Electronic Supplementary Material (ESI) for ChemComm.

The Pitfalls of Using J_{HF} Spin-Spin Coupling Constants to Infer Hydrogen Bond Formation in Organofluorine Compounds

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Computational Details

Conformational search calculations for all compounds were carried out in chloroform at the GFN2-xTB[1] level by applying the analytical linearized Poisson—Boltzmann (ALPB) solvent model to find the lowest energy conformers within calculated energies below than 100 kcal mol^{-1} using CREST 2.12 software.[2,3] This procedure resulted in two conformers for **1**-**3** . Compound **4** is rigid showing two conformers only for X = OH. The minima found for each compound were reoptimized and had their frequencies calculated at standard temperature and pressure values in ORCA 5.0.3 software using all possible combinations among M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets, considering the CPCM implicit solvent model. This procedure resulted in 36 theoretical levels for each conformer of each compound, being the best level for spin-spin coupling constant (SSCC) calculation for each case in comparison to experiment used for the remaining calculations (see below). Following this benchmarking study, PBE0/aug-pcJ-1/CPCM(chloroform) showed the best results in comparison to experiment for compounds **1** and **4** and B3LYP/aug-pcJ-1/CPCM(chloroform) for compounds **2** and **3**, respectively. This way, all further calculations were run in the most accurate theoretical level for each compound.

Spin-spin coupling constant calculations were run at the same level of optimization/frequency calculations for all levels, as this procedure showed to increase accuracy, since triplet instabilities are typically less pronounced close to the optimised equilibrium geometries.[4,5] Explicit solvation was run in a 50 ps GFN2-xTB metadynamics, being the most stable structure in the ensamble with five explicit solvent molecules reoptimized by QM/MM calculations at the best benchmark study identified DFT theoretical level in the QM region (solute plus one solvent molecule) and GFN2-xTB for the MM region (four solvent molecules) and considering the CPCM implicit solvent model to account for medium dielectric constant. The SSCC was then calculated for this DFT reoptimized geometry and compared with experiment. Also, SSCCs were decomposed into its FC (Fermi Contact), SD (Spin Dipolar), PSO (Paramagnetic Spin Orbit) and DSO (Diamagnetic Spin Orbit) Ramsey terms.

Natural Bond Orbitals[6] (NBO) calculations, including the, Natural Steric Analysis[7] (NSA) and Natural J-Coupling[8] (NJC) analysis were run for all molecules using the NBO 7.0 program.[9] 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,[10] using wave functions calculated at the best level identified by the benchmark studies. NCI isosurfaces were obtained for the same wave functions used for QTAIM calculations using the NCIPLOT V4.0 program.[11,12,13]

Results

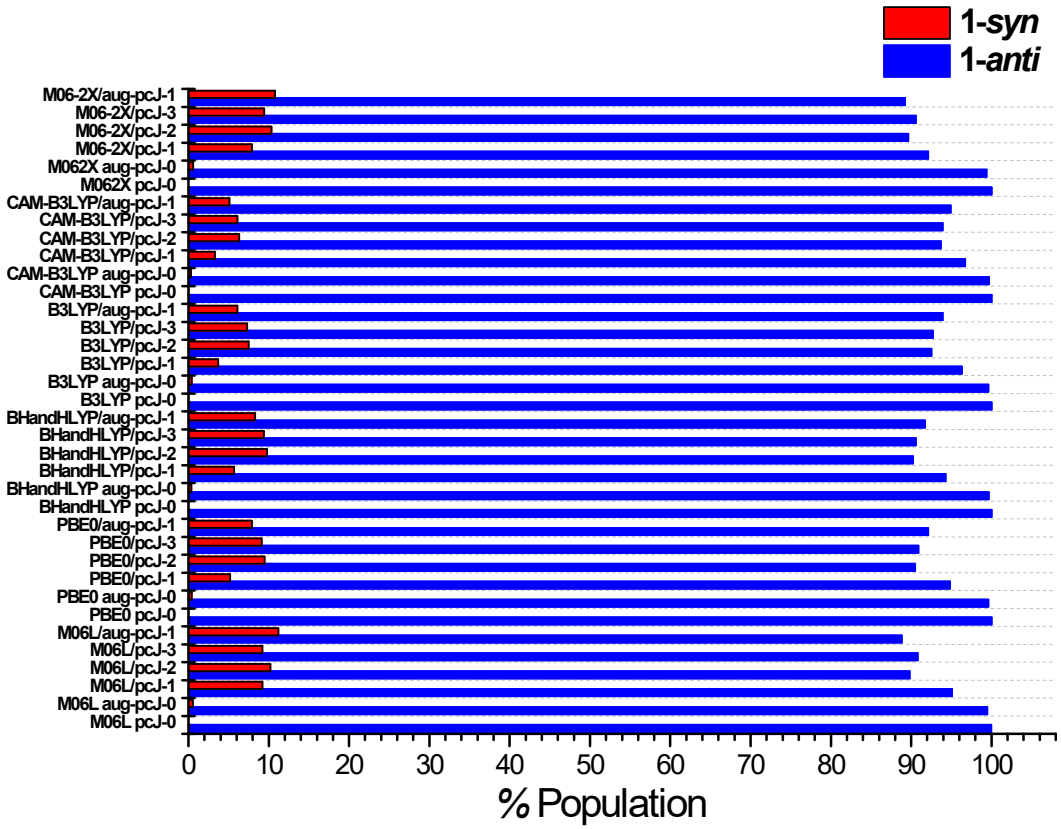


Figure S1. Conformer populations (*syn* vs *anti*) for **1** obtained at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model).

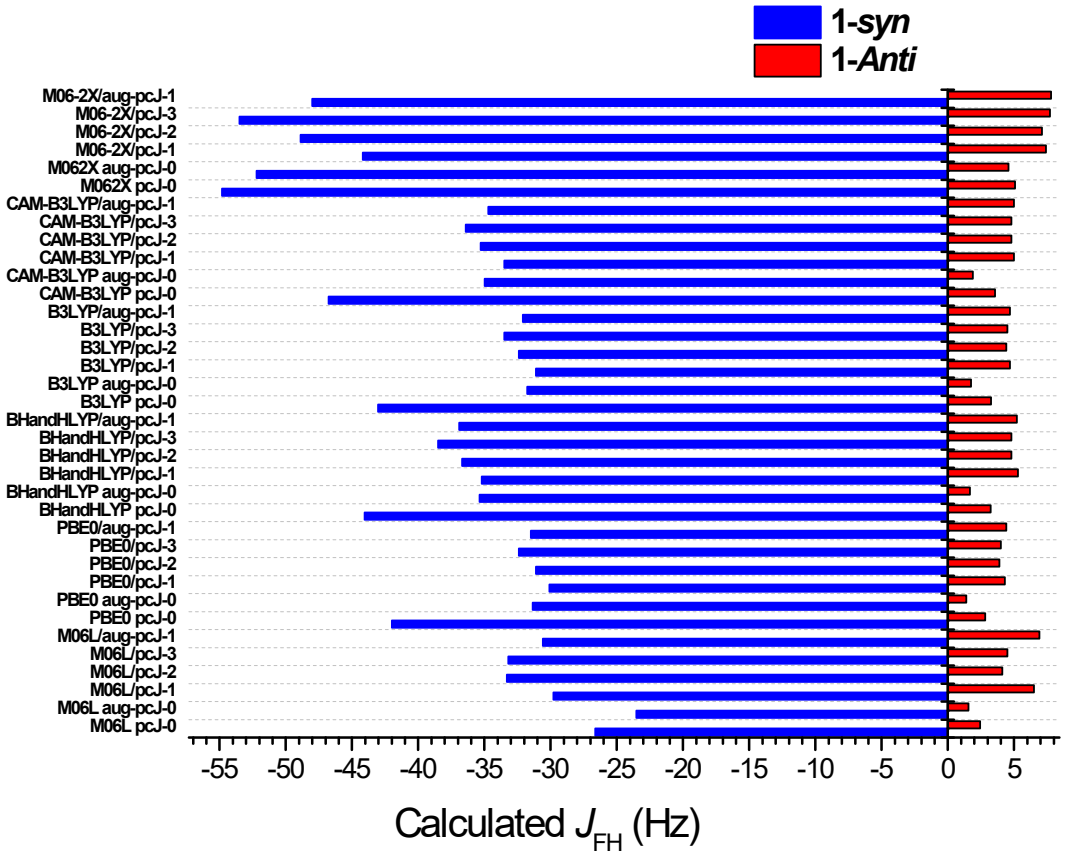


Figure S2. SSCCs obtained for for **1** *syn* and *anti* conformers obtained at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model).

