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Supporting Information

Sign Inversion of Circularly Polarized Luminescence by Geometry Manipulation of Four Naphthalene Units Introduced to a Tartaric Acid Scaffold

Tomoyuki Amako,[a] Kazuki Nakabayashi,[a] Tadashi Mori,[b] Yoshihisa Inoue,[b] Michiya Fujiki,[c]* and Yoshitane Imai[a]**

[a] Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan.

[b] Department of Applied Chemistry, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan.

[c] Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama, Ikoma, Nara 630-0192, Japan.

Correspondence to: (Y.I.) y-imai@apch.kindai.ac.jp. (M.F.) fujikim@ms.naist.jp.

(T.M.) tmori@chem.eng.osaka-u.ac.jp.

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1. General methods

Compounds (*S*)-**1**, (*R*)-**1** and (*S*)-**2** were purchased from Sigma-Aldrich Japan (Tokyo, Japan). These compounds were used after purification by recrystallization from chloroform. The solvent for the measurements of the optical properties was used as obtained and was purchased from the Wako Pure Chemical Industry. The preparation of compound (*R*)-**2** was reported previously.[1]

2. Measurement of solution-state fluorescence spectra

The solution-state fluorescence spectra and absolute photoluminescence quantum yields were measured using an Absolute PL Quantum Yield Measurement System (C9920-02, Hamamatsu Photonics) under air at ambient temperature. The samples were prepared in chloroform (1.0×10^{-3} M). The excitation wavelengths were 287 nm for (*S*)-**1** and 290 nm for (*S*)-**2**.

3. Measurement of solution-state CPL spectra

The solution-state CPL spectra were measured using a JASCO CPL-200 spectrofluoropolarimeter at ambient temperature. The instrument used a scattering angle of 0° from the excitation of unpolarized, monochromated incident light with a bandwidth of 10 nm. The samples were prepared in chloroform (1.0×10^{-3} M). The excitation wavelength was 290 nm. The CPL spectra were approached by a Simple Moving Average (SMA) method.

4. Measurement of solution-state CD and UV absorption spectra

The CD/UV-vis spectra of the solutions were recorded simultaneously at ambient temperature on a JASCO J-820 spectropolarimeter with a Peltier-controlled unit using a synthetic quartz cuvette with an optical path length of 1.0 cm (scanning rate: 100 nm/min, bandwidth: 2 nm, response time: 1 sec, a single accumulation). The samples were prepared in chloroform (1.0×10^{-5} M or 1.0×10^{-4} M).

5. Theoretical calculations

All calculations were performed on Linux-PCs using the Turbomole 6.5 or the Gaussian 09 (Rev. D.01) program suites.[2] The geometries were fully optimized at the dispersion-corrected density functional theory (3rd generation, DFT-D3)[3] with BJ dumping[4] with an AO basis-set of valence triple-ζ quality (in standard notation: H, [3s1p], C/O, [5s3p2d1f]) at the TPSS-D/def2-TZVP level[5] with a C_2 symmetry constraint. The convergence criterion for the optimization regarding the change of total energy between two subsequent optimization cycles was set to 10^{-7} E_h. The resolution-of-identity (RI) approximation[6] was employed for the perturbative corrections in all the geometry calculations throughout this study to facilitate the computational efficiency without any significant loss of accuracy, and the corresponding auxiliary basis-sets were taken from the Turbomole basis-set library. All excited-state calculations were performed with these DFT-D3 optimized ground-state geometries, thus, corresponding to the vertical transition approximation. Most of the CD spectra were calculated by the time-dependent density functional theory (TD-DFT) with long-range corrected functionals (CAM-B3 LYP) and a basis-set of TZVP.[7] The CD spectra were also calculated, for comparison purposes, by the most accurate time-dependent, second-order approximate coupled-cluster singles and doubles model[8] in conjunction with the resolution-of-identity method (RI-CC2 method)[9] with a basis-set of def2-TZVPP quality. Although most of the calculated rotational strengths of the dipole-length and velocity expressions only differed by less than 10%, some transitions significantly differed by ~20% with this relatively small basis-set. However, due to the size of the tetranaphthyl derivatives studied herein, calculations with a higher basis-set, even for the model compounds, were currently unfeasible. Thus, relatively robust length-gauge oscillators and rotational strengths were used throughout this study. The CD spectra were simulated by overlapping Gaussian functions for each transition for which the width of the band at 1/e height is fixed at 0.4 eV and the overall rotational strengths were scaled to one-third. These values are purely empirical and have no rigorous ground but are able to successfully reproduce and match to the experimental CD spectra, facilitating the interpretation of the spectra.

