Electronic Supplementary Information

Conformational analysis of 6-fluorosalicylic acid

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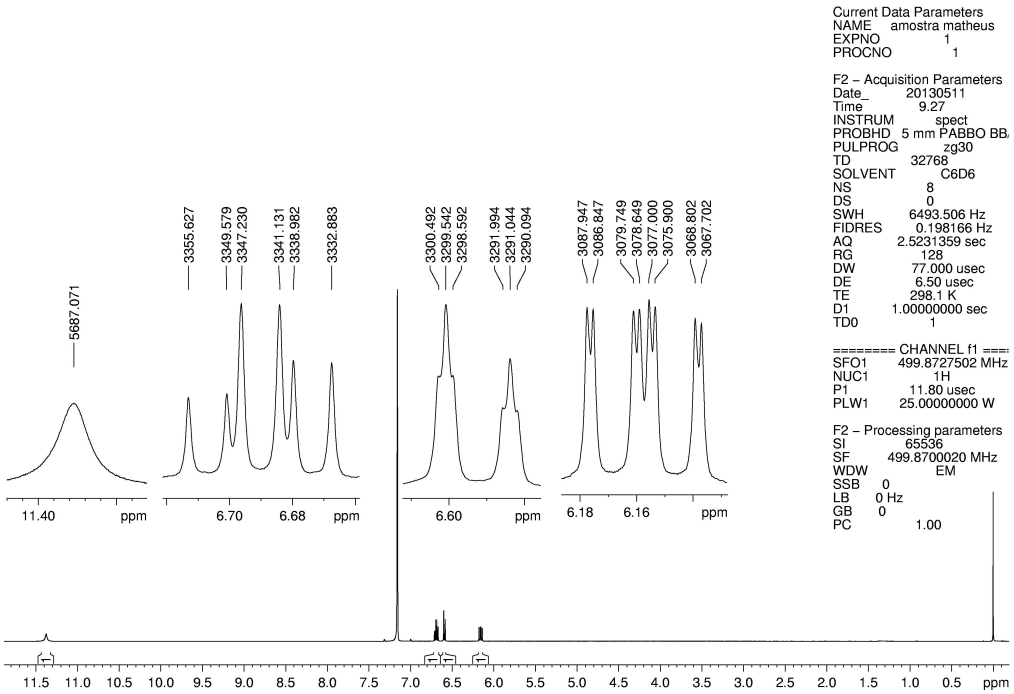


Figure S1. ^{1}H NMR spectrum of 6-fluorosalicylic acid in C_6D_6, at 499.87 MHz.

