Molecular design and experimental study on synergistic catalysts for synthesis of cyclocarbonate from styreneoxide and CO_2

Zhiqiang Zhang,[a] Haoyang Xu,[a] Dongjie Guo,[a] Junli Chen,[a] Junping Du,[a] Miaomiao Hou,[a] Yanda Zhang,[a] Liancai Xu,*[a] Hailong Wang*[b] and Guoqing Wang*[a]

[a] Department of Material and Chemical Engineering, Zhengzhou University of Light Industry, Henan, Zhengzhou, China, PRC.
[b] College of Biological, Chemical Sciences and Engineering, Jiaxing University, Zhejiang, Jiaxing, China, PRC.

Electronic Supplementary Information

Optimized geometries of various species in the reaction catalyzed by Ca.

Figure S1. Relative Gibbs free energy profile of the target reaction catalyzed by **Cb** in solvent of toluene.

Optimized geometries of various species in the reaction catalyzed by Cb.

Figure S2. Relative Gibbs free energy profile of the target reaction catalyzed by **Cc** in solvent of toluene.

Optimized geometries of various species in the reaction catalyzed by Cc.

Figure S3. Relative Gibbs free energy profile of the target reaction catalyzed by **Cd** in solvent of toluene.

Optimized geometries of various species in the reaction catalyzed by Cd.

Figure S4. Relative Gibbs free energy profile of the target reaction catalyzed by **Ce** in solvent of toluene.

Optimized geometries of various species in the reaction catalyzed by Ce.

Figure S5. Relative Gibbs free energy profile of the target reaction catalyzed by **Cf** in

solvent of toluene.

Optimized geometries of various species in the reaction catalyzed by Cf.

Figure S6. Relative Gibbs free energy profile of the target reaction catalyzed by **Ch** in solvent of toluene.

Optimized geometries of various species in the reaction catalyzed by Ch.

Figure S7. Relative Gibbs free energy profile of the target reaction catalyzed by **Cg** in solvent of toluene.

Optimized geometries of various species in the reaction catalyzed by Cg.

Figure S8. Relative Gibbs free energy profile of the target reaction catalyzed by **Cj** in solvent of toluene.

Optimized geometries of various species in the target reaction catalyzed by Cj.

Optimized geometries of various species in the side reaction denoted as S1 in Chart 3.

Optimized geometries of various species in the side reaction denoted as S2 in Chart 3.

Figure S9. Relative Gibbs free energy profile of the side reaction (denoted as S3 in Chart 4) in solvent of toluene.

Optimized geometries of various species in the side reaction denoted as S3 in Chart 4.

Figure S10. Relative Gibbs free energy profile of the side reaction (denoted as S4 in Chart 4) in solvent of toluene.

Optimized geometries of various species in the side reaction denoted as S4 in Chart 4.

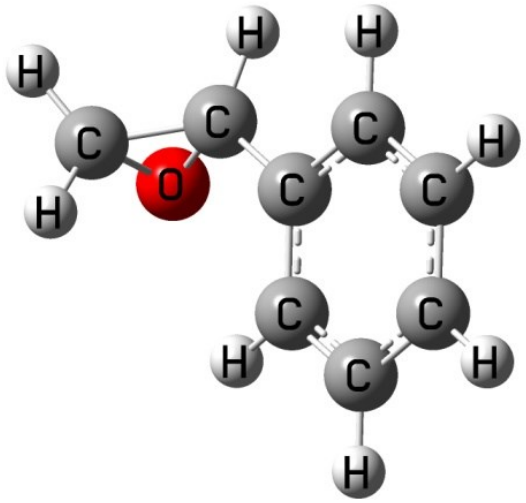
Figure S11. Relative Gibbs free energy profile of the side reaction (denoted as S5 in Chart 4) in solvent of toluene.

Optimized geometries of various species in the side reaction denoted as S5 in Chart 4.

Figure S12. Relative Gibbs free energy profile of the side reaction (denoted as S6 in Chart 4) in solvent of toluene.

Optimized geometries of various species in the side reaction denoted as S6 in Chart 4.

Optimized geometries of various species in the reaction catalyzed by Ca.

1	
HF=-384.67310770 C -0.149483 0.261608 -0.106510 C -1.596717 0.582135 -0.186134 O -2.475866 -0.446676 -0.607768 C -2.575247 -0.010274 0.733088 H -3.489634 0.531936 0.984330 H -2.222872 -0.723777 1.483150 H -1.831482 1.567722 -0.601527 C 0.781469 1.299700 -0.048656 C 2.141485 1.023430 0.055714 C 2.582950 -0.296674 0.093233 C 1.657679 -1.336570 0.023138 C 0.297873 -1.060552 -0.076138 H 0.436178 2.334023 -0.087282 H 2.859011 1.841362 0.101475 H 3.646934 -0.515536 0.169042 H 1.998235 -2.370932 0.039841 H -0.429503 -1.868210 -0.153302	

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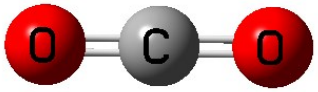
HF=-188.5626515 O 0.000000000 0.000000000 1.164177000 C 0.000000000 0.000000000 0.000000000 O 0.000000000 0.000000000 -1.164177000	

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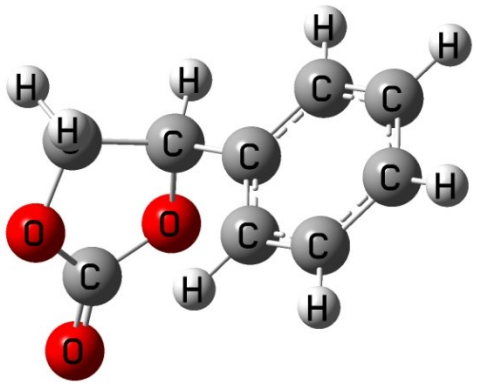
HF=-573.25354789 C 2.413132 0.366383 -0.330387 O 2.328352 0.075285 0.987751 C 1.392028 -0.974703 1.194737 C 0.607389 -1.033548 -0.125695 O 1.475589 -0.319230 -1.018763 C -0.757701 -0.409700 -0.079772 O 3.195955 1.126189 -0.810754 H 0.534564 -2.060839 -0.502745 H 1.940861 -1.901998 1.401102 H 0.763780 -0.721133 2.054449 C -1.881211 -1.169286 -0.398585 C -3.155488 -0.609623 -0.333922 C -3.309503 0.719793 0.044538 C -2.188716 1.487516 0.359615 C -0.919297 0.926305 0.299755 H -1.758148 -2.208724 -0.705823 H -4.026356 -1.211605 -0.587746 H -4.303095 1.162251 0.093114 H -2.305525 2.529617 0.652048 H -0.049046 1.535661 0.548017	

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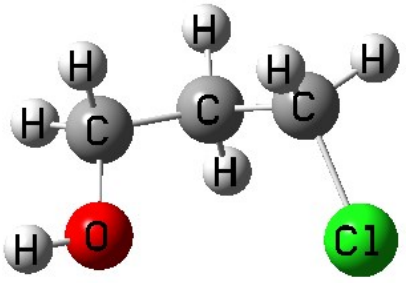
0 1 C -1.7814970 0.1747410 0.0981420 C -0.6394480 1.0274180 -0.4084470 C 0.6382220 0.9238720 0.4038980 H -0.4310320 0.7910150 -1.4613600 H -0.9724210 2.0769840 -0.3776790 O -1.4221420 -1.185186 -0.0038690 H -2.6866550 0.3949930 -0.4942450 H -1.9999900 0.4459340 1.14842700 Cl 1.6838340 0.462415000 -0.0839860 H 0.4244720 0.793679000 1.4716580 H 1.2574350 1.8174030 0.2795740 H -2.1435210 -1.7336550 0.330778000	

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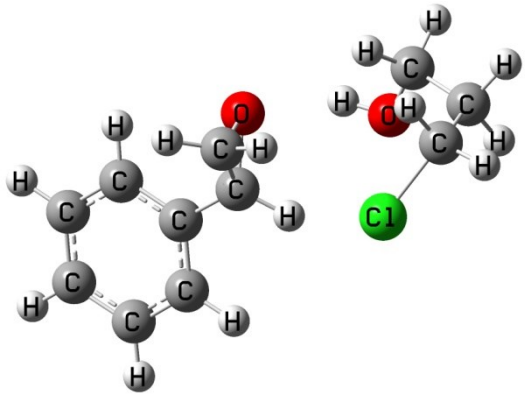
HF=-1038.55591493 C -4.357159 0.603422 0.385476 C -4.265878 -0.477161 -0.668034 C -3.157437 -1.501548 -0.475340 O -2.004343 -1.071773 -1.157595 Cl -2.902259 1.679420 0.460738 O 0.342463 -1.448758 0.322134 C 0.839946 -0.139573 0.029371 C 2.311543 0.019881 -0.055884 C 0.148553 -0.423278 1.289134 H -4.153887 -0.032295 -1.666858 H -5.241057 -0.990280 -0.655058 H -3.491517 -2.479771 -0.862917 H -2.955456 -1.638288 0.604901 H -4.464733 0.174395 1.388828 H -5.206602 1.267873 0.198703 H -1.219056 -1.501812 -0.770616 H -0.884637 -0.089200 1.412565 H 0.736258 -0.541986 2.202354 H 0.257396 0.385010 -0.735220 C 2.840953 1.104155 -0.756823 C 4.218022 1.294104 -0.827090 C 5.077775 0.393820 -0.203633 C 4.553707 -0.697949 0.486611 C 3.177881 -0.886135 0.559855 H 2.165998 1.803550 -1.251953 H 4.619995 2.143945 -1.376597 H 6.155562 0.537460 -0.261757 H 5.223047 -1.411651 0.964862 H 2.764693 -1.751268 1.078055	

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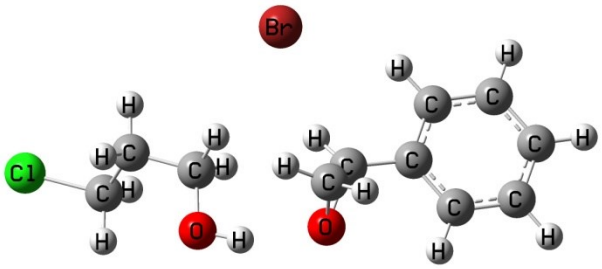
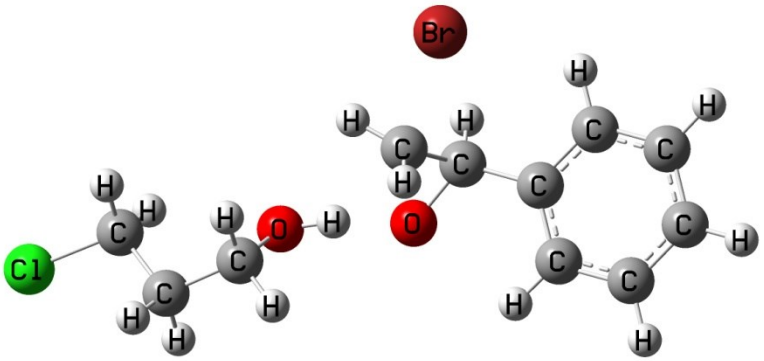
HF=-3612.68030900 C 3.645764 -1.692193 -0.166437 C 2.769105 -0.610642 -0.073020 C 3.157042 0.643232 -0.557077 C 4.420553 0.804063 -1.116791 C 5.300268 -0.274732 -1.203088 C 4.908511 -1.525359 -0.729333 C 1.424530 -0.742168 0.535222 C 1.240674 -1.210673 1.906184 O 0.943567 -2.069905 0.807533 Br 0.013900 2.426944 0.394804 O -1.954127 -1.980164 0.574315 C -1.998350 -0.607982 0.213191 C -3.438356 -0.143960 0.212703 C -4.239873 -0.895424 -0.821470 Cl -5.978760 -0.350305 -0.851147 H -3.877655 -0.300587 1.208752 H -3.452812 0.935125 0.004981 H -1.422392 0.028458 0.904243 H -1.555880 -0.448971 -0.788393 H -4.261561 -1.969496 -0.618283 H -3.854315 -0.726959 -1.833377 H -1.012914 -2.232526 0.613056 H 0.377350 -0.862949 2.478773 H 2.116973 -1.510530 2.487784 H 0.675660 -0.036251 0.161791 H 2.450355 1.475706 -0.476866 H 4.720224 1.782904 -1.490808 H 6.288192 -0.141930 -1.645064 H 5.587204 -2.375490 -0.802976 H 3.319252 -2.668779 0.192457	

TS6a-7a



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Br -2.153652 2.612460 -0.202489
O 2.582348 -0.806839 0.758597
C 2.979385 -0.576752 -0.563932
C 4.479719 -0.788116 -0.670130
C 5.210366 0.132108 0.276655
Cl 7.015286 -0.046116 0.110123
H 4.723181 -1.832482 -0.426312
H 4.809725 -0.599072 -1.702681
H 2.461310 -1.255404 -1.263304
H 2.733169 0.456478 -0.884916
H 4.969897 -0.089202 1.318994
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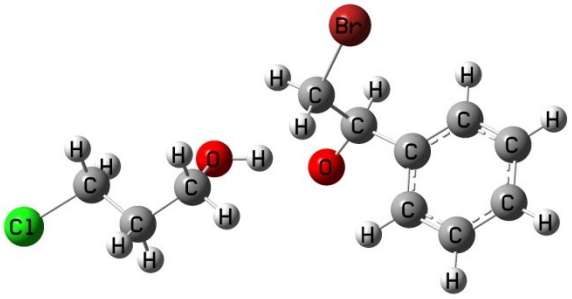
HF=-3612.66969741 C -2.120774 -2.035479 -0.362773 C -2.340607 -0.912201 0.437033 C -3.656323 -0.556483 0.737192 C -4.730298 -1.283108 0.226791 C -4.500358 -2.388410 -0.590246 C -3.188082 -2.762289 -0.882184 C -1.136518 -0.142414 0.978130 C -0.722209 0.958402 -0.013913 O -0.052855 -0.921061 1.154213 Br -2.077015 2.378250 -0.319853 O 2.380573 -0.090382 1.017453 C 2.629821 -0.342092 -0.327964 C 4.063199 -0.822550 -0.512809 C 5.021095 0.194914 0.051805 Cl 6.759488 -0.306794 -0.197646 H 4.200263 -1.782266 0.006528 H 4.274488 -0.983592 -1.581680 H 1.931727 -1.100294 -0.725776 H 2.486093 0.572877 -0.946748 H 4.883348 0.317216 1.128753 H 4.918146 1.170324 -0.437920 H 1.411036 -0.360008 1.192059 H 0.157227 1.486069 0.366556 H -0.511308 0.528604 -1.000699 H -1.492776 0.386841 1.902892 H -3.835813 0.299786 1.389895 H -5.751909 -0.988847 0.472183 H -5.338591 -2.960869 -0.989691 H -2.998304 -3.636498 -1.507202 H -1.084830 -2.330806 -0.534024	

8a

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Cl -6.265777 0.643619 -0.132368
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C -0.887762 -0.490245 1.984668
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Br 2.830222 -2.075935 -0.676041
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H -2.246068 -1.322063 -2.102192
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H 0.774989 -0.796812 -1.331911
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C 4.100638 2.299875 0.564705
C 3.652625 3.211426 -0.387519
C 2.406018 3.027559 -0.984443
C 1.615327 1.937563 -0.634575
H 3.649295 0.492859 1.659151
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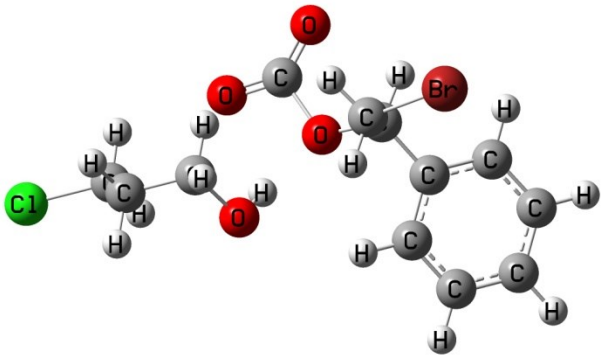

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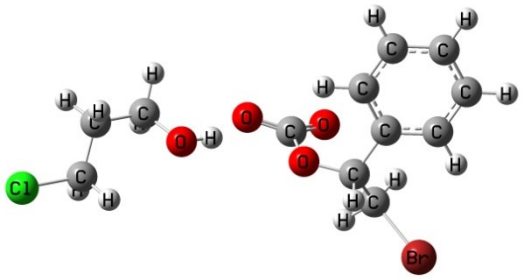
HF=-3801.25556102 C 5.777675 -0.641251 -0.236251 C 5.472712 0.803336 0.074977 C 4.098191 0.930427 0.709363 O 3.143145 0.425221 -0.177267 Cl 7.457455 -0.831196 -0.921851 O 1.188475 0.648197 1.679778 C -0.005431 0.347212 1.515451 O -0.980977 0.357890 2.271267 O -0.246975 -0.102390 0.170846 C -1.586653 -0.295619 -0.211031 C -2.345300 1.010369 -0.369234 C -2.287947 -1.311059 0.691263 Br -3.476613 -2.522279 -0.331608 H 5.506957 1.391992 -0.853697 H 6.236288 1.209265 0.755546 H 3.907679 1.992018 0.954613 H 4.077258 0.381125 1.670703 H 5.088644 -1.048188 -0.979760 H 5.746792 -1.267859 0.662220 H 2.282688 0.429346 0.317189 H -1.555579 -1.974445 1.153074 H -2.917477 -0.865897 1.461270 H -1.499483 -0.750229 -1.212088 C -3.741371 1.039434 -0.420012 C -4.422733 2.239024 -0.607075 C -3.719366 3.430988 -0.755372 C -2.327268 3.408162 -0.713006 C -1.646232 2.209761 -0.522252 H -4.311086 0.115546 -0.321481 H -5.512646 2.238846 -0.635509 H -4.251089 4.371699 -0.898956 H -1.762974 4.334739 -0.818963 H -0.558251 2.196077 -0.474345	

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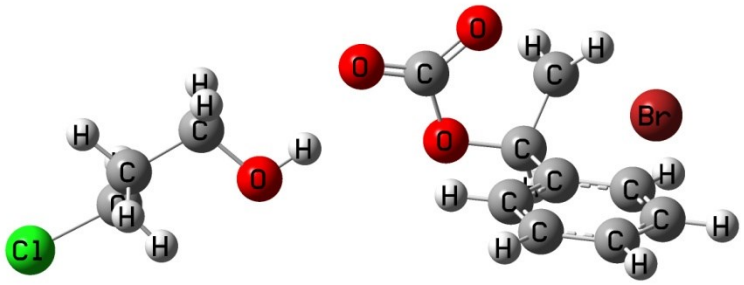

482.6(i)

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O 1.184289 -0.139046 1.822163
C 0.021999 -0.333564 1.471355
O -1.017607 -0.515356 2.169974
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H 4.082964 -0.708776 1.592842
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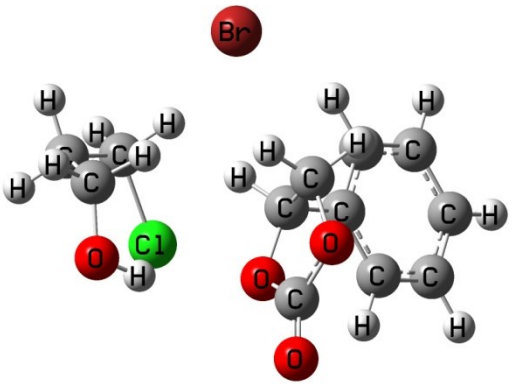
H -0.947938 4.319757 -0.154559

H -0.142926 1.986735 0.009262

10a	
HF=-3801.27505015 C 2.857589 0.456107 0.645992 C 1.760372 -0.263130 0.173166 C 1.758957 -1.659176 0.266878 C 2.843458 -2.316328 0.836831 C 3.940820 -1.596408 1.307979 C 3.943502 -0.208373 1.213367 C 0.585426 0.411130 -0.482364 C 0.577272 0.384552 -2.006306 O 0.601675 1.832841 -0.229552 C 1.112130 2.471444 -1.304808 O 1.224322 1.627789 -2.342476 O 1.430944 3.627189 -1.318585 Br -1.472248 -2.179876 -1.293528 O -2.404347 2.444674 0.341885 C -2.965370 1.189431 0.007841 C -3.344155 0.323417 1.204775 C -2.229445 -0.449284 1.871274 Cl -0.996591 0.633205 2.675722 H -3.880660 0.941869 1.941061 H -4.044091 -0.447213 0.839272 H -3.879846 1.421894 -0.554396 H -2.316316 0.613665 -0.674683 H -1.688924 -1.072030 1.143669 H -2.610308 -1.090790 2.672307 H -1.480399 2.323491 0.614494 H -0.443316 0.386182 -2.406723 H 1.142096 -0.442810 -2.441287 H -0.353363 0.000629 -0.100339 H 0.894478 -2.214279 -0.110576 H 2.829770 -3.403314 0.912823 H 4.787885 -2.116662 1.755501 H 4.793150 0.365820 1.582374 H 2.856472 1.544470 0.594795	

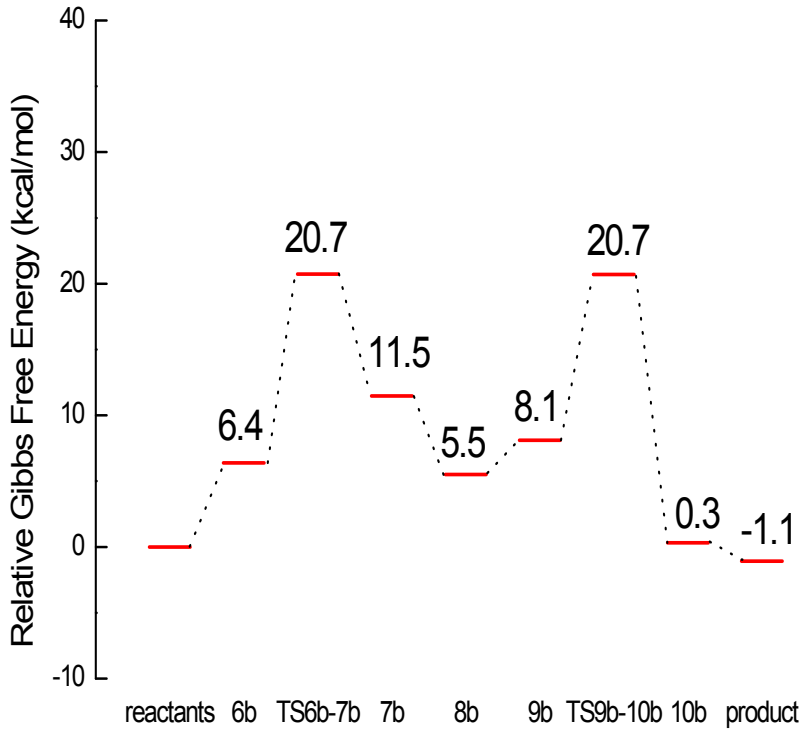
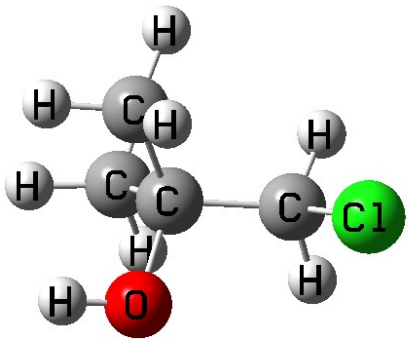


Figure S1. Relative Gibbs free energy profile of the target reaction catalyzed by **Cb** in solvent of toluene.

Optimized geometries of various species in the reaction catalyzed by Cb.

Cb			
			
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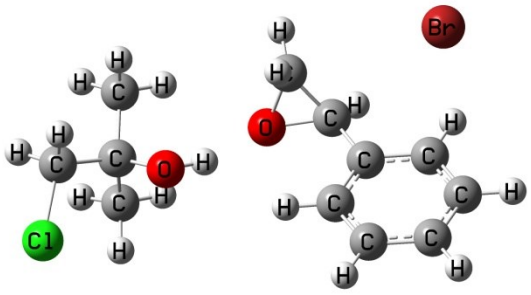
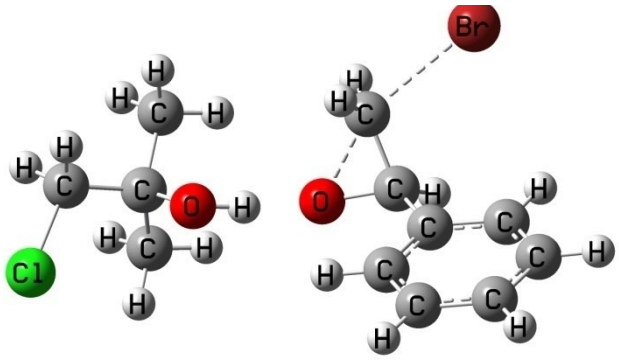
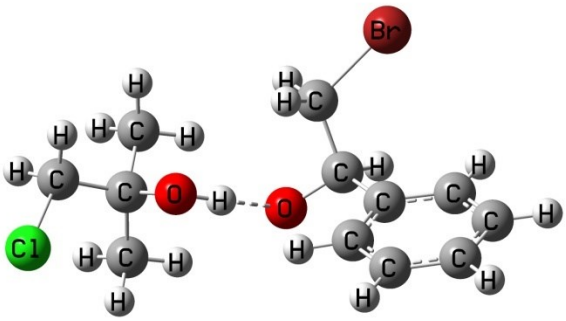
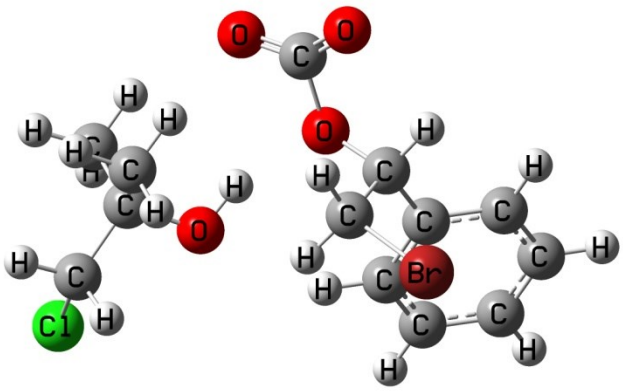
C	-1.998994000	-0.779652000	-0.422469000
Cl	2.019291000	0.002743000	-0.005110000
H	0.452170000	-1.744316000	0.225858000
H	0.442749000	-1.040812000	-1.418732000
C	-0.763982000	1.392525000	-0.607154000
O	-0.754164000	0.103115000	1.444857000
H	-2.913993000	-0.260397000	-0.104547000
H	-2.003558000	-1.778766000	0.032109000
H	-2.038215000	-0.885913000	-1.515308000
H	-1.700389000	1.920701000	-0.374329000
H	-0.683528000	1.327224000	-1.700958000
H	0.076206000	1.988225000	-0.232868000
H	-1.437306000	0.728630000	1.725094000

6b	
HF=-3651.97564286 C -4.864376 -0.780503 -0.547648 Cl -5.763526 0.685014 0.008593 C -3.480655 -0.938940 0.060552 O -2.707068 0.141847 -0.416600 C -2.919591 -2.261372 -0.468221 C -3.513744 -0.952999 1.583156 O -0.126033 -0.694007 0.278479 C 1.244460 -0.277748 0.124415 C 1.517815 1.179005 0.061981 C 0.545567 -0.970083 -0.953873 Br 4.329238 -1.730746 0.062434 H -4.776257 -0.688678 -1.635503 H -5.494430 -1.641412 -0.297075 H -1.900893 -2.405677 -0.084666 H -2.872408 -2.246182 -1.565956 H -3.527829 -3.120163 -0.149159 H -2.502875 -1.129544 1.974281 H -4.171780 -1.749688 1.960957 H -3.870488 0.009474 1.968489 H -1.787868 0.010269 -0.101415 H 0.771898 -2.022130 -1.137741 H 0.172967 -0.391417 -1.804952 H 1.967685 -0.877948 0.684668 C 2.851246 1.604344 0.063603 C 3.140849 2.963684 0.004543 C 2.115345 3.907476 -0.050418 C 0.788908 3.483680 -0.053132 C 0.492467 2.124197 0.010458 H 3.641031 0.847025 0.106942 H 4.181384 3.288162 0.005501 H 2.350391 4.971437 -0.092080 H -0.021330 4.211655 -0.093651 H -0.547501 1.798528 0.022535	

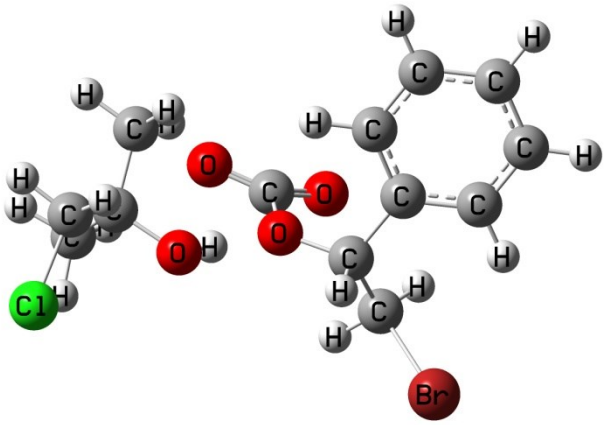
TS6b-7b	
HF=-3651.95441728 C -4.481741 -0.660639 -0.691100 Cl -5.383897 0.910561 -0.664454 C -3.216816 -0.681205 0.151253 O -2.313095 0.219017 -0.442577 C -2.669118 -2.110083 0.066977 C -3.479716 -0.310782 1.606138 O -0.206213 -0.210466 1.223217 C 1.171717 -0.071942 1.156038 C 1.719950 1.200815 0.576436 C 0.986082 -1.208281 0.266725 Br 3.264433 -2.040281 -0.497119 H -4.225726 -0.842267 -1.740504 H -5.190447 -1.420753 -0.342823 H -1.729850 -2.160756 0.632236 H -2.455243 -2.378226 -0.977220 H -3.370530 -2.844977 0.489748 H -2.538764 -0.378072 2.168064 H -4.218403 -0.986636 2.064114 H -3.852601 0.718098 1.676235 H -1.476410 0.178530 0.086340 H 0.836596 -2.189558 0.695466 H 0.683305 -1.021191 -0.758679 H 1.703525 -0.326704 2.090498 C 3.097323 1.434135 0.614759 C 3.629632 2.599952 0.076721 C 2.787715 3.560417 -0.484886 C 1.413713 3.338697 -0.512295 C 0.882082 2.164276 0.019167 H 3.749648 0.671162 1.041107 H 4.707740 2.760304 0.093400 H 3.204066 4.477293 -0.903432 H 0.746743 4.083718 -0.946716 H -0.193021 1.989762 0.006326	 **464.0(i)**