6. References

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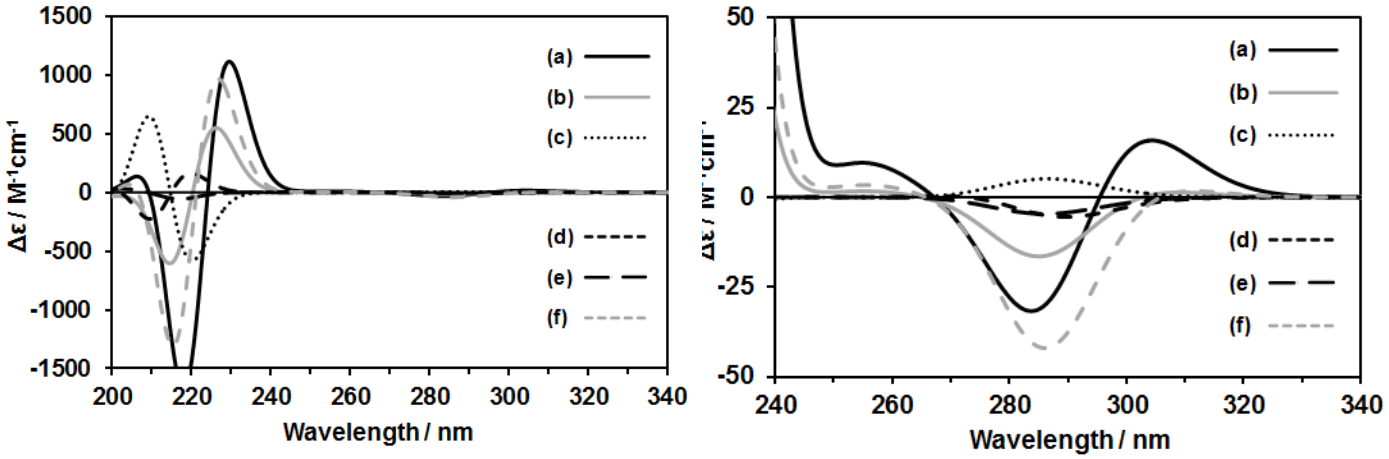

Fig. S1. Comparison of theoretical CD spectra for the full molecule of (*S*)-**1** with those of the model systems. Left: whole spectral region. Right: expanded at the long-wavelength region. (a) theoretical curve for the four-naphthalene model (A/B/C/D interactions were considered) (b-e) theoretical curves of each pair (A/B, A/C, A/D, and B/C, respectively) of the two-naphthalene sub-models (A/B, A/C, A/D, and B/C interactions were individually considered), (f) summation of the theoretical curves of four pairs of two-naphthalene sub-models (A/B, A/C, A/D, and B/C).

