Structure, Conformational Properties and Matrix Photochemistry of $CF_3C(O)SC(CH_3)_3$

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Supporting information

Figure S1. Clausius-Clapeyron plot for liquid $CF_3C(O)SC(CH_3)_3$

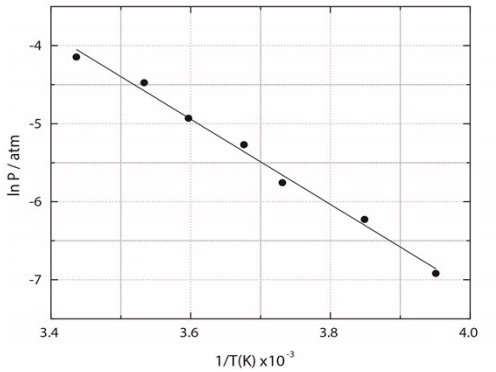


Figure S2. Vapour pressure curve of $CF_3C(O)SC(CH_3)_3$.

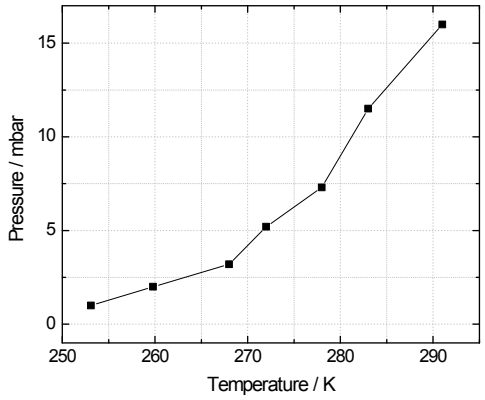
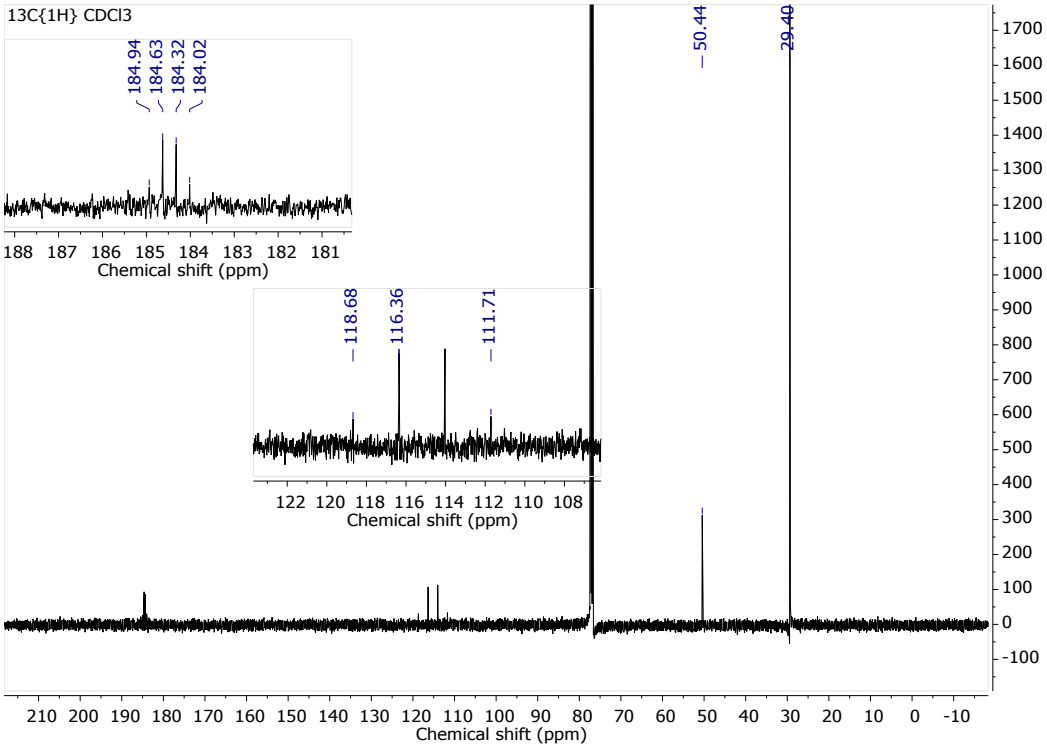
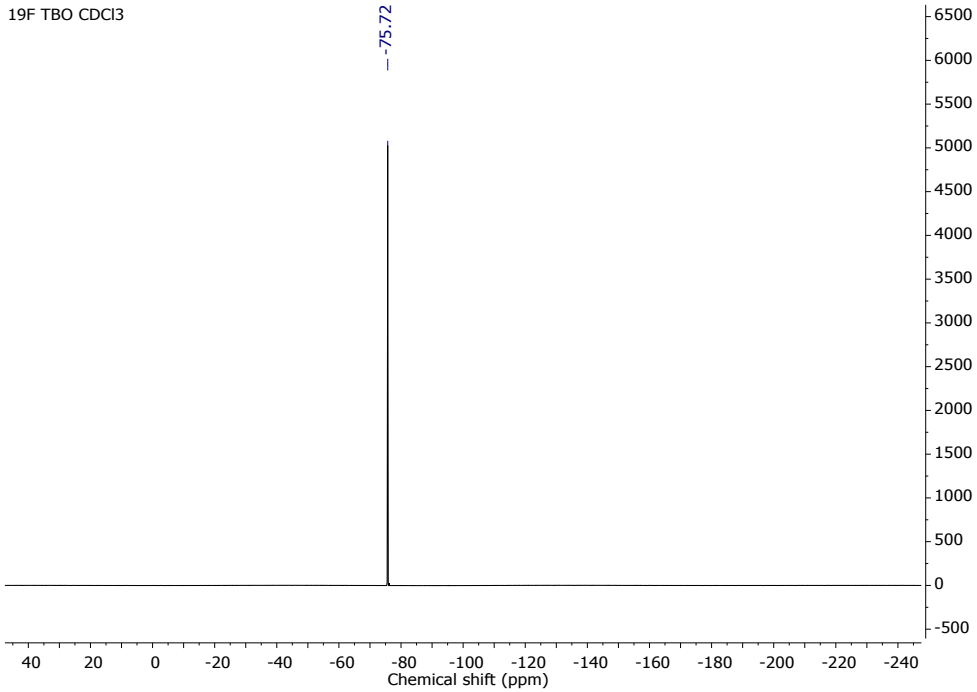


Figure S3. NMR ^{1}H, ^{19}F and ^{13}C spectra of $CF_3C(O)SC(CH_3)_3$**.** All samples were measured in $CDCl_3$.

