Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information:

Spectroscopic and Structural Studies on Phenyl and Pentafluorophenyl Trifluorothioacetate, and Pentafluorophenyl Trifluoroacetate, $CF_3C(O)SC_6H_5$, $CF_3C(O)SC_6F_5$ and $CF_3C(O)OC_6F_5$

Vanina M. Cayón, Mauricio F. Erben, Rosana M. Romano, Hans-Georg Stammler, Norbert W. Mitzel and Carlos O. Della Védova

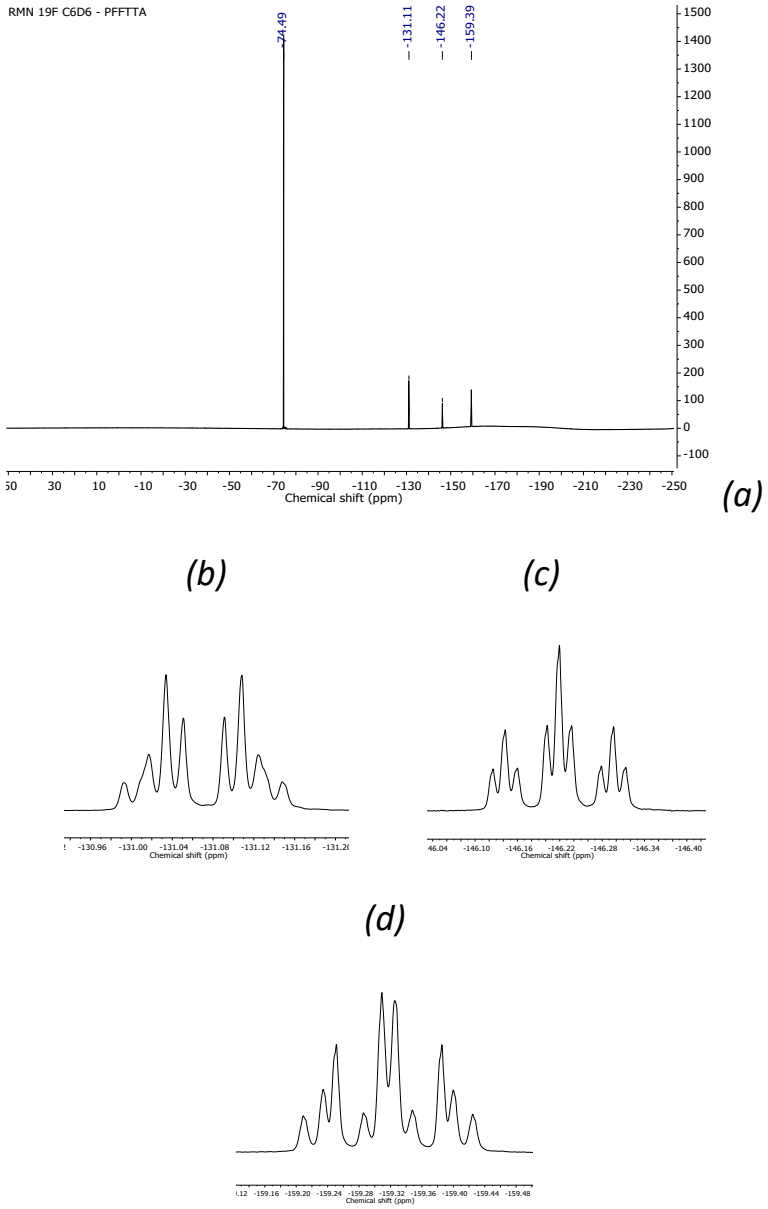


Figure S1. a) ^{19}F NMR spectrum of $CF_3C(O)SC_6F_5$. b, c, d, correspond to the enhanced signals.

Table S1. Crystal data and structure refinement for $CF_3C(O)SC_6H_5$

Identification code	$CF_3C(O)SC_6H_5$
Empirical formula	$C_8H_5F_3OS$
Formula weight	206.18
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.0609(5)
b/Å	5.4728(3)
c/Å	19.8700(12)
α/°	90
β/°	96.277(6)
γ/°	90
Volume/Å^3	871.32(9)
Z	4
ρ_{calc}g/cm^3	1.572
μ/mm^{-1}	0.374
F(000)	416.9
Crystal size/mm^3	0.6 × 0.32 × 0.26
Radiation/Å	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.124 to 52.086
Index ranges	-9 ≤ h ≤ 9, -6 ≤ k ≤ 6, -24 ≤ l ≤ 24
Reflections collected	9816
Independent reflections	2036 [R_{int} = 0.0443, R_{sigma} = 0.0747]
Reflections with *I > 2σ(I)*	1745
Data/restraints/parameters	2036/0/139
Goodness-of-fit on F^2	1.042
Final R indexes [*I > 2σ(I)*]	R_1 = 0. 0541, wR_2 = 0. 1609
Final R indexes [all data]	R_1 = 0. 0626, wR_2 = 0. 1675
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.44

