

Lib Search: Similarity EI Hybrid Search for Spectra Sent from Chromatogram Window

Video/Handout

James Little

Mass Spec Interpretation Services

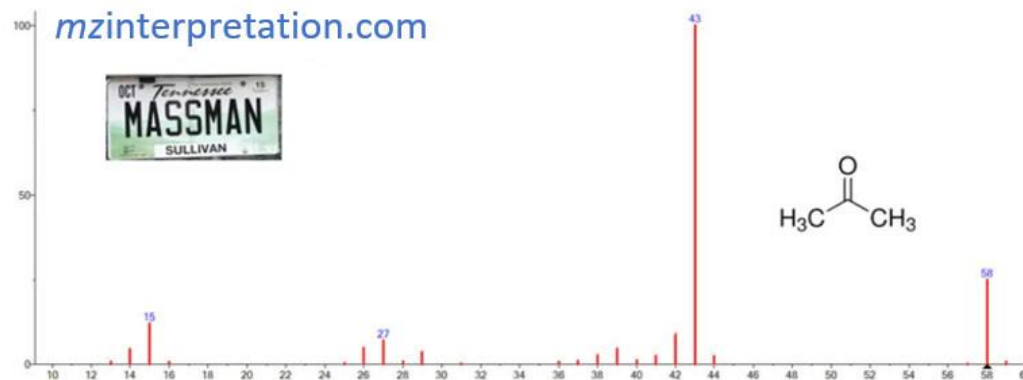
April 25, 2026

mzinterpretation.com

See **Full Course** on NIST26 with new **Integrated** Deconvolution/Library Searching for **EI GC-MS** and **LC-MS/MS**!

Mass Spec (m/z) Interpretation Services

Organic Mass Spectrometry



Lots of Previous Information on Lib Search and Other NIST Software on My Website

NIST Search of EI Mass Spectral Databases in Unknown Identifications

- **Extensive** Resources on Lib Search and Other Programs within NIST Search
- See [Link](#)
- However, no information on Chromatogram Window

Videos and Videos Zipped:

Part 0: Changes in EI NIST23 Program (V3.0)

Part I: Spectral Searches with NIST MS Search

Part II: Structure Searches with MS Search and Using MS Interpreter

Part III: AMDIS (NIST) for Processing EI Mass Spectral Data Files

Part IV: Advanced NIST Hybrid Search of EI and MS/MS Spectra

Part V: Creating and Sharing User EI and MS/MS Libraries

Part VI: Creating and Using Retention Indices in NIST Software

Part VII: Tracking Complex Coelution with AMDIS and NIST Search

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Part I: Spectral Searches with NIST MS Search

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Part IV: Advanced NIST Hybrid Search of EI Spectra

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Other Webinar Resources:

