Selective Etherification of β-Citronellene Catalyzed by Zeolite Beta

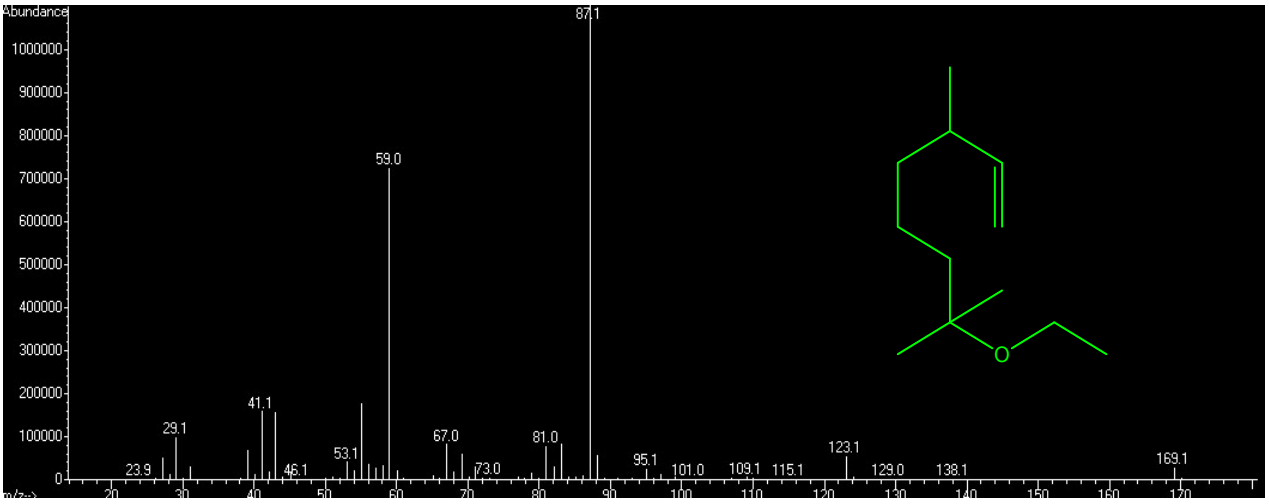
Supporting Information

1. Offline GC-MS characterization of the product mixture.

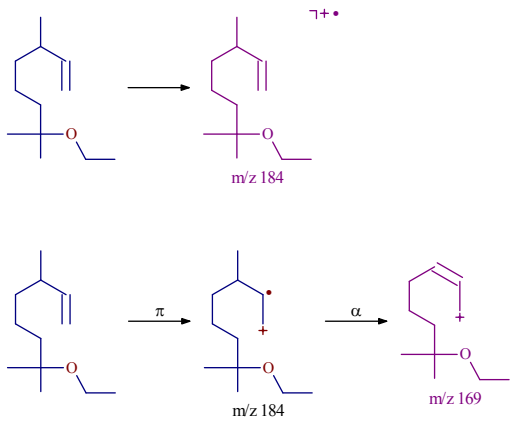
Identification of the products was done by gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890 N gas chromatograph (HP-1MS capillary column, 30 m, 0.25 mm ID, 0.25 μm film thickness) coupled to an Agilent 5973 MSD mass spectrometer. The mass spectra and fragmentation patterns of the two ethers were as shown below. The simulated mass spectral fragmentation pathways were done using the MassFrontier software of HighChem.

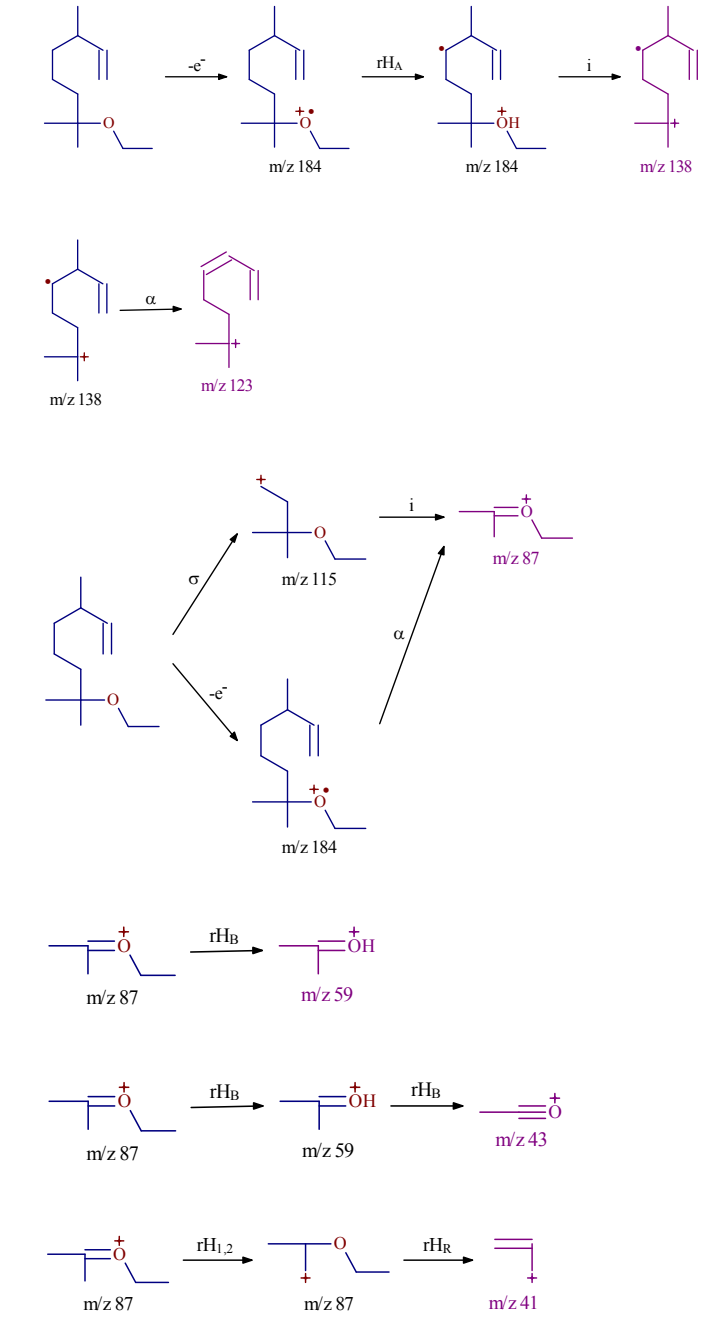
Product E-1:

GC-MS, 70eV, (fragment, relative intensity, mode of fragmentation) - m/z: 169 ([M-CH_3]$^+$, 2%, αC-C); 123 ([C_9H_{15}]$^+$, 6%, Rearrangement); 87 ([M-C_7H_{13}]$^+$, 100%, αC-C); 59 ([$(CH_3)_2C{=}OH$]$^+$, 70%, Rearrangement); 43 ([CH_3-C≡O]$^+$, 12%, Rearrangement); 41 ([$CH_2{=}CH{-}CH_2$]$^+$, 14%, Rearrangement).