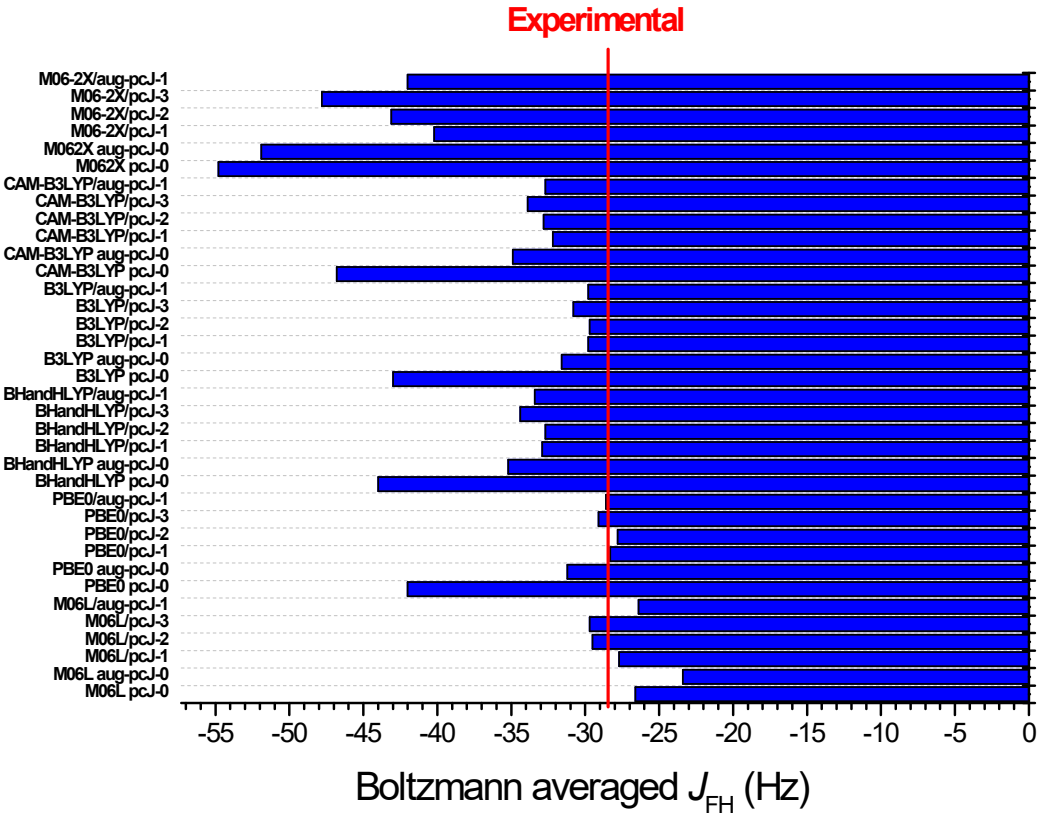
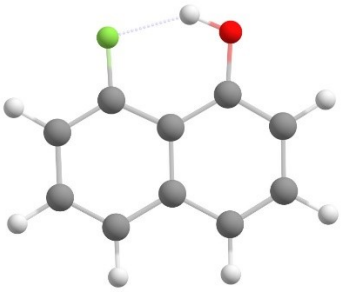


Figure S3. Boltzmann averaged SSCCs obtained from **1-*syn*** and **1-*anti*** conformers at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model). The experimental value (28.4 Hz is shown as a line in red for comparison).

Table S1. Cartesian coordinates (angstroms), absolute energy (atomic units) and lowest harmonic vibrational frequency (cm^{-1}) for the conformers of **1** obtained at the PBE0/aug-pcJ-1/CPCM(chloroform) level.

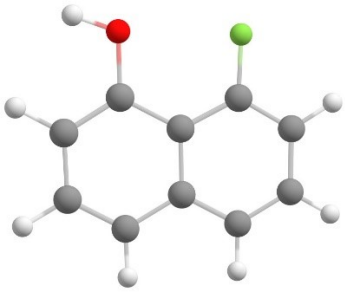


1-*syn*

Gibbs Free Energy (au)= -559.65498809

LHVF (cm^{-1})= 81.67

C	-1.257551	0.755030	0.000014
C	0.020247	0.153868	0.000006
C	0.046131	-1.277174	-0.000002
C	-1.176437	-1.994539	-0.000016
C	-2.382381	-1.345579	-0.000009
C	-2.430471	0.063628	0.000005
H	-3.369549	0.603822	0.000011
F	-1.327998	2.114414	0.000028
H	-1.136718	-3.078441	-0.000027
H	-3.309279	-1.907592	-0.000018
C	1.258477	0.862181	0.000005
C	2.447556	0.169376	0.000017
C	2.460748	-1.235114	0.000015
C	1.289477	-1.949177	0.000005
O	1.329834	2.213321	-0.000009
H	3.372509	0.734608	0.000023
H	3.413737	-1.752931	0.000023
H	1.298079	-3.033407	0.000001
H	0.446186	2.595747	0.000012



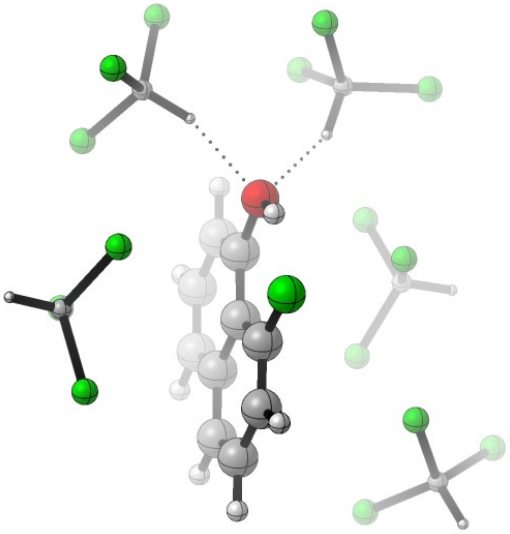
1-*anti*

Energy (au)= -559.65267387

LHVF (cm^{-1})= 63.64

C	-1.254644	0.774079	0.000011
C	0.019640	0.158546	0.000009
C	0.040232	-1.272789	0.000006
C	-1.181218	-1.989575	-0.000001
C	-2.384886	-1.335728	-0.000007
C	-2.426095	0.071575	0.000002
H	-3.364632	0.613174	0.000002
F	-1.336095	2.115692	0.000025
H	-1.143124	-3.073560	-0.000006
H	-3.313826	-1.894989	-0.000016
C	1.264785	0.853227	0.000003
C	2.449837	0.153356	0.000001
C	2.456371	-1.252556	0.000006
C	1.280275	-1.954730	0.000008
O	1.242113	2.206491	-0.000002
H	3.386148	0.703538	-0.000006
H	3.406308	-1.776006	0.000008
H	1.279490	-3.039105	0.000011
H	2.146769	2.535197	-0.000008

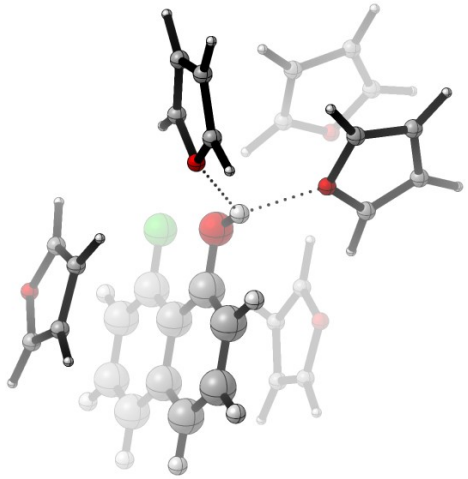
Table S2. Cartesian coordinates (angstroms), absolute energy (atomic units) and lowest harmonic vibrational frequency (cm^{-1}) for the most stable microsolvated ensemble of **1** and five THF molecules calculated at QM/MM: PBE0/aug-pcJ-1:GFN2-xTB/CPCM($CHCl_3$). The solute and the explicit $CHCl_3$ molecules directly coordinated to the O atom were also included in the QM region.



6	-1.782878000	-0.619064000	0.967045000
6	-1.133703000	0.182523000	0.005097000
6	-1.859609000	0.454471000	-1.194664000
6	-3.170877000	-0.057447000	-1.340547000
6	-3.751338000	-0.812079000	-0.357719000
6	-3.044304000	-1.106898000	0.824144000
1	-3.472401000	-1.711852000	1.613390000
9	-1.108290000	-0.930004000	2.107817000
1	-3.710771000	0.160454000	-2.255310000
1	-4.758227000	-1.192571000	-0.483024000
6	0.168876000	0.734290000	0.152316000
6	0.733023000	1.467630000	-0.860987000
6	0.017778000	1.713096000	-2.045497000
6	-1.249775000	1.222490000	-2.211999000
8	0.902751000	0.570672000	1.287816000
1	1.732909000	1.863231000	-0.721078000
1	0.484229000	2.297127000	-2.830740000
1	-1.804418000	1.414781000	-3.123340000
1	0.404863000	0.039333000	1.919423000
6	1.360105000	-2.233828000	-1.890650000
17	2.606360000	-0.990906000	-2.074834000
1	1.754685000	-3.185504000	-2.251187000
17	-0.062465000	-1.807169000	-2.842960000
17	0.921903000	-2.419796000	-0.191120000
6	3.867356000	-0.643326000	1.155016000
17	4.822229000	0.497643000	0.194925000
1	2.820802000	-0.445192000	0.959160000
17	4.133984000	-0.401099000	2.886164000
17	4.222434000	-2.311909000	0.689294000
6	1.392218000	3.482403000	2.691463000

17	1.307854000	2.868832000	4.349284000
1	1.054024000	2.689337000	2.036763000
17	3.052494000	3.887592000	2.240097000
17	0.326512000	4.878286000	2.483012000
6	-2.568450000	-4.263734000	-2.466292000
17	-2.100123000	-3.798164000	-0.826895000
1	-3.362384000	-5.010240000	-2.407891000
17	-1.189334000	-4.974835000	-3.313215000
17	-3.172802000	-2.860134000	-3.352872000
6	-2.711577000	3.181923000	1.597926000
17	-4.227227000	2.378504000	1.161688000
1	-2.938120000	4.109275000	2.126760000
17	-1.789553000	3.569132000	0.138409000
17	-1.770742000	2.147193000	2.670667000

Table S3. Cartesian coordinates (angstroms), absolute energy (atomic units) and lowest harmonic vibrational frequency (cm^{-1}) for the most stable microsolvated ensemble of **1** and five THF molecules calculated at QM/MM: PBE0/aug-pcJ-1:GFN2-xTB/CPCM(THF). The solute and the explicit THF molecules directly coordinated to the H(O) atom were included in the QM region.