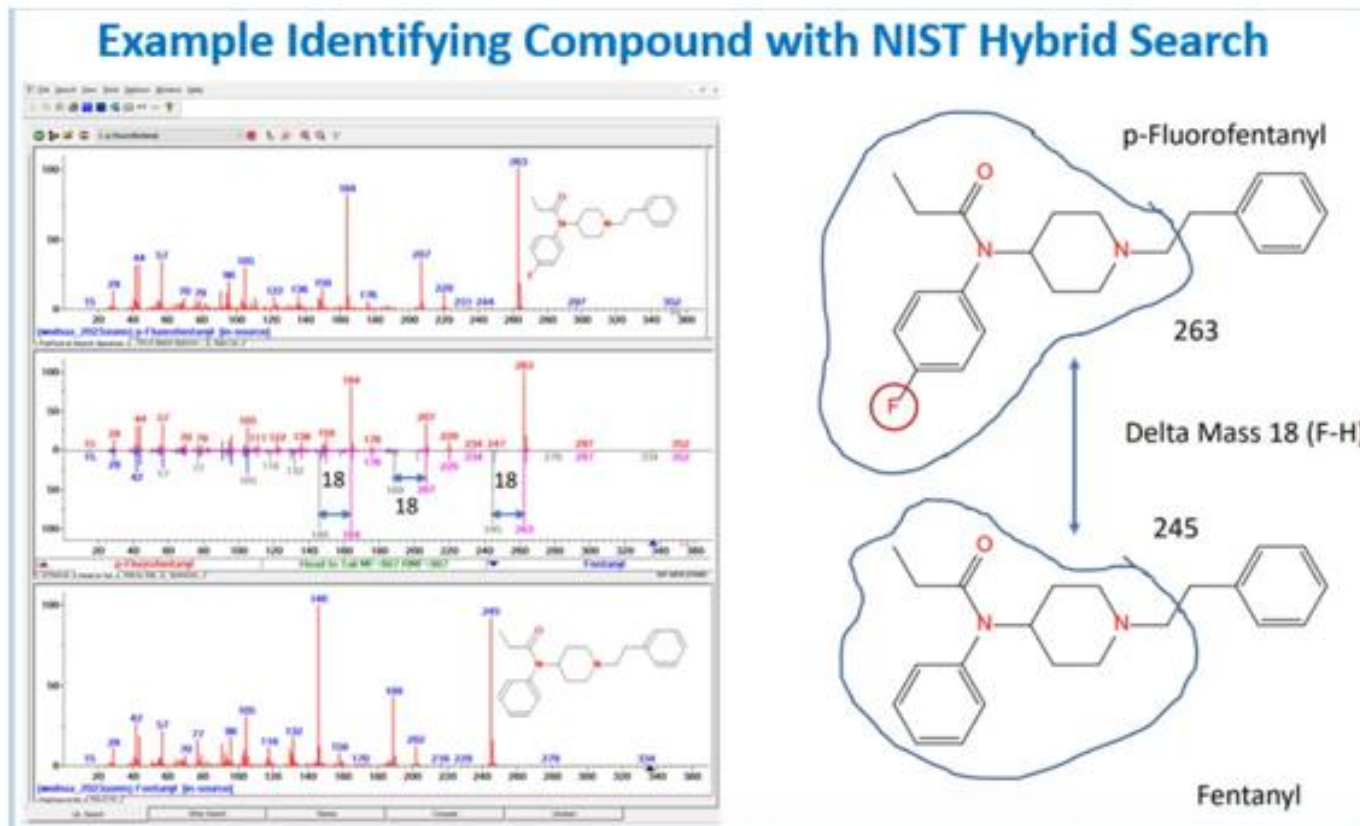
Power of NIST EI Hybrid Search for Unknown Identifications

- NIST EI hybrid search expands the power of traditional EI library matching by enabling detection of structurally related compounds through mass-shifted fragment alignment. This transforms the library from a static reference into a dynamic tool for identifying unknowns, analogs, and emerging compounds not explicitly represented in the database.
- Hybrid search integrates exact and mass-shifted peak matching into a single scoring process, allowing both direct spectral agreement and systematic mass differences to contribute to identification.
- While NIST EI hybrid search does not require a molecular ion, its effectiveness is significantly enhanced when the molecular weight of the unknown is known or constrained. In such cases, the mass difference (Δm) between unknown and library spectra can be interpreted directly, reducing false positives and enabling more confident structural insights.

More Detailed Information

Novel NIST Hybrid Search for Unknown Identifications

[See Link](#)



[Excel DeltaMass Table](#)

[PDF DeltaMass Table](#)

Videos

[YouTube: Advanced NIST Hybrid Search of EI Spectra](#)

[YouTube: Advanced NIST Hybrid Search for MS/MS \(Tandem\) Spectra](#)

[YouTube: Application NIST Hybrid in EI in Seized Drug Analyses](#)

Associated Handouts

[Handout: Advanced NIST Hybrid Search of EI Spectra](#)

[Handout: Advanced NIST Hybrid Search of MS/MS \(Tandem\) Spectra](#)

[Handout: Application NIST Hybrid in EI in Seized Drug Analyses](#)

Supporting Software Courses for Utilizing Hybrid Search

[NIST EI Search Software](#)

[NIST MSMS Search Software](#)

Setup of Hybrid Settings in Lib Search Window

#	Src.	MW	Formula	Name
1	A	0		Component at scan 781(10.601 min)...
2	A	0		Component at scan 1287(14.927 mi...
3	A	0		Component at scan 1424(10.688 mi...
4	L	0		TESTMIX2_180504_MAS011_06_s...
5	L	0		TESTMIX2_180504_MAS011_06_s...
6	L	0		Checkout_TestMix_AMSMS.834.83...

