Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Migration of methylethynyl group in a long-lived carbocation

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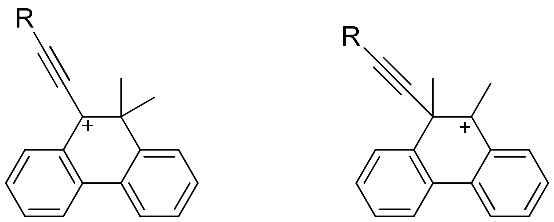
Electronic Supplementary Information

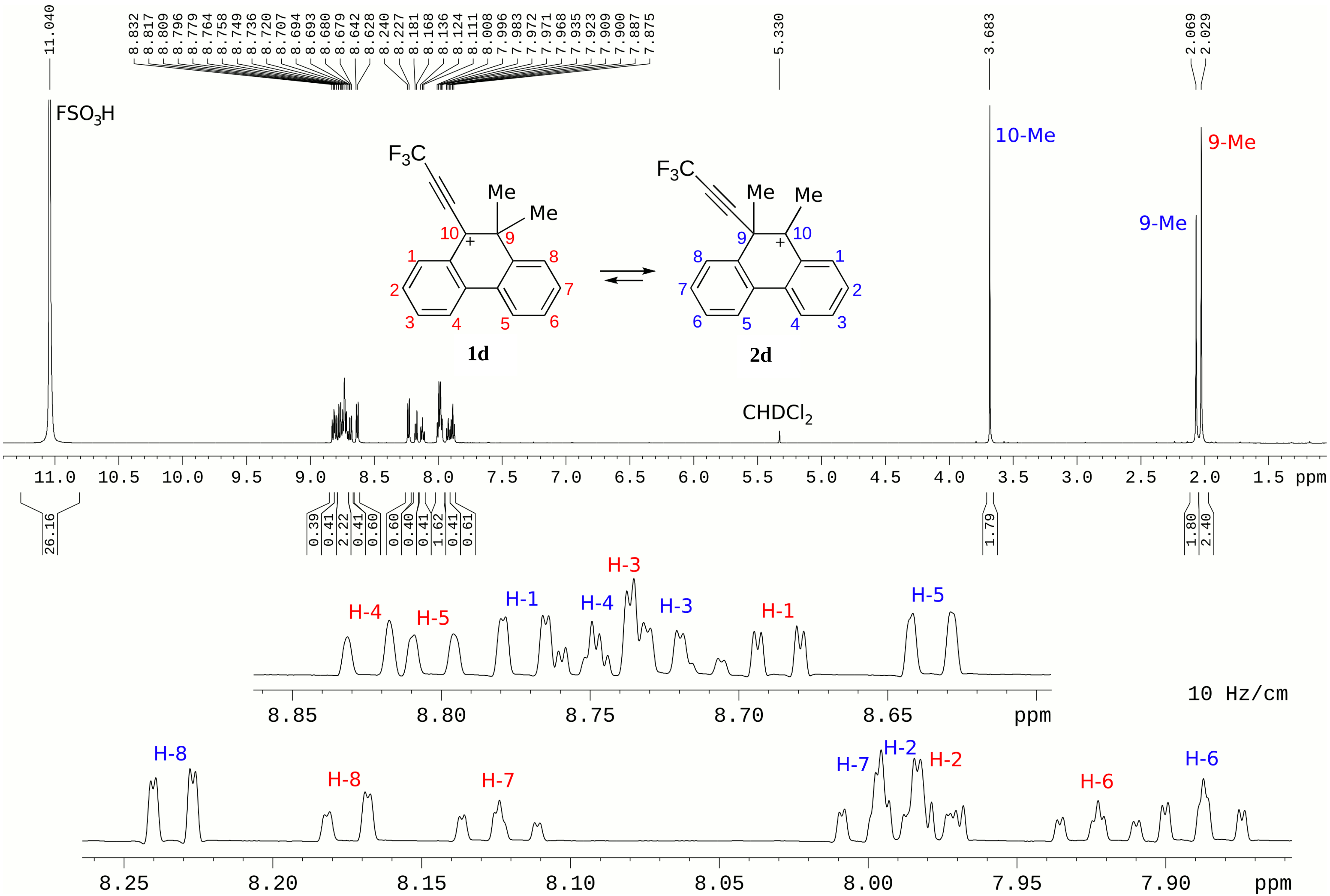


1a-d **2a-d**

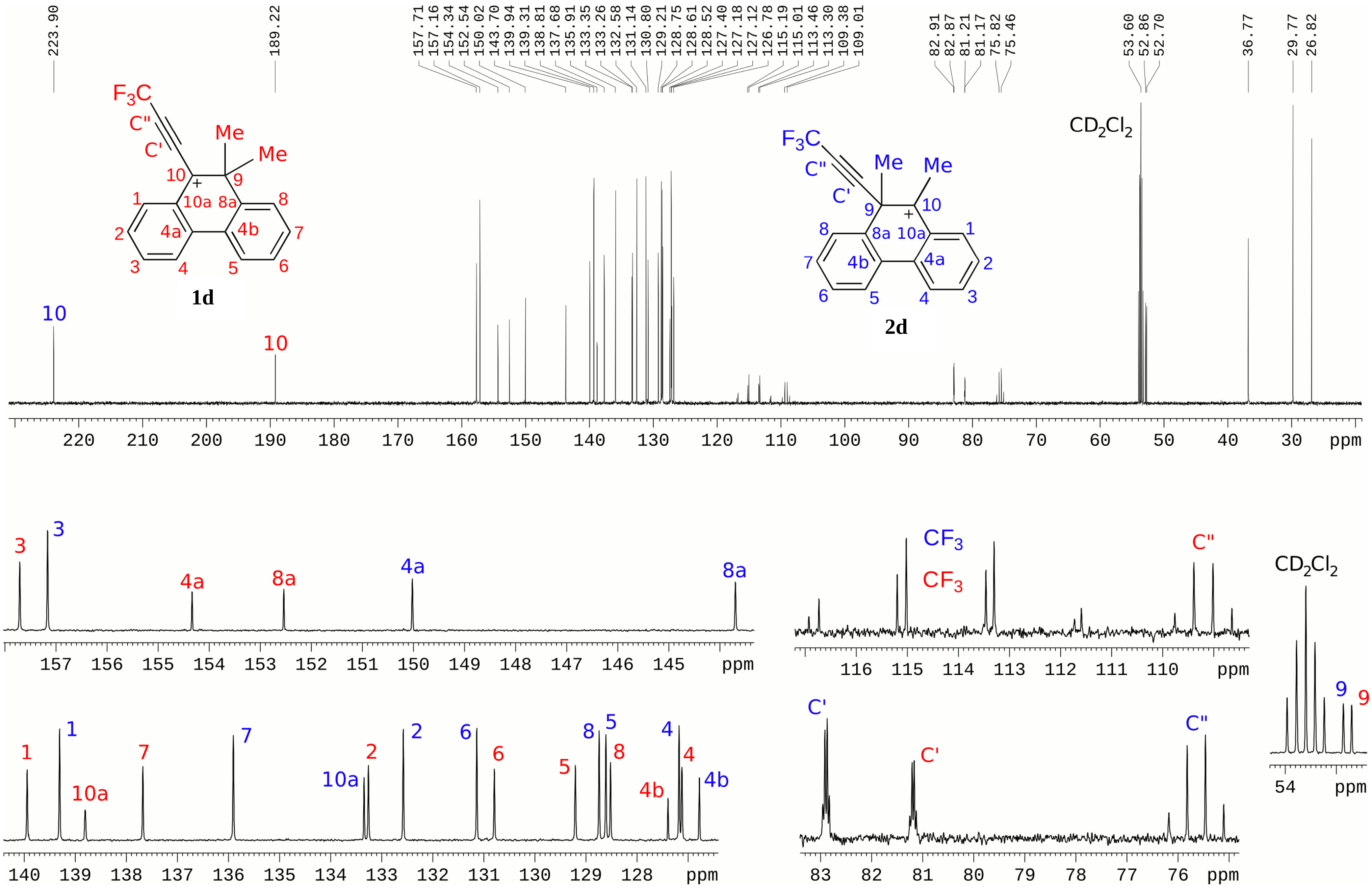
R = H (**a**), Me (**b**), Ph (**c**), CF_3 (**d**)

Table of content

^{1}H NMR spectrum of cations **1d** and **2d** in FSO_3H-SO_2ClF-CD_2Cl_2 at –50 °C

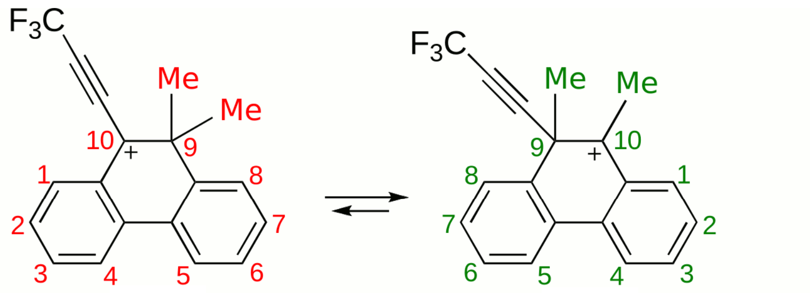


^{13}C NMR spectrum of cations **1d** and **2d** in FSO_3H-SO_2ClF-CD_2Cl_2 at –50 °C

