

Data Tables (DT) in NUTS: Publication Listings of NMR Data

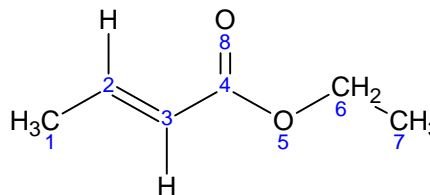
All literature describing the synthesis and characterization by NMR of new compounds require publication of the NMR data in standardized paragraphs (variations exist depending on the journal). These paragraphs include lists of chemical shifts, coupling (or multiplet) type, and coupling constant(s) for proton spectra, and chemical shift and multiplicity for ^{13}C spectra. NUTS provides tools within a routine called Data Tables (command **DT**) that greatly eases the generation (and thus improves the accuracy) of these data-list paragraphs.

→ **Print and use Section 16 in the NUTS Cheat Sheet to help you with this HW.**

Use the ^{13}C and ^1H data of **ethyl crotonate in acetone- d_6** in the **R:\ac300\Chem636\HW6** folder for this homework set.

– $\delta(\text{ppm})$ [$T_1(\text{s})$] assignments:

1 – 1.86 [40] 2 – 6.92 [41] 3 – 5.84 [13]
6 – 4.12 [9] 7 – 1.23 [9]



^{13}C Publication Listings:

Follow the instructions in the NUTS Cheat Sheet, Section 16 to create a data table for the ethyl crotonate ^{13}C spectrum. NUTS will provide the list of chemical shifts from a peak pick. You have to provide the multiplicities: this can be done based on chemical shifts for ethyl crotonate. Enter C CH CH2 or CH3 in column 3 of table (solv for the solvent peaks).

The initial Word export from the data table (following **dt cacs**) should look something like:

^{13}C NMR: (75.4 MHz,) delta 206.1 (solv), 166.5 (C), 145.0 (CH), 123.6 (CH), 60.4 (CH₂), 30.4 (solv), 30.2 (solv), 29.9 (solv), 29.6 (solv), 29.4 (solv), 17.9 (CH₃), 14.6 (CH₃);

Typically that listing would be edited to match publication standards (Journal and group variations exist). In general, the solvent name would be added to the beginning of the list, solvent chemical shifts would be removed, and font changes made to produce:

^{13}C NMR (75.4 MHz, CD_3OCD_3) δ 166.5 (C), 145.0 (CH), 123.6 (CH), 60.4 (CH₂), 17.9 (CH₃), 14.6 (CH₃);

DEPT spectra provide a general strategy for assigning ^{13}C multiplicities, as was done in HW#2 for your unknown. Edited-HSQC is a more powerful strategy that is quite similar to DEPT, but provides greatly increased sensitivity as well as one-bond proton correlations. We'll use this technique in a later lab in this course.

¹H Publication Listings:

1. Again, follow the instructions in the NUTS Cheat Sheet, Section 16, but now to create a data table for the ethyl crotonate ¹H spectrum you acquired in last week's lab (or you can use R:\ac300\Chem636\HW6\CGFECAH.001). Peak picks should not be used with proton spectra; many peaks will cluster to form a multiplet. Usually the center of the multiplet is the chemical shift, and the other peaks are separated by J-coupling. It is your knowledge that identifies the multiplets, and will produce the proper information. NUTS cursor tools are helpful in tabularizing the chemical shifts and J-couplings. Identifying the multiplets and making assignments is the business of Chem 605, but ethyl crotonate (with the help provided below) is simple enough to work with for this homework.
2. Start a new session of NUTS to work with the proton spectrum. In general, you can open a new spectrum in a session you've already been working in, but especially with nucleus changes, trouble (a software crash) can be avoided by starting in a new session.
3. Start with the most upfield triplet at 1.231 ppm. This is the 7 methyl in the structure above, with the 3 equivalent protons split by the two -CH₂- protons. The chemical shift (which is at the center) of the multiplet is just the position of the center peak. The multiplicity would be t for triplet.