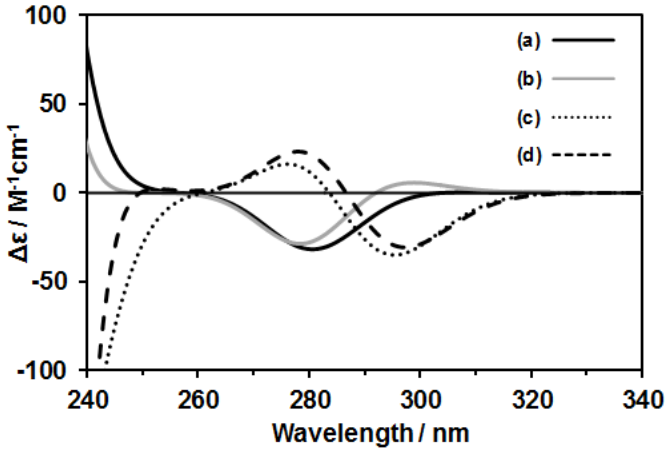

Fig. S2. Comparison of theoretical CD spectra for the full molecules of (*S*)-**2** to those of the model systems at the TD-DFT-CAM-B3 LYP/TZVP level. (a, c) theoretical curves of the full molecules. (b, d) theoretical curves for the four-naphthalene model. Spectra a and b are for the major conformer (*S*)-**2-I**, while c and d are for the minor conformer (*S*)-**2-II**.

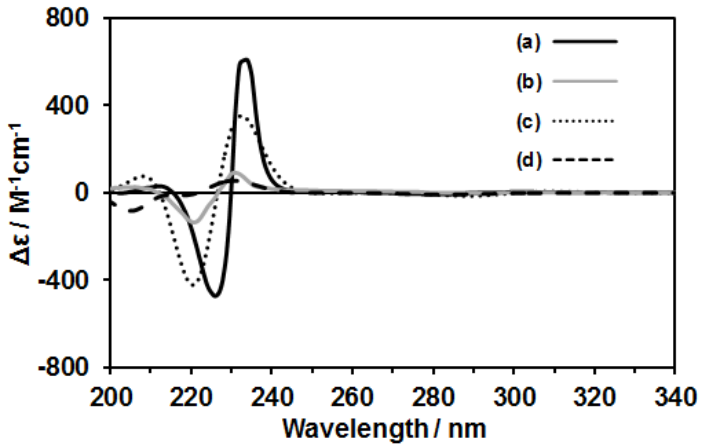

Fig. S3. The comparison at the main band region of the theoretical and experimental CD spectra of (*S*)-**1** and **-2**. (a) experimental curve of (*S*)-**1** (100 μ M in $CHCl_3$), (b) experimental curve of (*S*)-**2** (100 μ M in $CHCl_3$),(c) theoretical curve of (*S*)-**1** obtained at the TD-DFT-CAM-B3 LYP/TZVP level, (d) theoretical curve of (*S*)-**2** obtained at the TD-DFT-CAM-B3 LYP/TZVP level.

