Supplementary Materials

Talarodiolide, the new 12-membered macrodiolide, and GC/MS investigation of mycelial and culture filtrate extracts of *Talaromyces pinophilus*

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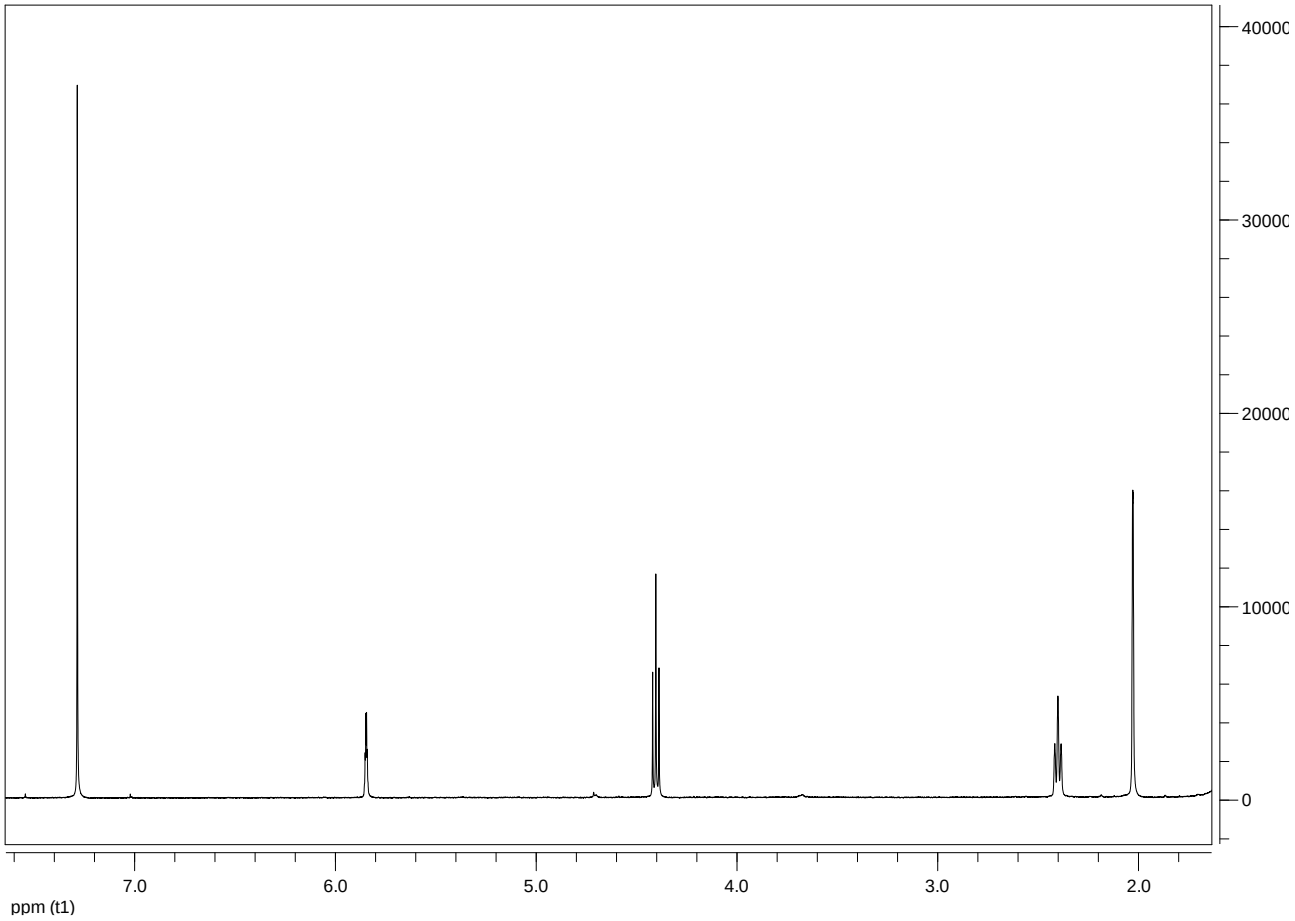


Figure S1. ^{1}H NMR spectrum of talarodiolide (**1**) recorded in $CDCl_3$ at 400 MHz

