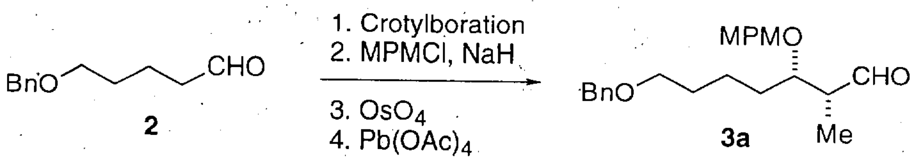
General Procedures and Methods.

NMR spectra were recorded on a Bruker DMX 500, AM 500, or AM 400 spectrometer. Chemical shifts are reported in parts per million (ppm). For ^{1}H NMR spectra, the central residual solvent peak (methanol, DMSO and chloroform) was used as the internal reference (3.30, 2.49 and 7.25 ppm) while the central solvent peak as the reference (49.0, 39.5 and 77.0 ppm, respectively) for ^{13}C NMR spectra. Fast atom bombardment (FAB) mass spectra were obtained with 3-nitrobenzyl alcohol or glycerol as the matrix. In order to save space, spectroscopic data is reported only selected compounds. Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on E. Merck kieselgel 60 (230-400) mesh silica gel. Preparative thin layer chromatography (PTLC) separations were performed on E. Merck pre-coated plates, silica gel 60F-254, layer thickness 0.50 mm. Reagents and solvents are commercial grade and were used as supplied, with the following exceptions. Benzene, ether, and THF were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from phosphorus pentoxide, and toluene was distilled from sodium. All reactions were conducted under an argon or nitrogen atmosphere. Reaction vessels were flame-dried or oven-dried and allowed to cool under an inert atmosphere.

Experimental Procedures for the Synthesis Summarized in Scheme 1.



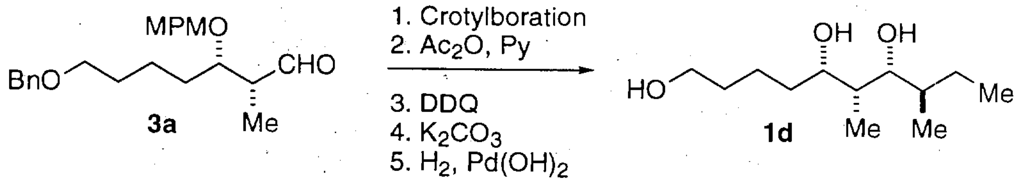
To a stirred mixture of potassium *tert*-butoxide (3.4 g, 27.8 mmol), THF (28 mL), and *cis*-2-butene (6.3 mL, 110 mmol), *n*-BuLi in THF (2.5 M, 27.8 mmol) was added at -78 °C. After complete addition of *n*-BuLi, the mixture was stirred at -45 °C for 10 min. The resulting solution was recooled to -78 °C, and to it was added dropwise (+)-methoxydiisopinocampheylborane in ether (1 M, 33.4 mmol). After the reaction mixture was stirred at -78 °C for 30 min, boron trifluoride etherate (4.7 mL, 37.3 mmol) was added dropwise. Then the aldehyde **2** (5.34 g, 27.8 mmol) in ether (5 mL) was added dropwise at -78 °C. The mixture was now stirred at -78 °C for 3 h and then treated with 3 N NaOH (41 mL, 122.4 mmol) and H_2O_2 (30%, 21 mL), and the resulting mixture was stirred overnight. The organic layer was separated and the aqueous layer was extracted with ether (100 mL x 2). The organic layers were combined, and dried ($MgSO_4$). After removal of the solvent, the residue was used for the next step without further purification.

To a crude alcohol (15.0 g, 97.4 mmol) and tetrabutylammonium iodide (3.6 g, 9.7 mmol) in DMF (250 mL) was added NaH (60% in mineral oil, 11.7 g, 292 mmol) at 0 °C. The mixture was stirred for 30 min. To the stirred mixture was added *p*-methoxybenzyl chloride (26.4 mL, 195 mmol) at 0 °C. The mixture was stirred and warmed to rt overnight. To the mixture was added saturated aqueous $Na_2S_2O_3$ (250 mL). The mixture was extracted with ether (300 mL x 2). The organic layers were combined, and dried ($MgSO_4$). After removal of ether, DMF was further removed by rotary evaporator under high vacuum to give the crude desired MPM ether.

The crude MPM ether (50 mmol) in a mixture of acetone (400 mL) and H_2O (50 mL) was treated with OsO_4 (0.3 M in toluene, 3.0 mL, 0.90 mmol) and 4-methylmorpholine *N*-oxide (12 g, 100 mmol) at rt. The reaction mixture was stirred at rt overnight. To the mixture was added saturated aqueous $Na_2S_2O_3$ solution (200 mL), and stirred for 1 h. The organic layer was separated and the aqueous layer was extracted with ether (200 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. At this stage, the crude material was separated by column chromatography over SiO_2 (Hex/EtOAc 3:1 then 1:2) to provide the pure diol.

To the diol (6.5 g, 16.2 mmol) in benzene (240 mL) was added lead(IV) acetate (8.6 g, 19.4 mmol) at rt. The mixture was stirred for 2 h at rt. To the mixture was then added saturated aqueous $NaHCO_3$ (200 mL). The organic layer was separated and the aqueous layer was extracted with ether (200 mL x 2). After removal of the solvent, the desired aldehyde **3a** (5.35 g, 52% overall from the aldehyde **2**) was used directly for the next step without any further purification.

The synthesis of **3b** from **2** was carried out under the same condition as the one given from **2** to **3a**, except *trans*-2-butene and (-)-methoxydiisopinocampheylborane used instead of *cis*-2-butene and (+)-methoxydiisopinocampheylborane.



To a stirred mixture of potassium *tert*-butoxide (0.70 g, 6.2 mmol), THF (6 mL), and *trans*-2-butene (0.70 g, 12.4 mmol), *n*-BuLi in THF (2.5 M, 6.2 mmol) was added at -78 °C. After complete addition of *n*-BuLi, the mixture was stirred at -45 °C for 10 min. The resulting solution was recooled to -78 °C, and to it was added dropwise (+)-

methoxydiisopinocampheylborane in ether (1 M, 7.5 mmol). After the reaction mixture was stirred at -78 °C for 30 min, boron trifluoride etherate (1.1 mL, 8.3 mmol) was added dropwise. Then the aldehyde **3a** (2.1 g, 5.6 mmol) in ether (2 mL) was added dropwise at -78 °C. The mixture was stirred at the same temperature for 3 h and then treated with 3 N NaOH (9 mL) and H_2O_2 (30%, 5 mL), and the resulting mixture was stirred overnight. The organic layer was separated and the aqueous layer was extracted with ether (20 mL x 2). The organic layers were combined, and dried ($MgSO_4$).

