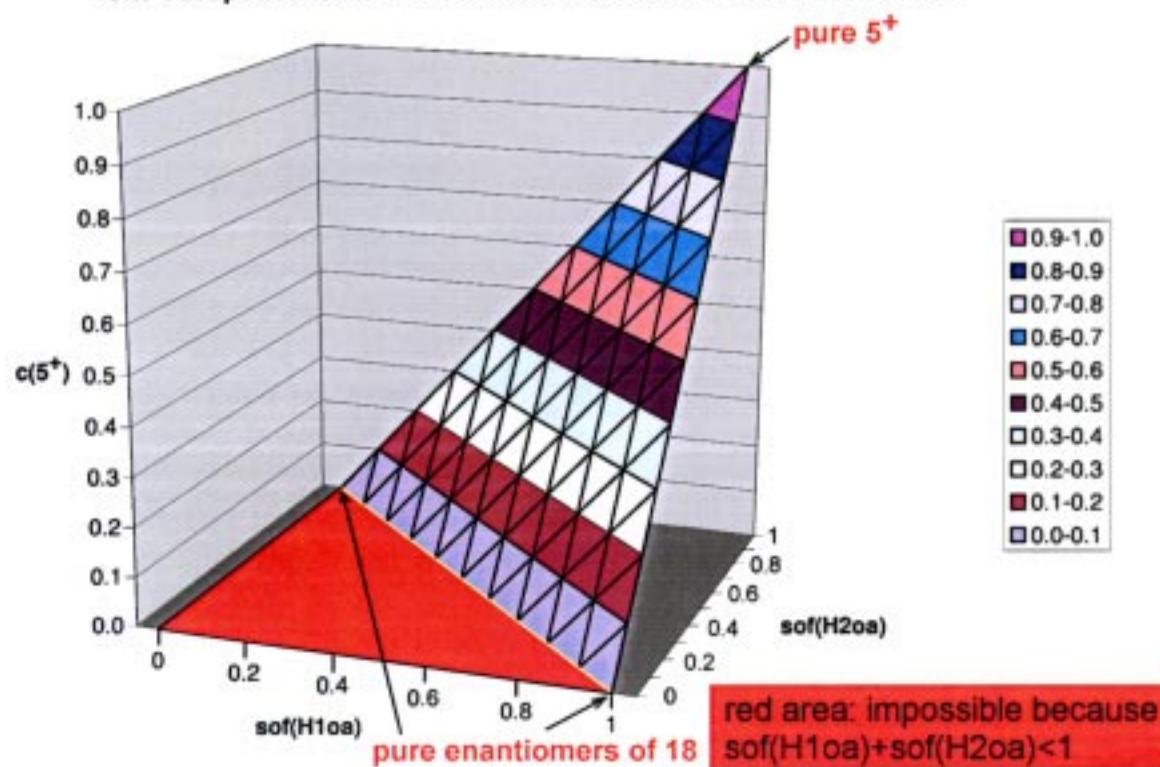


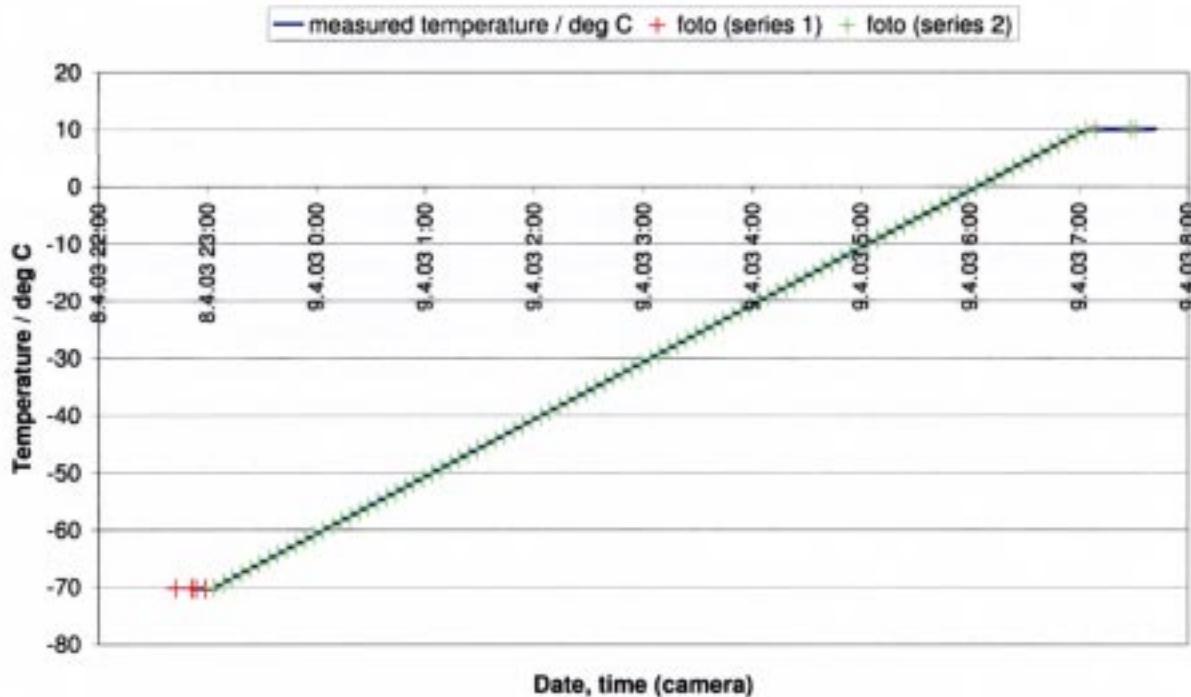
Fraction of 5^+ contributing to the observed structure as function of the hydrogen site occupation factors in the case of the assumed $5^+/18$ disorder



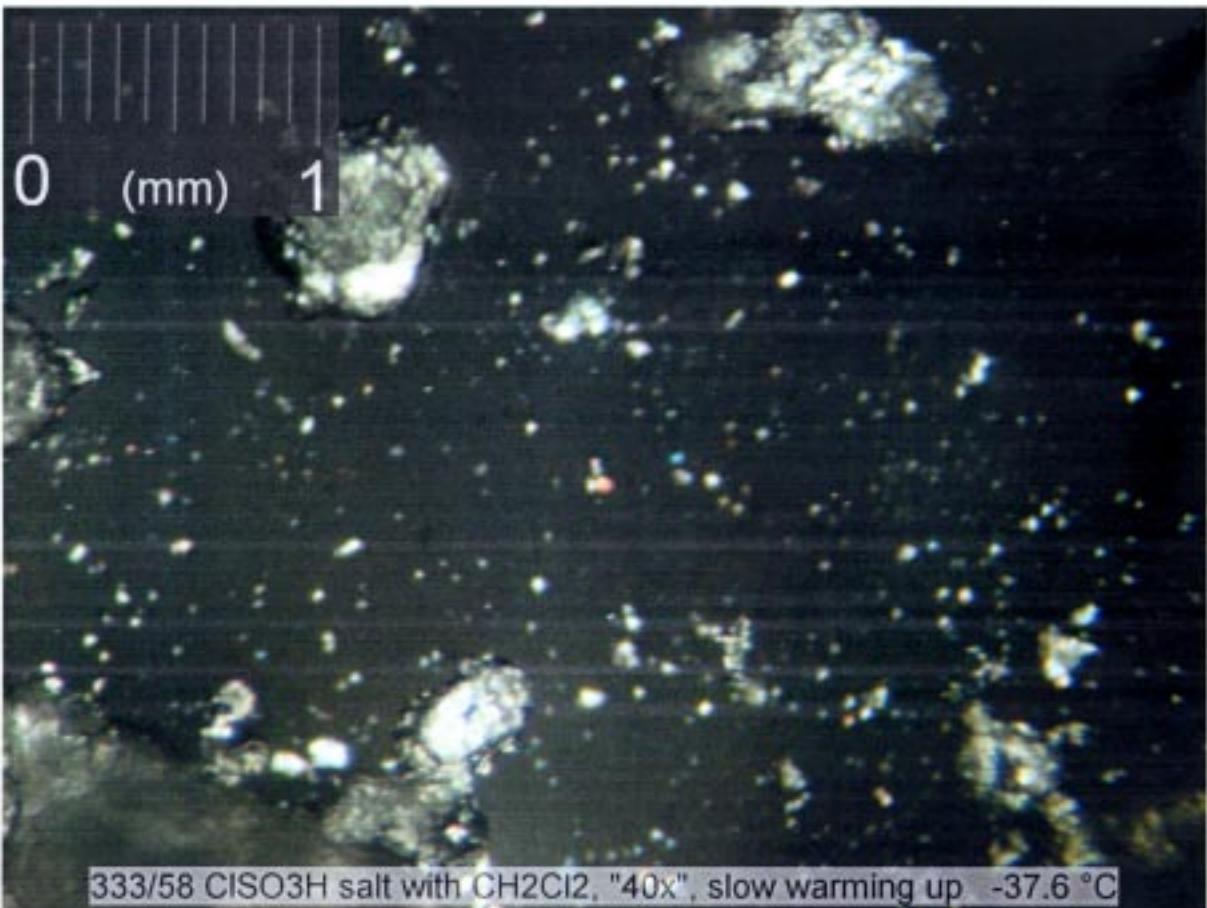
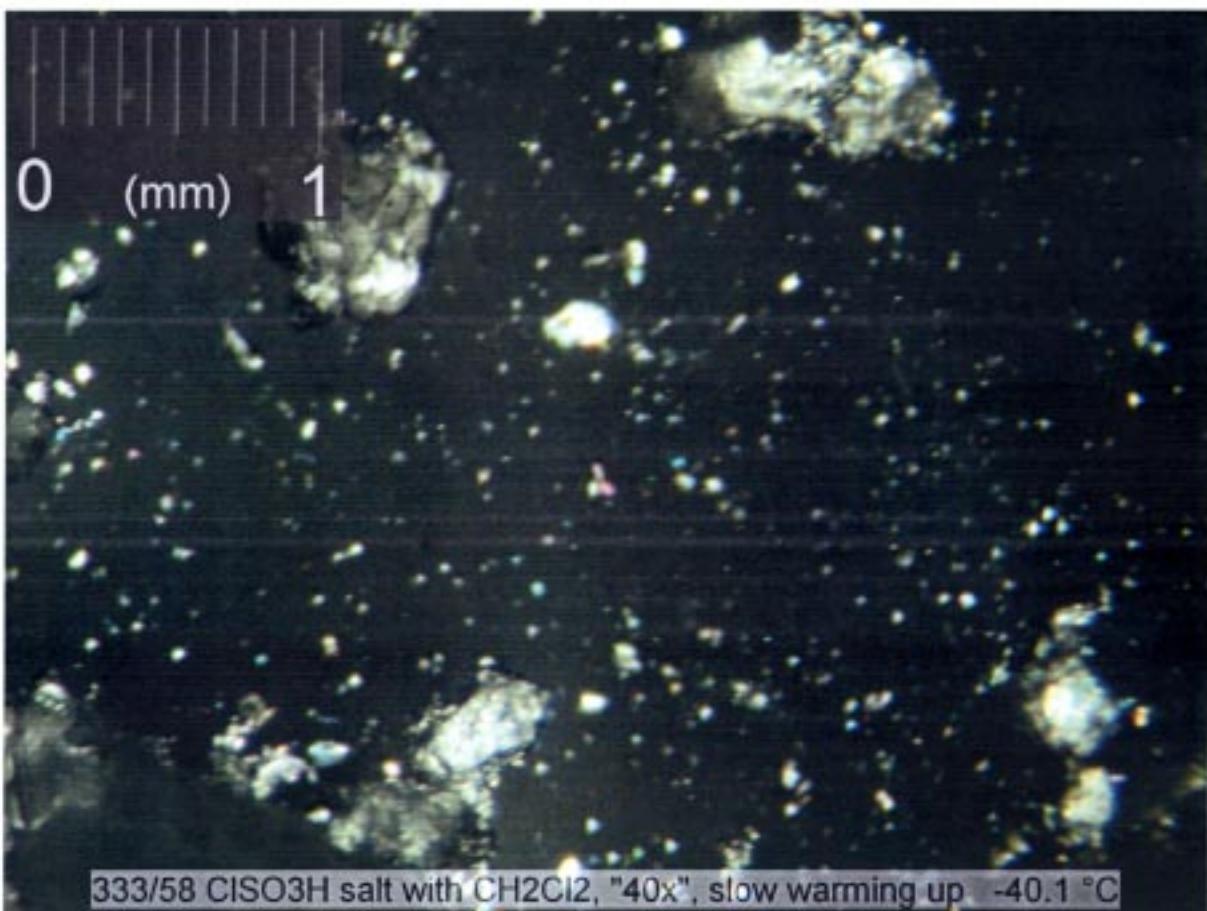
Thermal stability of crystalline $\mathbf{5}^+ \text{SO}_3\text{Cl}^- \cdot \text{CH}_2\text{Cl}_2$

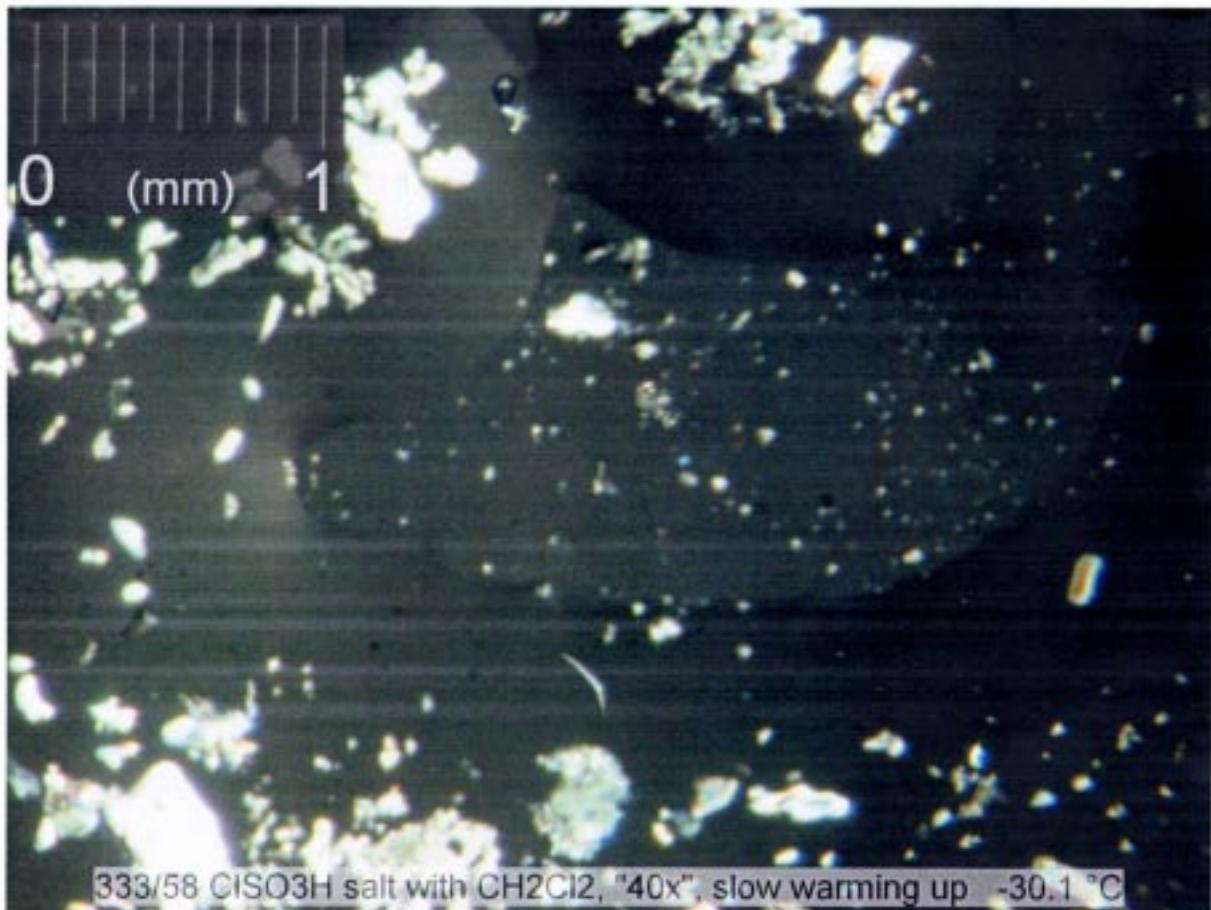
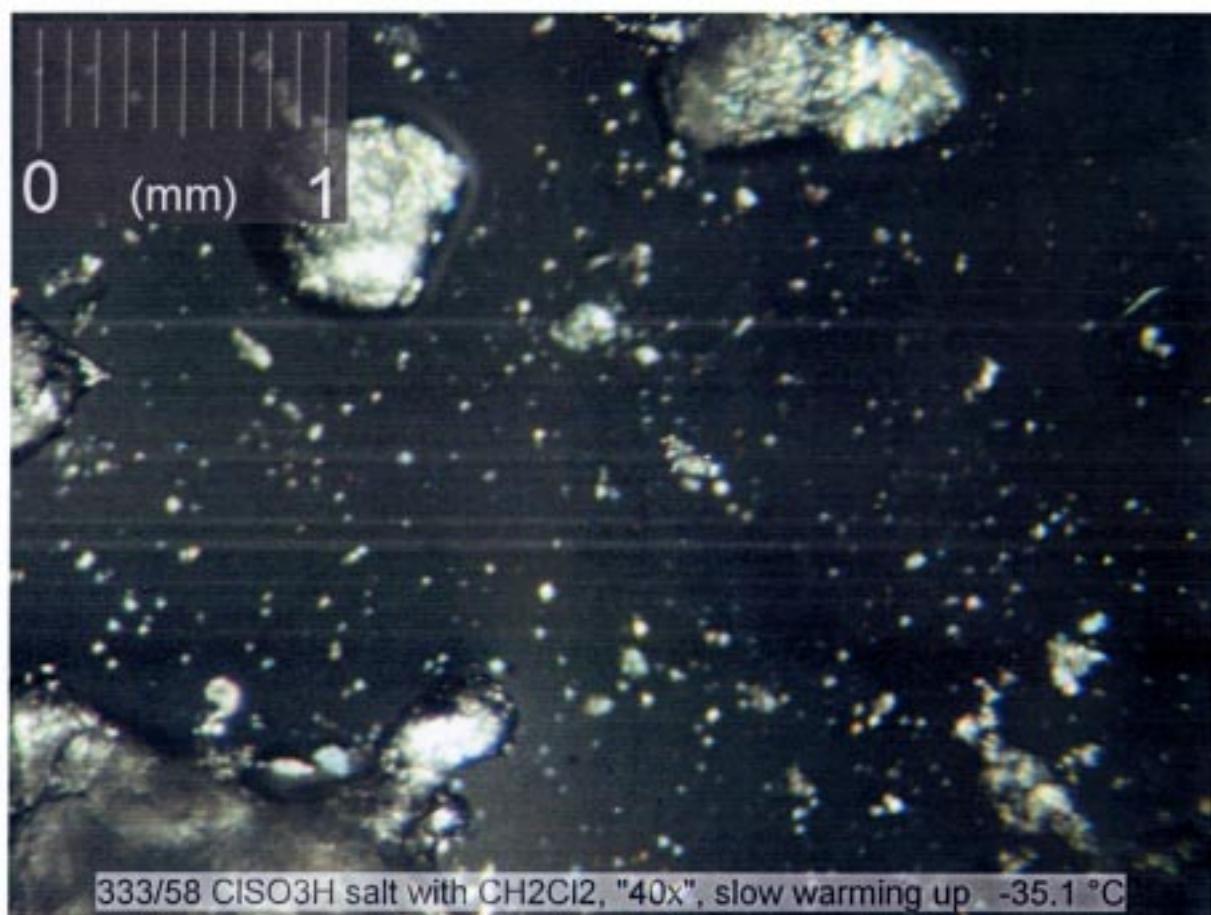
The thermal stability of a crystal sample was investigated on the cold stage of the low-temperature microscope described in fig. 6 of Laube, T. *Helv. Chim. Acta* **1994**, 77, 943. The crystals were covered with a per-fluorinated ether oil which protected them from traces of moisture during the investigation (about ten hours). The temperature of the cold stage was controlled by a Julabo FPW 80 cryostat connected via a serial cable to a computer running the Julabo program EasyTemp. The temperature/time function was stored on the computer. The same computer was used for remote control of a digital camera on the microscope via a USB cable. The experiment number was 333/58.

