

## Supporting Information

### Low valent lead and tin hydrides in reaction with heteroallenes

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## Data of crystallography

Table S1. Data of crystal structure determination.

	1	2	3	4	5	6
Emp. formula	C <sub>49</sub> H <sub>72</sub> N <sub>2</sub> Sn	C <sub>43</sub> H <sub>62</sub> N <sub>2</sub> Pb	C <sub>47</sub> H <sub>65</sub> NOSn	C <sub>47</sub> H <sub>65</sub> NOPb	C <sub>79</sub> H <sub>114</sub> O <sub>2</sub> Sn <sub>2</sub>	C <sub>73</sub> H <sub>100</sub> S <sub>2</sub> Sn <sub>2</sub>
<i>M</i> [g/mol]	807.77	816.16	778.69	867.19	1333.08	1279.08
$\lambda$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub>
<i>Z</i>	4	2	4	4	4	4
<i>a</i> [Å]	13.0631(8)	10.6529(3)	19.0046(14)	19.0155(7)	22.3552(4)	15.3777(3)
<i>b</i> [Å]	20.0701(12)	14.1442(4)	18.4257(12)	18.4067(7)	16.2894(3)	24.2581(4)
<i>c</i> [Å]	17.0055(11)	15.6309(4)	12.0392(8)	12.1142(4)	19.6949(4)	18.4918(3)
$\alpha$ [°]	90	108.6230(10)	90	90	90	90
$\beta$ [°]	97.061(3)	94.426(2)	99.420(5)	99.691(2)	96.3620(10)	91.9830(10)
$\gamma$ [°]	90	112.0080(10)	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	4424.6(5)	2016.66(10)	4159.0(5)	4179.6(3)	7127.8(2)	6893.9(2)
<i>D<sub>c</sub></i> [g/cm <sup>3</sup> ]	1.213	1.344	1.244	1.378	1.242	1.232
$\mu$ [mm <sup>-1</sup> ]	0.611	4.212	0.649	4.071	0.744	0.823
F(000)	1720	836	1648	1776	2816	2680
crystal size [mm]	0.22x0.20x0.18	0.17x0.15x0.14	0.17x0.15x0.13	0.19x0.14x0.12	0.18x0.16x0.14	0.16x0.14x0.11
$\theta$ range [°]	1.571 – 27.866	3.027 – 30.229	2.040 – 27.547	2.465 – 28.336	1.809 – 28.050	1.385 – 29.193
limiting indices	-17 ≤ <i>h</i> ≤ 17 -25 ≤ <i>k</i> ≤ 26 -22 ≤ <i>l</i> ≤ 22	-14 ≤ <i>h</i> ≤ 15 -19 ≤ <i>k</i> ≤ 20 -22 ≤ <i>l</i> ≤ 21	-24 ≤ <i>h</i> ≤ 24 -23 ≤ <i>k</i> ≤ 23 -15 ≤ <i>l</i> ≤ 15	-23 ≤ <i>h</i> ≤ 25 -24 ≤ <i>k</i> ≤ 24 -16 ≤ <i>l</i> ≤ 16	-29 ≤ <i>h</i> ≤ 29 -21 ≤ <i>k</i> ≤ 21 -26 ≤ <i>l</i> ≤ 26	-21 ≤ <i>h</i> ≤ 20 -32 ≤ <i>k</i> ≤ 33 -25 ≤ <i>l</i> ≤ 25
refl. coll.	153507	49601	36732	52598	58989	74582
ind. refl.	10496	11602	9533	10393	8614	33865
<i>R<sub>int</sub></i>	0.0323	0.0255	0.0827	0.0582	0.0602	0.0479
completeness	99.5	99.6	99.3	99.8	99.6	99.4
abs. correction	multi-scan	numerical	multi-scan	multi-scan	multi-scan	multi-scan
max., min. trans.	0.75, 0.65	0.75, 0.67	0.75, 0.61	0.75, 0.58	0.75, 0.69	0.6974, 0.7458
Para./restr.	481 / 0	450/2	497/18	500/1	401 / 1	1514 / 18
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0239, 0.0585	0.0291, 0.0644	0.0669, 0.1145	0.0693, 0.1587	0.0546, 0.1334	0.0373, 0.0718
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0278, 0.0608	0.0390, 0.0673	0.1157, 0.1287	0.0829, 0.1628	0.0795, 0.1436	0.0518, 0.0759
Goof on <i>F</i> <sup>2</sup>	1.019	1.087	1.258	1.295	1.029	0.979
peak / hole [ <i>e</i> · Å <sup>-3</sup> ]	1.199, -0.538	2.065, -3.753	1.121, -1.042	1.804, -3.410	1.920, -0.696	0.813, -0.479
CCDC	2063449	2063447	2063446	2063451	2063448	2063450

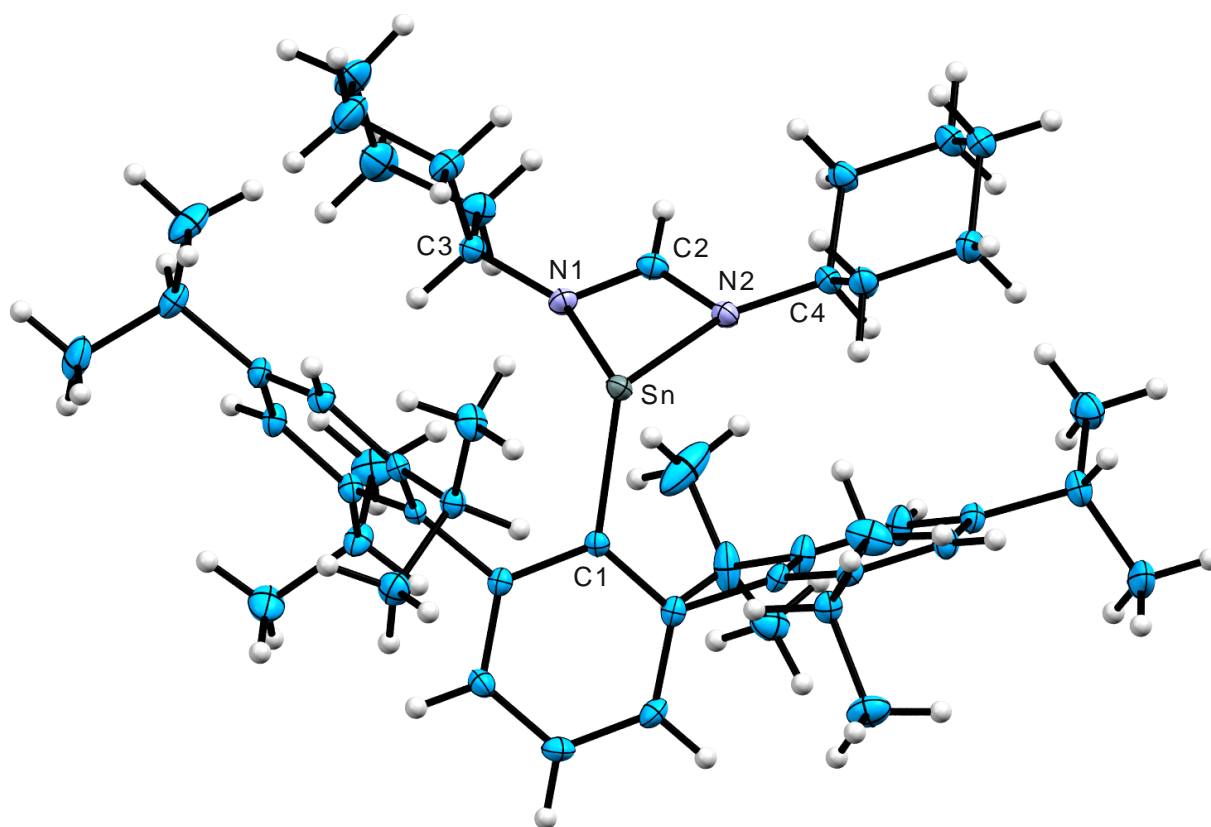


Figure S1. ORTEP (50% thermal ellipsoids) with selected atom labeling of **1**. Selected bond distances [ $\text{\AA}$ ] and angles [deg] for **1**: Sn–N1 2.2193(12), Sn–N2 2.2333(12), Sn–C1 2.2332(14), N1–C2 1.3214(19), N2–C2 1.3154(19), N1–Sn–N2 59.77(4), N2–C2–N1 114.58(13), C2–N1–Sn 91.66(9), C2–N2–Sn 91.21(9), N1–Sn–C1 101.84(5), C1–Sn–N2 107.87(5).

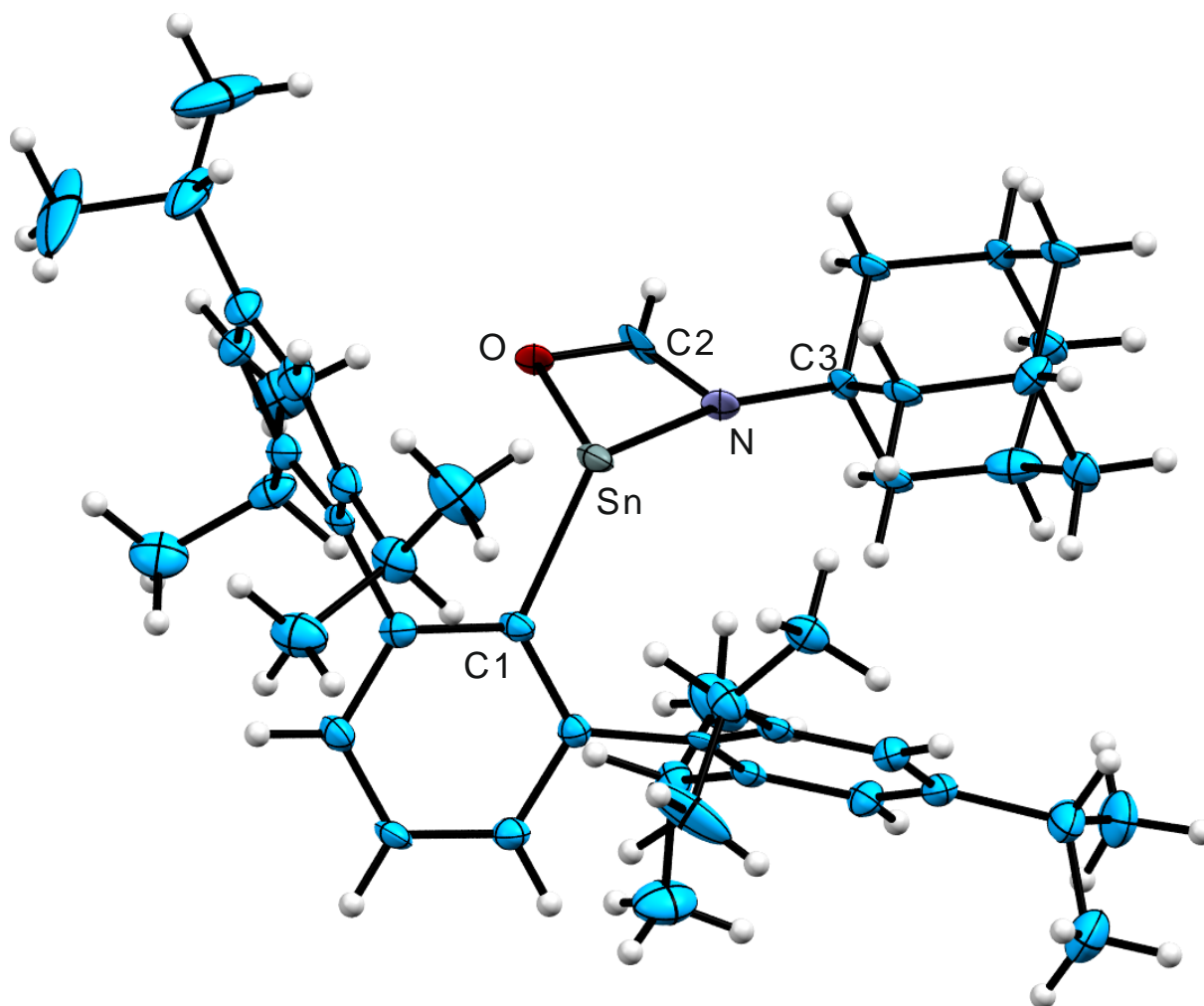
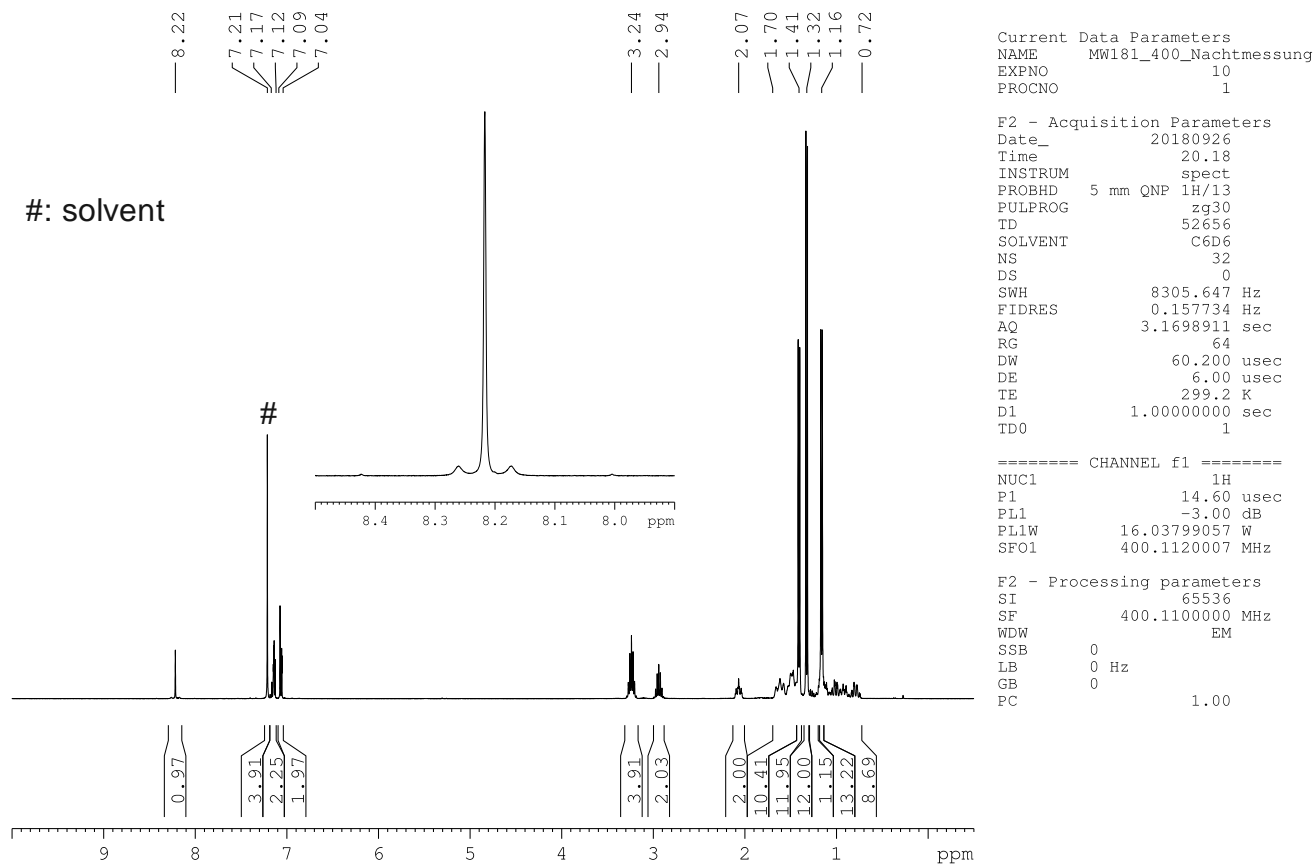
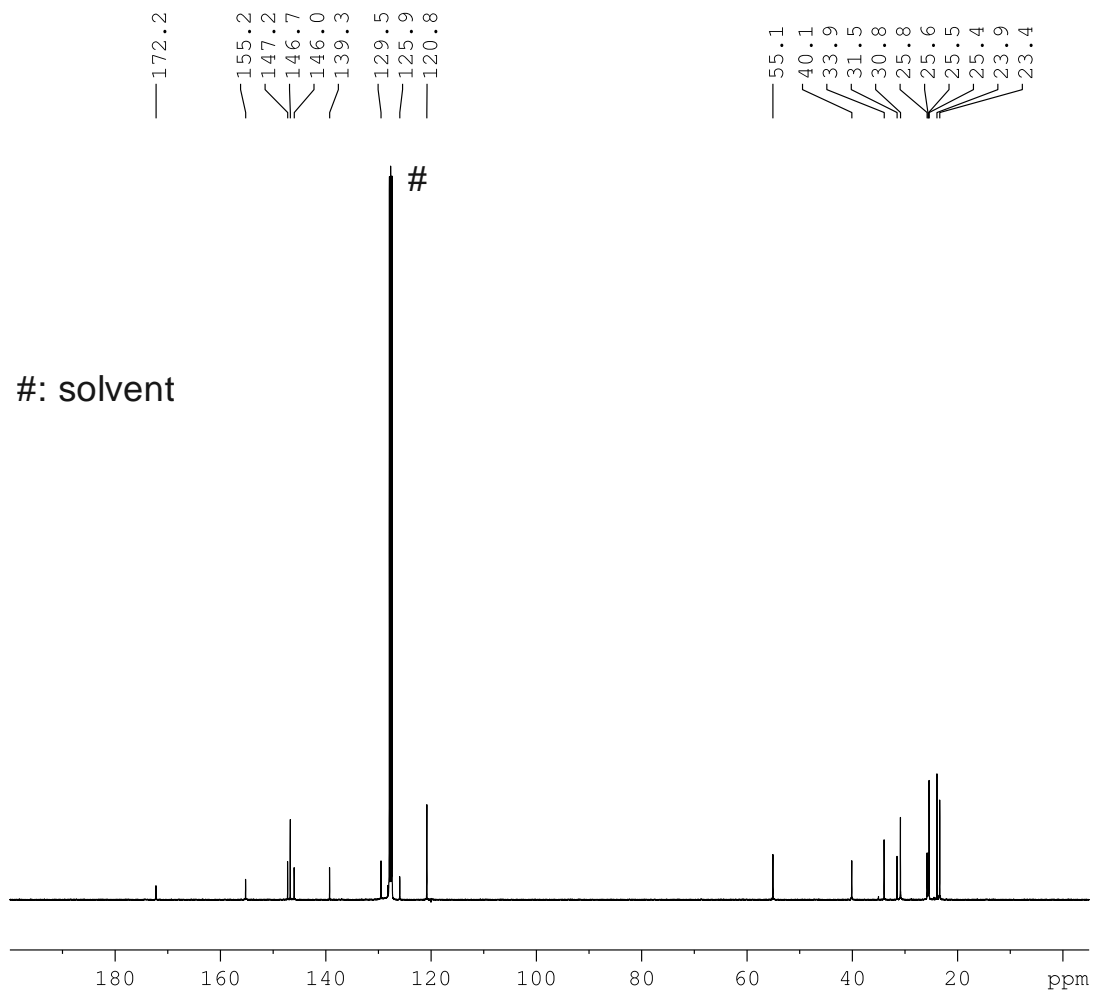