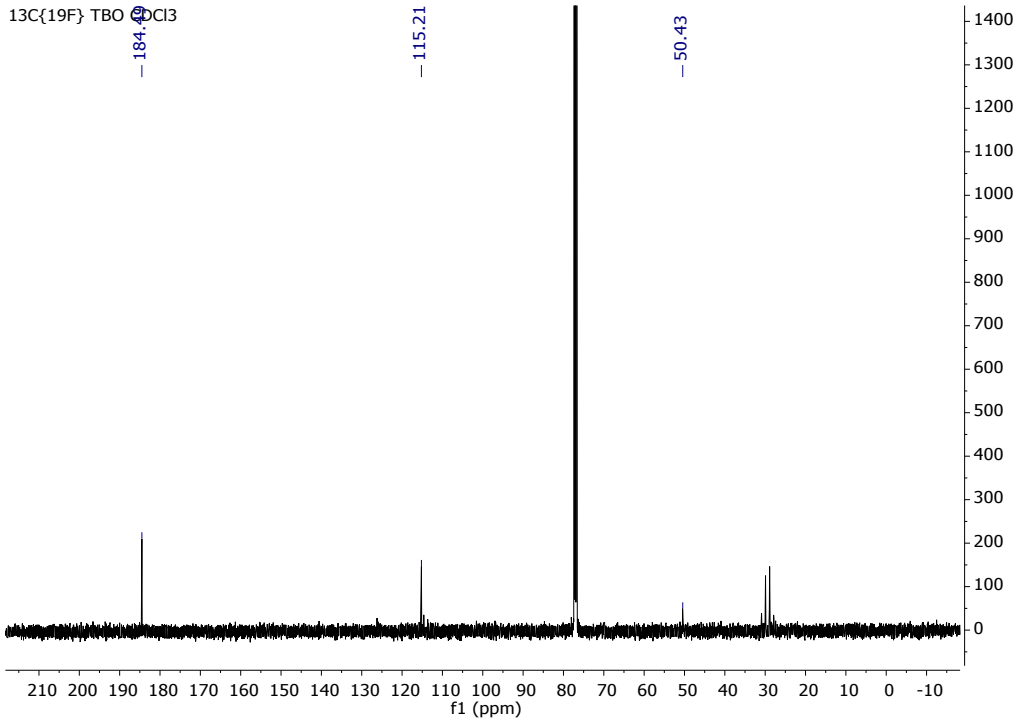
a) $^{13}C\{^{1}H\}$ NMR spectrum.

