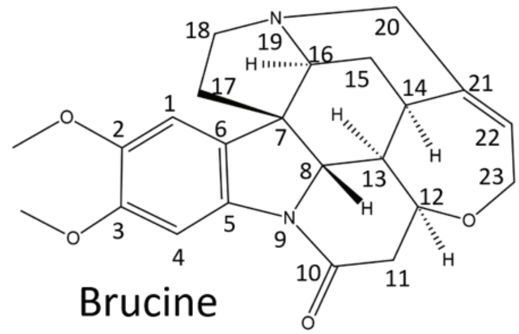
Exciting NMR Applications with Selective Excitation

INTRODUCTION

A very powerful and useful general NMR technique is to use selective excitation to focus directly on a resonance frequency or region to allow acquisition of very specific information to efficiently answer a specific question. Many experiments have been developed that are in essence 1-dimensional analogues of 2-dimensional experiments. In particular NOESY-1D[1] and TOCSY-1D have gained wide spread use and acceptance in the NMR community. The NOESY-1D and TOCSY-1D experiments can provide specific answers to questions in a fraction of the time needed for a full 2D result even with NUS techniques. In this Applications Note, we will explore the StepNoesy1D[2] experiment, which can yield information typically obtained by performing time consuming 3D experiments.

STEPNOESY

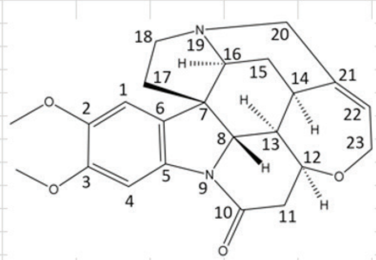
The StepNoesy experiment is really back-to-back TOCSY1D and NOESY1D pulse programs combined into a single sequence. We can use the TOCSY1D to reveal a fairly complete spin system for all resonances which are coupled to the selected peak. In this way a signal desired for nOe studies that might be buried under other resonances can be revealed and then selectively excited itself for the NOESY1D part. We will use Brucine as an example molecule to illustrate StepNoesy in action.



Brucine

As a general rule nOe measurements should not be undertaken until all primary assignments are complete. On first glance of the proton spectrum in Figure 1 Brucine might appear a complex example. As an aid to understanding the StepNoesy1D experiment we will briefly consider the NMR assignments for Brucine as they are conveniently observable by inspection of a table with a 4 minute edited HSQC result for a visual reference.

26.61	CH2	1.43	2.31	15	y
31.54	CH	3.11		14	y
42.18	CH2	1.81	1.86	17	y
42.35	CH2	2.59	3.04	11	y
48.07	CH	1.22		13	y
50.18	CH2	2.81	3.21	18	y
52.64	CH2	2.73	3.69	20	y
56.28	O-CH3	3.83		3-OCH3	y
56.42	O-CH3	3.79		2-OCH3	y
60.02	CH	3.89		16	y
60.3	CH	3.78		8	y
64.6	CH2	4	4.09	23	y
77.61	CH	4.23		12	y
100.83	CH	7.74		4	y
105.4	CH	6.64		1	y
128.61	CH	5.9		22	y
122.83	q			6	y
136.01	q			5	y
146.34	q			2	y
149.46	q			3	y
139.49	q			21	y
51.94	q			7	y
169	q			10	y



15N	assign	checked
43.93	19	y
151.89	9	y

Table 1. List of Brucine primary assignments for reference with interpreting StepNoesy result.