Figure S2. ORTEP (50% thermal ellipsoids) with selected atom labeling of **3**. Selected bond distances [ $\text{\AA}$ ] and angles [deg] for **3**: Sn–O 2.211(4), Sn–N 2.294(5), Sn–C1 2.258(3), O–C2 1.295(7), N–C2 1.296(8), O–Sn–C1 95.18(15), O–Sn–N 59.11(17), C1–Sn–N 106.28(16), O–C2–N 118.2(5), C2–N–Sn 88.7(4), C2–O–Sn 92.4(4).

## NMR spectroscopy

NMR Data of compound **1**<sup>1</sup>H-NMR of Ar\*SnN(Cy)C(H)N(Cy) in C<sub>6</sub>D<sub>6</sub> at RTFigure S3. <sup>1</sup>H NMR spectrum of **1**

$^{13}\text{C}\{^1\text{H}\}$ -NMR of Ar\*SnN(Cy)C(H)N(Cy) in  $\text{C}_6\text{D}_6$  at RT

Current Data Parameters  
 NAME MW181\_400\_Nachtmessung  
 EXPNO 11  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20180927  
 Time 1.41  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zgpg30  
 TD 53700  
 SOLVENT C6D6  
 NS 10000  
 DS 0  
 SWH 30864.197 Hz  
 FIDRES 0.574752 Hz  
 AQ 0.8699400 sec  
 RG 32800  
 DW 16.200 usec  
 DE 6.00 usec  
 TE 299.2 K  
 D1 1.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

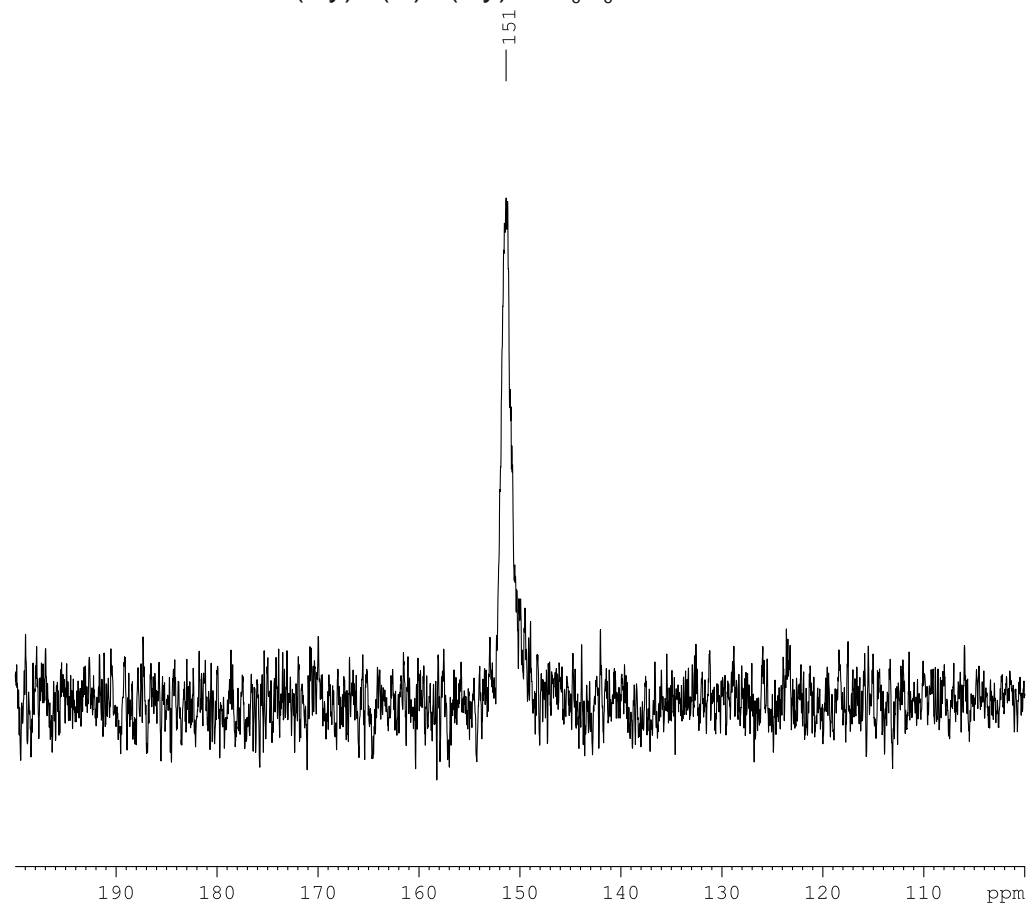
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 NUC1 13C  
 P1 13.50 usec  
 PL1 -4.16 dB  
 PL1W 78.55633545 W  
 SFO1 100.6198135 MHz

==== CHANNEL f2 =====  
 CPDPRG[2] waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 11.77 dB  
 PL13 13.14 dB  
 PL2W 16.03799057 W  
 PL12W 0.53474891 W  
 PL13W 0.39007664 W  
 SFO2 400.1120007 MHz

F2 - Processing parameters  
 SI 65536  
 SF 100.6077400 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S4.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1**

$^{119}\text{Sn}$ -NMR of  $\text{Ar}^*\text{SnN}(\text{Cy})\text{C}(\text{H})\text{N}(\text{Cy})$  in  $\text{C}_6\text{D}_6$  at RT



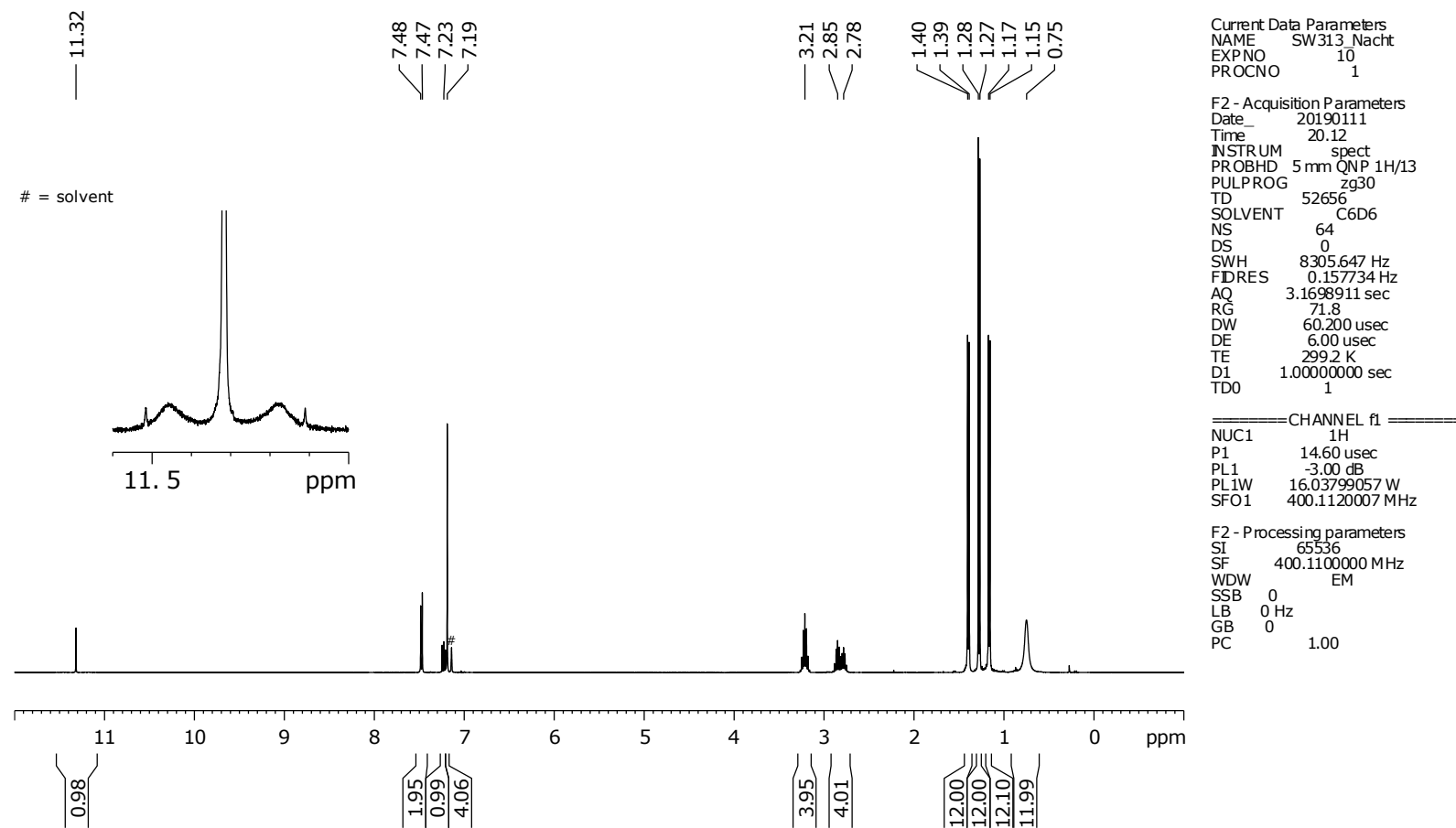
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EXPNO     11
PROCNO    1

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PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         32768
SOLVENT   C6D6
NS         4800
DS         0
SWH        74626.867 Hz
FIDRES     2.277431 Hz
AQ         0.2195456 sec
RG         14596.5
DW         6.700 usec
DE         5.50 usec
TE         299.2 K
D1         0.10000000 sec
TD0        1

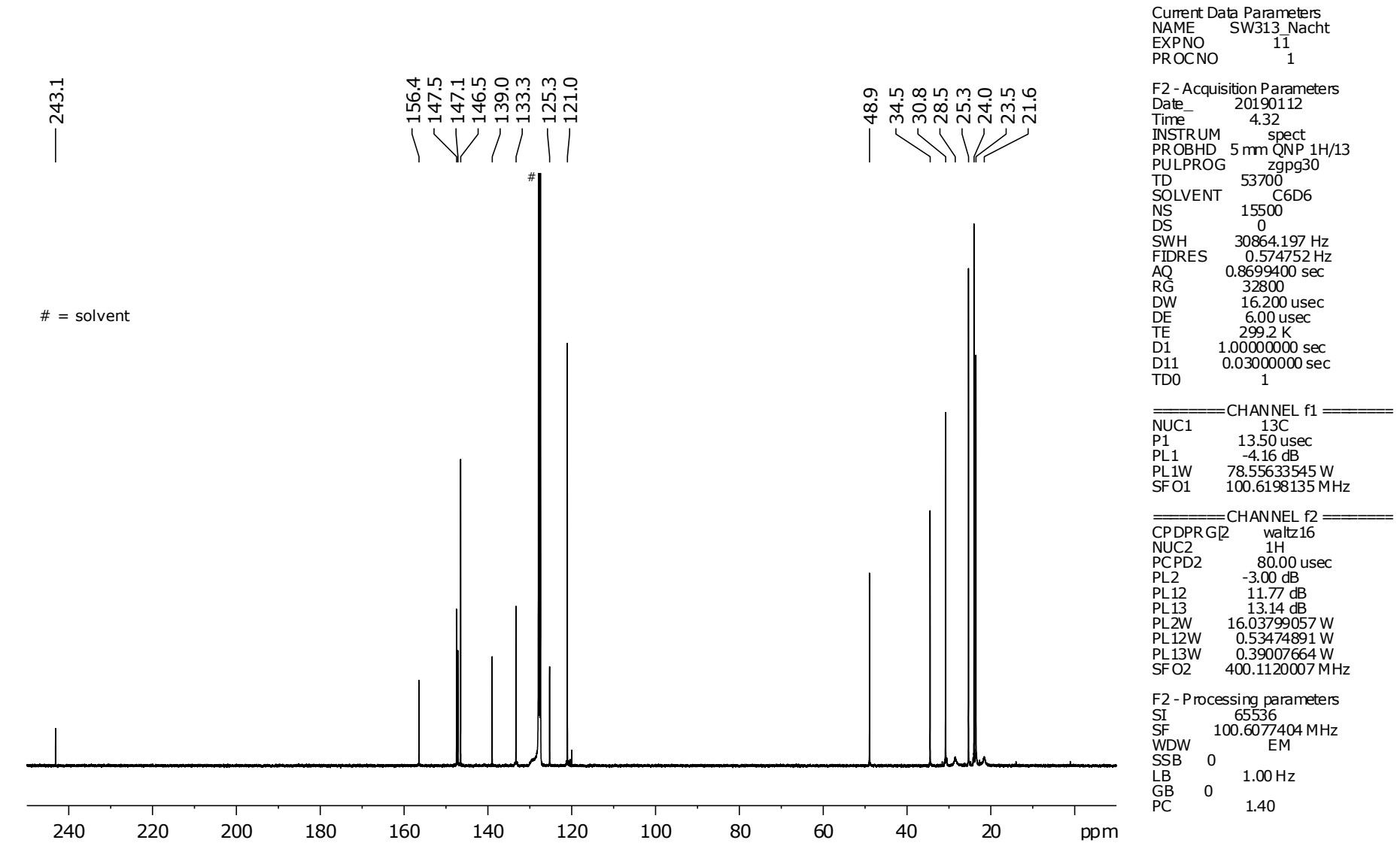
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P1        7.35 usec
PL1       0 dB
SFO1      93.3216955 MHz

