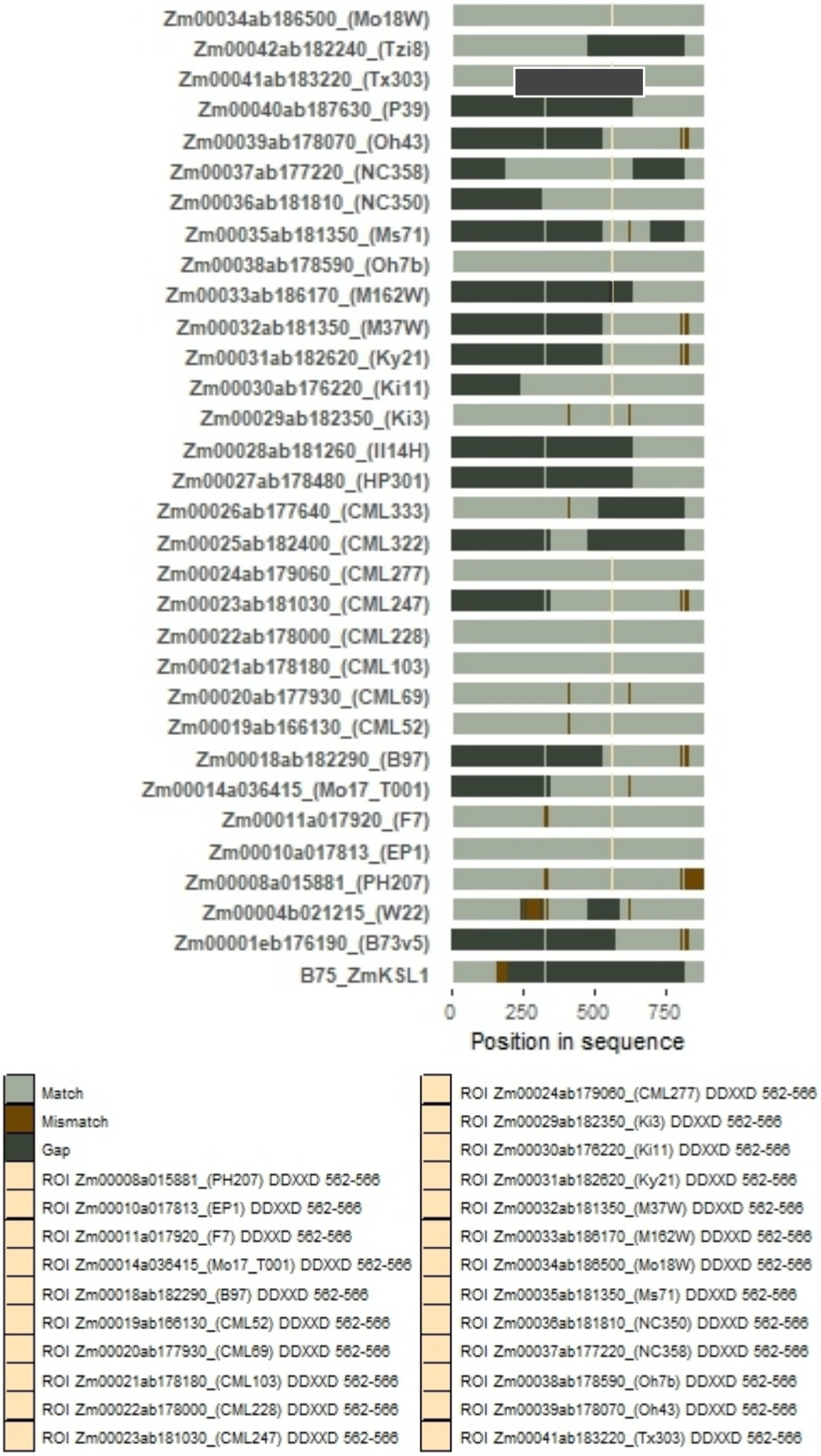
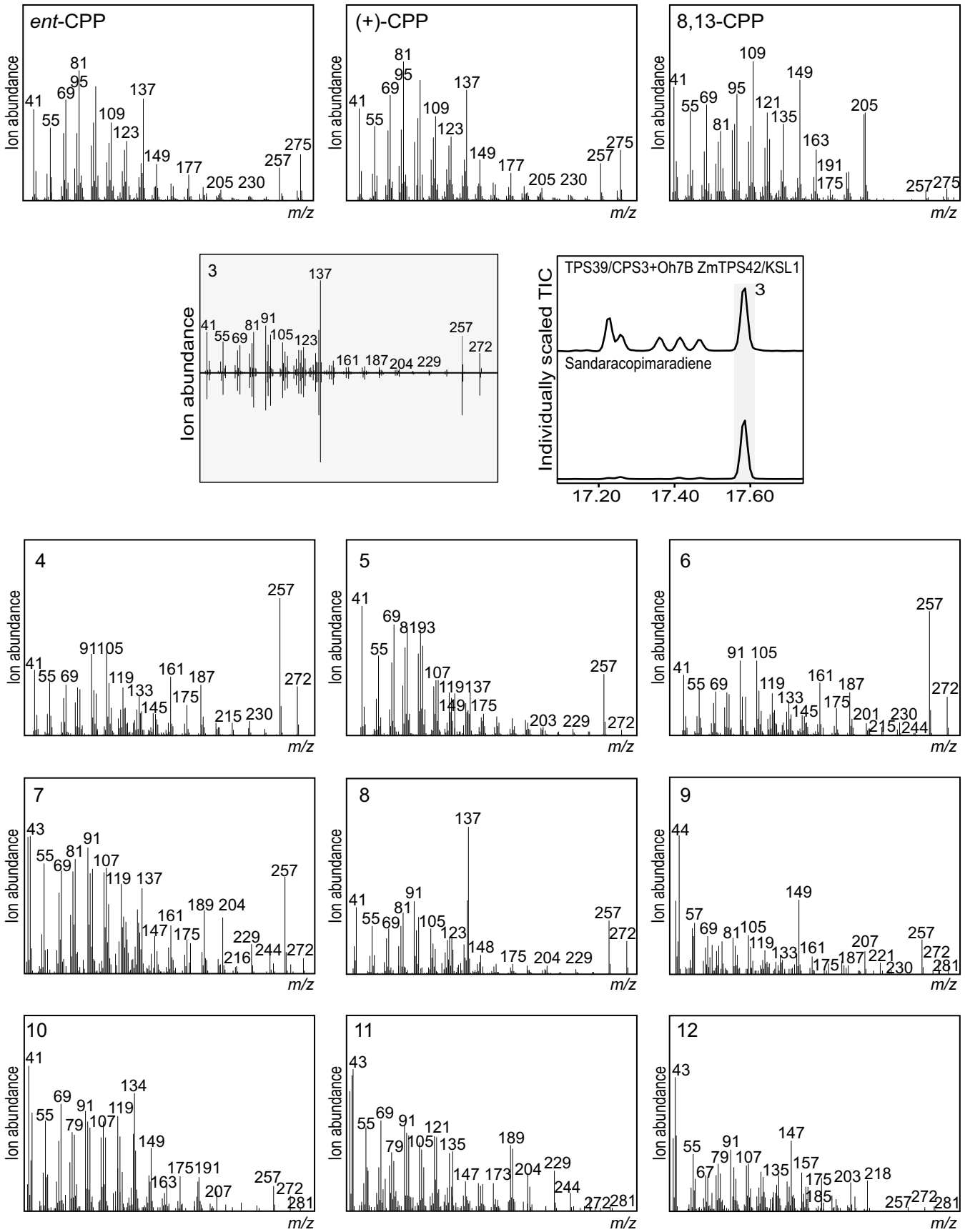
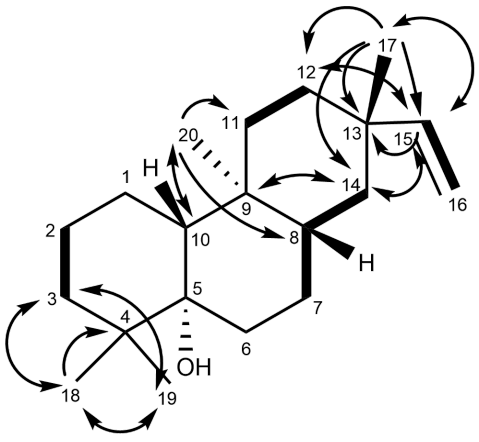


Supplementary Fig. S1 I Protein sequence alignment of ZmTPS42/KSL1 sequences derived from selected maize lines.



Supplementary Fig. S2 | Mass spectra of products from the pairwise reaction of ZmTPS42/KSL1 with different maize class II diterpene synthases. Mass spectrum of *Agrobacterium*-mediated *Nicotiana benthamiana* co-expression assays of ZmTPS38/CPS2/AN2, ZmTPS39/CPS3, and ZmTPS40/CPS4 alone as well as in combination with ZmTPS42/KSL1. *Ent*-CPP is the major product of ZmTPS38/CPS2/AN2. (+)-CPP is the major product of ZmTPS39/CPS3 and compounds **4** and **5** are minor products. Compounds **3-8** were found in the ZmTPS39/CPS3 + ZmTPS42/KSL1 combination and compounds **3**, **6-8** are unique to ZmTPS39/CPS3 + ZmTPS42/KSL1 combination. Compound **3** was identified as sandaracopimaradine by using a standard. 8,13-CPP is the major product of ZmTPS40/CPS4 and compounds **9-12** are minor products.