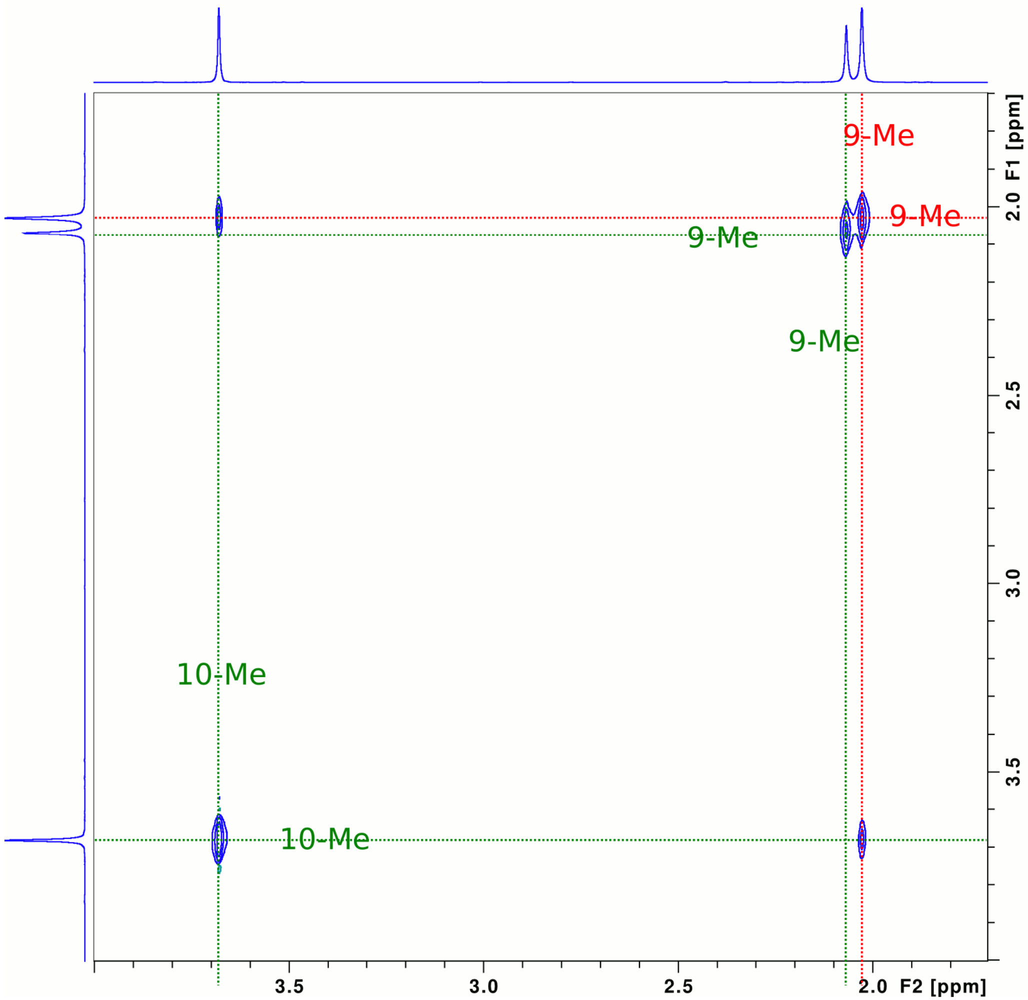


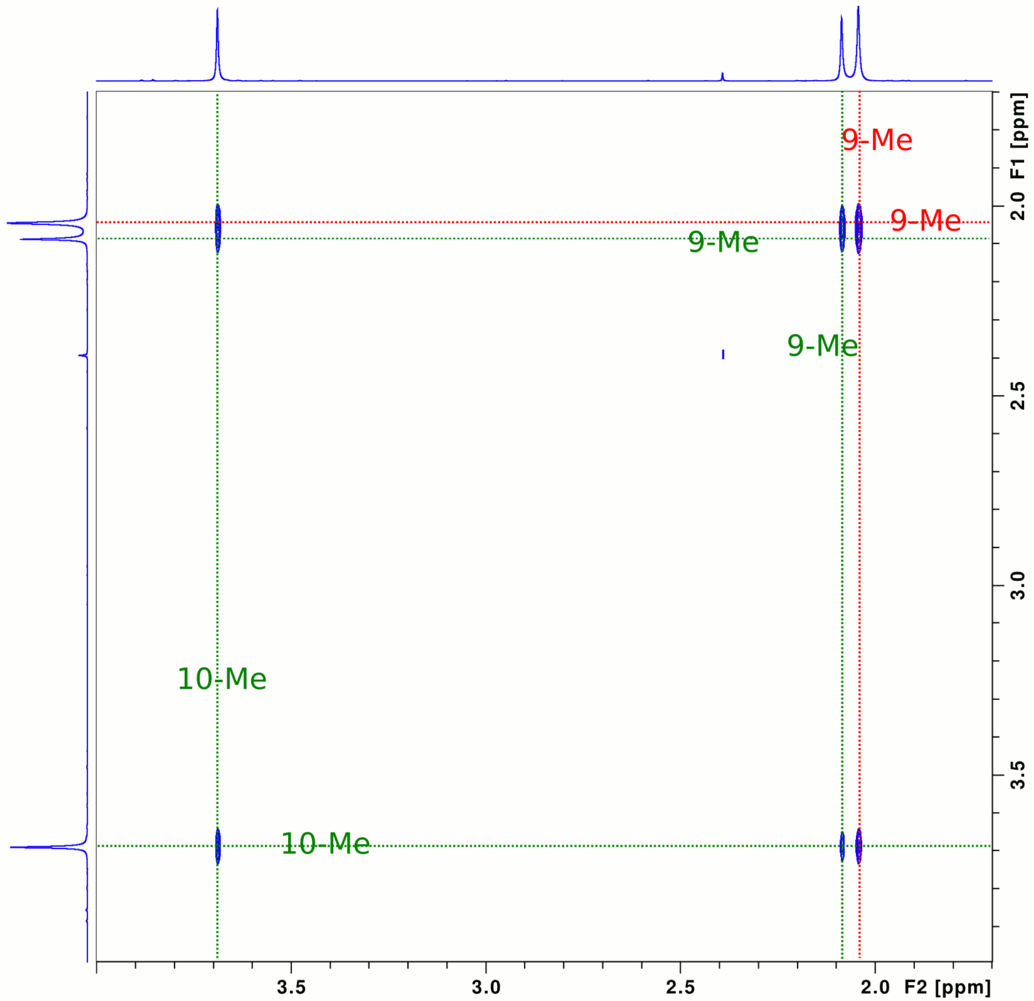
NOESY spectra (methyl region) of cations **1d** and **2d** in FSO_3H-SO_2ClF-CD_2Cl_2

Left: at –47 °C (mixing time 0.4 s)
Right: at –22.5 °C (mixing time 0.5 s)



