

Supporting Information

Genome Mining in *Streptomyces avermitilis*.
A Biochemical Baeyer-Villiger Reaction and
Discovery of a New Branch of the Pentalenolactone
Family Tree[†]

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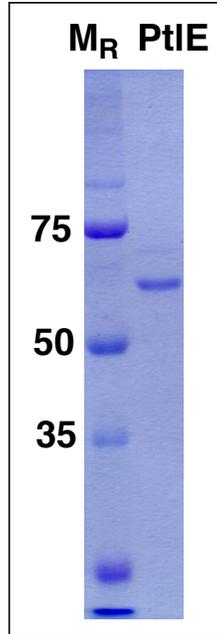


Figure S1. SDS-PAGE of recombinant PtIE. M_R , MW marker (kDa).

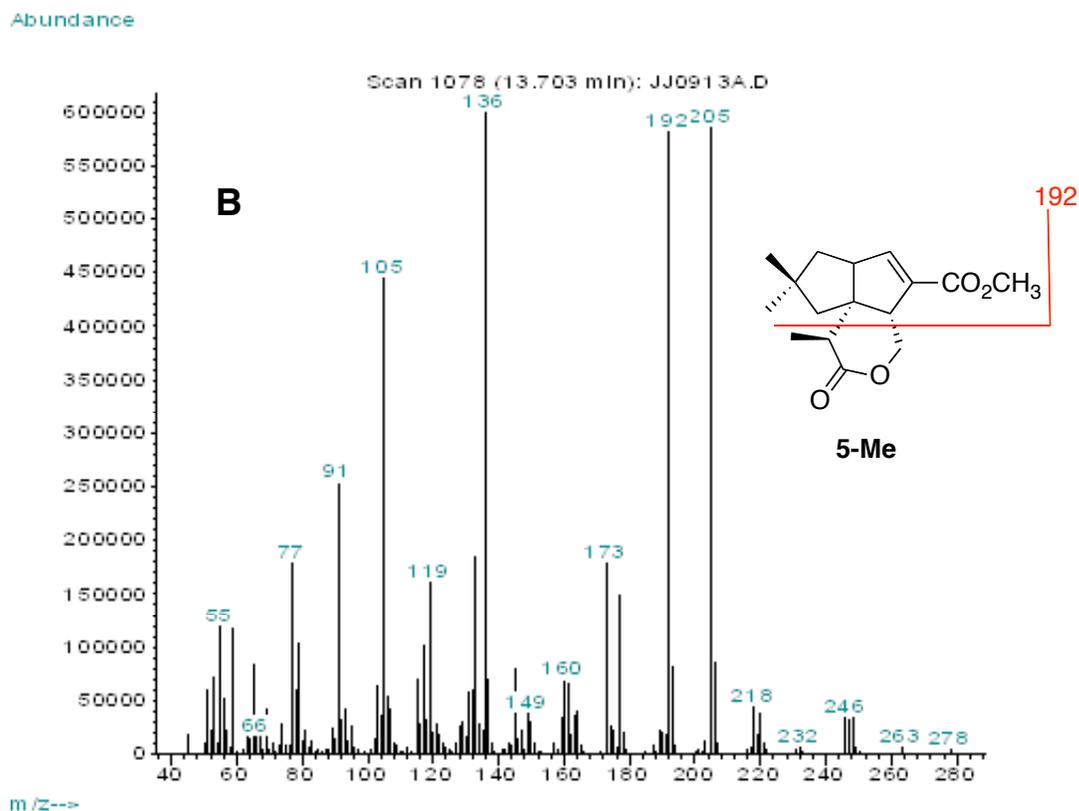
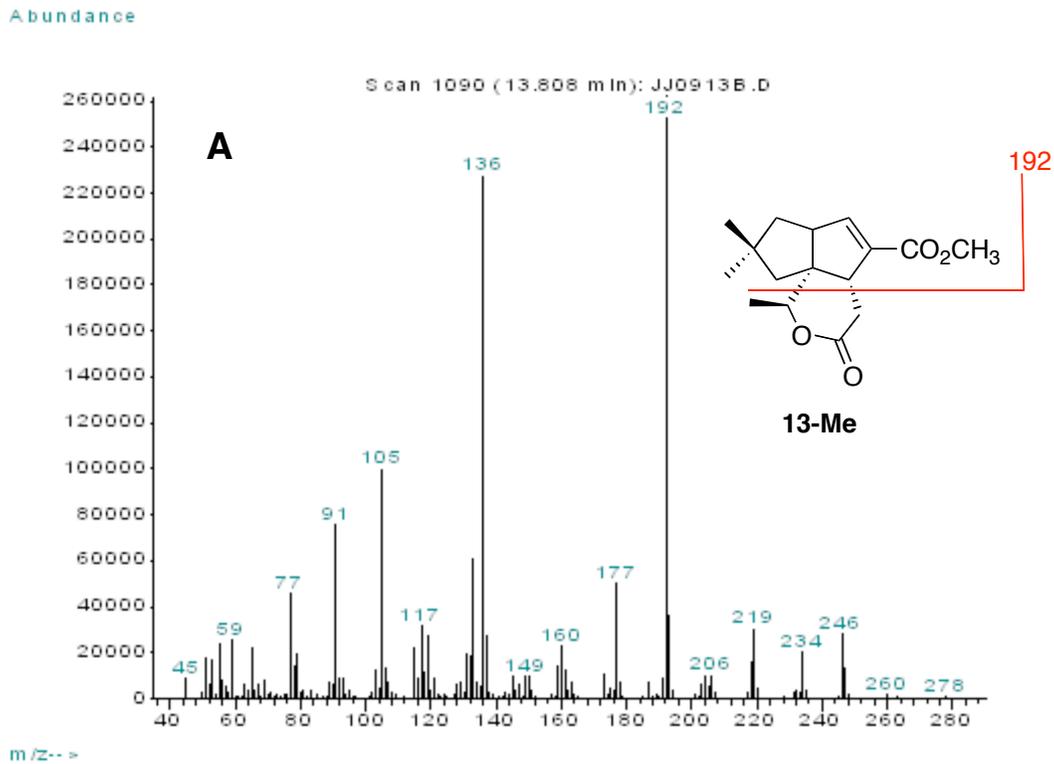


