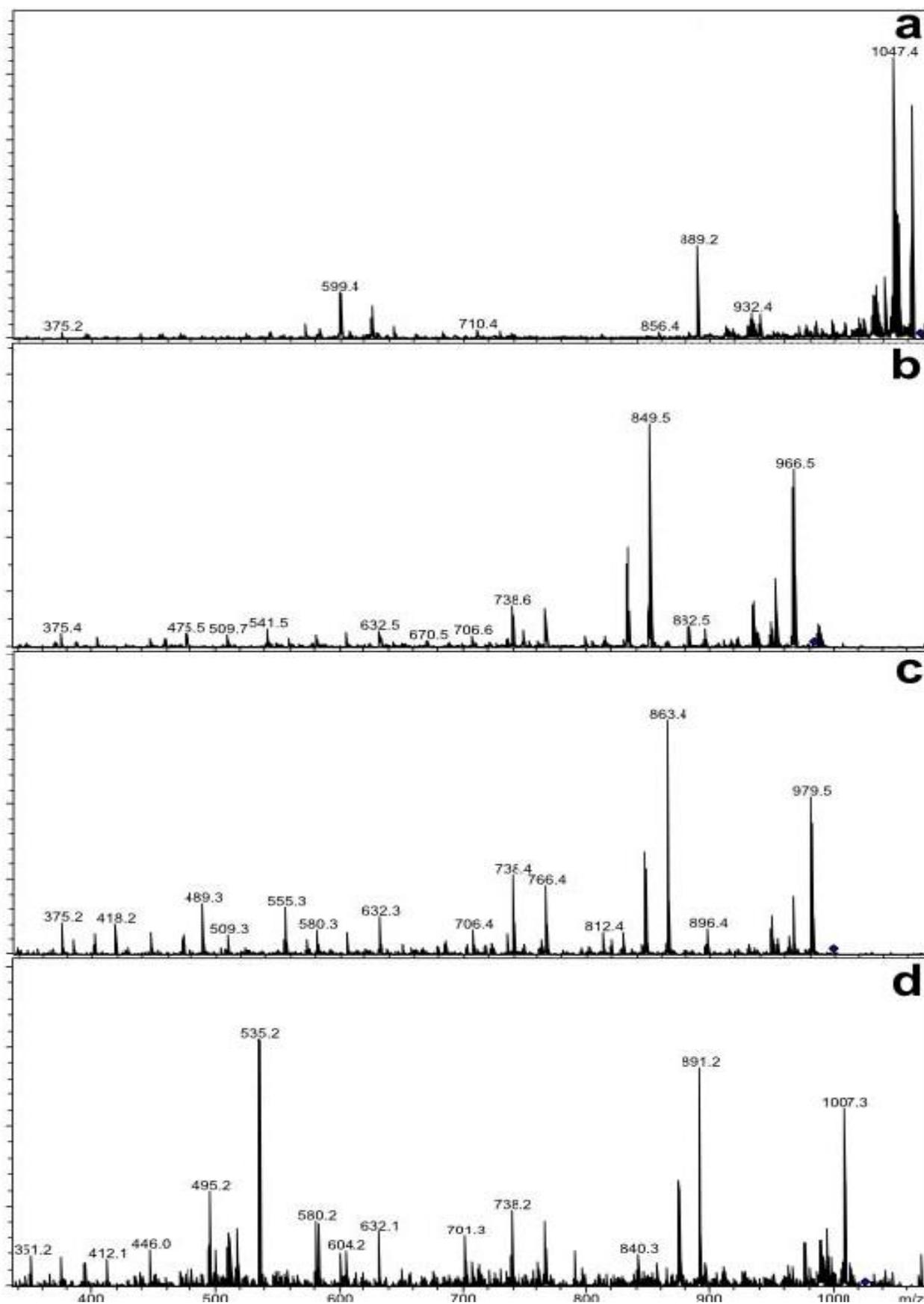
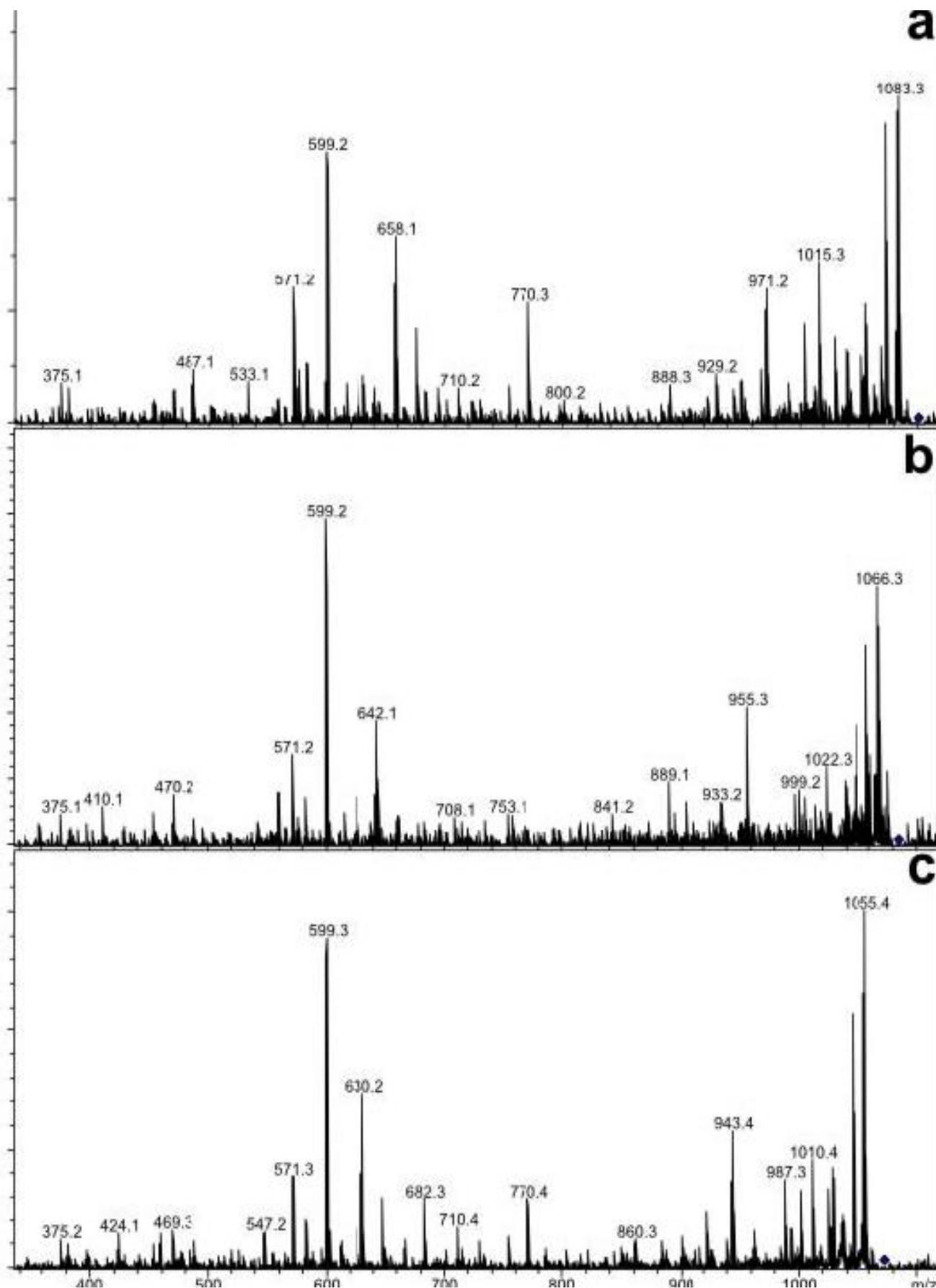


