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O–H Bond Dissociation Energies‡

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‡ In memory of our dear friend and colleague Athel Beckwith, in recognition of his many outstanding contributions to science.

Table AP1. B3-LYP/6-31G(2df,p)-optimized geometries (Å)

ROH molecules

H–OH

O	0.000000	0.000000	0.118794
H	0.000000	0.756678	-0.475174
H	0.000000	-0.756678	-0.475174

NH_2–OH

O	-0.724177	0.000201	-0.140249
H	-1.113355	-0.001060	0.740246
N	0.689108	-0.000184	0.156461
H	1.041450	-0.808319	-0.357654
H	1.041569	0.809062	-0.355827

HO–OH

O	0.000000	0.722922	-0.058820
H	0.790317	0.898277	0.470561
O	0.000000	-0.722922	-0.058820
H	-0.790317	-0.898277	0.470561

MeO–OH

O	1.165252	-0.265045	-0.105636
H	1.554059	-0.139528	0.771914
O	0.017641	0.609118	-0.014978
C	-1.121107	-0.226235	0.018746
H	-1.140319	-0.854273	0.919390
H	-1.972598	0.461666	0.032894
H	-1.177647	-0.863043	-0.871769

CF_3O–OH

O	1.876365	-0.004605	0.122289
H	2.143473	-0.056695	-0.809101
O	0.713381	0.834911	0.024294
C	-0.386126	0.004936	0.002829
F	-0.484861	-0.739860	1.093432
F	-1.430003	0.813400	-0.081361
F	-0.367878	-0.808581	-1.054354

CCl_3O–OH

O	-1.944903	0.138736	1.112081
H	-2.219340	-0.790869	1.034696
O	-0.529284	-0.009789	1.307959
C	0.111193	0.009797	0.091167
Cl	-0.177305	1.520880	-0.821965
Cl	1.827309	-0.142315	0.525597
Cl	-0.394376	-1.396183	-0.935515

F–OH

O	0.053330	0.702615	0.000000
H	-0.906617	0.848247	0.000000
F	0.053330	-0.718796	0.000000

Me–OH

O	-0.046498	-0.756503	0.000000
H	0.868774	-1.050409	0.000000
C	-0.046498	0.659137	0.000000
H	-1.092659	0.977865	0.000000
H	0.437431	1.084873	0.892050
H	0.437431	1.084873	-0.892050

Et–OH

O	1.198291	-0.209543	0.000000
H	1.941416	0.400601	0.000000
C	0.000000	0.554221	0.000000
H	-0.053770	1.206967	0.886620
H	-0.053770	1.206967	-0.886620
C	-1.171158	-0.413854	0.000000
H	-1.136166	-1.054958	0.885927
H	-2.120922	0.129527	0.000000
H	-1.136166	-1.054958	-0.885927

CF_3CH_2–OH

O	-1.928343	-0.222610	0.000040
H	-2.775474	0.231556	-0.000004
C	-0.906732	0.743419	-0.000022
H	-0.921033	1.385723	-0.891962
H	-0.921007	1.385806	0.891860
C	0.423088	0.005971	-0.000006
F	0.561738	-0.767924	-1.080104
F	1.426037	0.900306	-0.000093
F	0.561794	-0.767776	1.080192

t-Bu–OH

O	-0.486187	1.366215	0.000000
H	-1.448716	1.329506	0.000000
C	-0.000630	0.016442	0.000000
C	-0.486187	-0.706569	1.264561
H	-1.580772	-0.775043	1.277024
H	-0.090813	-1.726294	1.321068
H	-0.168997	-0.160918	2.157893
C	-0.486187	-0.706569	-1.264561
H	-1.580772	-0.775043	-1.277024
H	-0.168997	-0.160918	-2.157893
H	-0.090813	-1.726294	-1.321068
C	1.523859	0.147947	0.000000
H	1.856290	0.696991	-0.885642
H	1.856290	0.696991	0.885642
H	2.001661	-0.836195	0.000000

CF_3–OH

O	1.041383	0.874547	0.000000
H	1.859501	0.362553	0.000000
C	-0.004766	0.019929	0.000000
F	-1.119576	0.731239	0.000000
F	-0.004766	-0.781092	1.076641
F	-0.004766	-0.781092	-1.076641

CF_3CF_2–OH

O	1.709205	-0.454524	0.000000
H	2.161783	-1.308635	0.000000
C	0.376276	-0.669069	0.000000
F	-0.025847	-1.370614	1.082911
F	-0.025847	-1.370614	-1.082911
C	-0.355247	0.694139	0.000000
F	-0.025847	1.391449	1.083294
F	-0.025847	1.391449	-1.083294
F	-1.670124	0.491042	0.000000

PH_2–OH

O	0.039436	1.092102	0.000000
H	0.949899	1.400003	0.000000
P	0.039436	-0.570612	0.000000
H	-0.928465	-0.788823	1.025095
H	-0.928465	-0.788823	-1.025095

HS–OH

O	1.087950	0.024074	-0.117916
H	1.433535	0.029440	0.782924
S	-0.578107	-0.090678	0.009352
H	-0.887421	1.228821	0.010766

Cl–OH

O	0.036355	1.108499	0.000000
H	-0.908867	1.317352	0.000000
Cl	0.036355	-0.599138	0.000000

Br–OH

O	0.021447	1.462326	0.000000
H	-0.922213	1.675202	0.000000
Br	0.021447	-0.382109	0.000000

BH_2–OH

O	0.627140	-0.127136	-0.000039
H	1.111505	0.704109	-0.000058
B	-0.711202	0.031266	0.000046
H	-1.205933	1.122934	0.000083
H	-1.366686	-0.966282	0.000054

CH_2=CH–OH

O	-1.104561	-0.390189	0.000000
H	-1.892351	0.158746	0.000000
C	0.000000	0.410664	0.000000
C	1.236235	-0.073794	0.000000
H	-0.195970	1.481510	0.000000
H	2.081694	0.600505	0.000000
H	1.425701	-1.140473	0.000000

Ph–OH

O	2.301238	-0.111155	0.000041
H	2.671514	0.777613	0.000310
C	0.939864	-0.025168	0.000028
C	0.264287	1.195976	0.000007
C	0.219538	-1.221499	0.000008
C	-1.128518	1.216681	-0.000029
H	0.826829	2.126213	0.000013
C	-1.169644	-1.187168	-0.000041
H	0.764314	-2.158596	0.000032
C	-1.853328	0.028722	-0.000057
H	-1.645085	2.171049	-0.000040
H	-1.723443	-2.120469	-0.000058
H	-2.937220	0.048158	-0.000089

$PhCH_2$–OH

O	2.682173	-0.517078	-0.235313
H	3.600080	-0.334946	-0.016348
C	1.906353	0.604122	0.154059
H	2.120773	1.478444	-0.481405
H	2.143752	0.900739	1.189838
C	0.435939	0.268056	0.059938
C	-0.003834	-1.055842	0.086199
C	-0.507775	1.294730	-0.020822
C	-1.365588	-1.345561	0.034421
H	0.729341	-1.851161	0.137309
C	-1.868237	1.006360	-0.065135
H	-0.174529	2.328766	-0.052534
C	-2.301961	-0.317725	-0.038211
H	-1.694975	-2.379669	0.050540
H	-2.589177	1.815024	-0.128775
H	-3.362030	-0.545413	-0.078815

HC(O)–OH

O	-1.029271	-0.445398	0.000000
H	-0.646252	-1.337393	0.000000
C	0.000000	0.419697	0.000000
O	1.159212	0.116859	0.000000
H	-0.393273	1.447525	0.000000

MeC(O)–OH

O	-1.244022	-0.380736	0.000000
H	-1.860053	0.367279	0.000000
C	0.000000	0.158950	0.000000
O	0.191559	1.346831	0.000000
C	1.058510	-0.914853	0.000000
H	0.941655	-1.552981	0.880614
H	0.941655	-1.552981	-0.880614
H	2.045387	-0.454660	0.000000

$CF_3C(O)$–OH

O	0.812871	-1.651658	0.000000
H	0.533782	-2.580713	0.000000
C	-0.296489	-0.903362	0.000000
O	-1.422851	-1.304237	0.000000
C	0.087832	0.596196	0.000000
F	0.812871	0.886687	1.083002
F	0.812871	0.886687	-1.083002
F	-1.003744	1.345612	0.000000

$NH_2C(O)$–OH

O	-0.835188	-0.979345	0.002458
H	-1.739636	-0.640470	0.004715
C	-0.040579	0.125898	-0.001852
O	-0.464792	1.257218	0.005667
N	1.271967	-0.234548	-0.046245
H	1.946449	0.490582	0.122428
H	1.532734	-1.186640	0.142684

HOC(O)–OH

O	-1.086752	-0.681407	0.000015
H	-1.845957	-0.083969	0.000028
C	0.000000	0.103168	-0.000006
O	0.000000	1.306432	-0.000001
O	1.086751	-0.681408	-0.000011
H	1.845958	-0.083971	-0.000018

NC–OH

O	-0.148099	-1.110437	0.000000
H	0.714684	-1.548707	0.000000
C	0.000000	0.179537	0.000000
N	0.067158	1.336426	0.000000

CN–OH

O	-0.002237	-1.090793	0.000000
H	0.932251	-1.351997	0.000000
N	0.000000	0.237122	0.000000
C	-0.152393	1.403081	0.000000

ON–OH

O	0.893227	-0.588122	0.000000
H	1.760249	-0.155556	0.000000
N	0.000000	0.518302	0.000000
O	-1.113258	0.154052	0.000000

CH_2=N–OH

O	1.077718	0.265752	0.000003
H	1.786141	-0.387316	-0.000009
N	-0.068092	-0.528462	0.000001
C	-1.125088	0.175739	-0.000012
H	-1.112739	1.265438	0.000016
H	-2.067973	-0.359338	0.000036

O_2N–OH

O	1.121897	-0.563424	0.000143
H	1.717538	0.204865	0.000310
N	-0.147687	0.037287	-0.000131
O	-0.152771	1.248262	0.000041
O	-1.054593	-0.743072	-0.000107

Vertical RO• radicals

H–O•

O	0.000000	0.000000	0.106820
H	0.000000	0.000000	-0.854560

NH_2–O•

O	0.796794	0.000000	0.020816
N	-0.641270	0.000000	-0.137273
H	-0.942737	-0.809877	0.397193
H	-0.942728	0.809880	0.397193

HO–O•

O	0.055883	0.778868	0.000000
O	0.055883	-0.672926	0.000000
H	-0.894128	-0.847528	0.000000

MeO–O•

O	1.231343	-0.284246	-0.000152
O	0.082328	0.604633	0.001126
C	-1.065381	-0.222560	0.000148
H	-1.132130	-0.820243	0.913181
H	-1.905723	0.470961	-0.049186
H	-1.079224	-0.878448	-0.872673

CF_3O–O•

O	1.932995	-0.013695	0.002581
O	0.762409	0.829319	-0.018483
C	-0.339910	0.007591	0.003985
F	-0.382117	-0.769972	1.082583
F	-1.388265	0.823856	0.004672
F	-0.398926	-0.783943	-1.075775

CCl_3O–O•

O	1.926607	-0.026677	1.231447
O	0.488960	-0.011957	1.350393
C	-0.086519	-0.012203	0.097738
Cl	0.382979	-1.429978	-0.879780
Cl	-1.825136	-0.039912	0.445644
Cl	0.335956	1.492378	-0.815344