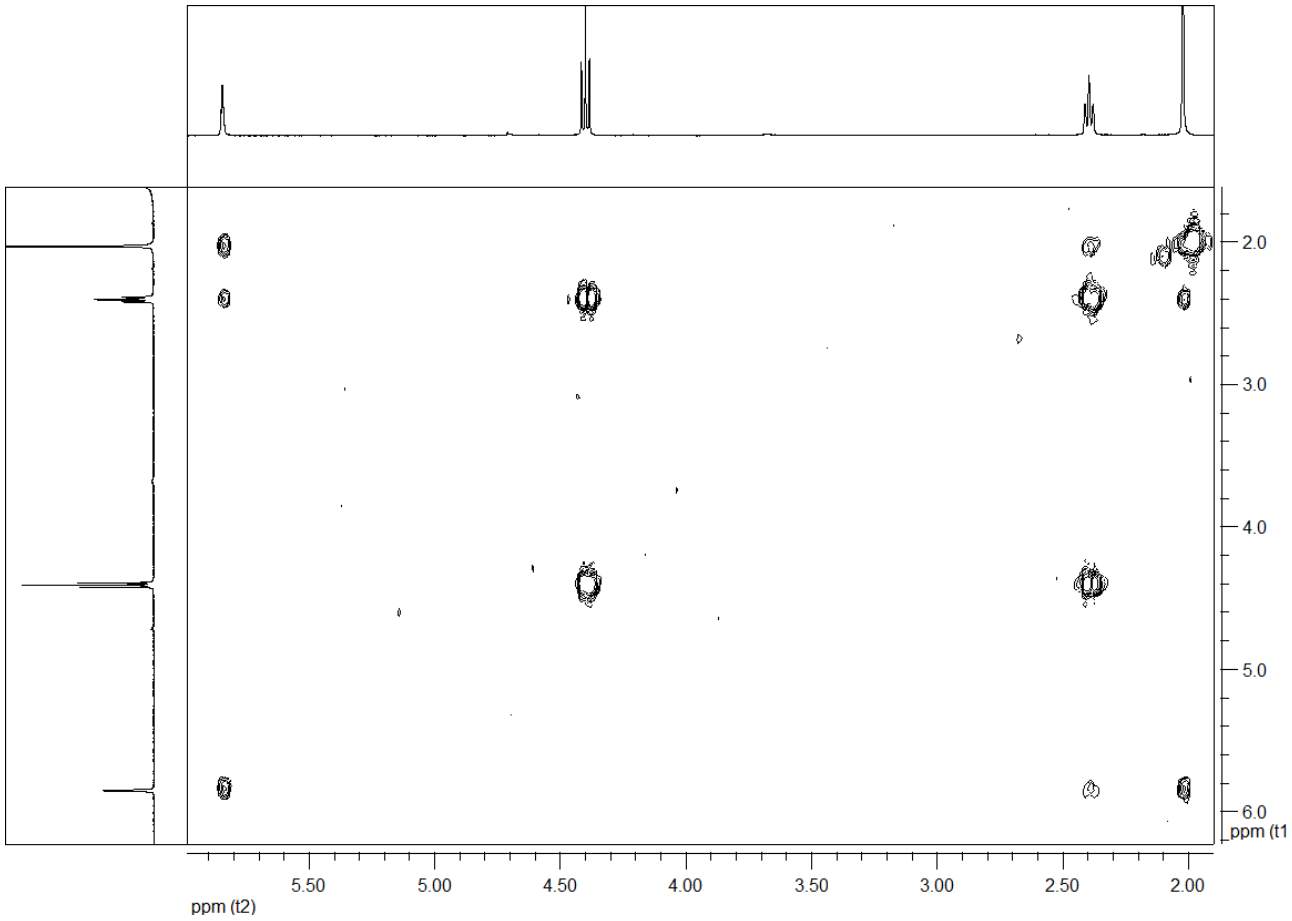


Figure S2. COSY spectrum of talarodiolide (**1**) recorded in $CDCl_3$ at 400 MHz

