Highly Efficient Epoxidation of Allylic Alcohols with Hydrogen Peroxide Catalyzed by Peroxoniobate-Based Ionic Liquids

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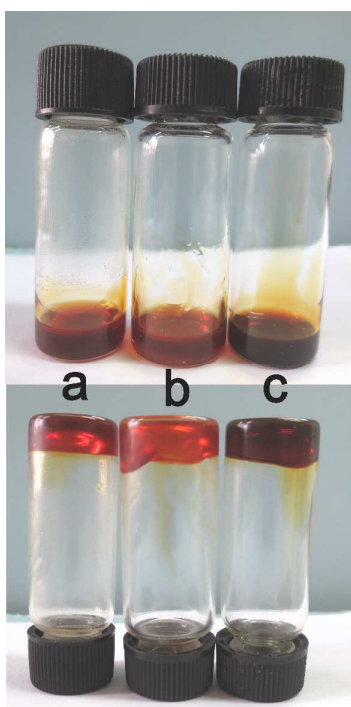## Characterization and activity test of ILs

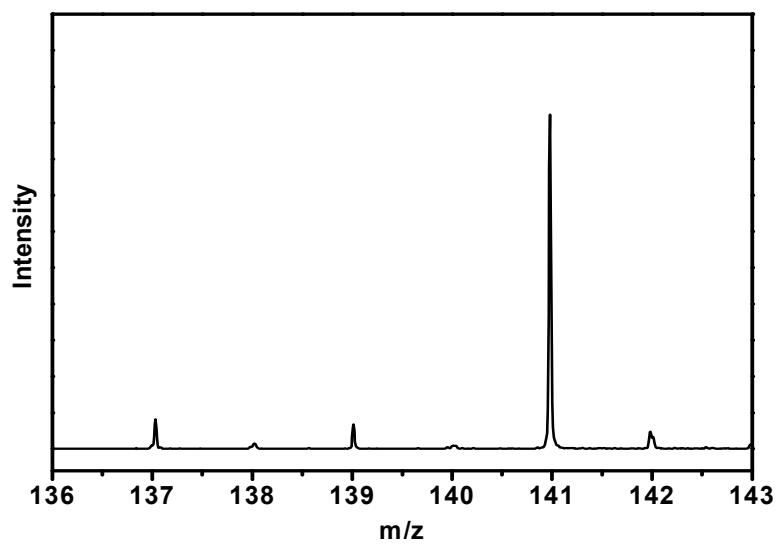**Figure S1.** Photographs of ILs catalyst: a) TPAIL; b) TBAIL; c) THAIL at 10 $^{\circ}$C.

Figure S2. Mass spectrum of $[Nb=O(O-O)(OH)_2]^-$

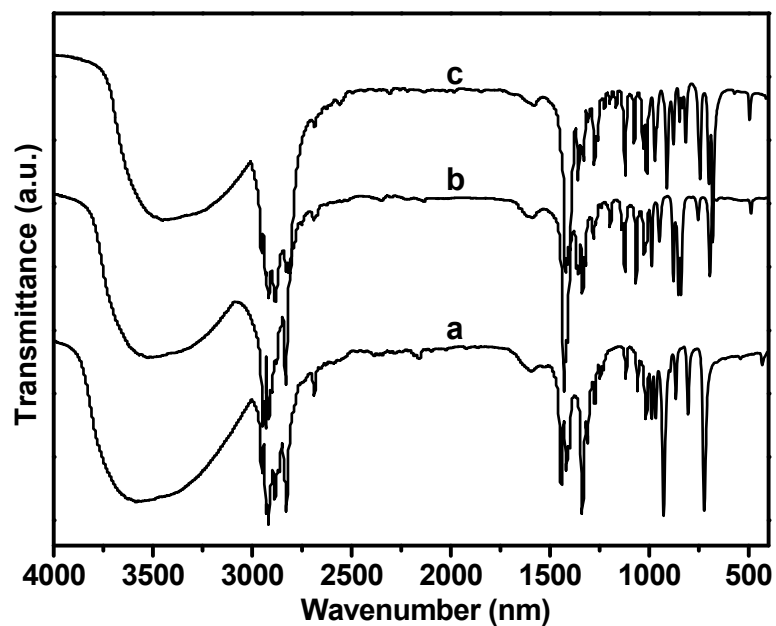**Figure S3.** FT-IR spectra of a) TPAOH; b) TBAOH; c) THAOH. The hydroxide precursor can be obtained by anion exchange between KOH and corresponding a quaternary ammonium halide salt in ethanol, following by drying carefully at room temperature.
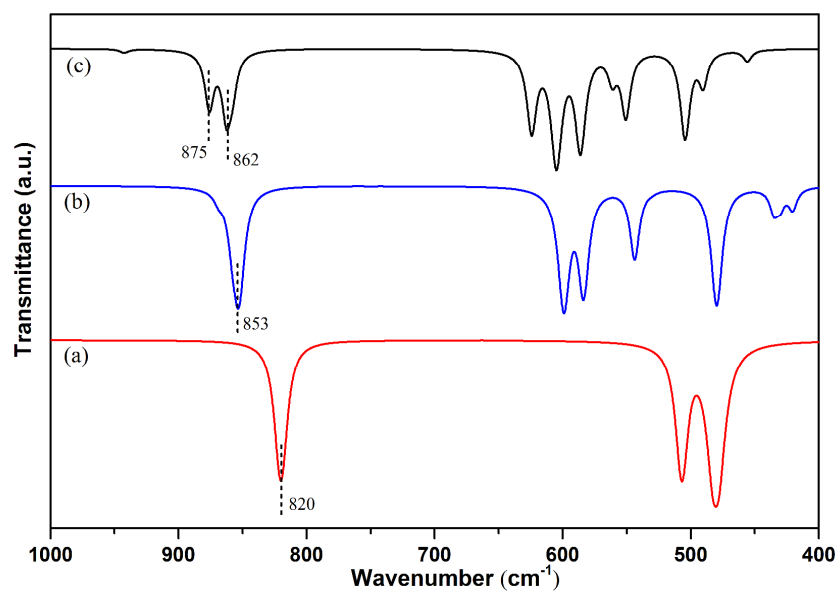
Figure S4. Simulated IR for three possible formed anions. (a) $[Nb(O\text{-}O)_4]^{3-}$; (b) $[Nb(O\text{-}O)_3(OOH)]^{2-}$; (c) $[Nb(O\text{-}O)_2(OOH)_2]^{-}$.

Table S1. Epoxidation catalyzed by TBA-IL in different solvents[a]

Entries	Solvents[b]	Conv. %[c]	Sel. %	
			epoxide	diol
1	none	96.4	≥99	<1
2	CH$_3$CN	53.9	≥99	<1
3	CH$_3$OH	40.8	88.3	11.7
4	EtOAc	35.6	≥99	<1
5	CH$_2$Cl$_2$	38.8	≥99	<1
6	H$_2$O	45.2	≥99	<1
7[d]	H$_2$O	61.9	≥99	<1

