**Supplementary Information**

# Trichodermamides D-F, Heterocyclic Dipeptides with a Highly Functionalized 1,2-oxazadecaline Core Isolated from the Endophytic Fungus *Penicillium janthinellum* HDN13-309

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# List of Supplementary information

**Table S1.** Cartesian coordinates of the four low-energy reoptimized conformers of (4*S*, 7*R*, 8*R*, 9*S*)**-1** calculated at B3LYP/6-31+G(d) level of theory with PCM solvent model for MeOH.

| Conformer **1a** | | Standard Orientation (Ångstroms) | | |
|---|---|---|---|---|
| I | Atom | X | Y | Z |
| 1 | C | -6.84467 | -1.43171 | -0.44619 |
| 2 | C | *-6.83425* | -0.1373 | -1.21917 |
| 3 | C | -5.47881 | 0.58107 | -1.09149 |
| 4 | C | -5.02953 | 0.57606 | 0.37339 |
| 5 | C | -4.78283 | -0.84975 | 0.88354 |
| 6 | C | -5.9368 | -1.74391 | 0.48595 |
| 7 | O | -3.88433 | 1.45424 | 0.55978 |
| 8 | N | -2.59968 | 0.96177 | 0.42601 |
| 9 | C | -2.40251 | -0.30263 | 0.32645 |
| 10 | C | -3.45401 | -1.37367 | 0.31943 |
| 11 | C | -0.96225 | -0.73676 | 0.18748 |
| 12 | N | -0.0432 | 0.26866 | 0.20736 |
| 13 | O | -0.68499 | -1.93274 | 0.06266 |
| 14 | C | 1.34561 | 0.16504 | 0.09576 |
| 15 | C | 2.01107 | 1.46839 | 0.16411 |
| 16 | O | 3.37253 | 1.49036 | 0.06612 |
| 17 | C | 4.12704 | 0.35314 | -0.09196 |
| 18 | C | 3.50723 | -0.90974 | -0.16073 |
| 19 | C | 2.07808 | -0.9769 | -0.06143 |
| 20 | O | 1.42361 | 2.53281 | 0.3033 |
| 21 | C | 5.51078 | 0.5165 | -0.18335 |
| 22 | C | 6.31251 | -0.63335 | -0.35264 |
| 23 | C | 5.71317 | -1.90671 | -0.41533 |
| 24 | C | 4.33381 | -2.03712 | -0.32222 |
| 25 | O | 6.05595 | 1.77282 | -0.18497 |
| 26 | O | 7.64513 | -0.40628 | -0.45001 |
| 27 | C | 8.52689 | -1.5223 | -0.62755 |
| 28 | C | 6.65343 | 2.18554 | 1.06149 |
| 29 | O | -5.6617 | 1.9052 | -1.58538 |
| 30 | O | -7.90029 | 0.68142 | -0.71387 |
| 31 | O | -4.60924 | -0.84381 | 2.30953 |
| 32 | H | -7.6527 | -2.12384 | -0.67184 |
| 33 | H | -7.01638 | -0.34003 | -2.28421 |
| 34 | H | -4.7442 | 0.05347 | -1.7154 |
| 35 | H | -5.79909 | 1.06374 | 0.97783 |

| | | | | |
|---|---|---|---|---|
| 36 | H | -5.98499 | -2.69448 | 1.0146 |
| 37 | H | -3.58607 | -1.74336 | -0.70415 |
| 38 | H | -3.1154 | -2.22653 | 0.91398 |
| 39 | H | -0.40029 | 1.21579 | 0.31566 |
| 40 | H | 1.58355 | -1.93849 | -0.11205 |
| 41 | H | 6.32325 | -2.79283 | -0.54289 |
| 42 | H | 3.88018 | -3.02252 | -0.37583 |
| 43 | H | 9.52792 | -1.09399 | -0.68049 |
| 44 | H | 8.30264 | -2.05326 | -1.559 |
| 45 | H | 8.46352 | -2.21019 | 0.22256 |
| 46 | H | 7.03735 | 3.19257 | 0.8897 |
| 47 | H | 5.89948 | 2.20644 | 1.85644 |
| 48 | H | 7.47392 | 1.51614 | 1.33765 |
| 49 | H | -4.86263 | 2.42282 | -1.38752 |
| 50 | H | -7.81745 | 1.55002 | -1.14727 |
| 51 | H | -5.42952 | -0.53017 | 2.72816 |

| Conformer **1b** | | Standard Orientation (Ångstroms) | | |
|---|---|---|---|---|
| I | Atom | X | Y | Z |
| 1 | C | -6.84008 | -1.33346 | -0.71424 |
| 2 | C | -6.82092 | 0.06827 | -1.26896 |
| 3 | C | -5.46601 | 0.75232 | -1.0148 |
| 4 | C | -5.03169 | 0.51249 | 0.43489 |
| 5 | C | -4.79177 | -0.97688 | 0.713 |
| 6 | C | -5.94191 | -1.79333 | 0.16479 |
| 7 | O | -3.88752 | 1.34731 | 0.77004 |
| 8 | N | -2.60121 | 0.87696 | 0.58345 |
| 9 | C | -2.40328 | -0.35627 | 0.2878 |
| 10 | C | -3.45591 | -1.40757 | 0.08949 |
| 11 | C | -0.96086 | -0.76933 | 0.11215 |
| 12 | N | -0.04158 | 0.21686 | 0.30788 |
| 13 | O | -0.68212 | -1.9323 | -0.19212 |
| 14 | C | 1.34959 | 0.12406 | 0.21735 |
| 15 | C | 2.01562 | 1.39603 | 0.50848 |
| 16 | O | 3.3795 | 1.42392 | 0.45426 |
| 17 | C | 4.13545 | 0.32091 | 0.13936 |
| 18 | C | 3.51516 | -0.91047 | -0.14779 |
| 19 | C | 2.08365 | -0.98313 | -0.1 |
| 20 | O | 1.42665 | 2.42959 | 0.79531 |
| 21 | C | 5.52216 | 0.4843 | 0.12486 |
| 22 | C | 6.32661 | -0.63253 | -0.18956 |
| 23 | C | 5.72566 | -1.87064 | -0.48989 |

| | | | | |
|---|---|---|---|---|
| 24 | C | 4.34349 | -2.00254 | -0.46639 |
| 25 | O | 6.07659 | 1.6836 | 0.48498 |
| 26 | O | 7.66394 | -0.41258 | -0.17064 |
| 27 | C | 8.5487 | -1.4982 | -0.47612 |
| 28 | C | 6.52761 | 2.50663 | -0.61039 |
| 29 | O | -5.64113 | 2.13914 | -1.29279 |
| 30 | O | -7.89029 | 0.79879 | -0.64866 |
| 31 | O | -4.63543 | -1.20006 | 2.12363 |
| 32 | H | -7.64596 | -1.97874 | -1.05648 |
| 33 | H | -6.99311 | 0.03956 | -2.35439 |
| 34 | H | -4.72621 | 0.32819 | -1.70742 |
| 35 | H | -5.80728 | 0.89946 | 1.1016 |
| 36 | H | -5.99567 | -2.8165 | 0.53305 |
| 37 | H | -3.573 | -1.60348 | -0.98288 |
| 38 | H | -3.12771 | -2.34783 | 0.54072 |
| 39 | H | -0.40022 | 1.13656 | 0.55661 |
| 40 | H | 1.58845 | -1.92112 | -0.3161 |
| 41 | H | 6.33746 | -2.73034 | -0.735 |
| 42 | H | 3.8892 | -2.96231 | -0.69472 |
| 43 | H | 9.55346 | -1.0828 | -0.39744 |
| 44 | H | 8.37945 | -1.8663 | -1.49383 |
| 45 | H | 8.42908 | -2.31464 | 0.24431 |
| 46 | H | 6.94018 | 3.40896 | -0.15586 |
| 47 | H | 7.30248 | 1.99228 | -1.18706 |
| 48 | H | 5.68565 | 2.77031 | -1.26033 |
| 49 | H | -4.8478 | 2.61675 | -0.99582 |
| 50 | H | -7.79778 | 1.72645 | -0.93175 |
| 51 | H | -5.46017 | -0.95432 | 2.57719 |

