

Electronic Supplementary Information for

**Stabilisation of transition states prior to and following eudesmane cation in
aristolochene synthase**

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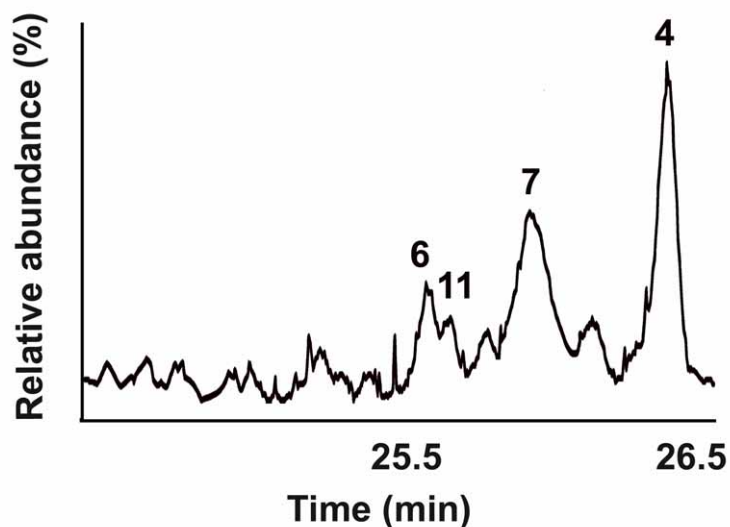


Fig. 1S: Total Ion Chromatogram of AS-F178C.