F–O•

O	0.000000	0.000000	-0.757154
F	0.000000	0.000000	0.673026

Me–O•

O	-0.004426	0.819392	0.000000
C	-0.004426	-0.600480	0.000000
H	1.037285	-0.916619	0.000000
H	-0.487660	-1.017819	0.889740
H	-0.487660	-1.017819	-0.889740

Et–O•

O	1.292562	-0.028847	0.000000
C	0.000000	0.574407	0.000000
H	-0.130187	1.209198	0.884603
H	-0.130187	1.209198	-0.884603
C	-1.033380	-0.532700	0.000000
H	-0.919305	-1.161308	0.883283
H	-2.041228	-0.115244	0.000000
H	-0.919305	-1.161308	-0.883283

CF_3CH_2–O•

O	-1.998930	-0.180545	0.000048
C	-0.951965	0.761027	-0.000026
H	-0.953142	1.397105	-0.890041
H	-0.953109	1.397207	0.889916
C	0.362388	0.004921	-0.000007
F	0.498984	-0.774936	-1.084230
F	1.383674	0.889118	-0.000079
F	0.499026	-0.774808	1.084302

t-Bu–O•

O	-0.521005	1.400533	0.000000
C	-0.034146	0.045861	0.000000
C	-0.521005	-0.672634	1.261596
H	-1.611947	-0.733760	1.275350
H	-0.131320	-1.690522	1.315451
H	-0.199319	-0.130887	2.150929
C	-0.521005	-0.672634	-1.261596
H	-1.611947	-0.733760	-1.275350
H	-0.199319	-0.130887	-2.150929
H	-0.131320	-1.690522	-1.315451
C	1.485953	0.176733	0.000000
H	1.816821	0.723407	-0.882888
H	1.816821	0.723407	0.882888
H	1.960781	-0.804707	0.000000

CF_3–O•

O	0.448436	1.328412	0.000000
C	0.019510	0.050937	0.000000
F	-1.308487	0.051435	0.000000
F	0.448436	-0.633101	1.080287
F	0.448436	-0.633101	-1.080287

CF_3CF_2–O•

O	-1.743112	0.480628	0.000000
C	-0.411906	0.690575	0.000000
F	-0.008178	1.399667	1.085812
F	-0.008178	1.399667	-1.085812
C	0.321406	-0.675624	0.000000
F	-0.008178	-1.378382	1.085967
F	-0.008178	-1.378382	-1.085967
F	1.642477	-0.479760	0.000000

PH_2–O•

O	0.077062	1.147992	0.000000
P	0.077062	-0.515096	0.000000
H	-0.886210	-0.728746	1.023615
H	-0.886210	-0.728746	-1.023615

HS–O•

O	0.053364	1.146232	0.000000
S	0.053364	-0.527199	0.000000
H	-1.280739	-0.734682	0.000000

Cl–O•

O	0.000000	0.000000	-1.157610
Cl	0.000000	0.000000	0.544757

Br–O•

O	0.000000	0.000000	-1.501598
Br	0.000000	0.000000	0.343223

BH_2–O•

O	-0.706942	-0.006142	-0.000035
B	0.643648	0.000890	0.000020
H	1.262701	-1.022463	0.000097
H	1.174597	1.067147	0.000076

CH_2=CH–O•

O	-1.237172	-0.152836	0.000000
C	0.000000	0.426390	0.000000
C	1.118646	-0.283635	0.000000
H	0.011686	1.511323	0.000000
H	2.072754	0.219052	0.000000
H	1.101059	-1.364213	0.000000

Ph–O•

O	-2.357178	0.011117	-0.000079
C	-0.990935	0.035203	-0.000041
C	-0.262553	1.222385	-0.000017
C	-0.326890	-1.189576	-0.000010
C	1.126927	1.180736	0.000032
H	-0.780445	2.174696	-0.000034
C	1.059936	-1.217812	0.000046
H	-0.909340	-2.100290	-0.000031
C	1.796136	-0.036445	0.000066
H	1.685061	2.107635	0.000048
H	1.569706	-2.172202	0.000070
H	2.876717	-0.065713	0.000106

$PhCH_2$–O•

O	2.753546	0.574623	-0.000120
C	1.967077	-0.608827	0.000078
H	2.189965	-1.220880	0.883149
H	2.189949	-1.221169	-0.882796
C	0.498293	-0.262552	0.000038
C	0.056567	1.056647	0.000045
C	-0.444239	-1.291796	-0.000009
C	-1.306216	1.340522	0.000019
H	0.782949	1.855309	0.000068
C	-1.802750	-1.008950	-0.000041
H	-0.112283	-2.323802	-0.000030
C	-2.239273	0.312479	-0.000022
H	-1.636828	2.371027	0.000026
H	-2.521017	-1.818285	-0.000077
H	-3.297852	0.535684	-0.000043

HC(O)–O•

O	-1.092729	-0.420680	0.000000
C	0.000000	0.363222	0.000000
O	1.130851	-0.028782	0.000000
H	-0.304976	1.416362	0.000000

MeC(O)–O•

O	-1.353457	0.087500	0.000000
C	0.000000	0.177918	0.000000
O	0.576434	1.233631	0.000000
C	0.641926	-1.180380	0.000000
H	0.321632	-1.741179	0.878005
H	0.321632	-1.741179	-0.878005
H	1.721363	-1.071923	0.000000

$CF_3C(O)$–O•

O	0.822852	-1.704520	0.000000
C	-0.284305	-0.954946	0.000000
O	-1.409926	-1.352751	0.000000
C	0.096243	0.546788	0.000000
F	0.822852	0.844538	1.087435
F	0.822852	0.844538	-1.087435
F	-0.998483	1.300603	0.000000

$NH_2C(O)$–O•

O	0.458031	1.259797	0.002240
C	0.126579	-0.061497	-0.001238
O	0.941823	-0.953278	0.004250
N	-1.221121	-0.216178	-0.033456
H	-1.584749	-1.142626	0.087380
H	-1.825710	0.572702	0.102311

HOC(O)–O•

O	-1.045990	-0.830567	0.000023
C	-0.072502	0.090181	-0.000055
O	-0.234227	1.281730	0.000017
O	1.111185	-0.537781	-0.000003
H	1.787268	0.151869	0.000025

NC–O•

O	-0.265458	-1.157109	0.000000
C	0.000000	0.112840	0.000000
N	0.303380	1.225690	0.000000

CN–O•

O	-0.366666	-1.095283	0.000000
N	0.000000	0.183205	0.000000
C	0.488888	1.246639	0.000000

ON–O•

O	1.046903	-0.461447	0.000000
N	0.000000	0.517133	0.000000
O	-1.046903	0.008956	0.000000

CH_2=N–O•

O	-1.166691	0.200128	0.000016
N	0.017728	-0.544602	-0.000007
C	1.038880	0.202476	-0.000020
H	0.975465	1.287496	0.000017
H	2.000690	-0.291157	0.000023

O_2N–O•

O	1.212593	-0.488391	-0.000174
N	-0.097764	0.039338	0.000174
O	-0.987723	-0.776565	-0.000067
O	-0.139327	1.230536	0.000090

Adiabatic RO• radicals

H–O•

O	0.000000	0.000000	0.108460
H	0.000000	0.000000	-0.867678

NH_2–O•

O	0.733700	-0.000002	0.012207
N	-0.540518	-0.000001	-0.049329
H	-1.043009	-0.868898	0.123824
H	-1.042966	0.868922	0.123821

HO–O•

O	0.055426	0.716421	0.000000
O	0.055426	-0.607978	0.000000
H	-0.886823	-0.867541	0.000000

MeO–O•

O	1.180952	-0.279608	-0.000002
O	0.158063	0.545035	0.000003
C	-1.090825	-0.182399	0.000003
H	-1.145875	-0.802597	0.897231
H	-1.875474	0.576263	-0.000081
H	-1.145822	-0.802683	-0.897173

CF_3O–O•

O	-1.890024	-0.025809	0.000116
O	-0.834869	0.768858	-0.002802
C	0.363779	-0.008997	-0.000041
F	0.418496	-0.768185	-1.073365
F	1.341376	0.871443	-0.004576
F	0.419735	-0.757749	1.080355

CCl_3O–O•

O	1.863961	-0.000888	1.242549
O	0.558856	-0.000264	1.347232
C	-0.097727	0.000151	0.049227
Cl	0.358016	-1.457669	-0.850876
Cl	-1.816826	-0.003580	0.461689
Cl	0.353153	1.461738	-0.846908

F–O•

O	0.000000	0.000000	-0.710043
F	0.000000	0.000000	0.631149

Me–O•

O	-0.011302	0.790571	0.000000
C	-0.011302	-0.571474	0.000000
H	1.060093	-0.865589	0.000000
H	-0.450934	-1.015067	0.908989
H	-0.450934	-1.015067	-0.908989

Et–O•

O	1.254674	-0.365045	-0.004941
C	0.183527	0.478421	-0.003555
H	0.311833	1.114421	0.899846
H	0.283796	1.205543	-0.834389
C	-1.189211	-0.194968	-0.000091
H	-1.287433	-0.858097	0.863964
H	-1.990036	0.550929	0.038424
H	-1.321451	-0.793155	-0.906439

CF_3CH_2–O•

O	-1.977760	-0.193317	0.000052
C	-0.986872	0.741524	-0.000028
H	-0.979657	1.367999	-0.906166
H	-0.979622	1.368090	0.906048
C	0.377248	-0.001475	-0.000007
F	0.512387	-0.766580	-1.080429
F	1.357305	0.907486	-0.000085
F	0.512432	-0.766445	1.080504

t-Bu–O•

O	-0.514292	1.358191	0.000000
C	-0.067088	0.059089	0.000000
C	-0.514292	-0.680800	1.276519
H	-1.605620	-0.754064	1.304388
H	-0.103956	-1.695134	1.310841
H	-0.184986	-0.135485	2.164823
C	-0.514292	-0.680800	-1.276519
H	-1.605620	-0.754064	-1.304388
H	-0.184986	-0.135485	-2.164823
H	-0.103956	-1.695134	-1.310841
C	1.485874	0.225595	0.000000
H	1.811921	0.767949	-0.889812
H	1.811921	0.767949	0.889812
H	1.938411	-0.770567	0.000000

CF_3–O•

O	0.444969	1.315617	0.000000
C	0.027830	0.024873	0.000000
F	-1.304019	0.090613	0.000000
F	0.444969	-0.638316	1.073176
F	0.444969	-0.638316	-1.073176

CF_3CF_2–O•

O	-1.717052	0.448013	0.000000
C	-0.436887	0.724919	0.000000
F	-0.002275	1.396041	1.084349
F	-0.002275	1.396041	-1.084349
C	0.316311	-0.697824	0.000000
F	-0.002275	-1.382688	1.083770
F	-0.002275	-1.382688	-1.083770
F	1.615752	-0.443003	0.000000

PH_2–O•

O	0.055769	1.068219	0.000000
P	0.055769	-0.435243	0.000000
H	-0.641341	-1.008558	1.103419
H	-0.641341	-1.008558	-1.103419

