

G2 and DFT rigorous description of the inversion process of oxane and thiane used as
simple ring systems modeling sugar components

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Cartesian Coordinates of conformers 1-7 and 10-16 (Angstroms) at MPW1K/6-
311++G(2d,2p) level of theory.

1			
C	-1.0383	-0.5891	-0.6762
O	-1.0523	-0.5567	0.7245
C	0.2394	-0.5972	1.2659
C	1.0756	0.5790	0.8157
C	1.1206	0.6390	-0.6998
C	-0.2891	0.5874	-1.2592
H	0.1199	-0.6075	2.3436
H	-0.5818	-1.5247	-1.0151
H	-2.0753	-0.5936	-0.9931
H	0.6336	1.4926	1.2082
H	2.0753	0.4974	1.2349
H	1.6379	1.5329	-1.0363
H	1.6883	-0.2116	-1.0768
H	-0.8211	1.5017	-1.0043
H	-0.2780	0.5114	-2.3436
H	0.7279	-1.5330	0.9755

2			
O	0.3552	-1.3762	-0.5840
C	1.3665	-0.5725	-0.0503
C	1.0181	0.9186	-0.0122
C	-0.8209	-1.2147	0.1555
C	-1.4701	0.1087	-0.1681
H	1.5922	-0.9271	0.9585
H	2.2464	-0.7457	-0.6585
H	1.6096	1.4400	-0.7569
H	1.3375	1.3137	0.9470
H	-0.5902	-1.2913	1.2221
H	-1.4769	-2.0404	-0.0975
H	-1.9691	0.0091	-1.1270
H	-2.2464	0.3165	0.5631

C	-0.4640	1.2672	-0.2437
H	-0.7480	2.0404	0.4620
H	-0.5547	1.7244	-1.2221

3

C	-0.8523	-1.0337	-0.8880
O	-1.0814	-1.0850	0.4923
C	0.1039	-0.9223	1.2313
C	1.0469	0.0977	0.6032
C	0.2403	1.1000	-0.1967
C	-0.4943	0.3816	-1.3250
H	-0.2101	-0.5926	2.2164
H	-0.0581	-1.7337	-1.1569
H	-1.7600	-1.3802	-1.3680
H	1.6278	0.5818	1.3821
H	1.7600	-0.3966	-0.0531
H	0.6014	-1.8875	1.3459
H	0.1270	0.3337	-2.2164
H	-1.3910	0.9310	-1.5943
H	-0.4815	1.5774	0.4606
H	0.8747	1.8875	-0.5907

4

C	-1.0690	-0.3716	-0.6156
C	-1.0336	-0.0993	0.8707
C	0.3076	-0.4995	1.4608
C	0.0142	0.4805	-1.2358
C	1.3803	0.0941	-0.6956
O	1.4065	-0.4882	0.5838
H	2.0408	0.9603	-0.6963
H	1.8266	-0.6459	-1.3563
H	0.0336	0.3950	-2.3181
H	-0.2029	1.5221	-1.0073
H	0.5413	0.1304	2.3181
H	0.2434	-1.5221	1.8262
H	-1.8175	-0.6294	1.4033
H	-1.2133	0.9629	1.0239
H	-2.0408	-0.1222	-1.0303
H	-0.8922	-1.4268	-0.8180

5

C	-1.1603	-1.3905	0.2615
C	-1.2419	0.1408	0.3278
C	1.2417	0.1404	0.3278
C	1.1595	-1.3910	0.2615
C	0.0000	0.7515	-0.2929
O	-0.0005	-1.8289	-0.3898
H	1.1943	-1.8233	1.2641

H	1.3229	0.4644	1.3626
H	2.1328	0.4953	-0.1803
H	0.0003	1.8289	-0.1591
H	0.0000	0.5643	-1.3626
H	-1.3229	0.4650	1.3626
H	-2.1328	0.4962	-0.1803
H	1.9873	-1.8056	-0.3013
H	-1.1953	-1.8228	1.2641
H	-1.9882	-1.8047	-0.3013