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6	-2.115486501	0.612541947	-2.575341368
6	-2.906425137	1.677212247	-3.054515448
6	-3.018188704	2.845098456	-2.355474906
6	-2.340998141	3.007979120	-1.141479277
1	-2.421868107	3.923909200	-0.578145601
9	-0.928607337	2.179315417	0.510045737
1	-3.426875917	1.547064593	-3.991993947
1	-3.628671591	3.653294421	-2.729270355
6	-0.630488604	-0.317686282	-0.865906556
6	-0.539307615	-1.477539167	-1.598818249
6	-1.223496470	-1.614349312	-2.809499622
6	-1.997064744	-0.595808618	-3.290604660
8	0.016517460	-0.165818171	0.306773497
1	0.067817160	-2.290015392	-1.224440160
1	-1.132492246	-2.538936287	-3.360688508
1	-2.528572408	-0.699566111	-4.224472775
1	0.521253036	-0.966794324	0.515007803
8	-4.230087565	0.591724356	0.325921728
6	-4.600677683	-0.250143373	-0.651539586
6	-4.012261815	-1.464450785	-0.487429044
6	-3.218599503	-1.355055208	0.680860768
6	-3.391621318	-0.083414923	1.128830310
1	-2.605781874	-2.116137267	1.117056269
1	-2.985847680	0.443195810	1.969521672
1	-5.274337270	0.127019002	-1.394657082
1	-4.122019352	-2.324637946	-1.114887410
8	1.653837340	1.031368142	-2.505450791
6	1.644811012	2.163064809	-1.778225774
6	0.938906626	3.132360003	-2.417351970

6	0.481856670	2.550174753	-3.625882718
6	0.947429160	1.273960365	-3.622946378
1	-0.111840244	3.018169706	-4.383577411
1	0.844218736	0.468882932	-4.322543004
1	2.169735768	2.153725286	-0.843905719
1	0.762280437	4.131489620	-2.076502671
8	-0.168907886	-2.604169468	1.991350267
6	0.188981464	-3.816625260	2.446506678
6	0.449773214	-3.768470313	3.779816270
6	0.233366243	-2.421891386	4.167764379
6	-0.140621351	-1.762218065	3.039680941
1	0.340824793	-2.011750176	5.150820146
1	-0.399070165	-0.739493366	2.851239447
1	0.220189132	-4.620147557	1.737287703
1	0.755352727	-4.580062637	4.407822685
8	2.400879520	-1.908555266	0.515290836
6	3.129179947	-1.162313366	-0.339082291
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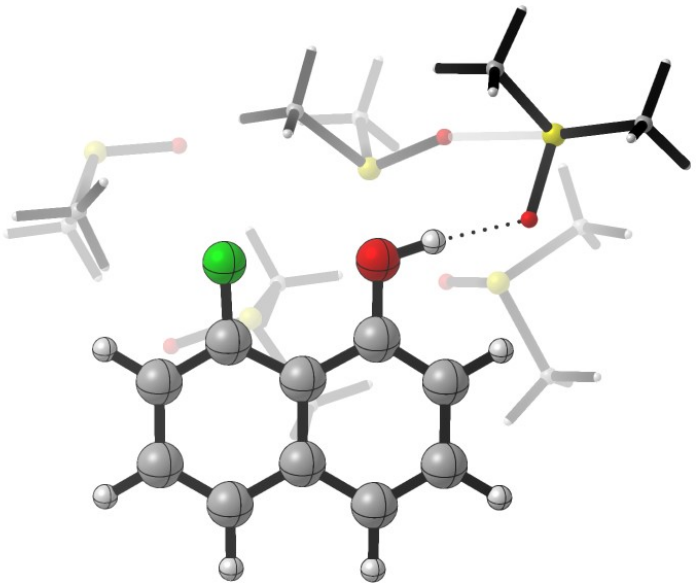
1	5.430182573	-2.418923486	1.592094205
1	2.855120785	-3.114266420	2.135381481
1	2.602592340	-0.626473415	-1.103617502
1	5.259820597	-0.770945765	-0.548032743
8	3.354586584	1.792392855	1.309183295
6	4.492762027	1.467447809	1.944175539
6	4.237009004	0.635274538	2.987678535
6	2.833953492	0.435677521	2.988801761
6	2.351535001	1.165057114	1.947518278
1	2.268932662	-0.168012569	3.669017947
1	1.358486843	1.312854952	1.572322236
1	5.404065056	1.885690241	1.565501447
1	4.949154081	0.215016328	3.667672140

Table S4. Cartesian coordinates (angstroms), absolute energy (atomic units) and lowest harmonic vibrational frequency (cm^{-1}) for the most stable microsolvated ensemble of **1** and five DMSO molecules calculated at QM/MM: PBE0/aug-pcJ-1:GFN2-xTB/CPCM(DMSO). The solute and the explicit DMSO molecule directly coordinated to the H(O) atom was included in the QM region.



6	0.311887000	-1.775770000	1.873845000
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6	2.161909000	-1.234414000	3.851364000
6	2.045380000	-2.503559000	3.352991000
6	1.101806000	-2.781999000	2.350435000
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9	-0.594387000	-2.097132000	0.938925000
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1	0.454422000	4.726509000	-2.292644000
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1	1.769476000	3.516123000	1.083579000
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1	1.947912000	4.636503000	-0.283610000
8	1.294041000	2.232415000	-1.518259000
16	2.264229000	-1.055101000	-0.667003000
6	3.108333000	0.258770000	0.296472000
6	2.903864000	-0.466960000	-2.280657000
1	2.500940000	-1.116963000	-3.049044000
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1	2.914325000	0.094927000	1.350670000
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1	-1.094438000	0.333654000	-4.231076000
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1	-2.506358000	-1.156226000	-2.621401000
1	-2.090085000	-1.420158000	-0.903648000
8	-1.797879000	1.394206000	-1.885216000
16	1.152722000	-4.210591000	-2.881137000
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1	1.549021000	-3.812439000	-0.537673000
1	1.067389000	-5.509053000	-0.866324000
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1	3.246257000	-5.348855000	-2.557201000
8	0.850700000	-2.786917000	-3.139832000
16	-3.215152000	2.978171000	-0.968440000
6	-4.398209000	1.625160000	-1.022240000
6	-4.417244000	4.217910000	-0.385854000
1	-5.152803000	4.406015000	-1.168374000
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1	-5.183708000	1.879947000	-1.734819000
1	-4.800281000	1.499784000	-0.017294000
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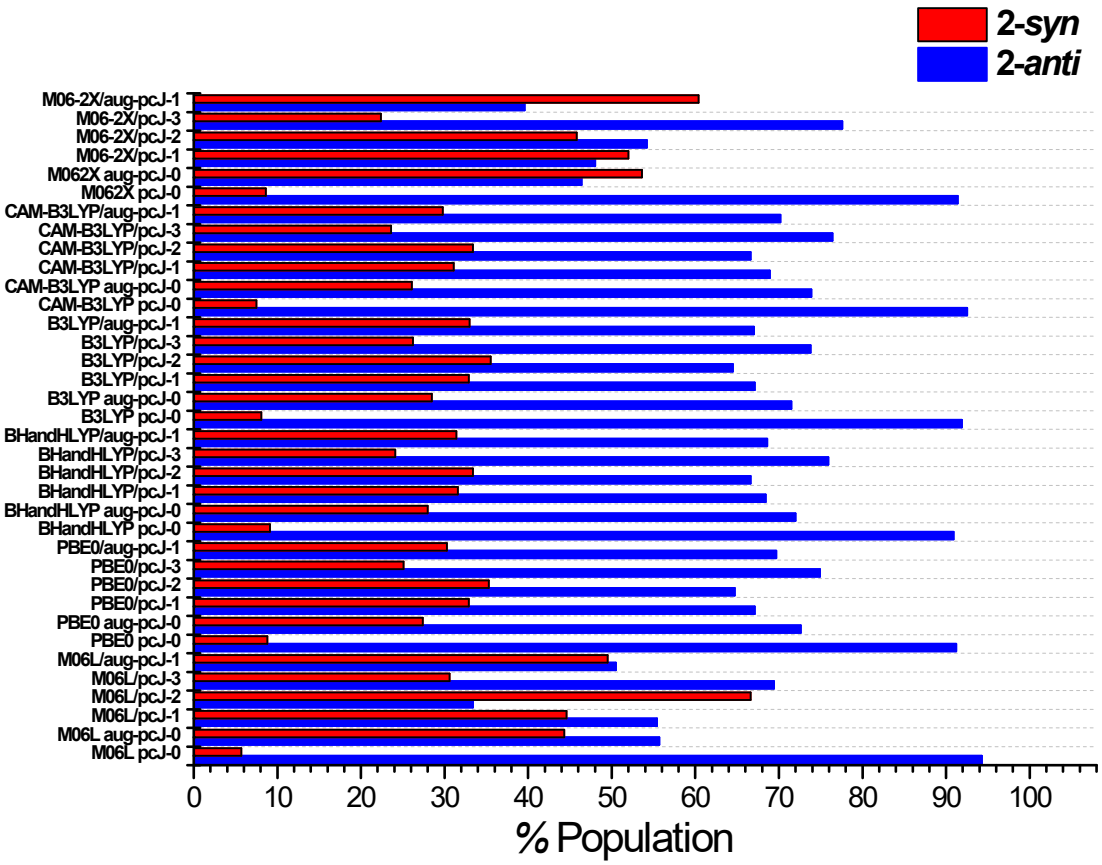


Figure S4. Conformer populations (*syn* vs *anti*) for **2** obtained at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model).

