Electronic Supplementary Information

Novel insights on biomass delignification with acidic deep eutectic solvents: a mechanistic study of β-O-4 ether bond cleavage and the role of the halide counterion on the catalytic performance.

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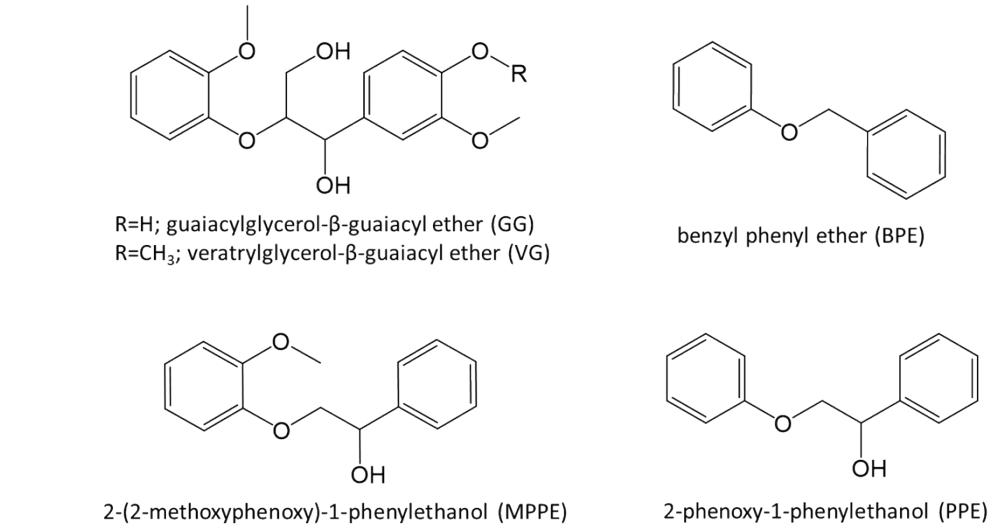
Lignin Model Compounds



Cleavage products

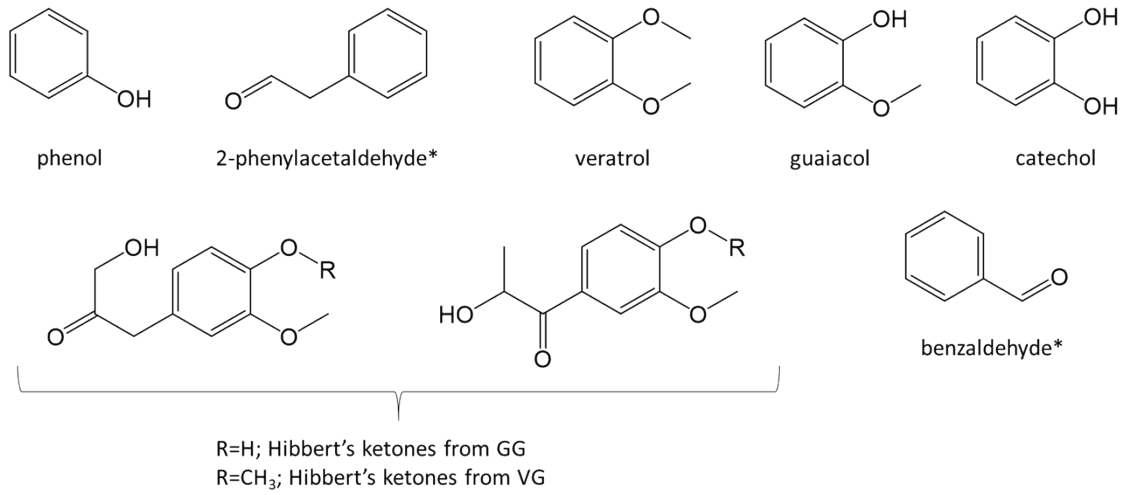


Figure S1. Main examples of lignin model compounds comprising a β-O-4 ether linkage and direct cleavage products formed through acid catalysed reactions reported in literature. *corresponding 2-phenylethenol and benzyl alcohol may coexist.

Table S1. Molar yields of PPE conversion, cleaved and non-cleaved products using neat pTSA:ChCl (1:1) at 120 °C.

Time (h)	PPE conversion (mol%)	Cleavage products (condensed) (mol%)	Non-cleaved products(mol%)		
			Esters[a] (mol%)	PPE-Cl (mol%)	Others[b] (mol%)
0.5	96.9 ± 2.5	42.8 ± 1.4 (7.0 ± 0.2)	0.0 ± 0.0	48.9 ± 1.0	5.2 ± 0.1
1.0	100.0 ± 0.0	54.6 ± 1.2 (8.9 ± 0.1)	0.0 ± 0.0	41.7 ± 1.1	3.7 ± 0.1
2.0	100.0 ± 0.0	67.5 ± 1.3 (12.1 ± 0.9)	0.0 ± 0.0	29.9 ± 1.2	2.6 ± 0.1
4.0	100.0 ± 0.0	78.8 ± 1.7 (15.5 ± 1.4)	0.0 ± 0.0	19.2 ± 1.4	2.0 ± 0.3

a) Comprises compounds **11**, **12** and **14** from Table 2; b) comprises other non-cleavage compounds, including **9** and **13** from Table 2, and others (*e.g.* PPE dimer).

Table S2. Molar yields of PPE conversion, cleaved and non-cleaved products using pTSA:ChCl (1:1)/H_2O at 120 °C.

Time (h)	PPE conversion (mol%)	Cleavage products (condensed) (mol%)	Non-cleaved products(mol%)		
			Esters[a] (mol%)	PPE-Cl (mol%)	Others[b] (mol%)
0.5	24.7 ± 2.3	20.2 ± 1.6 (1.6 ± 0.1)	0.0 ± 0.0	1.2 ± 0.1	3.4 ± 0.6
1.0	34.4 ± 2.2	29.7 ± 1.4 (2.2 ± 0.5)	0.0 ± 0.0	1.1 ± 0.4	3.6 ± 0.4
2.0	45.1 ± 1.5	40.6 ± 1.3 (5.5 ± 0.4)	0.0 ± 0.0	1.1 ± 0.1	3.4 ± 0.1
4.0	60.3 ± 2.0	54.5 ± 1.7 (8.5 ± 1.0)	0.0 ± 0.0	1.1 ± 0.1	4.7 ± 0.2

a) Comprises compounds **11**, **12** and **14** from Table 2; b) comprises other non-cleavage compounds, including **9** and **13** from Table 2, and others (*e.g.* PPE dimer).

Table S3. Molar yields of PPE conversion, cleaved and non-cleaved products using pTSA/H_2O at 120 °C.

Time (h)	PPE conversion (mol%)	Cleavage products (condensed) (mol%)	Non-cleaved products(mol%)		
			Esters[a] (mol%)	PPE-Cl (mol%)	Others[b] (mol%)
0.5	15.5 ± 2.7	12.1 ± 2.1 (0.0 ± 0.0)	0.0 ± 0.0	0.0 ± 0.0	3.3 ± 0.6
1.0	22.6 ± 1.0	18.4 ± 0.8 (0.0 ± 0.0)	0.0 ± 0.0	0.0 ± 0.0	4.2 ± 0.2
2.0	37.5 ± 1.4	31.3 ± 1.3 (0.0 ± 0.0)	0.0 ± 0.0	0.0 ± 0.0	6.2 ± 0.1
4.0	53.0 ± 1.7	45.2 ± 1.0 (2.7 ± 0.5)	0.0 ± 0.0	0.0 ± 0.0	7.8 ± 0.7
8.0	83.3 ± 2.2	70.8 ± 1.5 (9.3 ± 0.2)	0.0 ± 0.0	0.0 ± 0.0	8.8 ± 0.7

a) Comprises compounds **11**, **12** and **14** from Table 2; b) comprises other non-cleavage compounds, including **9** and **13** from Table 2, and others (*e.g.* PPE dimer).

Table S4. Molar yields of PPE conversion, cleaved and non-cleaved products using neat pTSA:ChBr (1:1) at 120 °C.

Time (h)	PPE conversion (mol%)	Cleavage products (condensed) (mol%)	Non-cleaved products(mol%)		
			Esters[a] (mol%)	PPE-Br (mol%)	Others[b] (mol%)
0.08	100.0 ± 0.0	62.3 ± 0.7 (9.5 ± 0.7)	0.0 ± 0.0	32.7 ± 0.6	5.0 ± 0.1
0.17	100.0 ± 0.0	83.8 ± 0.8 (16.6 ± 1.1)	0.0 ± 0.0	14.0 ± 0.8	2.1 ± 0.1
0.33	100.0 ± 0.0	96.0 ± 0.5 (22.6 ± 1.7)	0.0 ± 0.0	3.7 ± 0.3	0.3 ± 0.3
0.50	100.0 ± 0.0	98.5 ± 0.1 (25.0 ± 0.8)	0.0 ± 0.0	1.5 ± 0.1	0.0 ± 0.0
1.0	100.0 ± 0.0	100.0 ± 0.0 (24.8 ± 0.9)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
2.0	100.0 ± 0.0	100.0 ± 0.0 (25.5 ± 0.6)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
4.0	100.0 ± 0.0	100.0 ± 0.0 (26.0 ± 1.1)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
8.0	100.0 ± 0.0	100.0 ± 0.0 (25.8 ± 1.1)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

a) Comprises compounds **11**, **12** and **14** from Table 2; b) comprises other non-cleavage compounds, including **9** and **13** from Table 2, and others (*e.g.* PPE dimer).