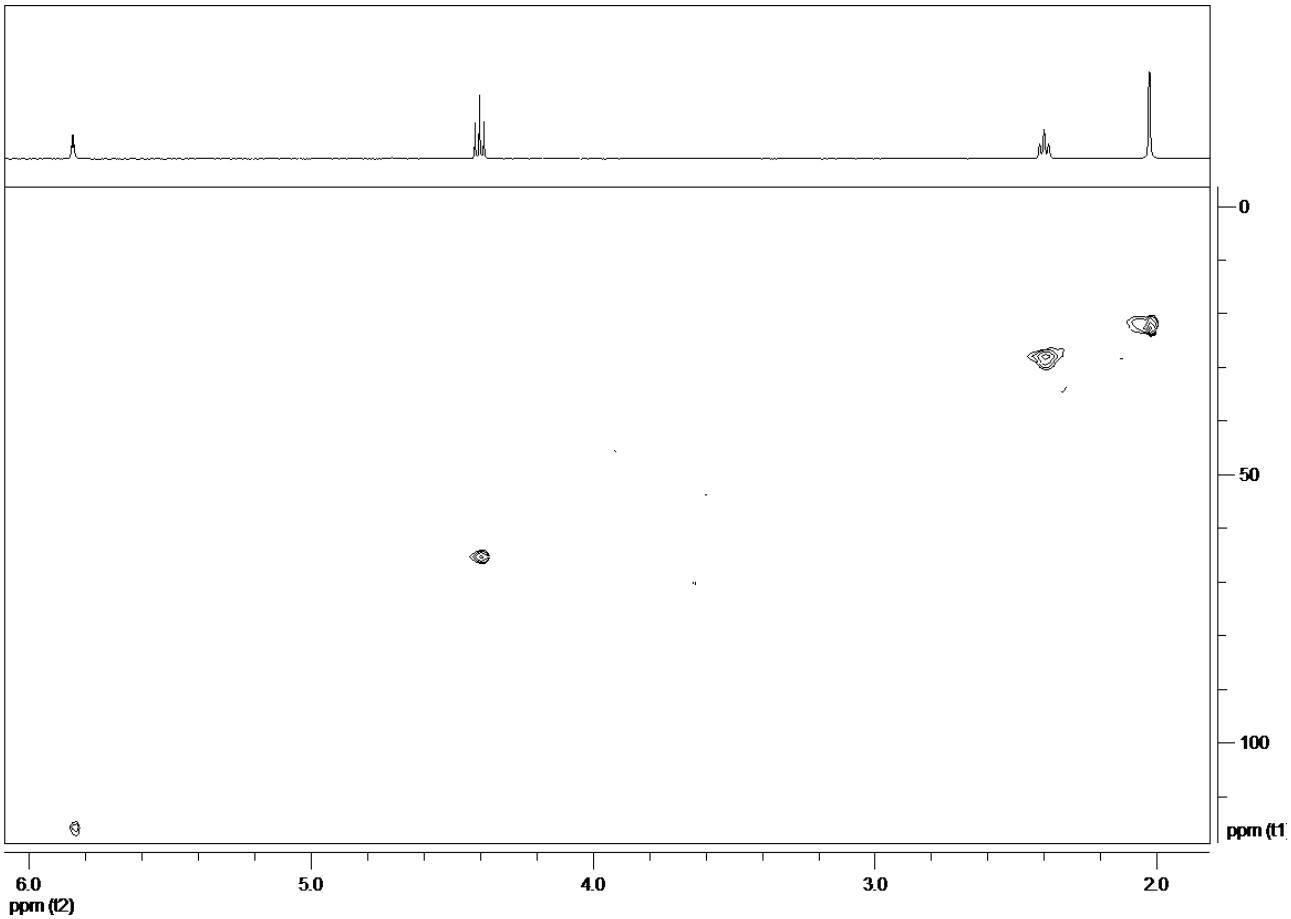


Figure S3. HSQC spectrum of talarodiolide (**1**) recorded in $CDCl_3$ at 400 MHz

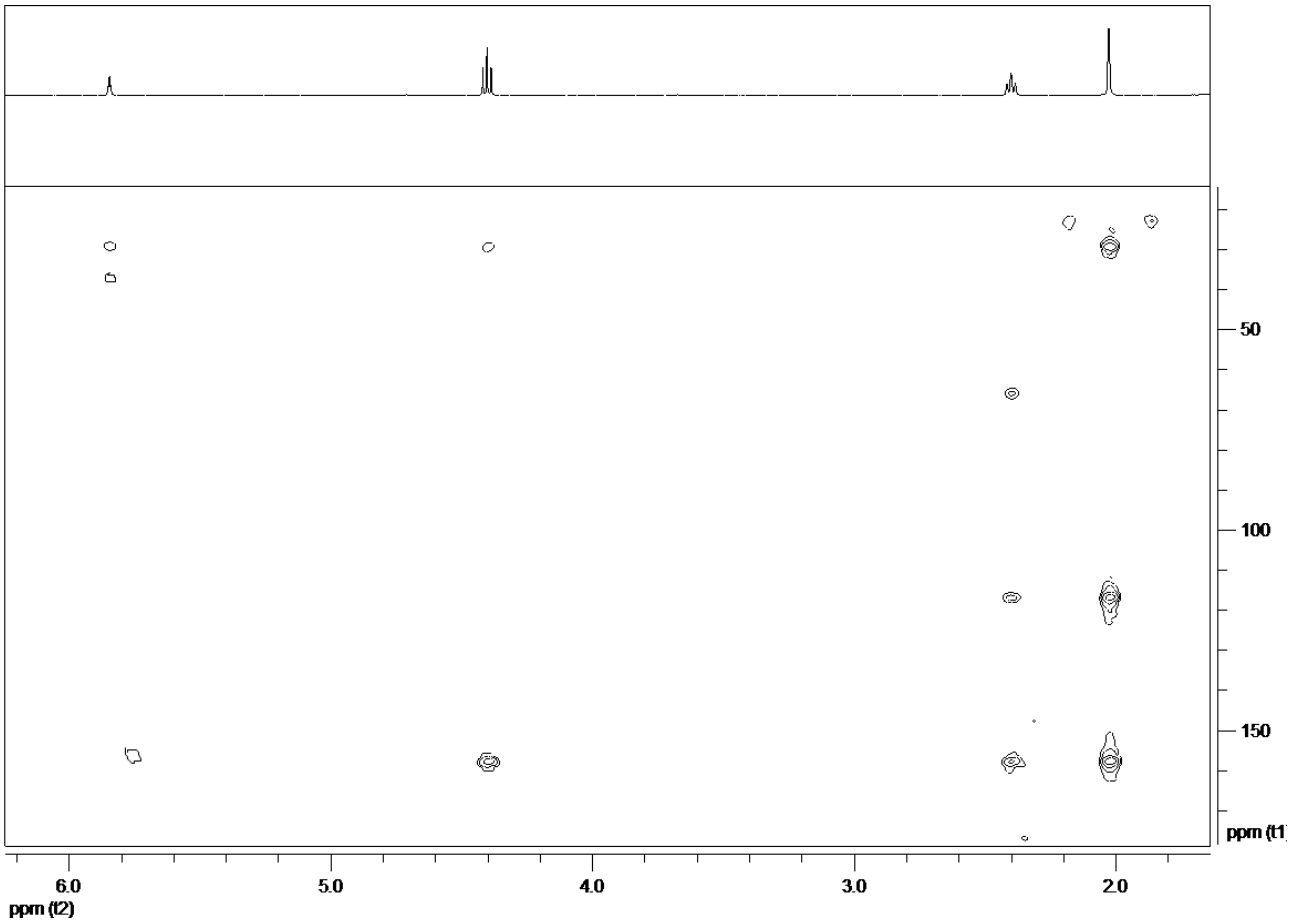


Figure S4. HMBC spectrum of talarodiolide (**1**) recorded in $CDCl_3$ at 400 MHz

