

Secrets of Structure Elucidation and Spectroscopic Databases



Reinhard Neudert
John Wiley & Sons





- John Wiley&Sons
- Laboratory Automation
- Structure Elucidation
- The SpecInf Internet Database
- Applications
- Links between Databases

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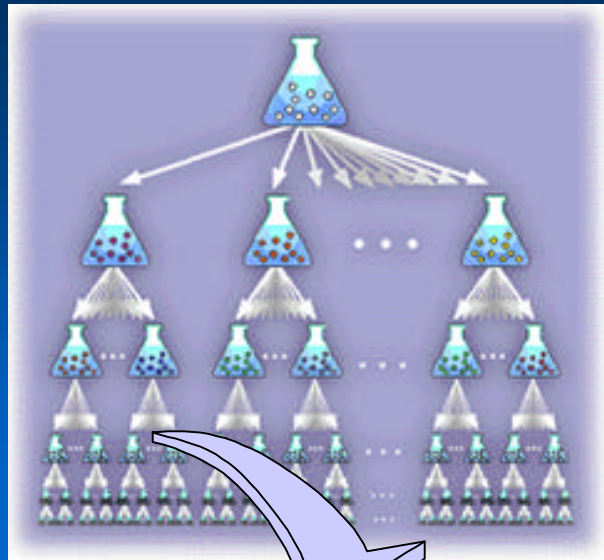
USA

Asia

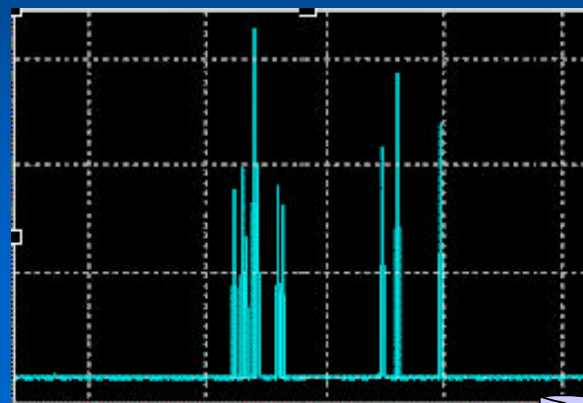


Canada

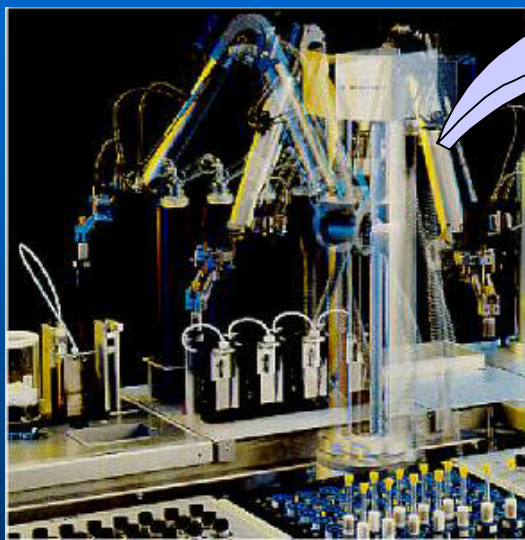
Laboratory Automation



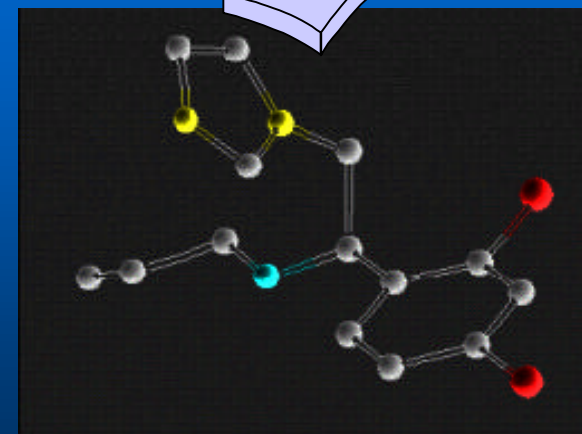
Combinatorial
Chemistry



Data Increase



Robots and Sample Changers



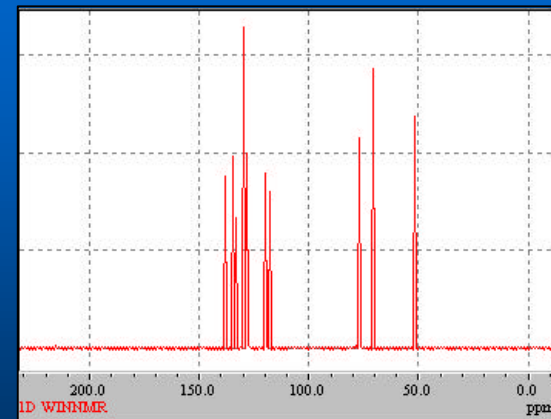
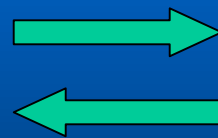
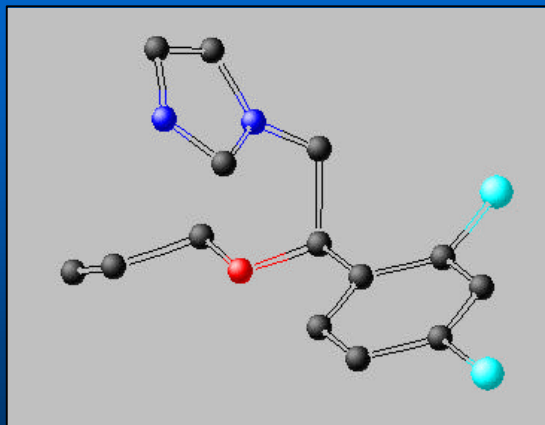
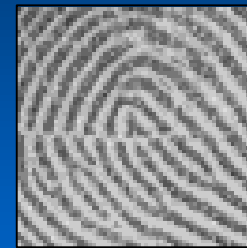
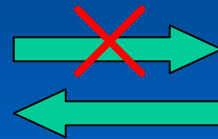
Bottleneck: Data Interpretation

Sensitivity and Structure Elucidation Potential



Technique	Required	Structure Elucidation Potential
^{13}C NMR	mg	very high
^1H NMR	μg	high
IR	ng	medium
EI/MS	<ng	medium
LC/MS	<ng	low

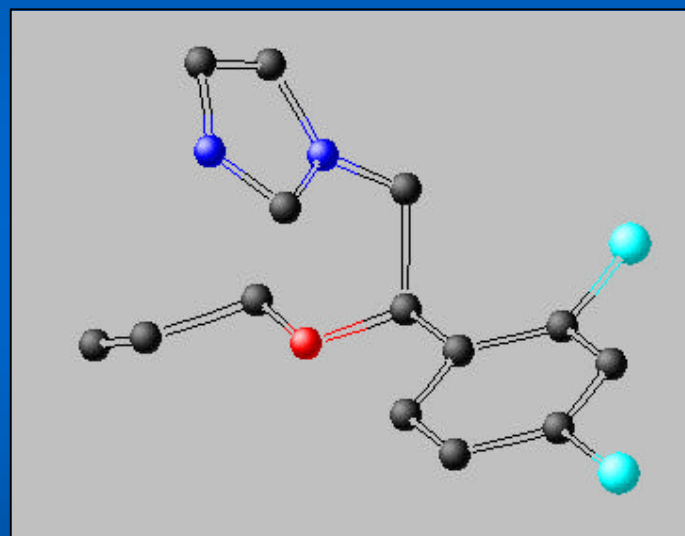
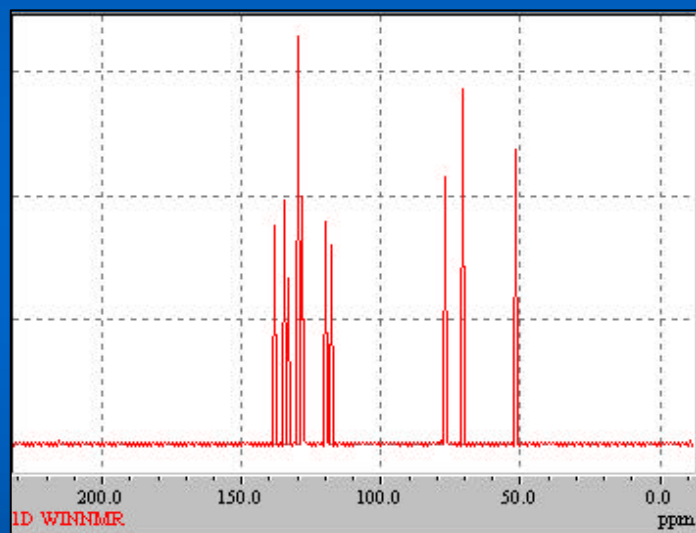
Fingerprints



Structure Elucidation



Spectrum Search
Structure Generator



Structure Search
Spectrum Prediction

Spectroscopic Databases: SpecInf



25 separate databases:

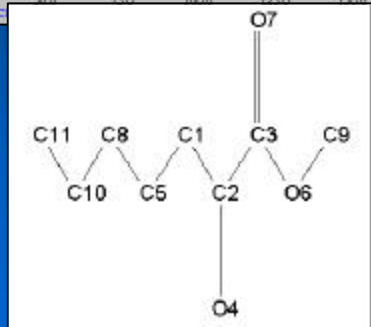
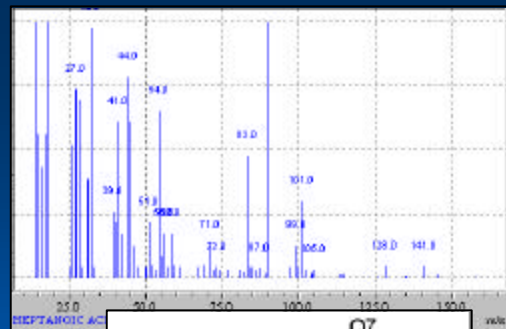
250,000 NMR Spectra

