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SUPPORTING INFORMATION

Organic fluorine involved intramolecular Hydrogen Bonds in the derivatives of Imides: NMR Evidence corroborated by DFT based theoretical calculations

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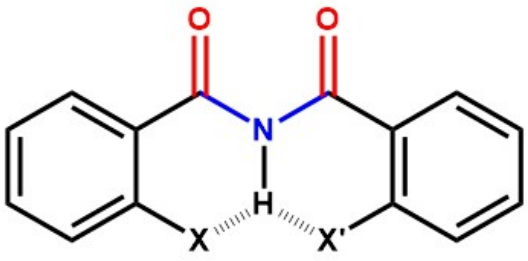
Chemical Structures of the molecules investigated

(a)

1. X=X'=F
2. X=X'=Cl
3. X=X'=H



(b)

4. X=H and X'=F
5. X=Cl and X'=F
6. X=OMe and X'=F
7. X=CF_3 and X'=F

Scheme. 1S: Chemical structures of 2-X-*N*'-(2-X'-benzoyl)benzamide[1] derivatives: (a) Group of symmetrically di-substituted molecules, where X = X') (b) asymmetrically di-substituted molecules (substituent X ≠ X').

800 MHz ^{13}C-^{1}H HSQC spectrum of molecule **1** in the solvent $CDCl_3$

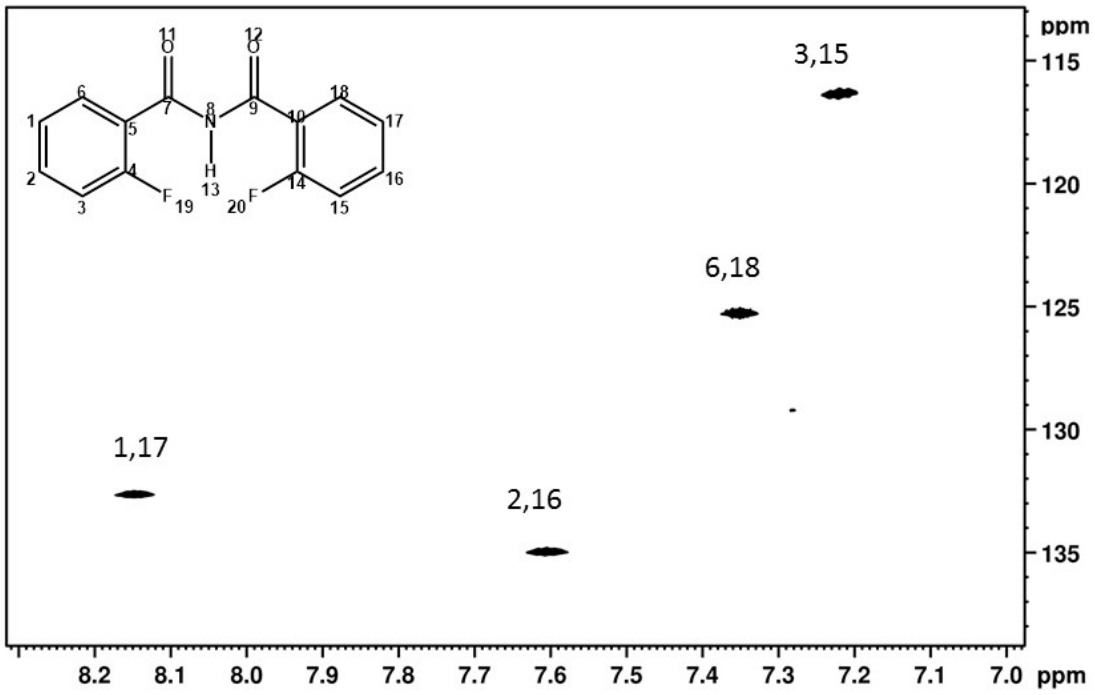


Fig.1S. 800 MHz two dimensional ^{1}H-^{13}C HSQC spectrum of molecule **1,** in the solvent $CDCl_3$. The chemical structure of the molecule is given as an inset. The atoms are numbered and the corresponding peak assignments are given.

500 MHz ^{13}C-^{1}H HSQC spectrum of molecule **2** in $CDCl_3$

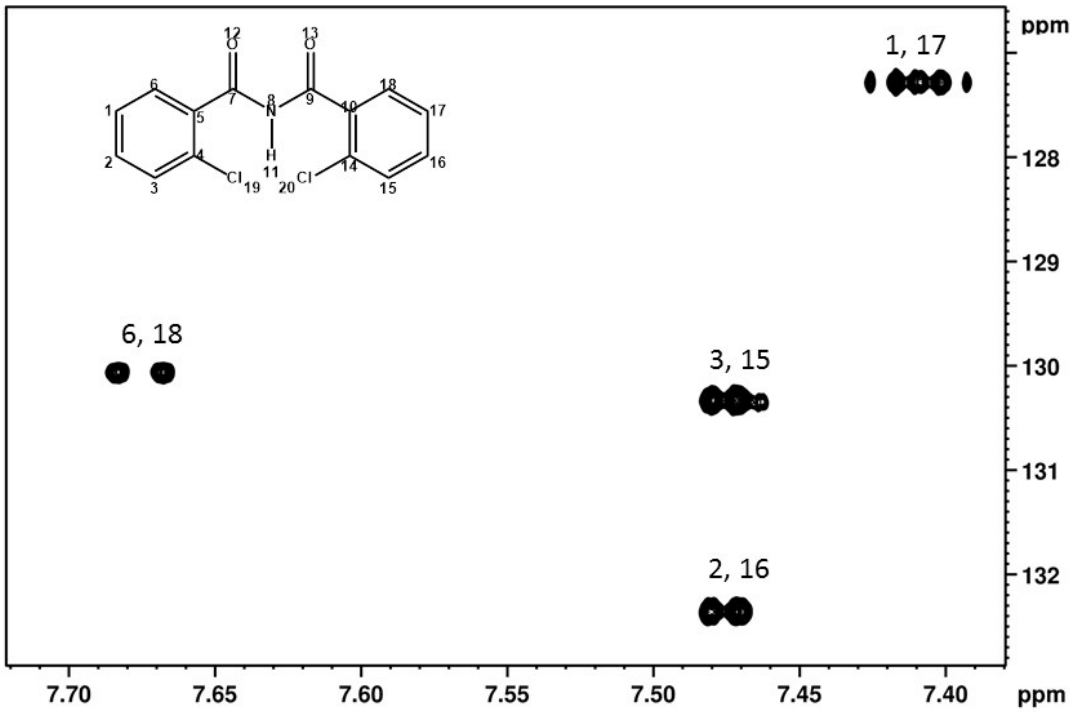


Fig.2S. 500 MHz two dimensional ^{1}H-^{13}C HSQC spectrum of molecule **2,** in the solvent $CDCl_3$. The chemical structure of the molecule is given as an inset. The atoms are numbered and the corresponding peak assignments are given.

400 MHz ^{15}N-^{1}H HSQC spectrum of molecule **2** in $CDCl_3$

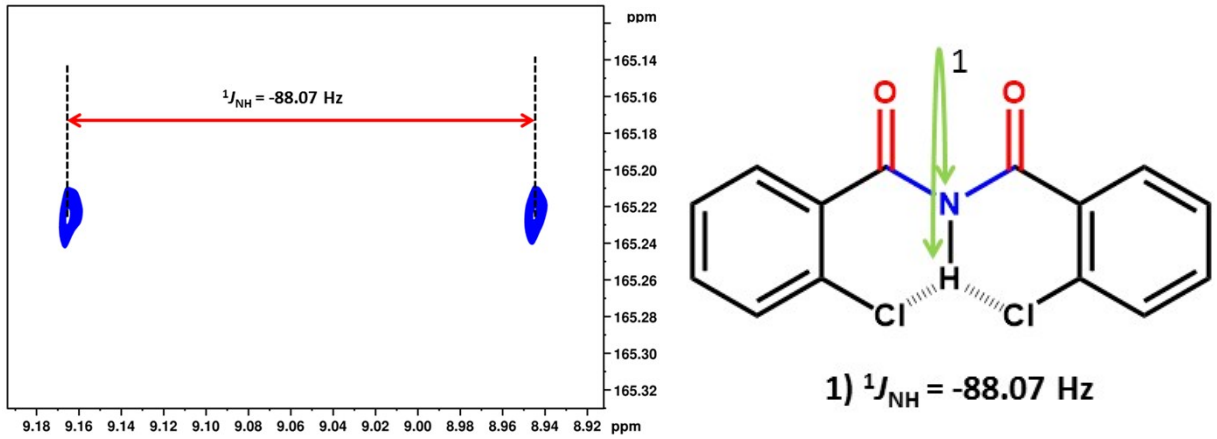


Fig.3S. 400 MHz two dimensional ^{15}N-^{1}H HSQC spectrum of molecule **2,** in the solvent $CDCl_3$. The separation providing the magnitude of the NH scalar coupling[2-4] is identified by a double headed arrow. The chemical structure of the molecule and the sign of the coupling is also given.

800 MHz ^{13}C-^{1}H HSQC spectrum of molecule **3** in $CDCl_3$

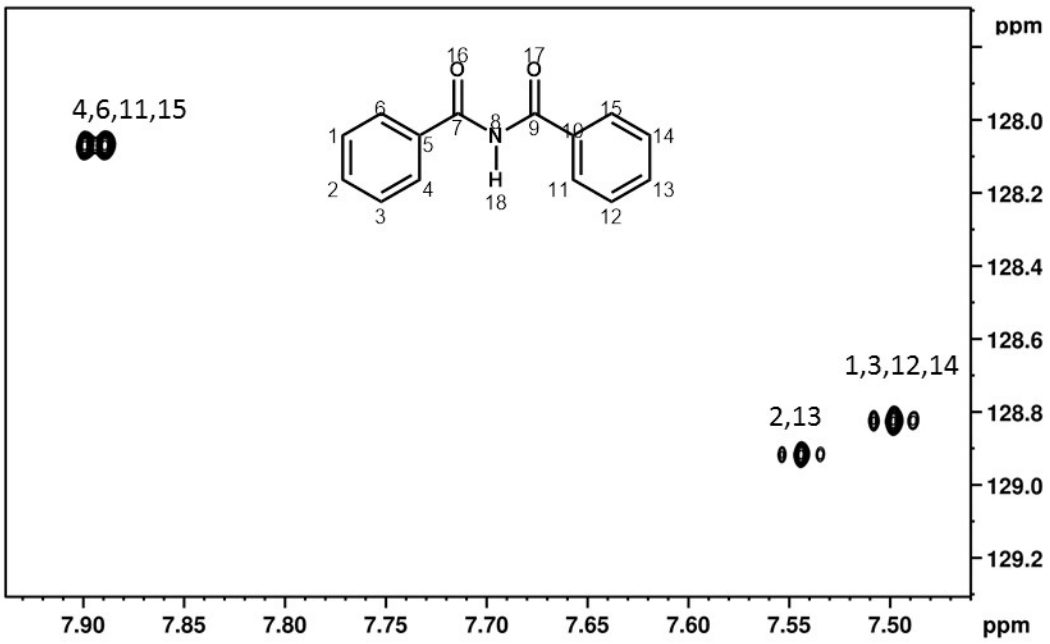


Fig.4S. 800 MHz two dimensional ^{13}C-^{1}H HSQC spectrum of molecule **3,** in the solvent $CDCl_3$. The chemical structure of the molecule is given as an inset. The atoms are numbered and the corresponding peak assignments are given.