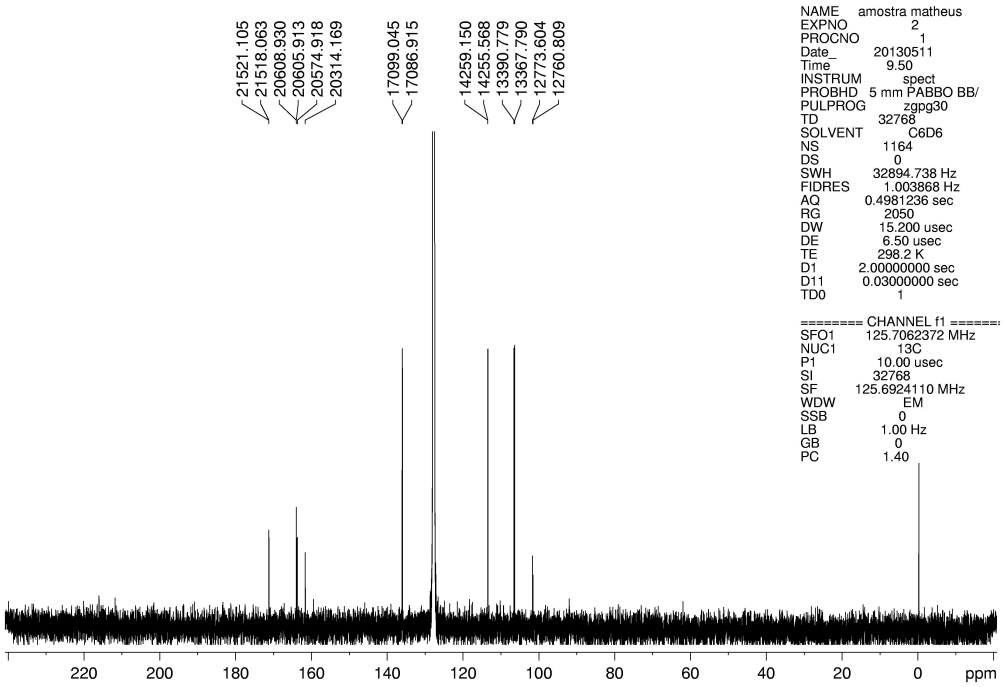


Figure S2. ^{13}C NMR spectrum of 6-fluorosalicylic acid in C_6D_6, at 125.69 MHz.

