Supporting Information

Rationale for the Acidity of Meldrum's Acid.

Consistent Relation of C-H Acidities to the Properties of Localized Reactive Orbital

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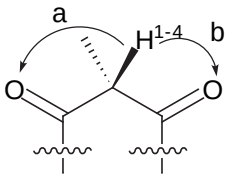
Contents

Table S1. Calculated Structural Values of the Relevant Carbonyl Compounds.[a]

compound	relative energy[b] (kcal / mol)	dihedral angle (°)[c]							
		H^1		H^2		H^3		H^4	
		a	b	a	b	a	b	a	b
1	-	85.7	-85.5	-29.9	30.1	-	-	-	-
2-a	0.0	99.3	-99.2	-	-	-	-	-	-
2-b	1.6	-55.7	55.7	-	-	-	-	-	-
3-a	0.0	92.4	-92.5	-	-	-	-	-	-
3-b	1.6	-74.2	74.2	-	-	-	-	-	-
4	-	-81.9	65.8	32.0	-48.8	-	-	-	-
5	-	104.7	104.7	13.0	-13.0	-	-	-	-
6	-	106.4	106.3	11.3	-11.5	-	-	-	-
7	-	140.7	123.2	21.7	119.3	-	-	-	-
8	-	-31.3	152.2	152.7	-30.6	-	-	-	-
9	-	-79.7	-	35.2	-	-	-	-	-
10	-	-79.4	-	33.4	-	-	-	-	-
11	-	-78.9	-	33.7	-	-	-	-	-
12	-	108.9	-	-7.2	-	108.9	-	7.2	-
13	-	111.3	-	109.8	-	4.8	-	-6.4	-
14-a	0.0	119.9	-	122.0	-	0.9	-	-	-
14-b	7.5	119.6	-	120.5	-	0.4	-	-	-
15-a	2.2	-56.4	-	174.2	-	-	-	-	-
15-b	0.0	81.7	-	161.6	-	-	-	-	-
15-c	3.0	138.9	-	106.7	-	-	-	-	-

[a] All the values were calculated at the B3LYP/6-311+G** (5d) level.
[b] To the most stable conformer of the molecule.
[c] Dihedral angles were defined as shown in the illustration on the right.



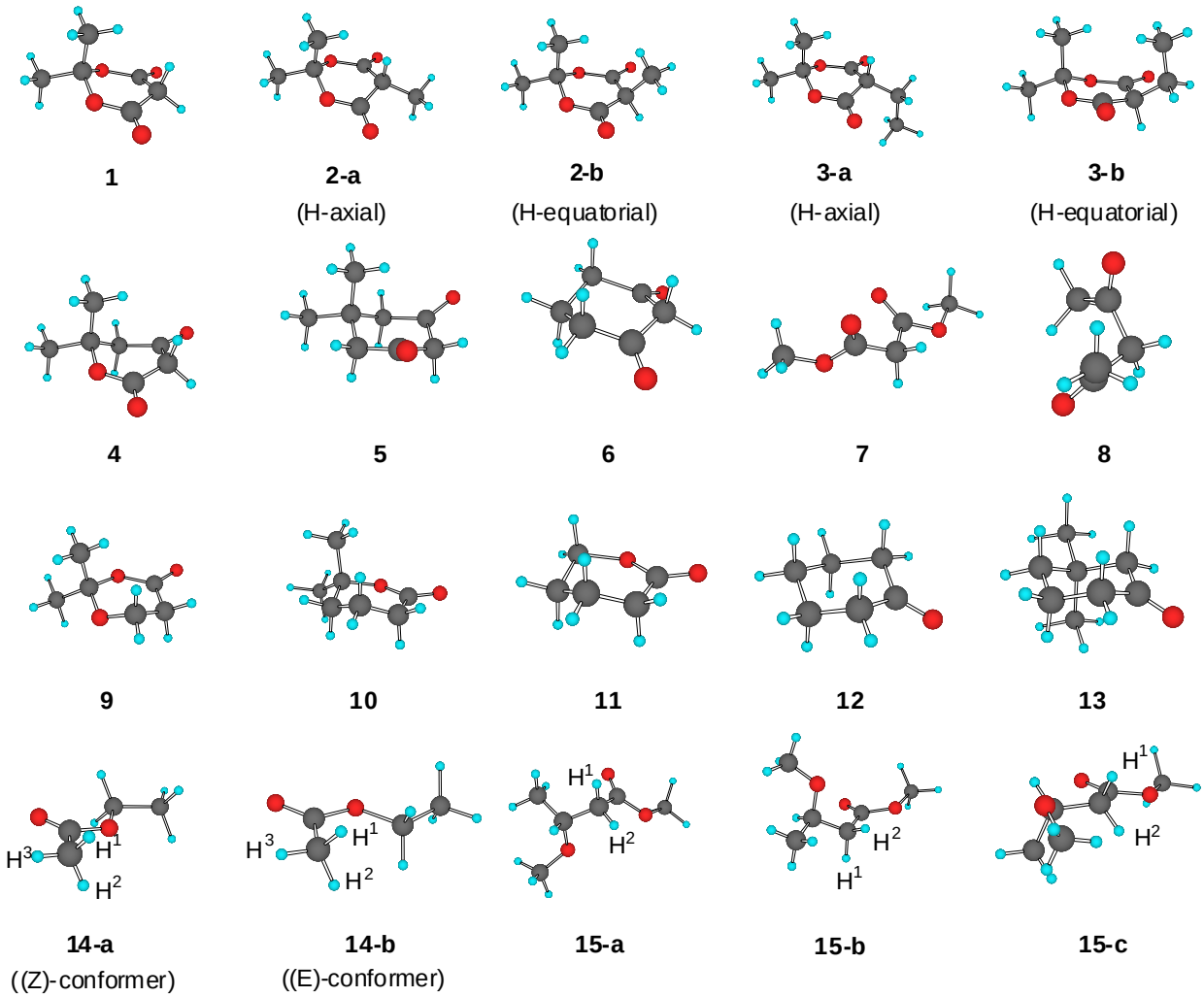


Figure S1. Stable conformations of the relevant carbonyl compounds.

Table S2-S16 The structures of the stationary point (stable structures) of **1-15**. Cartesian coordinates, number of imaginary frequencies, total energies of calculated species, and zero-point energies.

Table S2. 1 (Meldrum's acid)

Total Energy (au) = -534.5320647 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 86.90114 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.515966
3	8	0	1.223108	0.000000	2.108090
4	6	0	2.421692	0.194294	1.329629
5	8	0	2.369808	-0.559598	0.101123
6	6	0	1.235106	-0.596537	-0.645772
7	8	0	-0.993950	-0.021654	2.182635
8	6	0	3.547109	-0.414735	2.142350
9	6	0	2.628754	1.676460	1.034778
10	8	0	1.243044	-1.098284	-1.732497
11	1	0	-0.101079	1.035696	-0.343413
12	1	0	-0.880226	-0.532713	-0.355990
13	1	0	4.487775	-0.319692	1.598544
14	1	0	3.341448	-1.470663	2.319072
15	1	0	3.629299	0.098911	3.101008
16	1	0	3.554585	1.810553	0.473393
17	1	0	2.697384	2.228694	1.973193
18	1	0	1.808895	2.096011	0.449256

Table S3. 2 (methyl Meldrum's acid)

conformation 1 (**2-1**)

Total Energy (au) = -573.8572939 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies =0
Zero-point energy (kcal / mol) = 104.51204 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.099260

