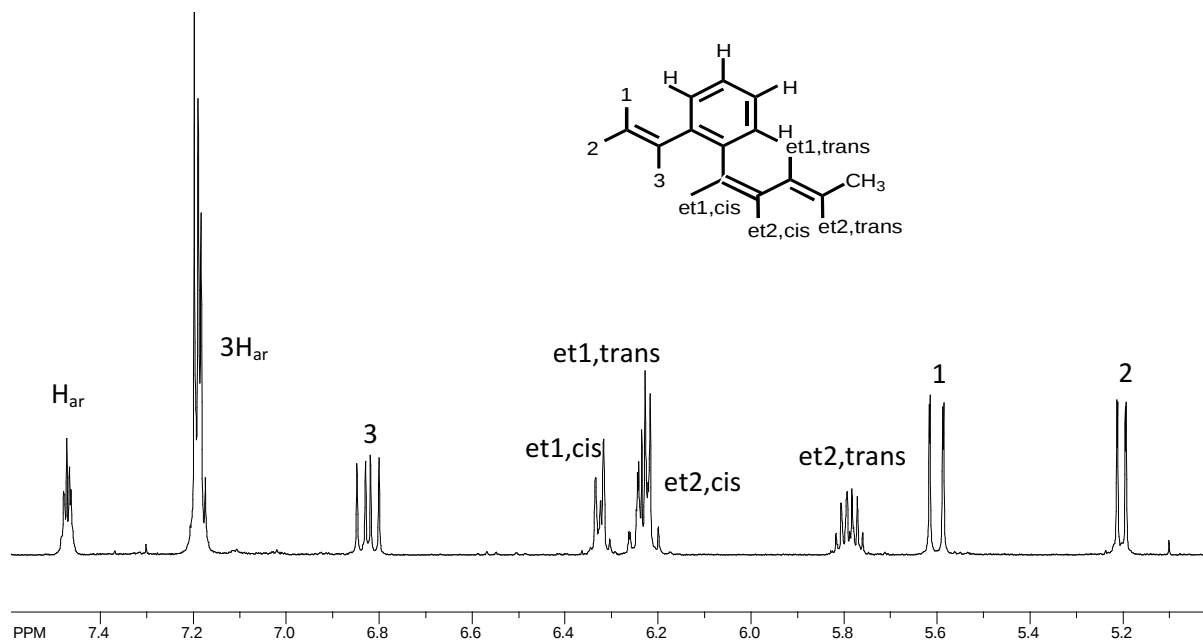


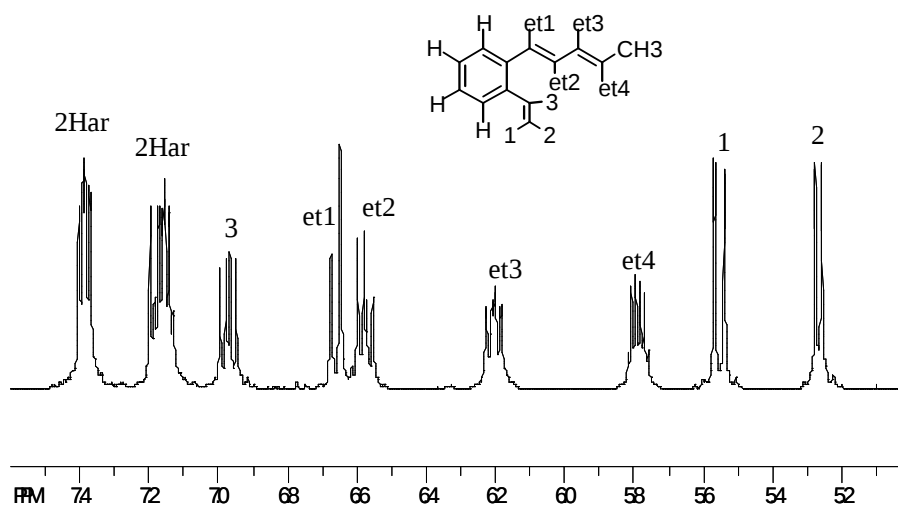
Thermal reaction of [3,4]-benzo-8-substituted-3*Z*,5*Z*,7*E*-octatetraenes and quantum-chemical study of the (8 π ,6 π)-electrocyclisation

Irena Škorić,^{a*} Fabijan Pavošević,^{a,b} Mario Vazdar,^b Željko Marinić,^c Marija Šindler-Kulyk,^a Mirjana Eckert-Maksić,^b Davor Margetić^{*b}

Supplementary information

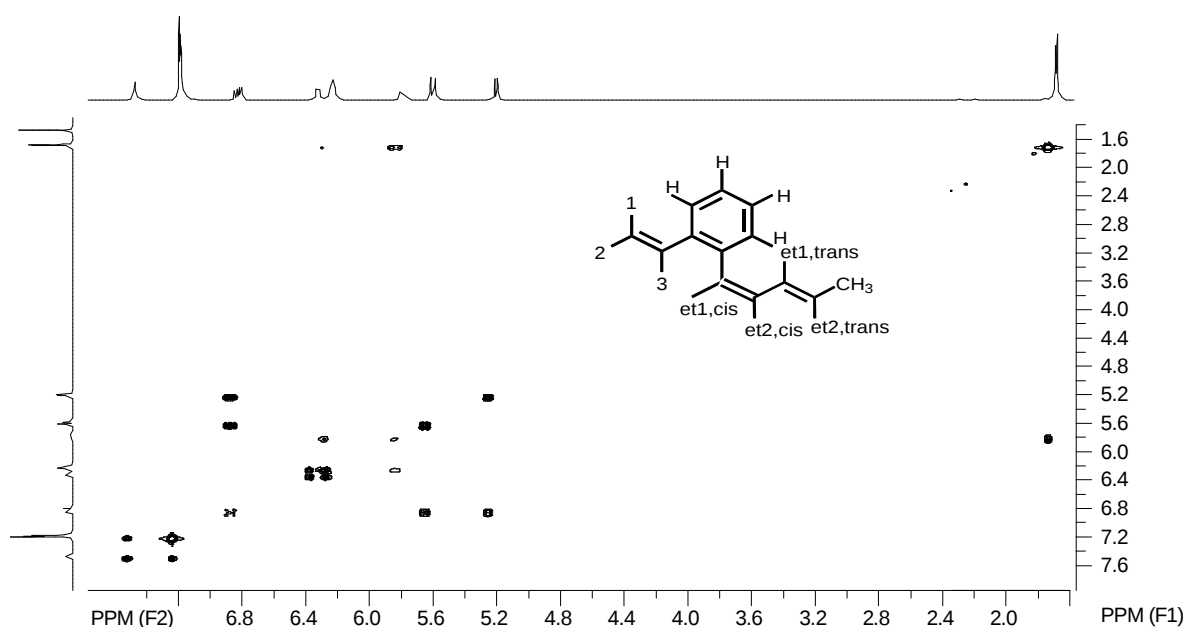


Part of the ¹H NMR spectrum (all the signals except for the methyl group) *cis,trans*-7a.

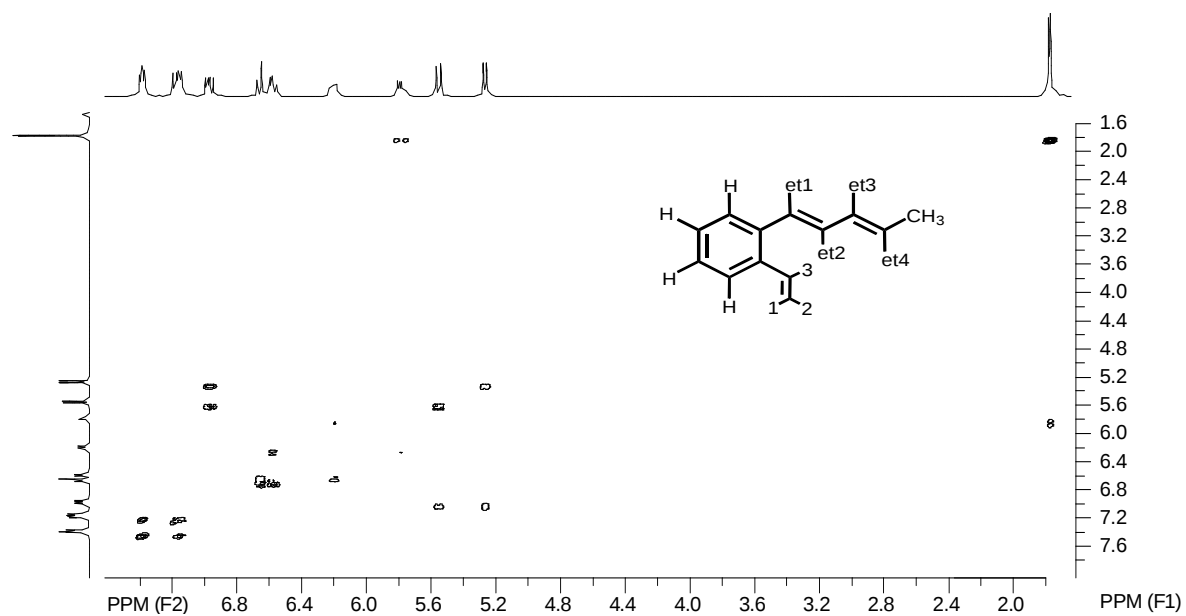


Part of the ¹H NMR spectrum (all the signals except for the methyl group) *trans,trans*-7a.

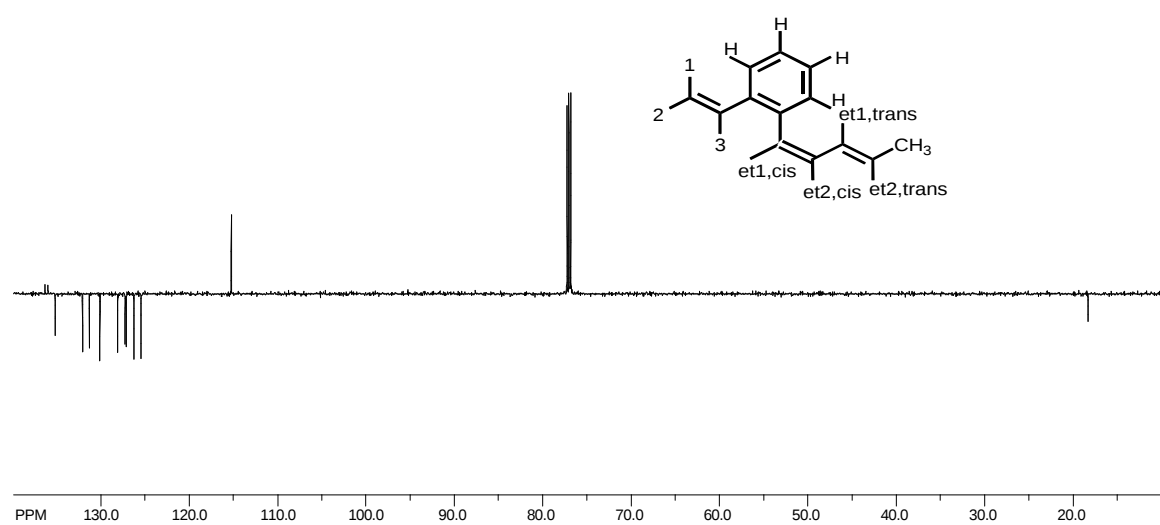
* Corresponding author. Tel.: +385-1-456-1008; fax: +385-1-468-0195



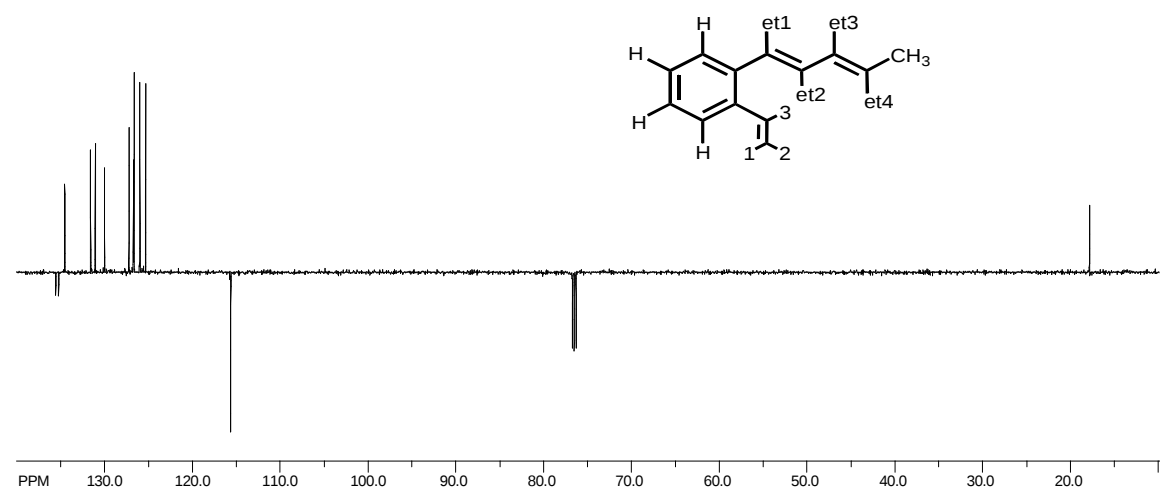
^1H - ^1H COSY NMR spectrum for *cis,trans*-7a.



