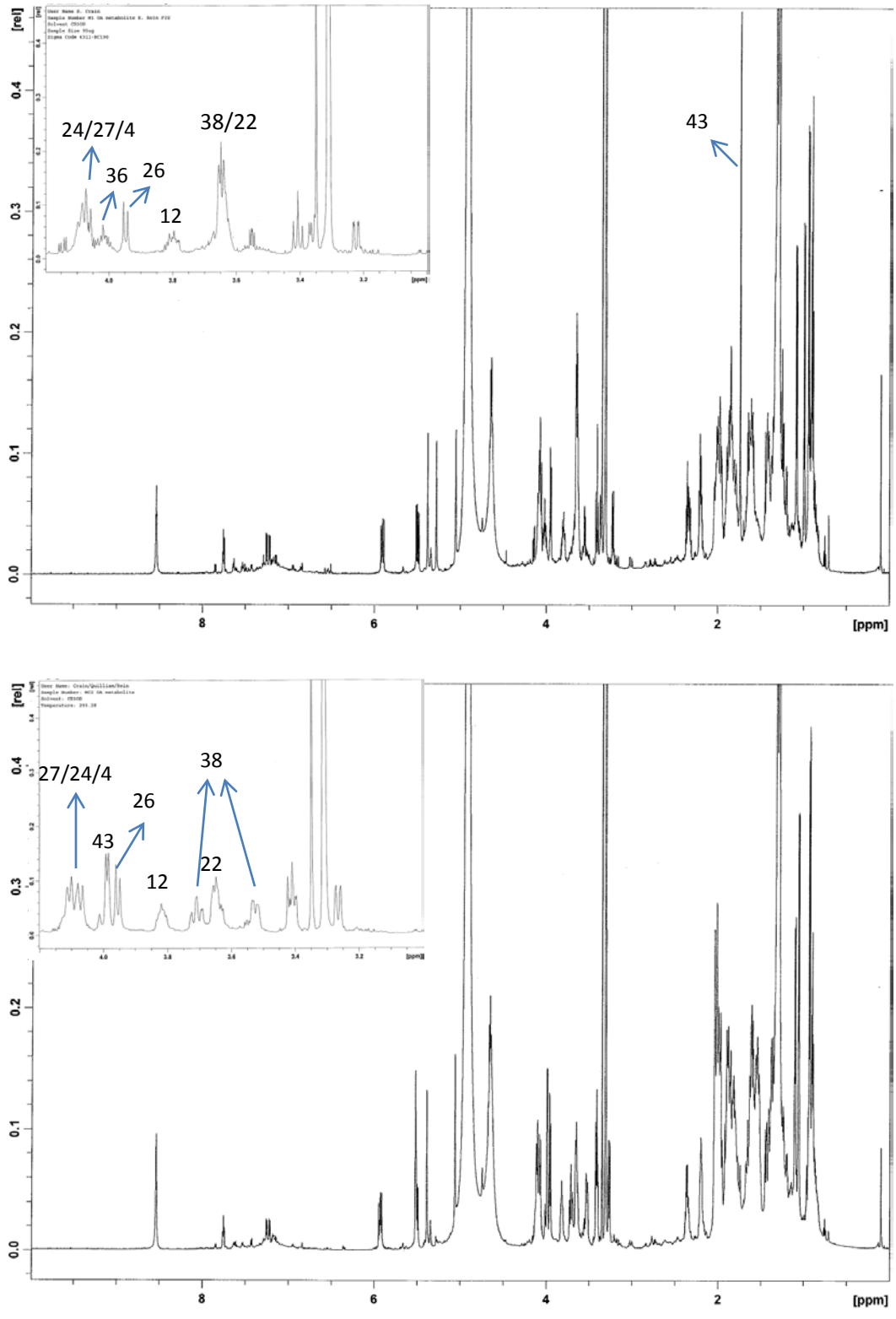
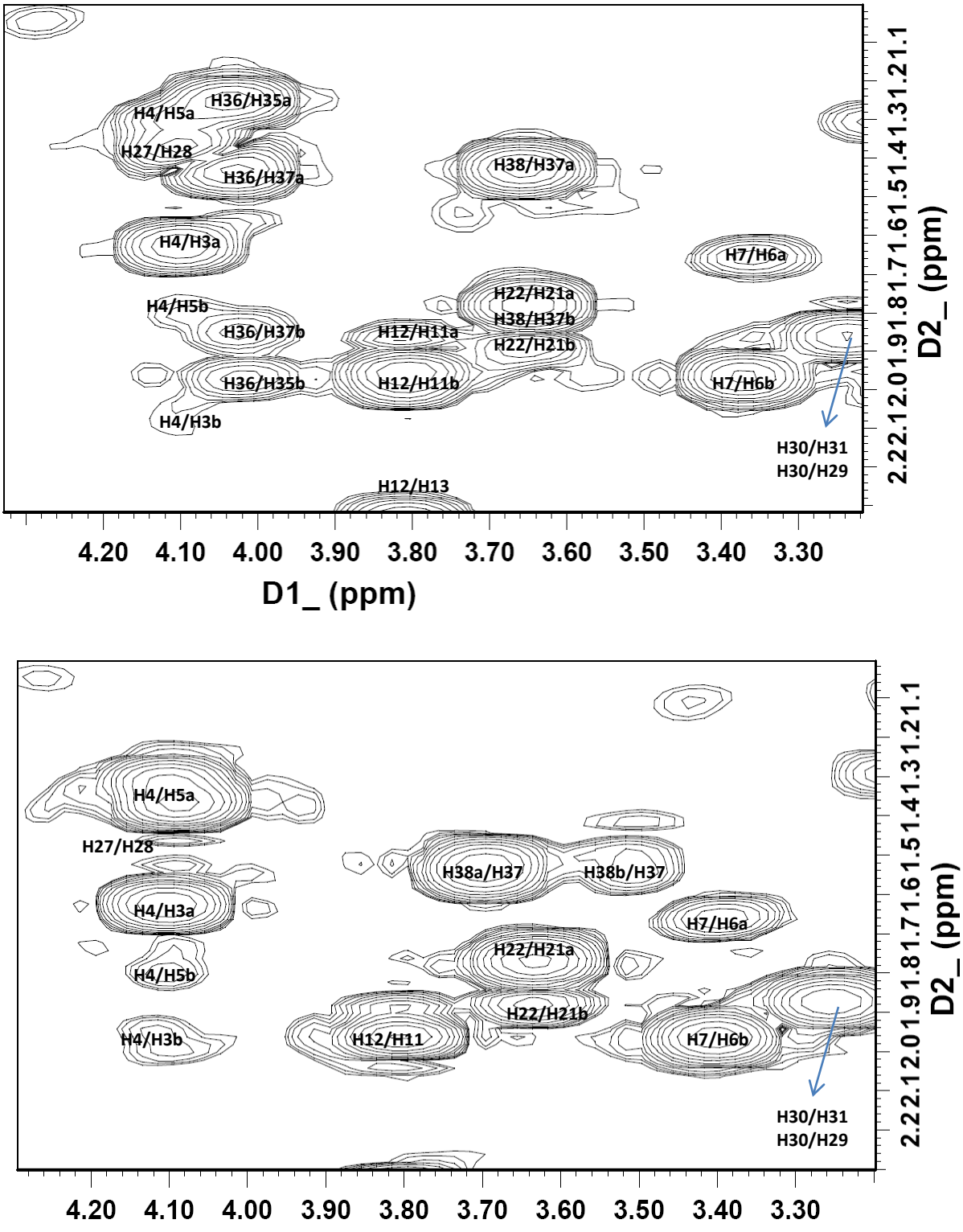
The structures of three human metabolites of the algal hepatotoxin okadaic acid

