ESI for:

Easy and Accurate Computation of Energy Barriers for Carbocations Solvation: An Expeditious Tool to Face Carbocation Chemistry

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1. Cartesian coordinates for the B3LYP optimized geometries of carbocations, and carbocation-water complexes at the transition state

NOTES: R^+ indicates carbocation. R^+-OH_2 indicates carbocation-water complex. fopt indicates fully optimized geometry. F indicates optimization with frozen (F) coordinates. TS indicates transition state. Frozen carbocation (R_F^+; see main text) geometries can be easily obtained by removing the water molecule from the frozen carbocation-water complex geometries at the transition state. TS structures were obtained by frozing the key C-O distance at 1.688 Å.

***t*-Bu$^+$ *C*$_{3h}$ fopt**

1 1
C 0.000090 0.000112 0.000476
C -1.019200 1.053742 -0.000522
C 1.422221 0.355723 0.001967
C -0.403027 -1.409340 -0.001275
H -1.679058 0.902973 0.871731
H -1.691427 0.896393 -0.861368
H -0.622851 2.069679 -0.005035
H 1.623378 0.973289 -0.891585
H 2.103596 -0.495296 0.031615
H 1.621282 1.044200 0.840282
H 0.040235 -1.899072 0.883613
H 0.085222 -1.919715 -0.848896
H -1.480879 -1.573875 -0.024228

***t*-Bu$^+$ *C*$_{3v}$ F**

1 1
C -0.001367 -0.001621 -0.053723
C -1.401703 -0.441852 -0.013955
C 0.317508 1.432491 -0.013768
C 1.081919 -0.993191 -0.013827
H -1.550600 -1.453752 -0.398384
H -2.089308 0.275806 -0.470510
H -1.672449 -0.474246 1.062262
H -0.484487 2.065922 -0.400446
H 0.425407 1.686988 1.060855
H 1.281796 1.668934 -0.472606
H 1.314883 -1.138369 1.061568
H 2.008397 -0.634087 -0.471041
H 0.788218 -1.972159 -0.400057

2 1 4 11 -90.0 F
2 1 3 9 90.0 F
4 1 2 7 90.0 F

***t*-Bu$^+$ C_s F**

1 1
C -0.010742 -0.034393 0.000839
C -0.040680 1.438644 0.000900
C 1.280762 -0.735428 0.000824
C -1.273010 -0.774307 0.000824
H 0.523849 1.814926 0.869171
H -1.047302 1.858704 0.002075
H 0.521378 1.814514 -0.869171
H 1.194200 -1.821700 -0.000336
H 1.874847 -0.404037 0.868942
H 1.876297 -0.402100 -0.865540
H -1.167892 -1.858688 -0.000046
H -1.876297 -0.440781 -0.862656
H -1.875046 -0.442230 0.865768

3 1 4 11 0.0 F
4 1 2 6 0.0 F
3 1 2 6 -180.0 F

TS *t*-Bu$^+$-OH$_2$ C_{3v} F

1 1
C -0.018883 0.131489 0.123661
C -1.320513 0.787486 -0.272401
C 1.218510 0.969029 -0.099044
C -0.050695 -0.656996 1.413001
H -2.169848 0.099147 -0.208477
H -1.268072 1.222667 -1.273320
H -1.511168 1.598966 0.439700
H 1.247096 1.390946 -1.106789
H 1.187559 1.801566 0.613539
H 2.140124 0.411632 0.099685
H -0.155318 0.058316 2.237788
H 0.876350 -1.213066 1.584848
H -0.907753 -1.335961 1.465561
O 0.148050 -1.027303 -1.092347
H 0.990487 -1.522909 -1.017162
H -0.584377 -1.678926 -1.087895

1 14 1.688 F

Bn$^+$ C_{2v} fopt

1 1
C -1.735368 -0.042344 0.485872
C -1.058680 -1.261536 0.269631
C 0.265961 -1.239717 -0.101670
C 0.946309 0.023091 -0.264932
C 0.223706 1.251667 -0.035469
C -1.100663 1.208846 0.334978
C 2.265585 0.055283 -0.634372
H -2.781858 -0.067881 0.778892
H -1.584620 -2.201688 0.396861
H 0.814707 -2.160846 -0.275573
H 0.740708 2.198801 -0.159907
H -1.658119 2.122559 0.511204
H 2.829919 -0.857400 -0.811809
H 2.798158 0.994717 -0.763883

TS Bn^+-OH_2 F

1 1

C	2.324207	0.000000	0.272820
C	1.651816	1.216997	0.110023
C	0.299460	1.221189	-0.211435
C	-0.389849	0.000000	-0.372114
C	0.299460	-1.221189	-0.211435
C	1.651816	-1.216997	0.110023
C	-1.806787	0.000000	-0.702399
H	3.382383	0.000000	0.516753
H	2.186708	2.154435	0.222981
H	-0.220863	2.164565	-0.361665
H	-0.220863	-2.164565	-0.361664
H	2.186708	-2.154434	0.222981
H	-2.218263	0.903885	-1.147056
H	-2.218262	-0.903886	-1.147055
O	-2.748242	0.000000	0.698674
H	-2.536179	0.786190	1.246217
H	-2.536173	-0.786187	1.246220

7 15 1.688 F

Ph(Me)CH^+ *C_s* fopt

1 1

C	-2.286582	-0.303766	0.000045
C	-1.861158	1.035903	-0.000007
C	-0.509631	1.313561	-0.000034
C	0.452203	0.246537	-0.000060
C	-0.014603	-1.110657	0.000045
C	-1.367770	-1.372365	-0.000032
C	1.802025	0.581144	0.000085
C	2.975133	-0.305626	-0.000008
H	-3.351121	-0.522096	0.000156
H	-2.590484	1.838874	-0.000049
H	-0.157044	2.341226	-0.000148
H	0.696162	-1.929332	0.000097
H	-1.729665	-2.395062	-0.000151
H	2.031354	1.647990	0.000295
H	3.603845	-0.058200	-0.870266
H	2.755436	-1.372736	-0.000592
H	3.603821	-0.059049	0.870453