F2 - Processing parameters
SI        65536
SF        93.2750580 MHz
WDW       EM
SSB       0
LB        5.00 Hz
GB        0
PC        3.00
```

Figure S5.  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum of **1**

NMR Data of compound **2** $^1\text{H}$ -NMR of Ar\*PbN(Dip)C(H)N(Dip) in  $\text{C}_6\text{D}_6$  at RTFigure S6.  $^1\text{H}$  NMR spectrum of **2**



$^{13}\text{C}$ -NMR of  $\text{Ar}^*\text{PbN}(\text{Dip})\text{C}(\text{H})\text{N}(\text{Dip})$  in  $\text{C}_6\text{D}_6$  at RTFigure S7.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2**

$^{207}\text{Pb}$ -NMR of  $\text{Ar}^*\text{PbN}(\text{Dip})\text{C}(\text{H})\text{N}(\text{Dip})$  in  $\text{C}_6\text{D}_6$  at RT

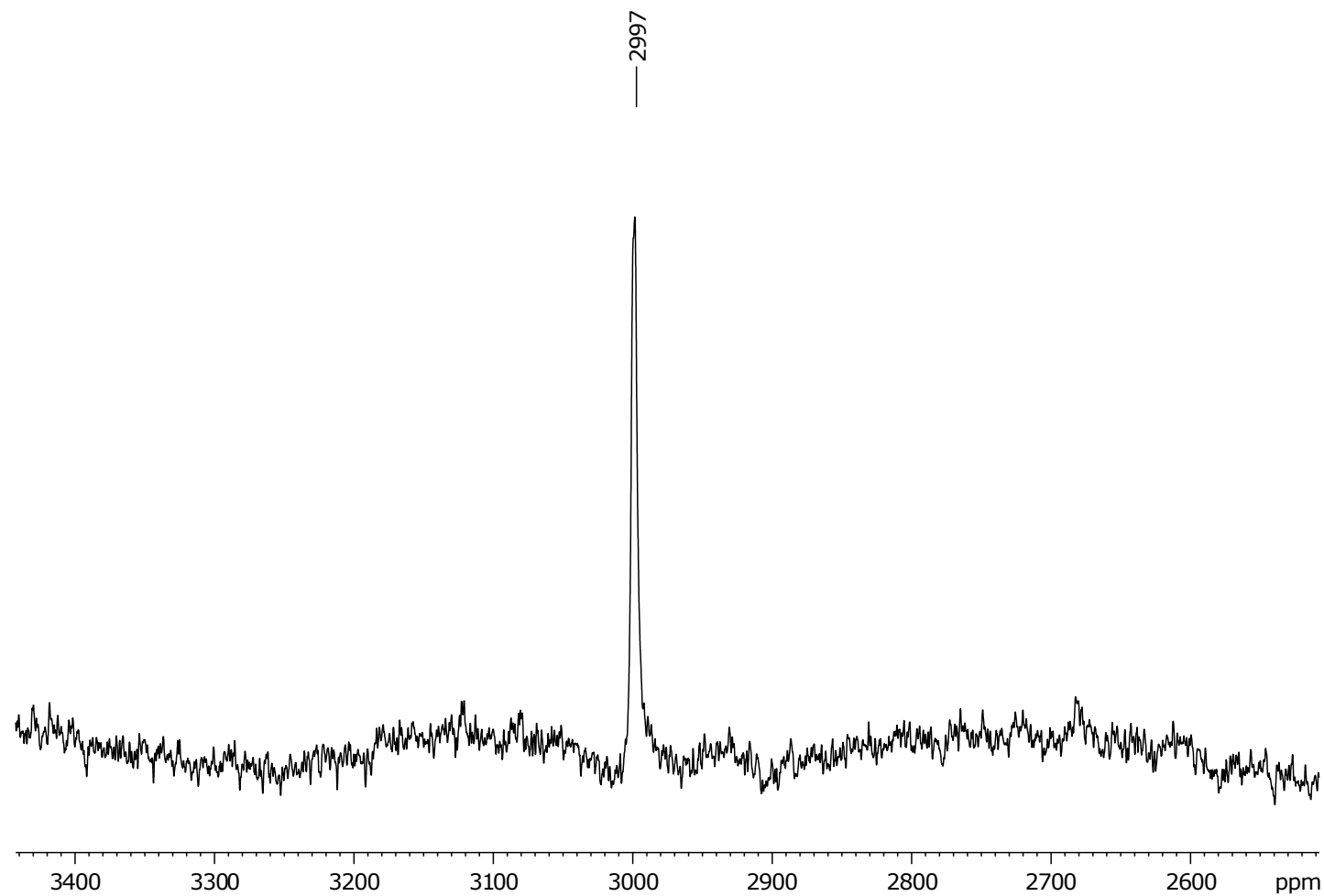


Figure S8.  $^{207}\text{Pb}\{^1\text{H}\}$  NMR spectrum of **2**

Current Data Parameters

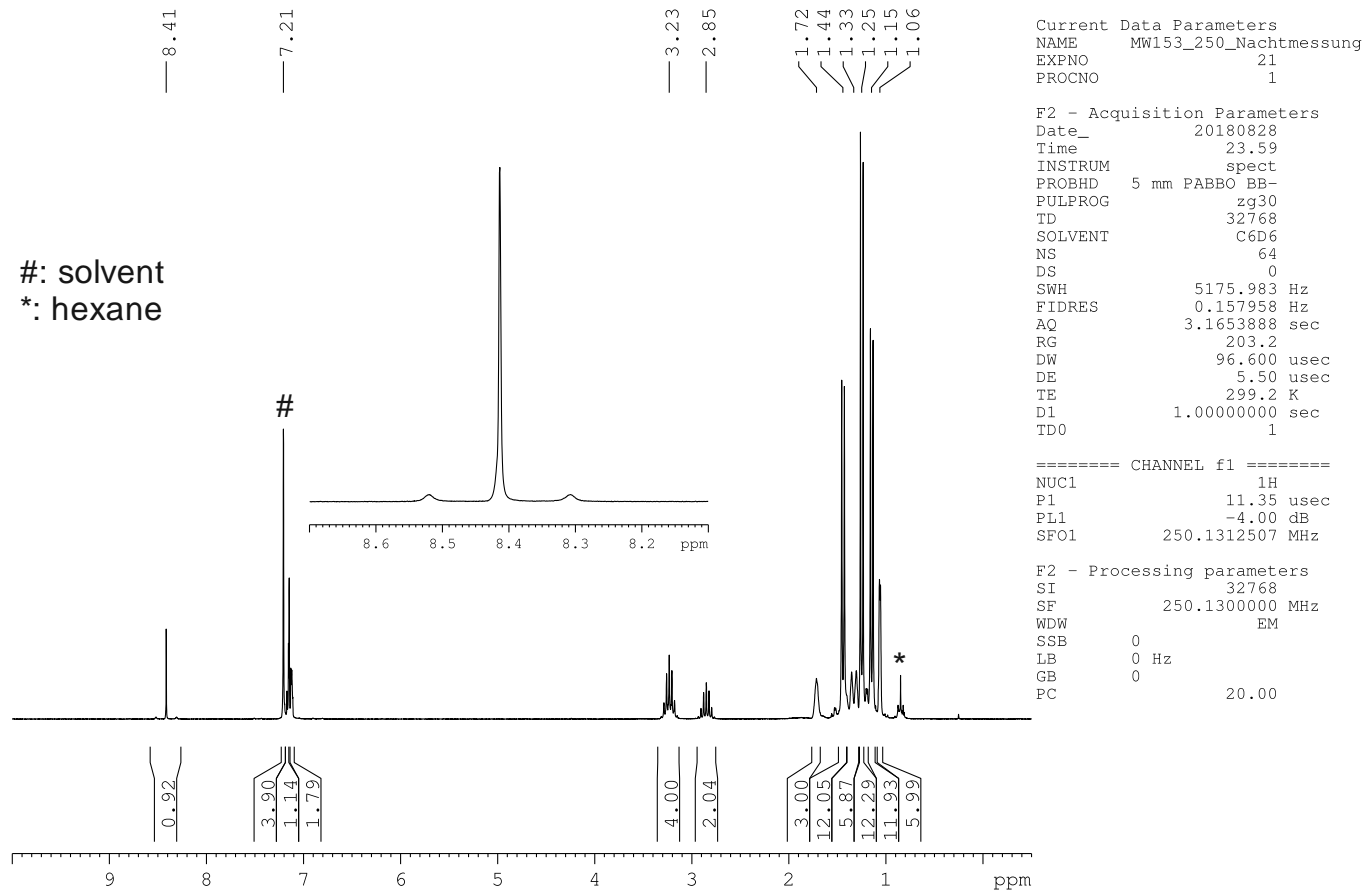
NAME SW313\_Pb  
EXPNO 11  
PROCNO 1

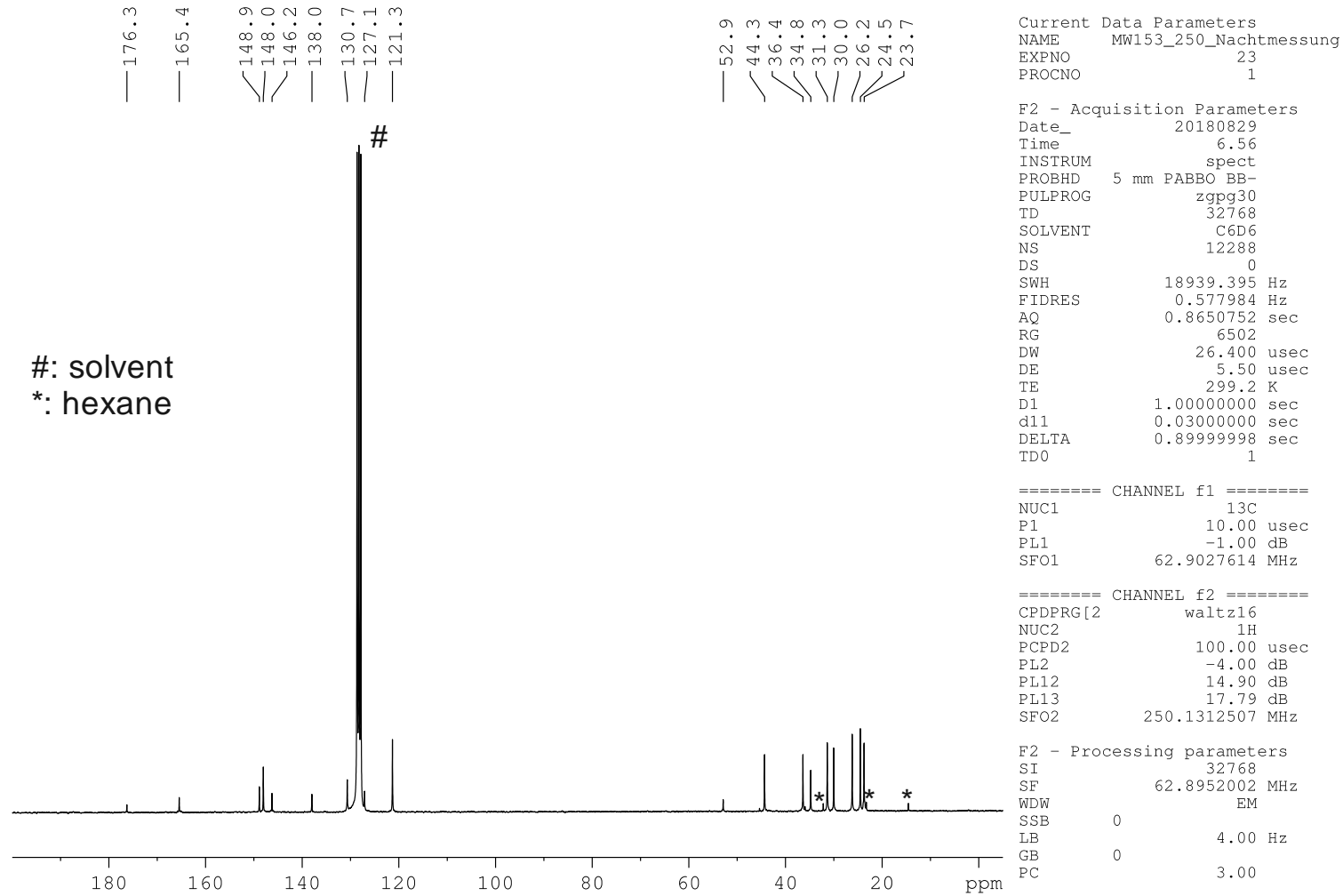
F2 - Acquisition Parameters

Date\_ 20190114  
Time 20.06 h  
INSTRUM spect  
PROBHD Z104275\_0338 (  
PULPROG zg30  
TD 14998  
SOLVENT C6D6  
NS 24450  
DS 0  
SWH 125000.000 Hz  
FIDRES 8.334445 Hz  
AQ 0.0599920 sec  
RG 8.91  
DW 4.000 usec  
DE 6.50 usec  
TE 298.0 K  
D1 0.20000000 sec  
TD0 1  
SFO1 63.0087553 MHz  
NUC1  $^{207}\text{Pb}$   
P1 12.50 usec  
PLW1 40.00000000 W

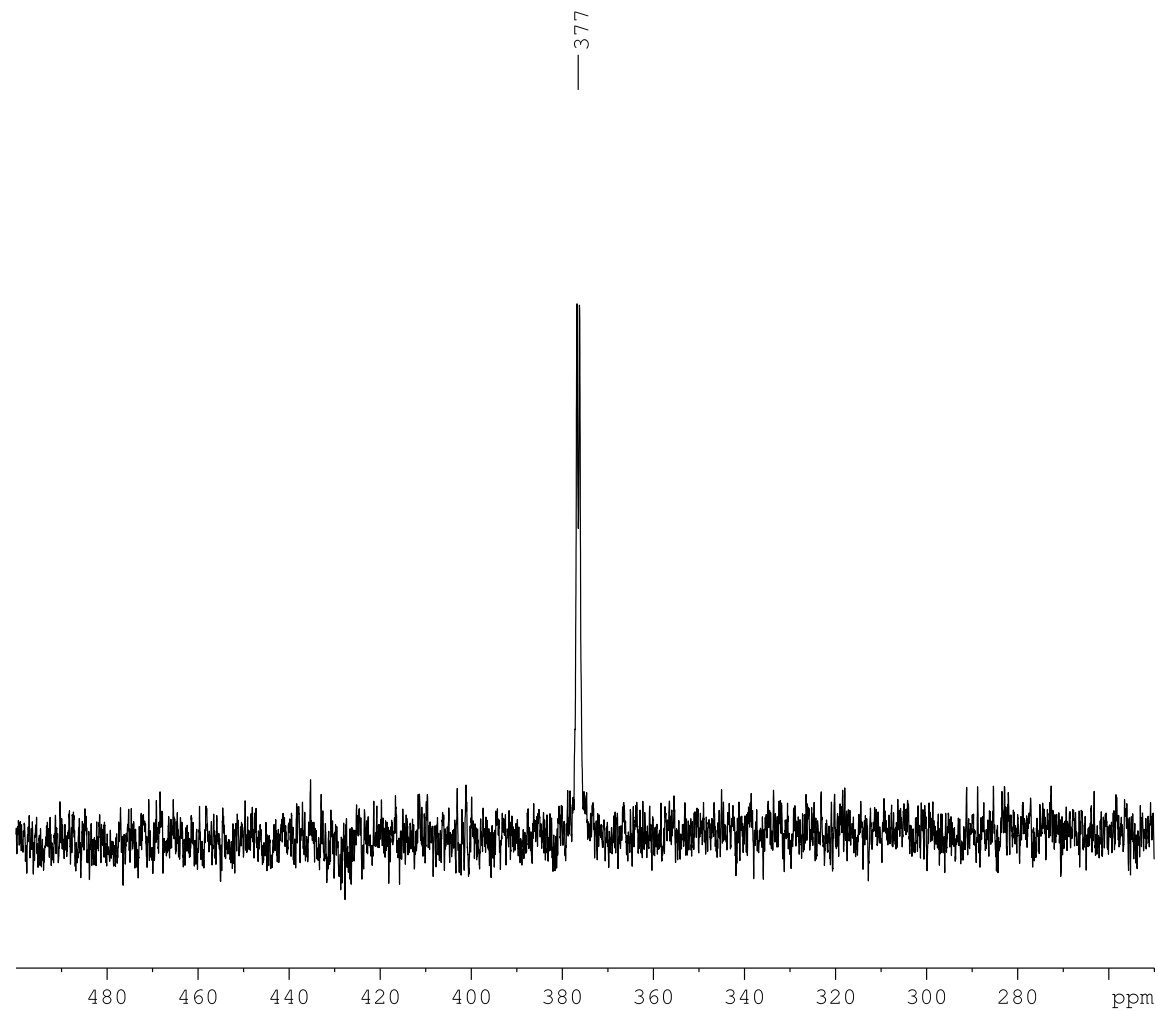
F2 - Processing parameters

SI 65536  
SF 62.7889938 MHz  
WDW EM  
SSB 0  
LB 50.00 Hz  
GB 0  
PC 3.00

NMR Data of compound **3**<sup>1</sup>H-NMR of Ar\*SnN(Ad)C(H)O in C<sub>6</sub>D<sub>6</sub> at RTFigure S9. <sup>1</sup>H NMR spectrum of **3**

$^{13}\text{C}\{^1\text{H}\}$ -NMR of Ar\*SnN(Ad)C(H)O in  $\text{C}_6\text{D}_6$  at RTFigure S10.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3**

$^{119}\text{Sn}$ -NMR of  $\text{Ar}^*\text{SnN}(\text{Ad})\text{C}(\text{H})\text{O}$  in  $\text{C}_6\text{D}_6$  at RT