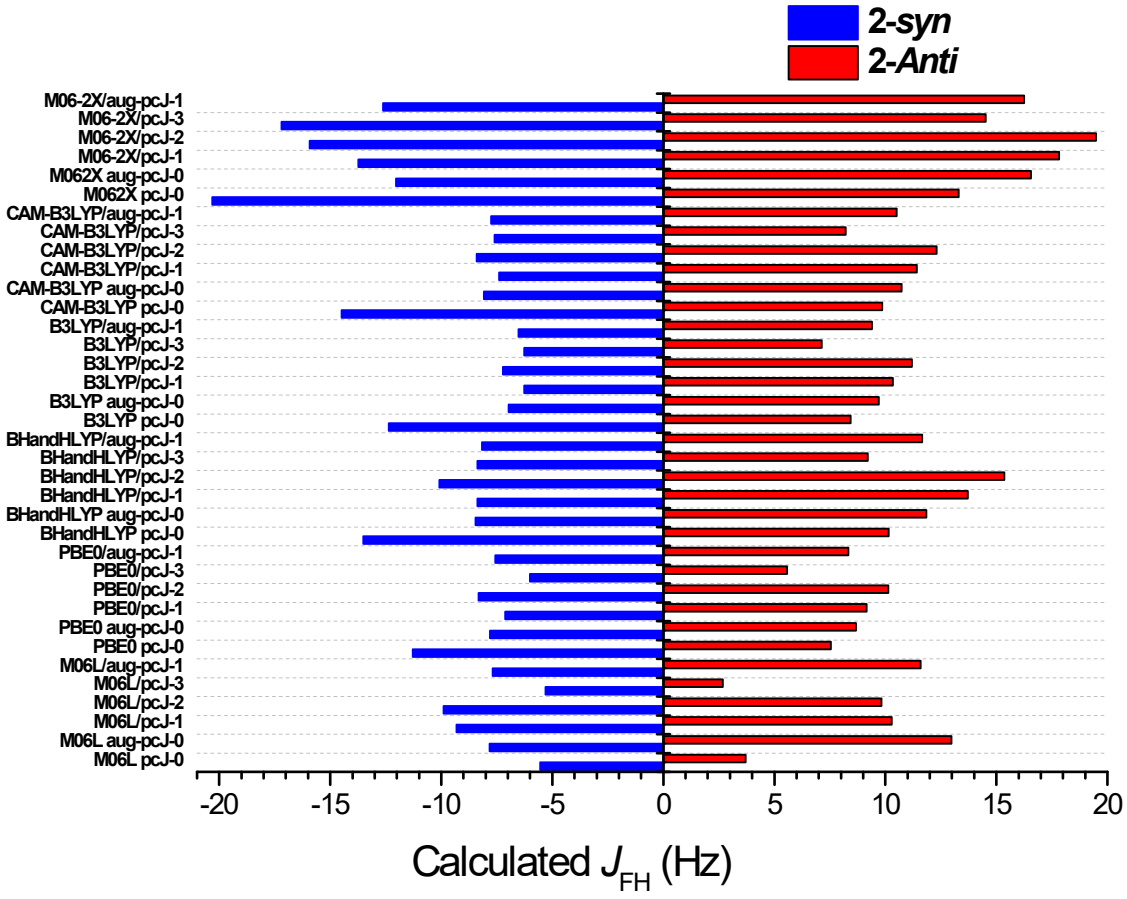


Figure S5. SSCCs obtained for for **2** *syn* and *anti* conformers obtained at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model).

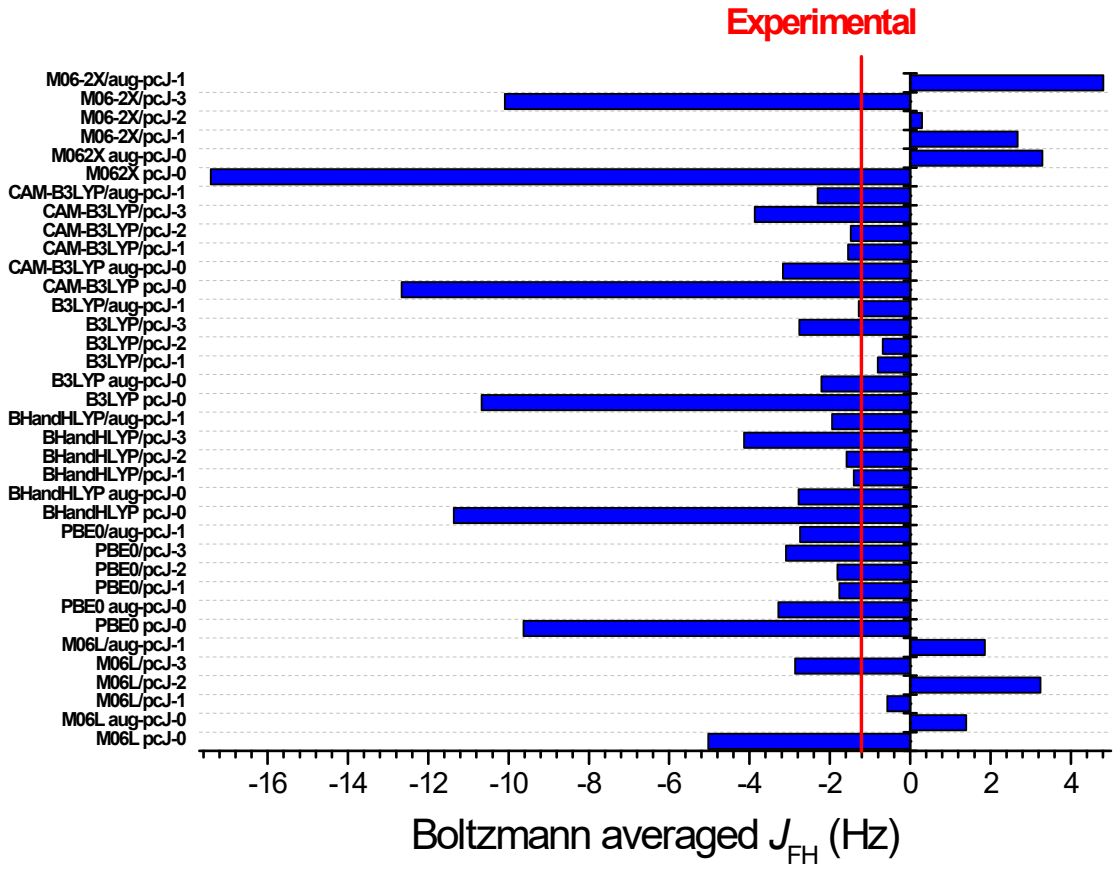
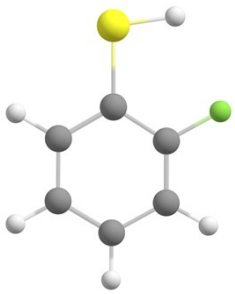


Figure S6. Boltzmann averaged SSCCs obtained from **2-*syn*** and **2-*anti*** conformers at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model). The experimental value (-1.2 Hz is shown as a line in red for comparison).

Table S2. Cartesian coordinates (angstroms), absolute energy (atomic units) and lowest harmonic vibrational frequency (cm^{-1}) for the conformers of **2** obtained at the B3LYP/aug-pcJ-1/CPCM(chloroform) level.

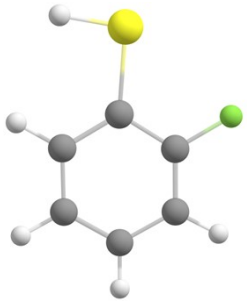


2-*syn*

Gibbs Free Energy (au)= -729.17882764

LHVF (cm^{-1})= 108.04

C	-0.455830	-1.498052	-0.009177
C	0.380771	-0.374754	-0.013729
C	-0.227096	0.878902	-0.008277
C	-1.601188	1.046624	0.000331
C	-2.418090	-0.083123	0.006106
C	-1.840877	-1.353860	0.001495
H	-0.013846	-2.487108	-0.014950
H	-2.012094	2.048404	0.003419
H	-3.494387	0.031919	0.013552
H	-2.467973	-2.236818	0.004838
S	2.148708	-0.601677	-0.019249
H	2.483791	0.703344	-0.082130
F	0.560708	1.989625	-0.012683



2-*anti*

Energy (au)= -729.17816092

LHVF (cm^{-1})= 153.42

C	-0.476907	-1.508574	-0.001732
C	0.373134	-0.396437	-0.000361
C	-0.219479	0.864337	0.000848
C	-1.589453	1.055560	0.000758
C	-2.421090	-0.064166	-0.000589
C	-1.860544	-1.342030	-0.001837
H	-0.051879	-2.504393	-0.002718
H	-1.985947	2.063082	0.001728
H	-3.495874	0.064324	-0.000675
H	-2.499872	-2.216286	-0.002899
S	2.154694	-0.492915	-0.000054
H	2.220350	-1.840947	-0.001292
F	0.597256	1.953002	0.002156