[a] Reaction conditions: 3-methyl-2-butene-1-ol (2 mmol), 30% aq. H$_2$O$_2$ (2 mmol), TBA-IL (0.05 mmol), 0 °C, 0.75 h. [b] 2 ml solvent was added if necessary. [c] GC conversion with dodecane as an internal standard. [d] 1 ml H$_2$O was used.
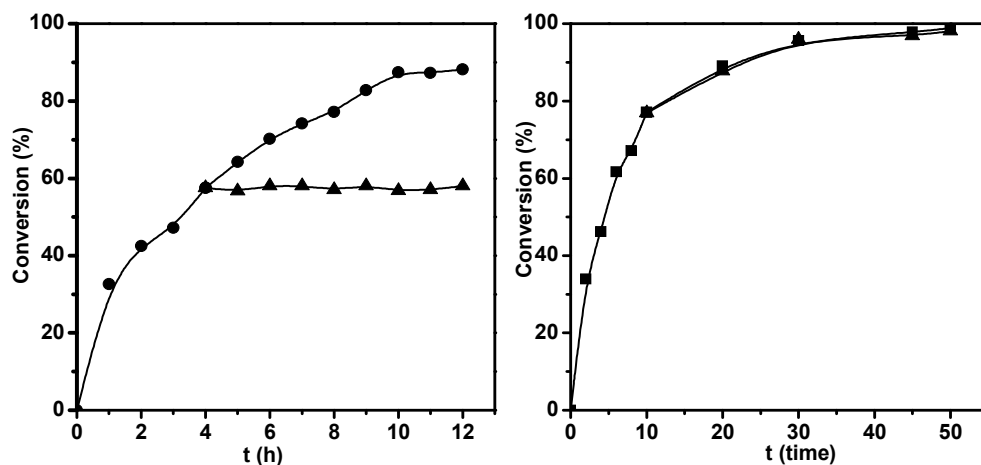
Figure S5. Time profile of the epoxidation reaction of 3-methyl-2-butene-1-ol catalyzed by TBAIL. a) Reaction conditions: 2 mmol of 3-methyl- 2-butene-1-ol, 2 mmol of 30% aqueous H_2O_2, 0.05mmol of the TBAIL, 2 mL EtOAc. After reaction for 4 h, 1 ml EtOAc was removed and stirred continuously (solid triangle point), indicating that reaction stopped immediately. The remained solution continued on the reaction (solid circle point); b) Reaction conditions: 4 mmol of 3-methyl-2-butene-1-ol, 4 mmol of 30 wt% aqueous H_2O_2, 0.1mmol of the TBAIL. After reaction for 10 min, the butylated hydroxytoluene (BHT) was added to the reaction mixture, which did not affect the reaction conversion (solid square point and solid triangle point).
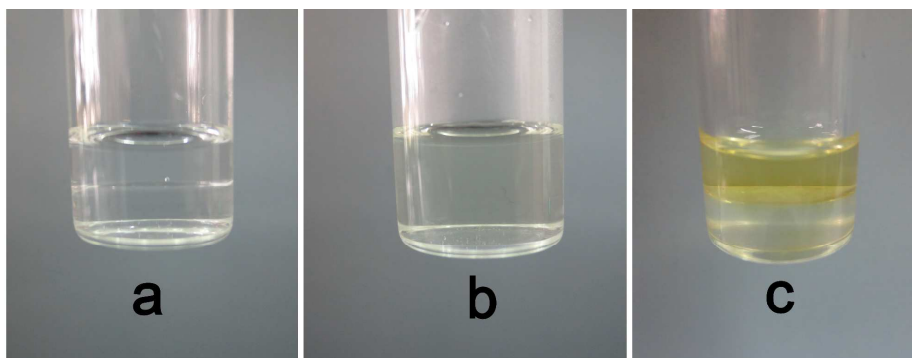
Figure S6. Photographs in water/oil phase: a) H_2O_2 and 3-methyl-2-butene-1-ol formed biphasic system; b) H_2O_2 and 3-methyl-2-butene-1-ol became homogeneous phase immediately after introduction of TBA-IL; c) H_2O and 3-methyl-2-butene-1-ol kept biphasic even if TBA-IL was added. Conditions: 4 mmol H_2O_2, 4 mmol 3-methyl-2-butene-1-ol and 0.1 mmol TBAIL under ice bath.
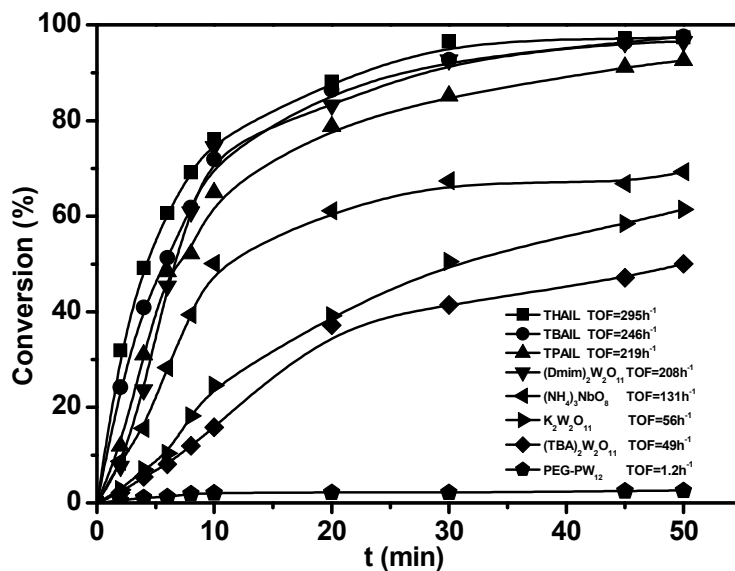
Figure S7. Conversion/time profiles of 3-methyl-2-butene-1-ol epoxidation reactions over the different catalysts. Reaction conditions: 3-methyl-2-butene-1-ol (2 mmol), H_2O_2 (2 mmol), catalyst (0.05 mmol), 0^oC. TOF was defined as the number of moles of the consumed allylic alcohol (3-methyl-2-butene-1-ol) per moles of catalyst per hour.
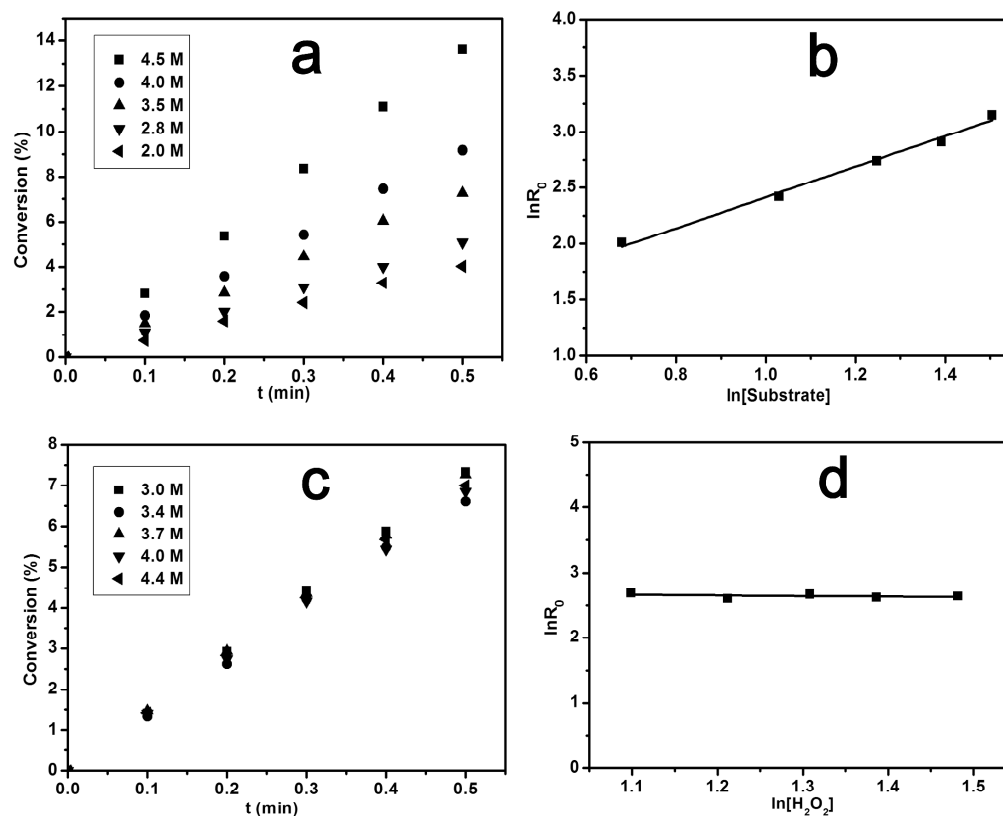
Figure S8. The relationship between the reaction rate (R_0) and the concentration of 1a and hydrogen peroxide. Reaction conditions for a and b: 3-methyl-2-butene-1-ol (2.0 M -4.5 M), H_2O_2 (4.0 M), TBAIL (0.083 M), 0^oC. Reaction conditions for c and d: 3-methyl-2-butene-1-ol (4.0 M), H_2O_2 (3.0 M-4.4 M), TBAIL (0.096 M), 0^oC. All reaction profiles have been attained at low conversions (<20%).
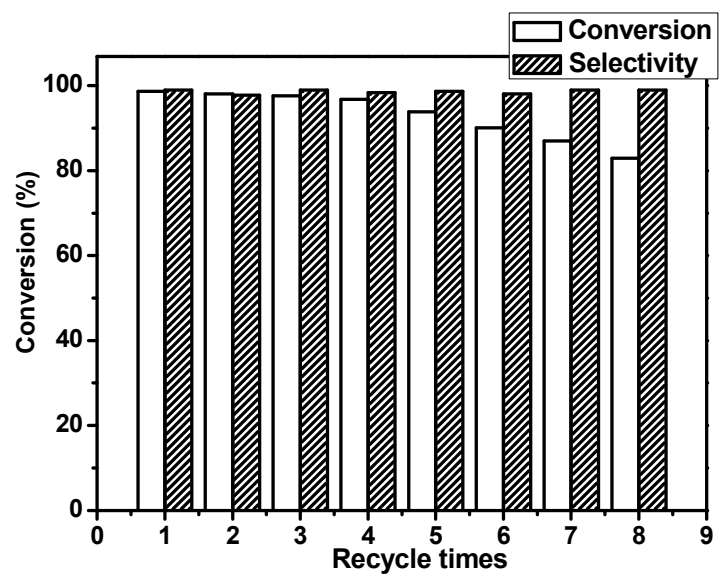
Figure S9. Recyclability of the TBAIL catalyst without any other solvent at 0 $^{\circ}$C for 0.75 h.