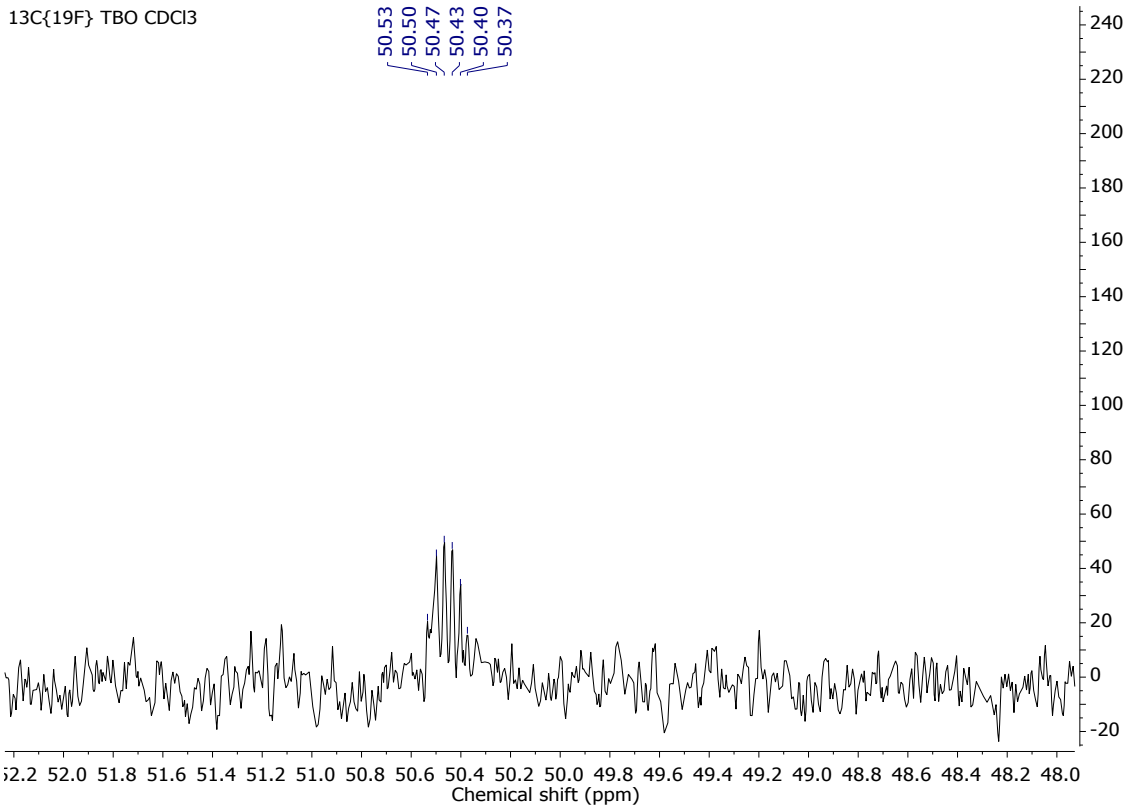


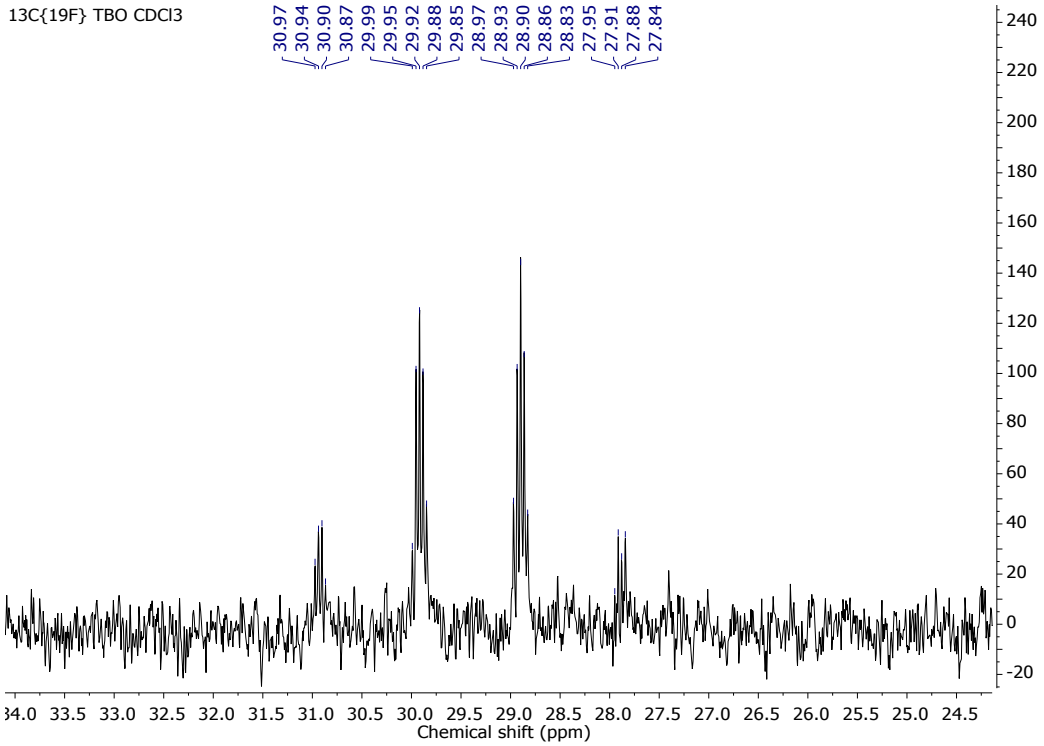
b) ^{19}F NMR spectrum.



c) $^{13}C\{^{19}F\}$ NMR spectrum.







d) ^{1}H NMR spectrum. (Signal at 7.28 ppm corresponds to a solvent impurity).