400 MHz ^{15}N-^{1}H HSQC spectrum of molecule **3** in $CDCl_3$

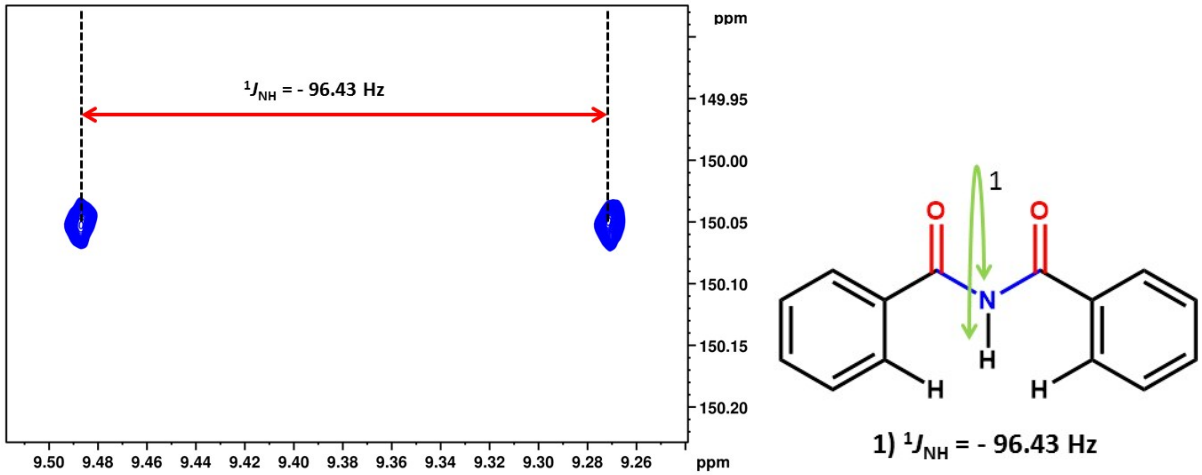


Fig.5S. 400 MHz 2D ^{15}N-^{1}H HSQC spectrum of molecule **3** in the solvent $CDCl_3$. The separation providing the magnitude of the coupling[2-4] is identified by double headed arrows. The chemical structure of the molecule and the sign of the coupling is also given.

^{1}H and $^{1}H\{^{19}F\}$ NMR spectra of molecule **4** in $CDCl_3$

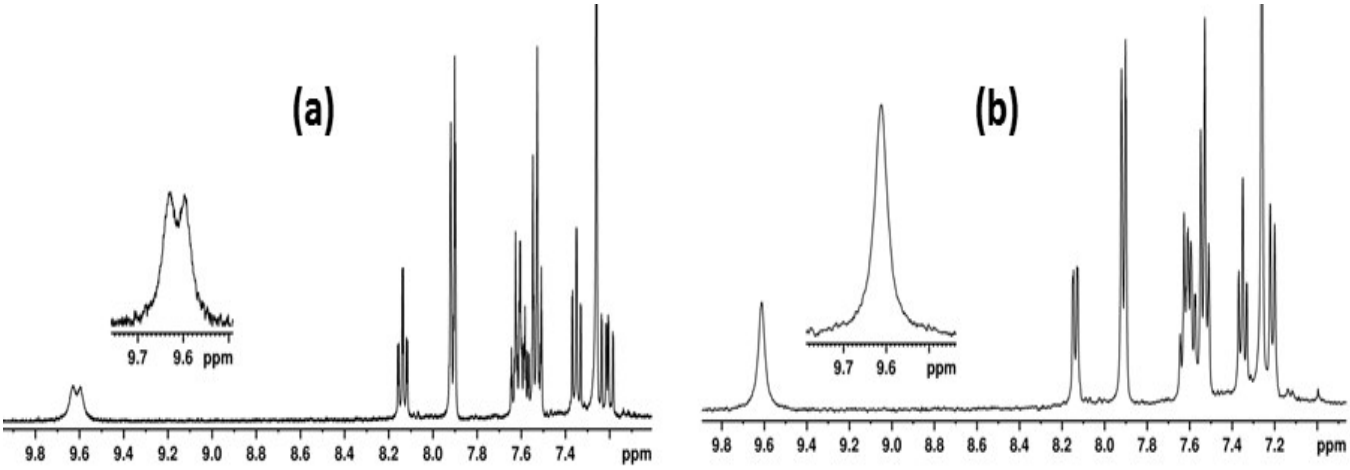


Fig.6S. 400 MHz **(a)** ^{1}H and **(b)** $^{1}H\{^{19}F\}$ NMR spectra of molecule **4** in the solvent $CDCl_3$.

500 MHz ^{13}C-^{1}H HSQC spectrum of molecule **4** in $CDCl_3$

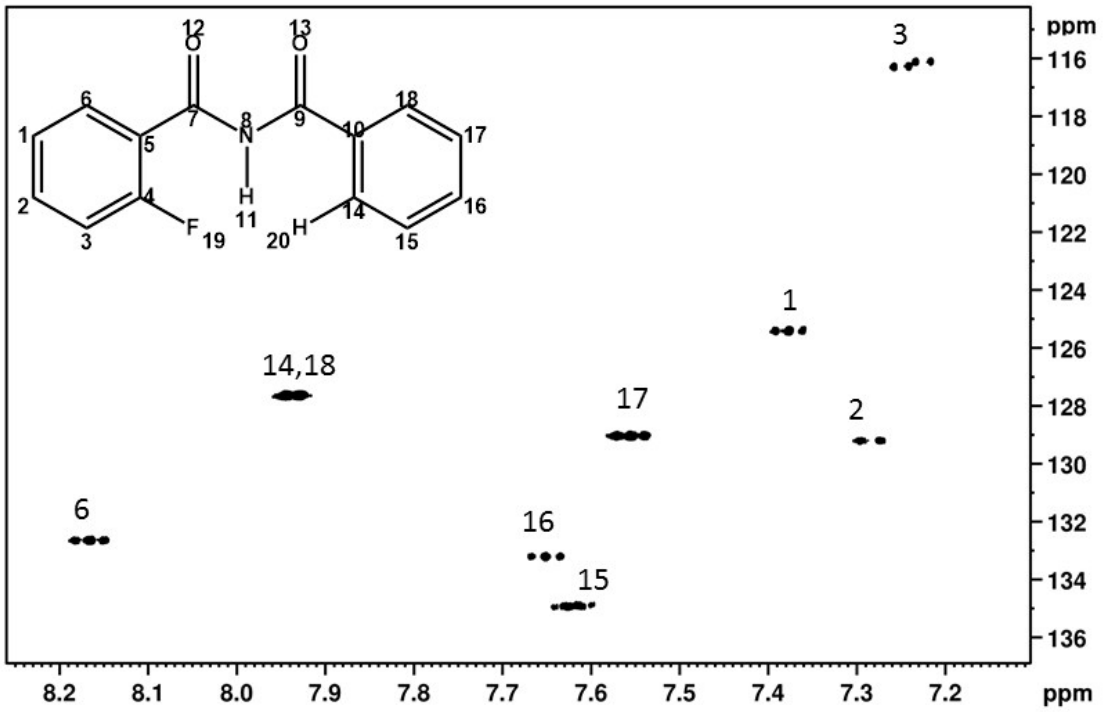


Fig.7S. 500 MHz ^{13}C-^{1}H HSQC spectrum of molecule **4** in the solvent $CDCl_3$. The chemical structure of the molecule is given as an inset. The atoms are numbered and the corresponding peak assignments are given.

800 MHz ^{15}N-^{1}H HSQC spectrum of molecule **4** in DMSO-d_6

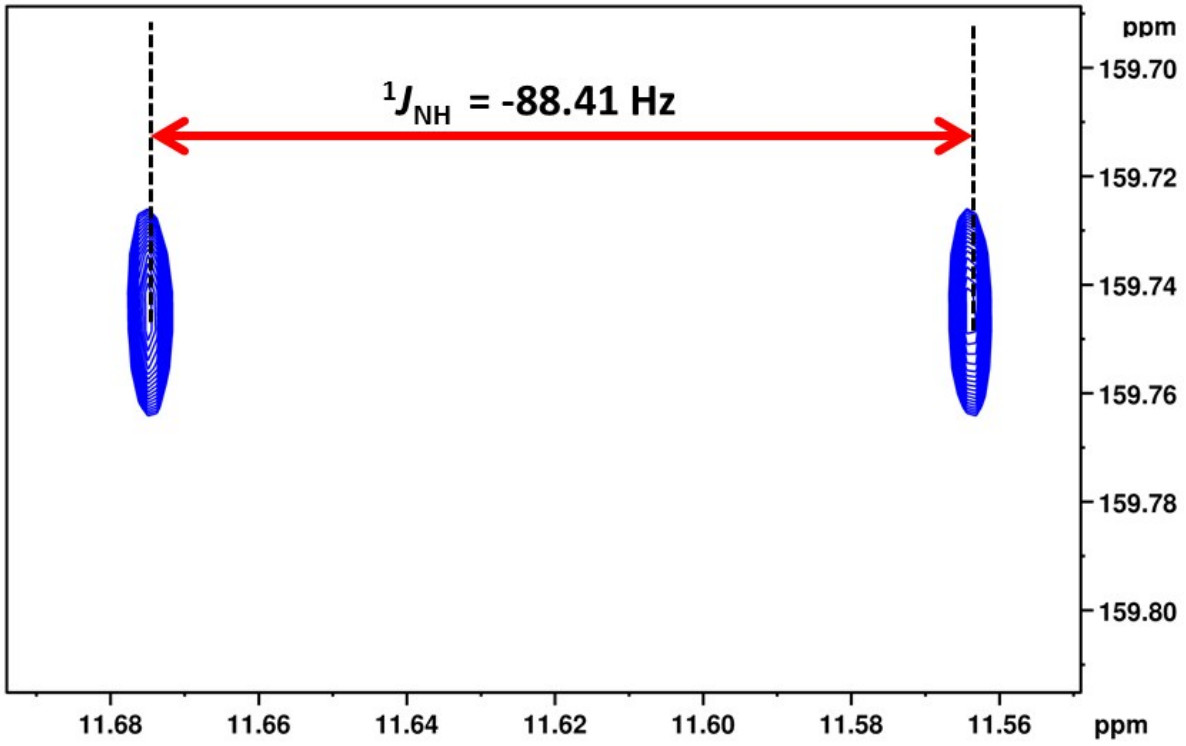


Fig.8S. 800 MHz ^{15}N-^{1}H HSQC NMR spectrum of molecule **4** in the solvent DMSO-d_6. The separation providing the magnitude of the coupling[2-4] is identified by double headed arrow. The value of the coupling and its sign is also given.