Supplementary details of the thermodynamic and concentration calculation

In order to obtain a quantitative estimation of the relative stability of various Nb anions, the conversion from the initial anion $[Nb=O(O-O)(OH)_2]^-$ (A) to $[Nb(O-O)_m(OOH)_{4-m}]^{(m-1)-}$ (m = 2, 3 and 4) (B) is calculated here. The reaction formula is written as

$$A + 3H_2O_2 \rightarrow B + (m-2)H^+ + 3H_2O \tag{1}$$
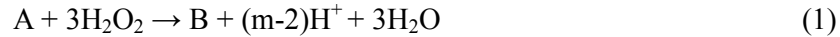
At 298 K, the Gibbs free energy change (ΔG) from A to B can be described as

$$\Delta G = G_B + (m-2) \Delta G_H^+(sol) + 3G_{H2O} - G_A - 3G_{H2O2} \tag{2}$$

where G_x(x=A, B, H$_2$O or H$_2$O$_2$) are the Gibbs free energies of A and B anions, H$_2$O, and H$_2$O$_2$, respectively, obtained from DFT calculation directly within the Gaussian package, with the entropies and zero-point energies included. In addition, it is worth noting that solvent model (PCM) was used to simulate water environment due to presence of 40 wt% H$_2$O$_2$, in which H$_2$O can be seen as solvent in the system. $\Delta G_H^+{}_{(sol)}$ is solvation free energy of H$^+$ in water at 298 K, which was obtained from experimental value, about -11.53 eV. [1]

Meanwhile, we quantitatively evaluated the relative concentrations of various anions. Firstly, assuming the initial concentration of $[Nb=O(O-O)(OH)_2]^-$ at 1 $mol*L^{-1}$ and considering the experimental condition of H$_2$O$_2$ (30 wt%)/TBAIL=40 (molar ratio), it gives the concentrations of H$_2$O$_2$ and H$_2$O to be 40 $mol*L^{-1}$ and 176.3 $mol*L^{-1}$, respectively. Secondly, at the equilibrium state the concentrations of these three anions $[Nb(O-O)_m(OOH)_{4-m}]^{(m-1)-}$ (m = 2, 3 and 4) can be calculated through Eqs. (3), (4) and (5) at 298 K:

$$-RT \ln \frac{C_1*(2C_1+C_2)^2*(176.30+3C_1+3C_2+3C_3)^3}{(1-C_1-C_2-C_3)*(40-3C_1-3C_2-3C_3)^3 C_\theta{}^2} = \Delta G_1 = 151930 J/mol \tag{3}$$

$$-RT \ln \frac{C_2*(2C_1+C_2)*(176.30+3C_1+3C_2+3C_3)^3}{(1-C_1-C_2-C_3)*(40-3C_1-3C_2-3C_3)^3 C_\theta} = \Delta G_2 = 15510 J/mol \tag{4}$$

$$-RT \ln \frac{C_3*(176.30+3C_1+3C_2+3C_3)^3}{(1-C_1-C_2-C_3)*(40-3C_1-3C_2-3C_3)^3} = \Delta G_3 = -22690 J/mol \tag{5}$$

where C_1, C_2, and C_3 are the concentrations of $[Nb(O-O)_4]^{3-}$, $[Nb(O-O)_3(OOH)]^{2-}$ and $[Nb(O-O)_2(OOH)_2]^-$, respectively, while ΔG_1, ΔG_2 and ΔG_3 are the corresponding Gibbs free energy changes from $[Nb=O(O-O)(OH)_2]^-$ to $[Nb(O-O)_4]^{3-}$, $[Nb(O-O)_3(OOH)]^{2-}$ and $[Nb(O-O)_2(OOH)_2]^-$, respectively. R is Molar gas constant, $8.314\ J*K^{-1}*mol^{-1}$. The calculated concentrations are showed in Table 1.

Supplementary details for Mechanism of allylic alcohol epoxidation

(1) The initial interaction forms in hydrogen bonding mechanism
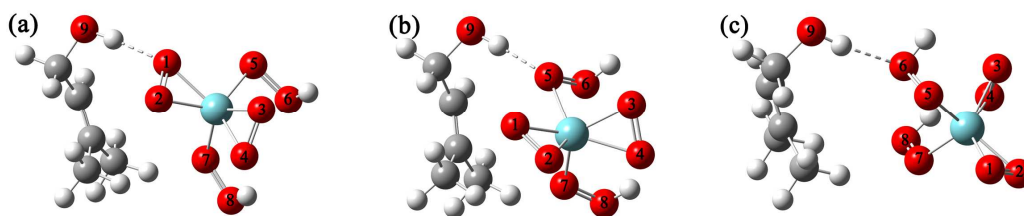
Figure S10. The initial interaction forms between allylic alcohol and $[Nb(O-O)_2(OOH)_2]^-$ in hydrogen bonding mechanism. (a), (b) and (c) represents three different hydrogen bonds, $O_9H\cdots O_1$, $O_9H\cdots O_5$ and $O_9H\cdots O_6$, respectively, in which (a) is the most stable one.

(2) The deprotonation and H back-donation process in metal-alcoholate bonding mechanism

In metal-alcoholate bonding mechanism, the deprotonation of the OH group in allylic alcohols is a prerequisite, in which the proton was transferred to the peroxo,[2] corresponding to an energy barrier of 0.26 eV (TS4, Figure S11a). In TS4, the O_9-H bond is elongated to 1.194 Å, at the same time the $Nb-O_1$ bond is also elongated and inclined to break. Indeed, when the proton is transferred to the O_1 atom, the $Nb-O_1$ bond is broken and forms an O_2O_1H species.

After oxidation of allylic alcohols in metal-alcoholate bonding mechanism, two intermediates IM2(3) (Figure S11b and S11c, respectively) are formed, corresponding