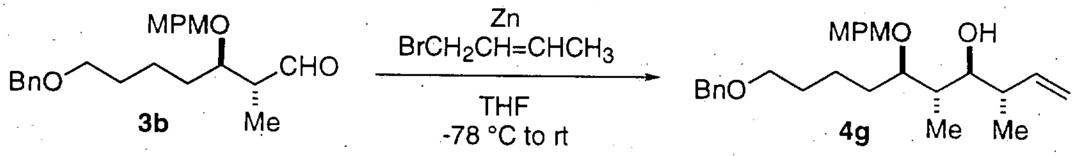
To the residue were added acetic anhydride (10 mL) and pyridine (20 mL) along with a catalytic amount of 4-(dimethylamino)pyridine. The reaction mixture was stirred for 4 h at rt. After reaction was completed, extra acetic anhydride and pyridine were removed by rotary evaporator under high vacuum. At this stage, the crude material was separated by column chromatography over SiO_2 (Hex/EtOAc 9:1) to provide the desired acetate (1.2 g) in overall 60% yield.

To the MPM ether (410 mg, 0.88 mmol) in a mixture of dichloromethane (10 mL) and water (1 mL) was added DDQ (300 mg, 1.31 mmol) at rt. The reaction mixture was vigorously stirred for 40 min. After the reaction was completed, saturated aqueous $NaHCO_3$ was added to it. The organic layer was separated and the aqueous layer was extracted with ether (20 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered, evaporated. The residue was carefully purified by column chromatography on SiO_2 (Hex/EtOAc 6:1) to provide the alcohol (230 mg) in 75% yield. This stage provides the best opportunity for separation of the pure diastereomer.

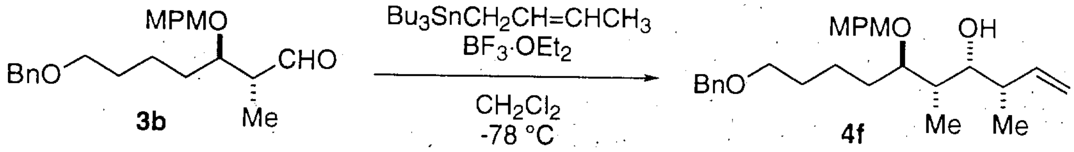
To the acetate (170 mg, 0.49 mmol) in methanol (5 mL) was added K_2CO_3 (1 g, 7.2 mmol) at rt. The reaction mixture was vigorously stirred for 2 h at rt. Then the mixture was treated with water (10 mL) and ether (20 mL). The organic layer was separated and the aqueous layer was extracted with ether (20 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered and evaporated *in vacuo*. The residue was purified on short column chromatography on SiO_2 to give the diol (140 mg) in 93% yield.

Then the diol (85 mg, 0.28 mmol) dissolved in ethanol (10 mL) was treated with $Pd(OH)_2$ (20%, 17 mg, 20% w/w) under hydrogen atmosphere at rt overnight. The mixture was filtered through a pad of Celite and washed with EtOAc. The filtrate was concentrated, and the resulting crude material was purified by column chromatography on SiO_2 (Hex/EtOAc 1:2) to provide the desired triol **1d** (47 mg) in 78% yield.

The synthesis of **1a~c and 1e~h** from **3a and 3b**, respectively, was carried out under the same condition given from **3a** to **1d**, except the Brown reagent used.



Crotylzinc addition to aldehyde: Crotyl bromide (1.6 mL, 11.4 mmol) was added to a suspension of zinc dust (0.85 g, 11.4 mmol) in THF (20 mL) at rt. The resulting mixture was warmed in order to initiate the exothermic reaction and stirred for 1 h at rt without cooling and then cooled to -78 °C and stirred for 10 min. A solution of the aldehyde **3b** (0.40 g, 1.1 mmol) in THF (3 mL) was added to the reaction mixture, and the resulting mixture was stirred and warmed to rt for 2 h, and poured into saturated aqueous NH_4Cl (30 mL). The separated aqueous layer was extracted with ether (30 mL x 2), dried ($MgSO_4$), filtered, concentrated and purified by column chromatography on SiO_2 (Hex/EtOAc 4:1) to provide the alcohols **4g** (0.41 g, 85%) in 5:1 diastereomeric ratio (the desired isomer is major). The corresponding triol was prepared in the same method as above.

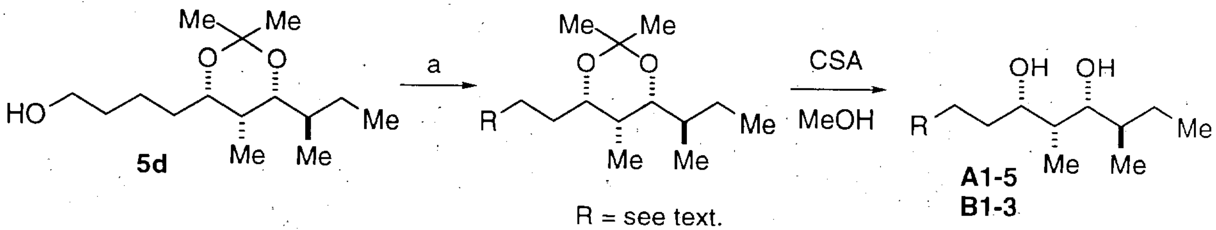


Preparation of crotyltributylstannane: Magnesium turnings (1.2 g, 49.4 mmol) were placed in a 100 mL round-bottomed flask equipped with a water condenser. THF (16 mL) was added, and the reaction was initiated by adding a small amount of crotyl bromide (0.3 mL, 2.5 mmol). The rapidly stirred mixture was then heated to reflux, and a solution of tributyltin chloride (3.4 mL, 12.4 mmol) and crotyl bromide (2.3 mL, 19.3 mmol) in THF (12 mL) was added slowly. After the addition was completed, the reaction mixture was heated at reflux overnight. The mixture was then cooled and hydrolyzed by saturated NH_4Cl solution. The aqueous layer was extracted with ether (30 mL x 2). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated. The crude product was highly pure and directly used for the following reaction.

Crotylstannane addition to aldehyde: To a solution of the aldehyde **3a** (0.20 g, 0.55 mmol) and crotyltributylstannane (0.38 g, 1.1 mmol) in CH_2Cl_2 (5 mL) was added dropwise boron trifluoride etherate (0.15 mL, 1.2 mmol) at -78 °C. The mixture was stirred for 2 h at the same temperature. Then the reaction mixture was poured into saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (20 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered, evaporated. The residue was purified by column chromatography on SiO_2 (Hex/EtOAc 6:1) to provide the alcohols **4f** (0.19 g, 82%) in 5:1 diastereomeric ratio (the desired isomer is major). The corresponding triol was prepared in the same method as above.

^{13}C and ^{1}H NMR Data for 1a~h in CD_3OD: see Table 1 and Table 3, respectively.
^{13}C and ^{1}H NMR Data for 1a~h in $(CD_3)_2SO$: see Table 5 and Table 7, respectively.
^{13}C and ^{1}H NMR Data for 1a~h in $CDCl_3$: see Table 9 and Table 12, respectively.

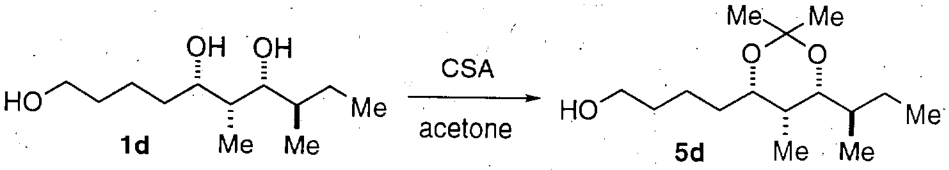
The synthesis of A1~5 and B1~3 was carried out as summarized below.



