Supporting Information

2-α-Hydroxyalkyl- and 2,7-Di(α-hydroxyalkyl)-1,8-bis(dimethylamino)naphthalenes: Stabilization of Non-Conventional *In/Out*–Conformers of "Proton Sponges" via N···H–O Intramolecular Hydrogen Bonding. A Remarkable Kind of Tandem Nitrogen Inversion

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Table of contents

General. The ^{1}H NMR spectra were recorded at the indicated field strengths; the internal reference was $SiMe_4$ (δ = 0.00 ppm). The melting points were not corrected. Chromatography was performed and the purity of the compounds was monitored by TLC on Al_2O_3 (Brockmann III) using $CHCl_3$ and MeCN as the eluents. Commercial Bu^nLi (1.6M solution in *n*-hexane), DMF, and $(EtO)_2CO$ were used. Solvents for preparation of organometallic compounds and those used in subsequent reactions were dried over sodium and benzophenone and were freshly distilled prior to any operation.

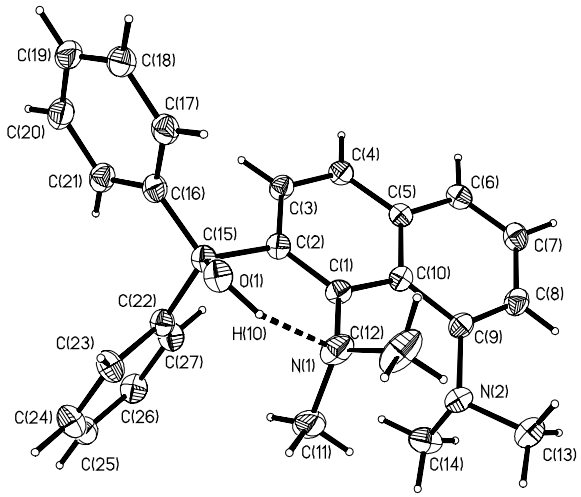

Figure S1. Molecular structure of compound **4e**.

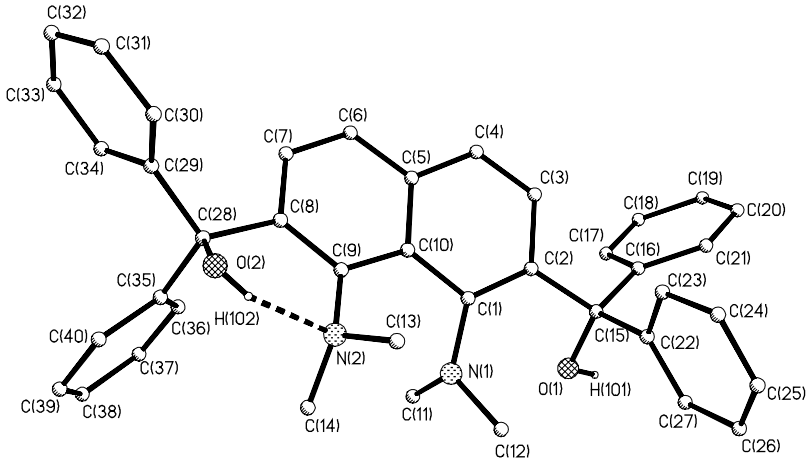

Figure S2. Molecular structure of diol **5e**.