1d **2d**





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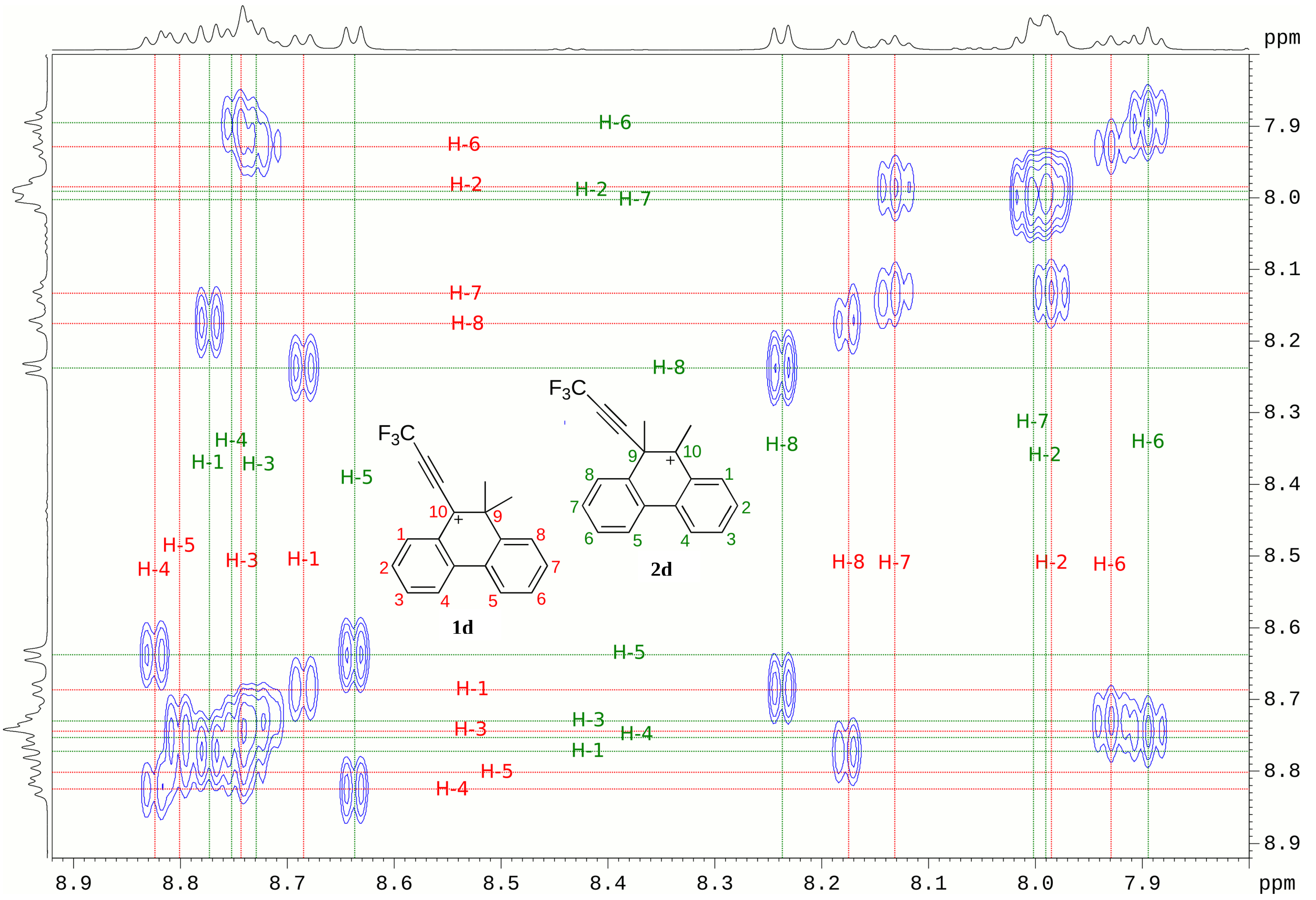
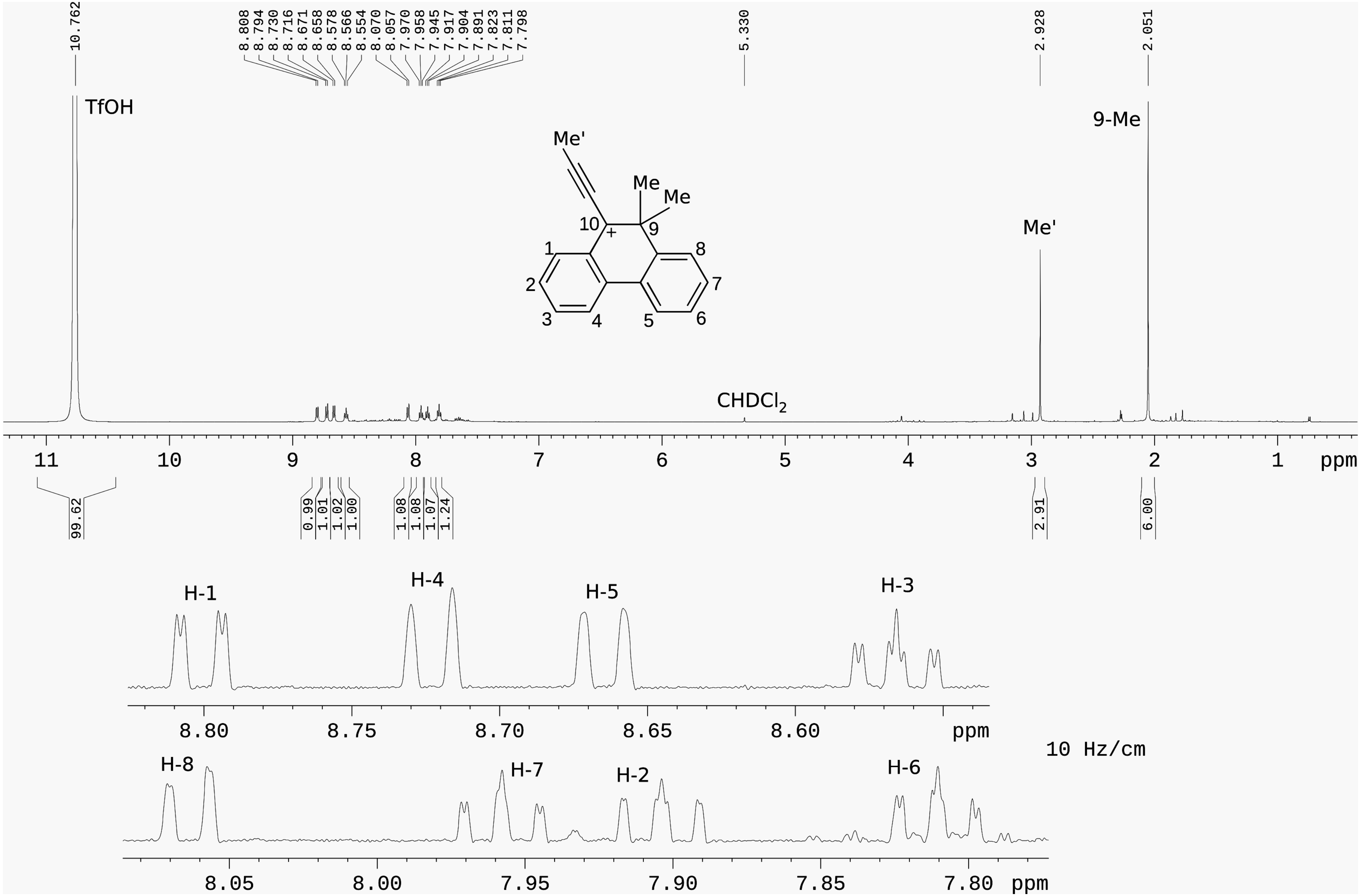