Simulated MS pattern of Ether E-1

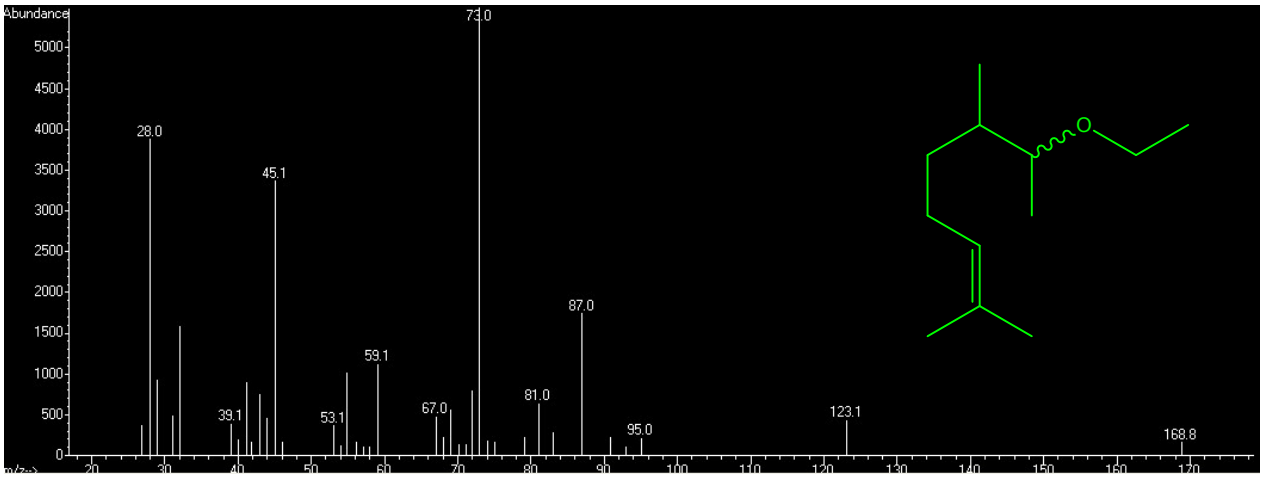




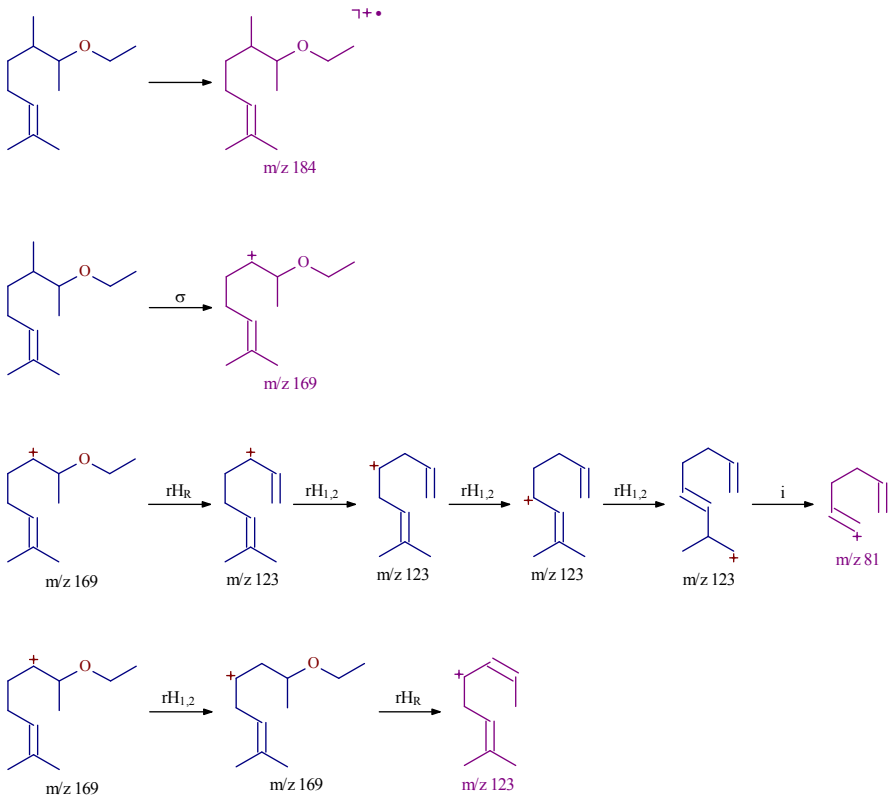
The experimentally observed MS fragmentation pattern for Product **E-1** is in agreement with the simulated pattern for 7-ethoxy-3,7-dimethyloct-1-ene (designated as **E-1**).

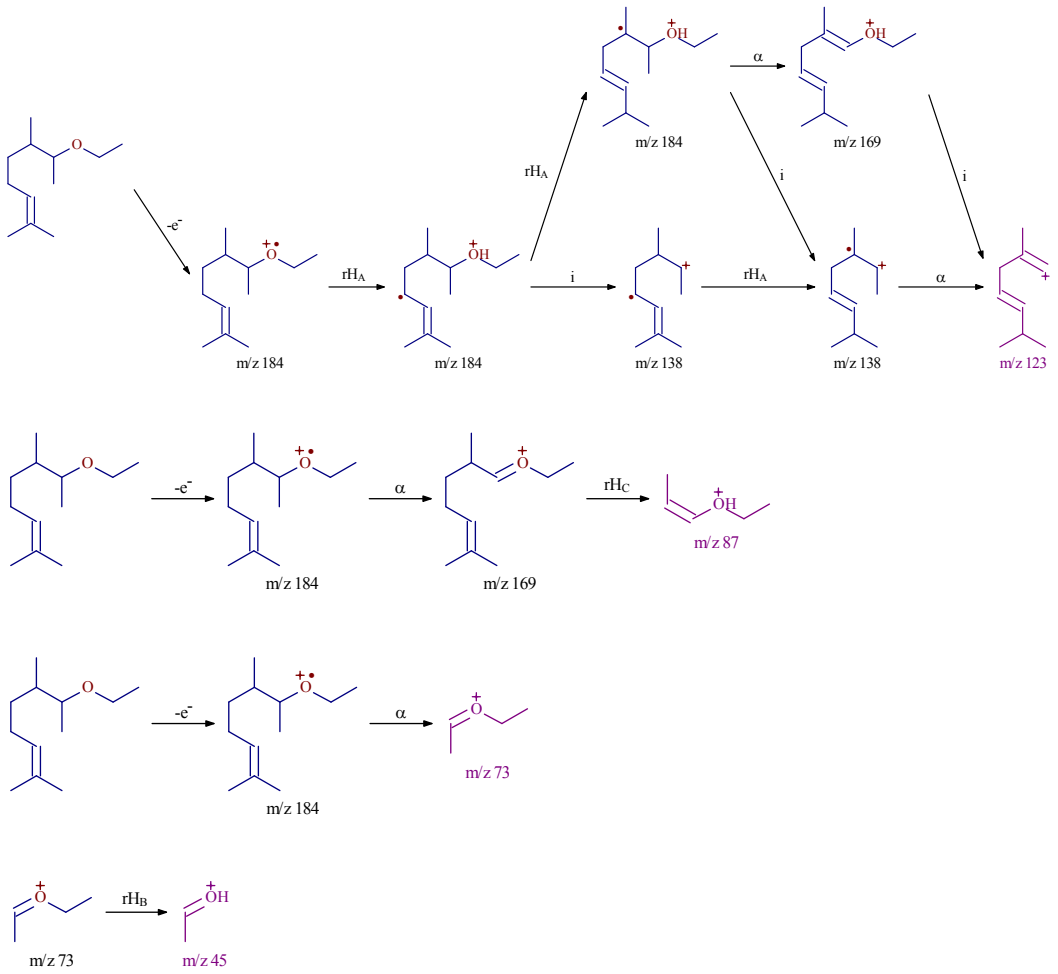
Product E-2:

GC-MS, 70eV, (fragment, relative intensity, mode of fragmentation) - m/z: 169 ([M-CH_3]$^+$, 3%, αC-C); 123 ([C_9H_{15}]$^+$, Rearrangement, 8%); 87 ([CH_3-CH=CH-OH-CH_2-CH_3]$^+$, Rearrangement, 20%); 81 ([CH_2=CH-(CH_2)$_2$-CH=CH]$^+$), 12%, Rearrangement); 73 ([M-C_8H_{15}]$^+$, 100%, αC-C); 45 ([CH_3-CH=OH]$^+$, 61%, Rearrangement); 28 ([CH_2=CH_2], 70%, Rearrangement).



