

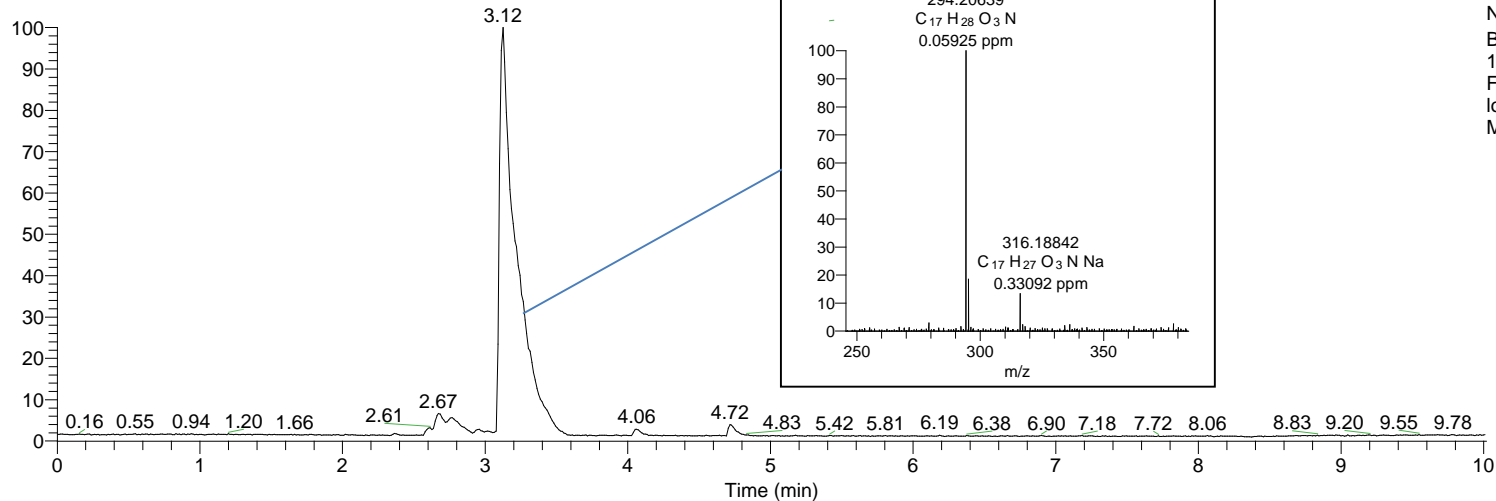
**Table S1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts for the  $\Delta\text{CYP107AK1}$  intermediates i and ii in  $\text{CD}_3\text{OD}$  with 0.1% TFA-d.

C No.	i			ii		
	$\delta_{\text{C}}$	Type	$\delta_{\text{H}}$ mult. (J in Hz)	$\delta_{\text{C}}$	Type	$\delta_{\text{H}}$ mult. (J in Hz)
1	23.0	CH <sub>2</sub>	1.76 m	22.9	CH <sub>2</sub>	1.74 m
2	30.4	CH <sub>2</sub>	1.75 m 1.22 m	30.4	CH <sub>2</sub>	1.74 m 1.23 m
3	29.0	CH <sub>2</sub>	2.11 m 1.14 m	29.0	CH <sub>2</sub>	2.11 m 1.14 m
4	45.2	CH	2.04 m	45.3	CH	2.04 m
5	41.1	CH	1.49 m	41.7	CH	1.42 m
6	34.6	CH <sub>2</sub>	1.68 ddd (12.7, 1.9, 0.2) 1.57ddd (12.7, 12.6, 6.7)	31.8	CH <sub>2</sub>	1.81 m 1.46 m
7	32.3	CH	2.58 m	39.5	CH	2.29 m
8	138.4	CH	6.18 dd (3.1, 2.8)	137.3	CH	6.22 dd (3.1, 2.8)
9	a	-	-	a	-	-
10	32.3	CH <sub>3</sub>	1.11 d (7.3)	29.4	CH <sub>2</sub>	1.54 m 1.37 m
11	-	-	-	12.6	CH <sub>3</sub>	1.00 t (7.3)
12	171.9	C=O	-	171.9	C=O	-
14	58.0	CH	4.50 m	a	CH	4.51 m
17	38.5	CH	1.96 m	38.6	CH	1.95 m
18	15.0	CH <sub>3</sub>	0.91 d (6.8)	15.0	CH <sub>3</sub>	0.91 d (6.8)
20	27.2	CH <sub>2</sub>	1.45 m 1.20 m	27.2	CH <sub>2</sub>	1.45 m 1.18 m
24	11.9	CH <sub>3</sub>	0.94 t (7.5)	11.8	CH <sub>3</sub>	0.95 t (7.3)