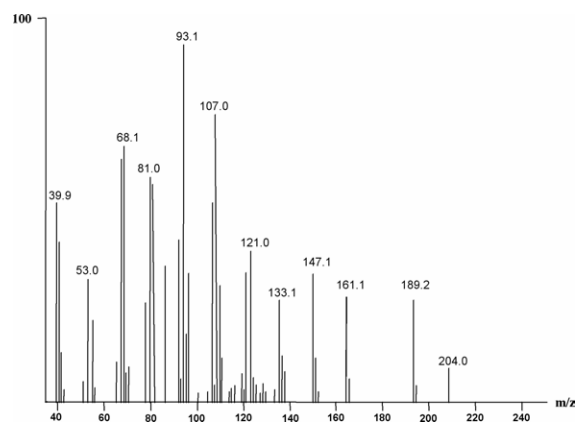


Fig. 2S: MS of germacrene A (4) produced by AS-F178C

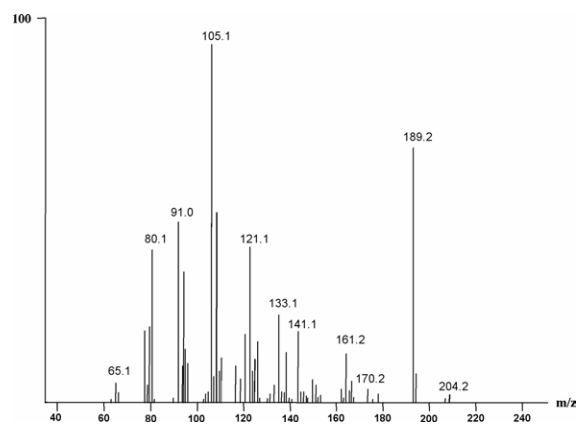


Fig 3S: MS of aristolochene (6) produced by AS-F178C

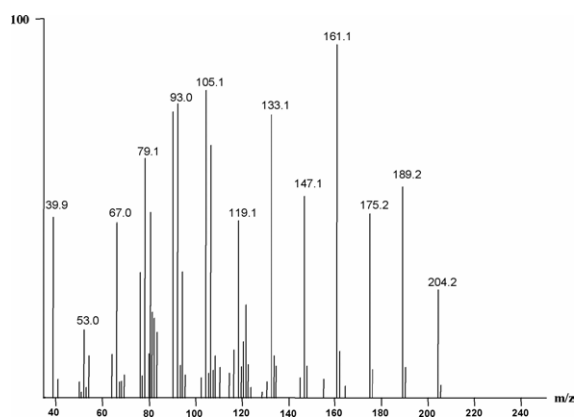


Fig 4S: MS of valencene (7) produced by AS-F178C

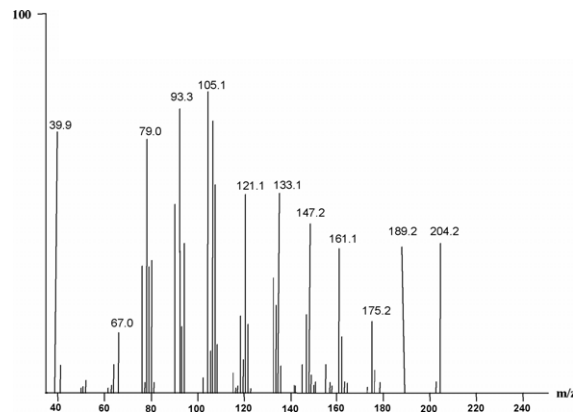


Fig 5S: MS of β -selinene (11) produced by AS-F178C

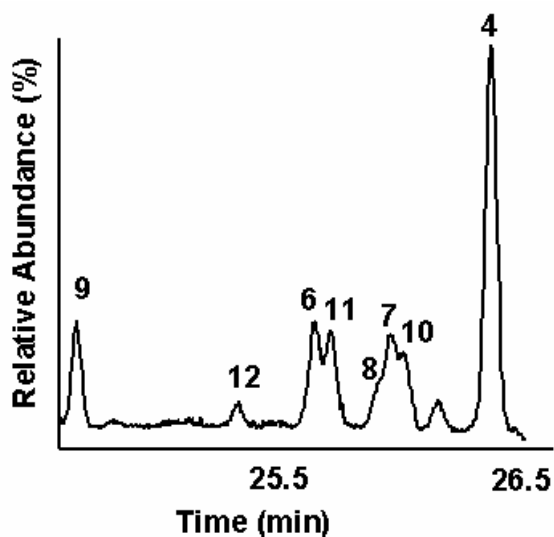


Fig. 6S: TIC of AS-F178V. All data for AS-F178V is from Forcat & Allemann, 2004.¹