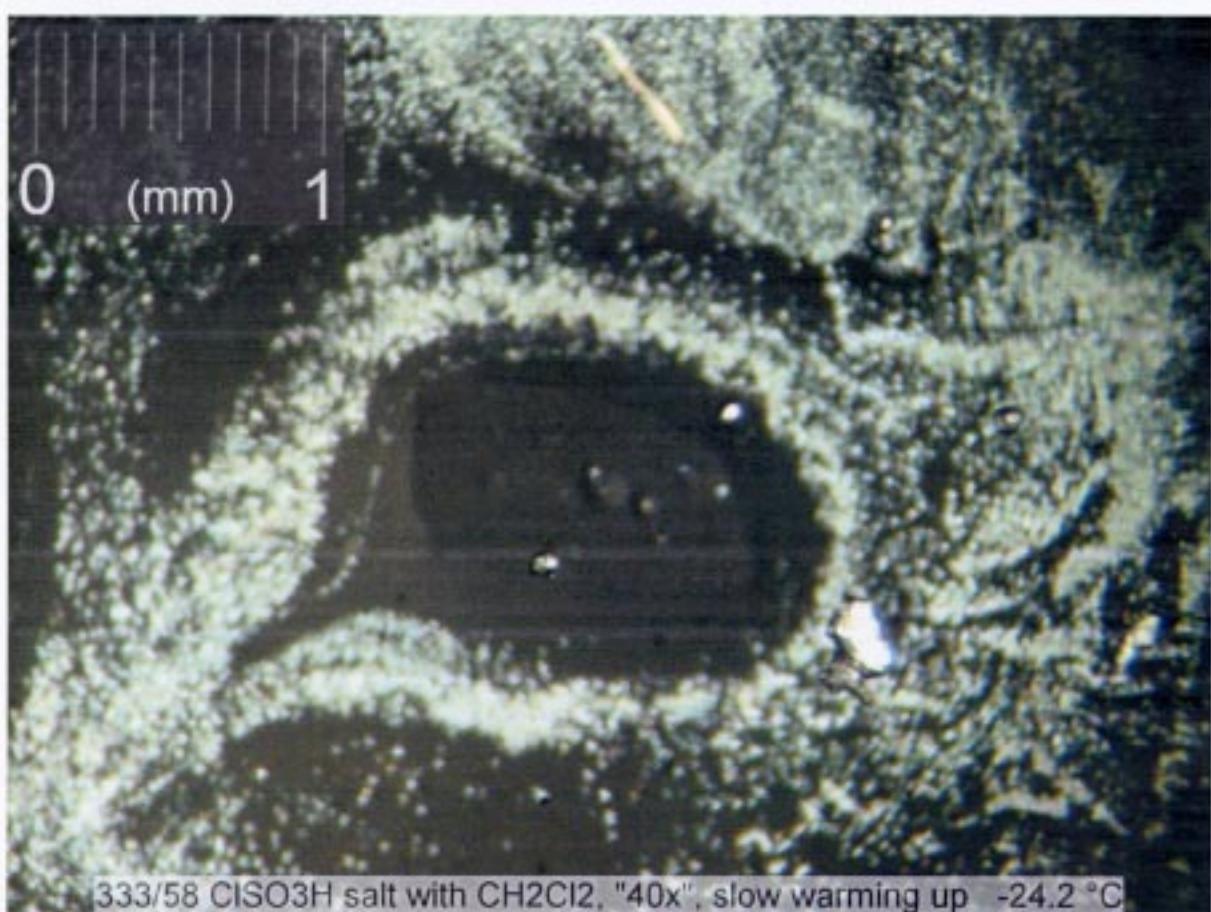
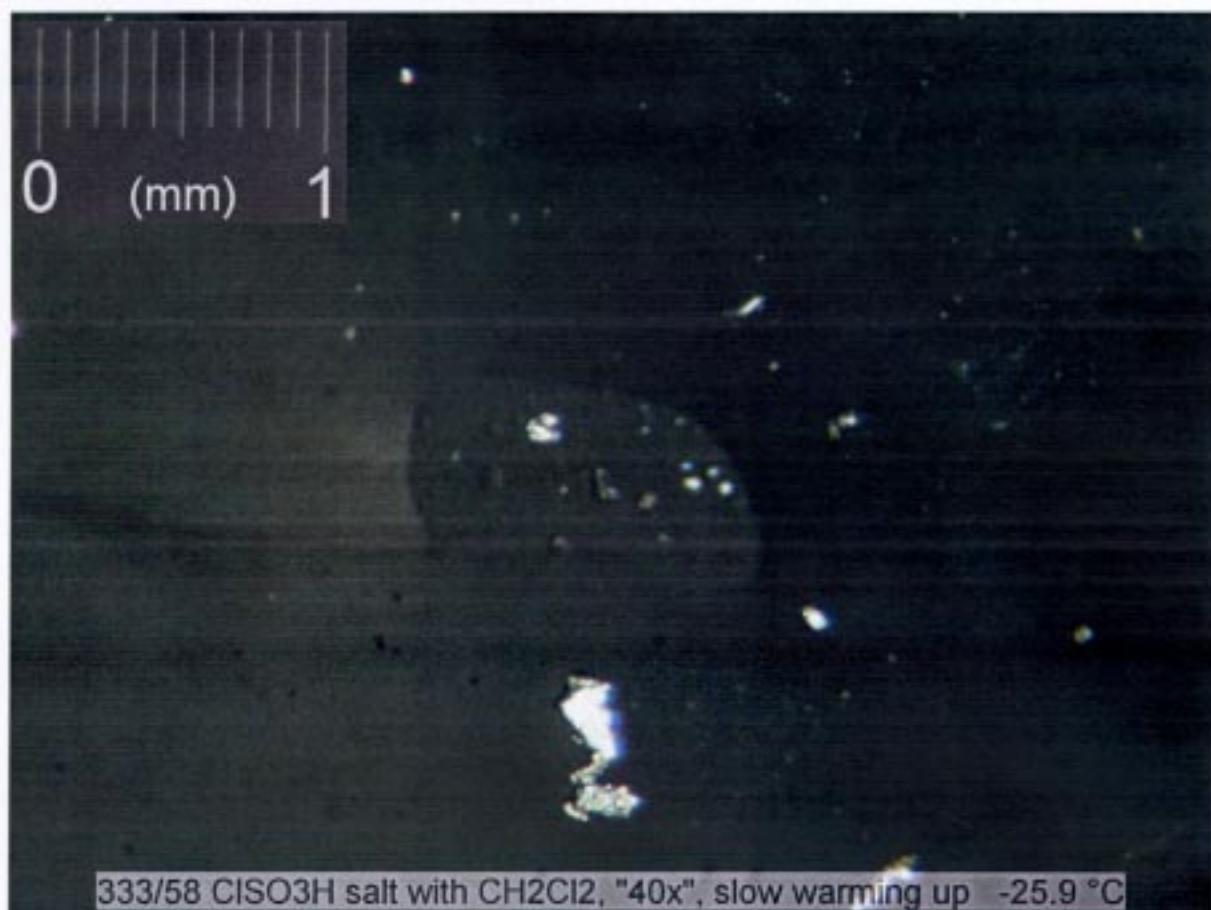
333/58: Slow warming up of the CISO_3H salt CH_2Cl_2 solvate on the cold stage of the LT microscope

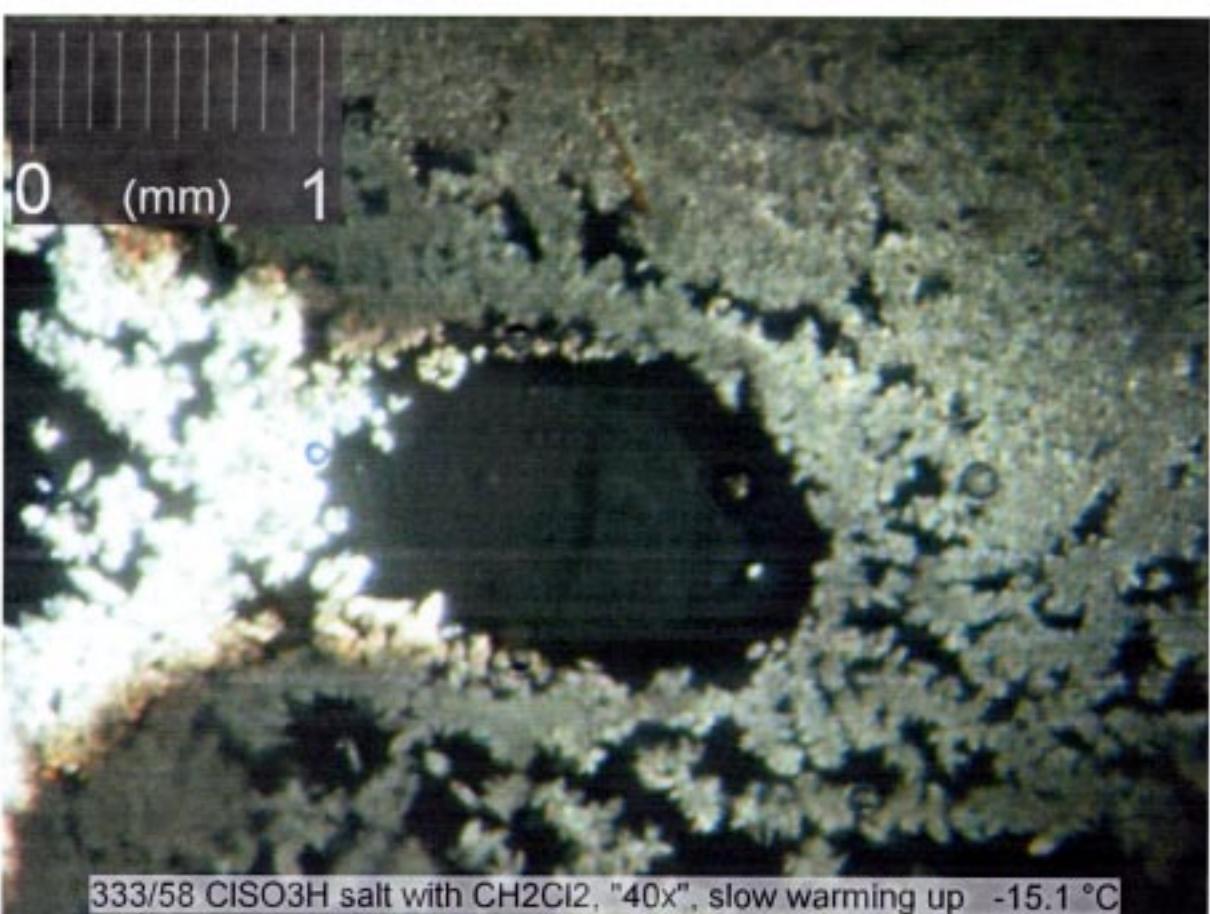
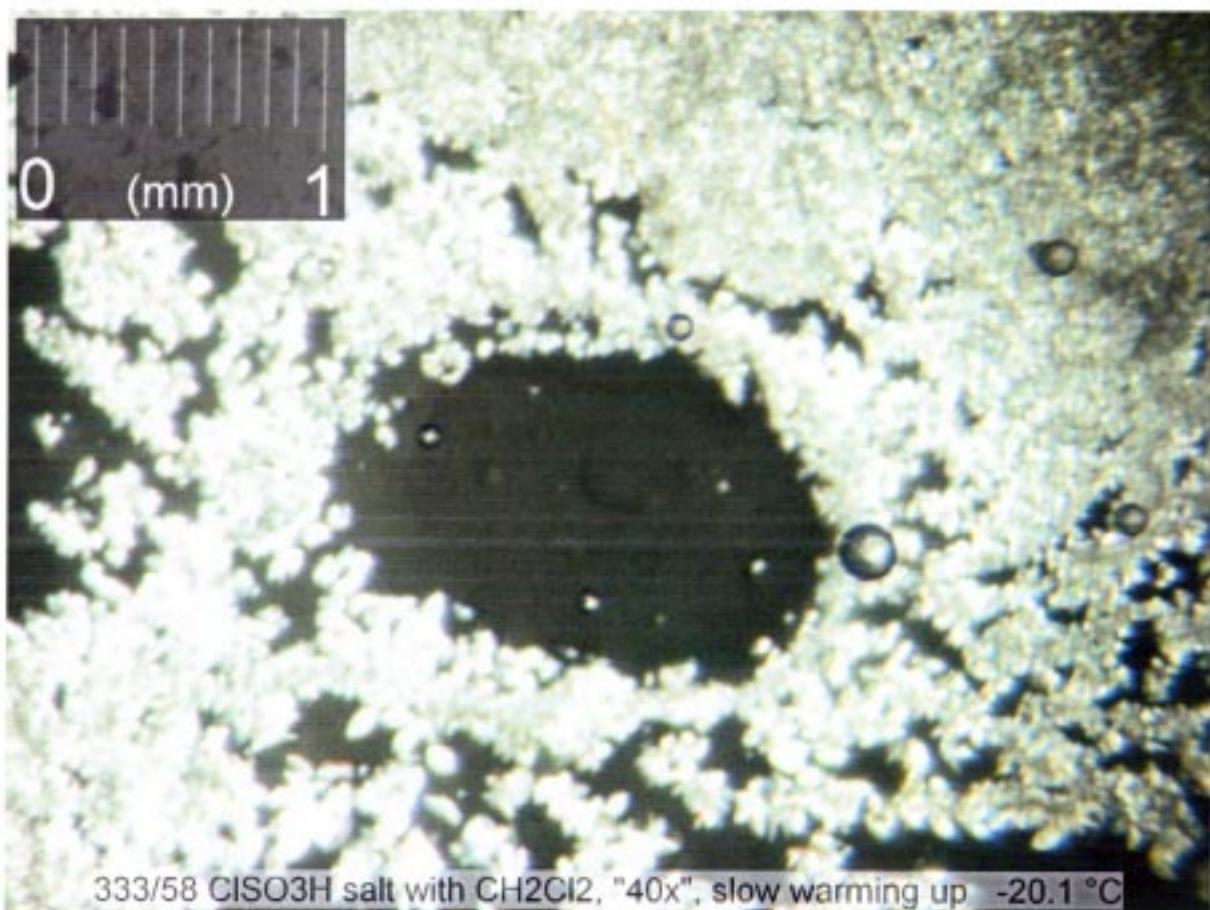


The following fotos show the melting and decomposition of the sample, and later crystallization of another compound and gas evolution.



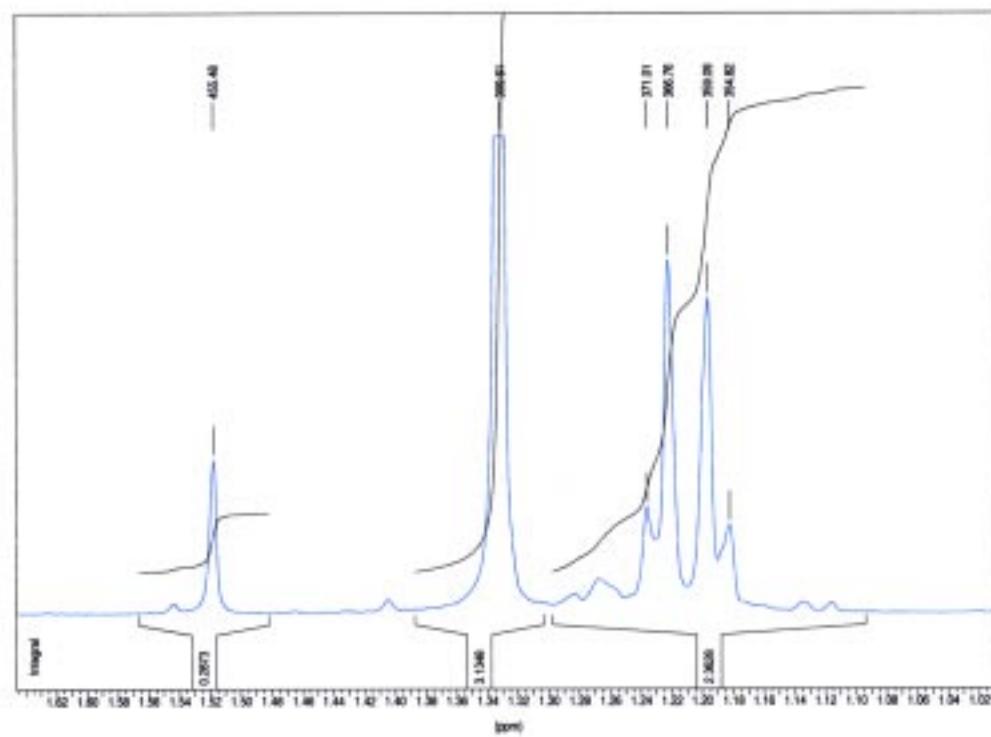
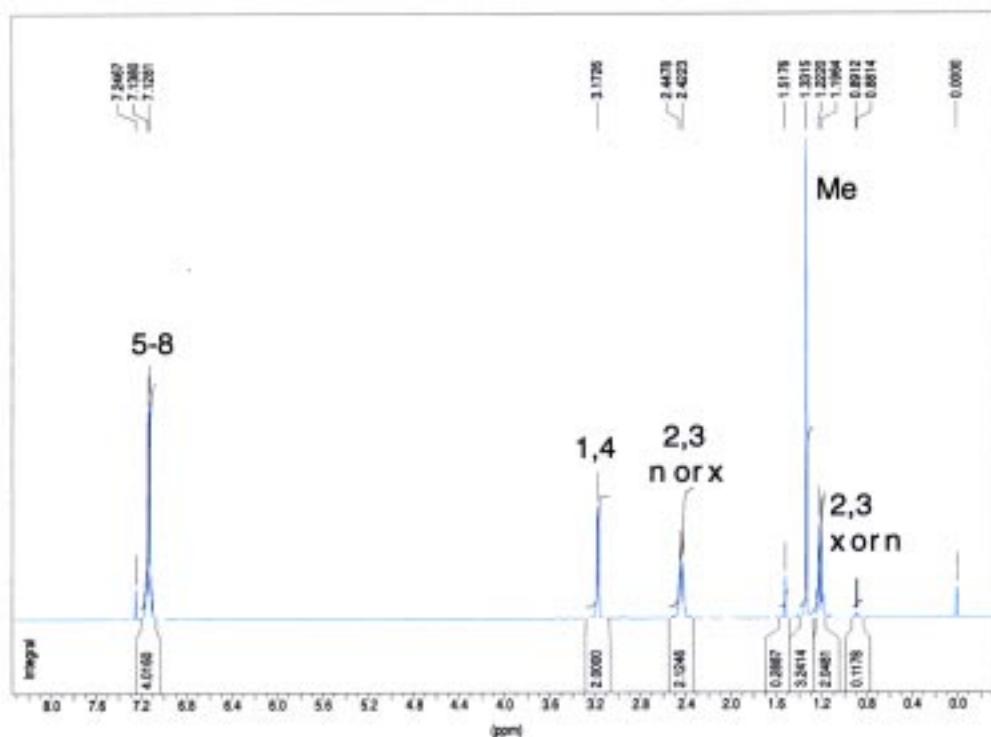