397,000 MS Spectra

32,000 IR Spectra

500,000 Structures

SpecInf : Basic Functions



Spectrum Search

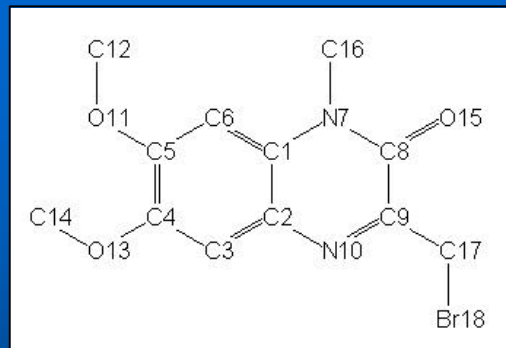
String Search



Cephalo%

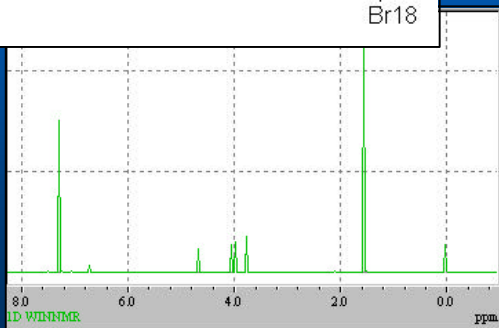
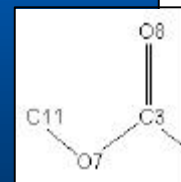
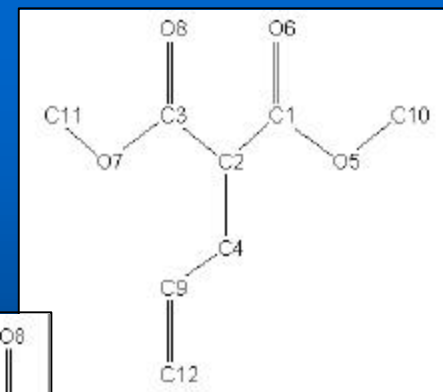
Cephalosporine

NMR, IR, MS
UV, NIR, Raman
Chemical Structures



Spectrum Prediction

Structure Search



Access through Web Browsers



Chemical Concepts SpecSurf Login Page - Netscape

Datei Bearbeiten Ansicht Gehe Communicator Hilfe

Zurück Vor Neu laden Anfang Suchen Guide Drucken Sicherheit Stop

Lesezeichen Adresse: <http://specinfo.wiley-vch.de:8080/specsurf/login.jsp> Verwandte Objek

T-Online Internet Neuigkeiten Interessantes Mitglieder Marktplatz



Welcome to SpecInfo on the Internet

Login

Please have a look [at the Illustrated Guide.](#) Username Did you setup your browser?
Password If not please [click here!](#)

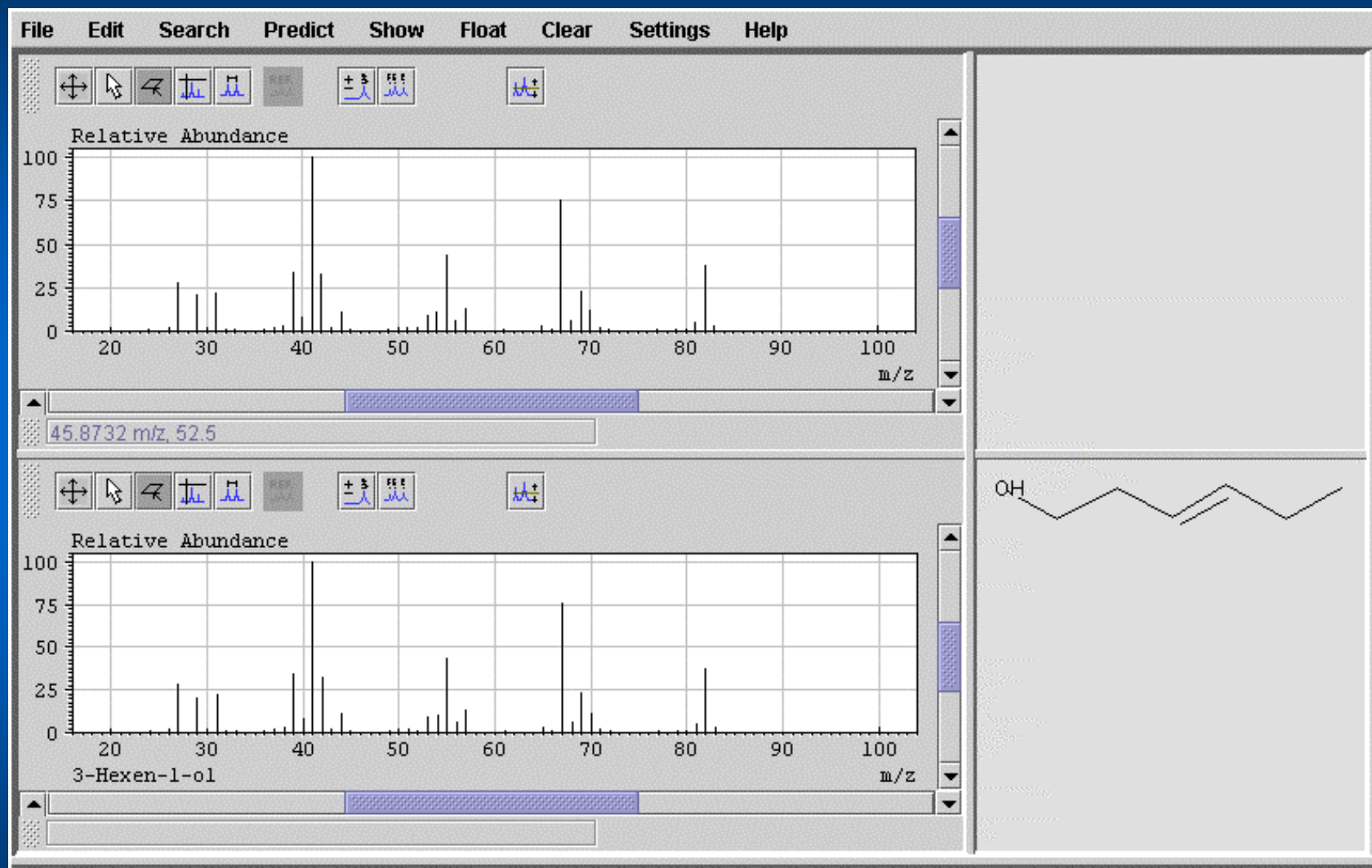
Screen Size

The applet has a size of about 500 kbyte and needs several minutes for the first download. Please allow some computation time after the download. You can follow this by watching your CPU usage meter on your task manager or system monitoring tool, generally CPU usage is 100% during this period.

