

Supplementary Information

An Effective Procedure for the Synthesis of Acid-Sensitive Epoxides: Use of 1-Methylimidazole as the Additive on Methyltrioxorhenium-Catalyzed Epoxidation of Alkenes with Hydrogen Peroxide

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1. GC analysis conditions

The conversions of alkenes and the yields of epoxides in Figures 1-4 and Tables 1-4 were determined by GC analysis except the yield of the epoxide from *cis*-4-decen-1-ol. The majority of the epoxides produced are stable under the GC analysis conditions indicated in Table S1.

Dimethylchromen oxide **8**, dihydrolinalool oxide **16**, 5,6-epoxy-6-methyl-2-heptanol **18**, 1-hydroxy-4,5-epoxydecane **20**, and β -pinene oxide **28** are unstable and produced corresponding rearrangement products under the standard GC analysis conditions (oven temperature $\geq 200^\circ\text{C}$, injection temperature $\geq 220^\circ\text{C}$). Under lower temperature GC analysis conditions indicated in Table S1 (lower oven and injection temperature), the rearrangement of **8**, **16**, **18**, and **28** were suppressed below 3%.

1-Hydroxy-4,5-epoxydecane **20** was unstable even under the lower temperature GC analysis conditions. Details of analysis of the epoxidation products of *cis*-4-decen-1-ol are described in next section.

Table S1 GC conditions for the analysis of epoxidations.

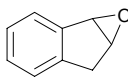
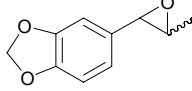
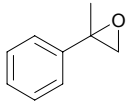
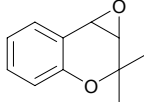
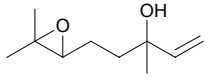
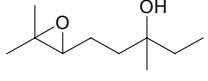
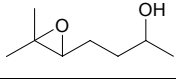
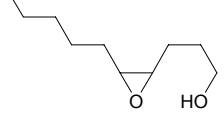
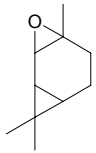
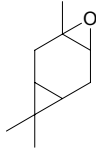
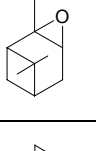
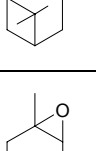
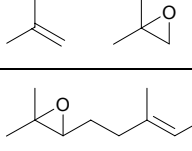
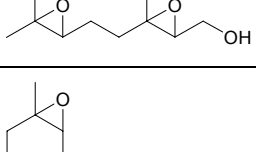
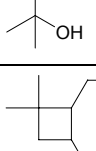
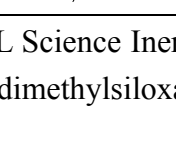
number	epoxide	temperature conditions
2		Oven: 50°C (2 min), 20°C /min to 250°C (3 min) Injection: 250°C, Detector: 260°C
		Oven: 50°C (2 min), 20°C /min to 270°C (7 min) Injection: 270°C, Detector: 280°C
		Oven: 50°C (2 min), 20°C /min to 200°C (5.5 min) Injection: 220°C, Detector: 250°C
8		Oven: 90°C (2 min), 20°C /min to 160°C (4.5 min), 20°C /min to 180°C (4 min) Injection: 180°C, Detector: 180°C
12		Oven: 50°C (2 min), 20°C /min to 210°C (5 min) Injection: 230°C, Detector: 250°C
16		Oven: 80°C (2 min), 20°C /min to 160°C (6 min) Injection: 160°C, Detector: 170°C
18		Oven: 70°C (2 min), 20°C /min to 150°C (6 min) Injection: 160°C, Detector: 170°C
20		Oven: 80°C (2 min), 20°C /min to 160°C (6 min) Injection: 160°C, Detector: 170°C

Table S1 GC conditions for the analysis of epoxidations (continued).

number	epoxide	temperature conditions
22		Oven: 50°C (2 min), 20°C /min to 200°C (5.5 min) Injection: 220°C, Detector: 250°C
24		Oven: 50°C (2 min), 20°C /min to 200°C (5.5 min) Injection: 220°C, Detector: 250°C
26		Oven: 50°C (2 min), 20°C /min to 200°C (5.5 min) Injection: 220°C, Detector: 250°C
28		Oven: 50°C (2 min), 20°C /min to 130°C (9 min) Injection: 130°C, Detector: 150°C
30 31		Oven: 50°C (2 min), 20°C /min. to 200°C (5.5 min) Injection: 220°C, Detector: 250°C
33 34		Oven: 50°C (2 min), 20°C /min. to 200°C (5.5 min) Injection: 220°C, Detector: 250°C
36		Oven: 50°C (2 min), 20°C /min. to 230°C (4 min) Injection: 240°C, Detector: 250°C
40		Oven: 80°C (2 min), 20°C /min. to 230°C (5.5 min) Injection: 240°C, Detector: 250°C

Column: GL Science Inert Cap 1 (30 m length x 0.25 mm ID x 0.25 µm film thickness, phase: polydimethylsiloxane)

2. Epoxidation of *cis*-4-decen-1-ol (19) and characterization of the products

Epoxidation procedure is described in Experimental section. Fig. S1 is the GC chromatogram of the reaction mixture.