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $CF_3C(O)SC_6H_5$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor

Atom	***x***	***y***	***z***	**U(eq)**
S(1)	1702.6(12)	6215.5(17)	3967.2(5)	28.0(3)
F(1)	4102(3)	2661(5)	5420.5(12)	44.3(6)
F(2)	2083(3)	5231(5)	5370.8(11)	43.1(6)
F(3)	1591(3)	1482(4)	5108.4(12)	44.2(6)
O(1)	3866(3)	2537(5)	4050.3(14)	32.1(6)
C(1)	2918(4)	3788(6)	4324.0(18)	23.1(7)
C(2)	2671(5)	3301(7)	5073.6(19)	29.1(8)
C(3)	2195(4)	6074(6)	3119.2(17)	20.4(7)
C(4)	3152(5)	7946(6)	2880.0(19)	25.9(8)
C(5)	3474(5)	7914(6)	2209.0(19)	26.1(8)
C(6)	2881(4)	6018(6)	1781.2(18)	25.4(8)
C(7)	1915(5)	4149(6)	2026.8(18)	25.7(8)
C(8)	1564(4)	4174(6)	2695.1(18)	25.1(7)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $CF_3C(O)SC_6H_5$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S(1)	24.7(5)	34.0(5)	26.3(4)	7.8(4)	7.7(4)	-0.5(4)
F(1)	39.7(14)	60.0(16)	32.1(12)	-0.1(12)	-1.7(10)	8.2(11)
F(2)	56.8(16)	46.2(14)	28.3(12)	3.6(12)	14.3(11)	-4.7(10)
F(3)	49.1(15)	48.8(14)	36.3(13)	-20.2(12)	11.8(12)	3.0(11)
O(1)	34.8(14)	30.8(13)	31.5(14)	12.6(12)	7.7(12)	0.9(12)
C(1)	24.0(17)	21.3(16)	24.7(17)	-0.9(14)	5.6(14)	-2.1(14)
C(2)	27.4(19)	32.0(18)	27.8(19)	-4.8(15)	3.2(15)	-1.7(16)
C(3)	14.6(15)	22.7(16)	24.3(16)	1.3(13)	3.6(12)	-0.6(13)
C(4)	25.7(18)	19.2(17)	32.9(19)	-2.4(14)	4.3(15)	-3.2(15)
C(5)	27.5(18)	18.3(16)	34(2)	-3.3(14)	8.8(15)	0.6(14)
C(6)	25.3(18)	25.5(17)	26.2(18)	-0.3(15)	7.0(15)	-0.3(14)
C(7)	28.0(19)	23.5(17)	25.3(17)	-4.5(15)	1.3(14)	-5.1(13)
C(8)	23.8(17)	21.0(16)	30.4(18)	-4.0(14)	3.1(15)	-1.9(13)

Table S4. Bond Lengths for $CF_3C(O)SC_6H_5$

Atom	-Atom	Length/Å	Atom	-Atom	Length/Å
S(1)	C(1)	1.754(4)	C(3)	C(4)	1.396(5)
S(1)	C(3)	1.775(3)	C(3)	C(8)	1.399(5)
F(1)	C(2)	1.325(4)	C(4)	C(5)	1.386(5)
F(2)	C(2)	1.322(4)	C(5)	C(6)	1.393(5)
F(3)	C(2)	1.329(4)	C(6)	C(7)	1.404(5)
O(1)	C(1)	1.200(4)	C(7)	C(8)	1.388(5)
C(1)	C(2)	1.547(5)			

Table S5. Bond Angles for $CF_3C(O)SC_6H_5$

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C(3)	S(1)	C(1)	100.24(16)	C(1)	C(2)	F(3)	109.4(3)
O(1)	C(1)	S(1)	127.2(3)	C(4)	C(3)	S(1)	118.7(3)
C(2)	C(1)	S(1)	113.2(2)	C(8)	C(3)	S(1)	120.0(3)
C(2)	C(1)	O(1)	119.6(3)	C(8)	C(3)	C(4)	121.2(3)
F(2)	C(2)	F(1)	108.2(3)	C(5)	C(4)	C(3)	119.1(3)
F(3)	C(2)	F(1)	108.2(3)	C(6)	C(5)	C(4)	120.6(3)
F(3)	C(2)	F(2)	107.8(3)	C(7)	C(6)	C(5)	119.8(3)
C(1)	C(2)	F(1)	110.5(3)	C(8)	C(7)	C(6)	120.3(3)
C(1)	C(2)	F(2)	112.5(3)	C(7)	C(8)	C(3)	119.0(3)