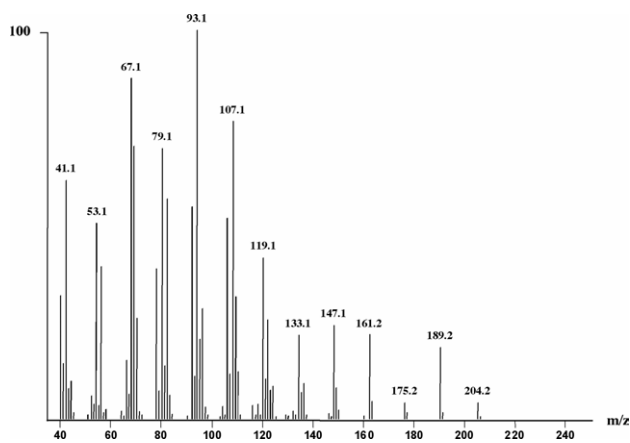


Fig. 7S: MS of germacrene A (4) produced by AS-F178V

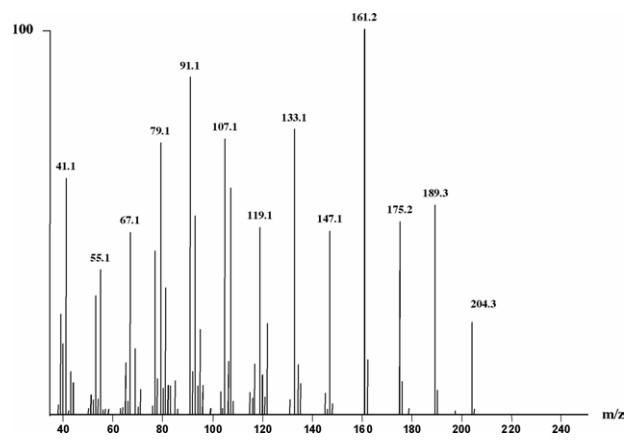


Fig 8S: MS of valencene (7) produced by AS-F178V

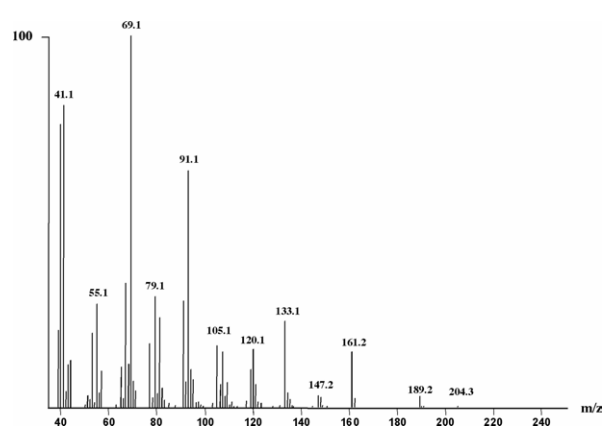
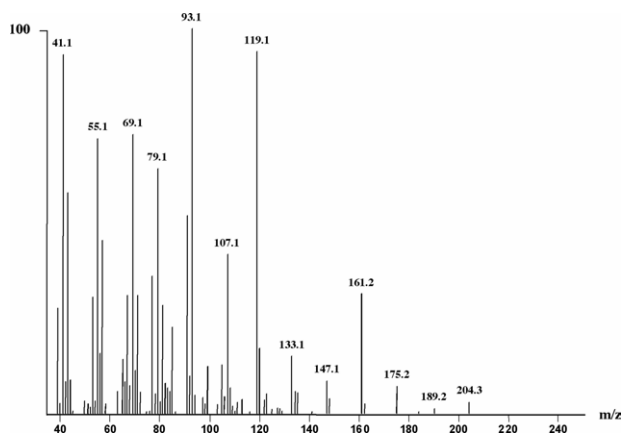


Fig 10S: MS of β -farnesene (9) produced by AS-F178V

100 -

Fig 9S: MS of α -farnesene (**8**) produced by AS-F178V

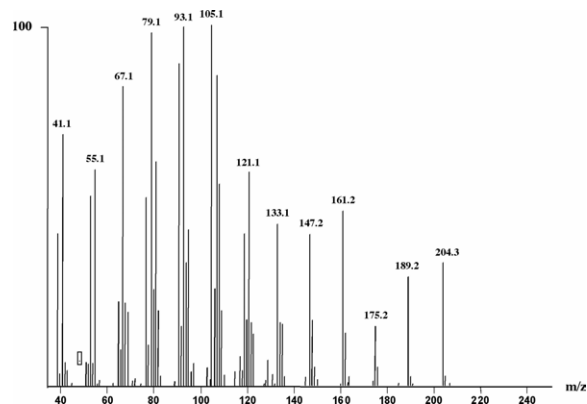
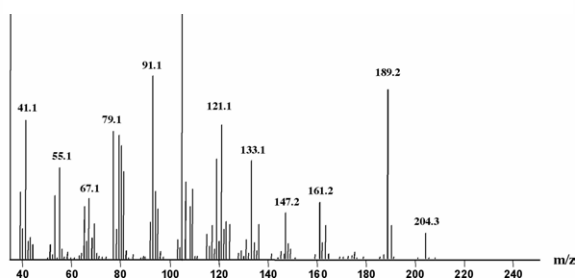


