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Supporting Information

Toward the Creation of NMR Databases in Chiral Solvents for Assignments of Relative and Absolute Stereochemistry: Scope and Limitation

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1. NMR database 1a~b (1,3-diol)

a. ^{13}C NMR Chemical shifts

	1a (syn)	**1a**	**1b** (anti)	**1b**	
DMBA	(*R*)	(*S*)	(*R*)	(*S*)	Average
1	61.210	61.198	61.265	61.253	61.232
2	33.219	33.242	33.293	33.313	33.267
3	22.107	22.106	22.614	22.628	22.364
4	38.429	38.445	38.138	38.169	38.295
5	71.458	71.475	67.739	67.676	69.587
6	43.644	43.654	44.458	44.59	44.087
7	71.176	71.216	67.473	67.394	69.315
8	40.752	40.813	40.492	40.522	40.645
9	18.635	18.651	19.175	19.189	18.913
10	14.106	14.114	14.133	14.135	14.122

b. relative (See Figure 1a in text)

	Black	Gray	Black	Gray
1	-0.021	-0.033	0.034	0.022
2	-0.048	-0.025	0.026	0.046
3	-0.257	-0.258	0.250	0.264
4	0.134	0.150	-0.157	-0.126
5	1.871	1.888	-1.848	-1.911
6	-0.443	-0.432	0.371	0.504
7	1.861	1.901	-1.842	-1.921
8	0.107	0.168	-0.153	-0.123
9	-0.278	-0.262	0.262	0.276
10	-0.016	-0.008	0.011	0.013

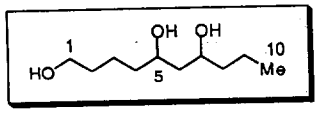
c. absolute (See Figure 1b in text)

	(*R*)-(*S*)	(*R*)-(*S*)
1	0.012	0.012
2	-0.023	-0.020
3	0.001	-0.014
4	-0.016	-0.031
5	-0.017	0.063
6	-0.010	-0.132
7	-0.040	0.079
8	-0.061	-0.030
9	-0.016	-0.014
10	-0.008	-0.002

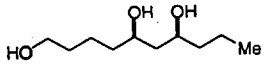
d. Assignment in DMBA

Correlation of carbon chemical shifts of **1a,b** in between DMSO-d_6 and (*R*)-DMBA. The *x*- and *y*-axes represent the region of 10~80 ppm and DMSO-d_6 contents (v/v%) in (*R*)-DMBA, respectively.

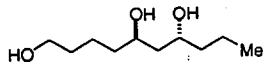
(See ref. 3 in text for assignment of ^{13}C NMR chemical shifts of **1a~b** in DMSO-d_6.)



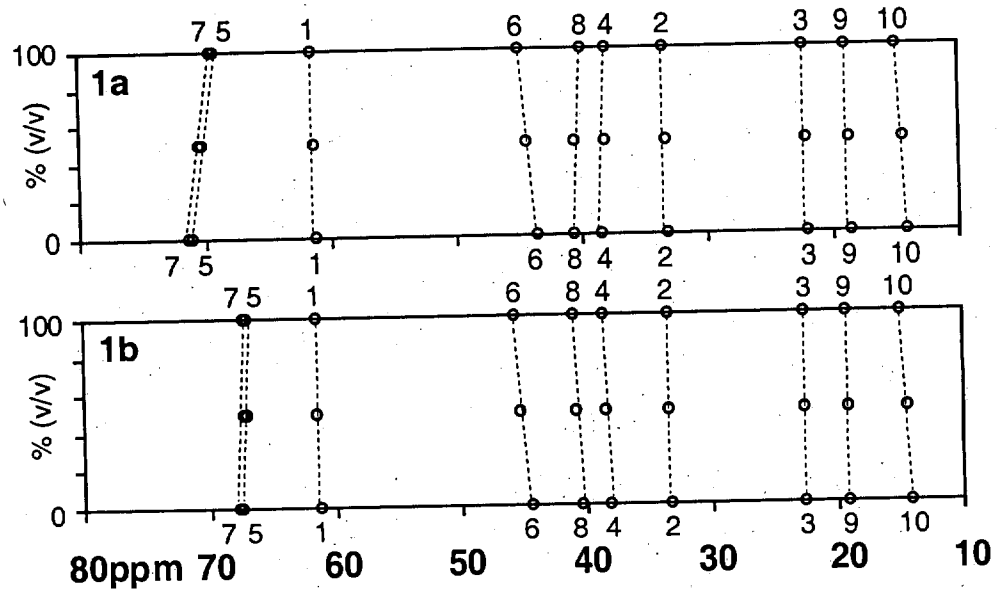
External Standard: Acetone-d_6 29.8ppm
in (*R*)-DMBA containing DMSO-d_6