HS–O•

O	0.053368	1.042435	0.000000
S	0.053368	-0.469587	0.000000
H	-1.280823	-0.826092	0.000000

Cl–O•

O	0.000000	0.000000	-1.082606
Cl	0.000000	0.000000	0.509461

Br–O•

O	0.000000	0.000000	-1.411128
Br	0.000000	0.000000	0.322544

BH_2–O•

O	-0.679586	-0.000520	-0.000093
B	0.601791	-0.000288	0.000140
H	1.218065	-1.040855	0.000040
H	1.209674	1.046453	0.000005

CH_2=CH–O•

O	-1.192364	0.118648	0.000000
C	0.000000	0.426731	0.000000
C	1.054318	-0.530947	0.000000
H	0.307247	1.492067	0.000000
H	2.095591	-0.227976	0.000000
H	0.810166	-1.587980	0.000000

Ph–O•

O	2.299394	-0.000079	-0.000056
C	1.049052	0.000091	-0.000037
C	0.289002	-1.237068	-0.000009
C	0.288863	1.237253	-0.000008
C	-1.085579	-1.223186	0.000029
H	0.857030	-2.160910	-0.000022
C	-1.085610	1.223129	0.000030
H	0.856952	2.161100	-0.000021
C	-1.781707	-0.000107	0.000048
H	-1.643282	-2.154102	0.000044
H	-1.643381	2.153996	0.000048
H	-2.866592	-0.000122	0.000079

$PhCH_2$–O•

O	-2.821813	0.519111	-0.056326
C	-1.973138	-0.532314	0.031621
H	-2.240064	-1.279156	-0.746901
H	-2.244990	-1.076407	0.965646
C	-0.485110	-0.237359	0.012659
C	-0.020484	1.076655	0.018385
C	0.433320	-1.289238	-0.004664
C	1.347851	1.335914	0.007193
H	-0.742453	1.885137	0.027984
C	1.800908	-1.031174	-0.014621
H	0.077700	-2.316661	-0.011846
C	2.261501	0.284213	-0.008582
H	1.701465	2.361933	0.010012
H	2.506589	-1.855367	-0.028740
H	3.327178	0.487448	-0.017490

HC(O)–O•

O	-1.042930	-0.258204	0.000000
C	0.000000	0.433058	0.000000
O	1.043002	-0.258180	0.000000
H	-0.000581	1.532723	0.000000

MeC(O)–O•

O	0.808020	-1.040958	0.001335
C	0.105408	0.001128	-0.006415
O	0.814282	1.037501	0.001394
C	-1.389468	0.004133	-0.002930
H	-1.765810	-0.803150	-0.635716
H	-1.743478	-0.170186	1.018220
H	-1.764771	0.969425	-0.348266

$CF_3C(O)$–O•

O	-1.622137	1.049910	0.000163
C	-0.948491	-0.000027	-0.010873
O	-1.622182	-1.049907	0.000127
C	0.592775	-0.000006	-0.005538
F	1.044395	1.086440	-0.620657
F	1.032119	-0.000518	1.252869
F	1.044468	-1.085903	-0.621530

$NH_2C(O)$–O•

O	0.761151	1.050244	0.002889
C	0.062145	0.000001	-0.001632
O	0.761163	-1.050237	0.002857
N	-1.284396	-0.000010	-0.028459
H	-1.780295	-0.868323	0.081671
H	-1.780311	0.868333	0.081361

HOC(O)–O•

O	0.897183	-0.931781	0.000055
C	0.054419	-0.002824	-0.000003
O	0.519538	1.152533	-0.000056
O	-1.240352	-0.286775	-0.000005
H	-1.737464	0.545130	0.000068

NC–O•

O	0.000000	0.000000	1.138537
C	0.000000	0.000000	-0.040702
N	0.000000	0.000000	-1.266297

CN–O•

O	0.000000	0.000000	1.099353
N	0.000000	0.000000	-0.118668
C	0.000000	0.000000	-1.327358

ON–O•

O	1.102101	-0.141082	0.000000
N	0.000000	0.322912	0.000000
O	-1.102101	-0.141466	0.000000

CH_2=N–O•

O	-1.187883	0.140254	0.000050
N	-0.068785	-0.342691	-0.000014
C	1.123648	0.115006	-0.000060
H	1.308494	1.186607	0.000028
H	1.934171	-0.599838	0.000030

O_2N–O•

O	0.914260	-0.827760	-0.000049
N	-0.001436	-0.001546	0.000102
O	-1.175176	-0.375285	-0.000089
O	0.262172	1.204397	0.000049

Hydrogenolyzed products

H–H

H	0.000000	0.000000	0.371396
H	0.000000	0.000000	-0.371396

NH_2–H

N	0.000000	-0.000052	-0.120627
H	0.809231	-0.467138	0.281516
H	-0.809357	-0.466919	0.281516
H	0.000126	0.934422	0.281359

HO–H

O	0.000000	0.118871	0.000000
H	0.756734	-0.475345	0.000000
H	-0.756734	-0.475619	0.000000

MeO–H

O	0.747782	0.121642	0.000002
C	-0.660302	-0.019383	0.000000
H	-1.035671	-0.543284	0.891911
H	-1.081642	0.989683	-0.000365
H	-1.035594	-0.543900	-0.891572
H	1.132462	-0.759341	0.000010

CF_3O–H

O	-1.292123	0.422683	0.002004
C	-0.003233	0.020026	-0.000400
F	0.290532	-0.734592	-1.069802
F	0.765429	1.096556	-0.014990
F	0.301396	-0.711259	1.082393
H	-1.859829	-0.357974	0.007952

CCl_3O–H

O	-0.093582	-0.000157	1.636994
C	-0.027968	0.000011	0.289936
Cl	0.853245	-1.463357	-0.333409
Cl	-1.695840	-0.002384	-0.323108
Cl	0.849056	1.465759	-0.333377
H	0.806637	0.000885	1.992638

F–H

F	0.000000	0.000000	0.091947
H	0.000000	0.000000	-0.827519

Me–H

C	0.000000	0.000365	0.000000
H	0.966893	-0.507686	0.000000
H	-0.560733	-0.287872	0.891205
H	-0.560733	-0.287872	-0.891205
H	0.154573	1.081242	0.000000

Et–H

C	-0.000017	0.765116	0.000000
H	-0.509698	1.163814	0.883086
H	-0.509698	1.163814	-0.883086
C	-0.000017	-0.765165	0.000000
H	0.509838	-1.163829	0.882996
H	-1.019676	-1.163798	0.000000
H	0.509838	-1.163829	-0.882996
H	1.019602	1.164123	0.000000

CF_3CH_2–H

C	-1.476495	-0.002657	-0.000015
H	-1.841136	0.511011	-0.891130
H	-1.841154	0.511118	0.891031
C	0.031677	-0.000633	0.000000
F	0.527247	-0.623506	-1.081055
F	0.522291	1.250161	-0.000075
F	0.527226	-0.623367	1.081145
H	-1.839678	-1.031983	0.000044

t-Bu–H

C	-0.372610	0.000101	0.000000
C	0.095677	-0.730642	1.264913
H	-0.267417	-1.763721	1.287002
H	1.191007	-0.763273	1.313674
H	-0.261508	-0.229856	2.171017
C	0.095677	-0.730642	-1.264913
H	-0.267417	-1.763721	-1.287002
H	-0.261508	-0.229856	-2.171017
H	1.191007	-0.763273	-1.313674
C	0.095677	1.461321	0.000000
H	-0.264797	1.996199	-0.885150
H	-0.264797	1.996199	0.885150
H	1.190976	1.520057	0.000000
H	-1.472073	0.000418	0.000000

CF_3–H

C	0.269811	0.200233	0.000000
F	-0.847260	0.928351	0.000000
F	0.269811	-0.578285	1.082735
F	0.269811	-0.578285	-1.082735
H	1.149866	0.852570	0.000000

CF_3CF_2–H

C	-0.603583	0.752432	0.000000
F	-0.231959	1.436456	1.096823
F	-0.231959	1.436456	-1.096823
C	0.119353	-0.604270	0.000000
F	-0.231959	-1.298930	1.083870
F	-0.231959	-1.298930	-1.083870
F	1.438513	-0.441601	0.000000
H	-1.690737	0.609981	0.000000

PH_2–H

P	0.000000	0.128881	0.000000
H	0.596637	-0.644376	1.033451
H	0.596637	-0.644376	-1.033451
H	-1.193273	-0.644461	0.000000

HS–H

S	0.000000	0.103439	0.000000
H	0.971446	-0.827589	0.000000
H	-0.971446	-0.827439	0.000000

Cl–H

Cl	0.000000	0.000000	0.071301
H	0.000000	0.000000	-1.212120

Br–H

Br	0.000000	0.000000	0.039511
H	0.000000	0.000000	-1.382872

BH_2–H

B	-0.000003	-0.000013	-0.000007
H	-1.176003	-0.192982	0.000012
H	0.755167	-0.921847	0.000012
H	0.420849	1.114893	0.000012

CH_2=CH–H

C	0.000007	0.663586	0.000000
C	0.000007	-0.663604	0.000000
H	0.921238	1.238234	0.000000
H	0.921348	-1.238147	0.000000
H	-0.921265	-1.238202	0.000000
H	-0.921406	1.238223	0.000000

Ph–H

C	1.306292	-0.485430	0.000039
C	1.073736	0.888317	0.000020
C	0.232538	-1.373932	0.000019
C	-0.232786	1.373954	-0.000019
H	1.909422	1.580621	0.000035
C	-1.073571	-0.888626	-0.000020
H	0.413942	-2.443879	0.000033
C	-1.306179	0.485637	-0.000039
H	-0.413887	2.443903	-0.000033
H	-1.909793	-1.580219	-0.000035
H	-2.323462	0.863621	-0.000068
H	2.323597	-0.863558	0.000069

$PhCH_2$–H

C	-2.420640	0.000163	0.008476
H	-2.827612	-0.875144	-0.506456
H	-2.805350	-0.021013	1.035805
C	-0.911335	0.000342	-0.010474
C	-0.193542	1.199881	-0.008423
C	-0.193944	-1.199665	-0.008423
C	1.198854	1.202539	0.002045
H	-0.733241	2.142662	-0.017097
C	1.198265	-1.202852	0.002048
H	-0.734031	-2.142246	-0.017118
C	1.900930	-0.000228	0.008083
H	1.735527	2.145929	0.001169
H	1.734641	-2.146414	0.001177
H	2.985816	-0.000505	0.013038
H	-2.827280	0.895653	-0.470511

HC(O)–H

C	-0.000002	0.525341	0.000000
O	-0.000002	-0.674506	0.000000
H	-0.937197	1.121901	0.000000
H	0.937221	1.122102	0.000000

MeC(O)–H

C	0.000000	0.461424	0.000000
O	1.201914	0.396840	0.000000
C	-0.928469	-0.727494	0.000000
H	-1.582160	-0.683411	0.879690
H	-1.582160	-0.683411	-0.879690
H	-0.361848	-1.659771	0.000000
H	-0.518336	1.448291	0.000000

$CF_3C(O)$–H

C	0.500682	-1.100682	0.000000
O	-0.250955	-2.029513	0.000000
C	0.017823	0.364982	0.000000
F	0.500682	0.987013	1.083309
F	0.500682	0.987013	-1.083309
F	-1.302382	0.452779	0.000000
H	1.605785	-1.190948	0.000000