400 MHz ^{1}H-^{15}N HSQC NMR spectrum of molecule **4** in $CDCl_3$

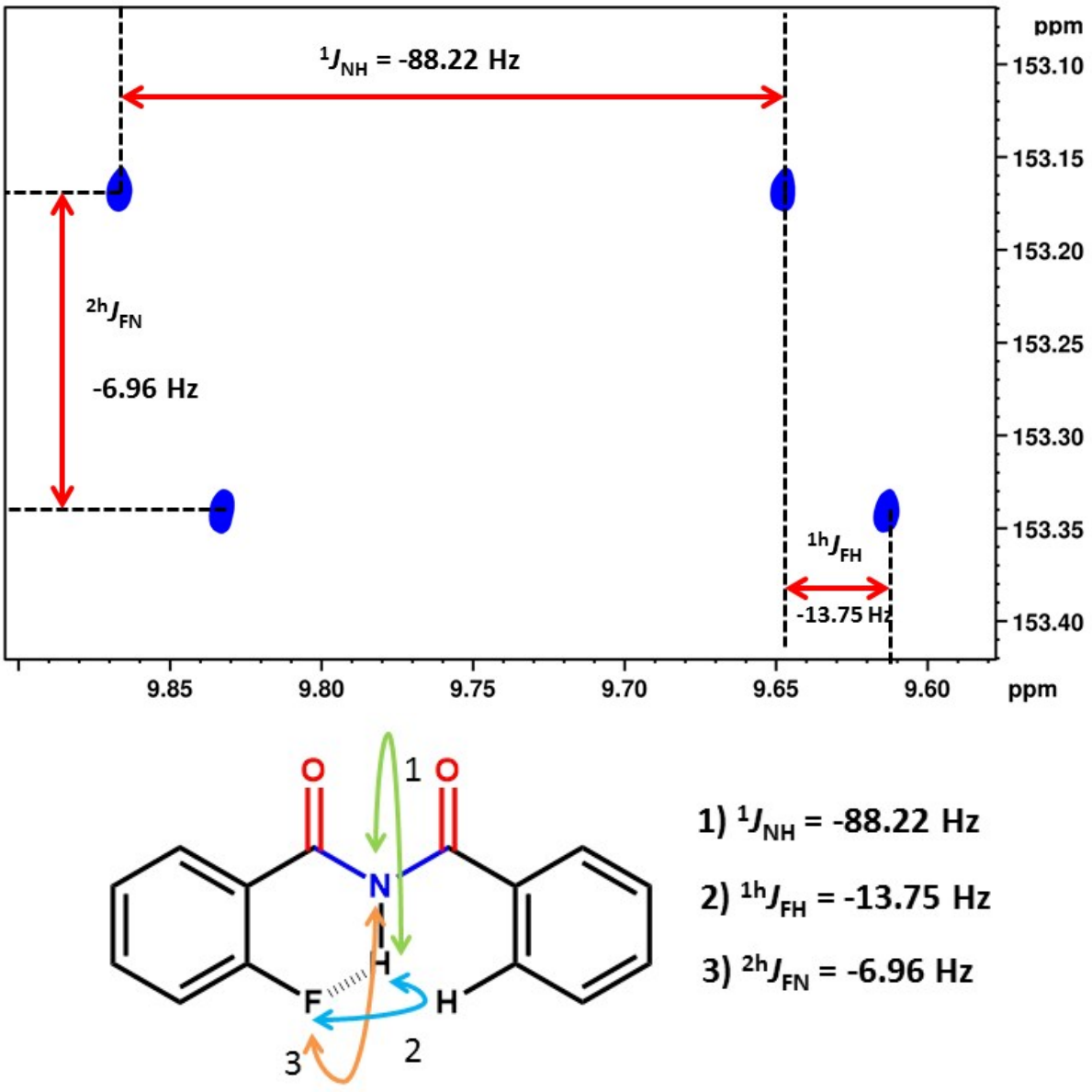


Fig.9S. 400 MHz ^{15}N-^{1}H HSQC NMR spectrum of molecule **4** in the solvent $CDCl_3$. The separation providing the magnitudes of the couplings[2-4] are identified by double headed arrows. The chemical structure of the molecule and the signs of the couplings are also given. The signs of the couplings are derived from the slopes of the displacement vector of cross-sections (Details are discussed in the main manuscript).

(a) 376 MHz ^{19}F and (b) 2D ^{19}F-^{1}H HOESY spectrum of molecule **4** in $CDCl_3$

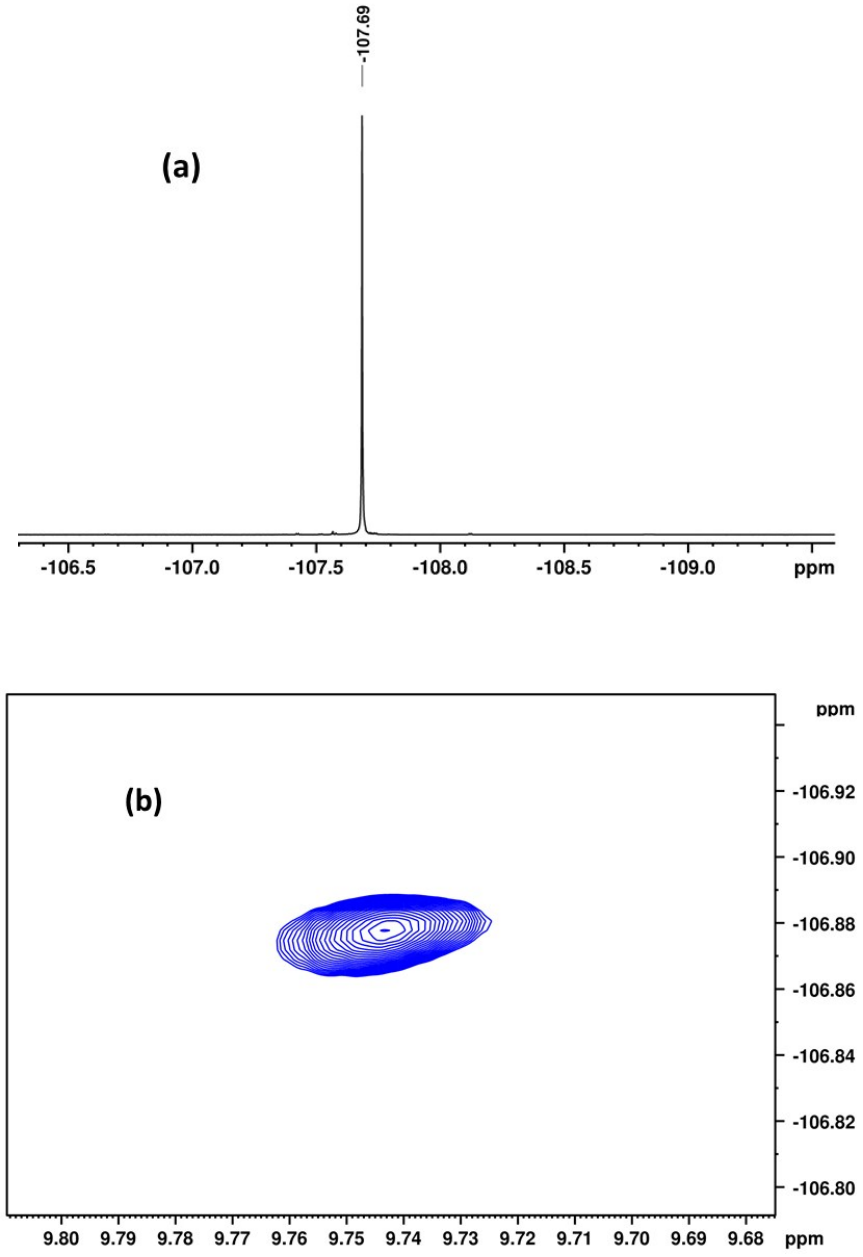


Fig.10S. (a) 376 MHz ^{19}F (b) 2D heteronuclear correlation ^{19}F-^{1}H HOESY[5] spectra of molecule **4** in the solvent $CDCl_3$.

400 MHz ^{1}H and $^{1}H\{^{19}F\}$ NMR spectra of molecule **5** in $CDCl_3$

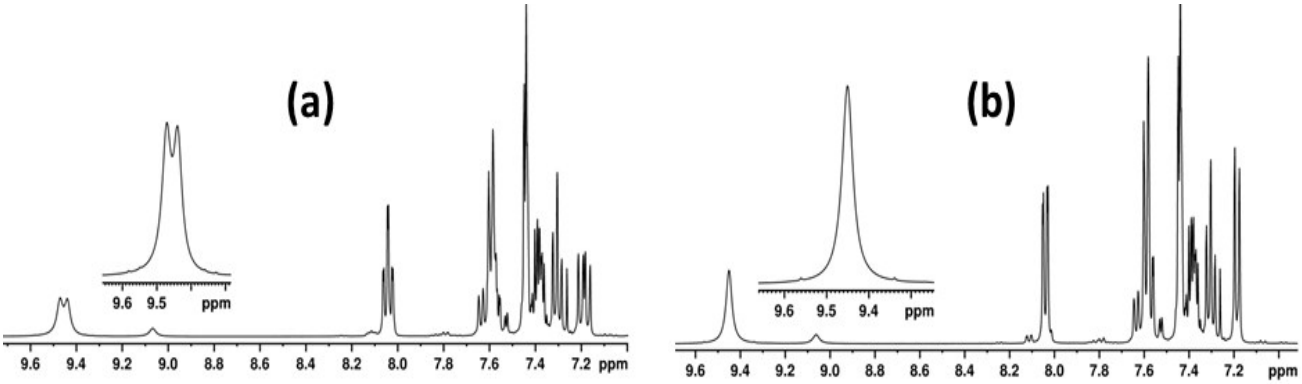


Fig.11S. 400 MHz **(a)** ^{1}H and **(b)** $^{1}H\{^{19}F\}$ spectra of molecule **5** in the solvent $CDCl_3$.

500 MHz ^{13}C-^{1}H HSQC spectrum of molecule **5** in $CDCl_3$

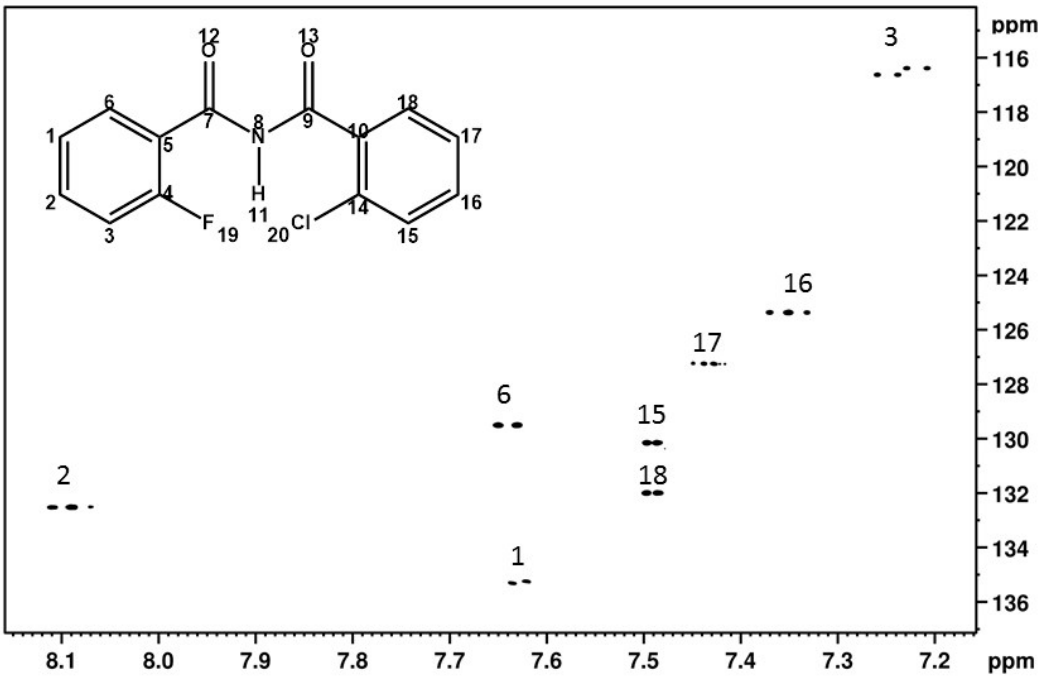


Fig.12S. The 500 MHz ^{1}H-^{13}C HSQC spectrum of the molecule **5** in solvent $CDCl_3$. The chemical structure of the molecule is given as an inset. The atoms are numbered and the corresponding peak assignments are given.