1a (syn)



1b (anti)



2. NMR database 2a~d (1,3,5-triol)

a. ^{13}C NMR chemical shifts

	2a	anti/anti	**2b**	syn/anti	**2c**	anti/syn	**2d**	syn/syn	
DMBA	(*R*)	(*S*)	(*R*)	(*S*)	(*R*)	(*S*)	(*R*)	(*S*)	Average
1	59.375	59.356	58.855	58.784	59.317	59.353	58.731	58.782	59.069
2	40.579	40.621	40.727	40.789	40.750	40.696	40.740	40.754	40.707
3	66.487	66.579	69.399	69.284	65.953	65.913	68.673	68.720	67.626
4	45.288	45.180	44.801	44.825	45.423	45.521	45.142	45.124	45.163
5	65.053	65.095	68.154	68.196	68.300	68.192	71.232	71.179	68.175
6	45.003	45.118	45.210	45.111	44.481	44.517	44.427	44.464	44.791
7	67.466	67.360	66.767	66.841	70.686	70.636	70.493	70.451	68.838
8	40.511	40.542	40.727	40.717	40.637	40.627	40.673	40.646	40.635
9	19.135	19.169	19.112	19.120	18.687	18.679	18.688	18.695	18.911
10	14.129	14.143	14.125	14.139	14.085	14.088	14.102	14.111	14.115

b. relative (See Graph below)

relative	Black	Gray	Black	Gray	Black	Gray	Black	Gray
1	0.306	0.287	-0.214	-0.285	0.248	0.284	-0.338	-0.287
2	-0.128	-0.086	0.020	0.082	0.043	-0.011	0.033	0.047
3	-1.139	-1.047	1.773	1.658	-1.673	-1.713	1.047	1.094
4	0.125	0.017	-0.362	-0.338	0.260	0.358	-0.021	-0.039
5	-3.122	-3.080	-0.021	0.021	0.125	0.017	3.057	3.004
6	0.212	0.327	0.419	0.320	-0.310	-0.274	-0.364	-0.327
7	-1.372	-1.477	-2.071	-1.997	1.849	1.799	1.656	1.614
8	-0.124	-0.093	0.092	0.082	0.002	-0.008	0.038	0.011
9	0.224	0.258	0.201	0.209	-0.224	-0.232	-0.223	-0.216
10	0.014	0.028	0.010	0.024	-0.030	-0.027	-0.013	-0.004

c. absolute (See Figure 3 in text)

absolute	*R-S*	*R-S*	*R-S*	*R-S*
1	0.019	0.071	-0.036	-0.051
2	-0.042	-0.062	0.054	-0.014
3	-0.092	0.115	0.040	-0.047
4	0.108	-0.024	-0.098	0.018
5	-0.042	-0.042	0.108	0.053
6	-0.115	0.099	-0.036	-0.037
7	0.106	-0.074	0.050	0.042
8	-0.031	0.010	0.010	0.027
9	-0.034	-0.008	0.008	-0.007
10	-0.014	-0.014	-0.003	-0.009