to the epoxidation process oxidized by the peroxo (O-O) and OOH, respectively. For the intermediates IM2(3), it requires to capture the proton back to finish the whole epoxidation process. Here, two transition states (TS7 and TS8) for two different epoxidation pathways, corresponding to IM2 and IM3, are calculated as showed in Figure S11d and S11e, respectively. In TS7 which has an energy barrier of 0.48 eV, the O_1-H and O_9-H bond are 1.285 Å and 1.143 Å, respectively, and the Nb-O_9 is elongated to 2.469 Å from the initial 2.088 Å, while the Nb-O_1 bond is shortened to 2.318 Å. In the other pathway, TS8 has an energy barrier of 0.23 eV, in which the O_1-H bond and Nb-O_9 bond are elongated to 1.241 Å and 2.268 Å, and the O_9-H bond and Nb-O_1 are shortened to 1.193Å and 2.230Å, respectively.
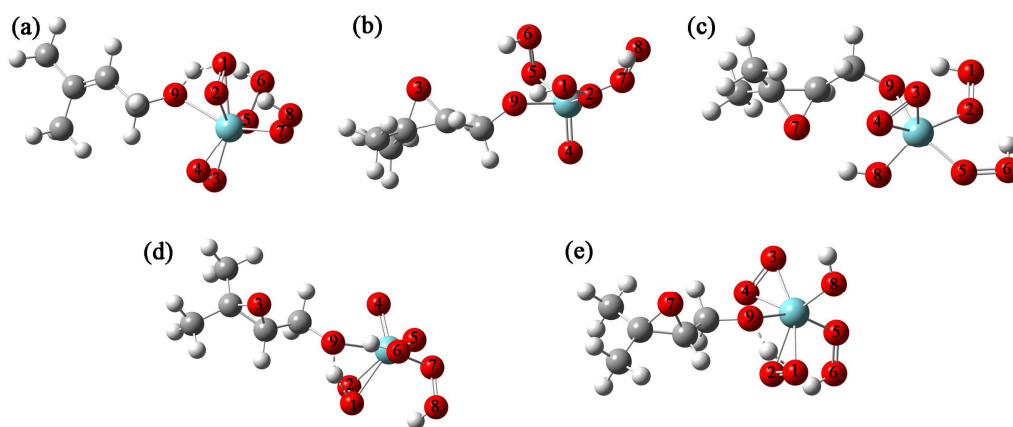
Figure S11. The optimized transition state structures and intermediate structures in metal-alcoholate bonding mechanism. (a) shows TS4 of the deprotonation process of the OH species; (b) and (c) correspond to the intermediate IM2 and IM3, respectively, which are produced from the epoxidation elementary process of OOH or the peroxo group (O-O) attacking the C=C bond of allylic alcohol. (d) and (e) describe the structures of transition states TS7(8), corresponding to the process that IM2(3) capture the proton back to form the final product and finish the whole epoxidation, respectively.

(3) The epoxidation of allylic alcohol with $W_2O_{11}^{2-}$

As reference to evaluate the activity of $[Nb(O\text{-}O)_2(OOH)_2]^-$ in catalyzing epoxidation of allylic alcohols, the commonly used dinuclear peroxotungstate ($W_2O_{11}^{2-}$) was exminated. Here, both the hydrogen bonding and metal-alcoholate bonding mechanisms were investigated. In hydrogen bonding mechanism, two kinds of hydrogen bonds, $O_{12}H\cdots O_1$ and $O_{12}H\cdots O_2$ (Figure S12a and S12b), were considered, whose distances are 1.845 Å and 1.822Å, respectively. The corresponding interaction energies are 0.70 eV and 0.75 eV, respectively, indicating that the peroxo (O-O) can serve as a more stable hydrogen bond with the OH group in allylic alcohol. Hence, we mainly focused on this stable interaction configuration ($O_{12}H\cdots O_2$) in the subsequent reaction. Under the assist of $O_{12}H\cdots O_2$, two transition states (TS9 and TS10) were discovered. TS9 (Figure S12c), describing that the O_7 atom of the peroxo ($O_7\text{-}O_8$) in W_2 attacks the C=C bond has a high energy barrier of 1.24 eV, in which two $C\text{-}O_7$ bonds are 2.007Å and 2.112Å, and the $O_7\text{-}O_8$ and $W_2\text{-}O_7$ bonds are elongated to 1.853Å and 2.157Å, respectively. And, TS10 (Figure S12d) is that the C=C bond is oxidized by the O_4 atom in peroxo ($O_4\text{-}O_5$) connecting to W_1 with two $C\text{-}O_4$ bonds of 1.885Å and 2.220Å, respectively, which has an energy barrier of 1.26 eV. In metal-alcoholate bonding mechanism, we also calculated two transition states (TS11 and TS12, see Figure S12f and S12g, respectively), which correspond to the initial state (Figure S12e) and the oxidative species are also similar with TS11 and TS12, respectively. The energy barriers are calculated to be 1.65 eV and 1.02 eV, respectively.
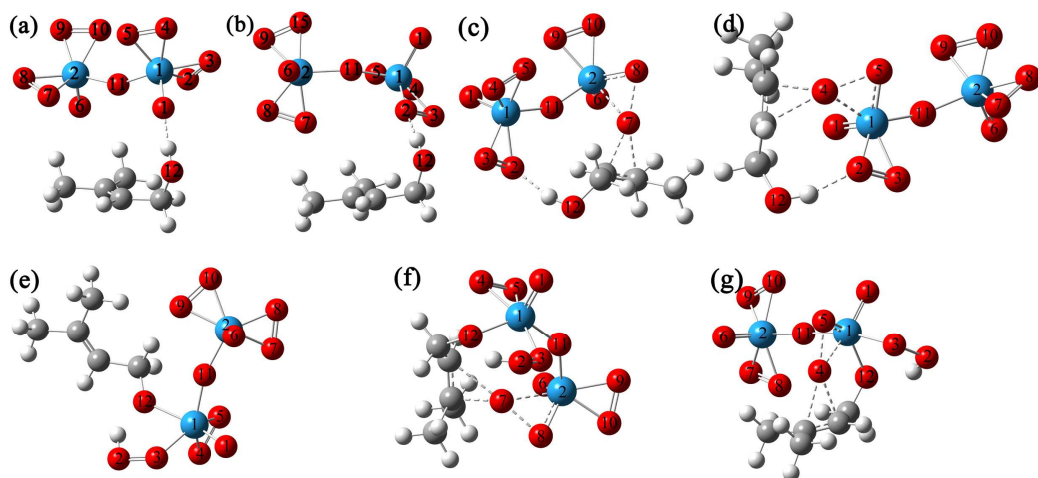
Figure S12. Optimized structures of various possible intermediate and transition sates in the epoxidation process with $W_2O_{11}{}^{2-}$. (a) and (b) are two initial interaction forms between allylic alcohol and $W_2O_{11}{}^{2-}$ via hydrogen bond; (c) and (d) are the possible transition states of the alcohols epoxidation following hydrogen bonding mechanism; (e) is the initial interaction form between allylic alcohol and $W_2O_{11}{}^{2-}$ via metal-alcoholate bond; (f) and (g) are the transition states of the epoxidation of allylic alcohols in metal-alcoholate bonding mechanism. Light green, red, white and grey balls represent W, O, H and C atom, respectively.

Table S2. Cartesian coordinates of some optimized structures.

[Nb=O(O-O)(OH)$_2$]$^-$

Atom	Coordinates /Å		
	x	y	z
Nb	0.14100	0.000011	0.089936
O	0.63572	0.001108	1.778992
O	-1.704490	0.741537	-0.148439
O	-1.70192	-0.74812	-0.145720
O	0.96364	1.59625	-0.791940
O	0.971235	-1.591330	-0.793637
H	0.446958	2.083537	-1.438802
H	0.458162	-2.079612	1.442605

Charge = -1; E = -433.911055 Hartree

Table S2. (Continued)

[Nb(O-O)$_2$(OOH)$_2$]$^-$

Atom	Coordinates /Å		
	x	y	z
O	-2.143388	-0.159169	-0.745516
O	-1.782811	-1.307440	0.123336
O	1.074482	2.016991	-0.292853
O	-0.355233	1.895150	-0.605481
O	2.350674	-1.166185	-0.721458
O	1.023038	-0.897100	-1.208193
O	0.091694	0.482729	1.837666
O	0.845708	-0.761075	1.557789
Nb	-0.295533	-0.051435	-0.010732
H	1.048220	2.308139	0.633206
H	2.235299	-1.030528	0.244479

Charge = -1; E = -659.359349 Hartree

Table S2. (Continued)

TS1

Atom	Coordinates /Å		
	x	y	z
O	-1.966757	2.016692	-0.238208
O	-0.495599	2.018083	-0.285938
O	-2.888678	-1.767456	-0.035270
O	-3.175601	0.341084	-0.212965
O	-0.034124	-1.684668	1.811070
O	-0.768304	-0.441837	1.722182
O	-0.797038	-0.775227	-1.663780
O	0.784650	-0.611957	-0.648463
Nb	-1.205392	0.172822	-0.121225
H	-2.733163	-2.047097	-0.952078
H	0.428569	-1.684172	0.946071
C	2.796874	-0.776833	-0.186522
C	2.384065	0.306266	0.541547
C	2.470486	1.745160	0.102213
O	1.826462	2.639648	0.989813
C	2.947547	-2.135763	0.444267
C	3.363575	-0.649514	-1.574352
H	2.053073	0.157621	1.565001
H	2.074722	1.850305	-0.914592
H	3.528124	2.043098	0.076261
H	0.872458	2.598776	0.783829
H	2.517415	-2.172703	1.446001
H	4.011853	-2.395265	0.520303
H	2.471288	-2.900878	-0.176358
H	3.039833	-1.493719	-2.187755
H	4.461712	-0.660411	-1.539078
H	3.039826	0.265279	-2.067822