## Supplementary Materials

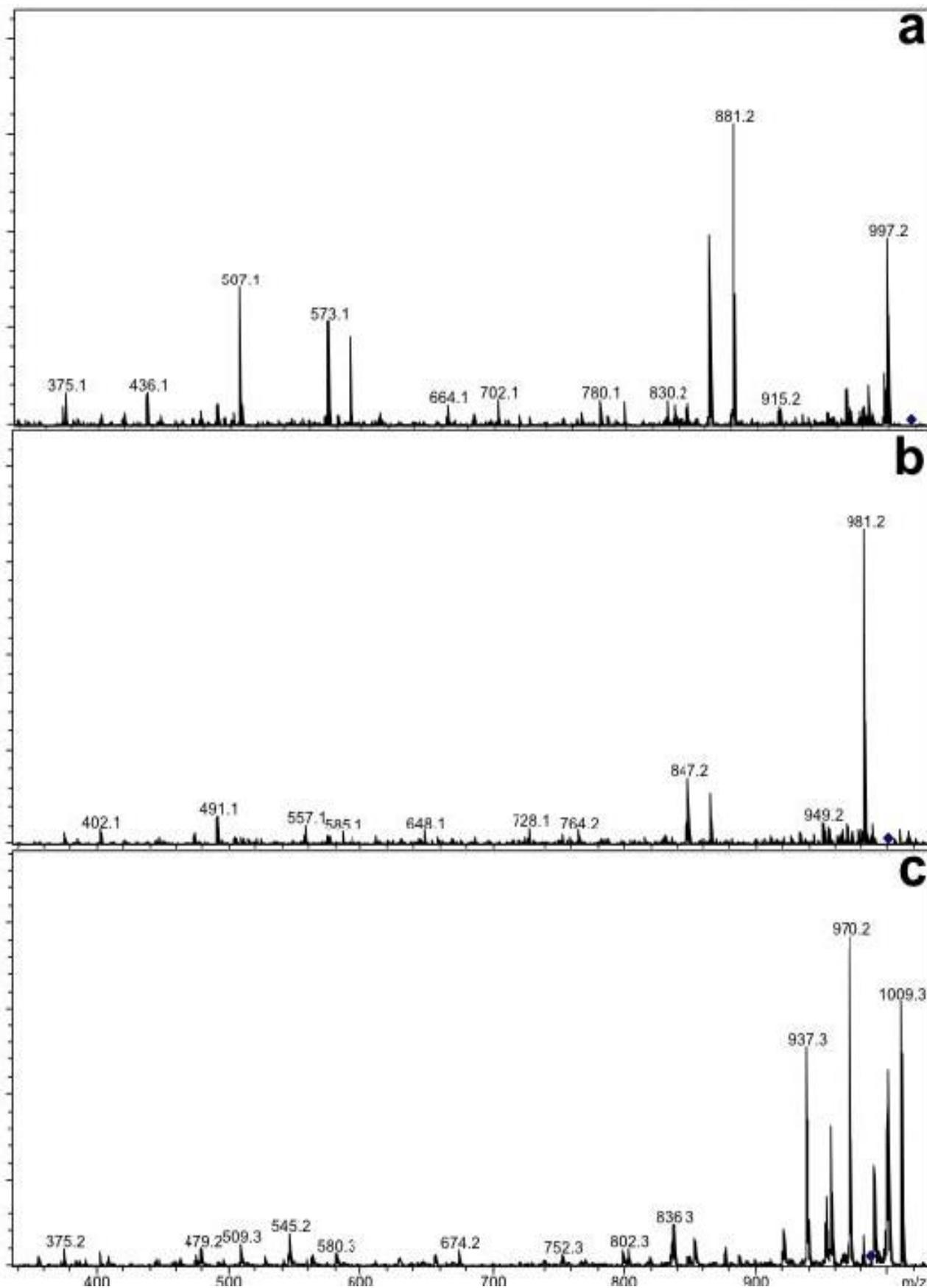
**Figure S1.** Electrospray ionization collision-induced dissociation MS/MS spectra for (a) MC-WR (1), (b) MC-WA (2), (c) MC-Waba (3) and (d) MC-WL (4).