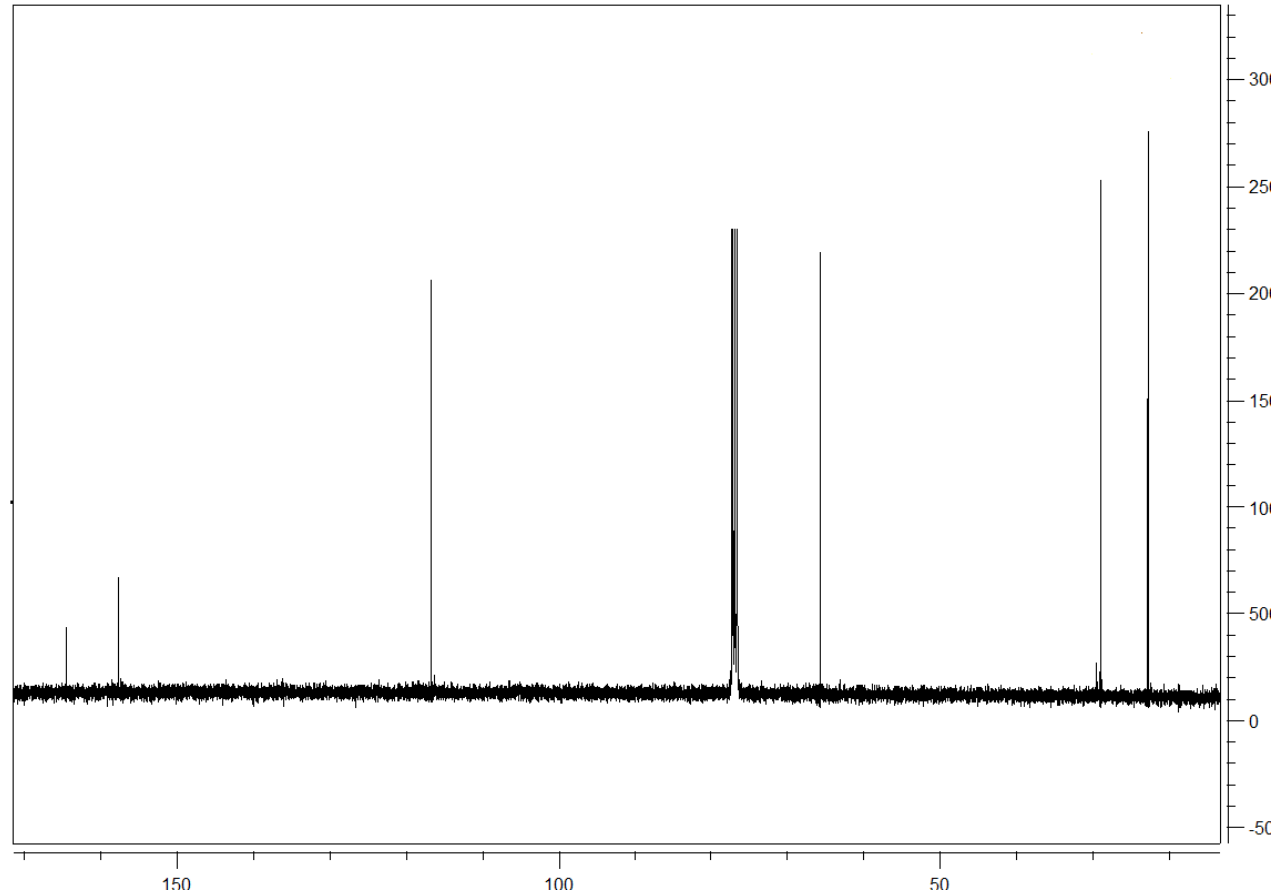


Figure S5. ^{13}C NMR spectrum of talarodiolide (**1**) recorded in $CDCl_3$ at 100 MHz

