

## Supporting Materials

Curvulin and Phaeosphaeride A from *Paraphoma* sp. VIZR 1.46 Isolated from *Cirsium arvense* as Potential Herbicides

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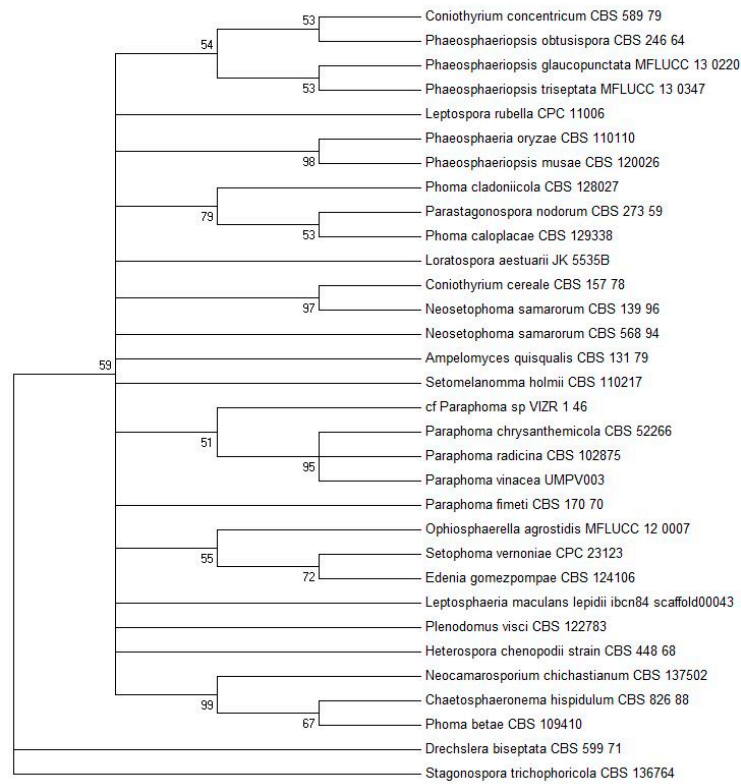
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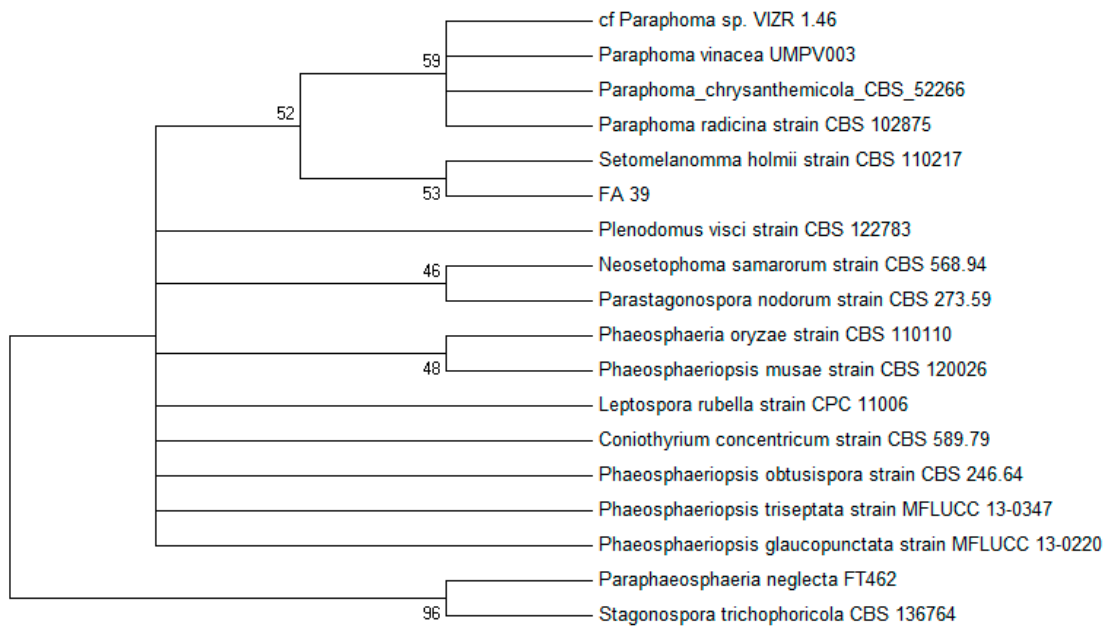
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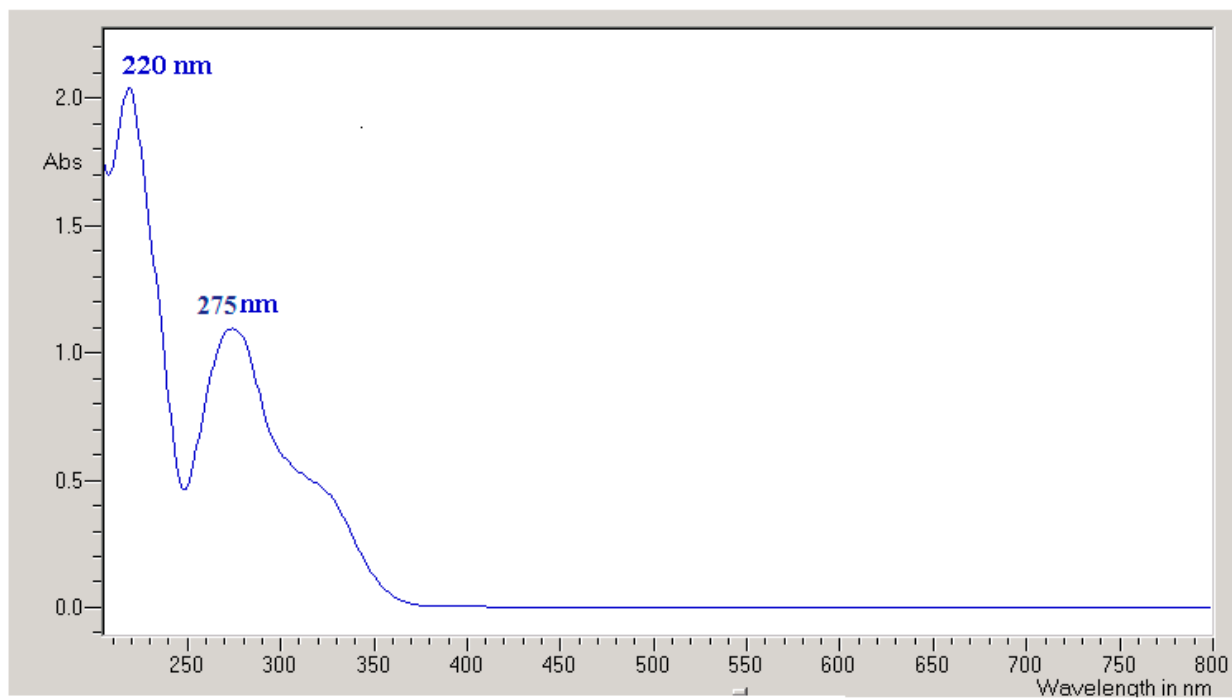
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**Figure S2** - A Bayesian 50 % majority rule consensus tree based on dataset of LSU alignment of cf *Paraphoma* sp. VIZR 1.46 and related species. Bootstrap support values for maximum likelihood equal to or greater than 40 % are given above the nodes. The tree is rooted to *Stagonospora trichophoricola*

