

Through Space J_{HF} Spin-Spin Coupling Constant Transmission Pathways in 2-(Trifluoromethyl)thiophenol: formation of unusual stabilizing bifurcated $\text{CF}\cdots\text{HS}$ and $\text{CF}\cdots\text{SH}$ interactions

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Experimental Procedures

Experimental Details

¹H, ¹⁹F, and ¹³C NMR spectra were obtained on a Bruker Avance spectrometer operating at 499.87 MHz for ¹H, 470.30 MHz for ¹⁹F, and 125.71 MHz for ¹³C using a BBFO probe with typical 90° pulse widths of 11.75 μ s for ¹H, 16.60 μ s for ¹⁹F, and 10.00 μ s for ¹³C. Spectra were recorded in 10 mg mL⁻¹ solutions with a probe temperature of 27.0 °C (BBFO) in C₆D₁₂, CDCl₃, CD₂Cl₂, or Acetone-d₆ (all acquired from Aldrich Chem., Co.) and referenced to the solvent residual signal.

Typical ¹H conditions were 32 scans, spectral width 7000 Hz, 64 k data points, giving an acquisition time of 4.7 s and zero filled to 128 k to give a digital resolution of 0.05 Hz. ¹⁹F spectra were typically acquired with 16 scans and a spectral width of 9398.5 Hz, and 64k data points zero filled to 128k to give a digital resolution of 0.07 Hz. ¹H-¹⁹F HETCOR (modulated with $J_{HF} = 3$ Hz) and ¹H-¹³C HMBC (modulated with a log-range $J_{HC} = 8$ Hz) experiments were performed using the Bruker standard pulse sequences. The E.COSY pattern used to determine the sign of the J_{HF} SSCCs was observed in the ¹H-¹³C{¹H}-HMBC spectra and referred to the correlation of the thiol proton with the carbon of the aromatic ring bond to the CF₃ group (³ J_{HC}), which was assumed to be positive. In order to do so, the resolution in the indirect dimension should be at least equal to the J_{CF} SSCC which is going to be used to observe the displacement vector. Typically, 4096 points were acquired in the ¹H dimension with a spectral window of 4746.835 Hz, giving a resolution of 1.16 Hz, and 2048 points in the ¹³C dimension with a spectral window of 20097.027 Hz, giving a resolution of 9.81 Hz. The resolution can be further increased by zero-filling the direct dimension to 8192 points and the indirect dimension to 4096 points. 64 scans/transient were used.

The IR spectra were recorded on a FTIR Shimadzu IRPrestige-21 spectrometer equipped with a CsI beamsplitter. The infrared spectrum was obtained in CH₂Cl₂ by using a 0.5 mm width NaCl round cell window with a concentration of 4 mM. The following IR spectrometer conditions were used: number of scans = 128, resolution = 1 cm⁻¹, spectral range = 650–4000 cm⁻¹. The equipment was purged with continuous dry nitrogen gas.

Computational Details

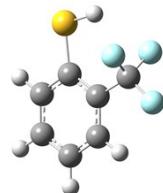
All optimization, frequency and energy calculations were done using the Gaussian16 Rev C.01 program.¹ The conformers were identified through scanning the FCCC(SH)/HSCC(CF₃) dihedrals at the same time from 0–180° in 10° steps at the M06-2X/6-311G(d,p) level. The two minima found in the potential energy surface (PES) were then reoptimized at the M06-2X/6-311++G** level and frequency calculations were carried out at the same level in order to identify each conformer as true energy minima, showing no negative frequencies. The same frequency energies were used to obtain enthalpies and Gibbs free energies at standard pressure (1 atm) and temperature (298.15 K). Cartesian coordinates, absolute energies and the lowest harmonic vibrational frequency are available for both conformers (**Table S1**).

Single point energy calculations were carried out on the optimized geometries for several DFT functionals and *ab initio* methods (**Table S2**). Additionally, single point DLPNO-CCSD(T)/CBS energy calculations were run using the ORCA 4.0.1 software² with the tightSCF option using the inbuilt “extrapolateEP3” command to obtain the CBS converged energies, which was then used as the benchmark (**Table S2**). Several basis-sets were tested in

combination with the DFT functional that showed the lowest relative error when compared to DLPNO-CCSD(T)/CBS results (**Table S3**). The population of the conformers at different solvents was computed at the M06/cc-pVTZ level using the integral equation formalism variant of the polarizable continuum model (IEFPCM) implicit solvation³ (**Table S4**). Natural Bond Orbitals⁴ (NBO) calculations, including the, Natural Coulomb Electrostatic⁴ (NCE), Natural Resonance Theory⁵ (NRT), Natural Steric Analysis⁶ (NSA) and Natural J-Coupling⁷ (NJC) analysis were done at the M06/cc-pVTZ level, except for the NJC analysis which was made at the PBE0/pcJ-1 level using the NBO 7.0 program.⁸ Topological analyses, evaluation of local properties and integral properties over the atomic basins (Ω) were carried out with the AIMALL program Version 19.10.12,⁹ using wave functions calculated at the M06/cc-pVTZ level. NCI isosurfaces were obtained with the same wave functions used for QTAIM calculations using the NCIPILOT V4.0 program.^{10,11,12} NMR spin-spin coupling constants (SSCCs) were obtained for both conformers at different levels of theory (**Table S5**). The SSCCs for different solvents were also calculated using the IEFPCM implicit solvation model (**Table S6**) at the PBE0/pcJ-1 level and were decomposed into its FC (Fermi Contact), SD (Spin Dipolar), PSO (Paramagnetic Spin Orbit) and DSO (Diamagnetic Spin Orbit) terms (**Table S7**). The bifurcated CF···HS H-bond energy formed for the dimer between thiophenol and (trifluoromethyl)benzene was calculated at the M06-2X/6-311G(d,p) level including the basis set superposition error (BSSE) correction as the energy difference between the dimer and its monomers (Figure S19).

Results

Table S1. Cartesian coordinates, absolute energy (atomic units) and lowest harmonic vibrational frequency (cm⁻¹) for the conformers of 2-(trifluoromethyl)thiophenol obtained at the M06-2X/6-311G(d,p) level.



cis-SH-CF₃

Energy (au)= -967.363064

LHVF (cm⁻¹)= 68.05

C	2.13770100	-1.72133300	-0.00002200	C	2.17566500	-1.67796500	-0.00483300
C	0.75130400	-1.69795500	-0.00002900	C	0.78819600	-1.68427400	-0.02326600
C	0.05778400	-0.48932500	-0.00001500	C	0.07441300	-0.48964100	-0.02177100
C	0.75720400	0.72640800	0.00001000	C	0.74710100	0.74055300	-0.00845300
C	2.15474800	0.68711000	0.00001900	C	2.14363900	0.73229400	0.00089200
C	2.83667900	-0.51955500	0.00000300	C	2.84914800	-0.46250100	0.01176600
H	2.66415700	-2.66689000	-0.00003400	H	2.72290400	-2.61172600	-0.00365200
H	0.19160800	-2.62395000	-0.00004700	H	0.24602200	-2.62074600	-0.03580700
H	2.70688100	1.61998300	0.00004300	H	2.68271700	1.67214500	-0.00508000
H	3.92008300	-0.51759600	0.00000900	H	3.93231100	-0.43886700	0.02401900



trans-SH-CF₃

Energy (au)= -967.361934

LHVF (cm⁻¹)= 54.94

C	-1.44487100	-0.52594700	-0.00002000	C	-1.43001400	-0.54316700	0.00656000
F	-1.96637600	0.09152900	-1.07678900	F	-1.97673400	0.23354600	-0.94291500
F	-1.96638100	0.09153100	1.07674500	F	-1.92463200	-0.12639700	1.18138300
F	-1.92545000	-1.77236000	-0.00002300	F	-1.89223400	-1.78418300	-0.19143000
S	0.06095600	2.35629100	0.00005400	S	-0.15083800	2.27418200	-0.03502300
H	-1.23746500	2.03507800	0.00008900	H	0.88296300	3.01378600	0.39216100

Table S2 Geometrical parameters (Bond lengths in Å and angles in °) for the conformers of 2-(trifluoromethyl)thiophenol obtained at the M06-2X/6-311G(d,p) level.

Cis	Trans
r(C11-F12)	1.346 Å
r(C11-F13)	1.346 Å
r(C11-F14)	1.336 Å
r(C4-S15)	1.772 Å
r(S15-H16)	1.338 Å
r(C1-C2)	1.387 Å
r(C2-C3)	1.393 Å
r(C3-C4)	1.403 Å
r(C4-C5)	1.398 Å
r(C5-C6)	1.386 Å
r(C6-C1)	1.390 Å
r(C3-C11)	1.503 Å
r(C1-H7)	1.082 Å
r(C2-H8)	1.082 Å
r(C5-H9)	1.084 Å
r(C6-H10)	1.083 Å
∠ (C2-C1-C6)	119.2 °
∠ (C2-C1-H7)	120.1 °
∠ (C1-C2-C3)	120.8 °
∠ (C1-C2-H8)	120.2 °
∠ (C6-C1-H7)	120.7 °
∠ (C1-C6-C5)	120.3 °
∠ (C1-C6-H10)	120.3 °
∠ (C3-C2-H8)	119.0 °
∠ (C2-C3-C4)	120.2 °
∠ (C2-C3-C11)	118.5 °
∠ (C4-C3-C11)	121.3 °
∠ (C3-C4-C5)	118.3 °
∠ (C3-C4-S15)	127.0 °
∠ (C3-C11-F12)	112.1 °
∠ (C3-C11-F13)	112.1 °
∠ (C3-C11-F14)	112.5 °
∠ (C5-C4-S15)	114.7 °
∠ (C4-C5-C6)	121.1 °

∠ (C4-C5-H9)	119.0 °	∠ (C4-C5-H9)	119.5 °
∠ (C4-S15-H16)	99.2 °	∠ (C4-S15-H16)	94.7 °
∠ (C6-C5-H9)	119.9 °	∠ (C6-C5-H9)	119.6 °
∠ (C5-C6-H10)	119.4 °	∠ (C5-C6-H10)	119.3 °
∠ (F12-C11-F13)	106.2 °	∠ (F12-C11-F13)	106.8 °
∠ (H16-S15-F12)	120.1 °	∠ (H16-S15-F12)	168.0 °
∠ (H16-S15-F12)	120.1 °	∠ (H16-S15-F12)	135.6 °

Table S3. Calculated populations (in percentage) from several DFT functionals and *ab initio* theoretical methods from single-point energy calculations corrected with the Gibbs free energies obtained from the M06-2X/6-311++G(d,p) level. The DLPNO-CCSD(T)/CBS energy was used as the benchmark to obtain the absolute errors (AE).

Method/6-311++G(d,p)	ΔE (<i>trans-cis</i>)	Population <i>Cis/Trans</i>	AE (kcal mol ⁻¹)
M06-2X	0.7091	67.0/33.0	0.43
M06	0.4983	62.2/37.8	0.22
M06-D3	0.4980	62.2/37.8	0.22
M11	0.7531	68.0/32.0	0.47
B3LYP	0.5707	63.9/36.1	0.29
B3LYP-D3	1.1464	75.9/24.1	0.87
MP2	-0.1133	47.2/52.8	0.39
MP3	-0.1477	46.3/53.7	0.43
MP4(D)	-0.2271	44.3/55.7	0.51
MP4(DQ)	-0.2098	44.8/55.2	0.49
MP4(SDQ)	-0.1762	45.6/54.4	0.46
DLPNO-CCSD(T)/CBS	0.2805	57.0/43.0	0.00

Table S4. Calculated populations (in percentage) obtained from the M06 functional using several basis sets corrected with the Gibbs free energies obtained from the M06-2X/6-311++G(d,p)//M06-2X/6-311++G(d,p) level.

M06/basis set	ΔE (<i>trans-cis</i>)	Population <i>cis/trans</i>	AE (kcal mol ⁻¹)
6-311++G(d,p)	0.4983	62.2/37.8	0.22
6-311++G(2d,p)	0.3443	58.5/41.5	0.06
6-311+G(d,p)	0.4955	62.1/37.9	0.22
cc-pVTZ	0.2491	56.2/43.8	0.03
cc-pVQZ	0.2053	55.1/44.9	0.08

may-cc-pVTZ	0.1529	53.8/46.2	0.13
jun-cc-pVTZ	0.1545	53.9/46.1	0.13
jul-cc-pVTZ	0.1496	53.7/46.3	0.13
aug-cc-pVTZ	0.1684	54.2/45.8	0.11
aug-cc-pVQZ	0.1912	54.8/45.2	0.09
DLPNO-CCSD(T)/CBS	0.2805	57.0/43.0	0.00

Table S5. Calculated populations (in percentage) at the M06/cc-pVTZ level in different solvents using the implicit IEFPCM solvation. The M06-2X/6-311++G(d,p) geometry was used in all cases and the thermochemistry from frequency calculation at this same level were used to obtain the Gibbs free energies. The dielectric constant (ϵ) is given for each solvent.

Solvent	ϵ	ΔE (<i>trans-cis</i>)	Population <i>Cis/Trans</i>
Cyclohexane	2.0165	-0.0751	48.1/51.9
Chloroform	4.7113	-0.3707	40.8/59.2
Dichloromethane	8.9300	-0.5112	37.5/62.5
Acetone	20.4930	-0.6141	35.1/64.9

Table S6. Boltzmann-averaged NMR spin-spin coupling constants (SSCCs) for 2-(trifluoromethyl)thiophenol obtained from a combination of several DFT levels and basis-sets using implicit IEFPCM cyclohexane solvation (values in Hz). The experimental J_{HF} was measured in C_6D_{12} . Basis sets marked with “*” indicate that the 6-311++G(d,p) basis set was used for C and S atoms and the indicated basis set for H and F.

Boltzmann-averaged SSCCs (Hz)						
	EPR-III*	aug-cc-pVTZ-J*	pcJ-1	aug-pcJ-1	pcJ-2	pcJ-3
M06	4.46	0.00	5.51	0.00	4.43	4.54
M06-L	3.73	3.68	4.10	3.73	3.47	3.26
PBE0	2.83	2.96	2.81	2.84	2.97	3.02
BHandH	3.36	3.42	3.23	3.25	3.55	3.57
Experimental			2.15			

Table S7. Experimental and Calculated Boltzmann-averaged (PBE0/pcJ-1 level using the IEFPCM approach) NMR spin-spin coupling constants (SSCCs) for 2-(trifluoromethyl)thiophenol obtained in several solvents.

