# Spectral Database for Instructors: A Living, Online NMR FID Database

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ABSTRACT: A Web-based resource has been developed to assist instructors of organic spectroscopy courses. This Web site is populated by NMR FID files that can be freely downloaded by registered users. Current offerings include FID files for ^{1}H and ^{13}C NMR, DEPT, ^{1}H–^{1}H COSY, HMQC, HMBC, TOCSY, and 1D NOE experiments. External users can also submit their own data for use by other instructors. By supplying users with the FID files, it will be easier for them to emphasize certain areas of the spectrum for use during in-class discussions, problem sets, and exams.

KEYWORDS: *Upper-Division Undergraduate, Graduate Education/Research, Organic Chemistry, Internet/Web-Based Learning, NMR Spectroscopy*
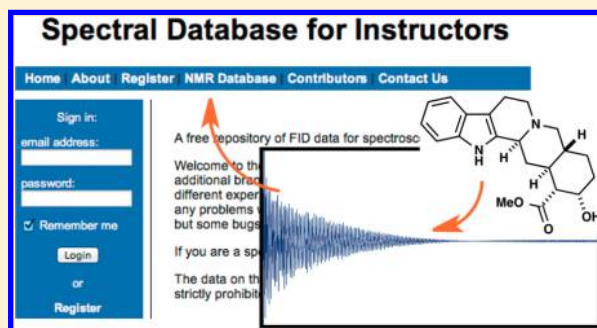
Structure elucidation is a fundamental skill for the practicing synthetic chemist. As students become more comfortable with this task, they will become more self-sufficient and better able to question the identity of what is in their flask. The ramifications of this are that the field will be expanded through the development of new reactions and the production of more complicated structures with confidence. Because of the importance of this skill, many universities and colleges have established courses on structural elucidation. Typically, these courses are populated by advanced undergraduate and first-year graduate students and are designed to give a more thorough and in-depth treatment of modern techniques for structural elucidation than is typically possible in an introductory organic chemistry course. Because of the ever-growing importance of 1-D and 2-D NMR in structure determination,[1] the bulk of these courses often focus on these techniques.

■ LACK OF AVAILABLE RESOURCES

One challenge that instructors face when preparing for these courses is the lack of available resources for finding suitable NMR spectra for homework assignments, exams, and in-class discussions. Although there are several textbooks available that contain a variety of spectral-based problems,[2] there is a limit to the number of spectra that can be included between the covers of a book. Also, the authors or publishers may feel the need to exclude more challenging spectra in order to make their text suitable for a wider audience. This is particularly true when it comes to problems involving 2-D NMR or Mosher analysis. At times, it would also be beneficial if the instructor had access to data that was more dynamic. For example, it would be very useful to expand each proton resonance when discussing coupling-constant analysis.[3] Furthermore, having problems for which the solutions are not readily available to students will always be a concern.

Given the era we live in, the Internet is a logical source for spectral problems. The Sigma-Aldrich Web site[4,5] and the *Spectral Database for Organic Compounds*[6] are both good sources for obtaining NMR spectra of commercially available or otherwise commonly occurring compounds. Unfortunately, both suffer from offering only one, unalterable view of each spectrum. There are several educational Web sites available that contain many good spectral problems.[7] However, these Web sites are often geared toward undergraduate students that are just being introduced to organic spectroscopy. The problems therefore tend to be somewhat elementary and are not suitable for advanced undergraduate or graduate level courses. One potential gold mine for spectra is the supporting information of published journal articles. Unfortunately, finding copies of the spectra themselves is not guaranteed, and those that do exist are again limited to the views provided by the original authors. Furthermore, these sources tend to be somewhat deficient in providing the actual spectra obtained during Mosher analysis[8] or from 2-D NMR techniques. The next logical alternative would be for instructors to pull material from their own research programs or from their departmental colleagues. Although this is a viable option for some, there are many instructors at smaller institutions that do not have highly active research programs. This is also an issue for newly appointed professors who have yet to build such internal databases. Because many research groups work with a limited number of compound classes, this solution may also limit the variety of compounds that students are challenged with. For all these reasons, course instructors need access to new sources of quality spectra.

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■ NEW WEB-BASED RESOURCE

We have addressed these deficiencies by creating a new Web-based resource: *Spectral Database for Instructors* (Figure 1).[9]

Figure 1. Welcome screen for the *Spectral Database for Instructors*.

The fundamental difference between our Web site and those currently available is that ours does not contain static scans of spectra. Instead our Web site is populated with the actual free induction decay (FID) data obtained on the spectrometer. FID files are the raw data collected by the spectrometer and can be processed by a number of third-party programs,[10] as well as the processing software supplied by the various instrument manufacturers. Another unique feature of this resource is that not only can users download the spectral data for the compounds of interest (Figure 2), but they can also upload their own data for others to use. This is accomplished using an online form (Figure 3). The range of spectral data currently available includes simple ^1H and ^{13}C spectra, DEPT, $^1H-^1H$ COSY, HMQC, HMBC, TOCSY, and 1D NOE. We have also made available a data set that will be useful for Mosher-type

Figure 2. Sample page for one compound in the *Spectral Database for Instructors*.