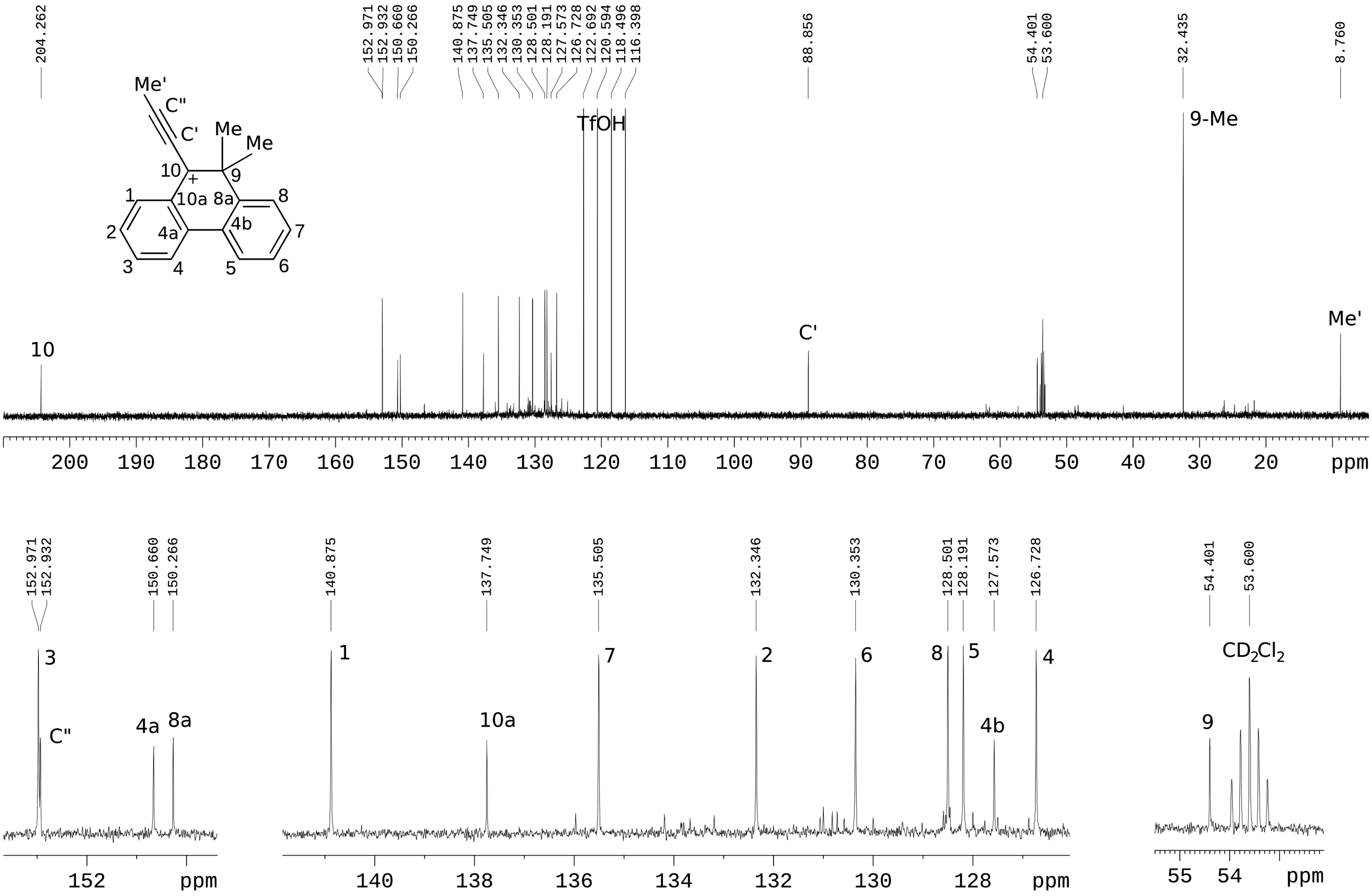
NOESY spectrum (aromatic region) of cations **1d** and **2d** in FSO_3H-SO_2ClF-CD_2Cl_2 at –22.5 ^oC (mixing time 0.5 s)