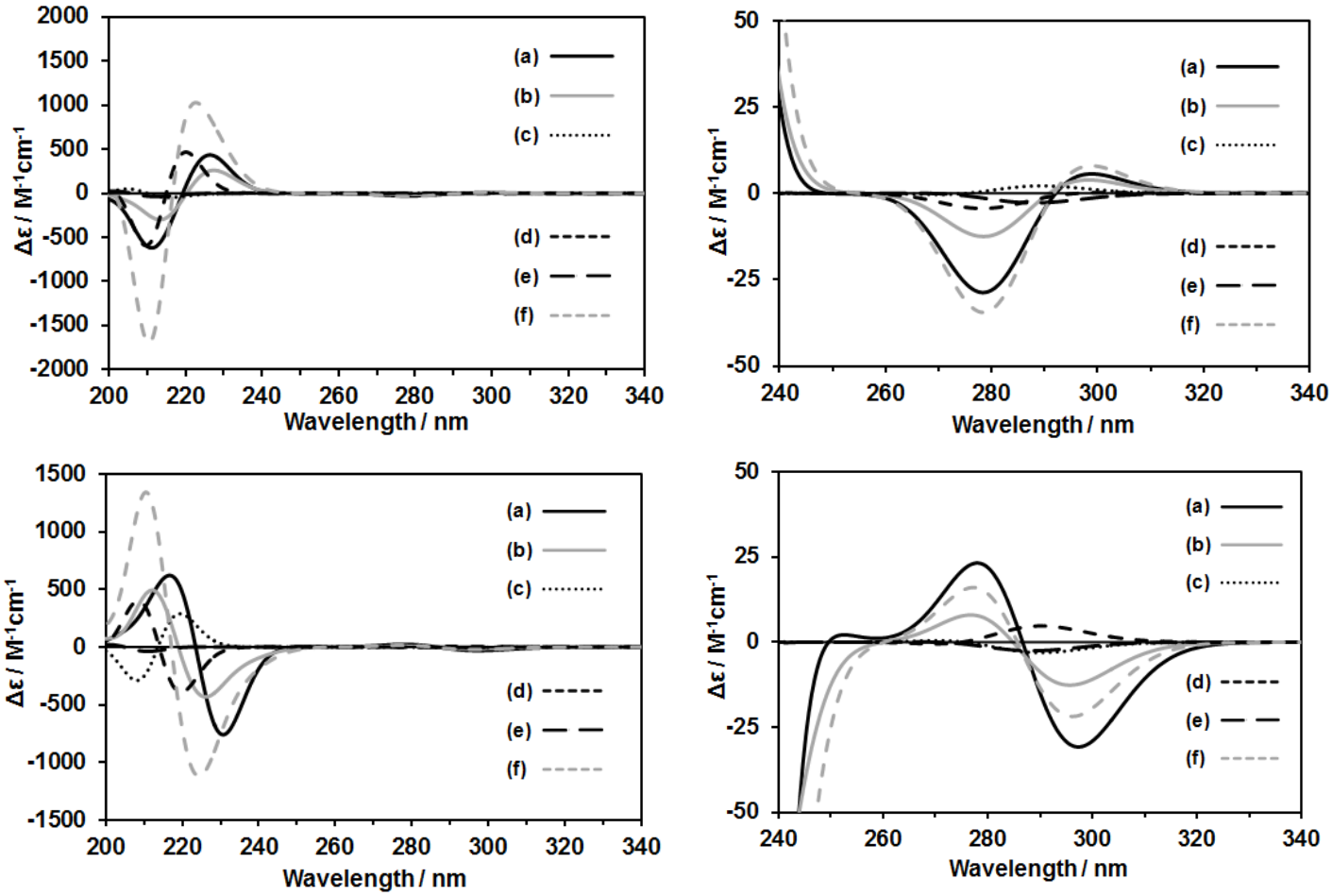

Fig. S4. Comparison of theoretical CD spectra for the full molecule of (*S*)-**2** to those of the model systems. Top: major conformer (*S*)-**2-I**. Bottom: minor conformer (*S*)-**2-II**. Left: whole spectral region. Right: expanded at the long-wavelength region. (a) theoretical curve for the four-naphthalene model (A/B/C/D interactions were considered) (b-e) theoretical curves of each pair (A/B, A/C, A/D, and B/C, respectively) of two-naphthalene sub-models (A/B, A/C, A/D, and B/C interactions were individually considered), (f) summation of the theoretical curves of four pairs of two-naphthalene sub-models (A/B, A/C, A/D, and B/C).

TABLE S1. Optimized Geometries of (*S*)-**1** and (*S*)-**2** at the DFT-D3-TPSS/def2-TZVP Level.

