Supporting Information

Structure, stereochemistry and synthesis of enantiopure cyclohexenone *cis*-diol bacterial metabolites derived from phenols

Derek R. Boyd,*[a] Narain D. Sharma,[a] John F. Malone,[a] Peter B. A. McIntyre,[a] Paul J. Stevenson,[a] Christopher C. R. Allen,[a] Marcin Kwit[a] and Jacek Gawronski*[c]

[a] *School of Chemistry and Chemical Engineering, Queen's University, Belfast, UK, BT9 5AG. FAX: (+44)-*

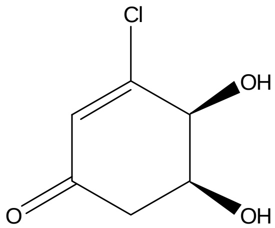
28-9097-4687; Tel(+44) 28 9097 4421; e-mail: ***dr.boyd@qub.ac.uk****,*

[b] *School of Biological Sciences, Queen's University, Belfast BT9 5AG, UK*.

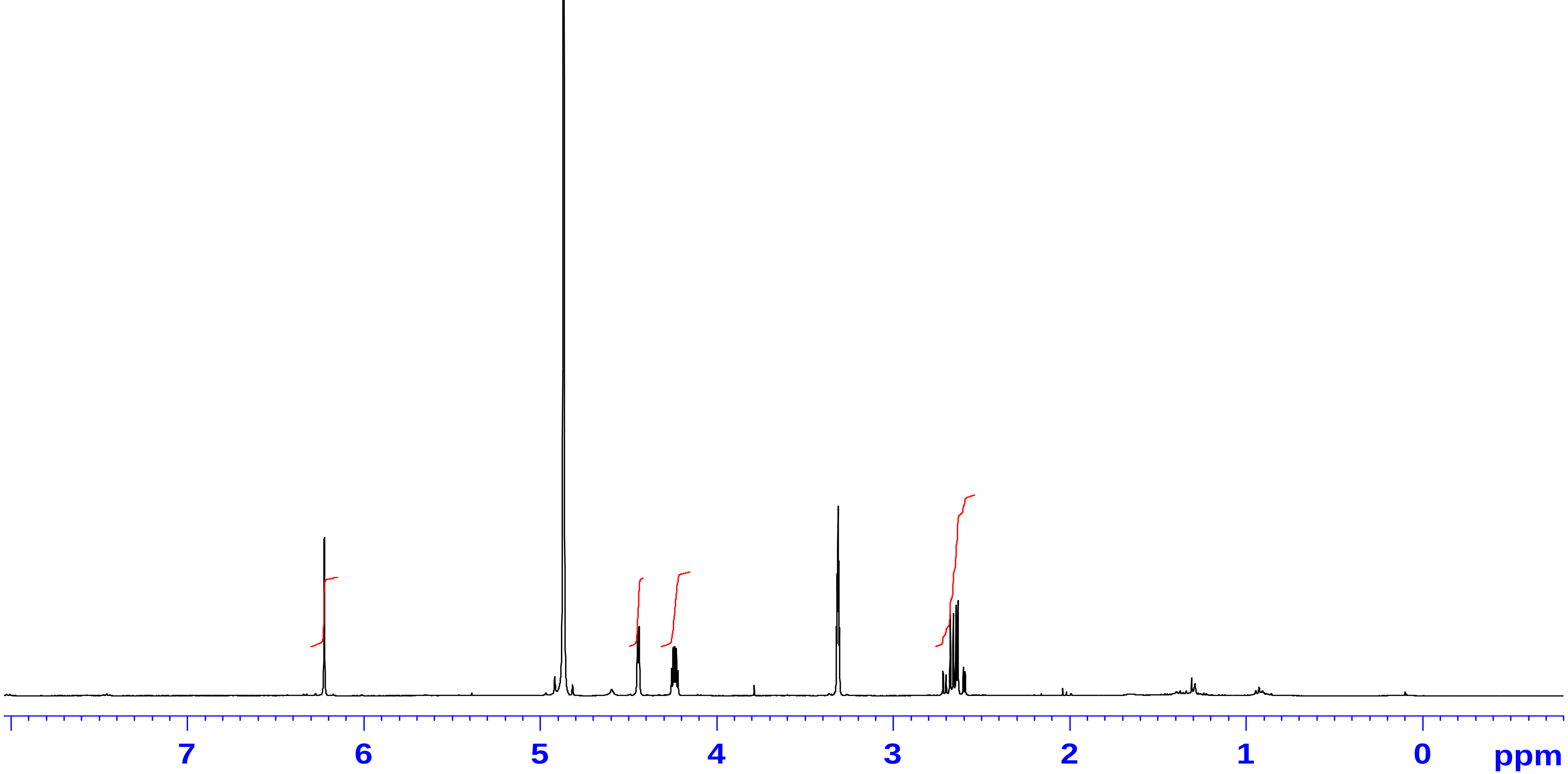
[c] *Department ofChemistry, A. Mieckiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland. . FAX:*

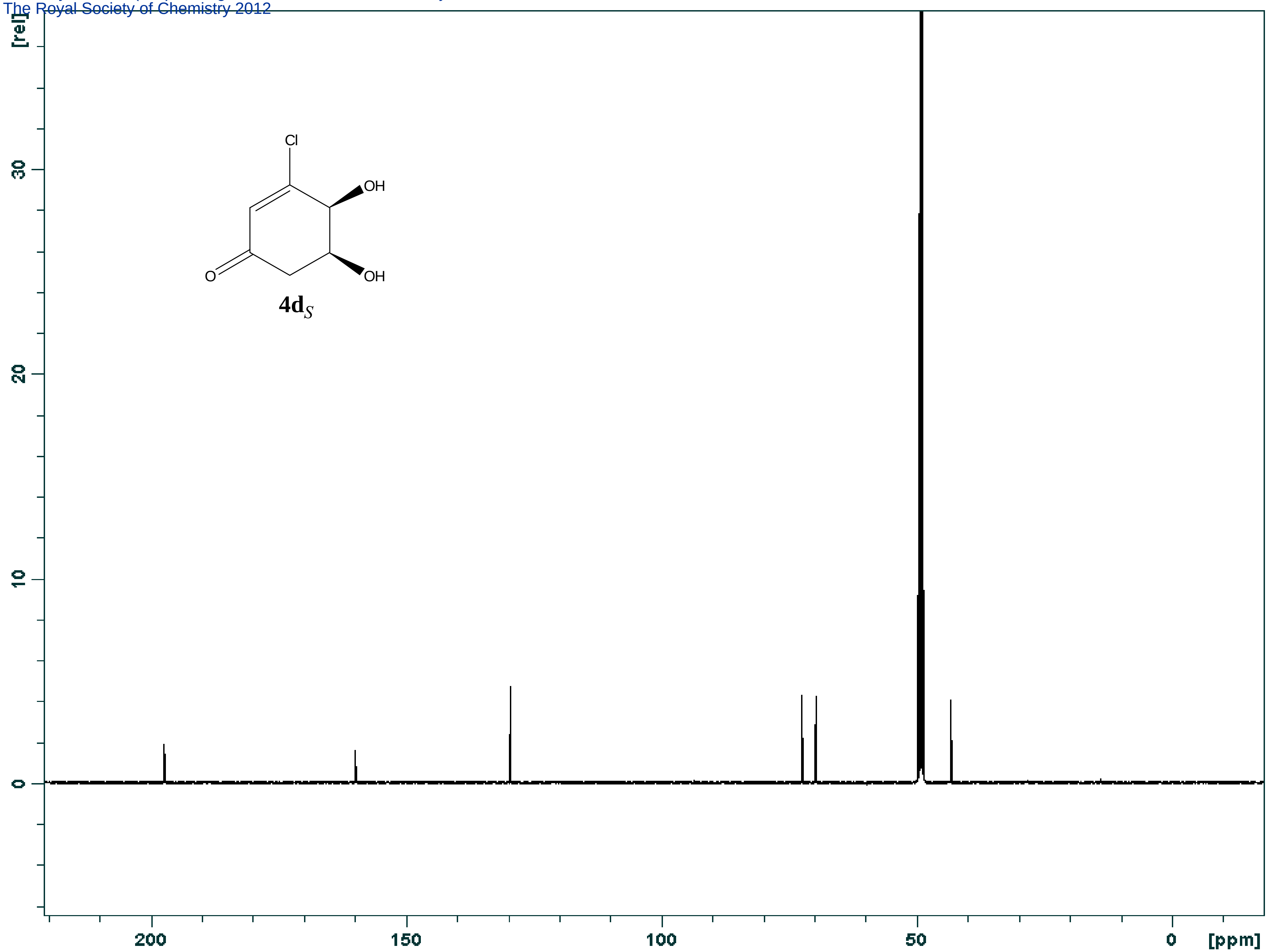
(+48)-61-8658-008; e.mail: gawronsk@amu.edu.pl

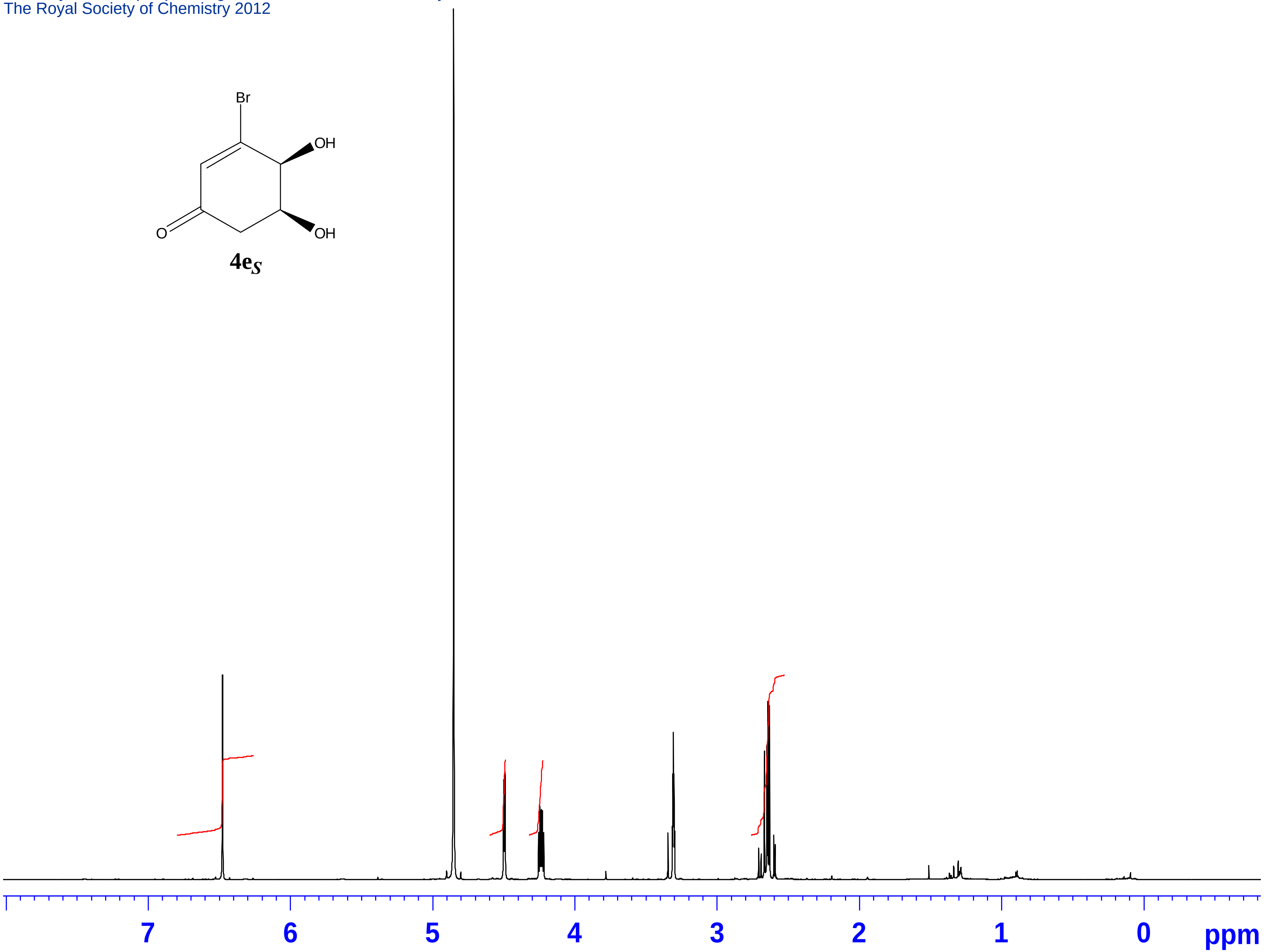
Index

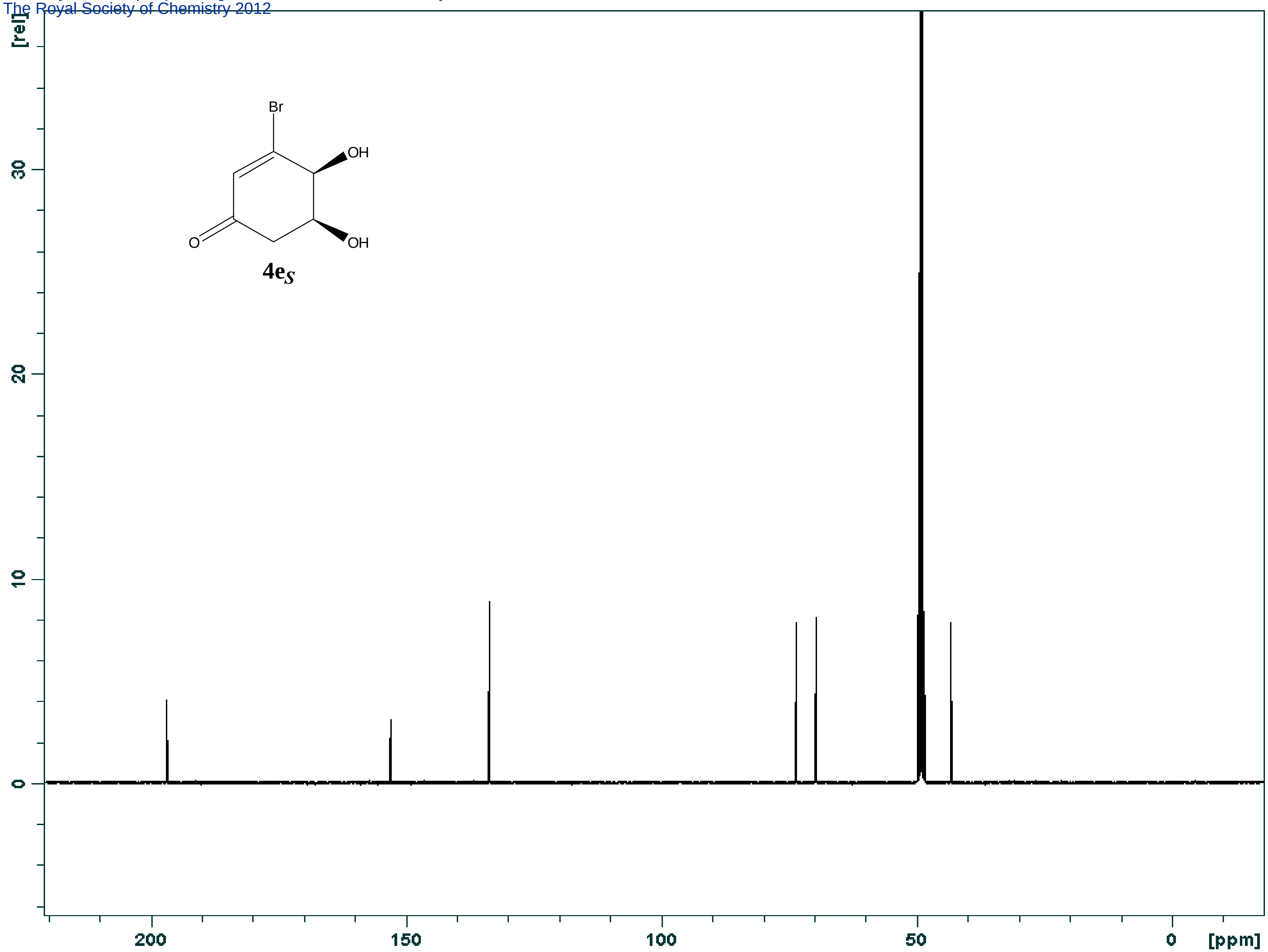


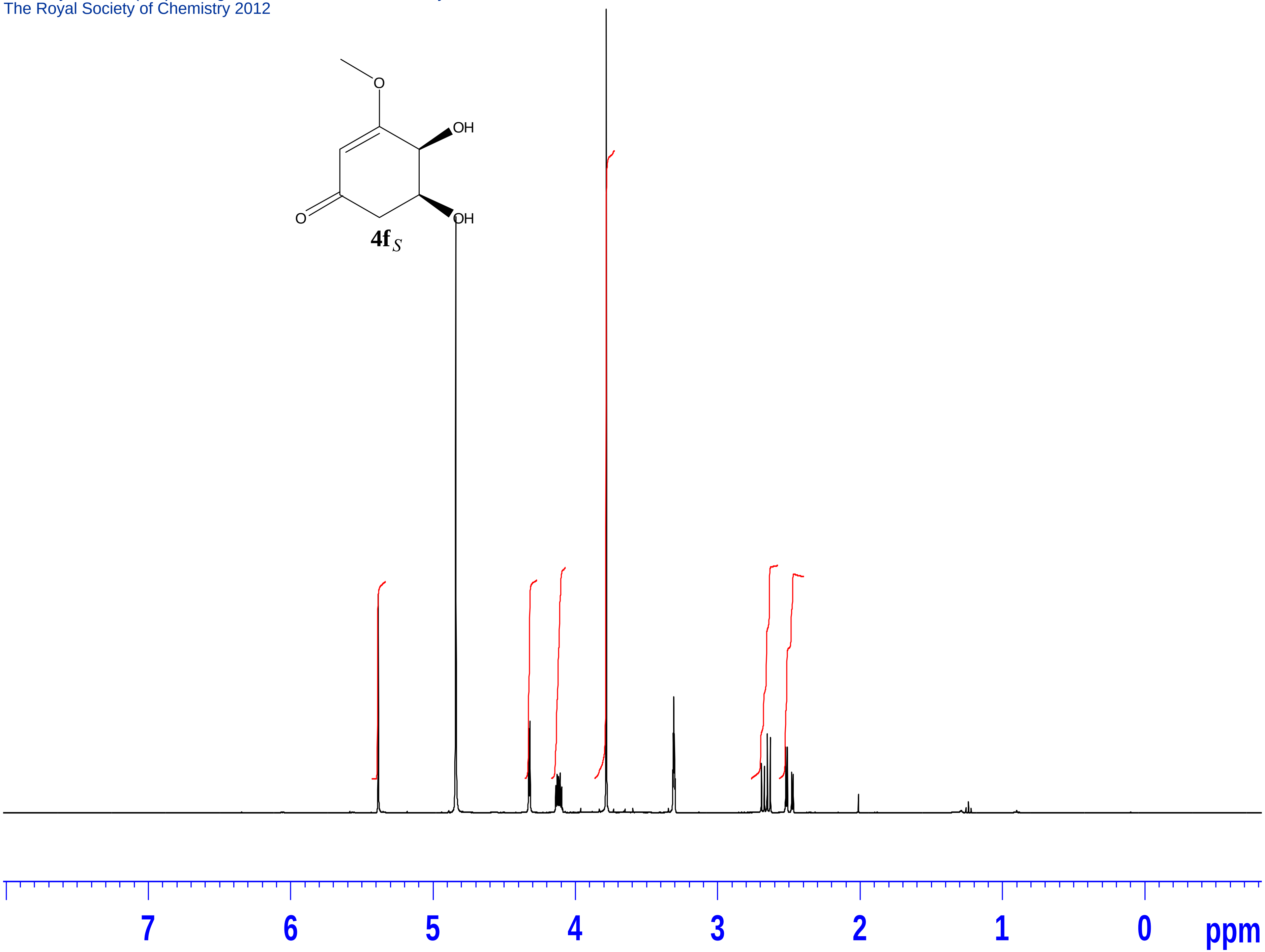
4d$_{S}$

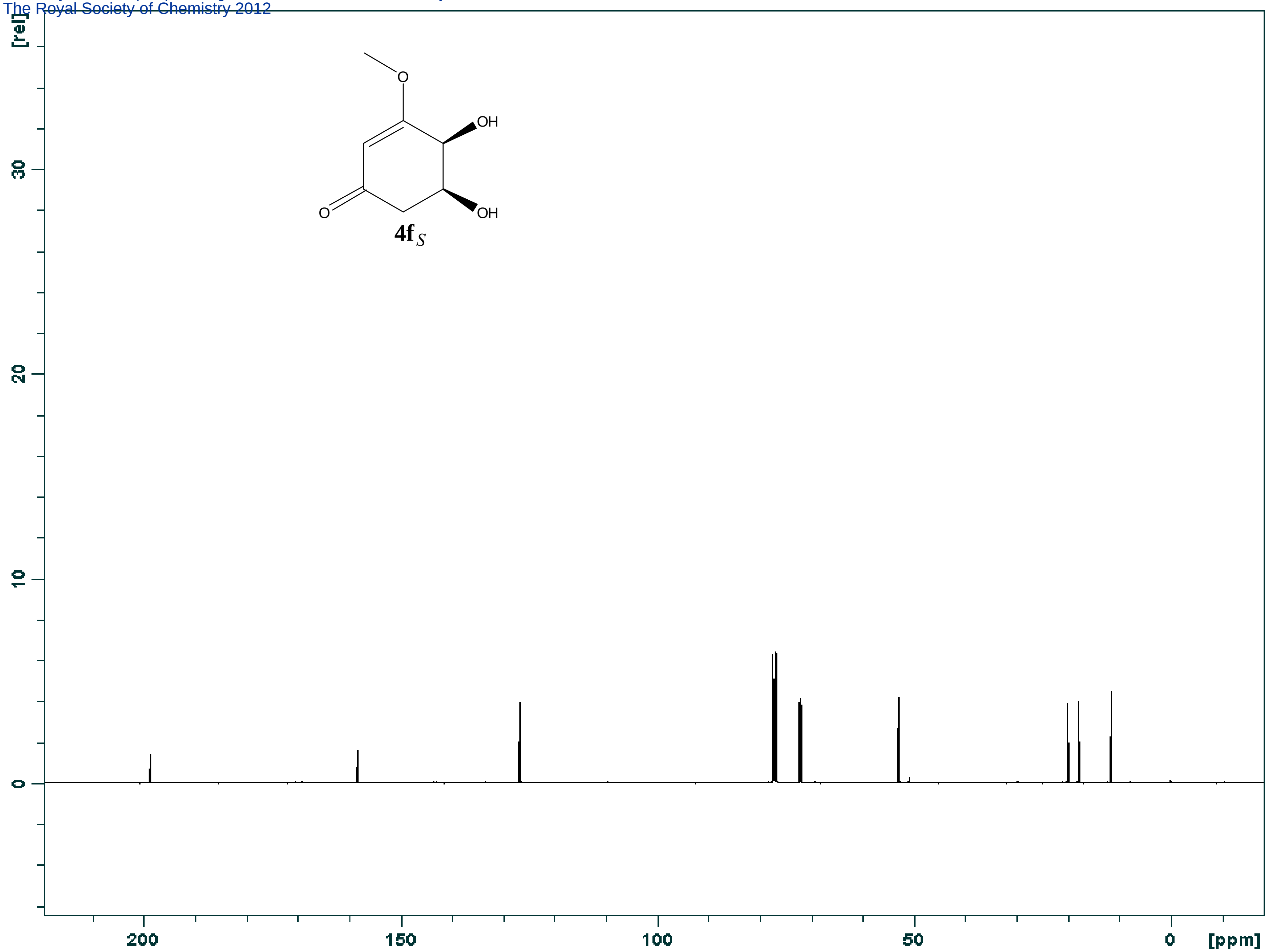



[rel]
30
20
10
0
Cl
OH
OH
O
4d$_S$
200
150
100
50
0
[ppm]

