Unexpected reactivity of 2-fluorolinalyl diphosphate in the active site of crystalline 2-methylisoborneol synthase

Mustafa Köksal[†,‡], *Wayne K. W. Chou*[§], *David E. Cane*[§,*], *and David W. Christianson*[†,*]

[†]Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, PA 19104-6323 USA; and [§]Department of Chemistry, Brown University, Box H, Providence, RI 02912-9108 USA

[‡]Current Address: Department of Molecular Biology and Genetics, Izmir Institute of Technology, Urla, Izmir, 35430 Turkey

*Authors to whom correspondence should be addressed: D.W.C.: Tel.: (215) 898-5714; e-mail: chris@sas.upenn.edu. D.E.C.: Tel: (401) 863-3588; e-mail: david_cane@brown.edu.

-- SUPPORTING INFORMATION --

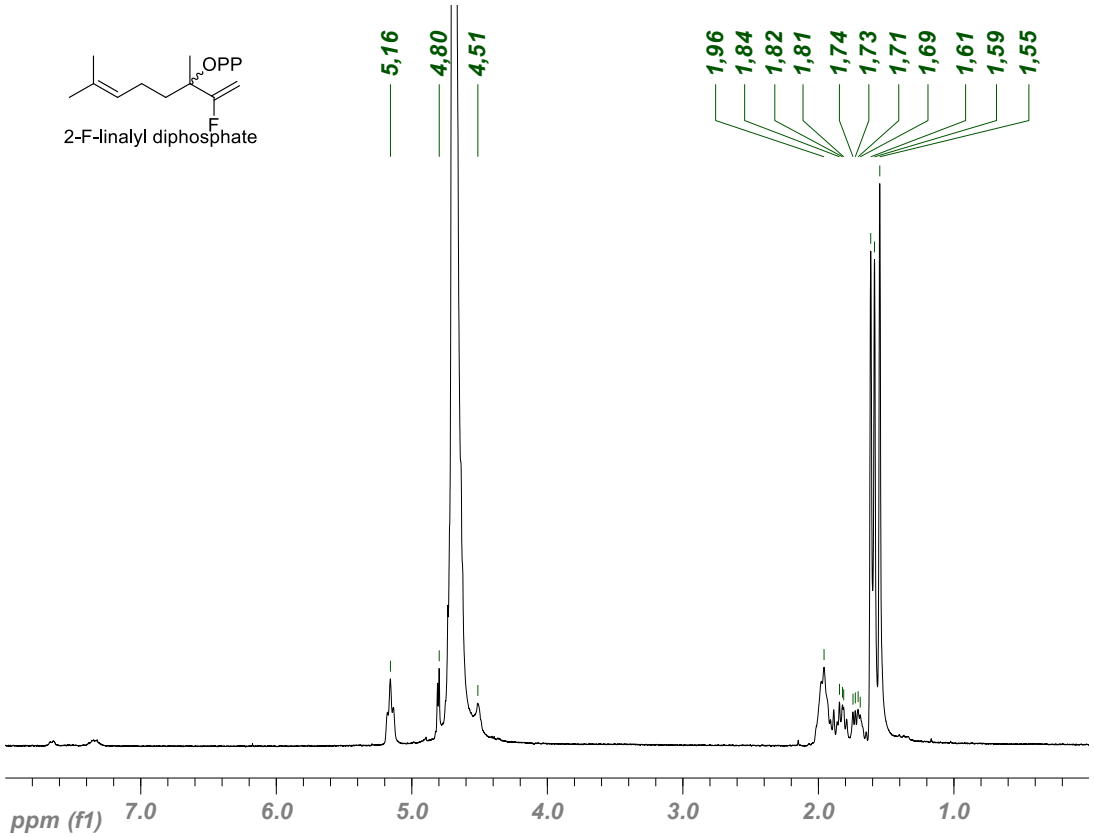

Figure S1. ^{1}H NMR (D_2O, 300 MHz) spectrum of 2FLPP.

