Supporting Information

Universal NMR Databases for Contiguous Polyols

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General Procedures and Methods.

The ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 500 spectrometer and a Mercury 400 spectrometer, respectively. The central residual solvent-signal [^1H NMR spectrum: 3.30 ppm (CD_3OD) and 2.49 ppm ($\text{DMSO}-d_6$); ^{13}C NMR spectrum: 49.0 ppm (CD_3OD) and 39.5 ppm ($\text{DMSO}-d_6$)] was used as the internal reference. For ^1H NMR spectra in $\text{C}_5\text{D}_5\text{N}$, the most up-field residual solvent-signal (7.19 ppm) was used as the internal reference. For ^1H and ^{13}C NMR spectra in D_2O , the residual solvent-signal of C_6D_6 in a WILMAD[®] coaxial insert (WGS-5BL, 50 mm L x 2 mm stem o.d.) was used as the external reference (^1H NMR spectrum: 7.15 ppm; ^{13}C NMR spectrum: 128.0 ppm). The apparent vicinal $^1\text{H}/^1\text{H}$ spin- coupling constants were extracted from 1D ^1H NMR spectra. Analytical thin chromatography (TLC) was performed with E. Merk pre-coated TLC plates, silica gel, 60F-254, layer thickness 0.25mm. Flash chromatography separations were performed on E. Merk kieselgel 60 (230-400) mesh silica gel, or on Silica (KP-Sil) by Biotage, Inc. Horizon[™] HPFC System. Reagents and solvents were commercial grade and were used as supplied. All reactions were conducted under an argon or nitrogen atmosphere. Reaction vessels were oven-dried and cooled under an inert atmosphere.

Experimental details on the synthesis outlined in Scheme 1

The enantiopure alcohol (*R*)-**A** was prepared from the benzoate of the alcohol ($\pm$)-**A** by using Oriyama's procedure.

Alcohol **A** (1.00 g, 3.84 mmol) and LiAlH_4 (300 mg, 7.68 mmol) in THF (50 ml) were stirred at rt for 1 day. The reaction was quenched with 15% aqueous sodium hydroxide (300ml) and water (300 ml). The mixture was extracted with ethyl acetate (300mlx3). The combined extracts were dried over anhydrous potassium carbonate, filtered through Celite and evaporated *in vacuo*. The residue was purified by chromatography over silica gel (20-25% EtOAc/hexane) to give the desired alcohol (0.82 g, 81%).

To a solution of alcohol (0.82g, 3.1 mmol), tetrabutylammonium iodide (230 mg, 0.63 mmol) and benzyl bromide (0.74 ml, 6.3 mmol) in DMF (30 ml) was added 50 % NaH (300 mg, 6.3 mmol). The mixture was stirred at rt for 1 d. The reaction was quenched with water (30 ml). The mixture was extracted with ether (50 mlx3) and the combined extracts were dried over anhydrous potassium carbonate, filtered through Celite and evaporated *in vacuo*. The residue was purified by chromatography over silica gel (10% EtOAc/hexane) to give the desired benzyl ether **B-1** (1.1 g, 95%).

To a solution of the benzyl ether **B-1** (101 mg, 0.290 mmol) in acetone (8 ml) and water (1 ml) were added NMO (67 mg, 0.66 mmol) and 0.1 M OsO₄ in toluene (0.15 ml, 0.15 mmol). The mixture was stirred at rt for 14 h. The reaction was quenched with saturated aqueous sodium hydrogensulfite (10 ml) and the mixture was extracted with ethyl acetate (10 mlx2). The combined extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The residue was purified by chromatography over silica gel (25% EtOAc/hexane) to give the diastereomeric mixture of alcohols (1:3, 77 mg, 69%). The diastereomeric mixture of alcohols and 10 % Pd/C (10 mg) in methanol (6 ml) were stirred under hydrogen for 7 h. The suspension was filtered through Celite and washed with MeOH. The combined filtrate was evaporated *in vacuo* to give the diastereomeric mixture of triols **1a** and **1d** (1:3, 39 mg, 95%). The mixture of triols **1a** and **1d** in pyridine (2 ml) was treated with Ac₂O (2 ml) and stirred for 14 h. The solvent was evaporated *in vacuo* and the residue was purified by chromatography over silica gel (25% EtOAc/hexane) to give the tetra-acetates, respectively. Each tetra-acetate was deacetylated by NaOMe in MeOH to give the desired triol **1a** and **1d** (□□□ 8 mg 21%, □□□23 mg 59%), respectively.

The stereochemical assignment of **1a** and **1d** are elucidated by the empirical rule on the stereoselectivity of dihydroxylation by OsO₄ and by the (pseudo)symmetry element observed in the NMR spectra of **1a**.

A solution of alcohol **A** (1.21 g, 4.65 mmol), quinoline (120mg) and Lindlar catalyst (120 mg) in hexane (30 ml) was stirred under hydrogen for 1 d. The suspension was filtered through Celite and washed with hexane. The filtrate was evaporated *in vacuo* to give the desired alcohol (1.10 g, 90%).

To a solution of alcohol (1.10 g, 4.19 mmol), tetrabutylammonium iodide (310 mg, 0.84 mmol) and benzyl bromide (1.00 ml, 8.38 mmol) in DMF (40 ml) was added 50 % NaH (402 mg, 8.38 mmol). The mixture was stirred at rt for 1 d. The reaction was quenched with water (40 ml). The mixture was extracted with ether (80 mlx3) and the combined extracts were dried over anhydrous potassium carbonate, filtered through Celite and evaporated *in vacuo*. The residue was purified by chromatography over silica gel (10% EtOAc/hexane) to give the desired benzyl ether **B-2** (1.44 g, 95%).

To a solution of the benzyl ether **B-2** (40 mg, 0.11 mmol) in acetone (8 ml) and water (1 ml) were added NMO (93 mg) and 1 M OsO₄ in toluene (0.2 ml). The mixture was stirred for 14 h. The reaction was quenched with saturated aqueous sodium hydrogensulfite (10 ml) and the mixture was extracted with ethylacetate (10 mlx2). The combined extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The residue was purified by chromatography over silica gel (25% EtOAc/hexane) to give the alcohols (□□□ 27 mg, □□□ 3 mg). Each alcohol and 10 % Pd/C (3 mg) in methanol (1 ml) were stirred under hydrogen for 7 h. The suspension was filtered through Celite and washed with MeOH. The combined filtrate was evaporated *in vacuo* to give the triol **1b** and **1c** (□□□ 14 mg quant. and □□□ 1.6 mg quant.), respectively.

The stereochemical assignment of **1b** and **1c** are elucidated by the empirical rule on the stereoselectivity of dihydroxylation by OsO₄ and by the (pseudo)symmetry element observed in NMR spectra of **1b**.

Experimental details on the synthesis outlined in Scheme 2

Tribenzyl *D*-xylopyranose was prepared from *D*-xylose in the known steps.

To (ethyl)triphenylphosphonium iodide (29.8 g, 71.2 mmol) in THF (200 ml) was added KHMDS (0.5 M in toluene, 143 ml) at 0 °C. The mixture was stirred at rt for 1h and then recooled to 0 °C. To the mixture was added tribenzylxylo *D*-xylopyranoside **C-1** (10.0 g, 23.8 mmol) in THF (100 ml) and the mixture was stirred at rt for 12 h. The reaction was quenched by acetone at 0 °C. The suspension was filtered through Celite and the filtered cake was washed with ether (100 ml). After removal of the solvent, ether (200ml) was added to the residue. The resulting suspension was filtered through Celite and washed with ether (100 ml). The solvent was evaporated *in vacuo* and the residue was purified by chromatography over silica gel (10-20% EtOAc/hexane) to give the pure alcohol (8.24g, 80%).

To oxaryl chloride (2.5 ml, 28.7 mmol) in dichloromethane (60 ml) was added dropwise dimethylsulfoxide (4.07 ml, 57.3 mmol) in dichloromethane (10 ml) at -78 °C over 5 min and the mixture was stirred for 2 min. The alcohol (4 g, 9.25 mmol) in dichloromethane (30 ml) was added to the solution at -78 °C over 5 min and the mixture was stirred for 5 min. Triethylamine (7.99 ml) was added to the solution and the mixture was stirred at rt for 1 h. The solution was diluted with chloroform (100 ml) and washed with 1 M HCl (200 ml) and aqueous saturated sodium hydrogencarbonate (200 ml). The organic layer was dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The residue was purified by chromatography over silica gel (10% EtOAc/hexane) to give the pure aldehyde (3.33 g, 84%).

To magnesium turnings (361 mg, 14.8 mmol) in THF (10 ml) was added 4-benzyloxybutyl bromide (3.60 g, 14.8 mmol) in THF (30 ml). The mixture was refluxed for 2 h. The prepared Grignard reagent was added to the solution of the aldehyde (3.19 g, 7.41 mmol) in THF (35 ml) at 0 °C and the mixture was stirred at rt for 1 h. The reaction was quenched with saturated aqueous ammonium chloride (50 ml) and water (50 ml) and the mixture was extracted with ethyl acetate (50 mlx3). The combined extracts were dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The residue was purified by chromatography over silica gel (0-15% EtOAc/hexane) to give the diastereomeric mixture of alcohols (3.27 g, 74%).

To the diastereomeric mixture of alcohols (3.27 g, 5.50 mmol) in DMF (50 ml) was added 50 % NaH (790 mg, 16.5 mmol), tetrabutylammonium iodide (406 mg, 1.1 mmol) and benzyl bromide (1.96 ml, 16.5 mmol). The mixture was stirred for 1 day. The reaction was quenched with water (100 ml) and the mixture was extracted with Et₂O (100 mlx3). The combined extracts were dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The residue was purified by Biotage chromatography (10% Et₂O/hexane) to give the pentabenzyl ethers **D-1** and **D-2** (mixture 1.91 g 51%, **D-1** 1.159 g, 31%).

The pentabenzyl ether **D-1** (mixture 200 mg, 0.292 mmol) and 20% $\text{Pd}(\text{OH})_2/\text{C}$ (20 mg) in EtOH (3 ml) was stirred under hydrogen for 12 h. The mixture was filtered and washed with methanol (10 ml). The combined filtrate was evaporated *in vacuo* to give the tetraol **2a** (mixture 69 mg, quant.).

The pentabenzyl ether **D-2** (mixture) gave the corresponding tetraol **2f** (mixture) in the same manner.

Tetraols (**2d** (mixture) and **2h** (mixture)), (**2g** (mixture) and **2b** (mixture)) and (**2e** (mixture) and **2c** (mixture)) were prepared from tribenzyl *D*-arabinopyranose **C-2**, tribenzyl *D*-ribopyranose **C-3**, and tribenzyl *D*-lyxopyranose **C-4** in the same manner, respectively.

The stereochemical assignment on a newly constructed chiral center (C.5) by the Grignard reaction is elucidated by the (pseudo)symmetry element on the NMR spectra of **2a**, **2b**, **2c**, and **2d** by ignoring the difference at the termini.

Experimental details on the synthesis outlined in Scheme 3

To a mixture of pentabenzyl ether **D-1** (900 mg, 1.31 mmol) and sodium acetate trihydrate (89.4 mg, 0.657 mmol) in dichloromethane (10 ml) and methanol (10 ml) was introduced O_3 at -78°C for 15 min. After 15 min, dimethylsulfide (10 ml) was added to the mixture and the mixture was stirred at rt for 2 h. The solution was

evaporated *in vacuo* and water (20 ml) was added to the residue. The mixture was extracted with Et₂O (20 mlx3). The combined extracts were dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The crude aldehyde was used for the next reaction.

To the crude aldehyde in Et₂O (13 ml) at 0 °C was added propylmagnesium bromide (6.55 mmol) in Et₂O (13 ml) prepared from 1-bromopropane (0.60 ml, 6.55 mmol) and magnesium turnings (160 mg, 6.55mmol). The mixture was stirred at rt for 1 h. The reaction was quenched with aqueous ammonium chloride (13 ml) and water (13 ml). The mixture was extracted with ethyl acetate (20 mlx3). The combined extracts were dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The residue was purified by Biotage chromatography (20% Et₂O/hexane) to give the corresponding alcohols (310 mg 33%, 273 mg 29%). The alcohols (310 mg, 0.433 mmol, 273 mg, 0.381 mmol) and 20% Pd(OH)₂/C (30 mg) in EtOH (2 ml) and ethyl acetate (1 ml) were stirred under hydrogen for 12 h, respectively. The mixture was filtered and washed with methanol (10 ml). The combined filtrate was evaporated *in vacuo* to give the pentaol **3a** (115 mg, quant) and **3e** (100 mg, quant.)

Pentaols (**3c** and **3f**), (**3k**, **3j**, **3p** and **3h**), (**3d**, **3m**, **3n**, and **3b**), and (**3g**, **3i**, **3o**, and **3l**) were prepared from the corresponding pentabenzyl ethers **D-2**, **D-3**, **D-4**, **D-5**, **D-6**, **D-7**, and **D-8** in the same manner, respectively.

The stereochemical assignment on a newly constructed chiral center (C.9) by the Grignard reaction is elucidated by the (pseudo)symmetry element of the molecule. The NMR spectrum of one (**2a**, **2b**, **2c**, and **2d**) of the two products by the Grignard reaction in each series shows a (pseudo)symmetric pattern while the other (**2f**, **2m**, **2e**, and **2n**) doesn't. The neither in the pair (**3g** and **3o**, **3h** and **3j**, **3i** and **3l**, **3k** and **3p**) have a (pseudo)symmetric pattern in the spectrum. But the spectrum of **3g**, **3i**, **3k**, and **3o** has a similar pattern with **3h**, **3j**, **3l**, and **3p** and they share the same relative configuration by ignoring the difference at the temini, respectively. Therefore, to share the same relative configuration for the structural cluster portion without inconsistency for all diastereomers, the whole stereochemistry including C.9 is elucidated logically.

Experimental details on the synthesis of heptaols 4a~d given in Figure 3

To the pentabenzyl ether **D-1** (1.44 g, 2.15 mmol) and sodium acetate trihydrate (292 mg, 2.15 mmol) in dichloromethane (10 ml) and methanol (10 ml) was introduced O_3 at -78°C for 20 min. After 15 min, dimethylsulfide (10 ml) was added to the mixture and the mixture was stirred at rt for 2 h. The solution was evaporated *in vacuo* and water (20 ml) was added to the residue. The mixture was extracted with Et_2O (20 mlx3). The combined extracts were dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The crude aldehyde was used for the next reaction.