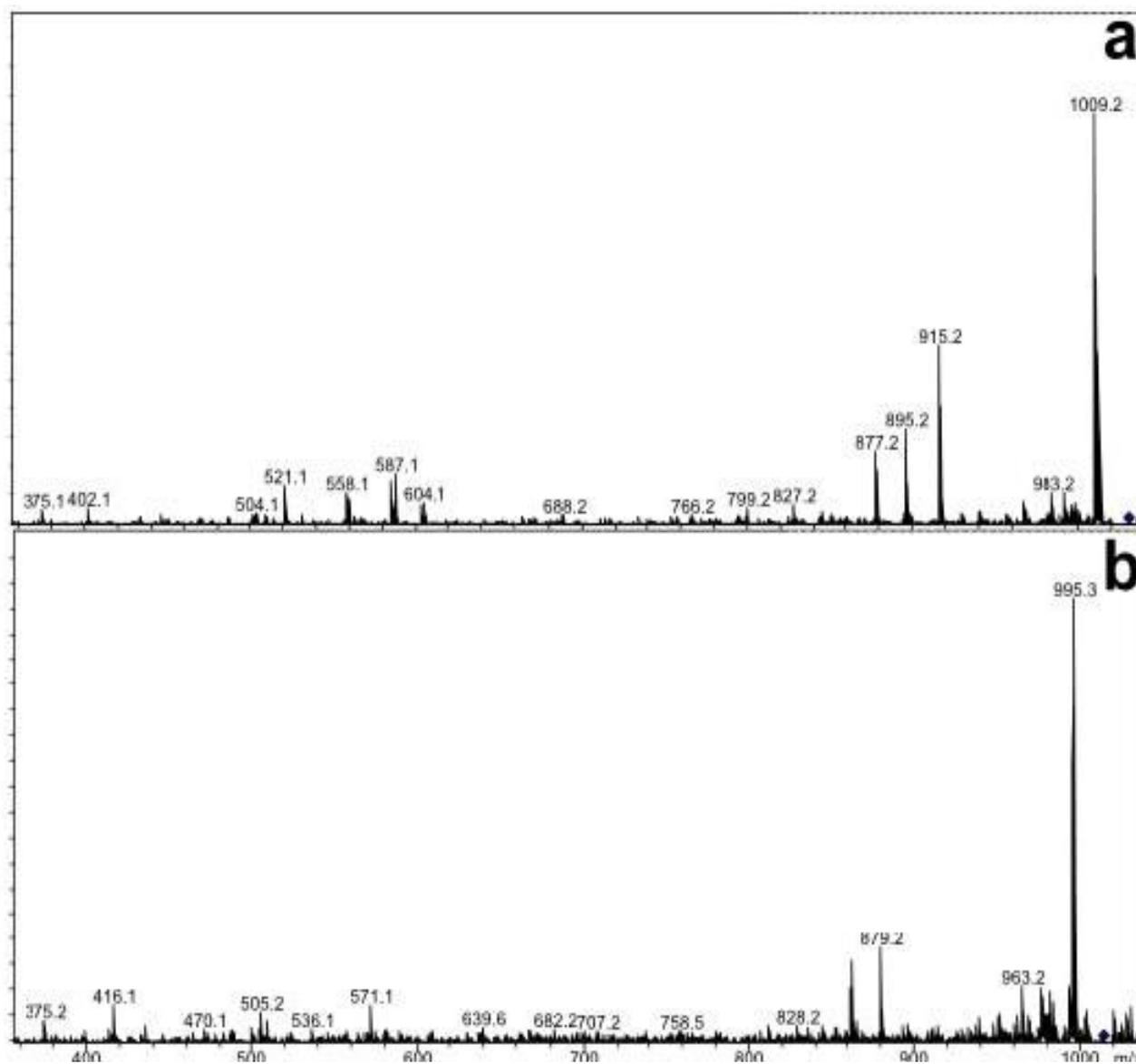
**Figure S2.** Electrospray ionization collision-induced dissociation MS/MS spectra for (a) MC-KynR (5), (b) MC-OiaR (6) and (c) MC-NfkR (7).



