Supporting Information

Metal-dependent regioselective homocoupling of stannyl- and alkyl-substituted alkynes on group 4 elements. Formation of unsymmetrical titanacyclopentadienes and symmetrical zirconacyclopentadienes.

Masayoshi Bando,[1] Kiyohiko Nakajima,[2] Zhiyi Song[1] and Tamotsu Takahashi[1]*

[1]Institute for Catalysis, Hokkaido University, Kita 21, Nishi 10, Sapporo 001-0021, Japan.
[2]Department of Chemistry, Aichi University of Education, Igaya, Kariya, Aichi 448-8542, Japan.

Correspondence to: tamotsu@cat.hokudai.ac.jp

Materials and Methods

General Information.

All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. ^{1}H NMR (at 400 or 600 MHz) and ^{13}C NMR (at 101 or 151 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane or given relative to the respective residual solvent peaks (^{1}H: $CHCl_3$ at 7.26, C_6H_6 at 7.16, ^{13}C: $CHCl_3$ at 77.0, C_6H_6 at 128.0). NMR yields were determined by using dichloromethane or mesitylene as internal standards. All yields were calculated according to the alkynes used in the formation of titanacyclopentadiene. Benzene, hexane and tetrahydrofuran were distilled from benzophenone-ketyl under nitrogen prior to use. All chemicals were obtained from commercial sources unless noted.

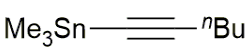
The following instruments were used for physical characterization of the compounds.

NMR	JEOL JNM-ECX400 (^{1}H: 400 MHz, ^{13}C: 101 MHz)
	JEOL JNM-ECX600 (^{1}H: 600 MHz, ^{13}C: 151 MHz)
GC	SHIMADZU GC-14B gas chromatograph
	SHIMADZU CBP1-M25-025 fused capillary column
	SHIMADZU CR-6A-Chromatopac integrator

Preparation for Stannyl-substituted Alkyne **1a** and **1b** and Diyne **1c**

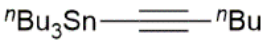
A typical procedure is given for the synthesis of **1a**. To a solution of 1-hexyne (5.74 ml, 50 mmol) in THF (100 mL) was added ^{n}BuLi (1.57 M in hexane, 35 mL, 55 mmol) dropwise at –78 °C. The reaction mixture was warmed up to 0 °C and stirred for 1h and 30 min. After Me_3SnCl (1.0 M in hexanes, 55 mL, 55mmol) was added at –78 °C, the mixture was warmed up to room temperature and stirred for 12 h. The solvent was removed under reduced pressure. **1a** was extracted with hexane and the organic phase was filtered and evaporated. Distillation of the residue gave **1a** (10.177 g, 41.5 mmol) as a colorless oil.

1-Trimethylstannyl-1-hexyne (1a)



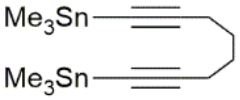
Isolated yield: 83%. CAS Registry Number [1191-12-4].
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.25 (s, 9H, satellites, $J_{HSn(119)}$ = 60.4, $J_{HSn(117)}$ = 57.7 Hz), 0.90 (t, J = 7.2 Hz, 3H), 1.35-1.45 (m, 2 H), 1.46-1.54 (m, 2 H), 2.24 (t, J = 7.1 Hz, 2 H). $^{13}C\{^1H\}$ NMR(101 MHz, $CDCl_3$): δ –7.8 (s, satellites, $J_{CSn(119)}$ = 404.5 Hz, $J_{CSn(117)}$ = 387.2 Hz), 13.6, 19.8, 21.9, 31.1, 81.8, 111.1. HRMS(FI) Calcd for $C_9H_{18}Sn$, $[M]^+$: 246.04318. Found: 246.04400.

1-Tributylstannyl-1-hexyne (1b)



Isolated yield: 88%. CAS Registry Number [35864-20-1].
^{1}H NMR (396 MHz, $CDCl_3$): δ 0.87-0.92 (two peaks (triplet) were overlapped, 12H), 0.93-0.97 (m, 6H), 1.26-1.64 (m, 16H), 2.24 (t, J = 6.9 Hz, 2H). $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): δ 10.9 (s, satellites, $J_{CSn(119)}$ = 383.4 Hz, $J_{CSn(117)}$ = 366.2 Hz), 13.6, 13.7, 19.8, 21.8, 27.0, 28.9, 31.2, 81.2, 111.9. HRMS(FD) Calcd for $C_{18}H_{36}Sn$, $[M]^+$: 372.18421. Found: 372.18505.

1,8-Bis(trimethylstannyl)-1,7-octadiyne (1c)

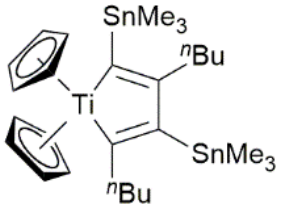


NMR yield: 71%. CAS Registry Number [178114-74-4].
^{1}H NMR (396 MHz, $CDCl_3$): δ 0.25 (s, 18H, satellites, $J_{HSn(119)}$ = 60.3, $J_{HSn(117)}$ = 57.8 Hz), 1.60-1.64 (m, 4H), 2.24-2.29 (m, 4H). $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): δ –7.8 (s, satellites, $J_{CSn(119)}$ = 405.3 Hz, $J_{CSn(117)}$ = 387.2 Hz), 19.6, 28.1, 82.3, 110.5. HRMS(FD) Calcd for $C_{14}H_{27}Sn_2$, $[M + H]^+$: 433.01571. Found: 433.01573.

Synthesis of Titanacyclopentadiene **2a**, **2b** and **7c**.

A typical procedure is given for the synthesis of **2a**. To a solution of Cp_2TiCl_2 (156 mg, 0.625 mmol) in THF (2.5 mL) was added ^{n}BuLi (1.57 M in hexane, 0.80 mL, 1.25 mmol) dropwise at –78 ºC. The reaction mixture was stirred for 1 h at the same temperature. After addition of **1a** (245 mg, 1 mmol), the mixture was warmed up to –10 ºC and stirred for 3 h to form bis(cyclopentadienyl)-titanacyclopentadiene **2a** (dark purple solution). The solvent was removed under reduced pressure. **2a** was extracted with hexane and the organic phase was filtered and evaporated.

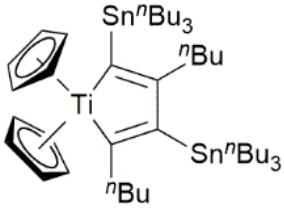
1,1-Bis(cyclopentadienyl)-2,4-dibutyl-3,5-bis(trimethylstannyl)-1-titanacyclopentadiene (2a)



NMR yield: 92%.

^{1}H NMR (396 MHz, $CDCl_3$): δ 0.04 (s, 9H, satellites, $J_{HSn(119)}$ = 48.3, $J_{HSn(117)}$ = 46.9 Hz), 0.15 (s, 9H, satellites, $J_{HSn(119)}$ = 48.3, $J_{HSn(117)}$ = 47.2 Hz), 0.90-0.96 (m, 6H), 1.18-1.31 (m, 8H), 1.67-1.71 (m, 2H), 1.80-1.84 (m, 2H), 6.13 (s, 10H). ^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$): δ –5.6 (s, satellites, $J_{CSn(119)}$ = 290.1 Hz, $J_{CSn(117)}$ = 277.5 Hz), –4.0 (s, satellites, $J_{CSn(119)}$ = 283.2 Hz, $J_{CSn(117)}$ = 271.8 Hz), 14.1, 14.5, 22.9, 23.6, 33.9, 34.1, 41.5, 43.1, 112.6, 134.8 (s, satellites, $J_{CSn(119)}$ = 367.8 Hz, $J_{CSn(117)}$ = 350.6 Hz), 141.8, 214.9 (s, satellites, $J_{CSn(119)}$ = 268.4 Hz, $J_{CSn(117)}$ = 257.0 Hz), 225.1. HRMS(FD) Calcd for $C_{28}H_{46}Sn_2Ti$, $[M]^+$: 668.11329. Found: 668.11601.

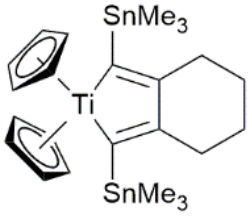
1,1-Bis(cyclopentadienyl)-2,4-dibutyl-3,5-bis(tributylstannyl)-1-titanacyclopentadiene (2b)



NMR yield: 93%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69-0.76 (m, 6H), 0.81-0.87 (m, 6H), 0.90-0.97 (m, 24H), 1.19-1.58 (m, 32H), 1.63-1.67 (m, 2H), 1.80-1.84 (m, 2H), 6.09 (s, 10H). ^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$): δ 12.1, 13.4, 13.7, 13.8, 14.2, 14.5, 23.3, 23.7, 27.7, 27.8, 29.5, 29.5, 34.3, 34.4, 42.0, 44.4, 112.5, 133.0 (s, satellites, $J_{CSn(119)}$ = 295.9 Hz, $J_{CSn(117)}$ = 282.1 Hz), 140.7, 215.0 (s, satellites, $J_{CSn(119)}$ = 203.5 Hz, $J_{CSn(117)}$ = 195.4 Hz), 224.8. HRMS(FD) Calcd for $C_{46}H_{82}Sn_2Ti$, $[M]^+$: 920.39566. Found: 920.39662.

8,8-Bis(cyclopentadienyl)-7,9-bis(trimethylstannyl)-8-titanabicyclo[4,3,0]-1,6-nonadiene (7c)



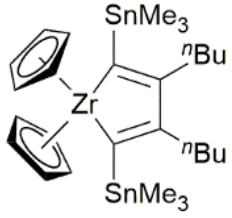
NMR yield: 94%.

^{1}H NMR (396 MHz, $CDCl_3$): δ 0.02 (s, 18H, satellites, $J_{HSn(119)}$ = 49.2, $J_{HSn(117)}$ = 47.1 Hz), 1.33-1.41 (m, 4H), 1.76-1.83 (m, 4H), 6.11 (s, 10H). ^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$): δ –6.0 (s, satellites, $J_{CSn(119)}$ = 294.7 Hz, $J_{CSn(117)}$ = 281.0 Hz), 23.5, 35.5, 113.3, 142.8 (s, satellites, $J_{CSn(119)}$ = 139.3 Hz, $J_{CSn(117)}$ = 133.6 Hz), 224.2 (s, satellites, $J_{CSn(119)}$ = 267.2 Hz, $J_{CSn(117)}$ = 254.7 Hz). HRMS(FD) Calcd for $C_{24}H_{36}Sn_2Ti$, $[M]^+$: 610.03489. Found: 610.03390.

Synthesis of Zirconacyclopentadiene **3a**, **3b** and **8a**.

A typical procedure is given for the synthesis of **3a**. To a solution of Cp_2ZrCl_2 (183 mg, 0.625 mmol) in THF (2.5 mL) was added ^{n}BuLi (1.57 M in hexane, 0.80 mL, 1.25 mmol) dropwise at –78 ºC. The reaction mixture was stirred for 1 h at the same temperature. After addition of **1a** (245 mg, 1 mmol), the mixture was warmed up to 20 ºC and stirred for 24 h to form bis(cyclopentadienyl)-zirconacyclopentadiene **3a** (red solution). The solvent was removed under reduced pressure. **3a** was extracted with hexane and the organic phase was filtered and evaporated.

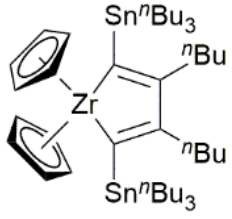
1,1-Bis(cyclopentadienyl)-3,4-dibutyl-2,5-bis(trimethylstannyl)-1-zirconacyclopentadiene (3a)



NMR yield: 90%.

^{1}H NMR (396 MHz, $CDCl_3$): δ 0.10 (s, 18H, satellites, $J_{HSn(119)}$ = 48.7, $J_{HSn(117)}$ = 46.4 Hz), 0.94 (t, J = 7.0 Hz, 6H), 1.27-1.40 (m, 8H), 1.79-1.89 (m, 4H), 6.16 (s, 10H). $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): δ –5.9, 14.1, 23.2, 33.9, 42.4, 111.5, 154.2 (s, satellites, $J_{CSn(119)}$ = 145.0 Hz, $J_{CSn(117)}$ = 139.3 Hz), 209.0 (s, satellites, $J_{CSn(119)}$ = 254.7 Hz, $J_{CSn(117)}$ = 243.3 Hz). HRMS(ESI) Calcd for $C_{28}H_{47}Sn_2Zr$, $[M + H]^+$: 711.07764. Found: 711.07619.

1,1-Bis(cyclopentadienyl)-3,4-dibutyl-2,5-bis(tributylstannyl)-1-zirconacyclopentadiene (3b)

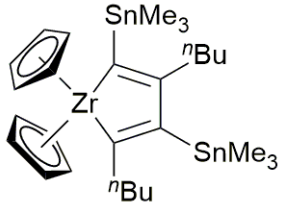


NMR yield: 96%.

^{1}H NMR (396 MHz, $CDCl_3$): δ 0.73-0.88 (m, 12H), 0.92-1.02 (m, 24H), 1.30-1.64 (m, 32H), 1.77-1.87 (m, 4H), 6.10 (s, 10H). $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): δ 12.0, 13.7, 14.1, 23.3, 27.7, 29.6, 33.8, 43.7, 111.5, 152.1 (s, satellites, $J_{CSn(119)}$ = 130.2 Hz, $J_{CSn(117)}$ = 124.5 Hz), 208.7 (s, satellites, $J_{CSn(119)}$ = 201.0 Hz, $J_{CSn(117)}$ = 193.0 Hz). HRMS(ESI) Calcd for $C_{46}H_{83}Sn_2Zr$, $[M + H]^+$: 965.36061. Found: 965.35993.

When the reaction mixture was stirred for 3 h instead of 24 h, the mixture of **3a** (57% NMR yield) and **8a** (34% NMR yield) was obtained.

1,1-Bis(cyclopentadienyl)-2,4-dibutyl-3,5-bis(trimethylstannyl)-1-zirconacyclopentadiene (8a)



NMR yield: 34%.

^{1}H NMR (600 MHz, $CDCl_3$): δ 0.18 (s, 9H, satellite peaks overlapped other peaks.), 0.21 (s, 9H, satellites, $J_{HSn(119)}$ = 49.2, $J_{HSn(117)}$ = 47.1 Hz), 0.93-0.96 (3H, The peaks overlapped the peaks of **3a**.), 1.00-1.02 (3H, The peaks overlapped other peaks.), 1.27-1.41 (m, 8H, The peaks overlapped the peaks of **3a**.), 1.99-2.01 (m, 2H), 2.47-2.49(m, 2H), 6.00 (s, 10H). $^{13}C\{^1H\}$ NMR(151 MHz, $CDCl_3$): δ –6.6, –4.0, 14.2, 14.3, 22.8, 23.1, 32.4, 33.6, 46.4, 49.1, 109.3, 129.0, 140.6, 194.7, 215.9.

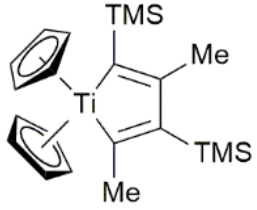
^{1}H NMR Monitoring Reaction of Alkyne **1a** with Cp_2ZrBu_2

To a solution of Cp_2ZrCl_2 (183 mg, 0.625 mmol) in *d*-THF (2.5 mL) was added ^{n}BuLi (1.57 M in hexane, 0.80 mL, 1.25 mmol) dropwise at –78 ºC. The reaction mixture was stirred for 1 h at the same temperature. After addition of **1a** (245 mg, 1 mmol) and mesitylene (69.5 μL, 0.50 mmol), the mixture was warmed up to 20 ºC and monitored by ^{1}H NMR. The ^{1}H NMR monitoring reaction showed that unsymmetrical complex **8a** was converted into symmetrical complex **3a** in 82% yield (Figure S24).

Reactions of Silyl-substituted Alkyne **4** with Cp_2TiBu_2

To a solution of Cp_2TiCl_2 (156 mg, 0.625 mmol) in THF (2.5 mL) was added ^{n}BuLi (1.57 M in hexane, 0.80 mL, 1.25 mmol) dropwise at –78 ºC. The reaction mixture was stirred for 1 h at the same temperature. After addition of 1-trimethylsilyl-1-propyne **4** (150 μL, 1 mmol), the mixture was warmed up to –10 ºC and stirred for 3 h, which gave a mixture of bis(cyclopentadienyl)-titanacyclopentadiene **5** (67% NMR yield) and **6** (19% NMR yield). When the reaction mixture was warmed up to 40 ºC and stirred for 24 h, **5** was completely converted into **6** (46% NMR yield). Column chromatography on alumina (eluent: benzene) and crystallization from toluene at –30 ºC afforded fine crystals of **6** for X-ray analysis. X-ray structure and crystallographic data of **6** were shown in Figure S1 and Table S1.

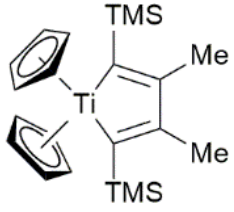
1,1-Bis(cyclopentadienyl)-2,4-dimethyl-3,5-bis(trimethylsilyl)-1-titanacyclopentadiene (5)



NMR yield: 67%.

^{1}H NMR (396 MHz, $CDCl_3$): δ –0.06 (s, 9H), 0.14 (s, 9H), 1.46 (s, 3H), 1.63 (s, 3H), 6.14 (s, 10H). $^{13}C\{^1H\}$ NMR(101 MHz, $CDCl_3$): δ 2.7, 4.0, 24.8, 27.4, 112.4, 139.7, 140.4, 209.0, 225.2.

1,1-Bis(cyclopentadienyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-titanacyclopentadiene (6)



NMR yield: 19% (–10 ºC, 3 h).

NMR yield: 46% (40 ºC, 24 h). Isolated yield: 23%.

CAS Registry Number [148540-24-3].

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.01 (s, 18H), 1.47 (s, 6H), 6.16 (s, 10H). $^{13}C\{^1H\}$ NMR(101 MHz, $CDCl_3$): δ 2.8, 23.3, 112.9, 138.4, 216.7.

X-ray Crystallographic Studies

All measurements were made on a Rigaku R-AXIS 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-2018/3. All caluculations were performed using the CrystalStructure crystallographic software package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to C(5) and C(6) atoms were located by difference Fourier maps and refined isotropically. The other hydrogen atoms were refined using the riding model. X-ray crystallographic data and refinement detail for compound **6** is summarized in Table S1.

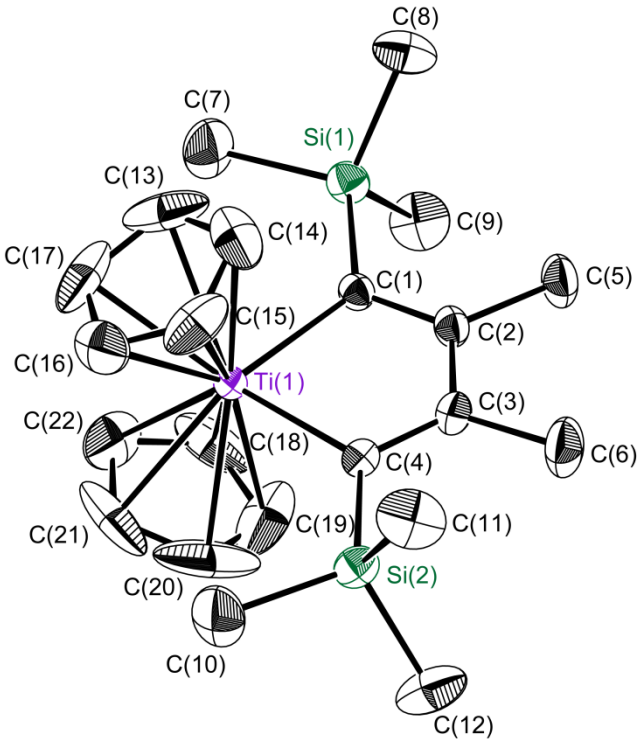


Fig. S1. X-ray Structure of **6**. All hydrogen atoms are omitted for clarity.