- Select Libraries
- Commercial Libraries e.g. Wiley
- User Libraries, etc.
- Results combined

Library Search Options

Available 3292820 Spectra in 5 Libraries

mainlib
replib
apci_msms_nist
hr_msms_nist
nist_ri

Included Libs:
mainlib
replib

- Similarity Radio Button selected
- Hybrid Search
- Normally use “In spectrum” box checked
- Software selects to select MW to limit Hybrid Search
- **Value** chosen **shown** in bottom right corner after search
- If chosen value not acceptable, **User can specify** by unclicking box and entering nominal molecular weight

Library Search Options

Search

Spectrum Search Type
 Identity Similarity
 EI Hybrid In spectrum 305

Spectrum Scoring Options
 Method: Full Spectrum Search (Score)
 Compound Ubiquity Correction

Presearch
 Default Fast Off Mass(Da) 1
 InChIKey
 blank = match search spectrum InChIKey

Other Options
 Automation Auto Report
 Apply Limits Use Constraints
 Use RI
 TMS mode: Off

- Save configuration
- Settings, Font and window sizes, etc.

PRE-RELEASE NIST MS Search 4.0 (EI)

File Search View Tools Options V

Open... Ctrl+O

Print Setup...

Print Report

Print Auto Report

Switch to Caller

Save Configuration

Restore Configuration

1 jl_ei_normal+others.ini

2 jl_hybrid.ini

3 settings_MSMS.INI

4 settings_EI.INI

Select Spectrum Type

Exit

Hybrid Search: Make Sure Library Results Contain Needed Properties

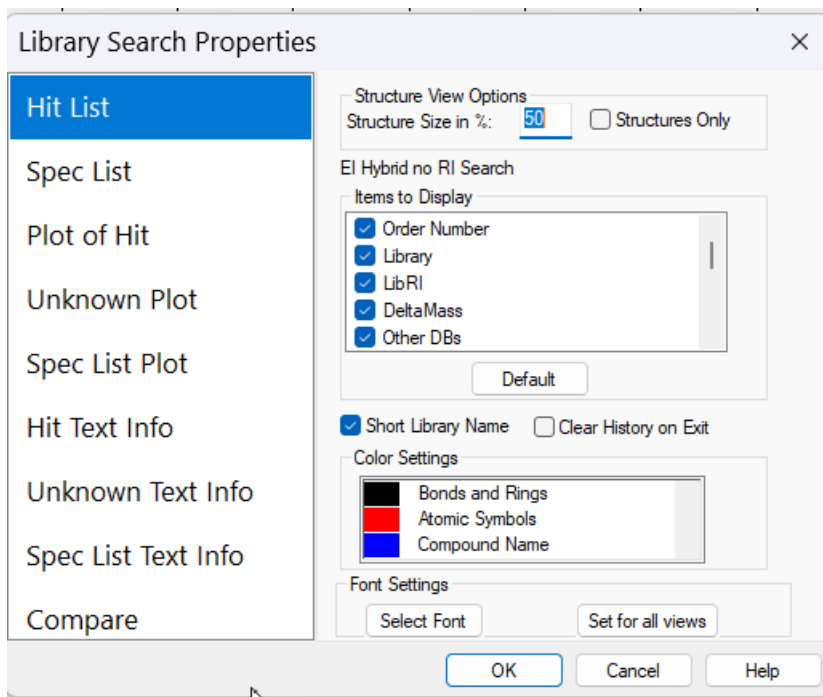
Incorrect Setup

#	Lib.	Match	LibRI	DeltaMass	DBs	Name
1	M	981	3086	-56	5	5-Nonadecylresorcinol, O,O-bis-TMS
2	M	976	3278	-84	5	5-Henicosylresorcinol, O,O-bis-TMS
3	M	976	2306	56	2	5-Undecylbenzene-1,3-diol, 2TMS deriv...
4	M	973	2877	-26	2	5-(8Z-Heptadecenyl)resorcinol, 2TMS
5	M	962	3084	-54	1	1,3-Benzenediol, 5-(10-nonadecenyl)-, (Z...
6	M	946	2676	2	6	Bilobol C15:1 (2TMS)
7	M	941	2502	28	3	1,3-Benzenediol, 5-tridecyl-, 2TMS
8	M	941	2889	-26	3	Bilobol C17:1 (2TMS)
9	M	914	1748	140	13	Olivetol, 2TMS derivative
10	M	901	3703	-236	1	5,5'-(4(Z)-Tetradecene-1,14-diyl)bisresor...