```
Current Data Parameters
NAME      MW153_250
EXPNO     11
PROCNO    1
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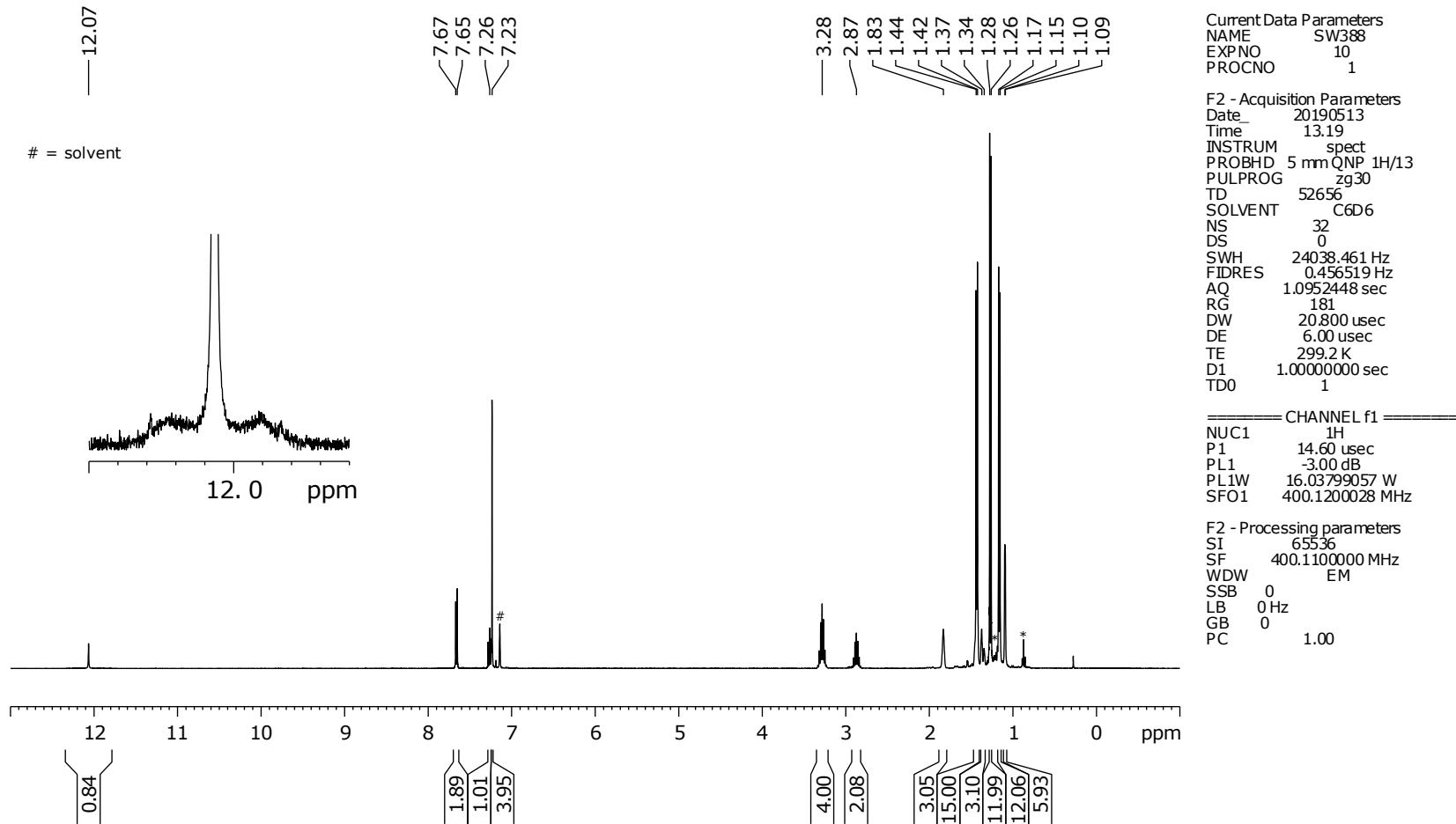
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F2 - Acquisition Parameters
Date_     20180827
Time      16.57
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         32768
SOLVENT   C6D6
NS         4700
DS         0
SWH        74626.867 Hz
FIDRES     2.277431 Hz
AQ         0.2195456 sec
RG         14596.5
DW         6.700 usec
DE         5.50 usec
TE         299.2 K
D1         0.10000000 sec
TD0        1
```

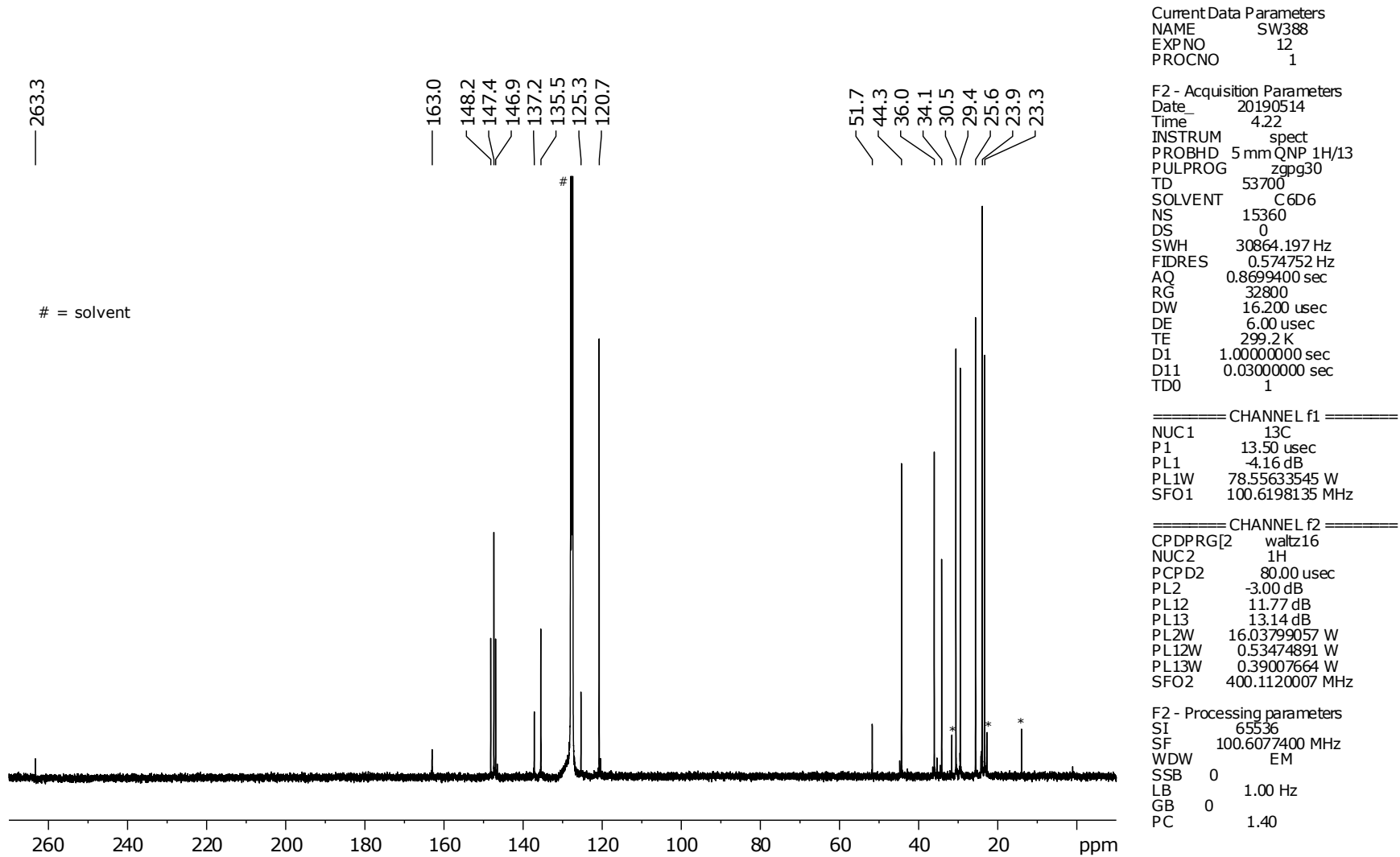
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NUC1      119Sn
P1        7.35 usec
PL1       0 dB
SFO1      93.3123680 MHz
```

```
F2 - Processing parameters
SI        65536
SF        93.2750580 MHz
WDW       EM
SSB       0
LB        8.00 Hz
GB        0
PC        3.00
```

Figure S11.  $^{119}\text{Sn}$  NMR spectrum of **3**

## NMR Data of compound 4

 $^1\text{H}$ -NMR of  $\text{Ar}^*\text{PbN}(\text{Ad})\text{C}(\text{H})\text{O}$  in  $\text{C}_6\text{D}_6$  at RTFigure S12.  $^1\text{H}$  NMR spectrum of 4

$^{13}\text{C}$ -NMR of  $\text{Ar}^*\text{PbN(Ad)C(H)O}$  in  $\text{C}_6\text{D}_6$  at RTFigure S13.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4**

$^{207}\text{Pb}$ -NMR of  $\text{Ar}^*\text{PbN}(\text{Ad})\text{C}(\text{H})\text{O}$  in  $\text{C}_6\text{D}_6$  at RT

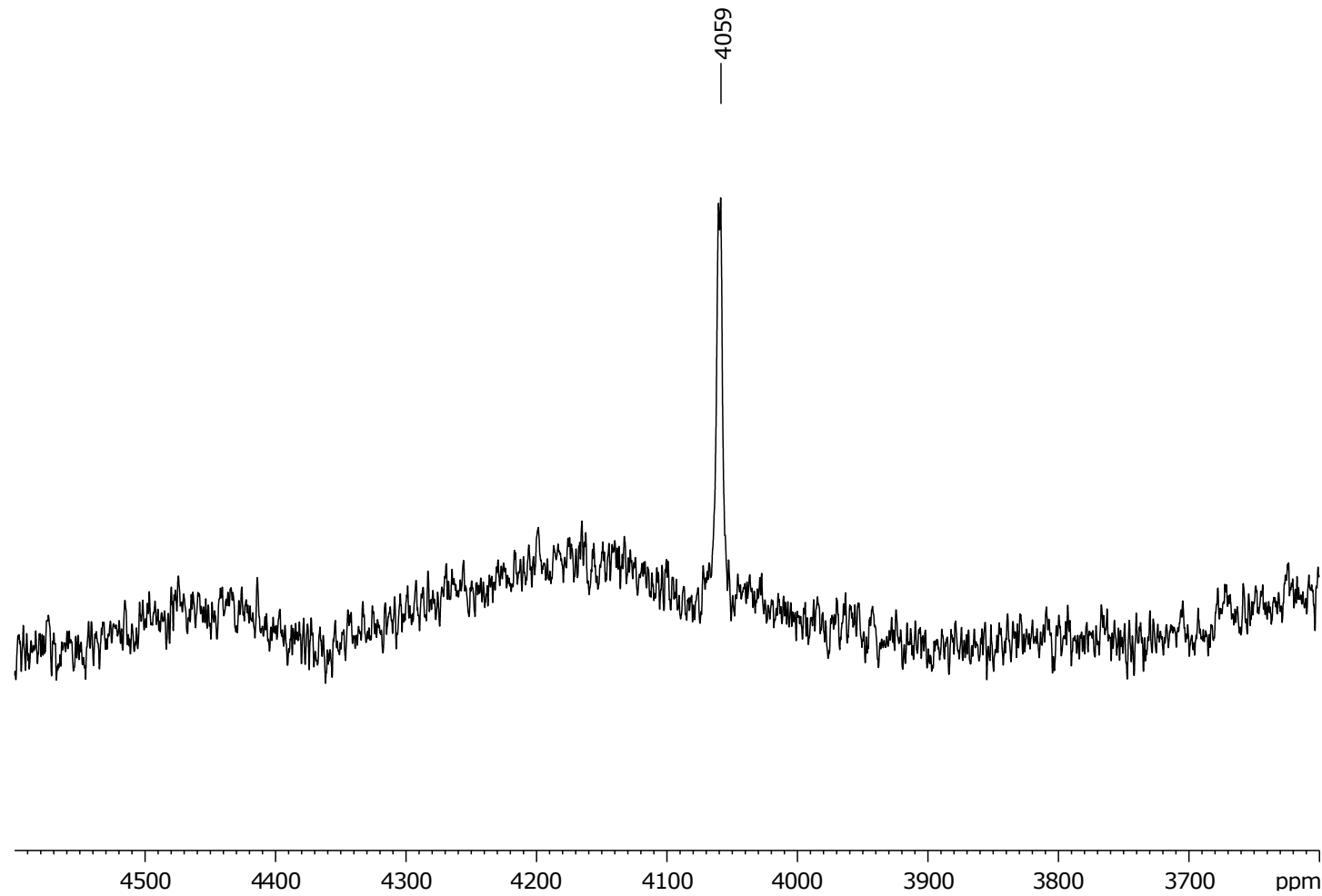


Figure S14.  $^{207}\text{Pb}$  NMR spectrum of **4**

Current Data Parameters

NAME SW388\_Pb  
EXPNO 13  
PROCNO 1

F2 - Acquisition Parameters

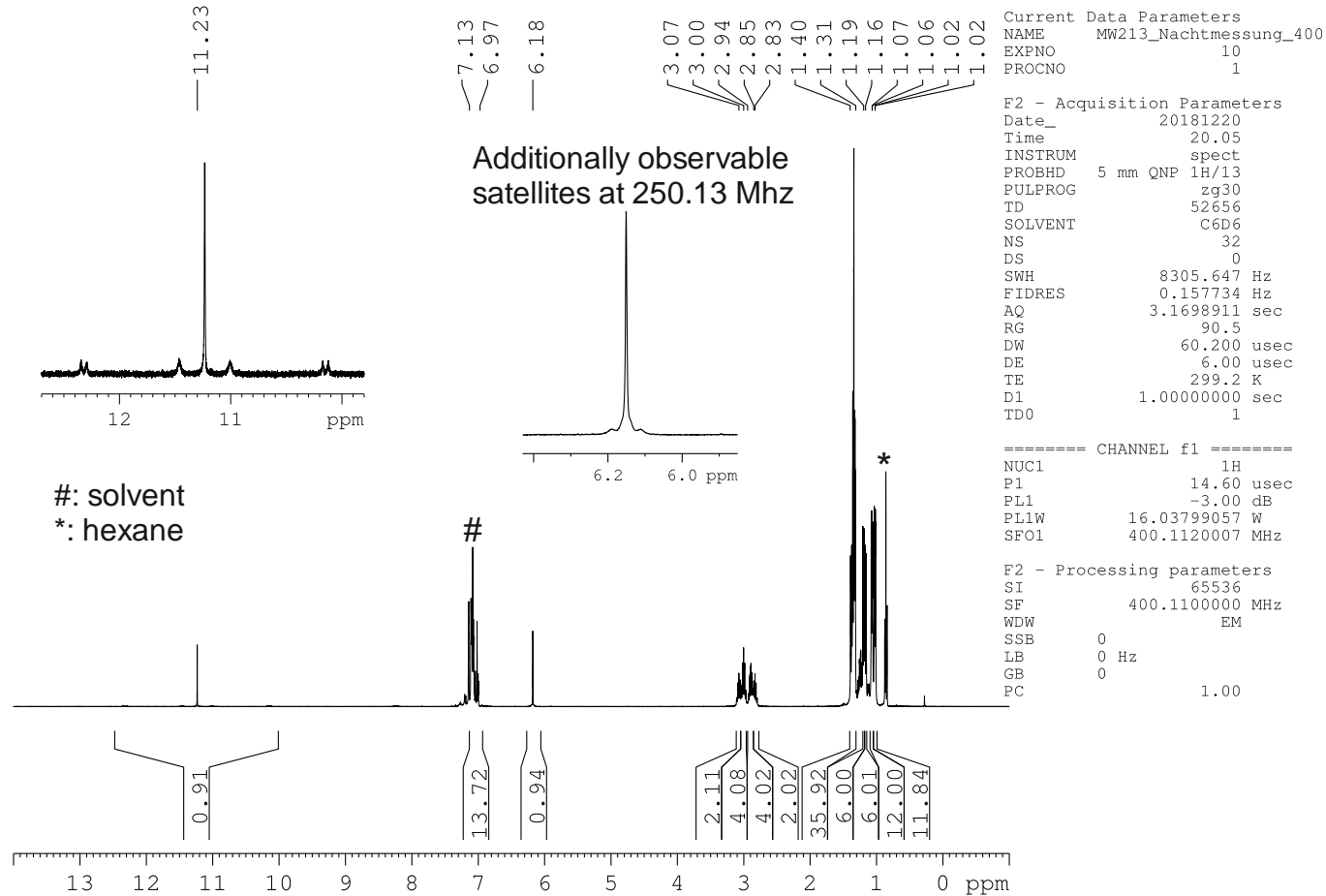
Date\_ 20190515  
Time 4.38 h  
INSTRUM spect  
PROBHD Z104275\_0338 (  
PULPROG zg30  
TD 14998  
SOLVENT C6D6  
NS 22528  
DS 0  
SWH 125000.000 Hz  
FIDRES 8.334445 Hz  
AQ 0.0599920 sec  
RG 204.67  
DW 4.000 usec  
DE 10.00 usec  
TE 298.0 K  
D1 0.20000000 sec  
TD0 1  
SFO1 63.0715443 MHz  
NUC1  $^{207}\text{Pb}$   
P1 12.50 usec  
PLW1 40.00000000 W