TS Ph(Me)CH$^+$-OH$_2$ F

1 1

C	-2.664826	0.173822	0.119231
C	-1.825741	1.269250	0.354156
C	-0.449644	1.139970	0.199107
C	0.100918	-0.095376	-0.199526
C	-0.754243	-1.192610	-0.429900
C	-2.130420	-1.056548	-0.272396
C	1.550467	-0.290617	-0.387922
C	2.450362	0.847864	-0.788651
H	-3.738804	0.283060	0.236804
H	-2.248418	2.223737	0.651350
H	0.187007	2.002204	0.373265
H	-0.337564	-2.144715	-0.750358
H	-2.784070	-1.901978	-0.461562
H	1.784670	-1.213694	-0.915185
H	2.321577	1.738262	-0.166271
H	2.187757	1.125932	-1.816147
H	3.502100	0.546098	-0.793659
O	2.161298	-0.791017	1.103999
H	2.757724	-0.138725	1.527579
H	1.416409	-0.966569	1.717587

7 18 1.688 F

Ph$_2$CH$^+$ *C$_2$* fopt

1 1

C	1.291504	-0.417969	0.038513
C	1.555800	0.936157	0.399902
C	2.852661	1.416214	0.394165
C	3.914566	0.571609	0.029770
C	3.685089	-0.770889	-0.301086
C	2.393875	-1.268524	-0.273911
C	0.000000	-0.999680	0.000000
C	-1.291504	-0.417969	-0.038513
C	-1.555800	0.936157	-0.399902
C	-2.852661	1.416214	-0.394165
C	-3.914566	0.571609	-0.029770
C	-3.685089	-0.770889	0.301086
C	-2.393875	-1.268524	0.273911
H	0.749878	1.572647	0.744598
H	3.054000	2.440582	0.690247
H	4.929459	0.958603	0.028534
H	4.515503	-1.418213	-0.562851
H	2.205185	-2.309265	-0.521973
H	0.000000	-2.089966	0.000000
H	-0.749878	1.572647	-0.744598
H	-3.053986	2.440582	-0.690247
H	-4.929459	0.958603	-0.028534
H	-4.515503	-1.418213	0.562851
H	-2.205185	-2.309265	0.521973

TS Ph_2CH^+-OH_2 F

1 1

C	1.346652	-0.351298	-0.126642
C	1.612545	0.842053	0.575676
C	2.903421	1.359298	0.594899
C	3.938638	0.713169	-0.090776
C	3.684405	-0.465028	-0.792550
C	2.394412	-0.993328	-0.811146
C	-0.004478	-0.990445	-0.207845
C	-1.342205	-0.315084	-0.222729
C	-1.503147	1.071691	-0.356324
C	-2.781697	1.627165	-0.333423
C	-3.904644	0.808373	-0.193520
C	-3.755018	-0.578572	-0.101579
C	-2.481743	-1.140518	-0.138909
H	0.828311	1.341778	1.132317
H	3.104873	2.271119	1.148498
H	4.941871	1.127914	-0.070532
H	4.483981	-0.971361	-1.323820
H	2.197506	-1.907367	-1.366475
H	-0.002632	-2.019015	-0.567687
H	-0.640844	1.711620	-0.503827
H	-2.901087	2.700873	-0.438939
H	-4.897528	1.247354	-0.179259
H	-4.627459	-1.220009	-0.026411
H	-2.371832	-2.224203	-0.116625
O	-0.065822	-1.074851	1.476927
H	0.683945	-1.553649	1.899738
H	-0.915387	-1.431107	1.826816

7 25 1.688 F

TS Ph_2CH^+-OH_2 F

1 1

C	1.346652	-0.351298	-0.126642
C	1.612545	0.842053	0.575676
C	2.903421	1.359298	0.594899
C	3.938638	0.713169	-0.090776
C	3.684405	-0.465028	-0.792550
C	2.394412	-0.993328	-0.811146
C	-0.004478	-0.990445	-0.207845
C	-1.342205	-0.315084	-0.222729
C	-1.503147	1.071691	-0.356324
C	-2.781697	1.627165	-0.333423
C	-3.904644	0.808373	-0.193520
C	-3.755018	-0.578572	-0.101579
C	-2.481743	-1.140518	-0.138909
H	0.828311	1.341778	1.132317
H	3.104873	2.271119	1.148498
H	4.941871	1.127914	-0.070532
H	4.483981	-0.971361	-1.323820
H	2.197506	-1.907367	-1.366475
H	-0.002632	-2.019015	-0.567687
H	-0.640844	1.711620	-0.503827
H	-2.901087	2.700873	-0.438939
H	-4.897528	1.247354	-0.179259
H	-4.627459	-1.220009	-0.026411
H	-2.371832	-2.224203	-0.116625
O	-0.065822	-1.074851	1.476927
H	0.683945	-1.553649	1.899738
H	-0.915387	-1.431107	1.826816