Conditions[a]
A1: PivCl, NEt_3, CH_2Cl_2; **A2**: (1) Dess-Martin; (2) $CH_2=PPh_3$, THF; **A3**: (1) TsCl, Py; (2) LAH, THF; **A4**: $RuCl_3$, $NaIO_4$, EtOAc–H_2O; **A5**: MeI, NaH, DMF; **B3**: (1) *o*-nitroselenocyanate, Bu_3P, THF; (2) MCPBA, NEt_3, CH_2Cl_2; **B1**: Starting from **B3**, (1) O_3, CH_3OH, -78°C; Me_2S, (2) $NaBH_4$, CH_3OH; **B2**: Starting from **B1**, PivCl, NEt_3, CH_2Cl_2.

For ^{13}C NMR spectra of **A1~5**, **B1~3**, see Table 15 and Table 17, respectively.

Strereochemical Assignment



A mixture of triol **1d** (50 mg, 0.23mmol) and CSA (5 mg, 0.02mmol) in acetone(1 mL) was stirred at room temperature for 15 min. Then the mixture was poured into saturated $NaHCO_3$ solution (10 mL). The aqueous layer was extracted with EtOAc(10 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered, evaporated. The residue was purified by column chromatography on SiO_2 (Hex/EtOAc 3:1) to provide acetonide **5d** (58 mg, 98%)

The synthesis of **5a~c** and **5e~h** from **1a~c** and **1e~h**, respectively, was carried out under the same condition given from **1d** to **5d**.

For the ^{13}C chemical shift of two methyl groups in the acetonide moiety, see Table shown below.

Table. ^{13}C NMR Chemical Shifts of Two Methyl Groups in Acetonide **5a~h**.

Compound	Chemical Shifts[a] of Two Methyl Groups (ppm)	C-5/C-7
5a	23.91, 25.64,	anti
5b	19.60, 30.06	syn
5c	23.83, 25.94	anti
5d	19.99, 30.36	syn
5e	19.87, 30.46	syn
5f	24.06, 25.13	anti
5g	19.81, 30.50	syn
5h	24.09, 25.35	anti

(a) ^{13}C NMR (100 MHz) was measured in CD_3OD.

NMR Database Sets

A. ^{13}C NMR Database Sets of Triol 1 in CD_3OD

Table 1. ^{13}C NMR Chemical Shifts in CD_3OD (ppm).

Position	Ave.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
1	62.95	62.94	62.89	62.91	62.91	63.00	62.97	63.01	62.97
2	33.70	33.70	33.68	33.69	33.66	33.72	33.69	33.72	33.70
3	23.48	23.92	23.50	23.73	23.37	23.25	23.46	23.25	23.35
4	34.94	35.30	35.91	35.48	35.74	33.03	34.99	33.39	35.69
5	74.71	72.66	75.20	72.60	76.70	74.98	75.04	75.01	75.47
6	41.02	41.14	40.46	39.71	39.93	42.72	41.04	42.61	40.53
7	78.21	76.42	78.96	80.13	80.18	77.65	75.98	80.59	75.73
8	38.42	38.03	38.17	38.61	38.75	38.08	38.55	38.41	38.79
9	26.17	28.13	27.13	24.21	25.83	28.25	26.77	22.68	26.39
10	11.86	12.24	11.62	12.04	11.39	12.39	11.39	12.47	11.35
11	10.06	10.54	7.77	11.03	6.57	11.74	10.50	12.21	10.09
12	14.92	12.66	14.56	16.56	15.52	12.14	15.38	17.15	15.38

Table 2. Difference in Carbon Chemical Shifts (ppm) between Average and Each of **1a~h** (CD_3OD).

Position	Ave.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
1	62.95	-0.01	-0.06	-0.04	-0.04	+0.05	+0.02	+0.06	+0.02
2	33.70	+0.01	-0.02	-0.01	-0.04	+0.02	-0.01	+0.02	+0.01
3	23.48	+0.44	+0.02	+0.25	-0.11	-0.23	-0.02	-0.23	-0.13
4	34.94	+0.36	+0.97	+0.54	+0.80	-1.91	+0.05	-1.55	+0.75
5	74.71	-2.05	+0.49	-2.11	+1.99	+0.27	+0.33	+0.30	+0.76
6	41.02	+0.12	-0.56	-1.31	-1.09	+1.70	+0.02	+1.59	-0.49
7	78.21	-1.79	+0.75	+1.92	+1.97	-0.56	-2.23	+2.38	-2.48
8	38.42	-0.39	-0.25	+0.19	+0.33	-0.34	+0.13	-0.01	+0.37
9	26.17	+1.96	+0.96	-1.96	-0.34	+2.08	+0.60	-3.49	+0.22
10	11.86	+0.38	-0.24	+0.18	-0.47	+0.53	-0.47	+0.61	-0.51
11	10.06	+0.48	-2.29	+0.97	-3.49	+1.68	+0.44	+2.15	+0.03
12	14.92	-2.26	-0.36	+1.64	+0.60	-2.78	+0.46	+2.23	+0.46

See Figure 1. in this supporting information.

Table 3. ^{1}H NMR Chemical Shifts in CD_3OD (ppm).

Position	Ave.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
1	3.555	3.555	3.554	3.554	3.554	3.558	3.553	3.555	3.555
2	1.553	1.559	1.552	1.558	1.550	1.556	1.559	1.543	1.548
3	1.391	1.378	1.363	1.368	1.500	1.374	1.382	1.380	1.382
3	1.540	1.535	1.492	1.509	1.500	1.578	1.568	1.578	1.563
4	1.405	1.396	1.492	1.392	1.366	1.361	1.442	1.345	1.449
4	1.518	1.559	1.492	1.550	1.366	1.550	1.519	1.538	1.567
5	3.741	3.948	3.663	3.960	3.674	3.804	3.552	3.783	3.542
6	1.679	1.617	1.635	1.686	1.643	1.737	1.694	1.783	1.638
7	3.429	3.496	3.419	3.321	3.377	3.390	3.552	3.278	3.600
8	1.507	1.487	1.574	1.549	1.500	1.494	1.471	1.532	1.450
9	1.158	1.282	1.146	1.114	1.102	1.304	1.085	1.108	1.119
9	1.551	1.449	1.448	1.634	1.719	1.416	1.439	1.529	1.775
10	0.908	0.919	0.902	0.911	0.907	0.918	0.890	0.906	0.912
11	0.855	0.801	0.920	0.882	0.897	0.768	0.899	0.790	0.880
12	0.877	0.841	0.905	0.904	0.823	0.829	0.957	0.962	0.798

Table 4. Difference in Proton Chemical Shifts (ppm) between Average and Each of **1a~h** (CD_3OD).