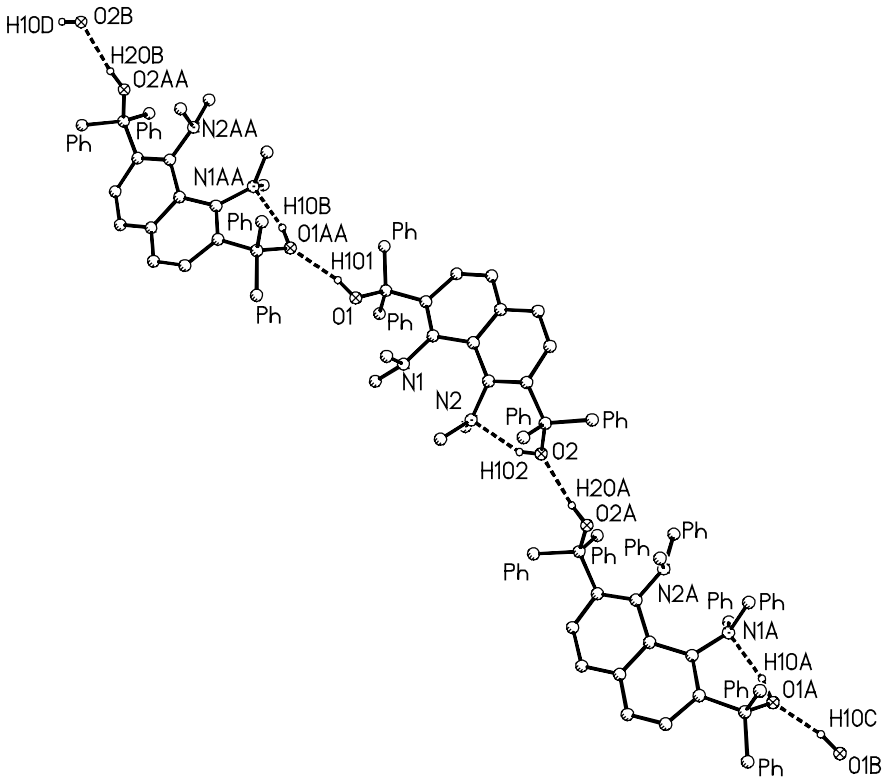

Figure S3. View along *b*-axis on crystal packing of diol **5e** showing the inter- and intramolecular H-bonding.