Correct Setup, dForm and pctRelForm Added

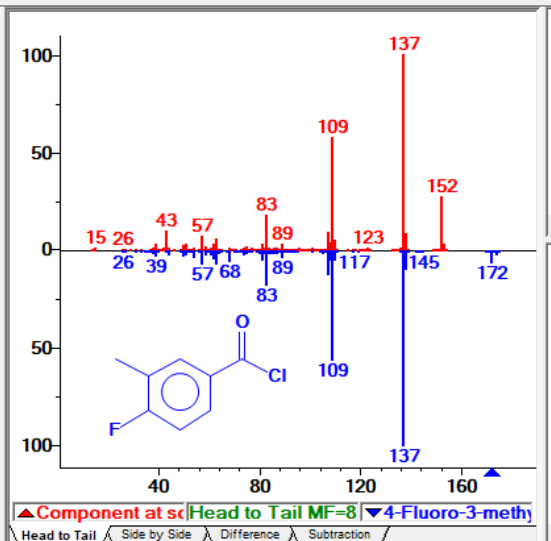
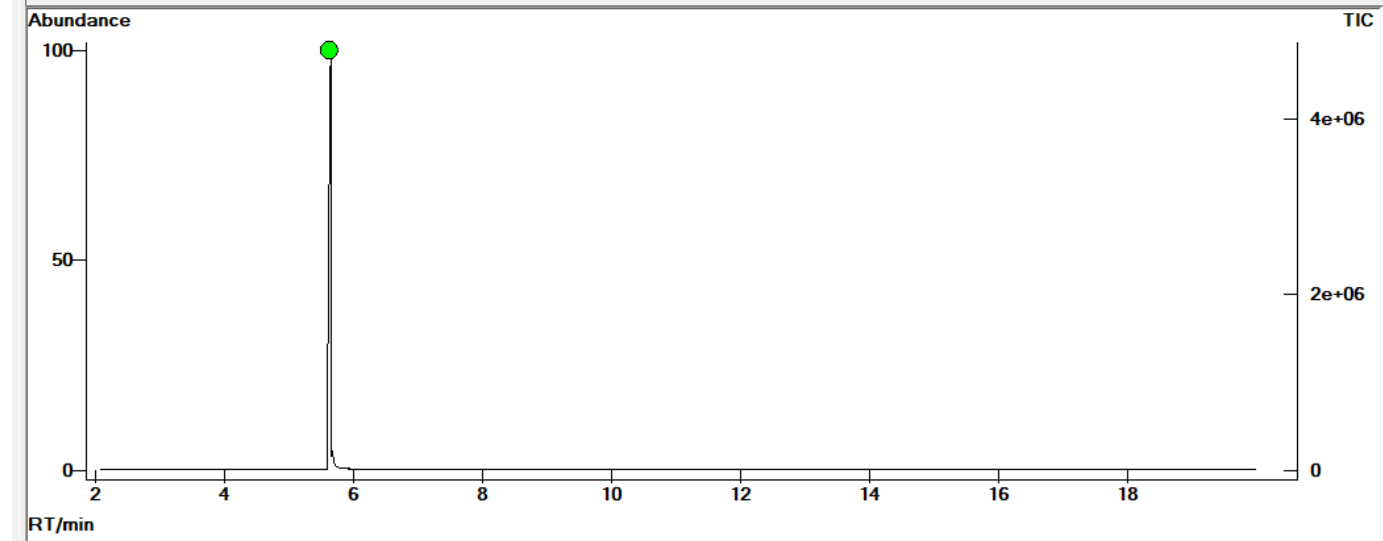
#	Lib.	Match	DeltaMass	dForm	pctRelForm	DBs	o.Match	Name
1	M	980	18	H-1F	8.8	28	46	Ethanone, 1-(4-methylphenyl)-
2	R	977	18	H-1F	8.8	11	51	Ethanone, 1-(3-methylphenyl)-
3	M	973	18	H-1F	8.8	12	60	Ethanone, 1-(2-methylphenyl)-
4	M	968	-16	O-1	1.6		752	3-Fluoro-4-methylbenzoic acid,
5	M	967	14	CH2	100	1	772	2-Fluoro-5-methylbenzaldehyd
6	M	964	-16	O-1	1.6		756	4-Fluoro-3-methylbenzoic acid,
7	M	963	14	CH2	100	1	775	4-Fluoro-3-methylbenzaldehyd
8	M	963	14	CH2	100	1	767	3-Fluoro-4-methylbenzaldehyd
9	M	961	14	CH2	100	1	776	4-Fluoro-2-methylbenzaldehyd
10	M	961	-16	O-1	1.6	1	756	2-Fluoro-5-methylbenzoic acid

Right Click and Select Properties to add



Added:

- dForm
- pctRelForm
- o.Match (essentially the standard EI Normal Match)