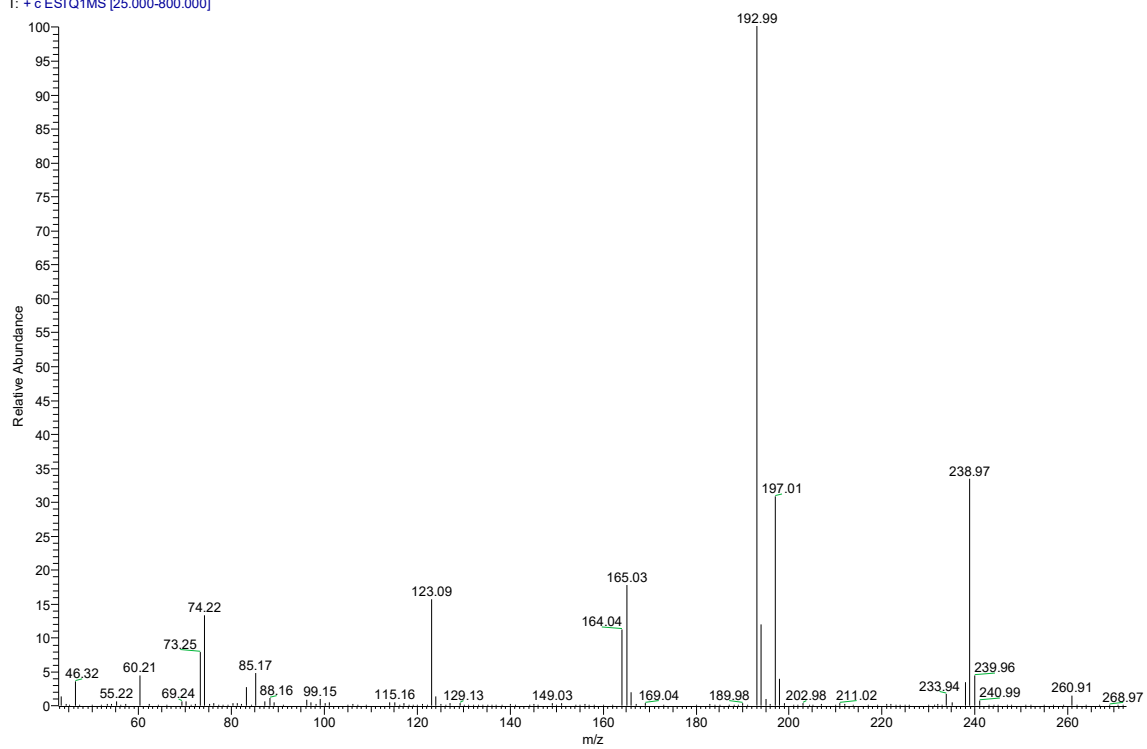
|   |                              |
|---|------------------------------|
| cf <i>Paraphoma</i> sp. VIZR 1.46           | GTTGCTTATCTAGACTTTTGTCTAGTGC |
| <i>Paraphoma chrysanthemicola</i> CBS 52266 | .....CG.....CG.....          |
| <i>Paraphoma radicina</i> CBS 102875        | .....CG.....CG.....          |
| <i>Paraphoma vinacea</i> UMPV003            | .....CG.....CG.....          |

**Figure S3** - Point differences in nucleotide sequences of LSU for strains *Paraphoma* sp. 1.46, *P. chrysanthemicola* CBS 522.66, *P. radicina* CBS 102875 and *P. vinacea* UMPV 003