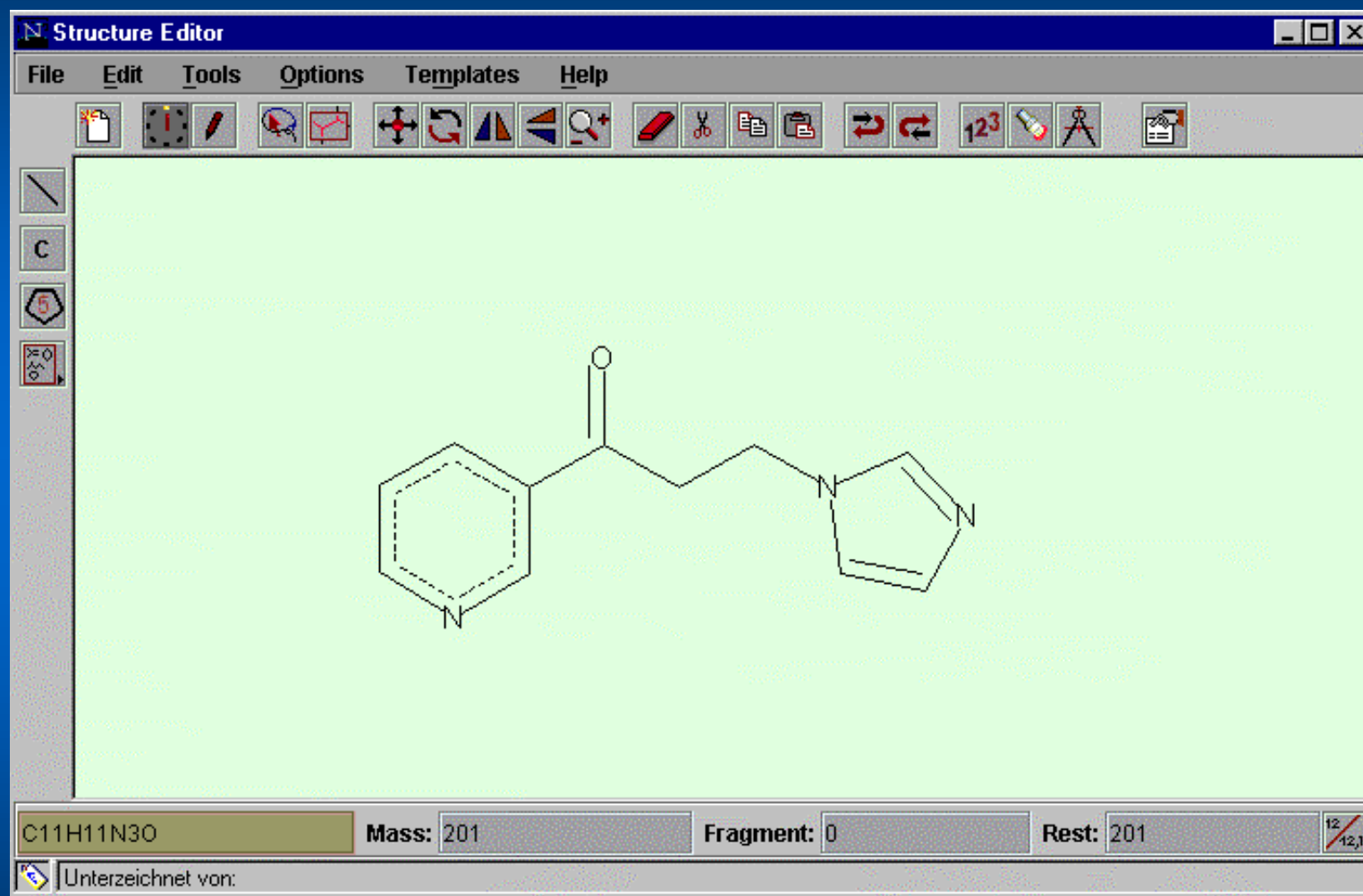
Swing installed

Applet SwingAvailable running

The Web Client SpecSurf

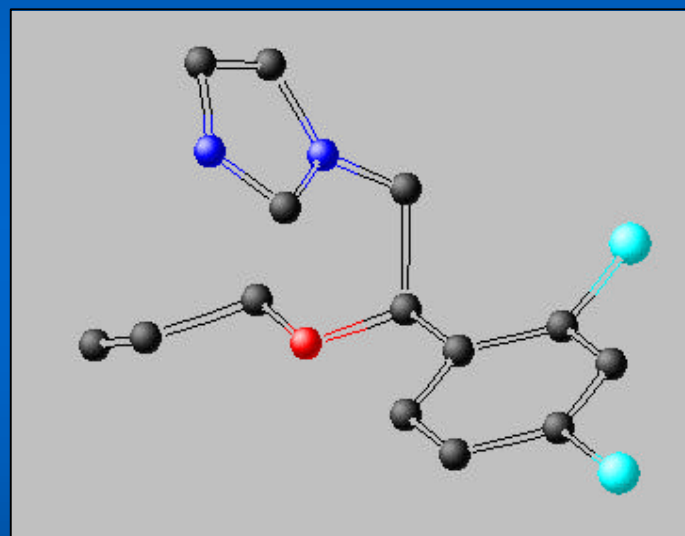
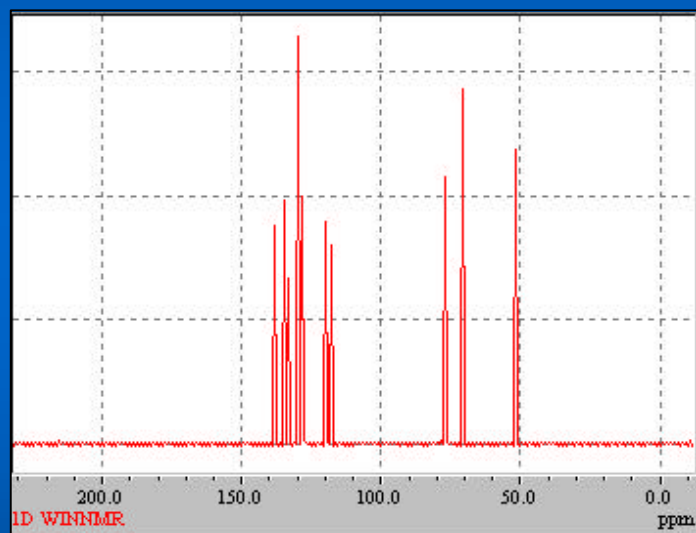
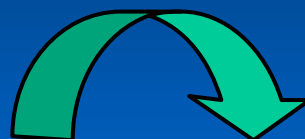


Structure Drawing



Applications

Spectrum Search



From Spectrum to Structure: Full Spectrum Search

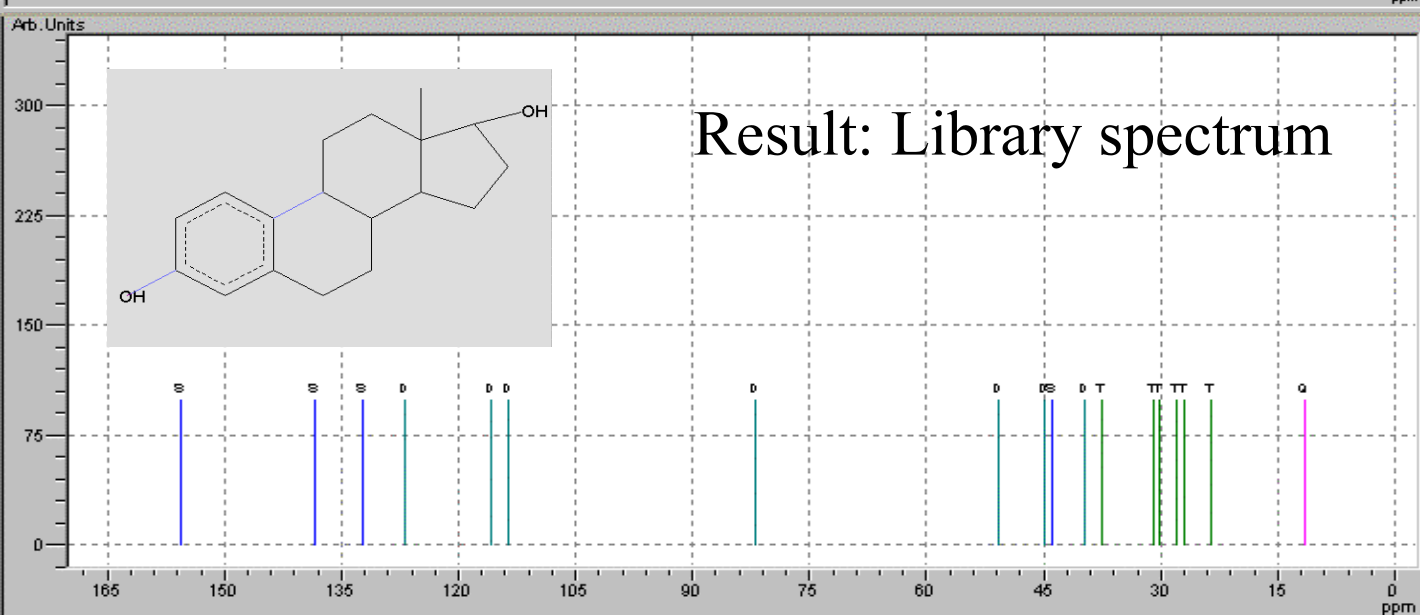
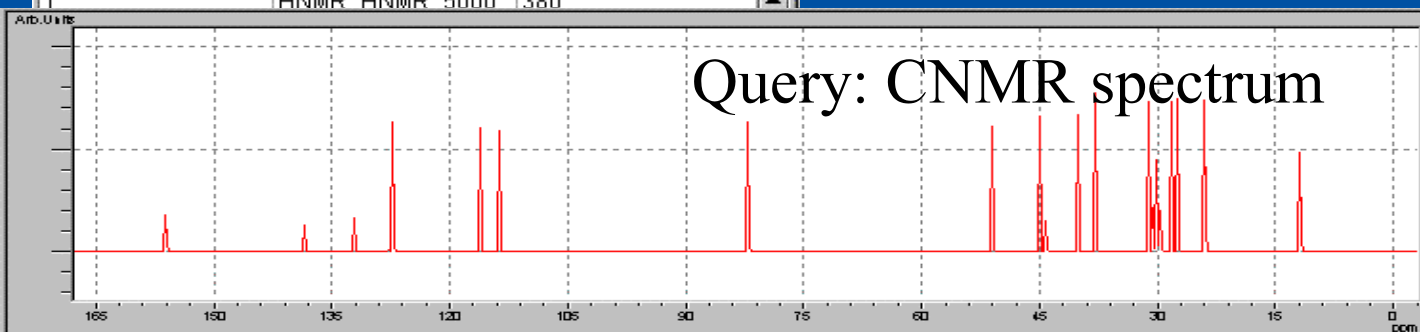


Case 1:
Query
contained
in the
Library

Database Preferences

Select Database(s)