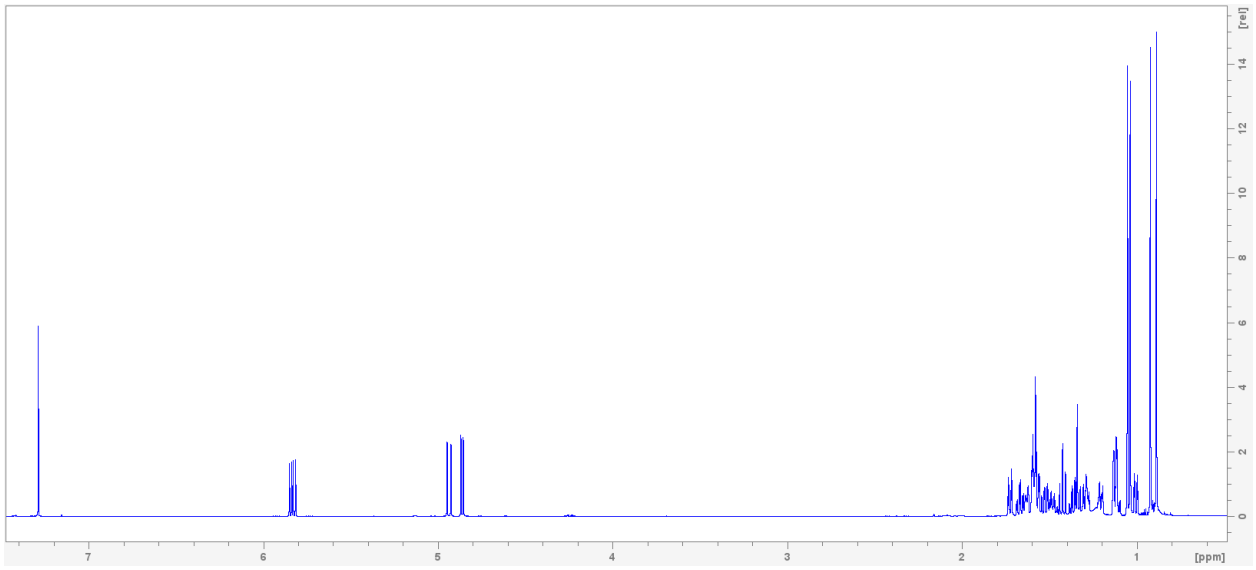
a



b

Position	δC (ppm)	δH (ppm)
1 a		1.626
b	21.183	1.358
2 a		1.589
b	22.094	1.477
3 a		1.665
b	36.906	1.121
4	38.843	
5	76.675	
6 a		1.722
b	32.623	1.572
7 a		1.524
b	25.07	1.121
8	41.669	1.2869
9	36.688	
10	48.63	1.338
11 a		1.585
b	35.083	1.111
12 a		1.578
b	31.95	1.204
13	36.361	
14 a		1.422
b	39.21	1.003
15	151.426	5.831
16 a		4.934
b	108.574	4.859
17	23.1	1.0507
18	24.42	0.884
19	24.01	1.0342
20	12.004	0.919

c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4
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2
1
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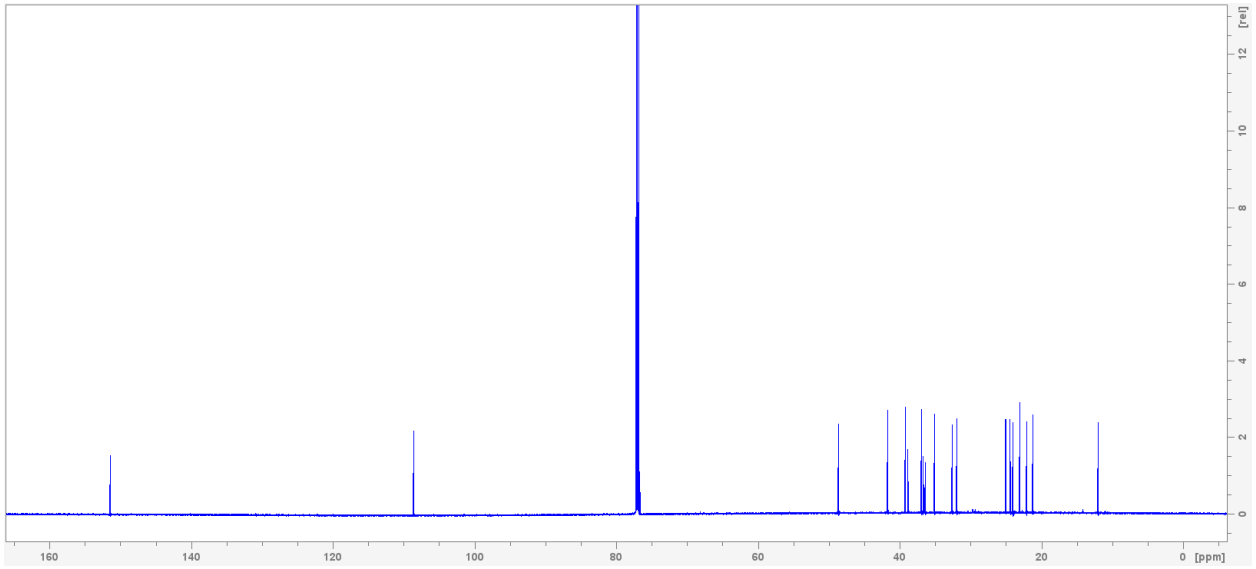
d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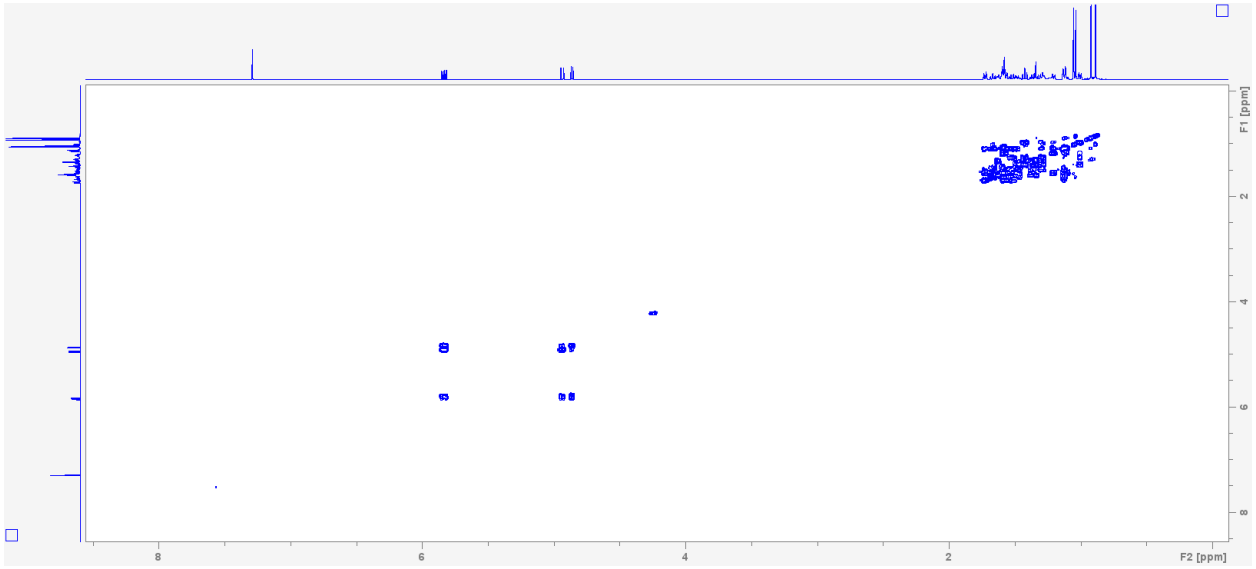
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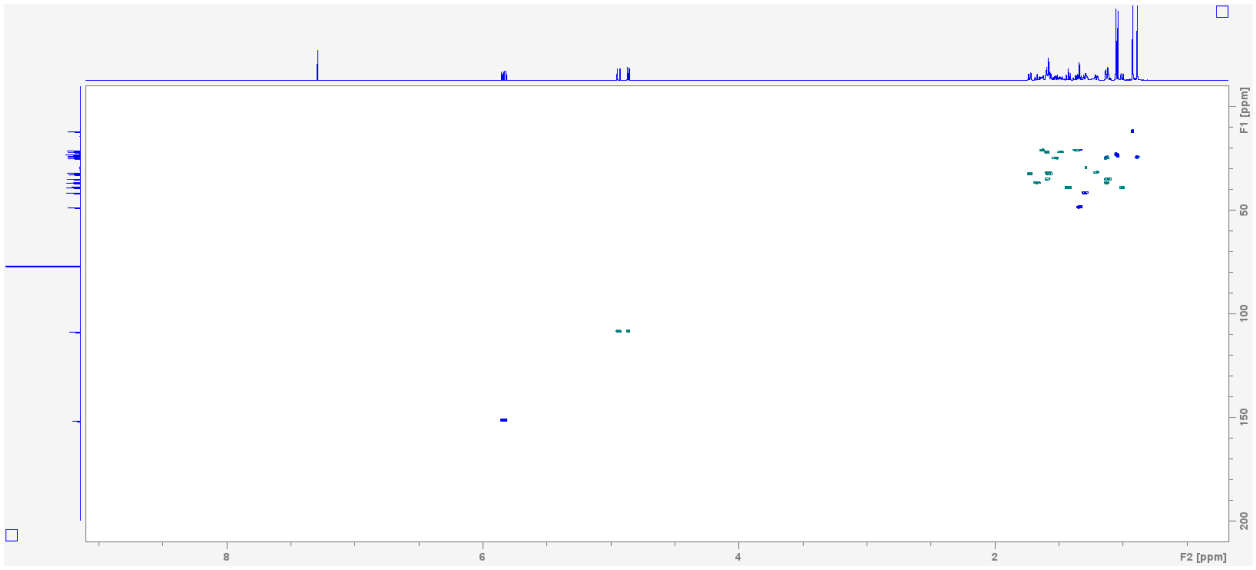
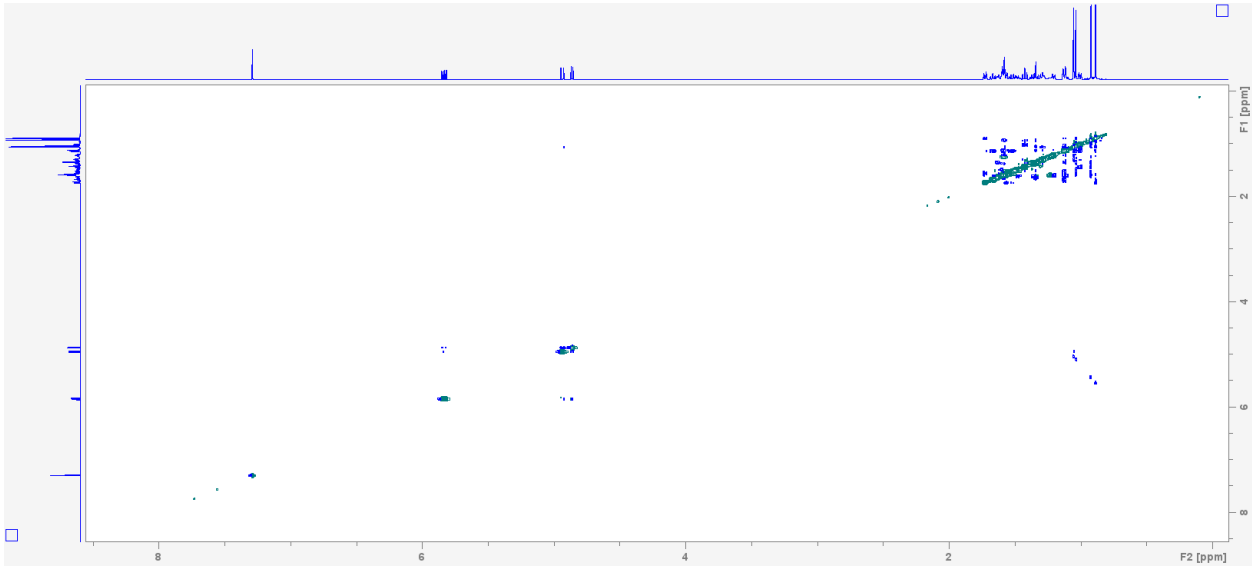
6
4
2
F2 [ppm]