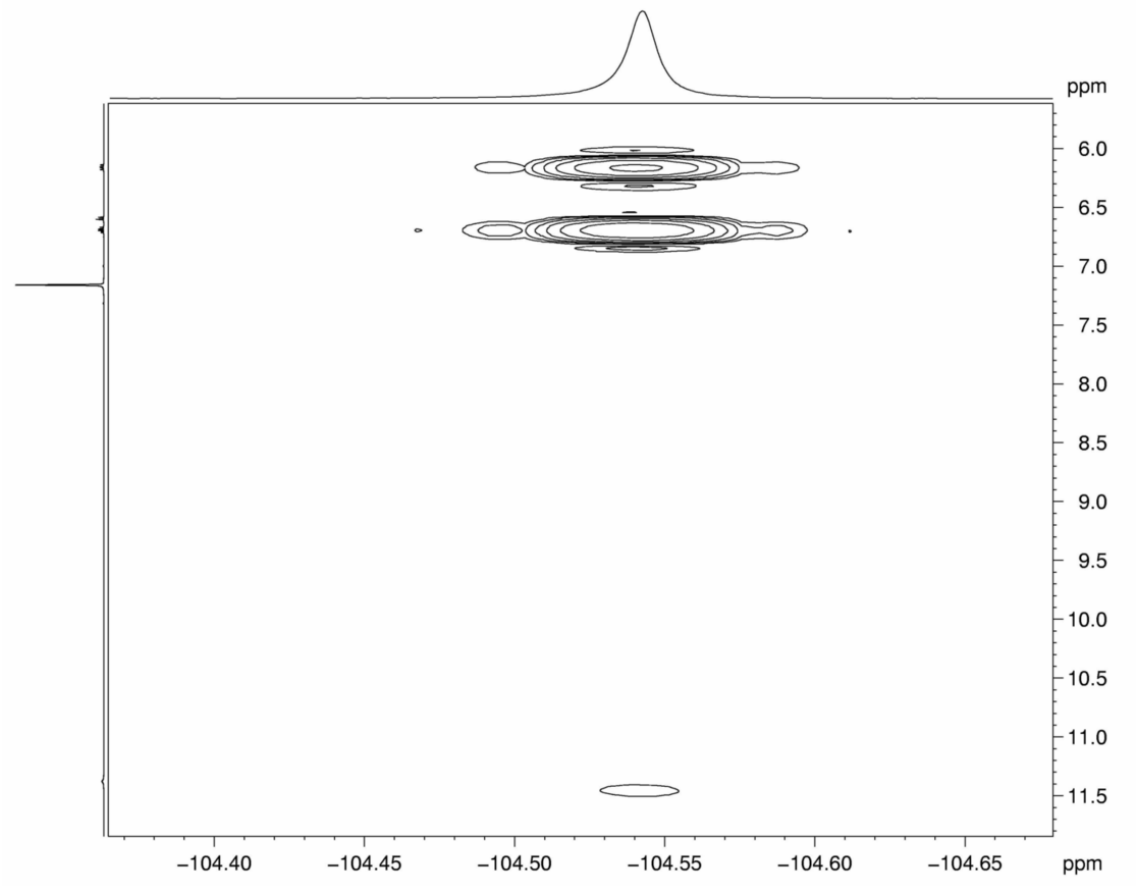


Figure S3. ^{1}H x ^{19}F HETCOR spectrum of 6-fluorosalicylic acid in C_6D_6, at 499.87 MHz for ^{1}H and 470.30 MHz for ^{19}F.

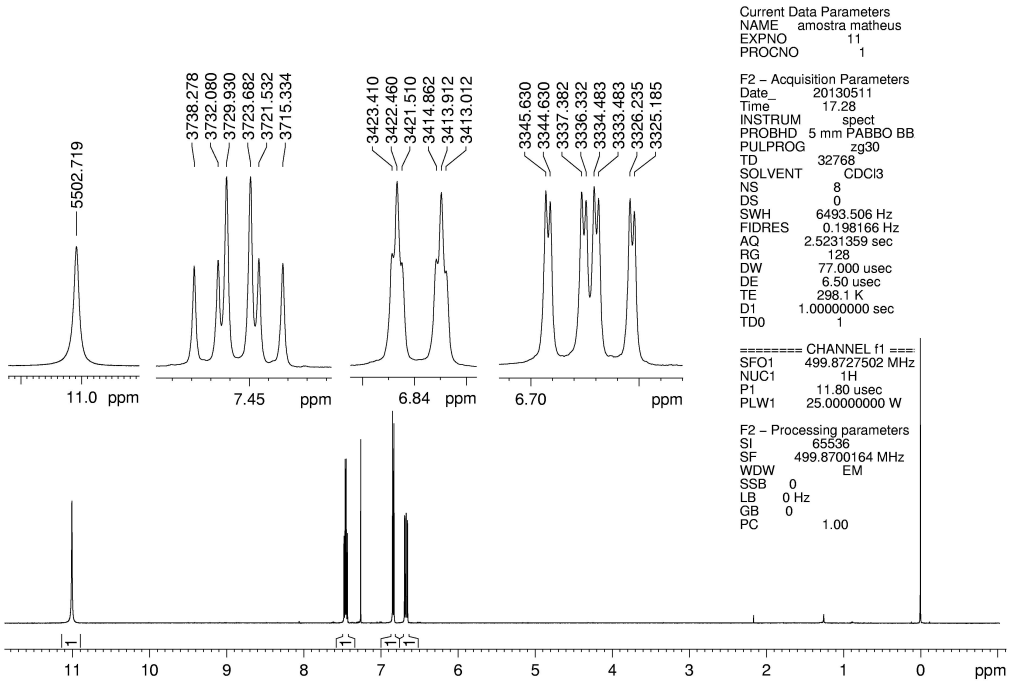


Figure S4. ^{1}H NMR spectrum of 6-fluorosalicylic acid in $CDCl_3$, at 499.87 MHz.

