Supporting Information

Assigning the Stereochemistry of Pairs of Diastereoisomers Using GIAO NMR Shift Calculation

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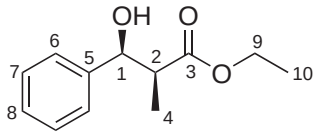
S-1 Complete ref. 48

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision D.01*, Gaussian, Inc., Wallingford, CT, 2004.

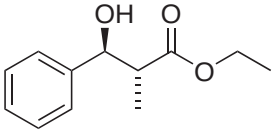
S-2 Calculated and experimental shifts

All calculated shifts were obtained as described in Computational Methods (Eq. 3 and Eq. 4). The older version of the software (see Computational Methods) was used for structures **1**–**7** and the newer version for **8**–**13**. The values of σ^{o} used in Eq. 4 were 191.561 ppm (^{13}C) and 31.752 ppm (^{1}H) for the older version, and 191.563 ppm (^{13}C) and 31.752 ppm (^{1}H) for the newer version; these values were obtained in B3LYP/6-31G(d,p) calculations on TMS.

All experimental shifts were taken from the references given in Fig. 1. Assignments of the experimental shifts were taken from these references and/or made using the reported multiplicities and intensities, and where assignment was incomplete the experimental shifts have been matched up in order with the calculated shifts for the corresponding structure. (Note that when comparing the experimental data with the alternative structure to decide which gave the best match, these resonances were re-assigned as required by matching up with the calculated shifts of the alternative structure). Not all of the shifts listed here were used for the calculations as explained in the Molecules Studied section.



1a



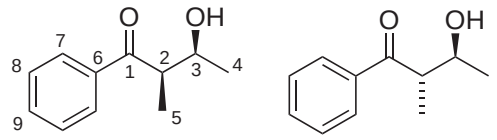
1b

Table S1: Calculated and experimental shifts (in ppm) for aldols **1**

Position	^{13}C calculated		^{13}C experimental	
	1a	**1b**	**1A**	**1B**
1	74.26	76.55	73.73	76.12
2	48.45	48.32	46.52	47.08
3	176.85	174.57	175.50	175.67
4	11.67	18.42	10.95*	14.27*
5	138.21	139.59	141.53	141.58
6	121.90	121.50	125.94†	126.53†
7	122.50	122.56	128.05†	128.24†
8	121.06	121.01	127.31	127.77
9	58.83	58.34	60.52	60.56
10	15.63	15.42	13.92*	13.98*

Position	^{1}H calculated		^{1}H experimental	
	1a	**1b**	**1A**	**1B**
1	5.27	4.76	5.09	4.75
2	2.47	2.74	2.77	2.80
4	1.14	1.38	1.12	1.02
6	7.43	7.35	7.22-7.35*	7.25-7.36*
7	7.38	7.34	7.22-7.35*	7.25-7.36*
8	7.23	7.20	7.22-7.35*	7.25-7.36*
9(R)	4.16	3.89	4.12†	4.18†
9(S)	4.16	3.92	4.12†	4.18†
10	1.19	0.91	1.21	1.25

*,† Assignments may be interchanged within each column.



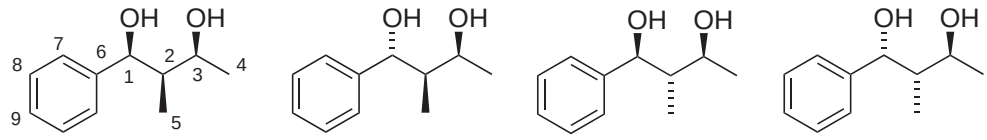
2a **2b**

Table S2: Calculated and experimental shifts (in ppm) for aldols **2**

Position	^{13}C calculated		^{13}C experimental	
	2a	**2b**	**2A**	**2B**
1	203.44	203.01	205.8	205.2
2	46.40	47.09	45.8	47.6
3	68.43	72.65	67.5	69.7
4	20.50	22.78	20.3	20.7
5	13.27	19.28	11.2	15.2
6	129.07	129.54	135.9*	136.4*
7	124.84	124.63	128.7†	128.6†
8	123.87	123.89	128.4†	128.3†
9	127.31	127.40	133.4*	133.2*

Position	^{1}H calculated		^{1}H experimental	
	2a	**2b**	**2A**	**2B**
2	3.04	3.12	3.42	3.51
3	4.35	3.90	4.24	4.14
4	1.11	1.11	1.26	1.31
5	1.40	1.48	1.18	1.26
7	8.13	8.12	7.94	7.99
8	7.54	7.54	7.50-7.56*	7.52-7.58*
9	7.55	7.56	7.50-7.56*	7.52-7.58*

*,† Assignments may be interchanged within each column.



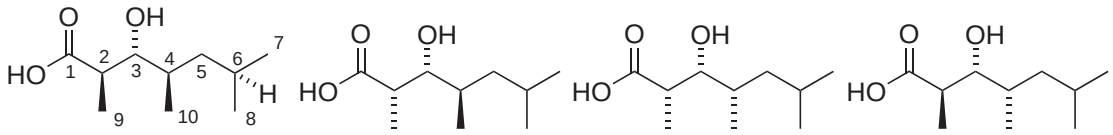
3a **3b** **3c** **3d**

Table S3: Calculated and experimental shifts (in ppm) for diols **3a–d**

Position	^{13}C calculated				^{13}C experimental			
	3a	**3b**	**3c**	**3d**	**3A**	**3B**	**3C**	**3D**
1	79.45	80.33	82.58	75.11	78.5*	77.7*	81.0*	74.7*
2	47.23	46.50	49.75	46.02	45.0*	44.4*	46.1*	45.7*
3	73.36	68.02	73.36	72.61	72.0*	68.9*	73.3*	70.9*
4	23.23	21.00	22.74	22.37	21.5*	18.9*	21.7*	21.9*
5	5.91	15.37	14.50	14.37	4.1*	12.0*	13.3*	11.3*
6	139.85	140.82	139.93	139.28	143.3*	143.7*	143.3*	142.7*
7	121.40	121.54	122.85	121.91	127.0*	126.4*	127.8*	127.0*
8	122.38	122.94	123.23	122.43	128.1*	128.2*	128.3*	128.0*
9	120.84	121.61	122.45	121.07	125.6*	127.6*	127.1*	126.1*

Position	^{1}H calculated				^{1}H experimental			
	3a	**3b**	**3c**	**3d**	**3A**	**3B**	**3C**	**3D**
1	5.31	4.98	4.57	5.45	5.03	4.70	4.54	5.08
2	1.46	1.78	1.71	1.64	1.70	1.95	1.85	1.82
3	4.30	4.15	4.01	4.04	4.22	4.05	3.92	3.80
4	1.10	1.05	1.12	1.28	1.22	1.21	1.26	1.28
5	0.83	1.05	0.46	0.87	0.82	0.82	0.79	0.79
7	7.43	7.49	7.48	7.46	7.40-7.20*	7.40-7.20*	7.40-7.20*	7.42-7.22*
8	7.36	7.40	7.40	7.37	7.40-7.20*	7.40-7.20*	7.40-7.20*	7.42-7.22*
9	7.20	7.27	7.31	7.22	7.40-7.20*	7.40-7.20*	7.40-7.20*	7.42-7.22*

* Assignments may be interchanged within each column.



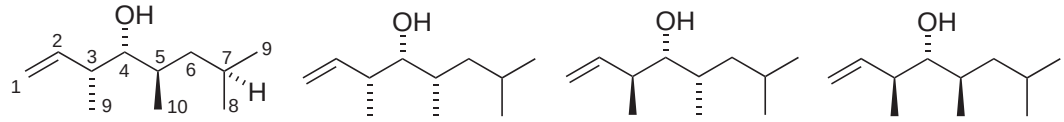
4a **4b** **4c** **4d**

Table S4: Calculated and experimental shifts (in ppm) for aldols **4a–d**

Position	^{13}C calculated				^{13}C experimental			
	4a	**4b**	**4c**	**4d**	**4A**	**4B**	**4C**	**4D**
1	171.69	173.29	173.25	171.52	181.4*	181.9*	181.6*	181.4*
2	40.76	40.43	40.05	41.30	39.4*	41.6*	42.1*	43.1*
3	80.31	77.54	76.56	78.86	78.2*	76.3*	75.6*	75.6*
4	38.33	35.27	35.74	38.07	33.4*	33.5*	33.3*	32.1*
5	43.79	44.18	40.53	42.02	42.3*	41.8*	42.6*	43.2*
6	27.57	27.66	27.06	27.42	25.2*	25.3*	25.0*	25.0*
7	21.25	21.45	25.57	24.92	21.3*	21.3*	23.6*	23.1*
8	24.99	24.76	20.26	20.94	24.3*	24.3*	21.6*	22.2*
9	18.11	11.79	11.72	17.27	16.6*	9.9*	11.1*	14.2*
10	16.09	15.31	16.69	16.31	14.6*	15.7*	14.5*	12.5*

Position	^{1}H calculated				^{1}H experimental			
	4a	**4b**	**4c**	**4d**	**4A**	**4B**	**4C**	**4D**
2	2.73	2.59	2.57	2.70	2.74*	2.74*	2.72*	2.66*
3	3.17	3.72	3.73	3.29	3.48*	3.67*	3.68*	3.61*
4	1.88	1.94	1.85	1.81	1.64*	1.62*	1.66*	1.66*
5(R)	1.82	1.92	1.01	1.07	1.18*	1.49*	1.07*	1.16*
5(S)	1.11	0.98	0.87	1.12	1.15*	1.04*	1.07*	1.24*
6	1.94	2.01	1.94	1.85	1.69*	1.67*	1.66*	1.70*
7	0.84	0.89	0.91	0.89	0.92†	0.85†	0.89†	0.86†
8	0.93	0.94	0.86	0.83	0.95†	0.93†	0.85†	0.85†
9	1.41	1.31	1.29	1.36	1.23†	1.22†	1.22†	1.18†
10	0.78	0.75	1.10	1.05	0.84†	0.85†	0.95†	0.89†

*,† Assignments may be interchanged within each column.



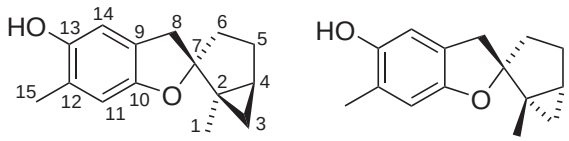
5a **5b** **5c** **5d**

Table S5: Calculated and experimental shifts (in ppm) for octenols **5a–d**

Position	^{13}C calculated				^{13}C experimental			
	5a	**5b**	**5c**	**5d**	**5A**	**5B**	**5C**	**5D**
1	111.67	111.70	113.59	113.39	114.7*	114.6*	116.3*	116.2*
2	138.81	138.34	138.39	136.97	141.8*	141.5*	141.5*	140.7*
3	44.33	45.48	46.40	45.13	40.4*	43.4*	43.6*	41.2*
4	80.02	78.33	77.52	80.53	79.5*	78.2*	79.5*	79.5*
5	36.43	36.32	35.97	37.21	33.3*	32.7*	31.9*	33.0*
6	41.61	43.27	43.38	41.09	40.2*	41.3*	42.0*	39.5*
7	27.66	27.15	27.13	27.40	25.3*	25.0*	25.1*	25.3*
8	21.03	24.34	24.06	20.71	21.3*	23.4*	23.3*	21.3*
9	25.25	21.82	22.19	25.64	24.4*	22.1*	22.2*	24.4*
10	14.80	17.32	17.92	18.30	13.9*	15.5*	16.7*	16.9*
11	16.64	14.54	14.88	16.77	16.5*	13.2*	12.8*	16.8*

Position	^{1}H calculated				^{1}H experimental			
	4a	**4b**	**4c**	**4d**	**4A**	**4B**	**4C**	**4D**
1 (*cis* to H)	5.24	5.21	5.26	5.31	5.07*	5.04	5.13*	5.12*
1 (*trans* to H)	5.38	5.40	5.48	5.43	5.07*	5.07	5.13*	5.12*
2	6.22	6.17	6.14	6.24	5.77*	5.72	5.75*	5.76*
3	2.47	2.42	2.48	2.51	2.41*	2.36*	2.30*	2.37*
4	3.40	3.33	3.40	3.26	3.20*	3.22*	3.16*	3.13*
5	1.95	1.94	1.85	1.72	1.66*	1.72-1.64*	1.67*	1.65*
6(R)	1.61	1.23	1.30	1.46	1.36*	1.18*	1.18*	1.26*
6(S)	1.17	1.21	1.42	1.34	1.36*	1.11*	1.25*	1.13*
7	1.89	1.85	1.90	1.87	1.66*	1.72-1.64*	1.72*	1.65*
8	0.87	0.91	0.91	0.85	0.83†	0.88†	0.87†	0.86†
9	0.94	0.88	0.89	0.94	0.92†	0.86†	0.86†	0.92†
10	1.04	1.09	1.00	1.08	1.03†	1.06†	0.99†	1.00†
11	0.89	0.91	0.98	0.93	0.89†	0.86†	0.89†	0.91†

*,† Assignments may be interchanged within each column.