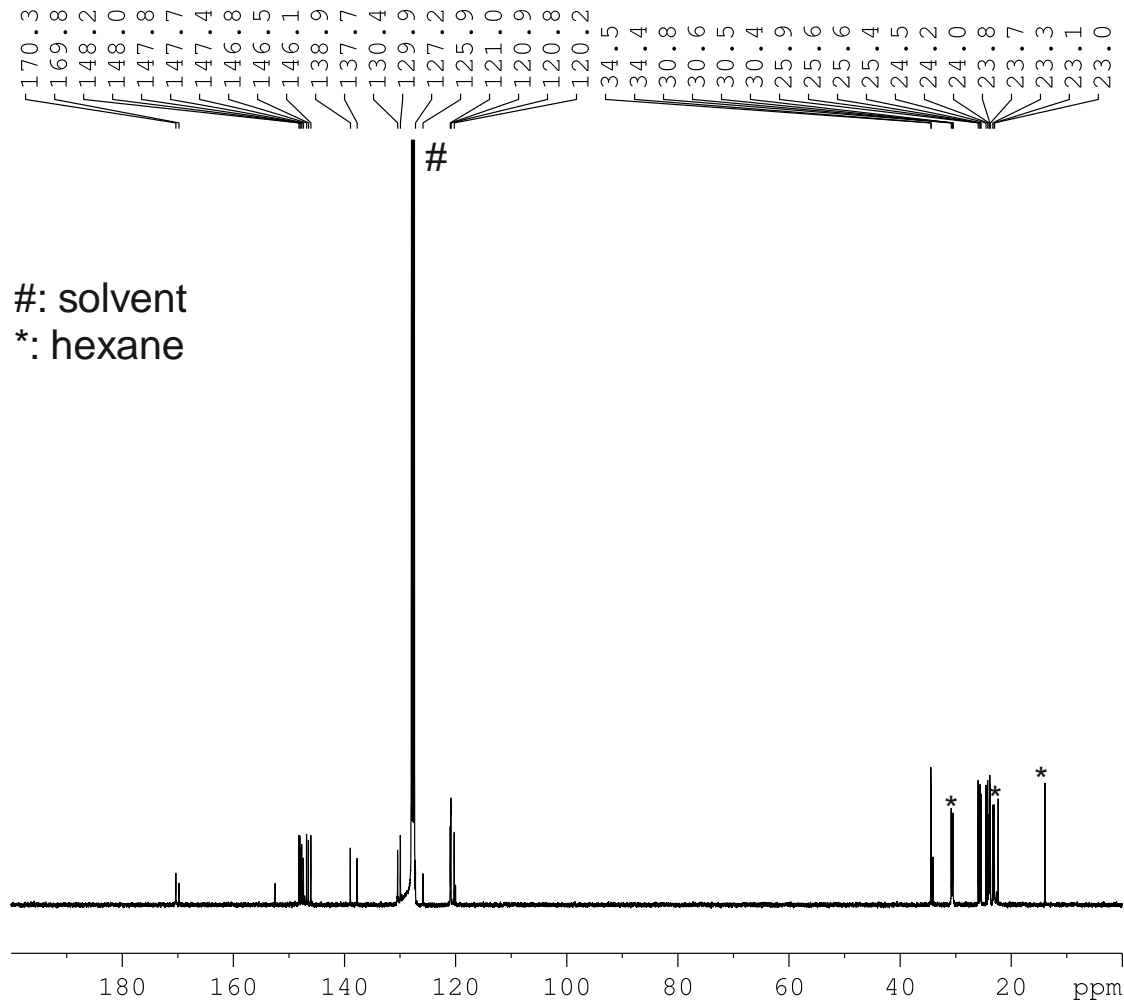
F2 - Processing parameters

SI 65536  
SF 62.7889938 MHz  
WDW EM  
SSB 0  
LB 50.00 Hz  
GB 0  
PC 3.00



## NMR Data of compound 5

 $^1\text{H}$ -NMR of  $\text{Ar}^*\text{Sn}(\text{H})\text{OC}(\text{H})\text{OSnAr}^*$  in  $\text{C}_6\text{D}_6$  at RTFigure S15.  $^1\text{H}$  NMR spectrum of 5

$^{13}\text{C}\{^1\text{H}\}$ -NMR of Ar\*Sn(H)OC(H)OSnAr\* in  $\text{C}_6\text{D}_6$  at RT

Current Data Parameters  
 NAME MW213\_Nachtmessung\_400  
 EXPNO 15  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20181221  
 Time 6.26  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zgpg30  
 TD 53700  
 SOLVENT C6D6  
 NS 10240  
 DS 0  
 SWH 30864.197 Hz  
 FIDRES 0.574752 Hz  
 AQ 0.8699400 sec  
 RG 32800  
 DW 16.200 usec  
 DE 6.00 usec  
 TE 299.2 K  
 D1 1.00000000 sec  
 D11 0.03000000 sec  
 TDO 1

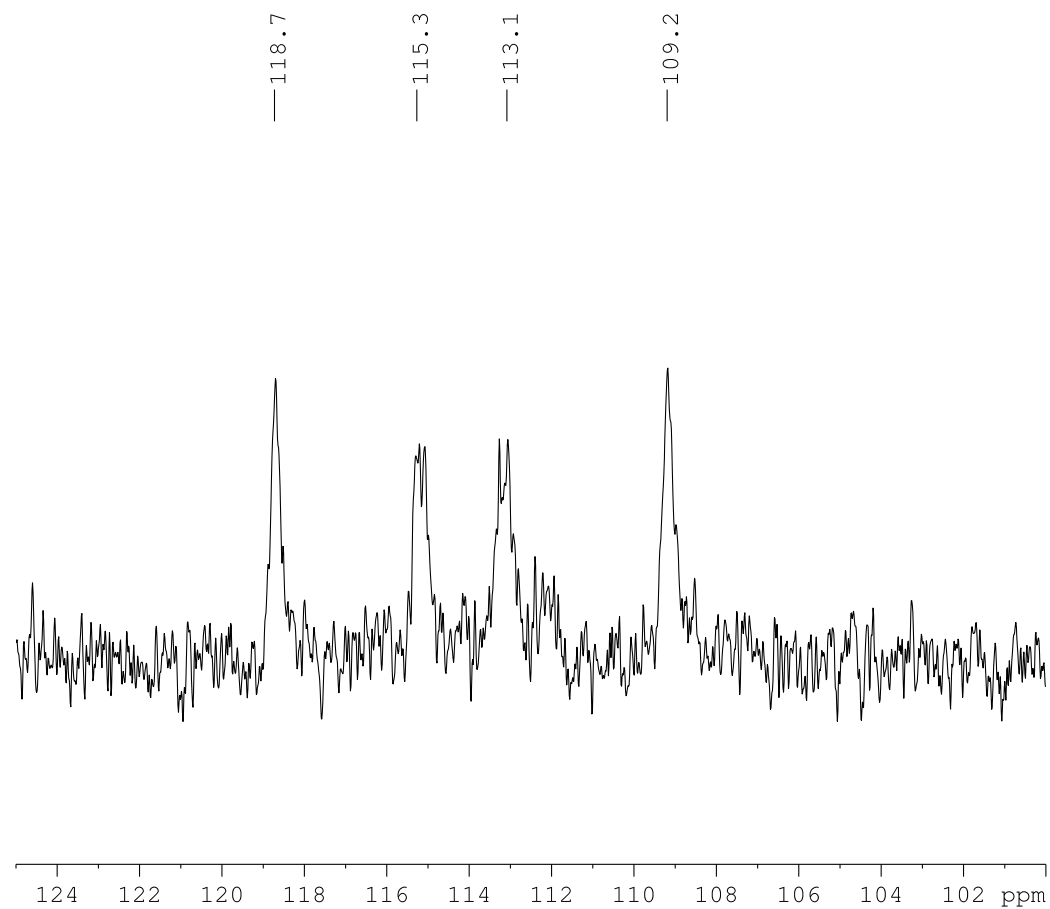
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 P1 13.50 usec  
 PL1 -4.16 dB  
 PL1W 78.55633545 W  
 SFO1 100.6198135 MHz

==== CHANNEL f2 =====  
 CPDPRG[2] waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 11.77 dB  
 PL13 13.14 dB  
 PL2W 16.03799057 W  
 PL12W 0.53474891 W  
 PL13W 0.39007664 W  
 SFO2 400.1120007 MHz

F2 - Processing parameters  
 SI 65536  
 SF 100.6077400 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S16.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 5

$^{119}\text{Sn}$ -NMR of  $\text{Ar}^*\text{Sn}(\text{H})\text{OC}(\text{H})\text{OSnAr}^*$  in  $\text{C}_6\text{D}_6$  at RT



```
Current Data Parameters
NAME          MW213_250
EXPNO         13
PROCNO        1

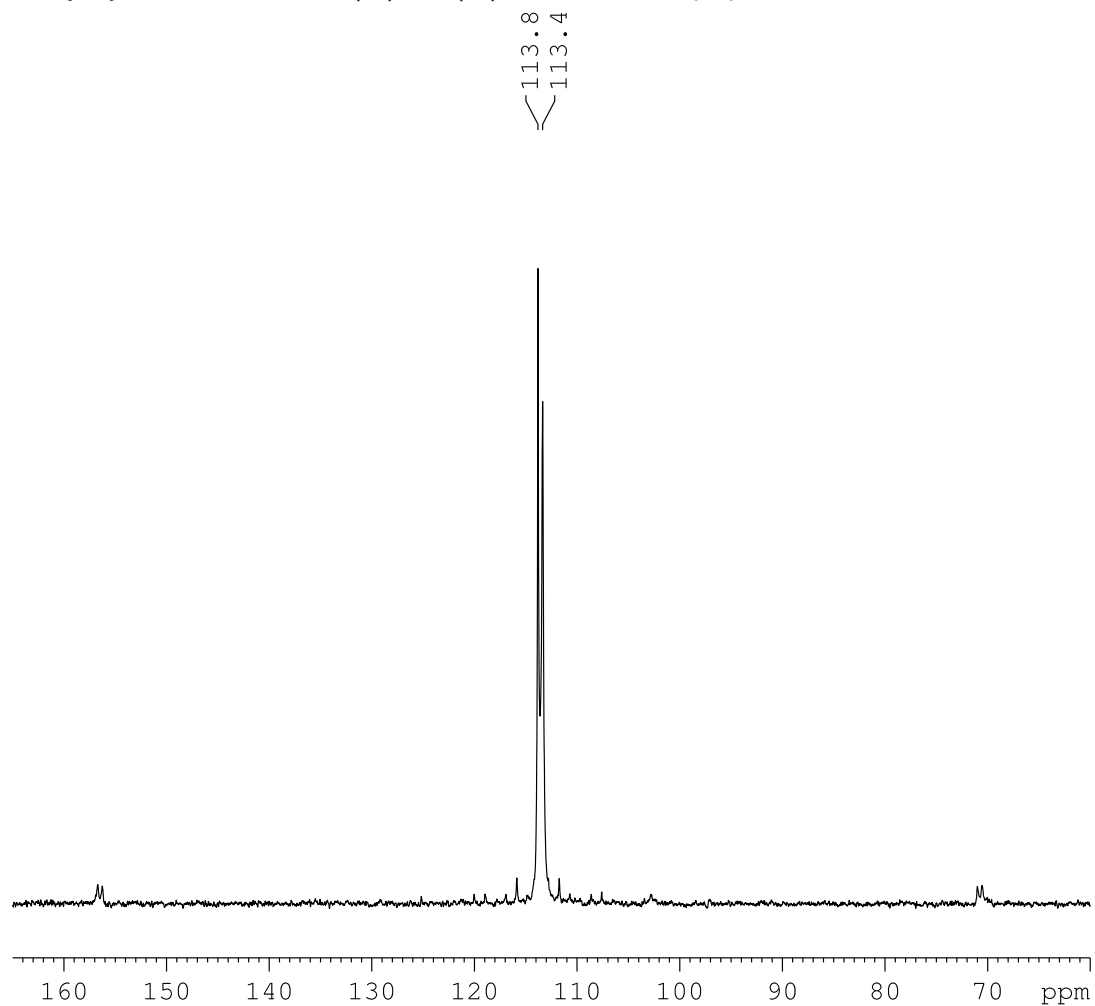
F2 - Acquisition Parameters
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Time          16.39
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            32768
SOLVENT       C6D6
NS            4500
DS            0
SWH           74626.867 Hz
FIDRES        2.277431 Hz
AQ            0.2195456 sec
RG            14596.5
DW            6.700 usec
DE            5.50 usec
TE            299.2 K
D1            0.10000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          119Sn
P1            7.35 usec
PL1           0 dB
SFO1          93.3170318 MHz

F2 - Processing parameters
SI            65536
SF            93.2750580 MHz
WDW           EM
SSB           0
LB            3.00 Hz
GB            0
PC            3.00
```

Figure S17.  $^{119}\text{Sn}$  NMR spectrum of **5**

$^{119}\text{Sn}\{^1\text{H}\}$ -NMR of  $\text{Ar}^*\text{Sn}(\text{H})\text{OC}(\text{H})\text{OSnAr}^*$  in  $\text{C}_6\text{D}_6$  at RT



Current Data Parameters  
 NAME MW222\_300\_Nachtmessung  
 EXPNO 15  
 PROCNO 1

F2 - Acquisition Parameters  
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 Time 4.10 h  
 INSTRUM spect  
 PROBHD Z104275\_0338 ( )  
 PULPROG zgig30  
 TD 39186  
 SOLVENT C6D6  
 NS 30720  
 DS 4  
 SWH 89285.711 Hz  
 FIDRES 2.278511 Hz  
 AQ 0.2194416 sec  
 RG 204.67  
 DW 5.600 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 0.10000000 sec  
 D11 0.03000000 sec  
 TD0 1  
 SFO1 111.9315658 MHz  
 NUC1  $^{119}\text{Sn}$   
 P1 12.10 usec  
 PLW1 12.00000000 W  
 SFO2 300.1312005 MHz  
 NUC2  $^1\text{H}$   
 CPDPRG[2] waltz16  
 PCPD2 90.00 usec  
 PLW2 8.26509953 W  
 PLW12 0.19511271 W

F2 - Processing parameters  
 SI 65536  
 SF 111.9203738 MHz  
 WDW EM  
 SSB 0  
 LB 5.00 Hz  
 GB 0  
 PC 1.40