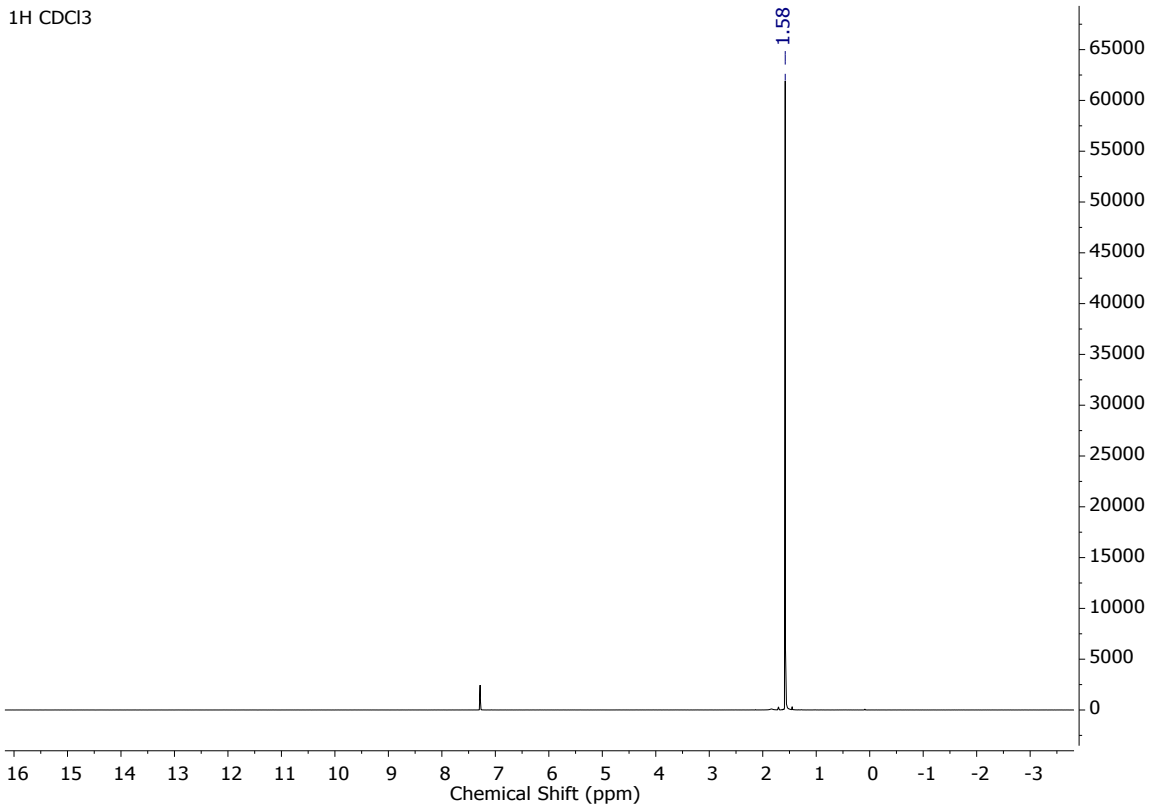
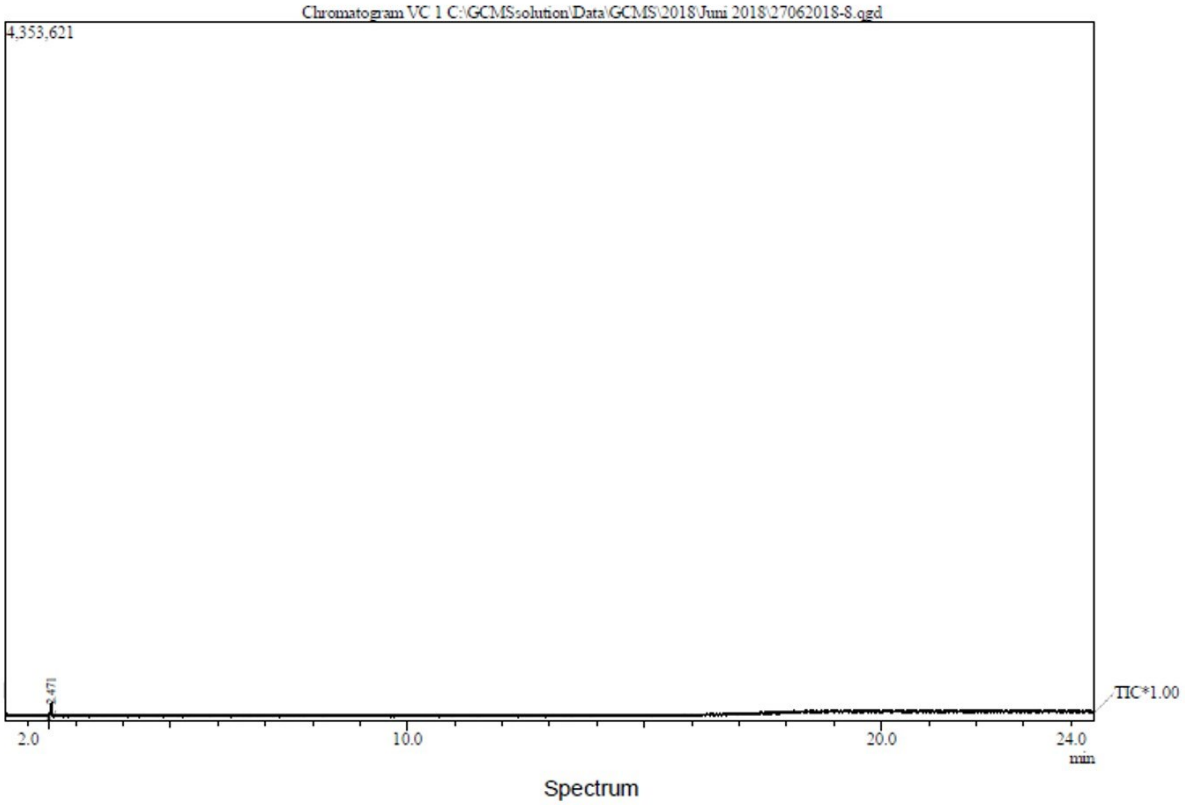


Figure S4. GC-MS chromatogram of $CF_3C(O)SC(CH_3)_3$.