$NH_2C(O)$–H

C	-0.163620	0.385401	0.000013
O	-1.195600	-0.244873	0.000056
N	1.083073	-0.157624	-0.000377
H	1.183669	-1.160155	0.000793
H	1.908187	0.416088	0.001295
H	-0.126847	1.494009	0.000030

HOC(O)–H

O	-1.117748	-0.091120	-0.000010
H	-1.041247	-1.058897	-0.000018
C	0.134757	0.397532	0.000000
O	1.135242	-0.261799	0.000010
H	0.092754	1.497054	0.000022

NC–H

C	0.000000	0.000000	-0.499688
N	0.000000	0.000000	0.652137
H	0.000000	0.000000	-1.566830

CN–H

N	0.000000	0.000000	0.430261
C	0.000000	0.000000	-0.739637
H	0.000000	0.000000	1.425998

ON–H

N	0.063286	0.579128	0.000000
O	0.063286	-0.622032	0.000000
H	-0.949293	0.922357	0.000000

CH_2=N–H

N	-0.668556	-0.153936	0.000068
C	0.585245	0.028784	-0.000183
H	1.086550	1.004893	0.000158
H	1.245785	-0.842341	0.000246
H	-1.163911	0.742296	0.000220

O_2N–H

N	0.000120	0.308313	0.000095
O	-1.095193	-0.219415	0.000020
O	1.095094	-0.219457	-0.000115
H	-0.000049	1.352787	0.000099

Table AP2. B3-LYP/6-31G(2df,p) ZPVEs and ΔH_{298} values (kJ mol^{-1}), and W3.2, W1w+T(Q), W2w, W1w and G4 vibrationless total energies (hartree)

	ZPVE	ΔH_{298}	W3.2	W1w+T(Q)	W2w	W1w	G4
					Substrates		
H–OH	55.3	9.9	–76.48448	–76.48369	–76.48395	–76.48304	–76.41832
NH_2–OH	104.0	11.0	–131.79835	–131.79742	–131.79731	–131.79602	–131.69500
HO–OH	68.6	11.0	–151.65503	–151.65314	–151.65377	–151.65143	–151.52070
MeO–OH	141.4	13.8		–190.96476	–190.96497	–190.96249	–190.81630
CF_3O–OH	84.0	17.2				–488.97881	–488.50587
CCl_3O–OH	68.4	20.6					–1569.24379
F–OH	36.3	10.0	–175.68049	–175.67696	–175.67915	–175.67525	–175.50279
Me–OH	132.5	11.2	–115.78474	–115.78400	–115.78384	–115.78285	–115.70222
Et–OH	206.3	13.9		–155.11203	–155.11130	–155.11040	–155.01281
CF_3CH_2–OH	147.7	18.6				–453.11419	–452.69030
t-Bu–OH	349.5	20.5				–233.76747	–233.63752
CF_3–OH	74.8	14.4				–413.81103	–413.40336
CF_3CF_2–OH	106.6	21.8					–651.14775
PH_2–OH	81.3	11.7	–419.13071	–419.12924	–419.12926	–419.12779	–418.24802
HS–OH	58.4	10.9	–475.60948	–475.60742	–475.60797	–475.60597	–474.45435
Cl–OH	34.1	10.2	–537.31390	–537.31189	–537.31243	–537.31045	–535.82397
Br–OH	33.1	10.4	–2681.21219	–2681.21017	–2681.21072	–2681.20872	–2649.38553
BH_2–OH	92.0	10.5	–101.96137	–101.96096	–101.96046	–101.95985	–101.88855
CH_2=CH–OH	145.6	12.6		–153.88286	–153.88179	–153.88092	–153.78122
Ph–OH	270.3	17.1				–307.47537	–307.40277
$PhCH_2$–OH	343.2	21.5					–346.70143
HC(O)–OH	87.7	10.8		–189.87749	–189.87773	–189.87537	–189.72639

MeC(O)–OH	159.7	14.5				–229.20971	–229.04369
$CF_3C(O)$–OH	101.3	19.0					–526.70217
$NH_2C(O)$–OH	133.1	13.8				–245.28511	–245.09871
HOC(O)–OH	103.1	12.3				–265.17558	–264.95947
NC–OH	56.1	11.2	–168.73156	–168.73066	–168.73002	–168.72843	–168.60785
CN–OH	53.0	12.2	–168.63601	–168.63533	–168.63443	–168.63299	–168.51359
ON–OH	52.8	10.9	–205.83633	–205.83441	–205.83375	–205.83094	–205.66374
CH_2=N–OH	115.4	11.7		–169.90193	–169.90104	–169.89960	–169.78146
O_2N–OH	69.0	11.7				–281.06320	–280.83005
				Vertical radicals			
H–O•	22.9	8.7					–75.71772787
NH_2–O•	68.2	10.5					–131.0357481
HO–O•	34.6	10.2					–150.8625675
MeO–O•	109.1	12.7					–190.1591607
CF_3O–O•	51.3	15.5					–487.8411199
CCl_3O–O•	36.0	19.0					–1568.578741
F–O•	5.1	8.8					–174.8299268
Me–O•	90.5	10.2					–115.0204851
Et–O•	175.8	12.8					–154.3286363
CF_3CH_2–O•	116.4	16.7					–452.0037704
t-Bu–O•	313.3	21.6					–232.9556975
CF_3–O•	39.1	12.4					–412.7026366
CF_3CF_2–O•	71.6	20.7					–650.4500331
PH_2–O•	46.9	11.2					–417.5766736
HS–O•	24.6	10.5					–473.8064577
Cl–O•	3.6	9.1					–535.1542059
Br–O•	3.1	9.2					–2648.712052

BH_2–O•	52.3	10.7					–101.2113688
CH_2=CH–O•	110.1	11.8					–153.1174249
Ph–O•	237.2	16.2					–306.7376198
$PhCH_2$–O•	304.7	19.3					–346.0200359
HC(O)–O•	47.2	10.2					–189.0308697
MeC(O)–O•	119.6	11.8					–228.3508023
$CF_3C(O)$–O•	61.5	18.0					–526.0055839
$NH_2C(O)$–O•	91.6	13.8					–244.4026906
HOC(O)–O•	64.3	12.6					–264.2654984
NC–O•	20.3	10.8					–167.9408433
CN–O•	18.9	11.3					–167.8485942
ON–O•	13.7	10.4					–204.9767473
CH_2=N–O•	79.1	11.8					–169.1117127
O_2N–O•	30.3	12.4					–280.1460061
				Adiabatic radicals			
H•	0.0	6.2	–0.50002	–0.49999	–0.50002	–0.49999	–0.50142
H–O•	21.8	8.7	–75.78409	–75.78271	–75.78350	–75.78226	–75.71777
NH_2–O•	68.9	10.7	–131.16309	–131.16183	–131.16186	–131.16038	–131.05907
HO–O•	36.6	10.0	–151.00595	–151.00359	–151.00418	–151.00160	–150.87079
MeO–O•	110.9	12.7		–190.31825	–190.31836	–190.31565	–190.16976
CF_3O–O•	52.6	16.1				–488.32013	–487.84930
CCl_3O–O•	36.5	19.6					–1568.58863
F–O•	6.8	8.7	–175.01245	–175.00842	–175.01031	–175.00610	–174.83407
Me–O•	94.0	10.4	–115.10481	–115.10342	–115.10360	–115.10229	–115.02189
Et–O•	167.1	13.6		–154.43117	–154.43076	–154.42952	–154.33255
CF_3CH_2–O•	118.0	16.9				–452.42619	–452.00468
t-Bu–O•	315.0	20.0				–233.08564	–232.95716

CF_3–O•	41.5	13.5				–413.10895	–412.70376
CF_3CF_2–O•	71.8	20.9					–650.45039
PH_2–O•	50.2	10.5	–418.48868	–418.48681	–418.48676	–418.48468	–417.60555
HS–O•	26.6	10.1	–474.98140	–474.97859	–474.97932	–474.97659	–473.82613
Cl–O•	5.0	8.9	–536.65304	–536.65009	–536.65084	–536.64829	–535.16104
Br–O•	4.3	8.9	–2680.54662	–2680.54369	–2680.54409	–2680.54163	–2648.71789
BH_2–O•	52.1	10.7	–101.28740	–101.28635	–101.28538	–101.28456	–101.21427
CH_2=CH–O•	109.7	11.8		–153.23659	–153.23511	–153.23394	–153.13493
Ph–O•	236.0	16.5				–306.82356	–306.75051
$PhCH_2$–O•	304.8	20.8					–346.02418
HC(O)–O•	50.9	10.5		–189.18660	–189.18462	–189.18207	–189.03403
MeC(O)–O•	123.0	14.7				–228.52115	–228.35661
$CF_3C(O)$–O•	64.9	18.8					–526.01023
$NH_2C(O)$–O•	96.2	13.9				–244.59576	–244.41090
HOC(O)–O•	65.8	12.1				–264.48506	–264.27108
NC–O•	26.2	9.7	–168.08516	–168.08388	–168.08241	–168.08065	–167.96069
CN–O•	23.2	10.5	–167.98344	–167.98229	–167.98075	–167.97906	–167.85983
ON–O•	22.8	10.2	–205.20109	–205.19910	–205.19798	–205.19515	–205.02844
CH_2=N–O•	82.5	11.2		–169.25802	–169.25548	–169.25396	–169.13559
O_2N–O•	27.2	13.4				–280.38527	–280.15338
				Hydrogenolysis products			
H–H	26.3	8.7					–1.17804
NH_2–H	88.9	10.0					–56.55147
HO–H	55.3	9.9					–76.41831
MeO–H	132.5	11.2					–115.70223
CF_3O–H	74.8	14.4					–413.40337
CCl_3O–H	60.0	17.5					–1494.13527

F–H	24.3	8.7	–100.43159
Me–H	115.8	10.0	–40.50941
Et–H	192.8	11.7	–79.81156
CF_3CH_2–H	135.5	15.2	–377.49757
t-Bu–H	339.3	17.7	–158.42628
CF_3–H	65.7	11.6	–338.17965
CF_3CF_2–H	97.6	18.8	–575.92360
PH_2–H	61.9	10.1	–343.02200
HS–H	39.0	10.0	–399.27334
Cl–H	17.4	8.7	–460.68534
Br–H	15.6	8.7	–2574.22990
BH_2–H	68.2	10.1	–26.59877
CH_2=CH–H	131.9	10.5	–78.57212
Ph–H	259.1	14.2	–232.19270
$PhCH_2$–H	329.7	19.1	–271.50297
HC(O)–H	68.8	10.0	–114.47940
MeC(O)–H	143.2	12.7	–153.79833
$CF_3C(O)$–H	86.1	17.0	–451.46204
$NH_2C(O)$–H	117.2	12.7	–169.86151
HOC(O)–H	87.7	10.8	–189.72639
NC–H	42.9	9.1	–93.40909
CN–H	41.4	9.8	–93.38491
ON–H	35.7	9.9	–130.44868
CH_2=N–H	103.1	10.2	–94.61209
O_2N–H	56.8	10.3	–205.65242

Table AP3. Performance of restricted and unrestricted variants of the HF, MP2, CCSD and CCSD(T) methods with the aug-cc-pV*n*Z+d basis sets (*n* = D, T, Q and 5) compared with eighteen BDEs and RSEs obtained with G4 as benchmarks (kJ mol^{-1})