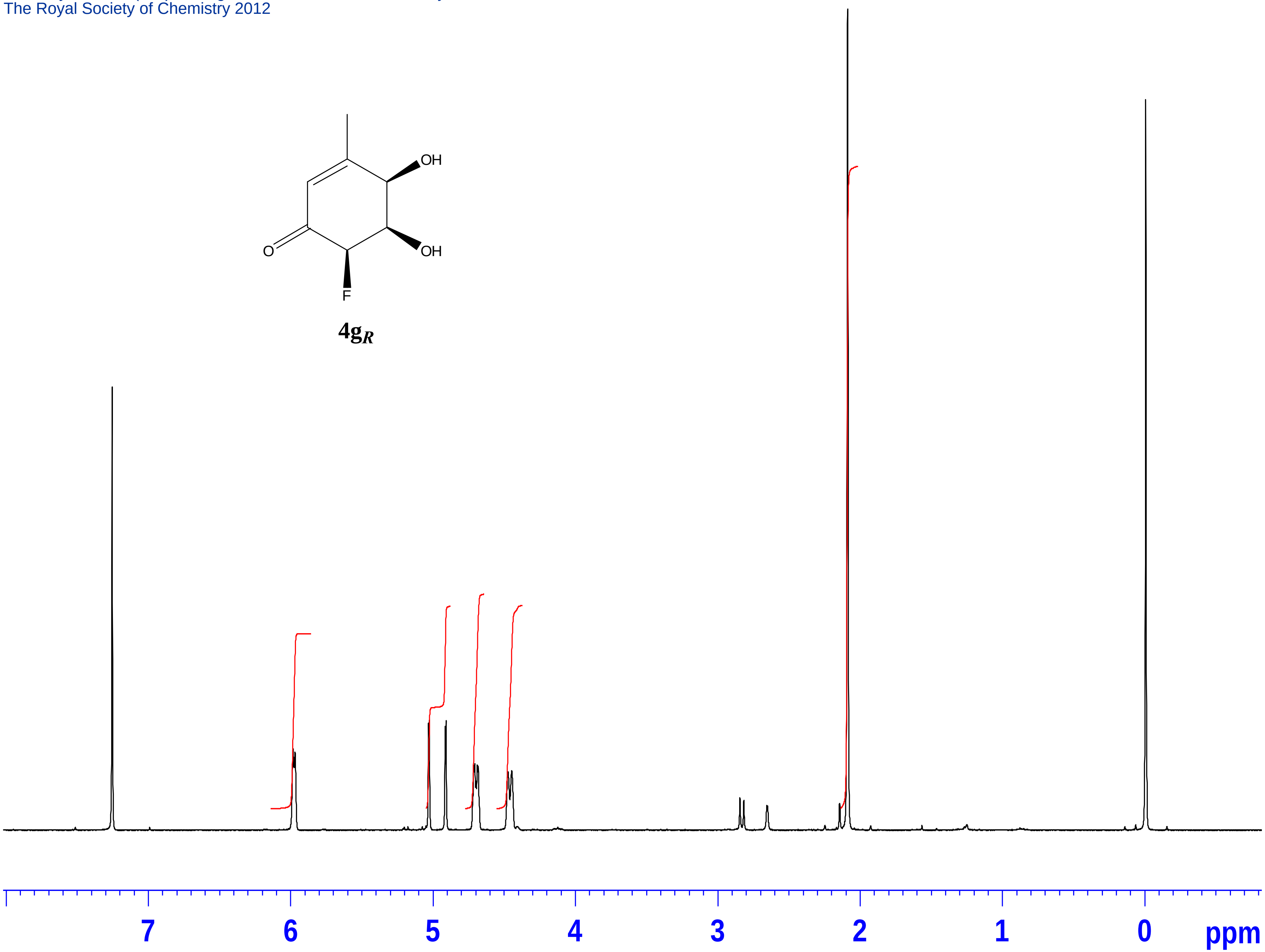

Br
OH
OH
O
4e$_S$
7
6
5
4
3
2
1
0
ppm

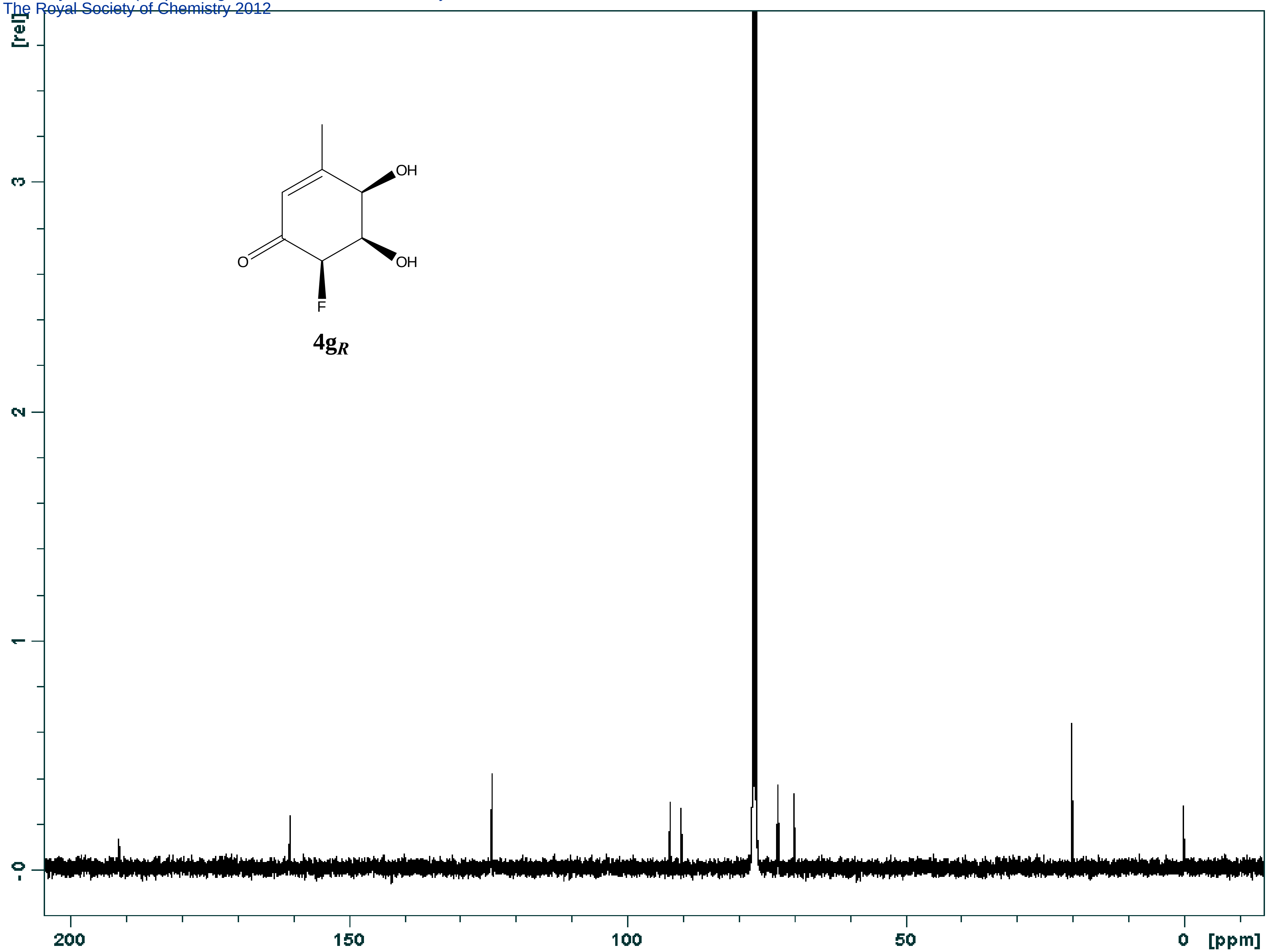

[rel]
30
20
10
0
Br
OH
OH
O
4e$_S$
200
150
100
50
0
[ppm]

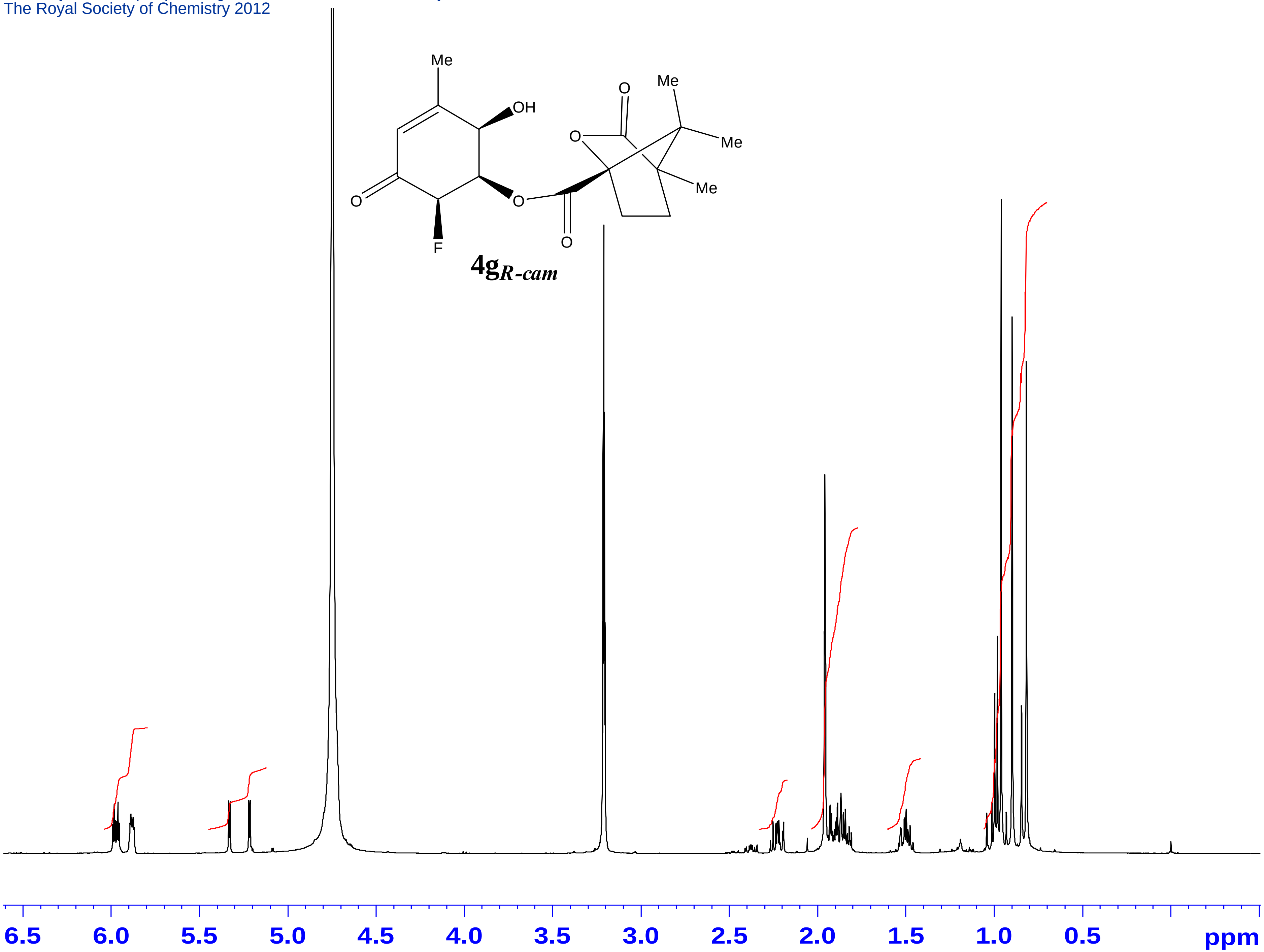

O
OH
OH
O
4f S
7
6
5
4
3
2
1
0
ppm

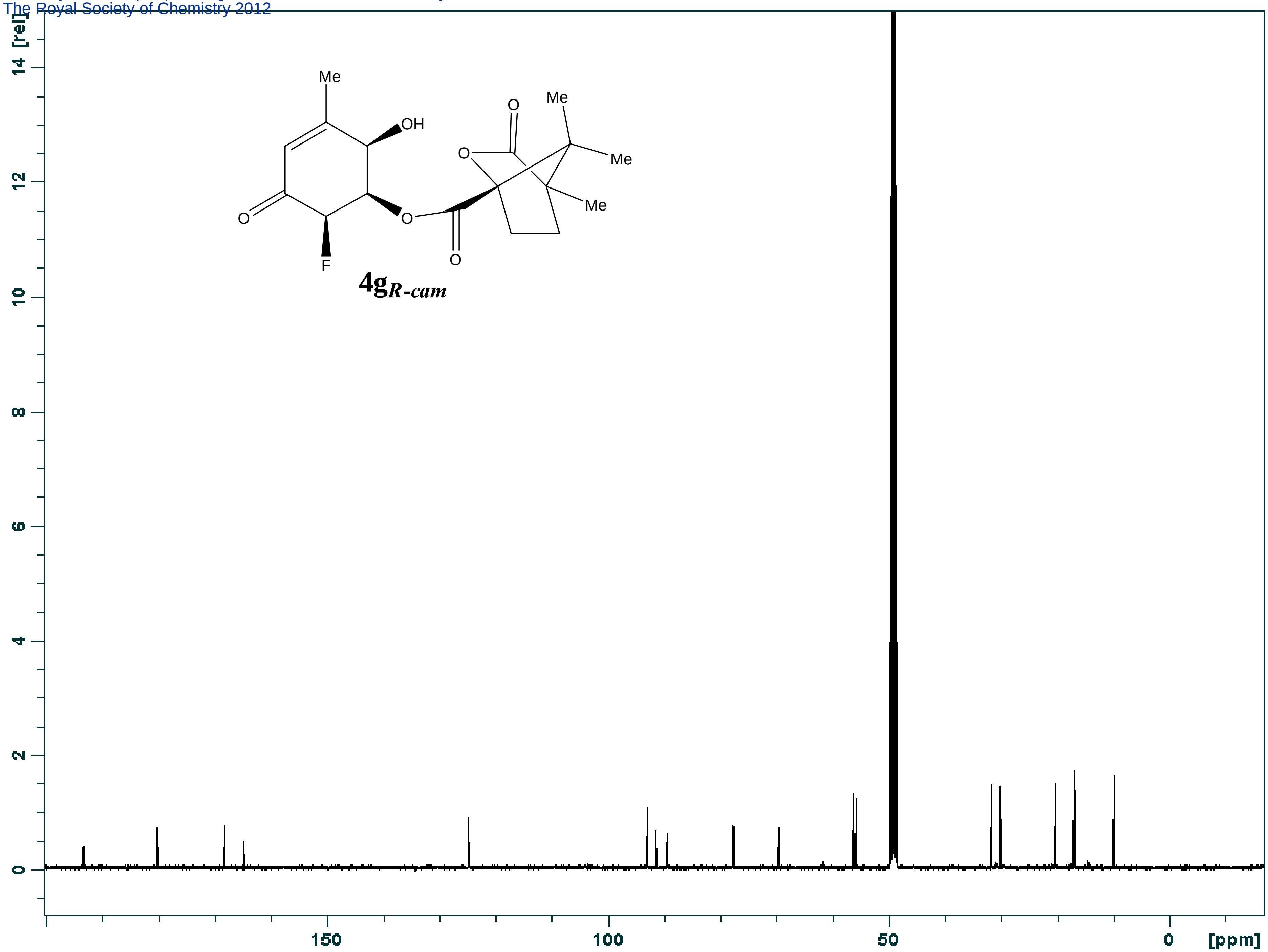


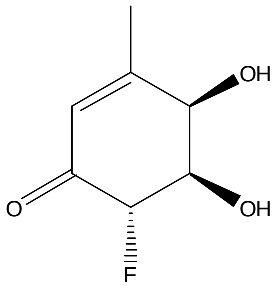
O
OH
OH
O
4f$_S$
[rel]
30
20
10
0
200
150
100
50
0
[ppm]


OH
OH
O
F
4g$_R$
7
6
5
4
3
2
1
0
ppm

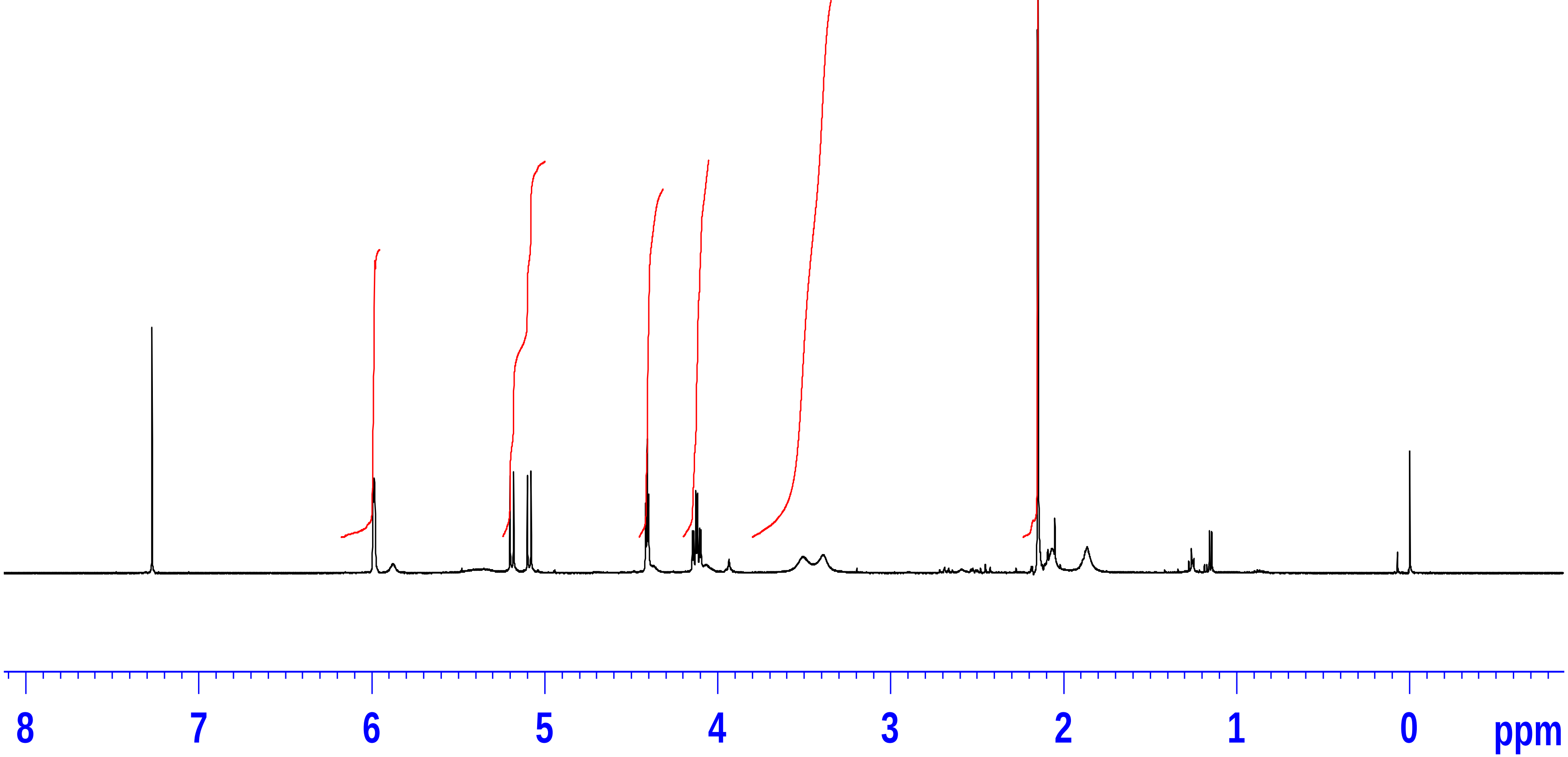

OH
OH
O
F
4g$_R$
[rel]
3
2
1
-0
200
150
100
50
0
[ppm]

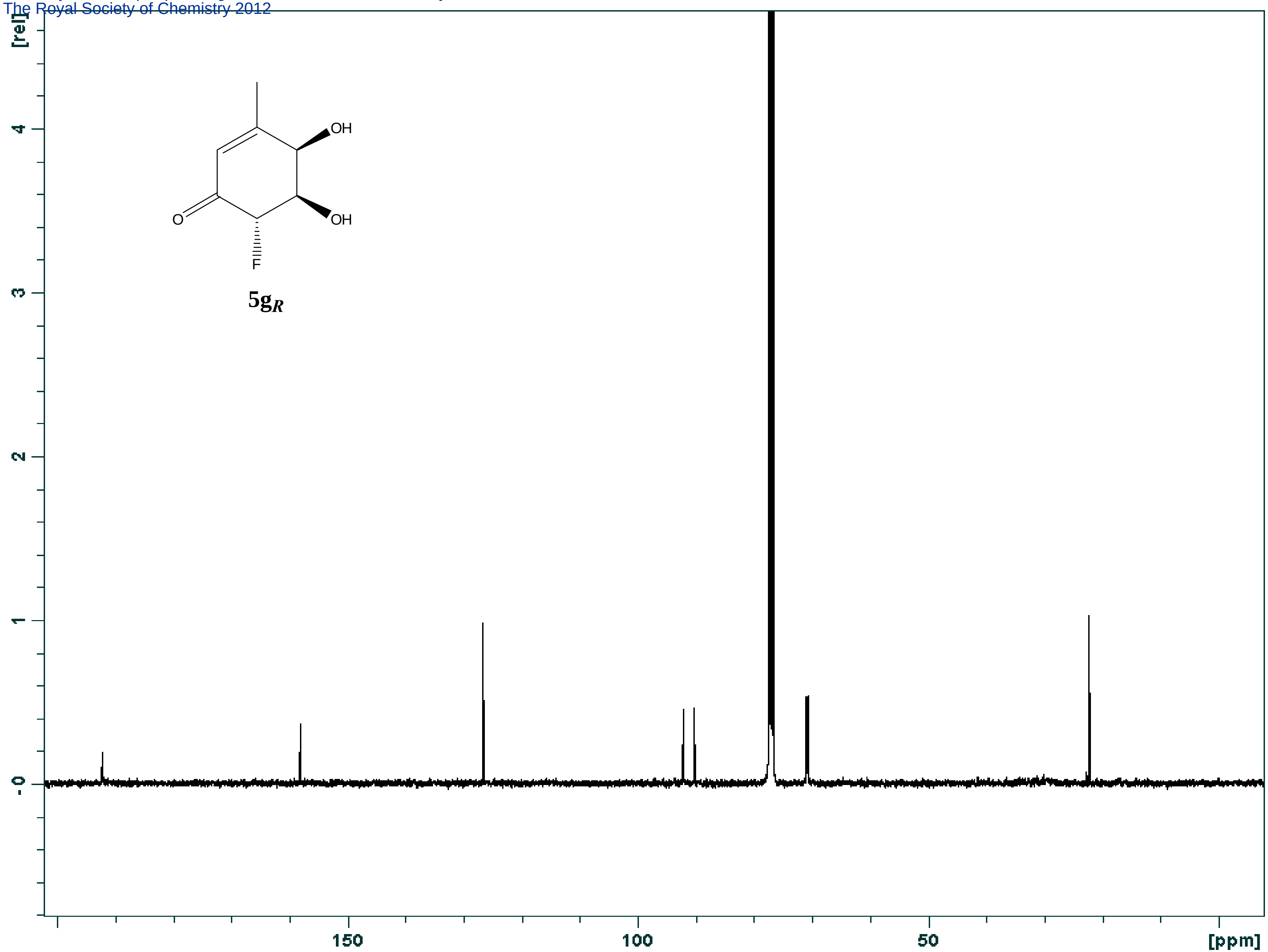

Me
OH
O
O
F
O
O
O
Me
Me
Me
4g*R-cam*
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


14 [rel]
12
10
8
6
4
2
0
Me
OH
O
F
Me
Me
Me
O
O
O
O
4g$_{R\text{-}cam}$
150
100
50
0
[ppm]