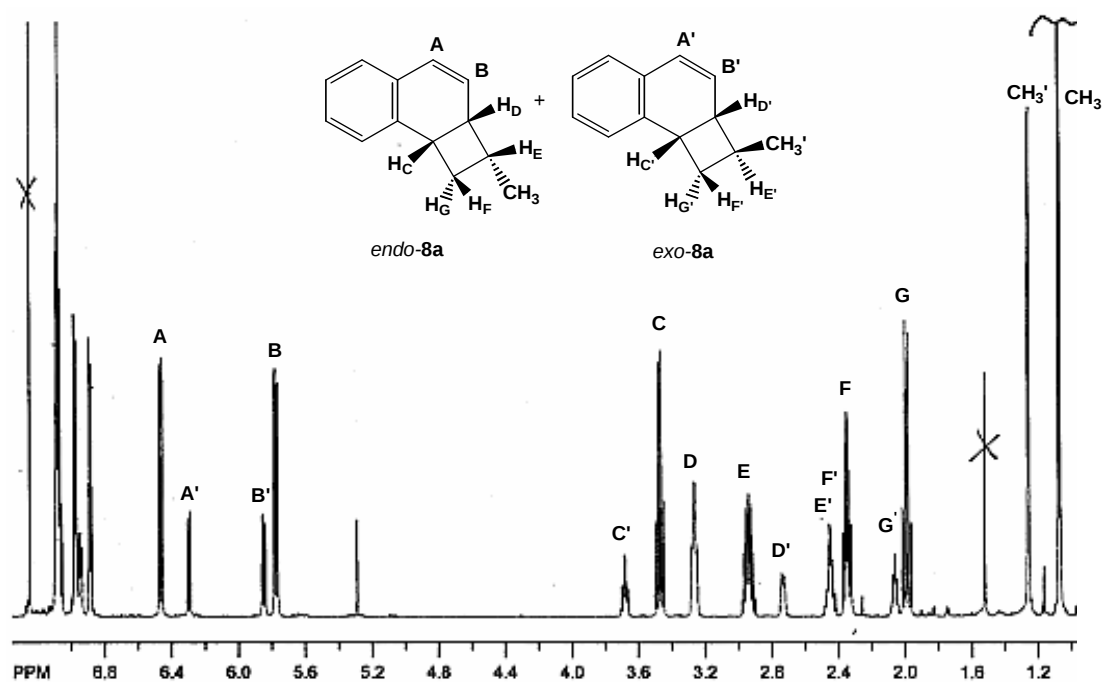
^1H - ^1H COSY NMR spectrum for *trans,trans*-7a.



^{13}C NMR spectrum for *cis,trans*-7a.

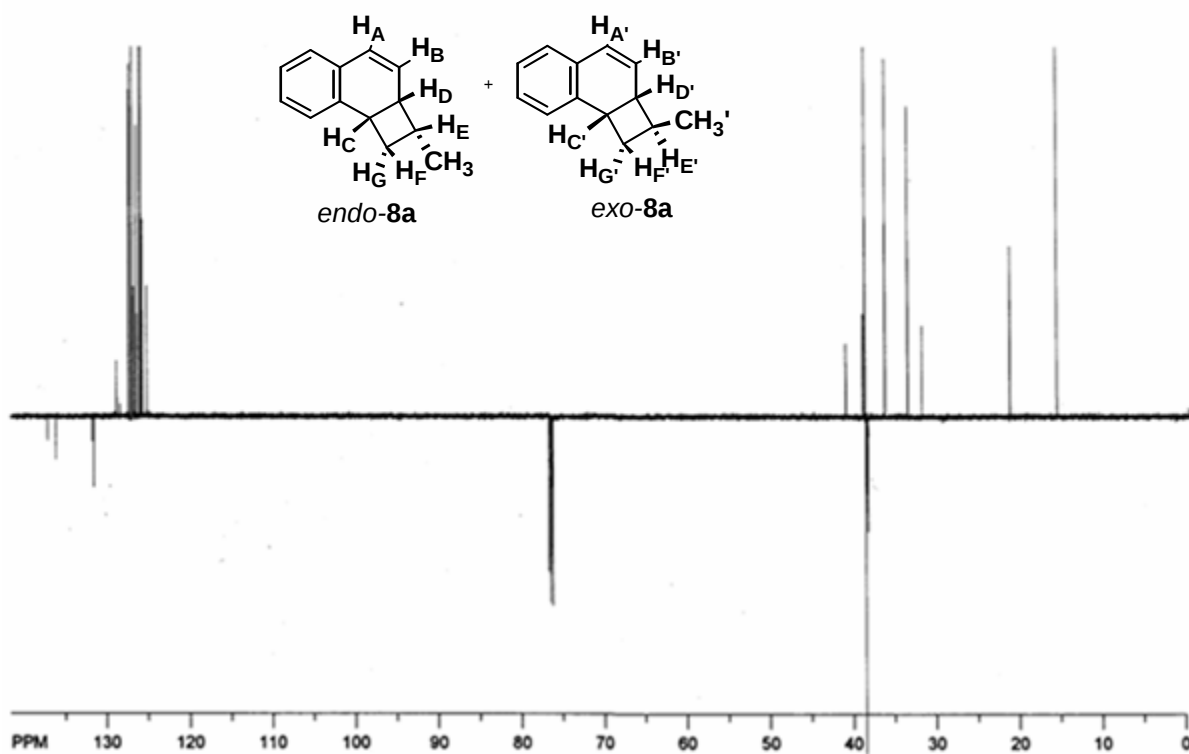


^{13}C NMR spectrum for *trans,trans*-7a.

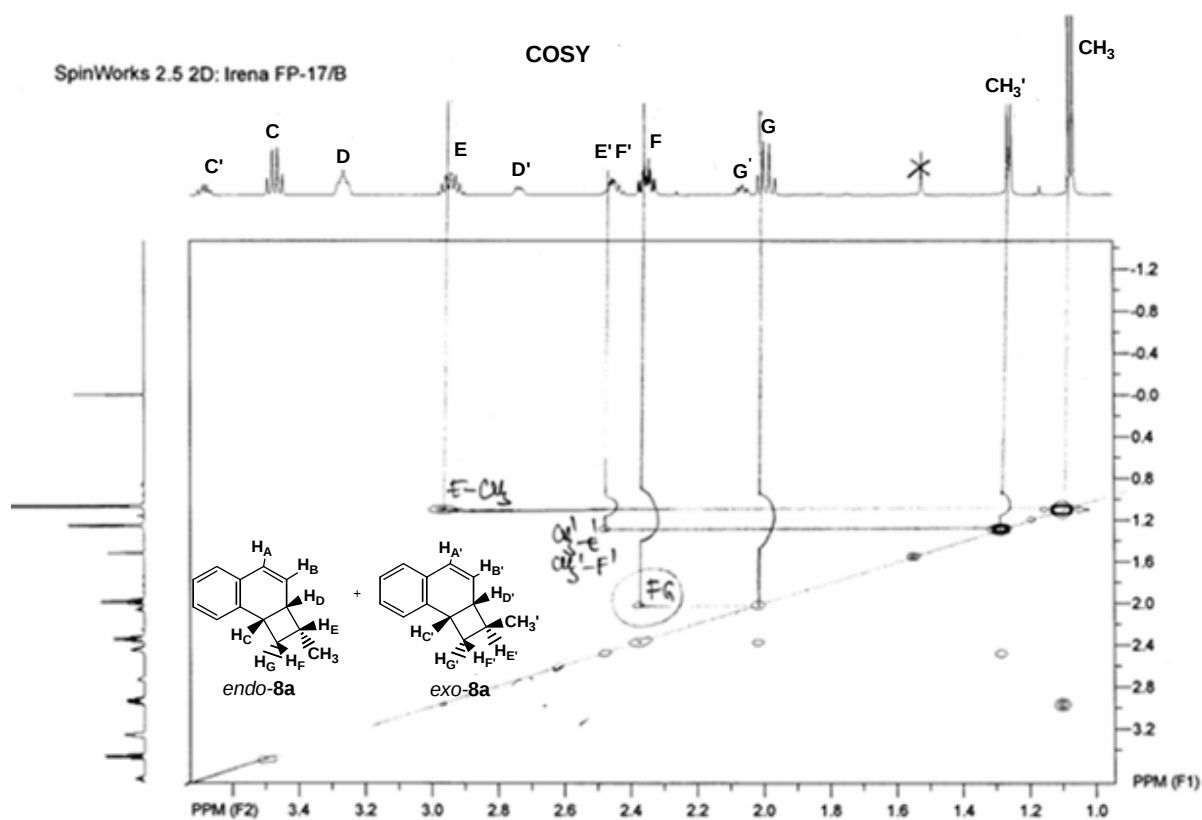


^1H NMR spectrum of reaction mixture of *endo-8a* and *exo-8a*.

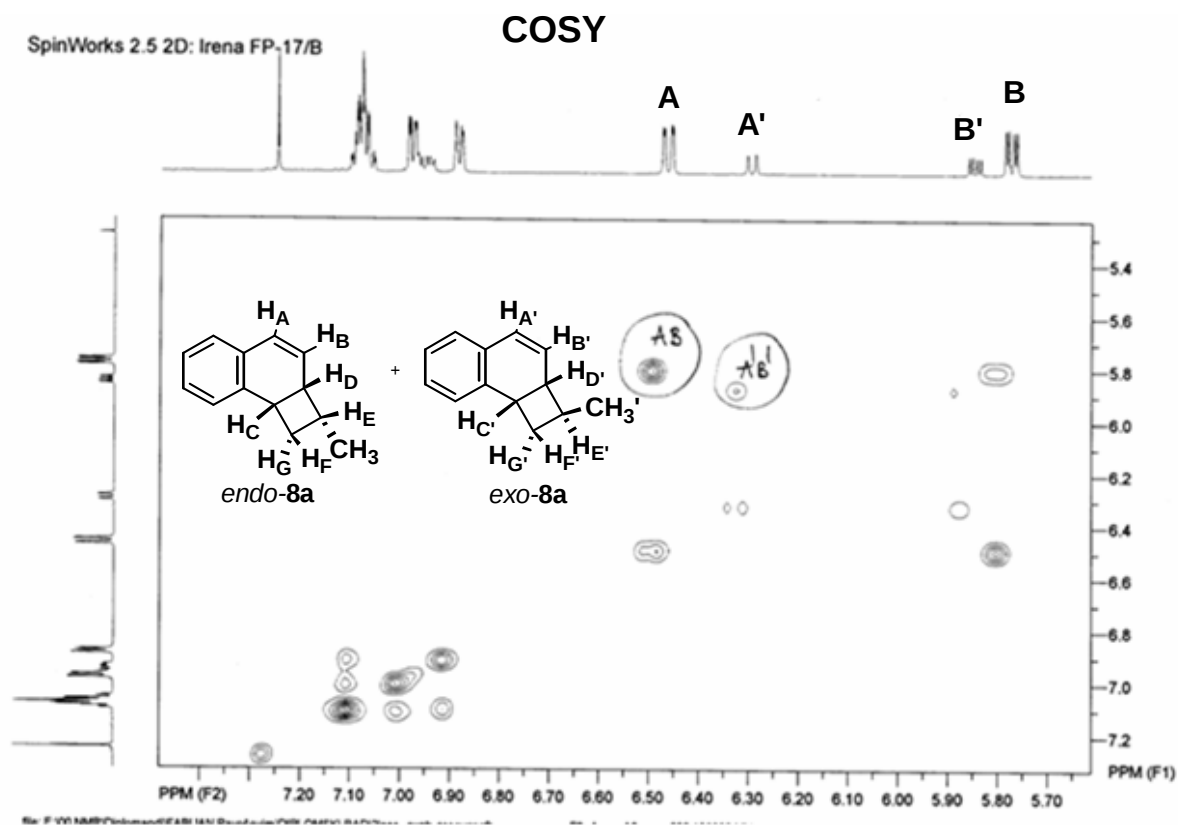
SpinWorks 2.5: Irena FP-17/B



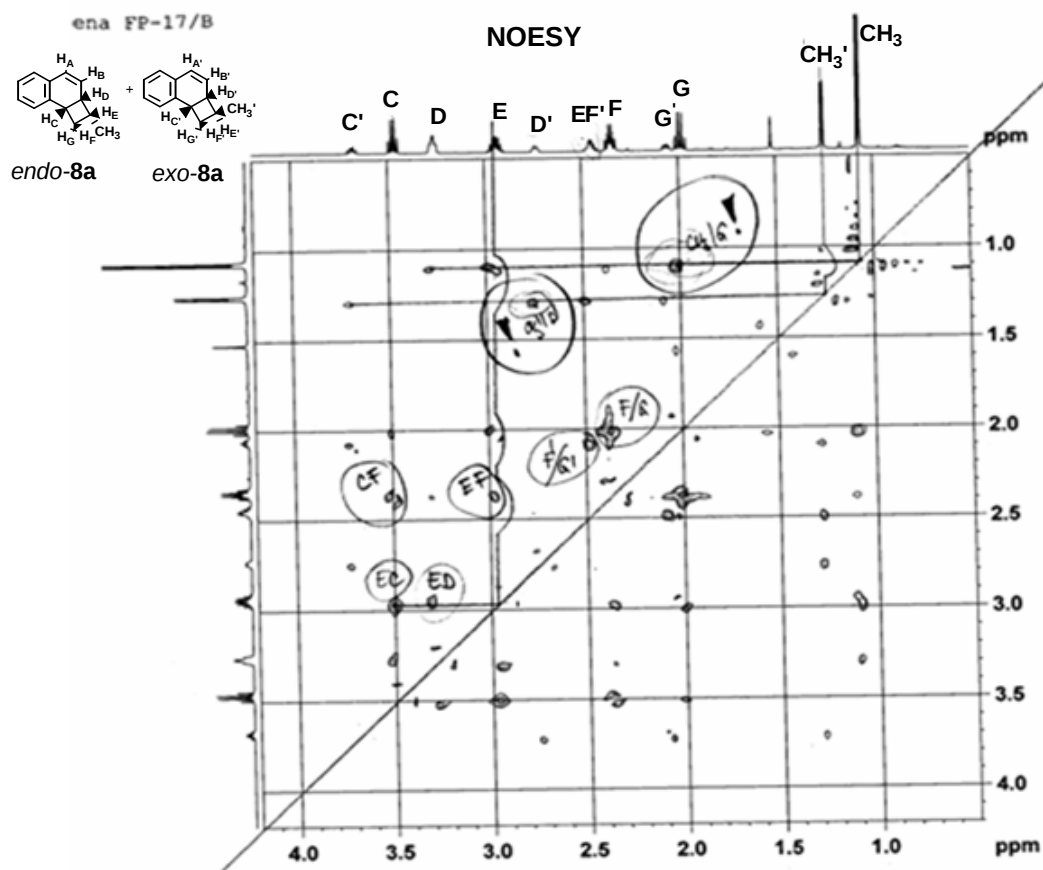
^{13}C NMR spectrum of reaction mixture of *endo-8a* and *exo-8a*.