Table S5. Molar yields of PPE conversion, cleaved and non-cleaved products using pTSA:ChBr (1:1)/H_2O at 120 °C.

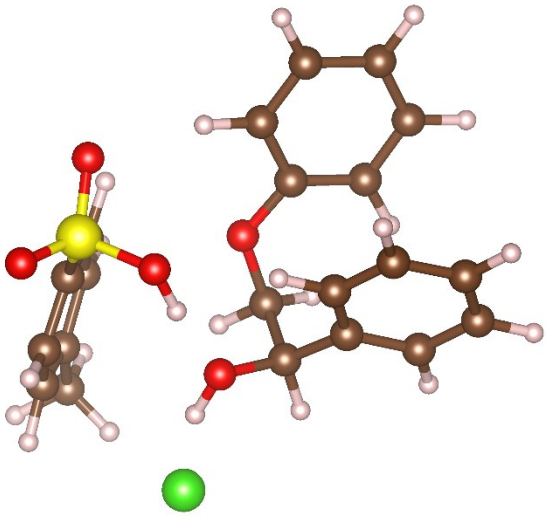
Time (h)	PPE Conversion (mol%)	Cleavage products (condensed) (mol%)	Non-cleaved products(mol%)		
			Esters[a] (mol%)	PPE-Br (mol%)	Others[b] (mol%)
0.5	22.8 ± 1.1	21.3 ± 1.0 (0.0 ± 0.0)	0.0 ± 0.0	0.0 ± 0.0	1.4 ± 0.1
1.0	34.2 ± 1.1	32.4 ± 1.0 (0.0 ± 0.0)	0.0 ± 0.0	0.0 ± 0.0	1.8 ± 0.1
2.0	58.3 ± 0.9	55.0 ± 0.8 (7.1 ± 0.2)	0.0 ± 0.0	0.0 ± 0.0	3.3 ± 0.1
4.0	81.4 ± 1.4	78.0 ± 1.1 (14.2 ± 0.3)	0.0 ± 0.0	0.0 ± 0.0	3.4 ± 0.3
8.0	99.6 ± 0.2	99.6 ± 0.2 (27.4 ± 1.5)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

a) Comprises compounds **11**, **12** and **14** from Table 2; b) comprises other non-cleavage compounds, including **9** and **13** from Table 2, and others (*e.g.* PPE dimer).

Table S6. Optimised coordinates (Å) of the initial state of the hydrogenation/dehydration step (Cl^-).

Colour code for spheres: H, white; C, brown; O, red; S, yellow; Cl, green.

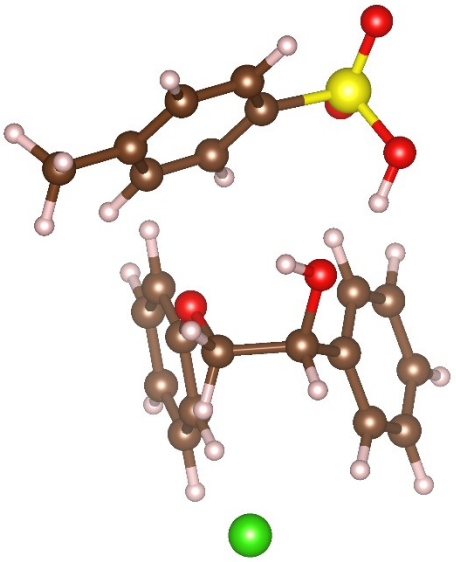
C	2.748994	-0.018836	1.797690
C	1.704379	-0.753892	1.238080
C	1.887519	-2.107826	0.939990
C	3.107182	-2.711273	1.199999
C	4.160143	-1.985461	1.754982
C	3.968849	-0.642236	2.046711
O	0.468331	-0.266241	0.941078
C	0.172182	1.121471	1.013820
C	0.422830	1.817427	-0.326627
C	1.866450	1.722922	-0.755936
C	2.347511	0.639146	-1.488693
C	3.709086	0.515758	-1.740121
C	4.602718	1.474068	-1.273675
C	4.125321	2.572602	-0.566691
C	2.763637	2.695414	-0.315781
O	-0.448491	1.258340	-1.301577
O	-0.344538	-1.241868	-1.781247
S	-1.461925	-2.254955	-1.319460
O	-0.812458	-3.317359	-0.574613
C	-2.442646	-1.282129	-0.212555
C	-2.241949	-1.378238	1.155192
C	-2.943314	-0.513793	1.989871
C	-3.814065	0.441411	1.467139
C	-4.021829	0.486051	0.085964
C	-3.343290	-0.372917	-0.759011
C	-4.464029	1.480787	2.336782
O	-2.268943	-2.608236	-2.468383
Cl	-2.504050	3.273192	-0.434715
H	3.237706	-3.759549	0.956007
H	5.115642	-2.458811	1.946308
H	2.648121	1.037619	2.000060
H	4.779564	-0.054277	2.462422
H	1.066605	-2.650475	0.483395
H	0.713874	1.610392	1.827839
H	-0.899396	1.187130	1.216240
H	1.664727	-0.126156	-1.837236
H	4.811409	3.334989	-0.214947
H	2.388126	3.551651	0.236916
H	4.073181	-0.343504	-2.291116
H	5.664514	1.368080	-1.464478
H	0.144779	2.867402	-0.194452
H	-1.286883	1.788766	-1.220192
H	-2.779110	-0.557003	3.061519
H	-1.526855	-2.091863	1.543684
H	-3.480382	-0.326072	-1.832930
H	-4.666360	1.250211	-0.329382
H	-4.080495	2.462680	2.041328
H	-5.547877	1.489797	2.198216
H	-4.249128	1.312553	3.393249
H	-0.477375	-0.258352	-1.525774



$G^{298.15\ K}$ = -2047.540837 a.u.

Table S7. Optimised coordinates (Å) of the intermediate state of the hydrogenation/dehydration step (Cl^-). Colour code for spheres: H, white; C, brown; O, red; S, yellow; Cl, green.

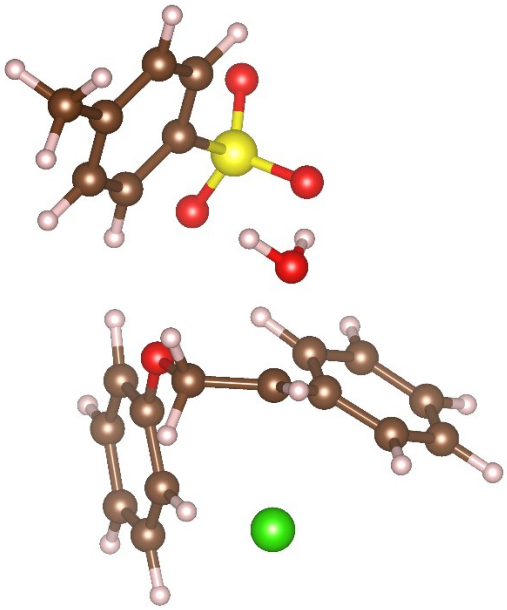
C	-3.425301	2.571213	0.331749
C	-2.312449	1.913075	0.859504
C	-2.224349	0.527543	0.832603
C	-3.259584	-0.200422	0.261397
C	-4.379731	0.425274	-0.271769
C	-4.456373	1.811290	-0.226837
S	-3.084670	-1.961447	0.096484
O	-2.480134	-2.108114	-1.363808
C	-3.514358	4.073839	0.383651
O	-4.394758	-2.562227	0.034591
O	-2.115477	-2.405449	1.072812
O	-0.707150	-0.178472	-1.641491
C	0.671192	0.250326	-1.627399
C	1.515325	-0.919684	-1.188286
C	1.064001	-1.783372	-0.191269
C	1.882276	-2.809029	0.267306
C	3.155952	-2.975023	-0.265767
C	3.602718	-2.118619	-1.267059
C	2.787057	-1.094050	-1.733290
C	0.827484	1.476261	-0.725717
O	0.724435	1.166181	0.659772
C	1.863328	0.916425	1.374910
C	1.656108	0.557394	2.707978
C	2.736021	0.276895	3.530766
C	4.034393	0.350039	3.033916
C	4.229048	0.709864	1.706255
C	3.158755	0.996634	0.863961
H	2.559726	-0.006546	4.562420
H	4.880228	0.123533	3.671944
H	3.356964	1.260468	-0.170570
H	5.231558	0.766888	1.298085
H	0.637427	0.495686	3.073612
H	1.755596	1.987411	-0.982881
H	0.004513	2.171445	-0.930997
H	0.079245	-1.656335	0.243697
H	4.595861	-2.239434	-1.684686
H	3.146284	-0.390276	-2.479168
H	1.520802	-3.470669	1.045846
H	3.798568	-3.768667	0.098946
H	0.970730	0.566242	-2.631292
H	-1.269489	0.600126	-1.708071
H	-1.484437	2.477096	1.276308
H	-1.345300	0.029037	1.220651
H	-5.171189	-0.172233	-0.708441
H	-5.324546	2.312447	-0.641110
H	-3.866449	4.401545	1.365728
H	-2.536634	4.528349	0.215372
H	-4.208001	4.456321	-0.366327
H	-1.656384	-1.562887	-1.472102
Cl	3.399719	2.202530	-2.816196



$G^{298.15\ K}$ = -2047.520610 a.u.