6

C	-1.2154	-0.1263	-0.5928
O	-1.1114	-0.2182	0.8081
C	0.1968	-0.1344	1.3212
C	-0.1320	0.7365	-1.1920
C	1.2429	0.1244	-0.9277
H	0.1921	-0.6848	2.2561
H	0.4348	0.9051	1.5581
H	-0.1979	1.7270	-0.7488
H	-0.3089	0.8603	-2.2561
H	1.5370	-0.5119	-1.7573
H	1.9885	0.9117	-0.8649
C	1.2235	-0.6901	0.3650
H	2.2001	-0.6972	0.8396
H	0.9720	-1.7270	0.1563
H	-1.1794	-1.1257	-1.0323
H	-2.2001	0.2805	-0.7980

7

C	-1.2508	-0.3490	-0.7673
C	-1.2771	-0.2935	0.7675
C	1.2113	-0.3208	0.6432
O	1.1627	-0.2659	-0.7672
C	0.0094	0.3044	1.3104
C	0.0013	0.2989	-1.3113
H	1.2825	-1.3695	0.9321
H	2.1278	0.1686	0.9661
H	0.0859	0.1504	2.3829
H	0.0205	1.3802	1.1545
H	-1.3985	-1.2959	1.1687
H	-2.1278	0.2811	1.1204
H	-1.2760	-1.3802	-1.1069
H	-2.1200	0.1428	-1.1949
H	0.0771	0.1515	-2.3829
H	-0.0192	1.3768	-1.1389

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C	1.0293	1.3645	0.2875
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S	2.0919	-0.0002	-0.2278
C	1.0285	-1.3642	0.2876
C	-0.3666	-1.2668	-0.2887
C	-1.0871	0.0007	0.1341
C	-0.3660	1.2678	-0.2887
H	1.5303	-2.2654	-0.0470
H	0.9971	1.3929	1.3739
H	1.5315	2.2654	-0.0471
H	-0.3051	-1.3084	-1.3739
H	-0.9410	-2.1345	0.0311
H	-2.0919	0.0010	-0.2796
H	-1.2028	0.0007	1.2183
H	-0.3045	1.3094	-1.3739
H	-0.9398	2.1358	0.0311
H	0.9963	-1.3926	1.3739

11

S	-2.0238	-0.0001	-0.4671
C	-1.0894	-1.3063	0.3443
C	0.3690	-1.3416	-0.0737
C	-1.0899	1.3065	0.3444
C	0.3683	1.3427	-0.0742
C	1.0731	0.0006	-0.3621
H	-1.1960	-1.1483	1.4141
H	-1.5731	-2.2474	0.1105
H	-1.1960	1.1481	1.4142
H	-1.5742	2.2474	0.1110
H	0.4384	1.9488	-0.9716
H	0.9166	1.8841	0.6932
H	0.4400	-1.9483	-0.9706
H	0.9174	-1.8822	0.6943
H	2.0238	0.0010	0.1604
H	1.3316	0.0005	-1.4142

12

C	-1.2805	-0.6862	-0.6353
S	-1.2770	-0.6495	1.1674
C	0.5225	-0.6896	1.4430
C	1.3200	-0.2447	0.2289
C	0.6756	0.9304	-0.4810
C	-0.5865	0.5220	-1.2413
H	0.7028	-0.0161	2.2743
H	-0.8256	-1.6140	-0.9657
H	-2.3235	-0.7286	-0.9270
H	2.3235	0.0131	0.5576
H	1.4351	-1.0752	-0.4640
H	0.8141	-1.6865	1.7545
H	-0.3370	0.2852	-2.2743

