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

Electronic Supplementary Information

The seeming lack of CF•••HO intramolecular hydrogen bonds in linear aliphatic fluoroalcohols in solution

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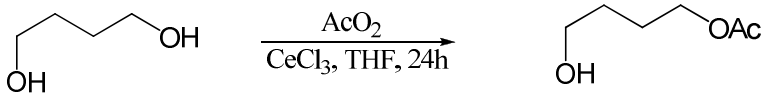
Synthesis of 4-fluorobutanol.

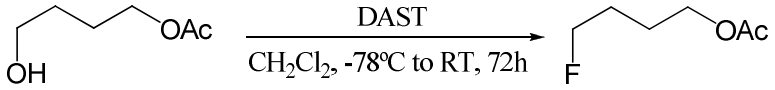
1. Mono acylation



(1) **(2)**

226 mmol (25.2 mL) of Acetic anhydride was added to a stirred solution of 1,4-butanediol (222 mmol; 19.7 mL) and 1g of CeCl3 in 500 mL of THF under nitrogen atmosphere. When judged complete by TLC (EtOAc/petroleum ether at 40:60 ratio), the reaction was diluted with 200 mL of Et_2O and washed twice with 50 mL of brine. The organics were dried with $MgSO_4$ and the solvent was evaporated, obtaining **2** as a crude product. The product was purified via flash column chromatography (EtOAc/petrol ether in 40:60 ratio) to provide the pure mono-acetate **2** in 55% yield.

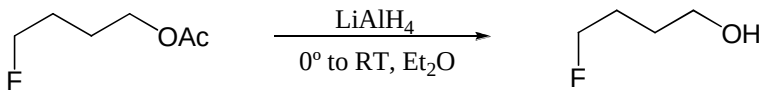
2. DAST Fluorination



(2) **(3)**

161.19 mmol (12.18 mL) of DAST was added dropwise to a stirred solution of **2** (30.74 mmol; 3.93 mL) in 300 mL of dichloromethane under nitrogen atmosphere and at -78ºC. The reaction mixture was warmed up to RT and was allowed to react for 72h. The workout was done by adding the reaction solution on water (50 mL) and extracted 3x with EtOAc (100 mL) before use of $MgSO_4$ as drying agent and careful solvent evaporation, since the product is volatile. The fluorinated product **3** was obtained in 81% yield after column chromatography (DCM/Et_2O in 50:50 ratio).

3. $LiAlH_4$ Reduction



(3) **(4)**

82.8 mmol (3.14 g) of $LiAlH_4$ was added carefully to a stirred solution of **3** (20.7 mmol; 2.95 mL) in 200 mL of Et_2O at 0ºC. The reaction mixture was warmed up to RT and

achieved completion after 1h as judged by TLC (100% Et_2O). The workup followed the procedure below:

1- The solution was diluted with ether (100 mL) and cooled down to 0ºC.

2- It was slowly added 3 mL of H_2O.

3- It was added 3 mL of NaOH

4- It was added 10 mL of H_2O

5- The mixture was warmed up to room temperature and stirred for 15 min.

6- $MgSO_4$ was added to the reaction mixture.

7- The reaction mixture was filtered.

The crude product **4** obtained in quantitative yield was purified by column chromatograpy (100% Et_2O), achieving 25% yield after careful solvent evaporation.

4: Colourless liquid; IR (0.03 M CCl_4 solution): υ = ~3639 cm^{-1} (%T = 83.1;medium), ~2962 cm^{-1} (%T = 70.2; strong), ~2900 cm^{-1} (%T = 79.8; strong), ~2877 cm^{-1} (%T = 83.8; medium), ~1474 cm^{-1} (%T = 93.3; weak), ~1445 cm^{-1} (%T = 91.7; weak), ~1434 cm^{-1} (%T = 93.0; weak), ~1388 cm^{-1} (%T = 88.7; weak), ~1043 cm^{-1} (%T = 65.1; strong), ~1008 cm^{-1} (%T = 74.9; strong), ~ 977 cm^{-1} (%T = 85.1; medium), ~945 cm^{-1} (%T = 83.4; medium). ^{1}H NMR (600.17 MHz, CD_2Cl_2 solution): δ 4.52 (2H, dt, $^3J_{H,F}$ = 47.4 Hz, $^3J_{HH}$ = 6.05 Hz), δ 3.69 (2H, m), δ 1.81 (2H, m), δ 1.69 (2H, m). ^{13}C (150.9 MHz, CD_2Cl_2 solution): δ 83.52 (d, $^1J_{FC}$ = 163.5 Hz), δ 62.73 (s), δ 29.10 (d, $^3J_{FC}$ = 5.01), 27.51 (d, $^2J_{FC}$ = 20.01).

(a) **(b)**

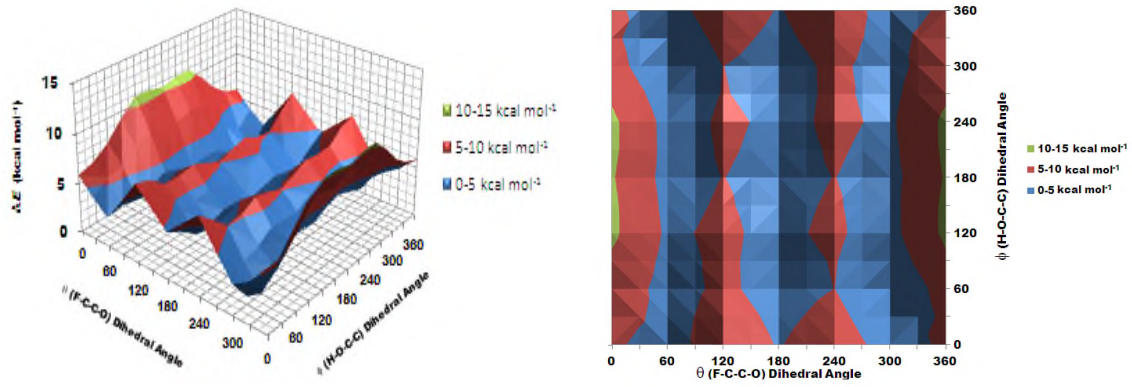


Figure S1: a) PES built by scanning the ϕ (H-O-C-C) and θ (F-C-C-O) dihedral angles of **FE** at the B3LYP/cc-pVDZ level. **b)** Contour map in the plane of ϕ and θ dihedral angles.

1 **2** **3** **4** **5**

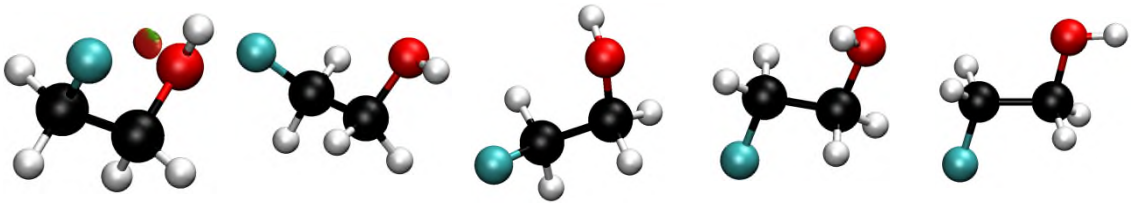
Figure S2: Molecular graphs for **FE** conformers obtained with the QTAIM. Green points represent BCPs.

Table S1: Relative energies of **FE** conformer (kcal mol^{-1}) obtained at different levels. If not otherwise stated, the aug-cc-pVDZ basis set was used.

	1	**2**	**3**	**4**	**5**
B3LYP	0.00	1.88	2.33	2.29	2.14
B3LYP-D3	0.00	2.10	2.47	2.39	2.28
B97D	0.00	2.16	2.29	2.34	2.58
MP2	0.00	2.05	2.58	2.38	2.19
MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ	0.00	1.96	2.46	2.34	2.17
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ	0.00	2.03	2.45	2.24	2.14

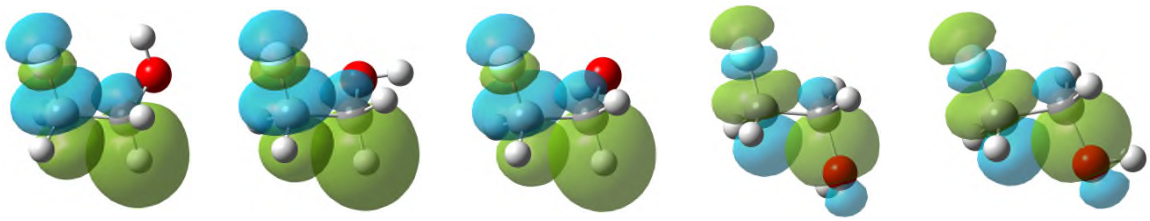
Table S2: Relative energies (Δ*E*) of **FE** conformer obtained for MP2/aug-cc-pVDZ optimised geometries. Thermal corrections to enthalpes (Δ*H*) and Gibbs free energies (Δ*G*) were obtained from B3LYP/aug-cc-pVDZ frequency calculations. Conformer populations (%P) are given for each case. Energies and populations are given separately for isolated molecule and by using the implicit IEF-PCM implicit solvent model for acetonitrile dielectric constant value.

Isolated					
	1	**2**	**3**	**4**	**5**
Δ*E* (kcal mol^{-1})	0.00	2.05	2.58	2.19	2.38
%P (Δ*E*)	92.0	2.9	1.2	2.3	1.7
Δ*H* (kcal mol^{-1})	0.00	1.92	2.43	2.40	2.20
%P (Δ*H*)	91.2	3.6	1.5	1.6	2.2
Δ*G* (kcal mol^{-1})	0.00	1.78	2.27	2.16	1.92
%P (Δ*G*)	88.0	4.3	1.9	2.3	3.4
Acetonitrile					
	1	**2**	**3**	**4**	**5**
Δ*E* (kcal mol^{-1})	0.00	0.59	0.72	1.85	2.10
%P (Δ*E*)	57.5	21.2	17.1	2.5	1.7
Δ*H* (kcal mol^{-1})	0.00	0.55	0.69	1.95	2.15
%P (Δ*H*)	56.4	22.4	17.6	2.1	1.5
Δ*G* (kcal mol^{-1})	0.00	0.58	0.71	1.83	1.94
%P (Δ*G*)	56.7	21.4	17.2	2.6	2.1



1 **2** **3** **4** **5**

Figure S3: FE NCI plots. The red/green NCI surface indicates a repulsive interaction between F and the OH group. The figures were obtained with a reduced density gradient (RDG) value of 0.6 au and the blue-green-red values ranging from -0.02 to 0.02.



1 **2** **3** **4** **5**

Figure S4: NBOs involved in $\sigma_{CH} \rightarrow \sigma^*_{CF}$ (conformers **1**-**3**) and $\sigma_{CO} \rightarrow \sigma^*_{CF}$ (conformers **4** and **5**) hyperconjugative interaction in **FE** (obtained at the B3LYP/aug-cc-pVDZ level; isosurface values 0.04 au).

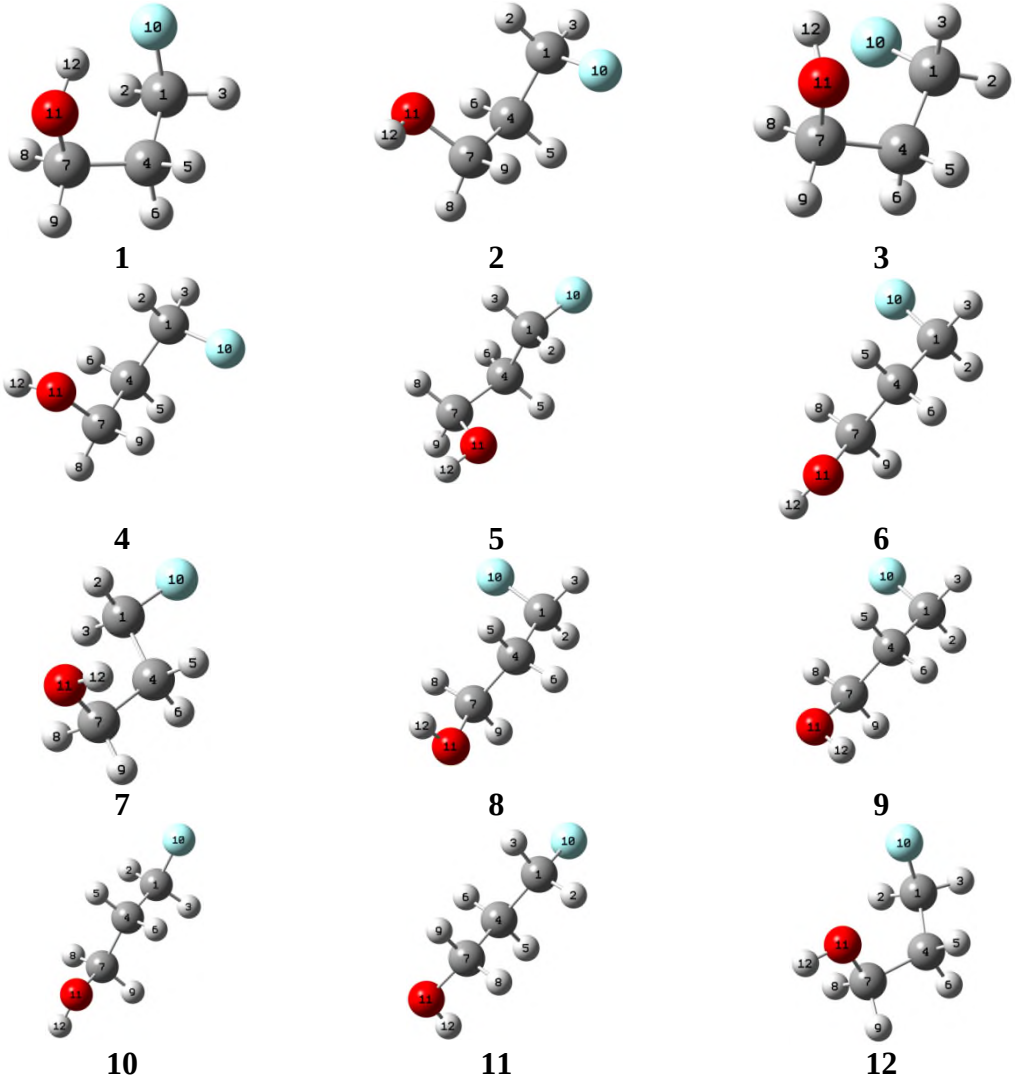


Figure S5: Geometrical representations of the **FP** conformers obtained at the MP2/aug-cc-pVDZ level.

Table S3: Relative energies of **FP** conformers (kcal mol^{-1}) obtained at different levels. If not otherwise stated, the aug-cc-pVDZ basis set was used. BHandH/EPR-III and SOPPA(CCSD)/EPR-III $^{1h}J_{F,H}$ SSCCs values (Hz) obtained for MP2/aug-cc-pVDZ geometries are also indicated in the table bottom.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
B3LYP	0.05	0.00	0.63	0.68	0.81	0.71	1.08	1.02	1.26	1.74	1.90	3.25
B3LYP-D3	0.00	0.19	0.65	0.80	1.10	1.06	1.28	1.30	1.54	2.19	2.27	3.66
B97D	0.00	0.34	0.45	0.68	1.19	1.06	1.14	1.11	1.29	2.12	2.00	3.44
MP2	0.17	0.00	0.61	0.81	1.00	1.08	1.40	1.41	1.65	2.28	2.46	3.66
MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ	0.17	0.00	0.56	0.78	0.95	1.02	1.31	1.33	1.56	2.14	2.31	3.56
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ	0.00	0.02	0.44	0.70	0.94	0.98	1.19	1.20	1.44	2.07	2.15	3.47
$^{1h}J_{F,H}$ (BHandH/EPR-III)	-12.67	-0.41	0.38	-0.32	-0.42	-0.50	-0.26	-0.19	-0.05	1.34	-0.77	-0.15
$^{1h}J_{F,H}$ [SOPPA(CCSD)/EPR-III]	-11.39	-0.24	0.23	-0.05	-0.38	-0.40	0.06	-0.04	0.33	1.78	-0.61	-0.10

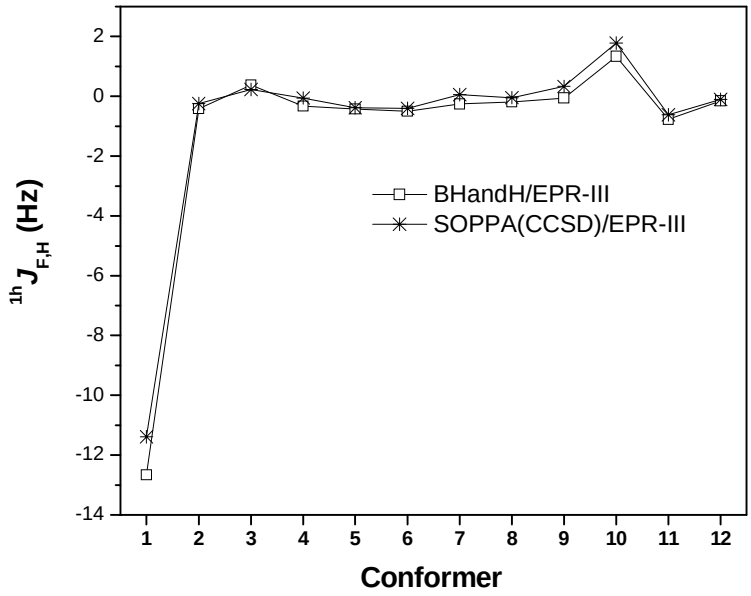


Figure S6: Comparison between SOPPA(CCSD)/EPR-III and BHandH/EPR-III calculated $^{1h}J_{F,H}$ SSCC values for **FP** conformers. BHandH/EPR-III $^{1h}J_{F,H}$ mean absolute deviation (MAD) from $^{1h}J_{F,H}$ SOPPA(CCSD)/EPR-III is of 0.29 Hz.

Table S4: Relative energies (Δ*E*)of **FP** conformer obtained for MP2/aug-cc-pVDZ optimised geometries. Thermal corrections to enthalpes (Δ*H*) and Gibbs free energies (Δ*G*) were obtained from B3LYP/aug-cc-pVDZ frequency calculations. Conformer populations (%P) are given for each case. Energies and populations are given separately for the isolated molecule and by using the implicit IEF-PCM implicit solvent model for cyclohexane and dichloromethane dielectric constant value.