#Hs is the number of protons represented by the multiplet; this number is clear based on integrations performed on the spectrum, but is enter (at least at the publication stage) as an integer; i.e., the integrals are rounded to the proper integer (3 in this case) based on the assignment of the multiplet (to the 7 methyl group).

A single J-coupling is reported for triplets; if you measure the two splittings, you will find them to be equal to 7.1 Hz. Use the NUTS cursor tools to enter the chemical shift and J-coupling data into the data table. Note that any cell can be manually edited by right-clicking on it.

4. The next peak at 1.861 ppm is the 1 methyl group. It is a doublet of doublets, multiplicity dd. Note now that the chemical shift, at the center of the multiplet, does not fall on any peak. Eyeballing the cursor to the center (when sufficiently expanded) is sufficiently accurate for entering this position in as the chemical shift. One large coupling comes from the 2 vinyl proton (6.9 Hz), and a smaller coupling from the 3 vinyl proton (1.8 Hz). Both of these couplings should be listed in one cell in the data table.
5. The next peak is the 6 methylene, a quartet with multiplicity symbol q. J-couplings are symmetric: the coupling observed on the 7 methyl should be identical in size to that measured on the 6 methylene.
6. Finally are the vinyl protons, which are slightly more complex. The multiplet at $\delta=5.841$ ppm is a doublet of quartet, dq. The larger coupling is to the other vinyl proton, with the smaller quartet coupling the methyl. Only two J-couplings would be entered into the table, as by definition, a quartet is represented by a single coupling constant (there are three protons coupling, but all by identical amounts).
7. The most downfield multiplet is slightly harder to see, but is still a doublet of quartets. The difference is the larger coupling to the methyl group.
8. You should be able to determine which vinyl group is which from the discussion above involving the 1 methyl group.

A final listing directly from **dt hacs** might look something like (assignments were included, and are listed first in the parens):

¹H NMR: (299.9 MHz,) delta 1.231 (H7, t, J = 7.1 Hz, 3H), 1.861 (H1, dd, J = 6.9, 1.8 Hz, 3H), 4.122 (H6, q, J = 7.1 Hz, 2H), 5.841 (H3, dq, J = 15.5, 1.8 Hz, 1H), 6.923 (H2, dq, J = 15.5, 6.9 Hz, qH);

Again, the listing must be cleaned up for publication, to something like:

¹H NMR (299.9 MHz, CD₃OCD₃) δ 1.231 (t, J = 7.1 Hz, 3H), 1.861 (dd, J = 6.9, 1.8 Hz, 3H), 4.122 (q, J = 7.1 Hz, 2H), 5.841 (dq, J = 15.5, 1.8 Hz, 1H), 6.923 (dq, J = 15.5, 6.9 Hz, qH);

→ Copy and paste your two paragraphs into Word. Clean them up as typical for a publication listing, and hand in at the due date.

Extra Credit: Look at the impurity multiplet at 6.367 ppm. From the change in J-couplings, can you guess what the impurity might be? It is harder to observe by being partially overlapped, but the other vinyl peak for this compound shows at 5.776 ppm. Can you identify where the methylene is at? Identifying such impurity peaks can obviously test data quality, both for sensitivity and resolution.

General recommendations for research work:

- a) Keep all peaks, including solvent peaks, in the peak pick and data tables.
- b) Make assignments in the 4th column for ¹³C, and 6th column for ¹H data. Assignments are typically not included in publication listing, but of course you will want to make them (at least of some compounds), and keep a record of them.
- c) Store the exported data table and numbered chemical structure files in a folder with the NMR data. Keep in mind that **File** → **Save** within NUTS will *not* save the data table; the **dt export** command is required to save the data table, written to a separate text file.
- d) Although the DT listing, and even a chemical structure, can be placed into NUTS spectra, NUTS is limited in many ways in these capabilities. Use of Word or PowerPoint, or a higher-ended drawing package (e.g., Illustrator or CorelDraw) is recommended for combined plots containing structures, spectra and text.