Table S8. Optimised coordinates (Å) of the transition state of the hydrogenation/dehydration step (Cl^-). Colour code for spheres: H, white; C, brown; O, red; S, yellow; Cl, green.

C	-4.470108	1.764300	0.410127
C	-3.290114	1.552055	1.123076
C	-2.574904	0.363464	0.991825
C	-3.040818	-0.622801	0.132614
C	-4.218156	-0.433287	-0.583995
C	-4.925611	0.752747	-0.439742
S	-2.043557	-2.089654	-0.188874
O	-1.408215	-1.760315	-1.496632
C	-5.259070	3.037696	0.578309
O	-2.983398	-3.202055	-0.273779
O	-1.066822	-2.144719	0.907348
O	-0.793283	0.775141	-1.785482
C	1.108119	1.441589	-1.101831
C	1.816703	0.226362	-1.493598
C	1.501786	-1.018585	-0.932172
C	2.142404	-2.161432	-1.389919
C	3.102861	-2.074948	-2.389083
C	3.411626	-0.840350	-2.958924
C	2.763240	0.302925	-2.526806
C	0.641649	1.794044	0.287820
O	0.522107	0.713504	1.175088
C	1.629860	0.244037	1.834847
C	1.400717	-0.894091	2.608513
C	2.447228	-1.442652	3.331892
C	3.718655	-0.872440	3.282534
C	3.932919	0.241372	2.482892
C	2.896900	0.810756	1.744293
H	2.269935	-2.331403	3.926687
H	4.535904	-1.307670	3.845406
H	3.106782	1.648810	1.087352
H	4.922147	0.678017	2.407558
H	0.414211	-1.344219	2.576895
H	1.312603	2.567301	0.665740
H	-0.355799	2.230807	0.211272
H	0.720087	-1.121693	-0.191389
H	4.159295	-0.769865	-3.739909
H	3.014541	1.274864	-2.932778
H	1.864936	-3.117548	-0.964193
H	3.606095	-2.970960	-2.735528
H	1.000500	2.221275	-1.836113
H	-1.555617	1.103235	-1.293474
H	-2.924810	2.324269	1.793761
H	-1.649271	0.197041	1.529837
H	-4.566681	-1.221290	-1.241854
H	-5.844210	0.903011	-0.998523
H	-6.028217	2.916722	1.346825
H	-4.614442	3.864581	0.880684
H	-5.760623	3.315788	-0.350591
H	-0.920671	-0.216370	-1.772112
Cl	3.141871	3.206633	-1.021291

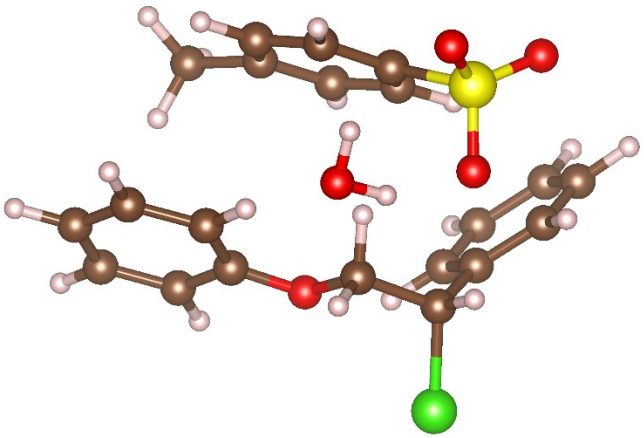


$G^{298.15\ K}$ = -2047.474054 a.u.

(-367.0536 cm^{-1})
d(C-O) = 2.127 Å
d(C-Cl) = 2.694 Å

Table S9. Optimised coordinates (Å) of the intermediate state between the hydrogenation/dehydration and enol-ether formation steps in the presence of pTSA with Cl^-. Colour code for spheres: H, white; C, brown; O, red; S, yellow; Cl, green.

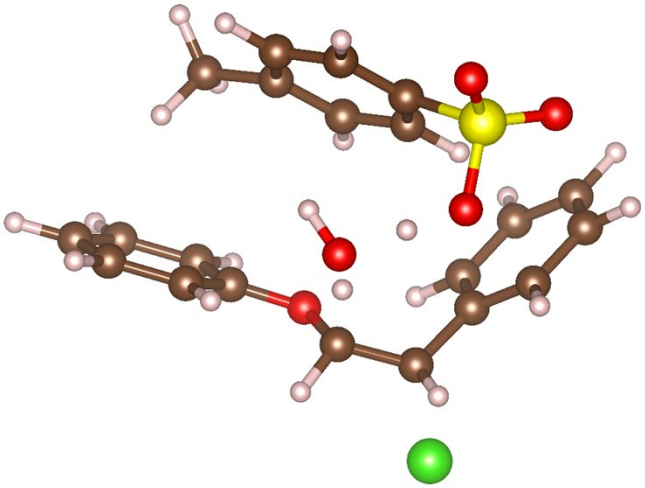
C	-1.619426	-1.474582	1.993008
C	-0.451146	-0.745245	2.214206
C	0.711189	-1.022609	1.504409
C	0.708283	-2.029888	0.546219
C	-0.437072	-2.787608	0.335227
C	-1.585986	-2.517504	1.067835
S	2.126925	-2.225214	-0.546084
O	2.012102	-1.064917	-1.478481
C	-2.904407	-1.109630	2.687279
O	1.893685	-3.502768	-1.237215
O	3.314580	-2.143697	0.303460
O	-0.256969	-1.965720	-2.821898
C	1.099632	1.743615	-1.303621
C	1.750434	1.858347	0.048988
C	2.987497	1.248632	0.251084
C	3.587220	1.277499	1.505986
C	2.956477	1.919273	2.565179
C	1.724408	2.539150	2.363530
C	1.124438	2.513303	1.111436
C	-0.207790	0.977491	-1.331907
O	-1.198478	1.665695	-0.585160
C	-2.416362	1.079047	-0.505241
C	-3.407447	1.816429	0.152417
C	-4.693050	1.312086	0.264690
C	-5.007892	0.061501	-0.265418
C	-4.014942	-0.668197	-0.906899
C	-2.718176	-0.175617	-1.039259
H	-5.452991	1.896531	0.771480
H	-6.011729	-0.336057	-0.175841
H	-1.967693	-0.775068	-1.545993
H	-4.240396	-1.644719	-1.320874
H	-3.140078	2.787579	0.551144
H	-0.541553	0.855031	-2.368644
H	-0.018425	-0.008703	-0.903973
H	3.445479	0.689698	-0.555961
H	1.228200	3.040860	3.187120
H	0.164626	2.987153	0.948064
H	4.529051	0.763583	1.654750
H	3.416383	1.930859	3.546959
H	1.777388	1.228943	-1.979539
H	0.054029	-2.852992	-2.608353
H	-0.450235	0.064387	2.937535
H	1.618205	-0.460278	1.690320
H	-0.408750	-3.587705	-0.392954
H	-2.486157	-3.099046	0.892255
H	-3.504156	-0.460492	2.041514
H	-3.499404	-1.997622	2.912687
H	-2.712283	-0.575831	3.620080
H	0.534326	-1.455263	-2.579419
Cl	0.847101	3.400640	-2.034443



$G^{298.15\ K}$ = -2047.536532 a.u.

Table S10. Optimised coordinates (Å) of the transition state of the enol-ether formation step in the presence of pTSA with Cl^-. Colour code for spheres: H, white; C, brown; O, red; S, yellow; Cl, green.

C	-0.745912	-2.508350	1.234483
C	-0.168135	-1.259975	1.477720
C	1.102458	-0.958049	1.005461
C	1.793732	-1.908844	0.264927
C	1.245229	-3.159299	0.008330
C	-0.017802	-3.454834	0.507517
S	3.281812	-1.419977	-0.591361
O	2.696105	-0.532322	-1.719103
C	-2.130458	-2.834521	1.724005
O	3.876381	-2.625001	-1.144779
O	4.089307	-0.598502	0.289820
O	0.307281	-0.716231	-2.093954
C	-0.182000	2.420228	-1.106594
C	0.683027	2.399137	0.110693
C	2.060445	2.250400	-0.041223
C	2.894533	2.171999	1.071954
C	2.353238	2.251543	2.348300
C	0.975851	2.407331	2.507104
C	0.144515	2.480751	1.398634
C	-1.148903	1.407100	-1.311269
O	-1.956666	1.154316	-0.160613
C	-2.892199	0.202561	-0.234517
C	-3.808191	0.153913	0.828302
C	-4.846631	-0.759894	0.821505
C	-4.995103	-1.659093	-0.235663
C	-4.075698	-1.626154	-1.276464
C	-3.024817	-0.710516	-1.289397
H	-5.551507	-0.769379	1.645618
H	-5.813206	-2.368787	-0.244973
H	-2.327664	-0.692712	-2.116570
H	-4.171969	-2.320817	-2.103867
H	-3.689765	0.875495	1.628000
H	-1.774946	1.557758	-2.193700
H	-0.228389	0.169628	-1.734960
H	2.485468	2.153453	-1.034099
H	0.550313	2.476962	3.502337
H	-0.922147	2.625012	1.508052
H	3.953856	2.000386	0.932316
H	2.997930	2.182466	3.217012
H	0.371616	2.633224	-2.015508
H	-0.028397	-1.443219	-1.554683
H	-0.723432	-0.501482	2.020230
H	1.547881	0.010692	1.193274
H	1.809340	-3.872130	-0.581294
H	-0.454913	-4.430870	0.321378
H	-2.460012	-2.122397	2.480776
H	-2.846676	-2.788219	0.899279
H	-2.165550	-3.840826	2.148371
H	1.595793	-0.634514	-1.912782
Cl	-1.062644	4.384071	-0.988013