Li Liu, Fujiang Guo, Sheila Crain, Michael A. Quilliam, Xiaotang Wang and Kathleen S. Rein

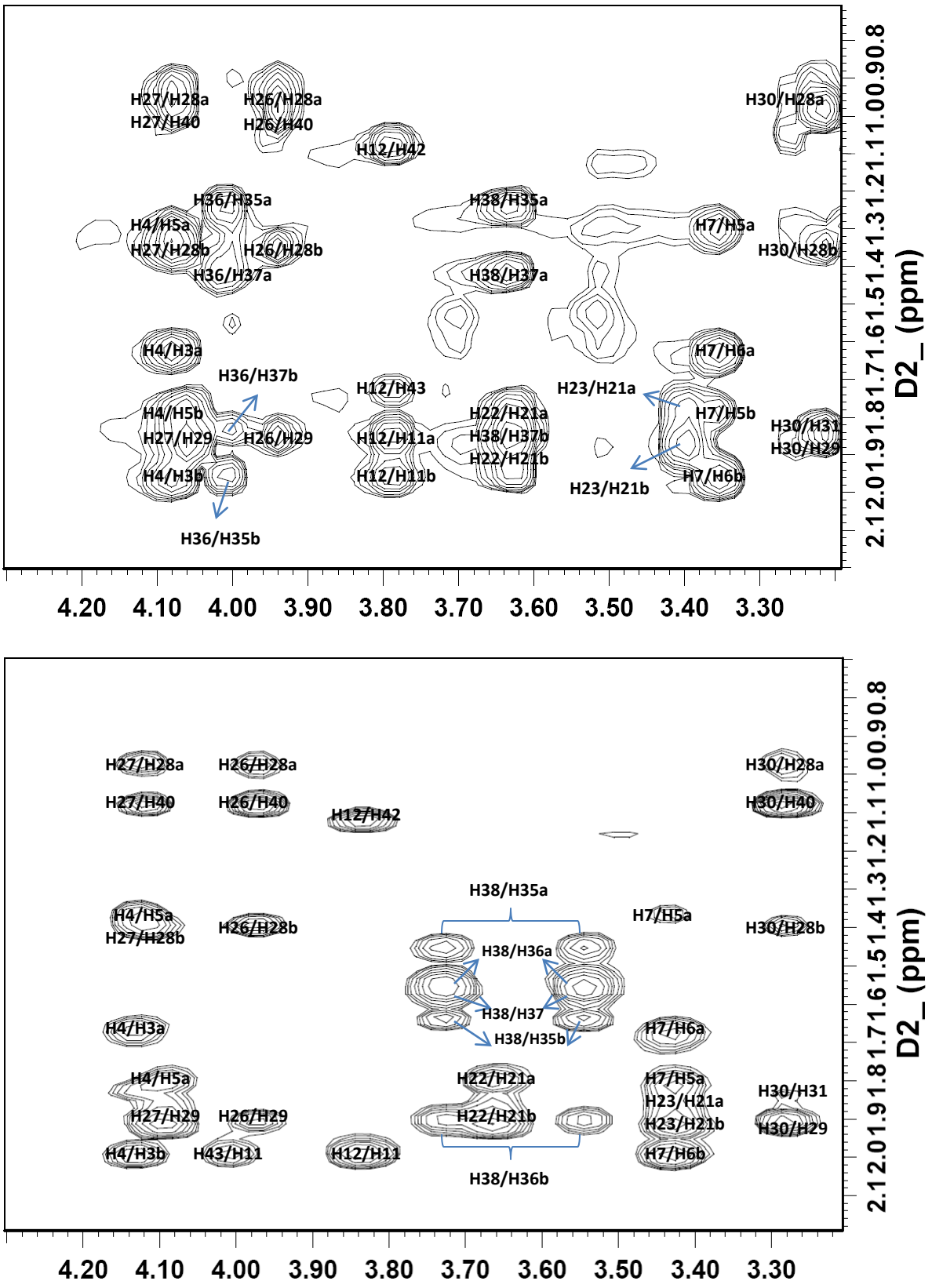
S1. ^{1}H NMR of metabolites 1 and 2.
S2. COSYs of metabolites 1 and 2 from 1.0-2.3 ppm and 3.2-4.3 ppm of ^{1}H NMR
S3. TOCSYs of metabolites 1 and 2 from 0.7-2.2 ppm and 3.2-4.3 ppm of ^{1}H NMR
S4. HSQCs of metabolites 1 and 2 from 55-85 ppm of ^{13}C NMR and 3.0-5.0 ppm of ^{1}H NMR
S5. HSQCs of metabolite 1 and 2 from 110-150 ppm of ^{13}C NMR and 3.5-5.5 ppm of ^{1}H NMR
S6. Table of ^{1}H and ^{13}C chemical shifts for metabolites 1 and 2 and COSY and TOCSY correlations for metabolite 1.
S7. HRESIMS of metabolite 1
S8. HRESIMS of metabolite 2
S9. HRESIMS of metabolite 4



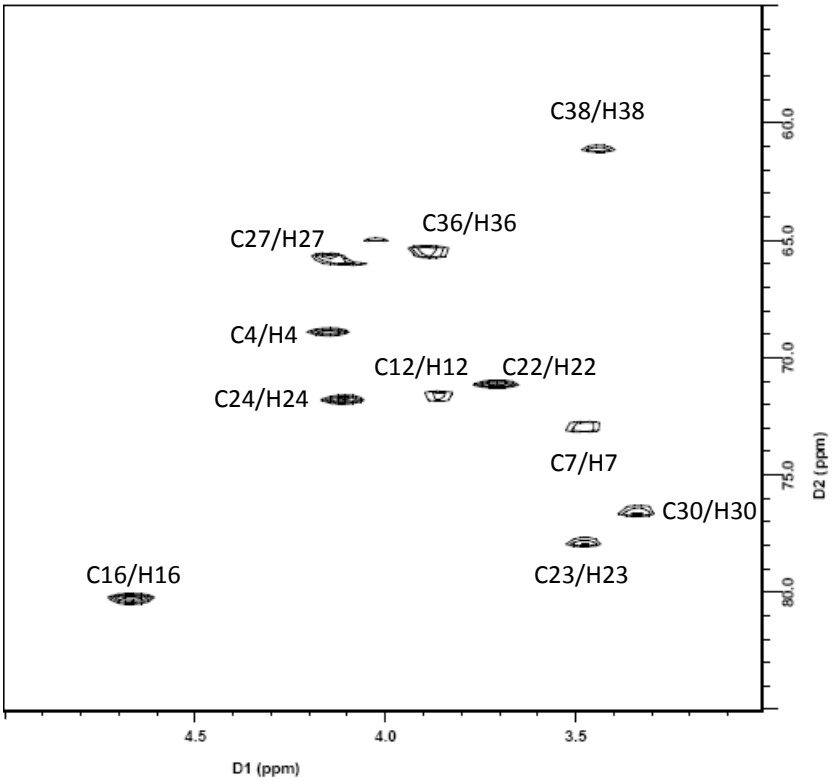
S1. ^{1}H NMR of metabolites1 (top) and 2 (bottom)