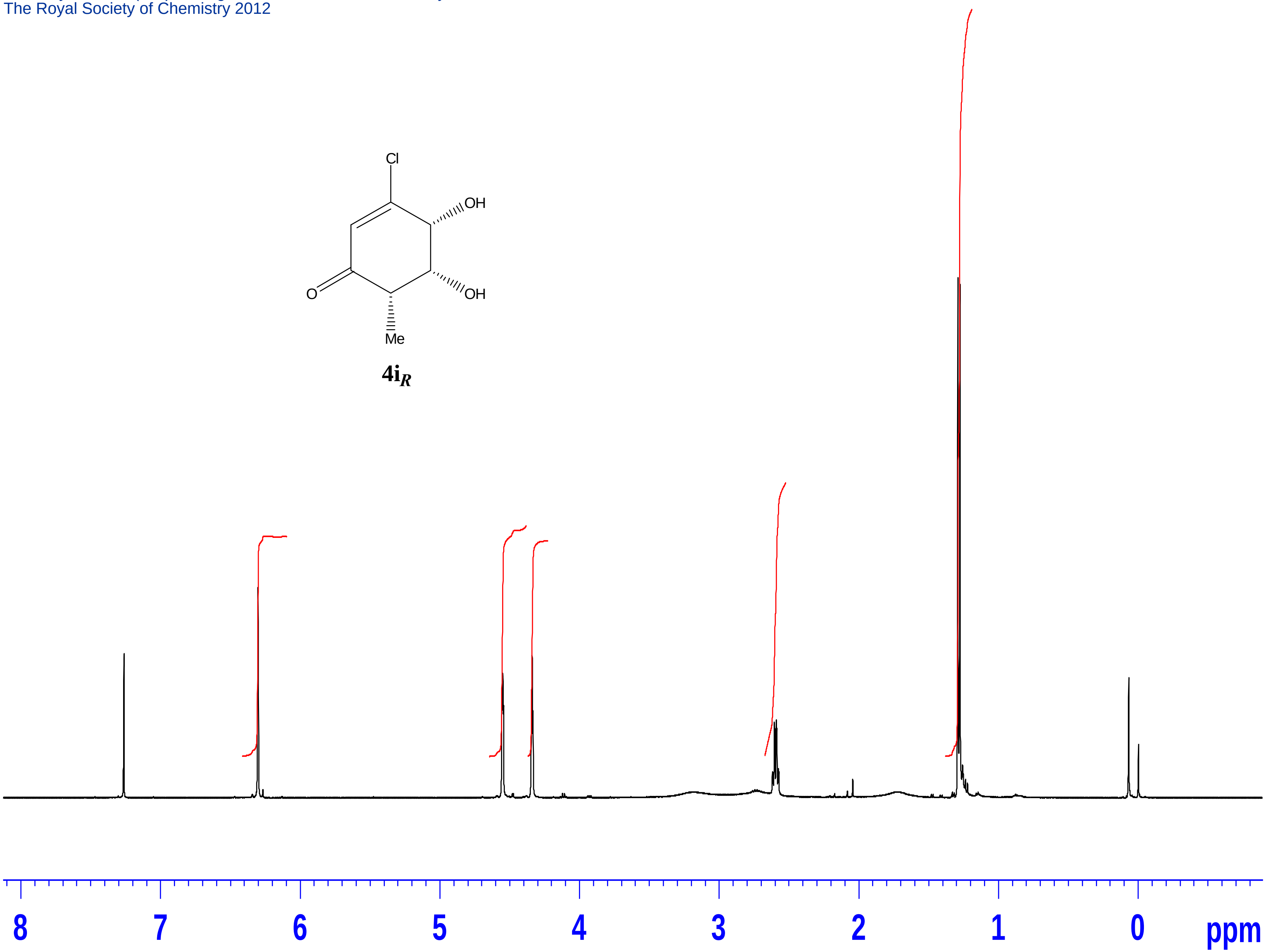


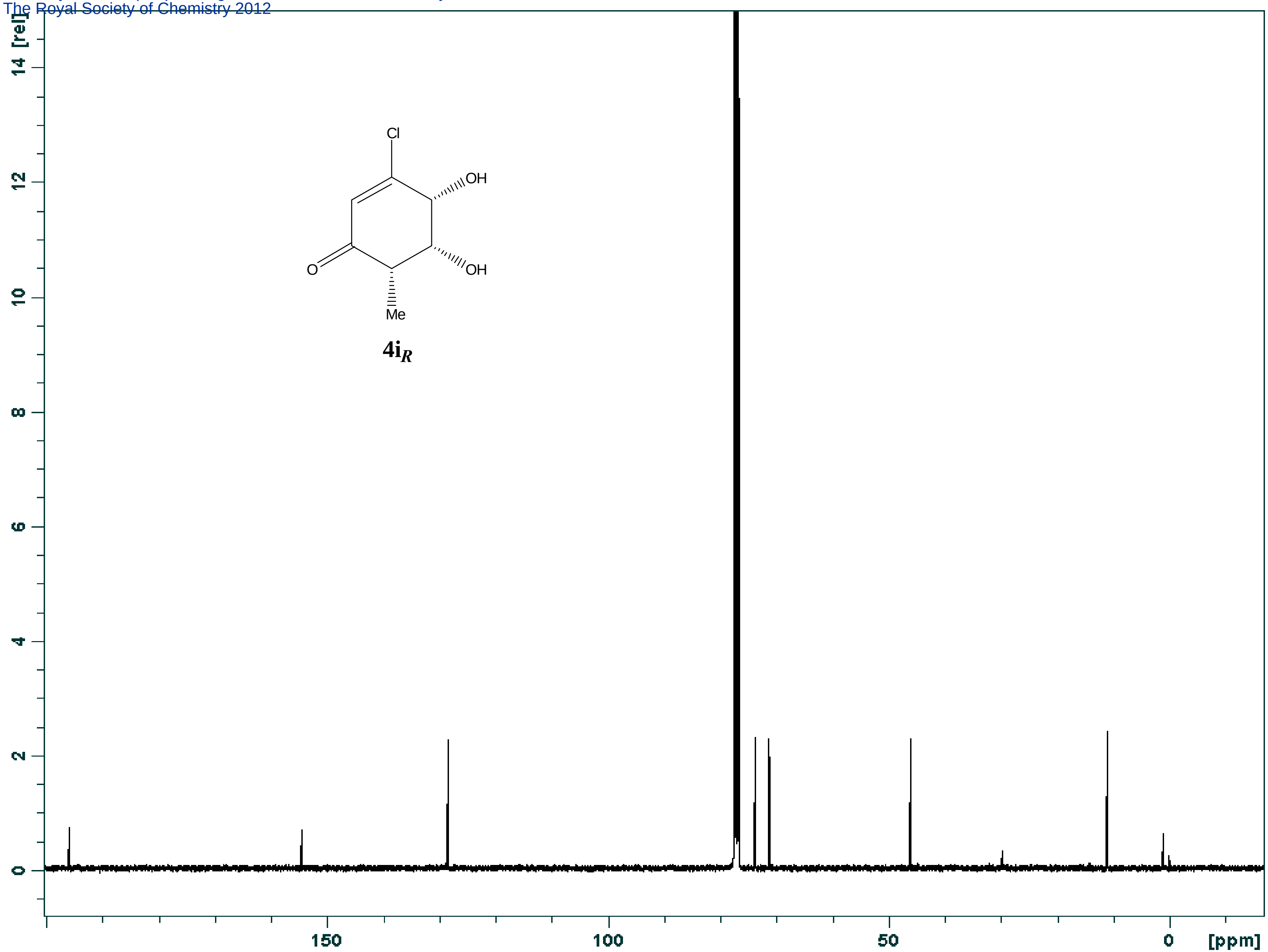
5g*R*




OH
OH
O
F
5gR
[rel]
4
3
2
1
-0
150
100
50
[ppm]

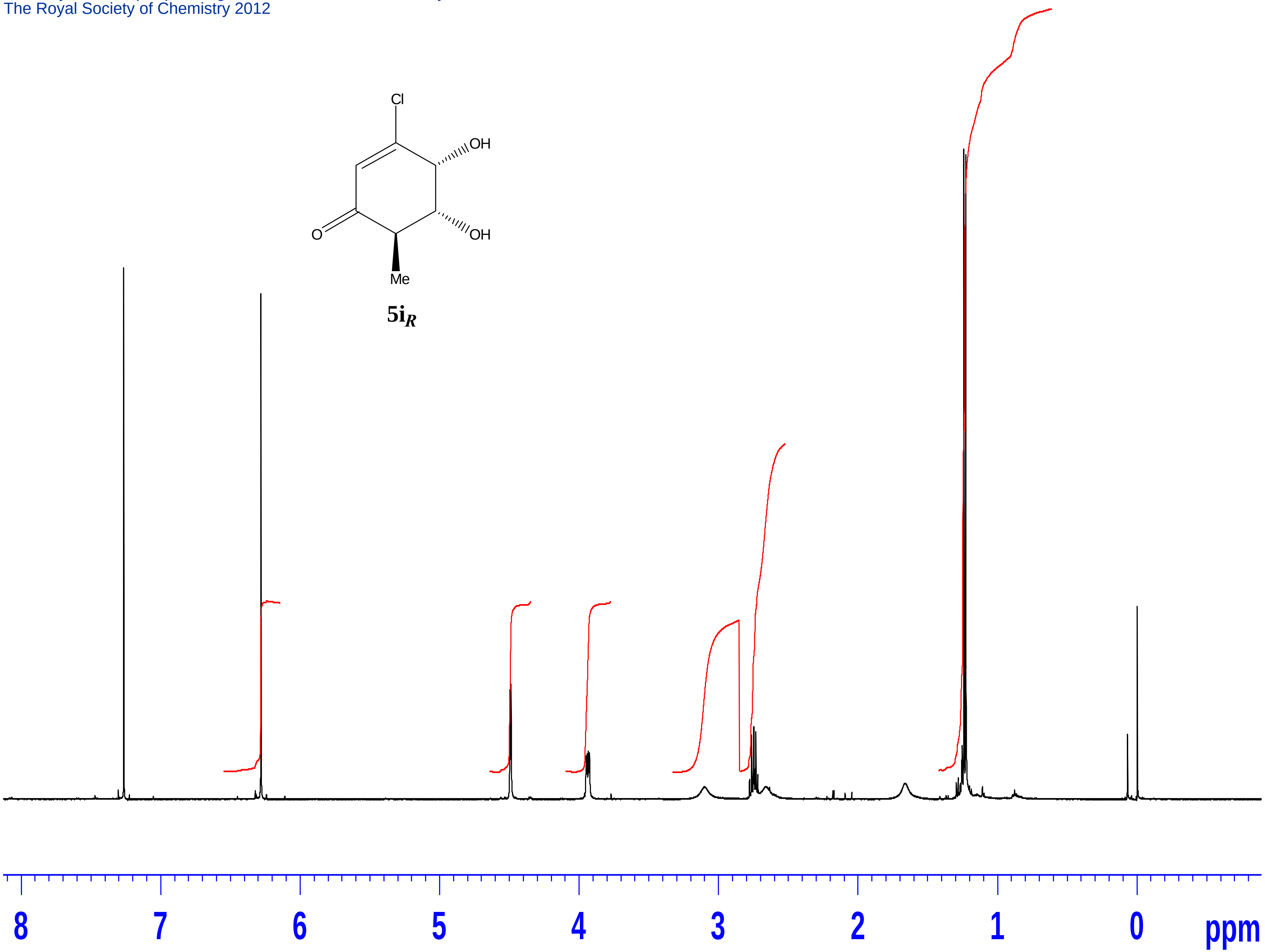
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



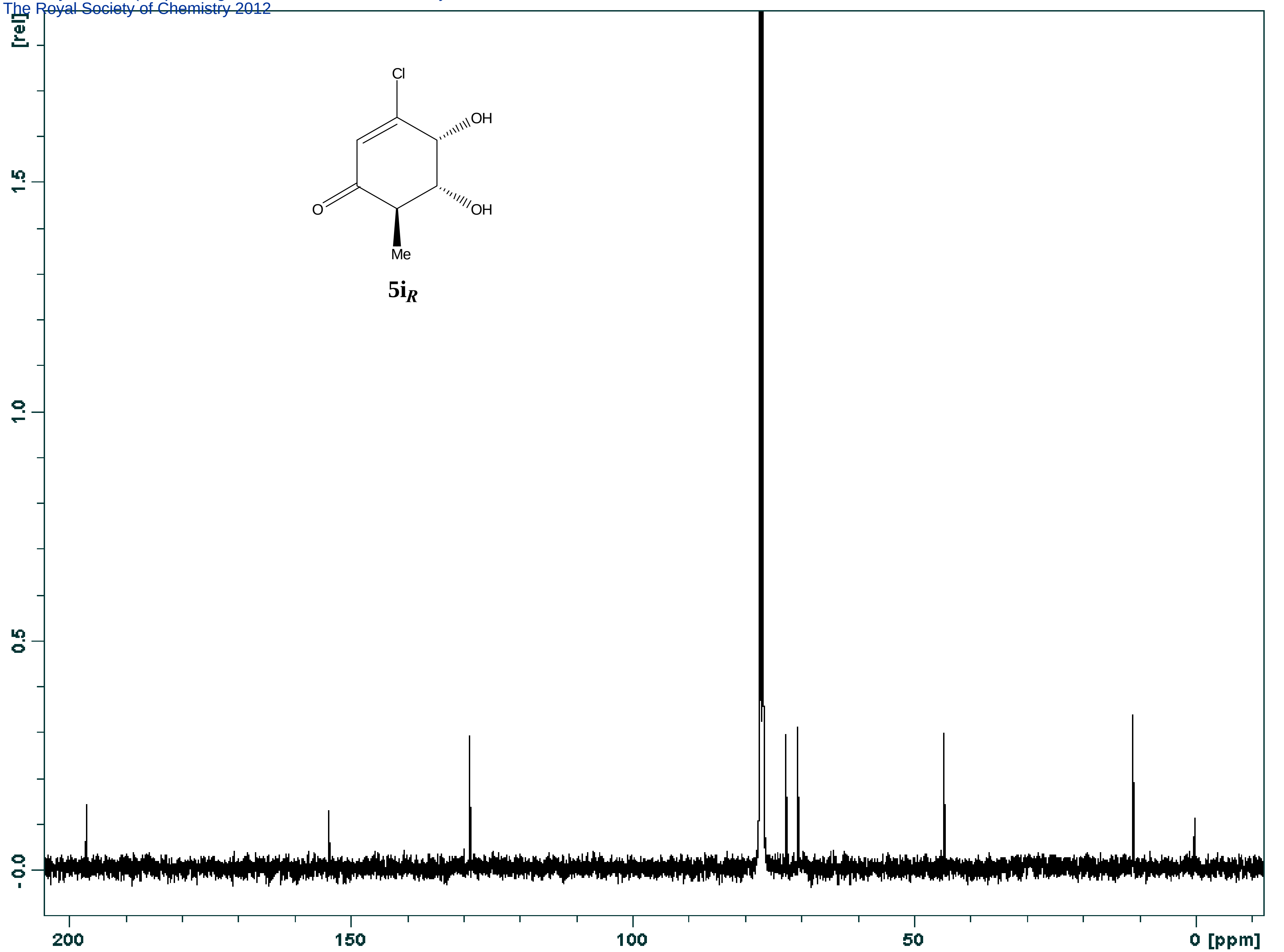


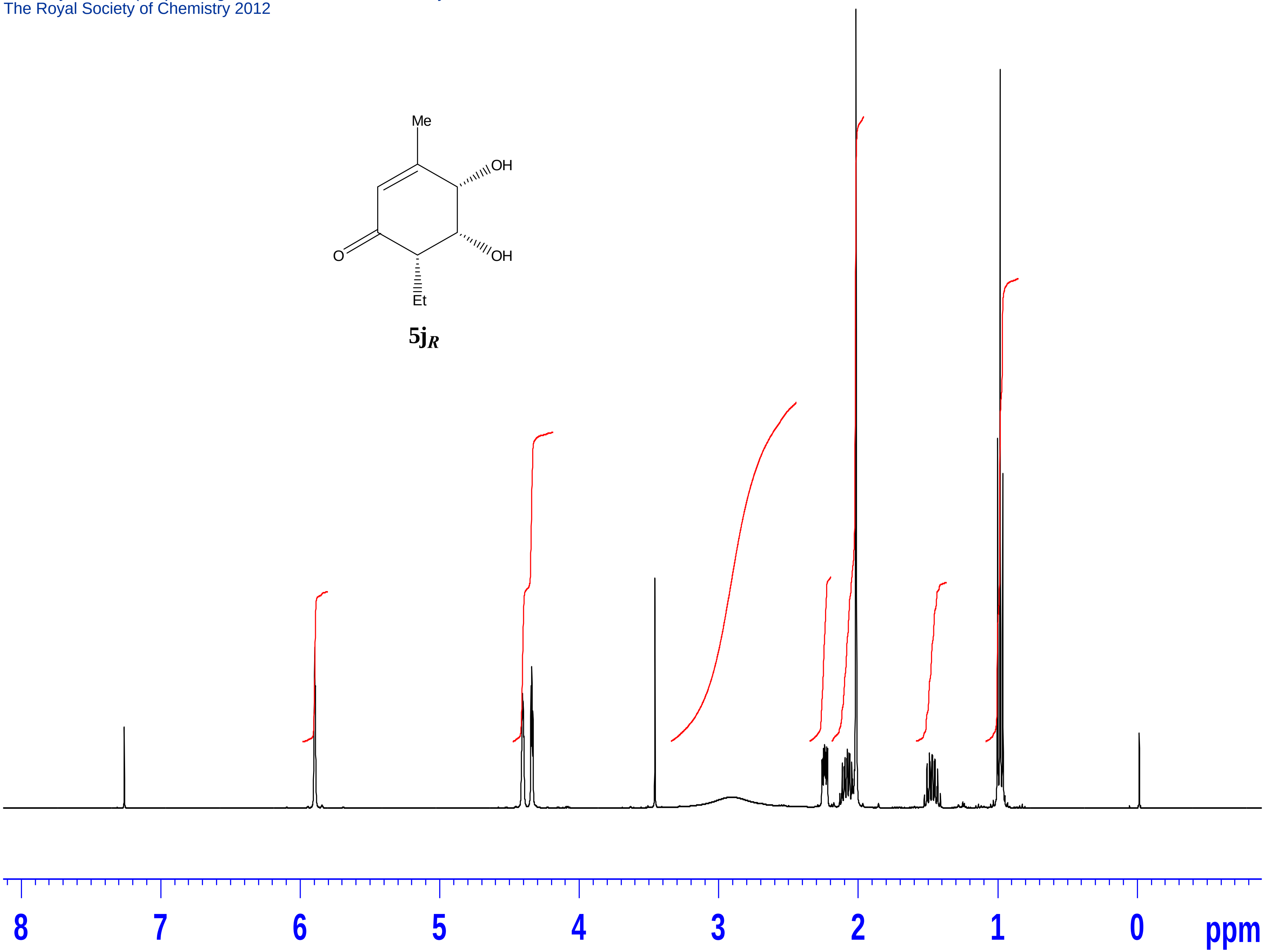
4i*R*

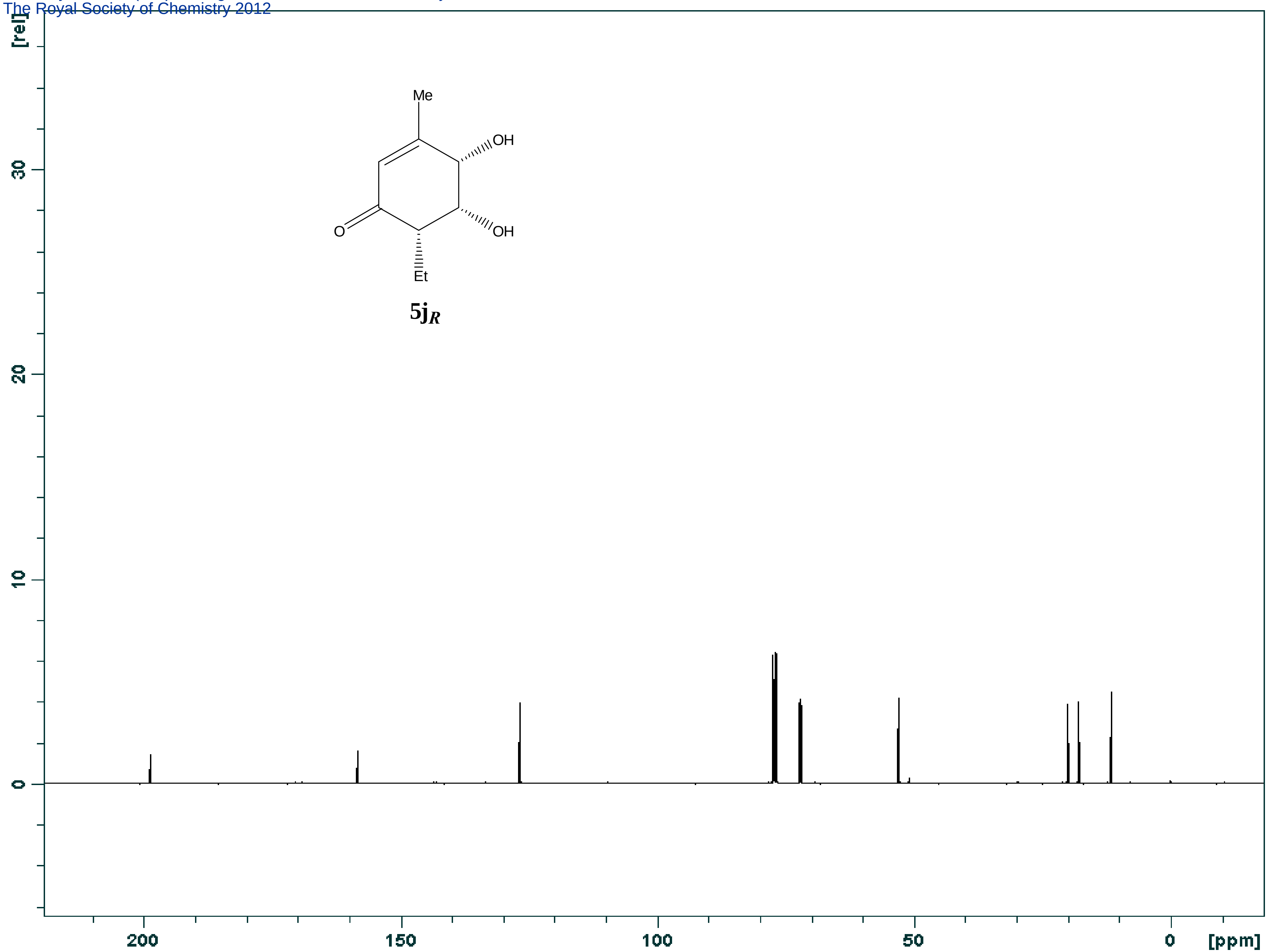
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



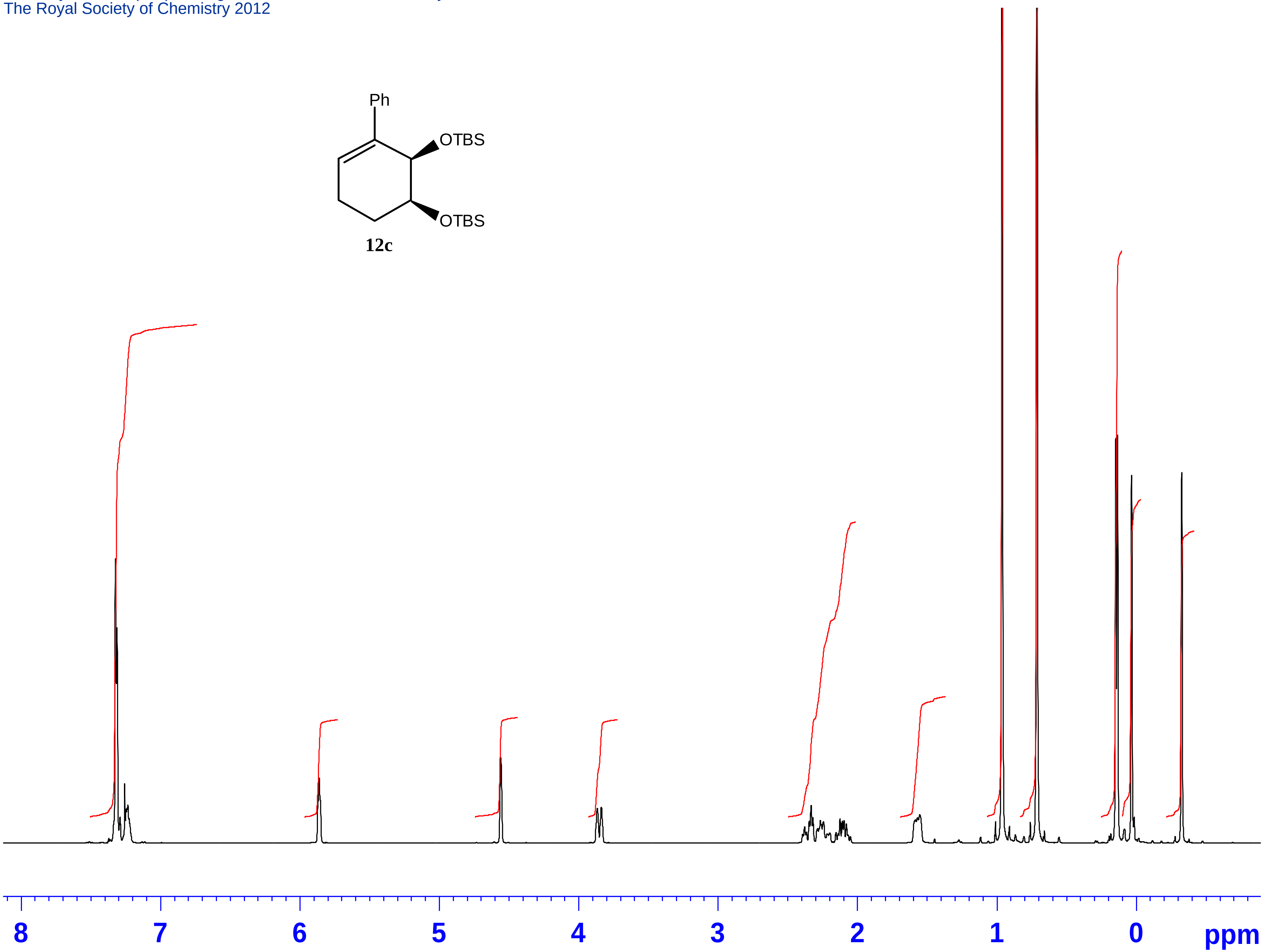
5i$_R$

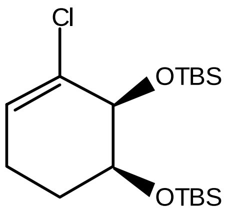

Cl
OH
OH
O
Me
5i_R
[rel]
1.5
1.0
0.5
-0.0
200
150
100
50
0 [ppm]


