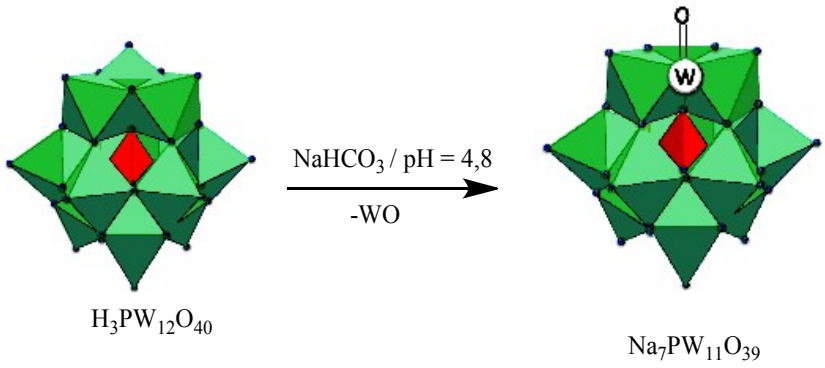
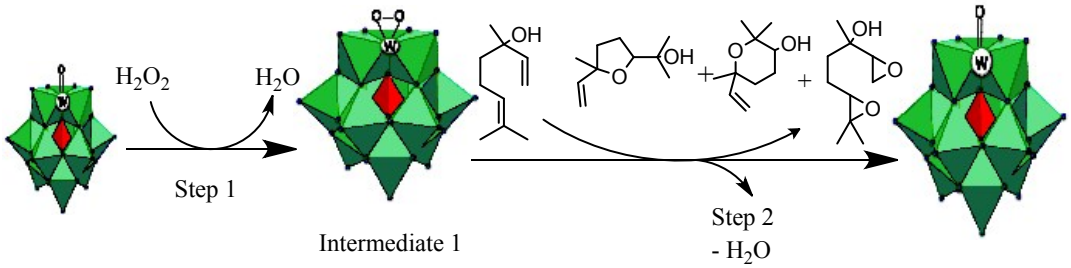
Supplemental material



Scheme SM1. Synthesis of lacunar sodium phosphotungstate catalyst



Scheme SM2. Reaction pathway of $Na_7PW_{11}O_{39}$-catalyzed oxidation reaction of linalool with H_2O_2 (adapted refs. 1,2)

