

Supporting Information

Engagement of CF₃ Group in N-H···F-C Hydrogen Bond in the Solution State: NMR Spectroscopy, DFT and MD Simulation Studies

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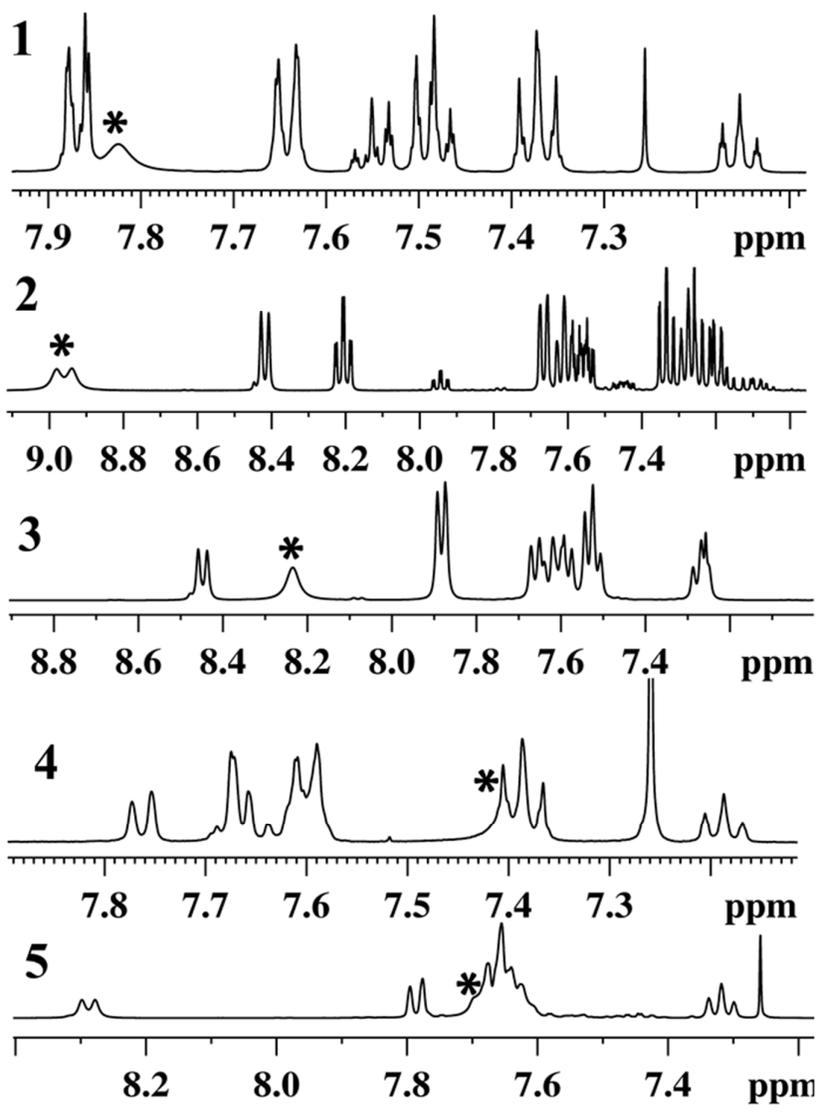
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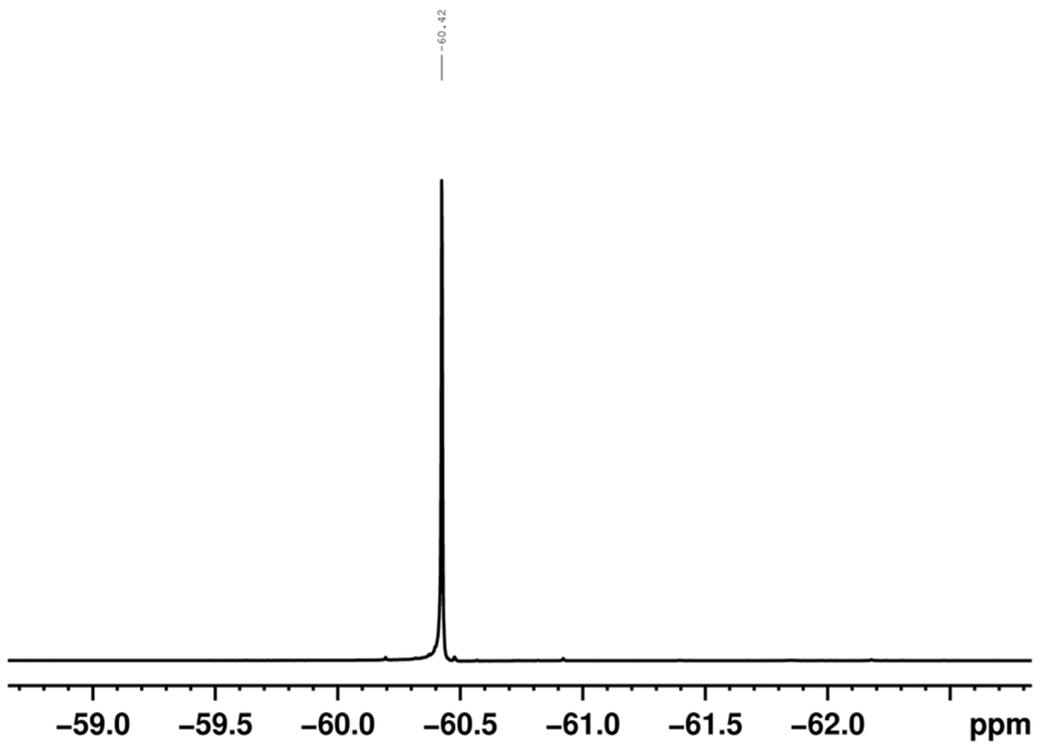
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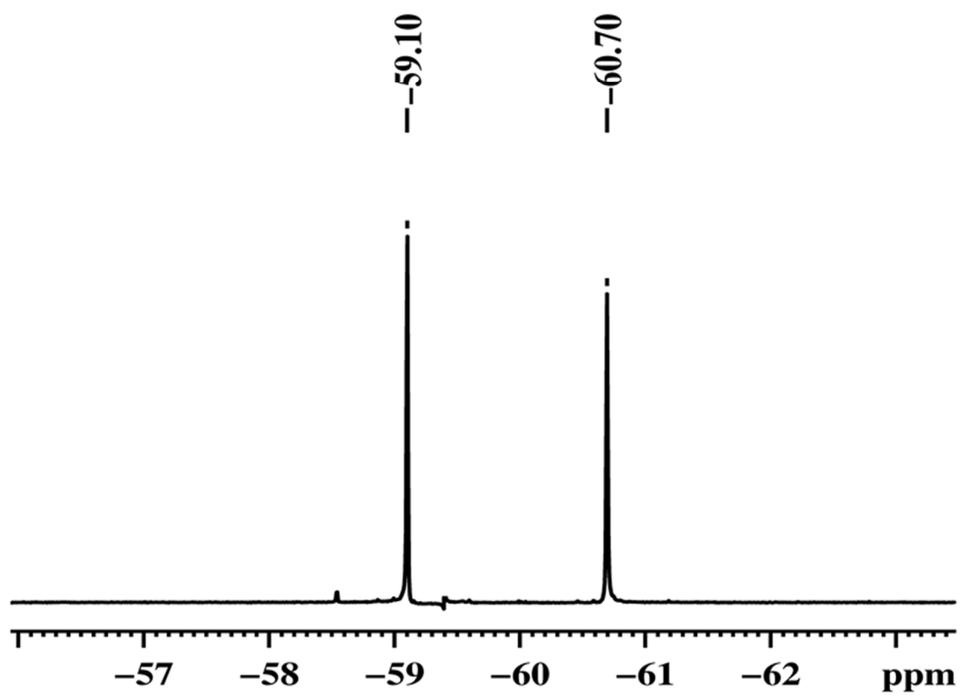
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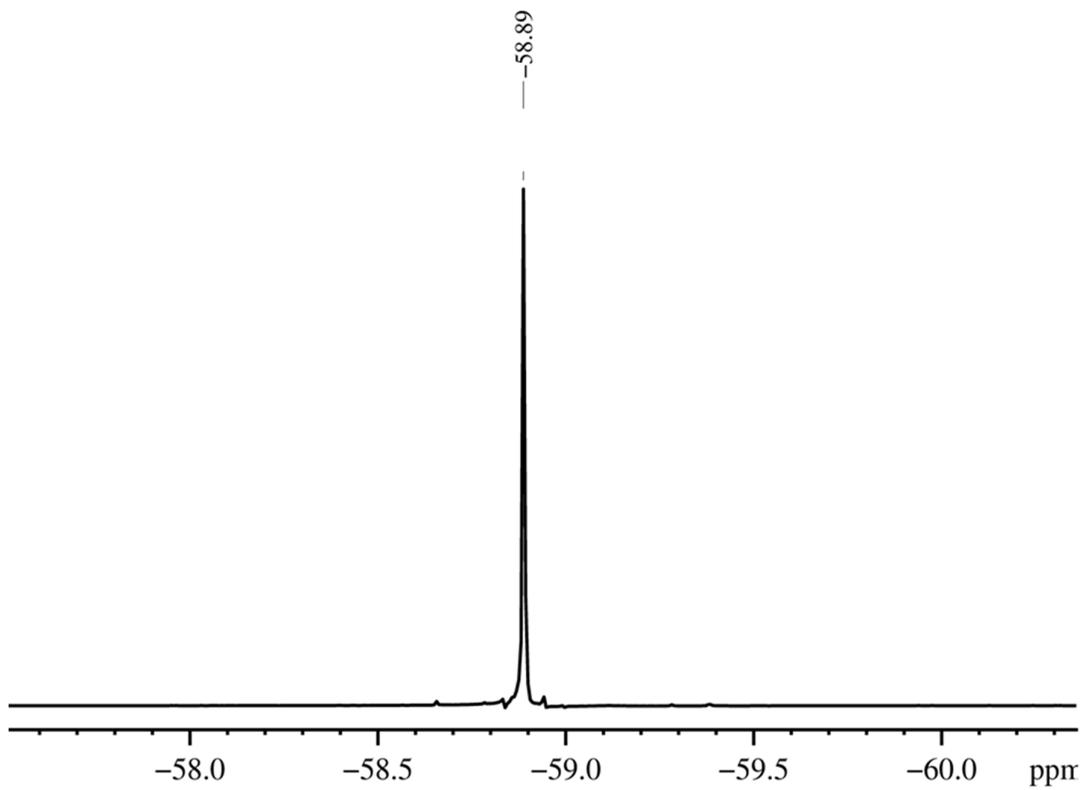
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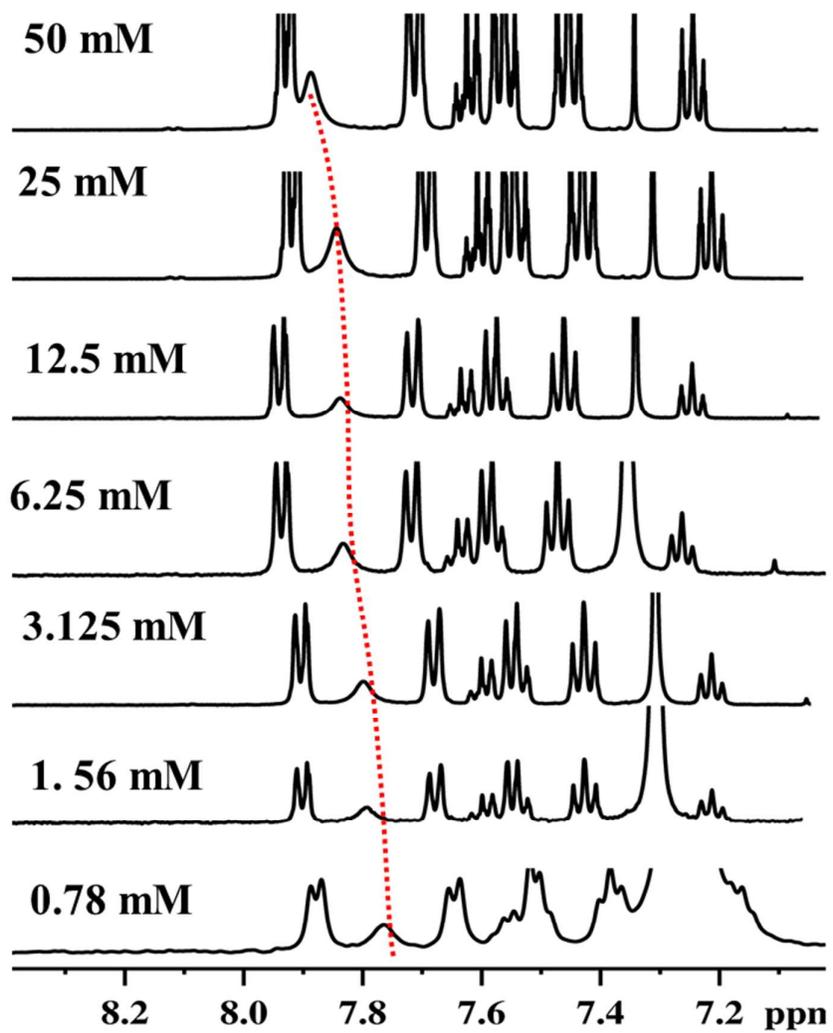