Table S1. X-ray Crystallographic Data and Refinement Details for Titanacyclopentadiene **6**.

	6
Formula	$C_{22}H_{34}Si_2Ti$
FW	402.57
T / K	298
Colour, shape	Orange, prism
Crystal size / mm	0.50 x 0.30 x 0.20
Crystal system	Triclinic
Space group, *Z*	*P*-1, 2
a / Å	9.709(5)
b / Å	10.178(6)
c / Å	12.212(6)
α / deg.	96.05(2)
β / deg.	95.99(2)
γ / deg.	104.28(2)
V / Å^3	1152.3(10)
D_x / Mg m^{-3}	1.160
F(000)	432
μ(Mo K$_a$) / mm^{-1}	0.478
T_{min}, T_{max}	0.7960, 0.9104
R_{int}	0.0231
Refln./param. ratio	5222/250
*R*1 [$F_o^2 > 2\sigma(F_o^2)$]	0.0430
*wR*2 (all refln)	0.1254
GoF	1.078

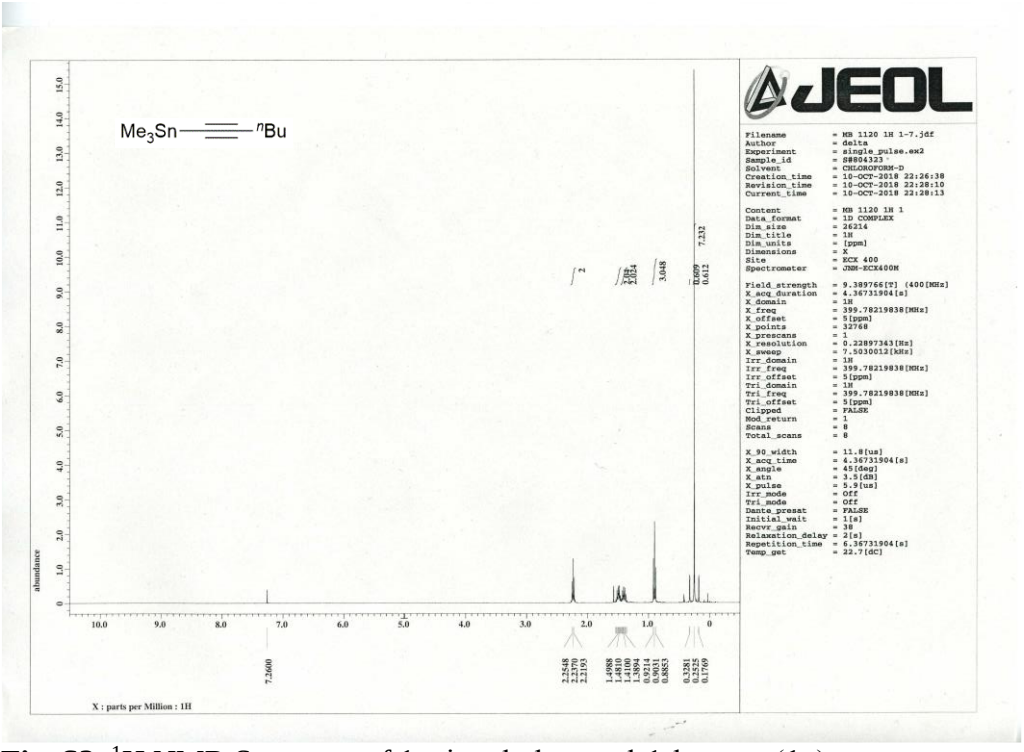


Fig. S2. ^{1}H NMR Spectrum of 1-trimethylstannyl-1-hexyne (**1a**).

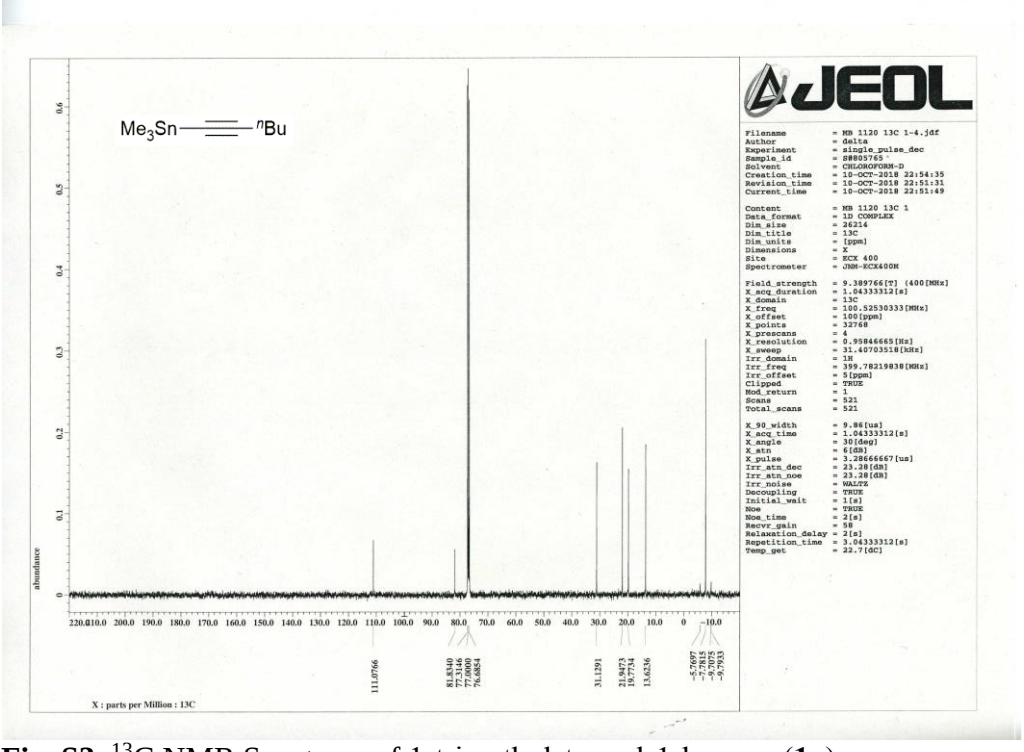


Fig. S3. ^{13}C NMR Spectrum of 1-trimethylstannyl-1-hexyne (**1a**).

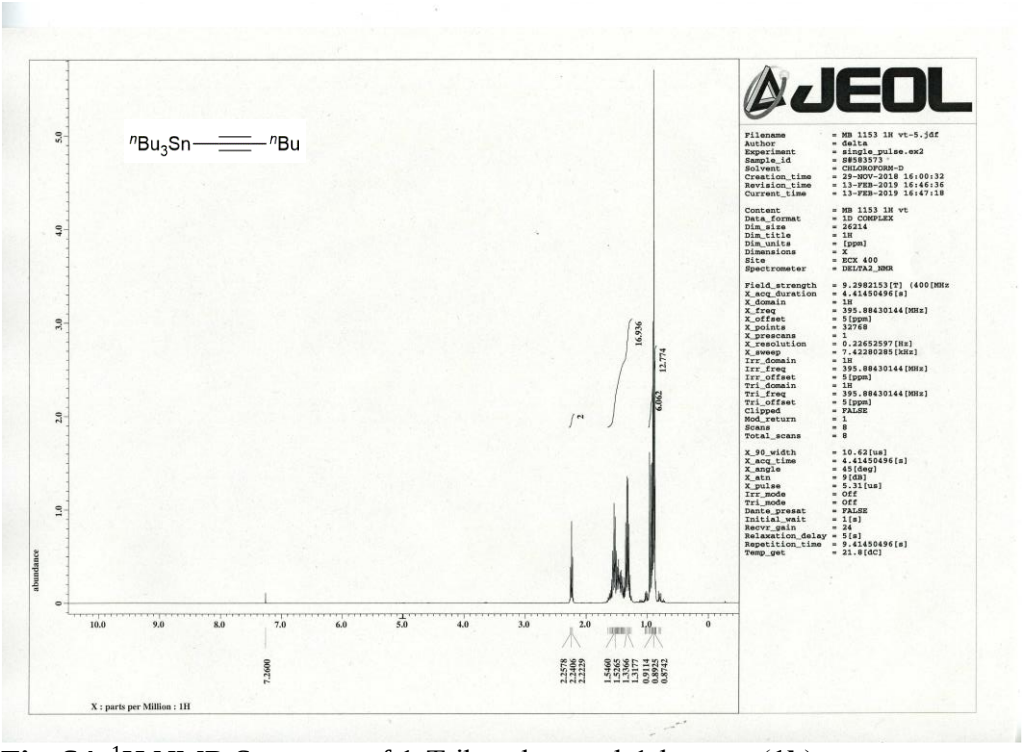


Fig. S4. ^{1}H NMR Spectrum of 1-Tributylstannyl-1-hexyne (**1b**).

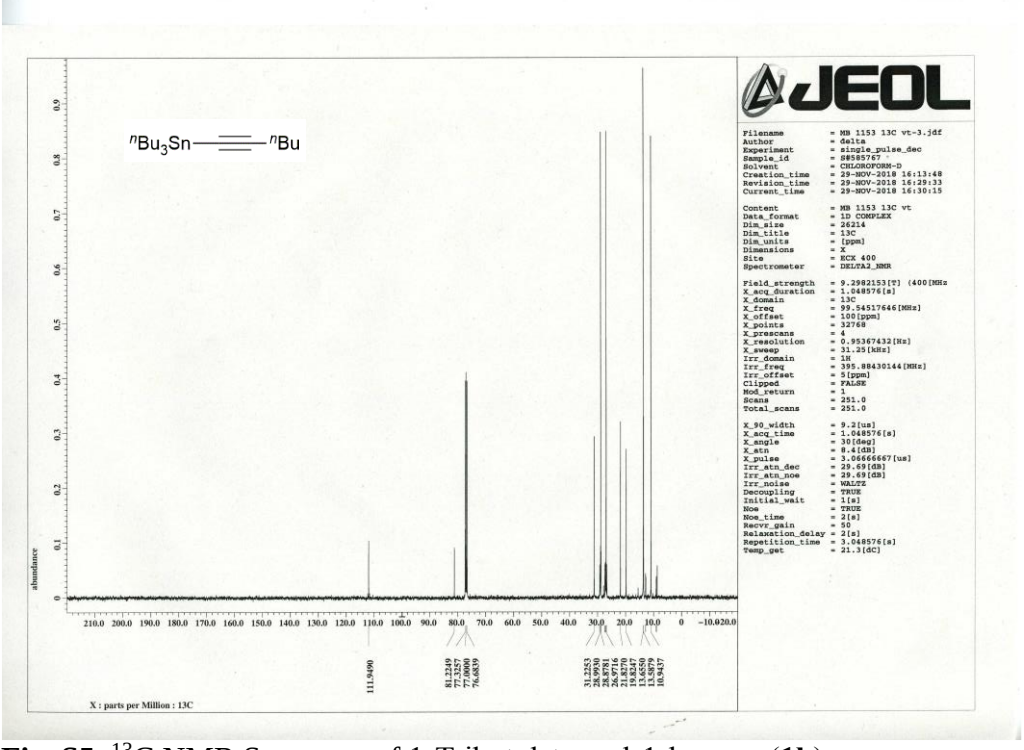


Fig. S5. ^{13}C NMR Spectrum of 1-Tributylstannyl-1-hexyne (**1b**).

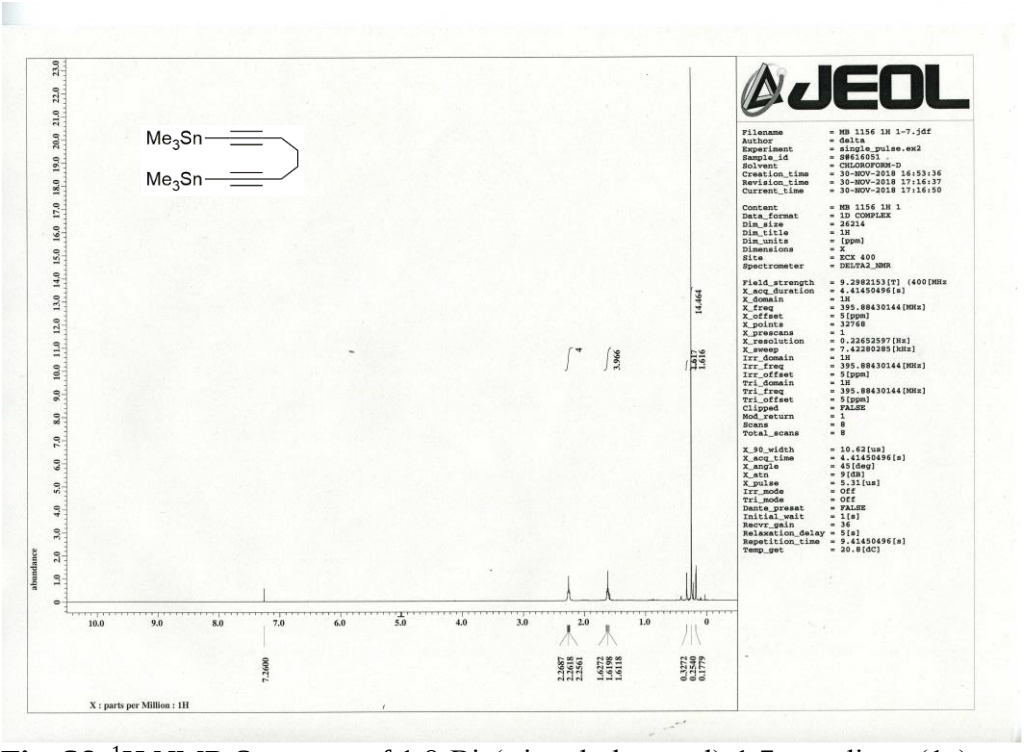


Fig. S6. ^{1}H NMR Spectrum of 1,8-Bis(trimethylstannyl)-1,7-octadiyne (**1c**).

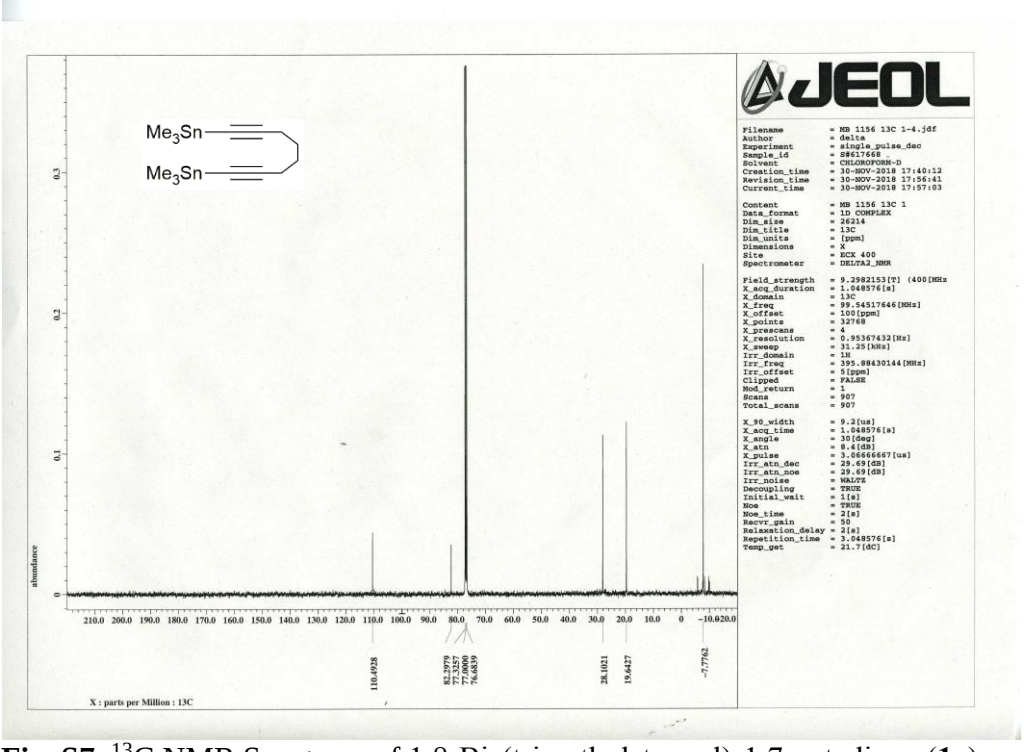


Fig. S7. ^{13}C NMR Spectrum of 1,8-Bis(trimethylstannyl)-1,7-octadiyne (**1c**).

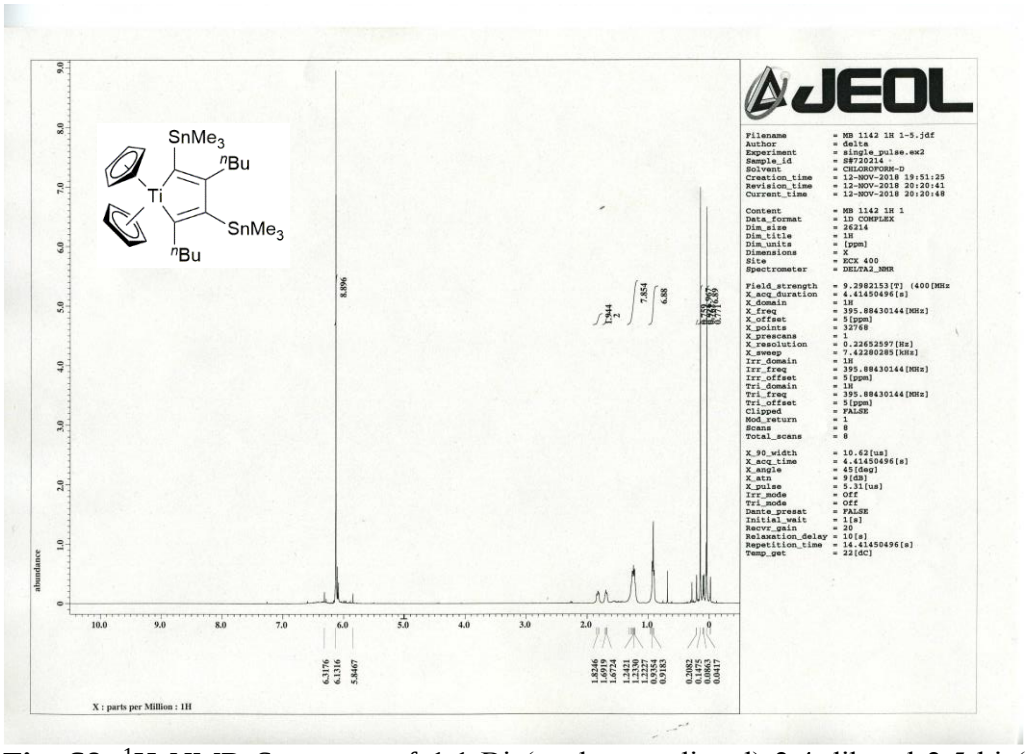


Fig. S8. ^{1}H NMR Spectrum of 1,1-Bis(cyclopentadienyl)-2,4-dibutyl-2,5-bis(trimethylstannyl)-1-titanacyclopentadiene (**2a**).

