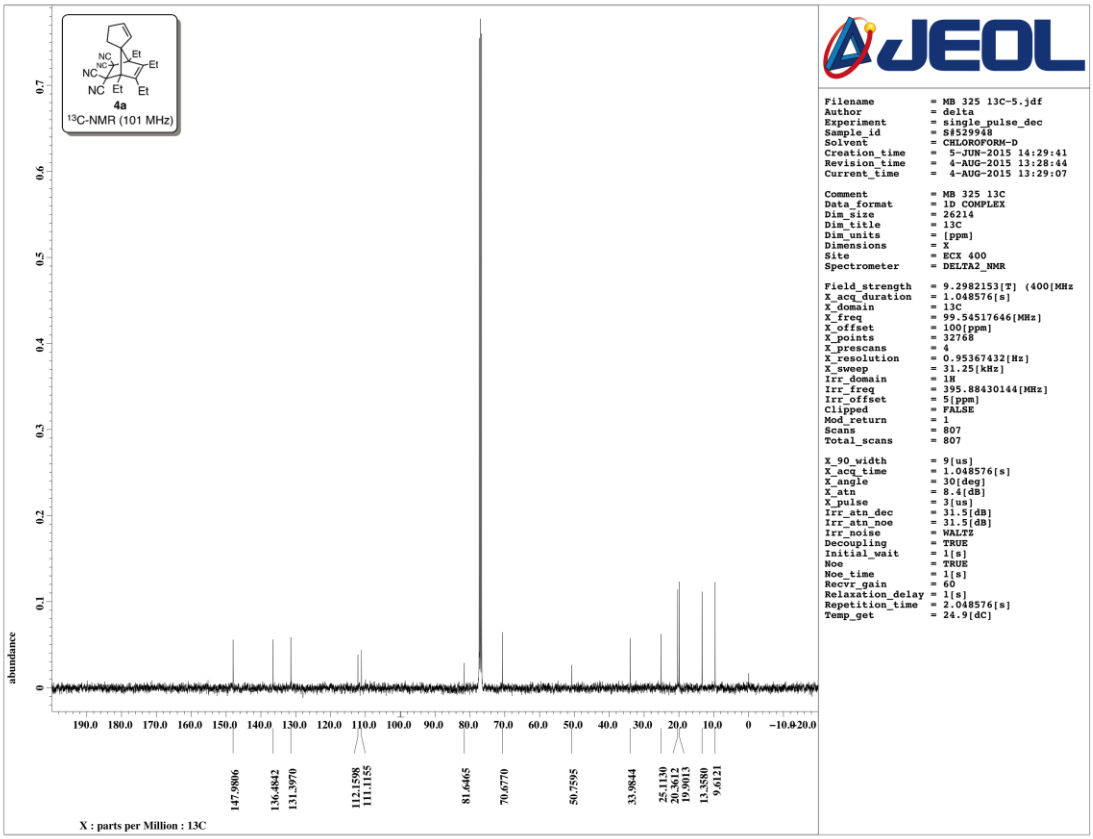



```
Filename          = MB 325 1H -4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#528387
Solvent           = CHLOROFORM-D
Creation_time     =  5-JUN-2015 13:59:46
Revision_time     =  4-AUG-2015 13:38:22
Current_time      =  4-AUG-2015 13:38:52

Comment           = MB 325 1H
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 4.41450496[s]
X_domain          = 1H
X_freq            = 395.88430144[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22652597[Hz]
X_sweep           = 7.42280285[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 395.88430144[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 11[us]
X_acq_time        = 4.41450496[s]
X_angle           = 45[deg]
X_atn             = 9[dB]
X_pulse           = 5.5[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 1[s]
Repetition_time   = 5.41450496[s]
Temp_get          = 24.5[dC]
```