| Conformer **1c** | | Standard Orientation (Ångstroms) | | |
|---|---|---|---|---|
| I | Atom | X | Y | Z |
| 1 | C | -6.79011 | -1.43287 | -0.52325 |
| 2 | C | -6.72617 | -0.1553 | -1.32223 |
| 3 | C | -5.38741 | 0.57603 | -1.11207 |
| 4 | C | -5.0386 | 0.58555 | 0.37868 |
| 5 | C | -4.8209 | -0.83069 | 0.91971 |
| 6 | C | -5.95601 | -1.72453 | 0.48031 |
| 7 | O | -3.90062 | 1.45746 | 0.64172 |
| 8 | N | -2.61015 | 0.96754 | 0.49676 |
| 9 | C | -2.41512 | -0.29799 | 0.39917 |
| 10 | C | -3.46772 | -1.36976 | 0.40878 |
| 11 | C | -0.97494 | -0.73531 | 0.25105 |

| | | | | |
|---|---|---|---|---|
| 12 | N | -0.05607 | 0.2694 | 0.25279 |
| 13 | O | -0.70193 | -1.93272 | 0.13498 |
| 14 | C | 1.33184 | 0.16395 | 0.12777 |
| 15 | C | 1.99886 | 1.46681 | 0.18619 |
| 16 | O | 3.35908 | 1.4873 | 0.07329 |
| 17 | C | 4.11062 | 0.34897 | -0.09105 |
| 18 | C | 3.48899 | -0.91362 | -0.15006 |
| 19 | C | 2.06108 | -0.97922 | -0.03482 |
| 20 | O | 1.41351 | 2.53183 | 0.32958 |
| 21 | C | 5.49329 | 0.51084 | -0.19865 |
| 22 | C | 6.292 | -0.64015 | -0.37496 |
| 23 | C | 5.69084 | -1.91315 | -0.42822 |
| 24 | C | 4.3126 | -2.04211 | -0.31884 |
| 25 | O | 6.03968 | 1.7665 | -0.20906 |
| 26 | O | 7.62341 | -0.4144 | -0.48783 |
| 27 | C | 8.50251 | -1.53132 | -0.67337 |
| 28 | C | 6.65108 | 2.18146 | 1.02995 |
| 29 | O | -5.5478 | 1.8942 | -1.62924 |
| 30 | O | -7.83067 | 0.66625 | -0.91405 |
| 31 | O | -4.84887 | -0.82334 | 2.35614 |
| 32 | H | -7.58267 | -2.1285 | -0.78897 |
| 33 | H | -6.82855 | -0.38139 | -2.39316 |
| 34 | H | -4.61065 | 0.04882 | -1.68269 |
| 35 | H | -5.8415 | 1.07252 | 0.93671 |
| 36 | H | -6.05022 | -2.658 | 1.03186 |
| 37 | H | -3.56579 | -1.7774 | -0.60502 |
| 38 | H | -3.1421 | -2.20091 | 1.04096 |
| 39 | H | -0.41054 | 1.21802 | 0.35729 |
| 40 | H | 1.56512 | -1.94047 | -0.07795 |
| 41 | H | 6.2986 | -2.80006 | -0.5612 |
| 42 | H | 3.85748 | -3.02717 | -0.36535 |
| 43 | H | 9.50308 | -1.10364 | -0.73837 |
| 44 | H | 8.26743 | -2.06373 | -1.60129 |
| 45 | H | 8.44829 | -2.21758 | 0.17868 |
| 46 | H | 7.03439 | 3.18756 | 0.85156 |
| 47 | H | 5.90578 | 2.20525 | 1.83292 |
| 48 | H | 7.47365 | 1.51163 | 1.2988 |
| 49 | H | -4.76597 | 2.42061 | -1.39062 |
| 50 | H | -7.71691 | 1.52861 | -1.35287 |
| 51 | H | -4.16185 | -0.22276 | 2.69307 |

| Conformer **1d** | Standard Orientation (Ångstroms) | | |
|---|---|---|---|

| I | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -6.75393 | -1.28927 | -0.87964 |
| 2 | C | -6.6575 | 0.11579 | -1.41861 |
| 3 | C | -5.33085 | 0.78757 | -1.01572 |
| 4 | C | -5.0413 | 0.50603 | 0.46101 |
| 5 | C | -4.84378 | -0.98938 | 0.72707 |
| 6 | C | -5.96205 | -1.77318 | 0.08302 |
| 7 | O | -3.91388 | 1.30012 | 0.93211 |
| 8 | N | -2.61888 | 0.84308 | 0.7257 |
| 9 | C | -2.42189 | -0.38059 | 0.38984 |
| 10 | C | -3.47305 | -1.43082 | 0.17081 |
| 11 | C | -0.97877 | -0.78917 | 0.19458 |
| 12 | N | -0.06086 | 0.19872 | 0.38208 |
| 13 | O | -0.70293 | -1.94985 | -0.11917 |
| 14 | C | 1.32944 | 0.11051 | 0.26937 |
| 15 | C | 1.99582 | 1.38368 | 0.55327 |
| 16 | O | 3.35822 | 1.41661 | 0.4746 |
| 17 | C | 4.11225 | 0.31715 | 0.14293 |
| 18 | C | 3.49128 | -0.91572 | -0.13664 |
| 19 | C | 2.06119 | -0.99335 | -0.06428 |
| 20 | O | 1.40803 | 2.41388 | 0.85435 |
| 21 | C | 5.49787 | 0.48536 | 0.10461 |
| 22 | C | 6.30044 | -0.62819 | -0.2263 |
| 23 | C | 5.6985 | -1.86755 | -0.51962 |
| 24 | C | 4.31746 | -2.0042 | -0.47265 |
| 25 | O | 6.054 | 1.68568 | 0.45813 |
| 26 | O | 7.63703 | -0.40403 | -0.22912 |
| 27 | C | 8.5203 | -1.48625 | -0.55102 |
| 28 | C | 6.49079 | 2.50984 | -0.6423 |
| 29 | O | -5.47546 | 2.18189 | -1.27256 |
| 30 | O | -7.78114 | 0.85098 | -0.91064 |
| 31 | O | -4.92387 | -1.25653 | 2.13628 |
| 32 | H | -7.53595 | -1.91492 | -1.30352 |
| 33 | H | -6.71232 | 0.09712 | -2.51646 |
| 34 | H | -4.5293 | 0.37934 | -1.64623 |
| 35 | H | -5.86511 | 0.88243 | 1.07155 |
| 36 | H | -6.08004 | -2.79339 | 0.44319 |
| 37 | H | -3.53738 | -1.64849 | -0.90247 |
| 38 | H | -3.16654 | -2.36424 | 0.65189 |
| 39 | H | -0.41754 | 1.11658 | 0.64051 |
| 40 | H | 1.56547 | -1.93229 | -0.27507 |
| 41 | H | 6.30885 | -2.72452 | -0.77748 |
| 42 | H | 3.86248 | -2.96489 | -0.69565 |
| 43 | H | 9.52481 | -1.06761 | -0.48807 |

| | | | | |
|---|---|---|---|---|
| 44 | H | 8.3356 | -1.85313 | -1.56644 |
| 45 | H | 8.41506 | -2.30424 | 0.16987 |
| 46 | H | 6.90649 | 3.41298 | -0.19228 |
| 47 | H | 7.26014 | 1.99726 | -1.22779 |
| 48 | H | 5.64086 | 2.77175 | -1.2825 |
| 49 | H | -4.70769 | 2.64903 | -0.90159 |
| 50 | H | -7.6503 | 1.78051 | -1.17149 |
| 51 | H | -4.25278 | -0.73138 | 2.6054 |