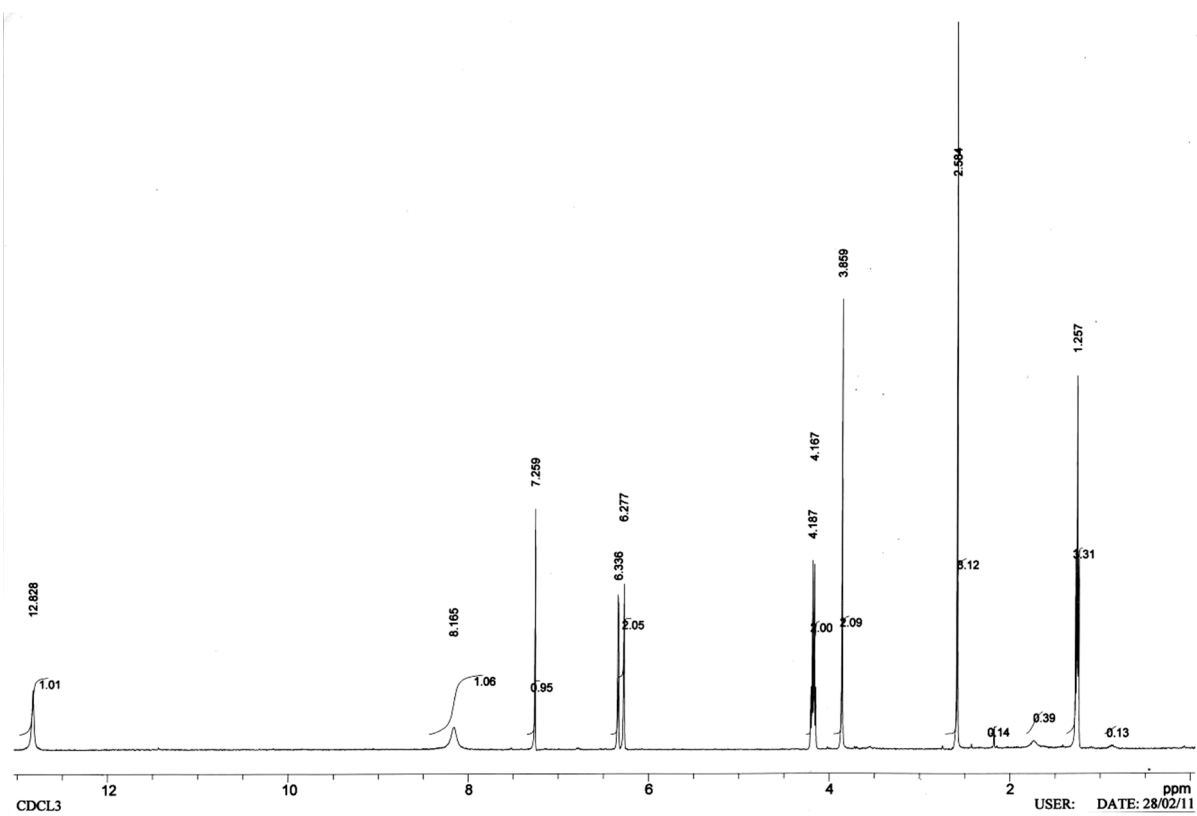


**Figure S4** – UV spectrum of curvulin, recorded in MeCN

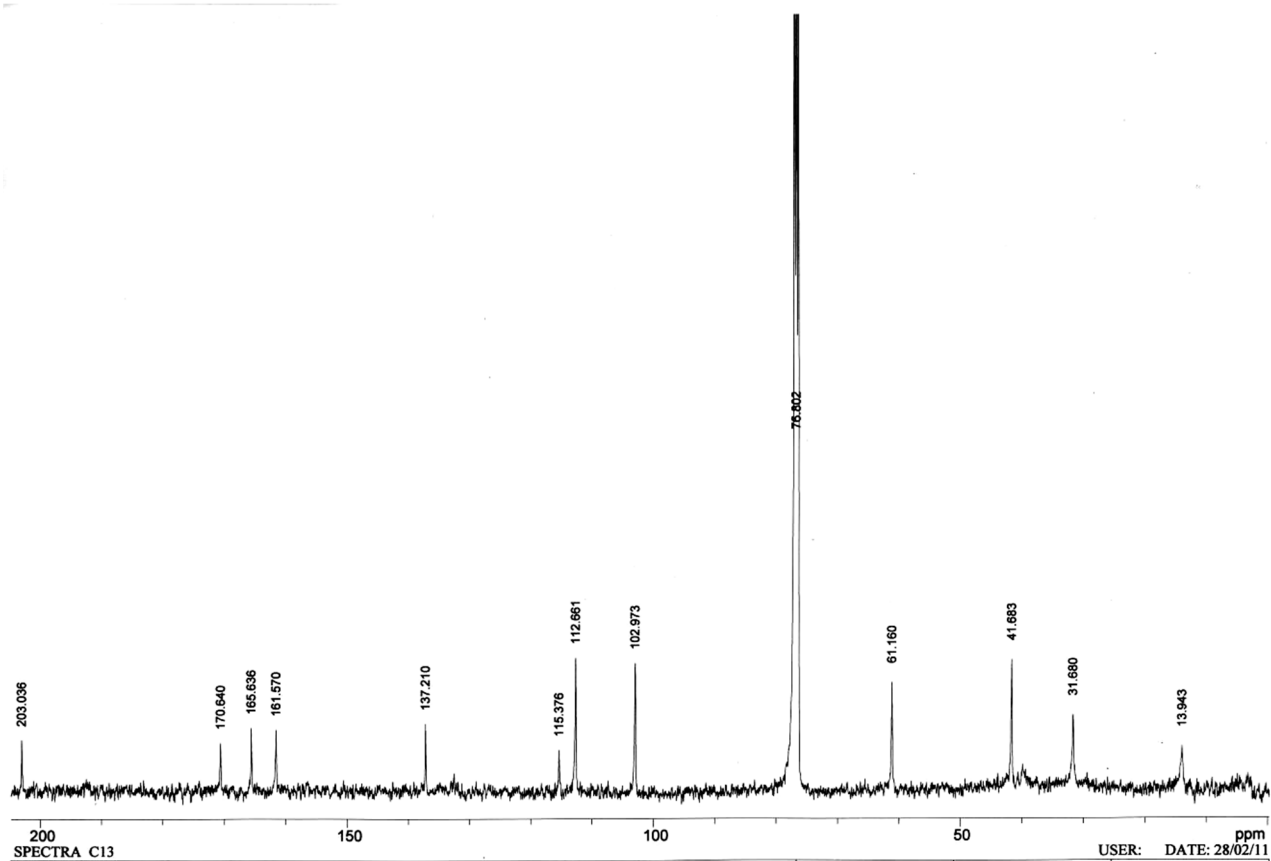
L#0141\_141209112637 #1189-1211 RT: 10.54-10.74 AV: 23 SB: 39 10.36-10.55, 10.73-10.87 NL: 1.04E6  
T: + c ESI Q1MS [25.000-800.000]