To the crude aldehyde in THF (10 ml) at 0°C was added pentynylmagnesium bromide that was prepared from 1-pentyn (3.60 ml, 21.5 mmol) and 18.3 ml (10.7 mmol) of 1 M ethylmagnesium bromide in THF by refluxing. The mixture was stirred at rt for 1 h. The reaction was quenched with aqueous ammonium chloride (10 ml) and water (20 ml). The mixture was extracted with ether (20 mlx3). The combined extracts were dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The residue was purified by Biotage chromatography (15-20% Et_2O /hexane) to give the alcohols (525 mg 33%, 265 mg 17%). A suspension of the alcohol (60 mg, 0.081 mmol), Lindlar catalyst (30 mg) and quinoline (10 mg) in ethyl acetate (1 ml) and hexane (1 ml) was stirred under hydrogen atmosphere for 1 day. The mixture was filtered and washed with ethyl acetate (5 ml). The combined filtrate was evaporated *in vacuo* to give the *cis*-olefins, respectively.

To the crude olefine in DMF (1 ml) were added tetrabutylammonium iodide (6.0 mg, 0.016 mmol) and 50 % NaH oil dispersion (12 mg, 0.24 mmol), benzyl bromide (29 μl , 0.24 mmol). The mixture was stirred at rt for 3 h. The reaction was quenched with water (2 ml) and the mixture was extracted with hexane (2 mlx3). The combined extracts were dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The residue was purified by Biotage chromatography (4% Et_2O /hexane) to give the heptabenzyl ether **E-1** (39 mg, 58%) and **E-2** (40 mg, 59%), respectively.

To a solution of heptabenzyl ether **E-1** (□□□□□, 40 mg, 0.048 mmol) and **E-2** (□□□□□, 40 mg, 0.048 mmol) in acetone (0.45 ml) and water (0.05 ml) were added *N*-methyl morpholine (11 mg, 0.096 mmol) and OsO₄ in toluene (0.1 M, 96 ul, 0.0096 mmol), respectively. The mixture was stirred at rt for 1 day. Saturated sodium sulfite was added to the mixture. After stirring the mixture for 10 min, the mixture was extracted by ether (1 mlx3). The combined extracts were dried over anhydrous magnesium sulfate, filtered through Celite and evaporated *in vacuo*. The residue was purified by PTLC (60% Et₂O/hexane) to give the diols (□□□□□□, 22 mg, 53%) and (□□□□□□, 28 mg, 67%) as the major product, respectively.

The diol (□□□□□□, 22 mg) and (□□□□□□, 28 mg) and Pd(OH)₂/C (10 mg) in ethanol (1 ml) and ethyl acetate (1 ml) were stirred at hydrogen atmosphere for 1 day, respectively. The mixture was filtered and washed with methanol (5 ml). The combined filtrate was evaporated *in vacuo* to give the alcohol **4a** (□□□□□□, 8.3 mg, quant.) and **4b** (□□□□□□, 10.2 mg, 97%), respectively.

Heptaols **4c** (□□□□□□) and **4d** (□□□□□□) were prepared from **D-6** in the same manner, respectively.

The stereochemical assignment on a newly constructed chiral center (C.9) by the Grignard reaction is elucidated by the (pseudo)symmetry element of the molecule by ignoring the difference at the termini. The stereochemical assignments at C10 and C.11 are elucidated by the empirical rule on the stereoselectivity of dihydroxylation by OsO₄.

NMR Data of Triols 1a~d.

Table 1. ^{13}C NMR chemical shifts of triols **1a~d** in CD_3OD / ppm

CD_3OD	1a SS	1b AA	1c SA	1d AS
1	62.879	62.986	62.910	62.970
2	33.642	33.718	33.672	33.718
3	23.115	22.955	23.335	22.993
4	34.506	33.247	34.575	34.461
5	73.513	73.975	71.495	72.731
6	76.660	78.291	76.926	76.903
7	73.308	73.801	72.580	71.116
8	36.956	35.803	36.986	37.062
9	19.952	19.800	19.808	20.142
10	14.484	14.522	14.529	14.499

Table 6. ^{13}C NMR chemical shifts of triols **1a~d** in D_2O / ppm

D_2O	1a SS	1b AA	1c SA	1d AS
1	61.948	62.010	61.981	62.021
2	31.527	31.541	31.502	31.587
3	21.576	21.604	21.718	21.484
4	32.596	31.110	32.662	31.986
5	72.058	71.827	70.614	71.329
6	76.040	77.391	76.049	76.035
7	71.899	71.637	71.154	70.392
8	35.046	33.588	34.461	35.125
9	18.512	18.534	18.413	18.652
10	13.567	13.566	13.609	13.541

Table 2. ^1H NMR chemical shifts of triols **1a~d** in CD_3OD / ppm

CD_3OD	1a SS	1b AA	1c SA	1d AS
1	3.56	3.56	3.56	3.56
5	3.64	3.59	3.81	3.59
6	3.20	3.29	3.15	3.15
7	3.64	3.59	3.61	3.82
10	0.94	0.94	0.95	0.95

Table 7. ^1H NMR chemical shifts of triols **1a~d** in D_2O / ppm

D_2O	1a SS	1b AA	1c SA	1d AS
1	3.63	3.64	3.63	3.63
5	3.76	3.73	3.83	3.71
6	3.36	3.50	3.36	3.36
7	3.76	3.73	3.72	3.84
10	0.93	0.93	0.93	0.93

Table 3. ^1H NMR $^3J_{\text{H,H}}$ of triols **1a~d** in CD_3OD / Hz

CD_3OD	1a SS	1b AA	1c SA	1d AS
5, 6	4.0	7.0	2.5	8.0
6, 7	4.0	7.0	8.0	2.5

Table 8. ^1H NMR $^3J_{\text{H,H}}$ of triols **1a~d** in D_2O / Hz

D_2O	1a SS	1b AA	1c SA	1d AS
5, 6	4.5	6.0	3.5	7.0
6, 7	4.5	6.0	7.0	3.5

Table 4. ^{13}C NMR chemical shifts of triols **1a~d** in $\text{DMSO}-d_6$ / ppm

$\text{DMSO}-d_6$	1a SS	1b AA	1c SA	1d AS
1	60.820	60.918	60.827	60.918
2	32.773	32.909	32.758	32.916
3	21.980	21.730	22.215	21.714
4	33.228	32.196	33.387	33.417
5	71.301	71.991	69.405	70.421
6	75.290	76.686	75.450	75.556
7	70.975	71.696	70.126	68.927
8	35.556	34.585	35.791	35.723
9	18.598	18.340	18.309	18.832
10	14.161	14.267	14.252	14.160

Table 9. ^1H NMR $^3J_{\text{H,H}}$ of triols **1a~d** in pyridine- d_5 / Hz

pyridine- d_5	1a SS	1b AA	1c SA	1d AS
5, 6	4.0	6.5	2.0	7.0
6, 7	4.0	6.5	7.0	2.0

Table 5. ^1H NMR chemical shifts of triols **1a~d** in $\text{DMSO}-d_6$ / ppm

$\text{DMSO}-d_6$	1a SS	1b AA	1c SA	1d AS
1	3.35	3.37	3.38	3.37
5	3.41	3.39	3.61	3.36
6	3.00	3.08	2.92	2.92
7	3.41	3.39	3.38	3.64
10	0.85	0.85	0.85	0.86
1-OH	4.32	4.30	4.31	4.30
5-OH	4.19	4.39	3.96	4.33
6-OH	4.06	4.33	4.11	4.12
7-OH	4.19	4.39	4.33	3.95

Chemical shift [^{13}C , ^1H , $^1\text{H}(\text{OH})$] and $^3J_{\text{H,H}}$ profiles of triols **1a-d**.

Graph 1. Difference in (A) ^{13}C chemical shifts, (B) ^1H chemical shifts between the average and the values of **1a-d**, $\Delta\delta = \delta_{\text{1a-d}} - \delta_{\text{ave}}$ in ppm, and (C) $^3J_{\text{H,H}}$ of **1a-d** in Hz, in CD_3OD .

Graph 2. Difference in (A) ^{13}C chemical shifts, (B) ^1H chemical shifts, and (C) hydroxy- ^1H chemical shifts between the average and the values of **1a-d** in $(\text{CD}_3)_2\text{SO}$, $\Delta\delta = \delta_{\text{1a-d}} - \delta_{\text{ave}}$ in ppm.

Graph 3. Difference in (A) ^{13}C chemical shifts, (B) ^1H chemical shifts between the average and the values of **1a-d**, $\Delta\delta = \delta_{\text{1a-d}} - \delta_{\text{ave}}$ in ppm, and (C) $^3J_{\text{H,H}}$ of **1a-d** in Hz, in D_2O .

Graph 4. $^3J_{\text{H,H}}$ of **1a-d** in $\text{C}_5\text{D}_5\text{N}$ in Hz.

NMR Data of Tetraols 2a~h.

Table 10. ^{13}C NMR chemical shifts of tetraols **2a-h** in CD_3OD / ppm

CD_3OD	2a □□□□ SSS	2b □□□□ AAA	2c □□□□ ASA	2d □□□□ SAS	2e □□□□ SSA	2f □□□□ ASS	2g □□□□ SAA	2h □□□□ AAS
1	62.902	62.986	62.986	62.932	62.895	62.986	62.910	62.986
2	33.634	33.718	33.733	33.687	33.649	33.718	33.657	33.718
3	23.206	23.046	23.046	23.456	23.031	22.963	23.380	22.986
4	34.256	32.603	34.552	34.552	34.051	34.256	34.491	32.747
5	72.974	73.945	72.883	71.541	74.491	72.512	71.708	74.210
6	75.325	76.660	73.725	73.596	73.285	76.197	75.257	75.356
7	75.272	76.607	73.710	73.543	76.213	73.315	75.409	75.325
8	72.747	73.824	72.754	71.298	72.367	74.286	74.044	71.465
9	36.713	35.113	37.047	37.009	36.729	36.509	35.250	36.948
10	20.043	19.899	19.899	20.286	19.815	19.876	19.831	20.217
11	14.461	14.522	14.529	14.499	14.506	14.476	14.529	14.468

Table 11. ^1H NMR chemical shifts of tetraols **2a-h** in CD_3OD / ppm

CD_3OD	2a □□□□ SSS	2b □□□□ AAA	2c □□□□ ASA	2d □□□□ SAS	2e □□□□ SSA	2f □□□□ ASS	2g □□□□ SAA	2h □□□□ AAS
1	3.56	3.56	3.56	3.56	3.56	3.56	3.56	3.57
5	3.70	3.73	3.62	3.83	3.66	3.62	3.83	3.70
6	3.49	3.50	3.59	3.48	3.66	3.37	3.43	3.58
7	3.49	3.50	3.59	3.48	3.36	3.65	3.57	3.42
8	3.70	3.73	3.62	3.83	3.62	3.66	3.70	3.84
11	0.95	0.95	0.95	0.95	0.95	0.94	0.95	0.95

Table 12. ^1H NMR $^3J_{\text{H,H}}$ of tetraols **2a-h** in CD_3OD / Hz

CD_3OD	2a □□□□ SSS	2b □□□□ AAA	2c □□□□ ASA	2d □□□□ SAS	2e □□□□ SSA	2f □□□□ ASS	2g □□□□ SAA	2h □□□□ AAS
5, 6	4.0	5.0	8.0	0	-	7.5	1.5	6.0
6, 7	-	-	-	-	1.5	1.5	7.5	7.5
7, 8	4.0	5.0	8.0	0	7.5	-	6.0	1.5

Table 13. ^{13}C NMR chemical shifts of tetraols **2a-h** in $\text{DMSO}-d_6$ / ppm

$\text{DMSO}-d_6$	2a □□□□ SSS	2b □□□□ AAA	2c □□□□ ASA	2d □□□□ SAS	2e □□□□ SSA	2f □□□□ ASS	2g □□□□ SAA	2h □□□□ AAS
1	60.828	60.919	60.934	60.850	60.828	60.919	60.821	60.926
2	32.757	32.909	32.924	32.788	32.780	32.894	32.742	32.917
3	22.055	21.881	21.759	22.299	21.919	21.661	22.207	21.828
4	33.061	31.308	33.531	33.486	32.894	33.098	33.334	31.483
5	70.749	71.849	70.393	69.306	72.425	70.195	69.619	72.135
6	73.548	75.171	71.978	71.847	71.432	74.625	73.692	73.804
7	73.487	75.156	71.963	71.787	74.701	71.485	73.715	73.698
8	70.385	71.530	70.097	68.935	69.892	72.054	71.811	69.253
9	35.366	33.652	35.905	35.806	35.450	35.199	33.834	35.647
10	18.672	18.505	18.392	18.893	18.308	18.498	18.445	18.825
11	14.159	14.258	14.281	14.176	14.250	14.167	14.266	14.138

Table 14. ^1H NMR chemical shifts of tetraols **2a-h** in $\text{DMSO}-d_6$ / ppm

$\text{DMSO}-d_6$	2a □□□□ SSS	2b □□□□ AAA	2c □□□□ ASA	2d □□□□ SAS	2e □□□□ SSA	2f □□□□ ASS	2g □□□□ SAA	2h □□□□ AAS
1	3.36	3.37	3.36	3.37	3.36	3.37	3.37	3.37
5	3.49	3.54	3.37	3.64	3.45	3.39	3.63	3.50
6	3.27	3.29	3.38	3.24	3.46	3.14	3.20	3.37
7	3.27	3.29	3.38	3.24	3.15	3.46	3.36	3.19
8	3.49	3.54	3.37	3.64	3.39	3.46	3.51	3.65
11	0.85	0.86	0.86	0.86	0.85	0.85	0.86	0.86
1-OH	4.32	4.30	4.31	4.32	4.32	4.31	4.32	4.31
5-OH	4.28	4.48	4.33	3.92	4.32	4.33	4.08	4.43
6-OH	4.15	4.59	3.98	4.12	4.00	4.26	4.38	4.50
7-OH	4.15	4.59	3.98	4.12	4.27	4.01	4.50	4.40
8-OH	4.28	4.48	4.33	3.92	4.32	4.33	4.42	4.07

NMR Data of Tetraols **2a~h** (continued).