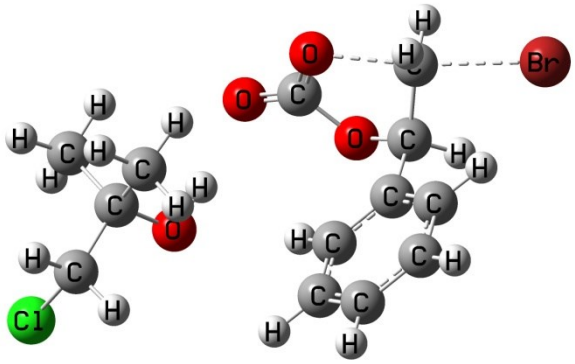
7b	
HF=-3651.97197052 C -4.285761 -0.537375 -0.609212 Cl -5.069413 1.050156 -1.012750 C -3.106581 -0.443832 0.347257 O -2.077558 0.234006 -0.314586 C -2.691154 -1.893309 0.639028 C -3.466834 0.254479 1.654693 O -0.177625 0.103259 1.481125 C 1.088773 -0.179699 1.111225 C 1.868154 1.009286 0.549419 C 0.962446 -1.293596 0.060662 Br 2.652536 -2.116357 -0.586176 H -3.944410 -0.950882 -1.564551 H -5.082533 -1.164329 -0.191618 H -1.793834 -1.866189 1.272122 H -2.441351 -2.417364 -0.295505 H -3.482475 -2.452261 1.162543 H -2.581291 0.255831 2.304691 H -4.296949 -0.252925 2.171598 H -3.753851 1.295419 1.461863 H -1.288166 0.248541 0.326644 H 0.403834 -2.128651 0.491497 H 0.453365 -0.926923 -0.838188 H 1.718710 -0.594684 1.940950 C 3.254000 1.109699 0.688528 C 3.951208 2.202077 0.177638 C 3.264027 3.224946 -0.473255 C 1.877569 3.142996 -0.601676 C 1.186665 2.050899 -0.082844 H 3.788937 0.313911 1.210634 H 5.034596 2.259171 0.294070 H 3.804511 4.084308 -0.872348 H 1.329040 3.944523 -1.098526 H 0.099508 1.994789 -0.144044	

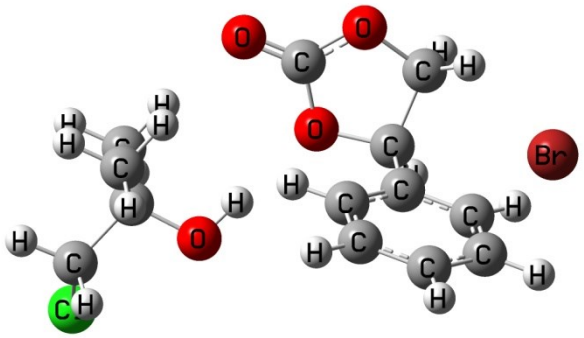
8b	
HF=-3840.56184694 C 3.877427 0.407102 1.240151 Cl 4.411964 2.104852 0.897980 C 3.109658 -0.257635 0.109452 O 1.897841 0.456756 -0.020854 C 2.831531 -1.693833 0.561530 C 3.880376 -0.265505 -1.202699 O -0.206173 -0.737606 -1.415583 C 0.155798 -2.072701 -1.937997 O -0.713279 -2.936259 -1.821224 C -1.375566 -0.655248 -0.626169 C -1.943307 0.736613 -0.733771 C -0.961532 -1.032844 0.786520 Br -2.487290 -1.011270 2.006176 O 1.304220 -2.049868 -2.387476 H 3.243948 0.465753 2.132128 H 4.789353 -0.155812 1.469352 H 2.239623 -2.201293 -0.212743 H 2.271099 -1.703314 1.507967 H 3.764474 -2.260824 0.698478 H 3.295619 -0.813919 -1.953989 H 4.857907 -0.757986 -1.083933 H 4.044378 0.760381 -1.554355 H 1.333845 0.017664 -0.699158 H -0.576399 -2.056589 0.795955 H -0.217096 -0.342147 1.195453 H -2.107910 -1.392941 -0.987795 C -3.221463 0.936666 -1.252491 C -3.749744 2.220199 -1.374568 C -2.997167 3.321963 -0.977764 C -1.716827 3.130761 -0.459502 C -1.201764 1.846650 -0.319949 H -3.805713 0.070442 -1.566205 H -4.751124 2.358885 -1.782743 H -3.403438 4.328574 -1.079398 H -1.117760 3.988053 -0.152982 H -0.194447 1.709736 0.076800	

9b

HF=-3840.55610634
C 4.589551 0.316369 -0.997664
Cl 5.233515 -1.349855 -1.310536
C 3.442822 0.378380 -0.002706
O 2.352001 -0.280410 -0.608416
C 3.118017 1.861537 0.196724
C 3.787494 -0.255592 1.338866
O 0.022792 0.075201 0.851467
C -0.147044 0.706420 2.174866
O -1.306999 0.704543 2.591274
C -1.134788 -0.253805 0.119759
C -1.869708 0.973428 -0.386595
C -2.008172 -1.241616 0.888481
Br -2.785854 -2.602734 -0.317154
O 0.934491 1.106729 2.604286
H 4.251401 0.693919 -1.968972
H 5.442412 0.906329 -0.643304
H 2.287598 1.946268 0.913921
H 2.825099 2.322143 -0.758223
H 3.976408 2.412078 0.610814
H 2.956796 -0.083442 2.038324
H 4.698596 0.191068 1.766499
H 3.946657 -1.334660 1.222687
H 1.573964 -0.181413 -0.014709
H -1.401105 -1.810177 1.594328
H -2.847001 -0.785031 1.413528
H -0.736281 -0.784305 -0.763111
C -3.221748 0.930103 -0.733615
C -3.863216 2.057570 -1.239712
C -3.162025 3.247622 -1.411246
C -1.811768 3.296696 -1.071841
C -1.172029 2.170441 -0.564742
H -3.785987 0.004753 -0.620262
H -4.920775 2.003052 -1.499157
H -3.664291 4.131709 -1.804156
H -1.251609 4.223784 -1.193618
H -0.119342 2.213332 -0.287432



TS9b-10b	
HF=-3840.54321837 C 4.661713 0.653403 0.420594 C 3.635965 -0.468811 0.449977 C 4.273460 -1.833695 0.677729 Cl 6.005620 0.423060 -0.772115 O 2.964368 -0.425728 -0.790524 C 2.675655 -0.140584 1.597344 O -0.737770 -1.204952 -1.121345 C -1.840661 -0.410048 -0.702538 C -2.540814 -1.131669 0.428071 C -0.108059 -1.815164 -0.051008 O 0.996901 -2.314687 -0.262162 O -0.773642 -1.768630 1.027108 C -1.395109 0.994279 -0.337888 Br -4.859749 -0.531084 -0.090846 H 4.168182 1.590608 0.140456 H 5.141503 0.765114 1.399436 H 1.867524 -0.883451 1.626208 H 2.218512 0.849178 1.455714 H 3.190793 -0.156904 2.569494 H 3.485758 -2.592621 0.770357 H 4.876571 -1.842487 1.598340 H 4.918883 -2.101954 -0.167168 H 2.291853 -1.144683 -0.793879 H -2.842991 -2.159969 0.286956 H -2.685884 -0.680382 1.399655 H -2.509507 -0.373865 -1.570643 C -2.319326 1.910100 0.176759 C -1.922753 3.203772 0.497719 C -0.602634 3.606844 0.303527 C 0.317522 2.699240 -0.211667 C -0.074071 1.400301 -0.531142 H -3.357256 1.604978 0.313515 H -2.654993 3.904302 0.899650 H -0.294948 4.622336 0.553814 H 1.355530 2.993803 -0.370957 H 0.661972 0.706087 -0.934854	 472.0(i)

10b	
HF=-3840.57210956 O -1.209527 -0.610809 2.581773 C -2.126619 -0.769681 1.469421 C -1.290486 -0.300084 0.283542 O 0.050445 -0.577055 0.769555 C 0.037897 -0.618330 2.119892 C -1.444701 1.163552 -0.039247 O 1.034773 -0.656441 2.792878 O 2.547793 0.065331 -0.722900 C 3.663127 -0.095887 0.131783 C 3.716139 -1.506204 0.700218 C 4.884905 0.247327 -0.705272 Cl 5.220843 -0.905742 -2.054984 C 3.606696 0.932249 1.263722 Br -4.059096 -1.703343 -0.982437 H 4.742526 1.228846 -1.170763 H 5.785352 0.260281 -0.080894 H 2.727348 0.733466 1.891110 H 3.528619 1.948489 0.852436 H 4.494462 0.876551 1.910856 H 2.845746 -1.673095 1.349697 H 4.622895 -1.655659 1.304791 H 3.706074 -2.248216 -0.106911 H 1.743886 -0.217678 -0.250294 H -2.410426 -1.823302 1.384010 H -3.013546 -0.162450 1.657126 H -1.484821 -0.932515 -0.589969 C -2.645212 1.579241 -0.627317 C -2.851398 2.925512 -0.902223 C -1.868603 3.869382 -0.604039 C -0.674897 3.456540 -0.022441 C -0.461826 2.107231 0.257784 H -3.398004 0.824171 -0.876102 H -3.788015 3.239132 -1.362612 H -2.034608 4.923824 -0.825419 H 0.102988 4.183424 0.210143 H 0.485553 1.796049 0.697428	

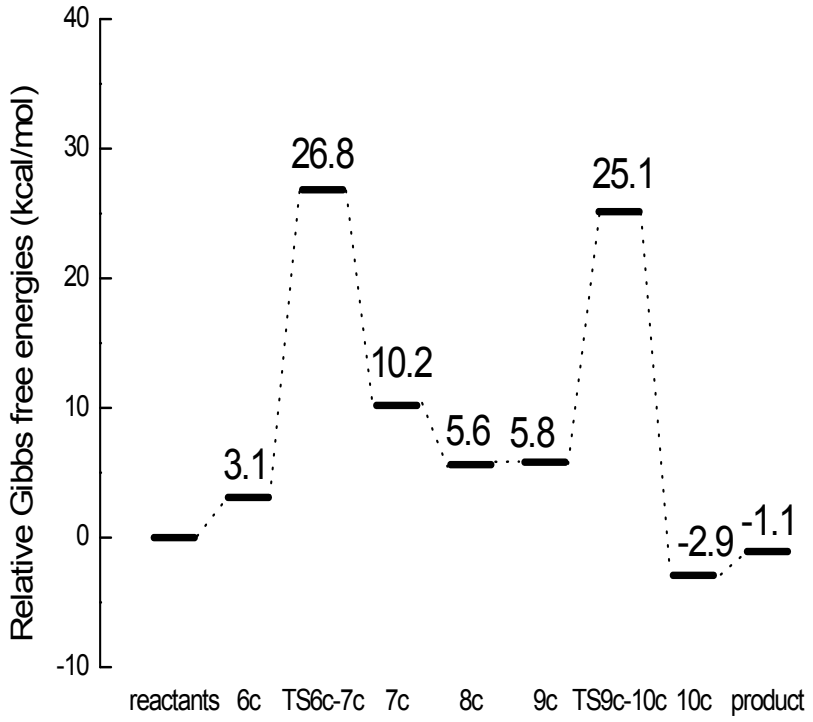
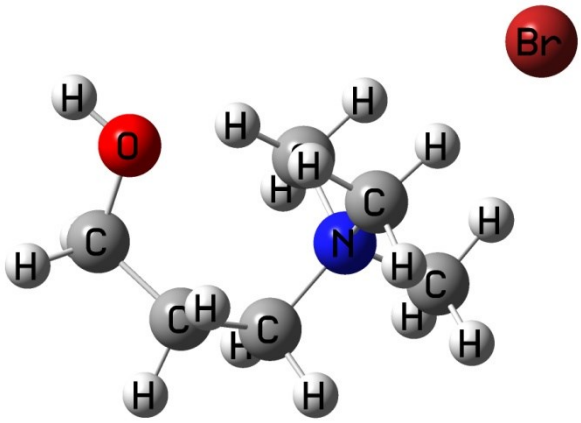
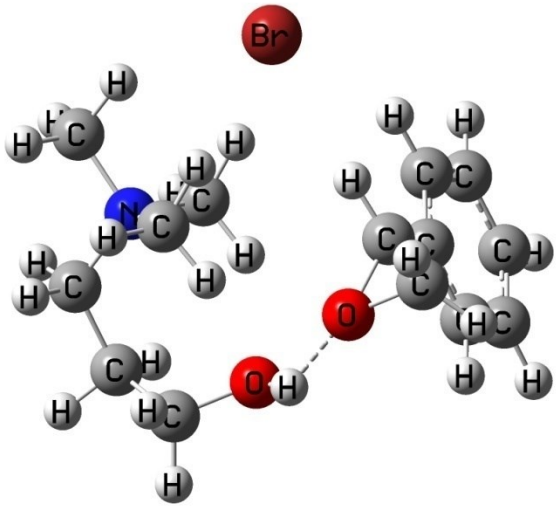
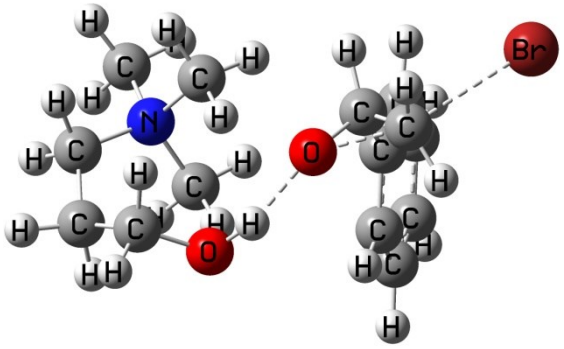


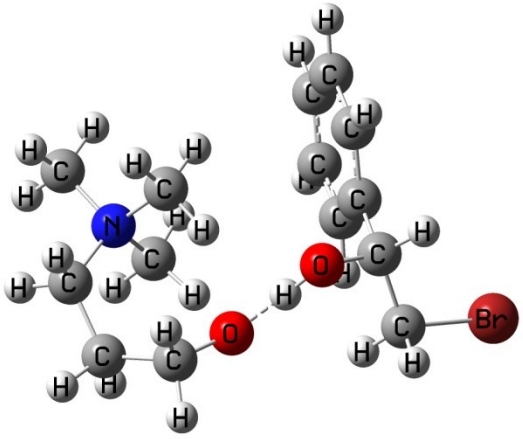
Figure S2. Relative Gibbs free energy profile of the target reaction catalyzed by **Cc** in solvent of toluene.

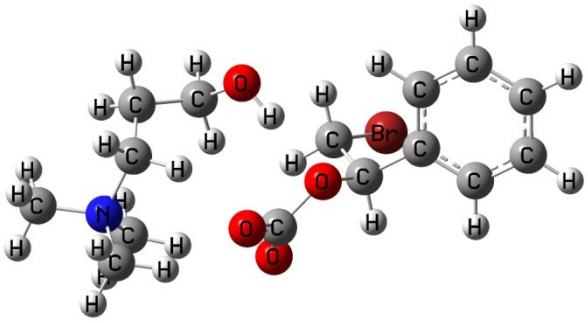
Optimized geometries of various species in the reaction catalyzed by Cc.

Cc	
HF=-2942.07557582 C -0.338135 1.906999 -0.276745 N 0.609892 0.761157 -0.056029 C 0.306311 0.139372 1.275841 C 2.011860 1.312785 -0.107102 C 3.168027 0.476764 0.422862 C 3.554711 -0.797202 -0.304468 O 2.723318 -1.849354 0.148123 C 0.362070 -0.249710 -1.141803 Br -2.933931 -0.377170 0.025586 H 3.032144 0.244299 1.488110 H 4.029722 1.159379 0.377106 H 4.609231 -1.023496 -0.083426 H 3.465739 -0.660143 -1.397859 H 2.182956 1.592065 -1.156814 H 1.976622 2.243000 0.475611 H 3.038464 -2.695384 -0.197799 H -0.697143 -0.548968 -1.067078 H 0.562308 0.233989 -2.104291 H 1.021179 -1.103682 -0.976193 H -0.763206 -0.129197 1.270112 H 0.926817 -0.752471 1.392096 H 0.525128 0.877460 2.056182 H -1.362778 1.496592 -0.284002 H -0.214542 2.622577 0.542808 H -0.089899 2.377613 -1.234356	

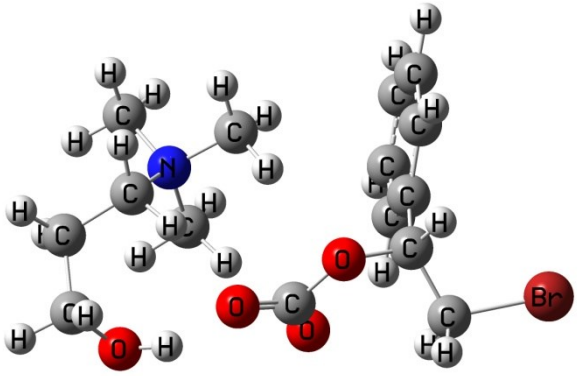
6c	
HF=-3326.77294779 C 2.237096 0.128983 0.258464 C 1.446274 0.392610 1.486766 C 1.964372 0.117151 2.827287 Br -0.943499 2.905628 0.117241 O 1.012915 -0.760981 2.244031 O 0.085030 -2.607757 0.362423 C -1.082387 -3.376326 0.530294 C -1.984495 -3.127171 -0.670470 C -2.937786 -1.938940 -0.652808 N -2.375933 -0.549828 -0.471398 C -3.436939 0.442654 -0.841711 C -2.013347 -0.290848 0.964458 C -1.188789 -0.310439 -1.362260 H -1.345527 -3.095240 -1.564501 H -2.643492 -3.997970 -0.804866 H -0.830177 -4.448579 0.568865 H -1.605958 -3.135031 1.472470 H -3.691712 -2.055006 0.138949 H -3.473744 -1.915182 -1.611753 H 0.504866 -2.362689 1.207136 H 1.598343 0.692947 3.679104 H 2.970240 -0.297391 2.933219 H 0.681845 1.172711 1.383093 H -1.720288 0.767206 1.040017 H -2.896687 -0.498411 1.578243 H -1.174434 -0.927505 1.244414 H -0.916549 0.748864 -1.249017 H -0.368083 -0.958353 -1.040912 H -1.490742 -0.534162 -2.392110 H -3.031692 1.448947 -0.655758 H -3.681447 0.315825 -1.901466 H -4.321564 0.255350 -0.223362 C 2.092655 0.993014 -0.830351 C 2.855256 0.796292 -1.979437 C 3.740676 -0.274872 -2.060740 C 3.866370 -1.153693 -0.985337 C 3.121692 -0.948997 0.170222 H 1.376931 1.817478 -0.761849 H 2.748362 1.482757 -2.818341 H 4.332482 -0.428862 -2.962242 H 4.549549 -1.999756 -1.047467 H 3.216020 -1.642759 1.006599	

TS6c-7c	
HF=-3326.71722613 C -0.913280 0.525361 0.359630 C -1.053309 -0.871626 -0.160913 C -2.008837 -1.774735 0.417507 Br -4.132017 -0.554725 -0.563909 O -0.276400 -1.875214 0.455445 O 2.027988 -1.293999 1.623256 C 3.005884 -2.116260 1.050788 C 4.178214 -1.251156 0.604218 C 4.128990 -0.574343 -0.757952 N 2.984480 0.378583 -1.074931 C 3.404205 1.217664 -2.234702 C 1.755984 -0.378000 -1.483970 C 2.665995 1.283597 0.080150 H 4.368243 -0.510184 1.394049 H 5.086348 -1.871330 0.552950 H 3.377655 -2.844476 1.790603 H 2.601966 -2.703779 0.206067 H 4.106771 -1.318516 -1.566161 H 5.041945 0.023361 -0.883020 H 1.113788 -1.594924 1.369572 H -2.323831 -2.651281 -0.131827 H -2.341822 -1.629603 1.439217 H -1.036170 -0.889830 -1.263693 H 0.978664 0.352716 -1.728736 H 2.001297 -0.982906 -2.363255 H 1.406473 -1.008952 -0.661429 H 1.899679 1.996489 -0.246265 H 2.279666 0.674572 0.904061 H 3.584224 1.809473 0.364441 H 2.561598 1.848801 -2.533008 H 4.250824 1.844793 -1.938550 H 3.692356 0.565078 -3.065352 C -1.128729 1.605273 -0.499933 C -0.945954 2.912171 -0.056927 C -0.533512 3.152216 1.254213 C -0.317410 2.079091 2.116337 C -0.498357 0.772660 1.667470 H -1.498301 1.405528 -1.507564 H -1.149083 3.745534 -0.728719 H -0.400987 4.173978 1.608342 H -0.008297 2.259377 3.145488 H -0.315768 -0.066419 2.339032	 538.1(i)

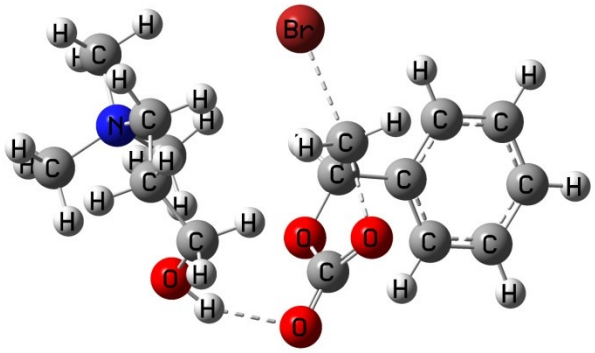
7c	
HF=-3326.76019658 C 1.124714 0.944324 0.597143 C 1.625275 -0.354854 1.204487 C 2.215797 -1.338978 0.213825 Br 3.852785 -0.635988 -0.590489 O 0.600094 -1.002080 1.912441 O -0.944813 -1.775304 -0.025378 C -1.926944 -2.614179 0.399463 C -3.265731 -2.401182 -0.327546 C -4.044426 -1.137591 -0.005758 N -3.374783 0.208529 -0.273983 C -4.440340 1.237207 -0.395765 C -2.474474 0.596857 0.866580 C -2.577398 0.165657 -1.541681 H -3.098189 -2.479481 -1.412529 H -3.961305 -3.216632 -0.065812 H -1.675936 -3.691332 0.259033 H -2.145907 -2.518453 1.499871 H -4.322409 -1.107973 1.057590 H -4.971037 -1.113638 -0.596661 H -0.023661 -1.381300 1.204766 H 2.500202 -2.251990 0.741822 H 1.520526 -1.598120 -0.591048 H 2.406211 -0.097290 1.939400 H -2.024707 1.569420 0.633705 H -3.084394 0.663176 1.773626 H -1.691794 -0.168451 0.940286 H -2.209918 1.178583 -1.738951 H -1.743321 -0.535714 -1.363066 H -3.236737 -0.167286 -2.351668 H -3.971253 2.220863 -0.499996 H -5.051751 1.021587 -1.278220 H -5.063392 1.218251 0.505044 C 0.862700 2.005216 1.469289 C 0.328277 3.205153 1.012810 C 0.045449 3.365700 -0.344355 C 0.287684 2.311060 -1.221400 C 0.810841 1.106413 -0.752267 H 1.083177 1.873567 2.530028 H 0.148848 4.021816 1.711556 H -0.344926 4.312549 -0.717300 H 0.083397 2.429793 -2.286389 H 0.983510 0.292168 -1.455537	

8c	
HF=-3515.34577447 C 2.616628 -0.870198 -0.262488 C 1.415672 -0.055596 -0.659691 C 1.210011 1.182188 0.196213 Br 2.714403 2.393616 0.013741 O 0.261855 -0.888464 -0.512118 C -0.869548 -0.594102 -1.315120 O -0.840767 0.434921 -2.000275 O -1.781071 -1.427685 -1.138704 O -1.062101 -0.696345 1.991173 C -1.800073 0.476613 1.767943 C -3.288074 0.195590 1.959637 C -3.842122 -0.777254 0.929932 N -4.595839 -0.142665 -0.240930 C -3.846506 0.982398 -0.894000 C -4.807630 -1.211297 -1.270923 C -5.916574 0.357335 0.224236 H -3.401866 -0.268873 2.948831 H -3.857492 1.137456 2.007675 H -1.484896 1.244237 2.493372 H -1.604221 0.885098 0.763713 H -4.569428 -1.473779 1.366138 H -3.024061 -1.353780 0.476678 H -0.630861 -0.982066 1.158705 H 0.329628 1.730942 -0.149055 H 1.119964 0.936725 1.259915 H 1.495139 0.257177 -1.710341 H -5.408163 -0.792358 -2.085129 H -3.816629 -1.523146 -1.625267 H -5.339460 -2.045084 -0.800876 H -6.453933 0.790406 -0.625394 H -6.490029 -0.478562 0.637149 H -5.772412 1.122043 0.992849 H -4.480191 1.373910 -1.696759 H -3.668121 1.769572 -0.156406 H -2.902718 0.613818 -1.317861 C 3.602823 -1.173588 -1.198124 C 4.712267 -1.934787 -0.837931 C 4.840926 -2.402381 0.466332 C 3.856894 -2.105300 1.408037 C 2.761181 -1.329500 1.048343 H 3.499031 -0.805066 -2.219425 H 5.478240 -2.160511 -1.578672	

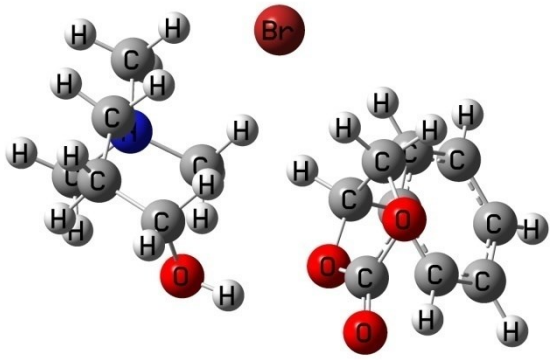
H 5.705601 -3.001219 0.749718 H 3.951075 -2.470831 2.429743 H 1.993993 -1.104162 1.791299	

9c	
HF=-3515.34875557 C -1.589187 0.815706 -0.267804 C -1.702297 -0.602454 -0.788755 C -2.519235 -1.537751 0.082387 Br -4.373099 -0.934883 0.082486 O -0.436151 -1.160812 -1.145346 C 0.439915 -1.638937 -0.155548 O 0.117055 -1.519040 1.033875 O 1.500499 -2.079779 -0.650680 O 3.649378 -2.219101 1.059409 C 4.620306 -2.079963 0.063878 C 4.873824 -0.613408 -0.291391 C 3.653933 0.046221 -0.930245 N 2.972276 1.133295 -0.105845 C 3.884424 2.294873 0.069141 C 1.765198 1.581531 -0.871312 C 2.530939 0.651189 1.247268 H 5.195057 -0.090523 0.621289 H 5.723628 -0.547878 -0.986916 H 5.558940 -2.519240 0.432950 H 4.337650 -2.632928 -0.848375 H 2.867158 -0.697779 -1.126616 H 3.905244 0.547520 -1.874046 H 2.771287 -2.333680 0.618627 H -2.513154 -2.547365 -0.337672 H -2.197155 -1.578044 1.121408 H -2.213202 -0.545997 -1.761817 H 1.217508 2.320800 -0.275275 H 2.096685 2.026223 -1.815593 H 1.122555 0.717097 -1.073224 H 2.126785 1.516264 1.784002 H 1.758324 -0.119649 1.145221 H 3.385526 0.225857 1.776846 H 3.340501 3.098002 0.576483 H 4.745543 1.996733 0.673021 H 4.221727 2.637797 -0.914443 C -1.702364 1.871687 -1.174621 C -1.557230 3.194749 -0.761797 C -1.298665 3.478766 0.577125	

C -1.193158 2.431532 1.492300 C -1.343043 1.111707 1.075698 H -1.916434 1.650666 -2.221953 H -1.664127 4.003248 -1.484289 H -1.198866 4.511428 0.910007 H -1.008792 2.645010 2.545153 H -1.236259 0.301430 1.793099	

TS9c-10c	
HF=-3515.31619237 C 2.783964 0.102713 0.384800 C 1.274941 0.142023 0.290844 C 0.773342 -0.222459 -1.089830 O 0.714682 1.398439 0.631723 C 0.668165 2.255086 -0.473308 O 1.093075 1.717889 -1.537599 O 0.173361 3.361599 -0.275028 Br -0.056897 -2.469480 -0.694989 O -2.426594 2.542085 0.177703 C -2.513492 2.021607 -1.128214 C -3.570669 0.937746 -1.194716 C -3.280407 -0.422648 -0.577378 N -3.243570 -0.551063 0.945945 C -4.304979 0.273820 1.586713 C -3.454139 -1.996320 1.265398 C -1.908227 -0.159256 1.511215 H -4.529868 1.337723 -0.834617 H -3.734697 0.709164 -2.258878 H -2.783256 2.815731 -1.843202 H -1.541113 1.623792 -1.466947 H -2.329885 -0.857419 -0.922709 H -4.078288 -1.111136 -0.886154 H -1.585024 3.055734 0.225034 H -0.240857 0.000866 -1.384864 H 1.447892 -0.560885 -1.867378 H 0.873812 -0.557802 1.033636 H -3.347867 -2.134385 2.345932 H -4.458281 -2.294454 0.946847 H -2.688371 -2.577742 0.737324 H -1.969408 -0.242695 2.601446 H -1.171962 -0.866256 1.115251 H -1.686704 0.870227 1.218611 H -4.333007 0.026775 2.652859 H -4.052802 1.330551 1.450966	 477.3(i)

H -5.271434 0.038471 1.127358 C 3.523741 1.215428 0.775451 C 4.910680 1.132715 0.877588 C 5.564566 -0.064729 0.604910 C 4.825313 -1.183030 0.224751 C 3.441585 -1.100374 0.114556 H 3.015070 2.152273 0.996964 H 5.481472 2.012074 1.172700 H 6.648660 -0.128276 0.687609 H 5.328109 -2.125683 0.012554 H 2.861723 -1.981429 -0.168419	

10c	
HF=-3515.36156400 O -2.798796 1.837497 1.509289 C -2.534554 2.428836 0.338434 O -1.630188 1.691516 -0.363399 C -1.412986 0.428387 0.296732 C -1.889569 0.744879 1.713256 O -3.006893 3.452173 -0.057454 C -2.144206 -0.691204 -0.389493 O 0.918085 2.167920 -1.592474 C 1.494979 2.454363 -0.332781 C 2.963603 2.070113 -0.343861 C 3.323740 0.640760 0.027065 N 3.173300 -0.463021 -1.018699 C 3.905365 -0.113685 -2.262896 C 3.759439 -1.701721 -0.411841 C 1.740270 -0.764951 -1.358000 Br 1.098722 -1.114603 2.116860 H 3.419540 2.398849 -1.289855 H 3.458856 2.664210 0.438534 H 1.407276 3.531017 -0.117813 H 0.978679 1.910332 0.478937 H 2.734726 0.292848 0.892327 H 4.388582 0.598373 0.293321 H -0.047731 2.258876 -1.507187 H -1.064778 1.073628 2.358266 H -2.425361 -0.078925 2.191365 H -0.335390 0.232125 0.315164 H 3.635846 -2.526895 -1.120455 H 4.823013 -1.533025 -0.213712 H 3.213136 -1.908983 0.519505 H 1.738553 -1.575171 -2.095047	

H 1.249219 -1.083195 -0.428261 H 1.278032 0.138170 -1.767585 H 3.921019 -0.991285 -2.917247 H 3.388335 0.707581 -2.767206 H 4.930247 0.178833 -2.009098 C -1.776867 -2.004496 -0.073589 C -2.465757 -3.071087 -0.639548 C -3.520259 -2.840396 -1.521894 C -3.882565 -1.534772 -1.838776 C -3.200120 -0.460987 -1.270232 H -0.956103 -2.175089 0.629022 H -2.179600 -4.091142 -0.386347 H -4.057649 -3.678616 -1.963214 H -4.704565 -1.346648 -2.527829 H -3.482985 0.559316 -1.527959	