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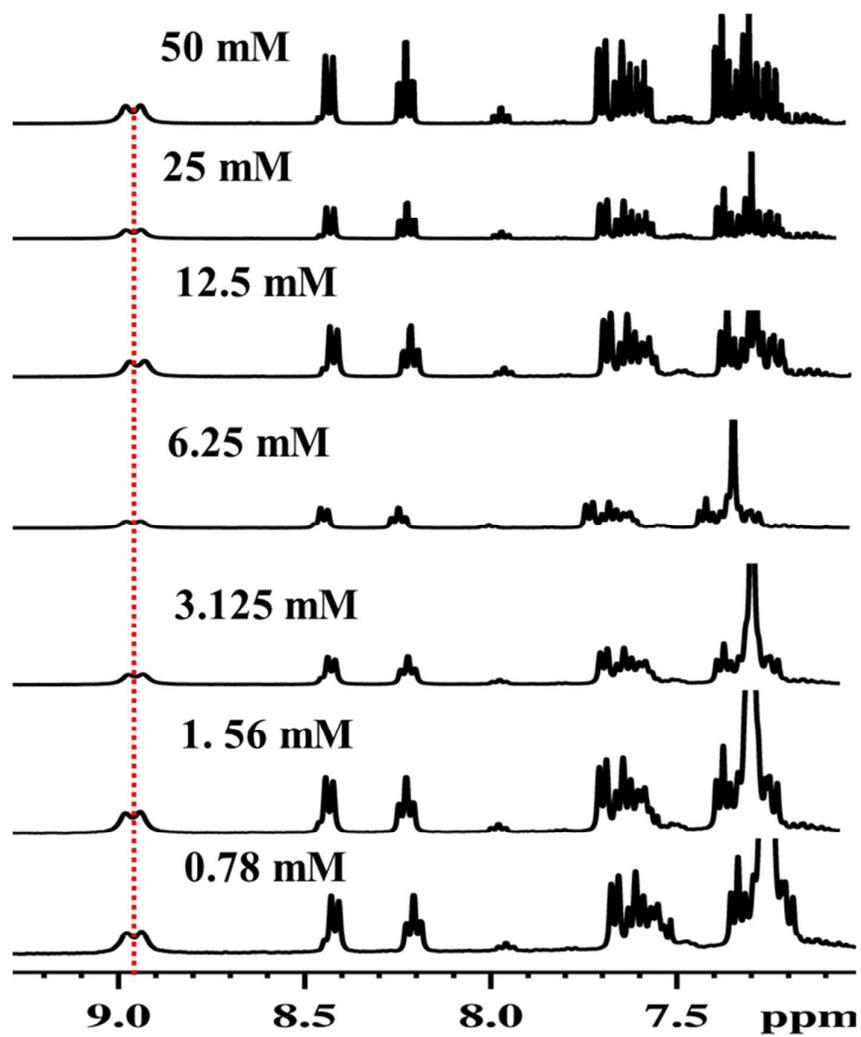
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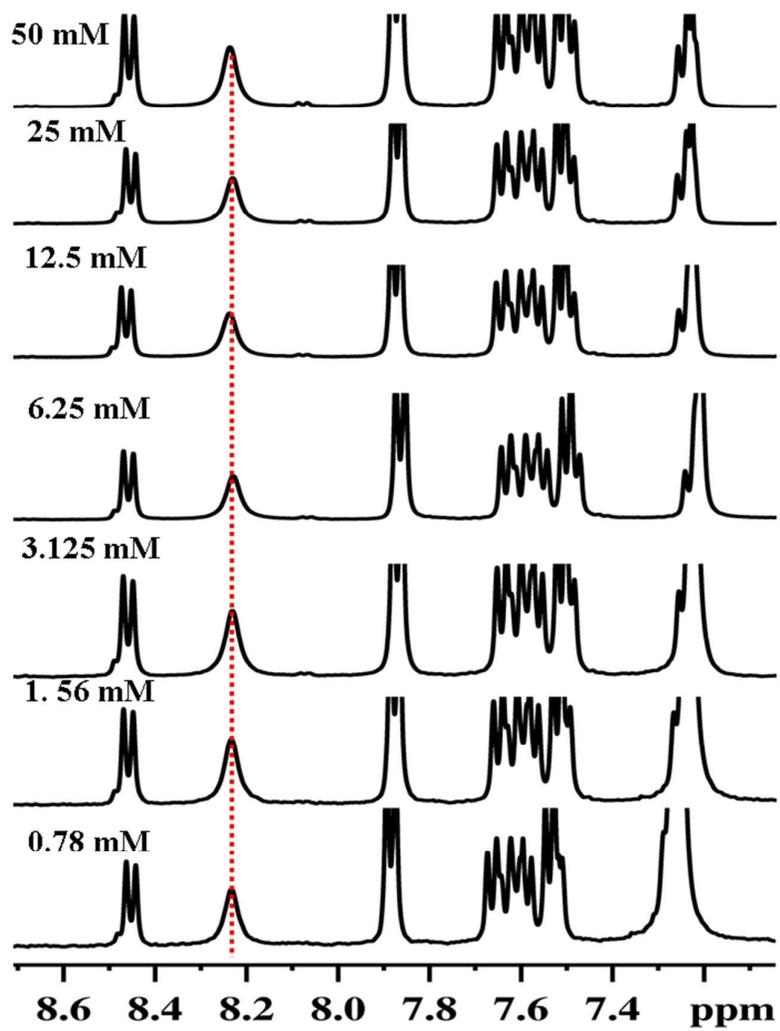
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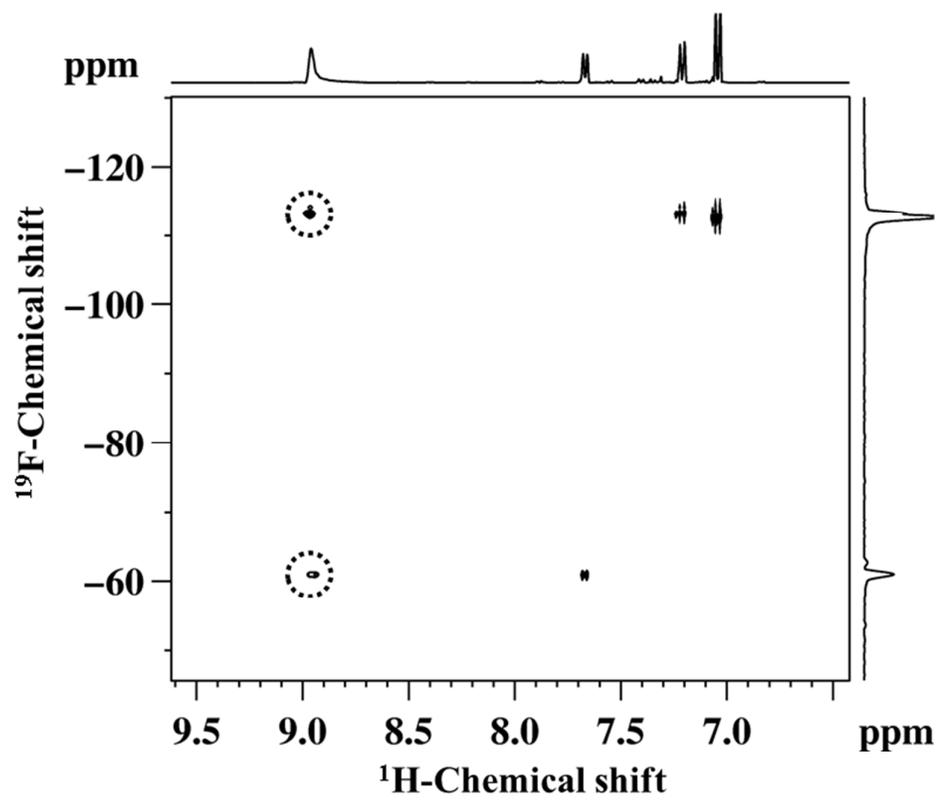
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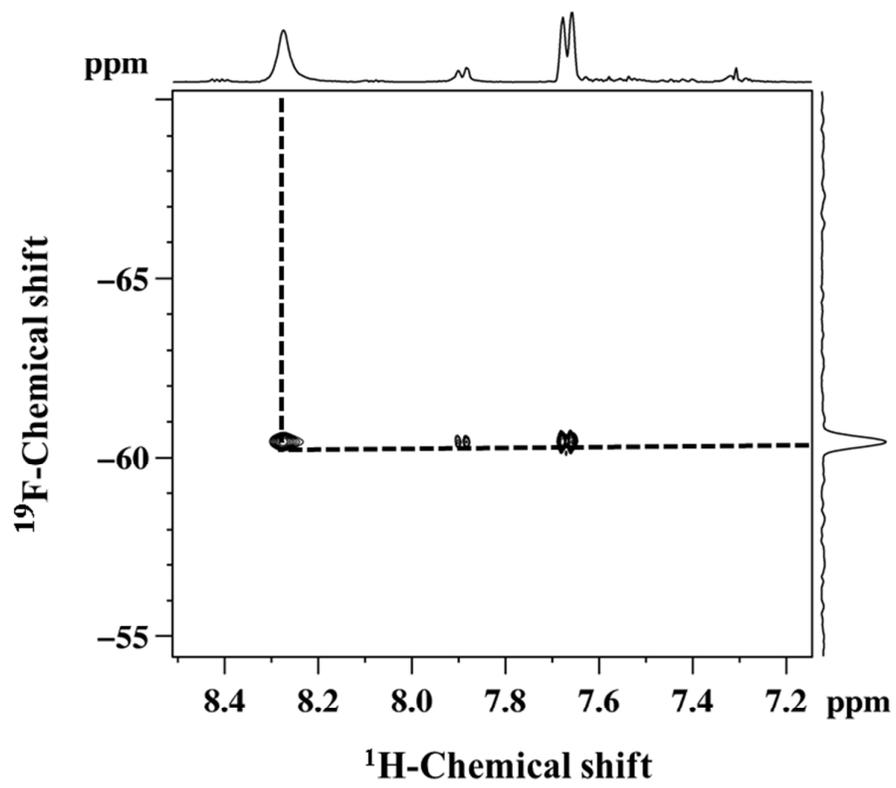
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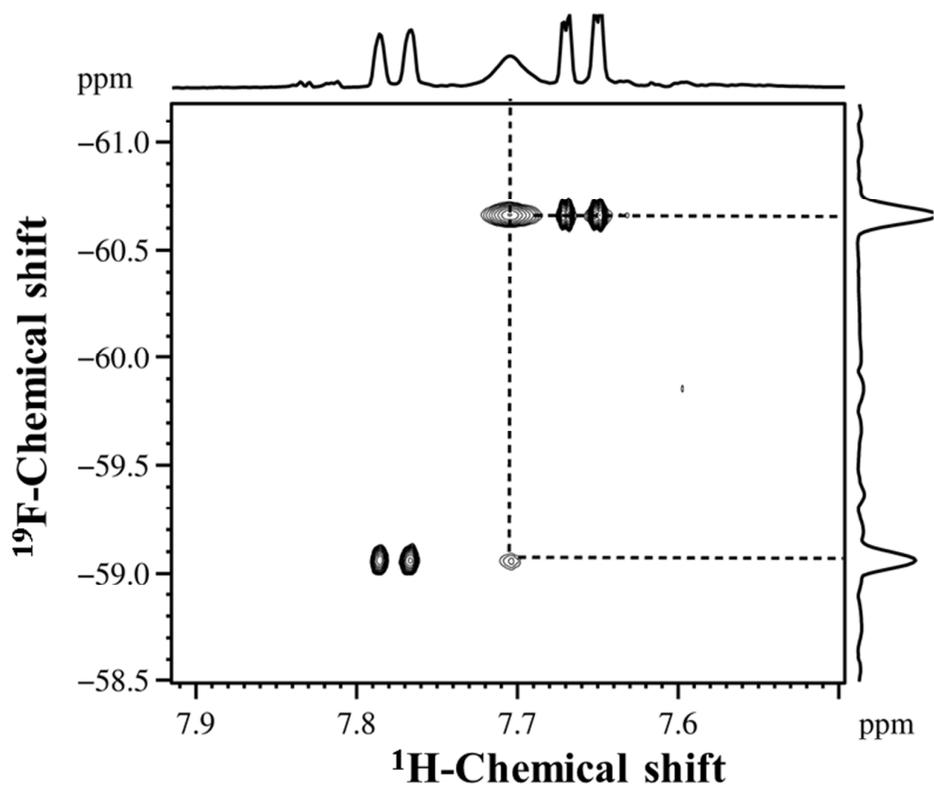
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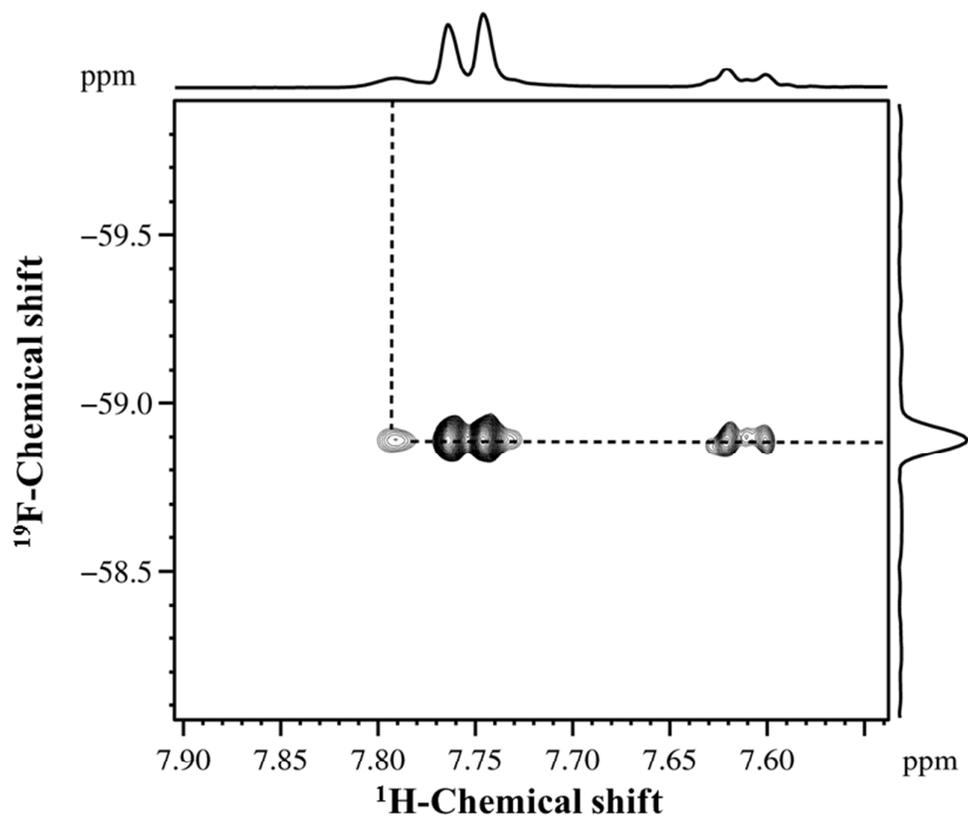
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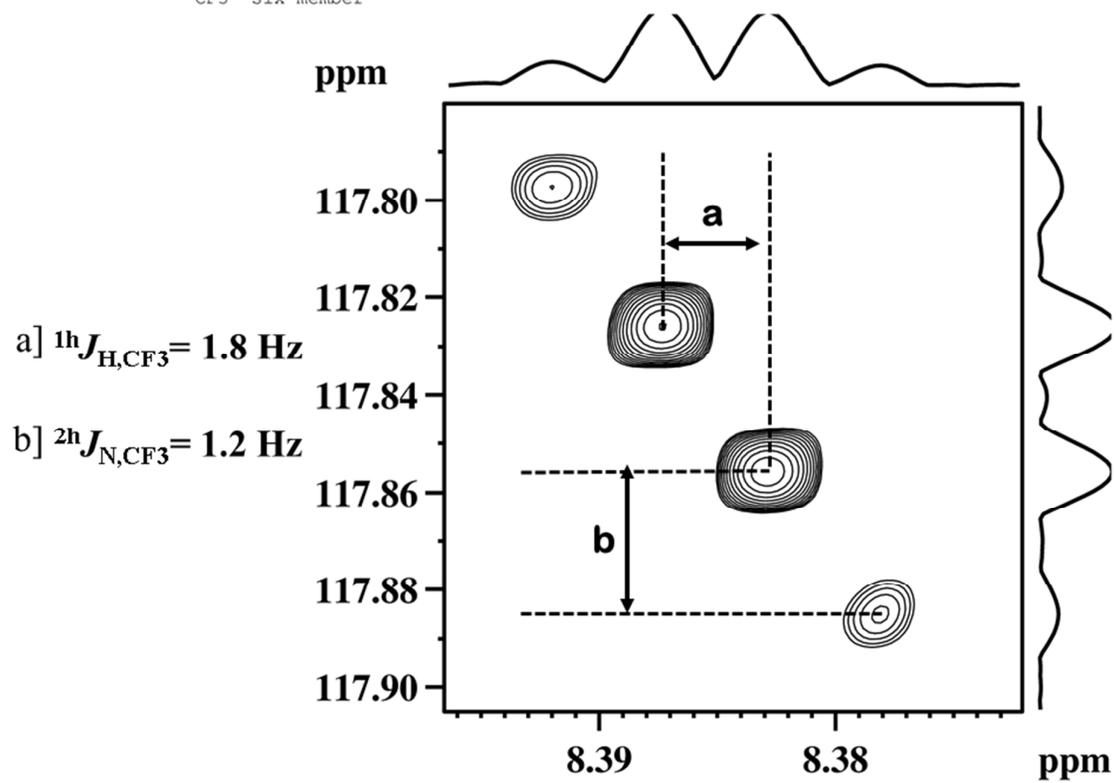