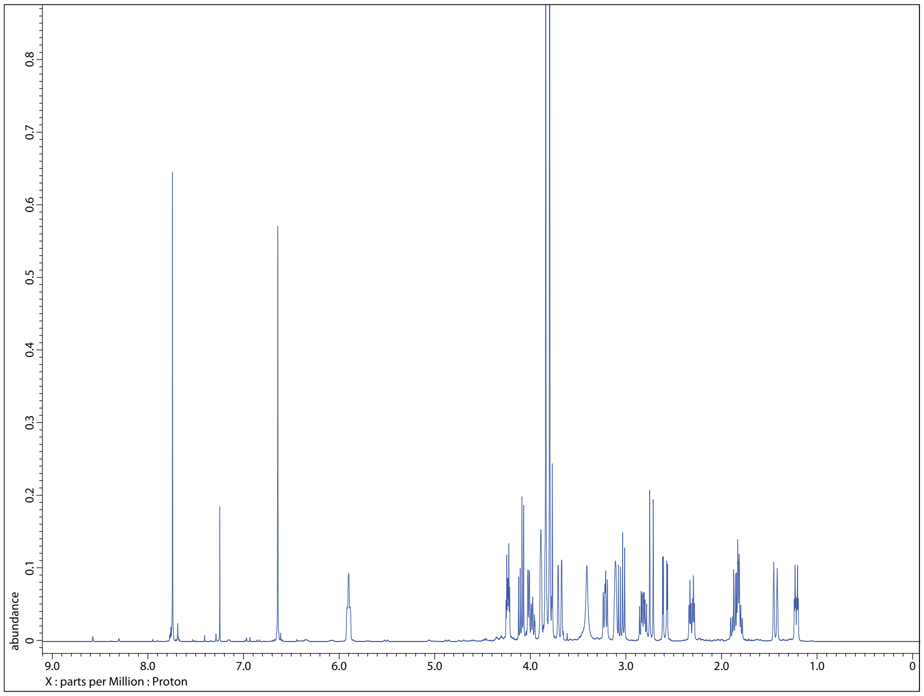


Figure 1. 1H NMR Spectrum for Brucine.

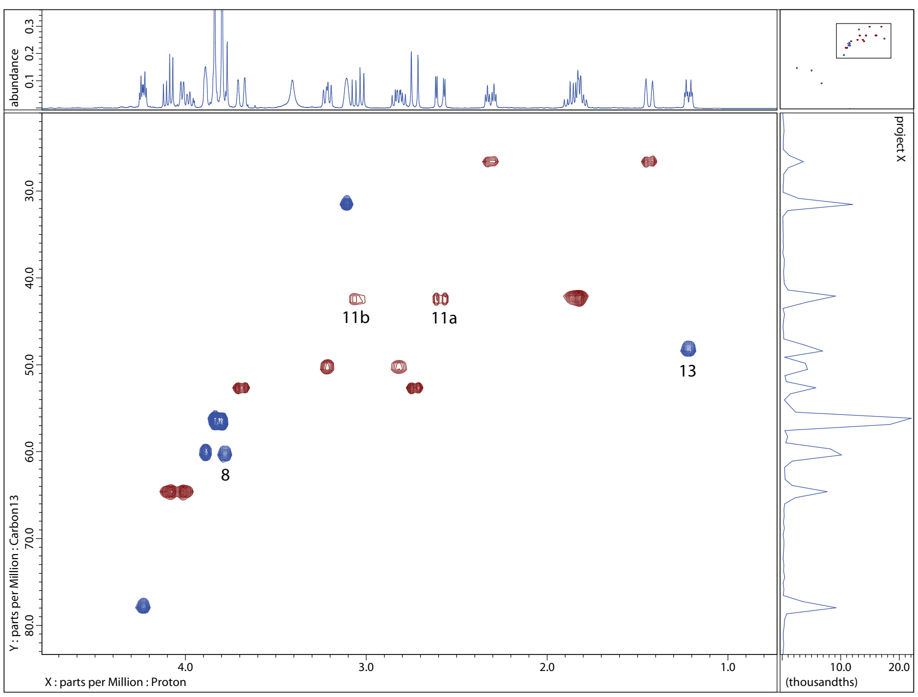
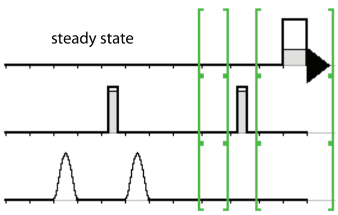


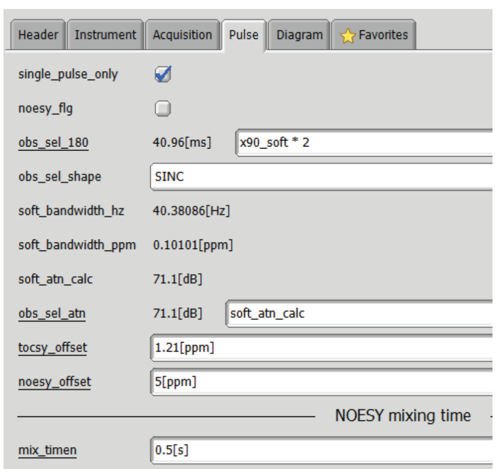
Figure 2. Expansion from edited HSQC for Brucine. The positions of H13 and H8 are labelled.

