Electronic Supplementary Material (ESI) for RSC Advances.

Formation of Dications Bearing $S(OH)_2^+$ Group from Long-lived 9,9-Dimethyl-10-R-phenanthrenium Cations in FSO_3H-$SbF_5/SO_2ClF/SO_2$: A Mechanistic Study

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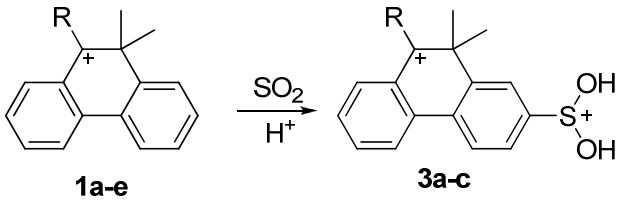
Electronic Supplementary Information



a R = PhC≡C
b R = Me
c R = OH
d R = MeC≡C
e R = CF_3C≡C

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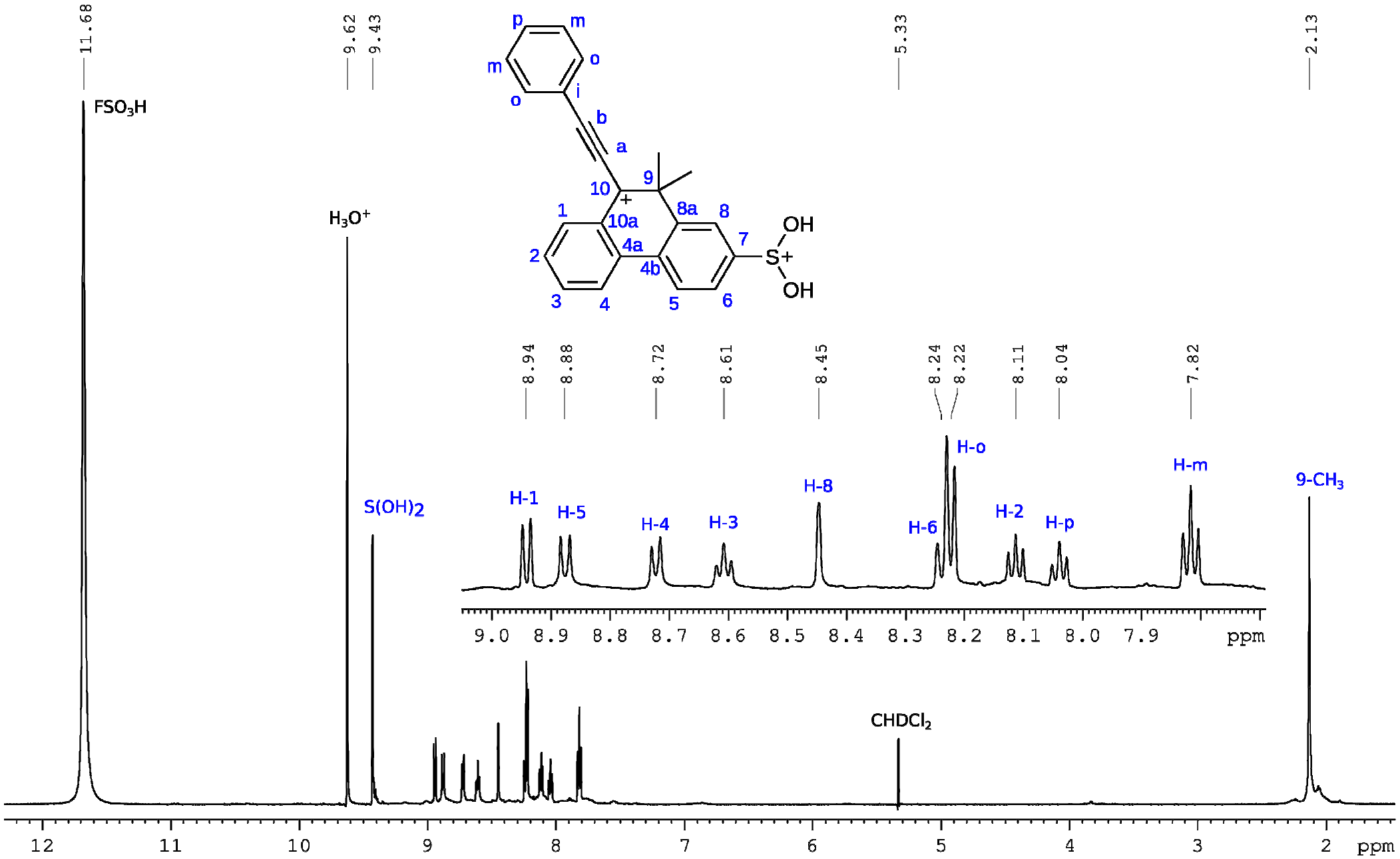
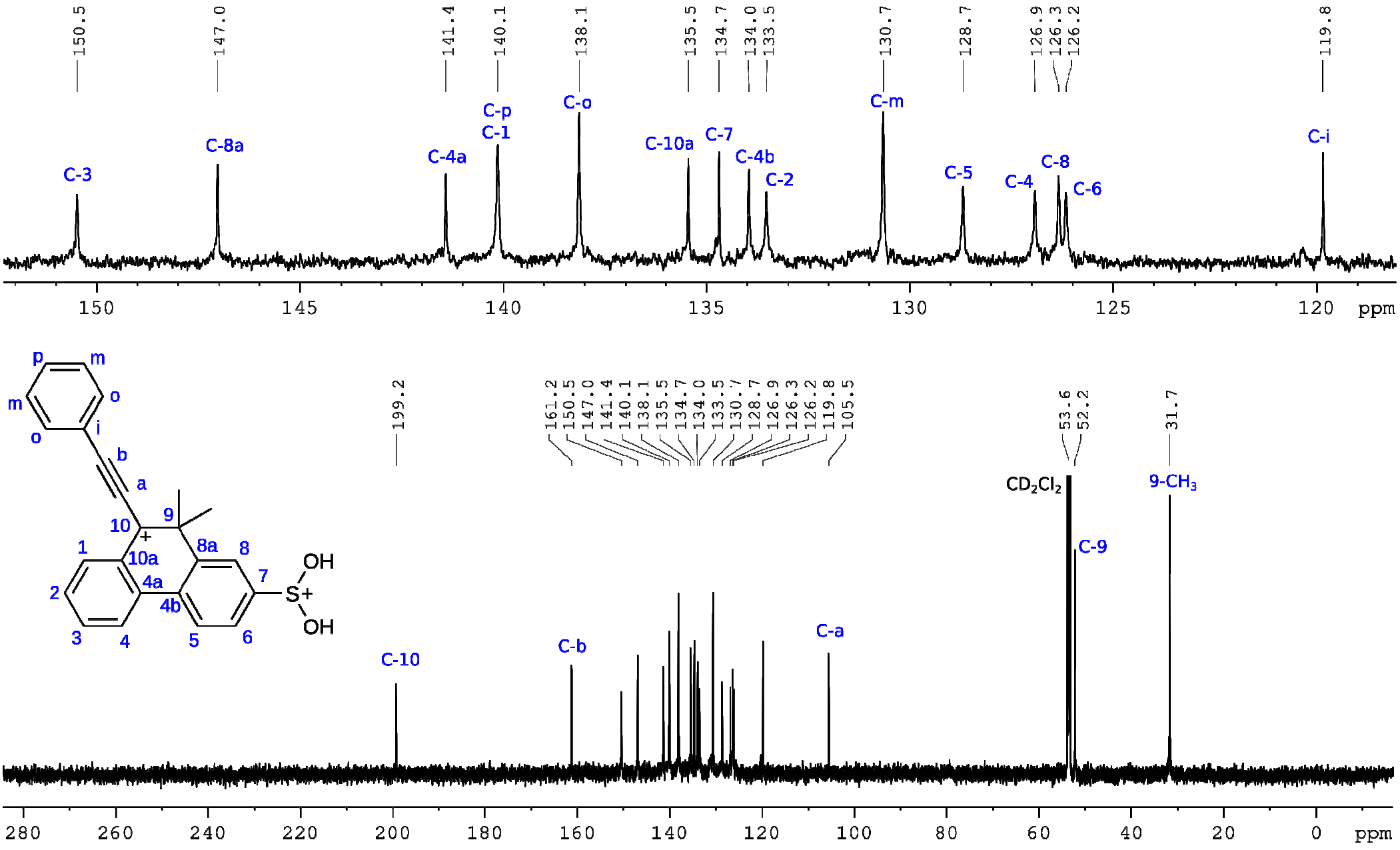
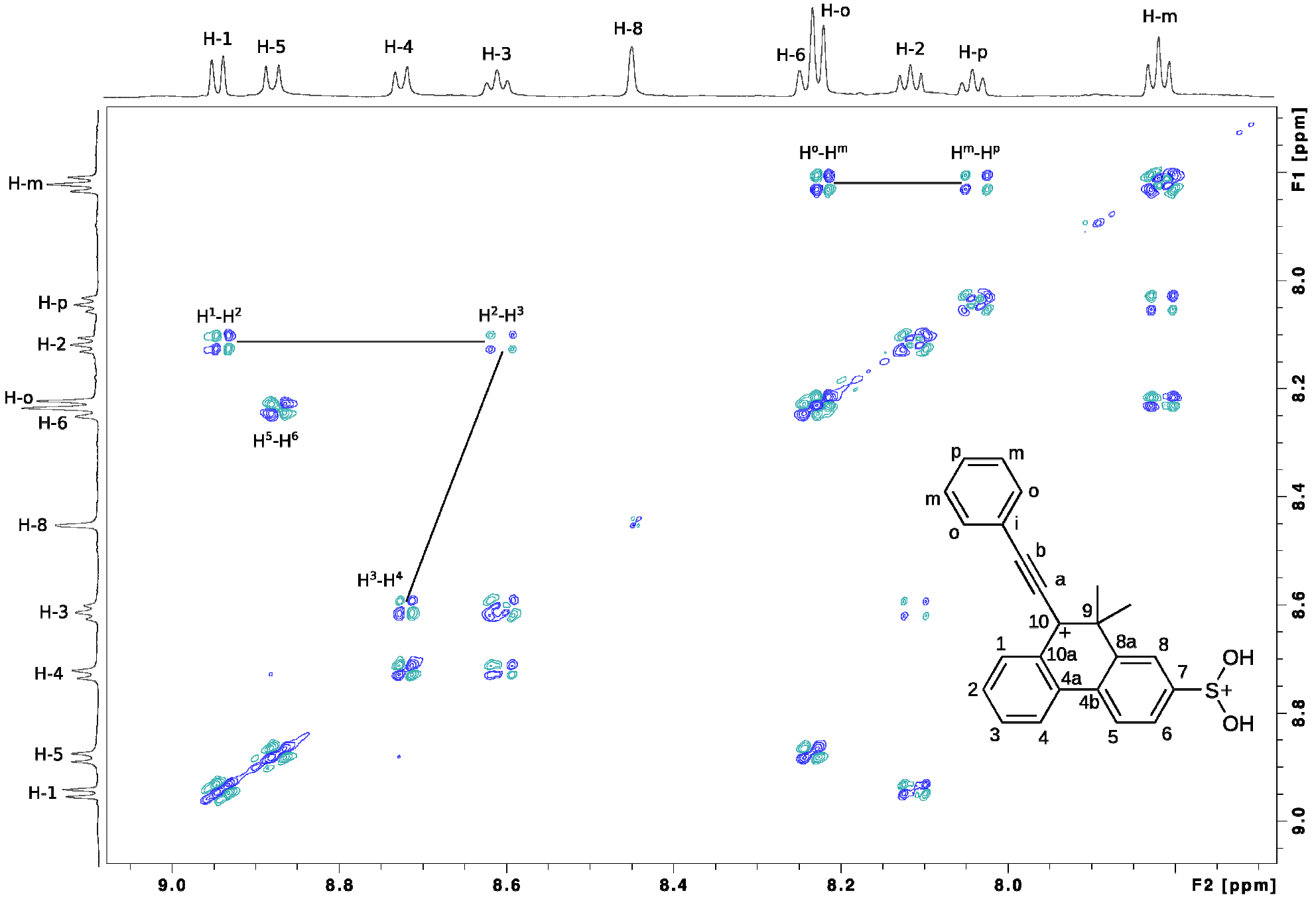
^{1}H NMR spectrum (600 MHz) of dication **3a** in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –81 ^{o}C