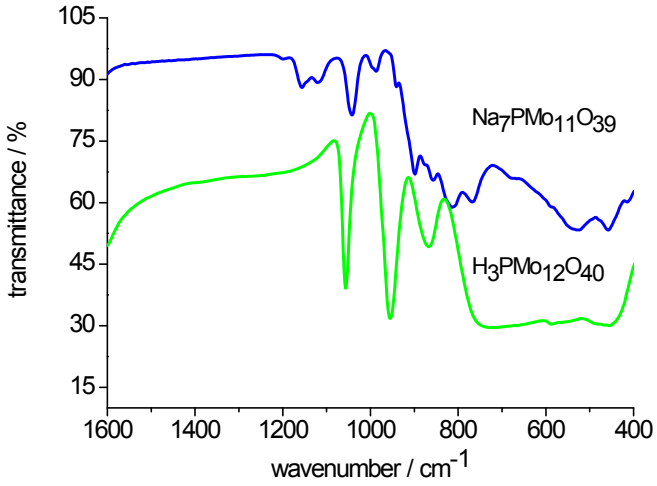


Figure SM1. FT-IR spectra of phosphomolybdic acid and its lacunar sodium salt

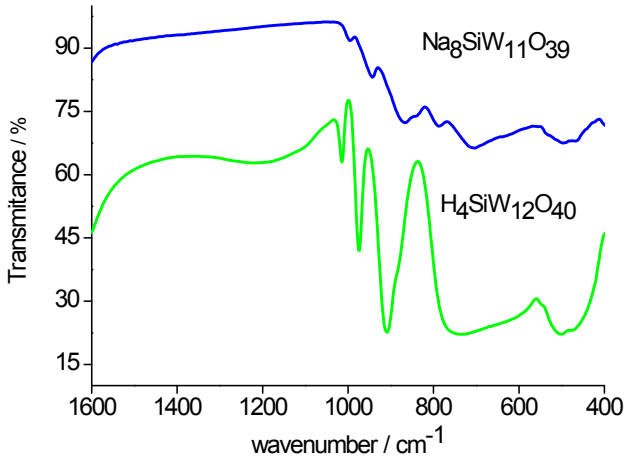


Figure SM2. FT-IR spectra of silicotungstic acid and its lacunar sodium salt

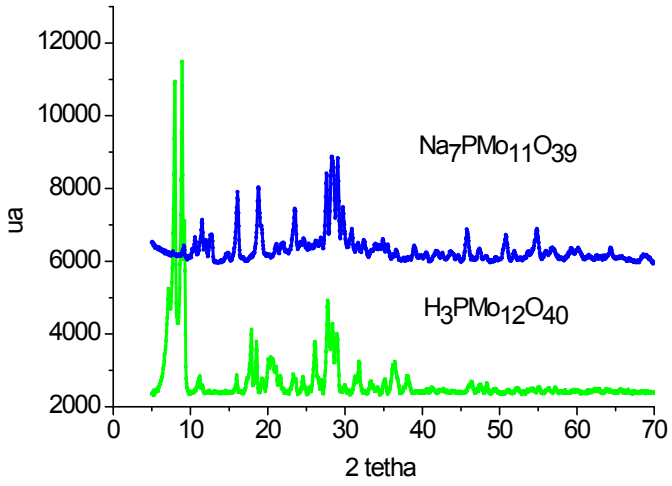


Figure SM3. Powdered XRD patterns of $Na_7PMo_{11}O_{39}$ lacunar salt and $H_3PMo_{12}O_{40}$ parent

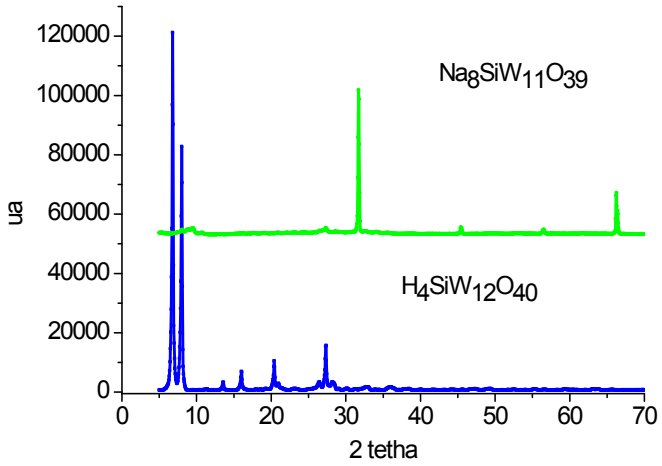


Figure SM4. Powdered XRD patterns of $Na_8SiW_{11}O_{39}$ lacunar salt and $H_4SiW_{12}O_{40}$ parent

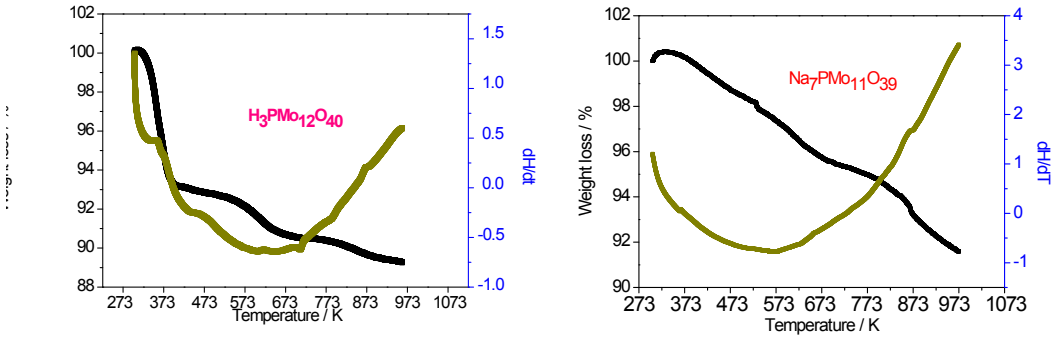


Figure SM5. TG/DSC curves: $H_3PMo_{12}O_{40}$ precursor (a) and $Na_7PMo_{11}O_{39}$ lacunar salt (b)

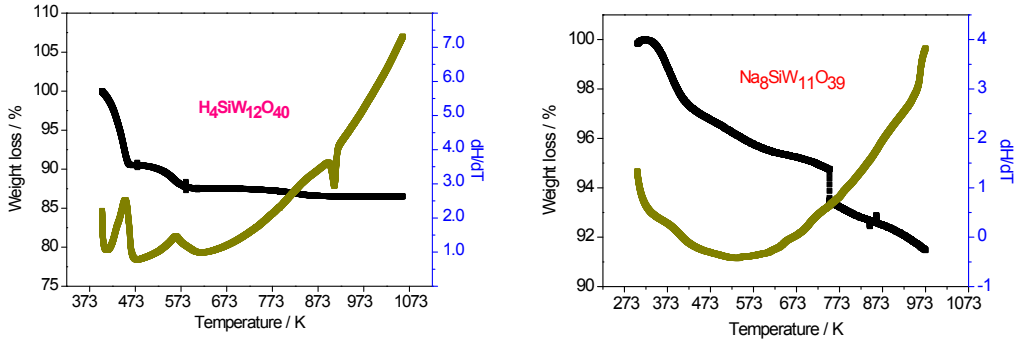


Figure SM6. TG/DSC curves: $H_4SiW_{12}O_{40}$ precursor (a) and $Na_8SiW_{11}O_{39}$ lacunar salt (b)