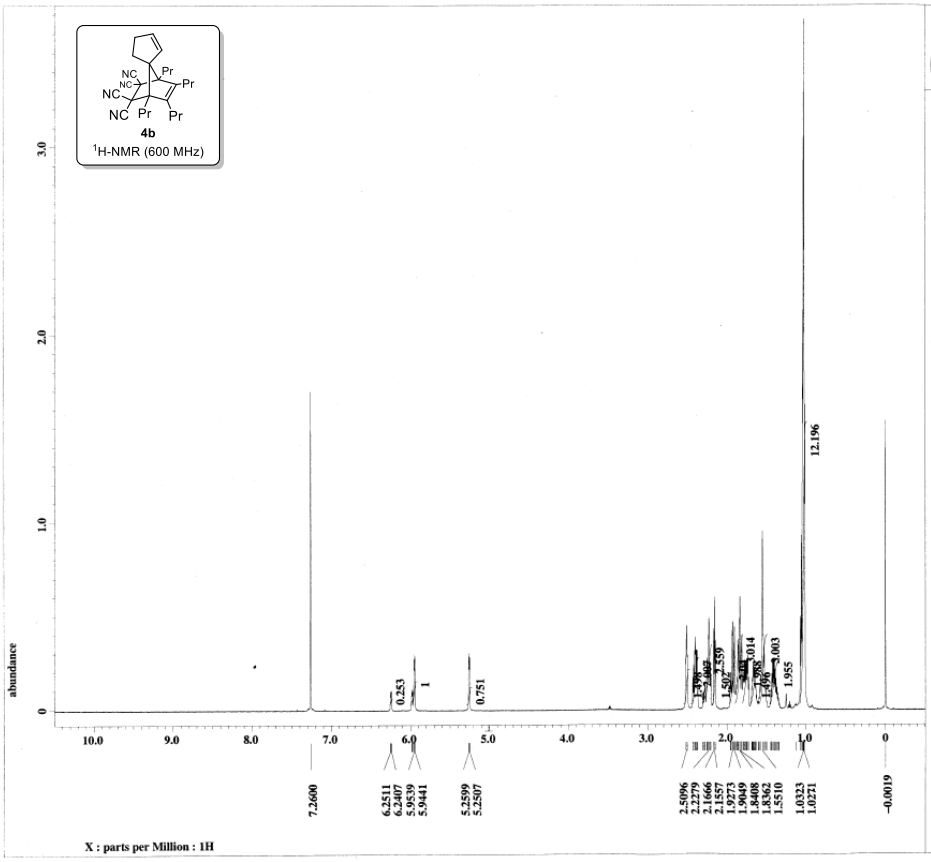



```
Filename          = MB 325 13C-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#529948
Solvent           = CHLOROFORM-D
Creation_time     =  5-JUN-2015 14:29:41
Revision_time     =  4-AUG-2015 13:28:44
Current_time      =  4-AUG-2015 13:29:07

Comment           = MB 325 13C
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_strength    = 9.2982153[T] (400[MHz
X_acq_duration    = 1.048576[s]
X_domain          = 13C
X_freq            = 99.54517646[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95367432[Hz]
X_sweep           = 31.25[kHz]
Irr_domain        = 1H
Irr_freq          = 395.88430144[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 807
Total_scans       = 807

X_90_width        = 9[us]
X_acq_time        = 1.048576[s]
X_angle           = 30[deg]
X_atn             = 8.4[dB]
X_pulse           = 3[us]
Irr_atn_dec       = 31.5[dB]
Irr_atn_noe       = 31.5[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 1[s]
Recvr_gain        = 60
Relaxation_delay  = 1[s]
Repetition_time   = 2.048576[s]
Temp_get          = 24.9[dC]
```