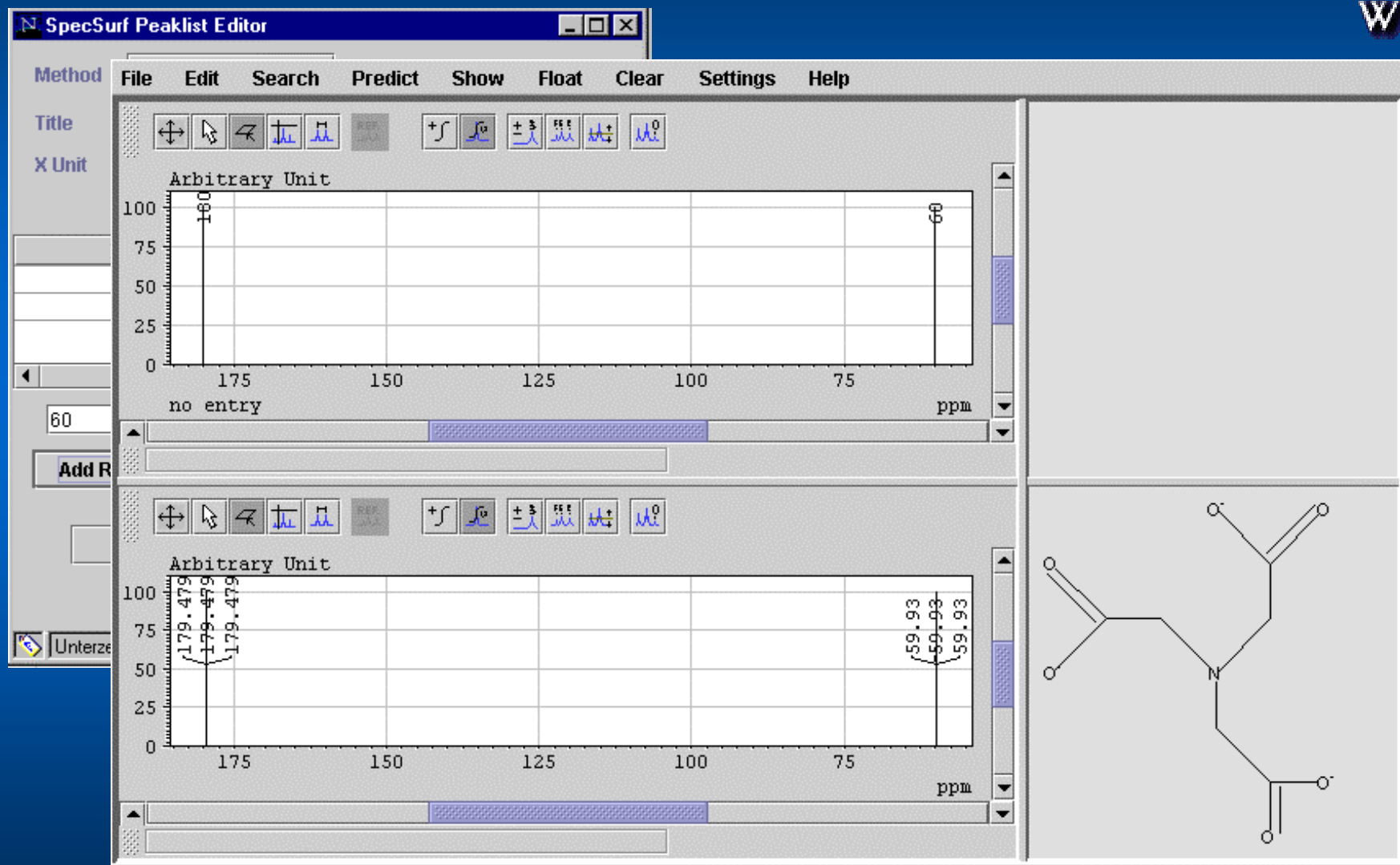
No	Name	Size in MByte
1	HNMR HNMR 5000	380



Unterzeichnet von:

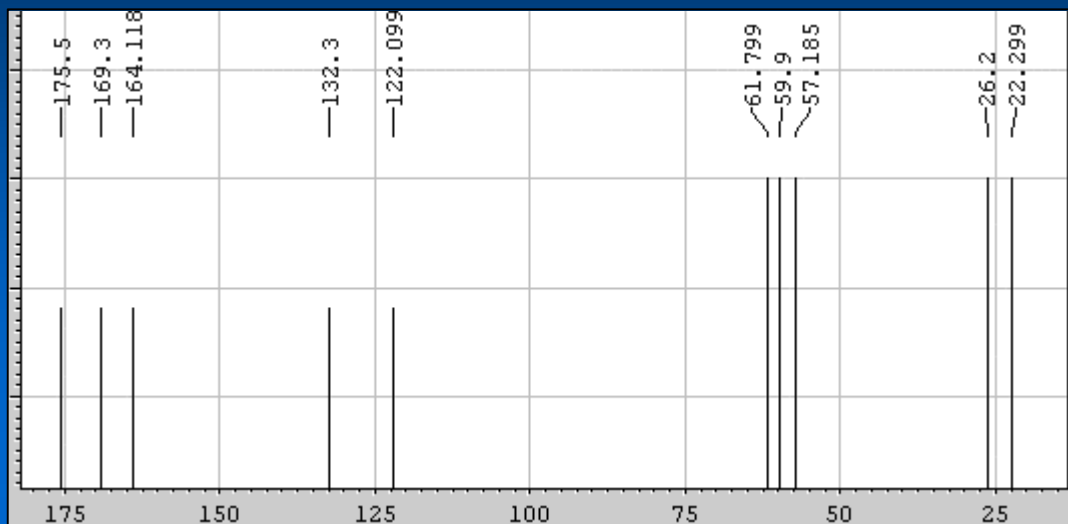
From Spectrum to Structure: Spectrum Search

From Spectrum to Structure: Peak List Search



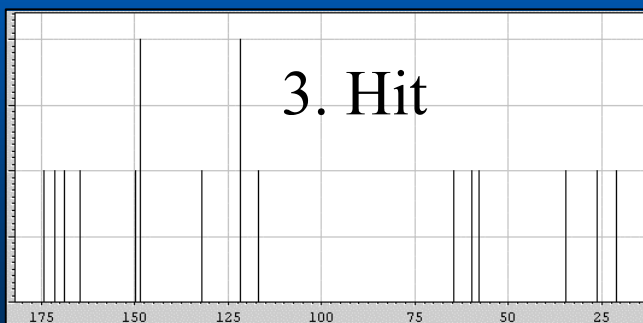
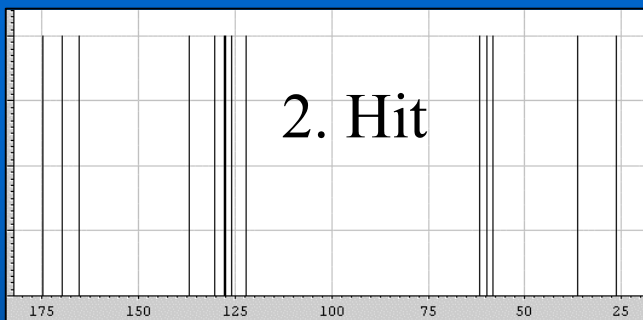
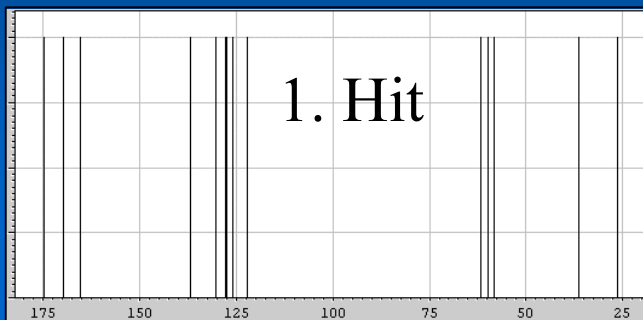
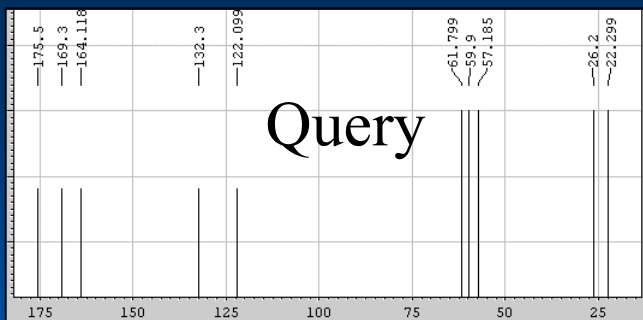
From Spectrum to Structure: Spectrum Search

Spectral and Structural Similarity

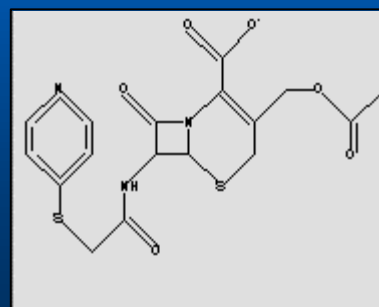
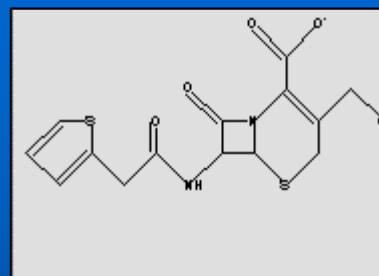
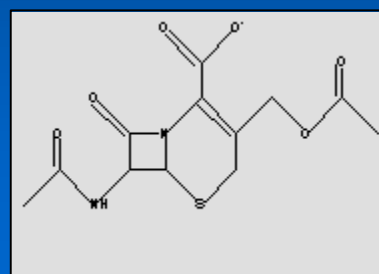
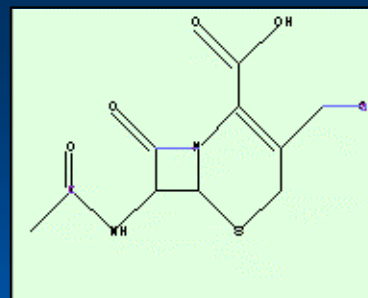