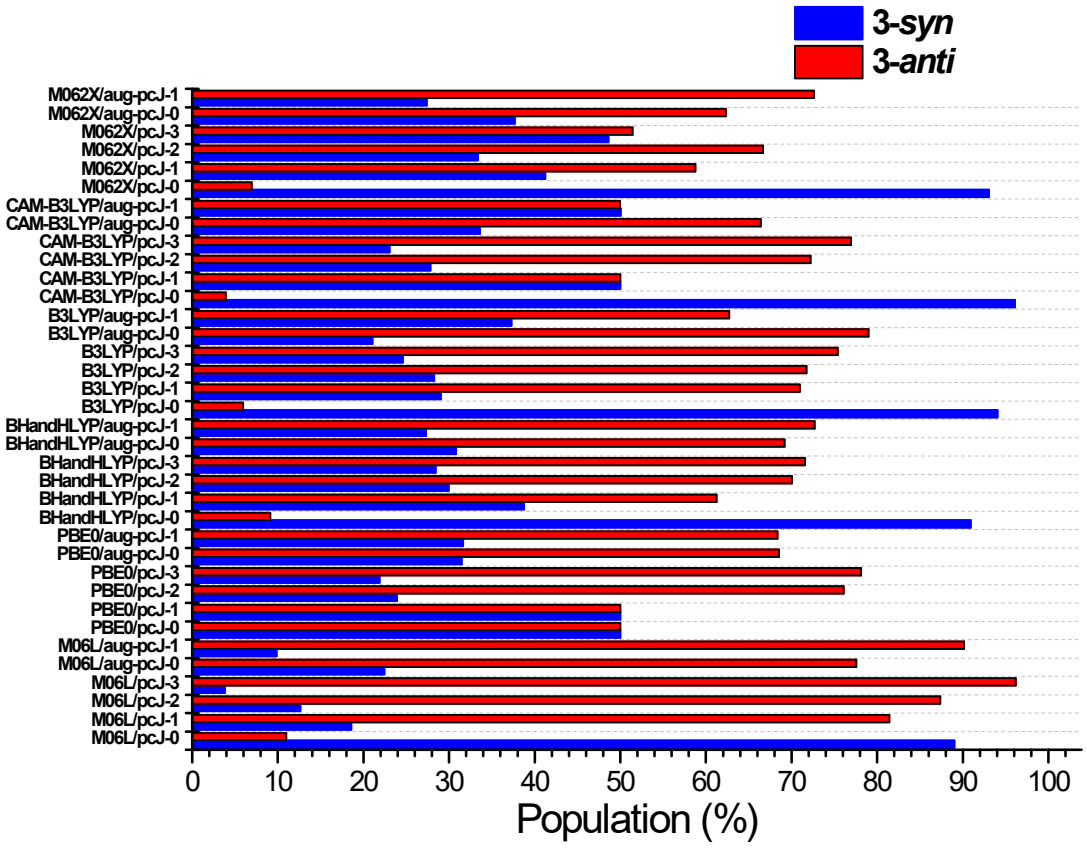


Figure S7. Conformer populations (*syn* vs *anti*) for **3** obtained at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model).

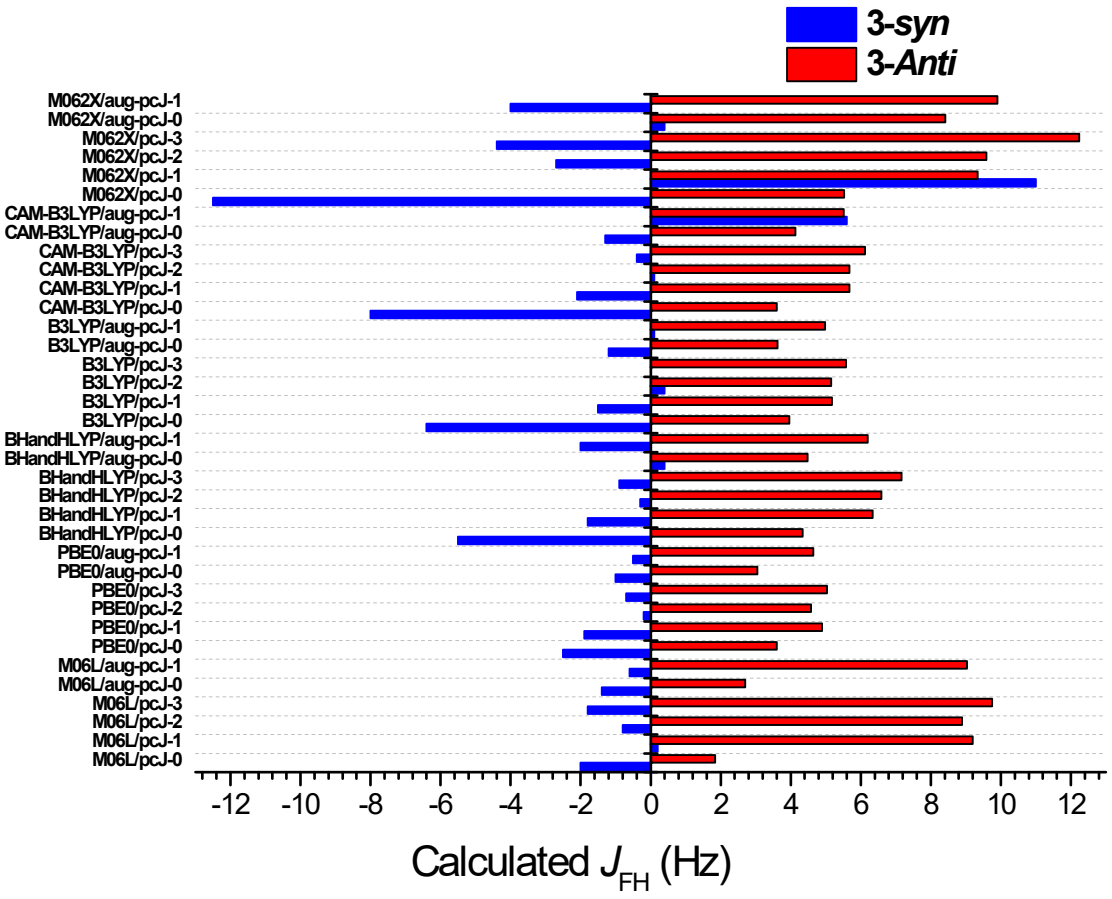


Figure S8. SSCCs obtained for for **3** *syn* and *anti* conformers obtained at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model).

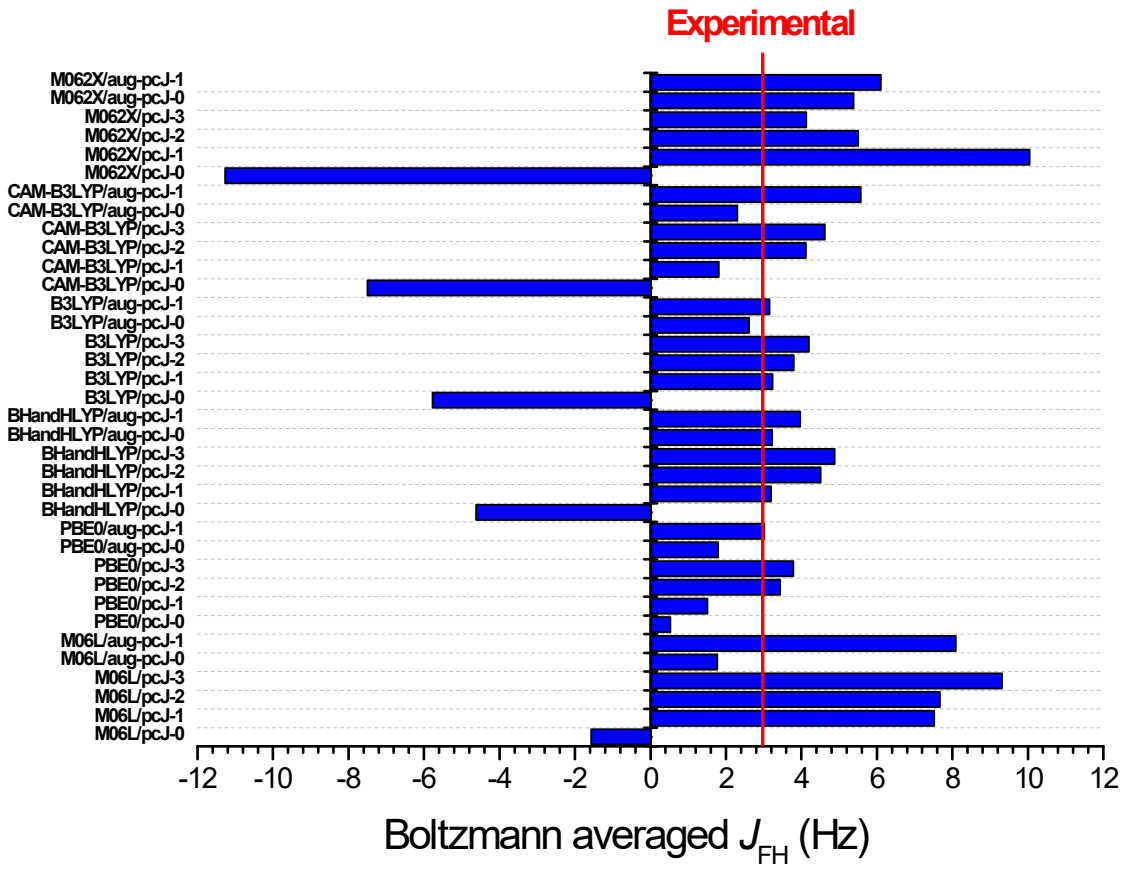
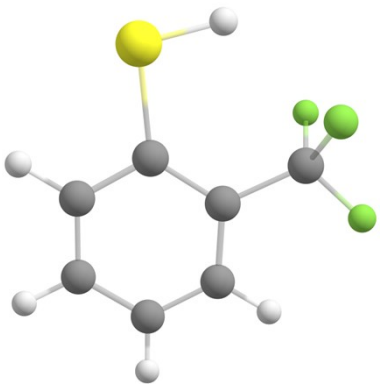


Figure S9. Boltzmann averaged SSCCs obtained from **3-*syn*** and **3-*anti*** conformers at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model). The experimental value (3.0 Hz is shown as a line in red for comparison).

Table S3. Cartesian coordinates (angstroms), absolute energy (atomic units) and lowest harmonic vibrational frequency (cm^{-1}) for the conformers of **3** obtained at the B3LYP/aug-pcJ-1/CPCM(chloroform) level.