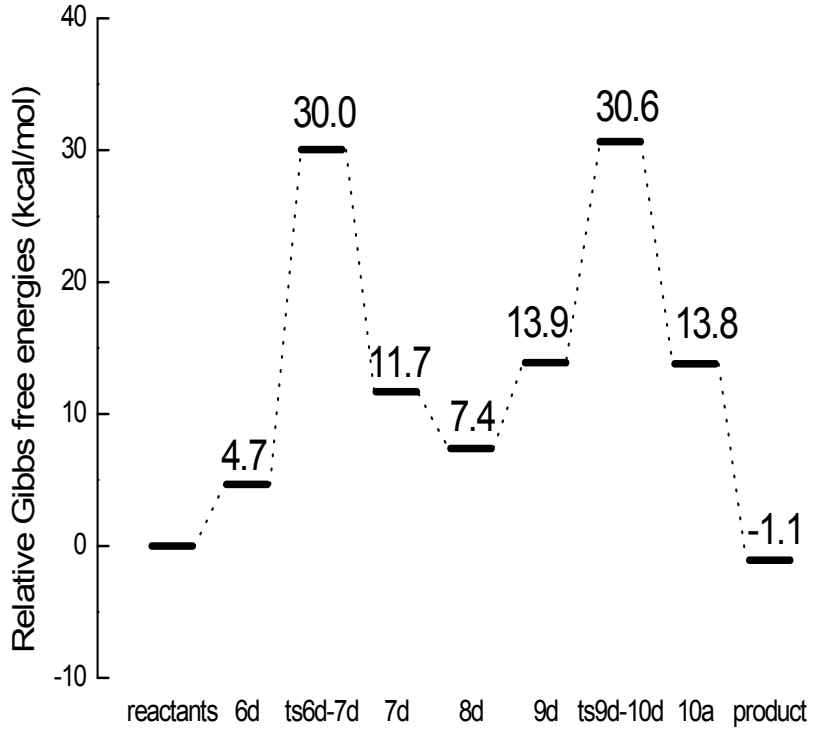
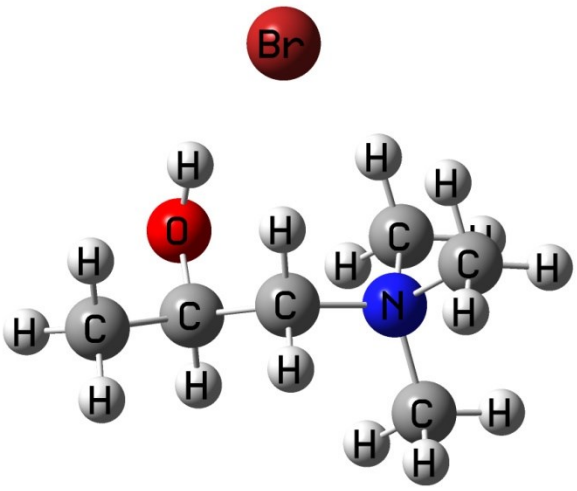
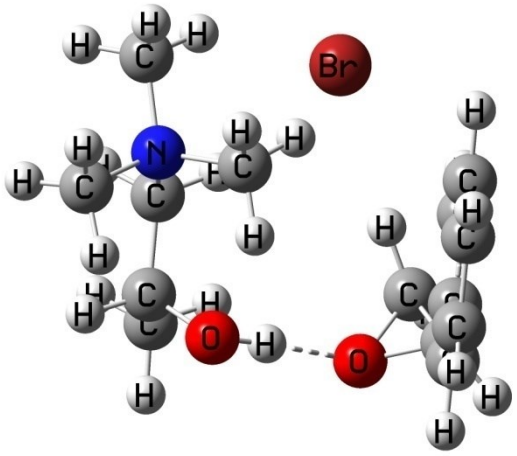
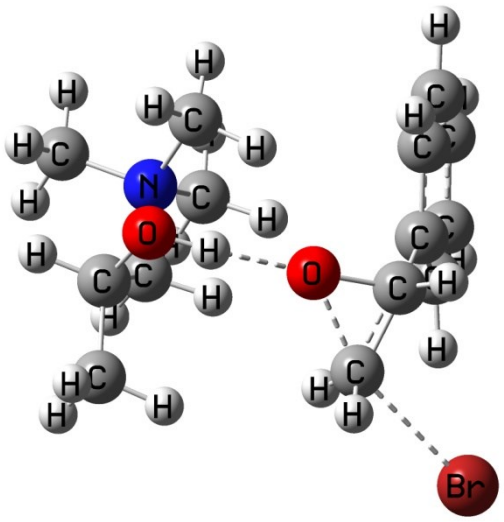


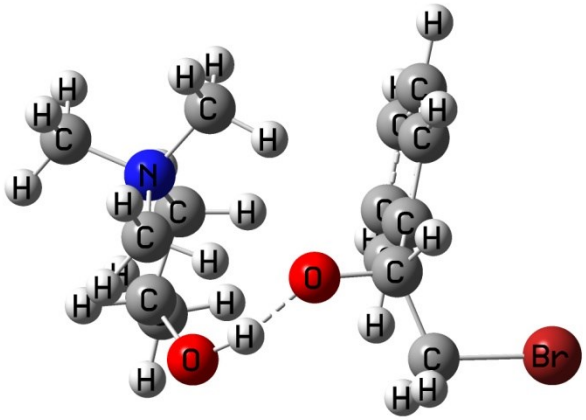
Figure S3. Relative Gibbs free energy profile of the target reaction catalyzed by **Cd** in solvent of toluene.

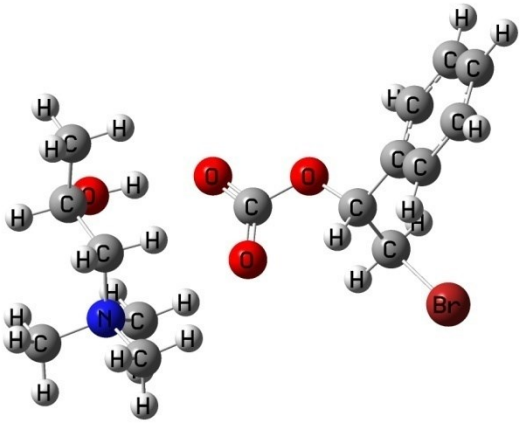
Optimized geometries of various species in the reaction catalyzed by Cd.

Cd	
HF=-2942.09263492 C 0.714359 2.834270 -0.758020 C 1.037186 1.663822 0.162256 C 1.008212 0.401552 -0.690162 N 1.476669 -0.898053 -0.040857 C 2.960582 -0.924110 0.027104 O 0.151224 1.610855 1.247883 C 0.921386 -1.127595 1.339746 C 0.989761 -2.011093 -0.917006 Br -2.202536 -0.334079 -0.069654 H 2.038807 1.819420 0.601629 H -0.032758 0.217729 -0.994918 H 1.644499 0.518412 -1.578143 H -0.269613 2.684593 -1.224756 H 1.465104 2.963835 -1.549945 H 0.669232 3.753393 -0.164162 H -0.719825 1.253220 0.943482 H 3.282214 -1.867107 0.481117 H 3.370491 -0.842653 -0.984959 H 3.306948 -0.086442 0.639634 H 1.364099 -2.960455 -0.519243 H -0.108742 -1.983020 -0.903974 H 1.367988 -1.850376 -1.931879 H 1.271891 -2.113766 1.664379 H 1.277107 -0.341257 2.007229 H -0.174077 -1.094289 1.271816	

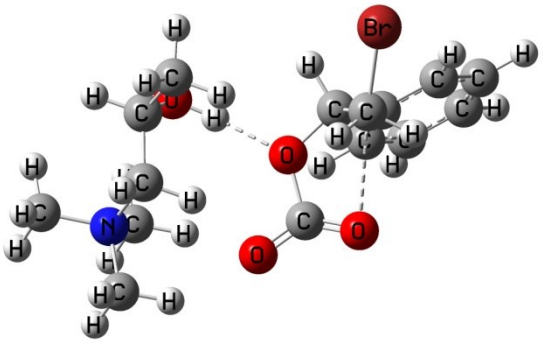
6d	
HF=-3326.78340669 C -1.855018 -2.127226 -2.211081 C -1.717051 -2.100469 -0.696955 O -0.403929 -2.365320 -0.269558 C -2.243493 -0.759139 -0.205920 N -2.186934 -0.515156 1.294851 C -0.782932 -0.209416 1.749946 C -3.028985 0.691470 1.580899 C -2.711743 -1.679392 2.051910 O 1.324756 -1.210010 -2.151969 C 2.473270 -0.438389 -1.759726 C 2.650624 -0.200397 -0.301553 C 1.396779 0.170297 -2.536240 Br -0.873253 2.453775 -0.663888 H -2.333304 -2.915463 -0.281364 H -1.708789 0.095704 -0.654920 H -3.305977 -0.670081 -0.476008 H -1.289931 -1.303926 -2.669739 H -2.903923 -2.032879 -2.521127 H -1.459263 -3.072272 -2.600187 H 0.232284 -1.923864 -0.877271 H 1.538523 0.321762 -3.607608 H 0.670444 0.829726 -2.046227 H 3.371949 -0.756395 -2.297546 H -2.782934 -1.402780 3.108920 H -3.705355 -1.939737 1.670387 H -2.025876 -2.523150 1.938254 H -2.947297 0.923540 2.648020 H -2.639686 1.522278 0.972364 H -4.068936 0.464361 1.323730 H -0.820292 -0.000239 2.825035 H -0.154962 -1.075235 1.533661 H -0.446419 0.674950 1.191559 C 3.252787 -1.193239 0.479433 C 3.426110 -1.007887 1.846556 C 3.000590 0.178346 2.446343 C 2.393039 1.165767 1.675846 C 2.225967 0.982228 0.304539 H 3.583998 -2.119453 0.006541 H 3.899359 -1.785481 2.444600 H 3.144222 0.328506 3.516056 H 2.048341 2.093736 2.132131 H 1.729944 1.757678 -0.278920	

TS6d-7d	
HF=-3326.73023578 C 1.649771 1.599145 -0.423954 C 1.055090 1.272048 0.796538 C 0.338468 2.250585 1.493840 C 0.185311 3.529375 0.967129 C 0.747991 3.843023 -0.271493 C 1.475327 2.875384 -0.960268 C 1.089982 -0.119585 1.358233 C 1.235222 -1.254350 0.476375 Br 3.667253 -1.314026 -0.449439 O -0.179882 -0.741388 1.357600 O -2.706826 -1.824659 1.475177 C -2.825804 -2.097745 0.104242 C -2.236546 -1.000589 -0.777612 N -2.850641 0.388326 -0.690691 C -4.231827 0.390278 -1.241249 C -2.131105 -3.400272 -0.270038 C -2.876023 0.920607 0.714418 C -1.986936 1.294671 -1.512474 H -3.907269 -2.206715 -0.082554 H -1.186885 -0.863719 -0.491907 H -2.306536 -1.281726 -1.837146 H -1.047549 -3.316140 -0.108161 H -2.305401 -3.680519 -1.317541 H -2.506179 -4.203425 0.372980 H -1.764894 -1.619558 1.679981 H 1.471587 -2.225962 0.886459 H 0.962319 -1.169631 -0.569132 H 1.623125 -0.189258 2.318013 H -2.414306 2.302449 -1.495234 H -0.979480 1.311772 -1.078265 H -1.950372 0.915862 -2.538752 H -4.621561 1.412893 -1.212555 H -4.207989 0.029321 -2.274689 H -4.865553 -0.258326 -0.630518 H -3.177880 1.972367 0.662878 H -3.573889 0.327687 1.307331 H -1.868334 0.817777 1.130441 H -0.102754 1.997779 2.460620 H -0.362485 4.287932 1.526368 H 0.634470 4.843862 -0.687067 H 1.943864 3.122849 -1.912478 H 2.274711 0.857974 -0.928223	 527.3(i)

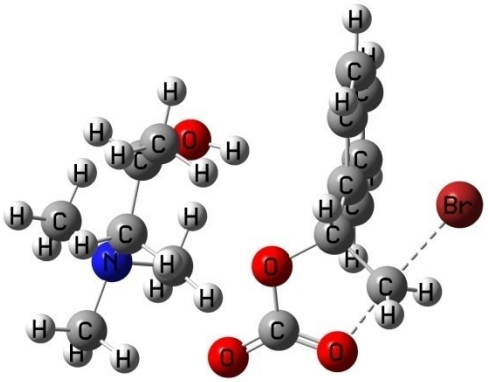
7d	
HF=-3326.76880836 C -0.965003 1.175296 0.955782 C -1.021444 0.754058 -0.376175 C -0.872167 1.714392 -1.377112 C -0.655600 3.055952 -1.066489 C -0.588976 3.460402 0.264869 C -0.750586 2.512296 1.275335 C -1.031610 -0.724306 -0.742992 C -2.007425 -1.536220 0.094340 Br -3.835742 -0.836948 -0.051333 O 0.221954 -1.252665 -0.597739 O 1.656640 -1.678988 1.586640 C 2.549881 -0.608883 1.640848 C 2.529544 0.233642 0.372722 N 3.221274 -0.374554 -0.849570 C 4.676901 -0.083331 -0.784131 C 2.241735 0.307439 2.819537 C 3.025384 -1.861778 -0.988977 C 2.628041 0.274403 -2.058822 H 3.566775 -1.026069 1.798265 H 1.486003 0.388046 0.074929 H 3.022139 1.203655 0.525919 H 1.287029 0.828386 2.659765 H 3.029125 1.058776 2.976632 H 2.149296 -0.299930 3.726420 H 0.968337 -1.534687 0.861507 H -2.036531 -2.569775 -0.259891 H -1.748439 -1.535607 1.159336 H -1.394573 -0.784726 -1.797537 H 3.177657 -0.061285 -2.945270 H 1.575954 -0.036439 -2.094361 H 2.705901 1.361651 -1.949234 H 5.174991 -0.541694 -1.644613 H 4.828289 1.000754 -0.802642 H 5.084725 -0.499786 0.142247 H 3.567059 -2.168425 -1.891001 H 3.433766 -2.361850 -0.108308 H 1.947865 -2.053060 -1.078268 H -0.928459 1.397948 -2.421552 H -0.549241 3.790425 -1.865154 H -0.426619 4.508207 0.514987 H -0.718327 2.820763 2.320852 H -1.081487 0.442851 1.757004	

8d	
HF=-3515.35893109 C 3.276919 1.858986 -0.771693 C 2.835090 0.905478 0.147351 C 3.484607 0.794423 1.376223 C 4.577786 1.602956 1.675293 C 5.022758 2.542342 0.749321 C 4.367080 2.669911 -0.473814 C 1.636926 0.046274 -0.156221 C 1.957553 -1.116944 -1.078776 Br 3.038546 -2.439183 -0.141358 O 0.665917 0.852390 -0.811532 C -0.666280 0.504083 -0.653980 O -0.928074 -0.498855 0.053611 O -1.451071 1.265813 -1.248650 O -4.179294 1.434964 -1.333462 C -4.431245 1.553146 0.038685 C -3.783324 0.439601 0.854700 N -4.166588 -0.991804 0.498171 C -5.632180 -1.192305 0.625914 C -3.933244 2.880878 0.593816 C -3.734098 -1.385951 -0.890971 C -3.444399 -1.880736 1.460858 H -5.527923 1.514572 0.153025 H -2.691592 0.467452 0.751889 H -4.052631 0.548924 1.915049 H -2.845513 2.958526 0.463707 H -4.173718 3.002627 1.659204 H -4.400487 3.700346 0.036858 H -3.193202 1.432320 -1.450783 H 1.041997 -1.631126 -1.381882 H 2.529577 -0.801711 -1.957904 H 1.217378 -0.355769 0.776184 H -3.693340 -2.921672 1.228997 H -2.370110 -1.704236 1.334489 H -3.764715 -1.637831 2.479302 H -5.855269 -2.256624 0.497767 H -5.958790 -0.860457 1.617475 H -6.141773 -0.617185 -0.151775 H -3.992470 -2.442680 -1.021499 H -4.251261 -0.749281 -1.609902 H -2.650934 -1.229894 -0.947862 H 3.129315 0.057468 2.097614 H 5.077789 1.502543 2.637898	

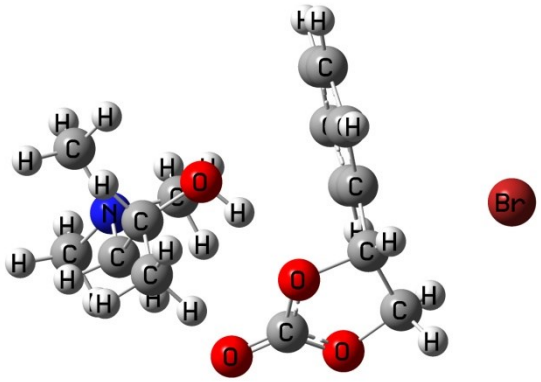
H 5.874576 3.179605 0.983409 H 4.702494 3.413100 -1.196222 H 2.744095 1.977649 -1.714686	

9d	
HF=-3515.34577893 C -1.656853 2.362093 -0.560934 C -2.153818 1.088400 -0.283148 C -3.536945 0.894230 -0.279631 C -4.402298 1.949494 -0.550927 C -3.898749 3.217965 -0.823794 C -2.521429 3.419389 -0.826786 C -1.213712 -0.075087 -0.041540 C -1.721549 -1.087488 0.984640 Br -2.644295 -2.584015 0.106885 O 0.115181 0.335550 0.250304 C 0.377158 0.942598 1.556493 O 1.574896 1.278415 1.635922 O -0.572182 0.991312 2.321169 O 1.839498 -0.241671 -1.856398 C 2.605276 -1.241434 -1.235298 C 3.221545 -0.768763 0.075611 N 4.220332 0.379436 0.003220 C 5.419706 -0.013945 -0.779158 C 1.777704 -2.485050 -0.939553 C 3.628217 1.631134 -0.589213 C 4.619947 0.690991 1.413501 H 3.390351 -1.509800 -1.961795 H 2.436203 -0.406261 0.753218 H 3.768994 -1.592805 0.554809 H 1.010586 -2.266964 -0.183663 H 2.396439 -3.317083 -0.576830 H 1.266263 -2.803675 -1.854594 H 1.174537 0.070817 -1.199272 H -0.893869 -1.543480 1.531967 H -2.426275 -0.668861 1.704542 H -1.097071 -0.609146 -1.001345 H 5.355515 1.501806 1.393633 H 3.718213 0.995481 1.958090 H 5.063250 -0.204944 1.860430 H 6.159780 0.790530 -0.718845 H 5.837811 -0.935643 -0.360415 H 5.137536 -0.170175 -1.823605 H 4.387091 2.417137 -0.507134	

H 3.364776 1.436095 -1.629220 H 2.733938 1.876709 -0.001666 H -3.951339 -0.094447 -0.082746 H -5.477883 1.777199 -0.542576 H -4.576372 4.045478 -1.029310 H -2.114093 4.409664 -1.027399 H -0.580736 2.530821 -0.549329	

TS9d-10d	
HF=-3515.31743112 C -1.518040 0.771163 2.742744 C -2.477909 1.013068 1.590586 O -1.902561 1.795047 0.568855 C -2.981036 -0.339356 1.097214 N -3.894761 -0.324315 -0.118447 C -3.143629 -0.013925 -1.385937 C -4.459265 -1.704845 -0.258051 C -4.998525 0.656106 0.053324 O -0.030551 -1.177272 0.367581 C -0.267013 -2.176691 -0.555401 O 0.767281 -2.540484 -1.187464 C 1.309261 -0.635187 0.302315 C 1.234481 0.723707 -0.345293 C 2.206109 -1.628426 -0.402664 O -1.430927 -2.564032 -0.659968 Br 4.222370 -0.495379 0.534478 H -3.327382 1.612259 1.956938 H -2.151734 -1.004596 0.829444 H -3.566889 -0.814748 1.897187 H -0.673936 0.148479 2.416164 H -2.010185 0.260014 3.580506 H -1.130375 1.730582 3.104293 H -0.987741 1.499482 0.395462 H 2.549042 -2.508840 0.123387 H 2.644217 -1.414595 -1.367649 H 1.632357 -0.533847 1.343209 H -5.083316 -1.734889 -1.157153 H -3.619733 -2.403073 -0.349930 H -5.065049 -1.931396 0.625215 H -5.707803 0.534853 -0.771829 H -5.503527 0.465041 1.006495 H -4.585325 1.668021 0.038780 H -3.860983 -0.064108 -2.212180	 524.7(i)

H -2.707751 0.982222 -1.297242 H -2.368236 -0.778537 -1.503071 C 1.527411 1.869104 0.395979 C 1.387120 3.133922 -0.169574 C 0.925696 3.265812 -1.476355 C 0.610949 2.127732 -2.217156 C 0.750874 0.864745 -1.649631 H 1.919212 1.755300 1.407260 H 1.643189 4.017297 0.412975 H 0.817623 4.253940 -1.920982 H 0.254466 2.223997 -3.242031 H 0.505391 -0.022008 -2.237485	

10d	
HF=-3515.33328293 O -0.016357 -1.410110 0.142395 C -0.267063 -1.974453 -1.047772 O 0.839610 -2.161595 -1.741276 C 2.001801 -1.713050 -0.974853 C 1.398407 -0.902375 0.161441 O -1.385175 -2.246185 -1.432844 C 1.313839 0.584241 -0.003334 O -1.863265 0.050792 1.909782 C -3.082901 -0.624148 1.734538 C -3.035607 -2.042717 2.277827 C -3.517980 -0.697120 0.274982 N -3.538770 0.611623 -0.502942 C -2.155887 1.048677 -0.913581 C -4.318149 0.361183 -1.751432 C -4.184553 1.700867 0.279843 Br 4.294635 -0.201027 0.439764 H -3.818435 -0.043196 2.312868 H -2.863106 -1.370022 -0.298648 H -4.546466 -1.082580 0.229636 H -2.287003 -2.636462 1.734151 H -4.005080 -2.550374 2.188194 H -2.753060 -2.019431 3.335700 H -1.150058 -0.480533 1.503783 H 2.544318 -2.594049 -0.622622 H 2.646056 -1.135323 -1.637128 H 1.794012 -1.175513 1.140644 H -4.285584 1.258494 -2.377399 H -3.860092 -0.481736 -2.279280	

H -5.354467 0.125545 -1.489744 H -4.305409 2.572601 -0.371150 H -5.164057 1.357492 0.629628 H -3.544018 1.959987 1.126594 H -2.254819 1.966394 -1.502742 H -1.555758 1.231625 -0.020604 H -1.717349 0.252619 -1.520688 C 1.132642 1.373482 1.133560 C 0.883474 2.735563 1.019915 C 0.815348 3.330205 -0.240353 C 0.996913 2.549302 -1.380396 C 1.239396 1.183605 -1.261846 H 1.232502 0.912872 2.117344 H 0.771293 3.340814 1.918250 H 0.646448 4.402526 -0.332016 H 0.971939 3.009072 -2.368106 H 1.400770 0.590986 -2.163487	

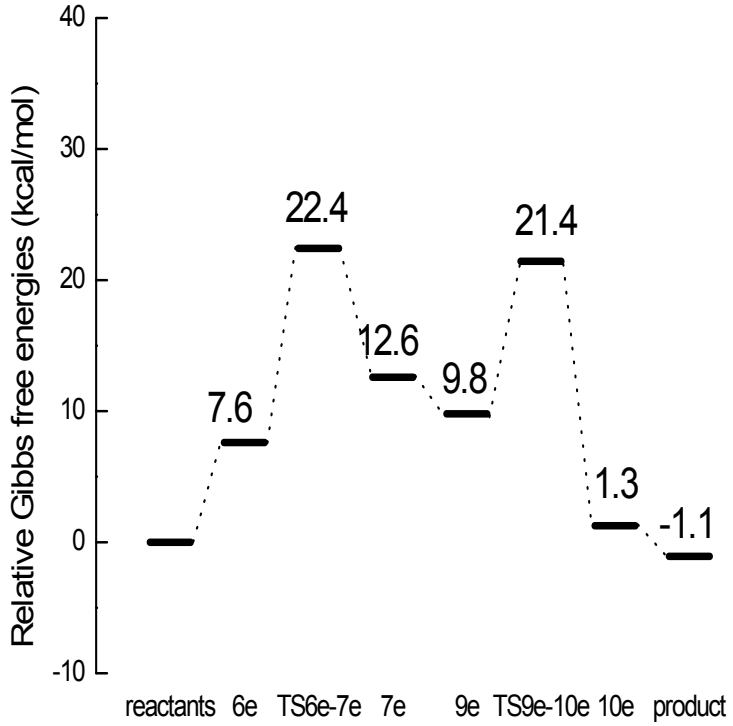
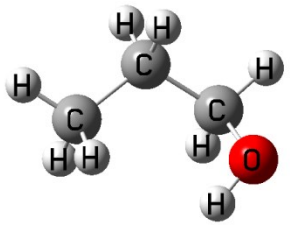
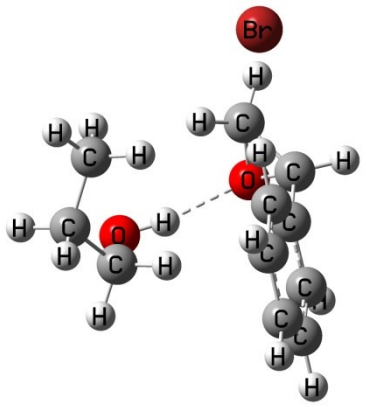


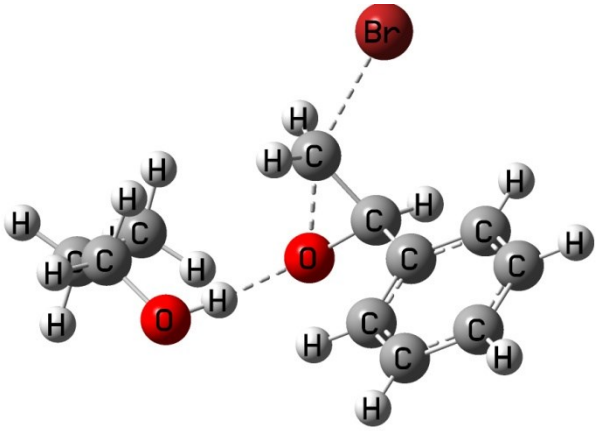
Figure S4. Relative Gibbs free energy profile of the target reaction catalyzed by **Ce** in solvent of toluene.

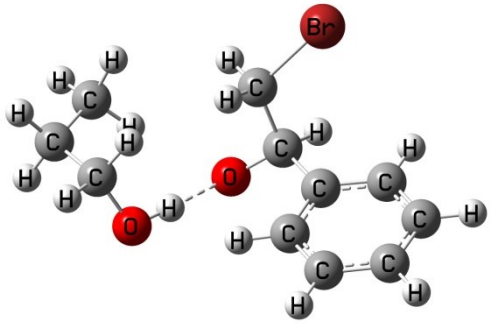
Optimized geometries of various species in the reaction catalyzed by Ce.