PBE0/pcJ-1 IEFPCM	Boltzmann-averaged SSCC (Hz)	Experimental (Hz)
Cyclohexane	2.81	2.15
Chloroform	3.39	3.00
Dichloromethane	3.66	3.50
Acetone	3.86	4.70

Table S8. Theoretical contribution of the four Ramsey terms for the J_{HF} (Hz) for conformers *cis* and *trans* of 2-(trifluoromethyl)thiophenol at the PBE0/pcJ-1-IEFPCM level in cyclohexane.

Conformer	FC	SD	PSO	DSO	Total	Experimental
<i>cis</i> -SH-CF ₃	-1.09	0.15	-1.50	1.60	-0.84	
<i>trans</i> -SH-CF ₃	6.86	-0.03	0.78	-1.41	6.20	2.15

Table S9. Atom-atom electrostatic interactions (kcal mol⁻¹) obtained at the M06/cc-pVTZ level for *cis*-2-(trifluoromethyl)thiophenol obtained at the M06/6-311++G(d,p) level.

Cis	C1	C2	C3	C4	C5	C6	H7	H8	H9	H10	C11	F12	F13	F14	S15	H16
C1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C2	8.17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3	5.746	7.289	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C4	3.515	2.979	6.315	0	0	0	0	0	0	0	0	0	0	0	0	0
C5	6.169	3.926	5.54	6.776	0	0	0	0	0	0	0	0	0	0	0	0
C6	8.752	3.714	3.925	3.2	8.418	0	0	0	0	0	0	0	0	0	0	0
H7	-13.98	-5.16	-3.995	-2.479	-4.278	-5.516	0	0	0	0	0	0	0	0	0	0
H8	-7.575	-10.98	-6.811	-3.049	-4.048	-3.775	6.418	0	0	0	0	0	0	0	0	0
H9	-4.478	-2.882	-4.019	-4.512	-13.43	-5.56	3.458	3.227	0	0	0	0	0	0	0	0
H10	-7.002	-3.256	-3.495	-2.825	-6.756	-10.91	5.908	3.688	6.001	0	0	0	0	0	0	0
C11	-21.03	-23.33	-47.38	-19.99	-20.05	-14.57	16.75	31.31	16.65	14.39	0	0	0	0	0	0
F12	5.774	5.683	10.1	5.668	5.939	4.217	-4.733	-7.692	-5.184	-4.304	-101.4	0	0	0	0	0
F13	5.774	5.682	10.1	5.668	5.939	4.217	-4.733	-7.692	-5.184	-4.304	-101.4	21.27	0	0	0	0
F14	6.401	7.102	9.873	4.523	5.235	4.148	-5.433	-11.95	-4.438	-4.228	-99.83	20.77	20.77	0	0	0
S15	-1.259	-1.025	-1.815	-2.073	-2.064	-1.132	0.995	1.213	2.055	1.164	9.086	-3.072	-3.072	-2.112	0	0
H16	-1.997	-1.743	-3.186	-2.695	-2.649	-1.647	1.612	2.17	2.491	1.703	20.12	-7.413	-7.414	-4.375	2.804	0

Table S10. Atom-atom electrostatic interactions (kcal mol⁻¹) obtained at the M06/cc-pVTZ level for *trans*-2-(trifluoromethyl)thiophenol obtained at the M06/6-311++G(d,p) level.

Trans	C1	C2	C3	C4	C5	C6	H7	H8	H9	H10	C11	F12	F13	F14	S15	H16
C1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C2	8.124	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3	5.361	6.958	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C4	3.462	3	5.957	0	0	0	0	0	0	0	0	0	0	0	0	0
C5	6.13	3.99	5.281	6.829	0	0	0	0	0	0	0	0	0	0	0	0
C6	8.758	3.801	3.767	3.243	8.602	0	0	0	0	0	0	0	0	0	0	0
H7	-13.79	-5.206	-3.778	-2.476	-4.313	-5.601	0	0	0	0	0	0	0	0	0	0
H8	-7.479	-11.11	-6.453	-3.05	-4.088	-3.837	6.425	0	0	0	0	0	0	0	0	0
H9	-4.294	-2.824	-3.689	-4.371	-13.17	-5.489	3.365	3.143	0	0	0	0	0	0	0	0
H10	-6.904	-3.284	-3.304	-2.82	-6.808	-11.07	5.913	3.694	5.842	0	0	0	0	0	0	0
C11	-20.72	-23.49	-44.69	-20	-20.25	-14.78	16.73	31.28	16.19	14.39	0	0	0	0	0	0
F12	5.548	5.554	9.416	5.715	5.966	4.21	-4.603	-7.401	-5.035	-4.233	-100.2	0	0	0	0	0
F13	5.656	5.734	9.345	5.435	5.829	4.212	-4.712	-7.773	-4.878	-4.233	-99.59	20.49	0	0	0	0
F14	6.367	7.221	9.437	4.578	5.344	4.253	-5.476	-12.01	-4.366	-4.271	-100.7	20.69	20.54	0	0	0
S15	-1.398	-1.179	-1.986	-2.328	-2.274	-1.275	1.121	1.392	2.137	1.288	10.77	-3.819	-3.392	-2.497	0	0
H16	-1.709	-1.324	-1.981	-2.33	-3.106	-1.68	1.394	1.565	3.536	1.78	10.19	-3.411	-3.321	-2.578	2.649	0

Table S11. Total energies (kcal mol⁻¹) obtained from the NBO analysis and energy differences between *cis*-2-(trifluoromethyl)thiophenol and *trans*-2-(trifluoromethyl)thiophenol at the M06/cc-pVTZ level on vacuum.

	<i>cis</i>	<i>trans</i>	ΔE (<i>cis-trans</i>) kcal mol ⁻¹
Lewis	-606429.52	-606429.71	0.19
Non Lewis	-577.85	-577.05	-0.80
Steric	254.85	254.65	0.20
Electrostatics	-297.99	-294.67	-3.33
Total energy	-607007.37	-607006.76	-0.61

Table S12. Popelier criteria for *cis*-2-(trifluoromethyl)thiophenol and *trans*-2-(trifluoromethyl)thiophenol in comparison to their meta analogues. Electron density at the BCP (ρ_{BCP}), Laplacian at the BCP ($\nabla^2\rho_{\text{BCP}}$), atomic charge $q(\text{A})$, atomic energy $E(\text{A})$, first intramolecular atomic dipole moment $\mu_1(\text{A})$ and the atomic volume $V(\text{A})$ are given in atomic units. Atomic distances are given in angstroms.

	Bond path	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	$q(\text{H16})$	$E(\text{H16})$	$\mu_1(\text{H16})$	$V(\text{H16})$	r_{H}	r_{H}^0	$\Delta r_{\text{H}} = r_{\text{H}}^0 - r_{\text{H}}$
<i>cis</i>	H16 - F12	0.0120	0.0488	-0.0196	-0.618	0.0213	0.418	4.46	-	-2.18
	H16 - F13	0.0120	0.0488							
<i>trans</i>	S15 - F12	0.0122	0.0538	-0.0607	-0.627	0.0409	0.499	-	2.28	-

Table S13. Total contributions of Hyperconjugative terms for each orbital, as well as total Lewis and Repolarization contributions for the J_{HF} SSCC for *cis*-TFT. All values are in Hz.

Orbital	Contribution/		Total
	F12-H16	F13-H16	
Lewis	-14.75	-12.49	
Repol.	0.05	1.45	
54.C3-C11*	-0.35	0.09	
55.C4-C5*	0.13	0.18	
61.C11-F12*	4.75	-0.14	
62.C11-F13*	-0.15	-2.89	
63.C11-F14*	-0.03	-0.08	
64.S15-H16*	-6.51	-5.74	
C1(ry)	-0.11	-0.09	
C2(ry)	0.19	0.33	
C3(ry)	2.84	5.09	
C4(ry)	-0.85	-0.97	
C5(ry)	-0.04	0.04	
C6(ry)	-0.07	-0.04	
C11(ry)	8.58	8.41	
F12(ry)	-1.07	0.44	
F13(ry)	0.45	-1.84	
265.F14(ry)	-0.14	0.19	
S15(ry)	-0.14	0	
315.H16(ry)	6.26	7.2	
Others	0.22	0.16	
(Total deloc.)	-13.97	-10.32	
NLMO	-0.73	-0.73	

Table S14. Total contributions of Hyperconjugative terms for each orbital, as well as total Lewis and Repolarization contributions for the J_{HF} SSCC for *trans*-TFT. All values are in Hz.

	F12-H16		F12-H16
Contribution/ Orbital	Total	Contribution/ Orbital	Total
Lewis	15.89	Lewis	2.99
Repol.	-1.28	Repol.	-0.29
C3-C4*	0.25	62.C11-F13*	0.11
54.C3-C11*	0.69	63.C11-F14*	-0.03
61.C11-F12*	0.8	64.S15-H16*	0.66
62.C11-F13*	0.46	C2(ry)	-0.08
63.C11-F14*	0.28	C3(ry)	-0.23
64.S15-H16*	4.85	C4(ry)	0.16
C2(ry)	0	C5(ry)	0.01
C3(ry)	-1.57	C6(ry)	0.02
C4(ry)	0.35	C11(ry)	-0.15
C5(ry)	-0.52	F12(ry)	0.01
C6(ry)	-0.04	F13(ry)	-0.45
C11(ry)	-0.38	S15(ry)	-0.1
F12(ry)	-0.78	315.H16(ry)	0.06
F13(ry)	-0.13	Others	0.11
S15(ry)	0.25	(Total deloc.)	-0.09
315.H16(ry)	-1.08	NLMO	2.8
Others	0.54	-	-
(Total deloc.)	-3.96	-	-
NLMO	18.57	-	-

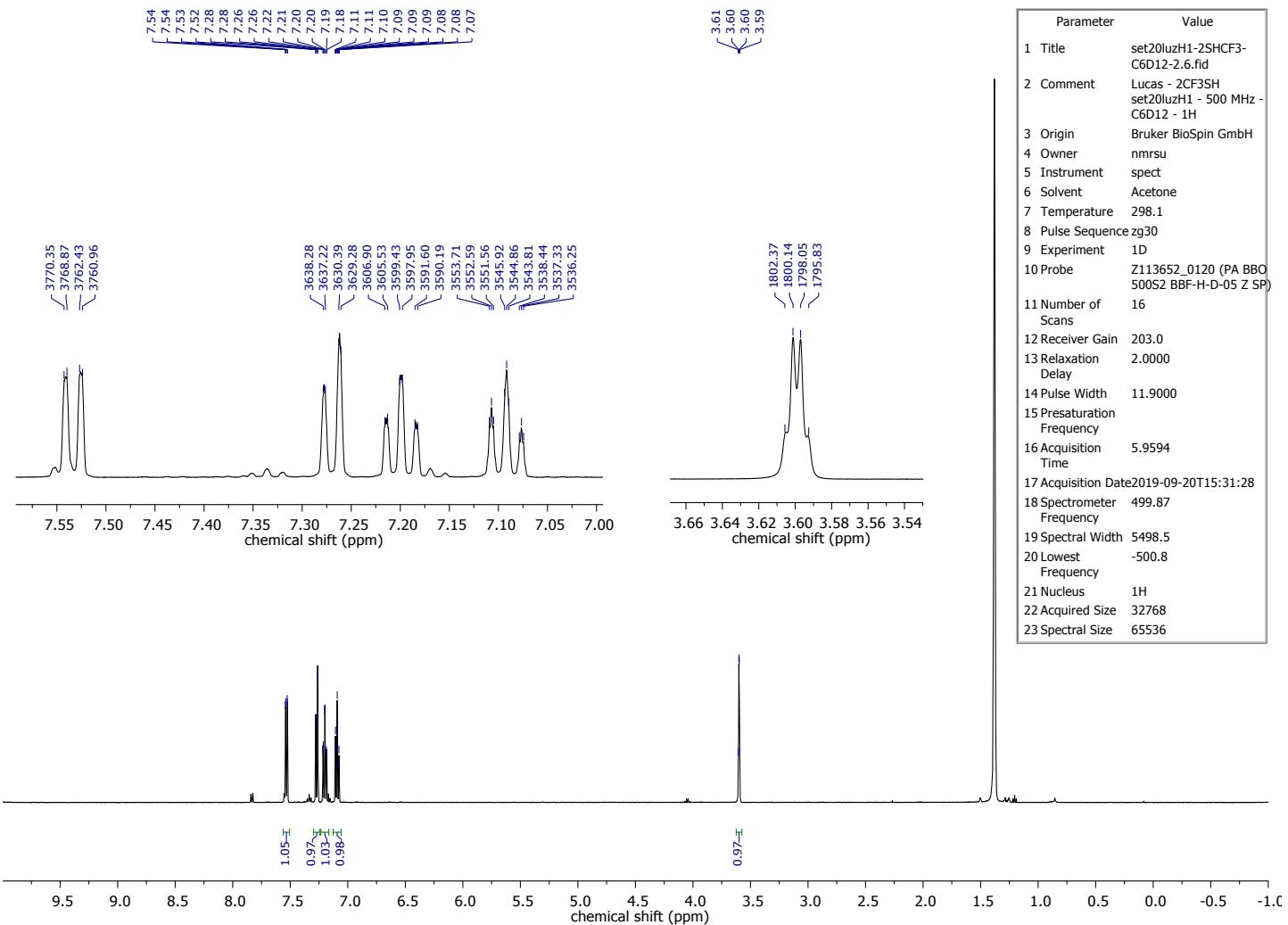


Figure S1. ^1H NMR Spectrum of 2-(trifluoromethyl)thiophenol in C_6D_{12} (500 MHz).