H	-1.2774	1.3589	-1.2714
H	0.4274	1.6865	0.2596
H	1.3820	1.3900	-1.1656

13

C	-1.1410	0.3627	-0.5531
C	-1.1121	0.0682	0.9316
C	0.1866	0.4290	1.6522
C	-0.0391	-0.4000	-1.2577
C	1.3263	0.2126	-1.0396
S	1.6474	0.8367	0.6401
H	1.4448	1.0730	-1.6897
H	0.4692	-0.3674	2.3291
H	0.0462	1.3211	2.2510
H	-0.2190	-0.4389	-2.3291
H	-0.0453	-1.4298	-0.9051
H	2.1090	-0.4962	-1.2828
H	-1.2930	-0.9969	1.0546
H	-1.9339	0.5746	1.4296
H	-1.0356	1.4298	-0.7401
H	-2.1090	0.0673	-0.9480

14

C	0.4501	-1.2672	0.2083
C	-1.0650	-1.3435	0.4491
C	-1.0650	1.3435	0.4491
C	0.4500	1.2672	0.2083
C	0.9046	0.0000	-0.4923
S	-1.9891	-0.0000	-0.3229
H	0.9588	-1.3466	1.1665
H	0.7679	-2.1250	-0.3768
H	1.9891	0.0001	-0.5623
H	0.5267	0.0000	-1.5100
H	0.9587	1.3467	1.1665
H	0.7678	2.1251	-0.3768
H	-1.2929	1.3316	1.5100
H	-1.4852	2.2574	0.0464
H	-1.4851	-2.2574	0.0464
H	-1.2928	-1.3316	1.5100

15

C	0.4355	-1.0936	-0.5010
C	1.2276	0.1770	-0.2096
C	-1.0120	1.3375	-0.3014
S	-2.0096	-0.0737	0.2549
C	0.3663	1.3195	0.3191
C	-0.6953	-1.3059	0.4794
H	-0.9520	1.3360	-1.3854

H	-1.5666	2.2197	-0.0037
H	0.8637	2.2679	0.1312
H	0.2552	1.2397	1.3973
H	1.7345	0.4897	-1.1190
H	2.0096	-0.0359	0.5149
H	0.0167	-1.0549	-1.5033
H	1.1028	-1.9518	-0.4802
H	-1.1712	-2.2679	0.3296
H	-0.3355	-1.2719	1.5033

16

C	0.3575	-1.3149	-0.3575
C	1.0757	0.0428	-0.4277
C	-1.0110	1.4456	-0.2107
S	-2.0883	-0.0255	-0.2370
C	0.3688	1.1503	0.3322
C	-0.9467	-1.2668	0.4073
H	-0.9380	1.8116	-1.2297
H	-1.5039	2.2061	0.3837
H	0.9590	2.0618	0.2722
H	0.3036	0.9034	1.3890
H	1.1720	0.3504	-1.4659
H	2.0883	-0.0547	-0.0486
H	0.1532	-1.6766	-1.3600
H	1.0022	-2.0540	0.1134
H	-1.4809	-2.2062	0.3171
H	-0.7842	-1.0955	1.4659

Supplementary Table 1.

Geometric data of oxane conformers at MP2/6-31G(d,p), [B3LYP/6-31G(d,p)] and {B3LYP/6-311++G(2d,2p)}.