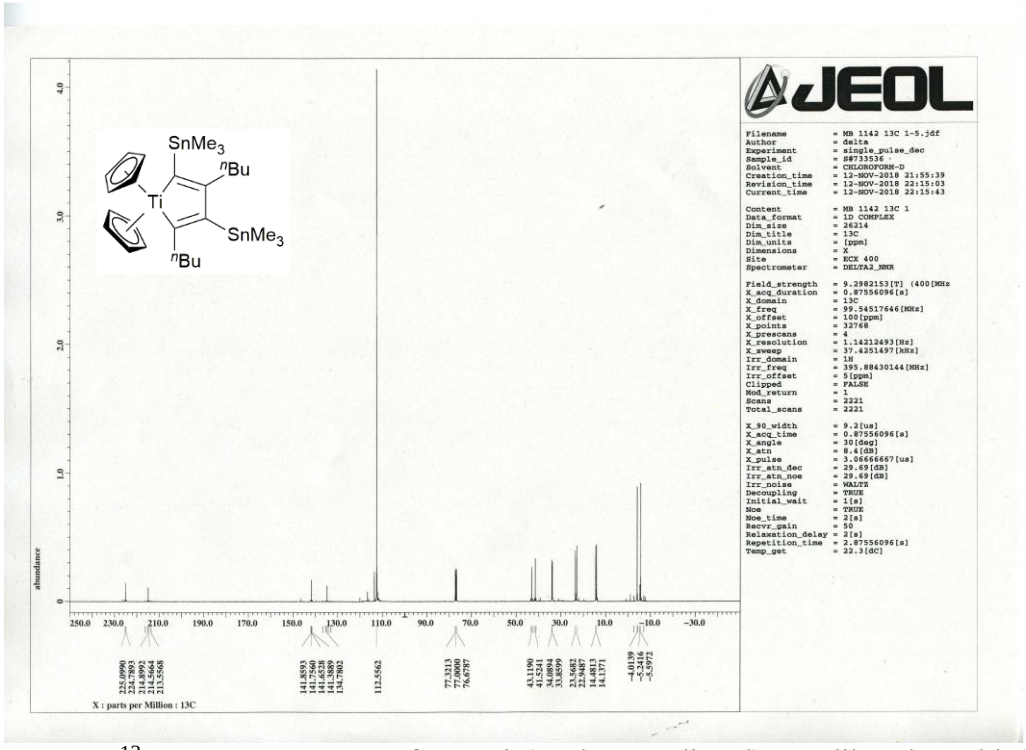


Fig. S9. ^{13}C NMR Spectrum of 1,1-Bis(cyclopentadienyl)-2,4-dibutyl-2,5-bis(trimethylstannyl)-1-titanacyclopentadiene (**2a**).

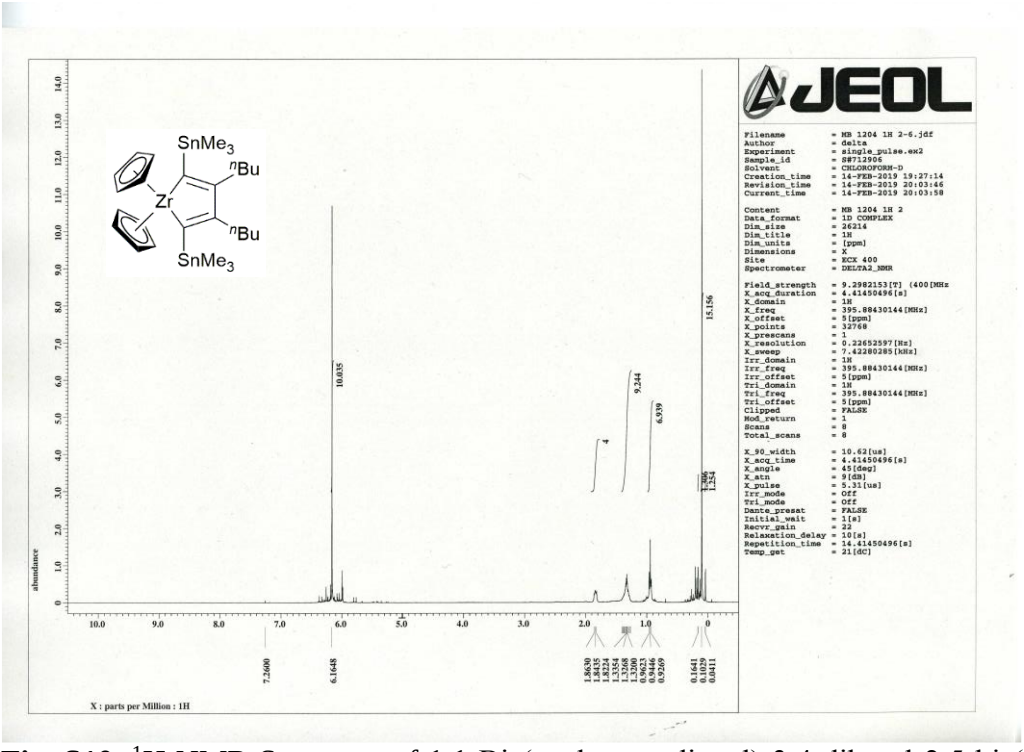


Fig. S10. ^{1}H NMR Spectrum of 1,1-Bis(cyclopentadienyl)-3,4-dibutyl-2,5-bis(trimethylstannyl)-1-zirconacyclopentadiene (**3a**).

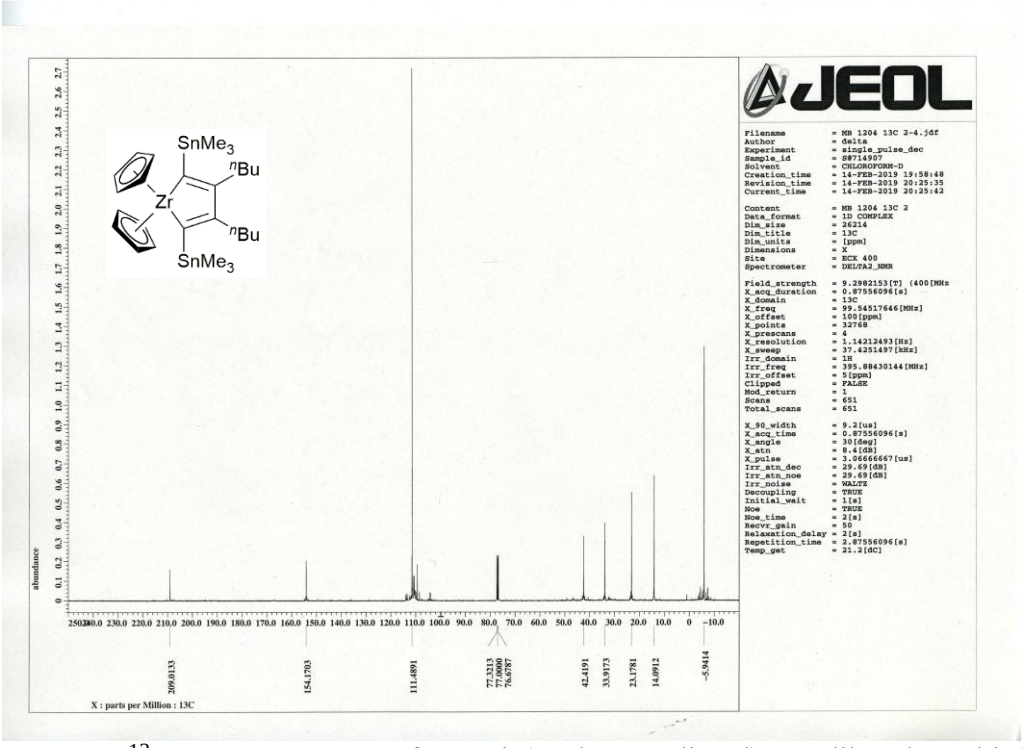


Fig. S11. ^{13}C NMR Spectrum of 1,1-Bis(cyclopentadienyl)-3,4-dibutyl-2,5-bis(trimethylstannyl)-1-zirconacyclopentadiene (**3a**).

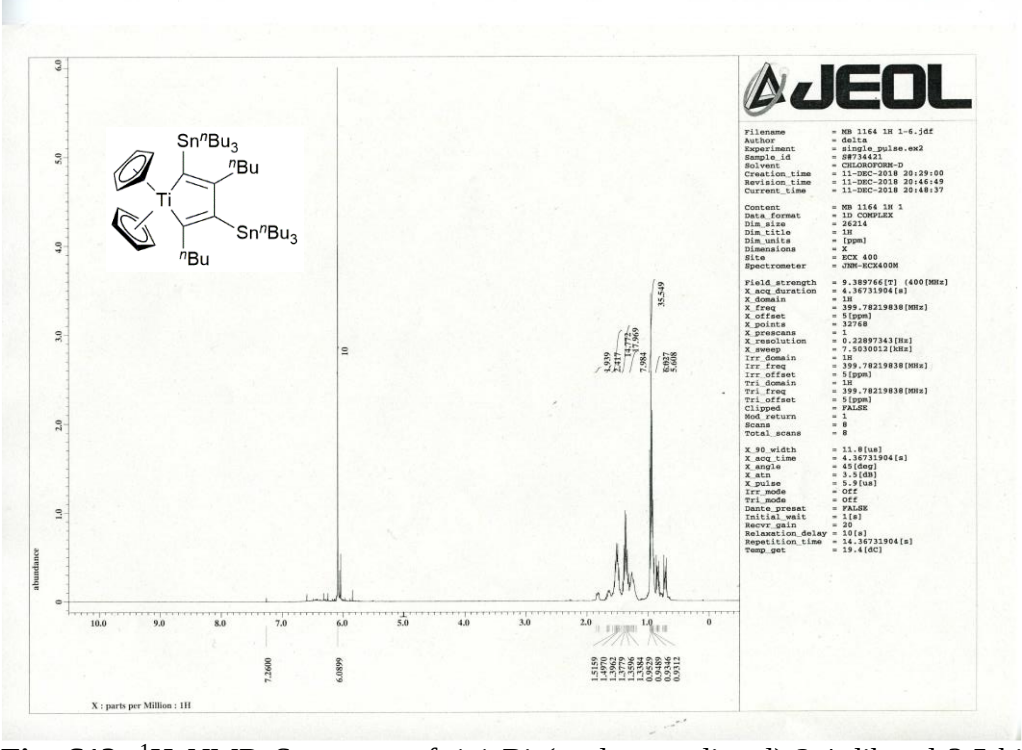


Fig. S12. ^{1}H NMR Spectrum of 1,1-Bis(cyclopentadienyl)-2,4-dibutyl-3,5-bis(tributylstannyl)-1-titanacyclopentadiene (**2b**).

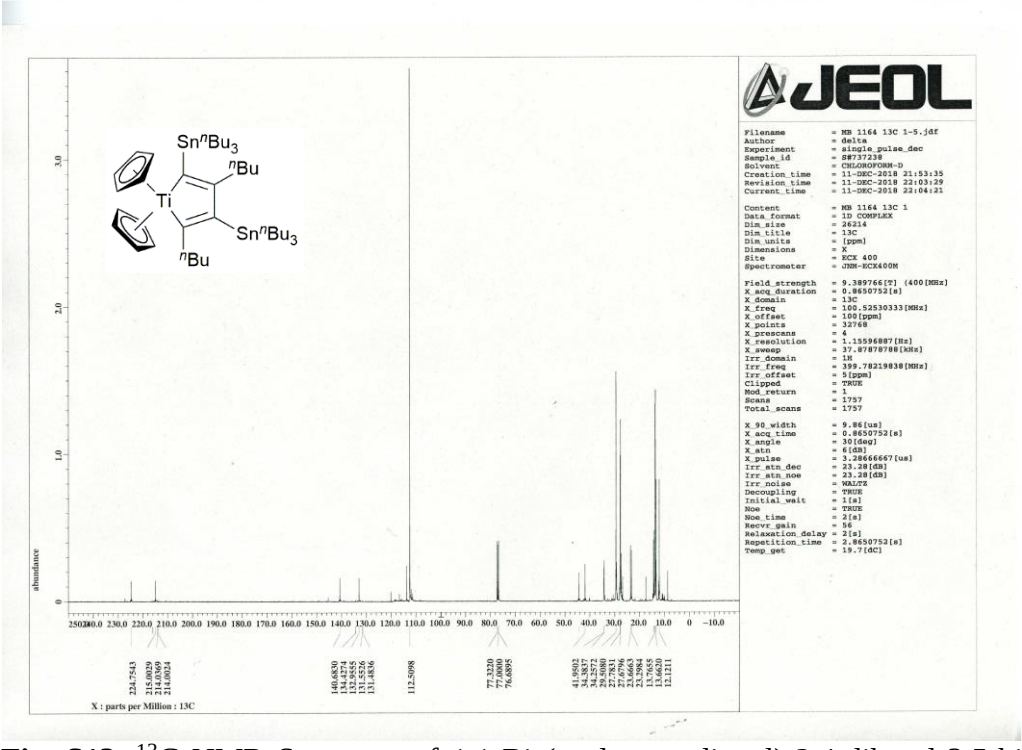


Fig. S13. ^{13}C NMR Spectrum of 1,1-Bis(cyclopentadienyl)-2,4-dibutyl-3,5-bis(tributylstannyl)-1-titanacyclopentadiene (**2b**).

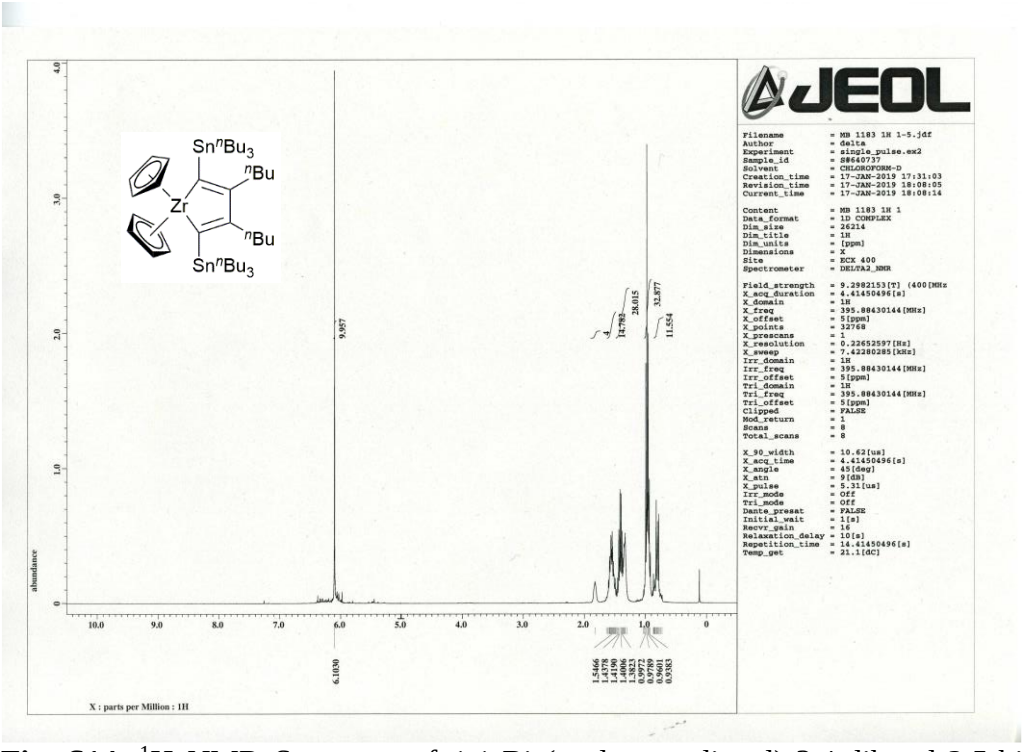


Fig. S14. ^{1}H NMR Spectrum of 1,1-Bis(cyclopentadienyl)-3,4-dibutyl-2,5-bis(tributylstannyl)-1-zirconacyclopentadiene (**3b**).

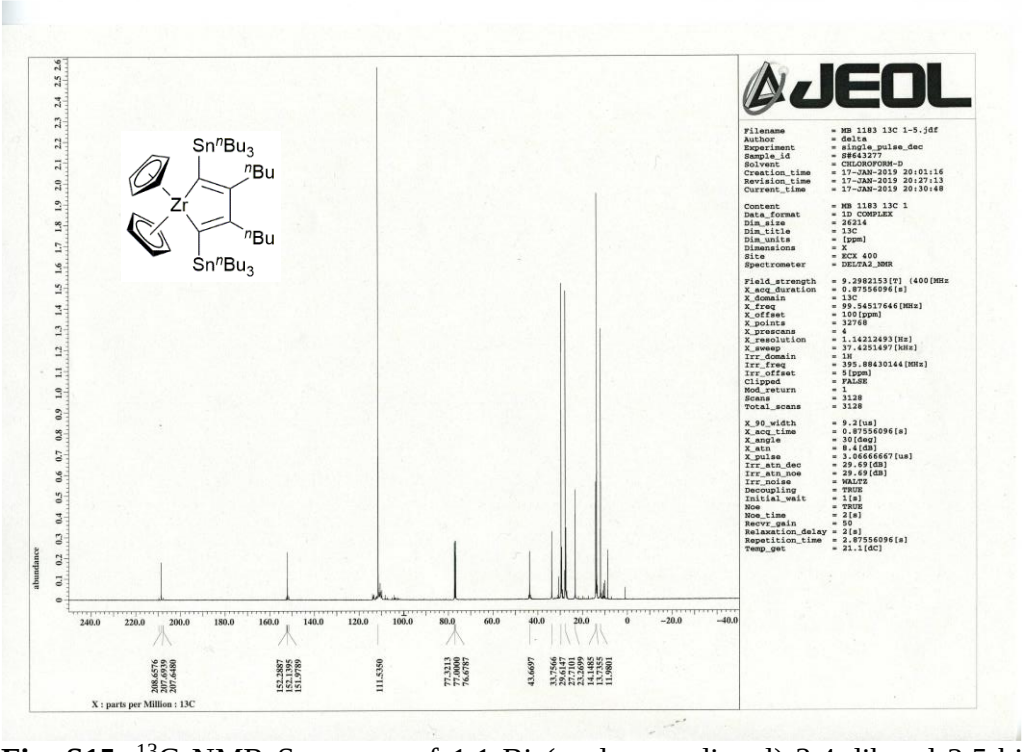


Fig. S15. ^{13}C NMR Spectrum of 1,1-Bis(cyclopentadienyl)-3,4-dibutyl-2,5-bis(tributylstannyl)-1-zirconacyclopentadiene (**3b**).