Me
OH
OH
O
Et
5j*R*
8
7
6
5
4
3
2
1
0
ppm

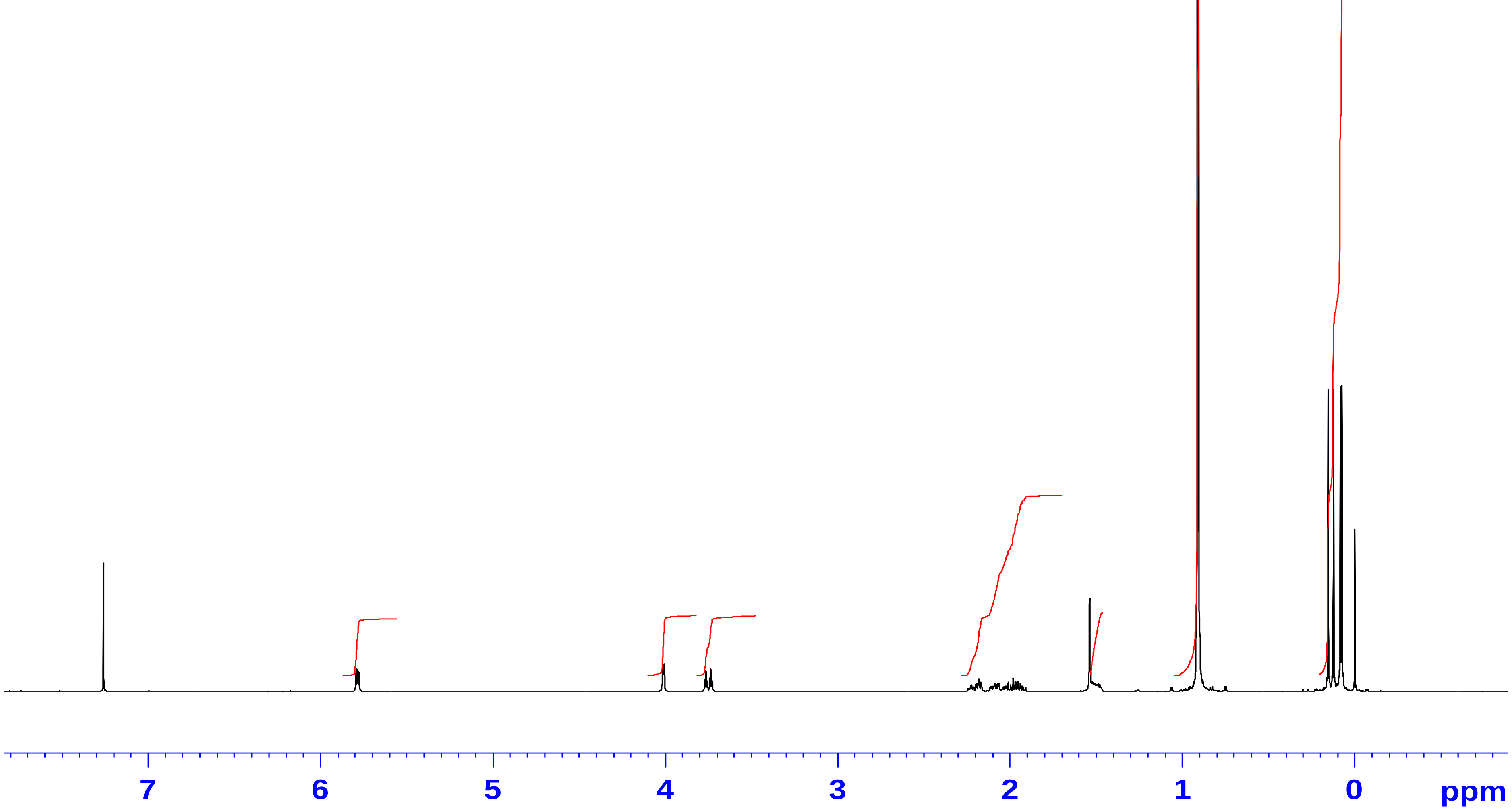

Me
OH
OH
O
Et
5j$_R$
[rel]
30
20
10
0
200
150
100
50
0
[ppm]

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

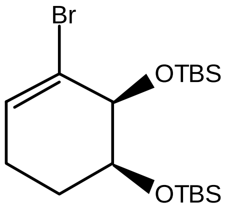




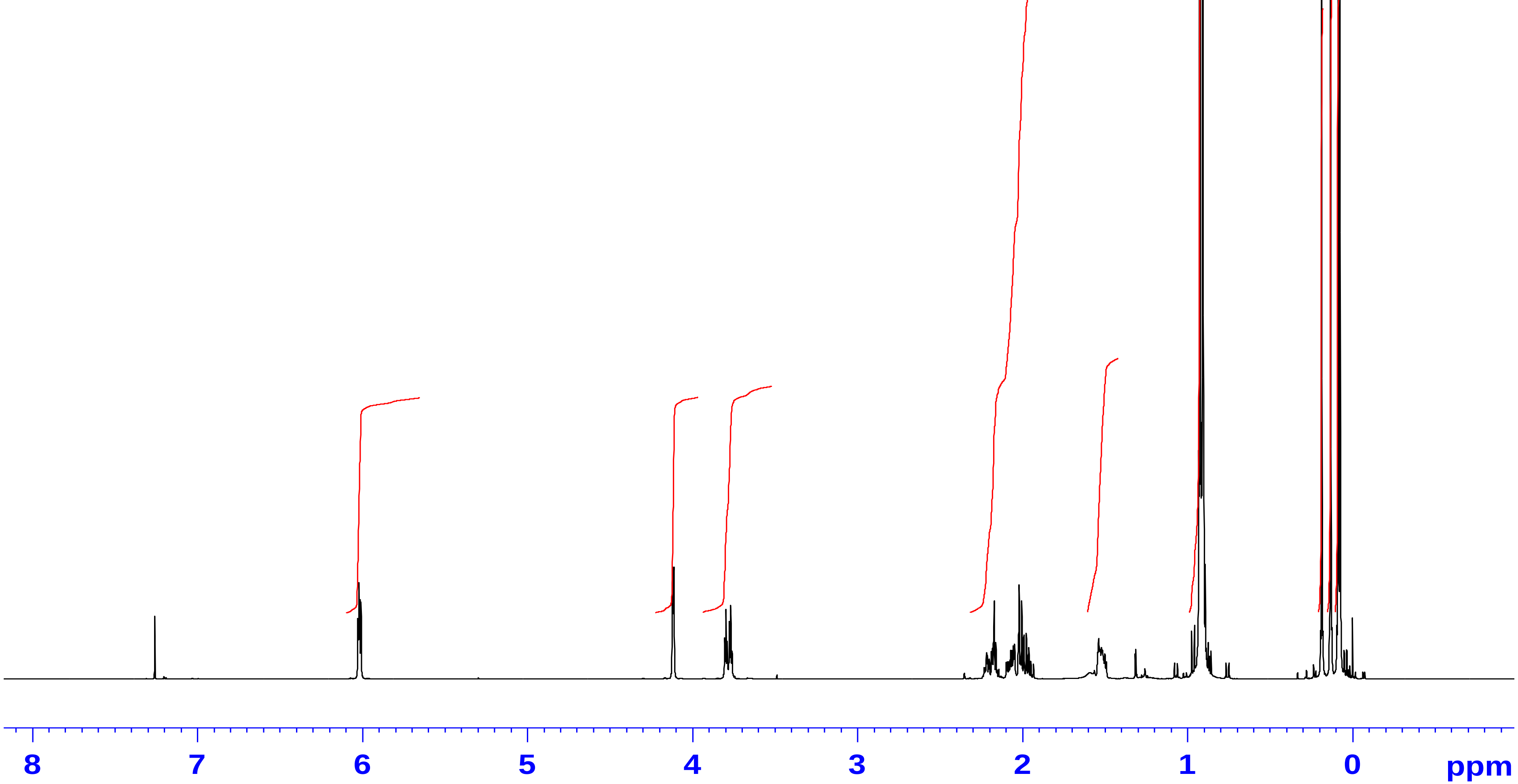
12d

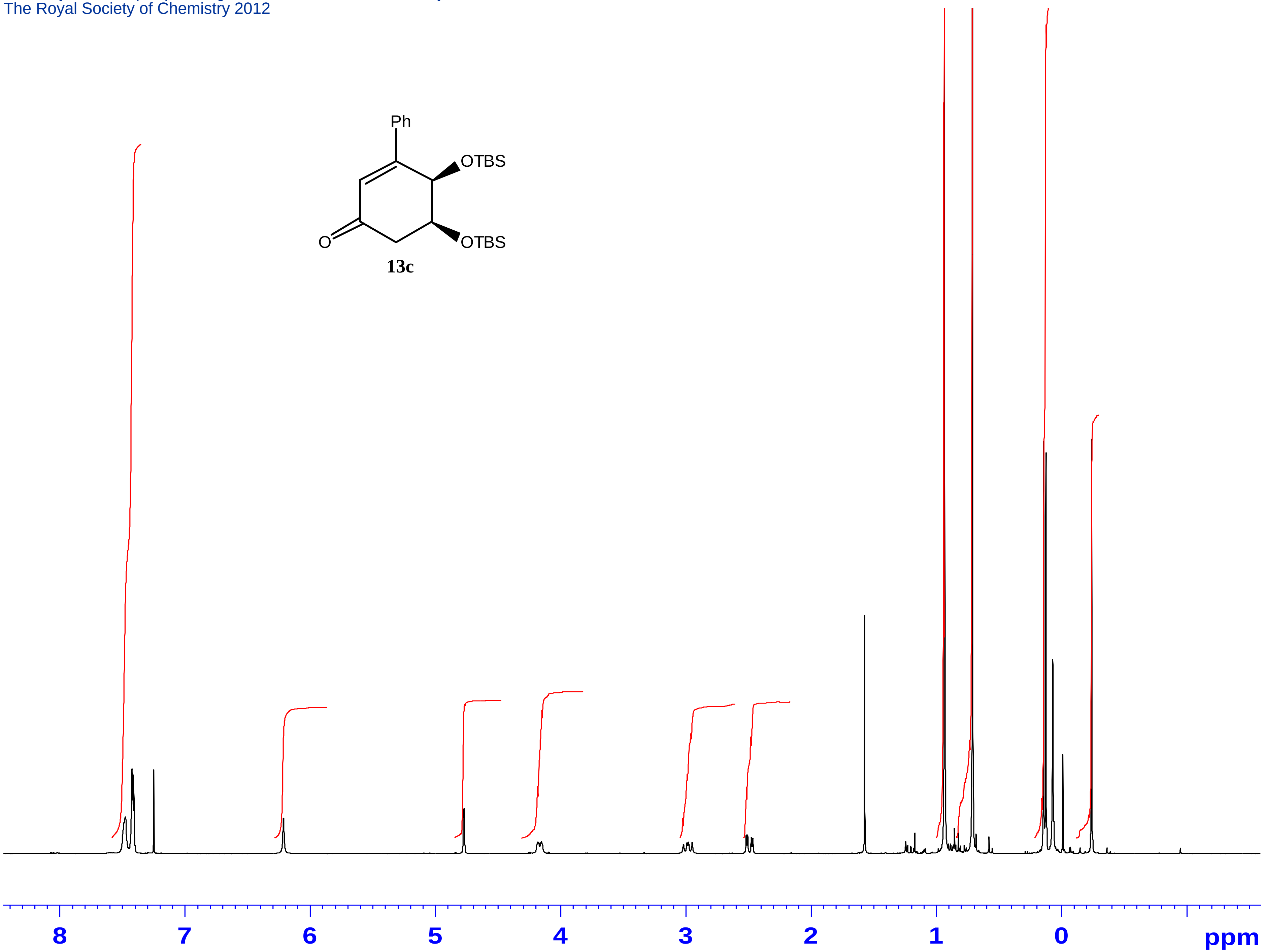


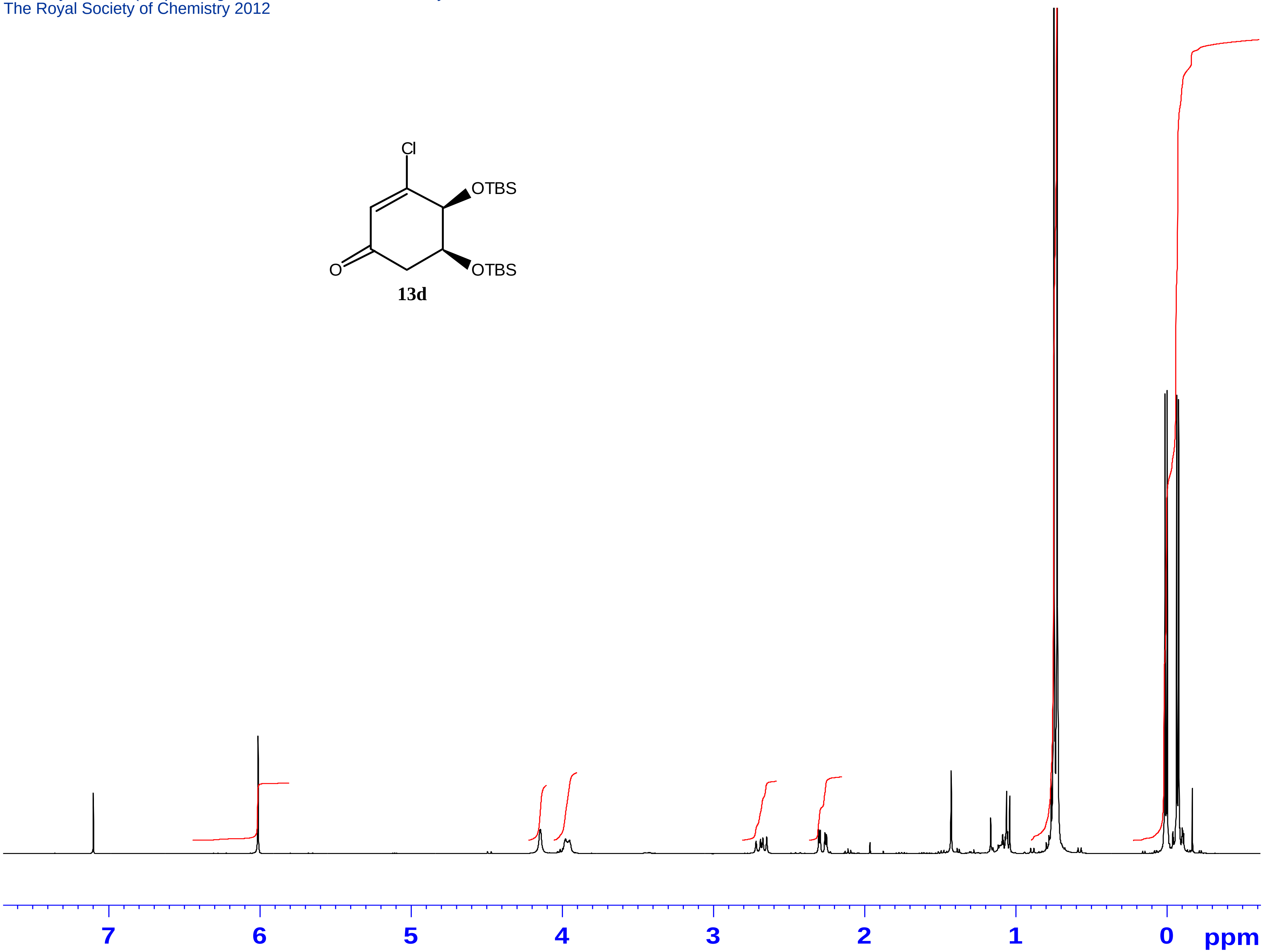
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

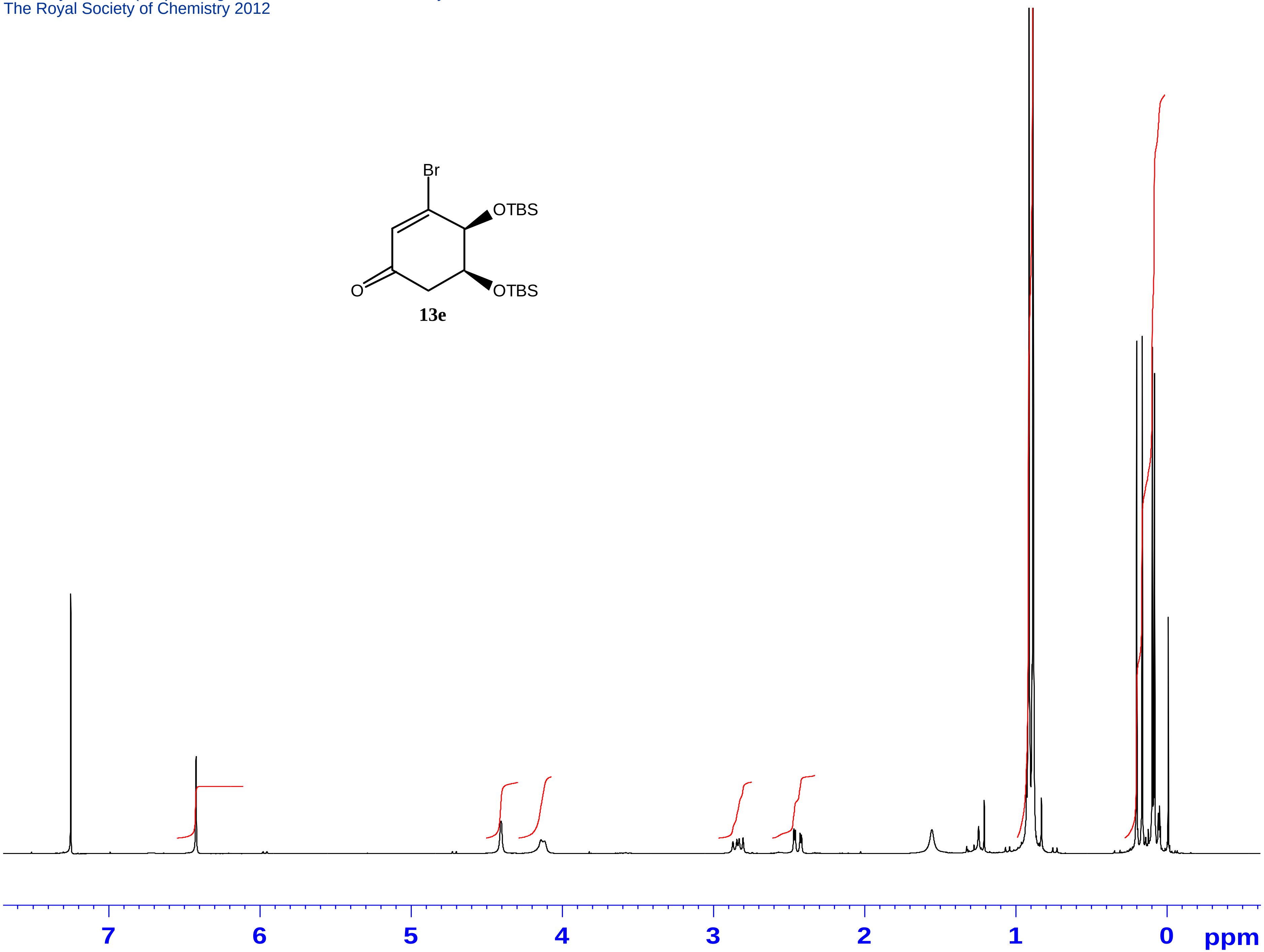


12e




Ph
OTBS
O
OTBS
13c
8
7
6
5
4
3
2
1
0
ppm


Cl
OTBS
O
OTBS
13d
7
6
5
4
3
2
1
0
ppm


Br
OTBS
OTBS
O
13e
7
6
5
4
3
2
1
0
ppm

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2012

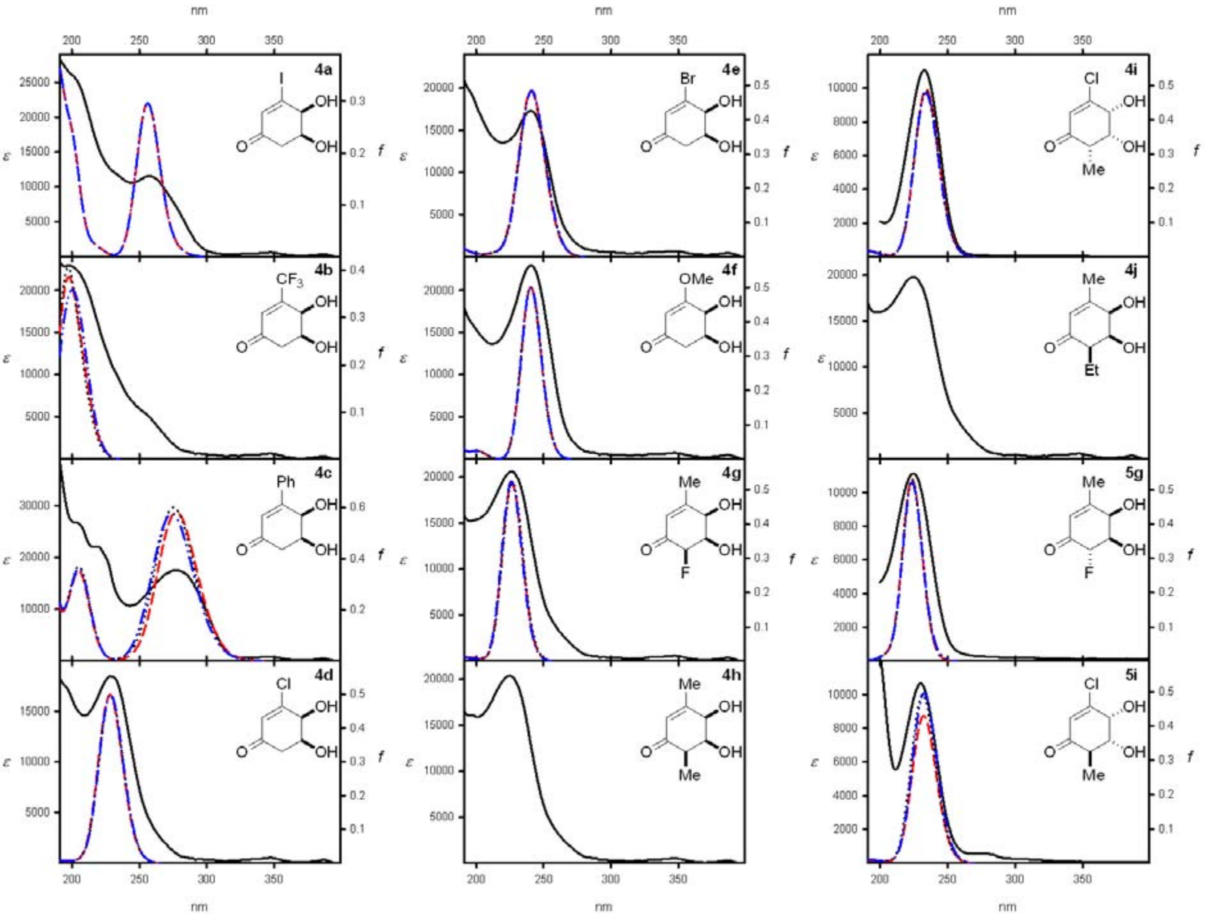


Figure A1. UV spectra spectra of *cis*-ketodiols **4a-4j**, **5g** and **5i**, experimental (in acetonitrile solutions, solid black lines) and $\Delta E_{\mathrm{B3LYP}}$ (red dashed lines), $\Delta G_{\mathrm{B3LYP}}$ (black dotted lines) and $\Delta E_{\mathrm{B2PLYP(D)}}$ (dash-dot-dot blue lines) Boltzmann averaged calculated at PCM/B2LYP/Aug-cc-pVTZ level. All calculated spectra were wavelength-corrected to match the experimental UV λ_{max}. Data for *cis*-diols **4h** and **4j** were taken from M. Kwit, J. Gawronski, D. R. Boyd, N. Sharma and M. Kaik, *Org. Biomol. Chem.* **2010**, *8*, 5635.

Computational details

Starting geometries of keto-*cis*-diols **4a**-**4g**, ***ent*-4i**, **5g** and ***ent*-5i** were obtained by optimisation at the B3LYP/6-311++G(d,p)[1] level of theory. From these geometries, for both *P* and *M* helicity enones, relaxed potential energy surfaces (PES) were obtained by changing the dihedral angles of H-C4-O-H, H-C5-O-H and, if necessary, of C2=C3-O-CH_3 and C2=C3-C_{Ar}=C_{Ar} in the range 0° to 360° by 30 degree steps. This allowed to identify the minimum energy structures which were further optimised in the acetonitrile and methanol solutions, using the polarizable continuum model (IEFPCM)[2] at the PCM/B3LYP/6-311++G(2d,2p) level of theory. The structures thus obtained were the real minimum energy conformers (no imaginary frequencies have been found). For all stable conformers the single point energy at the PCM/B2PLYP(D)/Aug-cc-pVTZ[3] were calculated. The total and free energy values were used to obtain the Boltzmann population of conformers at 298.15 K. For DFT calculations, only the results for conformers that differ from the most stable by less than 2 kcal mol^{-1} have been taken into account for further considerations, following a generally accepted protocol.[4]

The calculations of optical rotations were carried out for all stable conformers at four different wavelengths (589, 578, 546 and 436 nm), in the solvent and *in vacuo*, using the B3LYP/Aug-cc-pVTZ method. London orbitals (which ensure the origin independency of the results) have been used. Since the experimental data were recorded in methanol solution, optical rotations calculated with the use of the IEFPCM model were further taken into account.[5]

For all investigated compounds the ECD spectra were measured in acetonitrile solution and calculated at the IEFPCM/TDDFT/B2LYP/Aug-cc-pVTZ[3,6-7] level for all stable geometries optimised at the IEFPCM/B3LYP/6-311++G(2d,2p)

level, according to the procedure previously described.[8]
Note that in the case of **4a** all calculations were done using B3LYP hybrid functional and Aug-cc-pVDZ basis set for carbon, hydrogen and oxygen atoms and Aug-cc-pVDZ-PP basis set for iodine, with the use of the Conductor-like Screening Model (COSMO),[9] simulating acetonitrile or methanol solutions.