		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
	Δ*E*	0.17	0.00	0.61	0.81	1.00	1.08	1.40	1.41	1.65	2.28	2.46	3.66
	%P (Δ*E*)	25.2	33.3	11.9	8.5	6.2	5.3	3.1	3.1	2.1	0.7	0.5	0.1
Isolated	**Δ*H***	0.22	0.00	0.65	0.80	1.04	1.09	1.42	1.41	1.64	2.34	2.51	3.52
	%P (Δ*H*)	23.7	34.6	11.6	9.0	5.9	5.5	3.1	3.2	2.2	0.7	0.5	0.1
	Δ*G*	0.55	0.00	0.56	0.83	0.94	0.96	1.27	1.26	1.51	2.05	2.21	3.39
	%P (Δ*G*)	14.0	35.7	13.9	8.8	7.3	7.1	4.2	4.2	2.8	1.1	0.8	0.1
	Δ*E*	0.11	0.00	0.58	0.60	0.85	0.91	1.14	1.13	1.32	1.95	2.08	3.10
	%P (Δ*E*)	23.6	28.6	10.8	10.3	6.9	6.2	4.2	4.2	3.1	1.1	0.9	0.2
Cyclohexane	**Δ*H***	0.19	0.00	0.61	0.60	0.90	0.92	1.18	1.17	1.33	2.02	2.14	2.98
	%P (Δ*H*)	22.0	30.1	10.7	10.9	6.6	6.3	4.1	4.2	3.2	1.0	0.8	0.2
	Δ*G*	0.53	0.00	0.54	0.63	0.80	0.82	1.02	1.06	1.23	1.75	1.83	2.84
	%P (Δ*G*)	12.6	30.8	12.5	10.6	8.0	7.7	5.5	5.1	3.9	1.6	1.4	0.3
	Δ*E*	0.01	0.00	0.53	0.23	0.66	0.66	0.84	0.80	0.81	1.48	1.57	2.14
	%P (Δ*E*)	21.1	21.5	8.8	14.6	7.0	7.0	5.2	5.6	5.4	1.8	1.5	0.6
CH_2Cl_2	**Δ*H***	0.08	0.00	0.55	0.24	0.72	0.68	0.88	0.84	0.86	1.58	1.66	2.05
	%P (Δ*H*)	19.7	22.7	9.0	15.1	6.7	7.1	5.1	5.5	5.4	1.6	1.4	0.7
	Δ*G*	0.41	0.00	0.49	0.26	0.61	0.58	0.71	0.75	0.77	1.30	1.34	1.98
	%P (Δ*G*)	11.4	22.6	9.9	14.7	8.1	8.5	6.8	6.4	6.1	2.5	2.3	0.8

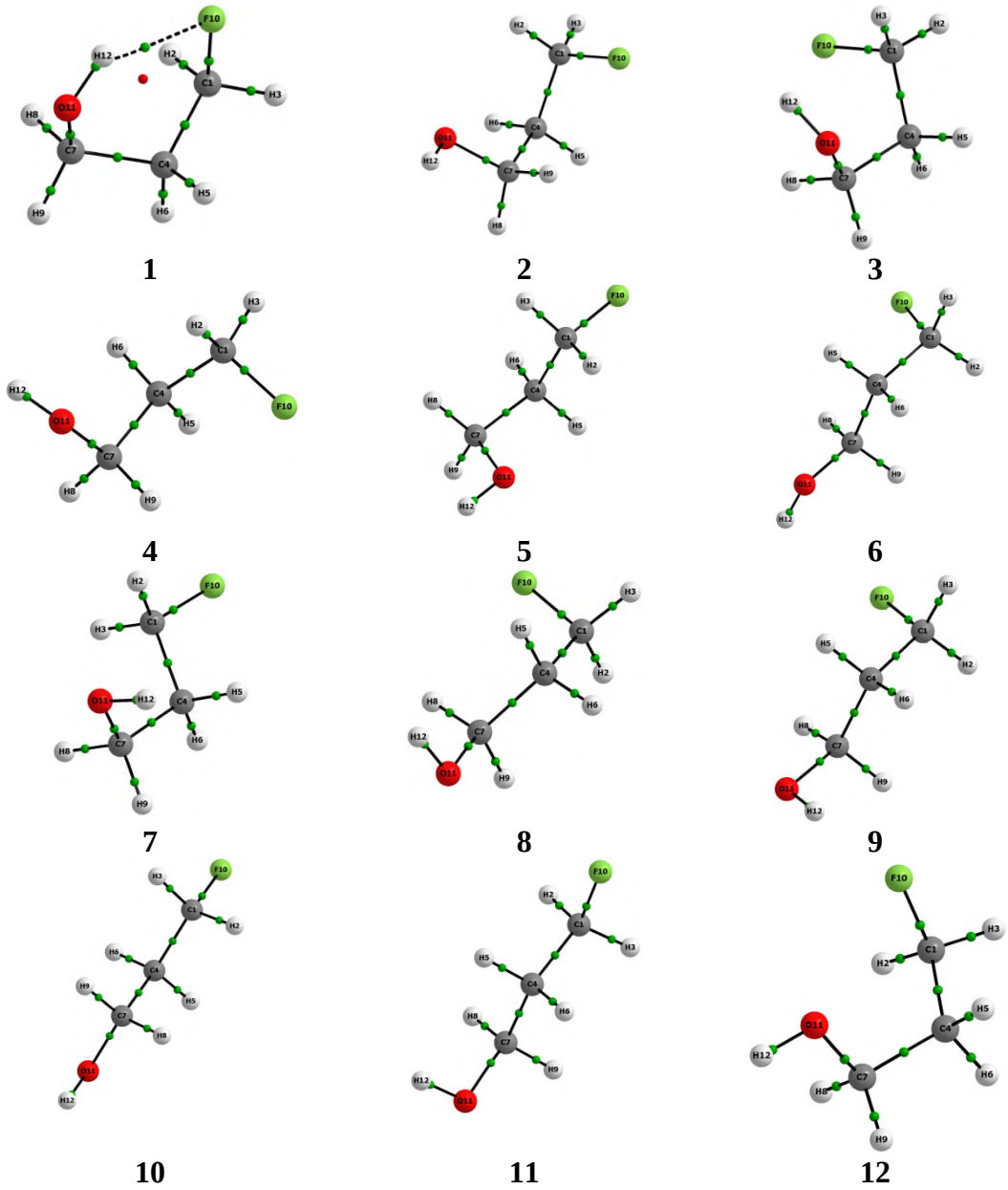


Figure S7: Molecular graphs of **FP** conformers obtained with the QTAIM. Green points represent BCPs; for conformer **1** the red point denotes a RCP.

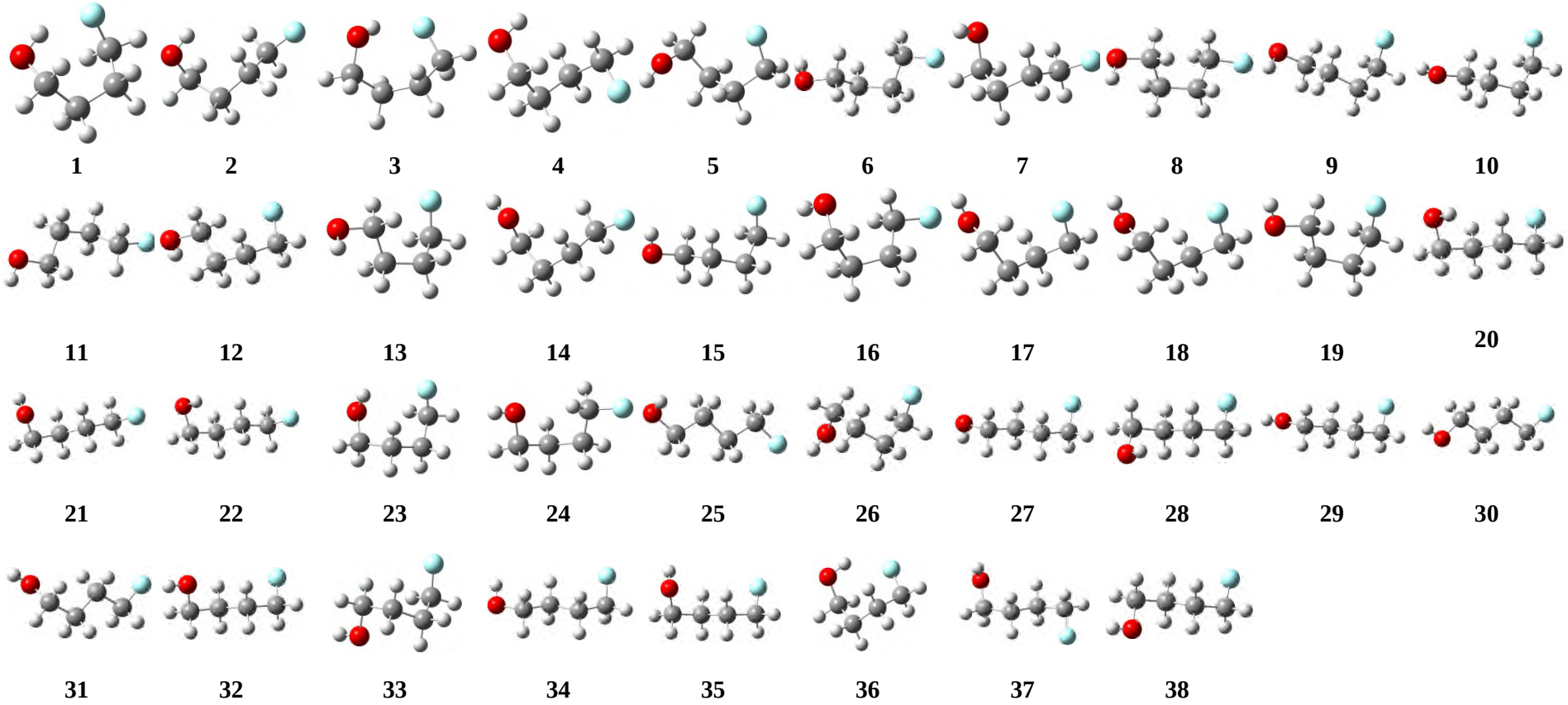


Figure S8: Geometrical representations of the **FB** conformers.

Table S5: Relative energies of **FB** conformer (kcal mol^{-1}) obtained at different levels. If not otherwise stated, the aug-cc-pVDZ basis set was used.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
B3LYP	0.12	2.39	2.48	1.95	2.01	2.15	1.93	2.04	1.85	1.68	1.82	1.78	1.74	1.70	1.61	1.70	1.42	1.53	1.30
B3LYP-D3	0.00	2.48	2.36	1.91	2.11	2.54	2.09	2.42	2.16	2.06	2.28	2.00	1.94	1.96	1.90	1.72	1.58	1.71	1.58
B97D	0.14	1.82	2.29	1.29	1.86	2.05	1.71	1.92	1.63	1.76	1.99	1.76	1.64	1.80	1.44	1.58	1.62	1.79	1.54
MP2	0.17	2.48	2.39	1.82	2.12	2.53	1.93	2.40	2.07	1.83	2.16	2.11	2.02	1.59	1.80	1.81	1.46	1.49	1.55
MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ	0.12	2.32	2.22	1.71	2.04	2.38	1.87	2.24	1.95	1.77	2.04	1.99	1.91	1.51	1.70	1.75	1.37	1.42	1.48
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ	0.06	2.36	2.16	1.79	2.07	2.41	1.95	2.28	2.01	1.90	2.16	1.97	1.91	1.71	1.74	1.76	1.50	1.56	1.56
	20	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**
B3LYP	1.34	1.14	1.20	1.25	1.27	1.10	0.95	0.96	0.89	0.76	0.81	0.78	0.66	0.66	0.70	0.53	0.57	0.38	0.00
B3LYP-D3	1.67	1.62	1.59	1.02	1.43	1.74	1.01	1.52	1.20	1.41	1.53	1.35	1.14	0.75	1.26	0.90	0.10	0.76	0.47
B97D	1.27	1.42	1.18	0.89	1.54	1.46	0.64	1.27	0.87	1.36	1.47	1.39	1.22	0.63	1.04	0.79	0.00	0.64	0.59
MP2	1.63	1.58	1.57	1.06	1.33	1.71	0.64	1.49	1.14	1.28	1.40	1.11	0.89	0.20	1.21	0.86	0.00	0.68	0.19
MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ	1.50	1.40	1.35	1.03	1.28	1.46	0.64	1.31	1.00	1.13	1.19	0.94	0.81	0.19	1.03	0.76	0.00	0.58	0.11
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ	1.55	1.48	1.43	1.02	1.40	1.53	0.77	1.36	1.07	1.27	1.33	1.14	1.01	0.45	1.10	0.84	0.00	0.67	0.33

Table S6: MP2/aug-cc-pVDZ calculated populations (%) and dipole moments (μ) of **FB** conformers, obtained for the isolated molecule and by using the implicit IEF-PCM implicit solvent model for cyclohexane and dichloromethane dielectric constant values. BHandH/EPR-III calculated $^{1h}J_{F,H}$ SSCCs obtained for isolated MP2/aug-cc-pVDZ geometries are also indicated (in Hz). Calculated SOPPA(CCSD)/EPR-III $^{1h}J_{F,H}$ SSCC values for conformers **1**, **3**, **23** and **36** are shown in parenthesis (Hz).

		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Isolated	**%P**	11.9	0.2	0.3	0.7	0.4	0.2	0.6	0.3	0.5	0.7	0.4	0.4	0.5	1.1	0.8	0.8	1.3	1.3	1.2
	μ	3.4	1.8	3.7	1.6	3.4	1.8	3.5	1.9	3.5	2.9	2.1	3.2	3.5	3.7	1.8	3.7	1.4	3.6	1.3
	$^{1h}J_{F,H}$	-30.26 (-22.58)	0.09 (0.39)	-17.24 (-12.04)	-0.19 (0.07)	1.21 (1.35)	-0.26 (-0.19)	-0.06 (-0.11)	-0.01 (-0.04)	-0.07 (-0.19)	-0.05 (-0.15)	0.36 (0.24)	-0.23 (-0.27)	1.95 (1.25)	-0.19 (-0.23)	0.02 (0.06)	-0.63 (-0.48)	-0.01 (-0.03)	-0.07 (-0.26)	-0.11 (-0.25)
Cyclohexane	**%P**	10.9	0.4	---	1.0	0.5	0.4	1.0	0.5	0.8	1.0	0.7	0.7	0.8	1.4	1.1	1.1	1.2	1.2	1.4
	μ	3.84	1.99	---	1.79	3.86	1.92	3.85	2.00	3.80	3.30	2.22	3.54	3.85	4.00	1.95	3.96	1.73	3.89	1.51
CH_2Cl_2	**%P**	6.8	0.6	---	1.2	0.7	0.7	1.2	0.8	1.2	1.3	0.9	0.8	1.1	1.4	1.2	1.1	0.9	0.8	1.2
	μ	4.42	2.19	---	2.03	4.54	2.11	4.25	2.14	4.27	3.83	2.41	4.01	4.29	4.40	2.17	4.32	2.37	4.37	1.72

		20	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**
Isolated	**%P**	1.0	1.1	1.1	2.7	1.7	0.9	5.4	1.3	2.3	1.8	1.5	2.4	3.6	11.4	2.1	3.7	15.9	5.0	11.5
	μ	3.3	3.5	1.8	2.3	3.9	1.8	2.4	3.3	1.6	3.3	2.2	3.7	3.5	1.6	1.7	1.9	3.4	1.7	2.1
	$^{1h}J_{F,H}$	-0.08 (-0.01)	-0.14 (-0.10)	0.03 (0.12)	-0.93 (0.12)	0.07 (0.00)	-0.27 (-0.21)	0.30 (0.11)	-0.08 (-0.09)	-0.18 (-0.05)	-0.05 (-0.23)	1.05 (0.82)	0.01 (-0.12)	-0.16 (-0.34)	0.10 (-0.00)	0.13 (0.09)	0.02 (0.05)	-11.99 (-8.26)	-0.32 (-0.25)	0.55 (0.26)
Cyclohexane	**%P**	1.7	1.9	2.0	1.9	1.9	1.7	5.5	2.4	3.5	2.9	2.5	3.4	4.3	9.3	3.5	4.9	13.9	6.6	11.8
	μ	3.67	3.83	2.03	2.49	4.17	1.92	2.55	3.62	1.76	3.68	2.29	3.96	3.81	1.77	1.89	2.12	3.83	1.83	2.26
CH_2Cl_2	**%P**	2.6	3.0	2.5	1.0	1.4	2.7	3.7	3.7	4.0	3.9	3.0	3.6	4.5	4.8	4.3	4.7	8.2	6.4	8.0
	μ	4.18	4.25	2.26	2.79	4.50	2.11	2.78	4.10	2.01	4.17	2.44	4.38	4.32	1.91	2.15	2.41	4.32	2.08	2.40

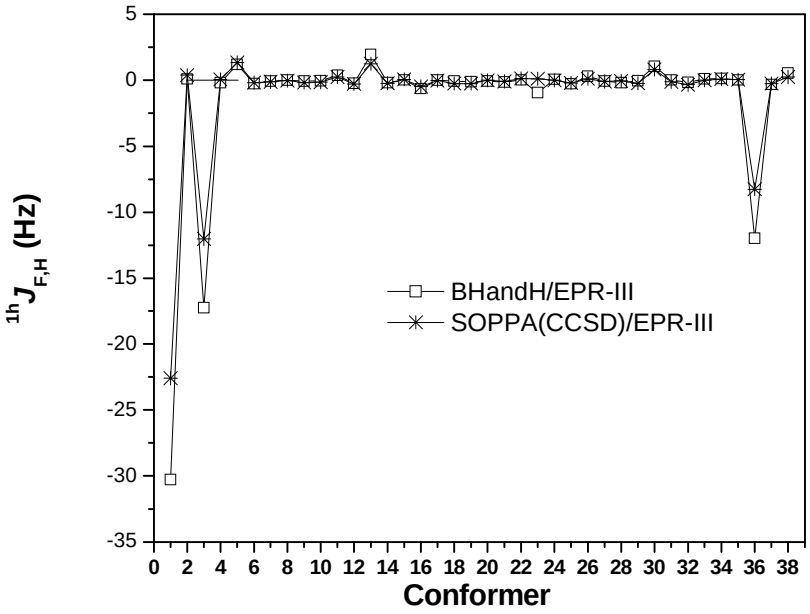


Figure S9: Comparison between SOPPA(CCSD)/EPR-III and BHandH/EPR-III calculated $^{1h}J_{F,H}$ SSCC values for **FB** conformers. BHandH/EPR-III $^{1h}J_{F,H}$ mean absolute deviation (MAD) from $^{1h}J_{F,H}$ SOPPA(CCSD)/EPR-III is of 0.58 Hz.