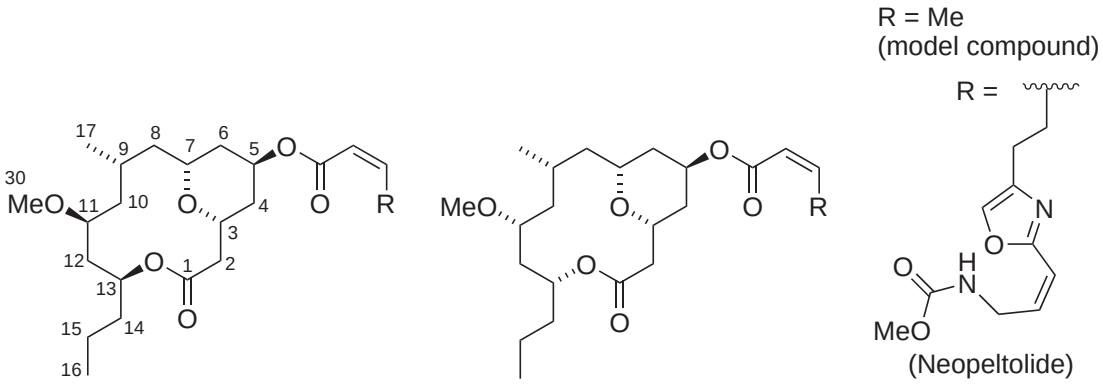
6a **6b**

Table S6: Calculated and experimental shifts (in ppm) for laurentristich-4-ol structures **6a** and **6b**

Position	^{13}C calculated		^{13}C experimental	
	6a	**6b**	**6A**	**6B**
1	17.36	19.17	15.2	16.3*
2	33.29	28.84	31.6	28.0*
3	16.68	18.03	14.5	16.1*
4	26.91	25.00	25.6	24.2*
5	28.69	25.98	26.2	26.9*
6	41.48	37.64	36.6	34.1*
7	96.65	95.49	98.2	97.5*
8	36.22	39.00	36.7	38.5*
9	120.29	119.65	125.6	125.2*
10	144.78	147.01	153.5	153.9*
11	108.77	108.32	111.1	112.0*
12	116.44	117.50	123.8	122.7*
13	141.94	142.44	149.4	147.3*
14	105.68	105.94	112.1	110.5*
15	18.51	17.53	16.5	14.5*

Position	^{1}H calculated		^{1}H experimental	
	6a	**6b**	**6A**	**6B**
1	1.20	1.10	1.06	1.11*
3(R)	0.31	0.90	0.29*	1.00†
3(S)	0.33	0.48	0.45*	0.39†
4	1.03	0.91	1.25	1.18†
5(R)	1.85	1.53	1.98†	1.60-1.77†
5(S)	1.60	2.33	1.64†	1.60-1.77†
6(R)	1.63	2.19	1.85‡	1.60-1.77†
6(S)	1.59	1.19	1.45‡	1.60-1.77†
8(R)	3.64	3.27	3.27$^{\#}$	3.46†
8(S)	3.09	2.73	2.89$^{\#}$	2.76†
11	6.26	6.58	6.41	6.64†
14	6.48	6.26	6.63	6.55†
15	2.05	2.09	2.12	2.19*

*,†,‡,$^{\#}$ Assignments may be interchanged within each column.



7a **7b**

Table S7: Calculated and experimental shifts (in ppm) for neopeltolide structures **7a** and **7b**

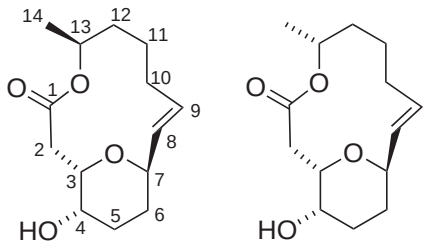
Position	^{13}C calculated		^{13}C experimental	
	7a	**7b**	**7A**	**7B**
1	167.68	169.15	173.0	174.7
2	43.20	43.07	43.2	43.2
3	71.88	72.70	71.3	72.8
4	38.42	39.42	36.2	36.2
5	72.45	72.34	69.2	69.1
6	39.28	39.19	37.4	38.8
7	75.81	75.71	77.0	76.5
8	45.28	46.08	45.2	45.6
9	34.29	38.01	32.6	35.6
10	44.47	46.85	43.5	46.0
11	76.12	83.34	77.1	84.5
12	41.87	44.04	41.0	41.3
13	73.60	72.30	73.9	75.7
14	39.16	40.41	37.9	37.1
15	22.24	21.41	20.0	19.7
16	15.46	15.31	14.1	14.2
17	27.76	27.16	26.0	25.2
30	54.52	55.84	56.4	56.6

(Table S7 continues. . .)

(Table S7 continued)

Position	^{1}H calculated		^{1}H experimental	
	6a	**6b**	**6A**	**6B**
2(R)	2.35	2.10	2.66*	2.26*
2(S)	2.27	2.34	2.26*	2.40*
3	4.47	4.30	4.04	4.02
4(R)	1.32	1.34	1.46†	1.45†
4(S)	1.50	1.57	1.78†	1.79†
5	4.52	4.53	5.17	5.19
6(R)	1.45	1.44	1.64‡	1.69‡
6(S)	1.32	1.34	1.49‡	1.30‡
7	3.91	4.03	3.55	3.69
8(R)	1.15	1.05	1.25$^\#$	1.25$^\#$
8(S)	1.57	1.39	1.36$^\#$	1.36$^\#$
9	1.61	1.58	1.38	1.24
10(R)	1.52	2.48	1.54§	2.28§
10(S)	1.33	1.12	1.08§	1.08§
11	3.67	3.03	3.64	3.23
12(R)	1.23	1.64	1.28¶	1.49¶
12(S)	2.16	1.71	1.83¶	1.83¶
13	5.13	5.26	5.14	5.24
14(R)	2.09	1.34	1.68$^\$$	1.48$^\$$
14(S)	1.53	1.50	1.48$^\$$	1.55$^\$$
15(R)	1.43	1.36	1.33$^\&$	1.33$^\&$
15(S)	1.47	1.35	1.33$^\&$	1.33$^\&$
16	0.98	0.93	0.92	0.92
17	0.97	0.99	0.94	0.94
30	3.20	3.29	3.23	3.30

*,†,‡,$^\#$,§,¶,$^\$$,$^\&$ Assignments may be interchanged within each column.



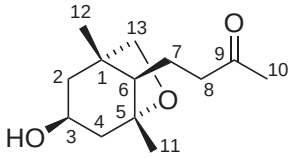
8a **8b**

Table S8: Calculated and experimental shifts (in ppm) for aspergillides A and B (**8a** and **8b**)

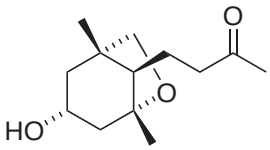
Position	^{13}C calculated		^{13}C experimental	
	8a	**8b**	**8A**	**8B**
1	168.52	169.70	170.1	169.8
2	41.30	41.33	40.5	39.9
3	72.09	72.40	74.0	69.8
4	68.92	68.81	66.7	67.2
5	29.75	29.63	21.7	27.8
6	26.14	25.50	21.9	22.6
7	70.53	70.34	71.3	71.5
8	127.51	125.85	132.1	129.0
9	136.06	135.40	137.0	138.2
10	32.96	35.22	31.0	30.7
11	27.96	29.85	23.6	25.3
12	34.53	35.46	32.1	32.1
13	68.44	72.58	71.5	69.6
14	20.63	22.26	18.5	19.2

Position	^{1}H calculated		^{1}H experimental	
	8a	**8b**	**8A**	**8B**
2(R)	2.19	2.41	2.39*	2.12*
2(S)	2.59	2.51	2.63*	2.71*
3	4.53	4.29	4.23	4.08
4	3.32	3.40	3.58	3.22
5(R)	1.51	1.46	1.71†	1.37†
5(S)	1.66	1.65	1.95†	1.55†
6(R)	2.03	2.04	2.21‡	1.78‡
6(S)	1.14	1.06	1.38‡	0.99‡
7	4.51	4.53	4.21	4.30
8	5.78	5.63	5.79	5.38
9	6.86	7.25	5.69	6.19
10(R)	2.19	2.05	2.28$^{\#}$	1.74$^{\#}$
10(S)	1.95	2.01	2.10$^{\#}$	2.04$^{\#}$
11(R)	1.84	2.03	1.81§	1.52§
11(S)	1.60	1.15	1.50§	1.34§
12(R)	1.94	1.92	1.88¶	1.61¶
12(S)	1.56	1.80	1.49¶	1.31¶
13	4.95	4.58	4.94	5.09
14	1.16	1.19	1.19	1.07

*,†,‡,$^{\#}$,§,¶ Assignments may be interchanged within each column.



9a



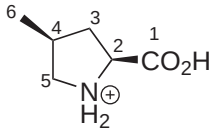
9b

Table S9: Calculated and experimental shifts (in ppm) for tanarifuranonol structures **9a** and **9b**

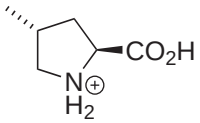
Position	^{13}C calculated		^{13}C experimental	
	9a	**9b**	**9A**	**9B**
1	44.27	44.09	43.0	42.3*
2	41.97	41.76	39.8	42.9†
3	64.88	64.92	66.2	66.3‡
4	43.76	41.15	41.5	39.2†
5	82.83	84.57	83.4	84.7*
6	54.35	54.62	53.6	53.1‡
7	21.80	23.12	18.5	18.6†
8	40.85	41.74	43.0	39.5†
9	202.58	203.51	207.8	208.0#
10	28.99	28.31	30.0	30.0#
11	26.41	26.72	25.4	25.9#
12	23.46	23.08	21.6	21.1#
13	76.82	76.37	77.2	77.0†

Position	^{1}H calculated		^{1}H experimental	
	9a	**9b**	**9A**	**9B**
2(R)	1.65	1.81	1.88*	1.55-1.67*
2(S)	1.40	1.83	1.41*	1.74*
3	4.34	3.84	4.06	3.88*
4(R)	1.90	1.66	1.67†	1.55-1.67*
4(S)	1.32	1.84	1.41†	1.81*
6	1.36	1.37	1.28	1.33*
7(R)	1.82	1.70	1.75‡	1.55-1.67*
7(S)	1.62	1.52	1.58‡	1.36-1.45*
8(R)	2.43	2.38	2.54#	2.51*
8(S)	2.38	2.33	2.54#	2.51*
10	1.99	2.02	2.15	2.13†
11	1.10	1.12	1.23	1.23†
12	0.91	0.86	0.98	0.93†
13(R)	3.59	3.56	3.42§	3.43*
13(S)	3.64	3.95	3.60§	3.92*

*,†,‡,#,§ Assignments may be interchanged within each column.



10a



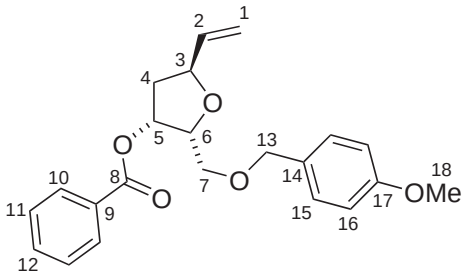
10b

Table S10: Calculated and experimental shifts (in ppm) for *cis* and *trans* methyl proline (**10a** and **10b**)

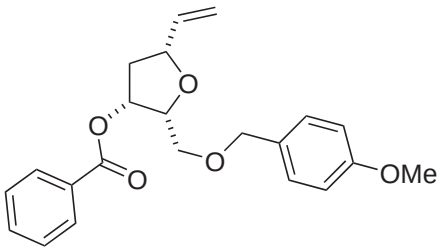
Position	^{13}C calculated		^{13}C experimental	
	10a	**10b**	**10A**	**10B**
1	163.99	164.73	173.0	172.8
2	66.43	65.43	60.7	59.9
3	35.06	35.63	36.9	36.4
4	38.25	36.30	33.7	32.2
5	50.85	51.42	52.7	52.9
6	16.05	15.60	16.4	16.6

Position	^{1}H calculated		^{1}H experimental	
	10a	**10b**	**10A**	**10B**
2	4.50	4.57	4.30	4.38
3(R)	2.07	2.88	1.64*	2.35*
3(S)	2.91	2.21	2.52*	1.94*
4	2.83	2.66	2.38	2.26*
5(R)	3.61	2.93	3.43†	2.83†
5(S)	3.13	3.78	2.87†	3.49†
6	1.44	1.44	0.99	0.99

*,† Assignments may be interchanged within each column.