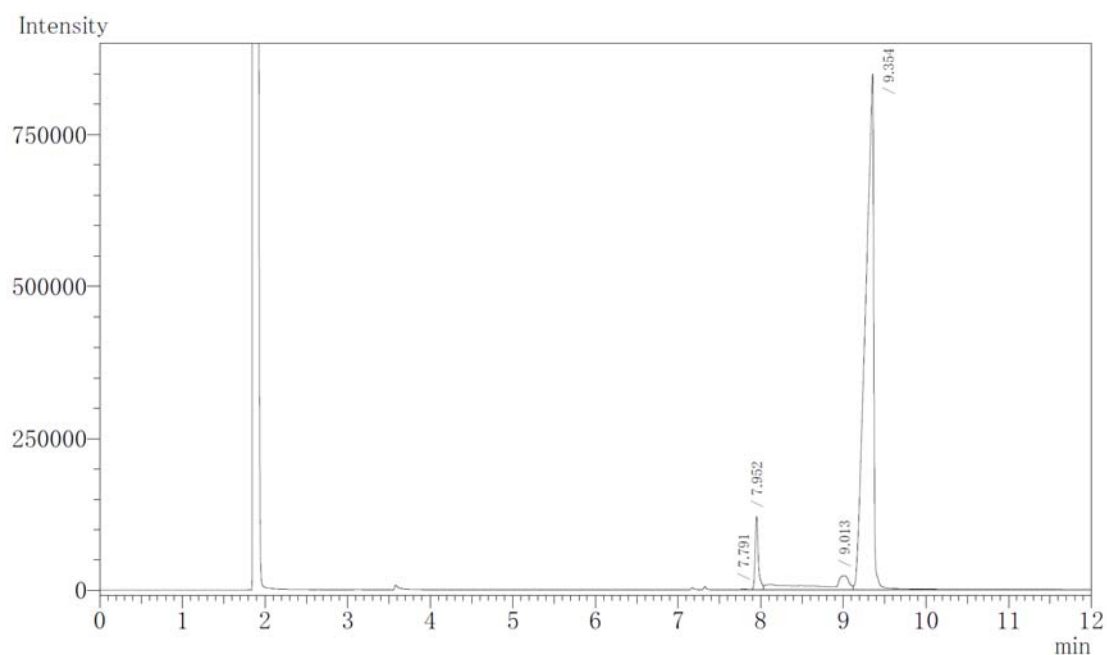


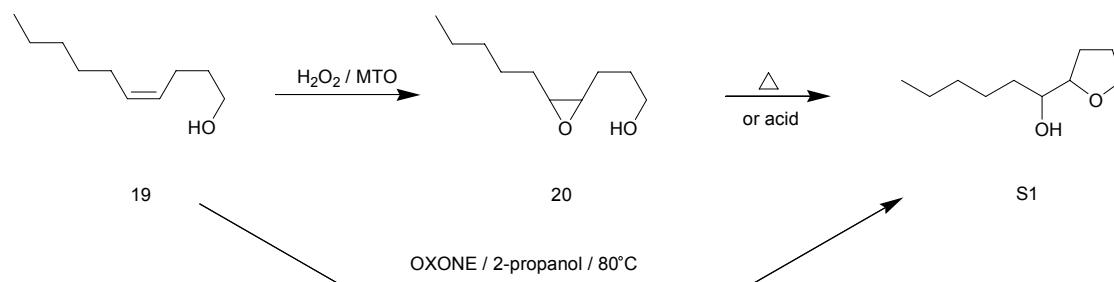
Fig. S1 GC chromatogram of the reaction mixture of *cis*-4-decen-1-ol **19** epoxidation.

Column: GL Science Inert Cap 1,

Oven temperature: 80°C (2 min), 20°C/min to 160°C (6 min),

Injection temperature: 160°C, FID temperature: 170°C

The product epoxide, 1-Hydroxy-4,5-epoxydecane **20**, was unstable under the GC analysis conditions. The peak at 9.3min is the epoxide **20**, and the peak at 7.9 min is the cyclization product, 1-(2-tetrahydrofuranyl)hexan-1-ol **S1**. **S1** is separately synthesized by oxidation of *cis*-4-decen-1-ol **19** by OXONE according to the reported procedure (Scheme S1).[1] The GC retention time of the separately synthesized **S1** was 7.9min (Fig. S2). Further, the attempt of the purification of **20** by distillation under reduced pressure (5 mmHg, 140 °C) resulted in the mixture of increased amount of **S1** and decreased amount of **20**. The chromatogram of the distillate is indicated in Fig. S3.