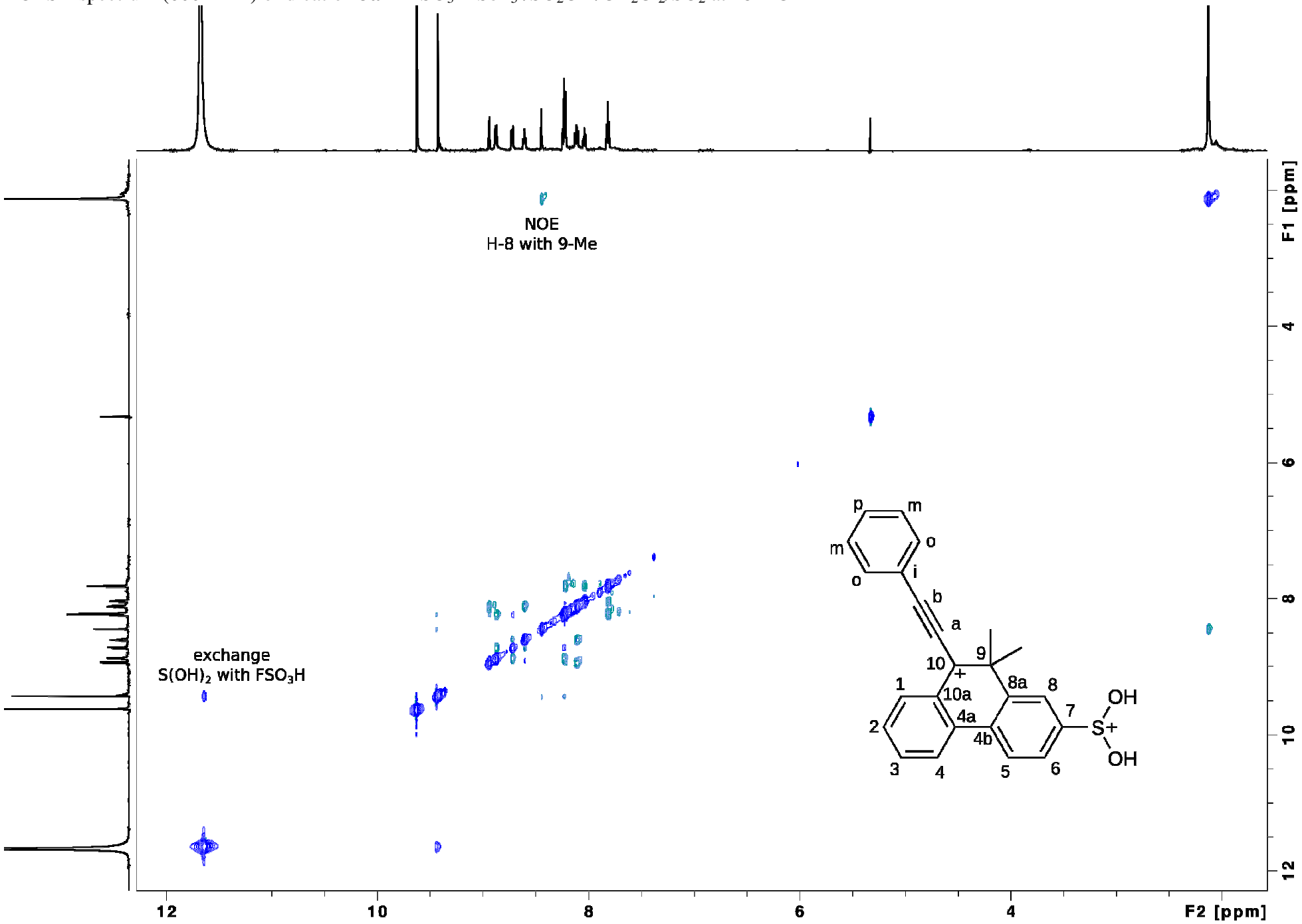
^{13}C NMR spectrum (151 MHz) of dication **3a** in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –81 ^{o}C



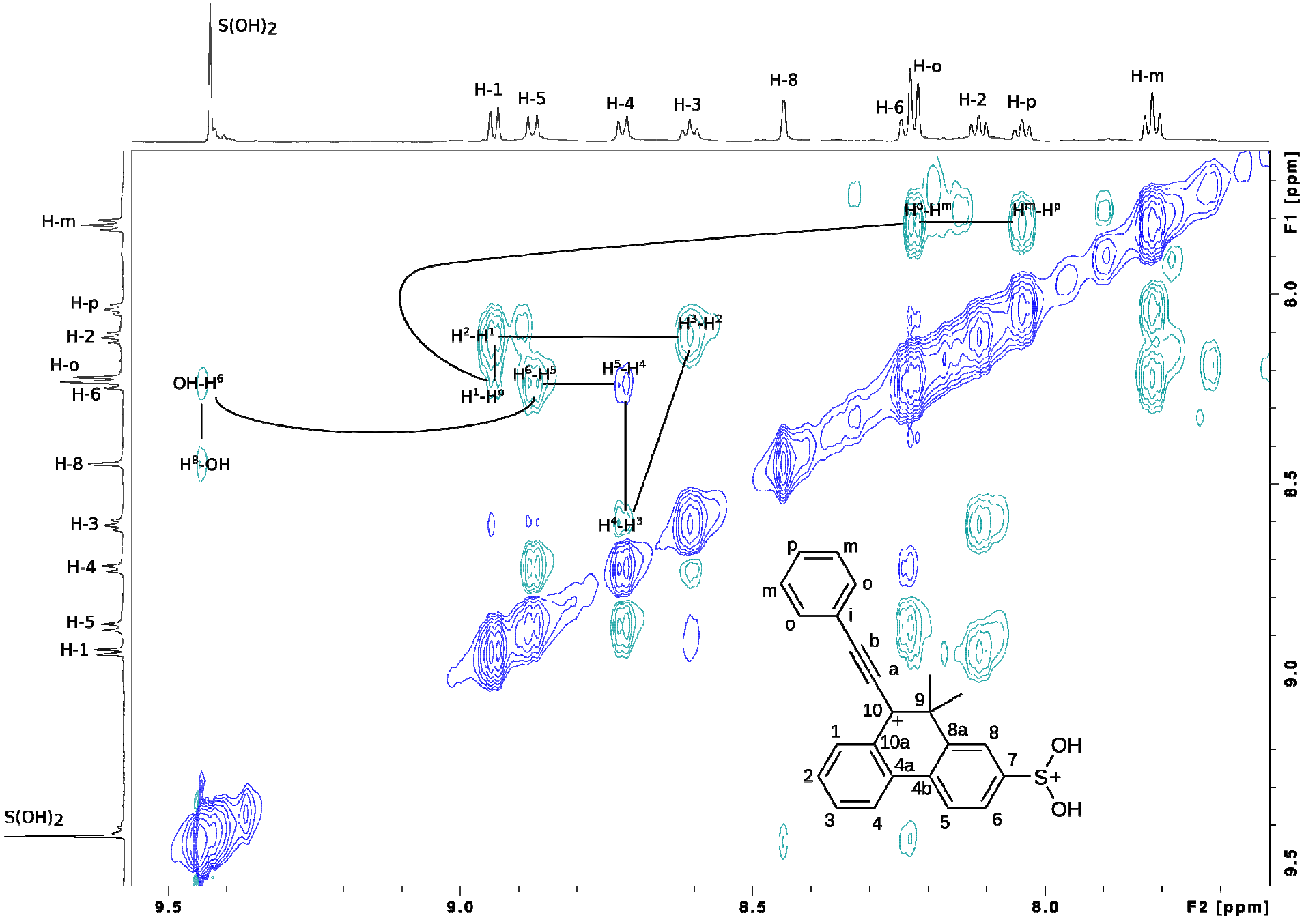
COSY spectrum (600 MHz) of dication **3a** in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –81 °C



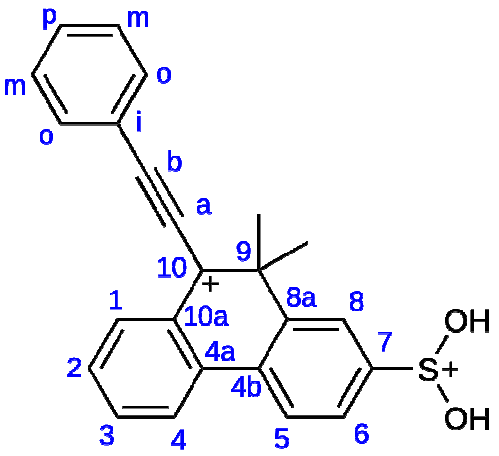
ROESY spectrum (600 MHz) of dication **3a** in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –81 °C



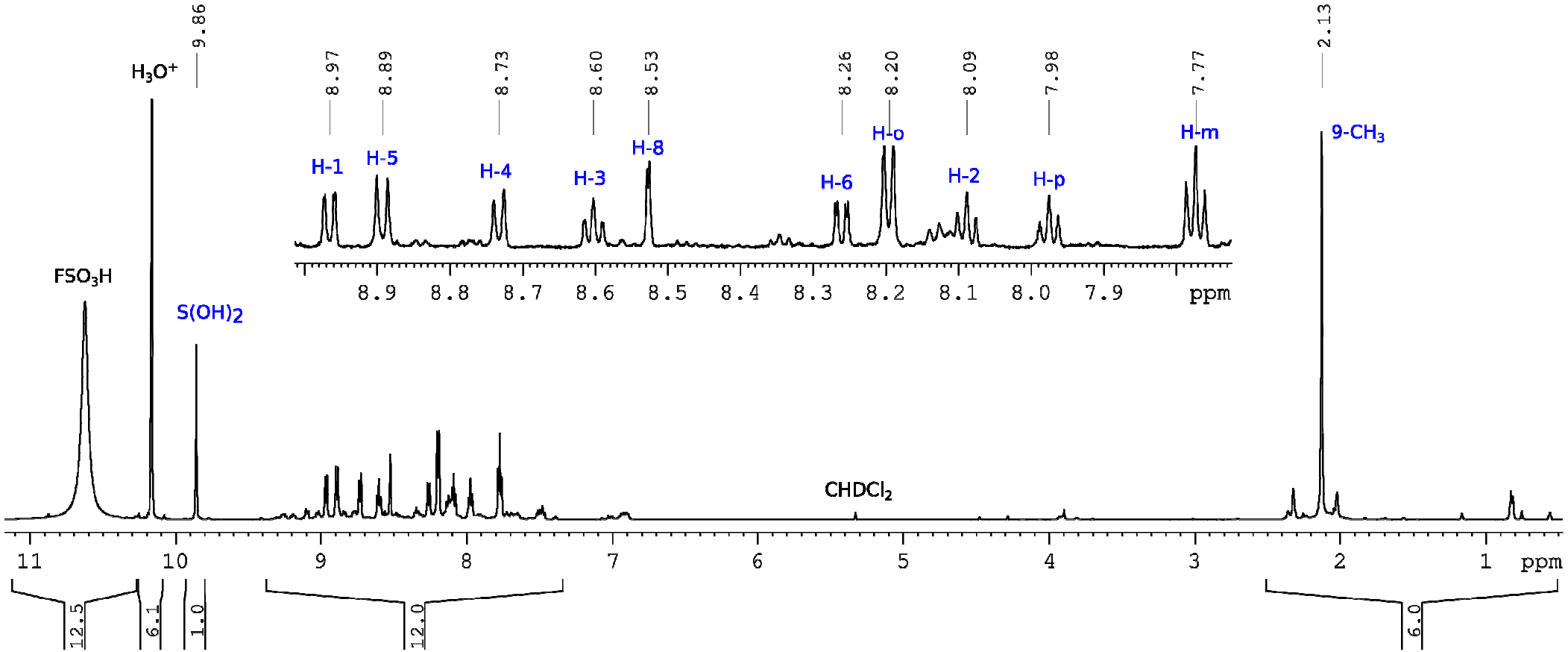
ROESY spectrum (600 MHz) of dication **3a** in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –81 °C (aromatics region)