Charge = -1; E = -931.036273 Hartree; IF = -493.8869

Table S2. (Continued)

TS2

Atom	Coordinates /Å		
	x	y	z
O	-1.066755	-0.505819	-0.574890
O	0.163749	-1.477640	-1.489770
O	1.646639	-0.028149	2.495379
O	0.498826	-0.417638	1.687305
O	2.227005	2.300352	-0.755836
O	1.006942	1.530617	-0.832777
O	2.699181	-1.311451	0.315170
O	2.996135	-0.291239	-0.703163
Nb	1.015118	-0.378040	-0.255405
H	2.358651	-0.570406	2.094498
H	2.900131	1.596203	-0.641082
C	-2.354408	1.240358	0.301471
C	-2.646204	-0.038407	0.683401
C	-3.615954	-0.990059	0.036919
O	-3.073131	-2.295042	-0.104121
C	-1.531572	2.132986	1.188248
C	-2.842912	1.880804	-0.967454
H	-2.239608	-0.382417	1.629983
H	-3.957813	-0.605837	-0.931397
H	-4.499207	-1.094680	0.679527
H	-2.178676	-2.146570	-0.457419
H	-1.164908	1.603536	2.067047
H	-2.135376	2.992996	1.510154
H	-0.669302	2.522890	0.639963
H	-2.003497	2.365065	-1.474598
H	-3.580422	2.662684	-0.740064
H	-3.292253	1.170165	-1.658884

Charge = -1; E = -931.045384 Hartree; IF = -452.0120

Table S2. (Continued)

TS3

Atom	Coordinates /Å		
	x	y	z
O	0.492191	2.083719	0.407850
O	1.304751	1.872848	-0.806735
O	0.352559	-0.092180	2.122023
O	-0.90643	-0.320028	0.857718
O	3.720711	-1.122683	0.214012
O	2.642970	-0.548754	0.986579
O	0.502215	-1.079565	-1.393236
O	1.899604	-0.689099	-1.618640
Nb	1.024017	0.141527	0.059761
H	0.038742	0.769320	2.424713
H	3.264747	-1.278516	-0.646914
C	-2.633558	-1.119782	-0.146980
C	-2.361905	0.107119	-0.684481
C	-2.873354	1.442473	-0.211823
O	-2.062383	2.524557	-0.618976
C	-2.205850	-2.386562	-0.835231
C	-3.511036	-1.314139	1.058909
H	-1.780142	0.143041	-1.601461
H	-3.004606	1.429031	0.877952
H	-3.863231	1.625532	-0.653344
H	-1.160491	2.414577	-0.240631
H	-1.509391	-2.193130	-1.649354
H	-3.087634	-2.912809	-1.226533
H	-1.716507	-3.057921	-0.12336
H	-3.061918	-2.050324	1.730954
H	-4.491221	-1.702668	0.751377
H	-3.668318	-0.393904	1.619263

Charge = -1; E = -931.047510 Hartree; IF = -401.6426

Table S2. (Continued)

TS4

Atom	Coordinates /Å		
	x	y	z
O	0.943075	1.920365	1.16091
O	0.745642	2.084075	-0.293723
O	1.450439	-2.017478	1.958677
O	1.249428	-0.577932	2.014934
O	3.756200	-0.146931	-1.464274
O	3.208742	0.124414	-0.169512
O	0.889906	-1.584068	-1.069220
O	1.112051	-0.332673	-1.812300
Nb	1.282066	0.248318	0.156635
H	0.548937	-2.319205	2.135530
H	2.928081	-0.338601	-1.967068
H	-0.238640	-1.272022	-0.670736
C	-4.355847	-0.065366	-0.150369
C	-3.168469	-0.469664	-0.618541
C	-1.867276	0.279658	-0.632619
O	-0.846802	-0.491271	-0.003096
C	-5.568185	-0.962187	-0.234357
C	-4.617278	1.276214	0.488070
H	-3.105705	-1.469131	-1.048079
H	-1.934915	1.239415	-0.118146
H	-1.571902	0.491707	-1.670002
H	-5.329759	-1.920810	-0.700378
H	-6.371210	-0.490622	-0.815606
H	-5.979654	-1.159515	0.763823
H	-5.085919	1.145688	1.471140
H	-5.318638	1.864664	-0.11724
H	-3.712510	1.867456	0.622469

Charge = -1; E = -931.054795 Hartree; IF = -1008.5062

Table S2. (Continued)

TS5

Atom	Coordinates /Å		
	x	y	z
O	-1.189607	0.091735	-1.058012
O	0.271913	-0.243565	-2.141530
O	1.425500	2.827096	0.736701
O	1.345328	2.029346	-0.449862
O	3.102083	-1.812149	-0.386592
O	2.720574	-0.427642	-0.439748
O	0.878234	-1.660796	1.993499
O	0.588753	-1.695581	0.569785
Nb	0.792687	0.126598	-0.403981
H	0.833045	2.303903	1.329186
H	2.307978	-2.194633	0.045999
H	0.639596	-0.728979	2.195999
C	-2.994504	-0.189447	-0.061776
C	-2.325407	0.824808	0.568304
C	-1.424960	0.677520	1.769427
O	-0.049270	0.780287	1.443897
C	-3.965309	0.114955	-1.168841
C	-2.929903	-1.630982	0.368357
H	-2.475001	1.836180	0.204036
H	-1.615271	-0.282291	2.265762
H	-1.675091	1.467172	2.493889
H	-3.963710	1.174409	-1.429213
H	-4.982479	-0.175209	-0.874378
H	-3.699065	-0.458740	-2.060343
H	-3.020388	-2.278427	-0.507266
H	-3.766277	-1.866856	1.040366
H	-1.991064	-1.878019	0.861241

Charge = -1; E = -931.038579 Hartree; IF = -512.7580

Table S2. (Continued)

TS6

Atom	Coordinates /Å		
	x	y	z
O	0.115153	-0.765030	1.990242
O	-1.341055	-0.955170	1.885526
O	0.243122	1.809471	1.211914
O	1.290663	0.870922	0.061348
O	-2.571421	1.924883	-1.359714
O	-1.522190	1.854312	-0.371364
O	-2.762415	-1.816669	-0.827349
O	-2.541521	-0.435267	-0.482733
Nb	-0.720704	0.087860	0.363352
H	-0.041560	2.529912	0.623518
H	-2.901738	0.996266	-1.331812
H	-1.869177	-2.053452	-1.146466
C	3.001790	-0.062497	-0.448896
C	2.081971	-0.487644	-1.371033
C	1.177436	-1.680694	-1.234752
O	-0.152727	-1.271611	-0.997447
C	3.891427	1.110243	-0.759729
C	3.338724	-0.806702	0.815308
H	1.963705	0.092079	-2.281005
H	1.513605	-2.347317	-0.432711
H	1.191967	-2.257983	-2.170589
H	3.594066	1.608706	-1.683546
H	4.934378	0.781918	-0.855826
H	3.84224	1.835115	0.056648
H	3.565966	-0.091324	1.608791
H	4.229268	-1.430804	0.661052
H	2.517193	-1.428347	1.165738

Charge = -1; E = -931.036206 Hartree; IF = -474.5635

Table S2. (Continued)