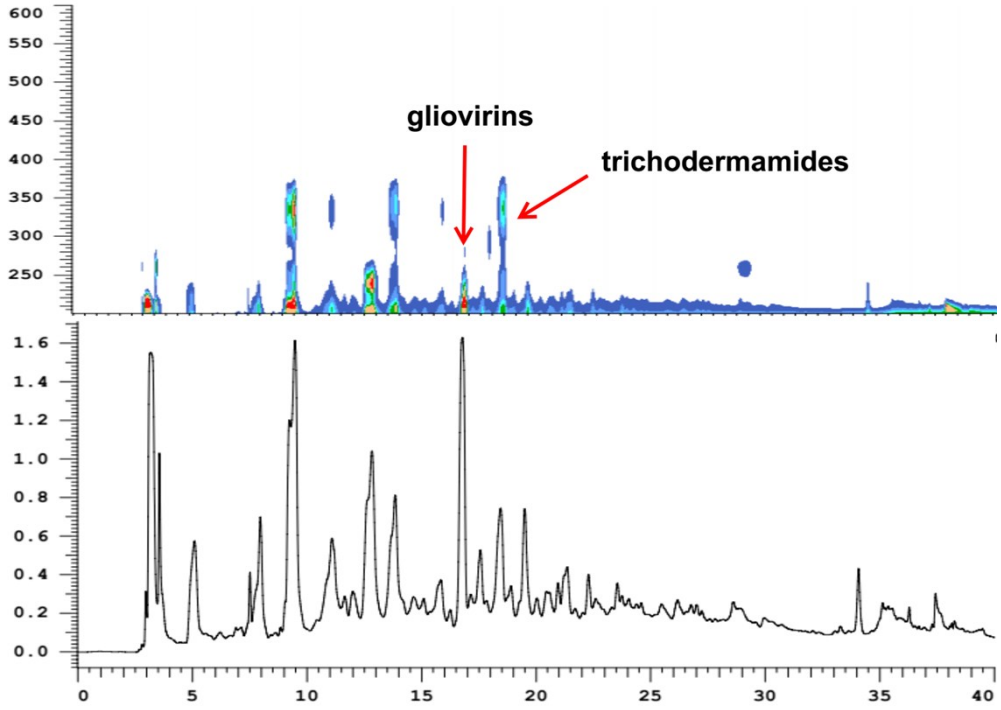


**Figure S1.** The HPLC-UV profiles of the EtOAc extract of reculturing HDN13-309.

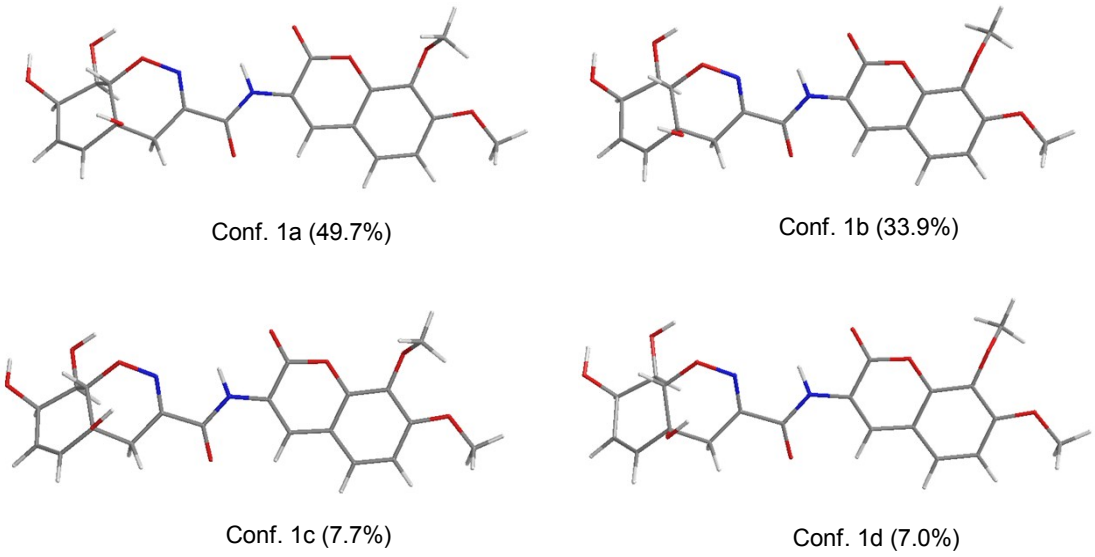


**Figure S2.** Conformations of lowest-energy conformers (>5% population) of (4*S*, 7*R*, 8*R*, 9*S*)-**1**.

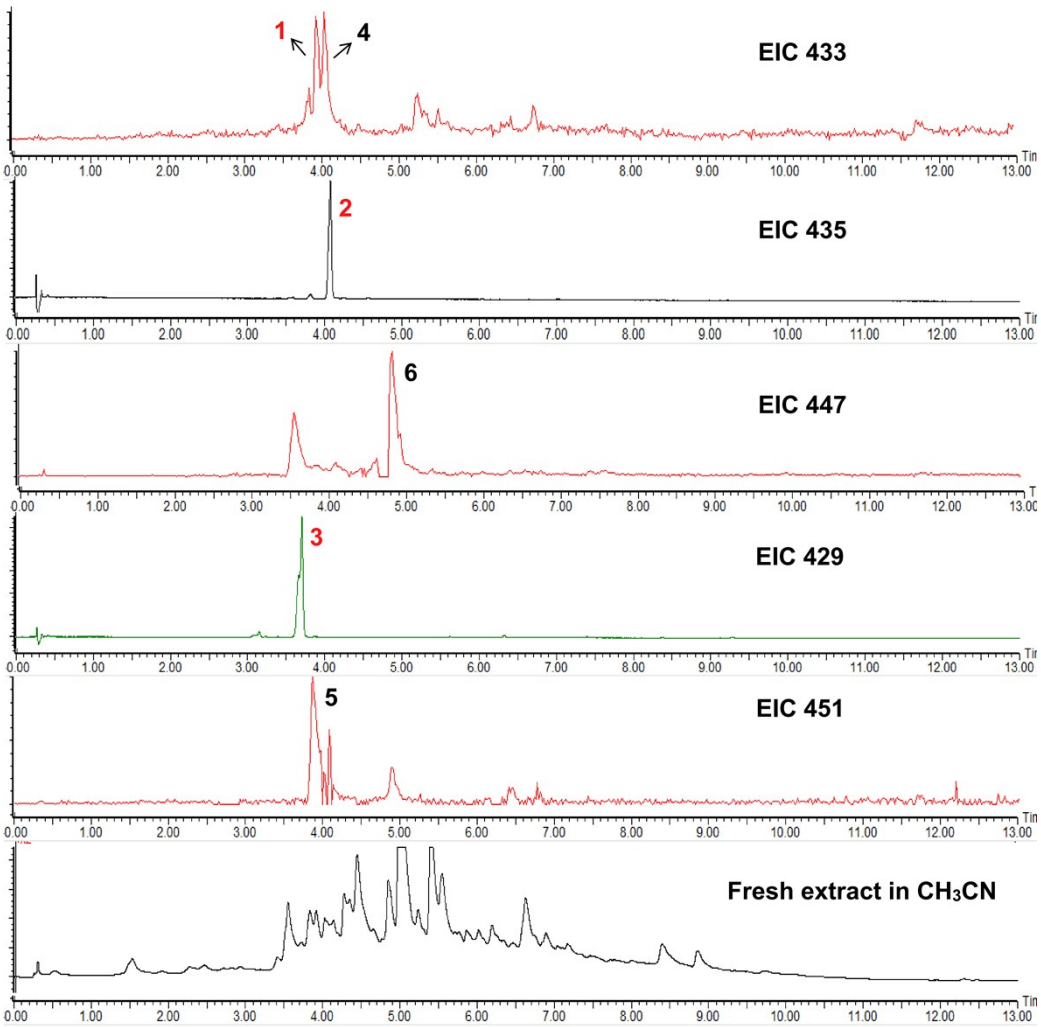


**Figure S3.** An extracted ion chromatogram for the $[M+H]^+$ signal of compounds **1-6** in the fresh $CH_3CN$ extract of *P. janthinellum* HDN13-309.