Fig 11S: MS of α -selinene (**10**) produced by AS-F178V

Fig 12S: MS of β -selinene (**11**) produced by AS-F178V

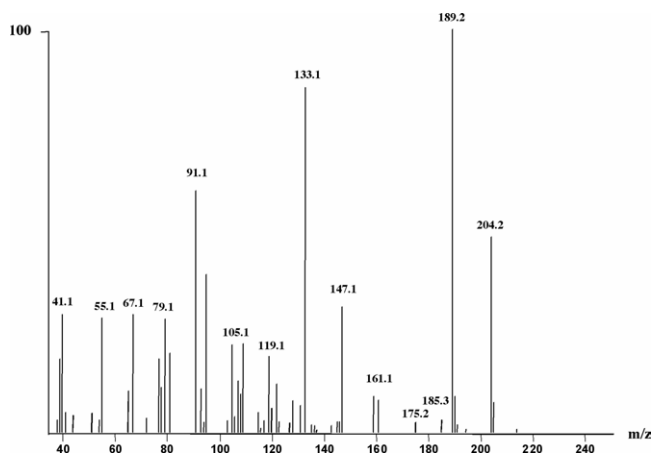


Fig. 13S: MS of selina-4,11-diene (**12**) produced by AS-F178V

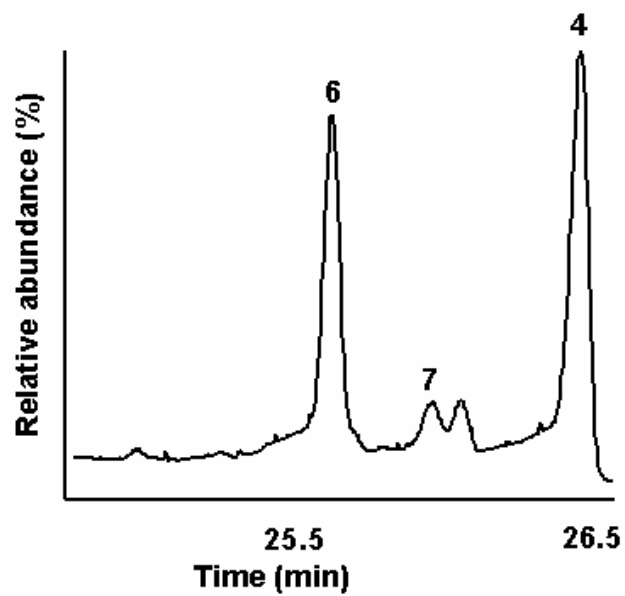


Fig. 14S: TIC of AS-F178I

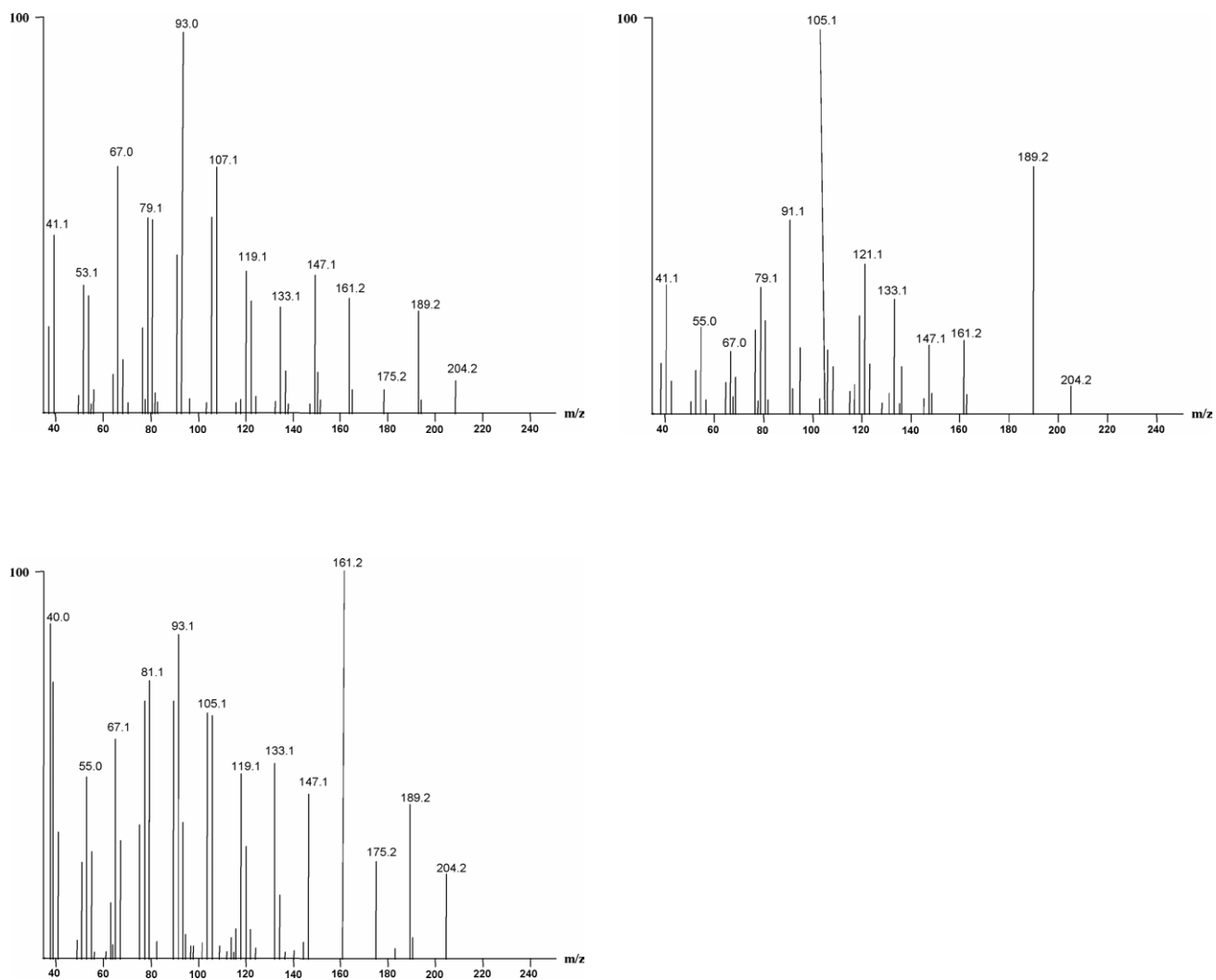


Fig 17S: MS of valencene (7) produced by AS-F178I

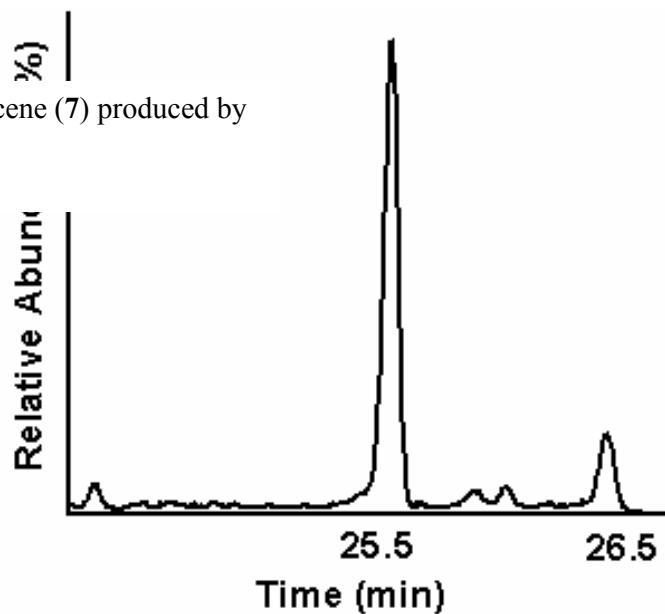


Fig. 18S: TIC of AS-F178Y.