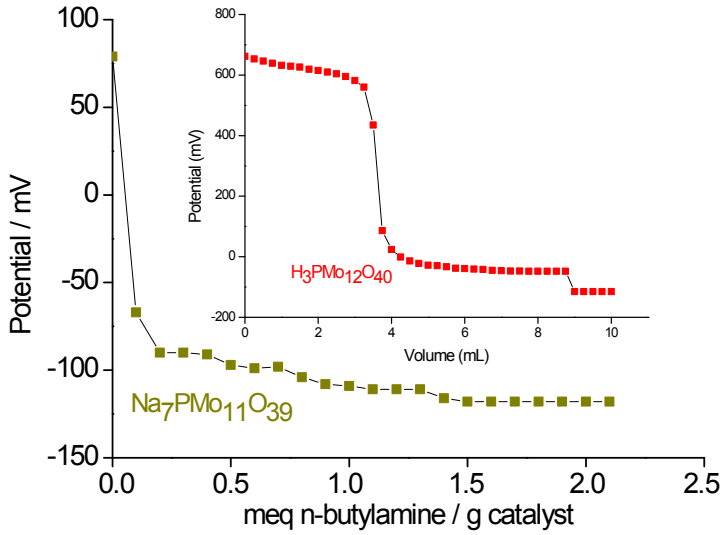


Figure SM7. Potentiometric titration curves with *n*-butylamine of $H_3PMo_{12}O_{40}$ and $Na_7PMo_{11}O_{39}$ salt

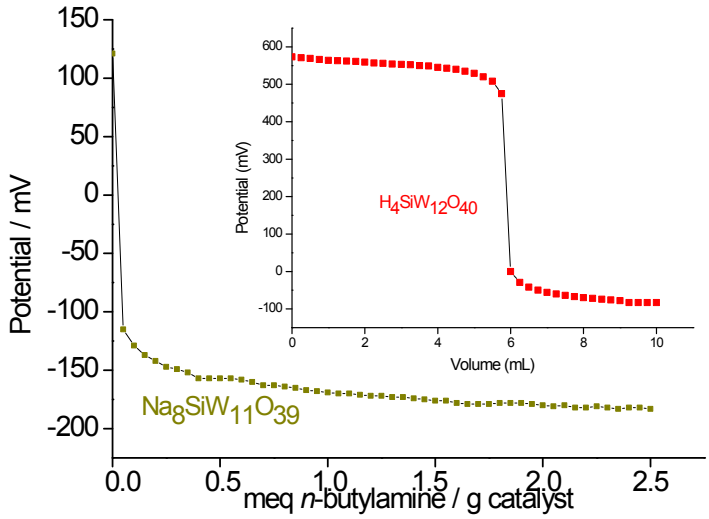
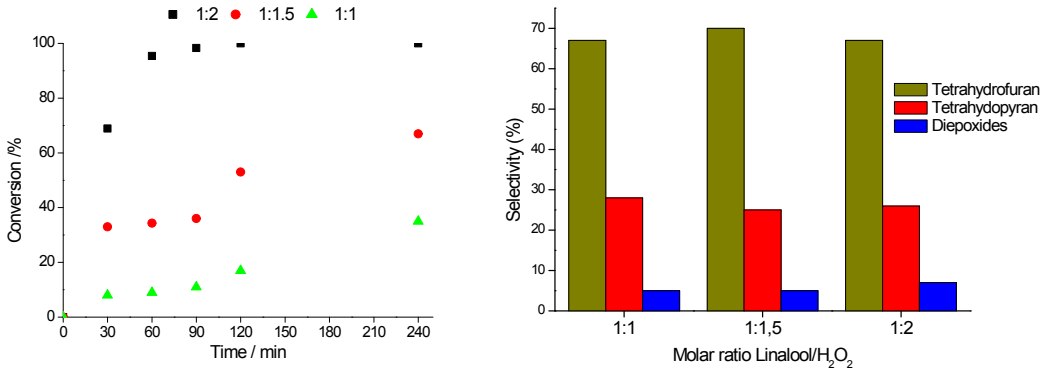


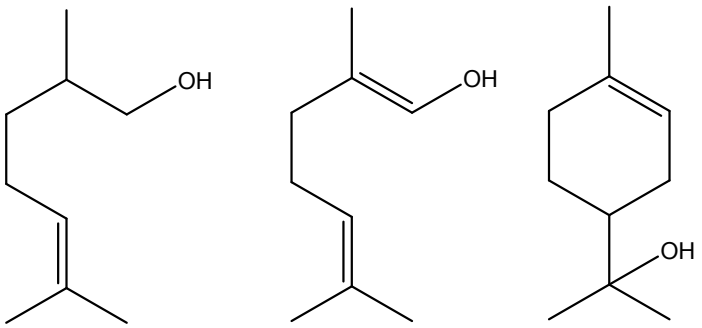
Figure SM8. Potentiometric titration curves with *n*-butylamine of $H_4SiW_{12}O_{40}$ and $Na_8SiW_{11}O_{39}$ salt.