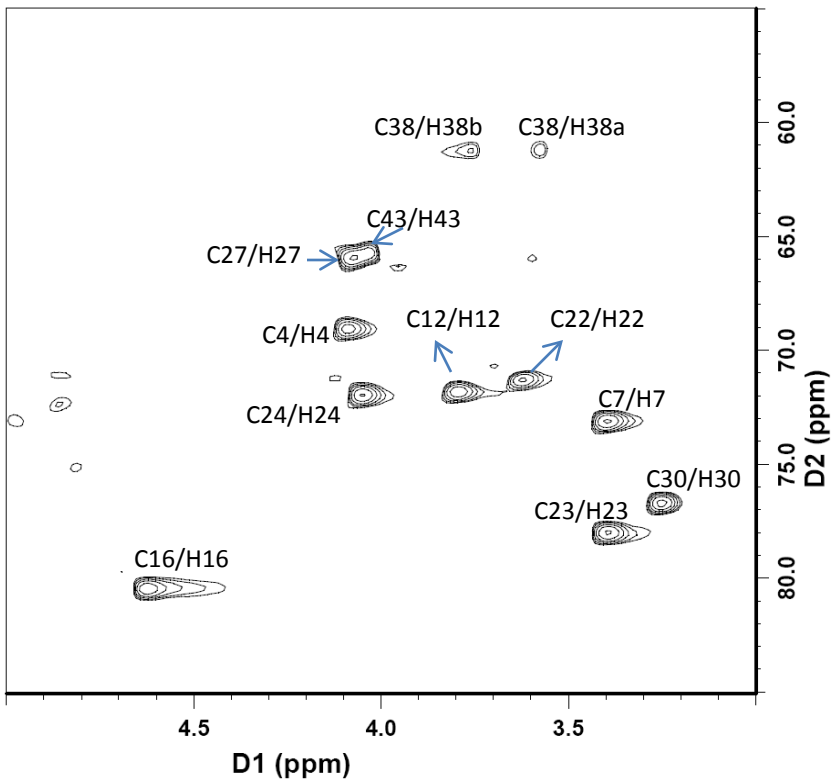


S2. COSY of metabolites1 (top) and 2 (bottom) from 1.0-2.3 ppm and 3.2-4.3 ppm of ^{1}H NMR

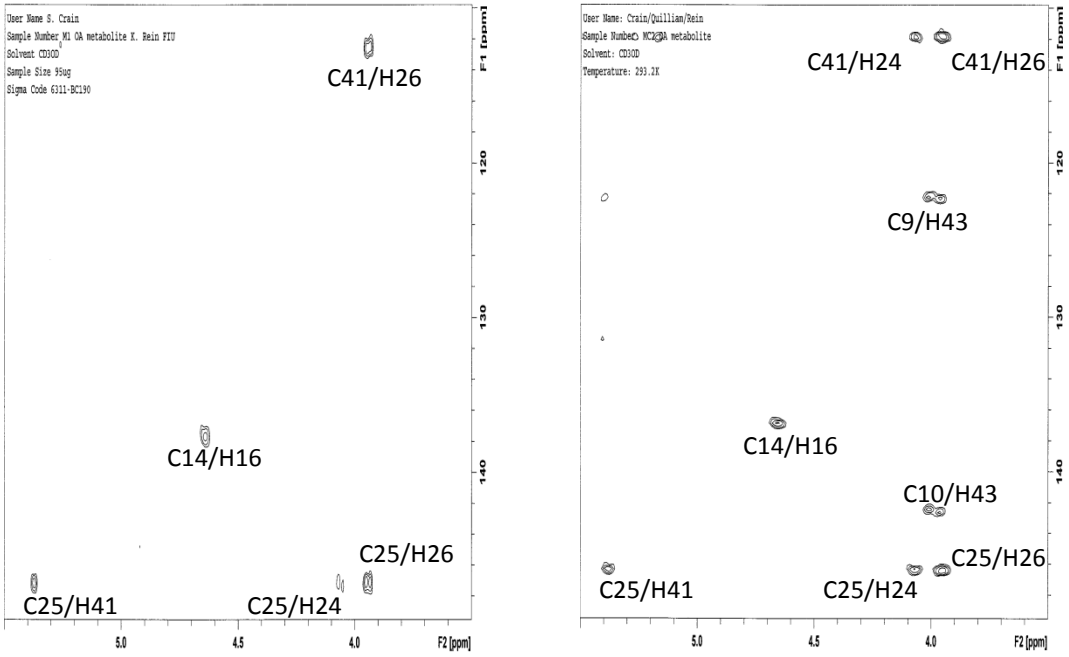


S3. TOCSY of metabolites 1 (top) and 2 (bottom) from 0.7-2.2 ppm and 3.2-4.3 ppm of ^{1}H NMR