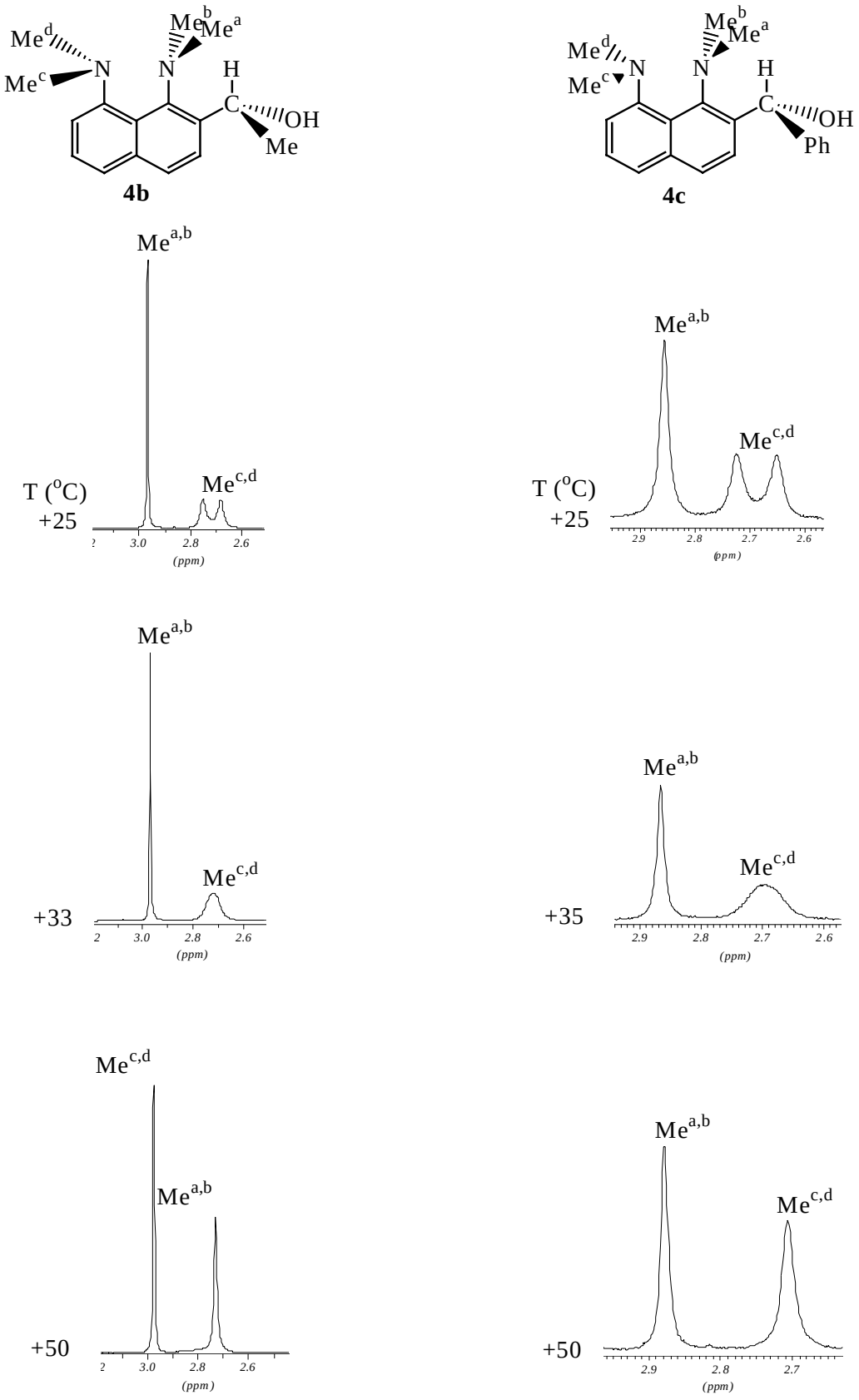

Figure S4. Temperature dependence of *N*-methyl signals in the ^{1}H NMR spectra of **4b** and **4c** (250 MHz, $CDCl_3$, $c = 6.45 \cdot 10^{-2}$ M for **4b** and $5.2 \cdot 10^{-2}$ M for **4c**).