Position	Ave.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
1	3.555	±0.000	-0.001	-0.001	-0.001	+0.003	-0.002	±0.000	+0.001
2	1.553	+0.006	-0.001	+0.005	-0.003	+0.002	+0.006	-0.010	-0.005
3	1.391	-0.013	-0.028	-0.023	+0.109	-0.017	-0.009	-0.011	-0.009
3	1.540	-0.005	-0.048	-0.031	-0.040	+0.038	+0.028	+0.038	+0.023
4	1.405	-0.009	+0.087	-0.013	-0.040	-0.044	+0.037	-0.060	+0.044
4	1.518	+0.041	-0.026	+0.032	-0.152	+0.032	+0.001	+0.020	+0.049
5	3.741	+0.207	-0.078	+0.219	-0.067	+0.063	-0.189	+0.042	-0.199
6	1.679	-0.062	-0.044	+0.007	-0.036	+0.058	+0.015	+0.104	-0.041
7	3.429	+0.067	-0.011	-0.108	-0.052	-0.039	+0.123	-0.151	+0.171
8	1.507	-0.020	+0.067	+0.042	-0.007	-0.013	-0.036	+0.025	-0.057
9	1.158	+0.124	-0.011	-0.044	-0.056	+0.146	-0.072	-0.049	-0.039
9	1.551	-0.102	-0.103	+0.083	+0.168	-0.135	-0.112	-0.022	+0.224
10	0.908	+0.011	-0.006	+0.003	-0.001	+0.010	-0.018	-0.002	+0.003
11	0.855	-0.053	+0.065	+0.027	+0.042	-0.087	+0.045	-0.065	+0.025
12	0.877	-0.037	+0.028	+0.027	-0.054	-0.048	+0.080	+0.084	-0.080

See Figure 2. in this supporting information.

B. ^{13}C NMR Database Sets of Triol 1 in $(CD_3)_2SO$

Table 5. ^{13}C NMR Chemical Shifts in $(CD_3)_2SO$ (ppm).

Position	Ave.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
1	60.82	60.74	60.78	60.77	60.77	60.92	60.84	60.91	60.82
2	32.78	32.75	32.79	32.78	32.78	32.95	32.78	32.65	32.81
3	22.29	22.70	22.26	22.48	22.12	22.32	22.16	22.26	22.05
4	33.62	34.22	34.84	34.43	34.63	31.49	33.34	31.77	34.24
5	71.63	69.66	72.14	69.72	73.75	71.72	71.92	71.63	72.53
6	39.75	39.82	39.11	38.52	38.49	41.56	39.89	41.41	39.22
7	75.07	73.18	75.56	77.02	77.10	74.51	72.90	77.41	72.88
8	36.70	36.23	36.46	36.78	37.05	36.41	36.89	36.65	37.15
9	24.77	26.79	25.91	22.57	24.30	26.87	25.41	21.39	24.97
10	11.62	11.95	11.44	11.85	11.17	12.15	11.16	12.12	11.14
11	9.79	10.06	8.06	10.59	6.82	11.15	10.31	11.54	9.83
12	14.66	12.36	14.10	16.46	15.28	12.03	15.06	16.86	15.11

Table 6. Difference in Carbon Chemical Shifts (ppm) between Average and Each of **1a~h** ($(CD_3)_2SO$).

Position	Ave.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
1	60.82	-0.08	-0.04	-0.05	-0.05	+0.10	+0.02	+0.09	±0.00
2	32.78	-0.04	+0.01	-0.01	-0.01	+0.16	±0.00	-0.13	+0.02
3	22.29	+0.41	-0.03	+0.19	-0.17	+0.02	-0.14	-0.03	-0.25
4	33.62	+0.60	+1.22	+0.81	+1.01	-2.13	-0.28	-1.85	+0.62
5	71.63	-1.97	+0.50	-1.92	+2.11	+0.08	+0.29	±0.00	+0.90
6	39.75	+0.07	-0.64	-1.23	-1.26	+1.80	+0.13	+1.66	-0.53
7	75.07	-1.89	+0.49	+1.95	+2.03	-0.56	-2.17	+2.34	-2.19
8	36.70	-0.47	-0.25	+0.08	+0.35	-0.29	+0.19	-0.05	+0.45
9	24.77	+2.01	+1.13	-2.20	-0.48	+2.09	+0.64	-3.38	+0.19
10	11.62	+0.33	-0.18	+0.23	-0.45	+0.52	-0.47	+0.50	-0.48
11	9.79	+0.26	-1.74	+0.79	-2.97	+1.36	+0.52	+1.75	+0.03
12	14.66	-2.30	-0.56	+1.80	+0.62	-2.62	+0.40	+2.20	+0.45

See Figure 5. in this supporting information.

Table 7. ^{1}H NMR Chemical Shifts in $(CD_3)_2SO$ (ppm).

Position	Ave.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
1	3.363	3.367	3.358	3.362	3.361	3.365	3.359	3.364	3.364
2	1.396	1.403	1.389	1.390	1.388	1.380	1.422	1.401	1.394
3	1.229	1.220	1.219	1.224	1.221	1.234	1.247	1.210	1.255
3	1.398	1.405	1.342	1.382	1.363	1.449	1.410	1.412	1.419
4	1.245	1.234	1.327	1.240	1.329	1.161	1.246	1.162	1.263
4	1.362	1.397	1.327	1.365	1.329	1.342	1.350	1.370	1.414
5	3.568	3.786	3.458	3.787	3.477	3.668	3.366	3.636	3.362
6	1.490	1.408	1.432	1.489	1.463	1.551	1.505	1.617	1.454
7	3.251	3.326	3.238	3.166	3.205	3.200	3.358	3.098	3.416
8	1.373	1.359	1.457	1.412	1.371	1.355	1.320	1.408	1.305
9	1.061	1.184	1.057	1.020	1.008	1.190	1.000	1.022	1.008
9	1.440	1.343	1.323	1.495	1.618	1.320	1.326	1.412	1.681
10	0.822	0.835	0.815	0.827	0.818	0.830	0.803	0.824	0.822
11	0.720	0.658	0.786	0.736	0.768	0.641	0.762	0.672	0.735
12	0.774	0.733	0.792	0.819	0.725	0.722	0.845	0.861	0.694

Table 8. Difference in Proton Chemical Shifts (ppm) between Average and Each of **1a~h** ($(CD_3)_2SO$).

Position	Ave.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
1	3.363	+0.004	-0.005	-0.001	-0.002	+0.002	-0.003	+0.001	+0.003
2	1.396	+0.007	-0.007	-0.006	-0.008	-0.016	+0.032	+0.005	+0.006
3	1.229	-0.009	-0.010	-0.005	-0.008	+0.005	+0.023	-0.019	+0.034
3	1.398	+0.007	-0.056	-0.016	-0.035	+0.051	+0.028	+0.014	+0.056
4	1.245	-0.011	+0.082	-0.005	+0.084	-0.084	+0.006	-0.083	-0.066
4	1.362	+0.035	-0.035	+0.003	-0.033	-0.020	-0.015	+0.008	+0.085
5	3.568	+0.219	-0.110	+0.220	-0.091	+0.101	-0.421	+0.069	-0.115
6	1.490	-0.082	-0.058	-0.001	-0.027	+0.061	+0.016	+0.127	-0.009
7	3.251	+0.075	-0.013	-0.085	-0.046	-0.051	+0.192	-0.153	+0.211
8	1.373	-0.014	+0.084	+0.039	-0.002	-0.018	-0.092	+0.035	-0.066
9	1.061	+0.123	-0.004	-0.041	-0.053	+0.129	-0.020	-0.039	+0.000
9	1.440	-0.097	-0.117	+0.055	+0.178	-0.120	-0.169	-0.028	+0.063
10	0.822	+0.013	-0.007	+0.005	-0.004	+0.008	-0.024	+0.002	+0.004
11	0.720	-0.062	+0.066	+0.016	+0.048	-0.079	+0.026	-0.048	-0.033
12	0.774	-0.041	+0.018	+0.045	-0.049	-0.052	+0.026	+0.087	-0.031

See Figure 6. in this supporting information.

