SUPPORTING INFORMATION

CycloBranch 2: Molecular Formula Annotations Applied to imzML Data Sets in Bimodal Fusion and LC-MS Data Files

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<pre>bool getcombination() {</pre>	Example:	
pos = 0;	$N = 4 \dots$ number of ite	ms
flag = 0;	P = 3 maximum numbe	r of combined items
do {		nput/output vector of length P
<pre>combination[pos]++;</pre>		
if (combination[pos] <= N) {	Output after 34 calls:	
	100	411
if (flag > 0) {		221
for (i = pos - 1; i >= 0; i) {	200	
<pre>combination[i] = combination[pos];</pre>	300	321
}	400	421
}	110	331
return true;	210	431
}	310	441
else {	410	222
flag = 1;	220	322
pos++;	320	422
}	420	332
<pre>} while (pos < P);</pre>	330	432
return false;	430	442
}	440	333
-	111	433
	211	443
	311	444

Figure S1. The basic algorithm used to generate the combinations of elements with repetitions from an input list of *N* elements (e.g., 1 = 'H', 2 = 'C', 3 = 'N', 4 = 'O') is shown. The maximum number of elements in a formula is limited by *P*. We used *P* = 200, if not stated otherwise. In the real implementation, two further optimizations were used. The first was based on the idea that the input list of elements was sorted by mass. For example, if the cumulative mass corresponding to the combination 411 (OHH) exceeded a user-defined upper mass limit, the combinations 511, 611, etc. were not generated (for $N \ge 6$). Since CycloBranch keeps statistics about the number of elements in a currently computed combination and since the user can define the maximum number of occurrences of any element, a similar approach was used to prune out unnecessary combinations of elements in the second case.

🌽 Settings			– 🗆 X
Search		Theoretical Spectrum/Spectra	
		Sequence/Compound Database File:	/siderophores/709_siderophores_and_secondary_metabolites.txt Select
Mode:	Compound Search - MS, LC-MS, MSI V De Novo Search Engine - MS/MS	Score Type:	Number of y-ions
	Compare Peaklist(s) with Spectrum of Searched Sequence - MS/MS Compare Peaklist with Database - MS/MS	Maximum Number of Reported Sequence Candidates:	1000
Maximum Number of Threads:	Compare Peakist (s) with Database - MS, MS Compare Peakist (s) with Database - MS, LC-MS, MSI Compound Search - MS, LC-MS, MSI	Peptide Sequence Tag:	
	Compound Search - MS, ECHNS, MSI		[M+Na]+
Experimental Spectrum/Spectra			[M+K]+ [M_k]_
Peptide Type:	Cyclic ~	Ion Types:	[M+Na-2H]-
File:	bno_03062019/HL_1to1_profile_BB7_01_4492.d/analysis.baf Select		[M+K-2H]-
Scan no.:	1		[M+Fe-2H]+
Precursor m/z Ratio:	0,000000		H Select All
Precursor Ion Adduct:			O Clear All
Charge:	2		N Add
Precursor m/z Error Tolerance:	1,000 ppm	Neutral Losses / Chemical Elements:	P:1 Remove
m/z Error Tolerance:	2,000 ppm		Default
Minimum Threshold of Relative Intensity:			HCON
Minimum Threshold of Absolute Intensity:			
m/z Ratio:	minimum: 650,000 文 maximum: 1400,000 文	Maximum Number of Combined Losses/Elements:	180
FWHM:	0,050000 Da	Report Unmatched Theoretical Peaks: Generate Full Isotope Patterns:	
Database of Building Blocks		Minimum Number of Isotopic Peaks:	4
Building Blocks Database File:	Select	Minimum Number of Spectra:	4
Maximum Number of Combined Blocks:	start: 1 🗘 middle: 1 🗘 end: 1 🗘	Minimum Number of Ion Types:	1
Incomplete Paths in De Novo Graph:	remove (speed up the search)	Basic Formula Check:	
Maximum Cumulative Mass of Blocks:	0,000 🗘	Advanced Formula Check: N/O Ratio Check:	M M
N-/C-terminal Modifications File:	Select	Isotope m/z Tolerance:	0,000 ppm
Miscellaneous		Isotope Intensity Tolerance:	10.000 %
Miscelial leous			
Disable Precursor Mass Filter:	Cyclic N-terminus:	Searched Sequence/Compound	
Internal Fragments:	Cydic C-terminus:	Sequence:	Edit
Enable Scrambling:	Regular Order of Ketide Blocks:	Modifications: N-terminal	C-terminal Branch
	-	Formula:	
OK Cancel Appl	У		Load Save 'example1_lcms.ini' Save As

Figure S2. CycloBranch's settings dialog configured for analysis of LC-MS data using the database-free approach.

🎤 Settings						-	- 0	×
Search			Theoretical Spectrum/Spectra					
			Sequence/Compound Database File:	1	siderophores/709 sideroph	hores_and_secondary_metabolites.txt	Select	
Mode:	Compound Search - MS, LC-MS, MSI	\sim	Score Type:		Number of v-ions			
			Maximum Number of Reported Sequence		,		÷	- -
Maximum Number of Threads:	1	* *	Peptide Sequence Tag:					
			replace bequerice ragi		[M+Na]+	^	Select All	í.
Experimental Spectrum/Spectra					[M+K]+		Clear All	i.
Peptide Type:	Cyclic	\sim	Ion Types:		[M-H]- [M+Na-2H]-			
File:	D:/raw_data/MSI/ITO14_new_reduced.imzML	Select			[M+K-2H]-		Reset	
Scan no.:	1	*			[M+Fe-2H]+	¥		
Precursor m/z Ratio:	0.000000	-			н c		Select All	
Precursor Ion Adduct:					0		Clear All	
Charge:	1	\$			N S:2		Add	
Precursor m/z Error Tolerance:	1.000 ppm	*	Neutral Losses / Chemical Elements:		5:2 P:1		Remove	il -
m/z Error Tolerance:	2.000 ppm	٢					Default	i.
Minimum Threshold of Relative Intensity:	0.500 %	٢					HCON	
Minimum Threshold of Absolute Intensity:	0	٢						
m/z Ratio:	minimum: 350.000	•	Maximum Number of Combined Losses/Ele		150		\$	3
FWHM:	0.001000 Da	-	Report Unmatched Theoretical Peaks: Generate Full Isotope Patterns:		コ マ			
Database of Building Blocks			Minimum Number of Isotopic Peaks:				•	a
Building Blocks Database File:		Select	Minimum Number of Spectra:	[50		•	ā
Maximum Number of Combined Blocks:	start: 1 🗘 middle: 1 🗘 end: 1	\$	Minimum Number of Ion Types:	[1		•	ā
Incomplete Paths in De Novo Graph:	remove (speed up the search)	\sim	Basic Formula Check:		2			
Maximum Cumulative Mass of Blocks:	0.000	\$	Advanced Formula Check: N/O Ratio Check:		2			
N-/C-terminal Modifications File:		Select	Isotope m/z Tolerance:		2.000 ppm		•	a
Miscellaneous			Isotope Intensity Tolerance:		5.000 %		•	_
Miscelarieuus			Searched Sequence/Compound					-
Disable Precursor Mass Filter:	Cydic N-terminus:						Edit	
Internal Fragments:	Cydic C-terminus:		Sequence:		11	10	Edit	
Enable Scrambling:	Regular Order of Ketide Blocks:		Modifications: N-termina	iinal	C-terminal	Branch		
			Formula:					
OK Cancel Apply	(Load Save 'example2_msi.	ni' Save A	As

Figure S3. CycloBranch's settings dialog configured for analysis of MSI data using the database-free approach.