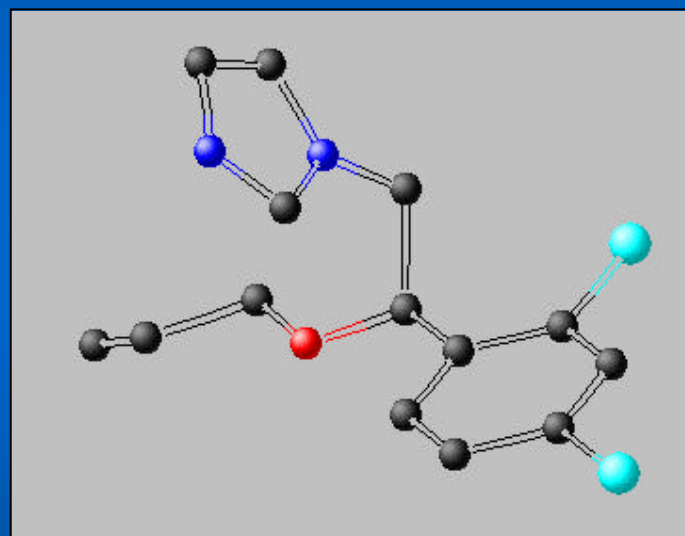
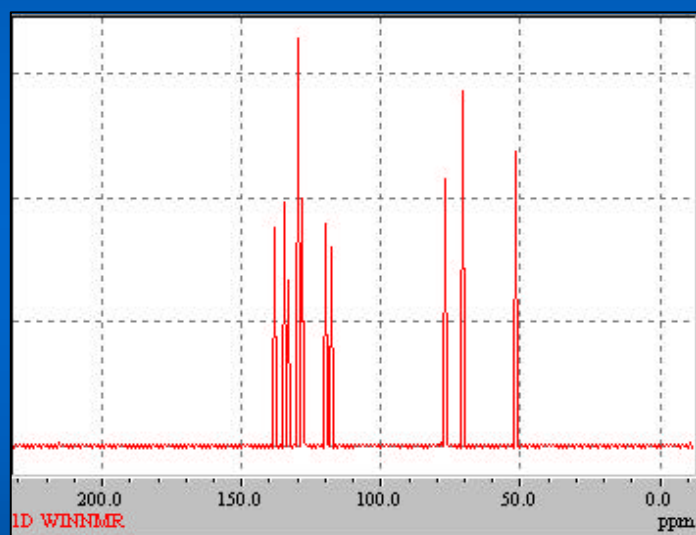
Case 2:
Query
not contained
in the
Library

Rank	Quality	Folder ID	Property
1/3	505	18:FO0000036681	7-Acetamido-cephalosporanic acid, anion
2/3	495	18:FO0000036689	7-(2-[2]Thienyl-acetamido)-desacetyl-cephalosporanic acid,...
3/3	408	18:FO0000029698	7-(Phenyl-acetamino)-cephalosporanic anion



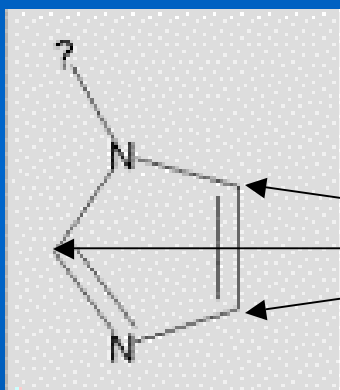
Similar
Spectra
correspond
to
Similar
Structures





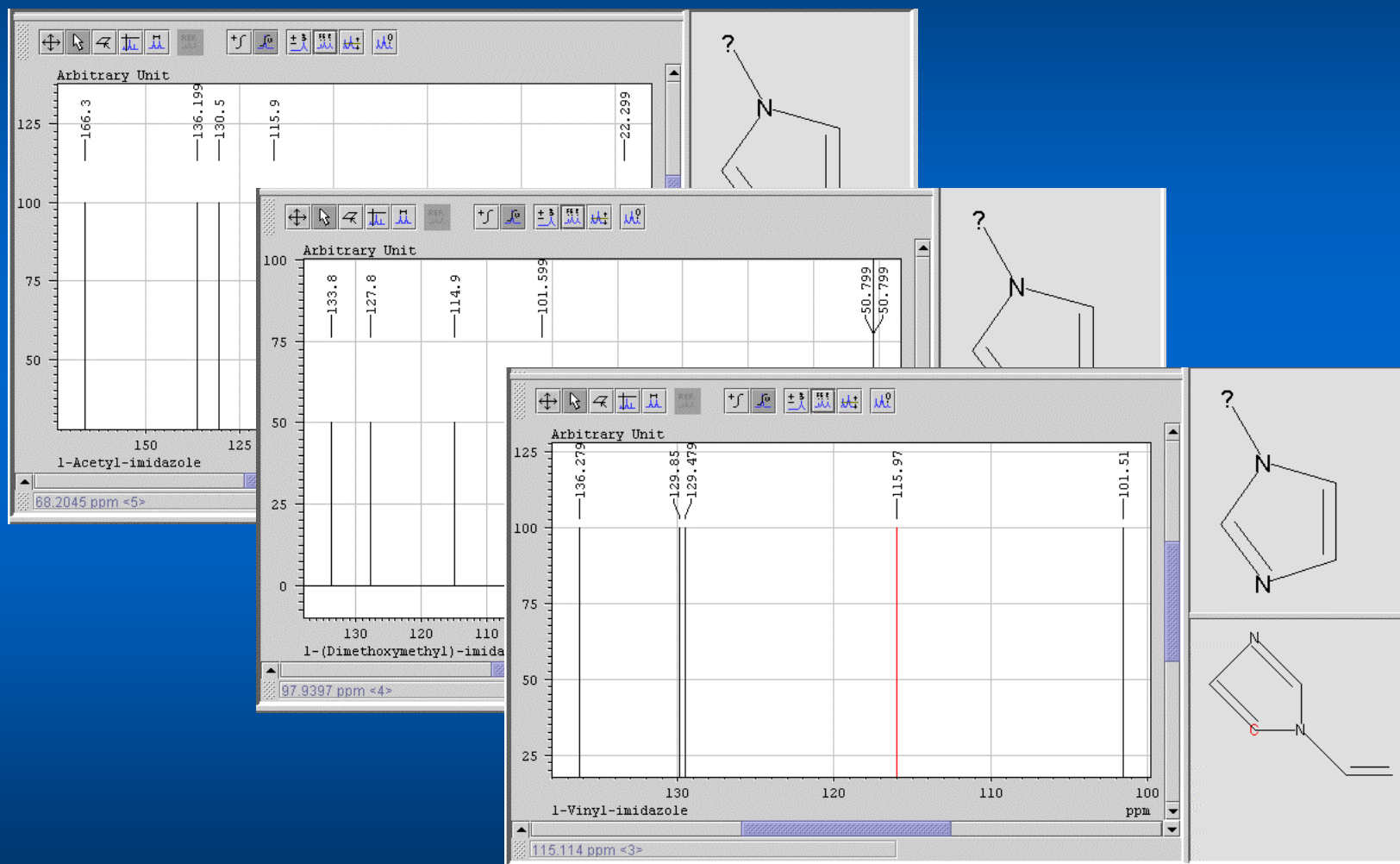
Structure Search

From Structure to Spectrum : Structure Search

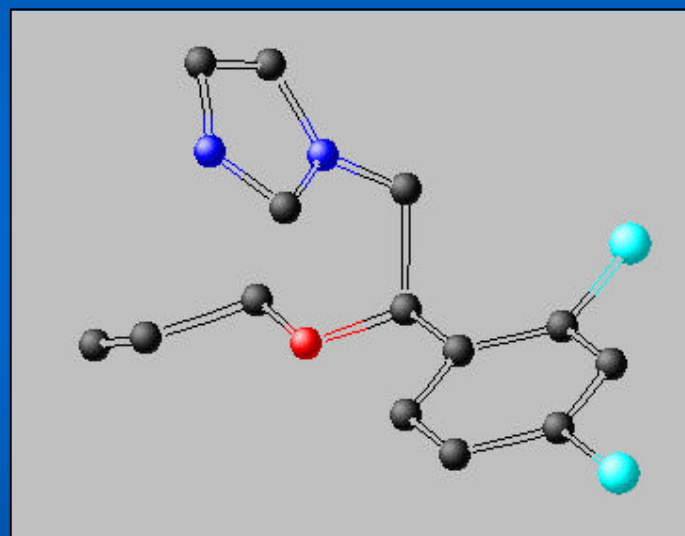
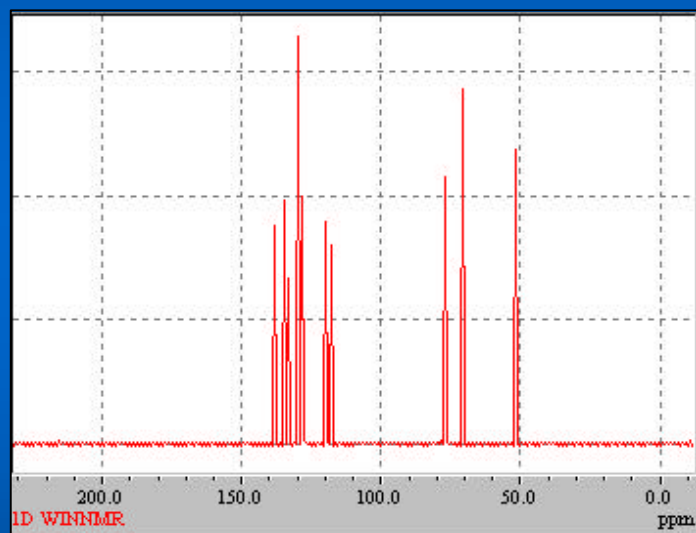


