An Estimate of the Rate Constants and Arrhenius Parameters for H-Atom Abstraction from Bu_3SnH by the 2,2-Dimethylvinyl Radical in PhMe. Kinetic Evidence for an Entirely Free Radical Mechanism for the O-Directed Hydrostannation of Alkynols with Stannanes and Et_3B/O_2

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Electronic Supplementary Information

(171 Pages Inclusive of Cover Pages)

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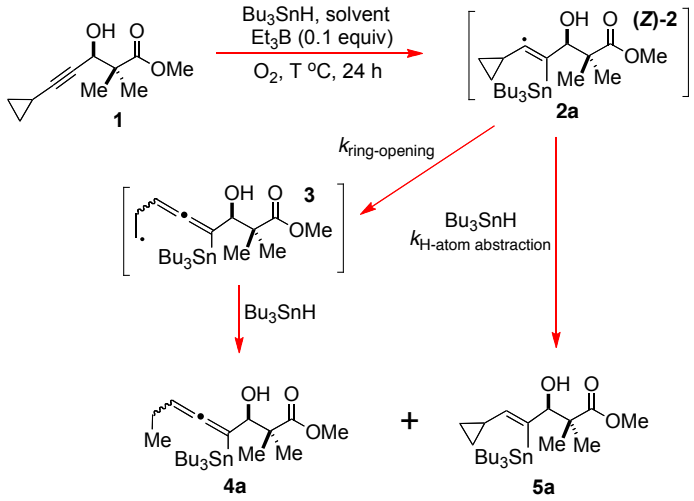
Part A. Experimental Section

Part 1. An Estimate of the $k_{H\text{-}atom}$ Abstraction Values for the 2,2-Dimethylvinyl Radical 6 from Bu_3SnH in PhMe Between 273 and 353K, and Estimates of the $k_{ring\text{-}opening}$ and Arrhenius Parameters for the Cyclopropane Ring-Opening of the α-Cyclopropyl-β-Tri-*n*-Butylstannylvinyl Radical 2a in Pentane and PhMe

1.1 The Averaged Ratios of 4a:5a Obtained from the O-Directed Hydrostannation of 1 with Bu_3SnH/cat. Et_3B as Determined by 600.13 MHz ^1H NMR Spectroscopy of the Crude Concentrated Hydrostannation Reaction Mixtures in $CDCl_3$



T °C	Run 1 Ratio **4a**:**5a**	Run 2 Ratio **4a**:**5a**	Run 3 Ratio **4a**:**5a**	Run 4 Ratio **4a**:**5a**	Run Total **4a**:**5a**	Final Averaged Value of **4a**:**5a**
Pentane						
20 °C	**HAW-VII-055** 1.51 : 1	**HAW-VII-056** 1.55 : 1	**HAW-VII-057** 1.44 : 1	—	$\frac{4.50}{3}$:1	**1.50 : 1**
25 °C	**HAW-VII-058** 1.58 : 1	**HAW-VII-059** 1.55 : 1	**HAW-VII-060** 1.66 : 1	—	$\frac{4.79}{3}$:1	**1.60 : 1**
30 °C	**HAW-VII-037** 2.12 : 1	**HAW-VII-041** 2.13 : 1	**HAW-VII-042** 1.93 : 1	—	$\frac{6.18}{3}$:1	**2.06 : 1**
PhMe						
20 °C	**HAW-II-189** 2.25 : 1	**HAW-VI-171** 2.22 : 1	—	—	$\frac{4.47}{2}$:1	**2.24 : 1**
25 °C	**HAW-VII-052** 2.47 : 1	**HAW-VII-053** 2.46 : 1	**HAW-VII-054** 2.58 : 1	—	$\frac{7.51}{3}$:1	**2.50 : 1**
30 °C	**HAW-VII-048** 2.885 : 1	**HAW-VIi-049** 2.76 : 1	—	—	$\frac{5.645}{2}$:1	**2.82 : 1**
40 °C	**HAW-VII-030** 4.33 : 1	**HAW-VII-034** 3.94 : 1	**HAW-VII-036** 4.71 : 1	—	$\frac{12.98}{3}$:1	**4.33 : 1**
60 °C	**HAW-IV-029** 10.84 : 1	**HAW-VII-029** 8.88 : 1	**HAW-VII-033** 9.70 : 1	**HAW-VII-035** 10.68 : 1	$\frac{40.10}{4}$:1	**10.03 : 1**
80 °C	**HAW-III-005** 20.44 : 1	**HAW-VI-164** 21.52 : 1	**HAW-VII-003** 20.22 : 1	—	$\frac{62.18}{3}$:1	**20.73 : 1**

1.2 Use of the Arrhenius Log A, E_a and $k_{\text{H-atom abstraction Bu3SnH}}$ Data Derived for the 2,2-Dimethylvinyl Radical (6) in Pentane to Calibrate the *In Situ*-Generated Stannylvinyl Radical (*Z*)-2a in Pentane and Provide Estimates for the $k_{\text{H-atom abstraction Bu3SnH}}$ Rate Constants of 6 and (*Z*)-2a in Pentane at 293 and 298 K

In the Supporting Information of their paper, Ingold and coworkers reported[7] that in pentane the 2,2-dimethylvinyl radical **6** abstracted the reactive H-atom of Bu_3SnH with a k= 2.96 x 10^8 mol^{-1} s^{-1} at 298 K. Ingold *et al.* also reported a log A of 9.67 for this process,[7] and an E_a = +1.624 ± 0.407 kcal mol^{-1}. After multiplication of 1.624 x 4184 J and including their errors, an E_a = +6794.816 J mol^{-1} ± 1702.888 J mol^{-1} was recorded.

The availability of this data allowed us to calculate the theoretical $k_{\text{H-atom abstraction}}$ values for the radical **6** from Bu_3SnH at 293 K and 303 K in pentane respectively, and using these values to calibrate the reaction of **2a** with Bu_3SnH thereafter allowed us to deduce the $k_{\text{ring-opening}}$ values for the stannylvinyl radical (***Z***)**-2a** (R = Bu) in pentane at these two temperatures, as well as at 298 K.

Those theoretical $k_{\text{H-atom abstraction}}$ calculations that we performed utilised the logarithmic form of the Arrhenius equation $k = Ae^{-Ea/RT}$ where:

$$\log k = \log A - \frac{E_a}{2.303RT}$$

where R = Gas Constant (8.314) and T = Absolute Temperature in K
and A = the Frequency or Pre-Exponential Factor

Thus, at 20 °C (293 K), the calculated $k_{\text{H-atom abstraction}}$ rate constant for **6** from Bu_3SnH **<u>in pentane</u>** was deduced using Ingold's reported log A = 9.67 and his E_a = 6794.816 J mol^{-1} (1.624 kcal mol^{-1}):

$$\log k_{\text{H-atom abstraction 293 K}} = 9.67 - \frac{6794.816}{2.303 \times 8.314 \times 293}$$

$$\log k_{\text{H-atom abstraction 293 K}} = 9.67 - \frac{6794.816}{5610.1126}$$

$$\log k_{\text{H-atom abstraction 293 K}} = 9.67 - 1.211173 = 8.458827$$

$$\therefore\ k_{\text{H-atom abstraction 293 K}} = 10^{8.458827} = 2.87625 \times 10^8\ mol^{-1}\ s^{-1}$$

Likewise, the $k_{\text{H-atom abstraction Bu3SnH}}$ rate constant for **6** at 30 ^{o}C (303 K) was calculated from:

$$\log k_{\text{H-atom abstraction 303 K}} = 9.67 - \frac{6794.816}{2.303 \times 8.314 \times 303}$$

$$\log k_{\text{H-atom abstraction 303 K}} = 9.67 - \frac{6794.816}{5801.5840}$$

$$\log k_{\text{H-atom abstraction 303 K}} = 9.67 - 1.1712 = 8.4988$$

$$\therefore \; k_{\text{H-atom abstraction 303 K}} = 10^{8.4988} = 3.153552 \times 10^{8} \text{ mol}^{-1} \text{ s}^{-1}$$

Although the experimentally determined $k_{\text{H-atom abstraction Bu3SnH}}$ quoted by Ingold *et al*.[6] for **6** at 25 ^{o}C (298 K) was 2.96 x 10^{8} mol^{-1} s^{-1}, such a *k* value would in actual fact require an Arrhenius energy of activation of E_a = 1.6347146 kcal mol^{-1} (6839.646 J mol^{-1}) to arrive at this figure (see below).

Importantly though, this E_a is only 0.01 kcal mol^{-1} different from the general mean value of E_a = +1.624 ± 0.407 kcal mol^{-1} (+6794.816 J mol^{-1} ± 1702.888 J mol^{-1}) that was reported in the SI of Ingold's paper,[7] and Ingold's team did claim a ± 25% level of error in the E_a they were reporting.[7]

The two calculations provided below have utilised the above E_a value (6839.646 J mol^{-1}) and Ingold's E_a = 6794.816 J mol^{-1}) to confirm this fact. They further show the veracity of our overall method of calculation for the two 273 K and 303 K $k_{\text{H-atom abstraction Bu3SnH}}$ values in pentane, and that our method of calculation is totally correct. Thus:

For E_a =1.6347146 kcal mol^{-1} x 4184 = 6839.646 J mol^{-1}

$$\log k_{\text{H-atom abstraction 298 K}} = 9.67 - \frac{6839.646}{2.303 \times 8.314 \times 298}$$

$$\log k_{\text{H-atom abstraction 298 K}} = 9.67 - \frac{6839.646}{5705.848316}$$

$$\log k_{\text{H-atom abstraction 298 K}} = 9.67 - 1.198708 = 8.471292$$

$$\therefore \; k_{\text{H-atom abstraction 298 K}} = 10^{8.471292} = 2.9600 \times 10^{8} \text{ mol}^{-1} \text{ s}^{-1}$$

$$= 2.96 \times 10^{8} \text{ mol}^{-1} \text{ s}^{-1}$$

For E_a = 1.624 kcal mol^{-1} x 4184 = 6794.816 J mol^{-1}

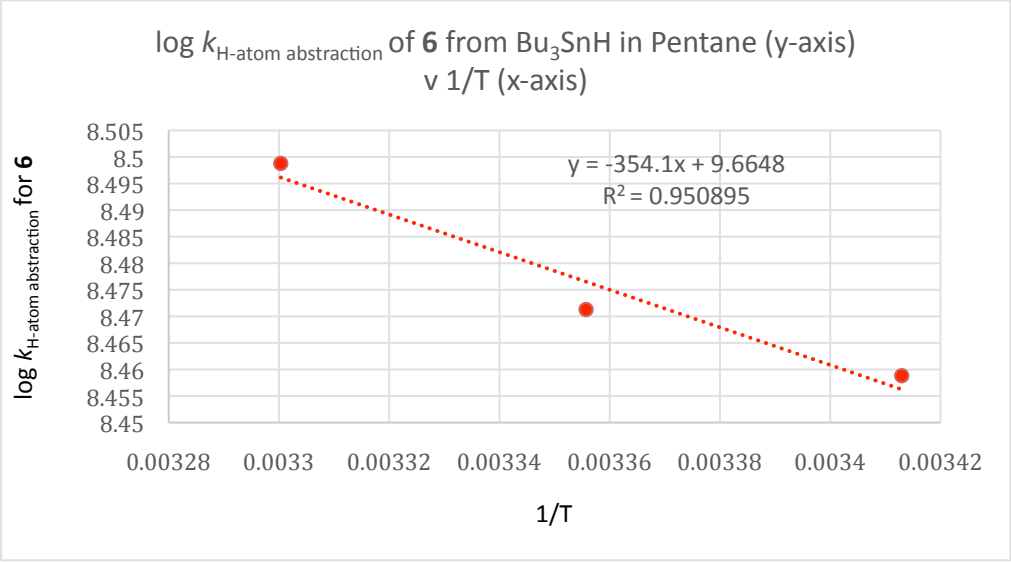
$$\log k_{\text{H-atom abstraction 298 K}} = 9.67 - \frac{6794.816}{2.303 \times 8.314 \times 298}$$

$$\log k_{\text{H-atom abstraction 298 K}} = 9.67 - \frac{6794.816}{5705.848316}$$

$$\log k_{\text{H-atom abstraction 298 K}} = 9.67 - 1.1908512 = 8.4791488$$

$$\therefore\ k_{\text{H-atom abstraction 298 K}} = 10^{8.4791488} = 3.014 \times 10^{8}\ mol^{-1}\ s^{-1}$$

When the two *calculated* log $k_{\text{H-atom abstraction 6 from Bu3SnH in pentane}}$ values at 293 K and 303 K (*calculated* using Ingold's E_a = 6794.816 J mol^{-1} = 1.624 kcal mol^{-1} data) were merged with Ingold's experimentally derived *k* value for **6** of 2.96 x 10^8 mol^{-1} sec^{-1} at 298 K,[7] the following three log $k_{\text{H-atom abstraction 6}}$ values emerged i.e. 8.458827; 8.471292; and 8.4988, and when these three resulting log $k_{\text{H-atom abstraction 6}}$ values were plotted against the following 1/T values (i.e. 1/293 K = 0.003413; 1/298 K = 0.003356; and 1/303 K = 0.0033) in Arrhenius format, the following Excel plot was obtained (see below). It consisted of a straight line plot that had a negative slope and an R^2 value of 0.950895 i.e. there was just a 5% deviation in the plotted points, with a 95% data fit when Ingold's experimental 298 K $k_{\text{H-atom abstraction}}$ value was included in the plot. This exercise was done ***solely*** to check the veracity of our two newly calculated *k* values for **6** when merged with his experimentally-derived *k* value, and as can be seen, the results are excellent (log A = 9.6648).[7]



With this task duly completed, the aforementioned $k_{\text{H-atom abstraction Bu3SnH}}$ values for **6** in pentane were used to calibrate the stannylvinyl radical **2a** (R = Bu) in pentane, to allow the rate constants for the cyclopropane ring-opening ($k_{\text{ring-opening}}$) event to be estimated for **2a** (R = Bu) at these three reaction temperatures. The latter data was secured at constant excess tin hydride concentration (0.2 M), by running 3 separate competition experiments at the temperatures of 293, 298 and 303 K, where the final ratio of allenyltin:vinyltin products **4a**:**5a** was established by 600.13 MHz ^{1}H NMR spectroscopy of the crude concentrated reaction mixtures in $CDCl_3$. The following equation of Baines,[13] Newcomb,[14] and Crich[15] was used to determine the $k_{\text{ring-opening}}$ values:

$$\frac{[\text{Vinyltin}]}{[\text{Allenyltin}]} = [(R)_3SnH] \times \frac{k_{\text{H-atom abstraction}}}{k_{\text{ring-opening}}} \qquad \text{(Eqn 1)}$$

which rearranges to Eqn 2:

$$k_{\text{ring-opening}} = [(R)_3SnH] \times k_{\text{H-atom abstraction}} \times \frac{[\text{Allenyltin}]}{[\text{Vinyltin}]} \quad \text{(Eqn 2)}$$

At 20 °C (293 K), from 3 independent reaction runs, the average ratio of **4a**:**5a** (R = Bu) was 1.50:1.

This allowed a $k_{\text{ring-opening 2a in pentane293 K}}$ = [0.2] x 2.88 x10^8 x 1.50/1 = 8.64 x 10^7 s^{-1} to be established, and a log $k_{\text{ring-opening 2a in pentane293 K}}$ = 7.936513742.

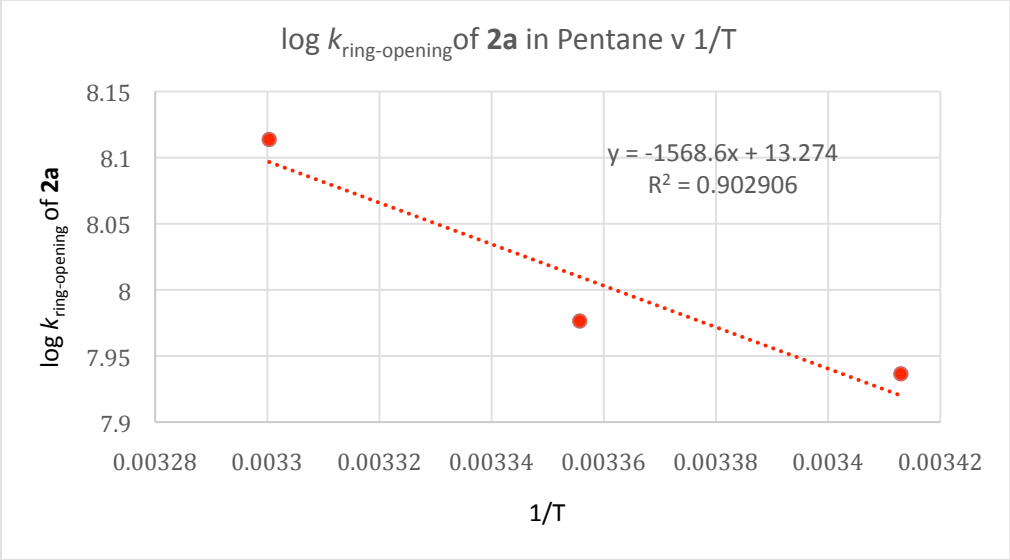
At 25 °C (298 K), from 3 independent reaction runs, the average ratio of **4a**:**5a** (R = Bu) was 1.60:1.

This led to a $k_{\text{ring-opening 2a in pentane298 K}}$ of [0.2] x 2.96 x10^8 x 1.60/1 = 9.472 x 10^7 s^{-1} which, in turn, gave a log $k_{\text{ring-opening 2a in pentane298 K}}$ = 7.976441689.

At 30 °C (303 K), from 3 independent reaction runs, the average ratio of **4a**:**5a** (R = Bu) was 2.06:1

Accordingly, a $k_{\text{ring-opening 2a in pentane303 K}}$ of [0.2] x 3.154 x10^8 x 2.06/1 = 1.299448 x 10^8 which gave rise to a log $k_{\text{ring-opening 2a in pentane303 K}}$ = 8.1137589.

An Excel Arrhenius plot of these values of log $k_{\text{ring-opening 2a}}$ in pentane v 1/T (i.e. 1/293 K = 0.003413; 1/298 K = 0.003356; and 1/303 K = 0.0033), employing the least-squares regression method, gave a straight-line output whose intercept provided the log A of the reaction, which was 13.274 (see below). The latter value enabled a Pre-Exponential or Frequency Factor A of 1.88 x 10^{13} s^{-1} to be deduced for the ring-opening process, which was consistent with an entirely free radical E_H1 ring-cleavage occurring within **2a** to give **3a**. The slope of the plot was -1568.6, while its R^2 = 0.902906. Such a net deviation confirmed that our data had given a reasonable fit of the averaged experimentally-derived **4a**:**5a** ratio determinations made. The deviation observed included the 5% deviation already present in Ingold's *k* calibrating data (see the earlier plot), and the 5% data point deviation in our own reaction run data. Most importantly though, the high magnitude of the log A (13.274) obtained for this ring-opening was unmistakeable, and it was a number that was sufficiently reliable to allow it to be confidently asserted that an entirely free radical, scissive, E_H1 ring-opening was occurring in **2a** in pentane to give **3a**.



The Arrhenius energy of activation for this cyclopropane radical ring-opening event was deduced from the expression E_a = -(slope) x 2.303*R*, which, for the ring-opening of the stannylvinyl radical **2a** (R = Bu) in pentane led to an E_a of +7.18 kcal mol^{-1} being calculated. Thus:

E_a = -(-1568.6) x 2.303 x 8.314 = +30034.207 J mol^{-1} = +30.034 kJ mol^{-1}, but to obtain the corresponding E_a in units of kcal mol^{-1}, this figure was divided by 4.184, which gave an E_a = 30.034/4.184 = +7.18 kcal mol^{-1}.

1.3 Estimation of the Rate Constants for H-Atom Abstraction ($k_{\text{H-atom abstraction Bu3SnH}}$) for the 2,2-Dimethylvinyl Radical (6) in PhMe and the Accompanying Arrhenius Parameter Determinations

The temperature dependent $k_{\text{H-atom abstraction Bu3SnH}}$ data for the 2,2-dimethylvinyl radical **6** from Bu_3SnH in PhMe was experimentally derived in the following way.

Free radical hydrostannation reactions were conducted on the alkynol **1** with Bu_3SnH/cat. Et_3B in PhMe over a 20-30 ^{o}C (293-303 K) temperature range, in an analogous manner to the way in which these reactions were run in pentane, and the averaged product ratios of **4a**:**5a** for 2-3 reaction runs were determined by 600.13 MHz ^{1}H NMR spectroscopy of the concentrated crude reaction mixtures in $CDCl_3$. The differences in the **4a**:**5a** product ratios, in pentane and PhMe, were then compared with respect to the allenyltin **4a** (R = Bu) component. This allowed us to estimate the differing rates of H-atom abstraction by (***Z***)**-2a** to give **5a** over the 293-303 K temperature range examined. It transpired that, within this narrow temperature window, the rate of H-atom abstraction of (***Z***)**-2a** from Bu_3SnH was approximately 1.47 x slower in PhMe than in pentane, where a larger quantity of **5a** was formed. As a result of this slower rate of H-atom abstraction by (***Z***)**-2a** in PhMe, more cyclopropane ring-opening product **4a** was formed in PhMe than in pentane.

The precise reduction in the rate of Bu_3SnH H-atom abstraction in PhMe was estimated by dividing the relative ratios of **4a** formed in the two reaction solvents at the temperature under investigation. Thus, at 293 K the **4a** ratio difference was 2.24/1.5 = 1.493; at 298 K it was 2.50/1.60 = 1.56; and at 303K it was 2.82/2.06 = 1.37. The average sum of these net reductions in the rate of H-atom abstraction in PhMe was thus 4.423/3 =1.47. Accordingly, we reduced the $k_{\text{H-atom abstraction Bu3SnH pentane}}$ values that we had obtained in pentane by a factor of 1.47. This gave rise to the following new reduced $k_{\text{H-atom abstraction Bu3SnH PhMe}}$ estimates for the rate of H-atom abstraction from the Bu_3SnH by the 2,2-dimethylvinyl radical **6** and **2a** in PhMe.

$$k_{\text{H-atom abstraction Bu3SnH by } \mathbf{6/2a} \text{ PhMe 293 K}} = \frac{2.88 \times 10^8 \text{ mol}^{-1}\text{ s}^{-1}}{1.47} = 1.959184 \times 10^8 \text{ mol}^{-1}\text{ s}^{-1}$$

$$k_{\text{H-atom abstraction Bu3SnH by } \mathbf{6/2a} \text{ PhMe 298 K}} = \frac{2.96 \times 10^8 \text{ mol}^{-1}\text{ s}^{-1}}{1.47} = 2.013605 \times 10^8 \text{ mol}^{-1}\text{ s}^{-1}$$

$$k_{\text{H-atom abstraction Bu3SnH by } \mathbf{6/2a} \text{ PhMe 303 K}} = \frac{3.154 \times 10^8 \text{ mol}^{-1}\text{ s}^{-1}}{1.47} = 2.145578 \times 10^8 \text{ mol}^{-1}\text{ s}^{-1}$$

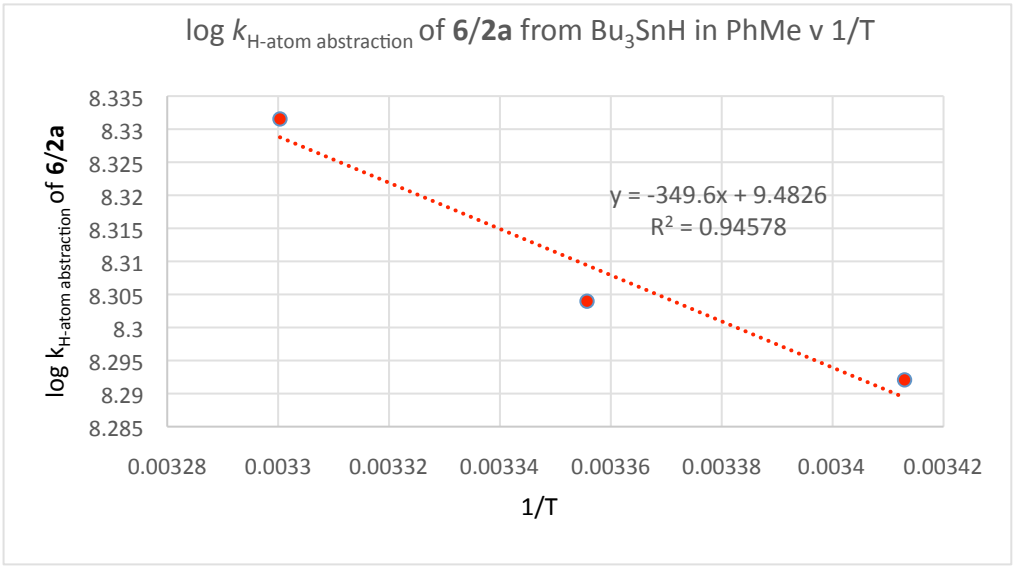
These *estimates*, in turn, gave rise to the following log $k_{\text{H-atom abstraction Bu3SnH 6/2a}}$ values in PhMe:

$$\log k_{\text{H-atom abstraction } \mathbf{6/2a} \text{ PhMe 293 K}} = 8.292075$$

$$\log k_{\text{H-atom abstraction } \mathbf{8/2a} \text{ PhMe 298 K}} = 8.303974$$

$$\log k_{\text{H-atom abstraction } \mathbf{6/2a} \text{ PhMe 303 K}} = 8.331544$$

When these three estimated log $k_{\text{H-atom abstraction Bu3SnH}}$ values for **6/2a** (R = Bu) in PhMe were plotted against the following 1/T values (i.e. 1/293 K = 0.003413; 1/298 K = 0.003356; and 1/303 K = 0.0033) in classical Arrhenius format, the following Excel plot was obtained via the least-squares regression method:



Significantly, this plot yielded a log A = 9.4826 (Frequency Factor A = 3.04 x 10^9 s^{-1}) and had a slope = -349.6 and an R^2 value of 0.94578, for seven *experimentally determined* **4a**:**5a** ratio measurements in PhMe. The fact that the R^2 value was 94.58% confirmed that the experimental data fit was good.

From that slope, an E_a = -(-349.6) x 2.303 x 8.314 = +6693.84 J mol^{-1} or +6.69384 kJ mol^{-1} was deduced, which translated into an E_a of +1.59879 kcal mol^{-1}, following multiplication by 0.238846 (i.e. +6.69384 kJ mol^{-1} x 0.238846 = E_a= +1.59879 kcal mol^{-1} or 1.6 kcal mol^{-1}). The close match of these Arrhenius parameters with the Ingold data for **6** and Bu_3SnH in pentane clearly corroborated the validity of our experimentally-derived Arrhenius plot for **6** (**2a**) and Bu_3SnH in PhMe and its integrity.

From these new, experimentally-determined, Arrhenius parameters for **6** in PhMe (log A= 9.4826 and E_a = 6693.84 J mol^{-1}) derived from this averaged Arrhenius plot, the following five ***additional*** new $k_{\text{H-atom abstraction Bu3SnH PhMe}}$ values were calculated. This allowed the entire 313-353 K temperature range to be fully calibrated and covered for **6**, which was to serve as the $k_{\text{H-atom abstraction Bu3SnH PhMe}}$ calibrant for **2a** (R = Bu) and later **13**.

At 313K: For E_a = 6693.84 J mol^{-1}

$$\log k_{\text{H-atom abstraction PhMe 313 K}} = 9.4826 - \frac{6693.84}{2.303 \times 8.314 \times 313}$$

$$\log k_{\text{H-atom abstraction PhMe 313 K}} = 9.4826 - \frac{6693.84}{5993.055}$$

$$\log k_{\text{H-atom abstraction PhMe 313 K}} = 9.4826 - 1.1169 = 8.3657$$

$$\therefore k_{\text{H-atom abstraction PhMe 313 K}} = 10^{8.3657} = 2.321133 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$$

At 323K: For E_a = 6693.84 J mol^{-1}

$$\log k_{\text{H-atom abstraction PhMe 323 K}} = 9.4826 - \frac{6693.84}{2.303 \times 8.314 \times 323}$$

$$\log k_{\text{H-atom abstraction PhMe 323 K}} = 9.4826 - \frac{6693.84}{6184.5269}$$

$$\log k_{\text{H-atom abstraction PhMe 323 K}} = 9.4826 - 1.082353 = 8.4002$$

$$\therefore k_{\text{H-atom abstraction PhMe 323 K}} = 10^{8.4002} = 2.513043 \times 10^{8}\ mol^{-1}\ s^{-1}$$

At 333K: For E_a = 6693.84 J mol^{-1}

$$\log k_{\text{H-atom abstraction PhMe 333 K}} = 9.4826 - \frac{6693.84}{2.303 \times 8.314 \times 333}$$

$$\log k_{\text{H-atom abstraction PhMe 333 K}} = 9.4826 - \frac{6693.84}{6375.9983}$$

$$\log k_{\text{H-atom abstraction PhMe 333 K}} = 9.4826 - 1.04985 = 8.43275$$

$$\therefore k_{\text{H-atom abstraction PhMe 333 K}} = 10^{8.43275} = 2.708631 \times 10^{8}\ mol^{-1}\ s^{-1}$$

At 343K: For E_a = 6693.84 J mol^{-1}

$$\log k_{\text{H-atom abstraction PhMe 343 K}} = 9.4826 - \frac{6693.84}{2.303 \times 8.314 \times 343}$$

$$\log k_{\text{H-atom abstraction PhMe 343 K}} = 9.4826 - \frac{6693.84}{6567.470}$$

$$\log k_{\text{H-atom abstraction PhMe 343 K}} = 9.4826 - 1.01924 = 8.46336$$

$$\therefore k_{\text{H-atom abstraction PhMe 343 K}} = 10^{8.46336} = 2.90643 \times 10^{8}\ mol^{-1}\ s^{-1}$$

At 353K: For E_a = 6693.84 J mol^{-1}

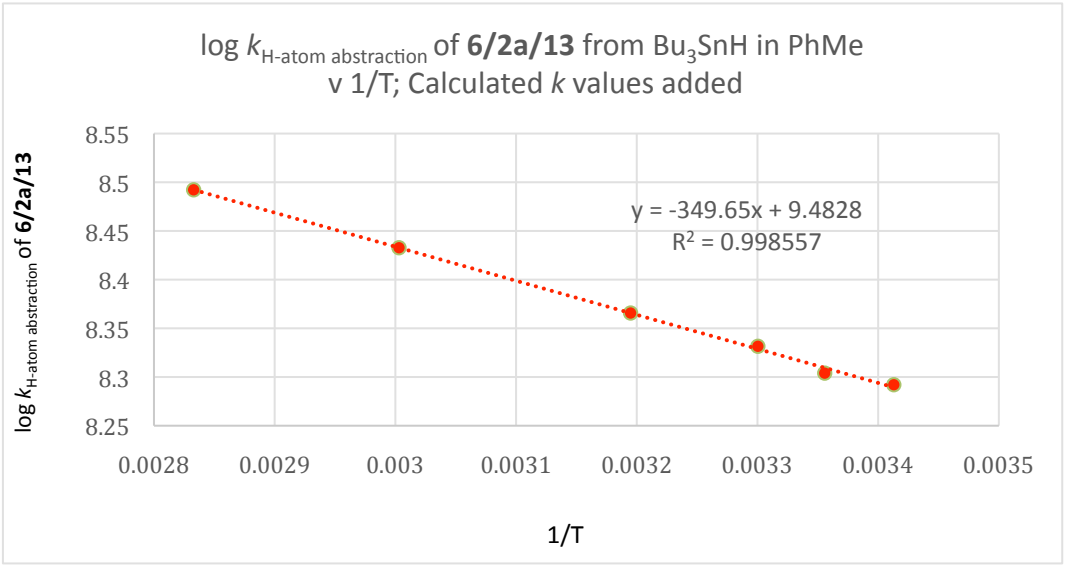
$$\log k_{\text{H-atom abstraction PhMe 343 K}} = 9.4826 - \frac{6693.84}{2.303 \times 8.314 \times 353}$$

$$\log k_{\text{H-atom abstraction PhMe 343 K}} = 9.4826 - \frac{6693.84}{6758.941}$$

$$\log k_{\text{H-atom abstraction PhMe 343 K}} = 9.4826 - 0.990368 = 8.49223$$

$$\therefore k_{\text{H-atom abstraction PhMe 343 K}} = 10^{8.49223} = 3.106204 \times 10^{8}\ mol^{-1}\ s^{-1}$$

With respect to the radical **6** (and the calibrated radicals **2a** and **13**), the calculated log $k_{\text{H-atom abstraction Bu3SnH}}$ values at 313K, 333K and 353 K were added to a new Arrhenius plot, alongside the 293 K, 298 K and 303 K log $k_{\text{H-atom abstraction Bu3SnH}}$ data, to check their numerical integrity. The output is shown below:



The fact that this Arrhenius plot now had an R^2 = 0.998557 indicated a near perfect fit of the data.

It used the following 1/T and log $k_{\text{H-atom abstraction Bu3SnH PhMe}}$ values:

1/293 K = 0.003412969.	log $k_{\text{H-atom abstraction 293K}}$ = 8.292075.
1/298 K = 0.003355704698.	log $k_{\text{H-atom abstraction 298K}}$ = 8.303974.
1/303 K = 0.00330033.	log $k_{\text{H-atom abstraction 303K}}$ = 8.331544.
1/313 K = 0.003194888.	log $k_{\text{H-atom abstraction 313K}}$ = 8.3657.
1/333 K = 0.003003.	log $k_{\text{H-atom abstraction 333K}}$ = 8.43275.
1/353 K = 0.0028328611.	log $k_{\text{H-atom abstraction 353K}}$ = 8.49223.

1.4 Estimation of the $k_{\text{ring-opening}}$ Rate Constants and Arrhenius Parameters for the Cyclopropane Ring-Opening of the Tri-*n*-Butylstannylvinyl Radical 2a in PhMe From The Averaged 4a:5a Ratios in PhMe

With this mix of calculated and experimentally-derived $k_{\text{H-atom abstraction Bu3SnH PhMe}}$ values in hand for **6** and **2a** (R = Bu) in PhMe, as well as the newly experimentally-derived **4a**:**5a** (R = Bu) ratios, the following $k_{\text{ring-opening 2a}}$ values were determined in PhMe at each specified temperature. As was the case with the pentane reaction runs, all product ratios were derived from reaction runs that were performed at a 0.2 M [Bu_3SnH]. The $k_{\text{ring-opening 2a PhMe}}$ values were again calculated using equation 2:

$$k_{\text{ring-opening}} = [(R)_3SnH] \times k_{\text{H-atom abstraction}} \times \frac{[\text{Allenyltin}]}{[\text{Vinyltin}]} \quad \text{(Eqn 2)}$$

These calculations are collated below:

At 293 K: $k_{\text{ring-opening 2a PhMe 293 K}} = [0.2] \times 1.959184 \times 10^8 \times 2.24/1 = 8.7771443 \times 10^7\ s^{-1}$.

At 298 K: $k_{\text{ring-opening 2a PhMe 298 K}} = [0.2] \times 2.013605 \times 10^8 \times 2.5/1 = 1.0068025 \times 10^8\ s^{-1}$.

At 303 K: $k_{\text{ring-opening 2a PhMe 303 K}} = [0.2] \times 2.145578 \times 10^8 \times 2.82/1 = 1.210106 \times 10^8\ s^{-1}$.

At 313 K: $k_{\text{ring-opening 2a PhMe 313 K}} = [0.2] \times 2.321133 \times 10^8 \times 4.33/1 = 2.0101011 \times 10^8\ s^{-1}$.

At 333 K: $k_{\text{ring-opening 2a PhMe 333 K}} = [0.2] \times 2.708631 \times 10^8 \times 10.03/1 = 5.4335138 \times 10^8\ s^{-1}$.

At 353 K: $k_{\text{ring-opening 2a PhMe 353 K}} = [0.2] \times 3.106204 \times 10^8 \times 20.73/1 = 1.2878322 \times 10^9\ s^{-1}$.

The 1/T and log $k_{\text{ring-opening 2a PhMe}}$ values that were used in the subsequent Arrhenius plot are listed below:

1/293 K = 0.003412969. log $k_{\text{ring-opening 2a PhMe 293 K}} = \log 8.7771443 \times 10^7\ s^{-1} = 7.943353$.

1/298 K = 0.003355704698. log $k_{\text{ring-opening 2a PhMe 298 K}} = \log 1.0068025 \times 10^8\ s^{-1} = 8.002944$.

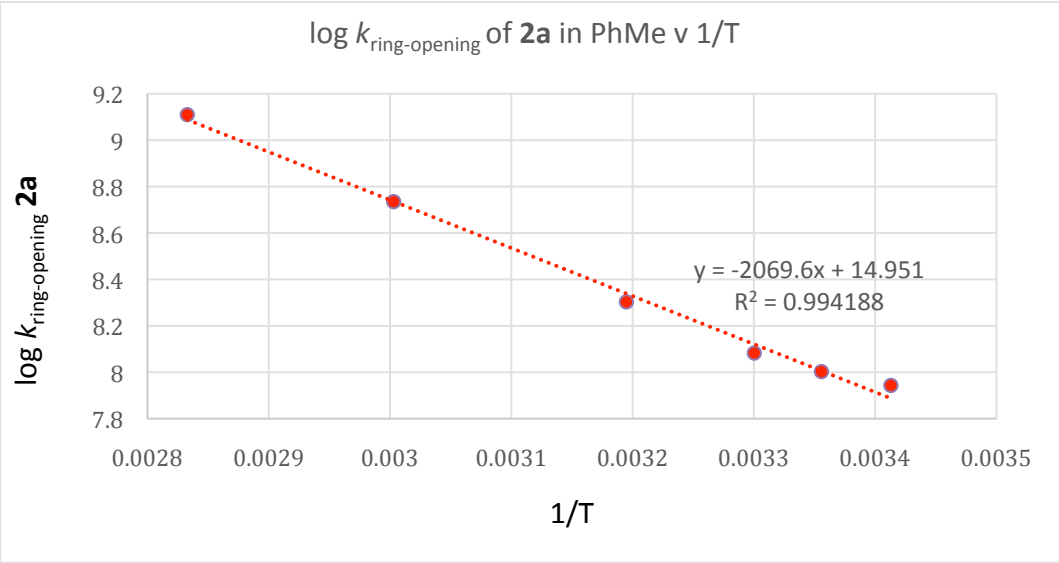
1/303 K = 0.00330033. log $k_{\text{ring-opening 2a PhMe 303 K}} = \log 1.210106 \times 10^8\ s^{-1} = 8.08282341$.

1/313 K = 0.003194888. log $k_{\text{ring-opening 2a PhMe 313 K}} = \log 2.0101011 \times 10^8\ s^{-1} = 8.3032179$.

1/333 K = 0.003003. log $k_{\text{ring-opening 2a PhMe 333 K}} = \log 5.4335138 \times 10^8\ s^{-1} = 8.735080$.

1/353 K = 0.0028328611. log $k_{\text{ring-opening 2a PhMe 353 K}} = \log 1.2878322 \times 10^9\ s^{-1} = 9.109859$.

That Arrhenius plot is shown below in Excel, and gave rise to the following Arrhenius expression for the ring-opening of radical **2a**: $\log k_{\text{ring-opening 2a}} = 14.951 - 9.47/2.303RT$.



Clearly, now that there were 6 experimental data points included in this Arrhenius Plot, from 17 independent reaction runs, a great improvement was seen in the overall R^2 score ($R^2 = 0.994188$), which lent considerable weight and confidence to the experimental accuracy of the experimental data that was deduced.

Our calculation of the E_a for the ring-opening of **2a** to give **3a** is presented below. It used the slope of -2069.6 derived from the above Arrhenius plot to deduce the final calculated figure for the E_a of the ring-opening of **2a**.

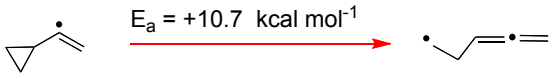
$$\therefore E_{a\ \text{ring-opening 2a}} = -(-2069.6) \times 2.303 \times 8.314 \text{ J mol}^{-1}$$

$$\therefore E_{a\ \text{ring-opening 2a}} = 39626.925 \text{ J mol}^{-1} = 39.6269 \text{ kJ mol}^{-1}$$

$$\therefore E_{a\ \text{ring-opening 2a}} = \frac{39.6269 \text{ kJ mol}^{-1}}{4.184} = +9.47 \text{ kcal mol}^{-1}$$

This E_a of +9.47 kcal mol^{-1} for the ring-opening of **2a** showed a reasonably good level of agreement with Guo's theoretical value[22] for the mechanistically analogous E_H1 ring-opening of the α-

cyclopropylvinyl radical **17**, if one also considers that the Bu_3Sn-substituent will almost certainly be hyperconjugatively stabilising **2a** while also accelerating the actual ring-opening event itself.



17 **18**

ΔG = - 4.3 kcal mol^{-1}

J. Shi, M. Zhang, Y. Fu, L. Liu, Q.-X. Guo *Tetrahedron* **2007**, *63*, 12681.

Our $\Delta S^{\ddagger}_{333\ K}$ calculation for the **2a→3a** conversion is also shown overleaf for comparison. It used two methods of calculation: the Avery $\Delta S^{\ddagger}$ equation[2a] and variants of the Bunnett $\Delta S^{\ddagger}$ equation.[28]

The origin of Avery's $\Delta S^{\ddagger}$ equation[2a] is shown below for ease of understanding (see p 67 of ref 2a):

Using statistical thermodynamics, Wynne-Evans and Eyring[26] have shown that the rate constant k_r is related to the Boltzmann Constant $k_{Boltzmann}$, Planck's Constant h, the reaction temperature T, and the standard free energy of activation ($-\Delta G^{\ddagger}$) by the following form of the Arrhenius Equation:

$$k_r = \frac{k_{Boltzmann}\,T}{h}\ \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right)$$

If we now incorporate $\Delta G = \Delta H - T\Delta S$ into this expression, it follows that:

$$k_r = \frac{k_{Boltzmann}\,T}{h}\exp\left(n + \frac{\Delta S^{\ddagger}}{R}\right)\exp\left(\frac{-\Delta H^{\ddagger}}{RT}\right)$$

Since the enthalpy of activation ($\Delta H^{\ddagger}$) is related to the activation energy (E_a) by $\Delta H = E_a - nRT$, where n (the molecularity) = 1 for all unimolecular or liquid phase reactions, it follows that:

$$k_r = \frac{k_{Boltzmann}\,T}{h}\exp\left(n + \frac{\Delta S^{\ddagger}}{R}\right)\exp\left(\frac{E_a}{RT}\right)$$ where

h = 6.62 x 10^{-34} mol^{-1} Planck's Constant
R = 8.314 J K^{-1} mol^{-1} Gas Constant
n = Molecularity of Reaction
$k_{Boltzmann}$ = 1.38 x 10^{-23} J K^{-1}

In this expression,

$\frac{k_{Boltzmann}\,T}{h}\exp\left(n + \frac{\Delta S^{\ddagger}}{R}\right)$ = A = Pre-Exponential or Frequency Factor

The A factor gives a measure of the number of successful molecular collisions with the correct orientation and energy to react. and thereby give rise to the product(s).

So, from a knowledge of the reaction temperature and the A factor, one can work out the entropy of activation ($\Delta S^{\ddagger}$). Assuming n = 1 (for a unimolecular reaction), and taking natural logarithms, allows further equation simplification to:

$$\ln A = \ln \frac{k_{Boltzmann}\,T}{h} + 1 + \frac{\Delta S^{\ddagger}}{R}$$

Further conversion of the natural logarithm terms in this equation into $\log_{10}$ values requires multiplication by a factor of 2.303, and further rearrangement thereafter gives Avery's equation,[2a (page 67)] since he is the chemist who popularised it.:

$$\Delta S^{\ddagger} = R\left[2.303 \log A - 2.303 \log \frac{k_{Boltzmann}\,T}{h} - 1\right]$$ Avery's equation for $\Delta S^{\ddagger}$ for unimolecular reactions

Taking the log A of 14.951 derived from the intercept of our above Arrhenius plot of the log $k_{ring\text{-}opening}$ of **2a** in PhMe vs 1/T (for our **2a→3a** conversion), and using it in Avery's $\Delta S^{\ddagger}$ equation (which, most importantly, takes into account the effect of reaction molecularity),[2a] we arrived at the final $\Delta S^{\ddagger}_{333\ K}$ value shown below after insertion of the relevant numerical values into that equation.

$$\Delta S^{\ddagger}_{333K} = 8.314 \left[(2.303 \times 14.951) - 2.303 \log \left(\frac{1.38 \times 10^{-23} \times 333}{6.626 \times 10^{-34}} \right) - 1 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333K} = 8.314 \left[(34.4322) - 2.303 \log \left(6.935406 \times 10^{12} \right) - 1 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333K} = 8.314 \left[(34.4322) - 2.303 \left(12.84107 \right) - 1 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333K} = 8.314 \left[(34.4322) - 29.5730 - 1 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333K} = 8.314 \left[(34.4322) - 30.5730 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333K} = 8.314 \left[+3.8592 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333K} = +32.085\ J\ K^{-1}\ mol^{-1}$$

$$\therefore \boxed{\Delta S^{\ddagger}_{333K} = \frac{+32.085\ J\ K^{-1}\ mol^{-1}}{4.184} = +7.67\ e.u. = +7.67\ cal\ K^{-1}\ mol^{-1}}$$

However, in order to check the overall veracity of our $\Delta S^{\ddagger}_{333\ K}$ determination, we also used Anslyn and Dougherty's simplified variant[27] of Bunnett's long-established $\Delta S^{\ddagger}$ equation[28] to confirm the general magnitude of the $\Delta S^{\ddagger}_{333\ K}$ value we had derived for the **2a→3a** conversion via the Avery equation.[2a]

Although not specified by Anslyn and Dougherty in their book,[27] their simplified variant of Bunnett's much earlier $\Delta S^{\ddagger}$ equation[28] produces an output that is in entropy units (i.e. 1 e.u. = 1 cal K^{-1} mol^{-1}). It was formulated entirely analogously to Alder, Baker and Brown's earlier simplified 1971 $\Delta S^{\ddagger}$ e.u. equation for a 298 K determination, which had $\Delta S^{\ddagger}_{298\ K} = 4.576$ (log A-13.23).[29] The $\Delta S^{\ddagger}$ values that emerge from these two equations thus require multiplication by a factor of 4.184 to convert them into the more familiar J K^{-1} mol^{-1} unit of quantification that one typically sees for $\Delta S^{\ddagger}$ values reported in the literature.

We ourselves have formulated our own simplified variant of the Bunnett $\Delta S^{\ddagger}$ equation[28] shown below on the left, which does the J K^{-1} mol^{-1} $\Delta S^{\ddagger}$ calculation directly.

Significantly, both of these simplified $\Delta S^{\ddagger}$ equations work very well indeed for providing this key Arrhenius parameter for both ***unimolecular*** and ***bimolecular*** reactions (in the liquid phase), without all of the complex calculations that the Avery equation and its variants require.

The **2a→3a** $\Delta S^{\ddagger}_{333\ K}$ calculations where we used our own and Anslyn-Dougherty's $\Delta S^{\ddagger}$ equations are shown below. They give identical results:

The $\Delta S^{\ddagger}$ Equation in Units of J K^{-1} mol^{-1}

$$\Delta S^{\ddagger}_{Temp\ K} = 2.303R\left[\log A - \log\left(\frac{e\,k_{Boltzmann}}{h_{Planck}}\right) - \log T\right]\ J\ K^{-1}\ mol^{-1}$$

e = Euler's Constant = 2.7182818

or

$$\Delta S^{\ddagger}_{Temp\ K} = 19.147\left[\log A - 10.753 - \log T\right]\ J\ K^{-1}\ mol^{-1}$$

This work

Bunnett's $\Delta S^{\ddagger}$ Equation in Entropy Units

$$\Delta S^{\ddagger}_{Temp\ K} = 4.576\left[\log k - \log\left(\frac{e\,k_{Boltzmann}}{h_{Planck}}\right) - \log T + \frac{E^{\ddagger}}{4.576T}\right]$$

where $\log k = \log A - \log \frac{E^{\ddagger}}{4.576T}$ and e = Euler's Constant

or

$$\Delta S^{\ddagger}_{Temp\ K} = 4.576\left[\log A - 10.753 - \log T\right]\ cal\ K^{-1}\ mol^{-1}\ or\ e.u.$$

Anslyn-Dougherty

2a →3a $\Delta S^{\ddagger}_{333\ K}$ Calculations

$$\Delta S^{\ddagger}_{333\ K} = 19.147\left[14.951 - 10.753 - 2.522\right]\ J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = 19.147\left[14.951 - 13.275\right]\ J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = 19.147\left[1.676\right]\ J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = +32.09\ J\ K^{-1}\ mol^{-1}$$

2a →3a $\Delta S^{\ddagger}_{333\ K}$ Calculations

$$\Delta S^{\ddagger}_{333\ K} = 4.576\left[14.951 - 10.753 - 2.522\right]\ cal\ K^{-1}\ mol^{-1}\ or\ e.u.$$

$$\Delta S^{\ddagger}_{333\ K} = 4.576\left[1.676\right]\ cal\ K^{-1}\ mol^{-1}\ or\ e.u.$$

$$\Delta S^{\ddagger}_{333\ K} = +7.669\ cal\ K^{-1}\ mol^{-1}\ or\ e.u.\ \times 4.184$$

$$\Delta S^{\ddagger}_{333\ K} = +32.09\ J\ K^{-1}\ mol^{-1}$$

Significantly, the $\Delta S^{\ddagger}$ values so obtained matched up perfectly well with the $\Delta S^{\ddagger}_{333\ K}$ value that we had derived using Avery's equation.[2a] This agreement thus confirmed that our method was sound.

Finally, the enthalpy of activation $\Delta H^{\ddagger}$ and the free energy of activation $\Delta G^{\ddagger}$ for the unimolecular ring-opening of **2a** were also calculated from the experimentally-derived data in the following way:

$$\Delta H^{\ddagger} = E_a - nRT \therefore \Delta H^{\ddagger} = 39.6269 - \frac{1 \times 8.314 \times 333}{1000}\ kJ\ mol^{-1}$$

$$\Delta H^{\ddagger} = 39.6269 - 2.77 = 36.86\ kJ\ mol^{-1} = +8.8\ kcal\ mol^{-1}$$

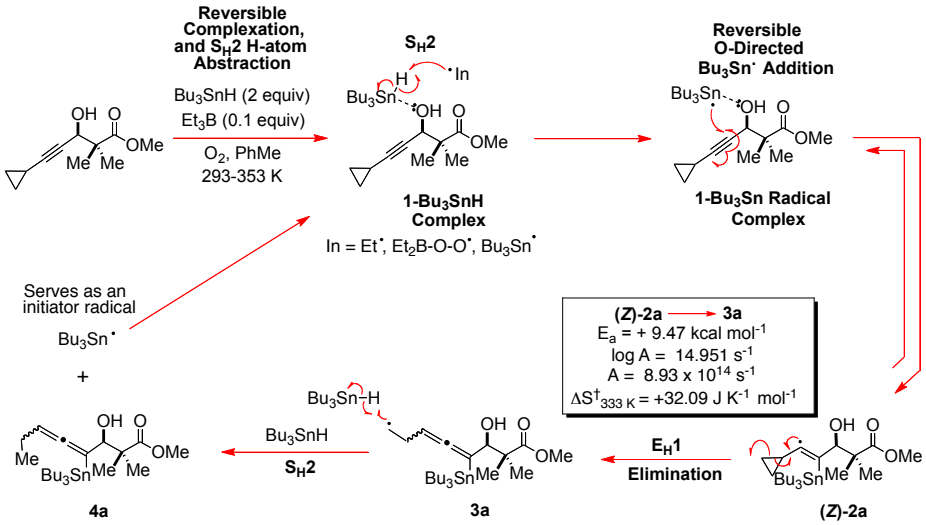
$$Since\ \Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \therefore \Delta G^{\ddagger} = 36.86 - \frac{333 \times 32.09}{1000}\ kJ\ mol^{-1}$$

$$\therefore \Delta G^{\ddagger} = 36.86 - 10.69 = 26.17\ kJ\ mol^{-1} = +6.25\ kcal\ mol^{-1}$$

1.5 Our Mechanistic Interpretation of The Arrhenius Parameters Obtained for the 2a→4a Conversion: <u>Support for An Entirely Free Radical E_H1 Mechanism For Cyclopropane Ring-Opening</u>

Clearly the ***<u>large</u>*** positive log A value of 14.951 that is seen here for the ring-opening of **2a** in PhMe at 333 K, and its accompanying $\Delta S^{\ddagger}_{333\ K}$ of +32.09 J K^{-1} mol^{-1} (+7.67 e.u.) only satisfactorily align with a *<u>single</u>* molecular entity (**2a**) entering the rate-determining step (r.d.s), and it undergoing homolytic cyclopropane ring-cleavage as shown in Scheme 4. The log A of 14.951 that was observed lies well within the range that one would normally see for cyclopropane radical homolyses,[2b] which typically give log A values of 13.29-16.11.[20] The fact that our log A sits right in the middle of this range of values possibly reflects some of the rotational freedom that is lost when the new C=C double bond forms in the r.d.s. Nonetheless, its high magnitude does strongly point to this being a *<u>unimolecular</u>* ring-opening event that is proceeding via a "very loose", but still cyclic, solvent-stabilised radicaloid activated complex, in which partial homolytic bond cleavage and partial radicaloid bond formation are both at advanced stages by the mid-point of the reaction.

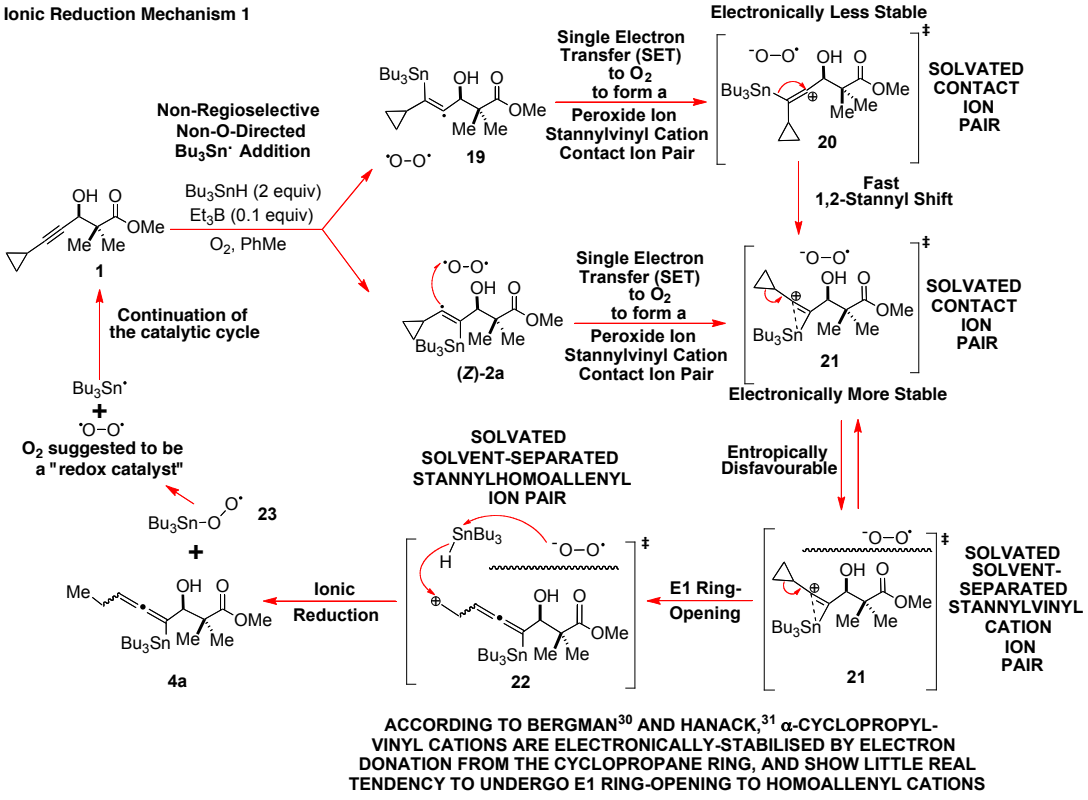
Once formed, the activated complex can then either revert to **2a** or eventually undergo full *<u>E_H1 homolytic ring-cleavage to produce the stannyl homoallenyl radical</u>* **3a** (Scheme 4),[3b,c] with **3a** then going on to H-atom abstract from the Bu_3SnH by the S_H2 pathway shown, to finally produce **4a**. A key component of this mechanistic scheme is **2a** itself arising from a reversible *<u>O-directed</u>* stannyl radical addition to the alkyne carbon that is α- to the propargylic alcohol group.[3,17-19]



Scheme 4. The sequential O-directed stannyl radical addition/E_H1/S_H2 mechanistic pathway that most satisfactorily rationalises the formation of **4a** from **3a** and **2a** in the non-polar PhMe solvent.

1.6 The Arrhenius Parameters Obtained for the 2a→4a Conversion in PhMe Do Not Support Stannylvinyl Cation Involvement in the Mechanism of the Cyclopropane Ring-Opening of 2a

The high log A of 14.951 observed for the ring cleavage of **2a** in PhMe over the temperature range 293-353K is at great odds with the stannylvinyl cationic mechanistic hypothesis that was recently put forward for alkyne hydrostannation,[6a-6d] and further propagated by two recent reviews,[6e,f] despite prior controverting reports.[3,4a] In the stannylvinyl cationic mechanistic theory,[6] a fast "outer sphere" single electron transfer (SET) oxidation event is proposed to occur involving the stannylvinyl radical and O_2. In the present instance, this would ultimately afford the solvent-separated solvated stannylvinyl cation ion pair **21**, which would subsequently undergo cyclopropane ring cleavage, ***either*** by the polar unimolecular mechanism of Scheme 5, where Bu_3SnH reduction of the carbocation **22** would occur (**Ionic Reduction Mechanism 1**) (see below) ***or*** by the direct bimolecular Bu_3SnH reduction mechanism shown in Scheme 6 (**Ionic Reduction Mechanism 2**) (see page 33).



Scheme 5. The *untenable* "outer sphere" SET/stannylvinyl cation reduction mechanism[6a-d] as applied to the alkynol **1** with $Bu_3SnH/Et_3B/O_2$ (**Ionic Reduction Mechanism 1**). It can be *ruled out* on the basis of the log A data reported here, our prior stannylvinyl radical EPR spectroscopy,[3d] and by our unsuccessful cation capture studies when **1** was hydrostannated in THF:H_2O (4:1).[3b,c]

Background. In the stannylvinyl cation mechanistic theory of alkyne hydrostannation with tin hydrides and radical initiators,[6] it is postulated[6a-d] that a ***non-coordinatively controlled***, ***non-regioselective***, addition of a tin radical occurs at *either* alkyne carbon of propargylically-oxygenated dialkyl acetylene substrates. As applied to **1**, this would require that a mixture of the stannylvinyl radicals **19** and **2a** is formed (Scheme 5), which would then engage in a fast "outer sphere" single electron transfer (SET) with O_2, to initially provide the solvent-caged contact ion pairs **20** and **21**. To arrive at **4a**, the theory[6] then demands that the less inductively stable of these two solvated stannylvinyl cation ion pairs, **20**, will undergo a fast, 1,2-tributylstannyl shift to produce the solvent-caged contact ion pair **21** *virtually exclusively*, which would then solvatively separate into its constituent ions, before engaging in cationic reduction either by the two-step **Ionic Reduction Mechanism 1** of Scheme 5, or by the one-step **Ionic Reduction Mechanism 2** of Scheme 6 (see page 33 of this SI).

Ionic Reduction Mechanism 1. Given that Sherrod and Bergman,[30] and Hanack[31] have both noted that α-cyclopropylvinyl cations generated from 1-cyclopropyl-1-iodoalkenes *do not willingly undergo cyclopropane ring-opening under solvolytic conditions*, one can reasonably assume that the transition of **21** into **22** would be rate-determining, if the **Ionic Reduction Mechanism 1** of Scheme 5 prevailed.

If one accepts this key tenet, then in the ***non-polar*** solvent ***PhMe***, one would expect a cationic unimolecular ring-opening of this sort to be associated with significant solvent electrostriction, and a massive loss in translational entropy, as the solvated contact ion pair **21** attempted to transit into the activated reaction complex that would produce **22**.

In such a mechanism, a solvent-induced dissociation of the peroxide anion away from the newly formed stannylvinyl cation of **21** would almost certainly be a requirement, to unmask the strong positive charge on the vinylic carbon, needed for the key fissive ring-opening event to effectively proceed.

However, given the very low dielectric constant of PhMe (ε = 2.38), it is hard to imagine how such a solvent could ever bring about such an effective charge separation, or solvatively stabilise the developing activated complex needed to induce cyclopropane ring-opening to give **22**. Rather, a polar activated complex of this sort would initially repel PhMe.

In fact, if initial electroneutrality already prevailed within the solvated contact ion pair form of **21** in PhMe, there would have to be significant solvent intercalation and massive bulk solvent reorganisation, to enable a full charge separation of that ion pair to occur. Only then could a stannylvinyl cation of sufficient electrophilicity be unmasked, to allow the requisite activated complex to satisfactorily form to enable the cyclopropane ring-opening to proceed (Scheme 5).

In our considered opinion, such a solvent-induced ionic charge separation would simply not be feasible in non-polar PhMe, due to the extremely strong attractive forces that would exist between the two oppositely charged ions in that solvent, as estimated by Coulomb's Law.

