The Anisotropy Effect of Three-Membered Rings in ^{1}H NMR Spectra−Quantification by TSNMRS and Assignment of the Stereochemistry

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Supporting Information

Table S1. X-Y-Z coordinates of compounds **1-36**. All energies are calculated at MP2/aug-cc-pVTZ theory level and given in atomic units.....S2-S25

Figure S1a-e. Structure and TSNMRS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red -0.1 ppm deshielding) of the substituted cyclopropanes **3**, **5-7**, **9-13**, and of the methyl-substituted oxirane, aziridine and thiirane **21-23**.....S26-S28

Table S2a-l. Computed and experimental δ(^{1}H)/ppm value of compound **24** to **36**.....S29-S33

Figure S2a-i. Structure and TSNMRS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red -0.1 ppm deshielding) of compounds **24**−**36**.....S34-S39

Figure S3. Preferred conformers of the studied *bis*- and *tris*-cyclic structures **24-36*syn/anti*** and the ring current effect of the three-membered ring (as TSNMRS Δδ(^{1}H)/ppm) on relevant protons in these *bis*- and *tris*-membered structures.....S40-43

Table S1. X-Y-Z coordinates of compounds **1-36**. All energies are calculated at MP2/aug-cc-pVTZ theory level and given in atomic units.

1 cyclopropane
MP2=-117.6254763

atomic number	atom	X	Y	Z
1	C	0.752339	-0.434360	0.000000
2	C	0.000000	0.868720	0.000000
3	C	-0.752357	-0.434376	0.000000
4	H	1.253763	-0.723788	0.910422
5	H	1.253763	-0.723788	-0.910422
6	H	0.000045	1.447679	-0.910421
7	H	0.000045	1.447679	0.910421
8	H	-1.253755	-0.723844	-0.910426
9	H	-1.253755	-0.723844	0.910426

2 methylcyclopropane
MP2=-156.8534782

atomic number	atom	X	Y	Z
1	C	0.945398	0.755065	-0.143639
2	C	0.945399	-0.755065	-0.143640
3	C	-0.178260	-0.000001	0.510464
4	H	0.723854	1.252360	-1.077107
5	H	1.663817	1.258324	0.485457
6	H	1.663817	-1.258323	0.485456
7	H	0.723856	-1.252360	-1.077109
8	H	-0.173516	-0.000003	1.592534
9	C	-1.536742	0.000000	-0.136097
10	H	-1.435241	-0.000009	-1.222537
11	H	-2.110677	0.883578	0.145380
12	H	-2.110685	-0.883568	0.145394

3 fluorocyclopropane
MP2=-216.7588507

atomic number	atom	X	Y	Z
1	C	0.873925	0.760984	-0.131578
2	C	0.873925	-0.760984	-0.131577
3	C	-0.246684	0.000000	0.481140
4	H	0.660122	1.238238	-1.075262
5	H	1.556920	1.283274	0.520008
6	H	1.556921	-1.283273	0.520008
7	H	0.660123	-1.238237	-1.075262
8	H	-0.393484	0.000000	1.550455
9	F	-1.443285	0.000000	-0.194469

4 chlorocyclopropane
MP2=-576.7464483

atomic number	atom	X	Y	Z
1	C	-0.598985	-1.175567	0.756760
2	C	-0.598985	-1.175567	-0.756760
3	C	-0.598985	0.113261	0.000000
4	H	0.323563	-1.448504	1.245091
5	H	-1.505726	-1.450436	1.273948
6	H	-1.505726	-1.450436	-1.273948
7	H	0.323563	-1.448504	-1.245091
8	H	-1.488669	0.722156	0.000000
9	Cl	0.860866	1.088410	0.000000

5 bromocyclopropane
MP2=-2689.7325912

atomic number	atom	X	Y	Z
1	C	-0.935012	-1.565393	0.756598
2	C	-0.935012	-1.565393	-0.756598
3	C	-0.935012	-0.276330	0.000000
4	H	-0.014432	-1.842698	1.246454
5	H	-1.843603	-1.838700	1.271942
6	H	-1.843603	-1.838700	-1.271942
7	H	-0.014432	-1.842698	-1.246454
8	H	-1.825503	0.331232	0.000000
9	Br	0.639194	0.784979	0.000000

6 iodocyclopropane
MP2=-7034.0744087

atomic number	atom	X	Y	Z
1	C	0.069823	-2.240278	0.755495
2	C	0.069823	-2.240278	-0.755495
3	C	-0.647261	-1.164938	0.000000
4	H	0.990931	-1.971178	1.248402
5	H	-0.537655	-2.973918	1.263987
6	H	-0.537655	-2.973918	-1.263987
7	H	0.990931	-1.971178	-1.248402
8	H	-1.724237	-1.196082	0.000000
9	I	0.093383	0.778379	0.000000

7 cyclopropanemethanol
MP2=-231.9777365

atomic number	atom	X	Y	Z
1	C	-0.312834	-0.151285	0.503023
2	C	-1.642597	-0.533090	-0.084147
3	C	-1.170380	0.895772	-0.163189
4	C	0.937149	-0.584331	-0.199780
5	H	-0.249116	-0.108575	1.581933
6	H	-2.448331	-0.761869	0.596068
7	H	-1.633743	-1.110680	-0.997127
8	H	-1.662475	1.626673	0.459862
9	H	-0.849611	1.255422	-1.131386
10	O	2.029730	0.301639	0.032347
11	H	0.731209	-0.673714	-1.273239
12	H	1.271235	-1.557037	0.159244
13	H	1.708865	1.193573	-0.142429

8 cyclopropanol
MP2=-192.7495343

atomic number	atom	X	Y	Z
1	C	0.232302	-0.012972	0.485625
2	C	-0.905703	-0.742723	-0.137717
3	C	-0.882156	0.773855	-0.139057
4	O	1.454974	-0.111968	-0.196510
5	H	0.305766	-0.019308	1.566206
6	H	-1.608482	-1.246986	0.506849
7	H	-0.688792	-1.228133	-1.076705
8	H	-1.566443	1.300895	0.508325
9	H	-0.660040	1.249136	-1.082443
10	H	1.911546	0.731182	-0.103261

9 cyanocyclopropane
MP2=-209.715821

atomic number	atom	X	Y	Z
1	C	0.225149	-0.000109	0.592397
2	C	1.250591	0.748341	-0.233150
3	C	1.250698	-0.748210	-0.233323
4	C	-1.137318	-0.000143	0.144771
5	H	0.355268	-0.000228	1.663839
6	H	2.024868	1.261358	0.315539
7	H	0.884751	1.251707	-1.114422
8	H	2.025028	-1.261258	0.315259
9	H	0.884936	-1.251418	-1.114719
10	N	-2.244224	0.000081	-0.241381

10 aminocyclopropane
MP2=-172.8895141

atomic number	atom	X	Y	Z
1	C	0.210658	-0.000013	0.489234
2	C	-0.924017	-0.754906	-0.138925
3	C	-0.923995	0.754947	-0.138878
4	N	1.453166	0.000000	-0.237842
5	H	0.239174	-0.000048	1.574089
6	H	-1.619430	-1.263746	0.510713
7	H	-0.705496	-1.241533	-1.076992
8	H	-1.619397	1.263767	0.510789
9	H	-0.705463	1.241627	-1.076915
10	H	2.006333	-0.816654	-0.007346
11	H	2.006276	0.816707	-0.007400

11 acetylcyclopropane
MP2=-270.0142209

atomic number	atom	X	Y	Z
1	C	-0.468344	-0.638498	0.000031
2	C	-1.647570	-0.037112	-0.743486
3	C	-1.647513	-0.037071	0.743609
4	C	0.786276	0.153543	-0.000034
5	O	0.769194	1.376864	-0.000083
6	C	2.071662	-0.631118	-0.000042
7	H	-0.374326	-1.714413	0.000058
8	H	-2.297881	-0.726079	-1.260063
9	H	-1.442222	0.902687	-1.234117
10	H	-2.297784	-0.726011	1.260273
11	H	-1.442128	0.902754	1.234174
12	H	2.922625	0.043362	-0.000102
13	H	2.105521	-1.277879	-0.878024
14	H	2.105580	-1.277793	0.878003

12 methyl cyclopropanecarboxylate
MP2=-345.1530837

atomic number	atom	X	Y	Z
1	C	0.956595	-0.636636	0.000061
2	C	2.103830	0.014043	0.745138
3	C	2.103864	0.013940	-0.745053
4	C	-0.321353	0.099852	-0.000020
5	O	-0.432795	1.309935	-0.000102
6	O	-1.373441	-0.745984	0.000025
7	C	-2.650426	-0.087123	-0.000043
8	H	0.889987	-1.712546	0.000135
9	H	2.780500	-0.649313	1.260935
10	H	1.868577	0.945361	1.237360
11	H	2.780560	-0.649488	-1.260725
12	H	1.868633	0.945188	-1.237415
13	H	-2.753954	0.534355	-0.886163
14	H	-2.753982	0.534483	0.885985
15	H	-3.385496	-0.884100	0.000004

13 phenylcyclopropane
MP2=-348.1957853

atomic number	atom	X	Y	Z
1	C	1.577625	0.638972	-0.000082
2	C	2.572248	-0.219099	-0.749661
3	C	2.572230	-0.218899	0.749750
4	C	0.140565	0.287709	-0.000042
5	H	1.781525	1.701664	-0.000222
6	H	3.381514	0.282510	-1.258888
7	H	2.171499	-1.085191	-1.256304
8	H	3.381486	0.282841	1.258865
9	H	2.171462	-1.084856	1.256608
10	C	-0.821692	1.303283	-0.000137
11	C	-2.182937	1.005636	-0.000100
12	C	-2.607822	-0.321398	0.000034
13	C	-1.659720	-1.343856	0.000129
14	C	-0.300240	-1.041516	0.000092
15	H	-0.496840	2.337454	-0.000242
16	H	-2.909152	1.808439	-0.000176
17	H	-3.663897	-0.556872	0.000063
18	H	-1.978263	-2.378531	0.000233
19	H	0.419121	-1.852457	0.000169

14 cyclopropanecarboxaldehyde
MP2=-230.7773741

atomic number	atom	X	Y	Z
1	C	-1.167015	-0.287192	-0.742276
2	C	-1.167081	-0.286986	0.742329
3	C	-0.310897	0.726908	-0.000073
4	C	1.142898	0.485006	0.000024
5	O	1.643617	-0.627743	0.000032
6	H	-2.030917	0.099197	-1.260284
7	H	-0.612558	-1.071703	-1.235438
8	H	-0.612668	-1.071358	1.235760
9	H	-2.031030	0.099550	1.260150
10	H	-0.633597	1.756939	-0.000233
11	H	1.784403	1.382901	-0.000229

15 vinylcyclopropane
MP2=-194.8527833

atomic number	atom	X	Y	Z
1	C	1.106286	0.861261	-0.199363
2	C	1.405951	-0.388644	0.586371
3	C	0.362631	-0.405172	-0.511994
4	C	-1.058435	-0.577274	-0.143925
5	C	-1.902824	0.405631	0.184906
6	H	1.842539	1.196869	-0.913708
7	H	0.572351	1.647771	0.311179
8	H	1.033905	-0.432181	1.599400
9	H	2.342012	-0.895800	0.406861
10	H	0.668806	-0.921545	-1.412963
11	H	-1.421523	-1.600736	-0.128525
12	H	-2.921612	0.187545	0.472404
13	H	-1.598134	1.443259	0.169376