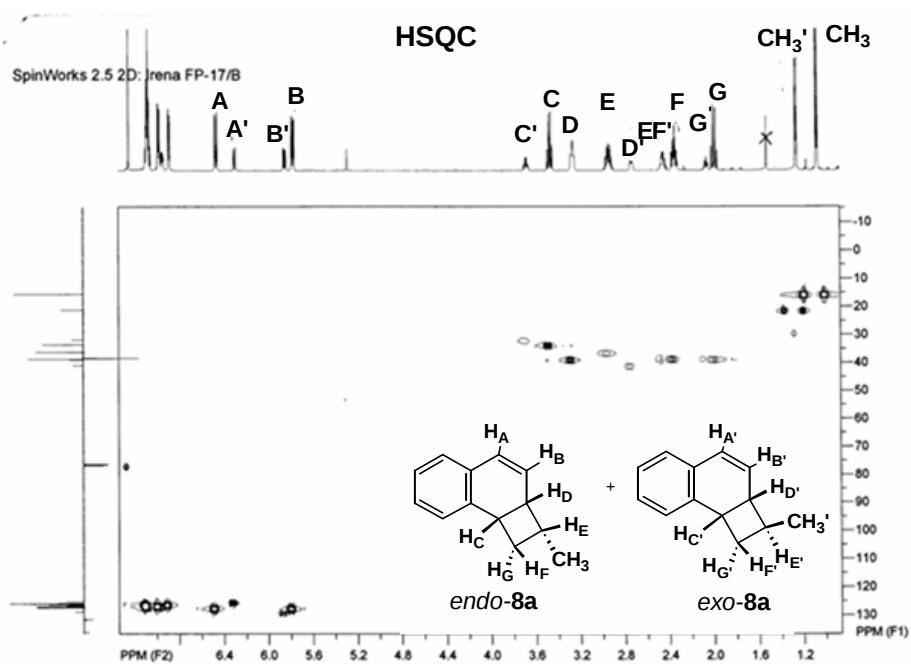
Part of the ^1H - ^1H COSY spectrum of reaction mixture of *endo*-8a and *exo*-8a.



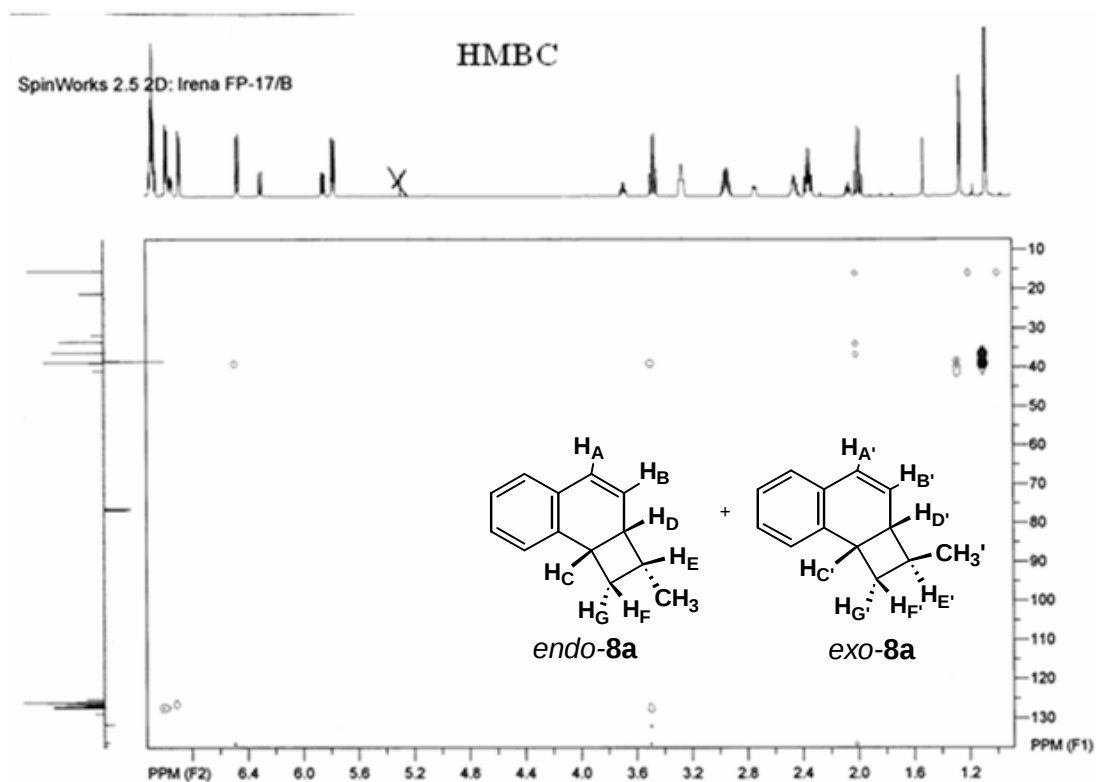
Part of the ^1H - ^1H COSY spectrum of reaction mixture of *endo*-8a and *exo*-8a.



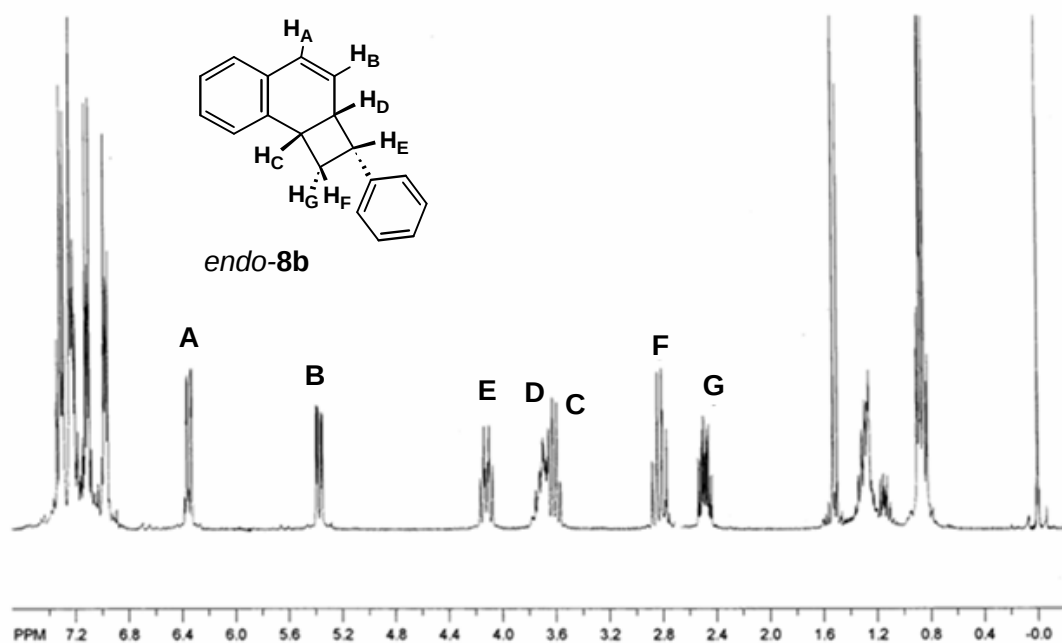
Part of the NOESY spectrum of reaction mixture of *endo-8a* and *exo-8a*.



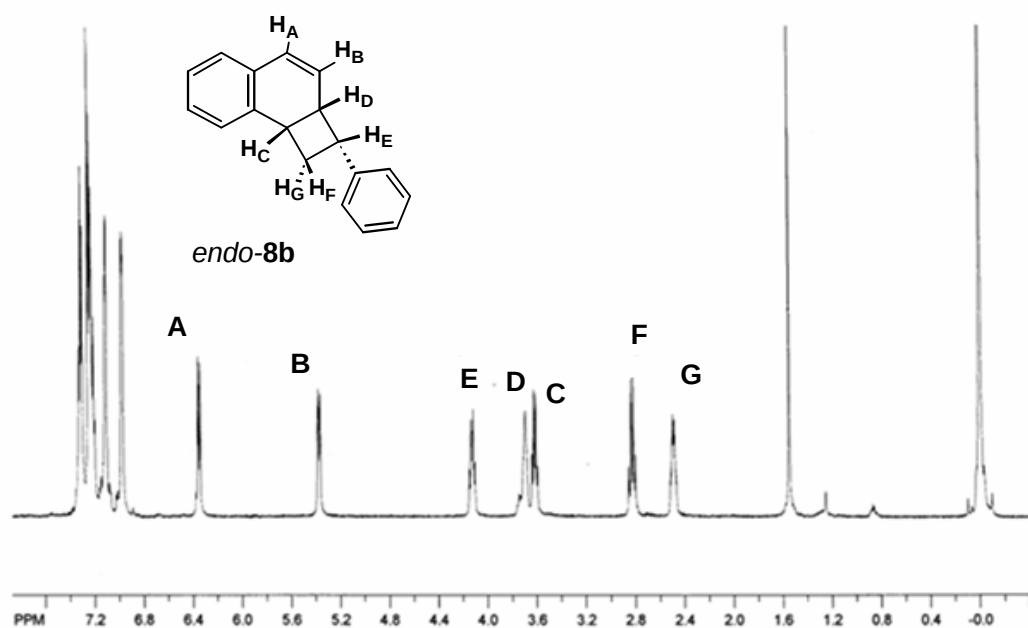
HSQC spectrum of reaction mixture of *endo-8a* and *exo-8a*.



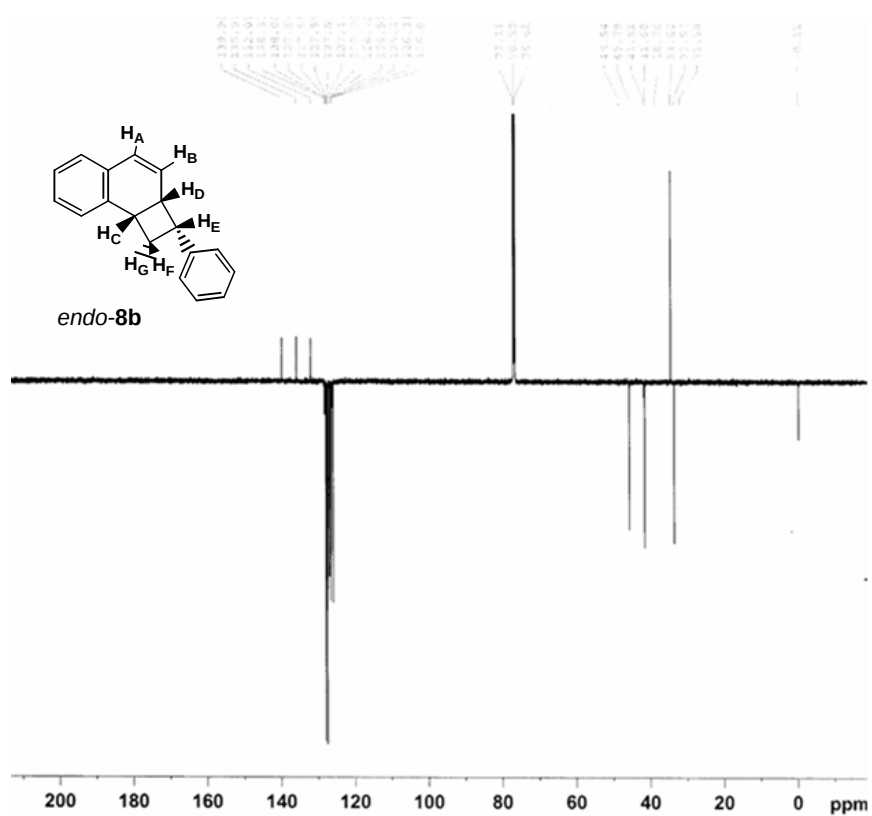
HMBC spectrum of reaction mixture of *endo-8a* and *exo-8a*.