**Figure S5** – ESI Mass spectrum of curvulin, recorded in positive mode

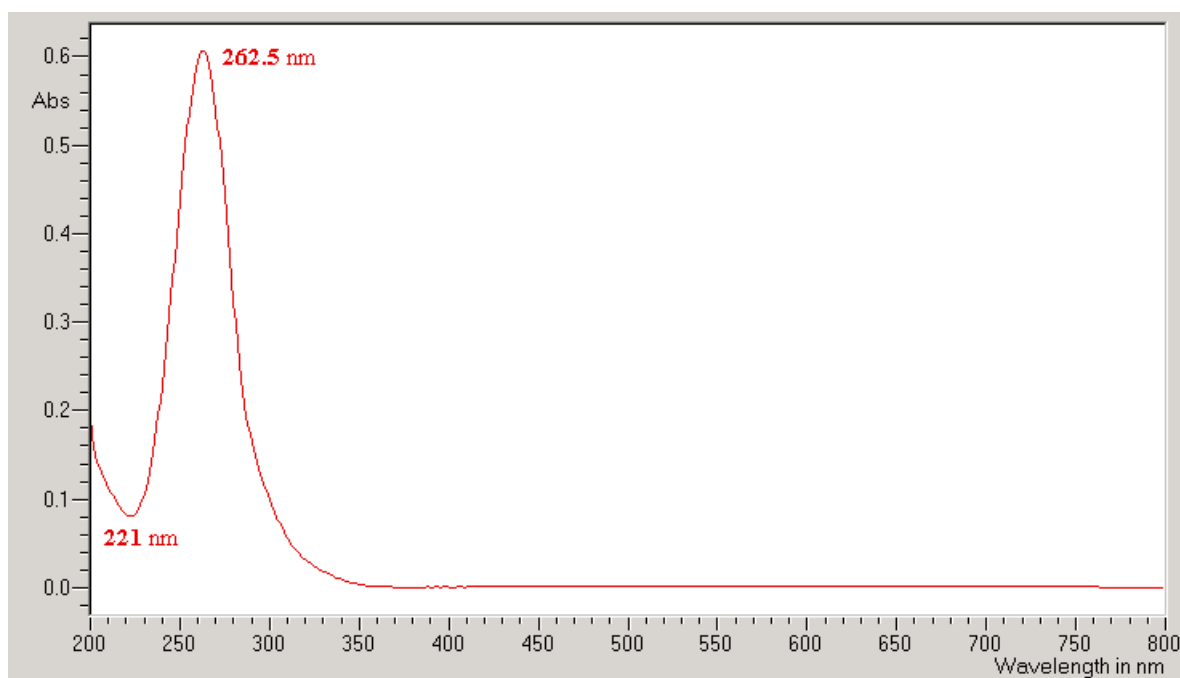


**Figure S6** - <sup>1</sup>H-NMR spectrum of curvulin (CDCl<sub>3</sub>, 400 MHz)



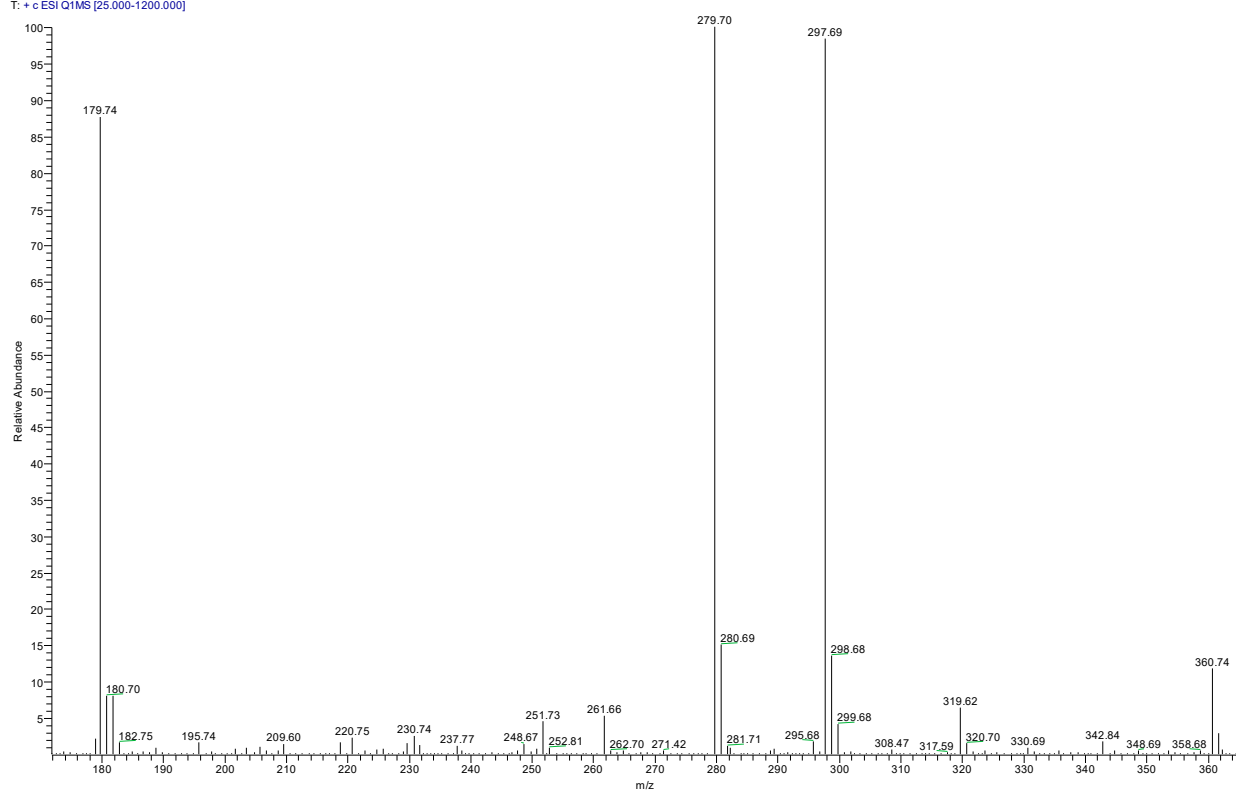
**Figure S7** –  $^{13}\text{C}$ -NMR spectrum of curvulin ( $\text{CDCl}_3$ , 100 MHz)



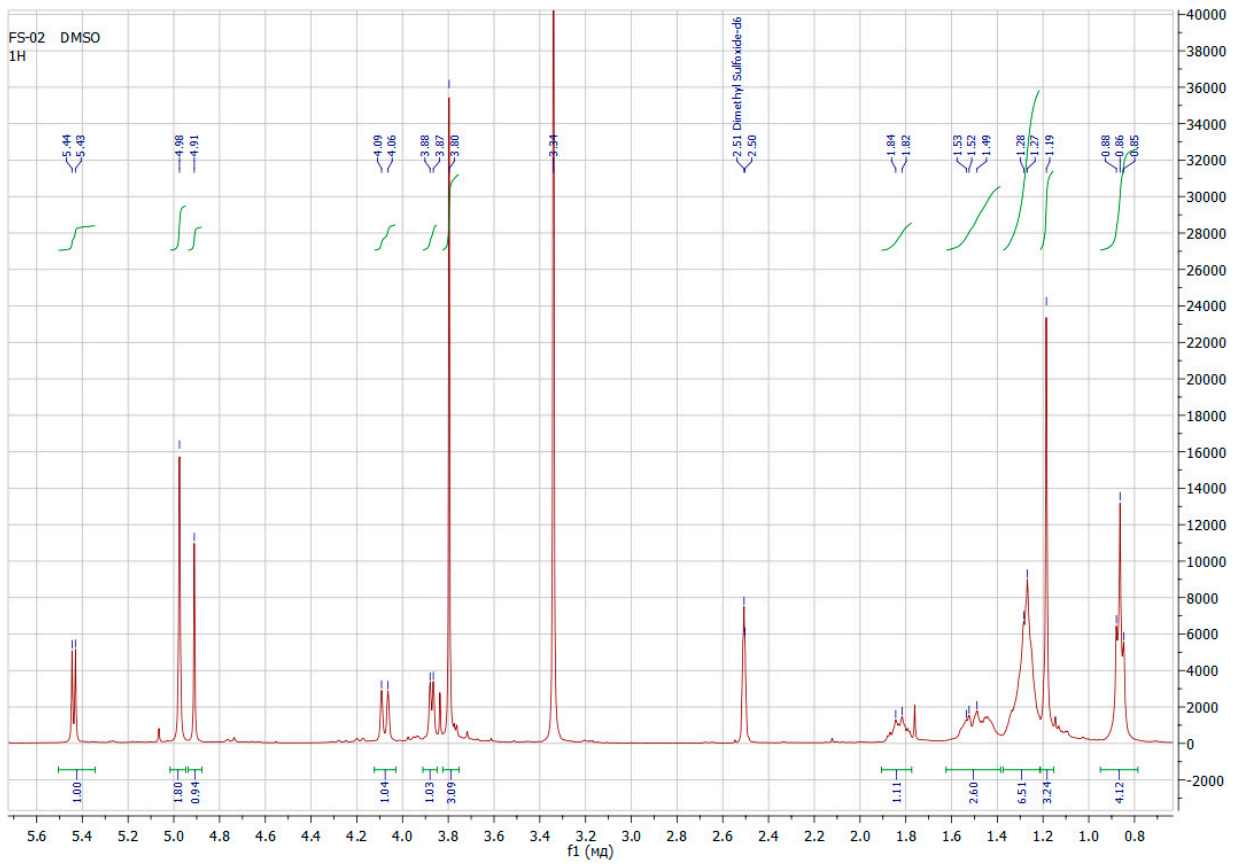


**Figure S8** – UV spectrum of phaeosphaeride A, dissolved in MeCN

L#0082 #3234-3310 RT: 20.44-20.92 AV: 77 NL: 1.11E5  
T: + c ESI Q1MS [25.000-1200.000]