**Figure S4.** [1]H NMR spectrum of trichodermamide D (**1**) in $d_6$-DMSO (500 MHz)

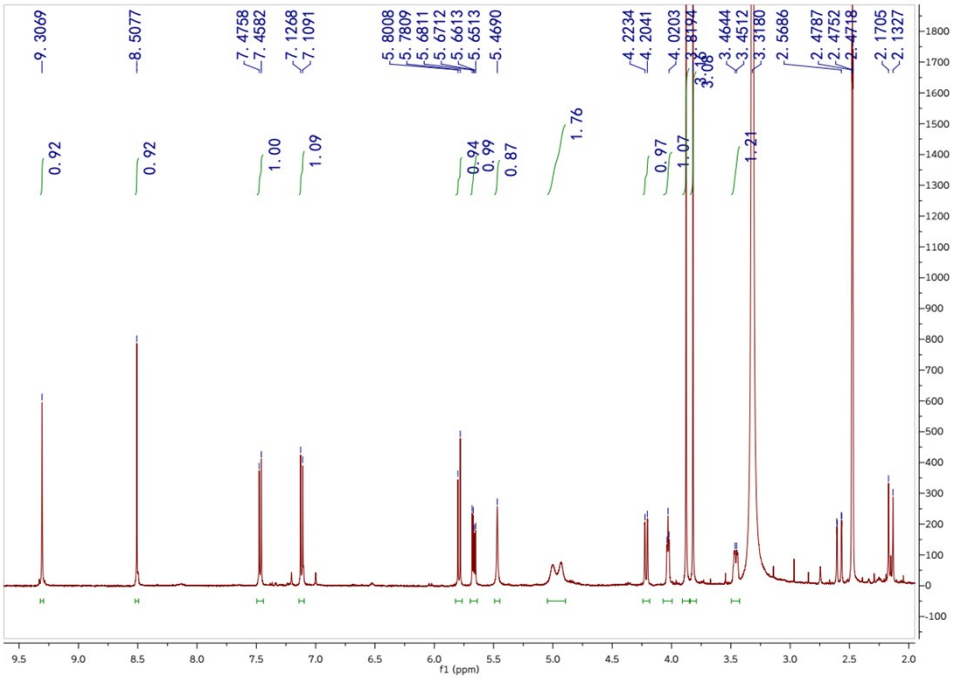

**Figure S5.** [13]C NMR spectrum of trichodermamide D (**1**) in $d_6$-DMSO (125 MHz)

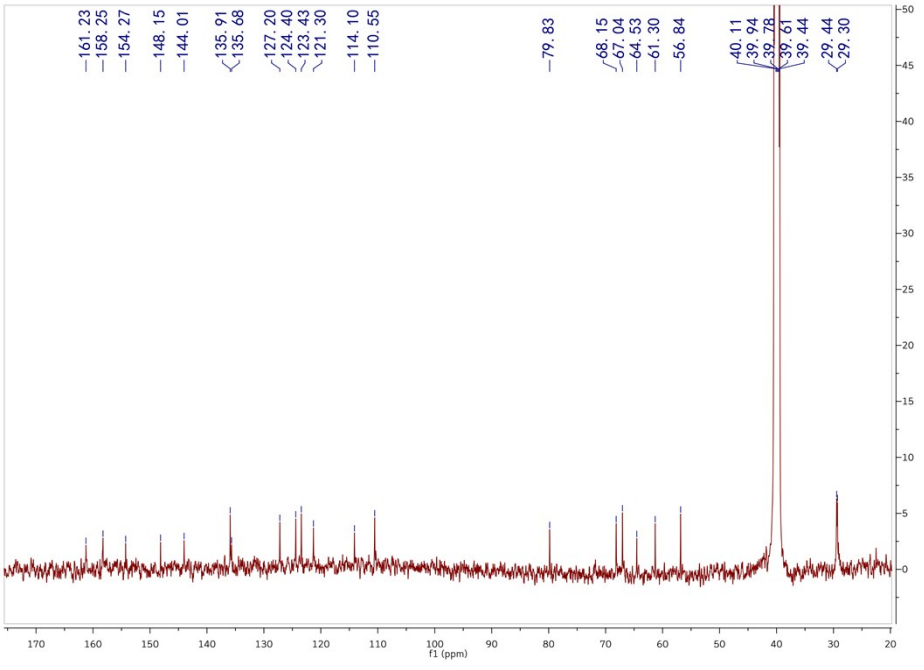

**Figure S6.** $^{1}H$-$^{1}H$ COSY spectrum of trichodermamide D (**1**)

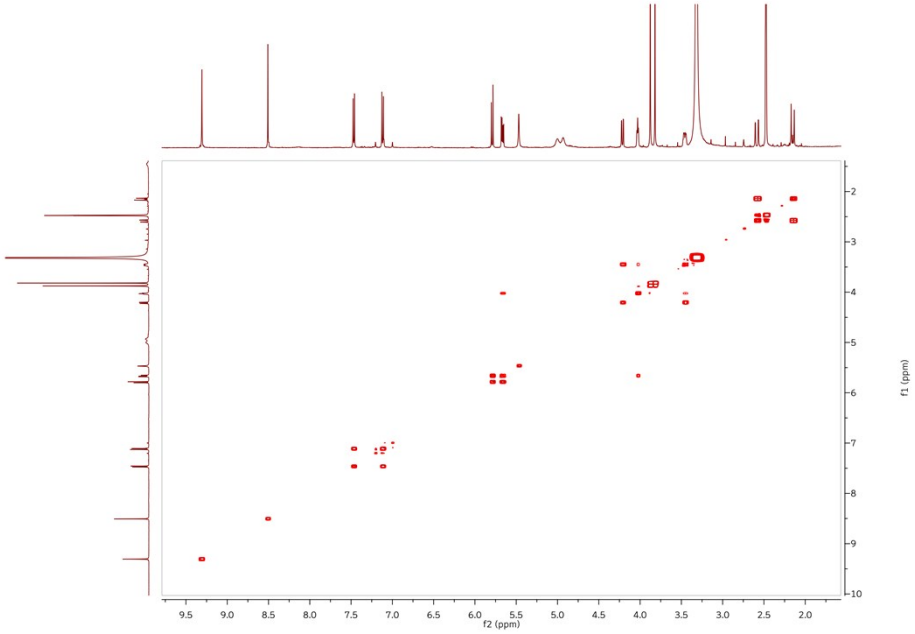


**Figure S7.** HSQC spectrum of trichodermamide D (**1**)

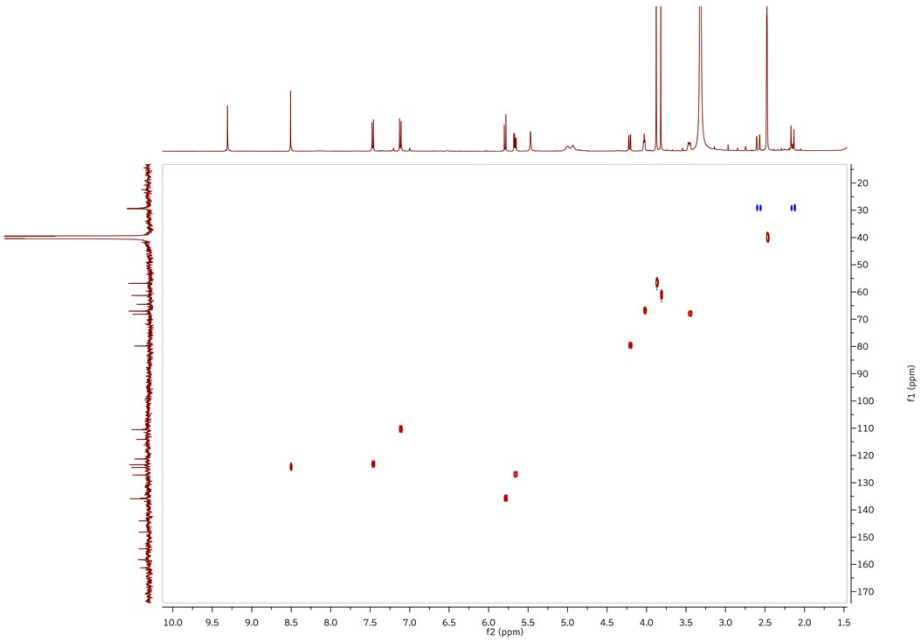