Table S6. Torsion Angles for $CF_3C(O)SC_6H_5$

Atom	Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Atom	Angle/˚
S(1)	C(1)	C(2)	F(1)	-143.2(3)	F(2)	C(2)	C(1)	O(1)	158.2(3)
S(1)	C(1)	C(2)	F(2)	-22.1(3)	F(3)	C(2)	C(1)	O(1)	-82.0(3)
S(1)	C(1)	C(2)	F(3)	97.8(3)	C(3)	C(4)	C(5)	C(6)	-1.2(4)
S(1)	C(3)	C(4)	C(5)	-176.9(3)	C(3)	C(8)	C(7)	C(6)	-0.4(4)
S(1)	C(3)	C(8)	C(7)	177.7(3)	C(4)	C(5)	C(6)	C(7)	1.4(4)
F(1)	C(2)	C(1)	O(1)	37.1(4)	C(5)	C(6)	C(7)	C(8)	-0.6(4)
S(1)	C(1)	C(2)	F(1)	-143.2(3)	F(2)	C(2)	C(1)	O(1)	158.2(3)
S(1)	C(1)	C(2)	F(2)	-22.1(3)	F(3)	C(2)	C(1)	O(1)	-82.0(3)
S(1)	C(1)	C(2)	F(3)	97.8(3)	C(3)	C(4)	C(5)	C(6)	-1.2(4)

Table S7. Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $CF_3C(O)SC_6H_5$

Atom	*x*	*y*	*z*	U(eq)
H(4)	3720(60)	9340(90)	3210(20)	43(13)
H(5)	4190(60)	9450(90)	2000(20)	37(12)
H(6)	3180(60)	6000(80)	1250(20)	34(11)
H(7)	1430(70)	2740(100)	1710(30)	60(15)
H(8)	890(60)	2680(100)	2890(20)	47(13)

Table S8. Crystal data and structure refinement for $CF_3C(O)SC_6F_5$

Identification code	$CF_3C(O)SC_6F_5$
Empirical formula	C_8F_8OS
Formula weight	296.14
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.59343(9)
b/Å	16.8308(3)
c/Å	10.18927(16)
α/°	90
β/°	93.3318(15)
γ/°	90
Volume/Å^3	957.62(3)
Z	4
ρ_{calc}g/cm^3	2.054
μ/mm^{-1}	0.446
F(000)	576.0
Crystal size/mm^3	0.629 × 0.26 × 0.243
Radiation/Å	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.678 to 73.424
Index ranges	-9 ≤ h ≤ 9, -27 ≤ k ≤ 28, -17 ≤ l ≤ 16

Reflections collected	30116
Independent reflections	4627 [R_{int} = 0.0188, R_{sigma} = 0.0118]
Reflections with *I > 2σ(I)*	4141
Data/restraints/parameters	4627/0/163
Goodness-of-fit on F^2	1.043
Final R indexes [*I > 2σ(I)*]	R_1 = 0.0306, wR_2 = 0.0863
Final R indexes [all data]	R_1 = 0.0351, wR_2 = 0.0895
Largest diff. peak/hole / e $Å^{-3}$	0.57/-0.52

Table S9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for $CF_3C(O)SC_6F_5$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor

Atom	***x***	***y***	***z***	**U(eq)**
S1	1222.5(4)	4604.4(2)	2295.1(2)	22.38(6)
F1	3793.4(13)	6645.5(4)	1836.9(7)	31.43(13)
F2	5150(2)	5812.0(5)	495.6(9)	64.6(3)
F3	1332(2)	5935.5(6)	677.0(10)	64.7(3)
F4	5655.8(11)	3601.0(4)	2366.5(6)	27.09(12)
F5	7107.1(10)	2529.7(3)	4219.8(6)	26.85(12)
F6	4491.6(12)	2283.1(3)	6331.4(6)	27.29(12)
F7	414.8(12)	3151.8(4)	6634.1(6)	30.48(13)
F8	-1036.2(9)	4218.3(3)	4807.1(6)	24.98(11)
O1	5290.2(13)	5289.7(4)	3207.8(7)	27.75(14)

C1	3618.1(16)	5290.4(5)	2418.5(8)	20.71(13)
C2	3459(2)	5931.2(6)	1328.9(9)	28.63(18)
C3	2267.1(13)	3939.6(4)	3530.5(7)	17.26(12)
C4	4346.8(14)	3496.0(5)	3407.5(8)	18.46(12)
C5	5099.6(14)	2945.7(4)	4348.7(8)	18.68(12)
C6	3770.0(15)	2823.3(5)	5438.2(8)	19.09(13)
C7	1706.1(15)	3259.6(5)	5586.3(8)	19.86(13)
C8	978.9(13)	3812.4(5)	4639.3(8)	18.04(12)