f

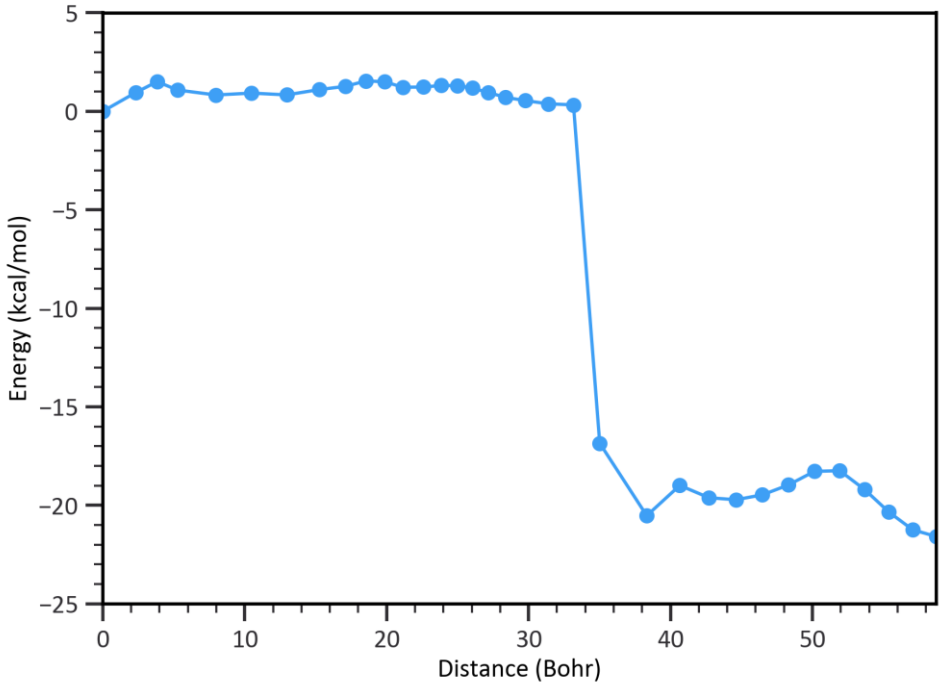


g



Supplementary Fig. S3 | NMR structural elucidation of compound **1** (5-rosanol). **a,** chemical structure depicted with key structural elements solved by experimental NMR including COSY (bold) and HMBC (arrows). Other structural elements including stereochemistry were confirmed utilizing computation NMR. **b**, 5-rosanol ^{13}C and ^{1}H assignments and chemical shift table. 5-rosanol NMR spectra: **c**, ^{1}H NMR; **d**, ^{13}C NMR; **e**, HSQC; **f**, COSY; **g**, NOESY.

a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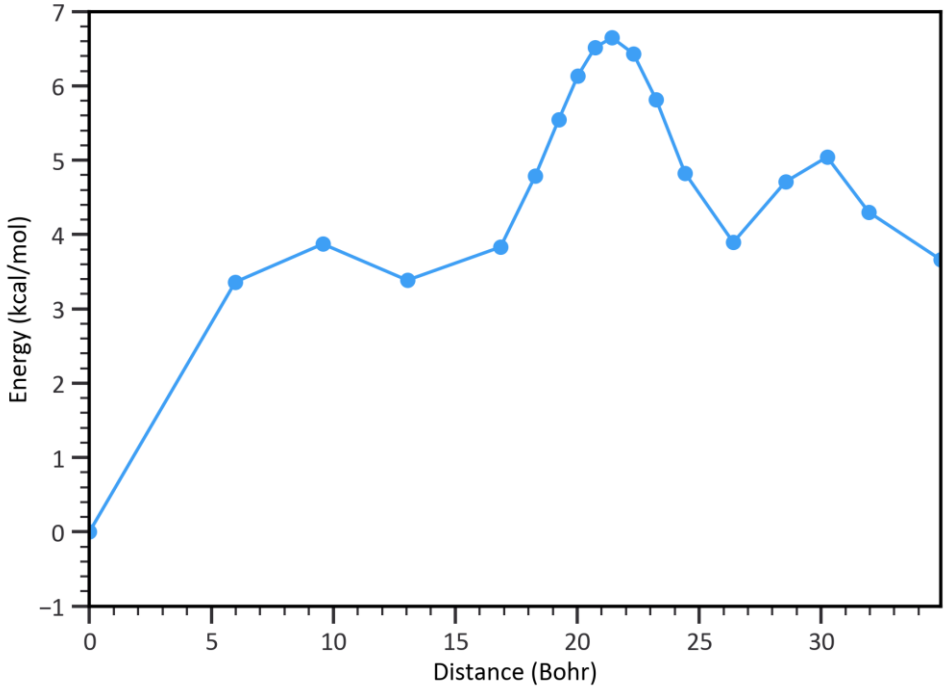
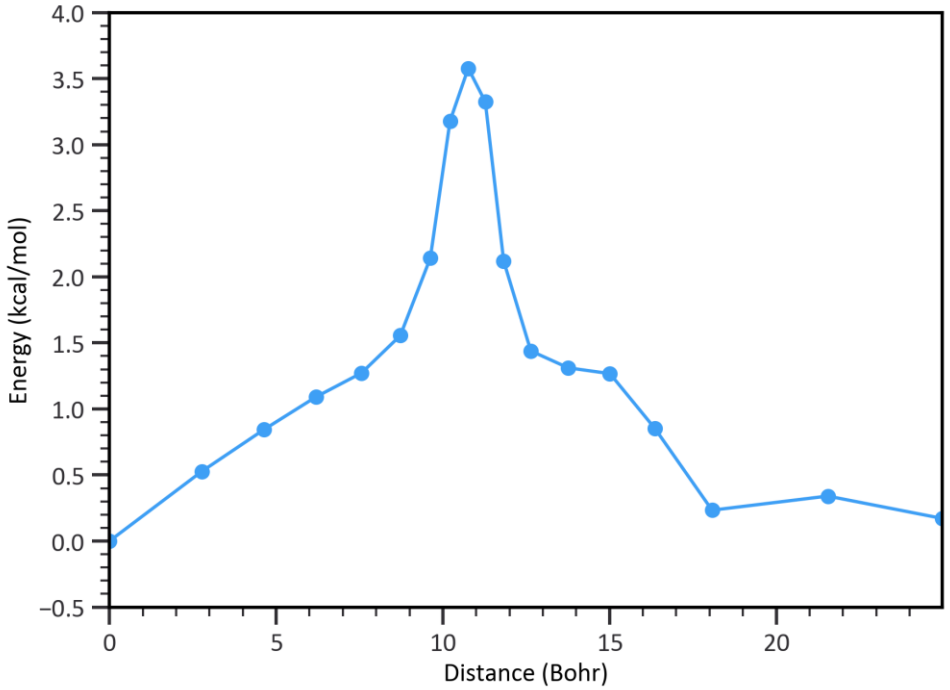
0
−5
−10
−15
−20
−25
Energy (kcal/mol)
0
10
20
30
40
50
Distance (Bohr)

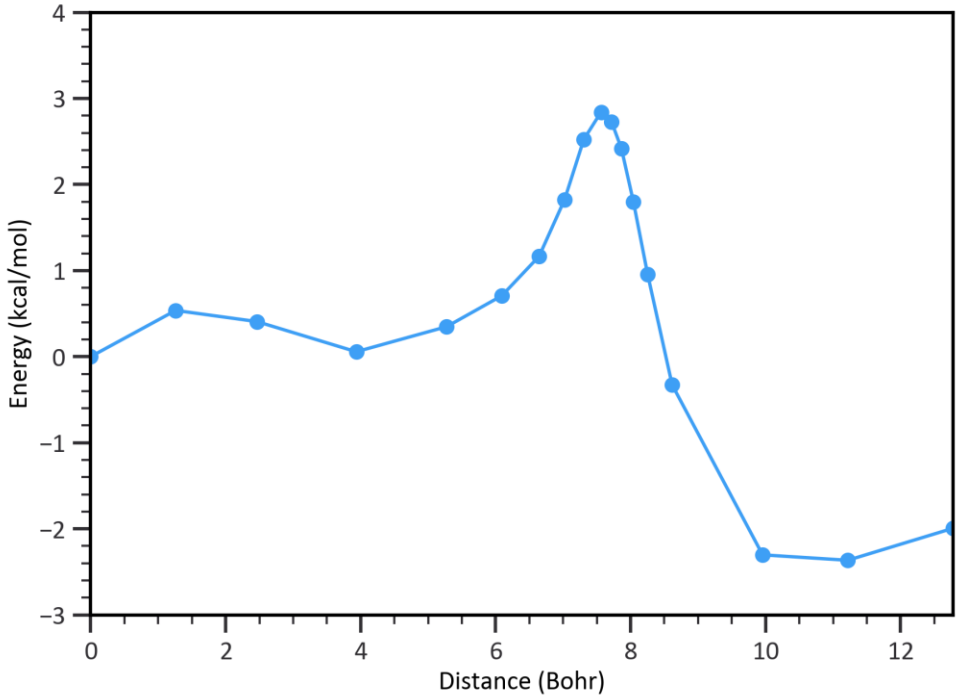
b


7
6
5
4
3
2
1
0
−1
Energy (kcal/mol)
0
5
10
15
20
25
30
Distance (Bohr)