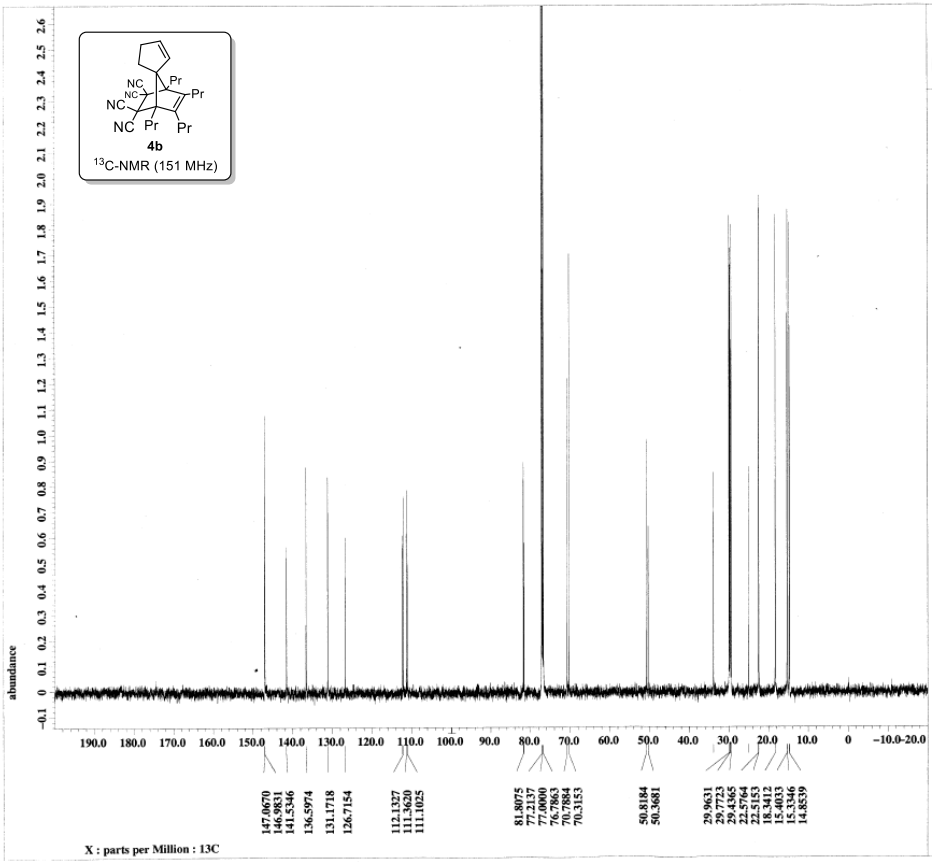


Filename = MB 799 1H-11.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#533291
Solvent = CHLOROFORM-D
Creation_time = 3-AUG-2017 14:49:48
Revision_time = 8-AUG-2017 19:01:26
Current_time = 8-AUG-2017 19:01:52

Content = MB 799 1H
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = DELTA2_NMR

Field_strength = 14.09636928[T] (600[M
X_acq_duration = 2.9097984[s]
X_domain = 1H
X_freq = 600.1723046[MHz]
X_offset = 5[ppm]
X_points = 32768
X_prescans = 1
X_resolution = 0.34366642[Hz]
X_sweep = 11.26126126[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 600.1723046[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8

X_90_width = 12.6[us]
X_acq_time = 2.9097984[s]
X_angle = 45[deg]
X_atn = 3.6[dB]
X_pulse = 6.3[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 54
Relaxation_delay = 5[s]
Repetition_time = 7.9097984[s]
Temp_get = 22[dC]



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Author = delta
Experiment = single_pulse_dec
Sample_id = S#427519
Solvent = CHLOROFORM-D
Creation_time = 8-AUG-2017 12:09:21
Revision_time = 8-AUG-2017 13:01:52
Current_time = 8-AUG-2017 13:02:06