Figure 3. Compound submission page for the *Spectral Database for Instructors*.

analysis. The contents of the database are freely available to instructors worldwide.

In addition to improving the education of the advanced undergraduate and graduate students at our home institution, we are confident that this will find widespread use for teaching students at universities and colleges around the world.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Claridge, T. D. W. *High-Resolution NMR Techniques in Organic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 2009. (b) Nicolaou, K. C.; Snyder, S. A. Chasing Molecules That Were Never There: Misassigned Natural Products and the Role of Chemical Synthesis in Modern Structure Elucidation. *Angew. Chem., Int. Ed.* **2005**, *44*, 1012−1044.

(2) Selected examples,: (a) Silverstein, R. M.; Webster, F. X.; Kiemle, D. J. *Spectrometric Identification of Organic Compounds*, 7th ed.; Wiley: Hoboken, NJ, 2005. (b) Simpson, J. H. *Organic Structure Determination Using 2-D NMR Spectroscopy*; Academic Press: Burlington, MA, 2008. (c) Crews, P.; Rodríguez, J.; Jaspars, M. *Organic Structure Analysis*, 2nd ed.; Oxford University Press: New York, 2010. (d) Field, L. D.; Sternhell, S.; Kalman, J. R. *Organic Structures from Spectra*, 4th ed.; Wiley: West Sussex, England, 2008. (e) Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Structural Spectroscopy*; Prentice-Hall: Upper Saddle River, NJ, 1998.

(3) (a) Hoye, T. R; Hanson, P. R.; Vyvyan, J. R. A Practical Guide to First-Order Multiplet Analysis in ^1H NMR Spectroscopy. *J. Org. Chem.* **1994**, *59*, 4096−4103. (b) Hoye, T. R.; Zhao, H. A Method for Easily Determining Coupling Constant Values: An Addendum to "A

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Practical Guide to First-Order Multiplet Analysis in ^{1}H NMR Spectroscopy". *J. Org. Chem.* **2002**, *67*, 4014–4016.

(4) Sigma−Aldrich. http://www.sigmaaldrich.com/ (accessed Apr 2013). Authors note: To access the spectra, you must go to the "Safety & Documentation" area for the compound of interest.

(5) Bound volumes of these spectra are also available, see: Pouchert, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, 1st ed.; Aldrich Chemical Company: Milwaukee, WI, 1993.

(6) National Institute of Advanced Industrial Science and Technology (AIST), Japan. *Spectral Database for Organic Compounds*, SDBS. http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng (accessed Apr 2013).

(7) (a) Merlic, C. A.; Fam, B. C.; Miller, M. M. WebSpectra: Online NMR and IR Spectra for Students. *J. Chem. Educ.* **2001**, *78*, 118−120. (b) Hunt, I. at the University of Calgary. http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-0.html (accessed Apr 2013). (c) Organic Chemistry at CU Boulder. http://orgchem.colorado.edu/Spectroscopy/Spectroscopy.html (accessed Apr 2013). (d) Interactive NMR Problems at Yale University. http://classes.yale.edu/02-03/chem220a/studyaids/nmr/Ynmr.html (accessed Apr 2013). (e) NMR problems at the University of Hartford. http://uhavax.hartford.edu/chemistry/pdb/nmr/problems.htm (accessed Apr 2013). (f) The Spectral Game. http://www.spectralgame.com/ (accessed Apr 2013).

(8) (a) Dale, J. A.; Mosher, M. S. Nuclear Magnetic Resonance Enantiomer Reagents. Configurational Correlations *via* Nuclear Magnetic Resonance Chemical Shifts of Diastereomeric Mandelate, *O*-Methylmandelate, and α-Methoxy-α-trifluoromethylphenylacetate (MTPA) Esters. *J. Am. Chem. Soc.* **1973**, *95*, 512−519. (b) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. High-Field FT NMR Application of Mosher's Method. The Absolute Configuration of Marine Terpenoids. *J. Am. Chem. Soc.* **1991**, *113*, 4092−4096. (c) Hoye, T. R.; Jeffrey, C. S.; Shao, F. Mosher ester analysis for the determination of absolute configuration of stereogenic (chiral) carbinol carbons. *Nat. Protoc.* **2007**, *2*, 2451−2458. (d) Hoye, T. R.; Erickson, S. E.; Erickson-Birkedahl, S. L.; Hale, C. R. H.; Izgu, E. C.; Mayer, M. J.; Notz, P. K.; Renner, M. K. Long-Range Shielding Effects in the ^{1}H NMR Spectra of Mosher-like Ester Derivatives. *Org. Lett.* **2010**, *12*, 1768−1771.

(9) The Harned Research Group. *Spectral Database for Instructors*. http://harned.chem.umn.edu/ (accessed Apr 2013).

(10) Some examples of third-party programs, include: (a) iNMR, http://www.inmr.net (accessed Apr 2013); (b) mNova, http://mestrelab.com (accessed Apr 2013); (c) NUTS, http://www.acornnmr.com/nuts.htm (accessed Apr 2013); (d) ACD/NMR, http://www.acdlabs.com/resources/freeware/nmr_proc/index.php (accessed Apr 2013). Questions regarding these programs should be directed to the appropriate software developer.

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