<sup>a</sup> No signal detected

**A**

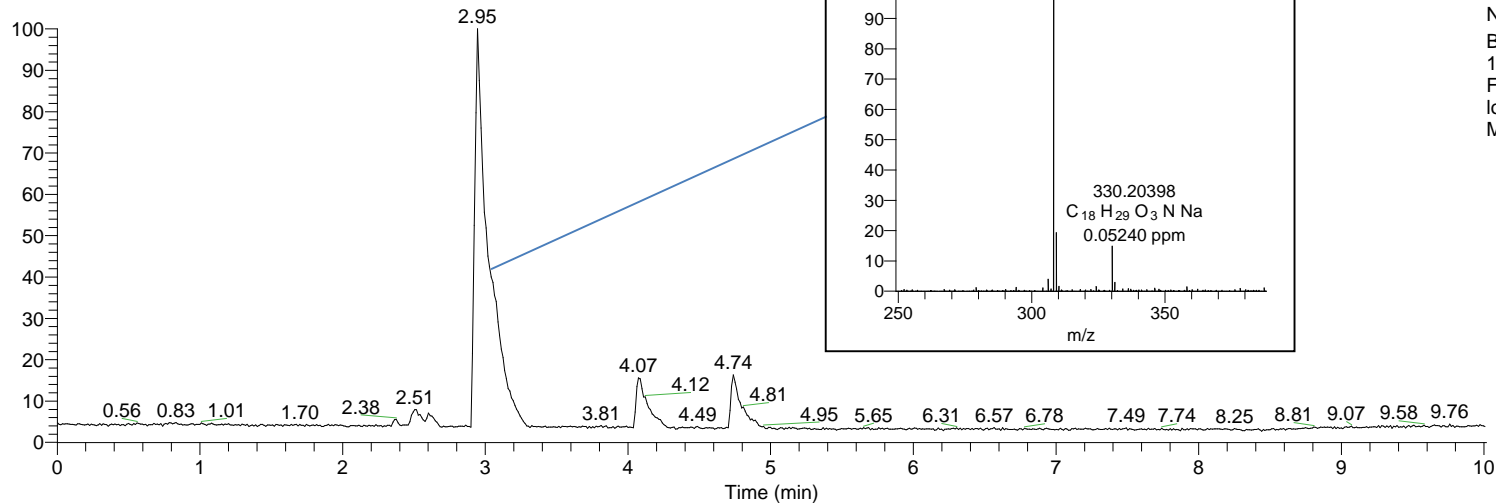
RT: 0.00 - 10.02



NL: 5.39E6  
Base Peak m/z=  
190.00000-2000.00000 F:  
FTMS (1,1) + p ESI Full  
lock ms [190.00-2000.00]  
MS CFA-ILE\_HCD\_B