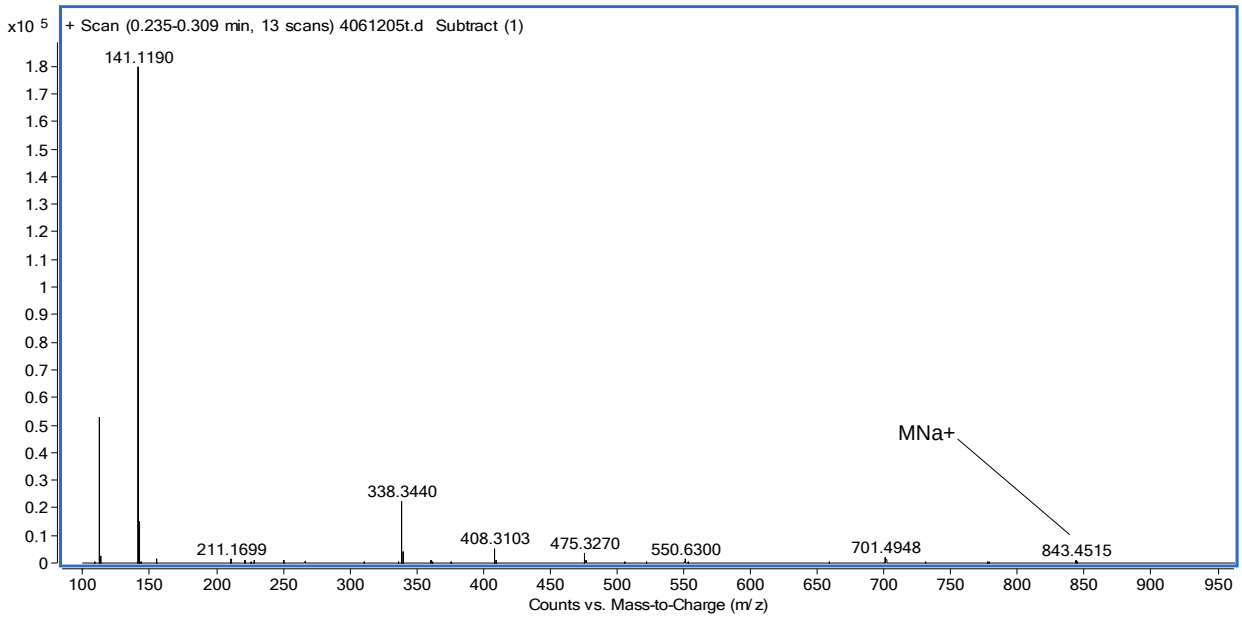
S4. HSQC of metabolite 1 (top) and 2 (bottom) from 55-85 ppm of ^{13}C NMR and 3.0-5.0 ppm of ^{1}H NMR

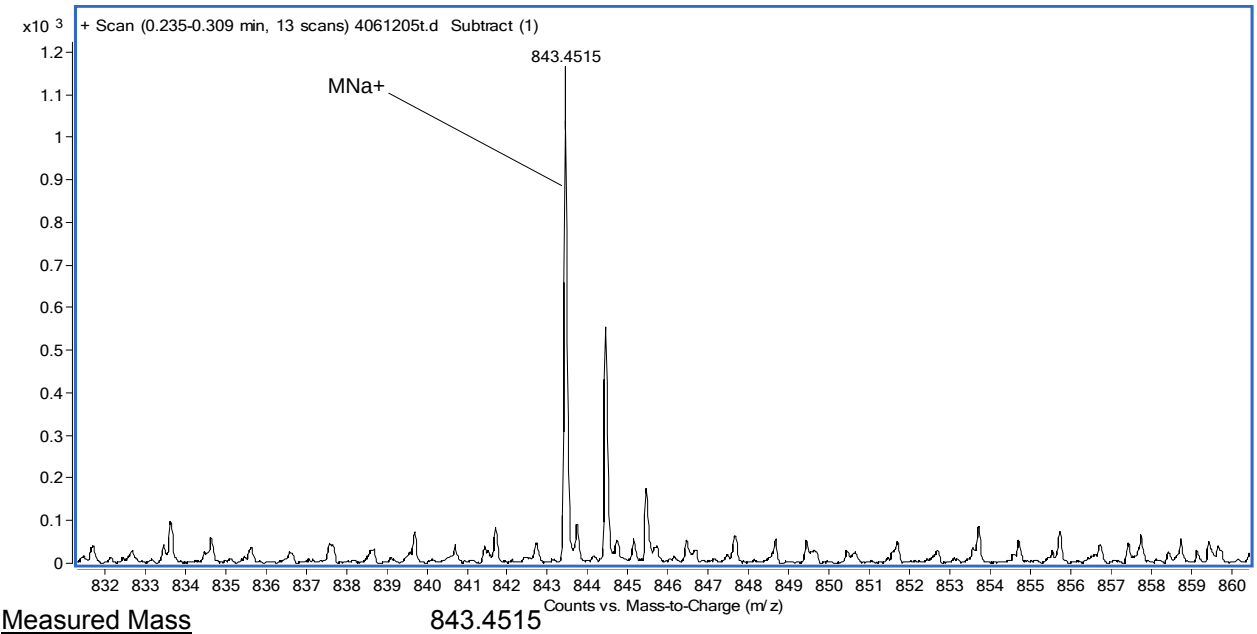


S5. HMBC of metabolite1 (left) and 2 (right) from 110-150 ppm of ^{13}C NMR and 3.5-5.5 ppm of ^{1}H NMR