11a



11b

Table S11: Calculated and experimental shifts (in ppm) for tetrahydrofurans **11**

Position	^{13}C calculated		^{13}C experimental	
	11a	**11b**	**11A**	**11B**
3	78.73	78.76	79.2*	79.3*
4	40.52	39.34	39.8*	39.5*
5	74.20	73.77	75.4*	75.0*
6	80.92	81.52	80.0*	80.7*
7	66.17	66.29	68.2*	68.2*
8	159.60	159.69	165.7*	165.8*
13	71.90	72.18	73.3*	73.3*
17	150.92	150.94	159.2*	159.2*
18	51.95	51.95	55.3*	55.3*
16	109.37	109.25	113.8§	113.8§
1	110.59	109.82	116.3§	116.4§
11	122.89	122.74	128.6§	128.6§
15	124.98	125.00	129.5§	129.5§
9	125.10	125.44	129.7§	129.7§
12	126.14	125.99	130.1§	130.1§
10	126.25	126.47	133.3§	133.3§
14	127.84	127.91	138.2§	138.7§
2	135.65	138.51		

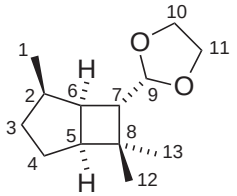
* Assignments may be interchanged within each column.
§ Only eight resonances (unassigned) reported for these nine environments.

(Table S11 continues. . .)

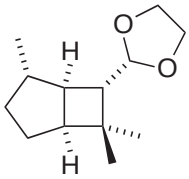
(Table S11 continued)

Position	^{1}H calculated		^{1}H experimental	
	11a	**11b**	**11A**	**11B**
1 (*cis* to H)	5.22	4.94	5.15	5.13
1 (*trans* to H)	5.49	5.22	5.29	5.28
2	6.09	5.94	5.89	5.94
3	4.69	4.57	4.71	4.47
4(R)	2.09	2.02	2.32*	1.92*
4(S)	1.78	2.33	2.07*	2.64*
5	5.45	5.40	5.69	5.60
6	4.57	4.49	4.38	4.17
7(R)	3.53	3.54	3.70†	3.75†
7(S)	3.77	3.79	3.70†	3.75†
10	7.81	7.74	7.99	7.98
11	7.37	7.35	7.44	7.44
12	7.47	7.46	7.82	7.58
13(R)	3.64	3.68	4.36‡	4.38‡
13(S)	4.84	4.82	4.51‡	4.52‡
15	7.30	7.27	6.76	6.77
16	6.41	6.43	7.16	7.18
18	3.07	3.06	3.74	3.75

*,†,‡ Assignments may be interchanged within each column.



12a



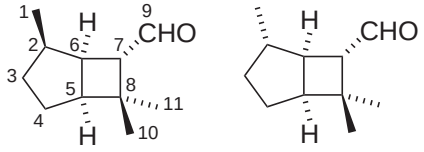
12b

Table S12: Calculated and experimental shifts (in ppm) for acetals **12**

Position	^{13}C calculated		^{13}C experimental	
	12a	**12b**	**12A**	**12B**
1	17.50	20.72	14.4*	19.7*
2	38.55	38.95	36.7*	38.1*
3	34.90	33.29	34.5*	34.0*
4	28.30	25.84	27.1*	24.9*
5	46.25	44.54	44.2*	46.2*
6	42.52	44.32	40.3*	43.0*
7	49.15	53.80	47.2*	49.8*
8	38.23	38.09	34.5*	34.1*
9	106.85	107.37	106.0*	106.1*
10	64.12	64.15	64.9*	64.6*
11	64.10	64.17	64.6*	64.9*
12	25.68	26.00	26.5*	26.3*
13	25.64	25.47	24.4*	24.4*

Position	^{1}H calculated		^{1}H experimental	
	12a	**12b**	**12A**	**12B**
1	0.97	0.82	0.92	0.79
2	1.83	2.00	1.71*	1.92*
3(R)	1.39	1.90	1.32*	1.87*
3(S)	1.57	1.39	1.66*	1.45*
4(R)	1.47	1.71	1.45*	1.65*
4(S)	1.74	1.68	1.68*	1.51*
5	2.18	2.21	2.13*	2.18*
6	2.63	2.37	2.48*	2.23*
7	1.99	1.69	1.81*	1.60*
9	5.35	5.37	4.90*	4.88*
10(R)	3.73	3.72	3.87-3.96*	3.89-3.97*
10(S)	3.65	3.65	3.77-3.83*	3.78-3.85*
11(R)	3.67	3.69	3.77-3.83*	3.78-3.85*
11(S)	3.71	3.70	3.87-3.96*	3.89-3.97*
12	0.91	0.91	0.89†	0.90†
13	1.15	1.13	1.15†	1.14†

*,† Assignments may be interchanged within each column.



13a **13b**

Table S13: Calculated and experimental shifts (in ppm) for aldehydes **13**

Position	^{13}C calculated		^{13}C experimental	
	13a	**13b**	**13A**	**13B**
1	16.31	20.55	13.9*	19.7*
2	38.35	39.81	36.4*	38.1*
3	34.50	33.26	34.2*	33.5*
4	28.36	25.90	27.2*	24.6*
5	45.71	44.20	47.2*	46.5*
6	43.46	43.83	38.8*	40.5*
7	56.37	61.90	53.2*	58.6*
8	41.53	41.35	38.4*	38.1*
9	201.89	202.28	204.3*	204.2*
10	26.38	26.68	27.1*	27.0*
11	26.28	26.48	24.5*	25.0*

Position	^{1}H calculated		^{1}H experimental	
	13a	**13b**	**13A**	**13B**
1	0.89	0.85	0.86	0.82
2	1.90	1.82	1.89*	1.47-1.91*
3(R)	1.39	1.89	1.30*	1.47-1.91*
3(S)	1.65	1.47	1.73*	1.20-1.35*
4(R)	1.56	1.77	1.47-1.58*	1.47-1.91*
4(S)	1.81	1.73	1.79*	1.47-1.91*
5	2.20	2.25	2.15	2.23
6	3.08	2.86	3.01	2.77
7	2.75	2.56	2.43	2.31
9	10.50	10.56	9.79	9.76
10	1.03	1.02	1.07†	1.08†
11	1.10	1.05	1.16†	1.15†

*,† Assignments may be interchanged within each column.

S-3 Expectation values and standard deviations

Expectation values and standard deviations of each of the parameters for both a correct assignment (two structures the right way round) and an incorrect assignment (two structures the wrong way round) obtained from an analysis of the values obtained for all pairs of structures in Fig. 1 are presented in Table S14.

As discussed in the main text, the values in Table S14 are not quite the same as the expectation values and standard deviations used to calculate the probabilities, because for each species values recalculated with the species in question removed from the data set were used.

Table S14: Expectation values and standard deviations of each of the parameters for both a correct assignment (two structures the right way round) and an incorrect assignemt (two structures the wrong way round).

	correl (carbon)	correl (proton)	correl (all)
Correct	0.99913 (0.00046)	0.99103 (0.01010)	0.99760 (0.00170)
Incorrect	0.99840 (0.00095)	0.98464 (0.01386)	0.99575 (0.00246)

	MAE (carbon)	MAE (proton)	MAE (all)
Correct	2.535 (0.604)	0.169 (0.048)	0.649 (0.144)
Incorrect	2.859 (0.759)	0.199 (0.052)	0.749 (0.176)

	CMAE (carbon)	CMAE (proton)	CMAE (all)
Correct	1.535 (0.436)	0.120 (0.058)	0.417 (0.126)
Incorrect	1.922 (0.518)	0.162 (0.068)	0.544 (0.158)

	CP1 (carbon)	CP1 (proton)	CP1 (all)
Correct	0.914 (0.338)	1.167 (0.661)	1.041 (0.401)
Incorrect	−0.324 (0.726)	−0.568 (1.033)	−0.446 (0.668)

	CP2 (carbon)	CP2 (proton)	CP2 (all)
Correct	0.575 (0.226)	0.527 (0.275)	0.551 (0.184)
Incorrect	−0.296 (0.396)	−0.238 (0.457)	−0.267 (0.338)

	CP3 (carbon)	CP3 (proton)	CP3 (all)
Correct	0.547 (0.253)	0.478 (0.305)	0.512 (0.209)
Incorrect	−0.487 (0.533)	−0.786 (0.835)	−0.637 (0.499)

S-4 Coordinates of Structures

Coordinates and energies (DFT, gas phase) are given for the global minimum conformer (according to the DFT gas phase energies) identified for each species.

Table S15. Coordinates (Ångstroms) for aldol **1a**

atom	x	y	z
C1	-5.142998	-1.513805	-0.115922
C2	-6.472720	-2.933430	-3.985874
C3	-5.865451	-1.685897	-3.863132
C4	-5.445776	-1.232392	-2.610784
C5	-5.628850	-2.021300	-1.462691
C6	-6.242507	-3.274985	-1.604772
C7	-6.661926	-3.727513	-2.857313
H8	-6.801690	-3.285991	-4.959664
H9	-5.720555	-1.064474	-4.742938
H10	-4.976122	-0.254025	-2.536805
H11	-6.400916	-3.907037	-0.732798
H12	-7.139015	-4.699694	-2.948640
C13	-3.627369	-1.725001	0.066909
H14	-3.108973	-1.374641	-0.835400
O15	-5.881829	-2.140064	0.936368
H16	-5.641439	-1.665828	1.757275
H17	-5.388739	-0.444445	-0.064341
C18	-3.225664	-3.170167	0.354190
H19	-3.683997	-3.543274	1.276480
H20	-3.512314	-3.834116	-0.466597
H21	-2.140086	-3.251118	0.480443
C22	-3.164625	-0.858743	1.216561
O23	-1.865749	-0.489239	1.042516
O24	-3.862367	-0.551270	2.175570
C25	-1.332945	0.315663	2.101716
H26	-1.910170	1.243131	2.186654
H27	-1.381002	-0.237730	3.046224
C28	0.110742	0.638841	1.770118
H29	0.696058	-0.280139	1.660604
H30	0.176861	1.173861	0.816975
H31	0.562575	1.254393	2.552935

Energy = -692.62129720293 hartree

Table S16. Coordinates (Ångstroms) for aldol **1b**

atom	x	y	z
C1	-3.333787	-0.986227	0.608070
C2	-3.658434	-0.884068	-3.711673
C3	-2.557302	-1.476493	-3.099265
C4	-2.458216	-1.495074	-1.706611
C5	-3.459463	-0.920372	-0.905029
C6	-4.560886	-0.326297	-1.539188
C7	-4.658917	-0.308640	-2.932417
H8	-3.735563	-0.866522	-4.795481
H9	-1.773358	-1.922090	-3.706098
H10	-1.587201	-1.960205	-1.249414
H11	-5.356018	0.132979	-0.955987
H12	-5.517596	0.158595	-3.407790
C13	-3.639005	-2.383123	1.180667
O14	-4.096259	0.038027	1.249610
H15	-5.024950	-0.267832	1.284430
H16	-2.290286	-0.741977	0.846275
C17	-5.074236	-2.758316	0.891206
O18	-5.156937	-4.041672	0.448184
O19	-6.025397	-2.004258	1.064455
C20	-6.487194	-4.470913	0.134837
H21	-7.109666	-4.429292	1.035590
H22	-6.912990	-3.822573	-0.639261
C23	-6.416490	-5.897269	-0.374124
H24	-5.779383	-5.958180	-1.262673
H25	-5.973141	-6.554579	0.381178
H26	-7.412496	-6.271142	-0.627184
H27	-2.982171	-3.116438	0.695010
C28	-3.414721	-2.452560	2.689107
H29	-3.605047	-3.465497	3.060981
H30	-2.382737	-2.188291	2.941443
H31	-4.084432	-1.776863	3.232233