**Figure S8.** HMBC spectrum of trichodermamide D (**1**)

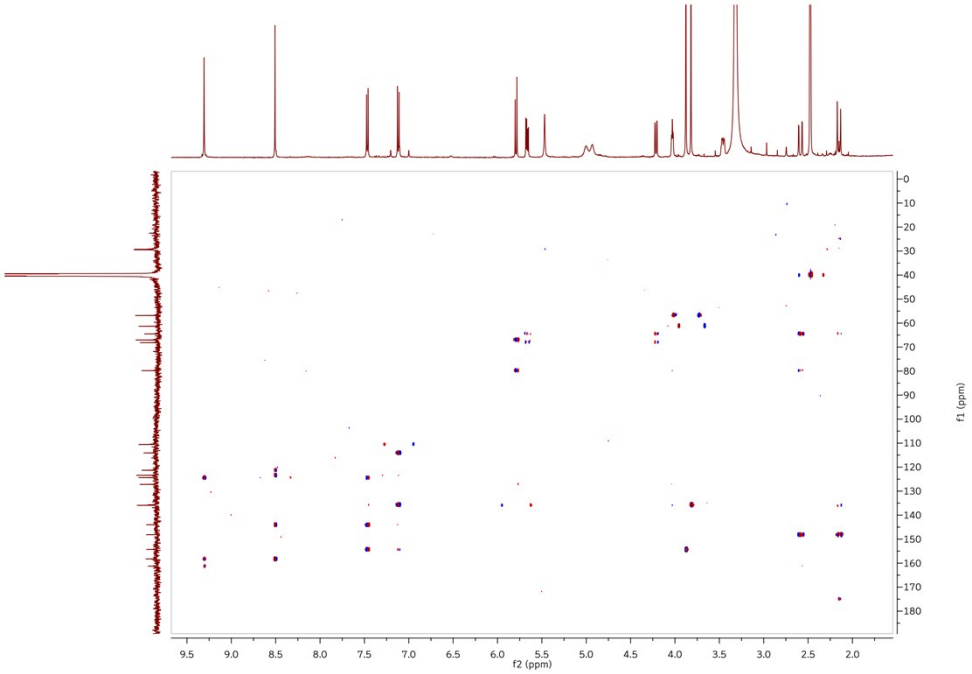


**Figure S9.** NOESY spectrum of trichodermamide D (**1**)

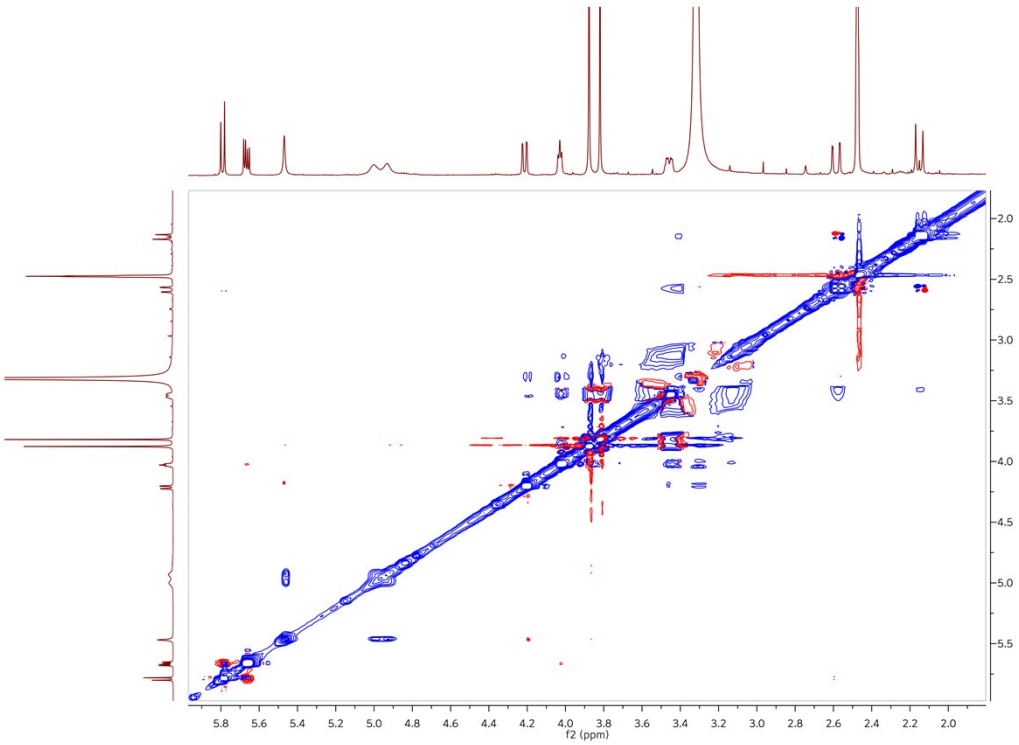

**Figure S10.** HRESIMS spectrum of trichodermamide D (**1**)

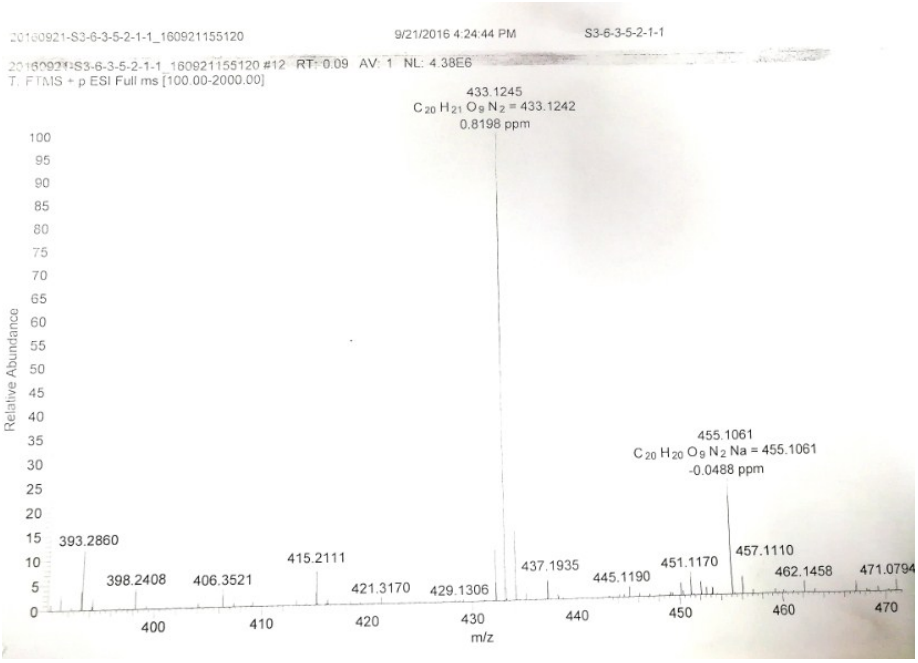


**Figure S11.** $^{1}$H NMR spectrum of trichodermamide E (**2**) in $d_6$-DMSO (500 MHz)

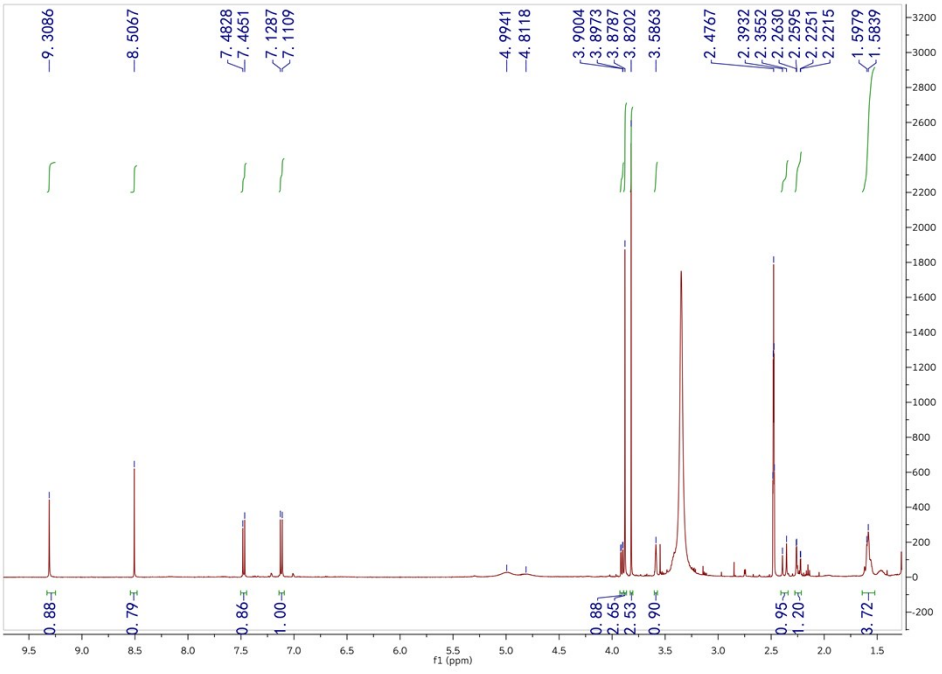