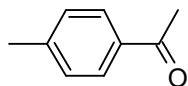
#	RT	Score	RI	dRI	Abund.Rel.	DotProd	R.Match	Prob	Max2Med	Lib	Dbs	Formula	LibRI	Lib ID
1	5.6502	810	1166	5	100	786				inlib	1	C8H6ClFO	1161	4-Fluoro-3-methylbenzoyl chl

- Library Search
- Library Search Options
- Send To
- Copy Selected Hits to Clipboard
- Export Selected Hits to Text File
- Show Selected
- Show All
- Properties

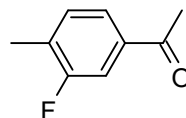
- Only Normal EI Search done in chromatogram
- Send to Lib Search for Novel Hybrid Search

➤ New in NIST26 dForm and pctRelForm, Delta Mass in Previous Versions

#	Lib.	Match	DeltaMass	dForm	pctRelForm	DBs	o.Match	Name
1	M	980	18	H-1F	8.8	28	46	Ethanone, 1-(4-methylphenyl)-



Best Hit, 134



Proposed MW 152

Or isomer

Addition of Fluorine Group

DeltaMass Difference in mass of query compound and library compound

dform highlights mass differences corresponding to plausible structural modifications, guiding interpretation.

pctRefForm Percent: Probability that a dForm is correct. Based on statistics of occurrences of each dForm relative to the most common (CH2 which is assigned 100%) – for high scoring hits (>900). The higher, the most likely correct – values like 0.01 are so rare, they are very likely accidental and wrong for example,

NOTE: *Much* more *Detailed* information on Hybrid Search Found on my Website at:
See [Link1](#) and [Link2](#)

Results Indicate Difference of Fluorine Group

- Note no. of spectra in results top bar
- Type of Search and Displayed results left and middle of bottom bar
- MW determined by computer to limit hybrid search
- Important Hybrid parameters DeltaMass, dform, pctRefForm in search results window

PRE-RELEASE NIST MS Search 4.0 (EI mode) - [EI Hybrid precursor = 152, Presearch Default - 63 spectra]

File Search View Tools Options Window Help

1.

#	Src.	MW	Formula	Name
1	A	0		

mainlib: replib; 431275 total spectra

#	Lib.	Match	DeltaMass	dForm	pctRefForm	DBs	Name
1	M	980	18	H-1F	8.8	28	Ethanone, 1-(4-methylphenyl)-
2	R	977	18	H-1F	8.8	11	Ethanone, 1-(3-methylphenyl)-
3	M	973	18	H-1F	8.8	12	Ethanone, 1-(2-methylphenyl)-
4	M	967	-16	O-1	1.6		3-Fluoro-4-methylbenzoic acid, methy
5	M	967	14	CH2	100	1	2-Fluoro-5-methylbenzaldehyde
6	M	964	-16	O-1	1.6		4-Fluoro-3-methylbenzoic acid, methy
7	M	963	14	CH2	100	1	4-Fluoro-4-methylbenzaldehyde
8	M	963	14	CH2	100	1	3-Fluoro-4-methylbenzaldehyde
9	M	961	-16	O-1	1.6	1	2-Fluoro-5-methylbenzoic acid methyl
10	M	961	14	CH2	100	1	4-Fluoro-2-methylbenzaldehyde
11	M	954	-16	O-1	1.6		2-Fluoro-3-methylbenzoic acid, methy
12	M	952	-2	H-2	2.2	3	2-Fluoro-4-methylbenzoic acid
13	M	951	-16	O-1	1.6		3-Fluoro-5-methylbenzoic acid, methy
14	R	948	4	C-1H-3F	1.2	7	Ethanone, 1-(3,4-dimethylphenyl)-
15	M	944	14	CH2	100	1	5-Fluoro-2-methylbenzaldehyde
16	M	943	4	C-1H-3F	1.2	14	Ethanone, 1-(2,4-dimethylphenyl)-
17	M	942	-2	H-2	2.2	2	4-Fluoro-3-methylbenzoic acid

Names Structures Spec List

PlotText of Search Spectrum Plot of Search Spectrum Spec List

(Text File)

Name: MW: N/A ID#: 13 DB: Text File
96 m/z Values and Intensities:

14	1	15	7	26	1	27	5	29	1
31	6	33	3	37	3	38	7	39	30
40	2	41	1	42	7	43	100	44	8
46	1	49	2	50	23	51	32	52	4
53	4	54	7	56	6	57	71	58	4
59	19	60	3	61	12	62	27	63	60
64	6	65	3	68	11	69	5	70	6
71	2	73	2	74	12	75	14	76	4
77	13	78	2	79	1	80	5	81	32
82	10	83	178	84	11	85	5	86	8
87	8	88	3	89	27	90	3	91	1

