Supporting Information

The Electrophilic Methylating Agent $[SO_2Me]^+$ − Parent of Two Cationic Species

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† passed away unexpectedly in march 2024

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1 ^{1}H NMR spectroscopy

1.1 ^{1}H NMR spectroscopy of [FS(OH)(OMe)][SbF_6]

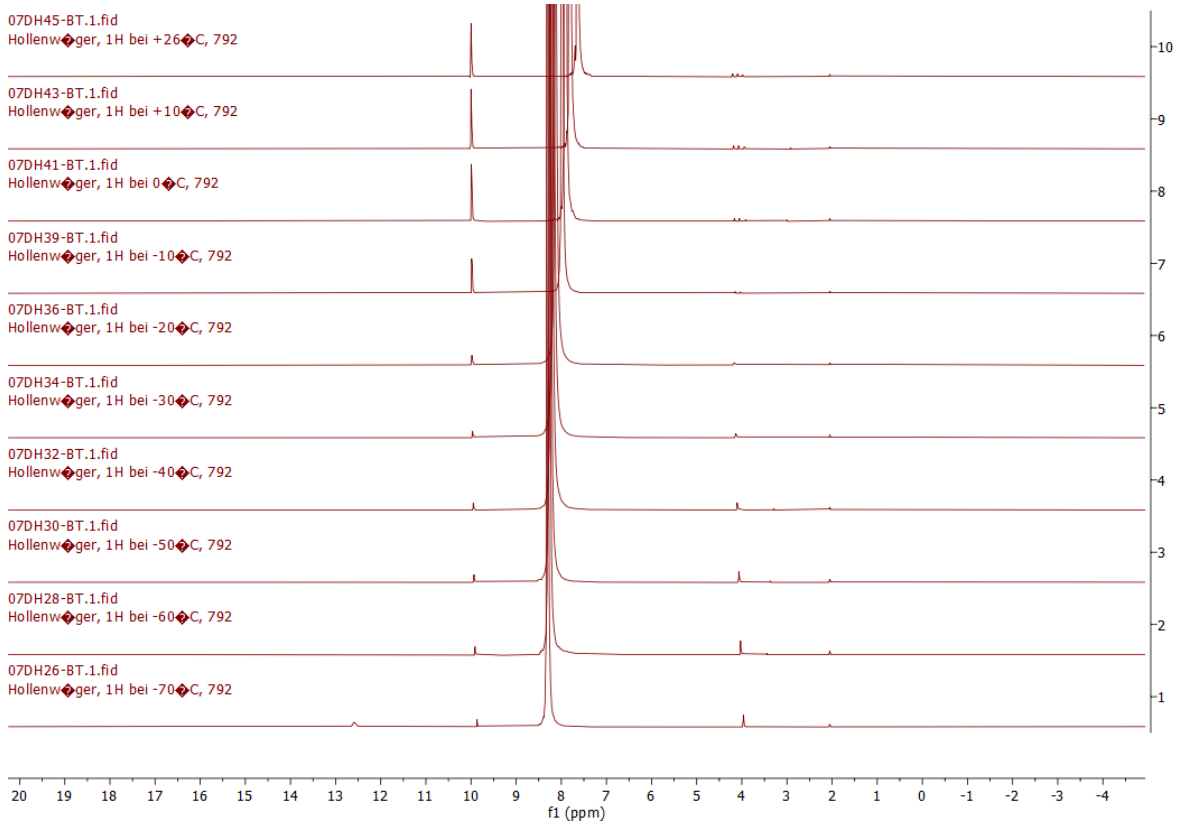

Figure S1. ^{1}H NMR spectra stack of [$FS(OMe)_2$][Sb_2F_{11}] at various temperatures. The NMR spectra are measured with acetone-d6 as external reference.

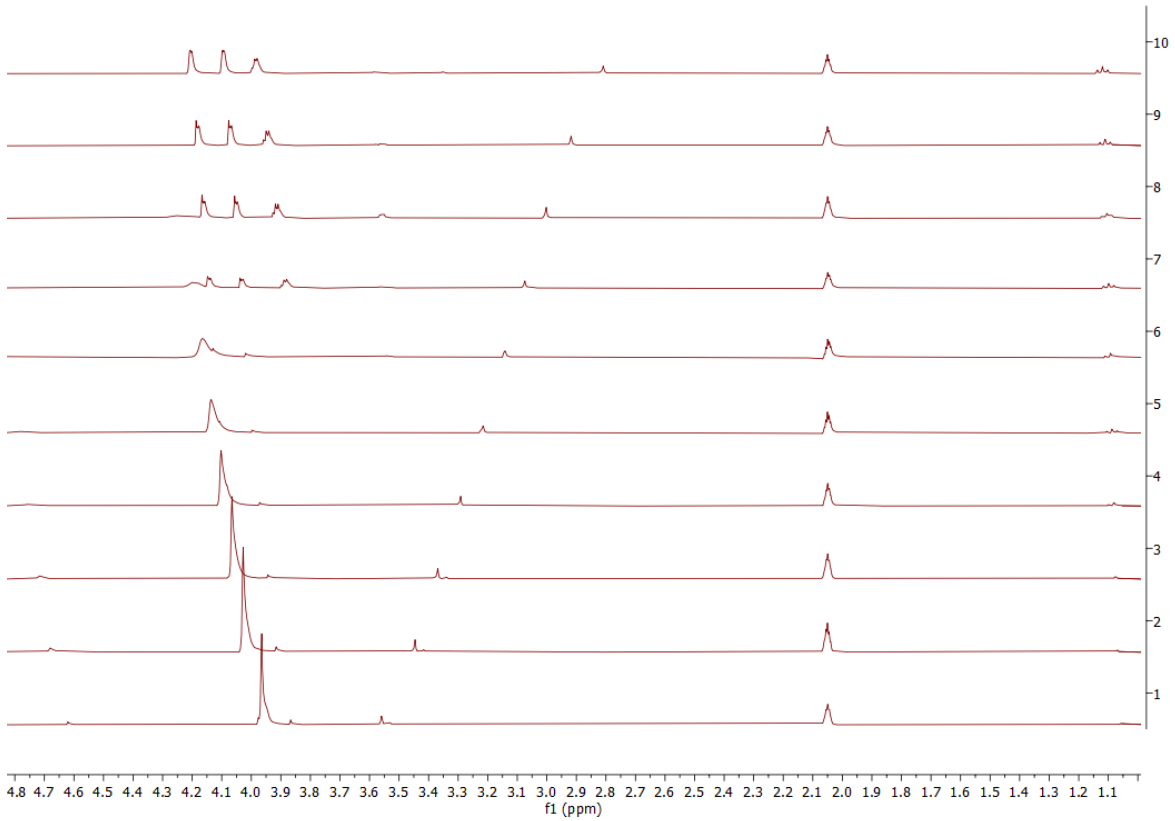

Figure S2. ^{1}H NMR spectra stack of [FS(OH)(OMe)][SbF_6] at various temperatures from 1.00 ppm to 4.80 ppm. The NMR spectra are measured with acetone-d6 as external reference.