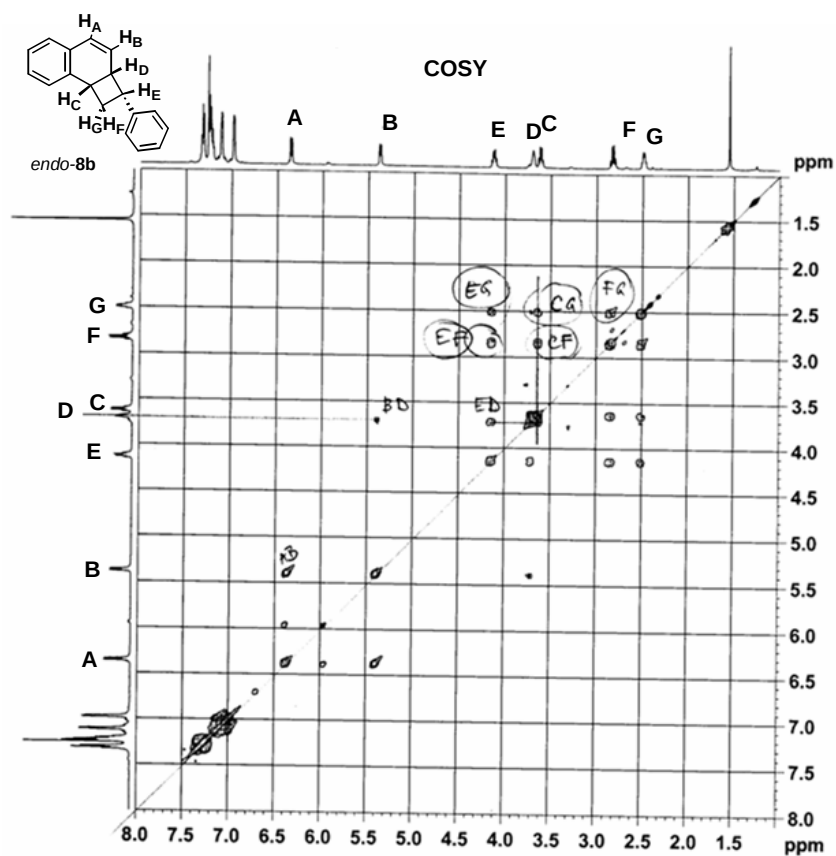
¹H NMR spectrum of *endo-8b* (300 MHz).



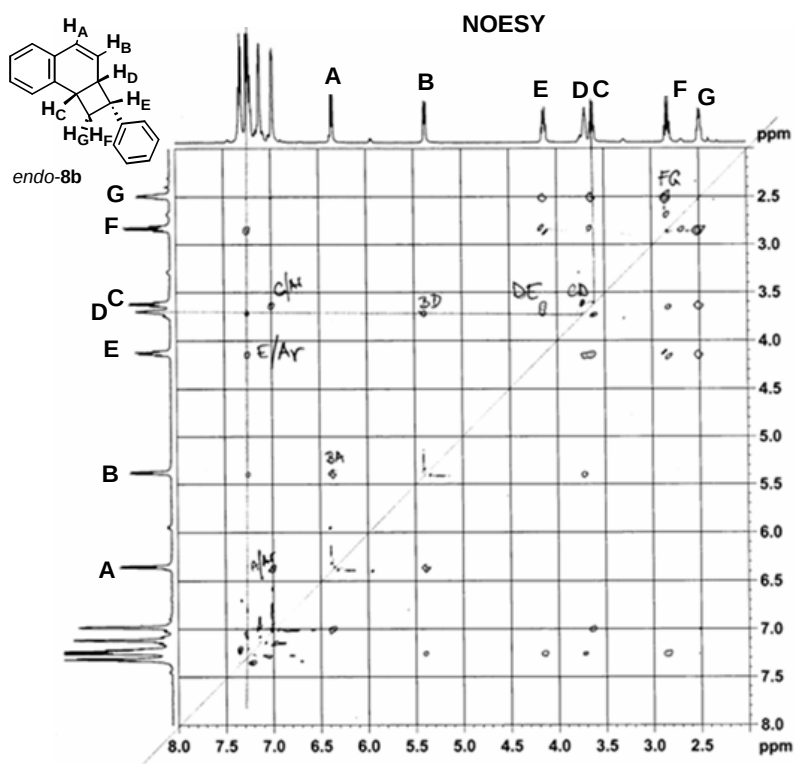
^1H NMR spectrum of *endo-8b* (600 MHz).



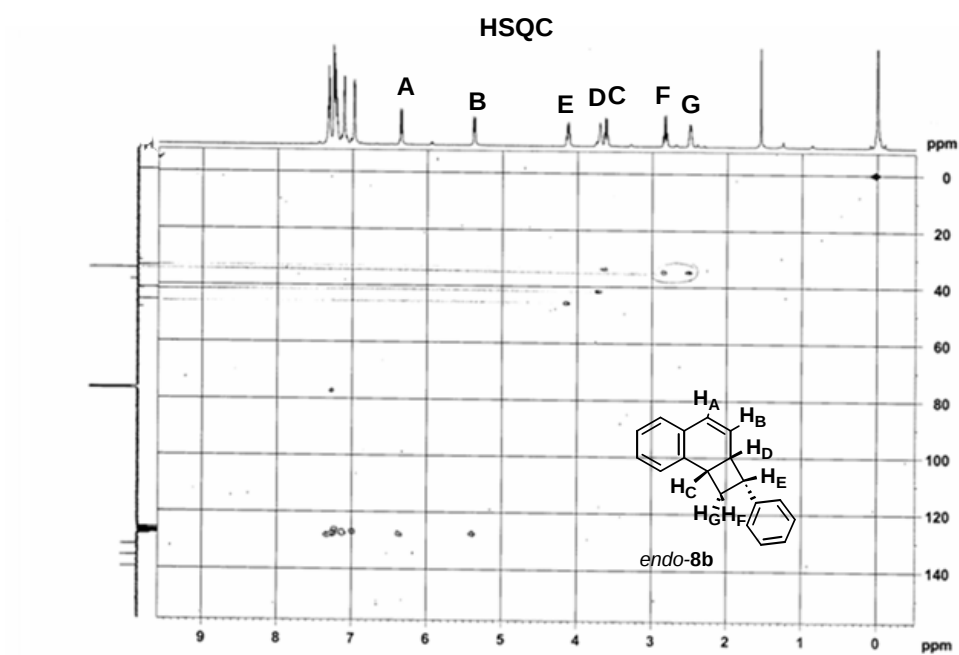
^{13}C NMR spectrum of *endo-8b*.



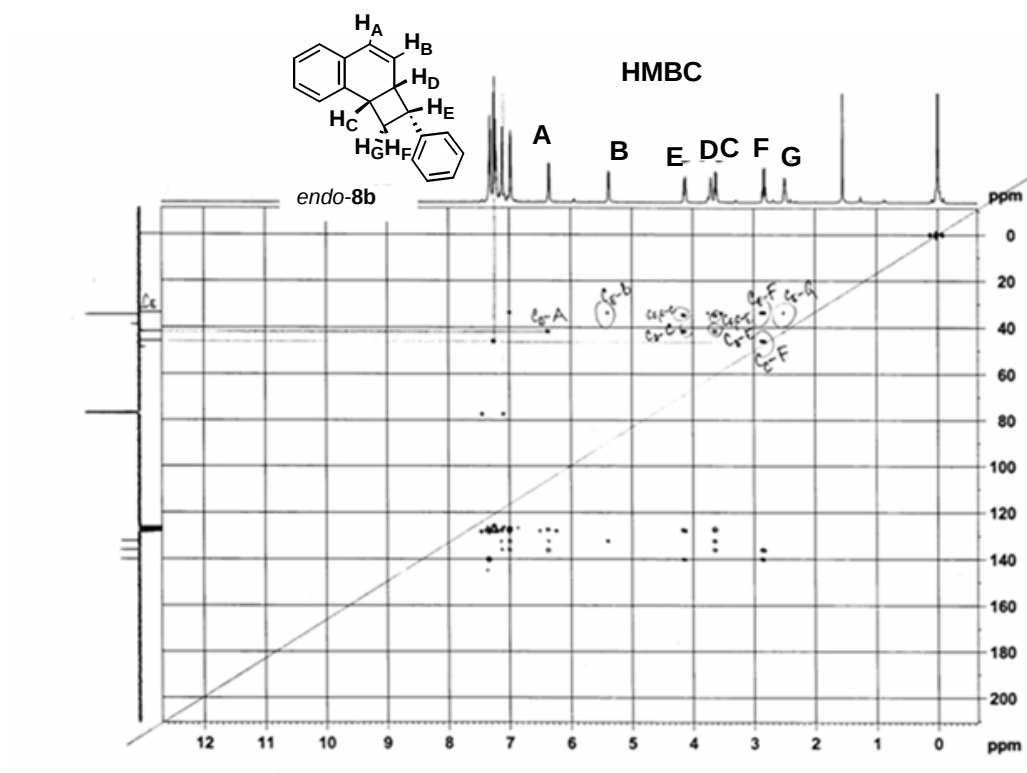
^1H - ^1H COSY NMR spectrum of *endo*-8b.



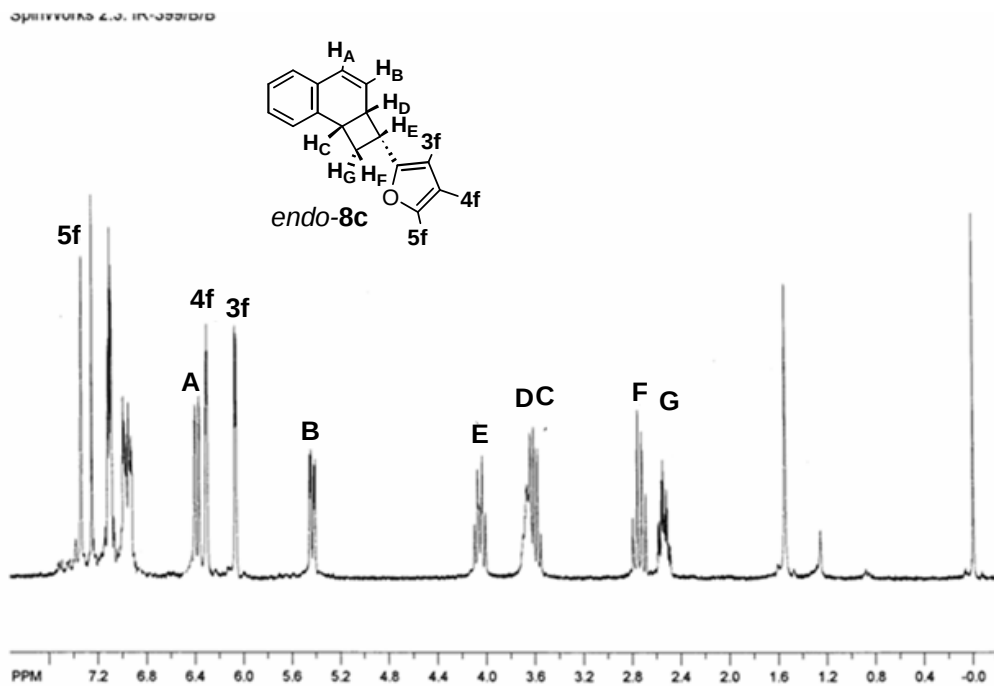
NOESY NMR spectrum of *endo*-8b.



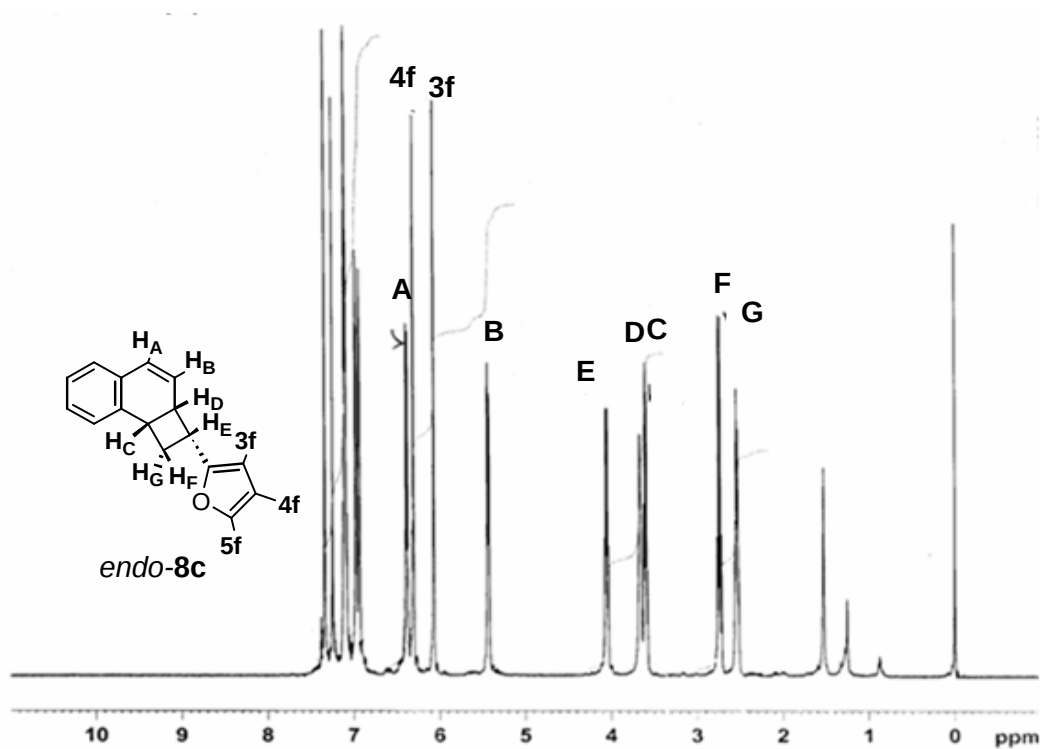
HSQC NMR spectrum of *endo-8b*.