TS7

Atom	Coordinates /Å		
	x	y	z
O	-3.781797	1.143003	-0.210141
O	1.169984	-1.047970	-1.744506
O	1.015377	2.727896	-0.135858
O	1.811852	1.712275	-0.771447
O	4.016161	-0.232050	1.014700
O	3.654694	-0.825304	-0.278294
O	0.942183	0.035694	1.859861
O	1.154136	-1.295774	1.262035
Nb	1.736040	-0.219953	-0.302573
H	0.145458	2.279292	-0.118233
H	3.707845	-0.913957	1.633509
H	-0.091904	0.341745	1.161585
C	-4.301596	-0.179705	0.032649
C	-2.937062	0.180435	0.462543
C	-1.665435	-0.279092	-0.209726
O	-0.569891	0.540390	0.142847
C	-5.408506	-0.232970	1.066382
C	-4.556944	-1.014646	-1.205616
H	-2.801859	0.403666	1.521855
H	-1.773344	-0.260559	-1.296324
H	-1.467389	-1.318149	0.092184
H	-5.177795	0.416412	1.912832
H	-5.546330	-1.253987	1.437275
H	-6.356222	0.098065	0.627518
H	-5.498814	-0.707504	-1.673001
H	-4.641060	-2.074729	-0.945027
H	-3.760560	-0.901635	-1.939660

Charge = -1; E = -931.127086 Hartree; IF = -590.4891

Table S2. (Continued)

TS8

Atom	Coordinates /Å		
	x	y	z
O	-1.466018	-2.142414	-0.451889
O	-1.000587	-1.201806	-1.493680
O	-2.015910	-0.892661	1.964918
O	3.779690	-0.510603	1.084595
O	-3.717273	1.544476	-1.027463
O	-3.455628	0.349067	-0.282541
O	-0.959897	1.762609	0.778224
O	-1.079909	1.567453	-0.678920
Nb	-1.634440	-0.258488	0.118616
H	-1.726690	-1.776814	2.207702
H	-2.808693	1.933624	-1.051091
H	0.063876	1.071971	0.898489
C	4.217945	0.116695	-0.137973
C	2.874369	0.389563	0.405329
C	1.587687	-0.149268	-0.171917
O	0.528871	-0.018072	0.757230
C	5.311584	1.148865	0.049372
C	4.429150	-0.820287	-1.309792
H	2.743399	1.336117	0.931361
H	1.694970	-1.204517	-0.430717
H	1.354631	0.404596	-1.092683
H	5.111172	1.767867	0.925758
H	5.386879	1.799867	-0.827825
H	6.280579	0.657168	0.189715
H	5.389978	-1.336218	-1.206077
H	4.447166	-0.261441	-2.251112
H	3.643668	-1.572033	-1.370681

Charge = -1; E = -931.136615 Hartree; IF = -1003.092.

References:

1. Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2007**, *111*, 408-422.

2. Kamata, K.; Yamaguchi, K.; Mizuno, N. *Chem. Eur. J.* **2004**, *10*, 4728-4734.

¹H NMR spectra of the isolated epoxides
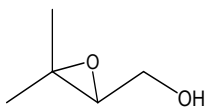
Crude product was purified by column chromatography using silica (petroleum ether/ethyl acetate = 1:1) ^{1}H NMR (400 MHz, CDCl$_3$), δ=NMR (400 MHz) δ =3.78 (d, 1H), 3.60 (dd, 1H), 2.93 (t, 1H), 2.70 (s, 1H), 1.24 (m, 6H).

.

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5	Owner	nmr
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8	Author	
9	Solvent	CDC13
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11	Pulse Sequence	zg30
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14	Relaxation Delay	1.0000
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18	Modification Date	2016-01-22T11:27:00
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20	Spectral Width	8223.7
21	Lowest Frequency	-1665.2
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

Crude product was purified by column chromatography using silica (petroleum ether/ethyl acetate = 1:2) ^{1}H NMR (400 MHz, CDCl$_3$), δ=3.74 (dd, 1H), 3.56 (dd, 1H), 2.57 (m, 1H), 2.38 (m, 1H), 2.32 (m, 1H), 1.28 (t, 3H).

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5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.5
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	101
14	Relaxation Delay	1.0000
15	Pulse Width	14.7500
16	Acquisition Time	3.9846
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18	Modification Date	2016-01-22T11:39:00
19	Spectrometer Frequency	400.13
20	Spectral Width	8223.7
21	Lowest Frequency	-1675.2
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

Crude product was purified by column chromatography using silica (petroleum ether/ethyl acetate = 2:1) ^{1}H NMR (400 MHz, CDCl$_3$), δ=3.85 (dd, 1H), , 3.56 (dd, 1H), 2.99 (m, 1H), 2.84 (m, 1H), 2.07 (s, 1H), 1.27 (m, 3H).

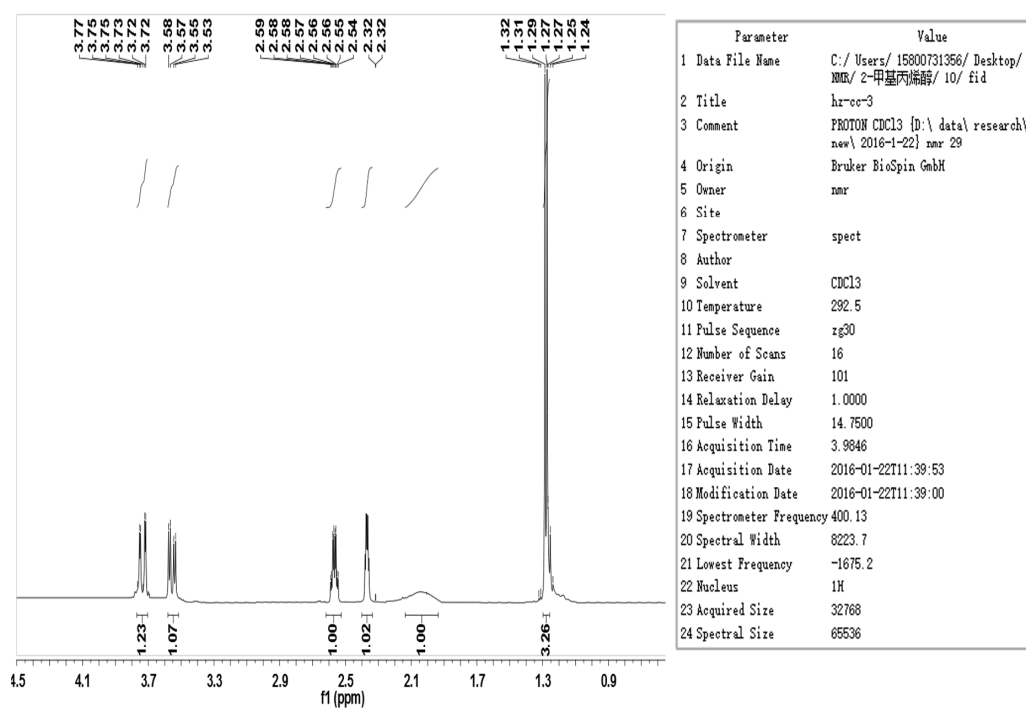|	Parameter	Value
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5	Owner	nmr
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8	Author	
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10	Temperature	292.5
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13	Receiver Gain	181
14	Relaxation Delay	1.0000
15	Pulse Width	14.7500
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18	Modification Date	2016-01-22T11:33:00
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20	Spectral Width	8223.7
21	Lowest Frequency	-1672.2
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

Crude product was purified by column chromatography using silica (petroleum ether/ethyl acetate = 2:1) ^{1}H NMR (400 MHz, CDCl$_3$), δ=5.01 (t, 1H), 3.75 (dd, 1H), 3.60 (dd, 1H), 2.91 (dd, 1H), 2.46 (s, 1H), 2.01 (dd, 2H), 1.68(m, 6H), 1.42 (m, 2H), 1.22 (d, 3H).