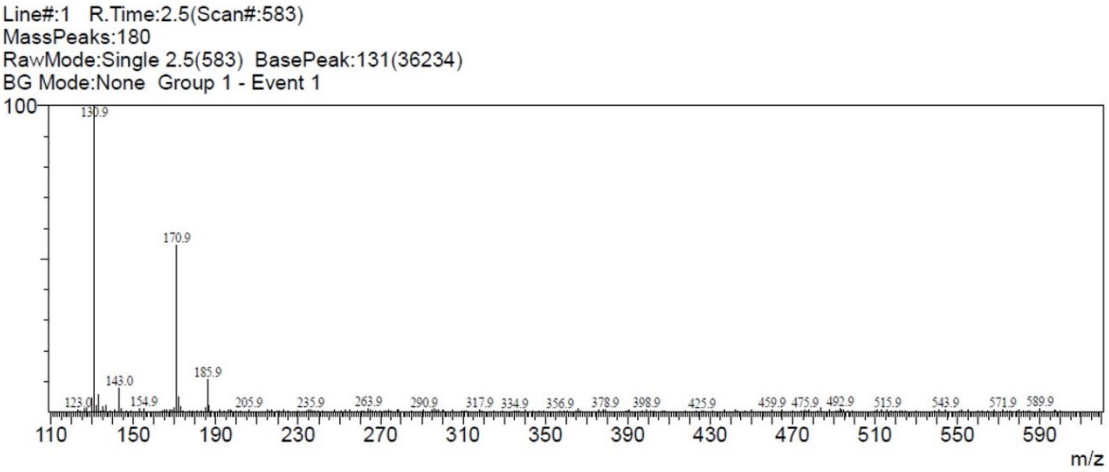


Table S1. Crystallographic data for $CF_3C(O)SC(CH_3)_3$

CCDC 2004500 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html

S1.1 Crystal data and structure refinement for $CF_3C(O)SC(CH_3)_3$

Empirical formula	$C_6H_9F_3OS$
Formula weight / g/mol	186.19
Temperature / K	94.0(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.34413(7)
b/Å	11.69960(6)
c/Å	11.73975(9)
α/°	90
β/°	95.4183(6)
γ/°	90
Volume / Å^3	1687.895(18)
Z	8
ρ_{calc} / g cm^{-3}	1.465
μ / mm^{-1}	0.376
F(000)	768
Crystal size/mm^3	0.619 × 0.305 × 0.269
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.314 to 102.782
Index ranges	$-27 \le h \le 27$, $-25 \le k \le 25$, $-24 \le l \le 25$
Reflections collected	350214
Independent reflections	18678 [R_{int} = 0.0420, R_{sigma} = 0.0143]
Data/restraints/parameters	18678/0/810
Goodness-of-fit on F^2	1.506
Final R indexes [I>=2σ (I)]	R_1 = 0.019
Final R indexes [all data]	R_1 = 0.037, wR_2 = 0.022
Largest diff. peak/hole / e Å^{-3}	0.23/–0.29
CCDC	2004500

S1.2 Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $CF_3C(O)SC(CH_3)_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized UIJ tensor

Atom	***x***	***y***	***z***	U_{eq}
S(1)	4449.52(4)	3493.43(4)	814.59(5)	16
S(2)	577.52(4)	4227.08(4)	3424.22(5)	17
F(1)	2984.6(5)	4702.2(6)	-717.4(6)	25
F(2)	1659.3(4)	4745.9(5)	351.6(7)	25
F(3)	2884.0(6)	6063.6(4)	513.4(7)	27
F(4)	2102.8(7)	5752.2(5)	4509.5(8)	30
F(5)	2163.4(6)	4704.4(7)	6038.0(7)	28
F(6)	3417.7(4)	4567.1(6)	4889.2(6)	25
O(1)	3103.4(4)	4339.8(4)	2249.4(4)	24
O(2)	2007.7(3)	2774.0(3)	4469.0(4)	23
C(1)	3378.19(17)	4256.35(18)	1290.0(2)	16
C(2)	2718.73(18)	4943.00(18)	331.2(3)	18
C(3)	5092.63(18)	2768.42(18)	2103.9(2)	15
C(4)	5986.2(2)	2068.9(3)	1611.4(3)	25
C(5)	4286.8(2)	1977.2(2)	2614.5(3)	22
C(6)	5582.5(2)	3635.5(2)	2972.3(3)	24
C(7)	1702.35(17)	3741.84(18)	4288.0(2)	16
C(8)	2355.15(18)	4716.2(2)	4928.7(3)	19
C(9)	-37.29(18)	2920.62(19)	2757.6(2)	17
C(10)	-973.5(3)	3399.0(3)	1950.0(4)	30
C(11)	-467.9(3)	2147.0(3)	3654.3(3)	27
C(12)	773.0(2)	2305.7(2)	2071.0(3)	22

S1.3 Anisotropic displacement parameters ($Å^2 \times 10^3$) for $CF_3C(O)SC(CH_3)_3$. 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)	17.09(2)	19.18(2)	12.28(2)	2.055(17)	3.406(16)	4.311(15)
S(2)	17.67(2)	13.232(18)	19.44(3)	-1.201(17)	-1.993(18)	2.374(14)
F(1)	28.5(2)	29.7(2)	17.0(2)	4.18(17)	2.72(17)	9.77(17)
F(2)	16.49(16)	26.83(19)	30.7(2)	3.67(19)	0.39(16)	2.30(13)
F(3)	31.8(2)	16.01(16)	32.2(3)	2.54(17)	0.6(2)	0.57(15)
F(4)	32.3(2)	16.57(16)	38.8(3)	1.28(19)	-5.3(2)	-5.99(16)
F(5)	29.6(2)	34.2(2)	20.8(2)	-7.6(2)	6.7(2)	-10.37(19)
F(6)	16.62(16)	33.7(2)	25.5(2)	-2.2(2)	1.52(15)	-5.76(15)
O(1)	26.07(14)	31.01(16)	16.85(16)	0.78(13)	7.56(13)	8.60(14)
O(2)	23.38(13)	15.25(11)	29.74(19)	2.75(12)	-5.26(14)	2.72(9)
C(1)	16.09(7)	17.44(7)	14.66(10)	0.26(7)	3.45(7)	2.19(6)
C(2)	17.33(8)	16.60(8)	19.19(11)	1.65(7)	2.17(7)	2.75(6)
C(3)	17.04(7)	14.80(7)	13.54(10)	0.94(7)	1.25(7)	0.29(6)
C(4)	25.71(10)	26.1(1)	22.63(14)	4.66(10)	5.57(10)	11.11(9)
C(5)	26.12(10)	19.36(8)	19.88(12)	3.94(9)	3.73(9)	-4.32(8)
C(6)	25.98(10)	21.15(9)	22.30(13)	-2.54(9)	-6.0(1)	-2.70(8)
C(7)	15.35(7)	14.17(7)	17.21(10)	0.87(7)	-0.04(7)	0.01(6)
C(8)	17.64(8)	18.87(8)	19.13(12)	-0.82(8)	1.12(8)	-3.87(6)
C(9)	16.29(8)	18.07(8)	16.51(11)	-2.61(7)	2.01(7)	-1.33(6)
C(10)	24.30(11)	35.25(13)	28.36(16)	-6.99(13)	-9.16(11)	4.02(11)
C(11)	29.52(12)	29.41(12)	23.90(15)	-1.98(11)	9.19(11)	-12.17(10)
C(12)	23.02(10)	21.96(9)	23.39(13)	-7.29(9)	7.58(10)	-2.40(8)