16 cyclopropanone
MP2=-191.5250435

atomic number	atom	X	Y	Z
1	C	0.379620	0.000000	-0.000044
2	C	-0.858721	-0.787302	0.000124
3	C	-0.858721	0.787302	0.000096
4	O	1.583449	0.000000	-0.000206
5	H	-1.160054	-1.277709	0.915501
6	H	-1.160276	-1.277741	-0.915163
7	H	-1.160048	1.277736	0.915461
8	H	-1.160281	1.277714	-0.915203

17 methylenecyclopropane
MP2=-155.6103373

atomic number	atom	X	Y	Z
1	C	0.314458	-0.000003	-0.000004
2	C	-0.931046	0.770431	-0.000046
3	C	-0.931052	-0.770428	0.000054
4	C	1.638070	-0.000001	-0.000005
5	H	2.193328	-0.928381	0.000051
6	H	-1.232307	1.264112	-0.913934
7	H	-1.232299	1.264235	0.913779
8	H	-1.232321	-1.264230	-0.913767
9	H	-1.232302	-1.264109	0.913946
10	H	2.193321	0.928383	-0.000065

18 oxirane
MP2=-153.5140453

atomic number	atom	X	Y	Z
1	O	0.000001	0.859435	-0.000003
2	C	0.731133	-0.376534	0.000001
3	C	-0.731134	-0.376533	0.000001
4	H	1.259686	-0.589269	0.919625
5	H	1.259686	-0.589275	-0.919621
6	H	-1.259687	-0.589267	0.919625
7	H	-1.259687	-0.589273	-0.919621

19 aziridine
MP2=-133.6527424

atomic number	atom	X	Y	Z
1	N	0.000006	0.860546	-0.172484
2	C	-0.739618	-0.400612	0.023220
3	C	0.739611	-0.400623	0.023219
4	H	-1.271038	-0.741926	-0.852066
5	H	-1.241423	-0.557142	0.967484
6	H	1.271027	-0.741941	-0.852067
7	H	1.241415	-0.557159	0.967484
8	H	0.000015	1.381757	0.697918

20 thiirane
MP2=-476.1367417

atomic number	atom	X	Y	Z
1	S	0.865233	0.000000	0.000000
2	C	-0.798450	0.739855	0.000000
3	C	-0.798450	-0.739855	0.000000
4	H	-1.065583	1.247013	-0.915939
5	H	-1.065583	1.247013	0.915939
6	H	-1.065583	-1.247013	-0.915938
7	H	-1.065583	-1.247012	0.915940

21 2-methyloxirane
MP2=-192.7463865

atomic number	atom	X	Y	Z
1	C	1.030533	0.622538	-0.063541
2	C	-0.152791	-0.032516	0.493816
3	O	0.825189	-0.792418	-0.239396
4	C	-1.498324	0.095709	-0.149959
5	H	1.859491	0.882914	0.581833
6	H	0.922741	1.208619	-0.968094
7	H	-0.143775	-0.246718	1.557674
8	H	-2.070001	0.897868	0.317420
9	H	-2.060773	-0.831300	-0.045035
10	H	-1.385700	0.313581	-1.210532

22 2-methylaziridine
MP2=-172.8837917

atomic number	atom	X	Y	Z
1	N	0.848804	-0.745428	-0.342073
2	C	0.982376	0.701167	-0.053495
3	C	-0.165591	-0.061620	0.482880
4	H	1.484786	-1.259479	0.259484
5	H	0.829340	1.336915	-0.914204
6	H	1.758595	1.015823	0.630131
7	H	-0.139197	-0.269693	1.546291
8	C	-1.527304	0.052839	-0.135070
9	H	-2.093035	0.868702	0.315707
10	H	-2.090536	-0.871245	-0.005819
11	H	-1.428468	0.242652	-1.202973

23 2-methylthiirane
MP2=-515.3677211

atomic number	atom	X	Y	Z
1	S	1.079674	-0.526882	-0.054833
2	C	-0.513464	0.169110	0.511513
3	C	0.367567	1.150690	-0.156249
4	H	-0.563831	0.242562	1.591471
5	C	-1.762077	-0.303407	-0.178497
6	H	0.873702	1.892672	0.445477
7	H	0.095493	1.458785	-1.157438
8	H	-2.582922	0.390339	0.013682
9	H	-2.055273	-1.289965	0.176713
10	H	-1.594107	-0.362640	-1.253174

24 bicyclo[3.1.0]hexane
MP2=-234.111845

atomic number	atom	X	Y	Z
1	C	-0.752889	-0.756429	-0.419091
2	C	-0.752882	0.756440	-0.419069
3	C	0.670801	1.218907	-0.190244
4	C	1.377650	-0.000004	0.426287
5	C	0.670792	-1.218907	-0.190243
6	C	-1.414529	-0.000005	0.704078
7	H	-1.386341	1.305261	-1.101378
8	H	-1.386330	-1.305231	-1.101431
9	H	0.739598	2.100892	0.448684
10	H	1.122575	1.468546	-1.153112
11	H	1.246807	-0.000005	1.508011
12	H	2.449694	-0.000012	0.234392
13	H	0.739571	-2.100889	0.448693
14	H	1.122581	-1.468559	-1.153100
15	H	-0.947362	-0.000028	1.679384
16	H	-2.494451	0.000012	0.719551

25 6-oxabicyclo[3.1.0]hexane
MP2=-270.0078681

atomic number	atom	X	Y	Z
1	C	-0.792948	-0.732498	-0.364208
2	C	-0.792947	0.732499	-0.364207
3	C	0.621752	1.223866	-0.201185
4	C	1.367518	0.000000	0.361720
5	C	0.621752	-1.223866	-0.201185
6	O	-1.271322	0.000000	0.785668
7	H	-1.546985	1.316540	-0.876065
8	H	-1.546986	-1.316539	-0.876066
9	H	0.693116	2.092983	0.452552
10	H	1.006789	1.506208	-1.184330
11	H	1.290359	0.000000	1.446061
12	H	2.423614	-0.000001	0.098680
13	H	0.693115	-2.092983	0.452552
14	H	1.006788	-1.506209	-1.184330

26s syn-3-bicyclo[3.1.0]hexanol
MP2=-309.2388011

atomic number	atom	X	Y	Z
1	C	-1.319747	-0.025543	1.068600
2	C	-1.177939	0.745268	-0.217961
3	C	-1.159314	-0.768243	-0.233301
4	H	-2.304544	-0.044585	1.512671
5	H	-0.489312	-0.015739	1.758120
6	C	0.208710	1.230279	-0.583995
7	H	-2.037121	1.288138	-0.585389
8	C	0.236378	-1.206455	-0.619478
9	H	-2.005884	-1.325325	-0.608801
10	C	1.135807	0.023084	-0.409266
11	O	1.682617	0.086442	0.914677
12	H	1.954493	0.043944	-1.133039
13	H	0.562895	2.061459	0.026580
14	H	0.219381	1.545241	-1.629497
15	H	0.250522	-1.485458	-1.676108
16	H	0.602958	-2.060673	-0.044892
17	H	2.242317	-0.688874	1.035346

26a anti-3-bicyclo[3.1.0]hexanol
MP2=-309.2377199

atomic number	atom	X	Y	Z
1	C	1.822101	-0.000001	0.732161
2	C	1.187505	-0.758492	-0.406034
3	C	1.187500	0.758501	-0.406025
4	H	2.901499	0.000007	0.768985
5	H	1.338074	-0.000012	1.699071
6	C	-0.239474	-1.216139	-0.217347
7	H	1.838507	-1.306945	-1.071422
8	C	-0.239482	1.216137	-0.217336
9	H	1.838498	1.306968	-1.071408
10	C	-0.966806	-0.000006	0.377062
11	H	-0.859922	-0.000008	1.460693
12	O	-2.372680	-0.000012	0.172457
13	H	-0.347030	-2.099734	0.412295
14	H	-0.681517	-1.443240	-1.192815
15	H	-0.681520	1.443242	-1.192807
16	H	-0.347047	2.099727	0.412310
17	H	-2.526163	0.000094	-0.779437

27 bicyclo[4.1.0]heptane
MP2=-273.3378325

atomic number	atom	X	Y	Z
1	C	0.963662	0.835387	-0.353057
2	C	1.034503	-0.672859	-0.474331
3	C	-0.210755	-1.505726	-0.276737
4	C	-1.308349	-0.762212	0.482494
5	C	-1.560348	0.593360	-0.167111
6	C	-0.351465	1.511610	0.004133
7	C	1.685236	0.017360	0.691867
8	H	1.604501	1.386352	-1.028284
9	H	1.717400	-1.046819	-1.226692
10	H	0.043603	-2.439488	0.231109
11	H	-0.606927	-1.775699	-1.260191
12	H	-1.025669	-0.620886	1.529877
13	H	-2.217591	-1.365565	0.482392
14	H	-2.446792	1.069285	0.256198
15	H	-1.754455	0.438984	-1.232944
16	H	-0.315991	1.859421	1.040340
17	H	-0.476227	2.400292	-0.616346
18	H	1.199054	-0.064270	1.655017
19	H	2.764190	0.056867	0.725979

28 7-oxabicyclo[4.1.0]heptane
MP2=-309.2372967

atomic number	atom	X	Y	Z
1	C	0.972175	0.840172	-0.298337
2	C	1.085839	-0.620593	-0.425436
3	C	-0.123831	-1.501472	-0.289461
4	C	-1.258451	-0.800554	0.452810
5	C	-1.540912	0.555327	-0.184683
6	C	-0.354472	1.505283	-0.023774
7	O	1.508484	0.040682	0.781191
8	H	1.731447	1.447751	-0.780212
9	H	1.909878	-1.018372	-1.010630
10	H	0.164087	-2.424472	0.218962
11	H	-0.456913	-1.778296	-1.294567
12	H	-0.982182	-0.666360	1.500313
13	H	-2.150645	-1.427479	0.426541
14	H	-2.434795	1.007844	0.247018
15	H	-1.741988	0.405874	-1.249827
16	H	-0.323188	1.896481	0.996227
17	H	-0.465665	2.362596	-0.690077

29 3-carene
MP2=-389.8079854

atomic number	atom	X	Y	Z
1	C	0.896200	0.894919	-0.670687
2	C	0.578058	-0.564273	-0.945467
3	C	-0.793817	-1.111581	-0.632691
4	C	-1.780662	-0.133919	-0.063381
5	C	-1.485171	1.151639	0.169885
6	C	-0.160373	1.802210	-0.085738
7	C	1.546847	-0.192058	0.149959
8	C	3.006942	-0.459698	-0.117499
9	C	1.142848	-0.376328	1.590423
10	H	1.552971	1.370484	-1.389366
11	H	1.039215	-0.982286	-1.832541
12	C	-3.136595	-0.700784	0.235323
13	H	-2.261982	1.789172	0.583102
14	H	-0.717092	-1.964034	0.054983
15	H	-1.227325	-1.520770	-1.551302
16	H	0.200748	2.249788	0.848114
17	H	-0.317709	2.641834	-0.769035
18	H	3.243721	-0.312635	-1.172132
19	H	3.638796	0.212075	0.468333
20	H	3.268680	-1.486627	0.148311
21	H	1.715167	0.296768	2.233201
22	H	0.083983	-0.179153	1.752392
23	H	1.352298	-1.398637	1.914194
24	H	-3.061173	-1.516736	0.958463
25	H	-3.589998	-1.117339	-0.667243
26	H	-3.805967	0.057334	0.639767