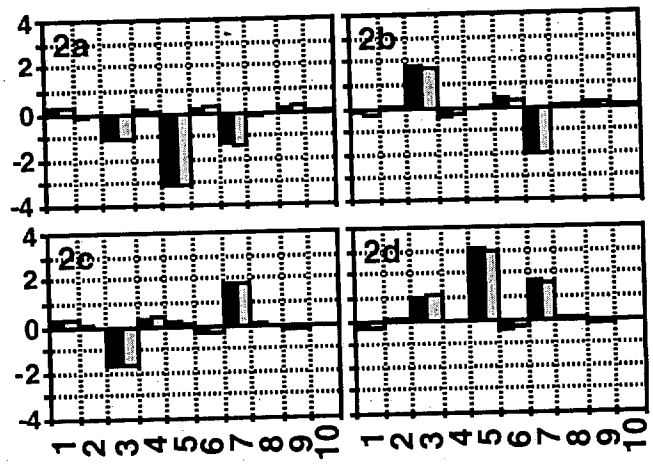
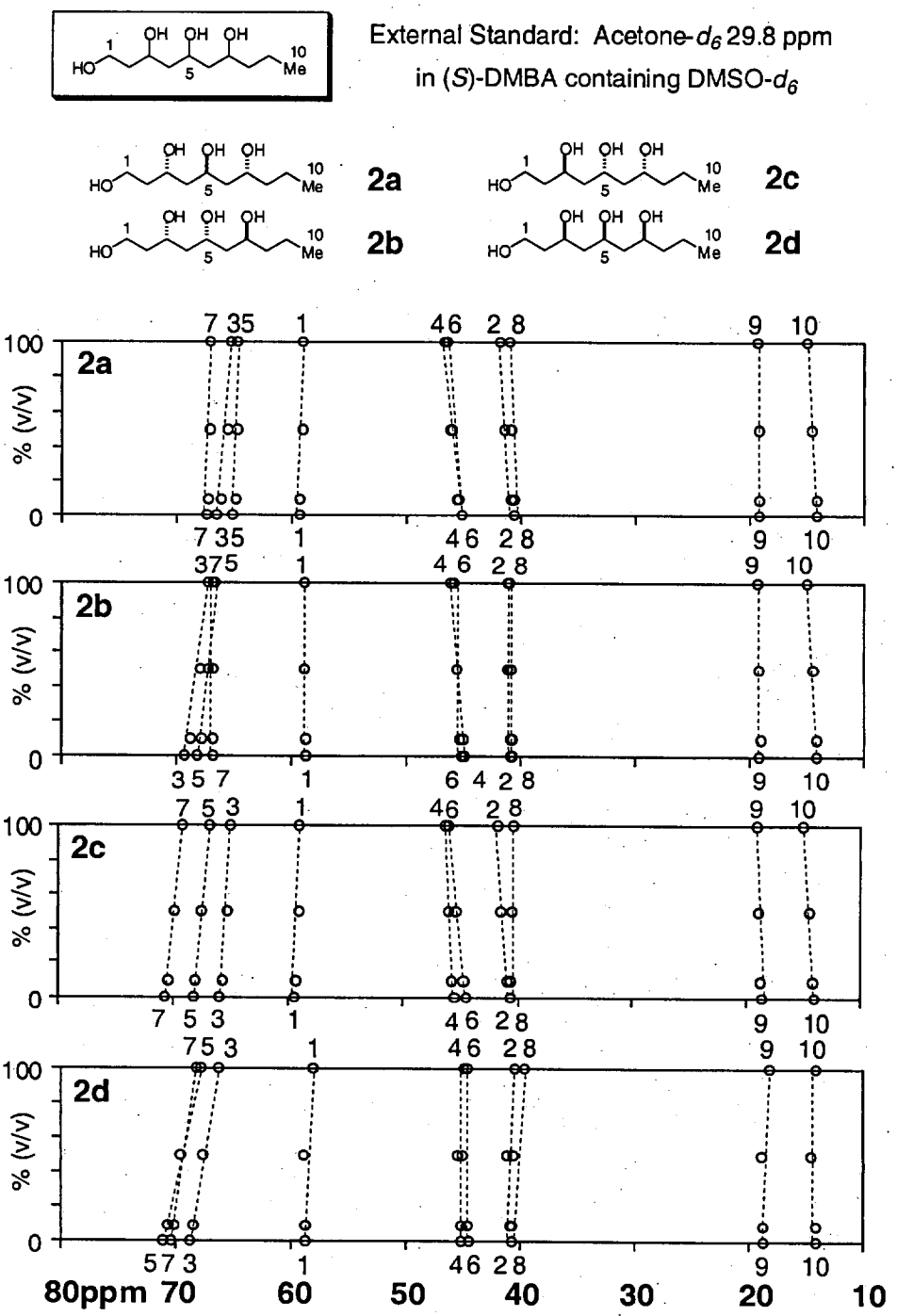


Figure Difference in carbon chemical shifts between the average and the values of **2a~d** (100 MHz, solid bar: (*R*)-DMBA, shadowed bar: (*S*)-DMBA). The *x*- and *y*-axes represent carbon number and $\Delta\delta$ ($\delta_{\mathbf{2a\sim d}}$-$\delta_{\mathbf{Ave}}$ in ppm), respectively.

d. Assignment in DMBA

Correlation of carbon chemical shifts of **2a~d** in between DMSO-d_6 and (*S*)-DMBA. The *x*- and *y*-axes represent the region of 10~80 ppm and DMSO-d_6 contents (v/v%) in (*S*)-DMBA, respectively.