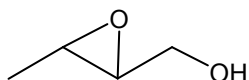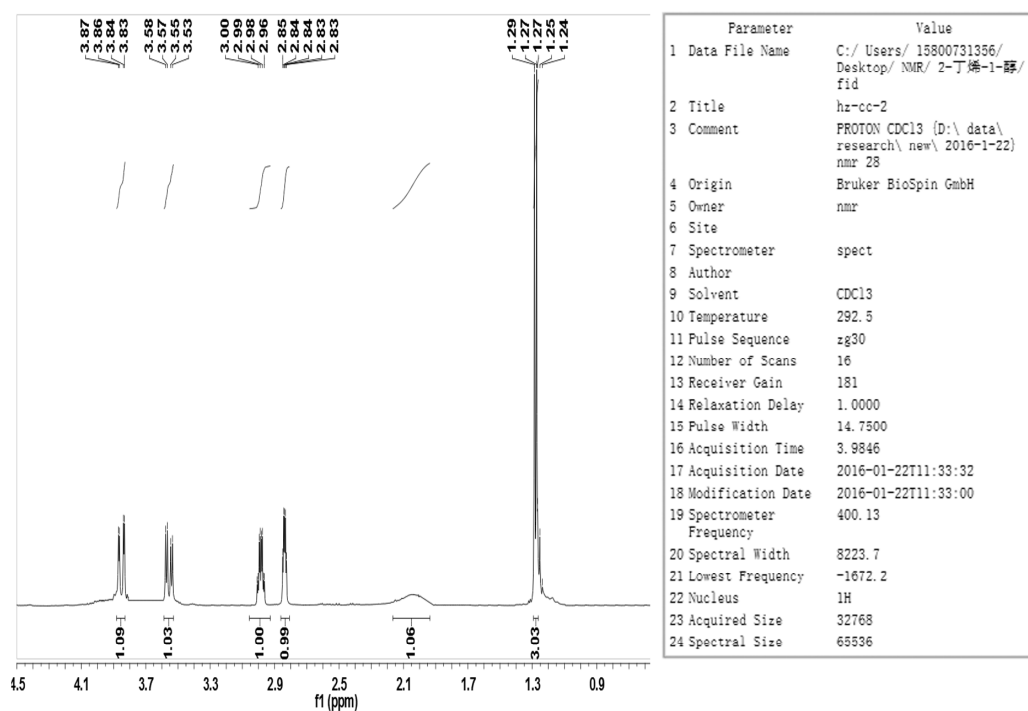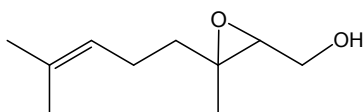| Parameter	Value
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6 Site	
7 Spectrometer	spect
8 Author	
9 Solvent	CDCl3
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12 Number of Scans	8
13 Receiver Gain	16
14 Relaxation Delay	1.0000
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17 Acquisition Date	2016-01-27T13:50:50
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19 Spectrometer Frequency	400.13
20 Spectral Width	8012.8
21 Lowest Frequency	-1563.0
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536

Crude product was purified by column chromatography using silica (petroleum ether/ethyl acetate = 1:2) ^{1}H NMR (400 MHz, CDCl$_3$), δ=3.71 (dd, 1H), 3.54 (dd, 1H), 2.56 (m, 2H), 2.35 (dd, 1H), 2.00 (s, 1H).

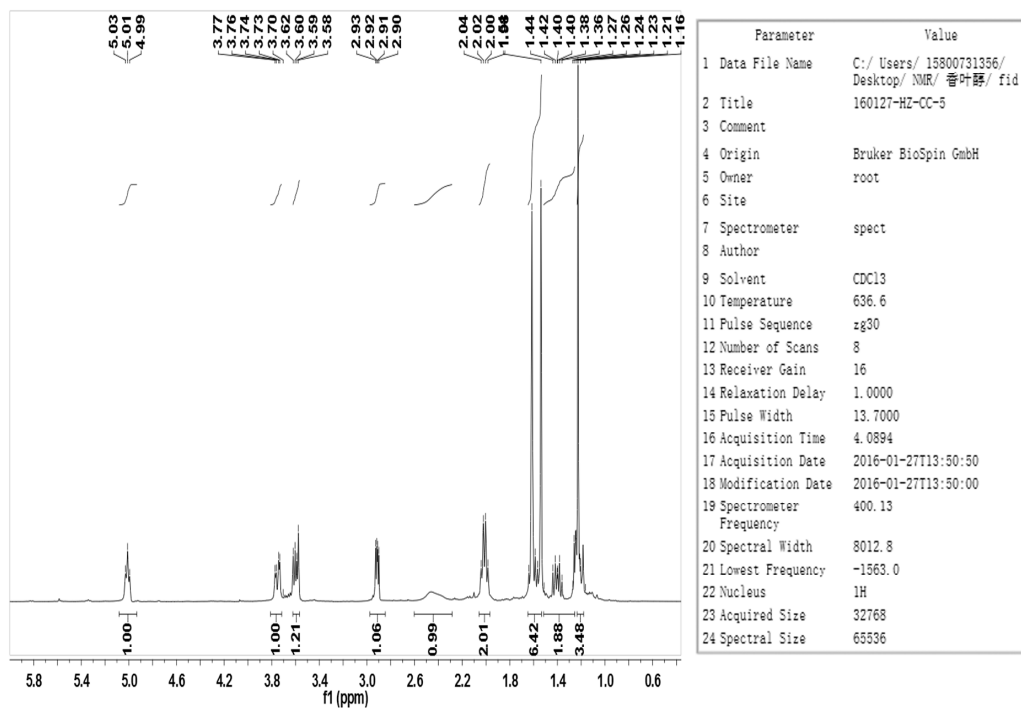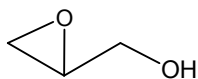|	Parameter	Value
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8	Author	
9	Solvent	CDCl3
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13	Receiver Gain	101
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19	Spectrometer Frequency	400.13
20	Spectral Width	8223.7
21	Lowest Frequency	-1675.2
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

Crude product was purified by column chromatography using silica (petroleum ether/ethyl acetate = 1:1) ^{1}H NMR (400 MHz, CDCl$_3$), δ=3.82 (dd, 1H), 3.56 (dd, 1H), 2.89 (m, 2H), 1.99 (s, 1H), 1.45 (m, 4H), 0.91 (m, 3H).
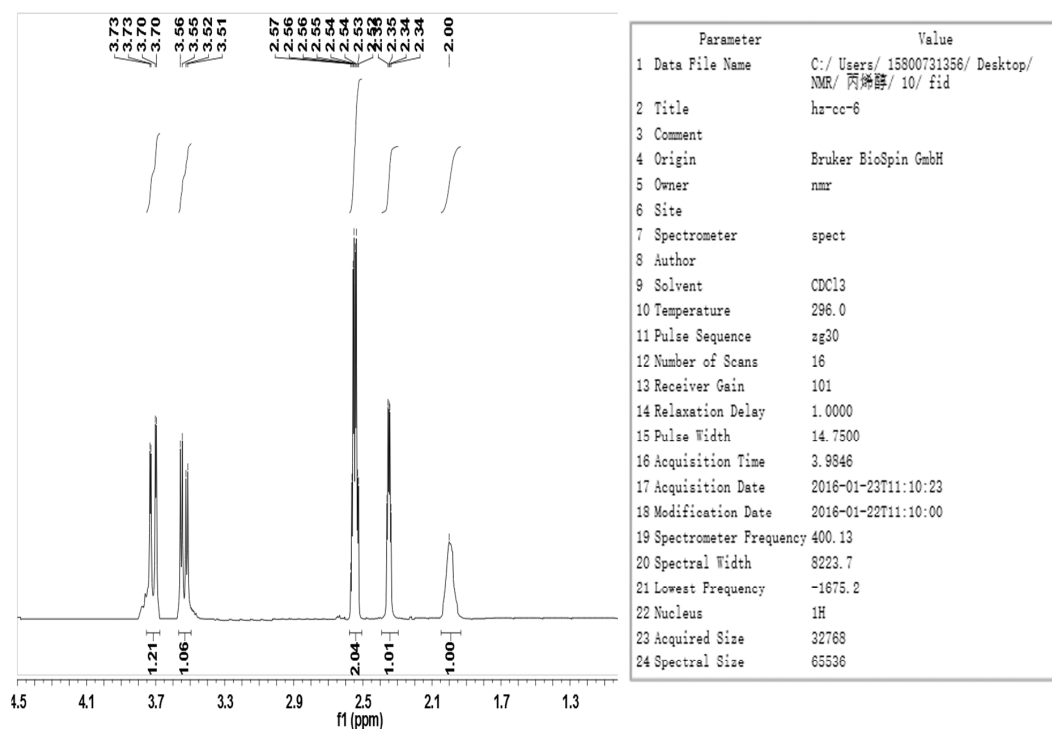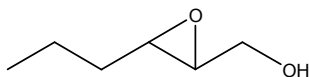
Crude product was purified by column chromatography using silica (petroleum ether/ethyl acetate = 1:1) ^{1}H NMR (400 MHz, CDCl$_3$), δ= 4.02 (dd, 1H), 3.3 (m, 2H), 2.44 (s, 1H), 1.77 (m, 2H), 1.58 (m, 2H), 1.25 (m, 2H).