30 2-carene
MP2=-389.808636

atomic number	atom	X	Y	Z
1	C	0.917154	0.928354	-0.606184
2	C	0.596963	-0.491975	-1.031401
3	C	-0.784091	-0.950422	-0.821093
4	C	-1.708216	-0.268394	-0.117875
5	C	-1.390602	1.054954	0.516484
6	C	-0.229760	1.799259	-0.151849
7	C	1.523710	-0.213557	0.160409
8	C	2.993455	-0.443275	-0.100748
9	C	1.095836	-0.579245	1.559888
10	H	1.624002	1.447740	-1.244564
11	H	1.094628	-0.876020	-1.913801
12	C	-3.090919	-0.800655	0.106285
13	H	-1.062307	-1.909306	-1.248551
14	H	-1.175887	0.901907	1.578489
15	H	-2.283134	1.687054	0.487778
16	H	0.131912	2.585374	0.515131
17	H	-0.616923	2.299873	-1.043533
18	H	3.254468	-1.491395	0.060053
19	H	3.603508	0.164612	0.571814
20	H	3.256254	-0.179240	-1.125969
21	H	0.033184	-0.804529	1.617846
22	H	1.323759	0.224645	2.263724
23	H	1.638152	-1.469595	1.884252
24	H	-3.838828	-0.116568	-0.301917
25	H	-3.301097	-0.897902	1.174684
26	H	-3.222875	-1.776907	-0.358946

31s syn-tricyclo[5.1.0.03,5]octane
MP2=-311.3286647

atomic number	atom	X	Y	Z
1	C	1.287701	-0.753439	-0.284892
2	C	1.287360	0.753813	-0.284636
3	C	-0.000308	1.530849	-0.453168
4	C	-1.287765	0.753461	-0.284634
5	C	-1.287443	-0.753786	-0.284498
6	C	0.000203	-1.530822	-0.453227
7	C	-1.633357	-0.000116	0.976480
8	C	1.633565	0.000051	0.976205
9	H	2.135107	-1.218710	-0.772248
10	H	2.134714	1.219499	-0.771695
11	H	-0.000324	1.931362	-1.470618
12	H	-0.000424	2.394229	0.218559
13	H	-2.135275	1.218751	-0.771790
14	H	-2.134885	-1.219425	-0.771449
15	H	0.000076	-1.931349	-1.470671
16	H	0.000414	-2.394194	0.218508
17	H	-2.670129	-0.000372	1.281139
18	H	-0.929485	0.000226	1.791993
19	H	0.930026	-0.000399	1.792008
20	H	2.670454	0.000318	1.280473

31a anti-tricyclo[5.1.0.$0^{3,5}$]octane
MP2=-311.3337647

atomic number	atom	X	Y	Z
1	C	1.326294	-0.751843	-0.370671
2	C	1.326303	0.751844	-0.370665
3	C	-0.020674	1.447054	-0.413760
4	C	-1.054339	0.758306	0.452521
5	C	-1.054342	-0.758305	0.452531
6	C	-0.020683	-1.447049	-0.413765
7	C	1.755821	-0.000007	0.864621
8	C	-2.198720	-0.000001	-0.164978
9	H	2.115183	-1.236386	-0.931653
10	H	2.115191	1.236384	-0.931650
11	H	-0.362371	1.476923	-1.452336
12	H	0.087740	2.484655	-0.092630
13	H	-1.257527	1.225691	1.406688
14	H	-1.257506	-1.225678	1.406706
15	H	-0.362395	-1.476915	-1.452337
16	H	0.087740	-2.484653	-0.092644
17	H	2.806312	-0.000015	1.115608
18	H	1.076760	-0.000006	1.705282
19	H	-3.148422	0.000014	0.349572
20	H	-2.258657	-0.000008	-1.245614

32s syn-3-norcarene oxide
MP2=-347.2316295

atomic number	atom	X	Y	Z
1	C	-1.298345	0.732237	-0.207731
2	C	-1.298332	-0.732250	-0.207729
3	C	-0.048220	-1.525277	-0.460070
4	C	1.243529	-0.754153	-0.318760
5	C	1.243521	0.754167	-0.318758
6	C	-0.048238	1.525278	-0.460068
7	C	1.575802	0.000005	0.945465
8	O	-1.380927	-0.000006	1.035159
9	H	-2.225696	1.237278	-0.461763
10	H	-2.225672	-1.237297	-0.461772
11	H	-0.122458	-1.910071	-1.481990
12	H	-0.043369	-2.396097	0.201800
13	H	2.086263	-1.220888	-0.812004
14	H	2.086254	1.220910	-0.812004
15	H	-0.122481	1.910073	-1.481987
16	H	-0.043399	2.396093	0.201806
17	H	2.607638	0.000005	1.265909
18	H	0.832035	-0.000005	1.726644

32a anti-3-norcarene oxide
MP2=-347.2301516

atomic number	atom	X	Y	Z
1	C	0.145373	-1.277886	0.754509
2	C	0.145373	-1.277886	-0.754509
3	C	-0.122845	-0.021204	-1.548947
4	C	-0.122845	1.246123	-0.737460
5	C	-0.122845	1.246123	0.737460
6	C	-0.122845	-0.021204	1.548947
7	C	1.442796	-1.394475	0.000000
8	O	-1.331549	1.501572	0.000000
9	H	-0.209896	-2.189508	1.216084
10	H	-0.209896	-2.189508	-1.216084
11	H	-1.097753	-0.089552	-2.036548
12	H	0.625007	0.069199	-2.340324
13	H	0.262433	2.131346	-1.234010
14	H	0.262433	2.131346	1.234010
15	H	-1.097753	-0.089552	2.036548
16	H	0.625007	0.069199	2.340324
17	H	1.965853	-2.339087	0.000000
18	H	2.073992	-0.514012	0.000000

33s syn-1,4-cyclohexadiene dioxide
MP2=-383.1243000

atomic number	atom	X	Y	Z
1	C	1.269688	-0.733189	-0.263650
2	C	1.269680	0.733203	-0.263629
3	C	-0.000005	1.529450	-0.379377
4	C	-1.269689	0.733197	-0.263627
5	C	-1.269681	-0.733196	-0.263651
6	C	0.000009	-1.529437	-0.379433
7	O	-1.477387	-0.000021	0.956286
8	O	1.477384	-0.000010	0.956287
9	H	2.163891	-1.239487	-0.614991
10	H	2.163880	1.239523	-0.614952
11	H	-0.000005	2.023276	-1.355622
12	H	-0.000004	2.320436	0.375464
13	H	-2.163890	1.239515	-0.614946
14	H	-2.163879	-1.239508	-0.614992
15	H	0.000011	-2.023217	-1.355700
16	H	0.000013	-2.320458	0.375370

33a anti-1,4-cyclohexadiene dioxide
MP2=-383.1296969

atomic number	atom	X	Y	Z
1	C	0.000076	-1.262778	0.734181
2	C	0.000076	-1.262778	-0.734181
3	C	-0.000043	-0.000014	-1.545647
4	C	-0.000043	1.262754	-0.734182
5	C	-0.000043	1.262754	0.734182
6	C	-0.000043	-0.000014	1.545647
7	O	1.212686	-1.516564	0.000000
8	O	-1.212647	1.516640	0.000000
9	H	-0.388237	-2.144409	1.233857
10	H	-0.388237	-2.144409	-1.233857
11	H	-0.879717	0.013592	-2.193437
12	H	0.879528	-0.013622	-2.193576
13	H	0.388332	2.144358	-1.233853
14	H	0.388332	2.144358	1.233853
15	H	-0.879717	0.013592	2.193437
16	H	0.879528	-0.013622	2.193576

34s syn-1,7-dimethyl-4-oxatricyclo[5.1.0.0^{3,5}]octane
MP2=-425.6914007

atomic number	atom	X	Y	Z
1	C	-0.731377	0.756864	0.065856
2	C	-0.731370	-0.756880	0.065840
3	C	0.510392	-1.506028	-0.374186
4	C	1.793792	-0.731152	-0.404111
5	C	1.793783	0.731161	-0.404117
6	C	0.510379	1.506029	-0.374189
7	C	-0.713461	-0.000020	1.376388
8	O	2.162752	0.000010	0.785772
9	C	-1.987988	1.511987	-0.296561
10	C	-1.987981	-1.511978	-0.296586
11	H	0.346528	-1.877803	-1.392728
12	H	0.639073	-2.390878	0.258653
13	H	2.634622	-1.241819	-0.864264
14	H	2.634603	1.241837	-0.864281
15	H	0.346506	1.877789	-1.392736
16	H	0.639077	2.390890	0.258634
17	H	-1.637653	-0.000055	1.941829
18	H	0.199841	-0.000010	1.951299
19	H	-2.119030	1.561482	-1.380160
20	H	-1.922273	2.535954	0.079003
21	H	-2.879514	1.062082	0.134902
22	H	-2.119040	-1.561438	-1.380186
23	H	-2.879481	-1.062053	0.134905
24	H	-1.922287	-2.535955	0.078953

34a anti-1,7-dimethyl-4-oxatricyclo[5.1.0.$0^{3,5}$]octane
MP2=-425.6902546

atomic number	atom	X	Y	Z
1	C	-0.773487	0.755373	0.087998
2	C	-0.773495	-0.755361	0.088001
3	C	0.532201	-1.506394	-0.085117
4	C	1.773773	-0.736838	0.274460
5	C	1.773802	0.736821	0.274485
6	C	0.532214	1.506396	-0.085041
7	C	-0.970118	0.000001	1.381997
8	H	0.628566	-1.828410	-1.126223
9	C	-1.942837	1.513194	-0.490646
10	C	-1.942872	-1.513183	-0.490576
11	O	2.383137	-0.000005	-0.801622
12	H	0.484059	-2.412756	0.525149
13	H	2.499108	-1.241130	0.904482
14	H	2.499140	1.241067	0.904542
15	H	0.628566	1.828496	-1.126121
16	H	0.484049	2.412712	0.525292
17	H	-1.961128	0.000033	1.817708
18	H	-0.150824	-0.000102	2.091150
19	H	-1.865928	1.574028	-1.578420
20	H	-1.951258	2.532903	-0.098696
21	H	-2.898624	1.057677	-0.241173
22	H	-1.865991	-1.573947	-1.578349
23	H	-2.898652	-1.057675	-0.241053
24	H	-1.951268	-2.532913	-0.098678