1.2 ^{1}H NMR spectroscopy of $[FS(OMe)_2][Sb_2F_{11}]$

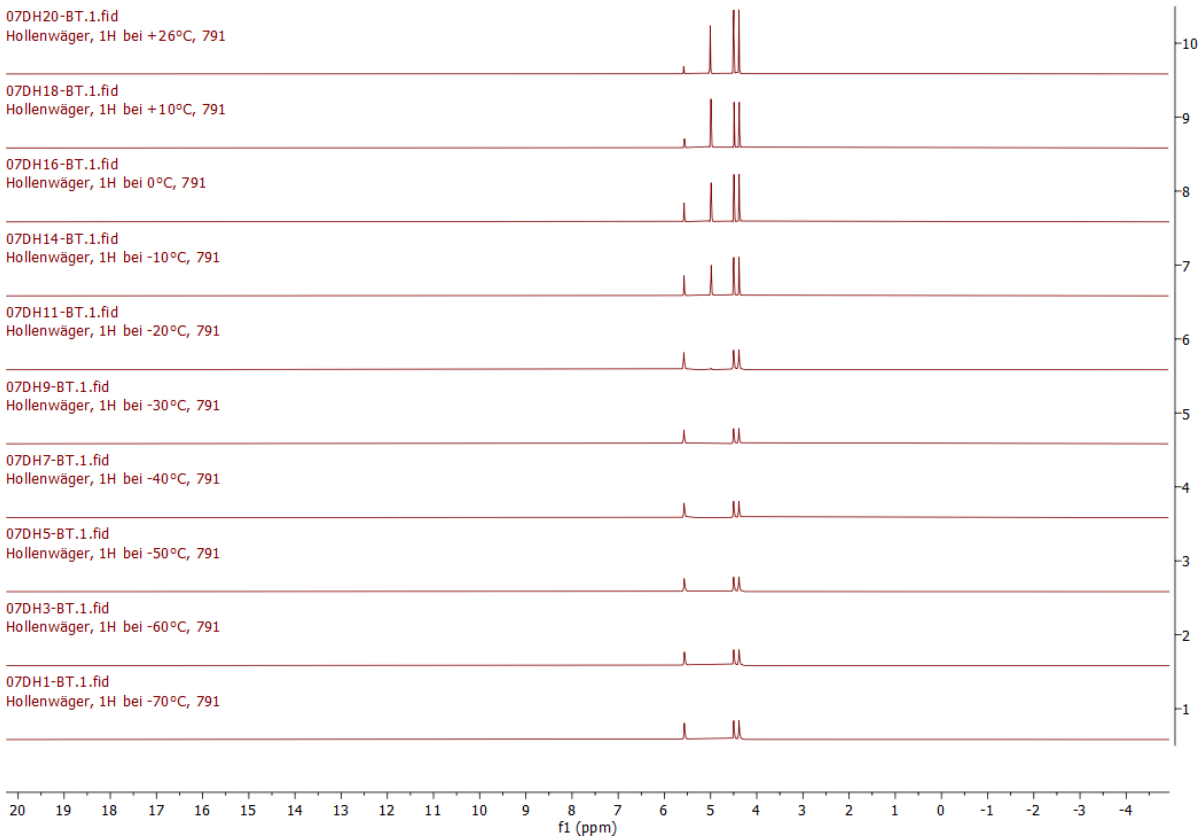

Figure S3. ^{1}H NMR spectra stack of $[FS(OMe)_2][Sb_2F_{11}]$ at various temperatures. The NMR spectra are measured with acetone-d6 as external reference.

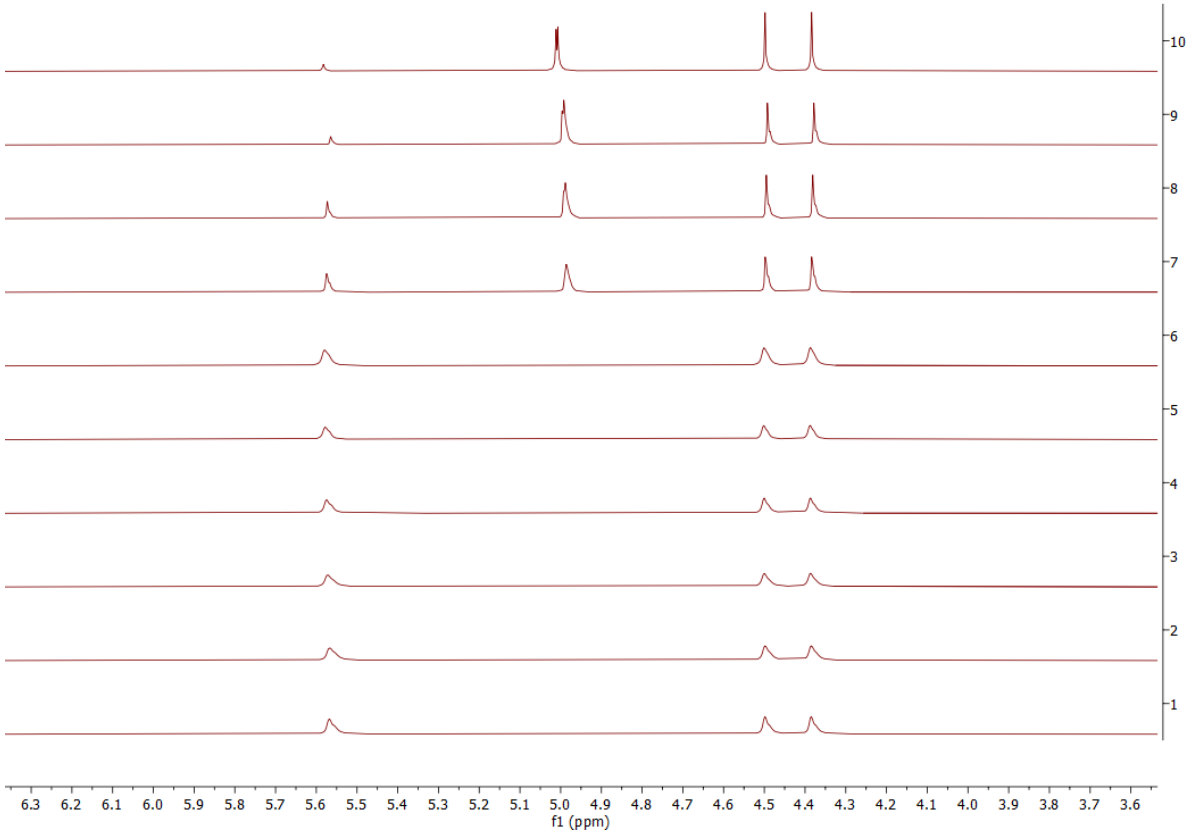

Figure S4. ^{1}H NMR spectra stack of $[FS(OMe)_2][Sb_2F_{11}]$ at various temperatures from 3.55 ppm to 6.35 ppm. The NMR spectra are measured with acetone-d6 as external reference.