According to Kreevoy[32] and Dill,[33] the electric field/force lines of two oppositely charged ions always penetrate very deeply into non-polar reaction solvents of low dielectric constant; much moreso than they ever do in solvents of high dielectric constant like H_2O (ε = 78.54). Indeed in PhMe, the electric field associated with two oppositely charged ions is so enormous that it would likely extend over a distance of some 210 Å (21 nm); the so-called Bjerrum length,[33-35] which corresponds to the distance at which the Coulombic energy of attraction of one mole of ion pairs is equal to the thermal energy *RT* required to separate them.[33]

How the Attractive Electrostatic Interaction Energy (*F*) Between Two Oppositely Charged Ions is Affected by the Solvent Medium and the Bjerrum Length ($L_{Bjerrum}$)

$$L_{Bjerrum} = \frac{k_e e^2 N_{Avogadro}}{\varepsilon_{Medium} RT}$$

where
k_e = the Coulomb or Electric Force Constant = $1/4\pi\varepsilon_o$
$e = q_1 = q_2 = e$ = charge on an electron = -1.6×10^{-19} C
$N_{Avogadro}$ = Avogadro's Number = 6.02214×10^{23}
ε_{Medium} = Medium Dielectric Constant
R = Gas Constant = 8.314 J mol^{-1} K^{-1}
T = Temperature in K and

$$k_e e^2 N_{Avogadro} = \frac{e^2 N_{Avogadro}}{4\pi\varepsilon_o} = 1.386 \times 10^{-4} \text{ J m mol}^{-1}$$

where
$\varepsilon_o = 8.85 \times 10^{-12}$ C^2 J^{-1}m^{-1} = the permittivity of a vacuum
$4\pi = 12.568$

Thus, for PhMe (ε_{Medium} = 2.38) at a T = 333 K

$$L_{Bjerrum\ PhMe} = \frac{1.386 \times 10^{-4} \text{ J m mol}^{-1}}{2.38 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 333 \text{ K}}$$

$$L_{Bjerrum\ PhMe} = \frac{1.386 \times 10^{-4} \text{ J m mol}^{-1}}{6589.178 \text{ J mol}^{-1}} = 210.3 \text{ Å}$$

Since the Electrostatic Interaction Energy $F = \frac{L_{Bjerrum}}{r} \times RT$ where r is the ion separation distance, it follows that for two oppositely charged ions separated by 2.81 Å in PhMe, the Electrostatic Interaction Energy F = 49.52 kcal mol^{-1} and F = 46.39 kcal mol^{-1} when they are separated by 3.0 Å

$$F_{333\ K} = \frac{210.3 \text{ Å}}{2.81 \text{ Å}} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 333 \text{ K} = \frac{207.2 \text{ kJ mol}^{-1}}{4.184} = 49.52 \text{ kcal mol}^{-1}$$

$$F_{333\ K} = \frac{210.3 \text{ Å}}{3.0 \text{ Å}} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 333 \text{ K} = \frac{194.1 \text{ kJ mol}^{-1}}{4.184} = 46.39 \text{ kcal mol}^{-1}$$

It further transpires that the Coulombic energy of attraction *F* between two oppositely charged ions in an ion pair depends upon the distance between them, and would be of the order of +50.6 kcal mol^{-1} if they were only 2.75 Å apart in PhMe at 333 K. This value does, however, change to +49.52 kcal mol^{-1} at 2.81 Å separation and *ca*. +46.39 kcal mol^{-1} at a 3.0 Å separation. Given that such high energies of attraction will always exist at such short ion separations in non-polar PhMe, it seems most unlikely that any solvent-mediated ion pair separation would ever be achievable in this solvent at such a temperature, unless the SET event involved long-range electron tunnelling; evidence for which has not been provided by the stannylvinyl cation-originating team,[6] in their published mechanistic work. Moreover, while we recognise that *F* calculations of this sort do *rather simplistically* treat the ions of an ion pair as rigid hard spheres, even so, they do give a very good idea of the separation energy *F* and the overall energy input needed to bring about a complete ion dissociation in PhMe, notwithstanding such calculations ignoring dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole type interactions.

Interestingly enough, the +50.6 kcal mol^{-1} energy input that we have calculated would be necessary to bring about a full ion separation of a typical contact ion pair in PhMe at 333 K, from an initial inter ion distance of 2.75 Å, accords very well with Alabugin's polarisable continuum model (PCM)-based calculation[17a] for the energy input (ΔE = +50.5 kcal mol^{-1}) required for trimethylstannylvinyl radical electron transfer to O_2 in PhMe at 110 ^{o}C, with accompanying formation of a separated solvated trimethylstannylvinyl cation superoxide anion ion pair.

Significantly, Alabugin's computational calculations[17a] confirmed that the energy input needed to induce formation of such a solvent separated ion pair would be far too high to allow that type of entity to ever readily form at temperatures of between 60 and 110 ^{o}C in PhMe, and the fact that our own *F* calculations have shown that a similar energy input would be needed to effect a contact ion pair ion separation in PhMe again indicates that the latter process would be equally energetically unfeasible in the **21** system.

It is also important to point out that any ion pairs, generated in a non-polar solvent medium like PhMe, would almost certainly cause considerable polarisation of the solvent in all of those regions of the solvent that became subject to their respective electric fields during ion separation. The resulting ion pair/solvent dipolar forces would then rapidly disperse through the bulk medium, to

greatly restrict the random movements of all those solvent molecules that fell within the zones of those electric fields, which, given the huge 210 Å Bjerrum length[33] of two oppositely charged ions in PhMe, would likely be a great many in number. This effect would also be multi-directional in its nature due to the random movement of the putative ion pairs and reagent diffusion.

One of the main manifestations of this would obviously be a very severe restriction of the mobility of all solvent molecules in the immediate vicinity of any putative developing charged activated complexes derived from **21** *en route* to **22** (a process known as electrostriction). Such charge development and solvent shell immobilisation would almost certainly ***NOT*** be associated with a high log A value, nor a strongly positive $\Delta S^{\ddagger}$ but, instead, with a much lower log A, and a large negative $\Delta S^{\ddagger}$.[2a,32]

It will thus be appreciated that the strongly positive $\Delta S^{\ddagger}_{333\,K}$ of +32.09 J K^{-1} mol^{-1} (+7.67 e.u.) that we have seen in the overall **2a**→**4a** transition ***in PhMe*** is ***NOT*** what one would normally expect to see for a genuinely cationic reaction pathway in which the rate-determining step was the unimolecular heterolytic ring-cleavage of solvent separated **21** to give **22**.

To illustrate this point still further, we draw very specific attention to the fact that most S_N1 reactions generally have large ***negative*** entropies of activation associated with them ***when organic solvents are the main or exclusive reaction medium***, notwithstanding entropically-favourable unimolecular bond-heterolysis occurring. This is due, primarily, to the substantial solvent reordering that is always required to achieve heterolysis in pure organic solvents,[32] or even aqueous binary organic solvent mixtures, when H_2O is present as only the minor solvent component.

Additionally, many pure, low polarity, organic solvents like PhMe or benzene do not have the ability to form multiple H-bonds, to favourably dissipate negative anionic charge through complexation, which further hampers their ability to mediate ion pair formation and ion separation.

Thus, Fainberg and Winstein[36] found that *t*-BuCl underwent hydrolysis in 3:2 EtOH: H_2O with a $\Delta S^{\ddagger}$ of -15.5 J K^{-1} mol^{-1} (-3.7 e.u.), and they noted that this $\Delta S^{\ddagger}$ value decreased to -27.6 J K^{-1} mol^{-1} (-6.6

e.u.) as the EtOH constituency increased to 4:1 EtOH:H_2O. Hughes and Cooper[37] likewise observed a log A of 11.89 at 25 ^oC in 4:1 EtOH: H_2O, which translated into a $\Delta S^{\ddagger}$ of -25.6 J K^{-1} mol^{-1} (-6.12 e.u.) for this heterolysis, which is in broad agreement with the Fainberg-Winstein $\Delta S^{\ddagger}$ determination that was reported subsequently.[36] These recorded values of $\Delta S^{\ddagger}$ are despite the $L_{Bjerrum}$ of two oppositely charged ions being just 15.66 Å in 4:1 EtOH:H_2O (w/w) (ε =35.72 at 298 K) and the *F* value being approximately +3.3 kcal mol^{-1} at 2.81 Å ion separation, which emphasises that it is not just electrostatic attractions and Field Effects that are dominating the magnitudes of the $\Delta S^{\ddagger}$ values of reactions that involve the formation of ion pairs. In entirely analogous fashion, the S_N1 hydrolysis of *t*-BuCl in 3:2 dioxane:H_2O was associated with a substantial negative $\Delta S^{\ddagger}$ of -29.29 J K^{-1} mol^{-1} (-7.0 e.u.).[36] It will thus be appreciated that for S_N1 reactions in binary solvent mixtures, and less polar solvents with large molecular masses, the processes of polar bond heterolysis are generally associated with much greater degrees of solvent reorientation and entropy loss, whenever those activated reaction complexes are attempting to form.

Only when neat 100% H_2O was used for the *t*-BuCl hydrolysis performed at 25 ^oC did Fainberg and Winstein[36] observe that it reacted with a large positive $\Delta S^{\ddagger}$ of +51.04 J K^{-1} mol^{-1} (+12.2 e.u.).

This ability of H_2O to essentially non-electrostrictively surround and stabilise a polar activated complex that is transitioning into an intimate ion pair is unique, for it allows for much more facile charge separation in the developing ion pair transition state, which can now become considerably looser and more entropically-free (and product-like) as measured by the large positive overall $\Delta S^{\ddagger}$.

Another way of thinking about such reactions is as follows. Whenever pure H_2O is employed as the reaction solvent for the S_N1 solvolysis of a *tert*-alkyl halide, due to its very high dielectric constant (ε = 78.54), this lowers the Bjerrum length between the two newly emerging oppositely charged ions to just 7.12 Å at 298 K, which means that the Coulombic energy of attraction *F* between the two ions is now a mere +1.5 kcal mol^{-1} when those ions are just 2.81 Å apart, which is negligible. Such a weak attractive interaction is relatively easy to thermally disrupt. This contrasts very profoundly, however, with the Coulombic energy of attraction *F* that exists between two such oppositely charged ions in PhMe at 3 Å separation, where the *F* can now be estimated to be approximately +46.39 kcal mol^{-1} at 333 K; a value so large that it effectively prohibits facile ion separation from ever occurring in that solvent at that temperature.

In essence, because of the very high dielectric constant of H_2O (ε = 78.54), when it solvates a nascent activated complex of a *tert*-alkyl halide that is separating into two oppositely charged ions, the super-efficient solvation that occurs serves to completely ablate the huge Coulombic attractive forces that would otherwise confound and prohibit heterolytic bond fission in a much lower dielectric solvent such as PhMe.

This greatly enhanced ability of H_2O to more effectively solvate and promote the transition of a neutral dipolar molecule into the loose polar activated complex needed to undergo full heterolysis is thus not associated with the severe electrostriction that is often seen in organic solvents, or the binary solvent mixtures in which they predominate, and this property helps to explain the huge positive increase in the $\Delta S^{\ddagger}$ that was seen by Fainberg and Winstein[36] during the hydrolysis of *t*-BuCl in 100% H_2O.

Basically, pure organic solvents and aqueous organic solvent mixtures always have much lower dielectric constants than pure H_2O itself, and this inevitably increases the Bjerrum lengths[33-35] that are associated with any developing activated complexes that are attempting to transit into ion pairs in those solvent media. This, in turn, leads to greatly increased solvent electrostriction and significanty decreased solvent movement[34] in the vicinity of the polar activated complex itself, as well as far beyond it. Such factors thus serve to make reactions that involve ion separation far harder to achieve in low polarity solvents. This is why solvolyses of tertiary alkyl halides are typically associated with substantive negative $\Delta S^{\ddagger}$ values in solvents that are primarily organic in their nature, but these are not the sole factors that determine outcome (*vide infra*).

In full agreement with these observations, Moelwyn-Hughes and Biordi[38] recorded a negative $\Delta S^{\ddagger}$ of -15.73 J K^{-1} mol^{-1} (-3.76 e.u.) for the solvolysis of *t*-BuCl in neat dry MeOH (ε = 32.7) at 25 ^{o}C, while Fainberg and Winstein[36] recorded a $\Delta S^{\ddagger}$ of -3.1 e.u. (-12.97 J K^{-1} mol^{-1}) for this same solvolysis in MeOH. Cowie and coworkers[39] also found that *t*-BuBr underwent hydrolysis in 70% Me_2CO:30% H_2O with a $\Delta S^{\ddagger}$ of -42.68 J K^{-1} mol^{-1} (-10.2 e.u.) at 50 ^{o}C. Acetone has an ε = 21.

Analogously, Sherrod and Bergman[30] observed a large negative $\Delta S^{\ddagger}$ of between -88.70 and -83.68 J K^{-1} mol^{-1} (-21.2 and -20.0 e.u.) for the high temperature S_N1 solvolysis of 1-cyclopropyl-1-iodoethylene with 1 equiv of Et_3N in MeOH, which proceeds via an α-cyclopropyl-vinyl cation.

The key point being made here is that, typically, the formation of solvated charged contact ion pairs, or solvent-separated ion pairs, is highly entropically disfavoured in solvents of low-polarity such as PhMe, due to the huge field effects and flux lines that inevitably arise, which require massive solvent reorganisation to occur, which inevitably translates into large negative $\Delta S^{\ddagger}$ values being seen for most such reactions, and accompanying log A values that fall well below 13.

A similar entropically unfavourable solvent reorganisation would almost certainly be required for any cyclopropane ring-opening event that involved the solvated contact ion pair **21** ***in non-polar PhMe***. It would thus be extremely unlikely that such an electronically-destabilised activated ring-opening complex would ever willingly form from the electroneutral solvated contact ion pair **21** in that solvent. We also doubt that any of the solvent separated ion pairs **21** or **22** would ever readily form in the mechanistic pathway to **4a** from the stannylvinyl radical **2a**.

In our view, the log A of 14.951 that was recorded for the ring-opening of stannylvinyl radical **2a** in PhMe at 333 K, and its accompanying $\Delta S^{\ddagger}$ of +32.09 J K^{-1} mol^{-1} (+7.67 e.u.), are totally incompatible with **Ionic Reduction Mechanism 1** (Scheme 5) being the source of **4a**. Nor does this log A support the idea that a stannylvinyl cation-containing ion pair[6] more generally is forming in the non-polar solvent PhMe under our O-directed free radical hydrostannation conditions,[3] contrary to the experimentally unsupported assertions of those who advance the stannylvinyl cationic theory.[6]

It is a log A value that only mechanistically aligns with the "electrically neutral", unimolecular, homolytic ring cleavage process shown in Scheme 4 being the r.d.s for this reaction in PhMe.[3b,c]

In this very connection, we must highlight here how we have hitherto been unable to trap the putative primary stannylhomoallenyl cation of the hypothesised contact ion pair **22** with H_2O,[3b,c] to obtain the corresponding primary alcohol, and we have been equally unsuccessful at trapping the stannylvinyl cations[6] of the putative ion pairs **20** and **21** with H_2O, notwithstanding Sherrod and Bergman having readily intercepted such α-cyclopropyl-stabilised vinyl cations with H_2O with great ease; these workers having secured α-cyclopropyl ketones in good yield from such efforts.[30] The fact that Velgraki and Stratakis[40] have also successfully trapped gold-stabilised α-cyclopropylvinyl cations in 4:1 THF:H_2O mixtures at rt, further substantiates our claim that **21** and **22** cannot be

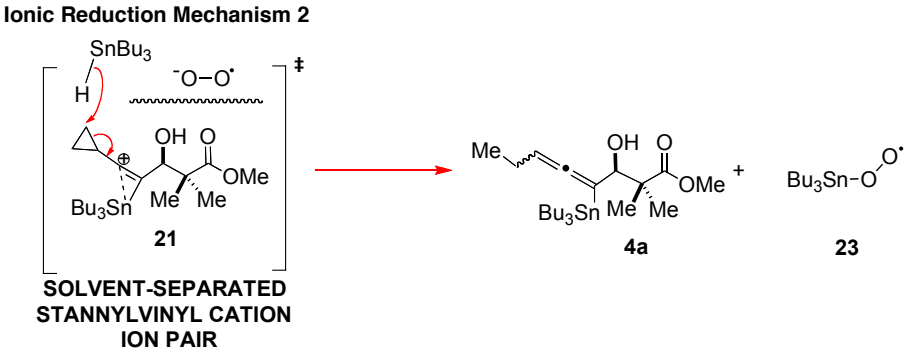
intermediates in the pathway where **2a** is converted into **4a**, as would be claimed by proponents of the stannylvinyl cation alkyne hydrostannation theory.[6]

Of great relevance here is the fact that Bergman[30] and Hanack[31] have each independently proposed that the positive charge in secondary α-cyclopropyl-vinyl cations is very strongly hyperconjugatively stabilised by electron-donation from the cyclopropane ring into the empty carbocation *p*-orbital; provided that this orbital is aligned *syn*- with respect to the two proximal C-C bonds of the cyclopropane ring. ***This cation-stabilisation effect would thus strongly disfavour spontaneous cyclopropane ring-opening***, due to the ring-opened primary carbocation of the new ion pair not enjoying such excellent charge stabilisation, nor any activated complex *en route* to it.

Finally, whenever PhMe or C_6H_6 have been used as the solvents for any of these O-directed alkyne hydrostannations, never has any product of electrophilic aromatic substitution of the aromatic solvent been encountered.[3] One would surely see such a product if a putative stannylvinyl cation[6] was indeed a genuine intermediate. Naturally this casts further doubt on the stannylvinyl cation mechanistic theory for alkyne hydrostannation[6] under the cat. Et_3B/O_2-initiated conditions.

On account of these collective outcomes, **Ionic Reduction Mechanism 1** can effectively be ruled out as playing any role in the transition of **2a**→**4a**.

Ionic Reduction Mechanism 2. The alternative **Ionic Reduction Mechanism 2** (Scheme 6) *can equally well be discounted* for explaining how the **2a**→**4a** conversion proceeds. This is because such a bimolecular "associative" "S_N2"-type ionic reduction of the stannylvinyl cation in **21** would lead to a considerable loss in translational entropy during the key "rate-determining" reductive ring-cleavage step. In fact, a bimolecular r.d.s of this sort would typically be associated with a much lower log A of 5-11, and a strongly negative entropy of activation[2] due to the massive decrease in translational entropy that would inevitably accompany formation of the solvated, charged, bimolecular activated complex in PhMe, and the strict requirements for correct orbital overlap and alignment to form the partial bonds of the activated reaction complex that would lead to stannylallene **4a**.

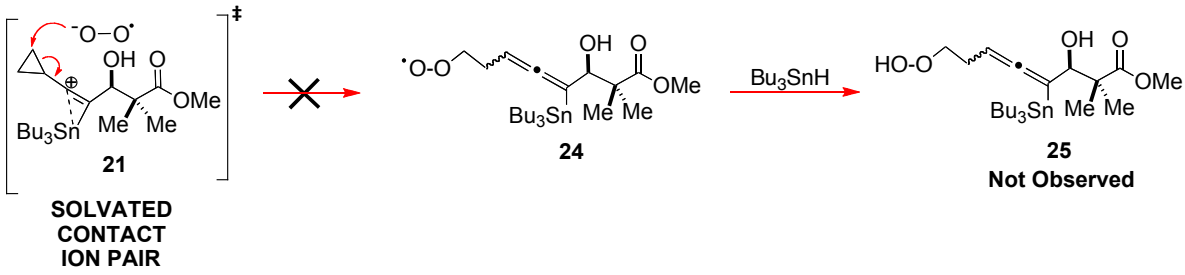


Scheme 6. **Ionic Reduction Mechanism 2,** proceeding via **21** (solvent-separated), would be incompatible with the high log A value of 14.951 observed for the conversion of **2a** into **4a**, due to the highly associative bimolecular nature of the solvated activated complex that would need to form, the requisite tin-stabilisation of the cation, and the substantial solvent reorganisation that would likely be required to separate the initially formed electroneutral contact ion pair into the solvent-separated charged ion pair needed to initiate such an S_N2-type ionic reduction event. Like **Ionic Reduction Mechanism 1**, **Ionic Reduction Mechanism 2**[6] can effectively be *ruled out* and considered *mechanistically unviable*[6] on the basis of the log A and the positive $\Delta S^{\ddagger}$ data[2] at hand.

Entropically unfavourable, solvent-mediated, contact ion pair separation of electrically neutral **21** would also likely be a key requirement for the aforementioned **Ionic Reduction Mechanism 2** to proceed in non-polar PhMe. Clearly, such an electrostrictive charge separation would be a necessity to unmask the full positive charge on the vinylic cation component of **21** to facilitate the aforementioned "S_N2" ionic reduction event. Like the concerted bimolecular reduction itself, such electrostrictive behaviour would once more be associated with a large negative $\Delta S^{\ddagger}$ in PhMe. On these grounds, this mechanistic thesis can equally well be rejected.

Further Comments. It is also difficult to imagine how any charged contact ion-pair such as **21** would not immediately self-react to some significant degree in PhMe to give **24** and thereafter **25** (Scheme 7), given the fact that the newly created superoxide anion would be negatively charged and far more nucleophilic than its neutral tri-*n*-butyltin hydride counterpart. The fact also that it would be sitting right at the heart of the solvated ion pair cage of **21** would seemingly mandate this.

Moreover, primary alkyl hydroperoxides are readily synthesised by direct S_N2 displacement of alkyl bromides with 2 equiv of aq. H_2O_2 in the presence of CF_3CO_2Ag, and they are not unduly unstable under neutral conditions, having previously been prepared and isolated by Davies and Roberts.[41] Yet, there was no sign of any hydroperoxide products such as **25** (or derivatives thereof) in the hydrostannation of **1** in PhMe (Scheme 7).



Scheme 7. Hydroperoxide products such as **25** were never seen in our free radical hydrostannations of **1**. If **Ionic Reduction Mechanism 2** was genuinely operative, one might see such products co-formed.

The presence of a nucleophilic hydroxy within the cationic component of ion pair **21** would provide yet another pathway for self-reaction, if such an ionic intermediate[6] was indeed genuinely forming in PhMe. Again, however, we saw no evidence for the formation of ether-type products in our hydrostannation of **1**, which further argues against the intermediacy of a stannylvinyl cation[6] in these O-directed dialkylacetylene free radical hydrostannations.[3,4,17-19]

Therefore, on the basis of us investigating this mechanistic problem in a manifold way,[28a] using a wide variety of experimental techniques, we have been able to firmly rule out the existence of stannylvinyl cations[6] in alkyne hydrostannation reactions mediated by tin hydrides under the cat. Et_3B/O_2 (or AIBN) initiated conditions, in both PhMe and in other solvents that include THF/H_2O.[3]

Some of those aforementioned experimental techniques have included EPR spectroscopy[3d] to characterise the triphenylstannylvinyl radicals of some of these O-directed dialkyl acetylene free radical hydrostannation reactions with Ph_3SnH/cat. Et_3B in PhMe. The fact that the shortest timescale of EPR spectroscopy is of the order of microseconds, yet we have been able to routinely observe triphenylstannylvinyl radicals for prolonged periods at temperatures of between -50 ^oC

and -10 ^{o}C in the presence of O_2,[3d] only helps to further confirm that the hypothesised[6] single electron transfer event involving O_2 ***is NOT*** *occurring* as stated in the various iterations of the stannylvinyl cation mechanistic theory that have so far appeared.[6]

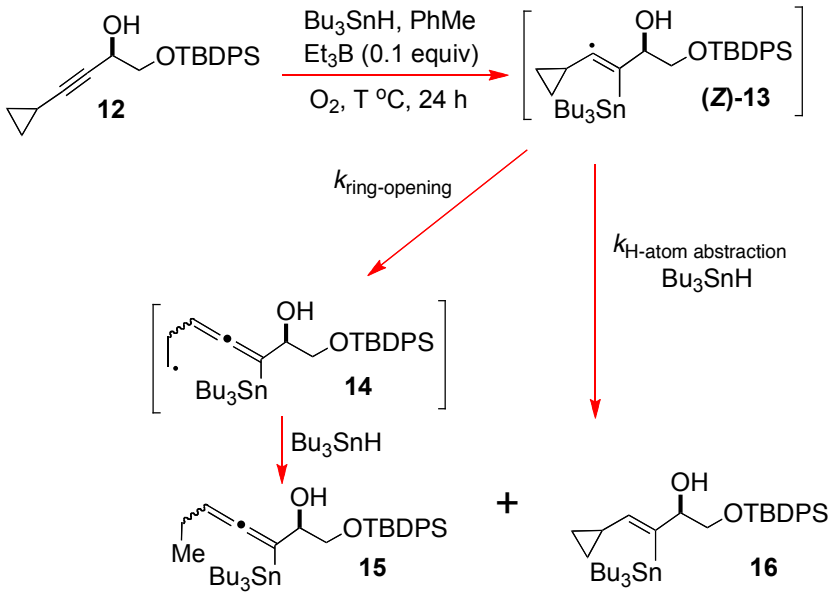
The above EPR work[3d] has also unambiguously confirmed that it is "O-directed" triphenylstannylvinyl radicals that are primarily being formed in these reactions and, this very fact, has allowed us to confidently ***restate*** that this process is indeed predominantly O-directed[3a,17-19,42] under the standard, reasonably concentrated, experimental reaction conditions that we[3] and others[6,16-19,42] typically use to run such free radical hydrostannation reactions. This counters other experimentally-unsupported proposals,[6,16] *which have not seemingly taken into account the changing regiochemistry[3] that is observed in these tin radical additions as the stannane concentration changes, which clearly rules out exclusive electronic regiocontrol in such propargylically-oxygenated dialkyl acetylene systems at higher stannane concentrations.*

In fact, it almost goes without saying that high stannane concentrations will promote intermolecular O-Sn coordination[3a,17-19] in these hydrostannations, but we will restate this here for the record. For this very reason, we strongly advise that all such processes are always generally conducted at higher stannane concentrations, within the limits of experimental expediency of course.

Finally, Alabugin and his team[17, 42] have gone to great lengths to provide very strong and convincing computational support for such a propargyloxy O-Sn radical coordination event beneficially occurring, in their recent NBO calculations and modelling of these O-directed alkyne free radical hydrostannation reactions. They have also shown that such O-coordinated Sn radicals generally always prefer to add to the α-alkyne carbon, due to this mode of addition giving rise to a significantly lower energy stannylvinyl free radical.[17,41] This powerfully elegant and insightful work by Alabugin and his team[17,42] warrants special commendation, for it has controverted many incorrect mechanistic ideas associated with the stannylvinyl cation theory,[6a-d] and it has very strongly supported not just our own 2005 experimental contributions to the O-directed disubstituted acetylene free radical hydrostannation area,[3,4] but also those excellent experimental contributions from the Alabugin laboratory themselves.[17,42] It has additionally confirmed the earlier O-directed assertions of the Taddei/Nativi[18] and Geilen/Willem[19] laboratories beforehand.

Part 2. An Estimate of the $k_{\text{ring-opening}}$ of the Cyclopropane Ring in the Tri-*n*-Butylstannylvinyl Radical 13 in PhMe at Different Temperatures and the Arrhenius Parameters Derived Therefrom

2.1 The Experimentally Determined Average Ratios of 15:16 Obtained from the O-Directed Hydrostannation of 12



T °C	Run 1 Ratio **15**:**16**	Run 2 Ratio **15**:**16**	Run 3 Ratio **15**:**16**	Run 4 Ratio **15**:**16**	Run Total **15**:**16**	Final Averaged Value of **15**:**16**
	LH-I-89	**LH-I-90**	**LH-I-93**	**LH-I-94**		
40 °C	2 x 0.47:1 = 0.94 : 1	2 x 0.43:1 = 0.86 : 1	2 x 0.40:1 = 0.80 : 1	2 x 0.44:1 = 0.88 : 1	$\frac{3.48}{4}$:1	**0.87 : 1**
	LH-I-91	**LH-I-92**	**LH-I-95**	**LH-I-96**		
50 °C	2 x 0.72:1 = 1.44 : 1	2 x 0.76:1 = 1.52 : 1	2 x 0.71:1 = 1.42 : 1	2 x 0.70:1 = 1.40 : 1	$\frac{5.78}{4}$:1	**1.45 : 1**
	LH-I-85	**LH-I-86**				
60 °C	2 x 0.97:1 = 1.94 : 1	2 x 1.02:1 = 2.04 : 1	——	——	$\frac{3.98}{2}$:1	**1.99 : 1**
	LH-I-77	**LH-I-78**	**LH-I-87**	**LH-I-88**		
70 °C	2 x 1.25:1 = 2.50 : 1	2 x 1.08:1 = 2.16 : 1	2 x 1.56:1 = 3.12 : 1	2 x 1.38:1 = 2.76 : 1	$\frac{10.54}{4}$:1	**2.64 : 1**
	LH-I-73	**LH-I-74**	**LH-I-83**			
80 °C	2 x 2.04:1 = 4.08 : 1	2 x 1.90:1 = 3.80: 1	2 x 2.50:1 = 5.0 : 1	——	$\frac{12.88}{3}$:1	**4.29 : 1**

The ratios of **15**:**16** were numerically determined by ^{1}H NMR spectroscopy of the crude concentrated reaction mixture in $CDCl_3$. The latter determination involved a comparison of the numerical integral of the olefinic resonance at δ 5.55 ppm for the vinyltin product **16** with the corresponding integral for ***one*** of the two allenyltin diastereomers of **15**. Specifically, the allenyltin **15** gave rise to two separate allenic proton signals at δ 4.77 and 4.71 ppm, which were attributable to the two geometric isomers that always formed non-stereoselectively as a 1:1 mixture. The allenic resonance at δ 4.71 ppm was the one that was typically used to make these ratio comparisons, since this signal was typically unobscured by impurities. However, in some instances, where there was an obvious overlapping impurity, it was found necessary to perform the integration on the δ 4.77 pm triplet of doublets in order to obtain an accurate quantifying integral value. In either case, it was always necessary to multiply the numerically measured integral for the δ 4.71 or 4.77 ppm resonance by a factor of 2, to obtain the real ratio of **15**:**16** formed in each reaction run at the specified temperature. The ratios of **15**:**16** were then averaged at those specific temperatures (eg. at 40 ^{o}C), and it is these averaged ratios that have been used for the various $k_{\text{ring-opening}}$ determinations shown below for the conversion of **13** into **14** and thence **15** at the various temperatures studied. While at higher temperatures above 70 ^{o}C there is an increased ±16-18% variation in the ratios obtained, relative to the averaged ratio, when these reactions are run below 70 ^{o}C, the deviations in ratio are much lower and correspond to an overall measurement error that is approximately ± 2.5-8% which, in both cases, is perfectly reasonable for a thermally mediated radical reaction. In fact, variable kinetics are often a hallmark of free radical reactions and such variations are thus to be expected.

2.2 The $k_{ring\text{-}opening}$ and Arrhenius Data Obtained for Stannylvinyl Radical 13 and Our Mechanistic Interpretation of That Data

As already indicated:

$$k_{ring\text{-}opening} = [(R)_3SnH] \times k_{H\text{-}atom\ abstraction} \times \frac{[Allenyltin]}{[Vinyltin]} \quad \text{(Eqn 2)}$$

Consequentially, using equation 2 and the above averaged ratios of **15**:**16** obtained at 0.2 M [Bu_3SnH] in PhMe, the following $k_{ring\text{-}opening}$ constants and their log $k_{ring\text{-}opening}$ values were determined for **13** at each temperature specified:

At 313 K: $k_{ring\text{-}opening\ \mathbf{13},\ 313\ K} = [0.2] \times 2.32 \times 10^8 \times 0.87/1 = 4.0368 \times 10^7\ s^{-1}$.

At 323 K: $k_{ring\text{-}opening\ \mathbf{13},\ 323\ K} = [0.2] \times 2.51 \times 10^8 \times 1.45/1 = 7.2790 \times 10^7\ s^{-1}$.

At 333 K: $k_{ring\text{-}opening\ 13,\ 333\ K} = [0.2] \times 2.71 \times 10^8 \times 1.99/1 = 1.07858 \times 10^8\ s^{-1}$.

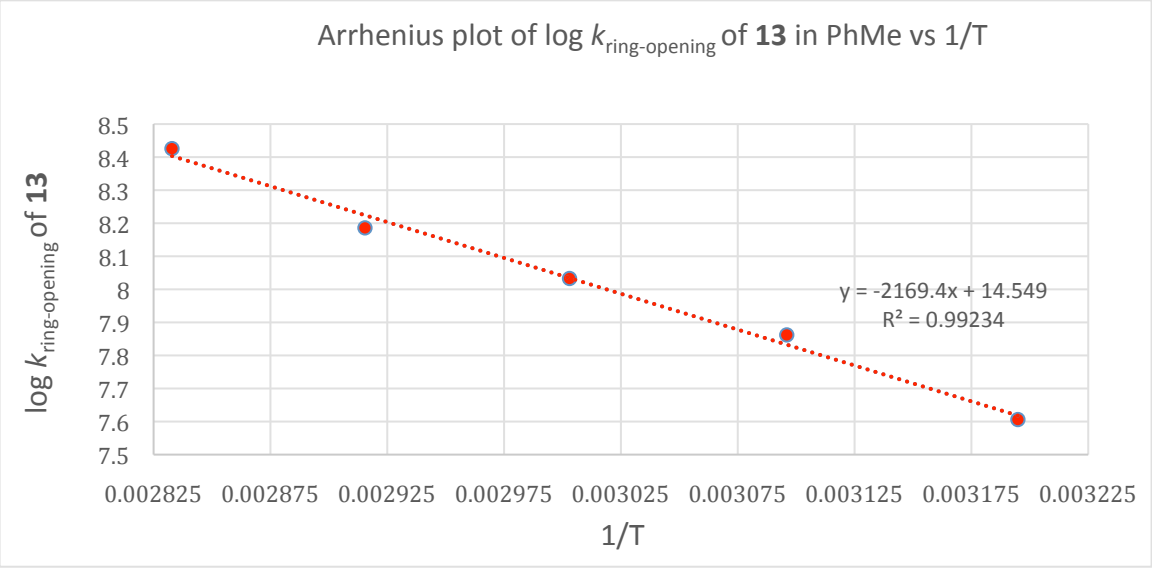
At 343 K: $k_{ring\text{-}opening\ \mathbf{13},\ 343\ K} = [0.2] \times 2.906 \times 10^8 \times 2.64/1 = 1.53437 \times 10^8\ s^{-1}$.

At 353 K: $k_{ring\text{-}opening\ \mathbf{13},\ 353\ K} = [0.2] \times 3.106 \times 10^8 \times 4.29/1 = 2.66495 \times 10^8\ s^{-1}$.

The corresponding 1/T values that were used in the same Arrhenius plot are as follows:

1/313 K = 0.003194888.	$\log k_{ring\text{-}opening\ \mathbf{13},\ 313\ K} = 7.60604$.
1/323 K = 0.003096.	$\log k_{ring\text{-}opening\ \mathbf{13},\ 323\ K} = 7.862072$.
1/333 K = 0.003003.	$\log k_{ring\text{-}opening\ 13,\ 333\ K} = 8.03285$.
1/343 K = 0.002915.	$\log k_{ring\text{-}opening\ \mathbf{13},\ 343\ K} = 8.185930$.
1/353 K = 0.0028328611.	$\log k_{ring\text{-}opening\ \mathbf{13},\ 353\ K} = 8.425688$.

The aforementioned log $k_{\text{ring-opening}}$ **13** values between 313-353 ^{o}K were then graphically displayed in the form of an Arrhenius plot (log $k_{\text{ring-opening}}$ of **13** v 1/T) in Excel; this plot is shown below. Importantly, its intercept furnished a log A of 14.549, which confirmed an E_H1 radical-induced ring-opening mechanism was again operating. The aforementioned Arrhenius plot also had a slope of -2169.4 and an r^2 = 0.99234, which indicated a 99.2% quality of data fit.



From that slope, the E_a was calculated to be 41537.809 J mol^{-1} or +9.921 kcal mol^{-1} (i.e. 9.92 kcal mol^{-1}). That E_a calculation is set out below to show our method.

From the slope: $E_{a\ \text{ring-opening}\ \mathbf{13}} = -(-2169.4) \times 2.303 \times 8.314$ J mol^{-1}

$\therefore\ E_{a\ \text{ring-opening}\ \mathbf{13}} = 41537.810$ J mol^{-1} = 41.5378 kJ mol^{-1}

$\therefore\ E_{a\ \text{ring-opening}\ \mathbf{13}} = 41.5378$ kJ mol^{-1} (x 0.238846) = +9.921 kcal mol^{-1}

This value compares very favourably with the experimentally-derived, two temperature point, E_a of +10.35 kcal mol^{-1} deduced for the cyclopropane ring-opening of **13** using the logarithmic form ($\log_{10}$) of the Arrhenius equation[2a (page 53)] shown below:

$$\log \frac{[k_2]}{[k_1]} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

which for the $k_{\text{ring-openings}}$ at 313 and 353 K gives

$$\log\left(\frac{2.66 \times 10^8}{4.04 \times 10^7}\right) = \frac{E_a}{2.303 \times 8.314}\left(\frac{353 - 313}{313 \times 353}\right)$$

which reduces to

$$\log\left(6.58416\right) = \frac{E_a}{2.303 \times 8.314}\left(\frac{40}{110489}\right)$$

$$\text{or} \quad 0.81850 = \frac{E_a}{2.303 \times 8.314}\left(\frac{40}{110489}\right)$$

which rearranges to

$$E_a = \frac{0.8185004 \times 2.303 \times 8.314 \times 110489}{40} \text{ J mol}^{-1}$$

$$= +43.289 \text{ kJ mol}^{-1}$$

which when divided by 4.184

gives an $E_{a\ \text{ring-opening for}\ \mathbf{13}} = +10.35$ kcal mol $^{-1}$

This used just two experimentally-determined $k_{\text{ring-opening}}$ values for **13** at 313 and 353 ^{o}K in PhMe to arrive at this calculated value, which is quite close in magnitude to Guo's $E_{a\ \text{ring-opening}\ \mathbf{13}}$ of +10.7 kcal mol^{-1} shown in Scheme 3 of our main paper.

However, given that our Arrhenius plot had used the five averaged $k_{\text{ring-opening of}\ \mathbf{13}\ \text{in PhMe}}$ data points v 1/T and it had an r^2 value of 0.99224, this value must be considered the more reliable of the two for the determination of the $E_{a\ \text{ring-opening}\ \mathbf{13}}$.

Nonetheless, the close level of agreement between the two E_a values is most reassuring, notwithstanding the 2 experimental data point calculation being +0.43 kcal mol^{-1} higher in magnitude than the E_a = +9.92 kcal mol^{-1} figure. Given the much greater degree of accuracy of the $E_{a\ \text{ring-opening}\ \mathbf{13}}$ = +9.92 kcal mol^{-1} value, we suggest that this is the E_a value that should be adopted in all future $k_{\text{ring-opening}}$ calculations involving **13** at different temperatures, and that it be used alongside our experimentally determined log A value of 14.549 in the following Arrhenius expression: $\log k_{\text{ring-opening}\ \mathbf{13}} = 14.549 - 9.92/2.303RT$.

With regard to this log A of 14.549, it resulted in a $\Delta S^{\ddagger}_{333\ K}$ = +24.39 J K^{-1} mol^{-1} (+5.83 e.u.) being estimated for the ring-opening of **13** at the mean reaction temperature of 333 K (60 ^{o}C). This was calculated as follows via the Avery equation[2a] (page 67 of Avery's book):

$$\Delta S^{\ddagger}_{333\ K} = 8.314 \left[(2.303 \times 14.549) - 2.303 \log \left(\frac{1.38 \times 10^{-23} \times 333}{6.626 \times 10^{-34}} \right) - 1 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = 8.314 \left[33.5063 - 2.303 \log \left(6.935406 \times 10^{12} \right) - 1 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = 8.314 \left[33.5063 - 2.303 \left(12.84107 \right) - 1 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = 8.314 \left[33.5063 - 29.5730 - 1 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = 8.314 \left[33.5063 - 30.5730 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = 8.314 \left[+2.933 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = +24.388\ J\ K^{-1}\ mol^{-1}$$

$$\therefore \Delta S^{\ddagger}_{333\ K} = \frac{+24.388\ J\ K^{-1}\ mol^{-1}}{4.184} = +5.83\ e.u. = +5.83\ cal\ K^{-1}\ mol^{-1}$$

It was also reconfirmed by calculation using the Hale and Anslyn/Dougherty[27] simplified $\Delta S^{\ddagger}$ equations. Thus:

$$\Delta S^{\ddagger}_{333\ K} = 19.147 \left[14.549 - 10.753 - 2.522 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = 19.147 \left[1.274 \right] J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = +24.39\ J\ K^{-1}\ mol^{-1}$$

$$\Delta S^{\ddagger}_{333\ K} = 4.576 \left[14.549 - 10.753 - 2.522 \right] cal\ K^{-1}\ mol^{-1}\ \text{or e.u.}$$

$$\Delta S^{\ddagger}_{333\ K} = 4.576 \left[1.274 \right] cal\ K^{-1}\ mol^{-1}\ \text{or e.u.}$$

$$\Delta S^{\ddagger}_{333\ K} = +5.830\ cal\ K^{-1}\ mol^{-1}\ \text{or e.u.} \times 4.184$$

$$\Delta S^{\ddagger}_{333\ K} = +24.39\ J\ K^{-1}\ mol^{-1}$$

Clearly, the high positive magnitude of this $\Delta S^{\ddagger}$ value once more confirmed that a non-associative, unimolecular, fissive E_H1 ring-opening was mechanistically operating in the transition of **13** into the activated complex that ultimately resulted in radical **14** (and thence **15**). This value further reflected the substantial bond-loosening and increase in entropy that was occurring in the activated complex as it was being formed, when compared with its precursor radical **13**. Of course, this activated complex had the choice of either reverting back to **13**, or ultimately eliminatively

transiting into the ring-opened homoallenyl radical **14**, which then could irreversibly H-atom abstract from the stannane via the S_H2 mechanistic pathway to give **15**. The fact that the frequency factor A of this unimolecular ring-opening of **13** to give **14** is 3.54 x 10^{14} s^{-1}, confirms that a substantial number of these activated complexes have sufficient translational energy to automatically transit into **14** at the mean reaction temperature of 333 K, once the inherent energy barrier has been overcome, and this establishes that this unimolecular process is strongly entropically favourable and has a product-like transition state. A log A = 14.549 most definitely does not align with an associative bimolecular ionic reductive ring-opening of a stannylvinyl cation intermediate, as would be advocated by some.[6] This log A value is slightly lower than that seen for the **2a→3a** transition, possibly because of the greater loss in overall rotational freedom/entropy encountered in going from **13→14**. This might be due to **13** having greater rotational freedom at the very outset. *However, most importantly, the large positive $\Delta S^{\ddagger}_{333\ K}$ of +24.39 J K^{-1} mol^{-1} (+5.83 e.u.) most definitely rules out a bimolecular ionic reductive ring cleavage of a putative α-cyclopropyl-β-tributylstannylvinyl cation[6] as having produced **15**, since bimolecular reactions always have negative $\Delta S^{\ddagger}$ values.*[2] The large positive $\Delta S^{\ddagger}_{333\ K}$ observed also confirmed that little in the way of solvent immobilisation or electrostriction had occurred, which further ruled out a stannylvinyl cation origin for **15** from the radical **2a**, as would be advocated by some.[6]

From the E_a of 41537.809 J mol^{-1} or +9.92 kcal mol^{-1} that was calculated for the ring-opening of **13** to give **14**, we have been able to estimate a free energy of activation $\Delta G^{\ddagger}_{333\ K}$ for this radical ring opening event in PhMe. This calculation is shown below:

$$\Delta H^{\ddagger} = E_a - nRT \therefore \Delta H^{\ddagger} = 41.53781 - \frac{1 \times 8.314 \times 333}{1000} \text{ kJ mol}^{-1}$$

$$\Delta H^{\ddagger} = 41.53781 - 2.77 = 38.77 \text{ kJ mol}^{-1} = +9.26 \text{ kcal mol}^{-1}$$

$$\text{Since } \Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \therefore \Delta G^{\ddagger} = 38.77 - \frac{333 \times 24.39}{1000} \text{ kJ mol}^{-1}$$

$$\therefore \Delta G^{\ddagger} = 38.77 - 8.12 = 30.65 \text{ kJ mol}^{-1} = +7.32 \text{ kcal mol}^{-1}$$

The composite $\Delta G^{\ddagger}$ value that we have determined here now puts a numerical figure on the fundamental energy input needed to bring about formation of the activated complex for the unimolecular radical ring-opening of the more rotationally free radical **13** to give **14**, and the relative contributions that the $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ terms make to that overall $\Delta G^{\ddagger}$, as **13** transits into the

activated complex that produces **14**. Although endergonic at +7.32 kcal mol^{-1}, this experimentally derived value of $\Delta G^{\ddagger}_{333\ K}$ is well below the immense Coulombic energy of attraction (*F* = +46.39 kcal mol^{-1}) that would be needed to separate the hypothetical stannylvinyl cation-superoxide anion pair[6] by 3 Å in PhMe, assuming that the hypothetical stannylvinyl cationic theory of reference 6 was invoked to be operating in this instance. Obviously, given the huge $\Delta G^{\ddagger}$ input that would be required to effect such an ion pair separation in the non-polar solvent, PhMe, it cannot possibly be proceeding by such a mechanism. In fact, PhMe would only serve to destabilise any developing polar transition state that could bring about cyclopropane bond fission into a stannylhomoallenyl cation, or which involved a direct S_N2 ionic reduction of a stannylvinyl cation to give **15**. Energetically therefore, one can state with high confidence that such an experimentally determined $\Delta G^{\ddagger}$ value of +7.32 kcal mol^{-1} is really only compatible with the much lower energy, radical-induced, β-scissive eliminative pathway giving rise to **15** from **13** (see Scheme 2/Table 2). A homolytic ring-opening of **13** to give **14** also more satisfactorily aligns with the Guo calculations of Scheme 3,[22] and all of the other experimental data that has so far been gathered to date in this area, *which collectively supports an exclusively free radical mechanism for these dialkyl acetylene O-directed hydrostannation reactions*[43] *with both cat. Et_3B/O_2 and AIBN initiators*.[3]

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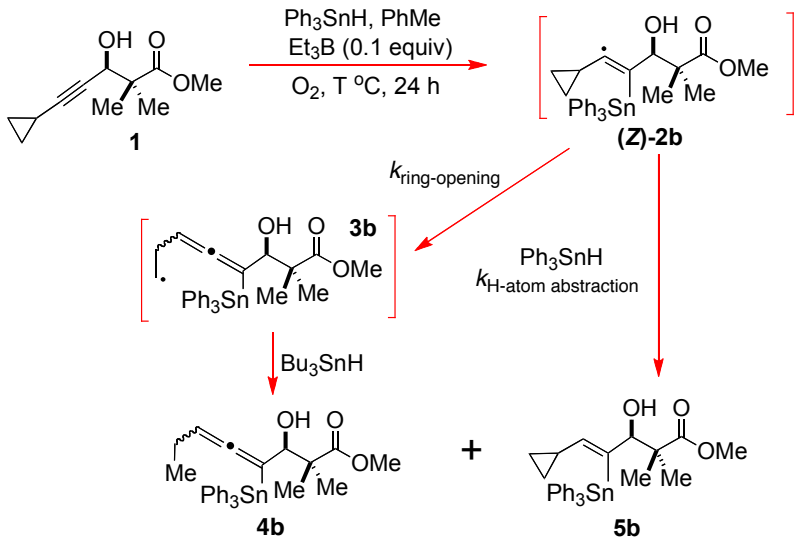
43. For an excellent new 2024 review on alkyne hydrometallation with Group IV metal hydrides, see the following Book Chapter by: T. Wiesner and M. Haas in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Elsevier, 2024: https://doi.org/10.1016/B978-0-323-96025-0.00125-3 (b) For McLaughlan and Roberts' recent highly regiocontrolled $PtCl_2$/XPhos-catalysed hydrostannation of terminal aryl acetylenes and propargylic alcohols, see: D. D. Roberts and M. G. McLaughlin, *Adv. Synth. Catal.*, 2023, **365**, 1602. (c) For McLaughlin's recent application of the $PtCl_2$/XPhos/Et_3SiH-catalyst system to the highly regiocontrolled hydroboration of terminal alkyl, aryl and heteroaryl acetylenes with HBPin, see: K. L. E. Hale, D. D. Roberts and M. G. McLaughlin, *Eur. J. Org. Chem.*, 2025, e202401355.

Part 3. Product Ratio Comparisons For the O-Directed Free Radical Hydrostannation of Alkynol 1 with Ph_3SnH in PhMe

3.1 The Experimentally Determined Average Ratios of 4b:5b Obtained from the O-Directed Hydrostannation of 1

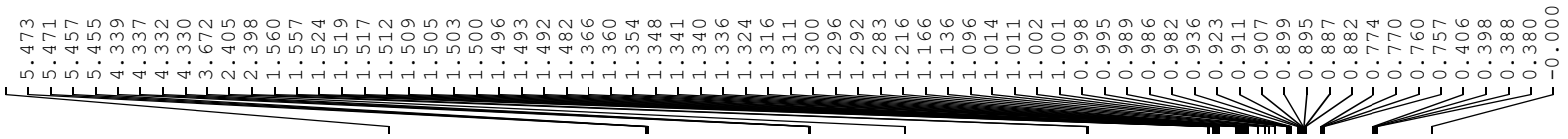


T °C	Run 1 Ratio **4b**:**5b**	Run 2 Ratio **4b**:**5b**	Run 3 Ratio **4b**:**5b**	Run 4 Ratio **4b**:**5b**	Run Total **4b**:**5b**	Final Averaged Value of **4b**:**5b**
20 °C (293 K)	**HAW-VII-069** 1: 4.58	**HAW-VII-070** 1: 4.75	**HAW-VII-071** 1: 4.62	**HAW-VII-072** 1: 4.88	$1 : \frac{18.83}{4}$	**1 : 4.71**
40 °C (313 K)	**HAW-VII-061** 1: 1.98	**HAW-VII-062** 1: 1.89	**HAW-VII-063** 1: 2.03	**HAW-VII-064** 1: 1.78	$1 : \frac{7.68}{4}$	**1 : 1.92**
60 °C (333 K)	**HAW-VII-065** 1.31 : 1	**HAW-VII-066** 1.87 : 1	**HAW-VII-067** 1.71 : 1	**HAW-VII-068** 1.35 : 1	$\frac{6.24}{4}$:1	**1.56 : 1**
80 °C (353 K)	**HAW-VII-074** 3.18 : 1	**HAW-VII-075** 2.47 : 1	**HAW-VII-079** 2.68 : 1	**HAW-VII-080** 3.39 : 1	$\frac{11.72}{4}$:1	**2.93 : 1**

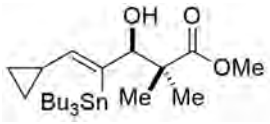
At 20 °C (293 K), from 4 independent reaction runs, the averaged ratio of **4b**:**5b** (R = Ph) was 1:4.71.

Assuming that the $k_{\text{H-atom abstraction Ph3SnH}}$ value for **2b** is approximately 6.95 faster than the $k_{\text{H-atom abstraction}}$ for **2a** from Bu_3SnH, this allows one to calculate a tentative $k_{\text{H-atom abstraction Ph3SnH}}$ value for **2b** as 1.36×10^9 mol^{-1} s^{-1} which, in turn, allows a tentative $k_{\text{ring-opening for 2b in PhMe 293 K}}$ of [0.2] x 1.36 $x10^9$ x 1/4.71 = 5.77 x 10^7 s^{-1} to be estimated.

Part B. The 600.13 MHz ^{1}H NMR and 150.90 MHz ^{13}C NMR Spectra of the Tributylstannylvinyltin 5a and Tributylstannylallene 4a in $CDCl_3$



Hamish Watson
HAW-V-047
Proton
Ref: 0.00ppm ($CDCl_3$-TMS)

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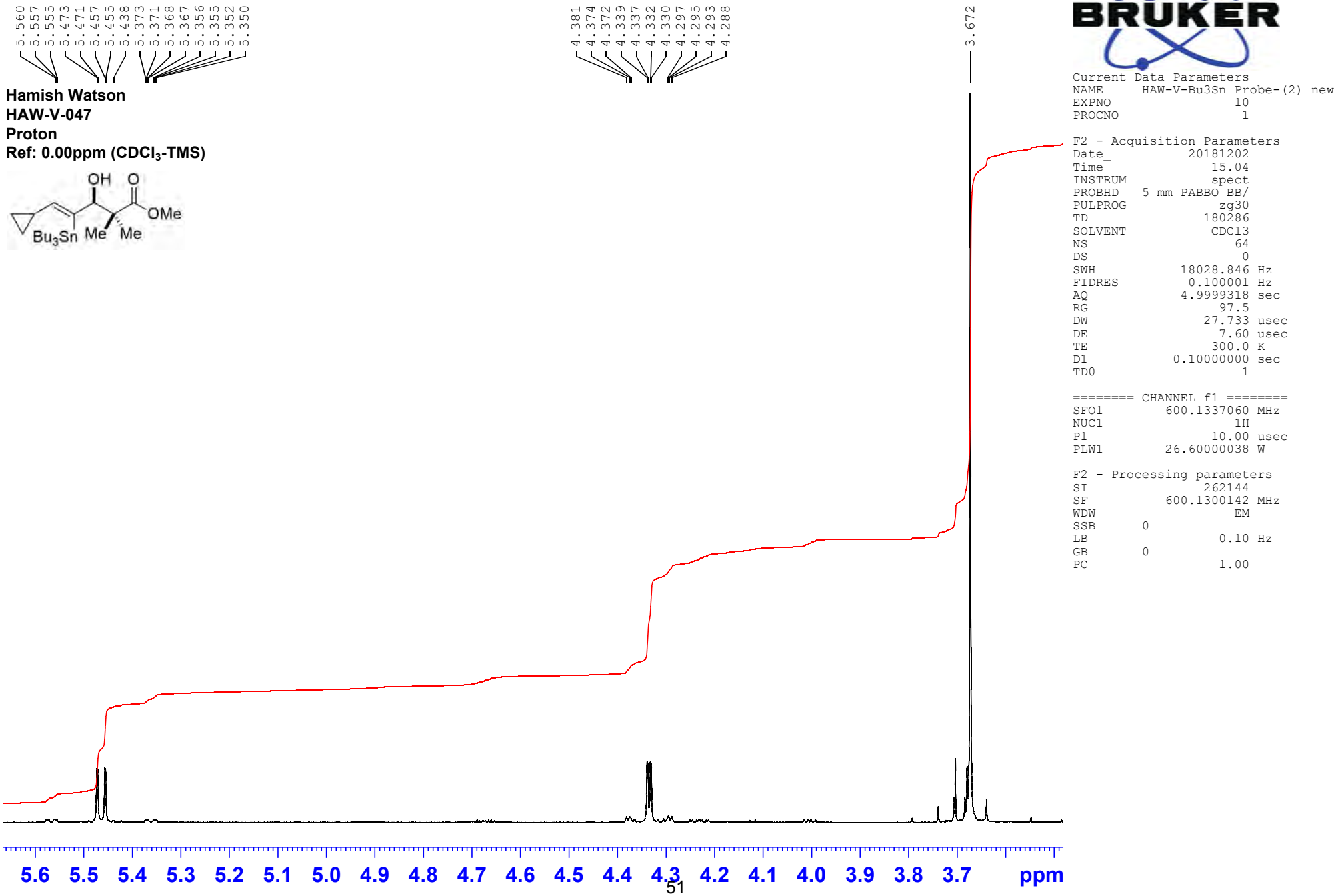
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Hamish Watson
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Hamish Watson
HAW-V-047
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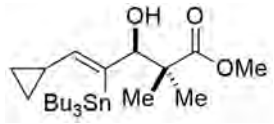

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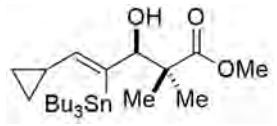


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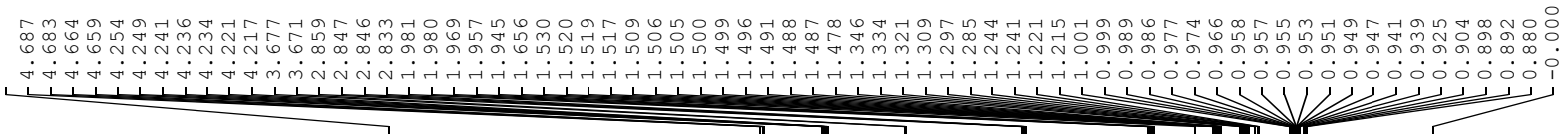

Hamish Watson
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Proton
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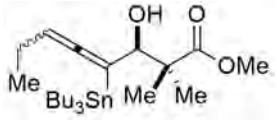


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TE                300.0 K
D1           0.10000000 sec
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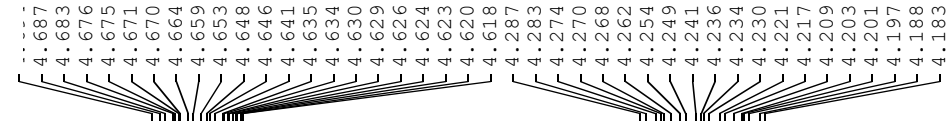
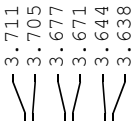
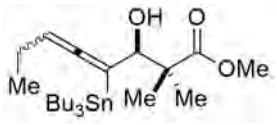
SF           600.1300100 MHz
WDW                  EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```





Hamish Watson
HAW-V-050
Proton
Ref: 0.00ppm ($CDCl_3$-TMS)

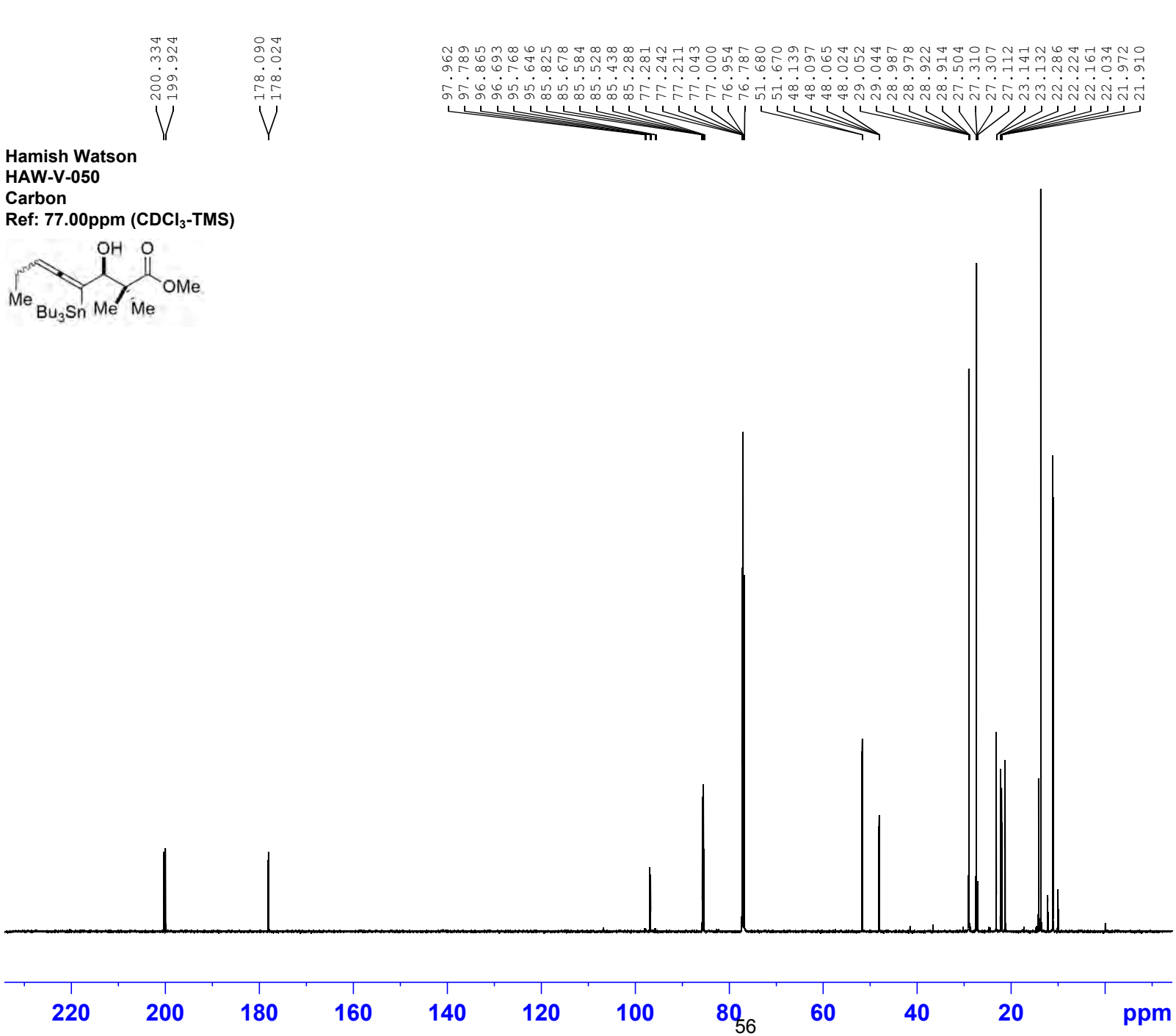



```
Current Data Parameters
NAME      HAW-V-Bu3Sn Probe-(1)
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20181130
Time                4.32
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                     64
DS                      0
SWH            18028.846 Hz
FIDRES          0.100001 Hz
AQ             4.9999318 sec
RG                 22.13
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300100 MHz
WDW                  EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```



BRUKER

Current Data Parameters
NAME HAW-V-Bu3Sn Probe-(1)
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181130
Time 5.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 119044
SOLVENT CDC13
NS 1024
DS 4
SWH 37500.000 Hz
FIDRES 0.315010 Hz
AQ 1.5872533 sec
RG 186.92
DW 13.333 usec
DE 7.73 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

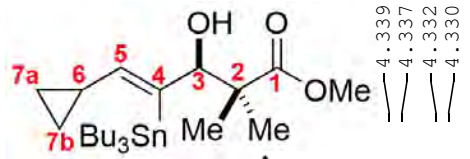
======== CHANNEL f1 ========
SFO1 150.9194058 MHz
NUC1 13C
P1 11.80 usec
PLW1 85.00000000 W

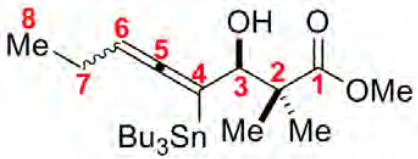
======== CHANNEL f2 ========
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz64
PCPD2 80.00 usec
PLW2 27.00000000 W
PLW12 0.43891999 W
PLW13 0.28090999 W

F2 - Processing parameters
SI 131072
SF 150.9028118 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Part C. The 600.13 MHz ^{1}H NMR Ratio Determinations For the Tributylstannylallene 4a and Tributylstannylvinyltin 5a in $CDCl_3$

HAW-VII-055
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
Pentane (*c* of sm = 0.1M),
20 °C, 24 h





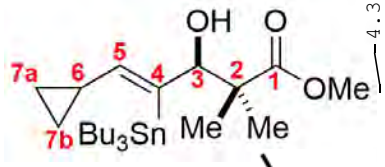