C. ^{13}C NMR Database Sets of Triol 1 in $CDCl_3$

Table 9. ^{13}C NMR Chemical Shifts in $CDCl_3$ (ppm).

Position	Ave.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
1	62.68	62.67	62.80	62.56	62.68	62.64	62.70	62.74	62.66
2	32.52	32.60	32.59	32.53	32.51	32.48	32.51	32.52	32.47
3	22.25	22.82	22.47	22.61	22.49	21.22	22.55	21.26	22.56
4	34.46	33.01	35.08	33.85	35.08	34.18	35.07	34.25	35.16
5	75.82	73.55	77.00	72.28	77.42	76.68	76.48	76.54	76.60
6	38.82	39.03	37.88	37.81	37.80	40.88	38.22	40.79	38.14
7	79.05	77.63	81.53	80.36	81.41	79.30	75.28	82.03	74.87
8	37.33	37.01	37.63	37.48	37.72	36.82	37.35	37.01	37.60
9	24.98	26.62	25.32	23.95	25.20	27.03	25.21	21.18	25.35
10	11.42	11.77	10.99	11.50	10.84	12.17	10.90	12.23	11.00
11	10.00	11.87	4.69	11.63	4.17	12.97	10.82	13.36	10.48
12	14.62	12.79	15.12	15.78	14.87	11.56	15.32	16.68	14.83

Table 10. Difference in Caobon Chemical Shifts (ppm) between Average and Each of **1a~h** ($CDCl_3$).

Position	Ave.	1 a	1 b	1 c	1 d	1 e	1 f	1 g	1 h
1	62.68	-0.01	+0.11	-0.12	±0.00	-0.04	+0.02	+0.05	-0.02
2	32.52	+0.07	+0.06	+0.01	-0.02	-0.04	-0.02	-0.01	-0.06
3	22.25	+0.57	+0.22	+0.36	+0.24	-1.03	+0.31	-0.98	+0.31
4	34.46	-1.45	+0.62	-0.61	+0.62	-0.28	+0.61	-0.21	+0.70
5	75.82	-2.27	+1.18	-3.54	+1.60	+0.86	+0.66	+0.72	+0.78
6	38.82	+0.21	-0.94	-1.01	-1.02	+2.06	-0.60	+1.97	-0.68
7	79.05	-1.42	+2.48	+1.31	+2.36	+0.25	-3.77	+2.98	-4.18
8	37.33	-0.31	+0.30	+0.15	+0.39	-0.50	+0.02	-0.31	+0.27
9	24.98	+1.64	+0.34	-1.03	+0.22	+2.05	+0.23	-3.81	+0.37
10	11.42	+0.35	-0.43	+0.07	-0.58	+0.74	-0.53	+0.81	-0.42
11	10.00	+1.87	-5.31	+1.63	-5.83	+2.97	+0.82	+3.36	+0.48
12	14.62	-1.83	+0.50	+1.16	+0.25	-3.06	+0.70	+2.06	+0.21

See Figure 7. in this supporting information.

Table 11. ^1H NMR Chemical Shifts in $CDCl_3$ (ppm).

Position	Ave.	1 a	1 b	1 c	1 d	1 e	1 f	1 g	1 h
1	3.641	3.639	3.650	3.628	3.639	3.640	3.644	3.647	3.644
2	1.581	1.589	1.599	1.569	1.572	1.578	1.570	1.581	1.590
3	1.402	1.389	1.404	1.355	1.381	1.437	1.387	1.454	1.409
3	1.529	1.566	1.498	1.538	1.381	1.579	1.573	1.575	1.524
4	1.433	1.403	1.418	1.367	1.398	1.431	1.505	1.445	1.499
4	1.578	1.564	1.556	1.533	1.546	1.604	1.590	1.605	1.622
5	3.734	3.846	3.803	3.916	3.812	3.637	3.616	3.632	3.612
6	1.683	1.782	1.680	1.756	1.638	1.620	1.684	1.677	1.629
7	3.495	3.499	3.465	3.329	3.449	3.519	3.634	3.423	3.641
8	1.516	1.521	1.512	1.570	1.465	1.528	1.488	1.574	1.467
9	1.123	1.213	1.032	1.112	1.111	1.298	1.017	1.109	1.095
9	1.514	1.385	1.404	1.662	1.706	1.374	1.360	1.478	1.743
10	0.885	0.897	0.864	0.890	0.889	0.905	0.856	0.888	0.892
11	0.864	0.838	0.873	0.930	0.859	0.731	0.966	0.753	0.963
12	0.867	0.874	0.956	0.840	0.767	0.817	0.966	0.963	0.750

Table 12. Difference in Proton Chemical Shifts (ppm) between Average and Each of **1a~h** ($CDCl_3$).

Position	Ave.	1 a	1 b	1 c	1 d	1 e	1 f	1 g	1 h
1	3.641	-0.002	+0.009	-0.013	-0.002	-0.001	+0.003	+0.006	+0.003
2	1.581	+0.008	+0.018	-0.012	-0.009	-0.003	-0.011	±0.000	+0.009
3	1.402	-0.013	+0.002	-0.047	-0.021	+0.035	-0.015	+0.052	+0.007
3	1.529	+0.037	-0.031	+0.009	-0.148	+0.050	+0.044	+0.046	-0.005
4	1.433	-0.030	-0.015	-0.066	-0.035	-0.002	+0.072	+0.012	+0.066
4	1.578	-0.014	-0.022	-0.045	-0.032	+0.027	+0.013	+0.027	+0.045
5	3.734	+0.112	+0.069	+0.182	+0.078	-0.097	-0.118	-0.102	-0.122
6	1.683	+0.099	-0.003	+0.073	-0.045	-0.063	+0.001	-0.006	-0.054
7	3.495	+0.004	-0.030	-0.166	-0.046	+0.024	+0.139	-0.072	+0.146
8	1.516	+0.005	-0.004	+0.054	-0.051	+0.012	-0.028	+0.058	-0.049
9	1.123	+0.090	-0.091	-0.011	-0.012	+0.175	-0.106	-0.014	-0.028
9	1.514	-0.129	-0.110	+0.148	+0.192	-0.140	-0.154	-0.036	+0.229
10	0.885	+0.012	-0.021	+0.005	+0.004	+0.020	-0.029	+0.003	+0.007
11	0.864	-0.026	+0.009	+0.066	-0.005	-0.133	+0.102	-0.111	+0.099
12	0.867	+0.007	+0.089	-0.027	-0.100	-0.050	+0.099	+0.096	-0.117

See Figure 8. in this supporting information.

D. Solvent Effect

1. CD_3OD vs $(CD_3)_2SO$

Table 13. $\Delta\delta$ ($\delta_{(CD3)2SO}$-δ_{CD3OD}) in ppm.