Energy = -692.62199943443 hartree

Table S17. Coordinates (Ångstroms) for aldol **2a**

atom	x	y	z
C1	-4.601224	-3.737673	-2.133118
C2	-5.375661	-2.629726	-1.794032
C3	-4.765641	-1.454246	-1.344402
C4	-3.371899	-1.382533	-1.229809
C5	-2.601954	-2.502247	-1.578993
C6	-3.214173	-3.674493	-2.027174
H7	-5.078600	-4.649635	-2.483713
H8	-6.458535	-2.679910	-1.883655
H9	-5.406888	-0.612470	-1.104097
H10	-1.516193	-2.468642	-1.503558
H11	-2.606465	-4.535651	-2.294376
C12	-2.653762	-0.158111	-0.753334
O13	-1.424553	-0.113092	-0.842933
C14	-3.438382	1.020200	-0.178411
H15	-4.340487	0.638456	0.311365
C16	-2.585408	1.698865	0.916985
H17	-2.181206	0.939144	1.597546
C18	-3.820571	1.963727	-1.318906
H19	-2.935655	2.362665	-1.826616
H20	-4.415273	1.445722	-2.078511
H21	-4.415973	2.806221	-0.955126
O22	-1.475956	2.395812	0.351395
H23	-0.958552	1.723015	-0.141079
C24	-3.383826	2.699863	1.743708
H25	-3.709781	3.552498	1.139343
H26	-4.260984	2.231595	2.200105
H27	-2.757588	3.112475	2.542639

Energy = -578.07292810041 hartree

Table S18. Coordinates (Ångstroms) for aldol **2b**

atom	x	y	z
C1	-4.954914	-3.530115	-1.834243
C2	-5.520748	-2.318365	-2.222565
C3	-4.758146	-1.149298	-2.185425
C4	-3.422900	-1.181201	-1.756209
C5	-2.860929	-2.405117	-1.373258
C6	-3.627407	-3.574240	-1.412078
H7	-5.547661	-4.441275	-1.864762
H8	-6.554829	-2.280900	-2.556590
H9	-5.214509	-0.210123	-2.494207
H10	-1.827767	-2.488289	-1.052061
H11	-3.186136	-4.523345	-1.116047
C12	-2.661713	0.107123	-1.735932
O13	-3.152756	1.100138	-2.277652
C14	-1.293393	0.179734	-1.060481
C15	-1.059675	1.565263	-0.418696
H16	-0.064919	1.567188	0.042860
O17	-1.049591	2.605897	-1.393271
H18	-1.889480	2.528577	-1.895838
C19	-2.074732	1.907388	0.667178
H20	-3.082134	2.032601	0.257664
H21	-2.102208	1.135907	1.442540
H22	-1.814324	2.862253	1.137115
H23	-1.243739	-0.555325	-0.250279
C24	-0.217136	-0.130067	-2.101966
H25	0.781754	-0.075771	-1.656899
H26	-0.344149	-1.135332	-2.516663
H27	-0.255588	0.571398	-2.942708

Energy = -578.07263310745 hartree

Table S19. Coordinates (Ångstroms) for diol **3a**

atom	x	y	z
C1	-4.491090	-1.296634	-2.587221
C2	-3.744088	-0.121500	-2.643127
C3	-2.484631	-0.063831	-2.043991
C4	-1.958107	-1.182857	-1.382213
C5	-2.721251	-2.360245	-1.333908
C6	-3.980401	-2.415791	-1.932884
H7	-5.472015	-1.339972	-3.053236
H8	-4.141938	0.751299	-3.154458
H9	-1.910612	0.859124	-2.102724
H10	-2.334982	-3.239358	-0.821080
H11	-4.563144	-3.332149	-1.887018
C12	-0.586102	-1.112384	-0.738175
C13	0.483455	-2.001888	-1.421832
C14	0.653901	-1.640729	-2.915794
H15	-0.307225	-1.745979	-3.430763
C16	1.662776	-2.524259	-3.643962
H17	2.687994	-2.323519	-3.317148
H18	1.439246	-3.585800	-3.502745
H19	1.641517	-2.309400	-4.718410
H20	-0.241892	-0.071140	-0.716931
H21	0.164363	-3.050994	-1.354254
C22	1.810027	-1.897973	-0.648162
H23	2.565168	-2.574572	-1.059228
H24	2.211108	-0.879499	-0.677068
H25	1.680117	-2.177950	0.402429
O26	1.058410	-0.277935	-3.044193
H27	1.148742	-0.089577	-3.994662
O28	-0.730178	-1.508050	0.633156
H29	-1.569962	-1.129660	0.946850

Energy = -579.26519246659 hartree

Table S20. Coordinates (Ångstroms) for diol **3b**

atom	x	y	z
C1	-3.762720	-4.211174	-2.074299
C2	-2.440594	-3.788565	-2.189804
C3	-2.151394	-2.432465	-2.353124
C4	-3.181789	-1.479756	-2.398857
C5	-4.509102	-1.922913	-2.286751
C6	-4.796683	-3.279379	-2.124376
H7	-3.987920	-5.267153	-1.949417
H8	-1.633624	-4.516143	-2.154736
H9	-1.111789	-2.124056	-2.445089
H10	-5.333912	-1.213917	-2.336766
H11	-5.829517	-3.608607	-2.041821
C12	-2.837414	-0.013725	-2.585554
C13	-2.666063	0.398508	-4.071064
C14	-4.014955	0.456542	-4.830631
H15	-4.553967	-0.487090	-4.702157
C16	-3.849216	0.681570	-6.329728
H17	-3.468904	1.684032	-6.550140
H18	-3.180248	-0.061484	-6.773810
H19	-4.822438	0.610772	-6.828620
H20	-2.026126	-0.346527	-4.563084
C21	-1.924813	1.745009	-4.132169
H22	-1.691169	2.024333	-5.163787
H23	-2.509668	2.554356	-3.683416
H24	-0.971587	1.684299	-3.595402
O25	-4.854946	1.495693	-4.330184
H26	-4.765613	1.476412	-3.353206
H27	-1.894833	0.168663	-2.052867
O28	-3.808354	0.819595	-1.943341
H29	-3.915956	0.464025	-1.041626

Energy = -579.26988682365 hartree

Table S21. Coordinates (Ångstroms) for diol **3c**

atom	x	y	z
C1	-4.014555	-1.926083	-3.961152
C2	-5.278157	-2.199427	-3.441542
C3	-5.447324	-2.374205	-2.066746
C4	-4.352646	-2.273270	-1.195269
C5	-3.084370	-2.002769	-1.733412
C6	-2.917709	-1.828689	-3.107949
H7	-3.884284	-1.789613	-5.031619
H8	-6.133368	-2.276193	-4.108341
H9	-6.442713	-2.586867	-1.682437
H10	-2.215936	-1.929815	-1.080886
H11	-1.931071	-1.617524	-3.512612
C12	-4.540890	-2.473396	0.295933
C13	-4.186128	-1.232951	1.165010
C14	-4.242301	-1.588693	2.674970
H15	-5.195097	-2.077510	2.910106
C16	-4.062689	-0.395737	3.607127
H17	-3.140557	0.147464	3.373029
H18	-4.906394	0.297604	3.551023
H19	-3.973063	-0.732557	4.646148
O20	-3.197919	-2.508987	3.002865
H21	-3.214201	-3.203231	2.308470
O22	-3.746636	-3.599568	0.696100
H23	-3.668841	-4.184360	-0.080780
H24	-5.582054	-2.755711	0.496258
C25	-5.107444	-0.056031	0.817752
H26	-4.800869	0.856337	1.338423
H27	-5.080159	0.177213	-0.251112
H28	-6.145195	-0.274915	1.090793
H29	-3.150609	-0.941614	0.942556

Energy = -579.2695440872 hartree

Table S22. Coordinates (Ångstroms) for diol **3d**

atom	x	y	z
C1	-4.713198	-3.643295	-2.181428
C2	-5.237845	-2.410587	-2.562722
C3	-4.584198	-1.230516	-2.201460
C4	-3.395726	-1.266833	-1.452818
C5	-2.880943	-2.517279	-1.079134
C6	-3.534878	-3.696934	-1.440608
H7	-5.219743	-4.562160	-2.463580
H8	-6.155154	-2.367769	-3.143722
H9	-5.007425	-0.277948	-2.511635
H10	-1.960118	-2.576411	-0.501830
H11	-3.120058	-4.656525	-1.144091
C12	-2.712951	0.032843	-1.060260
C13	-3.445775	0.772427	0.092426
C14	-2.924182	2.216711	0.290110
H15	-3.358867	2.633051	1.207025
C16	-3.272467	3.145412	-0.868046
H17	-2.730081	2.879513	-1.780488
H18	-4.346657	3.139938	-1.075118
H19	-2.974358	4.172054	-0.627240
O20	-1.504396	2.204609	0.453479
H21	-1.234846	3.108910	0.699478
C22	-3.318466	0.007699	1.422201
H23	-3.848173	0.537349	2.221750
H24	-3.762437	-0.989891	1.350786
H25	-2.274728	-0.105308	1.732561
H26	-4.516739	0.837304	-0.141981
H27	-2.701533	0.659419	-1.959050
O28	-1.342029	-0.199276	-0.732802
H29	-1.030838	0.625214	-0.302104

Energy = -579.26926740247 hartree

Table S23. Coordinates (Ångstroms) for aldol **4a**

atom	x	y	z
C1	-3.062827	0.512792	0.720354
H2	-3.442914	0.720541	-0.286346
C3	-4.266055	0.093026	1.615921
H4	-3.900945	-0.004798	2.646538
C5	-4.959141	-1.235764	1.244906
H6	-4.232040	-2.049815	1.343976
C7	-2.444379	1.830472	1.260722
H8	-2.114175	1.661905	2.294769
H9	-3.228958	2.596561	1.312931
C10	-1.261426	2.415221	0.460489
H11	-0.424097	1.708547	0.479447
C12	-0.775203	3.704656	1.130399
H13	-0.477689	3.516020	2.167366
H14	0.094232	4.112597	0.603885
H15	-1.558045	4.470818	1.135400
C16	-1.623695	2.698487	-0.997587
H17	-2.496861	3.355741	-1.069093
H18	-0.791292	3.185571	-1.517044
H19	-1.845796	1.774719	-1.540101
C20	-5.454282	-1.209886	-0.179529
O21	-5.418058	-2.421069	-0.766340
O22	-5.874665	-0.235593	-0.783447
H23	-5.784815	-2.271439	-1.663268
C24	-6.144843	-1.540749	2.160076
H25	-6.947745	-0.804210	2.045996
H26	-6.571745	-2.522123	1.924760
H27	-5.834248	-1.552100	3.209830
C28	-2.012403	-0.597651	0.622303
H29	-1.611609	-0.849183	1.609757
H30	-2.429613	-1.506957	0.180173
H31	-1.176703	-0.306551	-0.020284
O32	-5.228857	1.153215	1.645735
H33	-5.584703	1.249470	0.738916

Energy = -618.83658902923 hartree

Table S24. Coordinates (Ångstroms) for aldol **4b**

atom	x	y	z
C1	-1.763465	-3.695973	2.024836
H2	-2.567192	-3.337918	2.679016
C3	-0.735287	-2.538652	1.853834
H4	-0.004163	-2.834511	1.089621
C5	0.014415	-2.128606	3.141634
C6	-2.401845	-4.033485	0.648844
H7	-1.602037	-4.335983	-0.040791
H8	-2.839172	-3.120347	0.224594
C9	-3.490523	-5.127521	0.642104
H10	-3.051931	-6.080256	0.959386
C11	-4.009501	-5.327188	-0.785772
H12	-3.192087	-5.597942	-1.462474
H13	-4.751089	-6.132396	-0.821054
H14	-4.480842	-4.415933	-1.169595
C15	-4.658248	-4.797877	1.572167
H16	-5.093821	-3.822157	1.331849
H17	-5.448895	-5.551038	1.484932
H18	-4.341863	-4.782592	2.619390
C19	1.101962	-1.138155	2.793771
O20	2.097501	-1.115746	3.700847
O21	1.130721	-0.401832	1.820086
H22	2.715985	-0.429833	3.371733
C23	-1.132179	-4.937941	2.661206
H24	-0.296116	-5.307816	2.058643
H25	-0.763511	-4.728833	3.669435
H26	-1.857362	-5.748964	2.771497
O27	-1.447337	-1.407106	1.333214
H28	-0.776891	-0.740323	1.078373
C29	-0.887761	-1.517371	4.210235
H30	-0.306359	-1.237133	5.095787
H31	-1.382582	-0.608833	3.850416
H32	-1.657588	-2.224255	4.533224
H33	0.526661	-3.007388	3.548674
Energy = -618.83610626163 hartree			