2 Vibrational Data

2.1 Vibrational Data of $[FS(OMe)_2][Sb_2F_{11}]$

Table S 1. Assignment of experimental vibrational frequencies [cm^{-1}] of $[FS(OMe)_2][Sb_2F_{11}]$ and calculated vibrational frequencies [cm^{-1}] of $[FS(OMe)_2]^+$.

$[FS(OMe)_2][Sb_2F_{11}]$ exp. [a]		$[FS(OMe)_2]^+$ calc.[b,c]		
IR	Raman	IR/Raman	Assi	
3094(m)		3095(4/49)	ν_1	$\nu_{as}(CH)$
	3088(14)	3087(4/45)	ν_2	$\nu_{as}(CH)$
		3080(1/24)	ν_3	$\nu_{as}(CH)$
		3057(0/30)	ν_4	$\nu_{as}(CH)$
2987(m)	2994(65)	2975(1/119)	ν_5	$\nu_s(CH)$
	2855(15)	2960(2/128)	ν_6	$\nu_s(CH)$
1778(w)				
1445(s)	1447(20)	1440(17/5)	ν_7	$\delta(CH_2)$
		1432(20/4)	ν_8	$\delta(CH_2)$
		1424(16/5)	ν_9	$\delta(CH_2)$
		1422(17/3)	ν_{10}	$\delta(CH_2)$
		1417(0/1)	ν_{11}	$\gamma(CH_3)$
		1411(3/1)	ν_{12}	$\gamma(CH_3)$
1358(w)	1316(19)	1151(20/1)	ν_{13}	$\delta(CH_3)$
1300(w)		1139(8/2))	ν_{14}	$\delta(CH_3)$
	1171(14)	1125(1/1)	ν_{15}	$\delta(CH_3)$
1175(m)	1150(29)	1119(2/1)	ν_{16}	$\delta(CH_3)$
1022(vs)	1008(18)	1032(255/3)	ν_{17}	$\nu(SO)$
960(vs)	986(17)	975(432/2)	ν_{18}	$\nu(SO)$
	955(15)			
835(s)	838(27)	838(54/7)	ν_{19}	$\nu(CO)$
808(s)	813(20)	822(165/3)	ν_{20}	$\nu(CF)$
748(s)	757(58)	760(15/19)	ν_{21}	$\nu(CO)$
602(m)	604(14)			
555(s)	558(25)	538(13/3)	ν_{22}	$\delta(SO_2)$
	412(18)	417(6/1)	ν_{23}	$\delta(SOF)$
	394(19)	377(22/1)	ν_{24}	$\delta(SOF)$
	363(14)			
	348(14)			
		274(4/2)	ν_{25}	$\delta(SOC)$
	180(13)	180(8/1)	ν_{26}	$\delta(SOC)$
		131(4/0))	ν_{27}	$\tau(CH_3)$
		107(3/0)	ν_{28}	$\tau(CH_3)$
	97(27)	85(5/0)	ν_{29}	$\tau(CH_3)$
		79(1/0)	ν_{30}	$\tau(CH_3)$
700(vs)	684(18)			
673(vs)	647(100)			
660(vs)	572(26)			
494(s)	280(46)			
	230(17)			

[a] Abbrevations for IR intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder. Experimental Raman intensities are relative to a scale of 1 to 100. [b] Calculated on the M06-2X/aug-cc-pVTZ level of theory. Scaling factor 0.956. [c] IR intensities in km/mol; Raman intensities in $Å^4/u$.

2.2 Vibrational Data of [FS(OH)(OMe)][SbF_6]

Table S2. Experimental vibrational frequencies [cm^{-1}] of [FS(OH)(OMe)][SbF_6] and calculated vibrational frequencies [cm^{-1}] of [FS(OH)(OMe)]$^+$.

[FS(OH)(OMe)][SbF_6] (2) exp.[a]		**[FS(OH)(OMe)]$^+$ calc.[b,c]**	Assignment	
IR	Raman	IR/Raman		
3284(m)		3198(1598/133)	ν_1	ν(OH)
3111(m)		3094(4/49)	ν_2	ν_{as}(CH)
	3085(26)	3078(1/22)	ν_3	ν_{as}(CH)
	2986(59)	2974(1/117)	ν_4	ν_{as}(CH)
1628(w)				
	1584(50)			
1445(vw)	1449(51)	1433(17/5)	ν_5	δ(CH_2)
1418(vw)	1432(50)	1424(18/3)	ν_6	δ(CH_2)
1373(vw)		1412(4/1)	ν_7	δ(CH_2)
1319(vw)	1318(72)			
1292(vw)				
1234(vw)		1199(154/1)	ν_8	δ(SOH)
1209(vw)		1141(15/2)	ν_9	ρ(CH_3)
1153(vw)	1171(45)	1121(1/1)	ν_{10}	ρ(CH_3)
1020(w)	998(69)	1018(271/4)	ν_{11}	ν(SO)
959(w)		947(168/7)	ν_{12}	ν(SO)
879(vw)				
835(w)		841(187/4)	ν_{13}	ν(SF)
808(w)	817(40)			
	732(51)	766(30/16)	ν_{14}	ν(CO)
	689(71)			
586(w)	597(54)	588(55/1)	ν_{15}	δ(SOH)
555(w)		557(8/1)	ν_{16}	δ(SO_2)
492(w)		401(43/1)	ν_{17}	δ(SO_2)
		390(13/1)	ν_{18}	δ(SOF)
	134(42)	133(6/0)	ν_{19}	τ(CH_3)
	97(51)	77(4/0)	ν_{20}	τ(CH_3)
		26(0/0)	ν_{21}	δ(SOH)
Vibrations of anion SbF_6^-				
	680(81)			
658(vs)	653(100)			
	300(55)			
	230(56)			

[a] Abbreviations for IR intensities: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. Experimental Raman intensities are relative to a scale of 1 to 100. [b] Calculated on the M06-2X/aug-cc-pVTZ level of theory. Scaling factor: 0.956. [c] IR intensities in km/mol; Raman intensities in $Å^4/u$.