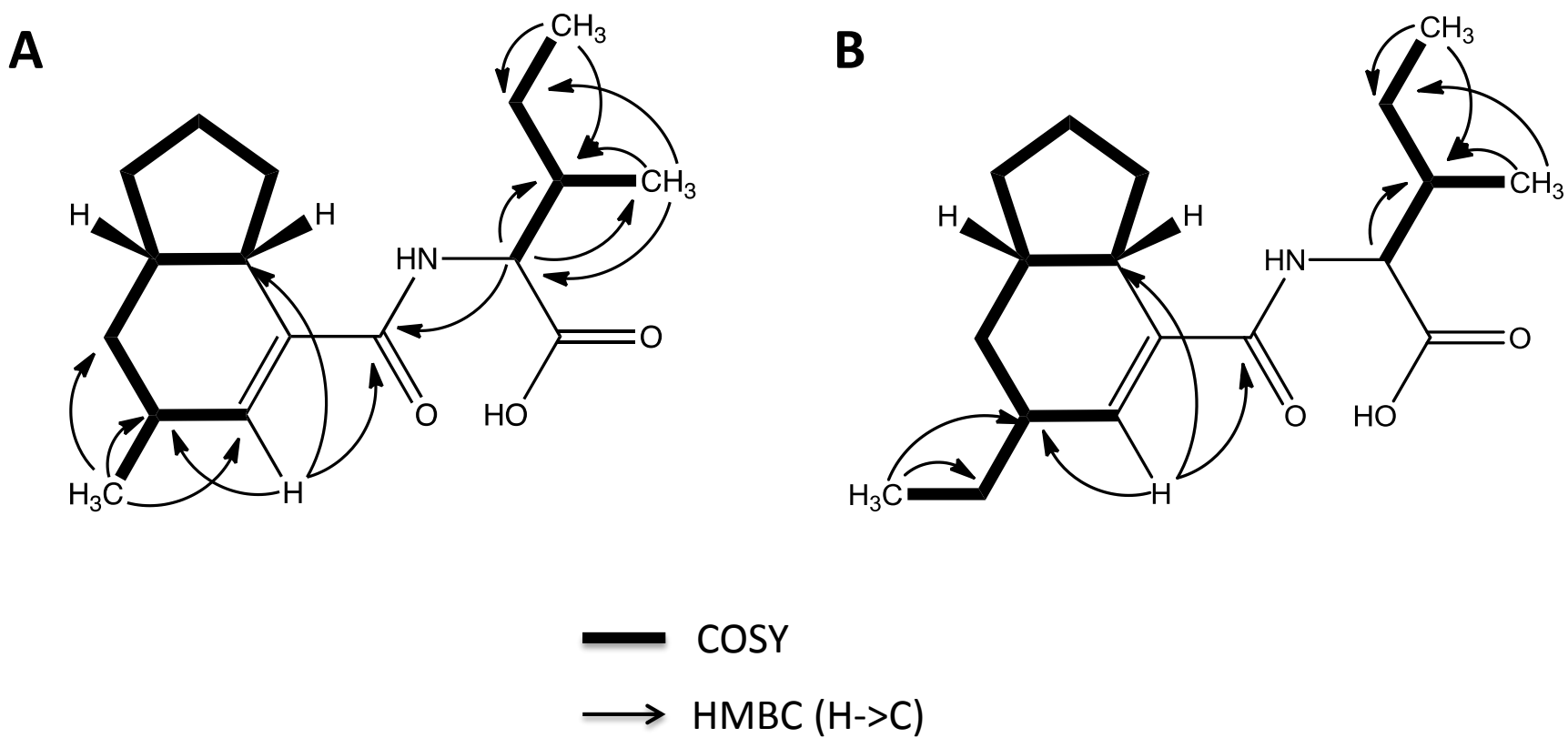
**B**

RT: 0.00 - 10.02

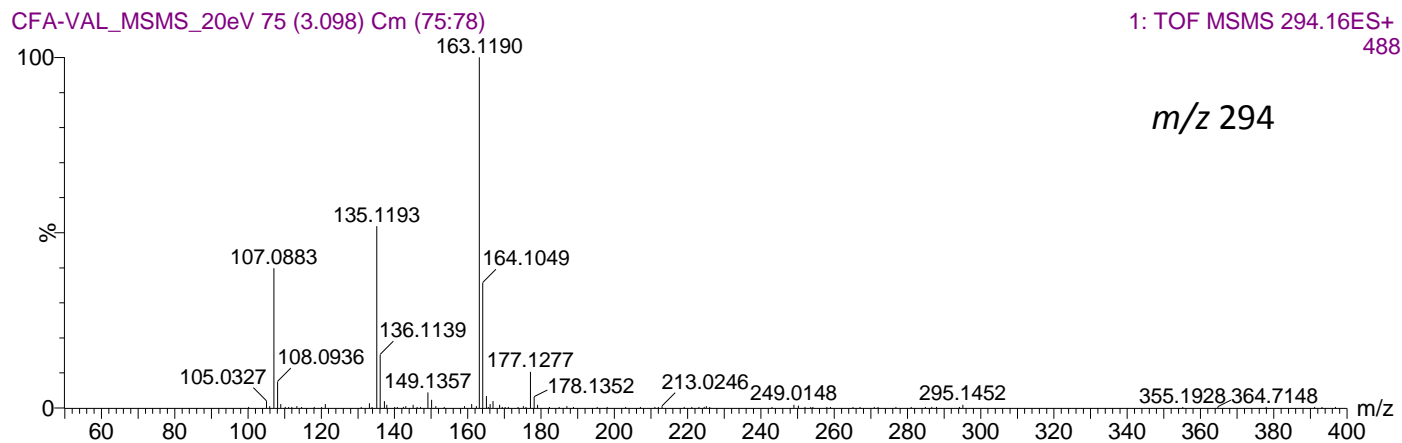
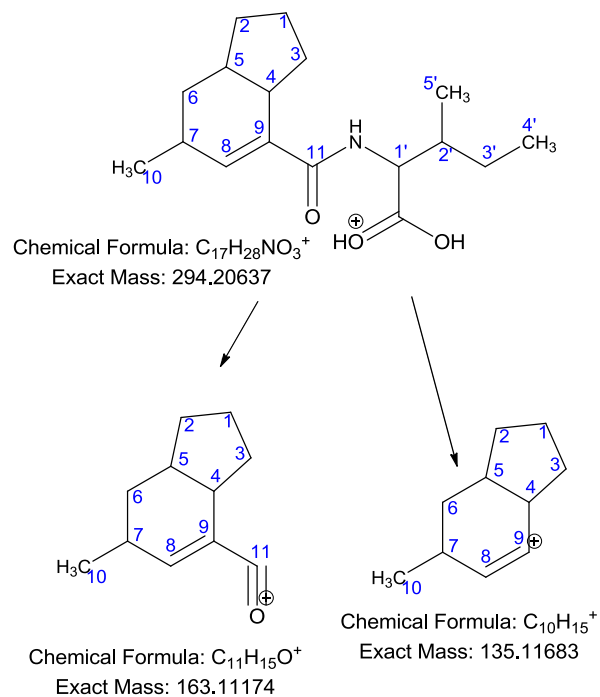