800 MHz ^{15}N-^{1}H HSQC spectrum of molecule **5** in DMSO-d_6

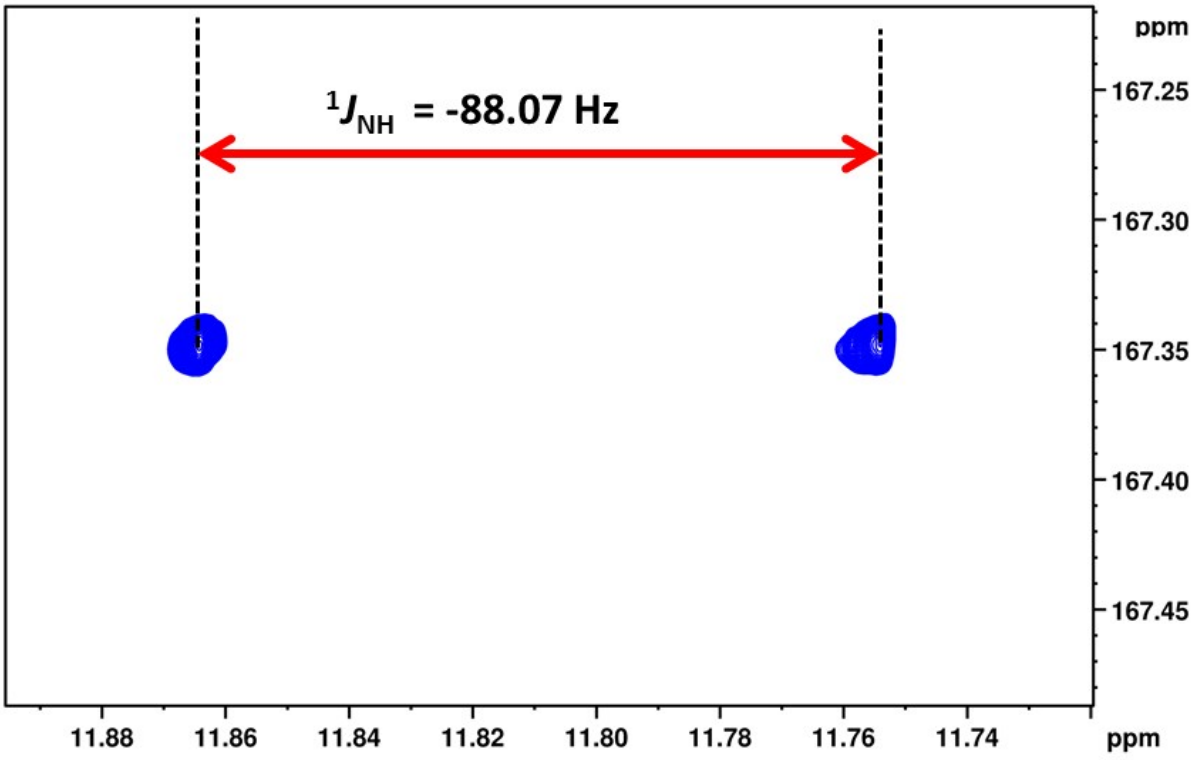


Fig.13S.800 MHz ^{15}N-^{1}H HSQC spectrum of molecule **5** in the solvent DMSO-d_6. The separation providing the magnitude of the coupling[2-4] is identified by a double headed arrow. The coupling strength and its sign is also given.

400 MHz ^{15}N-^{1}H HSQC spectrum of molecule **5** in $CDCl_3$

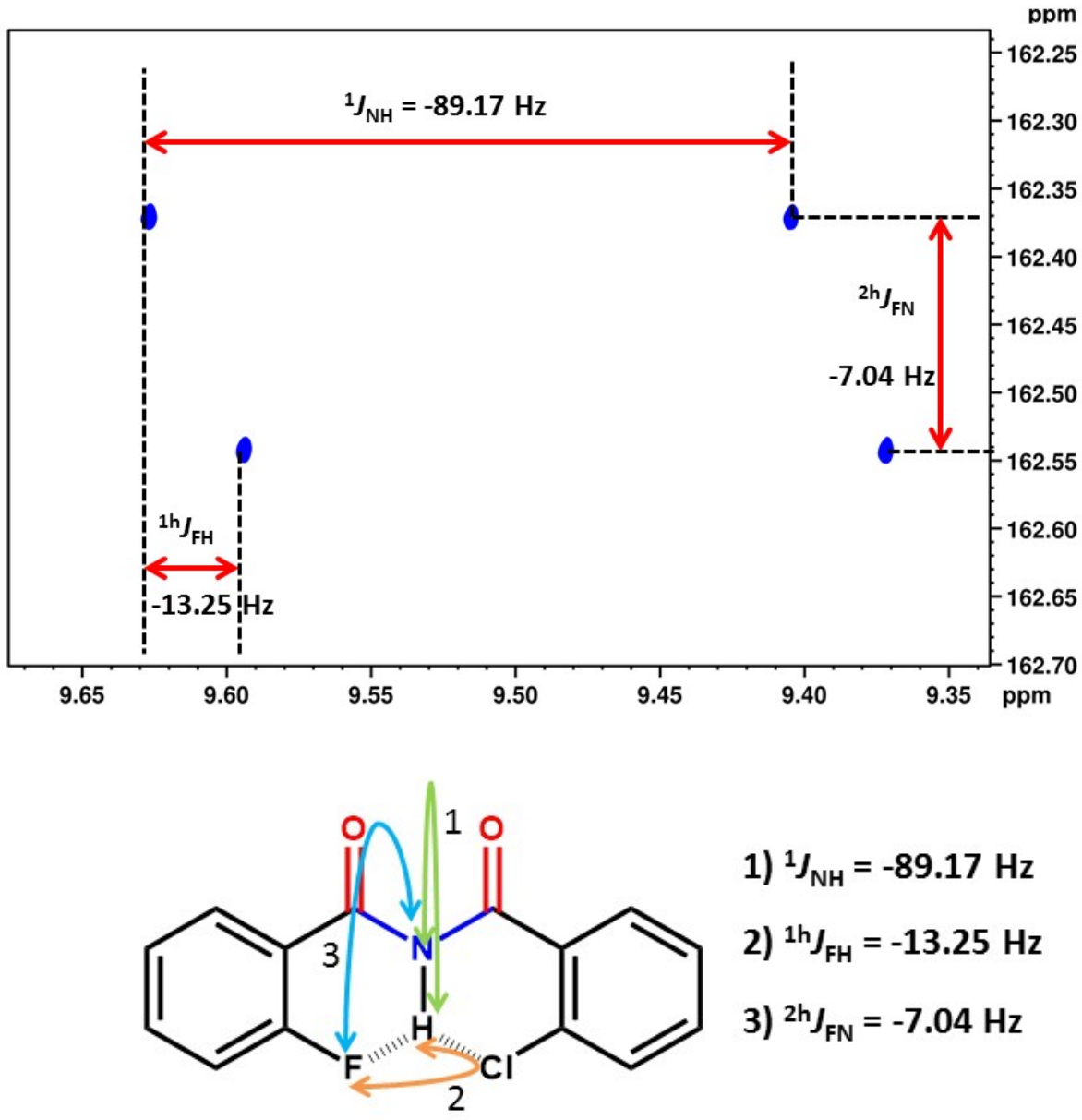


Fig.14S. 400 MHz ^{15}N-^{1}H HSQC spectrum of molecule **5** in $CDCl_3$. The separation providing the magnitudes of the couplings[2-4] are identified by double headed arrows. The chemical structure of the molecule and the signs of the couplings are also given.

376 ^{19}F and (b) 2D ^{19}F-^{1}H HOESY[5] NMR spectra of molecule **5** in $CDCl_3$

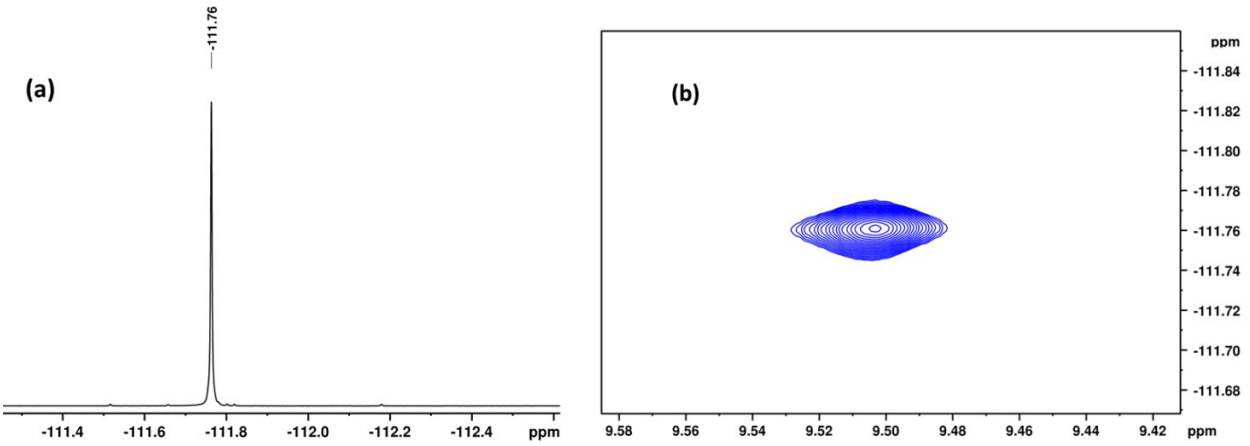


Fig.15S. (a) 376 ^{19}F and (b) 2D heteronuclear correlated ^{1}H-^{19}F HOESY[5] spectra of molecule **5** in the solvent $CDCl_3$ acquired on 400 MHz NMR spectrometer.

400 MHz (a) ^{1}H and **(b)** $^{1}H\{^{19}F\}$ spectra of molecule **6** in the solvent $CDCl_3$.

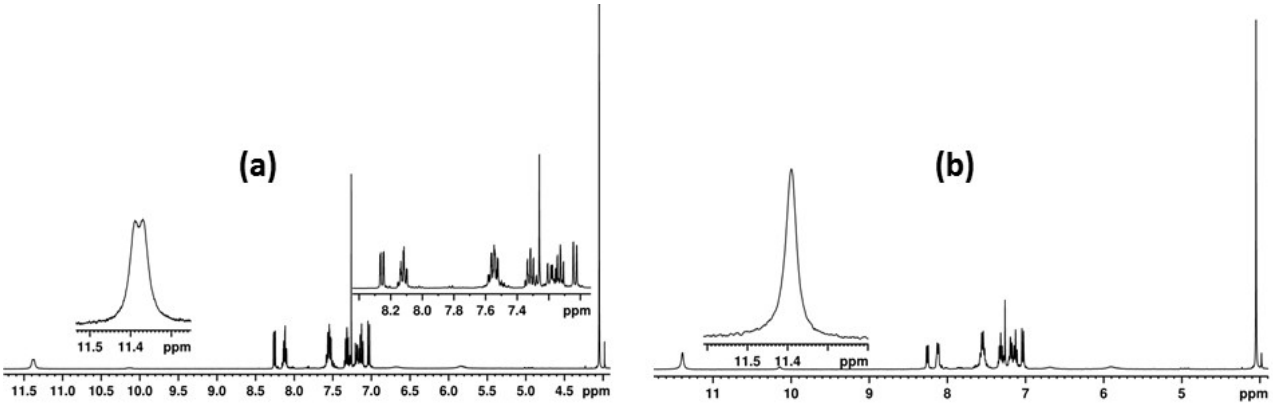


Fig.16S. 400 MHz (a) ^{1}H and **(b)** $^{1}H\{^{19}F\}$ NMR spectra of molecule **6** in the solvent $CDCl_3$.