Table S7: Relative energies (Δ*E*) of **FB** conformers obtained for MP2/aug-cc-pVDZ optimised geometries for the isolated molecule. Thermal corrections to enthalpes (Δ*H*) and Gibbs free energies (Δ*G*) were obtained from B3LYP/aug-cc-pVDZ frequency calculations. Conformer populations (%P) are given for each case.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Δ*E*	0.17	2.48	2.39	1.82	2.12	2.53	1.93	2.40	2.07	1.83	2.16	2.11	2.02	1.59	1.80	1.81	1.46	1.49	1.55
%P (Δ*E*)	11.9	0.2	0.3	0.7	0.4	0.2	0.6	0.3	0.5	0.7	0.4	0.4	0.5	1.1	0.8	0.8	1.3	1.3	1.2
Δ*H*	0.15	2.39	2.31	1.73	1.99	2.46	1.87	2.34	2.00	1.75	2.09	1.97	1.88	1.55	1.76	1.69	1.32	1.39	1.42
%P (Δ*H*)	10.7	0.2	0.3	0.7	0.5	0.2	0.6	0.3	0.5	0.7	0.4	0.5	0.6	1.0	0.7	0.8	1.5	1.3	1.2
Δ*G*	0.96	2.19	2.66	1.68	2.12	2.37	1.70	2.27	1.91	1.54	1.99	1.96	2.02	1.41	1.66	1.91	1.30	1.54	1.54
%P (Δ*G*)	3.4	0.4	0.2	1.0	0.5	0.3	1.0	0.4	0.7	1.3	0.6	0.6	0.6	1.6	1.0	0.7	1.9	1.3	1.3
	20	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**
Δ*E*	1.63	1.58	1.57	1.06	1.33	1.71	0.64	1.49	1.14	1.28	1.40	1.11	0.89	0.20	1.21	0.86	0.00	0.68	0.19
%P (Δ*E*)	1.0	1.1	1.1	2.7	1.7	0.9	5.4	1.3	2.3	1.8	1.5	2.4	3.6	11.4	2.1	3.7	15.9	5.0	11.5
Δ*H*	1.44	1.44	1.47	1.03	1.21	1.63	0.59	1.33	0.95	1.12	1.32	0.98	0.70	0.25	1.07	0.72	0.02	0.48	0.00
%P (Δ*H*)	1.2	1.2	1.1	2.4	1.8	0.9	5.1	1.5	2.8	2.1	1.5	2.7	4.2	9.1	2.3	4.1	13.4	6.1	13.8
Δ*G*	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42
%P (Δ*G*)	1.5	1.8	1.6	2.0	2.0	1.4	7.5	2.0	3.8	3.1	2.3	4.2	4.8	7.7	3.1	4.2	3.8	7.6	17.0

Table S8: Relative energies (Δ*E*) of **FB** conformer obtained for MP2/aug-cc-pVDZ optimised geometries for the IEF-PCM implicit solvent model using the cyclohexane dielectric constant value. Thermal corrected enthalpy (Δ*H*) and Gibbs free energies (Δ*G*) were obtained from B3LYP/aug-cc-pVDZ frequency calculations. Conformer populations (%P) are given for each case.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Δ*E*	0.15	2.09	---	1.53	1.92	2.06	1.58	1.92	1.67	1.53	1.78	1.78	1.66	1.36	1.48	1.51	1.45	1.47	1.35
%P (Δ*E*)	9.7	0.4	---	0.9	0.5	0.4	0.9	0.5	0.7	0.9	0.6	0.6	0.8	1.3	1.0	1.0	1.1	1.0	1.3
Δ*H*	0.26	2.14	---	1.59	1.92	2.13	1.69	2.01	1.73	1.61	1.84	1.75	1.65	1.48	1.55	1.54	1.40	1.48	1.33
%P (Δ*H*)	8.2	0.2	---	0.9	0.5	0.40	0.7	0.4	0.7	0.9	0.6	0.7	0.8	1.1	0.9	1.0	1.2	1.1	1.4
Δ*G*	1.11	2.26	---	1.81	2.14	2.19	1.83	2.12	1.76	1.74	1.94	1.92	1.90	1.66	1.63	1.87	1.59	1.78	1.58
%P (Δ*G*)	2.6	0.4	---	0.8	0.5	0.4	0.8	0.5	0.9	0.9	0.6	0.6	0.7	1.0	1.1	0.7	1.2	0.8	1.2
	20	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**
Δ*E*	1.24	1.16	1.16	1.17	1.17	1.23	0.55	1.05	0.81	0.93	1.02	0.83	0.70	0.24	0.82	0.62	0.00	0.44	0.10
%P (Δ*E*)	1.5	1.7	1.7	1.7	1.7	1.6	4.9	2.1	3.2	2.6	2.2	3.1	3.8	8.3	3.1	4.4	12.4	5.9	10.6
Δ*H*	1.18	1.15	1.19	1.20	1.15	1.27	0.65	1.04	0.74	0.88	1.06	0.81	0.60	0.36	0.80	0.58	0.15	0.36	0.00
%P (Δ*H*)	1.8	1.9	1.7	1.7	1.8	1.5	4.3	2.2	3.7	2.9	2.1	3.3	4.7	7.0	3.3	4.8	9.9	7.0	12.8
Δ*G*	1.11	1.22	1.59	1.36	1.12	0.89	1.09	0.76	0.91	0.92	0.77	0.66	0.69	0.80	0.67	0.97	0.37	0.00	1.11
%P (Δ*G*)	2.3	2.6	2.1	1.1	1.7	2.5	3.7	2.7	4.7	3.6	3.6	4.5	5.5	5.3	4.3	5.4	3.2	9.0	16.8

Table S9: Relative energies (Δ*E*) of **FB** conformer obtained for MP2/aug-cc-pVDZ optimised geometries for the IEF-PCM implicit solvent model using the dichloromethane dielectric constant value. Thermal corrected enthalpy (Δ*H*) and Gibbs free energies (Δ*G*) were obtained from B3LYP/aug-cc-pVDZ frequency calculations. Conformer populations (%P) are given for each case.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**
Δ*E*	0.12	1.59	---	1.12	1.49	1.49	1.14	1.37	1.12	1.08	1.32	1.36	1.19	1.05	1.12	1.19	1.32	1.38	1.13
%P (Δ*E*)	6.7	0.6	---	1.2	0.7	0.7	1.2	0.8	1.3	1.3	0.9	0.8	1.1	1.4	1.2	1.1	0.9	0.8	1.2
Δ*H*	0.08	1.51	---	0.97	1.32	1.44	1.13	1.35	1.06	1.01	1.26	1.20	1.05	1.04	1.05	1.08	1.15	1.20	0.96
%P (Δ*H*)	6.6	0.6	---	1.5	0.8	0.7	1.1	0.8	1.3	1.4	0.9	1.0	1.3	1.3	1.3	1.2	1.1	1.0	1.5
Δ*G*	1.26	1.90	---	1.37	1.87	1.83	1.60	1.80	1.42	1.44	1.71	1.73	1.61	1.53	1.43	1.73	1.83	1.68	1.53
%P (Δ*G*)	1.6	0.5	---	1.3	0.6	0.6	0.9	0.6	1.2	1.2	0.7	0.7	0.9	1.0	1.2	0.7	0.6	0.8	1.0
	20	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**
Δ*E*	0.68	0.61	0.70	1.25	1.07	0.65	0.47	0.48	0.42	0.44	0.60	0.49	0.36	0.32	0.39	0.33	0.00	0.15	0.01
%P (Δ*E*)	2.6	3.0	2.5	1.0	1.4	2.7	3.7	3.7	4.0	3.9	3.0	3.6	4.5	4.8	4.3	4.7	8.2	6.4	8.0
Δ*H*	0.49	0.46	0.61	1.10	0.90	0.58	0.90	0.58	0.41	0.34	0.20	0.26	0.50	0.33	0.11	0.26	0.22	0.13	0.00
%P (Δ*H*)	3.3	3.4	2.7	1.2	1.6	2.8	1.6	2.8	3.8	4.2	5.4	4.9	3.2	4.3	6.2	4.8	5.1	6.0	7.5
Δ*G*	3.25	3.60	2.67	0.75	1.15	3.60	2.59	3.93	5.66	4.78	4.27	4.49	5.82	2.87	5.15	5.84	1.92	8.70	13.10
%P (Δ*G*)	3.2	3.6	2.7	0.8	1.1	3.6	2.6	3.9	5.7	4.8	4.3	4.5	5.8	2.9	5.1	5.8	1.9	8.7	13.1

Table S10: Mean absolute deviations (MADs) over all respective conformers from the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ theoretical level. Values are given in kcal mol^{-1}.

	FE	**FP**	**FB**	**Total**
B3LYP/aug-cc-pVDZ	0.06	0.16	0.22	0.44
B3LYP-D3/aug-cc-pVDZ	0.08	0.13	0.13	0.34
B97D/aug-cc-pVDZ	0.17	0.09	0.18	0.44
MP2/aug-cc-pVDZ	0.07	0.16	0.08	0.31
MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ	0.04	0.10	0.09	0.23

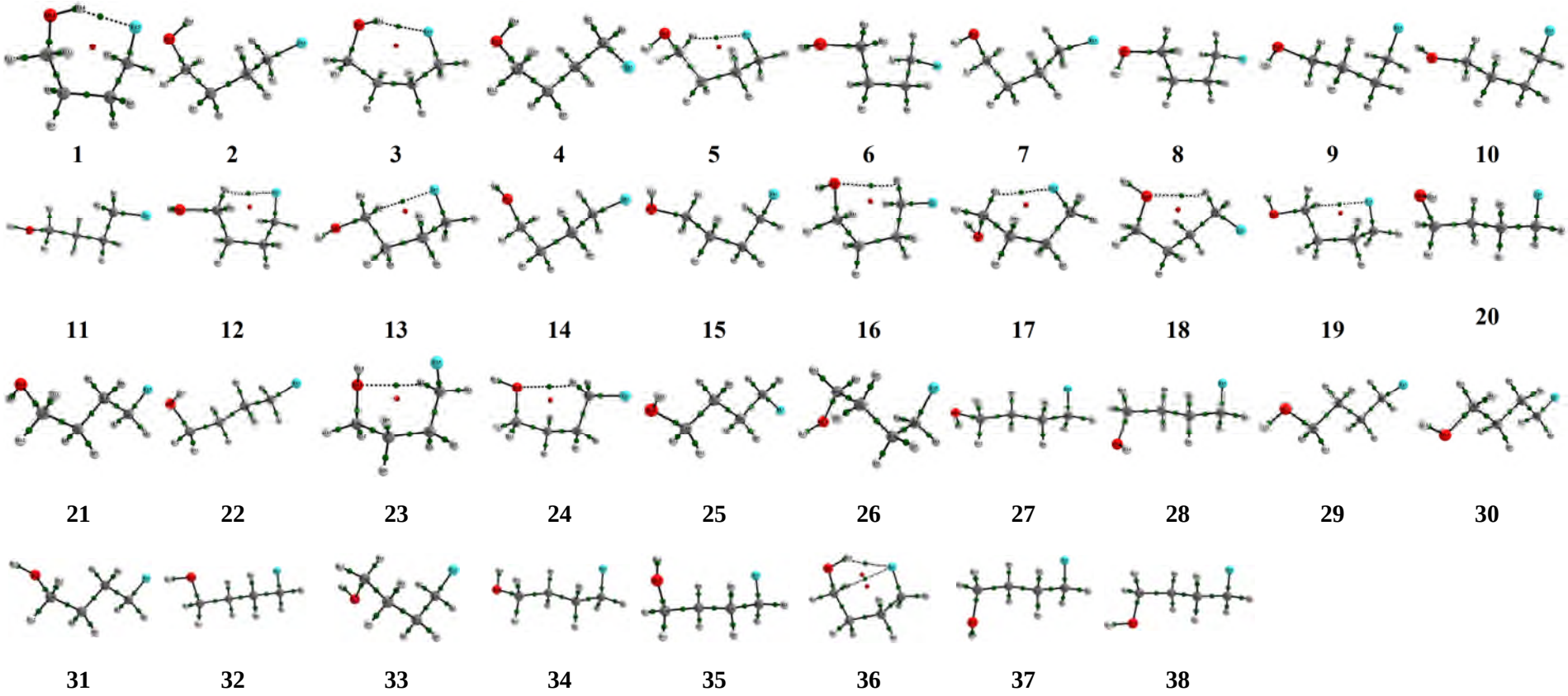
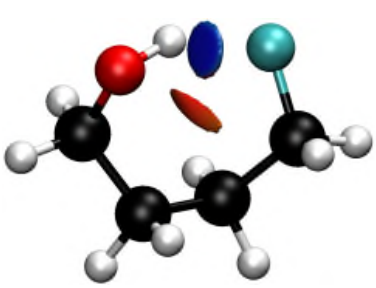
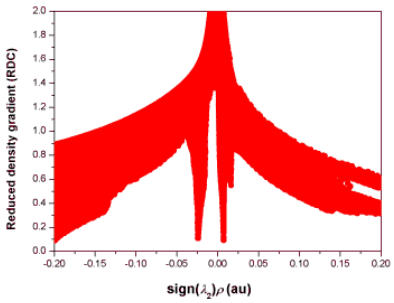
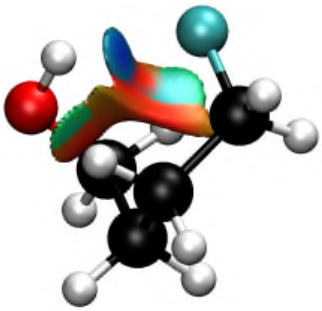


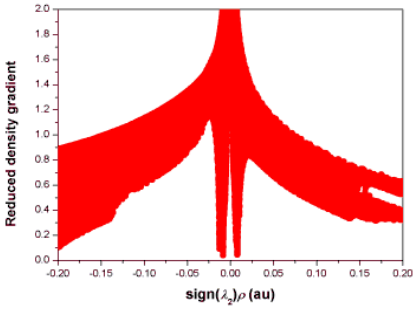
Figure S10: Molecular graphs of **FB** conformer obtained with the QTAIM. Green and points represent BCPs and RCPs, respectively.



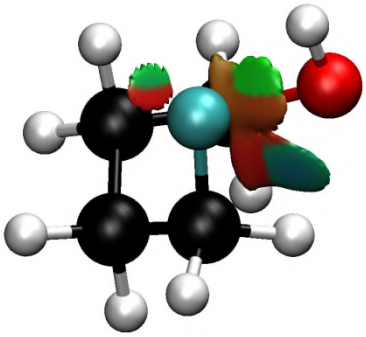


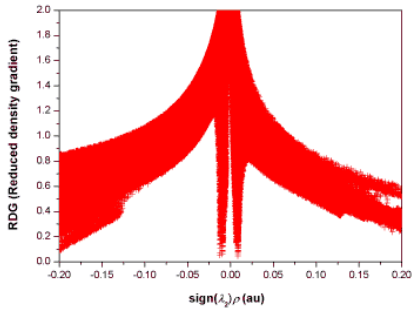
Conformer 1



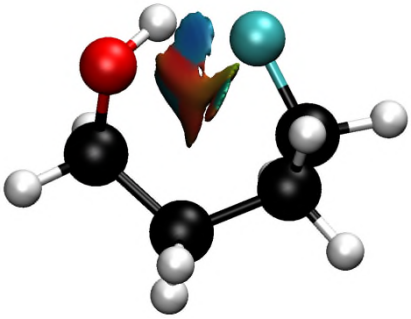


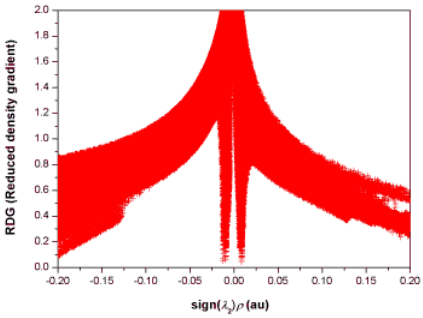
Conformer 3





Conformer 23

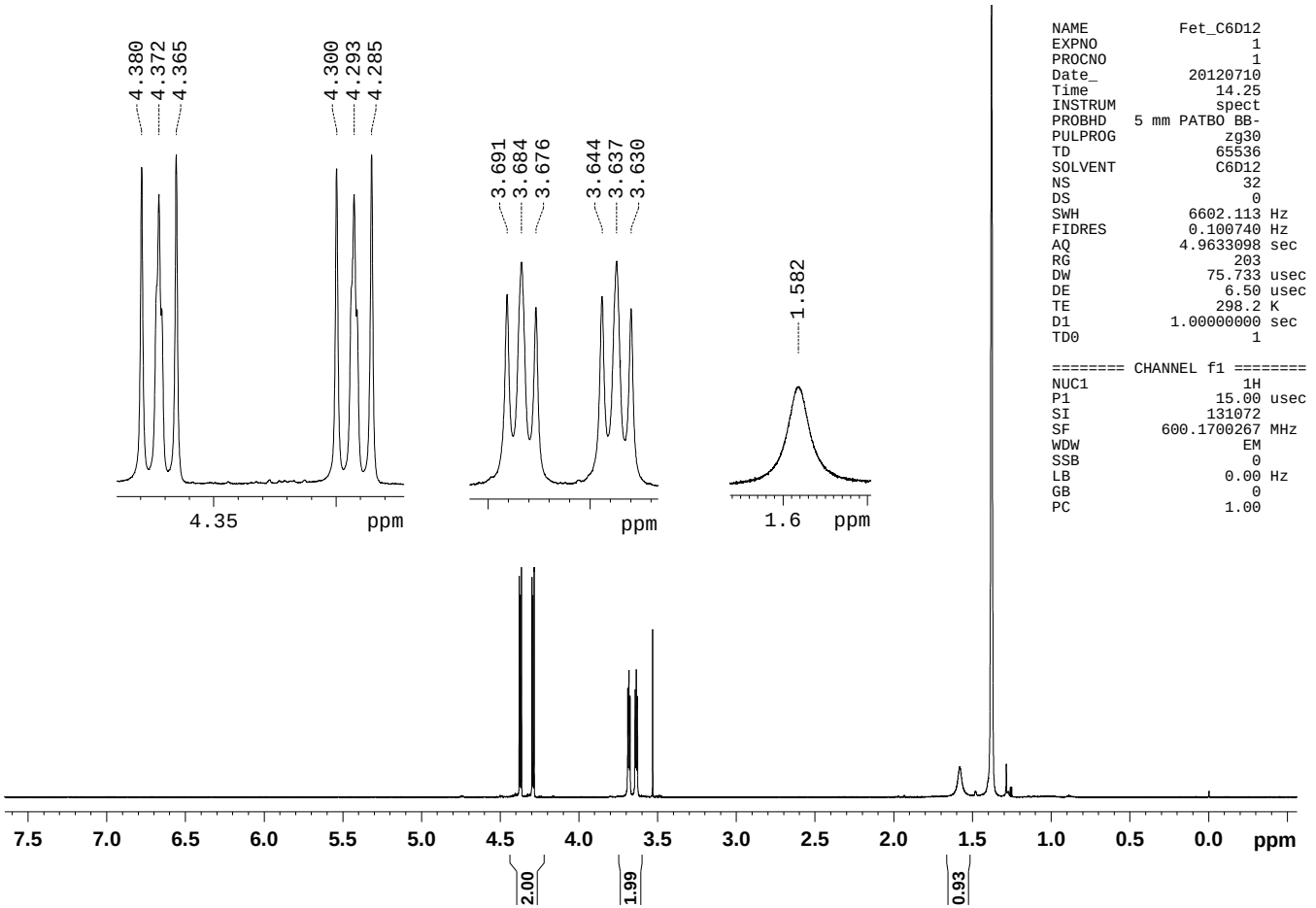




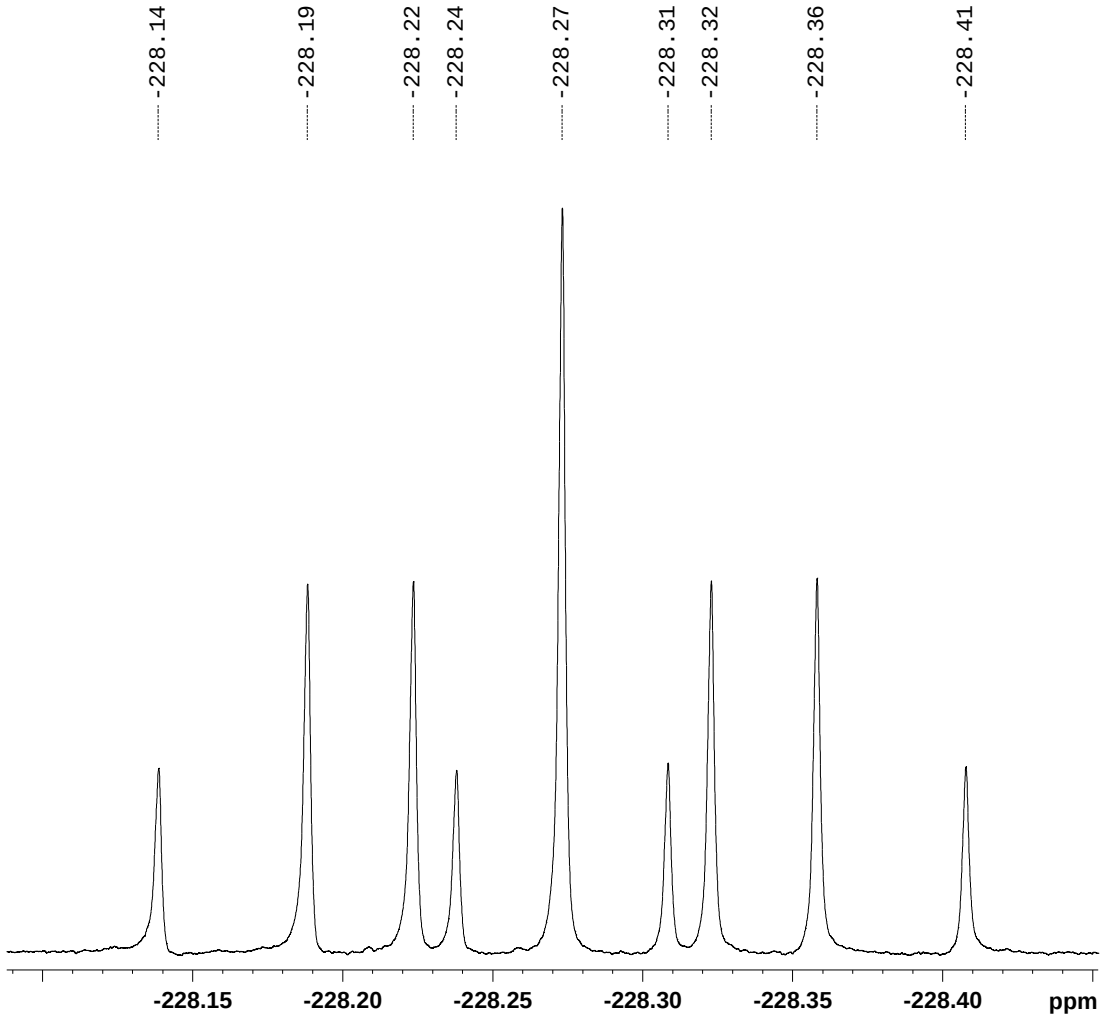
Conformer 36

Figure S11: NCI representations and RDG vs sign(λ_2)ρ plots of **FB** conformers which have appropriate geometry to form a CF···HO intramolecular hydrogen bond. The NCI plot were obtained with a reduced density gradient (RDG) value of 0.5 and the blue-green-red values ranging from -0.02 to 0.01 au.