NL: 1.85E6  
Base Peak m/z=  
190.00000-2000.00000 F:  
FTMS (1,1) + p ESI Full  
lock ms [190.00-2000.00]  
MS CFA-VAL\_HCD\_B

**Figure S1.** LC-HRMS analysis of the purified intermediates i (A) and ii (B) from the *S. scabiei*  $\Delta$ CYP107AK1 mutant.



**Figure S2.** Key COSY and HMBC correlations of the purified intermediates i (A) and ii (B) from the *S. scabiei*  $\Delta$ CYP107AK1 mutant.

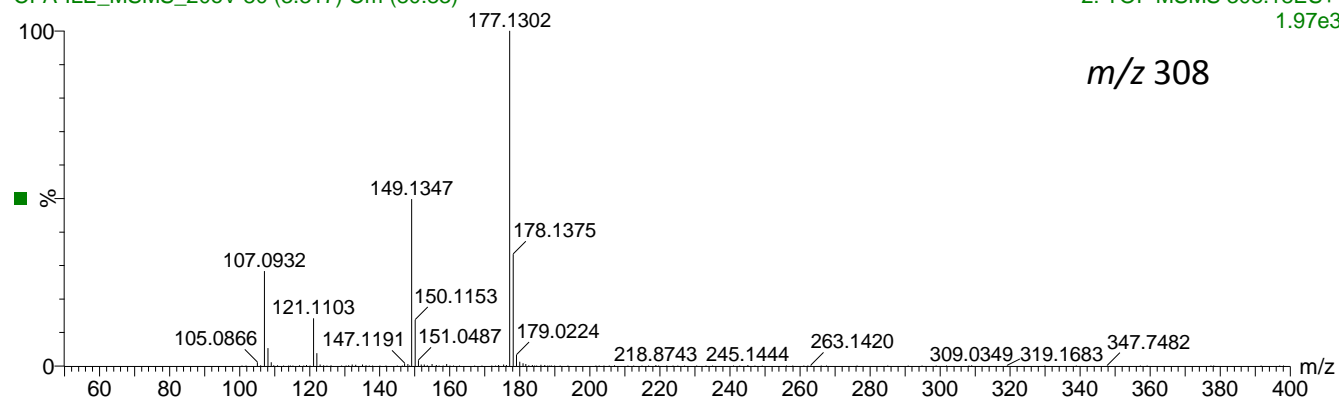
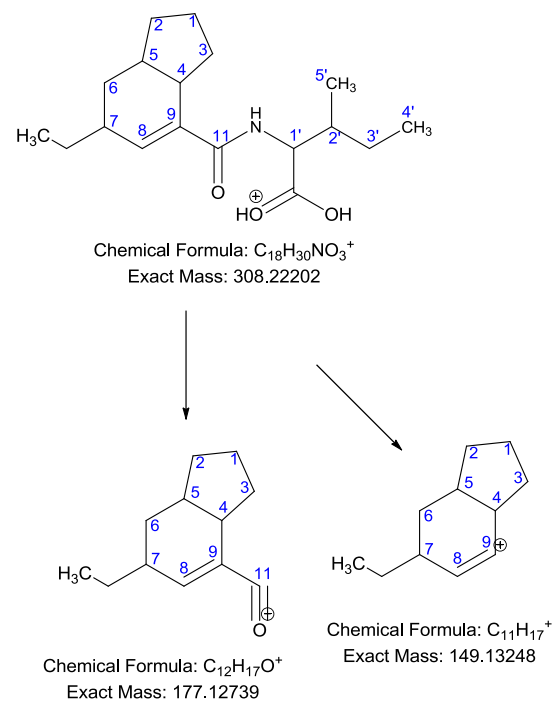
**A****B**

**Figure S3.** (A) Tandem MS spectrum of the purified intermediate *i*. The presence of the ion fragments at  $m/z$  163.1190 and 135.1193 confirm the proposed structure of *i*. (B) Expected fragmentation pattern of the intermediate *i*.

**A**

CFA-ILE ~ 1 ug/mL in MeOH 0.1%FA (FB)

CFA-ILE\_MSMS\_20eV 80 (3.317) Cm (80:83)

2: TOF MSMS 308.18ES+  
1.97e3**B**

**Figure S4.** (A) Tandem MS spectrum of the purified intermediate ii. The presence of the ion fragments at  $m/z$  177.1302 and 149.1347 confirm the proposed structure of ii. (B) Expected fragmentation pattern of the intermediate ii.