	1	2	3	4	5	6	7
O1-C2	1.426 [1.423] {1.424}	1.422 [1.418] {1.420}	1.425 [1.422] {1.423}	1.430 [1.427] {1.430}	1.425 [1.422] {1.423}	1.432 [1.429] {1.430}	1.425 [1.423] {1.424}
C2-C3	1.522 [1.531] {1.526}	1.545 [1.552] {1.546}	1.535 [1.544] {1.539}	1.529 [1.538] {1.534}	1.546 [1.555] {1.550}	1.520 [1.528] {1.523}	1.522 [1.530] {1.526}
C3-C4	1.528 [1.537] {1.533}	1.552 [1.560] {1.557}	1.535 [1.545] {1.542}	1.522 [1.530] {1.526}	1.527 [1.536] {1.537}	1.538 [1.548] {1.544}	1.546 [1.555] {1.553}
C4-C5	1.528 [1.537] {1.533}	1.546 [1.556] {1.553}	1.525 [1.534] {1.530}	1.522 [1.530] {1.526}	1.527 [1.536] {1.532}	1.538 [1.547] {1.544}	1.530 [1.538] {1.535}
C5-C6	1.522 [1.531] {1.526}	1.516 [1.528] {1.525}	1.536 [1.545] {1.540}	1.529 [1.538] {1.534}	1.546 [1.555] {1.550}	1.520 [1.528] {1.523}	1.521 [1.529] {1.524}
C6-O1	1.426 [1.423] {1.424}	1.424 [1.420] {1.421}	1.430 [1.427] {1.530}	1.430 [1.426] {1.430}	1.425 [1.422] {1.423}	1.432 [1.429] {1.430}	1.437 [1.433] {1.437}
C2-H1	1.100 [1.105] {1.100}	1.098 [1.103] {1.098}	1.097 [1.103] {1.097}	1.095 [1.100] {1.094}	1.098 [1.103] {1.097}	1.098 [1.093] {1.097}	1.100 [1.103] {1.097}
C2-H2	1.089 [1.094] {1.089}	1.089 [1.094] {1.088}	1.089 [1.094] {1.088}	1.093 [1.098] {1.092}	1.089 [1.093] {1.088}	1.090 [1.095] {1.090}	1.089 [1.092] {1.089}
C3-H3	1.092 [1.097] {1.093}	1.090 [1.094] {1.090}	1.091 [1.095] {1.091}	1.091 [1.096] {1.091}	1.091 [1.095] {1.091}	1.092 [1.097] {1.092}	1.090 [1.095] {1.091}
C3-H4	1.093 [1.097] {1.093}	1.091 [1.095] {1.091}	1.093 [1.097] {1.093}	1.093 [1.098] {1.093}	1.092 [1.097] {1.092}	1.091 [1.096] {1.091}	1.092 [1.096] {1.092}
C4-H5	1.095 [1.099] {1.095}	1.090 [1.094] {1.089}	1.090 [1.905] {1.090}	1.091 [1.095] {1.091}	1.091 [1.095] {1.091}	1.091 [1.09]6 {1.091}	1.091 [1.095] {1.090}
C4-H6	1.091 [1.096] {1.091}	1.089 [1.094] {1.088}	1.091 [1.096] {1.091}	1.093 [1.098] {1.094}	1.090 [1.095] {1.091}	1.091 [1.096] {1.091}	1.092 [1.096] {1.091}
C5-H7	1.092 [1.097] {1.093}	1.090 [1.095] {1.090}	1.091 [1.095] {1.091}	1.091 [1.096] {1.091}	1.091 [1.095] {1.091}	1.091 [1.096] {1.091}	1.092 [1.096] {1.091}
C5-H8	1.093 [1.097] {1.093}	1.092 [1.096] {1.092}	1.093 [1.097] {1.093}	1.093 [1.098] {1.093}	1.092 [1.097] {1.092}	1.092 [1.097] {1.092}	1.091 [1.097] {1.092}