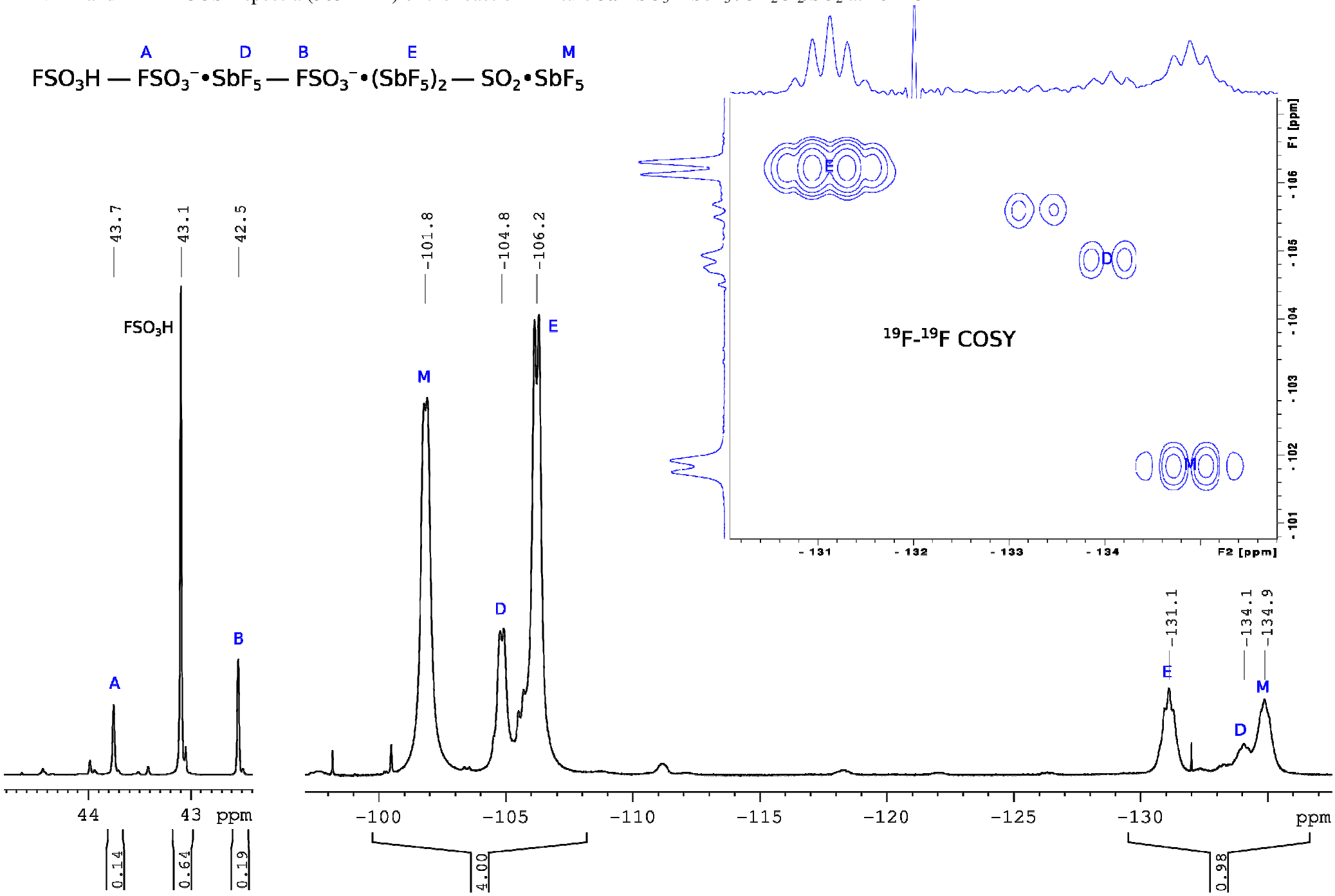
7-Dihydroxysulfonio-9,9-dimethyl-10-phenylethynylphenanthrenium dication (**3a**).Solution of carbinol **2a** (20 мг, 0.062 mmol.) in 0.13 g of CD_2Cl_2 was added to solution of FSO_3H (105 mg, 1.05 mmol.) and SbF_5 (235 mg, 1.09 mmol.) in 0.25 mL of liquid SO_2 placed into NMR tube at -70 °C and the mixture was stirred. Formation of cation **1a** was observed by NMR. The mixture was warmed to -61 °C and was kept for 2 h. ^{19}F NMR spectra (see at the next page) show that the mixture contains the following particles: SO_3F^- (HSO_3F), $SO_3F^-•SbF_5$, $SO_3F^-•(SbF_5)_2$, and $SO_2•SbF_5$ at ratio 64:13:19:37 (a sum of SO_3F is taken as 100). ^{19}F NMR spectrum (δ, ppm). SO_3F^- (HSO_3F): 43.1 s; $SO_3F^-•SbF_5$: 43.8 s (1F), -104.8 d (4F, *J* 99 Hz), -134.0 quintet (1F, *J* 99 Hz); $SO_3F^-•(SbF_5)_2$: 42.6 s (1F), -106.2 d (4F, *J* 104 Hz), -131.1 quintet (1F, *J* 104 Hz); $SO_2•SbF_5$: -101.8 d (4F, *J* 97 Hz), -134.9 quintet (1F, *J* 97 Hz).



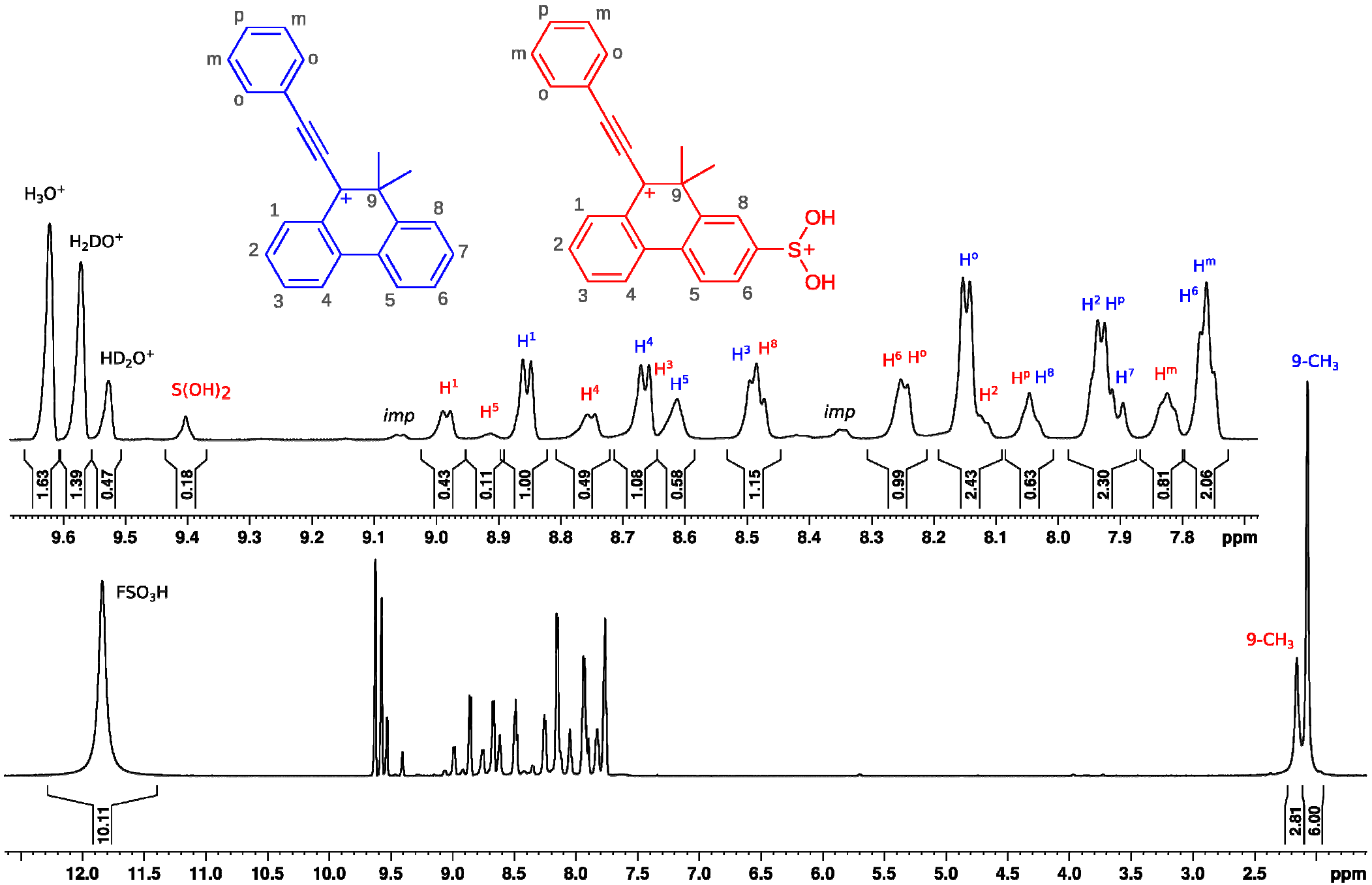
^1H NMR spectrum (600 MHz) of cation **1a** in FSO_3H-SbF_5 /CD_2Cl_2/SO_2 at –61 °C:



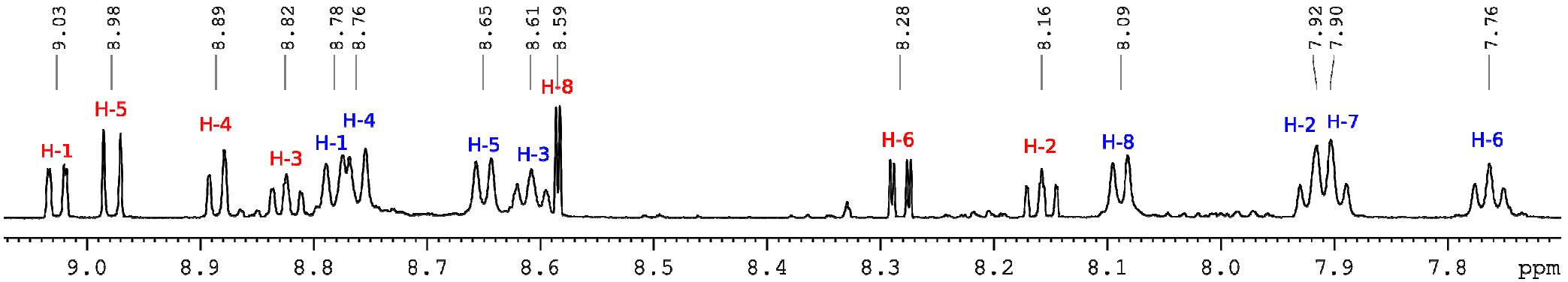
^{19}F NMR and ^{19}F-^{19}F COSY spectra (565 MHz) of the reaction mixture **3a**-FSO_3H-SbF_5 /CD_2Cl_2/SO_2 at –61 °C

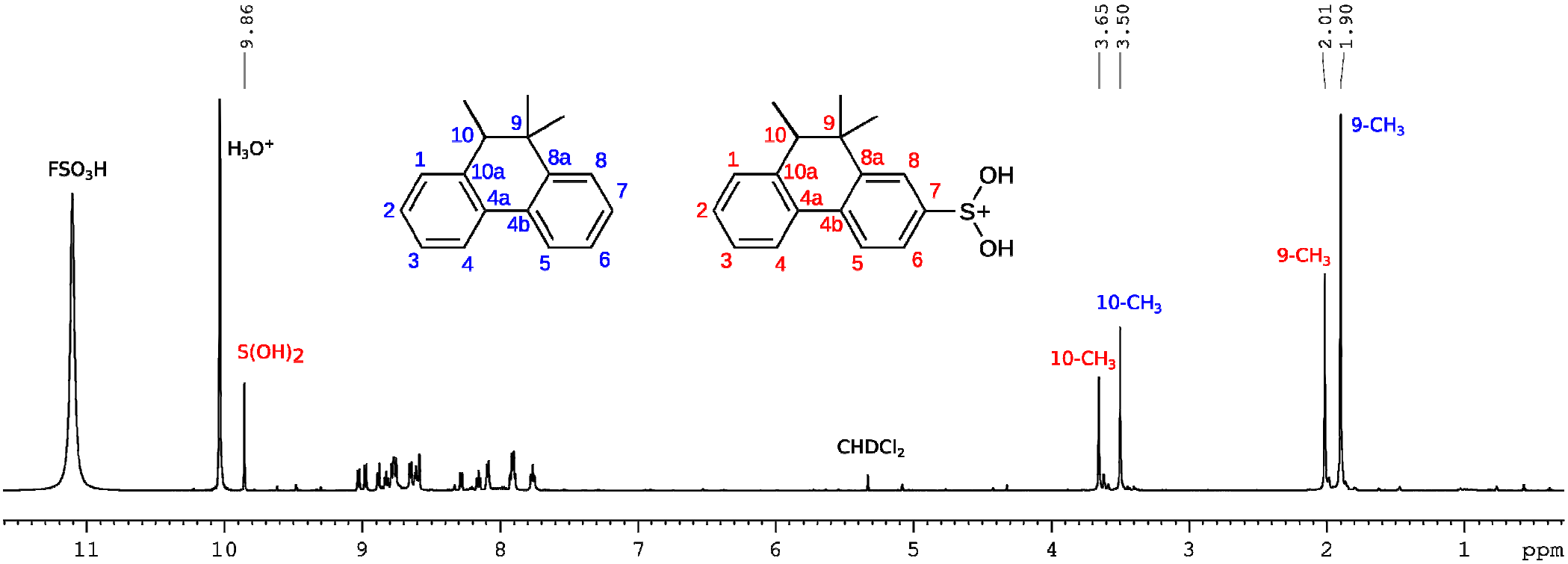


^{1}H NMR spectrum (600 MHz) of cations **1a** (blue) and **3a** (red) in FSO_3D-$SbF_5/SO_2ClF/SO_2$ at –100 °C (9-CH_3 of **1a** is referenced to 2.07 ppm)

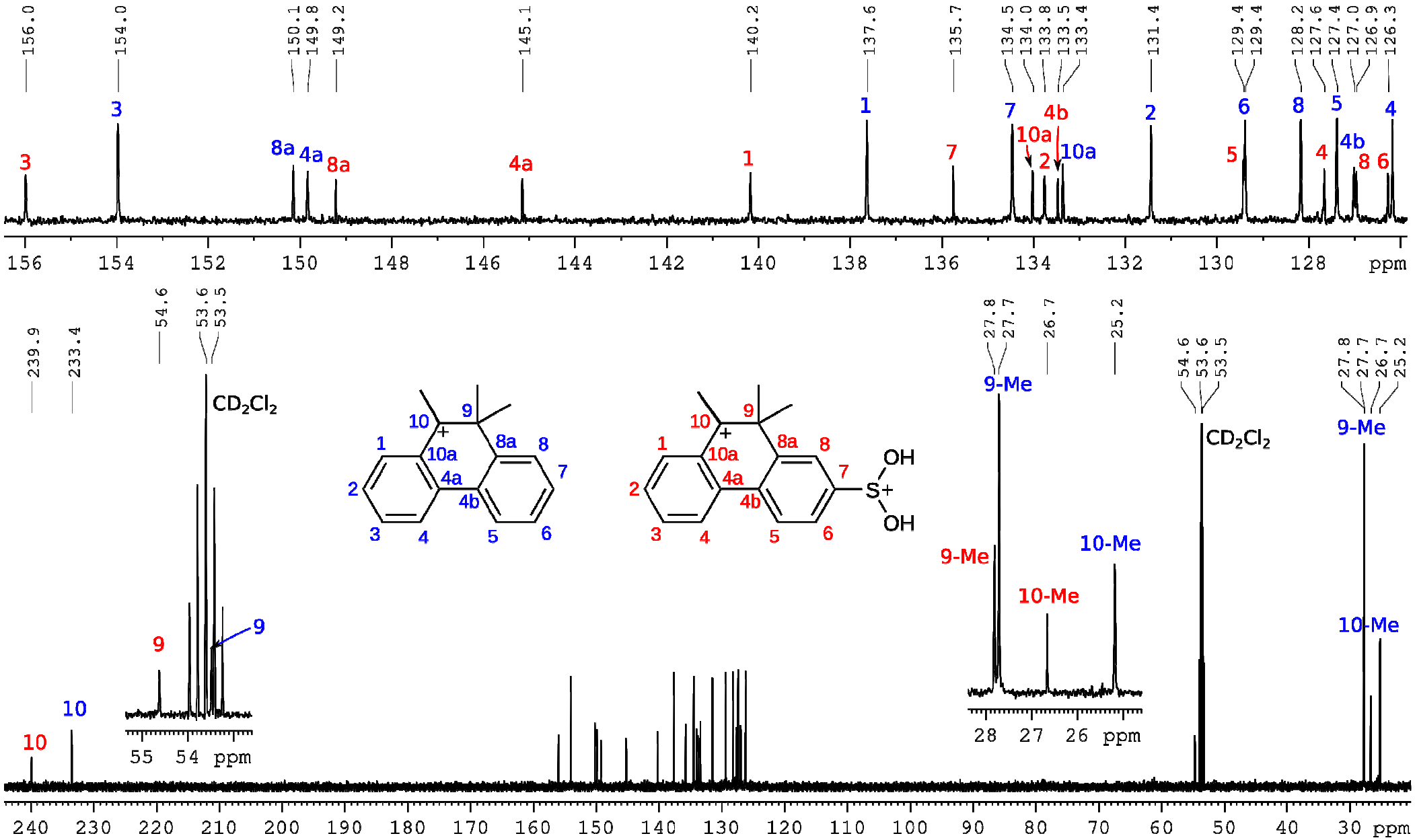


^{1}H NMR spectrum (600 MHz) of cations **1b** (blue) and **3b** (red) in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –71 °C

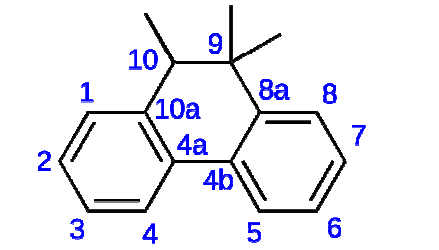


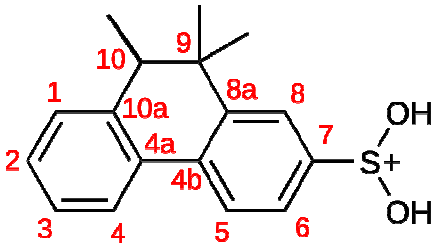


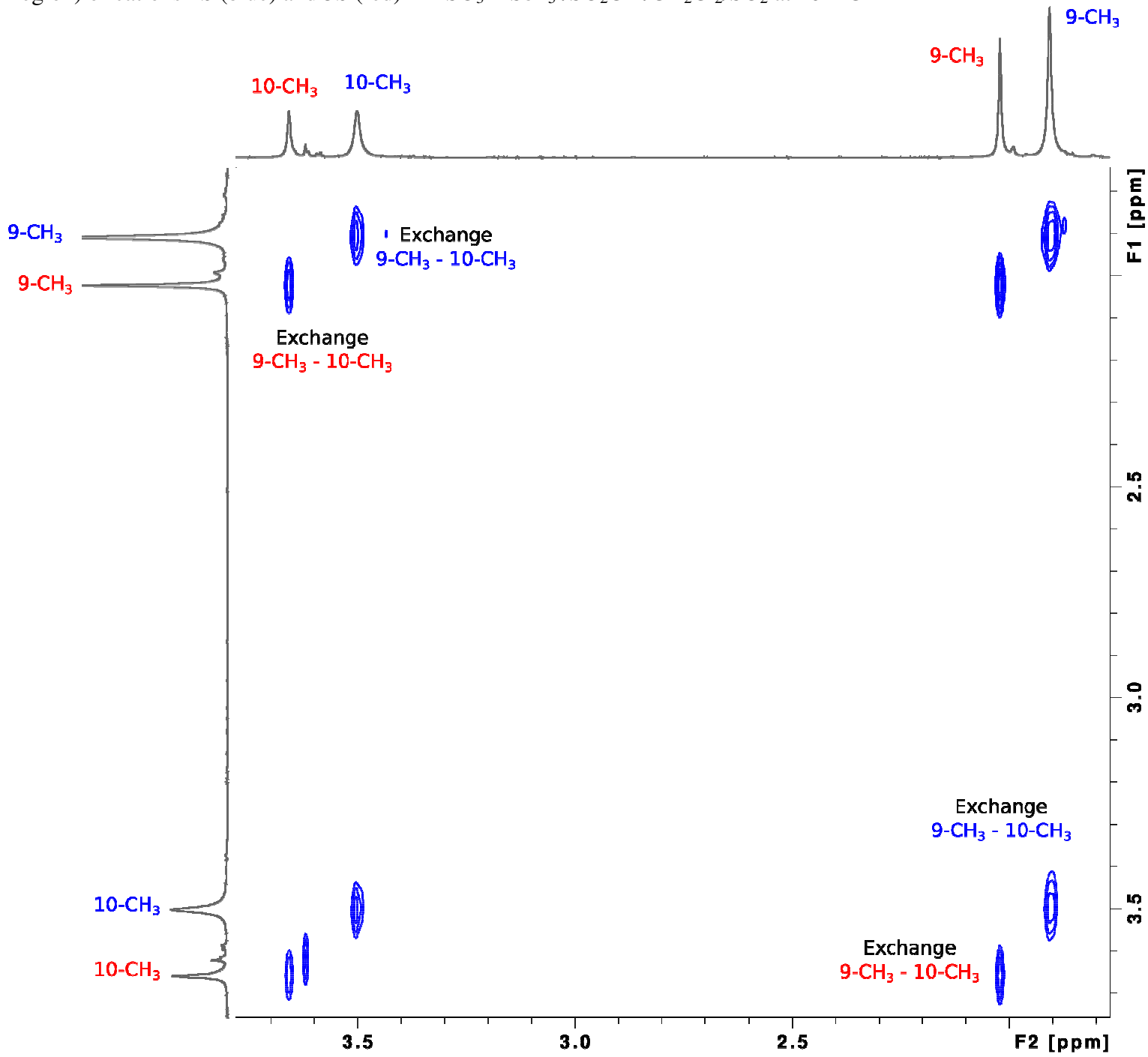
^{13}C NMR spectrum (151 MHz) of cations **1b** (blue) and **3b** (red) in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –71 ^{o}C