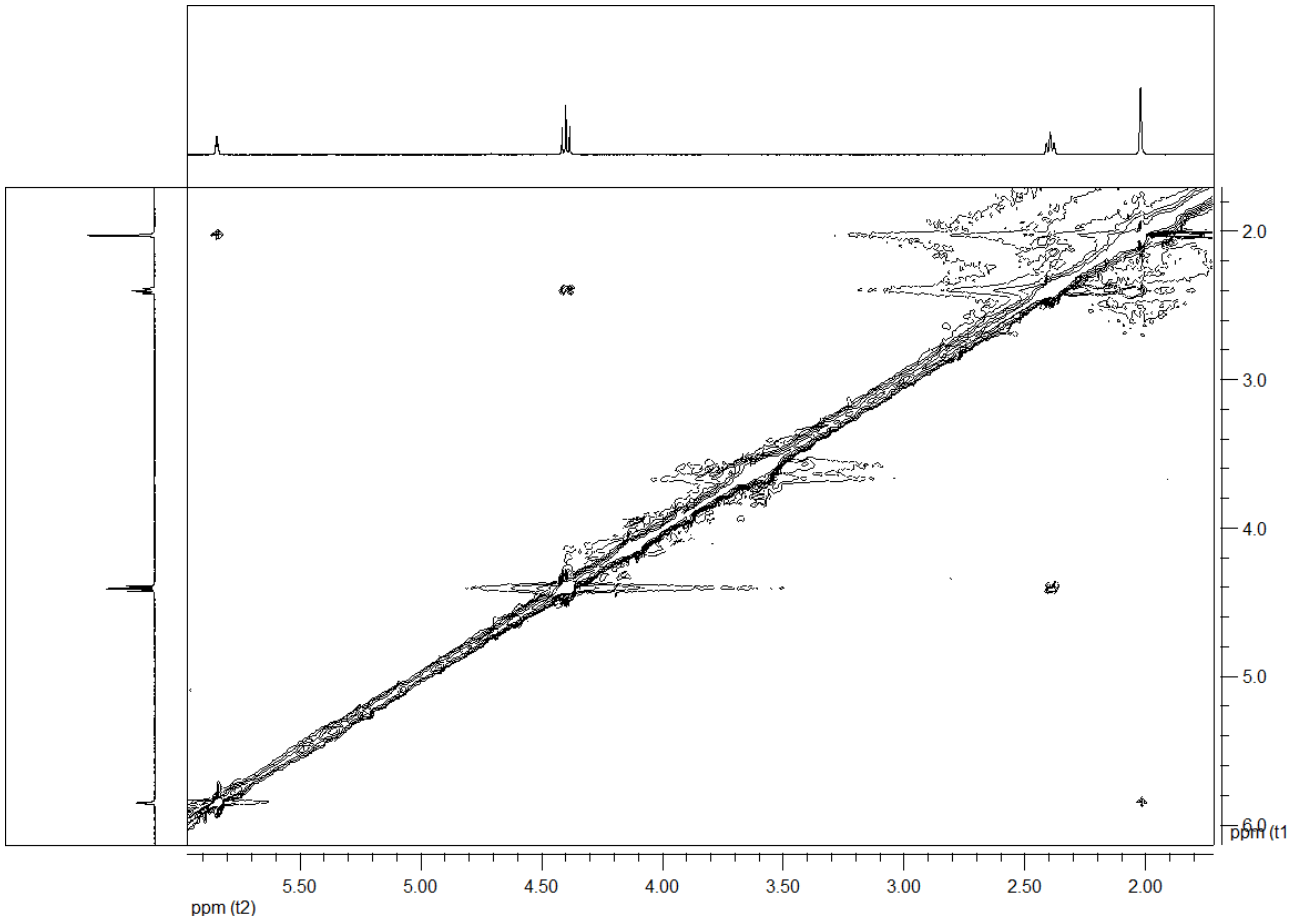
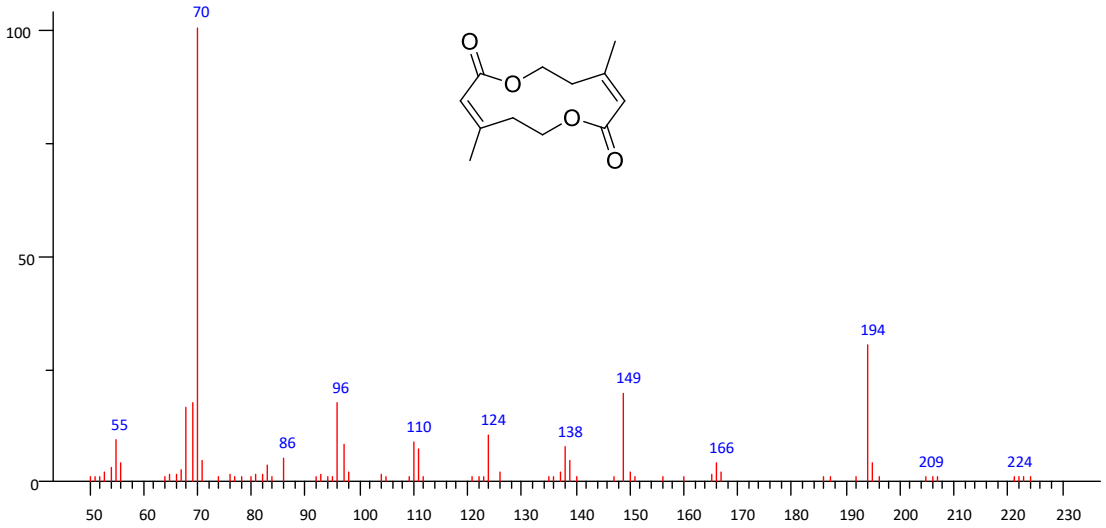
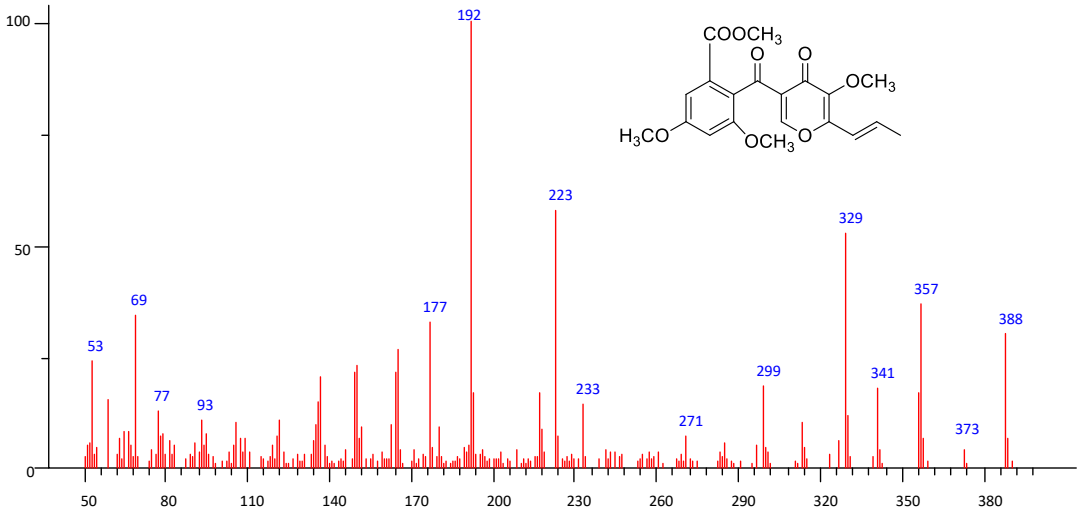
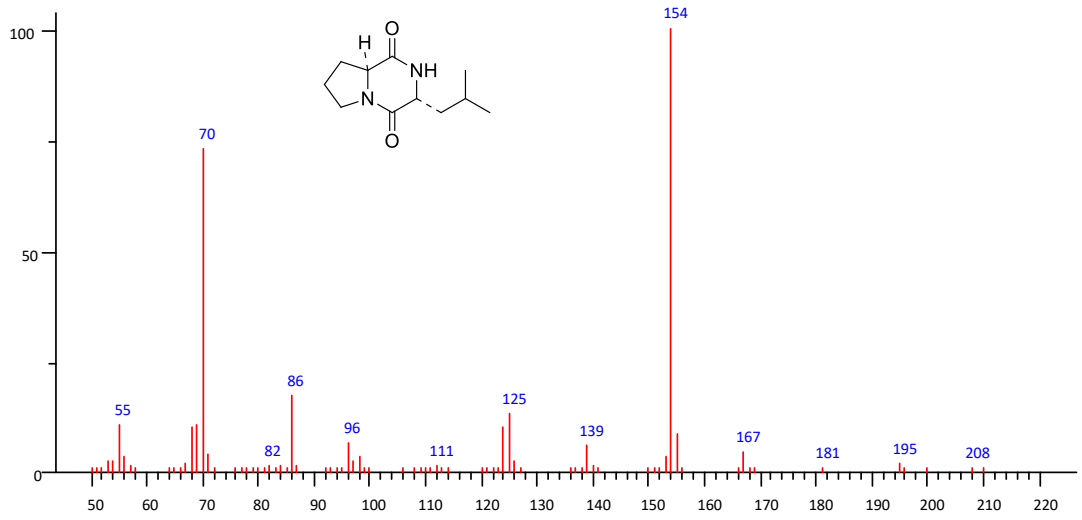