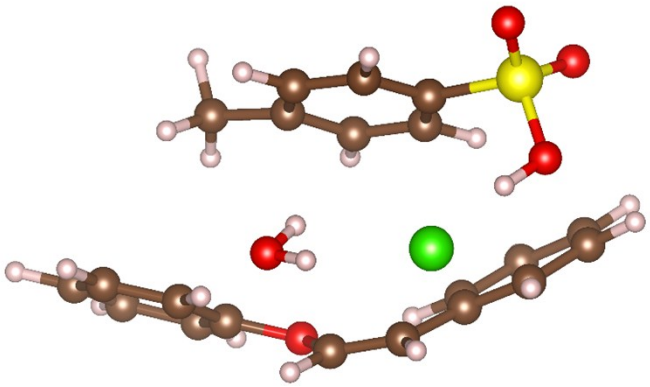


$G^{298.15\ K}$ = -2047.475301 a.u.

(-507.9738 cm^{-1})
d(C-H) = 1.599 Å
d(C-Cl) = 2.156 Å

Table S11. Optimised coordinates (Å) of the final state of the enol-ether formation step in the presence of pTSA with Cl^-. Colour code for spheres: H, white; C, brown; O, red; S, yellow; Cl, green.

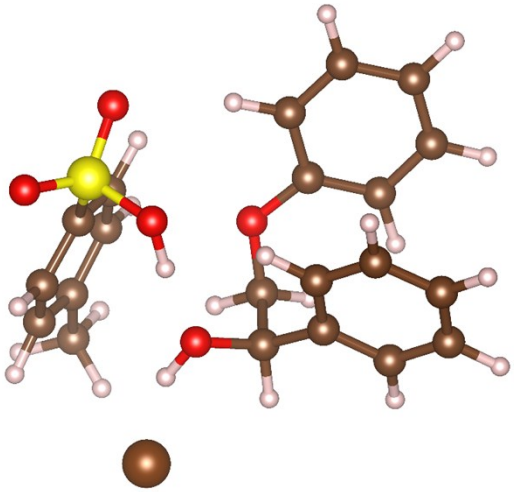
C	0.897854	-1.404392	-1.642363
C	0.313841	-0.140311	-1.741464
C	-1.033718	0.051243	-1.456152
C	-1.791222	-1.030471	-1.027659
C	-1.224074	-2.290150	-0.869368
C	0.115755	-2.469118	-1.184651
S	-3.542388	-0.830834	-0.748871
O	-3.666103	-0.288438	0.717823
C	2.319022	-1.641666	-2.083442
O	-4.139126	-2.147079	-0.847528
O	-4.019057	0.233547	-1.608465
O	1.047642	-2.090941	1.845738
C	0.376833	1.315620	1.836029
C	-0.419145	2.157725	0.938455
C	-1.810986	2.078733	1.065386
C	-2.650916	2.753425	0.190258
C	-2.110224	3.557074	-0.808466
C	-0.726391	3.675151	-0.922089
C	0.116719	2.981523	-0.061947
C	1.656222	0.957834	1.749885
O	2.505617	1.416663	0.772901
C	3.568536	0.639315	0.413120
C	4.518289	1.261528	-0.399202
C	5.622333	0.549813	-0.841479
C	5.797397	-0.781319	-0.468153
C	4.845827	-1.387852	0.341038
C	3.719491	-0.697113	0.781770
H	6.352712	1.038463	-1.476126
H	6.662473	-1.336890	-0.809272
H	2.960717	-1.216060	1.358248
H	4.958215	-2.428005	0.625313
H	4.364629	2.299382	-0.668683
H	2.092902	0.272878	2.465146
H	0.245574	-2.114515	2.392018
H	-2.228738	1.427916	1.824662
H	-0.299707	4.304884	-1.695393
H	1.189783	3.064239	-0.168680
H	-3.721968	2.611896	0.266289
H	-2.761378	4.074436	-1.503327
H	-0.168911	0.847207	2.649365
H	0.717763	-1.615519	1.074486
H	0.914168	0.706041	-2.060137
H	-1.494646	1.024826	-1.577359
H	-1.834933	-3.109200	-0.511240
H	0.566847	-3.447410	-1.060220
H	2.918494	-0.731009	-2.025945
H	2.800120	-2.402708	-1.467461
H	2.330134	-1.991059	-3.120670
H	-3.109145	-0.804350	1.414343
Cl	-1.953961	-1.470098	2.715046



$G^{298.15\ K}$ = -2047.541798 a.u.

Table S12. Optimised coordinates (Å) of the initial state of the hydrogenation/dehydration step in the presence of pTSA with Br^-. Colour code for spheres: H, white; C, small brown; O, red; S, yellow; Br, large brown.

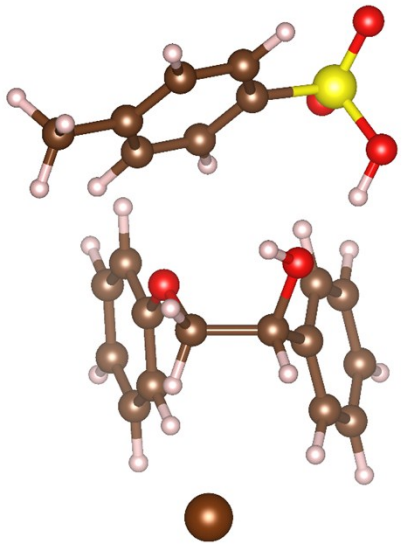
C	2.945393	0.201269	1.799868
C	2.057368	-0.691091	1.200057
C	2.491747	-1.971394	0.842733
C	3.803279	-2.346251	1.084873
C	4.701067	-1.461445	1.680513
C	4.260753	-0.192742	2.030669
O	0.751224	-0.432925	0.916908
C	0.195802	0.868189	1.046247
C	0.306818	1.654416	-0.262361
C	1.741033	1.851613	-0.687116
C	2.417573	0.907831	-1.457991
C	3.777543	1.054156	-1.705534
C	4.473896	2.145316	-1.196614
C	3.797980	3.105250	-0.450816
C	2.437975	2.958479	-0.203894
O	-0.441776	0.977929	-1.267110
O	0.143917	-1.465407	-1.813473
S	-0.784379	-2.677997	-1.405548
O	0.054431	-3.655117	-0.738532
C	-1.890243	-1.953791	-0.228127
C	-1.643121	-2.094187	1.128328
C	-2.468336	-1.423457	2.025087
C	-3.511426	-0.614230	1.575763
C	-3.754657	-0.521751	0.202491
C	-2.950778	-1.189041	-0.704250
C	-4.328391	0.223011	2.519571
O	-1.546122	-3.089532	-2.565334
Br	-2.949341	2.717430	-0.249153
H	4.128557	-3.338970	0.794901
H	5.728541	-1.755147	1.858360
H	2.647152	1.209521	2.048736
H	4.946653	0.517001	2.479568
H	1.788023	-2.638097	0.355792
H	0.636429	1.417958	1.882062
H	-0.868060	0.720072	1.247311
H	1.891815	0.041161	-1.839834
H	4.327748	3.969301	-0.065641
H	1.907403	3.705981	0.378550
H	4.297272	0.301440	-2.286685
H	5.536348	2.249709	-1.384549
H	-0.165905	2.625967	-0.089991
H	-1.359250	1.335210	-1.188034
H	-2.274250	-1.502215	3.089600
H	-0.804165	-2.690991	1.462394
H	-3.121266	-1.103711	-1.771070
H	-4.537948	0.134033	-0.155371
H	-4.169925	1.277388	2.270994
H	-5.394941	0.011735	2.410095
H	-4.044069	0.050069	3.558667
H	-0.180185	-0.540012	-1.543383



$G^{298.15\ K}$ = -4161.521273 a.u.

Table S13. Optimised coordinates (Å) of the intermediate state of the hydrogenation/dehydration step in the presence of pTSA with Br^-. Colour code for spheres: H, white; C, small brown; O, red; S, yellow; Br, large brown.