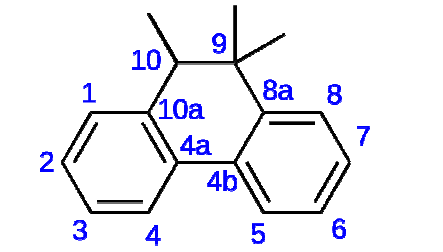
ROESY spectrum (600 MHz, methyl region) of cations **1b** (blue) and **3b** (red) in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –61 °C

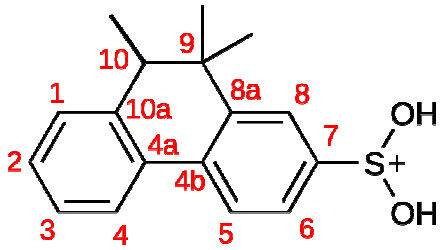


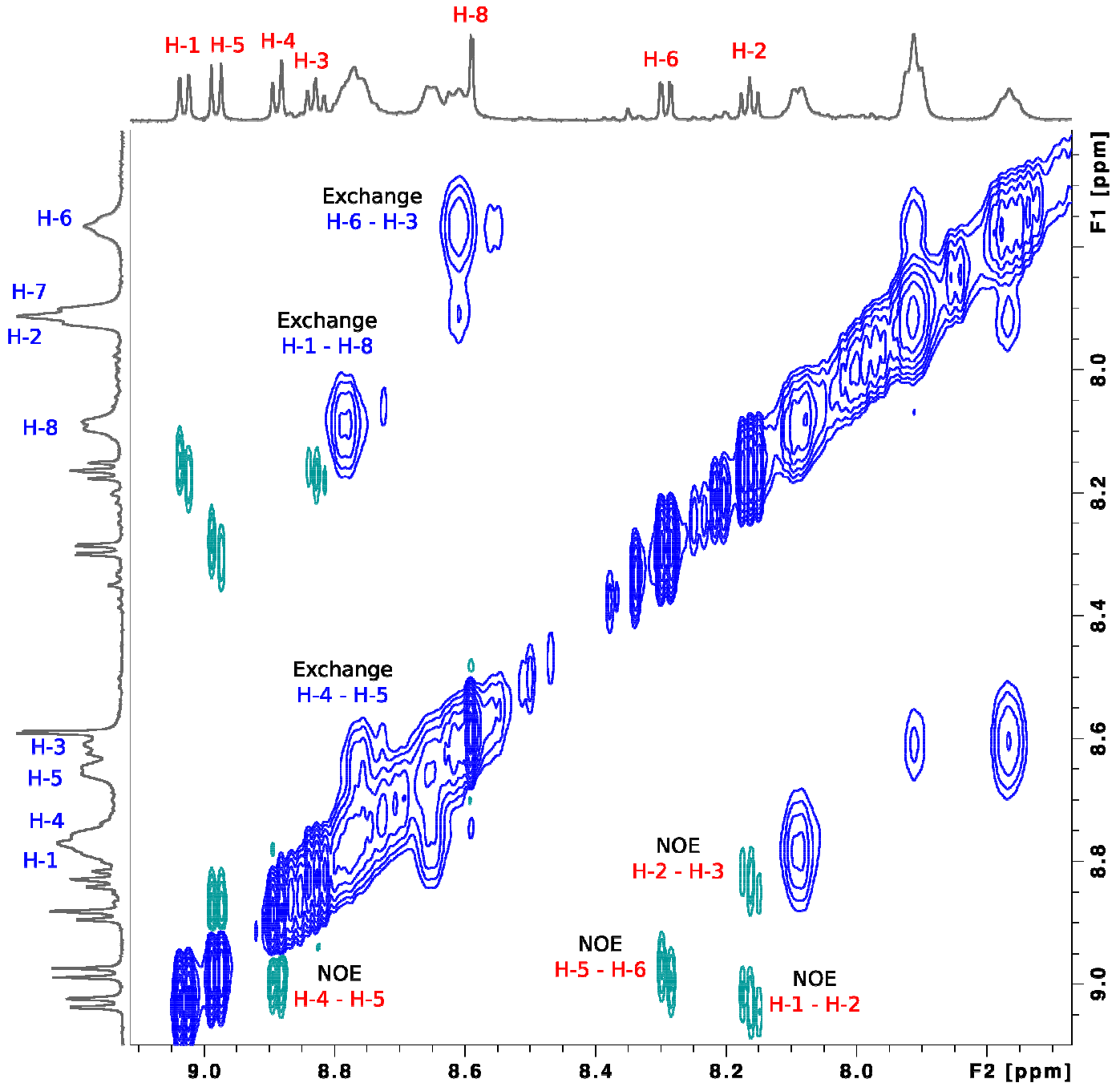




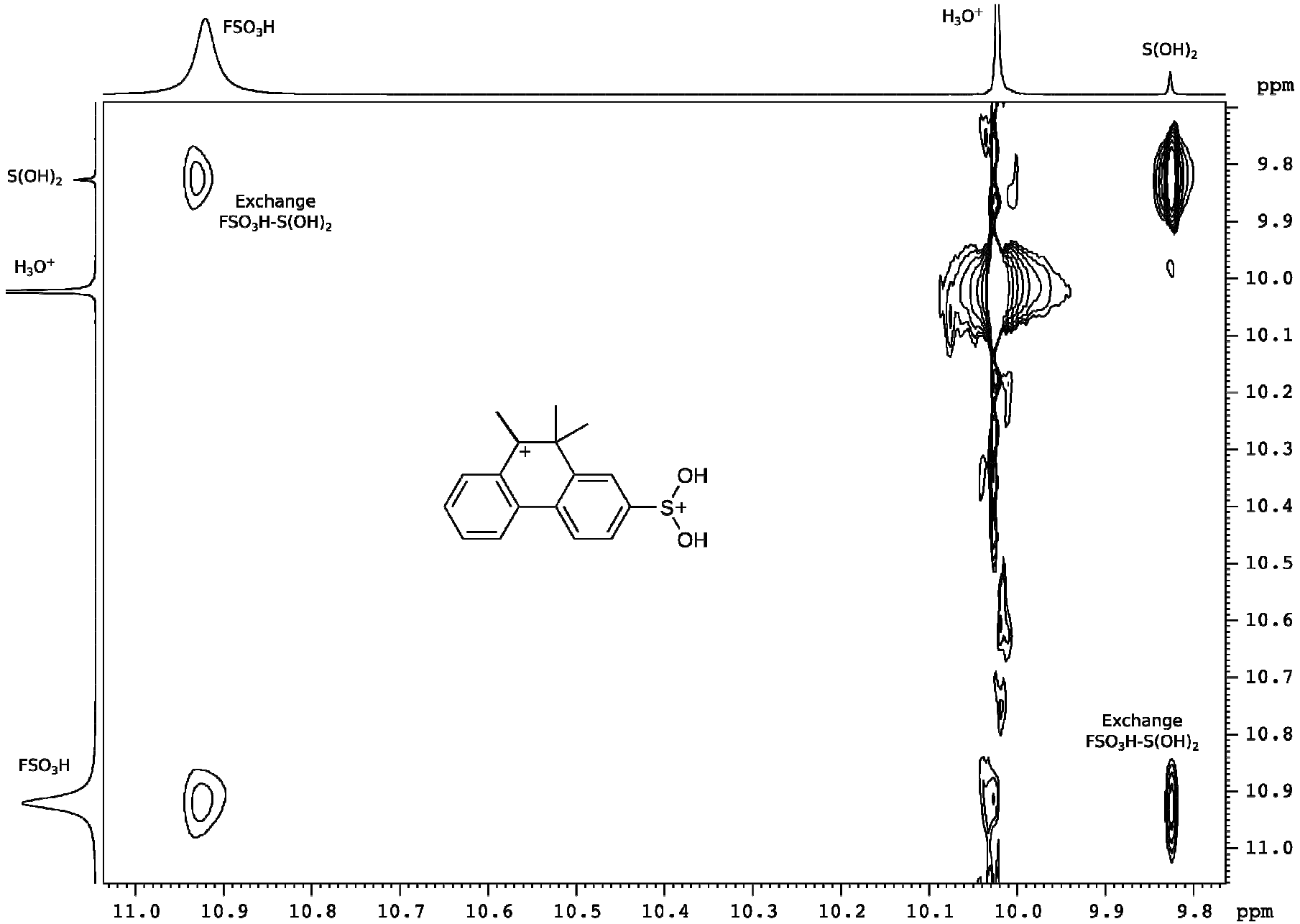
ROESY spectrum (600 MHz, aromatics region) of cations **1b** (blue) and **3b** (red) in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –61 °C