```
Current Data Parameters
NAME       HAW-VII-055-C
EXPNO                 40
PROCNO                 1

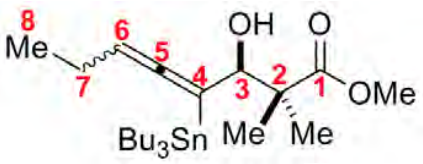
F2 - Acquisition Parameters
Date_           20191127
Time_              16.27
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300142 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-056
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
Pentane (*c* of sm = 0.1M),
20 °C, 24 h





4.339 4.337 4.332 4.330

4.250 4.245 4.237 4.232 4.230 4.225 4.217 4.212

H(3)
(dd)

2 x H(3)
(dd)
partially
overlapped

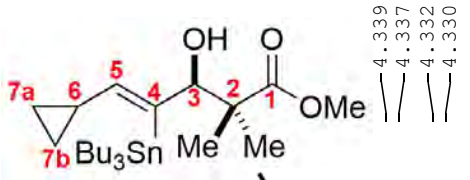

```
Current Data Parameters
NAME       HAW-VII-056-C
EXPNO                50
PROCNO                1

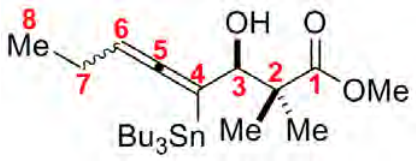
F2 - Acquisition Parameters
Date_          20191127
Time               16.36
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH            18028.846 Hz
FIDRES          0.100001 Hz
AQ              4.9999318 sec
RG                 60.48
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300141 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-057
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
Pentane (*c* of sm = 0.1M),
20 °C, 24 h





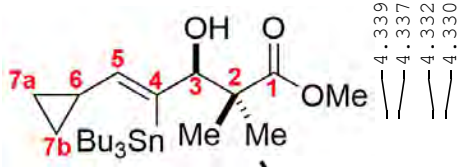

```
Current Data Parameters
NAME       HAW-VII-057-C
EXPNO                 10
PROCNO                 1

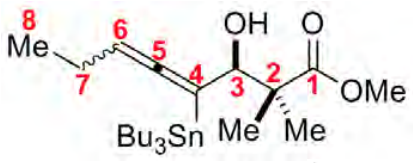
F2 - Acquisition Parameters
Date_           20191203
Time_              21.11
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ            4.9999318 sec
RG                 97.5
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300141 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-058
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
Pentane (*c* of sm = 0.1M),
25 °C, 24 h



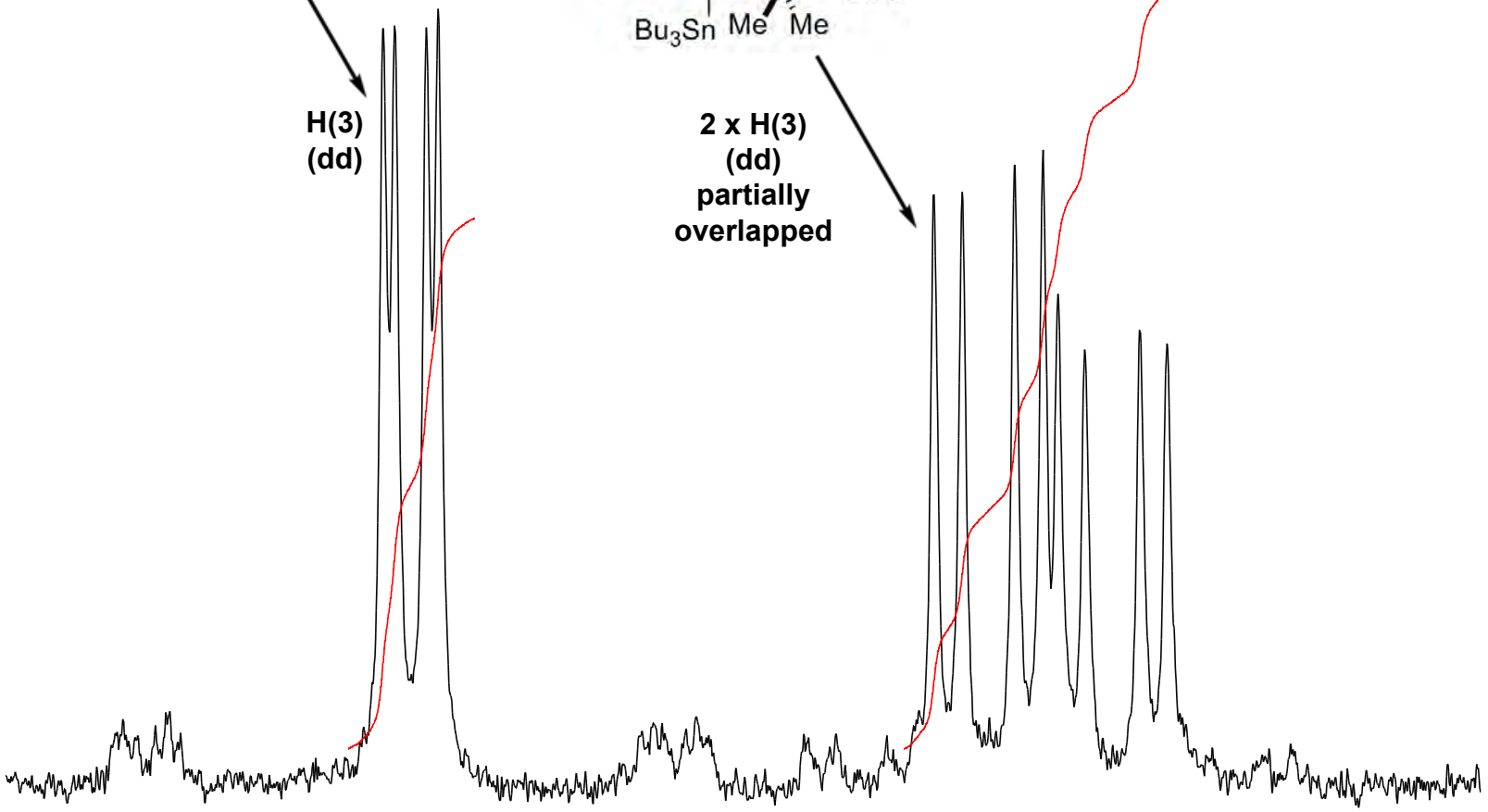


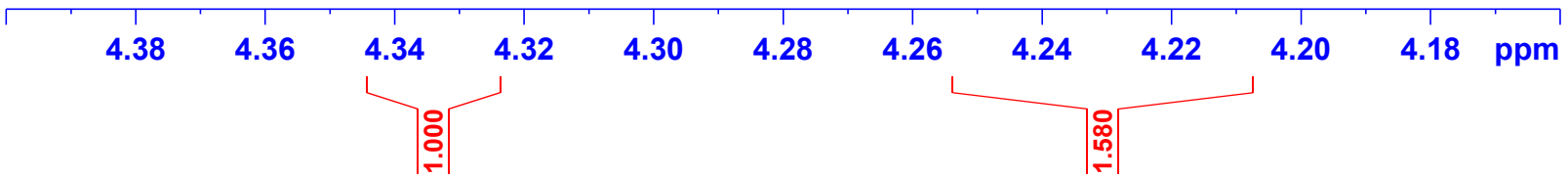
4.339 4.337 4.332 4.330

4.249 4.244 4.236 4.231 4.229 4.224 4.215 4.211

H(3)
(dd)

2 x H(3)
(dd)
partially
overlapped



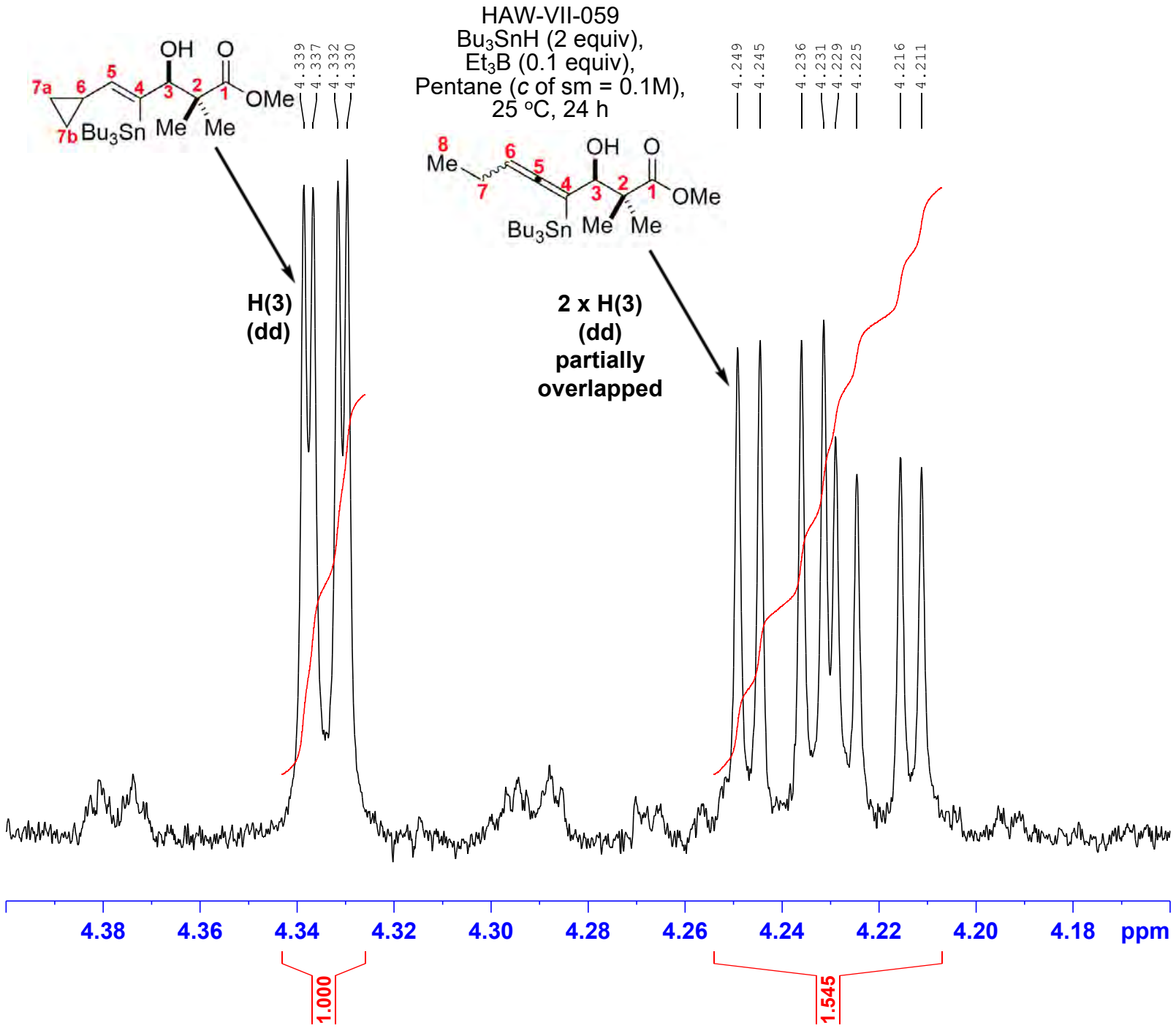



```
Current Data Parameters
NAME       HAW-VII-058-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191203
Time_             21.19
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                97.5
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                 1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300149 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

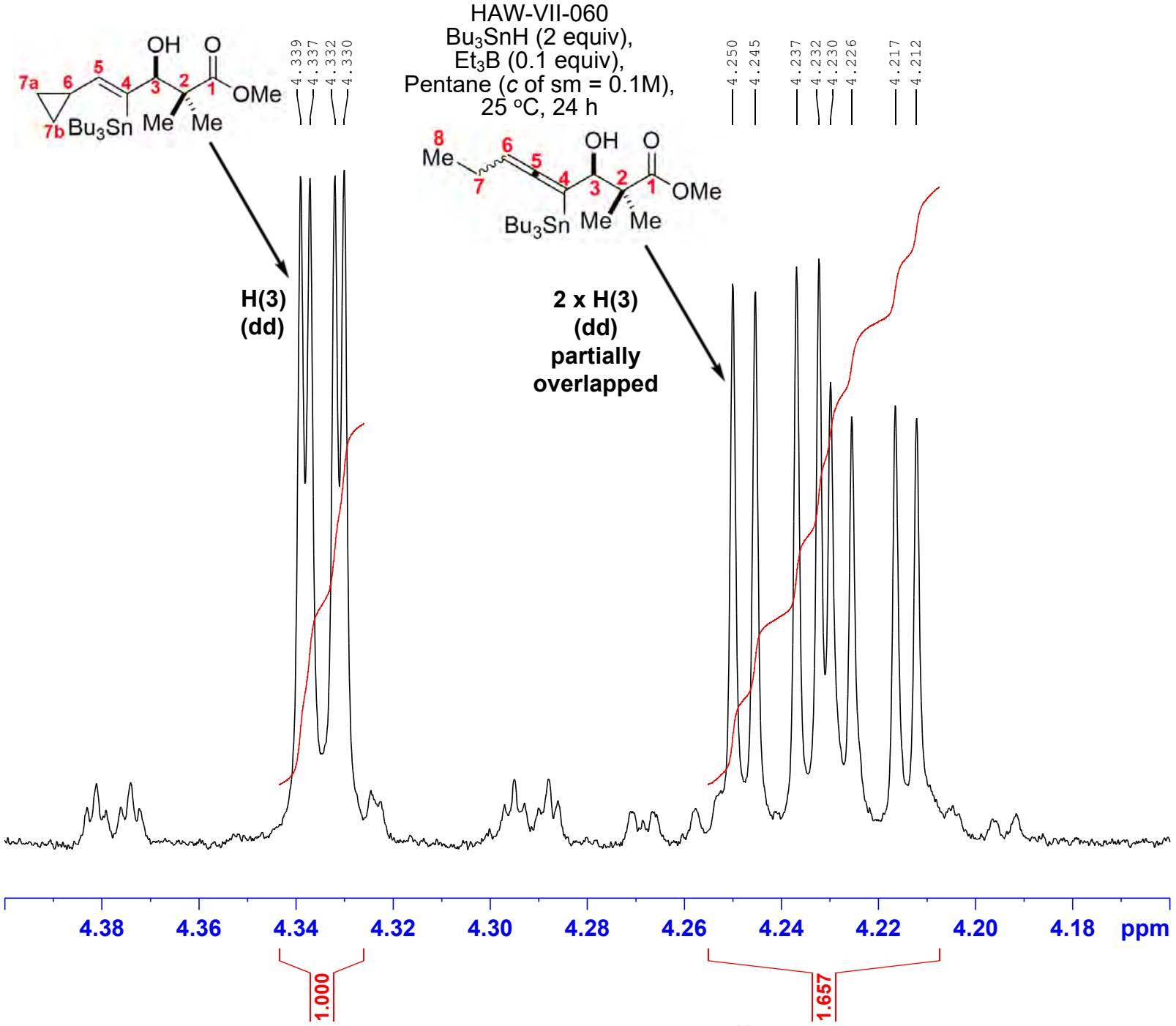



```
Current Data Parameters
NAME       HAW-VII-059-C
EXPNO                30
PROCNO                1

F2 - Acquisition Parameters
Date_          20191203
Time_             21.27
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                97.5
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                 1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300146 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```



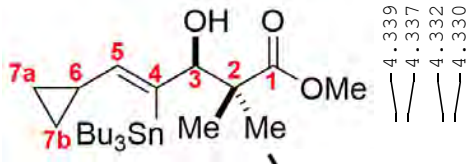

```
Current Data Parameters
NAME       HAW-VII-060-C
EXPNO                 40
PROCNO                 1

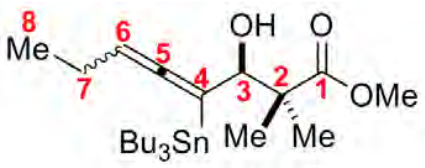
F2 - Acquisition Parameters
Date_           20191203
Time_             21.35
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD               180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ            4.9999318 sec
RG                 97.5
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300138 MHz
WDW                   EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-037
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
Pentane (*c* of sm = 0.1M),
30 °C, 24 h



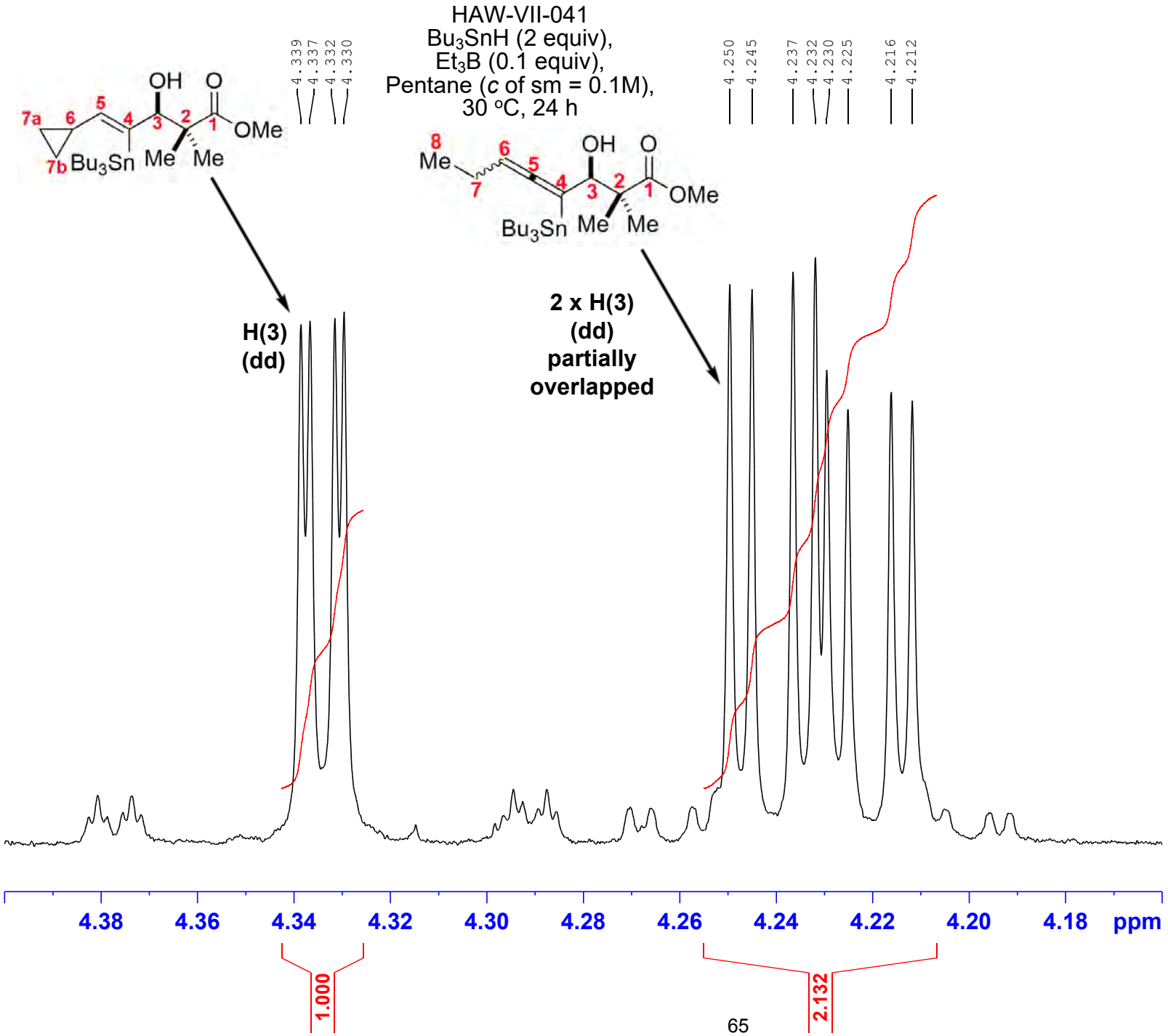



```
Current Data Parameters
NAME       HAW-VII-037-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191108
Time_              15.35
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                1H
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300136 MHz
WDW                 EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```



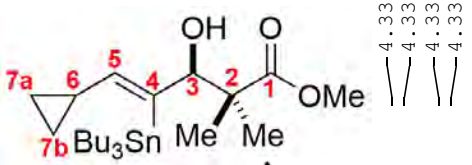

```
Current Data Parameters
NAME       HAW-VII-041-C
EXPNO                 10
PROCNO                 1

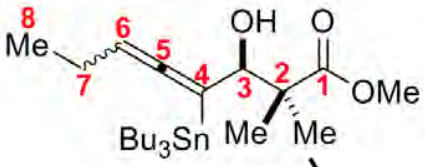
F2 - Acquisition Parameters
Date_           20191112
Time_             21.54
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD               180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300135 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-042
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
Pentane (*c* of sm = 0.1M),
30 °C, 24 h





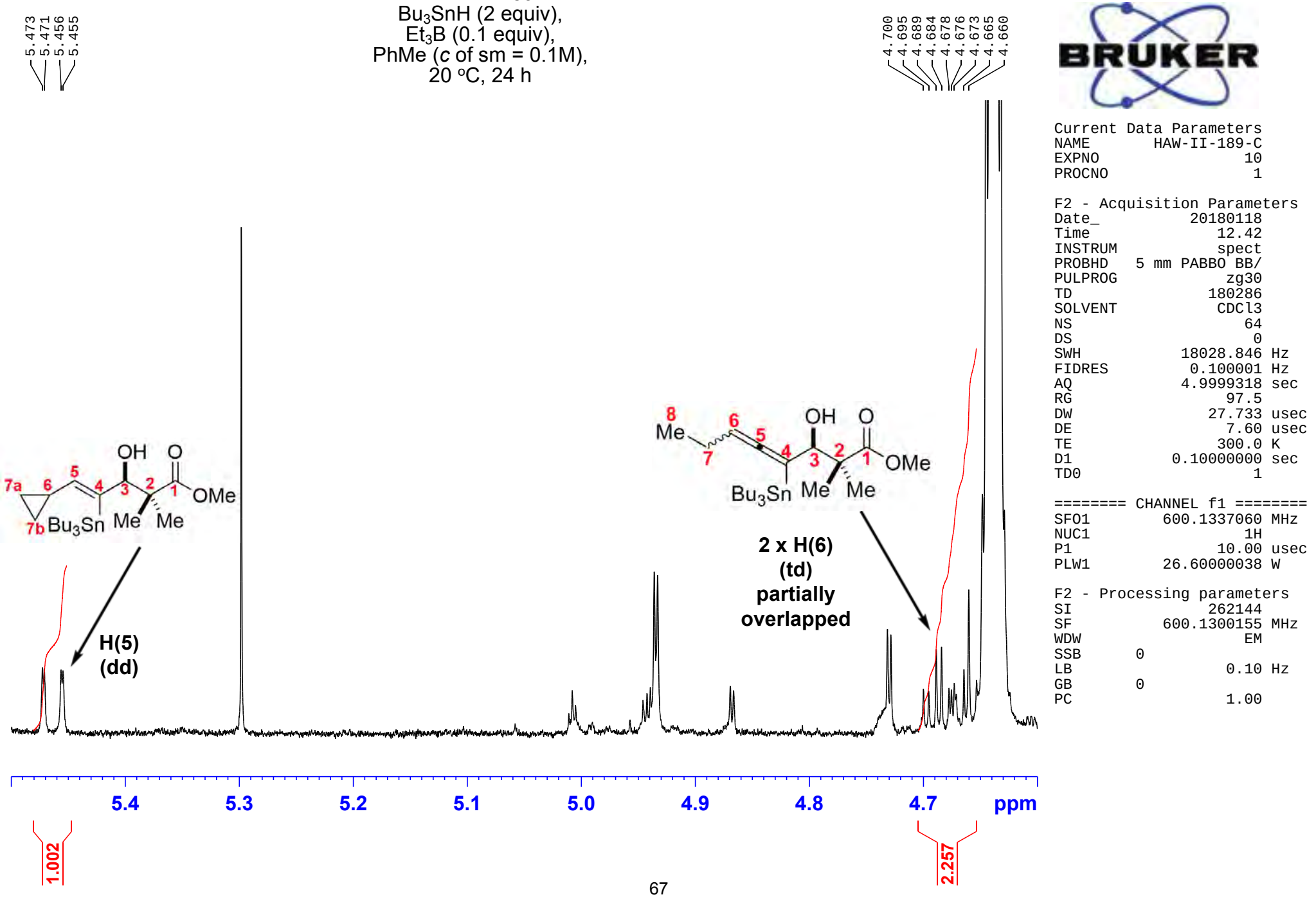

```
Current Data Parameters
NAME       HAW-VII-042-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191112
Time_              22.05
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                    68
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                 1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300134 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-II-189
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
20 °C, 24 h

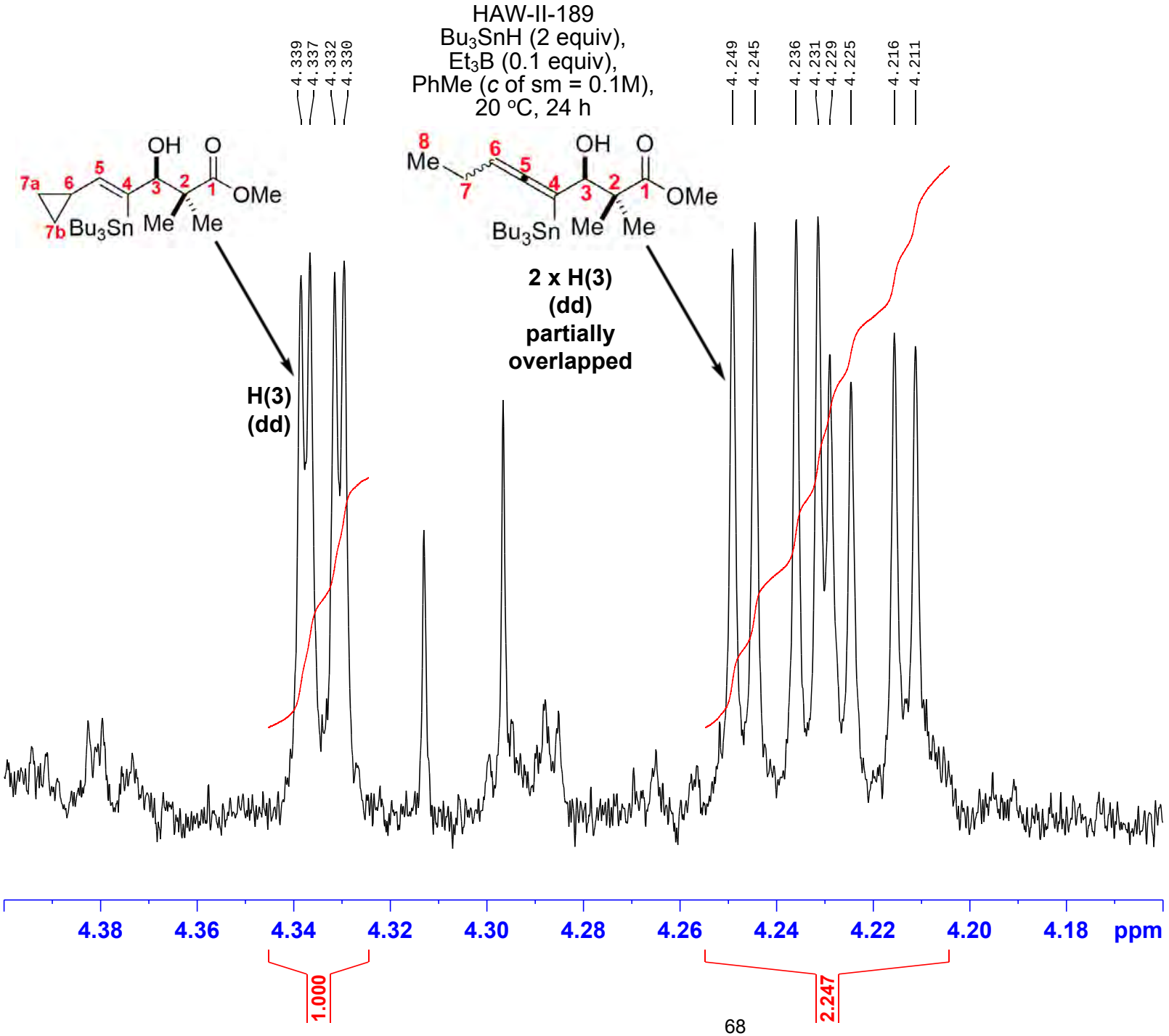



```
Current Data Parameters
NAME        HAW-II-189-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180118
Time               12.42
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ            4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                  7.60 usec
TE                 300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300155 MHz
WDW                 EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```



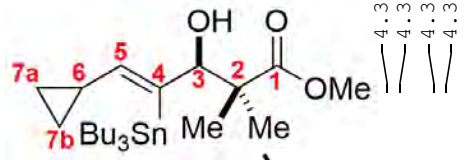
Current Data Parameters
NAME HAW-II-189-C
EXPNO 10
PROCNO 1

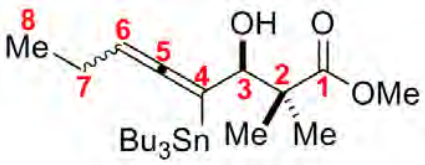
F2 - Acquisition Parameters
Date_ 20180118
Time 12.42
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 180286
SOLVENT CDCl3
NS 64
DS 0
SWH 18028.846 Hz
FIDRES 0.100001 Hz
AQ 4.9999318 sec
RG 97.5
DW 27.733 usec
DE 7.60 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1337060 MHz
NUC1 1H
P1 10.00 usec
PLW1 26.60000038 W

F2 - Processing parameters
SI 262144
SF 600.1300155 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

HAW-VI-171
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
20 °C, 24 h





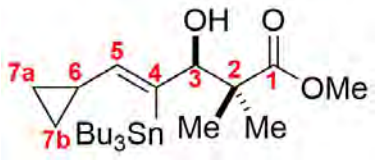

```
Current Data Parameters
NAME        HAW-VI-171-C
EXPNO                30
PROCNO                1

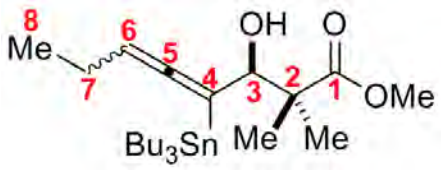
F2 - Acquisition Parameters
Date_          20190910
Time_             15.39
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                60.48
DW               27.733 usec
DE                7.60 usec
TE               300.0 K
D1            0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                 1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300139 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-052
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
25 °C, 24 h





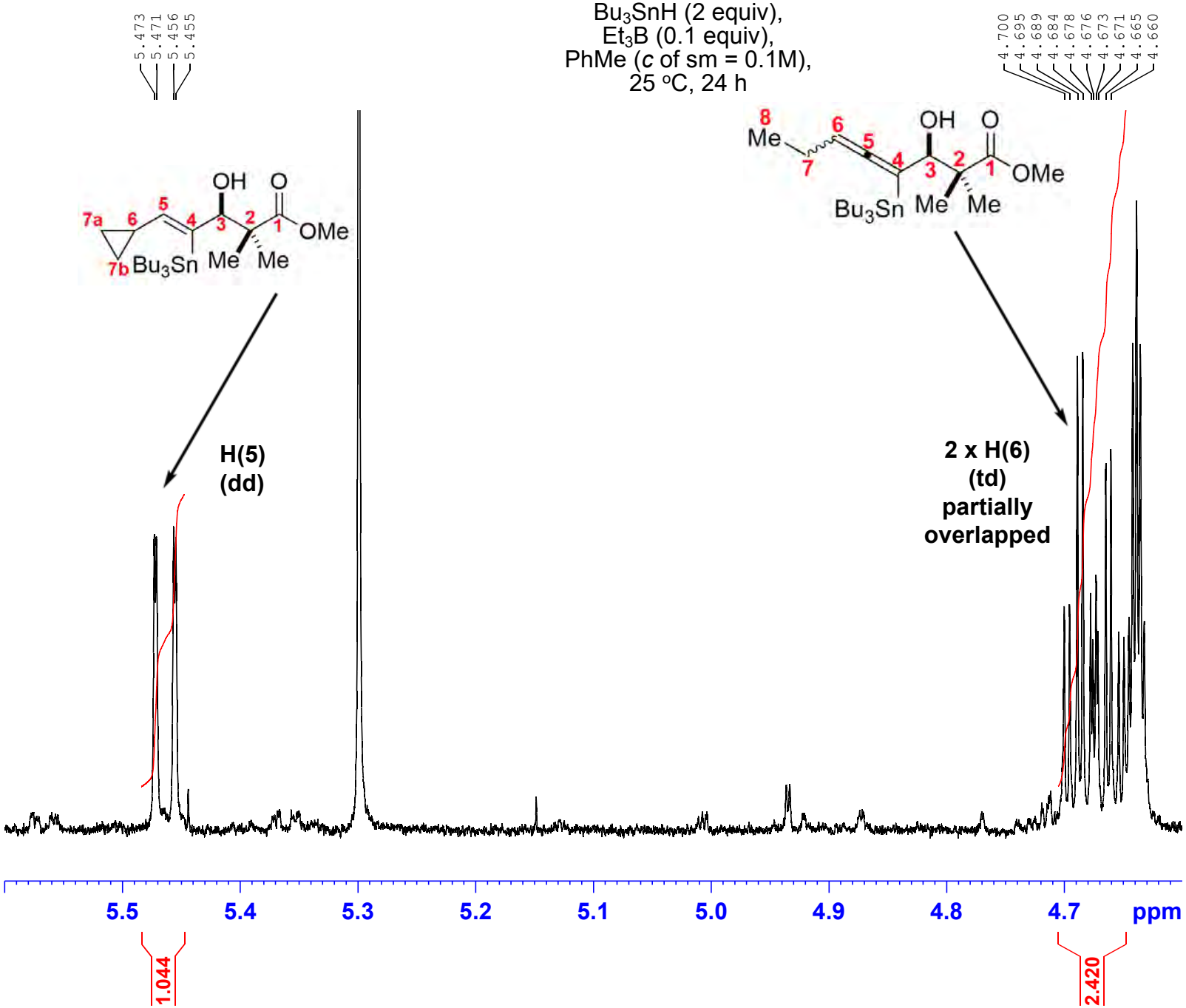

```
Current Data Parameters
NAME       HAW-VII-052-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191127
Time_             16.02
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                60.48
DW               27.733 usec
DE                7.60 usec
TE               300.0 K
D1            0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                 1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300142 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-053
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
25 °C, 24 h



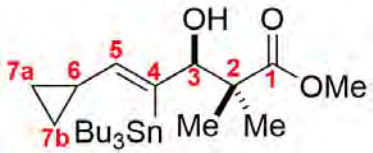

```
Current Data Parameters
NAME       HAW-VII-053-C
EXPNO                 20
PROCNO                 1

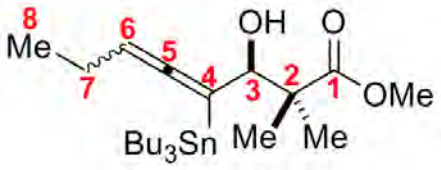
F2 - Acquisition Parameters
Date_           20191127
Time_              16.11
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300143 MHz
WDW                 EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-053
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
25 °C, 24 h





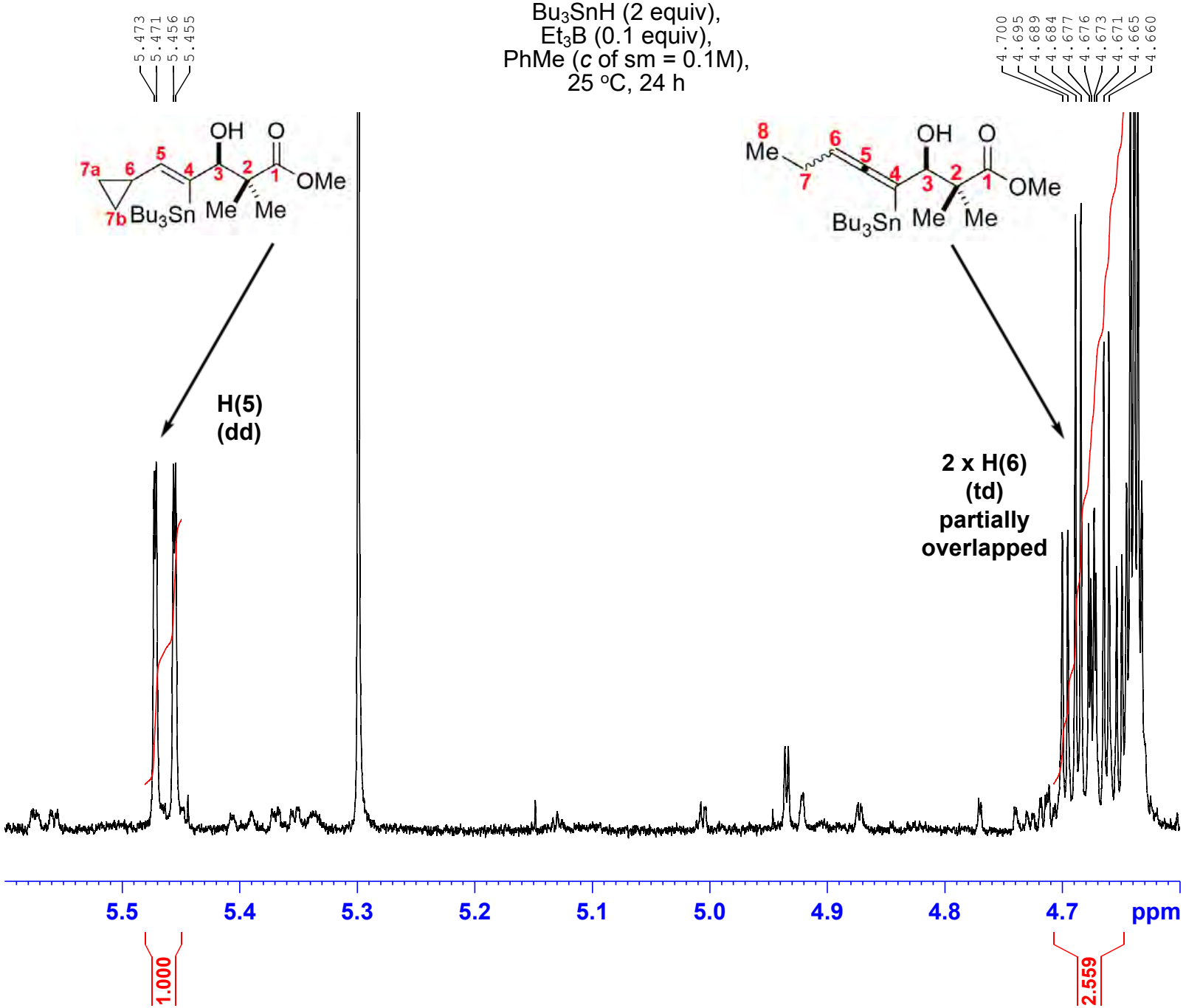

```
Current Data Parameters
NAME       HAW-VII-053-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191127
Time_              16.11
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300143 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-054
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
25 °C, 24 h



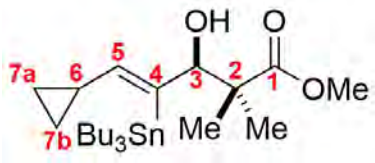

```
Current Data Parameters
NAME       HAW-VII-054-C
EXPNO                 30
PROCNO                 1

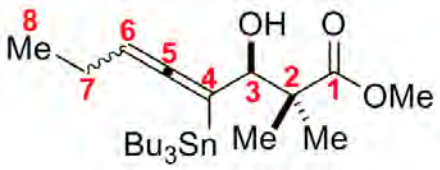
F2 - Acquisition Parameters
Date_           20191127
Time_             16.19
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                97.5
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1337060 MHz
NUC1                1H
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300142 MHz
WDW                 EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-054
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
25 °C, 24 h



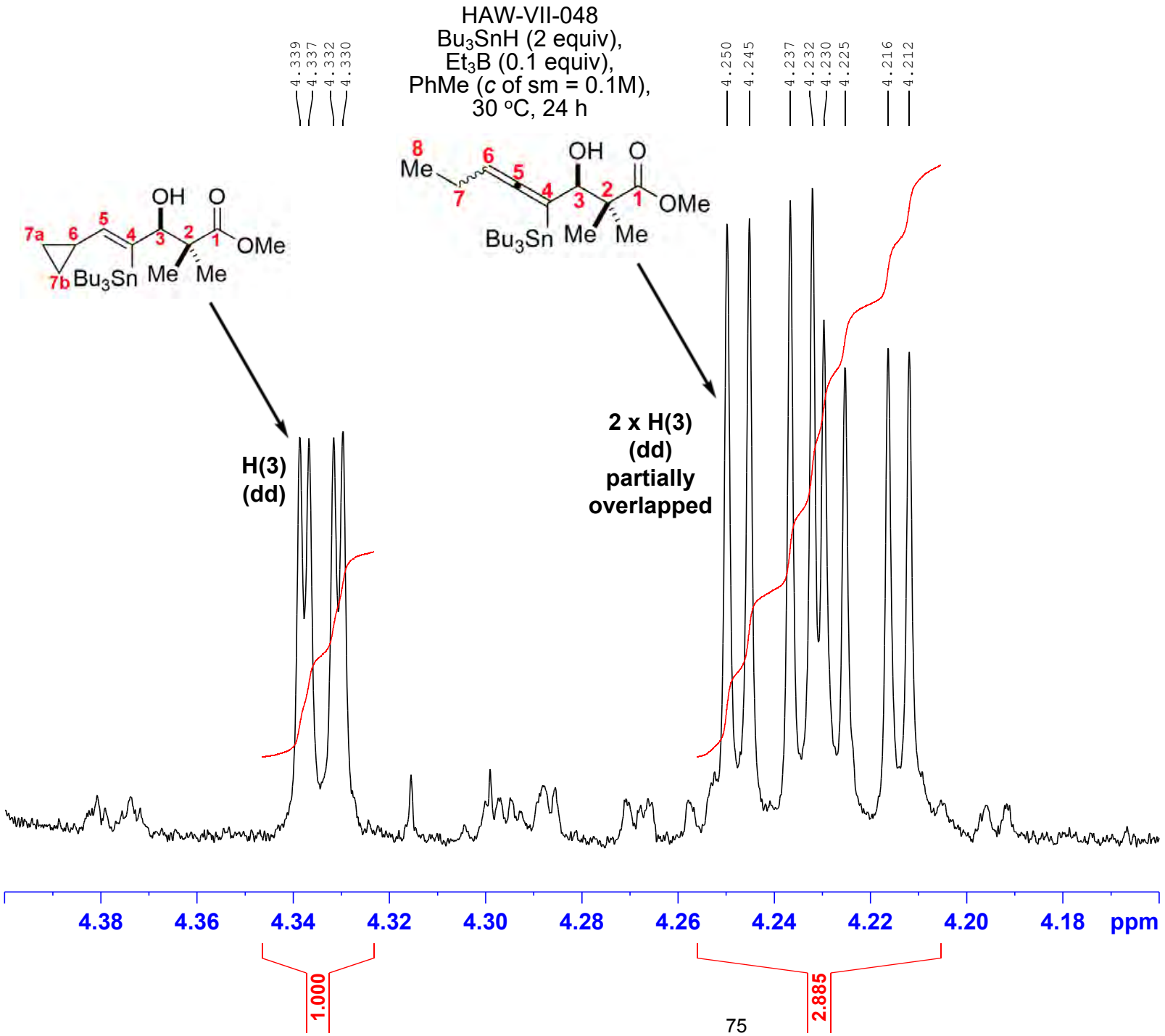



```
Current Data Parameters
NAME       HAW-VII-054-C
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191127
Time_             16.19
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD               180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300142 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```



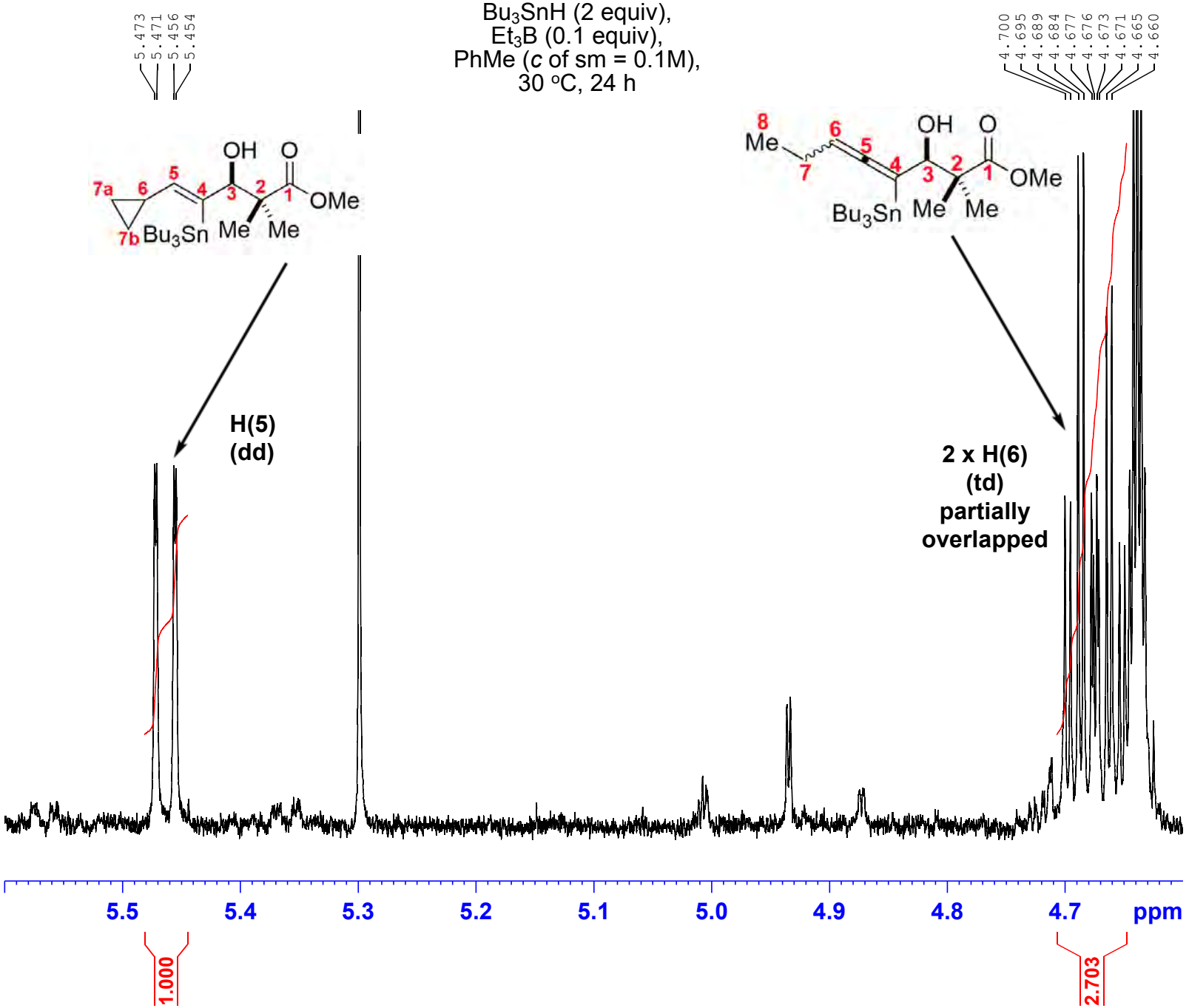

```
Current Data Parameters
NAME       HAW-VII-048-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191114
Time_              23.03
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300131 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-049
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
30 °C, 24 h



BRUKER

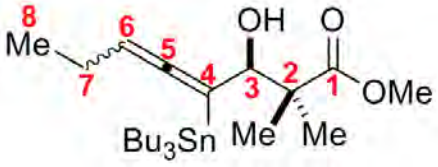
```
Current Data Parameters
NAME       HAW-VII-049-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191114
Time_              23.14
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300134 MHz
WDW                 EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-049
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
30 °C, 24 h



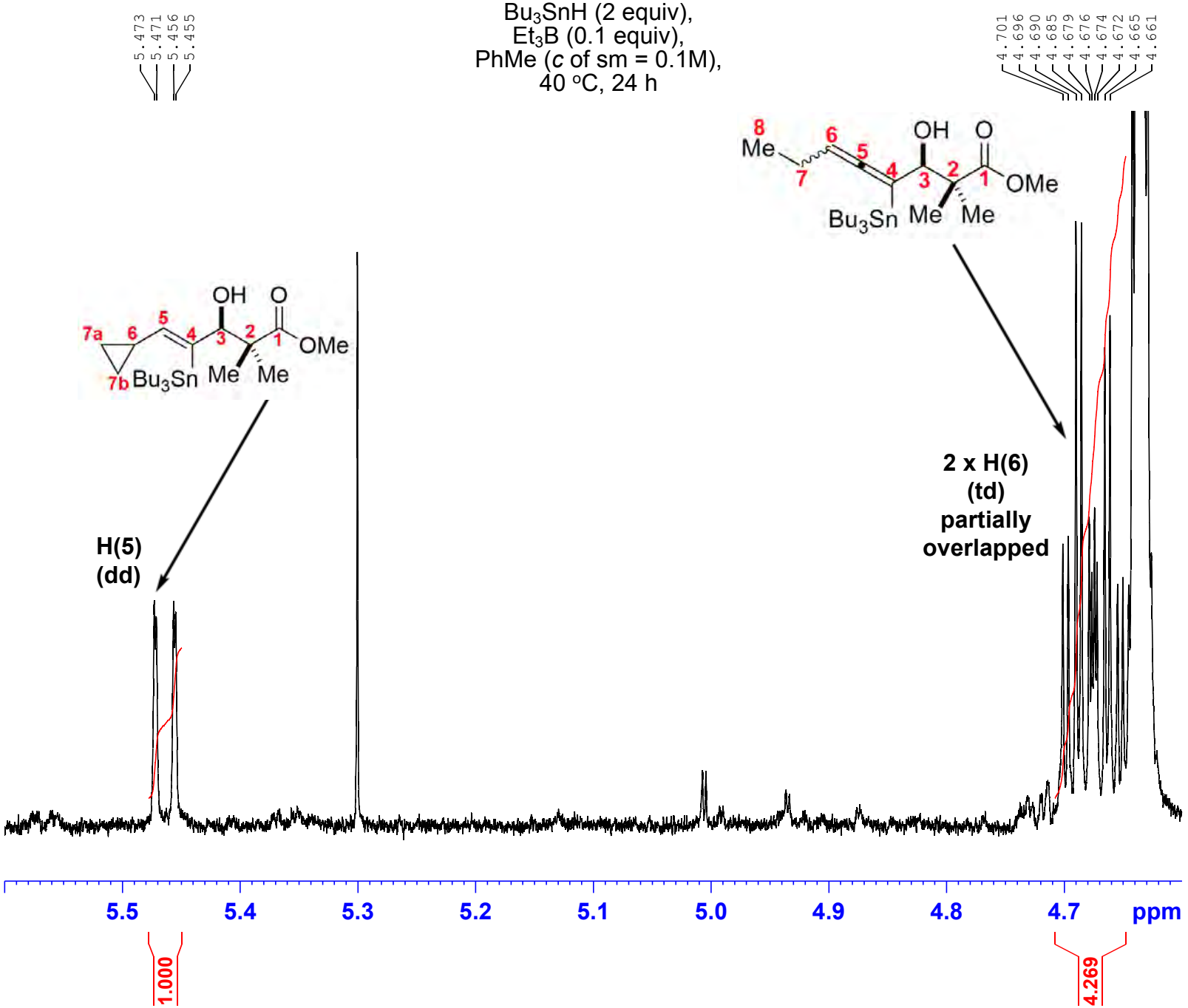

```
Current Data Parameters
NAME       HAW-VII-049-C
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20191114
Time_             23.14
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD               180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300134 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-030
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
40 °C, 24 h



BRUKER

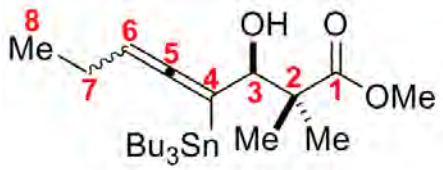
```
Current Data Parameters
NAME       HAW-VII-030-C
EXPNO                 10
PROCNO                 1

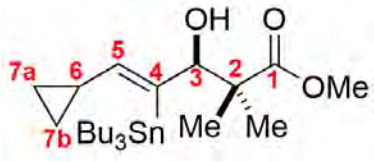
F2 - Acquisition Parameters
Date_           20191031
Time_              15.11
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ            4.9999318 sec
RG                 97.5
DW               27.733 usec
DE                7.60 usec
TE                298.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                1H
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300137 MHz
WDW                 EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-030
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
40 °C, 24 h

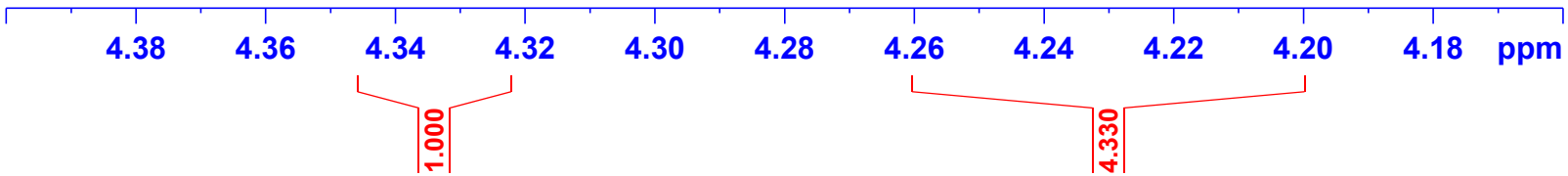




H(3)
(dd)

2 x H(3)
(dd)
partially
overlapped

4.339 4.338 4.332 4.330 4.248 4.243 4.235 4.230 4.227 4.223 4.214 4.209

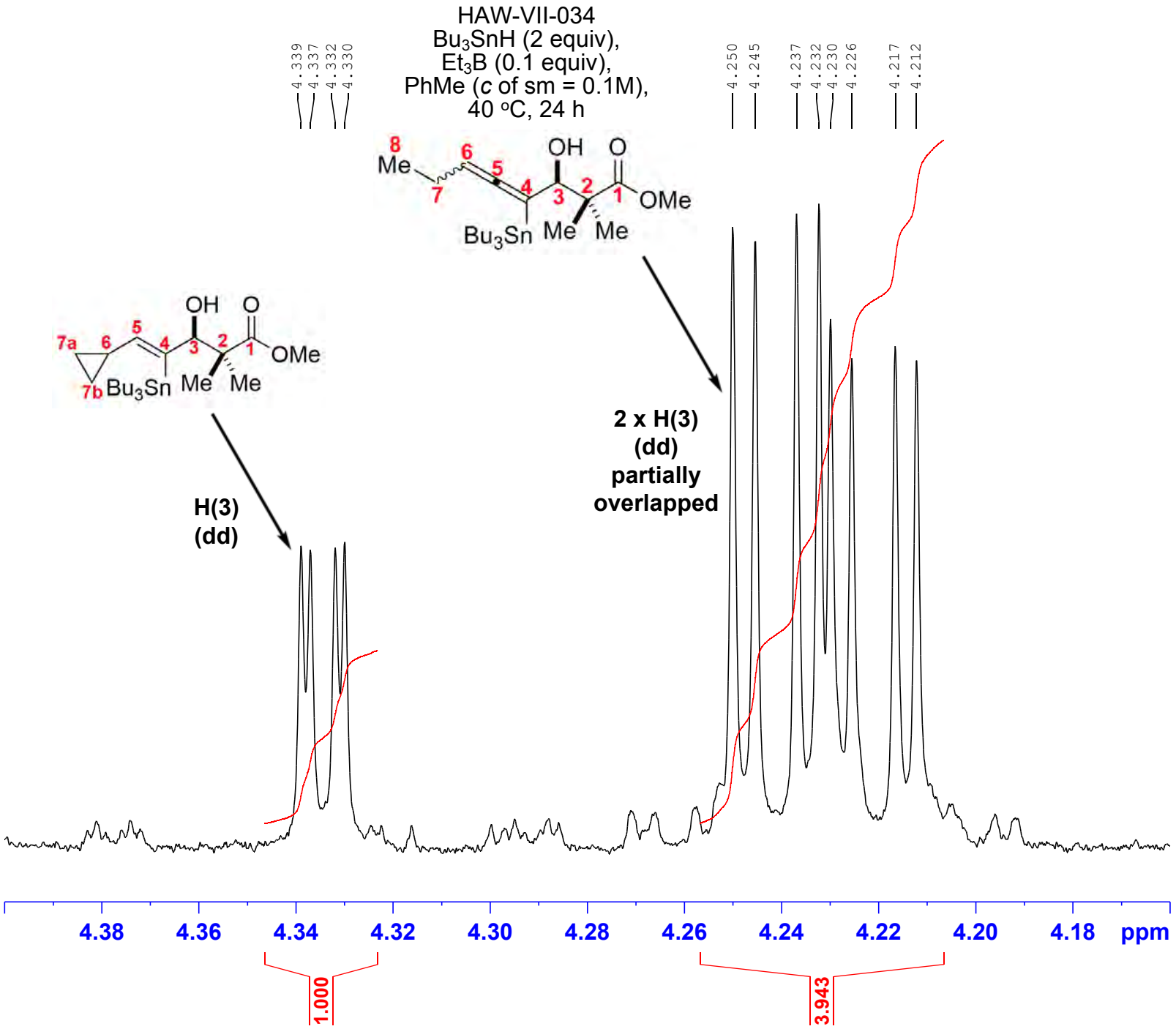



```
Current Data Parameters
NAME       HAW-VII-030-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191031
Time_              15.11
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                298.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300137 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```