7 25 1.688 F

Cumyl$^+$ C_S fopt

1 1

C	0.166122	-0.334991	-2.643800
C	-1.041061	-0.314194	-1.927261
C	-1.019165	-0.314087	-0.546265
C	0.222656	-0.313644	0.168610
C	1.434769	-0.324448	-0.595566
C	1.401123	-0.345215	-1.976089
C	0.251053	-0.303070	1.582748
C	-0.981979	-0.314453	2.420120
C	1.516617	-0.280182	2.369690
H	0.144272	-0.343307	-3.729965
H	-1.987564	-0.303116	-2.457214
H	-1.958679	-0.295639	-0.008286
H	2.395142	-0.334961	-0.095444
H	2.325592	-0.364639	-2.543411
H	-1.775589	0.207428	1.860000
H	-0.826065	0.275116	3.330093
H	-1.350464	-1.302582	2.690781
H	1.341675	0.168915	3.353394
H	2.353622	0.223160	1.888565
H	1.810500	-1.324432	2.567627

TS Cumyl$^+$-OH_2 F

1 1

C	2.917023	-0.006593	0.019323
C	2.212821	-1.211633	-0.024752
C	0.821724	-1.205737	-0.085761
C	0.106891	0.010619	-0.100131
C	0.833363	1.217169	-0.052288
C	2.224099	1.206048	0.004064
C	-1.390240	0.018226	-0.164764
C	-2.071046	-1.220007	-0.721009
C	-2.068736	1.299743	-0.606435
O	-1.800810	-0.002528	1.472412
H	4.001975	-0.012419	0.061259
H	2.745982	-2.157094	-0.021753
H	0.305178	-2.157851	-0.140319
H	0.322773	2.172834	-0.067004
H	2.766871	2.145535	0.033078
H	-1.835761	-1.285976	-1.789034
H	-3.159679	-1.143129	-0.634697
H	-1.741570	-2.149925	-0.253301
H	-3.156188	1.215182	-0.525431
H	-1.826718	1.467474	-1.661671
H	-1.742947	2.168767	-0.034377
H	-1.114273	-0.486908	1.977968
H	-2.674561	-0.403269	1.666504

7 10 1.688 F

(*p*-MeOPh)(C_6H_4)(CF_3)$_2$C$^+$ *Cs* fopt

1 1

C	-3.084048	-0.262373	0.017408
C	-2.267167	-1.436416	0.097478
C	-0.914498	-1.330984	0.086521
C	-0.248199	-0.029072	0.009723
C	-1.119662	1.140752	-0.063928
C	-2.476928	1.029825	-0.068866
O	-4.368144	-0.474989	0.028507
C	1.122925	0.058054	0.000859
C	1.971030	1.338267	0.029941
C	1.986267	-1.224512	-0.039264
F	3.280235	-0.964872	-0.184788
F	1.595692	-1.995559	-1.070373
F	1.808152	-1.914691	1.100981
F	2.827021	1.251975	1.053229
F	1.265181	2.469122	0.195113
F	2.642677	1.434012	-1.121700
F	-5.339607	0.606845	-0.043634
H	-2.764312	-2.397828	0.168171
H	-0.324691	-2.233360	0.156414
H	-0.681409	2.123105	-0.142457
H	-3.089451	1.920362	-0.141379
H	-6.306390	0.109371	-0.009213
H	-5.220707	1.146820	-0.985674
H	-5.219189	1.269246	0.816506

TS (*p*-MeO)(C_6H_4)(CF_3)$_2C^+$-OH_2 F

1 1
C 3.181837 -0.288087 0.074802
C 2.532044 0.914316 -0.272344
C 1.153508 0.999214 -0.206810
C 0.360337 -0.117420 0.165965
C 1.037873 -1.322329 0.518403
C 2.409389 -1.399923 0.485552
C -1.093606 -0.041992 0.216072
O 4.497731 -0.475961 0.056847
C 5.375822 0.587046 -0.352548
C -1.748043 1.353994 -0.007306
C -1.929473 -1.173503 -0.466496
F -2.089254 -0.827291 -1.743239
F -3.143201 -1.284300 0.116834
F -1.345715 -2.366553 -0.404388
F -1.237645 2.223497 0.890416
F -3.071141 1.293685 0.211136
F -1.528295 1.805259 -1.235655
O -1.542925 -0.325212 1.818333
H 3.098455 1.780048 -0.592460
H 0.698056 1.938145 -0.490451
H 0.479884 -2.188645 0.846975
H 2.925934 -2.310919 0.767592
H 6.379744 0.170994 -0.283000
H 5.281818 1.445820 0.319583
H 5.166810 0.883316 -1.385259
H -2.516687 -0.295841 1.961334
H -1.093329 0.319903 2.406552

7 18 1.688 F

(*p*-MeOPh)($Me)_2C^+$ fopt
1 1
C -1.368210 0.126190 -0.001404
C -0.767593 -1.163239 -0.000916
C 0.599014 -1.267441 -0.001495
C 1.456284 -0.112625 -0.001923
C 0.809600 1.175018 -0.002182
C -0.551682 1.291397 -0.002136
C 2.847839 -0.256729 -0.001495
O -2.666290 0.345245 -0.001221
C -3.613205 -0.747147 -0.000366
C 3.503800 -1.609726 -0.002197
C 3.801117 0.888184 0.000687
H -1.379486 -2.056931 -0.000244
H 1.038100 -2.258438 -0.000977
H 1.402405 2.080933 -0.002884
H -1.042587 2.258438 -0.002563
H -4.591476 -0.270035 -0.000504
H -3.490524 -1.353668 0.901062
H -3.490829 -1.354828 -0.901047
H 3.220840 -2.186249 0.887146
H 4.591461 -1.521606 -0.013672
H 3.202087 -2.197571 -0.877426
H 3.354218 1.880127 0.006836
H 4.459656 0.802078 -0.875809
H 4.465881 0.794006 0.871536