Scheme S1 Oxidations of *cis*-4-decen-1-ol

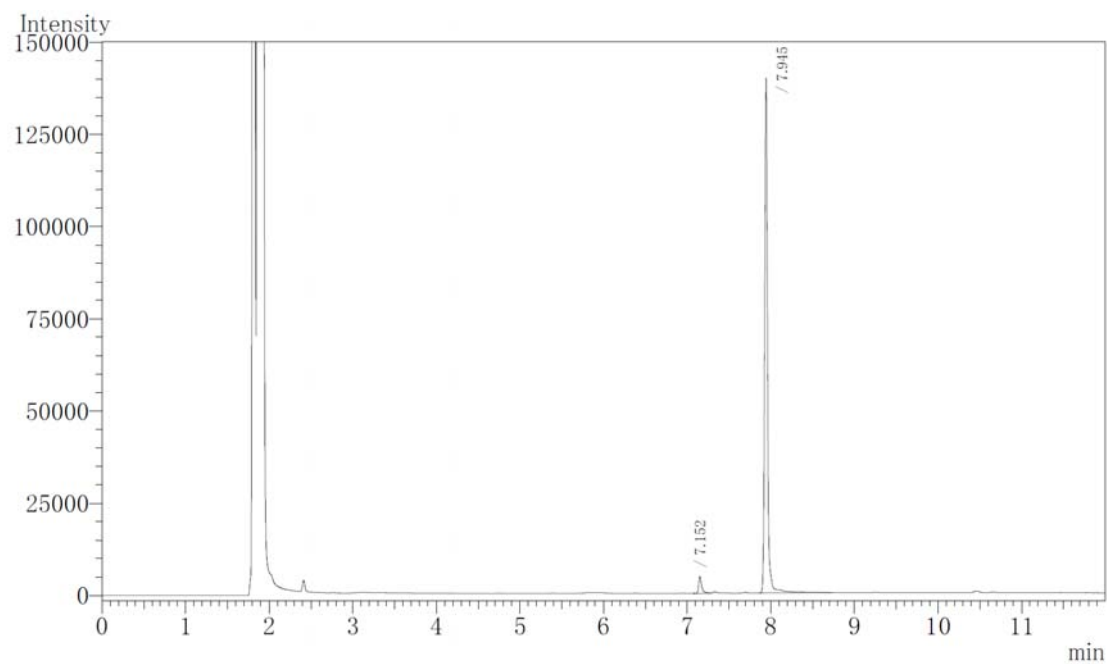


Fig. S2 GC chromatogram of the reaction mixture of *cis*-4-decen-1-ol **19** oxidation with OXONE.

Conditions: same with Fig S1. Peak at 7.1 min is *cis*-4-decen-1-ol **19**.