🌽 Settings						- 0	×
Search		T	heoretical Spectrum/Spectra				
		s	equence/Compound Database	File:		Select	
Mode:	Compare Peaklist(s) with Spectrum of Searched Sequence - MS/MS	~ s	core Type:		Sum of relative intensities of matched peaks		~
		÷ M	laximum Number of Reported S	equence Candidates:	100		*
Maximum Number of Threads:	1		eptide Sequence Tag:				
						Select A	
Experimental Spectrum/Spectra						Clear Al	
Peptide Type:	Other		on Types:			Reset	
File:	OXE/PCH_c325w1e15_UHR_onlinecal_000001.d/analysis.baf					Reset	
Scan no.:	1	-					
Precursor m/z Ratio:	325,067330	÷			H C	Select A	
Precursor Ion Adduct:					0	Clear Al	
Charge:	1	÷			N S:2	Add	
Precursor m/z Error Tolerance:	2,000 ppm		leutral Losses / Chemical Eleme	nts:	5.E	Remove	
m/z Error Tolerance:	2,000 ppm	÷				Default	5
Minimum Threshold of Relative Intensity:	5,000 %	•				HCON	-
Minimum Threshold of Absolute Intensity:	1	÷					_
m/z Ratio:	minimum: 100,000		faximum Number of Combined L		38		\$
FWHM:	0,001000 Da	-	teport Unmatched Theoretical P Senerate Full Isotope Patterns:				
Database of Building Blocks			linimum Number of Isotopic Pea		1		•
Building Blocks Database File:	BrickDatabases/inhouse_siderophores_blocks.txt Sele	lect M	finimum Number of Spectra:		1		*
Maximum Number of Combined Blocks:	start: 2 🗘 middle: 2 🗘 end: 2	÷ M	finimum Number of Ion Types:		1		* *
Incomplete Paths in De Novo Graph:	remove (speed up the search)	~	lasic Formula Check:				
Maximum Cumulative Mass of Blocks:	0,000	*	Advanced Formula Check: I/O Ratio Check:				
N-/C-terminal Modifications File:	Sele		sotope m/z Tolerance:		0,000 ppm		*
Miscellaneous		Is	sotope Intensity Tolerance:		10,000 %		\$
		Se	earched Sequence/Compound				
Disable Precursor Mass Filter:	Cyclic N-terminus:		equence:			Edit	
Internal Fragments:	Cydic C-terminus:			N-terminal	C-terminal Branch	ALCON C	
Enable Scrambling:	Regular Order of Ketide Blocks:			C14H16N2O3S2	o commu		5
OK Cancel Apply	1				Load Save 'example3_	nsms.ini' Sav	e As

Figure S4. CycloBranch's settings dialog configured for the analysis of the fragment ion mass spectrum of pyochelin $[C_{14}H_{16}N_2O_3S_2+H]^+$.