Rotatory strengths were calculated using both length and velocity representations. In the present study, the differences between the length and velocity of the calculated values of rotatory strengths were quite small and for this reason only the velocity representations were further used (see also Supplementary Information). The ECD spectra were simulated by overlapping Gaussian functions[10] for each transition, according to the procedure previously described.[11-15]

1 (a) Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004; (b) Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
2 (a) D. Marchesan, S. Coriani, C. Forzato, P. Nitti, G. Pitacco, K. Ruud, J. Phys. Chem. A **2005**, 109, 1449-1453; (b) B. Mennucci, J. Tomasi, R. Cammi, J. R. Cheeseman, M. Frisch, F. J. Devlin, S. Gabriel, P. J. Stephens, *J. Phys. Chem. A* **2002**, *106*, 6102-6113. (c) G. Scalmani, M. J. Frisch, B. Mennucci, J. Tomasi, R. Cammi, V. Barone, *J. Chem. Phys.* **2006**, *124*, 094107.
3 S. Grimme, *J. Chem. Phys.* **2006**, 124, 034108; (b) S. Grimme, F. Neese, *J. Chem. Phys.* **2007**, *127*, 154116; (c) L. Goerigk, S. Grimme, *J. Phys. Chem. A*, **2009**, *113*, 767.
4 (a) P. J. Stephens, D. M. McCann, E. Butkus, S. Stončius, J. R. Cheeseman, M. J. Frisch, *J. Org. Chem.* **2004**, *69*, 1948-1958; (b) P. J. Stephens, F. J. Devlin, J. R. Cheeseman, M. J. Frisch, O. Bortolini, P. Besse, *Chirality* **2003**, *15*, S57.
5 (a) M. Pecul, K. Ruud, T. Helgaker, *Chem. Phys. Lett.* **2004**, *388*, 110; (b) T. Helgaker, K. Ruud, K. L. Bak, P. Jørgensen, J. Olsen, *Faraday Discuss.* **1994**, *99*, 165.
6 R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Koelmel, *Chem. Phys. Lett.* **1989**, *162*, 165 (see also www.turbomole-gmbh.com for an overview of the TURBOMOLE program).
7 J. Gawronski, M. Kwit, P. Skowronek, *Org. Biomol. Chem.* **2009**, 7, 1562.
8 M. Kwit, J. Gawronski, D. R. Boyd, N. Sharma and M. Kaik, *Org. Biomol. Chem.* **2010**, *8*, 5635.
9 (a) A. Klamt and G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2*, **1993**, *5*, 799; b) A. Klamt and V. Jonas, *J. Chem. Phys.*, **1996**, *105*, 9972.
10 (a) N. Harada, P. Stephens, *Chirality*, **2010**, *22*, 229-233; (b) N. M. O'Boyle, A. L. Tenderholt, K. M. Langner. *J. Comp. Chem.*, **2008**, *29*, 839-845.
11 J Gawronski, M. Kwit, D. R. Boyd, N. D. Sharma, J. F. Malone, A. Drake, *J. Am. Chem. Soc.* **2005**, *127*, 4308.
12 M. Kwit, N. D. Sharma, D. R. Boyd, J. Gawronski, *Chem. Eur. J.* **2007**, *13*, 5812.
13 M. Kwit, N. D. Sharma, D. R. Boyd, J. Gawronski, *Chirality* **2008**, *20*, 609.
14 M. Kwit, J. Gawronski, D.R. Boyd, N. D. Sharma, M. Kaik, R. A. More O'Ferrall, J. S. Kudavalli, *Chem. Eur. J.* **2008**, *14*, 11500.

15 M. Kwit, J. Gawronski, L. Sbircea, N. D. Sharma, M. Kaik, D. R. Boyd, *Chirality*, **2009**, *21*, E37.

Table A1. Total energies (E_{tot}, in Hartree), relative energies (ΔE, ΔG in kcal mol^{-1}) and percentage populations of individual conformers of **4a-4g**, ***ent*-4i**, **5g** and ***ent*-5i** calculated at the PCM(MeCN)/B3LYP/6-311++G(2d,2p) level.

Conformer[a]	E_{tot}	ΔE	Population	ΔG	Population
4a(*M*1)[b]	-754.38000739	0.87	5	1.02	4
4a(*M*2)[b]	-754.38083059	0.35	13	0.16	18
4a(*M*3)[b]	-754.37977744	1.01	4	0.96	4
4a(*M*4)[b]	-754.38059932	0.50	10	0.32	13
4a(*P*1)[b]	-754.38010693	0.80	6	1.36	2
4a(*P*2)[b]	-754.38138924	0.00	23	0.11	19
4a(*P*3)[b]	-754.38122343	0.10	21	0.00	24
4a(*P*4)[b]	-754.38116156	0.14	18	0.22	16
4b(*M*2)	-796.43299657	0.15	17	0.00	25
4b(*M*3)	-796.43247009	0.48	10	0.33	14
4b(*M*4)	-796.43317079	0.04	21	0.14	19
4b(*P*1)	-796.43013745	1.94	1	2.44	
4b(*P*2)	-796.43294182	0.18	16	0.57	9
4b(*P*3)	-796.43282629	0.25	14	0.23	17
4b(*P*4)	-796.43322992	0.00	22	0.27	16
4c(*M*1a)	-690.389609	0.58	8	0.61	6
4c(*M*1b)	-690.390036	0.31	12	0.71	5
4c(*M*2a)	-690.389919	0.38	11	0.00	18
4c(*M*2b)	-690.389171	0.85	5	0.61	6
4c(*M*3a)	-690.389092	0.90	5	0.34	10
4c(*M*3b)	-690.38964	0.56	8	0.26	11
4c(*M*4a)	-690.389807	0.45	10	0.33	10
4c(*M*4b)	-690.39053	0.00	21	0.16	13
4c(*P*1a)	-690.388571	1.23	3	1.24	2
4c(*P*1b)	-690.38565	3.06		3.05	
4c(*P*2a)	-690.389426	0.69	6	0.5	7
4c(*P*2b)	-690.386438	2.57		2.16	
4c(*P*3a)	-690.38932	0.76	6	0.63	6
4c(*P*3b)	-690.386616	2.46		1.46	1
4c(*P*4a)	-690.38921	0.83	5	0.76	5
4c(*P*4b)	-690.386315	2.65		2.28	

4d(*M*2)	-918.90418258	0.56	8	0.72	9
4d(*M*3)	-918.90503293	0.02	21	0.41	13
4d(*M*4)	-918.90242934	1.66	1	1.91	1
4d(*P*1)	-918.90464944	0.26	14	0.00	27
4d(*P*2)	-918.90506780	0.00	22	0.30	16
4d(*P*3)	-918.90473508	0.21	15	0.44	13
4d(*P*4)	-918.90495274	0.07	19	0.15	21
4e(*M*1)	-3032.81705546	1.08	3	1.76	1
4e(*M*2)	-3032.81858179	0.13	17	0.20	19
4e(*M*3)	-3032.81794225	0.53	9	0.50	11
4e(*M*4)	-3032.81864704	0.09	18	0.30	16
4e(*P*1)	-3032.81616632	1.64	1	2.24	
4e(*P*2)	-3032.81838173	0.25	14	0.43	12
4e(*P*3)	-3032.81878449	0.00	22	0.33	15
4e(*P*4)	-3032.81853489	0.16	16	0.00	26
4f(*M*1a)	-573.85036476	1.13	4	1.49	2
4f(*M*1b)	-573.84535663	4.27		4.38	
4f(*M*2a)	-573.85216017	0.00	28	0.00	23
4f(*M*2b)	-573.84641244	3.61		3.47	
4f(*M*3a)	-573.85126861	0.56	11	0.06	21
4f(*M*3b)	-573.84616815	3.76		3.23	
4f(*M*4a)	-573.85195105	0.13	22	0.00	23
4f(*M*4b)	-573.84678075	3.38		2.93	
4f(*P*1a)	-573.84908161	1.93	1	7.13	
4f(*P*1b)	-573.84195287	6.41		5.99	
4f(*P*2b)	-573.84331373	5.55		3.88	
4f(*P*3a)	-573.85206462	0.06	25	0.07	21
4f(*P*3b)	-573.84368279	5.32		4.82	
4f(*P*4a)	-573.85115333	0.63	9	0.53	10
4f(*P*4b)	-573.84341928	5.48		4.79	
4g(*M*2)	-597.87503669	3.40		3.11	
4g(*M*3)	-597.87380314	4.17		0.43	22
4g(*M*4)	-597.87359201	4.31		3.90	

4g(*P*1)	-597.87678554	2.30		2.88	
4g(*P*2)	-597.88045504	0.00	65	0.00	45
4g(*P*4)	-597.87987332	0.37	35	0.19	33
***ent*-4i**(*M*1)	-958.213616	3.24		3.37	
***ent*-4i**(*M*2)	-958.2153897	2.12		2.45	
***ent*-4i**(*M*3)	-958.2138227	3.11		2.90	
***ent*-4i**(*M*4)	-958.2145679	2.64		2.95	
***ent*-4i**(*P*1)	-958.2172679	0.94	9	1.24	5
***ent*-4i**(*P*2)	-958.218772	0.00	44	0.11	33
***ent*-4i**(*P*3)	-958.2184069	0.23	30	0.00	41
***ent*-4i**(*P*4)	-958.2179049	0.54	17	0.40	21
5g(*M*1)	-597.87827223	1.16	6	0.88	9
5g(*M*2)	-597.87951638	0.38	25	0.2	29
5g(*M*3)	-597.88011916	0.00	48	0.00	41
5g(*M*4)	-597.87933478	0.49	21	0.38	21
5g(*P*1)	-597.87314245	4.38		4.43	
5g(*P*2)	-597.87615153	2.49		2.29	
5g(*P*4)	-597.87565705	2.80		2.70	
***ent*-5i**(*M*1)	-958.2172436	0.56	11	1.06	6
***ent*-5i**(*M*2)	-958.2181375	0.00	29	0.00	39
***ent*-5i**(*M*4)	-958.2176604	0.30	18	0.34	22
***ent*-5i**(*P*1)	-958.2161766	1.23	4	1.81	2
***ent*-5i**(*P*2)	-958.2175949	0.34	16	0.84	9
***ent*-5i**(*P*3)	-958.2174446	0.43	14	0.56	15
***ent*-5i**(*P*4)	-958.2168958	0.78	8	1.06	7

[a] Labels a-b refer to the rotamers due to the OMe or Ph substituents; [b] optimized at the COSMO(MeCN)/B3LYP/Aug-cc-pVDZ level.

Table A2. Total energies (E_{tot}, in Hartree), relative energies (ΔE, ΔG in kcal mol^{-1}) and percentage populations of individual conformers of **4a-4g**, ***ent*-4i**, **5g** and ***ent*-5i** calculated at the PCM(MeOH)/B3LYP/6-311++G(2d,2p) level.

Conformer[a]	E_{tot}	ΔE	Population	ΔG	Population
4a(*M*1)[b]	-754.379912	0.84	6	0.63	7
4a(*M*2)[b]	-754.380705	0.34	13	0.78	5
4a(*M*3)[b]	-754.379676	0.99	4	0.42	10
4a(*M*4)[b]	-754.380455	0.50	10	0.21	14
4a(*P*1)[b]	-754.379975	0.80	6	0.16	15
4a(*P*2)[b]	-754.381254	0.00	23	0.23	13
4a(*P*3)[b]	-754.381088	0.10	20	0.00	20
4a(*P*4)[b]	-754.381007	0.15	18	0.14	16
4b(*M*1)	-796.419509	0.86	6	1.09	4
4b(*M*2)	-796.420779	0.06	24	0.00	27
4b(*M*3)	-796.419417	0.91	6	0.16	21
4b(*M*4)	-796.420386	0.31	16	0.16	21
4b(*P*1)	-796.41917	1.07	5	1.68	2
4b(*P*2)	-796.420874	0.00	27	0.33	16
4b(*P*4)	-796.420375	0.31	16	0.62	9
4c(*M*1a)	-690.3895368	0.58	8	0.62	6
4c(*M*1b)	-690.3899706	0.30	12	0.71	5
4c(*M*2a)	-690.3898505	0.38	11	0.00	17
4c(*M*2b)	-690.389098	0.85	5	0.64	6
4c(*M*3a)	-690.3890224	0.90	5	0.35	10
4c(*M*3b)	-690.3895757	0.55	8	0.27	11
4c(*M*4a)	-690.3897271	0.46	10	0.34	10
4c(*M*4b)	-690.3904564	0.00	21	0.17	13
4c(*P*1a)	-690.3885016	1.23	3	1.36	2
4c(*P*1b)	-690.3855818	3.06		3.06	
4c(*P*2a)	-690.3893495	0.69	6	0.51	7
4c(*P*2b)	-690.3863629	2.57		2.18	
4c(*P*3a)	-690.3892501	0.76	6	0.63	6
4c(*P*3b)	-690.3865445	2.45		1.48	2
4c(*P*4a)	-690.3891194	0.84	5	0.78	5
4c(*P*4b)	-690.3862331	2.65		2.29	

4d(*M*1)	-918.8913331	0.80	6	1.32	3
4d(*M*2)	-918.8923292	0.17	17	0.31	17
4d(*M*3)	-918.8910392	0.98	4	0.55	11
4d(*M*4)	-918.8919791	0.39	11	0.63	10
4d(*P*1)	-918.8913462	0.79	6	1.27	3
4d(*P*2)	-918.8925969	0.01	22	0.33	16
4d(*P*3)	-918.8926013	0.00	22	0.00	28
4d(*P*4)	-918.891996	0.38	12	0.50	12
4e(*M*1)	-3032.81715796	1.10	4	1.63	1
4e(*M*2)	-3032.81859734	0.20	18	0.00	23
4e(*M*3)	-3032.81784649	0.67	9	0.47	10
4e(*M*4)	-3032.81856322	0.22	17	0.22	17
4e(*P*1)	-3032.81622499	1.69	1	2.05	
4e(*P*2)	-3032.81836769	0.34	14	0.32	13
4e(*P*3)	-3032.81891445	0.00	25	0.11	19
4e(*P*4)	-3032.81821873	0.44	12	0.20	17
4f(*M*1a)	-573.8394912	1.21	6	1.64	3
4f(*M*1b)	-573.8340909	4.60		4.66	
4f(*M*2a)	-573.8405366	0.55	18	0.64	17
4f(*M*2b)	-573.8336237	4.89		4.51	
4f(*M*3a)	-573.8393641	1.29	5	1.00	9
4f(*M*3b)	-573.8338856	4.73		4.12	
4f(*M*4a)	-573.8402057	0.76	12	1.05	8
4f(*M*4b)	-573.8346764	4.23		4.17	
4f(*P*1a)	-573.8390678	1.48	4	1.8	2
4f(*P*1b)	-573.832109	5.84		5.79	
4f(*P*2a)	-573.8395862	1.15	6	1.26	6
4f(*P*2b)	-573.8324129	5.65		5.04	
4f(*P*3a)	-573.8414202	0.00	45	0.00	50
4f(*P*3b)	-573.8311129	6.47		5.64	
4f(*P*4a)	-573.8388952	1.58	4	1.55	5
4f(*P*4b)	-573.8315158	6.22		5.98	
4g(*M*1)	-597.8645665	1.81	3	2.04	

4g(*M*2)	-597.8625819	3.05		2.66	
4g(*M*3)	-597.8604377	4.40		3.52	
4g(*M*4)	-597.8609482	4.08		3.70	
4g(*P*1)	-597.8648995	1.60	6	1.75	4
4g(*P*2)	-597.867449	0.00	73	0.00	80
4g(*P*4)	-597.8661301	0.83	18	0.96	16
***ent*-4i**(*M*1)	-958.2135581	3.23		3.34	
***ent*-4i**(*M*2)	-958.2153355	2.11		2.44	
***ent*-4i**(*M*3)	-958.2137648	3.10		2.89	
***ent*-4i**(*M*4)	-958.214504	2.64		2.94	
***ent*-4i**(*P*1)	-958.217207	0.94	9	1.23	5
***ent*-4i**(*P*2)	-958.2187039	0.00	44	0.10	34
***ent*-4i**(*P*3)	-958.2183477	0.22	30	0.00	40
***ent*-4i**(*P*4)	-958.2178286	0.55	17	0.39	21
5g(*M*1)	-597.8655892	0.56	14	1.16	7
5g(*M*2)	-597.8662542	0.14	28	0.40	25
5g(*M*3)	-597.8664815	0.00	35	0.00	48
5g(*M*4)	-597.866004	0.30	22	0.53	20
5g(*P*1)	-597.8615117	3.12		3.54	
5g(*P*2)	-597.8634057	1.93	1	2.31	
5g(*P*4)	-597.8629247	2.23		2.56	
***ent*-5i**(*M*1)	-958.217183	0.57	11	1.06	6
***ent*-5i**(*M*2)	-958.218084	0.00	29	0.00	39
***ent*-5i**(*M*4)	-958.217597	0.31	17	0.34	22
***ent*-5i**(*P*1)	-958.216118	1.23	4	1.81	3
***ent*-5i**(*P*2)	-958.217529	0.35	16	0.84	9
***ent*-5i**(*P*3)	-958.217386	0.44	14	0.56	15
***ent*-5i**(*P*4)	-958.216821	0.79	9	1.07	6

[a] labels a-b refer to the rotamers due to the OMe or Ph substituents; [b] optimized at the COSMO(MeCN)/B3LYP/Aug-cc-pVDZ level.

Table A3. Single-point energies (E_{tot}, in Hartree), relative energies (ΔE in kcal mol^{-1}) and percentage populations of individual conformers of **4a-4g**, ***ent*-4i**, **5g** and ***ent*-5i** calculated at the PCM/B2PLYP(D)/Aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) level.

Conformer[a]	$E_{tot(\mathrm{MeCN})}$	ΔE	Pop.	$E_{tot(\mathrm{MeOH})}$	ΔE	Pop.
4a(*M*1)[b]	not calculated			not calculated		
4a(*M*2)[b]	not calculated			not calculated		
4a(*M*3)[b]	not calculated			not calculated		
4a(*M*4)[b]	not calculated			not calculated		
4a(*P*1)[b]	not calculated			not calculated		
4a(*P*2)[b]	not calculated			not calculated		
4a(*P*3)[b]	not calculated			not calculated		
4a(*P*4)[b]	not calculated			not calculated		
4b(*M*1)				-795.96773809858	0.84	6
4b(*M*2)	-795.96742913525	0.70	11	-795.96902957660	0.03	24
4b(*M*3)	-795.96656380994	1.25	4	-795.96777289290	0.82	6
4b(*M*4)	-795.96752969804	0.64	12	-795.96855410669	0.33	15
4b(*P*1)	-795.96688187865	1.05	6	-795.96766734693	0.89	6
4b(*P*2)	-795.96855141389	0.00	38	-795.96907902508	0.00	26
4b(*P*3)	-795.96745600423	0.69	11			
4b(*P*4)	-795.96787374682	0.43	18	-795.96865054180	0.27	17
4c(*M*1a)	-689.90613583256	0.00	26	-689.90627504512	0.09	16
4c(*M*1b)	-689.90523583256	0.56	10	-689.90608604512	0.21	13
4c(*M*2a)	-	1.08	4	-	0.67	6

	689.90441338565			689.90535460003		
4c(*M*2b)	- 689.90474963244	0.87	6	- 689.90520144073	0.77	5
4c(*M*3a)	- 689.90390758355	1.40	3	- 689.90471259007	1.08	3
4c(*M*3b)	- 689.90095003877	3.25		- 689.90571859795	0.44	9
4c(*M*4a)	- 689.90439505731	1.09	4	- 689.90522542108	0.75	5
4c(*M*4b)	- 689.90548434818	0.41	13	- 689.90642608555	0.00	19
4c(*P*1a)	- 689.90341696385	1.71	1	- 689.90465633661	1.11	3
4c(*P*1b)	- 689.90102002943	3.21		- 689.90121002943	3.27	
4c(*P*2a)	- 689.90435600772	1.12	4	- 689.90508632981	0.84	4
4c(*P*2b)	- 689.90107803816	3.17		- 689.90160392655	3.03	
4c(*P*3a)	- 689.90599289631	0.09	24	- 689.90592524245	0.31	11
4c(*P*3b)	- 689.90253177959	2.26		- 689.90246575173	2.49	
4c(*P*4a)	- 689.90459417944	0.97	5	- 689.90499564792	0.90	5
4c(*P*4b)	- 689.90166419218	2.81		- 689.90158580904	3.04	
4d(*M*1)				- 918.45520398292	0.99	6
4d(*M*2)	- 918.45525551966	0.09	21	- 918.45607648108	0.44	15
4d(*M*3)	- 918.45405333068	0.84	6	- 918.45499009696	1.12	5

4d(*M*4)	-918.45467990060	0.45	11	-918.45572700753	0.66	10
4d(*P*1)	-918.45399255804	0.88	5	-918.45528803404	0.93	6
4d(*P*2)	-918.45532772212	0.04	22	-918.45622945238	0.34	17
4d(*P*3)	-918.45539776694	0.00	24	-918.45677701722	0.00	31
4d(*P*4)	-918.45458489344	0.51	11	-918.45568548713	0.68	10
4e(*M*1)	-3032.1689791660	0.65	7	-3032.1688771305	0.70	7
4e(*M*2)	-3032.1698441558	0.11	18	-3032.1698217325	0.11	18
4e(*M*3)	-3032.1684060242	1.01	4	-3032.1684041382	1.00	4
4e(*M*4)	-3032.1692652301	0.47	10	-3032.1692759330	0.45	10
4e(*P*1)	-3032.1687273044	0.81	6	-3032.1686948221	0.81	6
4e(*P*2)	-3032.1700123227	0.00	22	-3032.1699604878	0.02	24
4e(*P*3)	-3032.1699304763	0.05	20	-3032.1699934528	0.00	22
4e(*P*4)	-3032.1694768583	0.34	13	-3032.1694077046	0.37	12
4f(*M*1a)	-573.45816264424	0.90	8	-573.45914998319	1.24	6
4f(*M*1b)	-573.45296848498	4.16		-573.45388976062	4.54	
4f(*M*2a)	-573.45916307753	0.27	24	-573.46000761969	0.70	15
4f(*M*2b)	-	4.14		-	4.83	

	573.45300769731			573.45341749693		
4f(*M*3a)	-573.45785615828	1.09	6	-573.45905097111	1.30	5
4f(*M*3b)	-573.45256228706	4.42		-573.45374582576	4.63	
4f(*M*4a)	-573.45880422480	0.50	16	-573.45969940444	0.89	11
4f(*M*4b)	-573.45333139450	3.93		-573.45430078508	4.28	
4f(*P*1a)	-573.45752625270	1.30	4	-573.45892623955	1.38	5
4f(*P*1b)	-573.45082988050	5.50		-573.45191107473	5.78	
4f(*P*2a)				-573.45892606675	1.38	5
4f(*P*2b)	-573.45090788921	5.45		-573.45159778328	5.97	
4f(*P*3a)	-573.45960086344	0.00	37	-573.46111829323	0.00	50
4f(*P*3b)	-573.45001917495	6.01				
4f(*P*4a)	-573.45771869746	1.18	5	-573.45836490888	1.73	3
4f(*P*4b)	-573.45012491521	5.95		-573.45102701728	6.33	
4g(*M*1)				-597.48391307675	1.61	5
4g(*M*2)	-597.48046859907	3.27		-597.48130902477	3.25	
4g(*M*3)	-597.47821025926	4.69		-597.47931465763	4.50	
4g(*M*4)	-597.47817258091	4.71		-597.47966665535	4.28	

4g(*P*1)	-597.48335050149	1.47	7	-597.48445920543	1.27	8
4g(*P*2)	-597.48568629297	0.00	78	-597.48648039750	0.00	69
4g(*P*4)	-597.48416220972	0.96	15	-597.48519778949	0.80	18
***ent*-4i**(*M*1)	-957.74546901898	2.67		-957.74541169889	2.67	
***ent*-4i**(*M*2)	-957.74708977930	1.66	2	-957.74703801966	1.65	2
***ent*-4i**(*M*3)	-957.74558953368	2.60		-957.74553441694	2.60	
***ent*-4i**(*M*4)	-957.74615220352	2.25		-957.74609069282	2.25	
***ent*-4i**(*P*1)	-957.74847627490	0.79	10	-957.74841889712	0.79	10
***ent*-4i**(*P*2)	-957.74964967351	0.05	35	-957.74958482256	0.06	35
***ent*-4i**(*P*3)	-957.74973127688	0.00	38	-957.74967343921	0.00	38
***ent*-4i**(*P*4)	-957.74873029288	0.63	13	-957.74865627405	0.64	13
5g(*M*1)	-597.48341103594	0.58	16	-597.48433692207	0.78	12
5g(*M*2)	-597.48366022580	0.42	21	-597.48488865074	0.44	23
5g(*M*3)	-597.48432849048	0.00	42	-597.48558787065	0.00	47
5g(*M*4)	-597.48361102234	0.45	19	-597.48469593571	0.56	18
5g(*P*1)	-597.47999569131	2.72		-597.48095020561	2.91	
5g(*P*2)	-	1.68	2	-	2.06	

	597.48164799104			597.48230469157		
5g(*P*3)				-597.48185131165	2.34	
5g(*P*4)	-597.48060546830	2.34		-597.48185072083	2.35	
***ent*-5i**(*M*1)	-957.74812014614	0.76	8	-957.74806085064	0.77	8
***ent*-5i**(*M*2)	-957.74895554290	0.24	19	-957.74890431111	0.24	19
***ent*-5i**(*M*4)	-957.74847837578	0.54	11	-957.74841704220	0.54	11
***ent*-5i**(*P*1)	-957.74798976016	0.85	7	-957.74793445874	0.84	7
***ent*-5i**(*P*2)	-957.74898220377	0.22	19	-957.74892015191	0.23	19
***ent*-5i**(*P*3)	-957.74933716604	0.00	28	-957.74928017420	0.00	28
***ent*-5i**(*P*4)	-957.74828749988	0.66	10	-957.74821509151	0.67	8

[a] Labels a-b refer to the rotamers due to the OMe or Ph substituents.