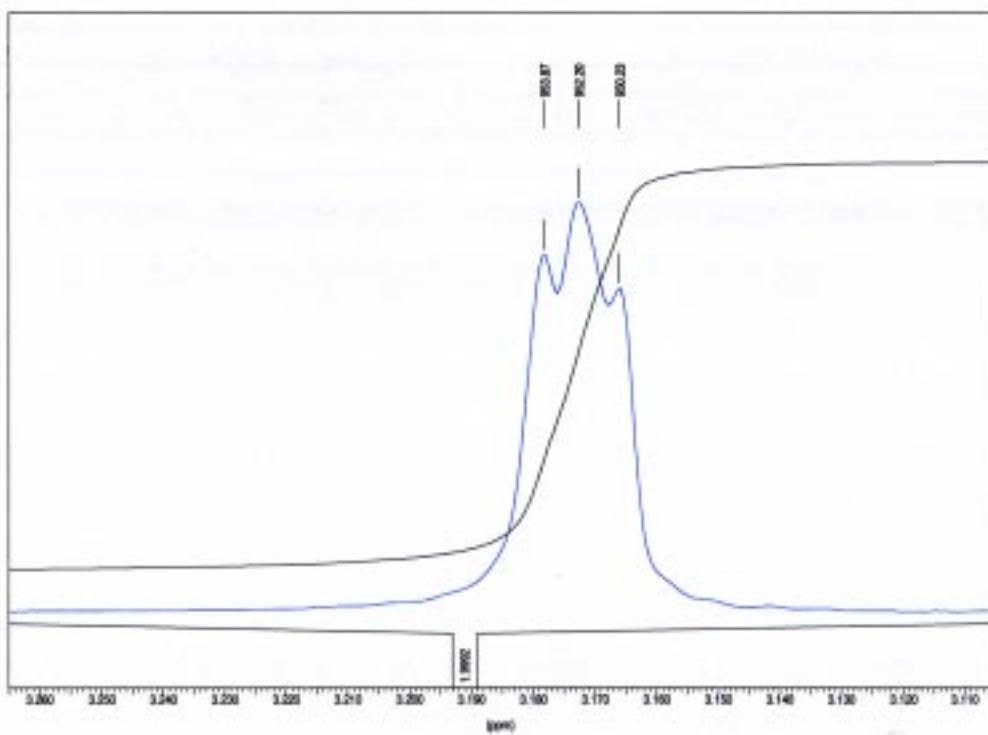
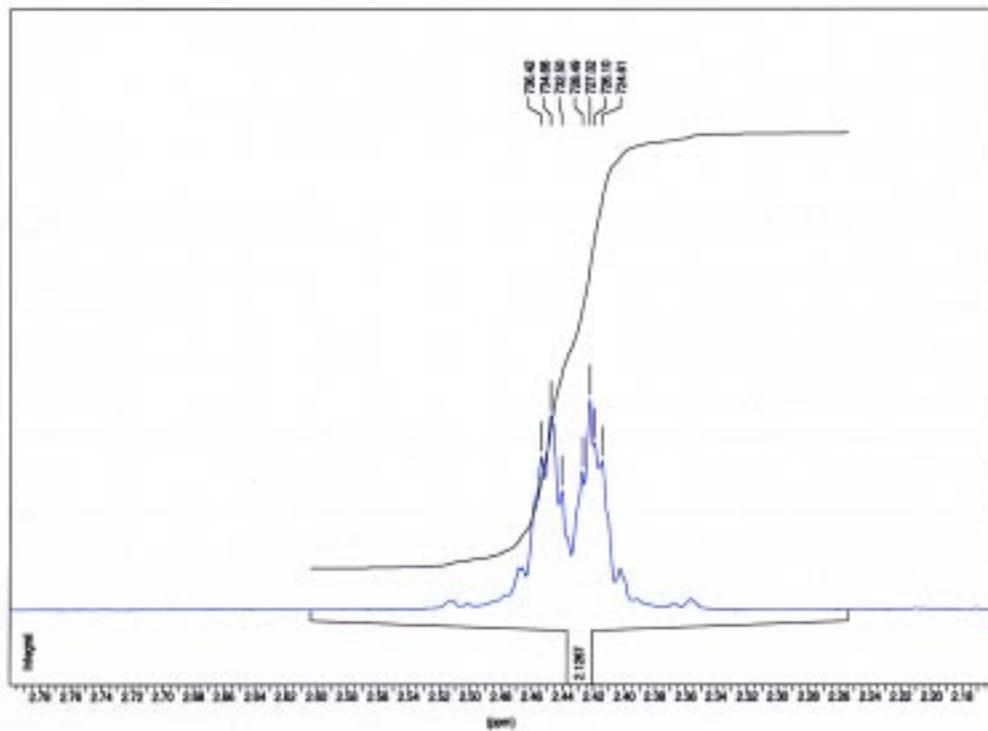


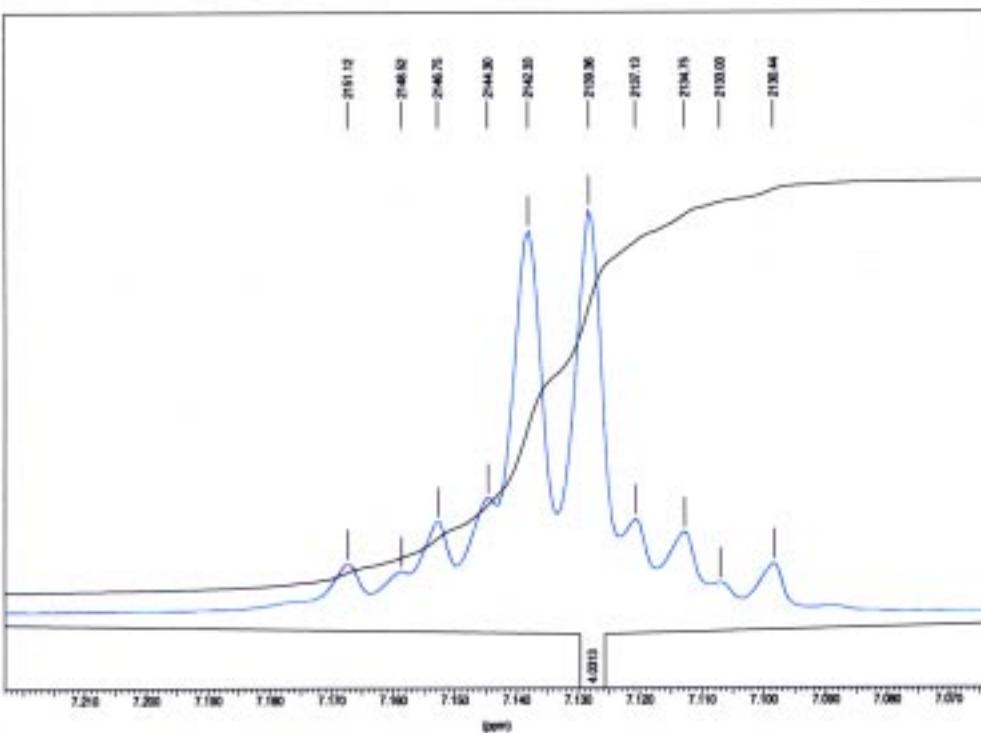


NMR spectra of 16, 17, 18, 5⁺

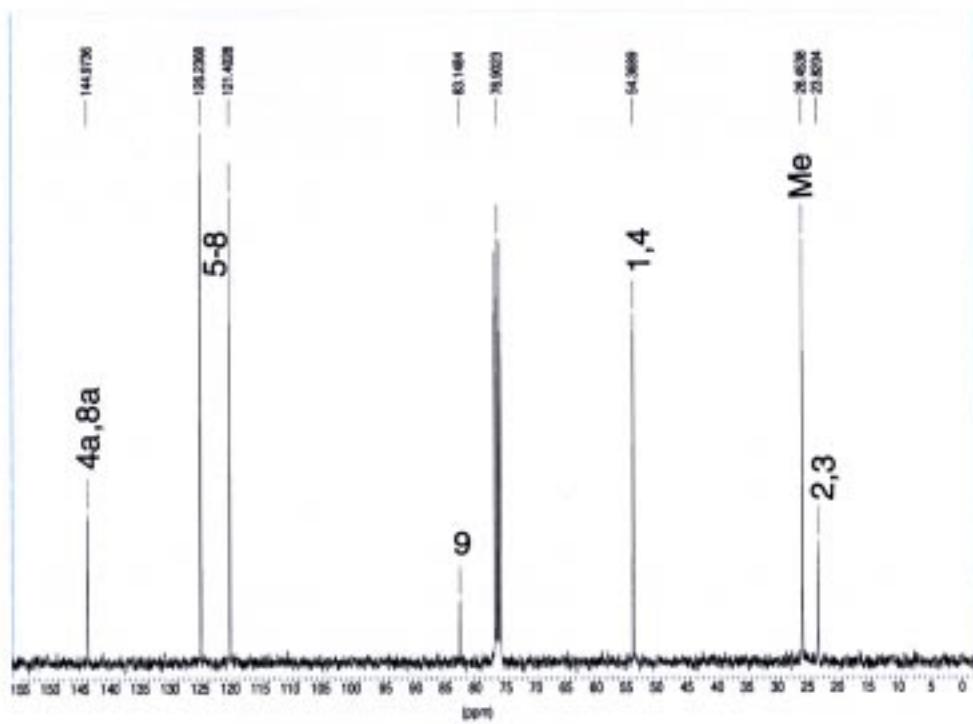
¹H-NMR spectrum of 16 (300 MHz, in CDCl₃)





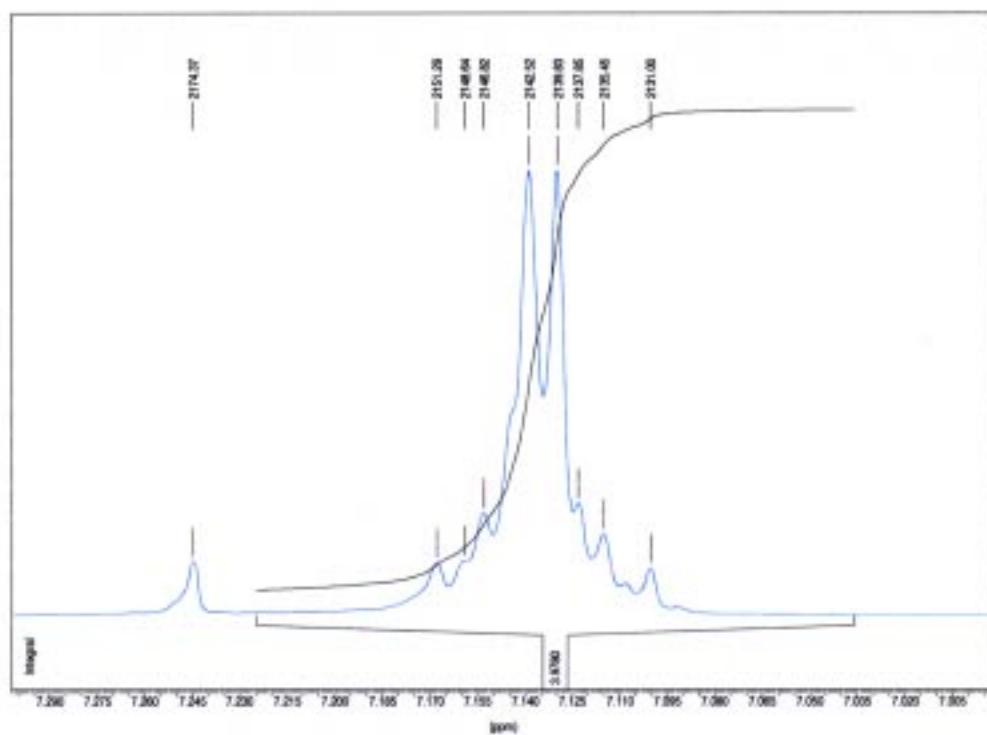
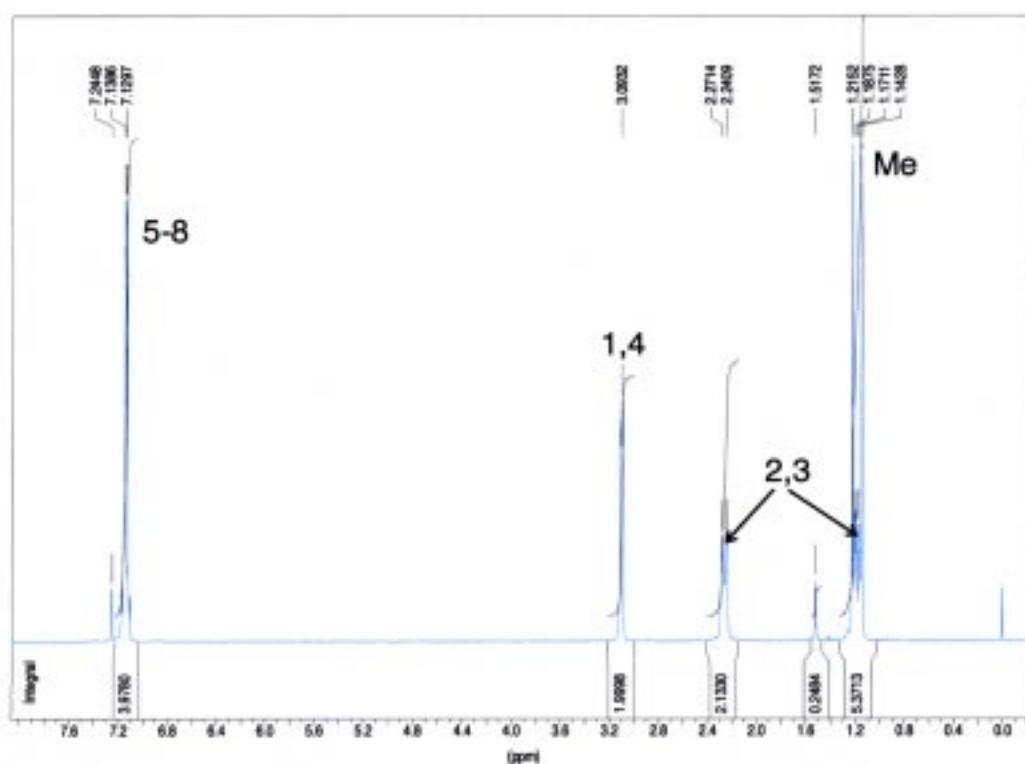


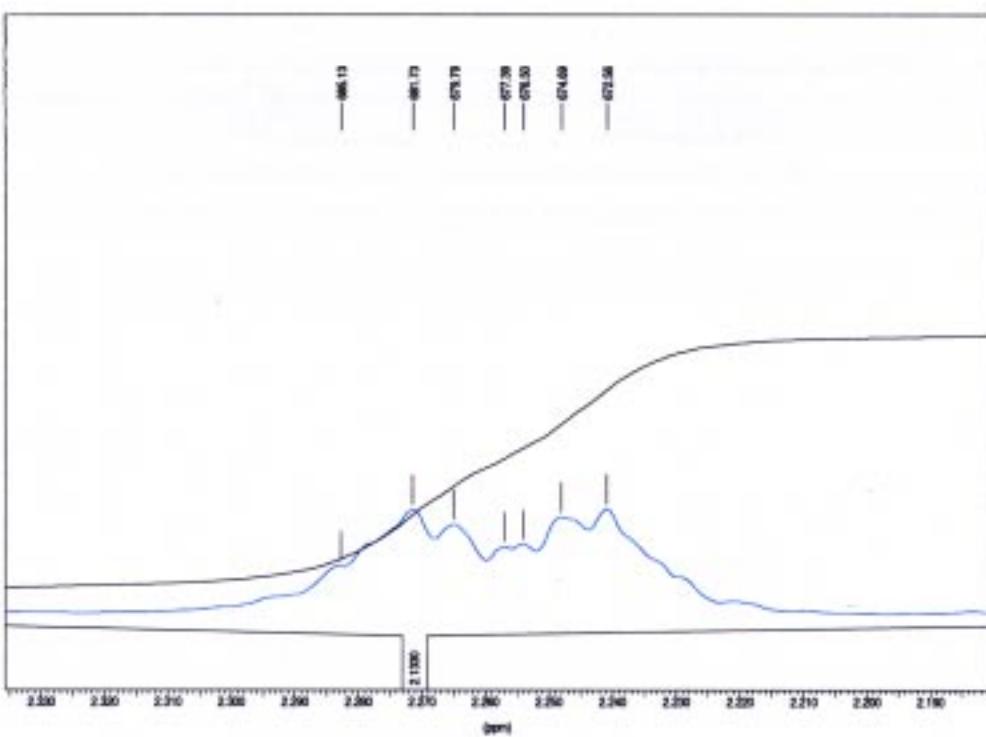
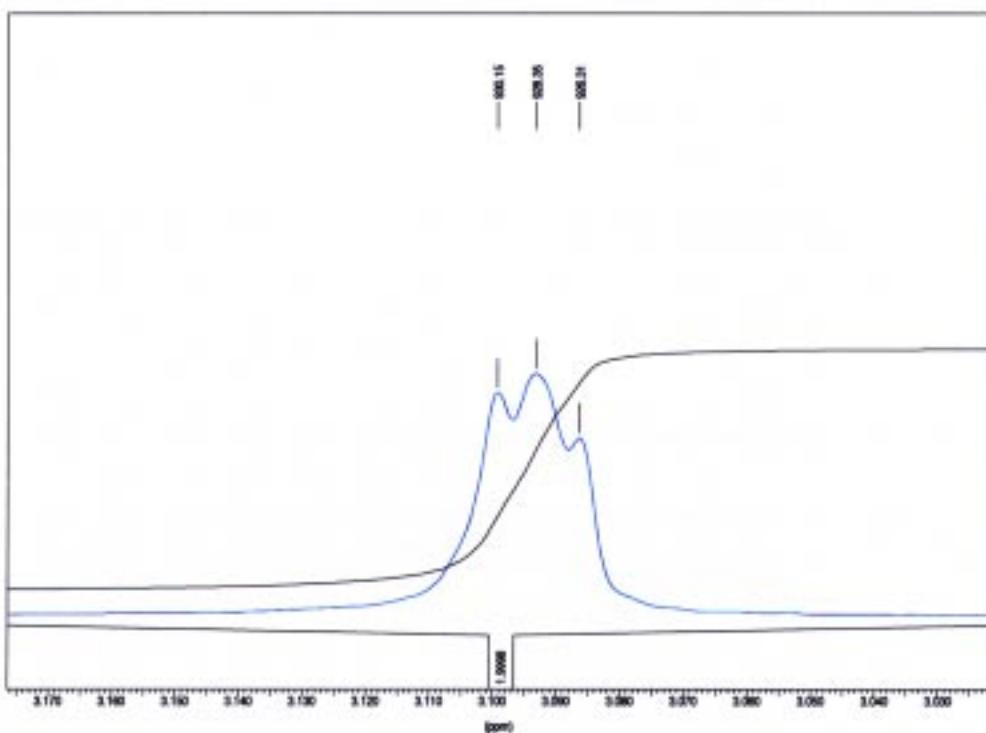
¹³C-NMR spectrum of **16** (in CDCl₃)

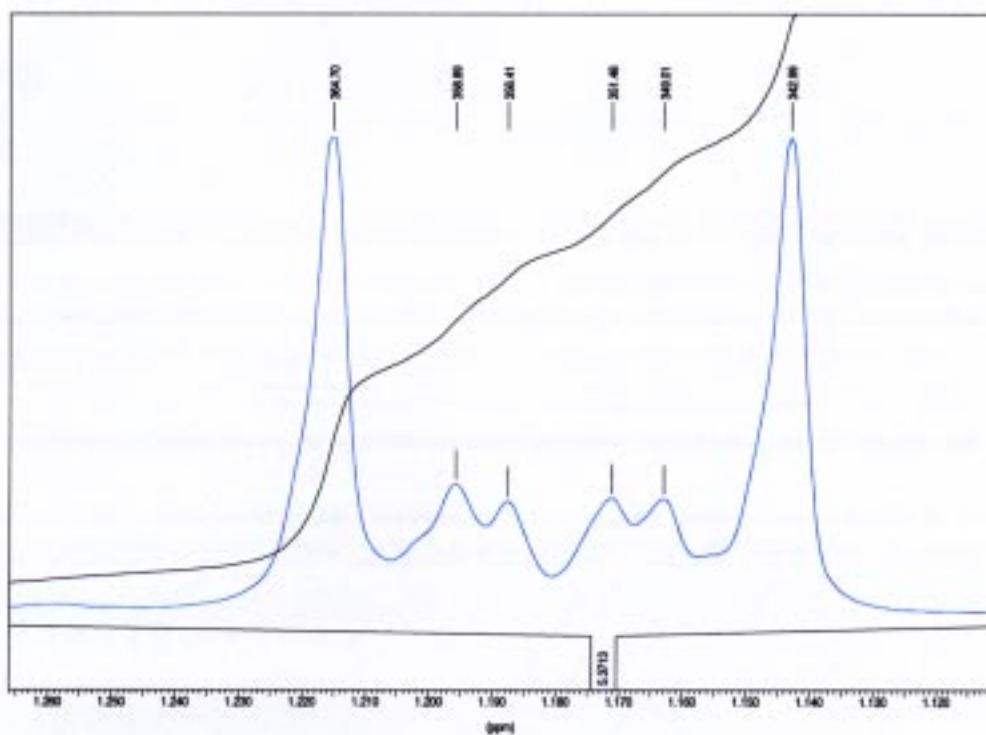


¹H-NMR spectrum of 17 (300 MHz, in CDCl₃)

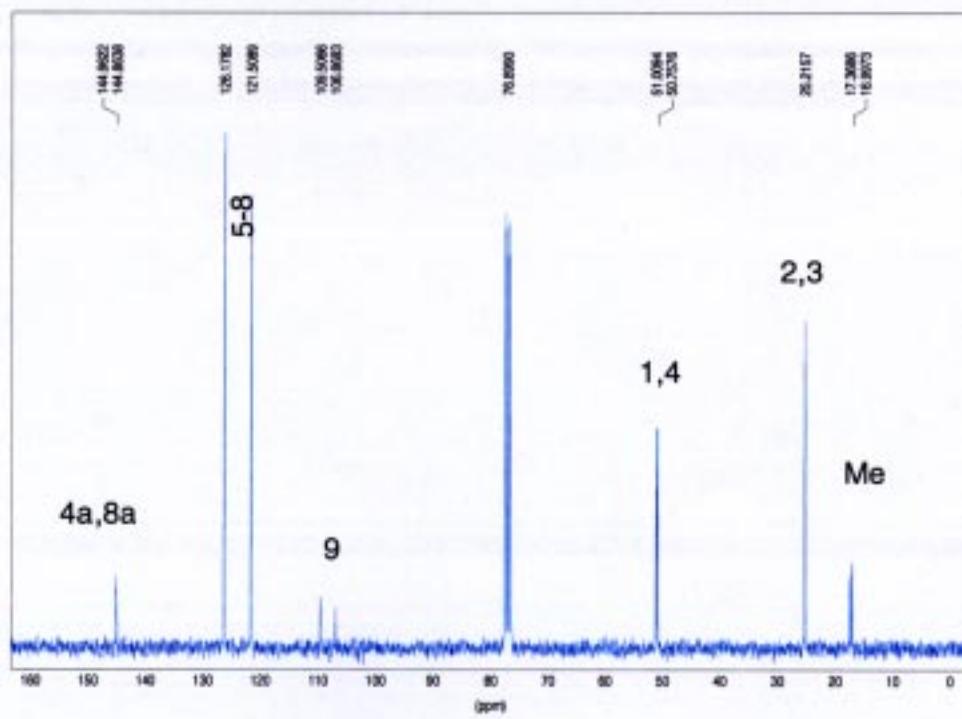
For NMR data of 9-fluorobenzonorbornane see: Adcock, W.; Angus, D. I.; Lowe, D. A. *Magn. Reson. Chem.* 1996, 34, 675-680. These authors assume that the F atom is *anti* to the benzene ring.