**Figure S3.** Electrospray ionization collision-induced dissociation MS/MS spectra for (a) MC-KynA (**8**), (b) MC-OiaA (**9**) and (c) MC-NfkA (**10**).

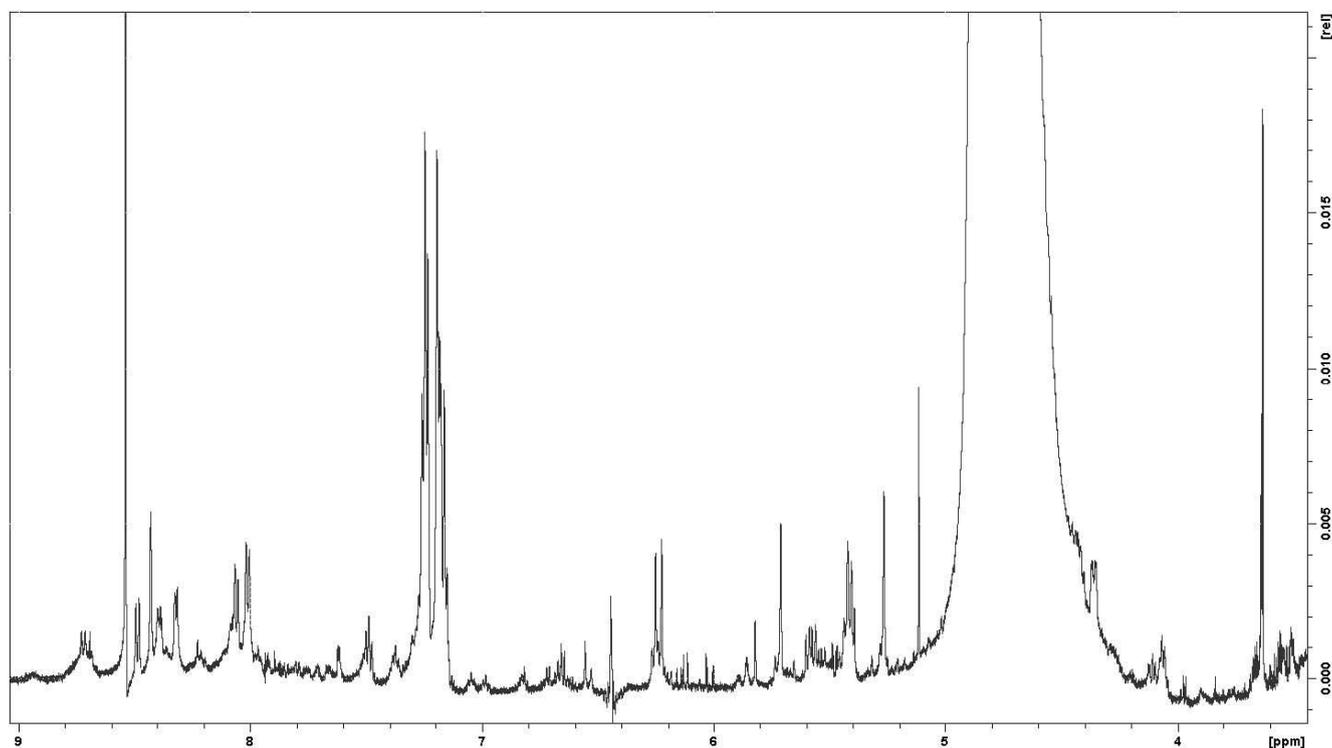


**Figure S4.** Electrospray ionization collision-induced dissociation MS/MS spectra for (a) MC-OiaAba (**12**) and (b) MC-NfkAba (**13**).