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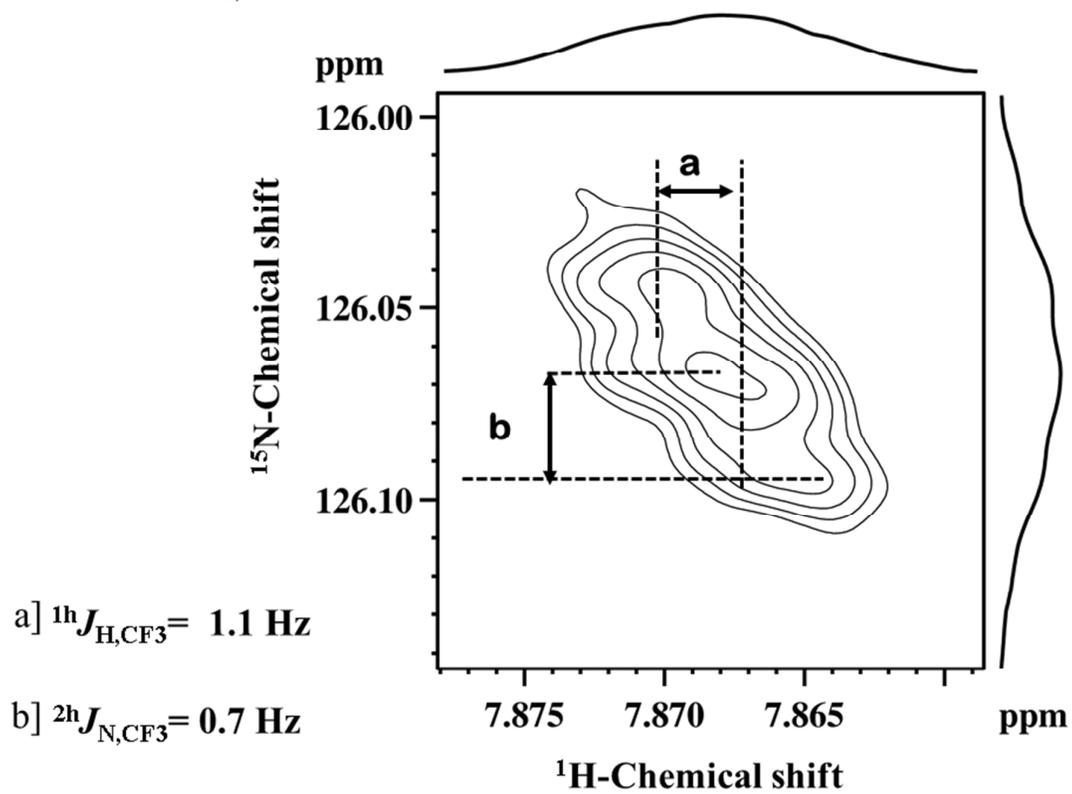


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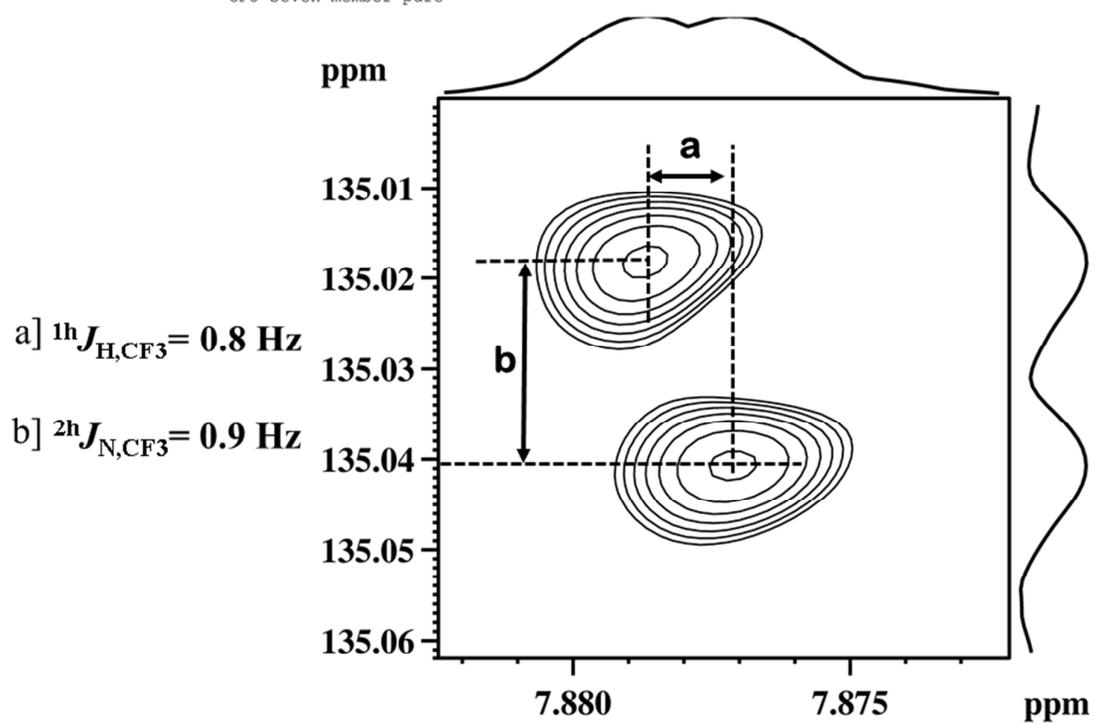
CF3 six member