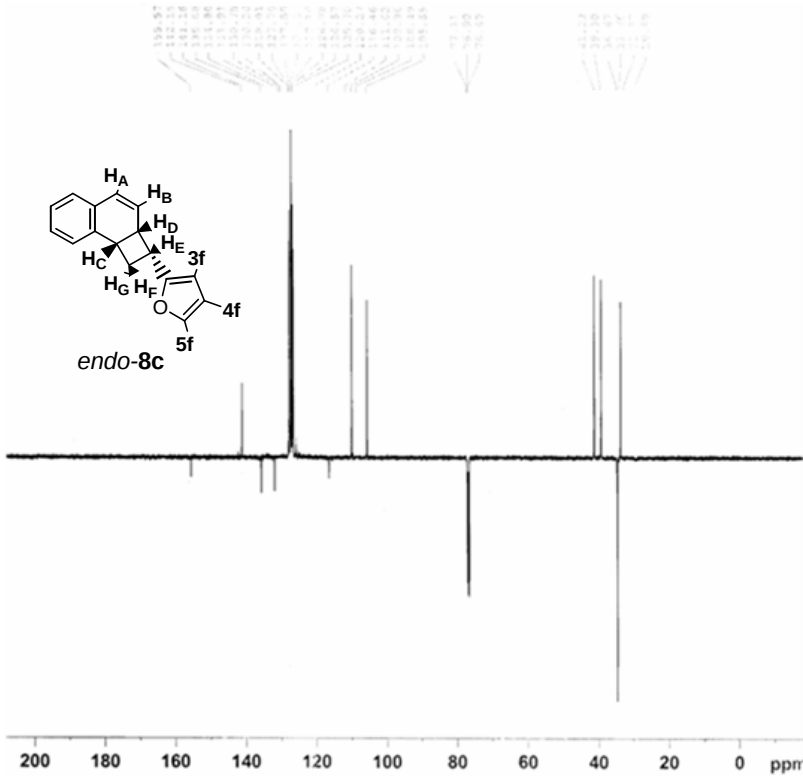
HMBC NMR spectrum of *endo-8b*.

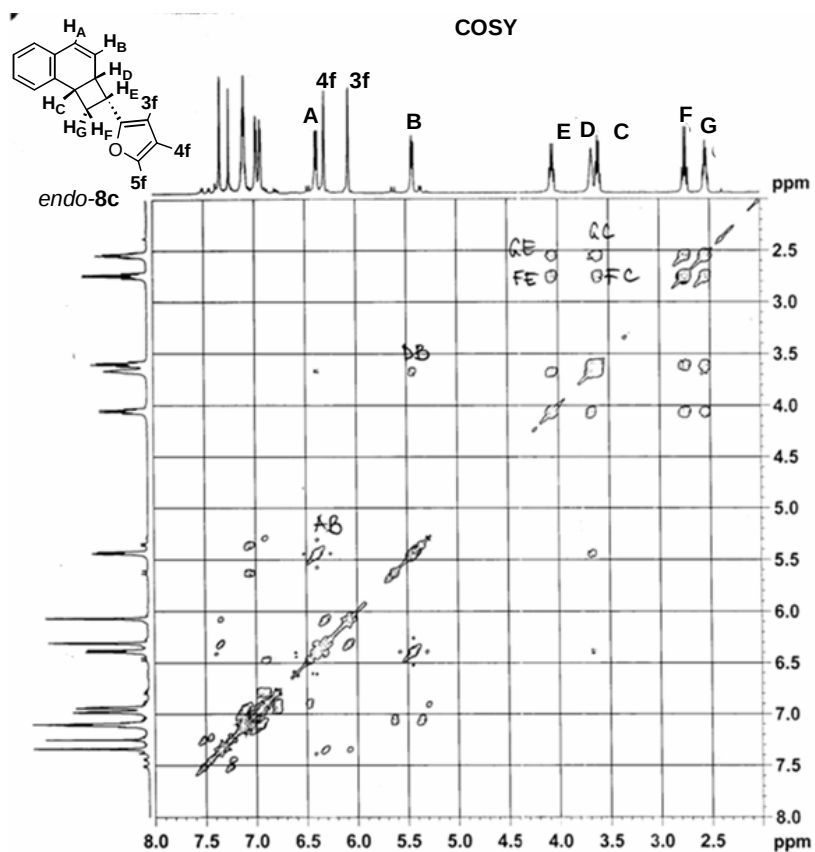


¹H NMR spectrum of *endo-8c* (300 MHz).

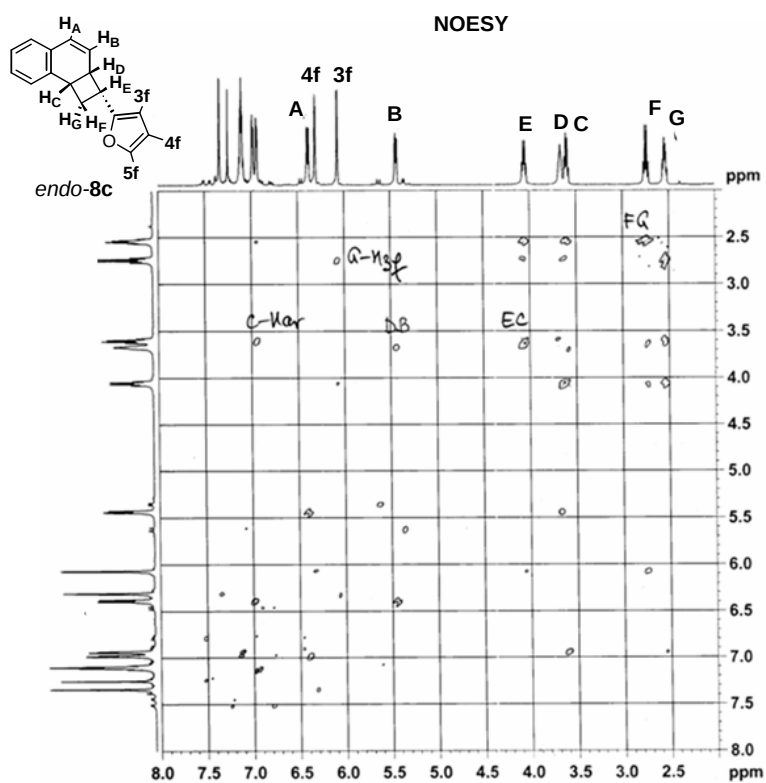


¹H NMR spectrum of *endo-8c* (600 MHz).

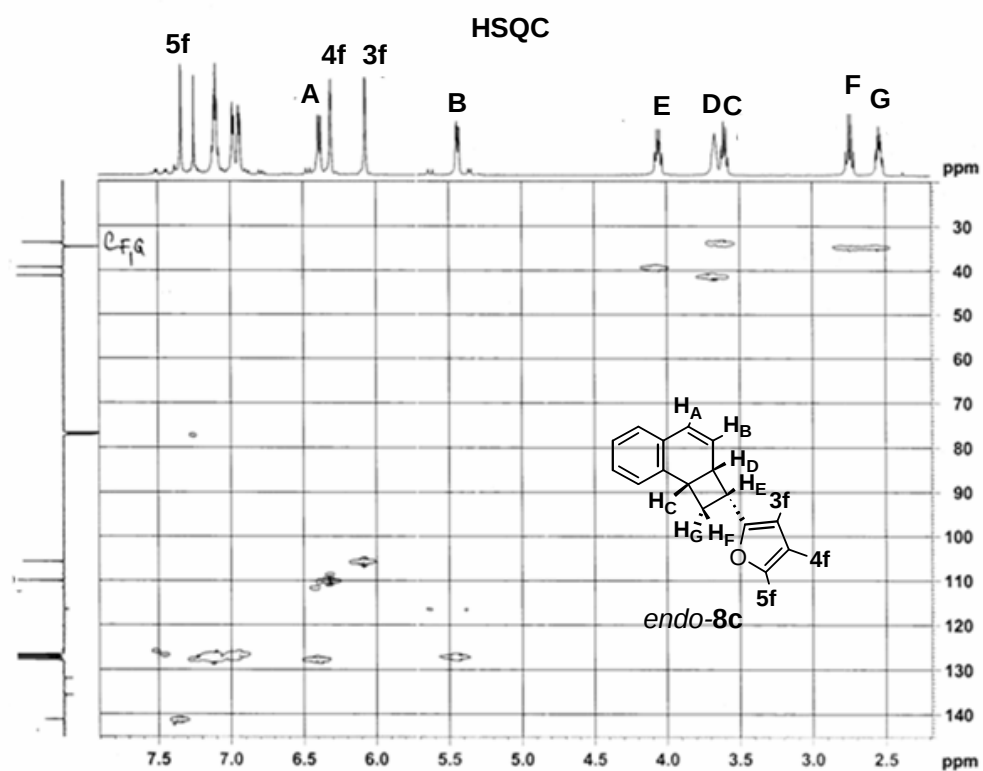
 ^{13}C NMR spectrum of *endo*-**8c**.



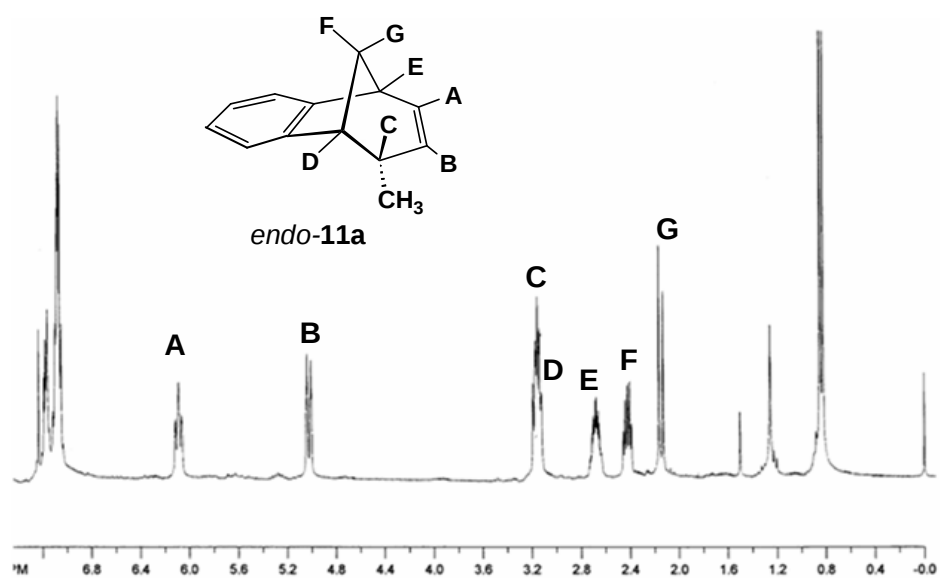
^1H - ^1H COSY NMR spectrum of *endo-8c*.



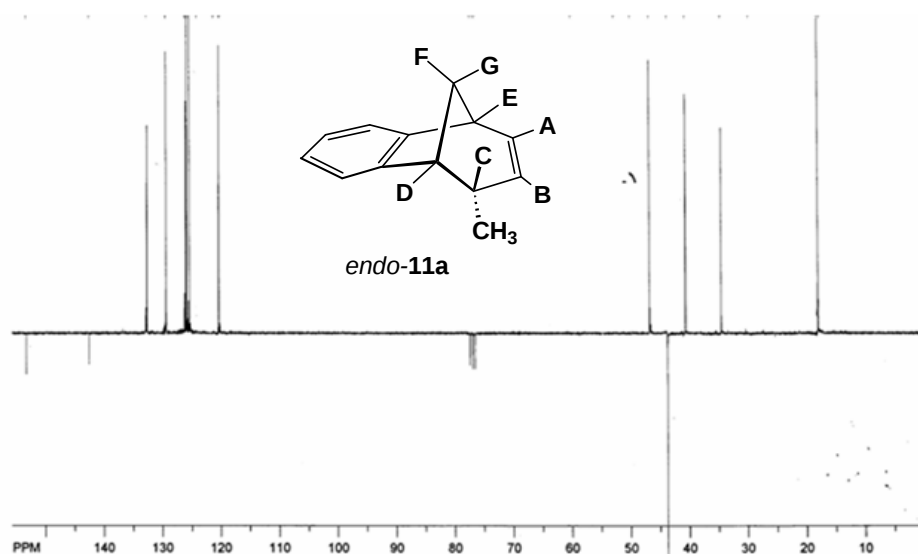
NOESY NMR spectrum of *endo-8c*.



HSQC NMR spectrum of *endo-8c*.



¹H NMR spectrum of *endo-11a*.



^{13}C NMR spectrum of *endo-11a*.

Table S1. Cartesian coordinates of optimized structures obtained at the M06/6-31+G(d,p) level of theory. The number of imaginary frequencies (NImag) is given in parenthesis.