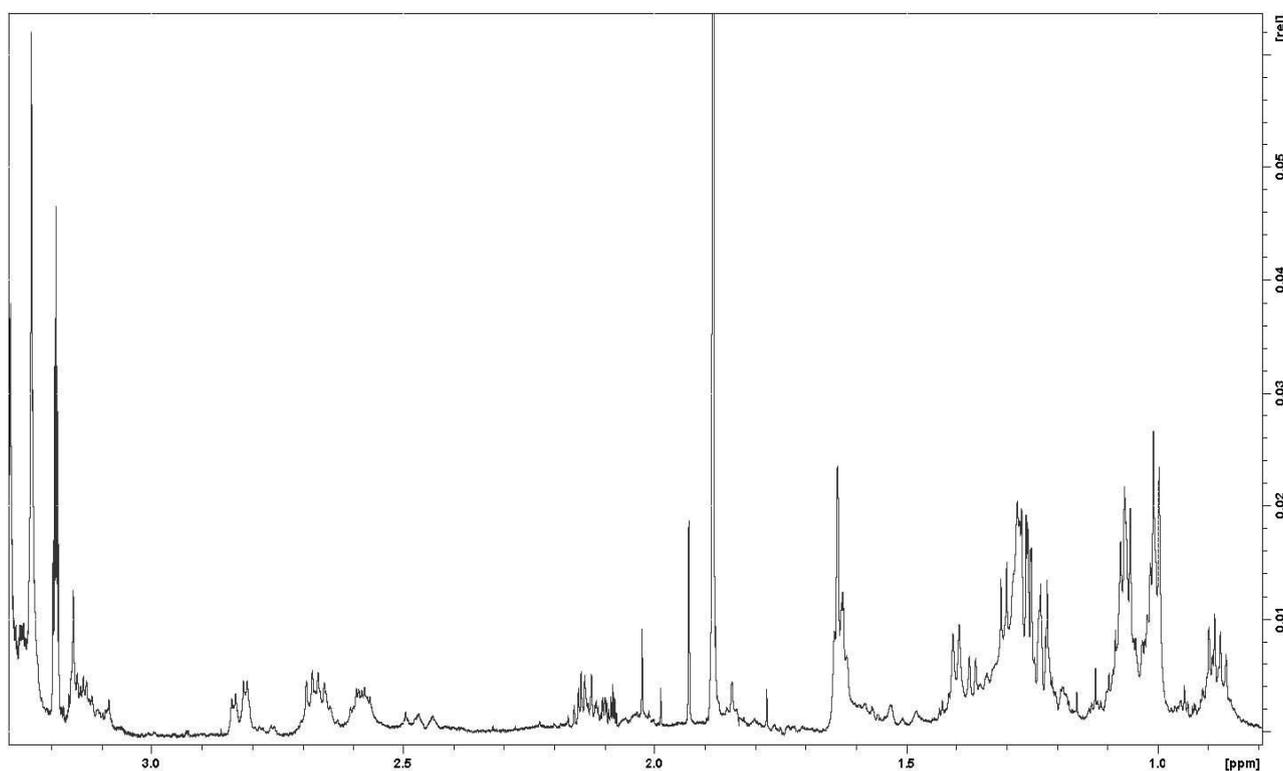


**Table S1.** High-resolution electrospray ionization mass spectrometry analysis of semi-pure mixtures of 1–3 and 5–10.

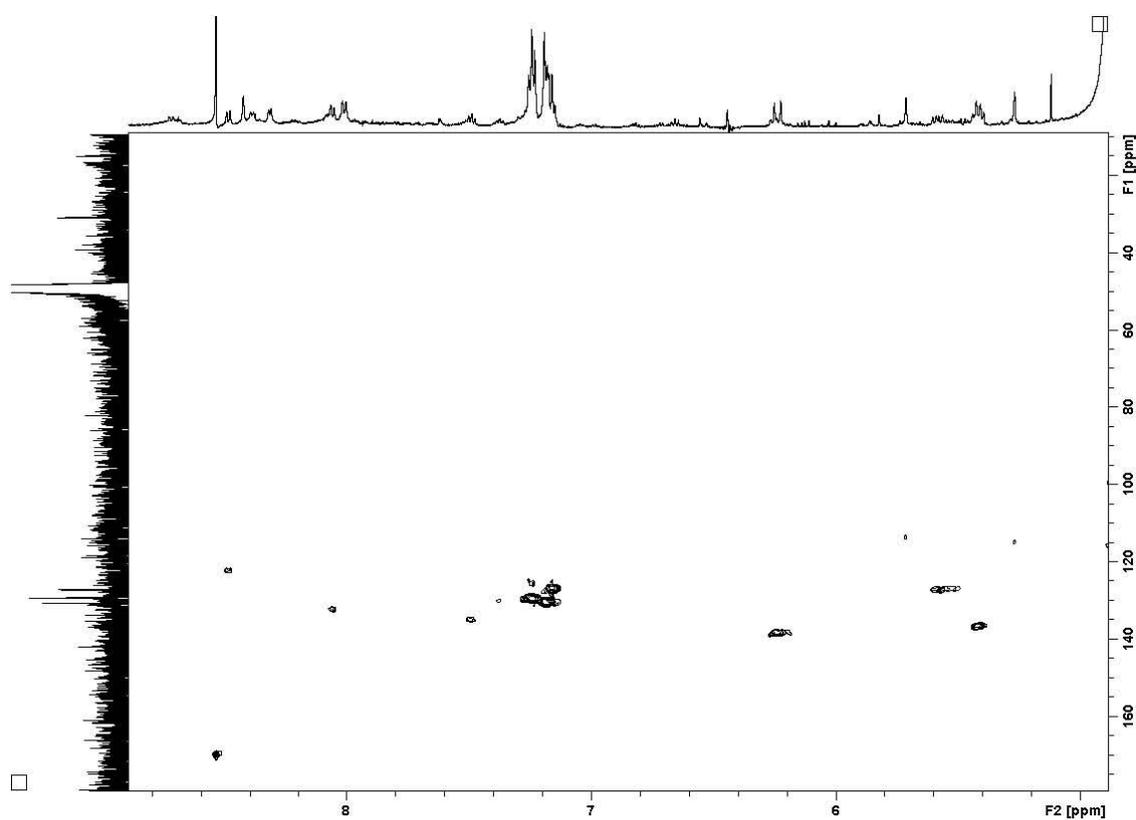
Microcystin	Measured <i>m/z</i>	Molecular Formula	Calculated <i>m/z</i>	Deviation (ppm)
MC-WR (1)	1068.5465	C54H74N11O12	1068.5513	−4.5
MC-WA (2)	1005.4650	C51H66N8O12Na	1005.4692	−4.3
MC-WAbA (3)	1019.4836	C52H68N8O12Na	1019.4849	−1.3
MC-KynR (5)	1072.5431	C53H74N11O13	1072.5462	−2.9
MC-OiaR (6)	1084.5449	C54H74N11O13	1084.5462	−1.2
MC-NfkR (7)	1100.5449	C54H74N11O14	1100.5411	+3.4
MC-KynA (8)	1009.4670	C50H66N8O13Na	1009.4642	+2.8
MC-OiaA (9)	1021.4634	C51H66N8O13Na	1021.4642	−0.8
MC-NfkA (10)	1037.4598	C51H66N8O14Na	1037.4591	+0.8