Position	Ave.	1a	1b	1c	1d	1e	1f	1g	1h
1	-2.13	-2.20	-2.11	-2.14	-2.14	-2.08	-2.13	-2.10	-2.15
2	-0.91	-0.95	-0.89	-0.91	-0.88	-0.77	-0.91	-1.07	-0.90
3	-1.19	-1.22	-1.24	-1.25	-1.25	-0.93	-1.31	-0.99	-1.30
4	-1.32	-1.08	-1.07	-1.05	-1.11	-1.54	-1.65	-1.62	-1.45
5	-3.08	-3.00	-3.06	-2.88	-2.95	-3.26	-3.12	-3.38	-2.94
6	-1.27	-1.32	-1.35	-1.19	-1.44	-1.17	-1.15	-1.20	-1.31
7	-3.13	-3.24	-3.40	-3.11	-3.08	-3.14	-3.08	-3.18	-2.85
8	-1.72	-1.80	-1.72	-1.83	-1.70	-1.67	-1.66	-1.76	-1.64
9	-1.40	-1.34	-1.22	-1.64	-1.53	-1.39	-1.36	-1.29	-1.42
10	-0.24	-0.29	-0.18	-0.19	-0.22	-0.25	-0.24	-0.35	-0.21
11	-0.26	-0.48	+0.29	-0.44	+0.25	-0.59	-0.19	-0.67	-0.26
12	-0.26	-0.30	-0.46	-0.10	-0.24	-0.11	-0.32	-0.29	-0.27

See Figure 3. in this supporting information. For δ_{CD3OD} and $\delta_{(CD3)2SO}$, see Table 1. and Table 5., respectively.

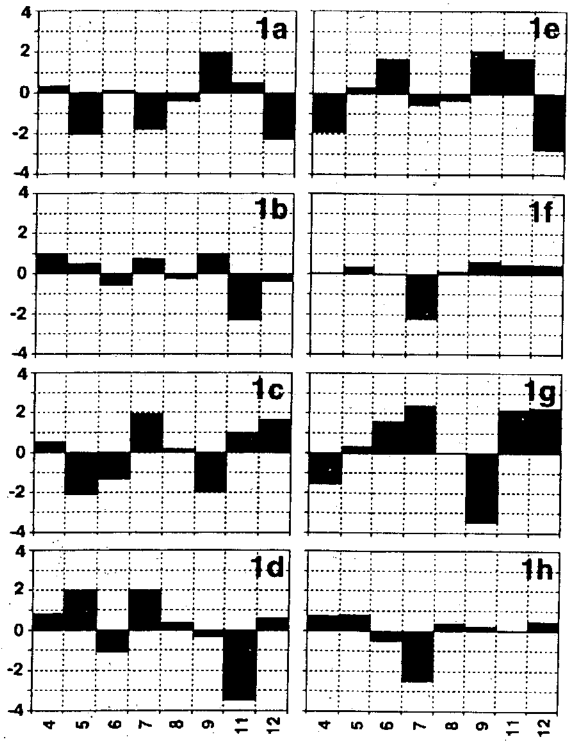
2. CD_3OD vs $CDCl_3$

Table 14. $\Delta\delta$ (δ_{CDCl3}-δ_{CD3OD}) in ppm.

Position	Ave.	1a	1b	1c	1d	1e	1f	1g	1h
1	-0.27	-0.27	-0.09	-0.35	-0.23	-0.36	-0.27	-0.27	-0.31
2	-1.17	-1.10	-1.10	-1.16	-1.15	-1.24	-1.19	-1.20	-1.23
3	-1.23	-1.10	-1.03	-1.13	-0.88	-2.03	-0.91	-1.99	-0.79
4	-0.48	-2.29	-0.83	-1.63	-0.66	+1.15	+0.08	+0.86	-0.53
5	+1.11	+0.89	+1.80	-0.32	+0.72	+1.70	+1.44	+1.53	+1.13
6	-2.20	-2.11	-2.58	-1.90	-2.13	-1.84	-2.82	-1.82	-2.39
7	+0.85	+1.21	+2.57	+0.23	+1.23	+1.65	-0.70	+1.44	-0.86
8	-1.09	-1.02	-0.54	-1.13	-1.03	-1.26	-1.20	-1.40	-1.19
9	-1.19	-1.51	-1.81	-0.26	-0.63	-1.22	-1.56	-1.50	-1.04
10	-0.44	-0.47	-0.63	-0.55	-0.55	-0.23	-0.49	-0.24	-0.35
11	-0.06	+1.33	-3.08	+0.60	-2.40	+1.23	+0.32	+1.15	+0.39
12	-0.30	+0.13	+0.56	-0.78	-0.65	-0.58	-0.06	-0.47	-0.55

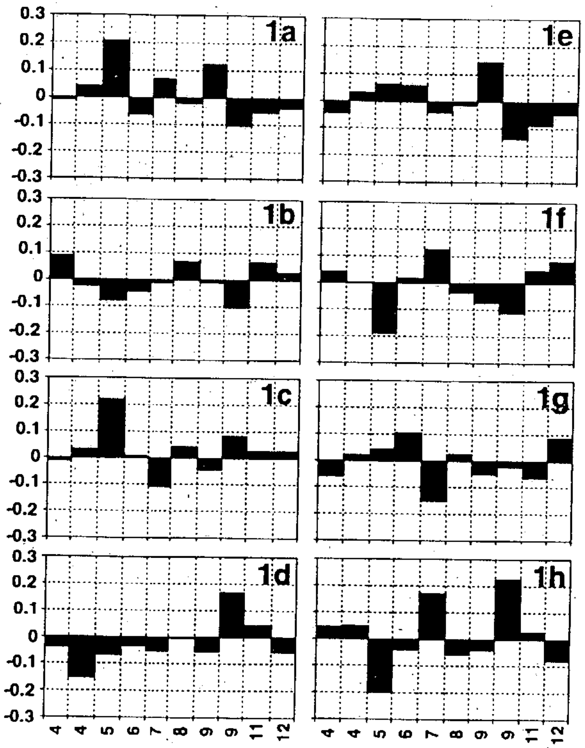
See Figure 4. in this supporting information. For δ_{CD3OD} and δ_{CDCl3}, see Table 1. and Table 9., respectively.

Figure 1. Difference in Carbon Chemical Shifts between Average and Each of **1a~h** (100MHz, CD_3OD).



See Table 2.

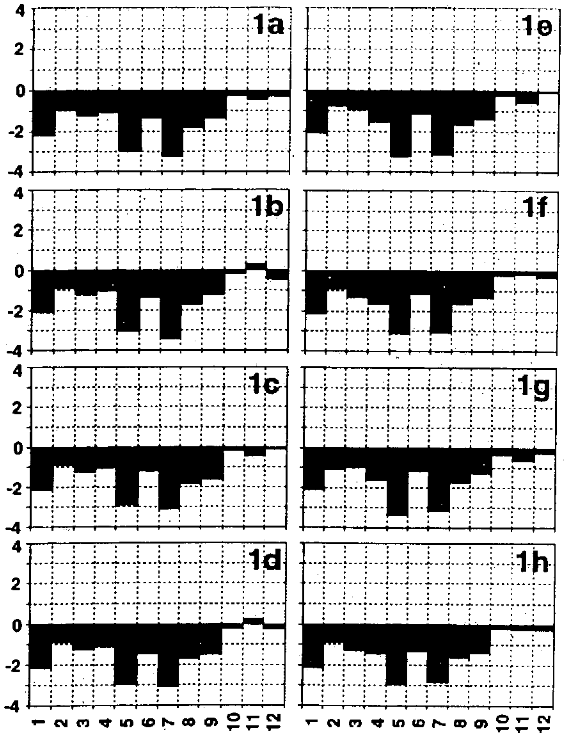
Figure 2. Difference in Proton Chemical Shifts between Average and Each of **1a~h** (500MHz, CD_3OD).