**Figure S9** – ESI Mass spectrum of phaeosphaeride A, recorded in positive mode



**Figure S10** -  $^1\text{H}$ -NMR spectrum of phaeosphaeride A (DMSO d-6, at 400 MHz)

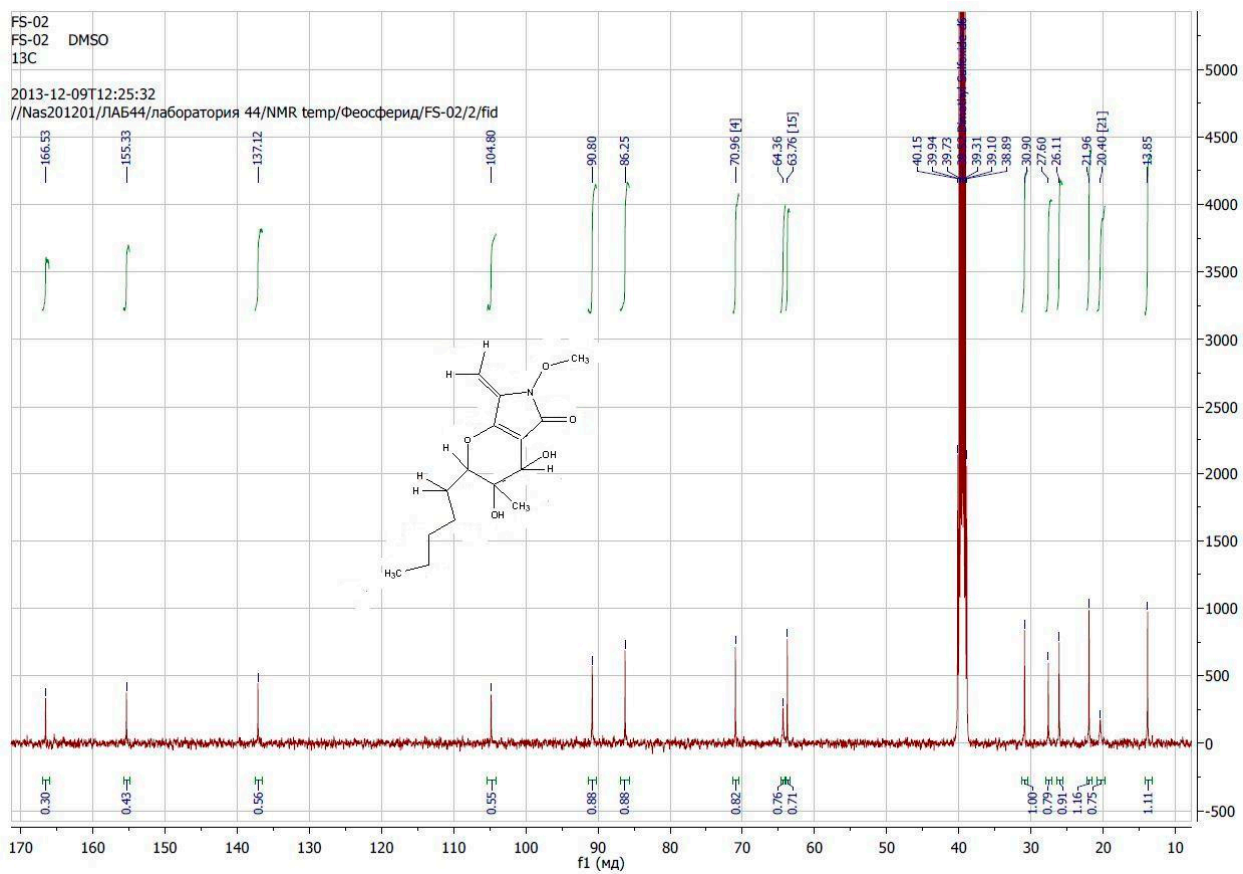
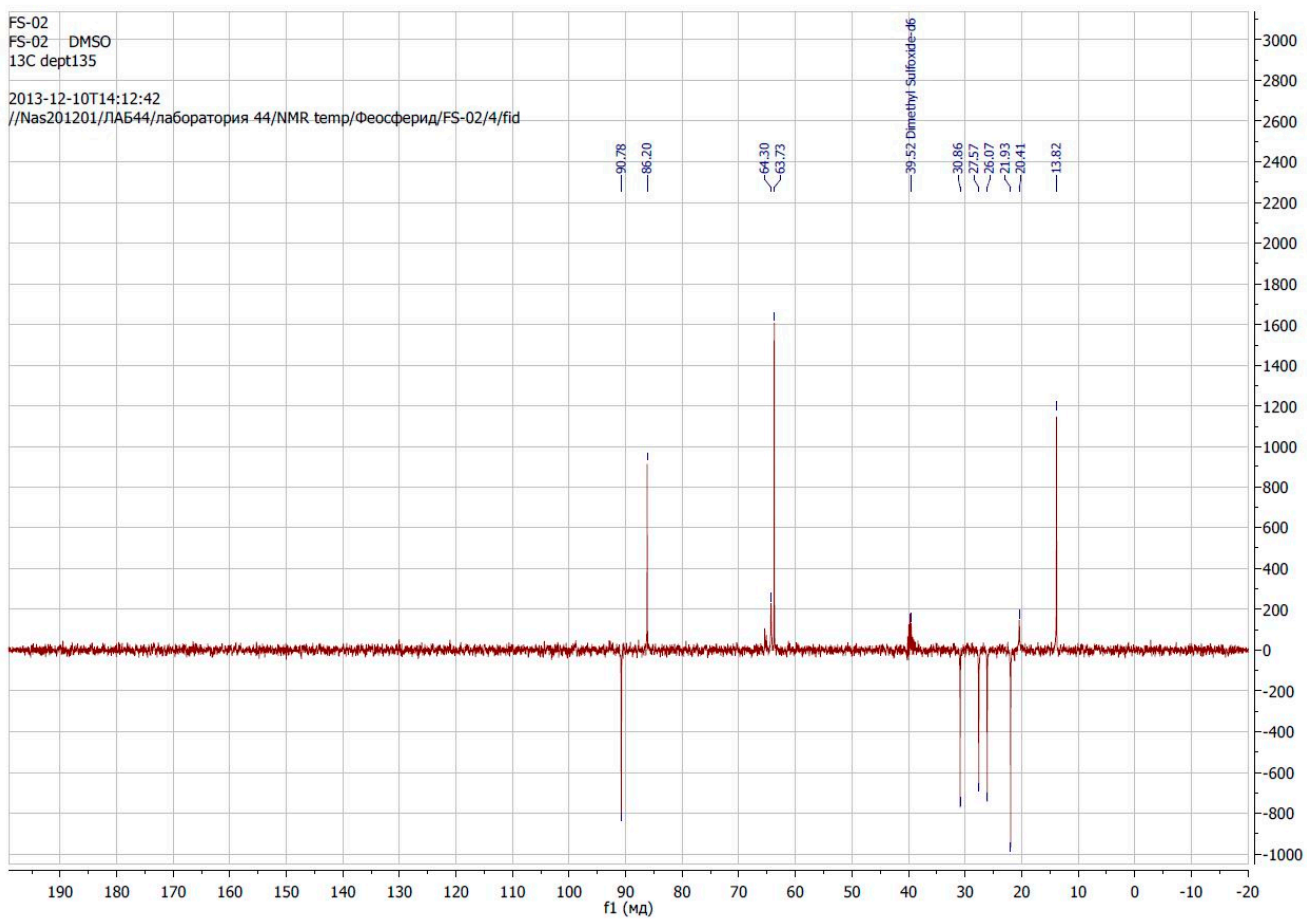