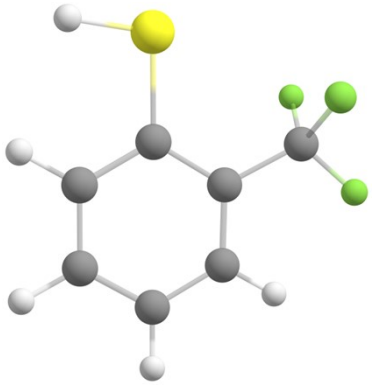


3-*syn*

Gibbs Free Energy (au)= -966.89668730

LHVF (cm^{-1})= 21.89

C	2.161928	0.687954	-0.000004
C	0.761086	0.728941	-0.000008
C	0.051884	-0.488590	-0.000005
C	0.753478	-1.699671	0.000002
C	2.142901	-1.724507	0.000002
C	2.846217	-0.521183	-0.000001
H	2.717847	1.617929	-0.000006
H	0.200740	-2.628672	0.000005
H	2.667324	-2.671423	0.000005
H	3.929622	-0.519401	-0.000002
S	0.073593	2.378682	0.000006
H	-1.238908	2.081269	0.000042
C	-1.450898	-0.535656	-0.000008
F	-1.991883	0.081352	-1.084623
F	-1.991887	0.081384	1.084587
F	-1.932272	-1.793684	0.000009



3-*anti*

Energy (au)= -966.89717735

LHVF (cm^{-1})= 19.66

C	2.145822	0.741054	0.179940
C	0.745767	0.742782	0.175121
C	0.071371	-0.490743	0.074112
C	0.801125	-1.679906	-0.009804
C	2.191561	-1.666706	-0.002497
C	2.860910	-0.448300	0.089739
H	2.680287	1.679215	0.257750
H	0.272537	-2.619838	-0.086321
H	2.742212	-2.596228	-0.069909
H	3.943969	-0.417244	0.094997
S	-0.153497	2.284260	0.308414
H	0.928053	3.083248	0.202991
C	-1.431287	-0.559575	0.032296
F	-2.010185	0.048065	1.100365
F	-1.944790	0.050485	-1.067183
F	-1.893041	-1.825926	0.015998

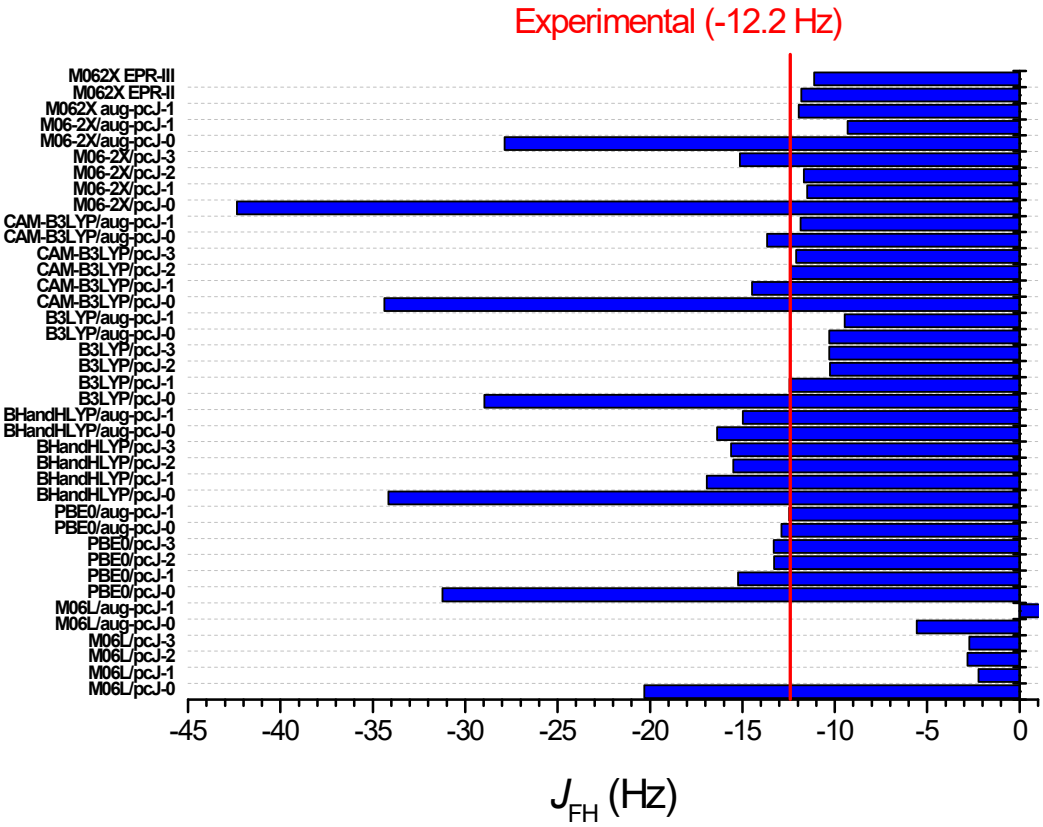
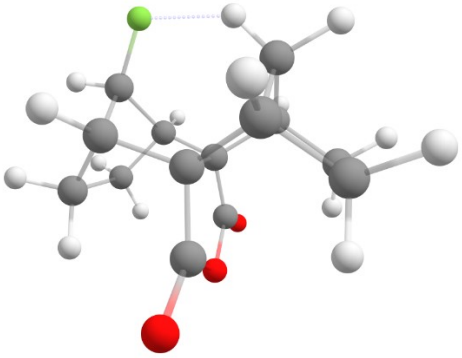


Figure S9. SSCCs obtained for compound **4** at M06L, M06-2X, B3LYP, CAM-B3LYP, BHandHLYP and PBE0 functionals and the pcJ-0, pcJ-1, pcJ-2, pcJ-3, aug-pcJ-0 and aug-pcJ-1 basis sets in chloroform (CPCM implicit solvent model). The experimental value (12.2 Hz is shown as a line in red for comparison).

Table S4. Cartesian coordinates (angstroms), absolute energy (atomic units) and lowest harmonic vibrational frequency (cm^{-1}) for **4** obtained at the PBE0/aug-pcJ-1/CPCM(chloroform) level.



Gibbs Free Energy (au)= -866.92024497

LHVF (cm^{-1})= 67.16

C	-1.464931	0.207466	-1.140229
C	-1.763193	1.679639	-0.768705
C	-1.760172	1.666651	0.795364
C	-1.462609	0.188326	1.140702
C	0.019085	-0.105267	0.770276
C	0.018239	-0.089235	-0.778179
C	-2.296298	-0.400429	-0.003616
C	0.693017	-1.440247	-1.150437
C	2.192823	-1.358224	-0.789771
C	2.188652	-1.381613	0.766393
C	0.686833	-1.467322	1.114972
C	0.228423	-2.381314	-0.030612
C	0.915183	1.047860	1.150829
C	0.911761	1.072121	-1.137492
O	1.397527	1.667924	0.012130
O	1.232112	1.449823	2.229480
O	1.226631	1.494235	-2.209139
H	0.802678	-3.311479	-0.039741
F	-2.516783	-1.768701	-0.012919
H	-1.750652	-0.071047	-2.153517
H	-1.045558	2.384361	-1.188311
H	-2.742718	1.963994	-1.155432
H	-1.039511	2.363028	1.223754
H	-2.737510	1.946029	1.191110
H	-1.746058	-0.107517	2.149718
H	-3.300111	0.029380	0.000360
H	0.495216	-1.752104	-2.175835
H	2.704837	-0.486789	-1.202316
H	2.702223	-2.235682	-1.191987
H	2.702039	-0.525714	1.208556
H	2.691142	-2.273821	1.144198
H	0.480212	-1.803109	2.131033
H	-0.823405	-2.623689	-0.037421

Table S5. Experimental *vs* theoretical J_{FH} SSCCs for **4X** (X = H, F, OH, Cl or CN). Theoretical values obtained at PBE0/aug-pcJ-1/CPCM(chloroform) level. Values in Hz.

X	Experimental	Theoretical
H	12.2	-12.5
F	17.5	-18.1
OH	18.7	-19.0
Cl	24.5	-25.7
CN	30.7	-33.6

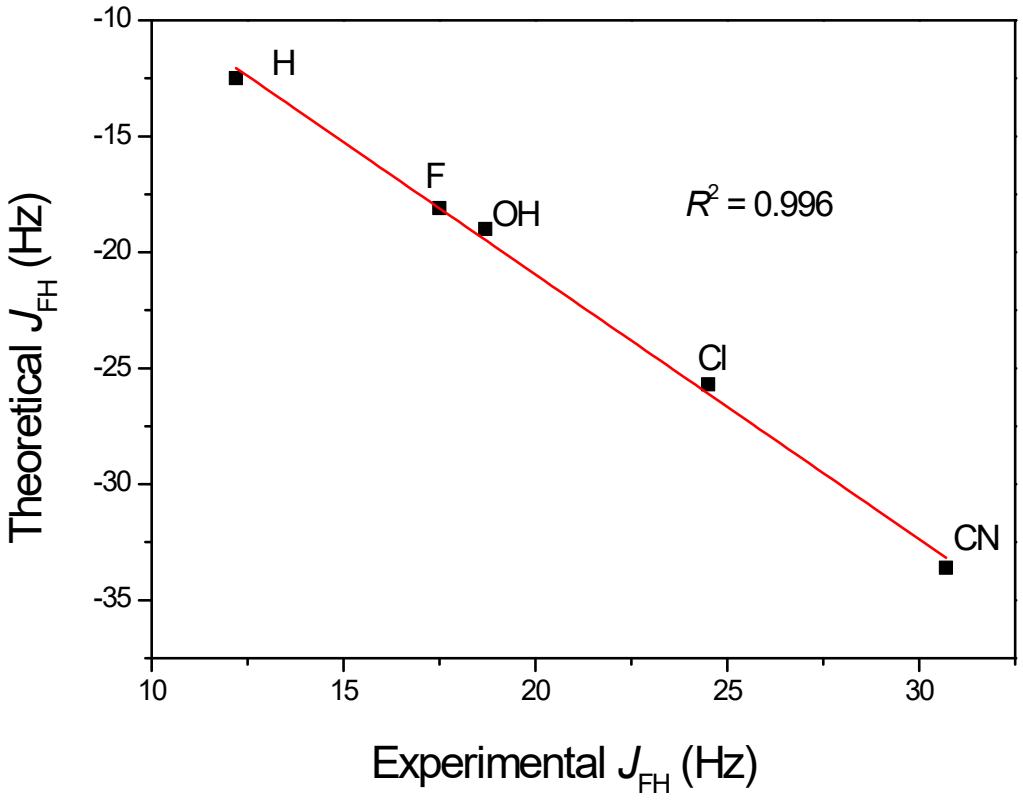


Figure S10. Experimental *vs* theoretical [PBE0/aug-pcJ-1/CPCM(chloroform)] J_{FH} SSCCs for **4X** (X = H, F, OH, Cl or CN). Obtained correlation coefficient is given in the figure.