(a) (b)

Figure SM9. Effect of oxidant load on kinetic curves of conversion (**a**) and products selectivity (**b**) of $Na_7PW_{11}O_{39}$-catalyzed oxidation reactions of linalool with H_2O_2

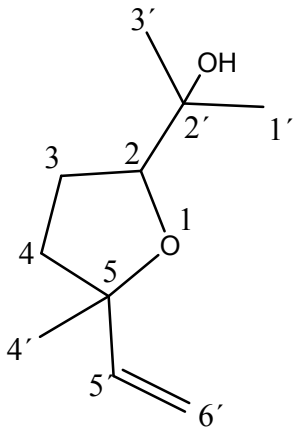
[a]Reaction conditions: Linalool (2.75 mmol); reaction time (4 h); $Na_7PW_{11}O_{39}$ (0.33 mol %); temperature (298 K); CH_3CN (10 mL)



β-citronellol geraniol α-terpineol

Figure SM10. Terpenic alcohols evaluated as substrates in $Na_7PW_{11}O_{39}$-catalyzed oxidation reactions with H_2O_2

Spectroscopic data of the main products of $Na_7PW_{11}O_{39}$-Catalyzed linalool oxidation by hydrogen peroxide.

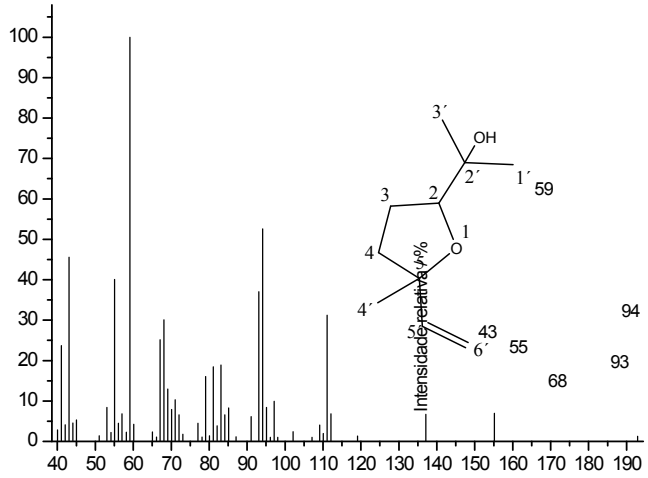


2-(5-methyl-5-vinyltetrahydrofuran-2-yl propan-2-ol) (1a)

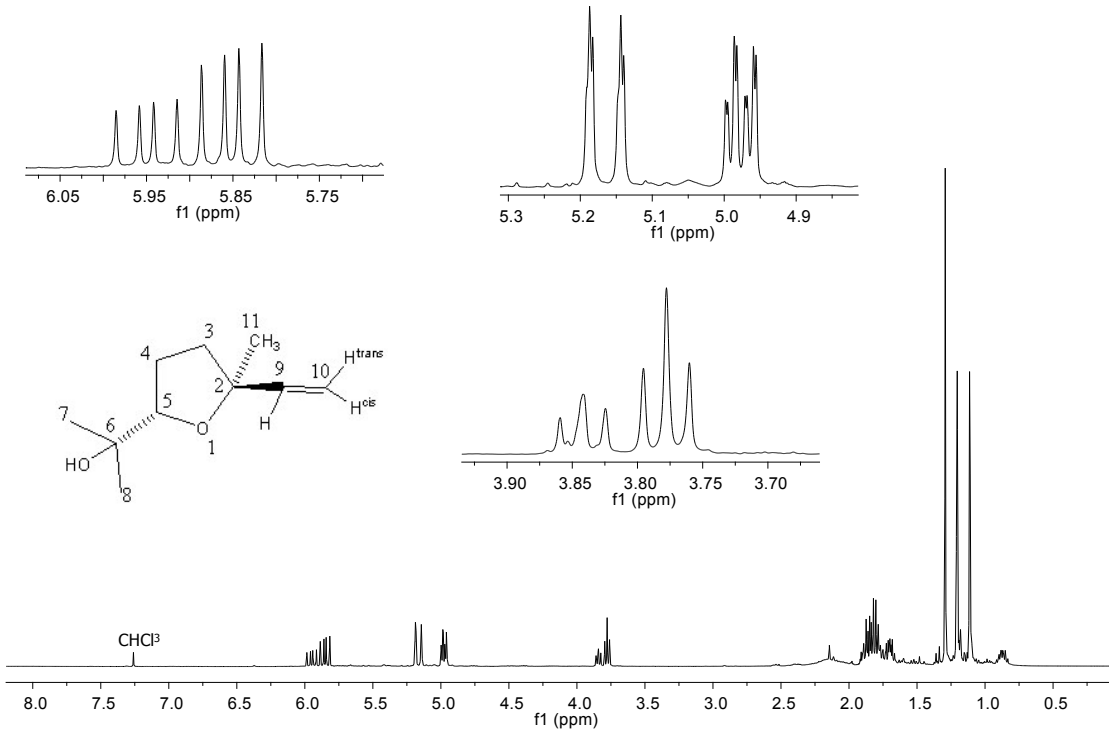
^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.11 (s, H7), 1.20 (s, H8), 1.29 (s, H11), 1.66-1.93 (m, H3 and H4), 3.78 (t, $J_{5,4}$=7, H5), 4.97 (dd, $J_{10cis,9cis}$=10.5, $J_{10cis,10trans}$=1.5, H10*cis*), 5.16 (dd, $J_{10trans,9cis}$=17.5, $J_{10cis,10trans}$=1.5, H*10trans*,), 5.85 (dd, $J_{10trans,9cis}$=17.5, $J_{10cis,9cis}$=10.5, H*9cis*).