🌽 Settings										- 🗆 ×
Search				Theoretic	tical Spectrum/Spec	tra				
				Sequenc	nce/Compound Data	base File:				Select
Mode:	Compound Search - MS, I	LC-MS, MSI		Score Type:			Number of y-ions			~
Maximum Number of Threads:							1000			*
Maximum Number of Threads:	1			'W '	Sequence Tag:					
Events and Construct Construct							[M+Cu-2H+K]+		1	Select All
Experimental Spectrum/Spectra	Curle						[M+Cu-3H]- [M+Zn-H]+			Clear All
Peptide Type:	Cyclic			Ion Type	bes:		[M+Zn-2H+Na]+			Reset
File:	A complex/EDTA_Zn_Na3	_pos_R240K_000001.0	d/analysis.bat ⊻ Se	elect			[M+Zn-2H+K]+ [M+Zn-3H]-			- Health
Scan no.: Precursor m/z Ratio:	1			*			H		`	Colorb All
Precursor m/z Ratio: Precursor Ion Adduct:	0.000000			•			с			Select All
Charge:	1			\$			O N			Clear All
Precursor m/z Error Tolerance:	1.000 ppm				Losses / Chemical E	Elements:	Na:3			Add
m/z Error Tolerance:	1.000 ppm			•						Remove
Minimum Threshold of Relative Intensity:	0.100 %			•						Default
Minimum Threshold of Absolute Intensity				•						HCON
m/z Ratio:	minimum: 0.000	🗘 maxii	mum: 500.000		ım Number of Combi	ined Losses/Elements:	100			•
FWHM:	0.001000 Da			Report U	Unmatched Theore					
Database of Building Blocks				Generate	ite Full Isotope Patti					
Building Blocks Database File:			50		m Number of Isotopi		3			÷
Maximum Number of Combined Blocks:	start: 1	middle: 1	¢ end: 1		m Number of Spectra m Number of Ion Typ		1			
Maximum Number of Combined Blocks: Incomplete Paths in De Novo Graph:	remove (speed up the se				m Number of Ion Tyj ormula Check:					•
Maximum Cumulative Mass of Blocks:	0.000	archy			ed Formula Check:					
N-/C-terminal Modifications File:	0.000		5	N/O Rati	itio Check:					
			30	1000000	e m/z Tolerance:		0.000 ppm			÷
Miscellaneous				Isotope I	e Intensity Tolerance	e:	10.000 %			\$
100 % - 90 % - 80 % - 70 % -		[M+Zn-H] 1+ <u>C11</u> 422.95408	0 <u>H13N2O8Na3</u> (1+ C10 H1)	[M+Zn-H] 1+ <u>C</u>	<u>C10H13N2O8Na3</u> (*	1+ C10 H12 N2 Na3 O8 68Z	in ()			
90 %			0 <u>H13N2O8Na3</u> (1+ C10 H1;			-H] 1+ <u>C10H13N2O8Na3</u> (1+)8 68Zn (97.26%);1-	+ C10 H12 N2 Na3 170	07 68Zn (2.74%);)
90 %	422.213		0H13N2O8Ne3 (1+ C10 H1: 423.954	[M+Zn-H] 1+ <u>C</u>	[M+Zn-	H] 1+ <u>C10H13N2O8Na3</u> (1+ 612	13C C9 H12 N2 Na3 ()8 68Zn [97.26%];1- I 428.307	+ C10 H12 N2 Na3 170 429.178	07 68Zn (2.74%];)
90%	422.213 Theoretical Intensity [%]	422.95408	423.954	[M+Zn-H] 1+ <u>C</u> 424.95281	[M+Zn- 425.95 425.695	H] 1+ <u>C10H13N2O8Na3</u> (1+ 612	13C C9 H12 N2 Na3 (428.307		07 68Zn (2.74%);) Name
90 % 80 % 70 % 60 % 40 % 10 % 40 % 10 % 420.471 421.342 Pattern Type Theoretical m/z		422.95408	423.954	[M+Zn-H] 1+ <u>C</u> 424.95281 424.825	[M+Zn- 425.95 425.695 y Error [ppm] -0.020882 1	H] 1+ <u>C10H13N2O8Na3</u> (1+ 612 426.566 L+ C10 H12 N2 Na3 O8 Zn ;	13C C9 H12 N2 Na3 (427.437 Summary Fo	428.307		1
90 % - 80 % - 70 % - 90 % - 1 - 10 % - 12 M+Zn-H] 1+ 421.954311 12 M+Zn-H] 1+ 421.954311	Theoretical Intensity [%] 00.000000 1.738718	422.95408 423.083 Experimental m/z 420.957267 421.954333	423.954 Relative Intensity [%] 100.00000 0.806750	[M+Zn-H] 1+ C 424.95281 424.825 Absolute Intensity 324407327 2617156	[M+Zn- 425.95 425.695 y Error [ppm] -0.020882 1 0.051775 1	H] 1+ <u>C10H13N2OBNa3</u> (1+ 612 426 566 I+ C10 H12 N2 Na3 O8 Zn ; I+ C10 H12 ISN N Na3 O8 Z	13C C9 H12 N2 Na3 (427.437	1 428.307 rmula	429.178	Name C10H13N2O8Na3 C10H13N2O8Na3
90% - 80% - 90% - 10% - 11 - 12 M+Zn-H] + 14 - 15 - 16 - 17 - <t< th=""><td>Theoretical Intensity [%] 00.000000 1.738718 1.120469</td><td>422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594</td><td>423.954 Relative Intensity [%] 100.00000 0.806750 10.762039</td><td>[N+Zn+H] 1= C 424.95281 424.825 Absolute intensity 324407327 2617156 34912843</td><td>[M+Zn- 425.95 425.695 y Error [ppm] -0.020882 1 0.051775 1 2 -0.142997 1</td><td>H] 1+ <u>C10H13N2O8Na3</u> (1+ 612 426.566 L+ C10 H12 N2 Na3 O8 Zn ;</td><td>13C C9 H12 N2 Na3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H</td><td>1 428.307 rmula</td><td>429.178</td><td>Name C10H13N208Na3 C10H13N208Na3 C10H13N208Na3</td></t<>	Theoretical Intensity [%] 00.000000 1.738718 1.120469	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594	423.954 Relative Intensity [%] 100.00000 0.806750 10.762039	[N+Zn+H] 1= C 424.95281 424.825 Absolute intensity 324407327 2617156 34912843	[M+Zn- 425.95 425.695 y Error [ppm] -0.020882 1 0.051775 1 2 -0.142997 1	H] 1+ <u>C10H13N2O8Na3</u> (1+ 612 426.566 L+ C10 H12 N2 Na3 O8 Zn ;	13C C9 H12 N2 Na3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H	1 428.307 rmula	429.178	Name C10H13N208Na3 C10H13N208Na3 C10H13N208Na3
90% - 80% - 90% - 10% Heoretical m/z 11 IM-Zn-H1 1+ 420.957276 1 12 IM-Zn-H1 1+ 421.960654 1 15 IM-Zn-H1 1+ 422.954164 5	Theoretical Intensity [%] 00.000000 1.738718	422.95408 423.083 Experimental m/z 420.957267 421.954333	423.954 Relative Intensity [%] 100.00000 0.806750	[M+Zn-H] 1+ C 424.95281 424.825 Absolute Intensity 324407327 2617156	[M+Zn- 425.99 425.695 y Error [ppm] -0.020882 1 0.051775 1 0.0142997 1 0.187223 1	H] 1+ <u>C10H13K2OBNa3</u> (1+ 612 426 566 L+ C10 H12 N2 Na3 O8 Zn ; L+ C10 H12 N2 Na3 O8 Zn ; L+ C10 H12 TSN N Na3 O8 Z + 13C C9 H12 N2 Na3 O8 Z	13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1;	1 428.307 rmula	429.178	Name C10H13N2O8Na3 C10H13N2O8Na3
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90% - 80% - 90% - 1 [M+Zn-H] 1+ 420.957276 1 [M+Zn-H] 1+ 422.95411 0 [M+Zn-H] 1+ 422.954164 5 [M+Zn-H] 1+ 422.961521 1 [M+Zn-H] 1+ 422.963986	Theoretical Intensity [%] 00.00000 1.738718 1.120469 7.371993 .643995	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.961448	423 954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230	(M+Zn+H) 1+ C 424.95281 424.825 Absolute Intensity 324407327 2617156 34912843 201784907 5142601	[M+Zn- 425.95 425.95 Fror [ppm] 1 0.001775 1 0.011775 1 0.011775 1 0.011775 1 0.011775 1 0.011775 1 0.011723 1 0.0117299 1 0.0117299 1 0.0116137 1	H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 426.566 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 N2 Na3 O8 Zn 1+ C10 H12 N2 Na3 O8 Zn 1+ C10 H12 N2 Na3 O8 Zn 1+ C10 H12 N2 Na3 O8 66Z 1+ C10 H12 N2 Na3 O8 66Z	13C C9 H12 N2 N3 (427.437 Summary Fo In ; in [97.26%];1+ C10 H 1; Zn ; Zn ;	1 428.307 rmula	429.178	Name C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3
90 % - 80 % - 90 % - 10 % - 11 [M-Zn-H] 1+ 420.957276 1 12 [M-Zn-H] 1+ 422.961521 1 15 [M-Zn-H] 1+ 422.961521 1 17 [M-Zn-H] 1+ 422.963986 0 18 [M-Zn-H] 1+ 423.951199 0	Theoretical Intensity [%] 00.00000 1.120469 7.371993 .643995 1.526410	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.961448 422.963767	423 954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.547469	[N+Zn+H] 1= C 424.95281 424.825 Absolute Intensity 324407327 2617156 34912643 201784907 5142601 1776029	[M+Zn- 425:95 425:95 y Error [ppm] 6.020822 1 0.051775 1 0.0142997 1 0.142997 1 0.017223 1 0.0172989 1 0.016137 1 0.0026753 1	H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 428.566 + C10 H12 N2 Na3 O8 Zn ; + 13C C9 H12 N2 Na3 O8 66Z + C10 H12 N2 Na3 O8 66Z + C10 H12 N2 Na3 O8 O7 + 13C2 C8 H12 N2 Na3 O8	13C C9 H12 N2 N3 (427 437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; Zn ; 662n ;	1 428.307 rmula	429.178	Name C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3 C10H13N2O8Na3
90 % - 80 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 10 % - 11 [M+Zn-H] 1 420.957276 12 [M+Zn-H] 1 420.95051 13 [M+Zn-H] 1 422.9511 14 [M+Zn-H] 1 422.963986 15 [M+Zn-H] 1 422.963986 16 [M+Zn-H] 1 423.95519 17 [M+Zn-H] 1 423.95529	Theoretical Intensity [%] 00.00000 1.120469 7.371993 .643995 .526410 .423818	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.961448 422.963767 423.951187	423.954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.547469 0.477537	(N+Zn+H) 1= C 424,95281 424,95281 Absolute Intensity 324407327 2617156 34912843 201784907 5142601 1776029 1549165	[M+Zn- 425:95 425:95 9 Error [ppm] -0.020822 1 0.051775 1 0.0187223 1 0.018723 1 0.018723 1 0.018723 1 0.018723 1 0.018753 1 0.026753 1 0.0384343 1	H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 428.566 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 N2 Na3 O8 66Z 1+ C10 H12 N2 Na3 O8 66Z 1+ C10 H12 N2 Na3 O8 66Z 1+ C10 H12 N2 Na3 O8 66Z	13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H n; Zn ; Zn ; E62n ; 1;	428.307 mula 12N2Na3 170 07	429.178 Zn [2,74%];	Name C10H13N2O8Na3