NMR Spectra



Spectrum S1: ^{1}H NMR spectrum of **FE** in cyclohexane-d_{12}.

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TD                32768
SOLVENT           C6D12
NS                   32
DS                    4
SWH            1231.527 Hz
FIDRES        0.037583 Hz
AQ           13.3038578 sec
RG                  203
DW              406.000 usec
DE                6.50 usec
TE               298.1 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
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WDW                  EM
SSB                   0
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GB                    0
PC                 1.00
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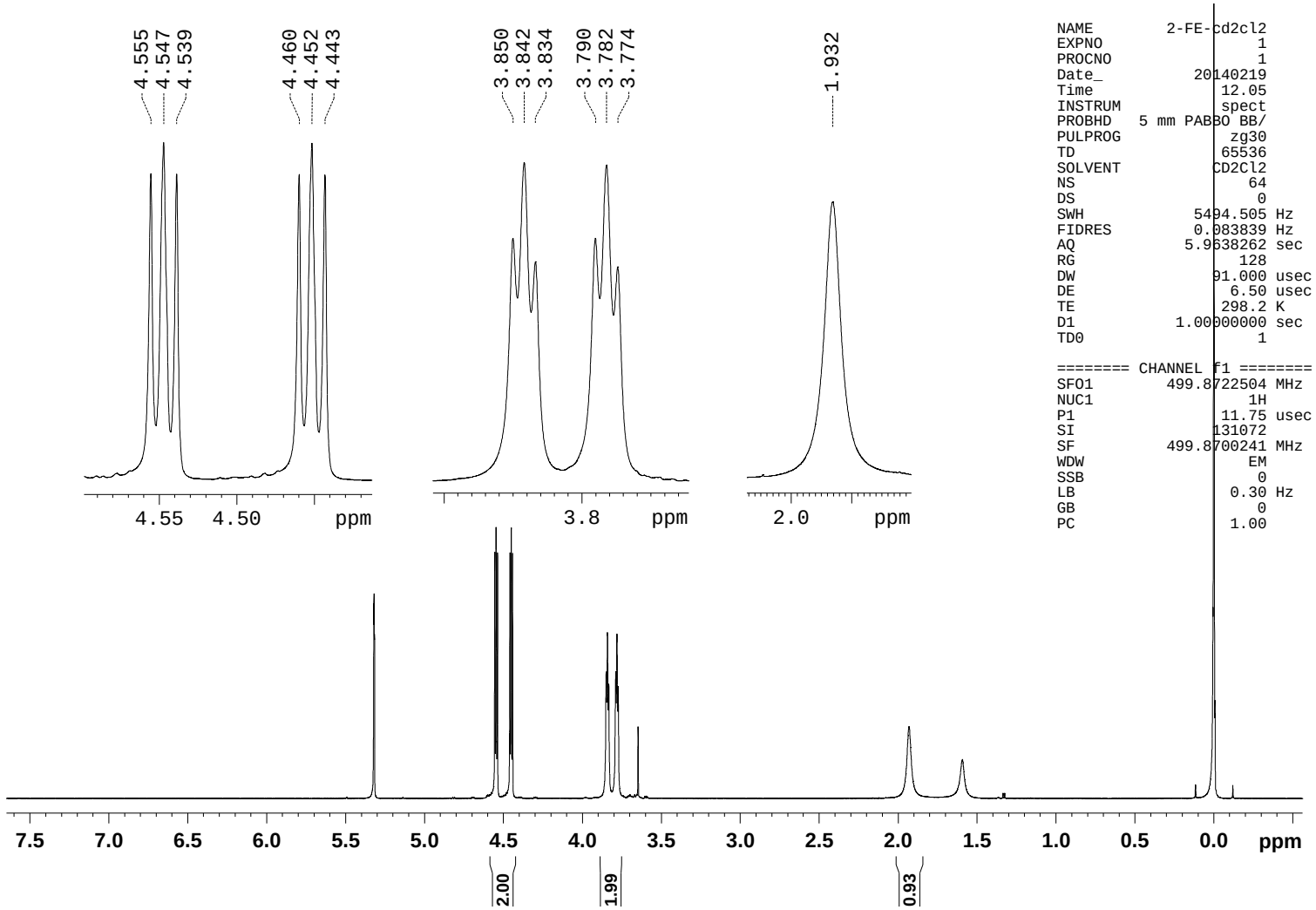
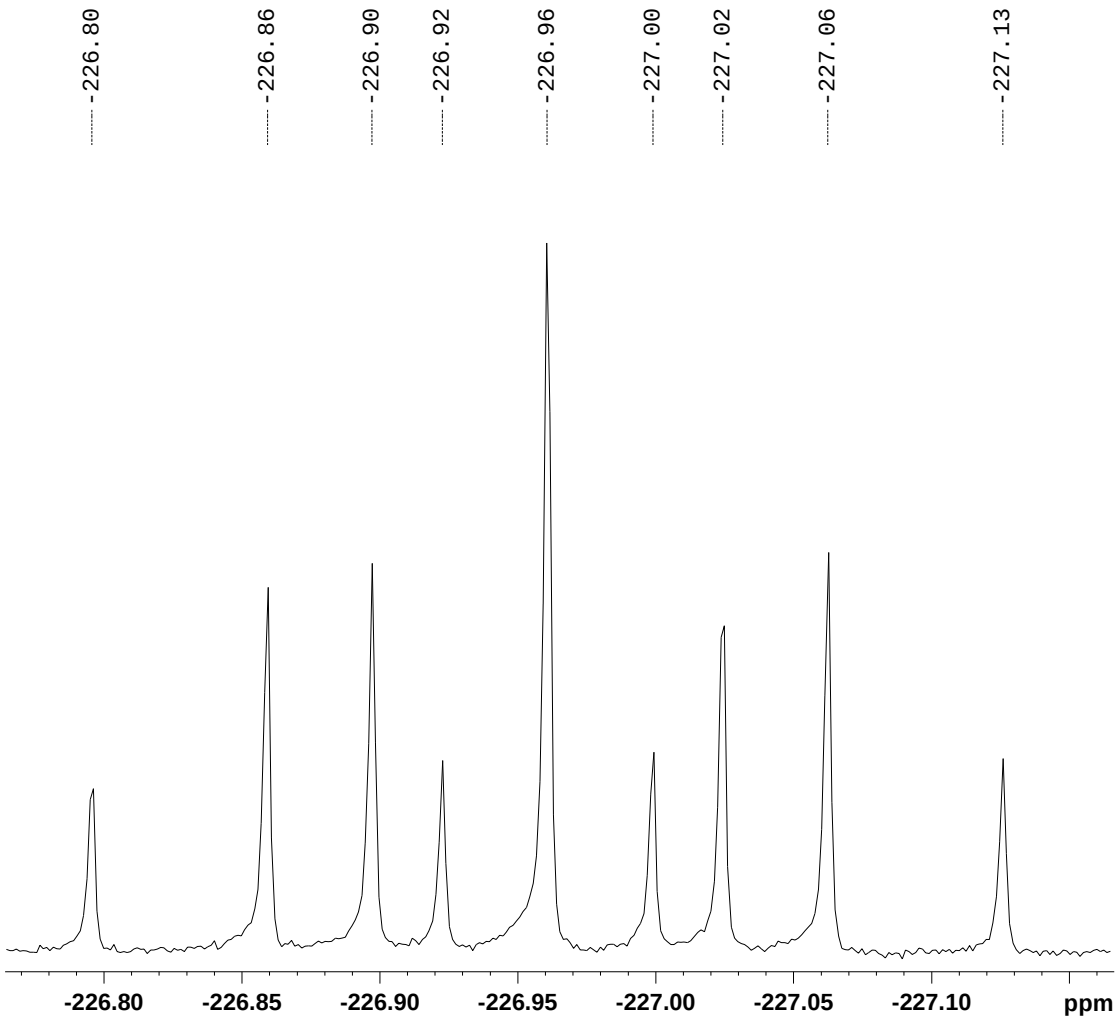
Spectrum S2: ^{19}F NMR spectrum of **FE** in cyclohexane-d_{12}.



Spectrum S3: ^{19}H NMR spectrum of **FE** in CD_2Cl_2.

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DS                      4
SWH             37500.000 Hz
FIDRES          0.286102 Hz
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RG                    203
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DE                   6.50 usec
TE                 298.2 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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SI                  65536
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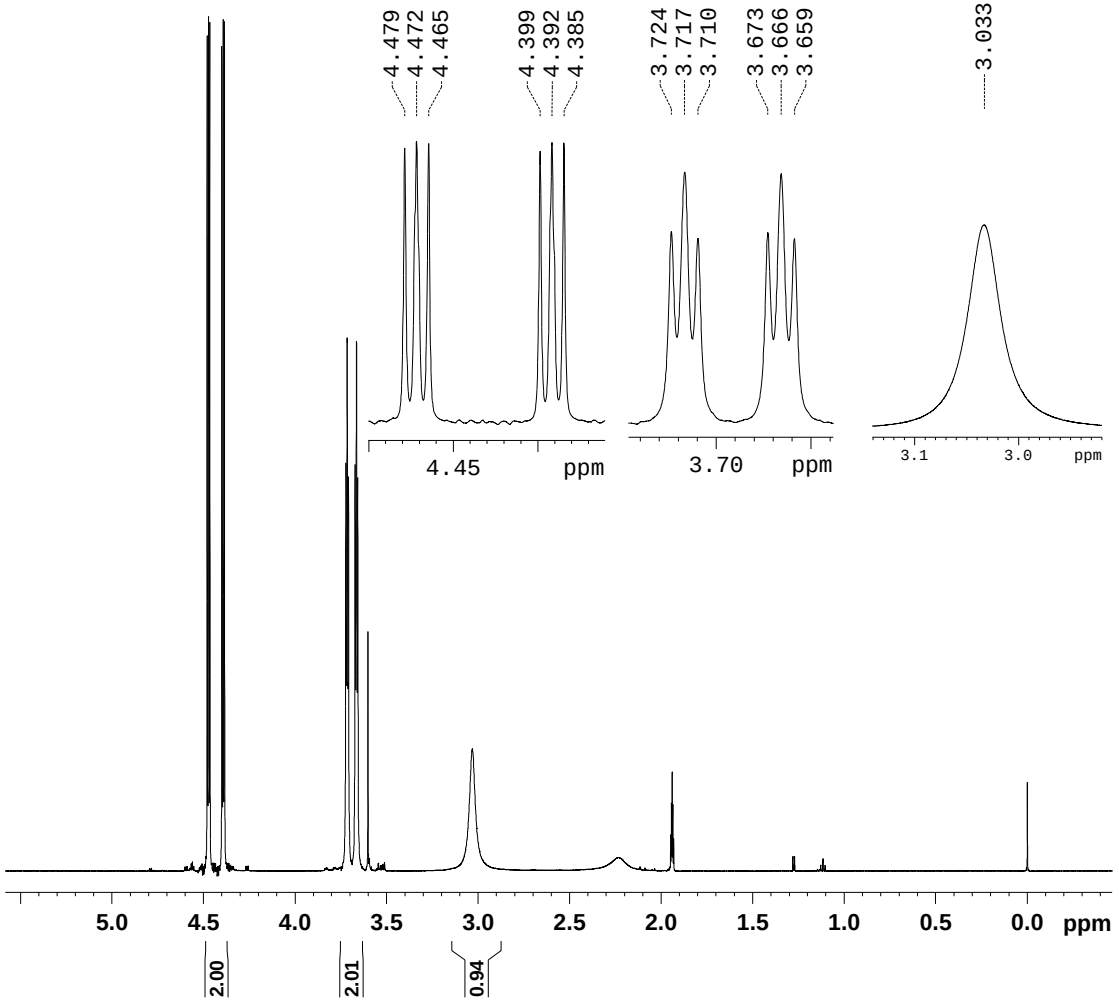
Spectrum S4: ^{19}F NMR spectrum of **FE** in CD_2Cl_2.