Figure S2. EI-Mass spectra of (A) neopentalenolactone D methyl ester (**13-Me**); (B) pentalenolactone D methyl ester (**5-Me**) isolated from *Streptomyces* UC5319

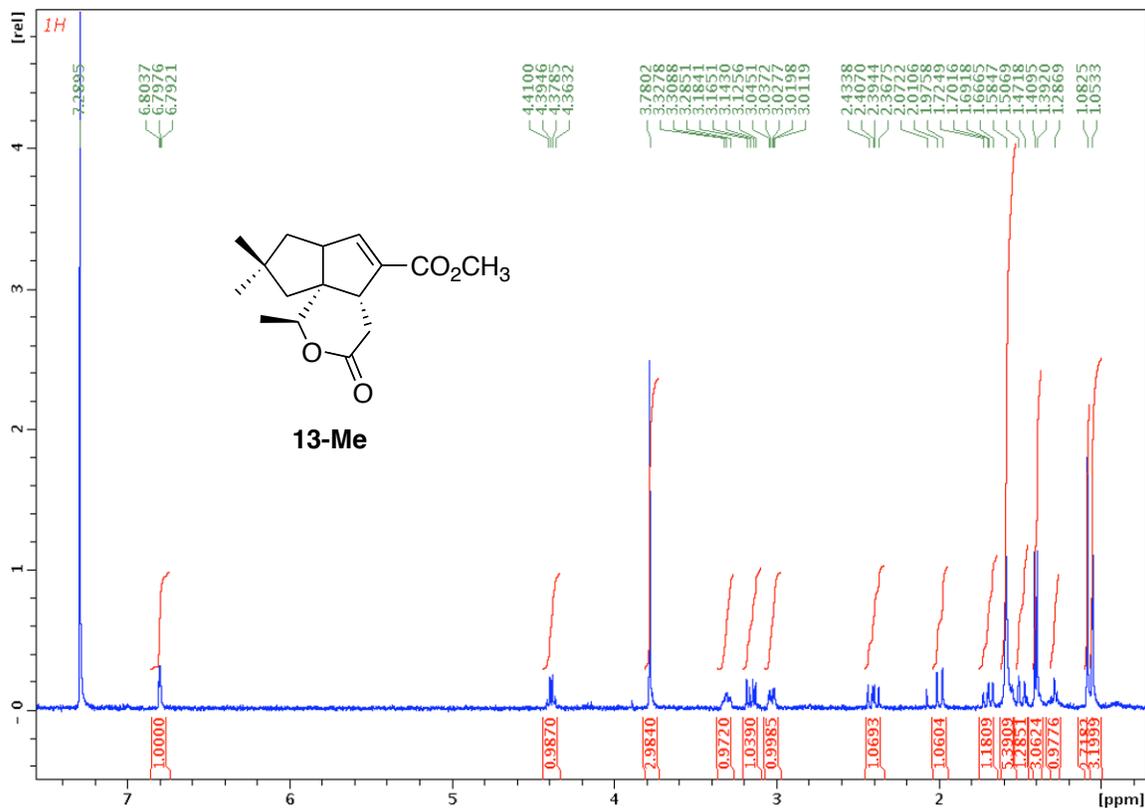


Figure S3. ^1H NMR spectrum (400 MHz, CDCl_3) of neopentalenolactone D methyl ester (**13-Me**).

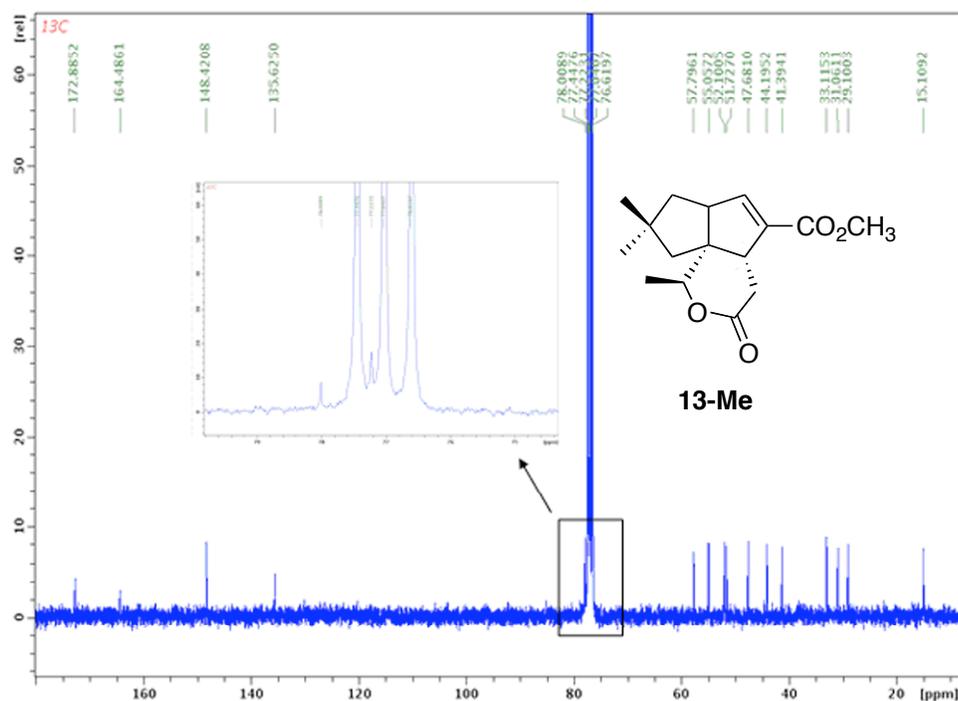


Figure S4. ^{13}C NMR spectrum (75 MHz, CDCl_3) of neopentalenolactone D methyl ester (**13-Me**).