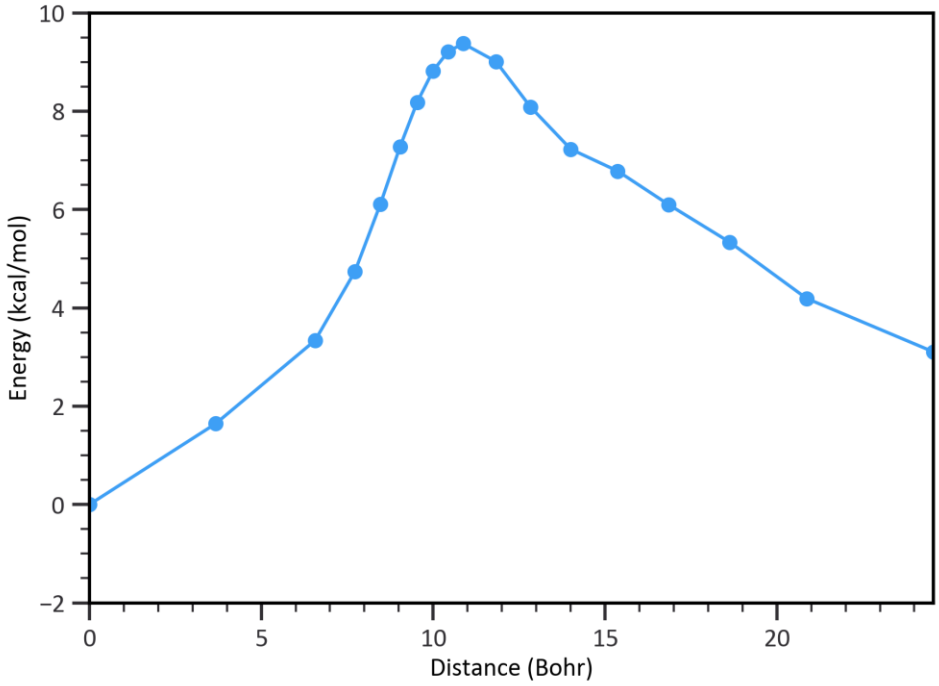
c


4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
Energy (kcal/mol)
0
5
10
15
20
Distance (Bohr)

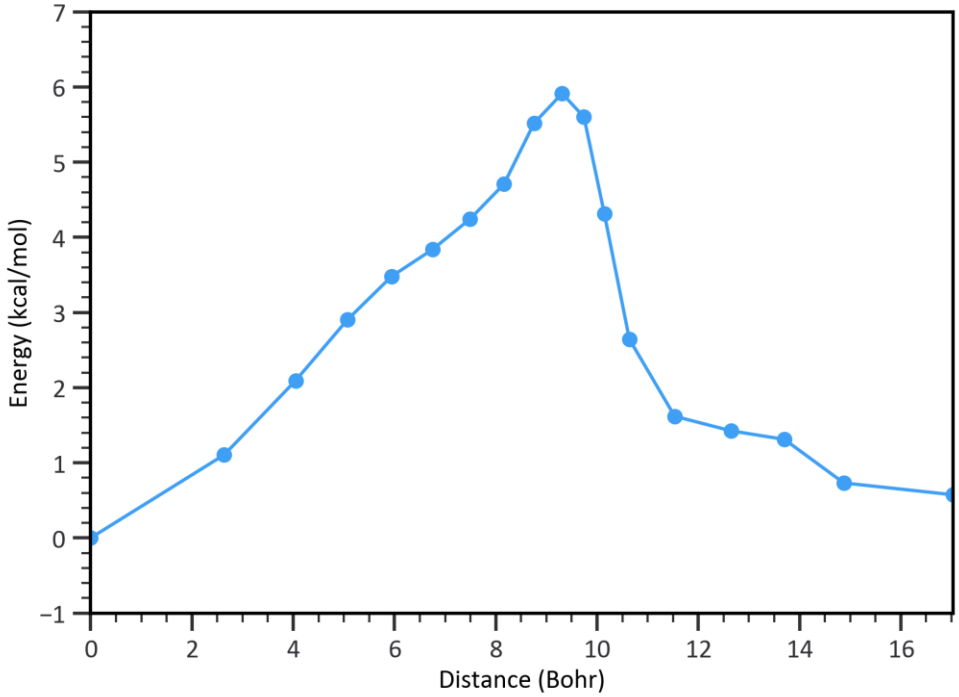
d


4
3
2
1
0
−1
−2
−3
Energy (kcal/mol)
0
2
4
6
8
10
12
Distance (Bohr)

e

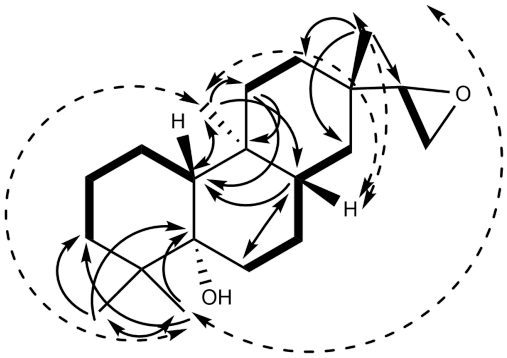


f



Supplementary Fig. S4 | MEP plots of the chemical steps in the ZmTPS42/KSL1-catalyzed mechanism, as obtained from RxnNet. **a**, MEP plot for the **I1** → **I2** step of the ZmTPS42/KSL1-catalyzed reaction mechanism generated using RxnNet. **b**, MEP plot for the **I2** → **I2^{NA}** step. **c**, MEP plot for the **I2^{NA}** → **I3** step. **d**, MEP plot for the **I3** → **I4** step. **e**, MEP plot for the **I4** →**I4^{NA}** step. **f**, MEP plot for the **I4^{NA}** → **I5** step.

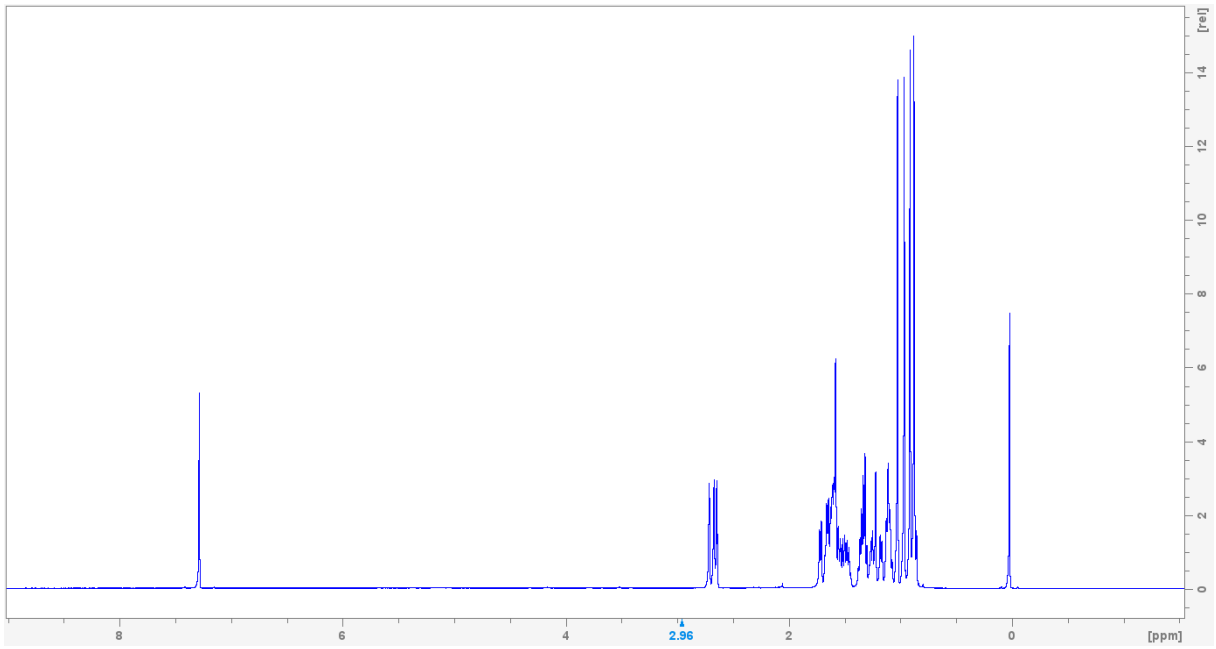
a



b

Position	δC (ppm)	δH (ppm)
1 a b	21.1785	1.626 1.358
2 a b	22.0695	1.589 1.477
3 a b	36.8689	1.665 1.121
4	38.8302	
5	76.6062	
6 a b	32.5735	1.722 1.572
7 a b	25.0819	1.524 1.121
8	41.1534	1.2869
9	36.7478	
10	48.5204	1.338
11 a b	34.5873	1.585 1.111
12 a b	29.3628	1.578 1.204
13	33.365	
14 a b	34.4213	1.422 1.003
15	61.1037	5.831
16 a b	43.4778	4.934 4.859
17	20.4828	1.0507
18	24.3954	0.884
19	23.977	1.0342
20	11.9278	0.919

c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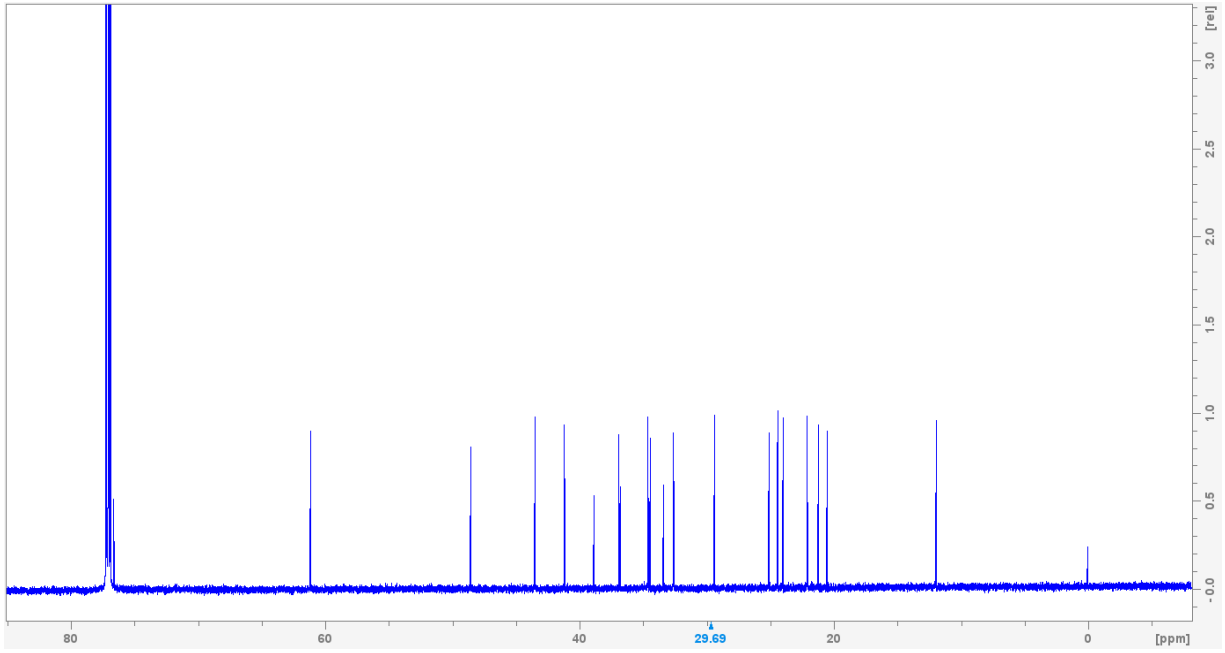
[ppm]