Figure S11 -  $^{13}\text{C}$  -NMR spectrum of phaeosphaeride A (DMSO d-6, at 100 MHz)



**Figure S12** -  $^{13}\text{C}$  DEPT spectrum of phaeosphaeride A (DMSO d-6, at 100 MHz)

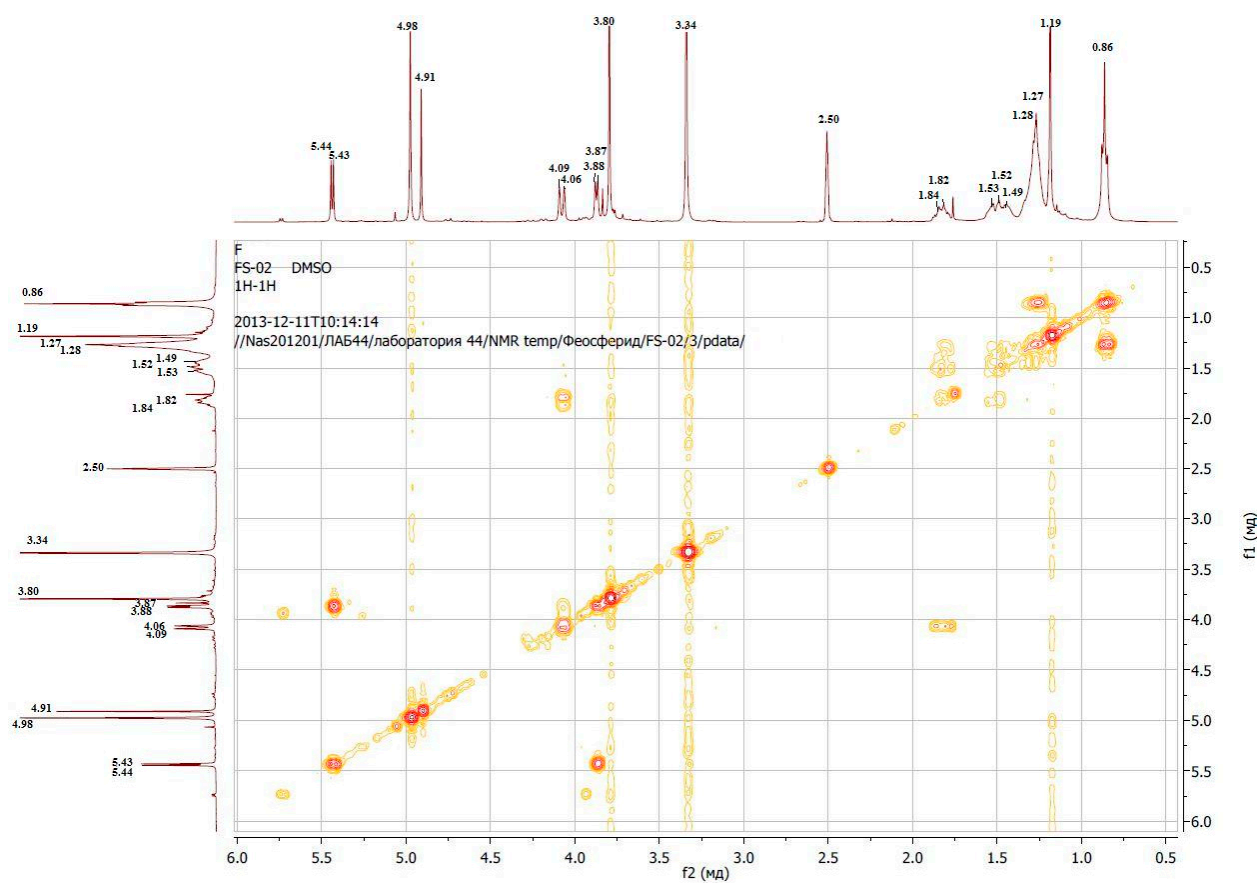
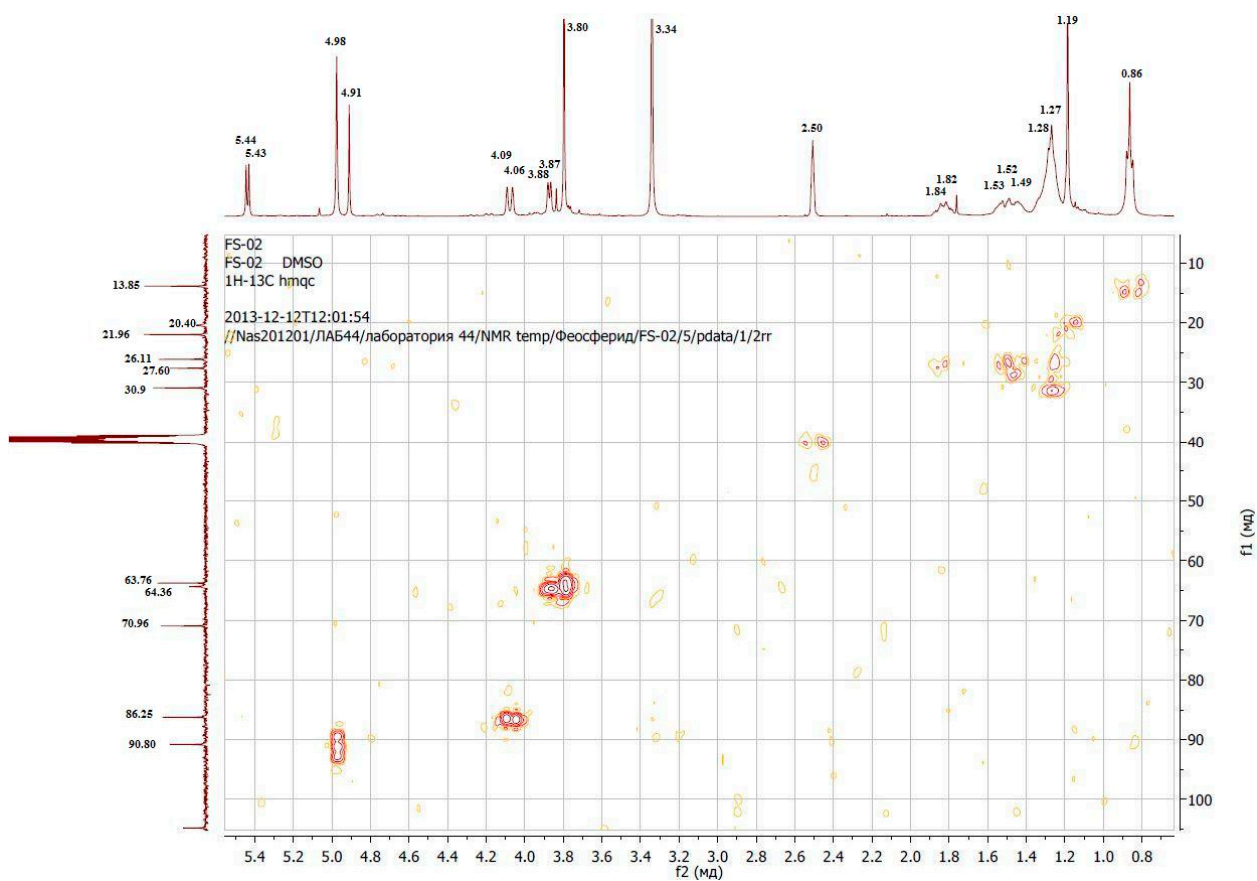