	MD		MAD		LD		SD		NO	
	BDE	RSE	BDE	RSE	BDE	RSE	BDE	RSE	BDE	RSE
					ROHF					
D	–87.6	–60.9	87.6	60.9	–148.5	–144.3	39.5	39.5	17	17
T	–86.8	–57.7	86.9	57.7	–144.5	–145.1	38.0	38.0	17	17
Q	–86.8	–56.8	86.9	56.8	–143.5	–144.8	37.8	37.8	17	17
5	–86.8	–56.7	86.9	56.7	–143.4	–144.9	37.7	37.7	17	17
					UHF					
D	–110.1	–49.7	110.1	49.7	–159.8	–113.9	33.7	33.7	18	17
T	–110.8	–46.8	110.8	46.8	–157.6	–115.2	31.9	31.9	18	17
Q	–110.9	–45.9	110.9	45.9	–156.8	–114.8	31.6	31.6	18	17
					ROMP2					
D	–7.5	–3.7	14.0	14.8	–51.2	40.0	19.0	19.0	9	9
T	6.6	1.3	16.9	14.4	–38.8	46.7	19.5	19.5	13	8
Q	11.5	3.5	19.8	14.6	41.6	50.6	20.1	20.1	14	9
5	13.0	4.0	20.9	14.7	43.3	51.3	20.2	20.2	15	9
					UMP2					
D	2.5	–13.4	11.0	16.2	–35.7	–38.1	14.4	14.4	8	12
T	17.5	–8.7	20.9	14.2	41.5	–32.7	15.5	15.5	15	10
Q	22.8	–6.6	25.5	13.4	46.6	35.4	16.1	16.1	17	10
					URCCSD					
D	–14.6	–15.1	15.9	15.1	–29.7	–35.9	10.3	10.3	13	13
T	–2.4	–11.2	6.9	11.2	–13.6	–26.0	7.8	7.8	4	9

Q	1.7	–9.0	5.5	9.0	18.2	–25.5	7.2	7.2	2	8
5	2.6	–8.5	5.4	8.5	19.8	–25.6	7.1	7.1	2	7
					UCCSD					
D	–15.5	–14.5	16.3	14.5	–29.9	–34.6	9.9	9.9	13	11
T	–3.4	–10.5	7.0	10.5	–13.8	–24.4	7.1	7.1	4	7
Q	0.6	–8.3	5.2	8.3	14.9	–22.5	6.5	6.5	2	6
					URCCSD(T)					
D	–16.0	–9.4	16.2	9.4	–25.4	–26.4	7.3	7.3	15	6
T	–2.7	–3.9	3.5	4.0	–7.9	–9.4	3.1	3.1	0	0
Q	1.5	–1.4	2.0	2.0	5.2	–5.2	2.0	2.0	0	0
					UCCSD(T)					
D	–15.6	–10.0	15.8	10.0	–25.5	–26.9	7.4	7.4	15	7
T	–2.2	–4.5	3.2	4.5	–6.7	–9.7	3.1	3.1	0	0
Q	1.9	–1.9	2.3	2.4	5.5	–5.5	2.1	2.1	0	0

Table AP4. Deviations from G4 values of vibrationless BDEs and RSEs calculated with wavefunction procedures with the 6-31+G(d,p) (B1), 6-311+G(2df,p) (B2) and 6-311+G(3df,2p) (B3) basis sets (kJ mol^{-1})

	Deviations for BDEs											
	ROHF			ROMP2			URCCSD			URCCSD(T)		
	B1	B2	B3	B1	B2	B3	B1	B2	B3	B1	B2	B3
HO–H	–146.3	–147.4	–143.7	–13.7	–5.0	4.2	–31.3	–24.7	–16.5	–28.1	–19.1	–10.0
NH_2O–H	–81.9	–87.7	–85.1	–9.2	–11.6	–5.7	–12.2	–14.9	–9.7	–12.5	–14.3	–8.5
HOO–H	–106.9	–112.3	–110.1	1.9	3.7	10.2	–18.3	–17.5	–12.1	–17.3	–15.3	–9.1
MeOO–H	–99.0	–104.7	–102.6	6.4	8.5	14.7	–16.7	–15.4	–10.3	–15.9	–13.6	–7.8
CF_3OO–H	–102.7	–109.5	–107.4	10.0	10.6	16.9	–11.3	–11.6	–6.1	–10.3	–9.2	–3.1
CCl_3OO–H	–100.8	–105.7	–103.4	7.4	12.6	19.4	–15.7	–11.7	–6.1	–14.6	–9.1	–2.7
FO–H	–124.4	–130.9	–127.9	–2.9	–1.5	6.2	–19.8	–19.8	–13.0	–17.9	–16.3	–8.7
MeO–H	–129.4	–130.9	–128.3	–3.7	2.8	9.5	–24.4	–20.4	–14.4	–22.2	–16.1	–9.5
EtO–H	–130.7	–132.2	–129.9	–4.3	2.5	9.2	–26.2	–22.1	–16.1	–24.3	–18.0	–11.3
CF_3CH_2O–H	–125.0	–128.1	–125.9	3.7	9.2	15.3	–18.0	–14.5	–9.1	–16.2	–10.5	–4.5
t-BuO–H	–127.0	–128.3	–126.3	1.9	9.6	15.7	–21.4	–15.6	–10.3	–19.6	–11.6	–5.7
CF_3O–H	–129.2	–131.5	–129.5	–0.6	7.4	13.2	–20.7	–14.5	–9.2	–18.3	–9.9	–4.1
CF_3CF_5O–H	–113.1	–118.5	–117.0	12.3	15.5	20.6	–10.3	–8.6	–4.0	–9.2	–5.5	–0.3
PH_2O–H	–22.4	–49.3	–49.4	–19.5	–27.3	–24.1	10.3	–0.4	2.3	4.6	–6.6	–3.6
HSO–H	–29.1	–46.2	–45.0	13.0	–10.8	–8.3	9.1	–2.9	0.1	5.5	–7.0	–3.5
ClO–H	–96.5	–103.7	–102.0	11.9	12.5	18.1	–14.9	–16.5	–12.3	–15.0	–15.5	–10.8
BrO–H	–100.4	–104.6	–104.6	35.5	31.3	31.3	–3.5	–7.6	–7.6	–1.5	–5.6	–5.6
BH_2O–H	–95.6	–98.2	–96.3	18.3	24.3	29.9	–16.8	–12.1	–7.1	–18.0	–11.7	–6.2
CH_2=CHO–H	–89.7	–89.8	–87.9	–27.7	–17.2	–11.7	–23.3	–15.0	–10.3	–22.6	–13.9	–8.7
PhO–H	–47.2	–49.6	–47.9	–31.2	–22.5	–17.0	–19.3	–12.2	–7.7	–23.2	–15.3	–10.4
$PhCH_2O$–H	–120.4	–122.0	–119.8	4.9	11.6	18.4	–17.5	–13.5	–7.5	–16.0	–9.9	–3.2
HC(O)O–H	2.0	–1.3	0.3	–44.3	–37.8	–33.4	–4.3	3.8	7.8	–19.2	–12.1	–7.8

$MeC(O)O–H$	0.2	–3.2	–1.6	–42.1	–36.4	–31.7	–2.9	4.5	8.8	–17.0	–10.7	–6.1
$CF_3C(O)O–H$	12.4	6.4	10.4	–37.7	–7.2	–23.7	2.9	11.3	15.2	–13.3	–11.3	–2.7
$NH_2C(O)O–H$	–9.2	–12.1	–10.5	–38.3	–33.9	–29.1	–4.4	1.8	6.2	–15.8	–10.5	–5.9
$HOC(O)O–H$	1.4	–1.9	–0.4	–34.7	–30.5	–25.8	–2.3	4.4	9.0	–14.9	–9.3	–4.5
NCO–H	–84.1	–91.9	–90.4	–2.8	2.3	7.0	–14.9	–12.1	–7.8	–18.2	–14.4	–9.7
CNO–H	–72.7	–77.7	–75.6	1.2	2.3	8.1	–13.3	–12.1	–6.9	–16.9	–15.1	–9.5
ONO–H	–30.8	–39.9	–36.3	–48.3	–52.9	–46.8	5.3	–1.1	5.1	–5.8	–12.1	–5.6
CH_2=NO–H	–51.4	–60.0	–57.7	–2.2	–7.8	–2.5	–2.7	–8.5	–3.8	–7.8	–13.5	–8.4
$O_2NO–H$	63.8	62.8	66.6	–94.5	–89.0	–83.7	11.9	20.1	25.9	–16.6	–11.0	–5.0
MD	–73.7	–79.0	–76.9	–10.6	–7.2	–2.4	–11.2	–9.0	–4.1	–14.8	–12.1	–6.5
MAD	78.9	83.5	81.9	18.9	18.0	19.7	13.7	12.0	9.3	15.4	12.1	6.5
LD	–146.3	–147.4	–143.7	–94.5	–89.0	–83.7	–31.3	–24.7	25.9	–28.1	–19.1	–11.3
SD	53.8	52.8	52.9	26.0	24.9	25.3	11.2	10.3	9.8	7.6	3.5	2.9
NO	27	27	28	16	18	22	22	21	11	25	22	3

	UHF			UMP2			UCCSD			UCCSD(T)		
	B1	B2	B3	B1	B2	B3	B1	B2	B3	B1	B2	B3
HO–H	–156.8	–160.2	–156.6	–13.7	–4.2	5.1	–31.4	–24.9	–16.7	–28.1	–19.2	–10.1
$NH_2O–H$	–102.0	–110.3	–108.1	–5.2	–6.3	–0.2	–13.2	–16.0	–10.8	–12.6	–14.3	–8.5
HOO–H	–122.5	–130.2	–128.3	1.8	4.8	11.2	–18.7	–18.1	–12.7	–17.3	–15.3	–9.1
MeOO–H	–115.3	–123.2	–121.5	5.7	8.9	15.1	–17.1	–16.0	–10.9	–15.9	–13.6	–7.9
$CF_3OO–H$	–117.4	–126.5	–124.7	10.2	12.0	18.2	–11.6	–12.0	–6.6	–10.3	–9.2	–3.1
$CCl_3OO–H$	–115.8	–123.0	–121.0	7.5	13.8	20.5	–16.1	–12.2	–6.6	–14.6	–9.1	–2.7
FO–H	–138.4	–147.2	–144.4	0.2	2.5	10.2	–20.1	–20.2	–13.4	–17.8	–16.2	–8.6
MeO–H	–142.1	–146.0	–143.6	–3.7	3.7	10.5	–24.6	–20.7	–14.7	–22.3	–16.1	–9.6
EtO–H	–143.5	–147.3	–145.2	–4.4	3.3	10.1	–26.4	–22.4	–16.4	–24.3	–18.0	–11.3
$CF_3CH_2O–H$	–137.4	–142.7	–140.7	3.6	10.1	16.2	–18.2	–14.8	–9.4	–16.2	–10.5	–4.5
t-BuO–H	–139.8	–143.3	–141.4	1.9	10.7	16.8	–21.6	–15.9	–10.6	–19.6	–11.6	–5.7
$CF_3O–H$	–140.3	–144.8	–143.0	–0.5	8.4	14.2	–20.9	–14.7	–9.5	–18.4	–9.9	–4.1