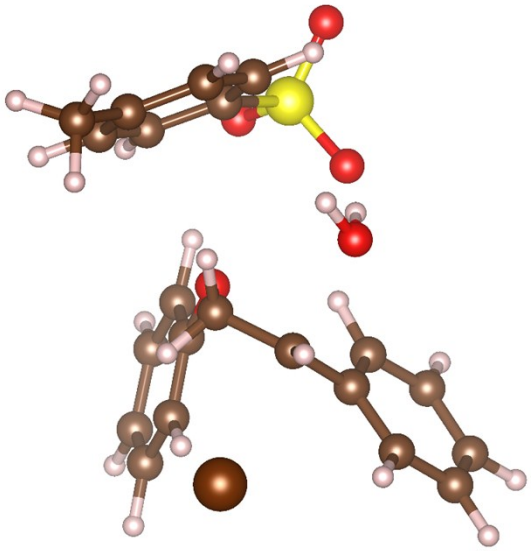
C	-3.468347	2.545040	1.202592
C	-2.483697	1.588516	1.459620
C	-2.542245	0.331390	0.873565
C	-3.591091	0.039418	0.011215
C	-4.584489	0.969928	-0.265661
C	-4.517973	2.217971	0.340339
S	-3.595193	-1.523951	-0.835295
O	-2.833122	-1.188150	-2.187228
C	-3.406992	3.896588	1.864353
O	-4.946853	-1.843706	-1.223931
O	-2.810341	-2.454076	-0.055033
O	-0.785462	0.342812	-1.541597
C	0.618923	0.506899	-1.253470
C	1.252416	-0.860954	-1.217416
C	0.574537	-1.942214	-0.656576
C	1.205575	-3.174684	-0.535711
C	2.515674	-3.332841	-0.974140
C	3.187966	-2.256888	-1.544958
C	2.560652	-1.022727	-1.672008
C	0.795542	1.277029	0.056875
O	0.452189	0.505879	1.202832
C	1.429369	-0.175112	1.874515
C	0.972474	-0.962830	2.932912
C	1.868911	-1.697537	3.692932
C	3.230627	-1.656190	3.406362
C	3.674265	-0.870239	2.350223
C	2.790483	-0.124517	1.575124
H	1.500222	-2.309776	4.508287
H	3.933253	-2.233699	3.994913
H	3.180146	0.466848	0.752242
H	4.729670	-0.829857	2.106527
H	-0.092502	-0.988857	3.133763
H	1.807202	1.682354	0.099734
H	0.105928	2.129842	0.061677
H	-0.441149	-1.829608	-0.295992
H	4.210381	-2.371350	-1.886331
H	3.094314	-0.164340	-2.071100
H	0.670998	-4.004750	-0.088720
H	3.011451	-4.291511	-0.868343
H	1.088738	1.112862	-2.034637
H	-1.234177	1.173968	-1.355875
H	-1.642707	1.820670	2.105013
H	-1.763281	-0.395061	1.065739
H	-5.392272	0.708030	-0.938539
H	-5.288102	2.954033	0.135700
H	-3.807802	3.841610	2.880300
H	-2.377283	4.250640	1.934576
H	-3.990155	4.634857	1.312381
H	-1.931609	-0.811954	-2.009865
Br	3.801287	2.433140	-1.424605



$G^{298.15\ K}$ = -4161.502960 a.u.

Table S14. Optimised coordinates (Å) of the transition state of the hydrogenation/dehydration step in the presence of pTSA with Br^-. Colour code for spheres: H, white; C, small brown; O, red; S, yellow; Br, large brown.

C	1.911850	-0.588217	2.051221
C	0.649577	-1.009302	1.641213
C	0.109095	-2.215909	2.089858
C	0.836510	-2.989456	2.981038
C	2.092891	-2.576277	3.423312
C	2.620450	-1.382486	2.950935
O	-0.142419	-0.322057	0.760819
C	0.228851	0.969029	0.358701
C	1.110045	1.020457	-0.870228
C	1.950045	-0.066650	-1.386143
C	1.538459	-1.405981	-1.323684
C	2.333201	-2.397475	-1.884360
C	3.532426	-2.074753	-2.506487
C	3.932898	-0.743322	-2.593266
C	3.143839	0.254862	-2.047725
O	-0.509627	0.577192	-2.206929
O	-1.634608	-1.682054	-1.545568
S	-2.887107	-1.786799	-0.740158
O	-2.708717	-2.571352	0.483809
C	-3.164546	-0.092522	-0.189884
C	-2.965841	0.266744	1.135770
C	-3.112221	1.596363	1.516067
C	-3.444295	2.581748	0.584434
C	-3.662569	2.197579	-0.740670
C	-3.534078	0.866656	-1.126795
C	-3.547205	4.026591	1.002340
O	-4.053147	-2.118326	-1.554788
Br	2.999538	2.676756	0.305843
H	0.417981	-3.926844	3.329618
H	2.656839	-3.186192	4.119167
H	2.363508	0.322008	1.670182
H	3.604093	-1.056165	3.268461
H	-0.862426	-2.517746	1.707556
H	0.726456	1.516467	1.159286
H	-0.702017	1.492132	0.129549
H	0.576546	-1.671261	-0.904283
H	4.864286	-0.483109	-3.081805
H	3.463549	1.288702	-2.074736
H	1.997459	-3.426073	-1.838689
H	4.151154	-2.856575	-2.932723
H	1.154307	1.967626	-1.379601
H	-1.242116	1.182236	-2.044446
H	-2.951001	1.878308	2.551990
H	-2.685065	-0.500419	1.846926
H	-3.733583	0.556810	-2.147801
H	-3.949454	2.946329	-1.472508
H	-2.553107	4.467331	1.118439
H	-4.089736	4.614402	0.260328
H	-4.063437	4.121932	1.959736
H	-0.902495	-0.320860	-1.999260

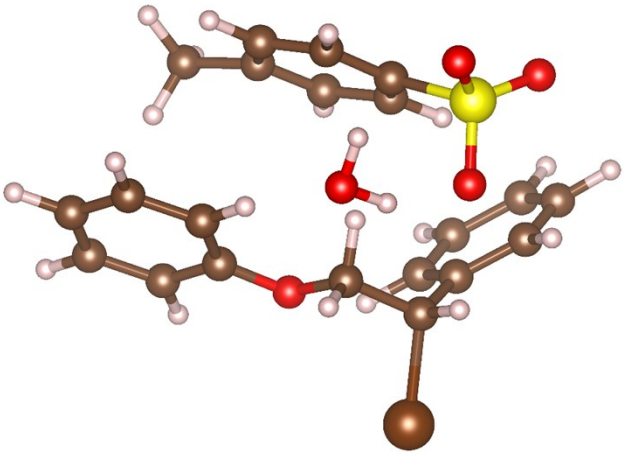


$G^{298.15\ K}$ = -4161.455695 a.u.

(-377.2325 cm^{-1})
d(C-O) = 2.146 Å
d(C-Br) = 2.774 Å

Table S15. Optimised coordinates (Å) of the intermediate state between the hydrogenation/dehydration and enol-ether formation steps in the presence of pTSA with Br^-. Colour code for spheres: H, white; C, small brown; O, red; S, yellow; Br, large brown.

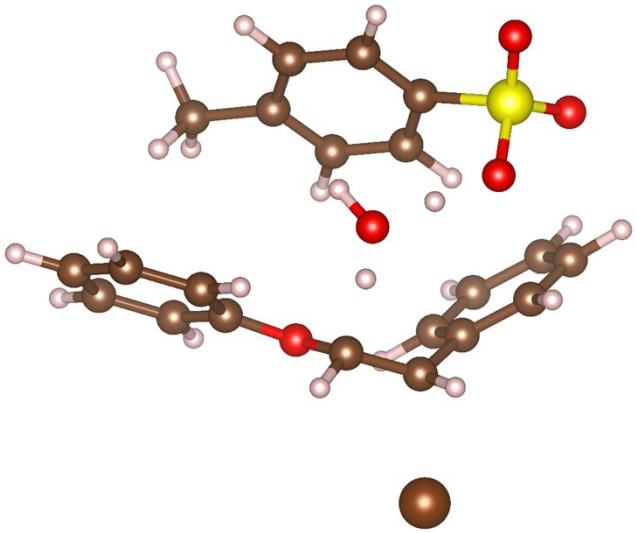
C	2.334671	1.538891	1.654664
C	1.026076	1.265363	2.054475
C	-0.059025	1.741055	1.328144
C	0.158825	2.483822	0.172817
C	1.454471	2.792858	-0.222525
C	2.531141	2.334310	0.526323
S	-1.225924	2.886099	-0.907080
O	-1.566619	1.578857	-1.543065
C	3.507864	0.938252	2.382112
O	-0.672460	3.837520	-1.883716
O	-2.294296	3.382745	-0.040487
O	0.744057	1.402800	-3.096560
C	-1.539650	-1.269343	-0.739574
C	-2.072684	-0.882225	0.611430
C	-3.047269	0.112660	0.681003
C	-3.508448	0.558549	1.915635
C	-3.002905	0.009405	3.087819
C	-2.036677	-0.993097	3.021778
C	-1.574847	-1.440560	1.790881
C	-0.069387	-0.985795	-0.969592
O	0.734188	-1.779458	-0.112396
C	2.074477	-1.603909	-0.202091
C	2.854874	-2.468242	0.574187
C	4.237096	-2.383701	0.536232
C	4.862413	-1.429935	-0.266250
C	4.079505	-0.570248	-1.026339
C	2.687892	-0.644410	-1.010884
H	4.829868	-3.063763	1.137837
H	5.943124	-1.360043	-0.295308
H	2.109633	0.045504	-1.618419
H	4.548839	0.179973	-1.652864
H	2.346136	-3.204018	1.185193
H	0.189722	-1.185813	-2.015098
H	0.086114	0.075646	-0.765858
H	-3.387187	0.589907	-0.229884
H	-1.638831	-1.423997	3.933849
H	-0.820727	-2.215247	1.731634
H	-4.233417	1.362430	1.951248
H	-3.351393	0.365522	4.050731
H	-2.088420	-0.733958	-1.509021
H	0.738419	2.367017	-3.073141
H	0.848422	0.658189	2.936768
H	-1.071965	1.535065	1.652158
H	1.601147	3.397473	-1.108067
H	3.544007	2.564720	0.209932
H	3.791052	-0.008054	1.910520
H	4.376174	1.599882	2.348583
H	3.265510	0.736551	3.427419
H	-0.143965	1.228604	-2.741864
Br	-1.909056	-3.191174	-1.112707



$G^{298.15\ K}$ = -4161.512085 a.u.