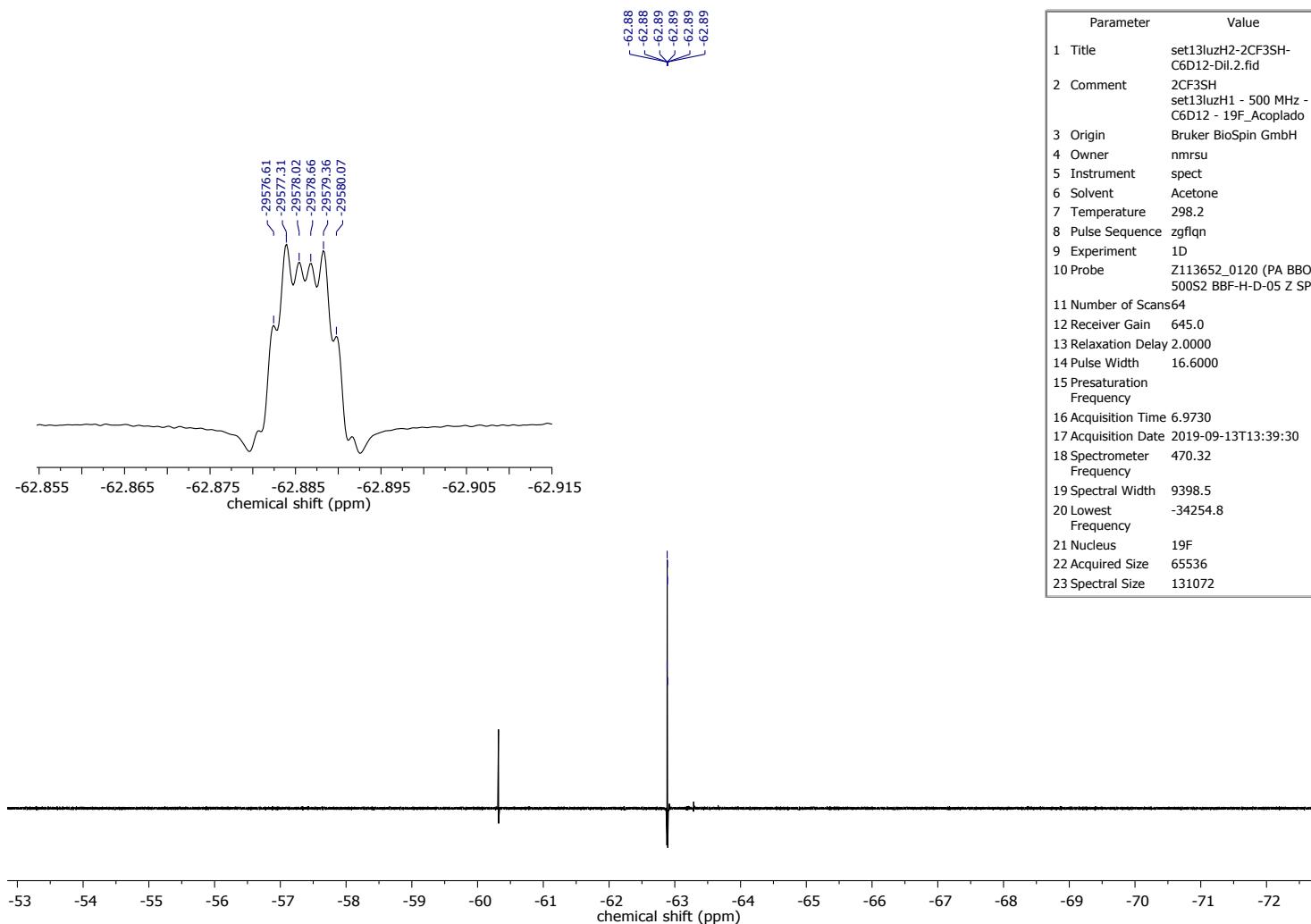


Figure S2. ^{19}F NMR Spectrum of 2-(trifluoromethyl)thiophenol in C_6D_{12} (470 MHz).

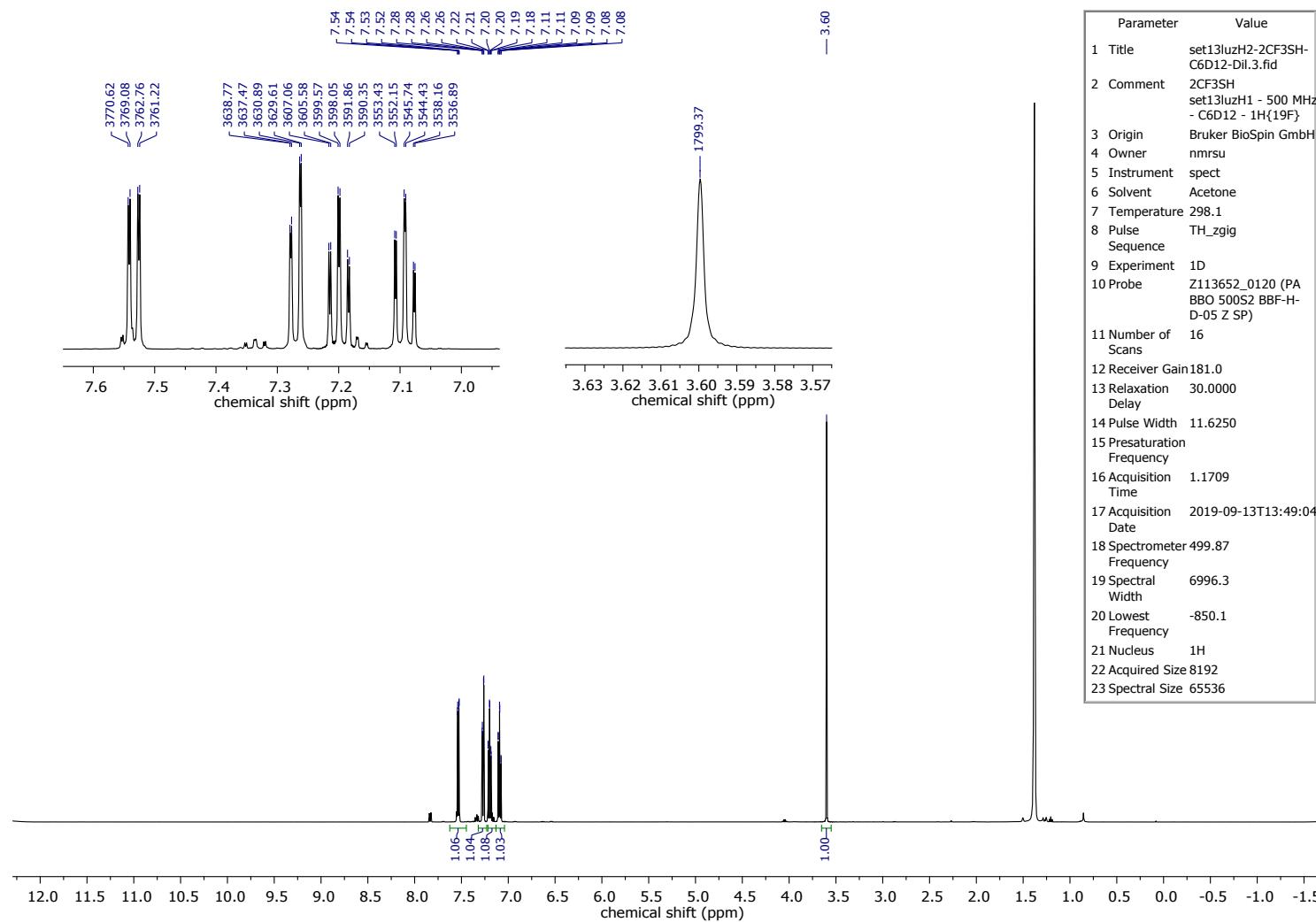


Figure S3. $^1\text{H}\{^{19}\text{F}\}$ NMR Spectrum of 2-(trifluoromethyl)thiophenol in C_6D_{12} (500 MHz).

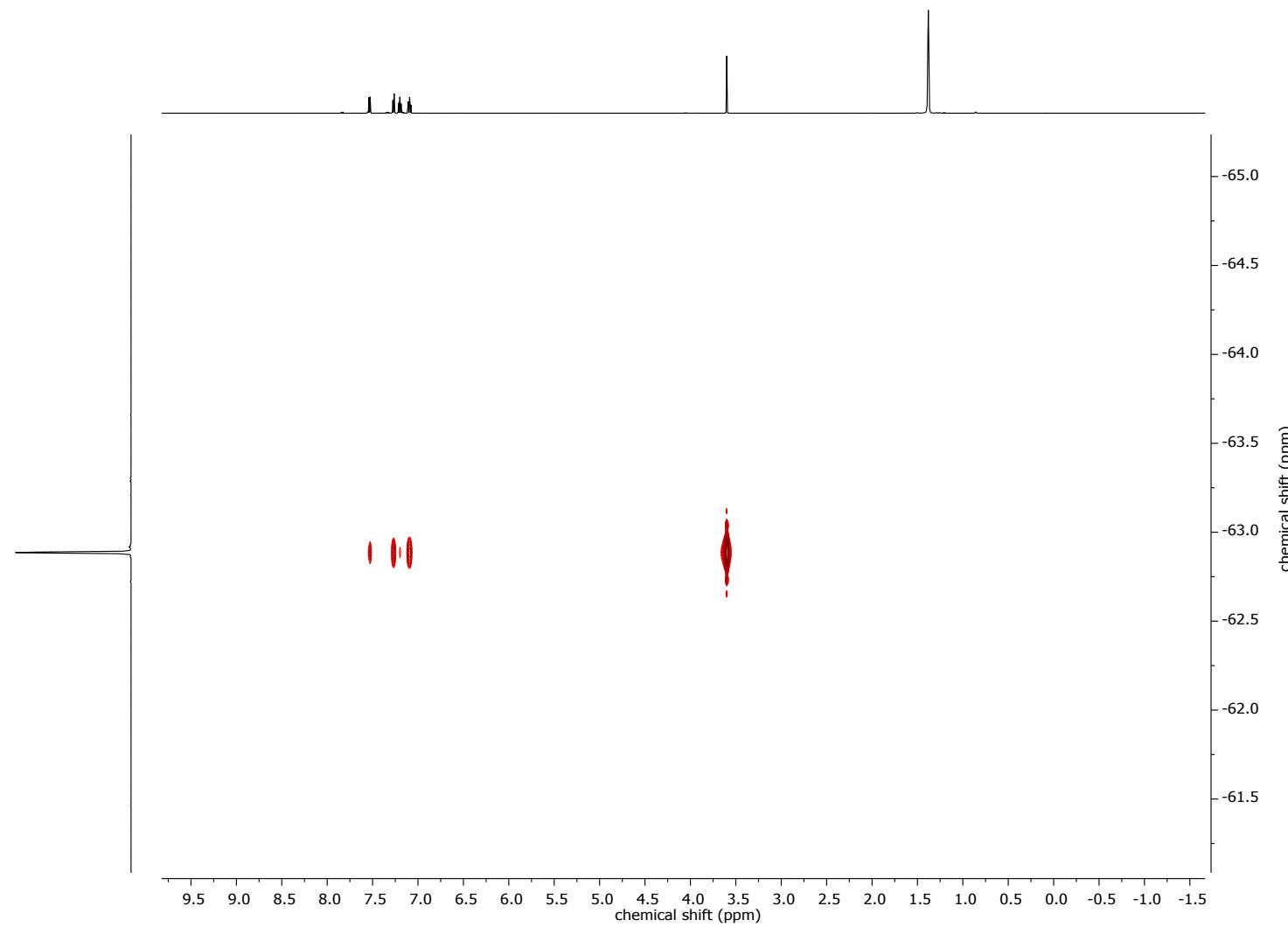


Figure S4. ^1H - ^{19}F { ^1H }-HETCOR Correlation Map of 2-(trifluoromethyl)thiophenol in C_6D_{12} (500 MHz).

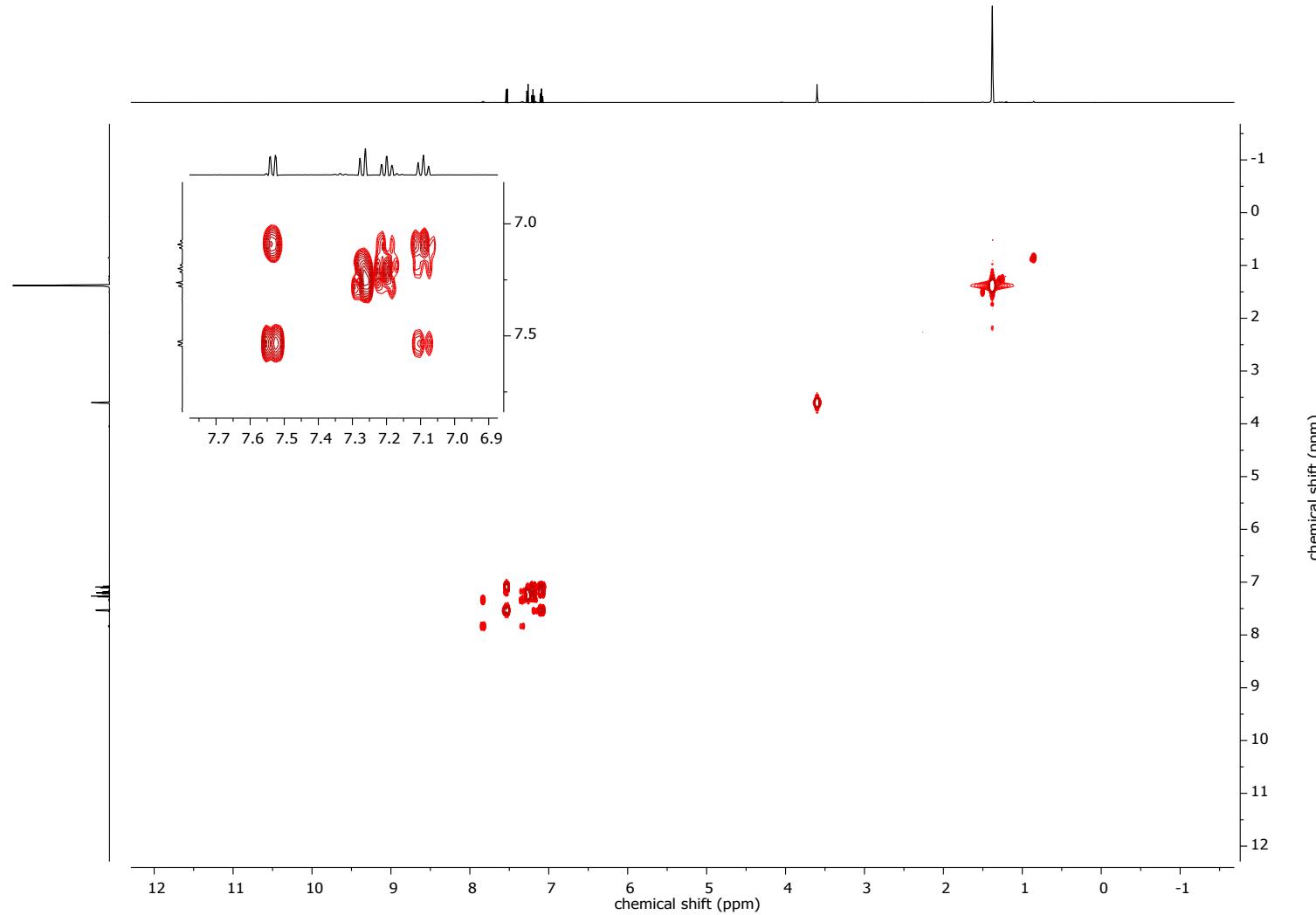


Figure S5. ^1H - ^1H -COSY Correlation Map of 2-(trifluoromethyl)thiophenol in C_6D_{12} (500 MHz).

