Supplemental material

Scheme SM1. Synthesis of lacunar sodium phosphotungstate catalyst

Scheme SM2. Reaction pathway of Na₇PW₁₁O₃₉-catalyzed oxidation reaction of linalool with H₂O₂ (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$_7$PMo$_{11}$O$_{39}$ lacunar salt and H$_3$PMo$_{12}$O$_{40}$ parent

Figure SM4. Powdered XRD patterns of Na$_8$SiW$_{11}$O$_{39}$ lacunar salt and H$_4$SiW$_{12}$O$_{40}$ parent
Figure SM5. TG/DSC curves: $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ precursor (a) and $\text{Na}_7\text{PMo}_{11}\text{O}_{39}$ lacunar salt (b)

Figure SM6. TG/DSC curves: $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ precursor (a) and $\text{Na}_8\text{SiW}_{11}\text{O}_{39}$ lacunar salt (b)
Figure SM7. Potentiometric titration curves with $n$-butylamine of H$_3$PMo$_{12}$O$_{40}$ and Na$_7$PMo$_{11}$O$_{39}$ salt.

Figure SM8. Potentiometric titration curves with $n$-butylamine of H$_4$SiW$_{12}$O$_{40}$ and Na$_8$SiW$_{11}$O$_{39}$ salt.
**Figure SM9.** Effect of oxidant load on kinetic curves of conversion (a) and products selectivity (b) of Na₇PW₁₁O₃₉-catalyzed oxidation reactions of linalool with H₂O₂

- Reaction conditions: Linalool (2.75 mmol); reaction time (4 h); Na₇PW₁₁O₃₉ (0.33 mol %); temperature (298 K); CH₃CN (10 mL)

**Figure SM10.** Terpenic alcohols evaluated as substrates in Na₇PW₁₁O₃₉-catalyzed oxidation reactions with H₂O₂
Spectroscopic data of the main products of Na$_7$PW$_{11}$O$_{39}$-Catalyzed linalool oxidation by hydrogen peroxide.

![Chemical Structure]

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

$^1$H NMR spectrum, $\delta$, 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, H10cis), 5.16 (dd, $J_{10trans,9cis}$=17.5, $J_{10cis,10trans}$=1.5, H10trans), 5.85 (dd, $J_{10trans,9cis}$=17.5, $J_{10cis,9cis}$=10.5, H9cis).

$^{13}$C NMR spectrum, $\delta$, 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) $\nu_{\text{max}}$ / cm$^{-1}$

3280, 2968, 1454, 1368, 1076, 975, 908.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 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$^{\text{trans}}$), 5.01 (d, $J = 6.1$ Hz, 1H$^{\text{cis}}$), 5.92-6.02 (m, 1H$^{7\text{cis}}$).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 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)

\[^{13}\text{C} \text{ NMR Spectrum of product (1b)}\]
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)