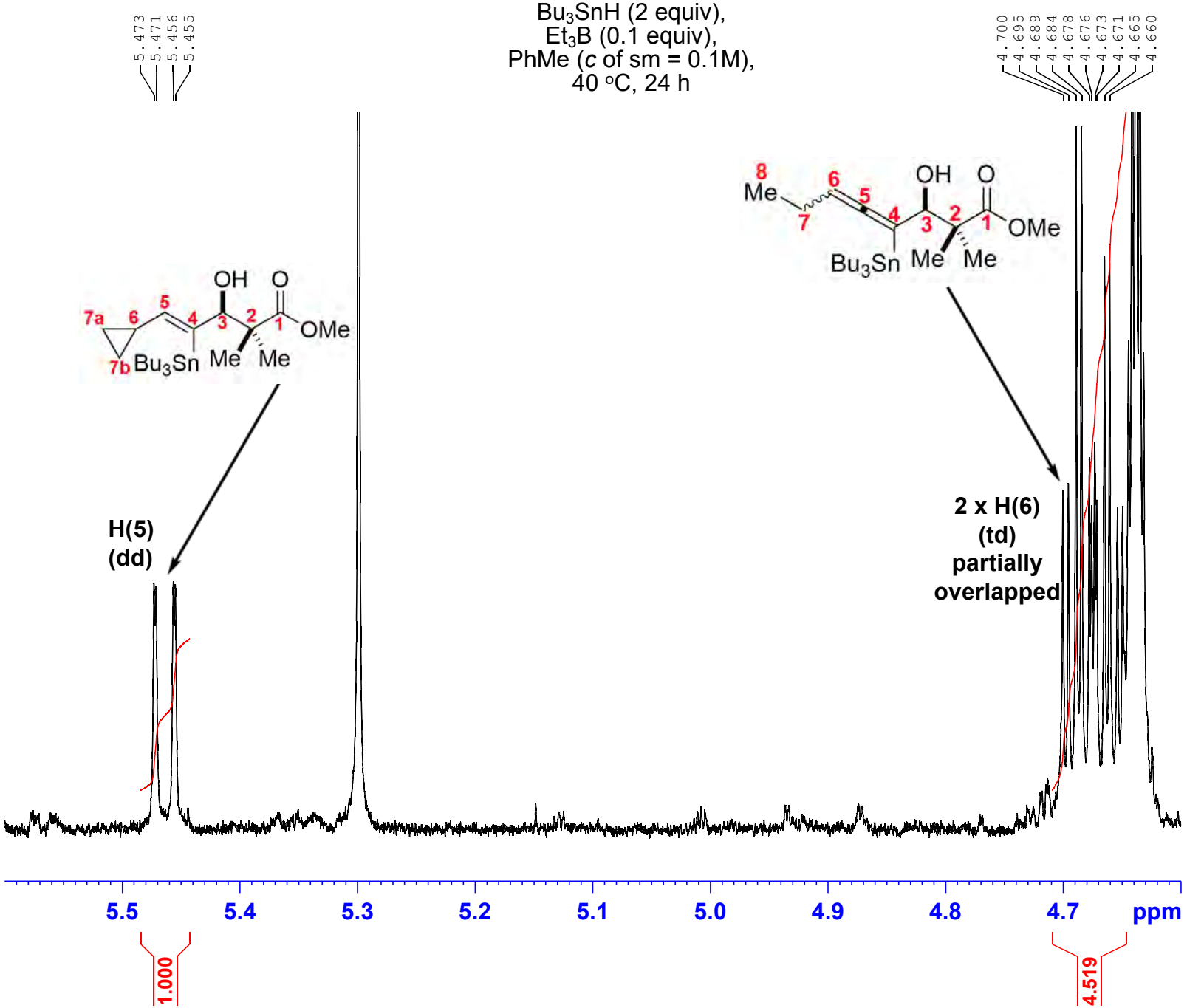

```
Current Data Parameters
NAME       HAW-VII-034-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191105
Time_             16.58
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH          18028.846 Hz
FIDRES        0.100001 Hz
AQ            4.9999318 sec
RG                97.5
DW               27.733 usec
DE                7.60 usec
TE               300.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1337060 MHz
NUC1                1H
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300129 MHz
WDW                 EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-036
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
40 °C, 24 h



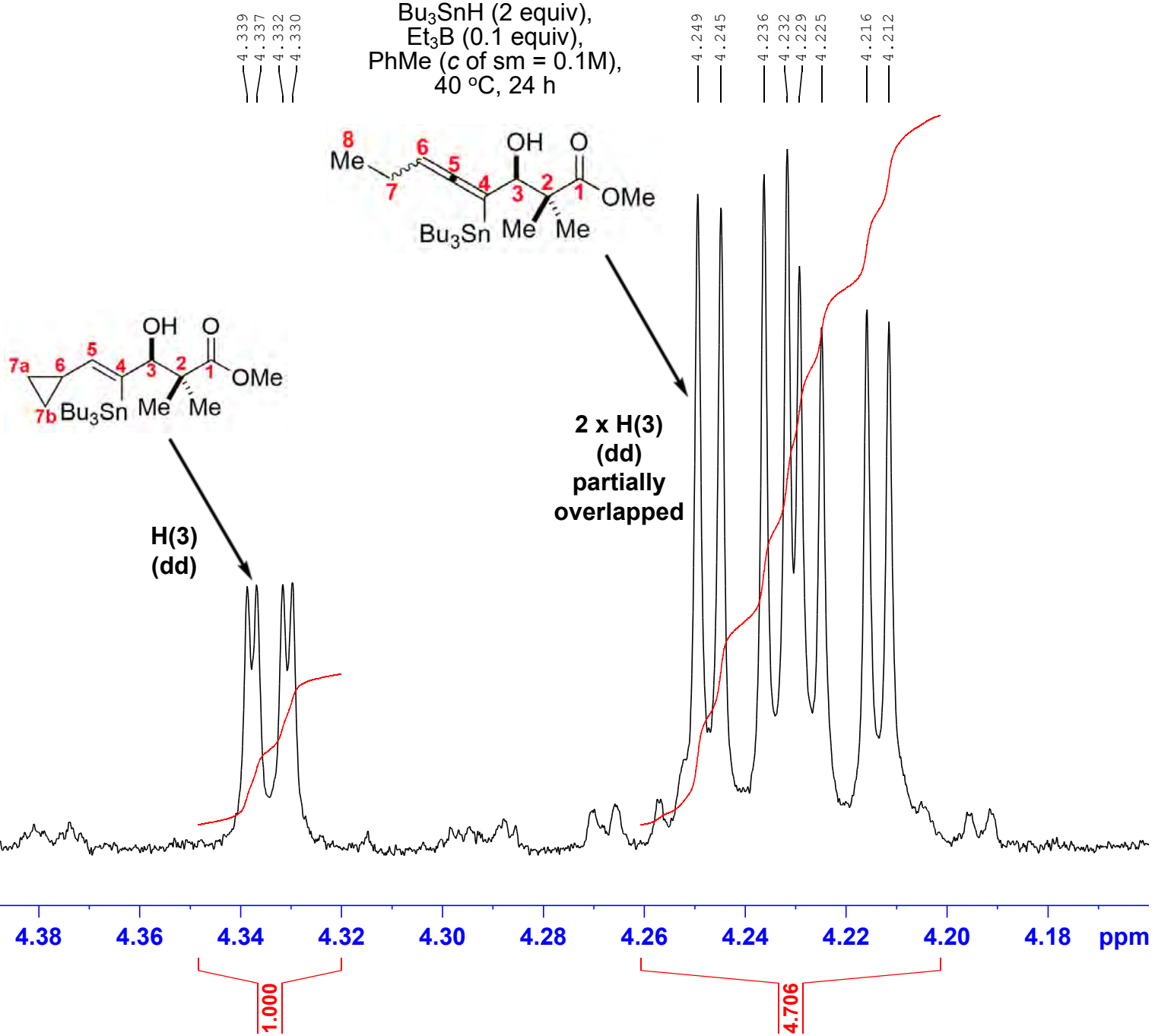

```
Current Data Parameters
NAME       HAW-VII-036-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191107
Time_             20.29
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                97.5
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                 1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300136 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-036
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
40 °C, 24 h



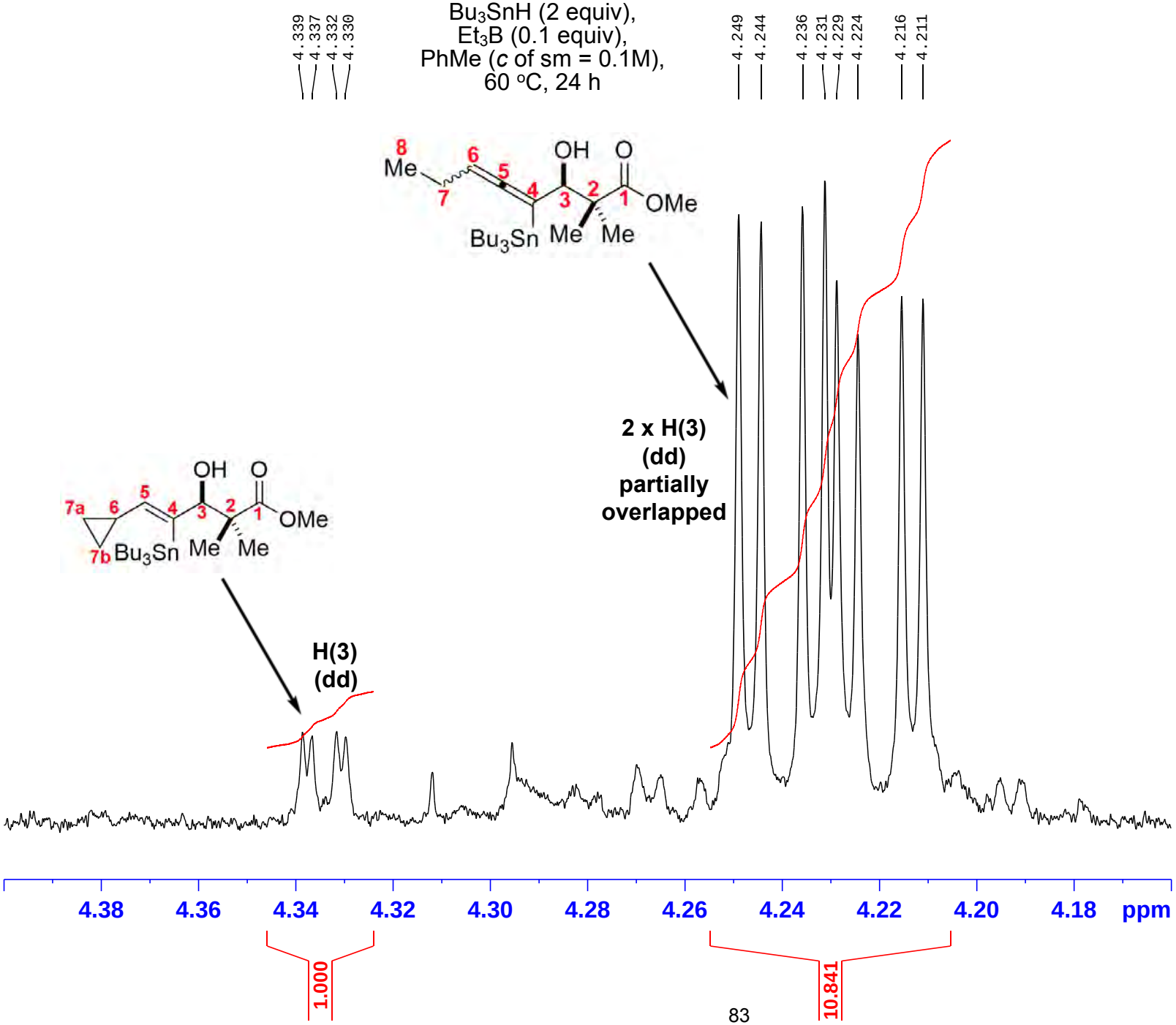

```
Current Data Parameters
NAME       HAW-VII-036-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191107
Time_             20.29
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                97.5
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                 1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300136 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-IV-029
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
60 °C, 24 h



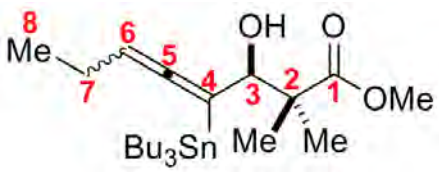

```
Current Data Parameters
NAME        HAW-IV-029-C
EXPNO                 20
PROCNO                 1

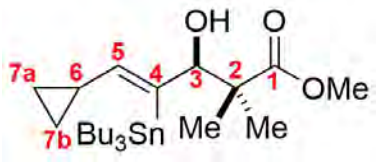
F2 - Acquisition Parameters
Date_           20180629
Time                1.26
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ            4.9999318 sec
RG                 97.5
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1337060 MHz
NUC1                   1H
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300152 MHz
WDW                   EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-029
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
60 °C, 24 h

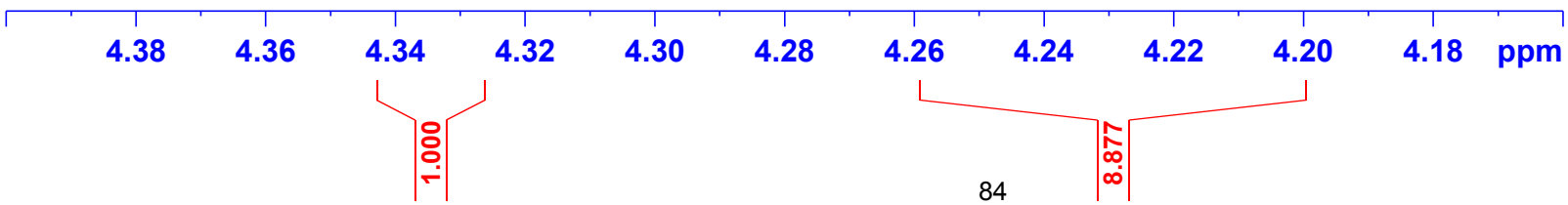




H(3)
(dd)

2 x H(3)
(dd)
partially
overlapped

4.339 4.337 4.332 4.330 4.248 4.244 4.235 4.230 4.227 4.223 4.214 4.210



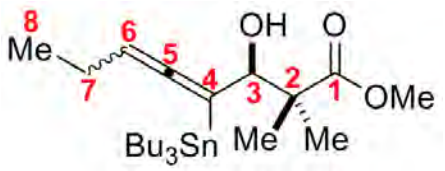

```
Current Data Parameters
NAME       HAW-VII-029-C
EXPNO                 10
PROCNO                 1

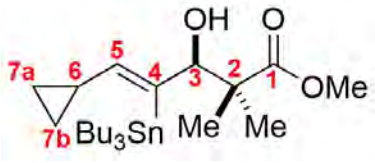
F2 - Acquisition Parameters
Date_           20191031
Time_              15.03
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                298.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300137 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-033
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
60 °C, 24 h

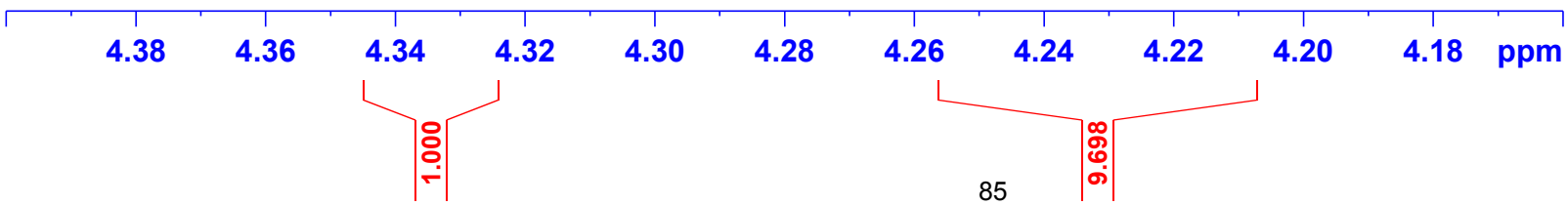




2 x H(3) (dd) partially overlapped

H(3) (dd)

4.339 4.337 4.332 4.330 4.250 4.245 4.237 4.232 4.230 4.225 4.216 4.212



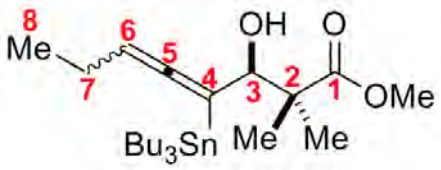

```
Current Data Parameters
NAME       HAW-VII-033-C
EXPNO                 10
PROCNO                 1

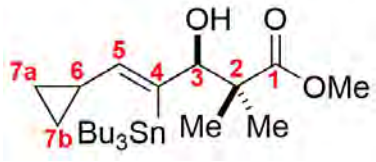
F2 - Acquisition Parameters
Date_           20191105
Time_             16.50
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                97.5
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                 1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300140 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-035
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
60 °C, 24 h





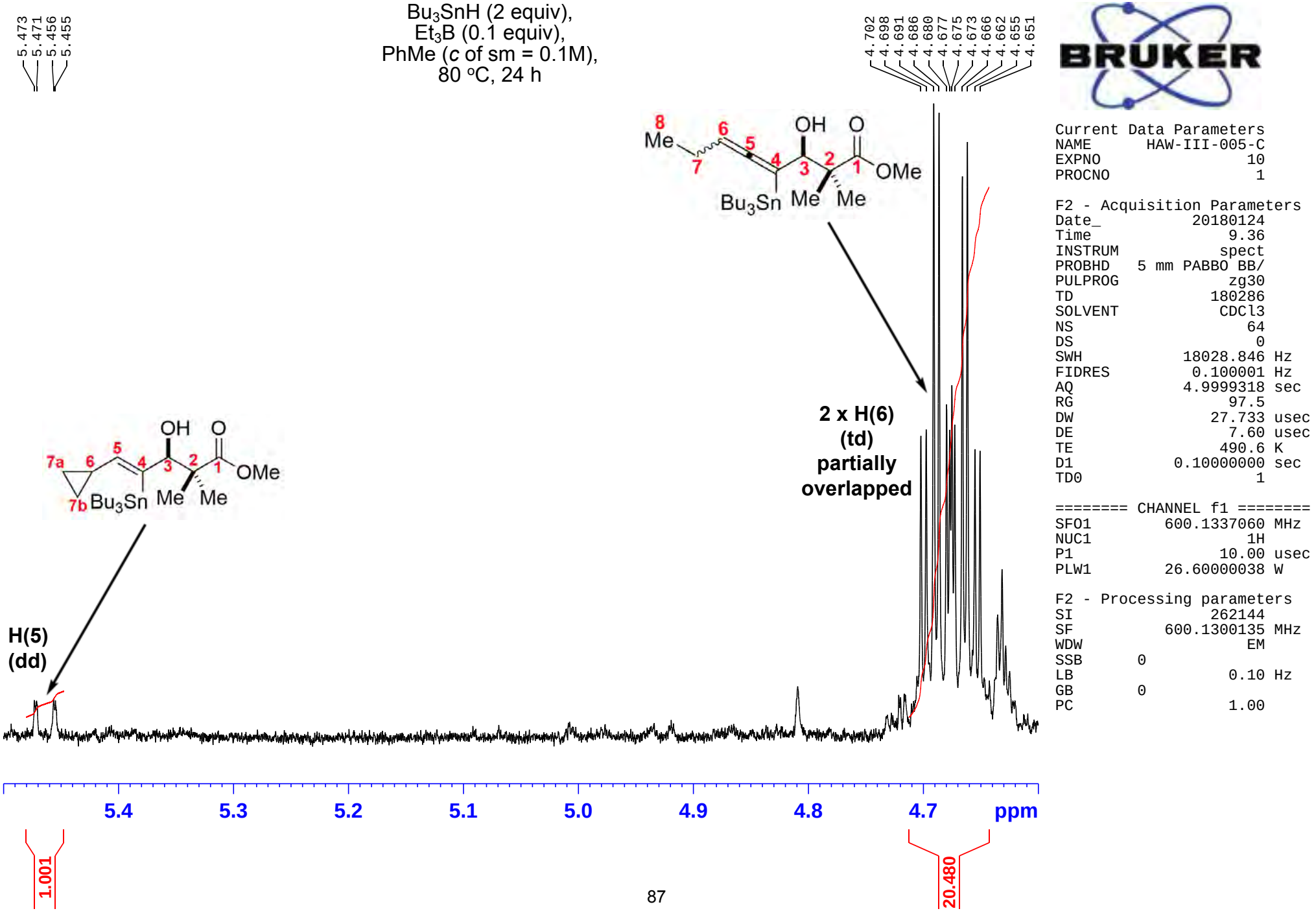

```
Current Data Parameters
NAME       HAW-VII-035-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191108
Time_               9.32
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300131 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-III-005
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
80 °C, 24 h



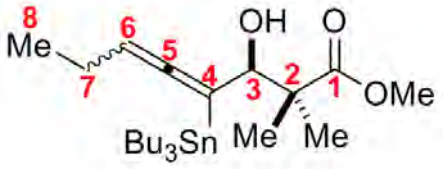

```
Current Data Parameters
NAME       HAW-III-005-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180124
Time                9.36
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ            4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                490.6 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300135 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-III-005
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
80 °C, 24 h



4.340 4.338 4.333 4.331

4.246 4.242 4.233 4.228 4.224 4.220 4.211 4.207

2 x H(3) (dd) partially overlapped

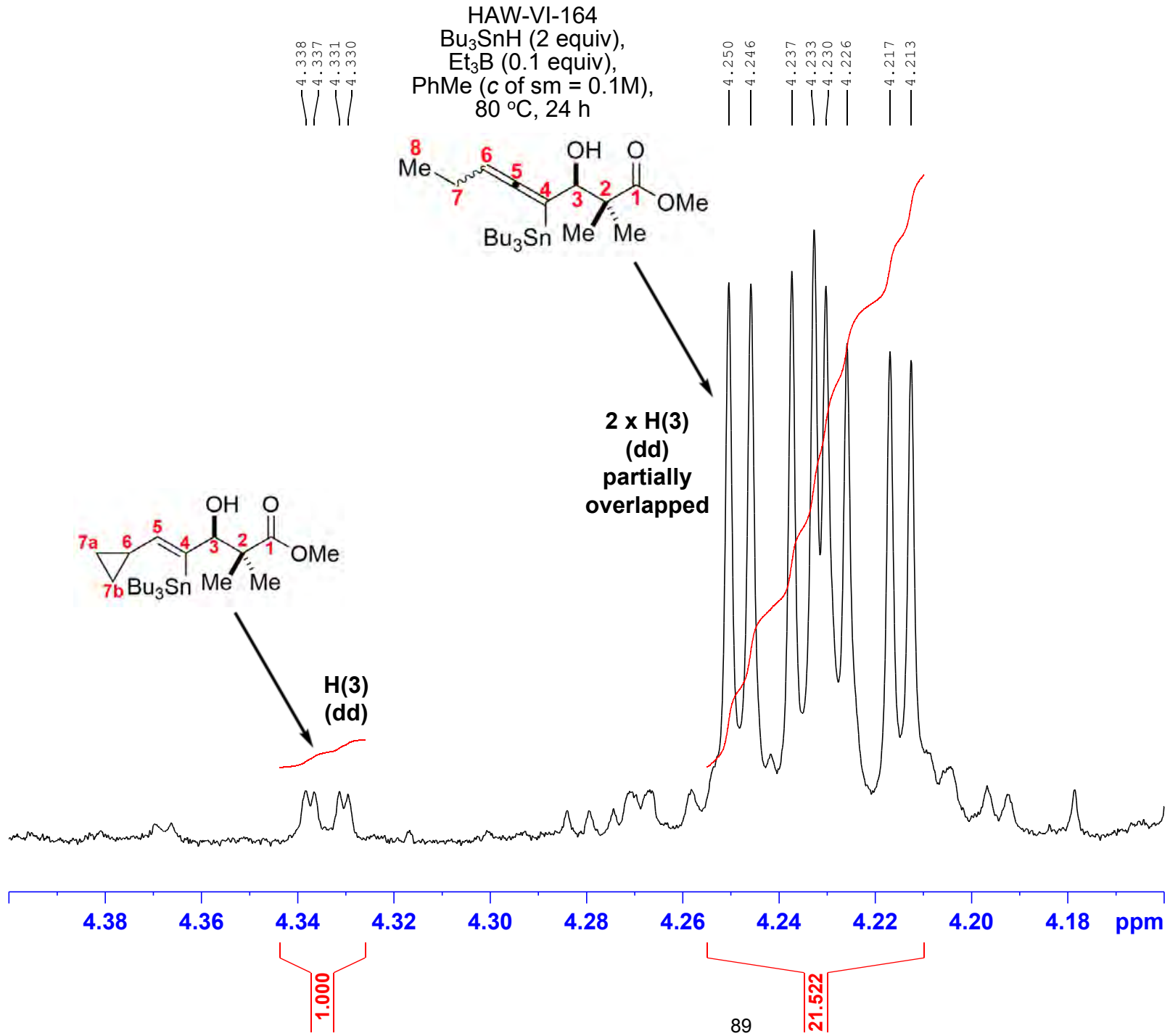
H(3) (dd)


```
Current Data Parameters
NAME       HAW-III-005-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180124
Time               9.36
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD               180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                490.6 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1337060 MHz
NUC1                1H
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300135 MHz
WDW                 EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```



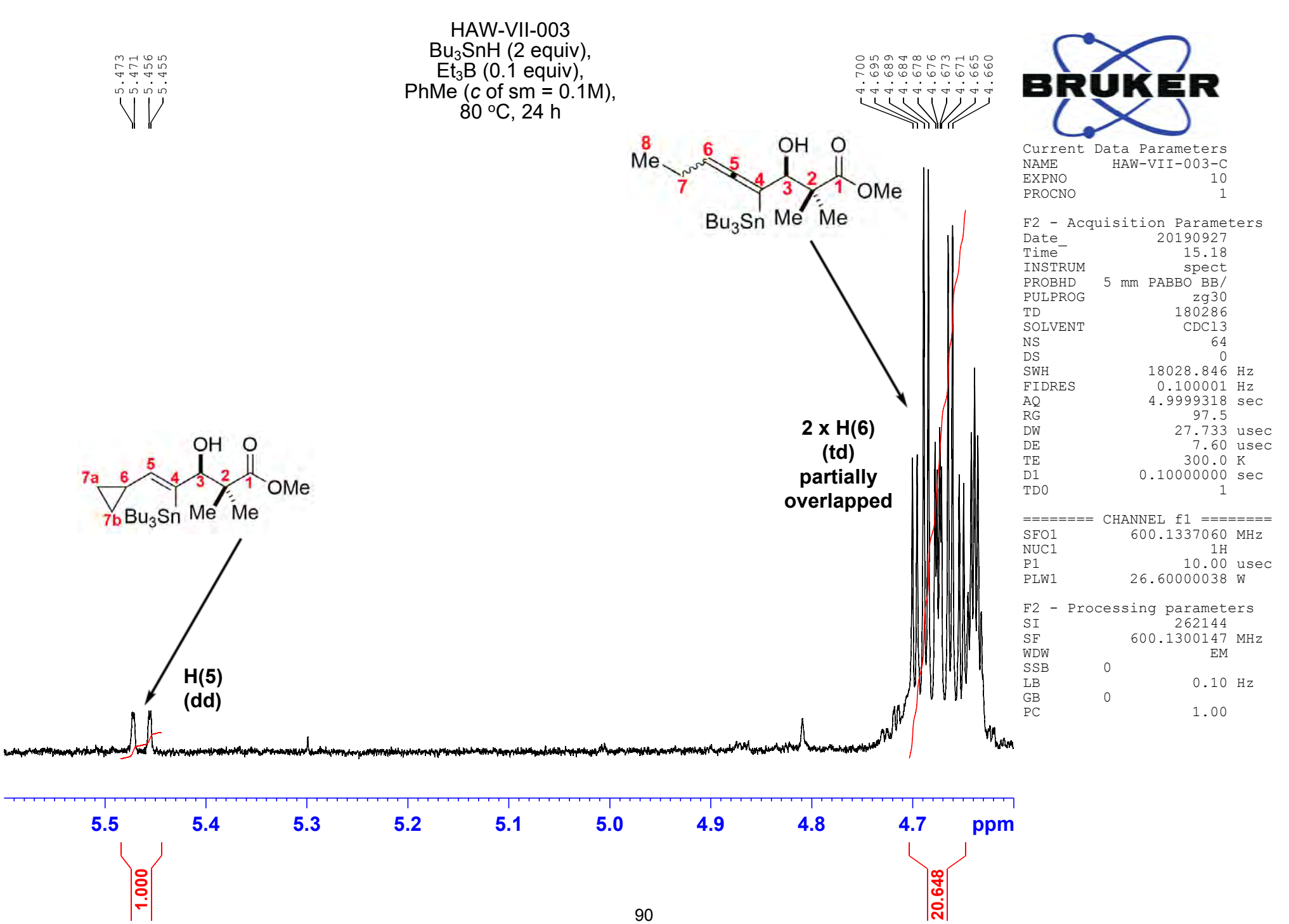

```
Current Data Parameters
NAME        HAW-VI-164-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190905
Time_             16.08
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD              180286
SOLVENT           CDCl3
NS                   64
DS                    0
SWH          18028.846 Hz
FIDRES        0.100001 Hz
AQ            4.9999318 sec
RG                97.5
DW               27.733 usec
DE                7.60 usec
TE               300.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1337060 MHz
NUC1                1H
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300137 MHz
WDW                 EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-003
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
80 °C, 24 h



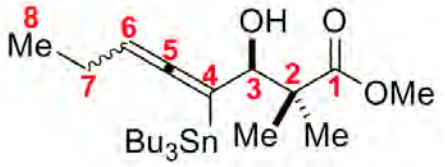

```
Current Data Parameters
NAME       HAW-VII-003-C
EXPNO                 10
PROCNO                 1

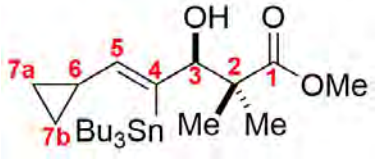
F2 - Acquisition Parameters
Date_           20190927
Time_              15.18
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                1H
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300147 MHz
WDW                 EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-003
Bu_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
80 °C, 24 h





4.339 4.337 4.332 4.330

4.250 4.245 4.237 4.232 4.229 4.225 4.216 4.212

2 x H(3) (dd) partially overlapped

H(3) (dd)

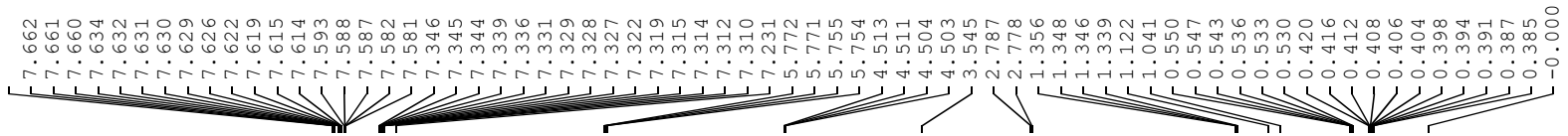

```
Current Data Parameters
NAME       HAW-VII-003-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190927
Time_              15.18
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD               180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

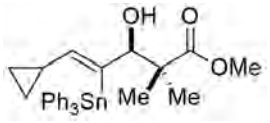
======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300147 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

Part D. The 600.13 MHz ^{1}H NMR and 150.90 MHz ^{13}C NMR Spectra of the Triphenylstannylvinyltin 5b and Triphenylstannylallene 4b in $CDCl_3$



Hamish Watson
HAW-V-044
Proton
Ref: 0.00ppm ($CDCl_3$-TMS)

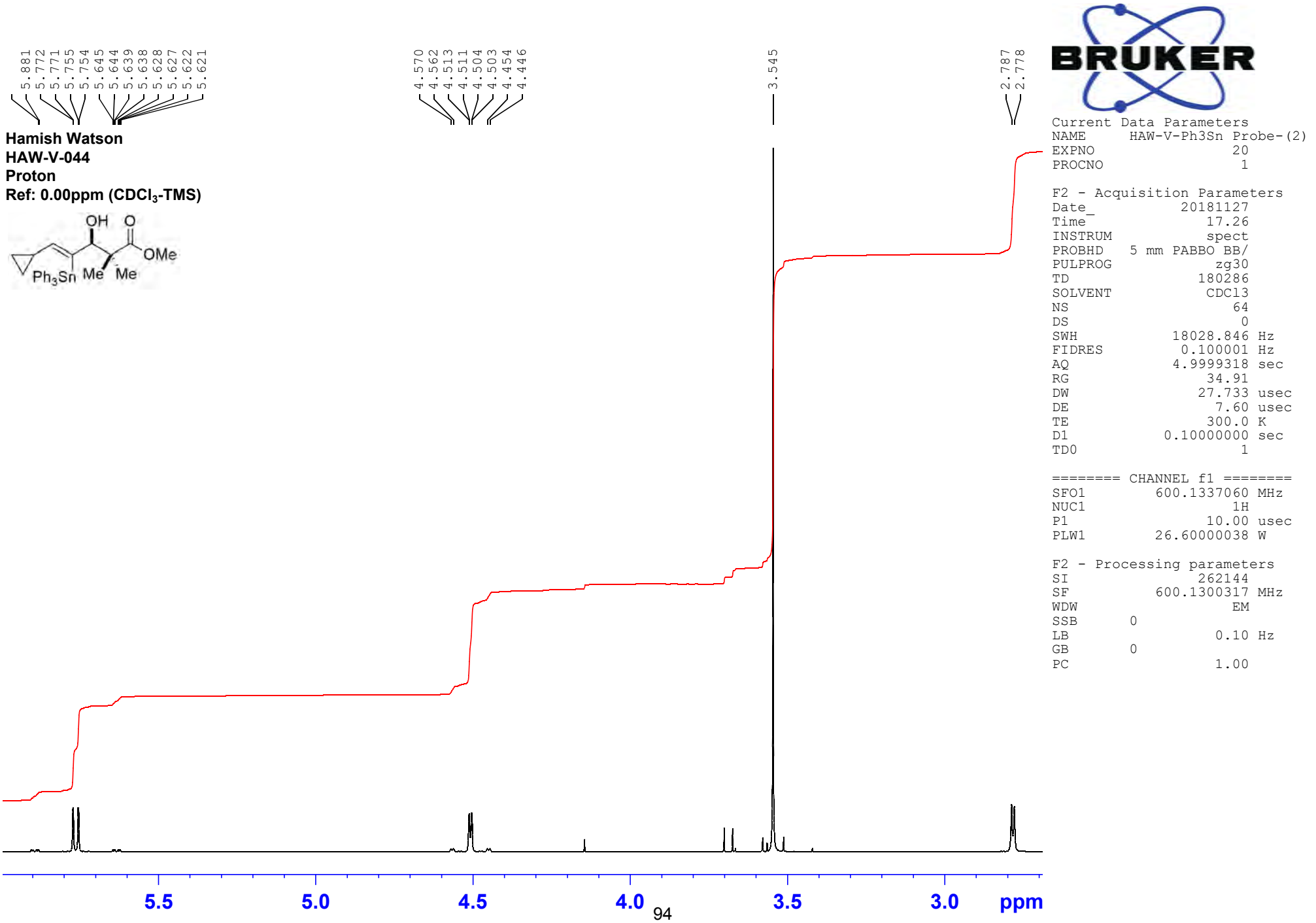



```
Current Data Parameters
NAME      HAW-V-Ph3Sn Probe-(2)
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_           20181127
Time                17.26
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                     64
DS                      0
SWH            18028.846 Hz
FIDRES          0.100001 Hz
AQ             4.9999318 sec
RG                  34.91
DW                 27.733 usec
DE                  7.60 usec
TE                 300.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300317 MHz
WDW                 EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```



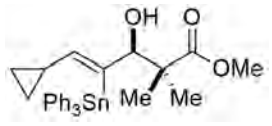

```
Current Data Parameters
NAME      HAW-V-Ph3Sn Probe-(2)
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_           20181127
Time                17.26
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                     64
DS                      0
SWH            18028.846 Hz
FIDRES          0.100001 Hz
AQ             4.9999318 sec
RG                  34.91
DW                 27.733 usec
DE                  7.60 usec
TE                 300.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                  10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300317 MHz
WDW                    EM
SSB       0
LB                  0.10 Hz
GB        0
PC                  1.00
```

Hamish Watson
HAW-V-044
Carbon
Ref: 77.00ppm ($CDCl_3$-TMS)



177.845
150.458
150.390
150.322
142.501
142.424
140.772
139.120
139.043
137.810
137.258
137.131
137.004
128.548
128.511
128.474
128.418
128.412
128.247
128.084
128.076
82.736
82.646
82.556
77.211
77.000
76.788
51.794
48.272
22.859
20.831
16.447
16.281
16.117
8.139
7.999


```
Current Data Parameters
NAME      HAW-V-Ph3Sn Probe-(2)
EXPNO                   21
PROCNO                   1

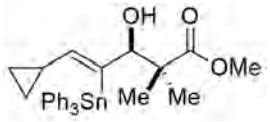
F2 - Acquisition Parameters
Date_             20181127
Time                 18.12
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                119044
SOLVENT             CDC13
NS                   1024
DS                      4
SWH              37500.000 Hz
FIDRES           0.315010 Hz
AQ               1.5872533 sec
RG                  186.92
DW                  13.333 usec
DE                    7.73 usec
TE                   300.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         150.9194058 MHz
NUC1                 13C
P1                 11.80 usec
PLW1         85.00000000 W

======== CHANNEL f2 ========
SFO2         600.1324005 MHz
NUC2                 1H
CPDPRG[2          waltz64
PCPD2              80.00 usec
PLW2         27.00000000 W
PLW12         0.43891999 W
PLW13         0.28090999 W

F2 - Processing parameters
SI                  131072
SF           150.9028187 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

Hamish Watson
HAW-V-044
Dept135
Ref: 77.00ppm ($CDCl_3$-TMS)



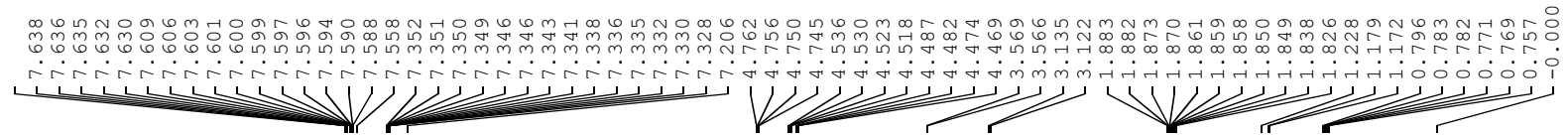

```
Current Data Parameters
NAME      HAW-V-Ph3Sn Probe-(2)
EXPNO                       22
PROCNO                       1

F2 - Acquisition Parameters
Date_             20181127
Time                 22.27
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG      deptsp135.b
TD                 119044
SOLVENT              CDCl3
NS                     256
DS                       4
SWH              35714.285 Hz
FIDRES           0.300009 Hz
AQ               1.6666160 sec
RG                  186.92
DW                  14.000 usec
DE                    7.44 usec
TE                   300.0 K
CNST2          145.0000000
D1              1.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                      1

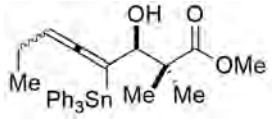
======== CHANNEL f1 ========
SFO1           150.9178962 MHz
NUC1                   13C
P1                   11.80 usec
P13                2000.00 usec
PLW0      0 W
PLW1           85.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5               0.500
SPOFFS5   0 Hz
SPW5           18.08300018 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                   1H
CPDPRG[2           waltz64
P3                   10.20 usec
P4                   20.40 usec
PCPD2                80.00 usec
PLW2           27.00000000 W
PLW12           0.43891999 W

F2 - Processing parameters
SI                   131072
SF             150.9028188 MHz
WDW                    EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```



Hamish Watson
HAW-V-043
Proton
Ref: 0.00ppm ($CDCl_3$-TMS)

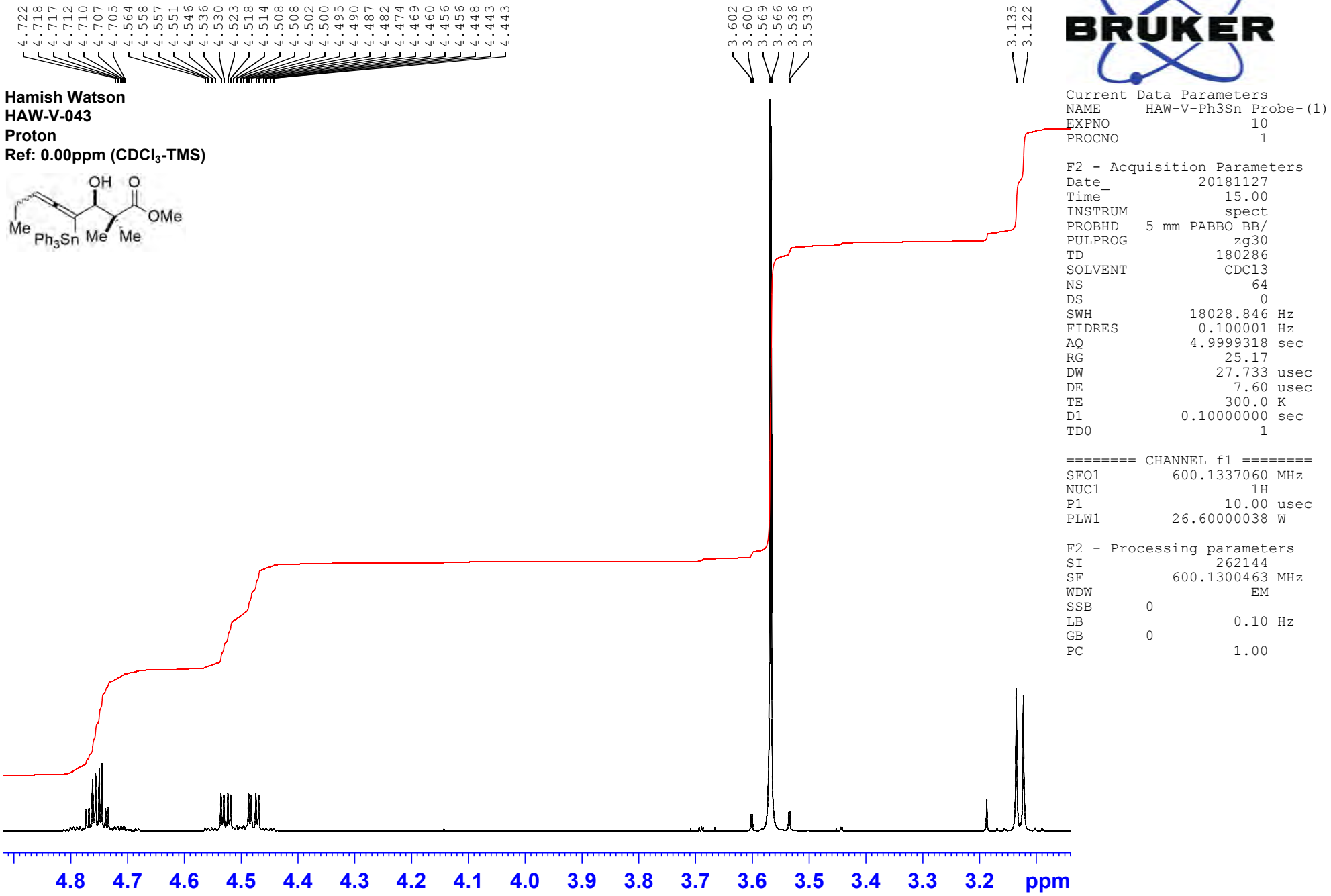



```
Current Data Parameters
NAME      HAW-V-Ph3Sn Probe-(1)
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20181127
Time                 15.00
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                 180286
SOLVENT             CDCl3
NS                     64
DS                      0
SWH            18028.846 Hz
FIDRES          0.100001 Hz
AQ              4.9999318 sec
RG                  25.17
DW                 27.733 usec
DE                  7.60 usec
TE                 300.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300463 MHz
WDW                   EM
SSB       0
LB                  0.10 Hz
GB        0
PC                  1.00
```

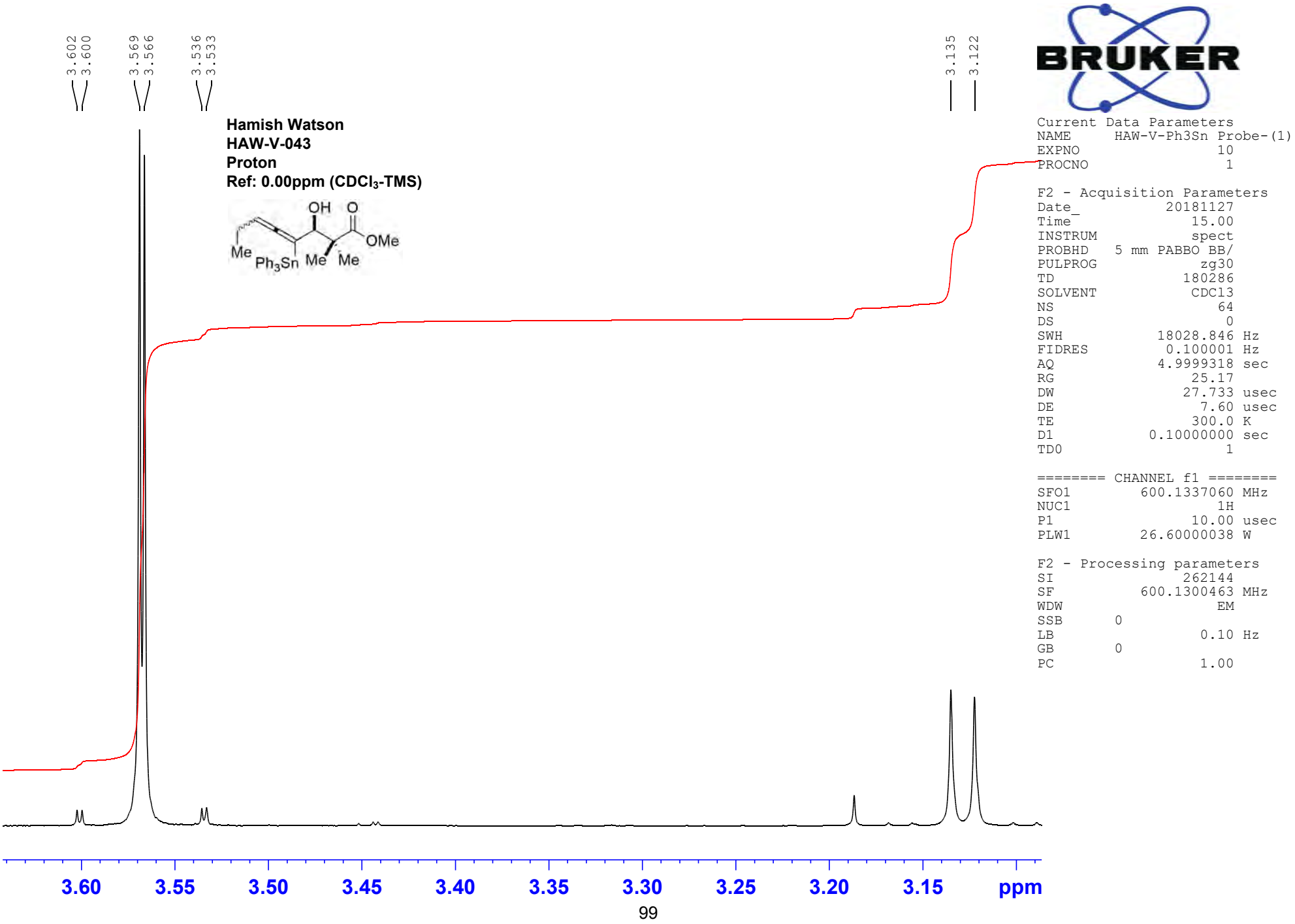



```
Current Data Parameters
NAME      HAW-V-Ph3Sn Probe-(1)
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_           20181127
Time                15.00
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                     64
DS                      0
SWH             18028.846 Hz
FIDRES          0.100001 Hz
AQ              4.9999318 sec
RG                  25.17
DW                 27.733 usec
DE                  7.60 usec
TE                 300.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                  10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300463 MHz
WDW                    EM
SSB       0
LB                  0.10 Hz
GB        0
PC                  1.00
```

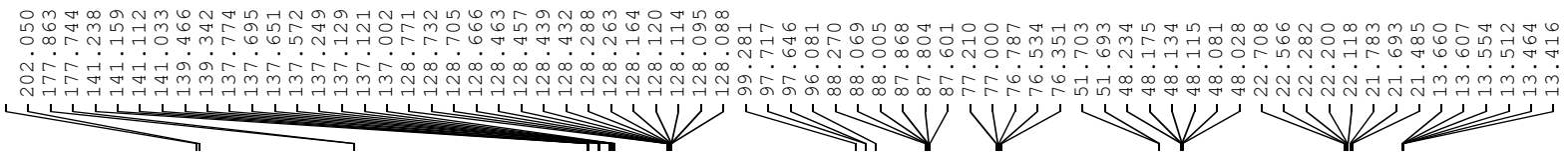



```
Current Data Parameters
NAME      HAW-V-Ph3Sn Probe-(1)
EXPNO                   10
PROCNO                   1

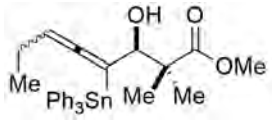
F2 - Acquisition Parameters
Date_           20181127
Time                15.00
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                     64
DS                      0
SWH             18028.846 Hz
FIDRES          0.100001 Hz
AQ              4.9999318 sec
RG                  25.17
DW                 27.733 usec
DE                  7.60 usec
TE                 300.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                  10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                 262144
SF           600.1300463 MHz
WDW                    EM
SSB       0
LB                  0.10 Hz
GB        0
PC                  1.00
```



Hamish Watson
HAW-V-043
Carbon
Ref: 77.00ppm ($CDCl_3$-TMS)




```
Current Data Parameters
NAME      HAW-V-Ph3Sn Probe-(1)
EXPNO                   11
PROCNO                   1

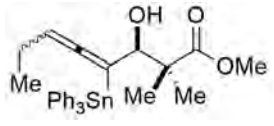
F2 - Acquisition Parameters
Date_             20181127
Time                 15.46
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                119044
SOLVENT             CDC13
NS                   1024
DS                      4
SWH              37500.000 Hz
FIDRES           0.315010 Hz
AQ               1.5872533 sec
RG                  186.92
DW                  13.333 usec
DE                    7.73 usec
TE                   300.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         150.9194058 MHz
NUC1                  13C
P1                  11.80 usec
PLW1         85.00000000 W

======== CHANNEL f2 ========
SFO2         600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz64
PCPD2               80.00 usec
PLW2         27.00000000 W
PLW12         0.43891999 W
PLW13         0.28090999 W

F2 - Processing parameters
SI                  131072
SF           150.9028244 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

Hamish Watson
HAW-V-043
Dept135
Ref: 77.00ppm ($CDCl_3$-TMS)



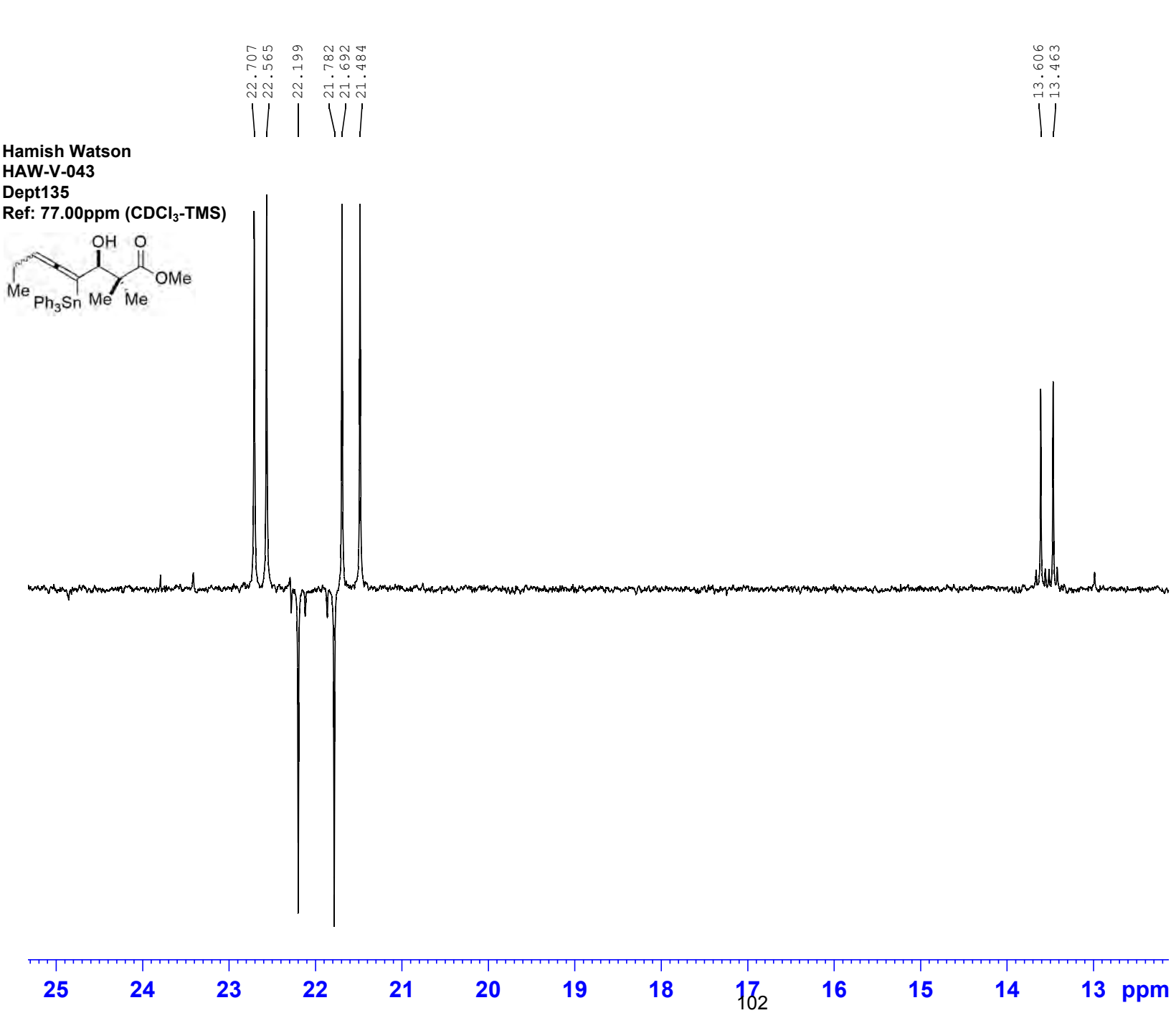
Current Data Parameters
NAME HAW-V-Ph3Sn Probe-(1)
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181127
Time 15.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG deptsp135.b
TD 119044
SOLVENT CDCl3
NS 256
DS 4
SWH 35714.285 Hz
FIDRES 0.300009 Hz
AQ 1.6666160 sec
RG 186.92
DW 14.000 usec
DE 7.44 usec
TE 300.0 K
CNST2 145.0000000
D1 1.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9178962 MHz
NUC1 13C
P1 11.80 usec
P13 2000.00 usec
PLW0 0 W
PLW1 85.00000000 W
SPNAM[5] Crp60comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 18.08300018 W

======== CHANNEL f2 ========
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz64
P3 10.20 usec
P4 20.40 usec
PCPD2 80.00 usec
PLW2 27.00000000 W
PLW12 0.43891999 W

F2 - Processing parameters
SI 131072
SF 150.9028246 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
Current Data Parameters
NAME      HAW-V-Ph3Sn Probe-(1)
EXPNO                       12
PROCNO                       1

F2 - Acquisition Parameters
Date_             20181127
Time                 15.58
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG       deptsp135.b
TD                  119044
SOLVENT              CDCl3
NS                     256
DS                       4
SWH              35714.285 Hz
FIDRES           0.300009 Hz
AQ               1.6666160 sec
RG                  186.92
DW                  14.000 usec
DE                    7.44 usec
TE                   300.0 K
CNST2          145.0000000
D1              1.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                      1

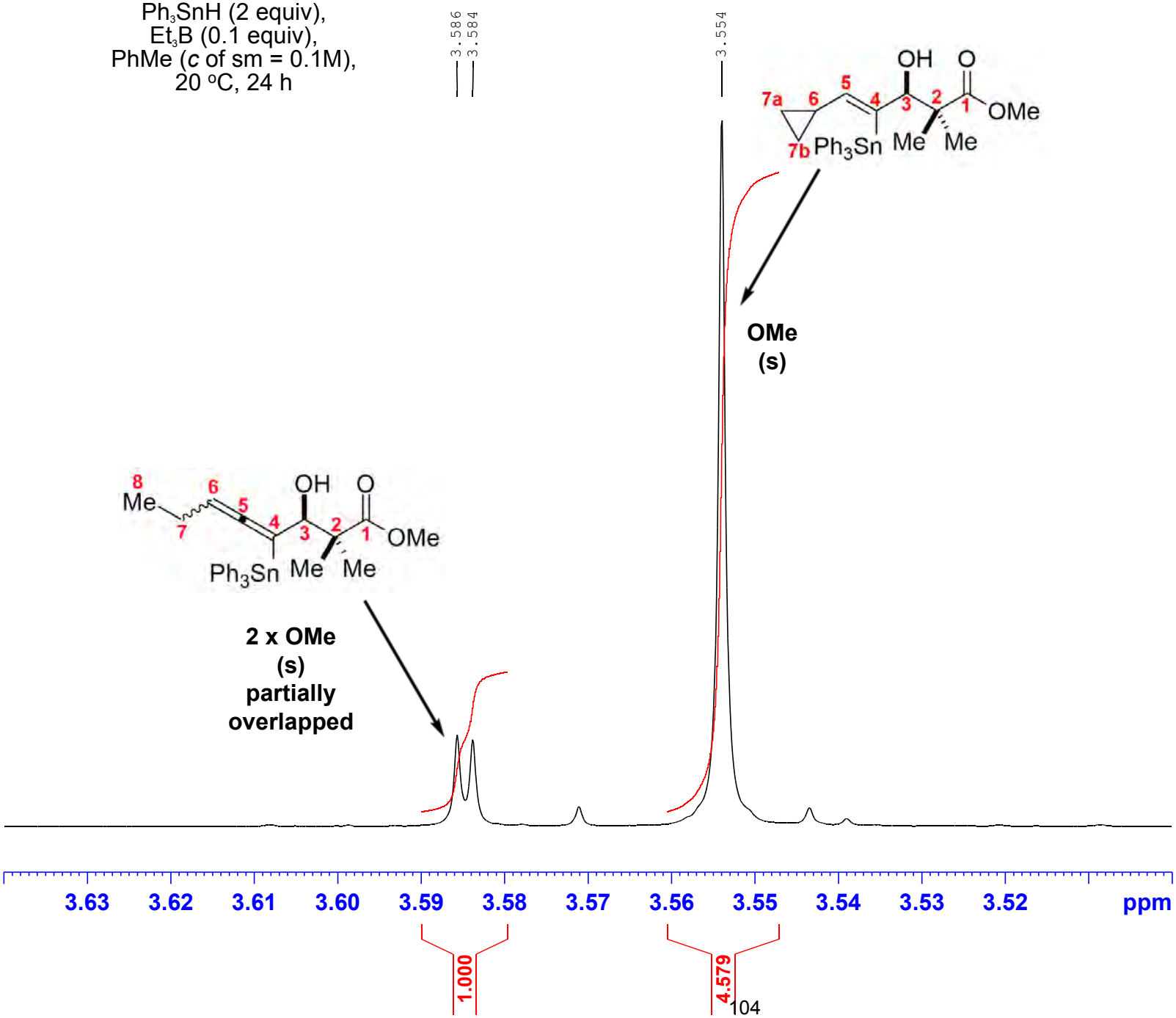
======== CHANNEL f1 ========
SFO1           150.9178962 MHz
NUC1                    13C
P1                    11.80 usec
P13                2000.00 usec
PLW0       0 W
PLW1           85.00000000 W
SPNAM[5]       Crp60comp.4
SPOAL5               0.500
SPOFFS5    0 Hz
SPW5           18.08300018 W

======== CHANNEL f2 ========
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2           waltz64
P3                    10.20 usec
P4                    20.40 usec
PCPD2                 80.00 usec
PLW2           27.00000000 W
PLW12           0.43891999 W

F2 - Processing parameters
SI                   131072
SF             150.9028246 MHz
WDW                     EM
SSB        0
LB                    1.00 Hz
GB         0
PC                    1.40
```

Part E. The 600.13 MHz ^{1}H NMR Ratio Determinations For the Triphenylstannylallene 4b and Triphenylstannylvinyltin 5b in $CDCl_3$

HAW-VII-069
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
20 °C, 24 h



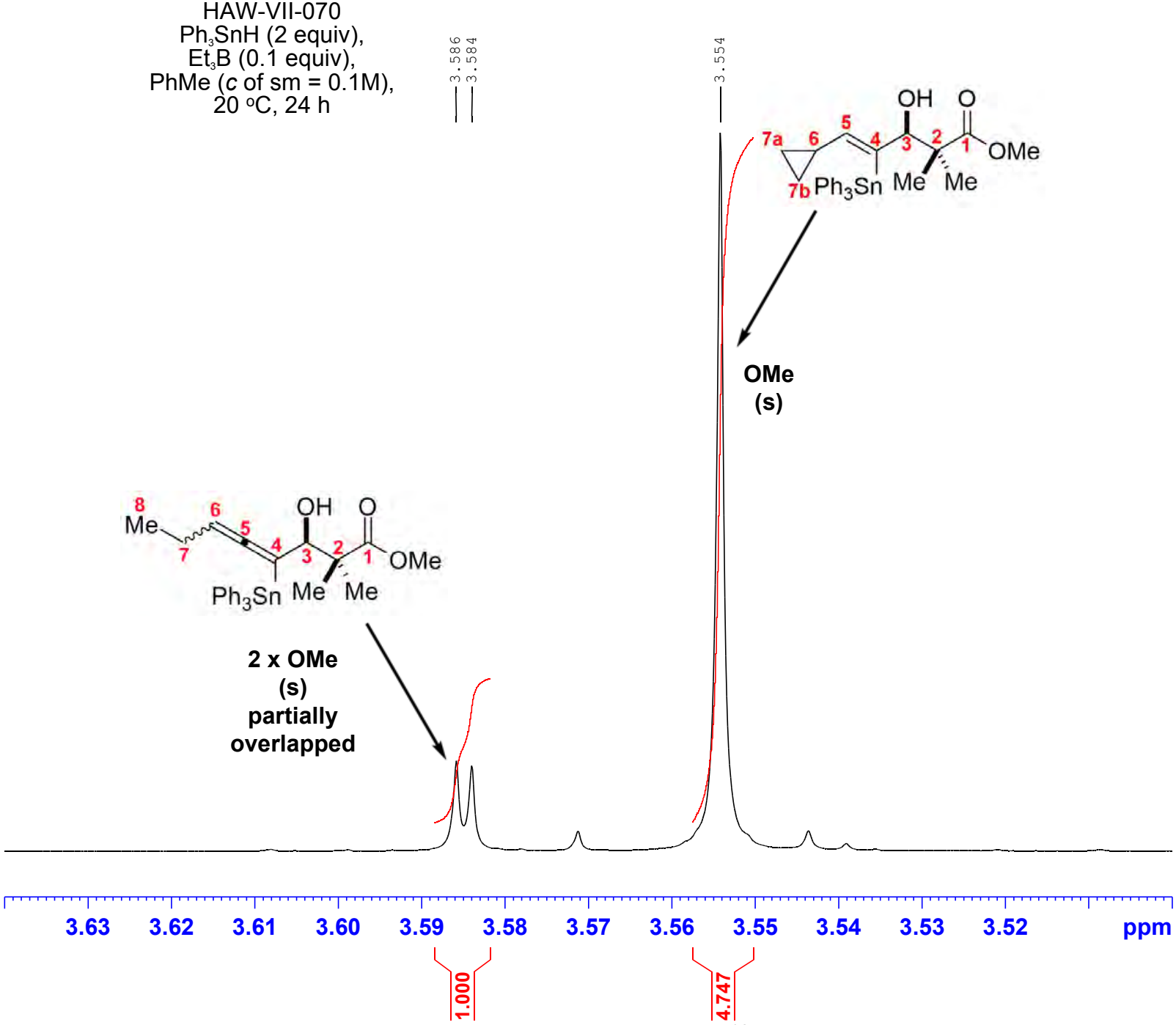