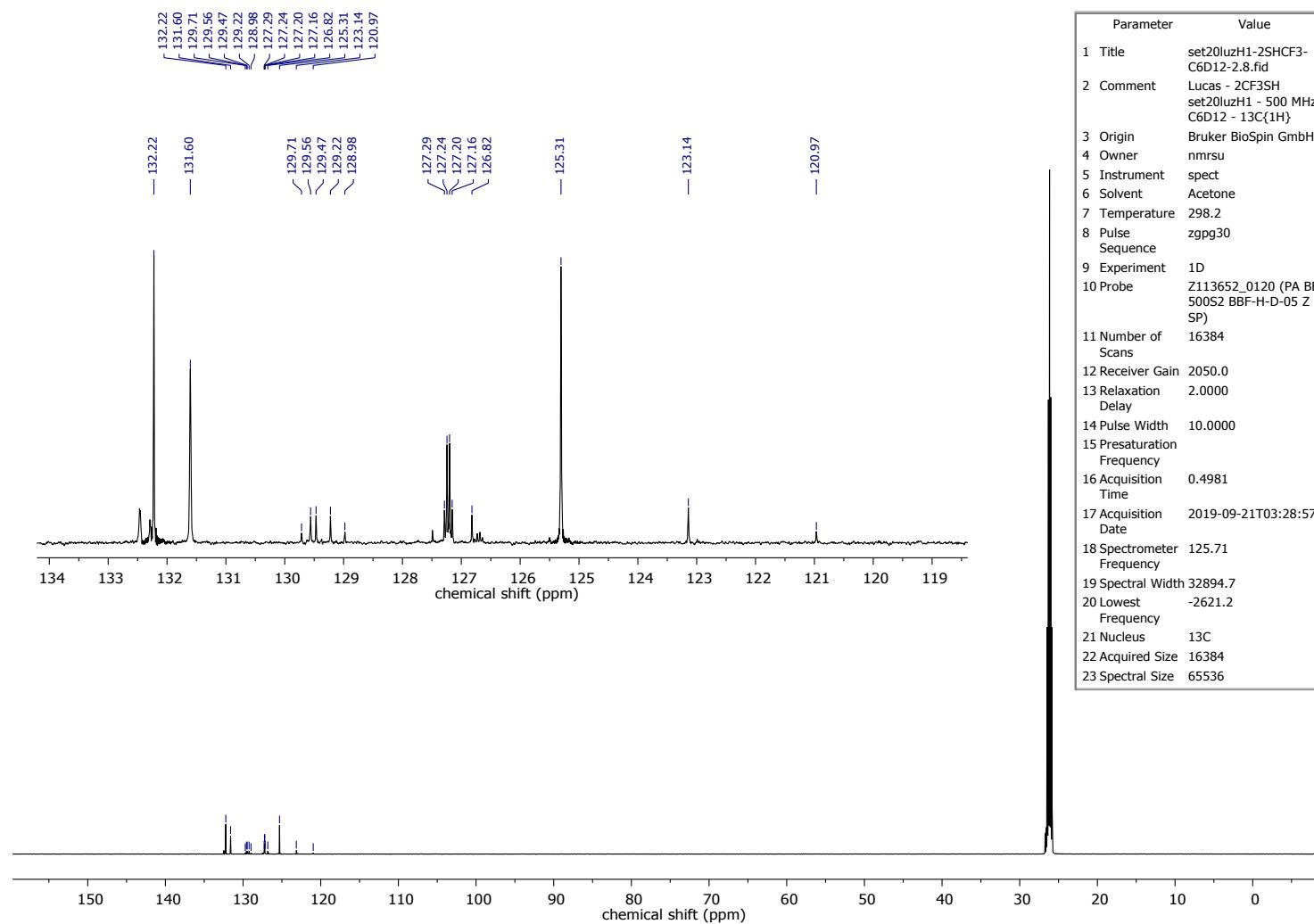


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 2-(trifluoromethyl)thiophenol in C_6D_{12} (126 MHz).

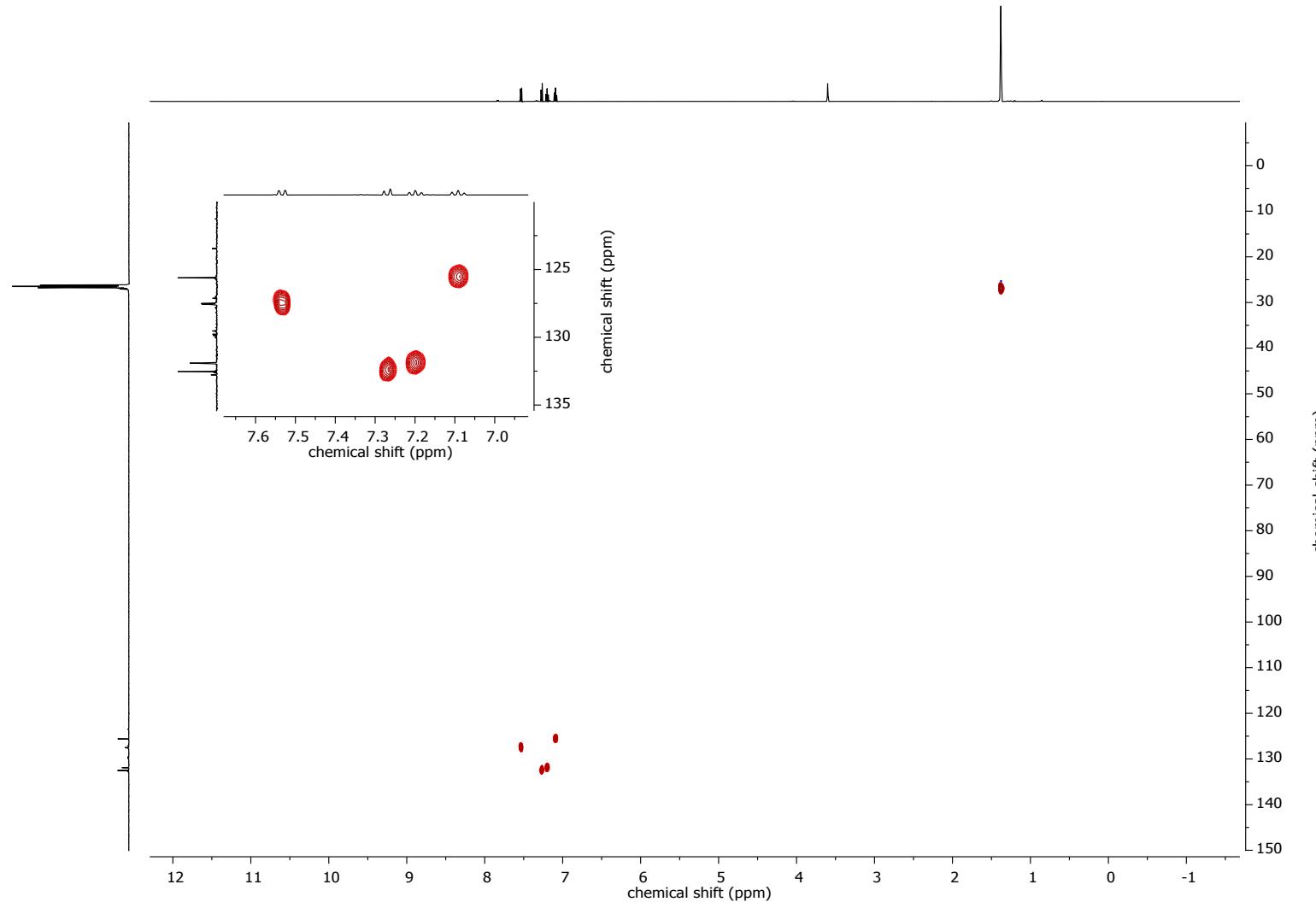


Figure S7. ^1H - $^{13}\text{C}\{^1\text{H}\}$ -HSQC Correlation Map of 2-(trifluoromethyl)thiophenol in C_6D_{12} (500 MHz).

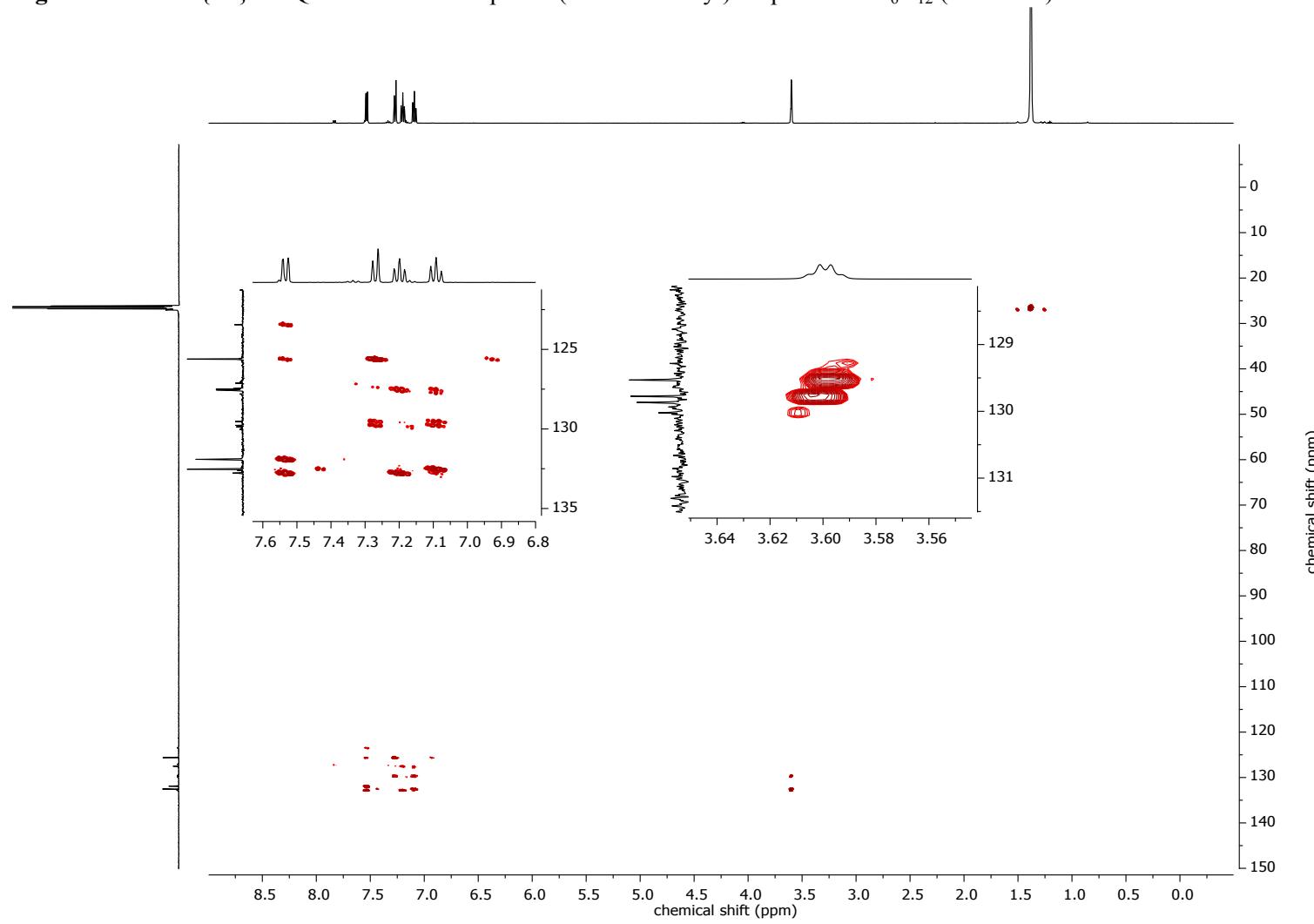


Figure S8. ^1H - $^{13}\text{C}\{^1\text{H}\}$ -HMBC Correlation Map of 2-(trifluoromethyl)thiophenol in C_6D_{12} (500 MHz).

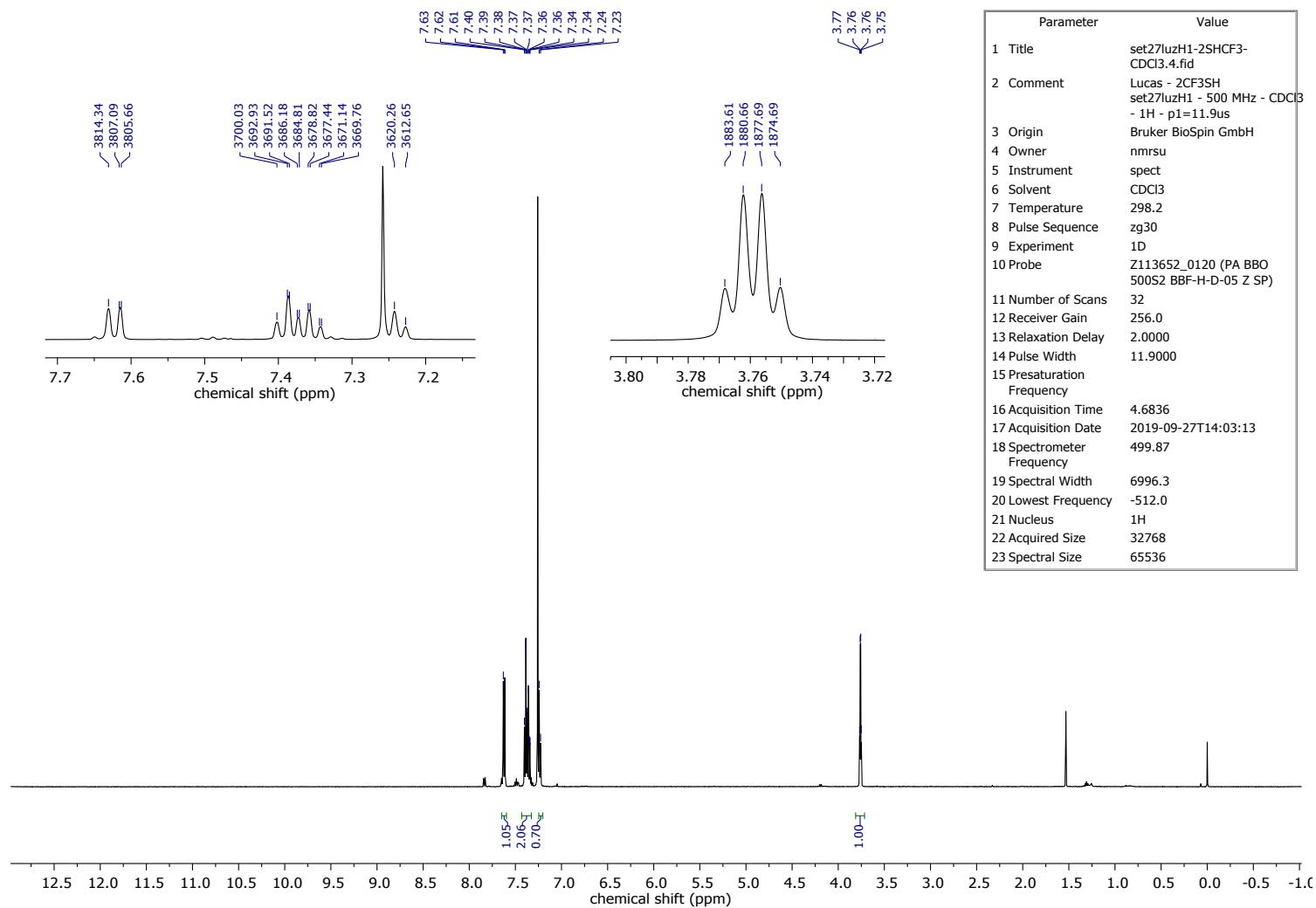


Figure S9. ^1H NMR Spectrum of 2-(trifluoromethyl)thiophenol in CDCl_3 (500 MHz).