**Figure S5.** Downfield region of the <sup>1</sup>H NMR spectrum of MC-NfkA (10; 600 MHz; CD<sub>3</sub>OH; electronic sculpturing suppression of the OH/H<sub>2</sub>O solvent peak and continuous wave suppression of the CHD<sub>2</sub>OH solvent peak).

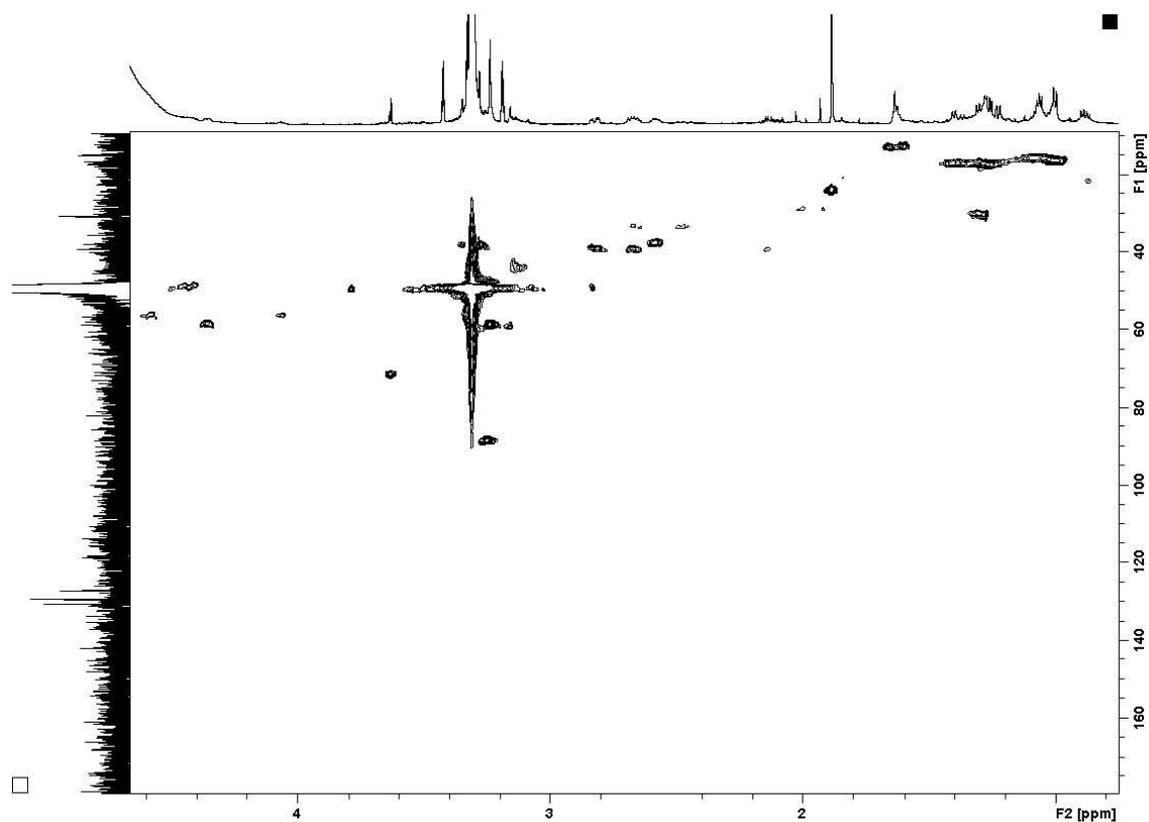
**Figure S6.** Upfield region of the  $^1\text{H}$  NMR spectrum of MC-NfkA (**10**; 600 MHz;  $\text{CD}_3\text{OH}$ ; electronic sculpturing suppression of the  $\text{OH}/\text{H}_2\text{O}$  solvent peak and continuous wave suppression of the  $\text{CHD}_2\text{OH}$  solvent peak).