Inf
varying substituents
on the C shif
Imidazole

Substructure Search Result



From Structure to Spectrum : Structure Search



Spectrum Prediction

From Structure to Spectrum : Spectrum Prediction

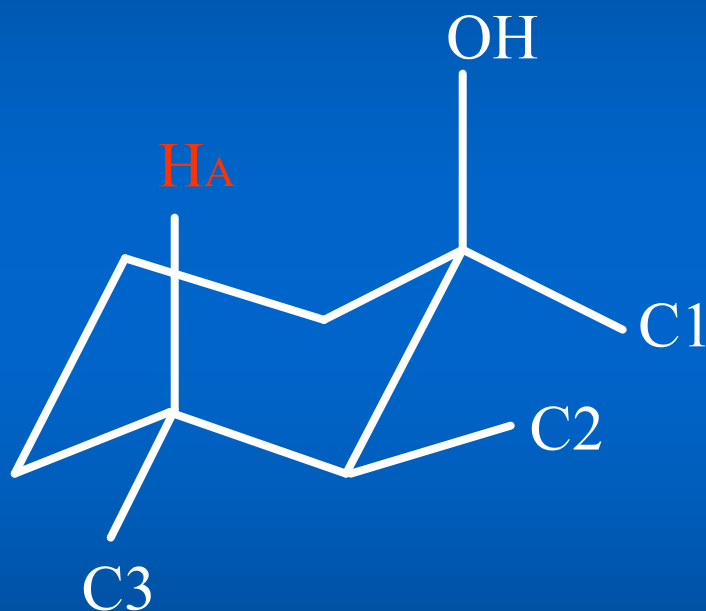


Strategies

- Rule Based Systems
- Database Based Systems

➤ Rule Based Systems

H_A Chemical Shift



1.44 ppm f

+0.15 ppm f C3 eq

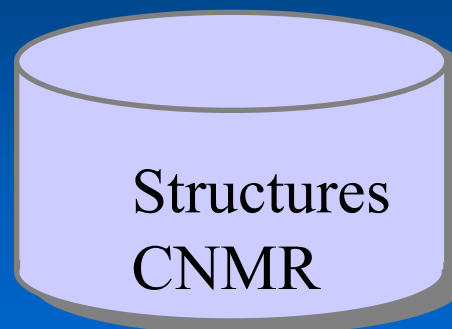
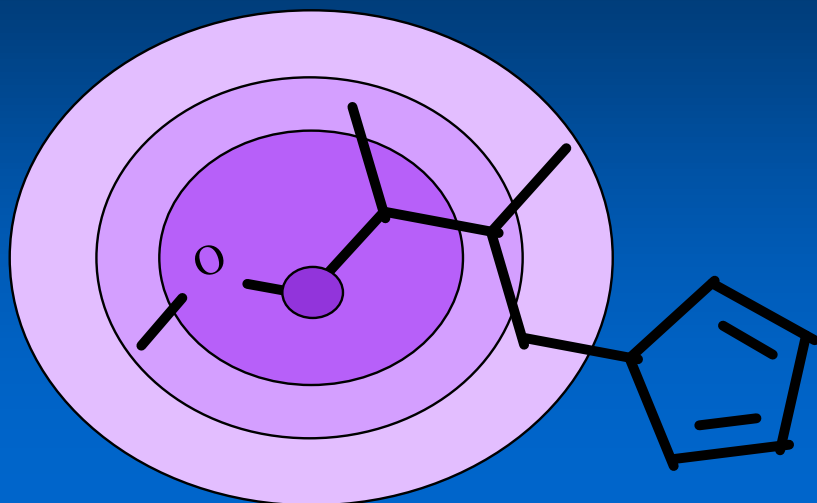
- 0.31 ppm f C2 eq

+0.03 ppm f C1 eq

+0.46 ppm f

1.77 ppm total

➤ Database Based Systems

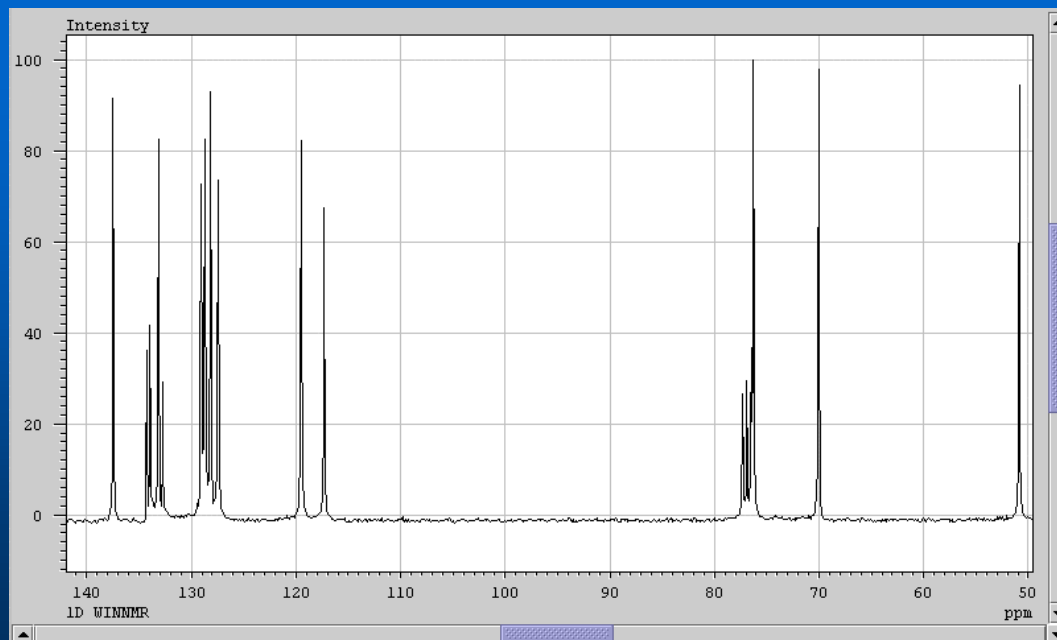
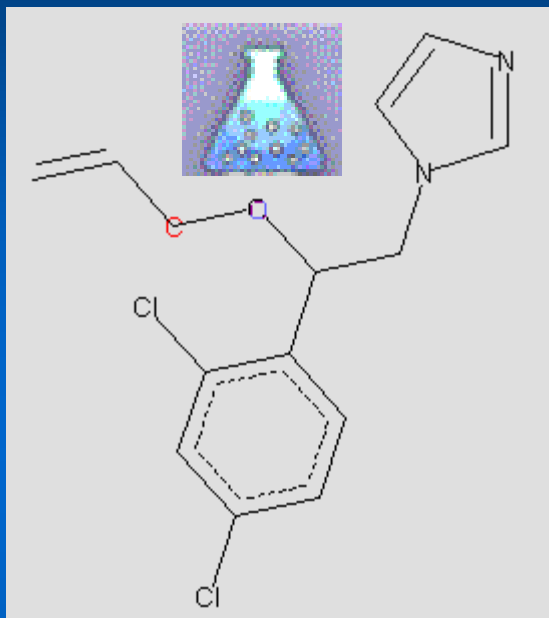


Substructure codes
(three spheres)

¹³CNMR chemical shift

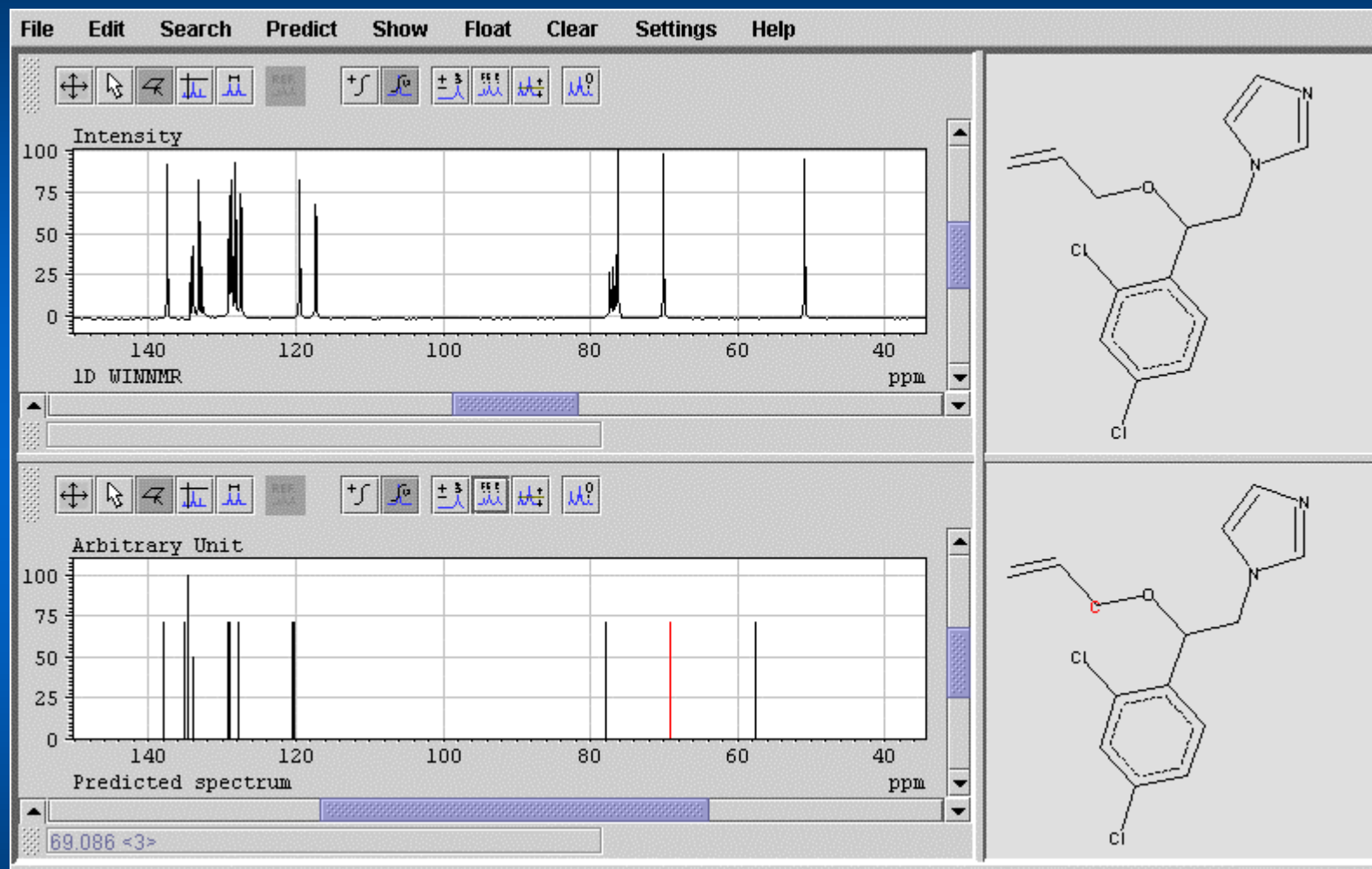
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	74.20 ppm
<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	72.20 ppm
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	71.80 ppm
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	71.50 ppm