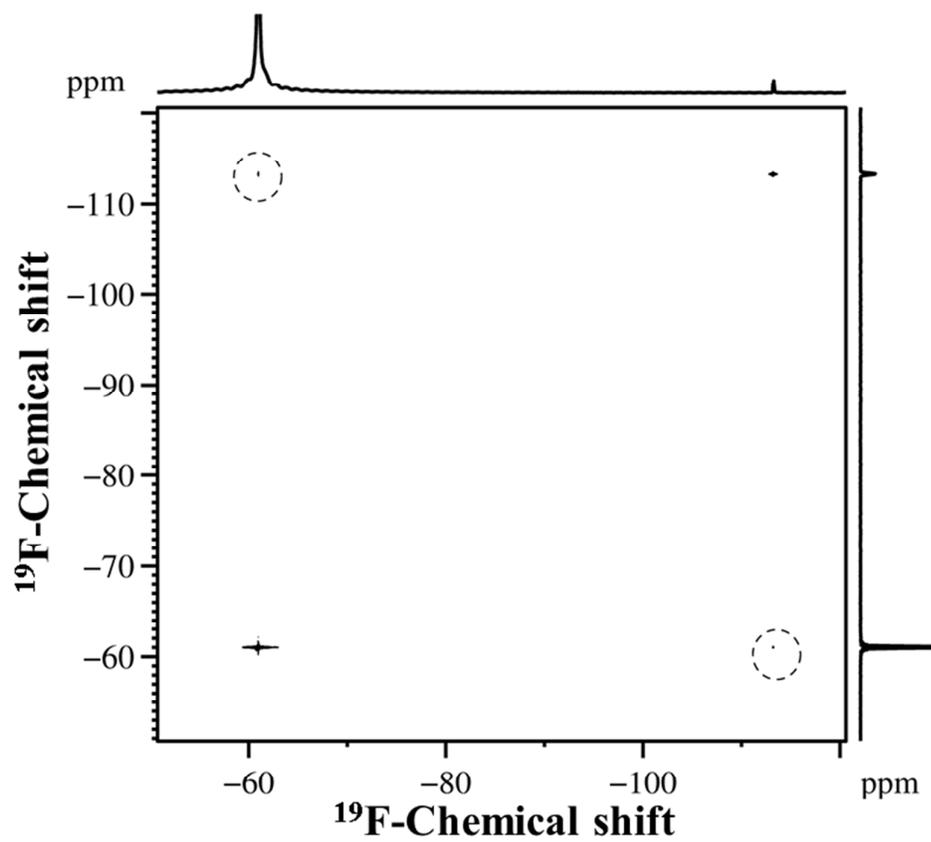
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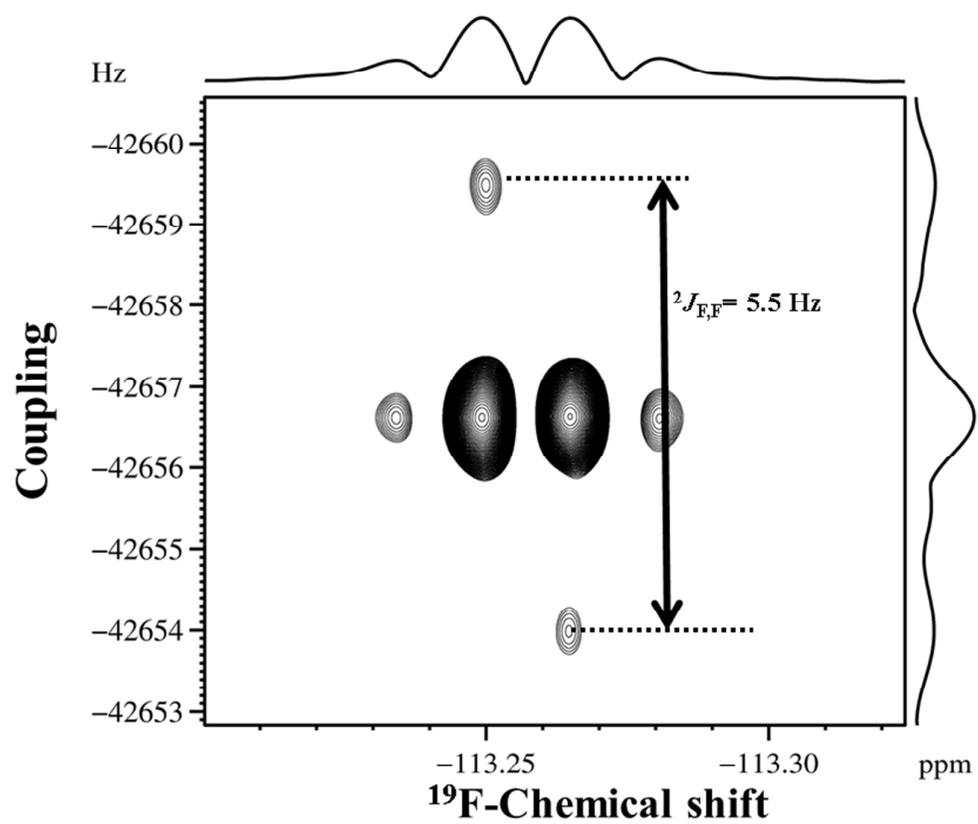
CF3 seven member pure



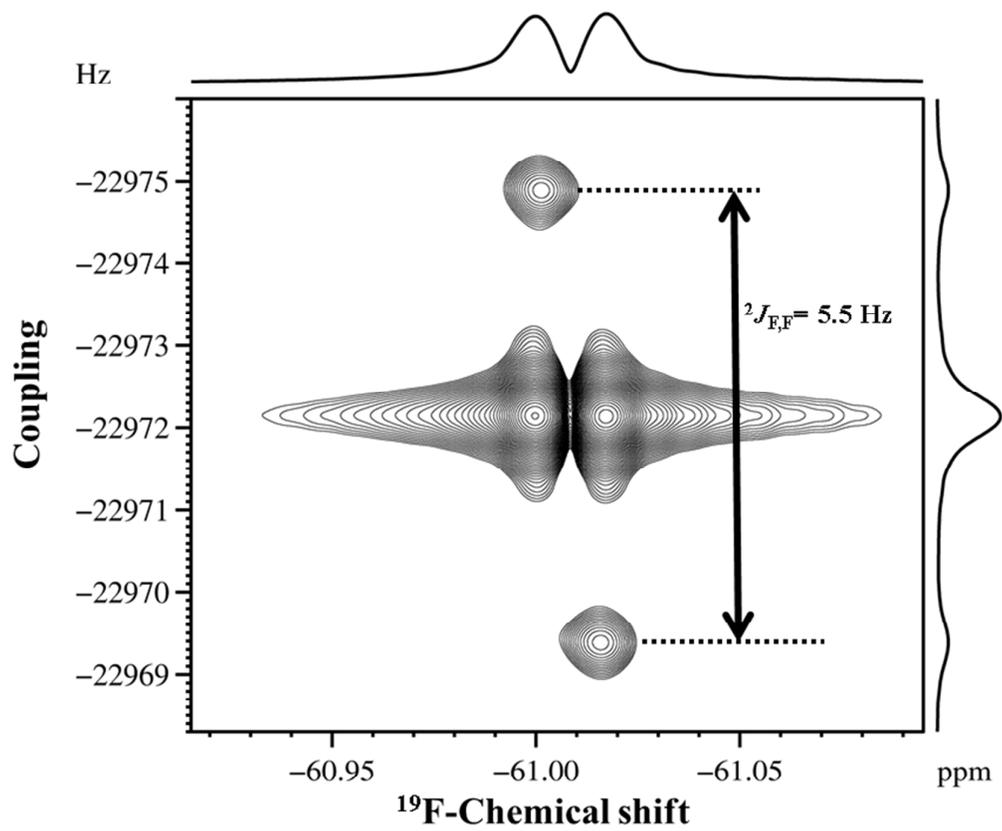
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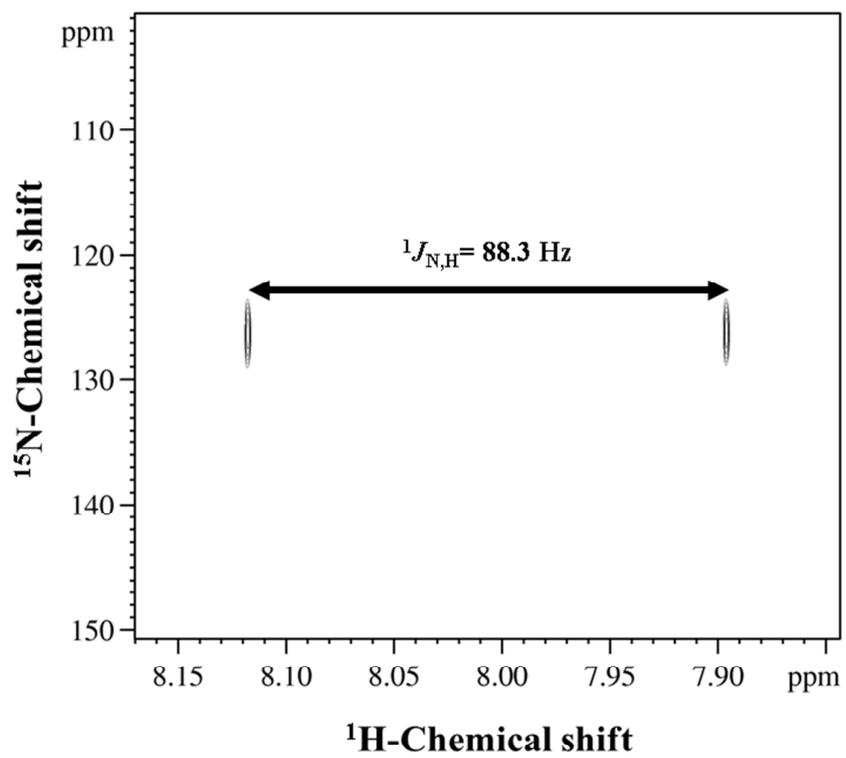
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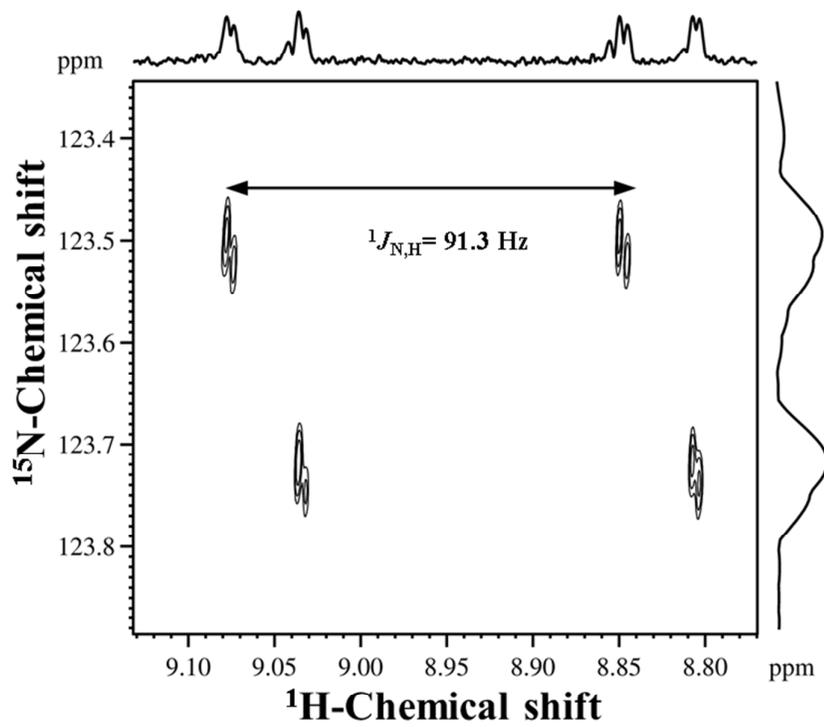