^{13}C NMR spectrum, δ, ppm: 24.0 (CH_3), 26.3 (C4), 26.7 (CH_3), 27.1 (CH_3), 37.4 (C3), 71.1 (C6), 83.0 (C2), 85.5 (C5), 111.3 (C10), 143.6 (C9).

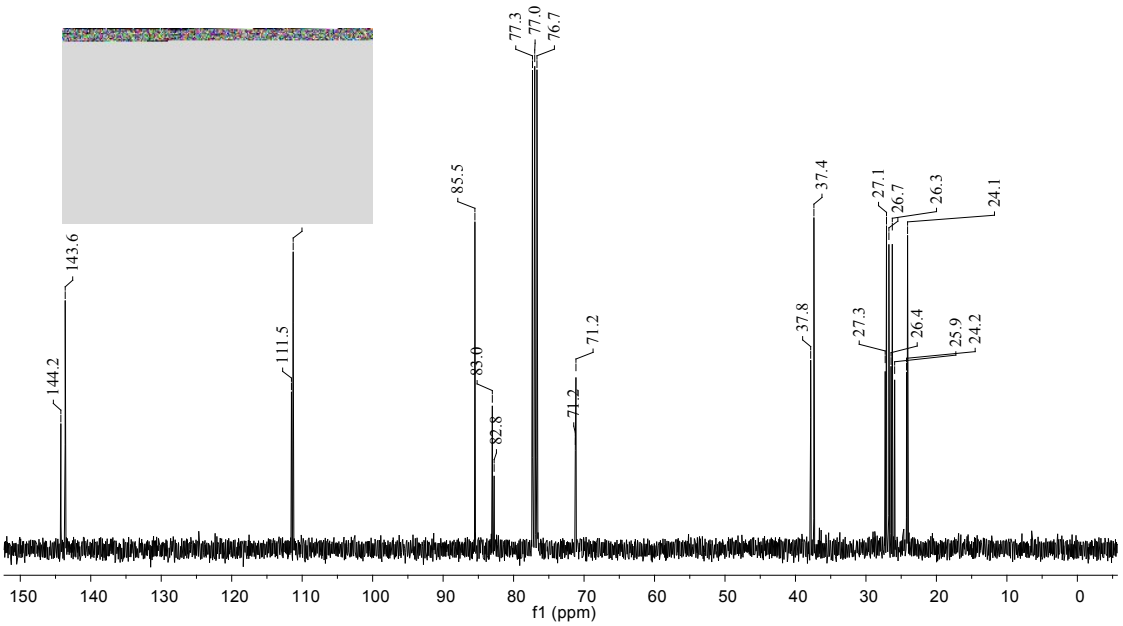
MS *m/z* (%) 170 (0.1), 155 (7), 137 (7), 111 (31), 94 (53), 93 (37), 68 (30), 59 (100), 55 (40), 43 (46).



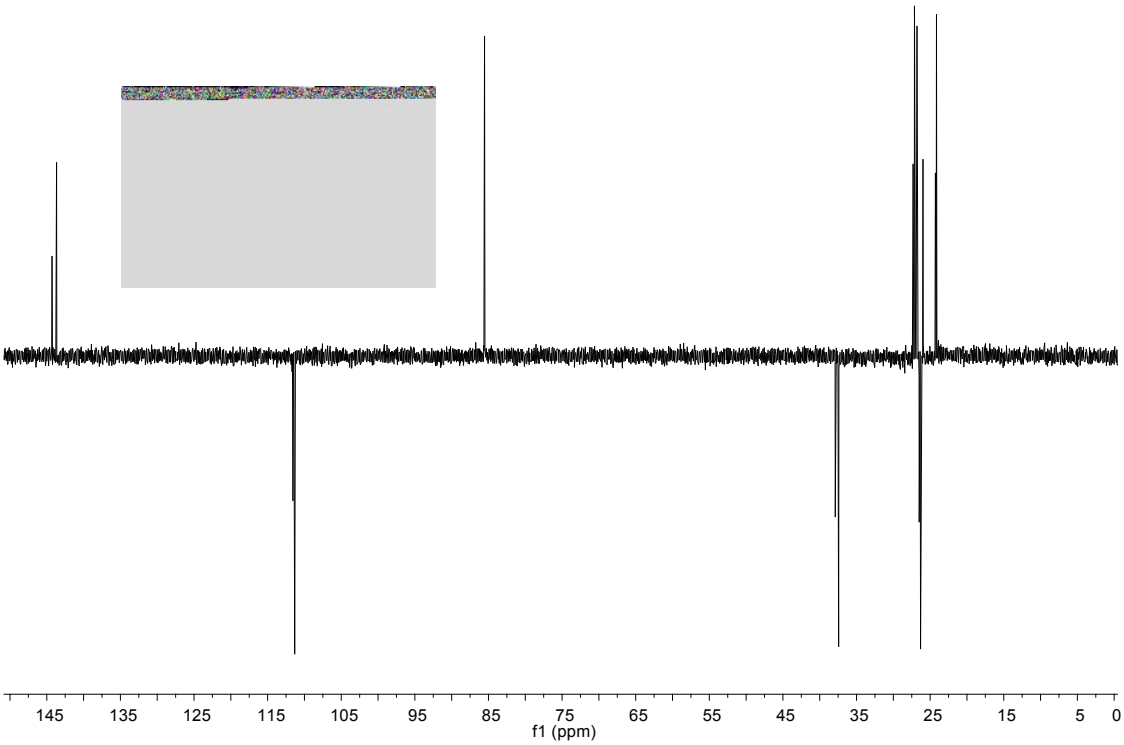
Mass spectrum of product (1a)