TS (*p*-MeOPh)(Me)$_2$C$^+$-OH$_2$ F

1 1

C	-2.070435	0.286803	-0.013904
C	-1.456002	-0.979910	-0.028126
C	-0.072535	-1.073335	-0.078624
C	0.749130	0.073533	-0.105845
C	0.111024	1.337315	-0.073921
C	-1.265483	1.443988	-0.037938
C	2.228101	-0.049058	-0.156873
O	-3.391415	0.497635	0.022629
C	-4.289308	-0.619732	0.031497
C	2.806440	-1.192816	-0.968239
C	3.033960	1.231102	-0.298234
H	-2.049162	-1.886032	-0.006241
H	0.367069	-2.065352	-0.086023
H	0.691317	2.252689	-0.107742
H	-1.753717	2.412587	-0.033238
H	-5.288848	-0.187057	0.053049
H	-4.135732	-1.237579	0.922960
H	-4.168349	-1.224834	-0.873429
H	2.334283	-2.150580	-0.748640
H	3.885799	-1.287118	-0.814351
H	2.639928	-0.966376	-2.027067
H	2.760290	1.994078	0.434412
H	2.859393	1.646303	-1.296557
H	4.107047	1.028785	-0.220239
O	2.596099	-0.566451	1.407168
H	3.505635	-0.358414	1.710039
H	1.958229	-0.167899	2.035934

7 25 1.688 F

Trityl$^+$ C_{3v} fopt

1 1

C	-1.369244	0.477380	0.000569
C	-1.720942	1.677102	-0.673540
C	-3.035946	2.119612	-0.683569
C	-4.022845	1.398976	-0.000107
C	-3.695455	0.221979	0.683819
C	-2.389232	-0.245778	0.674420
C	-0.000434	0.000837	0.000642
C	1.097219	0.947487	0.000230
C	0.982457	2.193083	0.673080
C	2.042110	3.088773	0.682240
C	3.225055	2.781467	-0.000853
C	3.354182	1.565894	-0.683417
C	2.312006	0.649956	-0.673088
C	0.271043	-1.423094	0.000833
C	-0.591844	-2.326964	-0.674376
C	-0.317885	-3.687189	-0.685140
C	0.798788	-4.182273	-0.000880
C	1.653989	-3.310947	0.684396
C	1.406642	-1.945630	0.675367
H	-0.964028	2.217904	-1.230948
H	-3.298766	3.021195	-1.227747
H	-5.048818	1.755234	-0.000571
H	-4.460838	-0.322700	1.227465
H	-2.130584	-1.139539	1.231476
H	0.079393	2.418122	1.229796
H	1.954455	4.024388	1.225370
H	4.047736	3.490512	-0.001149
H	4.266398	1.340795	-1.226772
H	2.400676	-0.276866	-1.229053
H	-1.438580	-1.941429	-1.231593
H	-0.967054	-4.365103	-1.230170
H	1.002841	-5.249012	-0.001597
H	2.507647	-3.702112	1.228741
H	2.051542	-1.275407	1.232992

TS Trityl^{+}-OH$_2$ F

1 1

C	-1.160752	-0.926846	0.089033
C	-2.239249	-0.491687	-0.695149
C	-3.303279	-1.351692	-0.970353
C	-3.315455	-2.646611	-0.453558
C	-2.244974	-3.094868	0.326159
C	-1.171269	-2.248227	0.582273
C	-0.003478	-0.011991	0.399632
C	-0.213241	1.455735	0.119415
C	-1.237104	2.170254	0.771551
C	-1.451035	3.514833	0.480873
C	-0.668807	4.158283	-0.482497
C	0.331078	3.451741	-1.150835
C	0.566973	2.110382	-0.848056
C	1.379690	-0.541873	0.107547
C	1.579369	-1.633938	-0.751834
C	2.869841	-2.090486	-1.026478
C	3.975137	-1.475769	-0.440002
C	3.791969	-0.380287	0.409756
C	2.509038	0.090506	0.668452
H	-2.242665	0.510938	-1.105483
H	-4.125178	-1.003150	-1.587981
H	-4.149944	-3.309163	-0.662213
H	-2.241904	-4.105387	0.722876
H	-0.326667	-2.634372	1.150860
H	-1.862199	1.675264	1.507944
H	-2.233460	4.058427	1.001543
H	-0.842752	5.204986	-0.713180
H	0.934730	3.942585	-1.907961
H	1.343558	1.571113	-1.378328
H	0.731974	-2.116505	-1.223923
H	3.005972	-2.929695	-1.701513
H	4.976697	-1.838675	-0.649832
H	4.648321	0.113444	0.858623
H	2.395061	0.976328	1.291197
O	-0.080654	-0.011550	2.085866
H	0.625271	0.553357	2.465837
H	0.041697	-0.921858	2.429049

7 35 1.688 F

Tropylium^{+} fopt

1 1

C	-1.362869	0.861084	-0.000046
C	-1.522949	-0.528625	-0.000275
C	-0.176468	1.602356	0.000259
C	-0.536255	-1.520218	0.000198
C	1.142792	1.137039	-0.000061
C	1.601500	-0.184555	-0.000229
C	0.854233	-1.367081	0.000153
H	-2.282150	1.441910	-0.000076
H	-2.550171	-0.885315	-0.000641
H	-0.295593	2.683212	0.000580
H	-0.897873	-2.545731	0.000458
H	1.913605	1.904037	-0.000122
H	2.681763	-0.308990	-0.000534
H	1.430481	-2.289230	0.000336

TS Tropylium^{+}-OH_2 F

1 1

C	-0.750927	-1.551916	-0.212981
C	0.515390	-1.264373	-0.645327
C	-1.718024	-0.686592	0.376271
C	1.222330	0.000032	-0.510204
C	-1.718045	0.686545	0.376284
C	-0.750973	1.551913	-0.212947
C	0.515352	1.264417	-0.645296
H	-1.068365	-2.585532	-0.335900
H	1.078357	-2.068913	-1.112536
H	-2.596985	-1.175231	0.788816
H	2.172574	0.000051	-1.041838
H	-2.597020	1.175148	0.788840
H	-1.068443	2.585522	-0.335841
H	1.078295	2.068987	-1.112480
O	1.805913	0.000010	1.073708
H	2.331598	-0.795542	1.308279
H	2.332070	0.795274	1.308197