3	1	0	2.155361	0.000000	-0.123896
4	6	0	1.320316	0.597238	-0.488141
5	1	0	1.359149	0.610240	-1.578309
6	1	0	1.419169	1.621501	-0.130660
7	6	0	-1.207583	0.842011	-0.401602
8	8	0	-1.146387	1.991053	-0.732250
9	6	0	-0.164513	-1.462987	-0.401397
10	8	0	0.739318	-2.175858	-0.730418
11	8	0	-1.433945	-1.950445	-0.378079
12	8	0	-2.412053	0.211017	-0.375319
13	6	0	-2.537447	-1.148377	0.083641
14	6	0	-2.638709	-1.196100	1.605555
15	1	0	-1.750650	-0.791175	2.092521
16	1	0	-3.502790	-0.614247	1.929903
17	1	0	-2.765199	-2.230631	1.928245
18	1	0	-4.646763	-1.123664	-0.317493
19	6	0	-3.769690	-1.704980	-0.604824
20	1	0	-3.641847	-1.647839	-1.685948
21	1	0	-3.914675	-2.746859	-0.316391

conformation 2 (**2-2**)

Total Energy (au) = -573.8548444 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 104.54319 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.386733	0.000000	0.120667
2	8	0	-0.731539	-1.189692	-0.355288
3	6	0	0.622999	-1.291771	-0.359778
4	6	0	1.425973	0.000072	-0.286212
5	6	0	0.622919	1.291903	-0.359549
6	8	0	-0.731671	1.189945	-0.354754
7	6	0	2.407905	-0.000052	0.904977
8	8	0	1.139097	2.366799	-0.482560
9	8	0	1.139204	-2.366655	-0.482815
10	6	0	-1.414798	-0.000533	1.645110
11	6	0	-2.766258	0.000126	-0.507891
12	1	0	2.031981	0.000161	-1.198933
13	1	0	3.034816	-0.890220	0.857537
14	1	0	3.036713	0.888702	0.856166
15	1	0	1.882003	0.001268	1.862443
16	1	0	-0.405318	0.000170	2.061608
17	1	0	-1.935942	0.888405	2.003638
18	1	0	-1.934456	-0.890584	2.003030
19	1	0	-3.314401	0.889760	-0.195233
20	1	0	-3.313927	-0.890265	-0.196561

21	1	0	-2.674229	0.000962	-1.594298

Table S4. 3 (ethyl Meldrum's acid)

conformation 1 (**3-1**)

Total Energy (au) = -613.1807558 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 122.38981 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.099670
3	6	0	1.469574	0.000000	-0.464031
4	1	0	1.947559	-0.882065	-0.033324
5	1	0	1.948731	0.880200	-0.030805
6	6	0	1.653046	0.002065	-1.984232
7	1	0	1.212868	0.893222	-2.437120
8	1	0	1.207403	-0.884776	-2.440285
9	1	0	2.717492	-0.000916	-2.231043
10	6	0	-0.740463	-1.276173	-0.392383
11	8	0	-0.199613	-2.323290	-0.606487
12	6	0	-0.740457	1.276675	-0.390687
13	8	0	-0.199824	2.324401	-0.602260
14	8	0	-2.092718	1.185929	-0.500931
15	8	0	-2.092744	-1.185672	-0.501721
16	6	0	-2.797816	0.000066	-0.092257
17	1	0	-3.578425	0.884573	1.707438
18	6	0	-3.011035	-0.001483	1.418776
19	1	0	-2.067303	0.001606	1.966625
20	1	0	-3.571443	-0.892536	1.705699
21	1	0	-4.674261	0.894928	-0.629370
22	6	0	-4.098493	0.001016	-0.872699
23	1	0	-4.681991	-0.885389	-0.620476
24	1	0	-3.883682	-0.005223	-1.941527

conformation 2 (**3-2**)

Total Energy (au) = -613.1781159 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 122.36346 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.100084
3	6	0	1.477834	0.000000	-0.444381
4	1	0	1.948890	0.881313	-0.005527
5	1	0	1.949245	-0.880671	-0.004621
6	6	0	1.684251	-0.000748	-1.960927
7	1	0	2.751331	-0.000557	-2.195238
8	1	0	1.250245	-0.890503	-2.426062
9	1	0	1.249732	0.888267	-2.427009
10	6	0	-0.727900	-1.293849	-0.344101
11	8	0	-0.226102	-2.375539	-0.224068
12	6	0	-0.728081	1.293816	-0.343994
13	8	0	-0.226290	2.375516	-0.223719
14	8	0	-2.040731	1.192907	-0.683751
15	8	0	-2.040734	-1.193014	-0.683674
16	6	0	-2.568266	-0.000224	-1.291669
17	6	0	-2.233424	-0.000175	-2.779165
18	1	0	-1.153027	-0.000242	-2.938789
19	1	0	-2.652716	-0.889900	-3.251340
20	1	0	-2.652631	0.889596	-3.251323
21	6	0	-4.056660	0.000057	-1.004305
22	1	0	-4.223958	-0.000167	0.073212
23	1	0	-4.515806	-0.889639	-1.437112
24	1	0	-4.515353	0.890192	-1.436686

Table S5. 4 (2,2-dimethylpyran-4,6-dione)

Total Energy (au) = -498.5967793 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 101.59831 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.535303
3	6	0	1.396236	0.000000	2.118887
4	6	0	2.444788	0.740403	1.300517
5	6	0	1.955777	1.518282	0.088081
6	8	0	0.788095	1.140845	-0.484227
7	8	0	2.573077	2.439472	-0.374588
8	8	0	1.675860	-0.531876	3.167177
9	6	0	0.586437	-1.289505	-0.583575
10	6	0	-1.400959	0.256741	-0.547453
11	1	0	3.178443	0.003824	0.952167
12	1	0	2.998804	1.424519	1.945686
13	1	0	-0.555724	-0.850402	1.934121
14	1	0	-0.495251	0.913707	1.889462

15	1	0	1.591924	-1.495972	-0.209407
16	1	0	-0.046769	-2.141359	-0.323230
17	1	0	0.636709	-1.215254	-1.671432
18	1	0	-2.079709	-0.542829	-0.240421
19	1	0	-1.378754	0.295041	-1.638246
20	1	0	-1.788757	1.208021	-0.178000

Table S6. 5 (dimedone)

Total Energy (au) = -462.6658085 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 116.72996 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.526150
3	6	0	1.370714	0.000000	2.178637
4	6	0	2.312836	1.090367	1.605994
5	6	0	2.399690	0.929555	0.066231
6	6	0	1.039586	0.937433	-0.608161
7	8	0	-1.031703	-0.003157	2.157152
8	6	0	3.714392	0.915851	2.211998
9	6	0	1.772052	2.489912	1.958398
10	8	0	0.780941	1.630668	-1.564742
11	1	0	1.239327	0.117274	3.256131
12	1	0	1.820199	-0.987114	2.002576
13	1	0	2.876675	-0.032956	-0.165074
14	1	0	3.009767	1.717563	-0.379743
15	1	0	-0.993606	0.225290	-0.385029
16	1	0	0.271180	-1.018156	-0.315555
17	1	0	4.403643	1.670963	1.822853
18	1	0	4.127918	-0.070219	1.979939
19	1	0	3.683998	1.021450	3.300402
20	1	0	2.431445	3.267739	1.563672
21	1	0	1.709900	2.616594	3.042700
22	1	0	0.772824	2.668094	1.549398

Table S7. 6 (1,3-cyclohexanedione)

Total Energy (au) = -384.0158858 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 82.13501 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.089151
3	6	0	1.430969	0.000000	-0.536353
4	8	0	2.376299	-0.202776	0.189120
5	6	0	-0.855201	1.147562	-0.536088
6	8	0	-1.584357	1.782655	0.189217
7	6	0	1.570114	0.281784	-2.022597
8	1	0	2.630341	0.383017	-2.257560
9	1	0	1.186927	-0.592017	-2.567148
10	6	0	-0.712026	1.428652	-2.022082
11	1	0	-1.263366	2.340120	-2.256098
12	1	0	-1.184939	0.600360	-2.567281
13	6	0	0.768009	1.529861	-2.433454
14	1	0	1.214003	2.417268	-1.971677
15	1	0	0.838647	1.671241	-3.514393
16	1	0	-0.467996	-0.932129	-0.348611