CF_3CF_5O–H	–125.4	–133.1	–131.6	12.0	16.2	21.3	–10.5	–8.9	–4.3	–9.2	–5.5	–0.3
PH_2O–H	–42.9	–68.8	–68.7	–1.9	–16.9	–13.8	8.9	–2.1	0.7	5.1	–6.1	–3.0
HSO–H	–52.3	–76.5	–76.1	19.6	2.5	6.2	7.9	–4.7	–1.7	5.4	–6.8	–3.3
ClO–H	–111.9	–122.9	–121.5	12.0	12.8	18.1	–15.2	–17.0	–12.9	–15.0	–15.5	–10.8
BrO–H	–119.1	–123.3	–123.3	36.2	32.0	32.0	–3.9	–8.0	–8.0	–1.4	–5.6	–5.6
BH_2O–H	–111.2	–115.9	–114.1	15.3	22.5	28.1	–17.2	–12.6	–7.5	–18.0	–11.8	–6.2
CH_2=CHO–H	–128.8	–129.6	–127.6	6.7	18.2	24.0	–25.2	–17.2	–12.5	–22.1	–12.8	–7.5
PhO–H	–149.9	–151.6	–150.1	84.6	99.0	105.1	–22.4	–15.5	–11.1	–17.0	–8.3	–3.1
$PhCH_2O$–H	–133.4	–137.4	–135.3	4.8	12.4	19.2	–17.7	–13.8	–7.8	–16.0	–9.9	–3.2
HC(O)O–H	–38.2	–44.0	–42.7	–7.7	0.9	5.4	–7.5	0.5	4.5	–19.3	–12.0	–7.7
MeC(O)O–H	–40.1	–45.9	–44.5	–6.3	1.4	6.2	–6.0	1.3	5.6	–17.1	–10.6	–5.9
CF_3C(O)O–H	–29.1	–34.9	–33.6	–2.9	5.0	9.9	–0.6	6.9	11.3	–13.2	–6.7	–2.0
NH_2C(O)O–H	–50.3	–55.4	–54.1	–3.8	2.7	7.6	–7.4	–1.3	3.1	–15.9	–10.4	–5.7
HOC(O)O–H	–39.7	–45.6	–44.4	4.0	9.5	14.1	–4.9	1.7	6.1	–14.8	–8.9	–4.1
NCO–H	–113.0	–121.1	–119.6	13.6	18.4	23.2	–17.3	–14.6	–10.3	–17.6	–13.6	–8.9
CNO–H	–101.2	–109.0	–107.1	11.1	14.5	20.4	–14.4	–13.4	–8.2	–16.5	–14.6	–8.9
ONO–H	–53.2	–63.7	–60.1	–32.7	–36.8	–30.6	3.9	–2.5	3.6	–5.4	–11.6	–5.1
CH_2=NO–H	–85.2	–95.2	–93.1	32.1	28.4	33.8	–2.7	–8.4	–3.7	–5.7	–11.3	–6.2
O_2NO–H	24.1	21.2	24.6	–52.5	–45.1	–39.4	8.2	16.3	22.0	–15.6	–9.9	–3.9
MD	–99.1	–106.4	–104.6	4.8	8.6	14.2	–12.4	–10.4	–5.5	–14.4	–11.4	–6.0
MAD	100.7	107.7	106.2	13.5	15.6	19.6	14.2	12.1	9.1	15.1	11.4	6.0
LD	–156.8	–160.2	–156.6	84.6	99.0	105.1	–31.4	–24.9	22.0	–28.1	–19.2	–11.3
SD	45.5	44.0	43.9	22.0	23.1	23.0	10.6	9.3	8.9	7.5	3.6	2.9
NO	31.0	31.0	31.0	13.0	17.0	24.0	20.0	20.0	14.0	25.0	19.0	3.0

Deviations for RSEs

	ROHF			ROMP2			URCCSD			URCCSD(T)		
	B1	B2	B3	B1	B2	B3	B1	B2	B3	B1	B2	B3

HO•	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NH_2O•	–64.4	–59.8	–58.6	–4.5	6.6	9.9	–19.1	–9.7	–6.8	–15.6	–4.8	–1.5
HOO•	–39.4	–35.1	–33.6	–15.5	–8.8	–6.0	–13.0	–7.1	–4.4	–10.8	–3.8	–0.9
MeOO•	–47.3	–42.8	–41.0	–20.0	–13.5	–10.5	–14.6	–9.2	–6.2	–12.2	–5.5	–2.2
CF_3OO•	–43.6	–38.0	–36.2	–23.6	–15.6	–12.6	–20.0	–13.1	–10.3	–17.8	–9.9	–6.9
CCl_3OO•	–45.5	–41.7	–40.2	–21.1	–17.6	–15.1	–15.6	–12.9	–10.4	–13.5	–9.9	–7.3
FO•	–21.9	–16.5	–15.8	–10.8	–3.5	–1.9	–11.5	–4.8	–3.5	–10.2	–2.8	–1.3
MeO•	–16.9	–16.5	–15.4	–10.0	–7.8	–5.3	–6.9	–4.3	–2.1	–5.8	–3.0	–0.5
EtO•	–15.6	–15.3	–13.7	–9.4	–7.5	–5.0	–5.1	–2.6	–0.4	–3.8	–1.1	1.3
CF_3CH_2O•	–21.3	–19.3	–17.7	–17.4	–14.2	–11.1	–13.2	–10.2	–7.4	–11.8	–8.6	–5.5
t-BuO•	–19.3	–19.1	–17.4	–15.6	–14.6	–11.5	–9.9	–9.0	–6.2	–8.5	–7.5	–4.3
CF_3O•	–17.1	–16.0	–14.2	–13.1	–12.4	–8.9	–10.6	–10.2	–7.2	–9.8	–9.2	–5.9
CF_3CF_5O•	–33.2	–28.9	–26.7	–25.9	–20.5	–16.3	–21.0	–16.1	–12.5	–18.9	–13.6	–9.7
PH_2O•	–123.9	–98.1	–94.3	5.8	22.3	28.3	–41.6	–24.2	–18.8	–32.7	–12.4	–6.4
HSO•	–117.2	–101.3	–98.7	–26.6	5.8	12.5	–40.4	–21.8	–16.6	–33.5	–12.1	–6.5
ClO•	–49.8	–43.7	–41.7	–25.6	–17.5	–13.9	–16.4	–8.2	–4.2	–13.1	–3.5	0.8
BrO•	–45.9	–42.9	–39.1	–49.1	–36.3	–27.1	–27.8	–17.1	–8.9	–26.6	–13.5	–4.4
BH_2O•	–50.7	–49.3	–47.4	–31.9	–29.3	–25.7	–14.4	–12.6	–9.4	–10.1	–7.4	–3.8
CH_2=CHO•	–56.6	–57.6	–55.8	14.0	12.2	15.9	–8.0	–9.7	–6.1	–5.4	–5.2	–1.3
PhO•	–99.2	–97.8	–95.7	17.6	17.5	21.3	–12.0	–12.5	–8.7	–4.8	–3.8	0.4
$PhCH_2O$•	–26.0	–25.4	–23.9	–18.6	–16.6	–14.2	–13.7	–11.2	–8.9	–12.1	–9.2	–6.8
HC(O)O•	–148.4	–146.2	–144.0	30.6	32.8	37.7	–27.0	–28.4	–24.3	–8.9	–7.0	–2.2
MeC(O)O•	–146.5	–144.3	–142.1	28.4	31.4	35.9	–28.4	–29.1	–25.2	–11.1	–8.4	–3.9
$CF_3C(O)O$•	–158.7	–153.8	–154.1	24.0	2.2	27.9	–34.2	–35.9	–31.6	–14.8	–7.8	–7.3
$NH_2C(O)O$•	–137.1	–135.3	–133.2	24.6	28.9	33.3	–26.9	–26.5	–22.7	–12.3	–8.6	–4.1
HOC(O)O•	–147.8	–145.5	–143.2	21.0	25.5	30.1	–29.0	–29.1	–25.4	–13.1	–9.8	–5.5
NCO•	–62.2	–55.5	–53.3	–10.9	–7.3	–2.8	–16.4	–12.6	–8.7	–9.9	–4.7	–0.3
CNO•	–73.7	–69.7	–68.0	–14.8	–7.3	–3.8	–18.0	–12.6	–9.6	–11.2	–4.0	–0.5
ONO•	–115.5	–107.5	–107.4	34.6	47.9	51.0	–36.6	–23.6	–21.5	–22.2	–7.0	–4.4
CH_2=NO•	–94.9	–87.5	–85.9	–11.5	2.8	6.8	–28.6	–16.2	–12.6	–20.2	–5.6	–1.6

O_2NO•	–210.1	–210.3	–210.3	80.8	84.0	88.0	–43.2	–44.8	–42.3	–11.5	–8.1	–5.0
MD	–72.6	–68.4	–66.7	–3.0	2.2	6.7	–20.1	–15.7	–12.4	–13.3	–7.0	–3.5
MAD	72.6	68.4	66.7	21.2	18.4	19.0	20.1	15.7	12.4	13.3	7.0	3.6
LD	–210.1	–210.3	–210.3	80.8	84.0	88.0	–43.2	–44.8	–42.3	–33.5	–13.6	–9.7
SD	53.8	52.8	52.9	26.0	24.9	25.3	11.2	10.3	9.8	7.6	3.5	2.9
NO	30	30	30	26	20	21	26	21	13	22	4	0

	UHF			UMP2			UCCSD			UCCSD(T)		
	B1	B2	B3	B1	B2	B3	B1	B2	B3	B1	B2	B3
HO•	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NH_2O•	–54.8	–49.8	–48.5	–8.5	2.1	5.4	–18.3	–8.9	–5.9	–15.6	–4.9	–1.6
HOO•	–34.2	–30.0	–28.3	–15.5	–9.0	–6.1	–12.7	–6.8	–4.1	–10.8	–3.9	–1.0
MeOO•	–41.4	–36.9	–35.1	–19.4	–13.1	–10.0	–14.3	–8.9	–5.8	–12.2	–5.6	–2.2
CF_3OO•	–39.4	–33.7	–31.9	–23.9	–16.1	–13.1	–19.8	–12.9	–10.1	–17.9	–10.0	–7.0
CCl_3OO•	–40.9	–37.1	–35.6	–21.2	–18.0	–15.4	–15.3	–12.7	–10.1	–13.6	–10.1	–7.4
FO•	–18.4	–13.0	–12.2	–13.9	–6.7	–5.1	–11.3	–4.7	–3.3	–10.3	–3.0	–1.5
MeO•	–14.6	–14.1	–13.0	–10.0	–7.8	–5.3	–6.9	–4.2	–2.0	–5.9	–3.0	–0.5
EtO•	–13.2	–12.9	–11.4	–9.3	–7.5	–5.0	–5.0	–2.6	–0.3	–3.9	–1.2	1.3
CF_3CH_2O•	–19.4	–17.4	–15.9	–17.3	–14.3	–11.1	–13.2	–10.1	–7.3	–11.9	–8.7	–5.6
t-BuO•	–17.0	–16.9	–15.2	–15.6	–14.8	–11.7	–9.8	–9.0	–6.1	–8.5	–7.6	–4.4
CF_3O•	–16.5	–15.3	–13.6	–13.2	–12.6	–9.1	–10.6	–10.2	–7.2	–9.8	–9.2	–6.0
CF_3CF_5O•	–31.4	–27.1	–24.9	–25.7	–20.4	–16.2	–20.9	–16.1	–12.5	–18.9	–13.7	–9.8
PH_2O•	–113.9	–91.3	–87.9	–11.8	12.8	18.9	–40.3	–22.9	–17.5	–33.2	–13.1	–7.1
HSO•	–104.5	–83.7	–80.5	–33.3	–6.7	–1.1	–39.3	–20.3	–15.0	–33.5	–12.3	–6.8
ClO•	–44.9	–37.3	–35.0	–25.7	–16.9	–13.0	–16.2	–7.9	–3.9	–13.2	–3.6	0.7
BrO•	–37.6	–36.9	–33.3	–49.9	–36.2	–26.9	–27.5	–16.9	–8.7	–26.7	–13.6	–4.5
BH_2O•	–45.6	–44.3	–42.5	–29.0	–26.6	–23.0	–14.2	–12.4	–9.2	–10.1	–7.4	–3.9
CH_2=CHO•	–28.0	–30.6	–29.0	–20.4	–22.4	–18.9	–6.2	–7.7	–4.2	–6.1	–6.4	–2.5
PhO•	–6.9	–8.6	–6.5	–98.3	–103.2	–100.0	–9.0	–9.4	–5.7	–11.1	–10.9	–7.0