Simulated MS pattern of Ether E-2





The experimentally observed MS fragmentation pattern for Product **E-2** is in agreement with the simulated pattern for 7-ethoxy-2,6-dimethyloct-2-ene (designated as **E-2**).

Isomer Identification

The chemical structures of the isomer products (Figure S1) were identified tentatively based on comparison of the mass spectra with literature data (NIST/EPA/NIH Mass Spectral Library Version 2.0d) and predicted fragmentation patterns (HighChem MassFrontier).

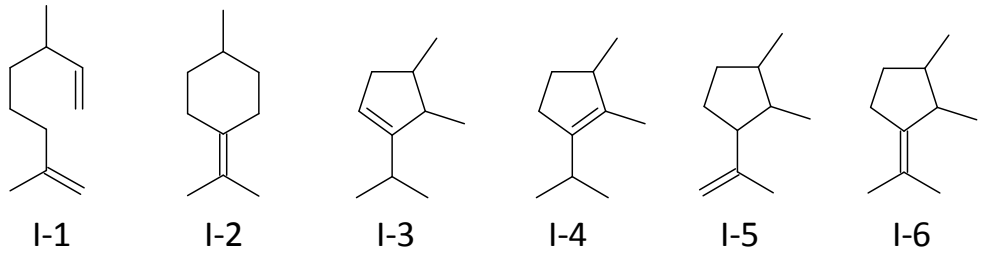


Figure S1. Chemical structures of β-citronellene isomers tentatively identified in the product mixture

2. Gas-phase thermodynamic equilibrium calculations

In order to predict the thermodynamic equilibrium of the etherification reaction of β-citronellene, gas-phase calculations have been performed with Gaussian09[1] using the B3LYP functional[2] and 6-311g(d,p) basis sets. All atoms were allowed to relax during geometry optimization, while the optimized structures were characterized as minima by frequency calculations. The partition functions for all gas-phase species included vibrational, rotational and translational degrees of freedom while the Gibbs free energy was calculated using statistical thermodynamics[3].

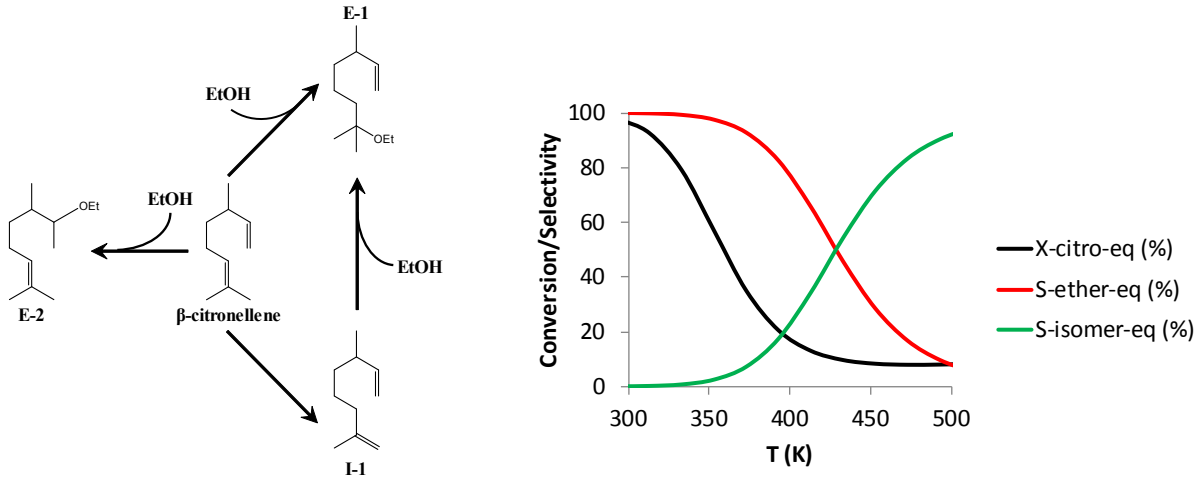
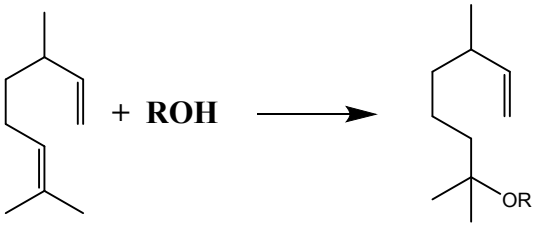
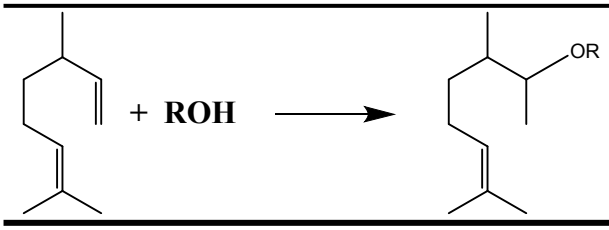


Figure S2. Reaction scheme of the etherification reaction of β-citronellene with ethanol (left) considered for the calculation of the thermodynamic equilibrium conversion and selectivity in the gas-phase (right)

Table S1. ΔG_r(353K) calculated for the gas-phase reactions with Gaussian09 (B3LYP/6-311g(d,p)).