Structure 7a (NImag = 0)

C	-2.047066	-2.207486	0.162063
C	-2.403618	-0.925644	0.552003
C	-1.657187	0.200401	0.170063
C	-0.533328	0.015668	-0.665781
C	-0.192304	-1.285226	-1.058291
C	-0.926594	-2.388547	-0.646922
H	-2.642321	-3.059979	0.480367
H	-3.278381	-0.777317	1.184380
H	0.666284	-1.415058	-1.714412
H	-0.637757	-3.385084	-0.972834
C	0.223532	1.145733	-1.233389
H	-0.382526	1.903978	-1.735158
C	1.556818	1.319676	-1.235715
H	1.939820	2.160026	-1.817891
C	-2.097538	1.498668	0.693060
H	-3.142509	1.518458	1.012112
C	-1.372572	2.608892	0.874933
H	-0.314514	2.665588	0.630032
H	-1.827167	3.497902	1.304394
C	2.568066	0.545164	-0.517273
H	3.542564	0.451267	-1.005273
C	2.420460	0.015419	0.704751

H	1.465307	0.146785	1.220921
C	3.474289	-0.749199	1.427068
H	3.138271	-1.770470	1.650895
H	4.395354	-0.816782	0.836894
H	3.718313	-0.284644	2.391157

Structure 12aTS (NImag = 1)

C	-3.234476	-0.969287	-0.384805
C	-2.009211	-1.506944	-0.107222
C	-0.865029	-0.718761	0.230139
C	-0.977773	0.720280	0.136661
C	-2.302470	1.224295	-0.081759
C	-3.388236	0.432815	-0.340991
H	-4.080234	-1.612234	-0.615383
H	-1.886305	-2.589204	-0.095470
H	-2.432503	2.305291	-0.084788
H	-4.358176	0.887132	-0.528719
C	-0.000142	1.772112	0.209081
H	-0.508520	2.731081	0.331043
C	1.372852	1.974897	0.113922
H	1.658416	3.008960	0.313918
C	0.258077	-1.462272	0.665474
H	0.218421	-2.533540	0.456289
C	1.428508	-0.950817	1.190602
H	1.389966	0.003010	1.706999
H	2.184921	-1.645707	1.554010
C	2.449601	1.120603	-0.147942
H	3.445101	1.486132	0.116630
C	2.324070	-0.205337	-0.552115
H	1.450204	-0.430080	-1.159931
C	3.525564	-1.057387	-0.827767
H	3.903683	-0.880715	-1.843259
H	4.338291	-0.839683	-0.124290
H	3.286864	-2.124791	-0.753705

Structure 13a (NImag = 0)

C	-3.339605	-0.831566	-0.329831
C	-2.124330	-1.359430	-0.602959
C	-0.904293	-0.701101	-0.167493
C	-1.018049	0.707676	0.227503
C	-2.333963	1.150655	0.646434
C	-3.443712	0.424557	0.371095
H	-4.245375	-1.366434	-0.605552

H	-2.031689	-2.338602	-1.071271
H	-2.416886	2.132921	1.110295
H	-4.425877	0.803566	0.643706
C	-0.035167	1.651069	0.089939
H	-0.335940	2.651605	0.412760
C	1.220805	1.666375	-0.637418
H	1.374920	2.638517	-1.114604
C	0.231312	-1.430207	-0.023125
H	0.200112	-2.459575	-0.390088
C	1.465643	-1.029684	0.701185
H	1.238890	-0.251336	1.446163
H	1.851911	-1.899800	1.251647
C	2.234566	0.799632	-0.845924
H	3.034192	1.183188	-1.485461
C	2.574932	-0.513101	-0.213855
H	2.726551	-1.257812	-1.012364
C	3.896629	-0.366951	0.543004
H	4.690033	0.019890	-0.107654
H	3.779845	0.334324	1.379996
H	4.231008	-1.329972	0.947703

Structure 15aTS (NImag = 1)

C	3.309777	-0.943693	0.175874
C	2.110261	-1.477107	-0.127413
C	0.865277	-0.712479	-0.237755
C	0.982119	0.759412	-0.038814
C	2.315936	1.247952	0.302250
C	3.413211	0.470169	0.410648
H	4.191227	-1.576003	0.246450
H	2.031865	-2.549794	-0.296036
H	2.409648	2.319052	0.472215
H	4.372813	0.911577	0.668477
C	0.061779	1.775802	-0.176723
H	0.524417	2.759847	-0.072581
C	-1.343185	1.914838	-0.465441
H	-1.595595	2.883551	-0.901062
C	-0.222052	-1.496063	-0.504758
H	0.027288	-2.555560	-0.584933
C	-1.681795	-1.250430	-0.630592
H	-1.944448	-0.900325	-1.637811
H	-2.182094	-2.223408	-0.521263
C	-2.376335	1.097496	-0.196913
H	-3.372360	1.417092	-0.514157
C	-2.276818	-0.251612	0.414094
H	-1.579620	-0.211156	1.264084

C	-3.634624	-0.740135	0.903383
H	-4.074238	-0.040413	1.623523
H	-4.333840	-0.836958	0.060940
H	-3.556116	-1.720502	1.386778

Structure 16a (NImag = 0)

C	3.298760	-0.801336	-0.046919
C	2.141553	-1.320813	-0.505835
C	0.837948	-0.686318	-0.287898
C	0.908099	0.749228	0.097530
C	2.153296	1.179741	0.728008
C	3.290899	0.457255	0.658256
H	4.233729	-1.340069	-0.180135
H	2.138080	-2.296997	-0.988994
H	2.154545	2.161502	1.199413
H	4.210550	0.835604	1.098378
C	0.038524	1.744397	-0.242821
H	0.380486	2.756382	-0.010759
C	-1.213269	1.674954	-0.966015
H	-1.355702	2.422867	-1.748876
C	-0.226589	-1.525884	-0.414603
H	0.056504	-2.525376	-0.757178
C	-1.666966	-1.482117	-0.027364
H	-2.275575	-1.844648	-0.872964
H	-1.810930	-2.244320	0.760871
C	-2.218491	0.830256	-0.697222
H	-3.118416	0.867226	-1.317279
C	-2.233544	-0.146923	0.436162
H	-1.586386	0.238958	1.239236
C	-3.646207	-0.330037	0.978495
H	-4.078499	0.624587	1.299278
H	-4.304772	-0.751961	0.205790
H	-3.659344	-1.013035	1.836123

Structure 14aTS (NImag = 1)

C	3.292135	-0.830075	0.177742
C	2.064011	-1.361663	0.460646
C	0.865828	-0.655533	0.139730
C	0.978088	0.729260	-0.230564
C	2.270781	1.227723	-0.576931
C	3.393091	0.467720	-0.392378
H	4.193508	-1.410005	0.361490
H	1.974241	-2.376529	0.846464

H	2.351026	2.254104	-0.931778
H	4.371370	0.871290	-0.642492
C	-0.051888	1.643249	0.060144
H	0.220496	2.693205	-0.065655
C	-1.179356	1.400040	0.854366
H	-1.424567	2.243574	1.509634
C	-0.374965	-1.288554	0.176418
H	-0.418829	-2.257745	0.682162
C	-1.448940	-1.042012	-0.847601
H	-1.146399	-0.239356	-1.533588
H	-1.653439	-1.936324	-1.454415
C	-1.935808	0.249595	1.075929
H	-2.498401	0.279938	2.016725
C	-2.605486	-0.600695	0.010054
H	-3.010997	-1.491757	0.513882
C	-3.742975	0.128883	-0.690394
H	-4.493066	0.481979	0.028793
H	-3.356618	1.005849	-1.227052
H	-4.248546	-0.523214	-1.413486

Structure 17aTS (NImag = 1)

C	-3.190716	-0.889490	0.012849
C	-1.988627	-1.324824	0.499274
C	-0.766478	-0.606605	0.289165
C	-0.904658	0.764642	-0.164088
C	-2.165783	1.159857	-0.717021
C	-3.269393	0.357710	-0.657124
H	-4.077715	-1.509502	0.118227
H	-1.921139	-2.304419	0.971074
H	-2.240585	2.162110	-1.136976
H	-4.216049	0.695433	-1.072315
C	-0.040239	1.796553	0.259393
H	-0.461301	2.802032	0.212542
C	1.119386	1.601552	1.007088
H	1.346666	2.329177	1.789061
C	0.421081	-1.305628	0.591830
C	1.603992	-1.510843	-0.325342
H	2.337645	-2.144849	0.195007
H	1.332346	-2.038790	-1.255616
C	1.917544	0.481667	0.858356
C	2.184925	-0.134044	-0.502368
H	2.684638	0.284133	1.613822
H	0.245075	-2.148840	1.269038
C	3.654291	-0.093668	-0.886074
H	3.822569	-0.574463	-1.857648
H	4.024973	0.936456	-0.949232

H	4.262439	-0.624912	-0.140423
H	1.598851	0.421358	-1.248451

Structure *endo*-8a (NImag = 0)

C	3.181708	-0.995102	-0.090766
C	1.891816	-1.420582	0.225334
C	0.830022	-0.522403	0.259312
C	1.068194	0.838414	-0.009445
C	2.363057	1.256389	-0.326965
C	3.416191	0.347559	-0.371996
H	3.999469	-1.711606	-0.117694
H	1.703139	-2.471881	0.443918
H	2.542557	2.311278	-0.533395
H	4.418610	0.687880	-0.621060
C	-0.033185	1.795743	0.083124
H	0.185224	2.827778	-0.193052
C	-1.252317	1.465835	0.532808
H	-2.018275	2.237080	0.623712
C	-0.572813	-0.973600	0.514936
H	-0.580643	-1.836977	1.194049
C	-1.466049	-1.265749	-0.715934
H	-1.161248	-0.645988	-1.570903
H	-1.553807	-2.305873	-1.049487
C	-1.618568	0.082154	0.958573
H	-1.891053	0.088729	2.025360
C	-2.651770	-0.627681	0.032458
H	-3.170190	-1.397349	0.622892
C	-3.653251	0.187841	-0.751860
H	-4.359247	0.710396	-0.093550
H	-3.147477	0.943639	-1.367176
H	-4.238448	-0.451591	-1.423876

Structure *exo*-8a (NImag = 0)

C	-2.920880	-1.259250	-0.161840
C	-1.624272	-1.464587	0.304124
C	-0.713004	-0.414926	0.395110
C	-1.120737	0.879157	0.019836
C	-2.426329	1.076504	-0.444015
C	-3.322958	0.019099	-0.540258
H	-3.614508	-2.094369	-0.227354
H	-1.308933	-2.463961	0.605991
H	-2.733250	2.081163	-0.733824
H	-4.332512	0.191245	-0.906111

C	-0.194639	2.007312	0.121423
H	-0.600805	2.999150	-0.077728
C	1.098749	1.849938	0.435081
H	1.758525	2.714769	0.494216
C	0.671571	-0.661946	0.936355
C	1.556128	-1.570040	0.048640
H	2.299360	-2.111717	0.649998
H	1.049532	-2.281717	-0.614503
C	1.665244	0.490985	0.653793
C	2.171397	-0.305370	-0.582467
H	2.459121	0.504141	1.415345
H	0.592241	-0.974393	1.987810
C	3.646586	-0.283449	-0.901748
H	3.894332	-0.975575	-1.715985
H	3.977514	0.718221	-1.204543
H	4.236014	-0.579153	-0.022369
H	1.577303	-0.003312	-1.458162

Structure 7b (NImag = 0)

C	-2.100512	-1.378431	1.810116
C	-2.174172	-0.012378	1.583457
C	-1.472239	0.603494	0.535422
C	-0.701845	-0.204325	-0.330844
C	-0.646110	-1.584130	-0.093254
C	-1.323655	-2.170144	0.966230
H	-2.650832	-1.825440	2.634463
H	-2.779708	0.612443	2.239168
H	-0.064567	-2.200773	-0.775661
H	-1.262615	-3.244654	1.121276
C	-0.055649	0.331352	-1.541236
H	-0.708139	0.916563	-2.193559
C	1.211968	0.141446	-1.954479
H	1.458062	0.506358	-2.953295
C	-1.576343	2.063139	0.429509
H	-2.468930	2.483358	0.899544
C	-0.695387	2.915313	-0.107417
H	0.242063	2.586368	-0.550259
H	-0.883838	3.985584	-0.093361
C	2.322643	-0.458144	-1.226314
H	3.086693	-0.936501	-1.842950
C	2.507359	-0.389517	0.105184
H	1.767381	0.152834	0.699735
C	3.617368	-0.952251	0.867488

C	4.616044	-1.756655	0.295771
C	3.693712	-0.685317	2.242016
C	5.650746	-2.263286	1.068995
H	4.578526	-1.993517	-0.765962
C	4.728951	-1.193671	3.018357
H	2.922314	-0.067920	2.700604
C	5.714159	-1.984519	2.434859
H	6.413867	-2.885059	0.606074
H	4.764905	-0.972383	4.082629
H	6.525019	-2.385852	3.038076

Structure 12bTS (NImag = 1)

C	4.072791	-1.791817	0.121524
C	2.783853	-1.807347	-0.327528
C	1.968491	-0.633539	-0.410822
C	2.489429	0.599278	0.145009
C	3.874174	0.569509	0.525245
C	4.639415	-0.562939	0.529269
H	4.660472	-2.706140	0.143684
H	2.348421	-2.738637	-0.687335
H	4.316914	1.500536	0.875344
H	5.673231	-0.518054	0.863074
C	1.877983	1.866175	0.413971
H	2.653550	2.603613	0.631850
C	0.619222	2.455972	0.554449
H	0.681627	3.532858	0.717703
C	0.739467	-0.812976	-1.080311
H	0.438315	-1.850894	-1.238849
C	-0.168001	0.177970	-1.416787
H	0.208614	1.179989	-1.600593
H	-1.044353	-0.101146	-2.000263
C	-0.681525	1.961161	0.509382
H	-1.482098	2.698566	0.434479
C	-1.004861	0.599671	0.422339
H	-0.330750	-0.067392	0.955858
C	-2.391846	0.107063	0.367682
C	-2.685623	-1.161281	0.882661
C	-3.425251	0.838259	-0.232400
C	-3.977254	-1.673860	0.828975
H	-1.883828	-1.744698	1.335112
C	-4.717082	0.329181	-0.284041
H	-3.213374	1.810442	-0.675899
C	-4.999721	-0.928056	0.248852
H	-4.185818	-2.658371	1.241611
H	-5.508185	0.911861	-0.750696

H -6.010680 -1.325892 0.204549

Structure 13b (NImag = 0)