Table B1. Structural parameters that characterize low-energy conformers of **4a-4g**, ***ent*-4i**, **5g** and ***ent*-5i** calculated at the PCM(MeCN)/B3LYP/6-311++G(2d,2p) level.

Diol	OH···O [Å]	OH···X [Å]	Torsion angle [°]			
			α[a]	β[b]	ω[c]	φ[d]
4a(*M*1)[e]	2.317		165.1	164.7	-177.1	
4a(*M*2)[e]	2.295	3.530	29.2	166.8	-178.3	
4a(*M*3)[e]	2.344		-61.1	-54.9	-178.6	
4a(*M*4)[e]	2.295		-70.6	38.4	180.0	
4a(*P*1)[e]	2.219		-160.2	-169.0	-179.6	
4a(*P*2)[e]	2.175		-161.4	38.8	177.3	
4a(*P*3)[e]	2.271	3.013	44.5	65.0	177.3	
4a(*P*4)[e]	2.257		-31.5	70.6	176.9	
4b(*M*2)	2.665		-18.8	-173.9	-179.0	
4b(*M*3)	2.645	2.618	-40.4	-45.2	-179.0	
4b(*M*4)	2.608		-49.5	38.9	178.9	
4b(*P*1)	2.337		-163.0	165.4	176.7	
4b(*P*2)	2.324		-166.4	-36.8	175.3	
4b(*P*3)	2.487	2.718	14.9	52.8	176.1	
4b(*P*4)	2.467		-30.3	58.9	175.6	
4c(*M*1a)	2.244		160.3	160.7	-177.4	34.6
4c(*M*1b)	2.275	2.505	159.3	163.3	-178.1	-26.3
4c(*M*2a)	2.243		36.2	163.4	-178.6	35.9
4c(*M*2b)	2.592	2.566	-29.6	-173.5	-179.6	-27.8
4c(*M*3a)	2.263		-67.1	-62.2	-179.4	34.4
4c(*M*3b)	2.256	2.570	-68.6	-65.9	179.9	-25.9
4c(*M*4a)	2.253		-72.3	37.4	179.7	34.5
4c(*M*4b)	2.255	2.526	-72.4	38.5	179.3	-25.8
4c(*P*1a)	2.167		-156.3	-170.3	-179.3	36.7
4c(*P*1b)	2.169		-154.4	-171.6	179.6	-49.9
4c(*P*2a)	2.133		-158.6	-37.9	177.6	37.1
4c(*P*2b)	2.132		-156.3	-39.6	176.3	-51.5
4c(*P*3a)	2.166		73.4	74.6	178.0	41.1
4c(*P*3b)	2.262		53.0	68.5	177.6	-57.7

4c(*P*4a)	2.191		-37.2	76.0	177.6	38.4
4c(*P*4b)	2.232		-33.4	73.2	176.8	-51.2
4d(*M*1)	2.513		157.8	177.6	-177.5	
4d(*M*2)	2.488	3.327	25.2	178.5	-179.1	
4d(*M*3)	2.583		-44.9	-51.5	-179.0	
4d(*M*4)	2.597		-50.4	38.9	179.5	
4d(*P*1)	2.439		-173.8	-165.2	178.5	
4d(*P*2)	2.393		-174.3	-34.0	177.2	
4d(*P*3)	2.491	2.948	32.1	50.1	177.0	
4d(*P*4)	2.515		-35.6	53.8	177.3	
4e(*M*1)	2.524		159.3	178.1	-178.4	
4e(*M*2)	2.498		24.1	179.6	-179.2	
4e(*M*3)	2.616	3.436	-41.6	-44.6	-178.6	
4e(*M*4)	2.594		-50.0	38.8	179.5	
4e(*P*1)	2.454		-174.8	-166.6	178.1	
4e(*P*2)	2.398		-174.4	-35.5	176.8	
4e(*P*3)	2.499	3.069	28.9	49.5	176.9	
4e(*P*4)	2.480		-33.1	56.7	177.0	
4f(*M*1a)	2.524		157.3	178.0	-179.5	1.5
4f(*M*1b)	2.534		161.3	179.0	180.0	-178.5
4f(*M*2a)	2.503	2.998	33.6	179.6	179.7	1.7
4f(*M*2b)	2.668		-34.7	-170.0	179.0	-179.2
4f(*M*3a)	2.581		-46.9	-45.2	180.0	1.5
4f(*M*3b)	2.551		-46.9	-46.2	179.5	-179.6
4f(*M*4a)	2.544		-56.4	41.8	178.6	1.1
4f(*M*4b)	2.542		-54.0	39.5	178.1	179.2
4f(*P*1a)	2.513		-178.0	-166.8	-179.9	-0.2
4f(*P*1b)	2.277		-165.2	-164.3	-179.0	-159.8
4f(*P*2b)	2.235		-166.0	-31.5	179.2	-149.7
4f(*P*3a)	2.464	2.488	51.7	54.1	178.8	0.4
4f(*P*3b)	2.545		173.7	31.8	178.8	-145.2
4f(*P*4a)	2.440		-42.2	62.6	180.0	0.0
4f(*P*4b)	2.713		-29.7	57.9	179.5	-157.9

4g(*M*2)	2.498		-8.6	178.8	-175.8
4g(*M*3)	2.565		-45.8	-41.2	-175.7
4g(*M*4)	2.616		-49.6	36.1	-178.3
4g(*P*1)	2.473		-170.9	-175.8	171.1
4g(*P*2)	2.416	2.778	-172.9	-35.8	169.5
4g(*P*4)	2.549		-37.5	56.6	170.3
***ent*-4i**(*M*1)	2.201		163.6	153.0	-174.5
***ent*-4i**(*M*2)	2.196	3.209	27.8	157.3	-175.1
***ent*-4i**(*M*3)	2.223		-71.1	-54.3	-176.0
***ent*-4i**(*M*4)	2.201		-78.8	33.1	-176.7
***ent*-4i**(*P*1)	2.175		-156.9	-170.6	175.8
***ent*-4i**(*P*2)	2.148		-160.0	-29.7	172.9
***ent*-4i**(*P*3)	2.207	2.616	61.9	70.7	173.1
***ent*-4i**(*P*4)	2.204		-26.1	72.5	172.3
5g(*M*1)	2.447		164.2	174.0	-170.7
5g(*M*2)	2.598		-27.2	-173.2	-171.7
5g(*M*3)	2.566	2.717	-43.8	-40.8	-171.5
5g(*M*4)	2.585		-47.8	33.8	-173.6
5g(*P*1)	2.467		-169.2	-175.0	179.7
5g(*P*2)	2.407		-171.1	-33.7	176.8
5g(*P*4)	2.537		-36.2	57.6	177.3
***ent*-5i**(*M*1)	2.212		162.5	159.0	-174.7
***ent*-5i**(*M*2)	2.197		30.5	162.2	-175.1
***ent*-5i**(*M*4)	2.193		-75.5	33.4	-177.5
***ent*-5i**(*P*1)	2.156		-157.1	-169.0	178.6
***ent*-5i**(*P*2)	2.120		-159.2	-36.5	175.8
***ent*-5i**(*P*3)	2.184	2.648	58.2	71.7	176.0
***ent*-5i**(*P*4)	2.183		-24.4	73.0	175.4

[a] H-C4-O-H; [b] H-C5-O-H; [c] C3-C2-C1=O; [d] φ = C2=C3-C_{Ar}-C_{Ar} or φ = C2=C3-O-CH_3; [e] optimized at the COSMO(MeCN)/B3LYP/Aug-cc-pVDZ level.

Table B2. Values of intra-ring torsion angles that characterize the low-energy conformers of **4a-4g**, ***ent*-4i**, **5g** and ***ent*-5i** calculated at the PCM(MeCN)/B3LYP/6-311++G(2d,2p) level.

Diol	Torsion angle[a] [°]					
	C_1	C_2	C_3	C_4	C_5	C_6
4a(*M*1)[b]	0.6	21.8	-48.4	53.8	-31.5	4.2
4a(*M*2)[b]	0.3	23.5	-49.7	54.1	-30.4	3.1
4a(*M*3)[b]	1.5	22.1	-49.5	54.6	-30.9	2.9
4a(*M*4)[b]	1.5	22.5	-49.2	53.2	-29.2	1.7
4a(*P*1)[b]	0.3	-24.1	48.2	-50.3	27.1	-1.4
4a(*P*2)[b]	0.6	-22.4	47.5	-53.0	31.2	-4.8
4a(*P*3)[b]	0.5	-21.9	47.0	-52.8	31.6	-5.1
4a(*P*4)[b]	0.9	-21.8	46.6	-52.2	31.5	-5.6
4b(*M*2)	-2.0	28.3	-52.9	53.5	-27.4	1.2
4b(*M*3)	-1.9	28.7	-53.8	54.5	-27.8	1.2
4b(*M*4)	-1.6	29.5	-54.4	53.3	-25.6	-0.9
4b(*P*1)	2.6	-24.9	48.0	-51.5	29.9	-4.8
4b(*P*2)	1.2	-23.1	48.9	-55.1	33.6	-6.4
4b(*P*3)	1.7	-24.2	49.4	-54.3	32.4	-5.6
4b(*P*4)	1.4	-23.3	49.1	-54.7	33.5	-6.4
4c(*M*1a)	1.4	21.2	-48.1	52.7	-30.9	3.7
4c(*M*1b)	-2.7	27.3	-51.3	51.2	-27.3	2.7
4c(*M*2a)	0.9	23.5	-50.0	53.2	-29.8	2.5
4c(*M*2b)	-2.2	28.6	-53.1	52.2	-26.5	1.0
4c(*M*3a)	2.3	22.5	-50.6	54.3	-30.2	1.8
4c(*M*3b)	-1.5	27.9	-53.3	52.8	-26.9	0.9
4c(*M*4a)	2.2	22.6	-50.0	52.9	-28.9	0.9
4c(*M*4b)	-1.4	27.7	-52.6	51.6	-25.9	0.3
4c(*P*1a)	-0.4	-23.5	48.4	-50.7	27.4	-1.4
4c(*P*1b)	0.7	-24.2	48.1	-49.7	26.9	-1.9
4c(*P*2a)	-0.2	-21.4	47.3	-52.6	31.6	-5.0
4c(*P*2b)	0.9	-21.9	46.9	-52.0	31.5	-5.7
4c(*P*3a)	-0.3	-21.6	47.5	-52.5	31.6	-4.8
4c(*P*3b)	2.9	-26.0	49.2	-50.7	28.6	-4.1
4c(*P*4a)	0.4	-21.7	47.1	-51.7	31.2	-5.2

4c(*P*4b)	1.7	-23.2	47.5	-51.5	30.3	-5.3
4d(*M*1)	0.3	22.5	-48.5	53.5	-30.6	3.7
4d(*M*2)	-0.2	25.1	-50.8	54.0	-29.2	2.1
4d(*M*3)	0.6	24.1	-50.7	54.8	-30.1	2.2
4d(*M*4)	0.6	25.2	-51.5	54.1	-28.5	0.7
4d(*P*1)	1.7	-24.6	47.7	-51.1	28.8	-3.4
4d(*P*2)	1.0	-23.8	49.1	-54.5	31.9	-4.8
4d(*P*3)	0.6	-22.6	47.9	-54.1	32.6	-5.4
4d(*P*4)	1.5	-24.1	48.9	-53.6	31.5	-5.0
4e(*M*1)	0.3	23.4	-49.5	53.7	-29.9	2.8
4e(*M*2)	-0.4	25.4	-51.0	53.9	-28.9	1.9
4e(*M*3)	0.4	24.2	-50.9	55.0	-30.3	2.5
4e(*M*4)	0.4	25.4	-51.7	54.1	-28.4	0.7
4e(*P*1)	1.86	-24.9	48.5	-51.9	29.2	-3.6
4e(*P*2)	1.00	-23.4	48.9	-54.6	32.3	-5.3
4e(*P*3)	1.16	-23.2	48.4	-54.1	32.4	-5.3
4e(*P*4)	1.32	-23.5	48.7	-54.0	32.2	-5.4
4f(*M*1a)	-0.6	25.7	-50.5	52.2	-27.6	1.3
4f(*M*1b)	1.2	23.3	-49.6	52.6	-28.4	1.2
4f(*M*2a)	-0.9	27.1	-51.9	52.9	-27.1	0.6
4f(*M*2b)	2.4	22.3	-49.2	52.8	-28.5	0.7
4f(*M*3a)	-0.3	26.6	-52.1	53.7	-27.8	0.8
4f(*M*3b)	2.0	23.4	-50.7	54.2	-29.0	0.8
4f(*M*4a)	-0.5	27.5	-52.6	52.7	-26.2	-0.6
4f(*M*4b)	1.9	24.3	-51.3	53.4	-27.5	-0.6
4f(*P*1a)	2.3	-27.6	50.3	-50.7	26.3	-1.3
4f(*P*1b)	-2.8	-19.7	45.9	-51.5	29.6	-1.9
4f(*P*2b)	-2.9	-18.7	46.3	-53.9	32.8	-4.2
4f(*P*3a)	2.3	-26.4	50.0	-52.2	29.0	-3.2
4f(*P*3b)	-3.4	-17.2	45.0	-53.8	34.0	-5.0
4f(*P*4a)	2.6	-27.5	50.6	-51.3	27.3	-2.1
4f(*P*4b)	-1.9	-20.0	46.7	-53.0	31.8	-3.9
4g(*M*2)	0.0	19.4	-44.4	50.0	-30.8	5.7

4g(*M*3)	0.6	19.0	-45.1	51.3	-31.7	5.9
4g(*M*4)	0.6	209	-46.5	50.3	-28.8	3.4
4g(*P*1)	3.2	-24.0	50.1	-58.1	38.8	-10.5
4g(*P*2)	3.3	-22.8	49.7	-59.2	40.9	-12.4
4g(*P*4)	3.8	-24.2	51.3	-60.1	41.2	-12.2
***ent*-4i**(*M*1)	1.5	16.1	-42.8	51.5	-33.4	7.9
***ent*-4i**(*M*2)	1.4	17.1	-43.8	52.0	-33.1	7.2
***ent*-4i**(*M*3)	2.4	16.5	-44.4	52.5	-32.8	6.4
***ent*-4i**(*M*4)	2.6	16.4	-43.9	51.9	-32.2	5.9
***ent*-4i**(*P*1)	0.7	-22.0	48.2	-54.2	32.7	-6.1
***ent*-4i**(*P*2)	0.7	-19.8	47.1	-55.9	36.5	-9.4
***ent*-4i**(*P*3)	1.2	-20.9	48.0	-56.2	36.7	-9.5
***ent*-4i**(*P*4)	1.0	-19.3	46.6	-55.6	37.2	-10.4
5g(*M*1)	-2.1	21.8	-48.1	55.5	-37.0	9.9
5g(*M*2)	-1.3	21.7	-48.8	56.5	-37.4	9.3
5g(*M*3)	-1.5	23.1	-50.5	57.7	-37.2	8.7
5g(*M*4)	-2.0	24.8	-51.3	56.0	-34.6	6.9
5g(*P*1)	2.0	-26.9	50.3	-505	26.8	-1.7
5g(*P*2)	2.7	-25.1	48.9	-51.7	30.2	-5.2
5g(*P*4)	3.4	-26.4	49.4	-50.8	29.1	-4.5
***ent*-5i**(*M*1)	0.1	20.0	-46.5	52.8	-32.8	6.8
***ent*-5i**(*M*2)	0.2	21.0	-47.9	54.2	-33.3	6.5
***ent*-5i**(*M*4)	1.4	20.5	-47.9	53.2	-31.4	4.3
***ent*-5i**(*P*1)	0.6	-22.4	47.0	-50.9	28.7	-3.6
***ent*-5i**(*P*2)	0.8	-20.4	46.0	-52.6	32.5	-7.0
***ent*-5i**(*P*3)	1.2	-21.2	46.5	-52.5	32.4	-6.9
***ent*-5i**(*P*4)	1.0	-19.8	45.2	-51.9	32.9	-7.7

[a] $C_1 = \tau$; C_2 = C2=C3-C4-C5; C_3 = C3-C4-C5-C6; C_4 = C4-C5-C6-C1; C_5 = C5-C6-C1-C2; C_6 = C6-C1-C2=C3; [b] optimized at the COSMO(MeCN)/B3LYP/Aug-cc-pVDZ level

Table C1. Experimental UV data for *cis*-ketodiols **4a-4j**, **5g** and **5i** measured in acetonitrile solution

Diol	Substituent at		λ_{max} [nm]	ε [M^{-1} cm^{-1}]
	C3	C6		
	H	H	210[a]	19200
	Me	H	224[a]	22500
4a	I	H	257	11600
4b	CF_3	H	198	22900
4c	Ph	H	277	17500
4d	Cl	H	228	18500
4e	Br	H	241	17300
4f	OMe	H	241	22900
4g	Me	F	226	20600
4h[a]	Me	Me	225	20400
4i	Cl	Me	233	11100
4j[a]	Me	Et	225	19800
5g	Me	F	224	11100
5i	Cl	Me	230	10600

[a] data taken from M. Kwit, J. Gawronski, D. R. Boyd, N. Sharma and M. Kaik, *Org. Biomol. Chem.* **2010**, *8*, 5635.

Table C2. Specific optical rotations for *cis*-ketodiols **4a**-**4g**, ***ent*-4i**, **5g** and ***ent*-5i**, calculated at the PCM(MeOH)/B3LYP/Aug-cc-pVTZ level and measured in methanol solution.

Diol	Conformer	Calculated opical rotations				Measured optical rotations			
		589 nm	578 nm	546 nm	436 nm	589 nm	578 nm	546 nm	436 nm
4a[a]	(*M*1)	22	27	48	633				
	(*M*2)	-128	-130	-134	-232				
	(*M*3)	-121	-128	-150	-237				
	(*M*4)	-163	-173	-204	-410				
	(*P*1)	-443	-461	-558	-1627				
	(*P*2)	-292	-313	-389	-1311				
	(*P*3)	-183	-197	-245	-967				
	(*P*4)	-317	-341	-430	-1595				
	***ΔE* Boltzmann averaged**	-224	-238	-290	-922	-38	-37	-42	-61
	***ΔG* Boltzmann averaged**	-231	-245	-299	-911				
4b	(*M*1)	41	47	68	394				
	(*M*2)	19	23	40	350				
	(*M*3)	42	45	56	190				
	(*M*4)	-16	-17	-20	-36				
	(*P*1)	-271	-286	-334	-657				
	(*P*2)	-210	-222	-265	-627				
	(*P*4)	-211	-223	-262	-541				
	***ΔE* Boltzmann averaged**	-63	-52	-52	98	-82	-86	-98	-147
	***ΔG* Boltzmann averaged**	-77	-80	-85	24				
	***ΔE* Boltzmann averaged**[b]	-99	-104	-119	-181				
4c	(*M*1a)	-634	-678	-823	-2375				
	(*M*1b)	668	715	885	2716				
	(*M*2a)	-693	-740	-903	-2469				
	(*M*2b)	648	694	855	2525				

	(*M*3a)	-686	-732	-897	-2501				
	(*M*3b)	561	600	736	2128				
	(*M*4a)	-766	-818	-1000	-2751				
	(*M*4b)	504	539	665	1945				
	(*P*1a)	-680	-725	-884	-2398				
	(*P*1b)	657	703	865	2457				
	(*P*2a)	-581	-622	-766	-2183				
	(*P*2b)	652	694	843	2201				
	(*P*3a)	-588	-628	-769	-2124				
	(*P*3b)	497	531	653	1810				
	(*P*4a)	-601	-642	-787	-2205				
	(*P*4b)	591	631	772	2098				
ΔE Boltzmann averaged		-95	-101	-120	-271	-20	-21	-21	+32
ΔG Boltzmann averaged		-211	-224	-272	-712				
ΔE Boltzmann averaged[b]		-74	-79	-93	-203				
4d	(*M*1)	-5	-3	5	151				
	(*M*2)	-75	-76	-81	-13				
	(*M*3)	8	9	14	90				
	(*M*4)	-53	-56	-64	-100				
	(*P*1)	-188	-198	-230	-445				
	(*P*2)	-115	-122	-147	-363				
	(*P*3)	-163	-171	-198	-375				
	(*P*4)	-125	-132	-156	-336				
ΔE Boltzmann averaged		-72	-76	-86	-126	-52	-54	-63	-109
ΔG Boltzmann averaged		-72	-75	-86	-134				
ΔE Boltzmann averaged[b]		-110	-116	-133	-237				
4e	(*M*1)	-115	-164	-194	-392				

	(*M*2)	-44	-84	-103	-271				
	(*M*3)	-106	-137	-160	-304				
	(*M*4)	-81	-118	-139	-294				
	(*P*1)	-44	-17	-14	+69				
	(*P*2)	-90	-66	-71	-47				
	(*P*3)	-15	+13	+20	+119				
	(*P*4)	-38	-34	-38	-47				
	ΔE Boltzmann averaged	-69	-79	-91	-156	-45	-47	-55	-96
	ΔG Boltzmann averaged	-69	-77	-88	-149				
	ΔE Boltzmann averaged[b]	-60	-62	-70	-104				
4f	(*M*1a)	-32	-32	-34	-8				
	(*M*1b)	-18	-19	-21	-19				
	(*M*2a)	-127	-132	-149	-227				
	(*M*2b)	-23	-24	-29	-57				
	(*M*3a)	-27	-28	-33	-68				
	(*M*3b)	-18	-20	-26	-79				
	(*M*4a)	-95	-100	-117	-232				
	(*M*4b)	-71	-76	-90	-199				
	(*P*1a)	-154	-161	-184	-314				
	(*P*1b)	-350	-369	-436	-922				
	(*P*2a)	-93	-98	-115	-233				
	(*P*2b)	-447	-474	-566	-1292				
	(*P*3a)	-163	-170	-194	-334				
	(*P*3b)	-447	-474	-566	-1293				
	(*P*4a)	-99	-104	-120	-219				
	(*P*4b)	-347	-367	-435	-954				
	ΔE Boltzmann averaged	-126	-132	-151	-258	-120	-127	-145	-219
	ΔG Boltzmann averaged	-128	-133	-152	-261				

	ΔE Boltzmann averaged[b]	-129	-135	-154	-264				
4g	(*M*1)	93	102	131	488				
	(*M*2)	27	31	49	308				
	(*M*3)	117	125	154	452				
	(*M*4)	57	62	79	265				
	(*P*1)	-216	-228	-268	-562				
	(*P*2)	-133	-141	-170	-404				
	(*P*4)	-136	-144	-172	-393				
	ΔE Boltzmann averaged	-132	-139	-167	-385	-103	-109	-129	-286
	ΔG Boltzmann averaged	-137	-145	-174	-409				
	ΔE Boltzmann averaged[b]	-128	-136	-163	-370				
***ent*-4i**	(*M*1)	67	72	92	324				
	(*M*2)	-19	-18	-13	114				
	(*M*3)	69	74	90	255				
	(*M*4)	3	3	6	60				
	(*P*1)	-144	-152	-181	-406				
	(*P*2)	-86	-92	-115	-328				
	(*P*3)	-128	-135	-161	-361				
	(*P*4)	-89	-96	-117	-313				
	ΔE Boltzmann averaged	-104	-111	-135	-342	+59	+88	+110	+219
	ΔG Boltzmann averaged	-106	-113	-137	-342				
	ΔE Boltzmann averaged[b]	-105	-111	-135	-331				
5g	(*M*1)	-74	-75	-76	13				
	(*M*2)	-136	-140	-152	-131				
	(*M*3)	-78	-81	-87	-74				
	(*M*4)	-84	-87	-94	-96				

	(*P*1)	-283	-297	-346	-669	
	(*P*2)	-225	-238	-282	-624	
	(*P*4)	-251	-265	-311	-628	
ΔE Boltzmann averaged		-96	-100	-107	-88	-92
ΔG Boltzmann averaged		-93	-96	-104	-87	
ΔE Boltzmann averaged[b]		-92	-95	-102	-81	
***ent*-5i[c]**	(*M*1)	-69	-70	-71	38	
	(*M*2)	-135	-140	-151	-115	
	(*M*4)	-117	-121	-137	-197	
	(*P*1)	-211	-222	-257	-476	
	(*P*2)	-141	-150	-178	-402	
	(*P*3)	-190	-199	-230	-429	
	(*P*4)	-154	-162	-191	-390	
ΔE Boltzmann averaged		-138	-144	-163	-241	+92
ΔG Boltzmann averaged		-139	-145	-163	-224	
ΔE Boltzmann averaged[b]		-151	-158	-181	-301	