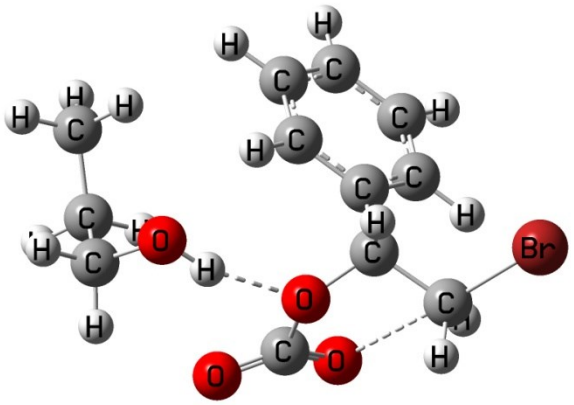
Ce			
HF=-194.2782446			
C	1.525332000	-0.501452000	0.104994000
C	0.622414000	0.662616000	-0.274024000
C	-0.779080000	0.537181000	0.296050000
O	-1.489662000	-0.579987000	-0.206689000
H	-0.734137000	0.502520000	1.400385000
H	-1.382699000	1.411452000	0.023468000
H	1.057378000	1.606132000	0.090943000
H	0.552188000	0.746722000	-1.368600000
H	-1.085306000	-1.389695000	0.132680000
H	2.550852000	-0.351360000	-0.253611000
H	1.572815000	-0.628607000	1.197015000
H	1.174205000	-1.447337000	-0.330887000

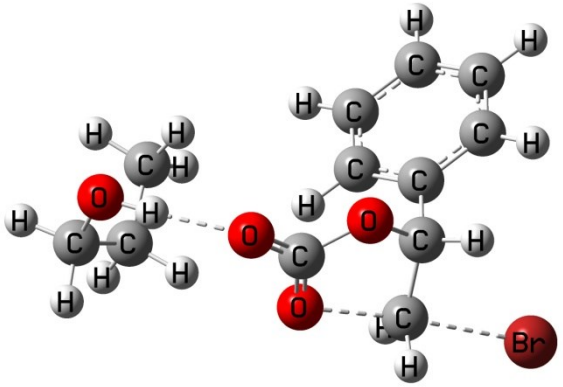


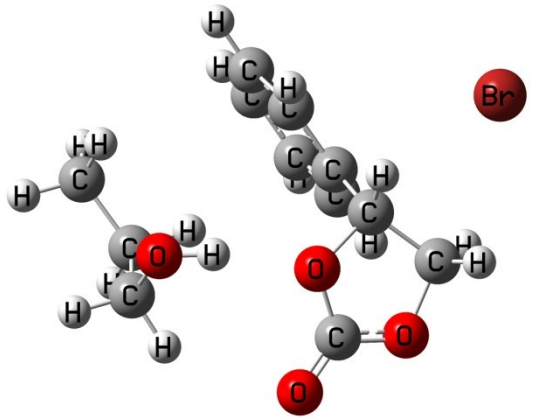
6e	
HF=-3153.07499946 C -0.752526 0.484018 1.774645 Br -3.144763 -0.208094 -0.318141 C -0.022922 -0.766934 1.806833 O 0.513172 0.394297 2.467513 C 0.756034 -1.281685 0.646818 O 1.986497 2.394433 0.992309 C 2.310878 1.884639 -0.285817 C 1.583552 2.638202 -1.386425 C 0.072235 2.482918 -1.337817 H 2.066234 0.811150 -0.350587 H 3.401414 1.976297 -0.436733 H 1.971629 2.276138 -2.354190 H 1.857209 3.704164 -1.316648 H 1.595005 1.685222 1.538348 H -1.626640 0.616164 2.410542 H -0.741261 1.086057 0.866507 H -0.364786 -1.527107 2.517419 H -0.418181 3.014739 -2.163845 H -0.240206 1.430348 -1.401635 H -0.334687 2.886976 -0.401587 C 2.037561 -1.792025 0.873659 C 2.810948 -2.259811 -0.183449 C 2.291086 -2.244805 -1.477851 C 1.004086 -1.760877 -1.700658 C 0.235086 -1.264980 -0.648510 H 2.437961 -1.790489 1.889295 H 3.816925 -2.637827 -0.000101 H 2.889351 -2.614709 -2.311045 H 0.591014 -1.754125 -2.709342 H -0.787748 -0.901518 -0.808607	

TS6e-7e	
HF=-3153.05222501 C 0.360081 0.936104 0.245225 Br -1.436234 2.599553 -0.382807 C -0.199848 -0.063845 1.143679 O 1.123043 -0.468106 1.156601 C -1.214818 -1.020993 0.581876 O 2.793373 -1.627224 -0.667761 C 3.585393 -0.589806 -1.180711 C 4.738547 -0.204005 -0.264255 C 4.277917 0.482224 1.012036 H 2.974355 0.309365 -1.395812 H 3.984350 -0.942227 -2.145159 H 5.425281 0.456273 -0.822094 H 5.301517 -1.120086 -0.023403 H 2.164539 -1.255673 -0.001580 H 0.913564 1.764330 0.664859 H 0.513922 0.660935 -0.793513 H -0.563393 0.357351 2.099133 H 5.122732 0.711733 1.676740 H 3.763198 1.427160 0.783104 H 3.560245 -0.138188 1.564224 C -0.818855 -2.188222 -0.068451 C -1.771071 -3.067560 -0.581497 C -3.128601 -2.791277 -0.440183 C -3.529271 -1.628310 0.217766 C -2.578139 -0.757540 0.737493 H 0.244793 -2.398077 -0.174071 H -1.448018 -3.975199 -1.092206 H -3.873713 -3.477410 -0.844383 H -4.589652 -1.399332 0.326873 H -2.884847 0.156715 1.246944	 459.6(i)

7e	
HF=-3153.06808662 C 0.282361 1.162481 0.126743 Br -1.146001 2.445703 -0.406798 C -0.111072 0.078713 1.142339 O 1.039434 -0.536794 1.468907 C -1.193410 -0.830270 0.558680 O 2.649292 -1.967939 -0.046045 C 3.248629 -1.129011 -0.984540 C 4.418355 -0.330847 -0.416753 C 3.974553 0.769914 0.534910 H 2.510762 -0.423065 -1.424017 H 3.608276 -1.762753 -1.813590 H 5.001198 0.099923 -1.250837 H 5.080851 -1.041551 0.103063 H 2.023256 -1.429657 0.537720 H 1.068872 1.787484 0.557449 H 0.626373 0.712042 -0.812159 H -0.595182 0.616500 2.000645 H 4.829583 1.243023 1.039834 H 3.431963 1.556321 -0.012292 H 3.280632 0.378679 1.293165 C -0.835338 -1.958425 -0.183790 C -1.810990 -2.791863 -0.725080 C -3.164059 -2.527392 -0.512682 C -3.530785 -1.416818 0.244861 C -2.550130 -0.583239 0.778103 H 0.224359 -2.184464 -0.314049 H -1.512595 -3.666328 -1.305486 H -3.926847 -3.186894 -0.929071 H -4.585127 -1.202523 0.427631 H -2.834842 0.282047 1.380274	

9e	
HF=-3341.65460968 C -2.072356 -1.024385 0.368801 Br -3.606060 -0.485021 -0.745689 C -0.769915 -0.536020 -0.243863 C -0.425309 0.917367 0.020217 O 0.301223 -1.395699 0.079889 C 0.671787 -1.539683 1.496798 O -0.161734 -1.102839 2.296416 O 1.764369 -2.096190 1.597258 O 2.713356 -1.480451 -1.450124 C 3.873551 -1.513434 -0.647159 C 4.159129 -0.174973 0.015478 C 4.453826 0.924499 -0.992650 H 3.779785 -2.291439 0.124997 H 4.710659 -1.781257 -1.316097 H 3.291517 0.087810 0.640589 H 5.010386 -0.295402 0.706315 H 1.938245 -1.592423 -0.858596 H -2.089300 -2.115955 0.380710 H -2.269260 -0.656180 1.374457 H -0.865465 -0.652269 -1.336757 H 4.600662 1.900639 -0.508694 H 5.362983 0.696106 -1.571244 H 3.628956 1.020175 -1.712628 C 0.754498 1.403064 -0.551657 C 1.161779 2.716871 -0.349789 C 0.393071 3.571680 0.438607 C -0.775733 3.094374 1.023630 C -1.178797 1.776316 0.818013 H 1.369537 0.724544 -1.148097 H 2.089769 3.069357 -0.801042 H 0.709913 4.601483 0.605197 H -1.378106 3.747108 1.655774 H -2.089059 1.420827 1.298193	

TS9e-10e	
HF=-3341.63824959 C 1.028369 -1.419027 -0.298491 C 0.998148 -0.486712 0.892841 C 1.046561 0.972334 0.509041 O -0.165264 -0.744420 1.687223 C -1.222050 -1.257901 0.968549 O -0.917891 -1.582500 -0.226145 O -2.303596 -1.345733 1.540297 Br 3.430741 -1.303460 -0.624969 O -4.885091 -0.573392 0.754296 C -4.950585 -0.737174 -0.637928 C -3.783195 -0.112333 -1.388773 C -3.583221 1.355825 -1.048118 H -5.024844 -1.807816 -0.910917 H -5.893046 -0.258596 -0.954478 H -2.865401 -0.680177 -1.167791 H -3.970207 -0.233021 -2.469554 H -4.015963 -0.909148 1.066376 H 1.123026 -2.485062 -0.145074 H 0.933339 -1.057013 -1.311754 H 1.844200 -0.716811 1.548884 H -2.789471 1.807679 -1.660667 H -4.506518 1.932850 -1.213842 H -3.306635 1.476579 0.007599 C 0.089443 1.523134 -0.346312 C 0.106808 2.882380 -0.640374 C 1.083565 3.708071 -0.086386 C 2.041668 3.164621 0.765017 C 2.014775 1.805560 1.064965 H -0.681679 0.883202 -0.779198 H -0.651525 3.299263 -1.303509 H 1.097640 4.772518 -0.320448 H 2.813700 3.800314 1.198079 H 2.770474 1.372030 1.720670	 500.6(i)

10e	
HF=-3341.66826194 O 0.415244 2.624529 1.135338 C 1.439593 1.815542 0.503558 C 0.652012 0.862691 -0.384691 O -0.632775 1.573438 -0.496904 C -0.741350 2.494949 0.478847 C 0.375384 -0.510839 0.150820 O -1.746585 3.109935 0.714451 O -3.189027 0.769886 -1.709451 C -3.873778 0.632716 -0.478820 C -3.520231 -0.654840 0.247578 C -3.883803 -1.894908 -0.552109 Br 3.601564 -0.256772 -0.549301 H -3.675395 1.504012 0.167177 H -4.947656 0.637330 -0.727160 H -2.439684 -0.655157 0.469300 H -4.036957 -0.660597 1.221782 H -2.279258 1.041140 -1.497225 H 2.098073 2.470612 -0.074975 H 2.027327 1.317903 1.275332 H 1.065719 0.803869 -1.394158 H -3.619779 -2.816618 -0.016071 H -4.963880 -1.923431 -0.766085 H -3.355519 -1.898657 -1.514196 C 0.063521 -1.530210 -0.747998 C -0.315892 -2.785960 -0.290848 C -0.396461 -3.034112 1.078026 C -0.094267 -2.018763 1.981735 C 0.295838 -0.766000 1.518368 H 0.146717 -1.335076 -1.817858 H -0.545644 -3.575734 -1.005538 H -0.694484 -4.018264 1.439441 H -0.149713 -2.205418 3.053801 H 0.537141 0.017217 2.237689	

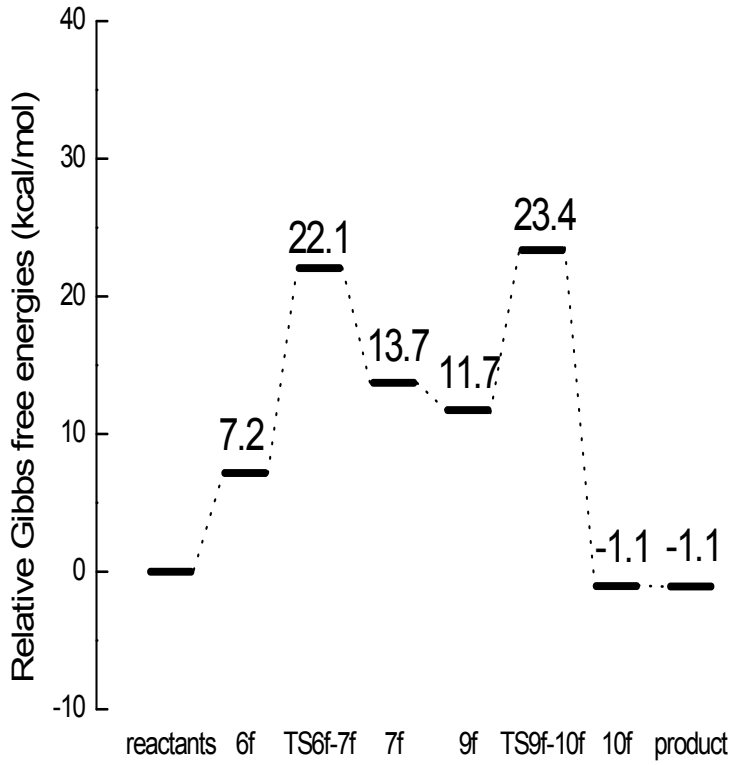
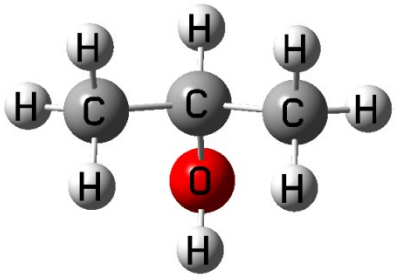
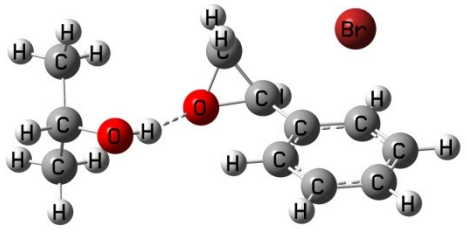


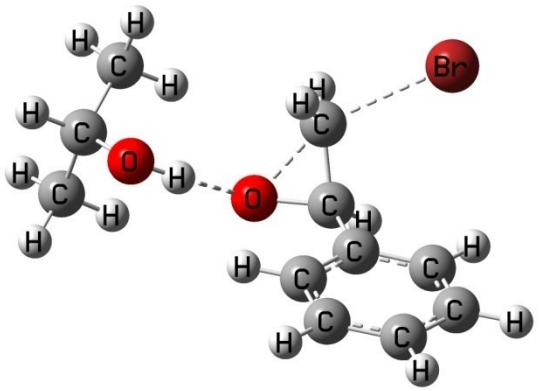
Figure S5. Relative Gibbs free energy profile of the target reaction catalyzed by **Cf** in solvent of toluene.

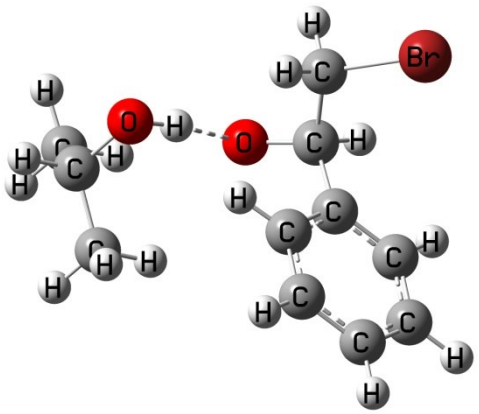
Optimized geometries of various species in the reaction catalyzed by Cf.

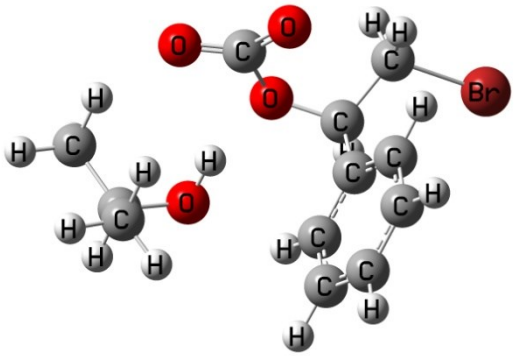
Cf			
HF=-194.2839693			
H	0.000019000	0.086675000	-1.473362000
C	0.000008000	0.040049000	-0.374681000
O	-0.000106000	1.406256000	0.024014000
C	1.258974000	-0.662857000	0.097940000
C	-1.258849000	-0.663063000	0.097909000
H	1.280744000	-0.714674000	1.198171000
H	2.153182000	-0.123134000	-0.235539000
H	1.309411000	-1.692291000	-0.281572000
H	-1.280687000	-0.714769000	1.198147000
H	-1.309032000	-1.692556000	-0.281474000
H	-2.153160000	-0.123582000	-0.235691000
H	-0.000429000	1.439511000	0.992199000

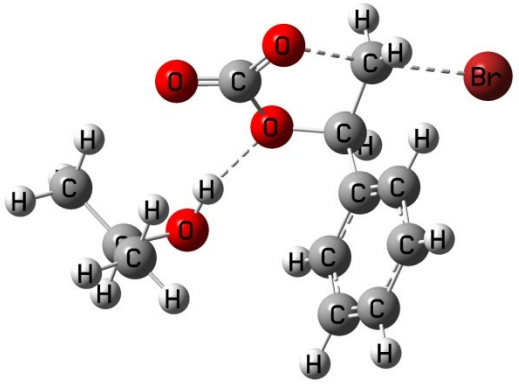


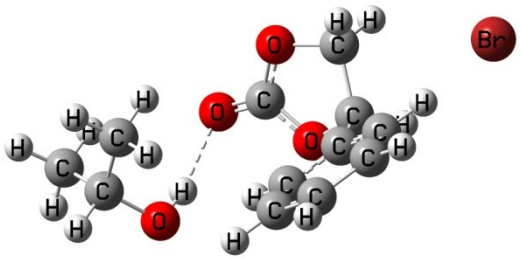
6f	
HF=-3153.08082672 C -4.186082 -1.680025 -0.917192 C -4.551306 -0.494655 -0.037118 C -4.494289 -0.860180 1.437568 O -3.728748 0.623030 -0.314299 O -1.197865 -0.494464 0.253335 C 0.210213 -0.226018 0.122196 C -0.540388 -0.842848 -0.966742 Br 3.134524 -2.006467 0.084455 C 0.641526 1.192364 0.063982 H -5.571540 -0.162762 -0.289531 H -3.184569 -2.052186 -0.656697 H -4.179737 -1.385819 -1.974619 H -4.898402 -2.507727 -0.787064 H -3.471375 -1.161017 1.707984 H -5.169418 -1.696506 1.670210 H -4.773385 0.000006 2.059264 H -2.812771 0.378451 -0.066182 H -0.421365 -1.913220 -1.145577 H -0.836384 -0.231607 -1.825224 H 0.856710 -0.898228 0.694222 C 2.014261 1.467331 0.069148 C 2.453496 2.785641 0.011775 C 1.539340 3.837686 -0.044738 C 0.173990 3.563390 -0.051241 C -0.272573 2.245298 0.008641 H 2.715358 0.627153 0.112785 H 3.523606 2.993002 0.015063 H 1.890774 4.869187 -0.084579 H -0.550375 4.377021 -0.092875 H -1.341676 2.034174 0.016919	

TS6f-7f	
HF=-3153.05765695 C -3.868141 -1.421749 -0.375824 C -4.154505 0.065700 -0.524387 C -4.639294 0.666465 0.787635 O -3.025736 0.757786 -1.010613 O -1.241458 0.139266 0.982837 C 0.134715 0.022594 1.068246 C -0.145088 -1.113463 0.201450 Br 2.008575 -2.368523 -0.246854 C 0.962884 1.147075 0.511740 H -4.934630 0.205971 -1.292523 H -3.095177 -1.572175 0.391675 H -3.496584 -1.837093 -1.321977 H -4.770263 -1.977122 -0.077623 H -3.860301 0.554114 1.555613 H -5.554912 0.169955 1.143737 H -4.845793 1.737824 0.664371 H -2.297743 0.614911 -0.356433 H -0.528504 -2.023571 0.641749 H -0.302262 -0.929697 -0.856991 H 0.512291 -0.269475 2.065663 C 2.343445 1.164992 0.726552 C 3.124856 2.192064 0.209235 C 2.530819 3.231759 -0.506674 C 1.153014 3.228393 -0.706889 C 0.372428 2.192578 -0.195343 H 2.802808 0.343626 1.277608 H 4.203843 2.181738 0.364869 H 3.142663 4.039555 -0.909586 H 0.678326 4.038800 -1.260910 H -0.707153 2.186074 -0.341587	 453.1(i)

7f	
HF=-3153.07358937 C -4.290907 -1.338475 0.777691 C -3.844126 -0.651078 -0.506885 C -3.741126 0.857178 -0.307840 O -2.632400 -1.191857 -0.968542 O -1.067560 -0.854454 1.147492 C 0.239545 -0.554194 1.006705 C 0.807856 -1.581036 0.023499 Br 2.762276 -1.395937 -0.327880 C 0.493542 0.866293 0.504170 H -4.590267 -0.850660 -1.298681 H -3.524122 -1.187385 1.551641 H -4.399873 -2.419290 0.613846 H -5.251305 -0.938407 1.139640 H -2.988502 1.076294 0.463477 H -4.705420 1.288125 0.005630 H -3.427164 1.348722 -1.239554 H -1.975579 -1.114006 -0.203083 H 0.678259 -2.589832 0.424480 H 0.332369 -1.504394 -0.960635 H 0.833423 -0.657661 1.954049 C 1.304270 1.763110 1.198097 C 1.458594 3.080953 0.767303 C 0.806444 3.518975 -0.382016 C -0.004470 2.628401 -1.088735 C -0.153738 1.317789 -0.649717 H 1.818252 1.417298 2.097936 H 2.093087 3.766718 1.331301 H 0.920526 4.549191 -0.721917 H -0.529174 2.961073 -1.985912 H -0.819808 0.634979 -1.181640	

9f	
HF=-3341.65984305 C 3.869848 0.854658 -0.217327 C 3.945499 -0.351003 -1.141093 C 4.568973 -1.544426 -0.435228 O 2.668292 -0.679987 -1.658189 O 0.694770 -1.048893 0.306961 C -0.539327 -0.540095 -0.161917 C -1.702124 -1.315676 0.430786 Br -3.295509 -1.134914 -0.706175 C 0.998195 -0.988343 1.747034 O 2.177699 -1.274013 1.947871 O 0.041595 -0.686364 2.466710 C -0.619980 0.968914 -0.043442 H 4.547935 -0.092224 -2.029242 H 3.273654 0.601661 0.672440 H 3.399084 1.707067 -0.726927 H 4.872494 1.158741 0.119717 H 3.961309 -1.804606 0.445146 H 5.590898 -1.315456 -0.096068 H 4.609634 -2.410479 -1.109785 H 2.086997 -0.915744 -0.900238 H -1.462990 -2.381665 0.442265 H -1.988934 -1.007170 1.434517 H -0.514282 -0.775641 -1.239869 C 0.263272 1.720953 -0.823205 C 0.283113 3.109490 -0.744745 C -0.588261 3.770808 0.118607 C -1.463639 3.029695 0.907885 C -1.477887 1.639783 0.826252 H 0.962713 1.197564 -1.480108 H 0.984936 3.676267 -1.357376 H -0.575986 4.858970 0.185528 H -2.138024 3.534719 1.599479 H -2.151551 1.075493 1.468185	

TS9f-10f	
HF=-3341.64043226 C 3.925781 0.798046 0.135966 C 4.159723 -0.218708 -0.969117 C 4.773579 -1.498472 -0.424281 O 2.963525 -0.491071 -1.679246 O 0.675497 -1.027188 0.008848 C -0.632859 -0.472173 -0.181761 C -1.591879 -1.228870 0.699640 Br -3.541734 -0.939353 -0.729132 C 0.898568 -1.441570 1.328292 O 2.046860 -1.731398 1.622602 O -0.170524 -1.460901 2.014473 C -0.587048 1.027375 0.022058 H 4.835053 0.215520 -1.725587 H 3.251271 0.374898 0.894988 H 3.469249 1.713126 -0.265378 H 4.870167 1.066771 0.632229 H 4.100464 -1.939033 0.325591 H 5.743586 -1.299745 0.056185 H 4.926279 -2.225346 -1.233006 H 2.295804 -0.825463 -1.046671 H -1.673108 -2.298865 0.565594 H -2.178112 -0.787914 1.489757 H -0.868429 -0.686081 -1.230352 C 0.389312 1.736923 -0.684462 C 0.522896 3.112045 -0.532713 C -0.315882 3.803452 0.339558 C -1.284360 3.104886 1.052891 C -1.414972 1.726092 0.898446 H 1.067546 1.197044 -1.348416 H 1.292830 3.643500 -1.092393 H -0.213541 4.881662 0.463055 H -1.946513 3.632262 1.739139 H -2.191857 1.205314 1.454359	 502.3(i)

10f	
HF=-3341.68107452 C 3.794496 0.414440 1.253206 C 4.609721 0.112757 0.005337 C 5.451547 -1.141529 0.175921 O 3.788425 0.019661 -1.146078 O 0.337624 -1.099315 -1.074301 C -0.836779 -0.472779 -0.500176 C -0.992929 -1.263509 0.796674 Br -4.153982 -0.836430 -0.016672 C 1.031233 -1.708143 -0.110046 O 2.144692 -2.159004 -0.260420 O 0.354622 -1.742723 1.036119 C -0.603921 1.003037 -0.307125 H 5.275195 0.967397 -0.199242 H 3.123416 -0.424952 1.488126 H 3.179278 1.312322 1.109998 H 4.449207 0.577341 2.122009 H 4.800151 -2.008571 0.359527 H 6.140738 -1.046253 1.027496 H 6.039205 -1.338016 -0.730083 H 3.251808 -0.794185 -1.066113 H -1.666810 -2.118617 0.682021 H -1.306539 -0.658683 1.649771 H -1.690886 -0.662560 -1.160087 C 0.648170 1.593175 -0.481053 C 0.813779 2.959213 -0.252019 C -0.264636 3.740174 0.150502 C -1.515513 3.147471 0.324301 C -1.691125 1.788247 0.094714 H 1.503705 1.003962 -0.814571 H 1.796825 3.408247 -0.397281 H -0.133144 4.807958 0.327619 H -2.368329 3.751388 0.634002 H -2.671614 1.314006 0.206354	

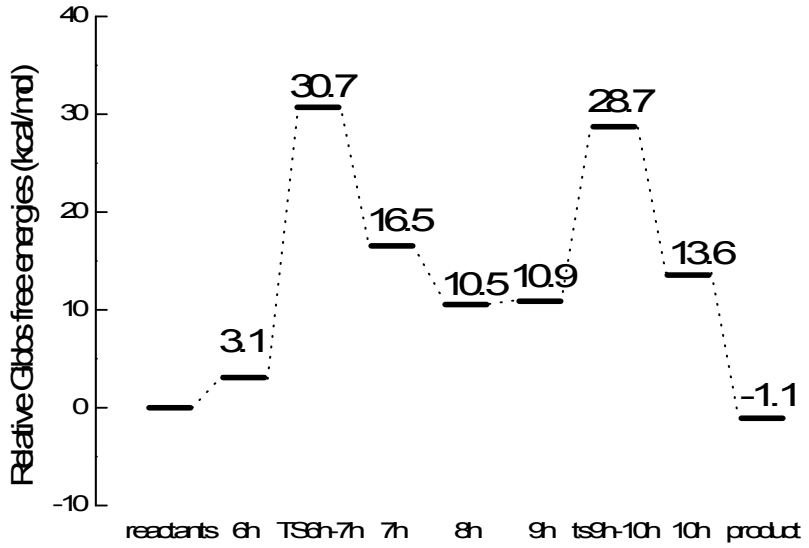
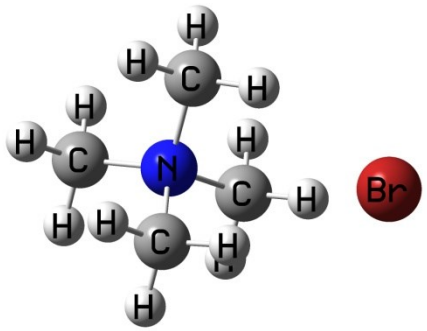
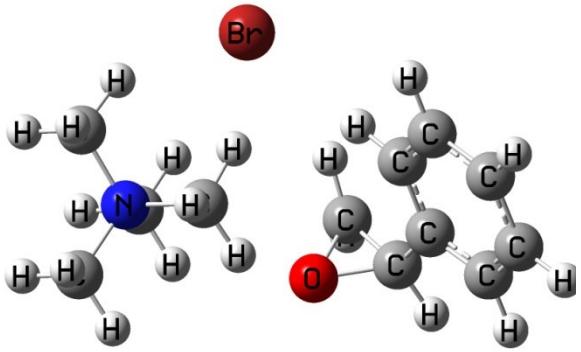
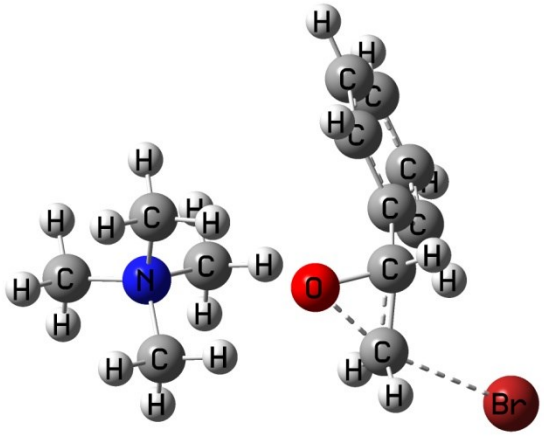


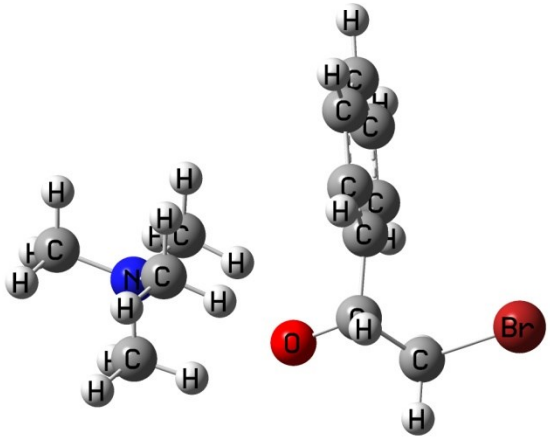
Figure S6. Relative Gibbs free energy profile of the target reaction catalyzed by **Ch** in solvent of toluene.

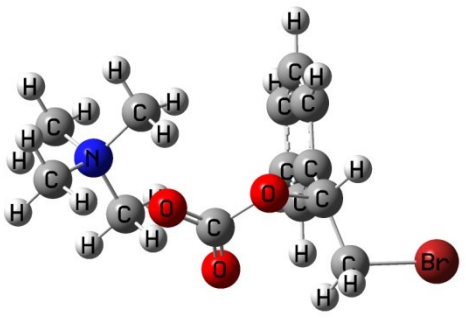
Optimized geometries of various species in the reaction catalyzed by Ch.

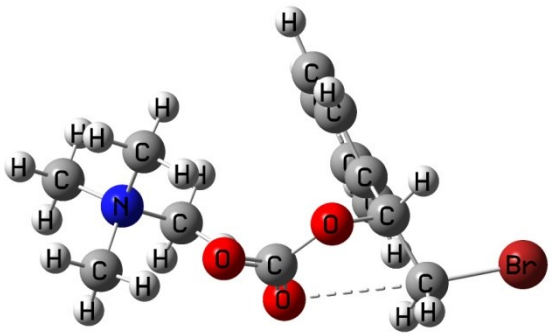
Ch	
HF=-2788.28398792 C 1.146950 -0.319351 1.376514 N 1.654910 -0.000169 0.000105 C 1.147088 -1.033328 -0.963753 C 3.139054 0.002074 -0.000745 C 1.144112 1.350572 -0.411922 Br -2.022976 0.000021 -0.000049 H 1.520288 1.566439 -1.417326 H 0.041420 1.302587 -0.397445 H 3.499209 -0.986624 0.301987 H 3.495756 0.235168 -1.009381 H 3.496005 0.760083 0.704162 H 1.524336 -1.307783 1.658655 H 1.523281 0.443738 2.065766 H 0.044232 -0.309145 1.330575 H 1.525198 -2.011064 -0.647494 H 0.044386 -0.999688 -0.930835 H 1.522948 -0.783139 -1.961304 H 1.519524 2.090081 0.303063	

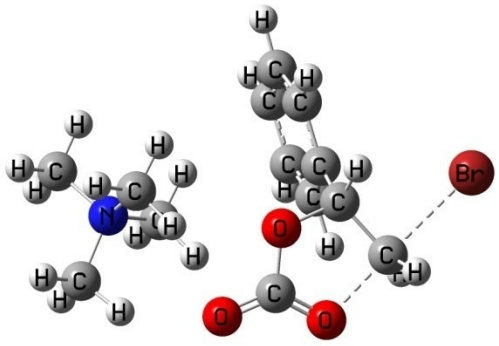
6h	
HF=-3172.97600610 C -2.455805 0.940593 -1.470162 C -1.881444 0.544931 -0.268631 C -2.517298 -0.400595 0.540146 C -3.741962 -0.931894 0.130782 C -4.323194 -0.530280 -1.069930 C -3.678809 0.405995 -1.874628 C -1.904713 -0.871371 1.808332 C -0.764614 -0.220326 2.454621 Br 1.347479 2.148319 0.248364 O -0.590289 -1.438756 1.731769 C 1.071626 -1.080958 -1.161106 N 2.450145 -1.332815 -0.619823 C 2.861300 -2.724102 -0.932982 C 2.452365 -1.133157 0.868490 C 3.400977 -0.358806 -1.244154 H 3.468073 -1.322247 1.232188 H 2.146757 -0.093191 1.059752 H -0.651452 -0.315251 3.537300 H -0.288438 0.656053 2.000184 H -2.576549 -1.454928 2.446604 H 2.884875 -2.855673 -2.019761 H 3.856369 -2.906643 -0.513810 H 2.136834 -3.414711 -0.489504 H 1.078476 -1.310028 -2.232105 H 0.362311 -1.716102 -0.620788 H 0.841826 -0.021579 -0.978075 H 3.376145 -0.497362 -2.330114 H 3.067014 0.653663 -0.967659 H 4.406097 -0.559763 -0.858401 H -4.245589 -1.667324 0.760710 H -5.281219 -0.948606 -1.375949 H -4.133445 0.724216 -2.812097 H -1.946701 1.688297 -2.078340 H -0.937457 1.001059 0.036750 H 1.735015 -1.831486 1.310301	

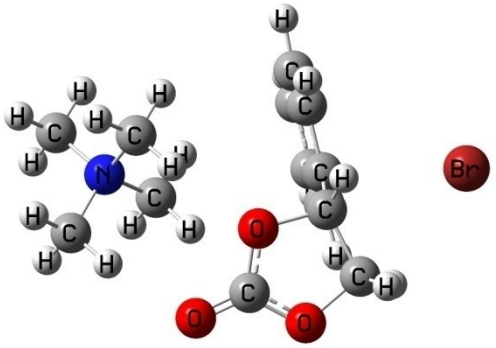
TS6h-7h	
HF=-3172.92192762 C 0.552913 2.705948 -1.200661 C 0.994398 1.573672 -0.515491 C 0.412004 1.231591 0.705986 C -0.568532 2.065137 1.255106 C -0.992413 3.204424 0.578752 C -0.438278 3.522606 -0.662595 C 0.721786 -0.055534 1.417153 C 1.096002 -1.232432 0.661929 Br 3.464094 -0.958676 -0.339773 O -0.400738 -0.896495 1.549120 C -2.138349 -0.222490 -1.141636 N -3.066968 -1.118184 -0.379148 C -3.366274 -0.493742 0.950900 C -2.400615 -2.442730 -0.153493 C -4.324966 -1.308103 -1.146946 H -3.097752 -3.089950 0.388615 H -2.161280 -2.879819 -1.128362 H 1.506924 -2.087144 1.179341 H 0.774764 -1.341372 -0.367638 H 1.279037 0.095560 2.355255 H -3.811058 0.491902 0.778168 H -4.070343 -1.141517 1.483522 H -2.412636 -0.411145 1.491969 H -2.638060 0.735040 -1.322429 H -1.247794 -0.063815 -0.526150 H -1.882992 -0.707330 -2.089411 H -4.802383 -0.334103 -1.294334 H -4.088245 -1.757365 -2.116773 H -4.991595 -1.968250 -0.582968 H -1.008460 1.802693 2.219589 H -1.748982 3.852758 1.021362 H -0.766967 4.413117 -1.197572 H 1.007109 2.961579 -2.157673 H 1.800479 0.952887 -0.913969 H -1.494421 -2.260894 0.438567	 511.4(i)