Table S25. Coordinates (Ångstroms) for aldol **4c**

atom	x	y	z
C1	-4.632519	0.391454	-1.637210
C2	-5.122330	1.157740	-0.372892
H3	-5.943457	1.824560	-0.668302
C4	-4.039267	1.979499	0.361950
C5	-3.921462	1.322554	-2.646405
H6	-3.034994	1.756501	-2.169161
H7	-4.591010	2.161193	-2.879631
C8	-3.460178	0.677458	-3.970680
H9	-4.331751	0.295906	-4.514531
C10	-2.482631	-0.476692	-3.744908
H11	-2.957836	-1.304849	-3.210963
H12	-2.121853	-0.872020	-4.700670
H13	-1.612494	-0.151690	-3.164476
C14	-2.805647	1.739568	-4.860201
H15	-1.912491	2.161091	-4.386421
H16	-2.507710	1.310704	-5.822929
H17	-3.502084	2.560134	-5.062762
C18	-4.686751	2.801288	1.452995
O19	-3.956430	3.879348	1.797810
O20	-5.747496	2.564631	2.009659
H21	-4.470552	4.306723	2.514982
O22	-5.677853	0.186369	0.525628
H23	-6.126129	0.682529	1.241175
C24	-2.932043	1.126270	0.974745
H25	-2.196623	1.754768	1.489394
H26	-3.327100	0.422352	1.715132
H27	-2.398041	0.556806	0.208359
H28	-3.605311	2.701044	-0.339040
C29	-5.821482	-0.335553	-2.290154
H30	-5.493198	-0.994290	-3.099425
H31	-6.350170	-0.969383	-1.570954
H32	-6.540930	0.380235	-2.701968
H33	-3.932370	-0.386881	-1.309725
Energy = -618.83613131512 hartree			

Table S26. Coordinates (Ångstroms) for aldol **4d**

atom	x	y	z
C1	-3.605762	0.347526	-0.236537
C2	-4.883041	1.236118	-0.168825
H3	-5.118332	1.566015	-1.189071
C4	-4.788917	2.498724	0.714477
C5	-2.355165	1.164706	-0.634971
H6	-2.187293	1.949589	0.112010
H7	-2.561491	1.679075	-1.583107
C8	-1.037338	0.374726	-0.780505
H9	-1.144482	-0.370911	-1.576478
C10	-0.644956	-0.344381	0.510774
H11	-1.371872	-1.118409	0.773995
H12	0.327002	-0.837381	0.400424
H13	-0.574327	0.356550	1.349448
C14	0.088137	1.324689	-1.202958
H15	0.264626	2.095562	-0.445005
H16	1.024345	0.776333	-1.352468
H17	-0.158476	1.825062	-2.145399
C18	-4.408755	2.141824	2.129661
O19	-3.654948	3.087254	2.721609
O20	-4.734309	1.132776	2.735033
H21	-3.502345	2.748425	3.628961
O22	-5.996435	0.434642	0.244336
H23	-5.820770	0.142254	1.161820
C24	-3.843268	-0.823759	-1.204409
H25	-3.015787	-1.538798	-1.178738
H26	-4.746004	-1.384433	-0.941159
H27	-3.955028	-0.466624	-2.233688
H28	-3.444836	-0.095461	0.753317
C29	-6.104659	3.275639	0.751423
H30	-5.988634	4.204082	1.321735
H31	-6.429501	3.540469	-0.259970
H32	-6.904366	2.700672	1.231030
H33	-4.015201	3.157074	0.303169
Energy = -618.83655450816 hartree			

Table S27. Coordinates (Ångstroms) for octenol **5a**

atom	x	y	z
C1	-3.247082	1.263716	1.041194
H2	-3.696926	2.167325	1.472712
H3	-2.250334	1.174426	1.494305
C4	-3.073890	1.497760	-0.474529
H5	-2.529349	0.654321	-0.913686
C6	-4.091484	0.028748	1.461775
H7	-5.098757	0.169117	1.052662
C8	-2.222390	2.750303	-0.707077
H9	-2.711970	3.644920	-0.307276
H10	-1.245403	2.652085	-0.222054
H11	-2.048293	2.909223	-1.776651
C12	-4.206247	-0.021827	3.013972
H13	-3.191042	-0.016515	3.432910
C14	-4.410933	1.642777	-1.201570
H15	-5.019637	2.437961	-0.758098
H16	-4.254208	1.887127	-2.257844
H17	-4.986091	0.712688	-1.167859
C18	-3.503499	-1.263937	0.888079
H19	-2.505066	-1.456812	1.294137
H20	-4.136872	-2.127281	1.110316
H21	-3.425642	-1.223412	-0.201967
C22	-4.986174	-1.238994	3.595978
H23	-4.512499	-2.162372	3.241613
H24	-3.803159	-1.450146	5.457835
C25	-6.446223	-1.272875	3.125322
H26	-6.989410	-0.364585	3.407002
H27	-6.506625	-1.374751	2.037302
H28	-6.975885	-2.131618	3.553139
C29	-5.777507	-1.147804	6.041962
C30	-4.823249	-1.281102	5.110819
H31	-6.820324	-0.980619	5.792865
H32	-5.529568	-1.206789	7.098214
O33	-4.836478	1.195957	3.440005
H34	-4.926803	1.151538	4.408258

Energy = -507.65637375111 hartree

Table S28. Coordinates (Ångstroms) for octenol **5b**

atom	x	y	z
C1	-3.749632	4.600806	-1.479441
H2	-3.955762	5.677225	-1.409409
H3	-2.658648	4.494524	-1.485398
C4	-4.268957	4.087533	-2.839375
H5	-5.351144	4.248655	-2.901828
C6	-4.318488	3.908271	-0.219373
C7	-3.985085	2.599061	-3.045330
H8	-2.916245	2.381594	-2.945566
H9	-4.526650	1.984556	-2.320163
H10	-4.302855	2.277966	-4.043251
C11	-3.779071	4.547453	1.094133
H12	-4.202038	5.557194	1.182292
C13	-3.628626	4.895227	-3.973095
H14	-2.540172	4.772680	-3.984432
H15	-4.015572	4.574052	-4.946056
H16	-3.849223	5.962288	-3.863084
C17	-2.228317	4.635532	1.218929
H18	-1.838179	5.203387	0.365808
H19	-2.159393	6.516278	2.388801
C20	-1.563470	3.253123	1.181657
H21	-1.924470	2.602530	1.985271
H22	-1.757897	2.748395	0.230130
H23	-0.475169	3.339144	1.277449
C24	-1.192754	5.071448	3.532887
C25	-1.853348	5.470559	2.437572
H26	-0.845625	4.052440	3.669267
H27	-0.978490	5.773313	4.334192
O28	-4.302250	3.782521	2.191344
H29	-3.946116	4.170051	3.010251
H30	-4.029716	2.850287	-0.224964
C31	-5.857228	3.939799	-0.212967
H32	-6.265460	3.482043	0.693845
H33	-6.229121	4.968452	-0.268741
H34	-6.272959	3.379843	-1.055747

Energy = -507.65636802746 hartree

Table S29. Coordinates (Ångstroms) for octenol **5c**

atom	x	y	z
C1	-2.255469	1.125965	0.050135
H2	-2.124726	0.579102	0.994335
H3	-1.549623	0.671767	-0.658198
C4	-1.845421	2.595035	0.278793
H5	-1.879841	3.133941	-0.674916
C6	-3.703490	0.887320	-0.451749
C7	-0.397703	2.653698	0.776386
H8	-0.286615	2.144528	1.739849
H9	0.279546	2.176809	0.059926
H10	-0.071386	3.691569	0.902394
C11	-4.008516	1.628177	-1.780372
H12	-3.836310	2.700783	-1.633622
C13	-2.760798	3.311088	1.272236
H14	-2.805132	2.776718	2.227209
H15	-2.400257	4.326370	1.470152
H16	-3.779503	3.400765	0.883201
C17	-5.450933	1.439760	-2.333961
H18	-5.626656	3.418391	-3.363615
C19	-5.942416	1.899848	-4.770995
C20	-5.678668	2.343980	-3.535078
H21	-6.010327	0.839212	-4.995040
H22	-6.102913	2.594747	-5.590047
O23	-3.058580	1.184210	-2.759344
H24	-3.274855	1.628261	-3.597978
H25	-4.387887	1.250673	0.322978
C26	-3.919879	-0.629876	-0.574087
H27	-4.957655	-0.870015	-0.822005
H28	-3.275819	-1.067805	-1.343813
H29	-3.694032	-1.129502	0.374503
C30	-6.531809	1.748543	-1.294662
H31	-7.531645	1.712971	-1.742802
H32	-6.523124	1.018746	-0.479600
H33	-6.394417	2.744877	-0.859369
H34	-5.569922	0.399648	-2.664000

Energy = -507.65711767941 hartree

Table S30. Coordinates (Ångstroms) for octenol **5d**

atom	x	y	z
C1	-5.627546	0.820362	-2.598972
H2	-5.067090	0.689457	-3.532244
H3	-6.455027	0.099736	-2.637108
C4	-6.224808	2.243785	-2.599488
H5	-6.853611	2.374926	-1.711407
C6	-4.710389	0.470112	-1.401930
C7	-7.129198	2.421489	-3.823374
H8	-6.563262	2.317098	-4.755414
H9	-7.930350	1.674810	-3.826883
H10	-7.597476	3.411560	-3.820670
C11	-4.128339	-0.967696	-1.508413
H12	-3.532158	-1.160226	-0.606282
C13	-5.147781	3.329173	-2.594949
H14	-4.453051	3.202442	-3.432123
H15	-5.598630	4.324052	-2.678181
H16	-4.569899	3.314149	-1.666164
C17	-3.247446	-1.244568	-2.760457
H18	-1.875301	-2.741441	-1.821365
C19	-2.793483	-3.624228	-3.483873
C20	-2.577364	-2.604305	-2.642802
H21	-3.478995	-3.538801	-4.322043
H22	-2.279710	-4.572116	-3.353289
O23	-5.224297	-1.893775	-1.483129
H24	-4.851533	-2.788125	-1.575794
C25	-2.156832	-0.191367	-2.970724
H26	-1.488590	-0.473985	-3.792519
H27	-2.586042	0.781011	-3.230937
H28	-1.545634	-0.063499	-2.070198
H29	-3.892058	-1.260004	-3.648831
C30	-5.461052	0.625463	-0.070030
H31	-4.841415	0.287208	0.767556
H32	-5.712539	1.672771	0.123131
H33	-6.390282	0.046259	-0.060627
H34	-3.867927	1.169678	-1.375841

Energy = -507.65692542959 hartree

Table S31. Coordinates (Ångstroms) for laurnetristich-4-ol (correct structure) **6a**

atom	x	y	z
O1	20.329617	-15.151571	0.516887
C2	20.831377	-16.895090	-1.118900
C3	21.205679	-16.282181	0.243885
C4	22.664335	-15.822317	0.314630
C5	23.178030	-16.156260	1.683874
C6	22.062033	-16.776588	2.474021
C7	21.059977	-17.278233	1.423839
H8	22.417667	-17.591240	3.111631
H9	21.595095	-16.015957	3.109692
H10	20.045931	-17.318810	1.834292
H11	21.346983	-18.291483	1.117533
C12	18.155094	-14.515862	-0.353970
C13	19.298706	-15.289603	-0.373004
H14	18.032930	-13.746413	0.400957
C15	17.170685	-14.754580	-1.324268
C16	18.552593	-16.530876	-2.295389
C17	19.500715	-16.277611	-1.319942
H18	18.724699	-17.298319	-3.040867
C19	17.385305	-15.762799	-2.284654
H20	21.513203	-16.580729	-1.916030
H21	20.785561	-17.987728	-1.096607
C22	15.910565	-13.938420	-1.338285
H23	15.036463	-14.587933	-1.226015
H24	15.893035	-13.213828	-0.517343
H25	15.831003	-13.380829	-2.277002
O26	16.417114	-15.977283	-3.226889
H27	16.708227	-16.692057	-3.815624
C28	23.782043	-16.837603	0.483534
C29	22.999969	-14.493119	-0.298687
H30	23.766483	-15.437854	2.236972
H31	23.576731	-17.888332	0.315161
H32	24.790737	-16.552868	0.201526
H33	24.069233	-14.268649	-0.219815
H34	22.735723	-14.482529	-1.360598
H35	22.457722	-13.683487	0.200187