d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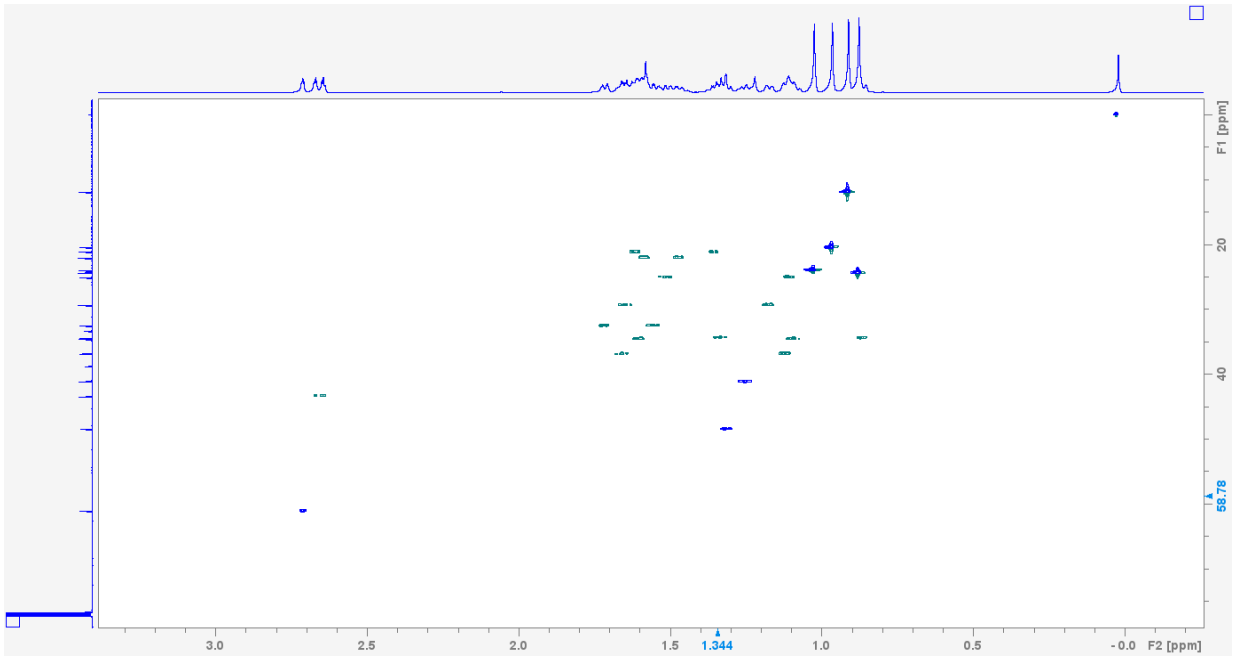
e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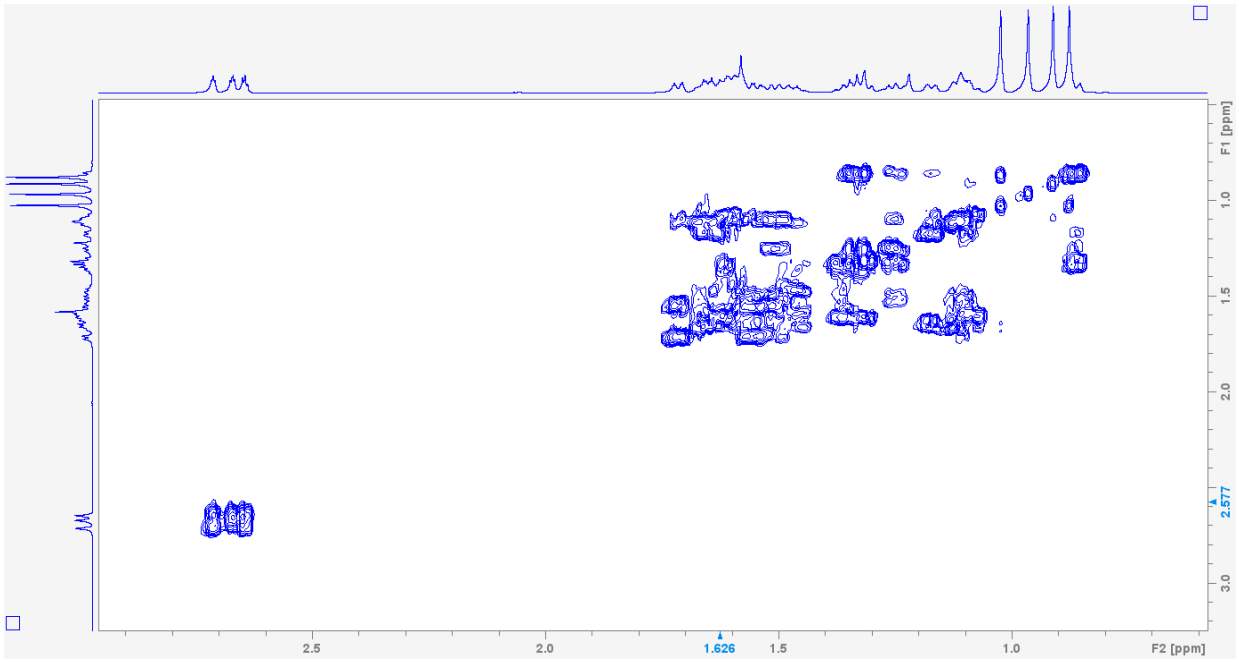
F2 [ppm]

f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1.5
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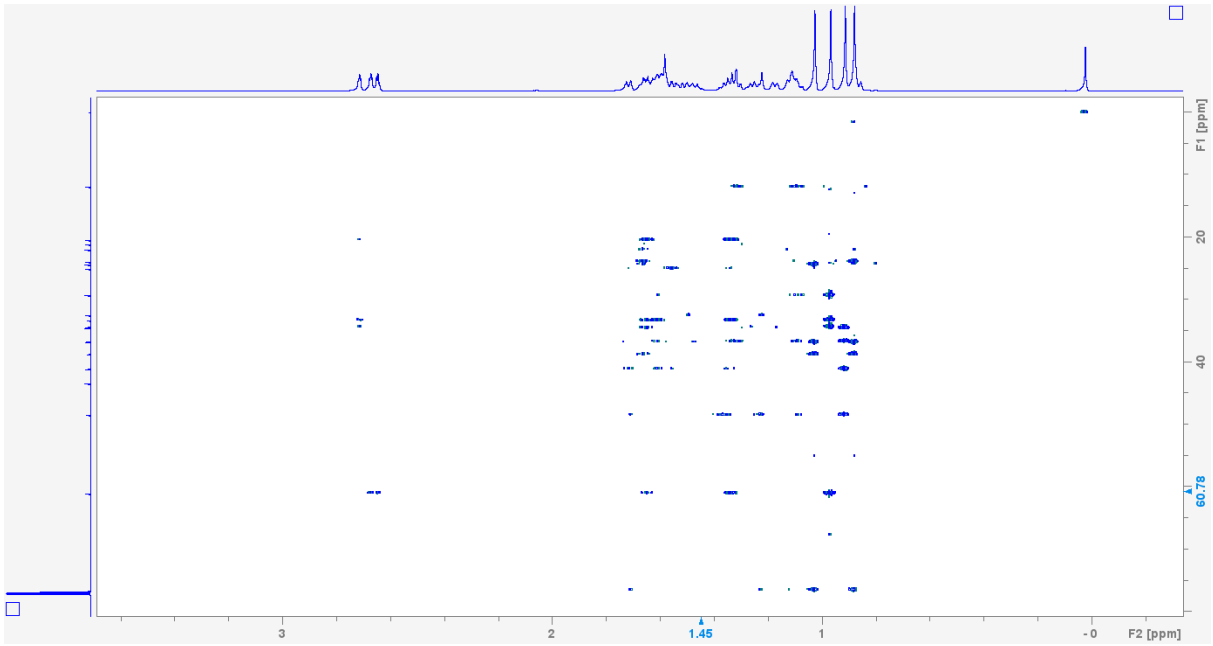
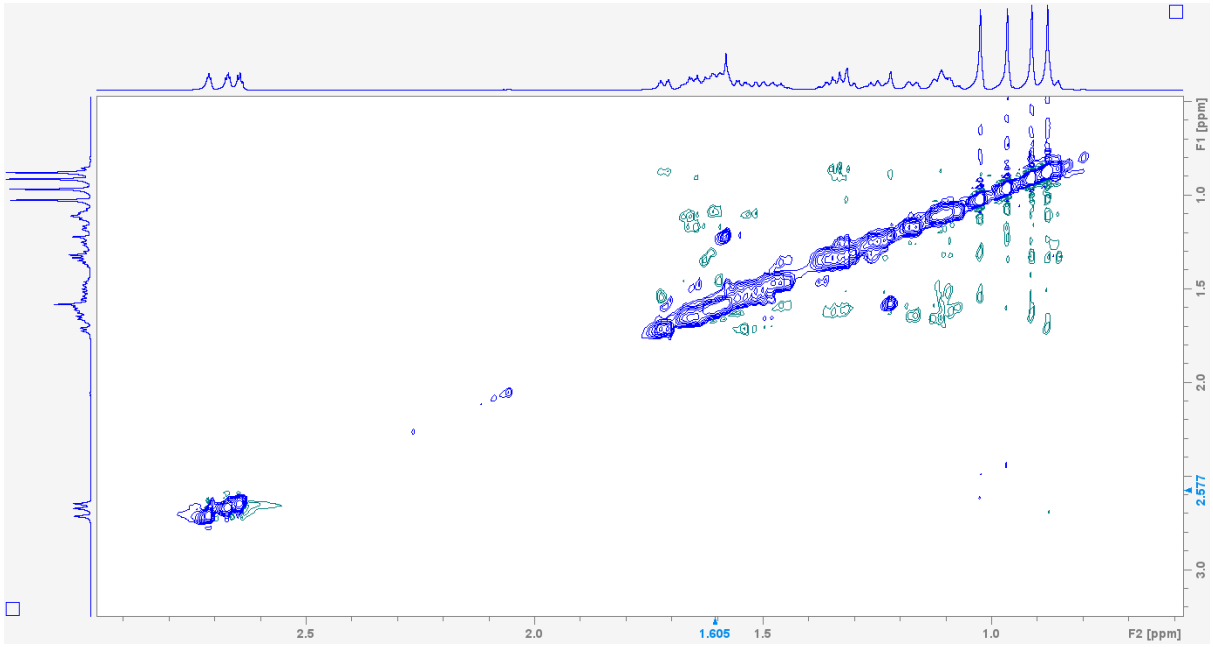
g

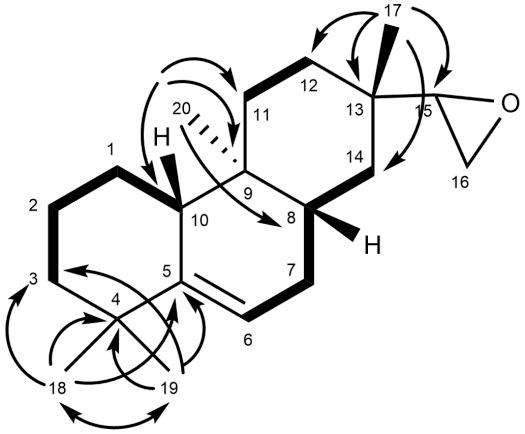


h



Supplementary Fig. S5 | NMR structural elucidation of compound **13** (epoxyrosanol). **a,** chemical structure depicted with key structural elements solved by experimental NMR including COSY (bold) and HMBC (arrows). **b**, Epoxyrosanol ^{13}C and ^{1}H assignments and chemical shift table. Epoxyrosanol NMR spectra: **c**, ^{1}H NMR; **d**, ^{13}C NMR; **e**, HSQC; **f**, COSY; **g**, HMBC; **h**, NOESY.