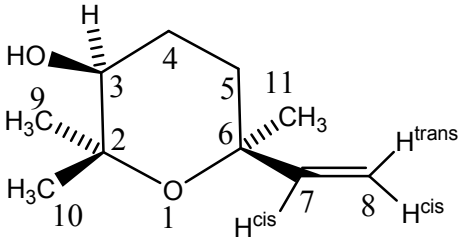
^{1}H NMR Spectrum of product (1a)



^{13}C NMR Spectrum of product (1a)



DEPT ^{13}C NMR Spectrum of product (1a)



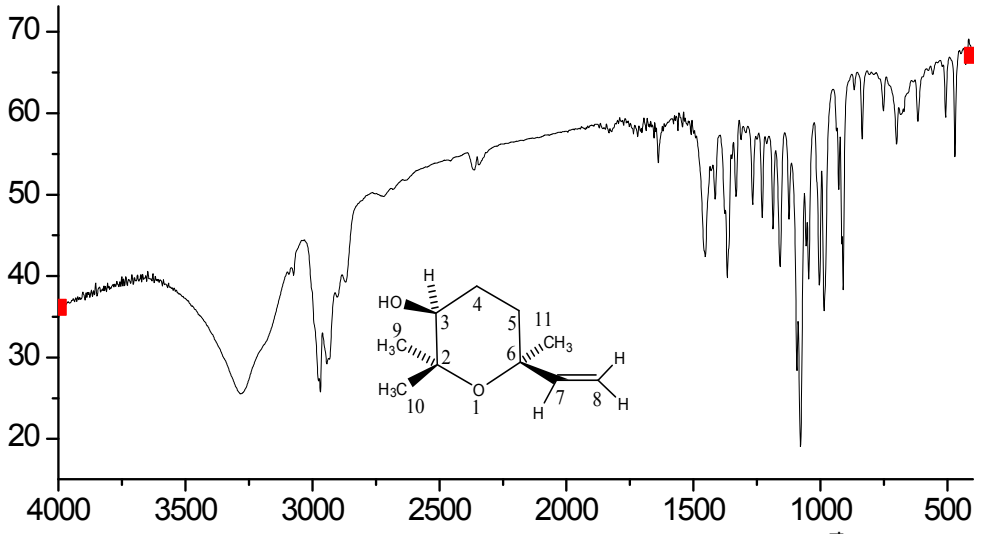
2,2,6-Trimethyl-6-vinyltetrahydro-2H-pyran-3-ol (1b)

2,2,6-trimethyl-6-vinyltetrahydro-2H-pyran-3-ol, colorless crystals, IR (film) ν_{max} / cm^{-1} 3280**,** 2968, 1454, 1368, 1076, 975, 908.