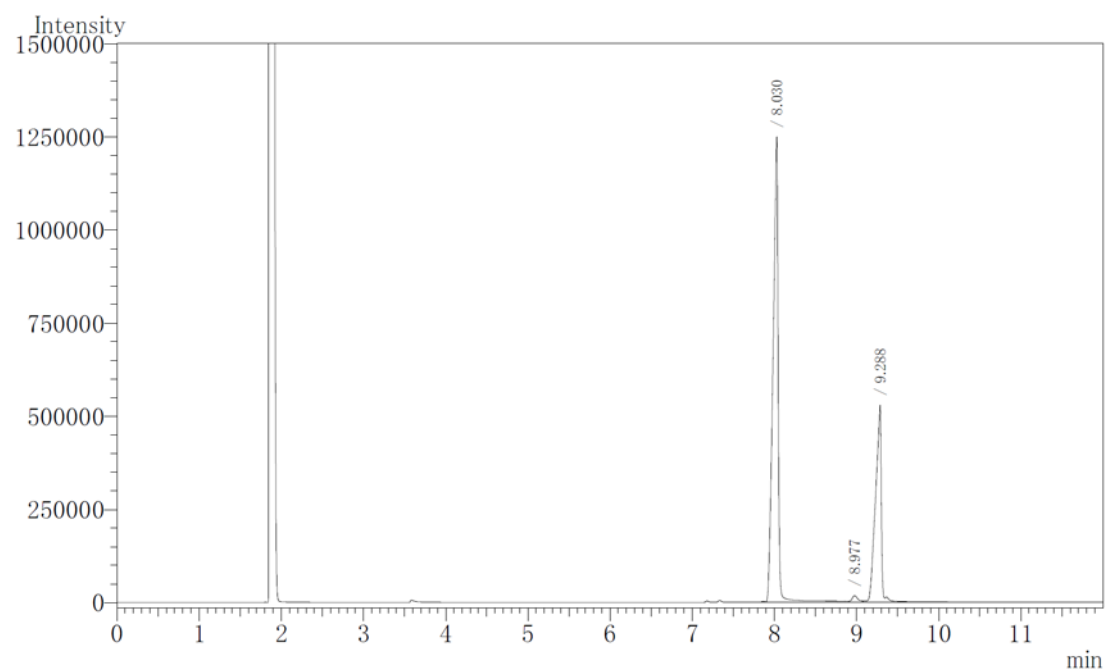


Fig. S3 GC chromatogram of the *cis*-4-decen-1-ol **19** epoxidation products obtained by distillation under reduced pressure.

Conditions: same with Fig S1.

Alternatively, 1-hydroxy-4,5-epoxydecane **20** was completely converted to 1-(2-tetrahydrofuran-2-yl)hexan-1-ol **S1** by treatment with acid (Fig. S4). (The CH₂Cl₂ solution of the epoxide **20** was stirred in the presence of diluted HCl).

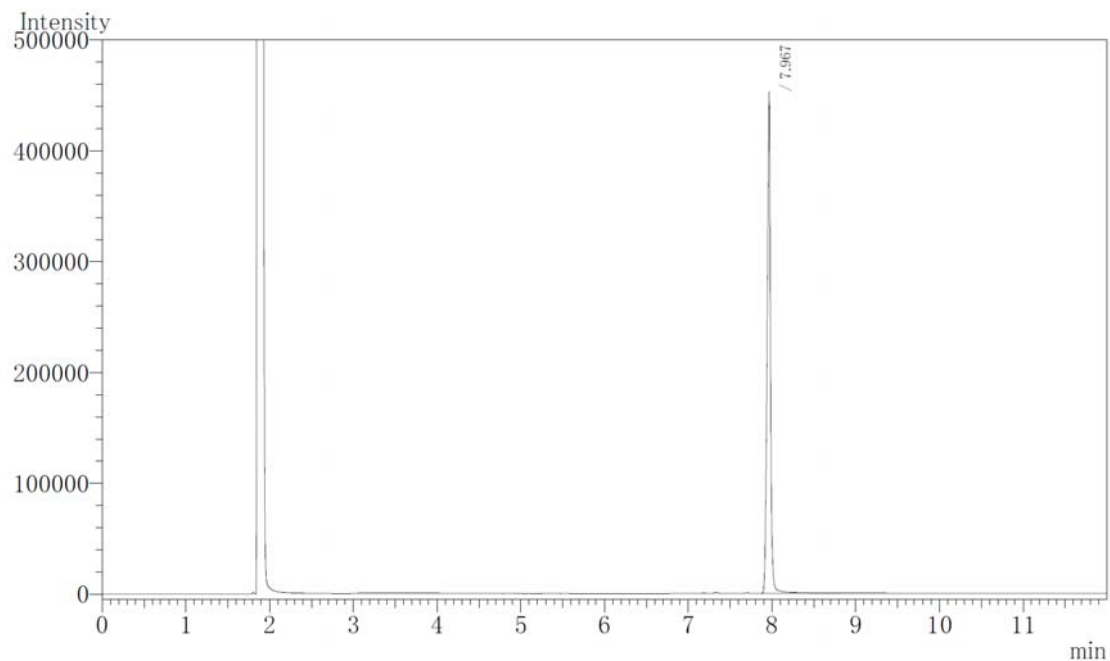


Fig. S4 GC chromatogram of reaction mixture by acid promoted rearrangement of 1-hydroxy-4,5-epoxydecane **20**.

Conditions: same with Fig S1.

The progress of the epoxidation of *cis*-4-decen-1-ol **19** was checked by GC analysis. After 4h, over 99% of the alkenol was consumed, and crude epoxide was isolated as described in Experimental section. The ¹H NMR indicated that the crude epoxide did not contain any cyclization product **S1**. ¹H NMR and ¹³C NMR of **20** and **S1** were indicated in Fig. S5-S8.