Figure S18.  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum of **5**

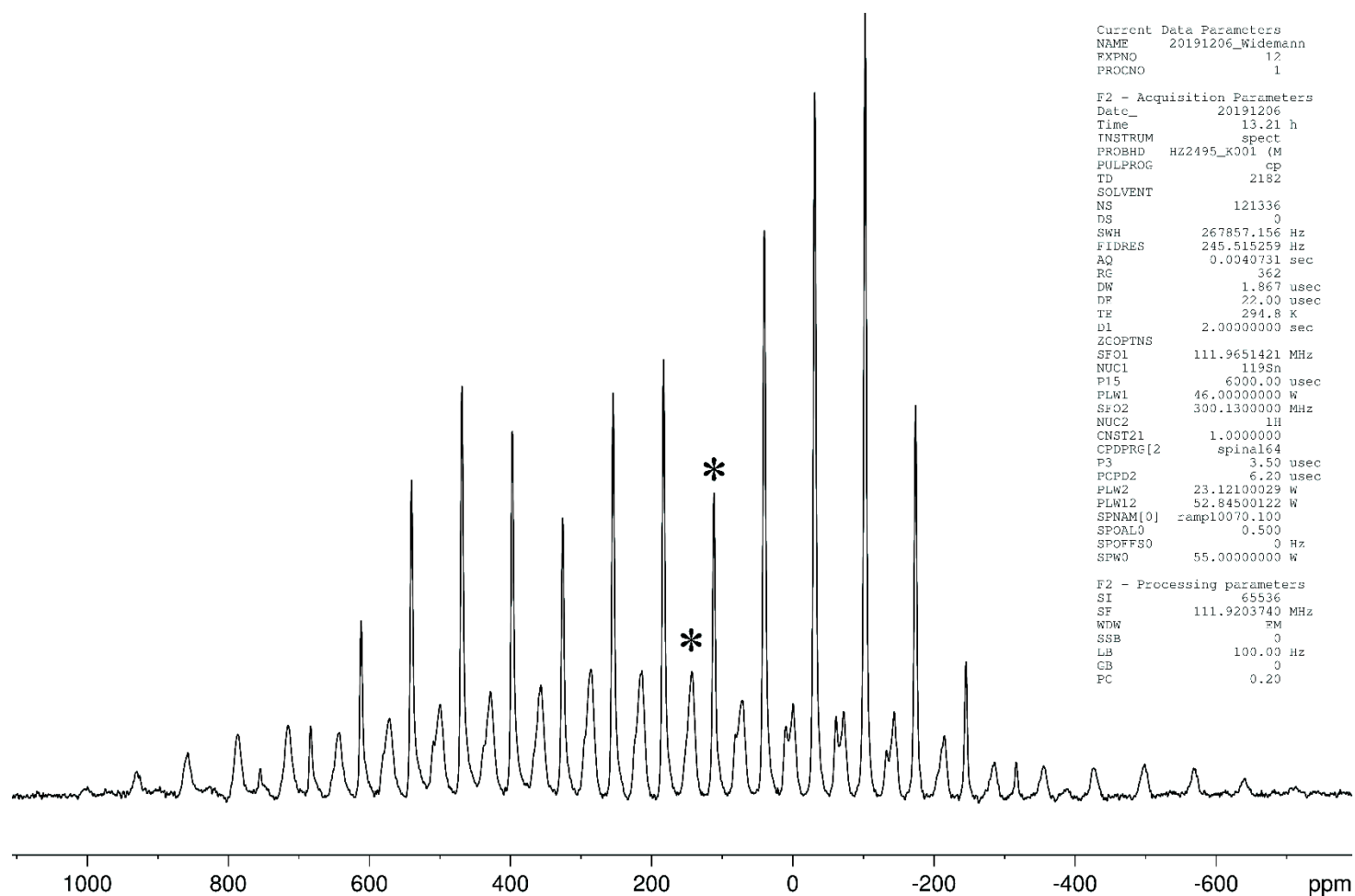


Figure S19. 111.9 MHz  $^{119}\text{Sn}$  CP/MAS NMR spectrum of **5** obtained at a spinning rate of 8 kHz. The isotropic peaks are indicated by asterisks. Sn-H:  $\delta_{\text{iso}} = 112$ ,  $\delta_{11} = 658(8)$ ,  $\delta_{22} = -62(6)$ ,  $\delta_{33} = -261(6)$ , span  $\Omega = 919(5)$ , skew  $\kappa = -0.57(2)$ ; Sn H-free:  $\delta_{\text{iso}} = 146$ ,  $\delta_{11} = 885(29)$ ,  $\delta_{22} = 218(20)$ ,  $\delta_{33} = -665(21)$ , span  $\Omega = 1550(11)$ , skew  $\kappa = 0.14(4)$ . The splittings in the spinning sidebands of the broader, H-free species visible in the region 0 to -200 ppm are ascribed to overlap with satellites due to  $^1J_{\text{Sn-119,Sn-117,119}}$  coupling (ca. 9200 Hz) associated with the strongest spinning sidebands of the Sn-H species, resulting in greater errors in the spinning sideband analysis.

S22

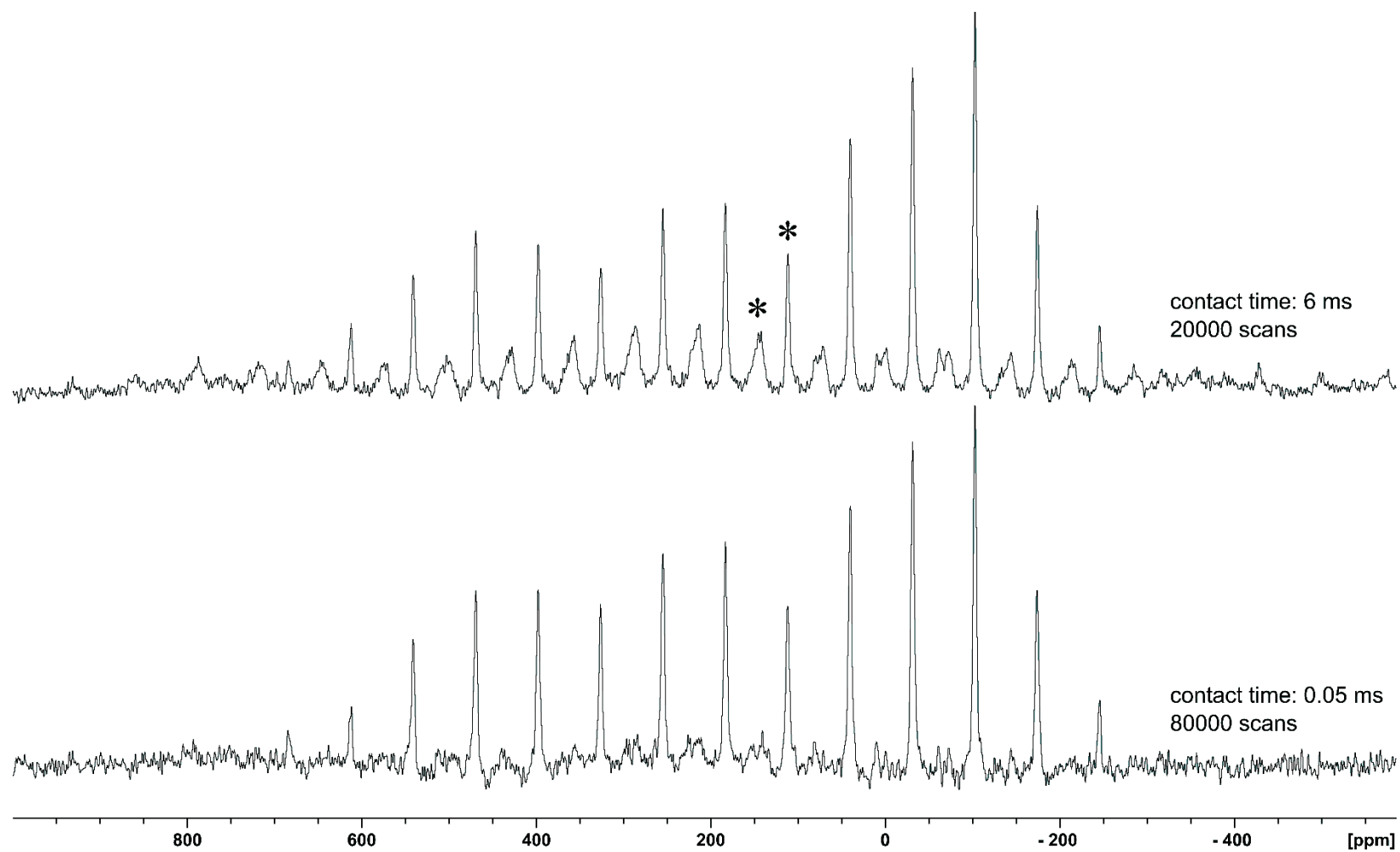
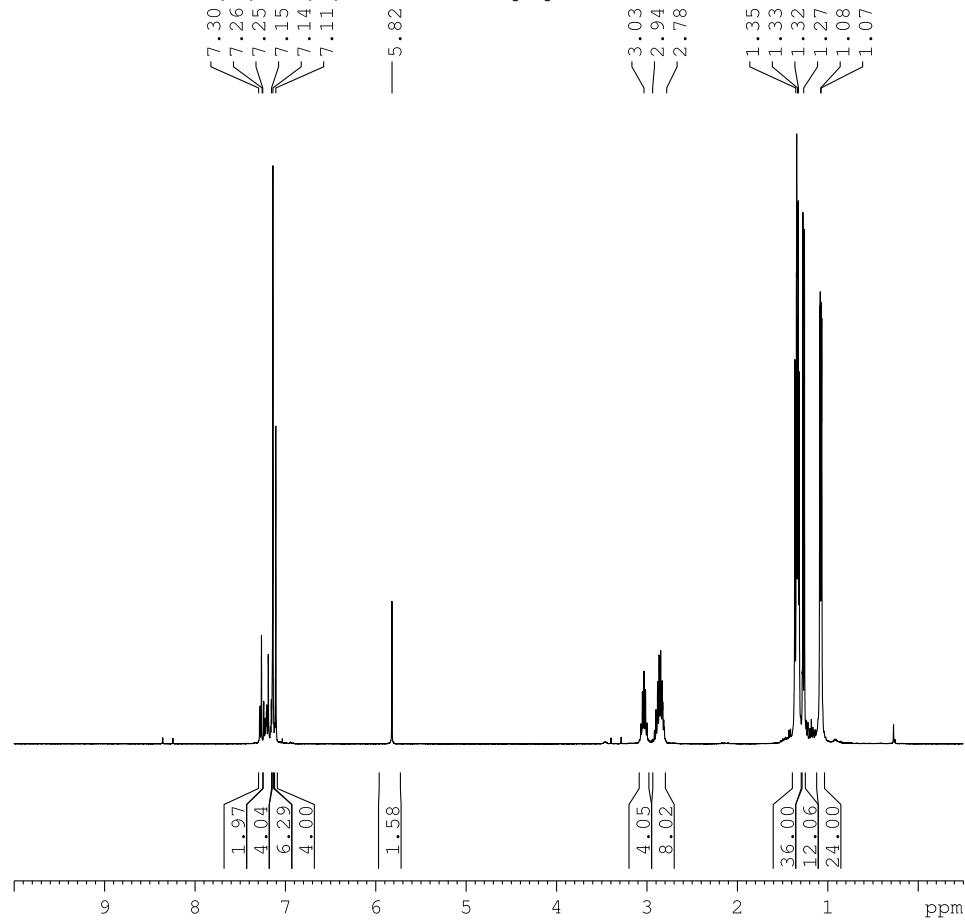


Figure S20. 111.9 MHz variable contact time  $^{119}\text{Sn}$  CP/MAS NMR spectra of **5** obtained at a spinning rate of 8 kHz. The isotropic peaks are indicated by asterisks. The upper spectrum was obtained after a contact time of 6 ms, the lower spectrum used a very short contact time of 0.05 ms to basically eliminate the contribution of the proton free Sn atom. NQS (non-quaternary suppression) experiments<sup>1</sup> turned out inconclusive.

## NMR Data of compound 6

<sup>1</sup>H-NMR of Ar\*Sn(H)2C(S)2SnAr\* in C<sub>6</sub>D<sub>6</sub> at RT

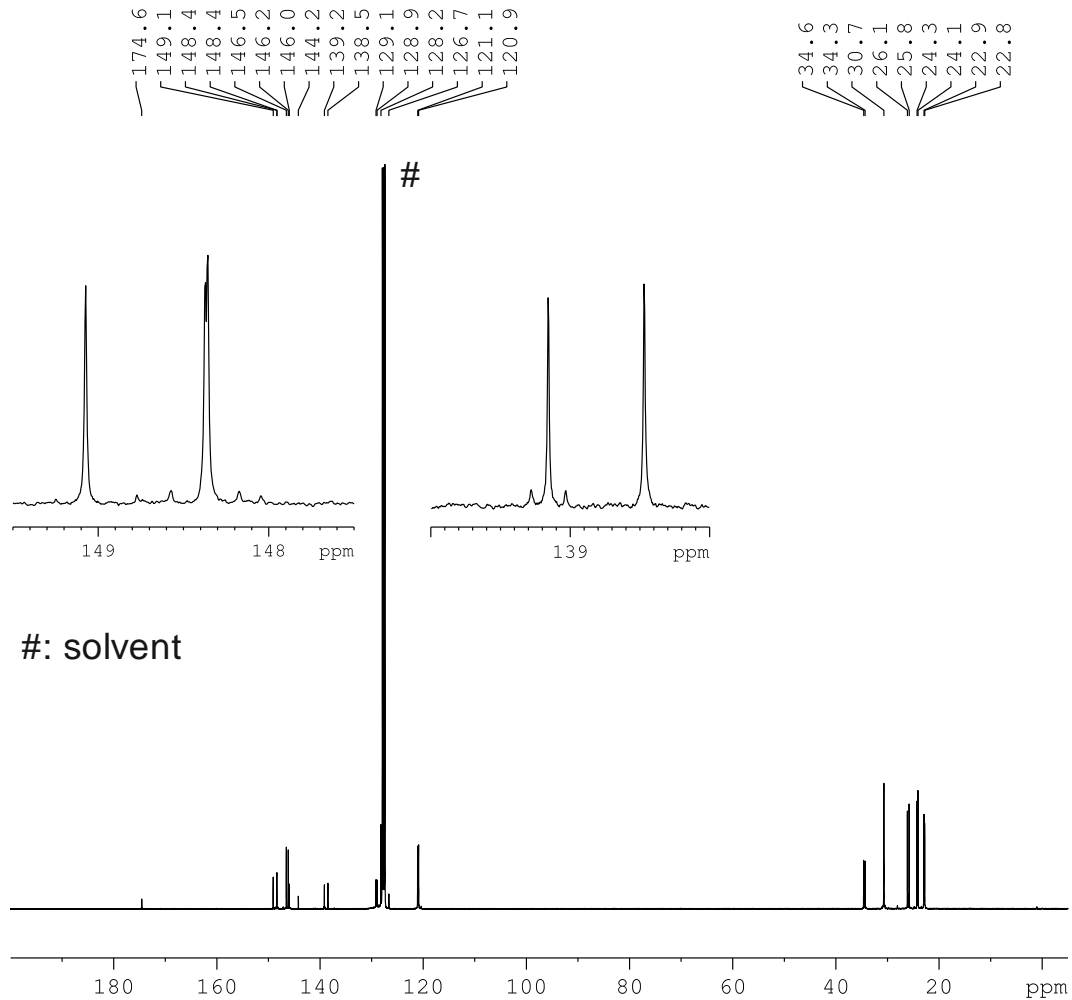
Current Data Parameters  
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 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190208  
 Time 20.04  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zg30  
 TD 52656  
 SOLVENT C6D6  
 NS 16  
 DS 0  
 SWH 8305.647 Hz  
 FIDRES 0.157734 Hz  
 AQ 3.1698911 sec  
 RG 57  
 DW 60.200 usec  
 DE 6.00 usec  
 TE 299.2 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 14.60 usec  
 PL1 -3.00 dB  
 PL1W 16.03799057 W  
 SFO1 400.1120007 MHz

F2 - Processing parameters  
 SI 65536  
 SF 400.1100000 MHz  
 WDW EM  
 SSB 0  
 LB 0 Hz  
 GB 0  
 PC 1.00

Figure S21. <sup>1</sup>H NMR spectrum of 6

$^{13}\text{C}\{^1\text{H}\}$ -NMR of  $\text{Ar}^*\text{Sn}(\text{H})_2\text{C}(\text{S})_2\text{SnAr}^*$  in  $\text{C}_6\text{D}_6$  at RT

Current Data Parameters  
 NAME MW262\_400\_Nachtmessung\_50mg  
 EXPNO 16  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190209  
 Time 0.46  
 INSTRUM spect  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zgpg30  
 TD 53700  
 SOLVENT C6D6  
 NS 15360  
 DS 0  
 SWH 30864.197 Hz  
 FIDRES 0.574752 Hz  
 AQ 0.8699400 sec  
 RG 32800  
 DW 16.200 usec  
 DE 6.00 usec  
 TE 299.2 K  
 D1 1.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 13.50 usec  
 PL1 -4.16 dB  
 PL1W 78.55633545 W  
 SFO1 100.6198135 MHz