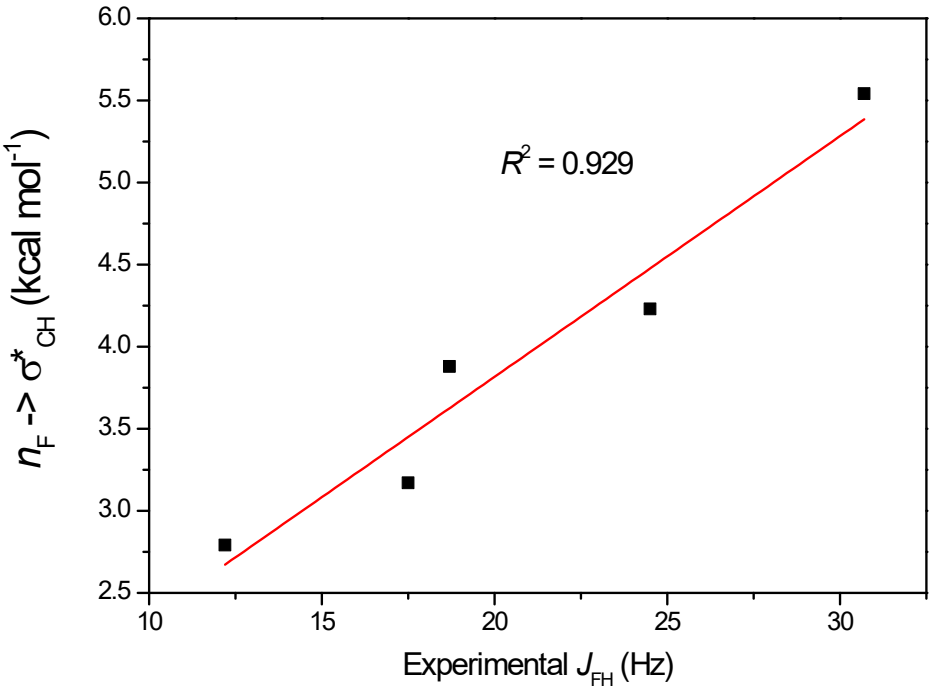


Figure S11. Correlation between experimental J_{FH} and $n_F \rightarrow \sigma^*CH$ hyperconjugation for **4X** (X = H, F, OH, Cl or CN) [calculated at PBE0/aug-pcJ-1/CPCM(chloroform)].

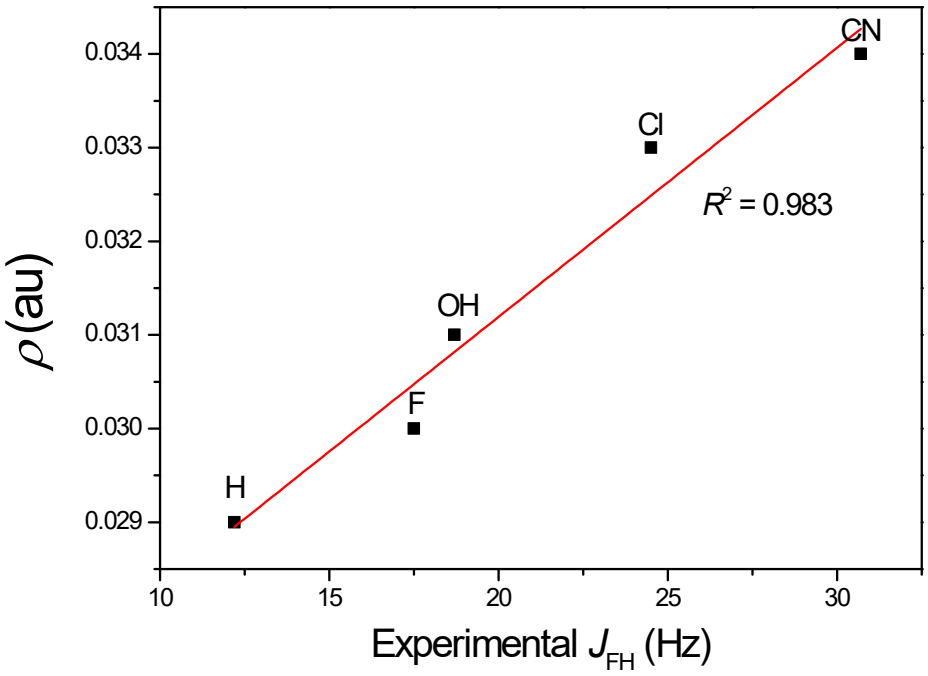


Figure S12. Correlation between experimental J_{FH} and electron density at BCP ρ (au) for **4X** (X = H, F, OH, Cl or CN) calculated at PBE0/aug-pcJ-1/CPCM(chloroform)].

NMR Experiments

^{1}H, ^{19}F, and ^{13}C NMR spectra were obtained on a Bruker Avance spectrometer operating at 499.87 MHz for ^{1}H, 470.30 MHz for ^{19}F, and 125.71 MHz for ^{13}C using a BBFO probe with typical 90° pulse widths of 11.75 µs for ^{1}H, 16.60 µs for 19F, and 10.00 µs for ^{13}C. Spectra were recorded in 10 mg mL^{-1} solutions with a probe temperature of 27.0 °C (BBFO) in $CDCl_3$, CD_2Cl_2, or Acetone-d_6 (all acquired from Aldrich Chem., Co.) and referenced to the solvent residual signal or TMS.

Typical ^{1}H 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. ^{19}F 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.

^{1}H-^{13}C HMBC (modulated with a long-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 ^{1}H-^{13}C-HMBC spectra and referred to the correlation of the thiol proton with the carbon of the aromatic ring bond to the fluorine, which was assumed to be negative. 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. Spectra in other solvents for **2** and **3** may be found in references 14 and 15.

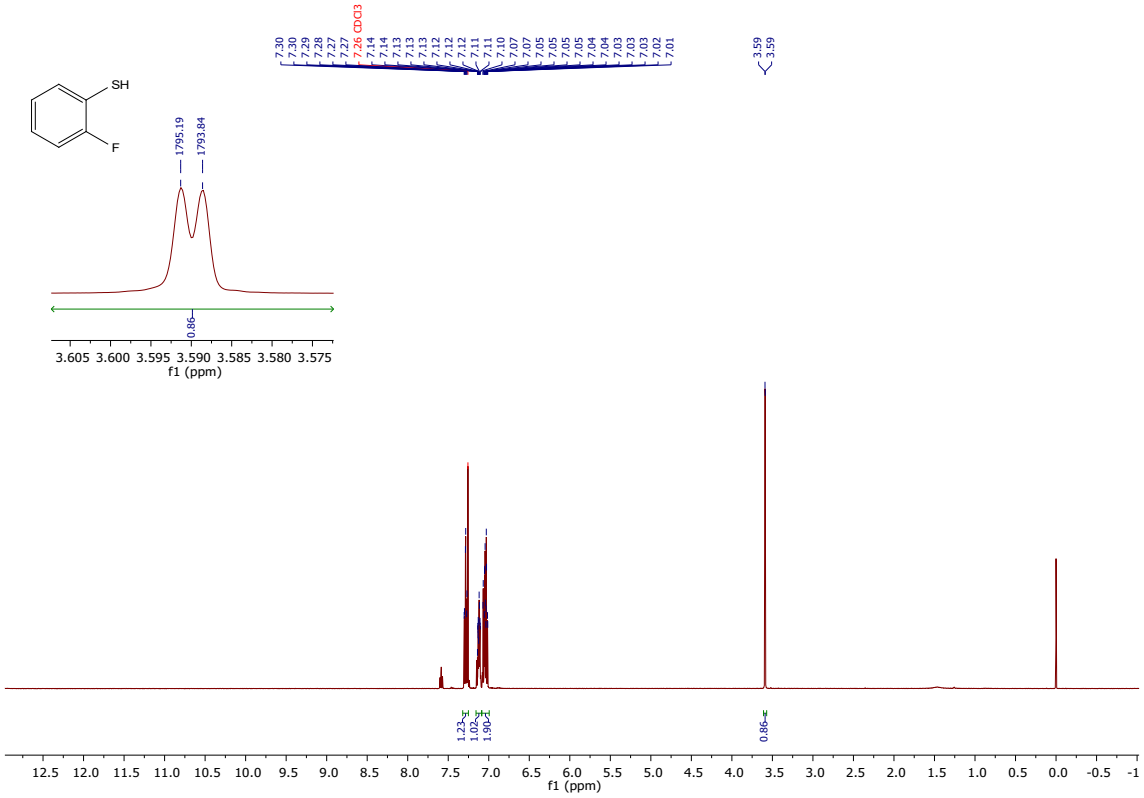


Figure S13. ^{1}H NMR Spectrum of 2-fluorothiophenol in $CDCl_3$.