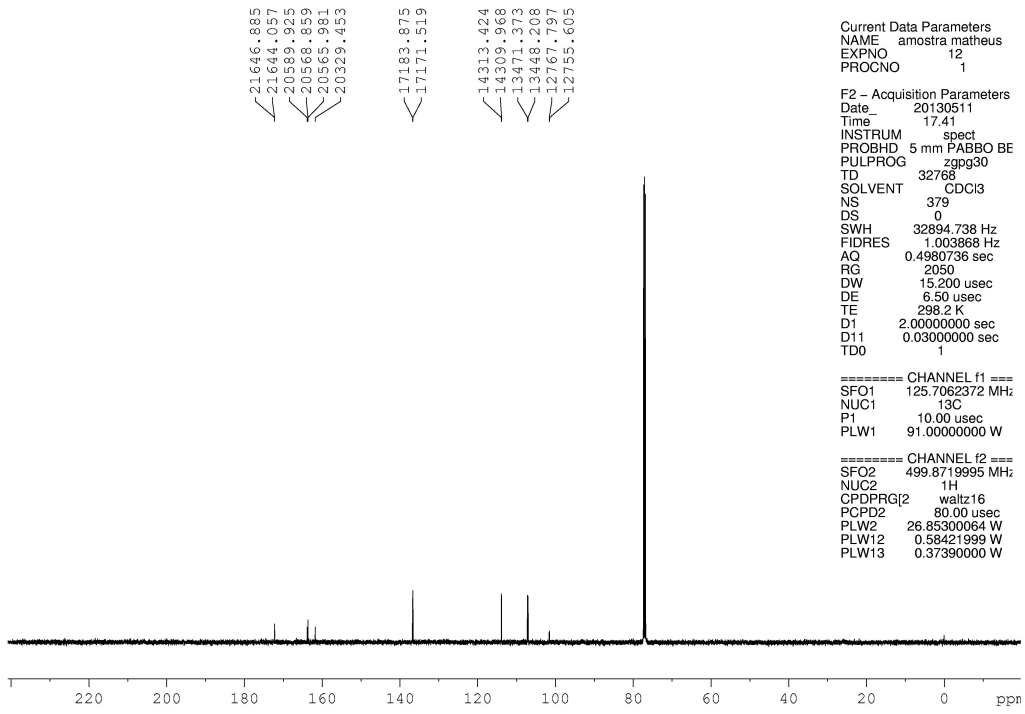


Figure S5. ^{13}C NMR spectrum of 6-fluorosalicylic acid in $CDCl_3$, at 125.69 MHz.