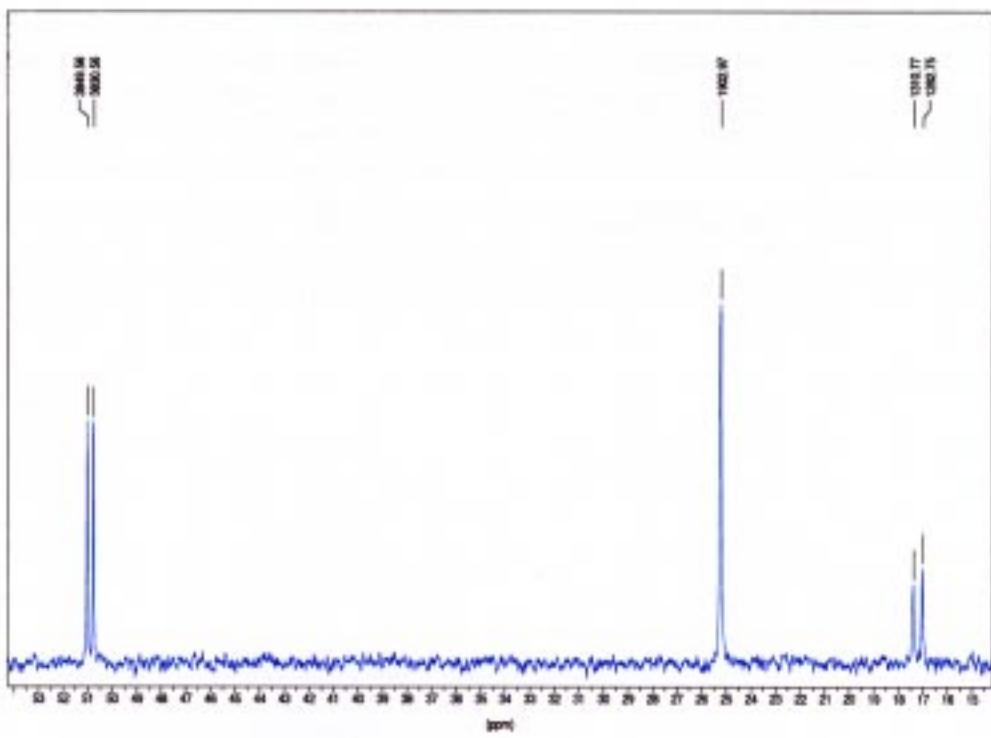
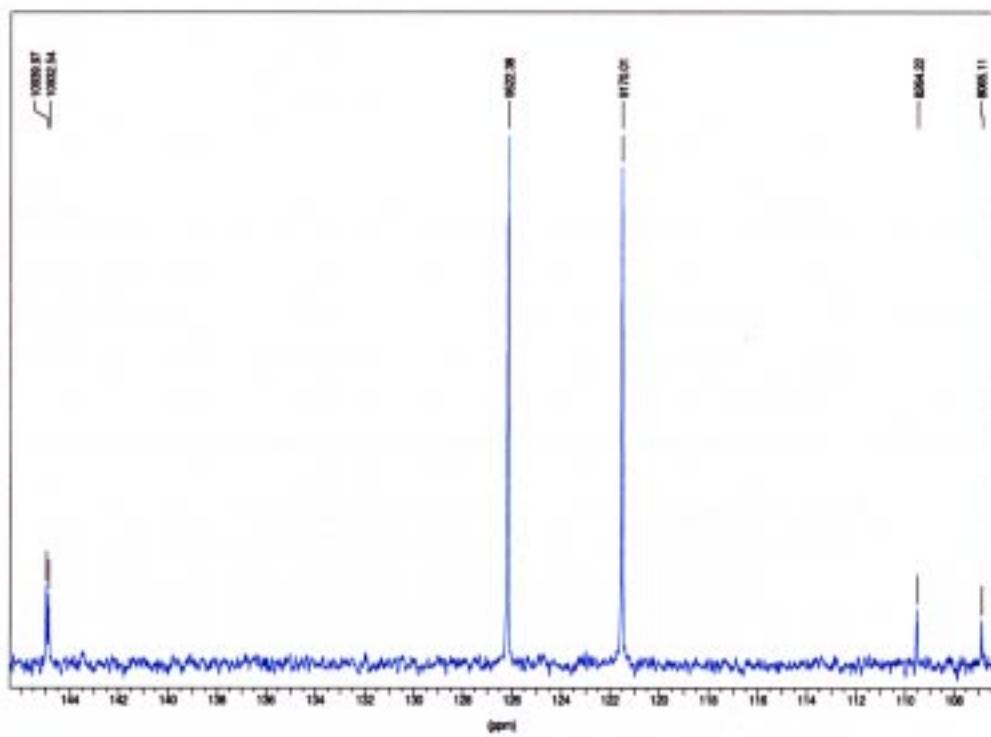




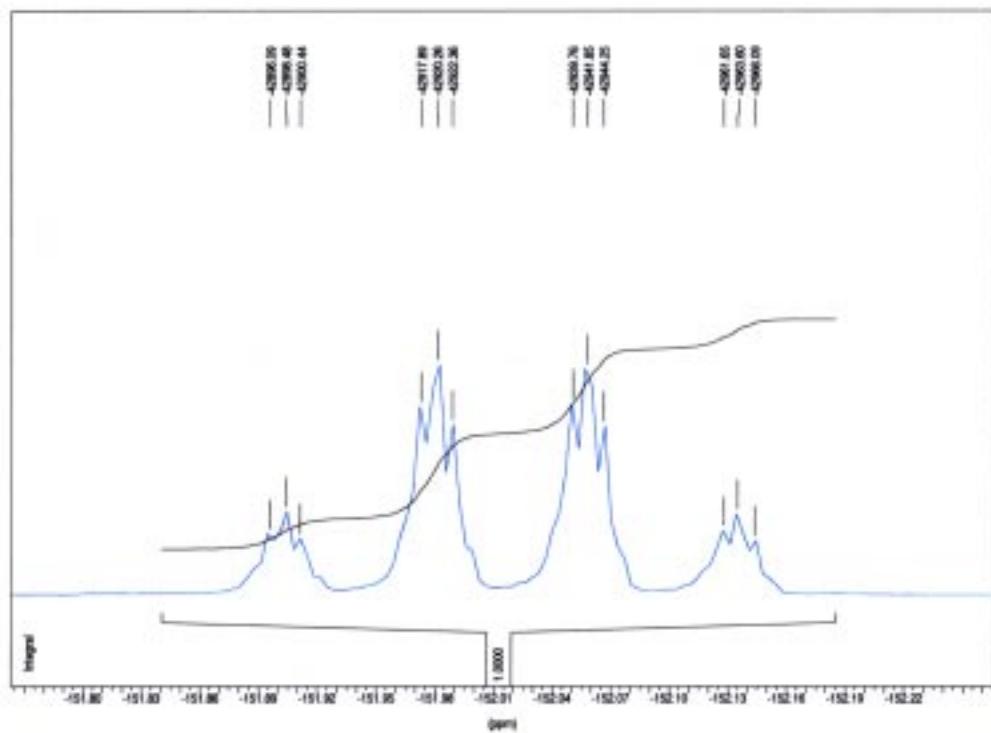
¹³C-NMR spectrum of **17** (in CDCl₃)



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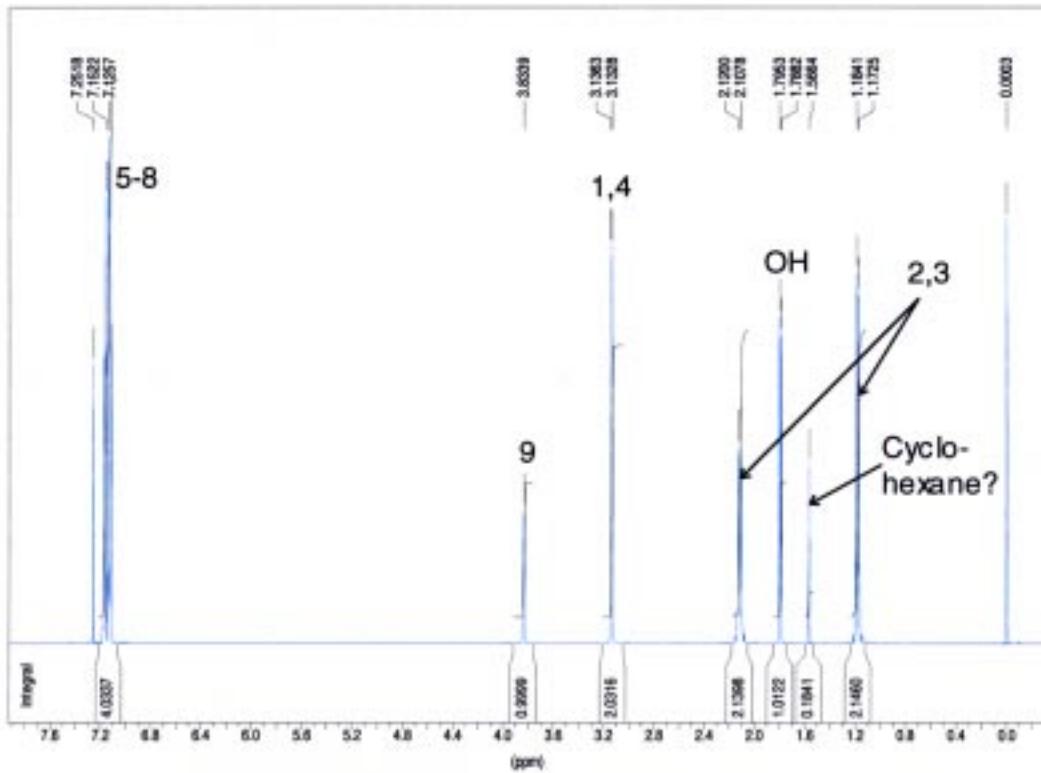


¹⁹F-NMR spectrum of **17** (in CDCl₃)

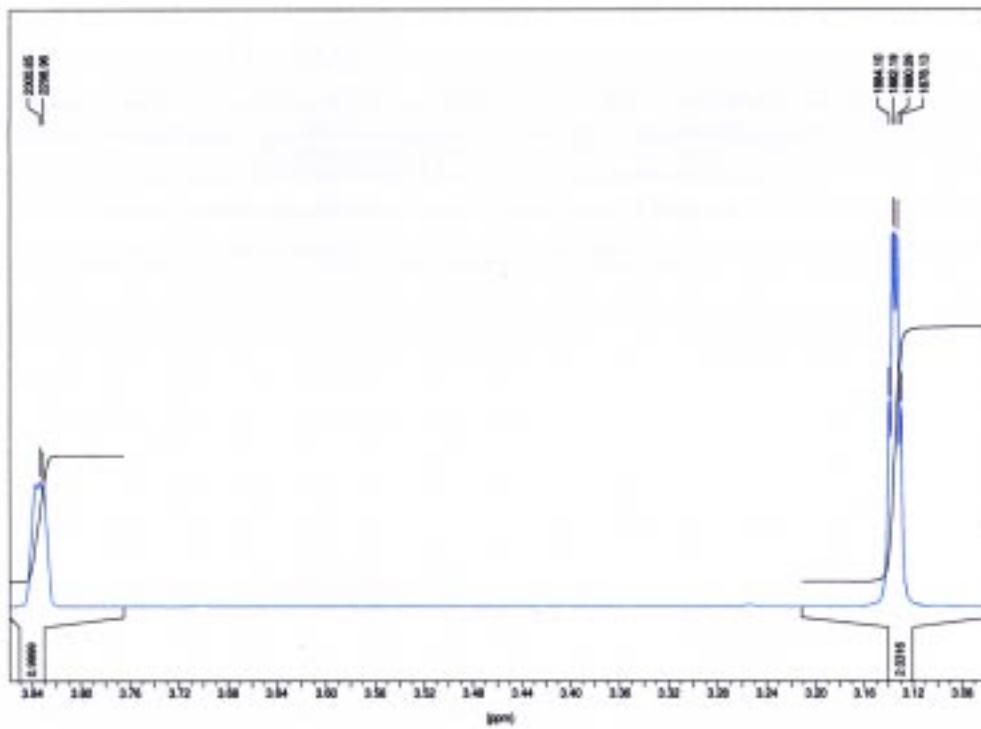
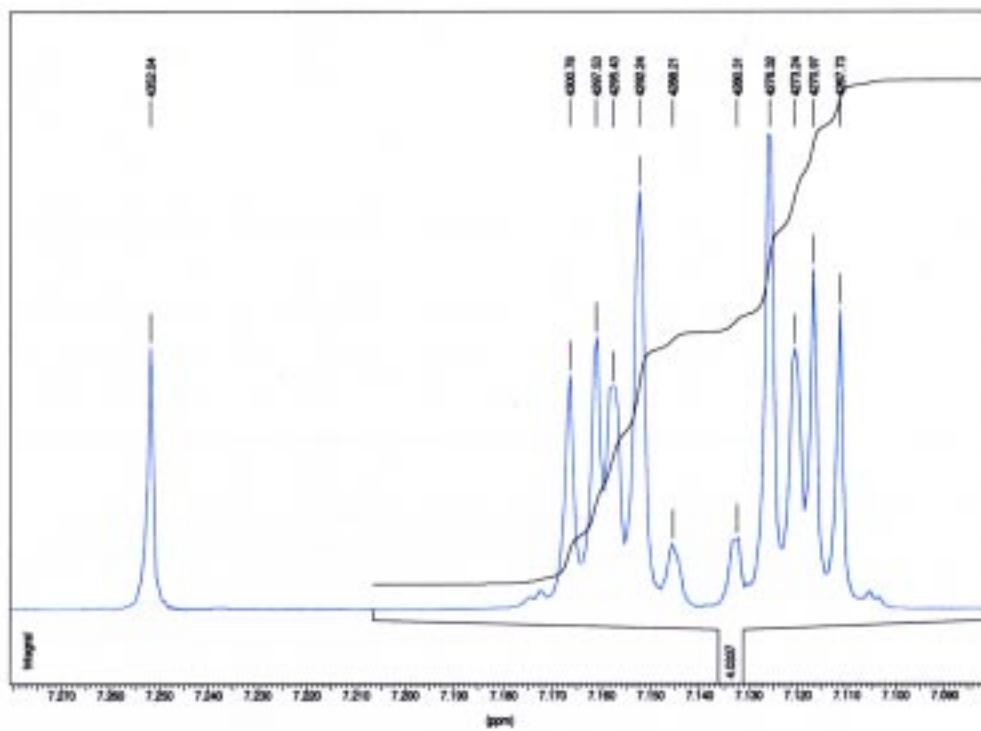


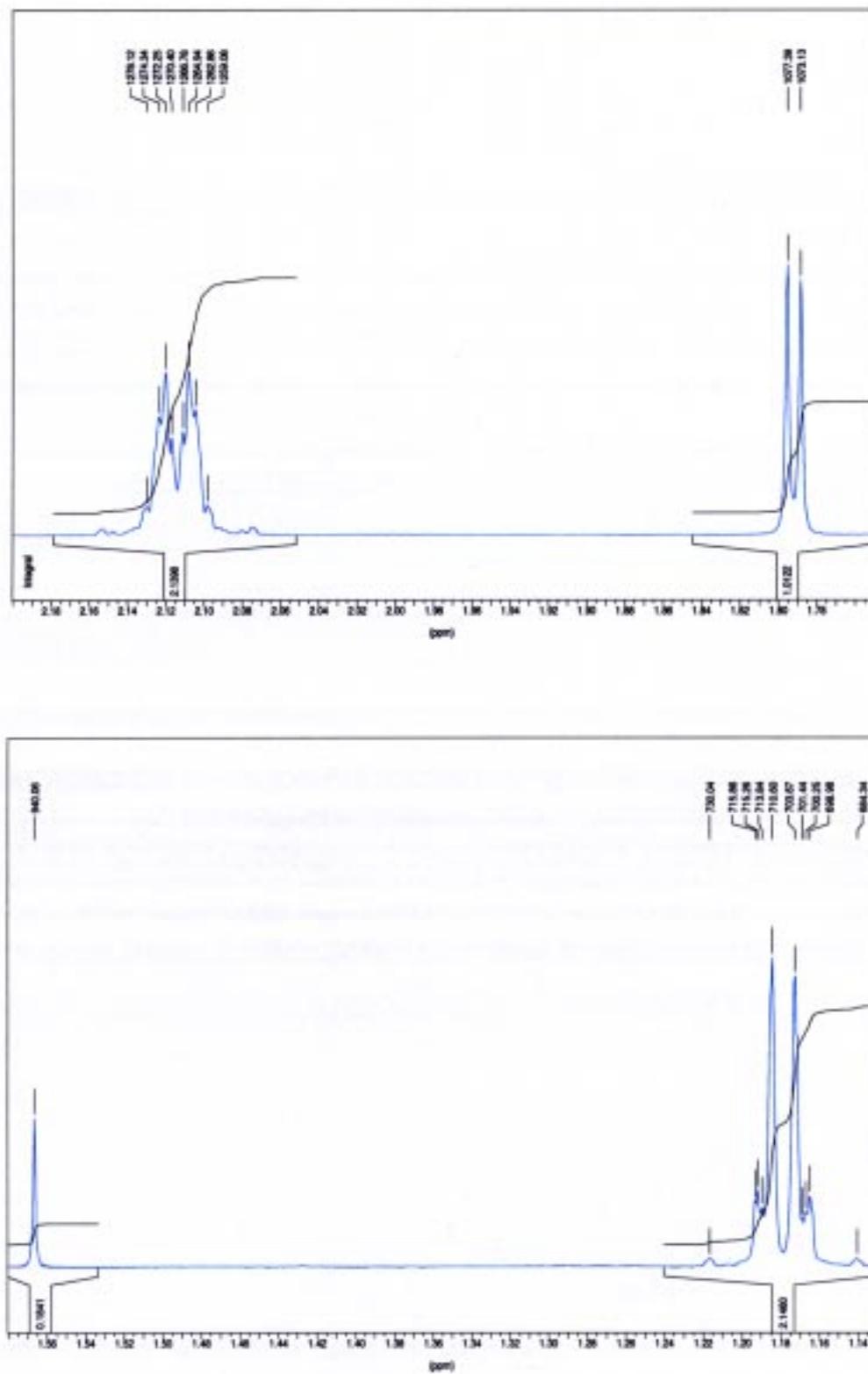
The large coupling must stem from the methyl hydrogens. The coupling partners for the smaller coupling constant could not be assigned.