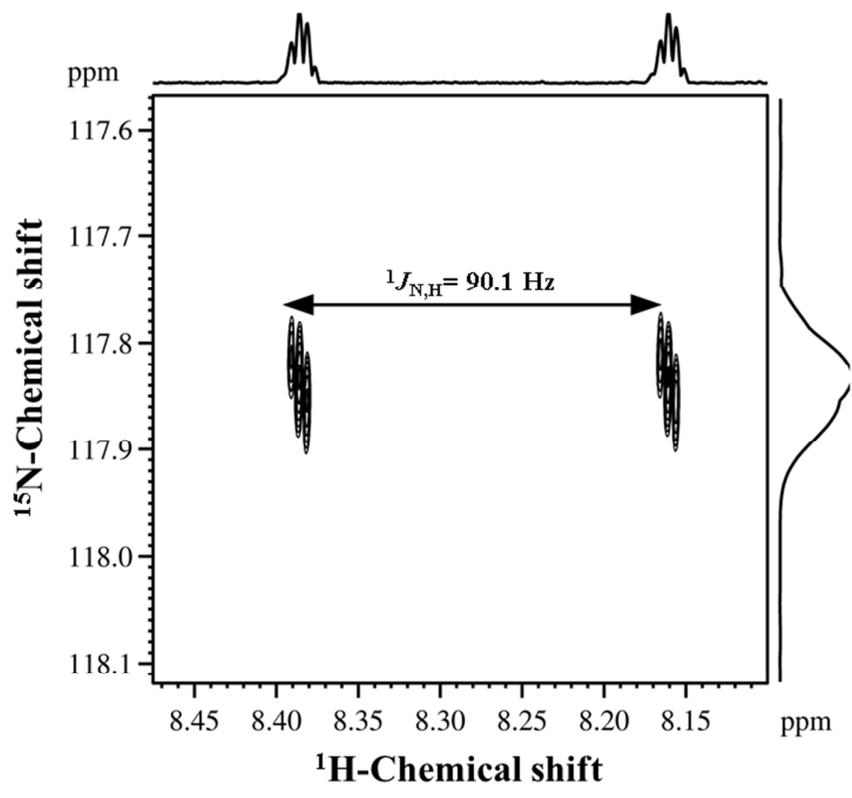
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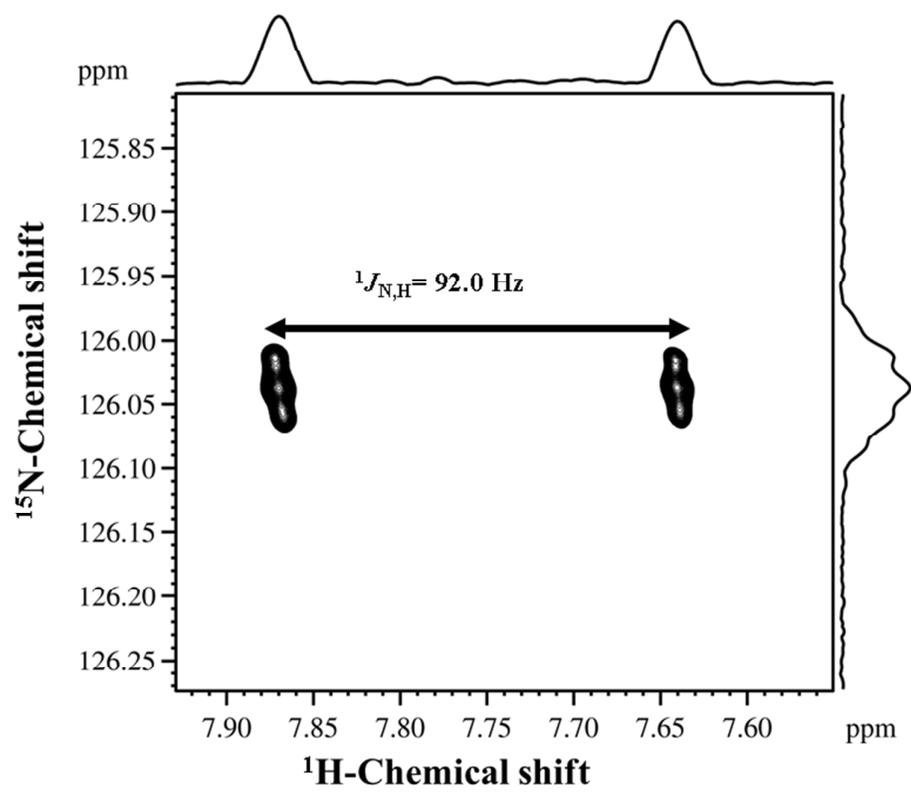
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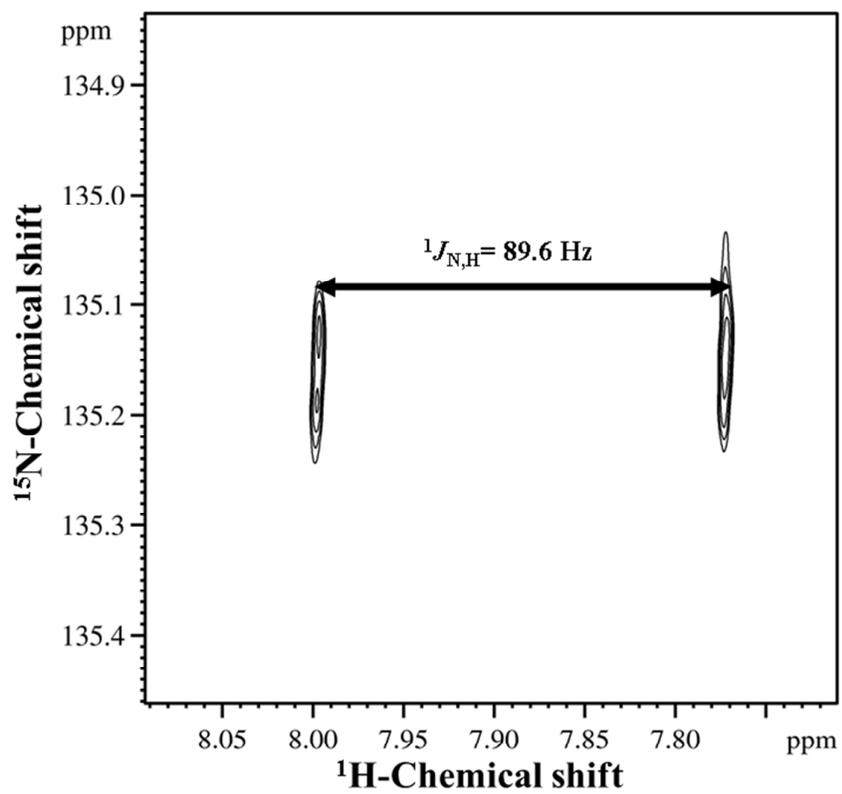




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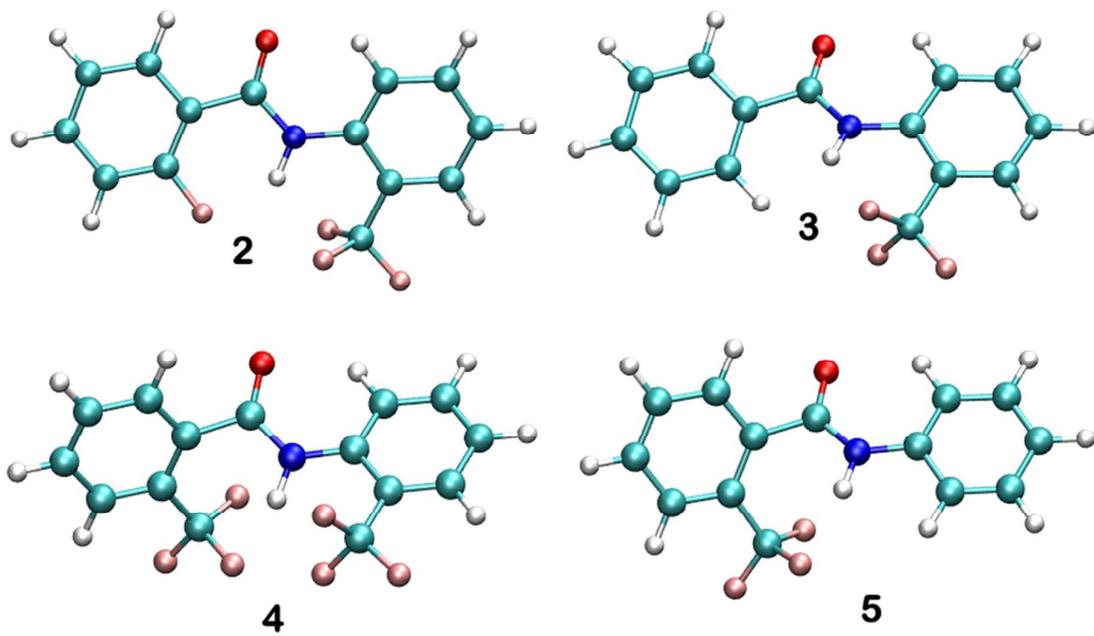


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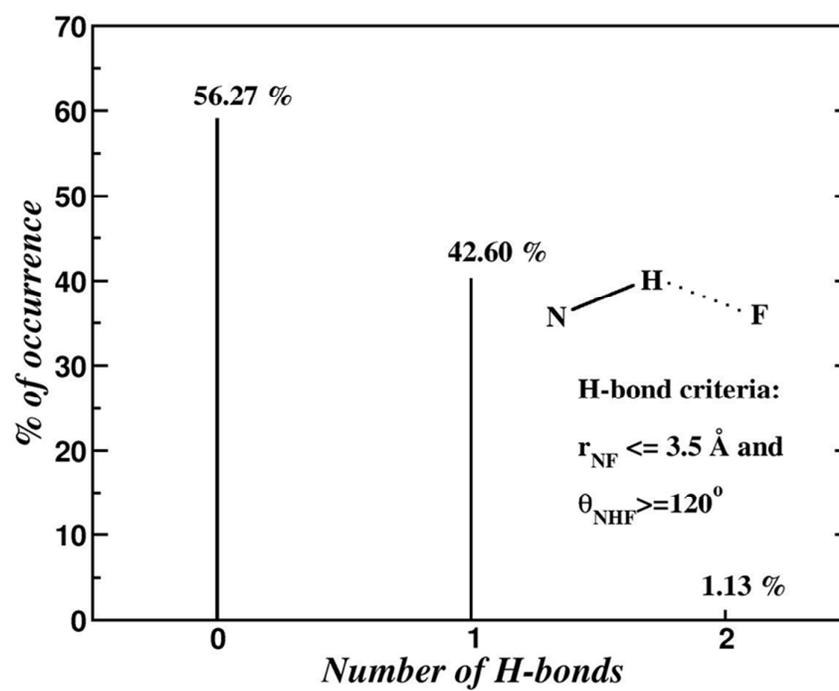
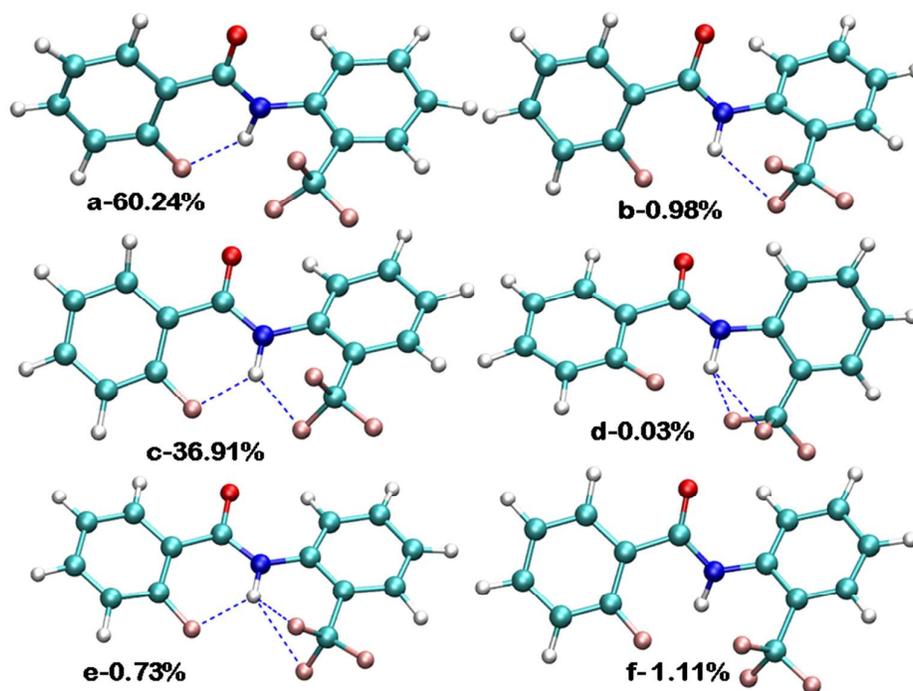
Table: ^{15}N - ^1H coupling constants in benzanilide (**1**) and its derivatives (**2-5**) in CDCl_3