Figure S6. NOESY spectrum of talarodiolide (**1**) recorded in $CDCl_3$ at 400 MHz

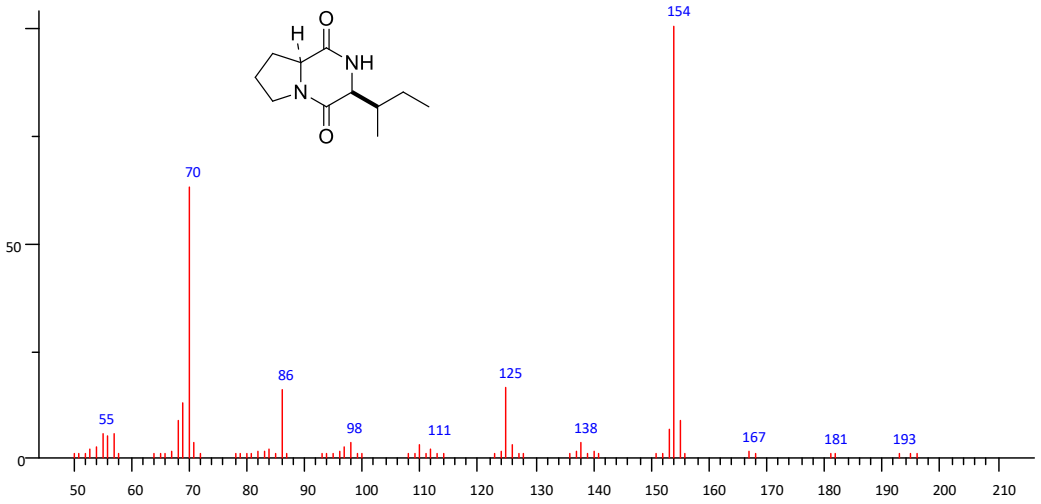
Table S1: Mass spectra of identified metabolites. RI represents the Kovats non isothermal retention index on HP5MS 30 m capillary column. Panel "MS peaks annotations" reports mass, formula (in square brackets) and normalized abundance (in round brackets) of identified fragments in mass spectra; the molecular ion is always represented by M; Me indicates methyl (-CH_3). Abundance is normalized taking abundance of base peak equal 100; for instance array 224 $[M]^+$ (5) represents a molecular ion with integer mass of 224 Dalton present in a mass spectrum at an abundance 5% the abundance of base peak; analogously array 209 $[M\text{-}Me]^+$ (4) represents ion of mass 209 Dalton and abundance 4% which has been formed from the molecular ion by loss of a methyl fragment (15 Dalton).