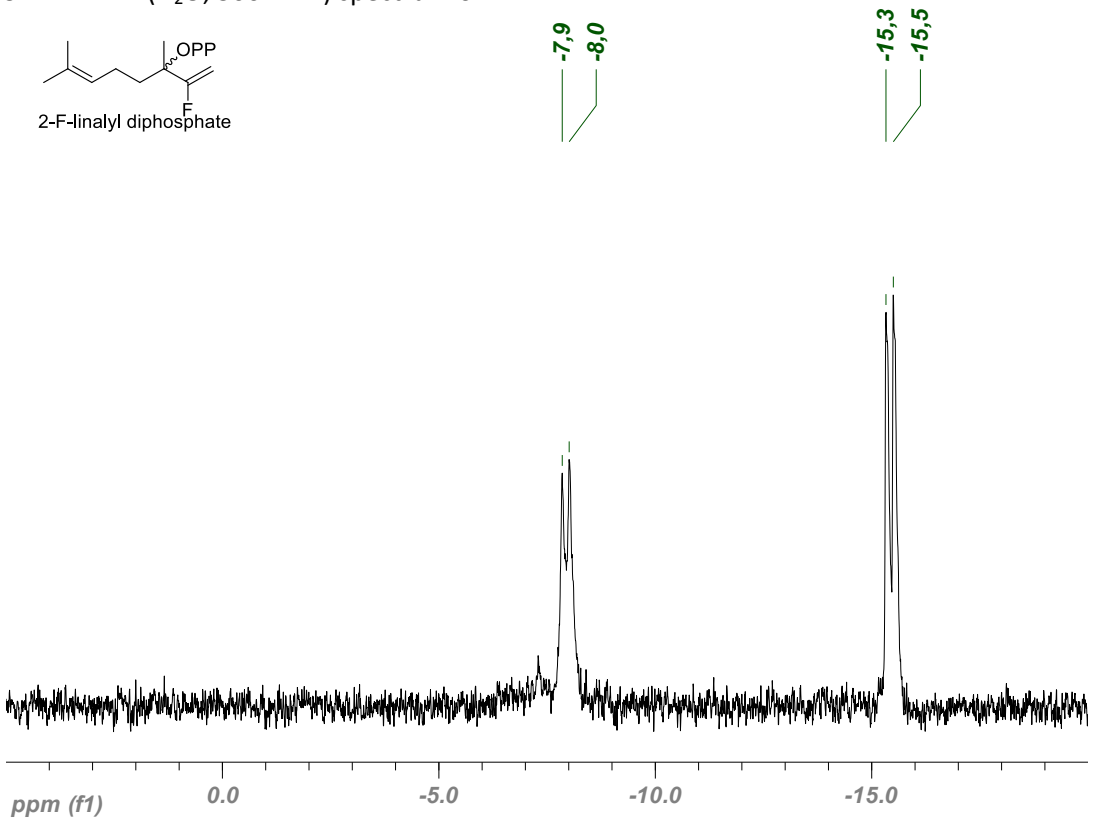

Figure S2. ^{31}P NMR (D_2O, 121 MHz) of 2FLPP.

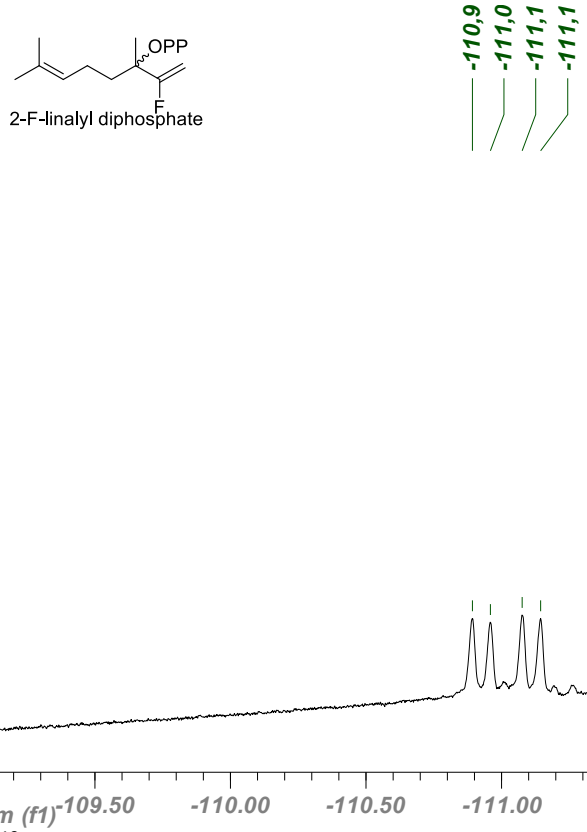

Figure S3. ^{19}F NMR (D_2O, 272 MHz) of 2FLPP.