Table 15. ^{13}C NMR chemical shifts of tetraols **2a-h** in D_2O / ppm

D_2O	2a SSS	2b AAA	2c ASA	2d SAS	2e SSA	2f ASS	2g SAA	2h AAS
1	61.978	62.016	62.046	62.024	61.963	62.046	61.993	62.039
2	31.542	31.542	31.603	31.565	31.550	31.595	31.512	31.572
3	21.629	21.887	21.493	21.971	21.470	21.440	21.887	21.864
4	32.475	29.949	32.490	32.877	32.308	32.119	32.740	29.798
5	71.914	72.209	71.231	70.344	72.725	71.057	70.238	72.263
6	74.121	74.788	72.634	72.240	72.756	74.303	73.203	73.870
7	74.098	74.735	72.634	72.217	74.356	72.771	73.855	73.264
8	71.732	72.035	71.087	70.124	70.897	72.589	72.043	70.063
9	34.925	32.392	34.955	35.357	34.530	34.758	32.210	35.236
10	18.565	18.808	18.414	18.922	18.361	18.414	18.778	18.853
11	13.582	13.567	13.628	13.620	13.613	13.605	13.582	13.590

Table 16. ^1H NMR chemical shifts of tetraols **2a-h** in D_2O / ppm

D_2O	2a SSS	2b AAA	2c ASA	2d SAS	2e SSA	2f ASS	2g SAA	2h AAS
1	3.64	3.64	3.64	3.65	3.63	3.64	3.64	3.67
5	3.79	3.85	3.70	3.92	3.74	3.73	3.90	3.89
6	3.61	3.67	3.68	3.58	3.70	3.56	3.48	3.78
7	3.61	3.67	3.68	3.58	3.55	3.70	3.75	3.50
8	3.79	3.85	3.70	3.92	3.73	3.75	3.88	3.93
11	0.94	0.94	0.94	0.96	0.94	0.94	0.94	0.96

Table 17. ^1H NMR $^3J_{\text{H,H}}$ of tetraols **2a-h** in D_2O / Hz

D_2O	2a SSS	2b AAA	2c ASA	2d SAS	2e SSA	2f ASS	2g SAA	2h AAS
5, 6	4.0	-	-	0	6.0	7.5	1.5	4.5
6, 7	-	-	-	-	2.5	2.5	8.5	8.5
7, 8	4.0	-	-	0	7.5	6.0	4.5	1.5

Chemical shift [^{13}C , ^1H , $^1\text{H}(\text{OH})$] and $^3J_{\text{H,H}}$ profiles of tetraols **2a-h**.

Graph 5. Difference in (A) ^{13}C chemical shifts and (B) ^1H chemical shifts between the average and the values of **2a-h**, $\Delta\delta = \delta_{\text{2a-h}} - \delta_{\text{ave}}$ in ppm, and (C) $^3J_{\text{H,H}}$ of **2a-h** in Hz, in CD_3OD . The $^3J_{\text{H,H}}$ indicated by an asterisk were not determined.

Graph 6. Difference in (A) ^{13}C chemical shifts, (B) ^1H chemical shifts, and (C) hydroxy- ^1H chemical shifts between the average and the values of **2a-h** in $(\text{CD}_3)_2\text{SO}$, $\Delta\delta = \delta_{\text{2a-h}} - \delta_{\text{ave}}$ in ppm.

Graph 7. Difference in (A) ^{13}C chemical shifts and (B) ^1H chemical shifts between the average and the values of **2a-h**, $\Delta\delta = \delta_{\text{2a-h}} - \delta_{\text{ave}}$ in ppm, and (C) $^3J_{\text{H,H}}$ of **2a-h** in Hz, in D_2O . The $^3J_{\text{H,H}}$ indicated by an asterisk were not determined.

NMR Data of Pentaols 3a~p.

Table 18. ^{13}C NMR chemical shifts of pentaols **3a-p** in CD_3OD / ppm

CD_3OD	3a SSSS	3b AAAA	3c ASSA	3d SAAS	3e SSSA	3f ASSS	3g SSAA	3h AASS
1	62.902	62.994	62.978	62.910	62.902	62.986	62.902	62.978
2	33.642	33.717	33.695	33.648	33.634	33.710	33.642	33.702
3	23.145	23.007	22.993	23.356	23.236	22.970	23.016	22.993
4	34.324	33.163	33.915	34.483	34.408	34.339	34.051	32.769
5	73.012	73.529	72.557	71.732	72.489	72.610	74.453	74.279
6	74.764	76.684	77.752	75.509	76.197	75.674	73.596	75.242
7	74.127	74.932	69.728	73.302	71.601	71.586	74.703	74.726
8	74.719	76.578	77.737	75.463	75.667	76.258	75.295	73.611
9	72.807	73.400	72.398	71.496	72.443	72.292	73.953	74.089
10	36.789	35.704	36.380	36.940	36.820	36.873	35.310	36.524
11	19.990	19.859	19.831	20.193	19.815	20.073	19.838	19.868
12	14.468	14.535	14.491	14.467	14.514	14.461	14.529	14.476

	3i SSAS	3j SASS	3k SASA	3l ASAS	3m SAAA	3n AAAS	3o ASAA	3p AASA
1	62.902	62.925	62.932	62.986	62.926	62.979	62.986	62.986
2	33.672	33.680	33.687	33.748	33.656	33.709	33.733	33.733
3	23.039	23.441	23.456	23.054	23.356	23.075	23.008	22.986
4	34.112	34.582	34.559	34.749	34.445	32.958	34.658	32.739
5	74.681	71.078	71.397	73.020	71.807	73.961	72.640	74.210
6	73.331	73.369	73.482	73.717	74.849	77.238	74.021	75.174
7	73.020	73.027	70.676	70.653	74.030	74.052	72.345	72.360
8	73.429	73.369	73.717	73.558	77.314	74.940	75.234	74.013
9	70.835	74.483	72.883	71.161	73.802	71.557	74.066	72.504
10	37.039	36.577	37.244	37.017	35.476	36.902	35.272	37.146
11	20.270	19.876	19.899	20.286	19.935	20.178	19.838	19.861
12	14.491	14.491	14.537	14.499	14.520	14.467	14.544	14.529

Table 19. ^1H NMR chemical shifts of pentaols **3a-p** in CD_3OD / ppm

CD_3OD	3a SSSS	3b AAAA	3c ASSA	3d SAAS	3e SSSA	3f ASSS	3g SSAA	3h AASS
1	3.56	3.56	3.56	3.56	3.56	3.56	3.56	3.57
5	3.72	3.74	3.64	3.87	3.70	3.64	3.68	3.70
6	3.54	3.63	3.45	3.55	3.53	3.46	3.67	3.59
7	3.76	3.74	4.07	3.80	3.95	3.95	3.67	3.66
8	3.54	3.63	3.45	3.55	3.45	3.53	3.58	3.66
9	3.72	3.74	3.64	3.87	3.64	3.71	3.70	3.70
12	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95

	3i SSAS	3j SASS	3k SASA	3l ASAS	3m SAAA	3n AAAS	3o ASAA	3p AASA
1	3.56	3.56	3.56	3.57	3.56	3.56	3.57	3.57
5	3.70	3.83	3.84	3.64	3.86	3.76	3.63	3.71
6	3.67	3.50	3.49	3.59	3.61	3.61	3.59	3.58
7	3.69	3.69	3.91	3.91	3.75	3.75	3.89	3.89
8	3.49	3.66	3.59	3.48	3.61	3.60	3.57	3.58
9	3.84	3.71	3.65	3.85	3.76	3.87	3.71	3.63
12	0.95	0.95	0.96	0.96	0.95	0.95	0.95	0.95

Table 20. ^1H NMR $^3J_{\text{H,H}}$ of pentaols **3a-p** in CD_3OD / Hz

CD_3OD	3a SSSS	3b AAAA	3c ASSA	3d SAAS	3e SSSA	3f ASSS	3g SSAA	3h AASS
5, 6	4.0	6.0	7.0	1.5	3.5	8.0	-	6.0
6, 7	4.5	6.0	2.5	7.0	5.0	2.0	-	7.5
7, 8	4.5	6.0	2.5	7.0	2.0	5.0	7.5	-
8, 9	4.0	6.0	7.0	1.5	7.5	3.5	6.0	-

	3i SSAS	3j SASS	3k SASA	3l ASAS	3m SAAA	3n AAAS	3o ASAA	3p AASA
5, 6	5.5	1.5	2.0	8.0	1.5	6.0	8.0	6.0
6, 7	1.5	8.5	8.5	1.0	7.0	6.0	0.0	8.0
7, 8	8.5	1.5	1.0	9.0	6.5	6.5	7.5	0.0
8, 9	1.5	5.0	8.0	2.0	6.0	1.5	6.0	8.0

NMR Data of Pentaols 3a~p (continued).

Table 21. ^{13}C NMR chemical shifts of pentaols **3a-p** in DMSO- d_6 / ppm

	3a SSSS	3b AAAA	3c ASSA	3d SAAS	3e SSSA	3f ASSS	3g SSAA	3h AASS
1	60.851	60.912	60.919	60.821	60.821	60.927	60.828	60.918
2	32.780	32.894	32.825	32.734	32.742	32.894	32.765	32.894
3	22.002	21.812	21.676	22.161	22.085	21.683	21.896	21.851
4	33.182	31.968	32.871	33.372	33.235	33.174	32.863	31.354
5	70.863	71.364	70.135	69.642	70.347	70.135	72.365	71.984
6	73.138	75.201	76.521	73.874	74.617	74.170	71.750	73.516
7	72.190	73.449	67.480	71.781	69.619	69.611	72.971	72.924
8	73.108	75.201	76.498	73.813	74.170	74.693	73.533	71.824
9	70.506	71.060	69.824	69.278	69.831	69.998	71.523	71.824
10	35.495	34.335	35.177	35.685	35.526	35.556	33.705	35.162
11	18.589	18.437	18.285	18.771	18.316	18.703	18.468	18.476
12	14.190	14.250	14.235	14.137	14.235	14.152	14.250	14.161

	3i SSAS	3j SASS	3k SASA	3l ASAS	3m SAAA	3n AAAS	3o ASAA	3p AASA
1	60.836	60.857	60.857	60.950	60.843	60.912	60.942	60.926
2	32.901	32.780	32.795	32.947	32.742	32.894	32.924	32.940
3	21.911	22.284	22.306	21.790	22.176	21.903	21.721	21.866
4	32.810	33.569	33.561	33.713	33.318	31.673	33.576	31.263
5	72.509	68.836	69.344	70.484	69.657	71.591	70.036	72.014
6	71.561	71.544	71.544	72.008	73.427	75.884	72.327	73.326
7	71.136	71.074	68.738	68.754	72.342	72.365	70.476	70.490
8	71.621	71.627	72.022	71.629	75.914	73.480	73.366	72.348
9	68.451	72.135	70.186	68.982	71.295	69.278	71.720	69.724
10	35.890	35.215	36.095	35.897	34.047	35.624	33.652	35.935
11	18.877	18.484	18.416	18.915	18.528	18.778	18.498	18.355
12	14.175	14.199	14.305	14.197	14.266	14.137	14.296	14.275

Table 22. ^1H NMR chemical shifts of pentaols **3a-p** in DMSO- d_6 / ppm

	3a SSSS	3b AAAA	3c ASSA	3d SAAS	3e SSSA	3f ASSS	3g SSAA	3h AASS
1	3.36	3.37	3.37	3.37	3.37	3.37	3.37	3.37
5	3.50	3.54	3.42	3.67	3.49	3.41	3.47	3.50
6	3.33	3.44	3.22	3.33	3.31	3.24	3.46	3.40
7	3.54	3.53	3.90	3.59	3.75	3.75	3.41	3.40
8	3.33	3.44	3.22	3.33	3.24	3.32	3.41	3.46
9	3.50	3.54	3.42	3.67	3.43	3.51	3.52	3.50
12	0.85	0.86	0.85	0.86	0.85	0.86	0.86	0.85
1-OH	4.33	4.30	4.31	4.32	4.31	4.31	4.32	4.31
5-OH	4.26	4.50	4.34	4.15	4.27	4.32	4.35	4.39
6-OH	4.22	4.76	4.51	4.52	4.31	4.40	4.17	4.50
7-OH	4.23	4.73	3.96	4.77	4.08	4.08	4.50	4.50
8-OH	4.22	4.76	4.51	4.52	4.40	4.32	4.50	4.18
9-OH	4.26	4.50	4.34	4.15	4.31	4.27	4.39	4.35

	3i SSAS	3j SASS	3k SASA	3l ASAS	3m SAAA	3n AAAS	3o ASAA	3p AASA
1	3.37	3.37	3.37	3.37	3.37	3.36	3.37	3.37
5	3.48	3.62	3.63	3.37	3.65	3.57	3.37	3.52
6	3.46	3.26	3.25	3.37	3.39	3.42	3.36	3.38
7	3.44	3.43	3.71	3.73	3.52	3.52	3.66	3.66
8	3.25	3.46	3.36	3.26	3.42	3.38	3.39	3.36
9	3.65	3.50	3.40	3.67	3.59	3.67	3.54	3.38
12	0.86	0.86	0.86	0.88	0.86	0.86	0.86	0.86
1-OH	4.32	4.32	4.33	4.33	4.33	4.31	4.31	4.31
5-OH	4.33	3.93	3.91	4.32	4.15	4.45	4.32	4.39
6-OH	3.99	4.10	4.03	3.98	4.57	4.72	4.13	4.44
7-OH	4.25	4.24	4.00	4.02	4.77	4.76	4.23	4.24
8-OH	4.11	4.00	3.96	4.05	4.72	4.57	4.45	4.12
9-OH	3.92	4.32	4.30	3.92	4.45	4.14	4.39	4.31

NMR Data of Petnaols 3a~p (continued).