**Figure S12.** $^{13}$C NMR spectrum of trichodermamide E (**2**) in $d_6$-DMSO (125 MHz)

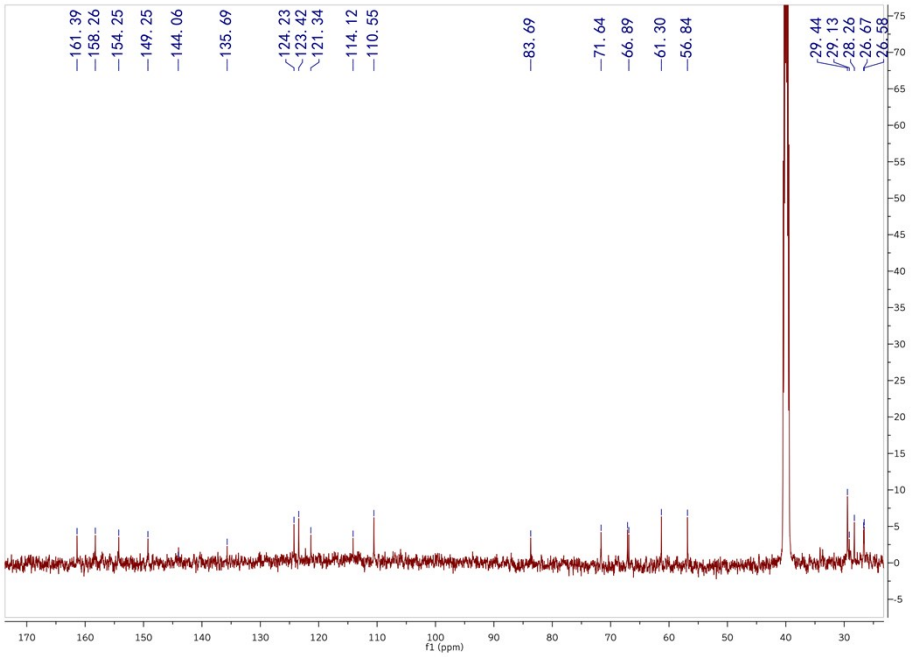


**Figure S13.** $^{1}$H-$^{1}$H COSY spectrum of trichodermamide E (**2**)

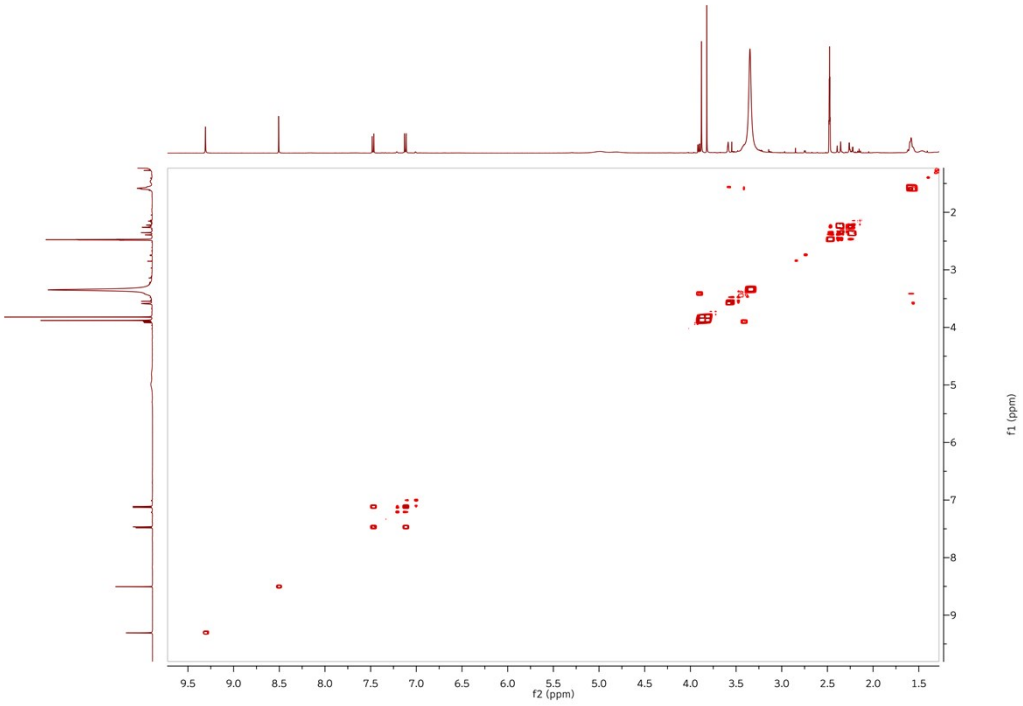

**Figure S14.** HSQC spectrum of trichodermamide E (**2**)

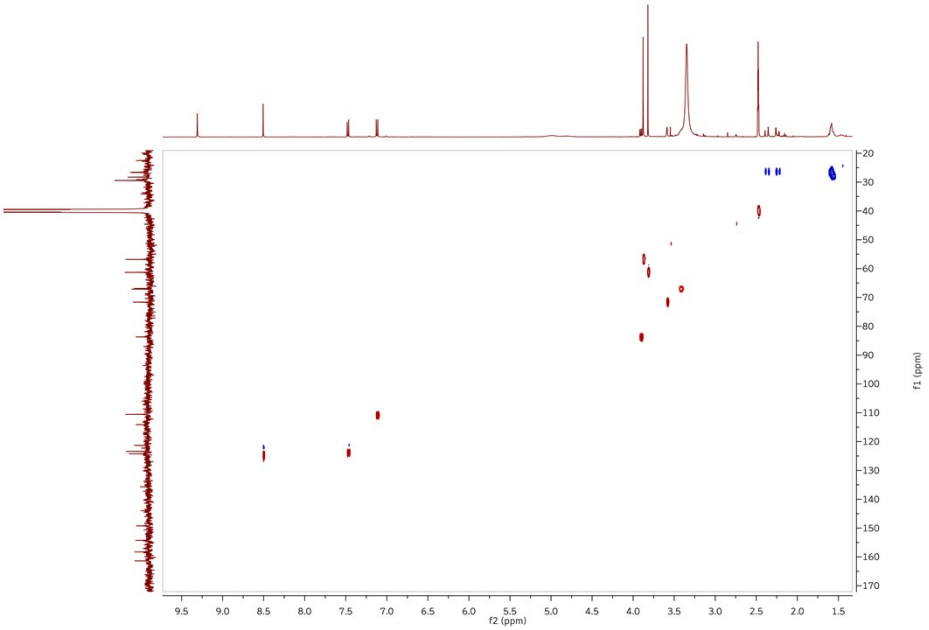


**Figure S15.** HMBC spectrum of trichodermamide E (**2**)

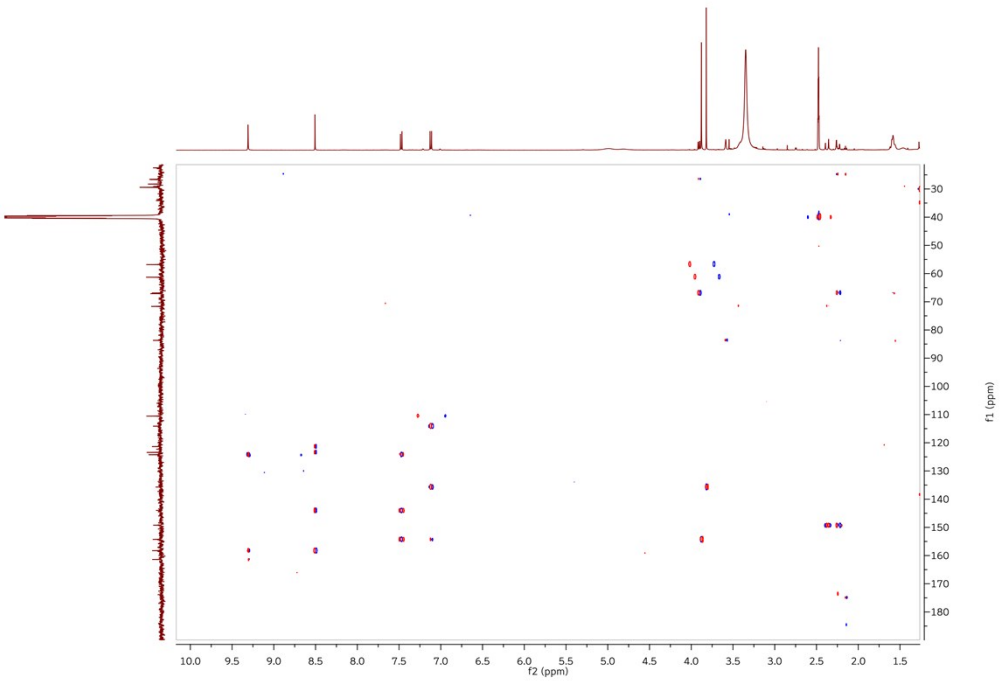