S1.4 Bond lengths for $CF_3C(O)SC(CH_3)_3$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(1)	C(1)	1.7311(2)	O(1)	C(1)	1.2105(5)
S(1)	C(3)	1.8477(2)	O(2)	C(7)	1.2059(4)
S(2)	C(7)	1.7357(2)	C(1)	C(2)	1.5499(3)
S(2)	C(9)	1.8473(2)	C(3)	C(4)	1.5301(3)
F(1)	C(2)	1.3337(7)	C(3)	C(5)	1.5226(3)
F(2)	C(2)	1.3304(5)	C(3)	C(6)	1.5224(3)
F(3)	C(2)	1.3409(6)	C(7)	C(8)	1.5492(3)
F(4)	C(8)	1.3340(6)	C(9)	C(10)	1.5299(4)
F(5)	C(8)	1.3454(8)	C(9)	C(11)	1.5217(4)
F(6)	C(8)	1.3283(6)	C(9)	C(12)	1.5231(3)

S1.5 Bond angles for $CF_3C(O)SC(CH_3)_3$

A	B	C	Angle/°	A	B	C	Angle/°
C(1)	S(1)	C(3)	104.761(12)	C(5)	C(3)	C(6)	111.99(3)
C(7)	S(2)	C(9)	104.529(11)	S(2)	C(7)	O(2)	129.02(3)
S(1)	C(1)	O(1)	129.15(3)	S(2)	C(7)	C(8)	113.187(16)
S(1)	C(1)	C(2)	113.45(2)	O(2)	C(7)	C(8)	117.76(3)
O(1)	C(1)	C(2)	117.37(3)	F(4)	C(8)	F(5)	108.07(6)
F(1)	C(2)	F(2)	107.94(5)	F(4)	C(8)	F(6)	107.66(5)
F(1)	C(2)	F(3)	107.87(5)	F(4)	C(8)	C(7)	113.38(4)
F(1)	C(2)	C(1)	113.75(3)	F(5)	C(8)	F(6)	107.28(5)
F(2)	C(2)	F(3)	107.55(4)	F(5)	C(8)	C(7)	109.36(3)
F(2)	C(2)	C(1)	110.30(3)	F(6)	C(8)	C(7)	110.88(4)
F(3)	C(2)	C(1)	109.23(4)	S(2)	C(9)	C(10)	102.470(19)
S(1)	C(3)	C(4)	101.844(19)	S(2)	C(9)	C(11)	110.82(2)
S(1)	C(3)	C(5)	110.821(17)	S(2)	C(9)	C(12)	110.548(16)
S(1)	C(3)	C(6)	110.822(17)	C(10)	C(9)	C(11)	110.70(3)
C(4)	C(3)	C(5)	110.16(2)	C(10)	C(9)	C(12)	109.89(3)
C(4)	C(3)	C(6)	110.77(2)	C(11)	C(9)	C(12)	112.01(2)

S1.6 Torsion angles (º) for $CF_3C(O)SC(CH_3)_3$

C(3)	S(1)	C(1)	O(1)	1.67(4)	S(1)	C(1)	C(2)	F(2)	130.65(4)
C(3)	S(1)	C(1)	C(2)	179.82(2)	S(1)	C(1)	C(2)	F(3)	-111.34(4)
C(1)	S(1)	C(3)	C(4)	177.200(19)	O(1)	C(1)	C(2)	F(1)	-172.39(5)
C(1)	S(1)	C(3)	C(5)	60.035(18)	O(1)	C(1)	C(2)	F(2)	-50.96(4)
C(1)	S(1)	C(3)	C(6)	-64.939(19)	O(1)	C(1)	C(2)	F(3)	67.04(5)
C(9)	S(2)	C(7)	O(2)	-2.94(3)	S(2)	C(7)	C(8)	F(4)	-14.99(4)
C(9)	S(2)	C(7)	C(8)	179.381(19)	S(2)	C(7)	C(8)	F(5)	105.67(4)
C(7)	S(2)	C(9)	C(10)	-176.39(2)	S(2)	C(7)	C(8)	F(6)	-136.23(4)
C(7)	S(2)	C(9)	C(11)	65.48(2)	O(2)	C(7)	C(8)	F(4)	167.04(5)
C(7)	S(2)	C(9)	C(12)	-59.323(19)	O(2)	C(7)	C(8)	F(5)	-72.29(5)
S(1)	C(1)	C(2)	F(1)	9.23(4)	O(2)	C(7)	C(8)	F(6)	45.80(4)
C(3)	S(1)	C(1)	O(1)	1.67(4)	S(1)	C(1)	C(2)	F(2)	130.65(4)