Table 23. ^{13}C NMR chemical shifts of pentaols **3a-p** in D_2O / ppm

D_2O	3a SSSS	3b AAAA	3c ASSA	3d SAAS	3e SSSA	3f ASSS	3g SSAA	3h AASS
1	61.978	62.028	62.031	61.982	61.971	62.039	61.986	62.046
2	31.535	31.560	31.565	31.491	31.512	31.580	31.580	31.610
3	21.607	21.730	21.516	21.828	21.690	21.463	21.432	21.910
4	32.536	31.021	31.656	32.773	32.634	32.126	32.232(a)	29.805
5	71.762	71.842	70.981	70.545	71.368	71.026	72.816	72.111
6	74.007	75.248	75.493	73.792	74.621	74.227	72.816	73.688
7	72.194	72.768	69.517	72.002	70.677	70.647	71.792	71.815
8	73.969	75.187	75.380	73.792	74.250	74.690	73.883	72.907
9	71.610	71.676	70.806	70.363	70.852	71.170	71.883	72.672
10	34.978	33.463	33.977	35.223	34.538	35.092	32.217(a)	34.705
11	18.550	18.666	18.436	18.772	18.376	18.641	18.800	18.398
12	13.582	13.591	13.567	13.538	13.605	13.560	13.613	13.651

	3i SSAS	3j SASS	3k SASA	3l ASAS	3m SAAA	3n AAAS	3o ASAA	3p AASA
1	61.978	62.001	62.016	62.069	61.982	62.035	62.062	62.054
2	31.550	31.542	31.565	31.633	31.507	31.567	31.618	31.603
3	21.455	21.955	21.963	21.470	21.821	21.768	21.478	21.910
4	32.232	32.877	32.915	32.885	32.773	31.014	32.824	29.767
5	73.135	69.904	70.139	71.155	70.644	72.017	70.935	72.323
6	72.748	72.020	72.073	72.551	73.428	75.468	72.611	73.696
7	70.791	70.768	69.092	69.070	72.351	72.388	70.162	70.222
8	72.058	72.801	72.543	72.111	75.529	73.481	73.688	72.665
9	69.699	72.983	71.041	69.934	71.827	70.462	72.111	70.844
10	35.342	34.690	35.365	35.387	33.463	35.223	32.164	35.319
11	18.899	18.406	18.414	18.914	18.688	18.772	18.808	18.444
12	13.590	13.605	13.673	13.613	13.584	13.569	13.598	13.681

(a) maybe interchanged

Table 24. ^1H NMR chemical shifts of pentaols **3a-p** in D_2O / ppm

D_2O	3a SSSS	3b AAAA	3c ASSA	3d SAAS	3e SSSA	3f ASSS	3g SSAA	3h AASS
1	3.63	3.64	3.64	3.64	3.63	3.64	3.63	3.67
5	3.78	3.86	3.73	3.95	3.77	3.74	3.77	3.89
6	3.62	3.79	3.58	3.68	3.61	3.60	3.72	3.80
7	3.85	3.83	3.99	3.87	3.95	3.96	3.68	3.71
8	3.62	3.79	3.58	3.68	3.60	3.61	3.77	3.74
9	3.78	3.86	3.73	3.95	3.74	3.78	3.87	3.80
12	0.93	0.94	0.94	0.94	0.94	0.94	0.94	0.96

	3i SSAS	3j SASS	3k SASA	3l ASAS	3m SAAA	3n AAAS	3o ASAA	3p AASA
1	3.64	3.65	3.65	3.65	3.64	3.64	3.64	3.67
5	3.79	3.90	3.93	3.73	3.94	3.87	3.71	3.89
6	3.73	3.60	3.59	3.68	3.70	3.79	3.67	3.79
7	3.78	3.79	3.97	3.96	3.84	3.84	3.88	3.91
8	3.59	3.73	3.69	3.57	3.79	3.70	3.75	3.69
9	3.90	3.81	3.75	3.93	3.88	3.95	3.88	3.74
12	0.94	0.94	0.96	0.94	0.94	0.94	0.95	0.97

Table 25. ^1H NMR $^3J_{\text{H,H}}$ of pentaols **3a-p** in D_2O / Hz

D_2O	3a SSSS	3b AAAA	3c ASSA	3d SAAS	3e SSSA	3f ASSS	3g SSAA	3h AASS
5, 6	4.5	6.0	7.0	2.0	4.0	7.5	6.5	4.0
6, 7	4.5	6.0	4.0	7.0	5.5	3.0	1.5	8.5
7, 8	4.5	6.0	4.0	7.0	3.0	6.0	8.5	1.5
8, 9	4.5	6.0	7.0	2.0	7.0	4.0	4.5	6.5

	3i SSAS	3j SASS	3k SASA	3l ASAS	3m SAAA	3n AAAS	3o ASAA	3p AASA
5, 6	7.0	1.0	1.5	8.5	2.0	5.5	8.5	4.5
6, 7	1.5	9.0	9.0	1.0	6.5	6.5	1.0	9.0
7, 8	9.0	1.5	1.0	9.5	6.5	7.0	9.0	1.0
8, 9	1.5	6.5	8.5	1.5	5.5	2.0	4.5	8.5

NMR Data of Petnaols **3a~p** (continued).

Table 26. $^3J_{\text{H,H}}$ of pentaols **3a-p** in pyridine-*d*6 / Hz

pyridine- <i>d</i> 6	3a □□□□□ SSSS	3b □□□□□ AAAA	3c □□□□□ ASSA	3d □□□□□ SAAS	3e □□□□□ SSSA	3f □□□□□ ASSS	3g □□□□□ SSAA	3h □□□□□ AASS
5, 6	4.0	6.0	7.0	1.0	-	7.5	4.5	-
6, 7	4.0	6.0	2.0	7.0	-	1.5	1.5	-
7, 8	4.0	6.0	2.0	7.0	-	4.0	7.5	-
8, 9	4.0	6.0	7.0	1.0	-	4.0	6.5	4.5
	3i □□□□□ SSAS	3j □□□□□ SASS	3k □□□□□ SASA	3l □□□□□ ASAS	3m □□□□□ SAAA	3n □□□□□ AAAS	3o □□□□□ ASAA	3p □□□□□ AASA
5, 6	-	-	-	7.0	1.5	6.5	7.5	6.5
6, 7	-	8.5	-	0.0	7.0	7.0	1.0	7.5
7, 8	9.0	0.0	-	9.0	7.0	6.5	7.5	0.0
8, 9	1.0	5.5	-	2.0	6.0	-	7.0	7.5

Chemical shift [^{13}C , ^1H , $^1\text{H}(\text{OH})$] and $^3J_{\text{H,H}}$ profiles of pentaols **3a~p** in CD_3OD and $\text{DMSO-}d_6$.

Graph 8. Difference in (A) ^{13}C chemical shifts and (B) ^1H chemical shifts between the average and the values of **3a~p** in CD_3OD , $\Delta\delta = \delta_{\text{3a~p}} - \delta_{\text{ave}}$ in ppm, and $^3J_{\text{H,H}}$ of **3a~p** in CD_3OD , in Hz. The $^3J_{\text{H,H}}$ indicated by an asterisk were not determined.

Graph 9. Difference in (A) ^{13}C chemical shifts (B) ^1H chemical shifts and (C) hydroxy- ^1H chemical shifts between the average and the values of **3a~p** in $(\text{CD}_3)_2\text{SO}$, $\Delta\delta = \delta_{\text{3a~p}} - \delta_{\text{ave}}$ in ppm.

Chemical shift [^{13}C , ^1H , $^1\text{H}(\text{OH})$] and $^3J_{\text{H,H}}$ profiles of pentaols **3a**~**p** in D_2O and pyridine- d_5 .

Graph 10. Difference in (A) ^{13}C chemical shifts and (B) ^1H chemical shifts between the average and the values of **3a**~**p** in D_2O , $\Delta\delta = \delta_{\text{3a-p}} - \delta_{\text{ave}}$ in ppm, and $^3J_{\text{H,H}}$ of **3a**~**p** in D_2O , in Hz.

Graph 11. The $^3J_{\text{H,H}}$ of **3a**~**p** in $\text{C}_5\text{D}_5\text{N}$ in Hz. The $^3J_{\text{H,H}}$ indicated by an asterisk were not determined.

Comparison at C9(C3'), C8(C4'), and C7(C5') for ^{13}C Δ and H7(H5') for ^1H Δ between Triols and Tetraols, cf., Panel B, Figure 5 in the Text.

Table 27. Comparison between ^{13}C chemical shifts at C3'(C9), C4'(C8), and C5'(C7) of triols **1a~d** and C3'(C10), C4'(C9), and C5'(C8) of tetraols **2a~h** in CD_3OD . Δ and $\Delta\Delta = \Delta(\text{tetraol}) - \Delta(\text{triol})$ are in ppm.

Relative configuration		Chemical shift Δ			$\Delta\Delta = \Delta(2) - \Delta(1)$		
C5'C6'C7'C8'		C3'	C4'	C5'	C3'	C4'	C5'
1a		19.95	36.96	73.31	$\Delta\Delta = \Delta(2) - \Delta(1\text{a})$		
2a		20.04	36.71	72.75	+0.09	-0.24	-0.56
2e		19.88	36.51	74.29	-0.08	-0.45	+0.98
1b		19.80	35.80	73.80	$\Delta\Delta = \Delta(2) - \Delta(1\text{b})$		
2g		19.83	35.25	74.04	+0.03	-0.55	+0.24
2b		19.90	35.11	73.82	+0.10	-0.69	+0.02
1d		20.14	37.06	71.12	$\Delta\Delta = \Delta(2) - \Delta(1\text{c})$		
2h		20.22	36.95	71.47	+0.07	-0.11	+0.35
2d		20.29	37.01	71.30	+0.14	-0.05	+0.18
1c		19.81	36.99	72.58	$\Delta\Delta = \Delta(2) - \Delta(1\text{d})$		
2c		19.90	37.05	72.75	+0.09	+0.06	+0.17
2e		19.82	36.73	72.37	+0.01	-0.26	-0.21

Table 28. Comparison between ^1H chemical shifts at H5'(H7) of triols **1a~d** and H5'(H8) of tetraols **2a~h** in CD_3OD . Δ and $\Delta\Delta = \Delta(\text{tetraol}) - \Delta(\text{triol})$ are in ppm.

Relative configuration	Chemical shift δ	$\delta = \delta(2) - \delta(1)$
C5'C6'C7'C8'	H5'	H5'
1a	3.64	$\delta = \delta(2) - \delta(1\mathbf{a})$
2a	3.70	+0.06
2e	3.66	+0.02
1b	3.59	$\delta = \delta(2) - \delta(1\mathbf{b})$
2g	3.70	+0.11
2b	3.73	+0.14
1d	3.82	$\delta = \delta(2) - \delta(1\mathbf{c})$
2h	3.84	+0.02
2d	3.83	+0.01
1c	3.61	$\delta = \delta(2) - \delta(1\mathbf{d})$
2c	3.62	+0.01
2e	3.62	+0.01

Average between the δ 's of Panel A and those of Panel B in Figure 5 in the Text, cf., Table 1 in the Text and Table 27 in the Supporting Information for ^{13}C δ as well as Table 2 and Table 28 for ^1H δ .

Table 29. Average of δ (tetraol 2)- δ (triol 1) at C3 and C3', C4 and C4', and C5 and C5' in CD_3OD in Table 1 in the Text and Table 27 in the Supporting Information in ppm.

Relative configuration	Average δ =(2)-(1)		
C5 C6 C7 C8 C5' C6' C7' C8'	C3 C3'	C4 C4'	C5 C5'
<div><div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div></div>	+0.09 -0.08	-0.25 -0.45	-0.55 +0.98
<div><div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div></div>	+0.03 +0.10	-0.53 -0.67	+0.24 -0.01
<div><div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div></div>	+0.06 +0.13	-0.10 -0.04	+0.28 +0.11
<div><div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div></div>	+0.07 -0.01	+0.08 -0.23	+0.16 -0.22

Table 30. Average of δ (tetraol 2)- δ (triol 1) at H5 and H5' in CD_3OD in Table 2 in the Text and Table 28 in the Supporting Information in ppm.

Relative configuration	Average δ =(2)-(1)
C5 C6 C7 C8 C5' C6' C7' C8'	H5 H5'
<div><div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div></div>	+0.06 +0.02
<div><div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div></div>	+0.11 +0.14
<div><div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div></div>	+0.02 +0.02
<div><div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div><div><div></div><div></div><div></div></div></div></div>	+0.02 +0.02

Comparison at C9(C3'), C8(C4'), and C7(C5') for ^{13}C Δ and H7(H5') for ^1H Δ between Triols and Pentaols, cf., Panel B, Figure 5 in the Text.

Table 31. Comparison between ^{13}C chemical shifts at C3'(C9), C4'(C8), and C5'(C7) of triols **1a~d** and C3'(C11), C4'(C10), and C5'(C9) of pentaols **3a~p** in CD_3OD . Δ and $\Delta\Delta = \Delta(\text{pentaol}) - \Delta(\text{triol})$ are in ppm.

Relative configuration		Chemical shift Δ			$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1})$		
C5'C6'C7'C8'C9'		C3'	C4'	C5'	C3'	C4'	C5'
1a	$\begin{bmatrix} \square & \square & \square \end{bmatrix}$	19.95	36.96	73.31	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1a})$		
3a	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.99	36.79	72.81	+0.04	-0.17	-0.50
3f	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	20.07	36.87	72.29	+0.12	-0.08	-1.02
3h	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.87	36.52	74.09	-0.08	-0.43	+0.78
3j	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.88	36.58	74.48	-0.08	-0.38	+1.18
1b	$\begin{bmatrix} \square & \square & \square \end{bmatrix}$	19.80	35.80	73.80	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1b})$		
3g	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.84	35.31	73.95	+0.04	-0.49	+0.15
3o	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.84	35.27	74.07	+0.04	-0.53	+0.27
3b	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.86	35.70	73.40	+0.06	-0.10	-0.40
3m	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.94	35.48	73.80	+0.13	-0.33	0.00
1d	$\begin{bmatrix} \square & \square & \square \end{bmatrix}$	20.14	37.06	71.12	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1c})$		
3d	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	20.19	36.94	71.50	+0.05	-0.12	+0.38
3n	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	20.18	36.90	71.56	+0.04	-0.16	+0.44
3l	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	20.29	37.02	71.30	+0.14	-0.04	+0.05
3i	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	20.27	37.04	70.84	+0.13	-0.02	-0.28
1c	$\begin{bmatrix} \square & \square & \square \end{bmatrix}$	19.81	36.99	72.58	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1d})$		
3k	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.90	37.24	72.88	+0.09	+0.26	+0.30
3p	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.86	37.15	72.50	+0.05	+0.16	-0.08
3c	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.83	36.38	72.40	+0.02	-0.61	-0.18
3e	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	19.82	36.82	72.44	+0.01	-0.17	-0.14

Table 32. Comparison between ^1H chemical shifts at H5'(H7) of triols **1a~d** and H5'(H9) of pentaol **3a~p** in CD_3OD . Δ and $\Delta\Delta = \Delta(\text{pentaol}) - \Delta(\text{triol})$ are in ppm.