7h	
HF=-3172.95555625 C 0.396132 2.580332 -1.281096 C 0.643379 1.221911 -1.116448 C 0.568876 0.621836 0.144880 C 0.272497 1.432721 1.240215 C 0.027935 2.797704 1.086542 C 0.086458 3.378006 -0.178020 C 0.620895 -0.896524 0.298875 C 1.787471 -1.514411 -0.459545 Br 3.512594 -0.751272 0.101982 O -0.534005 -1.460556 -0.146016 C -2.778163 0.270792 -0.949262 N -3.520204 -0.626258 0.000883 C -2.895992 -0.524064 1.361158 C -3.386594 -2.041490 -0.476356 C -4.949060 -0.236472 0.062528 H -3.941604 -2.688461 0.211753 H -3.816153 -2.106881 -1.481757 H 1.839913 -2.587644 -0.259701 H 1.709695 -1.356441 -1.540740 H 0.820517 -1.089887 1.385665 H -2.946574 0.520086 1.687952 H -3.460729 -1.168526 2.043919 H -1.851961 -0.863658 1.230820 H -2.804665 1.293578 -0.556683 H -1.744436 -0.117188 -0.985178 H -3.277709 0.218347 -1.922945 H -5.021509 0.800853 0.405069 H -5.390292 -0.328508 -0.935696 H -5.472952 -0.896622 0.761970 H 0.233585 0.979133 2.233874 H -0.195452 3.412146 1.959266 H -0.095483 4.444877 -0.304356 H 0.463140 3.028013 -2.273028 H 0.875046 0.609039 -1.989120 H -2.312695 -2.281521 -0.479329	

8h	
HF=-3361.54410025 C -0.439412 3.216128 -0.010100 C 0.007522 2.437269 -1.076669 C 0.628357 1.211681 -0.843615 C 0.812875 0.744694 0.458182 C 0.356037 1.531321 1.518995 C -0.263818 2.757433 1.294939 C 1.412211 -0.607425 0.794652 O 0.404031 -1.523078 1.208648 C 2.342504 -1.199801 -0.245362 Br 3.986771 -0.145473 -0.308118 C -4.270656 -1.519397 -0.083803 N -3.733411 -0.133108 -0.274895 C -4.848452 0.824436 -0.490534 C -2.833255 -0.120006 -1.475164 C -2.968439 0.270254 0.952027 H -4.933537 -1.513719 0.788069 H -4.830416 -1.797576 -0.982970 H 2.630367 -2.211890 0.050271 H 1.935817 -1.225243 -1.254498 H 2.006330 -0.475809 1.711972 H -2.470514 1.228105 0.760215 H -3.682078 0.368050 1.777096 H -2.240336 -0.517535 1.180034 H -2.414198 0.887439 -1.578621 H -2.017623 -0.849192 -1.341326 H -3.439648 -0.374256 -2.351196 H -4.431166 1.829128 -0.616594 H -5.402344 0.534697 -1.389408 H -5.514027 0.803583 0.378425 H 0.491227 1.164824 2.538194 H -0.593330 3.362551 2.139262 H -0.904182 4.184717 -0.193798 H -0.111807 2.794416 -2.099684 H 0.963055 0.612842 -1.687854 H -3.411704 -2.187471 0.086220 C -0.538244 -1.968345 0.260951 O -1.534874 -2.492957 0.788959 O -0.296207 -1.741938 -0.939158	

9h	
HF=-3361.54482601 C -3.936334 -1.613172 -0.795516 N -3.783016 -0.193328 -0.334742 C -3.438847 -0.183490 1.125057 C -2.691221 0.467006 -1.126381 C -5.052927 0.548592 -0.543392 O -1.463744 -2.513721 0.772958 C -0.519103 -1.890333 0.258446 O 0.467336 -1.519100 1.187554 C 1.434053 -0.564462 0.769902 C 2.340469 -1.122492 -0.310534 Br 4.065000 -0.203750 -0.288398 O -0.358286 -1.517152 -0.920911 C 0.790182 0.777461 0.479150 H -3.010338 -2.155603 -0.546433 H -4.787008 -2.053874 -0.264483 H 2.552917 -2.172718 -0.095806 H 1.939155 -1.041237 -1.320384 H 2.051950 -0.439304 1.672959 H -3.237940 0.850479 1.425305 H -4.295055 -0.585493 1.677178 H -2.564918 -0.829295 1.285829 H -2.515944 1.465789 -0.710438 H -1.781137 -0.150642 -1.073487 H -3.028853 0.541119 -2.165675 H -4.917555 1.584995 -0.217330 H -5.310246 0.524031 -1.607106 H -5.847911 0.073954 0.040626 H -4.124275 -1.603696 -1.873924 C 0.036169 1.360535 1.502031 C -0.593720 2.589028 1.324058 C -0.474840 3.260271 0.107473 C 0.263728 2.682637 -0.923126 C 0.885418 1.449313 -0.739344 H -0.050696 0.833300 2.453646 H -1.156166 3.036049 2.144361 H -0.943027 4.234530 -0.032199 H 0.364478 3.196983 -1.878373 H 1.448047 1.009575 -1.560874	

TS9h-10h	
HF=-3361.50948970 C 4.499887 -1.064426 0.434766 N 3.747054 0.052975 -0.217082 C 3.158241 -0.447323 -1.503237 C 2.653431 0.505171 0.704594 C 4.656437 1.195059 -0.495877 O 1.721042 -2.575893 0.373016 C 0.547431 -2.206868 0.293156 O 0.254136 -1.305023 -0.704554 C -1.045824 -0.686222 -0.553730 C -1.902848 -1.527227 0.362837 O -0.445612 -2.509855 1.019171 C -0.808895 0.727818 -0.088749 Br -3.874851 -0.152785 -0.280784 H 3.793072 -1.883383 0.612132 H 5.304455 -1.382083 -0.236415 H -2.409328 -2.398137 -0.031153 H -2.166458 -1.222332 1.364542 H -1.478134 -0.679324 -1.558850 H 2.546616 0.349102 -1.939272 H 3.984013 -0.712868 -2.171660 H 2.532896 -1.315909 -1.271602 H 2.041972 1.256635 0.193652 H 2.048249 -0.367813 0.956077 H 3.113363 0.931531 1.602320 H 4.079453 1.997583 -0.966513 H 5.085578 1.549696 0.446641 H 5.453494 0.863017 -1.168597 H 4.918826 -0.697341 1.377389 C -0.592108 1.723904 -1.040640 C -0.212028 3.007126 -0.655529 C -0.048057 3.309840 0.695683 C -0.272589 2.321362 1.653021 C -0.653081 1.041041 1.261547 H -0.744852 1.489696 -2.095529 H -0.068506 3.779678 -1.410430 H 0.232202 4.317049 1.001606 H -0.168275 2.553732 2.712350 H -0.824755 0.278764 2.022211	 524.7(i)

10h	
HF=-3361.52951674 C -1.640955 -1.934208 0.402461 O -0.509275 -2.674079 0.952652 C 0.594303 -2.383512 0.284466 O 0.365549 -1.480346 -0.677710 C -0.994450 -0.898221 -0.507964 O 1.695397 -2.833975 0.512581 C -0.796145 0.487966 0.031221 Br -3.803995 0.157714 -0.418901 C 4.273966 -1.048608 -0.114294 N 3.623935 0.285629 -0.312625 C 2.860995 0.275916 -1.601248 C 2.686851 0.551925 0.827295 C 4.657750 1.354943 -0.359606 H 3.489011 -1.813707 -0.047581 H 4.941327 -1.240124 -0.960675 H -2.278841 -2.632064 -0.145781 H -2.209437 -1.508876 1.229540 H -1.435766 -0.873856 -1.505265 H 2.379732 1.251315 -1.727601 H 3.566174 0.084528 -2.416328 H 2.095953 -0.504957 -1.547357 H 2.177622 1.508598 0.660804 H 1.951090 -0.253499 0.866812 H 3.270587 0.578997 1.752861 H 4.161590 2.321071 -0.495926 H 5.216799 1.352891 0.581253 H 5.335680 1.160024 -1.196562 H 4.848301 -1.018618 0.817200 C -0.512705 1.518311 -0.868429 C -0.148040 2.780683 -0.413896 C -0.049953 3.028770 0.956867 C -0.326542 2.003466 1.860300 C -0.695755 0.743259 1.399309 H -0.636272 1.331042 -1.936693 H 0.024823 3.584872 -1.129069 H 0.209803 4.023349 1.317492 H -0.277599 2.192550 2.932052 H -0.927561 -0.039881 2.121648	

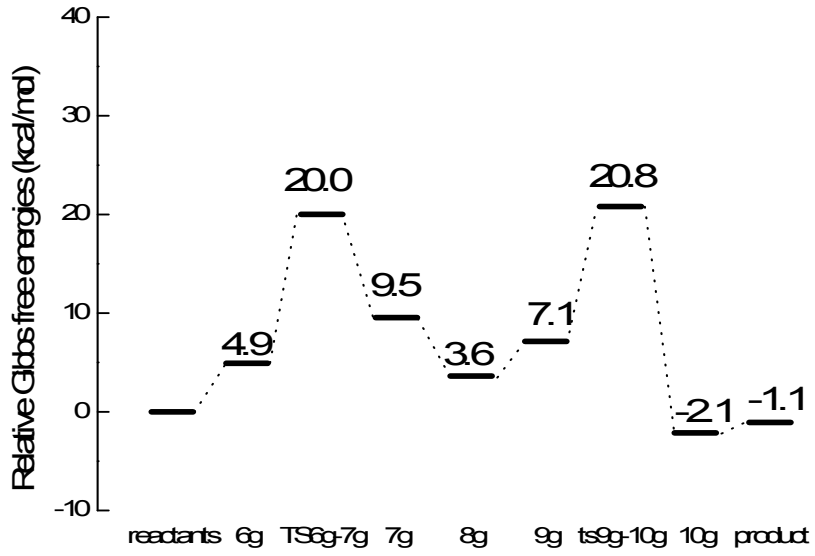
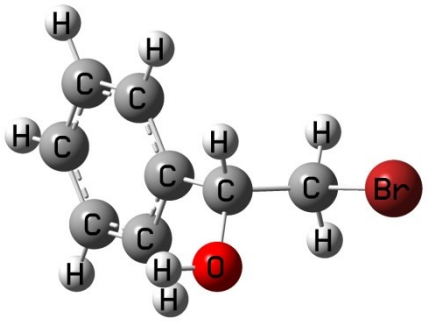
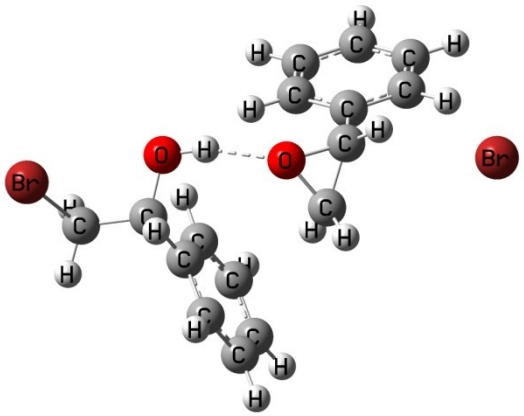
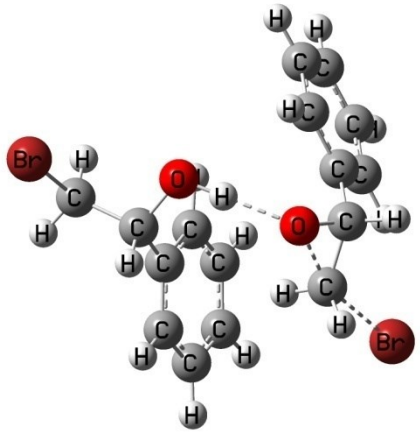


Figure S7. Relative Gibbs free energy profile of the target reaction catalyzed by **Cg** in solvent of toluene.

Optimized geometries of various species in the reaction catalyzed by Cg.

Cg	
HF=-2959.33106745 C 1.996657 -1.141405 0.592251 C 1.332437 0.047303 0.287810 C 2.022412 1.067428 -0.369996 C 3.364087 0.904073 -0.702482 C 4.022905 -0.283996 -0.393202 C 3.337168 -1.307410 0.256472 C -0.131194 0.205312 0.634087 C -0.963060 -0.131260 -0.580954 Br -2.859447 -0.235810 -0.185759 O -0.464214 1.523781 1.011097 H -0.387722 -0.505861 1.441341 H -0.837914 0.639162 -1.350173 H -0.675383 -1.104305 -0.989440 H 0.025633 1.753890 1.813032 H 1.501436 1.996826 -0.600936 H 3.897492 1.707249 -1.209009 H 5.073071 -0.409483 -0.652163 H 3.849141 -2.235436 0.506641 H 1.460132 -1.939228 1.109579	

6g	
HF=-5918.13302933 C -1.181484 2.143629 0.229980 C -2.186833 1.252565 -0.149509 C -3.525685 1.575984 0.101417 C -3.840122 2.773758 0.734557 C -2.834650 3.661810 1.116902 C -1.503201 3.341757 0.864581 C -1.890121 -0.039386 -0.818279 C -1.180988 -1.102984 -0.115609 O -0.513686 -0.334735 -1.120649 O 2.038408 0.735806 -0.751542 C 2.642591 -0.393547 -0.190979 H 2.609657 -1.249204 -0.893911 C 4.088153 -0.054080 0.087313 Br 5.109557 0.300205 -1.528061 C 2.002006 -0.822099 1.114006 Br -4.956977 -1.491368 -1.188997 H 4.150603 0.853033 0.698973 H 4.595900 -0.877446 0.598509 H 1.115890 0.491078 -0.985517 H -1.386158 -2.140530 -0.384426 H -0.828667 -0.920642 0.904165 H -2.604019 -0.362924 -1.580851 H -4.301153 0.866775 -0.207009 H -4.884907 3.016688 0.928486 H -3.088561 4.601468 1.608542 H -0.708344 4.031998 1.148959 H -0.139269 1.905770 0.018187 C 1.546359 0.132928 2.024293 C 0.938504 -0.261488 3.212073 C 0.801780 -1.615839 3.512812 C 1.270195 -2.573249 2.616383 C 1.867095 -2.175417 1.422949 H 1.629289 1.189657 1.769322 H 0.555462 0.491636 3.899603 H 0.311154 -1.924146 4.434986 H 1.148516 -3.633280 2.835998 H 2.204910 -2.923823 0.703190	

TS6g-7g	
HF=-5918.11375214 C -0.501944 2.746362 -0.574201 C -1.554702 1.829224 -0.589033 C -2.517942 1.884532 0.422017 C -2.422027 2.843605 1.427888 C -1.363210 3.750594 1.444645 C -0.401531 3.698148 0.436971 C -1.626750 0.835194 -1.724475 C -1.801986 -0.589198 -1.432473 Br -4.016357 -1.215681 -0.456432 O -0.412051 0.414606 -2.232305 O 1.948902 0.532269 -0.883389 C 2.201706 -0.692968 -0.273244 H 2.464922 -1.469939 -1.020990 C 3.373775 -0.521319 0.664618 Br 5.045748 -0.091494 -0.240953 C 1.032156 -1.208151 0.543623 H 3.186935 0.306128 1.357311 H 3.568542 -1.439477 1.227232 H 1.083114 0.486785 -1.381274 H -2.019316 -1.244354 -2.264207 H -1.292495 -0.997578 -0.569325 H -2.328672 1.207265 -2.498170 H -3.334889 1.161378 0.416035 H -3.176972 2.873219 2.214759 H -1.286412 4.493151 2.239774 H 0.435881 4.396484 0.441542 H 0.260621 2.680426 -1.349575 C 0.324959 -0.347911 1.388161 C -0.805549 -0.798803 2.062014 C -1.243769 -2.111826 1.900641 C -0.516634 -2.986724 1.098111 C 0.617239 -2.535018 0.426243 H 0.618571 0.701277 1.454425 H -1.382393 -0.104223 2.671659 H -2.174765 -2.436971 2.361472 H -0.866846 -4.007767 0.950599 H 1.157952 -3.204105 -0.246293	 4 02.4(i)

7g

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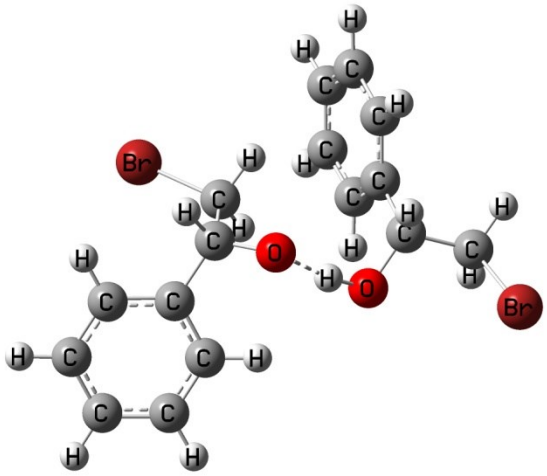
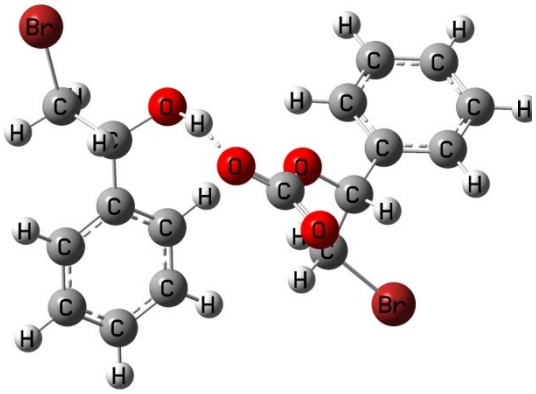
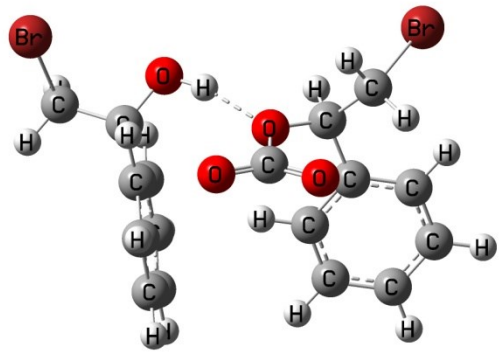
C 1.833153 -2.468003 0.443841
C 2.454183 -1.591191 -0.448118
C 3.837443 -1.685330 -0.615995
C 4.589701 -2.607048 0.108687
C 3.962659 -3.459994 1.015147
C 2.579725 -3.385566 1.178570
C 1.617021 -0.573514 -1.223145
C 1.530024 0.745761 -0.440570
Br 3.231698 1.730511 -0.159195
O 0.342678 -0.952946 -1.452788
O -1.535941 -0.947940 0.281092
C -2.318013 0.082125 -0.208548
H -2.406659 0.027268 -1.312438
C -3.702999 -0.005000 0.396160
Br -4.691526 -1.589101 -0.162725
C -1.763752 1.454426 0.142725
H -3.633614 -0.066571 1.488217
H -4.324079 0.851692 0.113653
H -0.723801 -1.011404 -0.352792
H 0.887232 1.448266 -0.978510
H 1.131046 0.571847 0.565407
H 2.190288 -0.351186 -2.160357
H 4.326661 -1.024401 -1.334085
H 5.669633 -2.662443 -0.036928
H 4.546946 -4.183832 1.584837
H 2.076969 -4.058686 1.874544
H 0.747956 -2.428104 0.537479
C -1.206817 1.679423 1.403226
C -0.631987 2.907109 1.713450
C -0.633178 3.938124 0.774552
C -1.205150 3.727787 -0.477604
C -1.772836 2.493087 -0.786724
H -1.166627 0.850491 2.110551
H -0.165487 3.057070 2.687206
H -0.159873 4.891565 1.007294
H -1.187305 4.520715 -1.225388
H -2.184273 2.312265 -1.781868

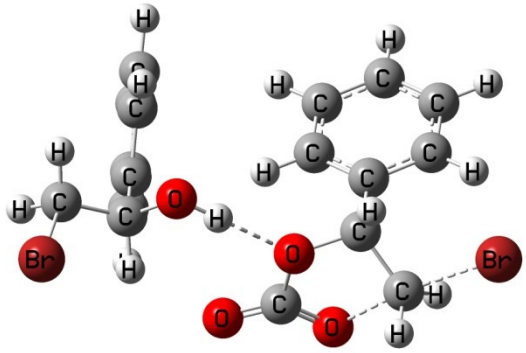


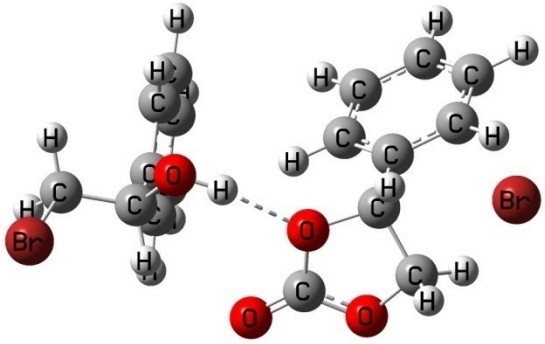
8g

HF=-6106.72024707
C -1.940013 -2.254383 -0.711848
C -2.799473 -1.516394 0.106000
C -4.134285 -1.908566 0.213985
C -4.610812 -3.009824 -0.492661
C -3.751068 -3.736714 -1.312635
C -2.413777 -3.357019 -1.416645
C -2.295132 -0.305448 0.847287
C -2.334409 0.956048 -0.007380
Br -4.147709 1.594635 -0.344084
O -0.945948 -0.502997 1.183839
C -0.451870 0.186984 2.357750
O 0.776031 0.019576 2.471244
O -1.279626 0.801783 3.026973
O 2.095061 -0.882603 0.321399
C 3.003678 0.159898 0.218588
H 3.483268 0.364201 1.197290
C 4.069184 -0.253330 -0.775980
Br 5.189143 -1.704752 -0.111125
C 2.393700 1.463153 -0.279779
H 3.595565 -0.624609 -1.691282
H 4.756214 0.560942 -1.020080
H 1.518720 -0.700432 1.117199
H -1.826211 1.768484 0.520205
H -1.880442 0.784426 -0.990293
H -2.890679 -0.128594 1.756234
H -4.800403 -1.340540 0.864822
H -5.656074 -3.303944 -0.397303
H -4.119384 -4.602526 -1.863137
H -1.731654 -3.930361 -2.044221
H -0.888864 -1.969677 -0.764693
C 1.063309 1.524011 -0.688471
C 0.523969 2.723385 -1.149802
C 1.304479 3.874512 -1.203062
C 2.630200 3.825151 -0.775676
C 3.169474 2.624461 -0.326389
H 0.458666 0.619435 -0.616011
H -0.520636 2.762818 -1.461566
H 0.876331 4.812256 -1.556541
H 3.245206 4.725158 -0.792353
H 4.203124 2.595439 0.026693



9g	
HF=-6106.71440391 C -1.732298 1.880000 0.019625 C -2.495728 0.710478 -0.008705 C -3.881189 0.819339 -0.147635 C -4.492039 2.067720 -0.235613 C -3.725421 3.228690 -0.199435 C -2.341505 3.127098 -0.073485 C -1.801718 -0.637958 0.041069 C -2.655505 -1.764327 0.618180 Br -3.662430 -2.703752 -0.800053 O -0.545341 -0.578676 0.673324 C -0.515888 -0.332280 2.132444 O 0.636106 -0.140549 2.516951 O -1.623643 -0.375110 2.670581 O 1.803570 -0.964106 -0.715074 C 2.579029 -0.027861 -0.015646 H 2.549118 -0.231865 1.068181 C 3.997904 -0.113965 -0.522765 Br 4.865407 -1.811000 -0.115863 C 2.111919 1.398703 -0.237392 H 4.026925 -0.021333 -1.614271 H 4.624875 0.661021 -0.071872 H 0.935884 -0.987045 -0.250051 H -2.018309 -2.529608 1.063975 H -3.395592 -1.437168 1.348393 H -1.551508 -0.914310 -0.998547 H -4.500844 -0.075941 -0.191201 H -5.576294 2.129975 -0.332125 H -4.202826 4.206509 -0.267124 H -1.723338 4.024975 -0.041488 H -0.650008 1.807923 0.134565 C 1.856221 1.868007 -1.528462 C 1.471354 3.188864 -1.736751 C 1.339723 4.056018 -0.652685 C 1.574288 3.588468 0.638555 C 1.955906 2.263917 0.845912 H 1.929902 1.174885 -2.367322 H 1.261358 3.541548 -2.746536 H 1.030992 5.089372 -0.813813 H 1.436582 4.251236 1.492751 H 2.083035 1.868170 1.854018	

TS9g-10g	
HF=-6106.69727435 C -1.292804 1.795489 -0.187203 C -2.310614 0.844835 -0.271405 C -3.597869 1.259078 -0.630303 C -3.857778 2.600658 -0.889260 C -2.840348 3.548305 -0.795590 C -1.558235 3.138946 -0.444131 C -2.027985 -0.623025 -0.013460 C -2.943604 -1.233817 1.023460 Br -4.671124 -2.123031 -0.471262 O -0.688547 -0.824811 0.422866 C -0.555249 -0.663696 1.818065 O 0.584763 -0.589013 2.246911 O -1.677087 -0.630052 2.404844 O 1.837079 -0.849319 -0.944321 C 2.711132 -0.238190 -0.030562 H 2.599152 -0.683473 0.971334 C 4.121607 -0.446043 -0.527552 Br 4.690253 -2.307240 -0.461551 C 2.476956 1.256019 0.081452 H 4.214416 -0.140468 -1.575527 H 4.839336 0.111137 0.081783 H 0.957251 -0.911577 -0.518721 H -2.775280 -2.254949 1.335994 H -3.719234 -0.664948 1.516296 H -2.114096 -1.191243 -0.947241 H -4.391942 0.517147 -0.723838 H -4.866702 2.905703 -1.167472 H -3.046899 4.599710 -0.996794 H -0.748194 3.863639 -0.363001 H -0.283768 1.488281 0.087880 C 2.378505 2.042321 -1.069693 C 2.193064 3.417564 -0.972097 C 2.103546 4.022023 0.281562 C 2.182709 3.241272 1.432276 C 2.366710 1.863272 1.332661 H 2.411285 1.558775 -2.046577 H 2.106599 4.019478 -1.876744 H 1.951200 5.098664 0.360456 H 2.077432 3.702478 2.413892 H 2.371822 1.236601 2.225003	 496.7(i)

10g	
HF=-6106.73118276 C -1.360595 1.914741 -0.090509 C -2.304445 0.889470 -0.161433 C -3.605335 1.176282 -0.592459 C -3.947383 2.475024 -0.949625 C -3.007349 3.502284 -0.870884 C -1.714382 3.216204 -0.445962 C -1.996685 -0.529452 0.239190 C -2.616850 -0.952689 1.566986 O -1.559976 -0.663290 2.515374 C -0.393954 -0.641805 1.873326 O -0.584196 -0.685890 0.535899 O 0.690424 -0.591519 2.390484 O 1.887490 -0.908600 -1.006523 C 2.722607 -0.248133 -0.089319 C 2.427440 1.234951 0.008349 H 2.628325 -0.689499 0.917830 C 4.144872 -0.401885 -0.573030 Br 4.778778 -2.239494 -0.500096 Br -4.744451 -2.253876 -0.569773 H 4.229617 -0.088087 -1.619665 H 4.833684 0.183926 0.042914 H 0.991979 -0.939817 -0.622936 H -2.843823 -2.023515 1.593573 H -3.504039 -0.379753 1.842903 H -2.271541 -1.242642 -0.547005 H -4.324609 0.354548 -0.675694 H -4.960110 2.684967 -1.293141 H -3.280532 4.520389 -1.149005 H -0.964811 4.005948 -0.386939 H -0.337981 1.706453 0.227323 C 2.455241 1.875130 1.247644 C 2.232339 3.247093 1.338203 C 1.979067 3.989998 0.187288 C 1.936743 3.353068 -1.051978 C 2.160684 1.982562 -1.140886 H 2.616546 1.280625 2.147507 H 2.238914 3.733901 2.312865 H 1.794729 5.062000 0.257669 H 1.712897 3.924781 -1.952436 H 2.097279 1.471056 -2.101618	

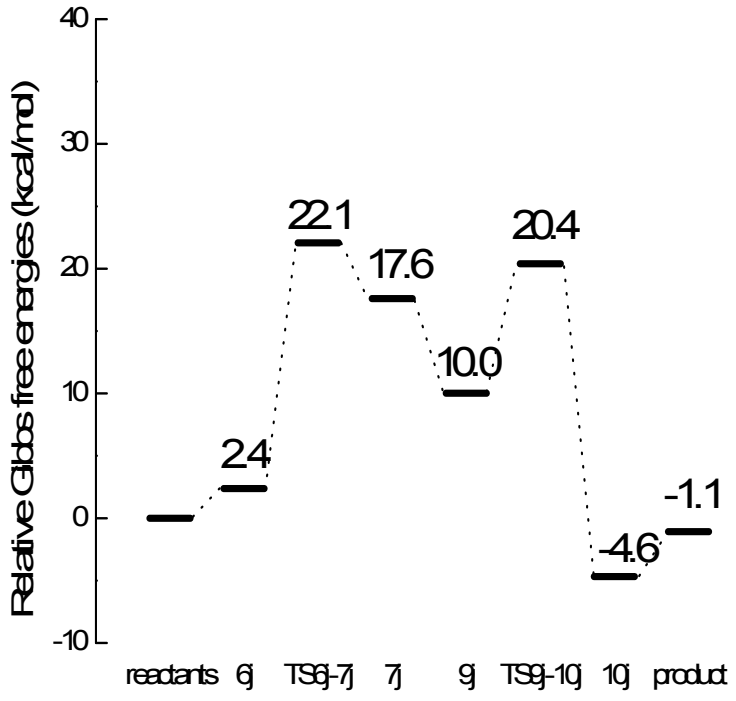
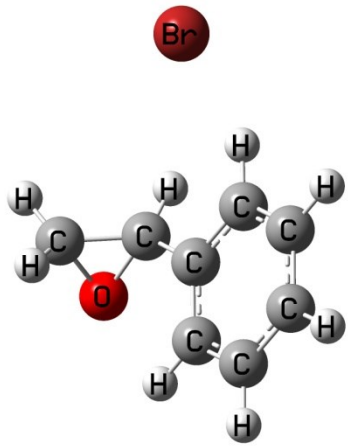
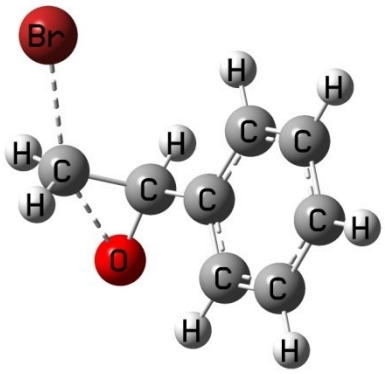
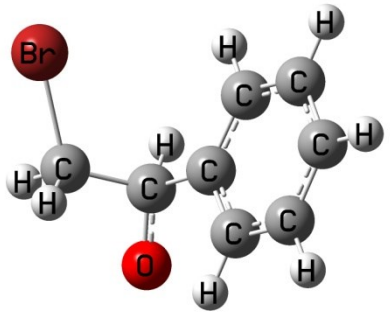


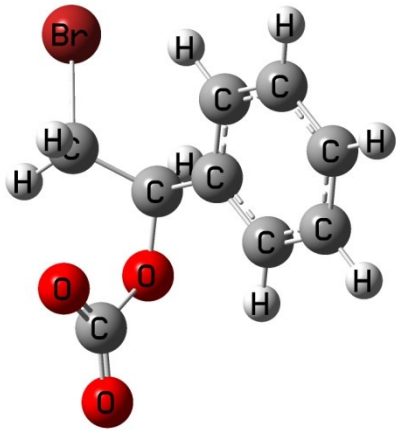
Figure S8. Relative Gibbs free energy profile of the target reaction catalyzed by **Cj** in solvent of toluene.