Table S16. Optimised coordinates (Å) of the transition state of the enol-ether formation step in the presence of pTSA with Br^-. Colour code for spheres: H, white; C, small brown; O, red; S, yellow; Br, large brown.

C	-1.352758	2.685847	1.134973
C	-1.072847	1.365985	1.495124
C	-1.849097	0.315297	1.019862
C	-2.909477	0.585873	0.163857
C	-3.217649	1.891479	-0.201543
C	-2.443426	2.934079	0.295044
S	-3.680944	-0.766368	-0.720176
O	-2.607466	-1.060742	-1.774907
C	-0.499012	3.825051	1.622519
O	-4.889551	-0.236096	-1.333151
O	-3.818634	-1.891802	0.188774
O	-0.824922	0.532467	-2.022551
C	1.373933	-1.559270	-0.870264
C	0.639481	-2.041168	0.329787
C	-0.513021	-2.804615	0.146964
C	-1.259476	-3.235791	1.241049
C	-0.851074	-2.910848	2.527417
C	0.303036	-2.148752	2.717184
C	1.044869	-1.715133	1.628593
C	1.578931	-0.192840	-1.114041
O	1.973645	0.571397	0.013723
C	2.107147	1.899115	-0.131930
C	2.742482	2.574227	0.920370
C	2.965618	3.937824	0.845191
C	2.553182	4.665491	-0.271990
C	1.907735	3.999073	-1.305241
C	1.676986	2.625620	-1.248752
H	3.470878	4.439241	1.663123
H	2.734166	5.731568	-0.332403
H	1.184099	2.126187	-2.072203
H	1.576839	4.547902	-2.179949
H	3.074180	1.988645	1.769288
H	2.186234	0.041999	-1.989012
H	0.144593	0.163186	-1.595438
H	-0.857349	-3.030977	-0.855870
H	0.627856	-1.899419	3.721338
H	1.958100	-1.150959	1.761831
H	-2.180473	-3.778593	1.074829
H	-1.433787	-3.238136	3.380776
H	1.145592	-2.110229	-1.776088
H	-1.066719	1.307909	-1.497779
H	-0.224213	1.148483	2.135617
H	-1.626378	-0.707692	1.295957
H	-4.048811	2.066957	-0.874449
H	-2.677957	3.957352	0.018947
H	0.159882	3.506100	2.430363
H	0.132863	4.201988	0.813908
H	-1.119608	4.649870	1.981105
H	-1.705573	-0.250381	-1.920417
Br	3.463506	-2.712862	-0.619165

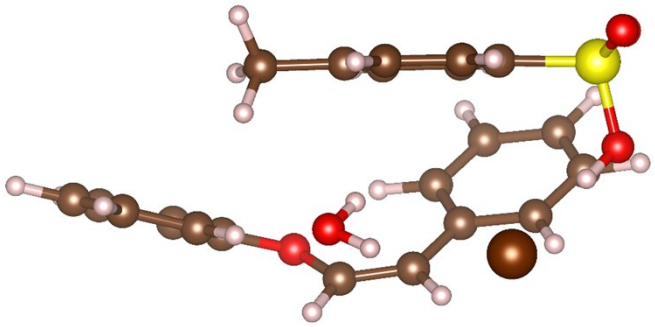


$G^{298.15\ K}$ = -4161.456868 a.u.

(-989.9281 cm^{-1})
d(C-H) = 1.554 Å
d(C-Br) = 2.400 Å

Table S17. Optimised coordinates (Å) of the final state of the enol-ether formation step in the presence of pTSA with Br^-. Colour code for spheres: H, white; C, small brown; O, red; S, yellow; Br, large brown.

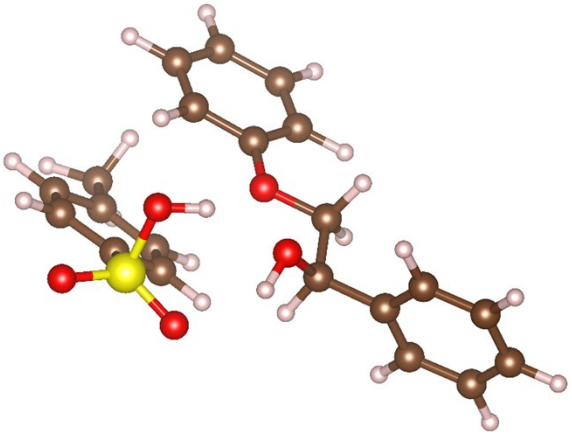
C	-0.562763	-1.284305	2.013527
C	-0.280579	0.073264	1.869442
C	1.014735	0.511029	1.602790
C	2.021391	-0.431974	1.464563
C	1.765557	-1.794605	1.585139
C	0.475765	-2.209365	1.864641
S	3.672919	0.086936	1.064253
O	3.664619	0.194344	-0.512836
C	-1.958434	-1.777189	2.288016
O	4.576333	-0.965875	1.478584
O	3.880280	1.435953	1.545624
O	-1.190834	-2.390233	-0.872857
C	-0.792479	0.859750	-1.796108
C	-0.072675	1.964409	-1.155125
C	1.316825	1.999512	-1.328685
C	2.095808	2.958338	-0.695682
C	1.493977	3.918024	0.111652
C	0.110530	3.908157	0.276561
C	-0.671271	2.942981	-0.347607
C	-2.068864	0.493767	-1.690473
O	-3.003745	1.191089	-0.964635
C	-4.051734	0.498449	-0.427412
C	-5.135209	1.268299	-0.002405
C	-6.230853	0.652612	0.581668
C	-6.259223	-0.731596	0.741075
C	-5.174277	-1.486248	0.314491
C	-4.060310	-0.886373	-0.268544
H	-7.068314	1.256282	0.912000
H	-7.116012	-1.212253	1.197202
H	-3.210124	-1.491894	-0.566247
H	-5.175689	-2.562525	0.443901
H	-5.091336	2.341427	-0.142263
H	-2.441578	-0.387708	-2.198314
H	-0.419162	-2.677533	-1.384197
H	1.788125	1.227011	-1.926192
H	-0.364060	4.653366	0.905788
H	-1.742944	2.938319	-0.205000
H	3.173242	2.918695	-0.795298
H	2.100881	4.654778	0.624659
H	-0.183612	0.201954	-2.410217
H	-0.834422	-1.585396	-0.475924
H	-1.079865	0.802629	1.954703
H	1.238880	1.566816	1.502397
H	2.569946	-2.504876	1.444133
H	0.254921	-3.268582	1.933227
H	-2.680448	-0.959600	2.292890
H	-2.249913	-2.490032	1.512023
H	-2.004408	-2.287299	3.254100
H	3.191968	-0.572496	-0.970191
Br	1.923100	-1.895882	-2.038041



$G^{298.15\ K}$ = -4161.520047 a.u.

Table S18. Optimised coordinates (Å) of the initial state of the hydrogenation/dehydration step in the presence of pTSA only. Colour code for spheres: H, white; C, small brown; O, red; S, yellow.

C	-0.816390	-1.584729	-0.909643
C	-0.716947	-2.901859	-0.470008
C	-1.828462	-3.738141	-0.571699
C	-3.021663	-3.276398	-1.107348
C	-3.098812	-1.961170	-1.565765
C	-2.003254	-1.119905	-1.478066
H	0.203524	-3.289396	-0.055595
H	-1.747574	-4.762770	-0.228584
H	-3.878590	-3.934329	-1.182627
H	-4.020008	-1.588108	-1.998271
H	-2.040596	-0.096058	-1.829506
O	0.179582	-0.658096	-0.792063
C	1.474976	-1.070220	-0.400053
H	1.953874	-1.630353	-1.211699
H	1.443083	-1.694822	0.498263
C	2.261054	0.191185	-0.074943
H	1.806356	0.665261	0.801273
C	3.700765	-0.164428	0.226026
C	4.081274	-0.503861	1.522689
C	5.390474	-0.884056	1.794768
C	6.329788	-0.921280	0.769829
C	5.955388	-0.577097	-0.525016
C	4.644842	-0.202398	-0.797922
H	3.351904	-0.457420	2.325743
H	5.679541	-1.140440	2.806903
H	7.352166	-1.210483	0.981170
H	6.686656	-0.598413	-1.324222
H	4.344231	0.079237	-1.800170
O	2.131513	1.059704	-1.188983
H	2.274759	1.958238	-0.867504
H	0.259119	1.350941	-1.570929
O	-0.464811	2.013530	-1.649797
S	-0.737928	2.697087	-0.234610
O	0.505553	2.671246	0.515941
O	-1.408381	3.935962	-0.519719
C	-1.888023	1.585003	0.526091
C	-3.224739	1.663282	0.154379
C	-4.112953	0.720129	0.651227
C	-3.679769	-0.296669	1.504473
C	-2.338622	-0.323731	1.891484
C	-1.435906	0.610983	1.405872
H	-3.553695	2.453623	-0.509876
H	-5.157840	0.767789	0.365311
C	-4.626031	-1.368615	1.971760
H	-1.995831	-1.097813	2.569346
H	-0.393870	0.592036	1.698736
H	-4.498639	-2.262590	1.353961
H	-4.427031	-1.647249	3.007745
H	-5.664294	-1.045191	1.892439

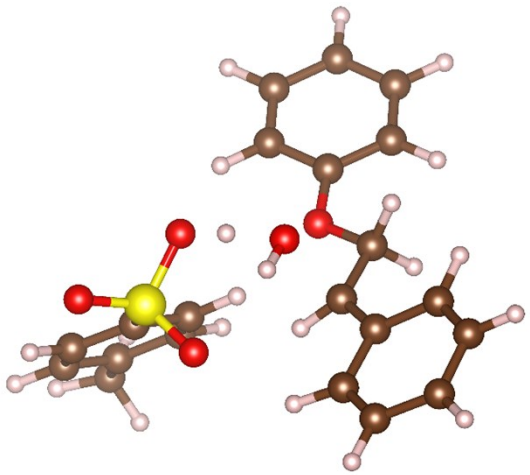


$G^{298.15\ K}$ = -1587.218374 a.u.