Relative configuration		Chemical shift Δ		$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1})$
C5 C6 C7 C8 C9		H5'	H5'	
1a	$\begin{bmatrix} \square & \square & \square \end{bmatrix}$	3.64	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1a})$	
3a	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.70	+0.06	
3f	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.71	+0.07	
3h	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.70	+0.06	
3j	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.71	+0.07	
1b	$\begin{bmatrix} \square & \square & \square \end{bmatrix}$	3.59	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1b})$	
3g	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.70	+0.11	
3o	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.71	+0.12	
3b	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.74	+0.15	
3m	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.76	+0.17	
1d	$\begin{bmatrix} \square & \square & \square \end{bmatrix}$	3.82	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1c})$	
3d	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.87	+0.05	
3n	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.87	+0.05	
3l	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.85	+0.03	
3i	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.84	+0.02	
1c	$\begin{bmatrix} \square & \square & \square \end{bmatrix}$	3.61	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{1d})$	
3k	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.65	+0.04	
3p	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.63	+0.02	
3c	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.64	+0.03	
3e	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.64	+0.03	

Average between the δ 's of Panel A and those of Panel B in Figure 5 in the Text, cf., Table 1 in the Text and Table 31 in the Supporting Information for ^{13}C δ as well as Table 2 and Table 32 for ^1H δ .

Table 33. Average of δ = δ (pentaol **3**) - δ (triol **1**) at C3 and C3', C4 and C4', and C5 and C5' in CD_3OD in Table 1 in the Text and Table 31 in the Supporting Information in ppm.

Relative configuration					Average δ = δ (3) - δ (1)		
C5	C6	C7	C8	C9	C3	C4	C5
C5'	C6'	C7'	C8'	C9'	C3'	C4'	C5'
$\square$	$\square$	$\square$	$\square$	$\square$	+0.04	-0.18	-0.50
$\square$	$\square$	$\square$	$\square$	$\square$	+0.12	-0.09	-1.02
$\square$	$\square$	$\square$	$\square$	$\square$	-0.09	-0.44	+0.86
$\square$	$\square$	$\square$	$\square$	$\square$	-0.08	-0.39	+1.18
$\square$	$\square$	$\square$	$\square$	$\square$	+0.04	-0.49	+0.23
$\square$	$\square$	$\square$	$\square$	$\square$	+0.04	-0.52	+0.25
$\square$	$\square$	$\square$	$\square$	$\square$	+0.06	-0.09	-0.43
$\square$	$\square$	$\square$	$\square$	$\square$	+0.13	-0.31	-0.01
$\square$	$\square$	$\square$	$\square$	$\square$	+0.04	-0.11	+0.31
$\square$	$\square$	$\square$	$\square$	$\square$	+0.03	-0.15	+0.38
$\square$	$\square$	$\square$	$\square$	$\square$	+0.13	-0.03	-0.03
$\square$	$\square$	$\square$	$\square$	$\square$	+0.12	-0.01	-0.35
$\square$	$\square$	$\square$	$\square$	$\square$	+0.08	+0.28	+0.30
$\square$	$\square$	$\square$	$\square$	$\square$	+0.04	+0.18	-0.09
$\square$	$\square$	$\square$	$\square$	$\square$	+0.01	-0.57	-0.18
$\square$	$\square$	$\square$	$\square$	$\square$	-0.01	-0.15	-0.13

Table 34. Average of δ = δ (pentaol **3**) - δ (triol **1**) at H5 and H5' in CD_3OD in Table 2 in the Text and Table 32 in the Supporting Information in ppm.

Relative configuration					Average δ = δ (3) - δ (1)	
C5	C6	C7	C8	C9	H5	H5'
C5'	C6'	C7'	C8'	C9'		
$\square$	$\square$	$\square$	$\square$	$\square$	+0.07	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.07	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.05	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.07	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.11	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.12	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.15	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.17	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.06	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.05	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.03	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.02	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.05	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.03	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.04	
$\square$	$\square$	$\square$	$\square$	$\square$	+0.04	

Comparison at C4, C5, and C6 for ^{13}C Δ and H5 and H6 for ^1H Δ between Tetraols and Pentaols.

Table 35. Comparison between ^{13}C chemical shifts at C4, C5, and C6 of tetraols **2a~h** and those of pentaols **3a~p** in CD_3OD . Δ and $\Delta\Delta = \Delta(\text{pentaol}) - \Delta(\text{tetraol})$ are in ppm.

Relative configuration		Chemical shift Δ			$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2})$		
C5 C6 C7 C8 C9		C4	C5	C6	C4	C5	C6
2a	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	34.26	72.97	75.33	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2a})$		
3a	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.32	73.01	74.76	+0.06	+0.04	-0.57
3e	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.41	72.49	76.20	+0.15	-0.48	+0.87
2f	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	34.26	72.51	76.20	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2f})$		
3f	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.34	72.61	75.67	+0.08	+0.10	-0.53
3c	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	33.92	72.56	77.75	-0.34	+0.05	+1.55
2g	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	34.49	71.71	75.26	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2g})$		
3d	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.48	71.73	75.51	-0.01	+0.02	+0.25
3m	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.45	71.81	74.85	-0.04	+0.10	-0.41
2b	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	32.60	73.95	76.66	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2b})$		
3n	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	32.96	73.96	77.24	+0.36	+0.01	+0.58
3b	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	33.16	73.53	76.68	+0.56	-0.42	+0.02

Relative configuration		Chemical shift Δ			$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2})$		
C5 C6 C7 C8 C9		C4	C5	C6	C4	C5	C6
2e	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	34.05	74.49	73.29	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2e})$		
3g	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.05	74.45	73.60	0.00	-0.04	+0.31
3i	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.11	74.68	73.33	+0.06	+0.19	+0.04
2c	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	34.55	72.88	73.73	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2c})$		
3o	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.66	72.64	74.02	+0.11	-0.24	+0.29
3l	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.75	73.02	73.72	+0.20	+0.14	-0.01
2d	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	34.55	71.54	73.60	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2d})$		
3k	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.56	71.40	73.48	+0.01	-0.14	-0.12
3j	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	34.58	71.08	73.37	+0.03	-0.46	-0.23
2h	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	32.75	74.21	75.36	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2h})$		
3p	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	32.74	74.21	75.17	-0.01	0.00	-0.19
3h	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	32.77	74.28	75.24	+0.02	+0.07	-0.12

Table 36. Comparison between ^1H chemical shifts at H5 and H6 of tetraol **2a~h** and those of pentaol **3a~p** in CD_3OD . Δ and $\Delta\Delta = \Delta(\text{pentaol}) - \Delta(\text{tetraol})$ are in ppm.

Relative configuration		Chemical shift Δ		$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2})$	
C5 C6 C7 C8 C9		H5	H6	H5	H6
2a	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	3.70	3.49	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2a})$	
3a	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.72	3.54	+0.02	+0.05
3e	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.70	3.53	0.00	+0.04
2f	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	3.62	3.37	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2f})$	
3f	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.64	3.46	+0.02	+0.09
3c	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.64	3.45	+0.02	+0.08
2g	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	3.83	3.43	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2g})$	
3d	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.87	3.55	+0.04	+0.12
3m	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.86	3.61	+0.03	+0.18
2b	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	3.73	3.50	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2b})$	
3n	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.76	3.61	+0.03	+0.11
3b	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.74	3.63	+0.01	+0.13

Relative configuration		Chemical shift Δ		$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2})$	
C5 C6 C7 C8 C9		H5	H6	H5	H6
2e	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	3.66	3.66	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2e})$	
3g	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.68	3.67	+0.02	+0.01
3i	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.70	3.67	+0.04	+0.01
2c	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	3.62	3.59	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2c})$	
3o	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.63	3.59	+0.01	0.00
3l	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.64	3.59	+0.02	0.00
2d	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	3.83	3.48	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2d})$	
3k	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.84	3.49	+0.01	+0.01
3j	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.83	3.50	0.00	+0.02
2h	$\begin{bmatrix} \square & \square & \square & \square \end{bmatrix}$	3.70	3.58	$\Delta\Delta = \Delta(\mathbf{3}) - \Delta(\mathbf{2h})$	
3p	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.71	3.58	+0.01	0.00
3h	$\begin{bmatrix} \square & \square & \square & \square & \square \end{bmatrix}$	3.70	3.59	0.00	+0.01

Comparison at C9(C4'), C8(C5'), and C7(C6') for ^{13}C and H8(H5') and H7(H6') for ^1H between Tetraols and Pentaols.

Table 37. Comparison between ^{13}C chemical shifts at C4'(C9), C5'(C8), and C6'(C7) of tetraols **2a~h** and C4'(C10), C5'(C9), and C6'(C8) of pentaols **3a~p** in CD_3OD . $\square$ and $\square\square$ = $\square$ (pentaol) - $\square$ (tetraol) are in ppm.

Relative configuration	Chemical shift $\square$			$\square\square=\square(3)-\square(2)$		
C5'C6'C7'C8'C9'	C4'	C5'	C6'	C4'	C5'	C6'
2a $\square\square\square\square$	36.71	72.75	75.27	$\square\square=\square(3)-\square(2a)$		
3a $\square\square\square\square\square$	36.79	72.81	74.72	+0.08	+0.06	-0.55
3e $\square\square\square\square\square$	36.87	72.29	76.26	+0.16	-0.46	+0.99
2e $\square\square\square\square$	36.73	72.37	76.21	$\square\square=\square(3)-\square(2f)$		
3e $\square\square\square\square\square$	36.82	72.44	75.67	+0.09	+0.07	-0.54
3c $\square\square\square\square\square$	36.38	72.40	77.74	-0.35	+0.03	+1.53
2h $\square\square\square\square$	36.95	71.47	75.33	$\square\square=\square(3)-\square(2g)$		
3d $\square\square\square\square\square$	36.94	71.50	75.46	-0.01	+0.03	+0.13
3n $\square\square\square\square\square$	36.90	71.56	74.94	-0.05	+0.09	-0.39
2b $\square\square\square\square$	35.11	73.82	76.61	$\square\square=\square(3)-\square(2b)$		
3m $\square\square\square\square\square$	35.48	73.80	77.31	+0.37	-0.02	+0.70
3b $\square\square\square\square\square$	35.70	73.40	76.58	+0.59	-0.42	-0.03

Relative configuration	Chemical shift $\square$			$\square\square=\square(3)-\square(2)$		
C5'C6'C7'C8'C9'	C4'	C5'	C6'	C4'	C5'	C6'
2f $\square\square\square\square$	36.51	74.29	73.32	$\square\square=\square(3)-\square(2e)$		
3h $\square\square\square\square\square$	36.52	74.09	73.61	+0.01	-0.20	+0.29
3j $\square\square\square\square\square$	36.58	74.48	73.37	+0.07	+0.19	+0.05
2c $\square\square\square\square$	37.05	72.75	73.71	$\square\square=\square(3)-\square(2c)$		
3p $\square\square\square\square\square$	37.15	72.50	74.01	+0.10	-0.25	+0.30
3k $\square\square\square\square\square$	37.24	72.88	73.72	+0.19	+0.13	+0.01
2d $\square\square\square\square$	37.01	71.30	73.54	$\square\square=\square(3)-\square(2d)$		
3l $\square\square\square\square\square$	37.02	71.16	73.56	+0.01	-0.14	+0.02
3i $\square\square\square\square\square$	37.04	70.84	73.43	+0.03	-0.46	-0.11
2g $\square\square\square\square$	35.25	74.04	75.41	$\square\square=\square(3)-\square(2h)$		
3o $\square\square\square\square\square$	35.27	74.07	75.23	+0.02	+0.03	-0.18
3g $\square\square\square\square\square$	35.31	73.95	75.30	+0.06	-0.09	-0.11

Table 38. Comparison between ^1H chemical shifts at H5'(H8) and H6'(H7) of tetraols **2a~h** and H5'(H9) and H6'(H8) of pentaols **3a~p** in CD_3OD . $\square$ and $\square\square$ = $\square$ (pentaol) - $\square$ (tetraol) are in ppm.