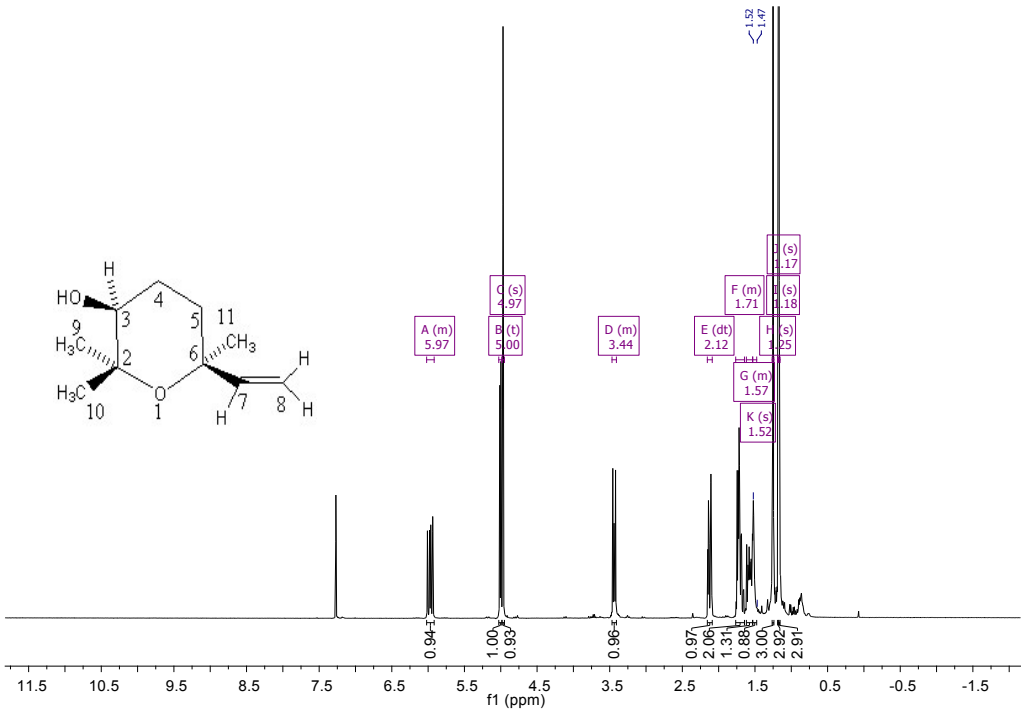
^{1}H NMR (600 MHz, $CDCl_3$) δ 1.17 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.52 (s, OH), 1.62 (m, $1H^{5}$), 1.64-1.77 (m, $2H^{4}$), 2.12 (dt, *J* = 13.7 e 3.8 Hz, $1H^{5}$), 3.41-3.47 (m, $1H^{3}$), 4,97 (s, $1H^{8trans}$), 5.01 (d, *J* = 6.1 Hz, $1H^{8cis}$), 5.92-6.02 (m, $1H^{7cis}$).

^{13}C NMR (150 MHz, $CDCl_3$) δ 20.8 (C10), 25.7 (C4), 29.5 (C9), 31.6 (C11), 32.5 (C5), 73.4 (C6), 74.8 (C3), 75.9 (C2), 110.6 (C8), 146.3 (C7).

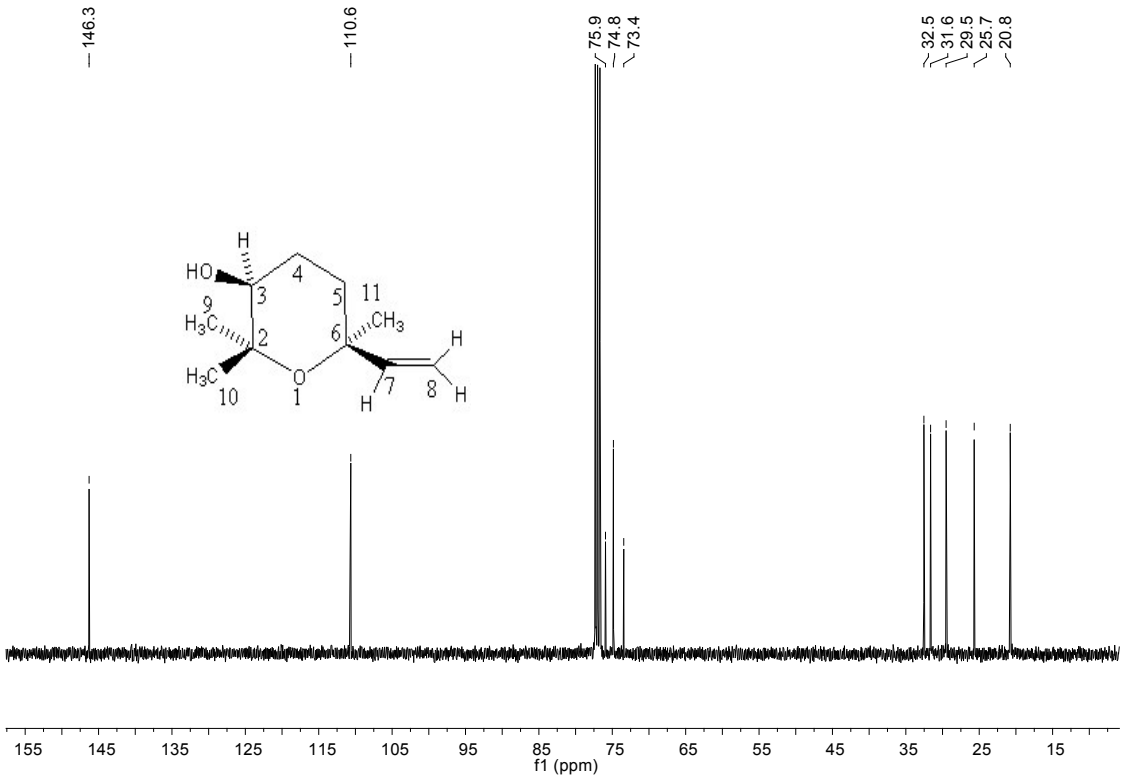
MS *m/z* (%) 170 (1), 155 (5), 94 (82), 79 (26), 68 (100), 67 (50), 59 (85), 43 (37)