(See ref. 3 in text for assignment of ^{13}C NMR chemical shifts of **2a~d** in DMSO-d_6.)



3. NMR database 3a~d (acetate-propionate)

a. ^{13}C NMR chemical shifts

	3a	anti/syn	**3b**	syn/anti	**3c**	syn/syn	**3d**	anti/anti	
DMBA	*R*	*S*	*R*	*S*	*R*	*S*	*R*	*S*	Average
1	61.216	61.237	61.219	61.210	61.160	61.147	61.247	61.269	61.213
2	33.284	33.318	33.364	33.370	33.251	33.263	33.302	33.312	33.308
3	22.536	22.61	23.161	23.158	22.880	22.903	21.965	21.981	22.649
4	35.655	35.694	**	**	35.541	35.567	34.613	34.675	35.291
5	74.324	74.411	71.250	71.352	75.787	75.793	74.473	74.507	73.987
6	42.124	42.076	42.144	42.082	40.968	40.970	44.282	44.306	42.369
7	71.019	71.135	74.127	74.179	75.510	75.493	74.339	74.298	73.763
8	36.593	36.567	38.111	38.123	37.888	37.871	37.243	37.163	37.445
9	19.677	19.685	19.173	19.161	19.419	19.399	18.524	18.549	19.198
10	14.144	14.161	14.186	14.181	14.143	14.130	14.258	14.263	14.183
11	11.592	11.669	11.569	11.621	5.213	5.205	12.695	12.687	10.281

b. relative (See Figure 4a in text)

	Black	Gray	Black	Gray	Black	Gray	Black	Gray
1	0.003	0.024	0.006	-0.003	-0.053	-0.066	0.034	0.056
2	-0.024	0.010	0.056	0.062	-0.057	-0.045	-0.006	0.004
3	-0.113	-0.039	0.512	0.509	0.231	0.254	-0.684	-0.668
4	0.364	0.403	**	**	0.250	0.276	-0.678	-0.616
5	0.337	0.424	-2.737	-2.635	1.800	1.806	0.486	0.520
6	-0.245	-0.293	-0.225	-0.287	-1.401	-1.399	1.913	1.937
7	-2.744	-2.628	0.364	0.416	1.748	1.730	0.576	0.535
8	-0.852	-0.878	0.666	0.678	0.443	0.426	-0.202	-0.282
9	0.479	0.487	-0.025	-0.037	0.221	0.201	-0.674	-0.649
10	-0.039	-0.022	0.003	-0.002	-0.040	-0.053	0.075	0.080
11	1.311	1.388	1.288	1.340	-5.068	-5.076	2.414	2.406

c. absolute (See Figure 4b in text)

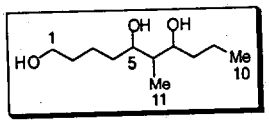
	R-S	*R-S*	*R-S*	*R-S*
1	-0.021	0.009	0.013	-0.022
2	-0.034	-0.006	-0.012	-0.010
3	-0.074	0.003	-0.023	-0.016
4	-0.039	**	-0.026	-0.062
5	-0.087	-0.102	-0.006	-0.034
6	0.048	0.062	-0.002	-0.024
7	-0.116	-0.052	0.017	0.041
8	0.026	-0.012	0.017	0.080
9	-0.008	0.012	0.020	-0.025
10	-0.017	0.005	0.013	-0.005
11	-0.077	-0.052	0.008	0.008

** Those peaks are hidden under the solvent peaks.

d. Assignment in DMBA

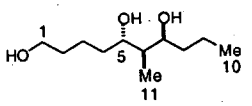
Correlation of carbon chemical shifts of **3a~d** in between DMSO-d_6 and (*R*)-DMBA. The *x*- and *y*-axes represent the region of 0~80 ppm and DMSO-d_6 contents (v/v%) in (*R*)-DMBA, respectively.

(See ref. 4 in text for assignment of ^{13}C NMR chemical shifts of **3a~d** in DMSO-d_6.)

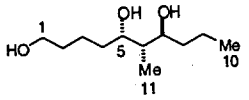


External Standard: Acetone-d_6 29.8 ppm
in (*R*)-DMBA containing DMSO-d_6

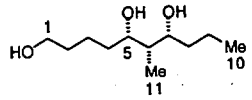
3a



3b



3c



3d