Reaction	R = Et	R = n-Pr	R = i-Pr
	29	30	40
	11	12	27

3. Atomic coordinates of the reaction intermediates inside the channel of zeolite beta

phys-a-citro

Si	0.580570200	1.197154490	14.320133113
Si	0.584133826	2.764264361	24.503128633
Si	0.735532812	10.190143667	14.273907646
Si	0.744882704	5.958906305	24.609207398
Si	1.624075540	9.612650273	9.713548691
Si	1.629518249	6.419713847	3.249506813
Si	1.874953856	1.757624315	3.070345589
Si	1.914494069	2.124237882	9.855031234
Si	2.123903435	8.736035205	5.164062566
Si	2.142046262	7.309714164	7.785248045
Si	2.231392112	11.705246123	4.990479258
Si	2.253423526	4.332599281	7.935941684
Si	2.634874877	11.953735761	7.918994762
Si	2.653448774	4.070152220	5.018059137
Si	3.557305709	1.337153887	14.674165746
Si	3.551781134	2.633888640	24.148824138
Si	3.710507297	10.290061884	14.432815096
Si	3.722708947	5.840152331	24.456878528
Si	3.978574229	10.645416853	11.491939497
Si	3.978514836	5.398224599	1.456916708
Si	4.054404645	1.518829831	11.743082899
Si	4.009526243	2.354737805	1.170512733
Si	5.434022067	11.508551879	4.690339341
Si	5.456655370	4.499901716	8.197825920
Si	5.306892203	8.555993478	5.080068828
Si	5.333247242	7.466120264	7.858136413
Si	5.671286190	11.975012889	7.633441695
Si	5.700735047	4.007107931	5.268025161
Si	5.946191617	9.940462347	16.322361109
Si	5.956238154	1.798296138	22.654411165
Si	5.897052248	2.158623296	16.207751718
Si	5.931569581	6.190217315	22.539264915
Si	6.312144448	9.868908900	9.560537411
Si	6.282810821	1.749931015	3.215911330
Si	6.281822499	2.078695210	9.651058429
Si	6.298057705	6.145224516	3.388949920
Si	6.464975736	12.076186806	18.251141947
Si	6.521455470	4.076160499	20.629587827
Si	6.926865565	8.586376167	20.821903659
Si	6.955857180	7.531792247	18.023764365
Si	6.760439136	11.547598418	21.177359416
Si	6.805830046	4.555356506	17.685010998
Si	8.215377955	2.397520062	24.717715769
Si	8.291858620	10.625943836	14.395106548
Si	8.256234712	5.443032506	24.480175349
Si	8.506491733	10.222535281	11.511962095
Si	8.516340948	5.824621218	1.484951662
Si	8.712906946	1.249385725	11.098846399

Si	8.682629314	2.618725813	1.737065805
Si	9.537958016	12.001799425	17.946577550
Si	9.554836821	4.142778898	20.942486695
Si	9.966313681	11.751584495	20.859569785
Si	10.009450355	4.344554307	18.025389194
Si	10.113233530	8.774064398	20.753825404
Si	10.160057153	7.334803004	18.131948719
Si	10.329469294	1.790759574	22.823128401
Si	10.405597856	2.176691644	16.047468765
Si	10.584469946	9.615816380	16.200164051
Si	10.591642349	6.501250848	22.713012008
Si	11.493625580	10.123281118	11.650414167
Si	11.488449745	5.932769880	1.317415562
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O	8.922304940	12.083721186	14.144023223
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O	8.536393982	11.826543228	11.183055780
O	8.587980893	4.238992311	1.843205249
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O	11.771857981	1.433059222	15.577793489
O	12.060651432	9.869453467	15.600789409
O	12.090196229	6.380744915	23.294600802
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C	8.656448742	4.751754842	12.400831620
C	6.370432868	5.738753658	12.042889132
C	4.947551962	5.191683301	12.233288820
C	4.442731798	5.192226649	13.679883671
C	2.952290834	5.003425046	13.754359225
C	2.152989676	5.380556292	14.766196518
C	2.650391431	6.019306348	16.032987668
C	0.669193595	5.148689105	14.715637160

C	6.434460783	7.232063389	12.402947028
H	7.183821757	4.853150523	13.909267662
H	9.434077353	4.371288430	13.067639990
H	8.928046452	4.959624136	11.361501744
H	6.640595887	5.641904436	10.979836494
H	4.272567865	5.808319904	11.615040286
H	4.889184357	4.174561921	11.822483573
H	4.719968943	6.136405778	14.173236673
H	4.960583869	4.398297712	14.243250124
H	2.489205708	4.508158386	12.893689518
H	3.729382384	6.218403579	16.022674438
H	2.438872862	5.357936032	16.890917049
H	2.119107960	6.965845090	16.227919833
H	0.346514737	4.521790172	15.561880566
H	0.119299177	6.100685998	14.816670540
H	0.364401762	4.664108082	13.776560222
H	6.265757272	7.407719489	13.474207192
H	7.417563104	7.635496339	12.147127068
H	5.662917819	7.783260594	11.846704465
H	7.999110907	3.006581689	12.385810088

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Si	0.592416305	1.201967616	14.314311622
Si	0.552619323	2.767869618	24.533852009
Si	0.750677145	10.179006612	14.289473807
Si	0.721515270	5.953312965	24.649114886
Si	1.634969425	9.585555846	9.734637475
Si	1.636515204	6.392670620	3.261848584
Si	1.858255720	1.691491529	3.086894246
Si	1.971736491	2.068664422	9.862693540
Si	2.158192265	8.689382287	5.215868851
Si	2.159519337	7.263295362	7.829485432
Si	2.269402321	11.647777358	5.013023731
Si	2.259358908	4.284209487	7.951301955
Si	2.688184030	11.906760740	7.931925916
Si	2.639510149	4.017515164	5.019648577
Si	3.591173588	1.331447685	14.657572997
Si	3.511091186	2.621420057	24.151952176
Si	3.731500227	10.282758654	14.454488868
Si	3.694501599	5.824278538	24.477502389
Si	3.988227067	10.610392908	11.514369389
Si	3.964657640	5.355370247	1.462478205
Si	4.116558594	1.482852381	11.728758726
Si	3.980814477	2.307839687	1.171572851
Si	5.472630870	11.443129413	4.707176798
Si	5.468855200	4.438273353	8.212803797
Si	5.323074726	8.505711522	5.117644714
Si	5.357251343	7.413401955	7.890259774
Si	5.719956209	11.914956731	7.657508062
Si	5.687493584	3.950289818	5.276430164
Si	5.972293442	9.984631347	16.334031148