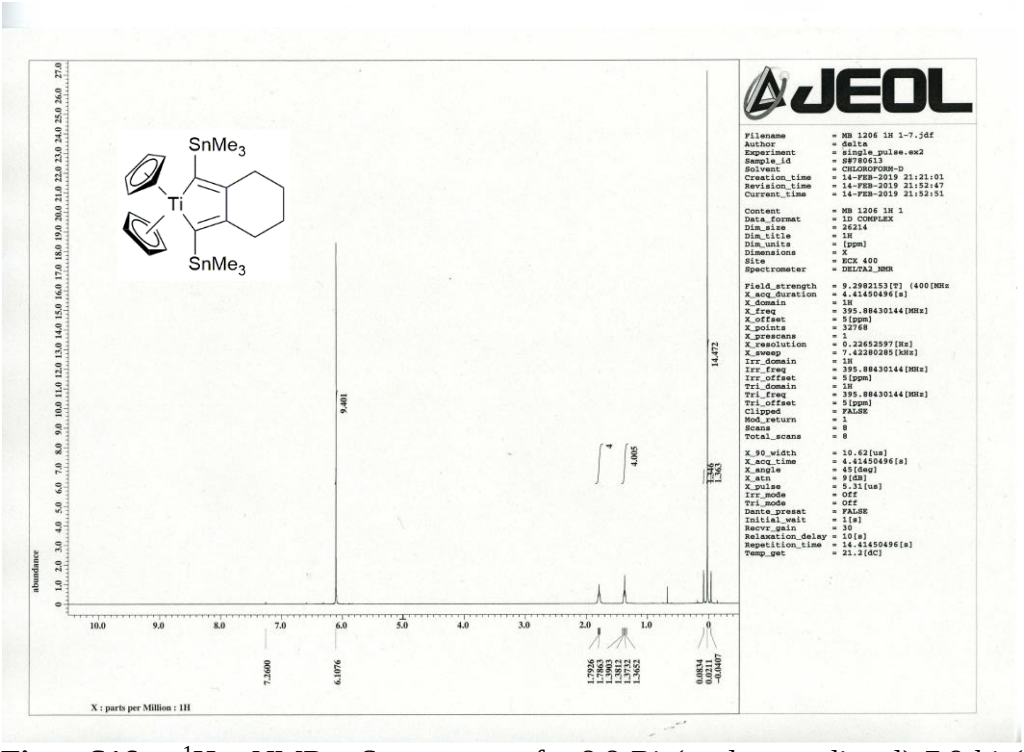


Fig. S16. ^{1}H NMR Spectrum of 8,8-Bis(cyclopentadienyl)-7,9-bis(trimethylstannyl)-8-titanabicyclo[4,3,0]-1,6-nonadiene (**7c**).

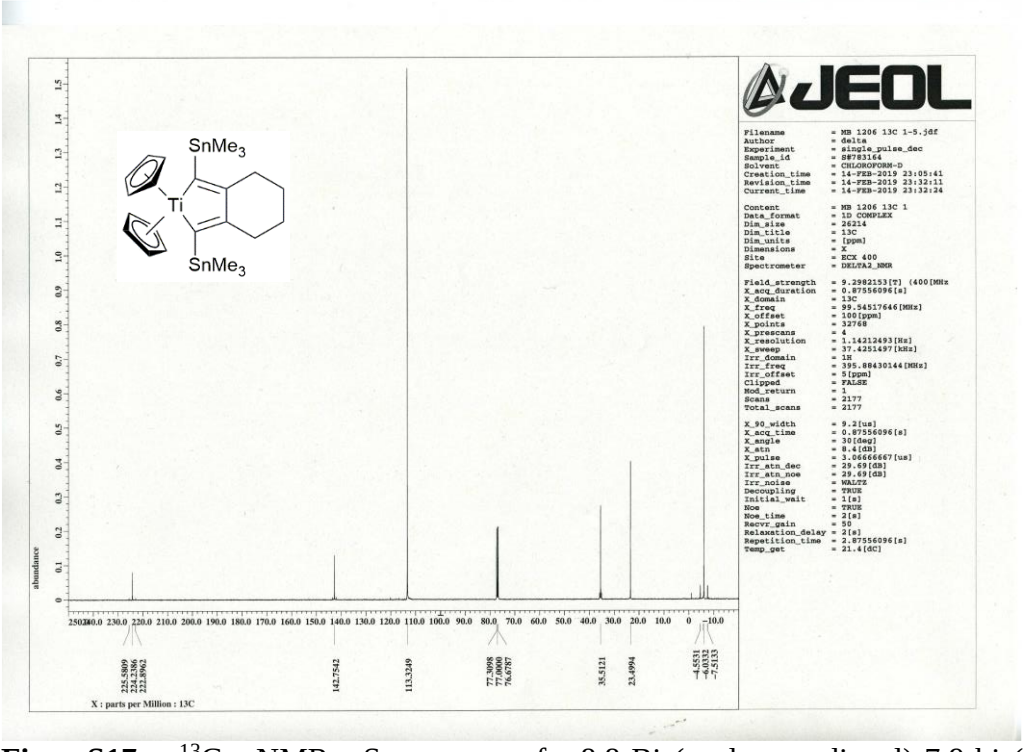


Fig. S17. ^{13}C NMR Spectrum of 8,8-Bis(cyclopentadienyl)-7,9-bis(trimethylstannyl)-8-titanabicyclo[4,3,0]-1,6-nonadiene (**7c**).

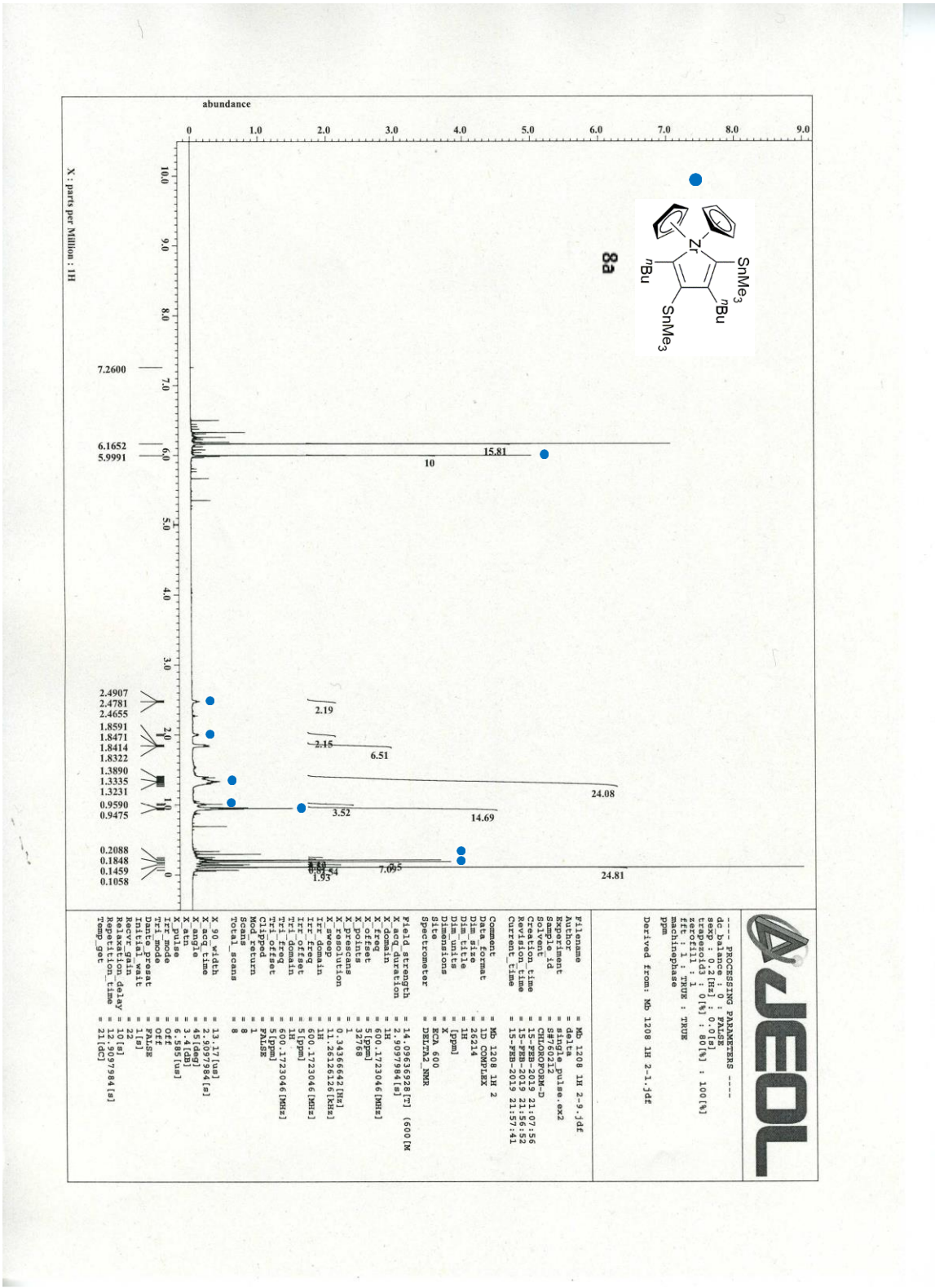


Fig. S18. ^{1}H NMR Spectrum of a mixture of **3a** and **8a**.

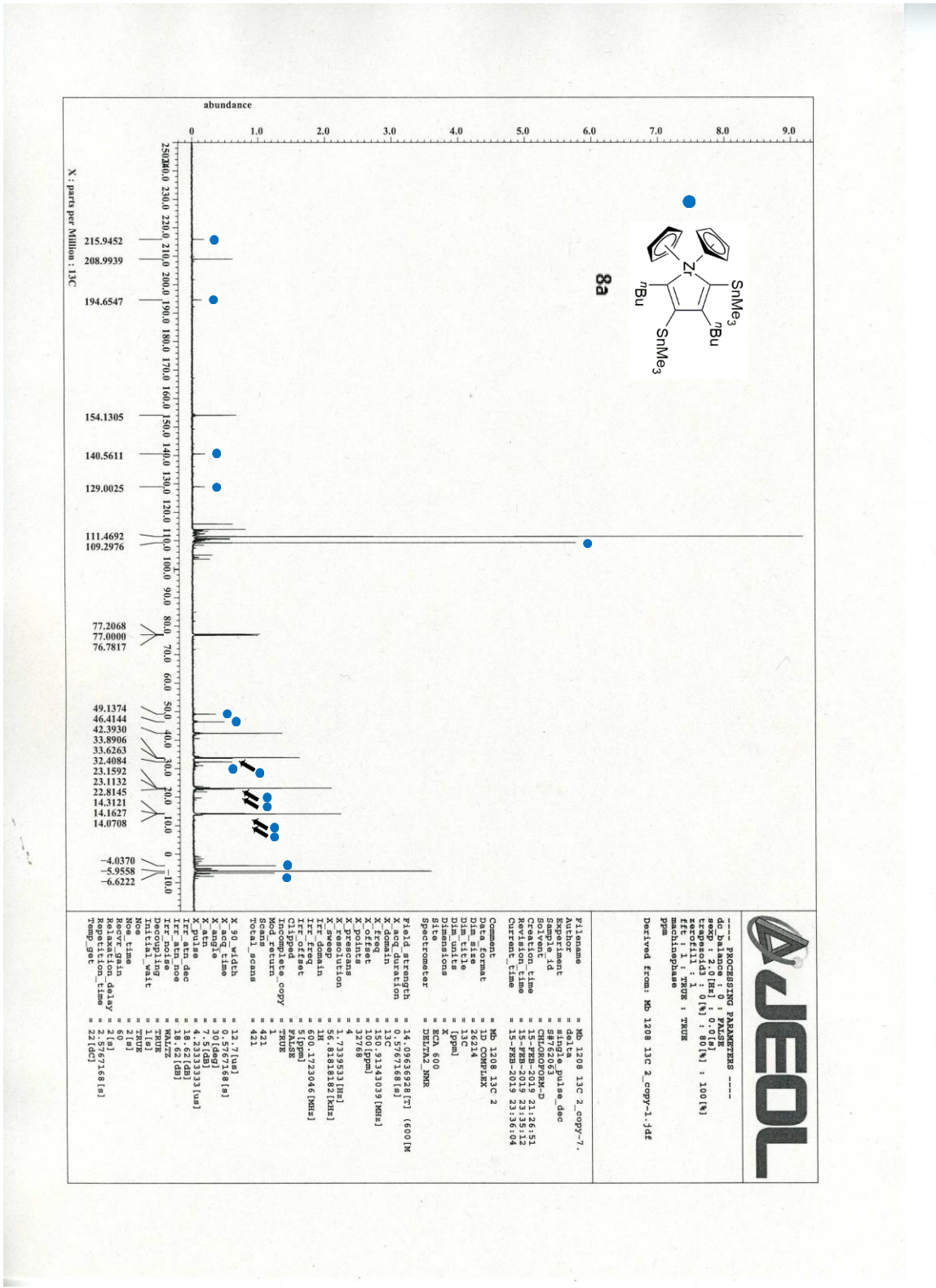


Fig. S19. ^{13}C NMR Spectrum of a mixture of **3a** and **8a**.

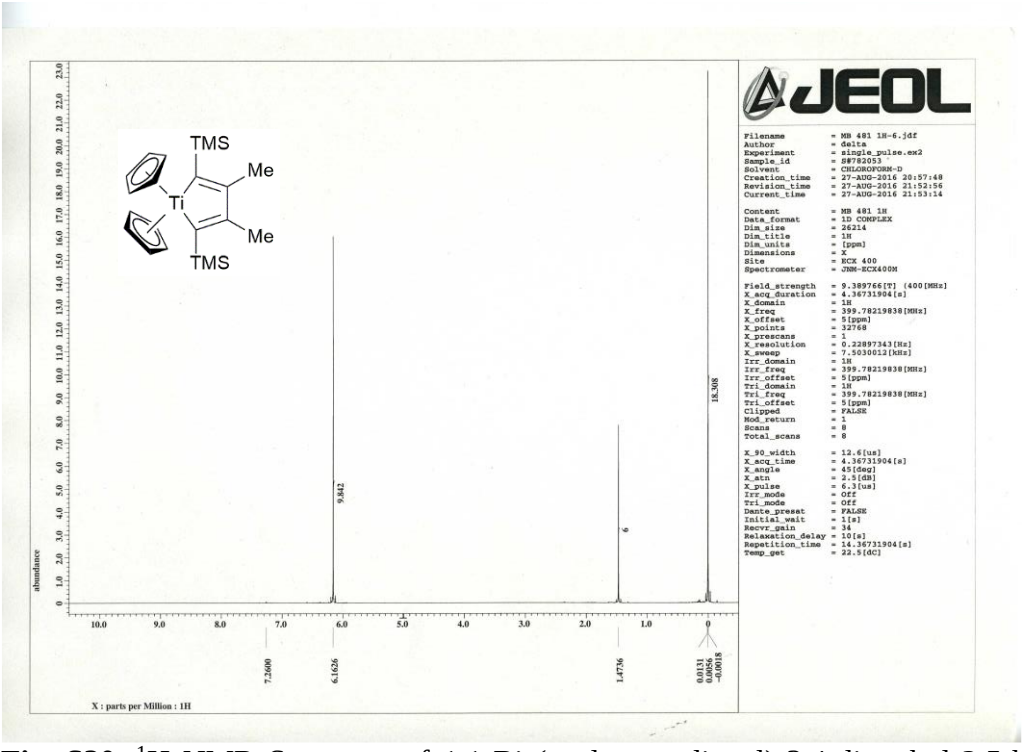


Fig. S20. ^{1}H NMR Spectrum of 1,1-Bis(cyclopentadienyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-titanacyclopentadiene (**6**).

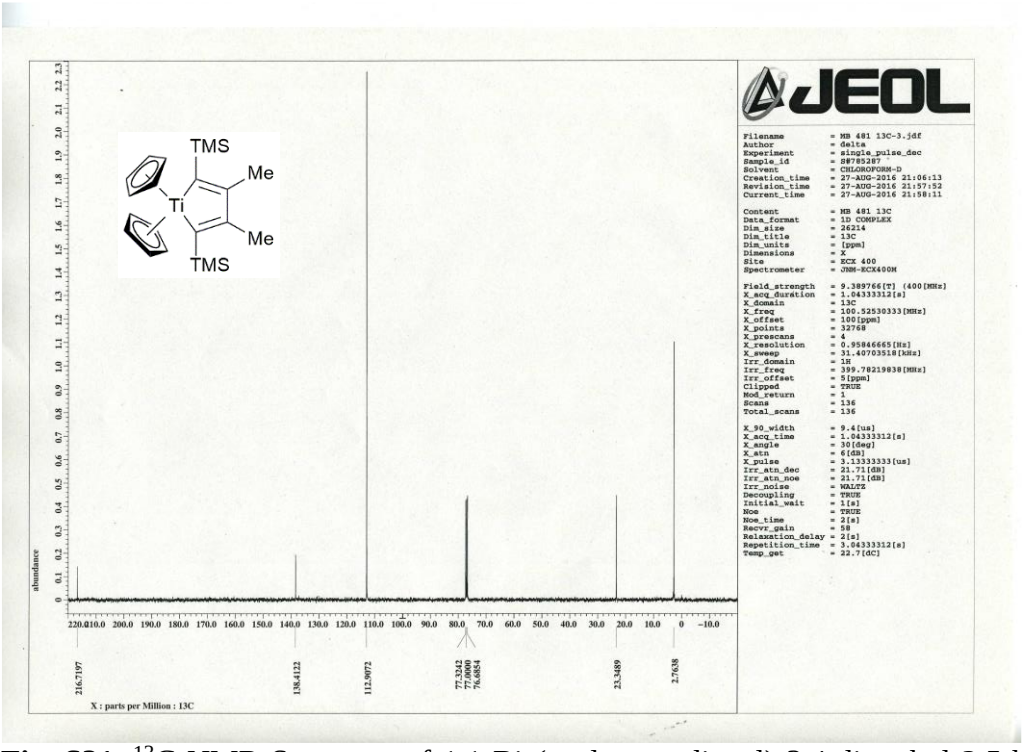


Fig. S21. ^{13}C NMR Spectrum of 1,1-Bis(cyclopentadienyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-titanacyclopentadiene (**6**).