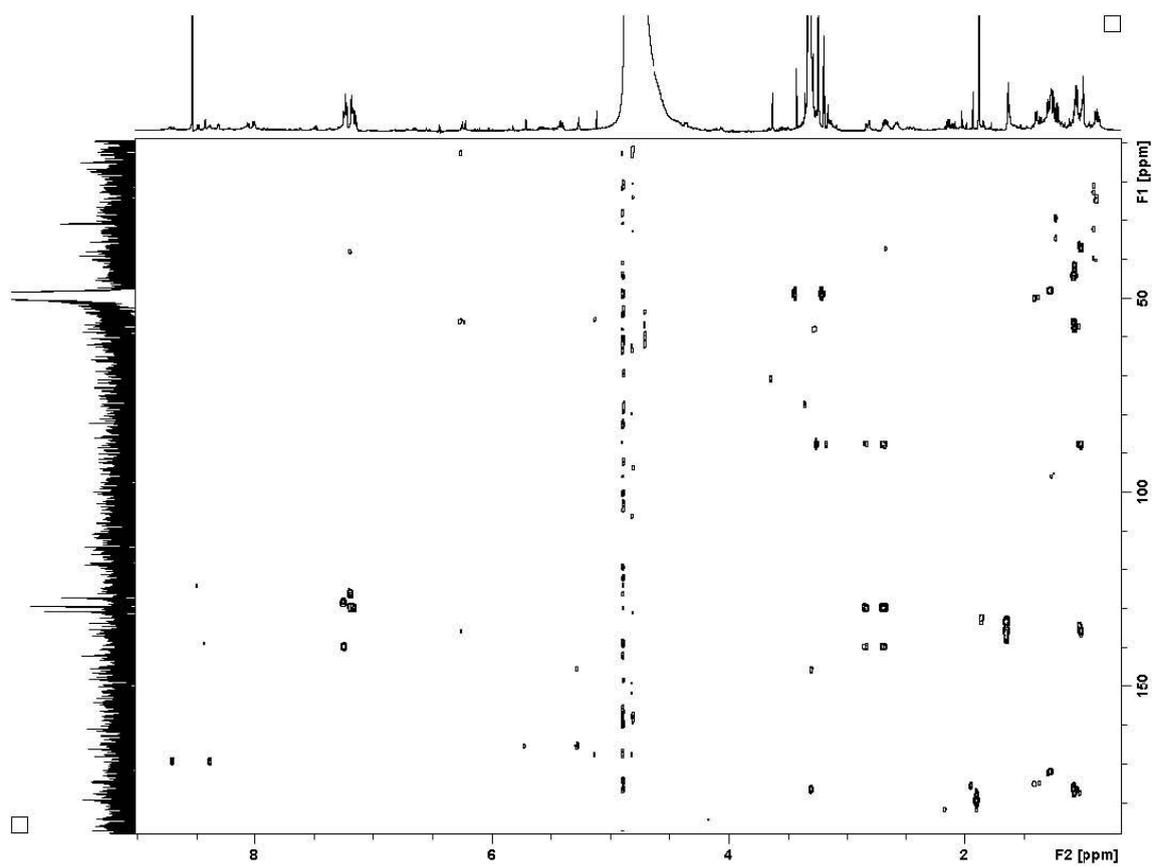
**Figure S7.** Downfield region of the  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of MC-NfkA (**10**;  $\text{CD}_3\text{OH}$ ; continuous wave suppression of the  $\text{OH}/\text{H}_2\text{O}$  solvent peak).



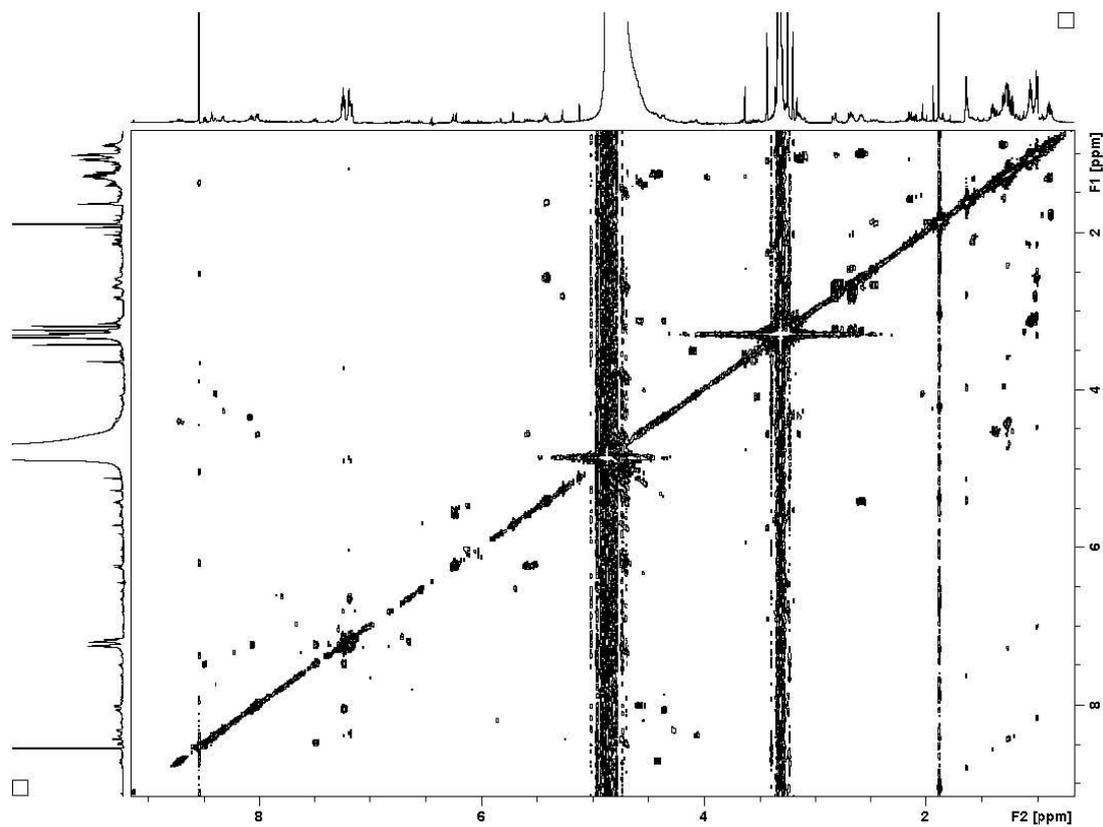
**Figure S8.** Upfield region of the  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of MC-NfkA (**10**;  $\text{CD}_3\text{OH}$ ; continuous wave suppression of the  $\text{OH}/\text{H}_2\text{O}$  solvent peak).