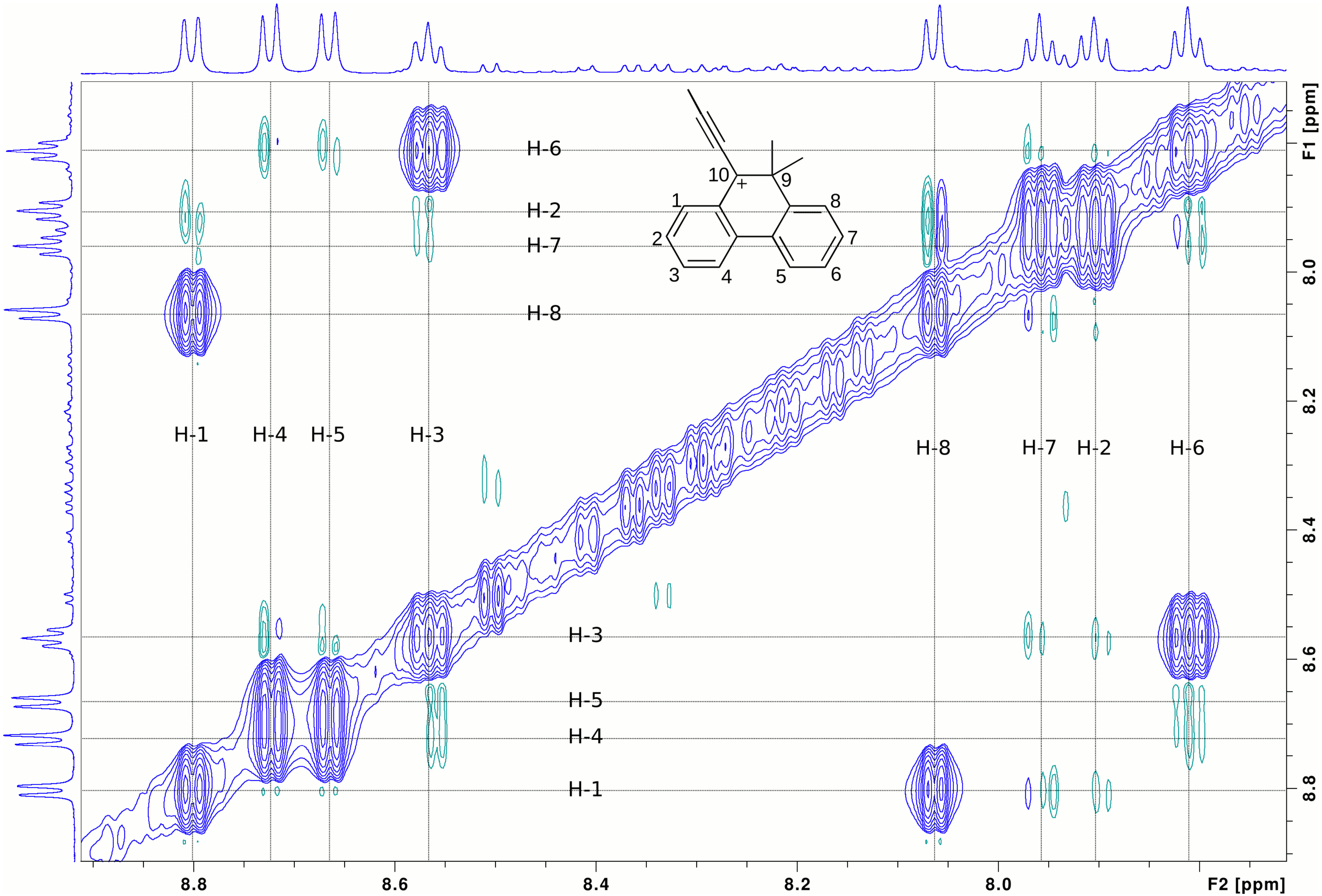
^{1}H NMR spectrum of cation **1b** in CF_3SO_3H-CD_2Cl_2 at 30 °C. Unpicked signals correspond to unidentified decomposition products.