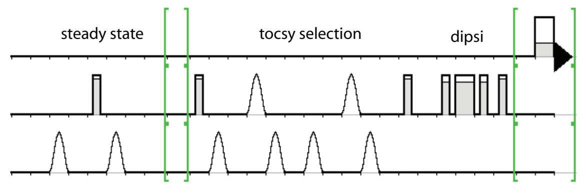
EXPERIMENT

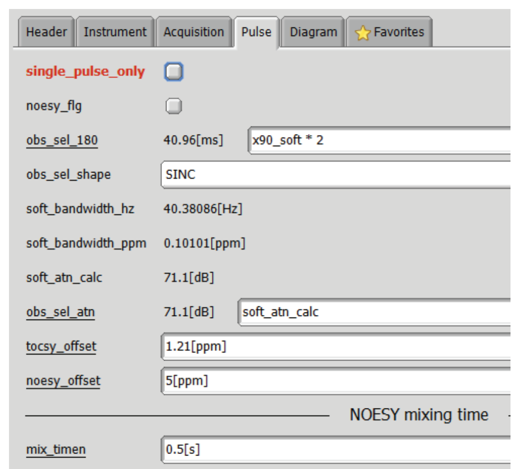
To obtain a StepNoesy result using Delta software the workflow is very simple.

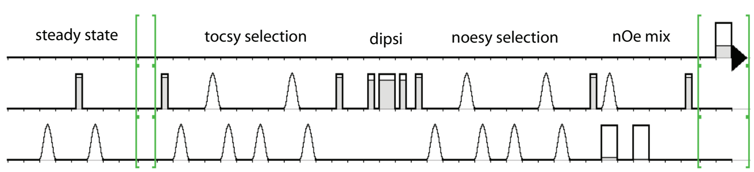
1. Choose StepNoesy1D_zqf experiment.
2. Check the "single pulse only" option in Pulse tab to obtain a simple 1H spectrum. From that result transfer the position desired for the TOCSY1D step.
3. Uncheck "single pulse only" and acquire the TOCSY1D. Inspect the result and transfer the position of the revealed resonance for the NOESY1D.
4. Check "NOESY flg" and acquire the full StepNoesy1D. Recommended to set number of transients to multiples of the full 128 step phase cycle.