90 % - 80 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 90 % - 10 % - 11 (M+Zn-H) 1 420.95121 12 (M+Zn-H) 1 422.961521 13 (M+Zn-H) 1 422.961521 14 (M+Zn-H) 1 423.95119 15 (M+Zn-H) 1 423.95529 16 (M+Zn-H) 1 423.95529 10 (M+Zn-H) 1 423.957542	Theoretical Intensity [%] 00.00000 1.120469 7.371993 .643995 .526410 .423818 .431010	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.961448 422.963767 423.9551187 423.955181	423.954 Relative Intensity [%] 100.00000 0.806750 0.762039 62.201094 1.585230 0.547469 0.477537 9.269733	[N+2n+1] 1= 0 424 95281 424 825 Absolute Intensity 32407327 2617156 34912643 201784907 5142601 1776029 1549165 30071694	[M+Zn- 425.99 425.99 1 0.00082 1 0.00175 1 0.0175 1 0.018723 1 0.018723 1 0.018723 1 0.018723 1 0.01875 1 0.01875 1 0.01875 1 0.01875 1 0.01843 1 0.0393516 1	H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 426.566 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 N2 Na3 O8 Zn ; 1+ 13C C9 H12 N2 Na3 O8 Z 1+ 13C C9 H12 N2 Na3 O8 662 1+ C10 H12 N2 Na3 O8 662 1+ C10 H12 N2 Na3 O8 66 1+ C10 H12 15N N Na3 O8 672	13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; Zn ; E2n ; E2n ; 52n ; 52n ; 52n ; 1; 52n ; 1;	428.307 mula 12N2Na3 170 07	429.178 Zn [2,74%];	Name C10H13N2C08Na3
Pattern Type Theoretical m/z 1 M-Zn-H1 2 M-Zn-H1 3 M-Zn-H1 4 20,471 420,471 421,342 1 M-Zn-H1 2 M-Zn-H1 3 M-Zn-H1 4 420,471 420,471 421,342	Theoretical Intensity [%] 00.00000 1.120469 7.371993 .643995 .526410 .423818 .431010 .380035	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.961448 422.963767 423.955181 423.955181 423.955786	423.954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.547469 0.477537 9.269733 6.890778	[N+2n+1] 1= 0 424 95281 424 95281 24407327 2617156 34912843 201784907 5142601 1776029 1549165 30071694 22354188	Image: marked state	H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 426.566 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 N2 Na3 O8 Zn ; 1+ 13C C9 H12 N2 Na3 O8 6622 1+ C10 H12 N2 Na3 O8 6622 1+ C10 H12 N2 Na3 O8 6722 1+ C10 H12 N2 Na3 O8 6722 1+ 13C C9 H12 N2 Na3 O8 6722 1+ 3C C9 H12 N2 N3 N3 N2 N3 N2 N3 N3 N2 N3 N3 N2 N3 N3 N3 N3 N3 N3 N2 N3	13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; Zn ; Zn ; Zn ; G2n ; 1; G2n ; 1; G2n ; 1; G2n ; C2n ;	428.307 mula 12N2Na3 170 07	429.178 Zn [2,74%];	Name C10H13N2O8Na3
Pattern Type Theoretical m/z 1 MALEAR-HI 2 MALEAR-HI 3 MALEAR-HI 4 20.471 420.471 421.342 Pattern Type Theoretical m/z 1 MALEAR-HI 2 MALEAR-HI 3 IM-Zn-HI 4 420.471 420.471 421.342 2 MALEAR-HI 1 420.957276 1 2 IM-Zn-HI 421.964311 0 3 IM-Zn-HI 421.960514 1 5 IM-Zn-HI 422.961521 1 7 IM-Zn-HI 423.95119 0 9 IM-Zn-HI 423.95529 8 10 IM-Zn-HI 423.957542 6 11 IM-Zn-HI 423.954876 0 12 IM-Zn-HI 424.952976 3	Theoretical Intensity [%] 00.00000 1.120469 7.371993 .643995 1.526410 4.23818 .431010 .380035 .177810	422.95408 423.083 Experimental m/z 420.957267 421.950394 421.960594 422.95005 422.961448 422.963767 423.951187 423.955181 423.9557376 423.9557376	423.954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.547469 0.477537 9.269733 6.890778 0.166790	[N+2n+1] 1= 0 424 95281 424 95281 424 95281 32407327 2617156 34912843 201784907 5142601 1549165 30071694 22354188 514000	Image: Constraint of the state	H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 426 566 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 15N N Na3 O8 Z 1+ 13C C9 H12 N2 Na3 O8 6622 1+ C10 H12 N2 Na3 O8 6622 1+ C10 H12 N2 Na3 O8 6722 1+ C10 H12 N2 Na3 O8 6722 1+ 3C C9 H12 N2 Na3 O8 672 1+ 3C C9 H12 N2 Na3 IBO	-13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; Zn ; Zn ; Zn ; G2n ; 1; G2n ; 1; G2n ; 1; G2n ; 1;	428.307 mula 12.N2.Na3 170 07) H12.N2.Na3 170 C	429.178 Zn [2.74%]; D7 662n [2.74%];	Name C10H13N2O8Na3
Pattern Type Theoretical m/z 1 MAZDARI 2 MAZDARI 3 MAZDARI 4 20.471 420.471 421.342 1 MAZDARI 1 MAZDARI 2 MAZDARI 3 MAZDARI 420.471 421.342 1 MAZDARI 1 MAZDARI 1 MAZDARI 2 MAZDARI 3 MAZDARI 420.471 421.342 420.471 421.342 420.471 421.342 420.471 421.342 420.471 421.342 420.471 421.342 5 MAZDARI 5 MAZDARI 6 MAZDARI 7 MAZDARI 7 MAZDARI 8 MAZDARI 9 MAZDARI 9 MAZDARI 9 MAZDARI 9 <td>Theoretical Intensity (%) 00.0000 1.120469 7.371993 .643995 1.526410 .423818 .431010 .380035 .177810 8.556447</td> <td>422.95408 422.083 Experimental m/2 420.957267 421.956394 422.95095 422.95108 422.963767 423.955181 423.955181 423.9557376 423.9557376 423.9557376</td> <td>Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.5474699 0.477537 9.269733 6.890778 0.166790 44.647402</td> <td>[N+2n+1] 1= 0 424 95281 424 95281 424 95281 34912843 201784907 5142601 1549165 30071694 22354188 514830444</td> <td>Image: constraint of the state state</td> <td>H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 426 566 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 15N N Na3 O8 Z 1+ 13C C9 H12 N2 Na3 O8 6622 1+ C10 H12 N2 Na3 O8 6622 1+ C10 H12 N2 Na3 O8 6722 1+ 3C C9 H12 N2 Na3 O8 6722 1+ 3C C9 H12 N2 Na3 O8 6722 1+ 3C C9 H12 N2 Na3 O8 6622 1+ 3C C9 H12 N2 N3 08 6622 1+ 3C C9 H12 N2 N3 08</td> <td>-13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; Zn ; i62n ; 1; i62n [97.26%];1+ C10 O7 Zn ; 1; i62n [90.84%];1+ 1;</td> <td>428.307 mula 12.N2.Na3 170 07) H12.N2.Na3 170 C</td> <td>429.178 Zn [2.74%]; D7 662n [2.74%];</td> <td>Name C10H13N2O8Na3 C10H13N2O8Na3</td>	Theoretical Intensity (%) 00.0000 1.120469 7.371993 .643995 1.526410 .423818 .431010 .380035 .177810 8.556447	422.95408 422.083 Experimental m/2 420.957267 421.956394 422.95095 422.95108 422.963767 423.955181 423.955181 423.9557376 423.9557376 423.9557376	Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.5474699 0.477537 9.269733 6.890778 0.166790 44.647402	[N+2n+1] 1= 0 424 95281 424 95281 424 95281 34912843 201784907 5142601 1549165 30071694 22354188 514830444	Image: constraint of the state	H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 426 566 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 N2 Na3 O8 Zn ; 1+ C10 H12 15N N Na3 O8 Z 1+ 13C C9 H12 N2 Na3 O8 6622 1+ C10 H12 N2 Na3 O8 6622 1+ C10 H12 N2 Na3 O8 6722 1+ 3C C9 H12 N2 Na3 O8 6722 1+ 3C C9 H12 N2 Na3 O8 6722 1+ 3C C9 H12 N2 Na3 O8 6622 1+ 3C C9 H12 N2 N3 08	-13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; Zn ; i62n ; 1; i62n [97.26%];1+ C10 O7 Zn ; 1; i62n [90.84%];1+ 1;	428.307 mula 12.N2.Na3 170 07) H12.N2.Na3 170 C	429.178 Zn [2.74%]; D7 662n [2.74%];	Name C10H13N2O8Na3
Pattern Type Theoretical m/z 1 [M+Zn-H] 1+ 421.342 2 [M+Zn-H] 1+ 420.957276 1 2 [M+Zn-H] 1+ 420.957276 1 3 [M+Zn-H] 1+ 421.96651 1 5 [M+Zn-H] 1+ 421.96654 1 5 [M+Zn-H] 1+ 422.961521 1 7 [M+Zn-H] 1+ 422.961321 1 7 [M+Zn-H] 1+ 423.95139 0 9 [M+Zn-H] 1+ 423.955259 8 10 [M+Zn-H] 1+ 423.955259 8 11 [M+Zn-H] 1+ 423.955259 8 12 [M+Zn-H] 1+ 423.955259 8 13 [M+Zn-H] 1+ 423.9556 0 14 [M+Zn-H] 1+ 423.956876 0 13 [M+Zn-H] 1+ 424.958510 1 14 [M+Zn-H] 1+ 424.958510 1 15 [M+Zn-H] 1+ 425.95011 0	Theoretical Intensity (%) 00.00000	422.95408 422.083 Experimental m/z 420.957267 421.954333 422.954085 422.954085 422.954085 422.954187 423.955181 423.955181 423.9557376 423.955787 423.955787 423.955787 423.957777 423.957777 423.957777 423.9577777 423.95777777777777777777777777777777777777	423.954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.547469 0.477537 9.269733 6.890778 0.166790 44.647402 2.007796	[N+2n+1] 1= 0 424 95281 424 95281 424 95281 3407327 2617156 34912843 201784907 5142601 1549165 30071694 22354188 514080 14839844 613436	Image: constraint of the state	H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 428.566 + C10 H12 N2 Na3 O8 Zn ; + C10 H12 N2 Na3 O8 Zn ; + C10 H12 15N N Na3 O8 Z + 13C C9 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 672 + C10 H12 N2 Na3 O8 672 + 13C C9 H12 N2 Na3 O8 672 + C10 H12 N2 Na3 O8 72 + C10 H12 N2 N3 72 + C10 H12	-13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; i62n ; 1; i62n ; 1; i62n [97.26%];1+ C11 O7 Zn ; 1; i62n [97.26%];1+ C11 S82n ;	428.307 mula 12.N2.Na3 170 07 0 H12.N2.Na3 170 0 3C C9 H12.N2.Na3 C	429.178 Zn [2.74%]; D7 662n [2.74%]; D8 672n [49.16%];	Name C10H13N2O8Na3