Unit	*Metabolite 1*				*Metabolite 2*	
	δ_H (J in Hz)[a]	δ_C	^{1}H-^{1}H COSY	TOCSY[b]	δ_H	δ_C
1	-	181.07			-	181.88
2	-	76.04			-	76.66
3a/b	1.63/2.06	46.19	4	4, 5a/b	1.63/1.97	46.22
4	4.09	69.20	3a/b, 5b	3a/b, 5, 44	4.11	69.03
5	1.29/1.80	33.92	4, 6a/b	3a/b, 6a/b	1.32/1.80	33.15
6	1.65/1.97	27.81	7, 5a/b	5a/b, 7	1.67/1.97	27.91
7	3.37	73.23	6a/b	6	3.41	73.09
8	-	96.62			-	96.83
9	5.28	123.49	43	11a/b, 12, 43	5.52	122.90
10	-	138.81			-	137.41
11	1.85/1.97	33.98	12	9, 12, 13, 14, 15, 16,	1.97	29.41
12	3.80	71.81	11a/b, 13	9, 11a/b, 13, 14, 15, 16, 42, 43	3.81	71.79
13	2.37	43.29	12, 14, 42	11a/b, 12, 14, 15, 16, 17, 42	2.36	43.16
14	5.91	137.68	15, 13	11a/b, 12, 13, 15, 16, 18, 42	5.93	137.52
15	5.50	132.12	14, 16	11a/b, 12, 13, 14, 16, 18, 42	5.51	132.00
16	4.65	79.58	15, 17a/b	11, 12, 13, 14, 15, 18	4.66	80.46
17	1.59/2.19	31.42	16, 18a/b	13, 18	2.19/1.60	31.36
18	1.86/2.21	37.10	17a/b	14, 15, 16, 17a/b,	2.20	37.35
19	-	106.14			-	106.87
20	1.85/2.00	38.01	21a		1.85/2.01	37.98
21	1.78/1.89	27.36	20, 22		1.78/1.90	27.47
22	3.64	71.38	21a/b, 23	24, 41	3.64	71.22
23	3.41	78.11	22, 24	24, 41	3.41	77.94
24	4.07	72.01	23, 41a	22, 23, 41	4.07	71.96
25	-	146.28			-	146.87
26	3.95	85.40	27	27, 28a/b, 29, 30, 40	3.95	86.19
27	4.08	66.11	26, 28b	26, 28a/b, 29, 30, 31, 40, 41	4.10	65.99
28	0.93/1.36	36.55	27, 29	26, 27, 29, 30	0.95/1.37	36.56
29	1.86	32.16	30, 40, 28a	26, 27, 28, 30, 31, 39	1.88	32.15
30	3.23	76.86	29, 31	26, 27, 28, 29, 31, 33, 39, 40	3.26	76.65
31	1.82	28.64	39, 32a/b	27, 29, 30, 39	1.82	28.60
32	1.42/2.01	27.33	31, 33	39	1.39/1.99	27.32
33	1.39	30.95	32	30, 39	1.29	30.56
34	-	97.88			-	97.29
35a/b	1.25/1.97	46.18	36	36, 37a/b, 38	1.43/1.62	36.85
36	4.02	64.91	35a,b; 37a,b	35a/b, 37a/b, 38	1.55/1.89	19.59
37a/b	1.43/1.84	35.99	36, 38	35a/b, 36, 38	1.52	26.33
38	3.64	59.70	37a,b	35a, 36, 37a/b	3.52/3.71	61.20
39	0.94	10.98	31	29, 30, 31, 32, 33	0.93	10.89
40	0.99	16.45	29	26, 27, 30	1.06	16.47
41	5.06/5.37	112.60	24	22, 23, 24, 27, 41	5.06/5.38	112.47
42	1.08	16.80	13	12, 13, 14, 15	1.10	16.83
43	1.74	23.04	9	9, 12	3.99	65.65
44	1.32	27.94		4	1.32	27.65

S6. Table of ^{1}H and ^{13}C chemical shifts for metabolites 1 and 2 and COSY and TOCSY correlations for metabolite 1.