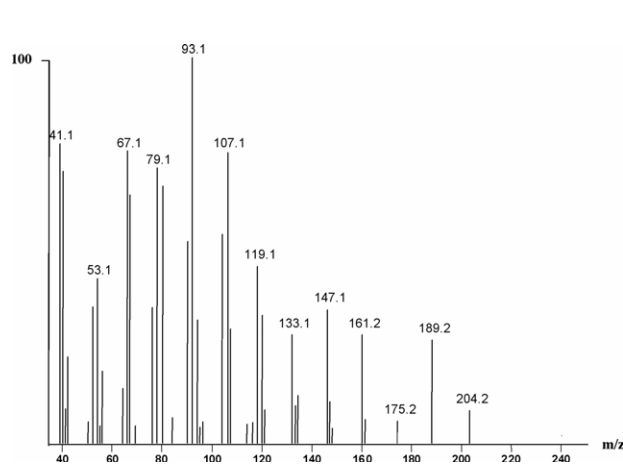


Fig. 19S: MS of germacrene A (4) produced by AS-F178Y

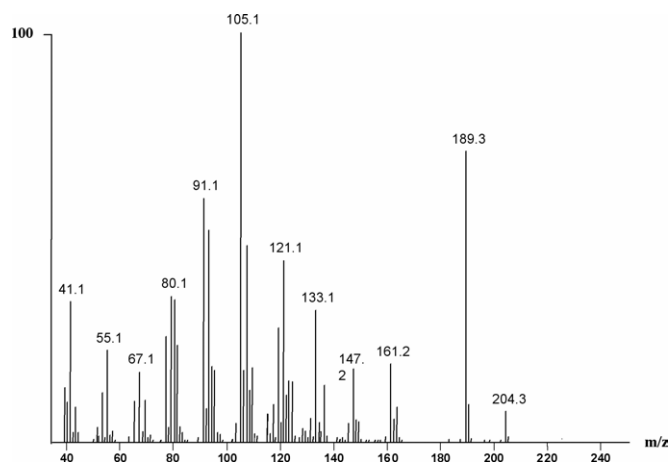


Fig 20S: MS of aristolochene (6) produced by AS-F178Y

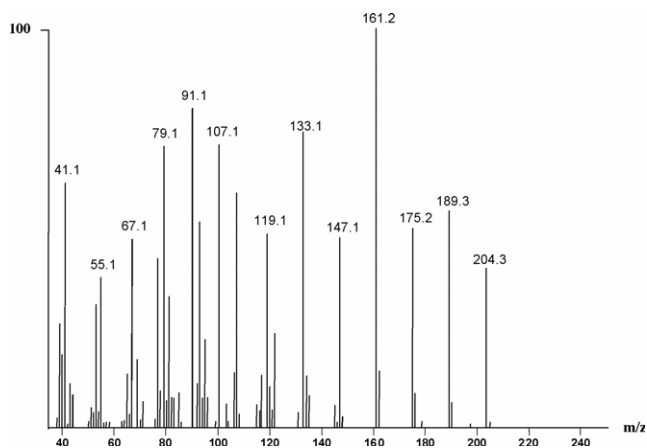


Fig. 21S: MS of valencene (7) produced by AS-F178Y

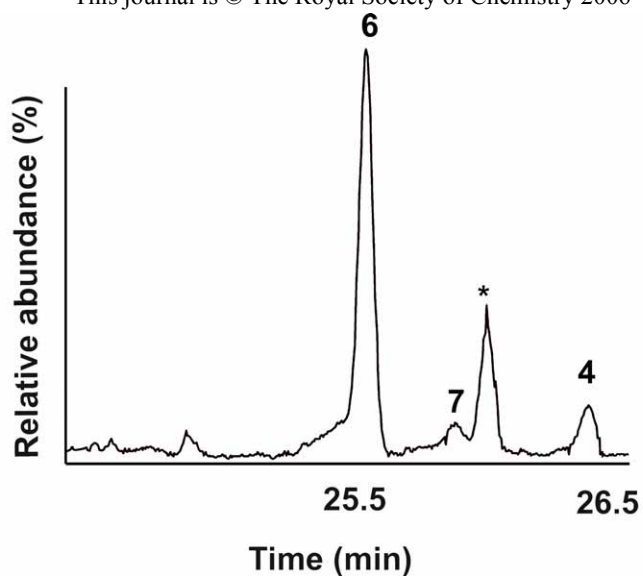


Fig. 22S: TIC of AS-F178W. * represents a non-terpene contaminant.