Table S10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $CF_3C(O)SC_6F_5$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S1	24.84(10)	21.49(9)	19.99(9)	2.47(6)	-5.68(7)	-4.30(7)
F1	44.2(3)	17.4(2)	32.7(3)	1.9(2)	1.9(2)	0.4(2)
F2	120.0(9)	37.4(4)	41.6(4)	9.2(3)	49.2(5)	14.9(5)
F3	84.9(7)	48.2(5)	55.3(5)	30.5(4)	-46.3(5)	-29.1(5)
F4	32.4(3)	25.2(2)	25.2(3)	0.82(19)	14.6(2)	0.4(2)
F5	21.7(2)	21.6(2)	37.5(3)	-1.7(2)	4.3(2)	4.27(18)
F6	35.9(3)	20.5(2)	25.0(2)	6.03(19)	-2.1(2)	0.1(2)
F7	37.5(3)	30.8(3)	24.7(3)	4.8(2)	15.4(2)	-0.5(2)
F8	18.6(2)	23.8(2)	33.1(3)	-0.7(2)	6.47(19)	1.90(18)
O1	28.0(3)	23.5(3)	30.9(3)	3.4(2)	-6.3(3)	-6.6(2)

C1	27.0(3)	16.9(3)	18.2(3)	0.4(2)	0.7(2)	-2.3(2)
C2	45.5(5)	20.0(3)	20.3(3)	2.6(3)	0.9(3)	-4.2(3)
C3	18.3(3)	16.5(3)	16.9(3)	-0.6(2)	0.6(2)	-2.6(2)
C4	20.0(3)	17.4(3)	18.5(3)	-1.5(2)	4.8(2)	-2.7(2)
C5	17.9(3)	15.4(3)	22.8(3)	-1.6(2)	1.7(2)	-1.2(2)
C6	22.7(3)	15.6(3)	18.7(3)	0.6(2)	-0.3(2)	-2.9(2)
C7	22.7(3)	19.0(3)	18.4(3)	-0.1(2)	5.1(2)	-3.3(2)
C8	16.5(3)	17.8(3)	20.0(3)	-1.4(2)	2.5(2)	-2.0(2)

Table S11. Bond Lengths for $CF_3C(O)SC_6F_5$

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S1	C1	1.7678(9)	F8	C8	1.3374(9)
S1	C3	1.7585(8)	O1	C1	1.1975(11)
F1	C2	1.3181(11)	C1	C2	1.5466(12)
F2	C2	1.3228(14)	C3	C4	1.3941(11)
F3	C2	1.3283(14)	C3	C8	1.3914(11)
F4	C4	1.3352(9)	C4	C5	1.3813(11)
F5	C5	1.3362(9)	C5	C6	1.3870(11)
F6	C6	1.3323(9)	C6	C7	1.3839(12)
F7	C7	1.3356(9)	C7	C8	1.3844(11)

Table S12. Bond Angles for $CF_3C(O)SC_6F_5$

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C3	S1	C1	98.38(4)	F4	C4	C5	118.77(7)
O1	C1	S1	127.32(7)	C5	C4	C3	121.27(7)
O1	C1	C2	119.53(8)	F5	C5	C4	120.47(7)
C2	C1	S1	113.12(6)	F5	C5	C6	119.58(7)
F1	C2	F2	107.45(9)	C4	C5	C6	119.95(7)
F1	C2	F3	107.09(9)	F6	C6	C5	119.53(7)
F1	C2	C1	110.68(7)	F6	C6	C7	120.60(7)
F2	C2	F3	109.45(10)	C7	C6	C5	119.87(7)
F2	C2	C1	109.98(9)	F7	C7	C6	120.56(7)
F3	C2	C1	112.05(8)	F7	C7	C8	119.85(7)
C4	C3	S1	121.38(6)	C6	C7	C8	119.59(7)
C8	C3	S1	120.86(6)	F8	C8	C3	120.35(7)
C8	C3	C4	117.69(7)	F8	C8	C7	118.02(7)
F4	C4	C3	119.96(7)	C7	C8	C3	121.62(7)

Table S13. Torsion Angles for $CF_3C(O)SC_6F_5$

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
S1	C1	C2	F1	131.92(8)	O1	C1	C2	F3	-169.35(10)
S1	C1	C2	F2	-109.51(9)	C1	S1	C3	C4	-65.33(7)
S1	C1	C2	F3	12.46(11)	C1	S1	C3	C8	117.66(7)

S1	C3	C4	F4	3.43(10)	C3	S1	C1	O1	-4.99(10)
S1	C3	C4	C5	-176.77(6)	C3	S1	C1	C2	173.03(6)
S1	C3	C8	F8	-2.57(10)	C3	C4	C5	F5	-179.50(7)
S1	C3	C8	C7	176.42(6)	C3	C4	C5	C6	0.37(12)
F4	C4	C5	F5	0.30(11)	C4	C3	C8	F8	-179.70(7)
F4	C4	C5	C6	-179.83(7)	C4	C3	C8	C7	-0.70(11)
F5	C5	C6	F6	-1.09(11)	C4	C5	C6	F6	179.04(7)
F5	C5	C6	C7	179.15(7)	C4	C5	C6	C7	-0.73(12)
F6	C6	C7	F7	0.64(12)	C5	C6	C7	F7	-179.59(7)
F6	C6	C7	C8	-179.40(7)	C5	C6	C7	C8	0.37(12)
F7	C7	C8	F8	-0.67(11)	C6	C7	C8	F8	179.37(7)
F7	C7	C8	C3	-179.68(7)	C6	C7	C8	C3	0.36(12)
O1	C1	C2	F1	-49.89(13)	C8	C3	C4	F4	-179.46(7)
O1	C1	C2	F2	68.68(12)	C8	C3	C4	C5	0.34(11)