```
Current Data Parameters
NAME       HAW-VII-069-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time_               4.07
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300218 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-070
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
20 °C, 24 h



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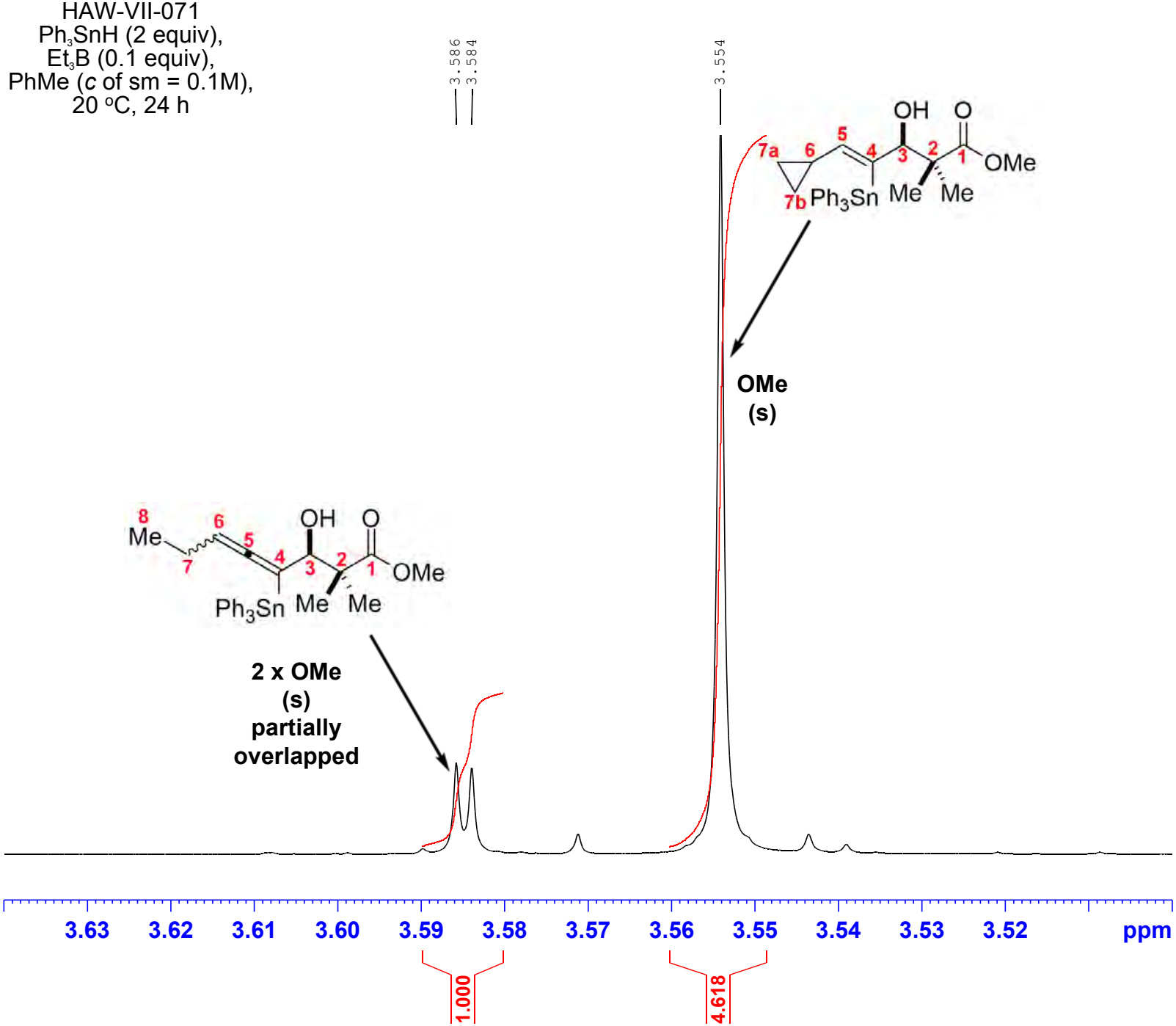
```
Current Data Parameters
NAME       HAW-VII-070-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time                4.15
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                     64
DS                      0
SWH            18028.846 Hz
FIDRES          0.100001 Hz
AQ              4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300214 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-071
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
20 °C, 24 h



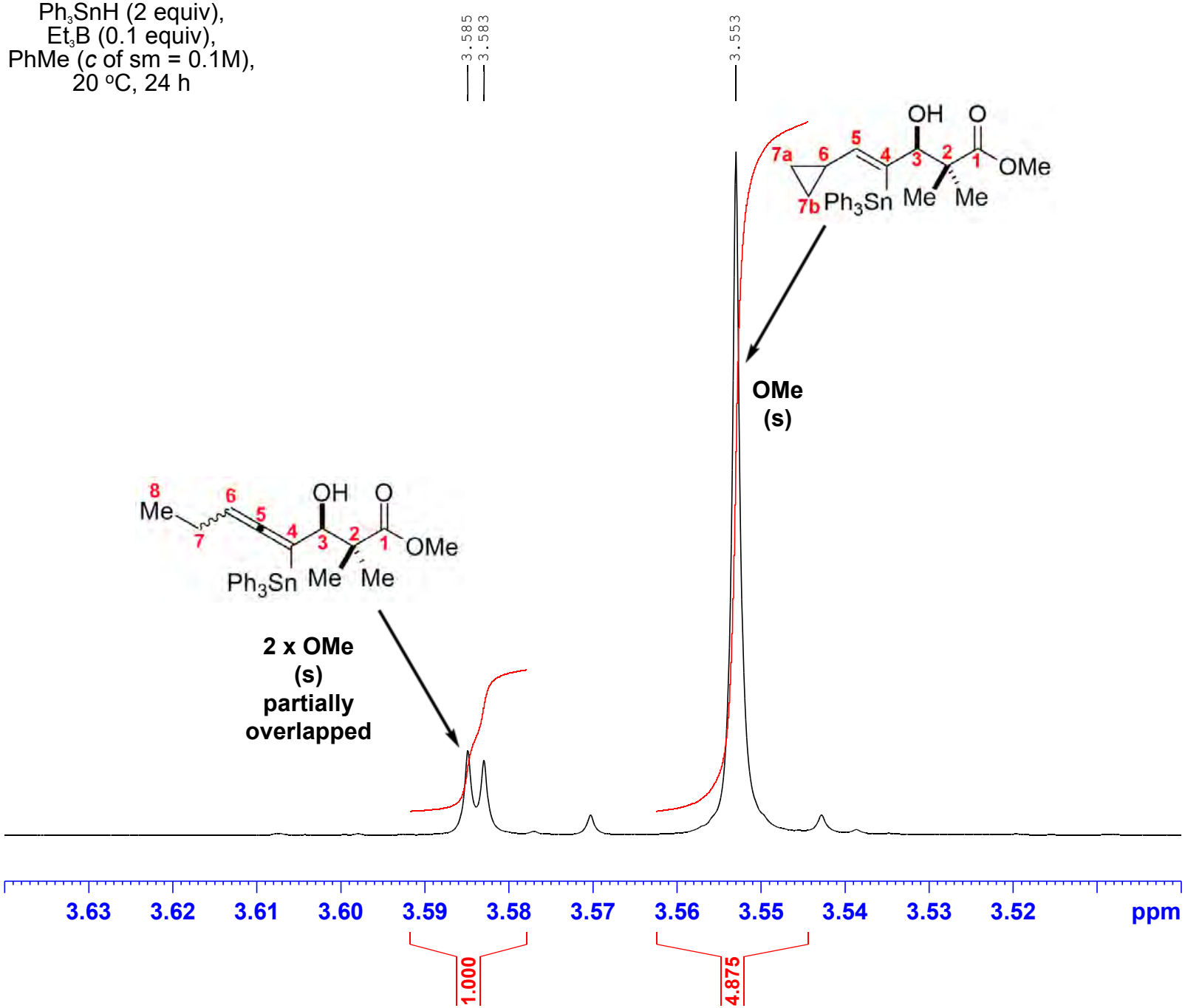

```
Current Data Parameters
NAME       HAW-VII-071-C
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time_               4.23
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300215 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-072
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
20 °C, 24 h



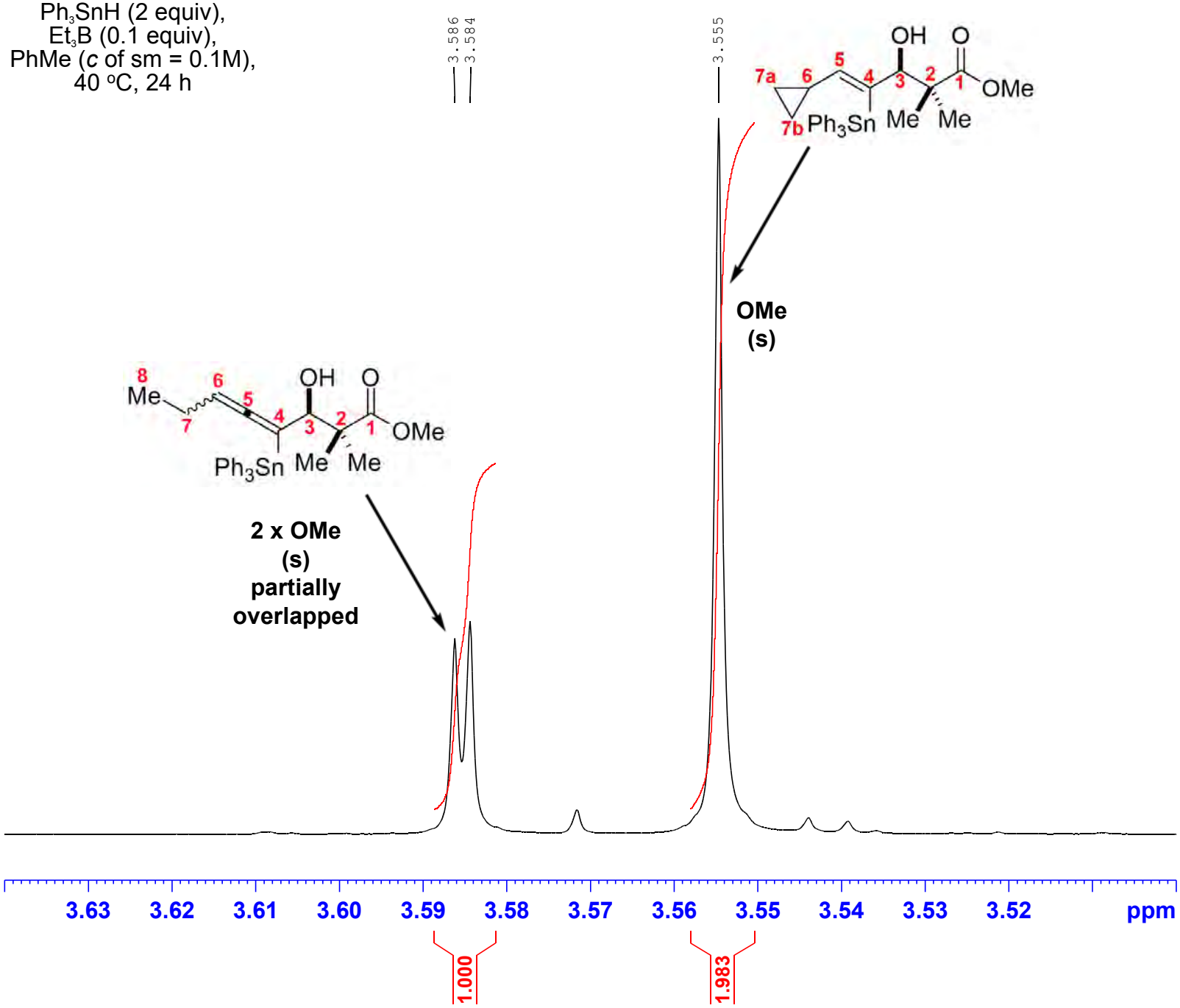

```
Current Data Parameters
NAME       HAW-VII-072-C
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time_               4.32
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                    68
DW               27.733 usec
DE                7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300236 MHz
WDW                   EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-061
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
40 °C, 24 h



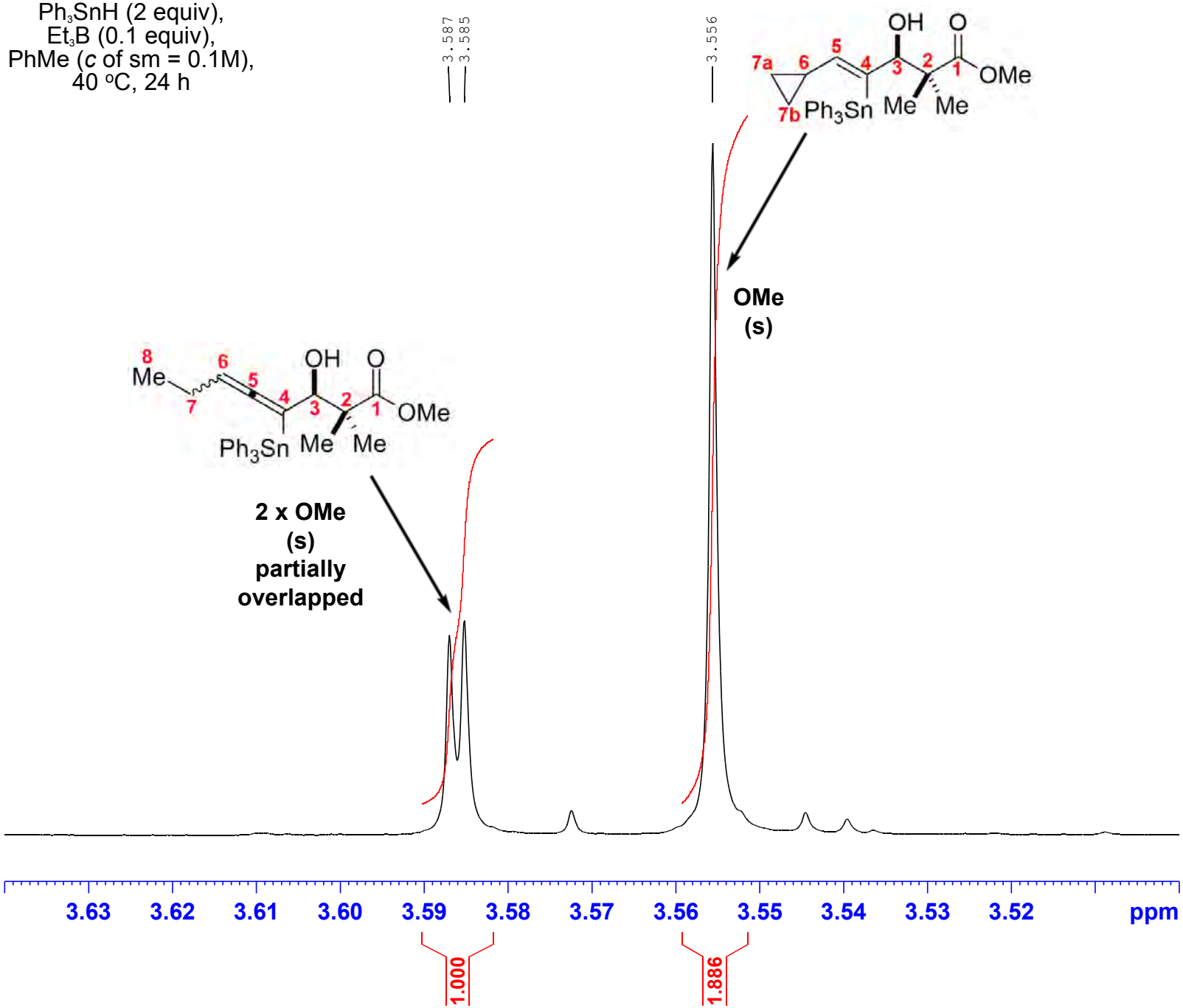

```
Current Data Parameters
NAME       HAW-VII-061-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time                3.01
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                     64
DS                      0
SWH            18028.846 Hz
FIDRES          0.100001 Hz
AQ              4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300208 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-062
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
40 °C, 24 h



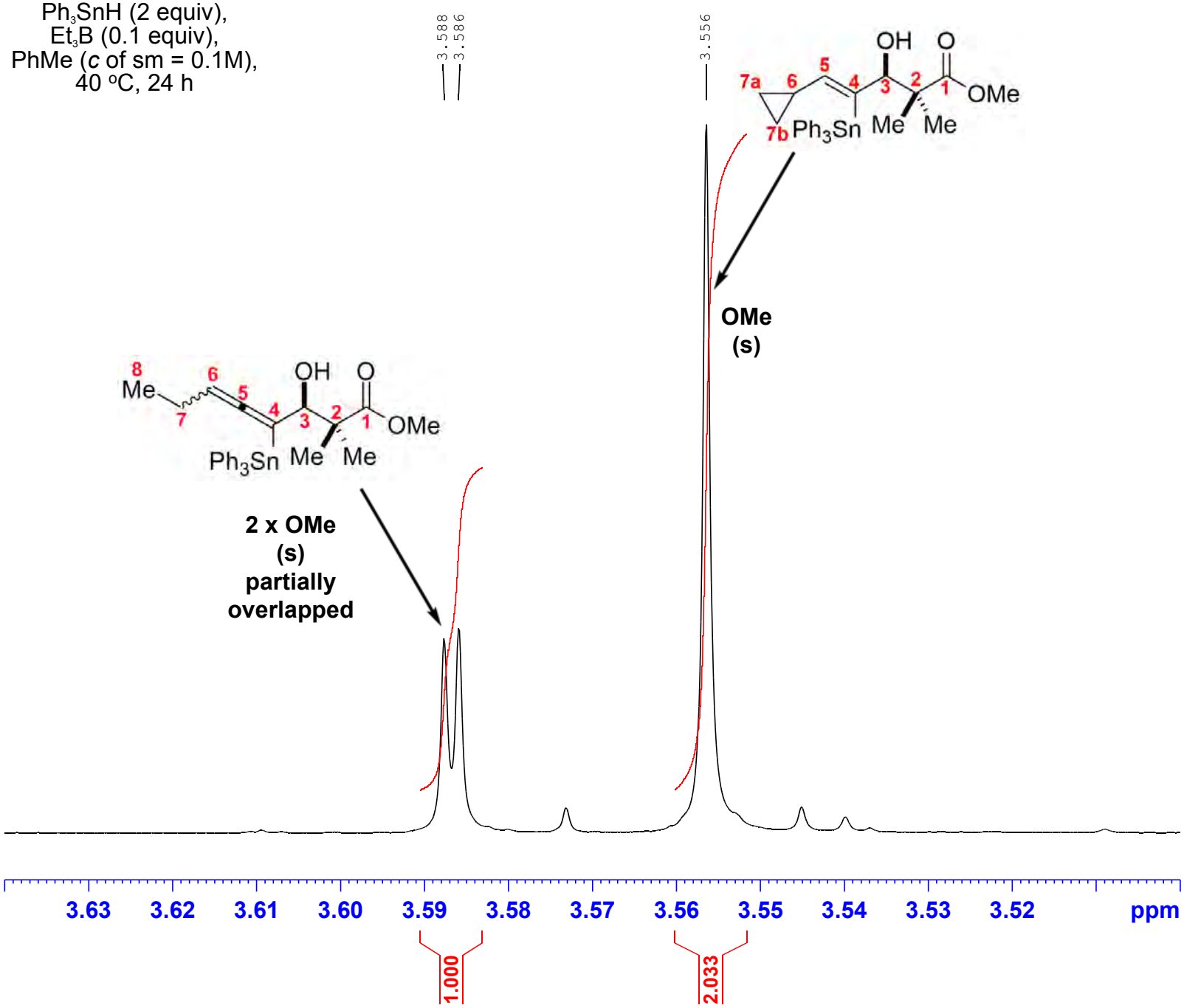

```
Current Data Parameters
NAME       HAW-VII-062-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time                3.09
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300192 MHz
WDW                  EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-063
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
40 °C, 24 h



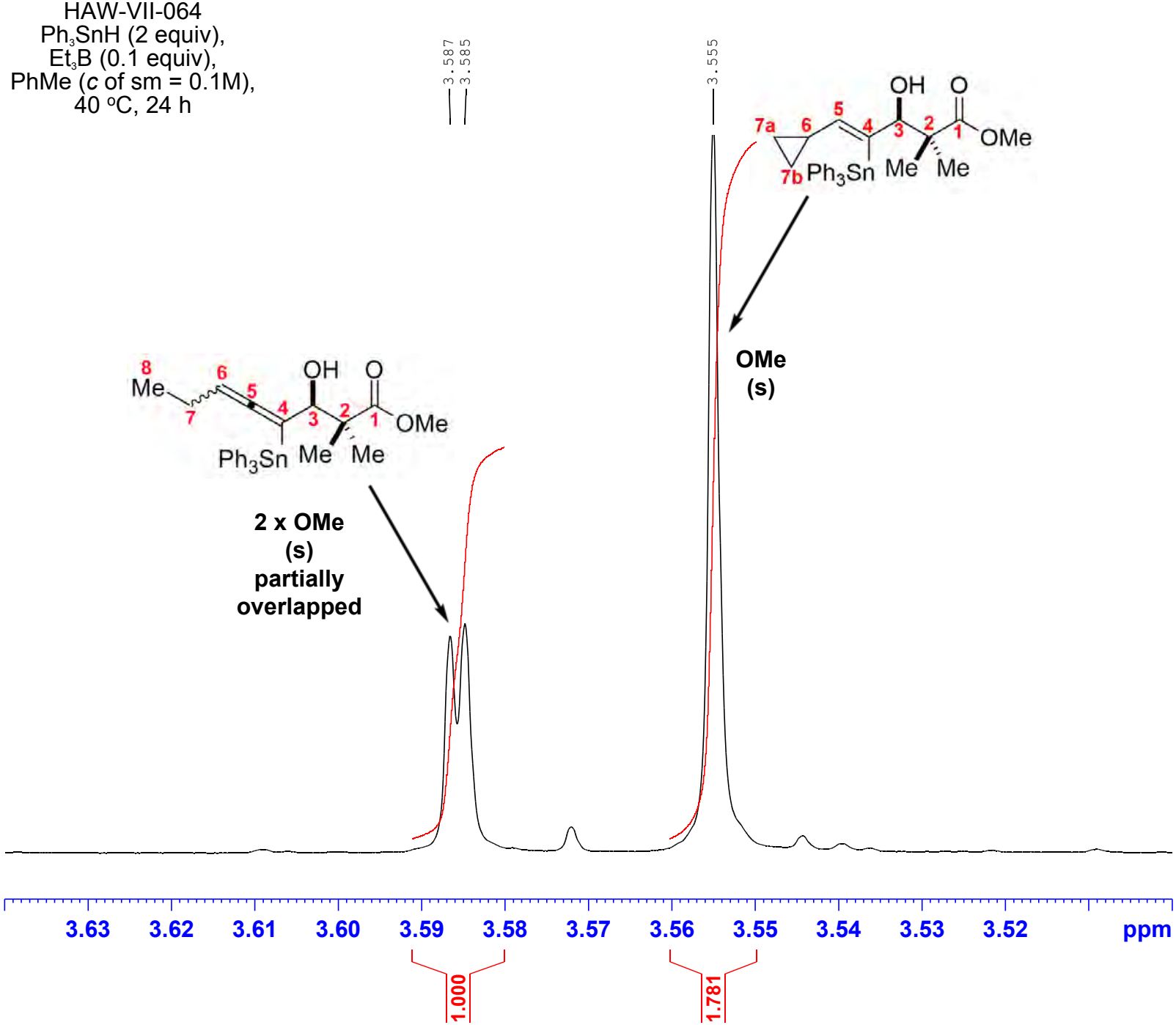

```
Current Data Parameters
NAME       HAW-VII-063-C
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time               3.17
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD               180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300175 MHz
WDW                  EM
SSB       0
LB                0.10 Hz
GB        0
PC                1.00
```

HAW-VII-064
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
40 °C, 24 h



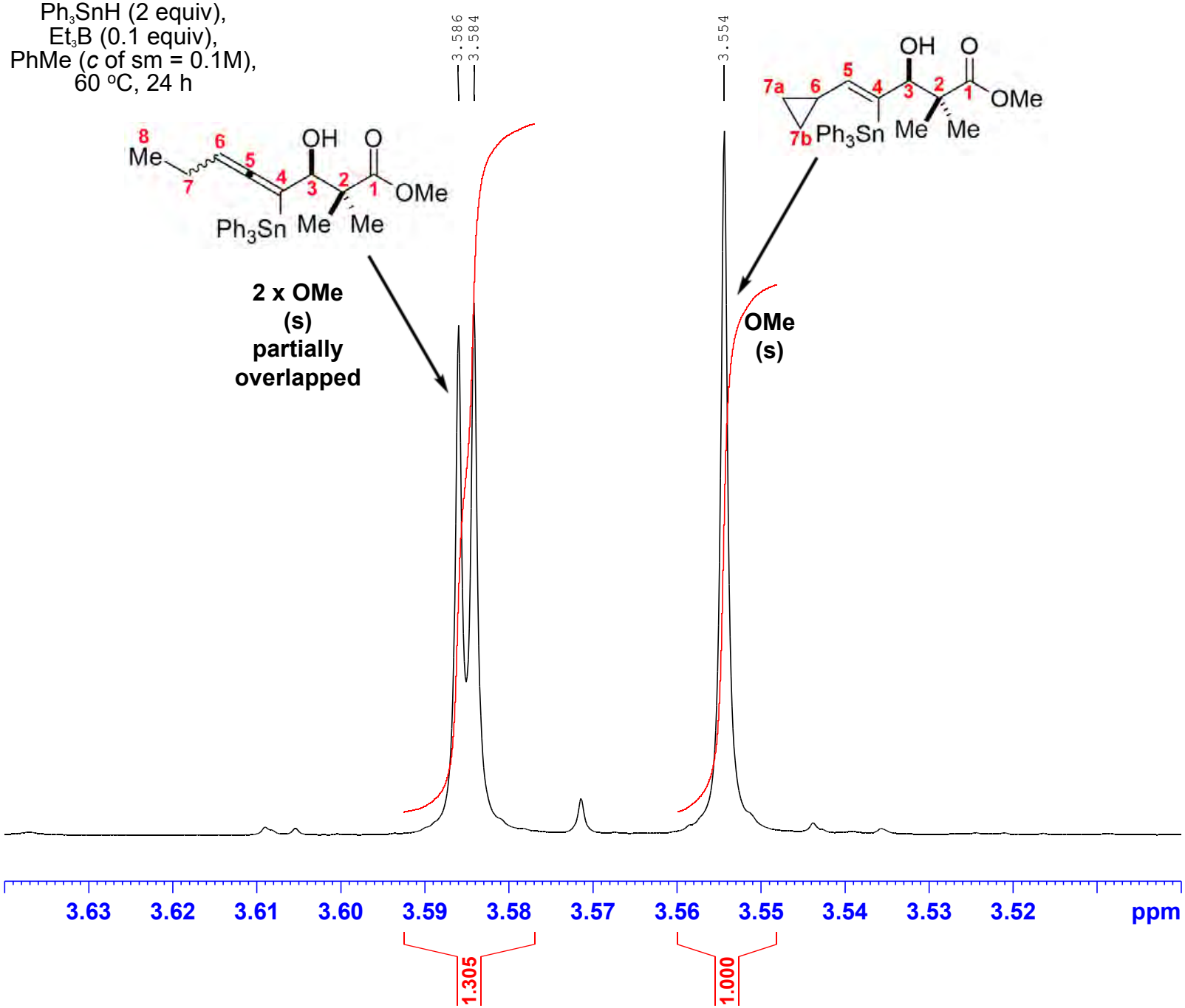

```
Current Data Parameters
NAME       HAW-VII-064-C
EXPNO                 60
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191219
Time_               2.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300204 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-065
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
60 °C, 24 h



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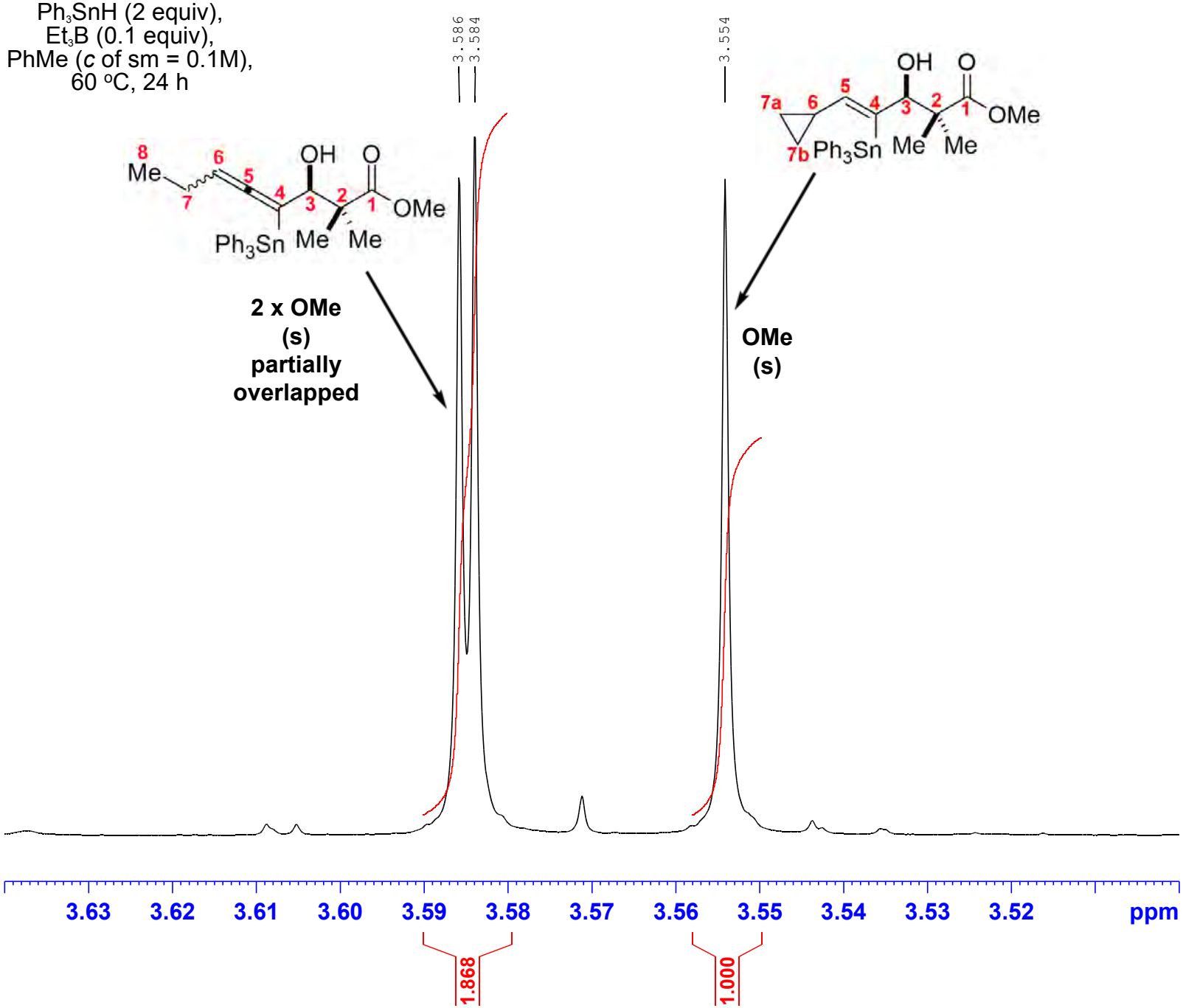
```
Current Data Parameters
NAME       HAW-VII-065-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time_               3.34
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300212 MHz
WDW                  EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-066
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
60 °C, 24 h



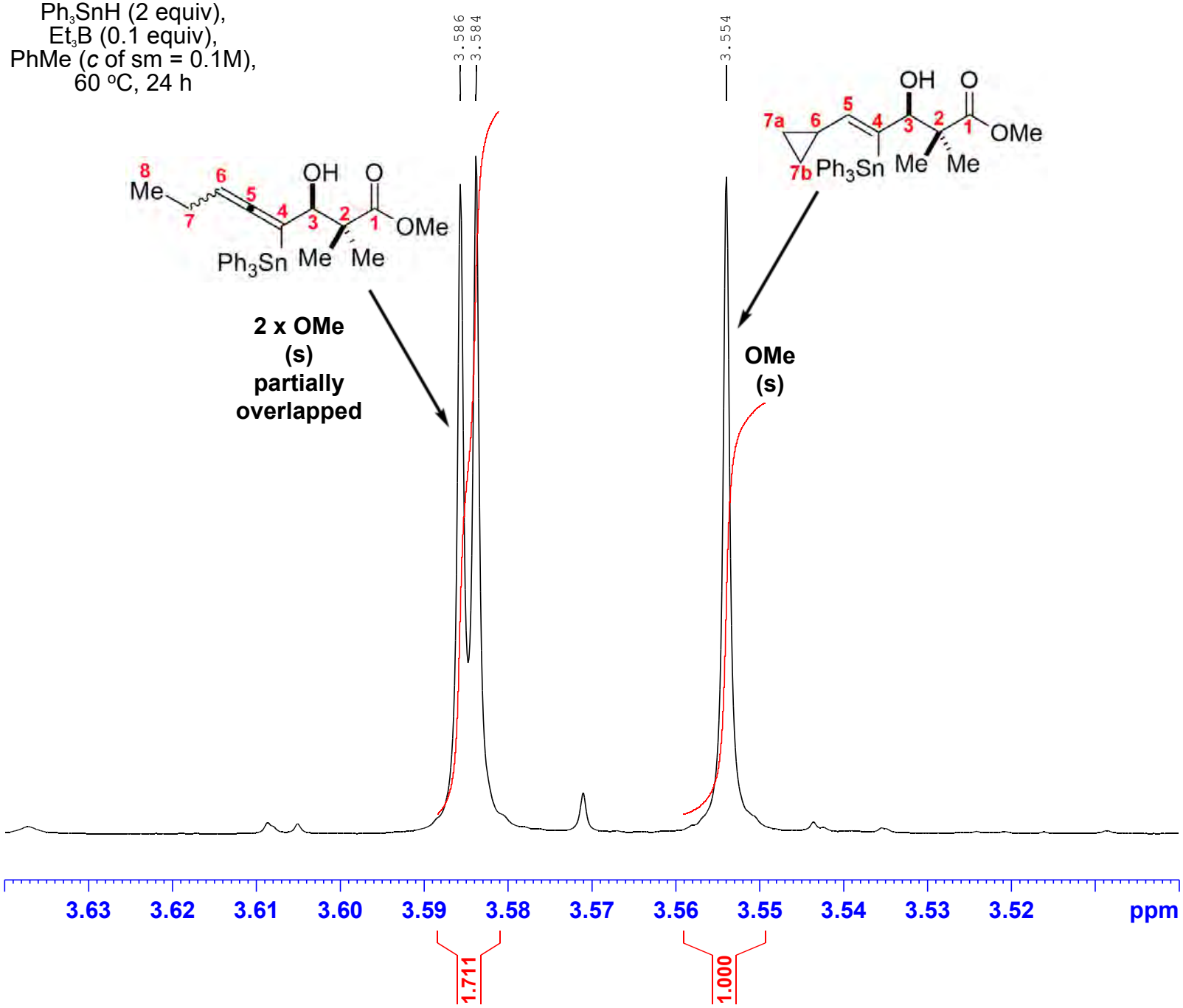

```
Current Data Parameters
NAME       HAW-VII-066-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time_               3.42
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300219 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-067
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
60 °C, 24 h



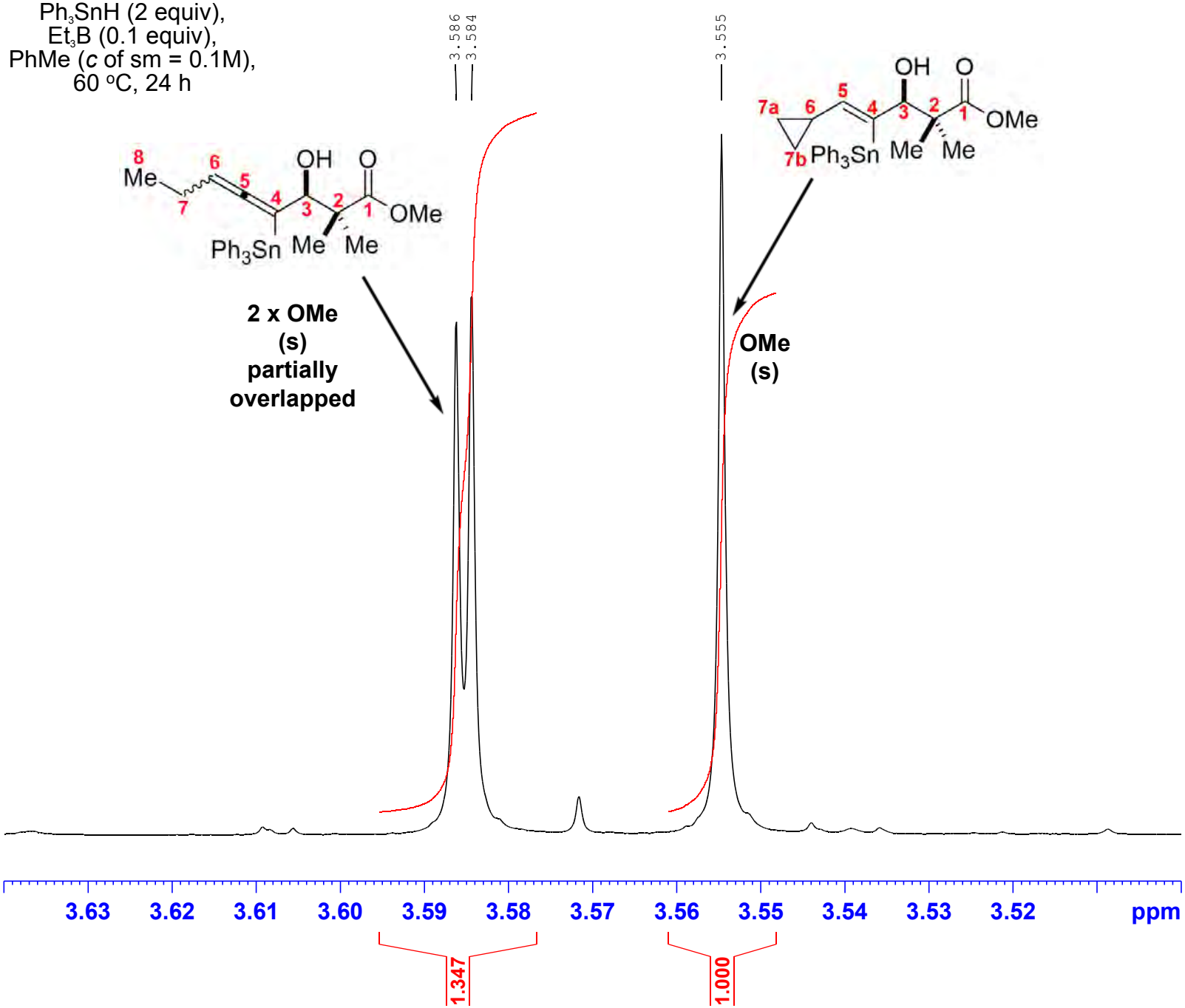

```
Current Data Parameters
NAME       HAW-VII-067-C
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191218
Time                3.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                     64
DS                      0
SWH            18028.846 Hz
FIDRES          0.100001 Hz
AQ              4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300222 MHz
WDW                  EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-068
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
60 °C, 24 h



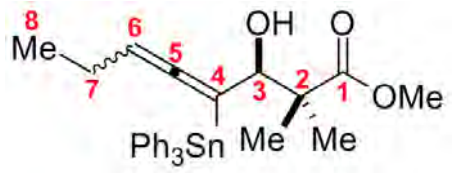
Current Data Parameters
NAME HAW-VII-068-C
EXPNO 40
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191218
Time 3.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 180286
SOLVENT CDCl3
NS 64
DS 0
SWH 18028.846 Hz
FIDRES 0.100001 Hz
AQ 4.9999318 sec
RG 97.5
DW 27.733 usec
DE 7.60 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.1337060 MHz
NUC1 1H
P1 10.00 usec
PLW1 26.60000038 W

F2 - Processing parameters
SI 262144
SF 600.1300208 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

HAW-VII-074
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
80 °C, 24 h



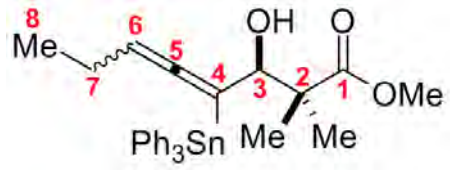

```
Current Data Parameters
NAME       HAW-VII-074-C
EXPNO                 80
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191219
Time_               3.07
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300192 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-075
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
80 °C, 24 h



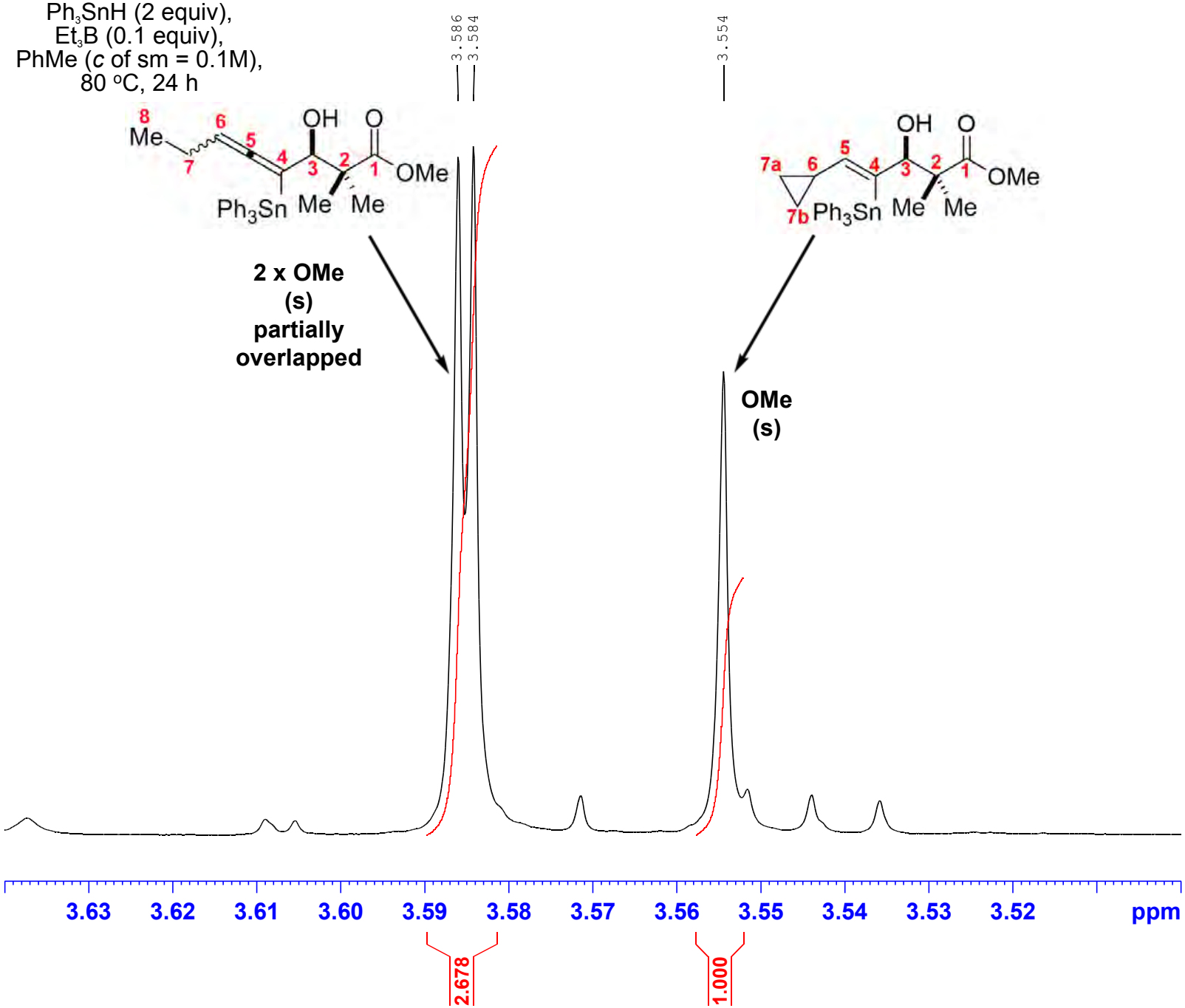

```
Current Data Parameters
NAME       HAW-VII-075-C
EXPNO                 90
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191219
Time_               3.15
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300183 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-079
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
80 °C, 24 h



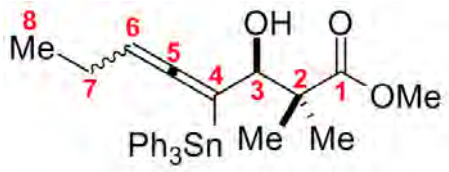

```
Current Data Parameters
NAME       HAW-VII-079-C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200115
Time_              11.21
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300215 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-080
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
80 °C, 24 h



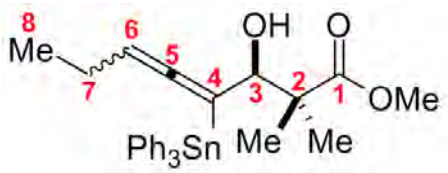

```
Current Data Parameters
NAME       HAW-VII-080-C
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200115
Time_              11.29
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH           18028.846 Hz
FIDRES         0.100001 Hz
AQ             4.9999318 sec
RG                  97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

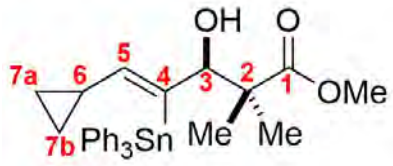
======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300187 MHz
WDW                   EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

HAW-VII-081
Ph_3SnH (2 equiv),
Et_3B (0.1 equiv),
PhMe (*c* of sm = 0.1M),
80 °C, 24 h



2 x OMe (s) partially overlapped



OMe (s)

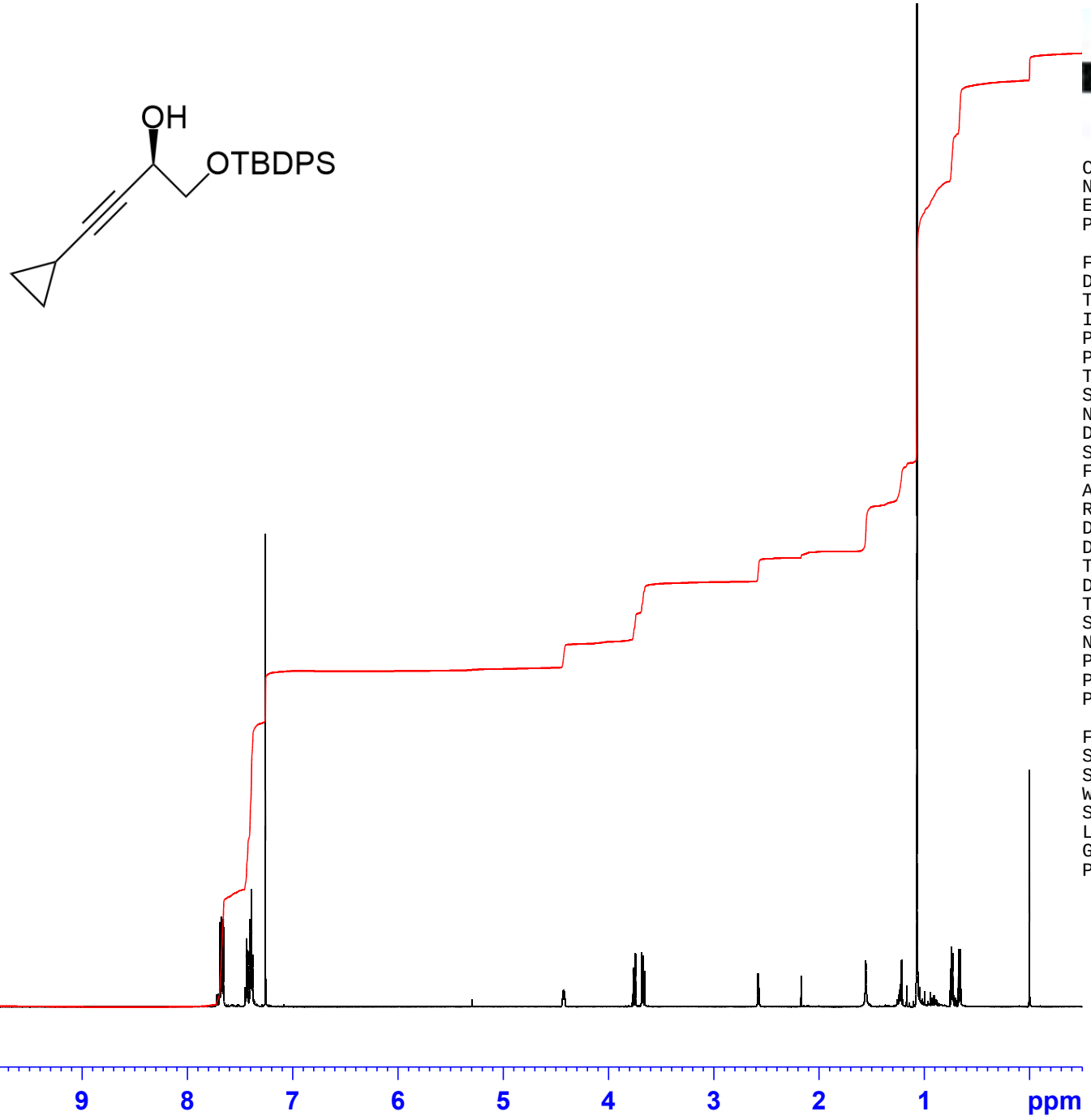

```
Current Data Parameters
NAME       HAW-VII-081-C
EXPNO                30
PROCNO                1

F2 - Acquisition Parameters
Date_          20200115
Time               11.37
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    64
DS                     0
SWH            18028.846 Hz
FIDRES          0.100001 Hz
AQ              4.9999318 sec
RG                 97.5
DW                27.733 usec
DE                 7.60 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1337060 MHz
NUC1                   1H
P1                 10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300170 MHz
WDW                  EM
SSB       0
LB                 0.10 Hz
GB        0
PC                 1.00
```

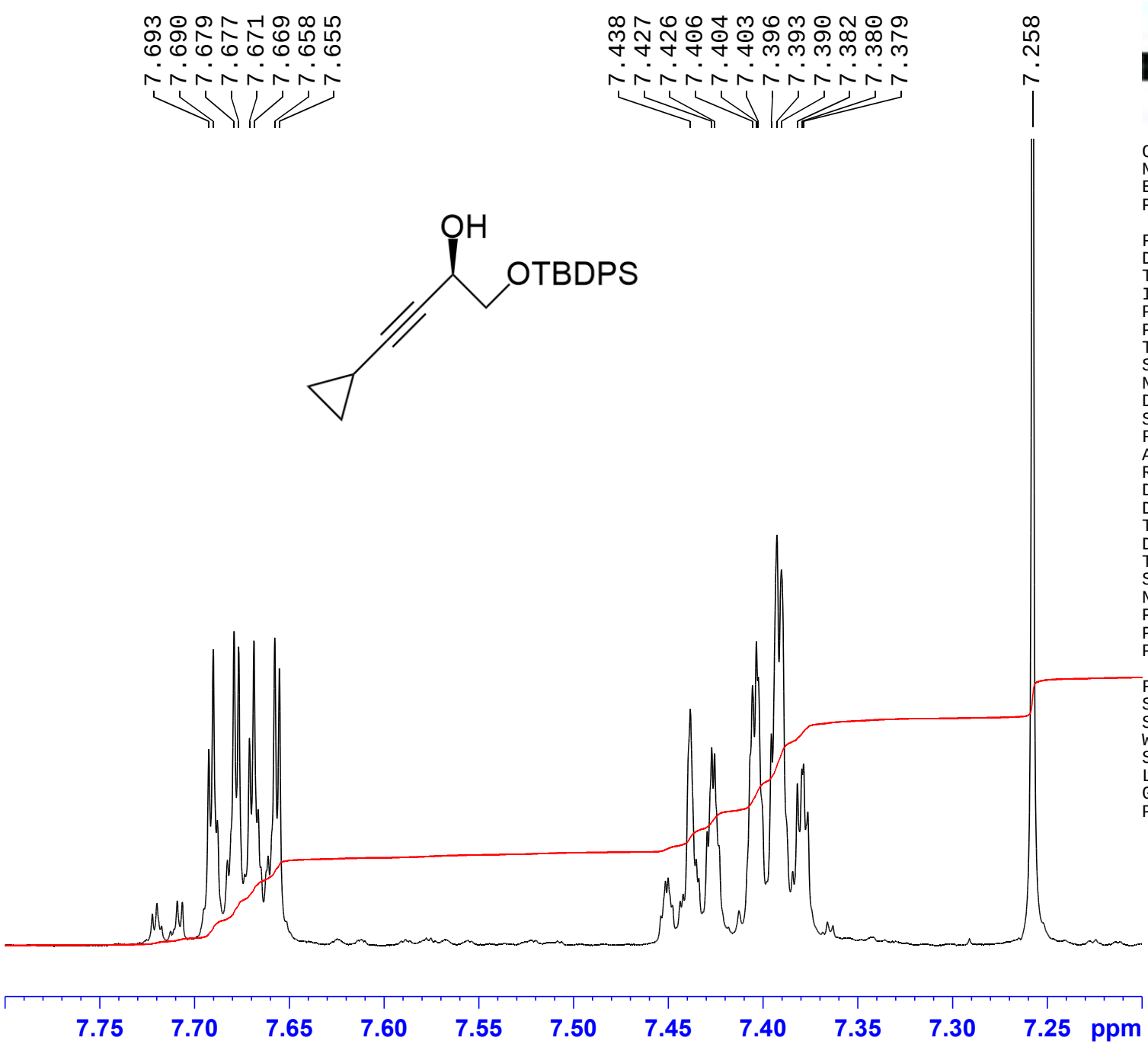
Part F. The 600.13 MHz ^{1}H NMR and 150.90 MHz ^{13}C NMR Spectra of the Cyclopropylpropargylic Alcohol 12 and the Tributylstannylallene 15 in $CDCl_3$




```
Current Data Parameters
NAME                  LH-I-71
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20220401
Time                   18.31 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                 zg30
TD                    180286
SOLVENT                CDCl3
NS                         16
DS                          0
SWH               18028.846 Hz
FIDRES             0.200003 Hz
AQ                 4.9999318 sec
RG                      97.5
DW                    27.733 usec
DE                     8.00 usec
TE                     300.0 K
D1               0.10000000 sec
TD0                         1
SFO1            600.1337060 MHz
NUC1                       1H
P0                    3.33 usec
P1                   10.00 usec
PLW1           26.60000038 W

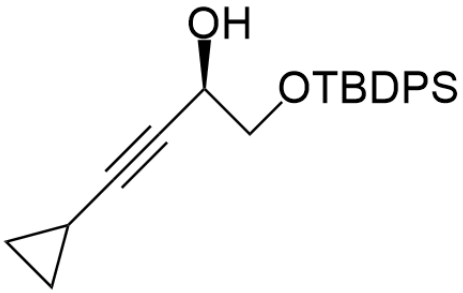
F2 - Processing parameters
SI                     262144
SF              600.1300153 MHz
WDW                        EM
SSB         0
LB                    0.10 Hz
GB          0
PC                    1.00
```




```
Current Data Parameters
NAME                  LH-I-71
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_                20220401
Time                   18.31 h
INSTRUM                 spect
PROBHD    Z114607_0188 (
PULPROG                 zg30
TD                    180286
SOLVENT                 CDCl3
NS                         16
DS                          0
SWH                18028.846 Hz
FIDRES              0.200003 Hz
AQ                  4.9999318 sec
RG                       97.5
DW                     27.733 usec
DE                      8.00 usec
TE                     300.0 K
D1                0.10000000 sec
TD0                         1
SFO1             600.1337060 MHz
NUC1                       1H
P0                      3.33 usec
P1                     10.00 usec
PLW1             26.60000038 W

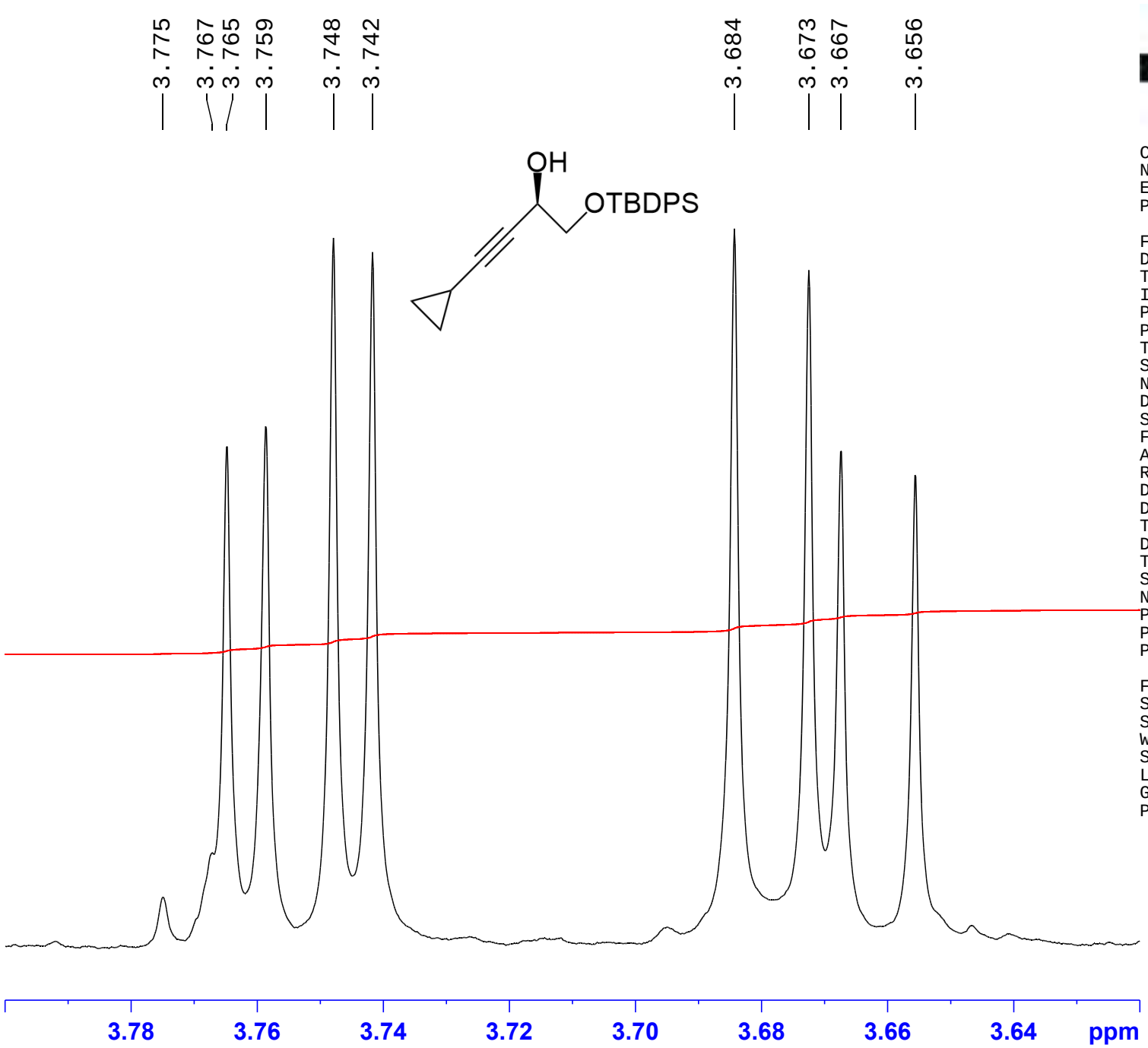
F2 - Processing parameters
SI                     262144
SF               600.1300153 MHz
WDW                        EM
SSB          0
LB                      0.10 Hz
GB           0
PC                      1.00
```




```
Current Data Parameters
NAME                  LH-I-71
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_                20220401
Time                   18.31 h
INSTRUM                 spect
PROBHD    Z114607_0188 (
PULPROG                 zg30
TD                    180286
SOLVENT                 CDCl3
NS                         16
DS                          0
SWH                18028.846 Hz
FIDRES              0.200003 Hz
AQ                  4.9999318 sec
RG                       97.5
DW                     27.733 usec
DE                      8.00 usec
TE                     300.0 K
D1                0.10000000 sec
TD0                         1
SFO1             600.1337060 MHz
NUC1                       1H
P0                      3.33 usec
P1                     10.00 usec
PLW1             26.60000038 W