4 15 1.688 F

Ph$(OMe)_2C^{+}$ *C_1* fopt

1 1

C	1.052840	-0.085935	-0.077195
C	-0.398317	-0.082758	-0.033407
O	1.628402	-1.229378	-0.265101
O	1.850572	0.928481	0.042903
C	1.487151	2.245984	0.565779
C	3.088417	-1.352685	-0.240924
C	-1.153719	1.027005	-0.471924
C	-2.541101	0.960392	-0.462338
C	-3.184981	-0.194024	-0.003741
C	-2.442443	-1.299239	0.426131
C	-1.055172	-1.256561	0.399490
H	2.365100	2.567723	1.123887
H	0.613008	2.169818	1.211546
H	1.310605	2.912233	-0.278513
H	3.508529	-0.789087	-1.074439
H	3.266463	-2.419137	-0.356018
H	3.470259	-0.984131	0.711907
H	-0.668338	1.911716	-0.866841
H	-3.122441	1.804475	-0.818578
H	-4.269980	-0.234620	0.011129
H	-2.947375	-2.193449	0.776577
H	-0.473664	-2.111433	0.725711

TS $Ph(OMe)_2C^+$-OH_2 F

1 1

C	1.089518	-0.145722	0.101083
O	-0.409858	0.009784	0.077986
O	1.563087	-1.369623	-0.192192
C	1.859598	0.828788	-0.375027
C	1.780344	2.200190	0.085751
C	1.393335	-1.830178	-1.560639
C	-1.024465	1.005799	-0.694985
C	-2.416451	1.078237	-0.761039
C	-3.201918	0.159937	-0.064015
C	-2.595771	-0.855726	0.682289
C	-1.208304	-0.938693	0.743158
H	2.618639	2.368797	0.767004
H	0.824790	2.416610	0.569804
H	1.896938	2.833169	-0.794002
H	0.332352	-1.863823	-1.822071
H	1.819606	-2.831696	-1.569565
H	1.944881	-1.177231	-2.240282
H	-0.427927	1.703785	-1.271869
H	-2.883912	1.848968	-1.365678
H	-4.284571	0.221653	-0.115274
H	-3.203548	-1.589597	1.202057
H	-0.753808	-1.772705	1.275468
O	1.508238	-0.206104	1.735210
H	0.982152	-0.907351	2.174323
H	1.248443	0.623166	2.188627

1 23 1.688 F

$Ph(OCH_2)_2C^+$ *C_{2v}* fopt

1 1

C	0.898346	-0.000001	-0.000001
C	-0.529578	0.000000	-0.000001
O	1.599739	1.097605	-0.021568
O	1.599739	-1.097606	0.021567
C	3.029910	-0.769126	-0.031066
C	3.029910	0.769127	0.031068
C	-1.227744	-1.229890	0.002680
C	-2.614124	-1.219765	0.002832
C	-3.303982	0.000000	0.000001
C	-2.614123	1.219765	-0.002832
C	-1.227743	1.229890	-0.002681
H	3.501400	-1.253466	0.823776
H	3.416371	-1.180099	-0.964401
H	3.416369	1.180100	0.964405
H	3.501402	1.253467	-0.823773
H	-0.680826	-2.166585	0.004060
H	-3.162468	-2.155876	0.004731
H	-4.390019	0.000001	0.000002
H	-3.162467	2.155876	-0.004730
H	-0.680825	2.166585	-0.004062

TS Ph(OCH$_2$)$_2$C-OH$_2$ F

1 1
C -0.825975 -0.007811 0.100517
C 0.652982 0.003674 -0.028149
O -1.471323 -1.077378 -0.367061
O -1.483370 1.133677 -0.130929
C -2.821494 0.813586 -0.627534
C -2.876324 -0.717621 -0.525426
C 1.342044 1.225515 -0.021791
C 2.731726 1.225702 -0.120313
C 3.427959 0.018265 -0.221508
C 2.737333 -1.196957 -0.230814
C 1.348010 -1.211442 -0.132552
H -3.552962 1.322380 0.000962
H -2.877145 1.188561 -1.650797
H -3.428611 -1.073413 0.347291
H -3.232268 -1.215194 -1.426770
H 0.796057 2.161930 0.034810
H 3.269958 2.168209 -0.126930
H 4.510727 0.024420 -0.301852
H 3.279715 -2.132447 -0.324221
H 0.806618 -2.152235 -0.165347
O -1.101267 -0.170440 1.757957
H -0.815507 0.631442 2.243334
H -0.606472 -0.927981 2.135204

1 21 1.688 F

(MeO)$_3$C$^+$ *C$_{3h}$* fopt

1 1
C 0.000153 -0.000275 0.000717
O 0.677231 1.093400 0.000366
O 0.608856 -1.133362 0.000320
O -1.285538 0.039505 0.000275
C -0.016235 2.395660 -0.000412
C -2.067642 -1.211533 -0.000366
C 2.083420 -1.183609 -0.000412
H 0.792450 3.122025 -0.004211
H -0.621735 2.473831 0.902359
H -0.627106 2.470291 -0.899826
H -3.100769 -0.873520 -0.002121
H -1.831680 -1.776184 0.901398
H -1.828934 -1.777176 -0.900787
H 2.308411 -2.247070 -0.007416
H 2.453354 -0.700974 0.903976
H 2.453415 -0.688980 -0.898239