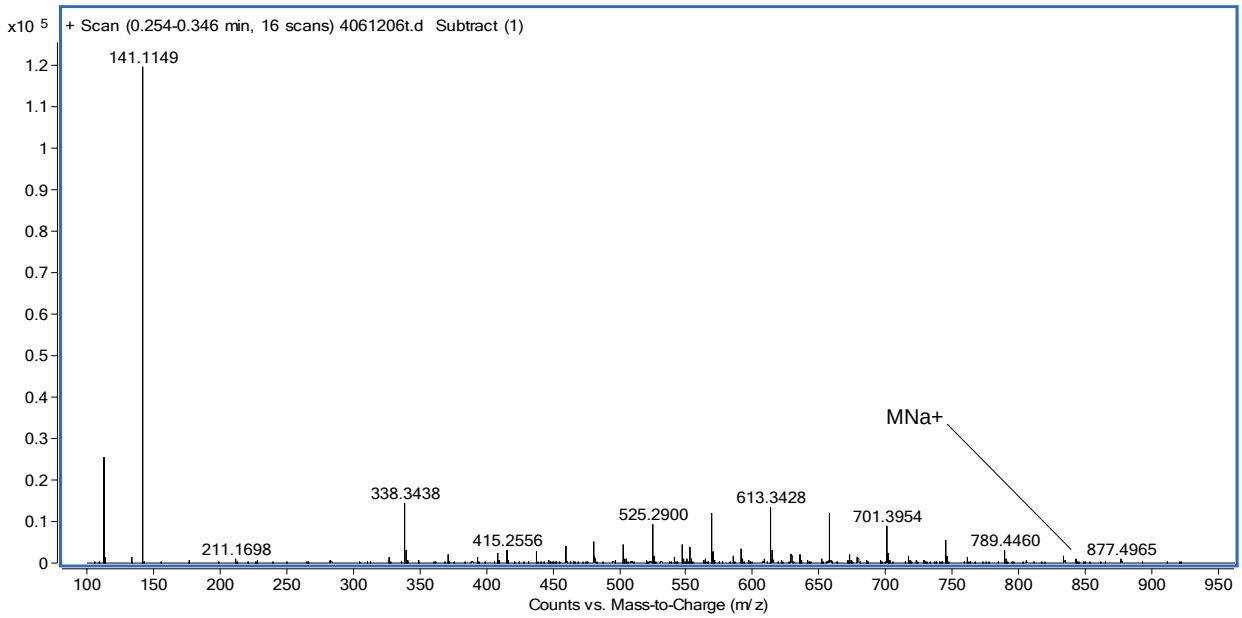


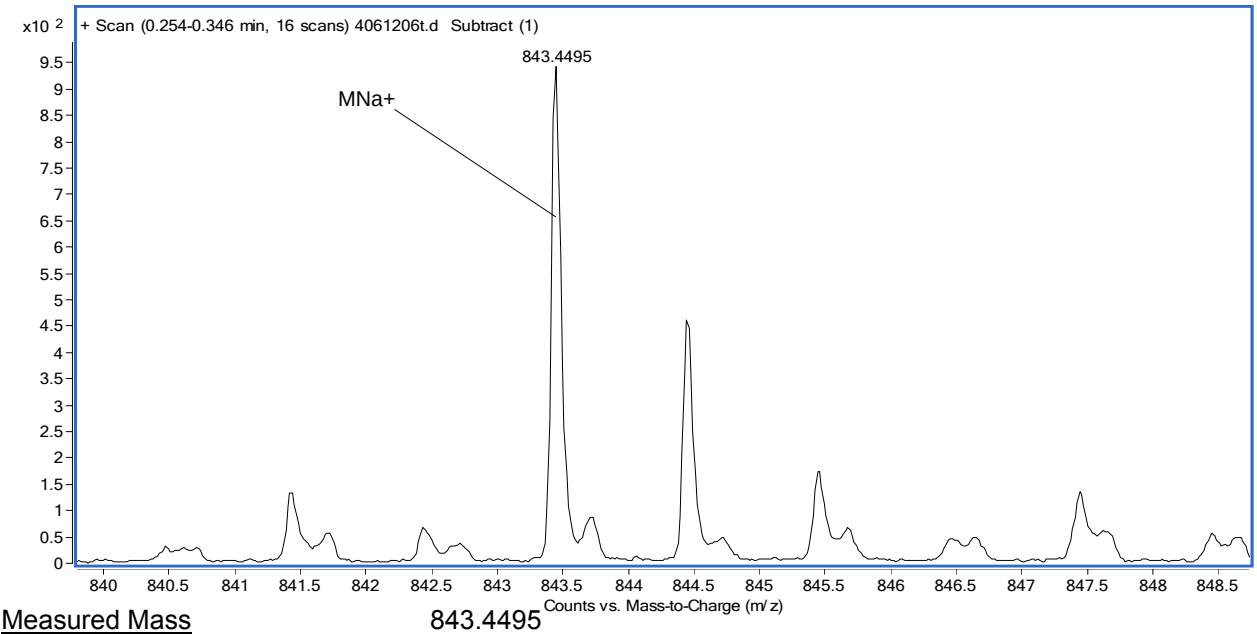
Measured Mass 843.4515

Element	Low Limit	High Limit
C	39	49
H	60	80
O	12	16
Na	0	1

Formula	Calculated Mass	mDaError	ppmError	RDB
C46 H67 O14	843.4525	-1.0	-1.2	13.5
C44 H68 O14 Na	843.4501	1.4	1.6	10.5