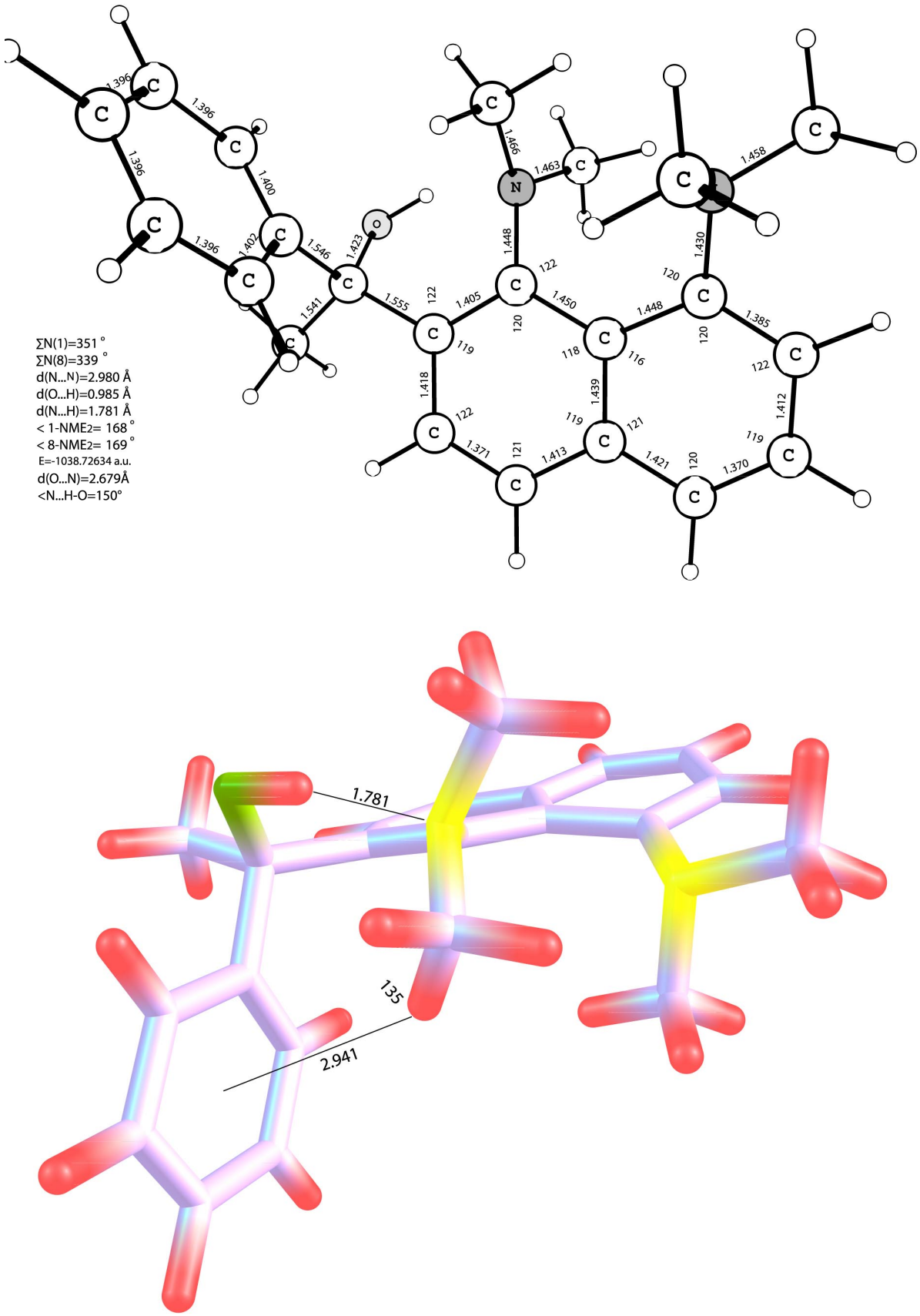

Figure S5. Calculated geometry (bond lengths and distances in Å, angles in degrees) and total energy for alcohol **4f** (compare with Table 4 and Figure 9, right).