Table S14. Experimental and computed wavenumbers (B3LYP/aug-cc-pVTZ) and assignment of the fundamental normal modes of vibrational corresponding to the lower energy forms of $CF_3C(O)OC_6F_5$

Experimental		**B3LYP/aug-cc-pVTZ**		**Assignment (% P.E.D.)/symmetry**
$FTIR_{gas}$[a]	**Matrix Ar**	**syn[b]**	**anti[b]**	
1836 (s)	1833.3	1807.2 (29)	1816.6 (86)	ν C=O (92)/A´
1625 (vw)	1623.7	1612.1 (1)	1610.4 (<1)	ν_{ring} CC (41) ; δ_{ring} CCC (25)/A´
-	1607.8	1610.0 (<1)	1605.7 (<1)	δ_{ring} CCC (22) ; ν_{ring} CC (54)/A´
1529 (vs)	1531.8	1489.4 (51)	1488.1 (78)	ν_{ring} CC(82)/A´´
-	1524.4	1484.5 (43)	1482.7 (75)	ν_{ring} CC (19) ; δ CCC (16)/A´
1476 (w)	1478.6	1439.8 (2)	1439.9 (10)	ν_{ring} CC (32) ;+ ν C-F (14) ; ν O-C (26)/A´
-	1344.5	1285.4 (<1)	1284.1 (3)	ν_{ring} CC (50) ; ν C-F (33)/A´
1342 (m)	1323.3	1271.4 (7)	1258.9 (20)	ν_{ring} CC (45) ; ν_{ring} C-F (38)/A´
-	1316.9	1259.1 (<1)	1256.7 (<1)	ν_{ring} CC (95)/A´´
1249 (s)	1242.1	1181.4 (50)	1180.6 (100)	ν_s CF_3 (81)/A´
	1203.4	1132.1 (6)	1170.3 (3)	ν_{ring} (C-F) (10) ; ν_{as} CF_3 (62)/A´´

1199 (s)	1192.3	1124.2 (31)	1127.2 (4)	ν_{as} CF_3 (66)/A´
-	1184.2	1117.7 (5)	1106.2 (45)	ν_{ring} (C-F)^{para} (22) ; ν (O-C) (25)/A´
1102 (vs)	1101.7	1070.1 (100)	1057.9 (90)	ν_{as} CF_3 (63) ; ν O-C(O) (30)/A´
1011 (m)	1005.2	984.1 (33)	985.4 (38)	ν_{as} (C-F)$^{meta\text{-}orto}$ (60)/A´´
993 (m)	990.1	965.4 (12)	982.1 (44)	ν (O-C) (17) ; ν_{ring} (C-F)^{para} (15)/A´
873 (w)	873.5	849.2 (3)	767.9 (<1)	ν (O-C(O)) (21) ; δ OCO (22) ; δ COC (20) /A´
-	777.4	770.1 (<1)	767.1 (<1)	[δ CCO (77) ; δ FCC (15)]$_{ring}$/A´´
-<	760.9	742.9 (2)	744.4 (<1)	δ_{oop} (O-C(O)-C) (60) + δ FCF (18)/A´´
758 (w)	755.5	739.9 (<1)	727.4 (3)	δ_{sim} CF_3 (43) /A´
-	720.4	715.4 (2)	704.6 (5)	τ_{ring} CCCC (21) ; δ_{oop} FCCC (out of ring plane) (24)/A´
712 (m)	715.4	650.6 (<1)	663.2 (3)	δ_{oop} FCCC$^{meta\text{-}orto}$(out of ring plane) (98)/A´´
-	710.2	635.7 (2)	651.1 (<1)	δ_{oop} FCCC^{para}(out of ring plane) (58) ; δ OCCC (21)/A´
641 (m)	641.7	616.4 (2)	578.5 (<1)	δ CF_3 (21) ; δ COC (22) ; δ CCO (23)/A´
-	573.6	565.3 (<1)	557.0 (<1)	δ CCC (20) ; ν CC (21) ; ν CF (24)/A´
-	555.1	534.5 (1)	505.7 (<1)	$\delta_{scissoring}$ CF_3 (56)/A´
-	-	501.4 (<1)	500.2 (<1)	$\delta_{rocking}$ CF_3 (73)/A´´
-	-	458.6 (<1)	462.6 (1)	δ CCC (29)/A´

-	-	433.4 (<1)	433.2 (<1)	δ CCC (52)/A´´
-	-	401.9 (<1)	419.5 (<1)	ν CC (15) ; δ FCF (41) ; δ CCO (13)/A´

[a] Band intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak . [b] Between parentheses, relative band intensity. The computed wavenumbers were corrected with a factor 0.968, as recommended for the used approximation.