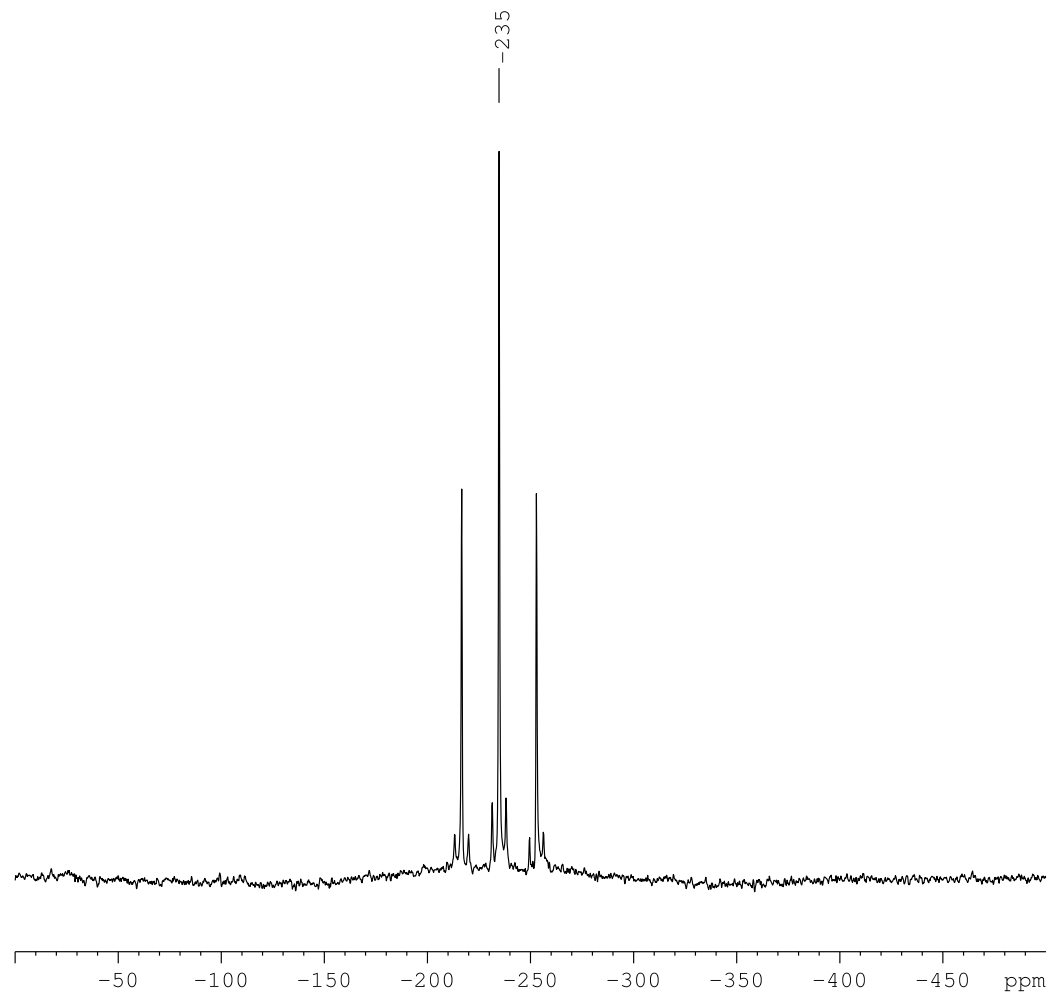
===== CHANNEL f2 =====  
 CPDPRG[2] waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 11.77 dB  
 PL13 13.14 dB  
 PL2W 16.03799057 W  
 PL12W 0.53474891 W  
 PL13W 0.39007664 W  
 SFO2 400.1120007 MHz

F2 - Processing parameters  
 SI 65536  
 SF 100.6077400 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S22.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **6**



$^{119}\text{Sn}$ -NMR of  $\text{Ar}^*\text{Sn}(\text{H})_2\text{C}(\text{S})_2\text{SnAr}^*$  in  $\text{C}_6\text{D}_6$  at RT

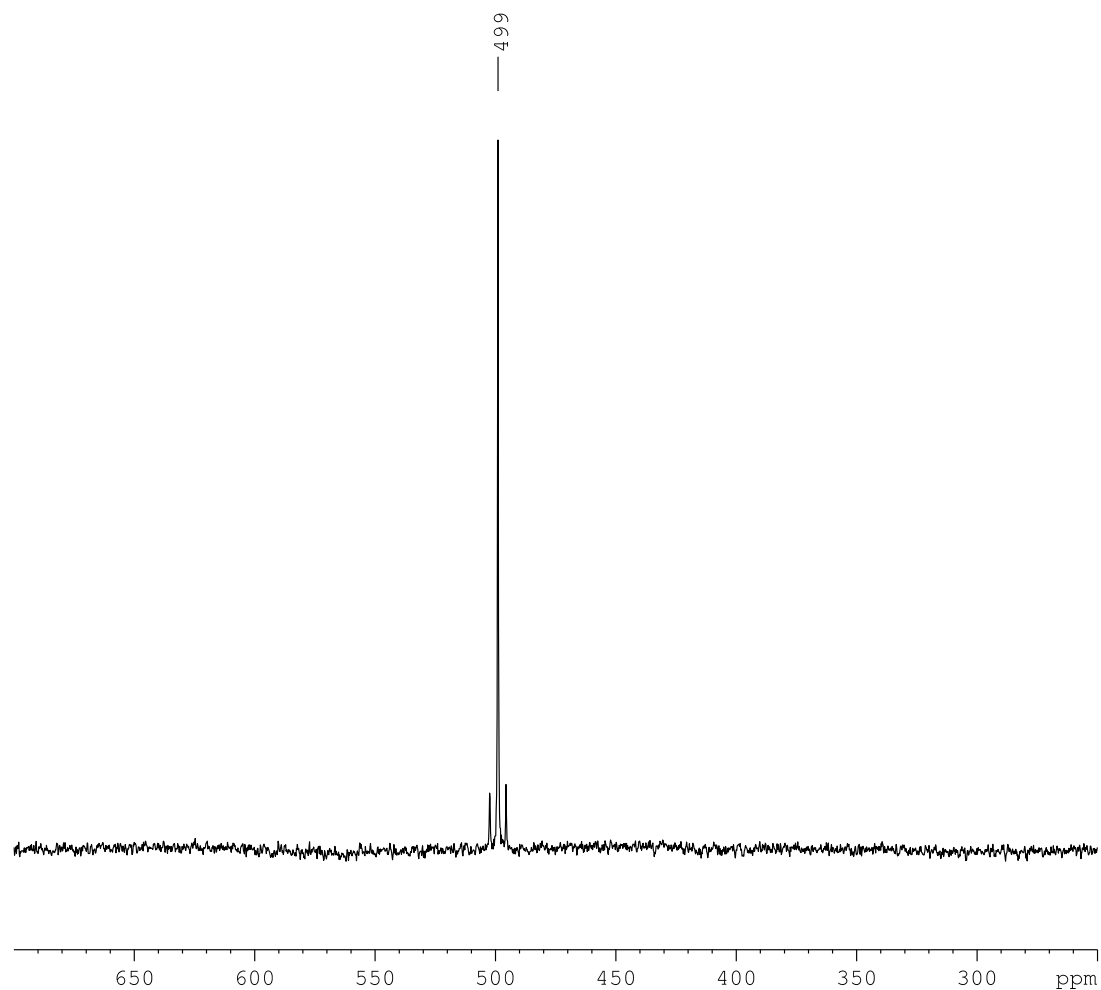


Current Data Parameters  
NAME MW262\_300\_Nachtmessung\_50mg  
EXPNO 11  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20190212  
Time 0.53 h  
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PULPROG zg30  
TD 11264  
SOLVENT C6D6  
NS 179200  
DS 1  
SWH 89285.711 Hz  
FIDRES 7.926644 Hz  
AQ 0.0630784 sec  
RG 204.67  
DW 5.600 usec  
DE 6.50 usec  
TE 298.0 K  
D1 0.02000000 sec  
TD0 1  
SFO1 111.8979900 MHz  
NUC1 119Sn  
P1 12.10 usec  
PLW1 12.00000000 W

F2 - Processing parameters  
SI 4096  
SF 111.9203740 MHz  
WDW EM  
SSB 0  
LB 40.00 Hz  
GB 0  
PC 1.40

Figure S23.  $^{119}\text{Sn}$  NMR spectrum of **6**

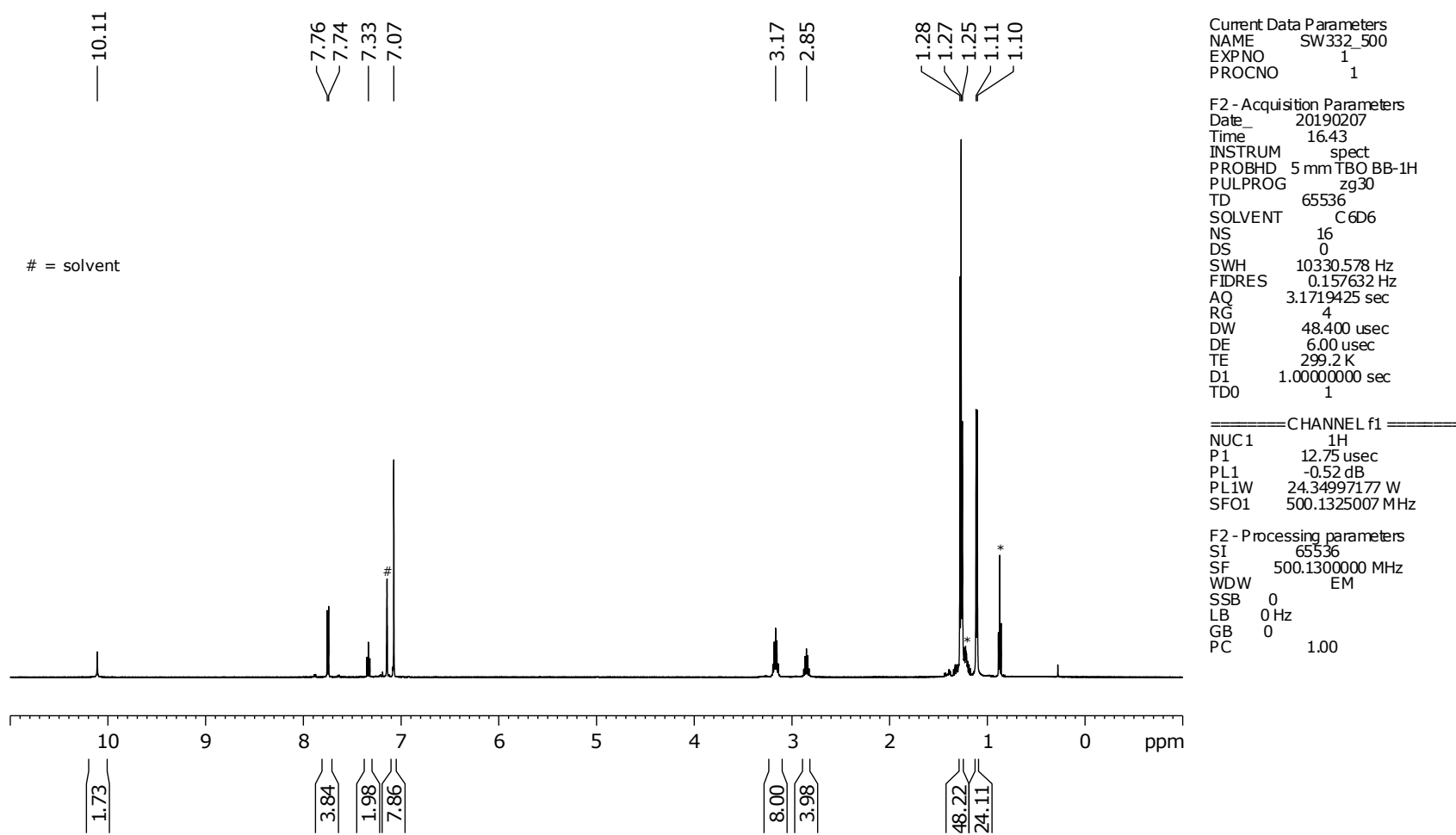
$^{119}\text{Sn}$ -NMR of  $\text{Ar}^*\text{Sn}(\text{H})_2\text{C}(\text{S})_2\text{SnAr}^*$  in  $\text{C}_6\text{D}_6$  at RT

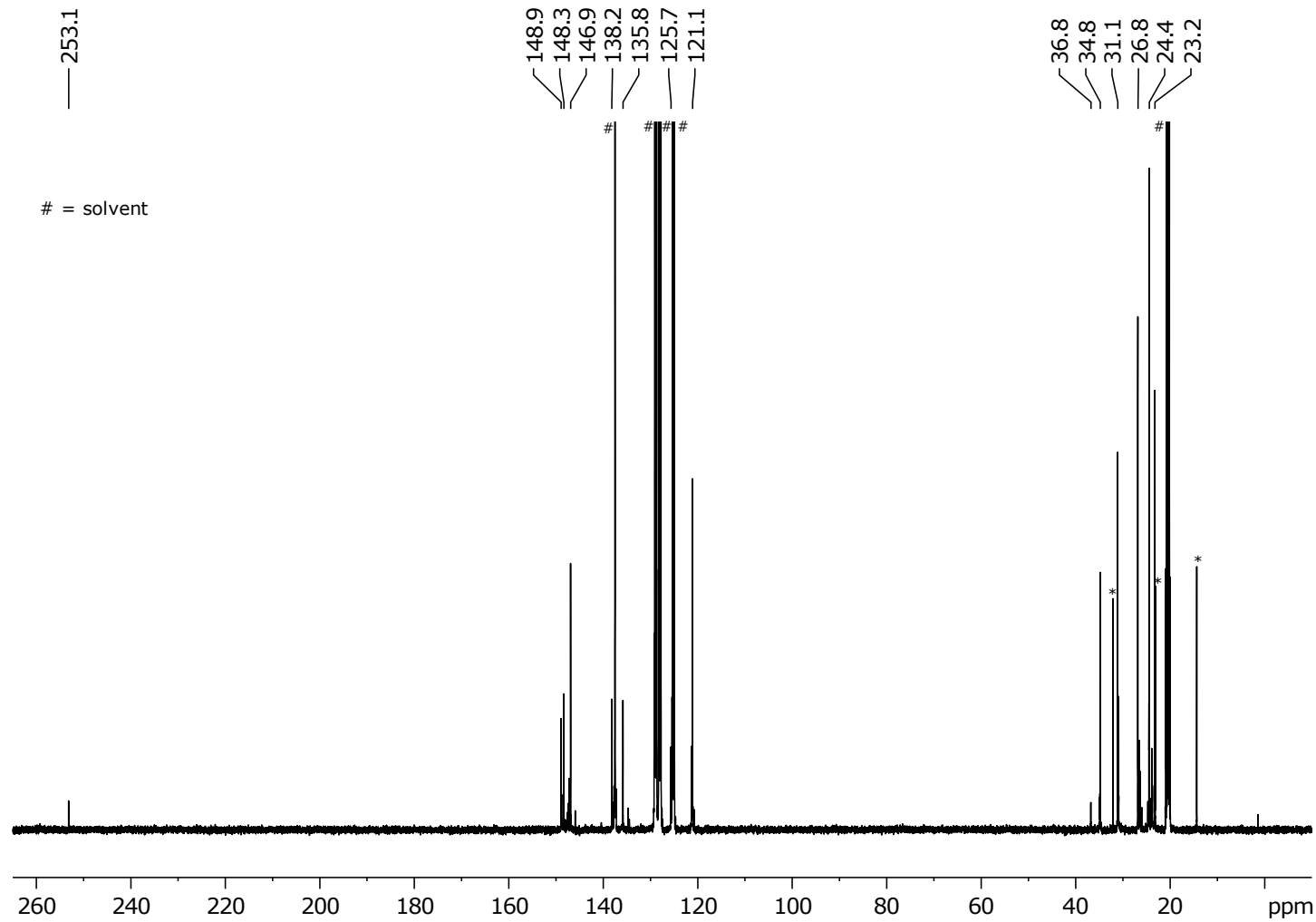
Current Data Parameters  
NAME MW242\_300\_Nachtmessung  
EXPNO 12  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20190201  
Time 23.41 h  
INSTRUM spect  
PROBHD Z104275\_0338 (  
PULPROG zg30  
TD 5120  
SOLVENT C6D6  
NS 122880  
DS 1  
SWH 89285.711 Hz  
FIDRES 17.438616 Hz  
AQ 0.0286720 sec  
RG 204.67  
DW 5.600 usec  
DE 6.50 usec  
TE 298.0 K  
D1 0.02000000 sec  
TD0 1  
SF01 111.9763340 MHz  
NUC1  $^{119}\text{Sn}$   
P1 12.10 usec  
PLW1 12.00000000 W