500 MHz ^{13}C-^{1}H HSQC spectrum of the molecule **6** in $CDCl_3$

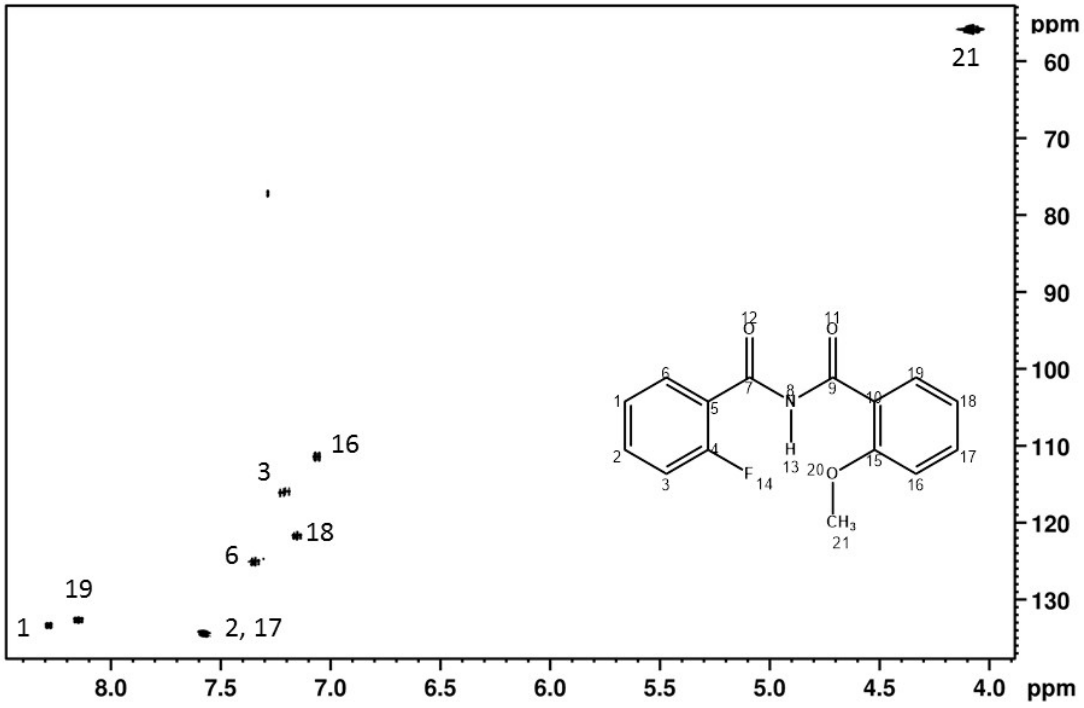


Fig.17S. 500 MHz ^{13}C-^{1}H HSQC spectrum of the molecule **6** in $CDCl_3$. The chemical structure of the molecules along with the numbering of the atoms is given as an inset. The peak assignments are also given.

800 MHz ^{15}N-^{1}H HSQC spectrum of the molecule **6** in DMSO-d_6

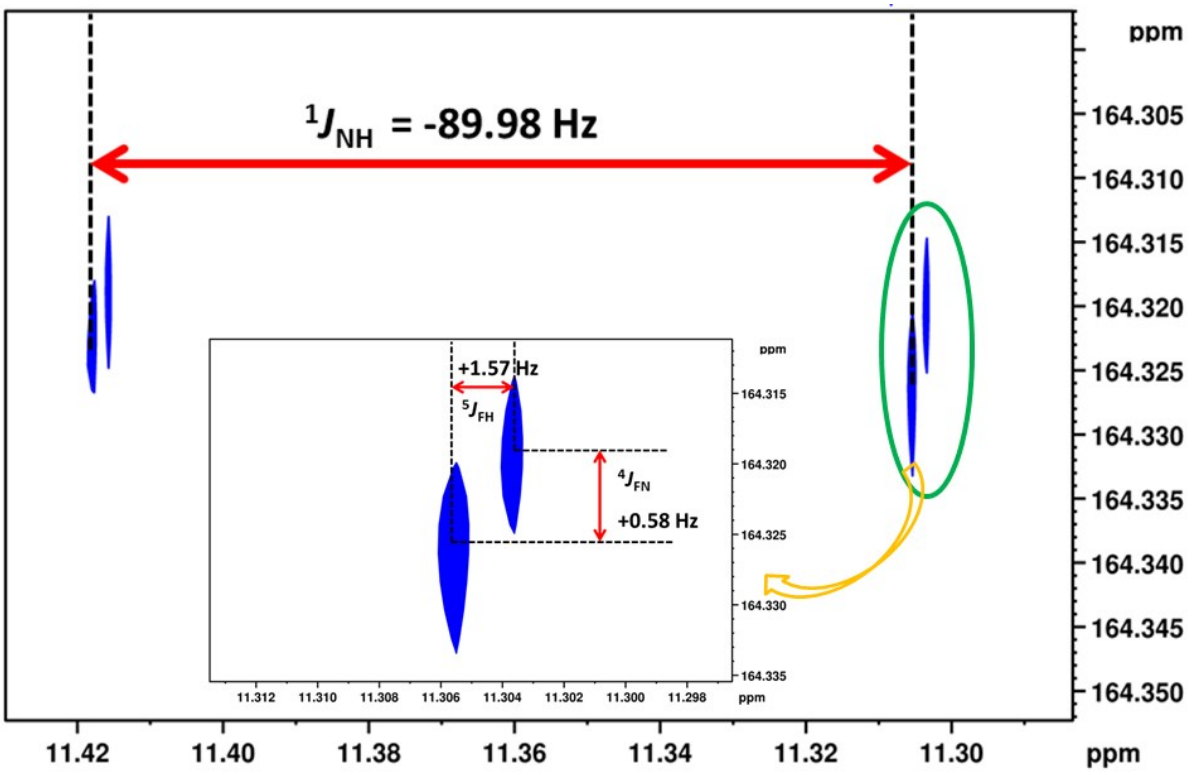


Fig.18Sa. 800 MHz ^{15}N-^{1}H HSQC spectrum of the molecule **6** in DMSO-d_6. The separation providing the magnitudes of the couplings [2-4] are identified by double headed arrows.

The molecule **6** containing methoxy group at the ortho position of one phenyl ring is forming strong HB and is not getting ruptured by the solvent DMSO. This has been already confirmed by titration study with the DMSO. When the ^{15}N-^{1}H HSQC spectrum of molecule **6** is acquired in the solvent DMSO-d_6, the couplings involving F atom are not detected as the multiplicity pattern disappears. The breaking of the fluorine involved HB yields a possibility of ring flip, resulting in the conformation where the F atom is trans to the imide proton and cis to the nitrogen atom. The proposed possible conformer structure is given in the Figure 18Sb.

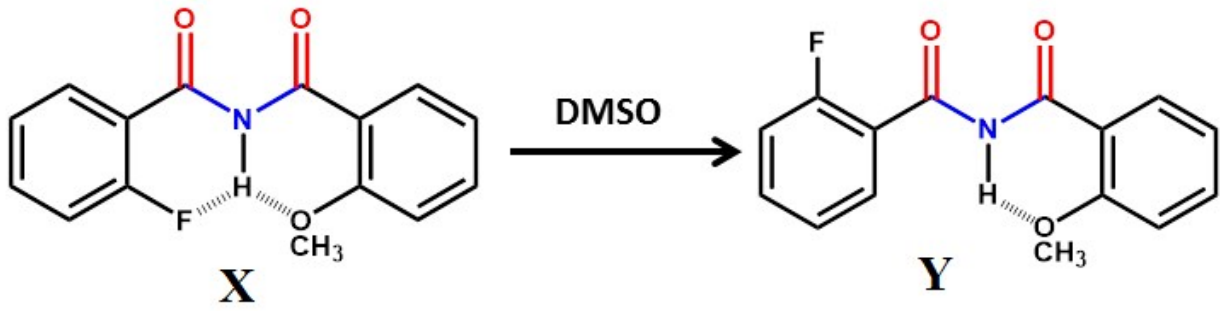


Fig.18Sb. The possible conformer of molecule **6** in the solvent chloroform (X) and in the solvent dimethyl sulphoxide (Y).

The measured $^{5}J_{FH}$ coupling is 1.57 Hz and $^{4}J_{FN}$ coupling is 0.58 Hz.

400 MHz ^{15}N-^{1}H HSQC spectrum of molecule **6** in the solvent $CDCl_3$.

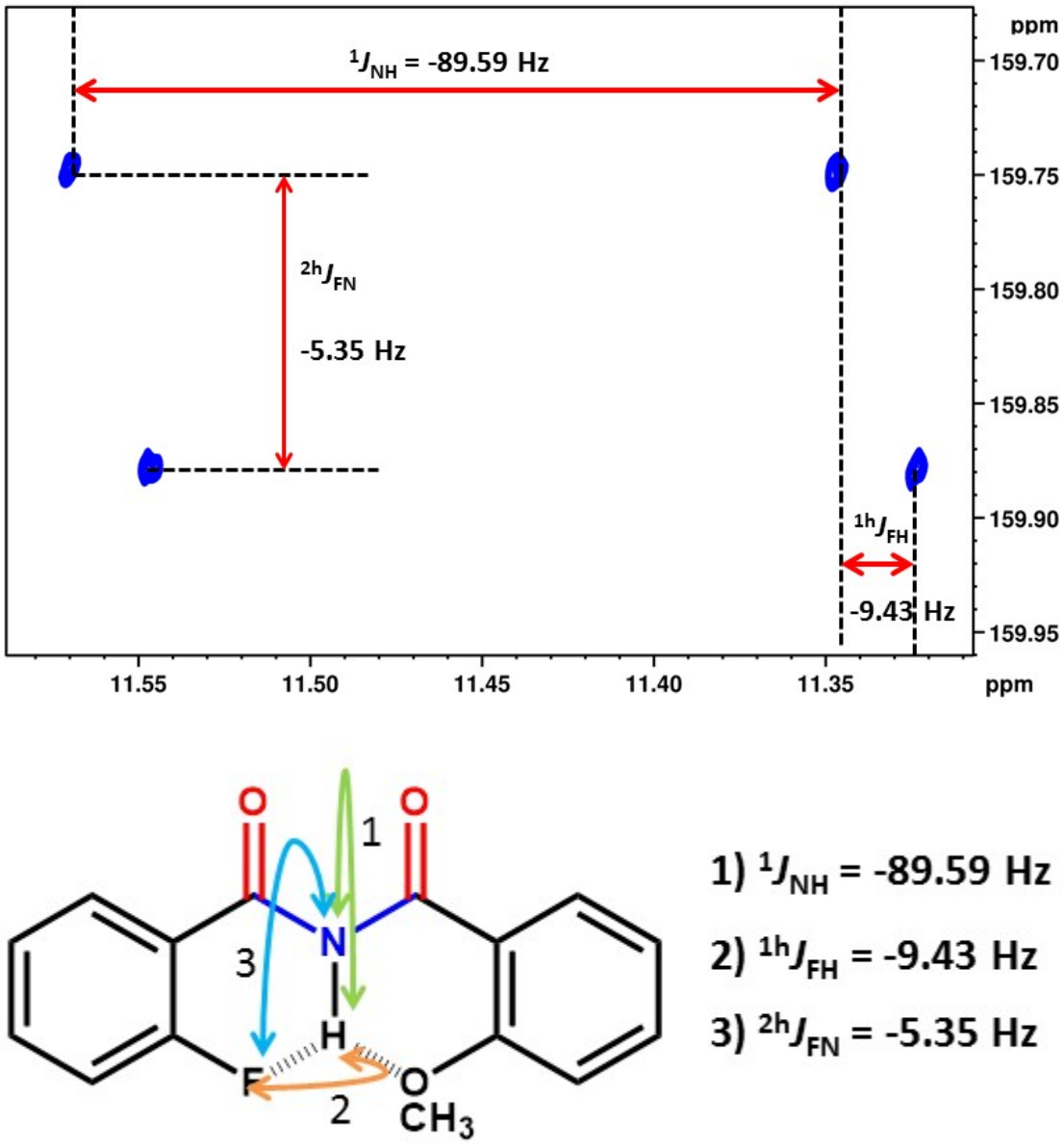


Fig.19S. 400 MHz ^{15}N-^{1}H HSQC spectrum of molecule **6** in the solvent $CDCl_3$. The separation providing the magnitudes[2-4] of the couplings are identified by double headed arrows. The chemical structure of the molecule, the measured magnitudes of the couplings and their signs are also given.