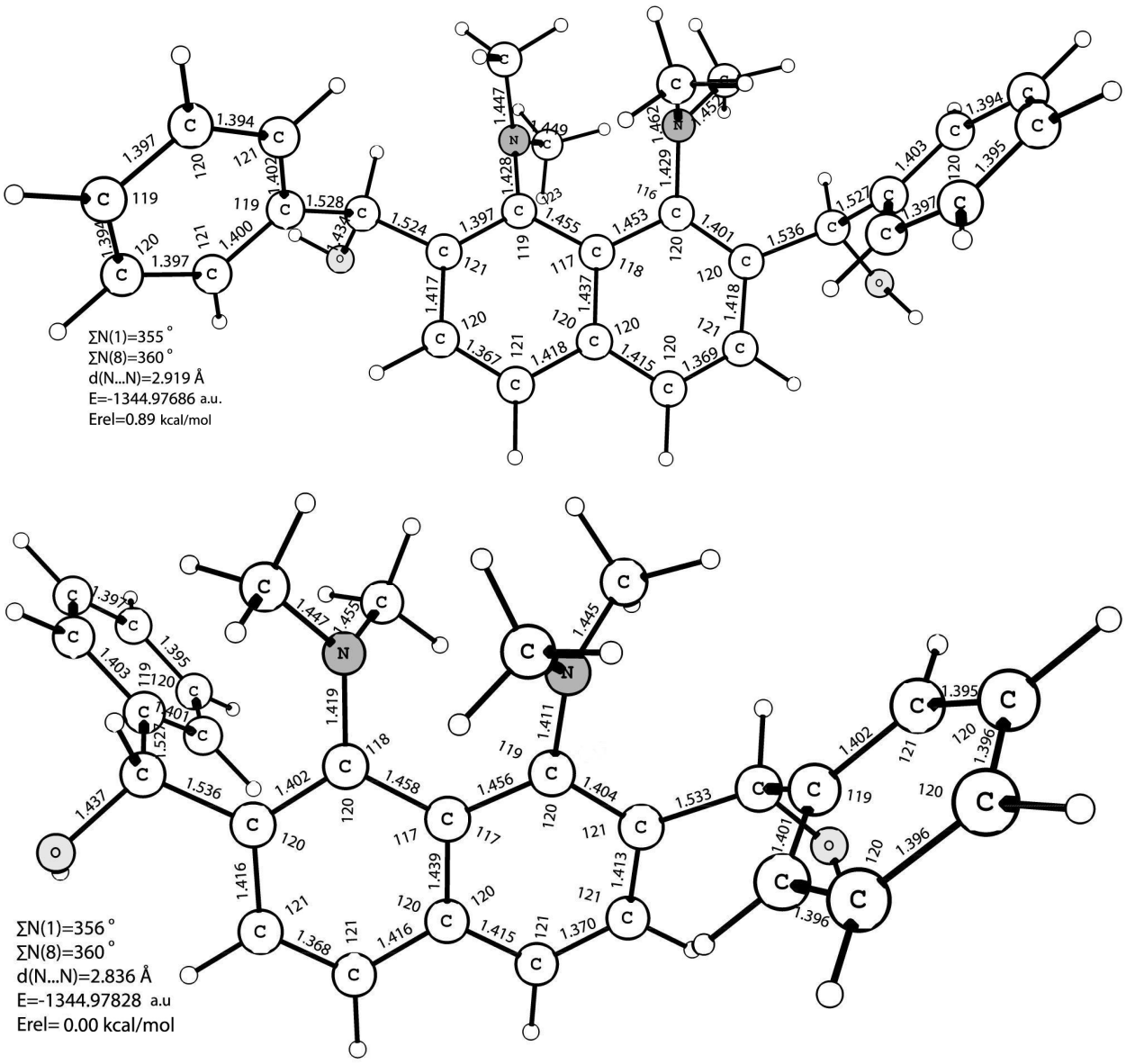

Figure S6. Calculated geometry (bond lengths and distances in Å, angles in degrees) and total energies for *cis*- (above) and *trans*-forms (below) of diol **5c**.

Table S1. Atomic Coordinates for Structure **4f**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.987118	-0.959775	2.477139
2	6	0	-0.476243	-2.007427	0.820237
3	6	0	3.487323	-2.805963	0.276960
4	6	0	1.844990	-2.289653	-1.406719
5	7	0	0.103087	-0.760838	1.328539
6	7	0	2.450845	-1.866979	-0.136192
7	6	0	1.784173	0.528039	-0.069339
8	6	0	2.149612	1.845319	-0.519068
9	6	0	2.814842	-0.484666	-0.163290
10	6	0	4.128755	-0.109153	-0.391033
11	6	0	4.489066	1.230377	-0.652179
12	6	0	3.506782	2.177396	-0.778832
13	6	0	0.441767	0.332255	0.441738
14	6	0	-0.533827	1.325481	0.252635
15	6	0	-0.165815	2.537846	-0.383912
16	6	0	1.139113	2.816962	-0.696563
17	6	0	-1.987220	1.177749	0.786552
18	1	0	1.291609	0.009952	2.877612
19	1	0	1.880395	-1.549440	2.239672
20	1	0	0.427533	-1.488586	3.258589
21	1	0	0.287481	-2.777846	0.668118
22	1	0	-0.993344	-1.822985	-0.120641
23	1	0	-1.215578	-2.385049	1.537424
24	1	0	4.281817	-2.955377	-0.475565
25	1	0	3.951705	-2.466452	1.206090
26	1	0	3.024460	-3.781259	0.459744
27	1	0	1.425332	-3.294687	-1.298493
28	1	0	2.583339	-2.307659	-2.226734
29	1	0	1.039094	-1.609710	-1.686080
30	1	0	4.898707	-0.870430	-0.442200
31	1	0	5.531222	1.482298	-0.824920
32	1	0	3.744190	3.196907	-1.069294
33	1	0	-0.914787	3.301386	-0.549254
34	1	0	1.414629	3.794652	-1.082640
35	8	0	-1.963668	0.737744	2.139369
36	1	0	-1.270454	0.038238	2.133065
37	6	0	-2.754599	2.512790	0.842755
38	1	0	-2.966104	2.919457	-0.149183
39	1	0	-3.709496	2.319991	1.337089
40	1	0	-2.202894	3.248519	1.434403
41	6	0	-2.809634	0.212760	-0.098608
42	6	0	-2.680915	0.193189	-1.494052
43	6	0	-3.763693	-0.620361	0.497613
44	6	0	-3.479256	-0.646981	-2.272530
45	1	0	-1.947097	0.832094	-1.977212
46	6	0	-4.562157	-1.460953	-0.279244
47	1	0	-3.859887	-0.602975	1.577717
48	6	0	-4.422318	-1.479731	-1.667771
49	1	0	-3.361759	-0.651488	-3.352840
50	1	0	-5.294088	-2.103993	0.202259
51	1	0	-5.041386	-2.135791	-2.273029