Table S15. Experimental and computed wavenumbers (B3LYP/aug-cc-pVTZ) and assignment of the fundamental normal modes of vibrational corresponding to the lower energy forms of $CF_3C(O)SC_6F_5$

Experimental	**B3LYP/aug-cc-pVTZ**		**Assignment (% P.E.D.)/symmetry**
$FTIR_{gas}$[a]	**syn[b]**	**anti[b]**	
1738 (s)	1743 (48)	1739 (96)	ν C=O (95)/A´
1642 (m)	1601 (8)	1599 (8)	ν_{ring} CC (62)/A´
-	1590 (1)	1588 (1)	ν_{ring} CC (59) ; δ CCC (10)/A´
1516 (sh)	1480 (55)	1480 (62)	δ CCC (53) ; ν_{ring} C-F (22)/A´
1493 (vs)	1465(100)	1463 (100)	ν_{ring} CC (53); ν_{ring} C-F (21) ; δ CCC (10)/A´´

1417 (w)	1379 (2)	1375 (1)	ν_{ring} CC (11) ; δ CCC (10) ; ν_{ring} C-F (42)/A´
1379 (w)	1263 (1)	1262 (3)	ν_{ring} CC (96)/A´
1277 (s)	1258 (2)	1257 (<1)	δ CCC (45) ; ν_{ring} C-F (29)/A´´
1208 (s)	1209 (46)	1214 (27)	ν_s CF_3 (57) ; ν F_3C-C(O) (12)/A´
1171 (s)	1135 (73)	1158 (52)	ν_{as} CF_3 (61)/A´
1096 (s)	1125 (80)	1127 (1)	ν_{as} CF_3 (86)/A´´
1107 (sh)	1124 (5)	1106 (50)	ν_{ring} C-F (74)/A´´
986 (s)	1077 (44)	1077 (32)	ν_{ring} (C-F)^{para} (64)/A´
936 (s)	969 (73)	970 (43)	ν_{ring} (C-F)$^{orto\text{-}meta}$ (95)/A´´
924 (s)	898 (97)	914 (53)	ν (C-S) (18) ;ν (C-F) (30) ; δ (C-C(O)-S) (27)/A´
865 (s)	837 (32)	833 (16)	ν_{ring} C-F (20) ; ν S-C_6F_5 (38)/A´
-	744 (<1)	744 (<1)	δ_{ring} (in plane) (96)/A´´
739 (s)	736 (33)	737 (<1)	ν C-F (22) ; ν (C-S) (10) ; δ_{sim} CF_3 (24)/A´
689 (w)	711 (1)	713 (11)	[τ (CCCC) (22) ; δ FCCC (34)]$_{ring}$; δ_{oop} (C-C(O)-S)(19)/A´´
-	670 (1)	667 (<1)	δ_{oop} (ring plane) (80)/A´

-	657 (<1)	659 (<1)	δ_{oop} (ring plane) (96)/A´´
647 (w)	646 (<1)	643 (1)	$\delta_{scissoring}$ CF_3 (13) ; δoop (ring plane) (13)/A´
587 (w)	576 (<1)	573 (<1)	δ_{ring} CCC (26)/A´
-	568 (1)	561 (2)	ν (C-S)(14) ; δ_{ring} CCC (10) ; δ CF_3 (19) /A´
513 (w)	505 (6)	507 (<1)	ν (C(O)-S)(14) ; δ_{ring} CCC (19)/A´
-	499 (1)	491 (<1)	δ CF_3 (81) ; δ OCSC (11)/A´
-	486 (3)	462 (<1)	$\delta_{rocking}$ CF_3 (42)/A´´
439 (w)	432 (<1)	432 (<1)	δ_{ring} CCC (39)/A´´
407 (w)	395 (<1)	400 (<1)	ν (C-S) (25) ; δ_{ring} CCC (10) ; δ FCF (14) ; δ CSC (12)/A´

[a] Band intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak . [b] Between parentheses, relative band intensity. The computed wavenumbers were corrected with a factor 0.968, as recommended for the used approximation.