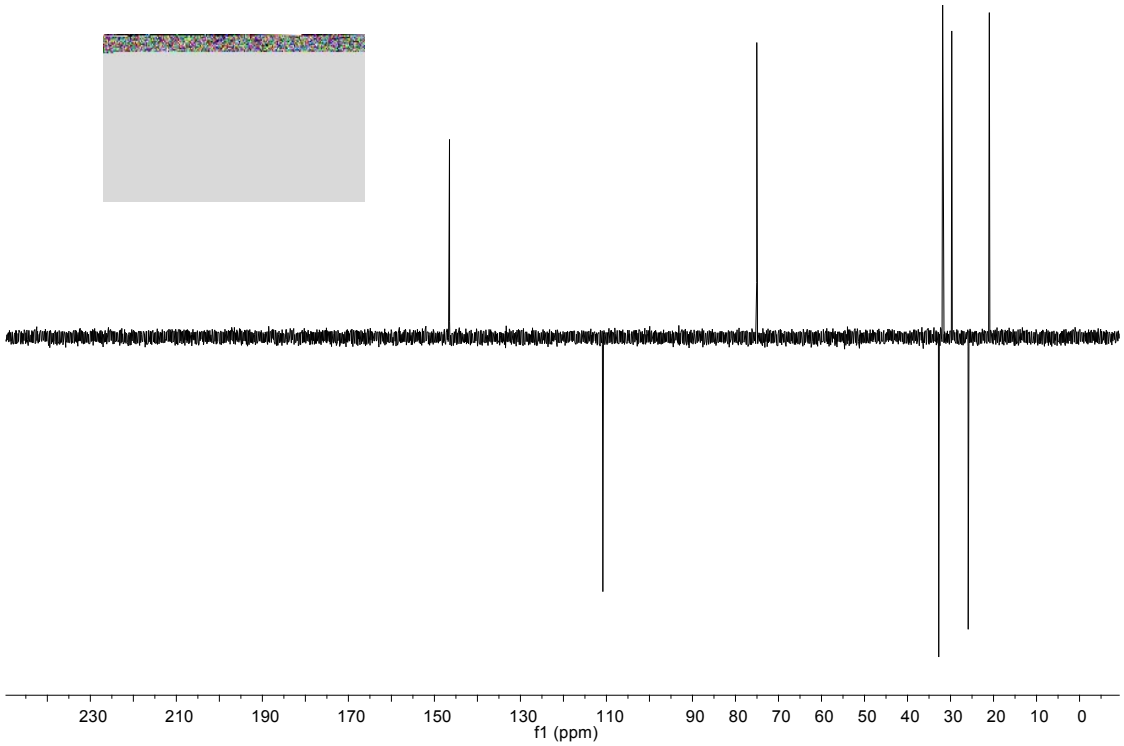
IR Spectrum of product (1b)



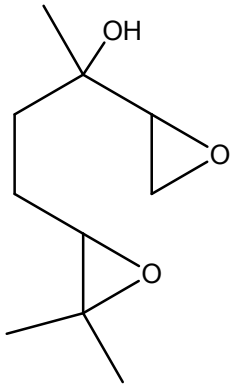
^{1}H NMR Spectrum of product (1b)



^{13}C NMR Spectrum of product (1b)

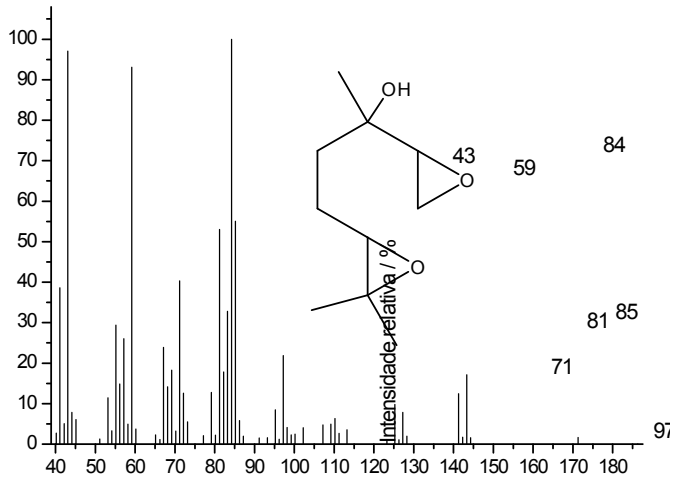


DEPT ^{13}C NMR Spectrum of product (1b)



Diepoxide (1c)

MS *m/z* (%) 186 (0.1), 143 (17), 97 (22), 84 (100), 85 (55), 81 (53), 71 (40), 59 (93), 43 (97).



Mass Spectrum of product (1c)