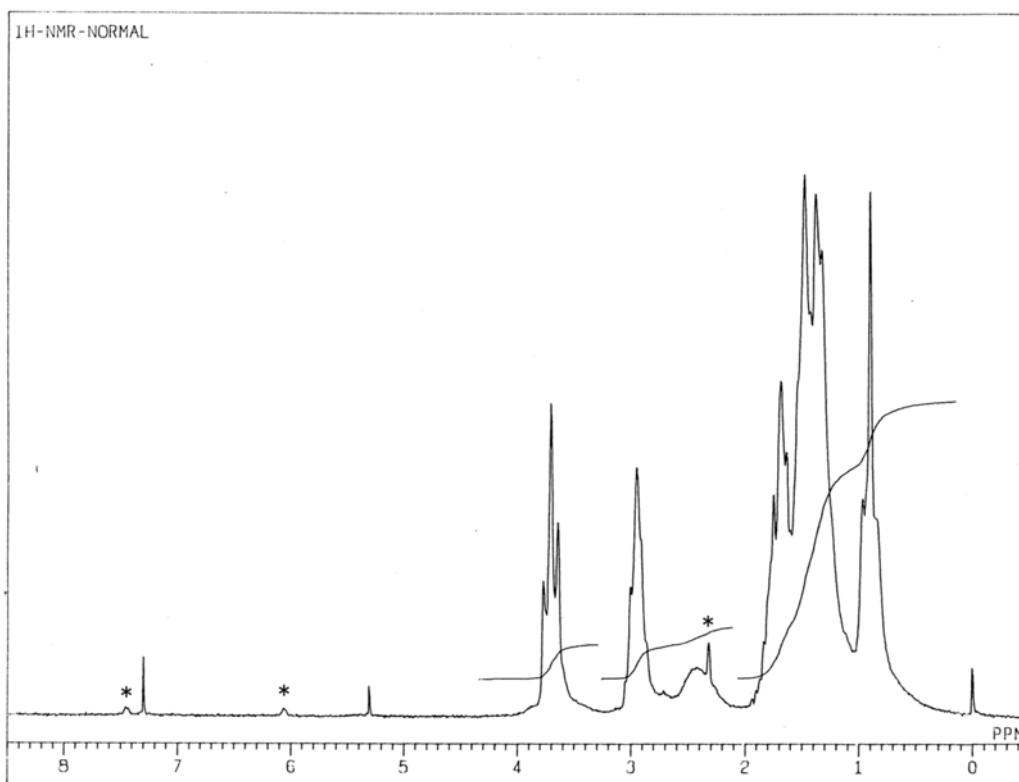


Fig. S5 ^1H NMR of crude 1-hydroxy-4,5-epoxydecane **20**. (*: 3-methylpyrazole)

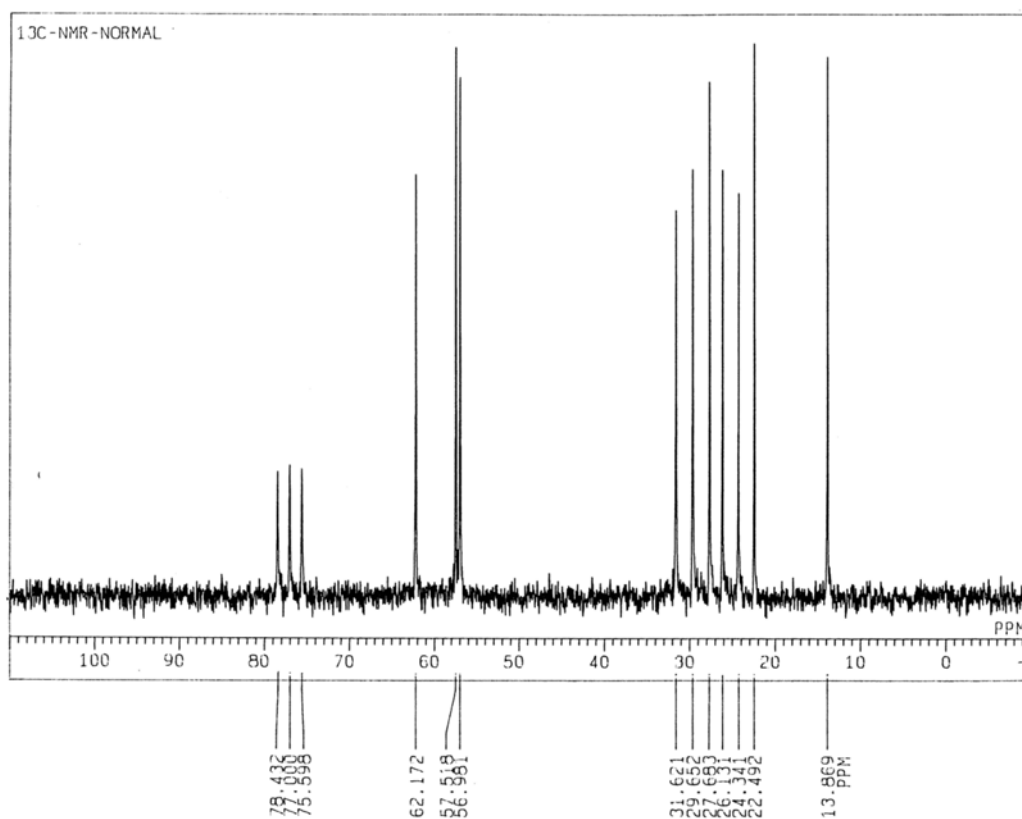


Fig. S6 ^{13}C NMR of crude 1-hydroxy-4,5-epoxydecane **20**.