Table S8. 7 (dimethyl malonate)

Total Energy (au) = -496.4115579 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 83.23913 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.092149
3	1	0	1.036097	0.000000	-0.341931
4	6	0	-0.692347	1.235385	-0.537083
5	6	0	-0.670136	-1.276723	-0.480944
6	8	0	-0.325848	1.865240	-1.496358
7	8	0	-1.625173	-1.340914	-1.210767
8	1	0	-1.588491	-3.741140	-0.035509
9	6	0	-0.554087	-3.636560	-0.364747
10	8	0	-0.031830	-2.349641	0.024525
11	1	0	0.082448	-4.367018	0.128984
12	1	0	-0.506512	-3.752854	-1.448010
13	8	0	-1.769854	1.543649	0.205386
14	6	0	-2.553705	2.662498	-0.253611
15	1	0	-1.947826	3.569241	-0.270086
16	1	0	-3.369126	2.756599	0.459696
17	1	0	-2.938373	2.465230	-1.254705

Table S9. 8 (acetylacetone)

Total Energy (au) = -345.902544 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 76.11847 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.509463
3	8	0	1.014007	0.000000	2.170681
4	6	0	-1.376926	0.039843	2.188994
5	6	0	-1.781728	1.509478	2.376970
6	6	0	-1.347742	2.162643	3.666733
7	8	0	-2.388590	2.097341	1.509991
8	1	0	-1.292370	-0.465630	3.151738
9	1	0	-2.131167	-0.439596	1.563759
10	1	0	-0.656252	0.789999	-0.377200
11	1	0	1.013520	0.129497	-0.377069
12	1	0	-0.406344	-0.950406	-0.362537
13	1	0	-1.543072	3.233523	3.631457
14	1	0	-1.899437	1.717774	4.501934
15	1	0	-0.286328	1.969638	3.848944

Table S10. 9 (2,2-dimethyl-1,3-dioxan-4-one)

Total Energy (au) = -460.4755595 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 98.93378 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.469942
3	8	0	1.306666	0.000000	1.991831
4	6	0	2.168815	0.993571	1.441357
5	6	0	2.347303	0.720026	-0.046362
6	6	0	1.034526	0.441820	-0.756121
7	6	0	-0.817765	1.213463	1.913288
8	6	0	-0.635110	-1.315702	1.883982
9	8	0	0.895577	0.546025	-1.945895
10	1	0	3.110572	0.906833	1.983058
11	1	0	1.771402	1.999344	1.617832
12	1	0	2.966989	-0.171787	-0.186360
13	1	0	2.840400	1.544194	-0.564694
14	1	0	-1.825303	1.145834	1.501042
15	1	0	-0.379522	2.150133	1.565157

16	1	0	-0.878431	1.235253	3.003341
17	1	0	-1.634296	-1.400317	1.455251
18	1	0	-0.704244	-1.365125	2.972209
19	1	0	-0.022506	-2.145093	1.529048

Table S11. 10 (6,6-dimethylpyranone)

Total Energy (au) = -424.5626888 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 114.11307 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.473023
3	6	0	1.431102	0.000000	2.027134
4	6	0	2.302591	1.065675	1.365030
5	6	0	2.326531	0.831324	-0.146251
6	6	0	0.975419	0.530939	-0.776746
7	6	0	-0.799222	1.232205	1.910087
8	6	0	-0.737213	-1.282885	1.850218
9	8	0	0.767010	0.677681	-1.953690
10	1	0	1.875684	-0.987747	1.859282
11	1	0	1.382524	0.146776	3.109959
12	1	0	3.319576	1.030346	1.764661
13	1	0	1.918821	2.066007	1.586780
14	1	0	2.951103	-0.040706	-0.377098
15	1	0	2.755349	1.670220	-0.696025
16	1	0	-1.789542	1.212939	1.451494
17	1	0	-0.309740	2.161396	1.610976
18	1	0	-0.919207	1.241838	2.996954
19	1	0	-1.740176	-1.286630	1.418801
20	1	0	-0.824976	-1.363865	2.937074
21	1	0	-0.199607	-2.157568	1.477781

Table S12. 11 (valerolactone)

Total Energy (au) = -345.9063669 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 79.67742 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Corrdinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000

2	1	0	0.000000	0.000000	1.090841
3	8	0	2.387087	0.000000	0.181072
4	1	0	-0.149210	-1.042383	-0.307893
5	6	0	1.416881	0.343618	-0.440338
6	8	0	1.590335	0.986460	-1.625183
7	6	0	-1.105699	0.878023	-0.593327
8	1	0	-2.083350	0.425949	-0.407471
9	1	0	-1.111974	1.857901	-0.102081
10	6	0	0.514424	1.692210	-2.292717
11	1	0	0.520806	2.721156	-1.916598
12	1	0	0.807227	1.711885	-3.342608
13	6	0	-0.851336	1.059368	-2.089036
14	1	0	-1.606010	1.704313	-2.549375
15	1	0	-0.895578	0.091242	-2.600579

Table S13. 12 (cyclohexanone)

Total Energy (au) = -309.9812031 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 94.31358 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.521348
3	6	0	1.430674	0.000000	2.098363
4	6	0	2.286170	-1.118676	1.491217
5	6	0	2.327556	-1.016545	-0.038412
6	6	0	0.911104	-1.030719	-0.649695
7	8	0	-0.679308	0.766598	-0.649000
8	1	0	-0.584255	0.853613	1.869406
9	1	0	-0.517109	-0.913197	1.846826
10	1	0	1.385622	-0.096430	3.187202
11	1	0	1.900159	0.968992	1.890635
12	1	0	1.874805	-2.093962	1.782400
13	1	0	3.301746	-1.075181	1.896767
14	1	0	2.917492	-1.833751	-0.463934
15	1	0	2.831670	-0.086091	-0.325846
16	1	0	0.458518	-2.017605	-0.480880
17	1	0	0.925730	-0.852718	-1.726375

Table S14. 13 (3,3-dimethylcyclohexanone)

Total Energy (au) = -388.6300301 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 128.95835 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.092553
3	1	0	1.046807	0.000000	-0.333349
4	6	0	-0.624329	1.297697	-0.487421
5	6	0	-0.794513	1.402690	-1.994026
6	8	0	-0.956538	2.185088	0.269667
7	1	0	-1.345906	2.316132	-2.223306
8	1	0	0.210465	1.500507	-2.427017
9	6	0	-1.474086	0.149101	-2.579674
10	1	0	-1.453518	0.200176	-3.672259
11	1	0	-2.530864	0.145901	-2.294144
12	6	0	-0.794713	-1.141996	-2.104410
13	1	0	-1.327788	-2.011515	-2.504613
14	1	0	0.220773	-1.184399	-2.519808
15	6	0	-0.700631	-1.266984	-0.565029
16	6	0	-2.101017	-1.406160	0.063841
17	1	0	-2.024161	-1.533192	1.147614
18	1	0	-2.621234	-2.280053	-0.340329
19	1	0	-2.730016	-0.530147	-0.113318
20	6	0	0.133435	-2.506851	-0.203288
21	1	0	0.245177	-2.604379	0.880843
22	1	0	-0.344762	-3.419433	-0.572924
23	1	0	1.134886	-2.451591	-0.641264

Table S15. 14 (ethyl acetate)

conformation 1 ((Z)-conformer)

Total Energy (au) = -307.8040782 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 73.70278 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.136194	-0.892100	0.000224
2	1	0	-3.105814	-0.398779	-0.015185
3	6	0	-1.042826	0.146218	-0.000701
4	1	0	-2.034304	-1.543641	-0.870581
5	1	0	-2.052332	-1.519903	0.890430
6	8	0	-1.211183	1.341724	-0.000048
7	8	0	0.176843	-0.434442	-0.001011
8	6	0	1.320383	0.455260	0.000587
9	1	0	1.263052	1.096135	0.883618