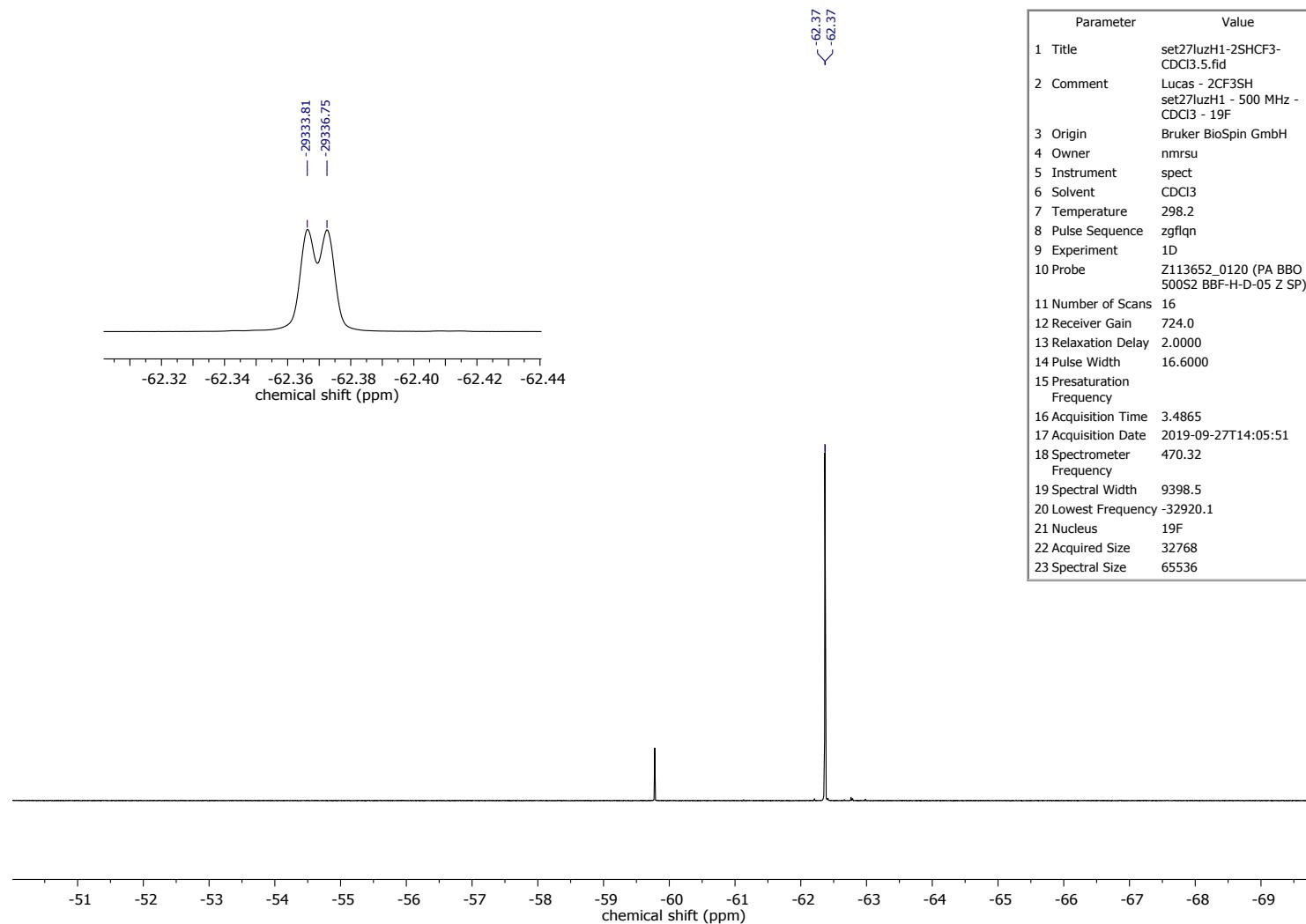


Figure S10. ^{19}F NMR Spectrum of 2-(trifluoromethyl)thiophenol in CDCl_3 (470 MHz).

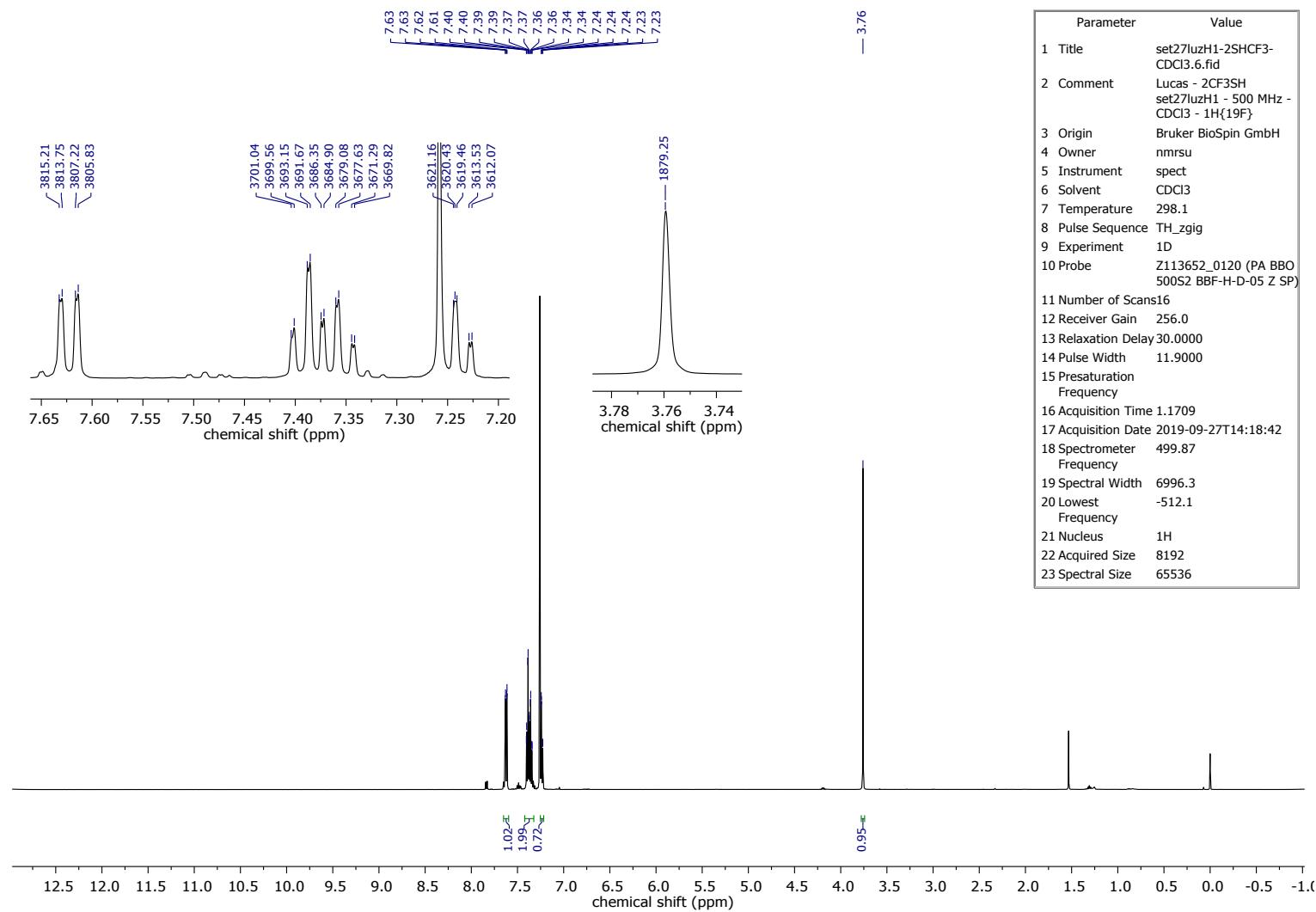


Figure S11. ^1H { ^{19}F } NMR Spectrum of 2-(trifluoromethyl)thiophenol in CDCl_3 (500 MHz).

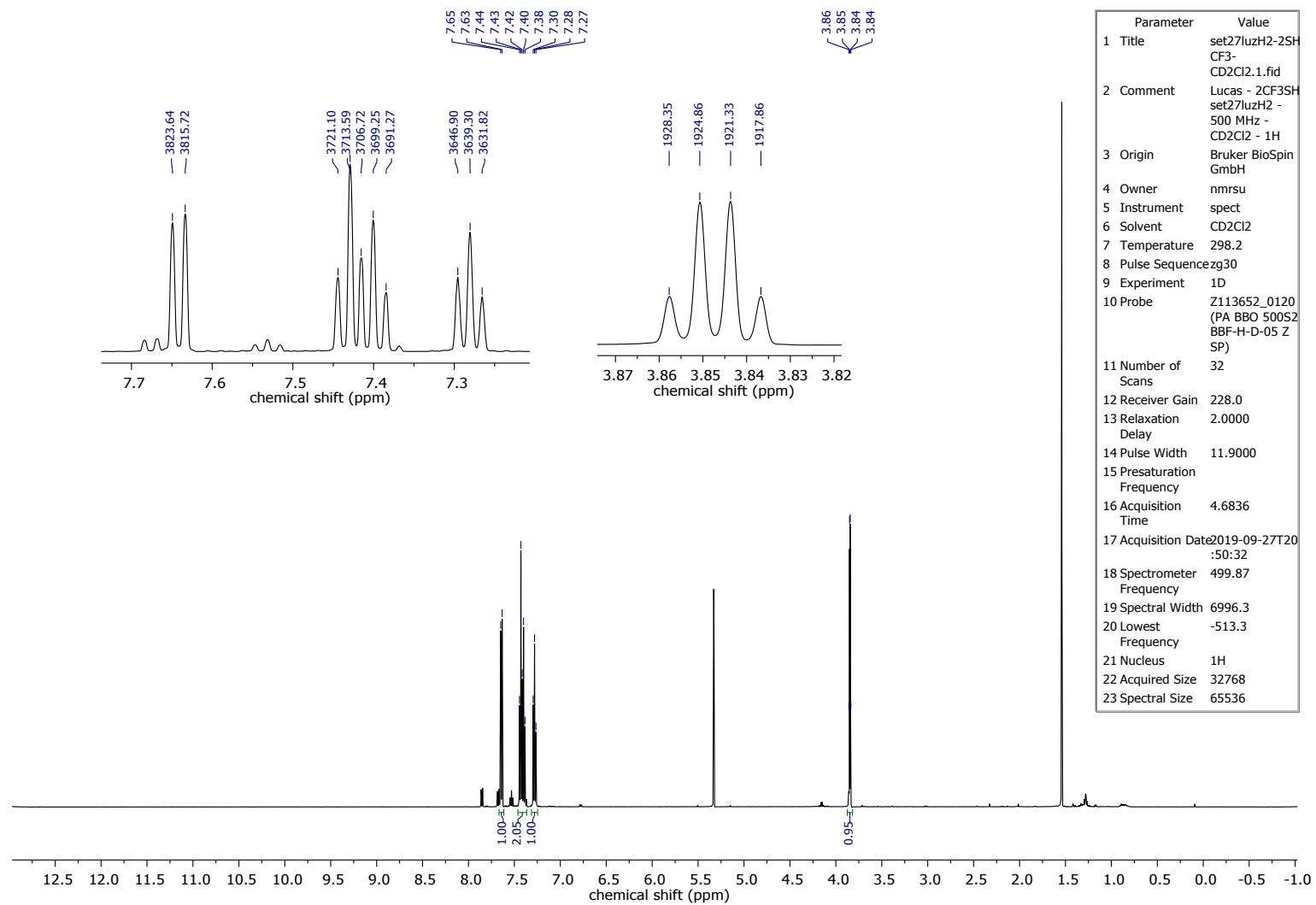


Figure S12. ^1H NMR Spectrum of 2-(trifluoromethyl)thiophenol in CD_2Cl_2 (500 MHz).