3 Crystallographic Data

Table S3. Crystal data and structure refinement of $[FS(OH)(OMe)][SbF_6]$, $[FS(OMe)_2][Sb_2F_{11}]$

	$[FS(OH)(OMe)][SbF_6]$	$[FS(OMe)_2][Sb_2F_{11}]$
Molecular Fomula	$CH_4F_7O_2SSb$	$C_2H_6F_{12}O_2SSb_2$
M_r[g·mol^{-1}]	334.86	565.65
Crystal size [mm^3]	0.163x0.365x0.438	0.762x0.355x0.200
Crystal system	Orthorhombic	monoclinic
Space group	*P*ca2$_1$	*P*2$_1$/n
a [Å]	13.5681(5)	9.7473(9)
b [Å]	10.8817(5)	12.6004(9)
c [Å]	22.3347(8)	10.6035(8)
α [°]	90	90
β [°]	90	100.743
γ [°]	90	90
V [Å^3]	3297.6(2)	1279.50(18)
Z	16	4
ρ_{calc} [g·cm^{-3}]	2.698	2.936
μ [mm^{-1}]	3.683	4.527
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073
F(000)	2496.0	1040.0
T [K]	102	103
h, k, l range	−10:17; −13:11; −28:26	−11:9; −14:13; −12:12
Measured reflexes	13848	8759
Unique reflexes	6546	2104
R_{int}	0.0249	0.0540
Parameters	450	174
R(F)/wR(F^2)[a] (all data)	0.0279/0.0665	0.0483/ 0.0894
Weighting scheme[b]	0.018600/5.787000	0.045400/0.894200
S (Gof)[c]	1.102	1.079
Residual density [e·Å^{-3}]	0.988/−0.959	1.256/−0.700
Device	Oxford XCalibur	Oxford XCalibur
CCDC	2368718	2368721

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$.

[b] $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma_c^2(F_0^2)+(xP)^2+yP]-1$; $P = (F_0^2+2F_c^2)/3$.

[c] GoF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = total number of parameters).

3.1 $[FS(OMe)_2][Sb_2F_{11}]$

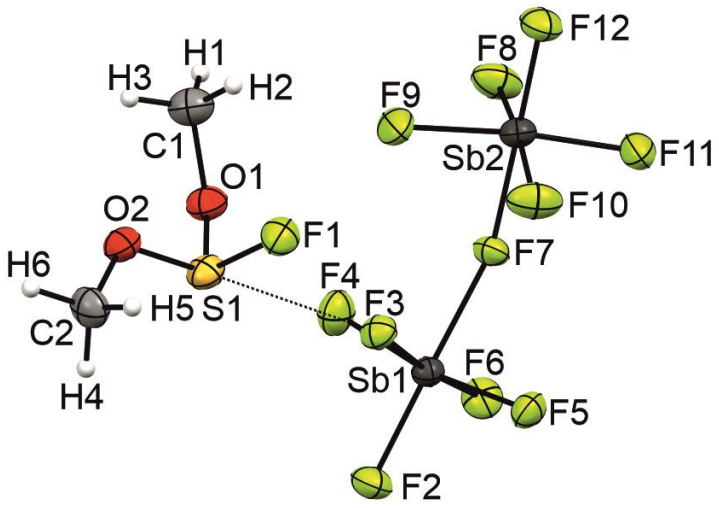

Figure S5. asymmetric unit of $[FS(OMe)_2][Sb_2F_{11}]$ (displacement ellipsoids 50% probability).

Table S4. Bond lengths, angles, torsions angles and donor-acceptor interactions of the asymmetric unit of $[FS(OMe)_2][Sb_2F_{11}]$, *i*=1-x,1-y,1-z, *ii*= -1/2+x,1.5-y,-1/2+z, *iii*= 1/2-x,1/2+y,1/2-z, *iv*= -1/2+x,1.5-y,1/2+z

Bond lengths [Å]		Bond angles [°]		Torsions angles [°]		Donor-acceptor interactions [Å]	
S1−O1	1.517(6)	O1−S1−O2	102.3(3)	O2−S1−O1−C1	44.7(7)	S1−F2*i*	2.996(5)
S1−O2	1.535(5)	O1−S1−F1	102.5(3)	F1−S1−O1−C1	-58.3(6)	C1(−H2) ···F10*ii*	2.970(9)
S1−F1	1.558(5)	O2−S1−F1	99.7(3)	O1−S1−O2−C2	169.3(5)	C2(−H6) ···F4*iii*	3.227(10)
O1−C1	1.476(9)	C1−O1−S1	122.0(5)	F1−S1−O2−C2	-85.6(6)	S1−F3	2.910(4)
O2−C2	1.488(9)	C2−O2−S1	117.5(4)			S1−F12*iv*	3.066(5)
Sb1−F2	1.855(4)	F4−Sb1−F6	90.3(2)				
Sb1−F3	1.863(4)	F4−Sb1−F2	96.2(2)				
Sb1−F4	1.849(4)	F6−Sb1−F2	92.8(2)				
Sb1−F5	1.857(4)	F4−Sb1−F5	169.6(2)				
Sb1−F6	1.854(4)	F6−Sb1−F5	91.20(19)				
Sb1−F7	2.031(4)	F2−Sb1−F5	94.0(2)				
Sb2−F7	2.028(4)	F3−Sb1−F3	88.44(19)				
Sb2−F8	1.852(4)	F6−Sb1−F3	173.66(19)				
Sb2−F9	1.858(4)	F2−Sb1−F3	93.5(2)				
Sb2−F10	1.843(4)	F5−Sb1−F3	88.95(18)				
Sb2−F11	1.861(4)	F4−Sb1−F7	84.37(19)				
Sb2−F12	1.860(4)	F6−Sb1−F7	86.40(18)				
		F2−Sb1−F7	179.03(18)				
		F5−Sb1−F7	85.47(18)				
		F3−Sb1−F7	87.29(17)				
		Sb2−F7−Sb1	146.4(2)				
		F10−Sb2−F8	170.9(2)				
		F10−Sb2−F9	91.0(2)				
		F10−Sb2−F11	89.5(2)				
		F10−Sb2−F7	85.75(19)				
		F12−Sb2−F11	93.6(2)				
		F12−Sb2−F7	179.25(18)				
		F11−Sb2−F7	87.11(18)				

F8−Sb2−F9	88.1(2)
F8−Sb2−F12	95.1(2)
F9−Sb2−F12	93.3(2)
F8−Sb2−F11	90.4(2)
F9−Sb2−F11	173.1(2)
F8−Sb2−F7	85.19(19)
F9−Sb2−F7	86.04(18)

3.2 [FS(OH)(OMe)][SbF$_6$]

Table S5. Bond lengths, angles, torsions angles and donor-acceptor interactions within the asymmetric unit of [FS(OH)(OMe)][SbF$_6$]