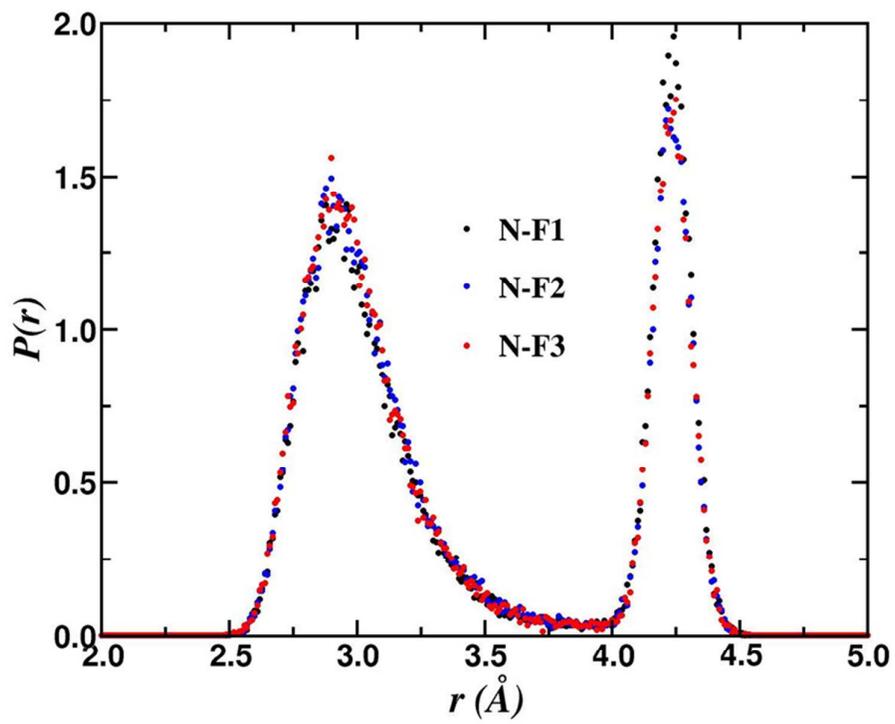
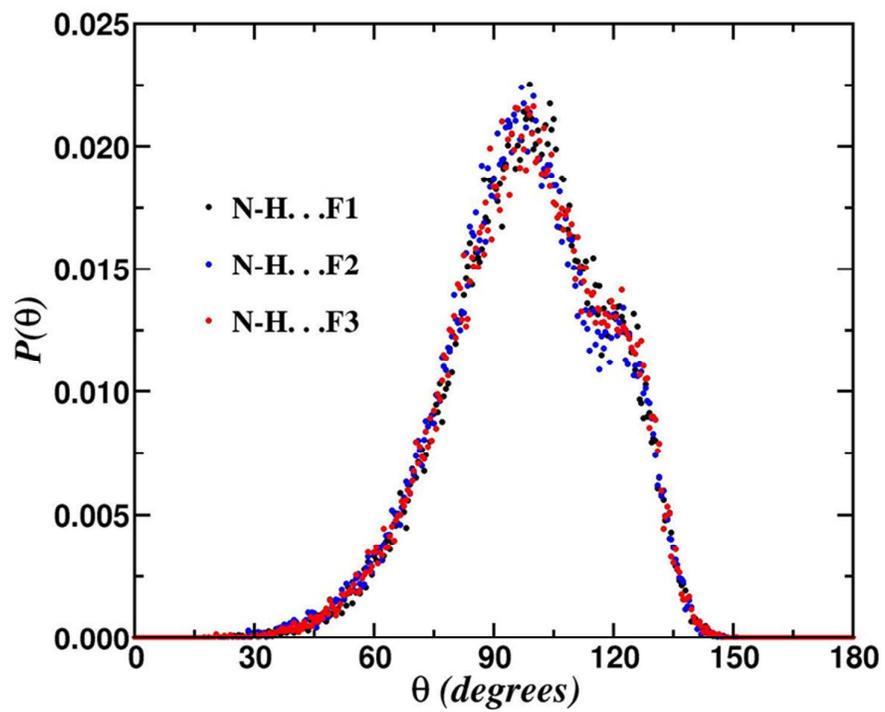
Molecule	$^1J_{\text{N,H}}$ (in Hz)
1	88.3
2	91.3
3	90.1
4	92.0
5	89.6

S23

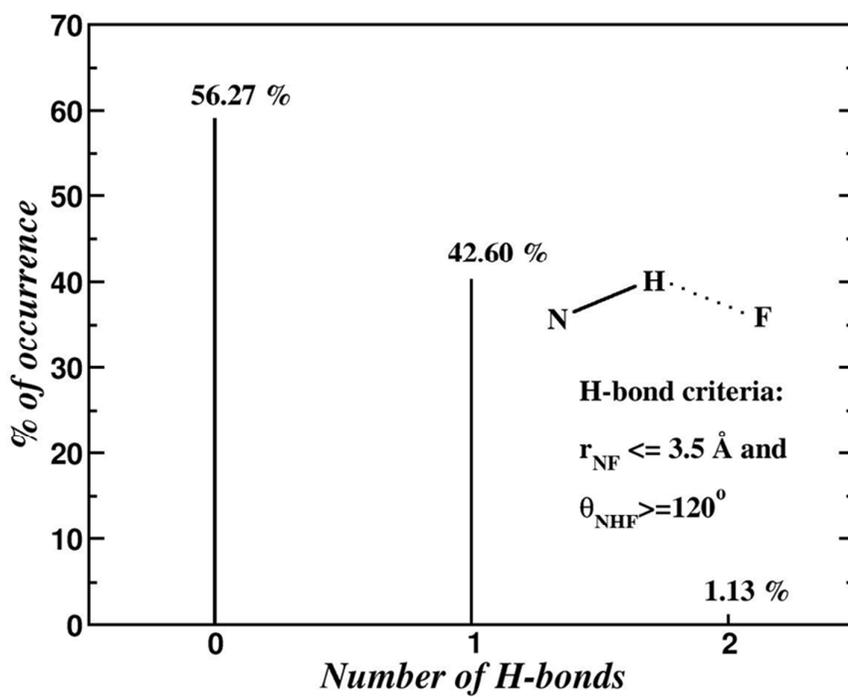
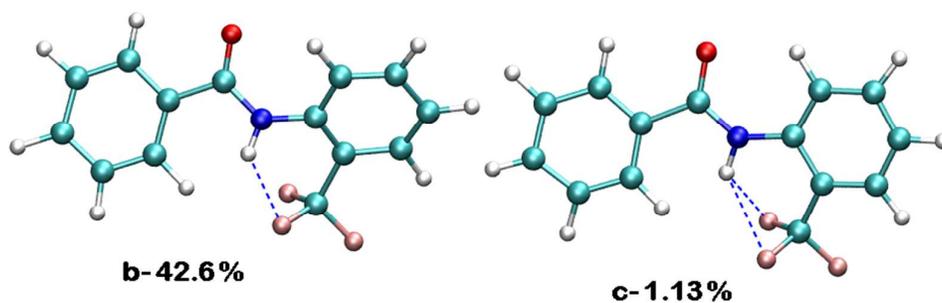
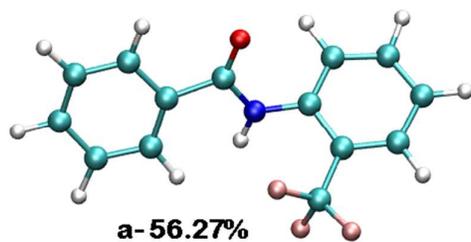