Si	5.917312279	1.833877035	22.638642007
Si	5.946264510	2.201078405	16.153374341
Si	5.898320402	6.234727775	22.553710022
Si	6.341275238	9.812328994	9.601423352
Si	6.264074621	1.698262007	3.221121464
Si	6.348407441	2.021175617	9.649643335
Si	6.274198536	6.098015098	3.407741948
Si	6.499125588	12.138253065	18.223321163
Si	6.503415105	4.132231968	20.625283503
Si	6.902482050	8.622570715	20.834975521
Si	6.960036339	7.562810780	18.042545460
Si	6.761748602	11.600910452	21.144294423
Si	6.809499048	4.596502534	17.668962518
Si	8.168449145	2.410530287	24.712193266
Si	8.320250630	10.693601860	14.410177221
Si	8.238165755	5.461541666	24.484583980
Si	8.550734950	10.235876817	11.513032601
Si	8.491529779	5.822863811	1.499098766
Si	8.746743045	1.263210694	11.113678276
Si	8.645097700	2.613600834	1.729205995
Si	9.571281685	12.047589469	17.940321585
Si	9.542222013	4.163845155	20.935422169
Si	9.972001705	11.778250365	20.870458502
Si	10.013690755	4.375803475	18.020395430
Si	10.102361785	8.795353307	20.795043471
Si	10.154550735	7.362224309	18.173733596
Si	10.298321933	1.819247871	22.832615769
Si	10.417914531	2.227010647	16.031369147
Si	10.579246082	9.630829827	16.203476706
Si	10.593228358	6.498836008	22.719363928
Si	11.515115464	10.097300023	11.664800759
Si	11.475481608	5.932491795	1.369855135
Si	11.681672145	1.111412306	11.531830788
Si	11.627887576	2.725088303	1.405194868
O	0.093250776	9.478706354	12.972856189
O	12.133164256	1.822452678	12.932427660
O	0.021500206	2.092195912	0.008191040
O	-0.001726924	6.580873531	0.048329037
O	0.138553997	9.677700747	10.323956009
O	0.129909822	6.351044492	2.690318741
O	0.494907530	2.406670790	2.604900862
O	0.680654456	1.296693349	10.426902966
O	0.814450406	11.779163069	14.100368893
O	0.780449230	4.344195050	24.788139809
O	1.477405393	0.338738272	3.890731699
O	1.492721413	3.402232563	9.073700884
O	1.772026788	8.085536438	9.155563395
O	1.823997668	7.867625343	3.877936100
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O	1.767419468	5.229787760	4.392099531
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O	2.655207342	2.700817253	4.084474085
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O	1.585952957	5.758215152	7.975054571
O	1.965803861	2.124167773	24.063431984
O	2.050436956	1.837974715	14.628763281
O	2.254931945	9.613615254	14.503693239
O	2.230569207	6.519479067	24.522452333
O	1.506043722	7.966785710	6.517542483
O	2.098691793	0.173209131	6.480552294
O	2.047737289	3.615199591	6.479515000
O	2.766500952	9.748378504	10.891541744
O	2.749776544	6.222647455	2.090218784
O	2.851977355	1.332142561	1.838981487
O	3.029230738	2.494904085	11.037740837
O	3.697114815	11.872661199	14.776959532
O	3.616535018	4.243920499	24.103578663
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O	3.404363060	3.834191619	1.305983722
O	3.760957476	8.783234634	5.412688342
O	3.770652483	7.200497184	7.684315236
O	3.851323651	11.566580693	4.638573884
O	3.849274040	4.350601251	8.295322275
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O	4.376911556	10.015466749	12.975251249
O	4.397773813	5.978881602	0.027249665
O	4.200780188	11.312279111	7.784898210
O	4.170891804	4.558907582	5.167298850
O	4.326572403	2.043974220	22.880286857
O	4.337045922	2.003029965	15.922795067
O	4.639731672	9.488384870	15.541910449
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O	5.313087279	10.585000943	10.591520885
O	5.284500089	5.302815864	2.393928250
O	5.406596373	2.161509094	1.921556515
O	5.546593136	1.532031870	10.977568480
O	6.073411147	12.075136595	6.086706980
O	6.046945369	3.768818491	6.844031259
O	5.539153584	11.009178334	17.526237318
O	5.512384621	5.223261655	21.329354739
O	6.179699217	0.249653363	22.416573247
O	6.183819434	3.806724743	16.407170740
O	6.014009690	7.979301010	6.505542294
O	6.351256736	1.421212235	17.534634418
O	6.381295668	2.677860855	21.326784060
O	6.720713005	8.656309297	16.879355520
O	6.609366803	7.586946238	22.037498536
O	6.259971987	10.056652252	21.231914141
O	6.343550298	6.155239010	17.510983968
O	5.975900070	9.897978173	4.600167014
O	5.991399159	5.977498325	8.314210246

O	5.635349171	8.444420751	9.102724231
O	5.485078617	7.392326245	3.962118248
O	5.803193992	1.207926001	8.349925734
O	5.771998621	2.511069568	4.543320477
O	6.270985724	8.046976060	19.439396624
O	6.079196452	0.104085262	3.457019399
O	6.081494630	3.619801822	9.468986796
O	6.706057594	10.822458312	8.370200164
O	6.682177019	5.056543969	4.600329342
O	6.139815462	0.106557437	19.797552828
O	6.177830236	3.996164990	19.046730289
O	6.744447254	2.331770116	23.948909546
O	6.773205713	1.716943517	14.887078054
O	6.968585706	10.749906289	15.316338216
O	6.923478461	5.453920996	23.545768980
O	7.681658582	9.400317098	10.413779084
O	7.606052319	6.584748034	2.625655575
O	7.840816212	1.986637246	2.984618611
O	7.939877032	1.774359355	9.787077401
O	8.024454571	11.561785976	18.106703315
O	8.021746512	4.729134995	20.772150278
O	7.853092629	10.035200013	12.973762693
O	7.822448203	6.046884390	0.029244487
O	8.126703117	1.965448301	12.410183233
O	7.952438515	2.052471211	0.361809168
O	8.381443236	11.704668057	21.196763961
O	8.433171328	4.471318885	17.616452349
O	8.492024762	8.819688778	20.641144273
O	8.539029258	7.341208406	18.276117556
O	8.974268670	12.136555415	14.227204175
O	8.778478255	3.929618582	24.624848651
O	8.629127823	11.793668165	11.092807431
O	8.551796854	4.232567627	1.831361971
O	9.285875619	1.416337933	24.052877271
O	9.478200378	2.688488605	14.820111689
O	9.407955961	9.659044465	15.073412044
O	9.454296374	6.338736988	23.870706061
O	10.193628950	0.265334359	19.396910560
O	10.143856303	3.705712571	19.501071470
O	10.767448996	8.076737798	19.496738099
O	10.008896725	9.511412522	11.553257388
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O	10.183812382	2.096611044	1.791995217
O	10.309781608	1.726458840	10.931805012
O	10.655029489	10.308066804	20.918140056
O	10.700291628	5.847087686	18.060298044
O	9.611455851	1.185550071	17.004026959
O	9.486450679	2.855454017	21.880422919
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O	10.594746390	8.141529254	16.835897403

O	10.498520936	7.999819248	22.138655007
O	10.724849421	0.502584928	21.996771819
O	10.850955672	3.511973778	16.946722820
O	11.453804357	11.701838147	11.789586192
O	11.446184125	4.320747549	1.239195705
O	11.638887050	2.548534032	23.356616441
O	11.797245101	1.495759794	15.570384932
O	12.061691882	9.812148449	15.596073528
O	12.084172266	6.358508160	23.316112057
Al	8.310362251	1.594695303	14.100302758
C	7.474745081	5.241008395	13.236881204
C	8.907602995	5.154585958	12.905484684
C	6.560952199	6.094009712	12.574436290
C	5.063935953	5.856806372	12.551335148
C	4.498350651	5.166776575	13.800796635
C	3.001217148	5.083252467	13.762808617
C	2.136980599	5.581600165	14.664956548
C	2.517063972	6.328968829	15.912865322
C	0.652868310	5.400372394	14.487034618
C	7.064011874	6.993463763	13.902027269
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H	9.242618099	5.972715707	12.255182240
H	6.962002173	6.618423615	11.699417259
H	4.566006429	6.826452455	12.392358100
H	4.856525404	5.246590259	11.655734068
H	4.833480226	5.691884000	14.707166275
H	4.917978182	4.149153375	13.859768425
H	2.589647228	4.540866319	12.904502143
H	3.599339528	6.425716389	16.064062852
H	2.095272126	5.819542476	16.795130589
H	2.083466445	7.342097551	15.896348751
H	0.222328593	4.876883055	15.357018672
H	0.148758562	6.381454345	14.434136320
H	0.417198252	4.830036354	13.577072339
H	7.487197954	6.499006212	14.796546916
H	7.770969601	7.740143268	13.536559859
H	6.099771722	7.388892547	14.246493996
H	8.997398991	4.190201090	12.365983943

phys-b-citro

Si	0.660687667	1.132906140	14.328345530
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Si	0.825351141	10.130860428	14.251292581
Si	0.840081201	5.914580210	24.612971018
Si	1.743927161	9.605419942	9.744121955
Si	1.735837882	6.416175850	3.241917196
Si	1.983831418	1.745929545	3.104616536
Si	2.061876486	2.146844172	9.880512010
Si	2.248483811	8.725891508	5.171543235
Si	2.303666268	7.302413706	7.778845673