Application 1: CNMR Conf



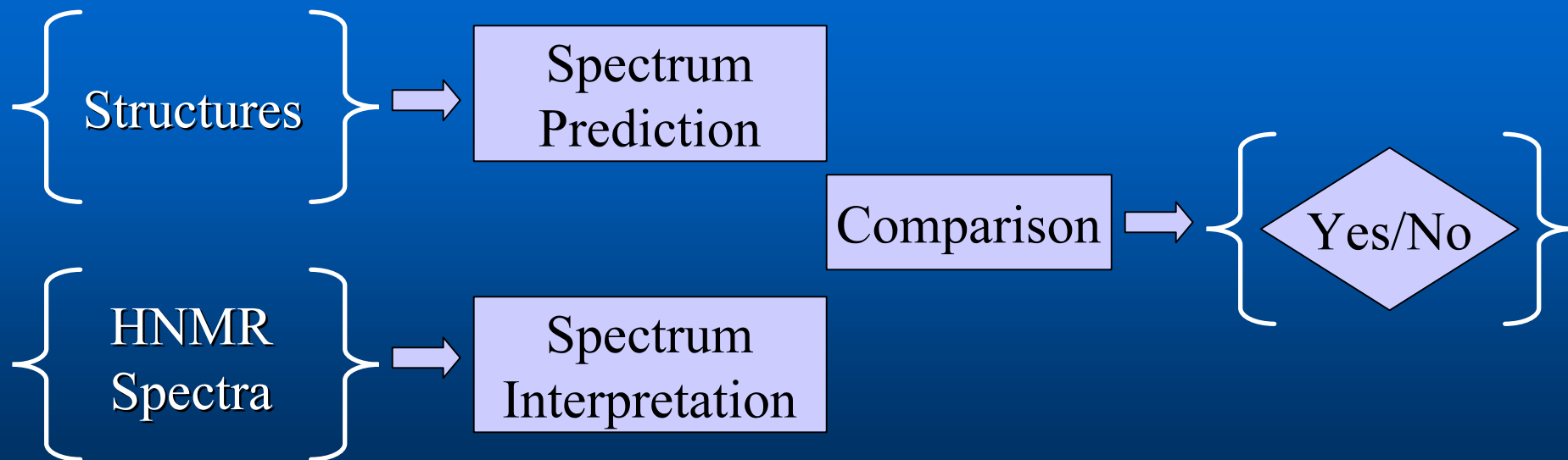
From Structure to Spectrum : Spectrum Prediction

CNMR Conf



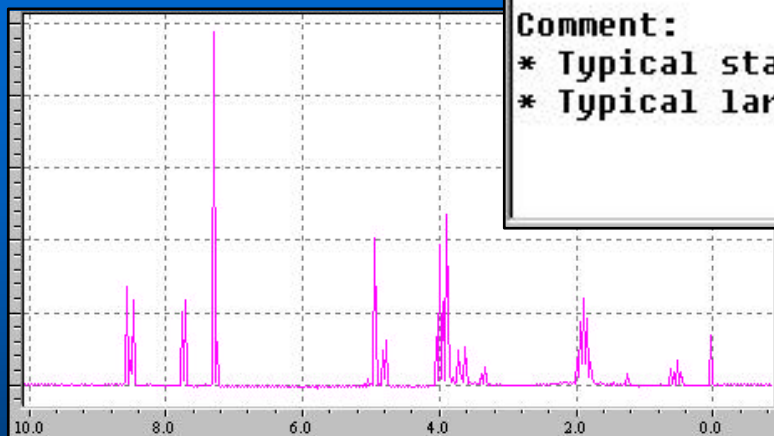
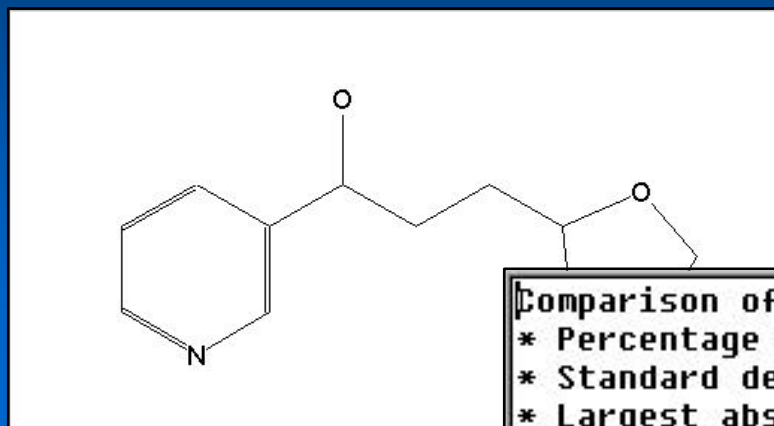
From Structure to Spectrum : Spectrum Prediction

Application 2: Automated HNMR Compatibility Check



From Structure to Spectrum : Spectrum Prediction

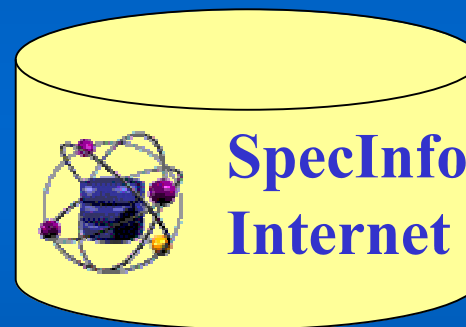
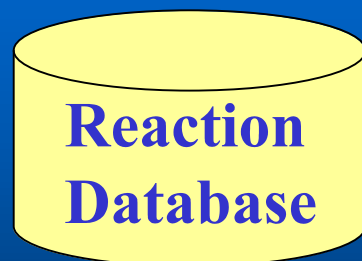
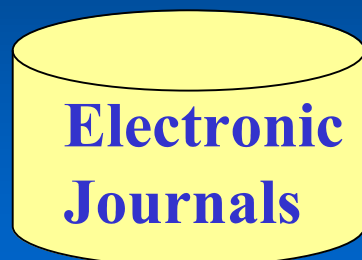
Yes/No



Comparison of ¹H-NMR shifts from spectrum and structure:
* Percentage of unexplained H atoms in spectrum = 0.00 %
* Standard deviation = 0.15 ppm
* Largest absolute deviation = 0.28 ppm

Comment:
* Typical standard deviations : 0.2 - 0.3 ppm
* Typical largest absolute deviations : up to 1 ppm

Hyperlinks between Databases



From the Electronic Journal to Spectra



Electronic Publishing Demo - Netscape

Datei Bearbeiten Ansicht Gehe Communicator Hilfe

Zurück Vor Neu laden Anfang Suchen Guide Drucken Sicherheit Stop

Lesezeichen Adresse: <http://specinfo.wiley-vch.de/ElectronicPublishing/index.html> Verwandte Objek

T-Online Internet Neuigkeiten Interessantes Mitglieder Marktplatz

Beltlike Aromatic Hydrocarbons by Metathesis Reaction with Tetradehydrodianthracene

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Institut für Organische Chemie der Technischen Universität Braunschweig^a,
Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig^b,
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Received Month Day, 199X

Keywords: Cycloadditions / Cyclophane / Metathesis / Photochemistry

A substructure of a (5,5) armchair nanotube was obtained by metathesis reactions with tetradehydrodianthracene. All C–C bonds are all unsaturated and form a full conjugated beltlike system. A set of molecular building blocks can be used to synthesize other sections of nanotubes as well.

One of the main motivations for the synthesis of cyclophanes is the preparation and investigation of compounds in which the π -electron system is spherically deformed by the introduction of bridging ligands (Scheme 1, left). [1] Fully conjugated belt- and tubelike structures can be viewed as an extreme example of such a deformation. (Scheme 1, right). [2] The p orbitals in these structures are perpendicular to the surface of a cylinder and their inner lobes point towards the axis of the cylinder.