TS $(MeO)_3C^+$-OH_2 F

1 1

C	-0.000512	-0.009402	0.027115
O	-1.252077	0.200996	-0.342143
O	0.832070	1.010040	-0.154200
O	0.508818	-1.210922	-0.197080
C	-2.144173	-0.946912	-0.487680
C	1.942551	-1.365582	-0.411334
C	0.296972	2.336054	-0.434434
H	-1.774387	-1.597503	-1.280174
H	-3.104159	-0.510700	-0.756073
H	-2.212937	-1.486942	0.458368
H	2.074601	-2.433321	-0.574112
H	2.504249	-1.042447	0.468652
H	2.250550	-0.794328	-1.287136
H	-0.299239	2.310492	-1.346373
H	1.178076	2.962332	-0.559457
H	-0.307038	2.694363	0.403667
O	-0.204887	-0.085612	1.700963
H	-0.584342	0.738589	2.069215
H	0.634207	-0.241497	2.181105

1 17 1.688 F

$(MeO)(OCH_2)_2C^+$ *C_1* fopt

1 1

C	0.245174	-0.280708	-0.003956
O	-0.700687	-1.162508	-0.032509
O	-0.113584	0.967304	0.026811
O	1.455101	-0.664177	-0.006558
C	-1.993644	-0.461740	0.040253
C	2.550511	0.331350	0.006792
C	-1.588370	1.027169	-0.034570
H	-2.456360	-0.752260	0.983683
H	-2.590014	-0.806482	-0.803678
H	3.450854	-0.277044	-0.006100
H	2.475859	0.920921	0.920385
H	2.470648	0.951788	-0.885695
H	-1.842823	1.515393	-0.975414
H	-1.916833	1.626307	0.813753

TS (MeO)(OCH$_2$)$_2$C$^+$–OH$_2$ F

1 1

C	-0.191063	0.121799	-0.178389
O	0.766665	0.552215	-0.994029
O	0.245431	-0.755392	0.734874
O	-1.342009	-0.039268	-0.767069
C	2.048068	0.175300	-0.415694
C	-2.410370	-0.730582	-0.050414
C	1.666153	-1.007415	0.474195
H	2.450514	1.026896	0.136697
H	2.710725	-0.075879	-1.239300
H	-3.214568	-0.806770	-0.774268
H	-2.718591	-0.135799	0.808048
H	-2.066909	-1.715537	0.257166
H	1.738804	-1.970105	-0.030131
H	2.181428	-1.041950	1.430849
O	-0.541289	1.432692	0.825725
H	-0.059624	1.568174	1.655133
H	-0.728889	2.274382	0.381616

1 15 1.688 F

Me(OMe)$_2$C$^+$ *C$_s$* fopt

1 1

C	-0.000997	0.409350	0.000001
C	-0.750532	1.696168	0.000001
O	-0.513358	-0.769142	0.000002
O	1.276134	0.497200	-0.000002
C	2.128640	-0.706025	-0.000003
C	-1.962583	-1.023314	0.000002
H	-1.830618	1.559902	0.000006
H	-0.451191	2.276302	-0.880553
H	-0.451184	2.276305	0.880551
H	3.140735	-0.309896	-0.000010
H	1.922471	-1.284836	-0.900469
H	1.922481	-1.284830	0.900468
H	-2.401331	-0.603187	0.905372
H	-2.039403	-2.108121	-0.000003
H	-2.401332	-0.603179	-0.905364

TS $Me(OMe)_2C^+$-OH_2 F

1 1

C	0.007303	0.285682	-0.179606
C	-0.746490	1.305166	-1.001408
O	-0.481211	-0.935305	0.011786
O	1.312012	0.317523	-0.412845
C	2.140001	-0.836166	-0.089035
C	-1.917224	-1.163982	0.012594
H	-1.748791	1.491564	-0.613107
H	-0.821252	0.916823	-2.022048
H	-0.181078	2.239004	-1.044530
H	3.146665	-0.532928	-0.369695
H	1.816886	-1.701408	-0.667829
H	2.097196	-1.060540	0.980575
H	-2.399049	-0.552304	0.778884
H	-2.028528	-2.220913	0.248211
H	-2.331859	-0.955016	-0.975374
O	-0.183745	0.938429	1.365310
H	0.249745	0.402142	2.060206
H	0.122082	1.864210	1.455431

1 16 1.688 F

$Me(OCH_2)_2C^+$ *C_1* fopt

1 1

C	0.685398	0.005095	-0.001903
C	2.161695	0.006584	0.000512
O	0.007987	-1.089535	-0.001291
O	0.000369	1.093385	-0.001607
C	-1.443674	0.766987	0.001184
C	-1.438070	-0.773716	0.000779
H	2.540959	1.027585	-0.041126
H	2.523582	-0.575172	-0.855049
H	2.516742	-0.494959	0.909077
H	-1.862228	1.220679	0.899247
H	-1.865832	1.221265	-0.894877
H	-1.854902	-1.230141	0.898232
H	-1.857265	-1.229750	-0.895766

TS Me(OCH$_2$)$_2$C$^+$-OH$_2$ F

1 1

C	-0.517800	-0.188283	0.067363
C	-1.825519	-0.883801	0.315693
O	0.211163	-0.631381	-0.952791
O	0.208121	0.109918	1.138921
C	1.595923	0.295964	0.714867
C	1.623801	-0.354941	-0.680313
H	-2.405901	-0.363049	1.080462
H	-1.598268	-1.890256	0.679499
H	-2.401393	-0.972470	-0.608040
H	1.810939	1.366053	0.698930
H	2.220850	-0.202496	1.455144
H	2.003060	0.303540	-1.462527
H	2.141361	-1.314276	-0.713354
O	-0.941013	1.348817	-0.487217
H	-1.475187	1.883860	0.135598
H	-1.380064	1.356635	-1.362683