376 MHz ^{19}F and **and** 2D ^{19}F-^{1}H HOESY spectra of the molecule **6** in $CDCl_3$.

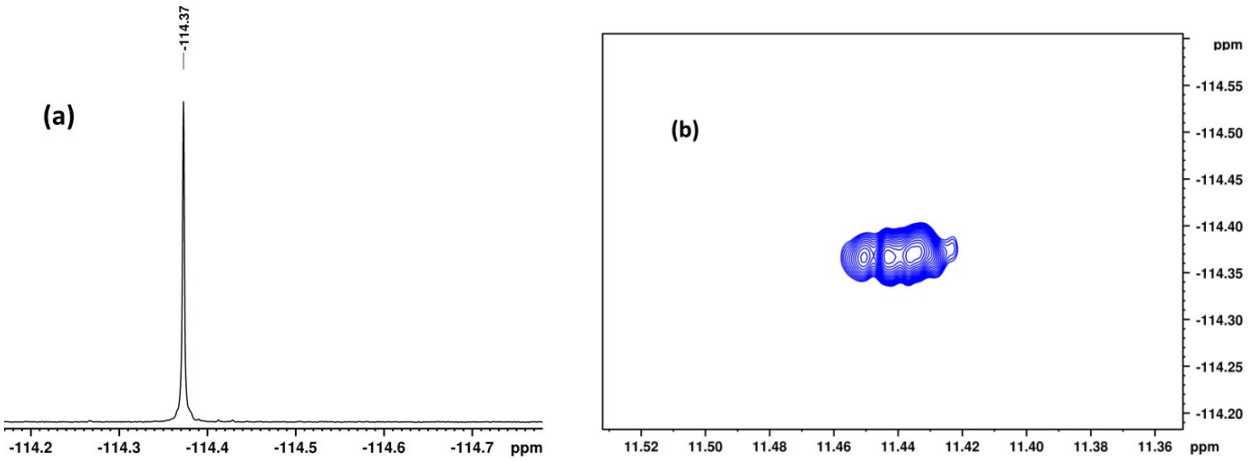


Fig.20S. (a) 1D ^{19}F and **(b)** 2D heteronuclear correlated ^{19}F-^{1}H HOESY spectra of molecule **6** in the solvent $CDCl_3$ acquired on a 400 MHz NMR spectrometer.

400 MHz ^{1}H and $^{1}H\{^{19}F\}$ spectra of molecule **7** in the solvent $CDCl_3$.

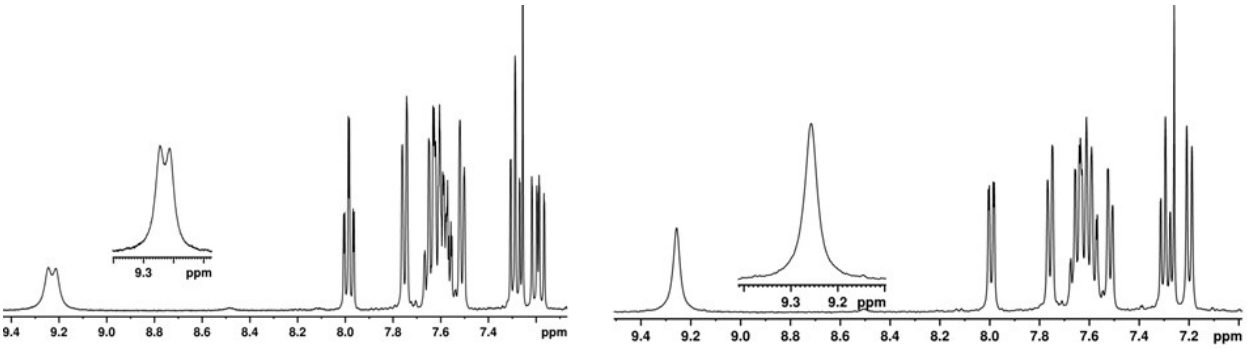


Fig.21S. 400 MHz (a) ^{1}H and **(b)** $^{1}H\{^{19}F\}$ NMR spectra of molecule **7** in the solvent $CDCl_3$.

500 MHz ^{13}C-^{1}H HSQC spectrum of molecule **7** in $CDCl_3$

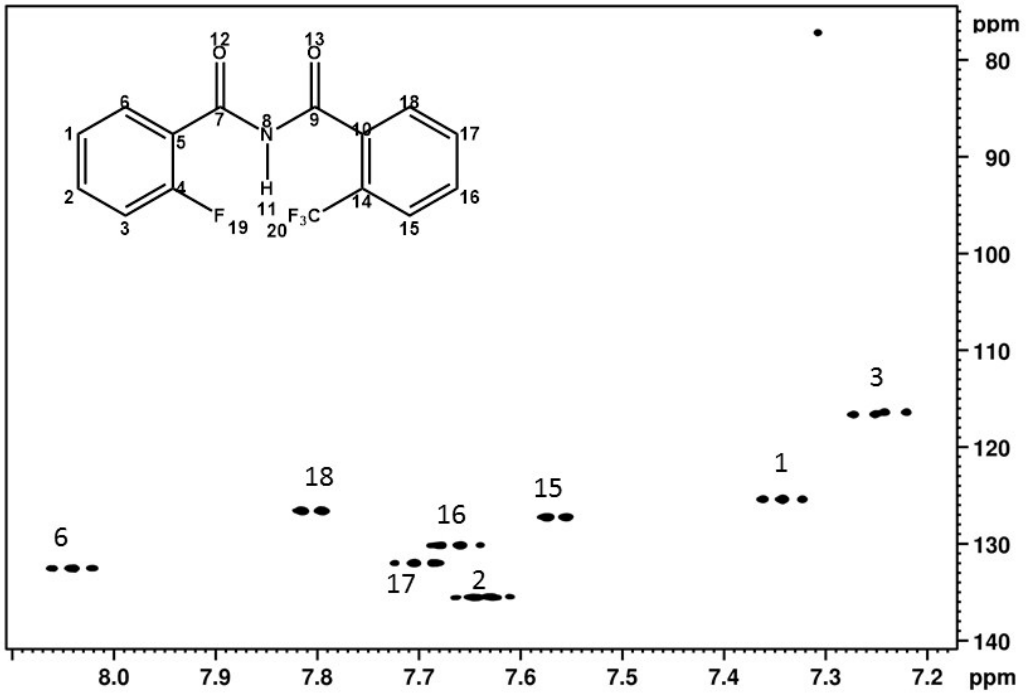
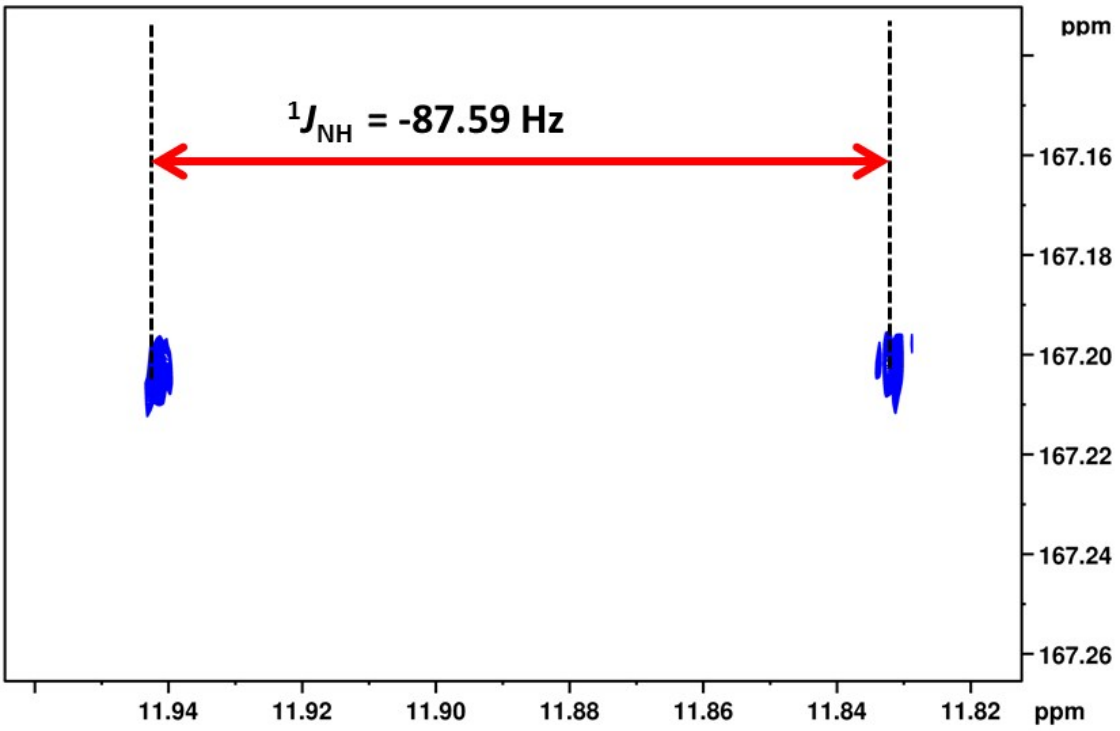


Fig.22S. 400 MHz ^{13}C-^{1}H HSQC spectrum of molecule **7** in the solvent $CDCl_3$. The chemical structure of the molecule is given as an inset. The atoms are numbered and the corresponding peak assignments are given.