(*S*)-**1**

C	0.0000000	0.0000000	-2.1691005
C	0.7721460	-1.0039768	-3.0171569
C	-0.7721460	1.0039768	-3.0171569
C	-0.5820081	-0.5055716	0.0702775
C	-1.8793490	-0.0555079	0.8173938
C	-2.8873990	-1.2087605	0.9302560
C	-2.4476164	1.2354154	0.1904542
C	0.5820081	0.5055716	0.0702775
C	1.8793490	0.0555079	0.8173938
C	2.8873990	1.2087605	0.9302560
C	2.4476164	-1.2354154	0.1904542
O	-0.8913029	-0.7250433	-1.3045778
O	-1.4040847	0.2155894	2.1568696
O	0.8913029	0.7250433	-1.3045778
O	1.4040847	-0.2155894	2.1568696
C	-2.6036232	-2.4663124	0.4301740
C	-4.1204706	-1.0091076	1.6412305
C	-3.4896332	-3.5528183	0.5949045
C	-4.6706227	-3.3881659	1.2754376
C	4.1204706	1.0091076	1.6412305
C	2.6036232	2.4663124	0.4301740
C	3.4896332	3.5528183	0.5949045
C	4.6706227	3.3881659	1.2754376
C	-4.5182441	0.2406430	2.1941316
C	-5.0131711	-2.1228281	1.8136763
C	-6.2312792	-1.9420573	2.5180920
C	-5.7081286	0.3810535	2.8755015
C	-6.5764672	-0.7185017	3.0436026
C	4.5182441	-0.2406430	2.1941316
C	5.0131711	2.1228281	1.8136763
C	6.2312792	1.9420573	2.5180920
C	5.7081286	-0.3810535	2.8755015
C	6.5764672	0.7185017	3.0436026
C	2.0281578	-2.4325866	0.7472236
C	3.3633979	-1.2668050	-0.9139140
C	2.4740583	-3.6815691	0.2688011
C	3.3717412	-3.7376567	-0.7693768
C	-2.0281578	2.4325866	0.7472236
C	-3.3633979	1.2668050	-0.9139140
C	-2.4740583	3.6815691	0.2688011
C	-3.3717412	3.7376567	-0.7693768
C	3.8357583	-0.1130847	-1.5969352
C	3.8372901	-2.5456664	-1.3769146
C	4.7567857	-2.6067533	-2.4569986
C	4.7293069	-0.2074560	-2.6400327
C	5.2027185	-1.4640493	-3.0770678
C	-3.8357583	0.1130847	-1.5969352
C	-3.8372901	2.5456664	-1.3769146
C	-4.7567857	2.6067533	-2.4569986
C	-4.7293069	0.2074560	-2.6400327
C	-5.2027185	1.4640493	-3.0770678
H	1.2270137	-1.7628274	-2.3795536
H	0.0844450	-1.4899243	-3.7162294
H	1.5573727	-0.4974033	-3.5844762
H	-1.2270137	1.7628274	-2.3795536
H	-0.0844450	1.4899243	-3.7162294
H	-1.5573727	0.4974033	-3.5844762
H	-0.2578348	-1.4431771	0.5296490
H	0.2578348	1.4431771	0.5296490
H	-2.1512073	0.0747332	2.7620166
H	2.1512073	-0.0747332	2.7620166
H	-1.6990399	-2.6309356	-0.1427550
H	-3.2246061	-4.5194458	0.1760661
H	-5.3590828	-4.2186004	1.4110801
H	1.6990399	2.6309356	-0.1427550
H	3.2246061	4.5194458	0.1760661
H	5.3590828	4.2186004	1.4110801
H	-3.8896504	1.1127827	2.0560176
H	-6.8910537	-2.7988160	2.6330089
H	-5.9821148	1.3520312	3.2782626
H	-7.5124814	-0.5947857	3.5806336
H	3.8896504	-1.1127827	2.0560176
H	6.8910537	2.7988160	2.6330089
H	5.9821148	-1.3520312	3.2782626
H	7.5124814	0.5947857	3.5806336
H	1.3650913	-2.3957592	1.6046337
H	2.1123131	-4.5924372	0.7377519
H	3.7385639	-4.6912552	-1.1415037
H	-1.3650913	2.3957592	1.6046337
H	-2.1123131	4.5924372	0.7377519
H	-3.7385639	4.6912552	-1.1415037
H	3.4666479	0.8596548	-1.3095206
H	5.0980188	-3.5853550	-2.7865199
H	5.0662580	0.6980576	-3.1371699
H	5.9071909	-1.5242732	-3.9019460
H	-3.4666479	-0.8596548	-1.3095206
H	-5.0980188	3.5853550	-2.7865199
H	-5.0662580	-0.6980576	-3.1371699
H	-5.9071909	1.5242732	-3.9019460