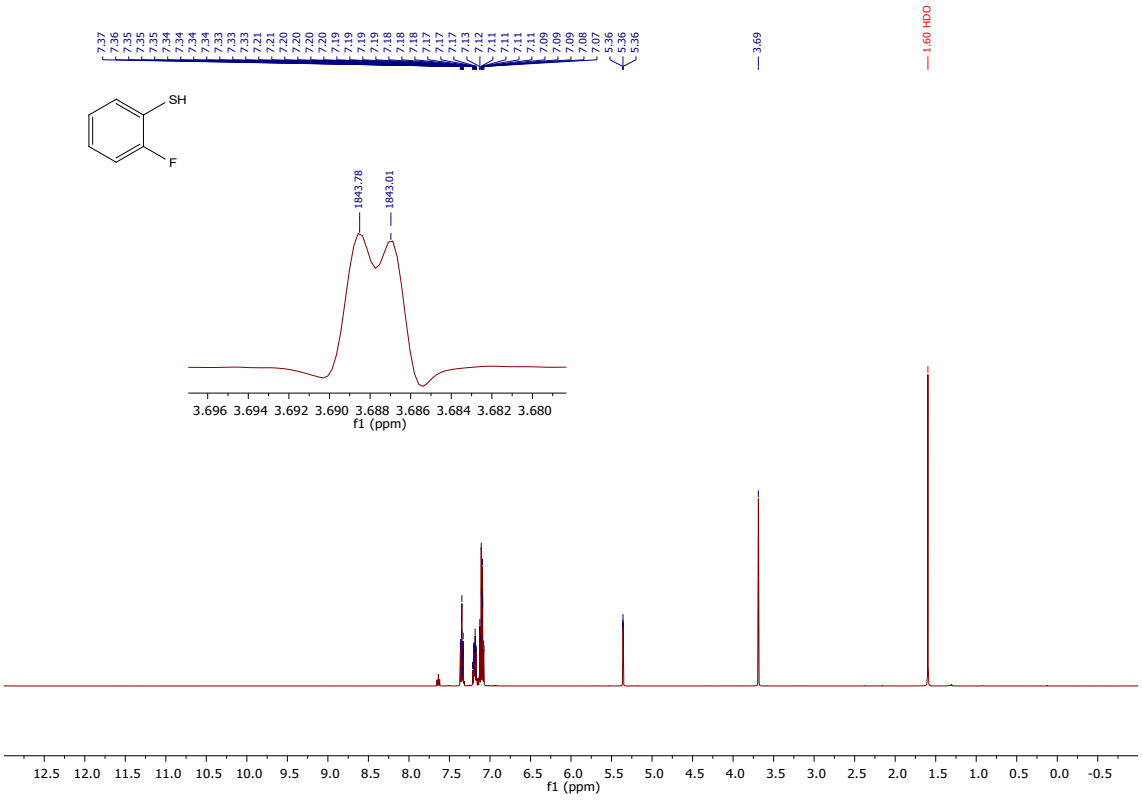


Figure S14. ^{1}H NMR Spectrum of 2-fluorothiophenol in CD_2Cl_2. In the amplification of the SH signal, a gaussian apodization was applied (GB = 0.5 LB = - 0.80) to visualize the coupling.

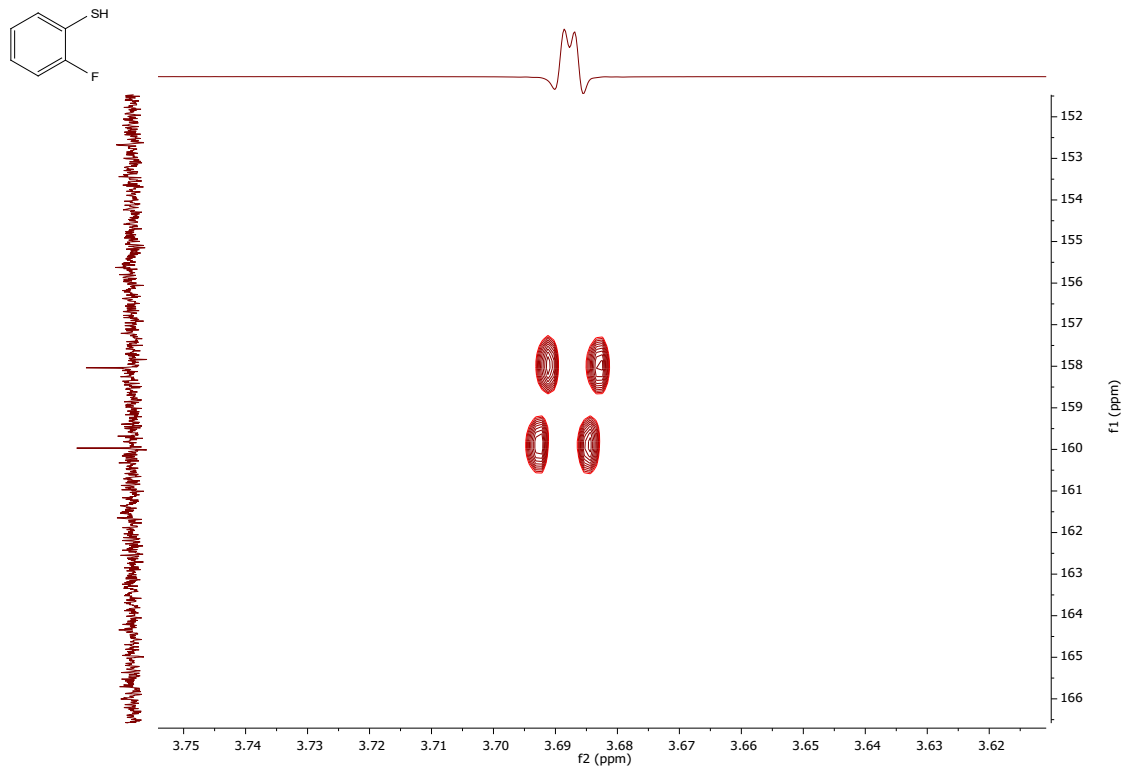


Figure S15. Ampliation of the ^{1}H-^{13}C-HMBC correlation map to better visualize S**H** – **C**F correlation.

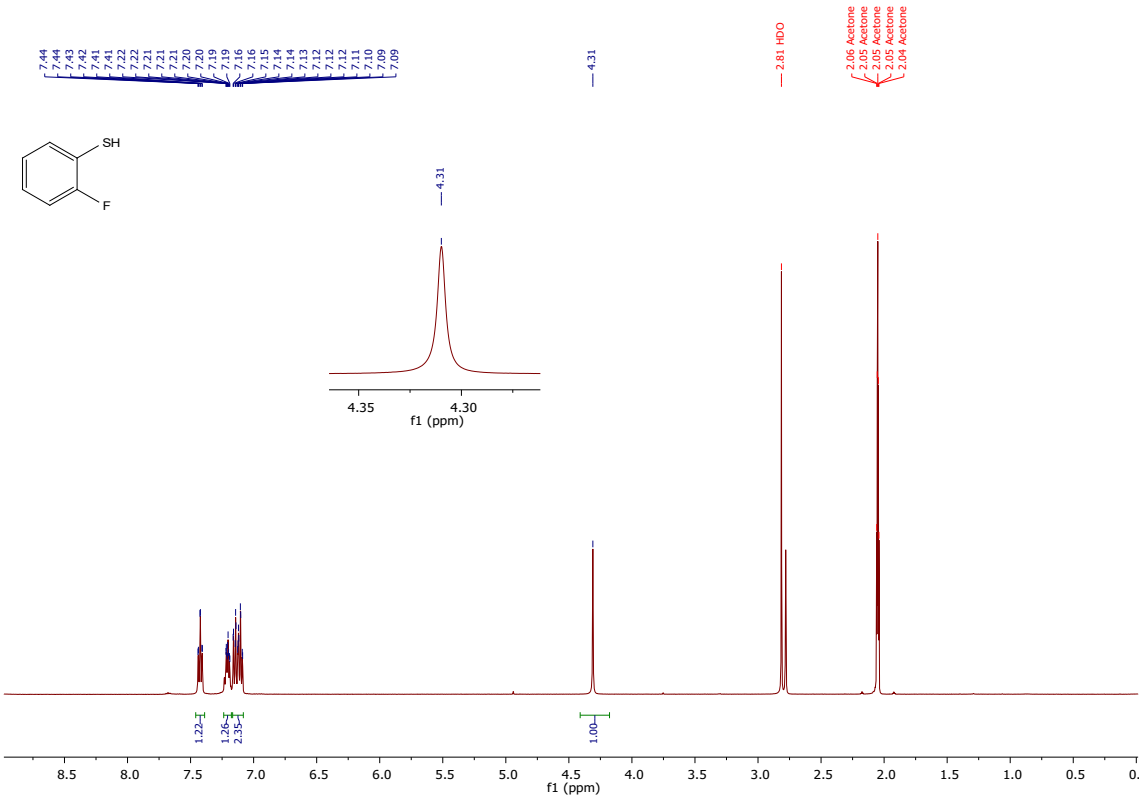


Figure S16. ^{1}H NMR Spectrum of 2-fluorothiophenol in Acetone-d_6.

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