Relative configuration	Chemical shift $\square$		$\square\square=\square(3)-\square(2)$	
C5'C6'C7'C8'C9'	H5'	H6'	H5'	H6'
2a $\square\square\square\square$	3.70	3.49	$\square\square=\square(3)-\square(2a)$	
3a $\square\square\square\square\square$	3.72	3.54	+0.02	+0.05
3e $\square\square\square\square\square$	3.71	3.53	+0.01	+0.04
2e $\square\square\square\square$	3.62	3.36	$\square\square=\square(3)-\square(2f)$	
3e $\square\square\square\square\square$	3.64	3.45	+0.02	+0.09
3c $\square\square\square\square\square$	3.64	3.45	+0.02	+0.09
2h $\square\square\square\square$	3.84	3.42	$\square\square=\square(3)-\square(2g)$	
3d $\square\square\square\square\square$	3.87	3.55	+0.03	+0.13
3n $\square\square\square\square\square$	3.87	3.60	+0.03	+0.18
2b $\square\square\square\square$	3.73	3.50	$\square\square=\square(3)-\square(2b)$	
3m $\square\square\square\square\square$	3.76	3.61	+0.03	+0.11
3b $\square\square\square\square\square$	3.74	3.63	+0.04	+0.13

Relative configuration	Chemical shift $\square$		$\square\square=\square(3)-\square(2)$	
C5'C6'C7'C8'C9'	H5'	H6'	H5'	H6'
2f $\square\square\square\square$	3.66	3.65	$\square\square=\square(3)-\square(2e)$	
3h $\square\square\square\square\square$	3.70	3.66	+0.04	+0.01
3j $\square\square\square\square\square$	3.71	3.66	+0.05	+0.01
2c $\square\square\square\square$	3.62	3.59	$\square\square=\square(3)-\square(2c)$	
3p $\square\square\square\square\square$	3.63	3.58	+0.01	-0.01
3k $\square\square\square\square\square$	3.65	3.59	+0.03	0.00
2d $\square\square\square\square$	3.83	3.48	$\square\square=\square(3)-\square(2d)$	
3l $\square\square\square\square\square$	3.85	3.48	+0.02	0.00
3i $\square\square\square\square\square$	3.84	3.49	+0.01	+0.01
2g $\square\square\square\square$	3.70	3.57	$\square\square=\square(3)-\square(2h)$	
3o $\square\square\square\square\square$	3.71	3.57	+0.01	0.00
3g $\square\square\square\square\square$	3.70	3.58	0.00	+0.01

Average between the δ 's in Table 35 and those in Table 37 for ^{13}C and between the δ 's in Table 36 and those in Table 38 for ^1H in the Supporting Information.

Table 39. Average of δ 's of (pentaol 3)-(tetraol 2) at C4 and C4', C5 and C5', and C6 and C6' in CD_3OD in Table 35 and Table 37 in ppm.

Relative configuration	δ 's of (3)-(2)			Relative configuration	δ 's of (3)-(2)		
C5 C6 C7 C8 C9 C5' C6' C7' C8' C9'	C4 C4'	C5 C5'	C6 C6'	C5 C6 C7 C8 C9 C5' C6' C7' C8' C9'	C4 C4'	C5 C5'	C6 C6'
$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.07	+0.05	-0.57	$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.01	-0.12	+0.30
	+0.16	-0.47	+0.93		+0.07	+0.19	+0.05
$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.09	+0.09	-0.54	$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.11	-0.25	+0.30
	-0.35	+0.04	+1.54		+0.20	+0.14	+0.00
$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	-0.01	+0.03	+0.19	$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.01	-0.14	-0.05
	-0.05	+0.10	-0.40		+0.03	-0.46	-0.17
$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.37	-0.01	+0.64	$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.01	+0.02	-0.19
	+0.58	-0.42	-0.01		+0.04	-0.01	-0.12

Table 40. Average of δ 's of (pentaol 3)-(tetraol 2) at H5 and H5', and H6 and H6' in CD_3OD in Table 36 and Table 38 in ppm.

Relative configuration	δ 's of (3)-(2)		Relative configuration	δ 's of (3)-(2)	
C5 C6 C7 C8 C9 C5' C6' C7' C8' C9'	H5 H5'	H6 H6'	C5 C6 C7 C8 C9 C5' C6' C7' C8' C9'	H5 H5'	H6 H6'
$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.02	+0.05	$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.03	+0.01
	+0.01	+0.04		+0.05	+0.01
$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.02	+0.09	$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.01	-0.01
	+0.02	+0.09		+0.03	0.00
$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.04	+0.13	$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.02	+0.01
	+0.03	+0.18		+0.01	+0.02
$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.03	+0.11	$\begin{bmatrix} \square & \square & \square & \square \\ \square & \square & \square & \square \\ \square & \square & \square & \square \end{bmatrix}$	+0.01	0.00
	+0.03	+0.13		0.00	+0.01

NMR Data of Heptaols 4a~d.

Table 41. ^{13}C NMR chemical shifts of heptaols **4a-d** in CD_3OD / ppm

	4a SSSSAA	4b SSSSAA	4c AAAAAA	4d AAASAA
1	62.903	62.903	62.994	62.986
2	33.626	33.626	33.717	33.709
3	23.242	23.242	23.030	23.090
4	34.392	34.392	32.951	33.019
5	72.460	72.460	73.704	73.741
6	76.002	76.002	76.275	77.276
7	71.951	71.951	74.545	73.961
8	73.704	73.704	75.152	72.262
9	73.704	73.704	74.523	72.573
10	77.299	77.299	76.199	75.221
11	73.704	73.704	73.567	73.961
12	35.537	35.537	35.476	35.188
13	19.935	19.935	19.882	19.867
14	14.520	14.520	14.535	14.542

Table 42. ^1H NMR chemical shifts of heptaols **4a-d** in CD_3OD / ppm

	4a SSSSAA	4b SSSSAA	4c AAAAAA	4d AAASAA
1	3.56	3.56	3.56	3.57
5	3.72	3.72	3.75	3.76
6	3.59	3.55	3.68	3.64
7	3.99	3.82	3.88	3.77
8	3.90	4.00	4.00	4.04
9	3.79	3.75	3.88	3.91
10	3.63	3.60	3.68	3.60
11	3.76	3.72	3.75	3.73

Table 43. ^1H NMR $^3J_{\text{H,H}}$ of heptaols **4a-d** in CD_3OD / Hz

	4a SSSSAA	4b SSSSAA	4c AAAAAA	4d AAASAA
5, 6	3.5	3.5	6.5	6.0
6, 7	5.0	4.0	6.0	6.0
7, 8	2.0	5.0	6.0	6.0
8, 9	7.0	1.5	6.0	0
9, 10	6.0	7.5	6.0	7.0
10, 11	6.0	6.0	6.5	6.0

Protocol for Predicting ^{13}C δ Profile of 4a at the First Order of Approximation, cf., Figure 4 and Graphs 8 and 9 in the Text.

Figure 1. A protocol for predicting the ^{13}C chemical shift profile for **4a** at the first order of approximation. Structural correlation of **4a** with the corresponding isomer of **1~3** and the observed δ and the predicted δ in CD_3OD with carbon number are shown in ppm. The ^{13}C chemical shift profiles for **4b~d** are predicted in the same protocol. See Table 48~51.

Protocol used for Refinement of ^{13}C δ Profiles for 4a with δ and ϵ given in Tables 29 and 39 in the Supporting Information, cf., Figure 6 and Graph 10 in the Text.

Figure 2. A protocol for refinement of the predicted ^{13}C δ profiles for 4a with δ and ϵ effects in Table 29 and 39. Structural correlation of 4a with the corresponding comparison of 1–3 and the predicted δ and the refinement in CD_3OD with carbon number are shown in ppm. The refinements for 4b–d are represented in the same protocol. See Table 48–51.

¹³C NMR Profiles predicted at the First Order of Approximation and their Refinements with Incorporation of ρ - and σ -Effects (Tables 29 and 39) for 4a~d, cf., Figures 1 and 2 in the Supporting Information and Figures 4 and 6 and Graphs 8~10 in the Text.

Table 44. The observed ¹³C chemical shifts δ (A), the predicted δ (B-1), and the difference $\delta\delta$ (B-2) = δ (predicted) - δ (observed), the refined predicted δ (C-1), and the difference δ (C-2) = δ (refined predicted) - δ (observed) at C3-C13 of **4a** in CD₃OD in ppm. See the procedure for **4a** in Figure 1 and 2 in the Supporting Information.

4a		C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
Observed $\square$ (A)		23.24	34.39	72.46	76.00	71.95	73.70	73.70	77.30	73.70	35.54	19.86
Prediction												
C5	C6	C7	C8	C9	C10	C11						
1a												
2a												
3e												
3g												
3m												
2b												
1b												
Predicted $\square$ (B-1)		23.12	34.51	73.51	75.33	71.60	74.70	74.03	76.61	73.80	35.80	19.80
$\square\square$ (B-2)		-0.12	+0.12	+1.05	+0.67	-0.35	+1.00	+0.33	-0.69	+0.10	+0.26	-0.06
Refinement												
C5	C6	C7	C8	C9	C10	C11						

Table 45. The observed ¹³C chemical shifts δ (A), the predicted δ (B-1), and the difference $\delta\delta$ (B-2) = δ (predicted) - δ (observed), the refined predicted δ (C-1), and the difference δ (C-2) = δ (refined predicted) - δ (observed) at C3-C13 of **4b** in CD₃OD in ppm. See the procedure for **4a** in Figure 1 and 2 in the Supporting Information.

4b		C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C12
Observed δ (A)		23.10	34.20	73.36	74.20	74.96	71.42	73.92	75.25	74.20	35.24	19.86
<div><div>Prediction</div><div><div>C5</div><div>C6</div><div>C7</div><div>C8</div><div>C9</div><div>C10</div><div>C11</div></div><div><div>1a</div><div>2a</div><div>3a</div><div>3e</div><div>3g</div><div>2g</div><div>1b</div></div></div>		23.12	34.51	73.51	75.33	74.13	71.60	74.70	75.41	73.80	35.80	19.80
Predicted δ (B-1)		23.12	34.51	73.51	75.33	74.13	71.60	74.70	75.41	73.80	35.80	19.80
$\delta\delta$ (B-2)		+0.02	+0.31	+0.15	+1.13	-0.83	+0.18	+0.78	+0.16	-0.40	+0.56	-0.06
<div><div>Refinement</div><div><div>C5</div><div>C6</div><div>C7</div><div>C8</div><div>C9</div><div>C10</div><div>C11</div></div></div>												
Total refinement		-0.25	-0.50	-1.04	+0.81	-0.27	-0.49	-0.03	+0.23	-0.53		
Refined predicted δ (C-1)		23.12	34.26	73.01	74.29	74.94	71.33	74.21	75.38	74.03	35.27	19.80
$\delta\delta$ (C-2)		+0.02	+0.06	-0.35	+0.09	-0.02	-0.09	+0.29	+0.13	-0.17	+0.03	-0.06

Table 46. The observed ^{13}C chemical shifts δ (A), the predicted δ (B-1), and the difference δ (B-2) = δ (predicted) - δ (observed), the refined predicted δ (C-1), and the difference δ (C-2) = δ (refined predicted) - δ (observed) at C3-C13 of **4c** in CD_3OD in ppm. See the procedure for **4a** in Figure 1 and 2 in the Supporting Information.

4c		C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
Observed δ (A)		23.03	32.95	73.70	76.28	74.55	75.15	74.52	76.20	73.57	35.19	19.88
<div> <div>Prediction</div> <div> <div>C5</div> <div>C6</div> <div>C7</div> <div>C8</div> <div>C9</div> <div>C10</div> <div>C11</div> </div> <div> <div>1b</div> <div>2b</div> <div>3b</div> <div>3b</div> <div>2b</div> <div>1b</div> </div> </div>		23.00	33.25	73.98	76.66	74.93	74.93	74.93	76.61	73.80	35.80	19.80
	Predicted δ (B-1)	23.00	33.25	73.98	76.66	74.93	74.93	74.93	76.61	73.80	35.80	19.80
	δ (B-2)	-0.03	+0.30	+0.28	+0.38	+0.38	-0.22	+0.41	+0.41	+0.23	+0.61	-0.06
	<div> <div>Refinement</div> <div> <div>C5</div> <div>C6</div> <div>C7</div> <div>C8</div> <div>C9</div> <div>C10</div> <div>C11</div> </div> <div> <div>1b</div> <div>2b</div> <div>3b</div> <div>3b</div> <div>2b</div> <div>1b</div> </div> </div>											
	Total refinement	-0.67	-0.43	-0.43	-0.43	-0.02	-0.43	-0.43	-0.43	-0.43	-0.67	
	Correlated refined δ (C-1)	23.00	32.58	73.55	76.23	74.50	74.91	74.50	76.18	73.37	35.13	19.80
	δ (C-2)	-0.03	-0.37	-0.15	-0.05	-0.05	-0.24	-0.02	-0.02	-0.20	-0.06	-0.06

Table 47. The observed ^{13}C chemical shifts δ (A), the predicted δ (B-1), and the difference δ (B-2) = δ (predicted) - δ (observed), the refined predicted δ (C-1), and the difference δ (C-2) = δ (refined predicted) - δ (observed) at C3-C13 of **4d** in CD_3OD in ppm. See the procedure for **4a** in Figure 1 and 2 in the Supporting Information.

4d		C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
Observed δ (A)		23.09	33.02	73.74	77.28	73.96	72.26	72.57	75.22	73.96	35.19	19.87
<div> <div>Prediction</div> <div> <div>C5</div> <div>C6</div> <div>C7</div> <div>C8</div> <div>C9</div> <div>C10</div> <div>C11</div> </div> <div> <div>1b</div> <div>2b</div> <div>3n</div> <div>3p</div> <div>3o</div> <div>2g</div> <div>1b</div> </div> </div>		23.00	33.25	73.98	76.66	74.05	72.36	72.35	75.26	73.80	35.80	19.80
	Predicted δ (B-1)	23.00	33.25	73.98	76.66	74.05	72.36	72.35	75.26	73.80	35.80	19.80
	δ (B-2)	-0.09	+0.23	+0.23	-0.62	+0.09	+0.10	-0.22	+0.04	-0.16	+0.61	-0.07
	<div> <div>Refinement</div> <div> <div>C5</div> <div>C6</div> <div>C7</div> <div>C8</div> <div>C9</div> <div>C10</div> <div>C11</div> </div> <div> <div>1b</div> <div>2b</div> <div>3n</div> <div>3p</div> <div>3o</div> <div>2g</div> <div>1b</div> </div> </div>											
	Total refinement	-0.67	-0.02	+0.66	-0.44	-0.10	+0.40	-0.44	+0.26	-0.53		
	Correlated refined δ (C-1)	23.00	32.58	73.96	77.32	73.61	72.26	72.75	74.82	74.06	35.27	19.80
	δ (C-2)	-0.09	-0.44	+0.22	+0.04	-0.35	0.00	+0.18	-0.40	+0.10	+0.08	-0.07

Protocol for Predicting ^1H NMR Profile of 4a at the First Order of Approximation, cf., Graphs 11 and 12 in the Text.

Figure 3. A protocol for predicting the ^1H chemical shift profiles for 4a at the first order of approximation. Structural correlation of 4a with the corresponding isomer of 1~3 and the observed δ and the predicted δ in CD_3OD with proton number are shown in ppm. The ^1H chemical shift profiles for 4b~d are predicted in the same protocol. See Table 53~55.