[a] calculated at the COSMO(MeOH)/B3LYP/Aug-cc-pVDZ level; [b] single-point energy calculated at the PCM/B2PLYP(D)/Aug-cc-pVTZ level; [c] measured for enantiomer

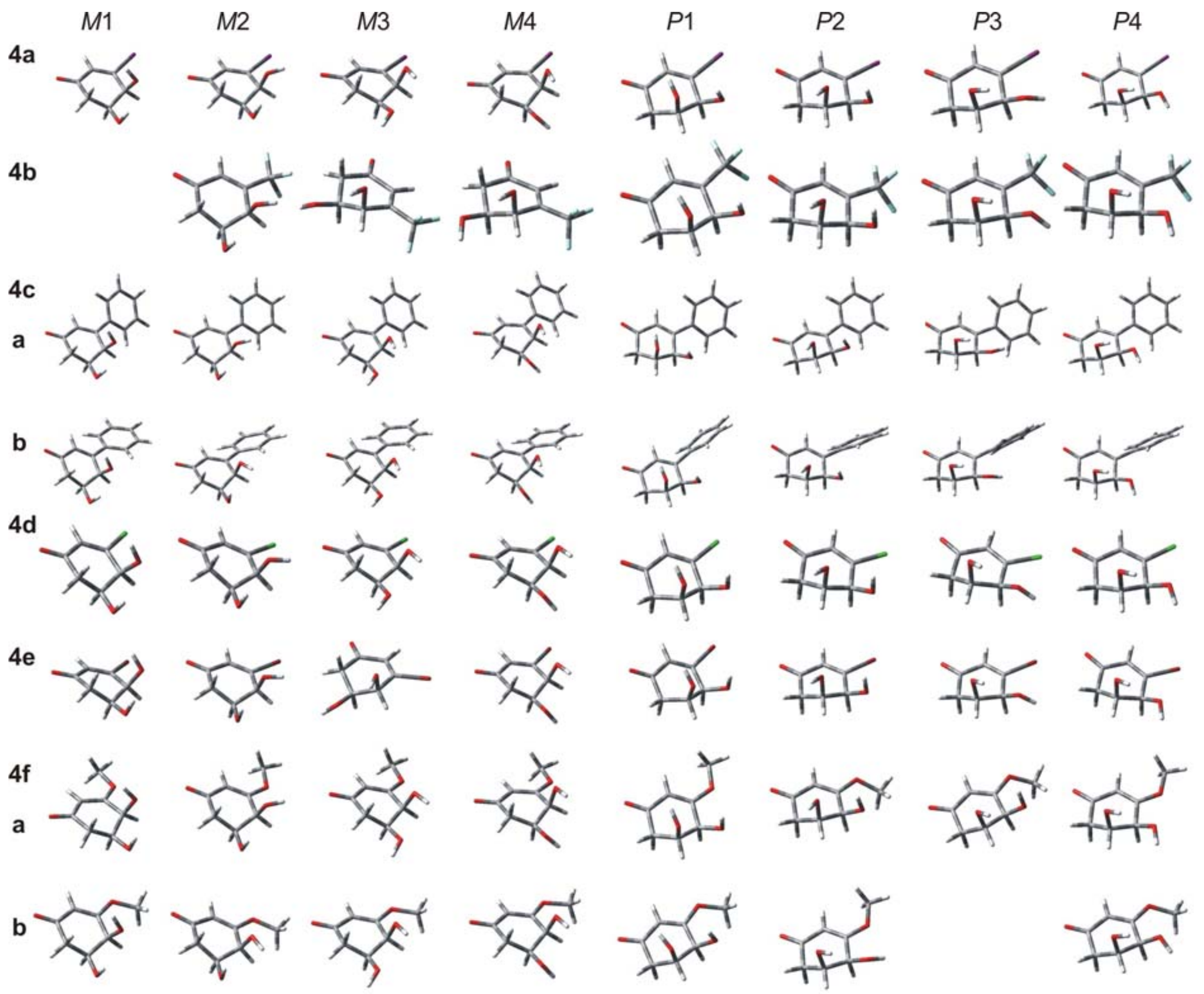


Figure A2. Structures of individual conformers of keto-*cis*-diols **4a**-**4f** calculated at the PCM/B3LYP/6-311++G(2d,2p) level.

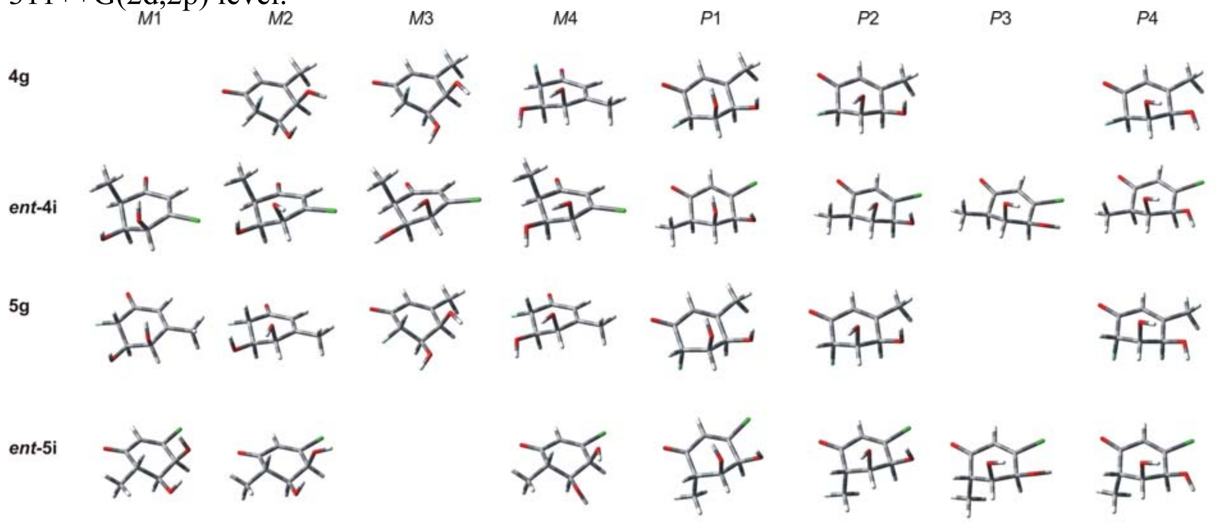
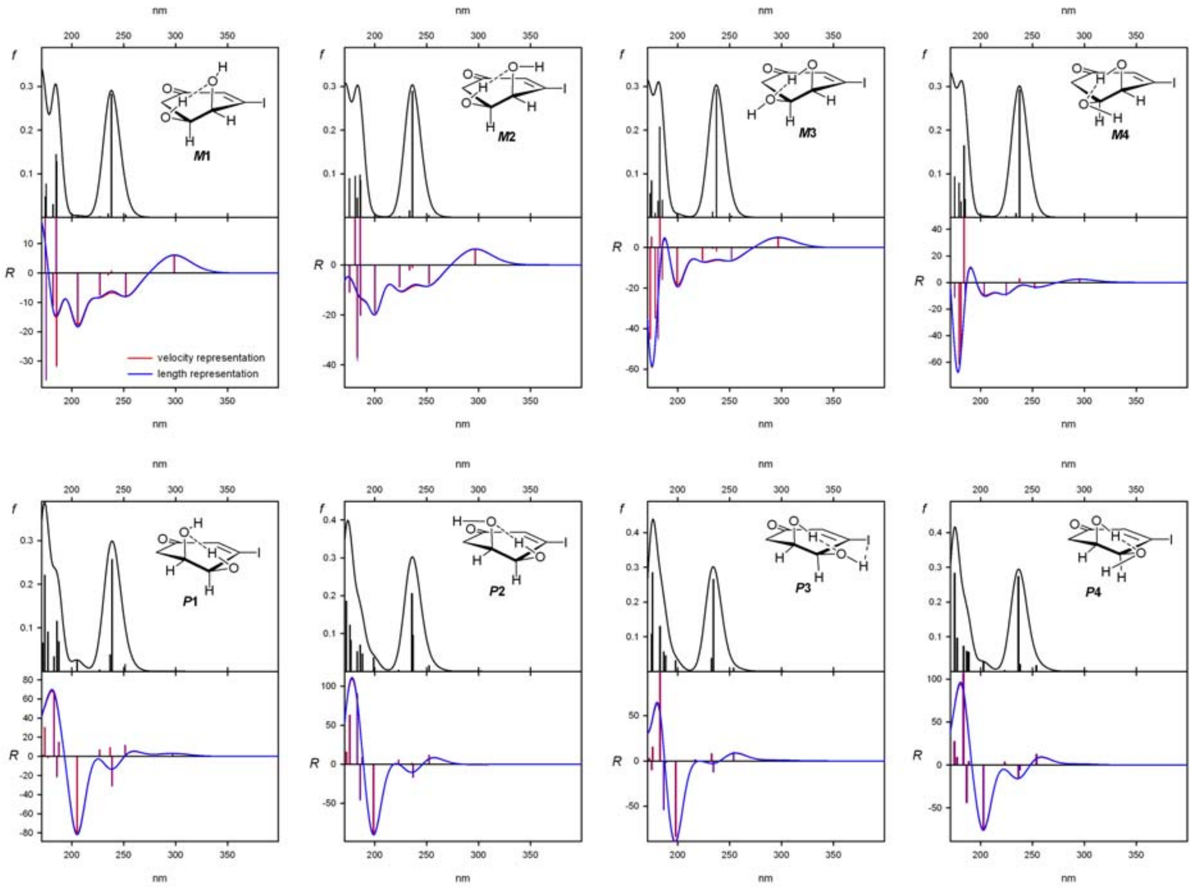


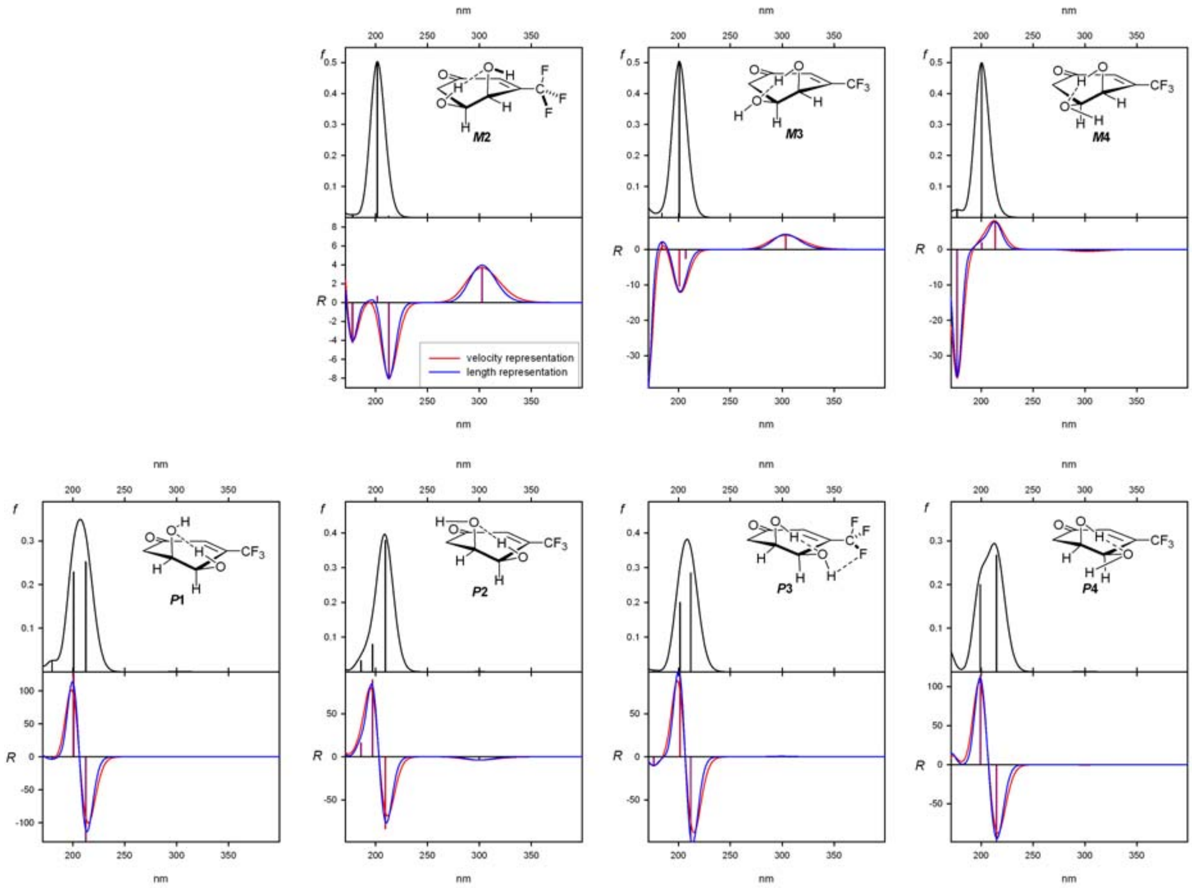
Figure A3. Structures of individual conformers of keto-*cis*-diols **4g**, ***ent*-4i**, **5g** and ***ent*-5i** calculated at the PCM/B3LYP/6-311++G(2d,2p) level.

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



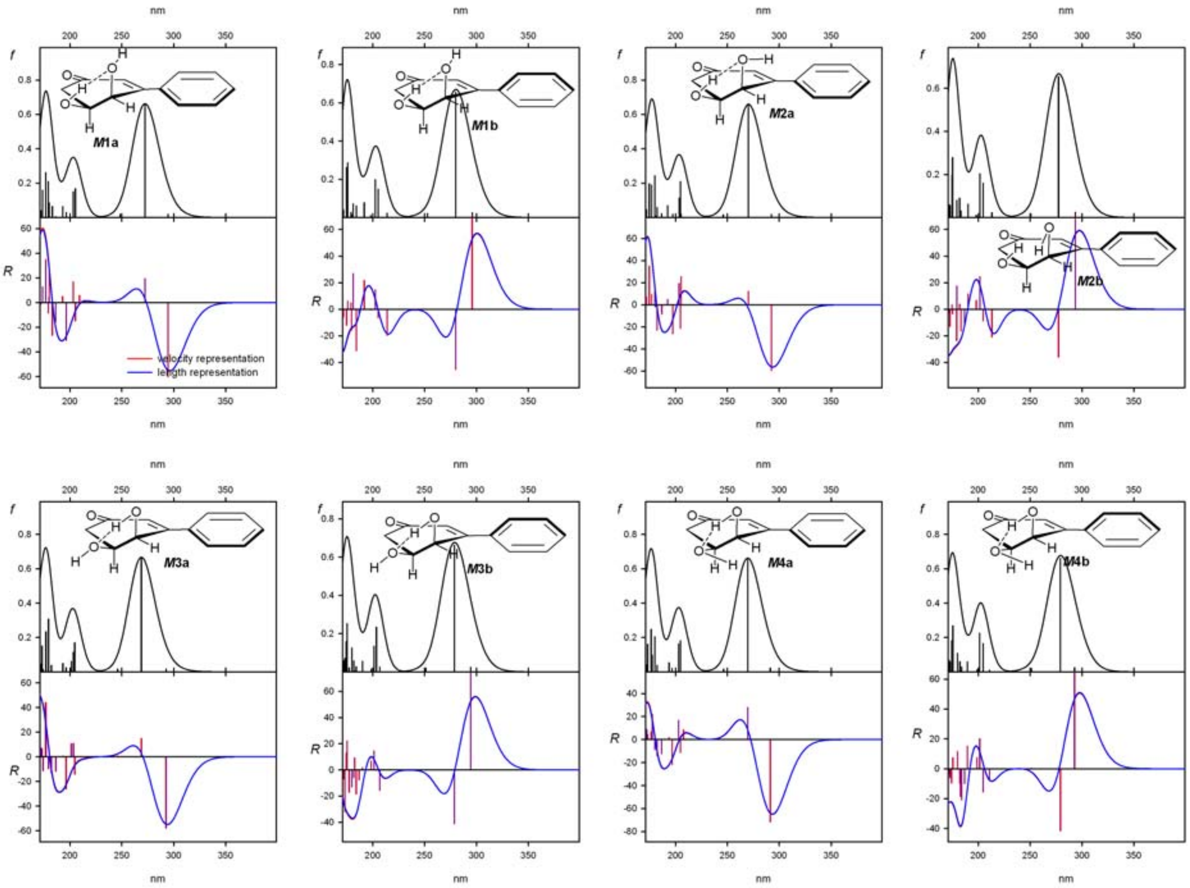
COSMO/TD-B2LYP/Aug-cc-pVDZ

Figure B1. UV and ECD spectra calculated at the COSMO/B2LYP/Aug-cc-pVDZ level for individual conformers of **4a**, optimized at the COSMO/B3LYP/Aug-CC-pVDZ level. Vertical bars represent rotatory strengths. Wavelength not corrected.

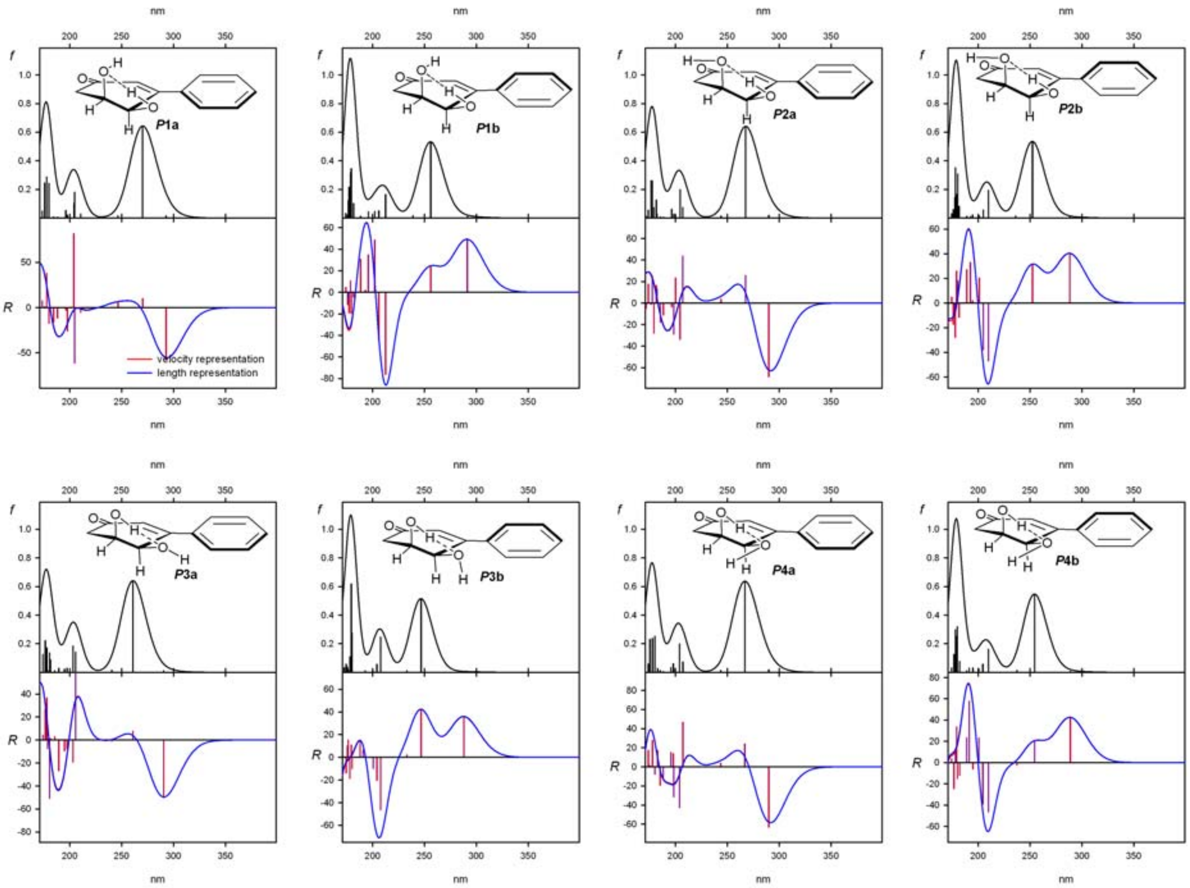


IEFPCM/TD-B2LYP/Aug-cc-pVTZ

Figure B2. UV and ECD spectra calculated at the PCM/B2LYP/Aug-cc-pVTZ level for individual conformers of **4b**, optimized at the PCM/B3LYP/6-311++G(2d,2p) level. Vertical bars represent rotatory strengths. Wavelength not corrected.

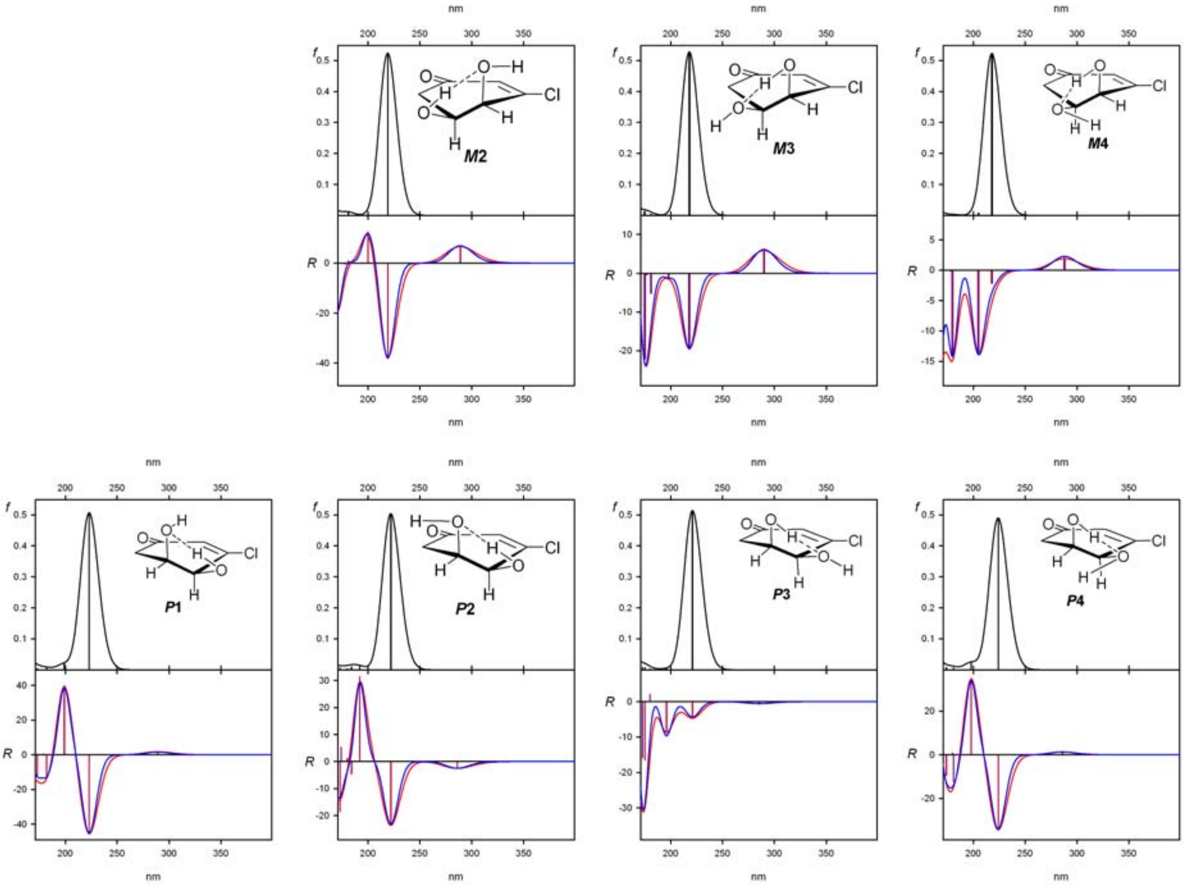


IEFPCM/TD-B2LYP/Aug-cc-pVTZ



IEFPCM/TD-B2LYP/Aug-cc-pVTZ

Figure B3. UV and ECD spectra calculated at the PCM/B2LYP/Aug-cc-pVTZ level for individual conformers of **4c**, optimized at the PCM/B3LYP/6-311++G(2d,2p) level. Vertical bars represent rotatory strengths. Wavelength not corrected.



IEFPCM/TD-B2LYP/Aug-cc-pVTZ

Figure B4. UV and ECD spectra calculated at the PCM/B2LYP/Aug-cc-pVTZ level for individual conformers of **4d**, optimized at the PCM/B3LYP/6-311++G(2d,2p) level. Vertical bars represent rotatory strengths. Wavelength not corrected.