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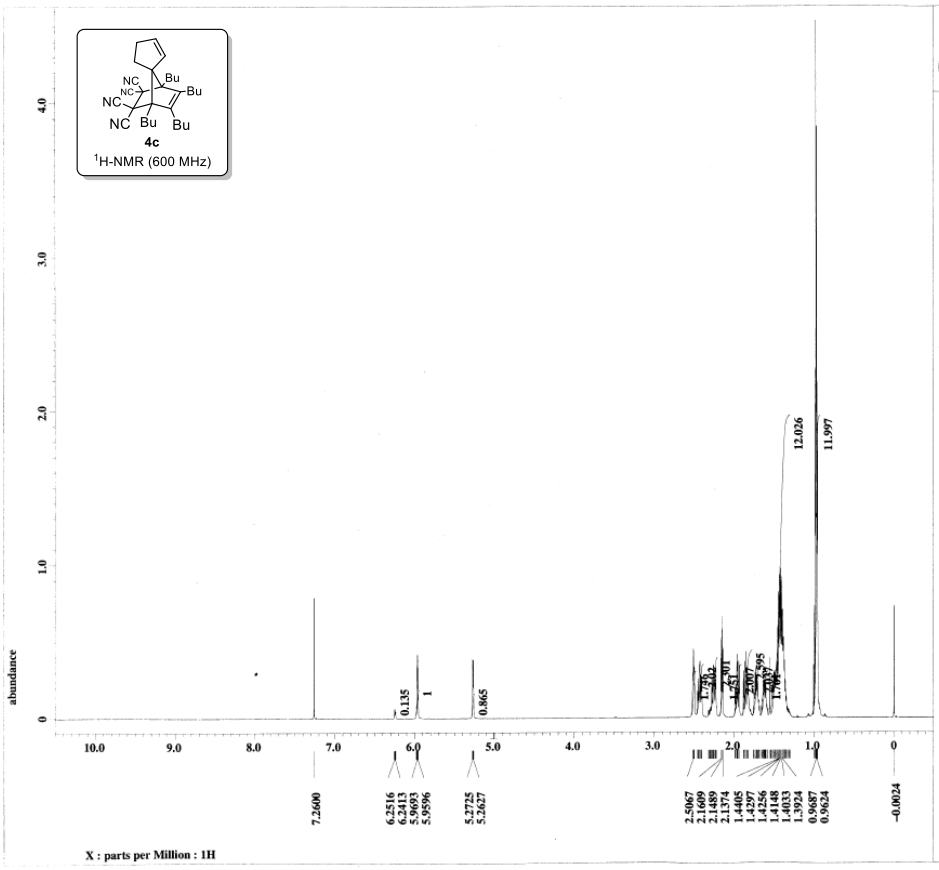
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = DELTA2_NMR

Field_strength = 14.09636928[T] (600[M
X_acq_duration = 0.868352[s]
X_domain = 13C
X_freq = 150.91343039[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.15160672[Hz]
X_sweep = 37.73584906[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 374
Total_scans = 374

X_90_width = 10.9[us]
X_acq_time = 0.868352[s]
X_angle = 30[deg]
X_atn = 7.5[dB]
X_pulse = 3.63333333[us]
Irr_atn_dec = 19.21[dB]
Irr_atn_noe = 19.21[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 78
Relaxation_delay = 2[s]
Repetition_time = 2.868352[s]
Temp_get = 22.6[dC]