Figure S13 -  $^1\text{H}, ^1\text{H}$  COSY spectrum of phaeosphaeride A (DMSO d-6, at 100 MHz)



**Figure S14** -  $^1\text{H},^{13}\text{C}$  HMQC spectrum of phaeosphaeride A (DMSO d-6)

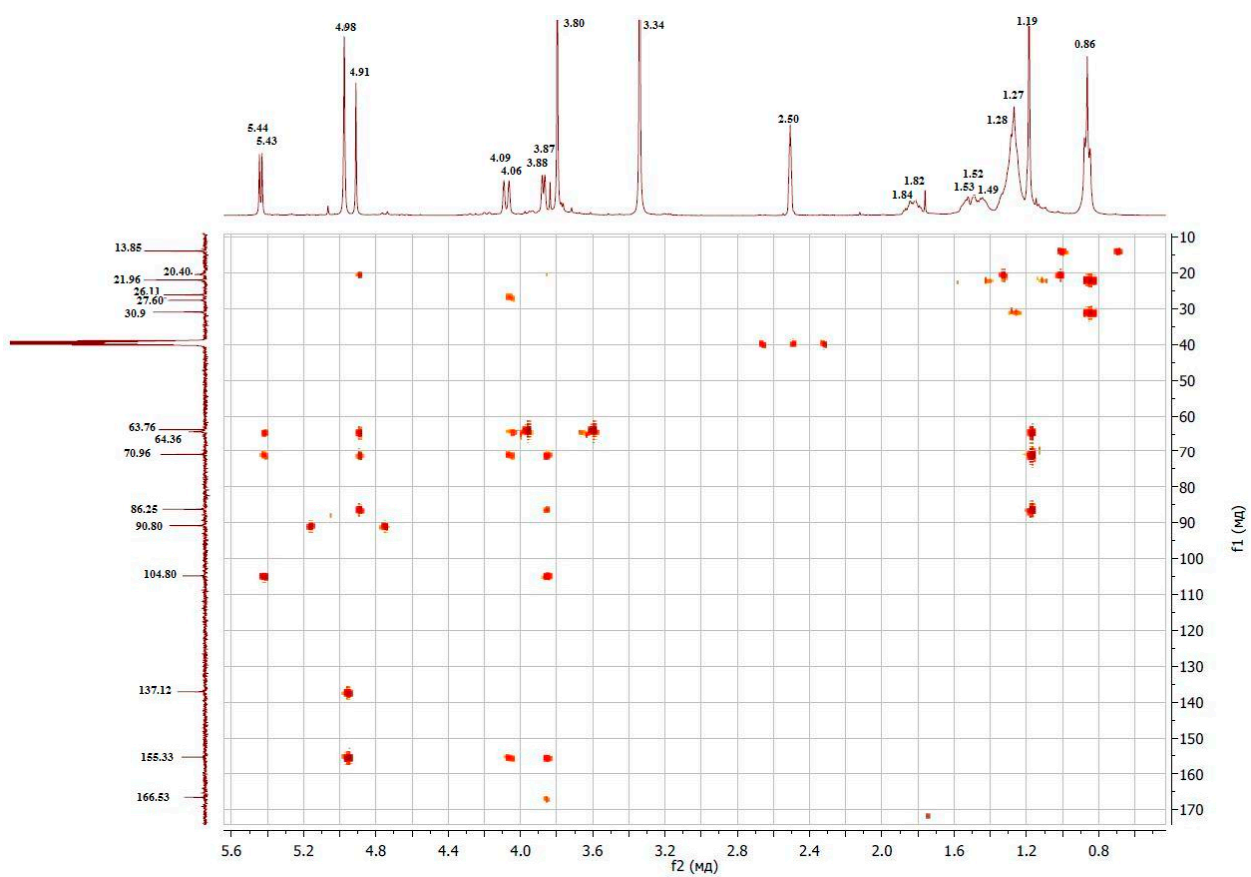
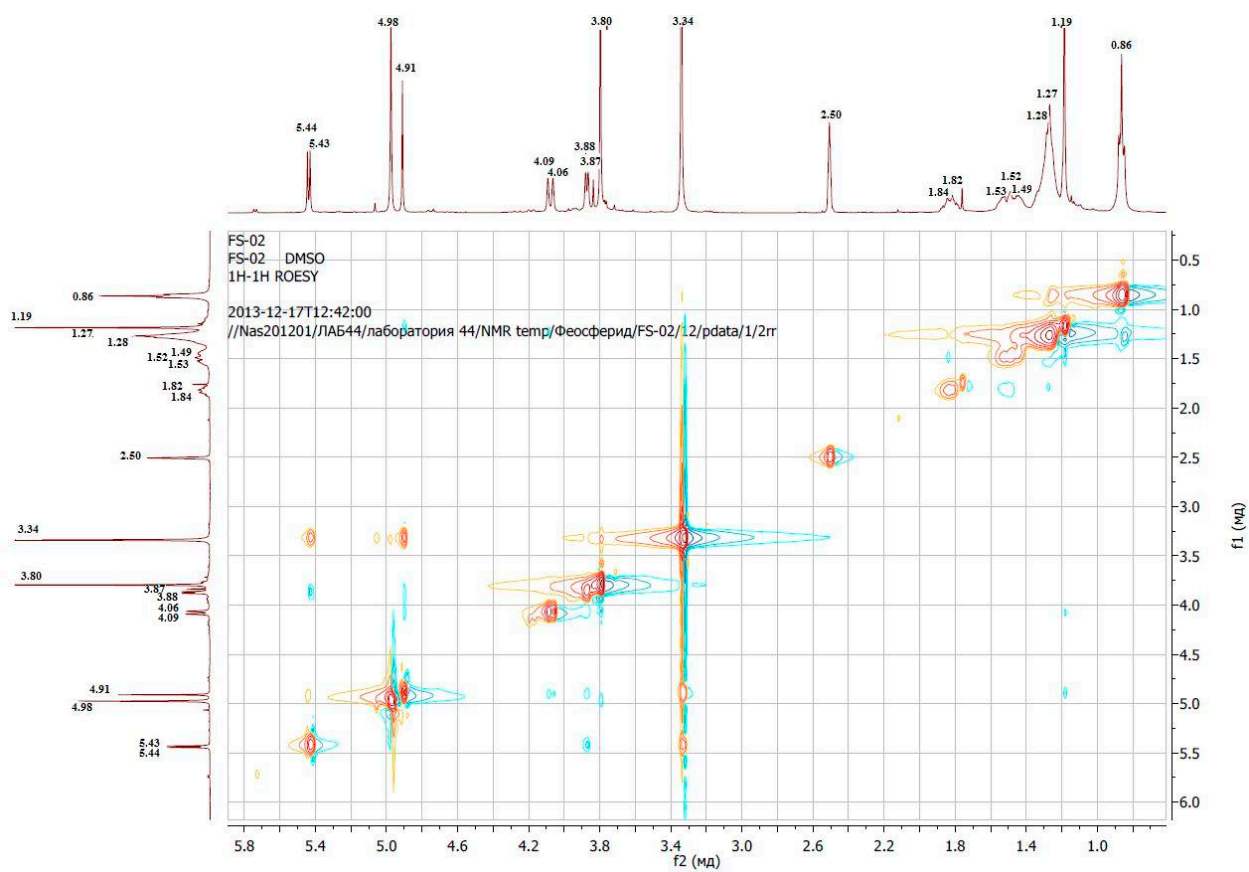
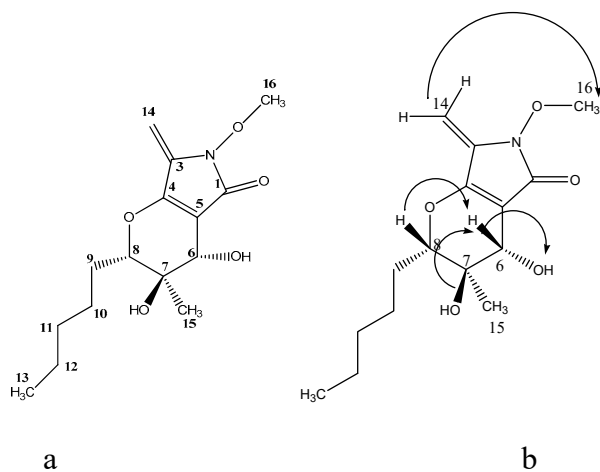