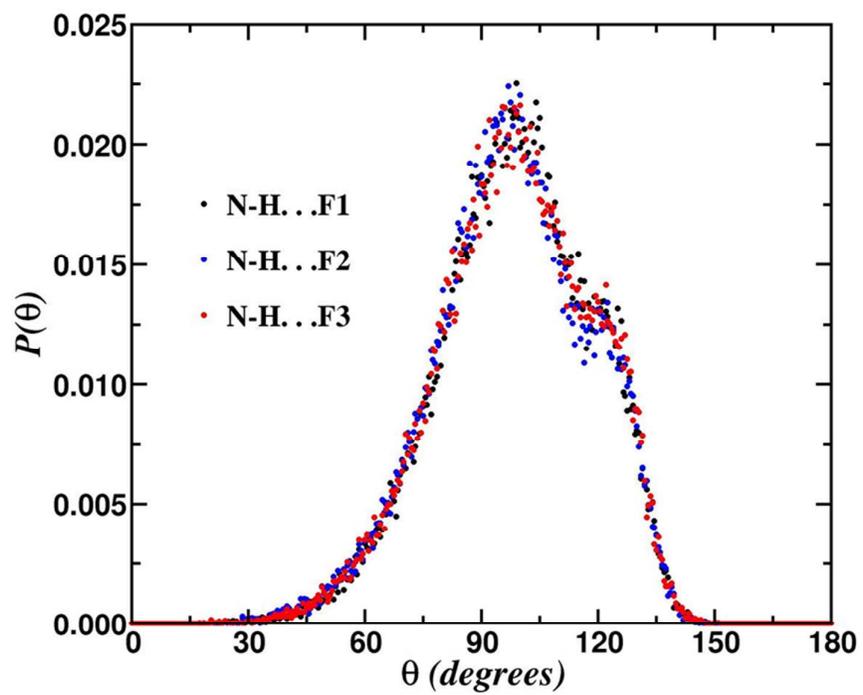
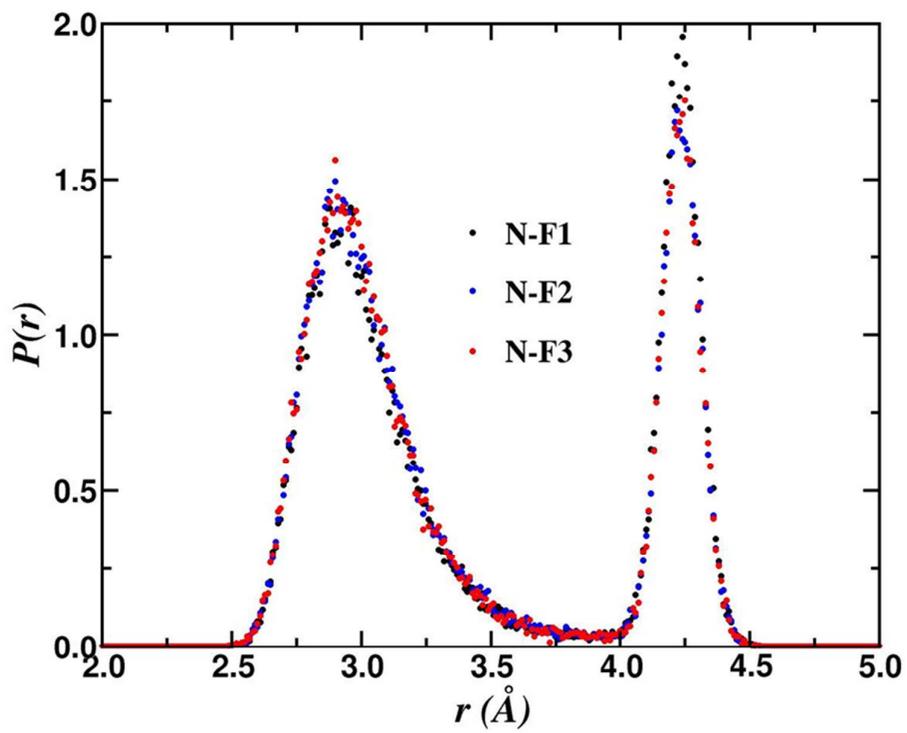
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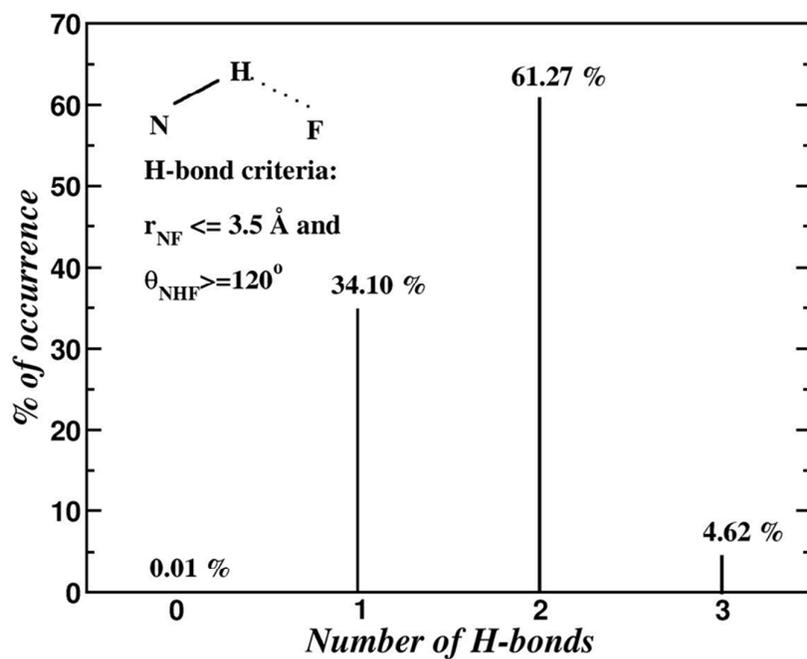
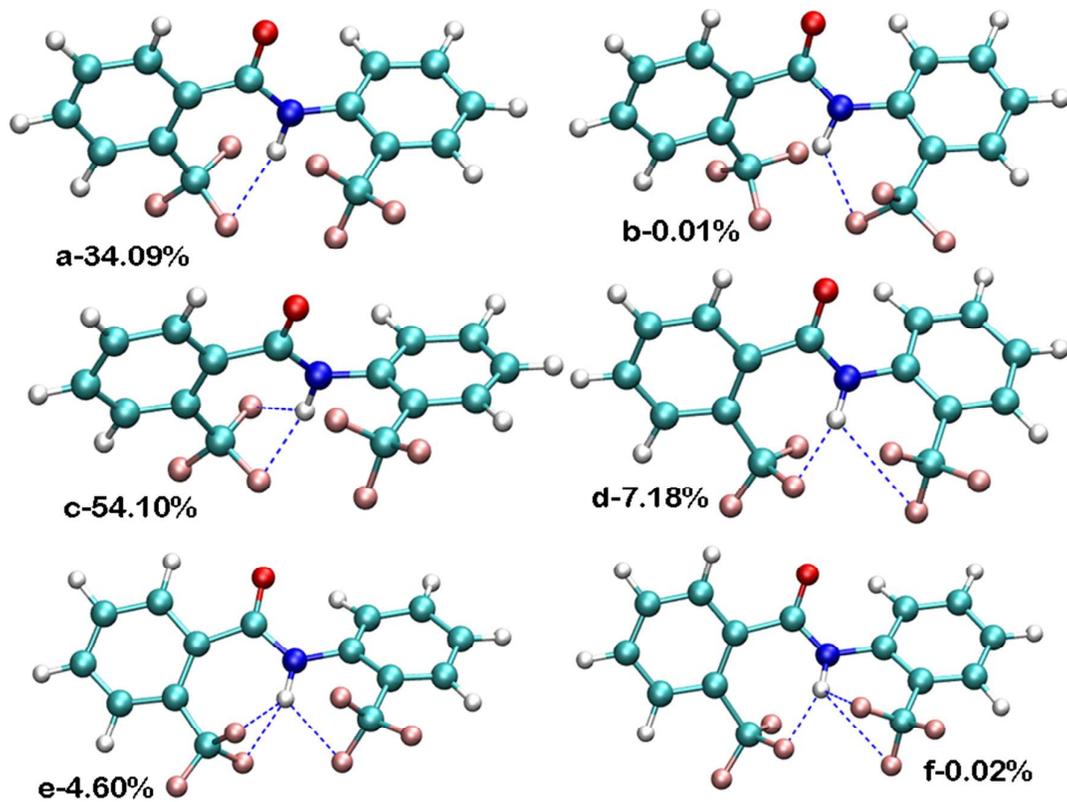


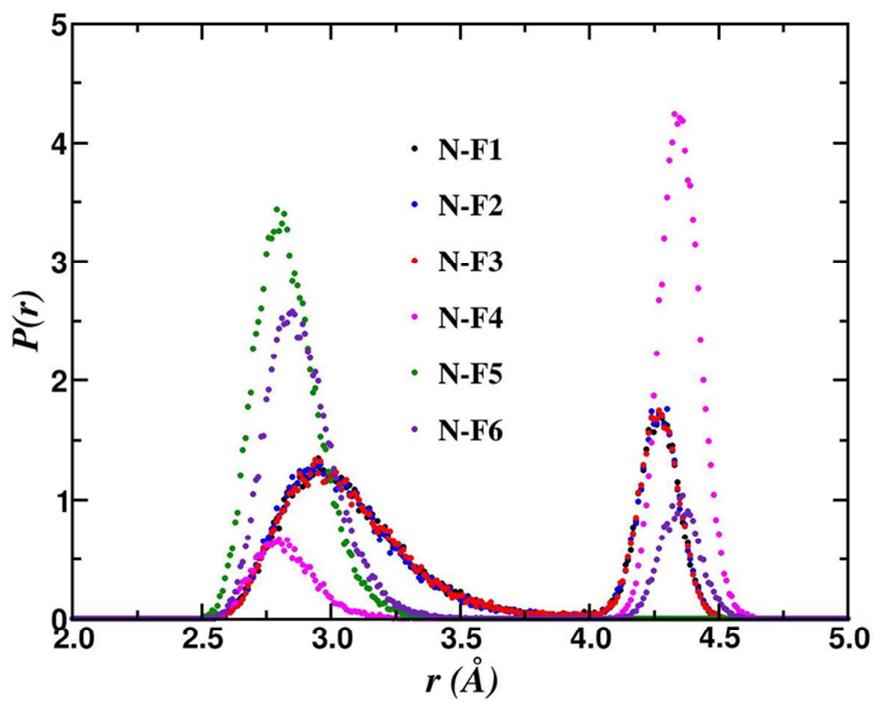
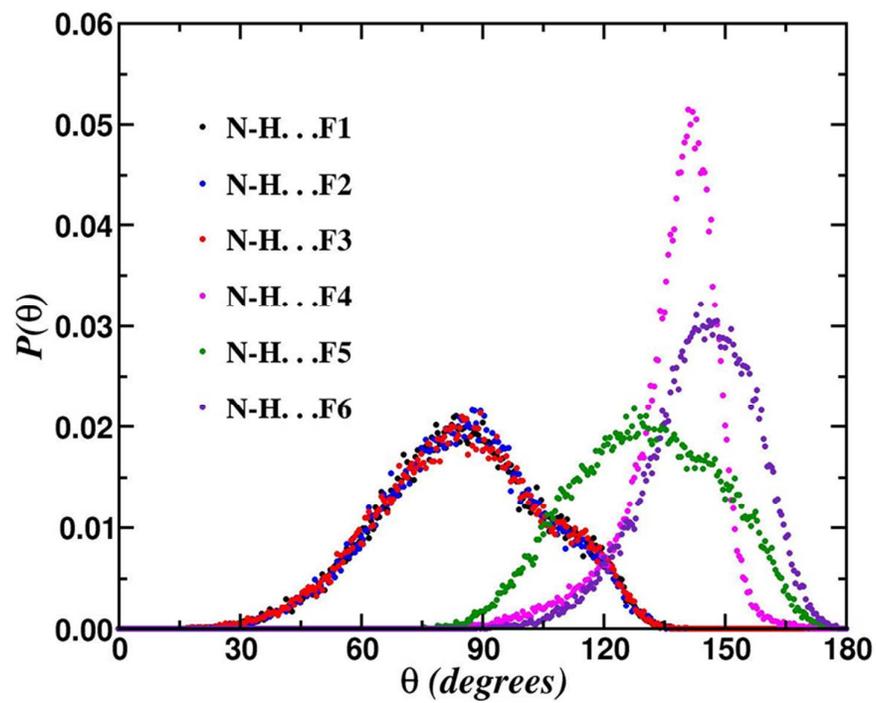
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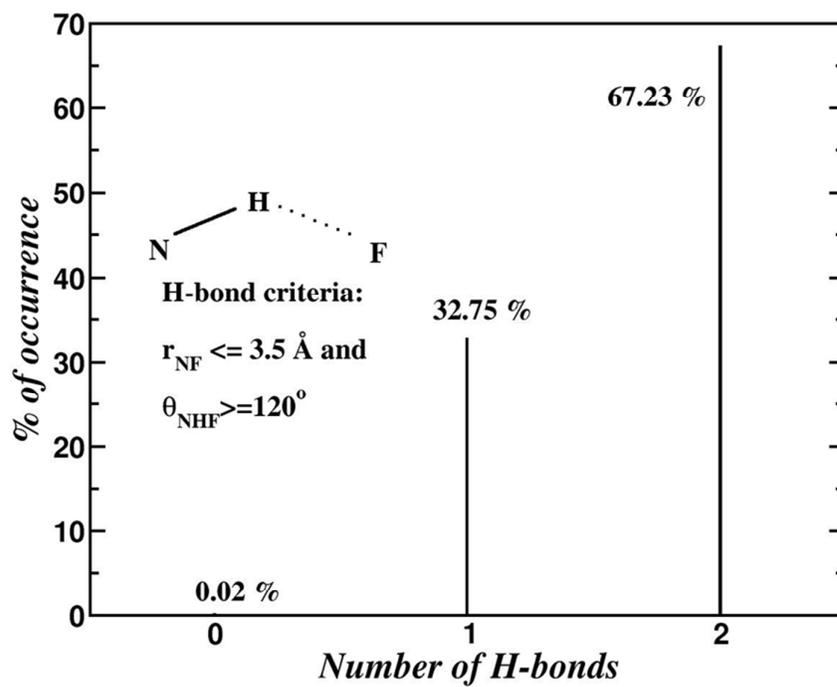
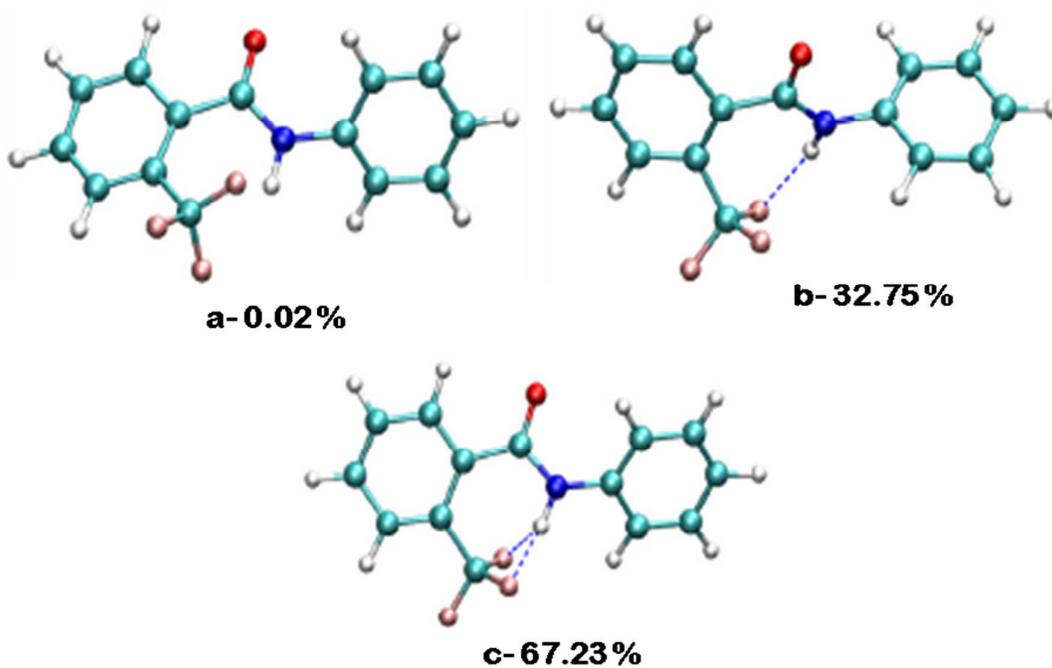