C6-H9	1.100 [1.105] {1.100}	1.099 [1.104] {1.099}	1.097 [1.103] {1.097}	1.095 [1.100] {1.094}	1.098 [1.103] {1.097}	1.090 [1.095] {1.090}	1.093 [1.099] {1.093}
C6-H10	1.089 [1.094] {1.089}	1.090 [1.095] {1.089}	1.090 [1.095] {1.090}	1.093 [1.099] {1.092}	1.089 [1.093] {1.088}	1.098 [1.103] {1.097}	1.095 [1.101] {1.095}
O1-C2-C3	111.4 [111.8] {111.9}	114.0 [114.1] {113.8}	110.1 [110.9] {111.0}	116.6 [116.7] {116.5}	111.8 [112.2] {112.2}	112.0 [112.7] {112.5}	111.3 [112.1] {112.1}
C2-C3-C4	109.9 [110.2] {110.4}	116.3 [115.8] {115.8}	109.3 [110.0] {110.2}	110.5 [111.0] {111.1}	109.6 [110.0] {110.3}	110.0 [110.6] {110.7}	110.9 [111.2] {111.3}
C3-C4-C5	109.9 [110.0] {110.1}	116.7 [116.9] {117.1}	109.2 [110.0] {110.1}	106.3 [107.0] {107.5}	109.6 [110.1] {110.3}	110.3 [110.8] {110.8}	110.9 [111.2] {111.2}
C4-C5-C6	109.9 [110.2] {110.4}	112.2 [113.0] {113.4}	108.8 [109.5] {109.8}	110.5 [111.0] {111.1}	109.6 [110.0] {110.3}	110.0 [110.6] {110.7}	110.5 [111.0] {111.0}
C5-C6-O1	111.4 [111.8] {111.9}	109.0 [110.3] {110.8}	112.1 [112.7] {112.7}	1116.6 [116.7] {116.5}	111.8 [112.2] {112.2}	112.0 [112.7] {112.5}	113.5 [113.8] {113.6}
C6-O1-C2	110.8 [112.1] {112.2}	108.7 [110.0] {109.9}	110.3 [112.0] {112.3}	123.1 [123.6] {123.4}	110.3 [111.9] {112.0}	114.2 [115.4] {115.5}	114.5 [115.5] {115.6}
O1-C2-C3-C4	57.2 [55.7] {55.4}	10.9 [12.9] {14.9}	30.5 [29.3] {30.8}	27.1 [25.6] {25.5}	2.6 [2.1] {2.3}	64.3 [61.7] {61.7}	56.8 [55.6] {54.7}
C2-C3-C4-C5	52.4 [51.3] {51.4}	13.0 [13.5] {13.3}	34.3 [33.0] {31.2}	63.1 [60.9] {61.0}	53.5 [52.0] {51.3}	29.3 [28.1] {28.3}	4.4 [5.7] {4.3}
C3-C4-C5-C6	52.4 [51.5] {51.4}	6.1 [1.8] {0.2}	63.5 [61.0] {60.8}	63.1 [61.1] {61.0}	53.4 [52.0] {51.3}	29.3 [28.3] {28.3}	47.6 [45.4] {46.6}
C4-C5-C6-O1	57.2 [55.7] {55.4}	50.0 [44.2] {41.5}	25.3 [24.6] {26.5}	27.1 [26.0] {25.5}	2.6 [2.1] {2.3}	64.3 [61.8] {61.7}	53.5 [53.1] {52.8}
C5-C6-O1-C2	61.8 [60.3] {59.7}	77.6 [74.7] {73.7}	41.0 [39.8] {37.5}	11.0 [11.7] {12.3}	61.4 59.8 59.4	31.4 [30.3] {30.3}	1.4 [3.4] {2.4}
C6-O1-C2-C3	61.8 [60.2] {59.7}	55.8 [57.2] {58.8}	72.6 [70.0] {69.4}	11.0 [11.9] {12.2}	61.4 [59.8] {59.4}	31.4 [30.4] {30.3}	54.3 [51.5] {52.0}

Supplementary Table 2.

Geometric data of thiane (X = O) conformers at MP2/6-31G(d,p), [B3LYP/6-31G(d,p)] and {B3LYP/6-311++G(2d,2p)}.