F2 - Processing parameters  
SI 4096  
SF 111.9203740 MHz  
WDW EM  
SSB 0  
LB 20.00 Hz  
GB 0  
PC 1.40

Figure S24.  $^{119}\text{Sn}$  NMR spectrum of **6**

NMR Data of compound **7** $^1\text{H}$ -NMR of  $(\text{Ar}^*\text{PbS})_2\text{CH}_2$  in  $\text{C}_6\text{D}_6$  at RTFigure S25.  $^1\text{H}$  NMR spectrum of **7**

$^{13}\text{C}$ -NMR of  $(\text{Ar}^*\text{PbS})_2\text{CH}_2$  in Tol- $d_8$  at RTFigure S26.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **7**

Current Data Parameters  
 NAME SW417\_500 - Kopie  
 EXPNO 12  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20190606  
 Time 23.16  
 INSTRUM spect  
 PROBHD 5 mm TBO BB-1H  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT Tol  
 NS 20480  
 DS 0  
 SWH 37878.789 Hz  
 FIDRES 0.577984 Hz  
 AQ 0.8650752 sec  
 RG 2050  
 DW 13.200 usec  
 DE 6.00 usec  
 TE 299.2 K  
 D1 1.0000000 sec  
 D11 0.03000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 11.00 usec  
 PL1 0 dB  
 PL1W 83.89700317 W  
 SFO1 125.7728799 MHz

===== CHANNEL f2 =====  
 CPDPRG[2] waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 0 dB  
 PL12 16.94 dB  
 PL13 21.51 dB  
 PL2W 21.60222244 W  
 PL12W 0.43701705 W  
 PL13W 0.15258029 W  
 SFO2 500.1325007 MHz

F2 - Processing parameters  
 SI 65536  
 SF 125.7577396 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

$^{207}\text{Pb}$ -NMR of  $(\text{Ar}^*\text{PbS})_2\text{CH}_2$  in Tol- $d_8$  at RT

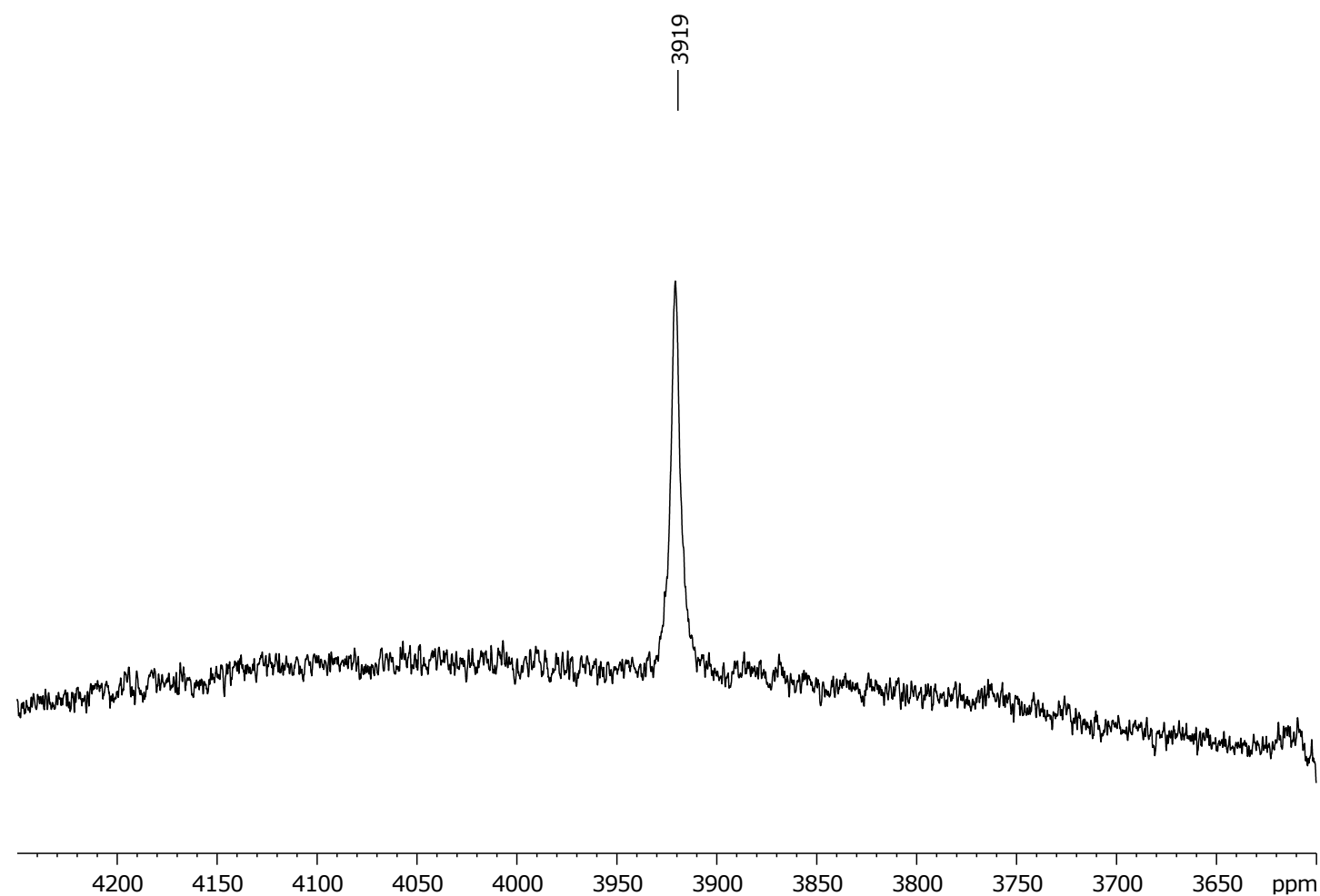


Figure S27.  $^{207}\text{Pb}$  NMR spectrum of **7**

Current Data Parameters

NAME SW413\_500  
EXPNO 11  
PROCNO 1

F2 - Acquisition Parameters

Date\_ 20190523  
Time 2.26  
INSTRUM spect  
PROBHD 5 mm TBO BB-1H  
PULPROG zg30  
TD 15608  
SOLVENT Tol  
NS 56320  
DS 0  
SWH 208333.328 Hz  
FIDRES 13.347856 Hz  
AQ 0.0374592 sec  
RG 2050  
DW 2.400 usec  
DE 17.40 usec  
TE 299.2 K  
D1 0.05000000 sec  
TD0 1

===== CHANNEL f1 =====

NUC1  $^{207}\text{Pb}$   
P1 9.50 usec  
PL1 0 dB  
SFO1 105.1010279 MHz

F2 - Processing parameters

SI 131072  
SF 104.6301920 MHz  
WDW EM  
SSB 0  
LB 50.00 Hz  
GB 0  
PC 1.40

## Quantum chemical calculations

On the basis of the molecular structure of **5** determined in the solid state the structure was optimized using the programme Orca4.2<sup>2, 3</sup> with BP86,<sup>4, 5</sup> Grimme's dispersion correction and Becke-Johnson damping (D3BJ)<sup>6</sup> making use of the resolution of identity (RI) approximation. The basis set chosen was def2-SVP on all light elements and def2-TZVP/ECP on Sn as implemented in ORCA4.2.<sup>7-10</sup> Absence of imaginary frequencies on this level of theory confirmed local minima on the PES. For all calculations *tight* convergence criteria for optimisations and *verytight* for SCF convergence were applied with *grid6* and *finalgrid7* gridsizes. On the basis of this optimized structure NMR chemical shifts were computed at SO-ZORA level with ADF,<sup>11, 12, 13</sup> including the crucial exchange correlation kernel (PBE density functional, basis sets: TZ2P for Sn, TZP for O, C, H).<sup>14</sup> The obtained <sup>119</sup>Sn NMR shieldings were converted to chemical shifts ( $\delta$ , in ppm) relative to the shieldings of tetramethyltin ( $\sigma[^{119}\text{Sn}]=2901.613$ ) calculated at identical computational level.

Table S2. Comparison of structural data of **5**, calculated structure, data of crystal structure analysis.

	X-ray data (Å)	calc. structure (Å)
Sn1–Sn2	2.8796(7)	2.924
Sn1–O1	2.226(2)	2.183
Sn2–O1'	2.097(3)	2.284
Sn2–C1'	2.267(2)	2.261
Sn1–C1	2.145(2)	2.195
O1–C2	1.241(3)	1.270, 1.262
Sn1–H1	1.79(2)	1.730
O1–C2–O1'	129.1(5)	128.1

Table S3. Principal components of the <sup>119</sup>Sn chemical shift tensor

	Sn–H (exp.) <sup>a</sup>	Sn (exp.) <sup>a</sup>	Sn–H (theor.) <sup>a</sup>	Sn (theor.) <sup>a</sup>
$\delta_{\text{iso}}$	112	146	78.1	197.7
$\delta_{11}$	658(8)	885(29)	642	937
$\delta_{22}$	–62(6)	218(20)	–86	453
$\delta_{33}$	–261(6)	–665(21)	–322	–797

<sup>a</sup> in ppm

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## Optimized geometry of 5

177

Sn2C73H100O2

H	8.844126000	4.922378000	2.830070000
O	10.451883000	6.883624000	3.966584000
C	13.377912000	6.273765000	2.800725000
C	8.900650000	2.824037000	0.919431000
C	12.819412000	5.421331000	1.705625000
C	13.029019000	4.465731000	-0.527101000
H	13.545697000	4.423071000	-1.487031000
C	13.166922000	7.667677000	2.808383000
C	14.290878000	7.826218000	4.975607000
C	14.490146000	4.182633000	3.791262000
H	13.589812000	3.628590000	3.479487000
C	13.463229000	5.351843000	0.458188000
H	14.333688000	5.983872000	0.275467000
C	9.620338000	0.668947000	2.550026000
H	9.896713000	-0.172731000	3.189058000
C	14.110630000	5.659595000	3.853515000
C	11.687356000	4.615913000	1.930978000
C	14.538310000	6.450655000	4.923038000
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C	11.296643000	3.665811000	0.963030000
C	13.631378000	8.417276000	3.897840000
H	13.451416000	9.494619000	3.922490000
C	12.056576000	1.336619000	2.560608000
H	12.624666000	2.242854000	2.310096000
C	10.607619000	1.579446000	2.161319000
C	7.951620000	1.880360000	1.329472000
H	6.915105000	2.012133000	1.021008000
C	14.970212000	3.586382000	5.117383000
H	15.923510000	4.031770000	5.439862000
H	15.143809000	2.509090000	4.992878000
H	14.235182000	3.713154000	5.923526000
C	11.967333000	3.597978000	-0.263920000
H	11.669963000	2.849574000	-1.000392000
C	12.461836000	8.362387000	1.652415000
H	11.904733000	7.590720000	1.099759000
C	8.288980000	0.795949000	2.144017000
C	14.732619000	8.652167000	6.169008000
H	14.295152000	9.657344000	6.043210000
C	10.243381000	2.669022000	1.330200000
C	13.500616000	8.974868000	0.694847000
H	13.006215000	9.435992000	-0.173209000
H	14.205378000	8.217629000	0.326654000



H	14.085341000	9.752818000	1.208984000
C	8.487306000	3.999545000	0.048309000
H	9.238432000	4.790905000	0.201062000
C	10.861223000	7.378222000	5.062469000
H	10.865612000	8.481136000	5.110043000
C	12.236861000	1.080770000	4.060089000
H	11.728336000	0.163858000	4.388407000
H	11.842453000	1.910409000	4.664543000
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H	7.499694000	-0.497812000	3.623679000
C	12.647529000	0.188204000	1.725535000
H	13.709883000	0.038946000	1.969133000
H	12.567292000	0.403594000	0.650896000
H	12.114794000	-0.754506000	1.922054000
C	7.118706000	4.576942000	0.431314000
H	7.072380000	4.793875000	1.507771000
H	6.298273000	3.886557000	0.185559000
H	6.935194000	5.512087000	-0.116375000
C	8.511342000	3.608078000	-1.439635000
H	8.239508000	4.466436000	-2.071884000
H	7.793791000	2.796870000	-1.635518000
H	9.506568000	3.259670000	-1.745500000
C	16.262710000	8.804261000	6.200365000
H	16.746438000	7.822984000	6.319201000
H	16.576403000	9.439976000	7.041876000
H	16.636734000	9.252026000	5.268912000
C	14.208480000	8.069566000	7.490798000
H	14.453413000	8.734752000	8.331868000
H	14.665001000	7.090622000	7.697891000
H	13.120526000	7.925744000	7.458427000
C	11.454085000	9.432544000	2.092522000
H	10.700187000	9.009160000	2.766899000
H	10.933981000	9.841869000	1.214345000
H	11.946448000	10.275095000	2.600471000
C	15.576884000	3.946070000	2.724657000
H	15.253032000	4.266054000	1.728394000
H	15.832007000	2.877049000	2.672979000
H	16.489081000	4.503084000	2.986612000
C	5.821161000	0.197011000	2.483248000
H	5.655106000	1.135337000	3.029661000
H	5.159166000	-0.569848000	2.909736000
H	5.509451000	0.352313000	1.439275000
C	7.491101000	-1.547167000	1.749306000
H	6.810727000	-2.342766000	2.087833000
H	8.522847000	-1.913844000	1.838951000
H	7.294204000	-1.357146000	0.683342000

O	11.256997000	6.767334000	6.093029000
Sn	11.486909000	4.509745000	6.349094000
C	8.212772000	6.146131000	6.950590000
C	12.495060000	2.579015000	8.976064000
C	8.723974000	5.289270000	8.061843000
C	8.408497000	4.413938000	10.317625000
H	7.870302000	4.430933000	11.266555000
C	8.364583000	7.547517000	6.982338000
C	7.304836000	7.711225000	4.782375000
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H	8.106719000	3.517573000	6.251916000
C	8.046977000	5.288615000	9.294134000
H	7.206056000	5.969892000	9.435413000
C	11.694956000	0.313138000	7.543202000
H	11.390142000	-0.576066000	6.985533000
C	7.534997000	5.528775000	5.863544000
C	9.813185000	4.412877000	7.866191000
C	7.102118000	6.326391000	4.801740000
H	6.598402000	5.854225000	3.958263000
C	10.121803000	3.480468000	8.887597000
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H	14.461764000	1.714353000	8.907271000
C	6.806031000	3.428880000	4.553279000
H	5.846283000	3.830491000	4.193189000
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C	13.035673000	0.447410000	7.906322000
C	6.876608000	8.543531000	3.588785000
H	7.187165000	9.582448000	3.793423000
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H	7.046371000	8.205077000	9.277782000
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C	12.942167000	3.804605000	9.758331000
H	12.159583000	4.570158000	9.634814000
C	9.098491000	0.838567000	5.986284000
H	9.621680000	-0.065897000	5.643835000

H	9.485666000	1.686123000	5.403545000
H	8.033823000	0.720875000	5.738463000
C	14.043293000	-0.632738000	7.557441000
H	13.516210000	-1.372183000	6.930912000
C	8.674418000	-0.101768000	8.301031000
H	7.608296000	-0.227083000	8.060349000
H	8.763988000	0.084599000	9.380350000
H	9.187372000	-1.049814000	8.079053000
C	14.257720000	4.399944000	9.240069000
H	14.195515000	4.609135000	8.162265000
H	15.108879000	3.723437000	9.406376000
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C	13.033970000	3.478884000	11.258736000
H	13.319741000	4.371450000	11.834894000
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C	5.349395000	8.533156000	3.413579000
H	4.988309000	7.515135000	3.203754000
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C	7.583184000	8.081131000	2.304850000
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H	7.276266000	7.060557000	2.035530000
H	8.672839000	8.070648000	2.433599000
C	10.041890000	9.287073000	7.853023000
H	10.902268000	8.804752000	7.374192000
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H	9.664426000	10.077921000	7.187606000
C	6.078723000	3.761678000	6.916998000
H	6.346431000	4.094645000	7.926131000
H	5.862867000	2.683360000	6.959965000
H	5.157689000	4.282783000	6.614675000
C	15.223713000	-0.084537000	6.743007000
H	14.874692000	0.396754000	5.819644000
H	15.917617000	-0.893003000	6.469908000
H	15.789857000	0.664475000	7.315810000
C	14.534507000	-1.353751000	8.824209000
H	15.220109000	-2.174684000	8.566639000
H	13.692307000	-1.770783000	9.393775000
H	15.073627000	-0.657815000	9.484315000
Sn	10.346487000	4.724059000	3.665370000