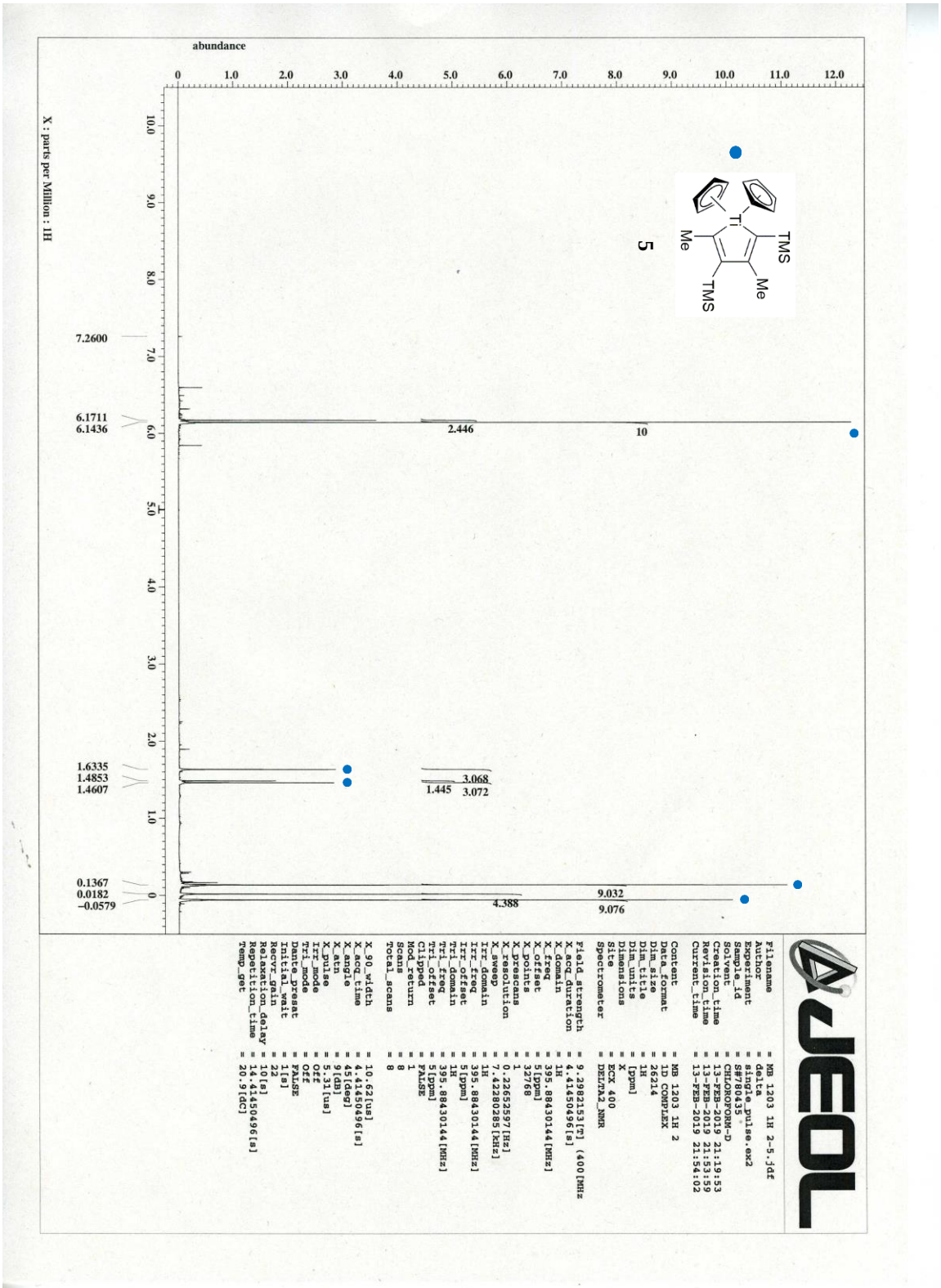


Fig. S22. [1]H NMR Spectrum of a mixture **5** and **6**.

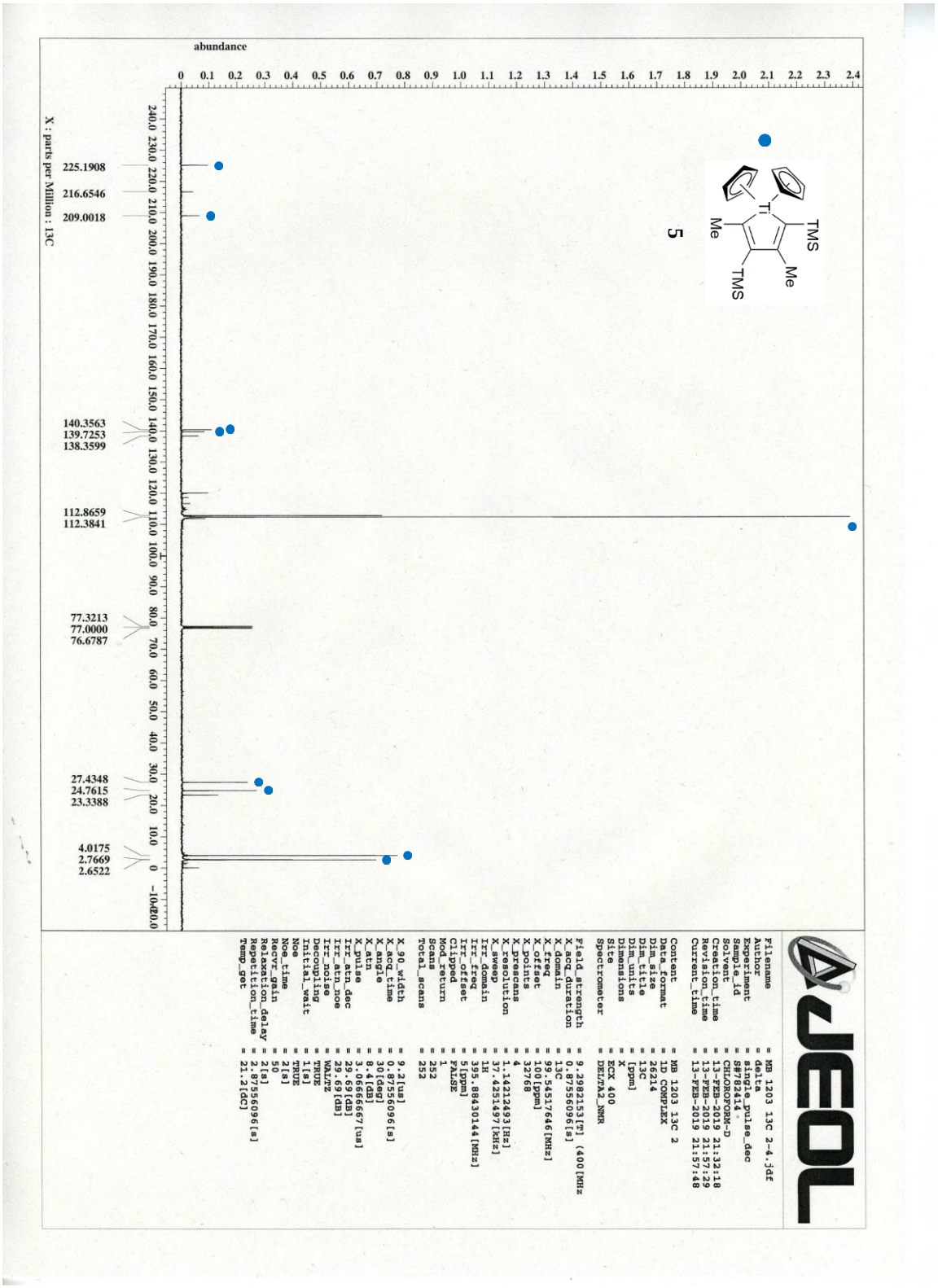


Fig. S23. ^{13}C NMR Spectrum of a mixture **5** and **6**.

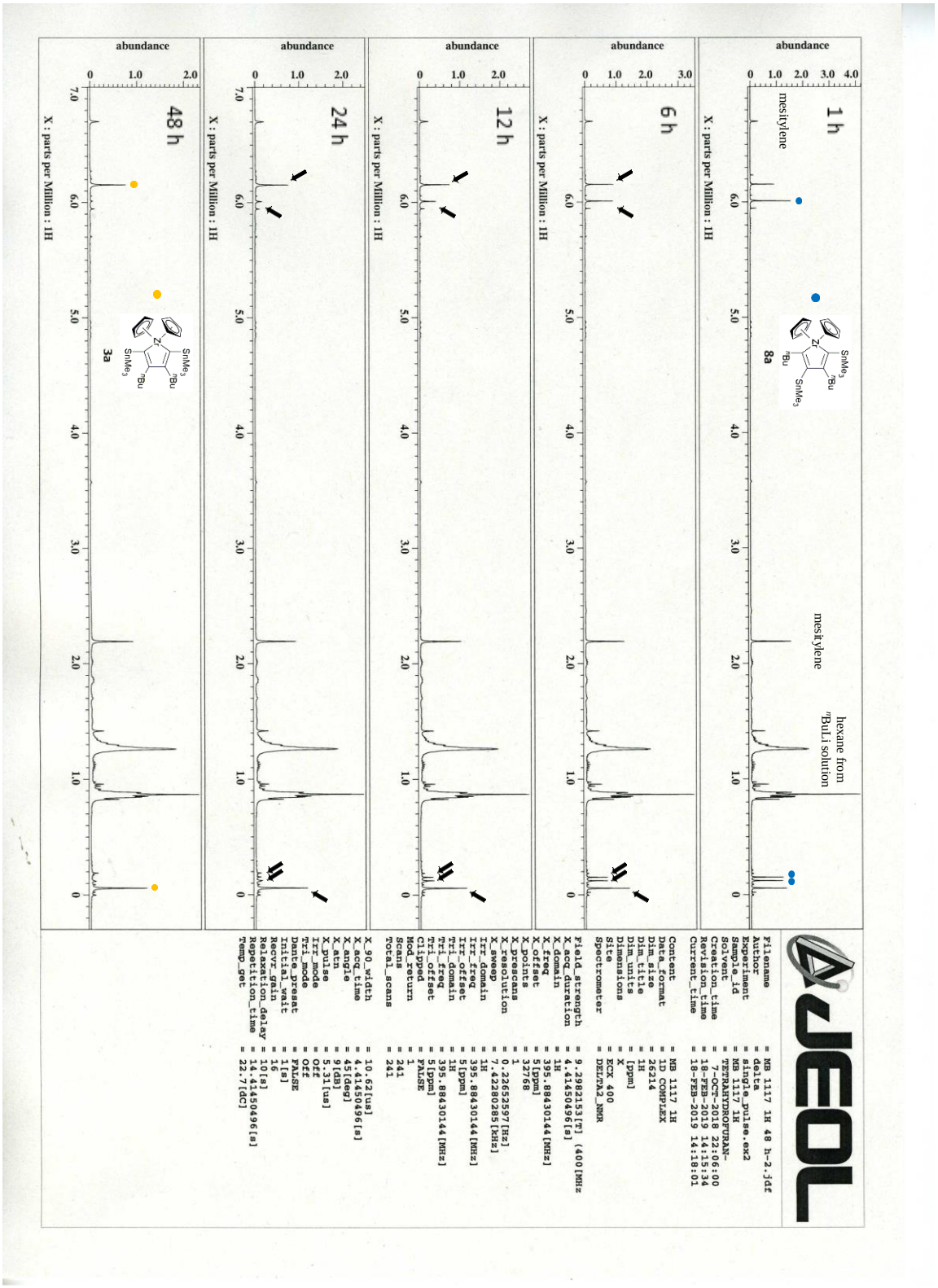


Fig. S24. ^{1}H NMR Monitoring Reaction of Alkyne **1a** with Cp_2ZrBu_2 (Conversion of **8a** into **3a**).

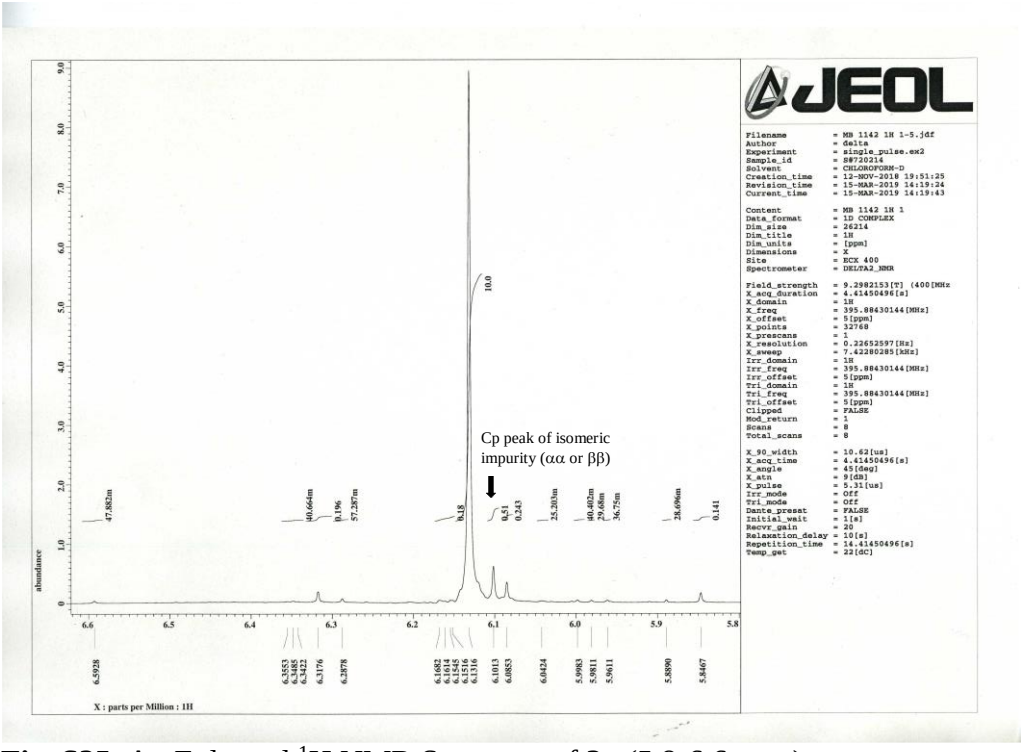


Fig. S25. An Enlarged ^{1}H NMR Spectrum of **2a** (5.8-6.6 ppm).

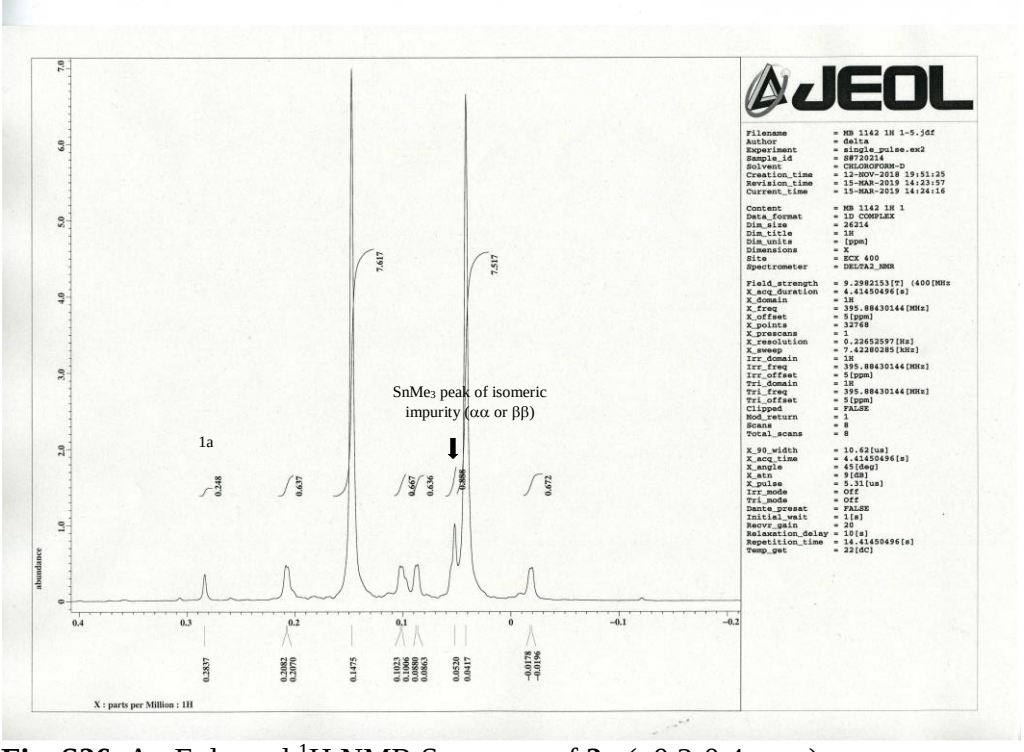


Fig. S26. An Enlarged ^{1}H NMR Spectrum of **2a** (–0.2-0.4 ppm).

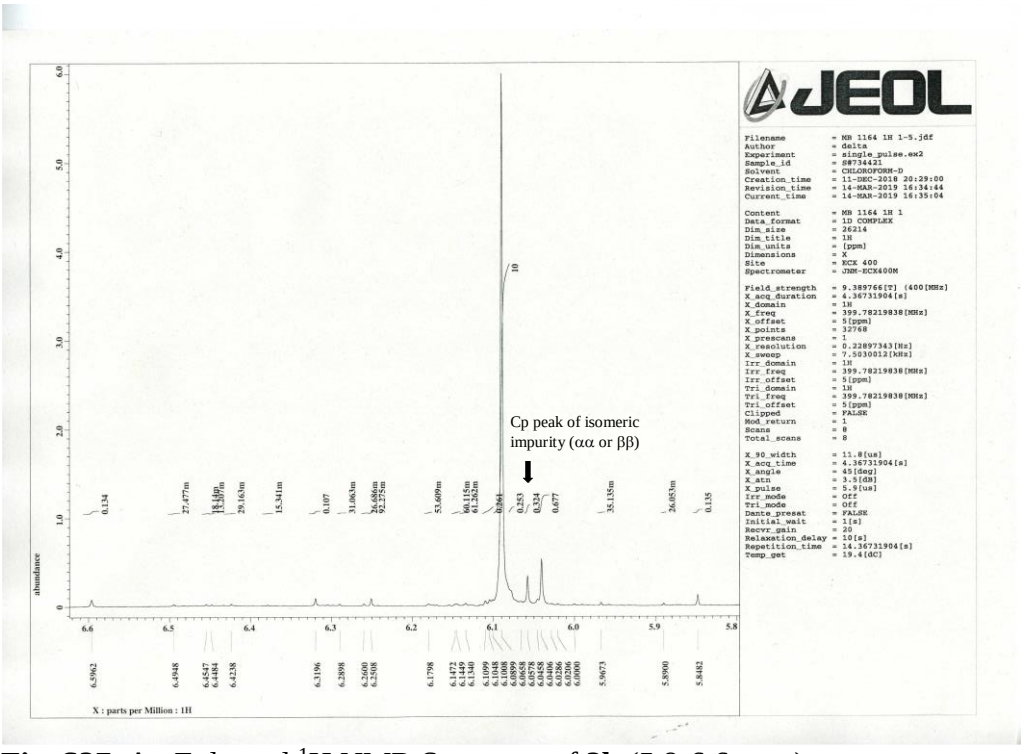


Fig. S27. An Enlarged ^{1}H NMR Spectrum of **2b** (5.8-6.6 ppm).

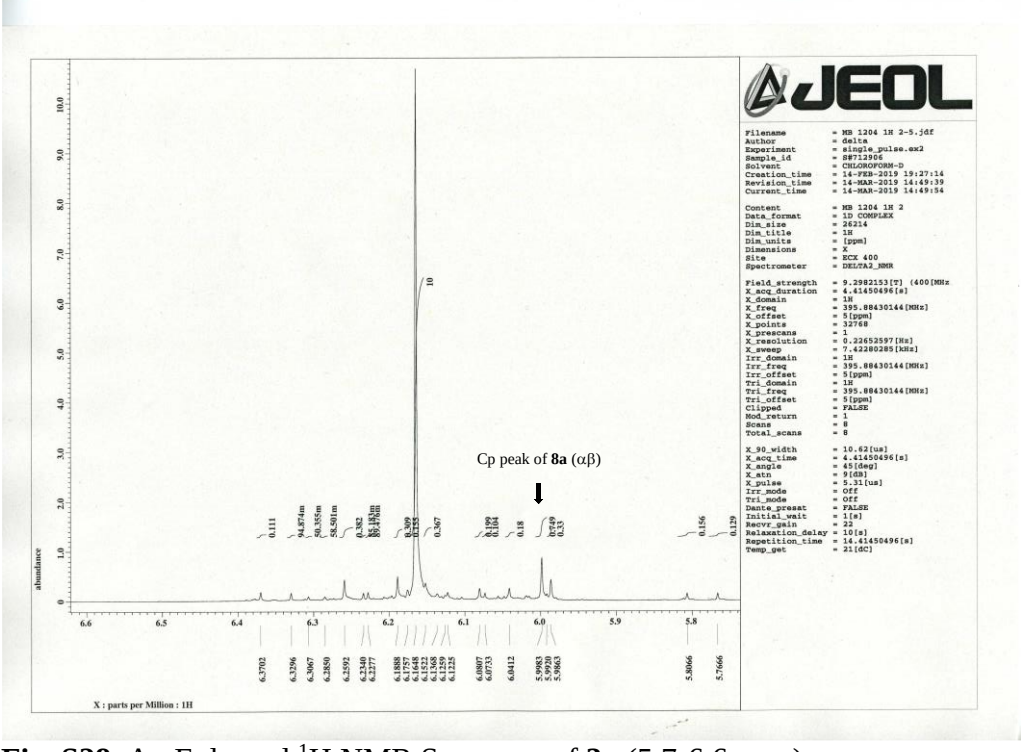


Fig. S28. An Enlarged ^{1}H NMR Spectrum of **3a** (5.7-6.6 ppm).