Total energy = -1038.72634 a.u.

Table S2. Atomic Coordinates for Diol **5c** (*cis*-form)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.766112	-2.133800	2.475616
2	6	0	1.338722	0.228086	2.750112
3	6	0	-2.363037	-0.377237	2.512939
4	6	0	-1.303535	1.431500	1.278876
5	7	0	1.289146	-0.923554	1.875114
6	7	0	-1.449205	-0.014304	1.444088
7	6	0	-0.011722	-0.955484	-0.300769
8	6	0	0.106945	-1.321140	-1.685388
9	6	0	-1.348968	-0.768250	0.234551
10	6	0	-2.458177	-1.204511	-0.502210
11	6	0	-2.266953	-1.765216	-1.790281
12	6	0	-1.038484	-1.753985	-2.394734
13	6	0	1.224869	-0.813129	0.452989
14	6	0	2.441857	-0.766346	-0.231340
15	6	0	2.493820	-0.932621	-1.637127
16	6	0	1.366483	-1.268217	-2.334511
17	6	0	3.775158	-0.694855	0.502860
18	1	0	0.935303	-2.980733	1.806242
19	1	0	-0.307176	-2.090759	2.715975
20	1	0	1.307302	-2.333701	3.410507
21	1	0	0.371158	0.453510	3.222496
22	1	0	1.644370	1.112422	2.186692
23	1	0	2.071059	0.067443	3.556200
24	1	0	-3.360869	0.084670	2.434532
25	1	0	-2.478949	-1.462318	2.559406
26	1	0	-1.937678	-0.052249	3.471925
27	1	0	-1.043258	1.888244	2.240271
28	1	0	-2.222069	1.914034	0.910791
29	1	0	-0.497516	1.645356	0.573727
30	1	0	-3.131248	-2.152772	-2.315762
31	1	0	-0.922473	-2.092872	-3.420698
32	1	0	3.455282	-0.881612	-2.136705
33	1	0	1.416515	-1.504039	-3.394121
34	6	0	4.642898	0.473779	0.036661
35	6	0	5.698157	0.277604	-0.862311
36	6	0	4.399388	1.769921	0.511038
37	6	0	6.485411	1.351858	-1.283138
38	1	0	5.900128	-0.725470	-1.223903
39	6	0	5.182661	2.843506	0.091746
40	1	0	3.592320	1.939381	1.219063
41	6	0	6.230143	2.638227	-0.809728
42	1	0	7.300474	1.180438	-1.980905
43	1	0	4.979921	3.840615	0.472590
44	1	0	6.843343	3.473679	-1.134740
45	6	0	-3.916486	-1.019025	-0.055688
46	1	0	-4.011939	-1.282879	0.997012
47	8	0	4.421378	-1.955523	0.281470
48	1	0	5.245567	-1.942786	0.788568
49	1	0	3.565258	-0.572965	1.569608
50	6	0	-4.457136	0.396883	-0.240657
51	6	0	-4.002768	1.241685	-1.261791
52	6	0	-5.517713	0.830466	0.568860
53	6	0	-4.589202	2.493647	-1.461590
54	1	0	-3.179671	0.923170	-1.893899
55	6	0	-6.100330	2.081654	0.374564

56	1	0	-5.889816	0.175419	1.352441
57	6	0	-5.636494	2.918018	-0.643526
58	1	0	-4.222786	3.138413	-2.255313
59	1	0	-6.915768	2.404059	1.015679
60	1	0	-6.087890	3.894004	-0.796158
61	8	0	-4.798812	-1.944615	-0.712801
62	1	0	-5.128725	-1.511680	-1.511429

Total energy = -1344.97686 a.u.