(*S*)-**2-I**

C	0.0000000	0.0000000	-2.7272516
C	-0.0874797	-1.2733097	-3.5589993
C	0.0874797	1.2733097	-3.5589993
C	-0.7388822	-0.2134994	-0.5238137
C	-1.7224061	0.5058795	0.4367800
C	-3.1757587	0.2057938	0.0617483
C	-1.4220748	2.0012043	0.4762630
C	0.7388822	0.2134994	-0.5238137
C	1.7224061	-0.5058795	0.4367800
C	3.1757587	-0.2057938	0.0617483
C	1.4220748	-2.0012043	0.4762630
O	-1.1416782	0.1116673	-1.8604877
O	-1.4815431	-0.1174172	1.7206897
O	1.1416782	-0.1116673	-1.8604877
O	1.4815431	0.1174172	1.7206897
C	-3.5416511	-1.0746817	-0.4350135
C	-4.1704816	1.1267093	0.3242809
C	-4.8572451	-1.3917944	-0.6717043
C	-5.8946954	-0.4563362	-0.4208154
C	4.1704816	-1.1267093	0.3242809
C	3.5416511	1.0746817	-0.4350135
C	4.8572451	1.3917944	-0.6717043
C	5.8946954	0.4563362	-0.4208154
C	-5.5386726	0.8315463	0.0937987
C	-6.5654913	1.7752880	0.3527359
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C	6.5654913	-1.7752880	0.3527359
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C	1.7454595	-2.8207138	-0.6401125
C	0.7708678	-2.5573114	1.5555189
C	1.4138003	-4.1553972	-0.6514723
C	0.7411424	-4.7522562	0.4463864
C	-1.7454595	2.8207138	-0.6401125
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C	-1.4138003	4.1553972	-0.6514723
C	-0.7411424	4.7522562	0.4463864
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C	-0.2674260	-4.5139202	2.6720667
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C	8.2369607	-0.1900117	-0.3944982
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C	7.2618630	0.7478697	-0.6562481
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H	0.9473705	1.2216711	-4.2330026
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H	-0.1976158	-2.1365686	-2.8978636
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H	0.8122578	1.2924927	-0.3431540
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H	-2.2794591	0.0383735	2.2522267
H	-2.7727020	-1.8137311	-0.6309530
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H	-3.9127330	2.1097424	0.7095291
H	3.9127330	-2.1097424	0.7095291
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H	5.1196411	2.3737814	-1.0582980
H	-6.2909036	2.7527870	0.7421250
H	-8.6639303	2.1931519	0.3157992
H	6.2909036	-2.7527870	0.7421250
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H	0.4908818	-1.9224425	2.3895322
H	1.6675661	-4.7735048	-1.5097692
H	-0.4908818	1.9224425	2.3895322
H	-1.6675661	4.7735048	-1.5097692
H	-0.5188032	-3.8850679	3.5226647
H	0.5188032	3.8850679	3.5226647
H	1.1338706	6.2831497	3.5081479
H	0.5561462	7.7118284	1.5547738
H	-1.1338706	-6.2831497	3.5081479
H	-0.5561462	-7.7118284	1.5547738
H	-9.2816522	-0.0445187	-0.5785680
H	9.2816522	0.0445187	-0.5785680
H	-7.5288802	-1.7266922	-1.0475945
H	7.5288802	1.7266922	-1.0475945
H	-0.6299672	6.7445028	-0.3889528
H	-2.2585893	2.3764471	-1.4854042
H	0.6299672	-6.7445028	-0.3889528
H	2.2585893	-2.3764471	-1.4854042

