Figure S1: Total ion chromatograms of the products obtained from incubations of FPP with AS (black), ASF178Y (blue), and ASF178V (red). Products are labelled as in the main text.
Figure S2: Mass spectra of product 3 from ASF178 catalysis (A) and of authentic germacrene A (B).
**Figure S3:** Mass spectra of product 6 from ASF178 catalysis (A) and of authentic valencene (B).
Figure S4: Mass spectra of product 7 from ASF178 catalysis (A) and of authentic α-selinene (B).
Figure S5: Mass spectra of product 8 from ASF178 catalysis (A) and of authentic β-selinene (B).
Figure S6: Mass spectra of product 9 from ASF178 catalysis (A) and of authentic selina-4,11-diene (B).
Figure S7: Mass spectra of product 10 from ASF178 catalysis (A) and of authentic (E)-β-farnesene (B).
**Figure S8:** Mass spectra of product 11 from ASF178 catalysis (A) and of authentic (E,E)-α-farnesene (B).
**Figure S9:** Determination of the absolute configuration of germacrene A produced by ASF178V.  

**A.** GC-trace of a racemic mixture of β-elemenes.  

**B.** GC-trace of a co-injection of racemic β-elemenes and the β-elemene produced from FPP by ASF178V.  

**C.** GC-trace of a co-injection of racemic β-elemenes and (+)-β-elemene produced from (S)-germacrene A. (S)-germacrene A was generated using wild type AS.  

**D.** Relation of (R)- and (S)-germacrene A to the β-elemenes formed in Cope rearrangements at increased temperatures. Method: The absolute configuration of germacrene A produced by ASF178V catalysis was determined using a GC equipped with a 30 m (0.25 mm) heptakis (-O-TBDMS-2, 3-di-O-methyl)-β-cyclodextrin (50% in OV17) chiral column. The method developed by de Kraaker et al.,¹ was used. Splitless injections
with an injector temperature of 250°C induced the Cope rearrangement of the enzymatically produced germacrene A.²

**Figure S10:** Relative orientation of residues Tyr 92, Phe 178, and Trp 334 in the active site of aristolochene synthase. Coordinates are from the X-ray structure of the apo-enzyme (pdb-file:1DI1).³
References