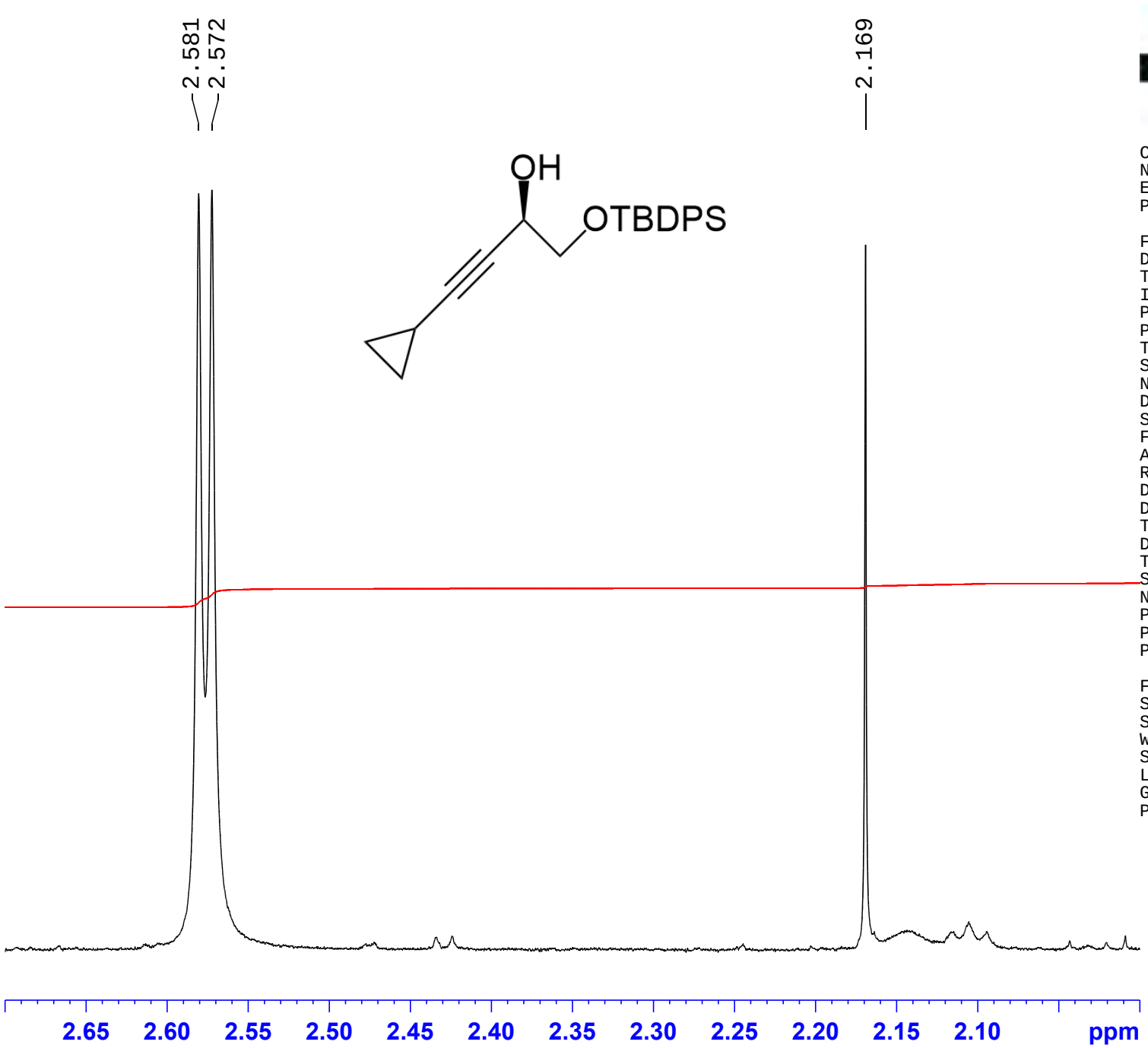
F2 - Processing parameters
SI                     262144
SF               600.1300153 MHz
WDW                        EM
SSB          0
LB                      0.10 Hz
GB           0
PC                      1.00
```




```
Current Data Parameters
NAME                  LH-I-71
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20220401
Time                  18.31 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                 zg30
TD                    180286
SOLVENT                CDCl3
NS                         16
DS                          0
SWH               18028.846 Hz
FIDRES             0.200003 Hz
AQ                 4.9999318 sec
RG                      97.5
DW                    27.733 usec
DE                     8.00 usec
TE                     300.0 K
D1               0.10000000 sec
TD0                         1
SFO1            600.1337060 MHz
NUC1                       1H
P0                     3.33 usec
P1                    10.00 usec
PLW1            26.60000038 W

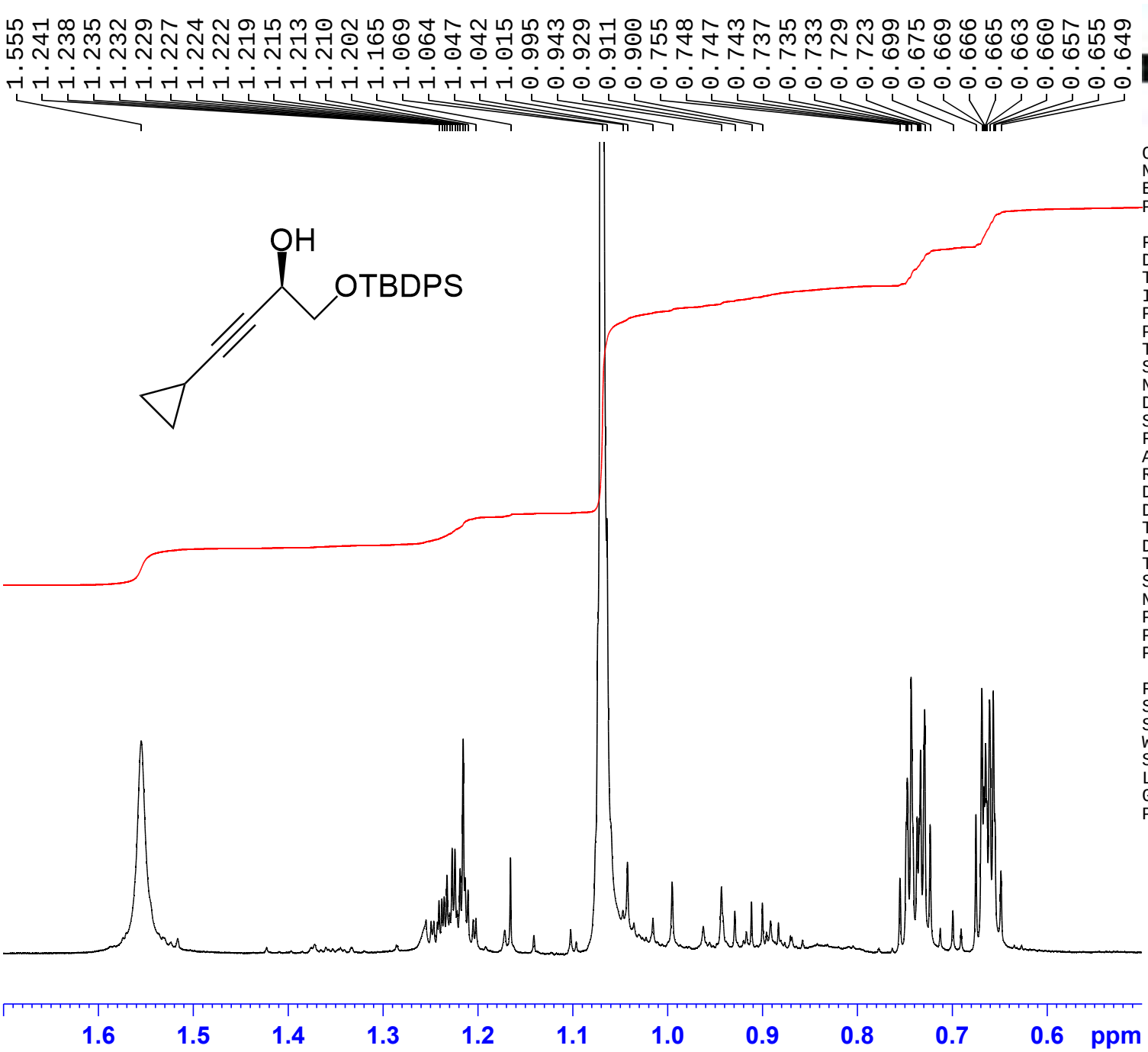
F2 - Processing parameters
SI                     262144
SF              600.1300153 MHz
WDW                        EM
SSB          0
LB                     0.10 Hz
GB           0
PC                     1.00
```




```
Current Data Parameters
NAME                  LH-I-71
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20220401
Time                  18.31 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                 zg30
TD                    180286
SOLVENT                CDCl3
NS                         16
DS                          0
SWH               18028.846 Hz
FIDRES             0.200003 Hz
AQ                 4.9999318 sec
RG                      97.5
DW                    27.733 usec
DE                     8.00 usec
TE                     300.0 K
D1               0.10000000 sec
TD0                         1
SFO1            600.1337060 MHz
NUC1                       1H
P0                    3.33 usec
P1                   10.00 usec
PLW1            26.60000038 W

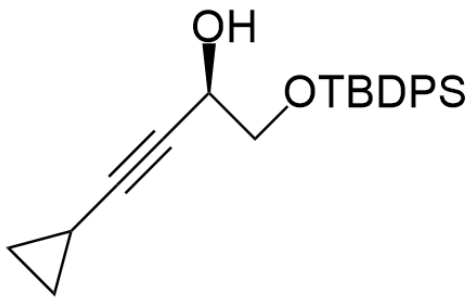
F2 - Processing parameters
SI                     262144
SF              600.1300153 MHz
WDW                        EM
SSB          0
LB                    0.10 Hz
GB           0
PC                     1.00
```



Current Data Parameters
NAME LH-I-71
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220401
Time 18.31 h
INSTRUM spect
PROBHD Z114607_0188 (
PULPROG zg30
TD 180286
SOLVENT CDCl3
NS 16
DS 0
SWH 18028.846 Hz
FIDRES 0.200003 Hz
AQ 4.9999318 sec
RG 97.5
DW 27.733 usec
DE 8.00 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
SFO1 600.1337060 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
PLW1 26.60000038 W

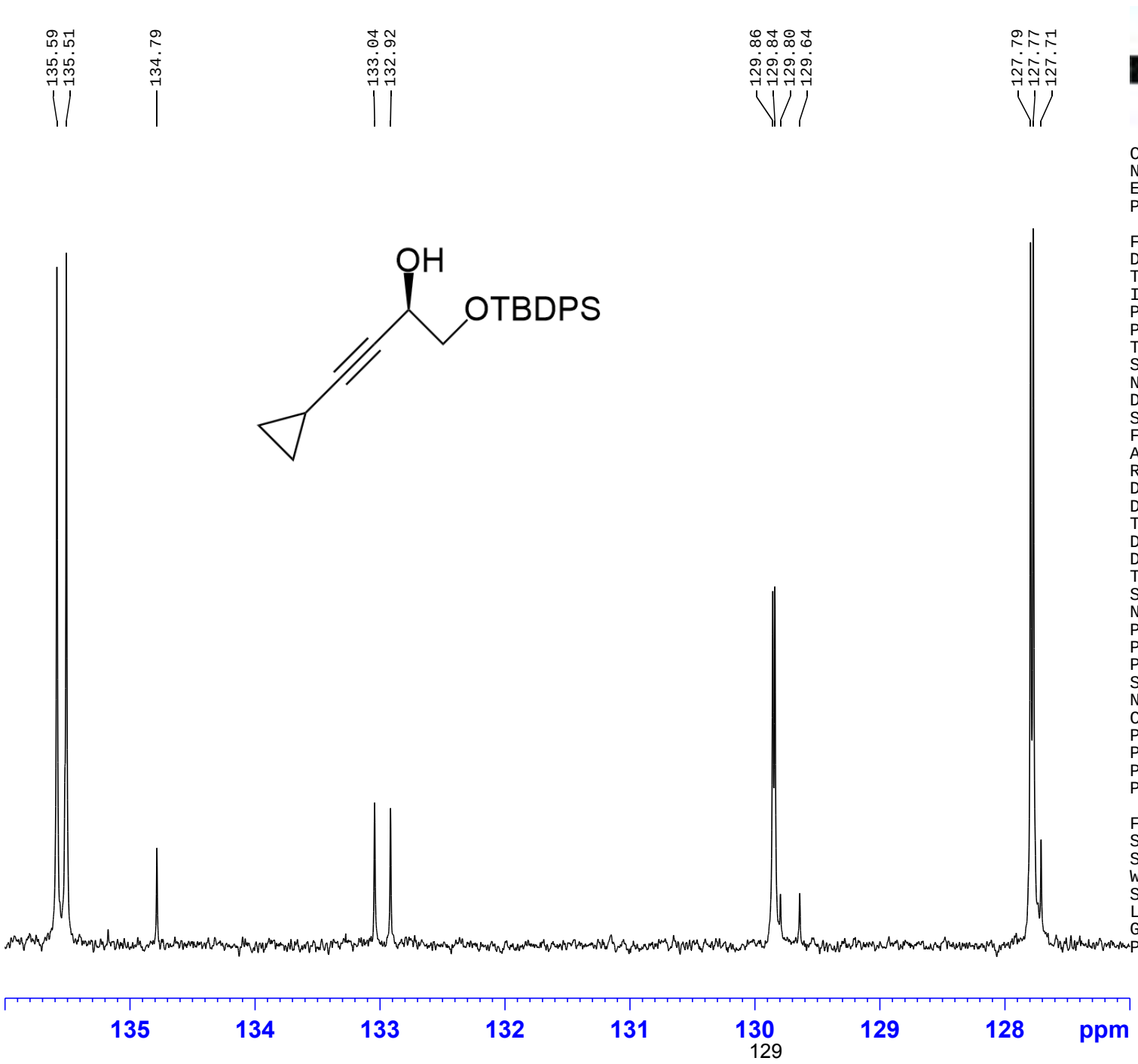
F2 - Processing parameters
SI 262144
SF 600.1300153 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00




```
Current Data Parameters
NAME                  LH-I-71
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_                20220401
Time                    20.00 h
INSTRUM                  spect
PROBHD   Z114607_0188 (
PULPROG                 zgpg30
TD                      119044
SOLVENT                  CDCl3
NS                         2000
DS                            4
SWH                 37500.000 Hz
FIDRES               0.630019 Hz
AQ                   1.5872533 sec
RG                      186.92
DW                      13.333 usec
DE                        6.53 usec
TE                       300.0 K
D1                  1.00000000 sec
D11                 0.03000000 sec
TD0                           1
SFO1               150.9194058 MHz
NUC1                        13C
P0                        3.93 usec
P1                       11.80 usec
PLW1               85.00000000 W
SFO2               600.1324005 MHz
NUC2                        1H
CPDPRG[2                waltz64
PCPD2                    70.00 usec
PLW2               27.00000000 W
PLW12               0.57327998 W
PLW13               0.28836000 W

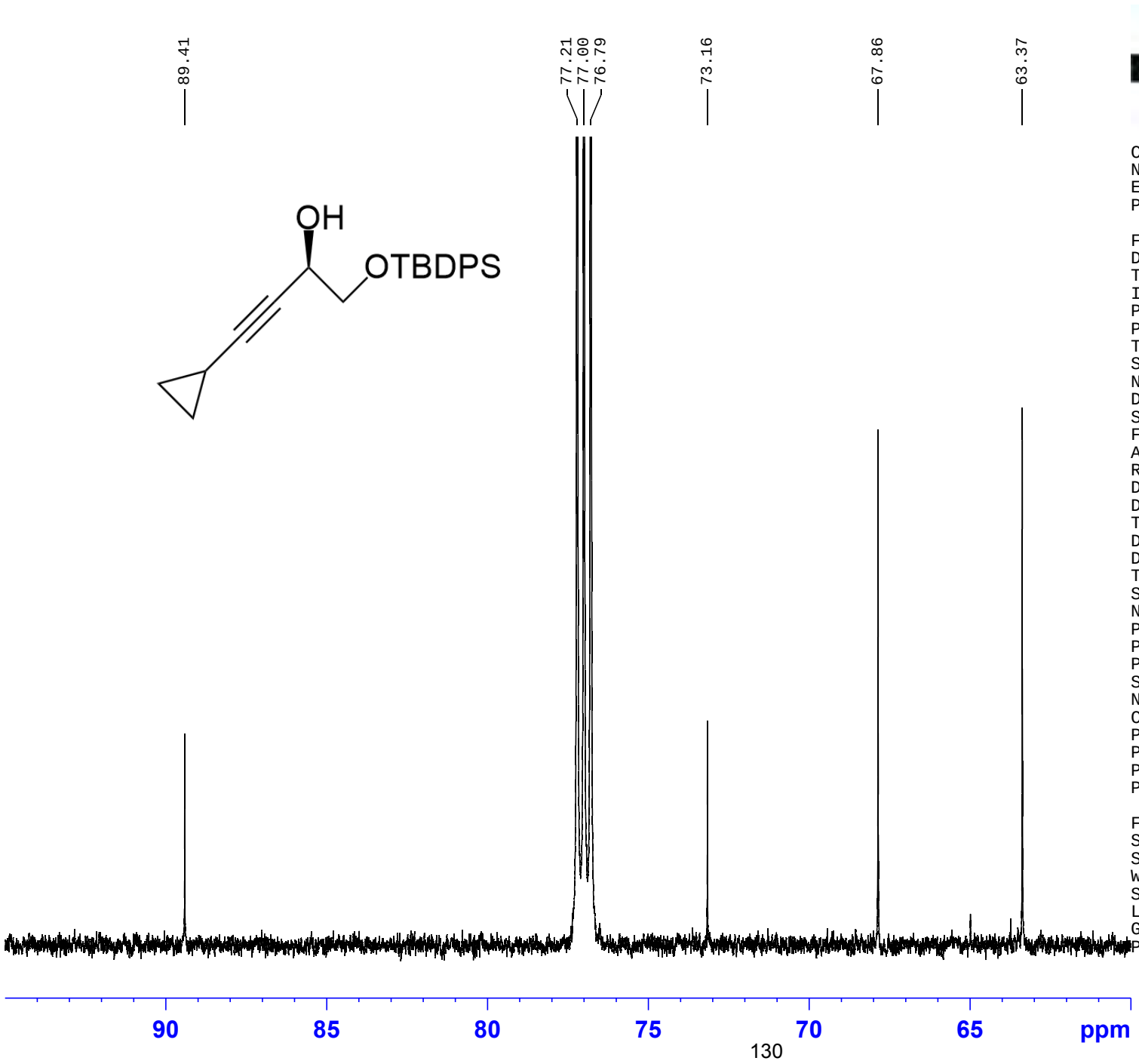
F2 - Processing parameters
SI                       131072
SF                 150.9028116 MHz
WDW                         EM
SSB             0
LB                       1.00 Hz
GB              0
PC                       1.40
```



Current Data Parameters
NAME LH-I-71
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220401
Time 20.00 h
INSTRUM spect
PROBHD Z114607_0188 (
PULPROG zgpg30
TD 119044
SOLVENT CDCl3
NS 2000
DS 4
SWH 37500.000 Hz
FIDRES 0.630019 Hz
AQ 1.5872533 sec
RG 186.92
DW 13.333 usec
DE 6.53 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9194058 MHz
NUC1 13C
P0 3.93 usec
P1 11.80 usec
PLW1 85.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz64
PCPD2 70.00 usec
PLW2 27.00000000 W
PLW12 0.57327998 W
PLW13 0.28836000 W

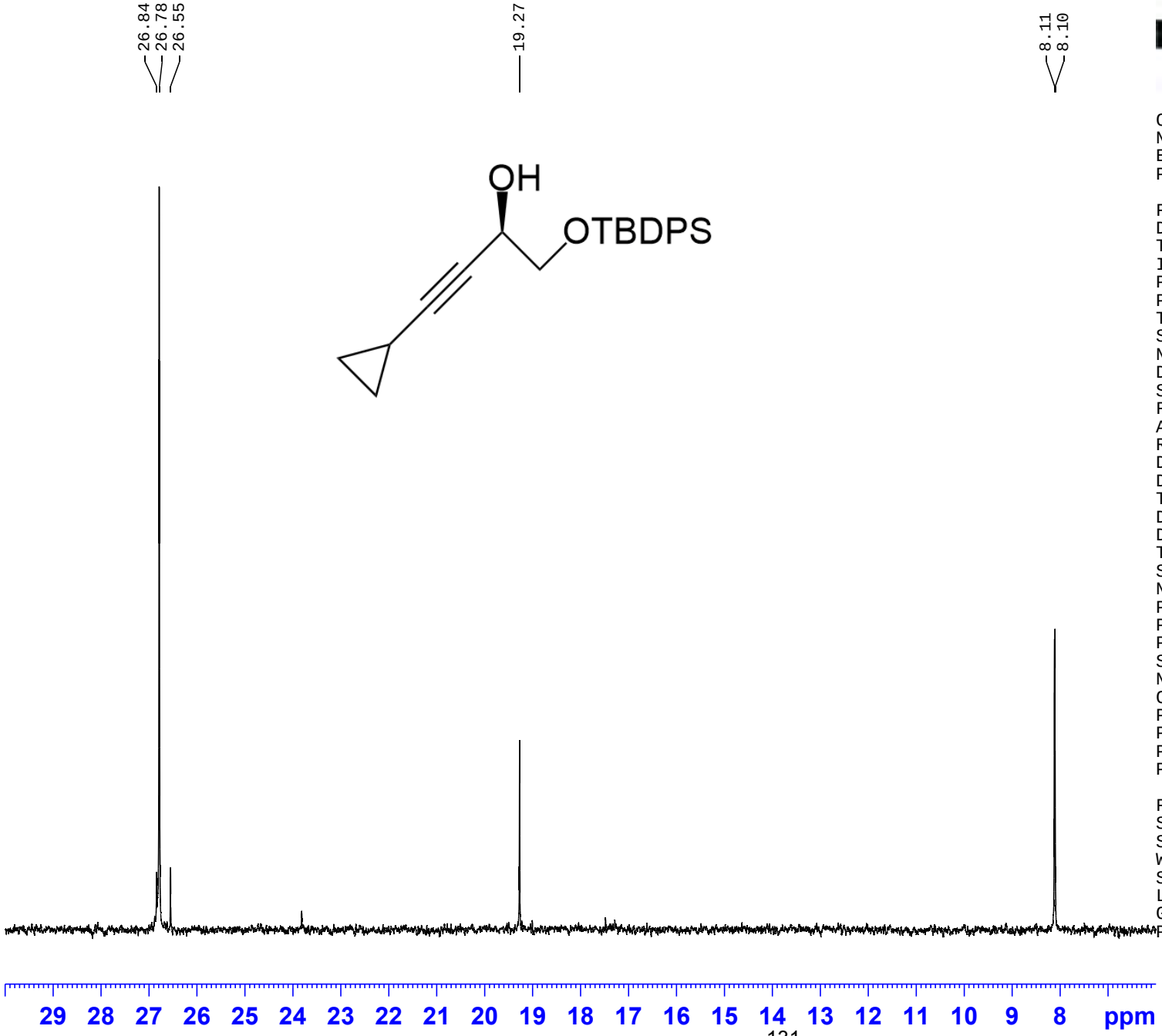
F2 - Processing parameters
SI 131072
SF 150.9028116 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
Current Data Parameters
NAME                  LH-I-71
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_               20220401
Time                  20.00 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG               zgpg30
TD                    119044
SOLVENT                CDCl3
NS                      2000
DS                         4
SWH               37500.000 Hz
FIDRES             0.630019 Hz
AQ                1.5872533 sec
RG                   186.92
DW                   13.333 usec
DE                     6.53 usec
TE                    300.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                        1
SFO1           150.9194058 MHz
NUC1                    13C
P0                    3.93 usec
P1                   11.80 usec
PLW1           85.00000000 W
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz64
PCPD2                 70.00 usec
PLW2           27.00000000 W
PLW12           0.57327998 W
PLW13           0.28836000 W

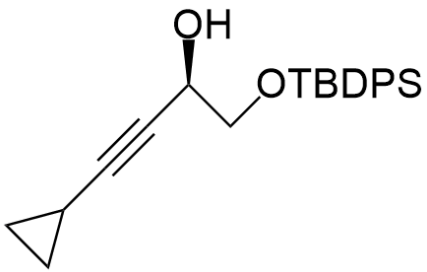
F2 - Processing parameters
SI                    131072
SF             150.9028116 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```




```
Current Data Parameters
NAME                  LH-I-71
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_               20220401
Time                   20.00 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                zgpg30
TD                     119044
SOLVENT                 CDCl3
NS                       2000
DS                          4
SWH                37500.000 Hz
FIDRES              0.630019 Hz
AQ                  1.5872533 sec
RG                     186.92
DW                     13.333 usec
DE                       6.53 usec
TE                      300.0 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                         1
SFO1             150.9194058 MHz
NUC1                      13C
P0                      3.93 usec
P1                     11.80 usec
PLW1             85.00000000 W
SFO2             600.1324005 MHz
NUC2                      1H
CPDPRG[2              waltz64
PCPD2                  70.00 usec
PLW2             27.00000000 W
PLW12             0.57327998 W
PLW13             0.28836000 W

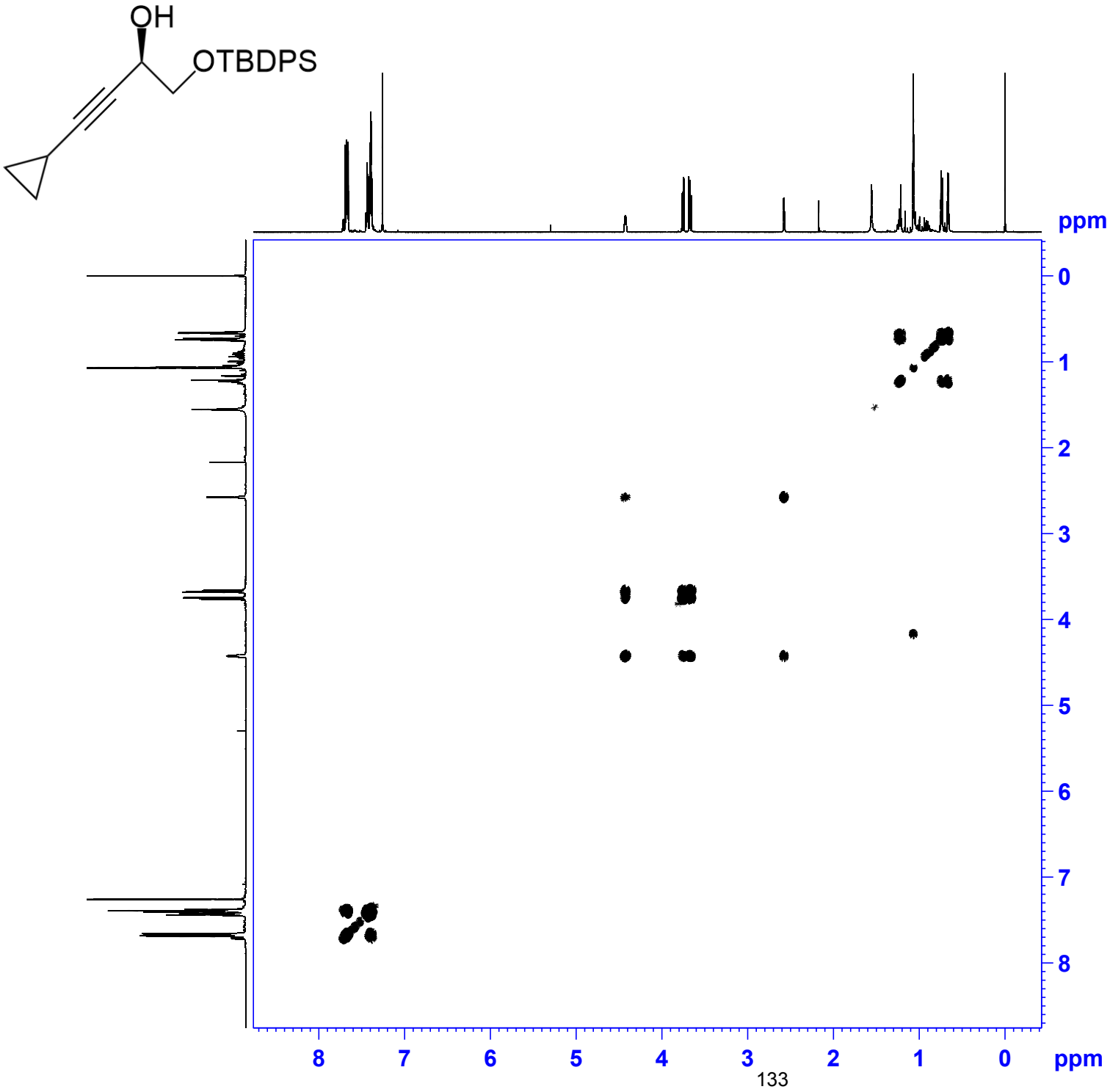
F2 - Processing parameters
SI                     131072
SF               150.9028116 MHz
WDW                       EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```




```
Current Data Parameters
NAME            LH-I-71
EXPNO                12
PROCNO                1

F2 - Acquisition Parameters
Date_          20220401
Time              20.46 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG     deptsp135.b
TD                119044
SOLVENT            CDCl3
NS                  1000
DS                     4
SWH            35714.285 Hz
FIDRES          0.600018 Hz
AQ             1.6666160 sec
RG                186.92
DW                14.000 usec
DE                 7.44 usec
TE                300.0 K
CNST2        145.0000000
D1            1.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1
SFO1         150.9178962 MHz
NUC1                  13C
P1                11.80 usec
P13             2000.00 usec
PLW0      0 W
PLW1         85.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5         18.08300018 W
SFO2         600.1324005 MHz
NUC2                  1H
CPDPRG[2         waltz64
P3                10.20 usec
P4                20.40 usec
PCPD2             70.00 usec
PLW2         27.00000000 W
PLW12         0.57327998 W

F2 - Processing parameters
SI                131072
SF           150.9027170 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



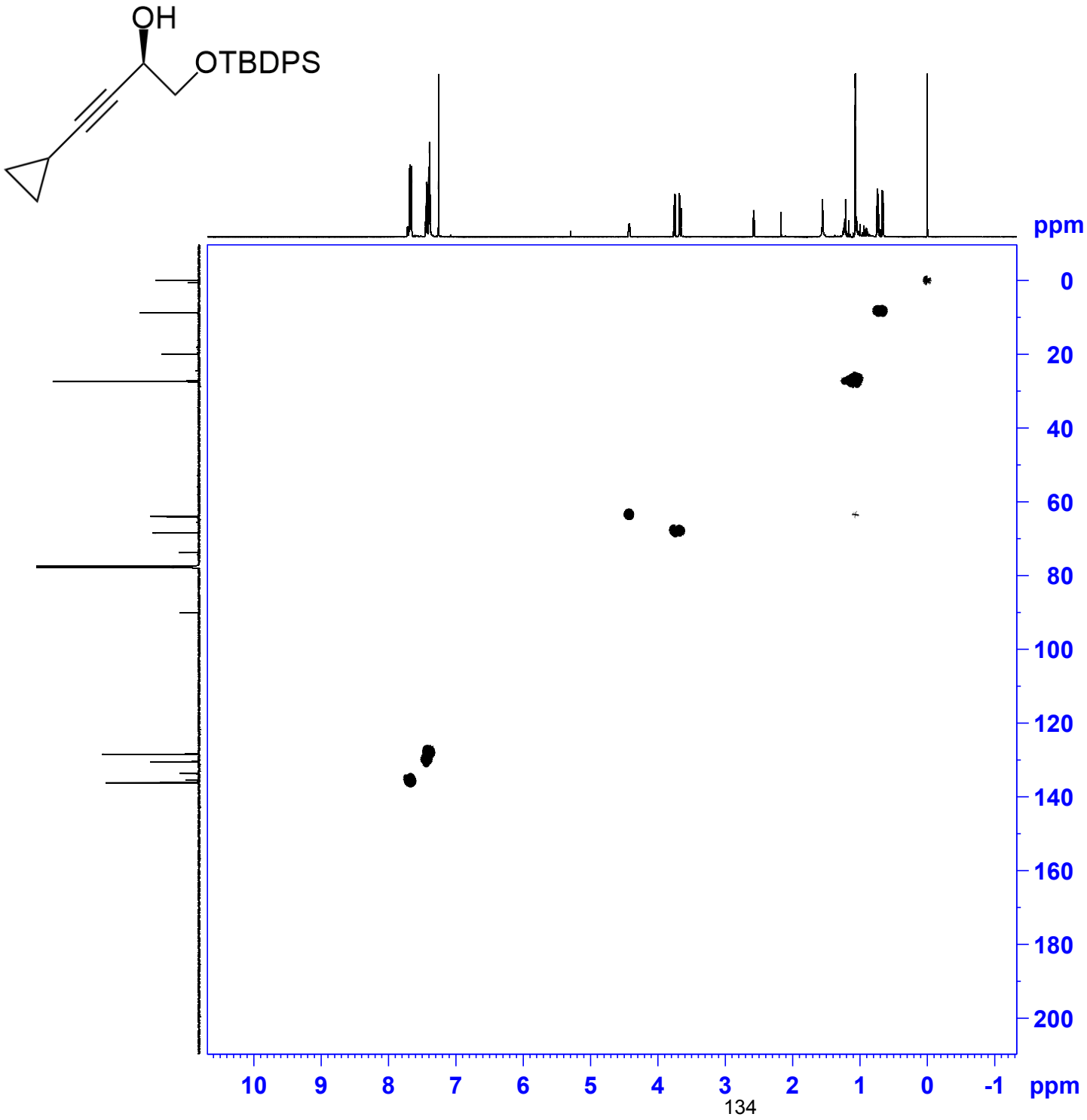
Current Data Parameters
NAME LH-I-71
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220401
Time 20.57 h
INSTRUM spect
PROBHD Z114607_0188 (
PULPROG cosygpmfppqf
TD 2048
SOLVENT CDCl3
NS 2
DS 8
SWH 5514.706 Hz
FIDRES 5.385455 Hz
AQ 0.1856853 sec
RG 186.92
DW 90.667 usec
DE 6.50 usec
TE 300.0 K
D0 0.00000300 sec
D1 0.87302327 sec
D11 0.03000000 sec
D12 0.00002000 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00018160 sec
TDav 1
SFO1 600.1325168 MHz
NUC1 1H
P1 10.00 usec
P17 2500.00 usec
PLW1 26.60000038 W
PLW10 4.25600004 W
GPNAM[1] SMSQ10.100
GPZ1 16.00 %
GPNAM[2] SMSQ10.100
GPZ2 12.00 %
GPNAM[3] SMSQ10.100
GPZ3 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 600.1325 MHz
FIDRES 43.020374 Hz
SW 9.176 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 600.1300153 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 600.1300153 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0



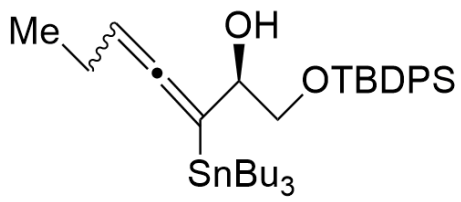

```
Current Data Parameters
NAME             LH-I-71
EXPNO                 14
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220401
Time              21.06 h
INSTRUM             spect
PROBHD   Z114607_0188 (
PULPROG  hsqcedetgpsp.3
TD                  1024
SOLVENT             CDCl3
NS                     2
DS                    32
SWH            7211.539 Hz
FIDRES        14.085036 Hz
AQ             0.0709973 sec
RG                186.92
DW                69.333 usec
DE                 6.50 usec
TE                300.3 K
CNST2       145.0000000
D0           0.00000300 sec
D1           0.80000001 sec
D4           0.00172414 sec
D11          0.03000000 sec
D16          0.00020000 sec
D21          0.00360000 sec
IN0          0.00001510 sec
TDav                   1
ZGOPTNS
SFO1        600.1328223 MHz
NUC1                1H
P1                10.00 usec
P2                20.00 usec
PLW1        26.60000038 W
SFO2        150.9178988 MHz
NUC2                13C
CPDPRG[2          garp4
P3                11.80 usec
P14              500.00 usec
P31             1730.00 usec
PCPD2             60.00 usec
PLW0     0 W
PLW2        85.00000000 W
PLW12        3.28760004 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3               0.500
SPOFFS3  0 Hz
SPW3        18.08300018 W
SPNAM[18  Crp60_xfilt.2
SPOAL18              0.500
SPOFFS18 0 Hz
SPW18        5.22629976 W
GPNAM[1]     SMSQ10.100
GPZ1                80.00 %
GPNAM[2]     SMSQ10.100
GPZ2                20.10 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                   256
SFO1          150.9179 MHz
FIDRES       258.692047 Hz
SW               219.408 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF          600.1300130 MHz
WDW                 QSINE
SSB                    2
LB       0 Hz
GB       0
PC                  1.40

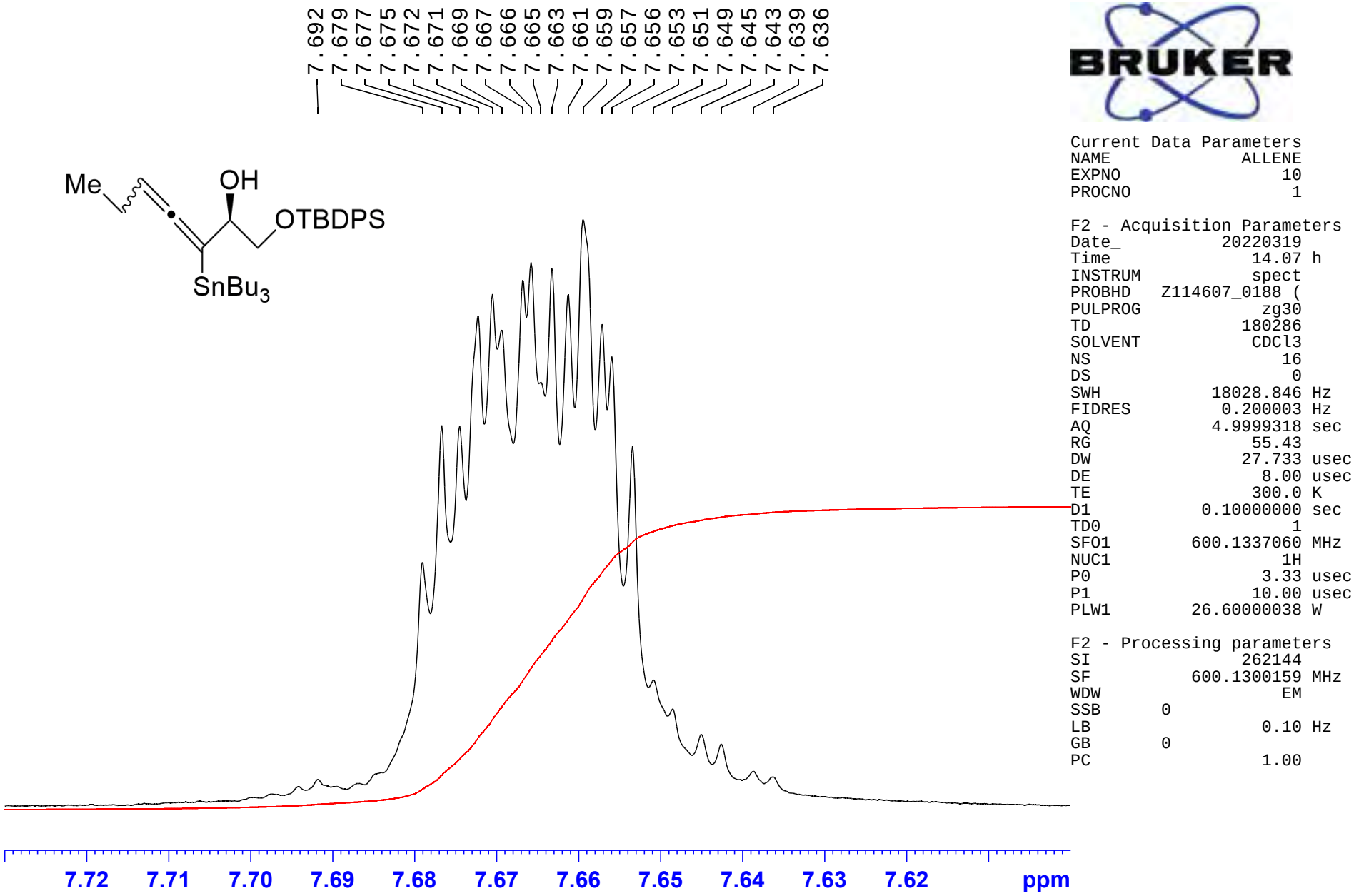
F1 - Processing parameters
SI                  1024
MC2       echo-antiecho
SF          150.9028010 MHz
WDW                 QSINE
SSB                    2
LB       0 Hz
GB       0
```




```
Current Data Parameters
NAME                  ALLENE
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20220319
Time                  14.07 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                zg30
TD                   180286
SOLVENT               CDCl3
NS                        16
DS                         0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                    55.43
DW                   27.733 usec
DE                    8.00 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                        1
SFO1           600.1337060 MHz
NUC1                      1H
P0                    3.33 usec
P1                   10.00 usec
PLW1           26.60000038 W

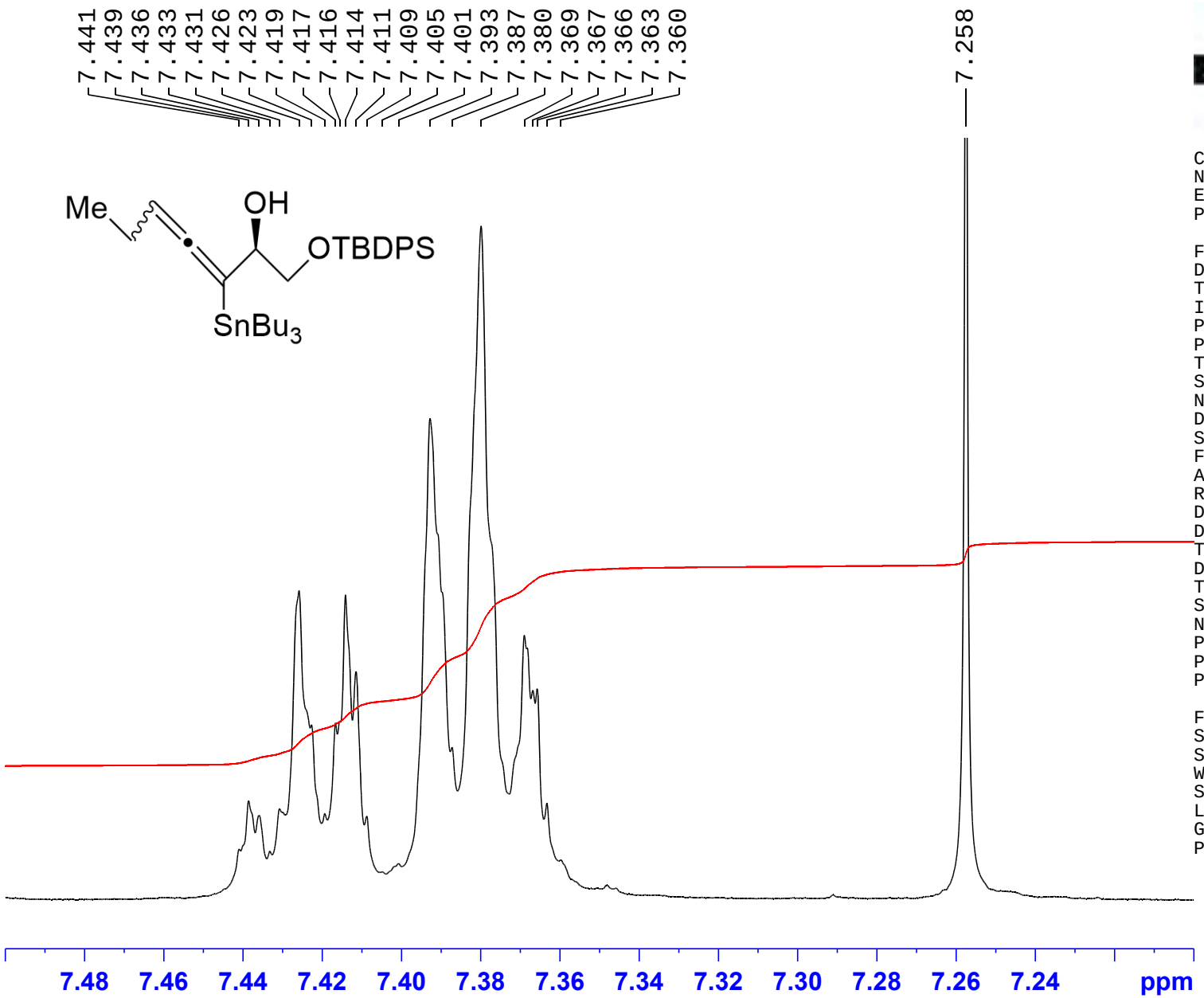
F2 - Processing parameters
SI                    262144
SF               600.1300159 MHz
WDW                       EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    1.00
```




```
Current Data Parameters
NAME                 ALLENE
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220319
Time                 14.07 h
INSTRUM               spect
PROBHD   Z114607_0188 (
PULPROG                zg30
TD                   180286
SOLVENT               CDCl3
NS                       16
DS                        0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                    55.43
DW                   27.733 usec
DE                    8.00 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                       1
SFO1           600.1337060 MHz
NUC1                    1H
P0                    3.33 usec
P1                   10.00 usec
PLW1           26.60000038 W

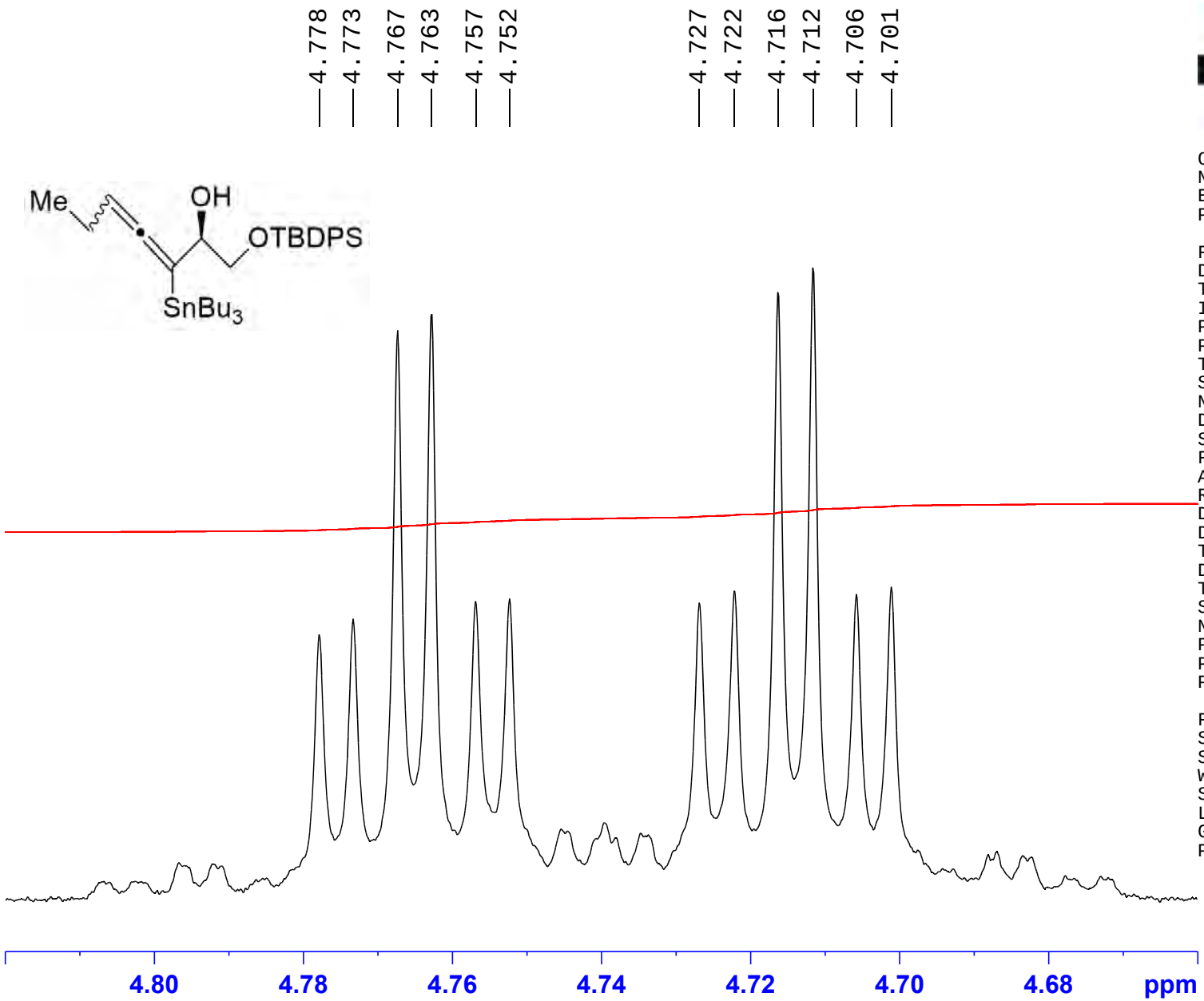
F2 - Processing parameters
SI                   262144
SF             600.1300159 MHz
WDW                     EM
SSB          0
LB                    0.10 Hz
GB           0
PC                    1.00
```



Current Data Parameters
NAME ALLENE
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220319
Time 14.07 h
INSTRUM spect
PROBHD Z114607_0188 (
PULPROG zg30
TD 180286
SOLVENT CDCl3
NS 16
DS 0
SWH 18028.846 Hz
FIDRES 0.200003 Hz
AQ 4.9999318 sec
RG 55.43
DW 27.733 usec
DE 8.00 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
SFO1 600.1337060 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
PLW1 26.60000038 W

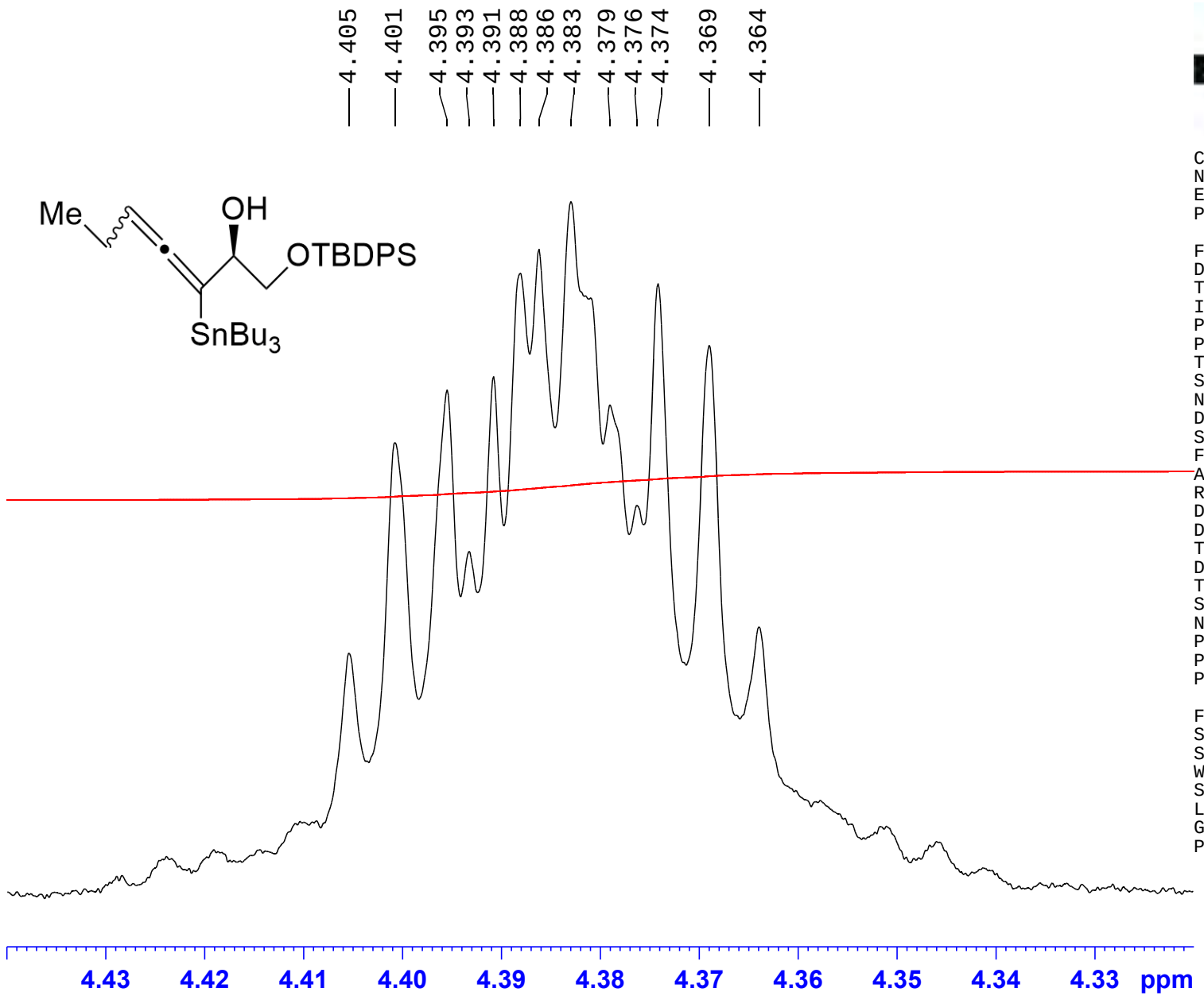
F2 - Processing parameters
SI 262144
SF 600.1300159 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00




```
Current Data Parameters
NAME                 ALLENE
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220319
Time                 14.07 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                zg30
TD                   180286
SOLVENT               CDCl3
NS                       16
DS                        0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                    55.43
DW                   27.733 usec
DE                    8.00 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                       1
SFO1           600.1337060 MHz
NUC1                    1H
P0                    3.33 usec
P1                   10.00 usec
PLW1           26.60000038 W

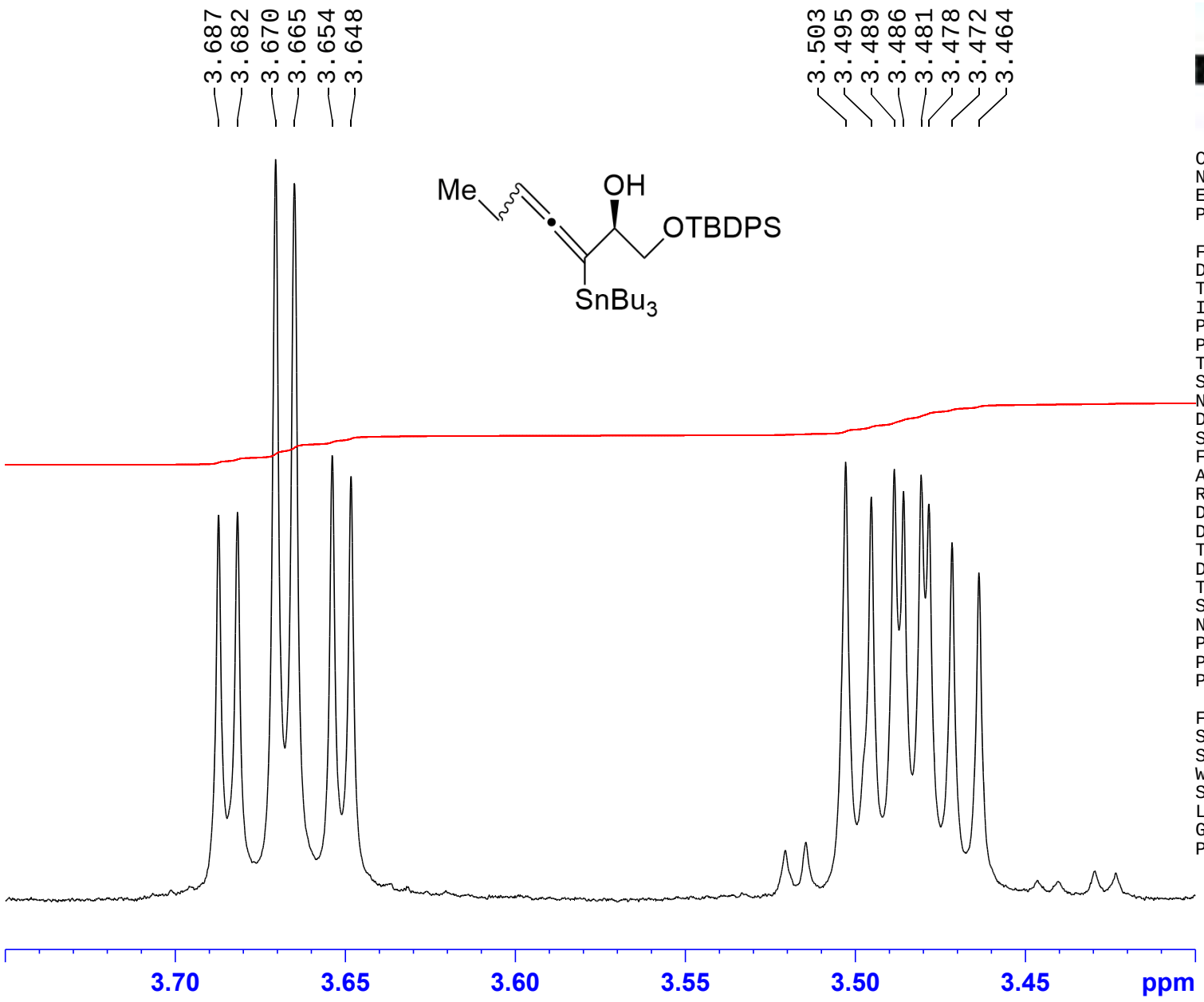
F2 - Processing parameters
SI                   262144
SF             600.1300159 MHz
WDW                      EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    1.00
```




```
Current Data Parameters
NAME                  ALLENE
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20220319
Time                  14.07 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                zg30
TD                   180286
SOLVENT               CDCl3
NS                        16
DS                         0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                    55.43
DW                  27.733 usec
DE                   8.00 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                        1
SFO1           600.1337060 MHz
NUC1                      1H
P0                   3.33 usec
P1                  10.00 usec
PLW1           26.60000038 W

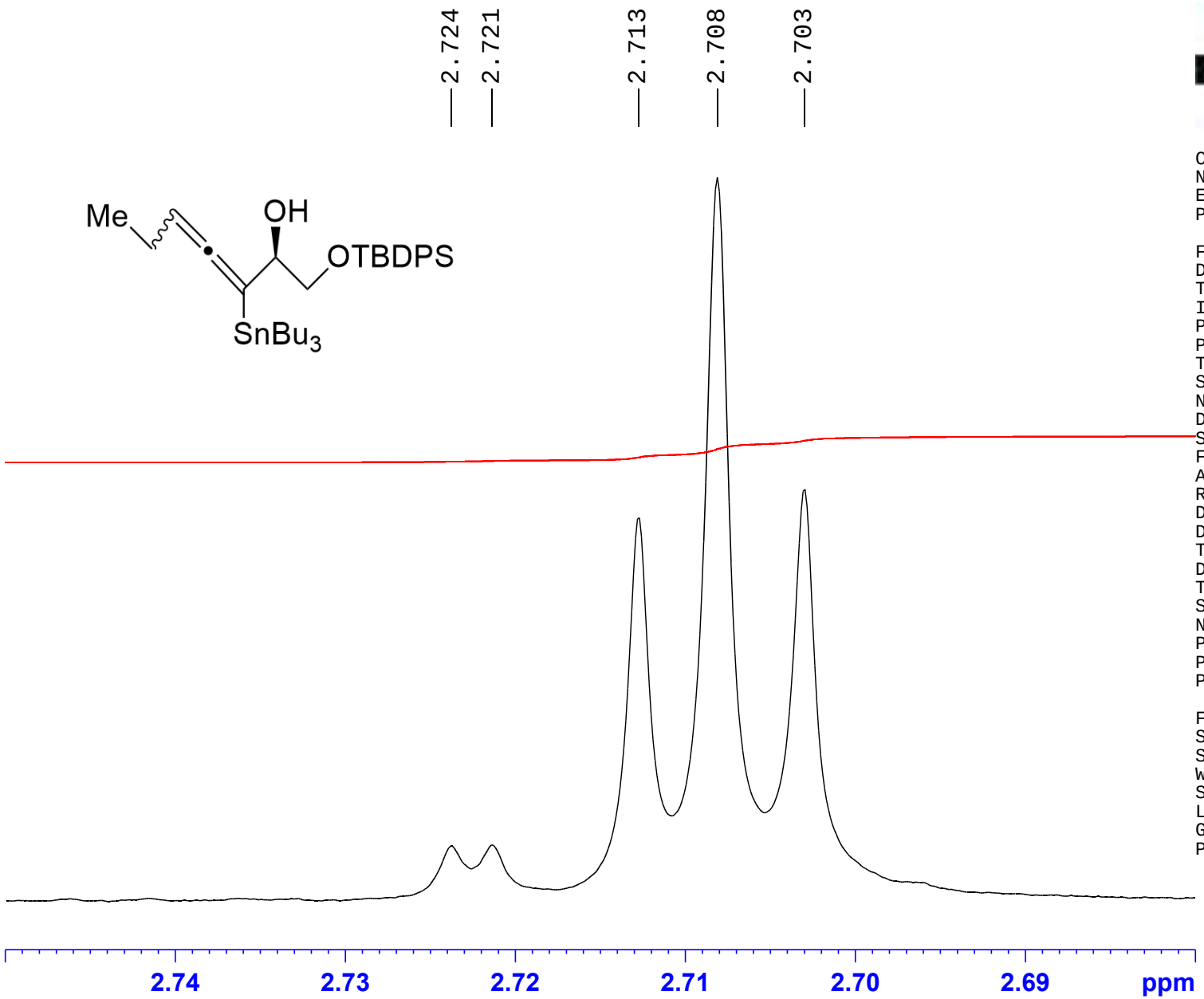
F2 - Processing parameters
SI                    262144
SF             600.1300159 MHz
WDW                       EM
SSB       0
LB                   0.10 Hz
GB        0
PC                    1.00
```




```
Current Data Parameters
NAME                  ALLENE
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20220319
Time                  14.07 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                zg30
TD                   180286
SOLVENT               CDCl3
NS                        16
DS                         0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                    55.43
DW                   27.733 usec
DE                    8.00 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                        1
SFO1           600.1337060 MHz
NUC1                      1H
P0                    3.33 usec
P1                   10.00 usec
PLW1           26.60000038 W