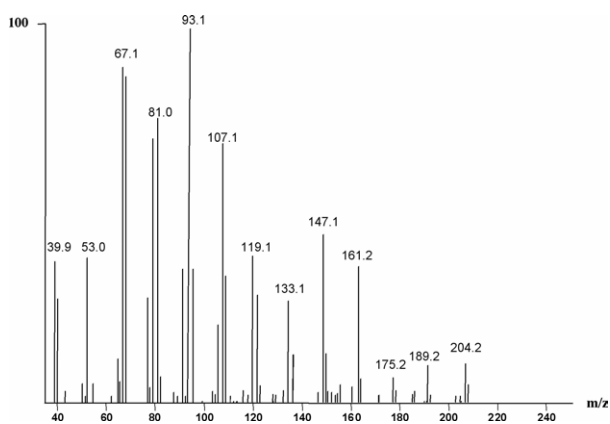


Fig. 23S: MS of germacrene A (4) produced by AS-F178W

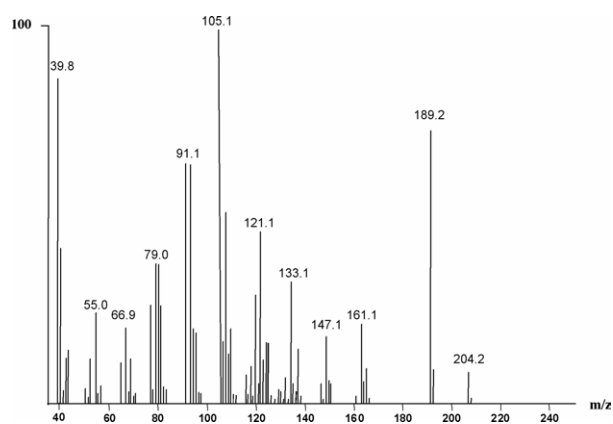


Fig 24S: MS of aristolochene (6) produced by AS-F178W

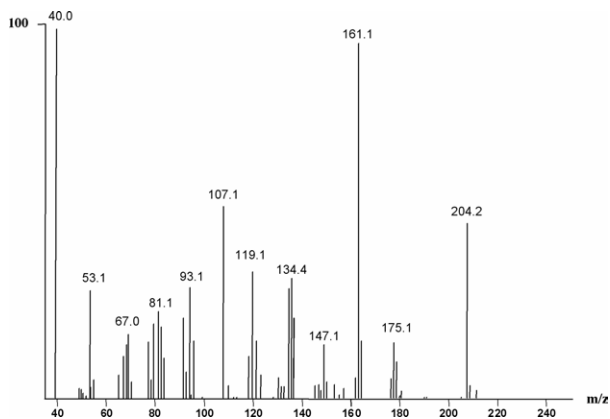


Fig 25S: MS of valencene (7) produced by AS-F178W

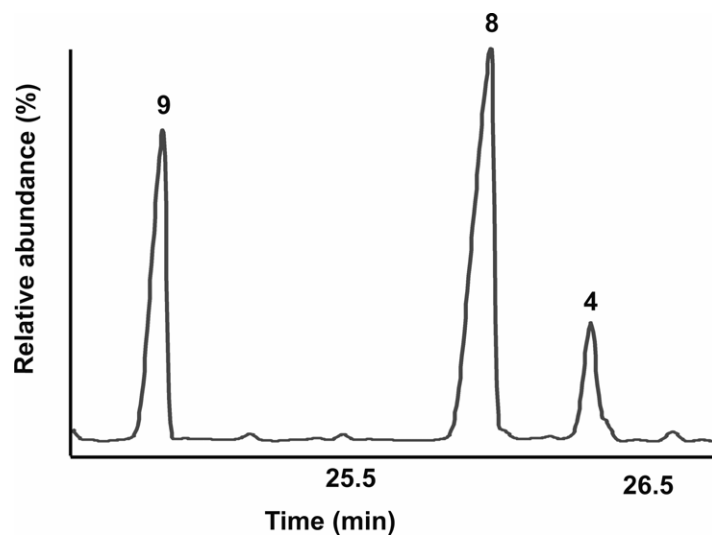


Fig. 26S: TIC of AS-F112A

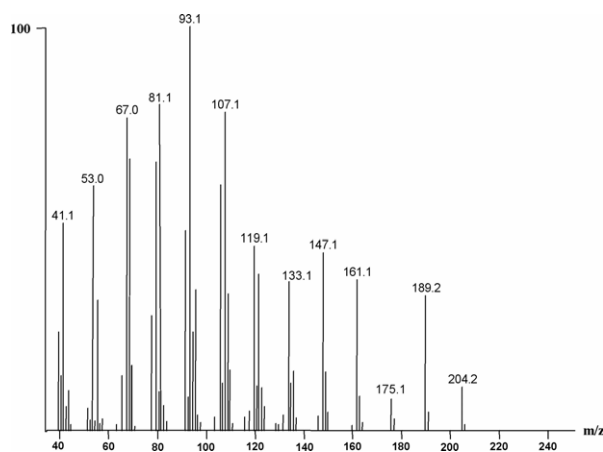


Fig. 27S: MS of germacrene A (4) produced by AS-F112A

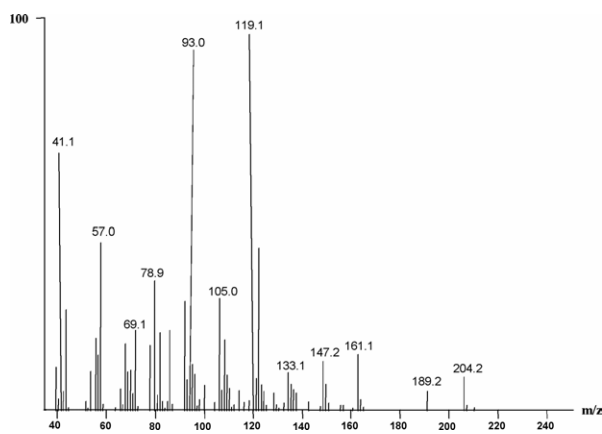


Fig 28S: MS of α -farnesene (8) produced by AS-F112A

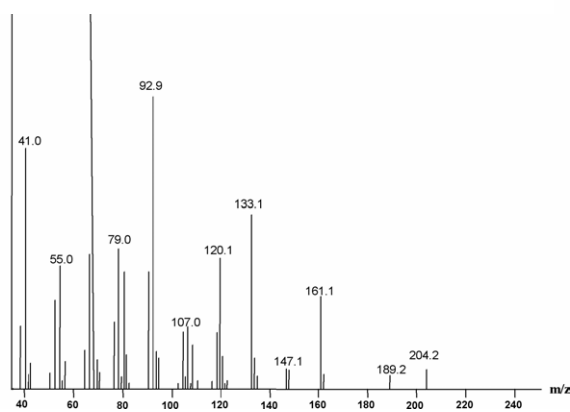


Fig 29S: MS of β -farnesene (9) produced by AS-F112A

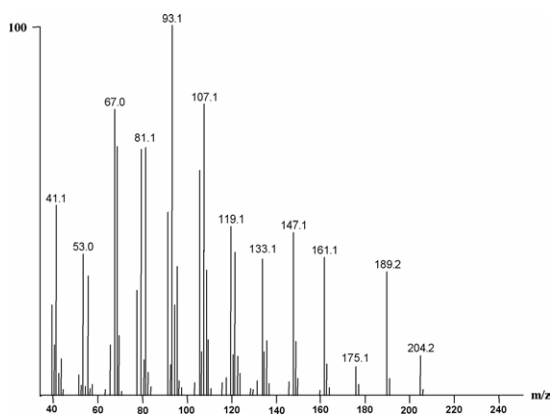


Fig. S30: Standard of germacrene A, **4**.