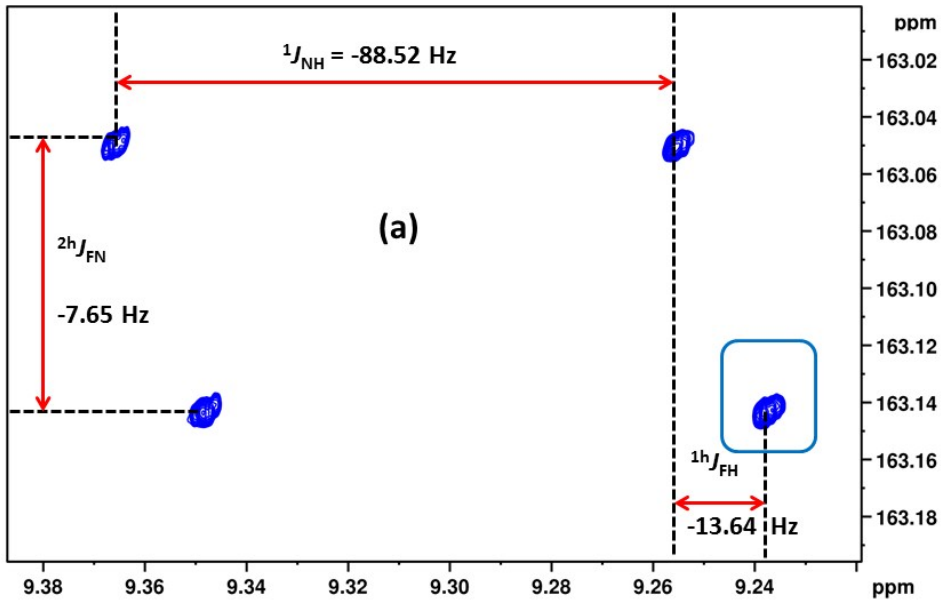
800 MHz ^{15}N-^{1}H HSQC spectrum of molecule **7** in the solvent DMSO-d_6

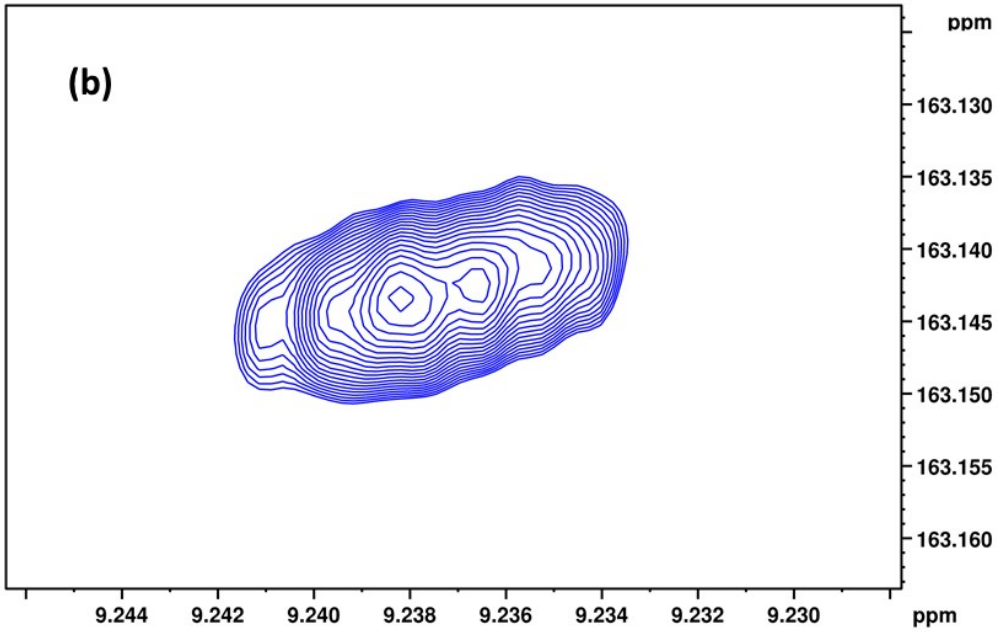


800 MHz ^{15}N-^{1}H HSQC spectrum of molecule **7** in the solvent DMSO-d_6. The separation providing the magnitude of the coupling[2-4] is identified by a double headed arrow.

The contours in the 2D ^{15}N-^{1}H HSQC spectrum of molecule showing multiple peaks are due to the through bond couplings with the single fluorine and also three fluorine atoms of the CF_3 group.

800 MHz ^{15}N-^{1}H HSQC spectrum of molecule **7** in the solvent $CDCl_3$





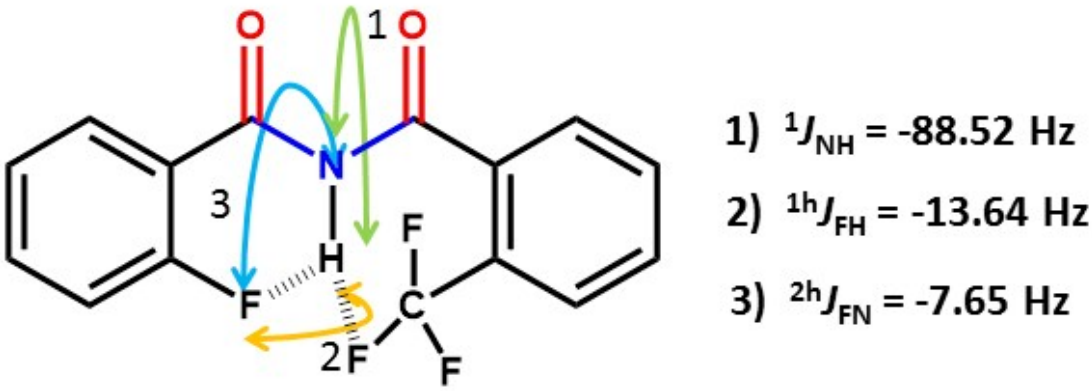


Fig.24S. (a) 800 MHz ^{15}N-^{1}H HSQC NMR spectrum of the molecule **7** in the solvent $CDCl_3$; (b) The zoomed region of the peak marked with a rectangle in Fig.7a. The separations providing the magnitudes[2-4] of the couplings are identified by double headed arrows. The chemical structure of the molecule and the signs of the couplings are also given.

376 MHz ^{19}F and 2D heteronuclear correlated ^{19}F-^{1}H HOESY[5] spectra of the molecule **7** in the solvent $CDCl_3$

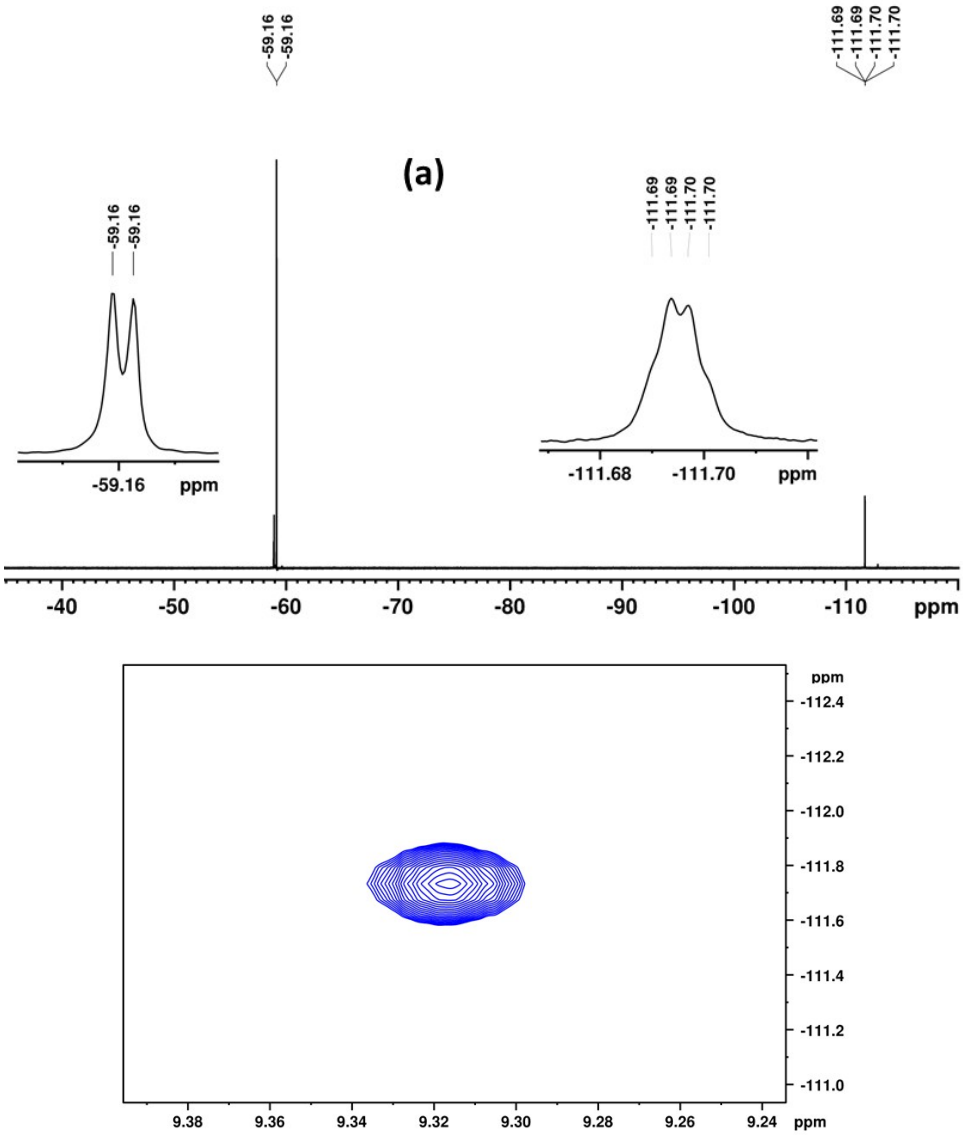


Fig.25S. (a) 376 MHz ^{19}F and (b) 2D heteronuclear correlated ^{19}F-^{1}H HOESY[5] spectra of the molecule **7** in the solvent $CDCl_3$ acquired on 400 MHz NMR spectrometer.

The ^{19}F spectrum of the molecule **7** is showinga doublet and a quartet, due to the F-F through space coupling, and is represented as F•••H•••F(CF_3). In the 2D ^{19}F-^{1}H HOESY spectrum of this molecule a strong correlation with the ortho substituted F atom is seen. On the other hand the correlation of proton with CF_3 group was hidden within the noise. This is may be due to the fast rotation of CF_3 group.

The plot of sign(λ_2(r))*ρ(r) as function 1 V/s **t**he reduced density gradient (RDG) as function 2 of molecules **2-7**.