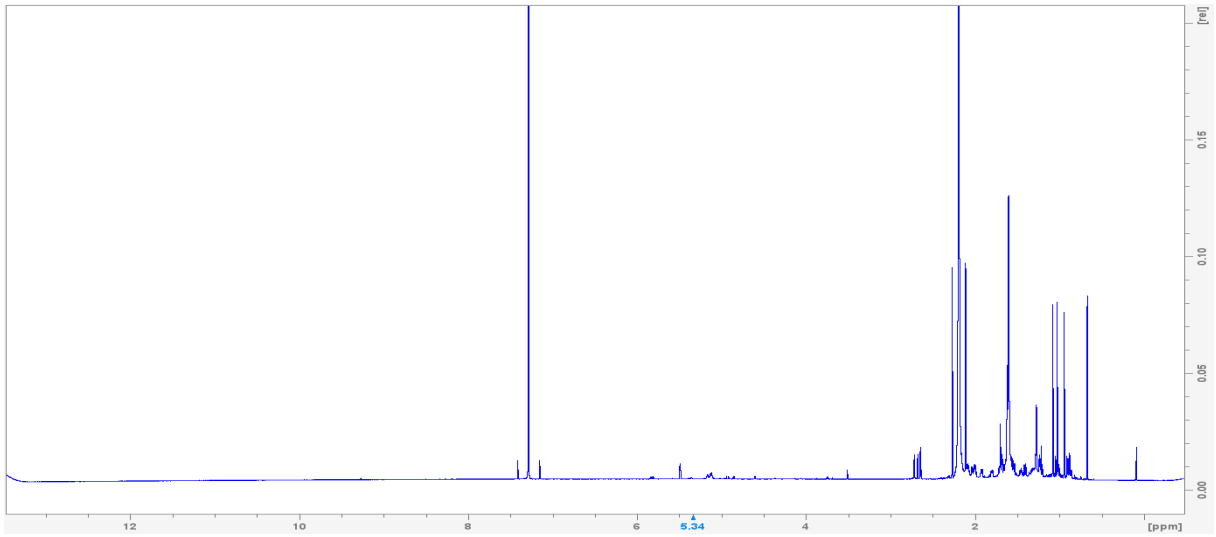
a



b

Position	δC (ppm)	δH (ppm)
1 a b	26.5654	1.802 2.093
2 a b	21.9358	1.595 1.539
3 a b	40.8027	1.412 1.237
4	35.8912	
5	145.8443	
6	116.2253	5.492
7 a b	30.2062	2.19 1.677
8	35.6569	1.455
9	34.8835	
10	47.1978	1.923
11 a b	33.7430	1.698 1.270
12 a b	29.8558	1.560 1.231
13	33.3388	
14 a b	34.2599	1.222 1.010
15	61.2331	2.72
16 a b	43.3800	2.678 2.644
17	19.5772	0.946
18	29.3412	1.029
19	29.7230	1.081
20	12.3750	0.674

c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10
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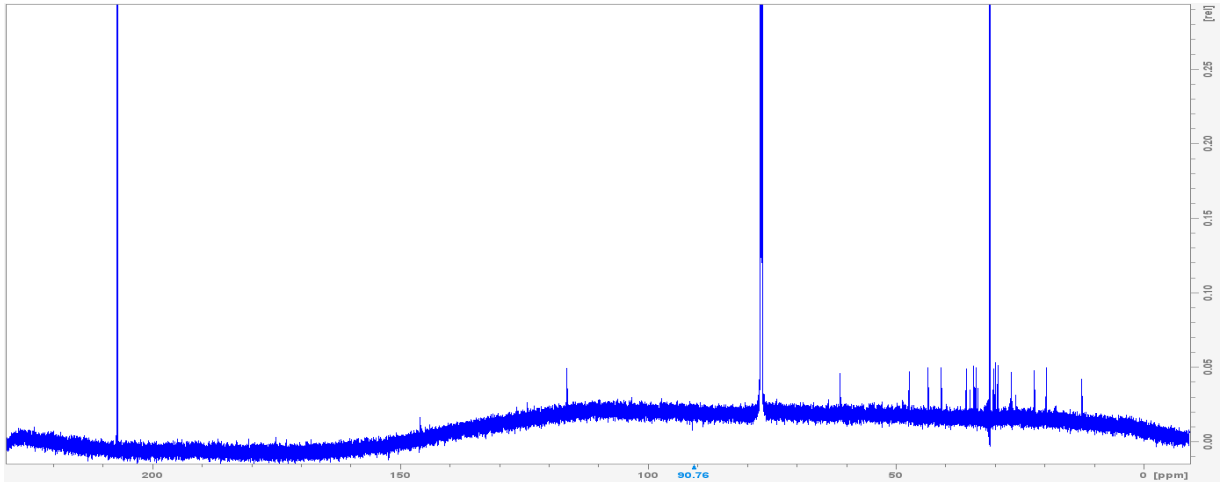
5.34
4
2
[ppm]

d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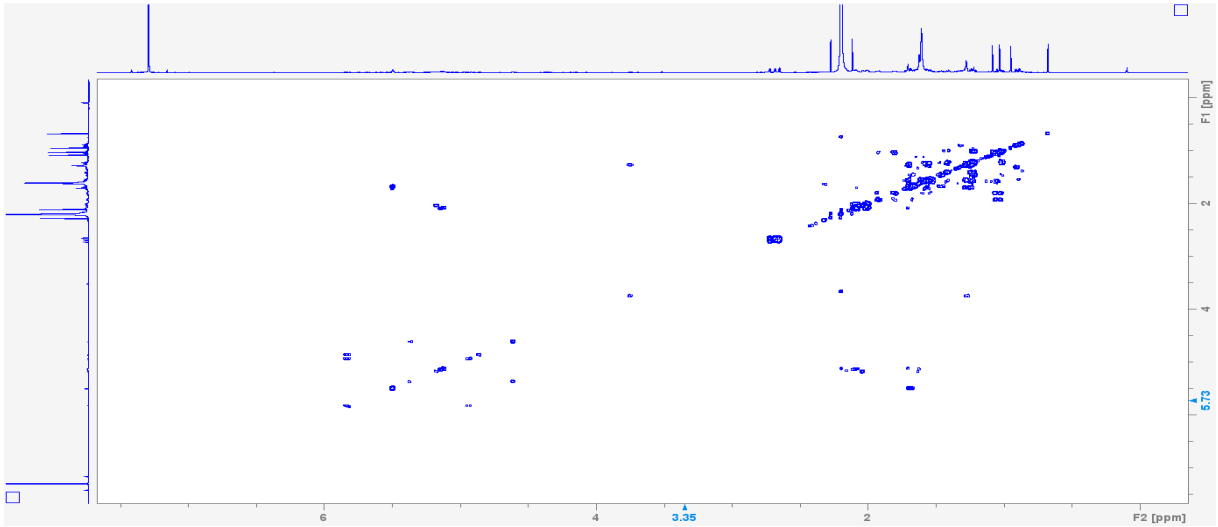
e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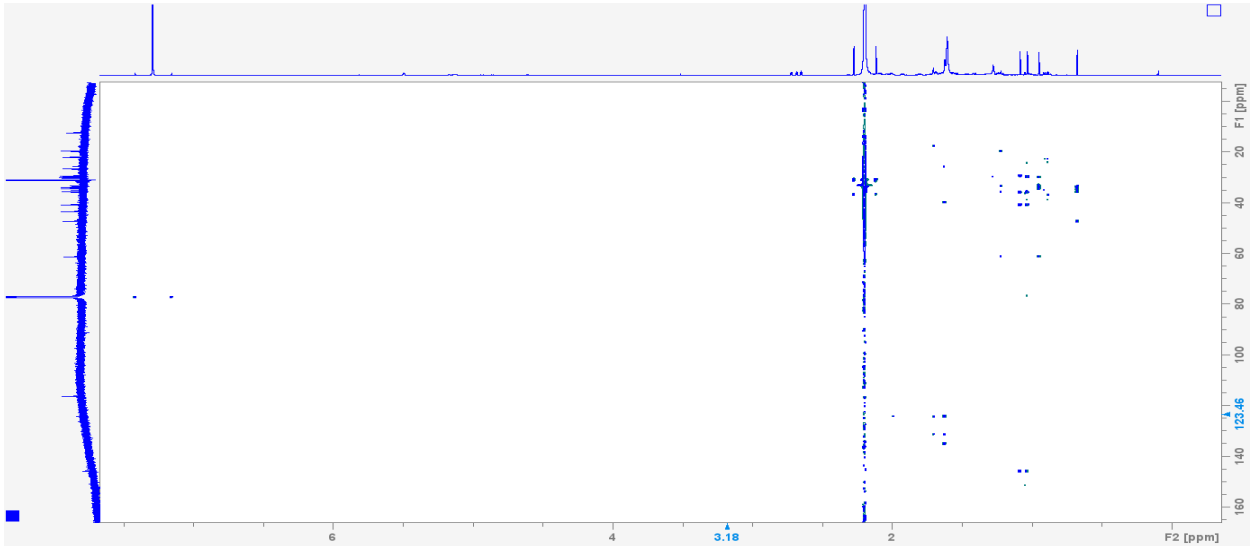
4
3.35
2
F2 [ppm]