Protocol used for Refinement of ^1H δ Profiles for **4a** with δ given in Tables 30 and 40 in the Supporting Information, cf., Graph 13 in the Text.

Figure 4. A protocol for refinement of predicted ^1H chemical shifts for **4a** with δ -effects in Table 30 and 40. Structural correlation of **4a** with the corresponding comparison of **1~3** and the predicted δ and the refinement in CD_3OD with proton number are shown in ppm. The refinements for **4b~d** are represented in the same protocol. See Table 48~51.

^{13}C δ Profiles predicted at the First Order of Approximation and their Refinements with Incorporation of α -Effect (Tables 30 and 40) for 4a~d, cf., Figures 3 and 4 in the Supporting Information and Graphs 11~13 in the Text.

Table 48. The observed ^1H chemical shifts δ (A), the predicted δ (B-1), and the difference $\delta\delta$ (B-2) $=\delta(\text{predicted})-\delta(\text{observed})$, the refined predicted δ (C-1), and the difference δ (C-2) $=\delta(\text{refined predicted})-\delta(\text{observed})$ at H5-H11 of **4a** in CD_3OD in ppm. See the procedure for **4a** in Figure 3 and 4

4a		H5	H6	H7	H8	H9	H10	H11	
Observed (A)		3.72	3.59	3.99	3.90	3.79	3.63	3.76	
<div><div>Prediction</div><div><div>C5</div><div>C6</div><div>C7</div><div>C8</div><div>C9</div><div>C10</div><div>C11</div></div><div><div>1a</div><div>2a</div><div>3e</div><div>3g</div><div>3m</div><div>2b</div><div>1b</div></div></div>		3.64							
			3.49						
				3.95					
					3.67				
						3.75			
							3.50		
								3.59	
Predicted (B-1)		3.64	3.49	3.95	3.67	3.75	3.50	3.59	
(B-2)		-0.08	-0.10	-0.04	-0.23	-0.04	-0.13	-0.17	
Refinement									
<div><div>C5</div><div>C6</div><div>C7</div><div>C8</div><div>C9</div><div>C10</div><div>C11</div></div>		+0.06							
			+0.04						
				+0.01					
					+0.18				
					+0.09				
						+0.01			
Total refinement		+0.06	+0.04	+0.01	+0.27	+0.01	+0.11	+0.14	
Refined predicted (C-1)		3.70	3.53	3.96	3.94	3.76	3.61	3.73	
(C-2)		-0.02	-0.06	-0.03	+0.04	-0.03	-0.02	-0.03	

Table 49. The observed ^1H chemical shifts δ (A), the predicted δ (B-1), and the difference $\delta\delta$ (B-2) $=\delta(\text{predicted})-\delta(\text{observed})$, the refined predicted δ (C-1), and the difference δ (C-2) $=\delta(\text{refined predicted})-\delta(\text{observed})$ at H5-H11 of **4b** in CD_3OD in ppm. See the procedure for **4a** in Figure 3 and 4

4b		H5	H6	H7	H8	H9	H10	H11	
		<div></div>	<div></div>	<div></div>	<div></div>	<div></div>	<div></div>	<div></div>	
Observed δ (A)		3.72	3.55	3.82	4.00	3.75	3.60	3.72	
<div><div><div>Prediction</div><div>C5C6C7C8C9C10C11</div><div>1a2a3a3e3g2g1b</div></div></div>		3.64	3.49	3.76	3.95	3.67	3.57	3.59	
		Predicted δ (B-1)	3.64	3.49	3.76	3.95	3.67	3.57	3.59
		$\delta\delta$ (B-2)	-0.08	-0.06	-0.06	-0.05	-0.08	-0.03	-0.13
		Refinement							
			+0.06	+0.05	+0.04	+0.01	+0.05	+0.09	+0.01
									+0.11
Total refinement		+0.06	+0.05	+0.04	+0.06	+0.09	+0.01	+0.11	
Refined predicted δ (C-1)		3.70	3.54	3.80	4.01	3.76	3.58	3.71	
$\delta\delta$ (C-2)		-0.02	-0.01	-0.02	+0.01	+0.01	+0.02	-0.01	

Table 50. The observed ^1H chemical shifts δ (A), the predicted δ (B-1), and the difference $\delta\delta$ (B-2) $=\delta(\text{predicted})-\delta(\text{observed})$, the refined predicted δ (C-1), and the difference $\delta\delta$ (C-2) $=\delta(\text{refined predicted})-\delta(\text{observed})$ at C4-C12 of **4c** in CD_3OD in ppm. See the procedure for **4a** in Figure 3 and 4

4c		H5	H6	H7	H8	H9	H10	H11
		δ	δ	δ	δ	δ	δ	δ
Observed δ (A)		3.75	3.68	3.88	4.00	3.88	3.68	3.75
Prediction								
C5		3.59						
C6			3.50					
C7				3.74				
C8					3.74			
C9						3.74		
C10							3.50	
C11								3.59
1b								
2b								
3b								
3b								
2b								
1b								
Predicted δ (B-1)		3.59	3.50	3.74	3.74	3.74	3.50	3.59
$\delta\delta$ (B-2)		-0.16	-0.18	-0.14	-0.26	-0.14	-0.18	-0.16
Refinement								
C5		+0.14						
C6			+0.13					
C7				+0.13				
C8					+0.13			
C9					+0.13			
C10						+0.13		
C11							+0.13	
Total refinement		+0.14	+0.13	+0.13	+0.26	+0.13	+0.13	+0.14
Refined predicted δ (C-1)		3.73	3.63	3.87	4.00	3.87	3.63	3.73
$\delta\delta$ (C-2)		-0.02	-0.05	-0.01	0.00	-0.01	-0.05	-0.02

Table 51. The observed ^1H chemical shifts δ (A), the predicted δ (B-1), and the difference $\delta\delta$ (B-2) $=\delta(\text{predicted})-\delta(\text{observed})$, the refined predicted δ (C-1), and the difference $\delta\delta$ (C-2) $=\delta(\text{refined predicted})-\delta(\text{observed})$ at C4-C12 of **4c** in CD_3OD in ppm. See the procedure for **4a** in Figure 3 and 4

4d		C5	C6	C7	C8	C9	C10	C11
		δ	δ	δ	δ	δ	δ	δ
Observed δ (A)		3.76	3.64	3.77	4.04	3.91	3.60	3.73
Prediction								
C5		3.59						
C6			3.50					
C7				3.75				
C8					3.89			
C9						3.89		
C10							3.57	
C11								3.59
1b								
2b								
3n								
3p								
3o								
2g								
1b								
Predicted δ (B-1)		3.59	3.50	3.75	3.89	3.89	3.57	3.59
$\delta\delta$ (B-2)		-0.17	-0.14	-0.02	-0.16	-0.02	-0.04	-0.14
Refinement								
C5		+0.14						
C6			+0.11					
C7				0.00				
C8					-0.01			
C9					+0.18			
C10						-0.01		
C11							0.00	
Total refinement		+0.14	+0.11	0.00	+0.17	-0.01	0.00	+0.11
Refined predicted δ (C-1)		3.73	3.61	3.75	4.06	3.88	3.57	3.70
$\delta\delta$ (C-2)		-0.03	-0.03	-0.02	+0.02	-0.03	-0.03	-0.03

Sub-grouped Internal and Terminal $^3J_{H,H}$ of Pentaols **3a-p in Tables 20, 25, and 26 in the Supporting Information, cf., Graphs 14 and 15 in the Text.**

Table 52. The observed internal $^3J_{H,H}$'s of pentaols **3a-p** in Hz.

		CD ₃ OD		D ₂ O		C ₅ D ₅ N	
	3a-p	$^3J_{H6,H7}$	$^3J_{H8,H7}$	$^3J_{H6,H7}$	$^3J_{H8,H7}$	$^3J_{H6,H7}$	$^3J_{H8,H7}$
SSS	SSSS	4.5	4.5	4.5	4.5	4.0	4.0
	SSSA	5.0	5.0	5.5	6.0	-	4.0
ASS	ASSS	2.0	2.0	3.0	3.0	1.5	-
	ASSA	2.5	2.5	4.0	4.0	2.0	2.0
SSA	SSAS	1.5	1.5	1.5	1.5	-	0.0
	SSAA	-	-	1.5	1.5	1.5	-
ASA	ASAS	1.0	1.0	1.0	1.0	0.0	-
	ASAA	0.0	0.0	1.0	1.0	1.0	0.0
SAS	SASS	8.5	8.5	9.0	9.0	8.5	9.0
	SASA	8.5	9.0	9.0	9.5	-	9.0
AAS	AASS	7.5	7.5	8.5	8.5	-	7.5
	AASA	8.0	7.5	9.0	9.0	7.5	7.5
SAA	SAAS	7.0	7.0	7.0	7.0	7.0	7.0
	SAAA	7.0	6.5	6.5	7.0	7.0	6.5
AAA	AAAS	6.0	6.0	6.5	6.5	7.0	7.0
	AAAA	6.0	6.0	6.0	6.0	6.0	6.0

Table 53. The observed terminal $^3J_{H,H}$'s of pentaols **3a-p** in Hz

		CD ₃ OD		D ₂ O		C ₅ D ₅ N	
	3a-p	$^3J_{H5,H6}$	$^3J_{H8,H9}$	$^3J_{H5,H6}$	$^3J_{H8,H9}$	$^3J_{H5,H6}$	$^3J_{H8,H9}$
SSA	SSAS	5.5	5.0	7.0	6.5	-	5.5
	SSAA	-	-	6.5	6.5	4.5	4.5
SSS	SSSS	4.0	4.0	4.5	4.5	4.0	4.0
	SSSA	3.5	3.5	4.0	4.0	-	4.0
SAA	SAAS	1.5	1.5	2.0	2.0	1.0	1.0
	SAAA	1.5	1.5	2.0	2.0	1.5	-
SAS	SASS	1.5	1.5	1.0	1.5	-	1.0
	SASA	2.0	2.0	1.5	1.5	-	2.0
ASA	ASAS	8.0	8.0	8.5	8.5	7.0	-
	ASAA	8.0	8.0	8.5	8.5	7.5	7.5
ASS	ASSS	8.0	7.5	7.5	7.0	7.5	-
	ASSA	7.0	7.0	7.5	7.0	7.0	7.0
AAA	AAAS	6.0	6.0	5.5	5.5	6.5	6.0
	AAAA	6.0	6.0	6.0	6.0	6.0	6.0
AAS	AASS	6.0	6.0	4.0	4.5	-	6.5
	AASA	6.0	6.0	4.5	4.5	6.5	7.0

Prediction of the Stereochemistry of 4a~d with Comparison of their $^3J_{H,H}$'s with the Sub-grouped $^3J_{H,H}$ Profiles in Table 3, Graphs 14 and 15 given in the Text, cf., Tables 43, 52, and 53 in the Supporting Information.

Graph 12. Prediction of the relative stereochemistry of **4a~d** with the sub-grouped, internal and terminal $^3J_{H,H}$'s of pentaols **3a~p**. The squared assignments next to each plot show the assignment of the sub-group for each observed $^3J_{H,H}$ with the adjacent glycols for internal $^3J_{H,H}$ and the adjacent and next glycols for terminal $^3J_{H,H}$. The x axis gives the observed $^3J_{H,H}$'s. The y axis represents proton number of **4a~d**. ● and ○ represent the *syn* and *anti* stereochemistry, respectively.

2D-Representation of the Internal and Terminal pairs of $^3J_{H,H}$ observed for pentaols **3a~p in CD₃OD, pyridine-*d*₅, and D₂O, cf., Table 16 in the Text.**

Graph 13. 2D-Representation of the internal (left graph) and terminal (right graph) $^3J_{H,H}$'s observed for pentaols **3a~p** in (A) CD₃OD, (B) C₅D₅N, and (D₂O). The x and y axes represent the two contiguous $^3J_{H,H}$'s indicated by arrows, with abbreviation of S=*syn* and A=*anti*. The Data are plotted for C₅D₅N by ignoring the difference at the termini.

Prediction of the Stereochemistry for 4a~d with 2D $^3J_{\text{H,H}}$ Profiles in Graph 15 in the Supporting Information, cf., Graphs 16 and 17 in the Text.

Graph 14. Prediction of the relative stereochemistry of 4a~d by plotting the observed, two contiguous $^3J_{\text{H,H}}$'s on the internal (A) and terminal (B) 2D-panels. The x and y axes represent $^3J_{\text{H,H}}$'s, with abbreviations of A=anti, S=syn. The filled circle gives the two contiguous $^3J_{\text{H,H}}$'s observed on 4a~d, with indications of the position and stereochemistry; for example, 5/6/7 (S/S) represents $^3J_{5,6}$ / $^3J_{6,7}$ (the relative configuration at 5/6 and 6/7 = syn and syn).

3D $^3J_{\text{H,H}}$ Profiles Created by Using the $^3J_{\text{H,H}}$'s Observed for Pentaols 3a~p in CD₃OD, cf., Graph 18 in the Text and Graph 15 in the Supporting Information.