Bond lengths [Å]							
S1−O1	1.532(6)	Sb1−F5	1.865(5)	Sb3−F21	1.864(5)		
S1−O2	1.507(6)	Sb1−F6	1.870(5)	Sb3−F22	1.871(5)		
S1−F1	1.549(5)	Sb1−F7	1.914(5)	Sb4−F23	1.903(5)		
O2−C1	1.486(11)	Sb1−F8	1.873(5)	Sb4−F24	1.873(5)		
S2−O3	1.528(7)	Sb1−F9	1.869(5)	Sb4−F25	1.871(5)		
S2−O4	1.526(7)	Sb1−F10	1.861(5)	Sb4−F26	1.864(5)		
S2−F2	1.561(6)	Sb2−F11	1.867(5)	Sb4−F27	1.855(5)		
O4−C2	1.486(11)	Sb2−F12	1.863(5)	Sb4−F28	1.874(5)		
S3−O5	1.521(7)	Sb2−F13	1.859(5)				
S3−O6	1.515(6)	Sb2−F14	1.863(5)				
S3−F3	1.556(6)	Sb2−F15	1.909(5)				
O6−C3	1.484(12)	Sb2−F16	1.868(5)				
S4−O7	1.522(7)	Sb3−F17	1.874(5)				
S4−O8	1.517(6)	Sb3−F18	1.875(5)				
S4−F4	1.559(6)	Sb3−F19	1.912(5)				
O8−C4	1.496(11)	Sb3−F20	1.863(5)				
Bond angles [°]							
O2−S1−O1	104.7(4)	F10−Sb1−F6	92.1(2)	F14−Sb2−F16	90.0(3)	F21−Sb3−F19	89.3(3)
O1−S1−F1	97.5(4)	F5−Sb1−F6	91.4(2)	F12−Sb2−F16	91.8(2)	F22−Sb3−F19	179.2(3)
O2−S1−F1	100.8(3)	F9−Sb1−F6	90.9(2)	F11−Sb2−F16	178.0(3)	F17−Sb3−F19	88.9(2)
C1−O2−S1	123.8(6)	F10−Sb1−F8	89.8(2)	F13−Sb2−F15	89.7(2)	F18−Sb3−F19	88.7(2)
O4−S2−O3	104.1(4)	F5−Sb1−F8	177.7(2)	F14−Sb2−F15	88.6(2)	F27−Sb4−F26	90.3(3)
O3−S2−F2	97.4(4)	F9−Sb1−F8	89.7(2)	F12−Sb2−F15	178.0(2)	F27−Sb4−F25	90.2(3)
O4−S2−F2	101.1(4)	F6−Sb1−F8	90.8(2)	F11−Sb2−F15	88.2(2)	F26−Sb4−F25	178.1(2)
C2−O4−S2	123.7(6)	F10−Sb1−F7	88.8(2)	F16−Sb2−F15	89.9(3)	F27−Sb4−F24	178.0(3)
O6−S3−O5	104.6(4)	F5−Sb1−F7	90.2(2)	F20−Sb3−F21	90.9(2)	F26−Sb4−F24	90.6(3)
O5−S3−F3	97.5(4)	F9−Sb1−F7	88.2(2)	F20−Sb3−F22	91.0(2)	F25−Sb4−F24	88.9(3)
O6−S3−F3	101.0(3)	F6−Sb1−F7	178.1(3)	F21−Sb3−F22	91.5(2)	F27−Sb4−F28	91.8(3)
C3−O6−S3	123.0(6)	F8−Sb1−F7	87.5(2)	F20−Sb3−F17	178.1(2)	F26−Sb4−F28	91.3(2)
O8−S4−O4	100.6(3)	F13−Sb2−F14	178.3(2)	F21−Sb3−F17	89.9(2)	F25−Sb4−F28	90.5(2)
O7−S4−F4	96.5(4)	F13−Sb2−F12	91.3(2)	F22−Sb3−F17	90.7(2)	F24−Sb4−F28	90.0(3)
O8−S4−F4	104.7(4)	F14−Sb2−F12	90.4(2)	F20−Sb3−F18	89.7(2)	F27−Sb4−F23	88.5(3)
C4−O8−S4	122.6(6)	F13−Sb2−F11	90.6(2)	F21−Sb3−F18	177.9(2)	F26−Sb4−F23	89.0(2)
F10−Sb1−F5	90.6(2)	F14−Sb2−F11	89.2(3)	F22−Sb3−F18	90.5(2)	F25−Sb4−F23	89.2(2)
F10−Sb1−F9	177.0(2)	F12−Sb2−F11	90.1(2)	F17−Sb3−F18	89.4(2)	F24−Sb4−F3	89.6(2)
F5−Sb1−F9	89.8(2)	F13−Sb2−F16	90.1(3)	F20−Sb3−F19	89.4(2)	F28−Sb4−F23	179.5(3)
Torsion Angles [°]							

O1−S1−O2−C1	-37.1(8)	O3−S2−O4−C2	34.9(8)	O5−S3−O6−C3	41.5(8)	O7−S4−O8−C4	-37.6(8)
F1−S1−O2−C1	63.7(7)	F2−S2−O4−C2	-65.7(8)	F3−S3−O6−C3	-59.4(8)	F4−S4−O8−C4	62.1(7)
Donor-acceptor interactions [Å]							
O1(−H1)···F23	2.544(9)	S1−F6	2.751(5)	O1−F6	2.913(8)		
C4(−H14)···F10	3.491(10)	S1−F14	2.743(6)	O1−F14	2.981(8)		

4 Quantum Chemical Calculations

The optimized structures are given with their cartesian coordinates x, y, z in angstrom. An illustration of the respective structures together with the calculated bond lengths in angstrom is shown next to the tables. The structures were calculated on the M062x/aug-cc-pVTZ level of theory.

4.1 [FS(OH)(OMe)]$^+$ in the gas phase

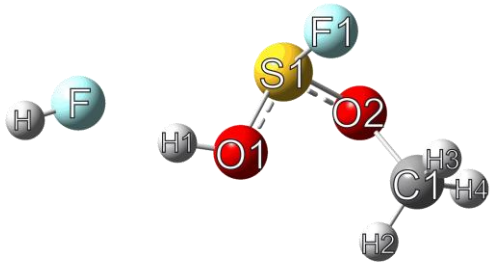

Figure S6. Optimized gas phase structure of [FS(OH)(OMe)]$^+$ on the M062x/aug-cc-pVTZ level of theory.

Table S6. Input matrix for the structure optimization of [FS(OH)(OMe)]$^+$ on the M062x/aug-cc-pVTZ level of theory.

opt freq=raman M062x/aug-*cc*-pvtz geom=connectivity

Symbolic Z-matrix:

Charge = +1 Multiplicity = 1

F	-3.115486	-0.315383	-0.040868
S	0.104833	0.370304	-0.481729
F	0.412262	1.485862	0.567334
O	1.481787	-0.237856	-0.692400
O	-0.581970	-0.654156	0.455693
C	2.271726	-0.856057	0.401408
H	2.349272	-0.144198	1.217116
H	3.232648	-1.042792	-0.060930
H	1.776433	-1.774554	0.695421
H	-1.571593	-0.639329	0.379593
H	-3.963954	-0.585875	0.223492

Calculation Type = FREQ

Calculation Method = RM062X

Basis Set = Aug-CC-pVTZ

Charge = 1

Spin = Singlet

Solvation = None

E(RM062X) = -789.14754 Hartree

RMS Gradient Norm = 9.908e-06 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 2.5311744 Debye

Polarizability (?) = 43.715 a.u.