Pattern Type Theoretical m/z 1 [M+Zn-H] 1+ 421.342 2 [M+Zn-H] 1+ 420.957276 1 2 [M+Zn-H] 1+ 420.957276 1 3 [M+Zn-H] 1+ 421.96651 1 5 [M+Zn-H] 1+ 421.96651 1 5 [M+Zn-H] 1+ 422.961521 1 7 [M+Zn-H] 1+ 422.961521 1 7 [M+Zn-H] 1+ 423.95139 0 9 [M+Zn-H] 1+ 423.955259 8 10 [M+Zn-H] 1+ 423.955259 8 11 [M+Zn-H] 1+ 423.955259 8 12 [M+Zn-H] 1+ 423.955259 8 13 [M+Zn-H] 1+ 424.952576 3 14 [M+Zn-H] 1+ 424.952510 1 15 [M+Zn-H] 1+ 424.955510 1 15 [M+Zn-H] 1+ 425.95011 0 15 [M+Zn-H] 1+ 425.95011 1 16 [M	Theoretical Intensity (%) 00.00000	422.95408 423.083 Experimental m/z 420.957267 421.954333 422.954085 422.954085 422.954085 422.953187 423.955181 423.955181 423.9557376 423.9557376 423.95473 424.952813 425.954993 425.954993 425.954993 425.954993 425.954993 425.954993 425.954993 425.954993 425.954993 425.954993 425.954993 425.954993 425.954993 425.954995 425.9549 425.955656 425.9549 425.95556565656565656565656565656565656565	423.954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.547469 0.477537 9.269733 6.890778 0.166790 44.647402 2.007796 0.304114	[N+2n+1] 1= 0 424 95281 424 95281 424 95281 3407327 2617156 34912843 201784907 5142601 1776029 1549165 30071694 22354188 541080 14839444 6513436 987542	Image: constraint of the state	H] 1+ <u>C10H13H2OBNa3</u> (1+ 612 426.566 + C10 H12 N2 Na3 O8 Zn ; + C10 H12 N2 Na3 O8 Zn ; + C10 H12 15N N Na3 O8 Z + 13C C9 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 672 + C10 H12 N2 Na3 O8 672 + 13C C9 H12 N2 Na3 O8 672 + C10 H12 N2 Na3 N2 O7 + C10 H12 N2 Na3 N2 O7 + C10 H12 N2 N3 N2 N2 N3 N2 N3	13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; G2n ;	428.307 mula 12.N2.Na3 170 07 0 H12.N2.Na3 170 0 3C C9 H12.N2.Na3 C	429.178 Zn [2.74%]; D7 662n [2.74%]; D8 672n [49.16%];	Name C10H13N2O8Na3
Pattern Type Theoretical m/z 1 [M+Zn-H] 1+ 421.342 2 [M+Zn-H] 1+ 420.957276 1 2 [M+Zn-H] 1+ 420.957276 1 2 [M+Zn-H] 1+ 421.954311 0 3 [M+Zn-H] 1+ 421.95651 1 5 [M+Zn-H] 1+ 421.961521 1 7 [M+Zn-H] 1+ 422.961521 1 7 [M+Zn-H] 1+ 423.95139 0 9 [M+Zn-H] 1+ 423.95259 8 10 [M+Zn-H] 1+ 423.955259 8 11 [M+Zn-H] 1+ 423.955259 8 12 [M+Zn-H] 1+ 423.955259 8 13 [M+Zn-H] 1+ 423.95563 1 14 [M+Zn-H] 1+ 424.955210 1 15 [M+Zn-H] 1+ 424.955210 1 16 [M+Zn-H] 1+ 424.955210 1 15 [M+Zn-H] 1+ 424.955510 1 15 [Theoretical Intensity (%) 00000 1.120469 1.120469 3.439995 3.526410 4.23818 4.23818 4.23818 4.23818 4.23818 4.23818 4.23818 4.23858 4.23858 4.23858 4.23858 4.24824 4.28758	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.96148 422.963767 423.955181 423.955181 423.955787 423.955787 424.952813 424.952813 424.952813 424.952813 424.952813 425.956124	423.954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.547469 0.477537 9.269733 6.890778 0.166790 44.647402 2.007796 0.304114 4.65914	[N+2n+1] 1= 0 424 95281 424 95281 424 95281 2407327 2617156 34912843 201784907 5142601 1549165 30071694 22354188 541000 14839444 6513436 987542 15201447	Image: constraint of the state	H] 1+ <u>C10H13H2O8Na3</u> (1+ 612 426.566 + C10 H12 N2 Na3 O8 Zn ; + C10 H12 N2 Na3 O8 Zn ; + C10 H12 N2 Na3 O8 G20 + 13C C9 H12 N2 Na3 O8 G62 + C10 H12 N2 Na3 O8 G62 + C10 H12 N2 Na3 O8 G72 + 13C C9 H12 N2 Na3 O8 G72 + C10 H12 N2 N2 N3 O8 G72 + C10 H12 N2 N3 N3 N2 N3 N3 N2 N3	-13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; I62n ; I; I62n ; I; I62n [97.26%];1+ C11 O7 Zn ; I; I62n [97.26%];1+ C11 O7 Zn ; I; I62n [97.26%];1+ C11 O7 6Zn ;	428.307 mula 12.N2.Na3 170 07 0 H12.N2.Na3 170 0 3C C9 H12.N2.Na3 C	429.178 Zn [2.74%]; D7 662n [2.74%]; D8 672n [49.16%];	Name C10H13N2O8Na3
90% 90% <td>Theoretical Intensity (%) 00000 1.120469 1.120469 3.43995 3.43995 3.526410 4.23818 4.23818 4.23818 4.23818 4.23818 4.23818 4.2385 4.2385 4.2385 4.2385 4.2385 4.2484 4.2875 8.2566 4.2875 8.2664 7.2975 8.2664 7.2975 8.2664 7.2975 8.2664 7.2975 8.2664 7.2975 8.2004 7.2975 8.2004 7.</td> <td>422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.954085 422.95448 422.955181 423.955181 423.955181 423.955787 423.955781 424.952813 424.952813 424.95281 425.9596124 425.9561570</td> <td>423.954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.477537 9.269733 6.890778 0.167690 44.647402 2.007796 0.304114 4.65914 0.190501</td> <td>[N+2n+1] + 0 424 95281 424 95281 424 95281 2407327 2617156 34912843 201784907 5142601 1549165 30071694 22354188 541080 14839444 6513436 987542 15201447 618000</td> <td>Image: product of the state of the</td> <td>H] 1+ <u>C10H13H2O3Na3</u> (1+ 612 426.566 + C10 H12 N2 Na3 O8 2n ; + C10 H12 N2 Na3 O8 2n ; + C10 H12 N2 Na3 O8 620 + 13C C9 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 672 + 13C C9 H12 N2 Na3 O8 672 + C10 H12 N2 Na3 O8 702 + C10 H12 N2 N3 N3 702 + C10 H12 N2 N3 N3 702 + C10 H12 N2 N3 702 + C10 H12 N2 N3 702</td> <td>-13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; 1; 162n ; 1; 162n [97.26%];1+ C11 07 Zn ; 1; 1662n [97.26%];1+ C11 07 Zn ; 1; 1662n ; 1; 662n ; 1; 662n ; 1; 662n ; 1; 662n ;</td> <td>428.307 mula 12.N2.Na3 170 07 0 H12.N2.Na3 170 0 3C C9 H12.N2.Na3 C</td> <td>429.178 Zn [2.74%]; D7 662n [2.74%]; D8 672n [49.16%];</td> <td>Name C10H13N2O8Nb3 C10H13N2O8Nb3</td>	Theoretical Intensity (%) 00000 1.120469 1.120469 3.43995 3.43995 3.526410 4.23818 4.23818 4.23818 4.23818 4.23818 4.23818 4.2385 4.2385 4.2385 4.2385 4.2385 4.2484 4.2875 8.2566 4.2875 8.2664 7.2975 8.2664 7.2975 8.2664 7.2975 8.2664 7.2975 8.2664 7.2975 8.2004 7.2975 8.2004 7.	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.954085 422.95448 422.955181 423.955181 423.955181 423.955787 423.955781 424.952813 424.952813 424.95281 425.9596124 425.9561570	423.954 Relative Intensity [%] 100.00000 0.806750 10.762039 62.201094 1.585230 0.477537 9.269733 6.890778 0.167690 44.647402 2.007796 0.304114 4.65914 0.190501	[N+2n+1] + 0 424 95281 424 95281 424 95281 2407327 2617156 34912843 201784907 5142601 1549165 30071694 22354188 541080 14839444 6513436 987542 15201447 618000	Image: product of the state of the	H] 1+ <u>C10H13H2O3Na3</u> (1+ 612 426.566 + C10 H12 N2 Na3 O8 2n ; + C10 H12 N2 Na3 O8 2n ; + C10 H12 N2 Na3 O8 620 + 13C C9 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 672 + 13C C9 H12 N2 Na3 O8 672 + C10 H12 N2 Na3 O8 702 + C10 H12 N2 N3 N3 702 + C10 H12 N2 N3 N3 702 + C10 H12 N2 N3 702 + C10 H12 N2 N3 702	-13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; 1; 162n ; 1; 162n [97.26%];1+ C11 07 Zn ; 1; 1662n [97.26%];1+ C11 07 Zn ; 1; 1662n ; 1; 662n ; 1; 662n ; 1; 662n ; 1; 662n ;	428.307 mula 12.N2.Na3 170 07 0 H12.N2.Na3 170 0 3C C9 H12.N2.Na3 C	429.178 Zn [2.74%]; D7 662n [2.74%]; D8 672n [49.16%];	Name C10H13N2O8Nb3
No No<	Theoretical Intensity (%) (%) (%) (%) (%) (%) (%) (%) (%) (%)	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.954085 422.95448 422.951187 423.955181 423.955181 423.955181 423.955181 424.952813 424.952813 424.95281 425.956124 425.9561570 426.953201	423.954 Relative Intensity [%] 100.000000 0.806750 10.762039 62.201094 1.585230 0.547469 0.477537 9.269733 6.890778 0.16790 44.647402 2.007796 0.304114 4.685914 0.190501 1.544104	[N+2n+1] + 0 424 95281 424 95281 424 95281 2407327 2617156 34912843 201784907 5142601 1549165 30071694 22354188 541080 6513436 987542 15201447 618000 5009185	Image: product of the state of the	H] 1+ <u>C10H13H2O3Na3</u> (1+ 612 426.566 + C10 H12 N2 Na3 O8 2n ; + C10 H12 N2 Na3 O8 2n ; + C10 H12 N2 Na3 O8 622 + 13C C9 H12 N2 Na3 O8 6622 + C10 H12 N2 Na3 O8 672 + 13C C9 H12 N2 Na3 O8 682 + 13C C9 H12 N2 Na3 O8 682 + C10 H12 N2 Na3 O8 702	-13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; 1; 162n ; 1; 162n [97.26%];1+ C11 07 Zn ; 1; 1662n [97.26%];1+ C11 07 Zn ; 1; 1662n ; 1; 662n ; 1; 662n ; 1; 662n ; 1; 662n ;	428.307 mula 12 N2 Na3 170 07 0 H12 N2 Na3 170 C	429.178 Zn [2.74%]; D7 662n [2.74%]; D8 672n [49.16%];	Name C10H13N2O8Nb3
No No<	Theoretical Intensity (%) Theoretical Intensity (%) 1.120469 1.120469 1.120469 1.120469 1.120469 1.120469 1.120469 1.12040 1.12040 1.12040 1.12040 1.20458 1.204	422.95408 423.083 Experimental m/z 420.957267 421.954333 421.960594 422.954085 422.954085 422.954085 422.956176 423.951187 423.955181 423.955181 423.955181 424.952813 424.952813 424.952813 425.956124 425.956124 425.9561270 426.957002 426.957002	423.954 Relative Intensity [%] 100.000000 0.806750 10.762039 62.201094 1.585230 0.547469 0.477537 9.269733 6.890778 0.166790 44.647402 2.007796 0.304114 4.685914 0.190501 1.544104 0.762328	[N+2n+1] + 0 424 95281 424 95281 424 95281 2407327 2617156 34912843 201784907 1217929 1549165 30071694 22354188 444393444 6513436 987542 15201447 618000 5007185 20185 20185 20185	Image: product of the state of the	H] 1+ <u>C10H13H2O3Na3</u> (1+ 612 426.566 + C10 H12 N2 Na3 O8 2n ; + C10 H12 N2 Na3 O8 2n ; + C10 H12 N2 Na3 O8 620 + 13C C9 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 662 + C10 H12 N2 Na3 O8 672 + 13C C9 H12 N2 Na3 O8 672 + C10 H12 N2 Na3 O8 702 + C10 H12 N2 N3 N3 702 + C10 H12 N2 N3 N3 702 + C10 H12 N2 N3 702 + C10 H12 N2 N3 702	-13C C9 H12 N2 N3 (427.437 Summary Fo In ; In [97.26%];1+ C10 H 1; Zn ; Zn ; i62n ; 1; i62n [97.26%];1+ C10 O7 Zn ; 1; i62n [97.26%];1+ C11 O7 Zn ; 1; i62n ; i221 ;	428.307 mula 12 N2 Na3 170 07 0 H12 N2 Na3 170 C	429.178 Zn [2.74%]; D7 662n [2.74%]; D8 672n [49.16%];	Name C10H13N2O8Nb3 C10H13N2O8Nb3