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TD                 65536
SOLVENT            CD3CN
NS                     4
DS                     0
SWH            12335.526 Hz
FIDRES          0.188225 Hz
AQ             2.6564426 sec
RG                    32
DW                40.533 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
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SI                131072
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WDW                   EM
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LB                 0.30 Hz
GB                     0
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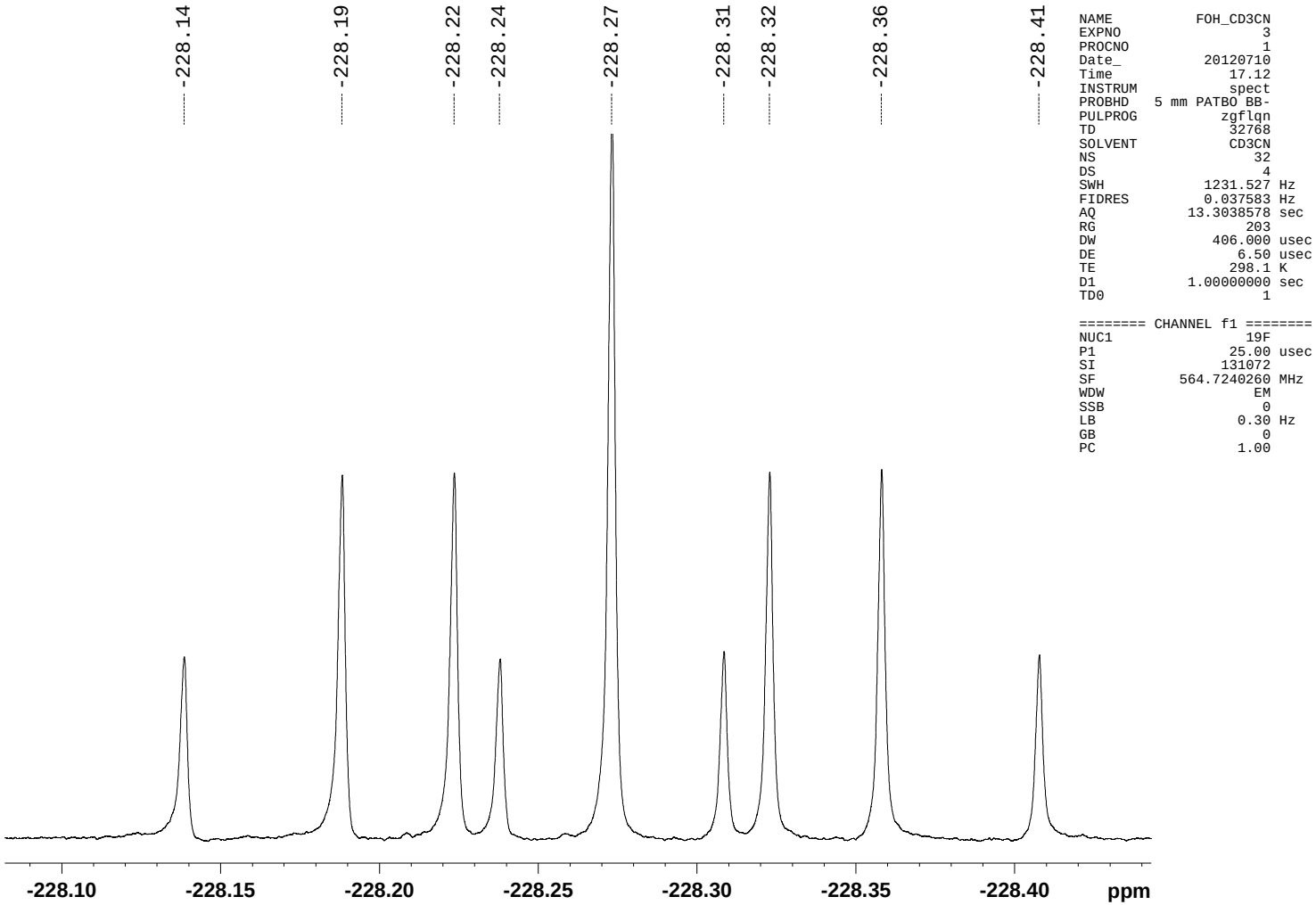
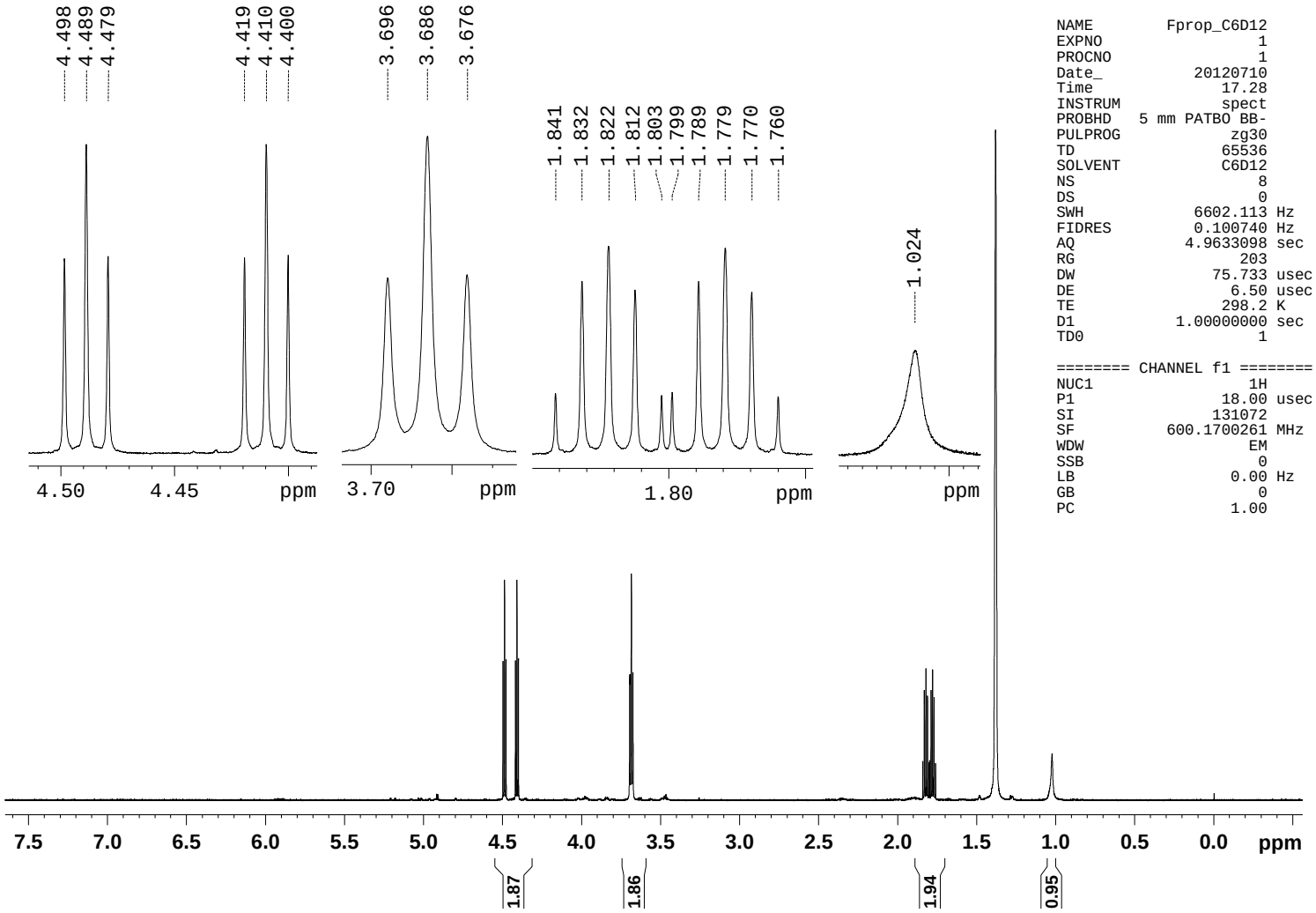
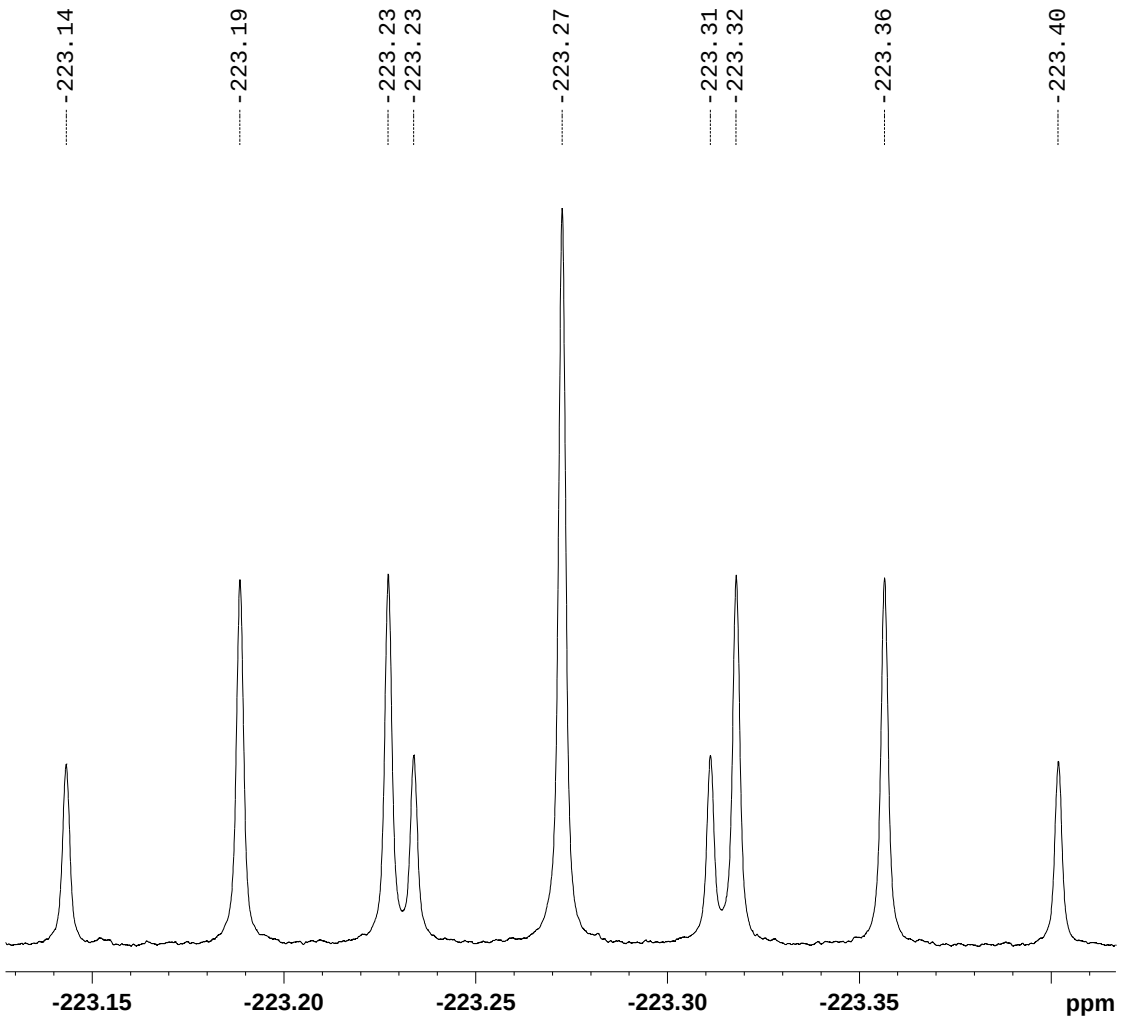
Spectrum S5: ^{1}H NMR spectrum of **FE** in CD_3CN.



Spectrum S6: ^{1}H NMR spectrum of **FE** in CD_3CN.

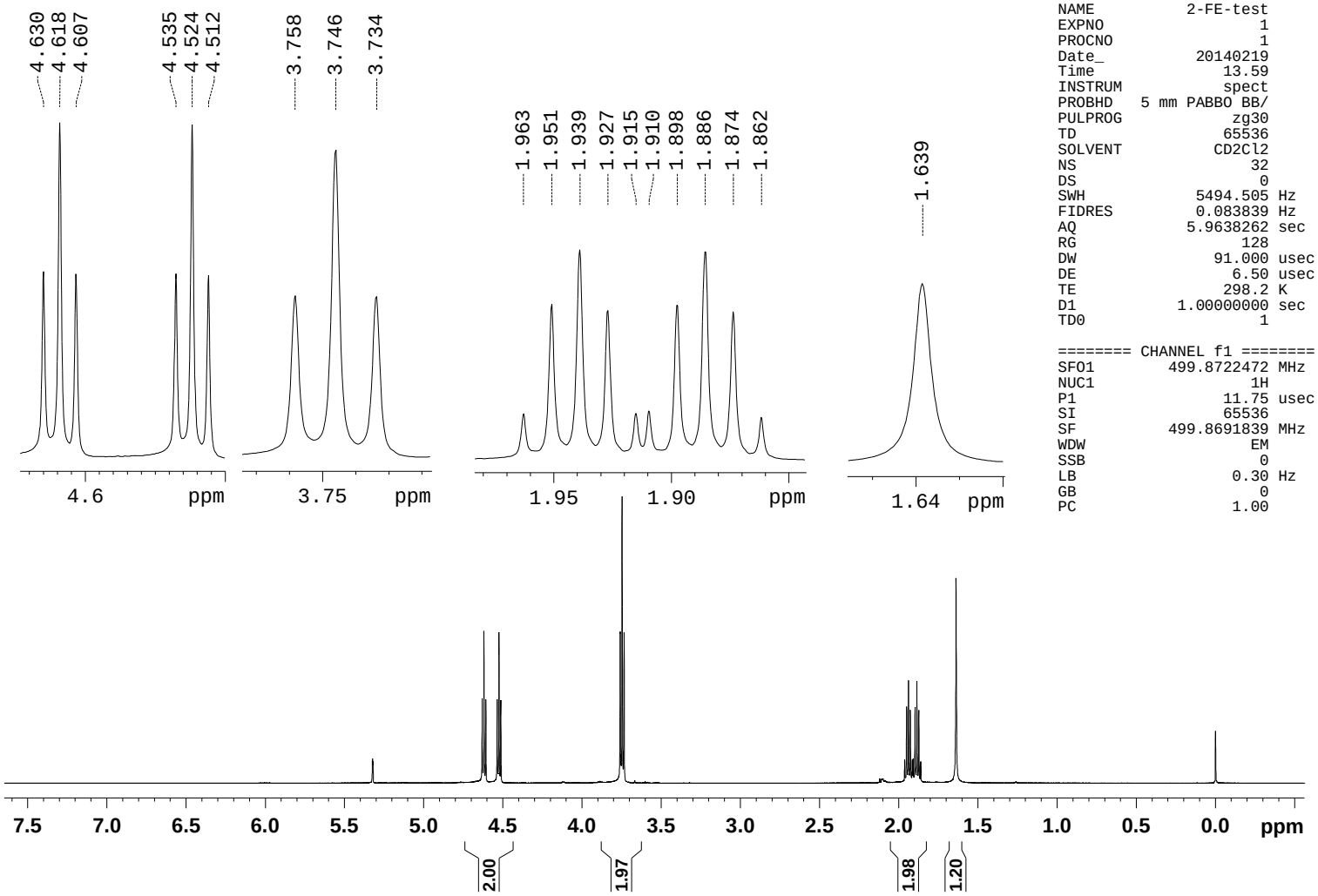


Spectrum S7: ^{1}H NMR spectrum of **FP** in cyclohexane-d_{12}.

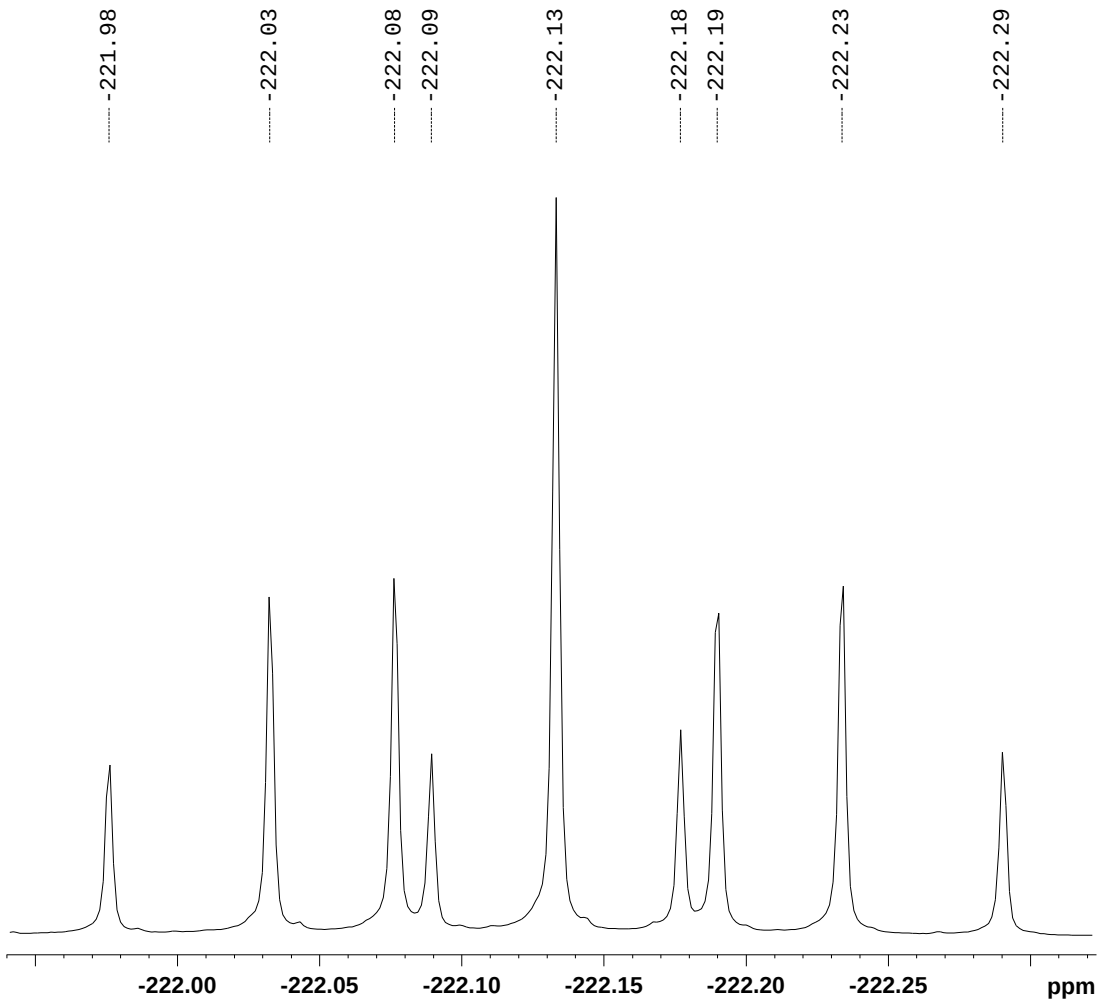



```
NAME          Fprop_C6D12
EXPNO                   3
PROCNO                  1
Date_            20120710
Time                17.33
INSTRUM             spect
PROBHD   5 mm PATBO BB-
PULPROG           zgflqn
TD                 65536
SOLVENT            C6D12
NS                    32
DS                     4
SWH             4290.618 Hz
FIDRES          0.065470 Hz
AQ              7.6371784 sec
RG                   203
DW                116.533 usec
DE                  6.50 usec
TE                298.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  19F
P1                  25.00 usec
SI                131072
SF          564.7240260 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Spectrum S8: ^{19}F NMR spectrum of **FP** in cyclohexane-d_{12}.

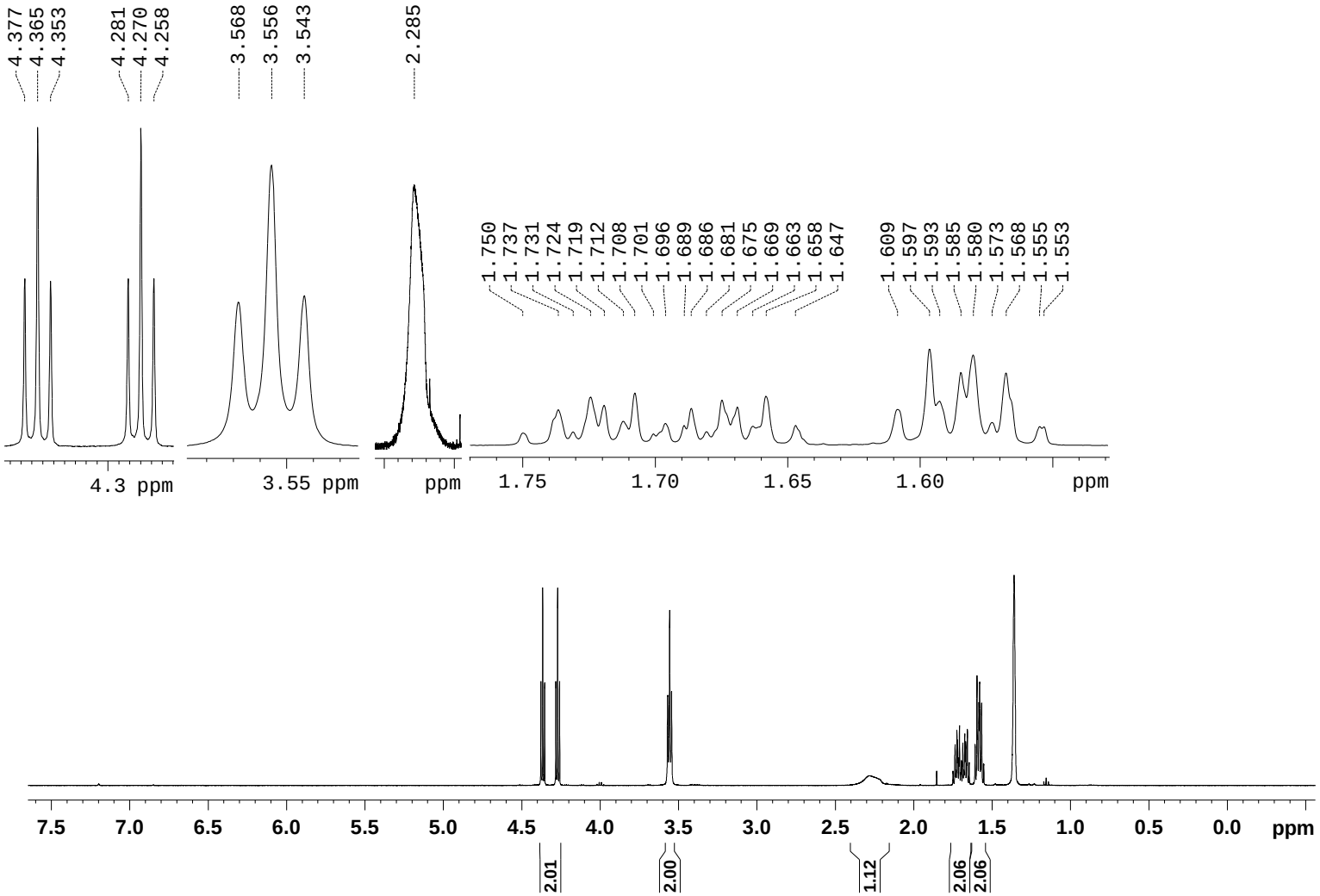


Spectrum S9: ^{1}H NMR spectrum of **FP** in CD_2Cl_2.

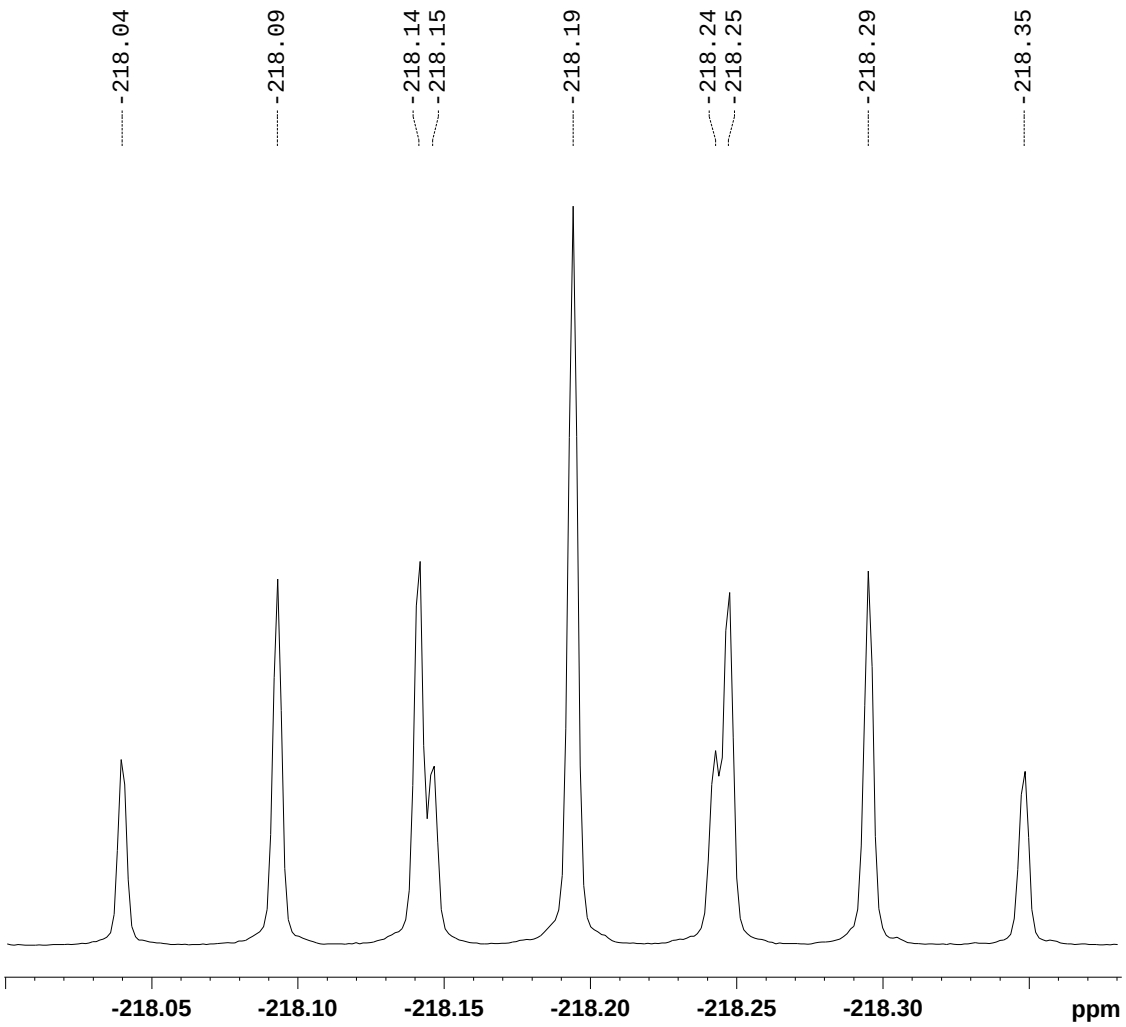



```
NAME          2-FE-test
EXPNO                 2
PROCNO                1
Date_          20140219
Time              14.00
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD               131072
SOLVENT          CD2Cl2
NS                  128
DS                    4
SWH           37500.000 Hz
FIDRES         0.286102 Hz
AQ            1.7476766 sec
RG                  322
DW               13.333 usec
DE                 6.50 usec
TE                298.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         470.2442565 MHz
NUC1                19F
P1                16.50 usec
SI                65536
SF           470.3477330 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Spectrum S10: ^{19}F NMR spectrum of **FP** in CD_2Cl_2.