	10	11	12	13	14	15	16
S1-C2	1.814 [1.838] {1.834}	1.810 [1.832] {1.828}	1.813 [1.836] {1.833}	1.836 [1.857] {1.855}	1.815 [1.838] {1.834}	1.825 [1.850] {1.846}	1.815 [1.829] {1.835}
C2-C3	1.524 [1.531] {1.527}	1.529 [1.536] {1.532}	1.532 [1.538] {1.534}	1.541 [1.549] {1.544}	1.547 [1.555] {1.555}	1.523 [1.530] {1.525}	1.524 [1.553] {1.527}
C3-C4	1.528 [1.537] {1.534}	1.554 [1.563] {1.560}	1.537 [1.549] {1.546}	1.524 [1.533] {1.530}	1.528 [1.528] {1.553}	1.535 [1.545] {1.542}	1.547 [1.560] {1.554}
C4-C5	1.528 [1.537] {1.534}	1.554 [1.563] {1.560}	1.527 [1.535] {1.532}	1.524 [1.533] {1.529}	1.528 [1.537] {1.533}	1.535 [1.545] {1.542}	1.528 [1.540] {1.533}
C5-C6	1.524 [1.531] {1.527}	1.528 [1.536] {1.532}	1.535 [1.538] {1.533}	1.522 [1.530] {1.527}	1.547 [1.555] {1.551}	1.523 [1.530] {1.525}	1.524 [1.531] {1.526}
C6-S1	1.814 [1.838] {1.834}	1.810 [1.832] {1.828}	1.830 [1.856] {1.854}	1.829 [1.854] {1.852}	1.815 [1.838] {1.834}	1.825 [1.849] {1.846}	1.833 [1.859] {1.855}
C2-H1	1.093 [1.097] {1.092}	1.092 [1.096] {1.091}	1.090 [1.094] {1.089}	1.088 [1.092] {1.087}	1.091 [1.095] {1.090}	1.091 [1.095] {1.092}	1.090 [1.091] {1.089}
C2-H2	1.090 [1.094] {1.089}	1.090 [1.093] {1.088}	1.090 [1.093] {1.088}	1.089 [1.093] {1.088}	1.089 [1.093] {1.088}	1.089 [1.093] {1.088}	1.090 [1.093] {1.089}
C3-H3	1.092 [1.097] {1.092}	1.090 [1.095] {1.090}	1.091 [1.095] {1.090}	1.091 [1.096] {1.091}	1.091 [1.096] {1.091}	1.092 [1.096] {1.091}	1.090 [1.092] {1.090}
C3-H4	1.093 [1.098] {1.094}	1.092 [1.097] {1.093}	1.093 [1.098] {1.094}	1.092 [1.097] {1.092}	1.093 [1.097] {1.093}	1.092 [1.097] {1.092}	1.093 [1.098] {1.093}
C4-H5	1.095 [1.100] {1.095}	1.090 [1.094] {1.090}	1.091 [1.095] {1.091}	1.091 [1.096] {1.091}	1.092 [1.096] {1.092}	1.092 [1.097] {1.092}	1.091 [1.096] {1.091}
C4-H6	1.092 [1.096] {1.092}	1.089 [1.093] {1.088}	1.092 [1.096] {1.092}	1.093 [1.098] {1.093}	1.090 [1.095] {1.090}	1.092 [1.097] {1.092}	1.092 [1.097] {1.092}
C5-H7	1.092 [1.097] {1.092}	1.090 [1.095] {1.090}	1.092 [1.097] {1.092}	1.092 [1.097] {1.092}	1.091 [1.096] {1.091}	1.092 [1.097] {1.093}	1.092 [1.097] {1.093}
C5-H8	1.093	1.092	1.092	1.093	1.093	1.092	1.092