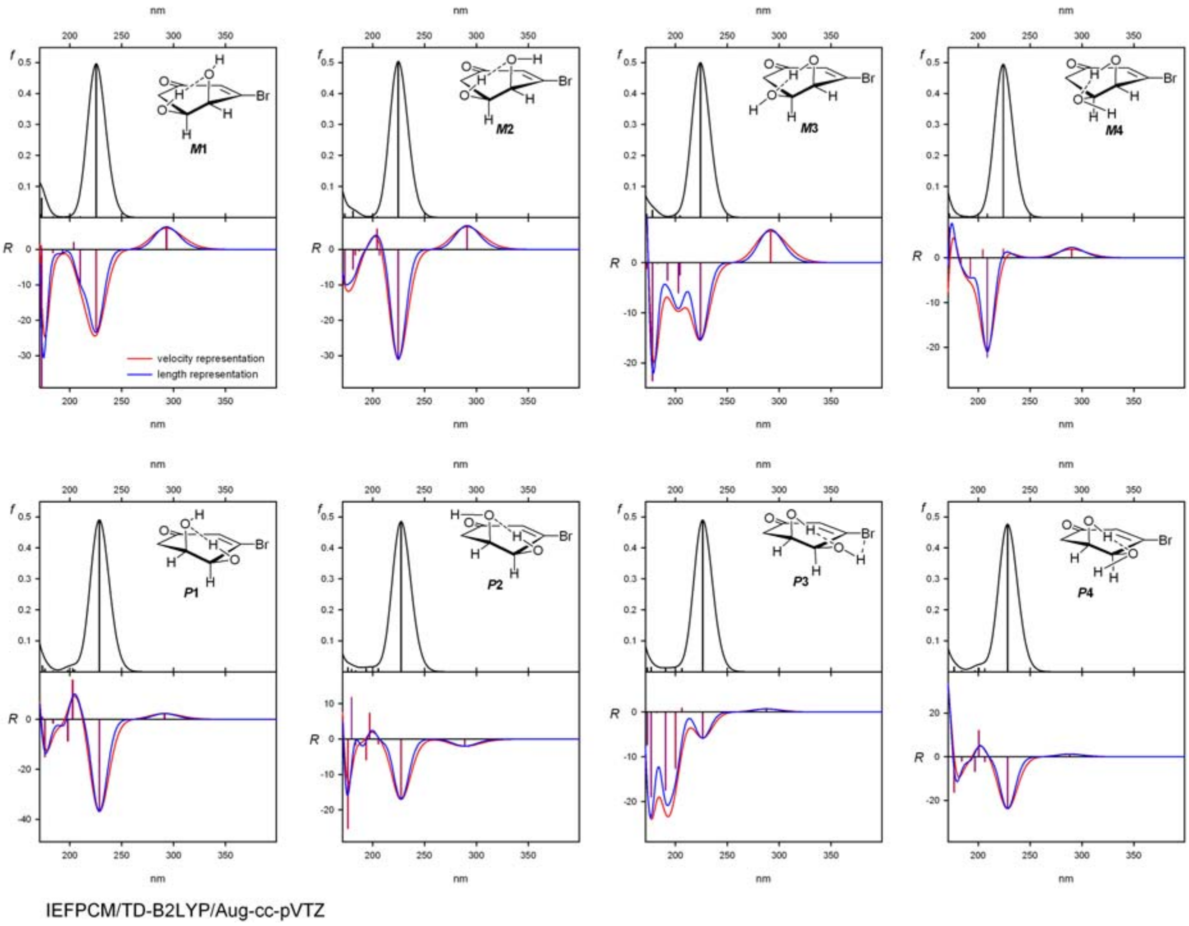
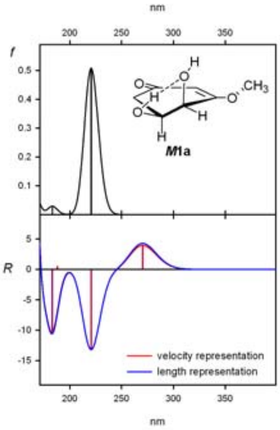
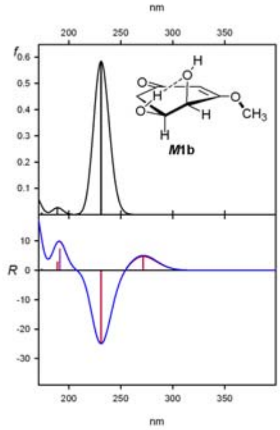
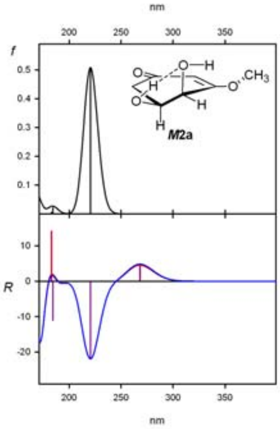
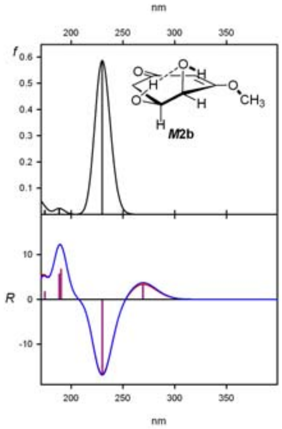


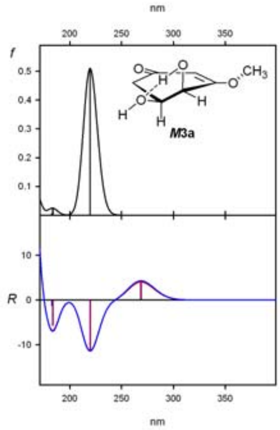
Figure B5. UV and ECD spectra calculated at the PCM/B2LYP/Aug-cc-pVTZ level for individual conformers of **4e**, optimized at the PCM/B3LYP/6-311++G(2d,2p) level. Vertical bars represent rotatory strengths. Wavelength not corrected.

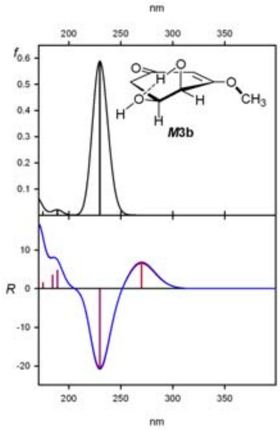


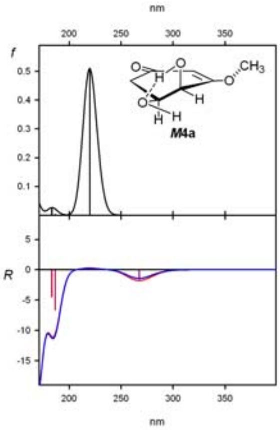


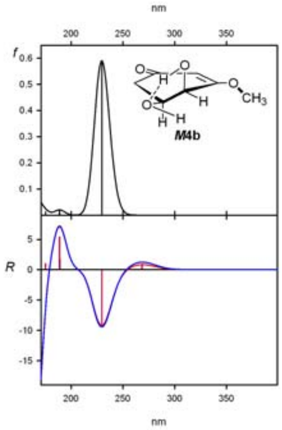




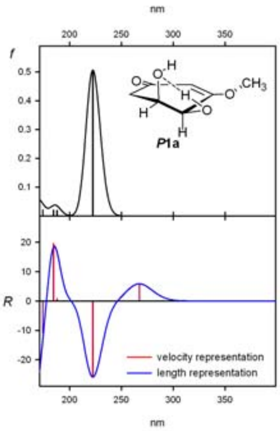


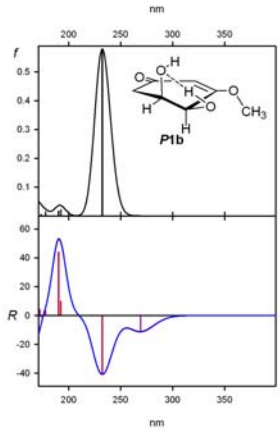


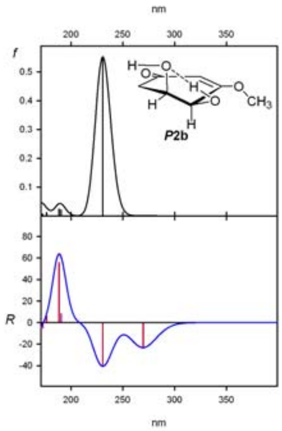


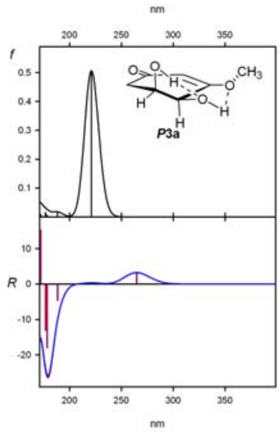


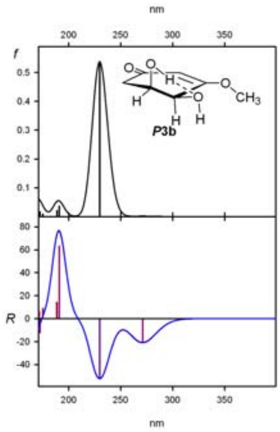
IEFPCM/TD-B2LYP/Aug-cc-pVTZ

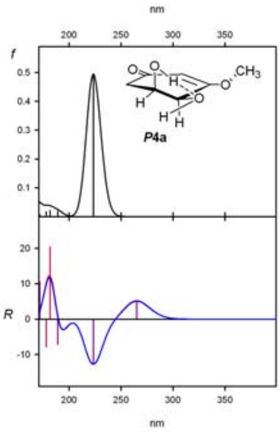


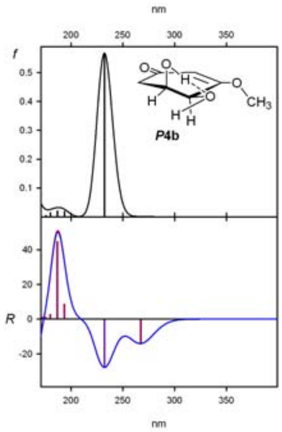












IEFPCM/TD-B2LYP/Aug-cc-pVTZ

Figure B6. UV and ECD spectra calculated at the PCM/B2LYP/Aug-cc-pVTZ level for individual conformers of **4f**, optimized at the PCM/B3LYP/6-311++G(2d,2p) level. Vertical bars represent rotatory strengths. Wavelength not corrected.

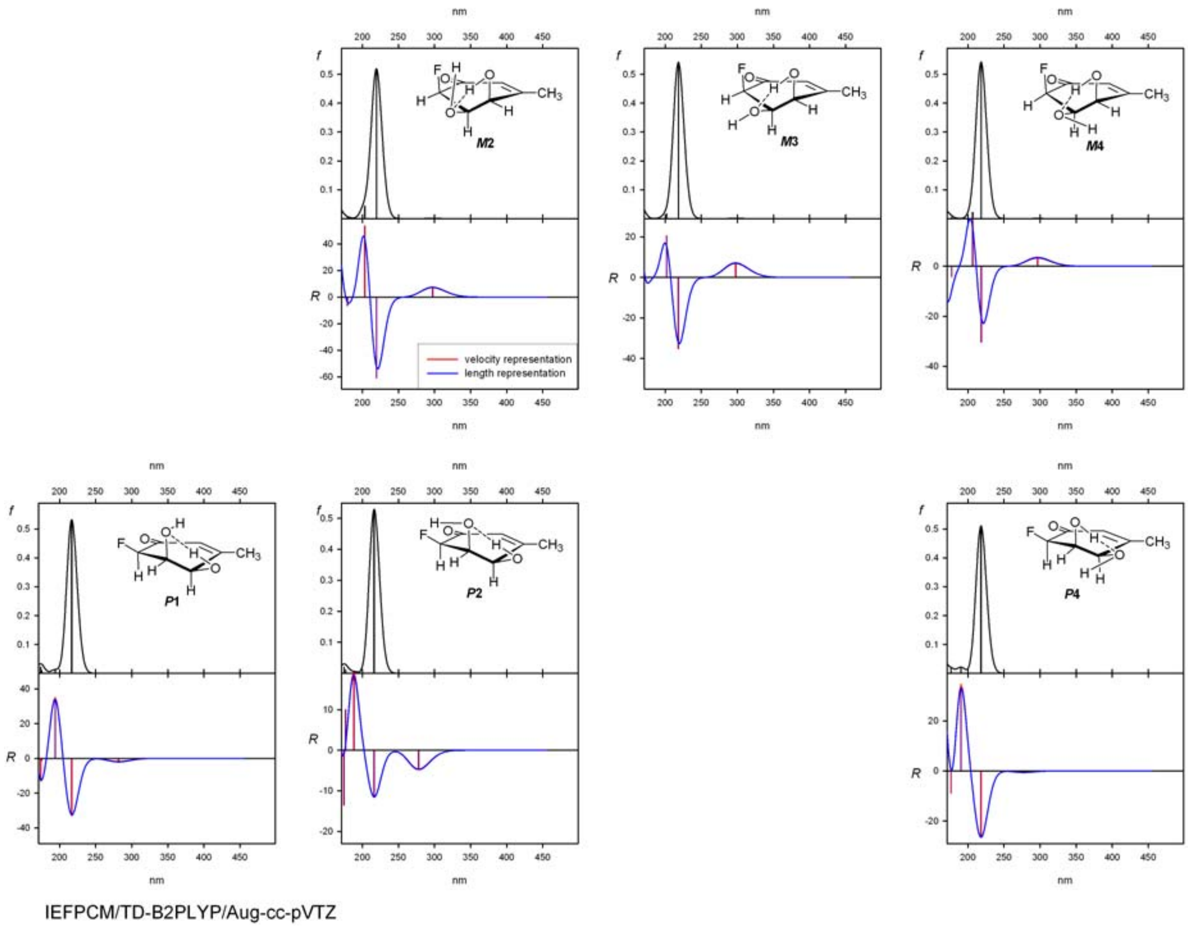


Figure B7. UV and ECD spectra calculated at the PCM/B2LYP/Aug-cc-pVTZ level for individual conformers of **4g**, optimized at the PCM/B3LYP/6-311++G(2d,2p) level. Vertical bars represent rotatory strengths. Wavelength not corrected.

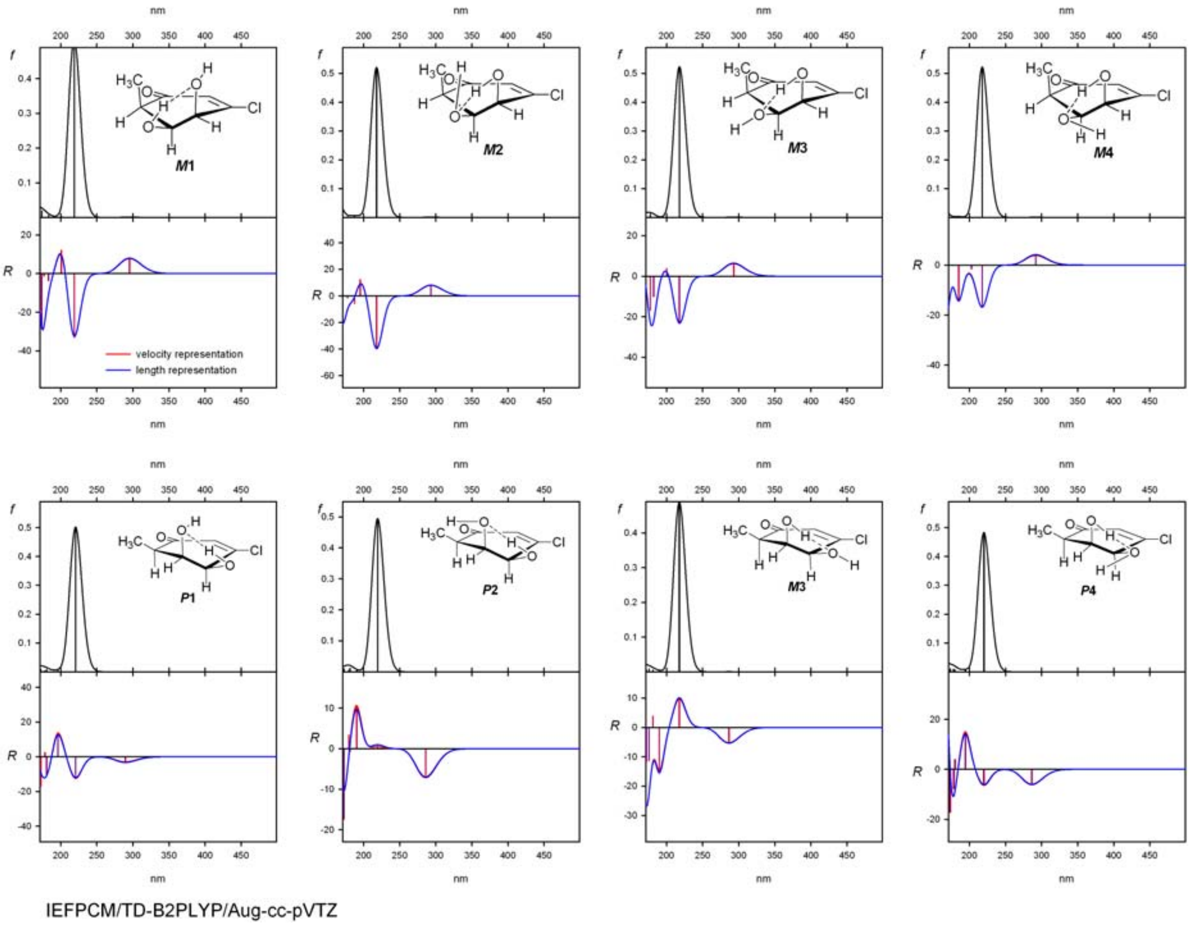
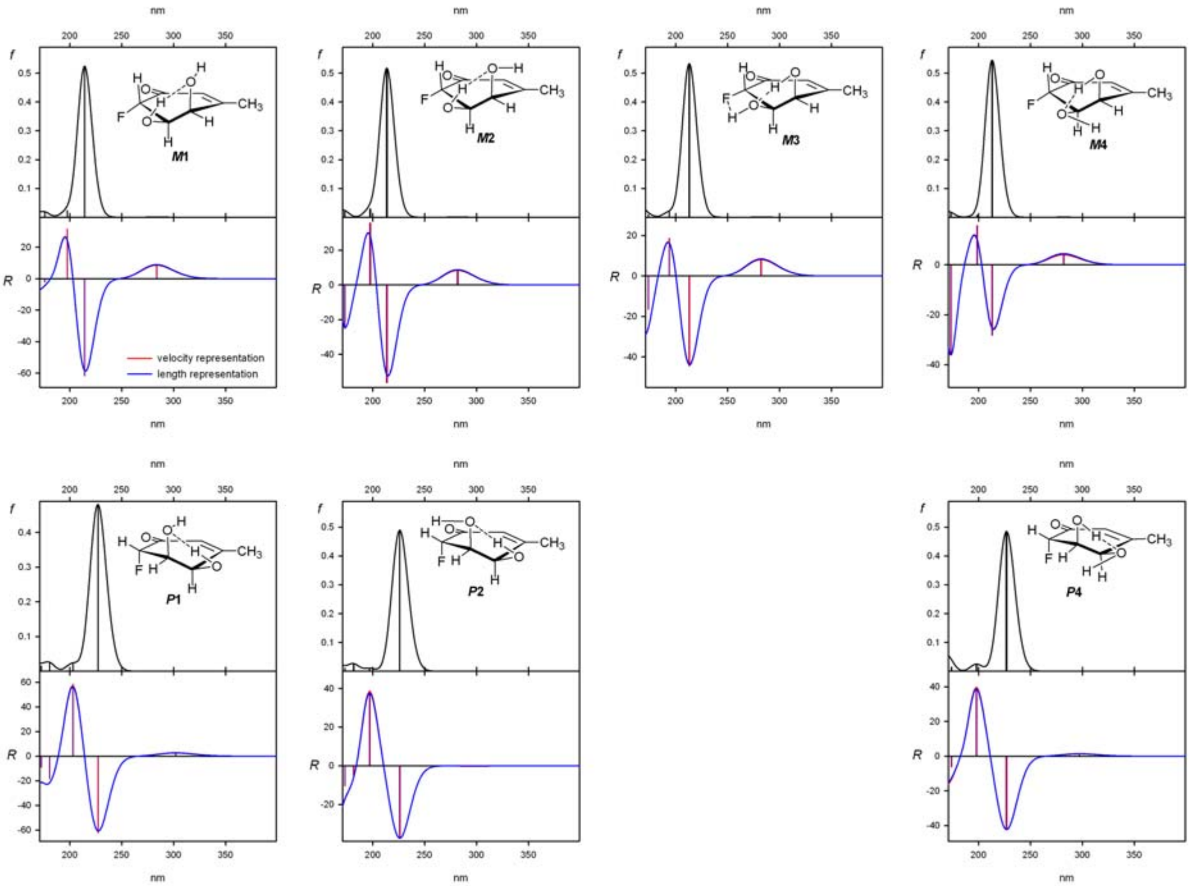


Figure B8. UV and ECD spectra calculated at the PCM/B2LYP/Aug-cc-pVTZ level for individual conformers of ***ent*-4i**, optimized at the PCM/B3LYP/6-311++G(2d,2p) level. Vertical bars represent rotatory strengths. Wavelength not corrected.



IEFPCM/TD-B2LYP/Aug-cc-pVTZ

Figure B9. UV and ECD spectra calculated at the PCM/B2LYP/Aug-cc-pVTZ level for individual conformers of **5g**, optimized at the PCM/B3LYP/6-311++G(2d,2p) level. Vertical bars represent rotatory strengths. Wavelength not corrected.

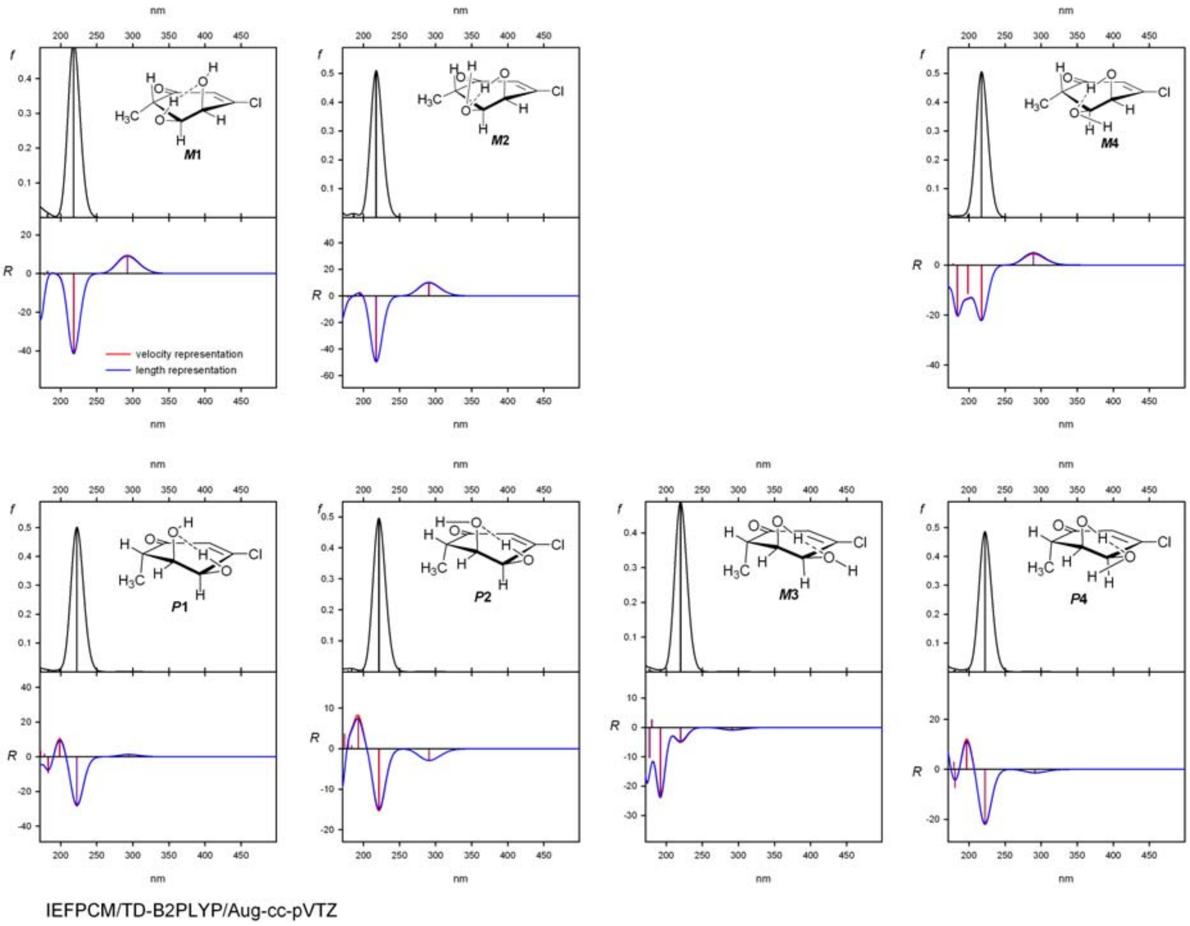


Figure B10. UV and ECD spectra calculated at the PCM/B2LYP/Aug-cc-pVTZ level for individual conformers of ***ent*-5i**, optimized at the PCM/B3LYP/6-311++G(2d,2p) level. Vertical bars represent rotatory strengths. Wavelength not corrected.