10	1	0	1.263871	1.098435	-0.880819
11	6	0	2.569937	-0.401539	0.000077
12	1	0	3.455169	0.240263	0.002038
13	1	0	2.607872	-1.040553	0.885236
14	1	0	2.609418	-1.037251	-0.887391

conformation 2 ((E)-conformer)

Total Energy (au) = -307.7919645 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 73.64028 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.500597
3	8	0	1.129104	0.000000	2.267330
4	6	0	2.402926	-0.007346	1.631571
5	6	0	3.373279	0.732780	2.531252
6	8	0	-0.964585	-0.004842	2.236928
7	1	0	-0.883003	0.518602	-0.393725
8	1	0	0.898470	0.491666	-0.406916
9	1	0	-0.019937	-1.030426	-0.378561
10	1	0	2.696358	-1.064934	1.499352
11	1	0	2.356678	0.454950	0.621150
12	1	0	3.418713	0.291896	3.536000
13	1	0	3.097690	1.788554	2.651822
14	1	0	4.384697	0.697838	2.107315

Table S16. 15 (methyl 3-methoxybutyrate)

conformation 1

Total Energy (au) = -461.6727638 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 112.29214 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.089751
3	1	0	1.035721	0.000000	-0.351492
4	6	0	-0.651180	-1.274935	-0.497966
5	8	0	-0.716340	-1.621651	-1.653783

6	8	0	-1.140215	-2.009454	0.521657
7	6	0	-1.795359	-3.237331	0.154951
8	1	0	-2.114130	-3.686945	1.092775
9	1	0	-1.105126	-3.896442	-0.373627
10	1	0	-2.655077	-3.031801	-0.484129
11	6	0	-0.579697	1.501445	-2.010540
12	1	0	-1.040283	2.448736	-2.300265
13	1	0	-1.054132	0.689052	-2.561706
14	1	0	0.472724	1.544867	-2.304687
15	6	0	-0.693356	1.277976	-0.501911
16	1	0	-0.212759	2.122202	0.017714
17	8	0	-2.047237	1.187357	-0.056639
18	6	0	-2.773815	2.401562	-0.080484
19	1	0	-2.247120	3.191746	0.473555
20	1	0	-2.966917	2.753677	-1.100907
21	1	0	-3.729248	2.205846	0.407183

conformation 2

Total Energy (au) = -461.6759187 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 112.11220 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.366016	0.392808	-0.309849
2	8	0	-2.169147	-0.345035	-0.620974
3	6	0	-1.168865	-0.255709	0.279440
4	6	0	0.021931	-1.097681	-0.129328
5	6	0	1.346876	-0.425944	0.222934
6	8	0	1.432448	0.732470	-0.611672
7	6	0	2.249914	1.771169	-0.102526
8	8	0	-1.245815	0.392857	1.294967
9	6	0	2.537292	-1.361679	0.011347
10	1	0	-0.060622	-2.053032	0.400837
11	1	0	-0.022341	-1.307758	-1.199455
12	1	0	-4.047252	0.201844	-1.136092
13	1	0	-3.145050	1.458010	-0.232010
14	1	0	-3.795175	0.045828	0.631206
15	1	0	3.301496	1.468447	-0.014893
16	1	0	1.305088	-0.104276	1.271691
17	1	0	2.568764	-1.714967	-1.022930
18	1	0	2.469706	-2.228860	0.674684
19	1	0	3.480162	-0.854131	0.227075
20	1	0	2.185250	2.598693	-0.809693
21	1	0	1.893297	2.110079	0.878909

conformation 3

Total Energy (au) = -461.6712334 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 112.17356 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.440674
3	6	0	1.212584	0.000000	2.035579
4	8	0	2.251029	0.018090	1.419931
5	6	0	1.070907	-0.054917	3.541181
6	6	0	2.378932	0.235746	4.294300
7	6	0	2.803752	1.702156	4.213177
8	8	0	2.309845	-0.257897	5.638502
9	6	0	1.427224	0.404889	6.528035
10	1	0	0.263255	0.621339	3.833816
11	1	0	0.735966	-1.067335	3.793403
12	1	0	-1.048509	0.003056	-0.289222
13	1	0	0.501316	-0.890565	-0.381469
14	1	0	0.506773	0.887459	-0.381181
15	1	0	3.164050	-0.374045	3.844190
16	1	0	2.022815	2.380737	4.568403
17	1	0	3.030950	1.960499	3.176939
18	1	0	3.704250	1.865848	4.809790
19	1	0	0.385501	0.380370	6.182992
20	1	0	1.717200	1.447679	6.703229
21	1	0	1.488198	-0.134311	7.473903

Table A1 – A15. The structures of the stationary point of the corresponding anions of **1**-**15**. Cartesian coordinates, number of imaginary frequencies, total energies of calculated species, and zero-point energies.

Table A1. 1 (the anion of Meldrum's acid)

Total Energy (au) = -533.9975606 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 78.12311 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.088719
3	6	0	1.432757	0.000000	-0.495549
4	8	0	2.343907	-0.499254	0.098872
5	6	0	-0.854731	1.149732	-0.495685
6	8	0	-1.796812	1.585444	0.100548
7	8	0	1.650887	0.638343	-1.675254
8	8	0	-0.476233	1.702031	-1.678186
9	6	0	0.546971	1.087216	-2.487762
10	6	0	-0.034124	-0.076831	-3.283971
11	1	0	0.743091	-0.511120	-3.914547
12	1	0	-0.846620	0.283768	-3.916519
13	1	0	-0.427180	-0.861237	-2.634938
14	6	0	1.100829	2.192176	-3.365429
15	1	0	1.899631	1.797704	-3.994648
16	1	0	0.307403	2.594197	-3.996672
17	1	0	1.499739	2.991283	-2.740280

Table A2. 2 (the anion of methyl Meldrum's acid)

Total Energy (au) = -573.3223057 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 95.8220 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.414575
3	8	0	1.268172	0.000000	2.044984
4	6	0	2.378490	0.433368	1.272293
5	8	0	2.399818	-0.174687	-0.011008

6	6	0	1.188804	-0.175914	-0.745574
7	8	0	-0.964881	-0.023259	2.173920
8	6	0	2.370410	1.965019	1.138094
9	6	0	3.623390	-0.061583	1.999624
10	8	0	1.306226	-0.356554	-1.954565
11	6	0	-1.319691	0.009467	-0.728617
12	1	0	-1.210755	0.476188	-1.711668
13	1	0	-1.719821	-1.001604	-0.897706
14	1	0	-2.069098	0.556900	-0.150677
15	1	0	3.246618	2.291909	0.572062
16	1	0	2.388656	2.423839	2.130126
17	1	0	1.471071	2.292683	0.615184
18	1	0	4.520812	0.229274	1.448280
19	1	0	3.662529	0.360634	3.006667
20	1	0	3.585691	-1.149760	2.070632

Table A3. 3 (the anion of ethyl Meldrum's acid)

Total Energy (au) = -612.647655 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 113.6483 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.443130
3	6	0	1.267139	0.000000	2.075344
4	6	0	2.354015	-0.507498	1.319817
5	6	0	2.187424	-1.035200	0.014069
6	8	0	0.884393	-0.975079	-0.536537
7	6	0	3.724937	-0.552625	1.953348
8	6	0	4.011936	-1.852914	2.728881
9	8	0	3.030977	-1.582281	-0.689210
10	8	0	1.266227	0.385159	3.241251
11	6	0	0.361194	1.397338	-0.529531
12	6	0	-1.402972	-0.416059	-0.427419
13	1	0	3.810098	0.282776	2.656707
14	1	0	4.486457	-0.425196	1.177445
15	1	0	3.249345	-2.009164	3.497095
16	1	0	3.998642	-2.712414	2.052132
17	1	0	4.993118	-1.822905	3.223050
18	1	0	0.352645	1.393449	-1.622502
19	1	0	-0.362816	2.130693	-0.164257
20	1	0	1.355868	1.684841	-0.186423
21	1	0	-1.508858	-0.343758	-1.512763
22	1	0	-2.141195	0.229685	0.053598
23	1	0	-1.576901	-1.448559	-0.120857