Figure S5. Analysis of spectrum containing ethylenediaminetetraacetic acid (EDTA) with zinc. CycloBranch's settings dialog configured for the analysis of direct infusion electrospray mass spectrum (ESI-MS) containing EDTA with three atoms of sodium and one atom of zinc (top); and fine isotope structure annotated using the database-free approach (bottom). The spectrum was collected in positive ion mode.

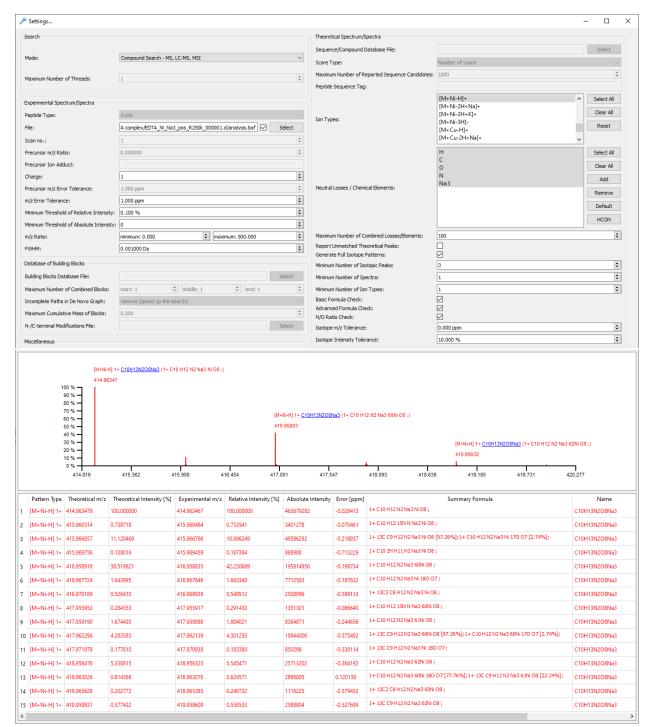


Figure S6. Analysis of spectrum containing EDTA with nickel. CycloBranch's settings dialog configured for the analysis of direct infusion ESI-MS containing EDTA with three atoms of sodium and one atom of nickel (top); and fine isotope structure annotated using the database-free approach (bottom). The spectrum was collected in positive ion mode.