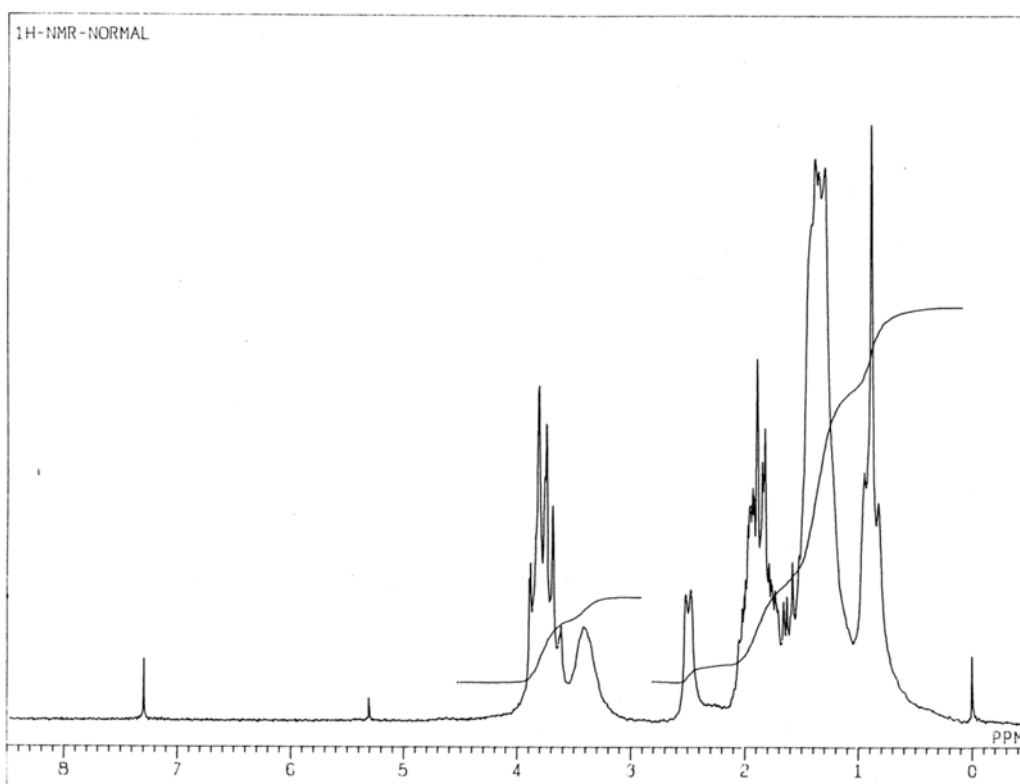


Fig. S7 ^1H NMR of 1-(2-tetrahydrofuranyl)hexan-1-ol **S1**.