Table A4. 4 (the anion of 2,2-dimethylpyran-4,6-dione)

Total Energy (au) = -498.0587603 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 93.6383 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.083401
3	6	0	1.273544	0.000000	-0.628927
4	8	0	2.372546	0.063526	-0.084792
5	6	0	-1.224253	0.085373	-0.684484
6	8	0	-2.365921	0.133267	-0.172853
7	8	0	1.315104	-0.065080	-2.039651
8	6	0	0.147571	-0.504785	-2.766581
9	6	0	-1.111032	0.172335	-2.214462
10	1	0	-2.011393	-0.270393	-2.650754
11	1	0	-1.104297	1.235236	-2.488747
12	6	0	0.413071	-0.087408	-4.215509
13	1	0	-0.421048	-0.380486	-4.861746
14	1	0	1.327581	-0.559539	-4.586946
15	1	0	0.539289	0.996534	-4.276394
16	6	0	0.048914	-2.037406	-2.670219
17	1	0	0.980107	-2.490967	-3.021161
18	1	0	-0.120947	-2.345494	-1.637064
19	1	0	-0.778092	-2.411092	-3.283533

Table A5. 5 (the anion of dimedone)

Total Energy (au) = -462.1249754 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 108.6603 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.540482
3	6	0	1.392506	0.000000	2.200773
4	6	0	2.463403	0.561078	1.467685
5	6	0	2.347051	1.113612	0.171458
6	6	0	0.950118	1.113910	-0.478997
7	8	0	1.475194	-0.476098	3.355917

8	8	0	3.281553	1.627671	-0.484554
9	6	0	0.473439	-1.368103	-0.532093
10	6	0	-1.423367	0.262465	-0.524978
11	1	0	3.443280	0.574887	1.936120
12	1	0	-0.547441	-0.862844	1.935767
13	1	0	-0.525688	0.895939	1.901173
14	1	0	0.496301	2.092080	-0.263651
15	1	0	1.096013	1.069749	-1.563985
16	1	0	1.482062	-1.597606	-0.182571
17	1	0	-0.194996	-2.168231	-0.193441
18	1	0	0.482554	-1.375727	-1.628223
19	1	0	-1.799658	1.227909	-0.170286
20	1	0	-2.119190	-0.514522	-0.185694
21	1	0	-1.443881	0.276196	-1.621517

Table A6. 6 (the anion of 1,3-cyclohexanedione)

Total Energy (au) = -383.4747553 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 74.0750 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.086557
3	6	0	1.257875	0.000000	-0.650248
4	8	0	2.369035	0.016228	-0.073086
5	6	0	-1.257001	0.042718	-0.650628
6	8	0	-2.367169	0.096346	-0.073843
7	6	0	1.258725	0.007700	-2.190424
8	1	0	2.159242	-0.521387	-2.517462
9	1	0	1.371712	1.052199	-2.516524
10	1	0	-1.333895	1.098533	-2.516989
11	6	0	-1.257088	0.050850	-2.190815
12	1	0	-2.175229	-0.446802	-2.518234
13	6	0	-0.009825	-0.592916	-2.799382
14	1	0	-0.007698	-0.480780	-3.892651
15	1	0	-0.028202	-1.670542	-2.592361

Table A7. 7 (the anion of dimethyl malonate)

Total Energy (au) = -495.8511605 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 74.2696 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.080776
3	6	0	1.285407	0.000000	-0.590238
4	8	0	2.367704	0.000058	0.012166
5	6	0	-1.257743	-0.000333	-0.641034
6	8	0	-1.593787	-0.000806	-1.822126
7	8	0	1.296132	-0.000480	-1.983960
8	8	0	-2.293992	-0.000401	0.346023
9	6	0	-3.607822	0.000256	-0.174806
10	1	0	-3.803214	-0.880273	-0.797576
11	1	0	-3.807015	0.888254	-0.785908
12	1	0	-4.276721	-0.006589	0.690530
13	6	0	2.581089	-0.000418	-2.577418
14	1	0	3.162070	-0.885348	-2.295212
15	1	0	2.407643	-0.000096	-3.656368
16	1	0	3.162232	0.884185	-2.294608

Table A8. 8 (the anion of acetylacetone)

Total Energy (au) = -345.353168 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 67.8834 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.085902
3	6	0	1.299307	0.000000	-0.590463
4	8	0	2.352614	-0.000159	0.085259
5	6	0	-1.250637	0.000142	-0.659690
6	8	0	-1.473489	0.000296	-1.894891
7	6	0	1.427048	0.000178	-2.114490
8	1	0	2.489278	-0.001078	-2.371685
9	1	0	0.926511	0.870380	-2.547721
10	1	0	0.924106	-0.868297	-2.548344
11	6	0	-2.496417	0.000095	0.249554
12	1	0	-3.104996	-0.880689	0.016970
13	1	0	-2.259182	-0.000385	1.317258
14	1	0	-3.104596	0.881329	0.017642

Table A9. 9 (the anion of 2,2-dimethyl-1,3-dioxan-4-one)

Total Energy (au) = -459.8866091 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0

Zero-point energy (kcal / mol) = 89.3832 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.425633
3	6	0	1.322094	0.000000	1.991803
4	6	0	2.274420	-0.868822	1.230320
5	6	0	1.976424	-1.461038	0.020338
6	8	0	0.657688	-1.130477	-0.521929
7	8	0	2.619076	-2.243037	-0.696194
8	6	0	0.629872	1.293105	-0.552893
9	6	0	-1.467004	-0.120865	-0.405785
10	1	0	3.238562	-1.086207	1.676010
11	1	0	1.657160	1.057627	2.071925
12	1	0	1.171519	-0.342040	3.027192
13	1	0	0.133475	2.172671	-0.130297
14	1	0	1.693561	1.325101	-0.312052
15	1	0	0.526090	1.310610	-1.640954
16	1	0	-2.036694	0.742958	-0.050685
17	1	0	-1.545985	-0.187191	-1.493264
18	1	0	-1.880596	-1.029569	0.035277

Table A10. 10 (the anion of 6,6-dimethylpyranone)

Total Energy (au) = -423.9663102 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 104.4440 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.531262
3	6	0	1.406584	0.000000	2.060386
4	6	0	2.538818	0.289329	1.318128
5	8	0	2.342418	0.641657	-0.087357
6	6	0	1.039162	0.994784	-0.547560
7	8	0	3.738667	0.285220	1.641486
8	6	0	0.717882	2.441226	-0.122761
9	6	0	1.112110	0.907264	-2.076956
10	1	0	1.573746	-0.243258	3.104390
11	1	0	-0.563495	-0.880843	1.881310
12	1	0	-0.600380	0.867772	1.878099
13	1	0	-0.994451	0.237961	-0.402557
14	1	0	0.279220	-0.995381	-0.365467

15	1	0	1.455278	3.122204	-0.558062
16	1	0	0.771039	2.533970	0.963412
17	1	0	-0.281817	2.743910	-0.457773
18	1	0	1.906850	1.559632	-2.450459
19	1	0	1.342790	-0.117081	-2.382669
20	1	0	0.163367	1.208335	-2.536836

Table A11. 11 (the anion of valerolactone)