Table S16. Experimental and computed wavenumbers (B3LYP/aug-cc-pVTZ) and assignment of the fundamental normal modes of vibrational corresponding to the lower energy forms of $CF_3C(O)SC_6H_5$

Experimental	**B3LYP/aug-cc-pVTZ**		**Assignment (% P.E.D.)/symmetry**
$FTIR_{liq}$[a]	**syn[b]**	**anti[b]**	
-	3088 (2)	3089 (1)	ν_{sim} CH (99)/A´
3065 (w)	3083 (3)	3085 (2)	ν_{asim} CH (99)/A´´
-	3076 (3)	3078 (2)	ν_{asim} CH (99)/A´
-	3069 (1)	3069 (1)	ν_{asim} CH (99)/A´
-	3060 (<1)	3060 (<1)	ν_{asim} CH (99)/A´
1715 (s)	1721 (86)	1712 (100)	ν C=O (96)/A´
1584 (w)	1566 (<1)	1564 (<1)	ν_{ring} CC (43)/A´
1572 (m)	1562 (<1)	1560 (<1)	ν_{ring} CC (45) ; δ CCC (11)/A´´
1434 (sh)	1461 (4)	1460 (3)	δ HCC (71)/A´
1383 (vw)	1425 (3)	1424 (2)	ν_{ring} CC (10) ; δ HCC (43)/A´´
1330 (vw)	1304 (1)	1303 (<1)	ν_{ring} CC (20) ; δ HCC (56)/A´´
-	1269 (<1)	1268 (<1)	ν_{ring} CC (70)/A´´

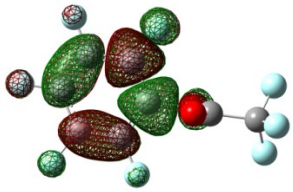
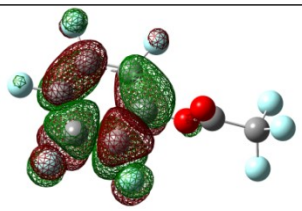
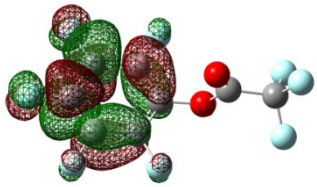
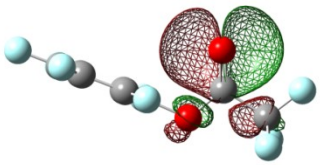
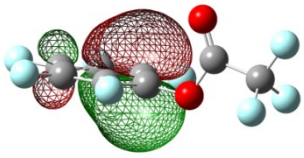
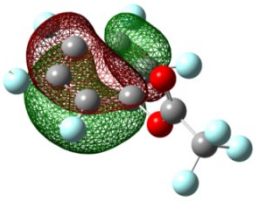
1274 (s)	1206 (49)	1207 (24)	ν F_3C-C(O) (28) ; ν_s CF_3 (44)/A´
-	1161 (<1)	1159 (<1)	δ CH (75)/A´
-	1143 (<1)	1148 (54)	ν_{ring} CC (10) ; δ CH (75)/A´´
1199 (s)	1136 (74)	1142 (<1)	ν_{as} CF_3 (73)/A´
1156 (s)	1120 (87)	1104 (49)	ν_{as} CF_3 (79)/A´´
-	1066 (<1)	1060 (<1)	ν_{ring} CC (12) ; δ CCC (29)/A´
-	1061 (1)	1059 (<1)	ν_{ring} CC (37) ; δ HCC (38)/A´´
-	1009 (1)	1008 (1)	ν_{ring} CC (44) ; δ CCC (22)/A´
-	987 (<1)	986 (<1)	ν_{ring} CC (13) ; δ CCC (59)/A´
-	985 (<1)	987 (<1)	τ HCCC (77)/A´´
-	966 (<1)	966 (<1)	τ HCCC (84) ; τ CCCC (11)/A´
-	914 (<1)	924 (33)	τ HCCC (99)/A´
927 (vs)	896 (100)	907 (30)	ν FC (28) ; ν CC (11) ; ν S-C(O) (18) ; δ OCS (28)/A´
-	830 (<1)	831 (<1)	τ HCCC (99)/A´´
743 (s)	743 (17)	744 (7)	τ HCCC (68) ; τ CCCC (14) ; τ SCCC (10)/A´´
704 (s)	709 (20)	711 (7)	δ_{sim} CF_3 (64)/A´
-	689 (3)	690 (7)	ν C-S (24) ; δ CCC (42)/A´

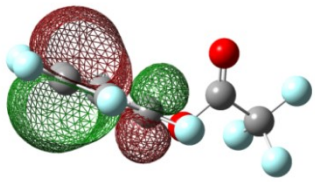
683 (m)	682 (6)	679 (3)	τ CCCC (68)/A´
-	669 (<1)	664 (<1)	δ oop C-C(O)-S (55) ; δ FCF (29)/A´´
-	608 (<1)	608 (<1)	δ_{ring} CCC (83)/A´´
-	583 (2)	564 (<1)	δ SCC (10) ; δ CSC (12) ; δ CF_3 (25)/A´
-	514 (1)	492 (3)	ν S-C(O) (21) ; $\delta_{rocking}$ CF_3 (39)/A´´
464 (w)	486 (1)	491 (<1)	δ CF_3 (79) ; δ OC-S-C (12)/A´´
451 (w)	455 (3)	467 (3)	ν S-C(O) (13) ; τ CCCC (19) ; δ OUT SCCC (25)/A´
428 (w)	415 (3)	401 (<1)	ν C-S (41) ; δ CCC (17)/A´

[a] Band intensity: vs = very strong, s = strong, m = medium, w = weak, vw = very weak . [b] Between parentheses, relative band intensity. The computed wavenumbers were corrected with a factor 0.968, as recommended for the used approximation.