Si	2.332251130	11.696623779	5.022762532
Si	2.371178264	4.348150042	7.964611116
Si	2.730381003	11.964998486	7.953042043
Si	2.753032935	4.072239169	5.036852738
Si	3.638212219	1.309562616	14.690190765
Si	3.638434390	2.585251922	24.168709006
Si	3.798552487	10.266097633	14.440085877
Si	3.820167418	5.792404302	24.457280088
Si	4.069674848	10.659597972	11.523893374
Si	4.079224376	5.385887432	1.457901868
Si	4.191950180	1.539941093	11.774272557
Si	4.115117700	2.339558010	1.192480599
Si	5.537655561	11.517329483	4.722513846
Si	5.581855090	4.488837725	8.211206404
Si	5.432803450	8.561764125	5.087616851
Si	5.462986397	7.438134825	7.839134394
Si	5.761449583	11.964150766	7.663493323
Si	5.800605456	4.013010837	5.282137141
Si	6.027421801	9.862620489	16.332401691
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Si	6.025767884	6.133719856	22.531052054
Si	6.379088216	9.840388760	9.566029756
Si	6.384501794	1.751604095	3.231367815
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Si	6.582262644	12.002215571	18.253329954
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Si	7.012013552	8.533361224	20.812079439
Si	7.040935801	7.456706057	18.020494204
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Si	6.909334926	4.466471326	17.705283303
Si	8.310447588	2.327244069	24.738854266
Si	8.378592788	10.547781739	14.407252369
Si	8.350786327	5.381450482	24.479361150
Si	8.585066921	10.171616138	11.522111747
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Si	8.788204810	2.588465388	1.756853909
Si	9.652145574	11.932752145	17.970474852
Si	9.663505918	4.063836892	20.943922118
Si	10.066786009	11.684140274	20.888605731
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Si	10.196968483	8.709487398	20.761016204
Si	10.252439057	7.278926854	18.135407308
Si	10.425787730	1.724547521	22.841882382
Si	10.514077726	2.104696148	16.074495835
Si	10.693057182	9.555841199	16.208827226
Si	10.695059258	6.422580459	22.709037632
Si	11.595408207	10.048821247	11.611363108
Si	11.588057096	5.915841110	1.325386476

Si	11.780750690	1.088744020	11.537653937
Si	11.750636090	2.724645614	1.396119572
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O	0.134275142	2.061815645	0.009471334
O	0.134849846	6.557852881	0.015637595
O	0.230694715	9.543813198	10.304461859
O	0.237992287	6.310670207	2.656607039
O	0.650420868	2.488008380	2.585882542
O	0.751405506	1.407600271	10.445703099
O	0.912546170	11.730850880	14.034948882
O	0.881552537	4.303466371	24.748760223
O	1.552801474	0.403637746	3.904201933
O	1.596072805	3.483376299	9.094282516
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O	1.870550782	7.906935804	3.841446630
O	1.831499022	10.804088705	8.643063294
O	1.886000635	5.281975554	4.399521502
O	2.817162945	1.140443068	8.850280708
O	2.773530500	2.746043818	4.115927612
O	1.656320462	10.223128556	5.027332173
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O	2.095653402	1.820078748	14.643621918
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O	2.350712788	6.474666562	24.479357269
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O	2.866984946	6.259063079	2.085510261
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O	3.898711482	7.162649789	7.551570183
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O	4.508669098	5.984335720	0.011346773
O	4.241495672	11.366868909	7.787014536
O	4.282640123	4.616251718	5.183527077
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O	5.645181945	1.620160447	11.050912986
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O	5.634827552	10.864441441	17.560739053
O	5.628650566	5.096544287	21.332782991
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O	6.130259343	8.023129007	6.467882081
O	6.413401304	1.276378666	17.550749440
O	6.535883288	2.560831432	21.373511350
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O	6.768074677	7.458281285	21.991734939
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O	6.433362356	6.015846428	17.605559120
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O	6.120581325	6.022595158	8.293982058
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O	5.648771194	7.482986590	3.908168571
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O	5.894995897	2.580760463	4.541600483
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O	6.139977277	0.166535122	3.465964164
O	6.194313963	3.660778759	9.464312421
O	6.755252948	10.861040518	8.343934931
O	6.785273332	5.133382854	4.617177881
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O	7.045811221	10.635054958	15.331763384
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O	7.927229522	9.877885683	12.975433057
O	7.922220264	5.979525074	0.015659303
O	8.238939066	1.987102932	12.480593794
O	8.112810407	1.992199051	0.397100289
O	8.479189448	11.610727651	21.234770957
O	8.532086931	4.338756634	17.657605195
O	8.591858089	8.763770733	20.586631604
O	8.636337095	7.295406117	18.204735878
O	8.997463550	12.008600621	14.147907065
O	8.898151327	3.852777201	24.629884953
O	8.603343706	11.787446098	11.225441488

O	8.684248997	4.209255454	1.840044297
O	9.432120375	1.336804855	24.082737683
O	9.578120730	2.537204063	14.846217548
O	9.510204898	9.588840424	15.091461436
O	9.572445360	6.257636428	23.876142301
O	10.268741789	0.187567235	19.417405554
O	10.284959846	3.618705761	19.514811809
O	10.861734963	7.979524514	19.471294361
O	10.071658144	9.531974308	11.466709092
O	10.080749109	6.482818688	1.472160655
O	10.330126392	2.079562580	1.841153987
O	10.370944561	1.675980453	10.965123692
O	10.760510200	10.218321908	20.900412708
O	10.778810771	5.756122758	18.035410080
O	9.671581120	1.061941936	17.013277364
O	9.607113102	2.753860162	21.888538609
O	10.472009990	10.666585811	17.374588848
O	10.538719240	5.273909487	21.570399640
O	10.750762389	8.059154884	16.815824030
O	10.558896060	7.911747684	22.111843644
O	10.833876441	0.396597612	22.014892671
O	10.947654821	3.396062727	16.964332398
O	11.601526890	11.662573290	11.669546474
O	11.527188086	4.307225586	1.174410204
O	11.775057088	2.454759843	23.343026306
O	11.876530718	1.347697866	15.608085318
O	12.159629640	9.807667679	15.583438427
O	0.030281210	6.328716998	23.287670188
Al	8.371544834	1.453618294	14.244923191
C	3.856592651	5.510038852	14.244038392
C	3.353780991	5.885697357	15.423293610
C	4.379773440	6.448510734	13.191096000
C	5.906430422	6.306858730	12.995301628
C	6.380564893	4.856398471	12.771334462
C	7.780647263	4.784624808	12.212420417
C	8.918927178	5.096799333	12.885710435
C	8.924061533	5.523470746	14.323812932
C	10.256117347	5.086183806	12.206567662
C	3.635495273	6.252095043	11.859802188
H	3.902512311	4.443600051	13.996775294
H	2.993934463	5.152534269	16.147349197
H	3.292307026	6.941585387	15.699836539
H	4.197400161	7.478147180	13.535248044
H	6.208793712	6.928561916	12.135701013
H	6.423377142	6.712659325	13.878040846
H	5.698190381	4.351466777	12.072431609
H	6.310213998	4.313301614	13.727518500
H	7.866678517	4.631071726	11.129508647
H	8.001928810	5.240583651	14.846617974
H	9.021880552	6.622482467	14.368013866
H	9.784529826	5.095076384	14.854044300