Table S3. Atomic Coordinates for Diol **5c** (*trans*-form)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.523103	-1.777710	1.003503
2	6	0	-1.798492	-2.073960	-1.410837
3	6	0	1.792344	-2.265482	1.038369
4	6	0	1.492396	-1.593355	-1.290777
5	7	0	-1.490552	-1.182876	-0.315697
6	7	0	1.311193	-1.262200	0.114048
7	6	0	-0.019870	0.815465	0.018661
8	6	0	0.003969	2.253435	0.075853
9	6	0	1.178004	0.108533	0.455435
10	6	0	2.195582	0.811395	1.116371
11	6	0	2.067602	2.204621	1.336340
12	6	0	1.040545	2.915347	0.777208
13	6	0	-1.239749	0.195699	-0.480464
14	6	0	-2.239041	0.995485	-1.056493
15	6	0	-2.066617	2.393331	-1.167616
16	6	0	-1.004228	3.013295	-0.564095
17	6	0	-3.598965	0.413332	-1.460317
18	1	0	-1.049375	-1.115299	1.729863
19	1	0	-0.986164	-2.734491	1.015844
20	1	0	-2.555317	-1.965043	1.338434
21	1	0	-1.159105	-2.968655	-1.369013
22	1	0	-1.606277	-1.581755	-2.366393
23	1	0	-2.843781	-2.425104	-1.402287
24	1	0	2.877432	-2.455202	0.986700
25	1	0	1.530797	-1.989991	2.062712
26	1	0	1.298073	-3.221800	0.819454
27	1	0	1.106503	-2.600076	-1.489972
28	1	0	2.549143	-1.567848	-1.601192
29	1	0	0.939976	-0.889589	-1.916029
30	1	0	2.838306	2.708729	1.906587
31	1	0	1.001725	3.997628	0.867988
32	1	0	-2.828671	2.970315	-1.678313
33	1	0	-0.920455	4.096720	-0.563032
34	6	0	3.535980	0.175132	1.514987
35	1	0	3.358832	-0.734279	2.090122
36	1	0	-3.460015	-0.397124	-2.178564
37	6	0	4.431904	-0.177638	0.329874
38	6	0	4.414532	0.561213	-0.860280
39	6	0	5.383611	-1.197918	0.473180
40	6	0	5.318347	0.277160	-1.886696
41	1	0	3.683189	1.352977	-0.990028
42	6	0	6.283266	-1.486344	-0.551700
43	1	0	5.420317	-1.763342	1.400843
44	6	0	6.252521	-0.748118	-1.737071

45	1	0	5.288396	0.856671	-2.805031
46	1	0	7.008726	-2.284952	-0.425664
47	1	0	6.951452	-0.971974	-2.537696
48	8	0	4.278152	1.000918	2.427473
49	1	0	4.810533	1.608736	1.896463
50	6	0	-4.415523	-0.129267	-0.288819
51	6	0	-5.356645	-1.140524	-0.527624
52	6	0	-4.346433	0.434067	0.992137
53	6	0	-6.196530	-1.591587	0.490488
54	1	0	-5.434273	-1.570067	-1.523240
55	6	0	-5.189343	-0.012500	2.011573
56	1	0	-3.620883	1.216355	1.193304
57	6	0	-6.115378	-1.027203	1.764993
58	1	0	-6.914891	-2.381100	0.288530
59	1	0	-5.119653	0.431810	3.000546
60	1	0	-6.768488	-1.375799	2.559746
61	8	0	-4.403275	1.356637	-2.185494
62	1	0	-4.823672	1.933217	-1.532057

Total energy = -1344.97828 a.u.