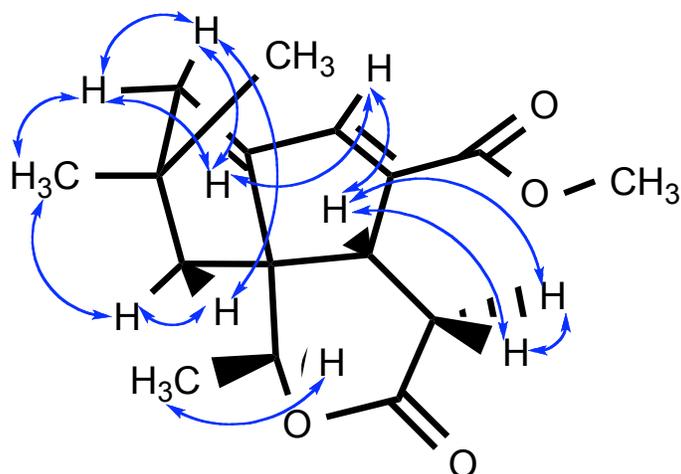
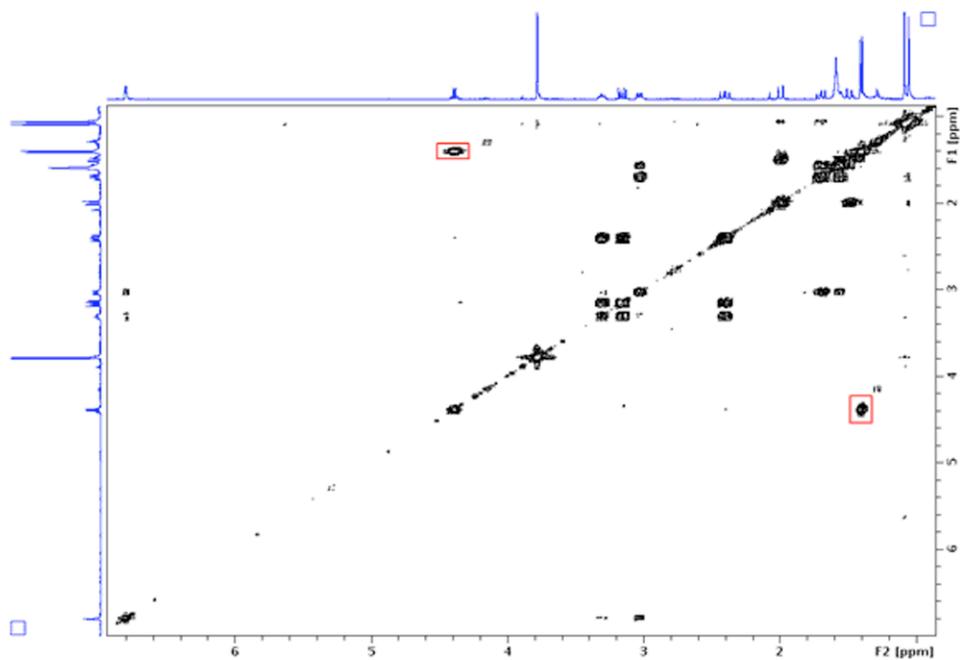


Figure S5. COSY spectrum and the observed ^1H - ^1H couplings of neopentalenolactone D methyl ester (**13-Me**). The H-9/H-10 crosspeaks are indicated by red boxes.

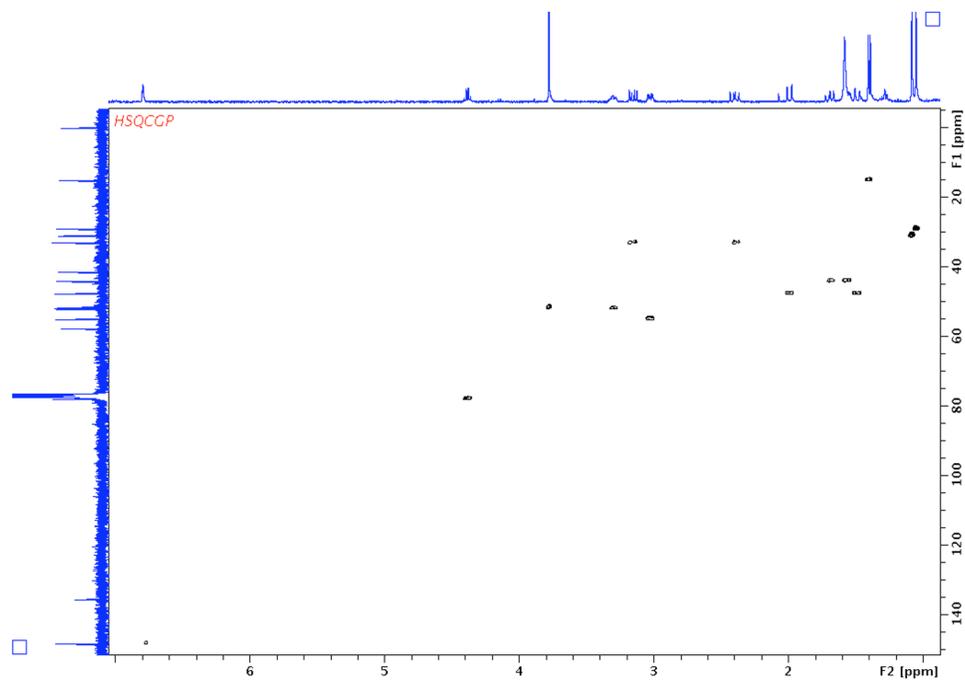


Figure S6. HSQC spectrum of neopentalenolactone D methyl ester (**13-Me**).