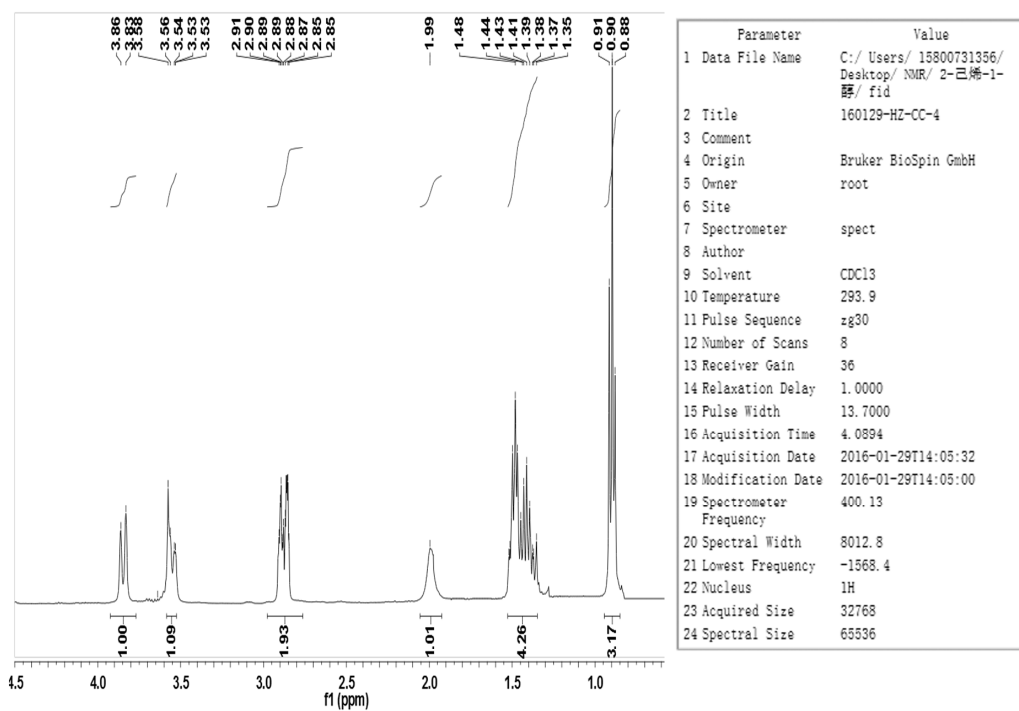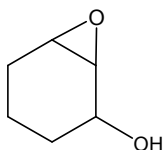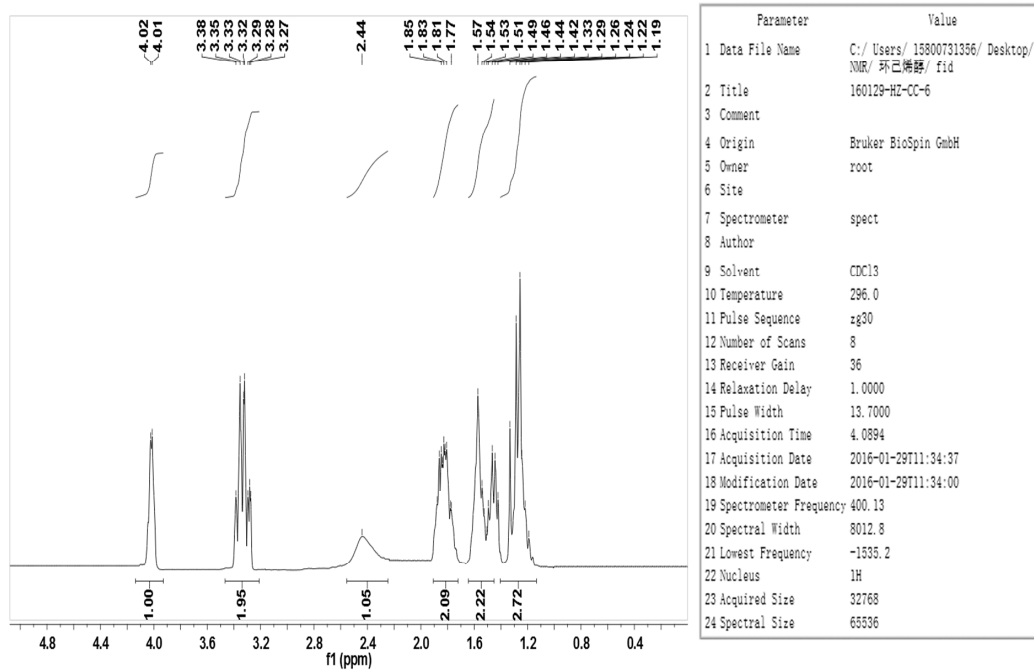| Parameter	Value
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6 Site	
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8 Author	
9 Solvent	CDCl3
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13 Receiver Gain	36
14 Relaxation Delay	1.0000
15 Pulse Width	13.7000
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19 Spectrometer Frequency	400.13
20 Spectral Width	8012.8
21 Lowest Frequency	-1535.2
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536

Crude product was purified by column chromatography using silica (petroleum ether/ethyl acetate = 5:1) ^{1}H NMR (400 MHz, CDCl$_3$), δ= 7.37 (m, 5H), 4.26 (m, 1H), 3.77 (dd, 1H), 3.73 (dd, 1H), 3.00 (d, 1H), 2.36 (s, 1H).

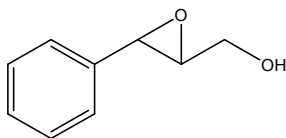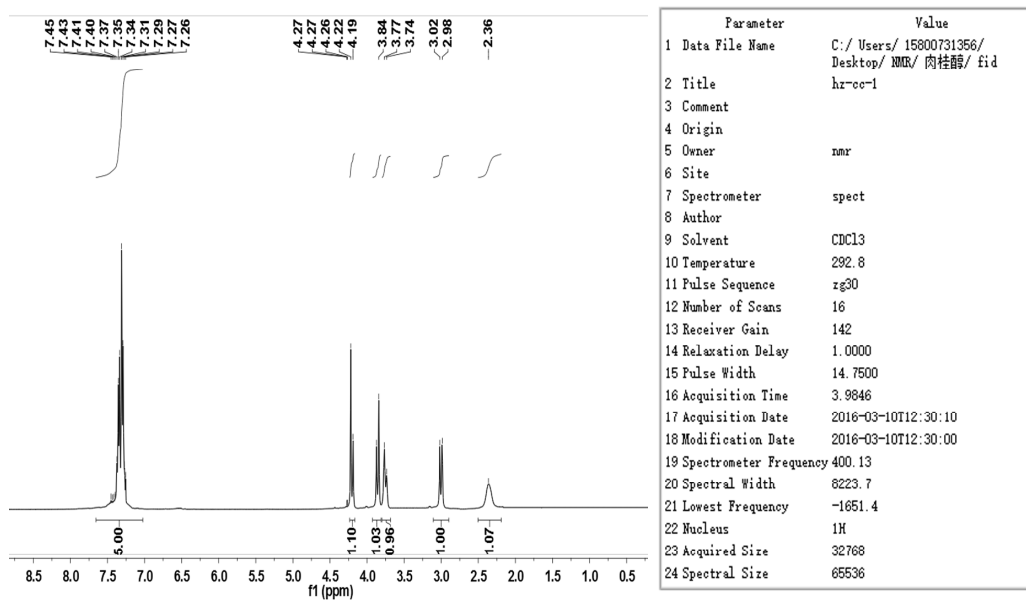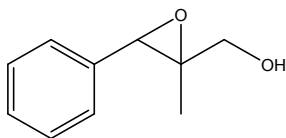|	Parameter	Value
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20	Spectral Width	8223.7
21	Lowest Frequency	-1651.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

Crude product was purified by column chromatography using silica (petroleum ether/ethyl acetate = 5:1) ^{1}H NMR (400 MHz, CDCl$_3$), δ=7.35 (m, 5H), 4.22 (m, 1H), 3.87 (dd, 1H), 3.78 (dd, 1H), 2.36 (s, 1H), 1.09 (s, 1H).

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8	Author	
9	Solvent	CDCl3
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