$PhCH_2O$•	–23.3	–22.8	–21.3	–18.5	–16.6	–14.1	–13.7	–11.1	–8.9	–12.1	–9.3	–6.9
HC(O)O•	–118.5	–116.1	–113.9	–6.0	–5.0	–0.2	–24.0	–25.4	–21.2	–8.8	–7.2	–2.4
MeC(O)O•	–116.6	–114.3	–112.1	–7.4	–5.5	–1.0	–25.5	–26.2	–22.3	–11.0	–8.6	–4.2
$CF_3C(O)O$•	–127.7	–125.3	–123.0	–10.8	–9.2	–4.7	–30.8	–31.8	–28.1	–14.9	–12.5	–8.1
$NH_2C(O)O$•	–106.5	–104.7	–102.5	–9.9	–6.8	–2.4	–24.0	–23.6	–19.8	–12.3	–8.8	–4.4
HOC(O)O•	–117.1	–114.6	–112.2	–17.7	–13.6	–9.0	–26.5	–26.6	–22.9	–13.3	–10.2	–6.0
NCO•	–43.8	–39.1	–36.9	–27.3	–22.5	–18.1	–14.2	–10.4	–6.4	–10.6	–5.6	–1.2
CNO•	–55.6	–51.2	–49.5	–24.8	–18.7	–15.3	–17.0	–11.5	–8.5	–11.6	–4.6	–1.2
ONO•	–103.6	–96.5	–96.5	19.0	32.7	35.8	–35.3	–22.4	–20.3	–22.7	–7.6	–5.0
CH_2=NO•	–71.5	–65.0	–63.5	–45.8	–32.5	–28.7	–28.7	–16.5	–13.0	–22.4	–7.9	–3.9
O_2NO•	–180.8	–181.4	–181.2	38.8	41.0	44.5	–39.6	–41.2	–38.7	–12.6	–9.3	–6.2
MD	–57.7	–53.8	–52.0	–18.5	–12.7	–9.0	–19.0	–14.6	–11.3	–13.7	–7.7	–4.1
MAD	57.7	53.8	52.0	22.2	18.4	15.8	19.0	14.6	11.3	13.7	7.7	4.2
LD	–180.8	–181.4	–181.2	–98.3	–103.2	–100.0	–40.3	–41.2	–38.7	–33.5	–13.7	–9.8
SD	45.5	44.0	43.9	22.0	23.1	23.0	10.6	9.3	8.9	7.5	3.6	2.9
NO	29	29	29	24	20	17	25	20	13	24	8	0

Table AP5. Deviations from G4 vibrationless BDEs (for ROH molecules) and RSEs (for RO• radicals) calculated with various DFT and G4(MP2)-type procedures (kJ mol^{-1})

	Deviations for BDEs														
	B-LYP	M06-L	B3-LYP	BMK	M06	M06-2X	LC-B-LYP	CAM-B3-LYP	UB2-PLYP	UB2K PLYP	UB2-PLYP-09	ROB2 PLYP	G3X (MP2)-RAD	G4 (MP2)	G4 (MP2)-6X
H	–10.9	–22.2	–11.9	–7.9	–3.2	–5.7	3.2	–8.6	–8.8	–8.1	–7.2	–6.6	–2.0	0.4	–0.6
NH_2	–31.2	–34.2	–23.8	–16.0	–14.3	–11.2	–17.1	–20.9	–16.0	–10.8	–12.9	–10.6	2.1	1.3	–1.2
HO	–26.5	–30.4	–19.2	–15.9	–8.7	–7.6	–10.7	–16.5	–13.2	–7.2	–9.7	–7.1	0.9	–0.4	–2.0
MeO	–28.9	–29.8	–19.5	–15.2	–7.7	–6.8	–10.9	–16.5	–12.6	–5.2	–8.6	–5.9	2.4	–1.1	–1.4
CF_3O	–23.2	–25.4	–14.0	–8.5	–2.9	0.2	–1.9	–10.1	–6.7	0.1	–2.8	–0.5	6.1	–4.5	0.8
CCl_3O	–21.9	–24.4	–12.7	–5.3	–1.9	0.9	–4.2	–9.9	–4.8	2.1	–1.0	1.3	6.3	–4.2	1.3
F	–21.8	–23.2	–15.9	–12.4	–3.4	–5.2	–6.2	–13.5	–11.0	–7.0	–8.1	–6.3	–1.3	–1.5	–2.5
Me	–29.3	–33.8	–21.8	–16.1	–12.2	–7.9	–3.6	–16.4	–11.1	–6.1	–7.6	–6.3	0.1	–0.1	1.2
Et	–31.7	–33.7	–22.7	–16.2	–11.6	–7.2	–3.3	–16.6	–10.4	–4.6	–6.5	–5.2	1.5	–1.0	1.2
CF_3CH_2	–25.7	–28.0	–15.8	–9.1	–4.1	–1.5	7.1	–8.5	–4.7	0.2	–1.0	0.2	5.8	–4.2	3.7
t-Bu	–29.8	–28.7	–20.1	–14.8	–5.8	–4.2	2.7	–12.5	–7.6	–1.6	–3.6	–2.6	4.3	–2.9	3.1
CF_3	–24.4	–26.6	–14.4	–4.2	0.1	1.2	9.0	–7.2	–4.7	–0.2	–1.4	–0.6	4.3	–3.8	2.1
CF_3CF_2	–33.6	–31.5	–16.2	–5.1	–2.8	3.4	13.2	–5.7	–1.7	4.4	2.9	4.5	9.1	–6.5	2.8
PH_2	–26.8	–26.3	–11.5	–2.6	0.1	8.4	3.1	–4.7	–8.1	–3.3	–5.8	–2.8	7.5	–5.1	–5.4
HS	–27.2	–30.3	–12.9	–7.8	–4.1	5.8	4.5	–5.8	–5.5	1.4	–2.1	0.6	–8.5	–2.3	–4.9
Cl	–33.8	–34.2	–21.5	–9.9	–11.4	–4.4	–2.6	–15.0	–10.3	–1.9	–5.4	–2.6	2.4	0.9	–0.7
Br	–36.7	–39.2	–22.0	–13.8	–11.9	–2.9	1.6	–13.5	–11.6	–0.3	–4.9	–2.6	1.3	0.8	–0.8
BH_2	–44.7	–39.4	–24.8	–13.0	–11.3	–1.0	1.1	–15.0	–7.0	5.4	–0.1	3.6	–0.6	0.1	–1.0
CH_2=CH	–24.0	–29.3	–15.5	–11.2	–13.4	–1.3	–2.4	–10.4	–8.2	–0.9	–4.2	–4.3	2.2	1.2	–0.3
Ph	–33.0	–28.5	–19.6	–11.4	–13.8	4.2	–4.1	–12.6	–0.5	19.0	9.7	–1.1	–17.1	1.6	4.9

$PhCH_2$	–33.3	–31.7	–19.8	–12.1	–8.8	–2.5	1.3	–12.5	–6.0	0.7	–1.8	–0.4	6.4	–4.5	3.7
HC(O)	–52.8	–45.0	–22.8	0.4	–2.8	15.9	24.4	–4.2	–16.5	–0.3	–9.9	–6.3	–1.9	–0.7	–3.7
MeC(O)	–55.1	–45.8	–24.8	–0.9	–3.2	15.4	23.1	–5.9	–16.8	–0.4	–9.0	–6.3	–0.2	–3.7	–2.2
$CF_3C(O)$	–52.4	–41.1	–19.5	7.1	3.5	23.5	31.9	0.8	–13.2	4.0	–5.6	–2.2	8.4	–4.5	–3.6
$NH_2C(O)$	–57.0	–48.4	–28.4	–5.3	–6.8	10.5	19.3	–9.7	–17.4	–1.4	–10.5	–7.2	0.3	–0.8	–0.7
HOC(O)	–57.3	–47.4	–26.9	–2.9	–5.3	13.3	21.5	–7.7	–8.7	8.3	6.1	9.4	0.2	–1.9	5.2
NC	–38.6	–45.4	–25.6	–14.9	–18.9	1.3	–1.4	–16.6	–11.2	–1.3	–5.6	–4.6	0.6	–1.0	–2.7
CN	–40.8	–43.7	–25.6	–7.9	–16.0	–2.2	1.5	–15.3	–13.0	–2.3	–7.4	–6.6	–1.3	0.1	–0.7
ON	–29.1	–39.2	–16.6	–2.3	–11.8	2.8	–0.1	–8.6	–21.1	–17.6	–20.1	–15.5	3.9	2.0	0.0
CH_2=N	–44.6	–49.7	–28.7	–15.0	–21.5	–10.1	–9.2	–19.6	–19.5	–6.1	–13.5	–12.7	0.2	1.9	–0.6
O_2N	–60.2	–46.8	–20.4	12.4	–0.4	32.9	36.7	2.5	–29.8	–14.2	–24.8	–16.7	–1.0	1.6	3.6
MD	–35.0	–34.9	–19.8	–8.3	–7.6	1.9	4.1	–10.9	–10.9	–1.8	–5.9	–4.0	1.4	–1.4	0.0
MAD	35.0	34.9	19.8	9.6	7.9	7.1	9.1	11.1	10.9	4.7	7.1	5.3	3.6	2.1	2.2
LD	–60.2	–49.7	–28.7	–16.2	–21.5	32.9	36.7	–20.9	–29.8	19.0	–24.8	–16.7	–17.1	–6.5	–5.4
SD	12.4	8.4	4.9	7.0	6.0	10.0	12.8	5.6	6.1	6.7	6.7	5.5	5.0	2.4	2.8
NO	31	31	31	15	12	8	10	17	17	4	5	4	1	0	0