**Figure S16.** NOESY spectrum of trichodermamide E (**2**)

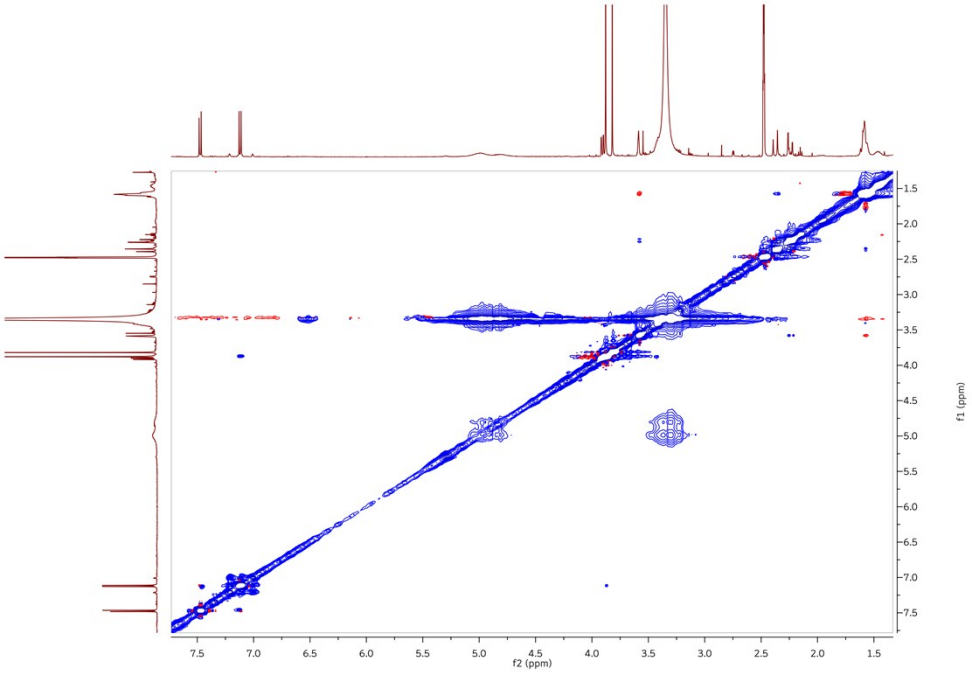


**Figure S17.** HRESIMS spectrum of trichodermamide E (**2**)

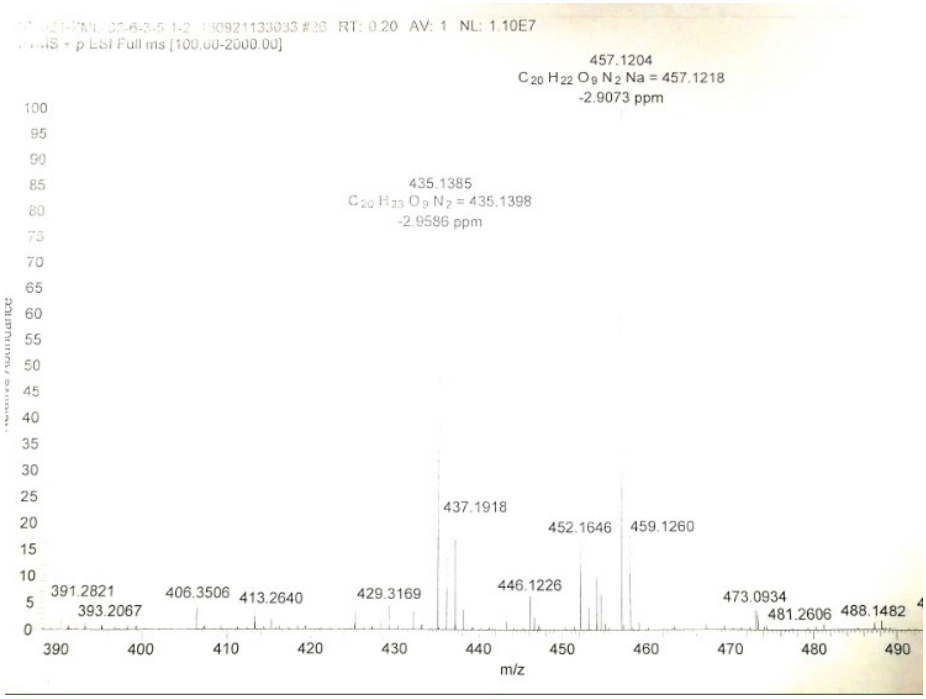

**Figure S18.** [1]H NMR spectrum of trichodermamide F (**3**) in $d_6$-DMSO (500 MHz)

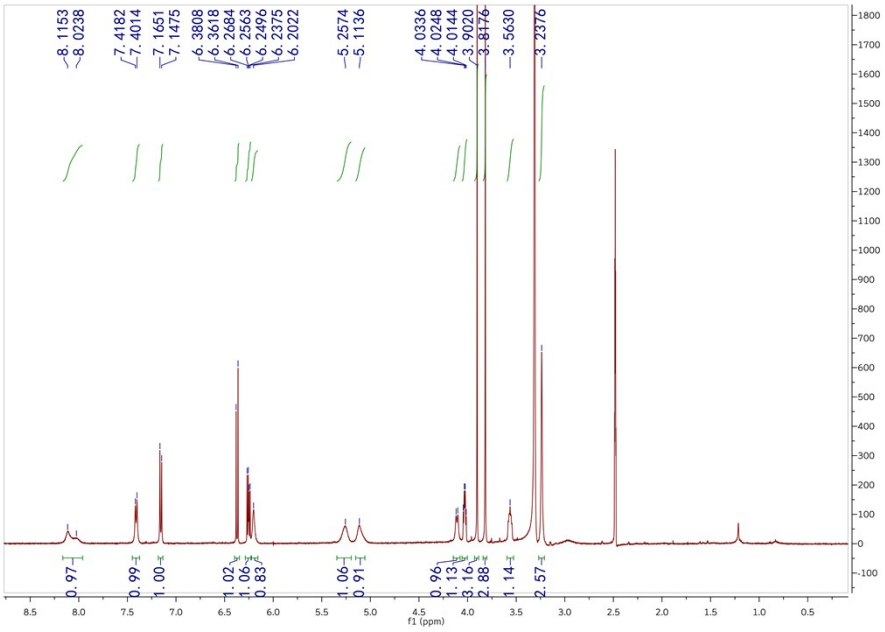


**Figure S19.** [13]C NMR spectrum of trichodermamide F (**3**) in $d_6$-DMSO (125 MHz)

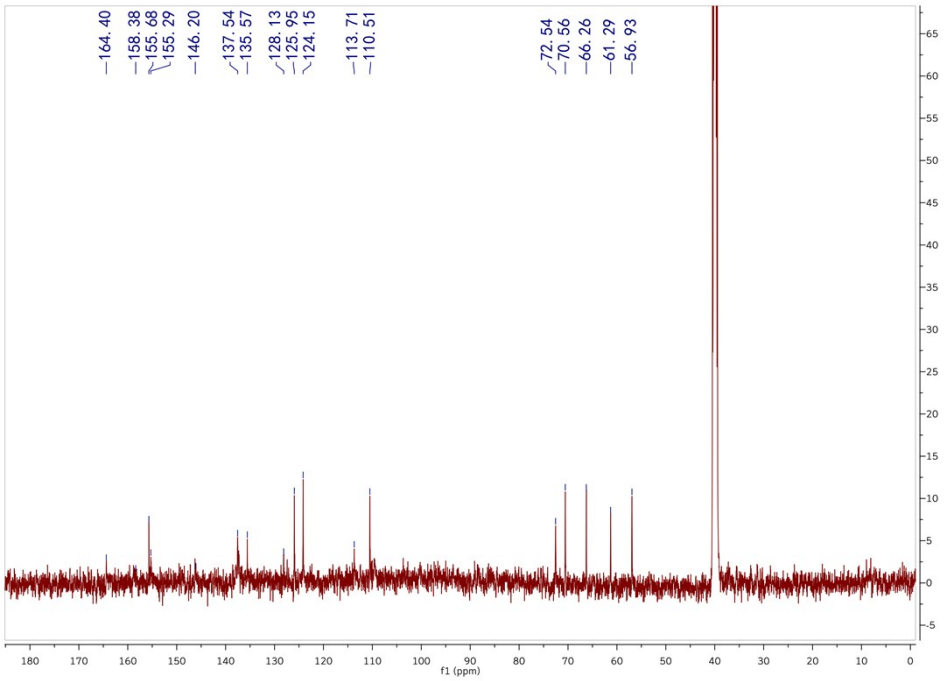