Figure S15 -  $^1\text{H}$ ,  $^{13}\text{C}$  HMBC spectrum of phaeosphaeride A (DMSO  $d_6$ )





**Figure S16** -  $^1\text{H}$ ,  $^1\text{H}$  ROESY spectrum of phaeosphaeride A (DMSO d-6, 400 MHz)



**Figure S 17** - a) Structure of phaeosphaeride A (**2**) (numbering of atoms is given according to those given by Maloney et al. 2006; b) Selected ROESY ( $^1\text{H}$  to  $^1\text{H}$ ) NMR correlations

**Table S1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of phaeosphaeride A (in DMSO-d<sub>6</sub>)<sup>a,b</sup>

| Position | $\delta\text{C}^c$ | $\delta\text{H}$ (J in Hz) | HMBC                                |
|----------|--------------------|----------------------------|-------------------------------------|
| 1        | 166.5 s            | -                          |                                     |
| 3        | 137.1 s            | -                          | H <sub>2</sub> -14                  |
| 4        | 155.3 s            | -                          | H-6, H <sub>2</sub> -14             |
| 5        | 104.8 s            | -                          | H-6                                 |
| 6        | 64.4 d             | 3.87 (d, 4.0)              |                                     |
| 7        | 71.0 s             | -                          | HO-6                                |
| 8        | 86.3 d             | 4.08 (d, 12 Hz,)           | HO-6, HO-7, H-6, H <sub>2</sub> -11 |
| 9        | 27.6 t             | 1.82 (m)1.52 (m)           |                                     |
| 10       | 26.1 t             | 1.49 (m, 2H)               |                                     |
| 11       | 30.9 t             | 1.27 (m, 2H)               |                                     |
| 12       | 22.0 t             | 1.28 (m, 2H)               |                                     |
| 13       | 13.9 q             | 0.86 (t, 6.4 Hz, 3H)       |                                     |
| 14       | 90.8 t             | 4.98 (s, 2H)               |                                     |
| 15       | 20.4 q             | 1.19 (s, 3H)               | HO-7                                |
| 16       | 63.8 q             | 3.80 (s, 3H)               |                                     |
| HO-6     |                    | 5.42 (d, 4.0)              |                                     |
| HO-7     |                    | 4.92 (s, 1H)               |                                     |

<sup>a</sup>The chemical shifts are in  $\delta$  values (ppm) from TMS. <sup>b</sup>2D  $^1\text{H}, ^1\text{H}$  (COSY)  $^{13}\text{C}, ^1\text{H}$  (HMQC) NMR experiments delineated the correlations of all the protons and the corresponding carbons.

<sup>c</sup>Multiplicities were assigned by DEPT spectrum.

**Table S2.** – Summary of three-way ANOVA analysis of the effect of adjuvants, solvents and wounding on phytotoxicity of phaeosphaeride A against *Cirsium arvense*

| Factors                       | SS       | DF  | MS       | F       | p        |
|-------------------------------|----------|-----|----------|---------|----------|
| adjuvant                      | 17,0727  | 5   | 3,4145   | 7,509   | 0,000001 |
| solvent                       | 1,4592   | 1   | 1,4592   | 3,209   | 0,074387 |
| wounding                      | 132,7092 | 1   | 132,7092 | 291,833 | 0,000000 |
| adjuvant x solvent            | 8,6860   | 5   | 1,7372   | 3,820   | 0,002335 |
| adjuvant x wounding           | 3,5335   | 5   | 0,7067   | 1,554   | 0,173474 |
| solvent x wounding            | 8,9253   | 1   | 8,9253   | 19,627  | 0,000014 |
| adjuvant x solvent x wounding | 4,7507   | 5   | 0,9501   | 2,089   | 0,067078 |
| Error                         | 120,0525 | 264 | 0,4547   |         |          |



Control



Phaeosphaeride A (ca. 0.25%) + Hasten (0.1%)



Phaeosphaeride A (ca. 0.25%) + water



Phaeosphaeride A (ca. 0.25%) + Biopower (0.1%)

**Figure S 18** – Effect of adjuvants on herbicidal activity of 0.5% semi-purified extract (ca. 0.25% phaeosphaeride A) from solid state culture of *Paraphoma* sp. VIZR 1.46 on *Cirsium arvense* plants (48 hours after treatment)