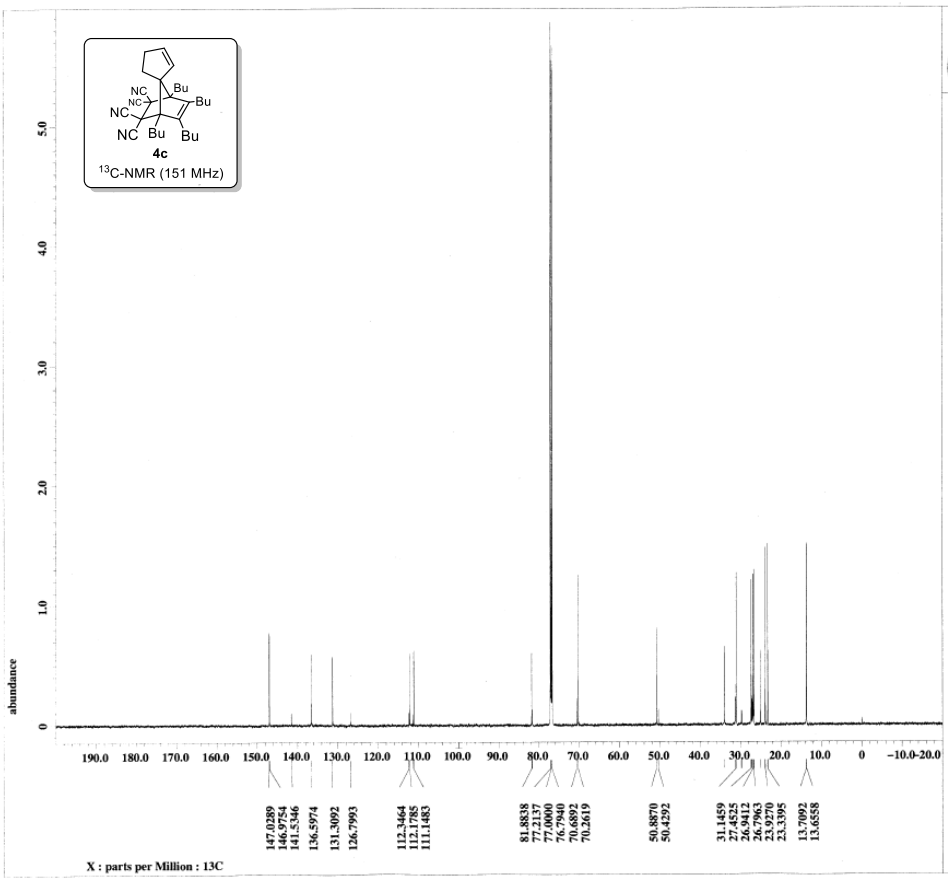



```
Filename          = MB 800 1H-6.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#342691
Solvent           = CHLOROFORM-D
Creation_time     =  2-AUG-2017 09:32:29
Revision_time     =  8-AUG-2017 12:57:10
Current_time      =  8-AUG-2017 12:57:55

Content           = MB 800 1H
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 600
Spectrometer      = DELTA2_NMR

Field_strength    = 14.09636928[T] (600[M
X_acq_duration    = 2.9097984[s]
X_domain          = 1H
X_freq            = 600.1723046[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.34366642[Hz]
X_sweep           = 11.26126126[kHz]
Irr_domain        = 1H
Irr_freq          = 600.1723046[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 600.1723046[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 12.6[us]
X_acq_time        = 2.9097984[s]
X_angle           = 45[deg]
X_atn             = 3.6[dB]
X_pulse           = 6.3[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 42
Relaxation_delay  = 5[s]
Repetition_time   = 7.9097984[s]
Temp_get          = 21.7[dC]
```