🎤 Settings								- 🗆 ×
Search				Theoretica	al Spectrum/Spec	tra		
					Compound Data			Select
Mode:	Compound Search - MS, LO	C-MS, MSI		Score Type			Number of y-ions	Unicet
				Maria		rted Sequence Candidates:		<u>.</u>
Maximum Number of Threads:	1			w.	equence Tag:	red Sequence Conductes.	1000	
				repute a	equence ray.		[M+Cu-H]+	∧ Select All
Experimental Spectrum/Spectra							[M+Cu-2H+Na]+	
Peptide Type:	Cyclic			Ion Types			[M+Cu-2H+K]+ [M+Cu-3H]-	Clear All
File:	k_accum0.1s_excpower22	%_8scans_000001.d/	/analysis.baf 🗹 Se	elect			[M+Zn-H]+	Reset
Scan no.:	1			•			[M+Zn-2H+Na]+	~
Precursor m/z Ratio:	0.000000			*			H C	Select All
Precursor Ion Adduct:							0	Clear All
Charge:	-1			•			N Na	Add
Precursor m/z Error Tolerance:	1.000 ppm				osses / Chemical	Elements:	IVG	Remove
m/z Error Tolerance:	1.000 ppm			÷				Default
Minimum Threshold of Relative Intensity:	0.100 %			÷				HCON
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Maximum Cumulative Mass of Blocks:	0.000				f Formula Check:			
N-/C-terminal Modifications File:			Se		N/O Ratio Check: Isotope m/z Tolerance: 0.000 ppm			÷
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100 % - 90 % - 70 % - 50 % - 40 % - 30 % - 20 % -				4+Cu-3H] 1- <u>C10H15N2C</u> 75.97757		H] 1- <u>C10H15N2O8Na1</u> (1-	13C C9 65Cu H12 N2 Na O8 (97.26%);1- C10 65Cu H12 N2 N	a 170 07 [2.74%];)
0 %					4			
373.026 373.68	9 374.352	375.015	375.679	376.342	377.005	377.668	378.331 378.994 379.658	
Pattern Type Theoretical m/z	Theoretical Intensity [%]	Experimental m/z	Relative Intensity [%]	Absolute Intensity			Summary Formula	Name
1 [M+Cu-3H] 1- 373.979285	100.000000	373.979281	100.000000	1359385103	-0.010574	1-C10 Cu H12 N2 Na O8 ;		C10H15N2O8Na1
2 [M+Cu-3H] 1- 374.976320	0.738718	374.976437	0.492215	6691094	0.311793	1- C 10 Cu H 12 15N N Na O8	B;	C10H15N2O8Na1
3 [M+Cu-3H] 1- 374.982664	11.120469	374.982701	9.424707	128118064	0.098870	1- 13C C9 Cu H12 N2 Na O8	8 [97.26%];1- C10 Cu H12 N2 Na 17O O7 [2.74%];	C10H15N2O8Na1
5 [M+Cu-3H] 1- 375.977478	44.571346	375.977569	46.324360	629726455	0.242500	1- C 10 65Cu H 12 N2 Na O8	;	C10H15N2O8Na1
	1.643995	375,983627	1.357417	18452521		1- C10 Cu H12 N2 Na 18O (07;	C10H15N2O8Na1
	0.526410	375.986086	0.432826	5883769	0.257002	1- 13C2 C8 Cu H12 N2 Na C		C10H15N2O8Na1
						1- C10 65Cu H12 15N N Na		
	0.329257	376.974707	0.278600	3787243	0.514552			C10H15N2O8Na1
	4.956543	376.980979	4.454966	60560147			08 [97.26%];1- C10 65Cu H12 N2 Na 17O O7 [2.74%];	C10H15N2O8Na1
10 [M+Cu-3H] 1- 376.986885	0.177810	376.987019	0.151329	2057140	0.0004077	1- 13C C9 Cu H12 N2 Na 18		C10H15N2O8Na1
11 [M+Cu-3H] 1- 377.981723	0.732751	377.981958	0.641498	8720423	0.619920	1- C10 65Cu H12 N2 Na 180	0 07 ;	C10H15N2O8Na1
12 [M+Cu-3H] 1- 377.984188	0.234628	377.984398	0.213427	2901290	0.556159	1- 13C2 C8 65Cu H 12 N2 N	a 08 ;	C10H15N2O8Na1
<								

Figure S7. Analysis of spectrum containing EDTA with copper. CycloBranch's settings dialog configured for the analysis of direct infusion ESI-MS containing EDTA with one atom of sodium and one atom of copper (top); and fine isotope structure annotated using the database-free approach (bottom). The spectrum was collected in negative ion mode.

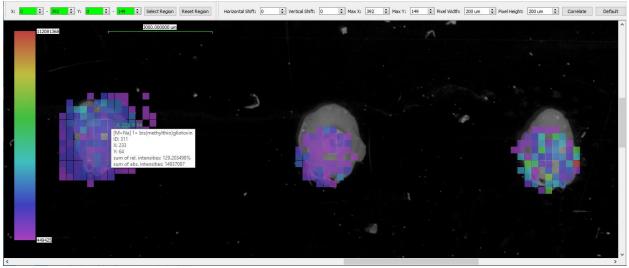


Figure S8. Fusion of identified compounds with an optical image. From left to right—dropletgenerated circles of bmGTX ($[C_{15}H_{20}N_2O_4S_2+Na]^+$, *m/z* 379.07567), FOXE ($[C_{27}H_{48}N_6O_9+K]^+$, *m/z* 639.31144), and TAFC ($[C_{39}H_{60}N_6O_{15}+Fe-2H]^+$, *m/z* 906.33041).

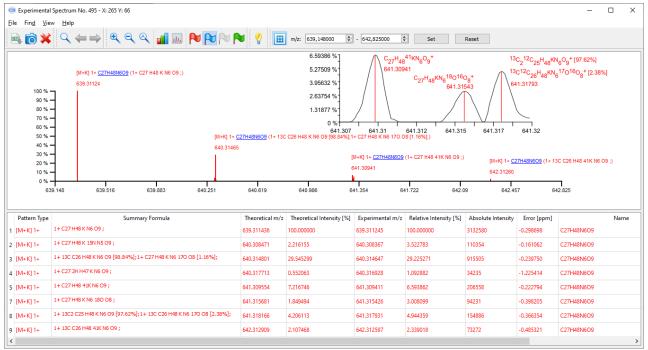


Figure S9. Dissecting ⁴¹K, ¹⁸O and ¹³C₂ (inset) from the $[M+K+2]^+$ ion of FOXE at FWHM = 0.001.

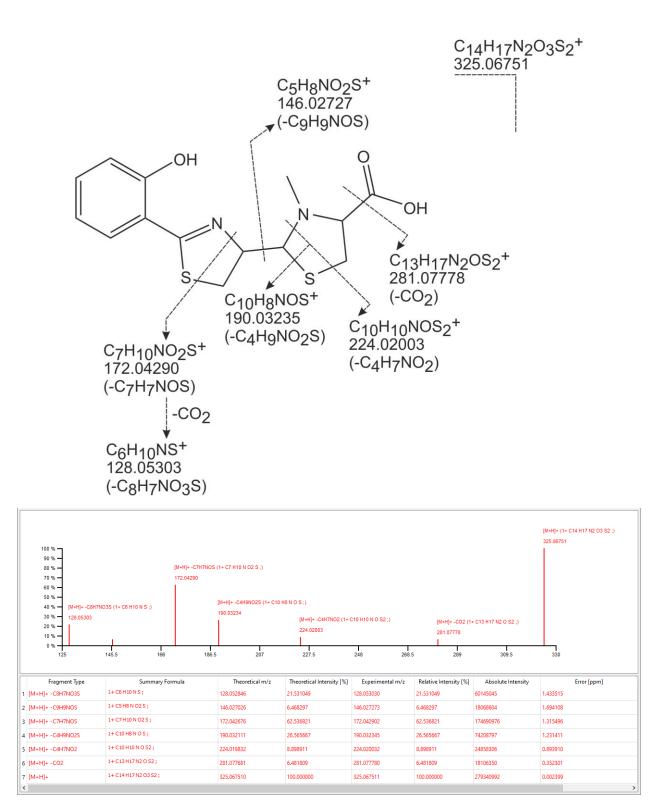


Figure S10. Structure of pyochelin and formulas of fragment ions suggested by CycloBranch.

Table S1. Number of generated combinations of elements for different m/z ranges [All = no filtering was applied; Sen. = Senior's filtering rules were applied; Adv. = advanced filtering rules (including the N/O rule) were used]. The maximum number of elements in a formula was limited to 200. S:1 and P:1 indicate that only one occurrence of sulfur and phosphorus was allowed, respectively.