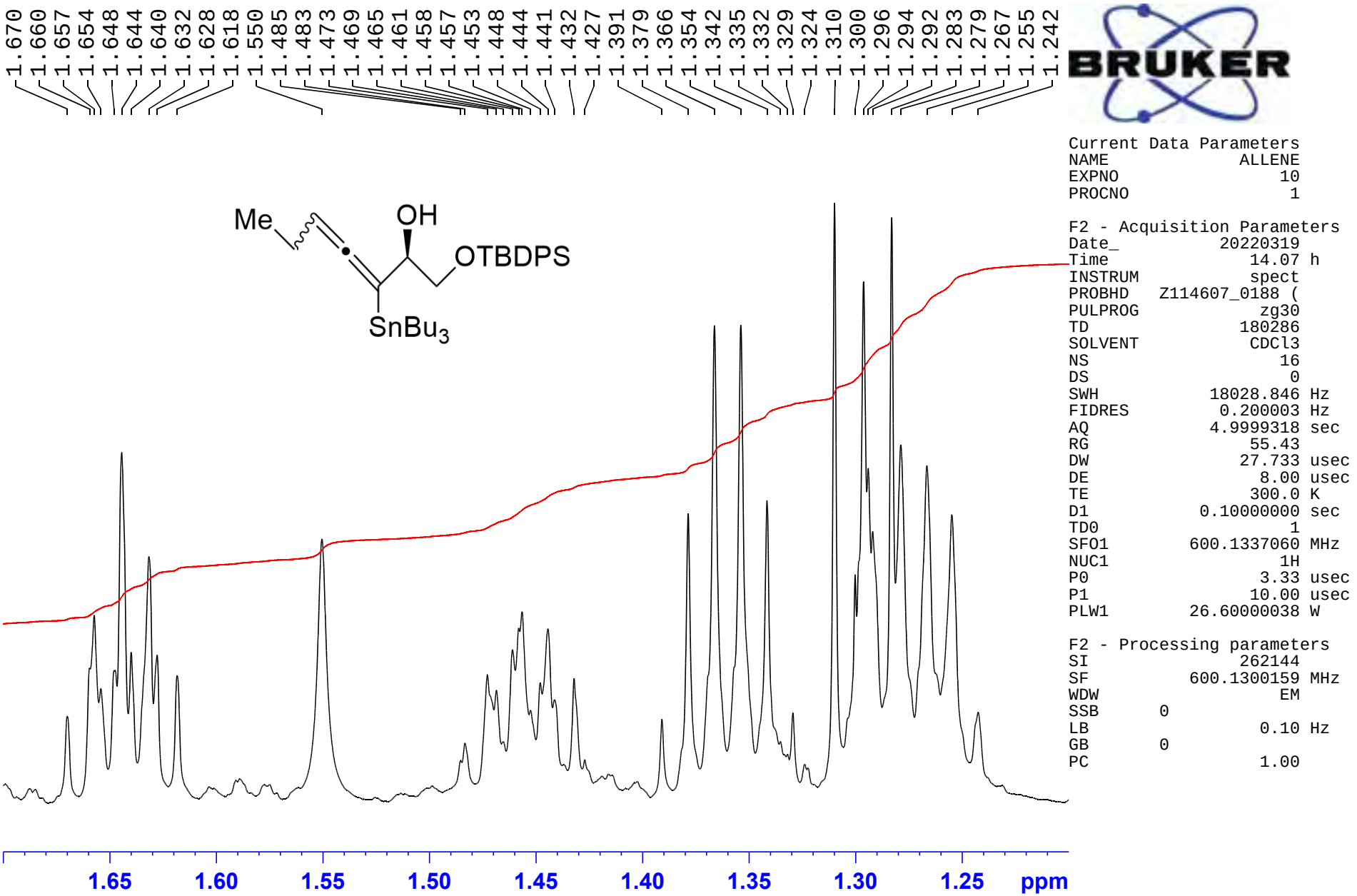
F2 - Processing parameters
SI                    262144
SF             600.1300159 MHz
WDW                       EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    1.00
```




```
Current Data Parameters
NAME                 ALLENE
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220319
Time                 14.07 h
INSTRUM                spect
PROBHD   Z114607_0188 (
PULPROG                zg30
TD                   180286
SOLVENT               CDCl3
NS                       16
DS                        0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                    55.43
DW                  27.733 usec
DE                   8.00 usec
TE                  300.0 K
D1              0.10000000 sec
TD0                       1
SFO1           600.1337060 MHz
NUC1                     1H
P0                   3.33 usec
P1                  10.00 usec
PLW1           26.60000038 W

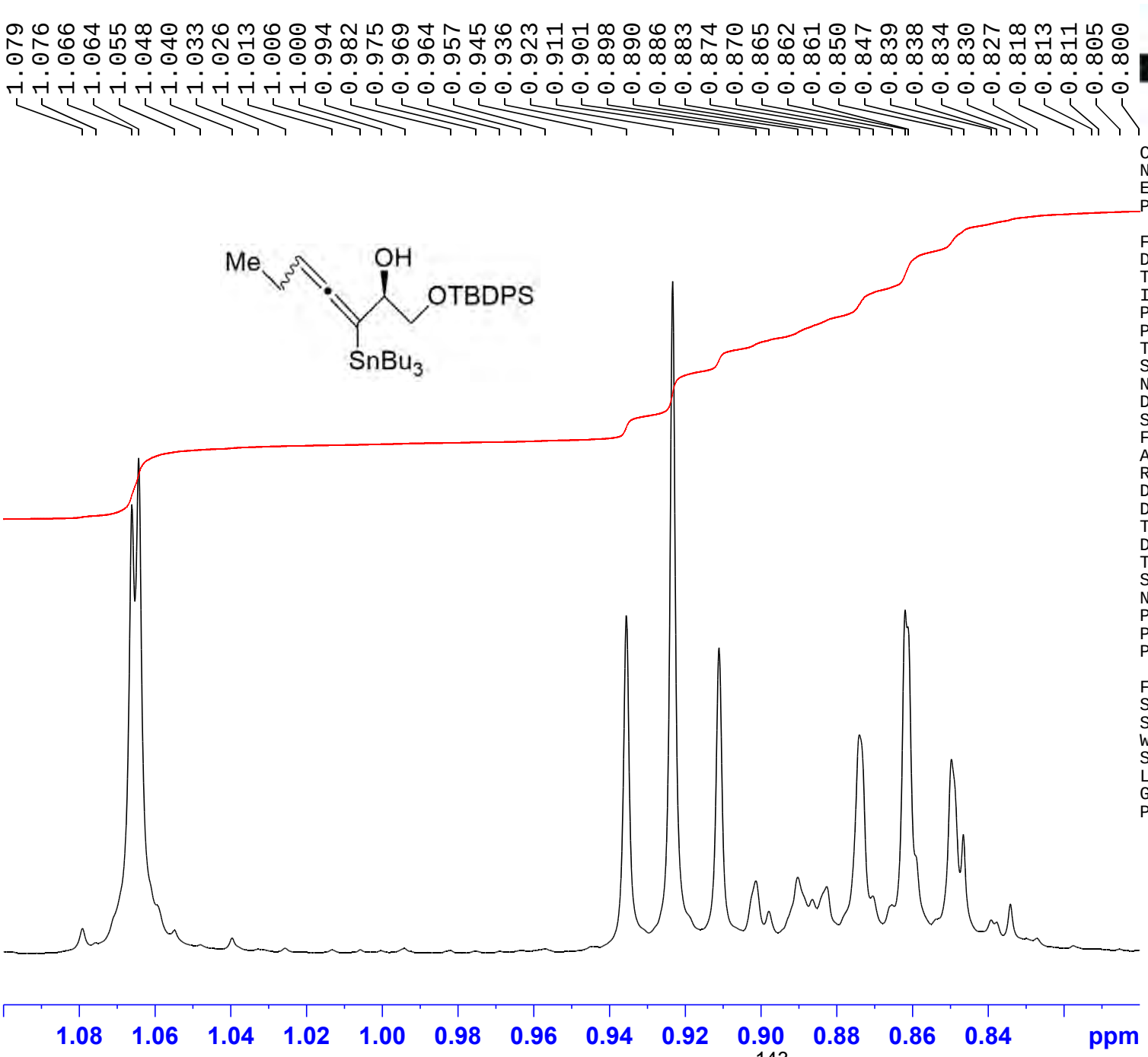
F2 - Processing parameters
SI                   262144
SF             600.1300159 MHz
WDW                      EM
SSB       0
LB                   0.10 Hz
GB        0
PC                   1.00
```




```
Current Data Parameters
NAME                 ALLENE
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220319
Time                 14.07 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                zg30
TD                   180286
SOLVENT               CDCl3
NS                       16
DS                        0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                    55.43
DW                   27.733 usec
DE                    8.00 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                       1
SFO1           600.1337060 MHz
NUC1                    1H
P0                    3.33 usec
P1                   10.00 usec
PLW1           26.60000038 W

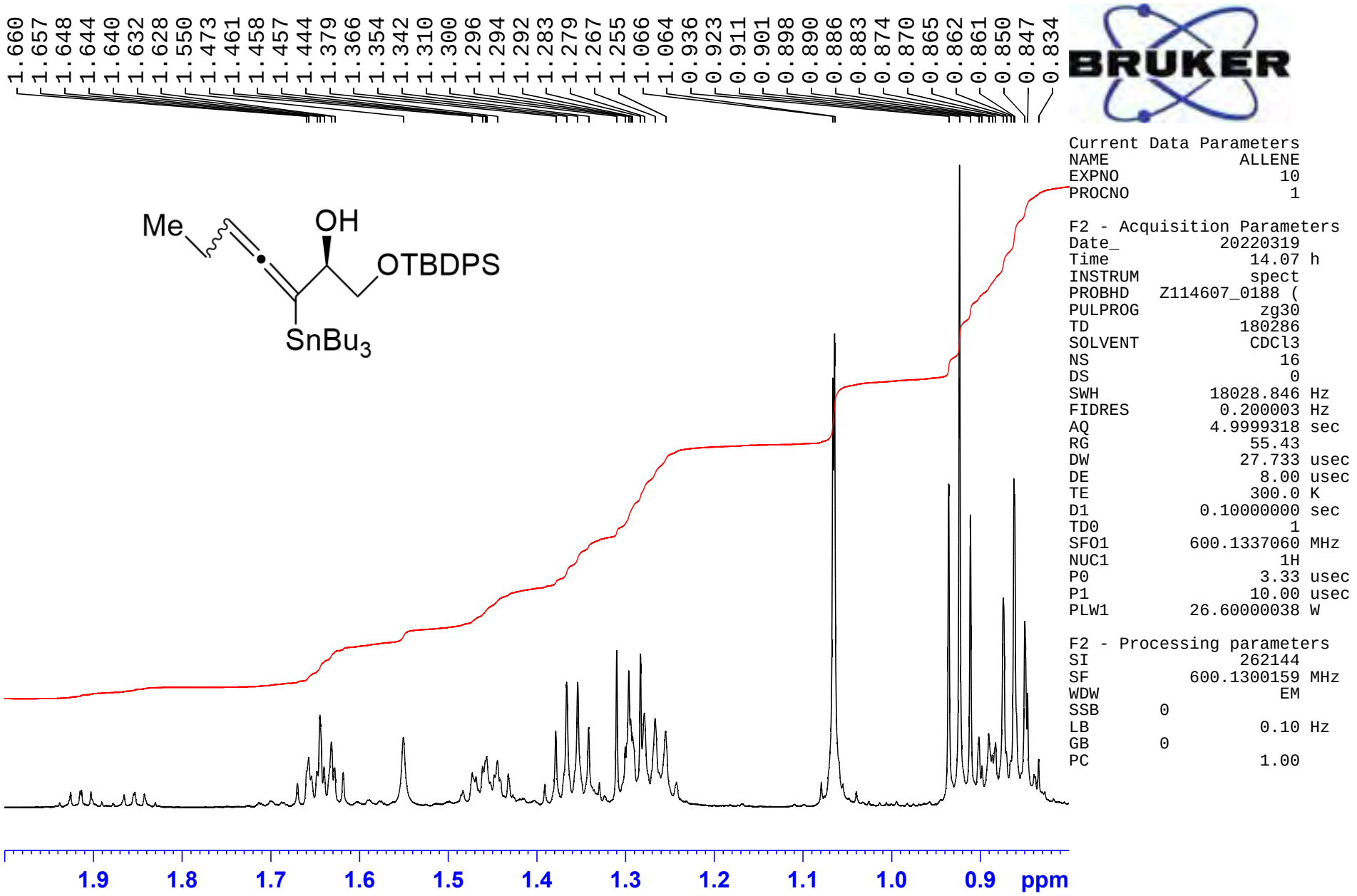
F2 - Processing parameters
SI                   262144
SF             600.1300159 MHz
WDW                      EM
SSB          0
LB                    0.10 Hz
GB           0
PC                    1.00
```




```
Current Data Parameters
NAME                 ALLENE
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220319
Time                 14.07 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                zg30
TD                   180286
SOLVENT               CDCl3
NS                       16
DS                        0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                    55.43
DW                   27.733 usec
DE                    8.00 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                       1
SFO1           600.1337060 MHz
NUC1                    1H
P0                    3.33 usec
P1                   10.00 usec
PLW1           26.60000038 W

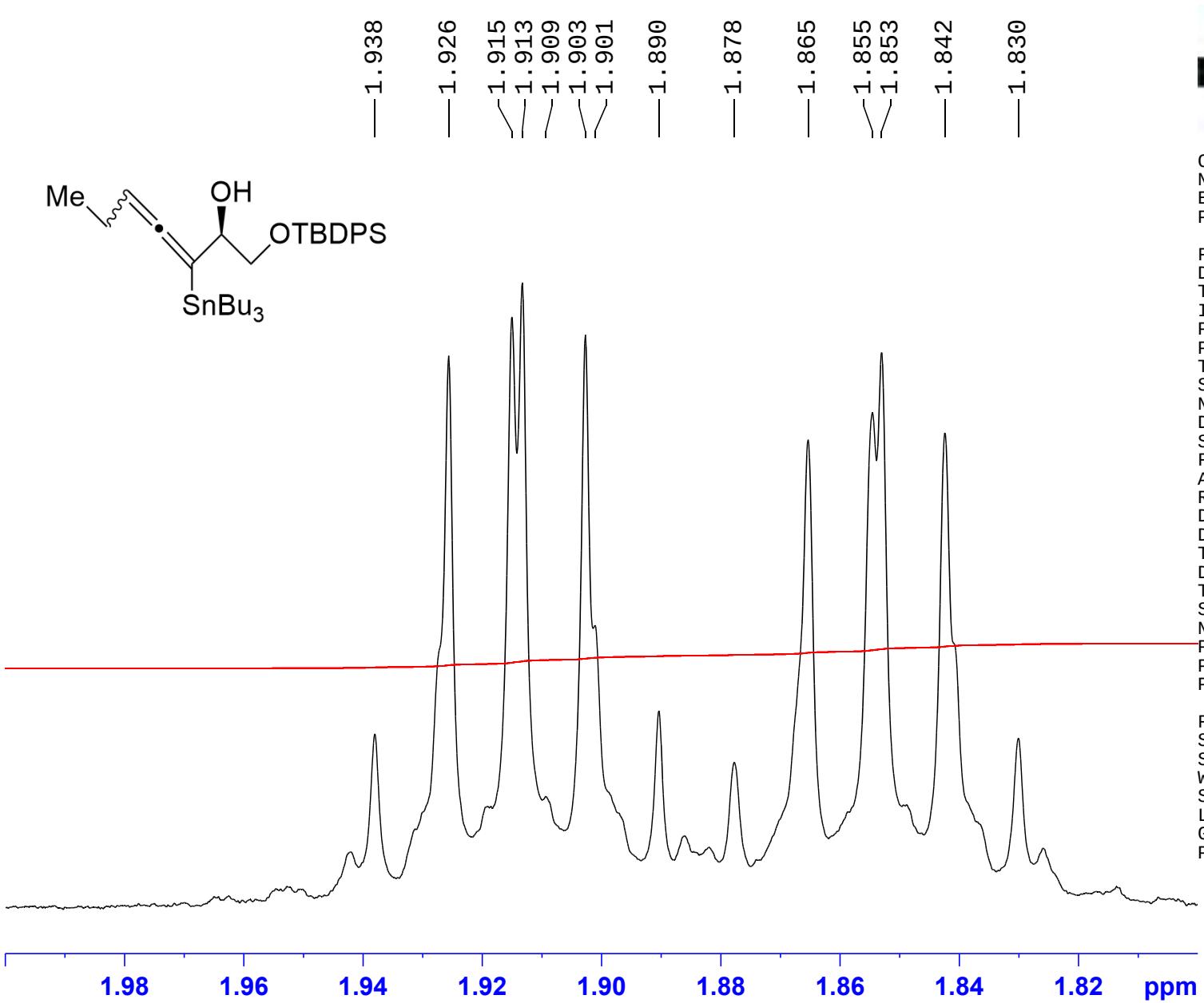
F2 - Processing parameters
SI                   262144
SF             600.1300159 MHz
WDW                     EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    1.00
```




```
Current Data Parameters
NAME                  ALLENE
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20220319
Time                  14.07 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                zg30
TD                   180286
SOLVENT               CDCl3
NS                        16
DS                         0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                    55.43
DW                   27.733 usec
DE                    8.00 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                        1
SFO1           600.1337060 MHz
NUC1                      1H
P0                    3.33 usec
P1                   10.00 usec
PLW1           26.60000038 W

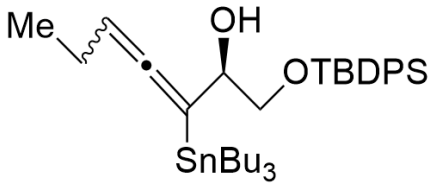
F2 - Processing parameters
SI                    262144
SF               600.1300159 MHz
WDW                       EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    1.00
```




```
Current Data Parameters
NAME                 ALLENE
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220319
Time                 14.07 h
INSTRUM              spect
PROBHD    Z114607_0188 (
PULPROG              zg30
TD                 180286
SOLVENT              CDCl3
NS                      16
DS                       0
SWH              18028.846 Hz
FIDRES            0.200003 Hz
AQ                4.9999318 sec
RG                   55.43
DW                  27.733 usec
DE                   8.00 usec
TE                  300.0 K
D1              0.10000000 sec
TD0                      1
SFO1           600.1337060 MHz
NUC1                    1H
P0                   3.33 usec
P1                  10.00 usec
PLW1           26.60000038 W

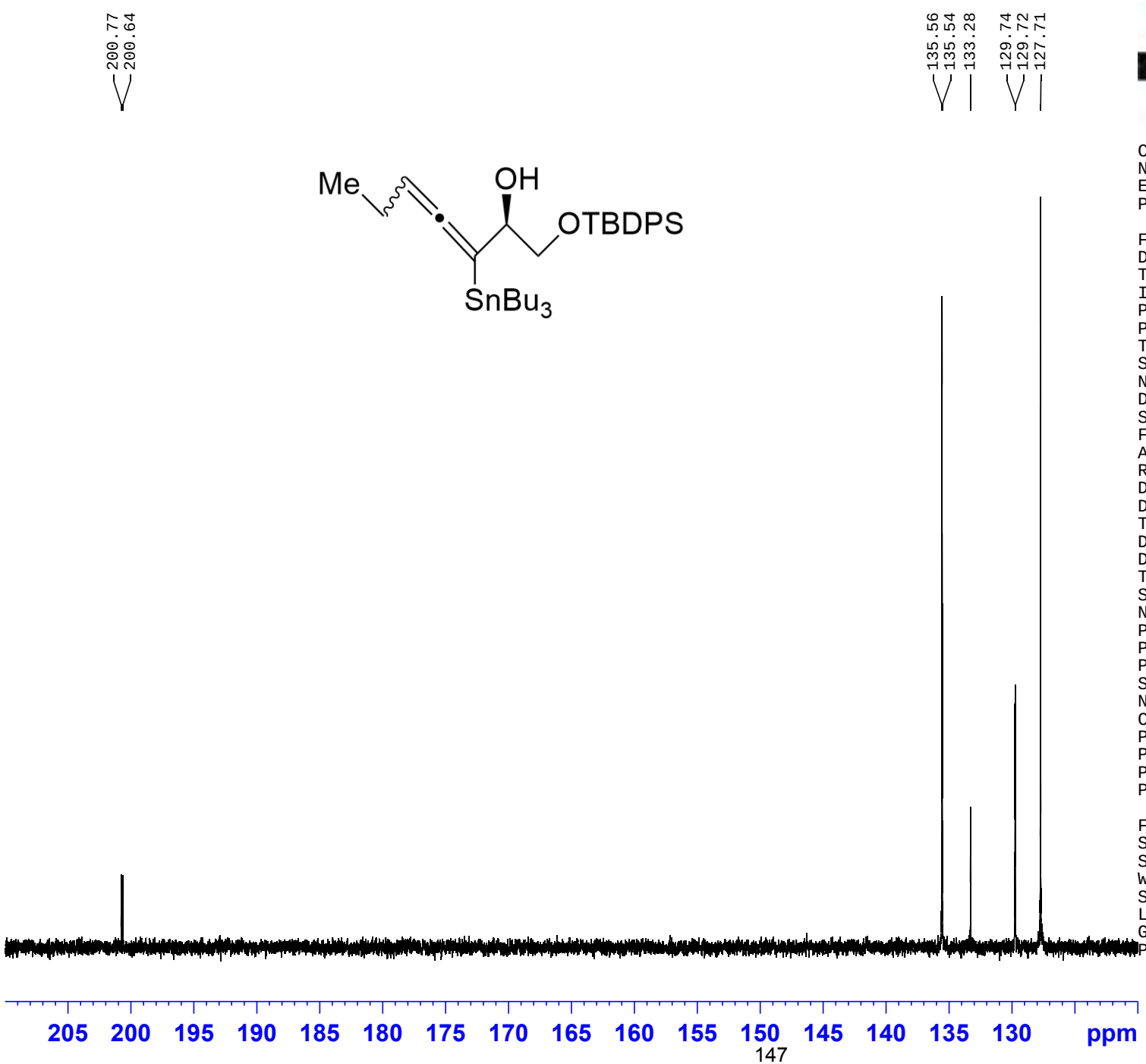
F2 - Processing parameters
SI                  262144
SF             600.1300159 MHz
WDW                     EM
SSB       0
LB                   0.10 Hz
GB        0
PC                   1.00
```




```
Current Data Parameters
NAME                  ALLENE
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_               20220319
Time                   15.36 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG               zgpg30
TD                    119044
SOLVENT                CDCl3
NS                      2000
DS                         4
SWH               37500.000 Hz
FIDRES             0.630019 Hz
AQ                1.5872533 sec
RG                   186.92
DW                   13.333 usec
DE                     6.53 usec
TE                    300.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                        1
SFO1           150.9194058 MHz
NUC1                    13C
P0                    3.93 usec
P1                   11.80 usec
PLW1           85.00000000 W
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2            waltz64
PCPD2                 70.00 usec
PLW2           27.00000000 W
PLW12           0.57327998 W
PLW13           0.28836000 W

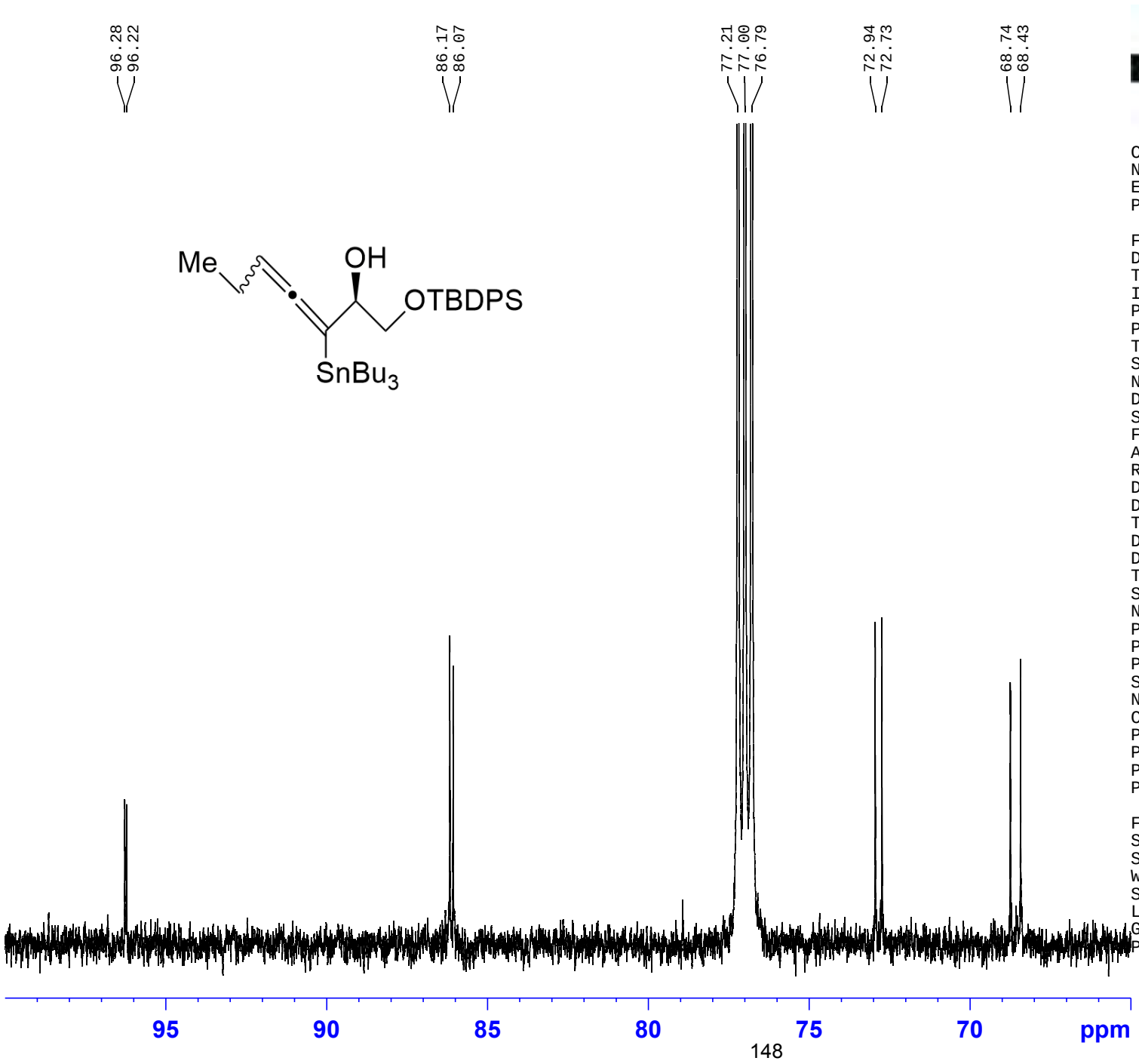
F2 - Processing parameters
SI                    131072
SF             150.9028116 MHz
WDW                       EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```



Current Data Parameters
NAME ALLENE
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220319
Time 15.36 h
INSTRUM spect
PROBHD Z114607_0188 (
PULPROG zgpg30
TD 119044
SOLVENT CDCl3
NS 2000
DS 4
SWH 37500.000 Hz
FIDRES 0.630019 Hz
AQ 1.5872533 sec
RG 186.92
DW 13.333 usec
DE 6.53 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9194058 MHz
NUC1 13C
P0 3.93 usec
P1 11.80 usec
PLW1 85.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz64
PCPD2 70.00 usec
PLW2 27.00000000 W
PLW12 0.57327998 W
PLW13 0.28836000 W

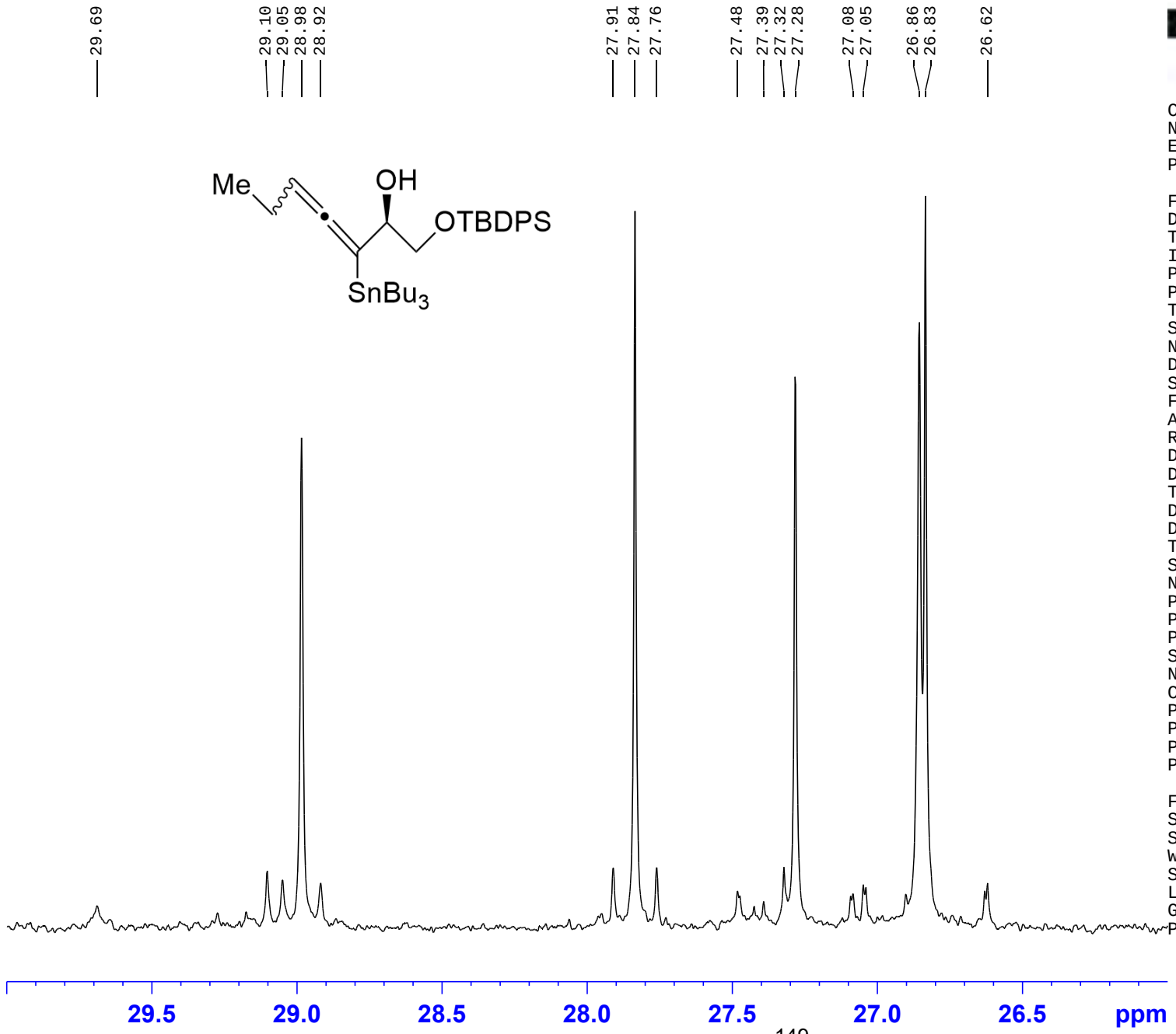
F2 - Processing parameters
SI 131072
SF 150.9028116 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
Current Data Parameters
NAME                 ALLENE
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220319
Time                 15.36 h
INSTRUM                spect
PROBHD   Z114607_0188 (
PULPROG              zgpg30
TD                   119044
SOLVENT               CDCl3
NS                     2000
DS                        4
SWH              37500.000 Hz
FIDRES            0.630019 Hz
AQ                1.5872533 sec
RG                   186.92
DW                   13.333 usec
DE                     6.53 usec
TE                    300.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1           150.9194058 MHz
NUC1                    13C
P0                    3.93 usec
P1                   11.80 usec
PLW1           85.00000000 W
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2            waltz64
PCPD2                70.00 usec
PLW2           27.00000000 W
PLW12           0.57327998 W
PLW13           0.28836000 W

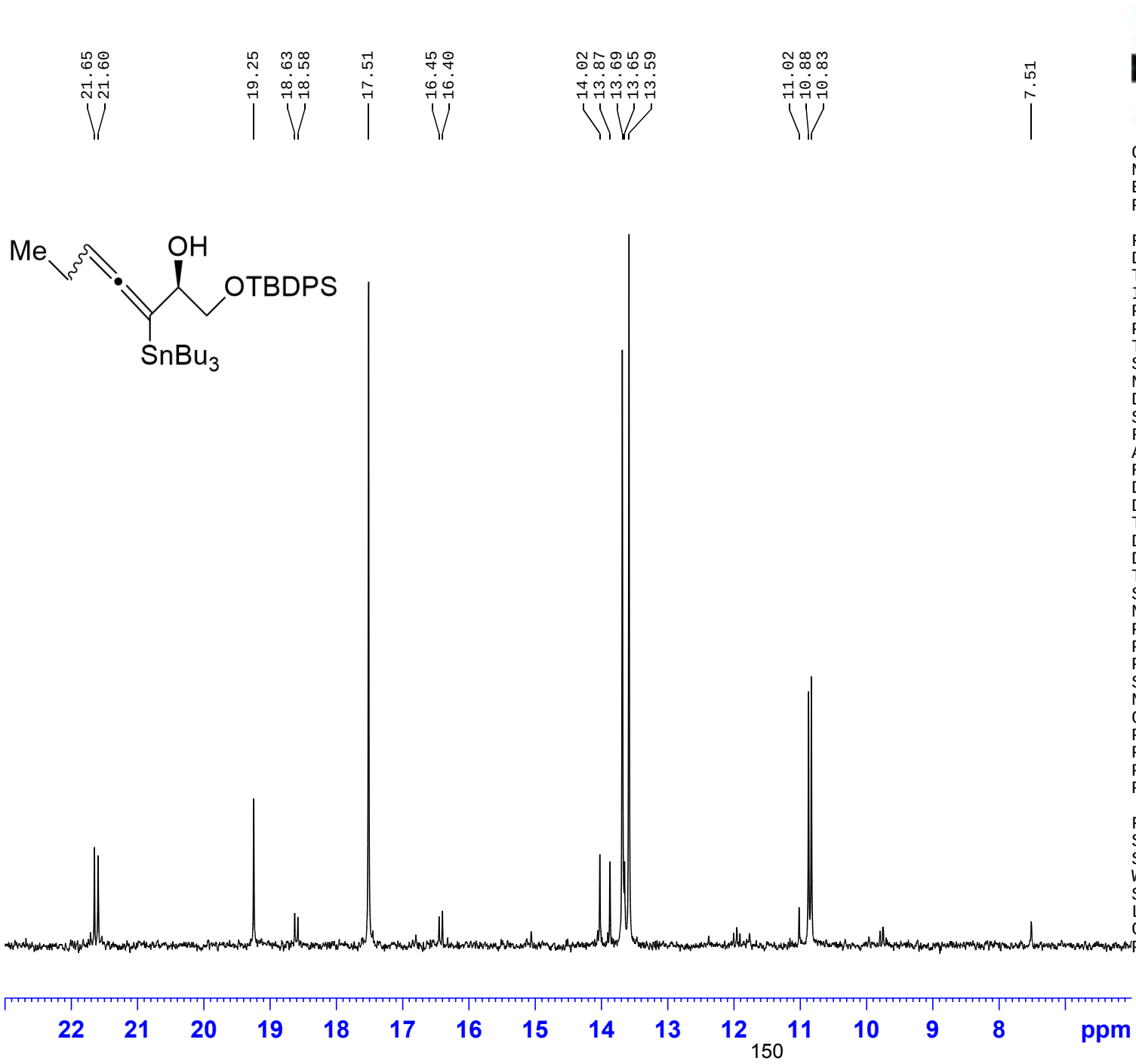
F2 - Processing parameters
SI                   131072
SF             150.9028116 MHz
WDW                      EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```




```
Current Data Parameters
NAME                 ALLENE
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220319
Time                 15.36 h
INSTRUM               spect
PROBHD    Z114607_0188 (
PULPROG              zgpg30
TD                   119044
SOLVENT               CDCl3
NS                     2000
DS                        4
SWH              37500.000 Hz
FIDRES            0.630019 Hz
AQ                1.5872533 sec
RG                   186.92
DW                   13.333 usec
DE                     6.53 usec
TE                    300.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                       1
SFO1           150.9194058 MHz
NUC1                   13C
P0                    3.93 usec
P1                   11.80 usec
PLW1           85.00000000 W
SFO2           600.1324005 MHz
NUC2                   1H
CPDPRG[2           waltz64
PCPD2                70.00 usec
PLW2           27.00000000 W
PLW12           0.57327998 W
PLW13           0.28836000 W

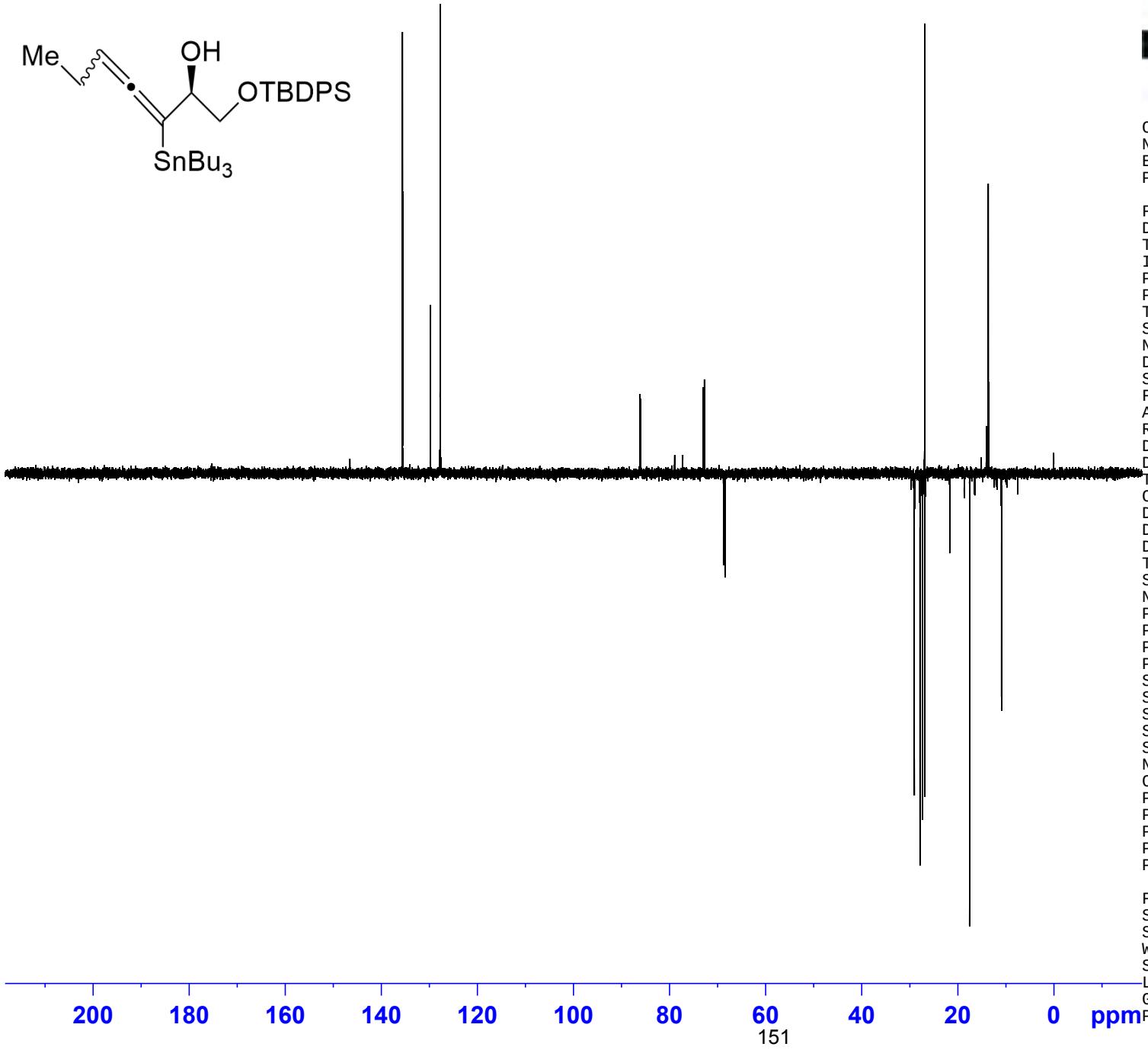
F2 - Processing parameters
SI                   131072
SF             150.9028116 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```




```
Current Data Parameters
NAME                  ALLENE
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_               20220319
Time                  15.36 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG               zgpg30
TD                    119044
SOLVENT                CDCl3
NS                      2000
DS                         4
SWH              37500.000 Hz
FIDRES            0.630019 Hz
AQ                1.5872533 sec
RG                   186.92
DW                   13.333 usec
DE                     6.53 usec
TE                    300.0 K
D1               1.00000000 sec
D11              0.03000000 sec
TD0                        1
SFO1           150.9194058 MHz
NUC1                    13C
P0                    3.93 usec
P1                   11.80 usec
PLW1            85.00000000 W
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2            waltz64
PCPD2                 70.00 usec
PLW2            27.00000000 W
PLW12            0.57327998 W
PLW13            0.28836000 W

F2 - Processing parameters
SI                    131072
SF             150.9028116 MHz
WDW                       EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```



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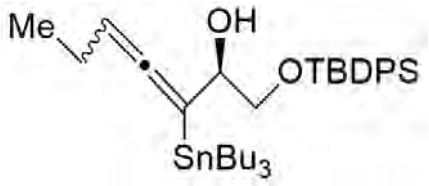
```
Current Data Parameters
NAME              ALLENE
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220319
Time               16.21 h
INSTRUM             spect
PROBHD   Z114607_0188 (
PULPROG      deptsp135.b
TD                119044
SOLVENT            CDCl3
NS                  1000
DS                     4
SWH            35714.285 Hz
FIDRES          0.600018 Hz
AQ             1.6666160 sec
RG                186.92
DW                14.000 usec
DE                 7.44 usec
TE                300.0 K
CNST2         145.0000000
D1             1.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1
SFO1          150.9178962 MHz
NUC1                  13C
P1                 11.80 usec
P13              2000.00 usec
PLW0      0 W
PLW1          85.00000000 W
SPNAM[5]      Crp60comp.4
SPOAL5              0.500
SPOFFS5   0 Hz
SPW5          18.08300018 W
SFO2          600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz64
P3                 10.20 usec
P4                 20.40 usec
PCPD2              70.00 usec
PLW2          27.00000000 W
PLW12          0.57327998 W

F2 - Processing parameters
SI                131072
SF          150.9028085 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



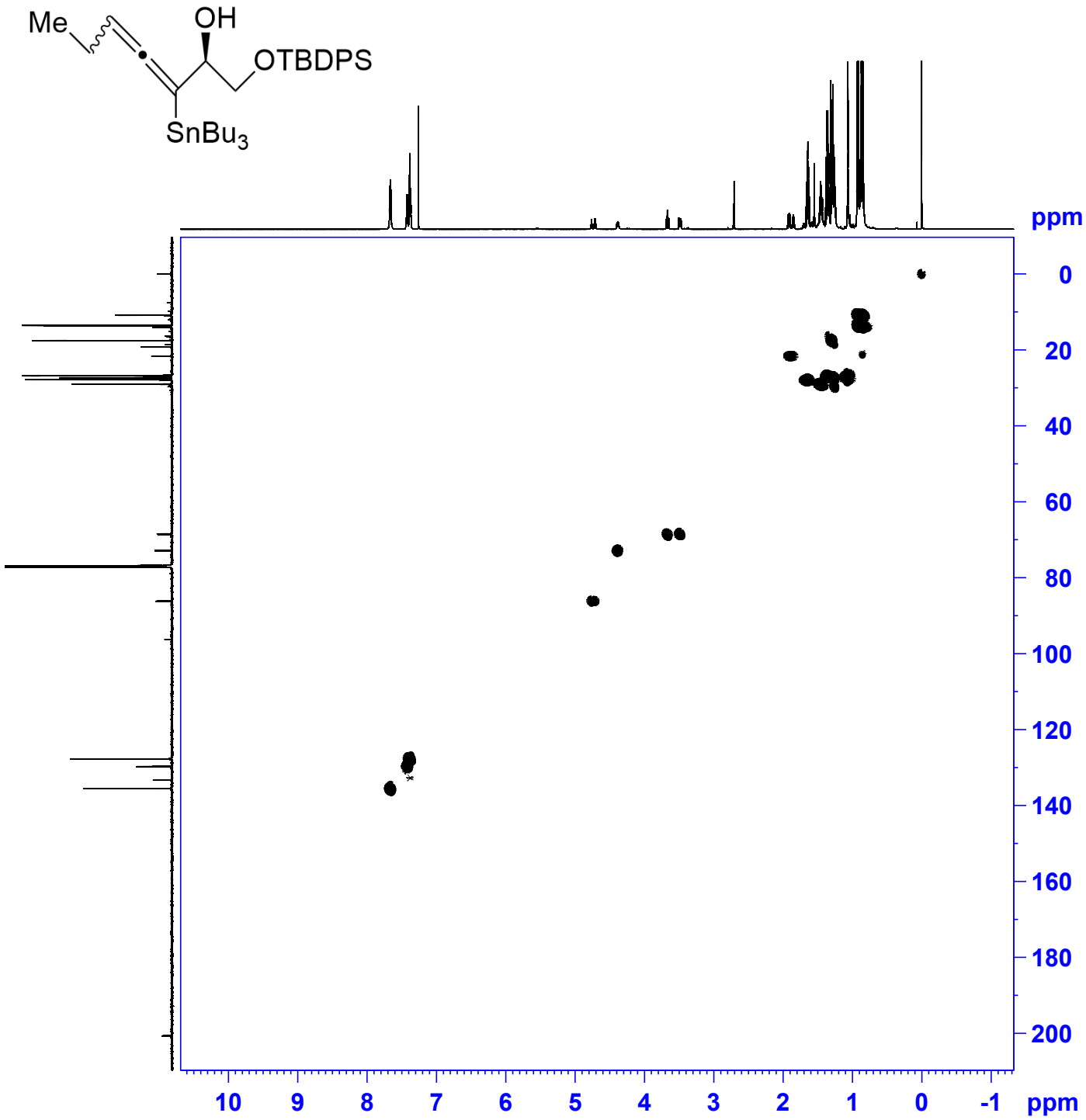

```
Current Data Parameters
NAME                 ALLENE
EXPNO                    13
PROCNO                    1

F2 - Acquisition Parameters
Date_              20220319
Time                 16.32 h
INSTRUM                spect
PROBHD   Z114607_0188 (
PULPROG    cosygpmfppqf
TD                     2048
SOLVENT             CDCl3
NS                        2
DS                        8
SWH               5514.706 Hz
FIDRES            5.385455 Hz
AQ               0.1856853 sec
RG                   186.92
DW                   90.667 usec
DE                     6.50 usec
TE                    300.0 K
D0               0.00000300 sec
D1               0.87302327 sec
D11              0.03000000 sec
D12              0.00002000 sec
D13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00018160 sec
TDav                      1
SFO1           600.1325169 MHz
NUC1                   1H
P1                    10.00 usec
P17                 2500.00 usec
PLW1           26.60000038 W
PLW10           4.25600004 W
GPNAM[1]       SMSQ10.100
GPZ1                  16.00 %
GPNAM[2]       SMSQ10.100
GPZ2                  12.00 %
GPNAM[3]       SMSQ10.100
GPZ3                  40.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                       256
SFO1              600.1325 MHz
FIDRES           43.020374 Hz
SW                    9.176 ppm
FnMODE                   QF

F2 - Processing parameters
SI                       1024
SF             600.1300139 MHz
WDW                    SINE
SSB          0
LB           0 Hz
GB           0
PC                     1.40

F1 - Processing parameters
SI                       1024
MC2                        QF
SF             600.1300151 MHz
WDW                    SINE
SSB          0
LB           0 Hz
GB           0
```




```
Current Data Parameters
NAME                 ALLENE
EXPNO                    14
PROCNO                    1

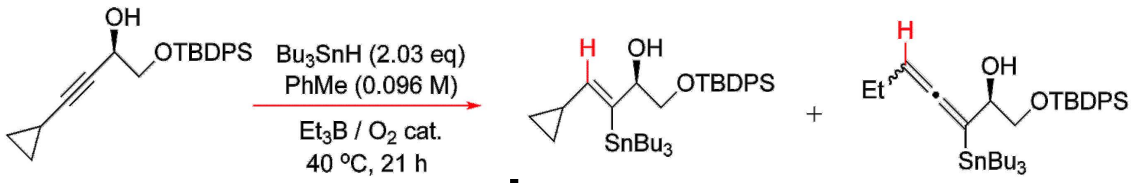
F2 - Acquisition Parameters
Date_              20220319
Time                 16.41 h
INSTRUM                spect
PROBHD   Z114607_0188 (
PULPROG  hsqcedetgpsp.3
TD                     1024
SOLVENT               CDCl3
NS                        2
DS                       32
SWH               7211.539 Hz
FIDRES           14.085036 Hz
AQ                0.0709973 sec
RG                   186.92
DW                   69.333 usec
DE                     6.50 usec
TE                    300.3 K
CNST2           145.0000000
D0               0.00000300 sec
D1               0.80000001 sec
D4               0.00172414 sec
D11              0.03000000 sec
D16              0.00020000 sec
D21              0.00360000 sec
IN0              0.00001510 sec
TDav                      1
ZGOPTNS
SFO1            600.1328223 MHz
NUC1                    1H
P1                     10.00 usec
P2                     20.00 usec
PLW1            26.60000038 W
SFO2            150.9178988 MHz
NUC2                    13C
CPDPRG[2                garp4
P3                     11.80 usec
P14                   500.00 usec
P31                  1730.00 usec
PCPD2                  60.00 usec
PLW0        0 W
PLW2           85.00000000 W
PLW12           3.28760004 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3                 0.500
SPOFFS3  0 Hz
SPW3           18.08300018 W
SPNAM[18  Crp60_xfilt.2
SPOAL18                0.500
SPOFFS18 0 Hz
SPW18           5.22629976 W
GPNAM[1]       SMSQ10.100
GPZ1                  80.00 %
GPNAM[2]       SMSQ10.100
GPZ2                  20.10 %
P16                 1000.00 usec

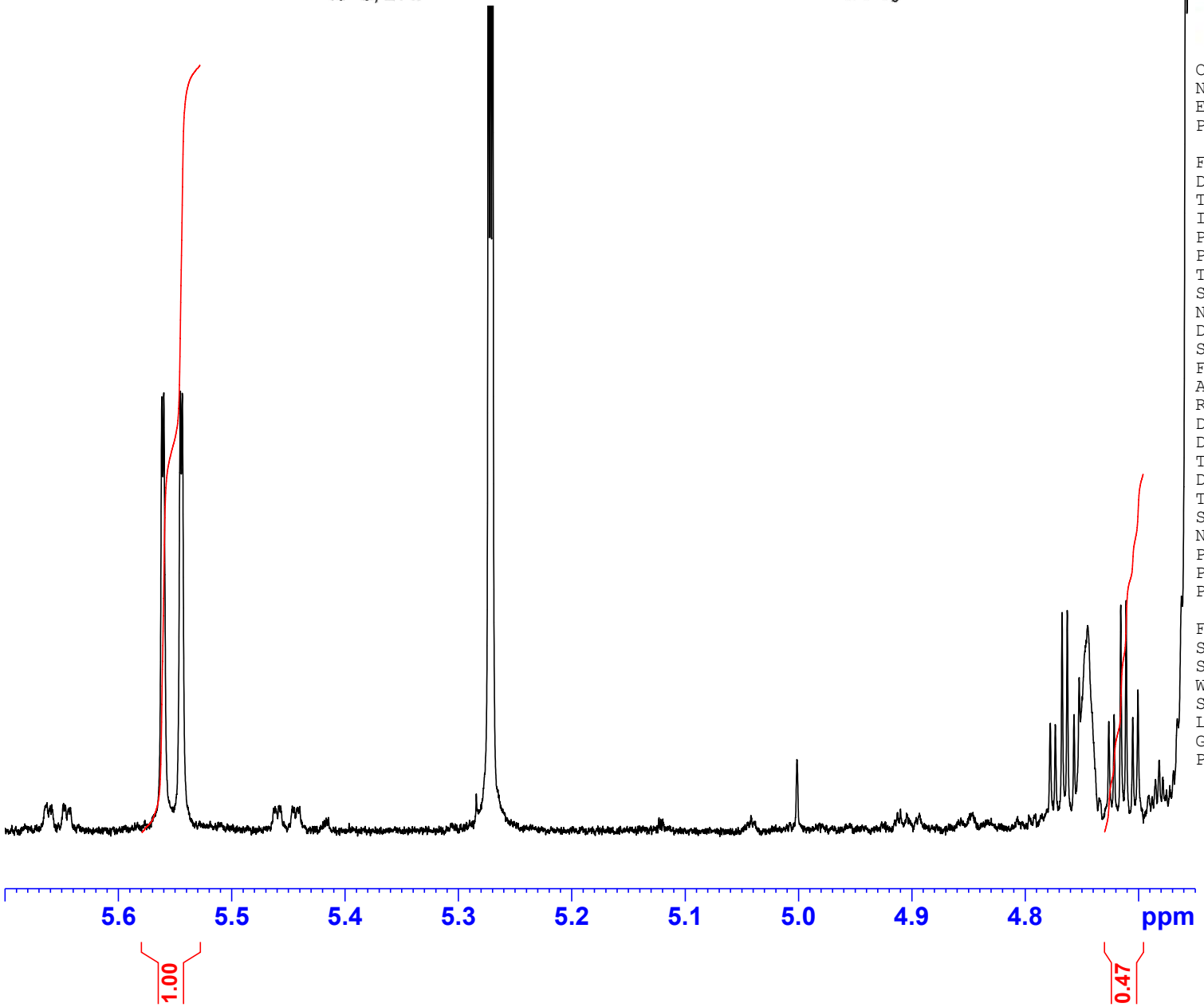
F1 - Acquisition parameters
TD                       256
SFO1              150.9179 MHz
FIDRES           258.692047 Hz
SW                  219.408 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                      1024
SF              600.1300128 MHz
WDW                    QSINE
SSB                        2
LB          0 Hz
GB          0
PC                      1.40

F1 - Processing parameters
SI                      1024
MC2          echo-antiecho
SF              150.9028016 MHz
WDW                    QSINE
SSB                        2
LB          0 Hz
GB          0
```

Part G. The 600.13 MHz ^{1}H NMR Ratio Determinations For the Tributylstannylallene 15 and Tributylstannylvinyltin 16 in $CDCl_3$ Over the 313 K-353 K Temperature Range

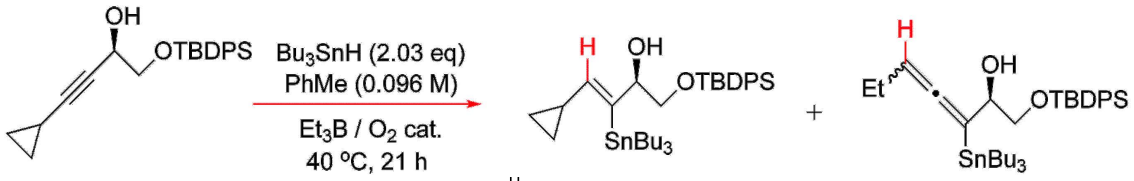


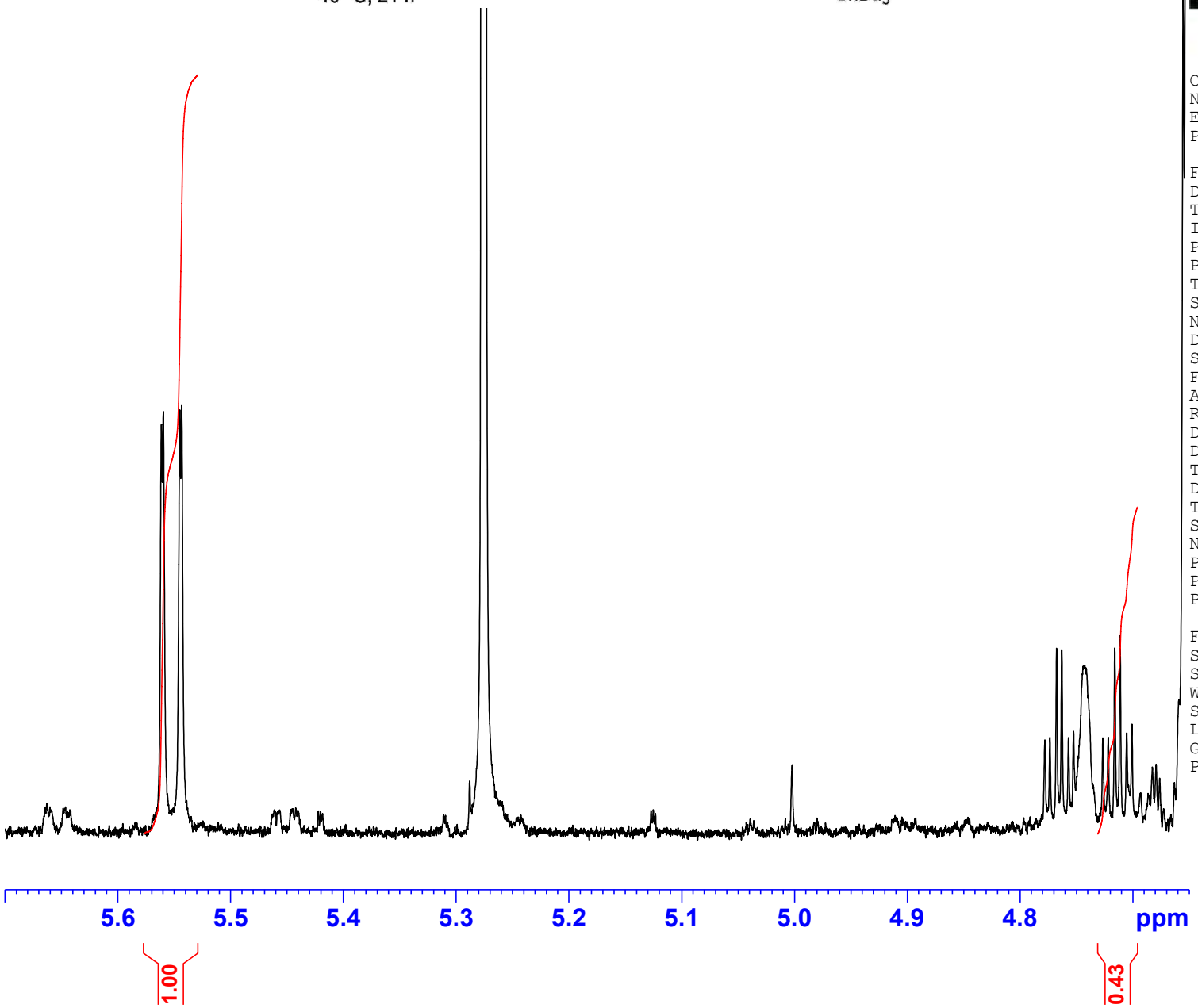



```
Current Data Parameters
NAME       LH-I-89 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220504
Time              12.07 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH           18028.846 Hz
FIDRES         0.200003 Hz
AQ            4.9999318 sec
RG                 22.13
DW               27.733 usec
DE                8.00 usec
TE               300.0 K
D1           0.10000000 sec
TD0                    1
SFO1        600.1337060 MHz
NUC1                1H
P0                3.33 usec
P1               10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300205 MHz
WDW                 EM
SSB                    0
LB                0.10 Hz
GB                     0
PC                1.00
```

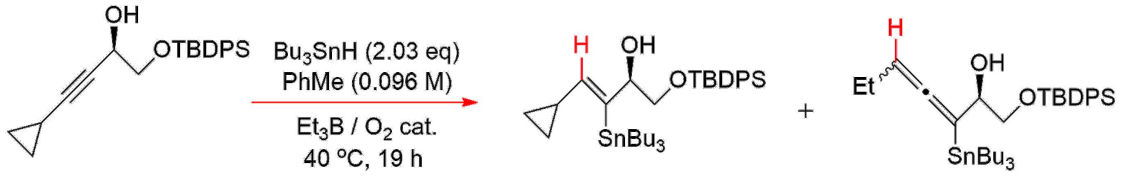


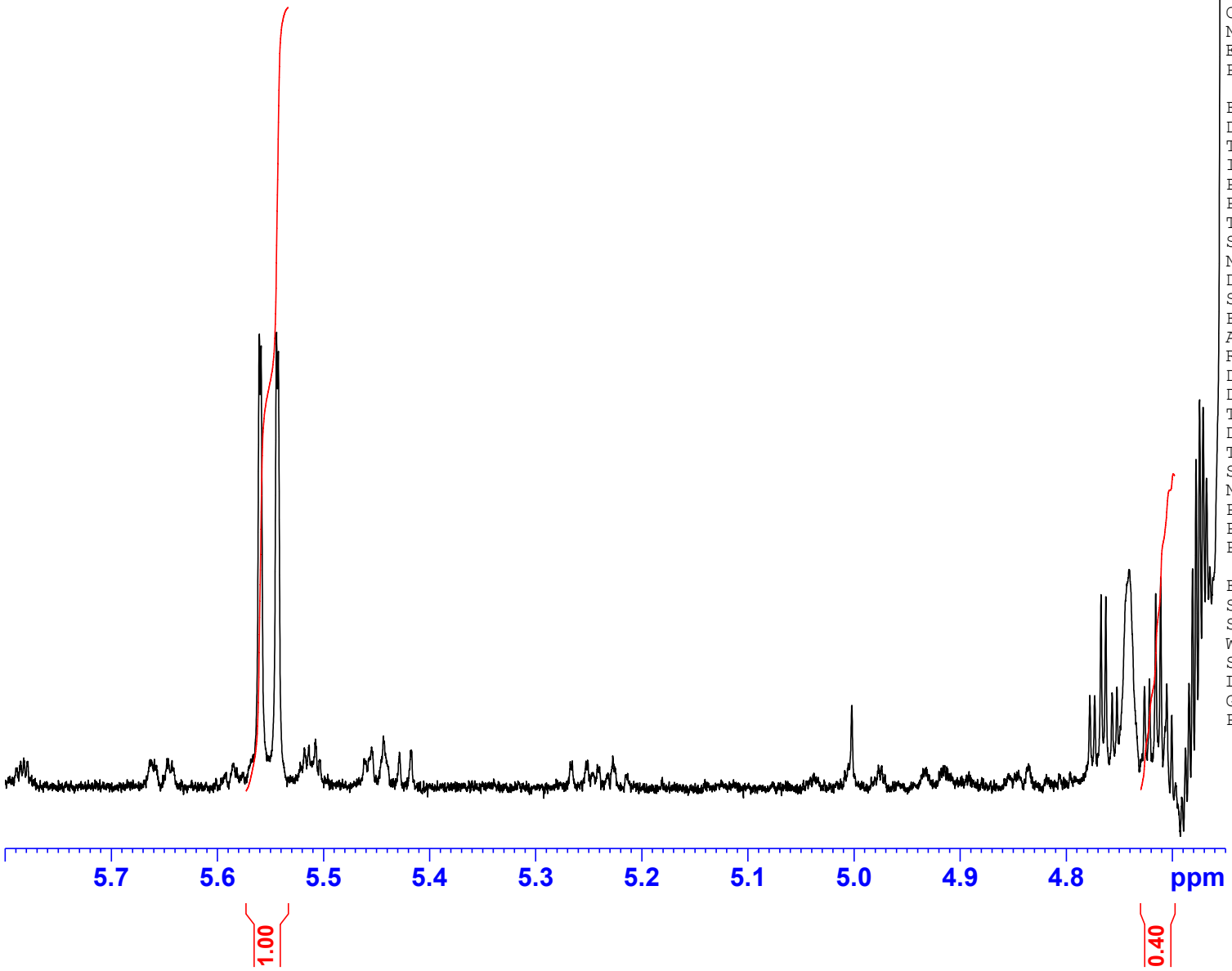