Talarodiolide **(1)**	RI: 2064	MS peaks annotations: 224 $[M]^{\bullet+}$ (5), 209 $[M\text{-}Me]^+$ (4), 194 $[M\text{-}2Me]^+$ (35), 149 $[M\text{-}2Me\text{-}CO_2\text{-}O]^+$ (60), 70 $[M\text{-}C_8H_9O_3]^+$ (100)
		
3-*O*-methylfunicone **(2)**	RI: 3006	MS peaks annotations: 388 $[M]^{\bullet+}$ (40), 373 $[M\text{-}Me]^+$ (15), 357 $[M\text{-}2Me]^+$, 223 $[M\text{-}C_9O_3H_9]^+$ (65), 192 $[M\text{-}2Me\text{-}C_9O_3H_9]^+$ (100)
		

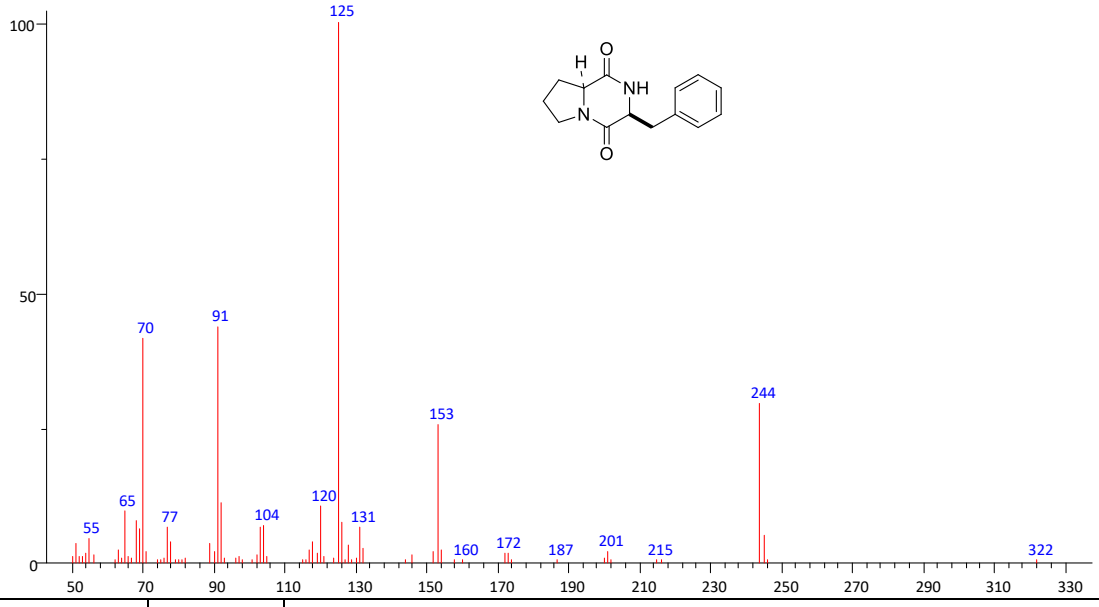
Cyclo-(Pro-Leu) **(3)**	RI: 2068	MS peaks annotations: 195 $[M\text{-}Me]^+$ (5), 154 $[M\text{-}C_4H_9]^+$ (100), 125 $[M\text{-}C_6H_{13}]^+$ (15), 111 $[M\text{-}C_7H_{15}]^+$ (3), 70 $[M\text{-}C_7NO_2H_{11}]^+$ (75)



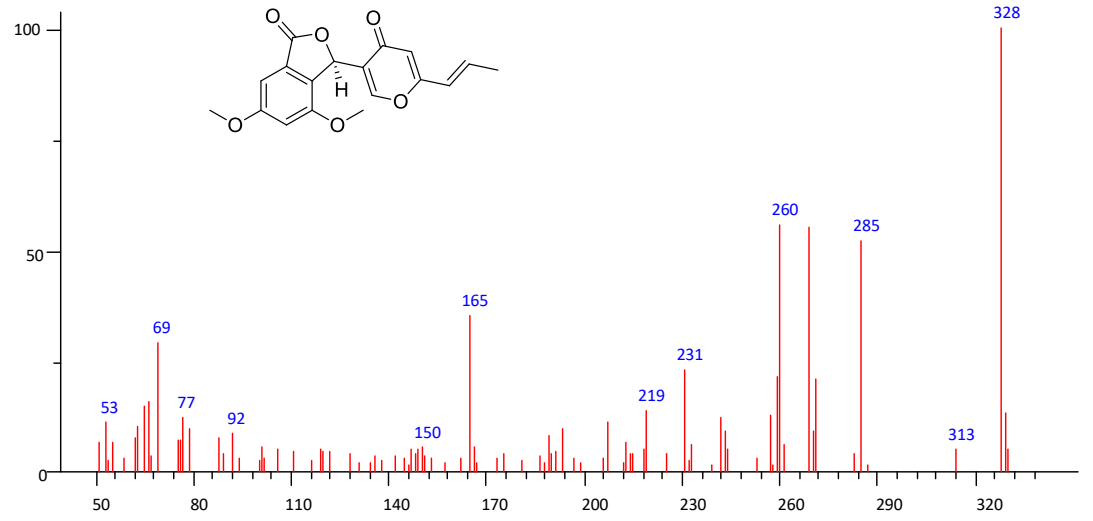
Cyclo-(Pro-Ile) **(4)**	RI: 2039	MS peaks annotations: 154 $[M\text{-}C_4H_9]^+$ (100), 125 $[M\text{-}C_6H_{13}]^+$ (120), 111 $[M\text{-}C_7H_{15}]^+$ (5), 70 $[M\text{-}C_7NO_2H_{11}]^+$ (65)