1 14 1.688 F

Ph(MeO)(Me)C$^+$ *C$_1$* fopt

1 1

C	1.678177	0.458328	-0.157654
C	0.275864	0.129379	-0.084625
O	2.658951	-0.371231	-0.025909
C	2.161850	1.853745	-0.395752
C	2.604813	-1.746200	0.464386
C	-0.632629	1.155762	0.285187
C	-1.992600	0.896637	0.355865
C	-2.480621	-0.370255	0.013504
C	-1.604202	-1.382706	-0.394806
C	-0.237656	-1.147705	-0.431473
H	3.204315	1.832657	-0.718353
H	2.118073	2.416031	0.548080
H	1.544357	2.375992	-1.129272
H	2.562164	-2.416031	-0.395233
H	1.752029	-1.882767	1.129288
H	3.548019	-1.876144	0.993057
H	-0.265015	2.141312	0.548706
H	-2.676346	1.679520	0.666977
H	-3.548035	-0.565918	0.053543
H	-1.991486	-2.352600	-0.689255
H	0.417603	-1.929703	-0.793228

TS Ph(MeO)(Me)C$^+$-OH$_2$ F

1 1

C	-1.222179	0.389987	0.029383
C	0.271104	0.186990	0.046010
O	-2.007194	-0.341372	-0.762764
C	-1.749798	1.811636	0.058737
C	-1.630980	-1.658678	-1.241127
C	1.096604	1.188294	-0.491875
C	2.479198	1.012662	-0.529523
C	3.054119	-0.151482	-0.018515
C	2.241488	-1.148272	0.526296
C	0.858007	-0.986952	0.553956
H	-2.835280	1.803626	0.193386
H	-1.555172	2.278658	-0.910677
H	-1.273657	2.412272	0.836848
H	-1.667146	-2.383034	-0.424305
H	-0.638800	-1.634168	-1.693778
H	-2.386154	-1.901097	-1.987318
H	0.672541	2.101884	-0.893538
H	3.105049	1.791060	-0.954385
H	4.131633	-0.281972	-0.042761
H	2.683183	-2.054771	0.928244
H	0.243200	-1.772740	0.980993
O	-1.639343	-0.201377	1.554378
H	-1.103845	0.170875	2.285252
H	-2.588631	-0.053711	1.749082

1 22 1.688 F

Me$_2$(OMe)C$^+$ *C$_s$* fopt

1 1

C	0.466583	-0.004026	0.000029
C	0.393172	1.478411	0.000029
O	-0.574600	-0.737028	-0.000032
C	1.755234	-0.726942	-0.000017
C	-1.947479	-0.204345	0.000014
H	1.388046	1.924410	0.001250
H	-0.161820	1.831591	0.880522
H	-0.159364	1.831408	-0.882128
H	1.617752	-1.808622	-0.000658
H	2.340134	-0.414015	0.876982
H	2.340805	-0.412962	-0.876161
H	-2.098374	0.386796	0.904509
H	-2.577759	-1.090178	-0.001390
H	-2.097672	0.389207	-0.903002

TS $Me_2(OMe)C^+$-OH_2 F

1 1

C	0.335204	0.126210	-0.140188
C	0.250528	1.440256	0.602304
O	-0.763802	-0.399199	-0.671701
C	1.511618	-0.060659	-1.070816
C	-2.078666	-0.098522	-0.126439
H	1.222788	1.719301	1.016933
H	-0.491346	1.421353	1.402721
H	-0.032065	2.213939	-0.120446
H	1.509025	-1.063031	-1.507682
H	2.464080	0.134616	-0.571113
H	1.407891	0.658632	-1.890220
H	-2.125394	-0.361683	0.933238
H	-2.763169	-0.721876	-0.699147
H	-2.318318	0.955711	-0.278437
O	0.631724	-0.940255	1.134202
H	1.476186	-0.820569	1.616132
H	0.594842	-1.864461	0.808846

1 15 1.688 F

$Ph(MeO)CH^+$ *Cs* fopt

1 1

C	-1.317944	0.531526	-0.000091
C	0.056980	0.223099	-0.000030
O	-2.221402	-0.379926	-0.000045
C	-3.642224	-0.036511	0.000092
C	0.975865	1.307434	0.000001
C	2.337117	1.052275	0.000047
C	2.790256	-0.274385	0.000031
C	1.890658	-1.355653	0.000001
C	0.529238	-1.118667	-0.000014
H	-1.647380	1.574144	-0.000258
H	-4.067075	-0.488339	-0.896316
H	-3.768108	1.048298	-0.000838
H	-4.066617	-0.486767	0.897508
H	0.607519	2.329818	-0.000014
H	3.047902	1.871687	0.000092
H	3.858401	-0.472002	0.000031
H	2.267381	-2.373079	-0.000045
H	-0.180479	-1.939056	-0.000030

TS Ph(MeO)CH$^+$-OH$_2$ F

1 1
C 1.256777 -0.750674 -0.149967
C -0.157948 -0.310919 -0.044995
O 2.222870 -0.074188 -0.749305
C 2.196025 1.373719 -0.868865
C -1.119042 -1.148485 -0.636152
C -2.465740 -0.791216 -0.610125
C -2.860448 0.386541 0.027137
C -1.910478 1.211835 0.638016
C -0.561015 0.872159 0.602047
H 1.368017 -1.805893 -0.401427
H 2.375340 1.835285 0.104902
H 1.243820 1.701230 -1.288940
H 3.014078 1.605432 -1.548737
H -0.813469 -2.068276 -1.128658
H -3.203562 -1.434613 -1.078551
H -3.910663 0.660658 0.055112
H -2.222673 2.120791 1.142478
H 0.165749 1.512646 1.091443
O 1.765724 -0.774921 1.459297
H 1.145260 -1.230366 2.065571
H 2.660561 -1.161789 1.564293