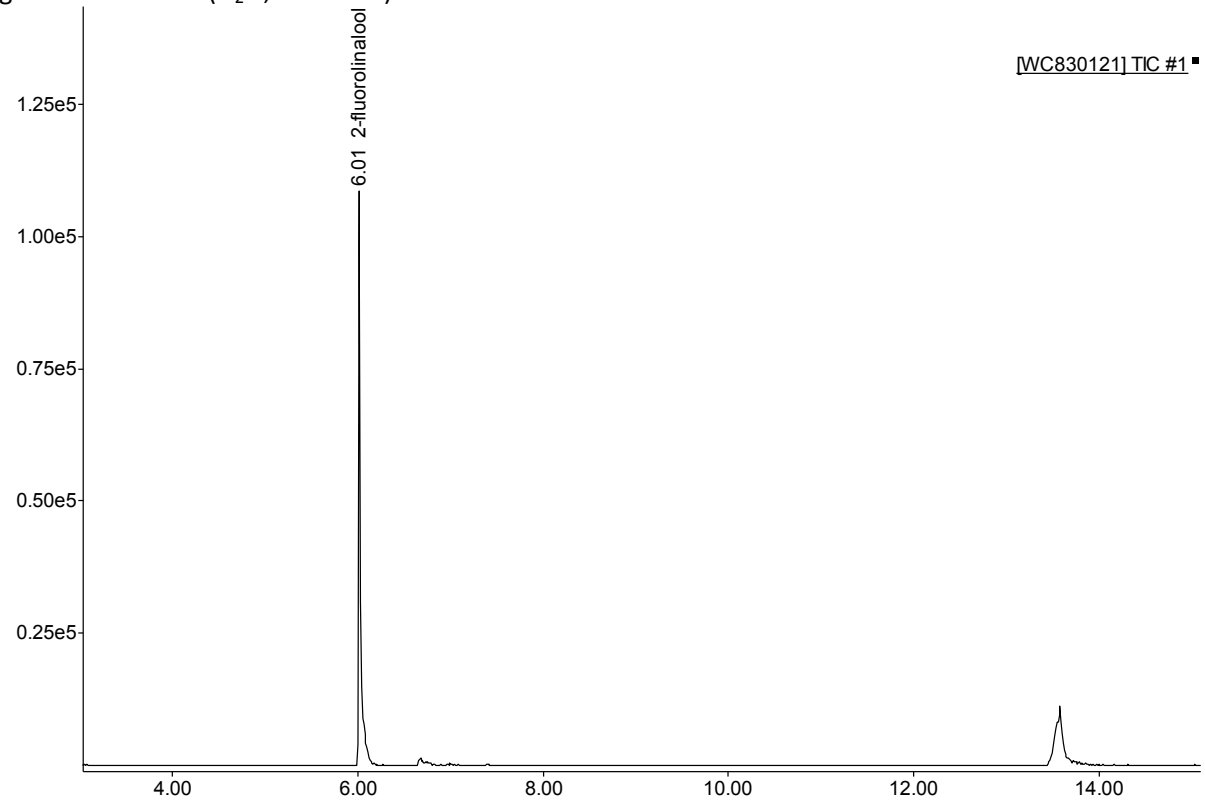

Figure S4. GC-MS TIC trace (non-chiral separation conditions) of pentane extract from the incubation of 2FLPP with MIBS (12 hrs).

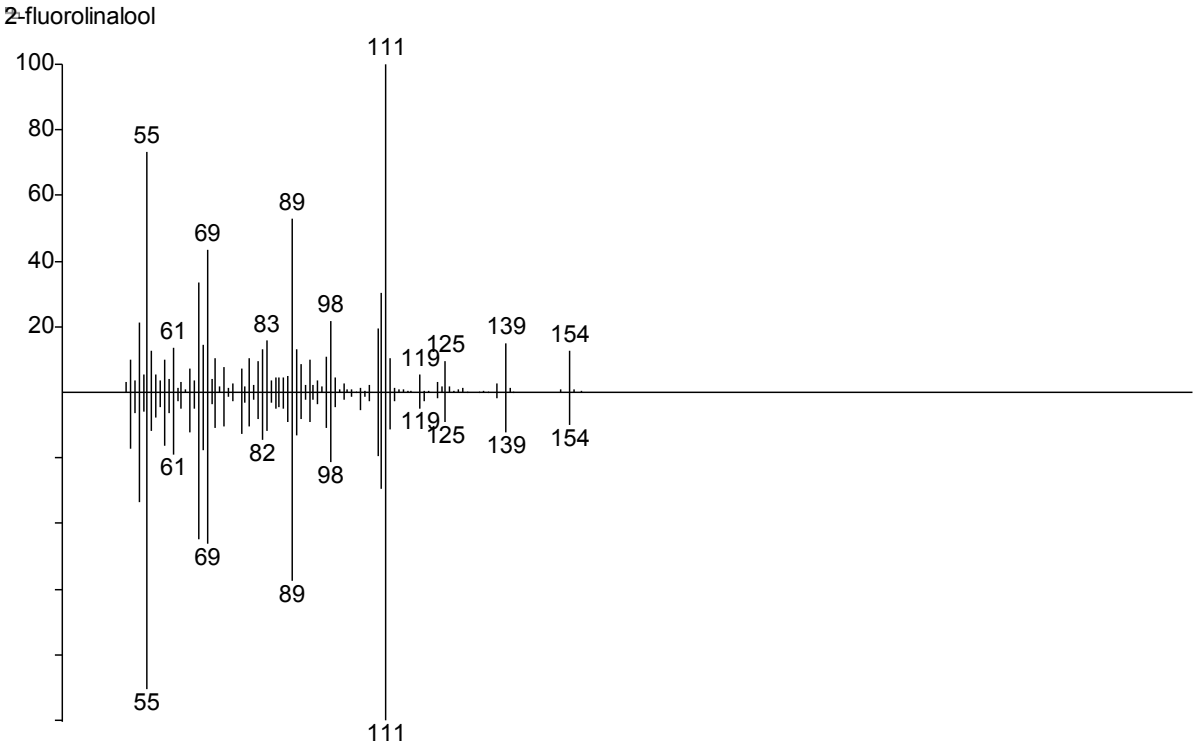

Figure S4b. Mass spectrum of peak at 6.01 min (bottom spectrum) and synthetic 2-fluorolinalool standard (top spectrum).