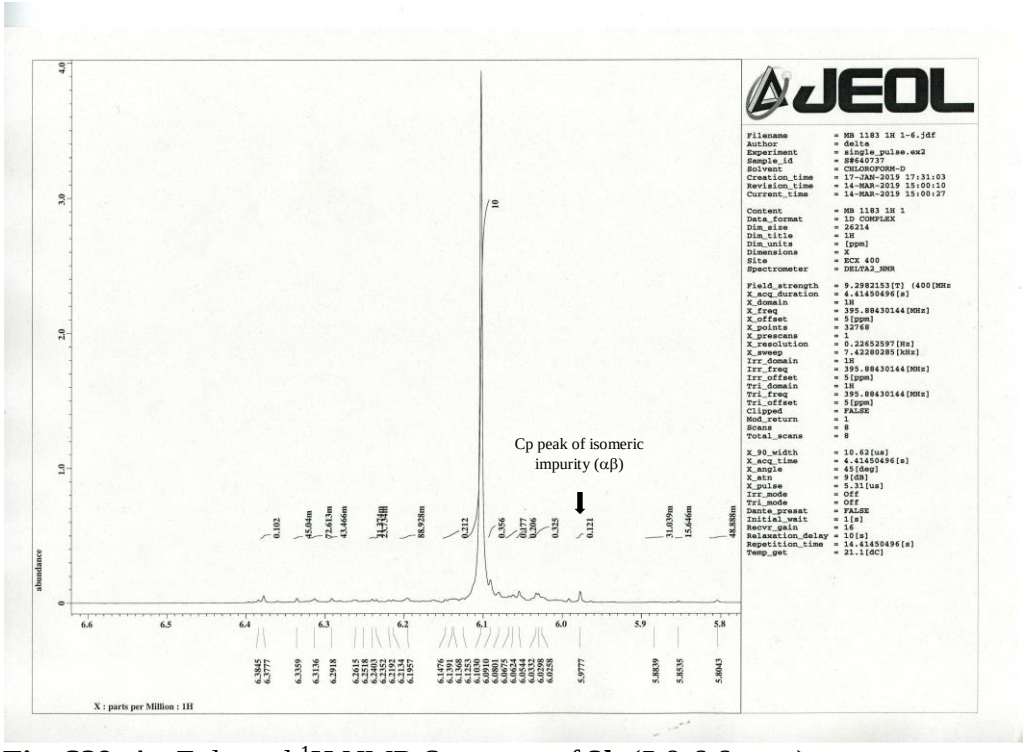


Fig. S29. An Enlarged ^{1}H NMR Spectrum of **3b** (5.8-6.6 ppm).

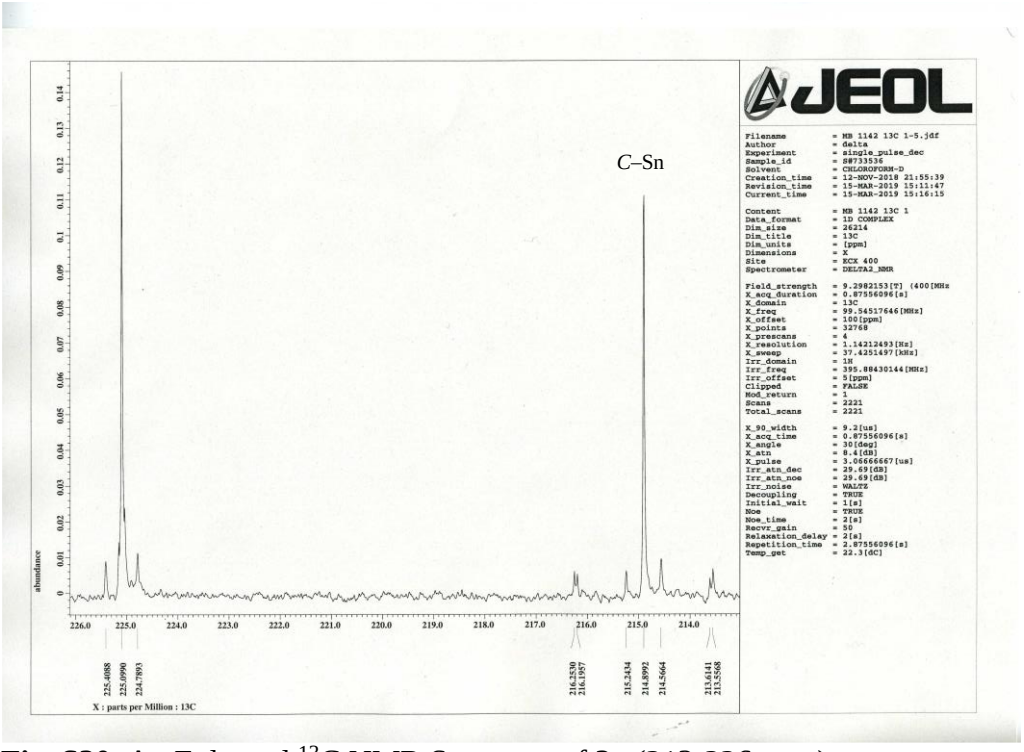


Fig. S30. An Enlarged ^{13}C NMR Spectrum of **2a** (213-226 ppm).

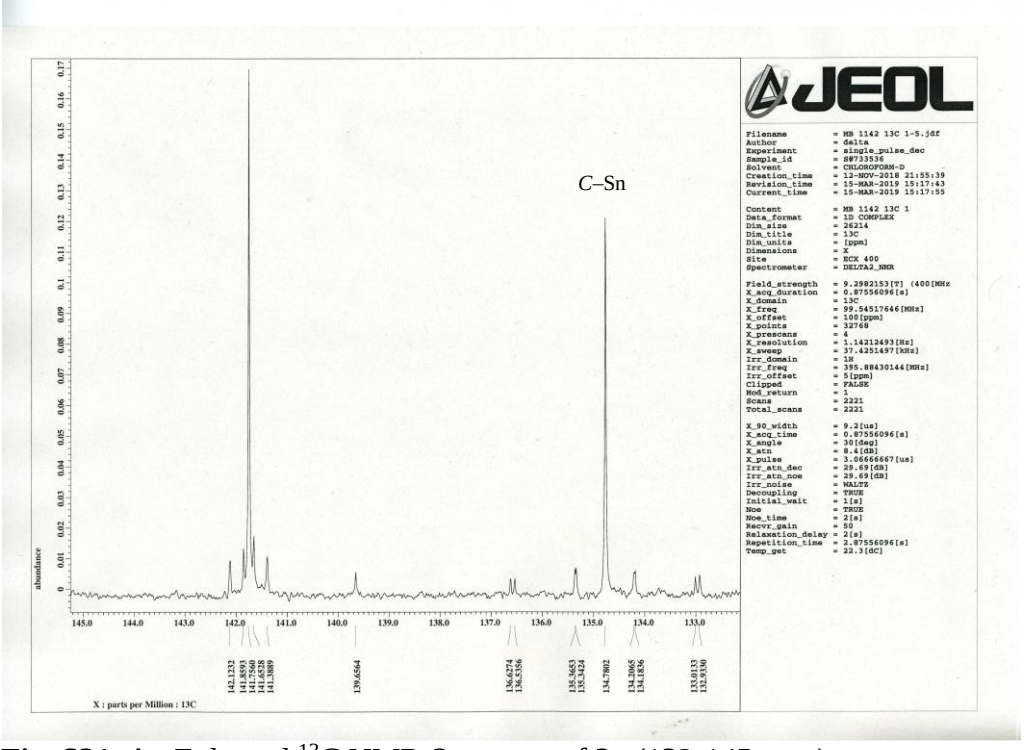


Fig. S31. An Enlarged ^{13}C NMR Spectrum of **2a** (132-145 ppm).

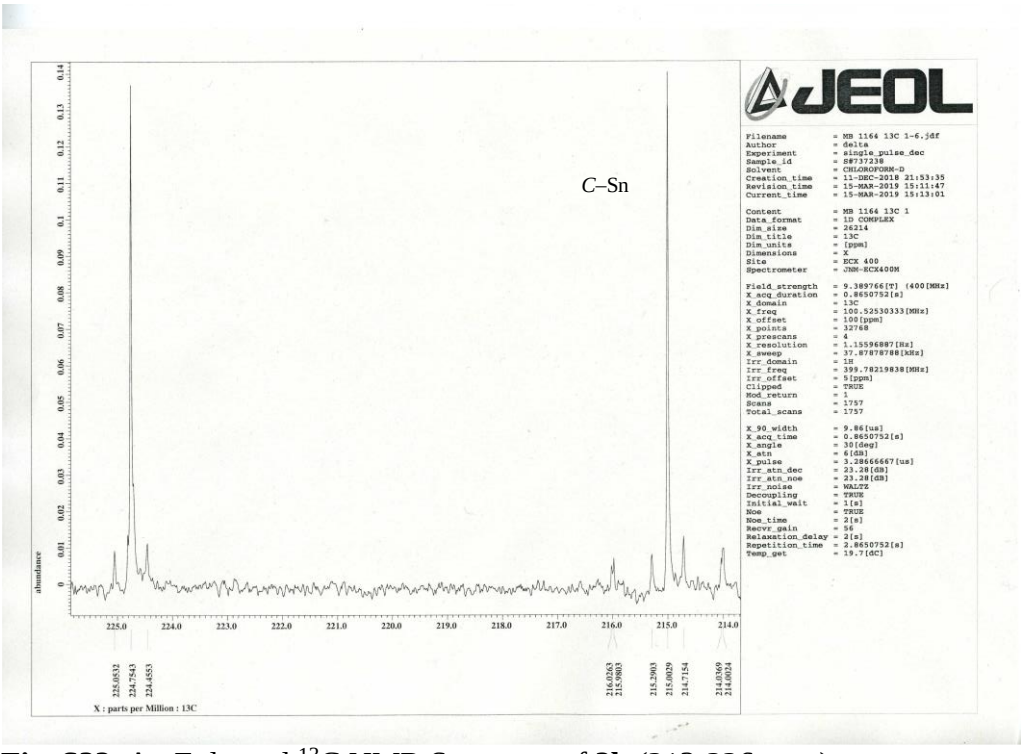


Fig. S32. An Enlarged ^{13}C NMR Spectrum of **2b** (213-226 ppm).

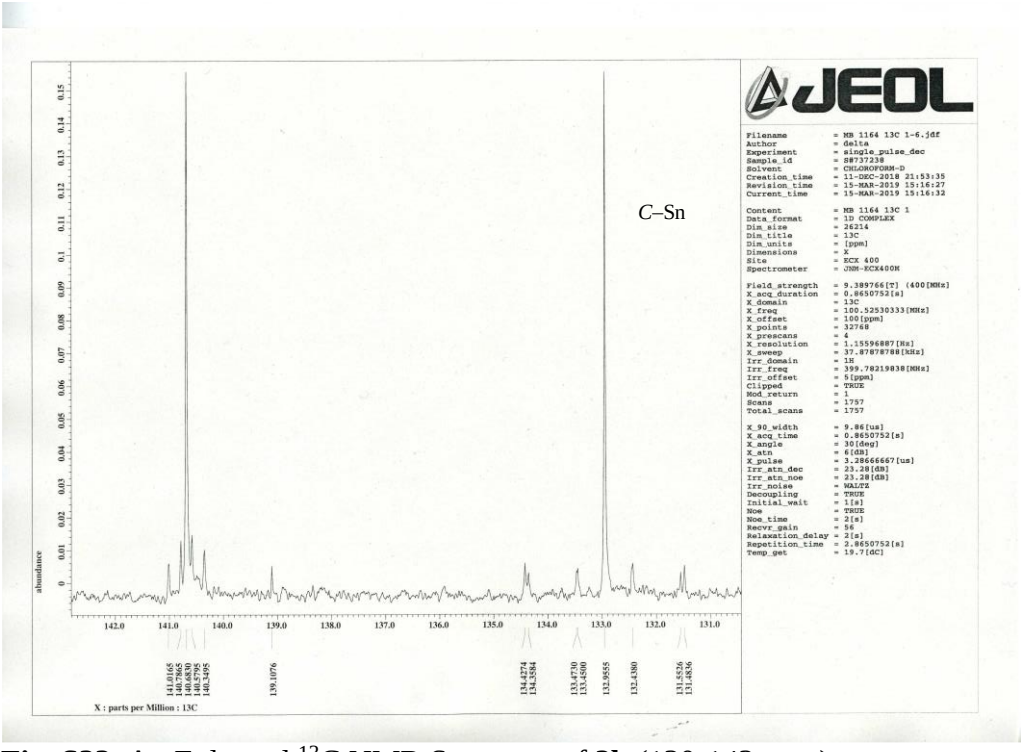


Fig. S33. An Enlarged ^{13}C NMR Spectrum of **2b** (130-143 ppm).

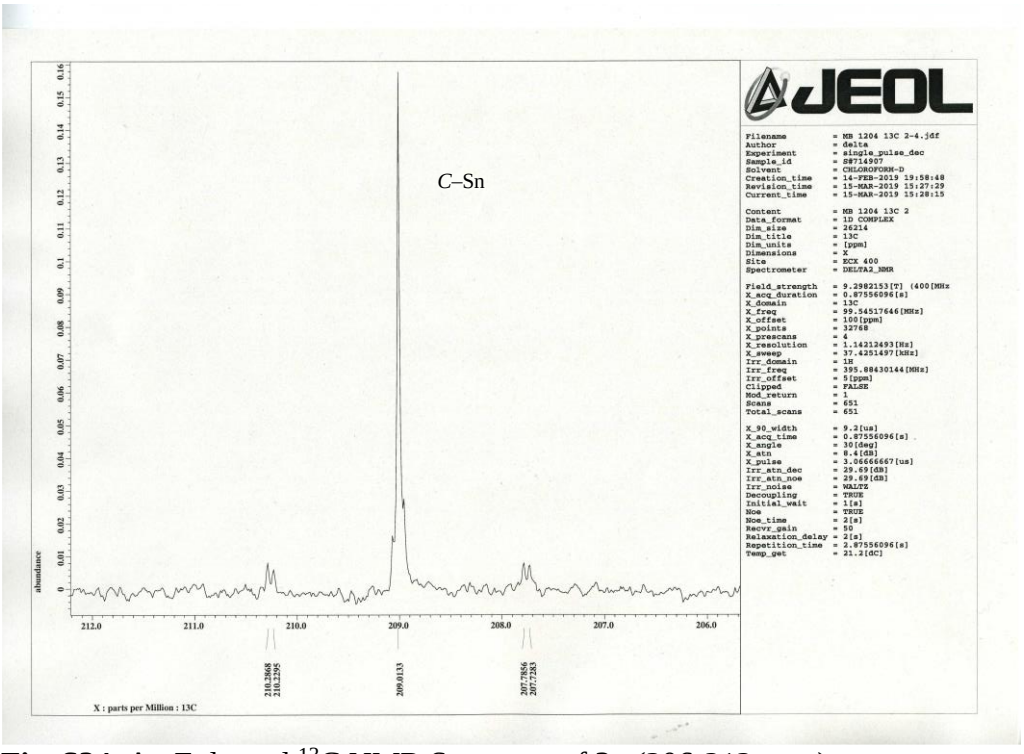


Fig. S34. An Enlarged ^{13}C NMR Spectrum of **3a** (206-212 ppm).

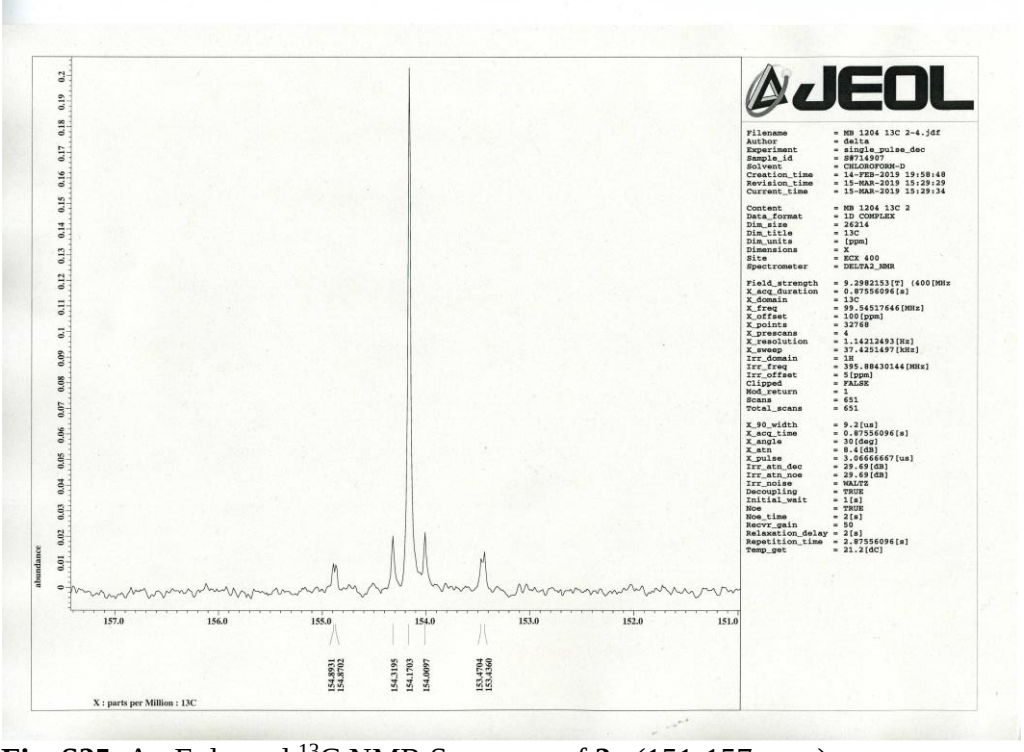


Fig. S35. An Enlarged ^{13}C NMR Spectrum of **3a** (151-157 ppm).