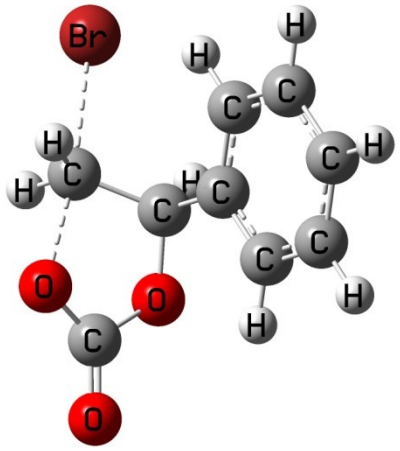
Optimized geometries of various species in the target reaction catalyzed by Cj.

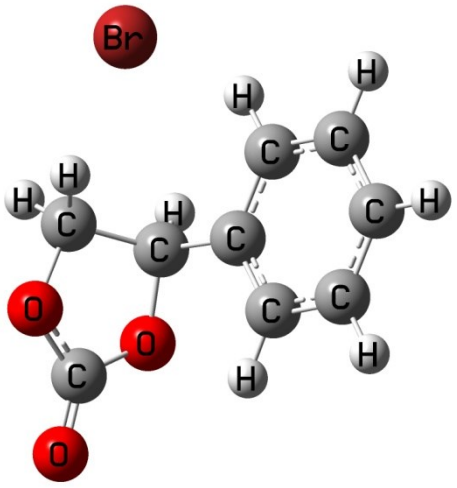
6j	
HF=-2958.78200772 C -3.554759 -0.344853 -0.002274 C -2.575932 0.638899 -0.126884 C -1.222997 0.294414 -0.130411 C -0.852839 -1.051515 -0.025712 C -1.835138 -2.028869 0.097510 C -3.186915 -1.684089 0.107700 C -0.161609 1.324438 -0.258682 O -0.586080 2.672052 -0.483817 C 0.018831 2.354601 0.760776 Br 2.758680 -0.552506 -0.015019 H 1.018135 2.764339 0.923360 H -0.658632 2.374883 1.620406 H 0.740464 1.015706 -0.795597 H 0.212970 -1.304151 -0.031581 H -1.539775 -3.074852 0.182432 H -3.950838 -2.456890 0.201427 H -4.608933 -0.064653 -0.003326 H -2.850391 1.688758 -0.233049	

TS6j-7j	
HF=-2958.74929527 C 3.257252 0.009358 -0.729208 C 2.212474 0.883601 -0.432250 C 1.126697 0.458162 0.330647 C 1.114399 -0.849536 0.823229 C 2.147703 -1.728682 0.516886 C 3.228075 -1.300939 -0.256511 C 0.011152 1.423439 0.659701 O 0.179979 2.716023 0.261268 C -1.141063 1.412356 -0.250884 Br -2.362060 -0.700132 -0.178092 H -2.018641 1.964676 0.059080 H -0.928616 1.347710 -1.312983 H -0.288249 1.270851 1.720934 H 0.262488 -1.180475 1.419118 H 2.114049 -2.754470 0.886076 H 4.041783 -1.988795 -0.490631 H 4.101845 0.353358 -1.328618 H 2.207462 1.917021 -0.779559	 413.6(i)

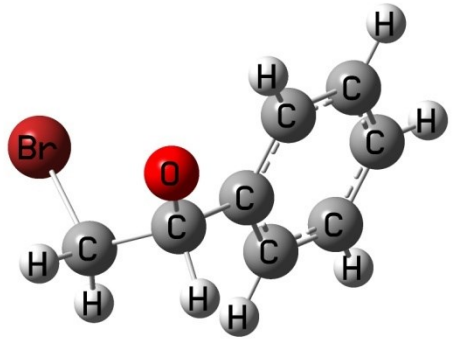
7j	
HF=-2958.75532756 C 3.116426 0.102110 -0.832803 C 2.029378 0.917443 -0.527221 C 1.012782 0.471270 0.318442 C 1.146303 -0.786806 0.909735 C 2.231475 -1.608471 0.611879 C 3.223071 -1.167745 -0.264370 C -0.157180 1.414307 0.626625 O 0.088331 2.703974 0.408199 C -1.344729 1.116426 -0.301931 Br -2.203988 -0.725976 -0.186768 H -2.164822 1.796267 -0.059975 H -1.053000 1.215594 -1.353154 H -0.491544 1.142311 1.671380 H 0.381568 -1.123458 1.612524 H 2.311524 -2.594179 1.074157 H 4.076908 -1.806509 -0.496449 H 3.898303 0.463681 -1.503871 H 1.928825 1.932448 -0.915468	

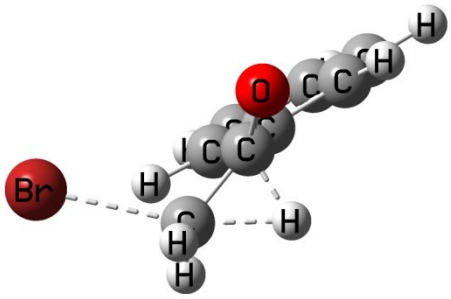
9j	
HF=-3147.35072813 C -2.285222 -0.297346 -0.523230 C -0.927699 -0.532653 -0.296362 C -0.537675 -1.788534 0.177517 C -1.481033 -2.781966 0.426164 C -2.833025 -2.540480 0.196601 C -3.228043 -1.292224 -0.279475 C 0.098860 0.542532 -0.614910 C 1.224201 0.631042 0.419516 Br 2.783029 -0.511714 -0.071815 O -0.478318 1.791069 -0.872409 C -1.039016 2.514055 0.271258 O -0.756897 2.021134 1.375812 O -1.690915 3.491696 -0.085334 H 1.633504 1.641055 0.449914 H 0.944751 0.313183 1.423215 H 0.565359 0.267066 -1.577026 H 0.517444 -2.000685 0.350909 H -1.153426 -3.751983 0.802131 H -3.573806 -3.316458 0.391531 H -4.284114 -1.083694 -0.453155 H -2.594790 0.683767 -0.881012	

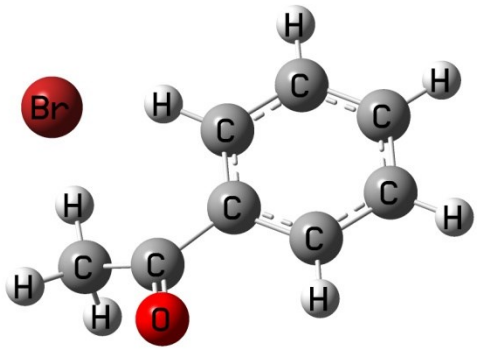
TS9j-10j	
HF=-3147.33949004 C -2.337394 -0.365386 -0.436094 C -0.960665 -0.544866 -0.297507 C -0.479426 -1.791050 0.118066 C -1.361062 -2.832401 0.388691 C -2.735276 -2.649107 0.247628 C -3.218064 -1.410797 -0.165903 C 0.003136 0.587476 -0.608654 C 0.955349 0.879772 0.531172 O -0.683124 1.774179 -0.952392 C -1.046199 2.526879 0.182631 O -0.466730 2.119725 1.238579 O -1.836517 3.438425 0.004079 Br 2.819647 -0.504148 -0.082404 H 1.600914 1.743847 0.459099 H 0.895715 0.364434 1.479711 H 0.588617 0.326914 -1.499826 H 0.595866 -1.943221 0.218632 H -0.968319 -3.796009 0.714431 H -3.425123 -3.465858 0.461620 H -4.290989 -1.250513 -0.274021 H -2.715765 0.603849 -0.757825	 478.7(i)

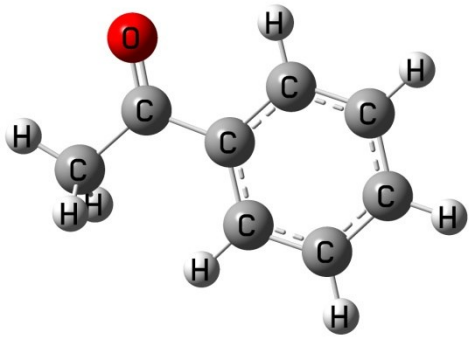
10j	
HF=-3147.38108060 O 0.972820 -2.185333 1.113804 C -0.174035 -1.356633 0.839396 C 0.241262 -0.632153 -0.435684 O 1.167378 -1.582276 -1.005784 C 1.658873 -2.370036 -0.024753 C 0.900634 0.706054 -0.237508 C 2.285505 0.863199 -0.284282 C 2.860327 2.112673 -0.058336 C 2.054266 3.212035 0.219639 C 0.669309 3.056161 0.265118 C 0.090522 1.811611 0.043902 O 2.587330 -3.117155 -0.156517 Br -3.077756 0.053586 -0.090422 H -1.051762 -1.993137 0.676928 H -0.350967 -0.695824 1.690742 H -0.618394 -0.539717 -1.105182 H -0.994958 1.676614 0.081878 H 0.029760 3.913006 0.475583 H 2.502779 4.190552 0.392260 H 3.943754 2.222657 -0.101399 H 2.921026 0.010978 -0.523001	

Optimized geometries of various species in the side reaction denoted as S1 in Chart 3.

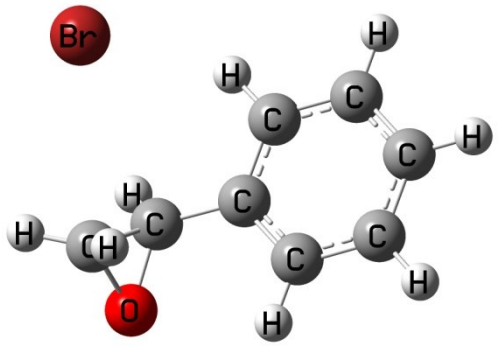
6 (same as 6j)	
TS6-7 (same as TS6j-7j)	
7 (same as 7j)	
11	
HF=-2958.74926315 C 3.252518 -0.852288 -0.245833 C 2.692730 -0.040334 -1.232279 C 1.532678 0.685919 -0.971180 C 0.921587 0.631257 0.279458 C 1.490985 -0.181598 1.261438 C 2.647280 -0.916698 1.010080 C -0.318891 1.515389 0.528957 C -1.474651 0.594494 1.001203 Br -1.948509 -0.822465 -0.300438 O -0.627492 2.340963 -0.441019 H -2.383264 1.196957 1.100053 H -1.271511 0.052130 1.935335 H -0.089261 2.018318 1.537547 H 1.030943 -0.225735 2.253152 H 3.077593 -1.545137 1.792413 H 4.160302 -1.422932 -0.449298 H 3.164598 0.021077 -2.215174 H 1.062935 1.347044 -1.701597	

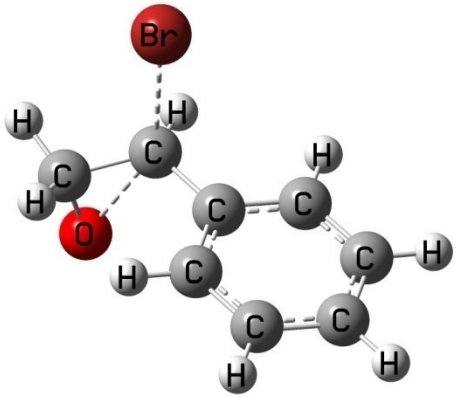
TS11-12	
HF=-2958.73008105 C 3.464873 -1.228867 -0.095173 C 3.601724 0.151026 -0.261196 C 2.490176 0.979335 -0.157319 C 1.228197 0.450661 0.124712 C 1.090320 -0.932188 0.263319 C 2.205792 -1.763602 0.163288 C 0.060185 1.417298 0.243105 C -1.089057 0.908373 1.003233 Br -2.550325 -0.544666 -0.205494 O -0.008635 2.377560 -0.584294 H -1.876362 1.637209 1.175179 H -0.910703 0.171297 1.783029 H 0.136607 1.792823 1.480478 H 0.099020 -1.362967 0.411572 H 2.083747 -2.842550 0.268268 H 4.335017 -1.881649 -0.175101 H 4.582282 0.580016 -0.473681 H 2.567583 2.056446 -0.306903	 -826.9(i)

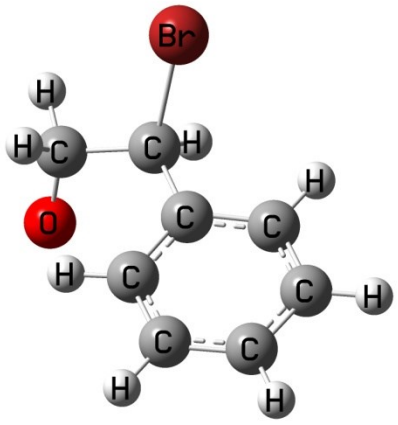
12	
HF=-2958.82023119 C 3.276527 -1.159120 -0.027688 C 3.241594 0.027293 -0.755927 C 2.116280 0.844643 -0.692297 C 1.006324 0.478916 0.071246 C 1.044748 -0.719521 0.791270 C 2.175401 -1.526831 0.745961 C -0.114405 1.471810 0.183675 C -0.812377 1.578269 1.514943 Br -2.262816 -0.751280 -0.317364 O -0.268460 2.329054 -0.672623 H -1.819026 1.976945 1.362476 H -0.882433 0.627139 2.047552 H -0.229343 2.287552 2.127597 H 0.161419 -1.038783 1.341667 H 2.187489 -2.465868 1.299365 H 4.157300 -1.801196 -0.065493 H 4.096548 0.322425 -1.365129 H 2.069743 1.781401 -1.246399	

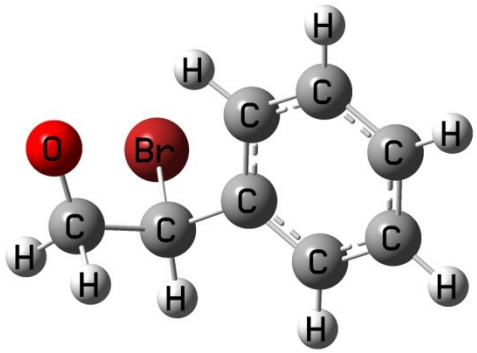
PHA	
HF=-384.71955362 C 2.582870 0.110114 0.000000 C 1.957975 -1.136966 -0.000025 C 0.572444 -1.217848 -0.000019 C -0.206636 -0.055588 0.000004 C 0.428413 1.191298 0.000016 C 1.817410 1.273069 0.000019 C -1.692370 -0.200829 0.000013 C -2.540492 1.044704 -0.000040 O -2.210770 -1.304169 0.000043 H -3.594391 0.753808 -0.000203 H -2.336408 1.662657 0.884505 H -2.336124 1.662729 -0.884474 H -0.157939 2.109117 0.000030 H 2.302913 2.247657 0.000042 H 3.669865 0.176004 0.000009 H 2.556769 -2.046319 -0.000047 H 0.063790 -2.180029 -0.000024	

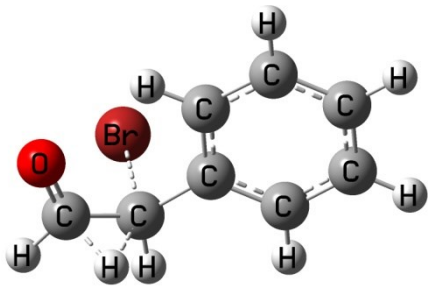
Optimized geometries of various species in the side reaction denoted as S2 in Chart 3.

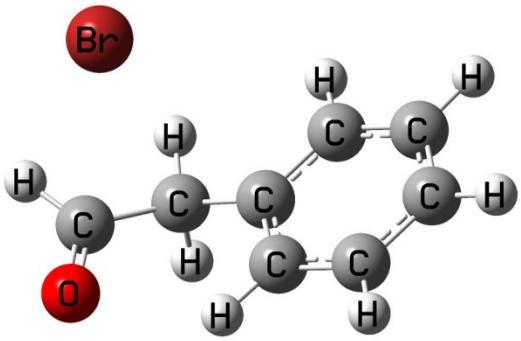
6' (6k)	
HF=-2958.78200845 C -3.554594 -0.345295 -0.002035 C -2.575914 0.638603 -0.126534 C -1.222915 0.294321 -0.130270 C -0.852561 -1.051555 -0.025827 C -1.834725 -2.029080 0.097216 C -3.186545 -1.684510 0.107588 C -0.161740 1.324601 -0.258561 O -0.586609 2.672014 -0.484293 C 0.018031 2.355189 0.760594 Br 2.758752 -0.552377 -0.014935 H 1.017124 2.765376 0.923341 H -0.659726 2.375447 1.619989 H 0.740529 1.015949 -0.795194 H 0.213268 -1.304089 -0.031719 H -1.539185 -3.075037 0.181851 H -3.950355 -2.457436 0.201182 H -4.608801 -0.065221 -0.002915 H -2.850536 1.688441 -0.232498	

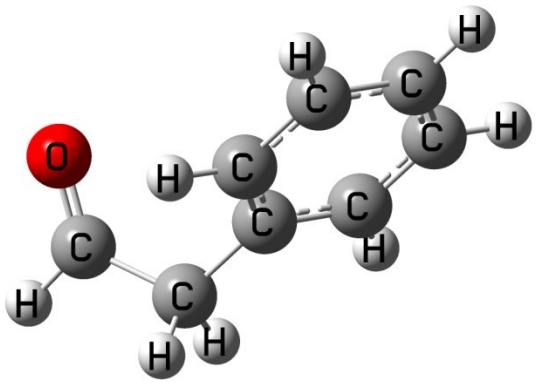
TS6'-7' (TS6k-7k)	
HF=-2958.74435384 C 2.610608 -0.095323 -1.260449 C 1.353070 0.441765 -1.021349 C 0.747059 0.309560 0.232275 C 1.423660 -0.403254 1.225421 C 2.680810 -0.949650 0.989224 C 3.282081 -0.796879 -0.257885 C -0.571066 0.888957 0.524515 O -0.167778 2.836441 0.453271 C -1.076218 2.060320 -0.198675 Br -1.990075 -0.978820 -0.136560 H -2.149642 2.252251 0.015551 H -0.974649 1.979863 -1.305662 H -0.892067 0.829152 1.561342 H 0.945218 -0.526169 2.198092 H 3.192065 -1.498108 1.780988 H 4.268534 -1.220573 -0.449030 H 3.072359 0.028381 -2.240652 H 0.832993 0.989389 -1.805674	 297.1 (i)

7' (7k)	
HF=-2958.74764277 C 2.848561 0.501765 -0.843510 C 1.536030 0.899741 -0.600361 C 0.707435 0.135648 0.226764 C 1.249351 -0.991617 0.851375 C 2.561182 -1.390388 0.615514 C 3.366914 -0.644834 -0.243105 C -0.698530 0.550825 0.524637 O -0.353404 2.828357 0.620829 C -1.128291 1.930099 0.022168 Br -1.949270 -0.887784 -0.248620 H -2.234540 2.004781 0.224690 H -1.068277 1.887199 -1.110885 H -0.902683 0.463873 1.599012 H 0.614469 -1.574246 1.521637 H 2.956709 -2.280659 1.106169 H 4.397995 -0.946667 -0.432235 H 3.481462 1.109579 -1.491344 H 1.150641 1.834287 -1.002889	

13	
HF=-2958.74363772 C 2.468832 0.315185 -1.308455 C 1.141831 0.427941 -0.909431 C 0.748296 -0.009110 0.363837 C 1.715314 -0.547521 1.214937 C 3.043653 -0.676441 0.810811 C 3.422854 -0.247855 -0.458787 C -0.632453 0.231355 0.851397 O -0.998085 2.360429 -0.307888 C -1.071796 1.728656 0.834519 Br -1.902430 -0.831091 -0.281929 H -0.386111 2.120511 1.666579 H -2.092283 1.696149 1.327835 H -0.780403 -0.185690 1.858280 H 1.417019 -0.872651 2.213950 H 3.779580 -1.110039 1.489206 H 4.460126 -0.342952 -0.783273 H 2.765897 0.672845 -2.295049 H 0.386704 0.893320 -1.539863	

TS13-14	
HF=-2958.73016504 C 2.577092 0.345025 -1.189340 C 1.308490 0.735368 -0.775187 C 0.786001 0.249640 0.431172 C 1.545270 -0.650166 1.187358 C 2.804536 -1.055094 0.761068 C 3.327148 -0.553162 -0.430491 C -0.516094 0.703005 0.930291 O -0.838088 2.741063 -0.373885 C -1.067387 2.026923 0.648127 Br -1.922368 -1.022859 -0.294424 H -0.219644 2.123863 1.594802 H -2.015446 2.172320 1.225097 H -0.872059 0.266559 1.862765 H 1.125484 -1.045862 2.113774 H 3.380169 -1.763280 1.357712 H 4.316801 -0.863909 -0.767572 H 2.980200 0.734572 -2.124515 H 0.701752 1.438064 -1.344142	 813.6(i)

14	
HF=-2958.80951743 C 2.652599 0.358458 -1.168044 C 1.538063 0.980947 -0.612792 C 0.979730 0.512846 0.579667 C 1.554853 -0.606899 1.184908 C 2.664147 -1.236358 0.629815 C 3.224648 -0.750635 -0.549413 C -0.161669 1.215914 1.262495 O -1.065345 2.503044 -0.565098 C -1.267554 1.767493 0.384786 Br -1.952537 -1.026367 -0.266539 H 0.240744 2.096765 1.800822 H -2.293458 1.605545 0.770906 H -0.610113 0.548797 2.009377 H 1.097891 -1.009752 2.089908 H 3.082423 -2.120327 1.112188 H 4.092653 -1.241909 -0.990432 H 3.067880 0.736780 -2.102873 H 1.074612 1.832014 -1.108780	

PHAD	
HF=-384.70365271 C -1.642836 -1.309752 0.231423 C -0.330010 -0.975980 0.543814 C 0.129561 0.332969 0.379159 C -0.750169 1.298993 -0.108420 C -2.066502 0.969114 -0.422629 C -2.515645 -0.336691 -0.252042 C 1.545138 0.690435 0.718113 O 2.415570 -0.787673 -0.989581 C 2.605750 0.049787 -0.143509 H 1.795913 0.412331 1.757614 H 3.640113 0.410401 0.074306 H 1.706191 1.779883 0.677006 H -0.400494 2.323760 -0.242724 H -2.741989 1.734810 -0.801380 H -3.544289 -0.597414 -0.496582 H -1.986896 -2.334600 0.362377 H 0.355165 -1.741029 0.910577	

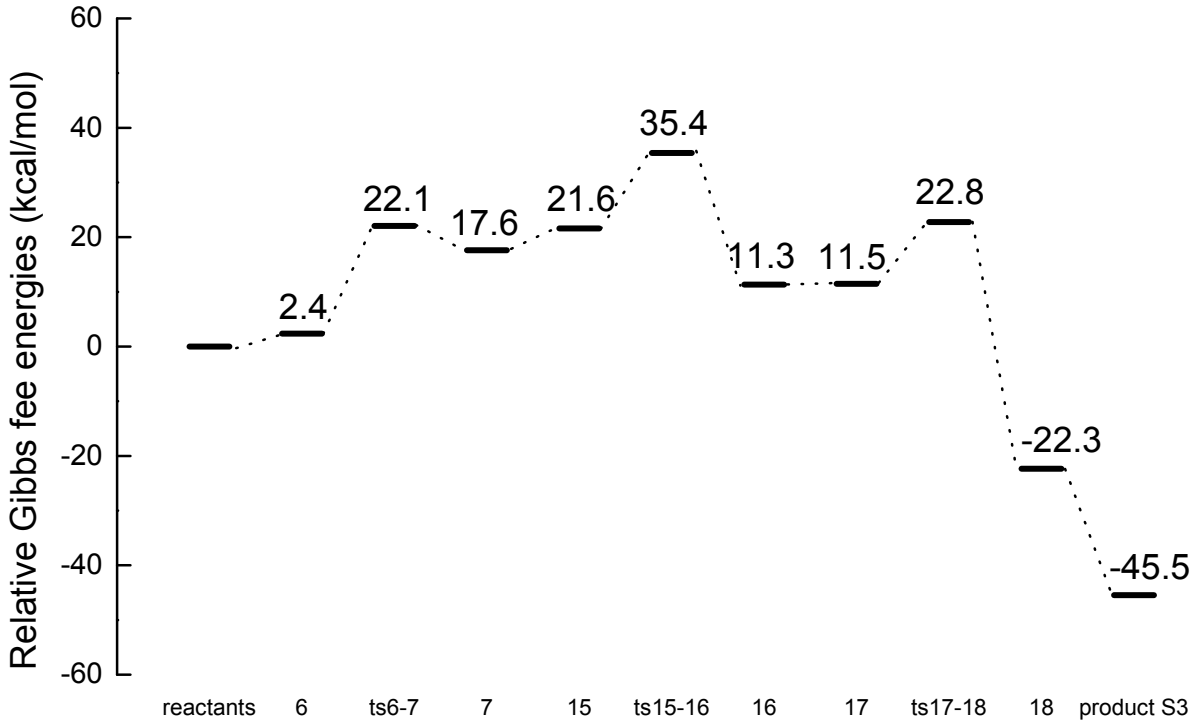
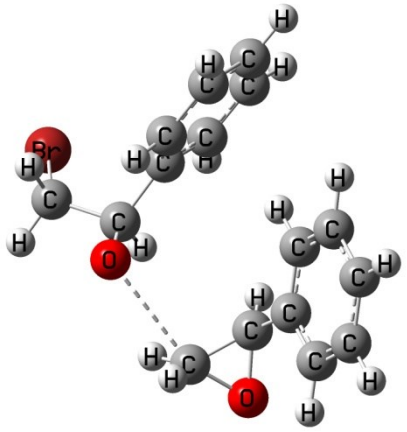
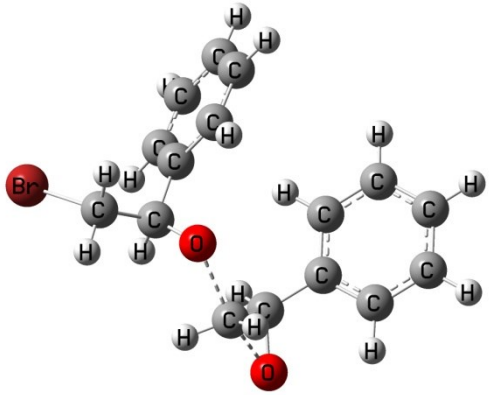


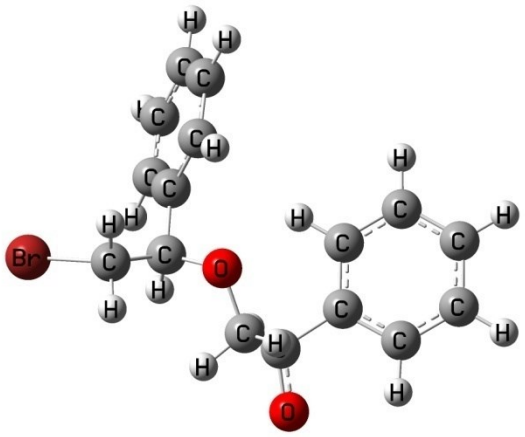
Figure S9. Relative Gibbs free energy profile of the side reaction (denoted as S3 in Chart 4) in solvent of toluene.

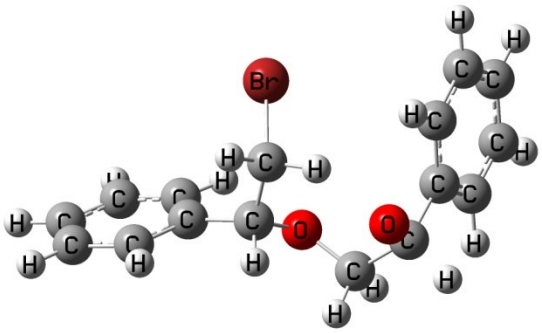
Optimized geometries of various species in the side reaction denoted as S3 in Chart 4.