	[1.098] {1.094}	[1.097] {1.093}	[1.097] {1.092}	[1.098] {1.093}	[1.097] {1.093}	[1.096] {1.091}	[1.096] {1.092}
C6-H9	1.093 [1.097] {1.092}	1.092 [1.096] {1.091}	1.091 [1.094] {1.089}	1.089 [1.093] {1.088}	1.091 [1.095] {1.090}	1.089 [1.093] {1.088}	1.089 [1.093] {1.088}
C6-H10	1.090 [1.094] {1.089}	1.090 [1.093] {1.088}	1.091 [1.094] {1.089}	1.090 [1.094] {1.089}	1.089 [1.093] {1.088}	1.091 [1.095] {1.090}	1.091 [1.095] {1.090}
S1-C2-C3	112.7 [112.9] {112.9}	112.9 [113.3] {113.3}	112.3 [112.9] {112.8}	119.0 [118.5] {118.2}	113.8 [114.0] {113.8}	111.5 [112.0] {111.9}	112.7 [111.9] {113.0}
C2-C3-C4	112.4 [112.9] {113.0}	117.8 [118.2] {118.2}	112.5 [113.5] {113.6}	115.3 [116.0] {116.0}	113.6 [114.4] {114.6}	111.9 [113.0] {112.9}	113.4 [111.2] {113.8}
C3-C4-C5	112.9 [113.3] {113.4}	120.6 [120.9] {120.9}	111.4 [112.6] {112.7}	109.8 [110.8] {110.7}	113.4 [113.5] {113.5}	112.9 [113.9] {113.9}	113.5 [114.1] {114.1}
C4-C5-C6	112.4 [112.9] {113.0}	117.8 [118.2] {118.2}	111.8 [112.6] {112.6}	111.9 [112.8] {113.0}	113.6 [114.4] {114.6}	111.9 [113.0] {112.9}	112.3 [114.1] {113.1}
C5-C6-S1	112.6 [112.9] {112.9}	56.1 [113.3] {113.3}	113.5 [113.5] {113.3}	115.4 [115.1] {115.6}	113.8 [114.0] {113.9}	111.5 [112.0] {111.9}	113.4 [112.4] {113.0}
C6-S1-C2	97.1 [98.0] {98.1}	92.1 [92.9] {93.1}	97.2 [98.7] {98.9}	106.5 [106.5] {106.6}	94.4 [96.2] {96.4}	98.9 [99.6] {99.7}	99.4 [99.2] {99.9}
S1-C2-C3-C4	61.6 [60.2] {59.9}	36.5 [35.2] {34.9}	38.6 [40.3] {40.6}	11.0 [9.8] {10.}5	8.8 [6.5] {6.5}	70.5 [67.9] {67.9}	56.2 [68.8] {54.1}
C2-C3-C4-C5	59.3 [59.3] {59.3}	6.3 [7.1] {7.4}	31.0 [26.0] {25.4}	58.1 [57.1] {58.0}	53.6 [54.1] {54.0}	35.5 [34.7] {34.7}	2.4 [3.9] {3.5}
C3-C4-C5-C6	59.3 [59.3] {59.3}	6.3 [7.1] {7.4}	73.1 [71.5] {71.4}	77.8 [75.7] {75.4}	40.3 [54.1] {54.0}	35.5 [34.7] {34.8}	62.0 [54.2] {62.2}
C4-C5-C6-S1	61.6 [60.1] {59.9}	36.6 [35.1] {34.9}	35.8 [40.5] {41.1}	44.3 [41.4] {40.0}	8.8 [6.5] {6.4}	70.5 [67.9] {67.9}	56.8 [53.3] {55.4}
C5-C6-S1-C2	55.5 [53.4] {53.1}	66.9 [65.2] {64.9}	25.2 [18.7] {18.1}	0.5 [2.1] {3.4}	57.7 [54.4] {54.2}	32.3 [31.2] {31.2}	1.2 [3.0] {0.5}
C6-S1-C2-C3	55.5 [53.4] {53.1}	66.9 [65.2] {64.9}	64.4 [60.2] {60.0}	16.2 [17.8] {18.2}	65.2 [54.4] {54.2}	32.3 [31.2] {31.2}	53.7 [61.0] {52.7}

Supplementary Table 3.

Energies and ZPE at MPW1K/6-311++G(2d,2p) and b3lyp/6-311++G(2d,2p) levels of theory. The relative energies with and without the ZPE-correction are included. Basically, the relative barriers are not affected (see following Supp. Table 4)