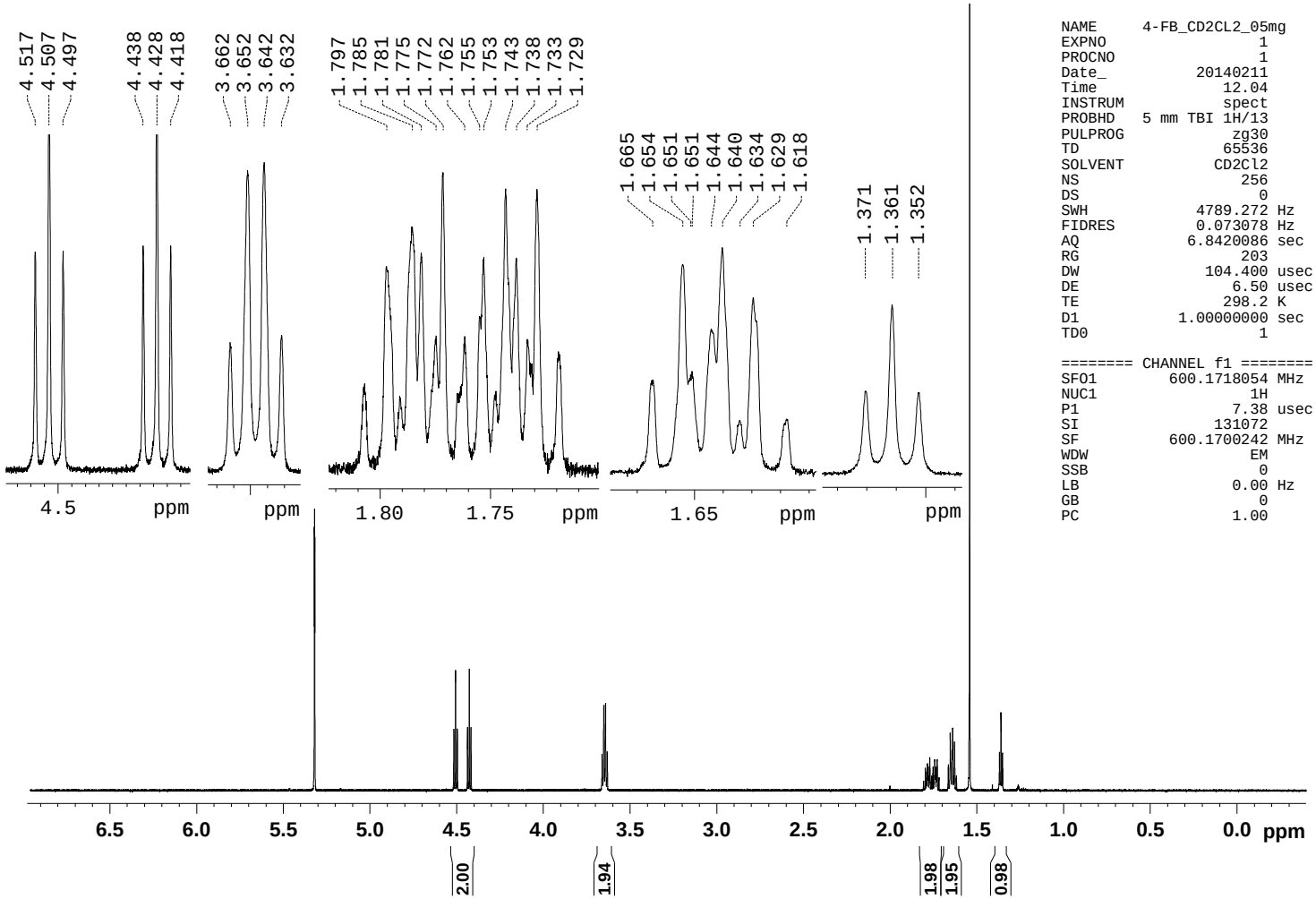


Spectrum S11: ^{1}H NMR spectrum of **FB** in cyclohexane-d_{12}.

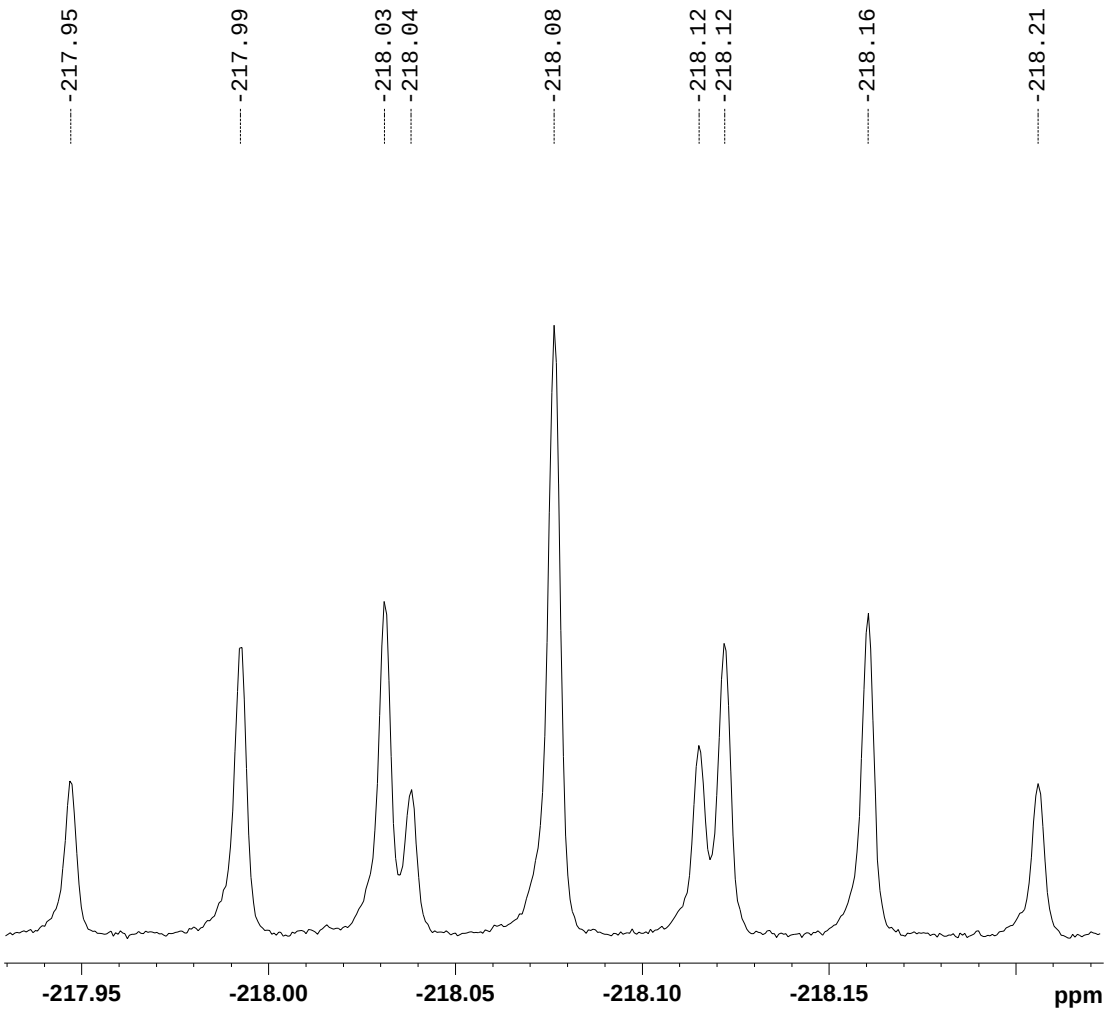



```
NAME      4-FB_cyclohex
EXPNO                 2
PROCNO                1
Date_          20140208
Time              11.48
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD               131072
SOLVENT         Acetone
NS                   64
DS                    4
SWH           37500.000 Hz
FIDRES         0.286102 Hz
AQ            1.7476766 sec
RG                  203
DW                13.333 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.2451972 MHz
NUC1                19F
P1                16.50 usec
SI                65536
SF          470.3477330 MHz
WDW                 EM
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00
```

Spectrum S12: ^{19}F NMR spectrum of **FB** in cyclohexane-$d_{12.}$



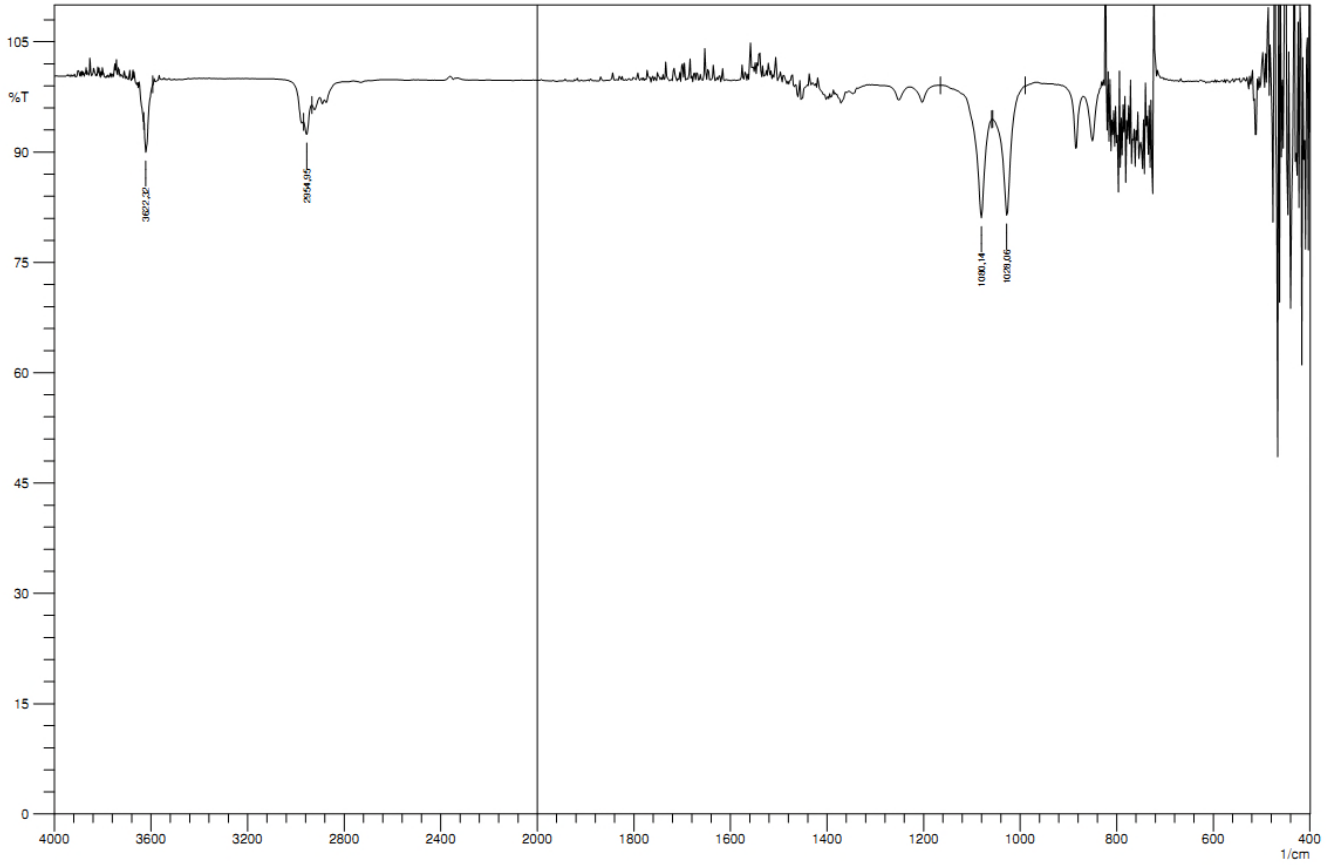
Spectrum S13: ^{1}H NMR spectrum of **FB** in CD_2Cl_2.