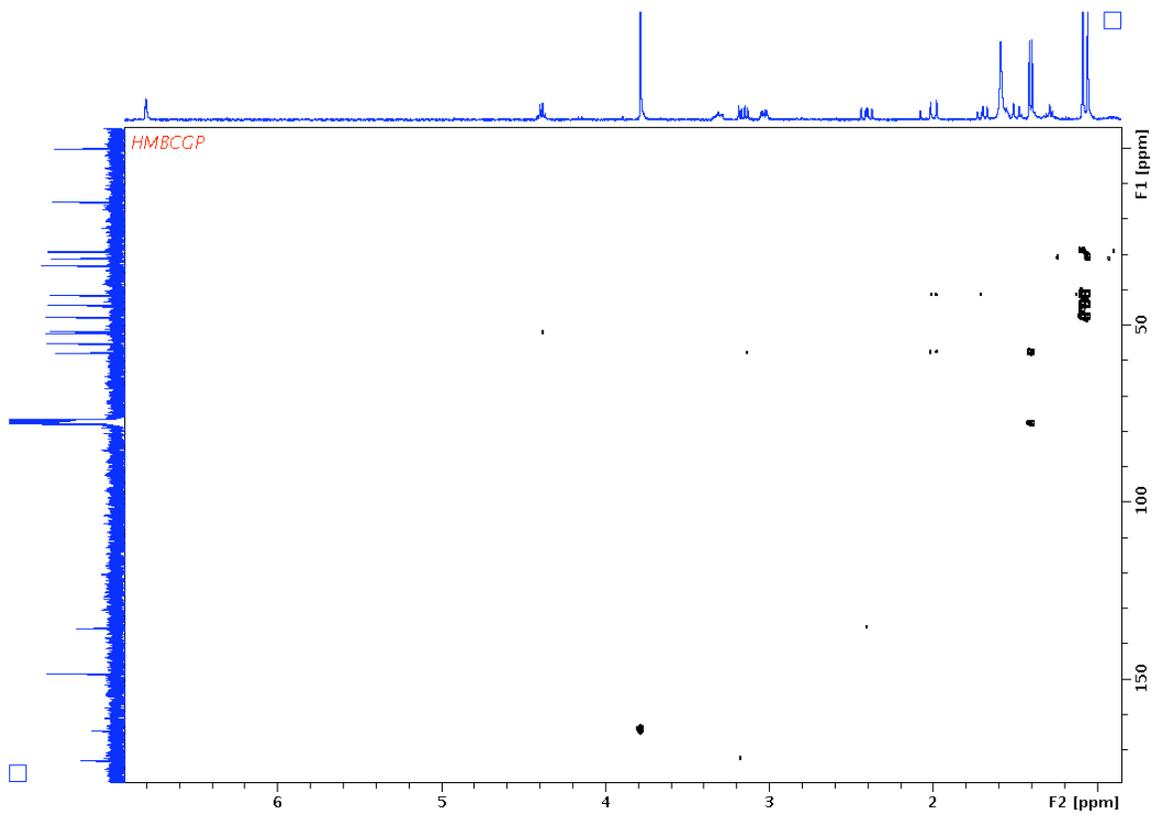


Figure S7. HMBC spectrum of neopentalenolactone D methyl ester (**13-Me**).