See Table 4.

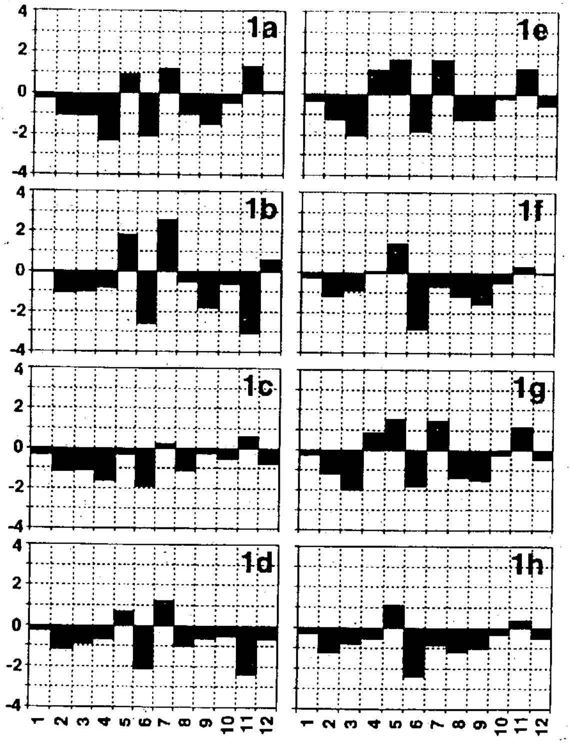
The x- and y- axes represent carbon number and $\Delta\delta$ ($\delta_{1a\text{-}h}$ - $\delta_{Ave.}$ in ppm), respectively, for all the graphs in this paper.

Figure 3. Difference in Carbon Chemical Shifts of **1a~h**, Δδ = δ($(CD_3)_2SO$) − δ(CD_3OD) in ppm (100MHz).



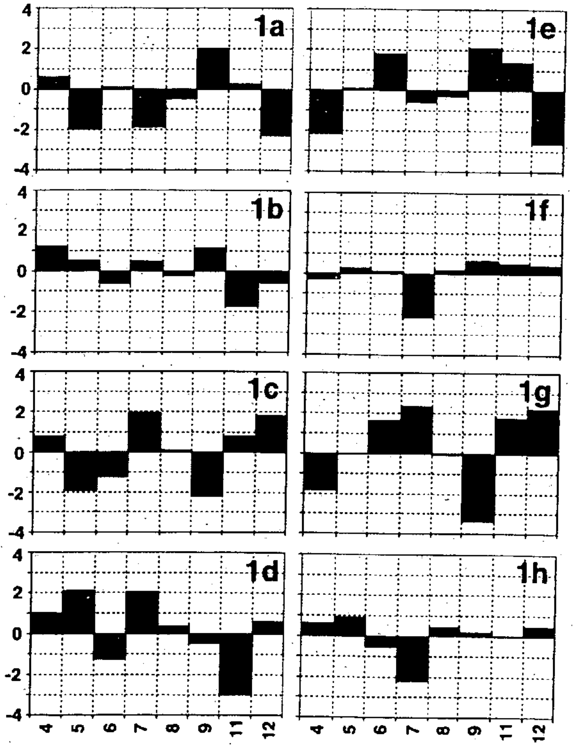
See Table 13.

Figure 4. Difference in Carbon Chemical Shifts of **1a~h**, Δδ = δ($CDCl_3$) − δ(CD_3OD) in ppm (100MHz).



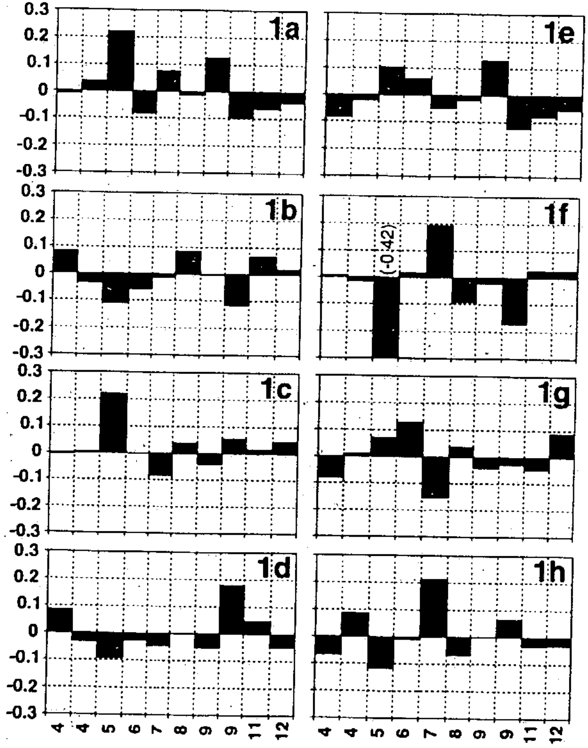
See Table 14.

Figure 5. Difference in Carbon Chemical Shifts between Average and Each of **1a~h** (100MHz, $(CD_3)_2SO$).



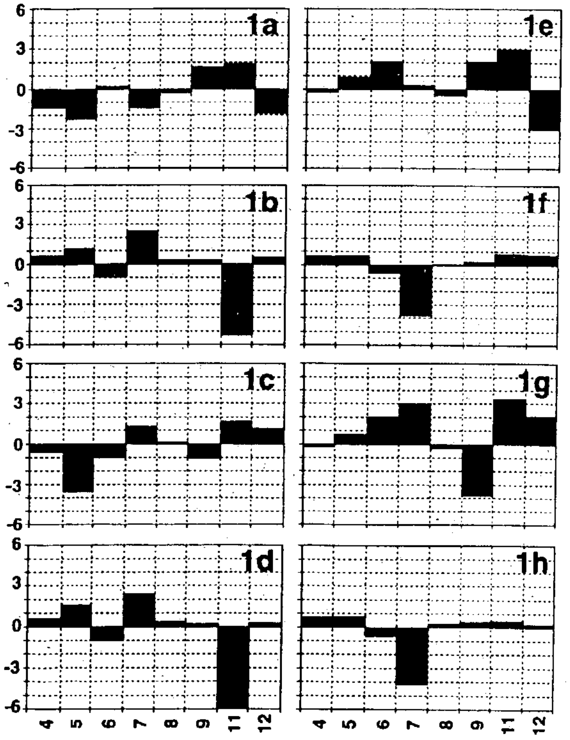
See Table 6.

Figure 6. Difference in Proton Chemical Shifts between Average and Each of **1a~h** (500MHz, $(CD_3)_2SO$).