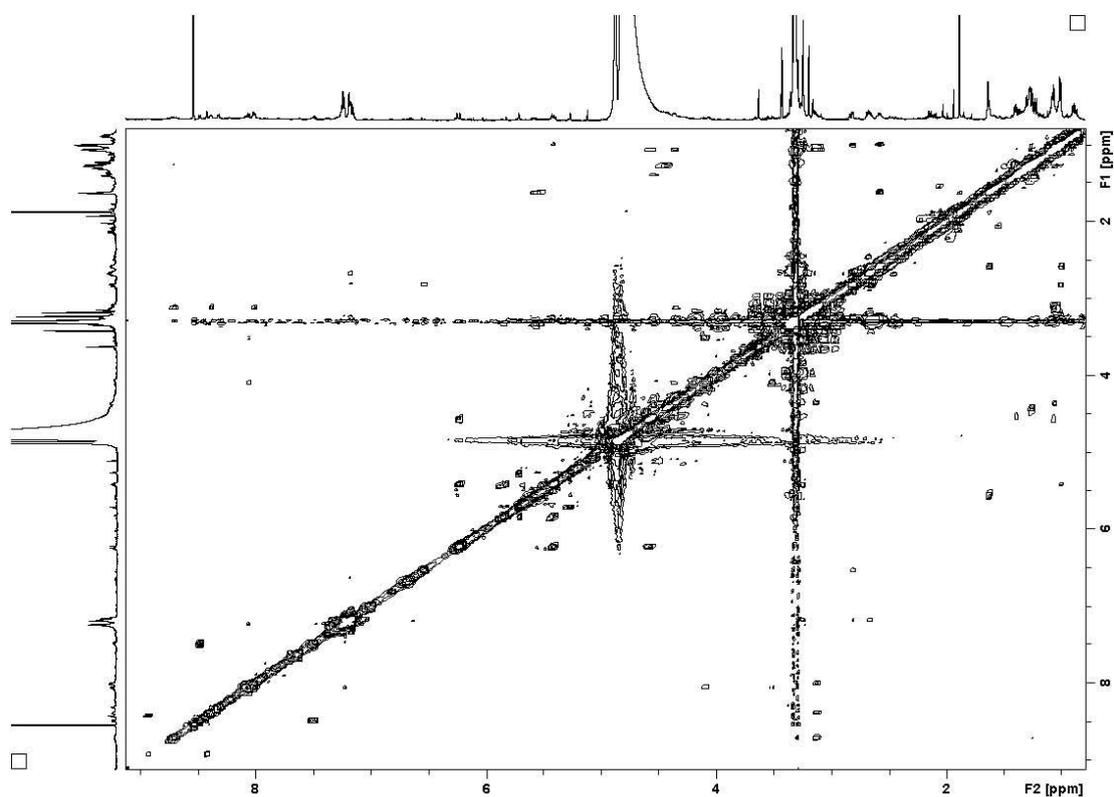
**Figure S9.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of MC-NfkA (**10**;  $\text{CD}_3\text{OH}$ ).



**Figure S10.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of MC-NfkA (**10**; CD3OH; continuous wave suppression of the OH/H<sub>2</sub>O solvent peak).



**Figure S11.**  $^1\text{H}$ - $^1\text{H}$  ROESY NMR spectrum of MC-NfkA (**10**; CD3OH; continuous wave suppression of the OH/H<sub>2</sub>O solvent peak).



**Figure S12.** Graphs depicting the oxidation of MC-WA into MC-KynA, MC-OiaA and MC-NfkA through (a) diffusion with atmospheric oxygen, (b) the application of stirring and (c) the application of hydrogen peroxide.