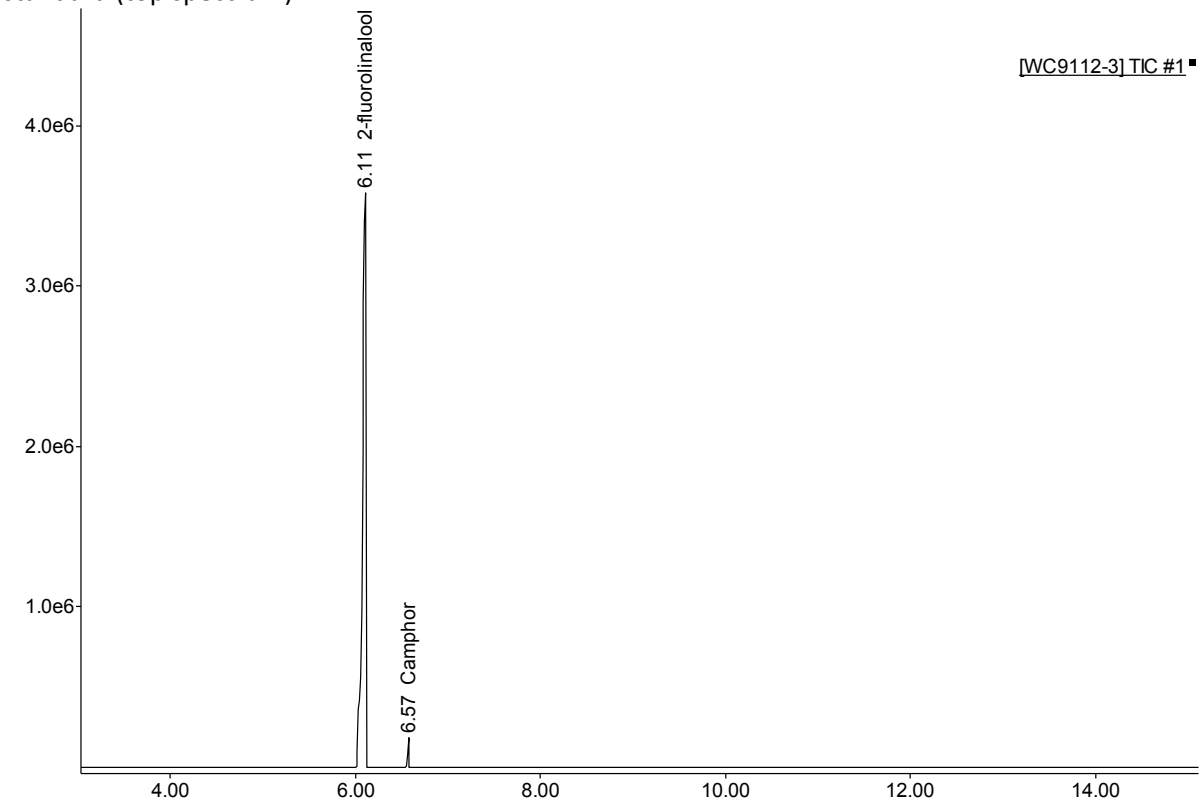

Figure S5a. GC-MS TIC trace (non-chiral separation conditions) of pentane extracts from the incubation of 2FLPP with MIBS, followed by incubation with phosphatase solution.

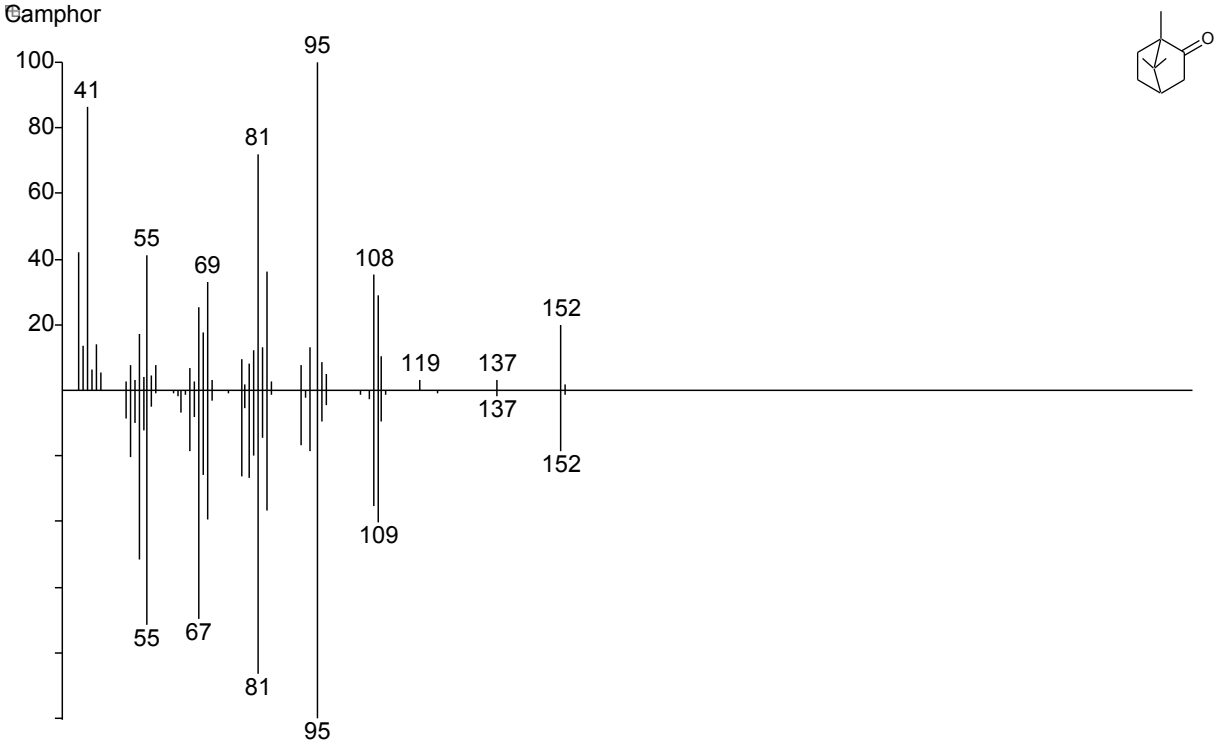

Figure S5b. Mass spectrum of peak at 6.57 min (bottom spectrum) and camphor standard (top spectrum).