**Figure S20.** $^{1}$H-$^{1}$H COSY spectrum of trichodermamide F (**3**)

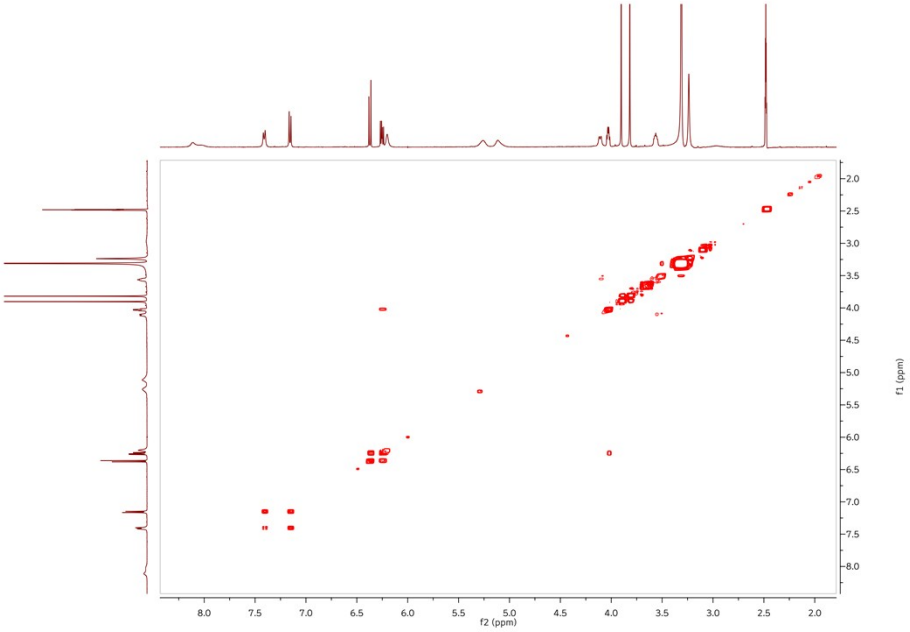


**Figure S21.** HSQC spectrum of trichodermamide F (**3**)

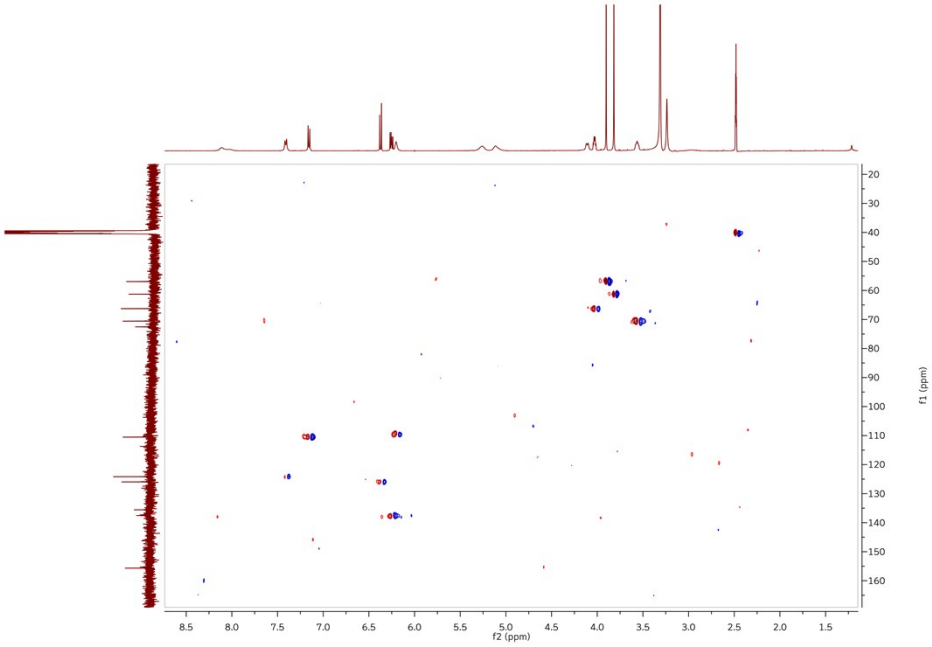

**Figure S22.** HMBC spectrum of trichodermamide F (**3**)

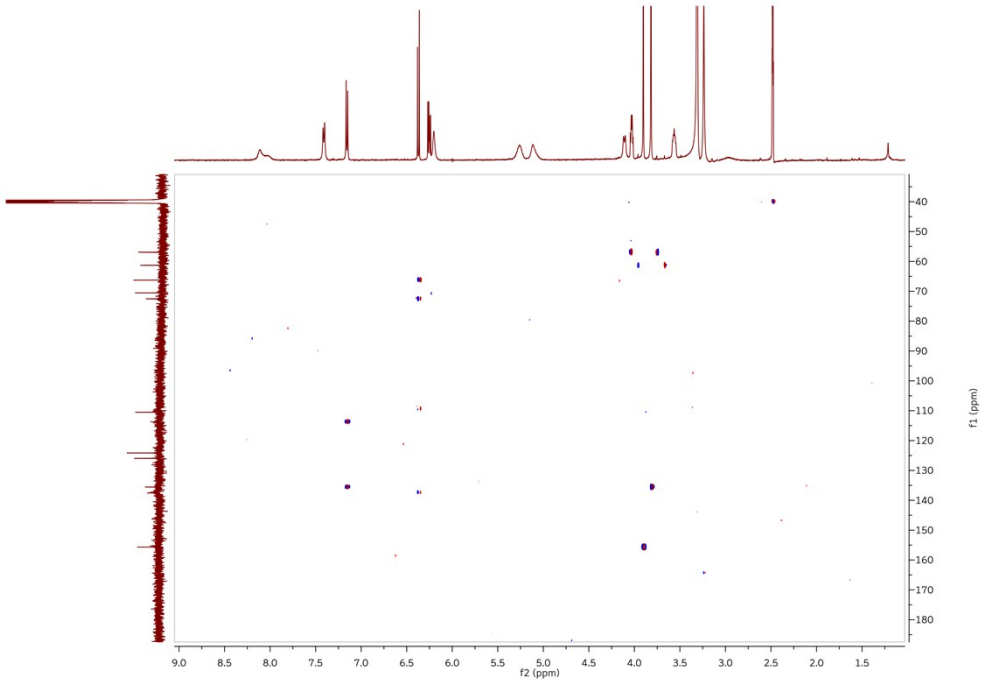


**Figure S23.** HRESIMS spectrum of trichodermamide F (**3**)