35s syn-3-carane epoxide
MP2=-464.9182571

atomic number	atom	X	Y	Z
1	C	0.730114	-0.887251	-0.673200
2	C	0.995986	0.581614	-0.954844
3	C	-0.059748	1.629662	-0.659555
4	C	-1.417316	1.111662	-0.258508
5	C	-1.694862	-0.306710	0.004019
6	C	-0.593618	-1.341391	-0.087880
7	C	1.781106	-0.140656	0.112785
8	C	-3.091736	-0.835693	-0.159710
9	O	-1.563976	0.633908	1.098610
10	H	1.132632	-1.569341	-1.412669
11	H	1.556162	0.774582	-1.861976
12	C	1.548264	0.178546	1.565330
13	C	3.216483	-0.464421	-0.222505
14	H	-0.203665	2.221918	-1.565430
15	H	0.280220	2.326935	0.112105
16	H	-2.257539	1.727197	-0.570129
17	H	-0.971001	-2.150884	-0.716077
18	H	-0.458520	-1.767746	0.911309
19	H	-3.230942	-1.249288	-1.159259
20	H	-3.817249	-0.040468	0.002914
21	H	-3.277379	-1.628718	0.566942
22	H	2.155902	1.036955	1.862297
23	H	1.848470	-0.668431	2.187299
24	H	0.505835	0.406350	1.777011
25	H	3.560022	-1.331572	0.346233
26	H	3.869286	0.377607	0.018951
27	H	3.331546	-0.688533	-1.283992

35a anti-3-carene epoxide
MP2=-464.9242678

atomic number	atom	X	Y	Z
1	C	0.741613	-0.339104	-1.008491
2	C	0.990535	1.017233	-0.366787
3	C	-0.039495	1.651938	0.538879
4	C	-1.387075	0.990117	0.517624
5	C	-1.640624	-0.325216	-0.083697
6	C	-0.538945	-1.101576	-0.758499
7	C	1.779722	-0.189967	0.076166
8	O	-2.014130	0.886984	-0.778082
9	H	1.143059	-0.440990	-2.009019
10	H	1.538837	1.712660	-0.989765
11	C	-2.805900	-1.145430	0.392643
12	C	1.487683	-0.779795	1.431404
13	C	3.228265	-0.260276	-0.334188
14	H	-0.187651	2.691680	0.239056
15	H	0.313188	1.676523	1.574562
16	H	-2.073572	1.311253	1.298325
17	H	-0.943595	-1.444079	-1.714308
18	H	-0.343077	-2.001838	-0.167648
19	H	-3.221554	-1.721126	-0.436096
20	H	-3.585964	-0.498432	0.790147
21	H	-2.492429	-1.844008	1.169737
22	H	0.432450	-0.713911	1.696307
23	H	2.058998	-0.261212	2.204925
24	H	1.773043	-1.834126	1.457896
25	H	3.572483	-1.296455	-0.372778
26	H	3.860859	0.279893	0.374103
27	H	3.373292	0.180750	-1.321108

36s 1,6-epoxydihydrocarvone
MP2=-538.8566091

atomic number	atom	X	Y	Z
1	C	0.264123	0.929822	0.655244
2	C	1.010074	0.107987	-0.411712
3	C	0.449448	-1.319254	-0.483431
4	C	-1.051940	-1.390376	-0.366415
5	C	-1.893710	-0.214694	-0.040340
6	C	-1.165745	1.072388	0.210557
7	O	-1.705329	2.148036	-0.000175
8	O	-1.578400	-1.220926	0.957905
9	H	0.694422	1.925827	0.753528
10	C	2.498401	0.100103	-0.182574
11	C	3.341567	0.409551	-1.176133
12	C	2.988801	-0.263653	1.188922
13	H	0.299127	0.414758	1.616940
14	H	0.825785	0.585823	-1.379773
15	H	0.865515	-1.929475	0.322418
16	H	0.762037	-1.775647	-1.424334
17	H	-1.549600	-2.181740	-0.920851
18	C	-3.325480	-0.127393	-0.461237
19	H	2.972820	0.691668	-2.154174
20	H	4.413700	0.389202	-1.029492
21	H	2.700909	0.496934	1.916884
22	H	4.073854	-0.350967	1.199815
23	H	2.565631	-1.209257	1.531727
24	H	-3.410717	0.432291	-1.391477
25	H	-3.906528	0.394961	0.297354
26	H	-3.730356	-1.128139	-0.597699

36a 1,6-epoxyisodihydrocarvone
MP2=-538.8555972

atomic number	atom	X	Y	Z
1	C	0.282917	1.162643	-0.030649
2	C	1.027353	-0.143991	-0.305024
3	C	0.466208	-1.249266	0.592521
4	C	-1.016815	-1.397532	0.400668
5	C	-1.881759	-0.252047	0.067362
6	C	-1.222837	1.085427	-0.140027
7	O	-1.903851	2.080479	-0.330708
8	O	-1.485208	-1.220327	-0.946969
9	H	0.628913	1.971898	-0.674727
10	C	2.516369	0.011681	-0.132176
11	C	3.347837	-0.295670	-1.136557
12	C	3.033664	0.512049	1.186348
13	H	0.470399	1.475649	1.003776
14	H	0.840218	-0.436851	-1.339552
15	H	0.659610	-1.027932	1.646463
16	H	0.959716	-2.196465	0.362119
17	H	-1.499820	-2.221394	0.919433
18	C	-3.340949	-0.239280	0.396540
19	H	4.420492	-0.201916	-1.026062
20	H	2.968079	-0.645944	-2.087830
21	H	2.699747	1.532753	1.380876
22	H	4.122277	0.507417	1.197287
23	H	2.683787	-0.105396	2.015455
24	H	-3.704230	-1.261551	0.481384
25	H	-3.893359	0.277370	-0.385979
26	H	-3.515291	0.287054	1.334730

Figure S1a. Structure and TSNMRS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red -0.1 ppm deshielding) of fluorocyclopropane **3.**

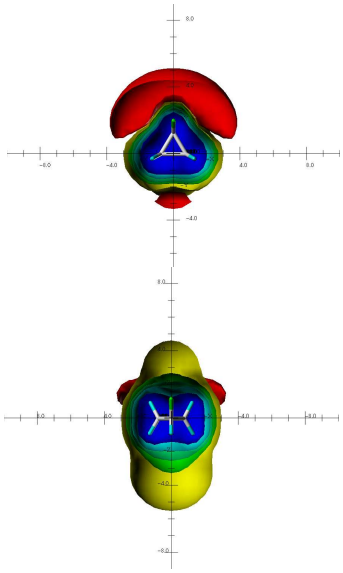


Figure S1b. ICSS of bromocyclopropane **5** (left), iodocyclopropane **6** (middle) and cyclopropanemethanol **7** (right).

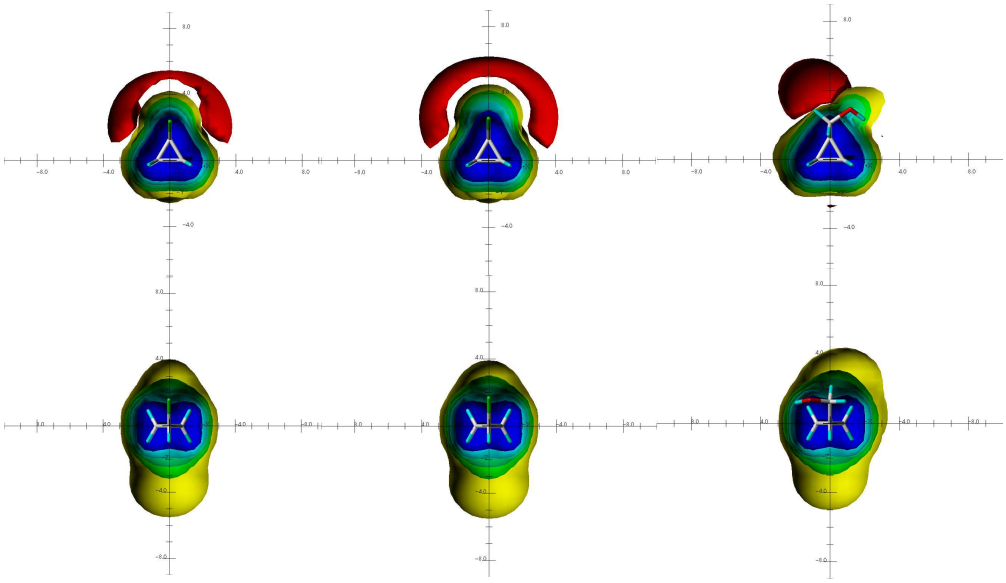


Figure S1c. ICSS of cyanocyclopropane **9** (left), aminocyclopropane **10** (middle) acetylcyclopropane **11** (right).

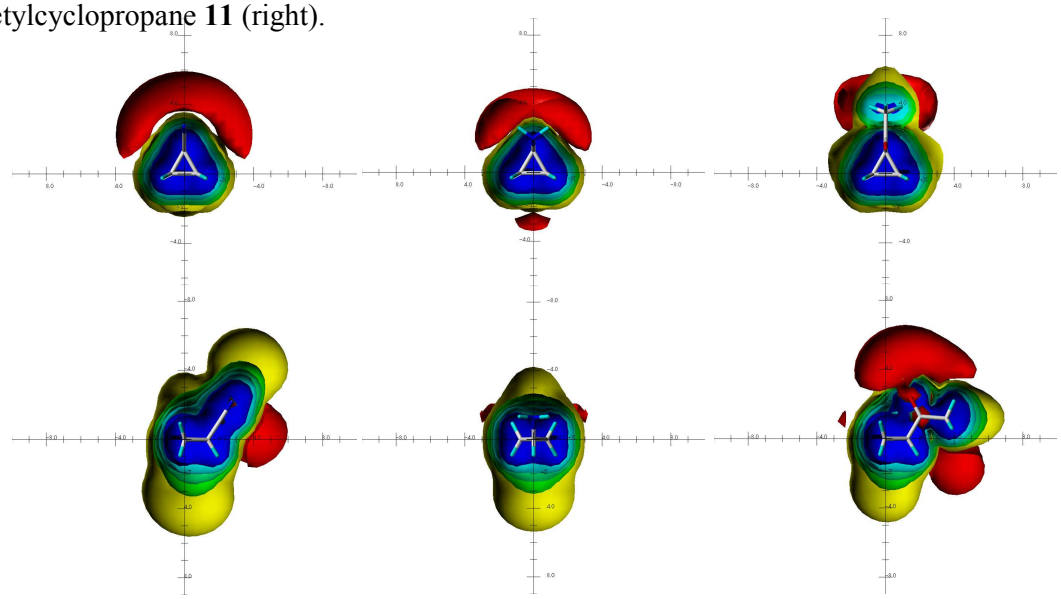


Figure S1d. ICSS of methyl cyclopropanecarboxylate **12** (left) and phenylcyclopropane **13** (right).

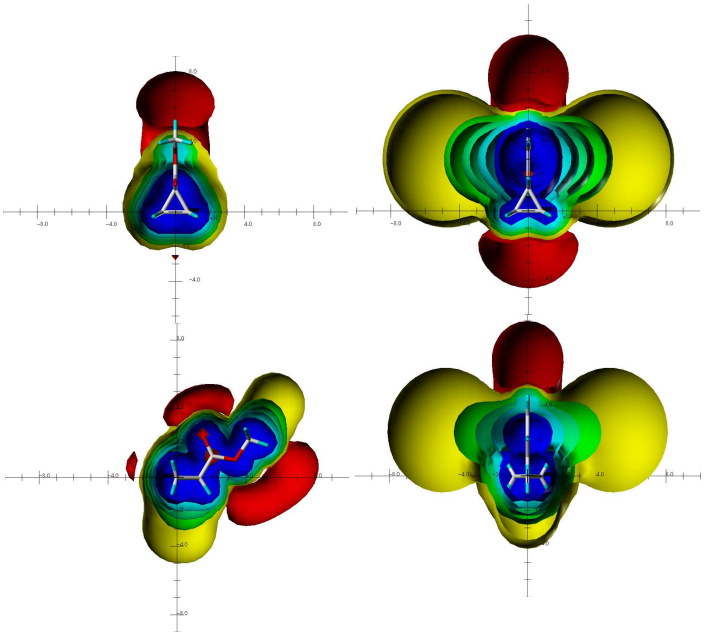


Figure S1e. ICSS of 2-methyloxirane **21** (left), 2-methylaziridine **22** (middle) und 2-methylthiirane **23** (right).