¹H-NMR spectrum of **18** (600 MHz; in CDCl₃)



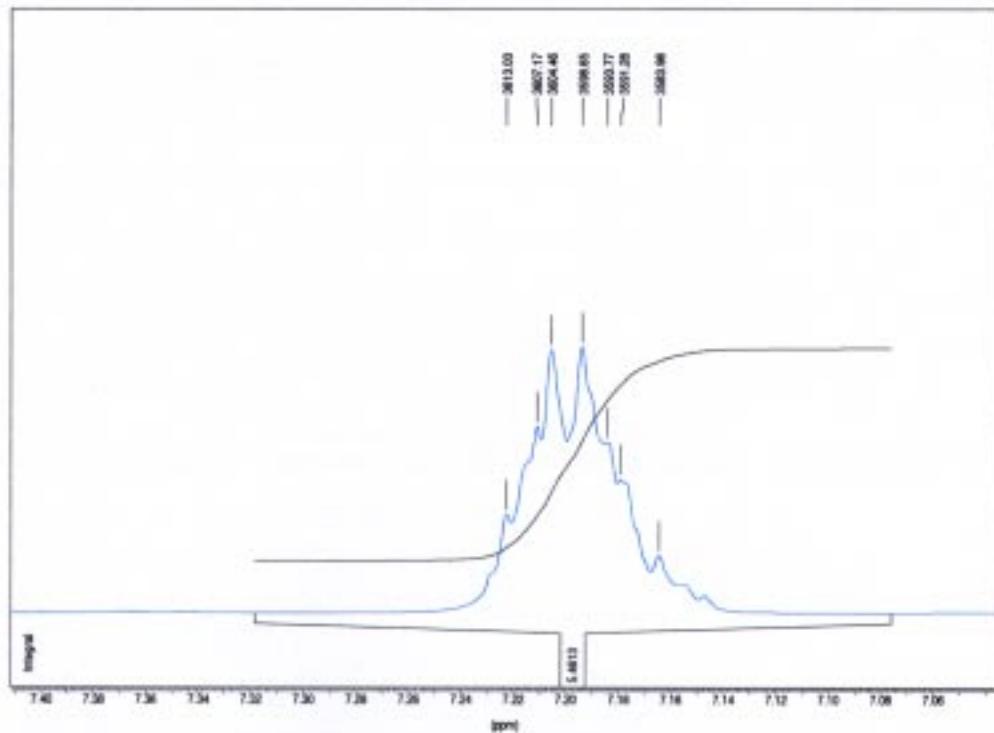
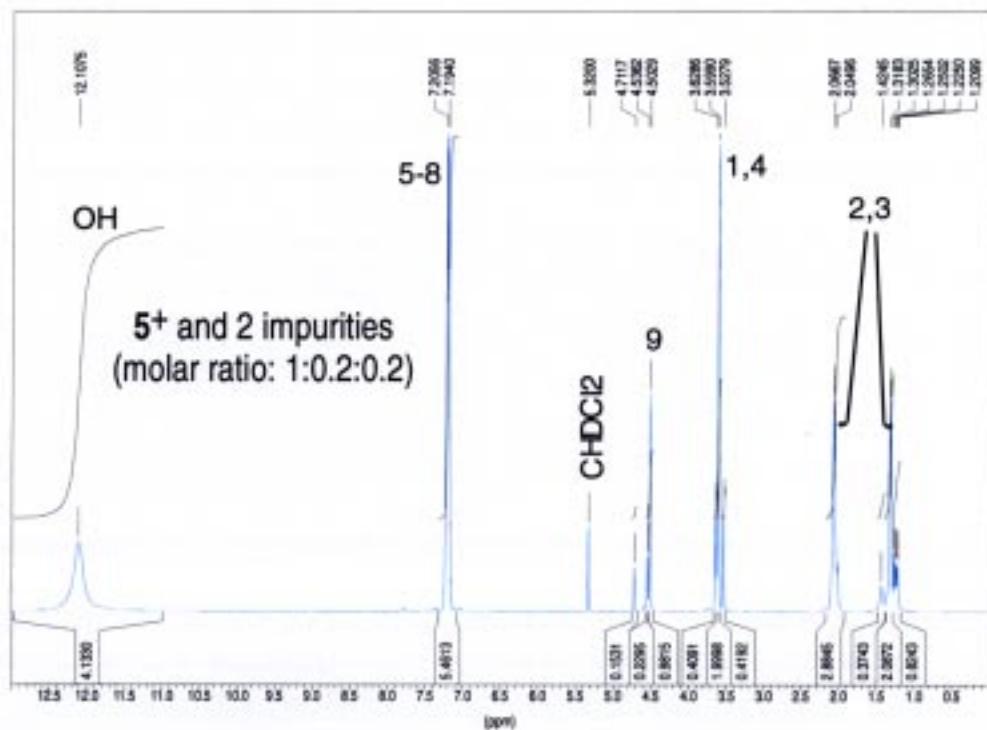
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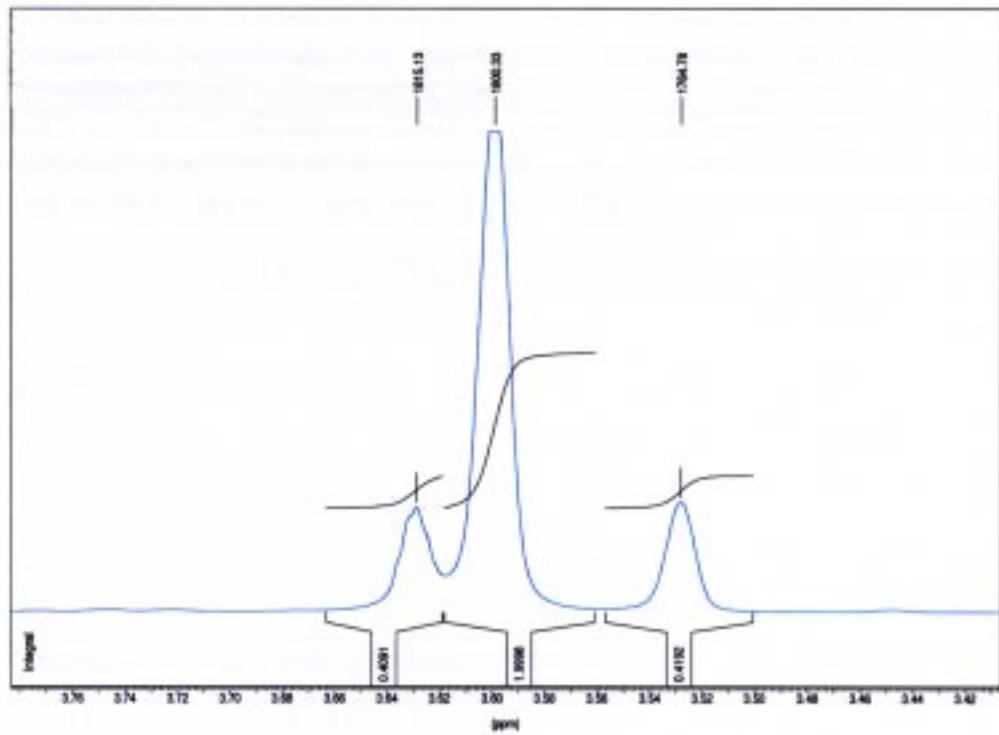
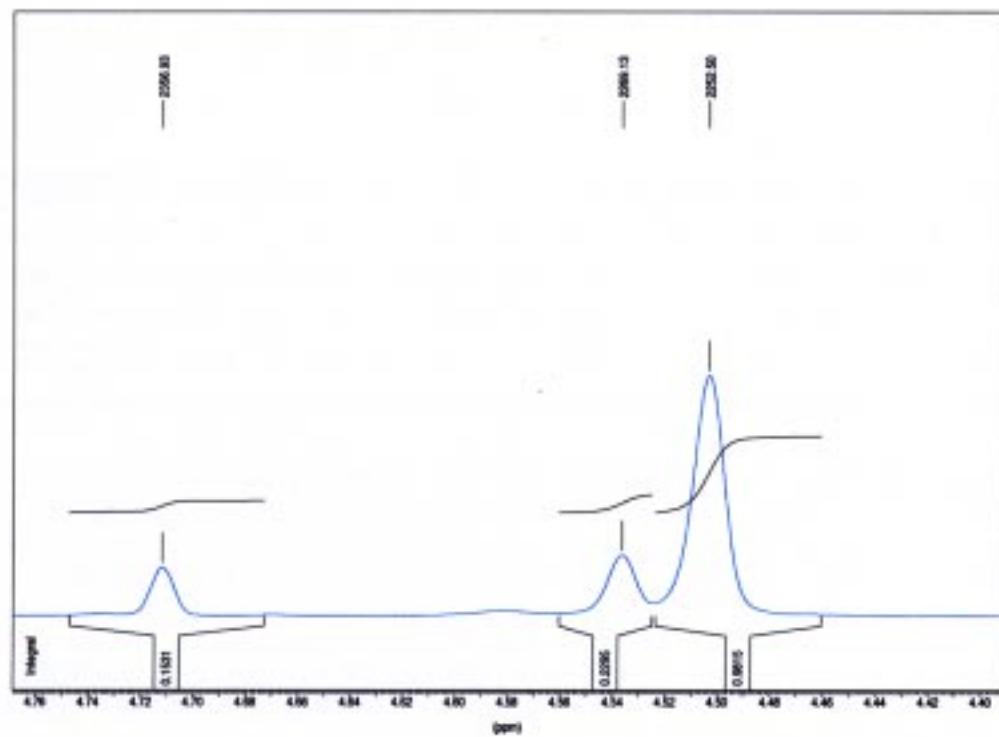


¹H-NMR spectrum of **5⁺** SO₃Cl⁻ or **18 · ClSO₃H** (500 MHz; 193 K; in CD₂Cl₂)

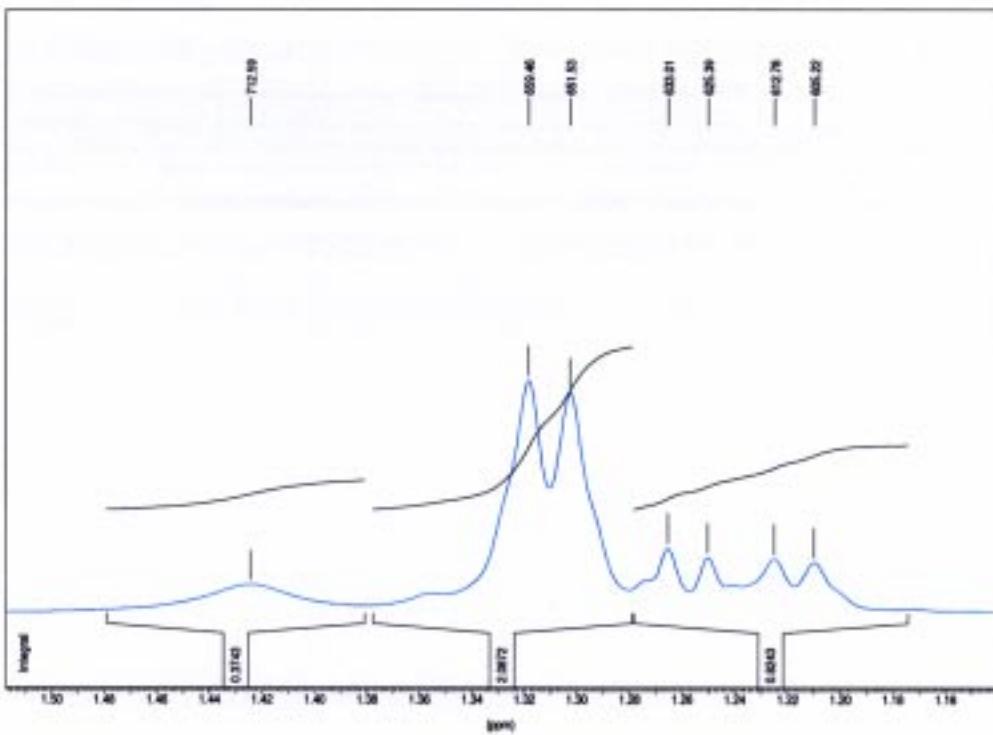
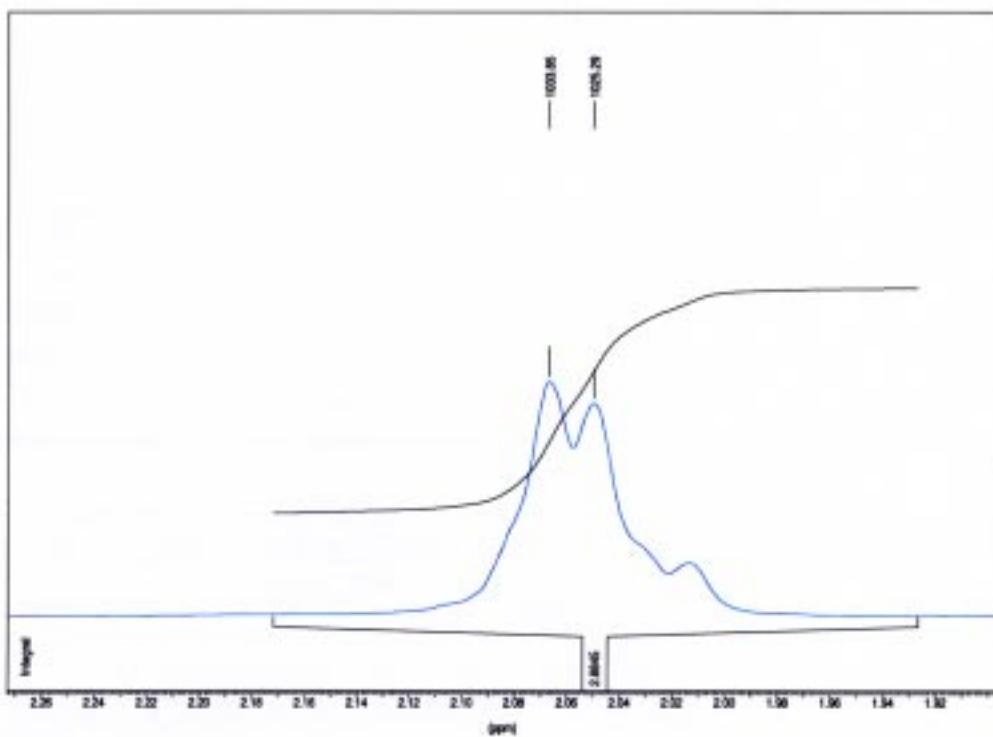
The sample has been prepared under nitrogen in a 5 mm NMR tube with a high vacuum valve in a cooling bath (-80 deg C) by adding a solution of ca. 10 mg of **18** in CD₂Cl₂ to a solution of ca. 45 mg of ClSO₃H in CD₂Cl₂. The NMR tube was stored on dry ice overnight before measurement could be carried out. This may have caused the partial decomposition of the sample.



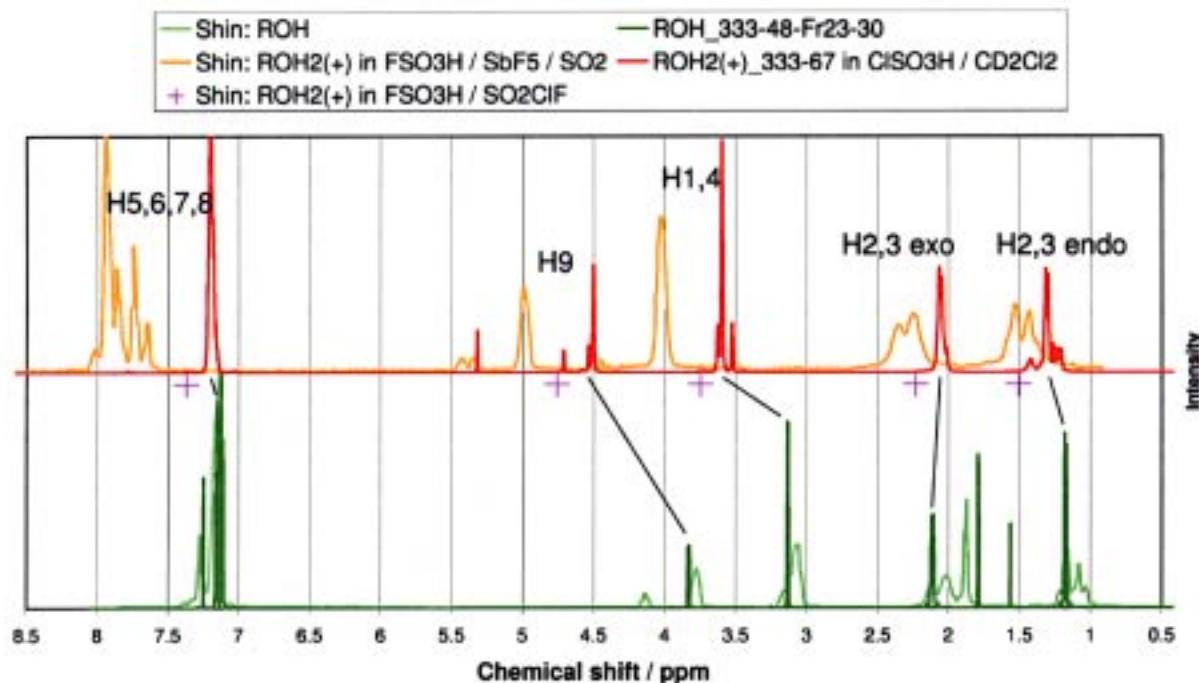
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¹H-NMR spectra of anti-benzonorborneol (ROH; in CDCl₃) and its protonated form (ROH₂⁺; in various superacids or CD₂Cl₂ at low temperature)



Spectra and peak positions labelled with "Shin" were taken from ref. 6a. ROH_333-48-Fr23-30 is a sample of **18**, for details of the spectra see above. ROH₂(+)_333-67 in ClSO₃H / CD₂Cl₂ is the spectrum of **5**⁺, for details of the spectra see above.

Results:

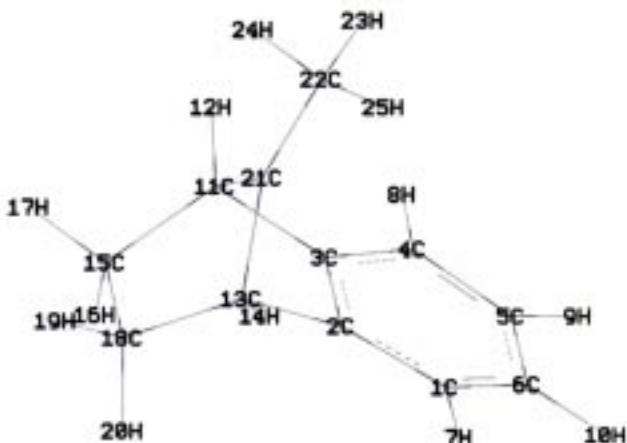
The spectra of **18** are practically identical. It is possible that the sample of Shin was not pure with regard to the stereoisomers. Our spectrum of **5**⁺ is very similar to the spectrum of Shin et al measured in FSO₃H/SO₂ClF, if one ignores a shift difference of 0.2 to 0.3 ppm for all signals. The **5**⁺ signals in the spectrum of Shin et al. measured in FSO₃H/SbF₅/SO₂ are much stronger shifted downfield (by 0.2 to 0.7 ppm) if compared with our spectrum.