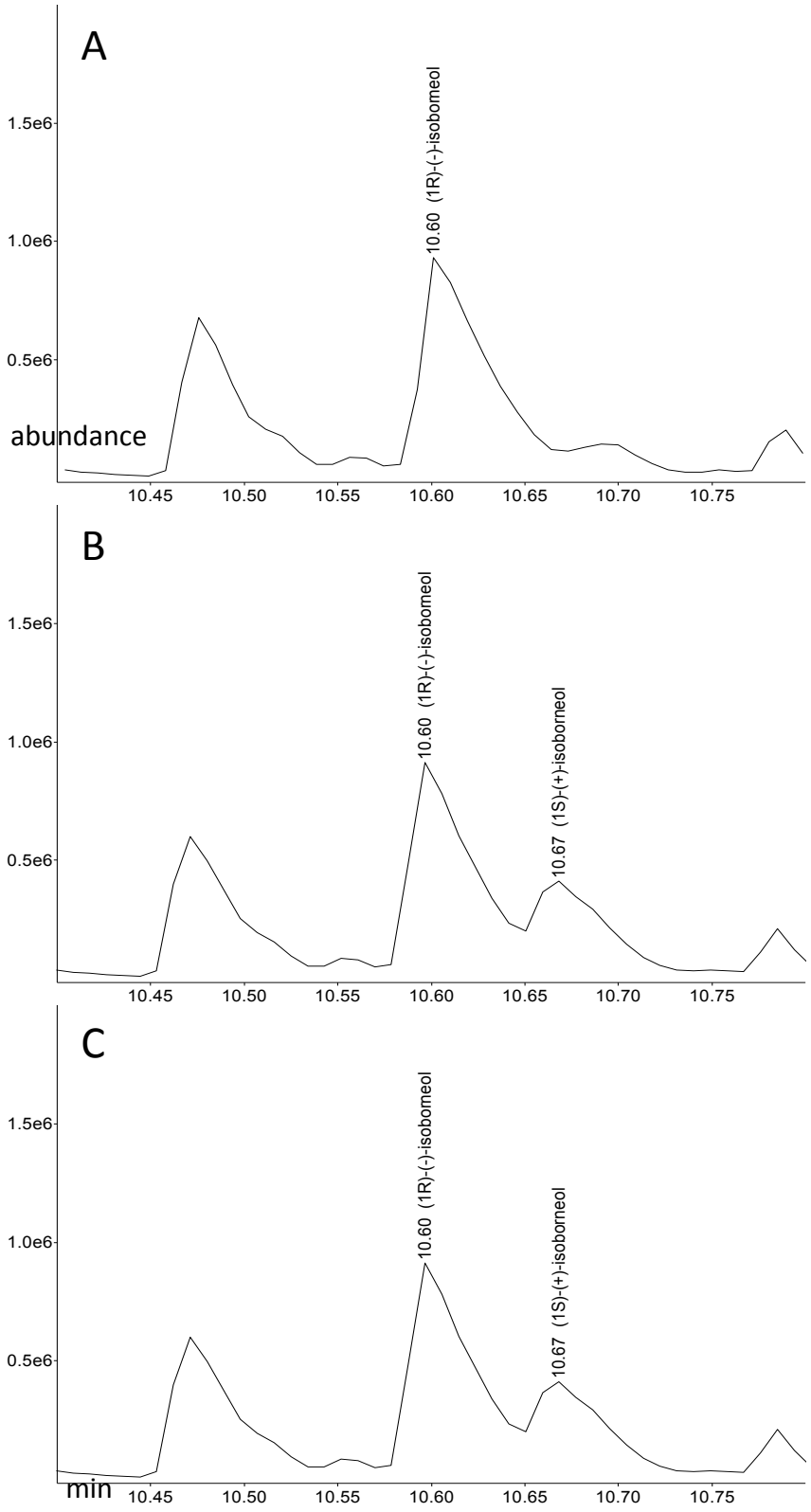

Figure S6a. GC-MS TIC traces (chiral separation conditions) of MIBS generated camphor reduced by $LiAlH_4$ (panel A), co-injected with (1*S*)-(+)-isoborneol (panel B) and co-injected with (1*S*)-(+)-isoborneol and (1*R*)-(-)-isoborneol (panel C).