```
Current Data Parameters
NAME       LH-I-90 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220504
Time              12.15 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    16
DS                     0
SWH           18028.846 Hz
FIDRES         0.200003 Hz
AQ            4.9999318 sec
RG                 27.87
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1
SFO1        600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300186 MHz
WDW                 EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```

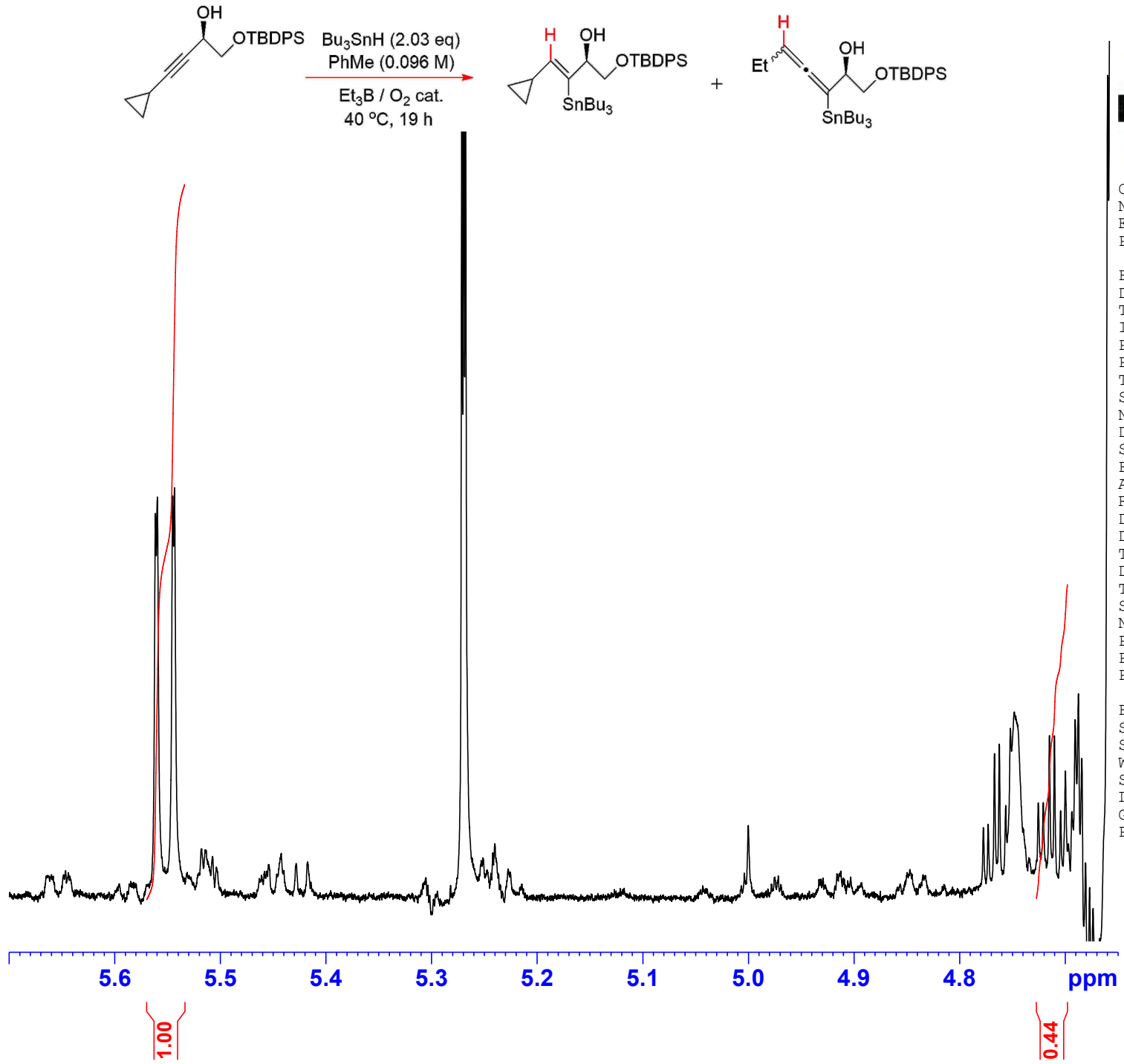





```
Current Data Parameters
NAME       LH-I-93 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220519
Time               15.05 h
INSTRUM             spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            18028.846 Hz
FIDRES          0.200003 Hz
AQ             4.9999318 sec
RG                 31.58
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1             0.10000000 sec
TD0                    1
SFO1         600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1         26.60000038 W

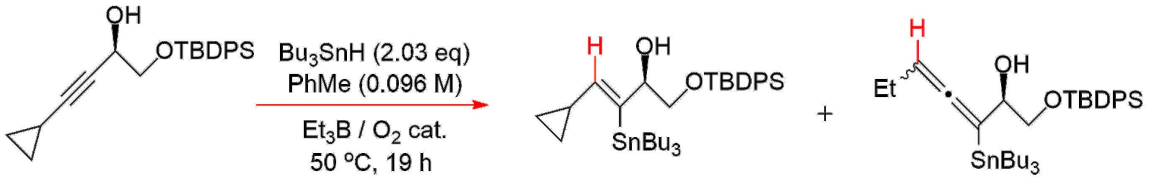
F2 - Processing parameters
SI                262144
SF         600.1300178 MHz
WDW                 EM
SSB                    0
LB                 0.10 Hz
GB                     0
PC                 1.00
```

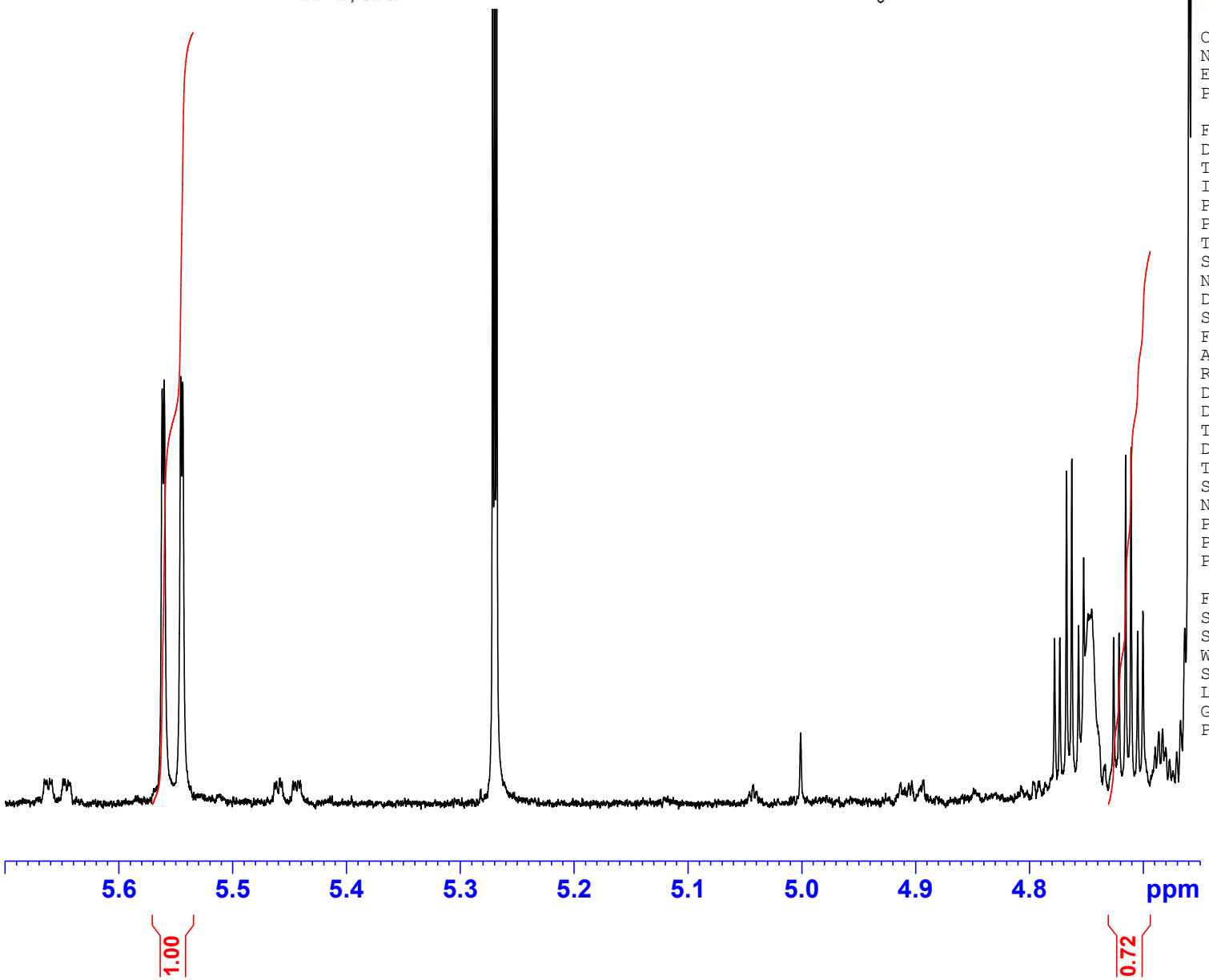



```
Current Data Parameters
NAME       LH-I-94 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220519
Time               15.11 h
INSTRUM             spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            18028.846 Hz
FIDRES          0.200003 Hz
AQ             4.9999318 sec
RG                 19.42
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1             0.10000000 sec
TD0                    1
SFO1         600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF         600.1300216 MHz
WDW                  EM
SSB                   0
LB                 0.10 Hz
GB                    0
PC                 1.00
```

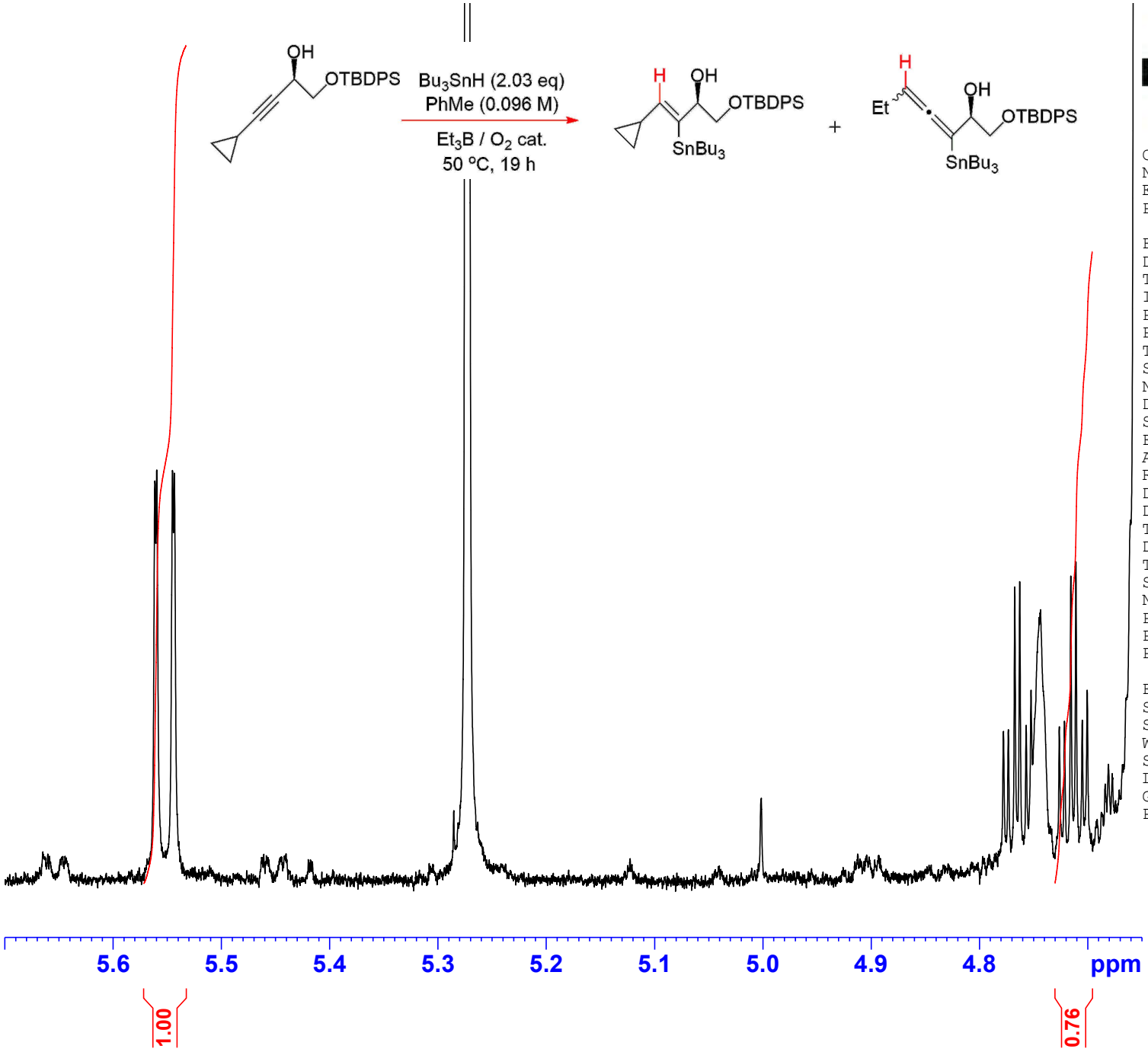





```
Current Data Parameters
NAME       LH-I-91 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220504
Time              11.31 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH           18028.846 Hz
FIDRES         0.200003 Hz
AQ            4.9999318 sec
RG                 13.75
DW               27.733 usec
DE                8.00 usec
TE               300.0 K
D1           0.10000000 sec
TD0                    1
SFO1        600.1337060 MHz
NUC1                1H
P0                3.33 usec
P1               10.00 usec
PLW1        26.60000038 W

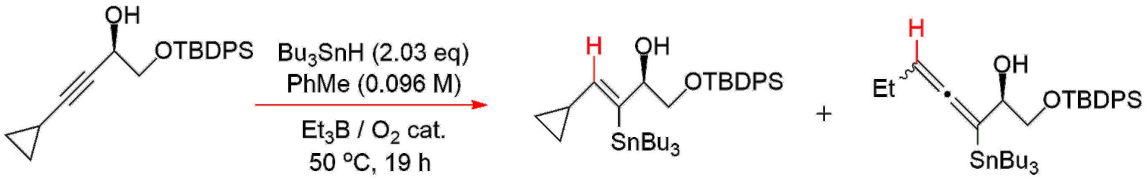
F2 - Processing parameters
SI                262144
SF          600.1300215 MHz
WDW                 EM
SSB                    0
LB                0.10 Hz
GB                     0
PC                1.00
```

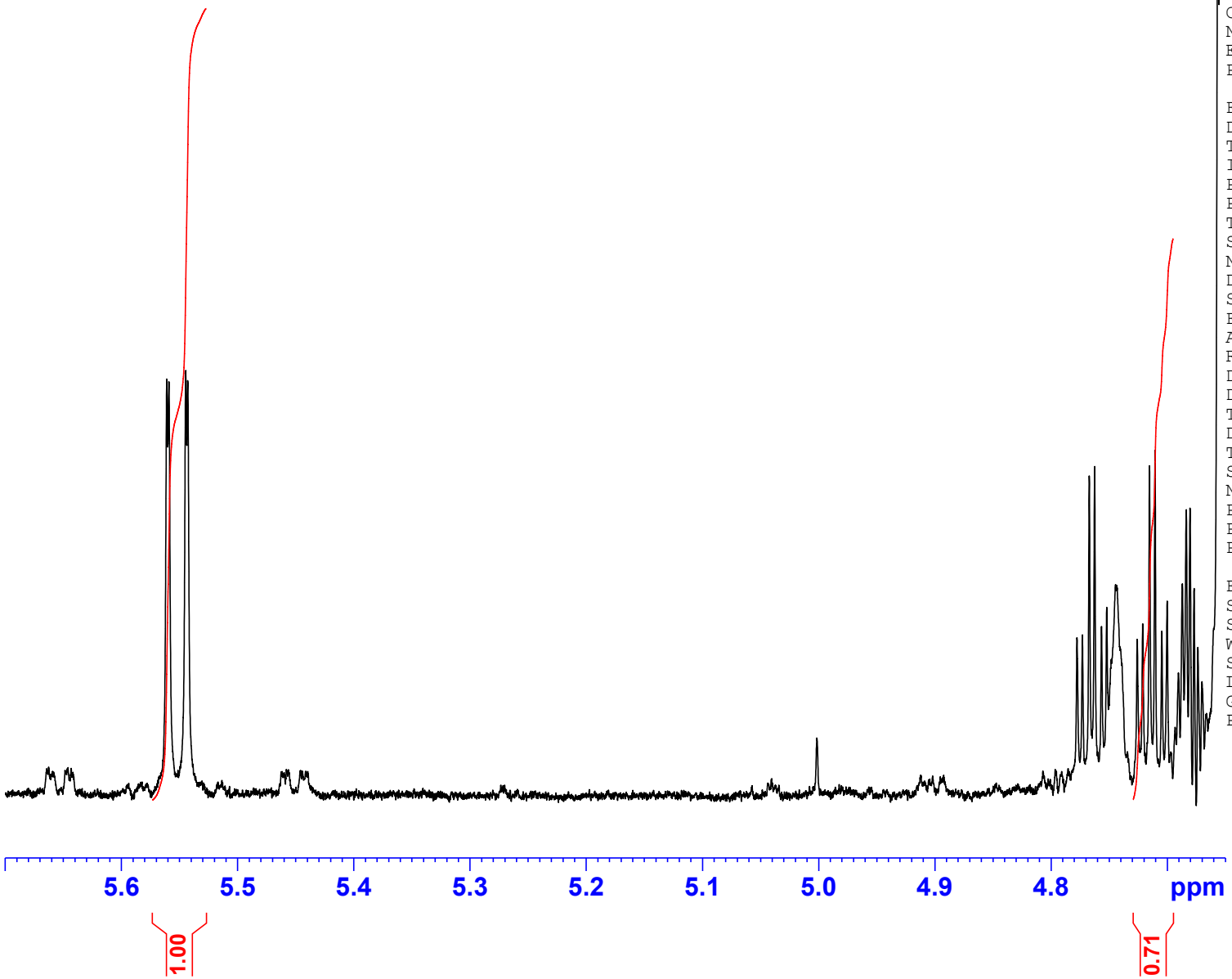



```
Current Data Parameters
NAME       LH-I-92 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220504
Time              11.40 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    16
DS                     0
SWH           18028.846 Hz
FIDRES         0.200003 Hz
AQ            4.9999318 sec
RG                 25.17
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1
SFO1        600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300198 MHz
WDW                 EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```

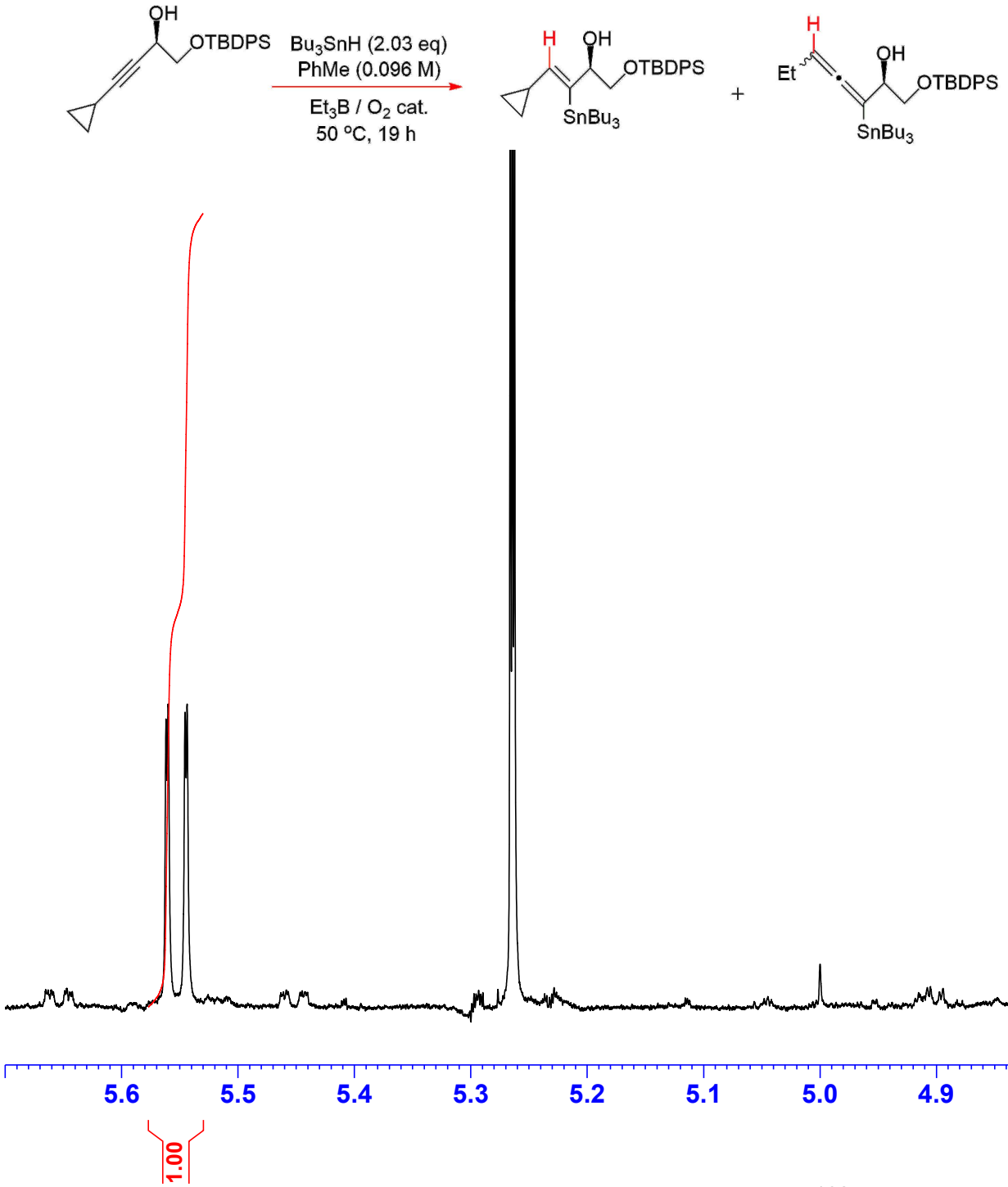





```
Current Data Parameters
NAME       LH-I-95 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220519
Time               15.19 h
INSTRUM             spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    16
DS                     0
SWH            18028.846 Hz
FIDRES          0.200003 Hz
AQ             4.9999318 sec
RG                 27.87
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1             0.10000000 sec
TD0                    1
SFO1         600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300215 MHz
WDW                 EM
SSB                    0
LB                 0.10 Hz
GB                     0
PC                 1.00
```



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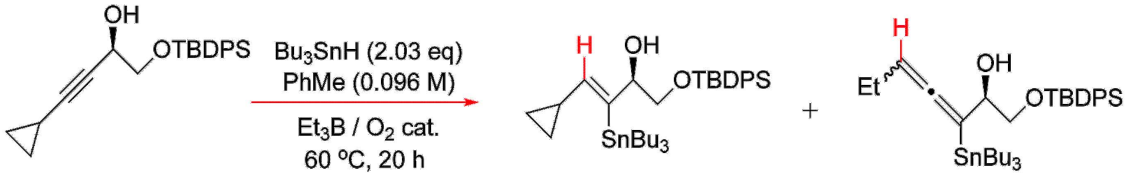
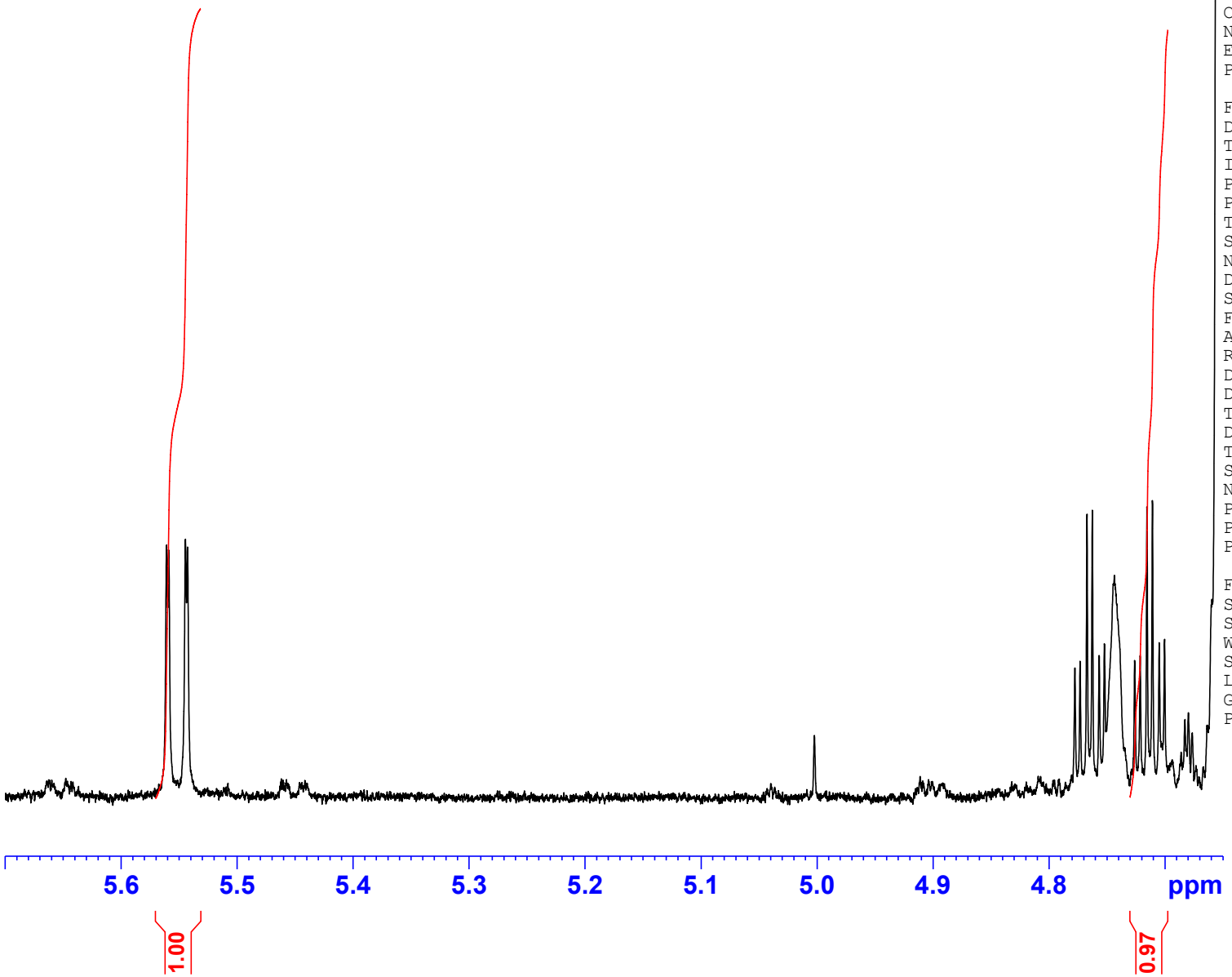
```
Current Data Parameters
NAME       LH-I-96 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220519
Time               15.25 h
INSTRUM             spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    16
DS                     0
SWH            18028.846 Hz
FIDRES          0.200003 Hz
AQ             4.9999318 sec
RG                 12.81
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1             0.10000000 sec
TD0                    1
SFO1         600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300248 MHz
WDW                 EM
SSB                    0
LB                 0.10 Hz
GB                     0
PC                 1.00
```

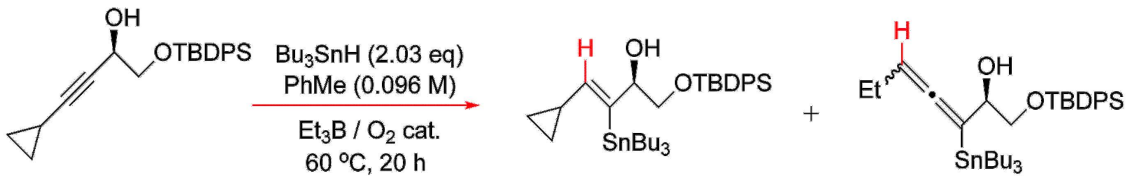


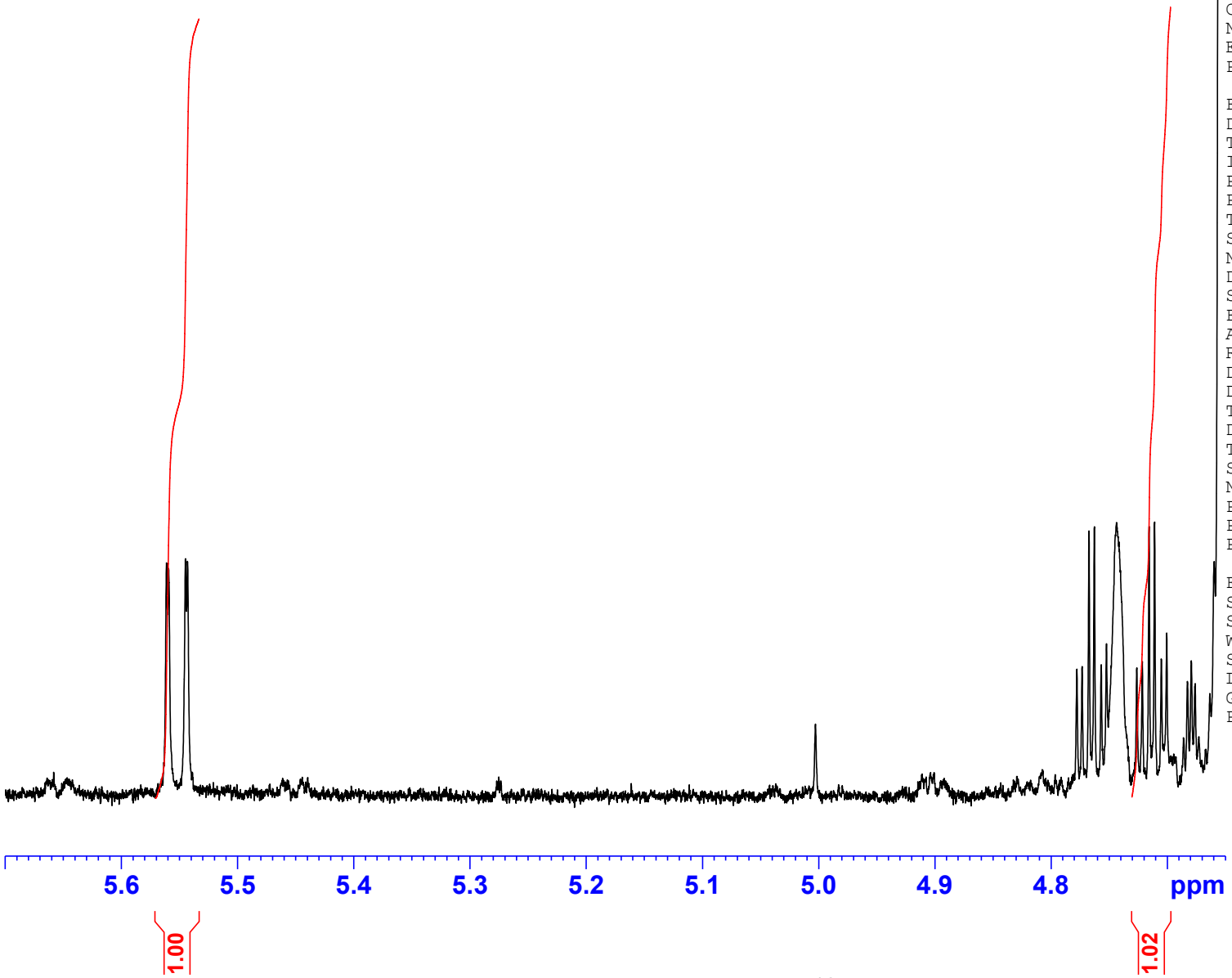



```
Current Data Parameters
NAME       LH-I-85 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220502
Time              13.59 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH           18028.846 Hz
FIDRES         0.200003 Hz
AQ            4.9999318 sec
RG                 27.87
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1
SFO1        600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300190 MHz
WDW                 EM
SSB                    0
LB                0.10 Hz
GB                     0
PC                 1.00
```

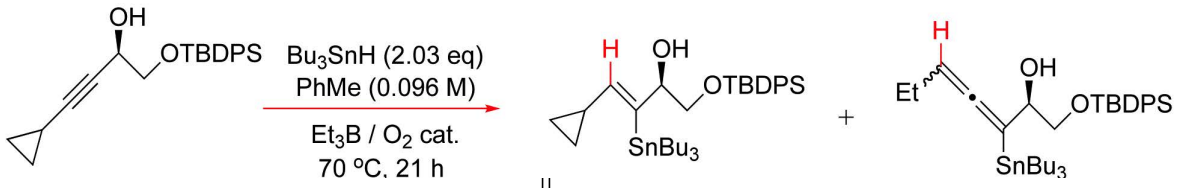


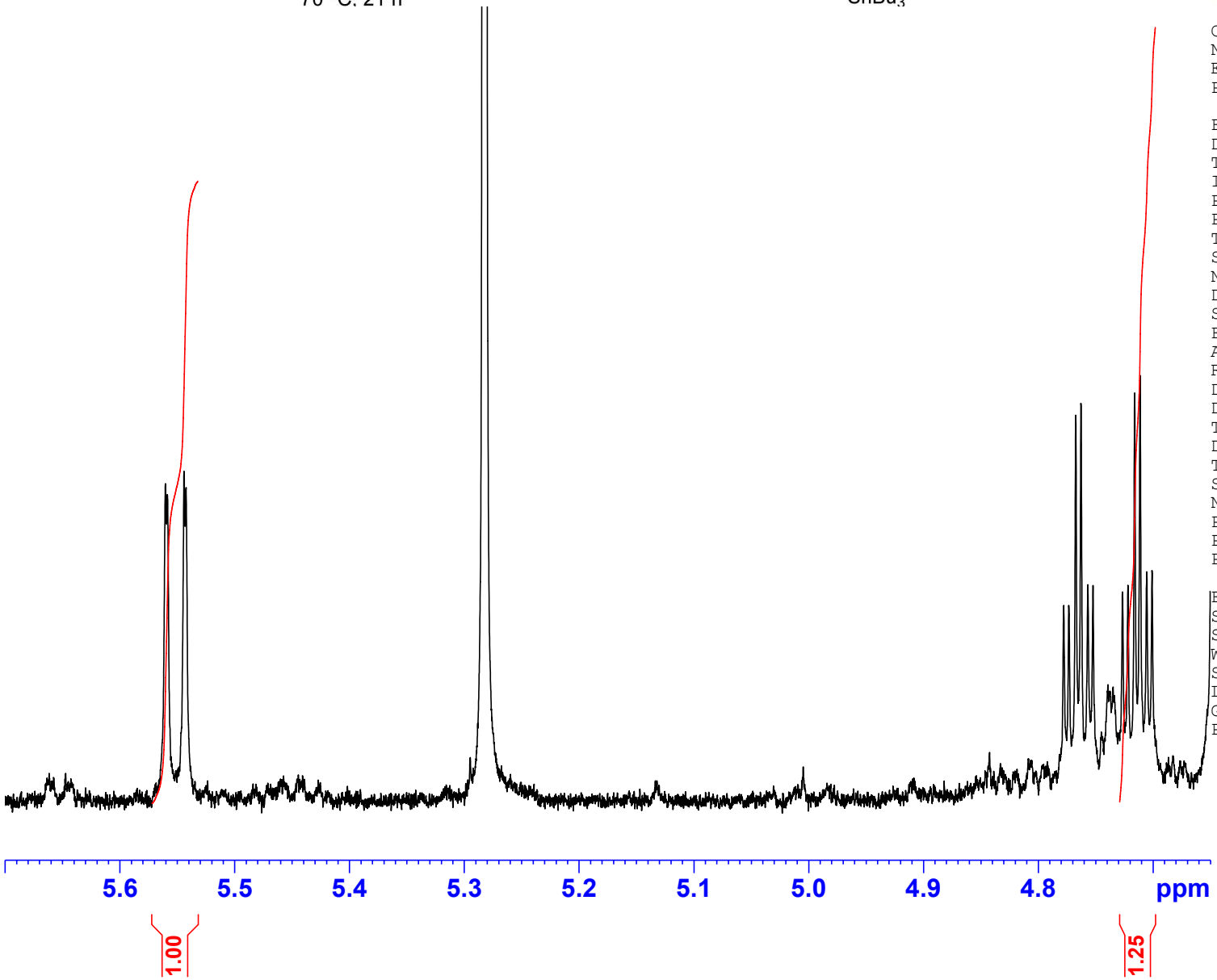



```
Current Data Parameters
NAME       LH-I-86 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220502
Time               14.08 h
INSTRUM             spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            18028.846 Hz
FIDRES          0.200003 Hz
AQ             4.9999318 sec
RG                 27.87
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1             0.10000000 sec
TD0                    1
SFO1         600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1         26.60000038 W

F2 - Processing parameters
SI                262144
SF           600.1300192 MHz
WDW                 EM
SSB                    0
LB                 0.10 Hz
GB                     0
PC                 1.00
```

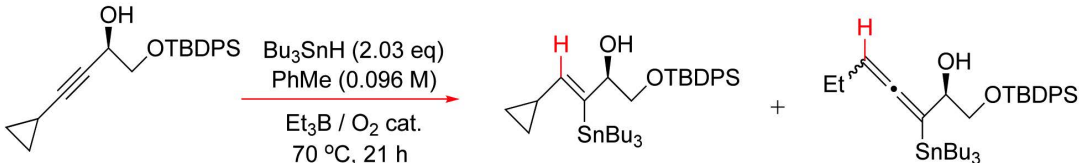


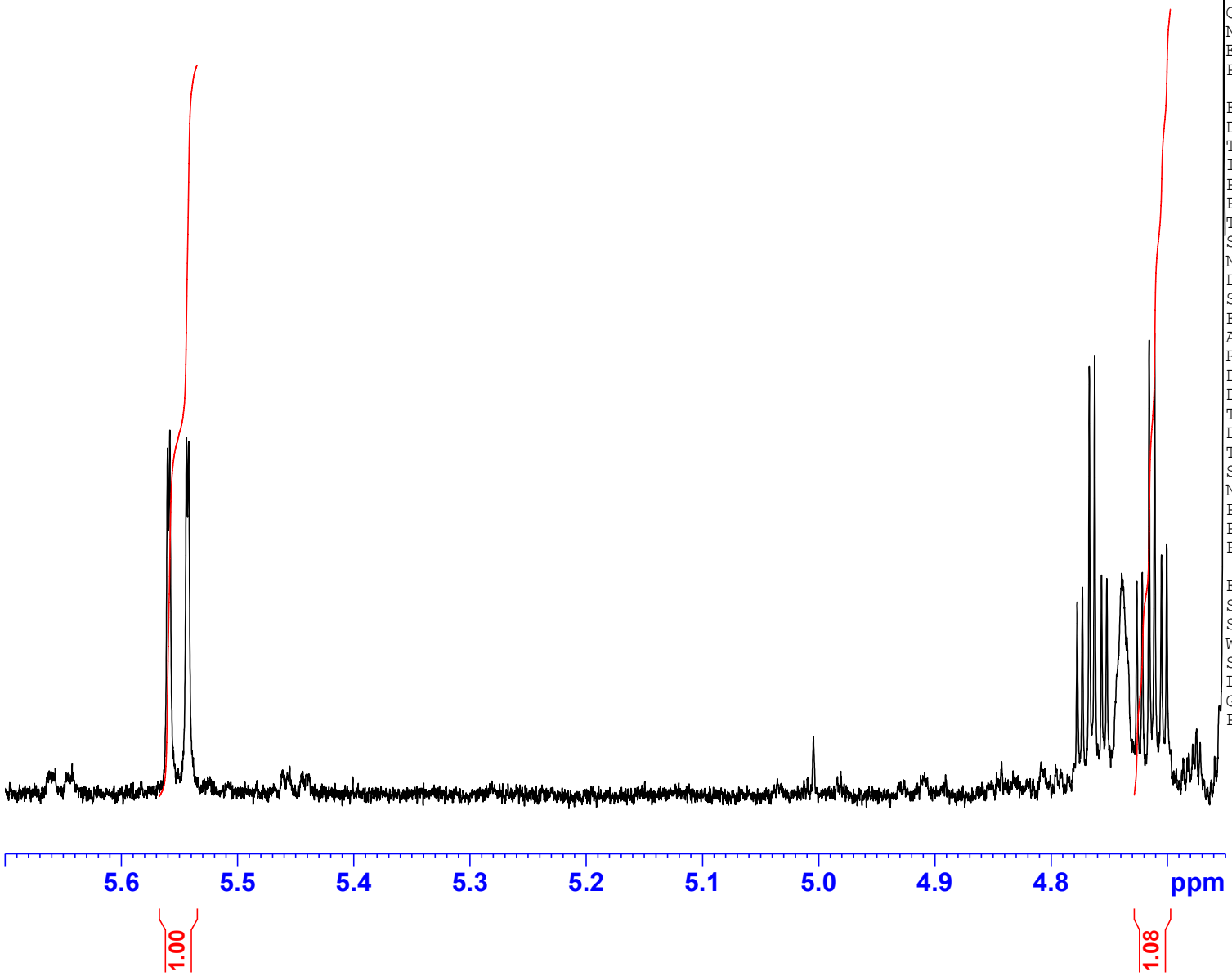



```
Current Data Parameters
NAME       LH-I-77 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220426
Time              21.11 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH           18028.846 Hz
FIDRES         0.200003 Hz
AQ             4.9999318 sec
RG                 49.63
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1
SFO1        600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300155 MHz
WDW                 EM
SSB                    0
LB                0.10 Hz
GB                     0
PC                1.00
```

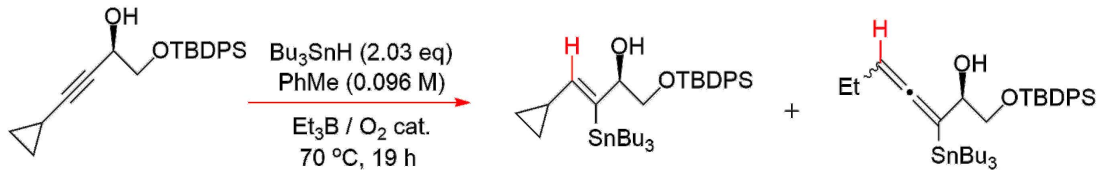


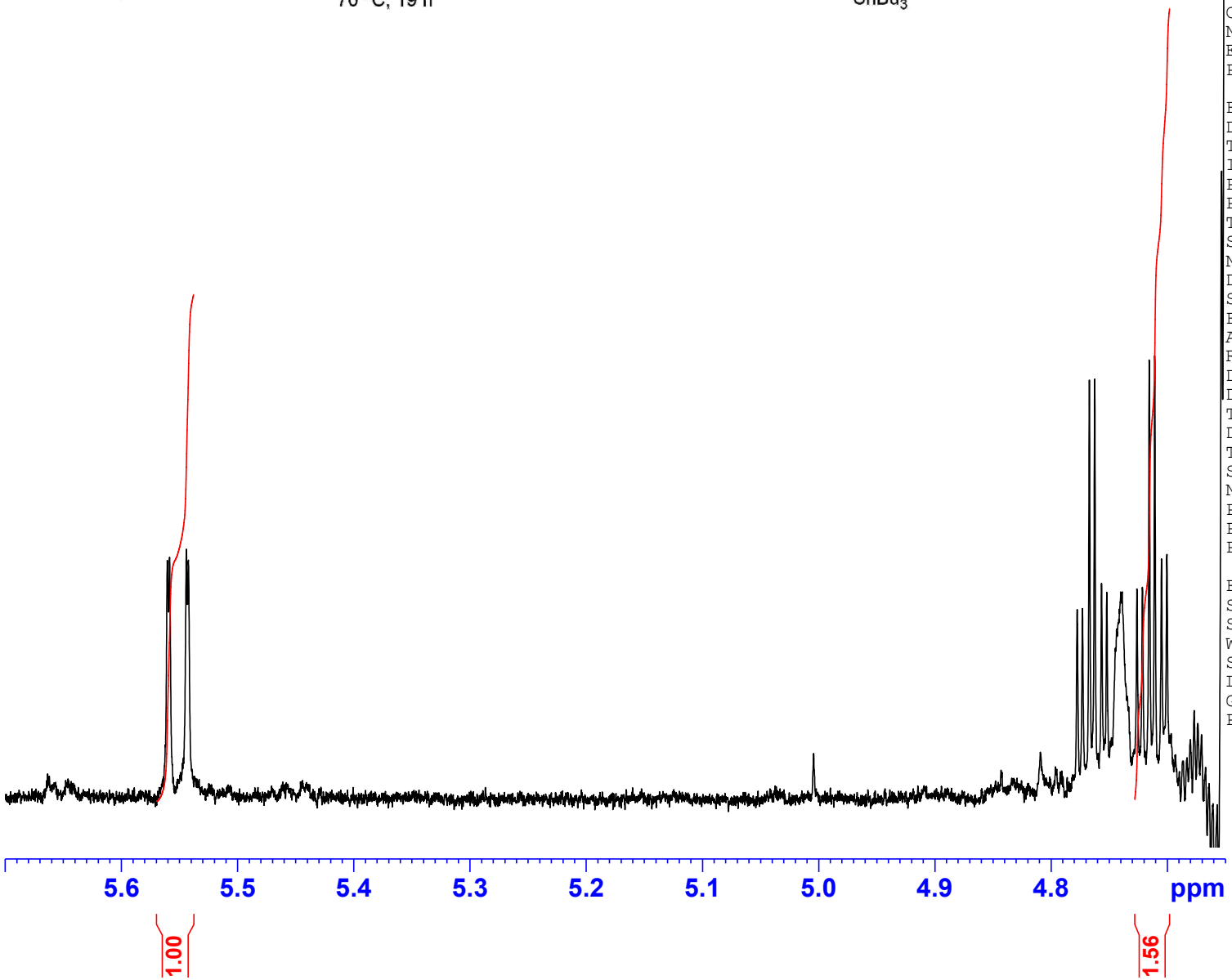



```
Current Data Parameters
NAME       LH-I-78 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220426
Time              16.31 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH           18028.846 Hz
FIDRES         0.200003 Hz
AQ             4.9999318 sec
RG                 43.25
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1
SFO1        600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300164 MHz
WDW                 EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```

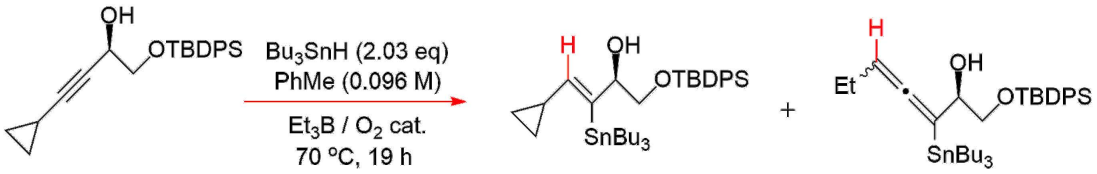


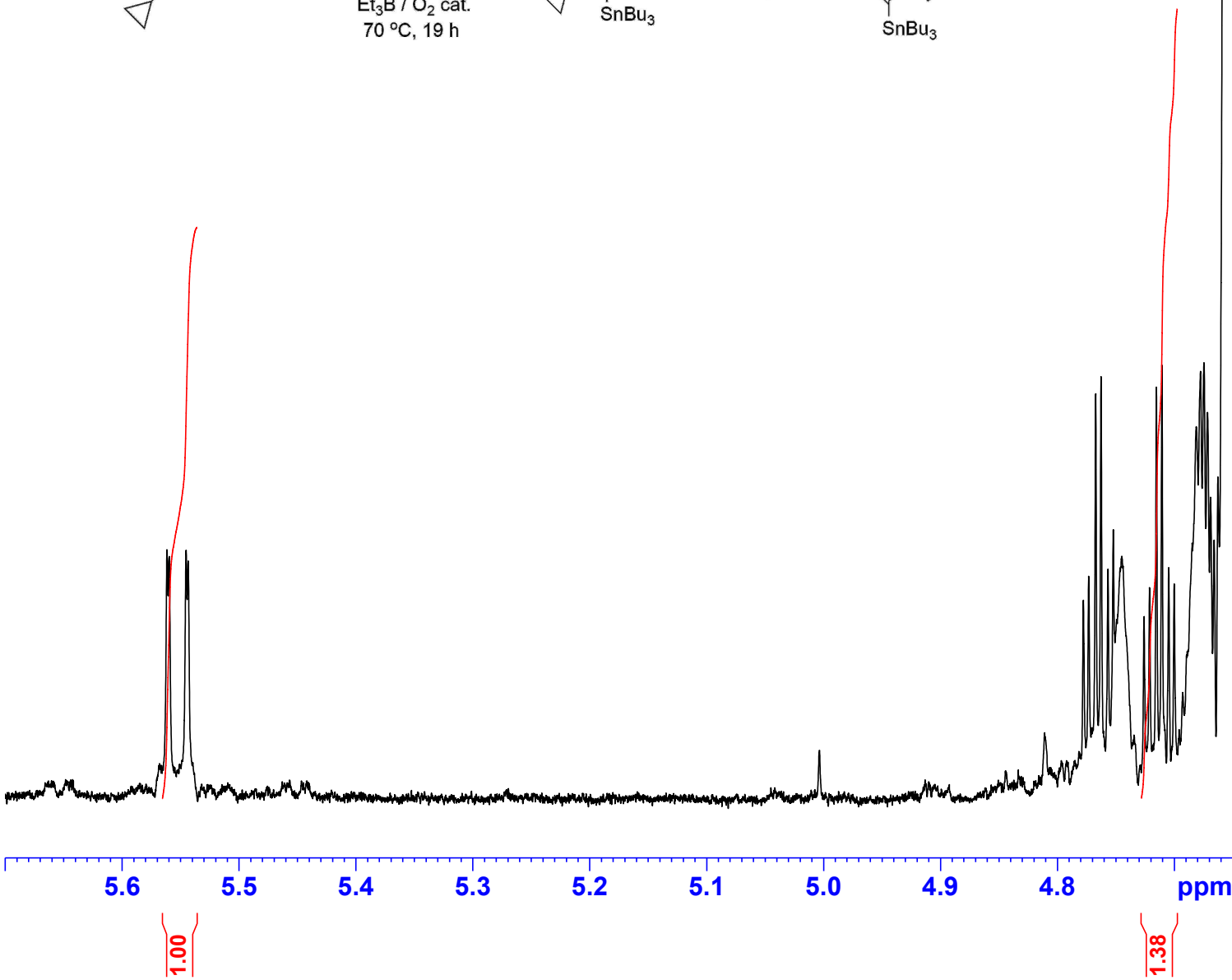



```
Current Data Parameters
NAME       LH-I-87 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220502
Time              14.16 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH           18028.846 Hz
FIDRES         0.200003 Hz
AQ            4.9999318 sec
RG                 34.91
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1
SFO1        600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300173 MHz
WDW                  EM
SSB                   0
LB                 0.10 Hz
GB                    0
PC                 1.00
```

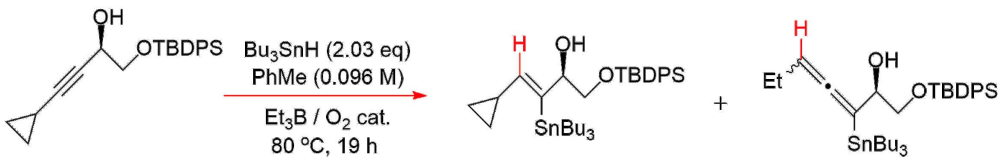





```
Current Data Parameters
NAME       LH-I-88 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220502
Time               14.25 h
INSTRUM             spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            18028.846 Hz
FIDRES          0.200003 Hz
AQ             4.9999318 sec
RG                 25.17
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1             0.10000000 sec
TD0                    1
SFO1         600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1         26.60000038 W

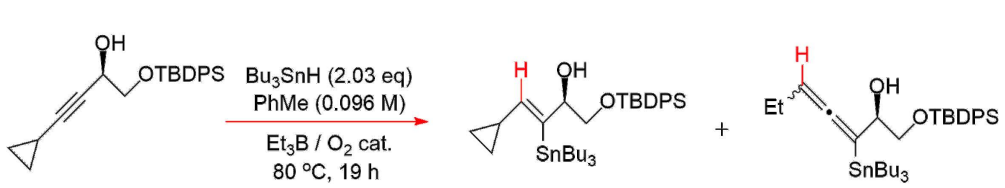
F2 - Processing parameters
SI                262144
SF           600.1300202 MHz
WDW                 EM
SSB                    0
LB                 0.10 Hz
GB                     0
PC                 1.00
```




```
Current Data Parameters
NAME                  LH-I-73
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_                20220407
Time                   18.07 h
INSTRUM                spect
PROBHD    Z114607_0188 (
PULPROG                 zg30
TD                    180286
SOLVENT                CDCl3
NS                         16
DS                          0
SWH                18028.846 Hz
FIDRES              0.200003 Hz
AQ                  4.9999318 sec
RG                       7.97
DW                     27.733 usec
DE                      8.00 usec
TE                     300.0 K
D1                 0.10000000 sec
TD0                         1
SFO1              600.1337060 MHz
NUC1                       1H
P0                      3.33 usec
P1                     10.00 usec
PLW1              26.60000038 W

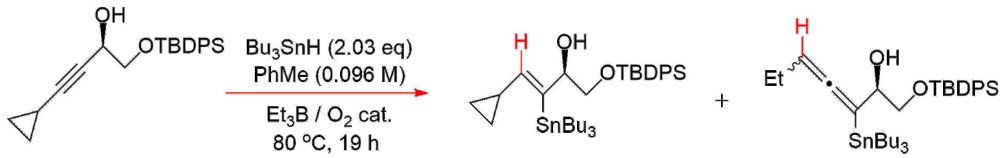
F2 - Processing parameters
SI                     262144
SF                600.1300252 MHz
WDW                        EM
SSB                         0
LB                       0.10 Hz
GB                          0
PC                       1.00
```

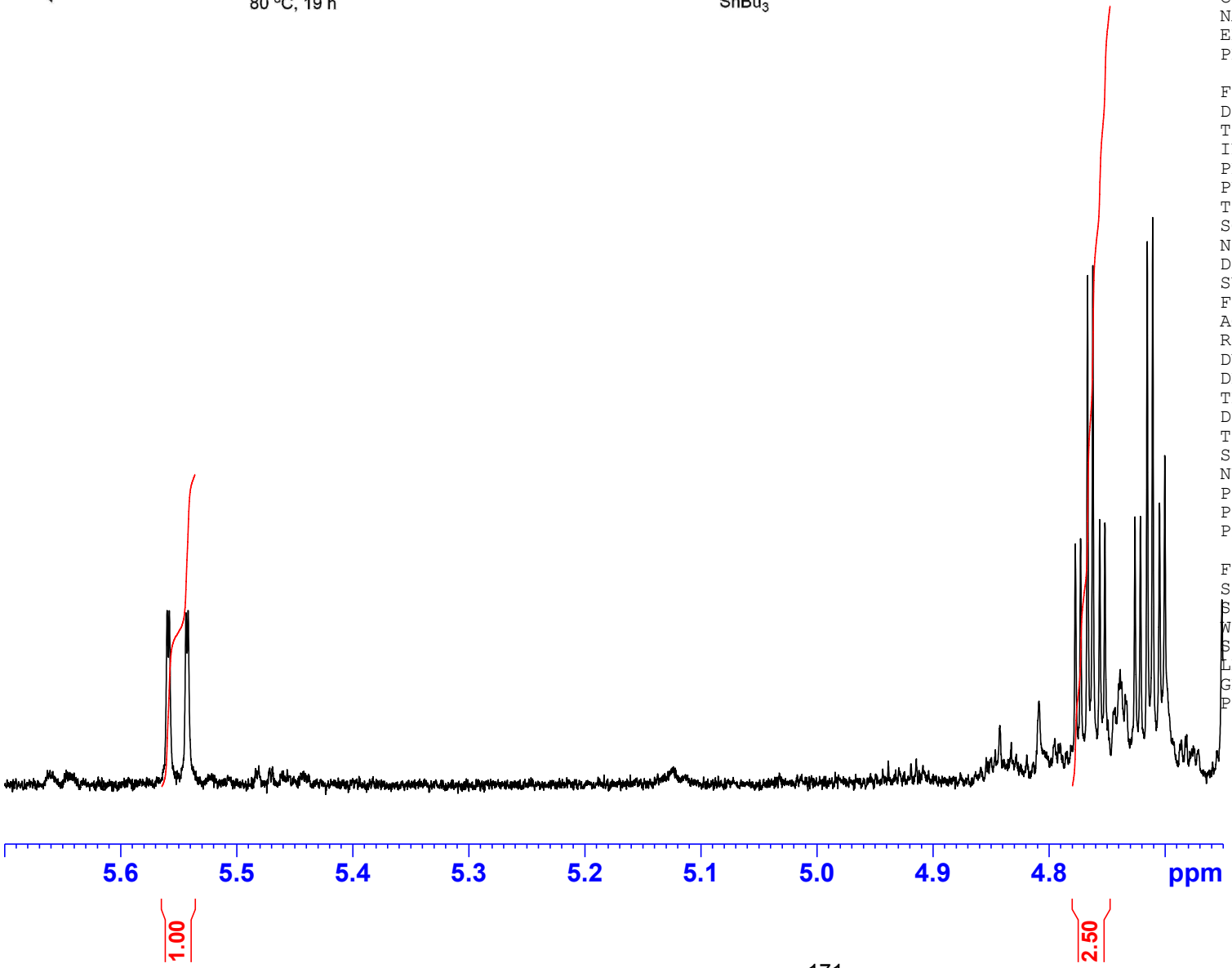



```
Current Data Parameters
NAME                  LH-I-74
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_                20220407
Time                    18.15 h
INSTRUM                 spect
PROBHD    Z114607_0188 (
PULPROG                 zg30
TD                    180286
SOLVENT                 CDCl3
NS                         16
DS                          0
SWH                 18028.846 Hz
FIDRES               0.200003 Hz
AQ                   4.9999318 sec
RG                          6.18
DW                     27.733 usec
DE                      8.00 usec
TE                     300.0 K
D1                  0.10000000 sec
TD0                         1
SFO1               600.1337060 MHz
NUC1                       1H
P0                      3.33 usec
P1                     10.00 usec
PLW1               26.60000038 W

F2 - Processing parameters
SI                      262144
SF                 600.1300288 MHz
WDW                        EM
SSB                         0
LB                       0.10 Hz
GB                          0
PC                       1.00
```






```
Current Data Parameters
NAME       LH-I-83 CRUDE
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220428
Time              20.33 h
INSTRUM            spect
PROBHD   Z114607_0188 (
PULPROG             zg30
TD                180286
SOLVENT             CDCl3
NS                    16
DS                     0
SWH           18028.846 Hz
FIDRES         0.200003 Hz
AQ             4.9999318 sec
RG                 49.63
DW                27.733 usec
DE                 8.00 usec
TE                300.0 K
D1           0.10000000 sec
TD0                    1
SFO1        600.1337060 MHz
NUC1                1H
P0                 3.33 usec
P1                10.00 usec
PLW1        26.60000038 W

F2 - Processing parameters
SI                262144
SF          600.1300168 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00
```