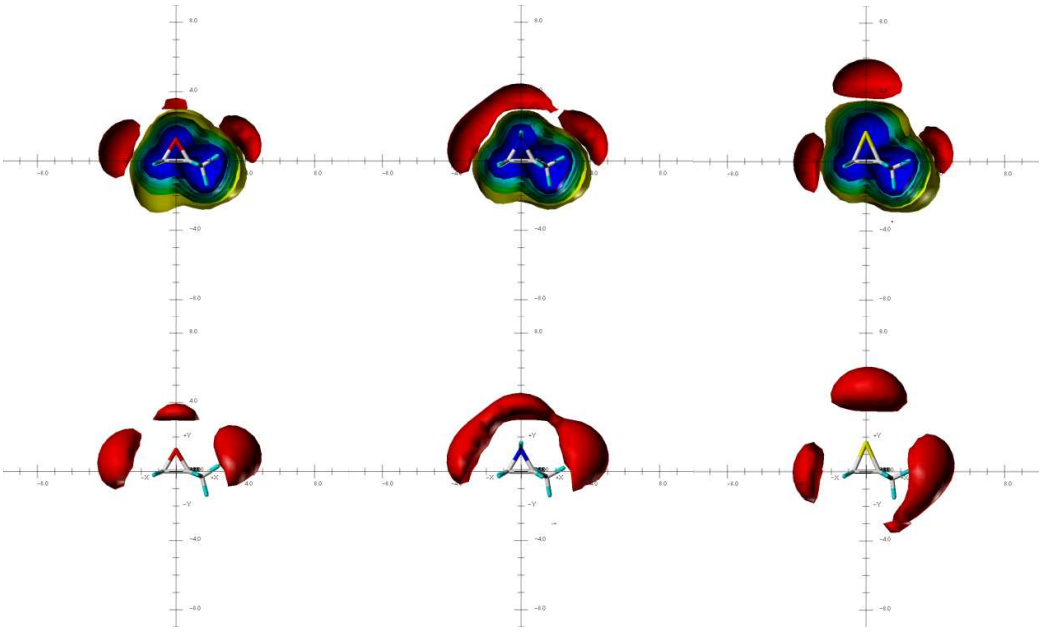
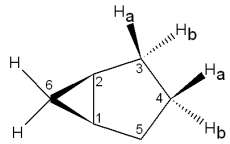


Table S2a. Computed and experimental δ(^{1}H)/ppm value of compound **24** and **25**

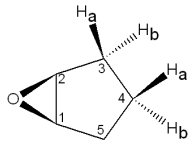
24



bicyclo[3.1.0]hexane

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [43]
1/ 2	1,11	1,17
3a/ 5a	1,78	1,70
3b/ 5b	1,72	1,62
4a	1,13	1,02
4b	1,45	1,42
6endo	0,11	0,11
6exo	0,18	0,26

25

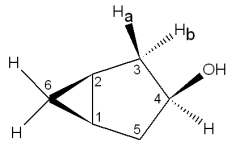


6-oxabicyclo[3.1.0]hexane

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [44]
1/ 2	3,24	3,46
3a/ 5a	1,99	2,02
3b/ 5b	1,44	1,55
4a	1,52	1,36
4b	1,38	1,55

Table S2b. Computed and experimental δ(^{1}H)/ppm value of compound **26** syn, anti

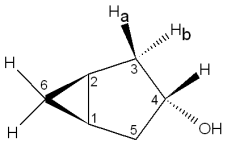
26s



syn-3-bicyclo[3.1.0]hexanol

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [42]
1	1,16	1,26
2	1,16	1,26
3a	2,02	1,71
3b	1,99	2,07
4	4,33	4,34
5a	1,57	1,71
5b	2,07	2,07
6endo	1,11	0,53
6exo	0,35	0,46
OH	0,03	

26a

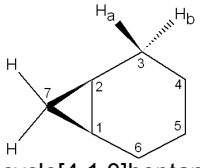


anti-3-bicyclo[3.1.0]hexanol

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [42]
1	1,07	1,25
2	1,07	1,25
3a	2,30	2,13
3b	1,29	1,67
4	3,79	3,97
5a	2,30	2,13
5b	1,29	1,67
6endo	0,02	0,01
6exo	0,17	0,33
OH	-0,67	

Table S2c. Computed and experimental δ(^{1}H)/ppm value of compound **27** and **28**

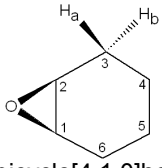
27



bicyclo[4.1.0]heptane

Proton	δ_{ber} [ppm]
1/ 2	0,78
3a	1,99
3b	1,97
4a	0,97
4b	1,39
5a	1,40
5b	1,11
6a	1,46
6b	2,13
7endo	-0,10
7exo	0,54

28



7-oxabicyclo[4.1.0]heptane

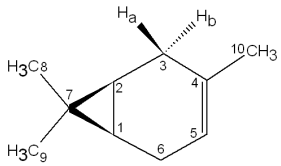
Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [44]
1/ 2	2,97	3,13
3a	2,15	1,99
3b	1,60	1,85
4a	1,60	1,41
4b	1,22	1,26
5a	1,46	1,41
5b	1,09	1,26
6a	1,90	1,99
6b	1,90	1,85

Table S2d. Computed and experimental δ(^{1}H)/ppm value of compounds **31-33** syn/anti

Compound	**31s**	**31a**	**32s**	**32a**	**33s**	**33a**
Proton	δ_{exp} [ppm] [40] [48]	δ_{calc} [ppm]	δ_{exp} [ppm] [49] [50]	δ_{exp} [ppm] [49] [50]	δ_{exp} [ppm] [46]	δ_{exp} [ppm] [46]
1/ 2	0,79-0,91	0,62	0,62	0,71	3,02	3,07-3,05
3a/ 6a	2,37-2,49	2,35	2,31	1,85	2,68	2,32-2,30
3b/ 6b	0,67-0,76	1,28	2,29	2,30	2,24	2,32-2,30
4/ 5	0,79-0,91	0,36	2,96	2,94	3,02	3,07-3,05
7endo	-0,19	0,55	0,62	-0,40		
7exo	0,64	0,19	0,26	0,55		
8endo	-0,19	-0,51				
8exo	0,64	0,78				

Table S2e. Computed and experimental δ(^{1}H)/ppm value of compound **29** and **30** (*average)

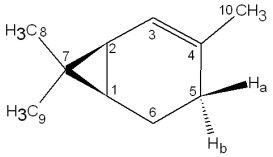
29



3-carene

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [39]
1	0,48	0,59
2	0,62	0,69
3a	1,98	1,80
3b	2,31	2,19
5	5,71	4,30
6a	2,17	1,96
6b	2,53	2,37
8exo*	1,08	1,04
9endo*	0,92	0,76
10*	1,74	1,61

30

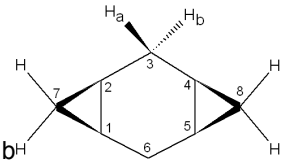


2-carene

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [51]
1	0,77	0,81
2	1,07	0,94
3	6,23	5,54
5a	1,72	1,60
5b	1,91	1,93
6a	1,98	1,82
6b	1,63	1,62
8exo*	1,14	1,06
9endo*	0,91	0,85
10*	1,84	1,66

Table S2f. Computed and experimental δ(^{1}H)/ppm value of compound **31** syn, anti

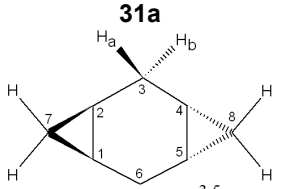
31s



syn-tricyclo[5.1.0.0^{3,5}]octane

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [40]
1/ 2	0,70	0,79-0,91
3a/ 6a	2,25	2,37-2,49
3b/ 6b	2,40	0,67-0,76
4/ 5	0,70	0,79-0,91
7endo/ 8endo	-0,22	-0,19
7exo/ 8exo	0,22	0,64

31a

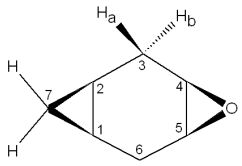


anti-tricyclo[5.1.0.0^{3,5}]octane

Proton	δ_{ber} [ppm]
1/ 2	0,62
3a/ 6a	2,35
3b/ 6b	1,28
4/ 5	0,36
7endo	0,55
7exo	0,19
8endo	-0,51
8exo	0,78

Table S2g. Computed and experimental δ(^{1}H)/ppm value of compound **32** syn, anti

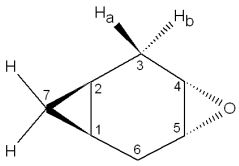
32s



syn-3-norcarene oxide

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [50]
1/ 2	0,62	0,62
3a/ 6a	2,53	2,31
3b/ 6b	2,20	2,29
4/ 5	2,91	2,96
7endo	0,98	0,62
7enxo	0,24	0,26

32a

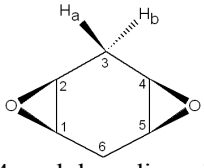


anti-3-norcarene oxide

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [50]
1/ 2	0,67	0,71
3a/ 6a	2,07	1,85
3b/ 6b	2,21	2,30
4/ 5	2,81	2,94
7endo	-0,55	-0,40
7enxo	0,56	0,55

Table S2h. Computed and experimental δ(^{1}H)/ppm value of compound **33** syn, anti

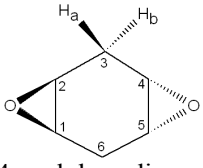
33s



syn-1,4-cyclohexadiene dioxide

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [46]
1/2	2,85	3,02
3a/ 6a	2,76	2,68
3b/ 6b	1,99	2,24
4/ 5	2,85	3,02

33a



anti-1,4-cyclohexadiene dioxide

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [46]
1/ 2	2,91	3,07-3,05
3a/ 3b/ 6a/ 6b	2,23	2,32-2,30
4/ 5	2,91	3,07-3,05

Table S2i. Computed and experimental δ(^{1}H)/ppm value of compound **34** syn,anti (*average)

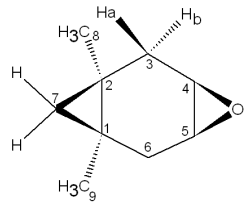
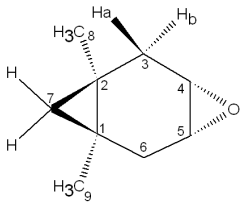
34s  syn-1,7-dimethyl-4-oxatricyclo[5.1.0.0^{3,5}]octane				**34a**  anti-1,7-dimethyl-4-oxatricyclo[5.1.0.0^{3,5}]octane		
Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [50]		Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [50]
3a/ 6a	2,40	2,36		3a/ 6a	2,08	1,74
3b/ 6b	1,90	1,85		3b/ 6b	1,81	2,13
4/ 5	2,97	3,10		4/ 5	2,82	3,06
7endo	1,42	0,97		7endo	0,02	0,07
7exo	-0,31	-0,20		7exo	-0,10	0,07
8*/ 9*	1,08	1,00		8*/ 9*	1,13	1,06