6/29/04

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Quantum chemical calculations

Structure and IR spectrum of Me-1⁺



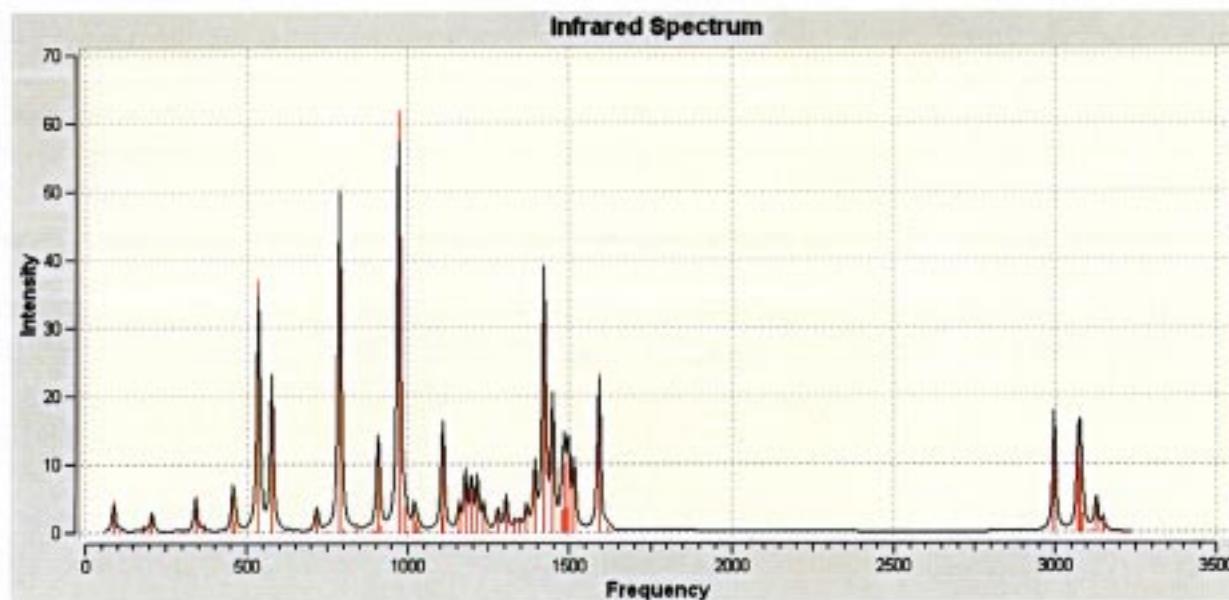
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Calculation Type	FREQ
Calculation Method	RB3LYP
Basis Set	6-311+G(d,p)
E(RB+HF-LYP)	-464.93021557 a.u.
RMS Gradient Norm	0.00000001 a.u.
Imaginary Freq	0
Dipole Moment	2.0128 Debye
Point Group	CS

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.155719	1.539804	1.429437
2	6	0	0.217608	0.335579	0.711498
3	6	0	0.217608	0.335579	-0.711498
4	6	0	0.155719	1.539804	-1.429437
5	6	0	0.189398	2.719307	-0.707511
6	6	0	0.189398	2.719307	0.707511
7	1	0	0.122504	1.543758	2.512043
8	1	0	0.122504	1.543758	-2.512043
9	1	0	0.205404	3.667941	-1.231155
10	1	0	0.205404	3.667941	1.231155
11	6	0	0.032720	-1.103866	-1.162083
12	1	0	-0.386318	-1.210920	-2.159152
13	6	0	0.032720	-1.103866	1.162083
14	1	0	-0.386318	-1.210920	2.159152
15	6	0	1.222592	-2.010774	-0.778077
16	1	0	2.151310	-1.628922	-1.202002
17	1	0	1.064628	-3.014473	-1.176308
18	6	0	1.222592	-2.010774	0.778077
19	1	0	1.064628	-3.014473	1.176308

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20	1	0	2.151310	-1.628922	1.202002
21	6	0	-0.915795	-1.124913	0.000000
22	6	0	-2.387830	-1.068736	0.000000
23	1	0	-2.791205	-0.598551	-0.897573
24	1	0	-2.727345	-2.116359	0.000000
25	1	0	-2.791205	-0.598551	0.897573



Zero-point correction= 0.214968 (Hartree/Particle)
Thermal correction to Energy= 0.224634
Thermal correction to Enthalpy= 0.225578
Thermal correction to Gibbs Free Energy= 0.180317
Sum of electronic and zero-point Energies= -464.715248
Sum of electronic and thermal Energies= -464.705582
Sum of electronic and thermal Enthalpies= -464.704638
Sum of electronic and thermal Free Energies= -464.749899

Potential energy surface of Me-1⁺

The potential energies were computed by optimising the structure at the B3LYP/6-31G(d) level with the constraints C4a-C9 = 1.5(0.2)2.3 Å and C8a-C9 = 1.5(0.2)2.3 Å ("relaxed potential energy surface scan") and then computing the energies at the level B3LYP/6-311++G(3df,3pd). The following energies were obtained (E(min) is here the minimal energy of these conformations; "2-21" and "3-21" are the lengths of the bonds C4a-C9 and C8a-C9, x and y the short names for these variables):

x	y	Energy / hartrees	(E - E(min)) / (kcal/mole)
"2-21"	"3-21"		
1.5	1.5	-464.91724964	28.9
1.7	1.5	-464.93359898	18.6
1.9	1.5	-464.93742699	16.2
2.1	1.5	-464.93664213	16.7
2.3	1.5	-464.92028639	27.0
1.5	1.7	-464.93359898	18.6
1.7	1.7	-464.95212888	7.0
1.9	1.7	-464.95680068	4.1
2.1	1.7	-464.95366351	6.0
2.3	1.7	-464.93754980	16.2
2.3	1.9	-464.94763557	9.8
2.1	1.9	-464.96131115	1.2
1.9	1.9	-464.96329518	0.0
1.7	1.9	-464.95680068	4.1
1.5	1.9	-464.93742699	16.2
1.5	2.1	-464.93664213	16.7
1.7	2.1	-464.95366351	6.0
1.9	2.1	-464.96131115	1.2
2.1	2.1	-464.96145695	1.2
2.3	2.1	-464.95226322	6.9
2.3	2.3	-464.94917069	8.9
2.1	2.3	-464.95226322	6.9
1.9	2.3	-464.94763557	9.8
1.7	2.3	-464.93754980	16.2
1.5	2.3	-464.92028639	27.0

A two-dimensional table of E – E(min) is shown below:

		"3-21"				
		1.5	1.7	1.9	2.1	2.3
"2-21"	1.5	28.9	18.6	16.2	16.7	27.0
	1.7	18.6	7.0	4.1	6.0	16.2
	1.9	16.2	4.1	0.0	1.2	9.8
	2.1	16.7	6.0	1.2	1.2	6.9
	2.3	27.0	16.2	9.8	6.9	8.9

The adjusted least-squares polynomial has the form

$$E_{\text{fit}} = \sum \text{coeff}_i \text{term}_i$$

with

i	coeff(i)	term(i)
1	2935.285116	1
2	-2771.664171	$x + y$
3	2790.735005	$x^2 + y^2$
4	-1593.964838	xy
5	-1099.568562	$x^3 + y^3$
6	450.3305595	$x^2y + xy^2$
7	148.3406157	$x^4 + y^4$
8	-13.61786771	$x^3y + xy^3$
9	-107.6457752	x^2y^2

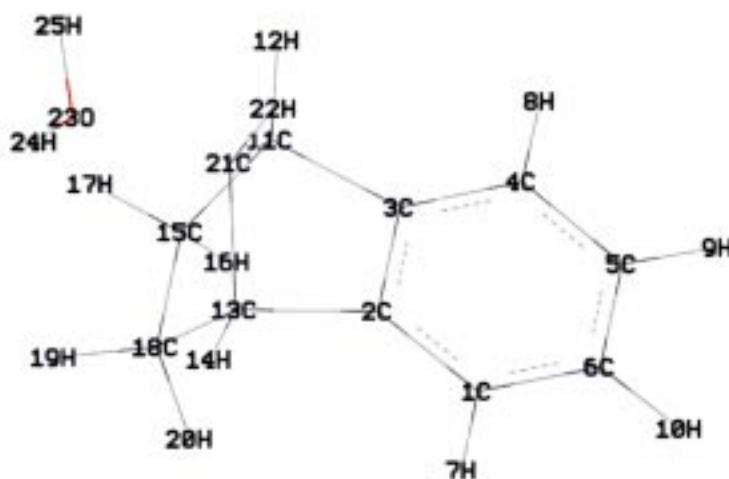
The minimum of the adjusted polynomial is at $x_{\min} = y_{\min} = 1.984 \text{ \AA}$ with $E_{\text{fit min}} = -0.3841 \text{ kcal/mole}$. The differences $E - E(\min) - E_{\text{fit}}$ (kcal/mole) are given in the following table (background colour for absolute values of differences: > 0.5 red, 0.3 - 0.5 orange, 0.1 - 0.3 yellow).

		"3-21"				
		1.5	1.7	1.9	2.1	2.3
"2-21"	1.5	-0.04	-0.04	0.60	-0.59	0.07
	1.7	-0.04	-0.46	0.01	0.20	0.29
	1.9	0.60	0.01	-0.20	-0.02	-0.39
	2.1	-0.59	0.20	-0.02	0.45	-0.04
	2.3	0.07	0.29	-0.39	-0.04	0.07

The symmetrical conformations have also been optimized at a higher level of theory (B3LYP/6-311+G(d,p)) for comparison, see the following table. These values were used in Figure 4.

x	y	(E - E(min)) /					
		Energy / hartrees	(kcal/mole)	C4a-C8a	C4a-C5	C5-C6	C6-C7
1.5	1.5	-464.8810259	30.3	1.44468	1.43861	1.36167	1.43082
1.7	1.7	-464.9171353	7.6	1.43061	1.42391	1.36986	1.42484
1.9	1.9	-464.9292605	0.0	1.42389	1.4088	1.37953	1.41779
2.1	2.1	-464.9281136	0.7	1.42237	1.39633	1.38839	1.41101
2.3	2.3	-464.9157321	8.5	1.41868	1.38647	1.39641	1.40347

Structure and IR and NMR spectrum of 5^+ (gas phase)



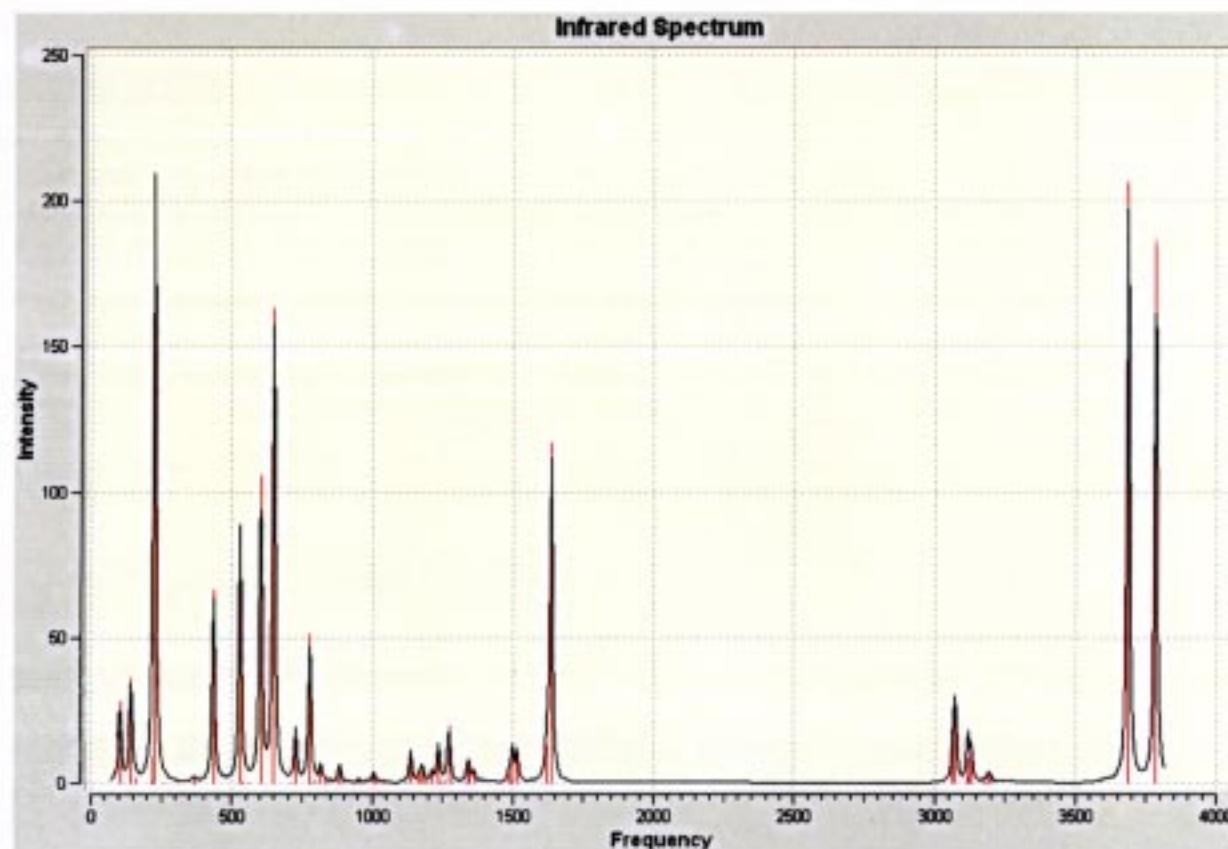
File Type	.log	
Calculation Type	FOPT	
Calculation Method	R83LYP	
Basis Set	6-311+G(d,p)	
E(RB+HF-LYP)	-502.05845466	a.u.
RMS Gradient Norm	0.00000034	a.u.
Imaginary Freq	0	
Dipole Moment	8.0595	Debye
Point Group	CS	

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.110666	1.792526	1.422162
2	6	0	-0.068277	0.604168	0.703676
3	6	0	-0.068277	0.604168	-0.703676
4	6	0	-0.110666	1.792526	-1.422162
5	6	0	-0.125683	2.987044	-0.699748
6	6	0	-0.125683	2.987044	0.699748
7	1	0	-0.123306	1.800483	2.505805
8	1	0	-0.123306	1.800483	-2.505805
9	1	0	-0.142520	3.931276	-1.230795
10	1	0	-0.142520	3.931276	1.230795
11	6	0	-0.033790	-0.852294	-1.151328
12	1	0	-0.389644	-1.037287	-2.163735
13	6	0	-0.033790	-0.852294	1.151328
14	1	0	-0.389644	-1.037287	2.163735
15	6	0	1.355005	-1.453803	-0.780040
16	1	0	2.153550	-0.845987	-1.203022
17	1	0	1.464296	-2.464821	-1.177015
18	6	0	1.355005	-1.453803	0.780040
19	1	0	1.464296	-2.464821	1.177015
20	1	0	2.153550	-0.845987	1.203022
21	6	0	-0.920051	-1.303978	0.000000

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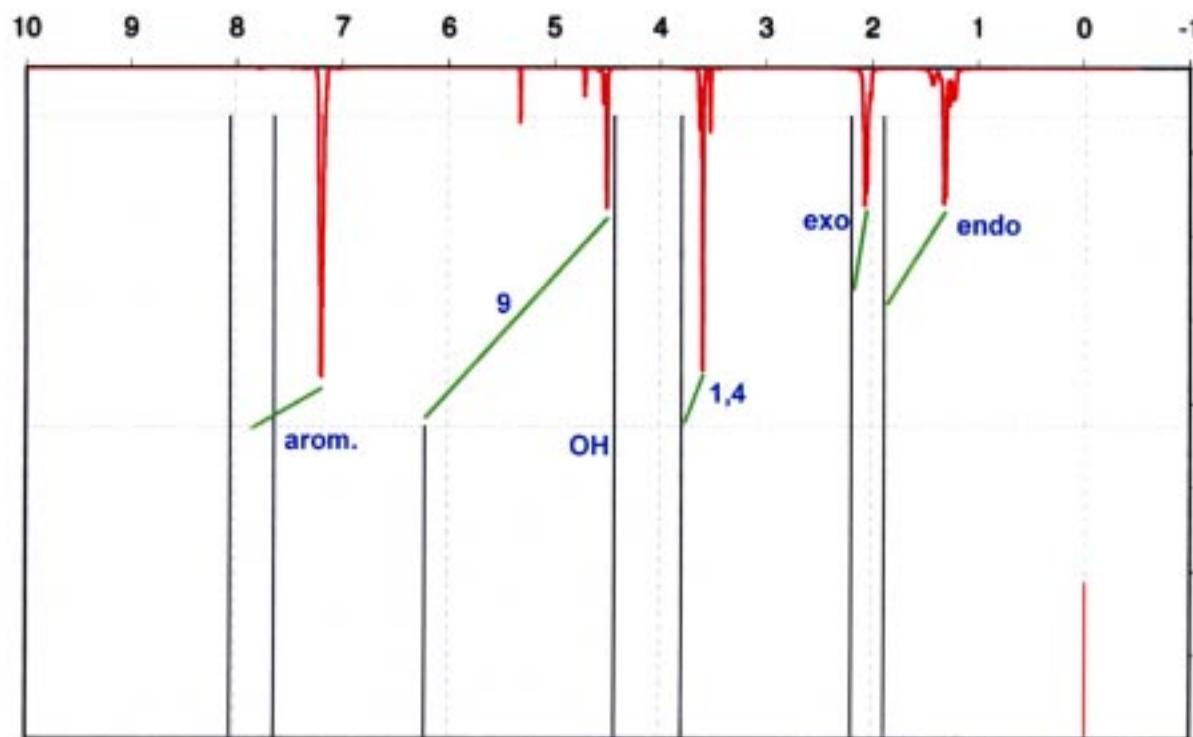
22	1	0	-1.978139	-1.060283	0.000000
23	8	0	-0.977030	-3.007054	0.000000
24	1	0	-1.404572	-3.379220	0.789904
25	1	0	-1.404572	-3.379220	-0.789904



Zero-point correction=	0.214666 (Hartree/Particle)
Thermal correction to Energy=	0.224754
Thermal correction to Enthalpy=	0.225698
Thermal correction to Gibbs Free Energy=	0.179832
Sum of electronic and zero-point Energies=	-501.843788
Sum of electronic and thermal Energies=	-501.833701
Sum of electronic and thermal Enthalpies=	-501.832757
Sum of electronic and thermal Free Energies=	-501.878623

NMR chemical shift calculation with the GIAO method (TMS absolute shielding value at the B3LYP/6-311++G(2d,2p) level of theory: H 31.6287); abscissa: chemical shift in ppm; red function: experimental ¹H-NMR spectrum; black lines: calculated ¹H-NMR spectrum rel. to TMS (red line); green lines connect corresponding signals; blue: assigned H positions.

File Type	.log
Calculation Type	SP
Calculation Method	B3LYP
Basis Set	6-311++G(2d,2p)
E(RB+HF-LYP)	-502.07634867 a.u.
RMS Gradient Norm	a.u.
Imaginary Freq	
Dipole Moment	8.0118 Debye
Point Group	CS



No.	nucleus	delta / ppm (relative to TMS)	H atom no. (chemical numbering)
9	H	8.0	6,7
10	H	8.0	6,7
7	H	7.6	5,8
8	H	7.6	5,8
22	H	6.2	9
24	H	4.4	(OH)
25	H	4.4	(OH)
12	H	3.8	1,4
14	H	3.8	1,4
17	H	2.2	2,3-exo
19	H	2.2	2,3-exo
16	H	1.9	2,3-endo
20	H	1.9	2,3-endo

Potential energy surface of $\mathbf{5}^+$ (gas phase)

Because of the slow convergence of many ab initio/DFT calculations on this system, the number of conformations (and scan dimensions) had to be kept at a minimum. Only a one-dimensional scan along the bending coordinate of the C9 bridge towards the C4a-C8a bond was possible, i. e. a relaxed scan with the constraints C4a-C9 = C8a-C9 = 1.7(0.1)2.4 Å. The following energies and selected geometry parameters were obtained for two different levels of theory (the colours correspond to those in Figure 11; the relative energies are depicted in Figure 10):

B3LYP/6-31G(d)//B3LYP/6-31G(d)

2-21 =	E(RB+HF-	(E - Emin) /	C9-O /	C4a-C8a /	C4a-C5 /	C5-C6 /	C6-C7 /
3-21	LYP)	(kcal/mole)	Ang	Ang	Ang	Ang	Ang
1.7	-501.9098412	8.132	2.85485	1.4344	1.42632	1.37274	1.426
1.8	-501.9164787	3.967	2.70304	1.43042	1.41853	1.37738	1.42327
1.9	-501.9196408	1.982	2.53102	1.42695	1.41103	1.38217	1.41957
2.0	-501.9205105	1.437	2.29101	1.42245	1.40376	1.38733	1.41484
2.1	-501.9212596	0.966	1.9279	1.41386	1.39647	1.39353	1.4073
2.2	-501.9227998	0.000	1.68997	1.40961	1.39144	1.39828	1.40181
2.3	-501.9212987	0.942	1.60751	1.41062	1.38881	1.40055	1.39988
2.4	-501.914946	4.928	1.56793	1.41244	1.38658	1.40219	1.39889

B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) [used for Figure 11]

2-21 =	(E - Emin) /		C9-O /	C4a-C8a /	C4a-C5 /	C5-C6 /	C6-C7 /
3-21	E(RB+HF-LYP)	(kcal/mole)	Ang	Ang	Ang	Ang	Ang
1.7	-502.0514695	5.949	2.90436	1.43243	1.42452	1.36942	1.42448
1.8	-502.0580789	1.802	2.79252	1.42832	1.41682	1.37419	1.42125
1.9	-502.0609499	0.000	2.64388	1.42559	1.40943	1.37901	1.41783
2.0	-502.0608522	0.061	2.46485	1.42359	1.40259	1.38379	1.41407
2.1	-502.0587773	1.363	2.13745	1.41757	1.39572	1.38947	1.40804
2.2	-502.0584413	1.574	1.71064	1.40725	1.38951	1.3959	1.39962
2.3	-502.0566909	2.673	1.61221	1.40797	1.38662	1.39835	1.39745
2.4	-502.0502231	6.731	1.57044	1.40981	1.38454	1.40003	1.39647