^{13}C NMR spectrum of cation **1b** in CF_3SO_3H-CD_2Cl_2 at 30 ^{o}C. Unpicked signals correspond to unidentified decomposition products.



NOESY spectrum of cation **1b** in CF_3SO_3H-CD_2Cl_2 at 28 °C (aromatic region; mixing time 0.7 s)



Blue cross-peaks are due to exchange, green ones are due to NOE

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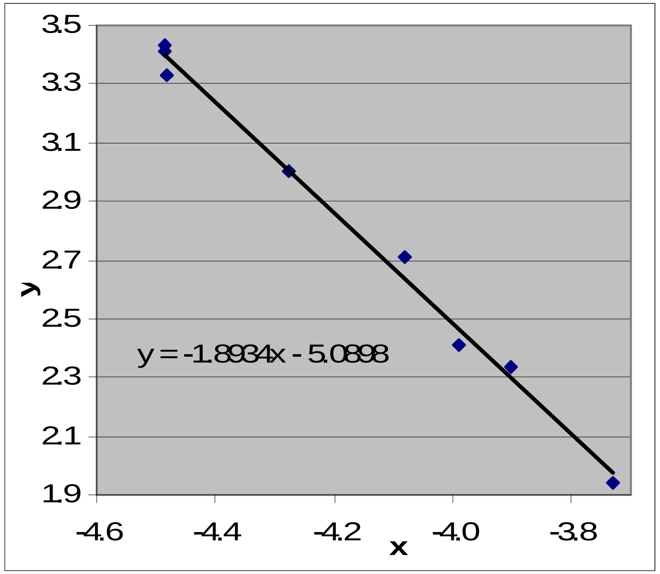
Equilibrium constant of **1d** ⇆ **2d** (K = **2d**/**1d**)

y = ax+b, where
a = ΔH, kJ/mole; b = ΔS, J deg.$^{-1}$ mole^{-1}; y = R*ln(K); x = -1000/T

t, °C	T, K	I_1	I_2	$K=I_1/(I_2-I_1)*2$	x=-1000/T	y=RlnK
-50.0	223.1	3	7.02	1.493	-4.482	3.329
-50.2	223.0	3	6.98	1.508	-4.484	3.413
-50.2	223.0	3	6.97	1.511	-4.484	3.433
-39.3	233.8	3	7.18	1.435	-4.276	3.005
-28.2	245.0	3	7.33	1.386	-4.082	2.712
-16.8	256.3	3	7.53	1.325	-3.901	2.336
-5.2	268.0	3	7.75	1.263	-3.731	1.942
-22.5	250.6	3	7.49	1.336	-3.990	2.410

I_1 – integral of **2d** 10-Me in ^{1}H NMR spectrum (see p. S2).
I_2 – integral of **2d** 9-Me and **1d** 9-Me in ^{1}H NMR spectrum (see p. S2).
R = 1.987*4.184 J/(mole*degree)



Parameters of the linear regression

ΔH, kJ	-1.893
stdEr ΔH	0.067
r^2	0.9924

ΔS, J deg.$^{-1}$ mole^{-1}	-5.090
stdEr ΔS	0.28
stdEr y	0.053

Extrapolation of equilibrium constant K to T = 177.6 K

T, K	ΔH, J	ΔS	ΔG=ΔH–T*ΔS	K=exp(–ΔG/R/T)
177.6	-1893	-5.090	-989	**1.954**

Rate constant of the reaction **1d** → **2d** at 177.6 K

y = ax+b, where
a = k, s^{-1}; y = –K/(K+1)*ln((K–γ)/(1+γ)); x = time–1340850000; γ = **2d**/**1d**
K = 1.954 (equilibrium constant at 177.6 K)

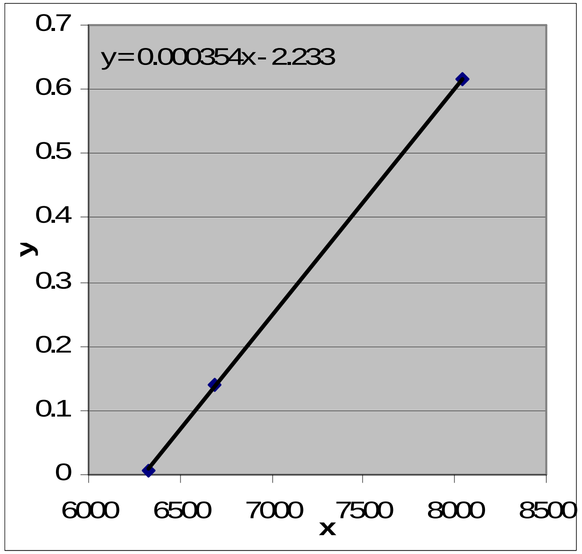
time, s	I_1	I_2	$\gamma=I_1/(I_2-I_1)*2$	x	y
1340856326	3	15.36	0.485	6326	0.0076
1340856693	3	12.48	0.633	6693	0.1402
1340858042	3	8.36	1.119	8042	0.6164

I_1 – integral of **2d** 10-Me in ^{1}H NMR spectrum (see p. S2).
I_2 – integral of **2d** 9-Me and **1d** 9-Me in ^{1}H NMR spectrum (see p. S2).