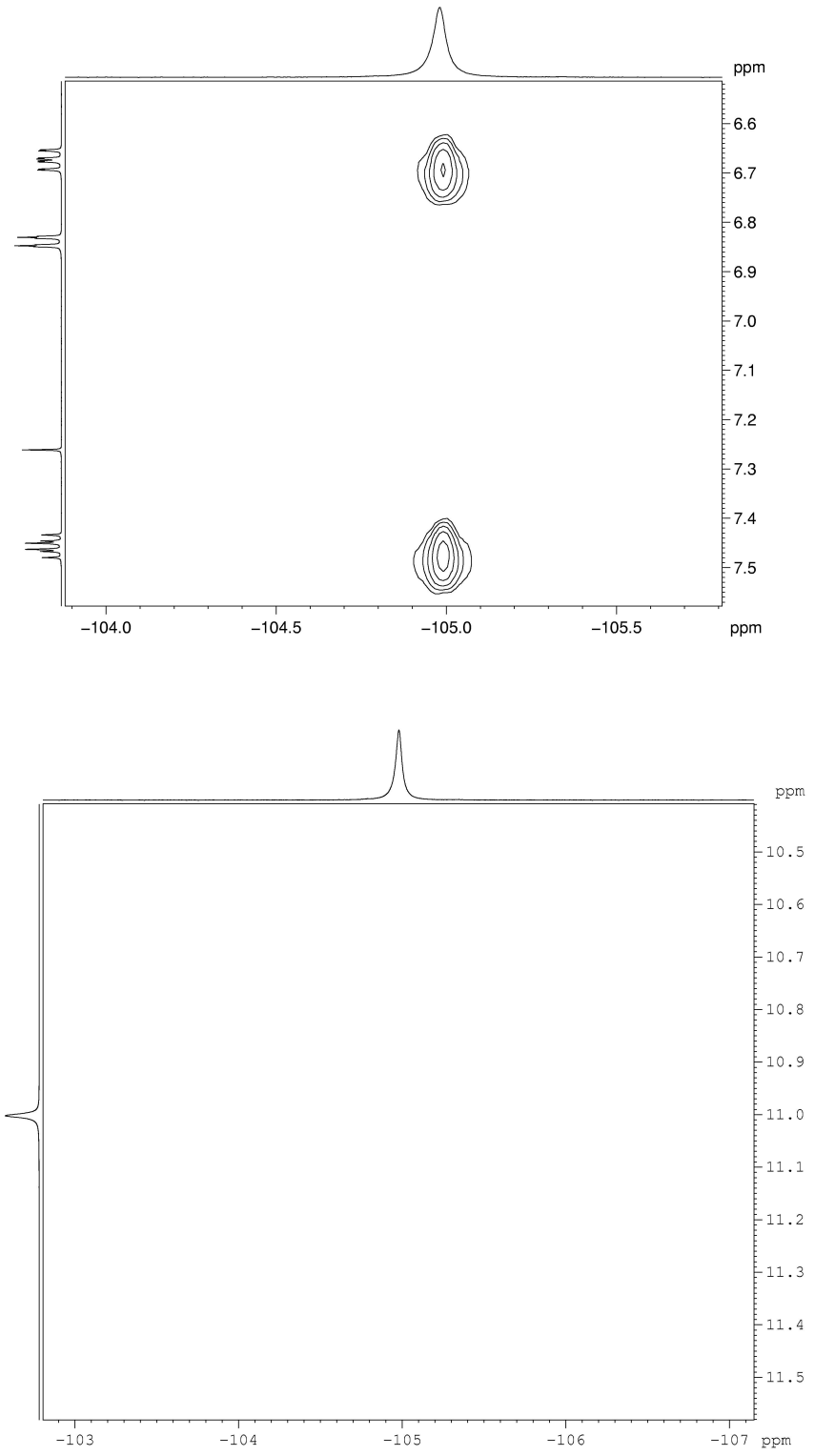


Figure S6. ^{1}H x ^{19}F HETCOR spectrum of 6-fluorosalicylic acid in $CDCl_3$, at 499.87 MHz for ^{1}H and 470.30 MHz for ^{19}F.