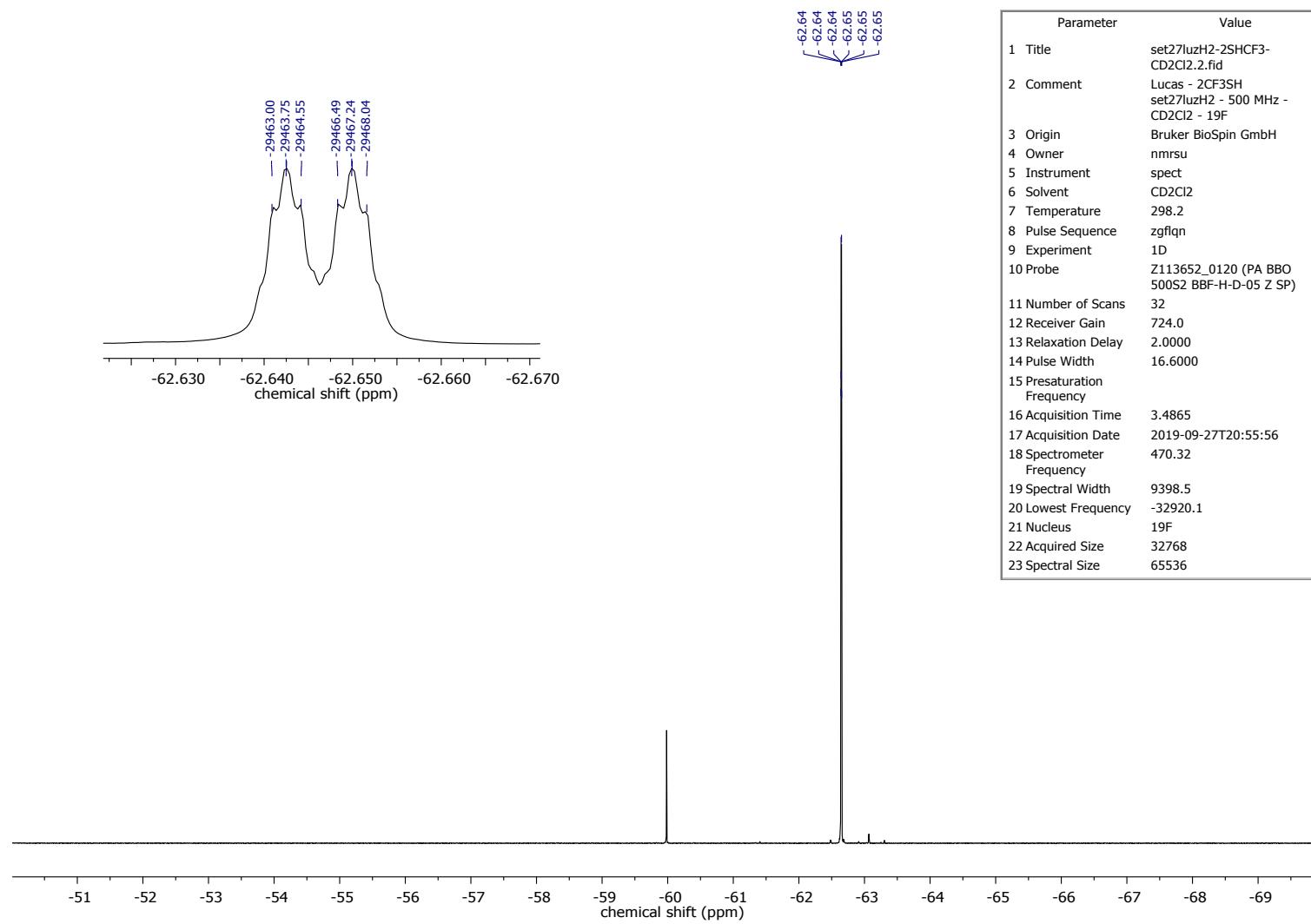


Figure S13. ^{19}F NMR Spectrum of 2-(trifluoromethyl)thiophenol in CD_2Cl_2 (470 MHz).

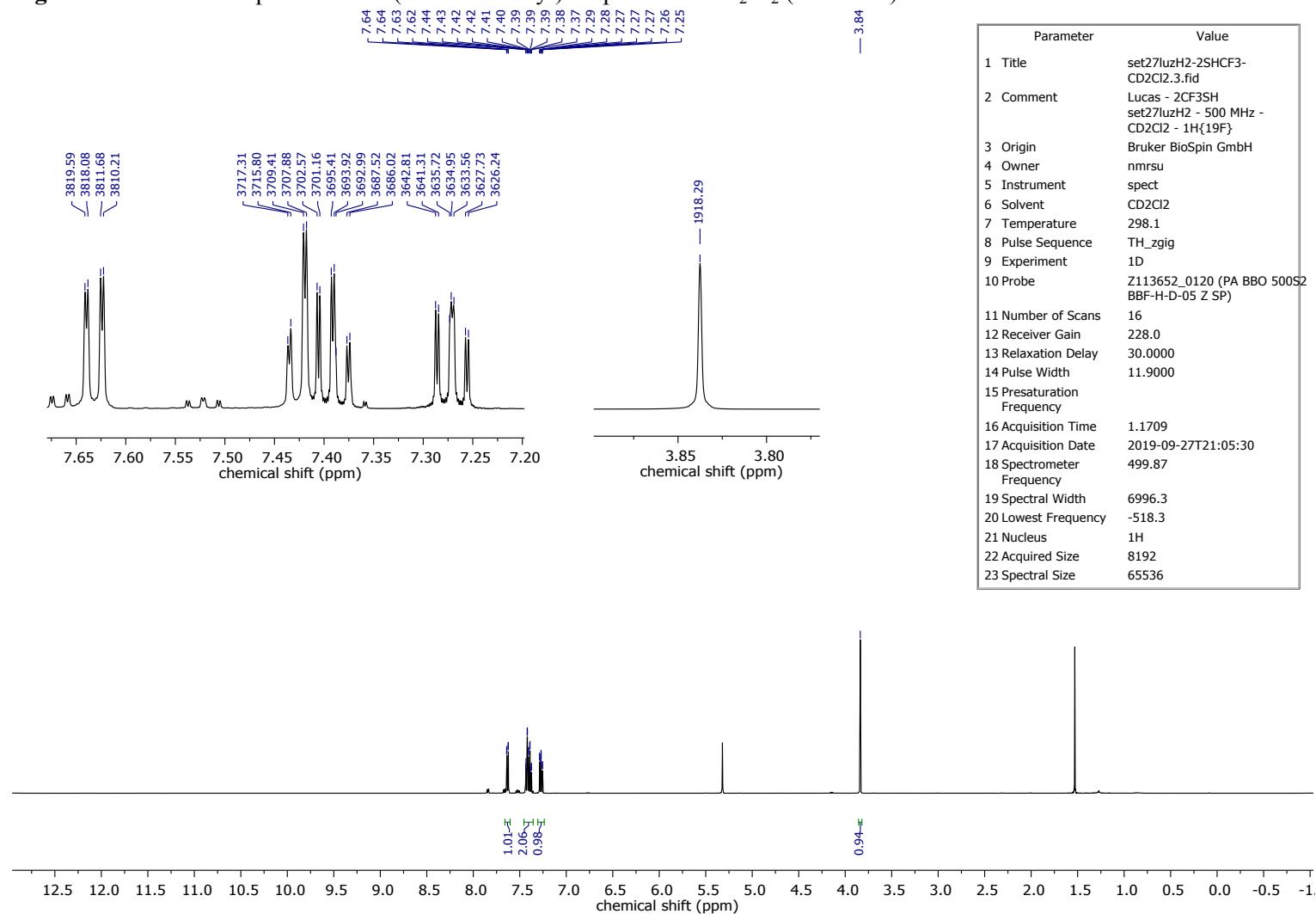


Figure S14. ^1H { ^{19}F } NMR Spectrum of 2-(trifluoromethyl)thiophenol in CD_2Cl_2 (500 MHz).

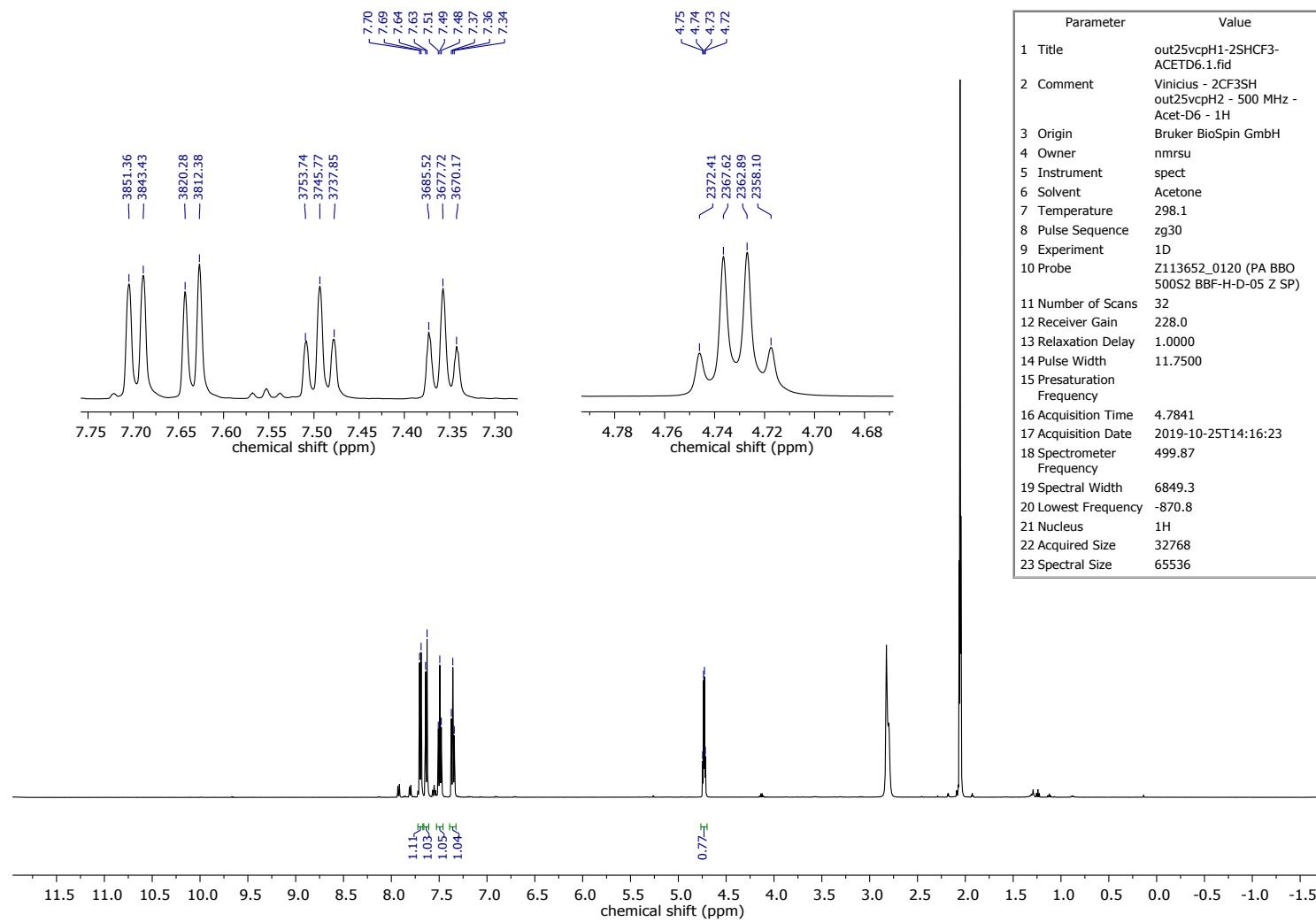
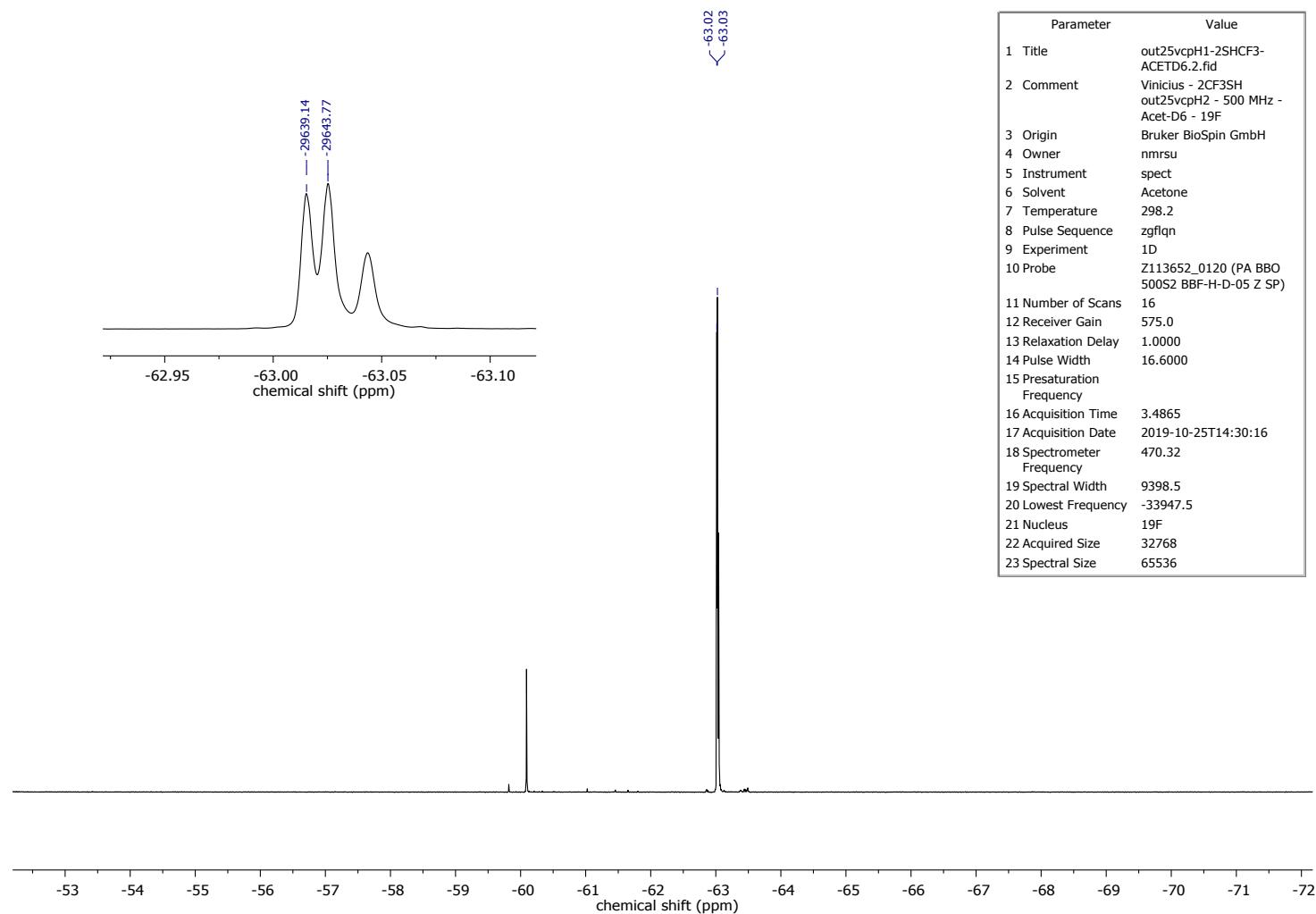


Figure S15. ^1H NMR Spectrum of 2-(trifluoromethyl)thiophenol in Acetone-d₆ (500 MHz).



Parameter	Value
1 Title	out25vcph1-2SHCF3-ACETD6.2.fid
2 Comment	Vinicio - 2CF3SH out25vcph2 - 500 MHz - Acet-D6 - 19F
3 Origin	Bruker BioSpin GmbH
4 Owner	nmsru
5 Instrument	spect
6 Solvent	Acetone
7 Temperature	298.2
8 Pulse Sequence	zgflqnm
9 Experiment	1D
10 Probe	Z113652_0120 (PA BBO 500S2 BBF-H-D-05 Z SP)
11 Number of Scans	16
12 Receiver Gain	575.0
13 Relaxation Delay	1.0000
14 Pulse Width	16.6000
15 Presaturation Frequency	
16 Acquisition Time	3.4865
17 Acquisition Date	2019-10-25T14:30:16
18 Spectrometer Frequency	470.32
19 Spectral Width	9398.5
20 Lowest Frequency	-33947.5
21 Nucleus	19F
22 Acquired Size	32768
23 Spectral Size	65536

Figure S16. ^{19}F NMR Spectrum of 2-(trifluoromethyl)thiophenol in Acetone-d₆ (470 MHz).