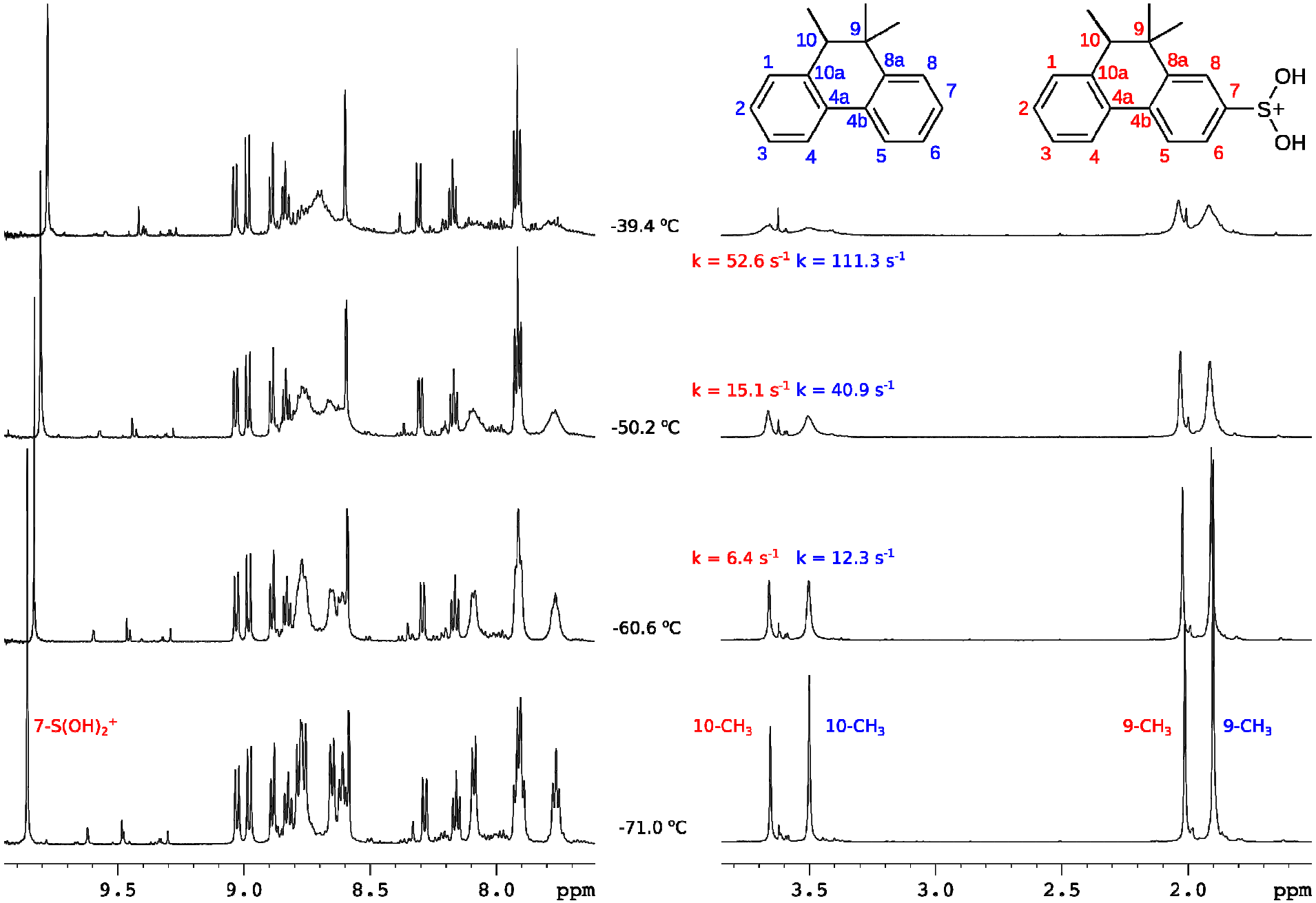




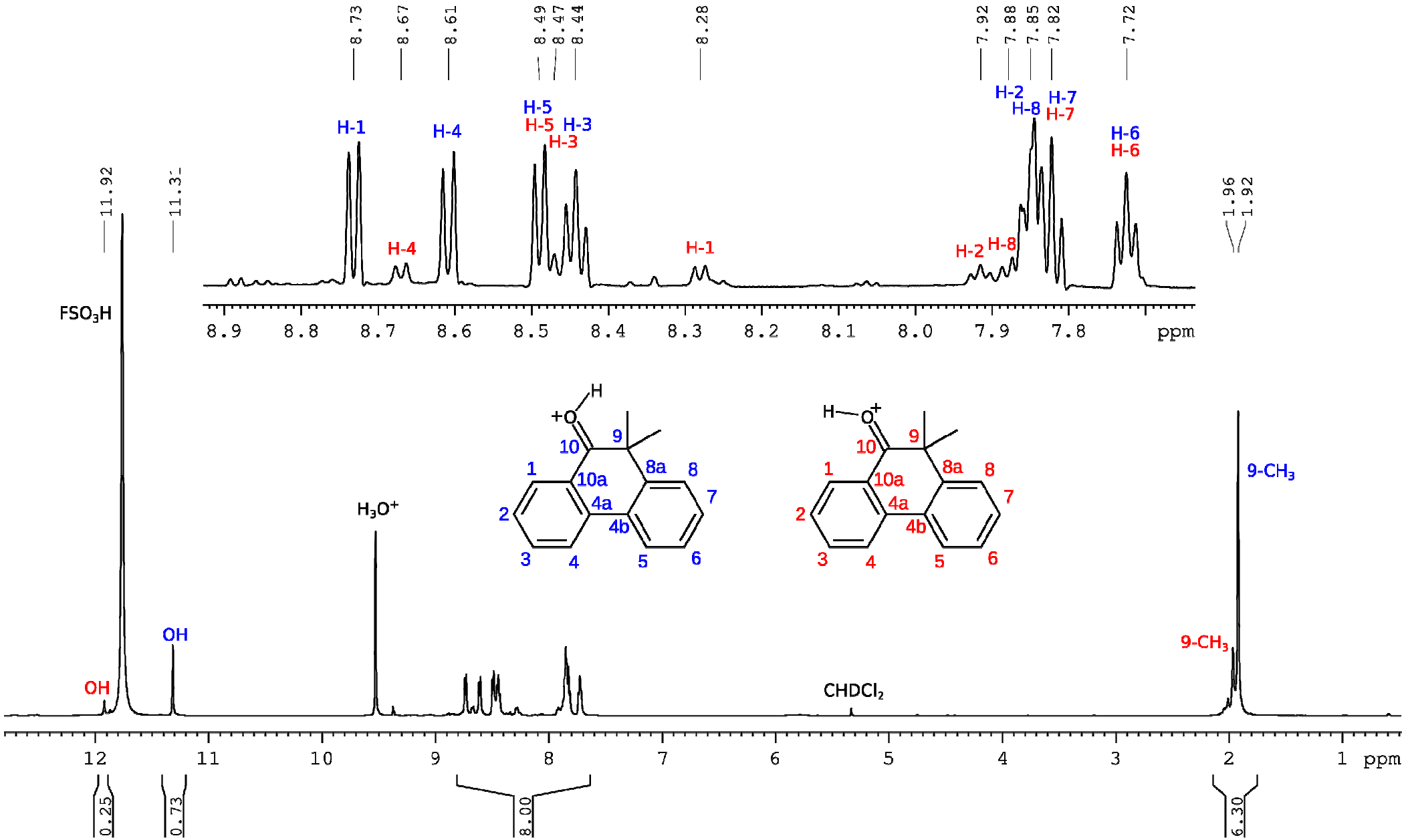
ROESY spectrum (600 MHz; FSO_3H, H_3O^+, $S(OH)_2^+$ signals) of cations **1b** and **3b** in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –61 °C, The exchange rate between protons of $S(OH)_2^+$ group of dication **3b** and protons of FSO_3H is k = 0.2 s^{-1}, pseudomonomolecular approximation.



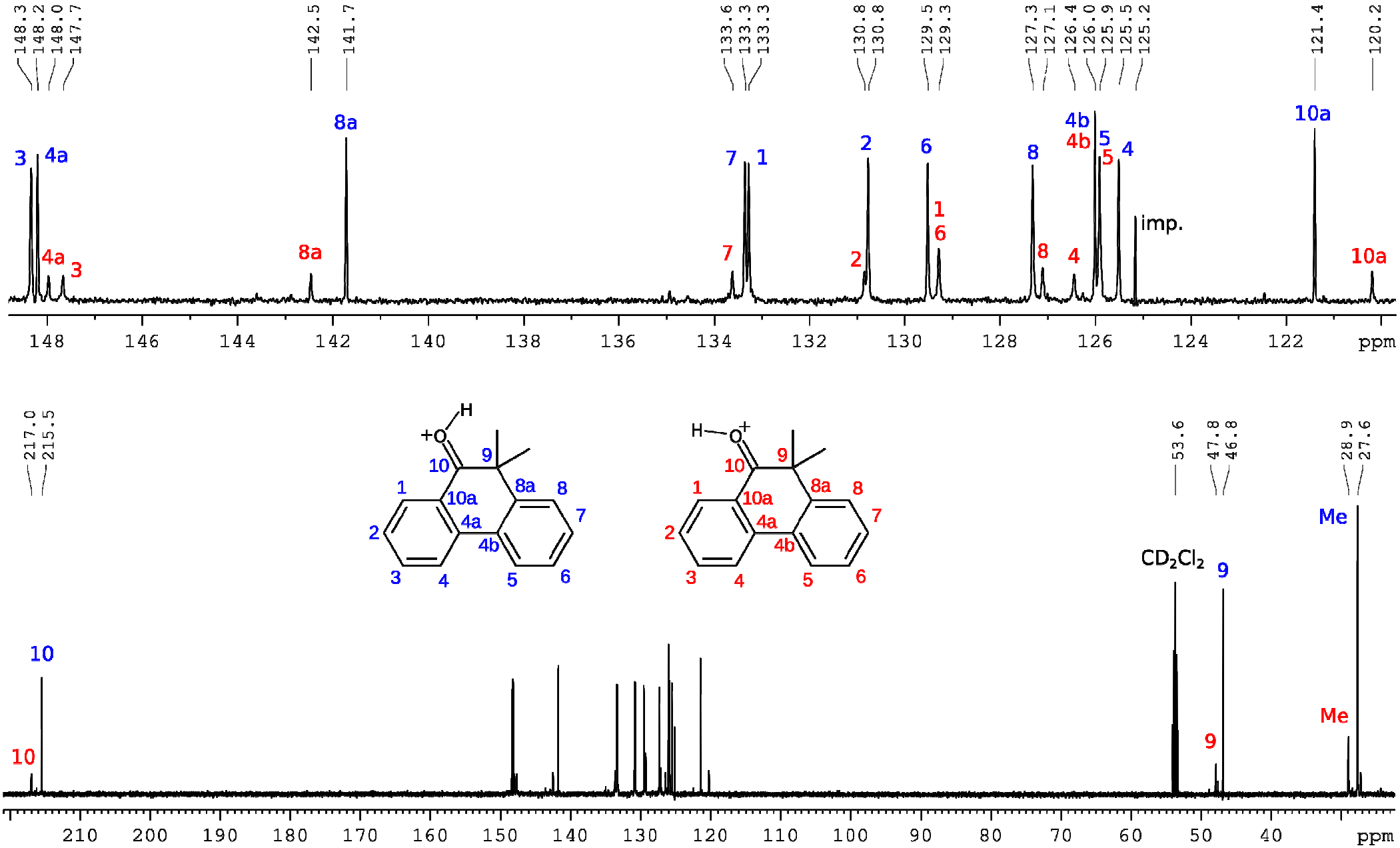
^{1}H DNMR spectra (600 MHz) of cations **1b** (blue) and **3b** (red) in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2.