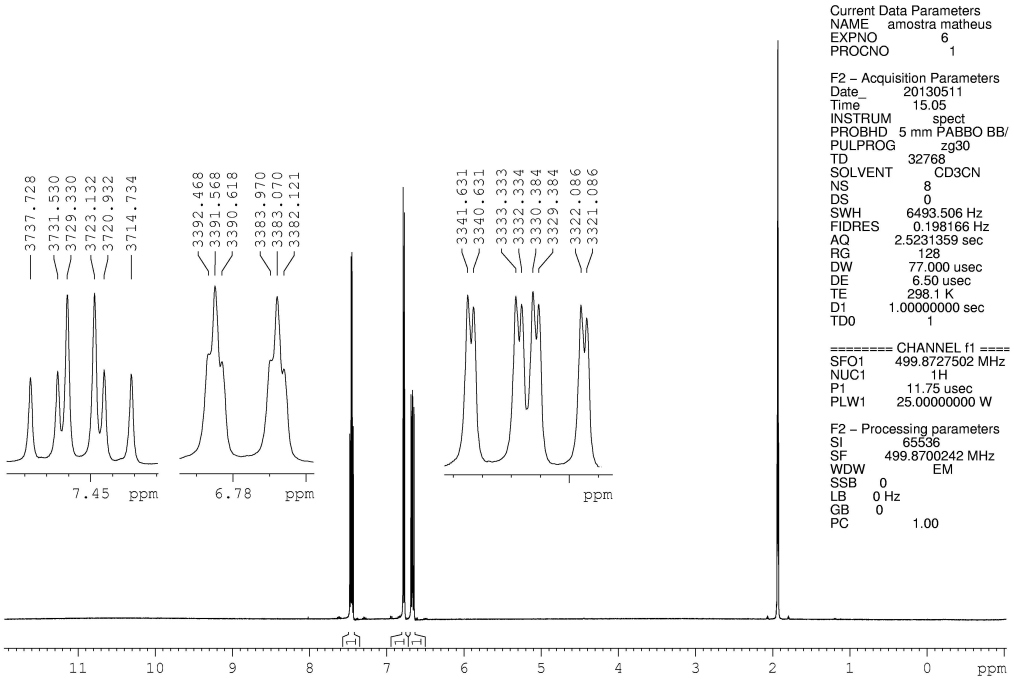


Figure S7. ^{1}H NMR spectrum of 6-fluorosalicylic acid in CD_3CN, at 499.87 MHz.

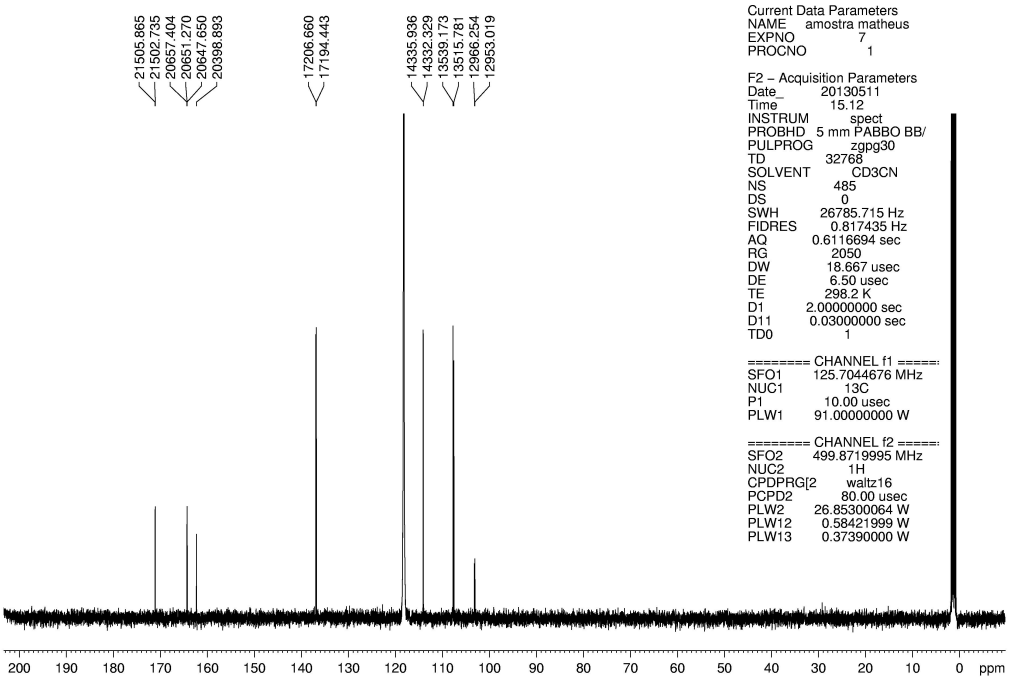


Figure S8. ^{13}C NMR spectrum of 6-fluorosalicylic acid in CD_3CN, at 125.69 MHz.