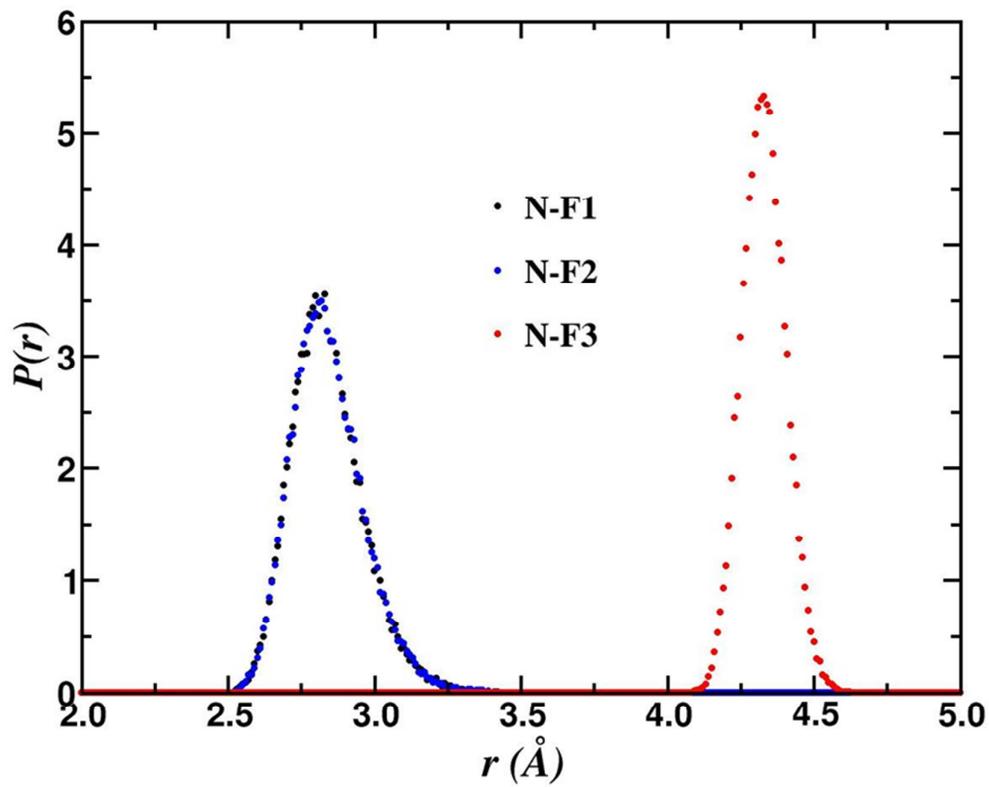
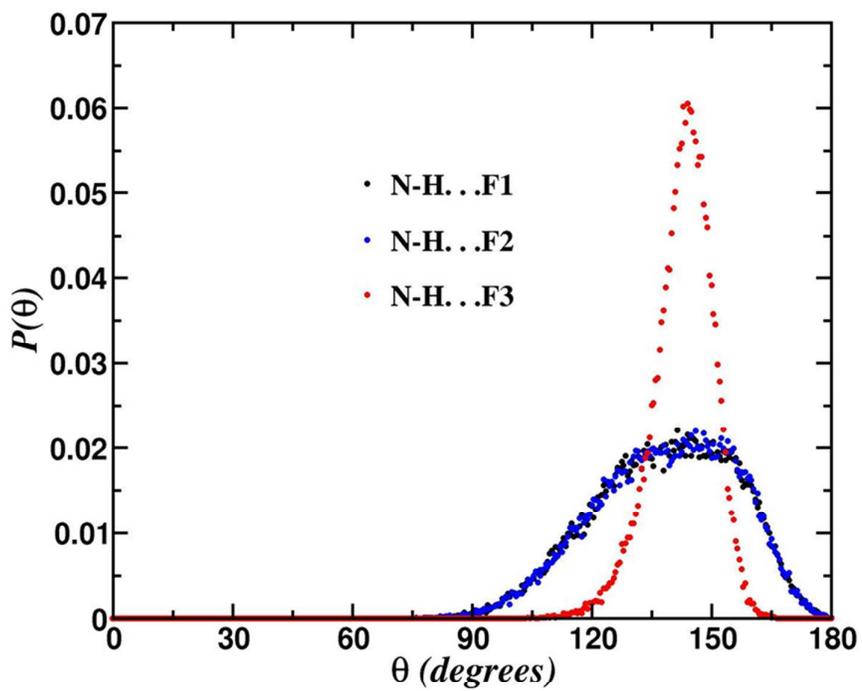
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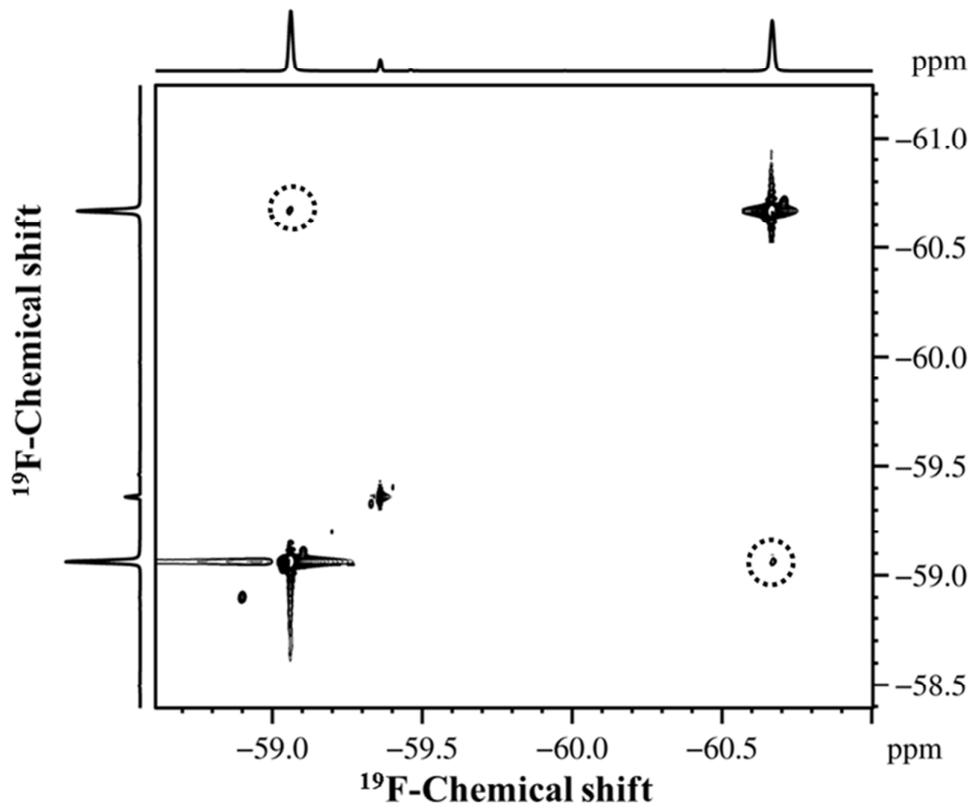




S30







S33

Table 2: Structural parameters obtained from DFT calculations

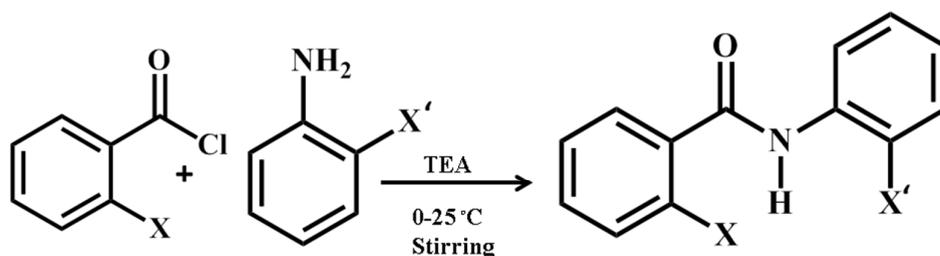
Parameter	Molecule 2	Molecule 3	Molecule 4	Molecule 5
N-H...F(a)	1.916	-	2.344	2.137
N-H...F(b)	2.176	2.229	2.155	-
N-H	1.010	1.009	1.010	1.007
N...F(a)	2.926	-	3.354	3.144
N...F(b)	3.186	3.238	3.165	-
\angle N-H...F(a)	139.96	-	127.47	128.20
\angle N-H...F(b)	127.15	128.76	120.16	-

General experimental remarks: Solvents were dried and distilled before use. All other reagents received from Aldrich were used without further purification. The investigated molecules **1-5** were synthesized according to the well known procedure [1].

The ^1H , ^{13}C and ^{19}F NMR spectra were recorded using Bruker 400 and 500 MHz NMR spectrometers. An Eurotherm temperature control unit was utilized to set the temperature to an accuracy of ± 1.0 K. The ^1H and ^{13}C chemical shifts were referenced relative to TMS and ^{19}F chemical shifts were referenced to trifluoroacetic acid. The experimental procedures for two dimensional ^{19}F - ^{19}F NOESY and ^1H - ^{19}F HOSEY experiments are well known [2].

General Procedure for Synthesis:

The substituted aniline (1 mM, 1 eq) was dissolved in dry dichloromethane (10 ml) and 1.8 mM of Triethylamine was added to it. Following which the required quantity of benzoyl chloride (1 mM, 1 eq) was added to the same solution, and the resulting mixture was stirred for nearly 2 Hrs between 0-25°C. The solution was washed with water, then mixed with saturated solution of NaCl and Sodiumbicarbonate solution. After this workup the organic layer was separated, dried with MgSO_4 .



	X	X'
1	-H	H
2	-F	CF ₃
3	-H	CF ₃
4	-CF ₃	CF ₃
5	-CF ₃	H

References:

- [1] P. Panini, D. Chopra *CrystEngComm*, **2012**, 14, 1972–1989.
- [2] J. Battiste, R. A. Newmark, *Prog. Nucl. Magn. Reson. Spectro.* **2006**, 48, 1–23.