Energy = -732.88755264812 hartree

Table S32. Coordinates (Ångstroms) for laurentristich-4-ol (originally proposed structure) **6b**

atom	x	y	z
O1	20.788347	-16.800112	-0.689974
C2	20.771433	-15.185383	-2.515532
C3	21.171175	-15.446563	-1.043996
C4	20.572115	-14.463420	-0.029289
C5	21.651701	-13.493246	0.351709
C6	22.898769	-13.830720	-0.413271
C7	22.708162	-15.288671	-0.848482
H8	21.441954	-12.436204	0.427612
H9	22.980196	-13.179341	-1.290343
H10	23.798086	-13.707328	0.197077
H11	23.061445	-15.965308	-0.059548
H12	23.289427	-15.528425	-1.745125
C13	19.159294	-13.998434	-0.225853
H14	18.772371	-13.481488	0.659083
H15	19.091293	-13.295619	-1.062114
H16	18.499023	-14.848560	-0.424941
C17	21.107147	-14.429150	1.395831
C18	20.505213	-18.804998	-2.032086
C19	20.653955	-17.439402	-1.894122
H20	20.493559	-19.441378	-1.153617
C21	20.376461	-19.334949	-3.324555
C22	20.531286	-17.078865	-4.272156
C23	20.666954	-16.587917	-2.986030
H24	20.527225	-16.403662	-5.119642
C25	20.391630	-18.460356	-4.429517
H26	19.795761	-14.707023	-2.628887
H27	21.518969	-14.606223	-3.065547
H28	20.488491	-14.003873	2.179338
H29	21.712782	-15.258053	1.745253
C30	20.216730	-20.814930	-3.520990
H31	21.026831	-21.204477	-4.145908
H32	20.246628	-21.351561	-2.566828
H33	19.254599	-21.032133	-3.995903
O34	20.257574	-18.995501	-5.681343
H35	20.281092	-18.275743	-6.332196

Energy = -732.87593525386 hartree

Table S33. Coordinates (Ångstroms) for neopeltolide (correct structure) **7a**

atom	x	y	z
C1	-6.651318	12.601052	-3.143882
C2	-5.335252	13.373853	-3.379944
C3	-4.052548	12.559107	-3.115121
C4	-3.763273	11.565884	-4.259826
C5	-2.602008	10.610699	-3.915704
O6	-2.938421	9.781355	-2.777524
C7	-3.934567	8.859516	-2.876658
C8	-4.355993	8.405501	-1.503754
C9	-5.776366	8.901393	-1.246025
C10	-6.242720	8.537043	0.167109
C11	-7.591361	9.185844	0.493774
C12	-7.591346	10.677530	0.139125
C13	-7.075480	10.893659	-1.283781
C14	-6.953862	12.384134	-1.634997
O15	-5.767442	10.326589	-1.373996
O16	-4.467814	8.478218	-3.909002
C17	-2.107430	9.815606	-5.136305
C18	-0.963166	8.860555	-4.787250
C19	-0.450911	8.133862	-6.021127
O20	-2.935548	13.465983	-3.071174
C21	-2.690656	13.975593	-1.766015
C22	-7.809848	13.370960	-3.791465
O23	-8.626490	8.549210	-0.297012
C24	-9.511872	7.642960	0.183987
O25	-10.517487	7.332136	-0.440185
C26	-10.046779	6.851896	2.480735
C27	-9.171660	7.018482	1.476209
H28	-9.698982	6.342147	3.377623
H29	-8.158266	6.649661	1.574194
C30	-11.474171	7.298246	2.522770
H31	-11.655524	7.850126	3.450822
H32	-11.747058	7.957536	1.695348
H33	-12.137319	6.428121	2.509088
H34	-6.594290	11.634591	-3.656811
H35	-5.340455	14.283180	-2.766071
H36	-5.298495	13.738379	-4.415757
H37	-4.122024	12.026906	-2.162364
H38	-4.660987	10.984333	-4.486887
H39	-3.498029	12.128893	-5.163824
H40	-1.753497	11.217611	-3.575964
H41	-4.286921	7.313971	-1.456800
H42	-3.660081	8.814519	-0.761308
H43	-6.454709	8.479622	-1.999169
H44	-6.301383	7.447318	0.260191
H45	-5.507649	8.899973	0.896728
H46	-7.811569	9.091899	1.562285
H47	-8.603018	11.088745	0.232664
H48	-6.940635	11.203200	0.849207
H49	-7.741817	10.407923	-2.008454
H50	-7.887608	12.890059	-1.360378
H51	-6.159641	12.833065	-1.025472
H52	-2.925110	9.245049	-5.588829
H53	-1.766919	10.522926	-5.903303
H54	-0.138009	9.420549	-4.332239
H55	-1.296239	8.118696	-4.053207
H56	0.366521	7.458098	-5.750793
H57	-1.244947	7.538830	-6.483499
H58	-0.073702	8.842210	-6.765613
H59	-2.412992	13.162481	-1.088310
H60	-1.854337	14.677328	-1.824619
H61	-3.563513	14.506710	-1.377091
H62	-8.754595	12.832728	-3.659132
H63	-7.919633	14.368605	-3.352646
H64	-7.644694	13.490222	-4.867599

Energy = -1311.40848233854 hartree

Table S34. Coordinates (Ångstroms) for neopeltolide (originally assigned structure) **7b**

atom	x	y	z
C1	-7.144014	7.550743	-6.308181
C2	-5.791281	8.060233	-5.744968
C3	-4.668801	8.026992	-6.801386
C4	-3.315161	8.439132	-6.184738
C5	-2.327673	7.262090	-6.089713
O6	-2.895617	6.253814	-5.230795
C7	-3.080004	5.012932	-5.759016
C8	-3.755792	4.106671	-4.765121
C9	-5.206826	3.902191	-5.184216
C10	-5.882661	2.833600	-4.321729
C11	-7.379179	2.736403	-4.633123
C12	-8.034516	4.119470	-4.620582
C13	-7.234767	5.114277	-5.468249
C14	-7.835879	6.528355	-5.373339
O15	-5.891025	5.144182	-4.990319
O16	-2.769560	4.667281	-6.891163
C17	-8.088455	8.736002	-6.548778
O18	-7.511837	2.157387	-5.955624
C19	-8.426680	1.217764	-6.297136
O20	-8.358092	0.609077	-7.356690
C21	-9.947418	-0.217446	-4.952157
C22	-9.529442	0.997097	-5.343171
H23	-10.796906	-0.267624	-4.273149
H24	-10.034925	1.885085	-4.984779
C25	-9.370224	-1.542392	-5.339178
H26	-10.080179	-2.089008	-5.967078
H27	-8.421304	-1.462351	-5.874856
H28	-9.185365	-2.135959	-4.437942
H29	-6.984393	7.063216	-7.278501
H30	-5.911798	9.091133	-5.385874
H31	-5.480746	7.475902	-4.874234
H32	-2.855230	9.244487	-6.770250
H33	-3.479468	8.844659	-5.177925
H34	-3.200458	3.162572	-4.743852
H35	-3.687293	4.551098	-3.765029
H36	-5.253410	3.629072	-6.246465
H37	-5.397009	1.864877	-4.487148
H38	-5.769021	3.094887	-3.261854
H39	-7.840393	2.086496	-3.882143
H40	-9.061776	4.064443	-4.996255
H41	-8.070969	4.472865	-3.582365
H42	-7.237467	4.802577	-6.520821
H43	-8.898953	6.461934	-5.637848
H44	-7.782261	6.892945	-4.339458
H45	-9.022964	8.400150	-7.010962
H46	-8.339087	9.240631	-5.609357
H47	-7.635036	9.471600	-7.220726
C48	-1.002630	7.733494	-5.467847
H49	-0.601058	8.576631	-6.043108
H50	-1.199488	8.101666	-4.452461
C51	0.069022	6.643785	-5.355759
H52	0.911780	7.048453	-4.782156
H53	-0.311246	5.787326	-4.788259
C54	0.592494	6.172567	-6.703650
H55	-0.183462	5.667632	-7.284898
H56	0.972594	7.013323	-7.292543
H57	1.413313	5.462594	-6.559747
O58	-5.024933	8.962441	-7.831342
C59	-4.438677	8.643088	-9.087865
H60	-3.347426	8.619482	-9.019140
H61	-4.813608	7.679884	-9.447072
H62	-4.726082	9.416102	-9.805534
H63	-4.620254	7.018903	-7.231311
H64	-2.144511	6.887353	-7.102886

Energy = -1311.40743994601 hartree

Table S35. Coordinates (Ångstroms) for apergillide A (**8a**)

atom	x	y	z
C1	-9.343910	0.399252	0.398314
C2	-9.104636	-1.112756	0.315178
C3	-9.477453	-1.756096	1.653085
C4	-8.794003	-1.056451	2.830547
C5	-8.876933	0.475167	2.762443
O6	-8.500545	0.927165	1.447522
H7	-10.398939	0.563748	0.642511
H8	-9.702044	-1.558651	-0.486951
H9	-10.564688	-1.707367	1.788575
H10	-9.193024	-2.814742	1.656084
H11	-9.199602	-1.429813	3.778064
H12	-7.732880	-1.338324	2.812478
H13	-8.134630	0.875846	3.463765
C14	-10.557964	2.326385	2.811282
C15	-10.214967	1.068896	3.143771
H16	-10.937435	0.418208	3.628608
H17	-9.806509	2.957897	2.336241
C18	-9.007528	1.130373	-0.897599
H19	-7.928410	1.294609	-0.994654
H20	-9.348055	0.577861	-1.780327
C21	-9.689018	2.478194	-0.914193
O22	-9.099982	3.550137	-0.932259
O23	-11.046328	2.329656	-0.929655
C24	-11.831781	3.539613	-0.861004
H25	-11.355935	4.325100	-1.461692
C26	-11.955121	4.017732	0.598016
H27	-10.955776	4.289626	0.952433
H28	-12.543264	4.943732	0.625520
O29	-7.730829	-1.382194	0.030464
H30	-7.207387	-0.733487	0.540339
C31	-11.931265	2.917733	2.932855
H32	-11.865577	3.913325	3.385443
C33	-12.602396	2.993880	1.552153
H34	-12.605403	1.990433	1.109320
H35	-13.655557	3.269004	1.690165
H36	-12.551147	2.303425	3.596711
C37	-13.189629	3.238094	-1.487062
H38	-13.684587	2.394458	-0.995137
H39	-13.849501	4.109781	-1.443696
H40	-13.063375	2.950698	-2.536797

Energy = -847.64811275423 hartree

Table S36. Coordinates (Ångstroms) for aspergillide B (**8b**)

atom	x	y	z
C1	-3.513429	14.537292	2.227155
C2	-2.278130	15.388148	1.906120
C3	-1.065041	14.470615	1.739434
C4	-0.900908	13.528185	2.933362
C5	-2.212125	12.857285	3.366791
O6	-3.261383	13.836940	3.468153
H7	-3.651546	13.818673	1.410115
H8	-2.430432	15.967925	0.989682
H9	-1.181252	13.876347	0.825059
H10	-0.151792	15.067007	1.630227
H11	-0.128226	12.780286	2.720412
H12	-0.531925	14.125009	3.778050
H13	-2.053312	12.456487	4.375724
C14	-3.926519	11.236154	2.529029
C15	-2.664908	11.701624	2.503348
H16	-1.943071	11.275133	1.812245
H17	-4.622218	11.666148	3.249672
C18	-4.788321	15.360615	2.402470
H19	-5.106331	15.440546	3.447432
H20	-4.658892	16.376383	2.011013
C21	-5.908852	14.734654	1.608097
O22	-6.496306	15.306479	0.699090
O23	-6.166315	13.466724	2.031051
C24	-7.177621	12.734739	1.311448
C25	-6.871512	11.229567	1.426144
H26	-6.820689	10.940369	2.482696
H27	-7.707727	10.670179	0.987399
O28	-2.025648	16.311832	2.967002
H29	-2.217084	15.838947	3.800039
C30	-4.498791	10.210051	1.600991
H31	-4.914416	9.382777	2.187665
C32	-5.582297	10.810479	0.691608
H33	-5.165657	11.649020	0.119692
H34	-5.850539	10.043800	-0.046878
H35	-3.707502	9.785396	0.971404
C36	-8.537226	13.050009	1.929411
H37	-9.337948	12.494496	1.431744
H38	-8.548138	12.802720	2.996721
H39	-8.761209	14.119062	1.852972
H40	-7.178071	13.015338	0.250657