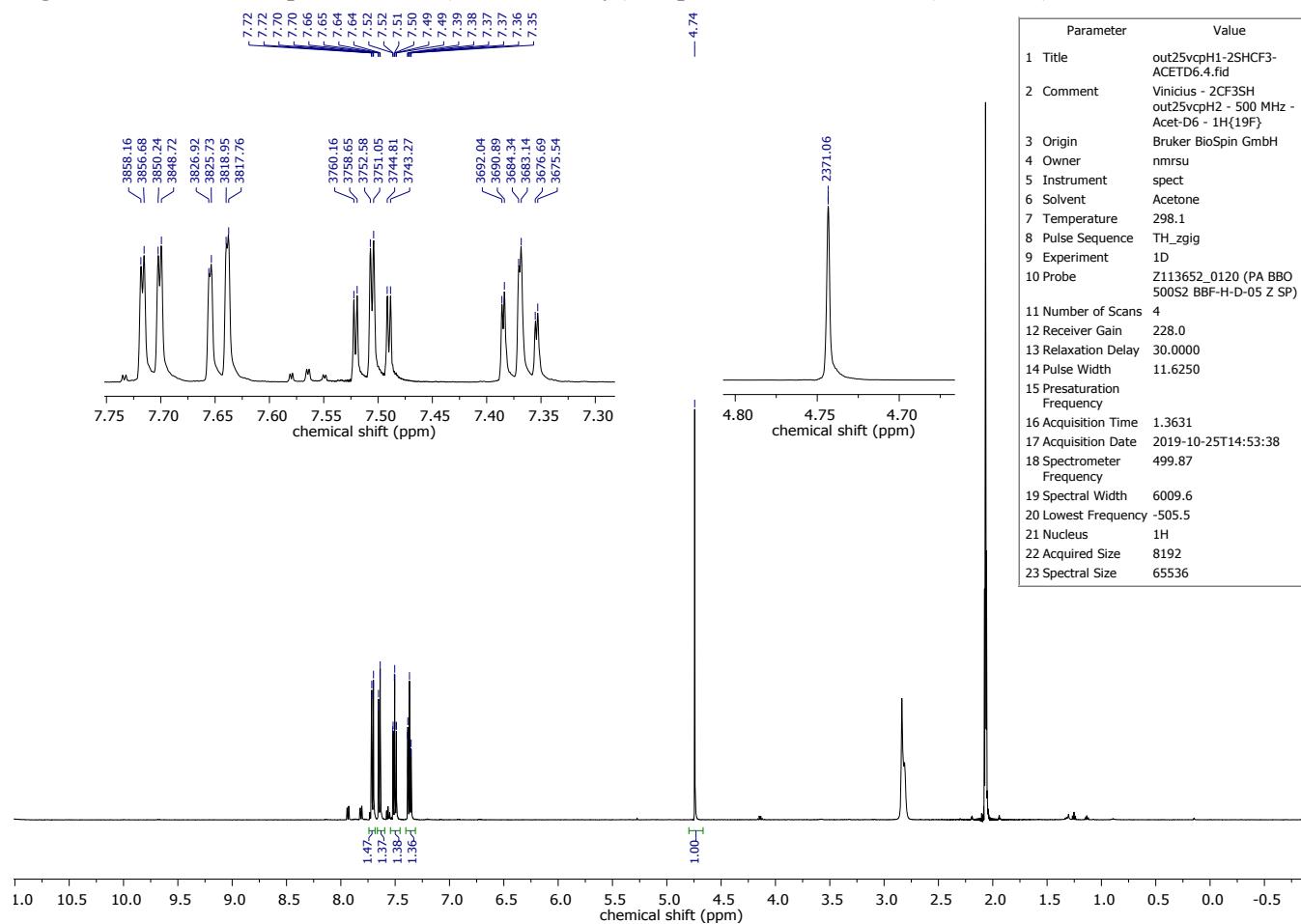


Figure S17. ^1H { ^{19}F } NMR Spectrum of 2-(trifluoromethyl)thiophenol in Acetone-d₆ (500 MHz).

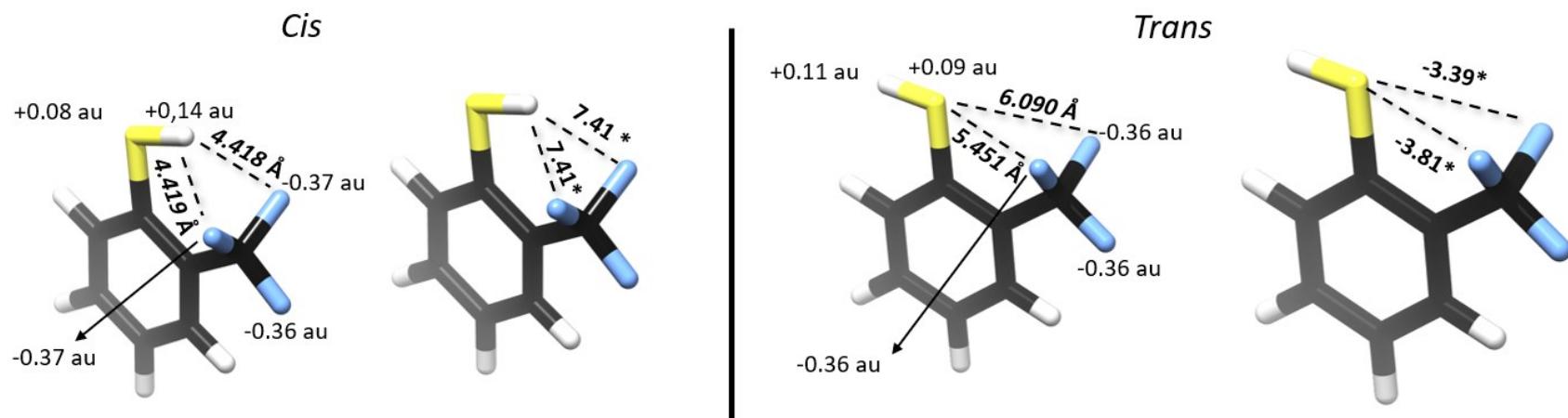


Figure S18 Main electrostatic interactions and charges obtained from the NCE analysis for *cis*-2-(trifluoromethyl)thiophenol and *trans*-2-(trifluoromethyl)thiophenol at the M06/cc-pVTZ level. * indicate values in kcal mol^{-1}

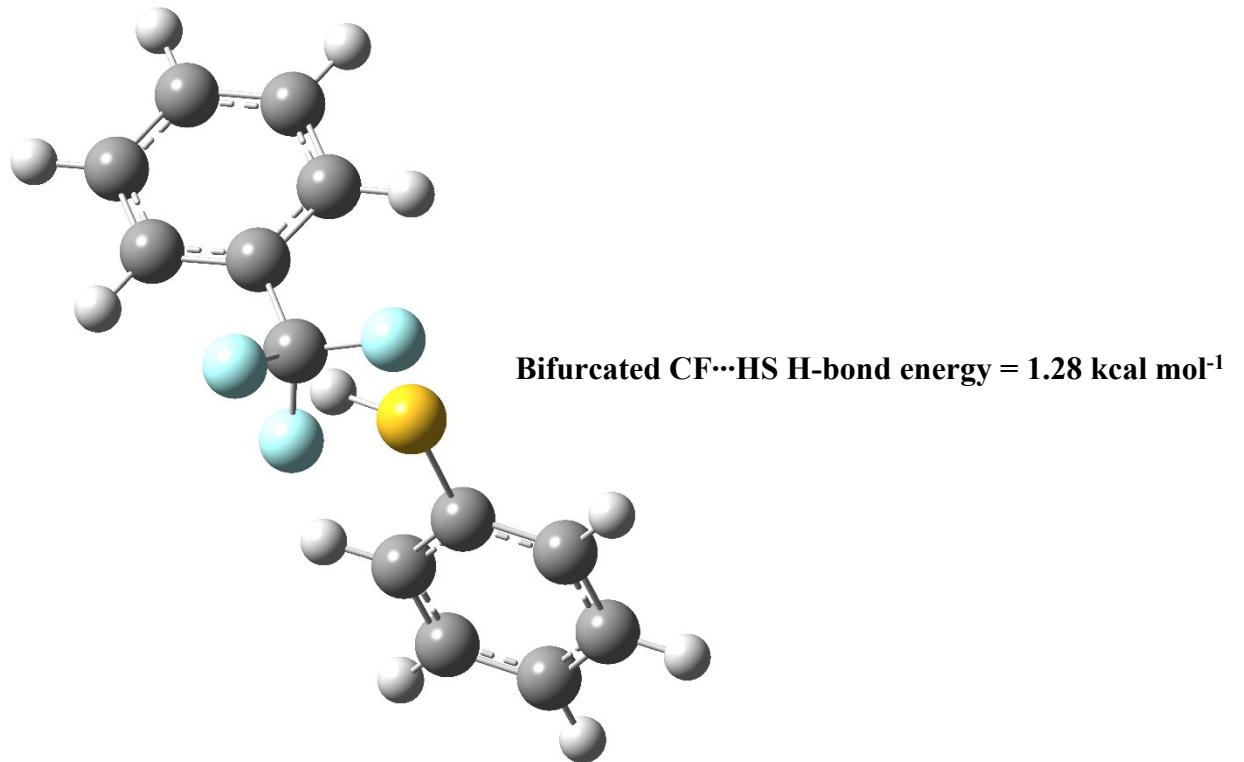
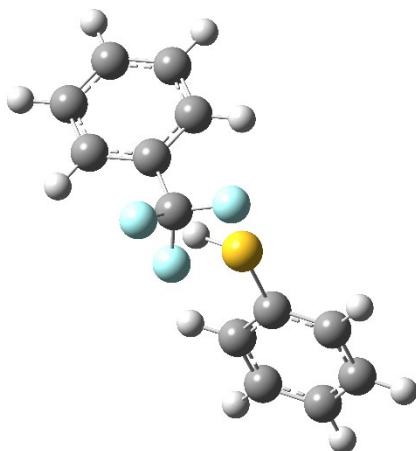


Figure S19: Dimer formed between (trifluoromethyl)benzene and thiophenol. The calculated M06-2X/6-311++G(d,p) $\text{CF}\cdots\text{HS}$ bifurcated H-bond energy is given in kcal mol⁻¹.

Table S15. Cartesian coordinates, counterpoise corrected energy (atomic units) and lowest harmonic vibrational frequency (cm^{-1}) for the dimer formed between (trifluoromethyl)benzene and thiophenol obtained at the M06-2X/6-311G(d,p) level.

Counterpoise corrected energy (au)= -1199.600921921930
 LHFV (cm^{-1})= 6.72



6	0	4.599562	-0.916529	-0.950635
6	0	4.085643	0.371624	-0.855430
6	0	3.029904	0.638366	0.016301
6	0	2.496991	-0.392213	0.790658
6	0	3.003527	-1.680723	0.674201
6	0	4.059067	-1.949117	-0.191650
1	0	5.420309	-1.113000	-1.630493
1	0	4.495238	1.168379	-1.465568
1	0	1.686643	-0.189955	1.481069
1	0	2.571144	-2.476084	1.269975
1	0	4.454793	-2.953739	-0.275447
16	0	2.434857	2.309184	0.126734
6	0	-1.102837	-0.185933	0.290980
9	0	-0.746702	0.714355	1.233452
6	0	-2.568593	-0.111309	-0.017410
6	0	-3.470725	-0.064577	1.042342
6	0	-3.012413	-0.125438	-1.333717
6	0	-4.832644	-0.027939	0.777587
1	0	-3.105309	-0.050924	2.062569
6	0	-4.379094	-0.087718	-1.591473
1	0	-2.297482	-0.158731	-2.146071
6	0	-5.286191	-0.039744	-0.539311
1	0	-5.540085	0.011582	1.596612
1	0	-4.732994	-0.093907	-2.614985
1	0	-6.349654	-0.009246	-0.743970
9	0	-0.337236	0.046102	-0.778226
9	0	-0.753938	-1.389012	0.777332
1	0	1.247384	2.003166	0.670877

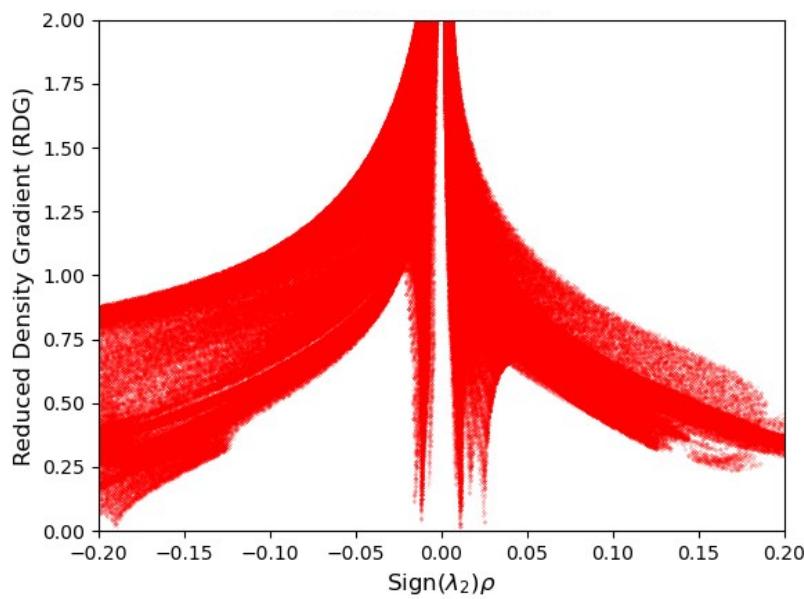
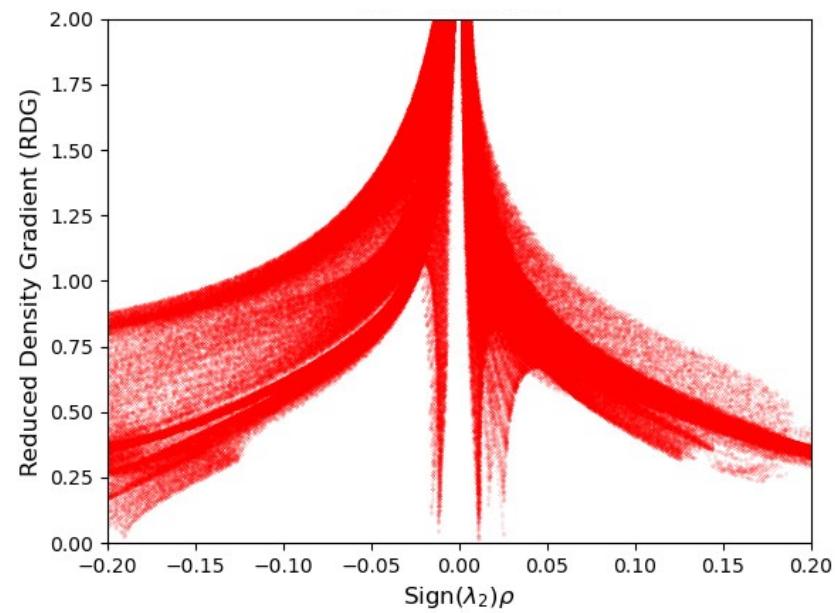


Figure S20. Reduced Density Gradient x Sign (λ_2) ρ obtained from NCI for *cis*-2-(trifluoromethyl)thiophenol (left) and *trans*-2-(trifluoromethyl)thiophenol (right) wavefunctions calculated at the M06/cc-pVTZ level.