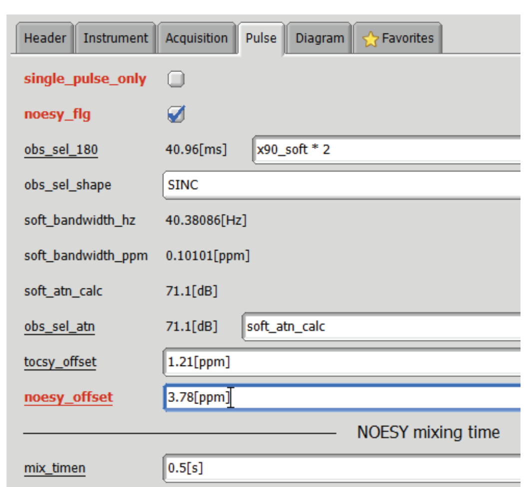












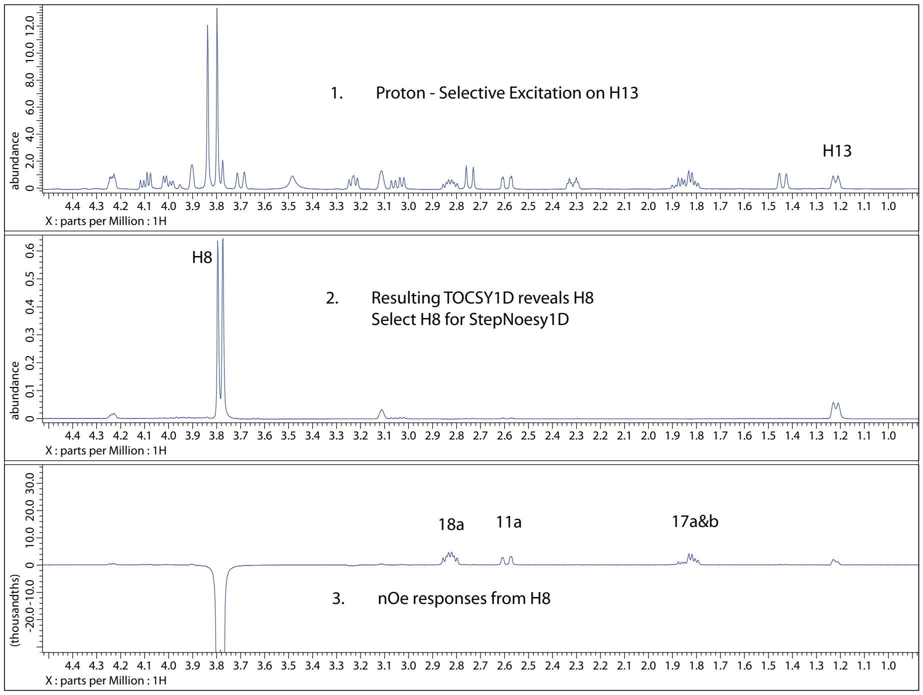


Figure 3. StepNoesy1D result showing nOe's from the buried H8 resonance to various protons in Brucine revealing important stereochemical information.

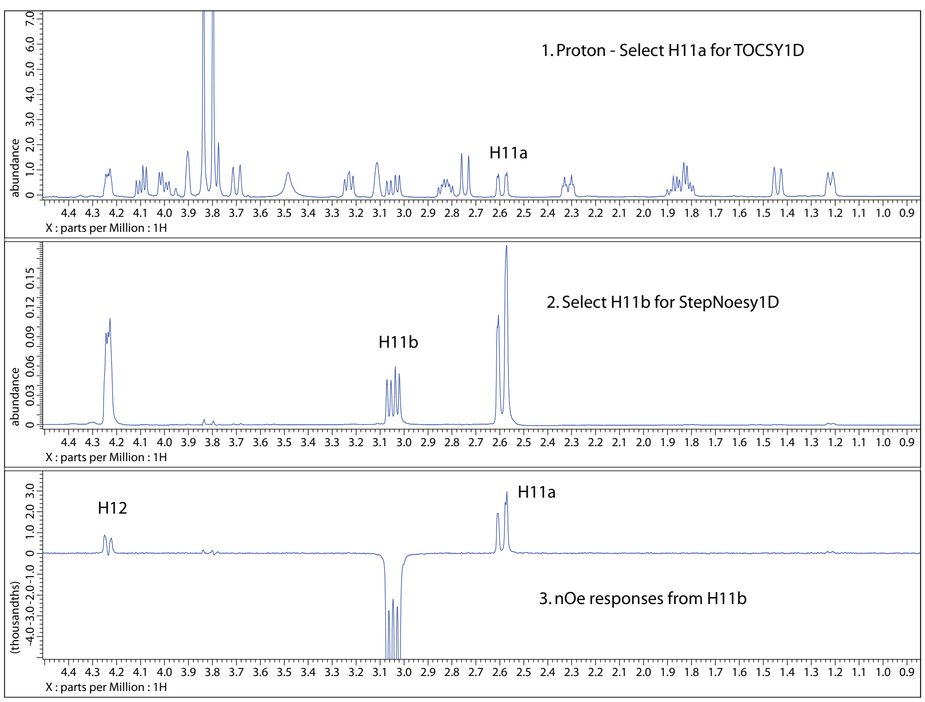


Figure 4. StepNOesy result showing nOe result from H-11b.

REFERENCES

[1] One-Dimensional NOE Experiments Using Pulsed Field Gradients. K Stott, J. Keeler, QN Van, AJ Shaka, J. Magn. Reson. 125(2) p 302-324 1997.

[2] Extending the limits of selective 1D NOESY with an improved selective TOCSY edited preparation function. Haitao Hu, Scott A. Bradley, Krish Krishnamurthy. J. Magn. Reson. Vol 171, Issue 2, Dec 2004 p 201-206.

AN-NM20180010