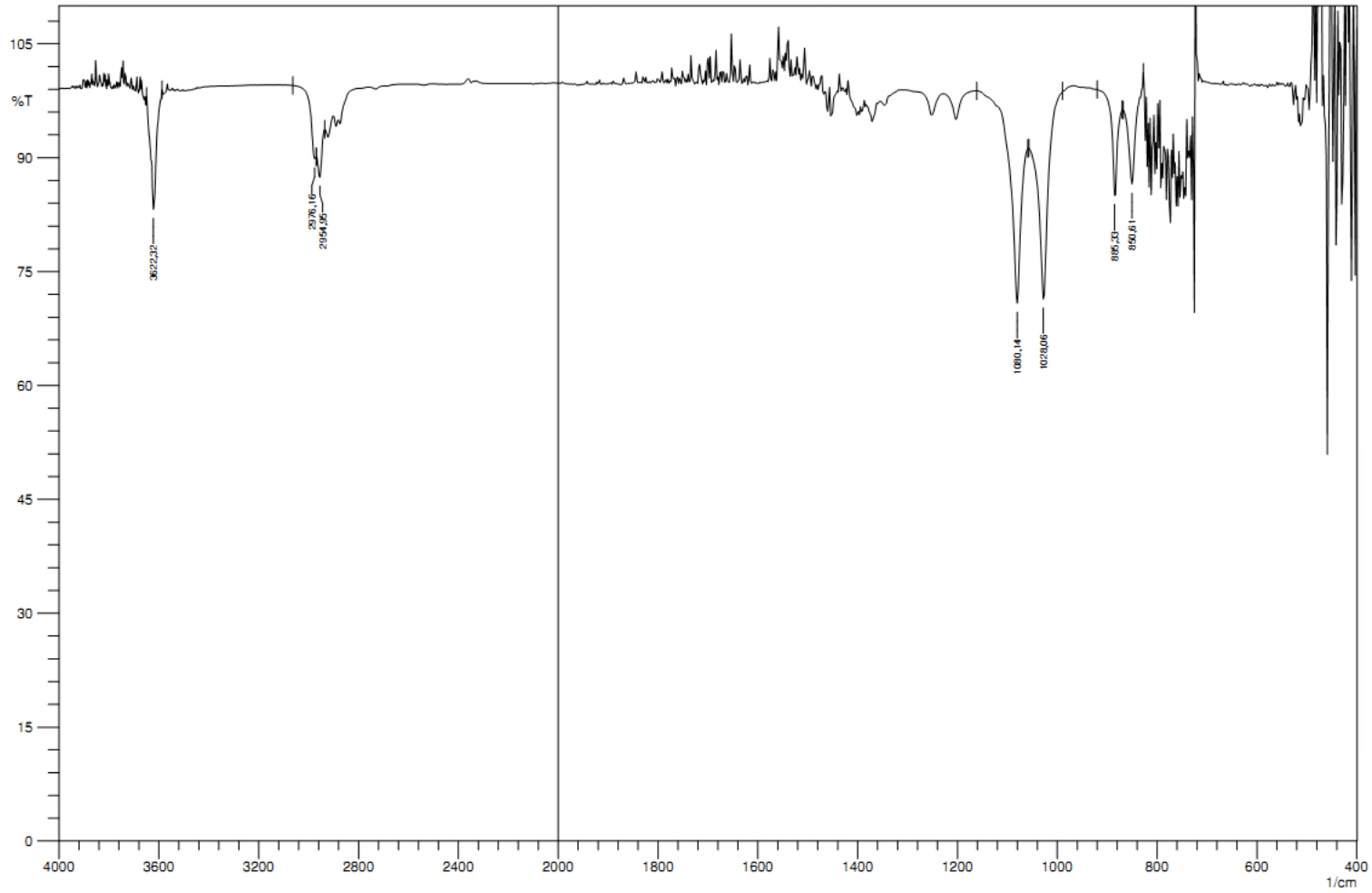

```
NAME      4-FB_CD2CL2_05mg
EXPNO                    2
PROCNO                   1
Date_             20140211
Time                 12.21
INSTRUM              spect
PROBHD   5 mm TBI 1H/13
PULPROG             zgflqn
TD                  131072
SOLVENT             CD2Cl2
NS                     256
DS                       0
SWH             22727.273 Hz
FIDRES           0.173395 Hz
AQ               2.8836341 sec
RG                     203
DW                  22.000 usec
DE                   6.50 usec
TE                  298.1 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          564.6009162 MHz
NUC1                  19F
P1                  29.77 usec
SI                  65536
SF            564.7240260 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Spectrum S14: ^{19}F NMR spectrum of **FB** in CD_2Cl_2.

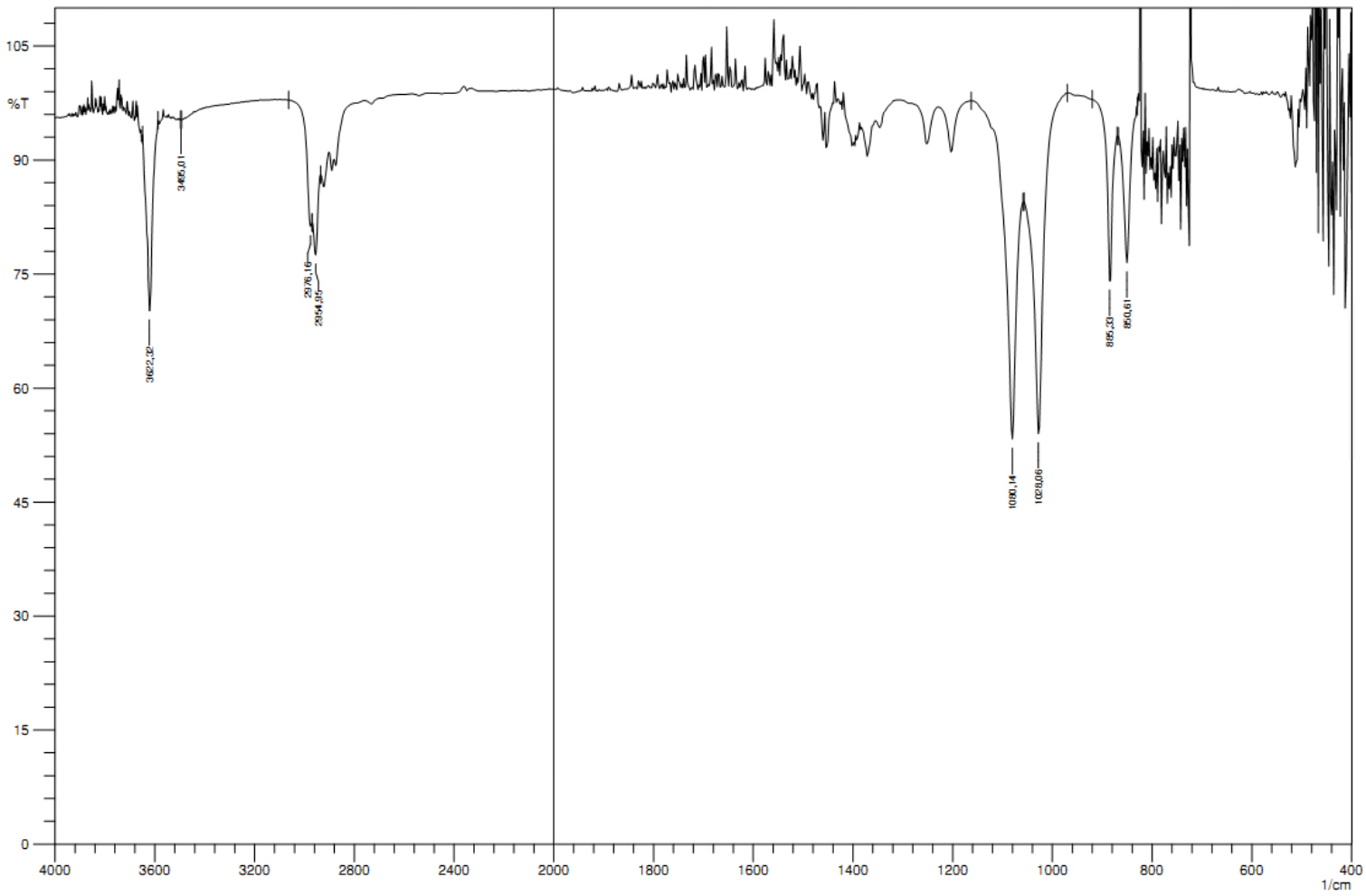
Infrared spectra



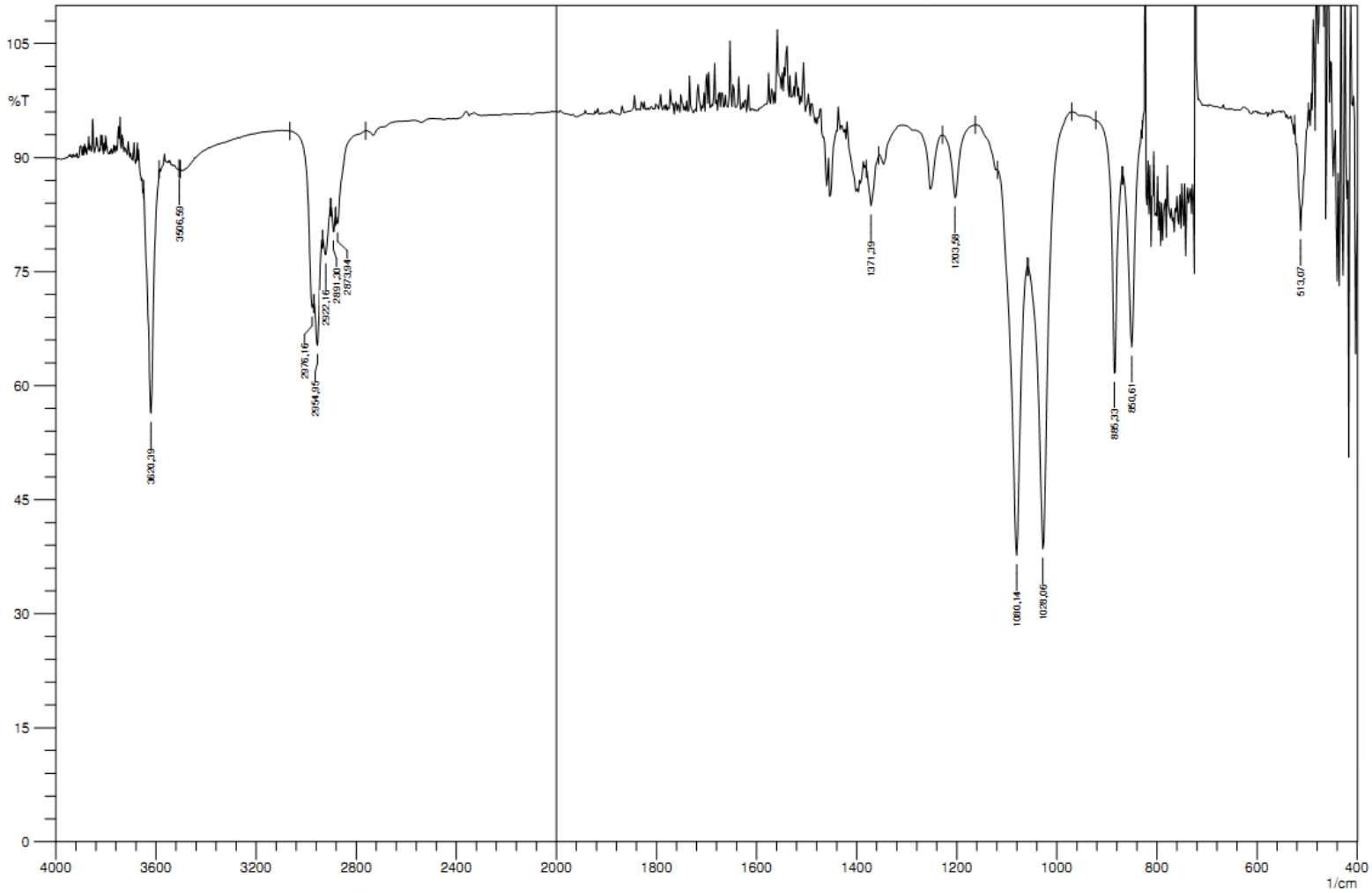
Spectrum S15: Infrared spectrum of **FE** in CCl_4. Concentration = 0.01M.



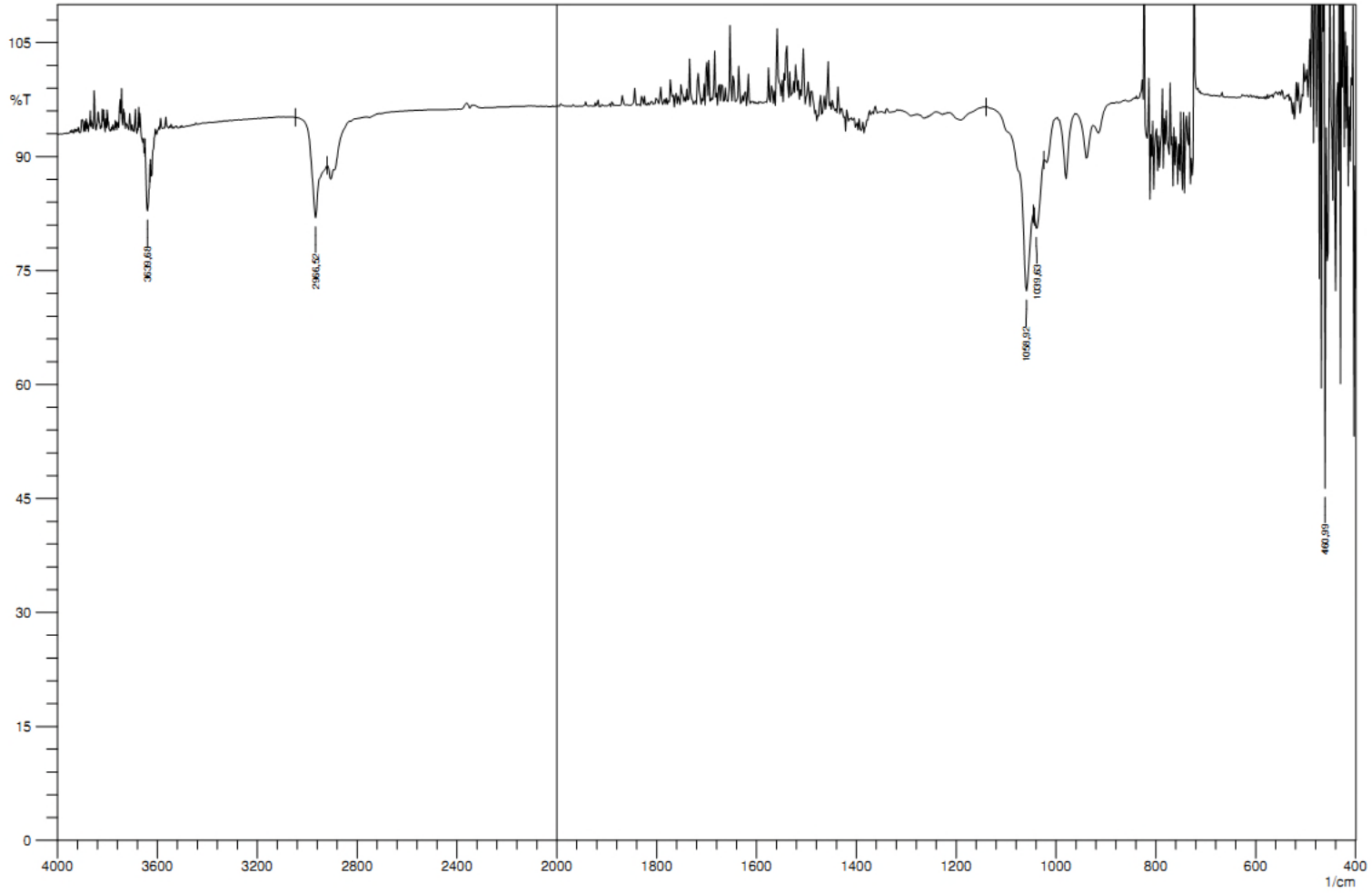