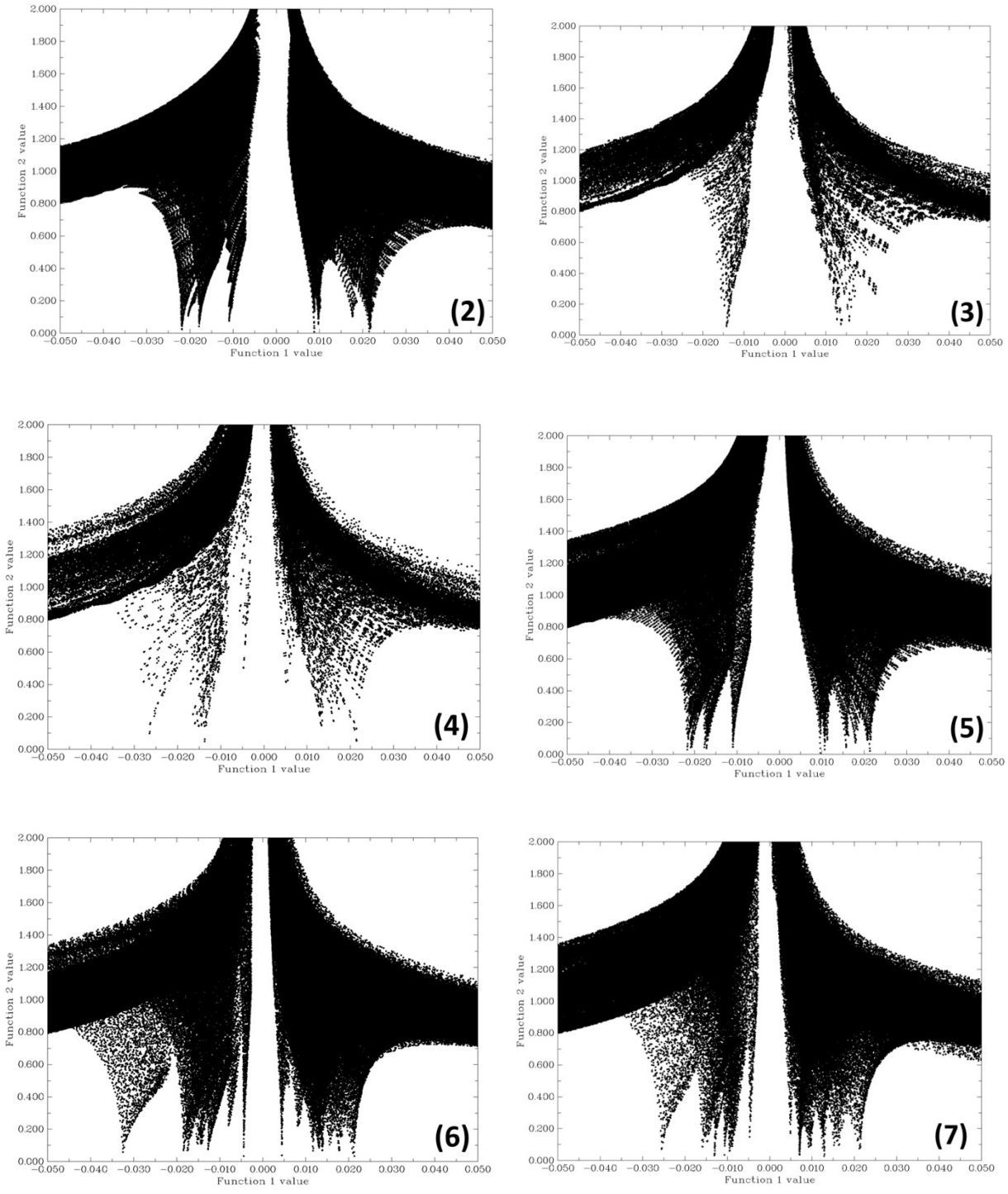


Fig.26S. The plot of sign(λ_2(r))*ρ(r) as function 1 V/s the reduced density gradient (RDG) as function 2 of molecules **2-7,** plotted using multiwfn[6] programme by utilizing wavefunction

(.wfn) files. The Wavefunction files were generated by Gaussian09[7] programme during DFT[8] structure optimization.

Coloured Isosurface plot of molecules **2-7**

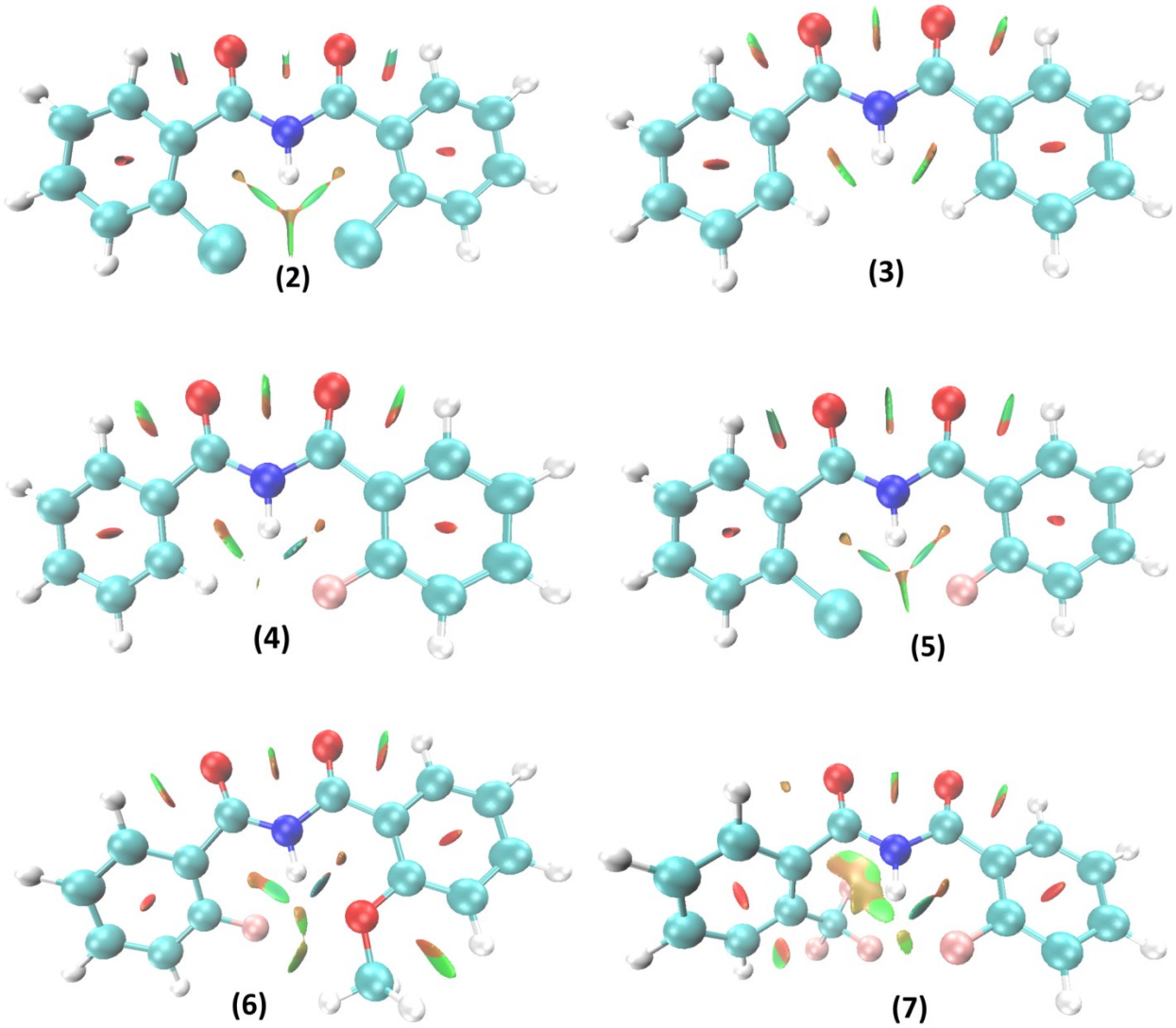


Fig.27S. Coloured Isosurface plot (green colour denotes weak H-bond and red colour stands for steric effect) of molecules **2-7**, ploted using VMD[9] programe.

There are four spikes on the left hand side (i.e. sign(λ_2(r))*ρ(r) is negative) in the Fig.29S(2) which denote four different weak interactions namely N-H---Cl, C-H---O HB, Cl---Cl and O---O interaction. These four non-covalent interactions can be seen in the Fig. 30S(2) as green coloured isosurface. The steric hindrance arising from the phenyl ring and other rings formed by four non-covalent interactions can be seen as the four type of spikes on right hand side (i.e. sign(λ_2(r))*ρ(r) is positive) in Fig.29S(2) and red isosurface in Fig. 30S(2). Similarly for all other molecules the H-bonds as spikes on left hand side and steric hindrance as spikes on right hand side in fig. 29S(3-7) can be seen. In the coloured isosurface plots Fig. 30S(3-7) the H-bonds as green isosurface and steric hindrance as red isosurface are visible.

The optimized structures with (3, -1) bond critical points (BCP) for the molecules **2-7**

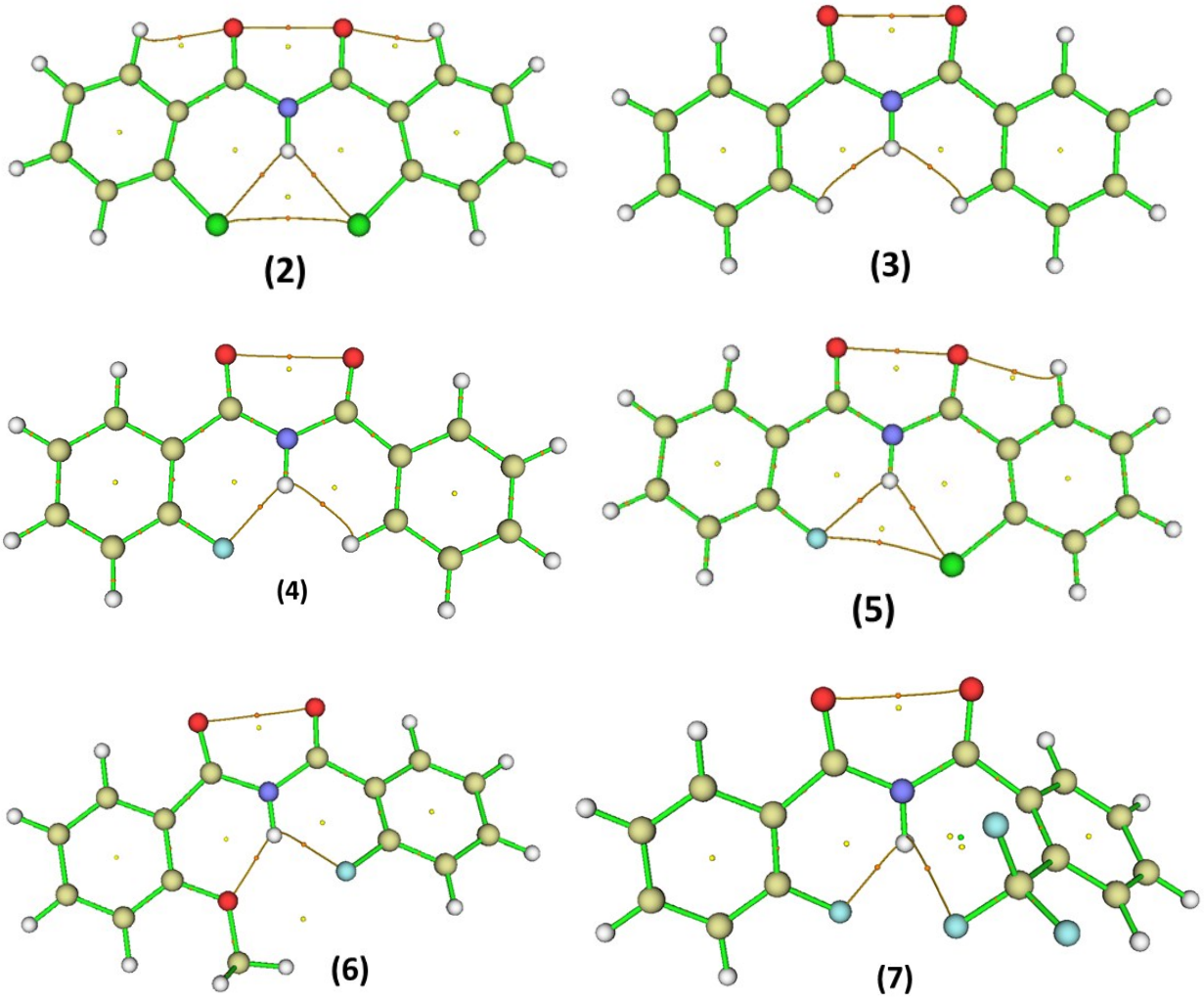


Fig.28S. The optimized structures with (3, -1) bond critical points (BCP) for the molecules **2-7**.

scan.gif

Fig.29S: The 3D optimized image and the animation file (.gif) of relaxed potential energy scan for the internal rotation of the phenyl ring through single bond of the molecule 1.

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