(*S*)-**2-II**

C	0.0000000	0.0000000	-2.2356530
C	-0.5902433	1.1320295	-3.0672880
C	0.5902433	-1.1320295	-3.0672880
C	0.5340671	0.5545011	-0.0284636
C	1.7608756	0.3994215	0.9105621
C	2.8577732	1.4053624	0.5508429
C	2.2475727	-1.0471680	0.8887061
C	-0.5340671	-0.5545011	-0.0284636
C	-1.7608756	-0.3994215	0.9105621
C	-2.8577732	-1.4053624	0.5508429
C	-2.2475727	1.0471680	0.8887061
O	1.0311443	0.5018642	-1.3700653
O	1.2615551	0.7718220	2.2180167
O	-1.0311443	-0.5018642	-1.3700653
O	-1.2615551	-0.7718220	2.2180167
C	2.5225270	2.6967460	0.0605503
C	4.1816099	1.1225959	0.8252032
C	3.4930108	3.6442652	-0.1595178
C	4.8601490	3.3707355	0.1042657
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C	-2.5225270	-2.6967460	0.0605503
C	-3.4930108	-3.6442652	-0.1595178
C	-4.8601490	-3.3707355	0.1042657
C	5.2078390	2.0784656	0.6134497
C	6.5703412	1.7910587	0.8843984
C	7.5468359	2.7372607	0.6628561
C	-5.2078390	-2.0784656	0.6134497
C	-6.5703412	-1.7910587	0.8843984
C	-7.5468359	-2.7372607	0.6628561
C	-1.9063820	1.9244071	1.9482848
C	-2.9440671	1.5381073	-0.1991829
C	-2.2663599	3.2527785	1.9045566
C	-2.9779995	3.7831844	0.7990144
C	1.9063820	-1.9244071	1.9482848
C	2.9440671	-1.5381073	-0.1991829
C	2.2663599	-3.2527785	1.9045566
C	2.9779995	-3.7831844	0.7990144
C	-3.3223386	2.9008248	-0.2772244
C	-4.0296784	3.4220604	-1.3924241
C	3.3223386	-2.9008248	-0.2772244
C	4.0296784	-3.4220604	-1.3924241
C	4.3798891	-4.7526856	-1.4455341
C	4.0401833	-5.6235805	-0.3824449
C	3.3558830	-5.1481523	0.7142058
C	-4.3798891	4.7526856	-1.4455341
C	-4.0401833	5.6235805	-0.3824449
C	-3.3558830	5.1481523	0.7142058
C	7.2027455	4.0136592	0.1593318
C	-7.2027455	-4.0136592	0.1593318
C	5.8879540	4.3224326	-0.1140459
C	-5.8879540	-4.3224326	-0.1140459
H	-0.9489574	1.9251983	-2.4065733
H	0.1703758	1.5384722	-3.7400792
H	-1.4299250	0.7611401	-3.6630015
H	0.9489574	-1.9251983	-2.4065733
H	-0.1703758	-1.5384722	-3.7400792
H	1.4299250	-0.7611401	-3.6630015
H	0.0653377	1.5239518	0.1769783
H	-0.0653377	-1.5239518	0.1769783
H	2.0349692	1.0468644	2.7371339
H	-2.0349692	-1.0468644	2.7371339
H	1.4868381	2.9397551	-0.1485345
H	4.4604192	0.1421026	1.2014955
H	3.2195196	4.6240023	-0.5441519
H	-4.4604192	-0.1421026	1.2014955
H	-1.4868381	-2.9397551	-0.1485345
H	-3.2195196	-4.6240023	-0.5441519
H	6.8306769	0.8077762	1.2689735
H	8.5872290	2.5059821	0.8732821
H	-6.8306769	-0.8077762	1.2689735
H	-8.5872290	-2.5059821	0.8732821
H	-1.3311193	1.5298594	2.7778474
H	-3.2067189	0.8738970	-1.0164713
H	-1.9962459	3.9179307	2.7215972
H	1.3311193	-1.5298594	2.7778474
H	3.2067189	-0.8738970	-1.0164713
H	1.9962459	-3.9179307	2.7215972
H	-4.2885697	2.7488319	-2.2062571
H	4.2885697	-2.7488319	-2.2062571
H	4.9195992	-5.1404292	-2.3050170
H	4.3226546	-6.6712715	-0.4363092
H	3.0935928	-5.8150752	1.5322553
H	-4.9195992	5.1404292	-2.3050170
H	-4.3226546	6.6712715	-0.4363092
H	-3.0935928	5.8150752	1.5322553
H	7.9822129	4.7508559	-0.0116452
H	-7.9822129	-4.7508559	-0.0116452
H	5.6206549	5.3026288	-0.5017500
H	-5.6206549	-5.3026288	-0.5017500