Spectrum S16: Infrared spectrum of **FE** in CCl_4. Concentration = 0.03M.



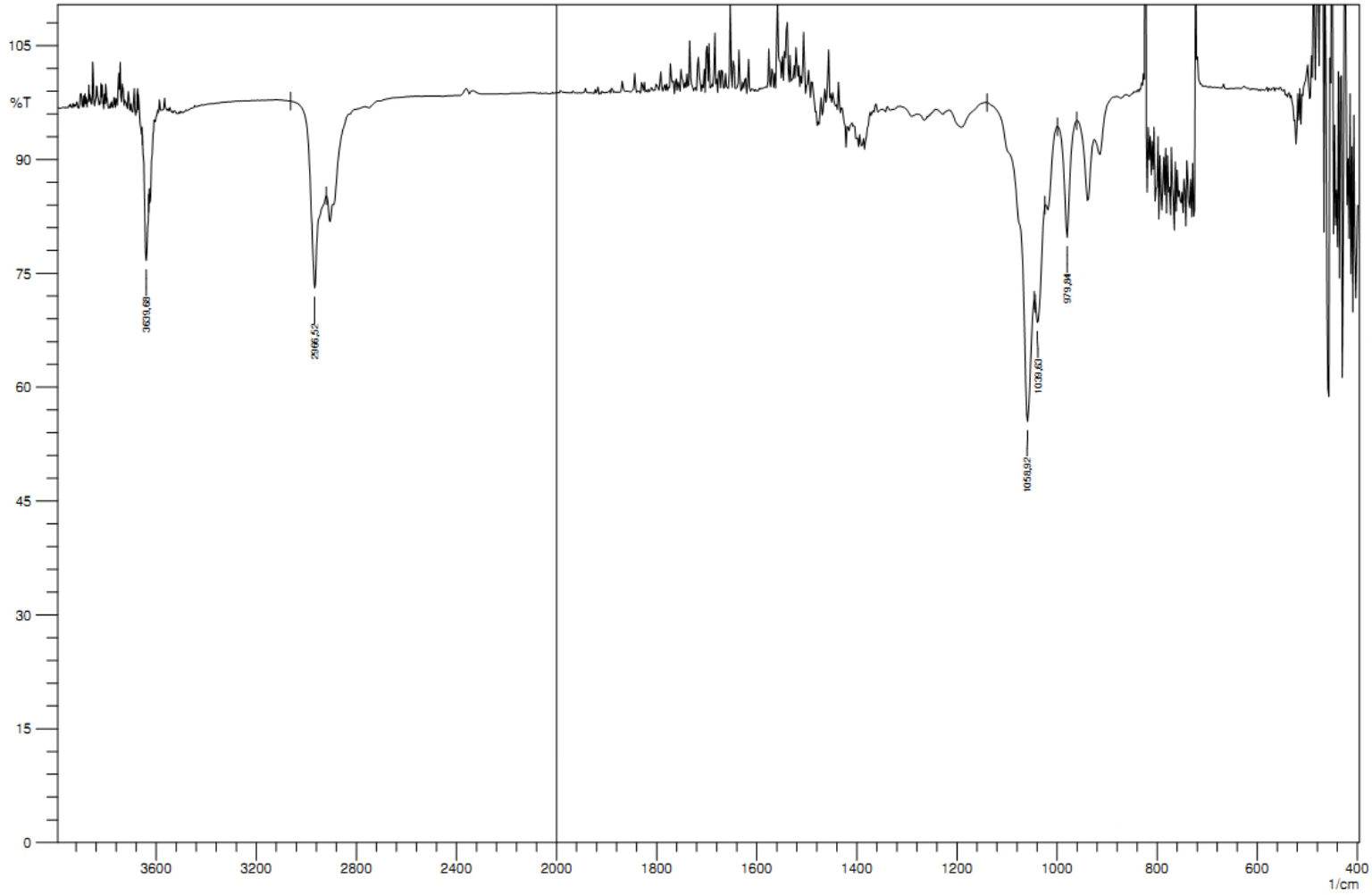
Spectrum S17: Infrared spectrum of **FE** in CCl_4. Concentration = 0.05M.



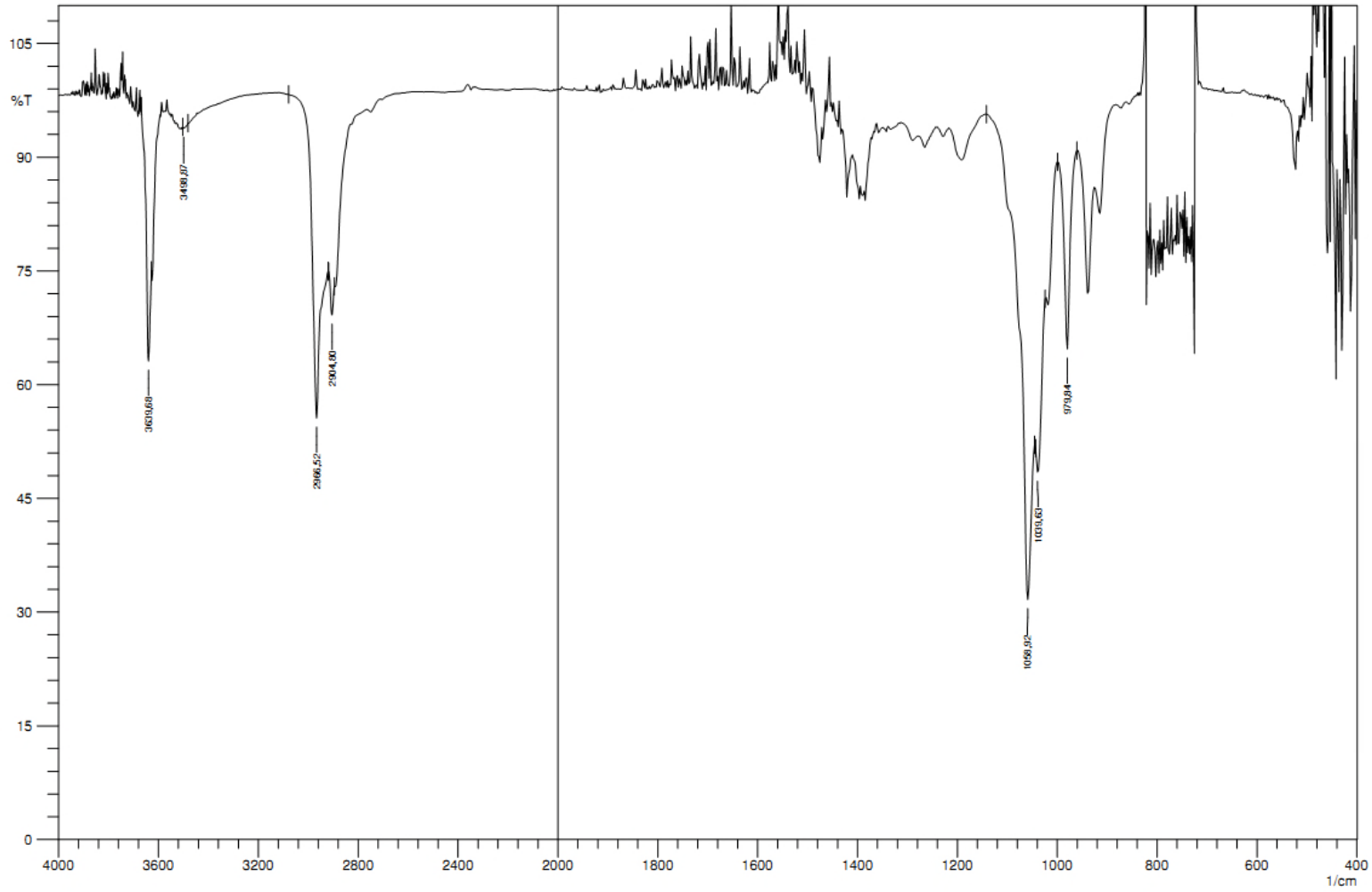
Spectrum S18: Infrared spectrum of **FE** in CCl_4. Concentration = 0.1M.



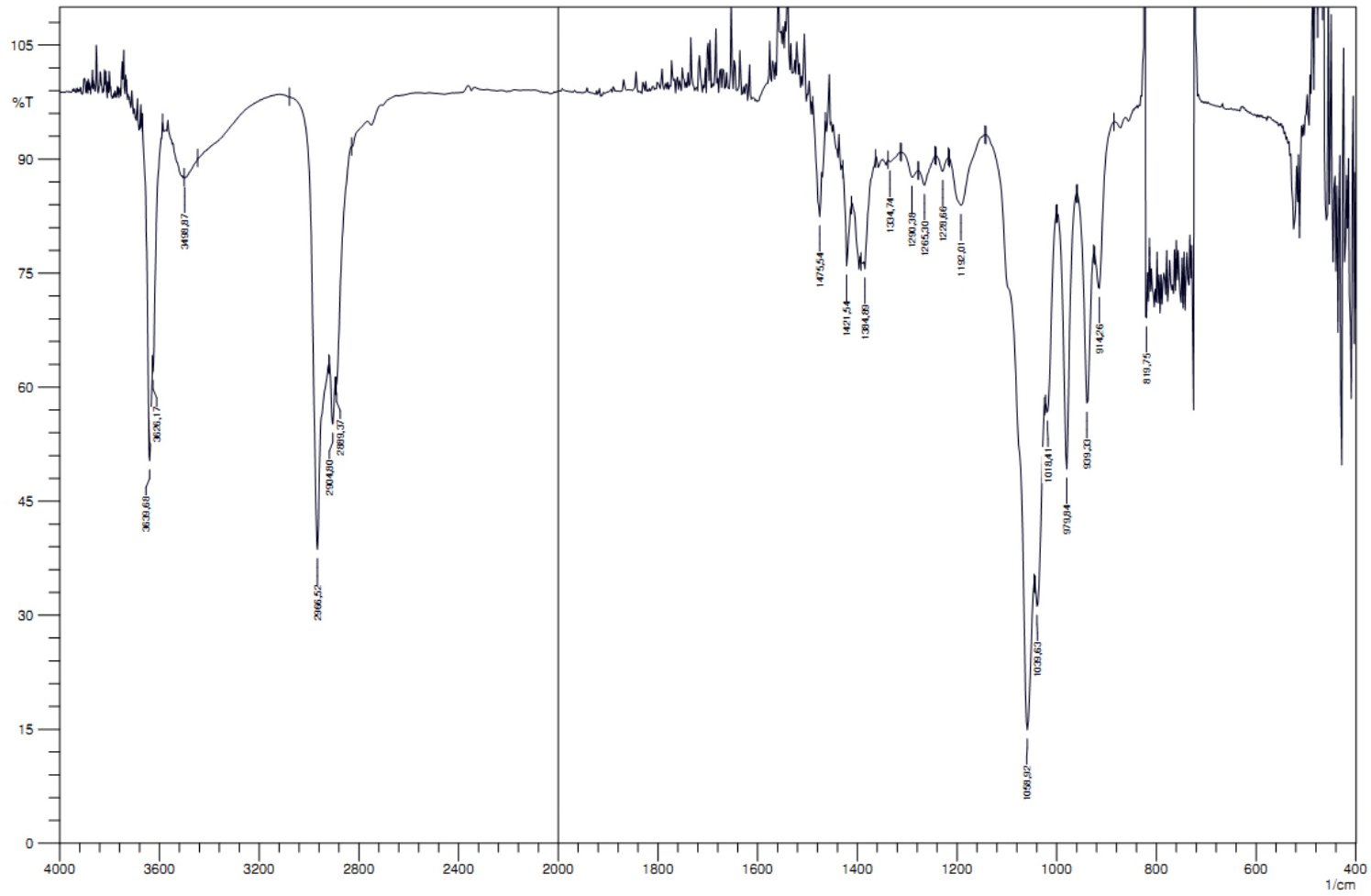
Spectrum S19: Infrared spectrum of **FP** in CCl_4. Concentration = 0.01M.



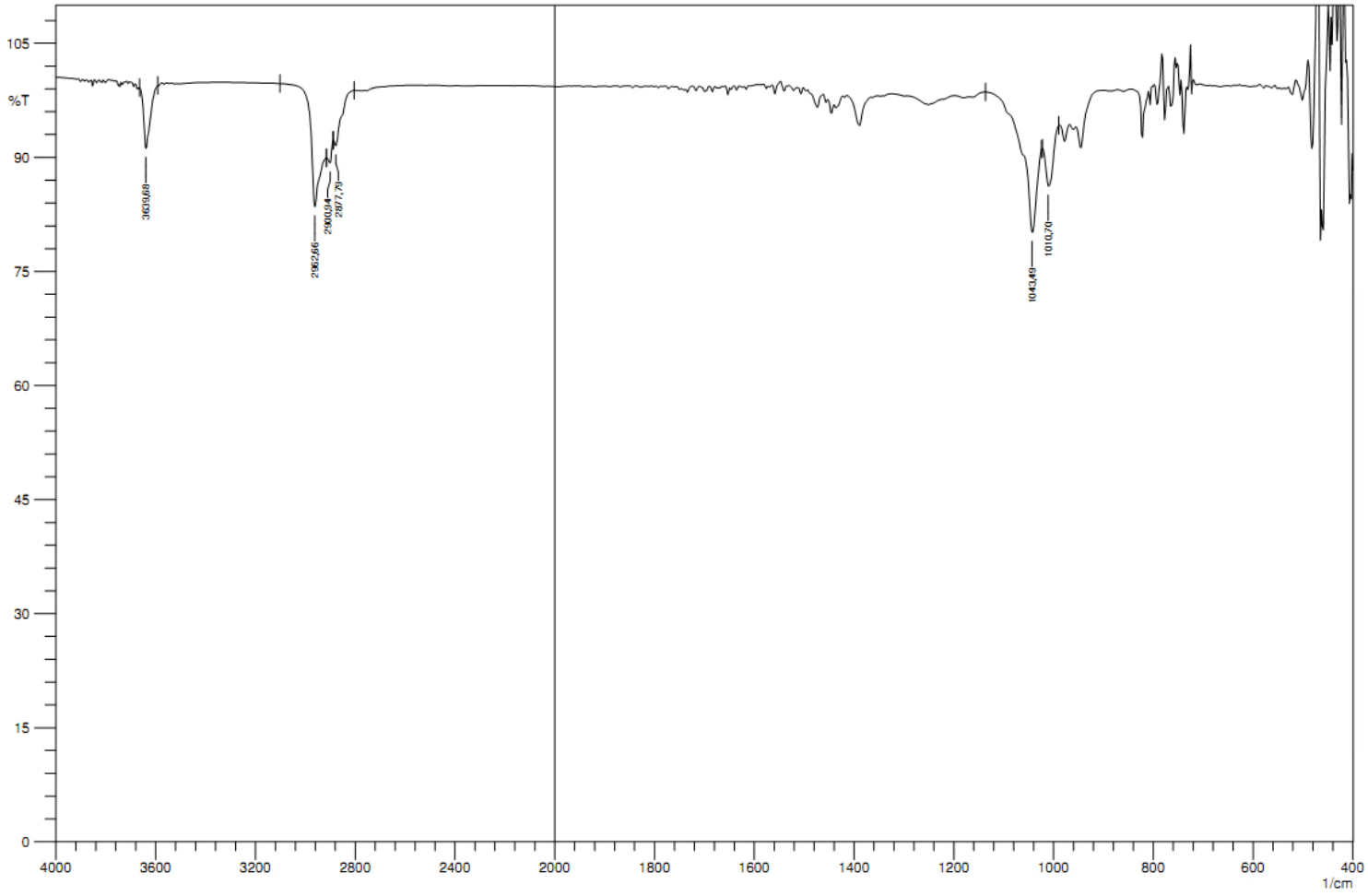
Spectrum S20: Infrared spectrum of **FP** in CCl_4. Concentration = 0.03M.



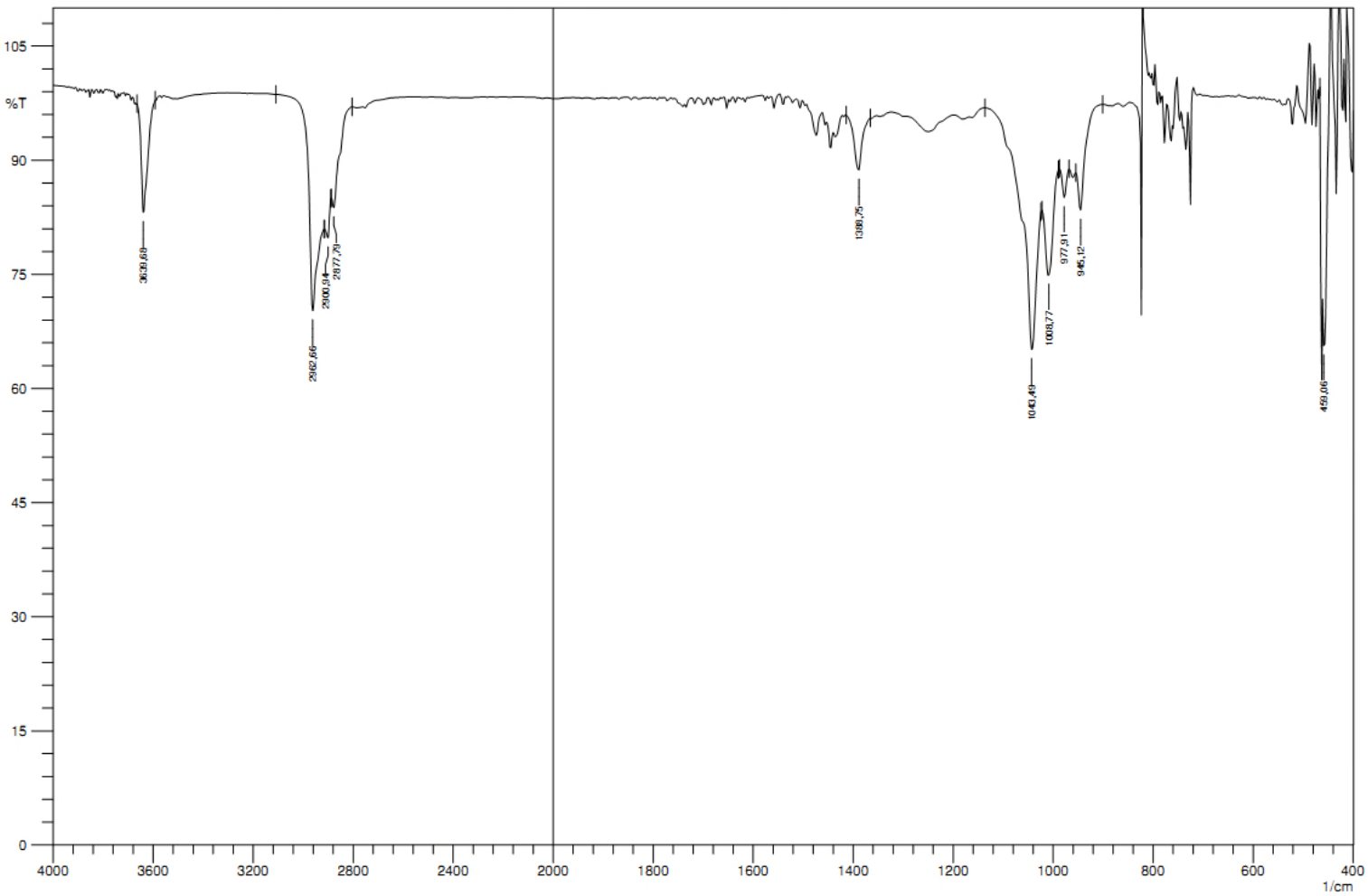
Spectrum S21: Infrared spectrum of **FP** in CCl_4. Concentration = 0.05M.



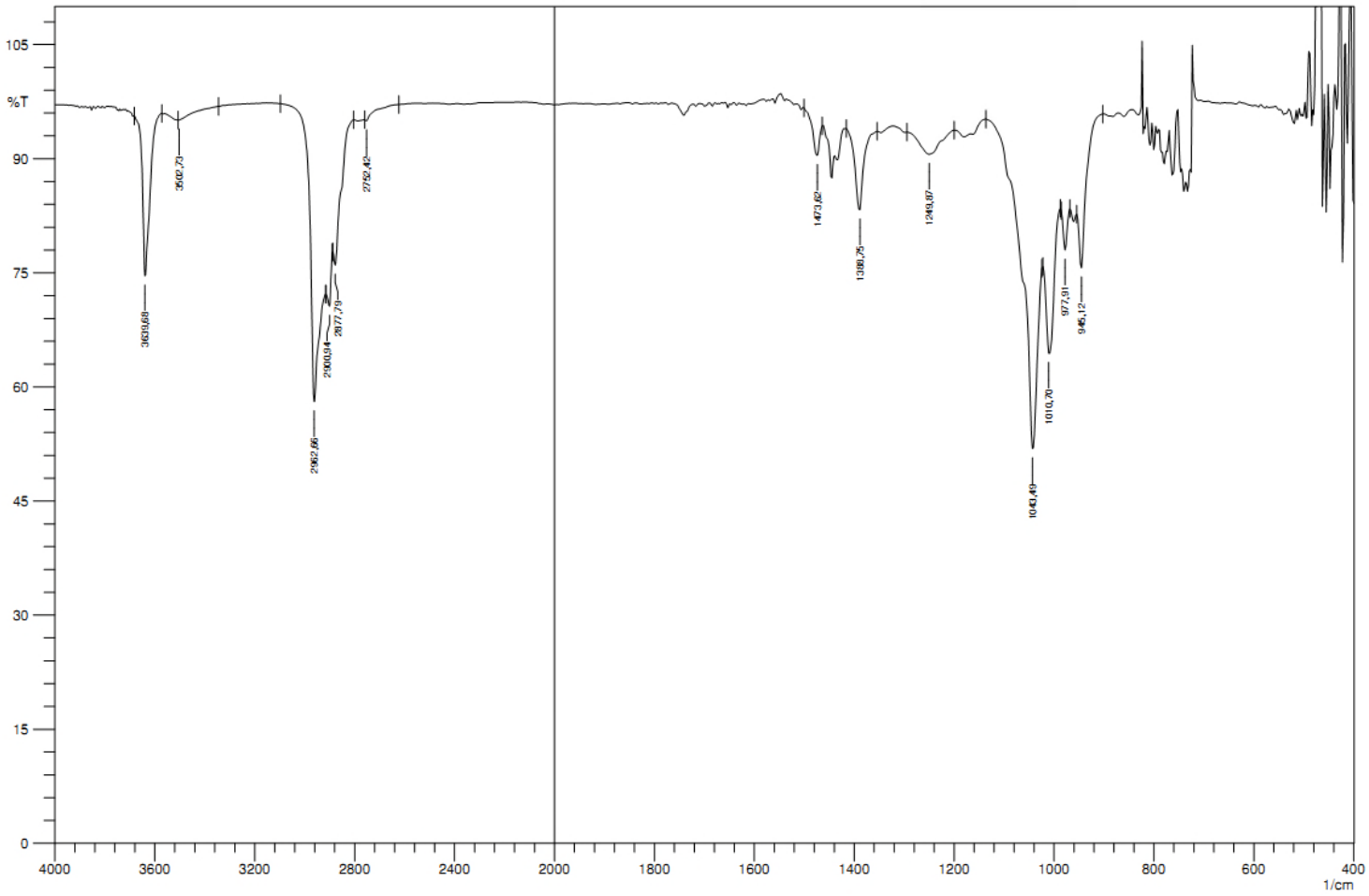
Spectrum S22: Infrared spectrum of **FP** in CCl_4. Concentration = 0.1M.



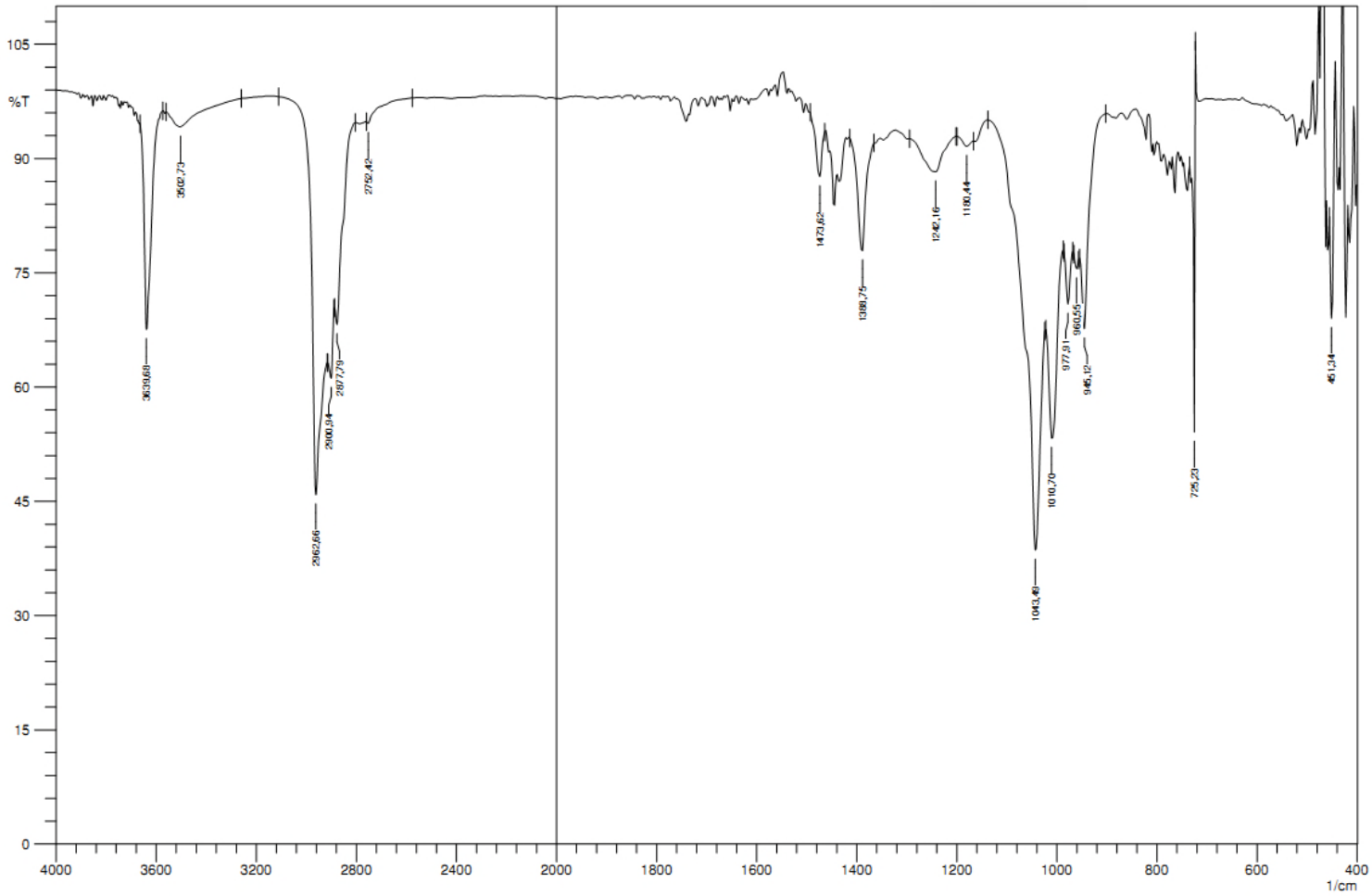
Spectrum S23: Infrared spectrum of **FB** in CCl_4. Concentration = 0.01M.



Spectrum S24: Infrared spectrum of **FB** in CCl_4. Concentration = 0.03M.



Spectrum S25: Infrared spectrum of **FB** in CCl_4. Concentration = 0.05M.



Spectrum S26: Infrared spectrum of **FB** in CCl_4. Concentration = 0.1M.