(singlet)

Table S19. Optimised coordinates (Å) of the transition state of the hydrogenation/dehydration step in the presence of pTSA only. Colour code for spheres: H, white; C, small brown; O, red; S, yellow.

C	-0.325048	2.811121	0.081975
C	0.216982	4.028706	-0.317225
C	-0.504734	5.199594	-0.087100
C	-1.746025	5.159771	0.529348
C	-2.273109	3.931665	0.929396
C	-1.569584	2.759273	0.712472
H	1.182778	4.078331	-0.802846
H	-0.082701	6.148036	-0.397536
H	-2.298168	6.074398	0.704466
H	-3.236419	3.889473	1.423358
H	-1.940568	1.793440	1.036210
O	0.279424	1.605356	-0.113565
C	1.633968	1.571037	-0.509735
H	2.242698	2.173958	0.172948
H	1.748562	1.955876	-1.532568
C	2.024420	0.128227	-0.443382
H	1.226646	-0.576731	-0.653507
C	3.320486	-0.336041	-0.614704
C	3.550151	-1.795445	-0.707436
C	4.794565	-2.279664	-0.890596
C	5.926796	-1.396010	-0.957046
C	5.738907	0.015923	-0.761738
C	4.509282	0.537193	-0.572984
H	2.681448	-2.440422	-0.623451
H	4.955594	-3.347447	-0.975508
H	6.919463	-1.793121	-1.114283
H	6.609142	0.661336	-0.751331
H	4.375678	1.597361	-0.401426
O	1.953614	-0.030779	1.469100
H	2.306216	-0.923166	1.604117
H	0.534611	-0.263460	1.670633
O	-0.457339	-0.568806	1.841423
S	-0.703133	-2.015204	1.297888
O	0.453862	-2.385687	0.483676
O	-1.100898	-2.905603	2.361140
C	-2.102679	-1.763000	0.234812
C	-3.175049	-2.635945	0.319071
C	-4.253227	-2.458537	-0.542517
C	-4.266729	-1.421537	-1.472406
C	-3.172317	-0.551179	-1.525486
C	-2.086398	-0.715389	-0.681297
H	-3.163439	-3.427848	1.057784
H	-5.099468	-3.133768	-0.483105
C	-5.429424	-1.231163	-2.410351
H	-3.178802	0.271272	-2.232988
H	-1.251318	-0.023495	-0.706909
H	-6.260730	-1.885870	-2.148576
H	-5.784211	-0.198802	-2.385591
H	-5.133581	-1.453520	-3.438723

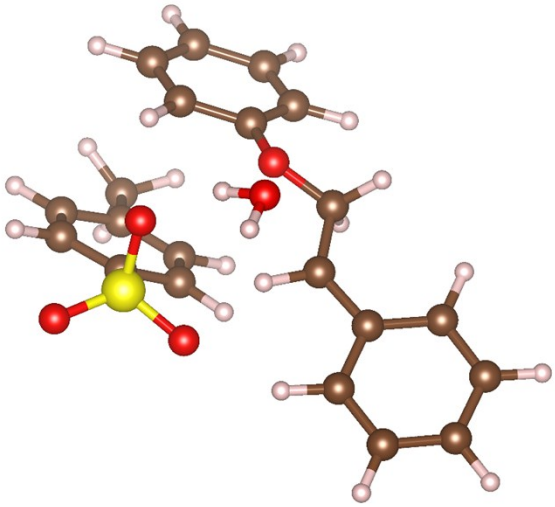


$G^{298.15\ K}$ = -1587.055296 a.u.

(triplet, -655.8568 cm^{-1})
d(C-O) = 1.920 Å
d(O-H) = 1.452 Å

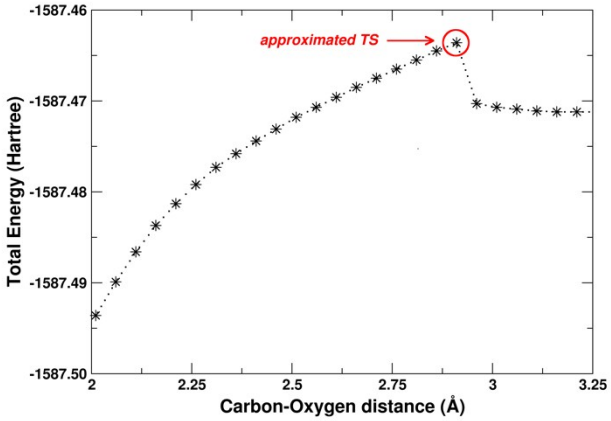
Table S20. Optimised coordinates (Å) of the approximated transition state of the hydrogenation/dehydration step in the presence of pTSA only. Colour code for spheres: H, white; C, small brown; O, red; S, yellow.

C	1.314910	-1.591988	1.127107
C	1.619514	-2.825407	0.563102
C	2.957626	-3.159097	0.352997
C	3.968351	-2.280598	0.713510
C	3.639924	-1.055395	1.294897
C	2.317336	-0.702713	1.503675
H	0.843296	-3.535561	0.304237
H	3.200866	-4.119694	-0.085519
H	5.005170	-2.546167	0.547780
H	4.422406	-0.358226	1.570517
H	2.018482	0.256519	1.913313
O	0.036133	-1.152298	1.357987
C	-1.016601	-1.713907	0.643878
H	-1.493542	-2.542146	1.184527
H	-0.680643	-2.110461	-0.334105
C	-1.963937	-0.642978	0.298608
H	-1.587876	0.381672	0.385870
C	-3.256904	-0.781061	-0.218543
C	-3.881425	0.419372	-0.643505
C	-5.152461	0.366791	-1.190379
C	-5.796712	-0.861204	-1.306458
C	-5.191779	-2.056803	-0.885929
C	-3.929360	-2.023650	-0.343980
H	-3.324570	1.349192	-0.541900
H	-5.640995	1.272957	-1.523568
H	-6.794151	-0.899510	-1.729938
H	-5.724634	-2.993577	-0.984075
H	-3.455085	-2.935904	-0.001656
O	-1.840860	0.463569	2.987664
H	-2.390653	1.251116	3.015134
H	-0.995382	0.823770	2.660190
O	0.125181	1.943568	1.711740
S	-0.052567	2.538325	0.366377
O	-1.360194	2.131946	-0.223878
O	0.244981	3.957382	0.280362
C	1.177445	1.682048	-0.620966
C	2.508516	2.066257	-0.501809
C	3.495758	1.311278	-1.118375
C	3.178547	0.161154	-1.845330
C	1.835969	-0.186205	-1.983321
C	0.837419	0.572591	-1.381302
H	2.753574	2.951669	0.073589
H	4.535850	1.605174	-1.018605
C	4.259192	-0.670187	-2.485462
H	1.572298	-1.063870	-2.565661
H	-0.210344	0.329765	-1.523606
H	3.967724	-1.721249	-2.525628
H	4.458375	-0.333170	-3.506700
H	5.191014	-0.598638	-1.921741



$G^{298.15\ K}$ = -1587.131334 a.u.

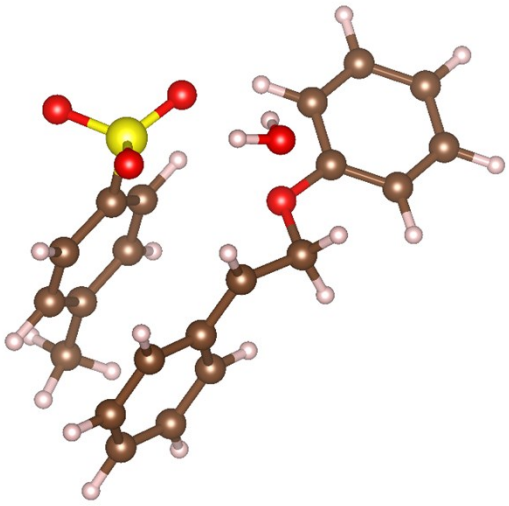
(singlet, -52.3477 cm^{-1})
d(C-O) = 2.910 Å



The Figure on the left shows the variation of the total energy upon climbing the eigenvector with a negative eigenvalue corresponding to the C^{α}-O bond cleavage. The point marked with the red circle was used as an approximate to the transition state. We used this procedure since we were unable to find a singlet TS structure using the usual approaches available in the Gaussian code.