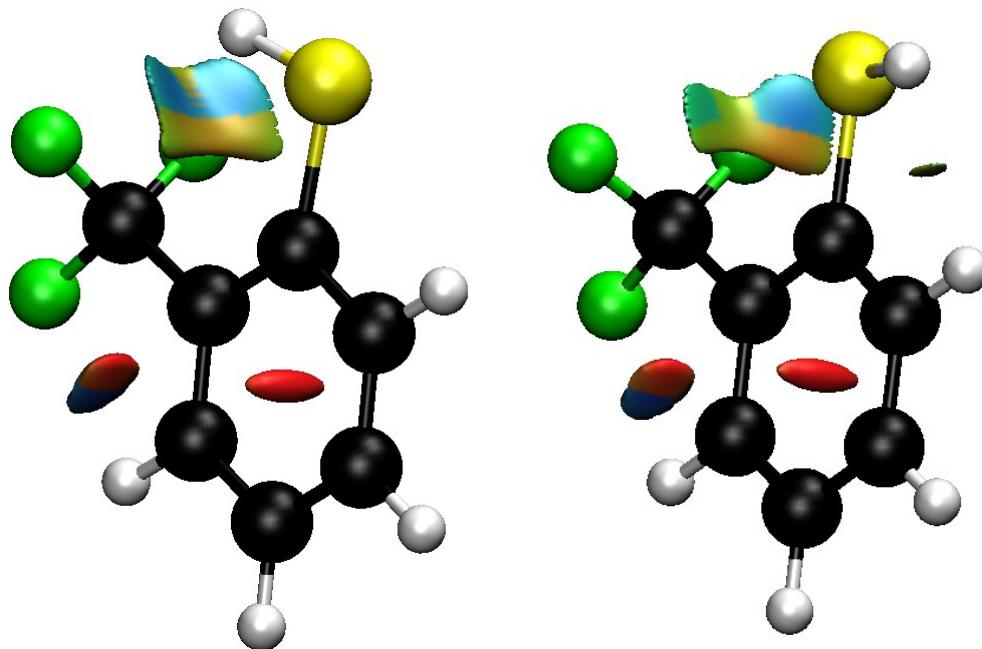


Figure S21. NCI isosurfaces for *cis*-TFT and *trans*-TFT obtained on M06/cc-pVTZ level electron densities, isosurfaces were plotted with an isovalue of 0.5 and a Color Scale Data Range from -0.2 to 0.2, with red surfaces representing steric crashes and blue surfaces representing stabilizing interactions.

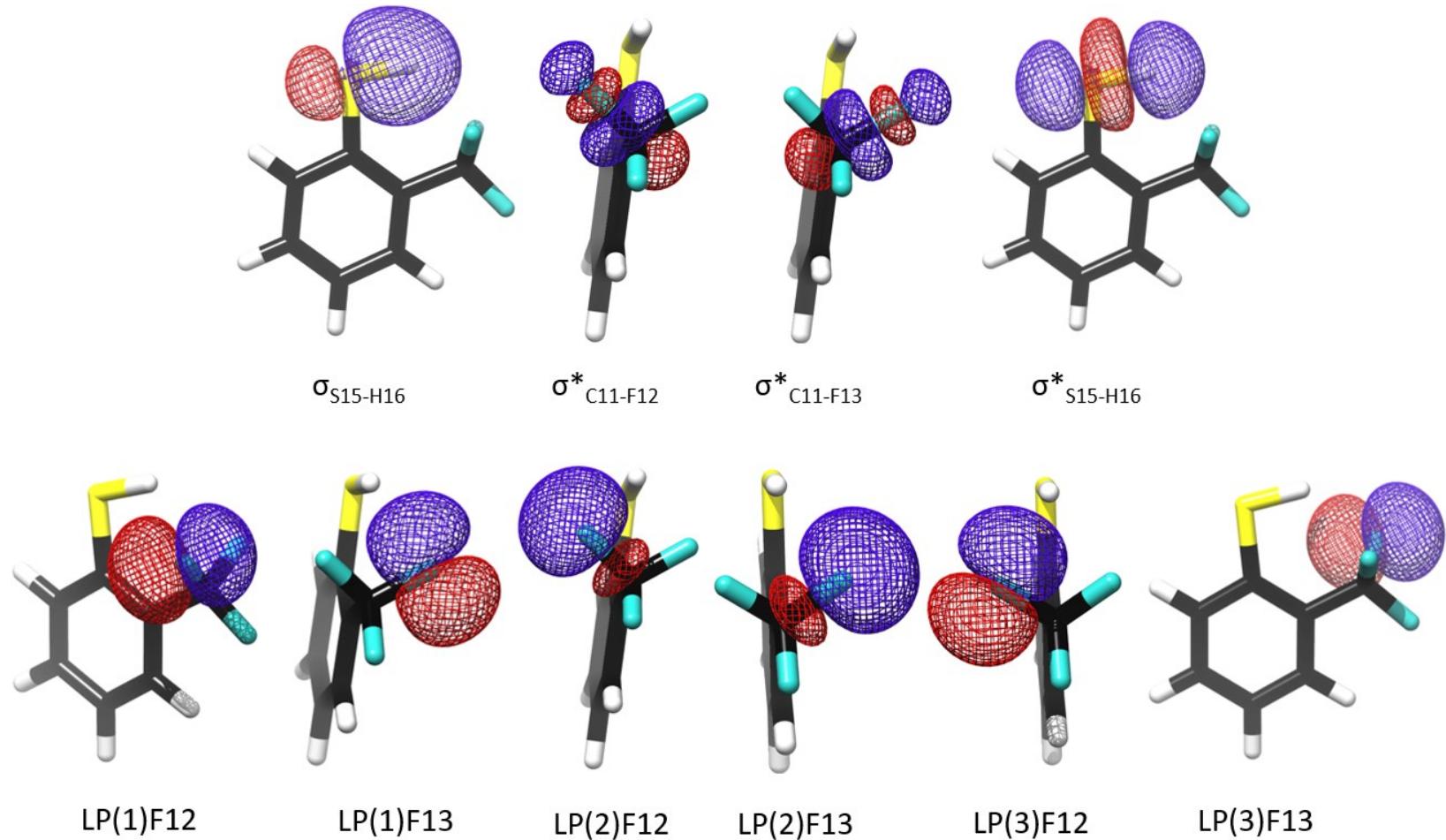


Figure S22. Orbitals that contribute to the *cis*-2-(trifluoromethyl)thiophenol $^{TS}J_{HF}$ SSCC Fermi contact calculated value. All orbital isosurfaces were obtained with isovalue of 0.02 au.

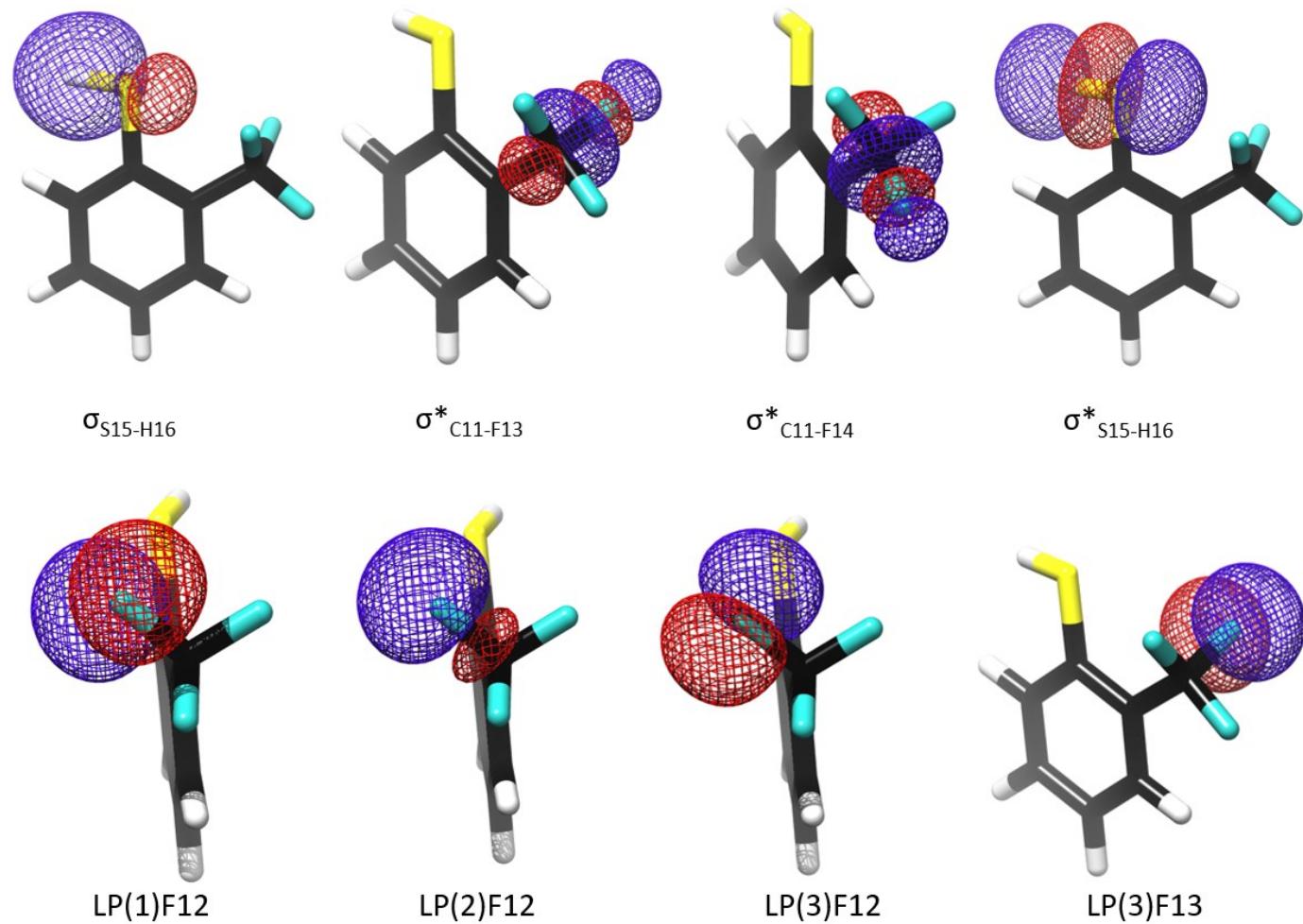


Figure S23. Orbitals that contribute to the *trans*-2-(trifluoromethyl)thiophenol ${}^{TS}J_{HF}$ SSCC Fermi contact calculated value. All orbital isosurfaces were obtained with isovalues of 0.02 a.u.

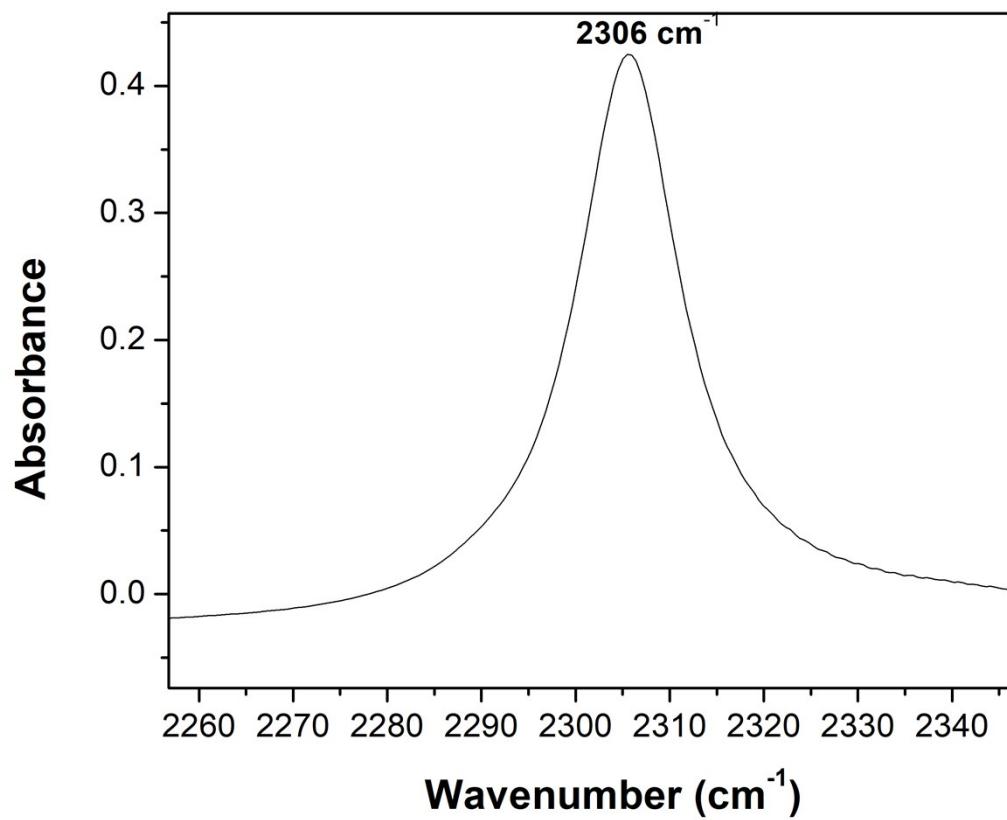


Figure S24: Experimental S-H bond stretch for 2-trifluoromethylphenol obtained in a 0.04 M concentration in CH_2Cl_2 .

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