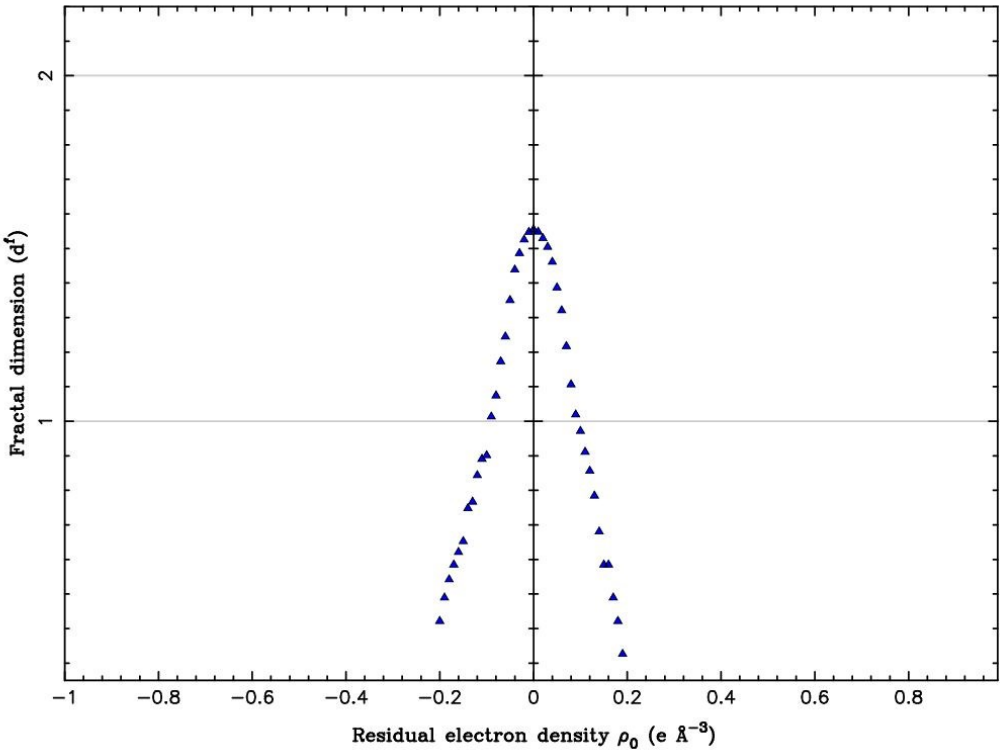
S1.7 Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for $CF_3C(O)SC(CH_3)_3$

Atom	*x*	*y*	*z*	U(eq)
H(4A)	6443.79	1630.91	2313.33	44(3)
H(4B)	6544.11	2621.79	1212.49	39(3)
H(4C)	5606.96	1448.32	1016.13	37(3)
H(5A)	3660.27	2454.68	2993.35	30(2)
H(5B)	4745.96	1479.1	3271.23	39(2)
H(5C)	3923.81	1406.8	1959.17	40(3)
H(6A)	4956.72	4157.84	3298.7	36(3)
H(6B)	6149.91	4171.78	2567.59	39(3)
H(6C)	6018.77	3154.3	3657.88	42(3)
H(10A)	-662.61	3952.47	1316.96	35(3)
H(10B)	-1553.84	3834.64	2434.13	48(3)
H(10C)	-1376.21	2660.31	1547.53	50(3)
H(11A)	184.58	1804.76	4236.96	31(3)
H(11B)	-1036.03	2619.74	4122.63	43(3)
H(11C)	-862.12	1427.61	3206.89	51(3)
H(12A)	1438.02	1943.76	2623.16	37(3)
H(12B)	343.45	1617.49	1605.84	36(2)
H(12C)	1080.02	2881.75	1454.9	44(3)

S1.8 Local coordinate system

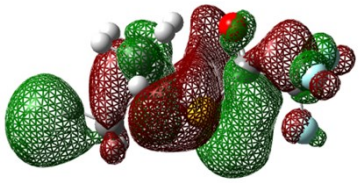
S(1) C(1) Z S(1) C(3) Y
S(2) C(7) Z S(2) C(9) Y
F(1) C(2) Z F(1) F(3) Y
F(2) C(2) Z F(2) F(3) Y
F(3) C(2) Z F(3) F(2) Y
F(4) C(8) Z F(4) F(6) Y
F(5) C(8) Z F(5) F(6) Y
F(6) C(8) Z F(6) F(5) Y
O(1) C(1) Z O(1) C(2) Y
O(2) C(7) Z O(2) C(8) Y
C(1) O(1) Z C(1) C(2) Y
C(2) F(2) Z C(2) F(1) Y
C(3) C(5) Z C(3) C(6) Y
C(4) H(4C) Z C(4) H(4A) Y
C(5) H(5B) Z C(5) H(5C) Y
C(6) H(6A) Z C(6) H(6B) Y
C(7) O(2) Z C(7) C(8) Y
C(8) F(6) Z C(8) F(4) Y
C(9) C(11) Z C(9) C(12) Y
C(10) H(10C) Z C(10) H(10A) Y
C(11) H(11C) Z C(11) H(11A) Y
C(12) H(12B) Z C(12) H(12A) Y
H(4A) C(4) Z H(4A) H(4B) Y
H(4B) C(4) Z H(4B) H(4A) Y
H(4C) C(4) Z H(4C) H(4B) Y
H(5A) C(5) Z H(5A) H(5B) Y
H(5B) C(5) Z H(5B) H(5A) Y
H(5C) C(5) Z H(5C) H(5A) Y
H(6A) C(6) Z H(6A) H(6B) Y
H(6B) C(6) Z H(6B) H(6A) Y
H(6C) C(6) Z H(6C) H(6A) Y
H(10A) C(10) Z H(10A) H(10B) Y
H(10B) C(10) Z H(10B) H(10A) Y
H(10C) C(10) Z H(10C) H(10B) Y
H(11A) C(11) Z H(11A) H(11B) Y
H(11B) C(11) Z H(11B) H(11C) Y
H(11C) C(11) Z H(11C) H(11B) Y
H(12A) C(12) Z H(12A) H(12C) Y
H(12B) C(12) Z H(12B) H(12C) Y
H(12C) C(12) Z H(12C) H(12A) Y

Figure S5. Fractal dimension plot [5]

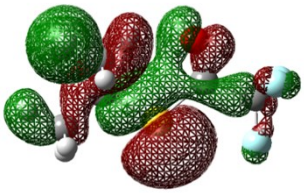


Plot generated with WinGX[6]

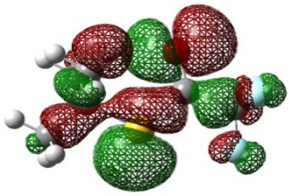
Figure S6. Diagrams of border molecular orbitals of *syn*-$CF_3C(O)SC(CH_3)_3$ calculated with the TD-B3LYP/cc-pVTZ approximation.