H	10.938952049	4.389952739	12.720748073
H	10.182086985	4.801893728	11.147790655
H	10.717270264	6.086026055	12.271897710
H	3.744532553	5.221174042	11.488808230
H	2.561170281	6.450460182	11.981001618
H	4.028951716	6.940768504	11.095813183
H	8.203358603	3.025001285	12.413857509

chem-b-citro

Si	0.633046462	1.203498767	14.278285225
Si	0.692967148	2.755113793	24.526156691
Si	0.799029589	10.208664707	14.238080419
Si	0.855301928	5.954199143	24.611508264
Si	1.707324311	9.630689780	9.731530759
Si	1.759392349	6.427990635	3.229660086
Si	2.008204195	1.745413876	3.096174942
Si	2.012533926	2.131361468	9.849918154
Si	2.268909129	8.731072840	5.179893650
Si	2.267700152	7.313087058	7.792235118
Si	2.350468439	11.695732177	5.005309870
Si	2.352243994	4.350404525	7.956375412
Si	2.729767336	11.966894655	7.934462937
Si	2.766046814	4.071273426	5.023306038
Si	3.605061862	1.371136495	14.684572138
Si	3.664113258	2.616311765	24.177791574
Si	3.763615067	10.321843299	14.458614970
Si	3.840224561	5.821161458	24.464104629
Si	4.034105894	10.670005855	11.529868634
Si	4.100193954	5.398587200	1.456785009
Si	4.135163435	1.548887560	11.758438638
Si	4.144710186	2.351174580	1.199333002
Si	5.558220915	11.523150490	4.735250794
Si	5.560591078	4.502418136	8.238252159
Si	5.445634449	8.570203516	5.116983296
Si	5.439917196	7.458439321	7.876411020
Si	5.755264698	11.983041439	7.678324910
Si	5.814234742	4.030747126	5.296371174
Si	5.995928899	9.914623471	16.343514646
Si	6.066917951	1.775081664	22.685189084
Si	5.975938710	2.143126602	16.181416922
Si	6.047443052	6.179428519	22.539457564
Si	6.367971218	9.866037532	9.598892101
Si	6.413066943	1.763097729	3.249913287
Si	6.381255730	2.072058202	9.685239988
Si	6.410415894	6.165717356	3.406913129
Si	6.554505916	12.064586876	18.254364016
Si	6.648087423	4.048417812	20.644379807
Si	7.019561575	8.581289534	20.815733265
Si	7.032342018	7.509357082	18.018391242
Si	6.864124407	11.541446534	21.179145704
Si	6.907686585	4.512877446	17.705951789

Si	8.332162415	2.374127961	24.735918907
Si	8.347824927	10.628542638	14.428435443
Si	8.377198073	5.427204790	24.484706567
Si	8.581119375	10.213566410	11.527160537
Si	8.629398541	5.823958603	1.491866084
Si	8.780839907	1.253634488	11.141806721
Si	8.811795657	2.618421221	1.761284352
Si	9.627996266	12.026157506	17.956699421
Si	9.692017443	4.124606270	20.926981992
Si	10.068655076	11.736603189	20.869411558
Si	10.121118342	4.339661036	18.001972950
Si	10.204858512	8.758732704	20.759016997
Si	10.250837399	7.344935802	18.122851185
Si	10.450557451	1.770050104	22.826942722
Si	10.453457524	2.186269609	16.020598993
Si	10.656263959	9.641730477	16.207190672
Si	10.714154034	6.484075695	22.708773691
Si	11.561941472	10.096669807	11.616374406
Si	11.605841844	5.953337192	1.331703932
Si	11.728130840	1.126892975	11.496393547
Si	11.776152757	2.757693481	1.401826968
O	0.111915725	9.489010542	12.945304257
O	0.010510725	1.834704476	12.898286177
O	0.146557131	2.102667570	0.007319191
O	0.140150968	6.590361263	0.012347108
O	0.194390778	9.623817044	10.296056492
O	0.254749087	6.369679808	2.656495846
O	0.681032885	2.502242426	2.582815482
O	0.699709078	1.366086227	10.375822085
O	0.907049140	11.800825084	13.993499068
O	0.891268085	4.342409303	24.737466528
O	1.572016995	0.395587292	3.879579114
O	1.558641871	3.475556711	9.065739350
O	1.940180788	8.161898200	9.114507044
O	1.934640769	7.906007807	3.844348492
O	1.821957899	10.804823542	8.610124754
O	1.898793596	5.267470045	4.360917115
O	2.804708177	1.143001726	8.830486430
O	2.800412052	2.731453348	4.121017269
O	1.671245042	10.223632156	5.017741385
O	1.670365897	5.822269408	7.981231221
O	2.121004086	2.114366075	24.101292795
O	2.060082495	1.880959198	14.653132015
O	2.294778381	9.627154276	14.450835314
O	2.371253668	6.505883988	24.493927690
O	1.608529411	8.012154157	6.481908660
O	2.142592521	0.206681859	6.475210577
O	2.153718810	3.690435985	6.479809182
O	2.798185328	9.815070373	10.922983162
O	2.875030587	6.270203426	2.058699656
O	3.032496871	1.366278122	1.880194053

O	3.044814342	2.541978084	11.049446856
O	3.704417028	11.912147337	14.789253544
O	3.761614410	4.236843278	24.112070014
O	3.514849545	0.041509278	11.640022777
O	3.548525746	3.871340987	1.321988927
O	3.872040163	8.823334959	5.379365617
O	3.870593816	7.196491797	7.604521675
O	3.937546845	11.629248393	4.652493051
O	3.940641726	4.396698853	8.315785707
O	4.314544693	1.927690622	13.315202804
O	4.334396055	2.015679813	25.542915046
O	4.444362335	10.094941377	12.988924530
O	4.540699135	5.997520991	0.013753420
O	4.240368630	11.365168055	7.787590378
O	4.292378349	4.621749205	5.177569550
O	4.479596472	2.021117084	22.915739950
O	4.355122732	2.027977814	15.954149615
O	4.624907656	9.519496049	15.567398687
O	4.705996365	6.605766807	23.342645839
O	5.349288943	10.644928707	10.592563644
O	5.405851713	5.370441410	2.409031158
O	5.578530713	2.242795609	1.941015948
O	5.576073477	1.628407785	11.024952334
O	6.128164128	0.009432841	6.117513304
O	6.155119410	3.846363730	6.868884599
O	5.616313197	10.904748614	17.584514315
O	5.653835505	5.144762210	21.337442309
O	6.293118871	0.185767164	22.460516697
O	6.294457374	3.729702672	16.435605742
O	6.123987501	8.019255855	6.502264936
O	6.350278842	1.332316722	17.551857597
O	6.558549962	2.608472705	21.378288357
O	6.701161334	8.542830144	16.824677424
O	6.776438209	7.511603785	22.000106900
O	6.366700552	9.995150477	21.267245045
O	6.434462774	6.064125662	17.600731622
O	6.085050944	9.985459366	4.649449800
O	6.084960954	6.041664191	8.348228492
O	5.635922594	8.523008444	9.074403414
O	5.655904896	7.492523433	3.934603086
O	5.814671114	1.268542970	8.392453856
O	5.931543985	2.595251617	4.562641611
O	6.376867670	8.031808709	19.419486230
O	6.176583088	0.176987836	3.488093300
O	6.179783370	3.678357147	9.490042000
O	6.747391543	10.891773106	8.383134028
O	6.799495377	5.148699227	4.627529414
O	6.229256007	0.045682322	19.836674680
O	6.299558084	3.869425439	19.076485509
O	6.897130757	2.260082998	23.998478423
O	6.771470801	1.609458866	14.910587297