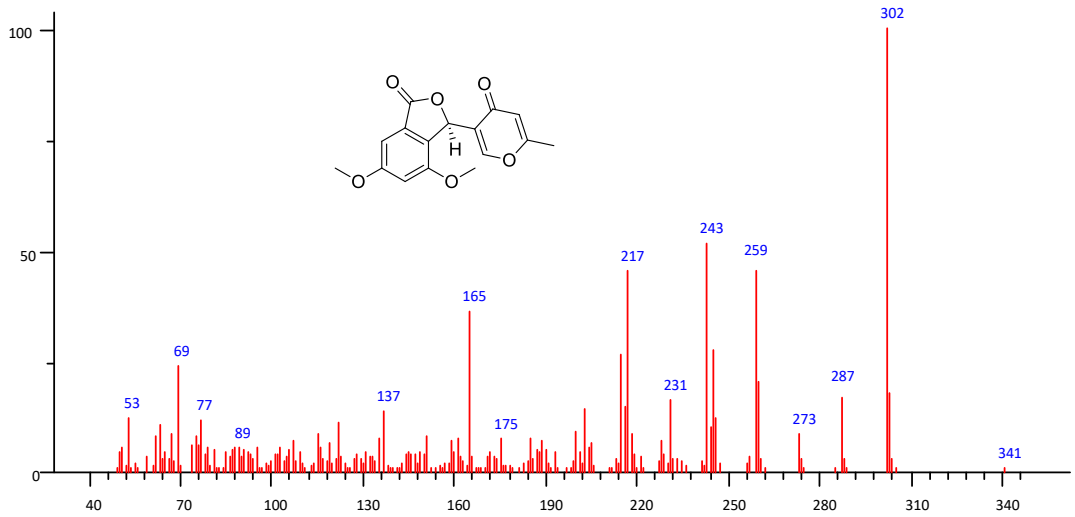
Cyclo (Pro-Phe) **(5)**	RI: 2443	MS peaks annotations: 244 $[M]^{\bullet+}$ (32), 215 $[M\text{-}C_2H_4]^+$ (3), 153 $[M\text{-}C_7H_7]$ (28), 125 $[M\text{-}C_3H_6\text{-}C_6H_5]$ (100)



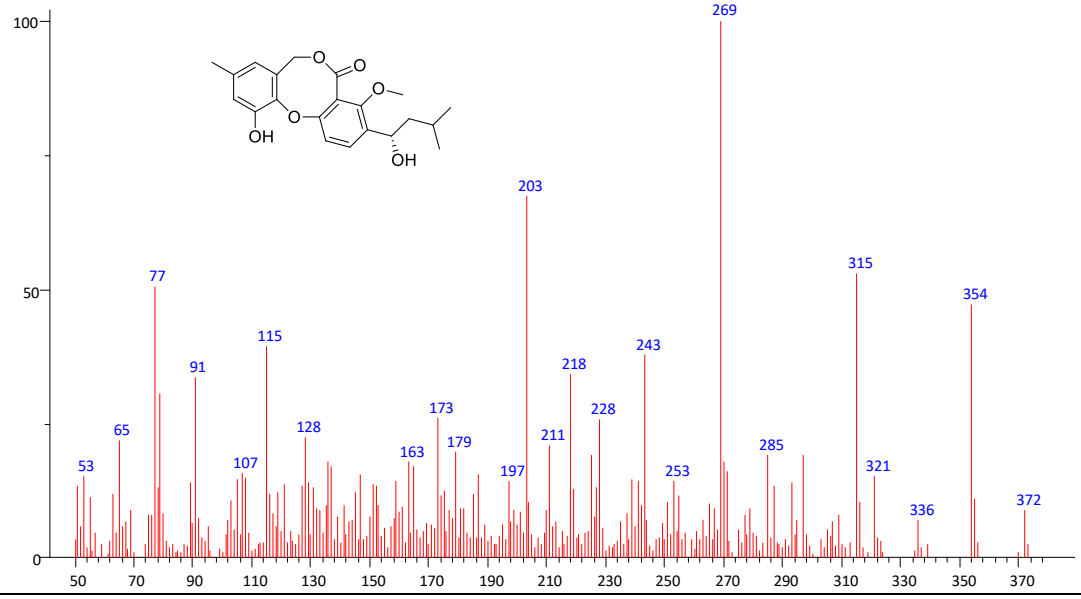
Vermistatin **(6)**	RI: 3105	MS peaks annotations: 328 $[M]^{\bullet+}$ (100), 313 $[M\text{-}Me]^+$ (10), 285 $[M\text{-}Me\text{-}C_2H_4]^+$ (48), 165 $[M\text{-}C_2H_4\text{-}C_8O_2H_8]^+$ (43)



Penisimplicissin **(7)**	RI: 2835	MS peaks annotations: 302 $[M]^{\bullet+}$ (100), 287 $[M\text{-}Me]^{+}$, 273 $[M\text{-}2Me]^{+}$ (17), 175 $[M\text{-}Me\text{-}C_6H_7O_2]$ (14), 165 $[M\text{-}C_8O_2H_8]^{+}$ (47)



Penicillide **(8)**	RI: 3103	MS peaks annotations: 372 $[M\text{-}Me]^{+}$ (16), 269 $[M\text{-}2Me\text{-}C_5OH_{10}]$ (100), 253 $[M\text{-}Me\text{-}OCH_3\text{-}C_5OH_{10}]$ (20)



1-glycerol-linoleate **(9)**	RI: 2076	MS peaks annotations: 354 $[M]^{\bullet+}$ (4), 336 $[M\text{-}OH]^+$, 262 $[M\text{-}C_3O_3H_7]^+$ (63), 234 $[M\text{-}C_4O_4H_7]^+$ (12)