Total Energy (au) = -345.3096066 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 69.9554 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.085193
3	6	0	1.323487	0.000000	-0.721716
4	1	0	1.849803	-0.975792	-0.662931
5	1	0	2.027065	0.724785	-0.277537
6	6	0	-1.249425	0.031371	-0.599410
7	8	0	-2.383408	0.098877	-0.094089
8	6	0	1.125183	0.338342	-2.202834
9	1	0	2.008521	0.074891	-2.802303
10	1	0	0.942685	1.413106	-2.324152
11	8	0	-1.283966	-0.000320	-2.057400
12	6	0	-0.102115	-0.413583	-2.711098
13	1	0	0.055378	-1.497760	-2.568268
14	1	0	-0.263844	-0.239537	-3.783144

Table A12. 12 (the anion of cyclohexanone)

Total Energy (au) = -309.3829542 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 84.8569 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.384706
3	1	0	0.969651	0.000000	-0.495547
4	8	0	1.015129	0.038148	2.157231
5	6	0	-1.373010	-0.011676	2.104222
6	1	0	-1.284938	-0.704783	2.949213

7	1	0	-1.518285	0.985339	2.545685
8	6	0	-1.230655	-0.055496	-0.873630
9	1	0	-1.115569	0.597516	-1.754741
10	1	0	-1.412394	-1.067015	-1.299342
11	6	0	-2.574602	-0.377449	1.222231
12	6	0	-2.503345	0.355479	-0.120390
13	1	0	-2.481158	1.438272	0.065898
14	1	0	-3.521153	-0.157248	1.738431
15	1	0	-3.397564	0.145733	-0.726121
16	1	0	-2.570165	-1.459573	1.027220

Table A13. 13 (the anion of 3,3-dimethylcyclohexanone)

Total Energy (au) = -388.0342039 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 119.5777 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.542369
3	6	0	1.418269	0.000000	2.130471
4	6	0	2.322298	1.005524	1.464146
5	6	0	2.080171	1.603005	0.239900
6	6	0	0.746618	1.265336	-0.476299
7	8	0	2.820271	2.442212	-0.373068
8	6	0	0.705047	-1.260084	-0.540056
9	6	0	-1.450124	0.011317	-0.516889
10	1	0	3.260101	1.248981	1.960583
11	1	0	1.337620	0.196089	3.212700
12	1	0	1.811254	-1.037253	2.071116
13	1	0	-0.571605	-0.864658	1.914515
14	1	0	-0.526376	0.903454	1.879152
15	1	0	0.970623	1.191676	-1.548176
16	1	0	0.090621	2.140688	-0.364800
17	1	0	0.238373	-2.174692	-0.152319
18	1	0	1.761099	-1.262785	-0.261972
19	1	0	0.647599	-1.289611	-1.634358
20	1	0	-1.988836	-0.898571	-0.219752
21	1	0	-1.476129	0.075457	-1.611193
22	1	0	-1.999316	0.872027	-0.119481

Table A14. 14 (the anion of ethyl acetate)

conformation 1 ((Z)-conformer)

Total Energy (au) = -307.1990433 (B3LYP/6-311+G** (5D))

Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 64.3499 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.000000	0.000000	1.082306
3	1	0	0.937665	0.000000	-0.539136
4	6	0	-1.204773	-0.024475	-0.669421
5	8	0	-2.383498	-0.014612	-0.258921
6	8	0	-1.009877	-0.087554	-2.118198
7	6	0	-2.134520	0.223777	-2.904746
8	1	0	-2.223637	1.318250	-3.033651
9	1	0	-3.047005	-0.113230	-2.402824
10	6	0	-1.977728	-0.439632	-4.269069
11	1	0	-2.824303	-0.191180	-4.921748
12	1	0	-1.056357	-0.111037	-4.760828
13	1	0	-1.930559	-1.527521	-4.159994

conformation 2 ((E)-conformer)

Total Energy (au) = -307.1952203 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 64.4723 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.487054	1.246662	-0.000410
2	6	0	-1.204101	-0.111206	0.000052
3	8	0	-1.965217	-1.091221	-0.000096
4	8	0	0.198922	-0.507625	0.000370
5	6	0	1.206999	0.471030	0.000403
6	6	0	2.559042	-0.235023	-0.000401
7	1	0	-2.528448	1.541993	-0.000162
8	1	0	-0.737289	2.024188	0.000470
9	1	0	1.124243	1.122286	-0.884065
10	1	0	1.125051	1.121527	0.885564
11	1	0	2.658724	-0.870694	-0.885196
12	1	0	2.659671	-0.871106	0.883998
13	1	0	3.379092	0.493799	-0.000668

Table A15. 15 (the anion of methyl 3-methoxybutyrate)

conformation 1

Total Energy (au) = -461.0763612 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 102.0030 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.409180
3	6	0	1.309834	0.000000	2.016711
4	8	0	2.286047	0.053210	1.244989
5	6	0	1.213216	-0.082471	3.400243
6	6	0	2.339234	-0.021279	4.348030
7	8	0	2.545548	1.389361	4.842234
8	6	0	3.199154	1.481932	6.076256
9	6	0	3.681435	-0.555746	3.838430
10	1	0	0.215338	-0.065388	3.822943
11	1	0	-1.049933	0.062247	-0.305433
12	1	0	0.553872	0.849790	-0.415902
13	1	0	0.442973	-0.914726	-0.416707
14	1	0	4.466093	-0.467785	4.599507
15	1	0	3.978091	-0.021625	2.936464
16	1	0	3.579180	-1.613067	3.576056
17	1	0	2.067374	-0.570547	5.266701
18	1	0	2.726702	0.840923	6.844057
19	1	0	3.132985	2.522164	6.414795
20	1	0	4.268145	1.210219	6.032584

conformation 2

Total Energy (au) = -461.0803166 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 101.9854 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.594559	-0.217099	-0.100470
2	8	0	2.420654	0.441129	-0.520836
3	6	0	1.210914	-0.021699	0.103834
4	8	0	1.310548	-0.967793	0.909402
5	6	0	0.104045	0.709953	-0.304056
6	6	0	-1.239637	0.391295	0.193078
7	6	0	-2.113512	1.628325	0.442585
8	8	0	-2.005795	-0.486026	-0.759139

9	6	0	-2.914526	-1.342903	-0.124651
10	1	0	0.233158	1.499766	-1.035385
11	1	0	4.411211	0.206522	-0.694510
12	1	0	3.544563	-1.299802	-0.264871
13	1	0	3.802201	-0.056819	0.965759
14	1	0	-3.722273	-0.806839	0.407365
15	1	0	-1.144197	-0.198120	1.113814
16	1	0	-2.144778	2.246349	-0.460880
17	1	0	-1.691984	2.229890	1.253334
18	1	0	-3.145279	1.365604	0.709204
19	1	0	-3.381032	-1.968304	-0.894346
20	1	0	-2.415917	-2.003966	0.603173

conformation 3

Total Energy (au) = -461.0818521 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 102.1542 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.195688	-1.675499	0.167307
2	1	0	1.776267	-2.538684	-0.479745
3	1	0	2.511772	-1.228720	-1.409344
4	6	0	2.262197	-1.561830	-0.395053
5	6	0	1.318155	-0.565954	0.294038
6	8	0	2.163899	0.633762	0.658192
7	1	0	1.059319	-0.931041	1.290311
8	6	0	2.273744	1.616456	-0.336772
9	1	0	2.783773	2.475916	0.112496
10	1	0	2.870478	1.284780	-1.206637
11	1	0	1.287840	1.930861	-0.704370
12	6	0	0.085876	-0.299567	-0.465740
13	1	0	0.114461	-0.274682	-1.549866
14	8	0	-1.457096	-0.159409	1.365506
15	6	0	-1.143298	-0.133745	0.162581
16	8	0	-2.200035	0.089203	-0.790193
17	6	0	-3.486412	0.222637	-0.227545
18	1	0	-3.539305	1.044909	0.495737
19	1	0	-3.810858	-0.689628	0.289609
20	1	0	-4.165154	0.425354	-1.062588

Table TS1, TS5, TS6, TS7, and TS8. The transition structures for deprotonation reaction with LiH of **1**, **5**, **6**, **7**, and **8**. Cartesian coordinates, number of imaginary frequencies, total energies of calculated species, and zero-point energies.