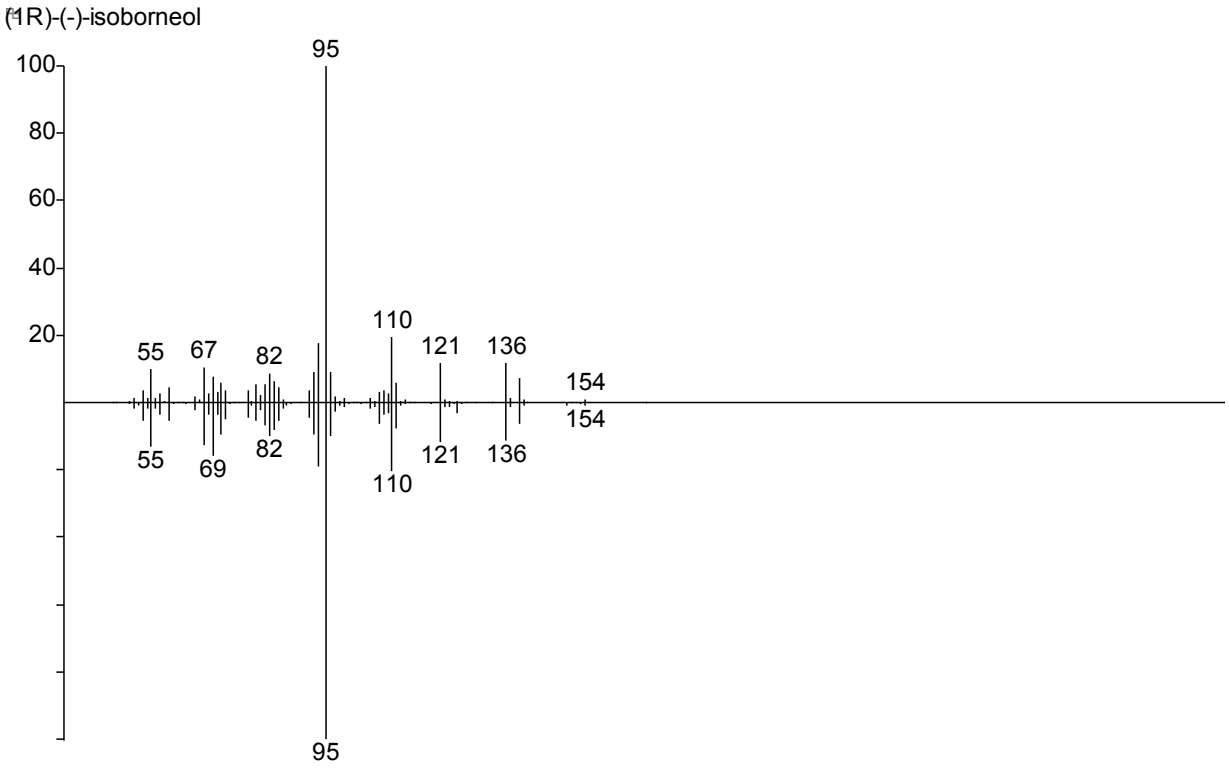

Figure S6b. Mass spectrum of peak at 10.60 min from Figure S6a panel A (bottom spectrum) and isoborneol standard (top spectrum).