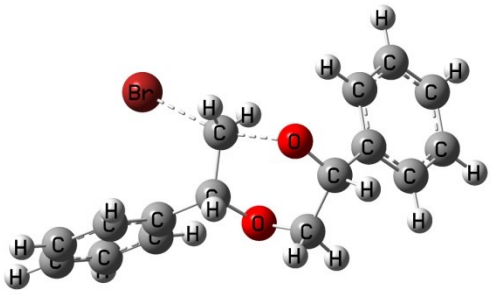
6 same as 6j
TS6-7 same as TS6j-7j
7 same as 7j

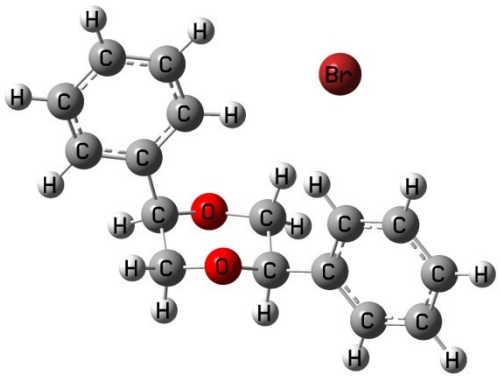
15	
HF=-3343.44808941 C 5.167752 -0.215531 0.350116 C 4.210425 -1.128635 -0.086590 C 2.926187 -0.695806 -0.419633 C 2.613415 0.660974 -0.312949 C 3.566692 1.570910 0.129732 C 4.849921 1.136765 0.460865 C 1.872837 -1.646530 -0.852524 O 2.247155 -3.006730 -1.039722 C 1.370894 -2.673386 0.048027 O -0.364985 -1.129657 1.548406 H 0.342114 -3.018423 -0.048117 H 1.808740 -2.747037 1.044158 H 1.179713 -1.257736 -1.607057 H 1.604236 0.996243 -0.555576 H 3.295793 2.622929 0.221269 H 5.598104 1.849580 0.808544 H 6.169061 -0.562961 0.607062 H 4.444163 -2.189386 -0.176630 C -1.178692 -0.701709 0.585116 C -2.597965 -0.909315 1.127437 Br -4.080807 -0.568072 -0.188971 C -0.967322 0.764745 0.186447 C -0.469652 1.651685 1.142977 C -0.194392 2.976504 0.817307 C -0.388353 3.432326 -0.488404 C -0.859450 2.549222 -1.458675 C -1.136121 1.224753 -1.120760 H -2.726078 -1.955115 1.417949 H -2.803337 -0.246254 1.975242 H -1.134257 -1.282269 -0.389281 H -1.494866 0.524931 -1.879131 H -0.998829 2.889893 -2.485817 H -0.161226 4.466666 -0.750631 H 0.196254 3.656165 1.576892 H -0.265769 1.244589 2.134715	

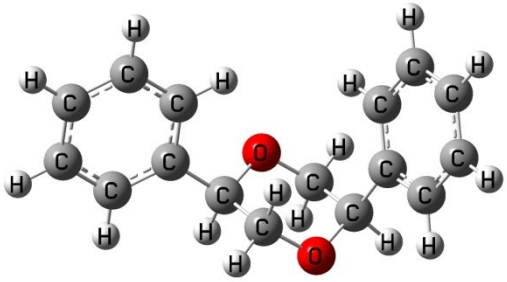
TS15-16	
HF=-3343.42662626 C -5.049233 -0.234521 -0.546503 C -4.113666 -1.144713 -0.059020 C -2.883435 -0.703953 0.428994 C -2.609872 0.665056 0.433965 C -3.539177 1.576801 -0.057610 C -4.765383 1.130277 -0.549936 C -1.866560 -1.696890 0.923880 O -2.293876 -2.987784 1.135844 C -1.089077 -2.406904 -0.085808 O 0.112205 -1.209951 -1.145957 H -0.224224 -2.975169 0.235885 H -1.592257 -2.671683 -1.007848 H -1.268129 -1.243575 1.742419 H -1.651235 1.019404 0.818797 H -3.300919 2.641371 -0.055614 H -5.496117 1.843583 -0.933503 H -6.008373 -0.592137 -0.924589 H -4.313590 -2.216270 -0.034917 C 1.087875 -0.710242 -0.349634 C 2.405142 -1.031108 -1.053842 Br 4.013999 -0.621620 0.038717 C 0.948637 0.785173 -0.084844 C 0.397995 1.603527 -1.072766 C 0.194412 2.960334 -0.842278 C 0.516350 3.517607 0.395907 C 1.044891 2.704999 1.396991 C 1.250239 1.347655 1.155638 H 2.461202 -2.104082 -1.255321 H 2.516500 -0.463205 -1.984174 H 1.141766 -1.202793 0.658784 H 1.650305 0.701433 1.939504 H 1.283133 3.126088 2.374407 H 0.343013 4.577826 0.583736 H -0.243701 3.584569 -1.622275 H 0.091216 1.134612 -2.008299	 563.6(i)

16	
HF=-3343.46103852 Br 3.754767 -1.106250 0.084833 C 2.127278 -1.137017 -1.004390 C 0.959932 -0.512491 -0.256544 C 1.115315 0.973297 -0.053009 C 0.842285 1.857782 -1.098158 C 0.922912 3.231913 -0.897877 C 1.266502 3.738144 0.355186 C 1.522556 2.861733 1.406092 C 1.442703 1.486708 1.200906 O -0.184954 -0.766655 -1.028261 C -0.938093 -1.909912 -0.569506 C -1.836306 -1.714104 0.680819 O -2.291340 -2.902248 1.055055 C -2.924108 -0.680622 0.334131 C -4.229003 -1.136842 0.142091 C -5.255807 -0.255010 -0.189346 C -4.995070 1.109072 -0.324020 C -3.696521 1.578255 -0.121706 C -2.674051 0.689139 0.204271 H -0.249189 -2.741401 -0.337780 H -1.569765 -2.210945 -1.416515 H -1.183104 -1.178947 1.448962 H -1.662675 1.068054 0.367930 H -3.479213 2.644494 -0.214229 H -5.798719 1.803870 -0.574548 H -6.271458 -0.630022 -0.333692 H -4.386947 -2.207203 0.287571 H 1.922429 -2.189783 -1.219928 H 2.356017 -0.600957 -1.931664 H 0.878701 -0.996330 0.732336 H 1.622857 0.794751 2.024556 H 1.771937 3.248701 2.393774 H 1.317593 4.815088 0.514865 H 0.697063 3.913245 -1.718028 H 0.524832 1.457075 -2.060736	

17	
HF=-3343.46778266 C -3.352071 -1.195141 1.182914 C -2.756294 -0.877711 -0.041951 C -2.965987 0.398350 -0.560498 C -3.722775 1.340964 0.132474 C -4.303615 1.016556 1.356643 C -4.117228 -0.264015 1.879909 C -1.903420 -1.893260 -0.829195 O -1.578446 -1.519025 -2.066583 C -0.684391 -2.278619 0.041633 O 0.208452 -1.215388 0.359077 C 1.132357 -0.841897 -0.629025 C 0.615573 0.261308 -1.534486 Br 0.292254 1.924774 -0.543483 C 2.451365 -0.524502 0.034587 C 2.507981 -0.038085 1.342739 C 3.735034 0.211216 1.949521 C 4.925162 -0.036978 1.266532 C 4.878546 -0.550980 -0.026654 C 3.646940 -0.808653 -0.625140 H 3.609642 -1.229124 -1.632790 H 1.573943 0.141525 1.871038 H 3.762975 0.600097 2.967623 H 5.884925 0.157532 1.745876 H 5.801486 -0.772523 -0.563191 H 1.290741 -1.694413 -1.321643 H 1.348535 0.510275 -2.311313 H -0.351130 -0.087816 -1.956709 H -0.995128 -2.684328 1.019043 H -0.130375 -3.065846 -0.503364 H -2.515148 -2.853285 -0.782339 H -2.524252 0.617998 -1.532885 H -3.860164 2.339041 -0.287921 H -4.898840 1.752394 1.899477 H -4.572327 -0.536076 2.834316 H -3.216870 -2.198564 1.596719	

TS17-18	
HF=-3343.45242814 C -3.945046 -1.213104 0.495429 C -3.124203 -0.454339 -0.345546 C -3.239362 0.934810 -0.293795 C -4.128179 1.550629 0.584997 C -4.928446 0.784122 1.428942 C -4.836302 -0.606405 1.375970 C -2.163504 -1.104893 -1.351084 O -1.433890 -0.224756 -2.074055 C -1.246365 -2.134438 -0.673239 O -0.203187 -1.537866 0.066645 C 0.723099 -0.806717 -0.717994 C 0.191424 0.593490 -0.965779 Br 1.732929 2.138708 -0.030159 C 2.076142 -0.908990 -0.055464 C 2.199689 -1.046113 1.326030 C 3.456608 -1.133435 1.913734 C 4.606288 -1.089452 1.127005 C 4.487904 -0.969448 -0.255071 C 3.227645 -0.887682 -0.838914 H 3.133529 -0.782758 -1.921737 H 1.298328 -1.073333 1.935718 H 3.541347 -1.228429 2.996595 H 5.591541 -1.145793 1.590601 H 5.379898 -0.938155 -0.881117 H 0.801036 -1.278682 -1.714011 H 0.317916 1.065051 -1.927534 H -0.559357 0.974942 -0.289934 H -1.776205 -2.786434 0.036656 H -0.807551 -2.769599 -1.466876 H -2.827352 -1.731222 -2.009864 H -2.621509 1.514070 -0.979354 H -4.194066 2.638989 0.612284 H -5.621396 1.264009 2.120729 H -5.462045 -1.220715 2.025279 H -3.894379 -2.303943 0.456073	 432.6(i)

18	
HF=-3343.52411341 C 3.811059 -1.236195 -0.395544 C 2.596647 -0.815342 0.160465 C 2.207965 0.511476 -0.012823 C 3.006327 1.388272 -0.746007 C 4.209114 0.961802 -1.298868 C 4.613804 -0.361273 -1.119782 C 1.762230 -1.868449 0.862072 O 0.895911 -1.413887 1.883526 C 0.981983 -2.728943 -0.130457 O -0.149722 -2.058739 -0.622879 C -1.050531 -1.765212 0.443820 C -0.362928 -0.882487 1.472468 Br -0.422154 2.824581 0.592029 C -2.278569 -1.116125 -0.122186 C -2.176656 0.083550 -0.831152 C -3.320102 0.689607 -1.340356 C -4.569581 0.099324 -1.162846 C -4.676787 -1.101039 -0.464025 C -3.532107 -1.703492 0.052428 H -3.610170 -2.644568 0.600840 H -1.211607 0.577152 -0.947516 H -3.224998 1.647507 -1.849956 H -5.463587 0.581512 -1.559195 H -5.651566 -1.567594 -0.319004 H -1.325807 -2.730056 0.921287 H -0.975035 -0.838287 2.382853 H -0.271596 0.151753 1.105241 H 1.605507 -2.990367 -0.995194 H 0.666797 -3.663721 0.377053 H 2.464525 -2.542309 1.382141 H 1.290964 0.921627 0.409666 H 2.655313 2.414133 -0.860612 H 4.831763 1.652837 -1.867681 H 5.559102 -0.710544 -1.536980 H 4.135064 -2.271257 -0.252383	

product of S3	
HF=-769.41861327 C -2.220590 0.751155 0.972623 C -2.369805 -0.323328 0.094703 C -3.253888 -0.194441 -0.980955 C -3.979090 0.975515 -1.172598 C -3.830035 2.040284 -0.284811 C -2.949063 1.925193 0.784967 C -1.628926 -1.637878 0.240896 O -0.869958 -1.935463 -0.932085 C -0.717134 -1.753966 1.448307 O 0.403309 -0.901152 1.340261 C 1.157112 -1.184830 0.169921 C 0.255325 -1.089063 -1.055270 C 2.301365 -0.222587 0.061323 C 2.129938 1.127731 0.374044 C 3.178846 2.025599 0.202162 C 4.405463 1.586264 -0.291574 C 4.581045 0.242123 -0.609076 C 3.532926 -0.656654 -0.429258 H 3.672184 -1.712238 -0.669649 H 1.170593 1.468177 0.763112 H 3.037560 3.075809 0.453903 H 5.224017 2.291807 -0.426156 H 5.538238 -0.110599 -0.990552 H 1.540050 -2.222877 0.239341 H 0.796553 -1.410054 -1.954023 H -0.059130 -0.038446 -1.195933 H -1.235075 -1.488304 2.377940 H -0.378941 -2.802855 1.529207 H -2.369485 -2.450791 0.293351 H -3.359715 -1.027214 -1.677093 H -4.665886 1.057402 -2.013880 H -4.398203 2.957990 -0.429748 H -2.821378 2.754036 1.480002 H -1.519133 0.684377 1.802361	

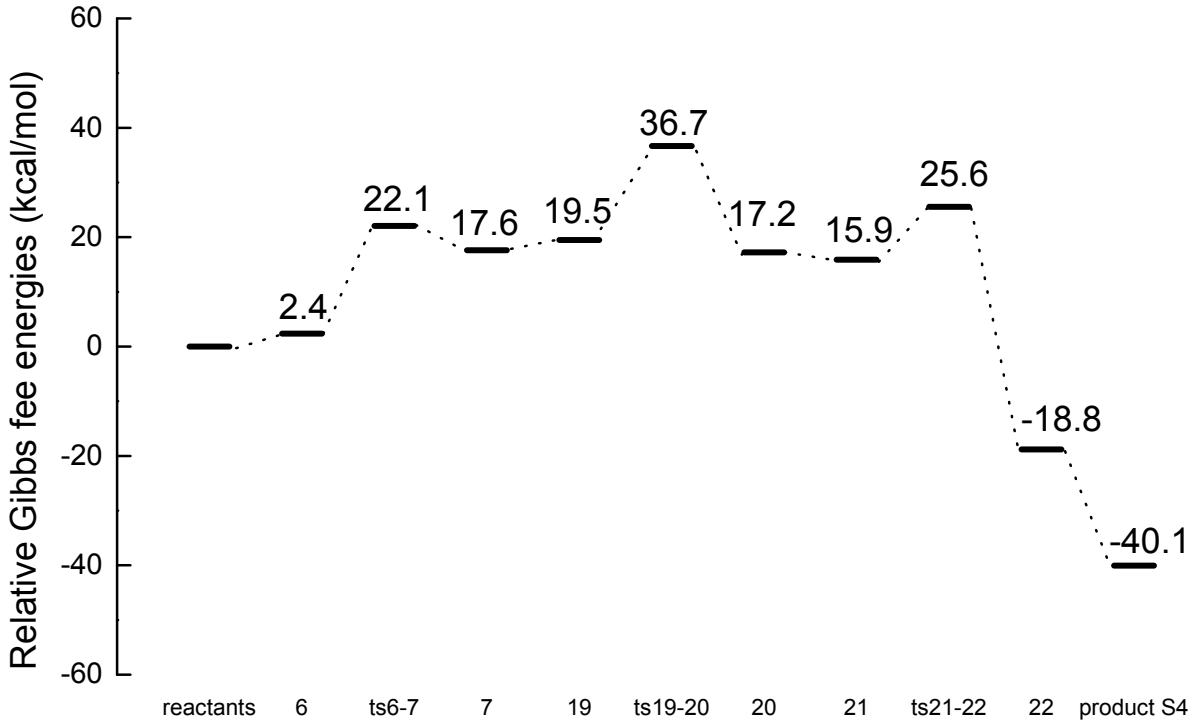
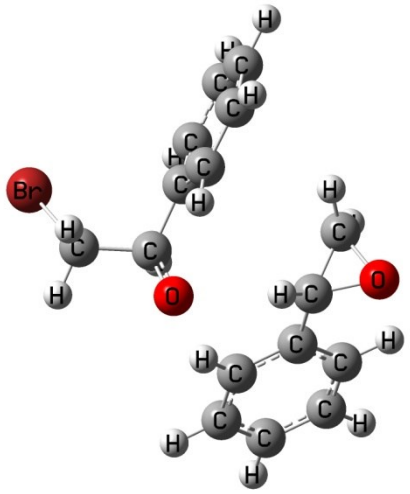
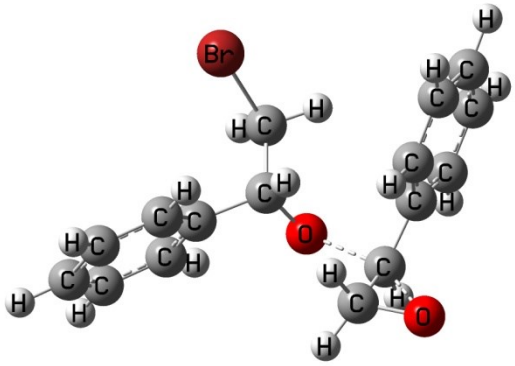


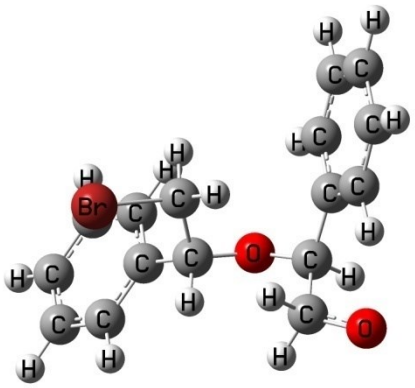
Figure S10. Relative Gibbs free energy profile of the side reaction (denoted as S4 in Chart 4) in solvent of toluene.

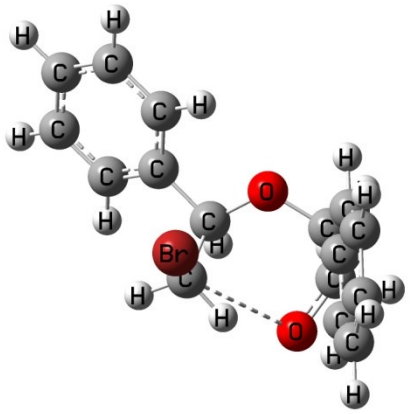
Optimized geometries of various species in the side reaction denoted as S4 in Chart 4.

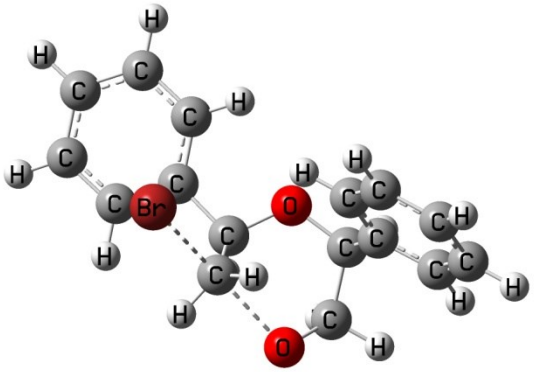
6 same as 6j
TS6-7 same as TS6j-7j
7 same as 7j

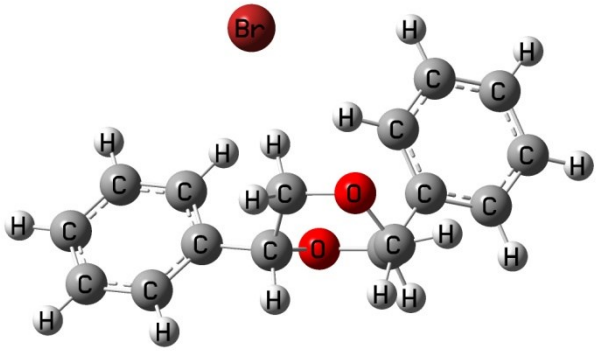
19	
HF=-3343.45429998 C 4.866597 -0.993417 -0.943248 C 4.158505 0.154606 -0.599120 C 2.987974 0.060566 0.157442 C 2.533150 -1.192490 0.582284 C 3.247046 -2.336486 0.233127 C 4.410064 -2.244475 -0.530060 C 2.200608 1.265815 0.522779 O 2.882864 2.523366 0.455029 C 1.846131 2.275041 -0.477908 O -0.110915 -0.381500 1.926984 H 0.939318 2.870671 -0.346843 H 2.175304 2.131830 -1.512782 H 1.512391 1.128026 1.365582 H 1.625466 -1.224249 1.204066 H 2.890835 -3.311774 0.566119 H 4.964260 -3.144743 -0.798275 H 5.781145 -0.912121 -1.532046 H 4.517302 1.140159 -0.898649 C -0.803623 -0.487308 0.785920 C -1.953311 -1.450372 1.103356 Br -3.087828 -1.989296 -0.461432 C -1.356816 0.836481 0.251972 C -1.653383 1.860088 1.153412 C -2.124427 3.092407 0.708175 C -2.287164 3.328331 -0.657842 C -1.964032 2.323293 -1.568755 C -1.491905 1.093468 -1.113531 H -1.547964 -2.390220 1.486924 H -2.648891 -1.010756 1.827006 H -0.236808 -0.945864 -0.079244 H -1.221425 0.308190 -1.822504 H -2.069952 2.502308 -2.639948 H -2.650162 4.294307 -1.011526 H -2.352629 3.880884 1.427303 H -1.472270 1.660503 2.210806	

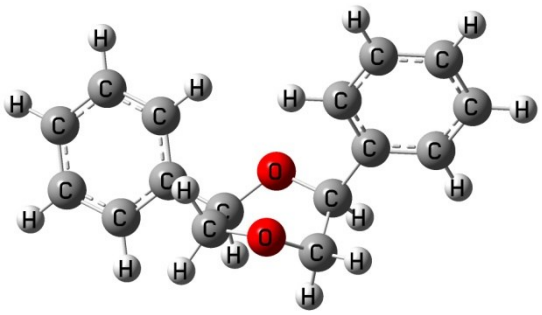
TS19-20	
HF=-3343.42323776 C -3.369103 0.764215 -1.246449 C -2.602757 -0.391274 -1.125136 C -2.441141 -1.013075 0.117388 C -3.098443 -0.463743 1.224972 C -3.874319 0.682486 1.104648 C -4.004034 1.311797 -0.133771 C -1.547325 -2.160796 0.314544 O -2.187450 -3.439160 -0.902846 C -0.934842 -2.886819 -0.787098 O -0.098143 -1.076488 1.271119 H -0.110061 -3.559411 -0.479974 H -0.580631 -2.277993 -1.646854 H -1.643898 -2.712543 1.242741 H -2.954117 -0.932418 2.198798 H -4.367189 1.098316 1.984071 H -4.594516 2.223070 -0.229626 H -3.466904 1.244325 -2.220378 H -2.132680 -0.828671 -2.004357 C 0.480981 -0.201414 0.406696 C 0.240170 1.190763 0.987819 Br 0.770835 2.656396 -0.238447 C 1.959897 -0.482630 0.180717 C 2.743756 -0.939022 1.242612 C 4.085027 -1.257250 1.054745 C 4.660381 -1.148757 -0.211984 C 3.878361 -0.728684 -1.285029 C 2.537052 -0.405361 -1.086757 H -0.829539 1.336420 1.166245 H 0.805301 1.350674 1.913641 H 0.009423 -0.192370 -0.607523 H 1.919832 -0.081396 -1.927086 H 4.311810 -0.660251 -2.283598 H 5.708970 -1.407132 -0.364210 H 4.684369 -1.607527 1.896378 H 2.263384 -1.064369 2.213680	 450.0(i)

20	
HF=-3343.45383691 C -4.439313 0.648956 0.393489 C -3.580057 -0.151915 -0.355686 C -2.483292 -0.773507 0.255610 C -2.300873 -0.604114 1.633321 C -3.163749 0.192988 2.381361 C -4.237561 0.829893 1.761739 C -1.503533 -1.603408 -0.549352 O -2.737542 -1.847846 -2.573624 C -1.594088 -1.387375 -2.085653 O -0.173764 -1.480341 0.025063 H -0.652808 -1.872063 -2.496003 H -1.416804 -0.273309 -2.267531 H -1.738888 -2.668727 -0.403823 H -1.452096 -1.092523 2.114895 H -2.996564 0.318424 3.452520 H -4.913461 1.459275 2.342339 H -5.280794 1.138215 -0.099569 H -3.734394 -0.356405 -1.420306 C 0.640142 -0.429184 -0.442018 C 0.102794 0.919664 0.022258 Br 1.225955 2.363800 -0.657865 C 2.027632 -0.699987 0.086935 C 2.262554 -0.740462 1.462435 C 3.531857 -1.015151 1.959024 C 4.591860 -1.238412 1.080773 C 4.367195 -1.200062 -0.292212 C 3.090262 -0.933604 -0.782382 H -0.900693 1.112209 -0.365491 H 0.102420 1.020058 1.111864 H 0.678114 -0.419155 -1.544115 H 2.909057 -0.905843 -1.857619 H 5.188019 -1.377935 -0.986830 H 5.589217 -1.446435 1.468335 H 3.698424 -1.049627 3.035682 H 1.432271 -0.579561 2.151560	

21	
HF=-3343.46109856 C -3.450794 0.833470 -0.603301 C -2.339078 0.406760 0.125181 C -2.531637 -0.496214 1.172319 C -3.800113 -1.001031 1.444503 C -4.898579 -0.598514 0.687390 C -4.719557 0.324168 -0.341336 C -0.978670 0.975062 -0.196849 C -0.344877 0.287457 -1.395092 Br 0.120125 -1.578845 -1.016458 O -0.209290 0.933475 0.975246 C 1.069445 1.609952 1.015718 C 1.146991 2.912615 0.184833 O 1.126778 2.790855 -1.143986 C 2.175214 0.603086 0.765468 C 3.026777 0.679394 -0.339789 C 4.014366 -0.284822 -0.534755 C 4.168309 -1.335681 0.366405 C 3.331063 -1.412531 1.478988 C 2.347578 -0.448178 1.672253 H 2.082024 3.404187 0.605123 H 0.313755 3.549961 0.617353 H 1.137235 1.911166 2.078155 H 1.679088 -0.514154 2.533679 H 3.442175 -2.229144 2.193915 H 4.933782 -2.095586 0.202259 H 4.661684 -0.221632 -1.410717 H 2.857027 1.495297 -1.047923 H -1.044608 0.263213 -2.237966 H 0.565746 0.832205 -1.670439 H -1.094150 2.020072 -0.541888 H -3.312329 1.571909 -1.396110 H -5.573664 0.662460 -0.928637 H -5.890683 -0.996596 0.901949 H -3.932338 -1.716114 2.257017 H -1.667658 -0.802250 1.758567	

TS21-22	
HF=-3343.44705404 C 3.123775 -1.051775 -0.461197 C 1.978032 -0.838268 0.303682 C 2.112895 -0.352374 1.601817 C 3.372815 -0.061190 2.115787 C 4.512385 -0.252052 1.337967 C 4.383205 -0.746672 0.041809 C 0.632724 -1.142136 -0.309488 C 0.153644 -0.173609 -1.375131 Br 1.250555 1.864318 -0.936196 O -0.303753 -1.276941 0.740720 C -1.624001 -1.682104 0.390108 C -1.663879 -2.397783 -0.980518 O -1.251711 -1.641756 -2.016367 C -2.594409 -0.525925 0.517927 C -3.964019 -0.763155 0.358808 C -4.892273 0.263528 0.492166 C -4.466529 1.557241 0.790975 C -3.106774 1.802878 0.958366 C -2.179679 0.770160 0.831776 H -2.713560 -2.770749 -1.098425 H -1.060352 -3.336550 -0.820530 H -1.906604 -2.432600 1.153275 H -1.118607 0.974208 0.973048 H -2.754348 2.808595 1.187318 H -5.190328 2.366685 0.888689 H -5.954088 0.054023 0.357163 H -4.305718 -1.772351 0.121480 H 0.570724 -0.270476 -2.369466 H -0.780318 0.353922 -1.285481 H 0.751619 -2.106101 -0.835957 H 3.021424 -1.436411 -1.478342 H 5.267293 -0.898821 -0.577647 H 5.497375 -0.008256 1.736856 H 3.464325 0.329166 3.129783 H 1.217990 -0.196407 2.201147	 444.1(i)

22	
HF=-3343.52007321 C -3.444421 -1.773686 -0.126693 C -2.241780 -1.070158 -0.198796 C -2.211862 0.175939 -0.829638 C -3.380444 0.708372 -1.364207 C -4.578941 0.000420 -1.295379 C -4.612288 -1.244870 -0.671911 C -1.000753 -1.632390 0.434939 C -0.597379 -0.831893 1.665703 Br -0.332558 2.813161 0.604911 O 0.049856 -1.612907 -0.521107 C 1.322130 -2.021896 -0.037582 C 1.278070 -2.282003 1.470053 O 0.676973 -1.235944 2.175631 C 2.371582 -1.010206 -0.424932 C 3.623877 -1.454384 -0.855962 C 4.628853 -0.546139 -1.180385 C 4.380907 0.822518 -1.086962 C 3.129518 1.269181 -0.667563 C 2.131312 0.360461 -0.328601 H 2.304255 -2.377168 1.849813 H 0.765389 -3.244994 1.664678 H 1.581737 -2.986284 -0.519468 H 1.169032 0.759220 -0.000445 H 2.901431 2.331936 -0.583424 H 5.160717 1.538264 -1.349015 H 5.600149 -0.907891 -1.519942 H 3.810535 -2.527856 -0.947081 H -1.355171 -0.971681 2.454526 H -0.544226 0.244366 1.425224 H -1.214123 -2.681700 0.723436 H -3.465697 -2.749640 0.363501 H -5.545596 -1.805105 -0.609745 H -5.491378 0.424726 -1.715491 H -3.346442 1.699416 -1.815508 H -1.296014 0.768982 -0.841642	

product of S4	
HF=-769.40966904 C 3.632761 0.699448 -0.368717 C 2.385638 0.090806 -0.224650 C 2.317486 -1.286507 -0.009406 C 3.484602 -2.041977 0.053737 C 4.728033 -1.428921 -0.085229 C 4.800563 -0.054255 -0.295204 C 1.147138 0.939033 -0.227751 C 0.862213 1.459270 1.185933 O 0.040603 0.178629 -0.660911 C -1.164452 0.924257 -0.770606 C -1.107402 2.168924 0.131075 O -0.488236 1.852429 1.349899 C -2.321938 0.030168 -0.416405 C -3.547690 0.208596 -1.058584 C -4.654740 -0.555323 -0.701339 C -4.541137 -1.514436 0.302115 C -3.318407 -1.701521 0.942873 C -2.214146 -0.932637 0.587761 H -2.122893 2.511635 0.361530 H -0.580901 2.998885 -0.375084 H -1.283514 1.266267 -1.817480 H -1.254674 -1.076025 1.083273 H -3.223394 -2.452099 1.726516 H -5.403310 -2.118477 0.581216 H -5.605072 -0.408019 -1.212657 H -3.634432 0.952816 -1.853057 H 1.540934 2.299612 1.419828 H 1.046308 0.655645 1.913715 H 1.310094 1.787833 -0.919853 H 3.688531 1.775096 -0.547504 H 5.768452 0.431102 -0.412457 H 5.639251 -2.023155 -0.036226 H 3.422383 -3.117833 0.211382 H 1.342196 -1.761296 0.091340	

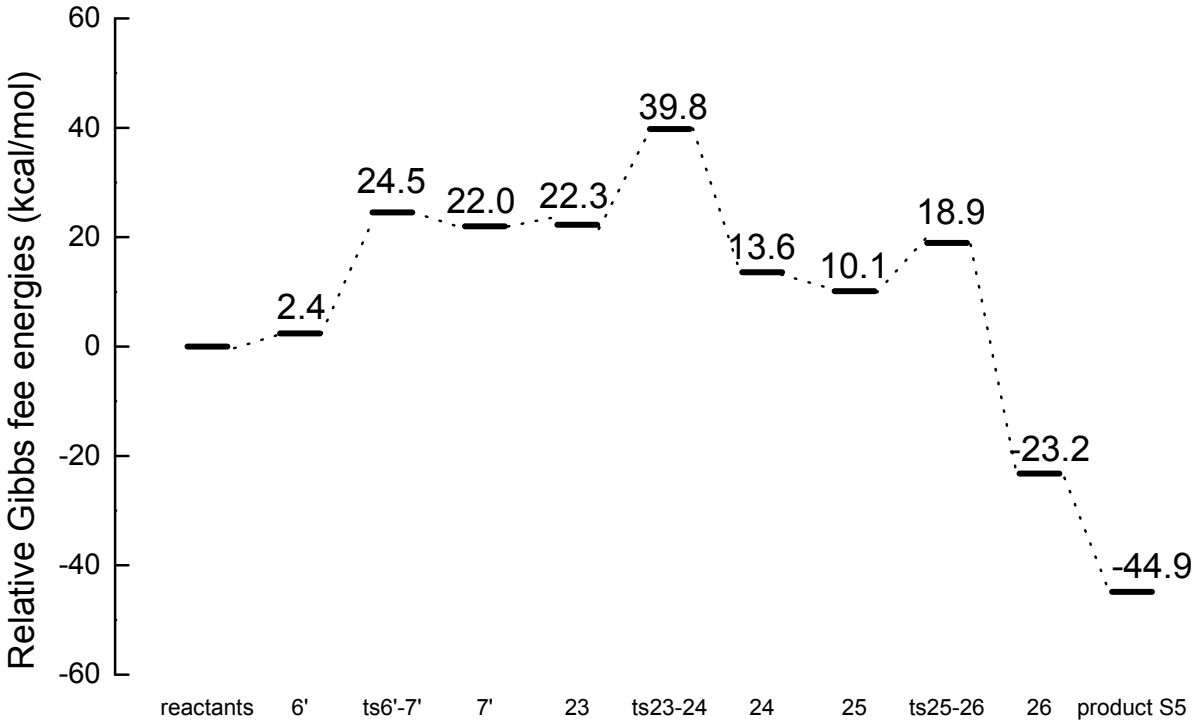
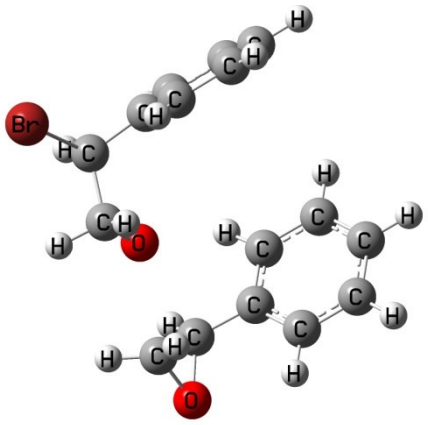
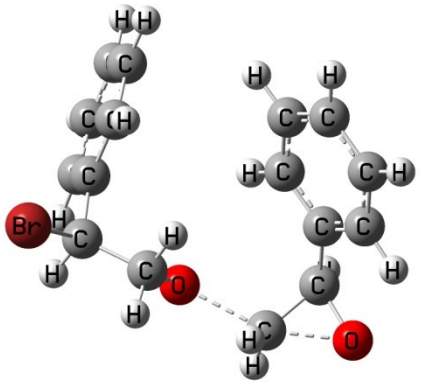


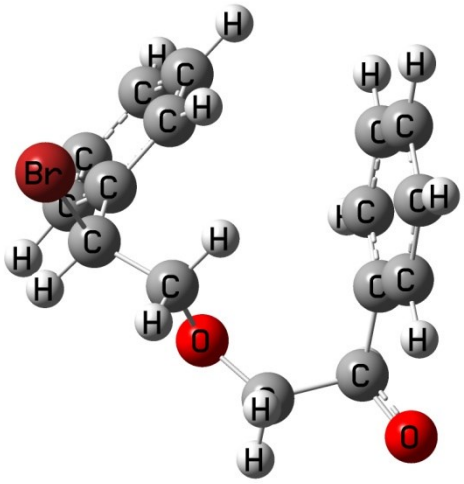
Figure S11. Relative Gibbs free energy profile of the side reaction (denoted as S5 in Chart 4) in solvent of toluene.