Table TS1. 1 (Meldrum's acid) with LiH

Total Energy (au) = -542.6485299 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 1
Zero-point energy (kcal / mol) = 88.7174 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.288958	0.771675	-0.049662
2	1	0	1.848540	0.593180	1.067680
3	1	0	2.671384	0.093782	1.930603
4	3	0	3.361978	-1.039057	0.843339
5	1	0	2.114293	1.268232	-0.556917
6	6	0	1.165014	-0.632587	-0.435636
7	6	0	0.071994	1.611403	-0.098805
8	8	0	0.054542	2.811172	-0.101568
9	8	0	2.154028	-1.363524	-0.555386
10	8	0	-0.048478	-1.179028	-0.528390
11	8	0	-1.122297	0.926953	-0.200259
12	6	0	-1.179822	-0.467894	0.073063
13	6	0	-1.161661	-0.724762	1.576660
14	1	0	-1.246101	-1.795011	1.772138
15	1	0	-2.006475	-0.210078	2.037409
16	1	0	-0.241076	-0.357738	2.036028
17	6	0	-2.414507	-1.000789	-0.624150
18	1	0	-2.492238	-2.078518	-0.474388
19	1	0	-3.301109	-0.515175	-0.214584
20	1	0	-2.355360	-0.788364	-1.691993

Table TS5. 5 (dimedone) with LiH

Total Energy (au) = -470.7821098 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 1
Zero-point energy (kcal / mol) = 118.6866 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.280153	1.573617	-0.125352
2	6	0	-0.961793	0.938069	-0.728259

3	6	0	-1.334573	-0.399773	-0.043059
4	6	0	-0.137019	-1.363867	-0.173928
5	6	0	1.212605	-0.785264	0.174318
6	6	0	1.449555	0.664873	0.084834
7	8	0	2.174212	-1.550113	0.369382
8	8	0	0.331592	2.754411	0.158509
9	6	0	-2.557385	-1.013582	-0.743326
10	6	0	-1.666170	-0.161751	1.443449
11	1	0	-1.778865	1.659510	-0.663695
12	1	0	-0.763636	0.754752	-1.793500
13	1	0	-0.041729	-1.690575	-1.220863
14	1	0	-0.278082	-2.276503	0.412591
15	1	0	2.104605	1.035358	0.876445
16	1	0	2.231036	0.670940	-0.835350
17	1	0	-2.823771	-1.975505	-0.294225
18	1	0	-2.364278	-1.179857	-1.807370
19	1	0	-3.425548	-0.353943	-0.658153
20	1	0	-1.952662	-1.098939	1.929764
21	1	0	-2.499215	0.539020	1.546419
22	1	0	-0.818665	0.254262	1.996057
23	3	0	3.748612	-0.981198	-0.485963
24	1	0	3.406309	0.256760	-1.585416

Table TS6. 6 (1,3-cyclohexanedione) with LiH

Total Energy (au) = -392.1325194 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 1
Zero-point energy (kcal / mol) = 84.1598 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.895659	1.703653	-0.166669
2	6	0	-1.658187	0.566688	0.532579
3	6	0	-1.220111	-0.782862	-0.014534
4	6	0	0.258321	-0.994507	-0.144588
5	6	0	1.152569	0.177963	-0.207487
6	6	0	0.615386	1.566499	0.044456
7	8	0	-2.014818	-1.647481	-0.324810
8	8	0	2.378171	0.003692	-0.315453
9	3	0	3.006807	-1.513159	0.603470
10	1	0	0.484985	-1.733901	-0.916308
11	1	0	0.732571	-1.549606	0.807000
12	1	0	-2.737544	0.654150	0.402793
13	1	0	-1.446825	0.587502	1.610556
14	1	0	1.194194	2.269146	-0.560656
15	1	0	0.869832	1.789166	1.091616
16	1	0	-1.124631	1.688309	-1.237939
17	1	0	-1.233106	2.672238	0.210246

18	1	0	1.819361	-2.111815	1.641856

Table TS7. 7 (dimethyl malonate) with LiH

Total Energy (au) = -504.5343657 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 1
Zero-point energy (kcal / mol) = 85.7386 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.974741	-0.770742	-0.641674
2	8	0	-1.664516	-0.594331	-0.057316
3	6	0	-1.251418	0.715517	0.101815
4	6	0	0.073548	0.780621	0.779336
5	6	0	1.158689	-0.019649	0.165167
6	8	0	2.261701	0.676268	-0.113691
7	6	0	3.401985	-0.076163	-0.581145
8	8	0	1.091792	-1.239358	0.014229
9	1	0	-3.009008	-0.309411	-1.628053
10	1	0	-3.732986	-0.321529	-0.001129
11	1	0	-3.123824	-1.846132	-0.717441
12	1	0	0.353338	1.815023	0.953192
13	1	0	-0.121684	0.131469	1.796080
14	1	0	3.687493	-0.826875	0.155897
15	1	0	4.193175	0.658024	-0.710911
16	1	0	3.170277	-0.564105	-1.528278
17	8	0	-1.952729	1.641786	-0.208171
18	3	0	-0.454295	-1.792427	1.032336
19	1	0	-0.392258	-1.011617	2.562228

Table TS8. 8 (acetylacetone) with LiH

Total Energy (au) = -354.0155936 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 1
Zero-point energy (kcal / mol) = 77.8577 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.711908	0.972482	-0.595099
2	6	0	1.350140	-0.376295	-0.003215
3	6	0	0.005039	-0.535169	0.646239
4	6	0	-1.199823	-0.061478	-0.034479
5	8	0	-1.357042	1.149596	-0.306409
6	8	0	2.159428	-1.283767	0.023790

7	6	0	-2.320060	-1.030679	-0.304709
8	1	0	0.068079	0.365058	1.569413
9	1	0	-0.083586	-1.551118	1.027394
10	1	0	1.775712	1.701700	0.227128
11	1	0	0.965703	1.320017	-1.313420
12	1	0	2.688898	0.909413	-1.072042
13	1	0	-3.175668	-0.513417	-0.737353
14	1	0	-1.981084	-1.822918	-0.978972
15	1	0	-2.617232	-1.518295	0.629617
16	1	0	0.068045	1.428134	2.183613
17	3	0	-0.470394	2.313875	0.824381

Table F1, F5, F6, F7, and F8. The optimized structures of entry **1**, entry **5**, entry **6**, entry **7**, and entry **8** with the dihedral angles of the C-H bonds of the reaction centers and the relevant carbonyl groups fixed on the value of the transitional structures for deprotonation reaction.