O	6.996588503	10.686977826	15.330992667
O	7.066106869	5.405168278	23.542592738
O	7.707962116	9.429822775	10.397250745
O	7.752403897	6.601879846	2.613537756
O	7.999046438	2.002708670	3.018566091
O	7.964848271	1.776032736	9.830231771
O	8.090114685	11.522733640	18.118881503
O	8.162583167	4.664393812	20.759558169
O	7.916684324	9.956124803	12.988671483
O	7.945571864	6.014209637	0.024217045
O	8.171460386	1.974932605	12.450062672
O	8.143280441	2.031224091	0.393360599
O	8.485025217	11.649122740	21.226118459
O	8.531786782	4.399419137	17.647981951
O	8.599164254	8.805034576	20.587102411
O	8.633814705	7.366291988	18.173661064
O	8.987294655	12.081577251	14.225549148
O	8.924401693	3.898009216	24.627064484
O	8.652148291	11.792866818	11.164152342
O	8.702912028	4.238681671	1.847931503
O	9.447198973	1.388567309	24.061744031
O	9.485217328	2.651918964	14.830293068
O	9.446971166	9.621599642	15.116724405
O	9.596392887	6.307889833	23.880169641
O	10.250456757	0.263319429	19.407657283
O	10.314318865	3.700197282	19.489983363
O	10.859944729	8.004977289	19.477154841
O	10.053809751	9.510012966	11.504622672
O	10.096478501	6.512087317	1.485854373
O	10.355112755	2.115630838	1.848675077
O	10.332043578	1.731125232	10.938031023
O	10.766051877	10.271010838	20.862274212
O	10.773957794	5.824475413	17.978163337
O	9.652436060	1.160878447	17.012540889
O	9.654477009	2.811427103	21.866850975
O	10.442260702	10.752579172	17.368619935
O	10.551365618	5.344017355	21.560753964
O	10.763141233	8.146864115	16.820682100
O	10.576089530	7.978313419	22.119030117
O	10.843018610	0.437147396	21.999949939
O	10.934293483	3.470324021	16.910272877
O	11.523726757	11.704937407	11.701300954
O	11.562745936	4.343243880	1.195238353
O	11.807421187	2.479011669	23.336406112
O	11.798143842	1.417433000	15.518511777
O	12.102087516	9.918953460	15.554978300
O	0.052110387	6.383271735	23.284477722
Al	8.317773732	1.536293991	14.147085286
C	3.751421697	5.569743750	14.079870512
C	3.264116723	6.029378630	15.235833424
C	4.260447361	6.430264656	12.954299498

C	5.801920795	6.359716491	12.831269111
C	6.358695551	4.927192086	12.837864148
C	7.791445145	4.873381140	12.317288973
C	8.873884553	5.476457006	13.028164037
C	8.796293712	5.769500185	14.465326082
C	10.106642716	5.827975319	12.303000917
C	3.592644011	6.049727985	11.623426372
H	3.798611885	4.488216510	13.910536764
H	2.919937398	5.347014496	16.015000213
H	3.201788510	7.101567317	15.438932610
H	4.008491205	7.478414849	13.180564879
H	6.099675794	6.868385005	11.897602748
H	6.251487146	6.925212366	13.662955879
H	5.760612841	4.277879740	12.184610948
H	6.289204137	4.498403957	13.848243888
H	7.873165015	5.017936853	11.227373561
H	7.979641944	5.237798054	14.965374636
H	8.593792691	6.859740636	14.543421384
H	9.758893520	5.600722697	14.966416695
H	11.010282080	5.683410099	12.910553940
H	10.181663716	5.327129423	11.329020563
H	10.034610062	6.920316263	12.103443412
H	3.824906616	5.012602641	11.339519325
H	2.498995798	6.133147744	11.697927174
H	3.932700004	6.719026724	10.818462743
H	8.145392365	3.762203725	12.424921902

4. Entropy calculations for adsorption and protonation of β-citronellene in zeolite beta

Adsorption and protonation entropies are defined as follows:
$\Delta S_{phys} = S_{phys} - S_{ZeOH} - S_{citro(g)}$
$\Delta S_{chem} = S_{phys} - S_{ZeOH} - S_{citro(g)}$
$\Delta S_{prot} = S_{chem} - S_{phys}$

The entropy of gas-phase β-citronellene ($S_{citro(g)}$) is calculated from statistical thermodynamics as follows:

$$S_{gas} = S_{vib} + S_{trans} + S_{rot}$$

$$S_{vib} = R\sum_{i=1}^{3N-6}\left[\frac{h\omega_i}{k_B T(e^{h\omega_i/k_B T}-1)} - \ln(1-e^{-h\omega_i/k_B T})\right]$$

$$S_{trans} = R\left\{\ln\left[\left(\frac{2\pi M\, k_B T}{h^2}\right)^{3/2}\frac{V^0}{N_A}\right] + \frac{5}{2}\right\}$$

$$S_{rot} = R\left\{\ln\left[\frac{\sqrt{\pi I_A I_B I_C}}{\sigma}\left(\frac{8\pi^2 k_B T}{h^2}\right)^{3/2}\right]+\frac{3}{2}\right\}$$

where, N is the number of atoms in the molecule, R is the universal gas constant, h is the Planck constant, k_B is the Boltzmann constant, T is the temperature (353 K), ω_i represent the vibrational frequencies obtained by a full hessian calculation with VASP, M is the molecular mass, V^0/N_A represents the molecular volume of an ideal gas and equals to k_BT/P^0 (with $P^0=1$ *bar*), while σ is the external symmetry number and I_A, I_B, I_C are the principal moments of inertia.

On the other hand, the entropy of the immobile surface species (S_{ZeOH}, S_{phys}, S_{chem}) is calculated from statistical thermodynamics as follows:

$$S_{immobile} = S_{vib}$$

$$S_{vib} = R\sum_{i=1}^{3N}\left[\frac{h\omega_i}{k_B T(e^{h\omega_i/k_B T}-1)} - \ln(1-e^{-h\omega_i/k_B T})\right]$$

where, N is the number of atoms considered in the partial hessian calculation, R is the universal gas constant, h is the Planck constant, k_B is the Boltzmann constant, T is the temperature (353 K), while ω_i represent the vibrational frequencies obtained by the partial hessian calculation with VASP.

Table S2. Adsorption and protonation entropies (J/mol/K) at 353K for β-citronellene in zeolite beta.

	ΔS_{phys}	ΔS_{chem}	ΔS_{prot}
β-double bond	-192	-171	21
α-double bond	-193	-176	17

5. References

1. Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
2. Becke, A.D., *Density-functional thermochemistry. III. The role of exact exchange*, J. Chem. Phys., **98** (1993) 5648-52.
3. Cramer, C.J., *Essentials of computational chemistry: theories and models*, Wiley, Cicester, 2nd edn, 2005.