Supplementary Information

Easy Epoxidation of Monoterpenes from Common Starting Materials

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Figure S1 shows the reaction progress monitored by thin layer chromatography (TLC) for the epoxidation of α -pinene. The plate shows a spot corresponding to the starting material α -pinene with Rf of 0.59. After three hours of reaction, the starting material began to disappear while a new spot appeared: the formed product with Rf of 0.82 corresponded to α -pinene epoxide product, 2,7,7-trimethyl-3-oxatricyclo-[4.1.1.02,4]octane. TLC analysis for epoxidation of β -pinene and limonene showed the same trend, pictures are not included.



Figure S1. TLC plate of starting material α -pinene (left) and crude product (right) after three hours of reaction.

Mass spectrometry and spectroscopy analysis for epoxidation of α -pinene (1)

Figure 5 in the article shows the mass spectrum of the chromatographic peak with a retention time of 9.45 min, which displays a base peak of m/z 67. Figure S2 shows the molecular ion and its fragments. The epoxide of α -pinene after losing one electron from the electron impact produces molecular ion **II**, which is a radical cation centered at the oxygen. Cation **III** forms by a methyl radical elimination that generates the carbonyl ion; cation **IV** results from the epoxide ring opening, which via a homolytic cleavage produces butanone **V** and the radical cation **VI**. After elimination of a methyl radical from **VI**, methylcyclobutenyl cation **VII** (m/z 67) is produced, which is the most abundant signal, suggesting the high stability of the fragment induced by the allyl cation resonance. Structure **IV**, obtained from the ring opening of the epoxide, reorganizes and contracts from a ring of six to five carbon atoms **IX**, which eliminates both an acyl radical yielding cation **XII** with m/z of 109 and an acyl cation **XI** with a signal at 43 m/z.



Figure S2. Proposed fragmentation mechanism of α -pinene epoxide (P1).



Figure S3. Full ¹H NMR (400 MHz, CDCl₃) of α -pinene epoxide (P1).



Figure S4. Full ¹³C NMR (100 MHz, CDCl₃) of α -pinene epoxide (**P1**).



Figure S5. Chromatographic profile of the epoxidation of β -pinene (2) with SPC and TAED.



Figure S6. Mass spectrum of β -pinene (2) corresponding to the chromatographic peak at 4.26 min in Figure S5.



Figure S7. Mass spectrum of β -pinene epoxide (**P2**) corresponding to the chromatographic peak at 6.0 and 6.26 min in Figure S5, two isomers with different retention times.



Figure S8. Proposed fragmentation mechanism of β -pinene epoxide (**P2**).



Figure S9. Full ¹H NMR (400 MHz, CDCl₃) of β -pinene epoxide (**P2**).



Figure S10. Full ¹³C NMR (100 MHz, CDCl₃) of β -pinene epoxide (**P2**).

Analysis and characterization of cyclohexene epoxide (P3)

After performing the epoxidation reaction, the product was purified by passing the crude product through a chromatography column. The epoxidized product yielded 68% and the corresponding ¹H and ¹³C NMR are shown as follows:



Figure S10. Full ¹H NMR (400 MHz, CDCl₃) of cyclohexene epoxide (P3).



Figure S11. Full ¹³C NMR (100 MHz, CDCl₃) of cyclohexene epoxide (P3).



Figure S12. Chromatographic profile of the epoxidation of limonene with SPC and TAED.



Figure S13. Mass spectrum of limonene corresponding to the chromatographic peak at 13.45 min.



Figure S14. Mass spectrum of *cis*-limonene epoxide corresponding to the chromatographic peak at 16.63 min.



Figure S15. Mass spectrum of *trans*-limonene epoxide corresponding to the chromatographic peak at 16.77 min.



Figure S16. Proposed fragmentation mechanism of limonene epoxide.



Figure S17. Full ¹H NMR (400 MHz, CDCl₃) of limonene epoxide.



Figure S18. Full ¹³C NMR (100 MHz, CDCl₃) of limonene epoxide.



Figure S19. Chromatographic profile of the epoxidation of α -terpinene (5) with SPC and TAED.



Figure S20. Mass spectrum of α -terpinene epoxides (**P5**).



Figure S21. Proposed fragmentation mechanism of α -terpinene epoxide (**P5**).

Analysis and characterization of (R)-carvone epoxide (P6)



Figure S22. Expanded chromatographic profile of the epoxidation of (*R*)-carvone (6) with SPC and TAED.



Figure S23. Mass spectrum of (*R*)-carvone epoxide (P6).



Figure S24. Proposed fragmentation mechanism (base peak) of (*R*)-carvone epoxide (P6).