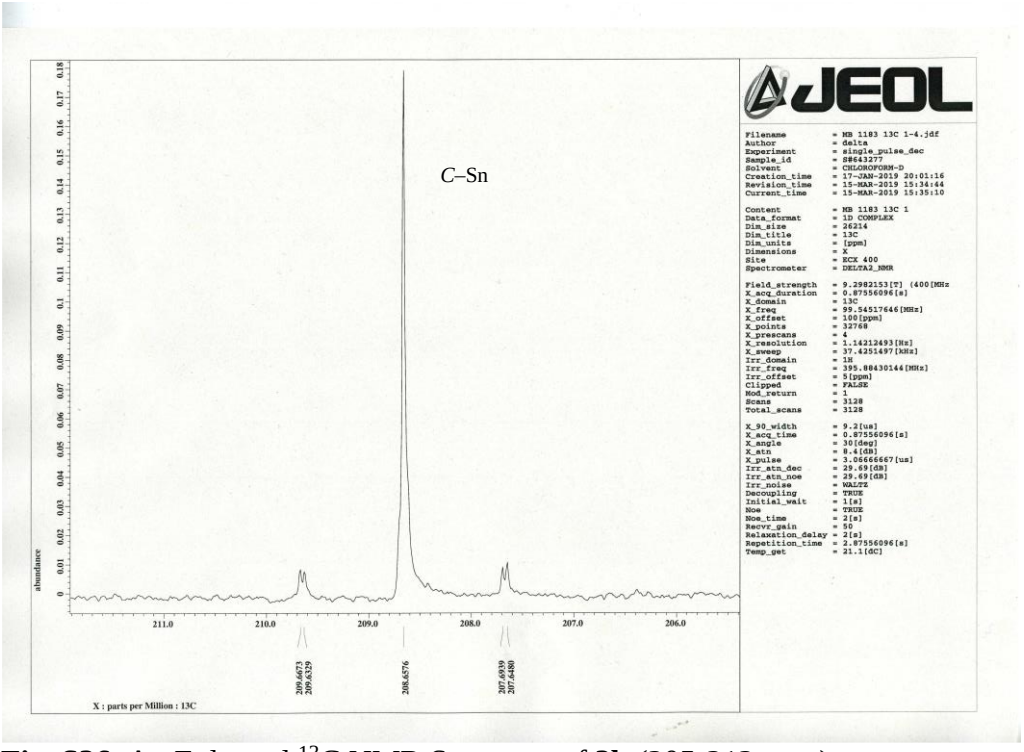


Fig. S36. An Enlarged ^{13}C NMR Spectrum of **3b** (205-212 ppm).

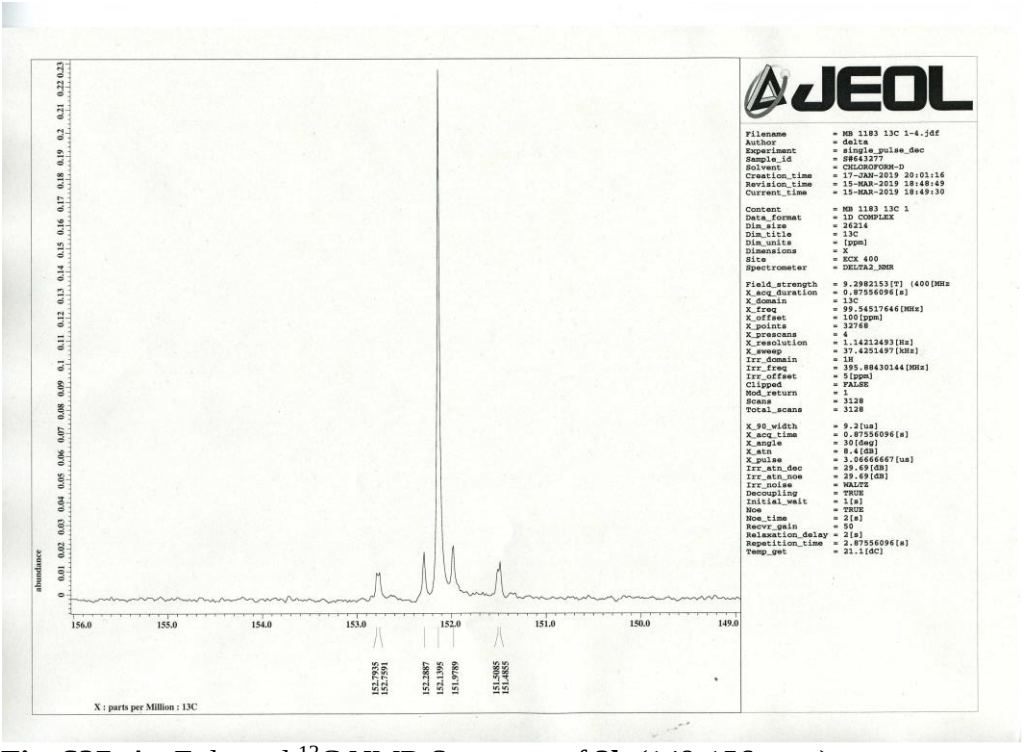


Fig. S37. An Enlarged ^{13}C NMR Spectrum of **3b** (149-156 ppm).

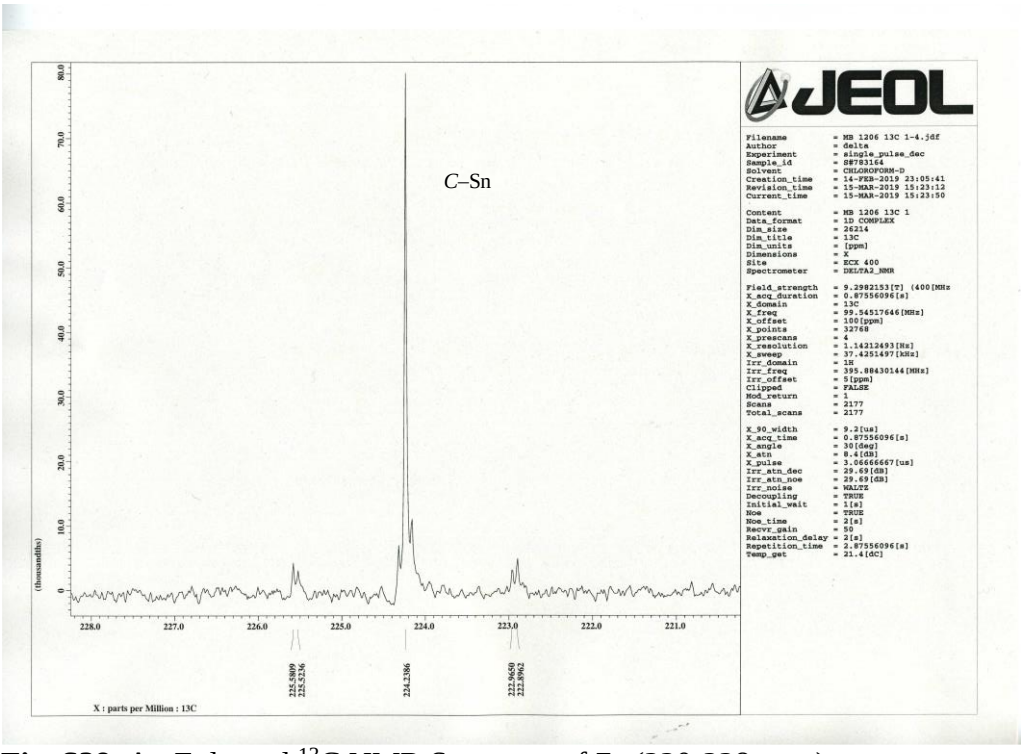


Fig. S38. An Enlarged ^{13}C NMR Spectrum of **7c** (220-228 ppm).

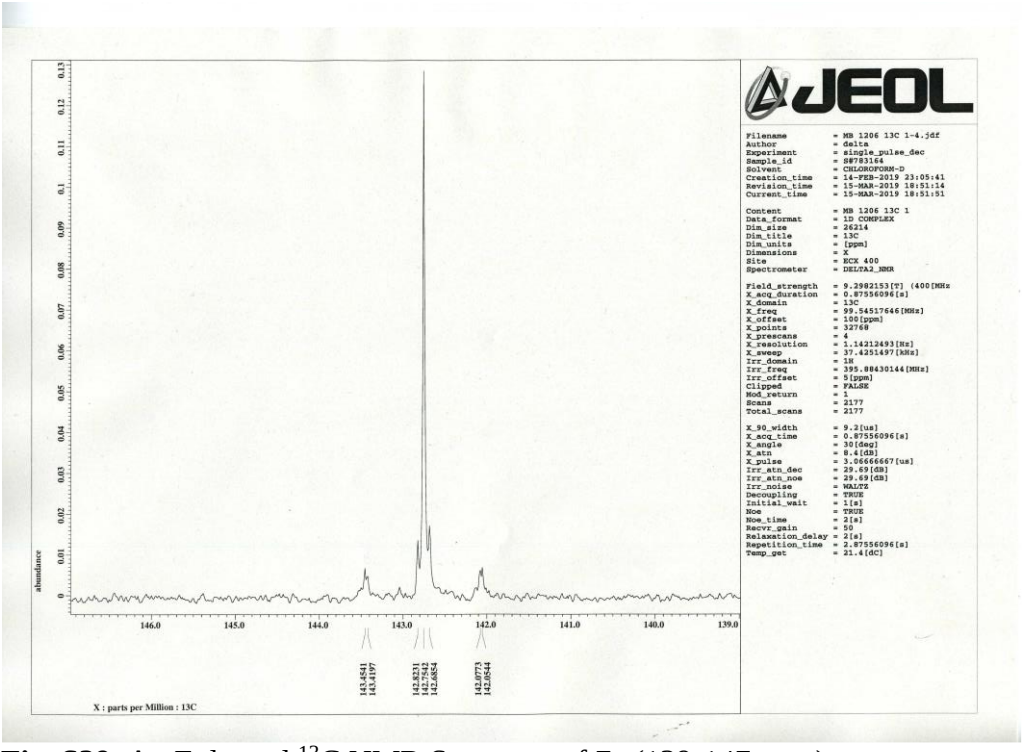


Fig. S39. An Enlarged ^{13}C NMR Spectrum of **7c** (139-147 ppm).

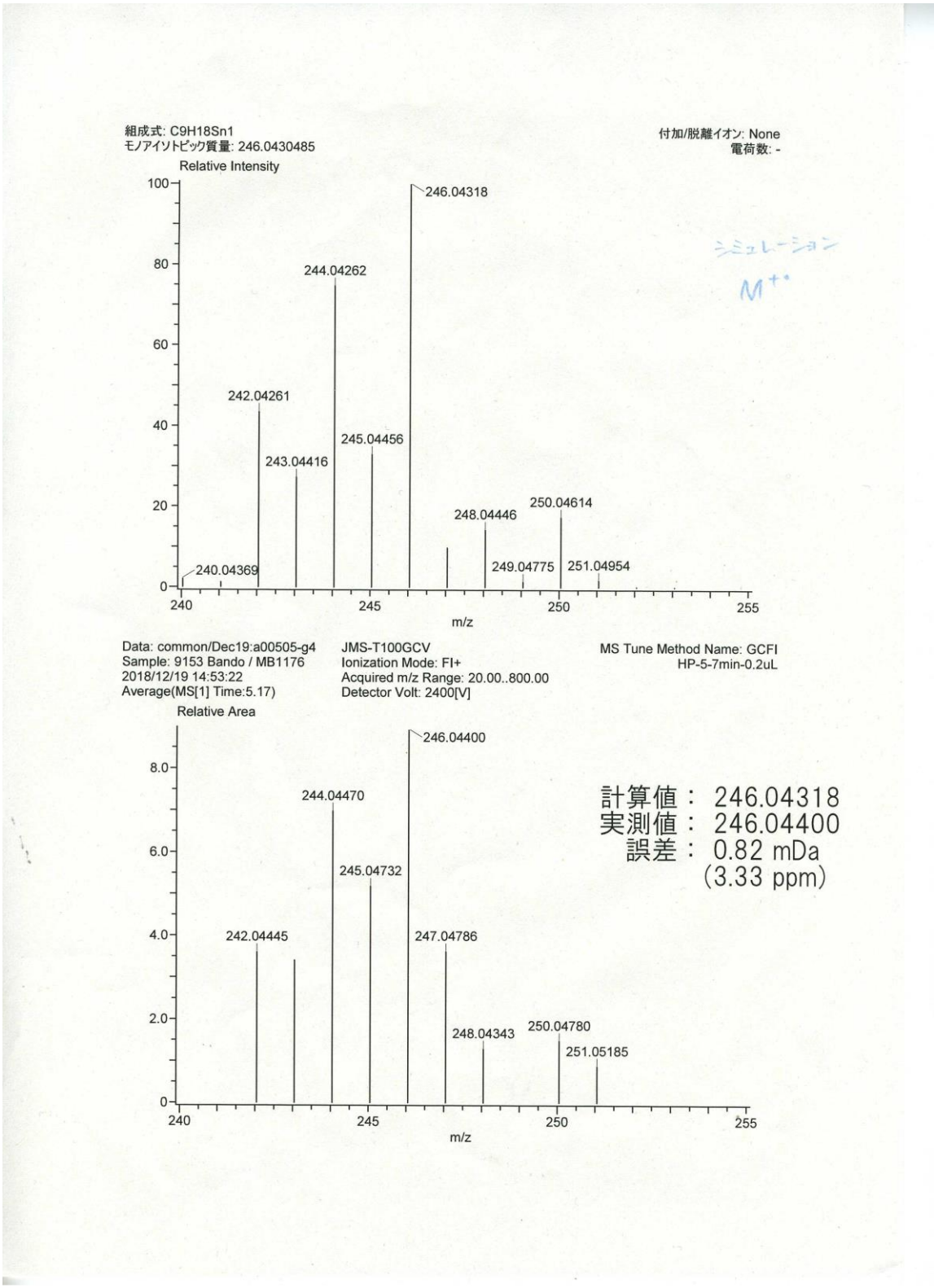


Fig. S40. Simulated mass (upper figure) and experimental mass (lower figure) (**1a**).

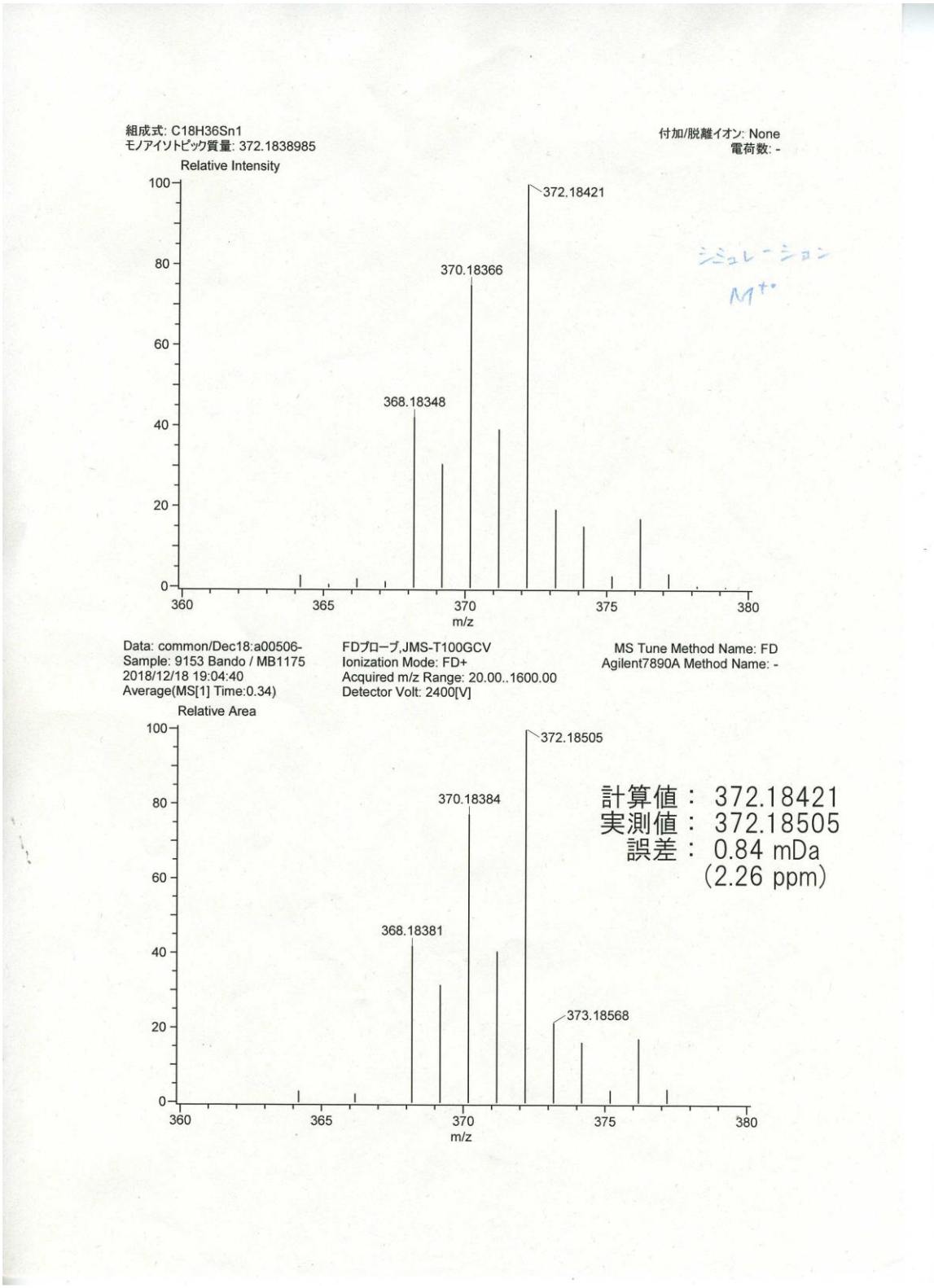


Fig. S41. Simulated mass (upper figure) and experimental mass (lower figure) (**1b**).

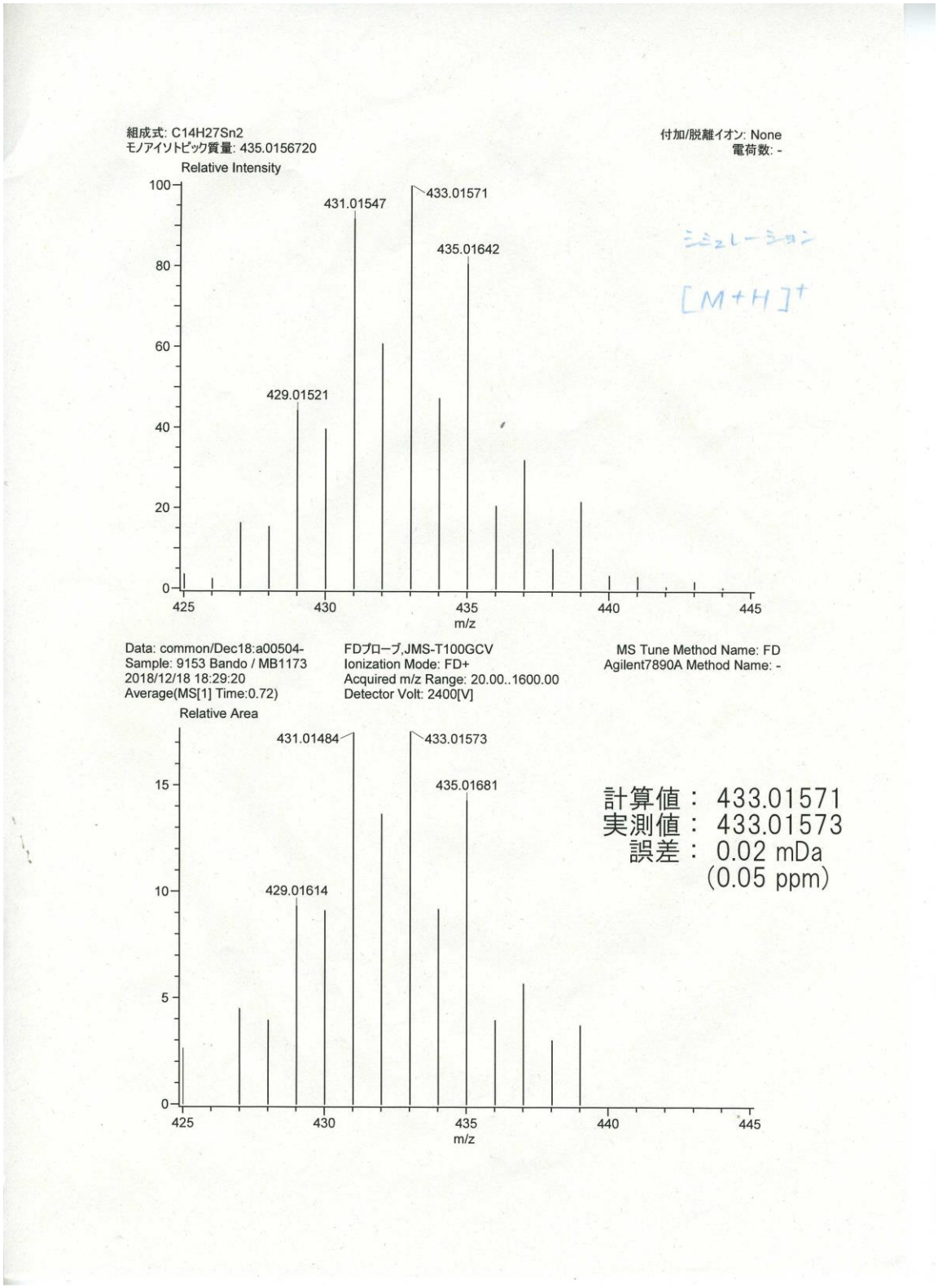


Fig. S42. Simulated mass (upper figure) and experimental mass (lower figure) (**1c**).