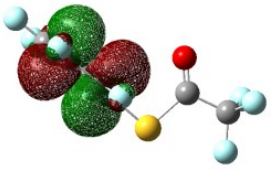
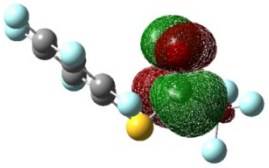
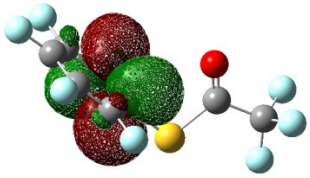
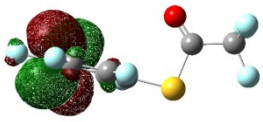
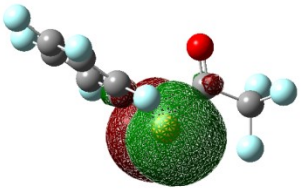
Table S 17. Schematic representation and approximate description of the first LUMO and HOMO for the compounds $CF_3C(O)SC_6H_5$, $CF_3C(O)SC_6F_5$ and $CF_3C(O)OC_6F_5$ calculated at the B3LYP/6-311++G ** level of approximation.

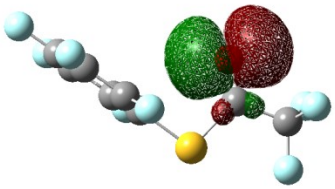
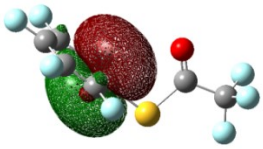
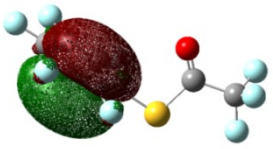
$CF_3C(O)OC_6F_5$

MO	Approximate description
 **LUMO+2 (71)**	**A´´ = π* (C–C)**
 **LUMO+1 (70)**	**A´´ = π* (C–C)**
 **LUMO (69)**	**A´´ = π* (C–C)**
 **HOMO (68)**	**A´ = n_p (O)**
 **HOMO-1 (67)**	**A´´ = π (C–C)**
 **HO**	**A´´ = π (C–C)**

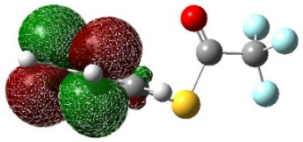
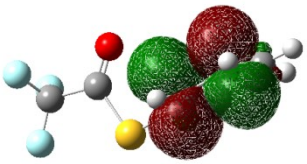
MO-2 (66)	
 HOMO-3 (65)	**A´´ = π (C–C)**

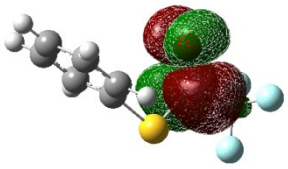
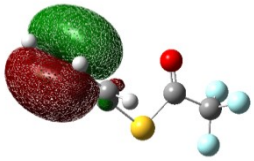
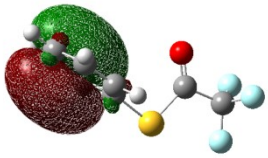
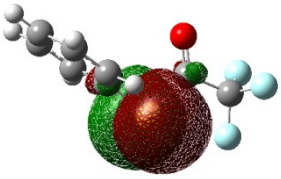
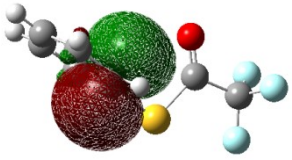
$CF_3C(O)SC_6F_5$

MO	Approximate description
 LU MO+3 (76)	**A´´ = π * (C–C)**
 LU MO+2 (75)	**A´´ = π * (C=O)**
 LUMO+1 (74)	**A´´ = π * (C–C)**
 LU MO (73)	**A´´ = π * (C–C)**
 HOMO (72)	**A´´ = n_p (S)**

 HOMO-1 (71)	A´ = n_p (O)
 HO MO-2 (70)	A´´ = π (C–C)
 H OMO-3 (69)	A´´ = π (C–C)

$CF_3C(O)SC_6H_5$

MO	Approximate description
 L UMO + 3 (56)	A´´ = π* (C–C)
 LUMO + 2 (55)	A´´ = π* (C–C)
 LUMO + 1 (54)	A´´ = π* (C–C)
	A´´ = π* (C=O)

 L UMO (53)	
 HOMO (52)	A´´ = π (C–C)
 HO MO-1 (51)	A´´= π (C–C)
 HOMO-2 (50)	A´´= n_p (S)
 HOMO-3 (49)	A´´= π (C–C)