S7. HRESIMS of metabolite 1



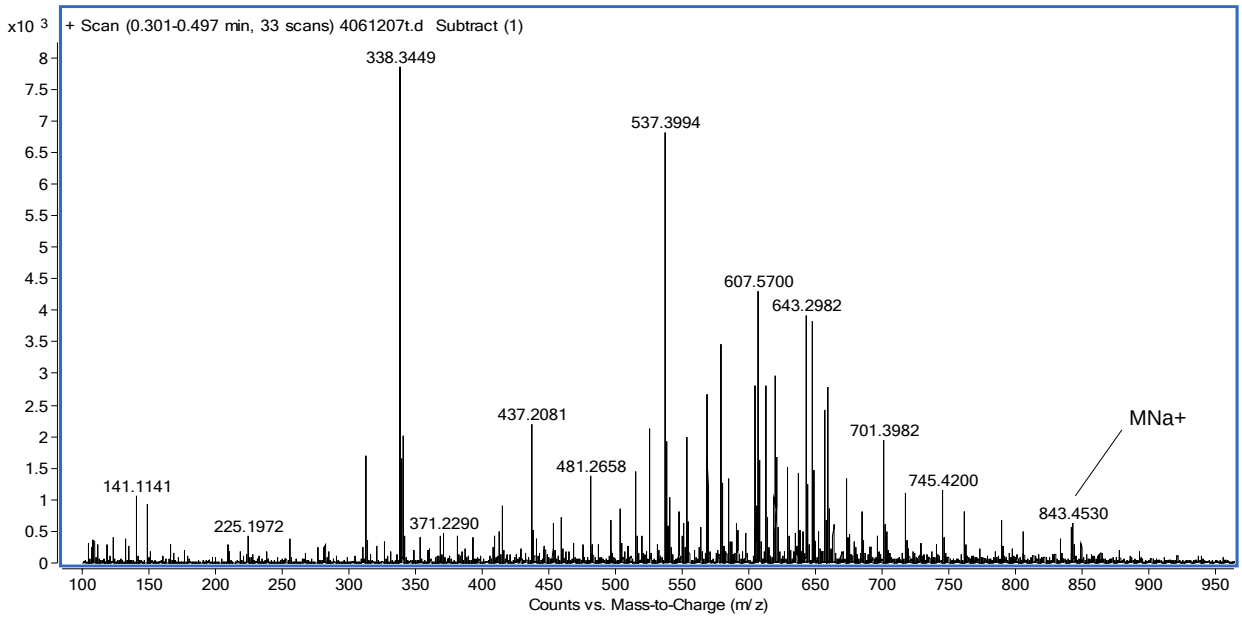


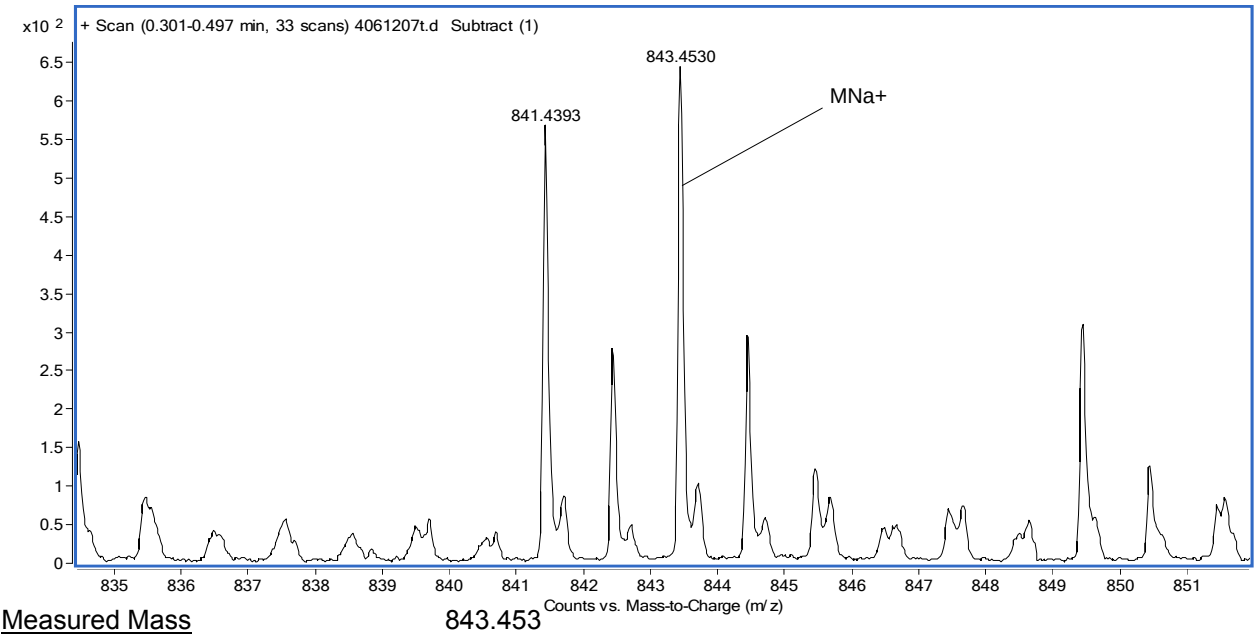
Measured Mass 843.4495

Element	Low Limit	High Limit
C	39	49
H	60	80
O	12	16
Na	0	1

Formula	Calculated Mass	mDaError	ppmError	RDB
C44 H68 O14 Na	843.4501	-0.6	-0.7	10.5
C46 H67 O14	843.4525	-3.0	-3.6	13.5

S8. HRESIMS of metabolite 2





Measured Mass 843.453

Element	Low Limit	High Limit
C	39	49
H	60	80
O	12	16
Na	0	1

Formula	Calculated Mass	mDaError	ppmError	RDB
C46 H67 O14	843.4525	0.5	0.6	13.5
C44 H68 O14 Na	843.4501	2.9	3.4	10.5

S9. HRESIMS of metabolite 4