Table S2k. Computed and experimental δ(^{1}H)/ppm value of compound **35** syn,anti (*average)

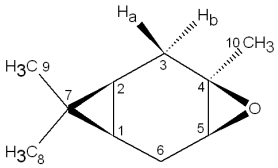
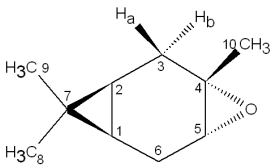
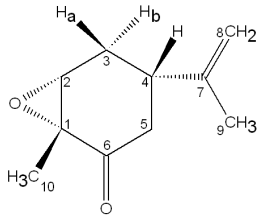
35s  syn-3-carane epoxide				**35a**  anti-3-carene epoxide		
Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [52]		Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [53]
1	0,37	0,51		1	0,31	0,45
2	0,41	0,55		2	0,39	0,53
3a	1,98	2,05 und 1,76		3a	1,51	1,49
3b	1,99			3b	2,09	2,15
5	2,75	2,86		5	2,64	2,83
6a	2,06	2,26 und 1,77		6a	1,64	1,64
6b	2,18			6b	2,31	2,30
8endo*	1,13	0,95		8exo*	1,04	1,01
9exo*	0,97	0,91		9endo*	0,75	0,73
10*	1,24	1,29		10*	1,18	1,26

Table S2l. Computed and experimental δ(^{1}H)/ppm value of compound **36** syn,anti (*average)

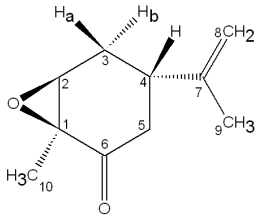
36s



1,6-epoxydihydrocarvone

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [41]
2	3,28	3,45
3b	2,21	2,37
3a	1,78	1,91
4	2,70	2,72
5a	1,89	2,03
5b	3,14	2,59
8	5,15	4,79
8	5,06	4,72
9*	1,79	1,72
10*	1,31	1,41

36a



1,6-epoxyisodihydrocarvone

Proton	δ_{ber} [ppm]	δ_{exp} [ppm] [41]
2	3,22	3,45
3a	2,15	1,91
3b	1,99	2,37
4	3,07	2,72
5a	2,36	2,03
5b	2,07	2,59
8	5,08	4,72
8	5,29	4,79
9*	1,76	1,72
10*	1,32	1,41

Figure S2a: ICSS (visualized as ICSSs: blue represents 5 ppm shielding, cyan 2 ppm shielding, greenblue 1 ppm, green 0.5 ppm shielding, yellow 0.1 ppm shielding and red -0.1 ppm deshielding) of bicyclo[3.1.0]hexane **24** (left) and bicyclo[4.1.0]heptan **27** (right) in X-Y-plane (above), X-Z-plane (middle) and Z-Y-plane (below)

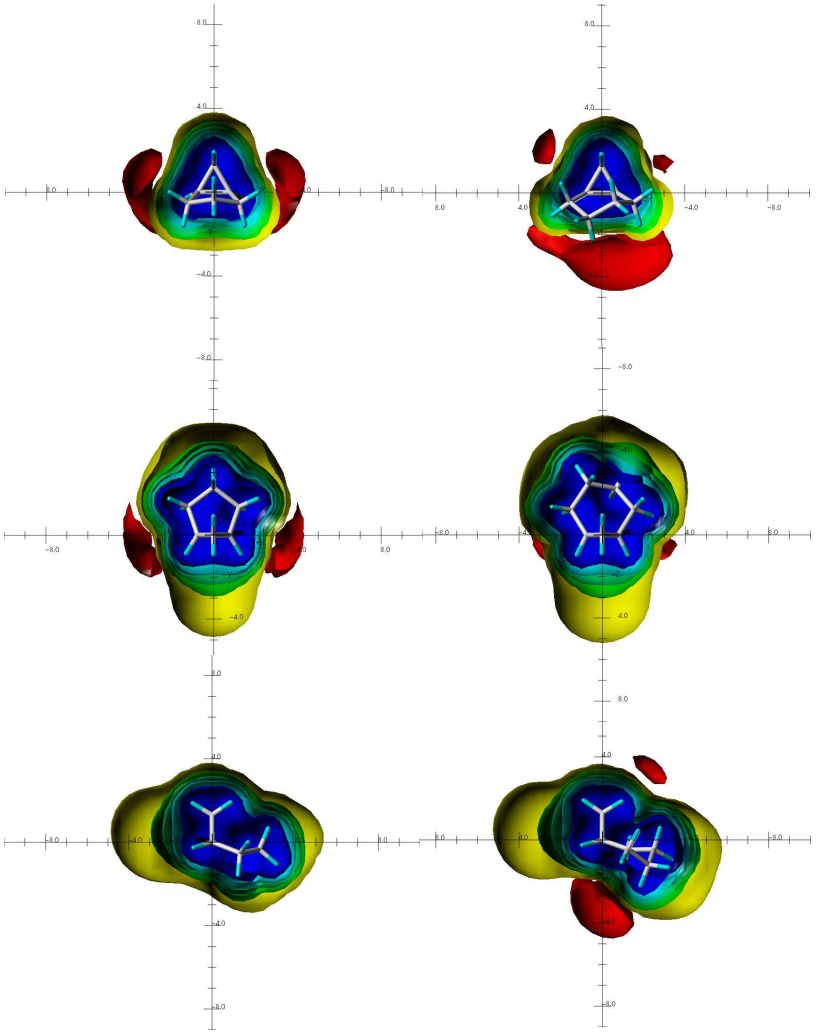


Figure S2b: ICSS of 6-oxabicyclo[3.1.0]hexane **25** (left) and 7-oxabicyclo[4.1.0]heptane **28** (right) in X-Y-plane (above), X-Z-plane (middle) and Z-Y-plane (below)

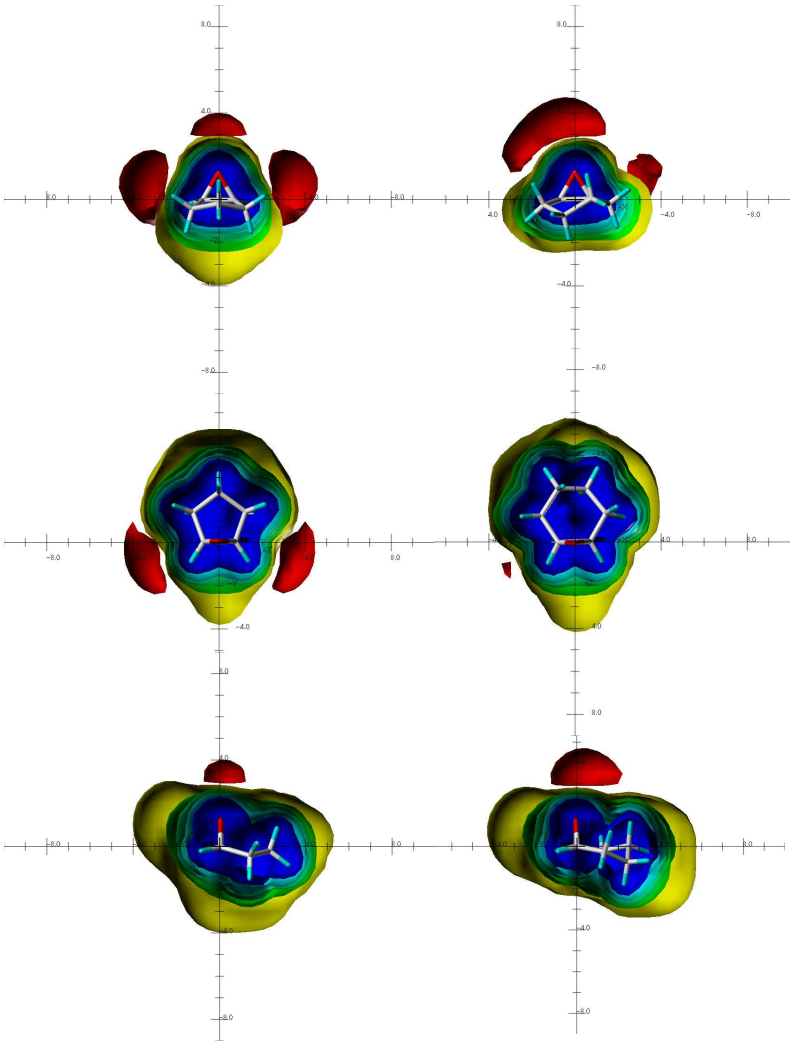


Figure S2c: deshielded areas of cyclopropane **1**, bicyclo[3.1.0]hexane **24**, bicyclo[4.1.0]heptan **27** (above) and oxirane**18**, 6-oxabicyclo[3.1.0]hexane **25**, 7-oxabicyclo[4.1.0]heptane **28** (below) – from left to right

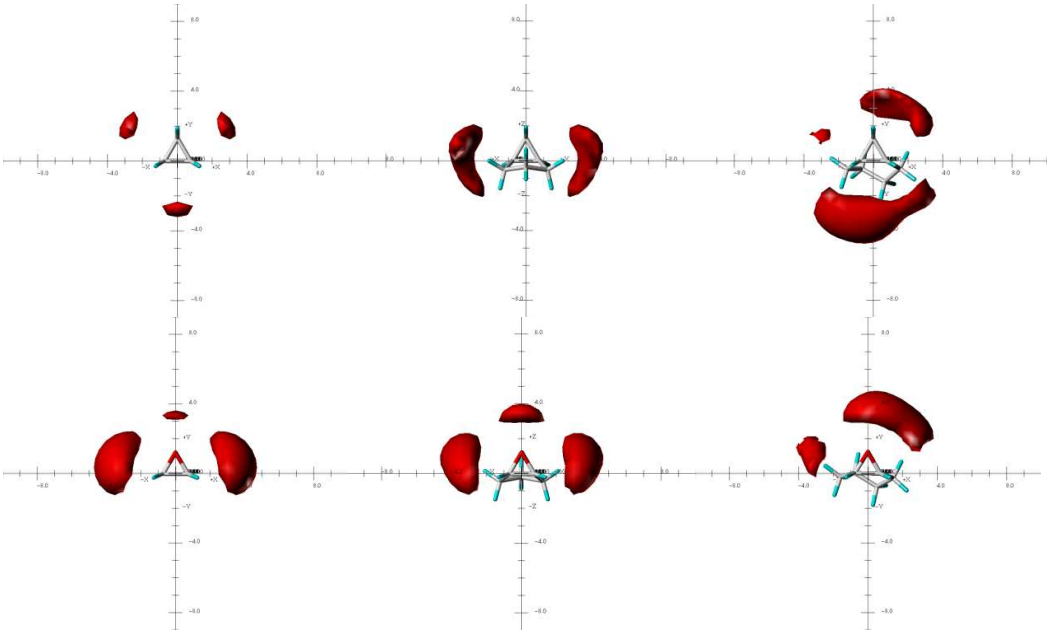


Figure S2d: ICSS of syn-3-bicyclo[3.1.0]hexanol **26s** und anti-3-bicyclo[3.1.0]hexanol **26a** in Z-Y-plane