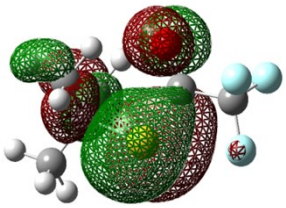
HOMO-3 (OM 45)



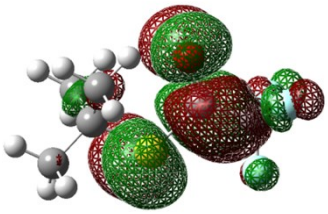
HOMO-2 (OM 46)



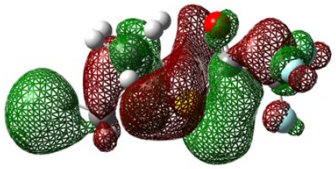
HOMO-1 (OM 47)



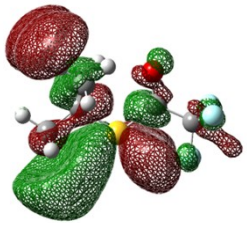
HOMO (OM 48)



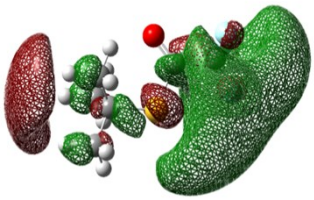
LUMO (OM 49)



LUMO+1 (OM 50)



LUMO+2 (OM 51)



LUMO+3 (OM 52)

Table S2. Calculated and assignment of the UV spectrum of *syn*-$CF_3C(O)SC(CH_3)_3$ using the TD-B3LYP/cc-pVTZ approximation

Transition (Contribution %)	***E* (eV)**	**$\lambda_{calculated}$(nm)**	***f****	**$\lambda_{experimental}$(nm)**
47→50 (12) / 47→52 (11)/ 48 → 49 (68)	5.4283	228.4	0.0875	238
47 → 50 (68) /47→51 (10)	6.9079	179.8	0.0204	203

*Oscillator force, with *f**>0.02

Table S3. Wavenumbers and assignment for the IR absorptions appearing after broadband UV-Visible photolysis of an 1:1000 Ar matrix containing $CF_3C(O)SC(CH_3)_3$ at about 10 K.

Ar-Matrix	Tentative assignment		Reported
	Molecule	**Vibrational mode**	**wavenumbers**
2999.8	$(CH_3)_3CSCF_3$	ν_{as}(C-H)	3029.9
2979.5	$(CH_3)_3CSCF_3$	ν_{as}(C-H)	3004.6
2952.7	$(CH_3)_3CSCF_3$	ν_{as}(C-H)	2998.8 2994.2
2937	$(CH_3)_3CSCF_3$	ν_{as}(C-H)	2938.1
2912.9	$(CH_3)_3CSCF_3$	ν_{as}(C-H)	2931.9 2930.0
2138.3	CO	ν(C=O)	2138.6[1]
2136.6	CO	ν(C=O)	
2133.1	CO	ν(C=O)	
2091.2	$^{13}C^{16}O$	$\nu(^{13}CO)$	2091.4[1]
2089.6	$^{13}C^{16}O$	$\nu(^{13}CO)$	
2047.9	OCS	ν(C=O)	2051.6[2]
1934.9	OCF_2	ν(C=O)	1941.4[3]
1906.3	OCF_2	$2(\nu_sCF_2)$	1913.5[3]
1477.2	$(CH_3)_3CSCF_3$	δ (CH_3)	1471.5
1467.7 1463.2	$(CH_3)_3CSCF_3$	δ (CH_3)	1455.8
1451.3 1443.7	$(CH_3)_3CSCF_3$	δ (CH_3)	1454.5
1397.8	$(CH_3)_3CSCF_3$	ρ CH_3	1391.5
1379.0 1373.1	$(CH_3)_3CSCF_3$	δ (CH_3)	1365.5
1369.7	$(CH_3)_3CSCF_3$	δ (CH_3)	1360.6
1354.9	SCF_2	ν(C=S)	1368[4]
1227.5 1219.4	OCF_2	$\nu_2(\nu_{as}CF_2)$	1237.8[3]
1184.7	SCF_2	$\nu_{as}(CF_2)$	1189[4]
1174.2	$(CH_3)_3CSCF_3$	$\nu_s(CC_3)$	1157.3
1146.5	$(CH_3)_3CSCF_3$	$\nu_{as}(CF_3)$	1093.9
1123.5	$(CH_3)_3CSCF_3$	$\nu_{as}(CF_3)$	1062.2
1111.6	$(CH_3)_3CSCF_3$	$\nu_s(CF_3)$	1053.1
1082.6	$(CH_3)_3CSCF_3$	δ (CH_3)	1019.1
1060.7	$(CH_3)_3CSCF_3$	δ (CH_3)	1010.2
1031.3 1025.1	$(CH_3)_3CSCF_3$	δ (CH_3)	965.4
964.5	OCF_2	$\nu_2(\nu_sCF_2)$	965.5[3]
893.1	$(CH_3)_3CSCF_3$	δ $C(CH_3)_3$	908.4
759.3 755.9	$(CH_3)_3CSCF_3$	ν(S-CF_3)	726.6
594.5	$(CH3)_3CSCF_3$	ν (S-CC_3)	560.5
552.5	$(CH3)_3CSCF_3$	$\delta(CF_3)$	524.2
541.6	$(CH3)_3CSCF_3$	$\delta(CF_3)$	518.1
496.4	$(CH_3)_3CSCF_3$	$\delta(CF_3)$	472.9

*This work, tentative assignment with B3LYP/aug-cc-pVTZ. Vibrational modes: δ = bending, ν = stretching, s = symmetric, as = antiymmetric.

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