The energies of both sets of structures has been computed again at a higher level of theory
(single point calculations; options: scf=tight int=ultrafine):

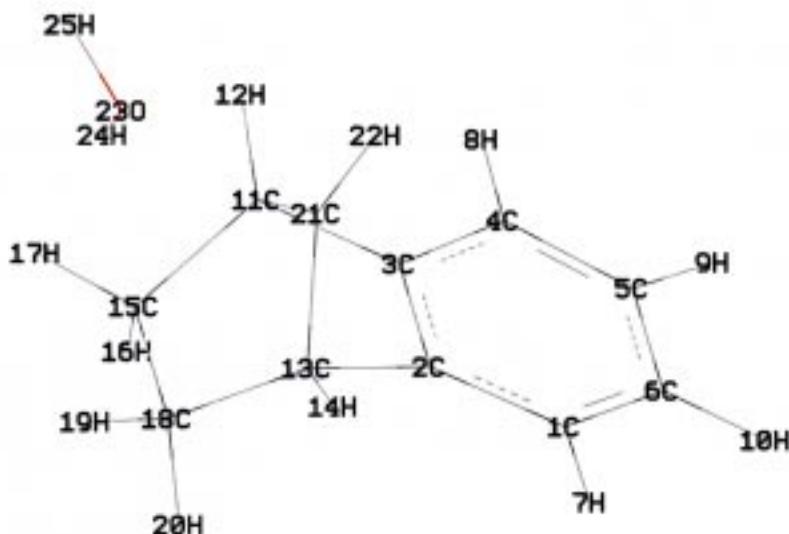
B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d)

2-21 = 3-21	E(RB+HF-LYP)	(E - Emin) / (kcal/mole)
1.7	-502.08772794	5.272
1.8	-502.09383194	1.442
1.9	-502.09612912	0.000
2.0	-502.09531251	0.512
2.1	-502.09354082	1.624
2.2	-502.09429526	1.151
2.3	-502.09259124	2.220
2.4	-502.08603146	6.336

B3LYP/6-311++G(3df,3pd)//B3LYP/6-311+G(d,p)

2-21 = 3-21	E(RB+HF-LYP)	(E - Emin) / (kcal/mole)
1.7	-502.08867872	5.183
1.8	-502.09464171	1.441
1.9	-502.09693774	0.000
2	-502.09630753	0.395
2.1	-502.09414812	1.751
2.2	-502.09465460	1.433
2.3	-502.09296824	2.491
2.4	-502.08640533	6.609

Structure and IR and NMR spectrum of the H-1⁺/water complex (absolute minimum on the 5⁺ potential energy surface; gas phase)

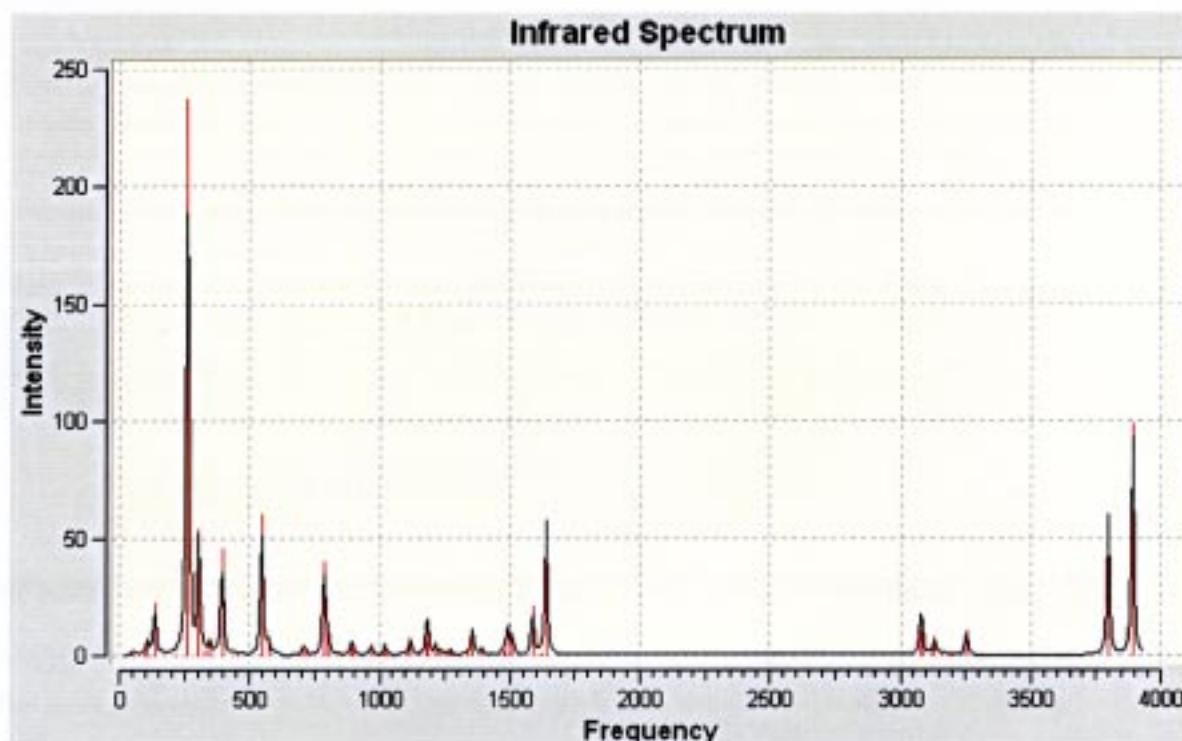


File Type	.log
Calculation Type	FREQ
Calculation Method	RB3LYP
Basis Set	6-311+G(d,p)
E(RB+HF-LYP)	-502.06122570 a.u.
RMS Gradient Norm	0.00000033 a.u.
Imaginary Freq	0
Dipole Moment	2.6874 Debye
Point Group	CS

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.146209	1.848470	1.428967
2	6	0	0.114327	0.666795	0.712409
3	6	0	0.114327	0.666795	-0.712409
4	6	0	-0.146209	1.848470	-1.428967
5	6	0	-0.299442	3.016583	-0.708102
6	6	0	-0.299442	3.016583	0.708102
7	1	0	-0.181537	1.845533	2.511435
8	1	0	-0.181537	1.845533	-2.511435
9	1	0	-0.436025	3.955623	-1.231459
10	1	0	-0.436025	3.955623	1.231459
11	6	0	0.145296	-0.782084	-1.166341
12	1	0	-0.257903	-0.944103	-2.161334
13	6	0	0.145296	-0.782084	1.166341
14	1	0	-0.257903	-0.944103	2.161334
15	6	0	1.446205	-1.516308	-0.777451
16	1	0	2.314538	-1.012095	-1.201681
17	1	0	1.421255	-2.532937	-1.170502
18	6	0	1.446205	-1.516308	0.777451

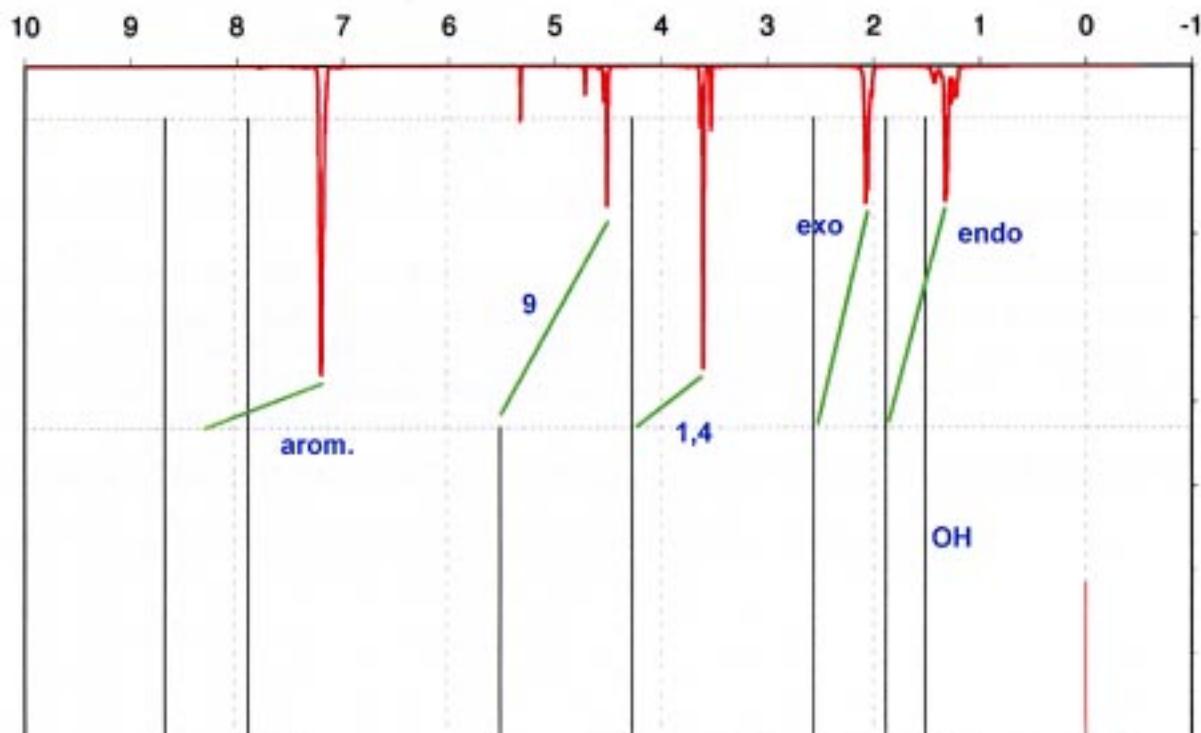
19	1	0	1.421255	-2.532937	1.170502
20	1	0	2.314538	-1.012095	1.201681
21	6	0	-0.775655	-0.908872	0.000000
22	1	0	-1.854504	-0.847333	0.000000
23	8	0	-1.383077	-3.406626	0.000000
24	1	0	-1.634858	-3.935970	0.765700
25	1	0	-1.634858	-3.935970	-0.765700



Zero-point correction=	0.210942 (Hartree/Particle)
Thermal correction to Energy=	0.222894
Thermal correction to Enthalpy=	0.223838
Thermal correction to Gibbs Free Energy=	0.172520
Sum of electronic and zero-point Energies=	-501.850284
Sum of electronic and thermal Energies=	-501.838332
Sum of electronic and thermal Enthalpies=	-501.837388
Sum of electronic and thermal Free Energies=	-501.888706

NMR chemical shift calculation with the GIAO method (TMS absolute shielding value at the B3LYP/6-311++G(2d,2p) level of theory: H 31.6287); abscissa: chemical shift in ppm; red function: experimental ^1H -NMR spectrum; black lines: calculated ^1H -NMR spectrum rel. to TMS (red line); green lines connect corresponding signals; blue: assigned H positions.

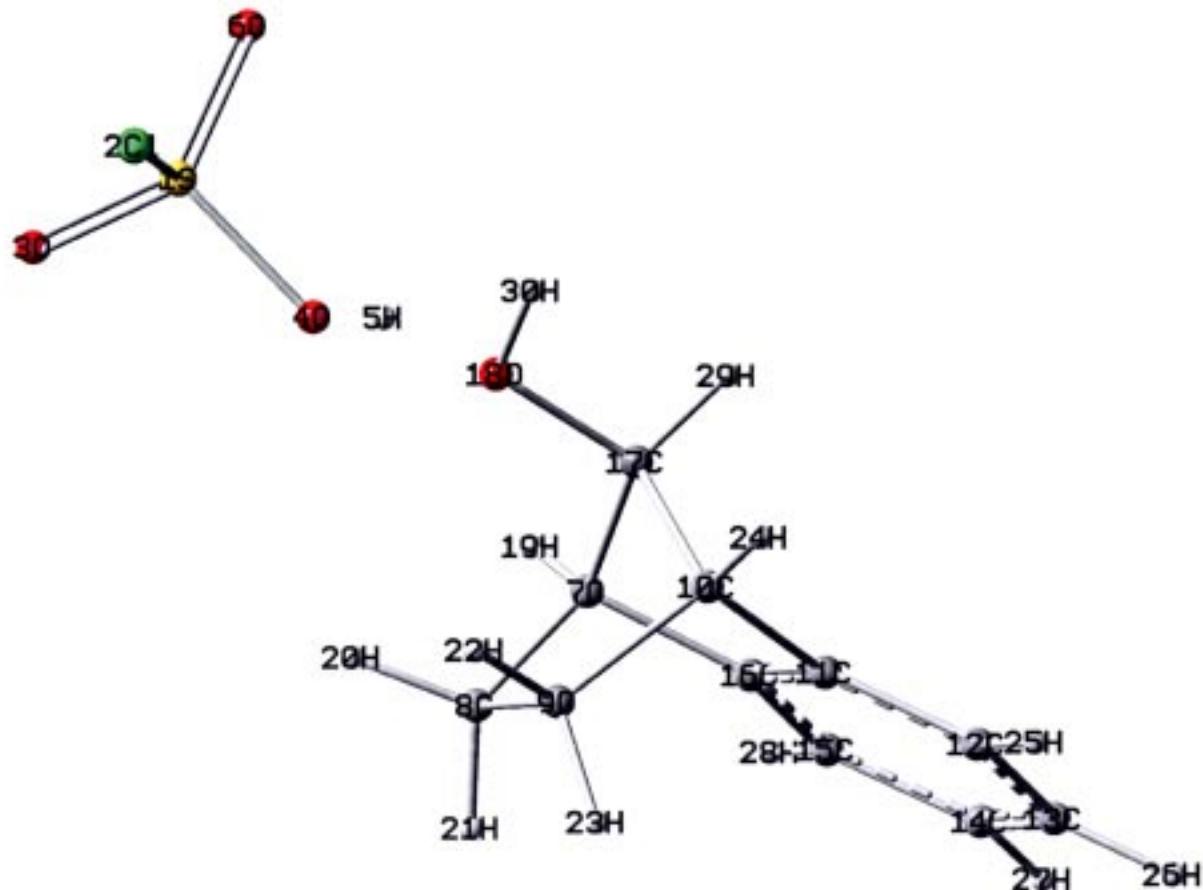
File Type	.log
Calculation Type	SP
Calculation Method	B3LYP
Basis Set	6-311++G(2d,2p)
E(RB+HF-LYP)	-502.07899952
RMS Gradient Norm	a.u.
Imaginary Freq	
Dipole Moment	2.5713 Debye
Point Group	CS



Potential energy surface of a partially constrained pair $\text{5}^+ \text{ClSO}_3^-$ or $\text{18} \cdot \text{ClSO}_3\text{H}$ upon movement of the O-proton H₂O between the positions H₂oa and H₂ob (arrangement of the ions or molecules as found in the crystal; solvent/phase: gas phase)

In order to estimate the energy profile of the proton movement between the oxygen atoms O (belonging to the cation 5^+) and O₂ (belonging to the chlorosulfonate anion) in the crystal, an isolated ion pair with a mutual arrangement as found in the crystal structure has been investigated by DFT methods. The following constraints were applied for approximate retention of the geometry found in the crystal. All other parameters were fully optimized. The atom numbers in the table refer to the DFT atom names as shown below, the corresponding atom names from the crystal structure are given in parentheses.

Type	Atom 1	Atom 2	Atom 3	Atom 4	value
distance	4 (O ₂)	18 (O)	-	-	2.5538 Å
angle	4 (O ₂)	18 (O)	17 (C ₉)	-	106.8143°
angle	1 (S)	4 (O ₂)	18 (O)	-	124.8876°
dihedral angle	7 (C ₁)	17 (C ₉)	18 (O)	4 (O ₂)	-41.4284°
dihedral angle	1 (S)	4 (O ₂)	18 (O)	17 (C ₉)	-158.9729°
dihedral angle	2 (Cl)	1 (S)	4 (O ₂)	18 (O)	-22.9373°



The computations were carried out without a solvent model. Such calculations can give only a very coarse estimate because the arrangement of the cations and anions in infinite chains is not taken into account, and the cooperative effects are thus omitted.

The following energies and selected structural parameters have been obtained using the constraints of the previous page and the additional constraint for O2-H2o. The colours in the following tables correspond to the colors of the graphs in Figure 15. The structures on the lines with dashed frames were also used for NMR calculations, see below.

B3LYP/6-31G(d)//B3LYP/6-31G(d)

(constraint)	E(RB+HF-LYP) / O(2)-H(2o) hartrees	(E - Emin) / (kcal/mole)	O-H(2o)	S-O(2)-H(2o)	O(2)-H(2o)-O	H(2o)-O-C(9)	Dipole Moment (μ)
0.9	-1586.18355798	6.873	1.69122	114.311	159.504	110.085	5.6419
1.0	-1586.19425668	0.159	1.58351	115.22	162.131	111.089	6.387
1.1	-1586.19229856	1.388	1.47554	116.864	164.926	111.394	7.3852
1.2	-1586.18669984	4.901	1.36819	118.637	167.823	111.311	8.6142
1.3	-1586.18202752	7.833	1.26354	120.022	169.99	111.154	9.9725
1.4	-1586.17950393	9.417	1.16161	120.81	170.99	111.286	11.3097
1.5	-1586.17726467	10.822	1.06467	120.438	169.275	112.647	12.4646
1.6	-1586.17180232	14.250	1.01273	116.639	154.958	115.345	13.2695
1.7	-1586.16524805	18.363	1.00077	113.837	140.623	116.177	13.801
1.02226 ^a	-1586.19451077	0.000	1.55994	115.499	162.593	111.206	6.5833
1.02233 ^b	-1586.19451065	0.000	1.55951	115.574	162.705	111.165	6.586

^a this parameter has not been constrained; energy minimum obtained starting from **5⁺CISO₃⁻**.

^b this parameter has not been constrained; energy minimum obtained starting from **18-CISO₃H**.

B3LYP/6-311++G(3df,3pd)//B3LYP/6-31G(d)

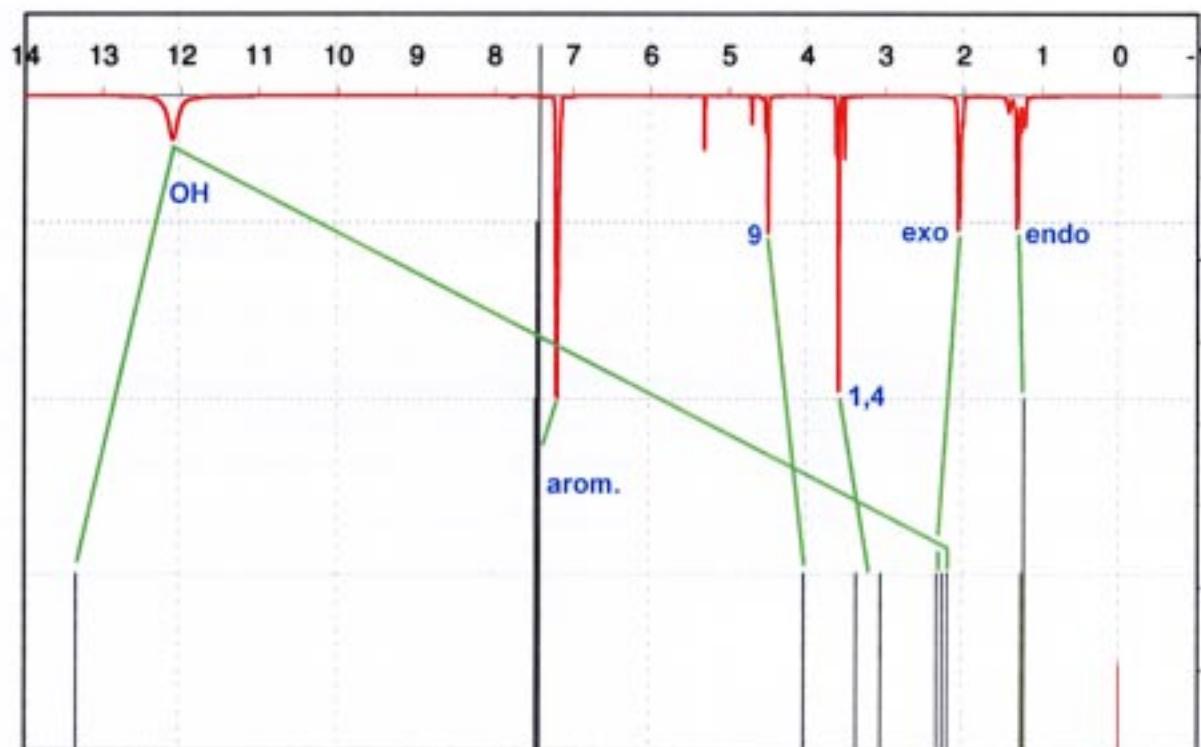
(constraint)	E(RB+HF-LYP) / O(2)-H(2o) hartrees	(E - Emin) / (kcal/mole)	Dipole Moment (μ)
0.9	-1586.57280116	5.903	5.5955
1.0	-1586.58220887	0.000	6.3102
1.1	-1586.57995289	1.416	7.2159
1.2	-1586.57433584	4.940	8.4031
1.3	-1586.56988109	7.736	9.7152
1.4	-1586.56763485	9.145	11.0047
1.5	-1586.56575696	10.324	12.1184
1.6	-1586.56021374	13.802	12.9014
1.7	-1586.55345992	18.040	13.4161

Although these constrained ion or molecule pairs are not expected to exist as minimum structures in solution (e. g. in methylene chloride, which was used as solvent for the ¹H NMR measurement, see above), the NMR spectra of the structures with O2-H2o = 1.0 Å

(corresponds to a pair **18-CISO₃H**) and with O2-H2o = 1.6 Å (corresponds to a pair **5⁺CISO₃⁻**) were computed using the GIAO method (a fully optimized structure of a pair **18-CISO₃H** and its NMR spectrum have been computed as well, see page S76). This allows to estimate the influence of the H2o position on the chemical shifts of the other protons.