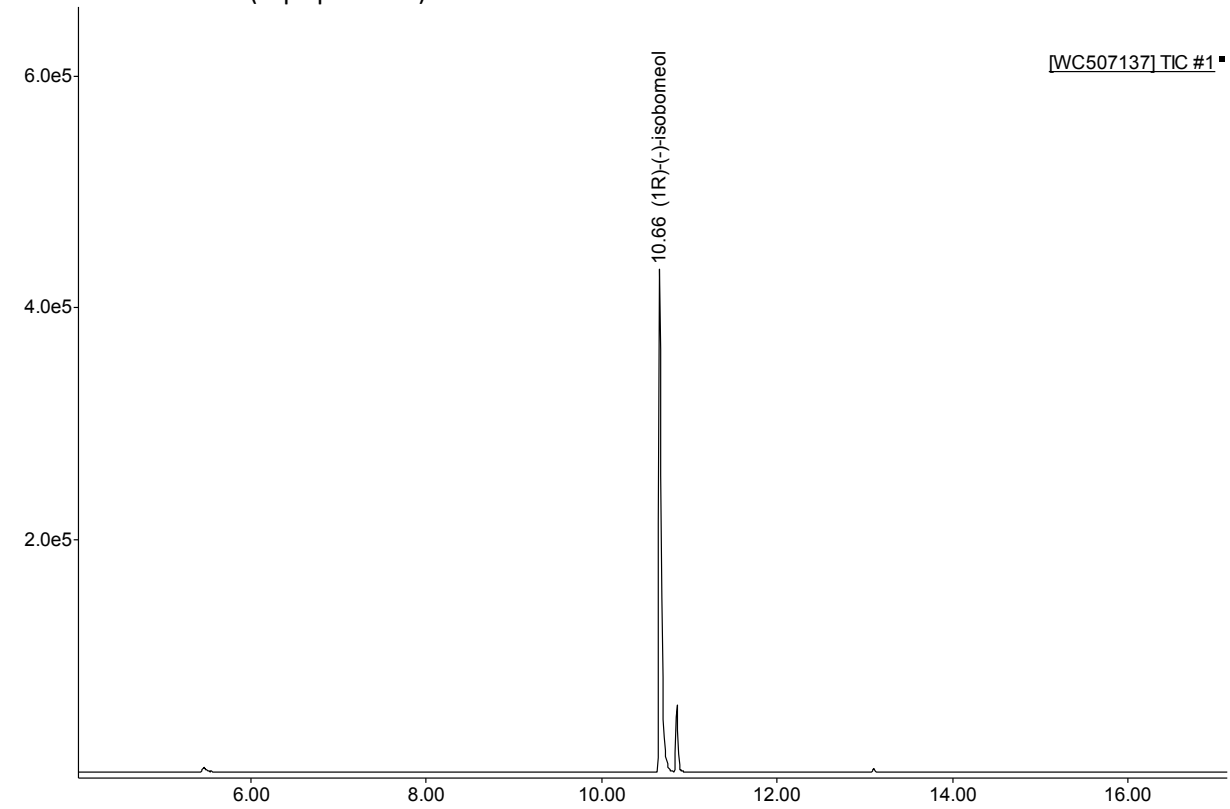

Figure S7a. GC-MS TIC trace (chiral separation conditions) of (1*R*)-(-)-isoborneol (from $LiAlH_4$ reduction of (1*R*)-(+)-camphor).

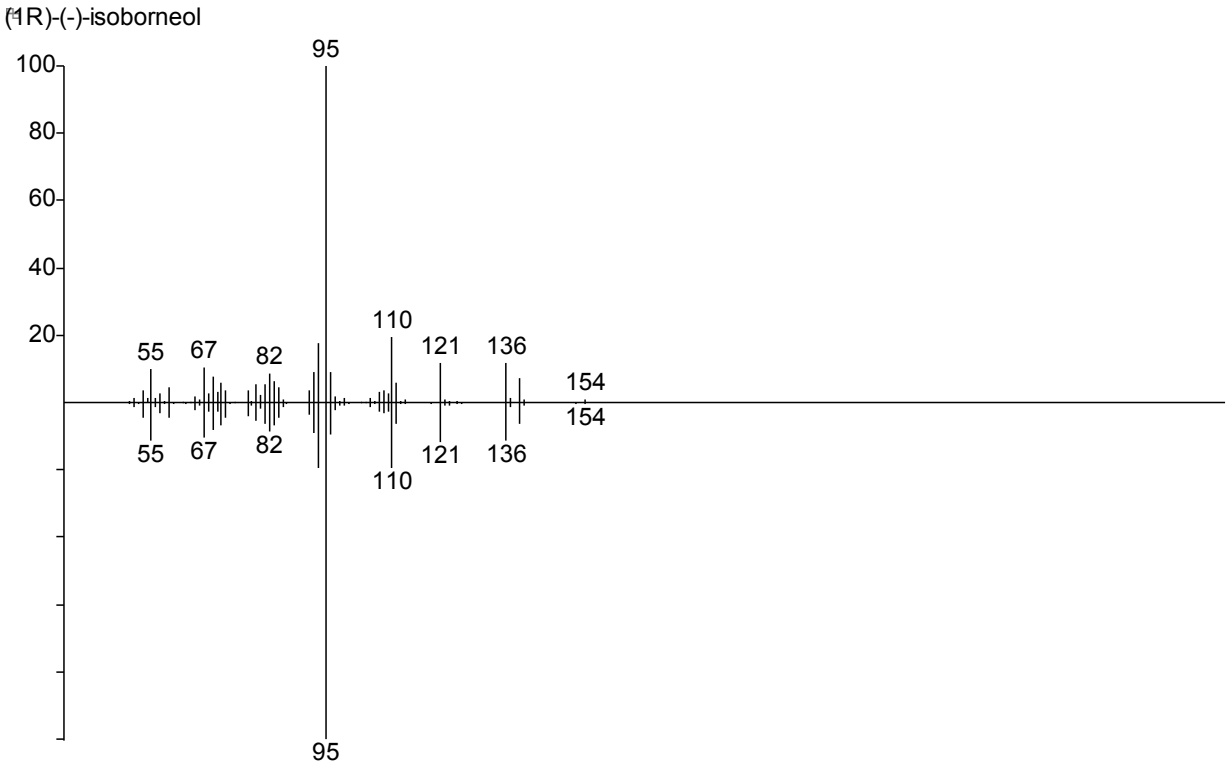

Figure S7b. Mass spectrum of peak at 10.66 min (bottom spectrum) and isoborneol standard (top spectrum)