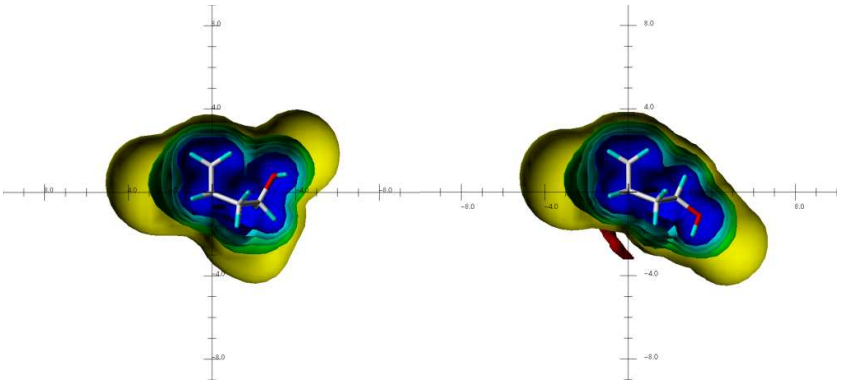


Figure S2e: ICSS of 3-carene **29** (left) and 2-carene **30** (right) in Z-Y-plane

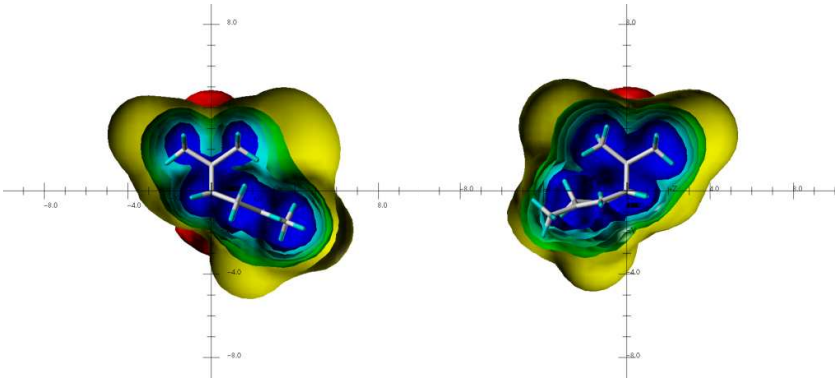
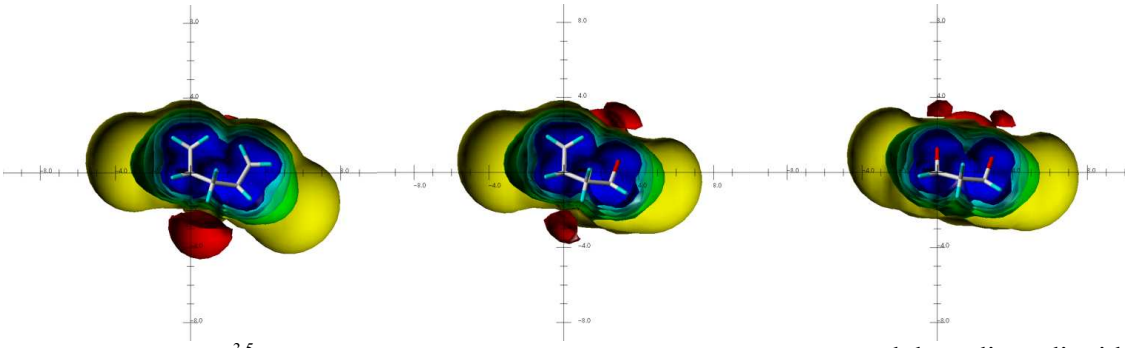
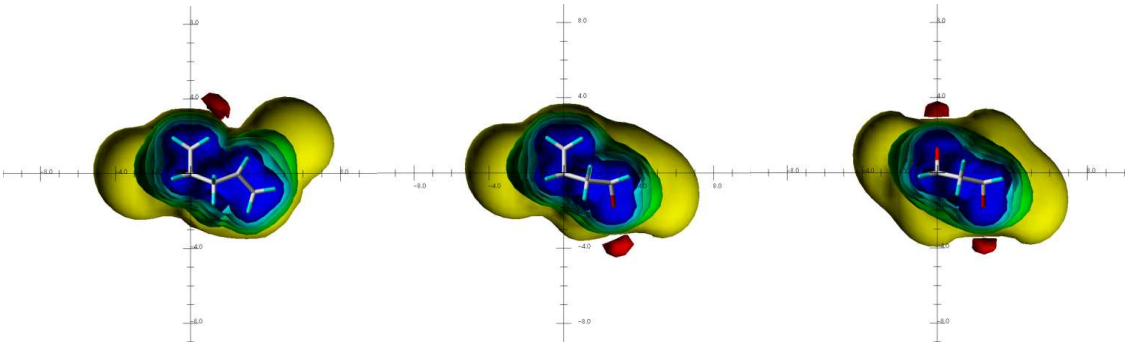


Figure S2f: ICSS of the symmetric tricyclo[5.1.0.$0^{3,5}$]octanes **31**-**33** syn/anti in Z-Y-plane



a)syn-tricyclo[5.1.0.$0^{3,5}$]octane **31s** b)syn-3-norcarene oxide **32s** c)syn-1,4-cyclohexadiene dioxide **33s**



d)anti-tricyclo[5.1.0.$0^{3,5}$]octane **31a** e)anti-3-norcarene oxide **32a** f)anti-1,4-cyclohexadiene dioxide **33a**

Figure S2g: ICSS of syn-1,7-dimethyl-4-oxatricyclo[5.1.0.0^{3,5}]octane **34s** (left) and anti-1,7-dimethyl-4-oxatricyclo[5.1.0.0]octane **34a** (right) in Z-Y-plane

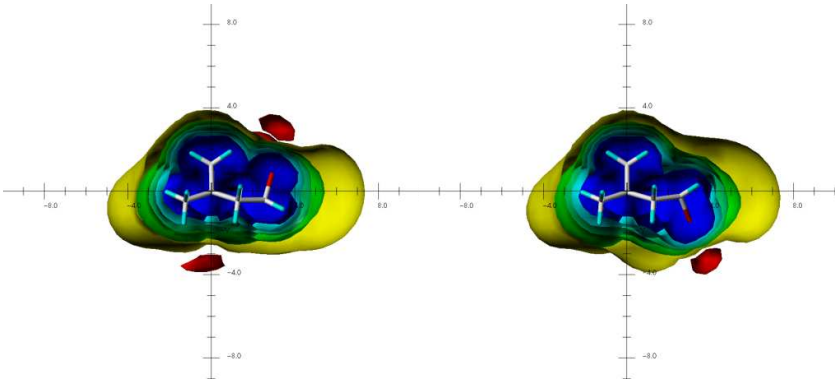


Figure S2h: ICSS of syn-3-carene epoxide **35s** (left) and anti-3-carene epoxide **35a** (right) in Z-Y-plane

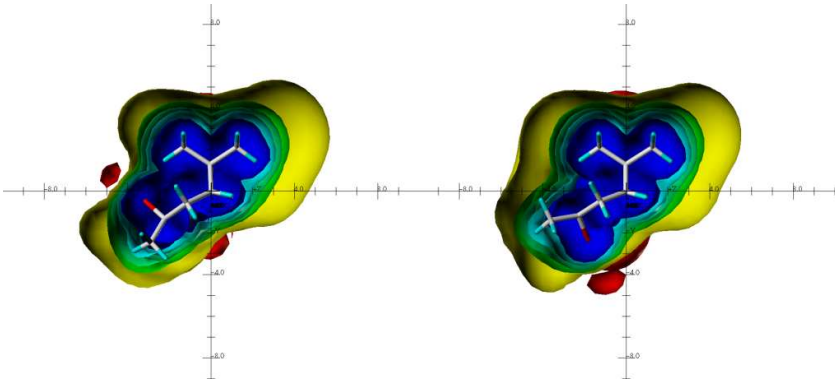


Figure S2i: ICSS of 1,6-epoxydihydrocarvone **36s** (left) and 1,6-epoxyisodihydrocarvone **36a** (right) in X-Z-plane (above) and X-Y-plane (below)

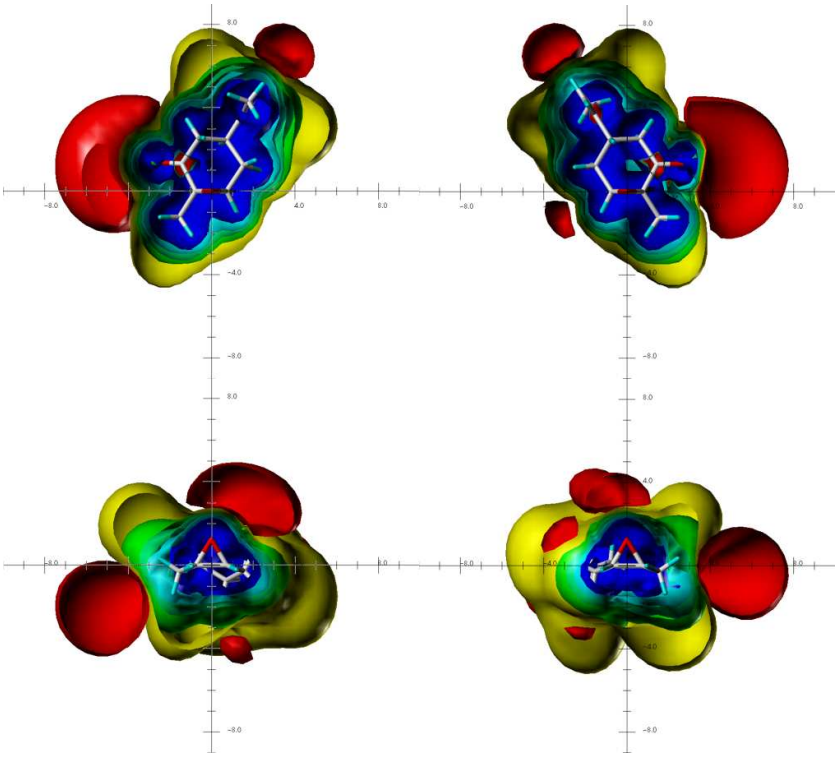
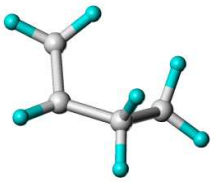
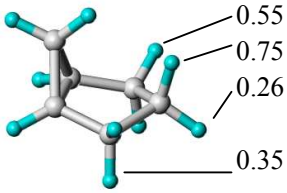
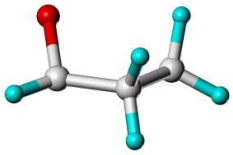
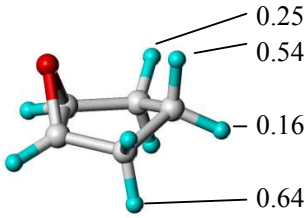
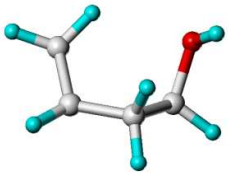
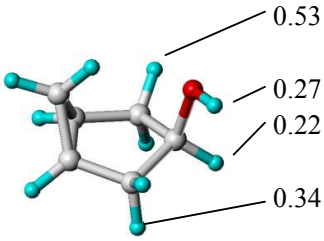
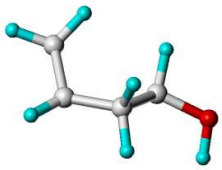
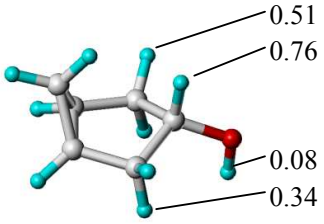
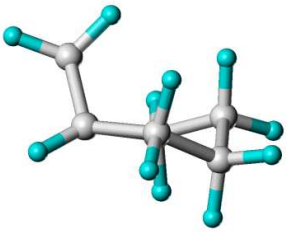
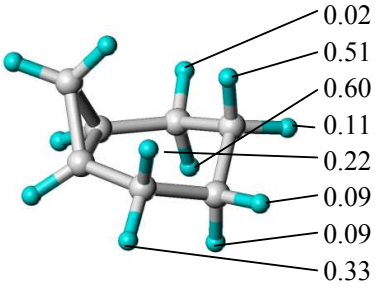
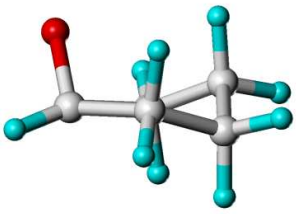
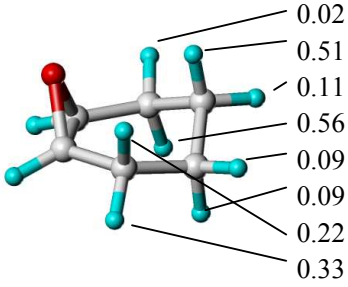
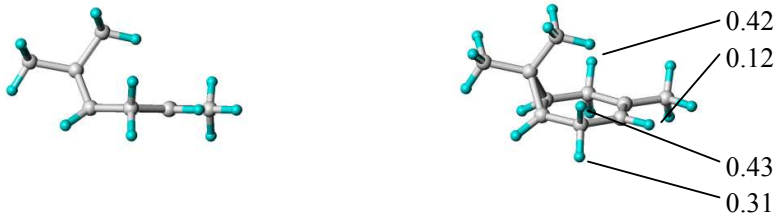