Table 54. Calculation for $^3J_{\text{H,H}}$ profiles composed of three contiguous $^3J_{\text{H,H}}$ in CD₃OD by using the $^3J_{\text{H,H}}$'s observed for pentaols 3a~p

SSS(S)					SSS(A)				AAA								
C5□ C8	3a	SSSS	4.0	4.5	4.5	3e	SSSA	3.5	5.0	2.0	3b	AAAA	6.0	6.0	6.0		
C8□ C5	3a	SSSS	4.5	4.5	4.0	3e	ASSS	2.0	5.0	3.5	3b	AAAA	6.0	6.0	6.0		
C6□ C9	3a	SSSS	4.5	4.5	4.0	3f	ASSS	2.0	5.0	3.5	3b	AAAA	6.0	6.0	6.0		
C9□ C6	3a	SSSS	4.0	4.5	4.5	3f	SSSA	3.5	5.0	2.0	3b	AAAA	6.0	6.0	6.0		
C5□ C8											3n	AAAS	6.0	6.0	6.5		
C8□ C5											3n	SAAA	6.5	6.0	6.0		
C6□ C9											3m	SAAA	7.0	6.5	6.0		
C9□ C6											3m	AAAS	6.0	6.5	7.0		
Average			4.25	4.5	4.25	Average			2.75	5.0	2.75	Average			6.19	6.13	6.19

SAS					ASA				ASS(S)								
C5□ C8	3j	SASS	1.5	8.5	1.5	3l	ASAS	8.0	1.0	9.0	3f	ASSS	8.0	2.0	5.0		
C8□ C5	3j	SSAS	1.5	8.5	1.5	3l	SASA	9.0	1.0	8.0	3i	SASS	8.5	1.5	5.5		
C6□ C9	3i	SSAS	1.5	8.5	1.5	3k	SASA	8.5	1.0	8.0	3h	AASS	7.5	-	-		
C9□ C6	3i	SASS	1.5	8.5	1.5	3k	ASAS	8.0	1.0	8.5	3e	ASSS	7.5	2.0	5.0		
C5□ C8	3k	SASA	2.0	8.5	1.0	3o	ASAA	8.0	0	7.5							
C8□ C5	3k	ASAS	1.0	8.5	2.0	3o	AASA	7.5	0	8.0	3g	AASS	7.5	-	-		
C6□ C9	3l	ASAS	1.0	9.0	2.0	3p	AASA	8.0	0	8.0	3j	SASS	8.5	1.5	5.0		
C9□ C6	3l	SASA	2.0	9.0	1.0	3p	ASAA	8.0	0	8.0							
Average			1.5	8.63	1.5	Average			8.13	0.5	8.13	Average			7.92	1.75	5.13

ASS(A)					AAS				(A)SSA								
C5□ C8	3c	ASSA	7.0	2.5	2.5	3h	AASS	6.0	7.5	1.5	3i	SSAS	5.5	1.5	8.5		
C8□ C5	3c	ASSA	7.0	2.5	2.5	3d	SAAS	7.0	7.0	1.5	3f	SSSA	5.0	2.0	8.0		
C6□ C9						3d	SAAS	7.0	7.0	1.5	3e	SSSA	5.0	2.0	7.5		
C9□ C6						3g	AASS	6.0	7.5	1.5	3h	SSAA	-	-	7.5		
C5□ C8						3p	AASA	6.0	8.0	0	3g	SSAA	-	-	7.5		
C8□ C5						3m	AAAS	6.5	7.0	1.5							
C6□ C9						3n	AAAS	6.0	6.5	1.5							
C9□ C6						3o	AASA	6.0	7.5	0	3j	SSAS	5.0	1.5	8.5		
Average			7.0	2.5	2.5	Average			6.31	7.25	1.13	Average			5.13	1.75	7.92

(A)SSA					SAA						
C5□ C8					3d	SAAS	1.5	7.0	7.0		
C8□ C5					3d	SAAS	1.5	7.0	7.0		
C6□ C9	3c	ASSA	2.5	2.5	7.0	3g	SSAA	1.5	7.5	6.0	
C9□ C6						3h	SSAA	1.5	7.5	6.0	
C5□ C8						3m	SAAA	1.5	7.0	6.5	
C8□ C5	3c	ASSA	2.5	2.5	7.0	3p	ASAA	0	8.0	6.0	
C6□ C9						3o	ASAA	0	7.5	6.0	
C9□ C6						3n	SAAA	1.5	6.5	6.0	
Average			2.5	2.5	7.0	Average			1.13	7.25	6.31

3D $^3J_{\text{H,H}}$ Profiles Created by Using the $^3J_{\text{H,H}}$'s Observed for Pentaols 3a~p in $\text{C}_5\text{D}_5\text{N}$, cf., Graph 18 in the Text and Graph 15 in the Supporting Information.

Table 55. Calculation for $^3J_{\text{H,H}}$ profiles composed of three contiguous $^3J_{\text{H,H}}$ in $\text{C}_5\text{D}_5\text{N}$ by using the $^3J_{\text{H,H}}$'s observed for pentaols 3a~p

SSS(S)					SSS(A)				AAA								
C5□ C8	3a	SSSS	4.0	4.0	4.0	3e	SSSA	-	-	-	3b	AAAA	6.0	6.0	6.0		
C8□ C5	3a	SSSS	4.0	4.0	4.0	3e	ASSS	-	-	-	3b	AAAA	6.0	6.0	6.0		
C6□ C9	3a	SSSS	4.0	4.0	4.0	3f	ASSS	1.5	4.0	4.0	3b	AAAA	6.0	6.0	6.0		
C9□ C6	3a	SSSS	4.0	4.0	4.0	3f	SSSA	4.0	4.0	1.5	3b	AAAA	6.0	6.0	6.0		
C5□ C8											3n	AAAS	6.5	7.0	6.5		
C8□ C5											3n	SAAA	6.5	7.0	6.5		
C6□ C9											3m	SAAA	7.0	7.0	6.0		
C9□ C6											3m	AAAS	6.0	7.0	7.0		
Average			4.0	4.0	4.0	Average			2.75	4.0	2.75	Average			6.25	6.5	6.25

SAS					ASA				ASS(S)								
C5□ C8	3j	SASS	-	8.5	0	3l	ASAS	7.0	0	9.0	3f	ASSS	7.5	1.5	4		
C8□ C5	3j	SSAS	0	8.5	-	3l	SASA	9.0	0	7.0	3i	SASS	9.0	-	-		
C6□ C9	3i	SSAS	-	9.0	1.0	3k	SASA	-	-	-	3h	AASS	-	-	4.5		
C9□ C6	3i	SASS	1.0	9.0	-	3k	ASAS	-	-	-	3e	ASSS	-	-	-		
C5□ C8	3k	SASA	-	-	-	3o	ASAA	7.5	1.0	7.5							
C8□ C5	3k	ASAS	-	-	-	3o	AASA	7.5	1.0	7.5	3g	AASS	7.5	1.5	4.5		
C6□ C9	3l	ASAS	0	9.0	2.0	3p	AASA	7.5	0	7.5	3j	SASS	8.5	0	5.5		
C9□ C6	3l	SASA	2.0	9.0	0	3p	ASAA	7.5	0	7.5							
Average			0.75	8.83	0.75	Average			7.67	0.33	7.67	Average			8.13	1.0	4.63

ASS(A)					AAS				(S)SSA								
C5□ C8	3c	ASSA	7.0	2.0	2.0	3h	AASS	-	-	-	3i	SSAS	-	-	9.0		
C8□ C5	3c	ASSA	7.0	2.0	2.0	3d	SAAS	7.0	7.0	1.0	3f	SSSA	4.0	1.5	7.5		
C6□ C9						3d	SAAS	7.0	7.0	1.0	3e	SSSA	-	-	-		
C9□ C6						3g	AASS	6.5	7.5	1.5	3h	SSAA	-	-	-		
C5□ C8						3p	AASA	6.5	7.5	0	3g	SSAA	4.5	1.5	7.5		
C8□ C5						3m	AAAS	7.0	7.0	1.5							
C6□ C9						3n	AAAS	7.0	6.5	-							
C9□ C6						3o	AASA	7.0	7.5	1.0	3j	SSAS	5.5	0	8.5		
Average			7.0	2.0	2.0	Average			6.86	7.14	1.0	Average			4.67	1.0	8.13

(A)SSA					SAA						
C5□ C8					3d	SAAS	1.0	7.0	7.0		
C8□ C5					3d	SAAS	1.0	7.0	7.0		
C6□ C9	3c	ASSA	2.0	2.0	7.0	3g	SSAA	1.5	7.5	6.5	
C9□ C6						3h	SSAA	-	-	-	
C5□ C8						3m	SAAA	1.5	7.0	7.0	
C8□ C5	3c	ASSA	2.0	2.0	7.0	3p	ASAA	0	7.5	6.5	
C6□ C9						3o	ASAA	1.0	7.5	7.0	
C9□ C6						3n	SAAA	-	6.5	7.0	
Average			2.0	2.0	7.0	Average			1.0	7.14	6.86

$3D\ ^3J_{H,H}$ Profiles Created by Using the $^3J_{H,H}$'s Observed for Pentaols 3a~p in D₂O, cf., Graph 18 in the Text and Graph 15 in the Supporting Information.

Table 56. Calculation for $^3J_{H,H}$ profiles composed of three contiguous $^3J_{H,H}$ in D₂O by using the $^3J_{H,H}$'s observed for pentaols 3a~p

SSS(S)					SSS(A)				AAA			
C5□ C8	3a SSSS	4.5	4.5	4.5	3e SSSA	4.0	5.5	3.0	3b AAAA	6.0	6.0	6.0
C8□ C5	3a SSSS	4.5	4.5	4.5	3e ASSS	3.0	5.5	4.0	3b AAAA	6.0	6.0	6.0
C6□ C9	3a SSSS	4.5	4.5	4.5	3f ASSS	3.0	6.0	4.0	3b AAAA	6.0	6.0	6.0
C9□ C6	3a SSSS	4.5	4.5	4.5	3f SSSA	4.0	6.0	3.0	3b AAAA	6.0	6.0	6.0
C5□ C8									3n AAAS	5.0	6.5	7.0
C8□ C5									3n SAAA	7.0	6.5	5.0
C6□ C9									3m SAAA	6.5	6.5	5.5
C9□ C6									3m AAAS	5.5	6.5	6.5
Average		4.5	4.5	4.5	Average	3.5	5.75	3.5	Average	6.0	6.25	6.0

SAS					ASA				ASS(S)			
C5□ C8	3j SASS	1.0	9.0	1.5	3l ASAS	8.5	1.0	9.5	3f ASSS	7.5	3.0	6.0
C8□ C5	3j SSAS	1.5	9.0	1.0	3l SASA	9.5	1.0	8.5	3i SASS	9.0	1.5	7.0
C6□ C9	3i SSAS	1.5	9.0	1.5	3k SASA	9.0	1.0	8.5	3h AASS	8.5	1.5	6.5
C9□ C6	3i SASS	1.5	9.0	1.5	3k ASAS	8.5	1.0	9.0	3e ASSS	7.0	3.0	5.5
C5□ C8	3k SASA	1.5	9.0	1.5	3o ASAA	8.5	1.0	9.0				
C8□ C5	3k ASAS	1.5	9.0	1.5	3o AASA	9.0	1.0	8.5	3g AASS	8.5	1.5	6.5
C6□ C9	3l ASAS	1.0	9.5	1.5	3p AASA	9.0	1.0	8.5	3j SASS	9.0	1.5	6.5
C9□ C6	3l SASA	1.5	9.0	1.0	3p ASAA	8.5	1.0	9.0				
Average		1.38	9.06	1.38	Average	8.81	1.0	8.81	Average	8.25	2.00	6.33

ASS(A)					AAS				Terminal AAS			
C5□ C8	3c ASSA	7.0	4.0	4.0	3h AASS				3h AASS	4.0	8.5	1.5
C8□ C5	3c ASSA	7.0	4.0	4.0	3d SAAS	7.0	7.0	2.0				
C6□ C9					3d SAAS	7.0	7.0	2.0				
C9□ C6					3g AASS				3g AASS	4.5	8.5	1.5
C5□ C8					3p AASA				3p AASA	4.5	9.0	1.0
C8□ C5					3m AAAS	6.5	6.5	2.0				
C6□ C9					3n AAAS	6.5	7.0	2.0				
C9□ C6					3o AASA				3o AASA	4.5	9.0	1.0
Average		7.0	4.0	4.0	Average	6.75	6.88	2.0	Ave.	4.38	8.75	1.25

(S)SSA					(A)SSA				SAA			
C5□ C8	3i SSAS	7.0	1.5	9.0					3d SAAS	2.0	7.0	7.0
C8□ C5	3f SSSA	6.0	3.0	7.5					3d SAAS	2.0	7.0	7.0
C6□ C9	3e SSSA	5.5	3.0	7.0	3c ASSA	4.0	4.0	7.0				
C9□ C6	3h SSAA	6.5	1.5	8.5								
C5□ C8	3g SSAA	6.5	1.5	8.5					3m SAAA	2.0	6.5	6.5
C8□ C5					3c ASSA	4.0	4.0	7.0				
C6□ C9												
C9□ C6	3j SSAS	6.5	1.5	9.0					3n SAAA	2.0	7.0	6.5
Ave.		6.33	2.0	8.25	Ave.	4.0	4.0	7.0	Ave.	2.0	6.88	6.75

SAAterminal				
C5□ C8				
C8□ C5				
C6□ C9	3g SSAA	1.5	8.5	4.5
C9□ C6	3h SSAA	1.5	8.5	4.0
C5□ C8				
C8□ C5	3p ASAA	1.0	9.0	4.5
C6□ C9	3o ASAA	1.0	9.0	4.5
C9□ C6				
Ave.		1.25	8.75	4.38

3D $^3J_{H,H}$ Profiles, cf., Graph 18 in the Text.

Graph 15. The $^3J_{H,H}$ profiles composed of three contiguous spin-coupling constants in (A) CD_3OD , (B) C_5D_5N , and (C) D_2O . The x and y axes represent proton number and $^3J_{H,H}$'s, with abbreviation of A=*anti* and S=*syn*.

Prediction of the Stereochemistry of 4a~d with Three Contiguous $^3J_{H,H}$ Profiles, cf., Graph 19 in the Text.

Graph 16. Comparisons of the $^3J_{H,H}$ profiles. The $^3J_{H,H}$ profiles of 4a~d are dissected into the four small $^3J_{H,H}$ profiles and each of them is compared with the $^3J_{H,H}$ profiles composed of three contiguous spin-coupling constants. The x and y axes represent proton number and $^3J_{H,H}$ constant, with indication of their relative stereochemistry, i.e., A=*anti* and S=*syn*.

100 MHz ^{13}C NMR spectrum of 4a in CD_3OD

500 MHz ^1H NMR spectrum of 4a in CD_3OD

100 MHz ^{13}C NMR spectrum of 4b in CD_3OD

500 MHz ^1H NMR spectrum of 4b in CD_3OD

100 MHz ^{13}C NMR spectrum of 4c in CD_3OD

500 MHz ^1H NMR spectrum of 4c in CD_3OD

100 MHz ^{13}C NMR spectrum of 4d in CD_3OD

500 MHz ^1H NMR spectrum of 4d in CD_3OD