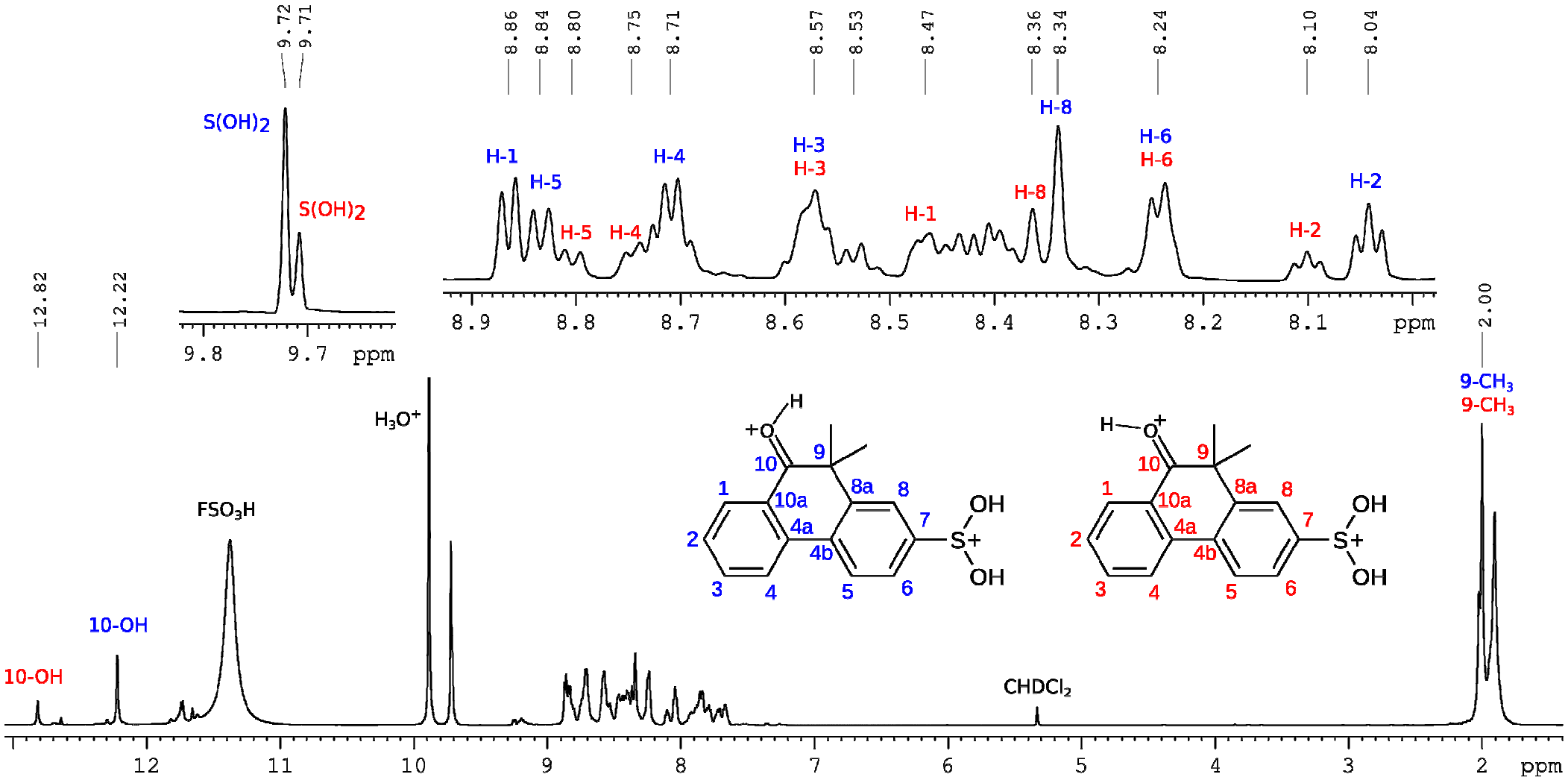
^{1}H NMR spectrum (600 MHz) of cations **(*E*)-1c** (blue) and **(*Z*)-1c** (red) in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2 at –91 °C



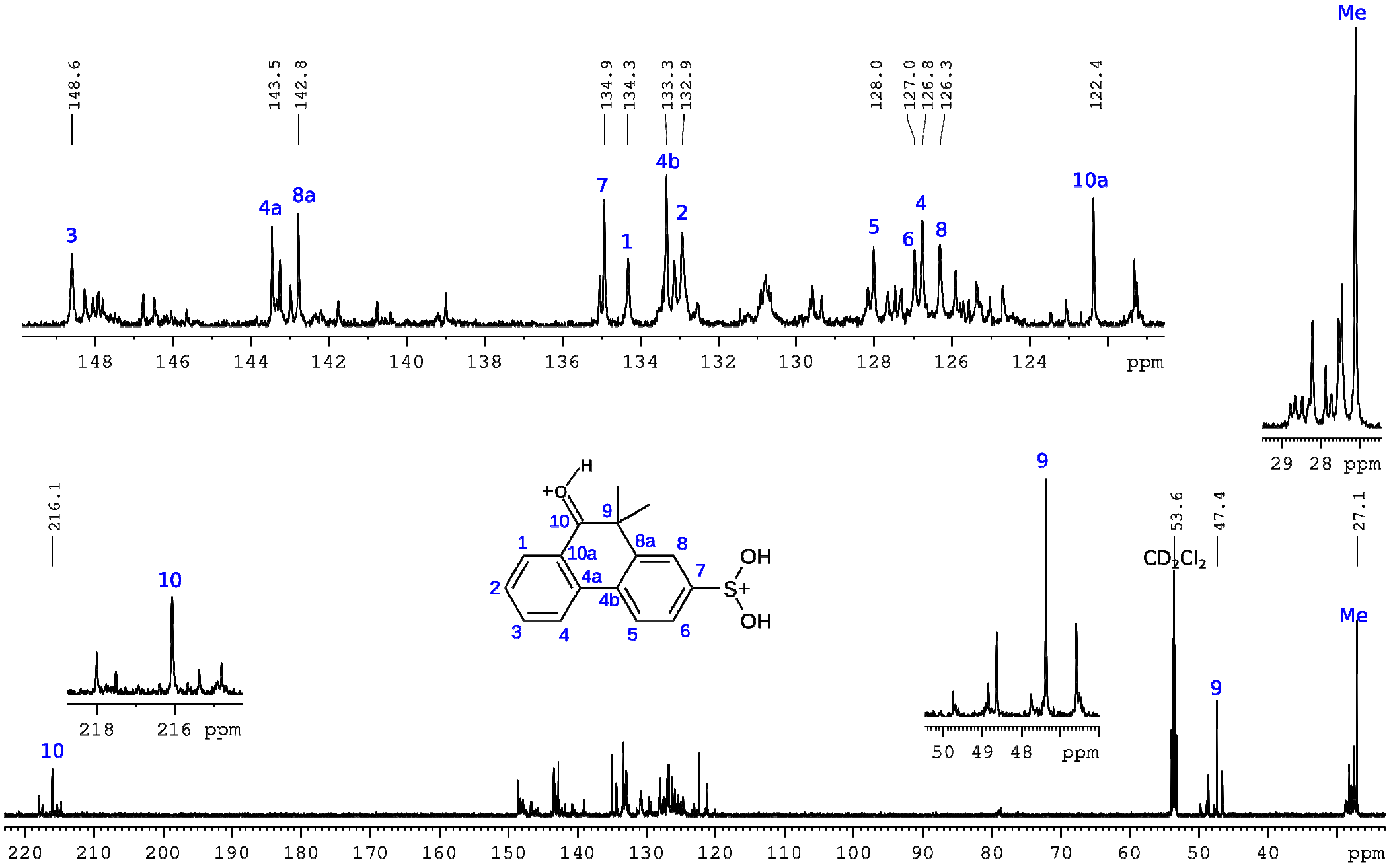
^{13}C NMR spectrum (151 MHz) of cations **(*E*)-1c** (blue) and **(*Z*)-1c** (red) in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2 at –91 °C



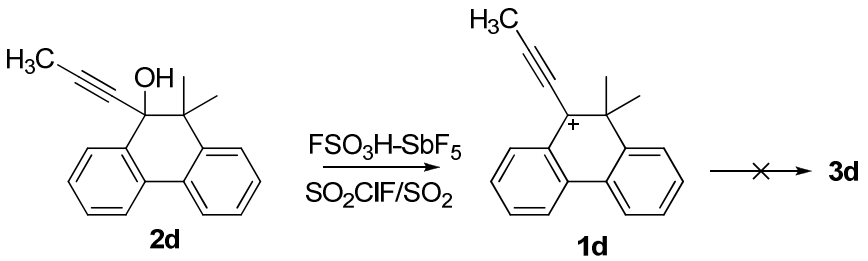
^{1}H NMR spectrum (600 MHz) of cations **(*E*)-3c** (blue) and **(*Z*)-3c** (red) in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –91 °C



^{13}C NMR spectrum (151 MHz) of cation (***E***)**-3c** in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –91 °C

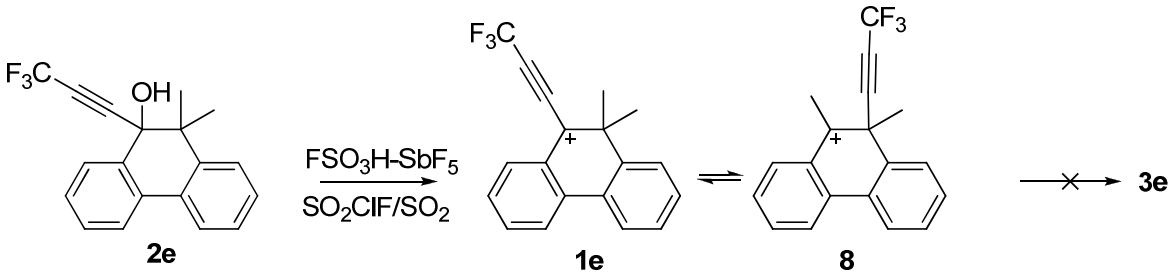


An attempt to generate 7-dihydroxysulfonio-9,9-dimethyl-10-methylethynylphenanthrenium dication (**3d**).



Solution of carbinol **2d**[1] (5 мг, 0.019 mmol.) in 0.14 mL of CD_2Cl_2 was added to solution of FSO_3H (145 mg, 1.45 mmol.) and SbF_5 (310 mg, 1.43 mmol.) in 0.25 mL of SO_2ClF/SO_2 (8% SO_2) placed into NMR tube at -95 °C and the mixture was stirred. Formation of cation **1d**[OBC] was observed at -100 °C. This cation at −71°C for 40 min transforms into a complex mixture of unidentified products, no sulfination reaction being observed.