Energy = -847.64554437329 hartree

Table S37. Coordinates (Ångstroms) for tanarifuranonol (correct structure) **9a**

atom	x	y	z
C1	4.013206	-3.137422	-5.580953
C2	5.352088	-3.853410	-5.327977
C3	5.600285	-4.975408	-6.337539
C4	4.331326	-5.759699	-6.693897
C5	3.076968	-4.863871	-6.838962
C6	2.806980	-4.098770	-5.530608
H7	5.414282	-4.231161	-4.300944
H8	6.181856	-3.139249	-5.420944
H9	6.021331	-4.538182	-7.251363
H10	4.515686	-6.303951	-7.630019
H11	4.155971	-6.541887	-5.943865
H12	1.888225	-3.512204	-5.678256
C13	2.626644	-4.974080	-4.274993
H14	2.099299	-5.897241	-4.541533
H15	3.594182	-5.291396	-3.875751
C16	1.844313	-4.294181	-3.147783
H17	1.932288	-4.904659	-2.241400
H18	2.248403	-3.304690	-2.925930
C19	0.357906	-4.154230	-3.437738
O20	-0.177748	-4.649616	-4.428134
C21	-0.446161	-3.382848	-2.423758
H22	-0.380665	-3.877506	-1.451631
H23	-0.064553	-2.361220	-2.354503
H24	-1.494336	-3.347572	-2.733410
O25	6.582579	-5.864043	-5.812066
H26	6.780239	-6.520040	-6.502662
C27	3.361616	-3.675113	-7.766875
H28	3.990001	-3.932840	-8.625191
H29	2.440951	-3.214660	-8.142837
O30	4.032873	-2.684857	-6.961018
C31	3.881162	-1.910884	-4.688312
H32	2.910845	-1.423450	-4.833584
H33	3.995702	-2.160114	-3.630084
H34	4.641316	-1.163318	-4.943303
C35	1.890712	-5.686995	-7.337546
H36	0.977647	-5.083233	-7.381386
H37	2.081208	-6.073379	-8.345025
H38	1.691395	-6.544648	-6.687366

Energy = -734.32441622718 hartree

Table S38. Coordinates (Ångstroms) for tanarifuranonol (originally proposed structure) **9b**

atom	x	y	z
C1	3.732125	-3.608875	-5.820389
C2	5.163284	-3.793368	-6.362311
C3	5.413914	-5.239846	-6.802812
C4	4.743439	-6.290087	-5.901344
C5	3.375599	-5.852796	-5.302578
C6	3.477333	-4.495400	-4.584367
H7	5.895307	-3.504115	-5.600030
H8	5.315919	-3.131275	-7.224501
H9	6.491772	-5.430530	-6.840472
H10	4.604215	-7.218000	-6.472039
H11	5.429376	-6.536182	-5.082232
H12	2.481820	-4.245010	-4.188754
C13	4.500317	-4.347906	-3.441131
H14	5.395898	-4.944052	-3.638364
H15	4.840331	-3.307260	-3.382253
C16	3.956632	-4.747096	-2.065573
H17	3.470364	-5.724261	-2.099465
H18	4.794731	-4.810644	-1.361724
C19	2.974892	-3.740173	-1.487267
O20	2.725801	-2.666173	-2.032491
C21	2.324244	-4.120018	-0.182786
H22	1.753370	-5.042594	-0.313504
H23	3.091612	-4.255722	0.583200
H24	1.643160	-3.325693	0.134957
O25	4.947025	-5.416325	-8.143973
H26	4.122921	-4.895750	-8.230845
C27	2.412925	-5.446838	-6.425745
H28	2.433661	-6.120351	-7.288041
H29	1.376338	-5.376241	-6.075763
O30	2.819739	-4.121957	-6.831357
C31	3.412364	-2.136980	-5.587475
H32	2.382352	-2.014258	-5.234343
H33	4.086456	-1.679793	-4.857478
H34	3.484443	-1.572213	-6.523903
C35	2.790854	-6.981747	-4.459529
H36	1.871151	-6.668386	-3.953801
H37	2.546267	-7.848145	-5.084373
H38	3.499452	-7.319379	-3.696833

Energy = -734.32821009833 hartree

Table S39. Coordinates (Ångstroms) for methyl proline **10a**

atom	x	y	z
C1	0.620501	0.442356	1.102963
C2	-0.565728	-0.499420	0.943650
C3	-1.366590	0.108162	-0.202241
C4	-0.284862	0.524078	-1.183826
H5	0.410196	1.292189	1.759452
H6	-1.155141	-0.561938	1.864519
H7	-0.233523	-1.516476	0.698751
H8	-1.894862	1.000751	0.158677
H9	0.128087	-0.319252	-1.746905
H10	-0.587014	1.326867	-1.861288
N11	0.805644	1.034413	-0.301509
H12	1.739152	0.750247	-0.652810
H13	0.814463	2.061280	-0.256404
C14	-2.375109	-0.854138	-0.804725
H15	-2.904443	-0.384881	-1.640407
H16	-1.890168	-1.761665	-1.179968
H17	-3.117195	-1.153052	-0.057280
C18	1.891313	-0.268884	1.542418
O19	1.816422	-0.832597	2.754456
O20	2.900659	-0.308782	0.853231
H21	2.689646	-1.248745	2.939813
Energy = -440.86739174764 hartree			

Table S40. Coordinates (Ångstroms) for methyl proline **10b**

atom	x	y	z
C1	0.530792	0.530018	1.309836
C2	-0.857199	-0.082102	1.452523
C3	-1.661553	0.552973	0.321232
C4	-1.192711	1.997467	0.345487
H5	1.015484	0.737085	2.268444
H6	-1.280956	0.191973	2.426945
H7	-0.859473	-1.174685	1.384351
H8	-1.374463	0.091349	-0.632895
H9	-1.314719	2.519511	-0.607066
H10	-1.638203	2.576556	1.160857
N11	0.266585	1.885263	0.641184
H12	0.811369	1.895306	-0.242159
H13	0.615809	2.668260	1.207674
C14	-3.162974	0.415003	0.503924
H15	-3.455132	-0.640123	0.511767
H16	-3.496319	0.864097	1.445598
H17	-3.698004	0.909695	-0.313258
C18	1.463120	-0.300273	0.433540
O19	1.771740	-1.502662	0.933862
O20	1.909349	0.111056	-0.628538
H21	2.385709	-1.938050	0.298685

Energy = -440.86808742786 hartree

Table S41. Coordinates (Ångstroms) for tetrahydrofuran **11a**

atom	x	y	z
C1	-0.603138	1.534726	-0.233931
C2	0.427853	1.387219	0.882357
C3	1.725835	1.330336	0.104775
C4	1.438957	2.367379	-0.981609
H5	0.230015	0.501492	1.493786
H6	0.428256	2.267398	1.537656
H7	2.610215	1.599229	0.692910
H8	1.563440	3.370779	-0.552892
O9	0.043625	2.228626	-1.317170
O10	1.881449	0.019259	-0.472975
C11	2.429708	-0.918325	0.337765
O12	2.788153	-0.743365	1.491636
C13	2.636122	-4.754088	-1.561406
C14	2.857150	-4.626797	-0.190773
C15	2.790388	-3.369315	0.412316
C16	2.494194	-2.233007	-0.353283
C17	2.274578	-2.368151	-1.730134
C18	2.348479	-3.627021	-2.330667
H19	2.694155	-5.731653	-2.033900
H20	3.083209	-5.505399	0.408197
H21	2.966095	-3.278584	1.482540
H22	2.064444	-1.501089	-2.351344
H23	2.191836	-3.725320	-3.402184
C24	2.304258	2.244165	-2.229743
H25	2.180104	1.257623	-2.691554
H26	1.983173	2.986300	-2.970841
O27	3.668993	2.484868	-1.883889
C28	-2.312144	3.411822	-0.262621
C29	-1.843423	2.252678	0.220342
H30	-3.224307	3.851260	0.127607
H31	-2.405193	1.761901	1.012669
H32	-1.800359	3.942982	-1.059789
H33	-0.888896	0.547766	-0.617374
C34	4.558520	2.238773	-2.973096
H35	4.122783	2.597267	-3.913523
H36	5.468216	2.823529	-2.795851
C37	5.711782	-1.925801	-3.166264
C38	5.240088	-1.267204	-4.303980
C39	4.859896	0.076140	-4.246898
C40	4.941222	0.781555	-3.041523
C41	5.417351	0.117592	-1.902540
C42	5.799489	-1.226814	-1.963090
H43	5.171689	-1.806443	-5.245606
H44	4.502707	0.562729	-5.151295
H45	5.487755	0.649526	-0.954954
H46	6.154650	-1.695373	-1.051493
C47	6.543462	-3.945086	-2.233646
H48	5.799595	-3.989021	-1.432156
H49	6.752989	-4.971800	-2.548783
H50	7.481990	-3.507811	-1.877164
O51	6.046428	-3.237425	-3.362515

Energy = -1228.90066724874 hartree

Table S42. Coordinates (Ångstroms) for tetrahydrofuran **11b**

atom	x	y	z
C1	3.886581	0.100191	1.101241
C2	3.331760	-1.320472	1.199165
C3	3.601045	-1.704728	2.640993
C4	3.402810	-0.356998	3.333747
H5	3.768068	-1.999699	0.460208
H6	2.247755	-1.290317	1.031946
H7	2.909063	-2.458362	3.033407
H8	2.325496	-0.167884	3.433240
O9	3.919248	0.642394	2.433544
O10	4.961292	-2.156366	2.779224
C11	5.183953	-3.455153	2.463073
O12	4.339515	-4.256555	2.095252
C13	9.338381	-4.470918	2.729059
C14	8.434187	-5.332704	2.109743
C15	7.082941	-4.989218	2.035015
C16	6.631143	-3.776687	2.573908
C17	7.545011	-2.916218	3.195889
C18	8.894832	-3.266318	3.274012
H19	10.389956	-4.739719	2.793554
H20	8.780106	-6.272292	1.686294
H21	6.383499	-5.667995	1.550762
H22	7.218198	-1.979884	3.641257
H23	9.598141	-2.602151	3.770550
C24	4.062055	-0.236158	4.702190
H25	5.142948	-0.404002	4.628135
H26	3.922671	0.781911	5.085824
O27	3.454430	-1.164361	5.601973
C28	5.624490	0.737113	-0.603425
C29	5.285470	0.161851	0.558188
H30	6.659328	0.753337	-0.931486
H31	6.067764	-0.284725	1.167524
H32	4.886817	1.207663	-1.245701
H33	3.216572	0.724890	0.499163
C34	4.124184	-1.219498	6.861666
H35	4.430187	-0.215006	7.178124
H36	3.404964	-1.585935	7.602840
C37	7.432085	-4.005551	6.776117
C38	7.609125	-2.709441	7.265390
C39	6.546309	-1.802671	7.289909
C40	5.285284	-2.181017	6.816788
C41	5.110949	-3.483794	6.329768
C42	6.176280	-4.390278	6.308321
H43	8.585452	-2.404535	7.634079
H44	6.714369	-0.802616	7.682257
H45	4.136952	-3.797287	5.957125
H46	5.989764	-5.383860	5.914973
C47	8.420984	-6.115396	6.318471
H48	8.128127	-6.124384	5.264028
H49	9.399302	-6.599463	6.395469
H50	7.716041	-6.689825	6.928543
O51	8.554484	-4.786672	6.807228