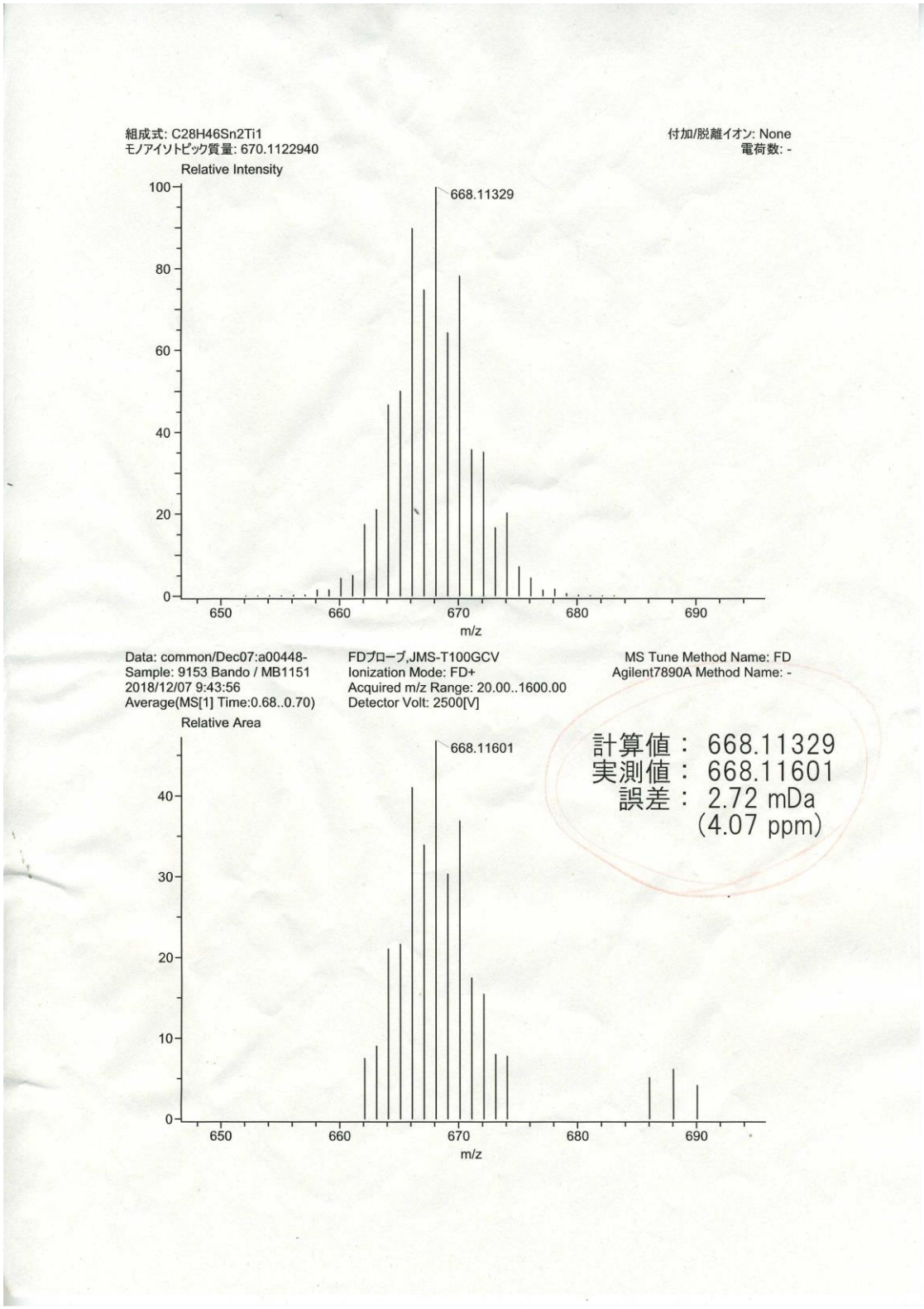


Fig. S43. Simulated mass (upper figure) and experimental mass (lower figure) (**2a**).

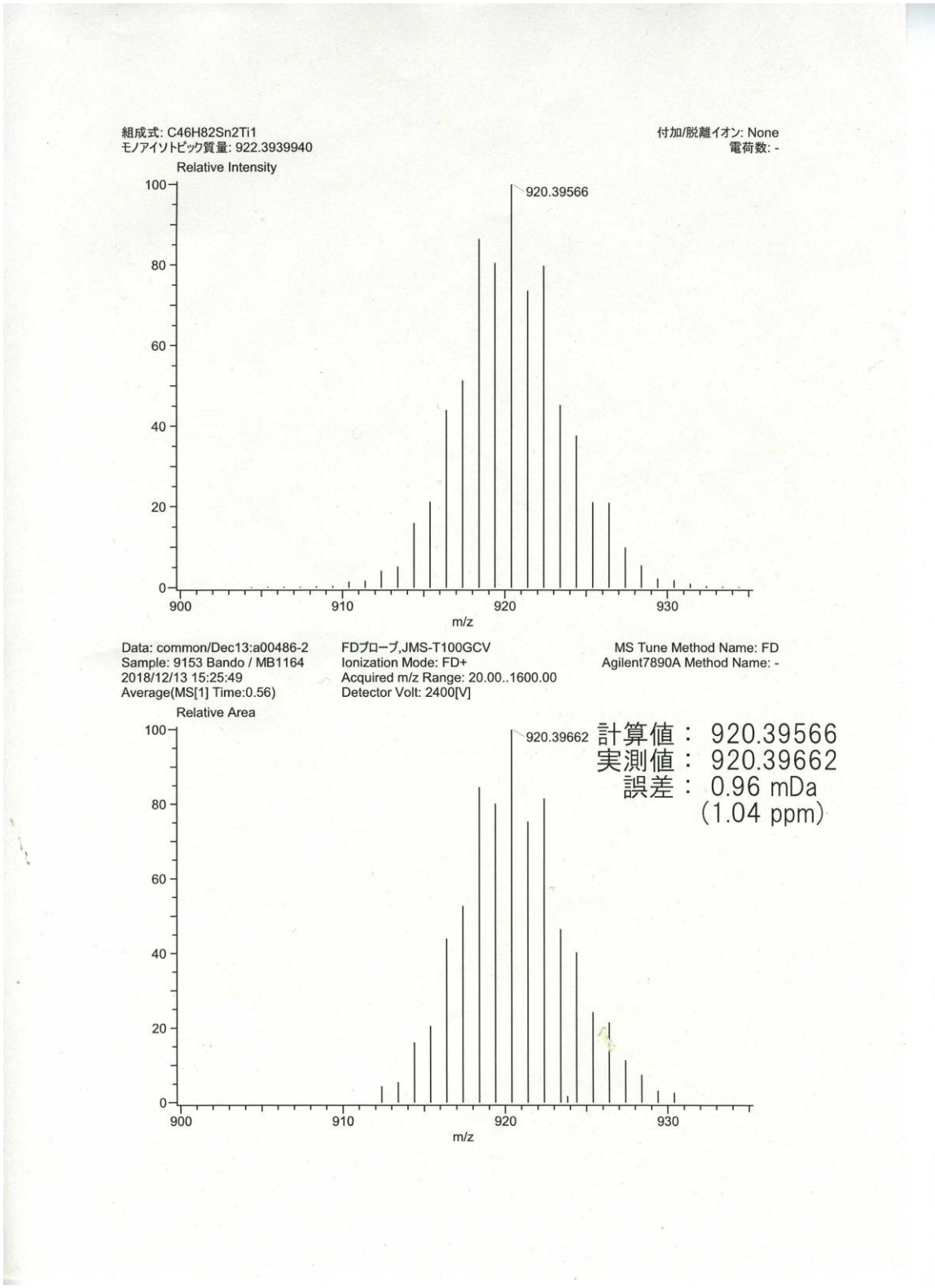


Fig. S44. Simulated mass (upper figure) and experimental mass (lower figure) (**2b**).

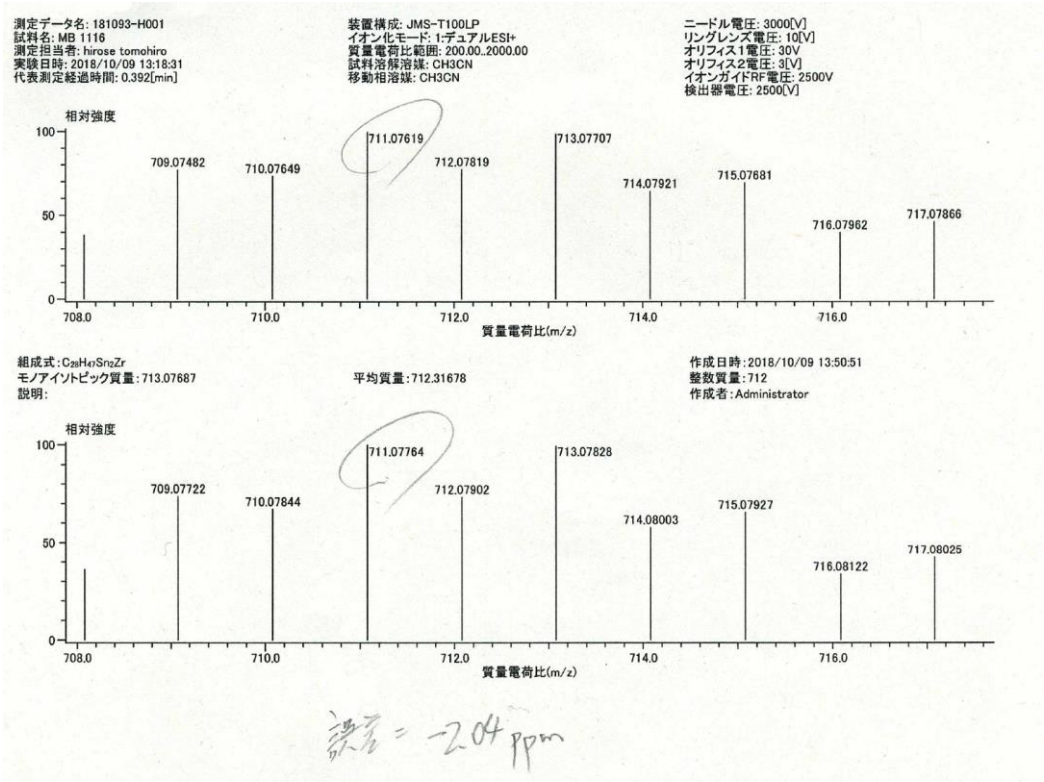


Fig. S45. Simulated mass (lower figure) and experimental mass (upper figure) (**3a**).

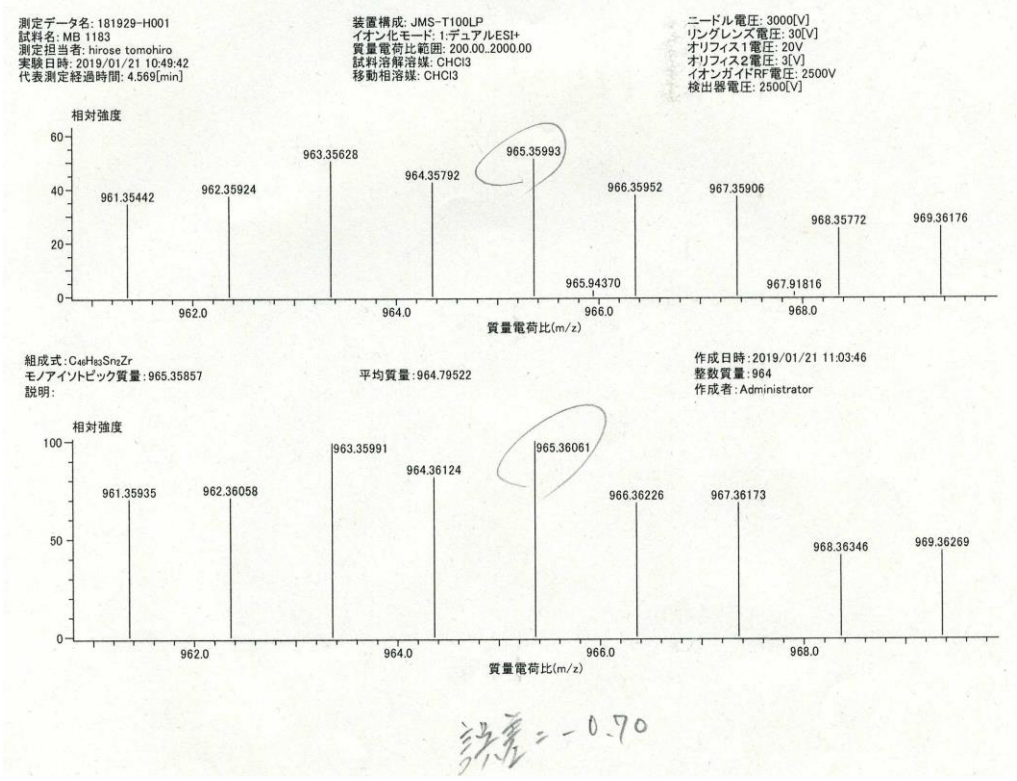


Fig. S46. Simulated mass (lower figure) and experimental mass (upper figure) (**3b**).

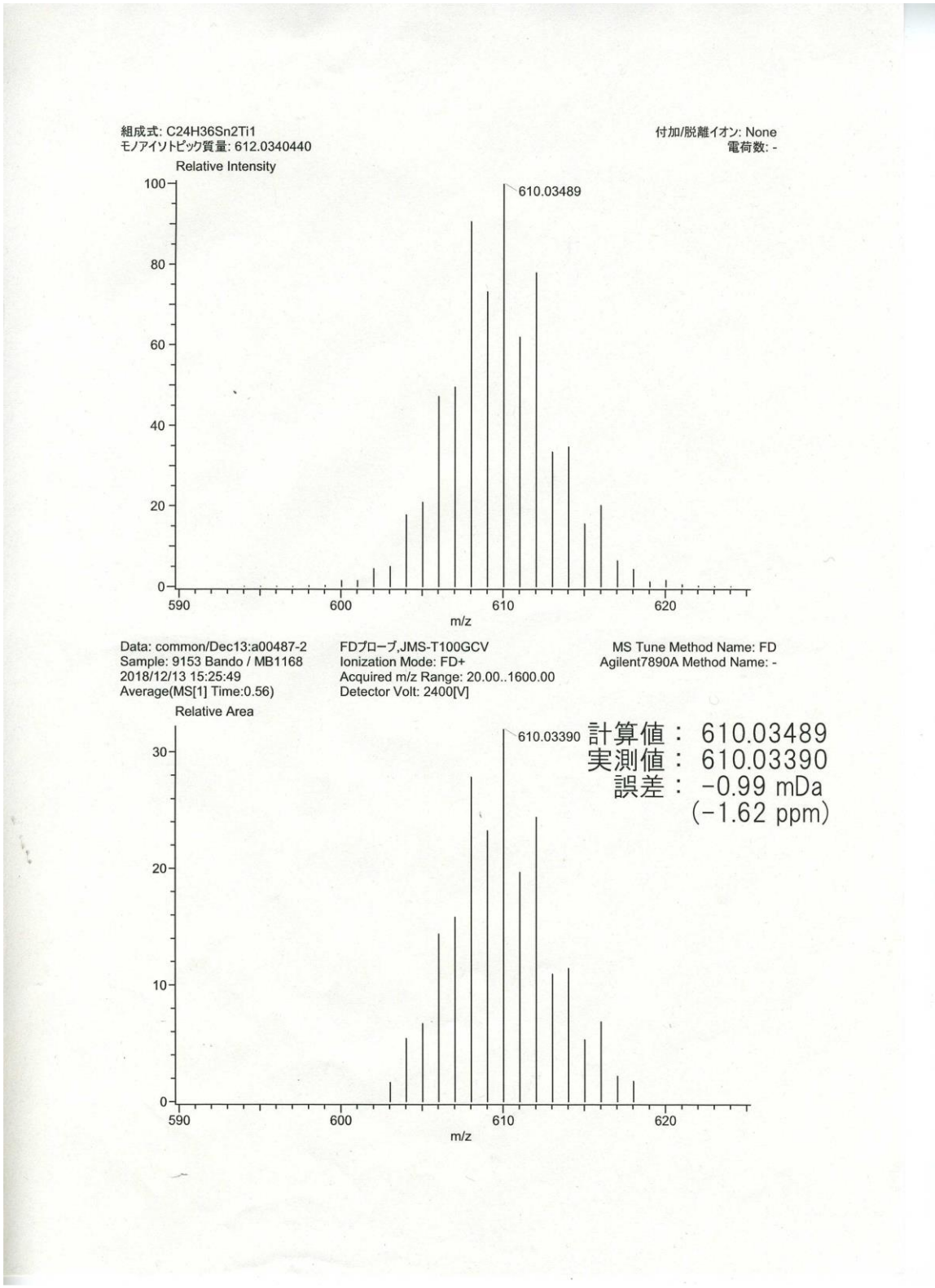
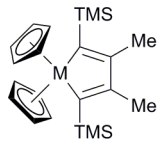


Fig. S47. Simulated mass (upper figure) and experimental mass (lower figure) (**7c**).



	M–C(Cp)	M–C(sp^2)	Si–C(sp^2)	Si–C(Me)	M–C(sp^2)–Si	Cent–M–C(sp^2)
Ti	2.358	2.145	1.871	1.869	129.36	105.88
Zr	2.51	2.246	1.865	1.864	128.64	106.64
Hf	2.488	2.223	1.870	1.863	130.05	107.36

Fig. S48. Comparison of Bond Distances (Å) and Angles (°) of X-ray Structures.

References

M = Ti
This study. CCDC 1900263

M = Zr
M. Westerhausen, M. H. Digeser, C. Gückel, H. Nöth, J. Knizek and W. Ponikwar, *Organometallics*, 1999, **18**, 2491.

M = Hf
M. B. Sabade, M. F. Farona, E. A. Zarate and W. J. Youngs, *J. Organomet. Chem*., 1988, **338**, 347.