Table S21. Optimised coordinates (Å) of the intermediate state between the hydrogenation/dehydration and enol-ether formation steps in the presence of pTSA only. Colour code for spheres: H, white; C, small brown; O, red; S, yellow.

C	-2.845746	-0.892289	-0.009595
C	-3.540123	-1.994939	-0.504822
C	-4.817951	-2.271468	-0.022931
C	-5.407919	-1.464243	0.938593
C	-4.712288	-0.354530	1.414213
C	-3.442209	-0.061827	0.943496
H	-3.104564	-2.635447	-1.259426
H	-5.352418	-3.129478	-0.413392
H	-6.402475	-1.685937	1.304449
H	-5.169294	0.299571	2.147306
H	-2.908939	0.825405	1.262295
O	-1.578135	-0.557757	-0.387969
C	-1.080934	-1.132377	-1.603080
H	-1.803157	-0.937349	-2.400258
H	-0.955472	-2.212869	-1.476767
C	0.210490	-0.471614	-1.936937
H	0.150528	0.449009	-2.501449
C	1.487836	-0.980540	-1.587436
C	2.652213	-0.349559	-2.095676
C	3.913919	-0.837849	-1.810688
C	4.066926	-1.960958	-0.994989
C	2.935550	-2.585183	-0.465849
C	1.667151	-2.107874	-0.750149
H	2.529897	0.523560	-2.728040
H	4.786727	-0.348728	-2.227629
H	5.055023	-2.351742	-0.782792
H	3.049743	-3.457634	0.168281
H	0.801780	-2.593854	-0.314924
O	-2.078537	1.560168	-2.507838
H	-1.418864	2.257417	-2.581140
H	-2.270067	1.558449	-1.562104
O	-1.430399	2.344722	0.262740
S	-0.012024	2.559104	0.055611
O	0.443947	2.784303	-1.303360
O	0.598669	3.541848	1.065214
C	0.934848	1.304074	0.846784
C	2.328452	1.291744	0.630077
C	3.092646	0.347598	1.276487
C	2.495415	-0.577069	2.144521
C	1.102795	-0.525824	2.369196
C	0.321501	0.423820	1.757700
H	2.763500	2.009624	-0.054315
H	4.159980	0.300705	1.099907
C	3.326066	-1.604268	2.849892
H	0.648076	-1.252125	3.033244
H	-0.748953	0.473190	1.906247
H	2.804394	-2.562072	2.893855
H	4.286108	-1.744935	2.353598
H	3.514642	-1.285654	3.880158

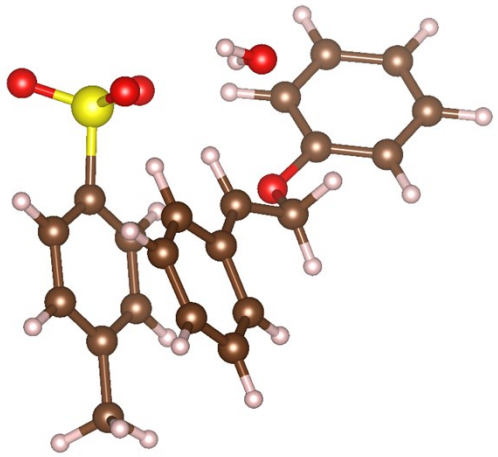


$G^{298.15\ K}$ = -1587.087855 a.u.

(triplet)

Table S22. Optimised coordinates (Å) of the intermediate state between the hydrogenation/dehydration and enol-ether formation steps in the presence of pTSA only. Colour code for spheres: H, white; C, small brown; O, red; S, yellow.

C	-3.121928	-0.938642	0.432071
C	-3.766702	-2.122141	0.097355
C	-5.151838	-2.117024	-0.045079
C	-5.876145	-0.949214	0.153426
C	-5.210511	0.226335	0.493443
C	-3.830173	0.241253	0.632936
H	-3.207705	-3.040454	-0.040816
H	-5.661928	-3.035765	-0.308346
H	-6.952753	-0.951857	0.038804
H	-5.767662	1.143949	0.637440
H	-3.275925	1.145090	0.865201
O	-1.761656	-0.858704	0.630010
C	-0.910941	-1.657858	-0.140133
H	-1.405286	-1.961266	-1.082505
H	-0.600741	-2.558405	0.398213
C	0.201230	-0.827658	-0.648146
H	-0.110823	0.148315	-1.004567
C	1.505682	-1.249411	-0.944494
C	2.283268	-0.386133	-1.756310
C	3.556311	-0.774440	-2.146037
C	4.070188	-1.986781	-1.700686
C	3.331474	-2.829666	-0.856231
C	2.058640	-2.469278	-0.478473
H	1.846889	0.565661	-2.055634
H	4.149290	-0.130528	-2.782473
H	5.068828	-2.284827	-1.999894
H	3.765825	-3.756732	-0.504568
H	1.488027	-3.104435	0.187959
O	-1.944281	0.534712	-2.104326
H	-1.291814	1.135186	-2.490650
H	-2.191563	1.037089	-1.313183
O	-1.297045	2.292889	0.108368
S	0.079075	2.654069	-0.280296
O	0.411491	2.125574	-1.635236
O	0.488435	4.027538	-0.054807
C	1.127547	1.617411	0.764694
C	2.504217	1.642178	0.571892
C	3.300177	0.697359	1.205026
C	2.747866	-0.270357	2.059218
C	1.375659	-0.248651	2.276616
C	0.559538	0.684081	1.626609
H	2.936781	2.383610	-0.091216
H	4.373210	0.701621	1.037693
C	3.639369	-1.280375	2.732847
H	0.925293	-0.969255	2.952408
H	-0.511363	0.700630	1.781688
H	3.054503	-2.057634	3.226368
H	4.305037	-1.756655	2.008473
H	4.265572	-0.800450	3.489001

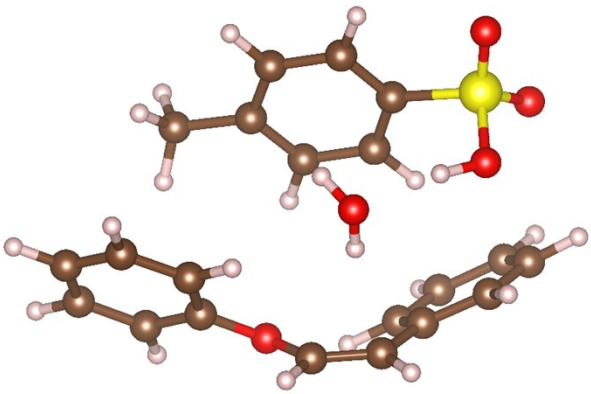


$G^{298.15\ K}$ = -1587.138532 a.u.

(singlet)

Table S23. Optimised coordinates (Å) of the final state of the enol-ether formation step in the presence of pTSA only. Colour code for spheres: H, white; C, small brown; O, red; S, yellow.

C	3.133163	-0.314801	1.171585
C	3.171489	0.815105	0.359588
C	4.220535	1.021640	-0.531035
C	5.246051	0.089022	-0.602813
C	5.229415	-1.041441	0.210912
C	4.174330	-1.235974	1.093683
O	2.171245	1.758634	0.361432
C	1.508175	1.971599	1.535566
C	0.232707	2.364597	1.588894
C	-0.701268	2.556920	0.469102
C	-2.068591	2.378326	0.709949
C	-2.994604	2.490844	-0.318802
C	-2.567410	2.817391	-1.601879
C	-1.212458	3.028043	-1.847392
C	-0.281518	2.895614	-0.824100
O	-2.896882	-0.532920	1.555891
S	-3.282144	-1.376101	0.250804
O	-4.078884	-0.489744	-0.557577
C	-1.678244	-1.610518	-0.479378
C	-1.017434	-0.514687	-1.023131
C	0.305627	-0.659167	-1.419160
C	0.962426	-1.890011	-1.302990
C	0.264153	-2.976093	-0.766842
C	-1.055044	-2.844485	-0.345622
C	2.372650	-2.058696	-1.797947
O	-3.781089	-2.670602	0.645634
O	-0.235562	-0.824831	2.106433
H	6.065936	0.250416	-1.292101
H	6.034351	-1.763404	0.156506
H	2.306207	-0.478081	1.853051
H	4.150553	-2.114133	1.727846
H	4.216106	1.914182	-1.144135
H	2.107038	1.835031	2.431348
H	-0.006522	0.064750	1.800672
H	-2.407046	2.108310	1.703803
H	-0.878395	3.295456	-2.843055
H	0.769241	3.061342	-1.019798
H	-4.040653	2.293167	-0.124257
H	-3.286689	2.900444	-2.407310
H	-0.161331	2.531060	2.586507
H	0.106791	-1.409109	1.418332
H	0.834813	0.197669	-1.823720
H	-1.531824	0.433154	-1.126047
H	-1.599489	-3.674531	0.088256
H	0.760331	-3.936418	-0.678720
H	2.934685	-1.127336	-1.720525
H	2.902127	-2.826751	-1.232905
H	2.362095	-2.361263	-2.848961
H	-2.019549	-0.800024	1.918714



$G^{298.15\ K}$ = -1587.206714 a.u.

(singlet)