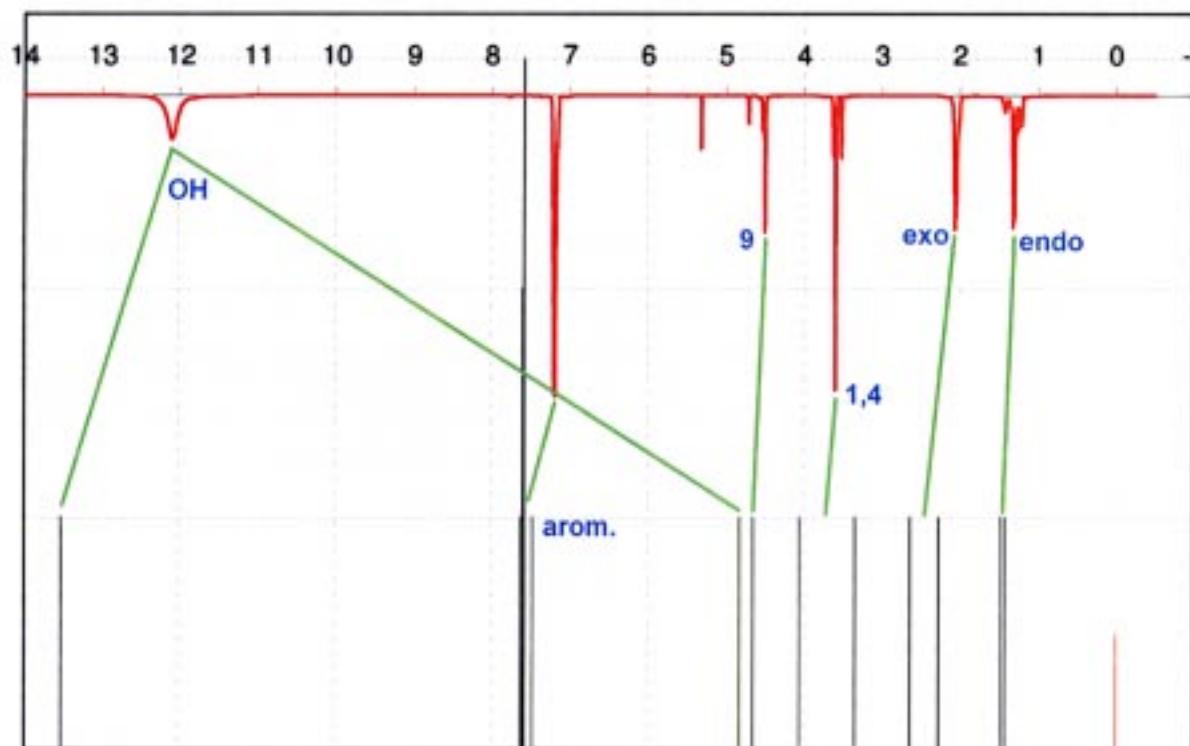
NMR chemical shift calculation with the GIAO method (TMS absolute shielding value at the B3LYP/6-311++G(2d,2p) level of theory: H 31.6287); abscissa: chemical shift in ppm; red function: experimental ^1H -NMR spectrum; black lines: calculated ^1H -NMR spectrum rel. to TMS (red line); green lines connect corresponding signals; blue: assigned H positions.

6-31G(d) O2-H2o = 1.0 Angstroem	
File Type	.log
Calculation Type	SP
Calculation Method	RB3LYP
Basis Set	6-311++G(2d,2p)
E[RB+HF-LYP]	-1586.52742325 a.u.
RMS Gradient Norm	a.u.
Imaginary Freq	
Dipole Moment	6.2830 Debye
Point Group	C1



NMR chemical shift calculation with the GIAO method (TMS absolute shielding value at the B3LYP/6-311++G(2d,2p) level of theory: H 31.6287); abscissa: chemical shift in ppm; red function: experimental ^1H -NMR spectrum; black lines: calculated ^1H -NMR spectrum rel. to TMS (red line); green lines connect corresponding signals; blue: assigned H positions.

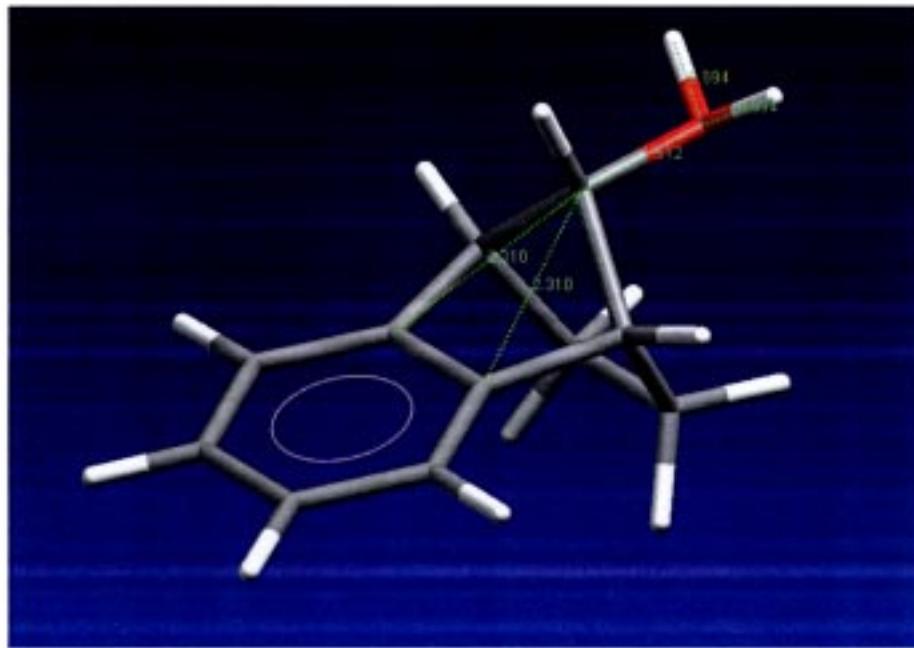
6-31G[d] O2-H2o = 1.6 Angstroem		
File Type	.log	
Calculation Type	SP	
Calculation Method	RB3LYP	
Basis Set	6-311++G(2d,2p)	
E(RB+HF-LYP)	-1586.50535418	a.u.
RMS Gradient Norm		a.u.
Imaginary Freq		
Dipole Moment	12.9910	Debye
Point Group	C1	



Semiempirical calculations (MOPAC; AM1) on **5⁺**, **18**, deprotonated **18**

Coordinates of **5⁺** (from a SYBYL-mol2 file). The entries are: atom name, x, y, z, SYBYL atom type

C1	-0.6936	-2.9486	0.0593	C.ar
C2	0.6964	-2.9480	0.0590	C.ar
C3	1.4254	-1.7436	0.0734	C.ar
C4	0.7162	-0.5628	0.0801	C.ar
C5	-0.7158	-0.5635	0.0806	C.ar
C6	-1.4238	-1.7450	0.0741	C.ar
C7	-1.1596	0.8839	0.0762	C.3
C8	-0.7719	1.4597	-1.3061	C.3
C9	0.7691	1.4601	-1.3071	C.3
C10	1.1589	0.8848	0.0748	C.3
C11	-0.0001	1.4446	0.9707	C.3
O12	0.0004	2.9543	0.8804	O.3
H13	-1.1733	2.4949	-1.4238	H
H14	0.0004	1.1790	2.0501	H
H15	-1.2415	-3.9051	0.0469	H
H16	1.2450	-3.9040	0.0465	H
H17	2.5253	-1.7593	0.0732	H
H18	-2.5237	-1.7618	0.0745	H
H19	-2.1933	1.0880	0.4114	H
H20	-1.1843	0.8243	-2.1263	H
H21	-0.8099	3.3055	1.3363	H
H22	1.1807	0.8246	-2.1277	H
H23	1.1699	2.4955	-1.4255	H
H24	2.1927	1.0903	0.4090	H
H25	0.7899	3.3077	1.3698	H

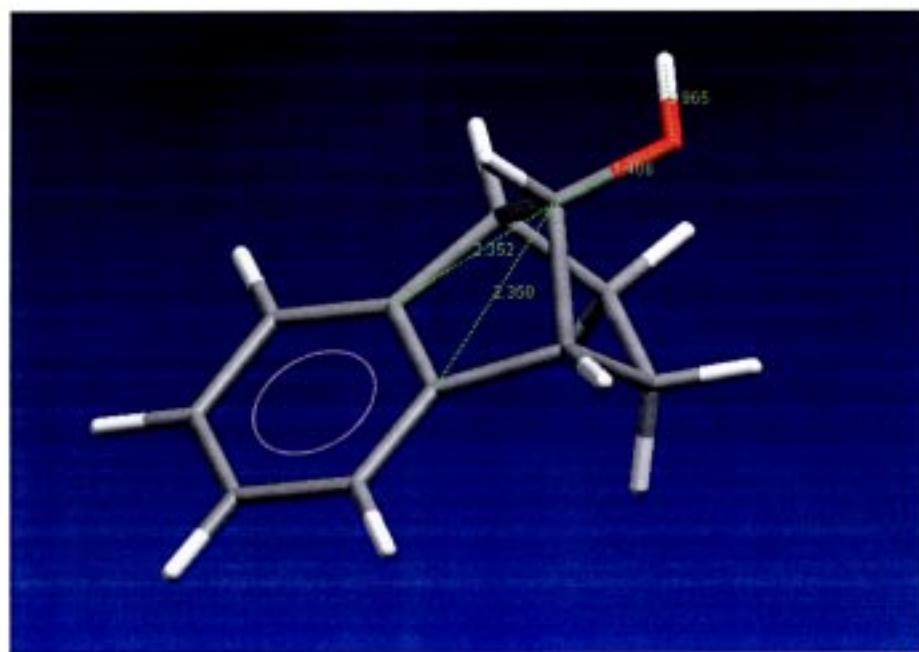


Coordinates of **18** (from a SYBYL-mol2 file)

C1	-0.6634	-2.9701	0.1859	C.ar
C2	0.7258	-2.9684	0.1878	C.ar
C3	1.4498	-1.7625	0.1923	C.ar
C4	0.7448	-0.5788	0.1949	C.ar
C5	-0.6875	-0.5808	0.1932	C.ar

X-ray Crystal Structures of a Benzonorbornenyl Cation and of a Protonated Benzonorbornenol
Thomas Laube J. Am. Chem. Soc.

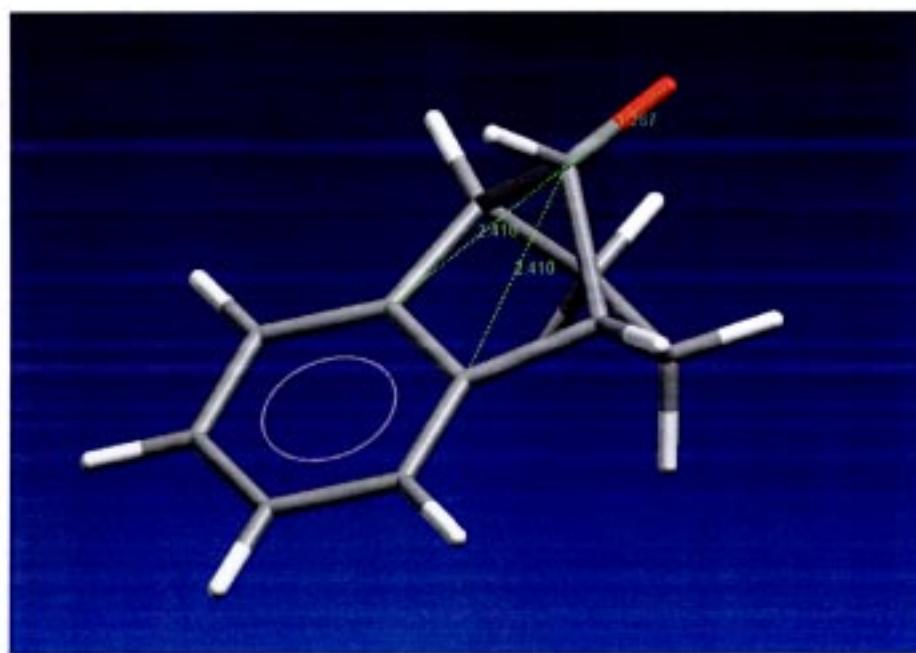
C6	-1.3902	-1.7660	0.1887	C.ar
C7	-1.1251	0.8645	0.1920	C.3
C8	-0.7451	1.4290	-1.1973	C.3
C9	0.7967	1.4310	-1.1980	C.3
C10	1.1802	0.8686	0.1914	C.3
C11	0.0284	1.4780	1.0771	C.3
O12	0.0986	2.8826	1.0771	O.3
H13	-1.1405	2.4674	-1.3038	H
H14	0.0246	1.0887	2.1238	H
H15	-1.2097	-3.9249	0.1831	H
H16	1.2744	-3.9220	0.1868	H
H17	2.5484	-1.7751	0.1945	H
H18	-2.4886	-1.7814	0.1877	H
H19	-2.1599	1.0672	0.5180	H
H20	-1.1588	0.7986	-2.0174	H
H21	-0.7641	3.1981	1.3730	H
H22	1.2099	0.8006	-2.0185	H
H23	1.1895	2.4706	-1.3026	H
H24	2.2115	1.0823	0.5207	H



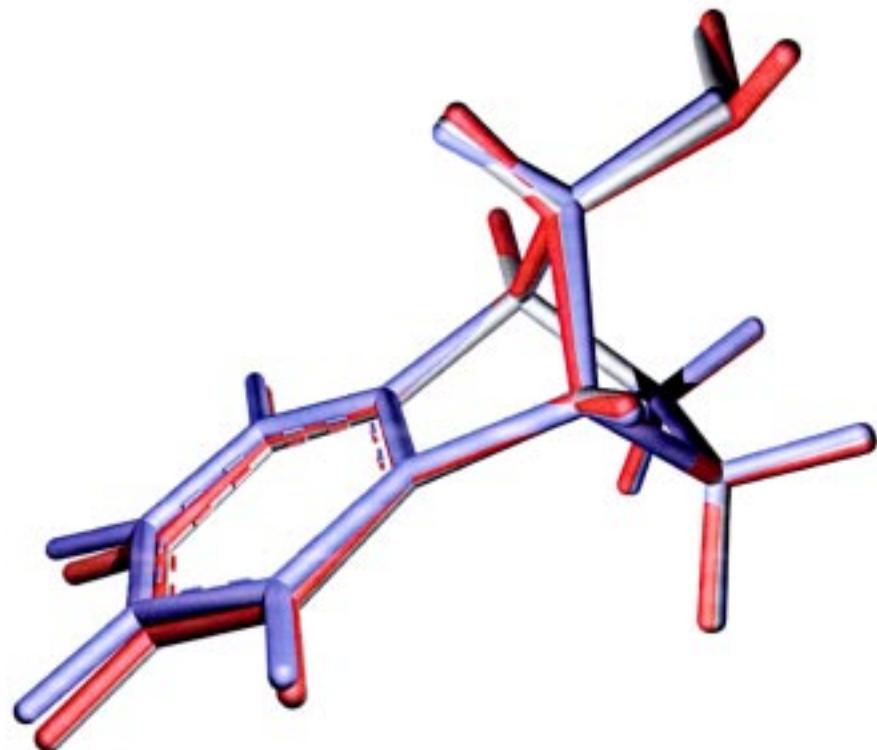
Coordinates of deprotonated **18** (from a SYBYL-mol2 file)

C1	-0.6942	-2.9028	0.1896	C.ar
C2	0.6949	-2.9027	0.1887	C.ar
C3	1.4139	-1.6980	0.1208	C.ar
C4	0.7186	-0.5069	0.0472	C.ar
C5	-0.7186	-0.5070	0.0482	C.ar
C6	-1.4134	-1.6983	0.1226	C.ar
C7	-1.1650	0.9175	0.0114	C.3
C8	-0.7708	1.4962	-1.3535	C.3
C9	0.7690	1.4962	-1.3544	C.3
C10	1.1648	0.9176	0.0108	C.3
C11	0.0004	1.6108	0.9465	C.3
O12	0.0004	2.8964	1.0155	O.3
H13	-1.1585	2.5405	-1.4323	H
H14	0.0011	1.0590	1.9339	H
H15	-1.2411	-3.8539	0.2462	H
H16	1.2420	-3.8538	0.2445	H
H17	2.5116	-1.7111	0.1318	H
H18	-2.5111	-1.7117	0.1348	H

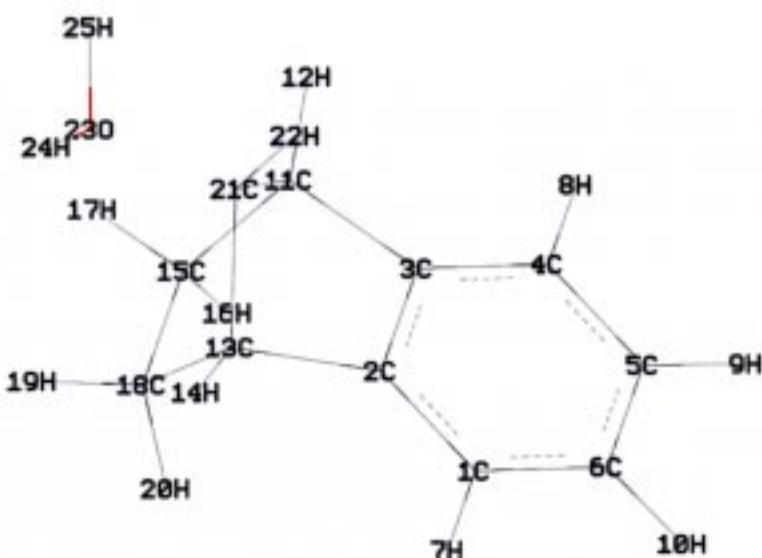
H19	-2.2014	1.1189	0.3240	H
H20	-1.1799	0.8948	-2.2000	H
H22	1.1769	0.8947	-2.2015	H
H23	1.1565	2.5487	-1.4337	H
H24	2.2015	1.1191	0.3215	H



Superposition of **5⁺** (red), **18** (grey), deprotonated **18** (blue) [least squares adjustment of C1, C2, C3, C4]



Structure and IR and NMR spectrum of 5^+ (in water)



File Type	.log
Calculation Type	FREQ
Calculation Method	RB3LYP
Basis Set	6-311+G(d,p)
E(RB+HF-LYP)	-502.16956852 a.u.
RMS Gradient Norm	0.00000862 a.u.
Imaginary Freq	0
Dipole Moment	21.9973 Debye
Point Group	C1

Polarizable Continuum Model (PCM)
=====

Model : PCM.
Atomic radii : UAO (Simple United Atom Topological Model).
Polarization charges : Total charges.
Charge compensation : None.
Solution method : Matrix inversion.
Cavity : GePol (RMin=0.200 OFac=0.890).
Default sphere list used, NSphG= 12.
Tesserae with average area of 0.200 Ang**2.
1st derivatives : Analytical V*U(x)*V algorithm (CHGder, D1EAlg=0).
Cavity 1st derivative terms included.
2nd derivatives : U-function 2nd derivative terms included.
Solvent : Water, Eps= 78.390000.