f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3.18
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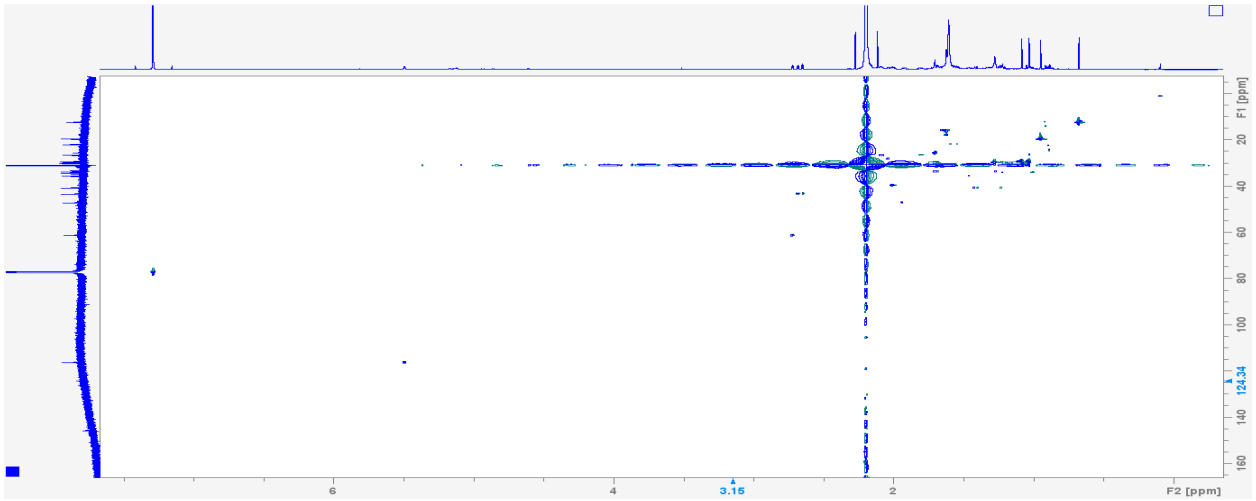
g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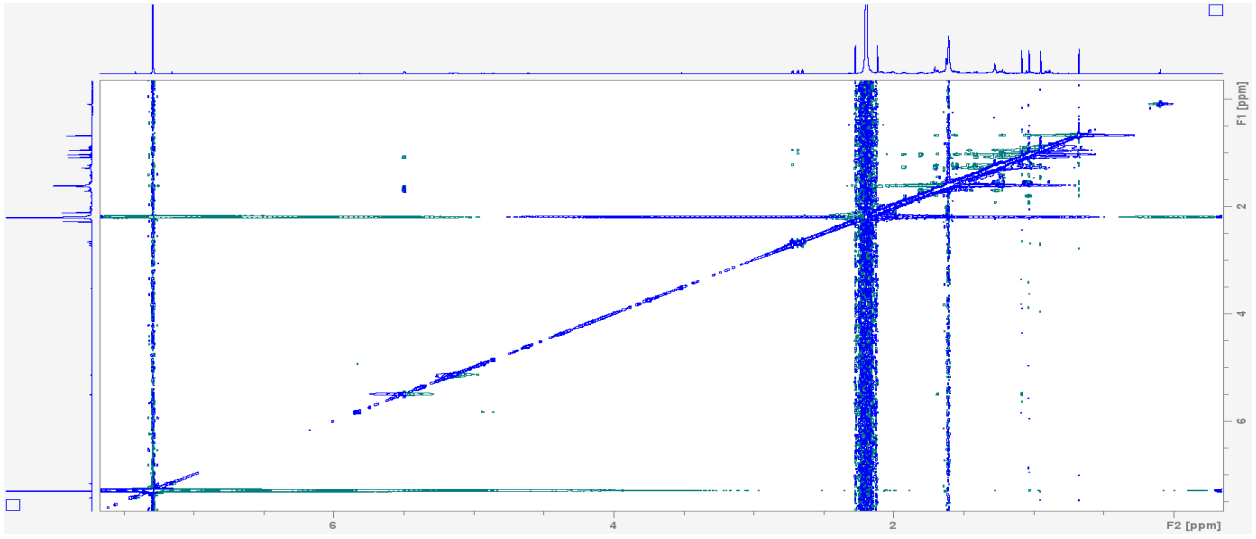
6
4
3.15
2
F2 [ppm]

h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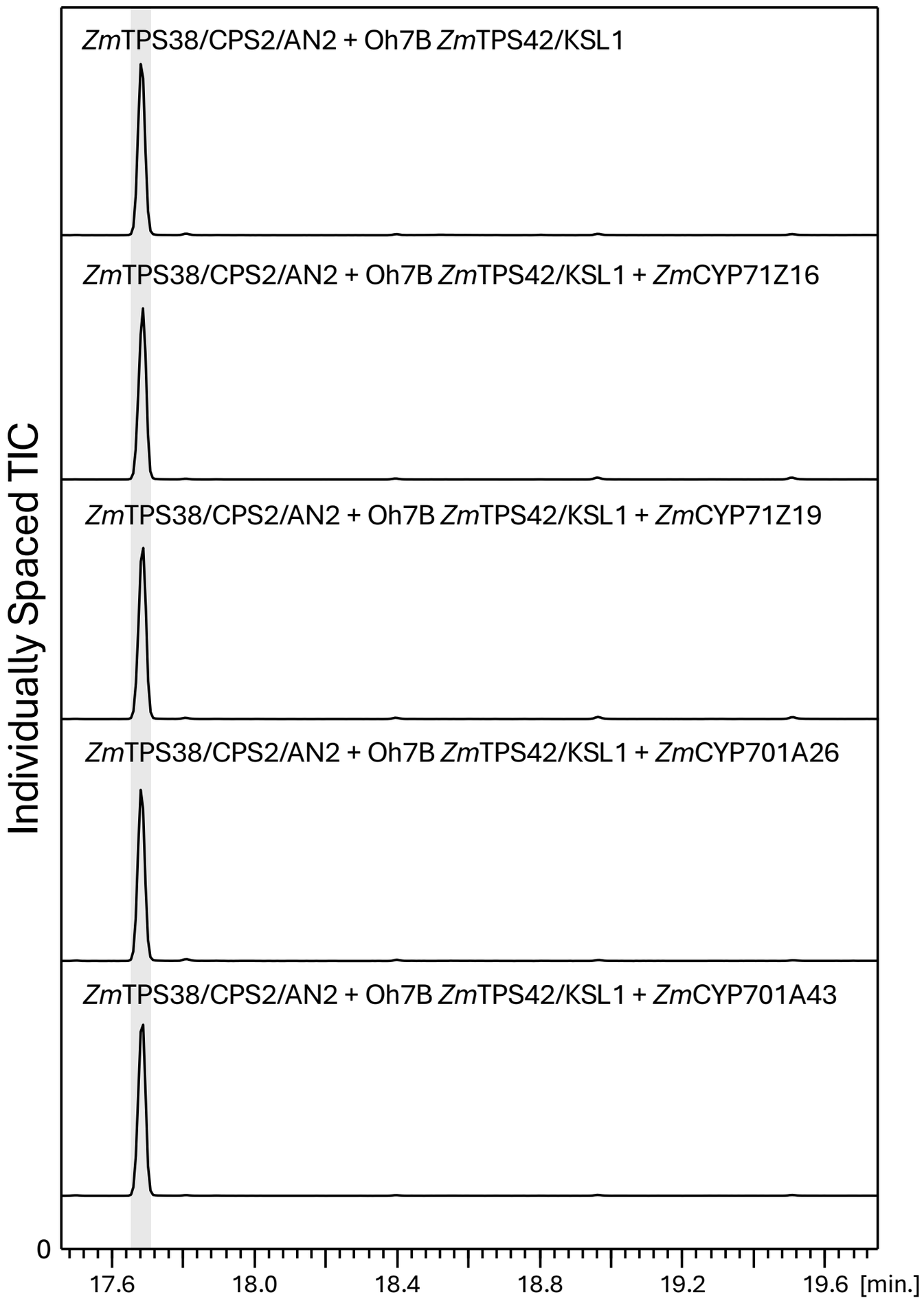
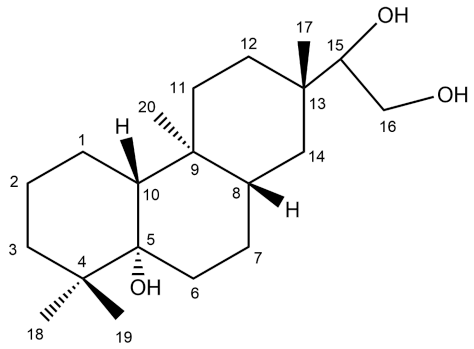
4
6
6
4
2
F2 [ppm]

Supplementary Fig. S6 | NMR structural elucidation of compound **14** (epoxyrosaene). **a**, chemical structure depicted with key structural elements solved by experimental NMR including COSY (bold) and HMBC (arrows). **b**, Epoxyrosaene 13C and 1H assignments and chemical shift table. Epoxyrosaene NMR spectra: **c**, 1H NMR; **d**, 13C NMR; **e**, HSQC; **f**, COSY; **g**, HMBC; **h**, NOESY.



Supplementary Fig. S7 | Functional analysis of maize P450 enzymes for 5-rosanol conversion. Individually scaled total ion chromatograms (TIC) of reaction products resulting from *Nicotiana benthamiana* co-expression assays of ZmTPS38CPS2/AN2 and ZmTPS42/KSL1 only, or with the addition of known maize diterpenoid-metabolic P450 enzymes, ZmCYP71Z16, ZmCYP71Z19, ZmCYP701A26, and ZmCYP701A43. Highlighted peak depicts 5-rosanol.