	MPW1K/6-311++G(2d,2p)			B3LYP/6-311++G(2d,2p)		
	Uncorrected energies	ZPE value	Corrected energies	Uncorrected energies	ZPE value	Corrected energies
E ₁	-271.78512	0.15047	-271.63465	-271.86381	0.14616	-271.71765
E ₂	-271.76818	0.15038	-271.61780	-271.84784	0.14597	-271.70187
E ₃	-271.77585	0.15034	-271.62551	-271.85456	0.14594	-271.70862
E ₄	-271.76834	0.14984	-271.61850	-271.84776	0.14542	-271.70234
E ₅	-271.77460	0.15024	-271.62436	-271.85363	0.14586	-271.70777
E ₆	-271.77457	0.15013	-271.62444	-271.85334	0.14580	-271.70754
E ₇	-271.77380	0.15001	-271.62379	-271.85273	0.14562	-271.70711
E ₁₀	-594.80319	0.14671	-594.65648	-593.84851	0.14265	-594.70586
E ₁₁	-594.78406	0.14624	-594.63744	-594.83040	0.14249	-594.68791
E ₁₂	-594.79415	0.14662	-594.64753	-594.83951	0.14250	-594.69701
E ₁₃	-594.78784	0.14654	-594.64130	-594.83417	0.14238	-594.69179
E ₁₄	-594.79130	0.14635	-594.64495	-594.83686	0.14223	-594.69463
E ₁₅	-594.79510	0.14668	-594.64842	-594.84045	0.14256	-594.69789
E ₁₆	-594.79351	0.14662	-594.64689	-594.83913	0.14249	-594.69664

Supplementary Table 4.

Energy barrier values at G2 enthalpy, MPW1K/6-311++G(2d,2p) and b3lyp/6-311++G(2d,2p) levels of theory. The relative energies with and without the ZPE-correction are included. These values are given in kcal/mol.

Generally, the magnitudes of the barriers are higher for the G2 and MPW1K/6-311++G(2d,2p) than for the b3lyp/6-311++G(2d,2p) one. In addition, in all cases, the barrier from the minima (1, 10) to the intermediaries (3, 12) is higher than that from the intermediaries to the transition states (2, 4, 11, 13).

	G2 enthalpy	MPW1K/ 6-311++G(2d,2p)		b3lyp/6-311++G(2d,2p)	
	Corrected barriers	Uncorrected barriers	Corrected barriers	Uncorrected barriers	Corrected barriers
$\Delta E^\ddagger_{1\rightarrow 2}$	10.5	10.6	10.6	10.0	9.9
$\Delta E^\ddagger_{3\rightarrow 2}$	4.8	4.8	4.8	4.2	4.2
$\Delta E^0_{1\rightarrow 3}$	5.7	5.8	5.7	5.8	5.7
$\Delta E^\ddagger_{3\rightarrow 4}$	4.5	4.7	4.4	4.3	3.9
$\Delta E^\ddagger_{1\rightarrow 4}$	10.2	10.5	10.1	10.1	9.6
$\Delta E^\ddagger_{3\rightarrow 5}$	0.2	0.8	0.7	0.6	0.5
ΔE^0	0.0	0.0	0.0	0.0	0.0
$\Delta E^\ddagger_{3\rightarrow 7}$	0.8	1.3	1.1	1.1	0.9
$\Delta E^\ddagger_{6\rightarrow 7}$	0.1	0.5	0.4	0.4	0.3
$\Delta E^0_{3\rightarrow 6}$	0.8	0.8	0.7	0.8	0.7
$\Delta E^\ddagger_{10\rightarrow 11}$	11.6	12.0	11.9	11.4	11.3
$\Delta E^\ddagger_{12\rightarrow 11}$	5.9	6.3	6.3	5.7	5.7
$\Delta E^0_{10\rightarrow 12}$	5.7	5.7	5.6	5.6	5.6
$\Delta E^\ddagger_{12\rightarrow 13}$	3.8	4.0	3.9	3.4	3.3
$\Delta E^\ddagger_{10\rightarrow 13}$	9.4	9.6	9.5	9.0	8.8
$\Delta E^\ddagger_{12\rightarrow 14}$	1.0	1.8	1.6	1.7	1.5
ΔE^0	0.0	0.0	0.0	0.0	0.0
$\Delta E^\ddagger_{12\rightarrow 16}$	0.2	0.4	0.4	0.2	0.2
$\Delta E^\ddagger_{15\rightarrow 16}$	0.4	1.0	1.0	0.8	0.8
$\Delta E^0_{12\rightarrow 15}$	0.6	0.6	0.6	0.6	0.6