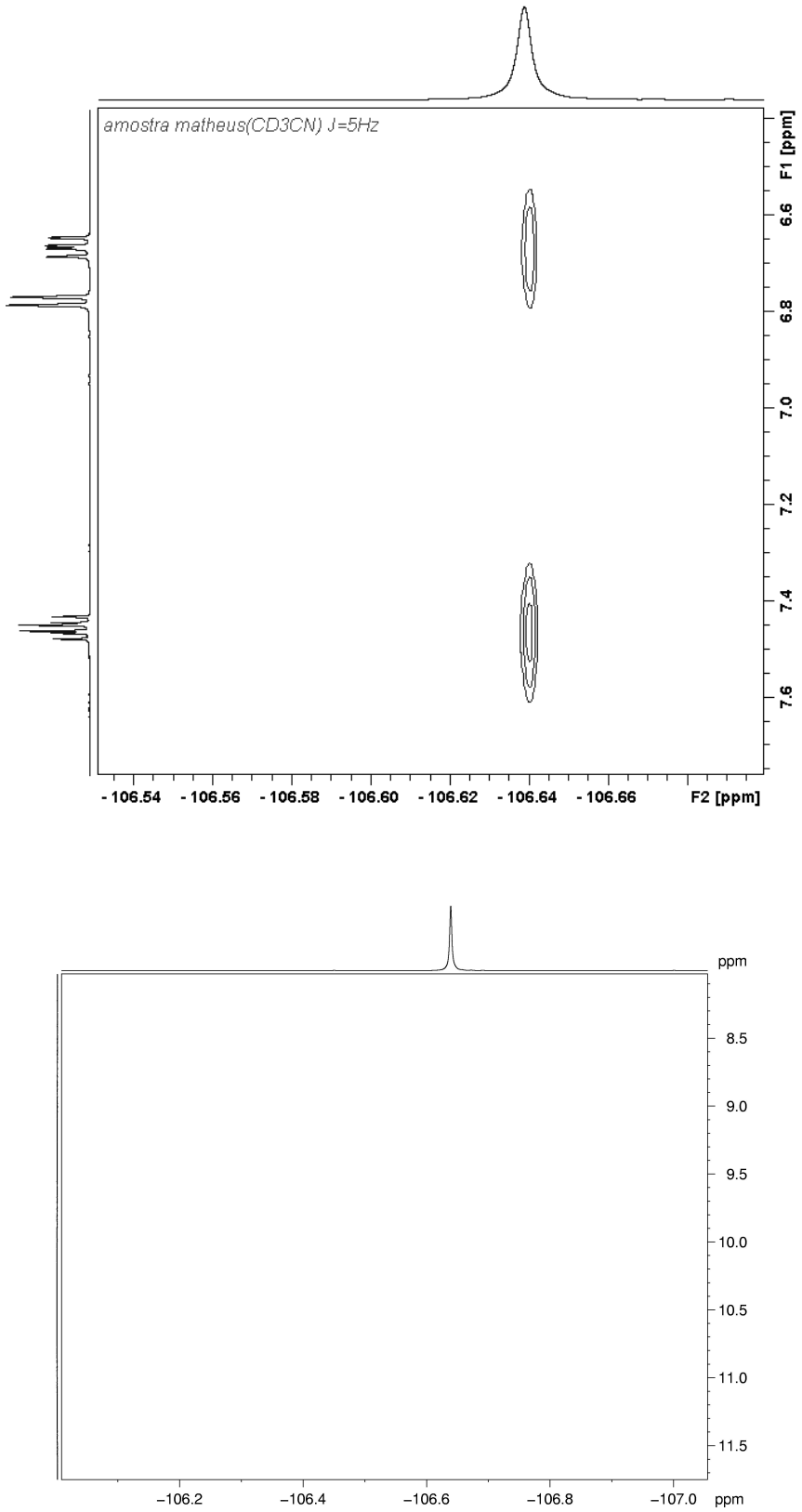
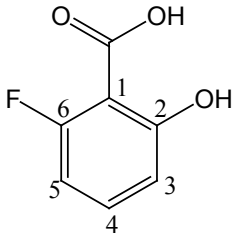


Figure S9. ^{1}H x ^{19}F HETCOR spectrum of 6-fluorosalicylic acid in CD_3CN, at 499.87 MHz for ^{1}H and 470.30 MHz for ^{19}F.

Table S1. NMR assignments for 6-fluorosalicylic acid (chemical shifts, δ, in ppm relative to TMS, and coupling constants, *J*, in Hz).