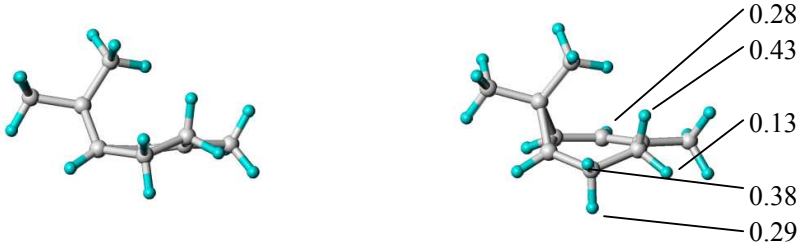
Figure S3: Preferred conformers of the studied *bis*- and *tris*-cyclic structures **24-36*syn/anti*** and the ring current effect of the three-membered ring (as TSNMRS $\Delta\delta(^1H)$/ppm on relevant protons in these *bis*- and *tris*-membered structures.

Number	View 1: C1 on C2	View 2: rotated
24		
25		
26s		
26a		
27		
28		

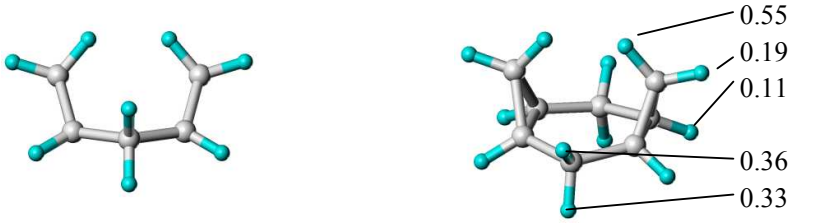
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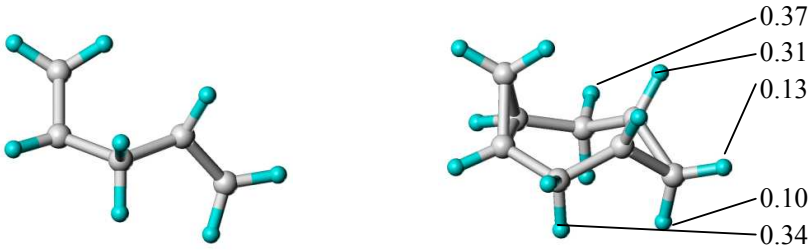
30



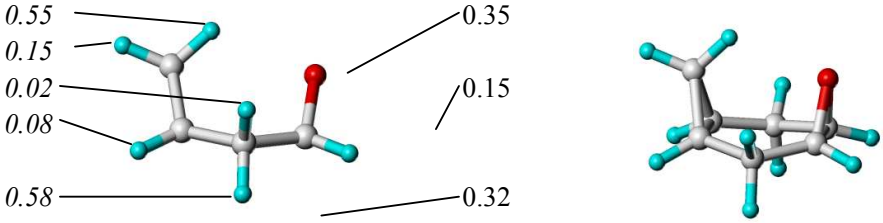
31s



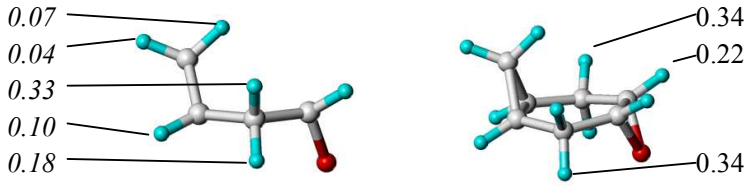
31a



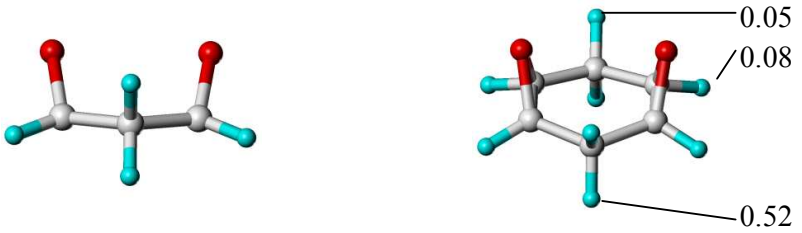
32s



32a



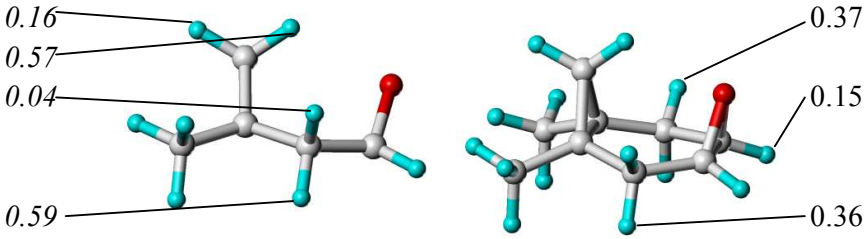
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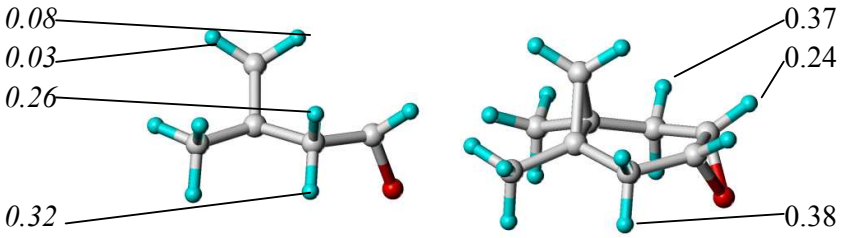
33a



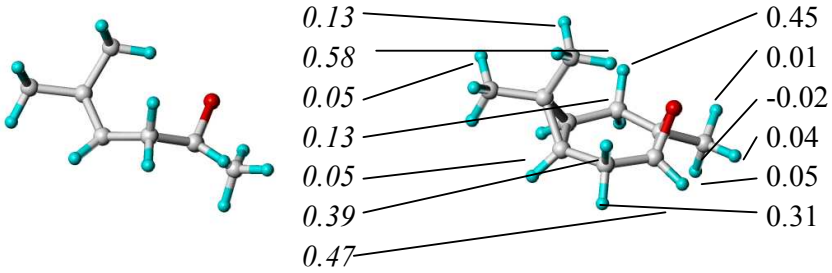
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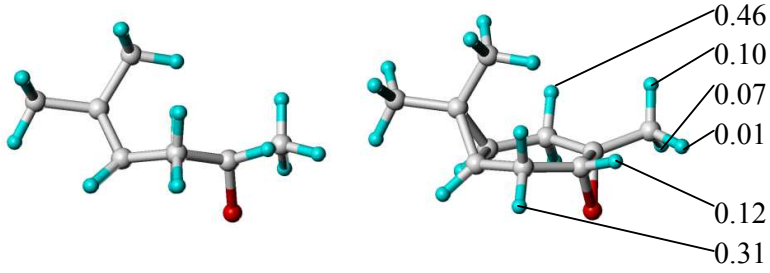
34a



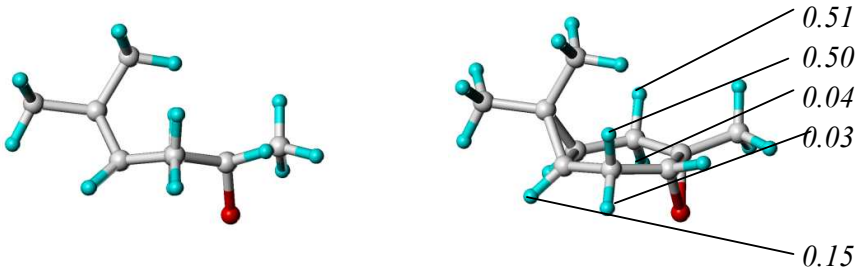
35s



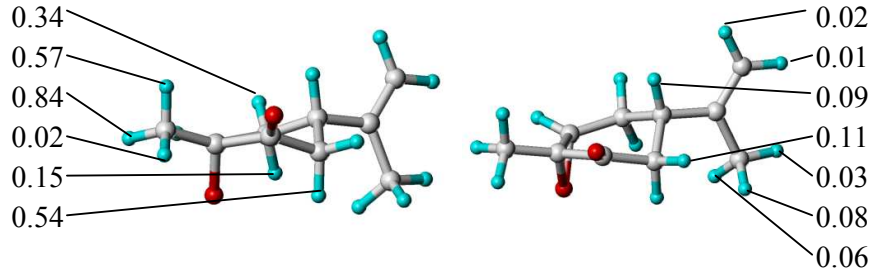
35a



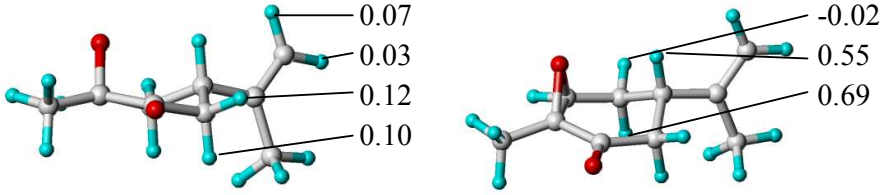
35a



36s


0.34
0.57
0.84
0.02
0.15
0.54
0.02
0.01
0.09
0.11
0.03
0.08
0.06

36a


0.07
0.03
0.12
0.10
-0.02
0.55
0.69