Parameters of the linear regression

k, s^{-1}	0.0003544
stdEr k	0.0000015

r^2	0.999983
stdEr y	0.0019



Kinetics of the reaction **1d** → **2d**

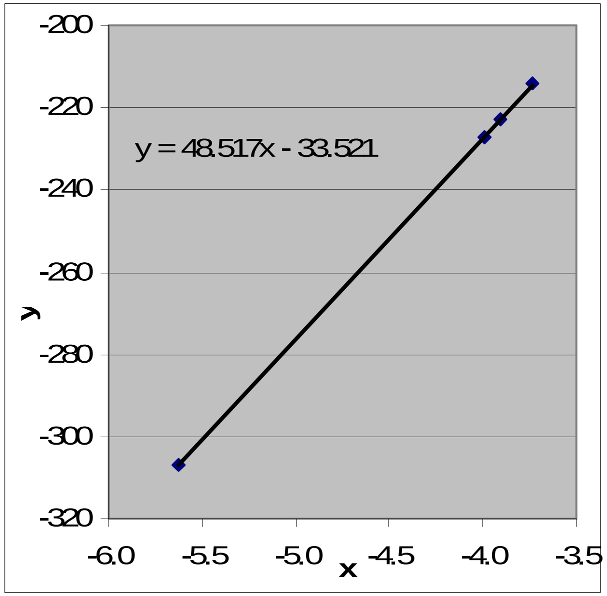
The Eyring equation $\Delta G^{\#} = -RT(\ln(k/T)-23.76)$; $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$
y = ax+b, where
a = $\Delta H^{\#}$, kJ; b = $\Delta S^{\#}$, J $deg.^{-1}$ $mole^{-1}$; y = R*(ln(k/T)-23.76); x = -1000/T
R = 1.987*4.184 J/(mole*degree); k – rate constant, s^{-1}

t, °C	T, K	k **1d**→**2d**	x	y	$\Delta G^{\#}$, kJ
-95.5	177.6	0.000354	-5.631	-306.7	55.66
-22.5	250.6	7	-3.990	-227.3	58.21
-16.8	256.3	12	-3.901	-223.0	58.42
-5.2	268.0	36	-3.731	-214.2	58.68

Parameters of the linear regression

$\Delta H^{\#}$, kJ	48.52
stdEr $\Delta H^{\#}$	0.20
r^2	0.999967

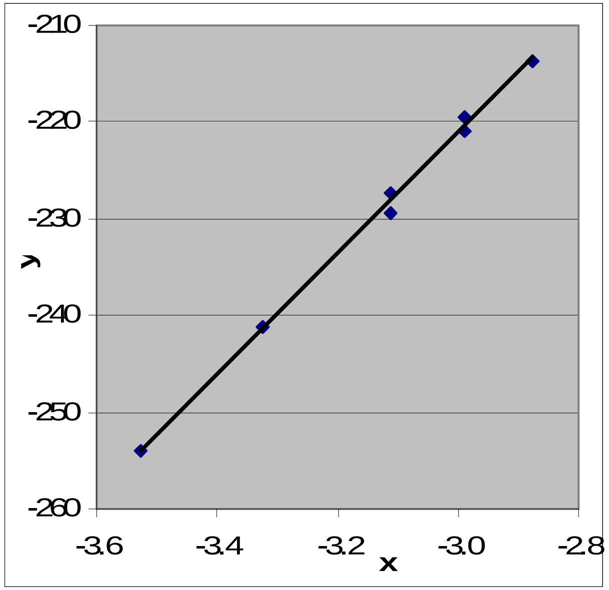
$\Delta S^{\#}$, J $deg.^{-1}$ $mole^{-1}$	-33.52
stdEr $\Delta S^{\#}$	0.86
stdEr y	0.301



Kinetics of the reaction **1b** → **1b'**

Eyring equotion $\Delta G^{\#} = -RT(\ln(k/T)-23.76)$; $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$
y = ax+b, where
a = $\Delta H^{\#}$, kJ; b = $\Delta S^{\#}$, J $deg.^{-1}$ $mole^{-1}$; y = R*(ln(k/T)-23.76); x = -1000/T
R = 1.987*4.184 J/(mole*degree); k – rate constant, s^{-1}

T, °C	T, K	k **1b**→**1b'**	x	y	$\Delta G^{\#}$, kJ
48.3	321.4	7	-3.112	-229.3	75.3
61.5	334.7	20	-2.989	-221.0	75.6
74.7	347.9	50	-2.876	-213.7	76.0
48.3	321.4	9	-3.112	-227.3	74.7
61.4	334.5	24	-2.991	-219.4	75.0
27.9	301.1	1.59	-3.323	-241.1	74.2
10.5	283.7	0.32	-3.527	-254.0	73.6