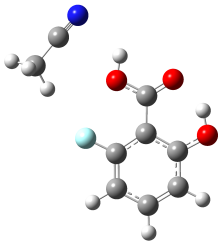


Parameter	(O)H/(COO)H	H-3	H-4	H-5	C-1	C-2	C-3	C-4	C-5	C-6	C(OOH)
C_6D_6											
δ	11.36	6.59	6.69	6.16	101.6	163.9	113.4	136.0	106.4	162.6	171.2
J		$^3J_{HH}$ = 8.4 $^4J_{HH}$ = $^5J_{HF}$ = 1.0	$^3J_{HH}$ = 8.4 $^4J_{HF}$ = 6.0	$^3J_{HF}$ = 10.9 $^3J_{HH}$ = 8.4 $^4J_{HH}$ = 1.0	$^2J_{CF}$ = 12.8	$^3J_{CF}$ = 3.0	$^4J_{CF}$ = 3.6	$^3J_{CF}$ = 12.1	$^2J_{CF}$ = 23.0	$^1J_{CF}$ = 260.7	$^3J_{CF}$ = 3.0
$CDCl_3$											
δ	11.00	6.84	7.45	6.67	101.5	163.6	113.8	136.6	107.1	162.7	172.2
J		$^3J_{HH}$ = 8.4 $^4J_{HH}$ = $^5J_{HF}$ = 1.0	$^3J_{HH}$ = 8.4 $^4J_{HF}$ = 6.2	$^3J_{HF}$ = 11.2 $^3J_{HH}$ = 8.4 $^4J_{HH}$ = 1.0	$^2J_{CF}$ = 12.2	$^3J_{CF}$ = 2.8	$^4J_{CF}$ = 3.4	$^3J_{CF}$ = 12.4	$^2J_{CF}$ = 23.2	$^1J_{CF}$ = 260.5	$^3J_{CF}$ = 2.8
CD_3CN											
δ	-	6.78	7.45	6.66	103.1	164.3	114.0	136.8	107.6	163.3	171.1
J		$^3J_{HH}$ = 8.4 $^4J_{HH}$ = $^5J_{HF}$ = 1.0	$^3J_{HH}$ = 8.4 $^4J_{HF}$ = 6.2	$^3J_{HF}$ = 11.2 $^3J_{HH}$ = 8.4 $^4J_{HH}$ = 1.0	$^2J_{CF}$ = 13.2	$^3J_{CF}$ = 3.7	$^4J_{CF}$ = 3.6	$^3J_{CF}$ = 12.3	$^2J_{CF}$ = 23.4	$^1J_{CF}$ = 258.5	$^3J_{CF}$ = 3.2

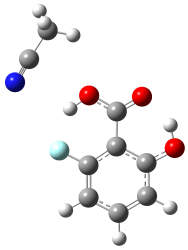
Table S2. Thermodynamic parameters obtained for **1** using the PCM model in benzene and acetonitrile, at the WB97XD/6-311++g(d,p) level.

Conformer	Benzene			Acetonitrile		
	ΔG_{rel} (%)	ΔH_{rel}	$T\Delta S_{rel}$	ΔG_{rel} (%)	ΔH_{rel}	$T\Delta S_{rel}$
1a	0.0 (84)	0.0	0.0	0.0 (76)	0.0	0.0
1b	1.0 (16)	0.7	-0.2	0.7 (23)	0.4	-0.2
1c	3.6 (0)	3.8	0.3	2.6 (1)	3.0	0.3

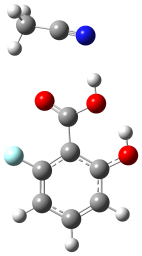
Table S3. Thermodynamic parameters obtained for **1** using an explicit acetonitrile solvent, at the WB97XD/6-311++g(d,p) level.



1a



1b



1c

Conformer	ΔG_{rel} (%)	ΔH_{rel}	$T\Delta S_{rel}$
1a	0.0 (63)	0.0	0.0
1b	0.9 (14)	1.6	0.7
1c	0.6 (23)	-0.2	-0.8