Deviations for RSEs

	B-LYP	M06-L	B3-LYP	BMK	M06	M06-2X	LC-B-LYP	CAM-B3-LYP	UB2-PLYP	UB2K PLYP	UB2-PLYP-09	ROB2 PLYP	G3X (MP2)-RAD	G4 (MP2)	G4 (MP2)-6X
NH_2	20.3	12.0	11.9	8.1	11.1	5.4	20.2	12.3	7.2	2.7	5.7	4.0	0.0	–0.9	0.5
HO	15.6	8.2	7.3	8.0	5.5	1.8	13.8	8.0	4.5	–0.9	2.4	0.5	–4.0	0.8	1.4
MeO	18.0	7.6	7.6	7.3	4.5	1.0	14.1	7.9	3.9	–3.0	1.4	–0.7	–2.9	1.5	0.8
CF_3O	12.3	3.2	2.1	0.6	–0.2	–5.9	5.0	1.5	–2.1	–8.2	–4.5	–6.1	–4.4	4.9	–1.4
CCl_3O	11.0	2.2	0.8	–2.6	–1.3	–6.6	7.3	1.4	–4.0	–10.2	–6.2	–7.9	–8.1	4.6	–1.9
F	10.9	1.0	4.0	4.5	0.2	–0.5	9.4	4.9	2.3	–1.1	0.8	–0.3	–8.3	1.9	1.8

Me	18.4	11.6	9.9	8.2	9.0	2.2	6.8	7.8	2.3	–2.0	0.4	–0.3	–0.6	0.5	–1.8
Et	20.8	11.5	10.8	8.3	8.4	1.5	6.5	8.0	1.6	–3.5	–0.8	–1.4	–2.1	1.4	–1.8
CF_3CH_2	14.8	5.8	3.9	1.2	1.0	–4.2	–3.9	–0.1	–4.1	–8.3	–6.2	–6.8	–3.5	4.6	–4.4
t-Bu	18.9	6.5	8.2	6.9	2.6	–1.5	0.5	3.9	–1.2	–6.5	–3.7	–4.0	–7.8	3.3	–3.8
CF_3	13.6	4.4	2.5	–3.7	–3.3	–7.0	–5.8	–1.4	–4.1	–7.9	–5.8	–6.1	–6.3	4.2	–2.7
CF_3CF_2	22.7	9.3	4.3	–2.8	–0.4	–9.2	–10.1	–2.9	–7.0	–12.5	–10.2	–11.2	–6.2	6.9	–3.5
PH_2	15.9	4.1	–0.4	–5.3	–3.3	–14.2	0.1	–3.9	–0.7	–4.8	–1.4	–3.8	–11.0	5.5	4.7
HS	16.3	8.1	1.0	–0.1	0.9	–11.6	–1.4	–2.8	–3.3	–9.6	–5.1	–7.2	–9.5	2.7	4.3
Cl	22.9	12.0	9.6	2.0	8.2	–1.4	5.8	6.4	1.6	–6.2	–1.9	–4.0	6.5	–0.5	0.1
Br	25.8	17.0	10.1	5.9	8.7	–2.8	1.6	5.0	2.9	–7.8	–2.3	–4.0	–4.3	–0.4	0.1
BH_2	33.8	17.2	12.9	5.1	8.1	–4.7	2.1	6.5	–1.8	–13.6	–7.1	–10.2	–3.3	0.3	0.4
CH_2=CH	13.1	7.1	3.6	3.3	10.2	–4.4	5.5	1.9	–0.6	–7.2	–3.0	–2.3	–1.4	–0.8	–0.3
Ph	22.1	6.3	7.7	3.5	10.6	–10.0	7.2	4.0	–8.3	–27.1	–16.9	–5.5	–4.2	–1.2	–5.5
$PhCH_2$	22.4	9.5	8.0	4.2	5.7	–3.2	1.9	3.9	–2.7	–8.8	–5.4	–6.2	15.1	4.9	–4.3
HC(O)	41.9	22.8	10.9	–8.3	–0.4	–21.6	–21.2	–4.3	7.8	–7.8	2.7	–0.3	–8.4	1.1	3.1
MeC(O)	44.2	23.6	12.9	–7.0	0.0	–21.2	–19.9	–2.7	8.0	–7.8	1.8	–0.3	–0.1	4.1	1.5
$CF_3C(O)$	41.5	18.9	7.6	–15.0	–6.7	–29.2	–28.8	–9.4	4.4	–12.1	–1.6	–4.4	–1.7	4.9	3.0
$NH_2C(O)$	46.1	26.2	16.5	–2.6	3.6	–16.2	–16.1	1.2	8.6	–6.8	3.2	0.6	–10.3	1.2	0.1
HOC(O)	46.4	25.2	15.1	–5.0	2.1	–19.0	–18.3	–0.8	–0.1	–16.4	–13.4	–16.0	–2.3	2.3	–5.8
NC	27.7	23.2	13.7	7.0	15.7	–7.0	4.5	8.0	2.4	–6.8	–1.6	–2.0	–2.1	1.4	2.1
CN	29.9	21.5	13.7	0.0	12.9	–3.6	1.7	6.8	4.2	–5.8	0.1	0.0	–2.5	0.3	0.1
ON	18.2	17.0	4.7	–5.6	8.6	–8.5	3.3	0.0	12.3	9.5	12.8	8.9	–0.7	–1.6	–0.6
CH_2=N	33.7	27.5	16.8	7.1	18.3	4.4	12.4	11.0	10.7	–2.1	6.3	6.1	–5.9	–1.5	0.0
O_2N	49.3	24.6	8.6	–20.3	–2.8	–38.6	–33.5	–11.1	21.0	6.1	17.6	10.1	–2.2	–1.2	–4.3
MD	24.1	12.8	8.0	0.4	4.4	–7.6	–0.9	2.3	2.1	–6.3	–1.3	–2.6	–3.3	1.8	–0.6
MAD	24.1	12.8	8.0	5.5	5.6	8.7	9.3	4.8	4.7	7.5	4.9	4.5	4.7	2.3	2.1
LD	49.3	27.5	16.8	–20.3	18.3	–38.6	–33.5	12.3	21.0	–27.1	17.6	–16.0	15.1	6.9	–5.8
SD	12.4	8.4	4.9	7.0	6.0	10.0	12.8	5.6	6.1	6.7	6.7	5.5	5.0	2.4	2.8
NO	30	16	11	2	6	8	11	3	3	6	5	4	3	0	0

Table AP6. Comparison of UMP2/6-31+G(d) and UCCSD(T)/6-31+G(d) BDEs (for ROH molecules) and RSEs (for RO• radicals) with G4 values (kJ mol^{-1})

		Present study		Previous study[a]	
	G4	UMP2	UCCSD(T)	UMP2	UCCSD(T)
			BDEs		
H	494.2	449.7	434.0	448.9	429.3
MeO	355.6	333.1	309.5	388.3	328.4
Ph	367.3	425.9	318.8	425.1	318.0
MeC(O)	457.1	422.1	409.8	559.8	549.4
$NH_2C(O)$	458.8	423.8	410.2	543.5	476.1
HOC(O)	459.6	435.4	414.7	484.1	406.7
NO_2	426.1	345.3	381.8	513.4	386.6
			Deviations from G4		
H		–44.5	–60.3	–45.3	–64.9
MeO		–22.5	–46.1	32.7	–27.2
Ph		58.5	–48.5	57.8	–49.3
MeC(O)		–35.0	–47.2	102.8	92.3
$NH_2C(O)$		–35.1	–48.7	84.7	17.3
HOC(O)		–24.2	–44.9	24.5	–52.9
NO_2		–80.9	–44.4	87.2	–39.5
			RSEs		
MeO	138.6	116.6	124.5	60.7	100.8
Ph	126.9	23.9	115.2	23.8	111.3
MeC(O)	37.2	27.6	24.1	–110.9	–120.1
$NH_2C(O)$	35.4	26.0	23.8	–94.6	–46.9
HOC(O)	34.6	14.3	19.3	–35.1	22.6

NO_2	68.1	104.4	52.2	–64.4	42.7
			Deviations from G4		
MeO		–22.0	–14.1	–77.9	–37.8
Ph		–103.0	–11.7	–103.1	–15.6
MeC(O)		–9.5	–13.0	–148.0	–157.2
$NH_2C(O)$		–9.4	–11.6	–129.9	–82.2
HOC(O)		–20.4	–15.4	–69.8	–12.0
NO_2		36.3	–15.9	–132.5	–25.4

[a] Y. Fu, L. Liu, Y. Mou, B.-L. Lin, Q.-X. Guo, *J. Mol. Struct.* **2004**, *674*, 241.

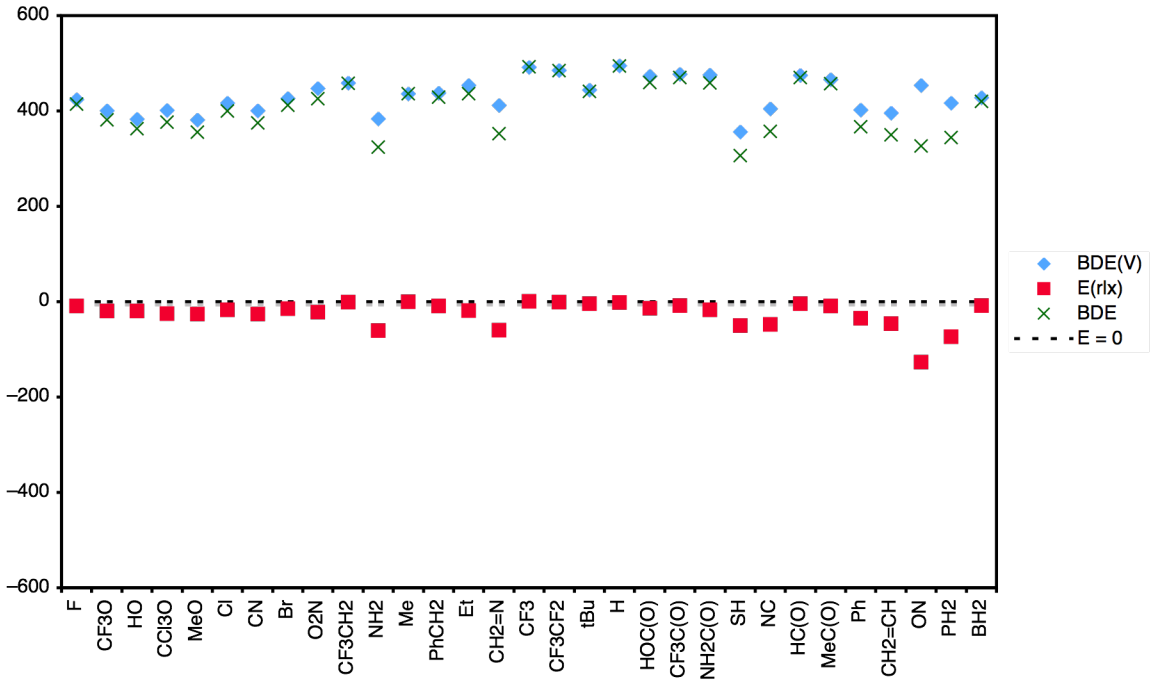

Fig. AP1. G4 vertical bond dissociation energy (BDE_V), geometric relaxation energy (E_{rlx}) and (adiabatic) BDE values corresponding to the dissociation of ROH molecules (298 K, kJ mol^{-1})