C	-3.304349	-0.892223	-0.358807
C	-2.080465	-1.342095	-0.719499
C	-0.872640	-0.696809	-0.234925
C	-1.021132	0.652013	0.322132
C	-2.338472	0.997808	0.820018
C	-3.430264	0.268739	0.487155
H	-4.199611	-1.422537	-0.674550
H	-1.968764	-2.255909	-1.301688
H	-2.439882	1.915699	1.397816
H	-4.417042	0.577317	0.824452
C	-0.073230	1.638629	0.264359
H	-0.397114	2.588377	0.699041
C	1.159831	1.773544	-0.488559
H	1.263556	2.791240	-0.876020
C	0.290543	-1.395600	-0.195701
H	0.290742	-2.375298	-0.680859
C	1.516267	-1.037888	0.563606
H	1.271336	-0.354237	1.390327
H	1.944152	-1.946854	1.008738
C	2.204911	0.976123	-0.795836
H	2.978702	1.449454	-1.404599
C	2.601216	-0.381194	-0.302831
H	2.764820	-1.035782	-1.174212
C	3.917735	-0.307460	0.446711
C	4.919221	-1.252077	0.215604
C	4.129656	0.666042	1.426533
C	6.105657	-1.228906	0.944086
H	4.764575	-2.016122	-0.546719
C	5.312832	0.692155	2.158289
H	3.356746	1.411350	1.613489
C	6.305416	-0.255466	1.919121
H	6.876842	-1.970333	0.746914
H	5.461277	1.456399	2.918132
H	7.231048	-0.234392	2.489651

Structure 15bTS (NImag = 1)

C	4.479149	0.908641	-1.105544
C	3.299740	1.461385	-0.758885
C	2.217501	0.747030	-0.077779
C	2.499051	-0.667904	0.290500

C	3.791241	-1.191282	-0.144483
C	4.727325	-0.473174	-0.799676
H	5.234298	1.499603	-1.617645
H	3.109211	2.505342	-1.001949
H	3.995091	-2.233878	0.092856
H	5.668239	-0.935106	-1.088566
C	1.779723	-1.577482	1.035511
H	2.347793	-2.491952	1.219868
C	0.494310	-1.652756	1.680335
H	0.471007	-2.361269	2.510350
C	1.100223	1.513629	0.101833
H	1.206953	2.522239	-0.300874
C	-0.259937	1.270863	0.644652
H	-0.274670	1.359141	1.738980
H	-0.907744	2.075722	0.273082
C	-0.679754	-1.081964	1.358247
H	-1.544667	-1.297114	1.987993
C	-0.884667	-0.115110	0.247064
H	-0.339965	-0.470589	-0.640147
C	-2.342468	0.023727	-0.118302
C	-2.801883	-0.359324	-1.378229
C	-3.264263	0.534408	0.801730
C	-4.148566	-0.239379	-1.715023
H	-2.093676	-0.759582	-2.102813
C	-4.609406	0.656252	0.470321
H	-2.923439	0.842908	1.790922
C	-5.056638	0.268199	-0.791239
H	-4.488125	-0.545094	-2.702164
H	-5.312228	1.055800	1.198109
H	-6.108215	0.362472	-1.051713

Structure 16b (NImag = 0)

C	3.280798	-0.834576	0.005283
C	2.130547	-1.344033	-0.481194
C	0.826481	-0.702137	-0.288808
C	0.896321	0.730049	0.106769
C	2.131294	1.150644	0.763313
C	3.265504	0.420870	0.715198
H	4.214366	-1.380081	-0.108451
H	2.131353	-2.317695	-0.969214
H	2.128732	2.130041	1.239465
H	4.177121	0.791599	1.177839
C	0.037000	1.731637	-0.242299
H	0.380447	2.740307	0.001215
C	-1.203179	1.675615	-0.984712

H	-1.332282	2.436084	-1.757632
C	-0.238593	-1.536314	-0.443860
H	0.048289	-2.535814	-0.782895
C	-1.686104	-1.496851	-0.087468
H	-2.273088	-1.852322	-0.949067
H	-1.851718	-2.261301	0.692939
C	-2.218968	0.834352	-0.746289
H	-3.110902	0.893358	-1.372738
C	-2.252102	-0.156712	0.378885
H	-1.602399	0.215092	1.186284
C	-3.646517	-0.321359	0.941018
C	-3.925825	0.040327	2.259556
C	-4.684169	-0.842002	0.160867
C	-5.204217	-0.114806	2.790317
H	-3.128468	0.451565	2.877618
C	-5.962772	-0.998993	0.685843
H	-4.494071	-1.130510	-0.873303
C	-6.227532	-0.635762	2.004487
H	-5.399720	0.173927	3.820658
H	-6.755821	-1.406856	0.062932
H	-7.226682	-0.757997	2.415887

Structure 14bTS (NImag = 1)

C	4.754568	-0.633223	-0.419239
C	3.609472	-1.336972	-0.154091
C	2.346339	-0.681332	-0.087246
C	2.329703	0.751470	-0.041738
C	3.526727	1.448237	-0.377007
C	4.703308	0.775467	-0.576251
H	5.701346	-1.154962	-0.537461
H	3.630911	-2.423769	-0.083379
H	3.501192	2.536801	-0.409772
H	5.611133	1.324461	-0.815367
C	1.298327	1.441192	0.632603
H	1.491420	2.504006	0.792719
C	0.306656	0.881547	1.435798
H	0.071680	1.495530	2.312466
C	1.150413	-1.407234	-0.055915
H	1.232880	-2.477981	0.154825
C	-0.076320	-1.006546	-0.830163
H	0.043656	-0.007054	-1.266552
H	-0.303821	-1.700955	-1.651194
C	-0.322242	-0.373628	1.422416
H	-0.726132	-0.650458	2.403763
C	-1.102417	-1.002074	0.278257
H	-1.277696	-2.052938	0.557590

C	-2.453716	-0.384370	0.006112
C	-3.603449	-1.176435	0.022766
C	-2.587983	0.976365	-0.288217
C	-4.856424	-0.631269	-0.247613
H	-3.514004	-2.238259	0.252401
C	-3.835928	1.525404	-0.561844
H	-1.703654	1.612536	-0.293032
C	-4.975793	0.723332	-0.541348
H	-5.739610	-1.265978	-0.227621
H	-3.921059	2.585789	-0.789428
H	-5.951823	1.154813	-0.751085

Structure 17bTS (NImag = 1)

C	4.547331	-0.979595	0.453805
C	3.439603	-1.425823	-0.212575
C	2.211228	-0.687478	-0.246808
C	2.294861	0.702918	0.160632
C	3.448351	1.110904	0.906308
C	4.531037	0.296067	1.073243
H	5.428962	-1.611734	0.528198
H	3.438143	-2.425091	-0.646087
H	3.466740	2.130676	1.288219
H	5.397701	0.642235	1.631396
C	1.536545	1.723065	-0.451527
H	1.962379	2.724863	-0.377384
C	0.518427	1.508857	-1.378431
H	0.440190	2.203289	-2.217411
C	1.081997	-1.389637	-0.715996
C	-0.247985	-1.536621	-0.014368
H	-0.888104	-2.188911	-0.624175
H	-0.157636	-2.019421	0.973187
C	-0.313916	0.405971	-1.324317
C	-0.817066	-0.140373	0.003899
H	-0.945744	0.186340	-2.188706
H	1.356754	-2.269970	-1.307446
H	-0.335256	0.434950	0.806498
C	-2.310659	-0.020997	0.173833
C	-3.193768	-0.679206	-0.688440
C	-2.846827	0.759787	1.199846
C	-4.570436	-0.562884	-0.527525
H	-2.802728	-1.293864	-1.499678
C	-4.224279	0.877397	1.368115
H	-2.170693	1.282860	1.875273
C	-5.091292	0.215811	0.503817
H	-5.240434	-1.082802	-1.208824

H	-4.619986	1.489112	2.175858
H	-6.167443	0.306233	0.631285

Structure *endo-8b* (NImag = 0)

C	3.162127	-1.186491	-0.143859
C	1.853452	-1.551553	0.172047
C	0.832904	-0.606958	0.192452
C	1.131597	0.738834	-0.092220
C	2.444935	1.096192	-0.407151
C	3.457304	0.141506	-0.436584
H	3.947790	-1.938377	-0.160713
H	1.618562	-2.591430	0.399908
H	2.670607	2.139866	-0.624377
H	4.474794	0.434623	-0.684262
C	0.069500	1.742549	-0.028806
H	0.328558	2.757002	-0.332776
C	-1.165431	1.472984	0.417352
H	-1.909139	2.268592	0.471656
C	-0.589704	-0.992297	0.450254
H	-0.638904	-1.845146	1.140808
C	-1.493364	-1.257137	-0.779879
H	-1.144315	-0.665601	-1.635093
H	-1.631239	-2.294054	-1.104572
C	-1.582922	0.116403	0.878488
H	-1.859396	0.156124	1.943351
C	-2.652828	-0.575171	-0.032929
H	-3.169371	-1.324534	0.585239
C	-3.680064	0.260787	-0.732783
C	-4.856949	0.598477	-0.055069
C	-3.495772	0.758092	-2.024457
C	-5.822451	1.405553	-0.646983
H	-5.014129	0.214751	0.953661
C	-4.462577	1.561615	-2.624588
H	-2.586981	0.517063	-2.572465
C	-5.628660	1.888867	-1.939493
H	-6.731168	1.651757	-0.101983
H	-4.302603	1.932854	-3.634527
H	-6.383787	2.514691	-2.409341

Structure *exo-8b* (NImag = 0)

C	-2.785779	-1.319883	0.710519
C	-1.502600	-1.014578	1.158186
C	-0.701742	-0.094688	0.485465

C	-1.207565	0.541924	-0.663750
C	-2.498881	0.230699	-1.104476
C	-3.285825	-0.693727	-0.428510
H	-3.393491	-2.042133	1.250719
H	-1.111186	-1.499734	2.053023
H	-2.883164	0.728216	-1.994520
H	-4.286802	-0.922847	-0.786470
C	-0.397917	1.523806	-1.385295
H	-0.879864	2.052980	-2.207396
C	0.882454	1.769253	-1.075121
H	1.459105	2.497683	-1.643398
C	0.665523	0.247027	1.018435
C	1.686887	-0.913733	0.968987
H	2.426594	-0.832786	1.775106
H	1.293152	-1.936950	0.954016
C	1.557523	1.009407	0.010687
C	2.225767	-0.353138	-0.366670
H	2.291410	1.631124	0.541647
H	0.553497	0.722893	2.003462
H	1.655523	-0.791767	-1.198437
C	3.685515	-0.385924	-0.689202
C	4.645520	0.017600	0.245985
C	4.124975	-0.794395	-1.951222
C	5.999820	0.009756	-0.069509
H	4.331492	0.343026	1.237796
C	5.479814	-0.803460	-2.273145
H	3.389231	-1.109334	-2.690645
C	6.422641	-0.401874	-1.331875
H	6.729536	0.324618	0.673332
H	5.798066	-1.125544	-3.262218
H	7.481639	-0.409510	-1.578876

Structure 7c (NImag = 0)

C	2.533540	2.566801	-0.251226
C	3.064709	1.555826	0.535377
C	2.721377	0.208474	0.341793
C	1.834452	-0.119435	-0.707926
C	1.314095	0.913240	-1.499449
C	1.646113	2.241731	-1.275705
H	2.813925	3.601965	-0.071810
H	3.758068	1.803781	1.338363
H	0.643710	0.648136	-2.314896
H	1.228517	3.019340	-1.910809
C	1.520540	-1.511732	-1.074024
H	2.386827	-2.151607	-1.257722

C	0.302325	-2.058160	-1.253740
H	0.277906	-3.070343	-1.661042
C	3.302132	-0.767672	1.271041
H	4.216262	-0.425611	1.762412
C	2.821459	-1.967192	1.618558
H	1.892787	-2.366258	1.216667
H	3.345110	-2.579293	2.348148
C	-1.000729	-1.493528	-0.936467
H	-1.846072	-1.865188	-1.517171
C	-1.252601	-0.619399	0.059401
H	-0.440805	-0.265943	0.697197
C	-2.543189	-0.090291	0.393481
C	-2.945079	0.774574	1.377678
O	-3.624414	-0.461156	-0.352647
C	-4.351120	0.942582	1.226002
H	-2.298837	1.230671	2.116531
C	-4.707319	0.171248	0.163823
H	-5.011376	1.554222	1.825649
H	-5.648603	-0.027396	-0.327911

Structure 12cTS (NImag = 1)

C	-3.941204	-1.674479	-0.329650
C	-2.650635	-1.807294	0.094104
C	-1.795173	-0.690628	0.363823
C	-2.273199	0.633023	0.016614
C	-3.662531	0.713332	-0.341450
C	-4.467875	-0.376156	-0.518298
H	-4.559768	-2.552140	-0.499253
H	-2.243991	-2.799298	0.285881
H	-4.075178	1.703584	-0.527235
H	-5.502768	-0.241807	-0.823651
C	-1.617559	1.901618	-0.061553
H	-2.365822	2.690474	-0.163569
C	-0.337223	2.462059	-0.116983
H	-0.362993	3.552612	-0.113525
C	-0.578549	-1.015833	0.996996
H	-0.315742	-2.075616	0.993292
C	0.361877	-0.122777	1.485361
H	0.020775	0.852254	1.820962
H	1.220090	-0.522715	2.023619
C	0.945192	1.927557	-0.148864
H	1.768550	2.617541	0.042642
C	1.236330	0.558681	-0.253588

H	0.579697	-0.035194	-0.883325
C	2.607794	0.083003	-0.243538
C	3.814554	0.623379	0.104850
O	2.778383	-1.226362	-0.587848
C	4.783507	-0.411511	-0.049766
H	3.991279	1.640633	0.429629
C	4.099974	-1.509414	-0.469006
H	5.848745	-0.346369	0.125997
H	4.392366	-2.518030	-0.721973