Head to Tail Side by Side Difference Subtraction

Head to Tail MF=980 RMF=988

Ethanone, 1-(4-methylphenyl)-

Name: Ethanone, 1-(4-methylphenyl)-
Formula: C9H10O
MW: 134 ExactMass: 134.073165 CAS#: 122-00-9 NIST#: 228482 ID#: 149258 DB: mainlib
Contributor: Japan AIST/NIMC Database- Spectrum MS-NW-53
InChIKey: GNKZMNRKLCJAY-UHFFFAOYSA-N Non-stereo
62 m/z Values and Intensities:

(mainlib) Ethanone, 1-(4-methylphenyl)-

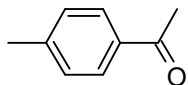
PlotText of Hit Plot of Hit

Lib. Search Other Search Names Compare Librarian Chromatogram

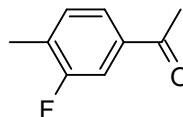
Type of Search: EI Hybrid Displayed: EI Hybrid 152

Proposed Structure Consistent with 3 Hits

#	Lib.	Match	DeltaMass	dForm	pctRelForm	DBs	o.Match	Name
1	M	980	18	H-1F	8.8	28	46	Ethanone, 1-(4-methylphenyl)-



Hit #1
MW 134

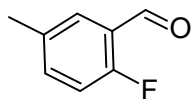


Proposed MW 152

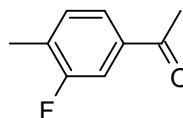
Or isomer

Addition of Fluorine Group

#	Lib.	Match	DeltaMass	dForm	pctRelForm	DBs	o.Match	Name
5	M	967	14	CH2	100	1	772	2-Fluoro-5-methylbenzaldehyde



Hit #5
MW 138

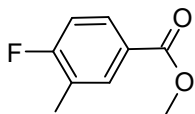


Proposed MW 152

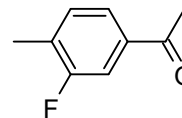
Or isomer

Addition of Fluorine Group

#	Lib.	Match	DeltaMass	dForm	pctRelForm	DBs	o.Match	Name
6	M	964	-16	O-1	1.6		756	4-Fluoro-3-methylbenzoic acid, methyl e



Hit #5
MW 168



Proposed MW 152

Or isomer

Addition of Fluorine Group

Getting Structure for Proposed Unknown for MS Interpreter

Send Library Structure to Drawing Program

The screenshot shows a software interface with a search results table, a mass spectrum plot, and a context menu. The table lists search results with columns for #, Lib., Match, DeltaMass, dForm, pctRelForm, DBs, and Name. The mass spectrum plot shows relative intensity versus m/z with peaks at 43, 51, 57, 63, 69, 75, 83, 89, 95, and 109. The context menu is open, showing options like 'Send To', 'Find name in Names tab', and 'Copy Structure to Clipboard'. The 'Send To' sub-menu is also visible, listing 'Spec List', 'Compare List', 'MS Interpreter', and 'Default Structure Editor'.

#	Lib.	Match	DeltaMass	dForm	pctRelForm	DBs	Name
1	M	980	18	H-1F	8.8	28	Ethanone, 1-(3-methylphenyl)-
2	R	977	18	H-1F	8.8	11	Ethanone, 1-(3-methylphenyl)-

Edit Library Best Hit, and select and copy proposed structure to clipboard with copy command

The screenshot shows the ACD/ChemSketch software interface. The title bar indicates the file path: [C:\NIST26\MSSEARCH\nistms2.mol]. The menu bar includes File, Edit, Pages, Tools, Templates, Options, Documents, and Add. The toolbar contains various drawing and editing tools. The main workspace shows a chemical structure of 1-(3-methylphenyl)ethanone and a mass spectrum plot. The mass spectrum plot shows relative intensity versus m/z with peaks at 43, 51, 57, 63, 69, 75, 83, 89, 95, and 109. The chemical structure is shown in a 2D representation.

Structure Drawn in Drawing Program, Unknown Spectrum sent to MS Interpreter and Proposed Structure Inserted

- Detailed MS Interpreter Help
- [See link](#)
- Paste in structure copied in Drawing Program
- Use either Paste/Edit or
- Or click on structure box and Keyboard Ctrl V
- Very good fit to proposed structure
- Isotope ratios very consistent
- Position of methyl and fluorine on aromatic ring uncertain