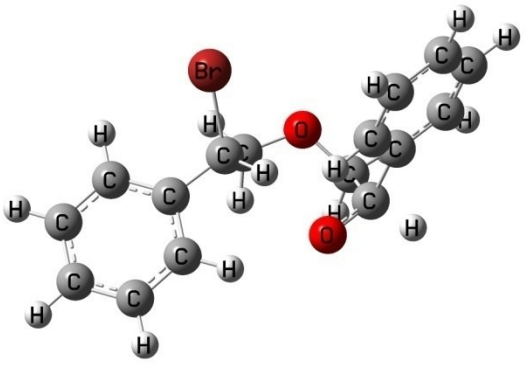
Optimized geometries of various species in the side reaction denoted as S5 in Chart 4.

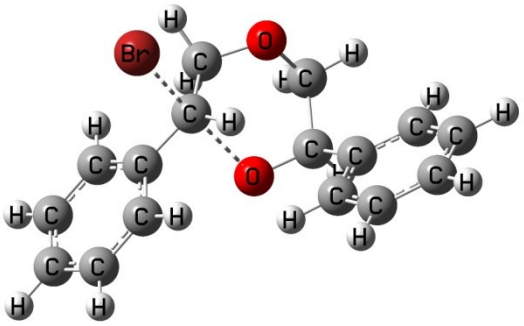
6' same as 6k
TS6'-7' same as TS6k-7k
7' same as 7k

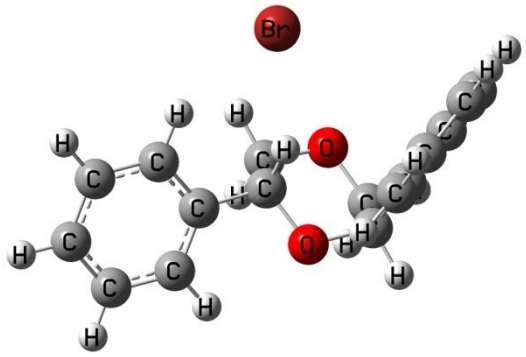
23	
HF=-3343.44679699 C -2.451776 1.940864 0.033388 C -2.086199 0.657597 0.432223 C -2.929251 -0.420900 0.142155 C -4.139147 -0.202371 -0.520606 C -4.499647 1.084574 -0.911979 C -3.655411 2.159846 -0.636290 C -2.494979 -1.778768 0.554747 O -3.486245 -2.814370 0.539279 C -2.440363 -2.876953 -0.412128 O 0.129012 -0.887833 1.901523 H -1.716321 -3.683553 -0.269429 H -2.739734 -2.685477 -1.447949 H -1.778055 -1.795476 1.386905 H -4.798176 -1.050190 -0.712704 H -5.447660 1.250976 -1.425524 H -3.937904 3.168487 -0.941031 H -1.788967 2.777998 0.256572 H -1.158800 0.447092 0.988622 C 0.787143 -1.361936 0.848829 C 2.099296 -0.563716 0.679683 Br 3.246593 -1.426573 -0.719563 C 1.876478 0.874683 0.349730 C 1.405063 1.290183 -0.898837 C 1.099709 2.625747 -1.135287 C 1.263579 3.574470 -0.126038 C 1.709063 3.168140 1.128793 C 2.019900 1.829848 1.356834 H 1.086637 -2.446256 0.902642 H 0.257261 -1.270339 -0.151975 H 2.689898 -0.671138 1.595699 H 2.342631 1.502511 2.345206 H 1.818527 3.895912 1.933188 H 1.025161 4.621934 -0.313976 H 0.725608 2.928662 -2.113507 H 1.266236 0.548676 -1.685760	

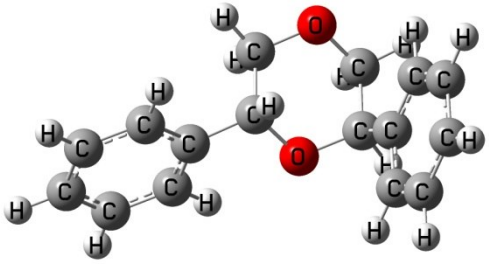
TS23-24	
HF=-3343.42089279 C -1.982808 1.666771 -1.420535 C -2.012394 1.086331 -0.157133 C -3.015789 0.169760 0.174174 C -3.985073 -0.153707 -0.772699 C -3.960957 0.435515 -2.037094 C -2.960774 1.347672 -2.364837 C -3.036849 -0.468354 1.535849 O -3.954201 -1.472732 1.761427 C -2.160389 -1.600473 1.758840 O -0.213102 -0.975831 1.652137 H -1.951836 -1.909464 2.773397 H -2.011629 -2.300980 0.943340 H -2.977178 0.313822 2.319482 H -4.745792 -0.881722 -0.490990 H -4.724825 0.177997 -2.772455 H -2.935190 1.803649 -3.355384 H -1.186509 2.368368 -1.674492 H -1.234917 1.302724 0.580439 C 0.341003 -1.388427 0.494941 C 1.805863 -0.938496 0.479799 Br 2.721428 -1.702667 -1.121290 C 1.968679 0.545321 0.518946 C 1.597800 1.363584 -0.551085 C 1.657687 2.748010 -0.437628 C 2.091748 3.339497 0.748551 C 2.448764 2.532771 1.824975 C 2.395691 1.146901 1.702235 H 0.346515 -2.500638 0.349235 H -0.136372 -0.975406 -0.434824 H 2.327956 -1.408548 1.320372 H 2.647683 0.512974 2.552638 H 2.770840 2.982236 2.764348 H 2.134045 4.425189 0.836286 H 1.365004 3.372060 -1.282655 H 1.247433 0.903517 -1.475887	 557.0(i)

24	
HF=-3343.46034050 C 1.848816 1.045945 2.128687 C 1.982234 1.270170 0.758255 C 2.798087 0.456111 -0.029594 C 3.509760 -0.571877 0.594856 C 3.369080 -0.813822 1.957939 C 2.532882 -0.007400 2.734489 C 2.934582 0.632008 -1.549184 O 4.117661 0.289368 -2.046936 C 1.851884 -0.243448 -2.238079 O 0.471334 -0.051829 -1.855988 H 1.905469 -0.028251 -3.313514 H 2.132607 -1.300978 -2.081159 H 2.610068 1.702442 -1.741060 H 4.180592 -1.155727 -0.038493 H 3.919068 -1.631547 2.428376 H 2.428025 -0.189443 3.805202 H 1.208500 1.696601 2.730414 H 1.432016 2.083239 0.275874 C 0.005703 -0.974115 -0.923271 C -1.496721 -0.785340 -0.824719 Br -2.182558 -2.207286 0.368502 C -1.935280 0.554390 -0.335389 C -1.505767 1.057704 0.894878 C -1.862702 2.338965 1.293198 C -2.669451 3.130620 0.475529 C -3.096168 2.639418 -0.754213 C -2.731420 1.355379 -1.151681 H 0.213282 -2.011147 -1.249077 H 0.470037 -0.846464 0.073458 H -1.953372 -1.009559 -1.795041 H -3.050069 0.974428 -2.122819 H -3.712044 3.256447 -1.407864 H -2.946916 4.136318 0.790398 H -1.506431 2.724222 2.248511 H -0.866374 0.445878 1.532422	

25	
HF=-3343.47148145 C -4.801007 0.150793 -0.084347 C -3.883114 -0.781830 0.389961 C -2.647277 -0.971708 -0.237694 C -2.368880 -0.212779 -1.373498 C -3.279991 0.725337 -1.855386 C -4.500948 0.915395 -1.212590 C -1.615930 -2.003709 0.261799 O -0.539959 -2.137552 -0.518767 C -1.278386 -1.706512 1.743813 O -0.668174 -0.449587 2.019529 C 0.682716 -0.344982 1.678359 C 0.931937 0.175796 0.271567 Br 0.496794 2.105656 0.252064 C 2.329099 -0.103026 -0.179979 C 3.442317 0.602673 0.281784 C 4.728171 0.212010 -0.082654 C 4.915299 -0.901977 -0.899284 C 3.809269 -1.628650 -1.337222 C 2.522162 -1.237406 -0.977935 H -5.756218 0.283711 0.427202 H -4.134997 -1.382708 1.267700 H -1.416371 -0.397969 -1.871022 H -3.034351 1.313301 -2.741425 H -5.215185 1.650477 -1.586225 H -2.224736 -2.959766 0.369701 H -2.183356 -1.721181 2.373010 H -0.604858 -2.515841 2.084540 H 1.163845 0.326214 2.410220 H 1.168705 -1.337015 1.740042 H 0.210028 -0.322866 -0.391048 H 3.292900 1.478697 0.914558 H 5.588430 0.779778 0.273443 H 5.922093 -1.207058 -1.186653 H 3.948568 -2.511080 -1.962080 H 1.640153 -1.814083 -1.270440	

TS25-26	
HF=-3343.45848503 C -4.808350 -0.038060 -0.594791 C -3.946339 -0.084627 0.497752 C -2.661261 -0.624396 0.384929 C -2.276531 -1.145944 -0.851211 C -3.134673 -1.107885 -1.948163 C -4.404084 -0.547446 -1.828163 C -1.699868 -0.736971 1.578320 O -0.466041 -1.184493 1.251374 C -1.615395 0.570896 2.380701 O -0.854110 1.574514 1.743910 C 0.499184 1.231714 1.559129 C 0.713991 0.451786 0.284381 Br 1.707362 2.128242 -1.054720 C 1.775287 -0.551674 0.126660 C 2.757858 -0.762154 1.095351 C 3.723479 -1.749552 0.921915 C 3.712121 -2.555468 -0.212862 C 2.726199 -2.358571 -1.180797 C 1.771854 -1.367584 -1.009243 H -5.801946 0.399035 -0.483623 H -4.285840 0.307194 1.458942 H -1.284671 -1.594967 -0.911184 H -2.808627 -1.517145 -2.905414 H -5.074771 -0.508402 -2.687043 H -2.219102 -1.444825 2.285474 H -2.599511 1.024154 2.571357 H -1.151642 0.329431 3.357120 H 1.060279 2.173231 1.545927 H 0.847513 0.622840 2.410421 H -0.118940 0.416207 -0.405143 H 2.776115 -0.145113 1.992913 H 4.486542 -1.895225 1.687163 H 4.465992 -3.332071 -0.343970 H 2.704097 -2.983603 -2.073761 H 1.007248 -1.203749 -1.769683	 338.8(i)

26	
HF=-3343.52545010 C 3.992395 -0.043490 0.266841 C 3.050674 -0.939947 -0.231866 C 1.939446 -1.299786 0.529574 C 1.791714 -0.740961 1.802000 C 2.721539 0.164648 2.295784 C 3.830523 0.513756 1.529418 C 0.887008 -2.282134 0.044674 O -0.419732 -1.882534 0.432464 C 0.865521 -2.540066 -1.452995 O 0.504852 -1.390676 -2.170568 C -0.750920 -0.889158 -1.746488 C -0.807243 -0.673798 -0.239012 Br 0.676158 2.468221 -0.680395 C -2.194236 -0.300499 0.188266 C -3.135506 -1.276867 0.523947 C -4.437665 -0.917188 0.862542 C -4.811933 0.425215 0.863200 C -3.875262 1.401197 0.525792 C -2.571410 1.046443 0.190172 H 4.834624 0.252621 -0.357524 H 3.165379 -1.312834 -1.248297 H 0.904448 -0.988821 2.384646 H 2.565158 0.622534 3.272096 H 4.547457 1.244329 1.902534 H 1.040280 -3.249777 0.553020 H 1.841577 -2.869898 -1.832512 H 0.132897 -3.351904 -1.636986 H -0.894309 0.071014 -2.256227 H -1.548576 -1.601814 -2.045821 H -0.106250 0.143814 0.004839 H -2.830744 -2.323119 0.531394 H -5.162418 -1.687592 1.128993 H -5.830839 0.709578 1.129131 H -4.158154 2.453976 0.530324 H -1.814892 1.801635 -0.052052	

product of S5	
HF=-769.41786698 C 3.957225 -0.618007 1.065266 C 3.047918 0.327769 0.592646 C 2.209623 0.028588 -0.481568 C 2.290330 -1.240124 -1.065017 C 3.192734 -2.185744 -0.593633 C 4.033131 -1.874714 0.474596 C 1.211578 1.007165 -1.068125 O -0.105500 0.452942 -1.076127 C 1.161322 2.381701 -0.424319 O 0.612171 2.325229 0.874694 C -0.686755 1.773826 0.839267 C -0.675202 0.379767 0.222701 C -2.068154 -0.170590 0.131302 C -2.839999 -0.009233 -1.019692 C -4.153793 -0.469993 -1.053638 C -4.711385 -1.087088 0.063072 C -3.946041 -1.248069 1.215918 C -2.631054 -0.794628 1.246339 H 4.602325 -0.369350 1.906871 H 2.984570 1.297901 1.082744 H 1.624209 -1.481259 -1.894113 H 3.244726 -3.167875 -1.061604 H 4.742964 -2.612265 0.846445 H 1.445957 1.141888 -2.135604 H 2.158450 2.829752 -0.337035 H 0.540962 3.039412 -1.060273 H -1.054027 1.742656 1.872264 H -1.358962 2.420917 0.241895 H -0.052662 -0.277668 0.859443 H -2.396891 0.467090 -1.892505 H -4.745121 -0.346697 -1.960025 H -5.739099 -1.446098 0.034562 H -4.371897 -1.735608 2.091804 H -2.027739 -0.931924 2.145909	

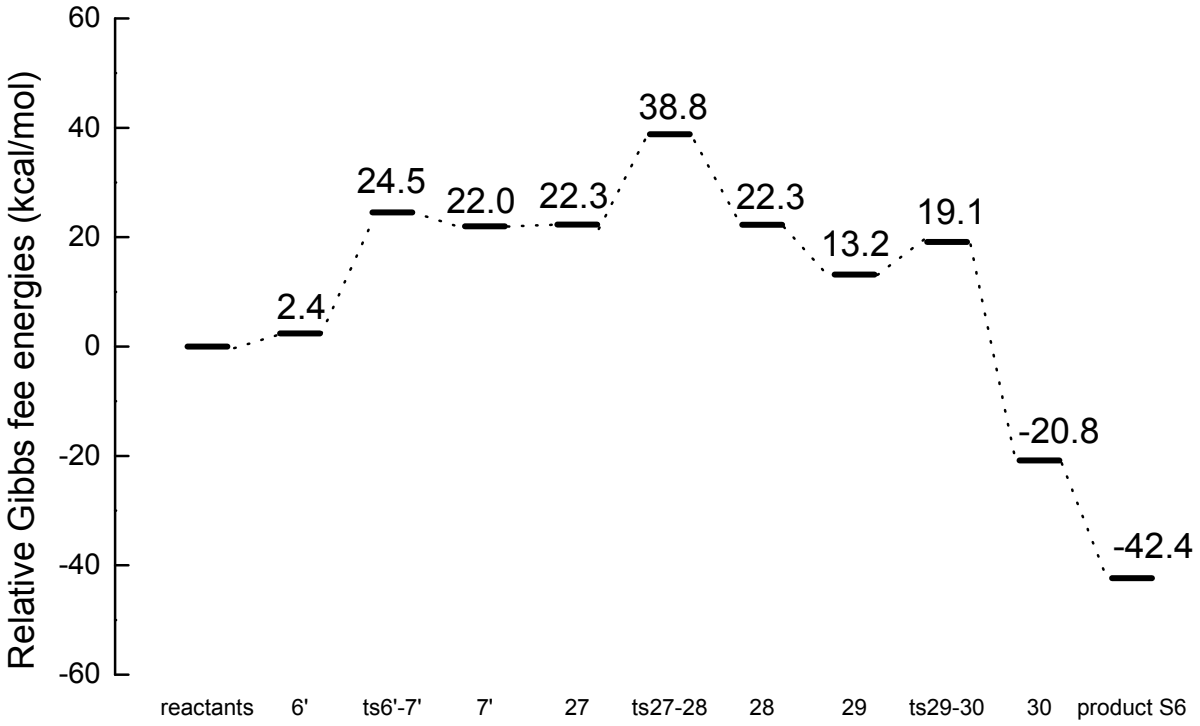
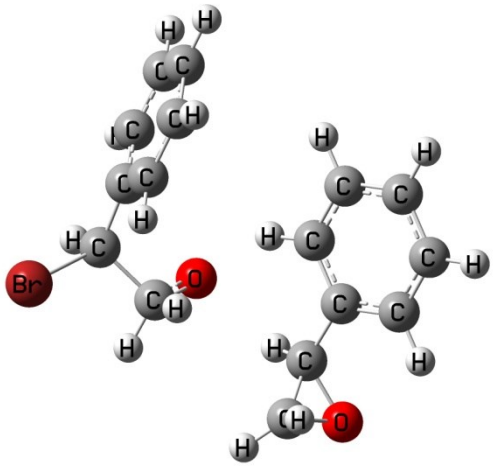
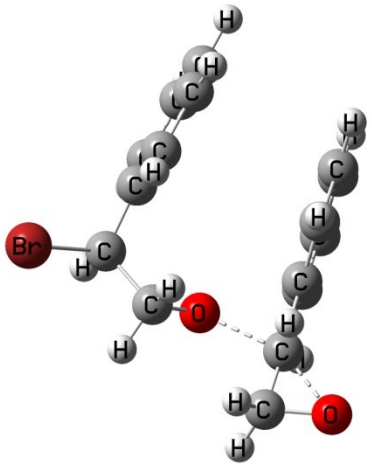


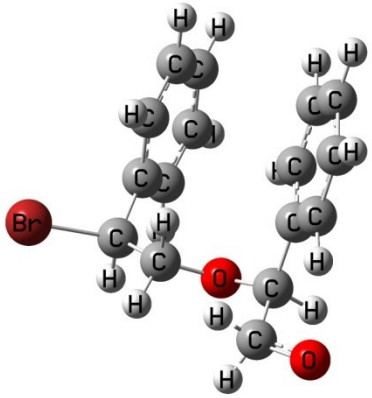
Figure S12. Relative Gibbs free energy profile of the side reaction (denoted as S6 in Chart 4) in solvent of toluene.

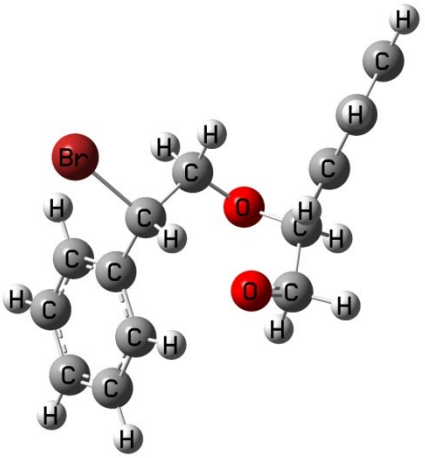
Optimized geometries of various species in the side reaction denoted as S6 in Chart 4.

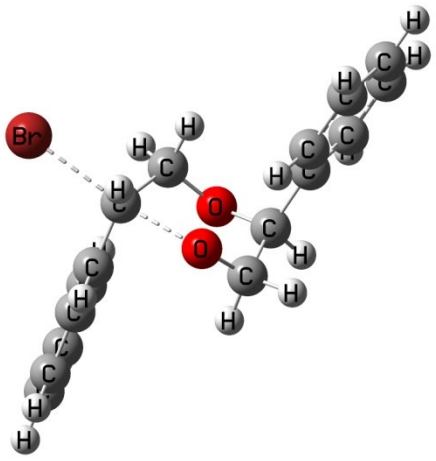
6' same as 6k
TS6'-7' same as TS6k-7k
7' same as 7k

27	
HF=-3343.44679625 C -4.498843 1.084642 -0.912561 C -4.138428 -0.202365 -0.521353 C -2.928948 -0.420933 0.142171 C -2.086234 0.657576 0.433137 C -2.451743 1.940922 0.034472 C -3.654953 2.159958 -0.635925 C -2.494855 -1.778892 0.554726 O -3.486181 -2.814441 0.538856 C -2.439967 -2.877007 -0.412203 O 0.129042 -0.887670 1.901971 H -1.716002 -3.683641 -0.269300 H -2.738976 -2.685424 -1.448110 H -1.778304 -1.795751 1.387180 H -1.159061 0.446982 0.989906 H -1.789201 2.778088 0.258335 H -3.937388 3.168650 -0.940543 H -5.446510 1.251093 -1.426730 H -4.797164 -1.050236 -0.714216 C 0.786986 -1.361814 0.849156 C 2.099101 -0.563612 0.679730 Br 3.246236 -1.426708 -0.719489 C 1.876249 0.874739 0.349573 C 1.404998 1.290153 -0.899071 C 1.099762 2.625723 -1.135675 C 1.263527 3.574521 -0.126488 C 1.708831 3.168270 1.128436 C 2.019603 1.829991 1.356625 H 1.086454 -2.446135 0.902984 H 0.256901 -1.270293 -0.151537 H 2.689840 -0.670888 1.595672 H 2.342244 1.502738 2.345050 H 1.818230 3.896096 1.932793 H 1.025182 4.621980 -0.314543 H 0.725837 2.928574 -2.113981 H 1.266239 0.548599 -1.685962	

TS27-28	
HF=-3343.42062976 C 2.655453 0.954214 2.047707 C 2.677840 -0.190280 1.254382 C 2.487294 -0.104636 -0.128186 C 2.262134 1.156973 -0.691702 C 2.243321 2.300185 0.096569 C 2.443662 2.205686 1.473750 C 2.491578 -1.288102 -0.999447 O 4.032992 -2.194248 -0.551986 C 2.728777 -2.633004 -0.509659 O 0.484791 -1.124439 -1.510060 H 2.443679 -3.439134 -1.213091 H 2.321209 -2.875249 0.493987 H 2.653499 -1.133119 -2.059043 H 2.065879 1.220977 -1.761849 H 2.050127 3.269796 -0.363514 H 2.424885 3.101751 2.095628 H 2.811374 0.865994 3.123562 H 2.878872 -1.161247 1.704098 C -0.285610 -1.517019 -0.476411 C -1.651342 -0.837866 -0.620298 Br -2.897553 -1.574826 0.760645 C -1.602092 0.651321 -0.518101 C -1.213998 1.294511 0.659598 C -1.096716 2.677798 0.705552 C -1.366621 3.444880 -0.427220 C -1.728406 2.812249 -1.613266 C -1.851088 1.425283 -1.650945 H -0.468810 -2.620651 -0.420614 H 0.110874 -1.234822 0.536192 H -2.108067 -1.150995 -1.565363 H -2.115159 0.924479 -2.583057 H -1.919621 3.398983 -2.512083 H -1.272034 4.530540 -0.389602 H -0.779357 3.160156 1.630152 H -0.990392 0.697780 1.544465	 460.9(i)

28	
HF=-3343.45601602 C -3.959366 0.878118 -1.480136 C -3.531841 -0.113216 -0.600325 C -2.439397 0.114053 0.247400 C -1.805023 1.360583 0.198109 C -2.235336 2.352214 -0.681720 C -3.315989 2.115164 -1.528060 C -1.957085 -0.962582 1.197727 O -3.786302 -2.492791 1.089001 C -2.482408 -2.385134 0.862492 O -0.515246 -0.877644 1.346563 H -1.815389 -3.077881 1.466603 H -2.169799 -2.589017 -0.214668 H -2.330479 -0.746860 2.210181 H -0.952131 1.547784 0.852933 H -1.721240 3.315146 -0.702835 H -3.656663 2.889359 -2.217457 H -4.809477 0.682581 -2.135638 H -4.045830 -1.073928 -0.499181 C 0.202150 -1.351248 0.247824 C 1.638937 -0.896079 0.444412 Br 2.713395 -1.706786 -1.001786 C 1.821212 0.586505 0.466051 C 1.514638 1.379425 -0.641765 C 1.598591 2.763669 -0.562873 C 1.998591 3.376297 0.624342 C 2.294356 2.594114 1.737008 C 2.211126 1.206532 1.651995 H 0.173686 -2.451483 0.180302 H -0.186669 -0.952413 -0.708170 H 2.038632 -1.345435 1.360470 H 2.423185 0.592604 2.528039 H 2.589491 3.063313 2.675070 H 2.060544 4.462447 0.686081 H 1.341745 3.368714 -1.431811 H 1.185027 0.905556 -1.566811	

29	
HF=-3343.46790183 C -4.292350 0.328253 -1.046607 C -3.089800 -0.373142 -0.967610 C -2.650125 -0.877191 0.260668 C -3.429399 -0.649484 1.400337 C -4.625736 0.057557 1.323567 C -5.062919 0.548079 0.093371 C -1.366795 -1.668588 0.392840 O -0.460828 -1.358080 -1.884194 C -0.797704 -2.232811 -0.927648 O -0.402281 -0.961945 1.203944 H -1.596925 -2.974890 -1.238218 H 0.053109 -2.892914 -0.580560 H -1.587991 -2.547329 1.027273 H -3.078331 -1.034941 2.360206 H -5.220672 0.224254 2.222615 H -5.999436 1.103456 0.026435 H -4.627436 0.715287 -2.009836 H -2.441577 -0.541117 -1.833041 C -0.118716 0.382289 0.921882 C 0.871434 0.550909 -0.224411 Br 1.180893 2.522064 -0.332384 C 2.162637 -0.176380 -0.022386 C 3.045070 0.144285 1.012655 C 4.185877 -0.619863 1.229706 C 4.465878 -1.707043 0.401731 C 3.582697 -2.036674 -0.623786 C 2.431446 -1.280695 -0.835744 H -1.033210 0.954919 0.689050 H 0.310121 0.801114 1.845977 H 0.390896 0.237809 -1.165338 H 1.685376 -1.536736 -1.599144 H 3.786205 -2.897498 -1.261317 H 5.364016 -2.303282 0.567723 H 4.866702 -0.361121 2.041538 H 2.833832 1.003942 1.650688	

TS29-30	
HF=-3343.45868238 C 4.400904 0.342520 1.326858 C 3.180407 -0.281378 1.074096 C 2.860886 -0.711013 -0.218152 C 3.780537 -0.478270 -1.245386 C 4.997023 0.151282 -0.997537 C 5.312046 0.563513 0.296129 C 1.558546 -1.408174 -0.556194 O 0.328585 -1.063740 1.462701 C 0.810810 -2.012674 0.631171 O 0.699406 -0.543480 -1.301924 H 1.522497 -2.718596 1.136321 H 0.012163 -2.668330 0.189647 H 1.787239 -2.208808 -1.281966 H 3.525363 -0.796898 -2.258295 H 5.700388 0.320546 -1.813662 H 6.262719 1.057919 0.498719 H 4.636566 0.671020 2.339714 H 2.437917 -0.435260 1.859240 C 0.249218 0.646899 -0.686664 C -0.834597 0.480658 0.365165 Br -1.905029 2.549301 0.035265 C -1.963154 -0.436130 0.141865 C -2.396327 -0.751221 -1.148573 C -3.434491 -1.654486 -1.349423 C -4.072440 -2.240487 -0.258535 C -3.653337 -1.922562 1.034047 C -2.601019 -1.037301 1.231123 H 1.079981 1.209830 -0.231866 H -0.133715 1.243436 -1.522654 H -0.625922 0.781365 1.378307 H -2.233706 -0.819523 2.232307 H -4.140049 -2.383378 1.894117 H -4.889646 -2.945804 -0.413161 H -3.752498 -1.895572 -2.364038 H -1.907285 -0.286790 -2.003144	 322.5(i)

30

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C -2.890446 -0.822794 0.205683
C -3.855525 -0.747572 1.214013
C -5.038726 -0.041435 1.026985
C -5.273507 0.608454 -0.183554
C -1.626423 -1.608345 0.496168
O -0.183690 -0.999759 -1.370199
C -0.837025 -2.064651 -0.717562
O -0.757164 -0.906772 1.370998
H -1.495017 -2.533325 -1.463720
H -0.108380 -2.820083 -0.373886
H -1.919220 -2.508353 1.061591
H -3.659983 -1.247165 2.164792
H -5.777593 0.006072 1.826793
H -6.196885 1.166655 -0.336543
H -4.483483 1.068112 -2.134694
H -2.374041 -0.177751 -1.782610
C -0.133652 0.203838 0.727251
C 0.654934 -0.214630 -0.507472
Br 1.636607 3.067910 -0.096511
C 1.971628 -0.897469 -0.211261
C 2.855401 -0.295570 0.691852
C 4.076956 -0.889151 0.987801
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C 2.374077 -2.068318 -0.856305
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H 0.868950 0.716277 -1.057235
H 1.723059 -2.512805 -1.608217
H 3.899372 -3.570408 -1.087881
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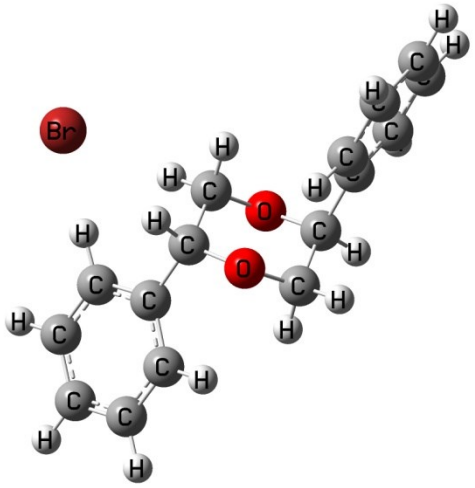
H 2.591375 0.664732 1.137236



product of S6	
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