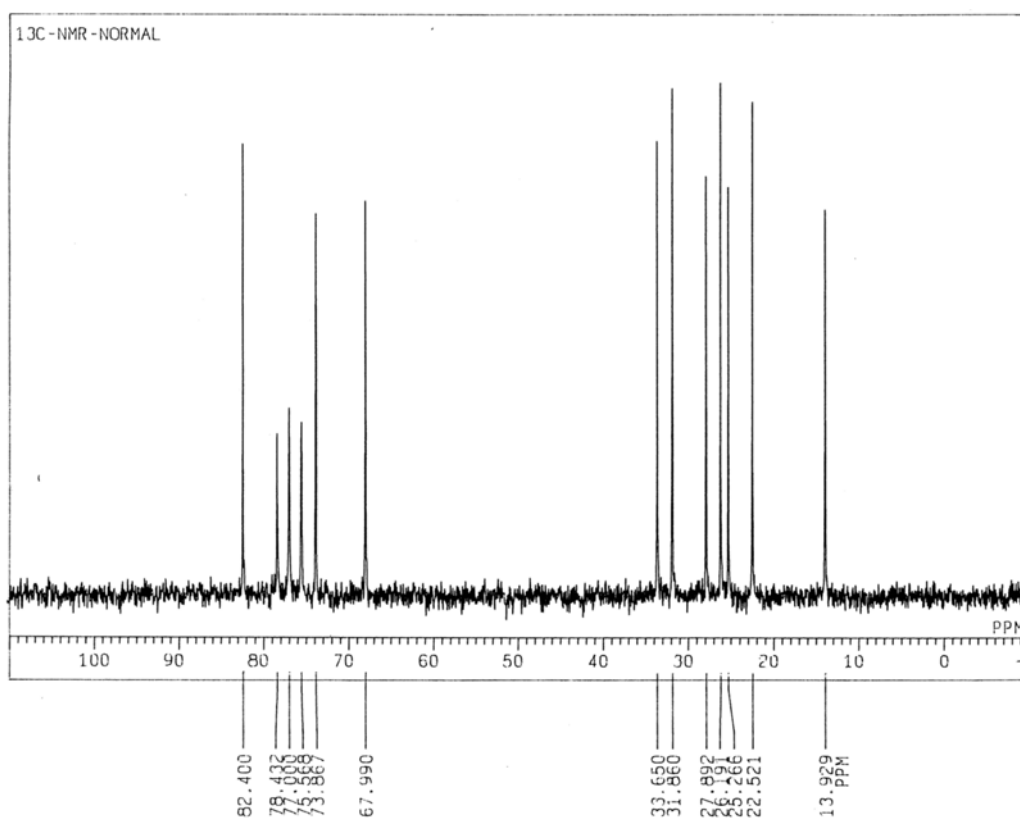


Fig. S8 ^{13}C NMR of 1-(2-tetrahydrofuranyl)hexan-1-ol **S1**.

3. NMR spectra of isosafrole oxide (mixture of isomers)

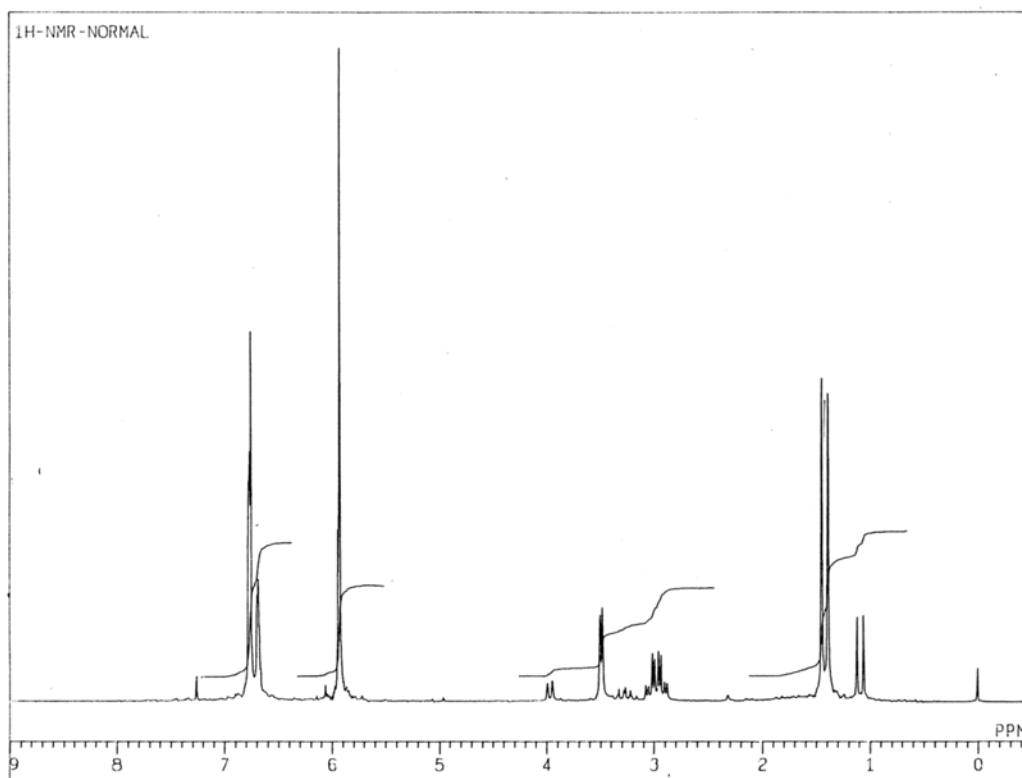


Fig. S9 ^1H NMR of isosafrole oxide.