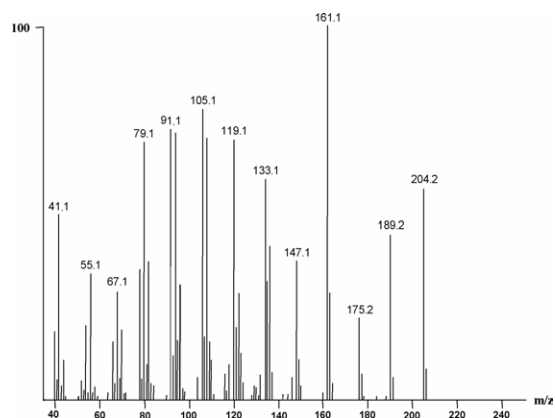


Fig. S31: Standard of valencene, **7**.

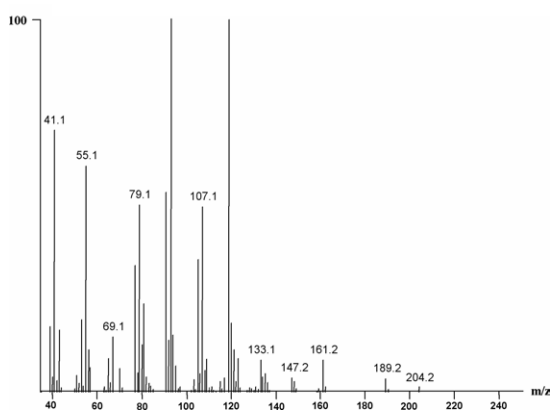


Fig. S32: Standard of α -farnesene, **8**.

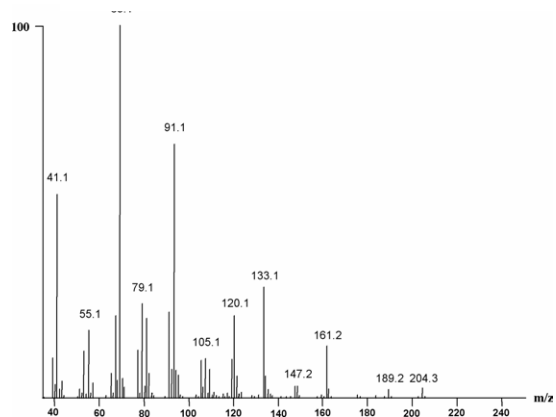


Fig. S33: Standard of β -farnesene, **9**.

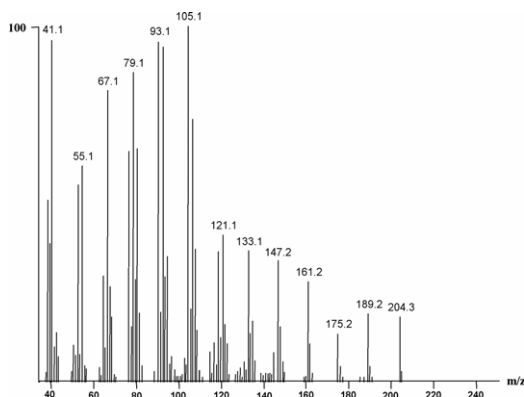


Fig. S34: Standard of β -selinene (**11**).

For standards **10** and **12**, see Forcat & Allemann, 2004.¹

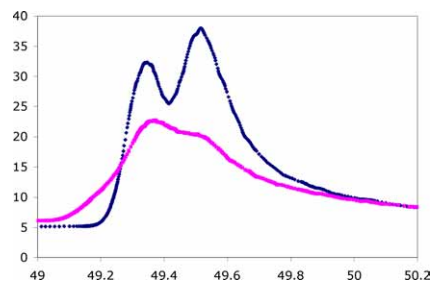


Fig. S35: Determination of the absolute configuration of germacrene A produced by AS-F112A. --- GC- trace of a racemic mixture of β -elemenes. --- GC- trace of a co-injection of racemic β -elemenes and the β -elemene produced from FPP by AS-F112A.

References for ESI

1. S. Forcat and R. K. Allemann, *Chem. Commun.*, 2004, 2094-2095.
2. M. J. Calvert, P. R. Ashton and R. K. Allemann, *Journal of the American Chemical Society*, 2002, **124**, 11636-11641.
3. M. J. Calvert, S. E. Taylor and R. K. Allemann, *Chemical Communications*, 2002, 2384-2385.