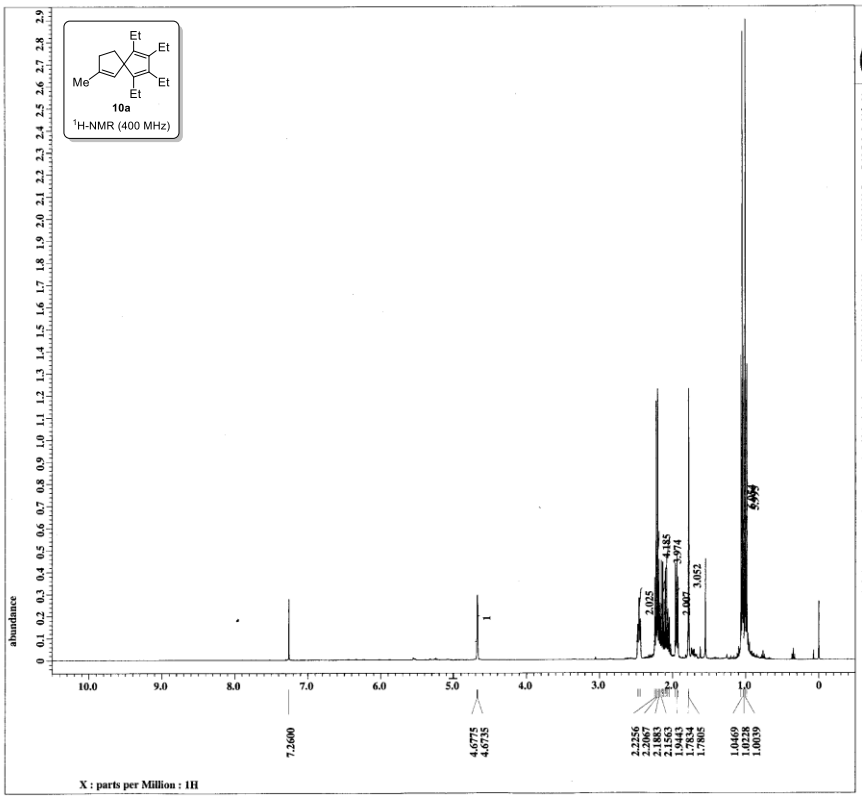



```
Filename          = MB 800 13C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#344476
Solvent           = CHLOROFORM-D
Creation_time     =  2-AUG-2017 11:52:14
Revision_time     =  2-AUG-2017 11:54:11
Current_time      =  2-AUG-2017 11:54:36

Content           = MB 800 13C
Data_format       = 1D COMPLEX
Dim_size          = 32768
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 600
Spectrometer      = DELTA2_NMR

Field_strength    = 14.09636928[T] (600[M
X_acq_duration    = 0.868352[s]
X_domain          = 13C
X_freq            = 150.91343039[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.15160672[Hz]
X_sweep           = 37.73584906[kHz]
Irr_domain        = 1H
Irr_freq          = 600.1723046[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 2902
Total_scans       = 2902

X_90_width        = 10.9[us]
X_acq_time        = 0.868352[s]
X_angle           = 30[deg]
X_atn             = 7.5[dB]
X_pulse           = 3.63333333[us]
Irr_atn_dec       = 19.21[dB]
Irr_atn_noe       = 19.21[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 80
Relaxation_delay  = 2[s]
Repetition_time   = 2.868352[s]
Temp_get          = 22.6[dC]
```



JEOL

```
Filename          = MB 758 1H c2-6.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = ##751632
Solvent           = CHLOROFORM-D
Creation_time     = 28-MAY-2017 19:53:04
Revision_time     = 28-MAY-2017 21:02:34
Current_time      = 28-MAY-2017 21:03:02

Content           = MB 758 1H c2
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = JNM-ECX400M

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 4.36731904[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 1
X_resolution      = 0.22897343[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 12.6[us]
X_acq_time        = 4.36731904[s]
X_angle           = 45[deg]
X_atn             = 2.5[dB]
X_pulse           = 6.3[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 9.36731904[s]
Temp_get          = 22.3[dC]
```

X-ray crystallographic data and refinement details for compound 4a

All measurements were made on a Rigaku R-RAXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods (SHELXS-2013/1) and refined on F^2 using SHELXL-2017/1. All caluculations were performed using the CrystalStructure crystallographic software package. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms attached to carbon atoms were refined isotropically. The cyclopentene ring were found to be disordered with two possible positions of atoms C(2) and C(24) with site occupancy factors for C(2)/C(24) = 0.53/0.47. The hydrogen atoms (H(25), H(26)) attached to atom C(2) and those (H(27), H(28)) attached to atom C(24) were also refined with the occupancy factors in line with each attached carbon atom. X-ray crystallographic data and refinement details for compound **4a** are summarized in Table S19.

Table S19. X-ray crystallographic data and refinement details for compound **4a**

	4a
Formula	$C_{23}H_{26}N_4$
FW	358.48
T / K	298
Colour, shape	Colorless, prism
Crystal size / mm	0.30 x 0.30 x 0.30
Crystal system	Monoclinic
Space group, *Z*	$P2_1/n$, 4
a / Å	10.439(3)
b / Å	12.582(4)
c / Å	15.443(6)
β / deg.	92.263(14)
V / Å^3	2026.8(11)
D_x / Mg m^{-3}	1.175
F(000)	768
μ(Mo K$_a$) / mm^{-1}	0.071
T_{min}, T_{max}	0.976, 0.982
R_{int}	0.0249
Refln./param. ratio	4626/365
$R1$ [$F_o^2 > 2\sigma(F_o^2)$]	0.0429
*wR*2 (all refln)	0.1263
GoF	1.029