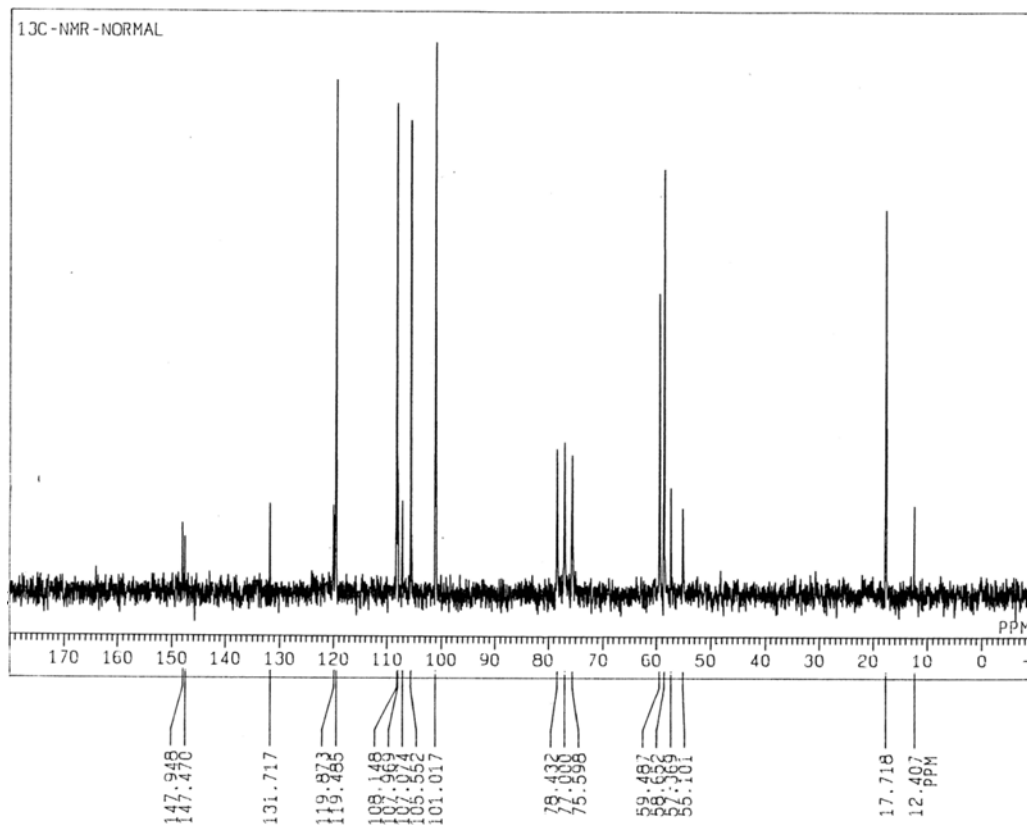


Fig. S10 ^{13}C NMR of isosafrole oxide.

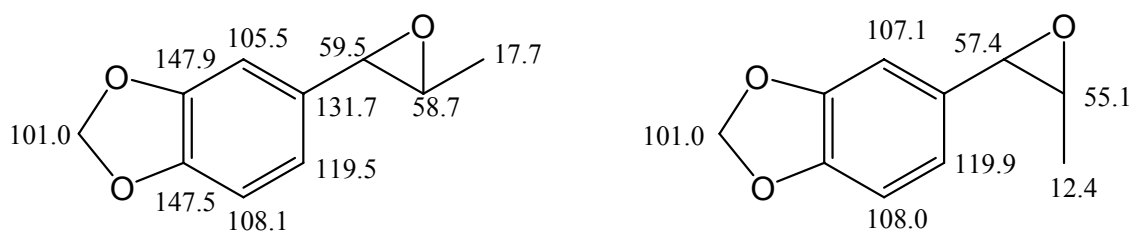


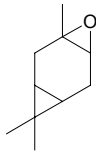
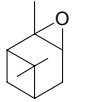
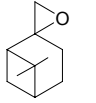
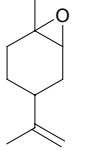
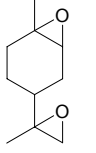
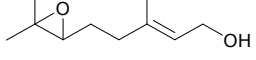
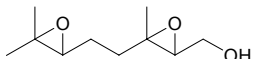
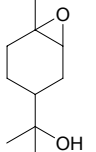
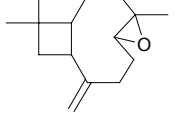
Fig. S11 Assignment of ^{13}C NMR signals of *trans*- and *cis*-isosafrole epoxide (δ in ppm).

Isosafrole epoxide is a known compound,[2] but NMR data was not found in literatures. The ratio of *trans*- and *cis*-isomer was approximately 4:1 by ^1H NMR (Fig. S9). The assignment of the signals of ^{13}C NMR (Fig. S10) are as indicated in Fig. S11. The signals of quaternary carbons in *cis*-isomer were not observed (Fig. S10).

4. NMR references for the known epoxides

number	epoxide	references
2		[3], [4], [5]
		[6]
8		[7]
12		[7], [8]
16		[7]
18		[7]
22		[9]

(continued)

number	epoxide	references
24		[5], [9], [10], [11], [12], [13], [14]
26		[5], [8], [9], [10], [11], [13], [14]
28		[15]
30		[9], [10], [11], [12], [13], [16]
31		[9], [12]
33		[10], [12]
34		
36		[13]
40		[13]

5. References

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