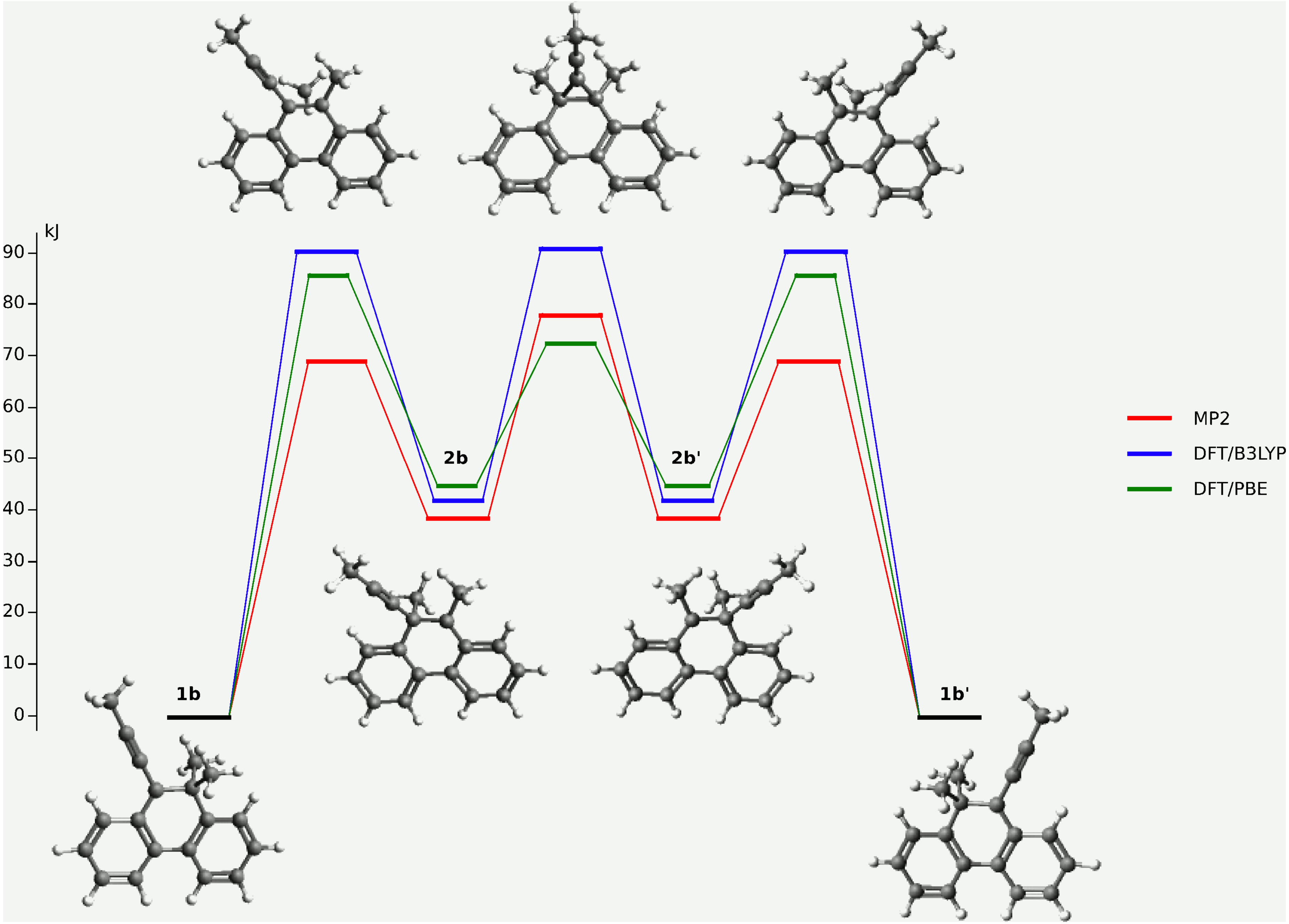


Parameters of the linear regression

$\Delta H^{\#}$, kJ	62.2
stdEr $\Delta H^{\#}$	1.6
r^2	0.9967

$\Delta S^{\#}$, J $deg.^{-1}$ $mole^{-1}$	-34.4
stdEr $\Delta S^{\#}$	5.0
stdEr y	0.87

Quantum chemical calculations (basis Λ1 (cc-pVDZ), PRIRODA program)



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Optimized coordinates of cation **1b** by RI-MP2/Λ1

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36
Energy -731.85703833
C    1.03529781  -1.50218756   0.01436759
C    1.91976671  -0.35443345   0.00132741
C    1.37449781   0.94771858  -0.01138719
C   -0.10941955   1.19743949  -0.01206712
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C    2.24263500   2.04460898  -0.02365524
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C    1.51444416  -2.82300170   0.02789553
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H    3.76865559  -1.49638697   0.01049267
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H   -1.39785889  -4.59385040   0.04921177
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H    0.04253429   2.94054475  -1.30460994
H   -0.24791344   1.42937299  -2.18808276
H   -5.42077337   0.11461426   0.89636655
H   -5.20041390   1.61831111  -0.02582251
H   -5.42667806   0.07235632  -0.87424900
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Optimized coordinates of cation **2b** by RI-MP2/Λ1

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36
Energy -731.84237326
C   -2.01205654   1.75199969  -0.16886023
C   -0.87934608   0.92991098  -0.05422888
C    0.39875373   1.58497028   0.06837211
C    0.46501685   3.01035411   0.14214837
C   -0.67271049   3.76703450   0.05749401
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C   -0.97992097  -0.51418307  -0.02533336
C    0.19619645  -1.28788805   0.00119546
C    1.54460888  -0.63240371  -0.12383956
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C    2.57303152  -1.32991550   0.63851462
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C    4.44596845  -2.66461393   2.00278841
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H    3.98128832  -3.34867456   2.71764809
H    5.07980207  -3.24844713   1.33053856
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Optimized coordinates of TS **1b** → **2b** by RI-MP2/Λ1

36
Energy -731.83066803

C	-0.74037083	1.27905607	0.05725436
C	0.71625954	1.29070859	0.05989948
C	1.46276619	2.48161797	-0.00602868
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C	2.83576268	0.06418816	0.15872578
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C	-2.85741608	0.04414078	0.14243904
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C	-1.49323565	2.46461714	-0.00052428
C	-0.72658858	-1.20085449	0.21061513
C	0.70311893	-1.19000063	0.20242688
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H	-3.42611991	3.37724128	-0.02970258
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H	3.34115474	-4.95321947	0.52925375
H	3.51103965	-4.24581941	2.14559234

Optimized coordinates of TS **2b** → **2b’** by RI-MP2/Λ1

36
Energy -731.82728662

C	-1.92422871	1.71603690	0.52072075
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