Structure 13c (NImag = 0)

C	4.479893	-1.003911	0.015025
C	3.278333	-1.446828	0.451062
C	2.058700	-0.708204	0.172202
C	2.212249	0.686229	-0.256637
C	3.489162	1.037623	-0.847421
C	4.574858	0.239851	-0.707868
H	5.376226	-1.597856	0.176436
H	3.182281	-2.415834	0.939165
H	3.576104	2.010477	-1.329851
H	5.536350	0.552365	-1.108382
C	1.321871	1.696626	-0.006733
H	1.645788	2.671655	-0.380499
C	0.179690	1.805890	0.880851
H	0.162296	2.788500	1.361191
C	0.867948	-1.360228	0.194417
H	0.878260	-2.385586	0.573189
C	-0.420590	-0.881479	-0.365982
H	-0.252841	-0.121521	-1.143116
H	-0.944496	-1.723529	-0.837707
C	-0.856884	1.021617	1.244339
H	-1.536646	1.464312	1.975333
C	-1.355381	-0.279151	0.695788
H	-1.440249	-1.010116	1.516286
C	-2.734224	-0.089004	0.155045
C	-3.404959	0.973163	-0.369311
O	-3.515852	-1.204116	0.096038
C	-4.685800	0.483081	-0.776974
H	-3.022353	1.982317	-0.455066
C	-4.696263	-0.839753	-0.472839
H	-5.490485	1.042648	-1.234634
H	-5.429409	-1.625265	-0.584460

Structure 15cTS (NImag = 1)

C	4.234124	-1.395551	0.222045
C	3.018278	-1.656405	-0.297019
C	1.930389	-0.679996	-0.391786
C	2.240522	0.694424	0.088964
C	3.574349	0.881261	0.654543
C	4.517440	-0.081159	0.727762
H	4.992598	-2.173102	0.265161
H	2.801799	-2.655835	-0.670414
H	3.803810	1.875749	1.032956
H	5.489259	0.137466	1.163491
C	1.512186	1.864213	0.047150
H	2.102561	2.721443	0.378030
C	0.196874	2.294886	-0.352581
H	0.157156	3.351011	-0.625222
C	0.781481	-1.206966	-0.912151
H	0.870214	-2.266598	-1.156958
C	-0.588796	-0.689543	-1.147761
H	-0.658403	-0.120478	-2.082738
H	-1.250616	-1.554928	-1.280085
C	-0.978879	1.643967	-0.344204
H	-1.866693	2.171621	-0.693108
C	-1.147817	0.210845	0.015937
H	-0.565843	-0.014269	0.920921
C	-2.563242	-0.132625	0.312237
C	-3.198710	-0.651025	1.397177
O	-3.458760	0.067737	-0.695523
C	-4.579344	-0.775164	1.039497
H	-2.734004	-0.908372	2.340329
C	-4.678496	-0.326142	-0.236920
H	-5.388227	-1.147538	1.653510
H	-5.499033	-0.221503	-0.931542

Structure 16c (NImag = 0)

C	4.363063	-0.976360	0.348860
C	3.259730	-1.434144	-0.277678
C	1.985361	-0.709817	-0.281776
C	2.093062	0.730395	0.075216
C	3.250531	1.100561	0.885367
C	4.330716	0.302624	1.015871
H	5.267445	-1.579062	0.377856
H	3.264061	-2.423213	-0.733732
H	3.246097	2.095396	1.328327
H	5.192410	0.633081	1.590995
C	1.357344	1.766811	-0.422174
H	1.728157	2.762524	-0.165773

C	0.228651	1.752063	-1.327602
H	0.257854	2.478592	-2.142101
C	0.898302	-1.483753	-0.552633
H	1.160480	-2.510097	-0.824632
C	-0.576702	-1.341547	-0.388244
H	-1.081266	-1.686324	-1.303330
H	-0.890458	-2.059352	0.390572
C	-0.863414	0.987787	-1.196283
H	-1.660031	1.054812	-1.938208
C	-1.100637	0.052693	-0.045643
H	-0.558592	0.422942	0.837526
C	-2.542617	0.002350	0.324164
C	-3.239047	0.343648	1.441476
O	-3.397440	-0.481745	-0.621539
C	-4.613977	0.052935	1.170216
H	-2.816773	0.756040	2.348893
C	-4.650594	-0.442538	-0.092345
H	-5.459969	0.196402	1.828717
H	-5.444433	-0.797113	-0.733427

Structure 14cTS (NImag = 1)

C	-4.495572	-0.579620	0.236158
C	-3.357875	-1.297377	-0.017727
C	-2.075527	-0.674512	0.016234
C	-2.021153	0.759550	0.056008
C	-3.216267	1.466645	0.381737
C	-4.416626	0.815750	0.483993
H	-5.459716	-1.080877	0.277651
H	-3.402791	-2.377046	-0.155120
H	-3.165580	2.550010	0.483895
H	-5.320934	1.373584	0.715706
C	-0.948006	1.462530	-0.531962
H	-1.108889	2.537801	-0.631761
C	0.054449	0.923555	-1.339537
H	0.319722	1.570663	-2.182721
C	-0.901773	-1.432065	0.011143
H	-1.001005	-2.490793	-0.245902
C	0.292245	-1.084659	0.861353
H	0.139979	-0.113996	1.351080
H	0.480014	-1.829796	1.647289
C	0.659528	-0.337120	-1.355941
H	1.107969	-0.591147	-2.322418
C	1.373035	-1.000852	-0.180421

H	1.630225	-2.023117	-0.498940
C	2.632410	-0.313845	0.211437
C	3.003742	0.452159	1.273848
O	3.667613	-0.414265	-0.669327
C	4.358194	0.847938	1.034517
H	2.387143	0.703589	2.127233
C	4.706298	0.297652	-0.156196
H	4.986696	1.458925	1.668453
H	5.609227	0.310322	-0.749085

Structure 17cTS (NImag = 1)

C	-4.319182	-0.839812	-0.454780
C	-3.186682	-1.383371	0.084933
C	-1.950062	-0.662304	0.167471
C	-2.038890	0.774654	-0.022914
C	-3.220395	1.290862	-0.649099
C	-4.317114	0.512613	-0.882590
H	-5.210740	-1.449856	-0.577957
H	-3.174954	-2.435215	0.367800
H	-3.245698	2.355397	-0.877905
H	-5.204622	0.939399	-1.343865
C	-1.249464	1.689729	0.704368
H	-1.670896	2.691601	0.799644
C	-0.195539	1.335012	1.545568
H	-0.080055	1.889420	2.479068
C	-0.807255	-1.429659	0.468315
C	0.487809	-1.464751	-0.308044
H	1.160024	-2.190673	0.167187
H	0.349007	-1.788497	-1.352725
C	0.624557	0.253982	1.285809
C	1.058783	-0.078999	-0.134621
H	1.296859	-0.106472	2.067256
H	-1.058999	-2.389746	0.931585
H	0.570905	0.623682	-0.823122
C	2.523031	0.062131	-0.337071
C	3.287681	0.874715	-1.116954
O	3.329007	-0.750282	0.406515
C	4.651105	0.542550	-0.841878
H	2.913906	1.622751	-1.804328
C	4.614876	-0.445574	0.088174
H	5.538533	0.981153	-1.278000
H	5.376326	-1.013753	0.602312

Structure *endo*-8c (NImag = 0)

C	-4.365354	-0.515337	0.515189
C	-3.194548	-1.220447	0.235935
C	-2.030513	-0.554723	-0.132501
C	-2.041352	0.848210	-0.243340
C	-3.217505	1.546805	0.039448
C	-4.374338	0.872703	0.420142
H	-5.266236	-1.050716	0.805977
H	-3.182776	-2.307845	0.310821
H	-3.221089	2.632766	-0.048971
H	-5.282232	1.430737	0.637055
C	-0.833482	1.547790	-0.681036
H	-0.862514	2.637496	-0.672363
C	0.260156	0.911275	-1.121892
H	1.122204	1.483826	-1.466004
C	-0.745360	-1.285292	-0.361678
H	-0.939486	-2.290964	-0.758524
C	0.252963	-1.371998	0.820349
H	0.141877	-0.499187	1.476639
H	0.249412	-2.279798	1.432216
C	0.360999	-0.577210	-1.183062
H	0.496483	-0.902694	-2.224511
C	1.402664	-1.178847	-0.181706
H	1.741222	-2.149046	-0.573091
C	2.568413	-0.366366	0.214913
C	2.902909	0.338396	1.330564
O	3.535297	-0.209872	-0.735186
C	4.158145	0.967449	1.054011
H	2.322108	0.405080	2.241415
C	4.491349	0.603114	-0.210107
H	4.733538	1.605739	1.710972
H	5.333822	0.818541	-0.850995

Structure *exo-8c* (NImag = 0)

C	3.992628	-1.304867	0.526165
C	2.755132	-1.515911	-0.077463
C	1.902712	-0.453905	-0.370300
C	2.310346	0.856866	-0.058159
C	3.557037	1.059591	0.544787
C	4.394078	-0.009152	0.841337
H	4.640343	-2.149645	0.748752
H	2.441348	-2.529377	-0.329806
H	3.864248	2.077300	0.784179
H	5.358094	0.167050	1.312832
C	1.444779	1.995325	-0.366374
H	1.859857	2.990042	-0.203393

C	0.191916	1.845517	-0.817964
H	-0.427502	2.716597	-1.026158
C	0.583043	-0.711000	-1.052241
C	-0.429932	-1.513239	-0.202322
H	-1.120851	-2.083112	-0.834323
H	-0.033031	-2.167240	0.582628
C	-0.391158	0.488850	-0.993994
C	-1.069904	-0.178957	0.247027
H	-1.093793	0.452142	-1.836277
H	0.770794	-1.119572	-2.055381
H	-0.591014	0.191438	1.163409
C	-2.530270	-0.077806	0.406226
C	-3.337483	0.411400	1.388664
O	-3.295800	-0.533590	-0.628234
C	-4.683658	0.246906	0.935020
H	-3.002428	0.836769	2.326056
C	-4.596717	-0.329702	-0.290806
H	-5.592890	0.519643	1.453687
H	-5.328464	-0.648678	-1.018738

Table S2. Single point energies and total energies obtained at M06/6-311+G(d,p)//M06/6-31G+(d,p) level of theory. ZPVE values are taken from M06/6-31+G(d,p) method.^a

Structure	E_{sp}	ZPVE	E_{tot}
7a	-503.469450	0.239657	-503.229793
12aTS	-503.438132	0.238869	-503.199263
13a	-503.463044	0.241202	-503.221842
15aTS	-503.452341	0.240728	-503.211613
16a	-503.458024	0.241044	-503.216980
14aTS	-503.443682	0.239197	-503.204485
17aTS	-503.439379	0.239004	-503.200375
endo-8a	-503.506683	0.241935	-503.264748
exo-8a	-503.505685	0.241868	-503.263817
7b	-695.104818	0.280115	-694.824703
12bTS	-695.073478	0.281019	-694.792459
13b	-695.094003	0.283256	-694.810747
15bTS	-695.082572	0.283283	-694.799289
16b	-695.087562	0.282843	-694.804719
14bTS	-695.073193	0.282007	-694.791186

17bTS	-695.069305	0.281649	-694.787656
endo-8b	-695.137696	0.284623	-694.853073
exo-8b	-695.137104	0.284746	-694.852358
7c	-692.924143	0.249830	-692.674313
12cTS	-692.889529	0.251035	-692.638494
13c	-692.910049	0.253266	-692.656783
15cTS	-692.898863	0.253219	-692.645644
16c	-692.904253	0.252624	-692.651629
14cTS	-692.889496	0.251916	-692.637580
17cTS	-692.886662	0.251802	-692.634860
endo-8c	-692.955134	0.254598	-692.700536
exo-8c	-692.954761	0.254731	-692.700030

^a all energies are given in atomic units

Table S3. ΔE_{final} are obtained by adding ΔG_{solv} calculated at the CPCM/HF/6-31G(d) level of theory to the ΔE_{tot} calculated at M06/6-311+G(d,p)//M06/6-31+G(d,p) level of theory. ΔE_{final} values are given relative to **7a**, **7b** and **7c**, respectively.^b

Structure	ΔE_{tot}	ΔG_{solv}	ΔE_{final}
7a	0.0	4.1	0.0
12aTS	80.2	-5.4	70.7
13a	20.9	-6.4	10.4
15aTS	47.7	-6.9	36.8
16a	33.6	-6.3	23.3
14aTS	66.4	-5.7	56.7
17aTS	77.2	-6.0	67.2
endo-8a	-91.8	-4.2	-100.1
exo-8a	-89.3	-3.3	-96.7
7b	0.0	5.0	0.0
12bTS	84.7	-2.7	77.0
13b	36.6	-3.6	28.0
15bTS	66.7	-4.5	57.2
16b	52.5	-4.3	43.1
14bTS	88.0	-3.8	79.1

17bTS	97.3	-4.1	88.1
<i>endo</i>-8b	-74.5	-2.6	-82.1
<i>exo</i>-8b	-72.6	-3.3	-81.0
7c	0.0	2.5	0.0
12cTS	94.0	-4.9	86.7
13c	46.0	-5.3	38.3
15cTS	75.3	-5.0	67.8
16c	59.6	-4.9	52.2
14cTS	96.4	-5.0	89.0
17cTS	103.6	-4.4	96.7
<i>endo</i>-8c	-68.8	-4.1	-75.4
<i>exo</i>-8c	-67.5	-4.4	-74.3

^b all relative energies are given in kJ mol⁻¹