Point Group = C1

Job cpu time: 0 days 5 hours 11 minutes 5.9 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -789.14754 Hartree

Zero-point Energy Correction = 0.072817 Hartree

Thermal Correction to Energy = 0.082168 Hartree

Thermal Correction to Enthalpy = 0.083112 Hartree

Thermal Correction to Free Energy = 0.036427 Hartree

EE + Zero-point Energy = -789.07473 Hartree

EE + Thermal Energy Correction = -789.06538 Hartree

EE + Thermal Enthalpy Correction = -789.06443 Hartree

EE + Thermal Free Energy Correction = -789.11112 Hartree

E (Thermal) = 51.561 kcal/mol

Heat Capacity (Cv) = 28.614 cal/mol-kelvin

Entropy (S) = 98.258 cal/mol-kelvin

Opt Tab Data Section:

Step number = 1

Maximum force = 0 Converged

RMS force = 0 Converged

Maximum displacement = 4.9e-05 Converged

RMS displacement = 2.2e-05 Converged

Predicted energy change = -3.272345e-12 Hartree

4.2 [FS(OH)(OMe)]$^+$ solvated with water

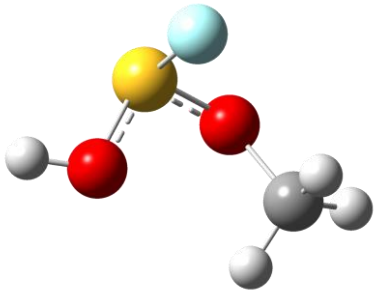

Figure S7. Optimized water solvated structure of [FS(OH)(OMe)]$^+$ on the M062x/aug-cc-pVTZ level of theory.

Table S7. Input matrix for the structure optimization of [FS(OH)(OMe)]$^+$ on the M062x/aug-cc-pVTZ level of theory.

opt=(calcall,tight) freq=raman aug-cc-pvtz scrf=(solvent=water) geom=connectivity m062x

Symbolic Z-matrix:

Charge = +1 Multiplicity = 1

S	0.846738	-1.143627	0.592160
F	-0.899997	-0.148551	-0.689000
O	0.724717	1.203817	0.428791
O	-1.866871	0.082318	0.407447
C	-1.614637	-0.572572	1.234184
H	-2.816612	-0.181786	-0.037265
H	-1.824082	1.130058	0.679375
H	1.568547	1.680415	0.317031
H	0.846738	-1.143627	0.592160

Calculation Type = FREQ

Calculation Method = RM062X

Basis Set = Aug-CC-pVTZ

Charge = 1

Spin = Singlet

Solvation = scrf=solvent=water

E(RM062X) = -688.7646 Hartree

RMS Gradient Norm = 2.5313e-05 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 2.7667907 Debye

Polarizability (?) = 46.511 a.u.

Point Group = C1

Job cpu time: 0 days 1 hours 22 minutes 10.6 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -688.7646 Hartree

Zero-point Energy Correction = 0.061462 Hartree

Thermal Correction to Energy = 0.067831 Hartree

Thermal Correction to Enthalpy = 0.068776 Hartree

Thermal Correction to Free Energy = 0.03093 Hartree

EE + Zero-point Energy = -688.70314 Hartree

EE + Thermal Energy Correction = -688.69677 Hartree

EE + Thermal Enthalpy Correction = -688.69583 Hartree

EE + Thermal Free Energy Correction = -688.73367 Hartree

E (Thermal) = 42.565 kcal/mol

Heat Capacity (Cv) = 20.252 cal/mol-kelvin

Entropy (S) = 79.653 cal/mol-kelvin

Opt Tab Data Section:

Step number = 1

Maximum force = 0 Converged

RMS force = 0 Converged

Maximum displacement = 4.4e-05 Converged

RMS displacement = 2e-05 Converged

Predicted energy change = -1.734397e-12 Hartree

4.3 Transition state of $[FS(OH)(OMe)]^+$ solvated with water

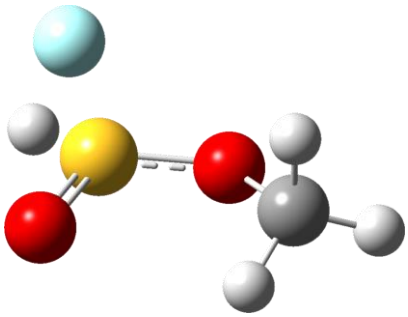

Figure S8. Optimized water solvated structure of the Transition state of $[FS(OH)(OMe)]^+$ on the M062x/aug-cc-pVTZ level of theory.

Table S8. Input matrix for the structure optimization of $[FS(OH)(OMe)]^+$ on the M062x/aug-cc-pVTZ level of theory.

# opt freq aug-cc-pvtz scrf=(solvent=water) geom=connectivity m062x			
Symbolic Z-matrix:			
Charge = +1	Multiplicity = 1		
S	-0.468248	-0.488616	-0.459645
F	-1.176815	1.169102	-0.079717

O	0.986717	-0.148863	-0.642975
O	-0.782049	-0.677763	0.984327
C	1.896038	0.340761	0.423528
H	1.673194	1.392852	0.563424
H	2.880765	0.181704	0.006586
H	1.722406	-0.247325	1.316662
H	-1.206640	0.537152	0.913120

Calculation Type = FREQ

Calculation Method = RM062X

Basis Set = Aug-CC-pVTZ

Charge = 1

Spin = Singlet

Solvation = scrf=solvent=water

E(RM062X) = -688.69477 Hartree

RMS Gradient Norm = 2.6933e-05 Hartree/Bohr

Imaginary Freq = 1

Dipole Moment = 1.6485653 Debye

Polarizability (?) = 48.871 a.u.

Point Group = C1

Job cpu time: 0 days 1 hours 2 minutes 0.3 seconds.

Thermo Tab Data Section:

Imaginary Freq = 1

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -688.69477 Hartree

Zero-point Energy Correction = 0.056725 Hartree

Thermal Correction to Energy = 0.062587 Hartree

Thermal Correction to Enthalpy = 0.063531 Hartree

Thermal Correction to Free Energy = 0.026975 Hartree

EE + Zero-point Energy = -688.63804 Hartree

EE + Thermal Energy Correction = -688.63218 Hartree

EE + Thermal Enthalpy Correction = -688.63124 Hartree

EE + Thermal Free Energy Correction = -688.66779 Hartree

E (Thermal) = 39.274 kcal/mol

Heat Capacity (Cv) = 18.746 cal/mol-kelvin

Entropy (S) = 76.939 cal/mol-kelvin

Opt Tab Data Section:

Step number = 1

Maximum force = 7e-06 Converged

RMS force = 3e-06 Converged

Maximum displacement = 0.000409 Converged

RMS displacement = 0.000203 Converged

Predicted energy change = -9.781114e-10 Hartree

4.4 Optimized structure of $[S(O)(OMe)]^{+}\cdot HF$ solvated with water

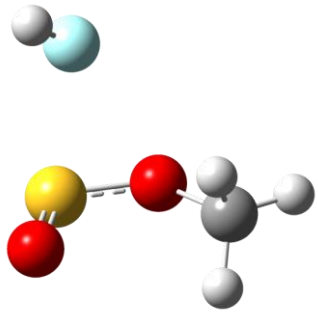

Figure S9. Optimized water solvated structure of the Transition state of $[FS(OH)(OMe)]^{+}$ on the M062x/aug-cc-pVTZ level of theory.