Table F1. 1 (Meldrum's acid)

Total Energy (au) = -534.5 298904 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 0
Zero-point energy (kcal / mol) = 86.7614 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.649128	0.110735	0.209501
2	1	0	-1.954465	0.256518	1.250229
3	1	0	-2.577115	0.131078	-0.365356
4	6	0	-0.826996	1.326366	-0.176412
5	8	0	-1.249472	2.445594	-0.150613
6	6	0	-1.008570	-1.245535	-0.004931
7	8	0	-1.640415	-2.255357	-0.134246
8	8	0	0.461101	1.075443	-0.538134
9	8	0	0.340696	-1.268598	-0.144855
10	6	0	1.131889	-0.072679	0.018140
11	6	0	1.424603	0.157466	1.496858
12	1	0	1.952797	-0.706349	1.903167
13	1	0	2.046073	1.046296	1.615461
14	1	0	0.507227	0.300016	2.072507
15	6	0	2.377120	-0.278826	-0.819805
16	1	0	3.020669	0.598851	-0.747645
17	1	0	2.096515	-0.432722	-1.862014
18	1	0	2.919516	-1.155509	-0.463673

Table F5. 5 (dimedone)

Total Energy (au) = -462.6621185 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 1
Zero-point energy (kcal / mol) = 116.3818 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.750283	1.415468	-0.225328
2	6	0	-0.614725	1.036992	-0.757980
3	6	0	-1.196949	-0.182110	0.006599
4	6	0	-0.262120	-1.388542	-0.210017
5	6	0	1.229133	-1.143681	-0.013009
6	6	0	1.764993	0.287881	-0.111914

7	8	0	2.000963	-2.067880	0.107794
8	8	0	1.018125	2.533460	0.156643
9	6	0	-2.589817	-0.509953	-0.555466
10	6	0	-1.317296	0.137534	1.509877
11	1	0	-1.269242	1.907197	-0.679765
12	1	0	-0.518996	0.777518	-1.821156
13	1	0	-0.353660	-1.735859	-1.249012
14	1	0	-0.545737	-2.238671	0.416581
15	1	0	2.419269	0.483926	0.742269
16	1	0	2.434566	0.288167	-0.981684
17	1	0	-3.010750	-1.391974	-0.063392
18	1	0	-2.547062	-0.712533	-1.629875
19	1	0	-3.280885	0.322817	-0.396519
20	1	0	-1.769537	-0.702981	2.043742
21	1	0	-1.944523	1.018347	1.672111
22	1	0	-0.347153	0.337872	1.974634

Table F6. 6 (1,3-cyclohexanedione)

Total Energy (au) = -384.0123114 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 1
Zero-point energy (kcal / mol) = 81.6842 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.229155	1.121910	-0.025658
2	6	0	-0.158321	1.686870	-0.345960
3	6	0	-1.255770	0.974361	0.467552
4	6	0	-1.292959	-0.487712	0.074918
5	6	0	0.039569	-1.225310	0.099846
6	6	0	1.326546	-0.399594	-0.011994
7	8	0	-2.301414	-1.040448	-0.304075
8	8	0	2.400189	-0.956684	-0.004158
9	1	0	0.037660	-1.985354	-0.686981
10	1	0	0.132141	-1.792129	1.035098
11	1	0	-2.242781	1.405356	0.296910
12	1	0	-1.026854	1.053595	1.538912
13	1	0	1.999400	1.497752	-0.703386
14	1	0	1.533636	1.437638	0.981676
15	1	0	-0.374675	1.578566	-1.414513
16	1	0	-0.178053	2.758487	-0.134073

Table F7. 7 (dimethyl malonate)

Total Energy (au) = -496.4089168 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 1
Zero-point energy (kcal / mol) = 83.3089 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.989918	-0.877058	-0.532753
2	8	0	-1.763164	-0.657501	0.191337
3	6	0	-1.264239	0.585415	0.145612
4	8	0	-1.790356	1.507943	-0.425840
5	6	0	0.030832	0.704666	0.938228
6	6	0	1.157250	-0.166597	0.400271
7	8	0	1.207525	-1.367271	0.460201
8	8	0	2.111217	0.599050	-0.168551
9	6	0	3.237181	-0.108622	-0.725100
10	1	0	-2.849107	-0.658831	-1.592010
11	1	0	-3.783505	-0.242502	-0.136311
12	1	0	-3.225663	-1.928160	-0.385137
13	1	0	0.326155	1.750731	0.919346
14	1	0	-0.160963	0.399997	1.970016
15	1	0	3.750558	-0.675981	0.052175
16	1	0	3.887917	0.660842	-1.133707
17	1	0	2.906198	-0.790683	-1.509093

Table F8. 8 (acetylacetone)

Total Energy (au) = -345.9009802 (B3LYP/6-311+G** (5D))
Number of Imaginary Frequencies = 1
Zero-point energy (kcal / mol) = 75.8967 (B3LYP/6-311+G** (5D))

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.739994	1.143775	-0.311394
2	6	0	1.293444	-0.255002	0.040893
3	8	0	1.950470	-1.234891	-0.228300
4	6	0	-0.013887	-0.408252	0.841293
5	6	0	-1.240007	0.175952	0.137295
6	6	0	-2.201327	-0.821335	-0.468064
7	8	0	-1.413232	1.372611	0.062653
8	1	0	0.116655	0.116626	1.793485
9	1	0	-0.139324	-1.472414	1.041647
10	1	0	2.029043	1.664793	0.608022
11	1	0	0.928137	1.725727	-0.751303
12	1	0	2.596713	1.096173	-0.982177
13	1	0	-2.990418	-0.302616	-1.010537
14	1	0	-1.666505	-1.503293	-1.137207
15	1	0	-2.641506	-1.437583	0.323100

Figure D1. Correlation between the absolute value of the deviation of the dihedral angle between the C-H bond and the adjacent C=O bond from the perpendicular angle (Δ_{DA}) and Experimental $\Delta G°_i$. Filled; dicarbonyl compounds **1**-**8** (sum of Δ_{DA} was used). Outlined; monocarbonyl compounds **9**-**15**.

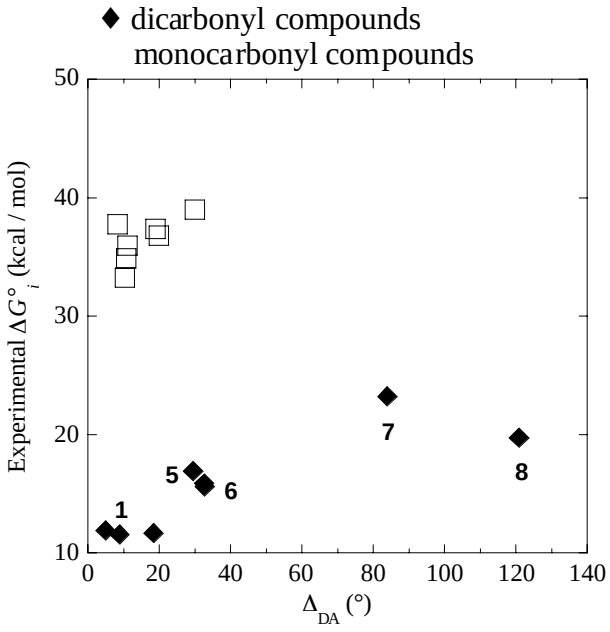


Table O1 and Figure O2. The calculated energetic values of HOMO and occupied RHO of the corresponding anions.[a]

Table O1.

compound	E_{HOMO} (kcal / mol)[b]	λ_{occ} (kcal / mol)[c]	f_{occ} (a. u.)	ρ_{occ}
1	-73.5	-75.3	0.7662	6.375
2	-80.0	-85.0	0.6708	4.953
3	-81.8	-87.0	0.6729	4.856
4	-77.3	-81.3	0.6710	5.177
5	-71.1	-75.1	0.6441	5.383
6	-69.0	-72.8	0.6423	5.536
7	-74.4	-77.3	0.7025	5.704
8	-66.9	-70.3	0.6667	5.949
9	-51.7	-53.6	0.6972	8.164
10	-45.1	-73.4	0.2210	1.889
11	-42.9	-68.9	0.2157	1.965
12	-36.1	-37.5	0.6446	10.80
13	-38.9	-63.1	0.2276	2.261
14-b	-44.4	-73.1	0.2119	1.890
15-b	-52.0	-53.3	0.7090	8.342

[a] All the values were calculated at the RHF/6-31G* (5d)//B3LYP/6-311+G** (5d) level.
[b] The energy levels of HOMOs.
[c] The energy levels of the occupied RHOs. The carbon atoms of the carbonyl groups were used as the reaction centers.

Figure O2. Correlation between the experimental ionization energy and the energy level of occupied RHO of the corresponding anions.