1 19 1.688 F

Xanthylium$^+$ C_{2v} fopt

1 1
C 1.215782 1.080164 -0.000007
C 2.491730 1.710835 0.000050
C 3.648556 0.972980 0.000066
C 3.580912 -0.452407 0.000025
C 2.339068 -1.108629 -0.000040
C 1.185767 -0.349875 -0.000050
C 0.000019 1.770523 -0.000024
C -1.215765 1.080192 -0.000066
C -2.491695 1.710876 -0.000060
C -3.648538 0.973036 -0.000071
C -3.580932 -0.452354 -0.000090
C -2.339090 -1.108585 -0.000104
C -1.185779 -0.349852 -0.000092
O -0.000012 -1.011971 -0.000121
O 4.647655 -1.247670 0.000032
O -4.647645 -1.247615 -0.000140
C 5.975042 -0.694107 0.000104
C -5.975059 -0.694198 0.000374
H 2.537393 2.795899 0.000085
H 4.608240 1.474225 0.000101
H 2.297330 -2.191345 -0.000074
H 0.000030 2.858242 0.000005
H -2.537357 2.795941 -0.000047
H -4.608194 1.474327 -0.000055
H -2.297359 -2.191302 -0.000136
H 6.641227 -1.555596 0.000112
H 6.144695 -0.094520 0.899812
H 6.144777 -0.094482 -0.899563
H -6.641177 -1.555737 0.000475
H -6.145157 -0.094481 -0.899169
H -6.144535 -0.094714 0.900188

TS Xanthylium^{+}-OH_2 F

1 1

C	-1.231018	0.900936	-0.200497
C	-2.490456	1.451579	-0.518458
C	-3.648971	0.700257	-0.441326
C	-3.574168	-0.653339	-0.033824
C	-2.332113	-1.229260	0.273482
C	-1.183914	-0.459740	0.182153
C	-0.000191	1.677800	-0.221326
C	1.231549	0.902497	-0.199217
C	2.491741	1.454634	-0.511349
C	3.649183	0.702154	-0.436577
C	3.573343	-0.653552	-0.035680
C	2.331120	-1.229936	0.269774
C	1.183341	-0.459472	0.180561
O	-0.000191	-1.084752	0.458635
O	-4.630263	-1.470816	0.076190
O	4.628957	-1.471922	0.071264
C	-5.940329	-0.989581	-0.248017
C	5.939594	-0.989746	-0.249515
H	-2.548160	2.488975	-0.840322
H	-4.599219	1.149676	-0.700442
H	-2.275258	-2.273334	0.558421
H	-0.000641	2.549871	-0.871806
H	2.549677	2.495118	-0.821561
H	4.600330	1.152989	-0.689846
H	2.273603	-2.274725	0.551869
H	-6.606204	-1.836551	-0.086059
H	-5.994143	-0.674255	-1.295599
H	-6.229403	-0.163516	0.410911
H	6.604721	-1.838157	-0.092074
H	6.228866	-0.167721	0.414319
H	5.994139	-0.668409	-1.295210
O	0.018112	2.592712	1.197116
H	-0.839578	2.523593	1.668326
H	0.716091	2.263283	1.802335

7 32 F 1.688

Table S1.

B3LYP/6-31G(d)//SMD calculated $\Delta G^{\neq}$ values for the water solvation of a selected set of carbocations (R^+; see Fig. 1 in the main text), together with the corresponding calculated ΔG and Λ values required to use Marcus Eq 3 (see the main text), in water solution. All data in kcal/mol. The symmetry group of the most stable R^+ conformation used for the computations are given into parenthesis.

R^+	Λ_i	Λ_o^{EL}	ΔG	$\Delta G^{\neq}$ [a]
t-Bu$^+$ (C_{3v})	15.7	6.27	-35.0	7.49
Bn$^+$ (C_{2v})	13.3	4.96	-31.2	5.94
Ph(Me)CH$^+$ (C_s)	15.5	5.37	-25.6	10.0
Benzhydryl$^+$ (C_2)	8.48	4.74	5.16	21.6
Cumyl$^+$ (C_s)	15.8	4.71	-21.7	11.1
(*p*-MeOPh)(CF$_3$)$_2$C$^+$ (C_s)	15.7	4.96	-19.5	12.1
(*p*-MeOPh)(Me)$_2$C$^+$ (C_s)	16.0	4.87	-15.7	13.7
Trityl$^+$ (C_{3v})	11.0	4.31	-8.54	11.4
Tropylium$^+$ (D_7)	17.3	5.35	1.75	23.6
Ph(MeO)$_2$C$^+$ (C_1)	26.2	4.57	-14.9	24.2
Ph(CH$_2$O)$_2$C$^+$ (C_{2v})	16.7	4.90	6.64	24.9
(MeO)$_3$C$^+$ (C_{3h})	14.3	5.35	-20.2	13.9
(MeO)(CH$_2$O)$_2$C$^+$ (C_1)	19.4	5.90	-22.2	15.5
Me(CH$_2$O)$_2$C$^+$ (C_s)	16.6	5.76	-9.08	18.0
Me(MeO)$_2$C$^+$ (C_1)	16.6	5.60	-11.9	16.6
Ph(MeO)(Me)C$^+$ (C_1)	15.2	5.00	-27.2	8.86
Me$_2$(MeO)C$^+$ (C_s)	16.6	5.92	-18.0	14.4
Ph(MeO)CH$^+$ (C_s)	22.3	5.30	-17.8	19.4
Xanthylium$^+$ (C_{2v})	17.8	5.11	1.26	22.9