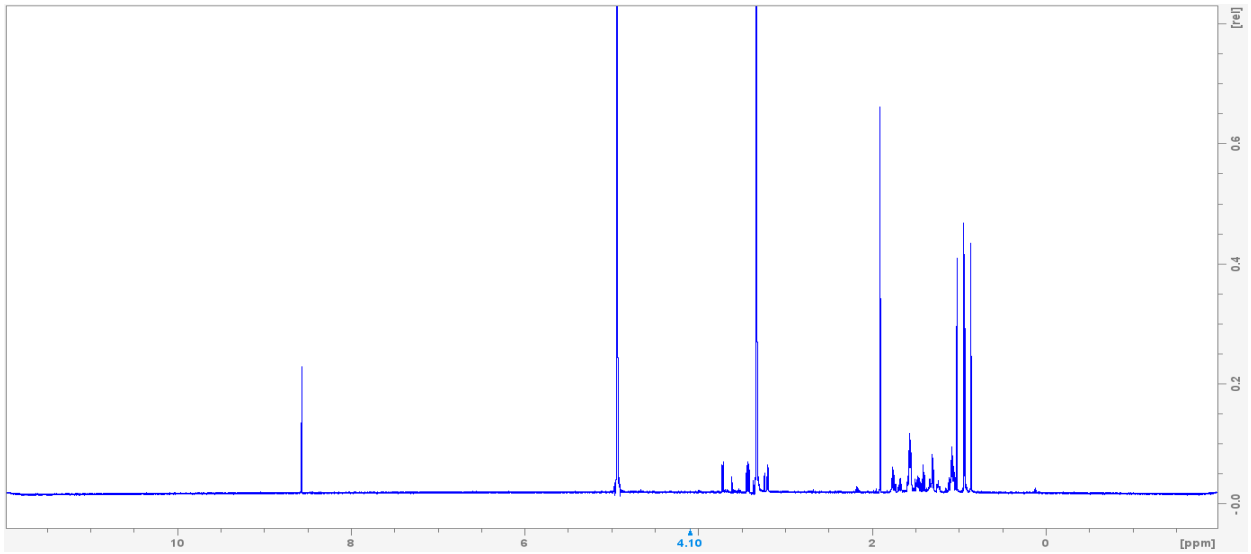
a



b

Position	δC (ppm)	δH (ppm)
1 a b	20.6	1.578 1.469
2 a b	21.94	1.567 1.506
3 a b	36.49	1.749 1.063
4	38.49	
5	76.45	
6 a b	31.94	1.778 1.571
7 a b	25.13	1.571 1.092
8	41.21	1.251
9	36.41	
10	48.69	1.31
11 a b	34.7	1.596 1.119
12 a b	28.99	1.683 1.083
13	36.39	
14 a b	35.79	1.412 1.093
15	81.71	3.2
16 a b	62.15	3.45 3.72
17	18.39	0.935
18	23.75	0.863
19	23.2	1.026
20	11.14	0.945

c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8
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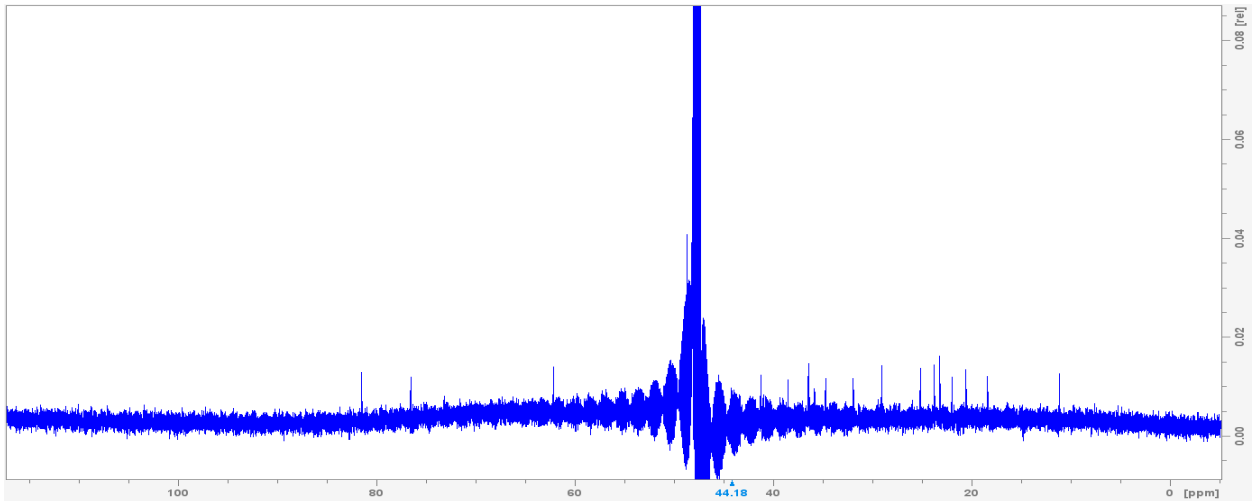
[ppm]

d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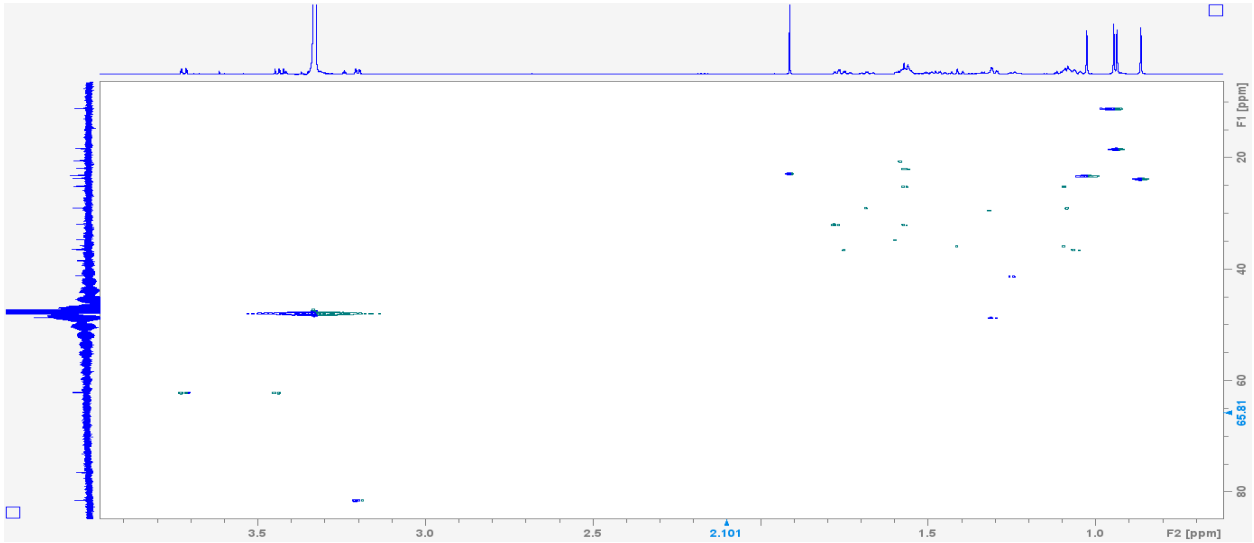
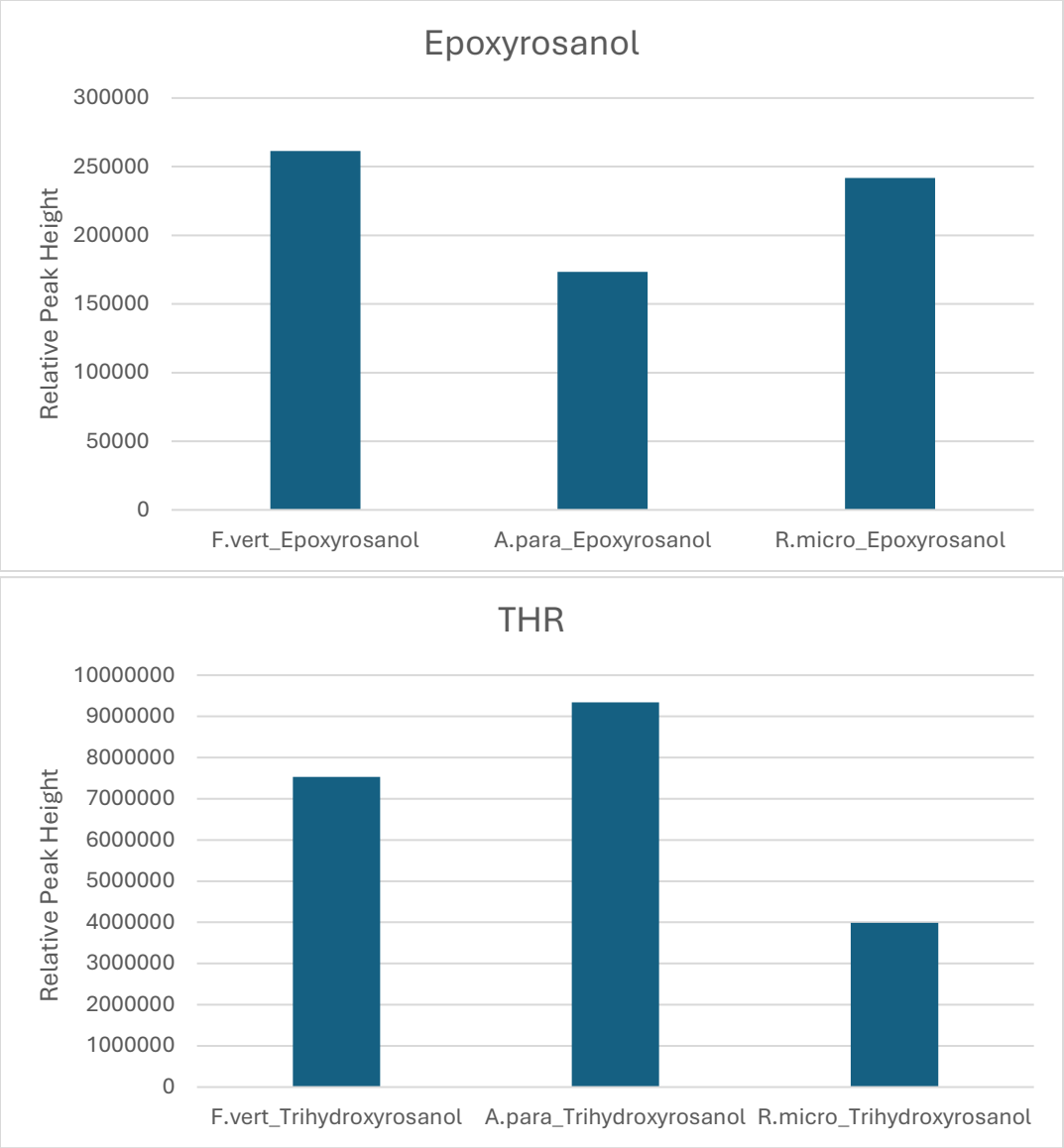
e


F1 [ppm]
20
40
60
65.81
80
3.5
3.0
2.5
2.101
1.5
1.0
F2 [ppm]

Supplementary Fig. S8 | NMR structural elucidation of compound **15** (trihydroxyrosanol, THR). **a**, chemical structure. **b**, Trihydroxyrosanol 13C and 1H assignments and chemical shift table. Trihydroxyrosanol NMR spectra: **c**, 1H NMR; **d**, 13C NMR; **e**, HSQC.



Supplementary Fig. S9 | Recovered epoxyrosanol and trihydroxyrosanol (THR) from fungal bioactivity assays. A total amount of 50 ug/mL assays were extracted after 48 h using 80% methanol and analyzed by LC-MS/MS. F.vert = *Fusarium ferticilliodies*; A. para = *Aspergillus parasiticus*; R. micro = *Rhizopus microspores*.