	$m/z \leq 500$			m/z	$s \le 1,000 \text{ I}$	Da	$m/z \le 2,000 \text{ Da}$		
Element s	All	Sen.	Adv.	All	Sen.	Adv.	All	Sen.	Adv.
HCON	934,19	120,3	29,9	8,101,5	1,730,8	399,8	46,132,9	17,758,0	3,331,
	2	83	59	35	38	94	61	42	530
HCONS	3,757,	620,2	122,	65,355,	16,723,	2,962,	796,949,	352,440,	29,991
	914	12	476	150	250	328	136	391	,863
HCONS	13,306	2,496,	308,	444,85	121,96	8,596,	11,113,5	5,140,83	82,784
P	,477	101	917	0,486	4,934	749	84,055	5,916	,488
HCONS	1,681,	225,4	55,5	15,438,	3,350,8	775,5	90,392,9	35,076,5	6,604,
:1	008	03	11	135	10	99	45	65	713
HCONS	3,024,	416,6	101,	29,436,	6,446,3	1,495,	177,165,	69,119,4	13,068
:1P:1	190	00	546	430	84	144	660	26	,349

Table S2. Time required to generate combinations of elements for different m/z ranges [mm:ss] (MALDI-MS or direct infusion ESI).

	m/	$z \leq 500$	Da	m/z	≤1,000) Da	$m/z \le 2,000 \text{ Da}$			
Elements	All	Sen.	Adv.	All	Sen.	Adv.	All	Sen.	Adv.	
HCON	0:00	0:00	0:00	0:02	0:02	0:02	0:21	0:26	0:26	
HCONS	0:00	0:00	0:00	0:17	0:20	0:22	5:34	6:53	7:29	
HCONSP	0:02	0:02	0:02	1:27	1:47	2:06	52:05	69:38	86:24	
HCONS:1	0:00	0:00	0:00	0:07	0:07	0:08	2:03	2:09	2:15	
HCONS:1P:1	0:00	0:00	0:00	0:09	0:10	0:11	2:16	2:37	2:39	

Comments on Conventional Mass Spectra Settings:

Go to the CycloBranch's settings dialog (i.e., click on "Search" \rightarrow "Settings" in the main window) and select the mode "Compound Search – MS, LC-MS, MSI". Define the minimum and maximum m/z ratios to limit the number of generated molecular formulas. The smaller the difference between the maximum and minimum m/z ratio is, the faster the search. Click on the HCON button to define the chemical elements H, C, O, and N in the field "Neutral Losses/Chemical Elements". Any custom element can be added. Heteroatoms such as Na or K need not be added if $[M+Na]^+$ or $[M+K]^+$ ions are searched. The heteroatoms used in the names of ion types are included automatically, and thus, computational time can be saved. Define the maximum number of atoms in a generated molecular formula (e.g., 150 or 180) in the field "Maximum Number of Combined Losses/Elements". The smaller the number is, the faster the search. See the sample configuration in **Figure S2** for LC-MS data and that in **Figure S3** for MSI data. The following options can be used to reduce the number of false-positive annotations of peaks:

(1) Enable the option "Generate Full Isotope Patterns" and define the "Minimum Number of Isotopic Peaks" (e.g., 2). The theoretical isotopic patterns of compounds are generated and compared with the experimental spectrum. The "Minimum Number of Isotopic Peaks" (i.e., the minimum number of annotated peaks in an isotopic pattern used to report a given compound) is used to remove false-positive formulas.

(2) If LC-MS data are processed, define the minimum number of consecutive scans in which an ion must be detected to be considered a match in the field "Minimum Number of Spectra" (e.g., 2). If MSI data are processed, the field determines the minimum number of single-pixel spectra that must be detected for every compound (e.g., 50). Note that this criterion can be combined with the "Minimum Number of Isotopic Peaks".

(3) Define a minimum number of ions that must be matched to annotate a given compound. For example, if $[M+H]^+$ and $[M+Na]^+$ ions are selected, "Charge" = 2, and "Minimum Number of Ion Types" = 2, any pair of ions from the set of ions $[M+H]^+$, $[M+Na]^+$, $[M+2H]^{2+}$, and $[M+Na+H]^{2+}$ must be matched, otherwise the formula is discarded. This option can be combined with the "Minimum Number of Isotopic Peaks" and "Minimum Number of Spectra". If MALDI-MS, direct infusion ESI-MS, and MSI data are processed, the ions must be detected in the same spectrum. If LC-MS data are processed, the ions may occur at different retention times, which is advantageous, especially if $[M+H]^+$ and $[M+Fe-2H]^+$ ions are searched.

(4) Enable the option "Basic Formula Check" to discard formulas that do not meet Senior's rules.

(5) Enable the option "Advanced Formula Check" to check the advanced filtering rules, as stated in the manuscript.

(6) Enable the option "N/O Ratio Check" to remove formulas with a number of nitrogen atoms larger than the number of oxygen atoms.

(7) Define "Isotope m/z Tolerance" τ_{mz} in ppm.

(8) Define "Isotope Intensity Tolerance" τ_{int} in %.

Comments on Standard Product Ion Mass Spectra Settings:

In the settings dialog, select the mode "Compare Peaklist(s) with Spectrum of Searched Sequence - MS/MS" and define the peptide type "Other". In this mode, a single theoretical spectrum of a compound is compared with all experimental MS/MS spectra in an input file. The result of each comparison corresponds to one row in the output report. To perform the comparison, enter the molecular formula of a neutral compound into the field "Searched Sequence/Compound - Formula". Define an input list of chemical elements in the field "Neutral Losses/Chemical Elements". Click on the HCON button to use the default chemical elements and set the "Maximum Number of Combined Losses/Elements". The upper bound on the number of combined elements is the number of elements in the formula corresponding to the precursor ion of the analyzed spectrum. For example, if the precursor corresponds to $[C_{14}H_{16}N_2O_3S_2+H]^+$, use a value of 38 or lower. Note that the maximum number of occurrences of single elements can be limited by a colon. For example, S:1 and P:1 can be used to allow only one occurrence of sulfur or phosphorus, respectively. Furthermore, define the minimum m/z ratio to be as large as possible (see the impact of m_{min} below). See the sample configuration in **Figure S4**.

To perform a comparison of a single experimental MS/MS spectrum with multiple theoretical spectra (i.e., database compounds), select the mode "Compare Peaklist with Database – MS/MS" and define the peptide type as "Other". In this case, the database of compounds "Sequence/Compound Database File" does not have to include the sequence of building blocks for any compound. The mandatory items for every compound in the database are only the name and molecular formula. Because the database may contain many compounds, a precursor mass filter is enabled by default. This filter can optionally be disabled by the checkbox "Disable Precursor Mass Filter" to make a comparison of the experimental spectrum with all compounds in the database. Note that the type of peptide in the database is ignored in this search mode, and all the compounds are used.

The algorithm for annotation of peaks in product ion mass spectra works a similar way like the algorithm for conventional mass spectra:

(1) The input list of elements (e.g., H, C, O, and N) is loaded, and combinations of elements are generated. The number of generated combinations is limited by the maximum number of elements in a formula according to the "Maximum Number of Combined Losses/Elements" (e.g., 150).

(2) A combination of elements is discarded if $m_{\text{total}} > m_{1+} - m_{\min}$ where m_{total} is the total mass of the combination, m_{1+} is the mass of singly charged precursor ion, and m_{\min} is the minimum m/z ratio.

(3) If a theoretical product ion mass spectrum of a single compound, e.g., $C_aH_bN_cO_d$, is generated, any combination of elements $C_wH_xN_yO_z$ is limited by the condition $w \le a, x \le b, y \le c$, and $z \le d$. If theoretical spectra of multiple compounds from a database are generated (within a specified precursor m/z error tolerance), the maximum numbers of elements are used. For example, given another database compound, $C_eH_fN_gO_h$, then $w \le \max(a,e), x \le \max(b,f), y \le$ $\max(c,g)$, and $z \le \max(d,h)$. (4) Senior's rules no. 1 and 3 are checked. In this case, the sum of valences of all atoms in a formula had to be even and greater than or equal to $2 * (n - \alpha)$ where α was the maximum number of independent molecules of neutral losses. We did not use $\alpha = 1$ but an empirically determined value $\alpha = 10$ what means that at the most ten neutral losses could occur simultaneously (i.e., a molecular graph could include up to α components). The reason was that multiple neutral losses of molecules such as water of ammonia did not meet the criterion 2 * (n - 1).

(5) The remaining combinations of elements are applied as hypothetical neutral losses to a single molecular formula or a database of molecular formulas. Note that atoms in the formula of an annotated fragment ion form a subset of atoms in the formula of the precursor ion, what is an important difference from the MS¹ approach. Similar to the MS¹ approach, the presence of a monoisotopic peak is checked in the experimental spectrum while the theoretical spectrum is being generated to save the computer's main memory (i.e., unnecessary isotopic patterns of fragment ions are not generated).