Energy = -1228.89987363562 hartree

Table S43. Coordinates (Ångstroms) for acetal **12a**

atom	x	y	z
C1	-0.828859	0.027088	-1.654304
C2	-0.188070	-1.294292	-2.089009
C3	-1.315745	-2.313818	-1.947796
C4	-1.986520	-1.904577	-0.643944
C5	-1.885226	-0.375009	-0.593554
H6	0.612464	-1.548377	-1.381317
H7	-2.027326	-2.241208	-2.778133
H8	-0.945944	-3.343228	-1.914885
H9	-3.014976	-2.267891	-0.570248
H10	-1.427490	-2.333504	0.197066
H11	-0.096375	0.757372	-1.287766
H12	-1.622829	-0.066787	0.427716
C13	-1.961562	0.665829	-2.519907
C14	-2.915885	0.585284	-1.278024
H15	-2.298386	-0.006088	-3.323392
C16	-4.281342	-0.013305	-1.613482
H17	-4.833970	-0.262223	-0.701171
H18	-4.884496	0.695718	-2.191168
H19	-4.193950	-0.926938	-2.210259
C20	-3.088031	1.872620	-0.461789
H21	-3.620437	1.668971	0.474065
H22	-2.123734	2.320836	-0.199114
H23	-3.665664	2.618226	-1.018217
H24	-1.271894	2.737206	-2.387410
C25	-1.643153	2.025585	-3.131744
C26	-1.308136	2.054251	-5.374054
C27	-2.420614	3.001305	-5.020452
H28	-0.629560	2.445490	-6.135895
H29	-1.694222	1.081604	-5.697719
H30	-2.057810	4.030497	-4.925303
H31	-3.254685	2.974966	-5.725845
O32	-0.626085	1.870351	-4.134946
O33	-2.834340	2.557960	-3.729994
C34	0.401603	-1.233640	-3.485594
H35	0.881104	-2.184103	-3.741468
H36	-0.360193	-1.031234	-4.244867
H37	1.155719	-0.442628	-3.552454

Energy = -659.06795479565 hartree

Table S44. Coordinates (Ångstroms) for acetal **12b**

atom	x	y	z
C1	-0.822220	0.047542	-1.590758
C2	-0.179796	-1.242331	-2.106544
C3	-1.270250	-2.298107	-1.909639
C4	-1.959444	-1.902346	-0.610015
C5	-1.892274	-0.372904	-0.554404
H6	0.087644	-1.156465	-3.165739
H7	-1.990315	-2.251053	-2.734872
H8	-0.879357	-3.319787	-1.876354
H9	-2.981999	-2.284876	-0.548941
H10	-1.406011	-2.324657	0.237490
H11	-0.112627	0.796651	-1.217835
H12	-1.659126	-0.059687	0.472281
C13	-1.941640	0.661506	-2.484799
C14	-2.921741	0.573216	-1.264160
H15	-2.245502	-0.022301	-3.292360
C16	-4.271792	-0.044785	-1.624379
H17	-4.840007	-0.295713	-0.722258
H18	-4.871834	0.652993	-2.218747
H19	-4.160223	-0.960635	-2.213593
C20	-3.125881	1.864289	-0.461828
H21	-3.676449	1.661741	0.463658
H22	-2.172544	2.325226	-0.181739
H23	-3.698961	2.599182	-1.036958
H24	-1.270263	2.739321	-2.361890
C25	-1.615185	2.014059	-3.105799
C26	-1.213086	2.009990	-5.337382
C27	-2.340439	2.956236	-5.031053
H28	-0.513728	2.394205	-6.083878
H29	-1.584695	1.031045	-5.659001
H30	-1.985612	3.988587	-4.940022
H31	-3.152672	2.915409	-5.760829
O32	-0.567584	1.846281	-4.075873
O33	-2.790912	2.529333	-3.747317
C34	1.084220	-1.559246	-1.311232
H35	1.837636	-0.779291	-1.466159
H36	0.891676	-1.615059	-0.234777
H37	1.514689	-2.513397	-1.631817

Energy = -659.06849939244 hartree

Table S45. Coordinates (Ångstroms) for aldehyde **13a**

atom	x	y	z
C1	-0.717020	-0.530625	-0.500778
C2	-0.374024	-2.020092	-0.421400
C3	-0.891830	-2.585494	-1.741696
C4	-2.220192	-1.863698	-1.927516
C5	-2.010786	-0.458366	-1.348834
H6	-0.939426	-2.470655	0.405288
H7	-0.215086	-2.351059	-2.571174
H8	-1.015155	-3.672388	-1.710062
H9	-2.547288	-1.851770	-2.970620
H10	-2.994084	-2.382874	-1.348420
H11	-0.811043	-0.062229	0.486929
H12	-2.901006	-0.169384	-0.773856
C13	0.005129	0.373864	-1.549859
C14	-1.390305	0.731875	-2.156013
H15	0.598380	-0.221156	-2.260572
C16	-1.434315	0.612662	-3.678597
H17	-2.465786	0.657055	-4.044362
H18	-0.873586	1.428291	-4.148274
H19	-0.996117	-0.327110	-4.029853
C20	-1.983323	2.074508	-1.710871
H21	-3.023682	2.167108	-2.042070
H22	-1.975480	2.182293	-0.620832
H23	-1.420712	2.912623	-2.136131
C24	1.105420	-2.266561	-0.189582
H25	1.308121	-3.339328	-0.107483
H26	1.721106	-1.872231	-1.004104
H27	1.435910	-1.784347	0.736387
C28	0.911016	1.507883	-1.008564
O29	0.728684	2.188718	0.000169
H30	1.818161	1.682973	-1.611746

Energy = -505.22687174513 hartree

Table S46. Coordinates (Ångstroms) for aldehyde **13b**

atom	x	y	z
C1	-0.749611	-0.582153	-0.528680
C2	-0.344214	-2.058472	-0.545986
C3	-0.948777	-2.589188	-1.847905
C4	-2.274243	-1.851157	-1.984675
C5	-2.040728	-0.466315	-1.373130
H6	0.745808	-2.170532	-0.552310
H7	-0.298677	-2.334803	-2.693076
H8	-1.077774	-3.675955	-1.851348
H9	-2.618947	-1.804689	-3.021376
H10	-3.045549	-2.379938	-1.411665
H11	-0.830827	-0.144572	0.473935
H12	-2.924767	-0.173967	-0.790547
C13	-0.012392	0.349185	-1.538134
C14	-1.398338	0.730757	-2.153476
H15	0.592644	-0.232611	-2.251041
C16	-1.425685	0.640068	-3.678426
H17	-2.452219	0.702906	-4.055237
H18	-0.850579	1.457949	-4.126311
H19	-0.993952	-0.297729	-4.042326
C20	-1.983699	2.071074	-1.691220
H21	-3.018987	2.179954	-2.033201
H22	-1.988275	2.158941	-0.599371
H23	-1.407794	2.911106	-2.094329
C24	-0.898077	-2.774467	0.683616
H25	-0.452908	-2.364099	1.596520
H26	-1.983539	-2.661771	0.773101
H27	-0.666922	-3.843890	0.646191
C28	0.890046	1.464514	-0.953308
O29	0.695913	2.119135	0.070480
H30	1.806409	1.651995	-1.538606

Energy = -505.22762736835 hartree

S-5 Comparison of theory levels

Calculations were carried out on aldols **1** using the methods given in Table S47. The methods show the levels of theory (either molecular mechanics using the MMFF force field, or *ab initio* using B3LYP/6-31G(d,p) implemented by the stated package) used to obtain (i) the geometries on which to calculate the shielding constants, (ii) the energies of these geometries (needed for the Boltzmann averaging) and (iii) the shielding constants themselves. "+sol" indicates that a continuum model of the chloroform solvent was used (see Computational Methods).

Table S47: Definitions of the calculation methods

Method	Structures	Energies	Shift calculation
A	MMFF	MMFF	Jaguar
B	MMFF	Jaguar	Jaguar
C	MMFF	Jaguar (+sol)	Jaguar
D	MMFF	MMFF	Gaussian
E	MMFF	Gaussian	Gaussian
F	MMFF	Gaussian (+sol)	Gaussian
G	MMFF	MMFF	Gaussian (+sol)
H	MMFF	Gaussian	Gaussian (+sol)
I	MMFF	Gaussian (+sol)	Gaussian (+sol)
J	Jaguar	Jaguar	Jaguar
K	Jaguar	Jaguar (+sol)	Jaguar
L	Gaussian	Gaussian	Gaussian
M	Gaussian	Gaussian (+sol)	Gaussian
N	Gaussian	Gaussian	Gaussian (+sol)
O	Gaussian	Gaussian (+sol)	Gaussian (+sol)
P	Jaguar (+sol)	Jaguar (+sol)	Jaguar
Q	Gaussian (+sol)	Gaussian (+sol)	Gaussian
R	Gaussian (+sol)	Gaussian (+sol)	Gaussian (+sol)

The values of the each of the parameters obtained for both correct (A=**a**, B=**b**) and incorrect (A=**b**, B=**a**) assignment combinations of aldols **1** are plotted in Fig. S1.

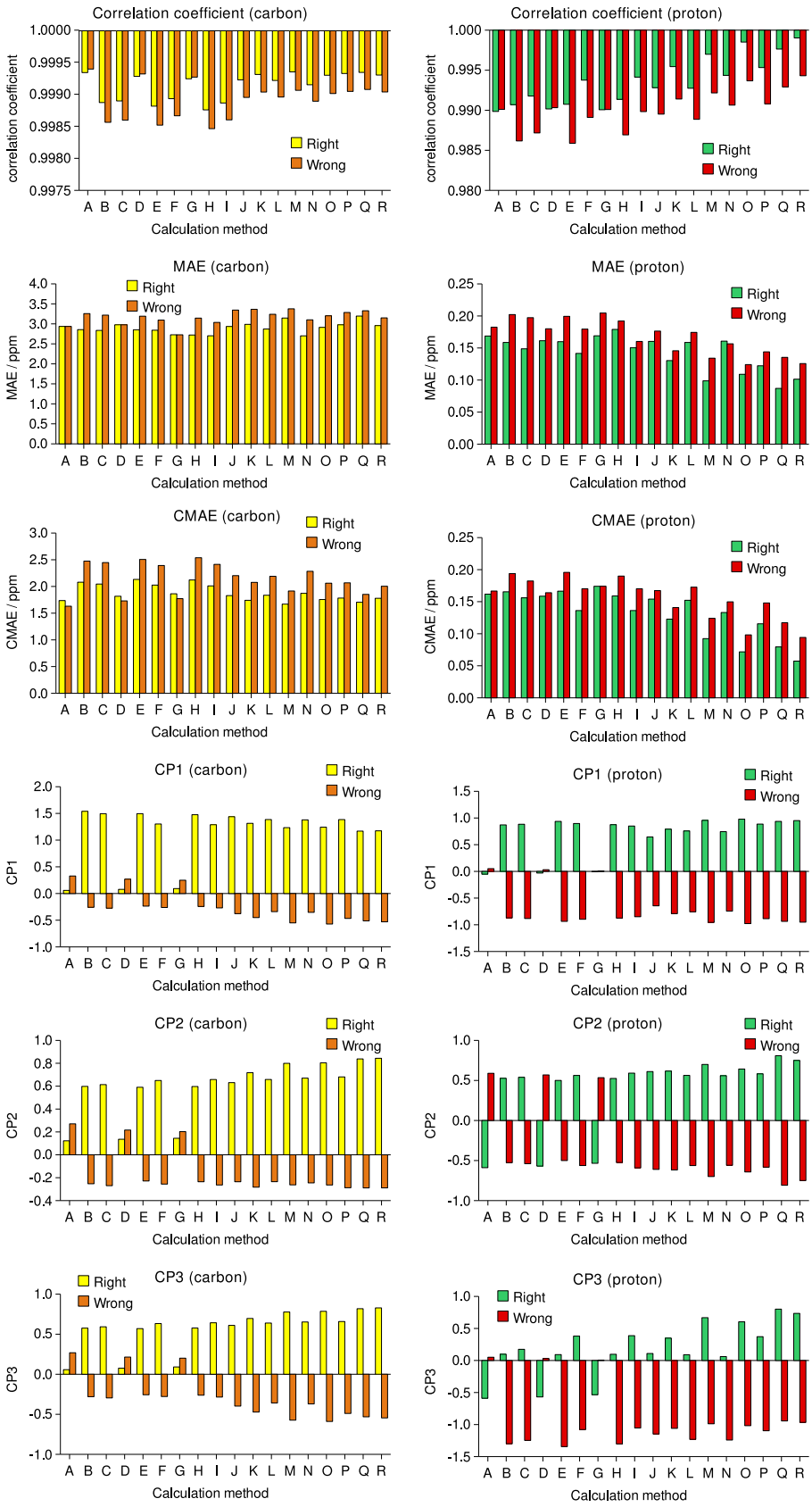


Figure S1: The effect of including geometry optimisation and/or solvation