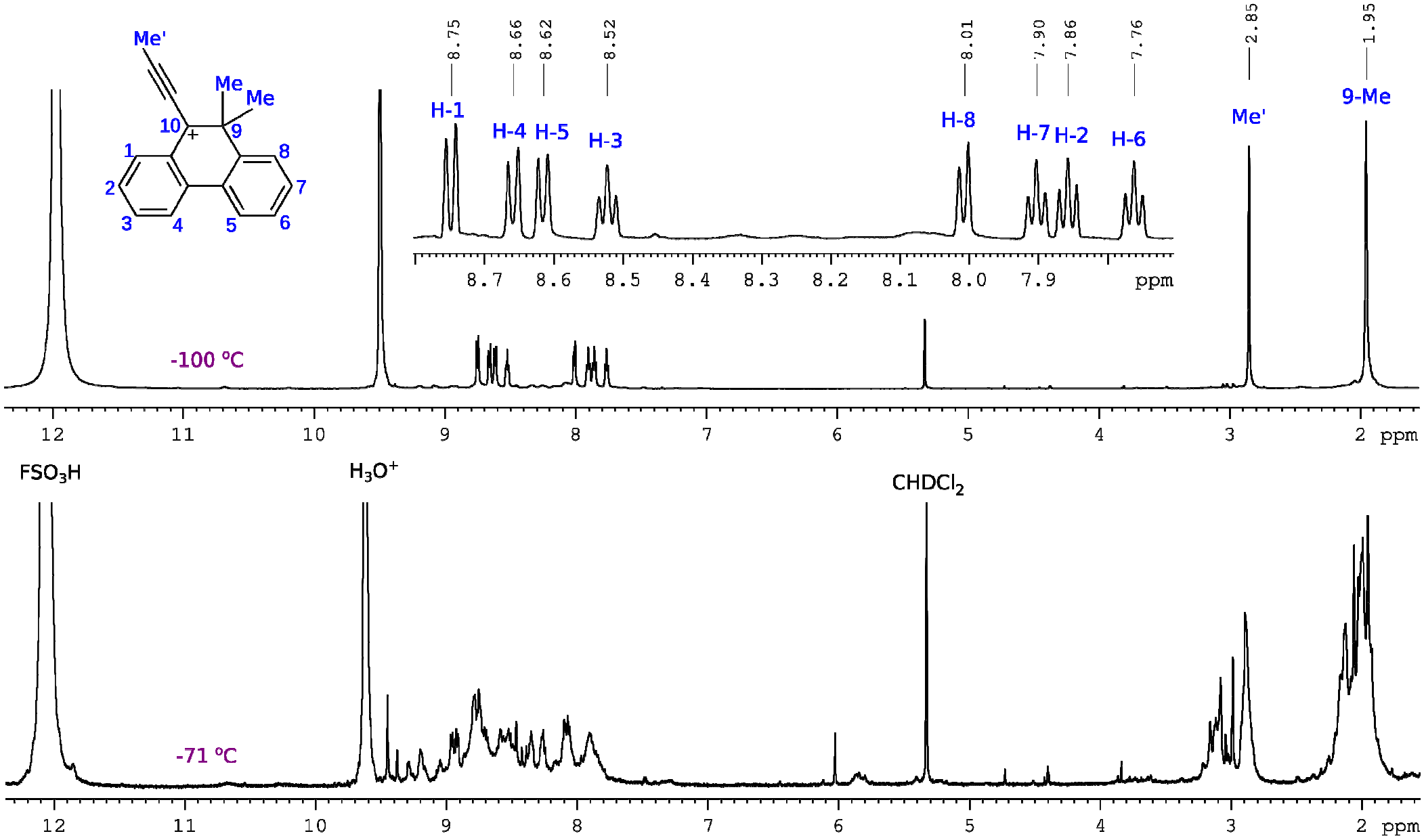
An attempt to generate 7-dihydroxysulfonio-9,9-dimethyl-10-trifluoromethylethynylphenanthrenium dication (**3e**).



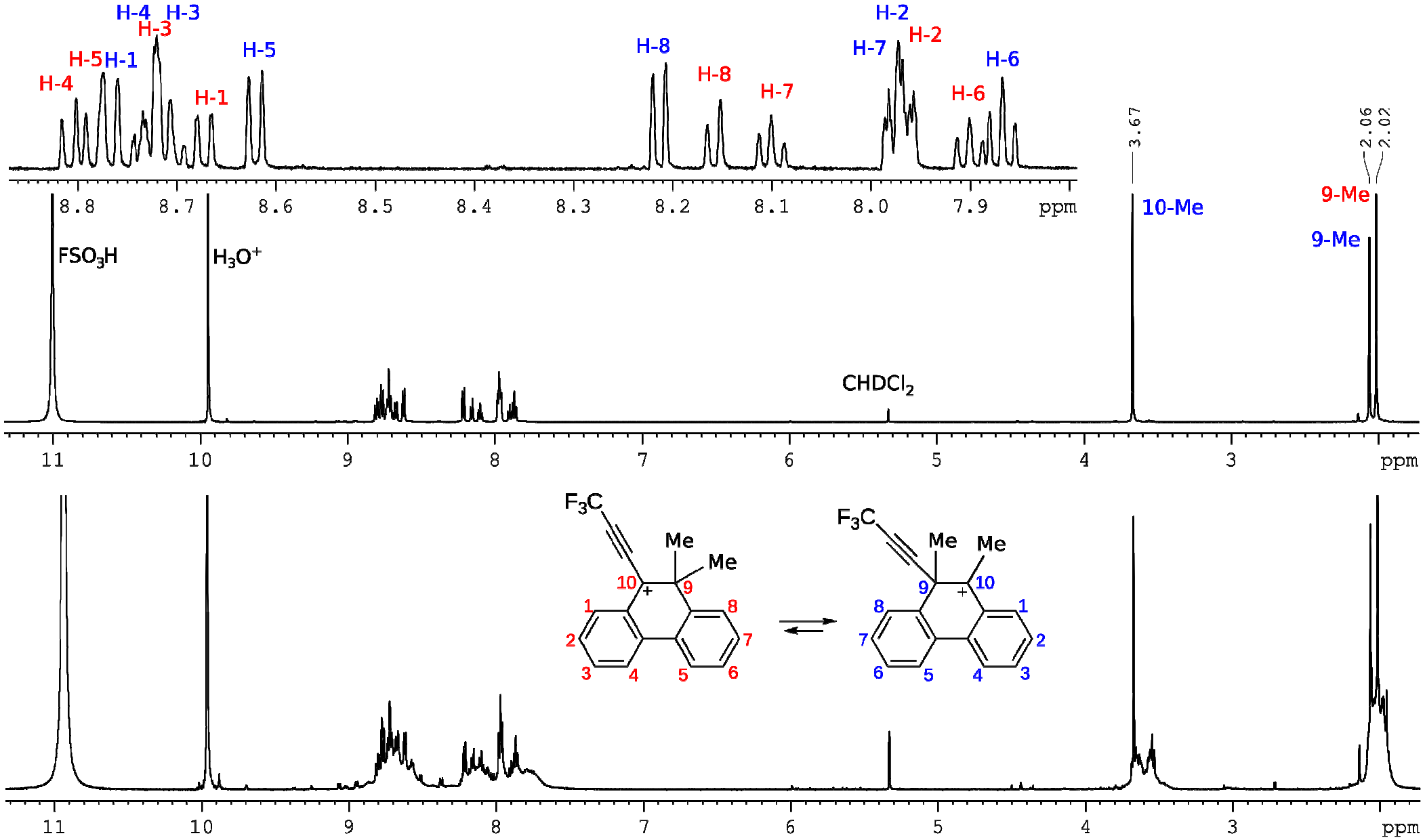
Solution of carbinol **2e**[1] (20 мг, 0.063 mmol.) in 0.13 mL of CD_2Cl_2 was added to solution of FSO_3H (125 mg, 1.26 mmol.) and SbF_5 (290 mg, 1.33 mmol.) in 0.25 mL of SO_2ClF/SO_2 (8% SO_2) placed into NMR tube at -95 °C and the mixture was stirred. Formation of a mixture of cation **1e** and its isomer **8** [OBC] was observed. The content of dication **3e** in the mixture was less than 2% (if any) at -39 °C. At -39 °C these cations are quickly (for 10 min) decomposed.

[1] V.A. Bushmelev, A.M. Genaev, G.E. Sal'nikov, and V.G. Shubin, *Russ. J. Org. Chem*., 2013, **49**, 853-859.
[OBC] G.E. Salnikov, A.M. Genaev, V.A. Bushmelev and V.G. Shubin, *Org. Biomol. Chem.*, 2013, **11**, 1498-1501.

^{1}H NMR spectra (600 MHz) of cation **1d** in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –100 °C (top) and after 40 min at –71 °C (bottom). The signal assignments are taken from *Org. Biomol. Chem.*, 2013, **11**, 1498-1501.



^{1}H NMR spectra (600 MHz) of the equilibrium mixture of cation **1e** (red) and its isomer (blue) in FSO_3H-SbF_5 /SO_2ClF/CD_2Cl_2/SO_2 at –39 °C (top) and at the same temperature after keeping the mixture for 10 min at –29 °C (bottom). The signal assignments are taken from *Org. Biomol. Chem.*, 2013, **11**, 1498-1501.



Comparison of chemical shifts between dications **3** and cations **1**

^{1}H NMR chemical shifts, δ(**3**)-δ(**1**)=difference

	H1	H2	H3	H4	H5	H6	H8	9-Me	10
(*E*)**3c**-(*E*)**1c**	8.86-8.73=0.13	8.04-7.85=0.19	8.57-8.44=0.13	8.71-8.61=0.10	8.83-8.49=0.34	8.24-7.72=0.52	8.34-7.85=0.49	2.00-1.92=0.08	12.22-11.31=0.91
(*Z*)**3c**-(*Z*)**1c**	8.47-8.28=0.19	8.10-7.92=0.18	8.57-8.47=0.10	8.75-8.67=0.08	8.80-8.49=0.31	8.24-7.72=0.52	8.36-7.88=0.48	2.00-1.96=0.04	12.82-11.92=0.90
3a-**1a***	8.94-8.84=0.10	8.11-7.92=0.19	8.61-8.50=0.11	8.72-8.67=0.05	8.88-8.60=0.28	8.23-7.76=0.47	8.45-8.04=0.41	2.13-2.07=0.06	**
3b-**1b**	9.03-8.78=0.25	8.16-7.72=0.44	8.82-8.61=0.21	8.89-8.76=0.13	8.98-8.65=0.33	8.28-7.76=0.52	8.58-8.09=0.49	2.01-1.90=0.11	3.65-3.50=0.15

* **1a** in HSO_3F-SbF_5(1:1)-SO_2ClF at -91 °C; H7 7.90 ppm;
** Hm 7.82-7.76=0.06, Hp 8.04-7.92=0.12, Ho 8.22-8.15=0.07

^{13}C NMR chemical shifts, δ(**3**)-δ(**1**)=difference

	C1	C2	C3	C4	C4a	C10a	C10
(*E*)**3c**-(*E*)**1c**	134.3-133.2=1.1	132.9-130.7=2.2	148.6-148.3=0.3	126.8-125.5=1.3	143.5-148.2=-4.7	122.4-121.4=1.0	216.1-215.5=0.6
3a-**1a***	140.1-139.4=0.5	133.5-132.1=1.4	150.5-150.9=-0.4	126.9-126.5=0.4	141.4-148.4=-7.0	135.5-136.4=-0.9	199.2-198.9=0.3
3b-**1b****	140.2-137.6=2.6	133.8-131.4=2.4	156.0-154.0=2.0	127.7-126.3=1.4	145.1-149.8=-4.7	133.8-133.4=0.4	239.9-233.4=6.5

	C4b	C8a	C5	C6	C7	C8	C9	9-Me
(*E*)**3c**-(*E*)**1c**	133.3-126.0=7.0	142.8-141.7=1.1	128.0-125.9=2.1	127.0-129.5=-2.5	134.9-133.3=1.6	126.3-127.3=-1.0	47.4-46.8=0.6	27.1-27.6=-0.5
3a-**1a***	134.0-127.6=6.4	147.0-148.8=-1.8	128.7-127.7=1.0	126.2-130.1=-3.9	134.7-134.8=-0.1	126.3-128.3=-2.0	52.2-52.7=-0.5	31.7-32.8=-1.1
3b-**1b****	133.5-127.0=6.5	145.2-149.8=-4.6	129.4-127.4=2.0	126.3-129.4=-3.1	135.7-134.5=1.2	127.0-128.2=-1.2	54.6-53.5=1.1	27.8-27.7=0.1

* **1a** in TfOH-CD_2Cl_2 at -7 °C; 105.5-101.7=3.8 (Ca), 119.8-120.7=-0.9 (Ci), 130.7-130.9=-0.2 (Cm), 138.1-137.4=0.7 (Co), 140.1-138.5=1.6 (Cp), 161.2-152.3=8.9 (Cb)
** 10-Me 26.7-25.2=1.5