Table S9. Input matrix for the structure optimization of $[FS(OH)(OMe)]^{+}$ on the M062x/aug-cc-pVTZ level of theory.

opt freq aug-cc-pvtz scrf=(solvent=water) geom=connectivity m062x

Symbolic Z-matrix:

Charge = +1 Multiplicity = 1

S	-0.146813	-0.794632	-0.449079
F	-1.752499	1.118497	0.058408
O	0.823518	0.342780	-0.672934
O	-0.126838	-1.274783	0.884385
C	1.615958	0.962470	0.411432
H	0.913043	1.385800	1.122256
H	2.200145	1.719029	-0.093263
H	2.231962	0.189436	0.858017
H	-2.492824	1.034575	0.612376

Calculation Type = FREQ

Calculation Method = RM062X

Basis Set = Aug-CC-pVTZ

Charge = 1

Spin = Singlet

Solvation = scrf=solvent=water

E(RM062X) = -688.75103 Hartree

RMS Gradient Norm = 1.2761e-05 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 0.26565543 Debye

Polarizability (?) = 48.533 a.u.

Point Group = C1

Job cpu time: 0 days 1 hours 5 minutes 14.3 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -688.75103 Hartree

Zero-point Energy Correction = 0.058636 Hartree

Thermal Correction to Energy = 0.066588 Hartree

Thermal Correction to Enthalpy = 0.067533 Hartree

Thermal Correction to Free Energy = 0.025208 Hartree

EE + Zero-point Energy = -688.69239 Hartree

EE + Thermal Energy Correction = -688.68444 Hartree

EE + Thermal Enthalpy Correction = -688.6835 Hartree

EE + Thermal Free Energy Correction = -688.72582 Hartree

E (Thermal) = 41.785 kcal/mol

Heat Capacity (Cv) = 23.433 cal/mol-kelvin

Entropy (S) = 89.08 cal/mol-kelvin

Opt Tab Data Section:

Step number = 1

Maximum force = 1.8e-05 Converged

RMS force = 8e-06 Converged

Maximum displacement = 0.001038 Converged

RMS displacement = 0.000459 Converged

Predicted energy change = -6.241065e-09 Hartree

4.5 $[FS(OMe)_2]^+$

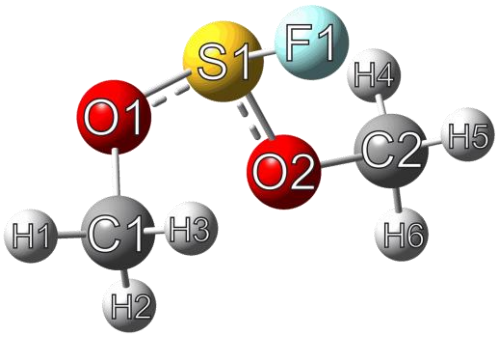

Figure S10. Optimized gas phase structure of $[FS(OMe)_2]^+$ on the M062x/aug-cc-pVTZ level of theory.

Table S 10. Input matrix for the structure optimization of $[FS(OMe)_2]^+$ on the M062x/aug-cc-pVTZ level of theory.

opt freq=raman M062x/aug-*cc*-pvtz geom=connectivity

Symbolic Z-matrix:

Charge = +1 Multiplicity = 1

S	0.048359	0.467458	-0.544311
F	0.001917	1.393761	0.721092
O	0.838993	-0.723707	0.045097
O	-1.367648	-0.077165	-0.598728
C	2.307947	-0.593352	0.158887
H	2.707570	-0.191814	-0.769315
H	2.649102	-1.607887	0.322247
H	2.526306	0.043408	1.010273
C	-1.983657	-0.867769	0.497273
H	-1.512593	-1.843783	0.510533
H	-1.852325	-0.327300	1.429360
H	-3.025559	-0.922101	0.208133

Calculation Type = FREQ

Calculation Method = RM062X

Basis Set = Aug-CC-pVTZ

Charge = 1

Spin = Singlet

Solvation = None

E(RM062X) = -727.97532 Hartree

RMS Gradient Norm = 3.244e-06 Hartree/Bohr

Imaginary Freq = 0

Dipole Moment = 1.7591638 Debye

Polarizability (?) = 49.984667 a.u.

Point Group = C1

Job cpu time: 0 days 5 hours 14 minutes 57.4 seconds.

Thermo Tab Data Section:

Imaginary Freq = 0

Temperature = 298.15 Kelvin

Pressure = 1 atm

Frequencies scaled by = 1

Electronic Energy (EE) = -727.97532 Hartree

Zero-point Energy Correction = 0.090431 Hartree

Thermal Correction to Energy = 0.098321 Hartree

Thermal Correction to Enthalpy = 0.099265 Hartree

Thermal Correction to Free Energy = 0.057546 Hartree

EE + Zero-point Energy = -727.88489 Hartree

EE + Thermal Energy Correction = -727.877 Hartree

EE + Thermal Enthalpy Correction = -727.87606 Hartree

EE + Thermal Free Energy Correction = -727.91778 Hartree

E (Thermal) = 61.697 kcal/mol

Heat Capacity (Cv) = 25.003 cal/mol-kelvin

Entropy (S) = 87.805 cal/mol-kelvin

Opt Tab Data Section:

Step number = 1

Maximum force = 0 Converged

RMS force = 0 Converged

Maximum displacement = 0.000126 Not converged

RMS displacement = 4.1e-05 Not converged

Predicted energy change = -1.219271e-11 Hartree

4.6 MEP calculations of $[SO_2Me]^+$ and $[FS(OMe)_2]^+$

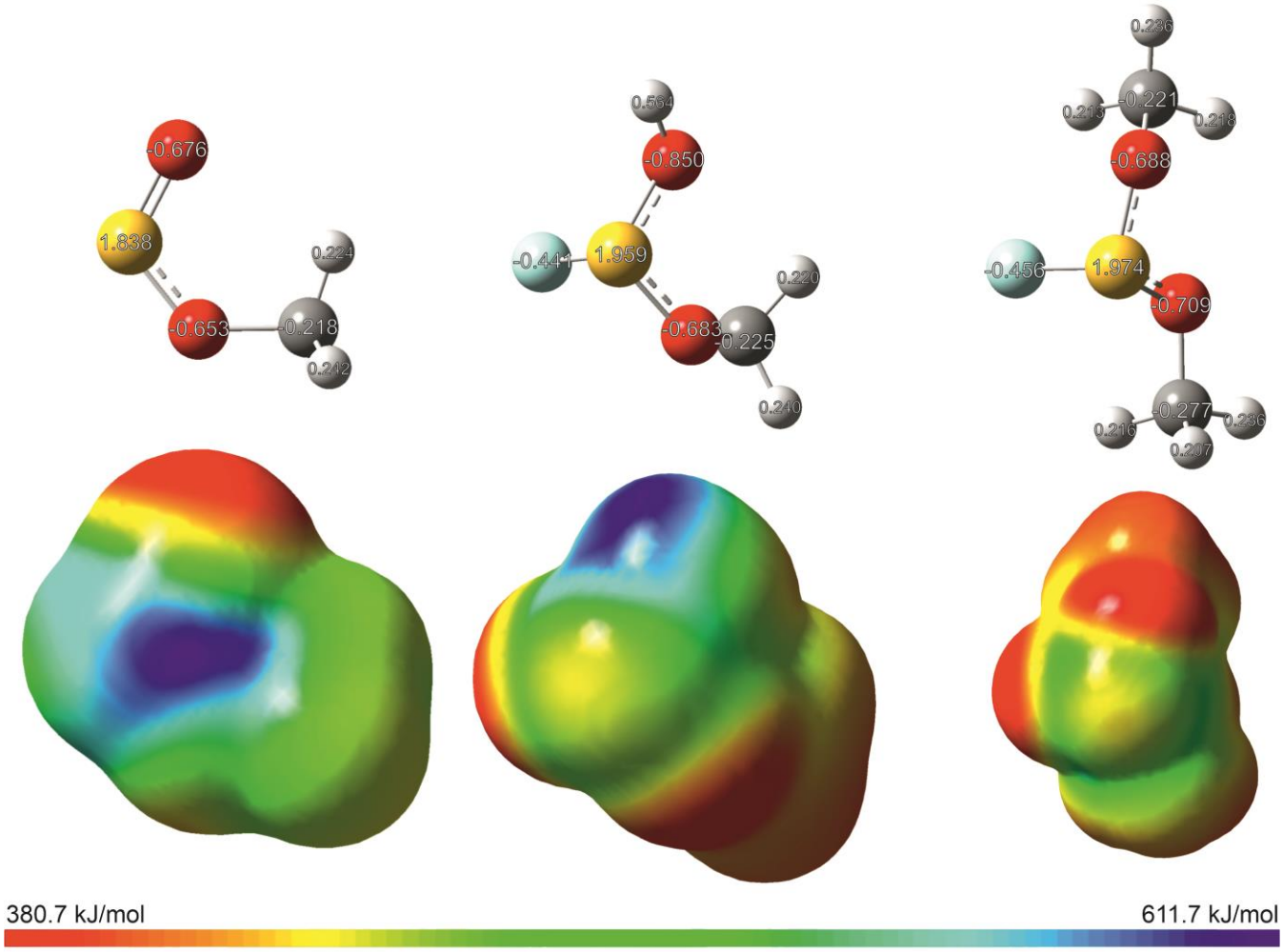

Figure S11. Molecular 0.0004 bohr^{-3} 3D isosurfaces with mapped electrostatic potential as color scale from 380.7 kJ/mol (red) to 611.7 kJ/mol (blue). The electrostatic potential isosurfaces and the NPA charges have been calculated for $[SO_2Me]^+$, $FS(OH)(OMe)]^+$ and $FS(OMe)_2]^+$.

5 Experimental Section

General

Caution! The hydrolysis of SbF_5 and the prepared salts $[SO_2Me][SbF_6]$, $[FS(OH)(OMe)][SbF_6]$ and $[FS(OMe)_2][Sb_2F_{11}]$ might form HF which burns skin and causes irreparable damage. Safety precautions must be taken while using and handling these materials.

Apparatus and Materials

Apparatus and Materials: All reactions were carried out using standard Schlenk techniques on a stainless-steel vacuum line. The salt syntheses were carried out in FEP/PFA reactors with stainless steel valves. Before each reaction or NMR measurement, the stainless-steel vacuum line and the reactors were dried with fluorine. A Bruker MultiRam FT-Raman spectrometer with Nd: YAG laser excitation (λ = 1064 nm) was used for Raman measurements. The measurement was performed after the transfer of the sample into a cooled (-196°C) glass cell under a nitrogen atmosphere and subsequent evacuation of the glass cell. Low-temperature IR spectroscopy was carried out on a Bruker Vertex-80V FTIR spectrometer using a cooled cell with a single crystal CsBr plate on which small amounts of the samples were placed.[1] Single crystal X-ray diffraction studies were performed on an Oxford XCalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector operating with Mo-Kα radiation (λ = 0.7107 Å). Measurements were performed at 173 K. The CrysAlisPro 1.171.39.46e program (Rigaku Oxford Diffraction, 2018) was used for data acquisition and reduction.[2] The structures were solved utilizing SHELXT[3] and SHELXL-2018/3[4] of the WINGX software package.[5] The structures were checked using the software PLATON.[6] The absorption correction was performed using the SCALE3 ABSPACK multiscan method.[7] Visualization was done with the software Mercury.[8] NMR spectra were recorded on a Bruker AV400 NMR instrument. The spectrometer was externally referenced to $CFCl_3$ for ^{19}F NMR and to tetramethylsilane for ^1H NMR spectra. For visualization and evaluation, the software MestReNova Version 14.3.2 was used.[9] The spectra were recorded inside a 4 mm FEP tube liner. The samples were transferred with nitrogen pressure from a reaction tube to the NMR FEP tube. The FEP tube was cooled down to −196 °C, evacuated, flame sealed, and at −60 °C tested for leakage. Immediately before the NMR measurement, the sealed FEP tube was

placed in a standard glass NMR tube filled with 0.2 mL of acetone d6 as an external reference and warmed to −60 °C. Quantum chemical calculations were performed using the Gaussian09 and Gaussian16 software packages,[10] and the GaussView 6 software package was used to visualize the calculated structures and mapped MEP surfaces.[11] Unless otherwise stated, all calculations were performed at the M06-2X/aug-cc-pVTZ level of theory.

$[SO_2Me][SbF_6]$: For the synthesis of $[SO_2Me][SbF_6]$ first antimony pentafluoride (280 mg, 1.292 mmol, 1.0 eq.) was condensed into a reactor (FEP tube). Methyl fluoride (44 mg, 1.292 mmol, 1.0 eq) and SO_2 as solvent were added at −196°C. The reaction was warmed up to −60°C and mixed. The solvent was removed at −78°C and $[SO_2Me][SbF_6]$ was obtained.

$[FS(OMe)_2][Sb_2F_{11}]$: To the $[SO_2Me][SbF_6]$ salt Methyl fluoride (220 mg, 6.46 mmol, 5.0 eq) and SO_2 were added. The reaction mixture was warmed up to 5°C and mixed. The solvent was removed at −78°C and $[FS(OMe)_2][Sb_2F_{11}]$ was obtained.

$[FS(OH)(OMe)][SbF_6]$ To the $[SO_2Me][SbF_6]$ salt anhydrous HF was added as solvent and reagent. The reaction mixture was warmed up to 5°C and mixed. The solvent was removed at −78°C and $[FS(OMe)_2][Sb_2F_{11}]$ was obtained.

6 References

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