Scheme 1. Spherically deformed π systems in a cyclophane (left) and in a beltlike conjugated system (right)



Dokument: Übermittelt

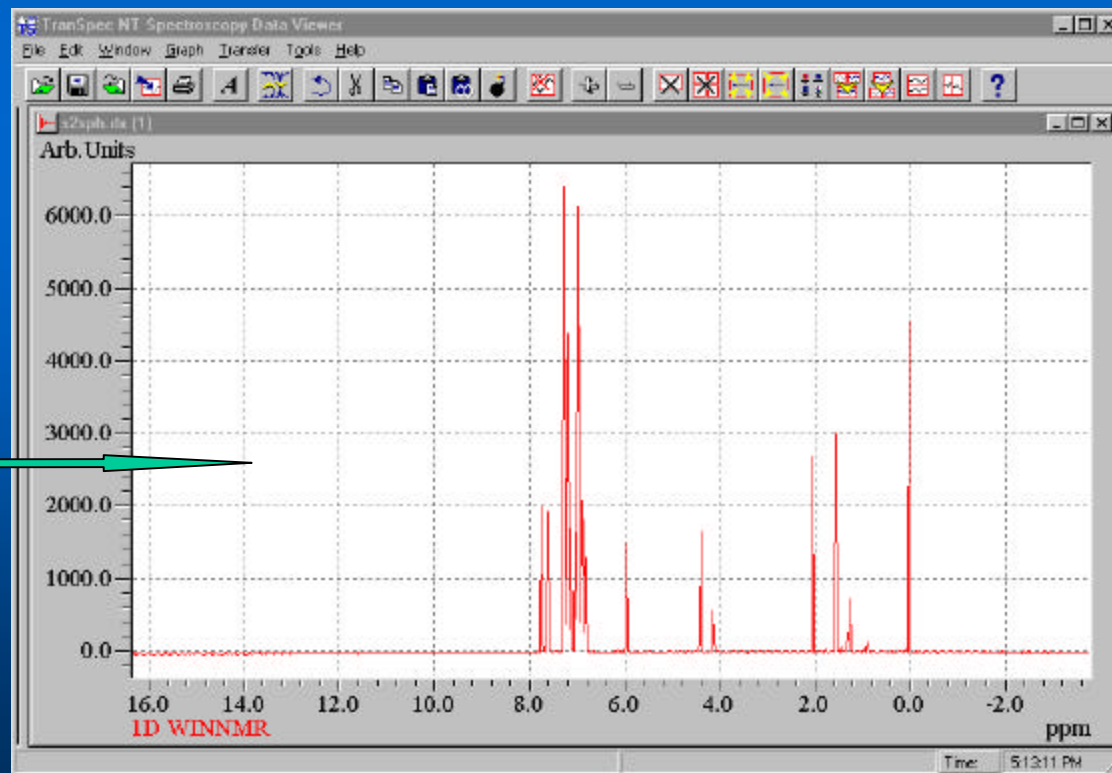
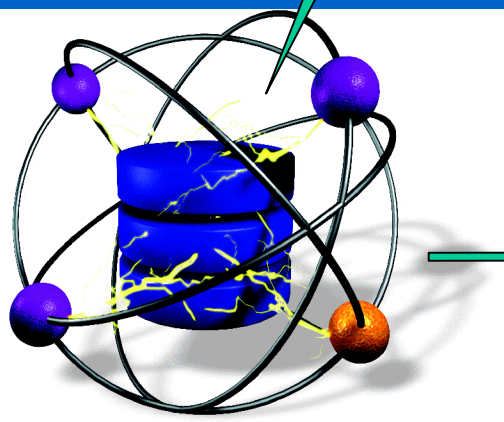
Experimental Section



Experimental Section

2: A solution of **1** (100 mg, 0.284 mmol) and α -pyrone were added to a reaction mixture. After reaction two portions of α -pyrone were added. The mixture was purified by column chromatography with hexane/ethyl acetate (2:1). Yield: 15%. M.p. 229 °C (decomp.). – **¹H NMR** (400 MHz, CDCl₃): δ = 6.90 (m, 10 H, CH, arom.), 5.95 (dd, *J* = 10.0, 2.0 Hz, CH, arom.), 4.90 (m, 2 H, CH₂, saturated). – **¹³C NMR** (100.5 MHz, CDCl₃): δ = 144.38 (C_q), 143.56 (C_q), 142.09 (C_q), 142.87 (C_q, arom.), 126.38 (CH, arom.), 126.38 (CH, arom.), 124.78 (CH, arom.), 124.71 (CH, arom.), 66.12 (C_q, saturated), 61.78 (C_q, saturated), 49.00 (w, C=C, olef), 1451.15 (s, C=C, arom.), 1361 (m), 1700 (sh), 280 nm (200, sh). – MS (70 eV): *m/z* 170 (M⁺), 155 (M⁺), 140 (M⁺), 125 (M⁺), 110 (M⁺), 95 (M⁺), 80 (M⁺), 65 (M⁺), 50 (M⁺), 35 (M⁺), 20 (M⁺), 15 (M⁺), 10 (M⁺), 5 (M⁺), 4.90.

5 (Kammermeier, page 1). – Method *a* from Scheme 1. The mixture was heated at reflux for 16 h. After removal of the solvent by distillation the residue was purified by column chromatography with hexane/dichloromethane (2:1). **5** was obtained as a white solid. Yield: 15%. M.p. 100 °C (decomp.). – **¹H NMR** (400 MHz, CDCl₃): δ = 7.47 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 7.30 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 7.15 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 7.00 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 6.85 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 6.70 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 6.55 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 6.40 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 6.25 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 6.10 (d, *J* = 8.0 Hz, 2 H, CH, arom.), 5.95 (dd, *J* = 10.0, 2.0 Hz, CH, arom.), 4.90 (m, 2 H, CH₂, saturated).



SpecInf Internet

Reaction Database-Spectroscopic Data



Search

About the Encyclopedia

Encyclopedia of Reagents

WILEY
InterScience®

PERSONAL
HOME PAGE

JOURNAL
FINDER

JOURNAL
SEARCH

REFERENCE
WORKS

HELP

CONTACT
US

LOGOUT

e-EROS Encyclopedia of Reagents for Organic Synthesis

A to Z SEARCH HELP

Abbreviations and Lists

A - Bru

But - Dia

Dib - Dio

Dip - K

L - M

N - Sin

Sod - Trim

Trip - Z

Text only search

Please enter a term or phrase to search on:

Begin Search

Reset

Structure & Metadata search

To perform a structure search select 1 from the top 3 terms in the first drop-down menu. For metadata searching, select from the 9 remaining terms.

Structure exact

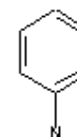
Structure ->

and

Please choose...

Begin Search

Reset



Browse Hit List

<

87

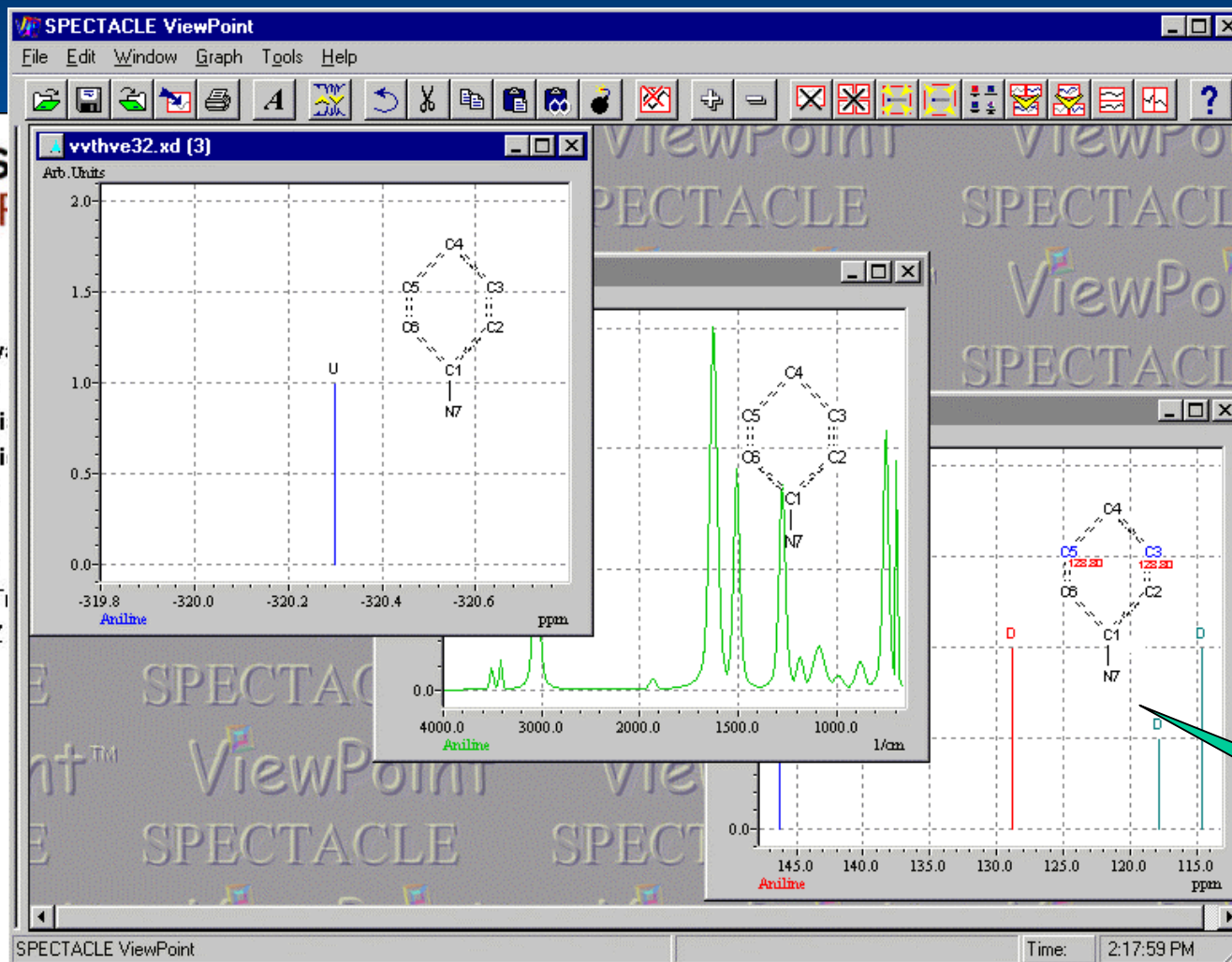
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Reaction Database-Spectroscopic Data



WILEY
InterS
e-ET

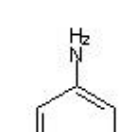
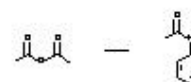
- Abbrev:
- A - Bru
- But - Di
- Dib - Di
- Dip - K
- L - M
- N - Sin
- Sod - T
- Trip - Z



... Browse Hit List ...

< 87 >

2 [Acetoacetic Acid](#)
[Addition and Condensation Reactions](#)





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