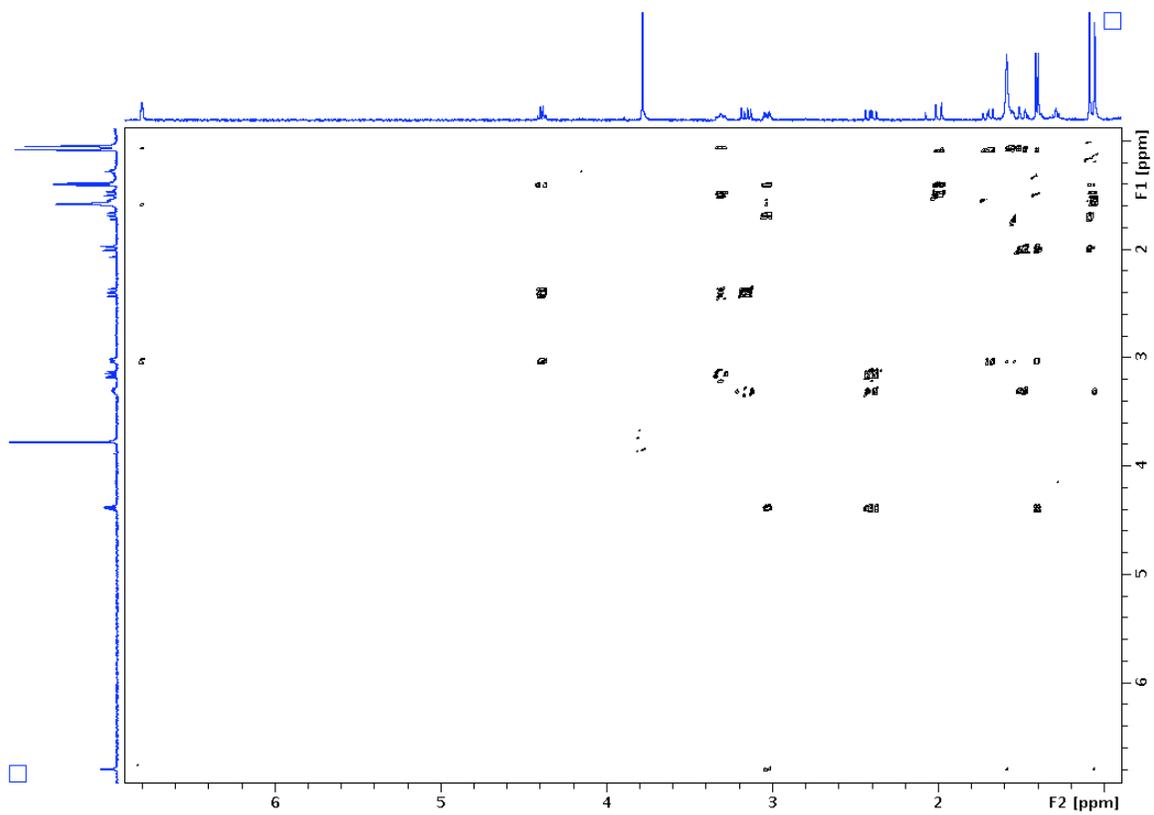


Figure S8. NOESY spectrum of neopentalenolactone D methyl ester (**13-Me**).

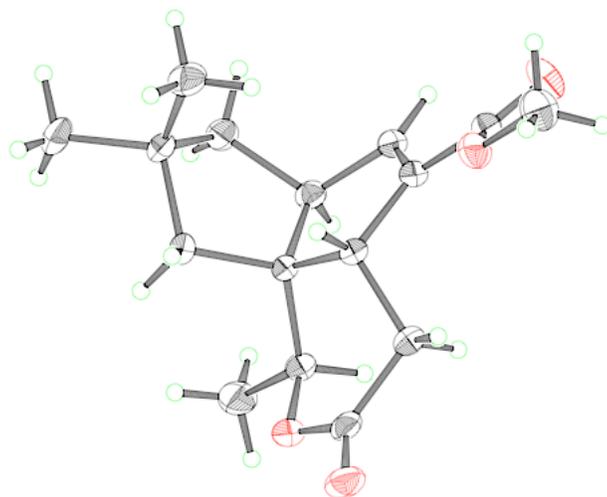


Figure S9. X-ray crystal structure of neopentalenolactone D methyl ester (**13-Me**).

Figure S10. (Following page) Alignment of *S. avermitilis* PtlE (Q82IY8, SAV2994) with known Baeyer-Villigerases and putative monooxygenases: A7HSA3 (cyclohexanone monooxygenase, 59% identity, 73% similarity) from *Parvibaculum lavamentivorans* DS-1; Q1D8E0 (53% identity, 69% similarity) from *Myxococcus xanthus* DK 1622; Q89NI1 (53% identity, 68% similarity) from *Bradyrhizobium japonicum* USDA 110; Q1T7B5 (cyclopentadecanone monooxygenase, CpdB, 52% identity and 68% similarity) from *Pseudomonas* sp. HI-70; A0AD32 (SAMR0677, 52% identity, 66% similarity) from *S. ambofaciens* ATCC 23877; SCAB11301 (51% identity, 64% similarity) from *S. scabies* 87.22; B1VPM8 (SGR6949, 48% identity, 60% similarity) from *S. griseus* IFO 13350; and Q9RL17 (SCO0300, 48% identity, 60% similarity) from *S. coelicolor* A3(2).