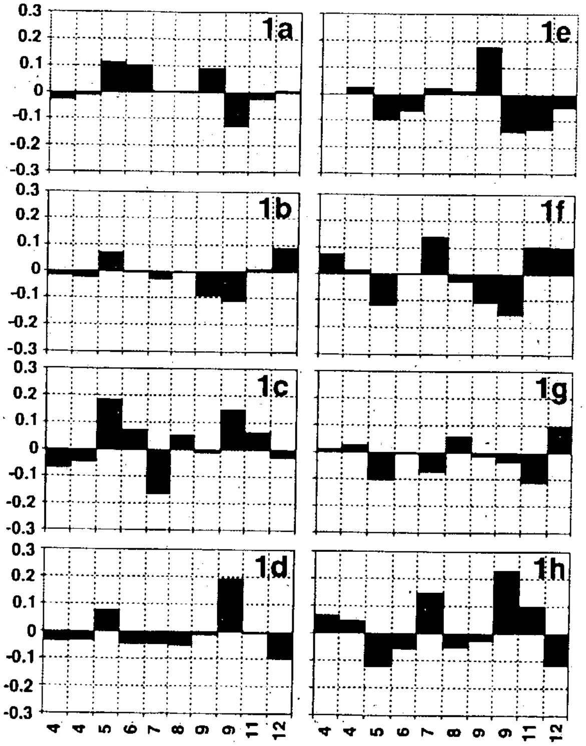
See Table 8.

Figure 7. Difference in Carbon Chemical Shifts between Average and Each of **1a~h** (100MHz, $CDCl_3$).



See Table 10.

Figure 8. Difference in Proton Chemical Shifts between Average and Each of **1a~h** (500MHz, $CDCl_3$).



See Table 12.

Experimental and Predicted Increments (ppm) of ^{13}C NMR Chemical Shifts

See Table 1 in text.

Table 15. Assignment of ^{13}C NMR Chemical Shifts (ppm, CD_3OD, 100MHz).

Obs.	1 d	A 1	A 2	A 3	A 4	A 5	B 1	B 2	B 3
1	62.91	65.62	(-CH=)	14.52	(-CO-)	73.78	(-OH)	(-O-)	(=CH2)
2	33.66	29.82	34.94	23.91	34.74	30.66	63.0	65.7	(-CH=)
3	23.37	23.55	26.51	29.35	22.59	23.64	30.3	26.4	31.39
4	35.74	35.50	35.47	35.71	35.28	35.72	32.4	32.3	35.25
5	76.70	76.38	76.46	76.62	76.09	76.46	76.5	76.0	75.84
6	39.93	40.09	40.01	39.90	40.16	39.99	40.2	40.2	40.04
7	80.18	79.87	80.05	80.12	79.71	79.96	79.9	79.7	79.90
8	38.75	38.38	38.74	38.72	38.77	38.74	38.8	38.8	38.73
9	25.83	25.81	25.83	25.81	25.87	25.83	25.9	25.9	25.79
10	11.39	11.44	11.48	11.48	11.48	11.48	11.4	11.4	11.50
11	6.57	6.80	6.72	6.68	6.88	6.76	6.8	6.9	6.86
12	15.52	15.53	15.59	15.59	15.56	15.57	15.6	15.6	15.61

Table 16. Experimental Increments (ppm).

Dif.	1 d	A 1	A 2	A 3	A 4	A 5	B 1	B 2	B 3
1	63.0	-2.7	(-CH=)	+48.4	(-CO-)	-10.9	(-OH)	(-O-)	(=CH2)
2	33.5	+3.8	-1.3	+9.7	-1.1	+3.0	63.3	-2.7	(-CH=)
3	20.4	-0.2	-3.1	-6.0	+0.8	-0.3	27.3	+3.8	-1.1
4	35.7	+0.2	+0.3	±0.0	+0.5	±0.0	31.7	+0.1	-2.8
5	70.6	+0.3	+0.2	+0.1	+0.6	+0.2	70.6	+0.5	+0.6
6	40.1	-0.2	-0.1	±0.0	-0.2	-0.1	40.1	±0.0	+0.2
7	74.6	+0.3	+0.1	+0.1	+0.5	+0.2	74.6	+0.2	±0.0
8	37.3	+0.4	±0.0	±0.0	±0.0	±0.0	37.3	±0.0	±0.0
9	24.1	±0.0	±0.0	±0.0	±0.0	±0.0	24.1	±0.0	+0.1
10	11.8	-0.1	-0.1	-0.1	-0.1	-0.1	11.8	±0.0	-0.1
11	8.0	-0.2	-0.1	-0.1	-0.3	-0.2	8.0	-0.1	-0.1
12	13.9	±0.0	-0.1	-0.1	±0.0	-0.1	13.9	±0.0	-0.1

Table 17. Predicted ^{13}C NMR Chemical Shifts[a] (ppm).

Estd.	1 d	A 1	A 2	A 3	A 4	A 5	B 1	B 2	B 3
1	63.0	67.3	(-CH=)	14.0	(-CO-)	72.4	(-OH)	(-O-)	(=CH2)
2	33.5	30.2	33.8	23.4	33.6	31.0	63.3	67.6	(-CH=)
3	20.4	20.6	24.1	26.6	19.5	20.7	27.3	24.0	27.6
4	35.7	35.4	35.8	35.4	35.1	35.7	31.7	31.9	35.4
5	70.6	70.6	70.7	70.6	70.3	70.6	70.6	70.3	70.7
6	40.1	40.1	40.1	40.1	40.1	40.1	40.1	40.1	40.2
7	74.6	74.6	74.6	74.6	74.6	74.6	74.6	74.6	74.6
8	37.3	37.3	37.3	37.3	37.3	37.3	37.3	37.3	37.3
9	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1
10	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8
11	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
12	13.9	13.9	13.9	13.9	13.9	13.9	13.9	13.8	13.9

[a] CS ChemNMR Pro version 1.0.

Table 18. Predicted Increments (ppm).

Dif.	1 d	A 1	A 2	A 3	A 4	A 5	B 1	B 2	B 3
1	63.0	-4.3	(-CH=)	+49.0	(-CO-)	-9.4	(-OH)	(-O-)	(=CH2)
2	33.5	+3.3	-0.3	+10.1	-0.1	+2.5	63.3	-4.3	(-CH=)
3	20.4	-0.2	-3.7	-6.2	+0.9	-0.3	27.3	+3.3	-0.3
4	35.7	+0.3	-0.1	+0.3	+0.6	±0.0	31.7	-0.2	-3.7
5	70.6	±0.0	-0.1	±0.0	+0.3	±0.0	70.6	+0.3	-0.1
6	40.1	±0.0	±0.0	±0.0	±0.0	±0.0	40.1	±0.0	-0.1
7	74.6	±0.0	±0.0	±0.0	±0.0	±0.0	74.6	±0.0	±0.0
8	37.3	±0.0	±0.0	±0.0	±0.0	±0.0	37.3	±0.0	±0.0
9	24.1	±0.0	±0.0	±0.0	±0.0	±0.0	24.1	±0.0	±0.0
10	11.8	±0.0	±0.0	±0.0	±0.0	±0.0	11.8	±0.0	±0.0
11	8.0	±0.0	±0.0	±0.0	±0.0	±0.0	8.0	±0.0	±0.0
12	13.9	±0.0	±0.0	±0.0	±0.0	±0.0	13.9	±0.1	±0.0