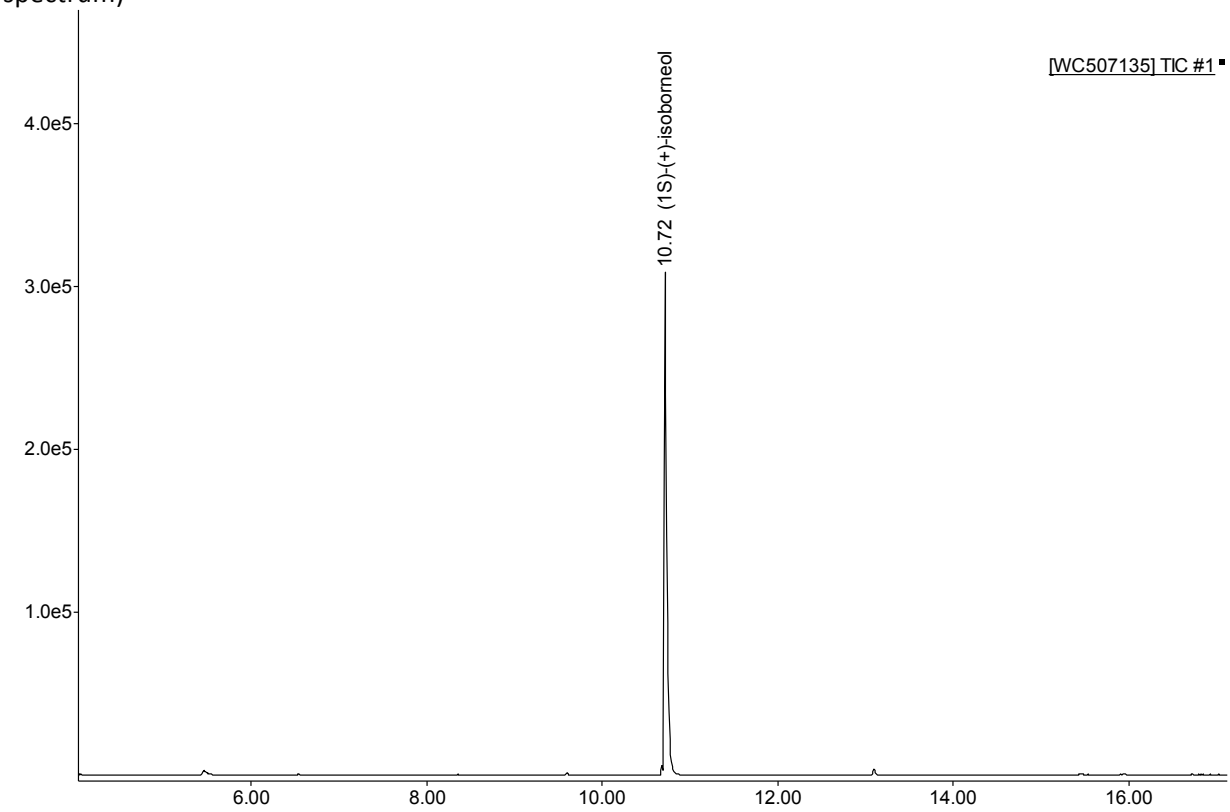

Figure S8a. GC-MS TIC trace (chiral separation conditions) of (1*S*)-(+)-isoborneol (from $LiAlH_4$ reduction of (1*S*)-(-)-camphor).

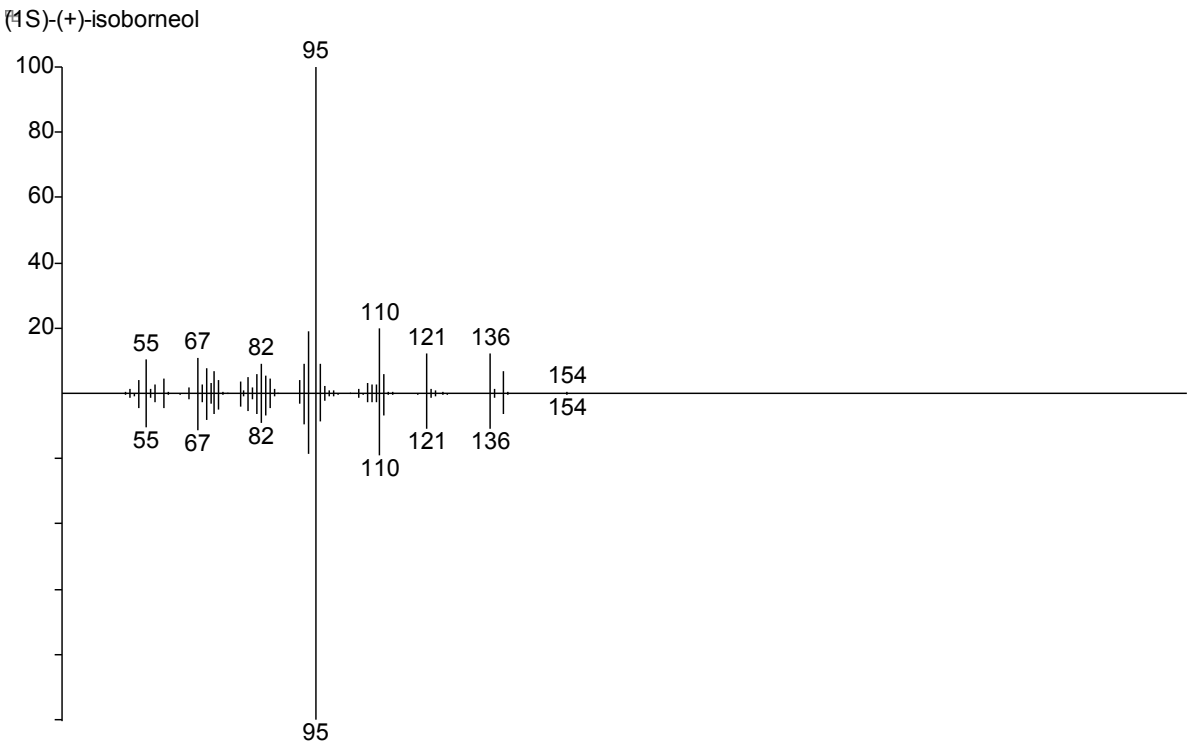

Figure S8b. Mass spectrum of peak at 10.72 min (bottom spectrum) and isoborneol standard (top spectrum).