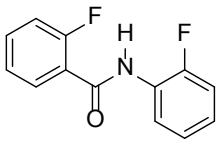
Application of ^{14}N decoupled HETCOR for ^{19}F-mediated amide hydrogen bonds with ROYALPROBE™ HFX

Product used：Nuclear Magnetic Resonance (NMR)

Fluorine and nitrogen containing organic compounds are often found in a variety of fields such as pharmaceutical and material sciences. Such compounds show unique properties based on their conformations and orientations, which are often induced by hydrogen bonds between N-H and F atoms. Therefore, analysis of molecular conformations and inter-molecular interactions are important. Here, we report ^{14}N decoupled ^{1}H–^{19}F HETCOR as an example of hydrogen bonds analysis between N-H and F for fluorinated benzanilide (**1**) as a demonstration.



fluorinated benzanilide (**1**)

Measurements of ^{1}H NMR with ^{14}N decoupling

NMR spectroscopy is a powerful tool for analysis of hydrogen bonds, and its *J* coupling value provides the information of hydrogen bond. Fig.1(A) shows ^{1}H NMR spectrum of **1**. Amide ^{1}H signal is observed in the lowest magnetic field region, ca 8.77 ppm. In this case, severe line broadening is arising from quadrupolar ^{14}N. In contrast, measurement of ^{1}H NMR under the ^{14}N decoupling condition, resulted in the sharp amide ^{1}H signal observation as double of a doublet (Fig.1(B)). This splitting signal is derived from bifurcated hydrogen bond bridges between N-H (11) and two F (F5, F6) atoms.

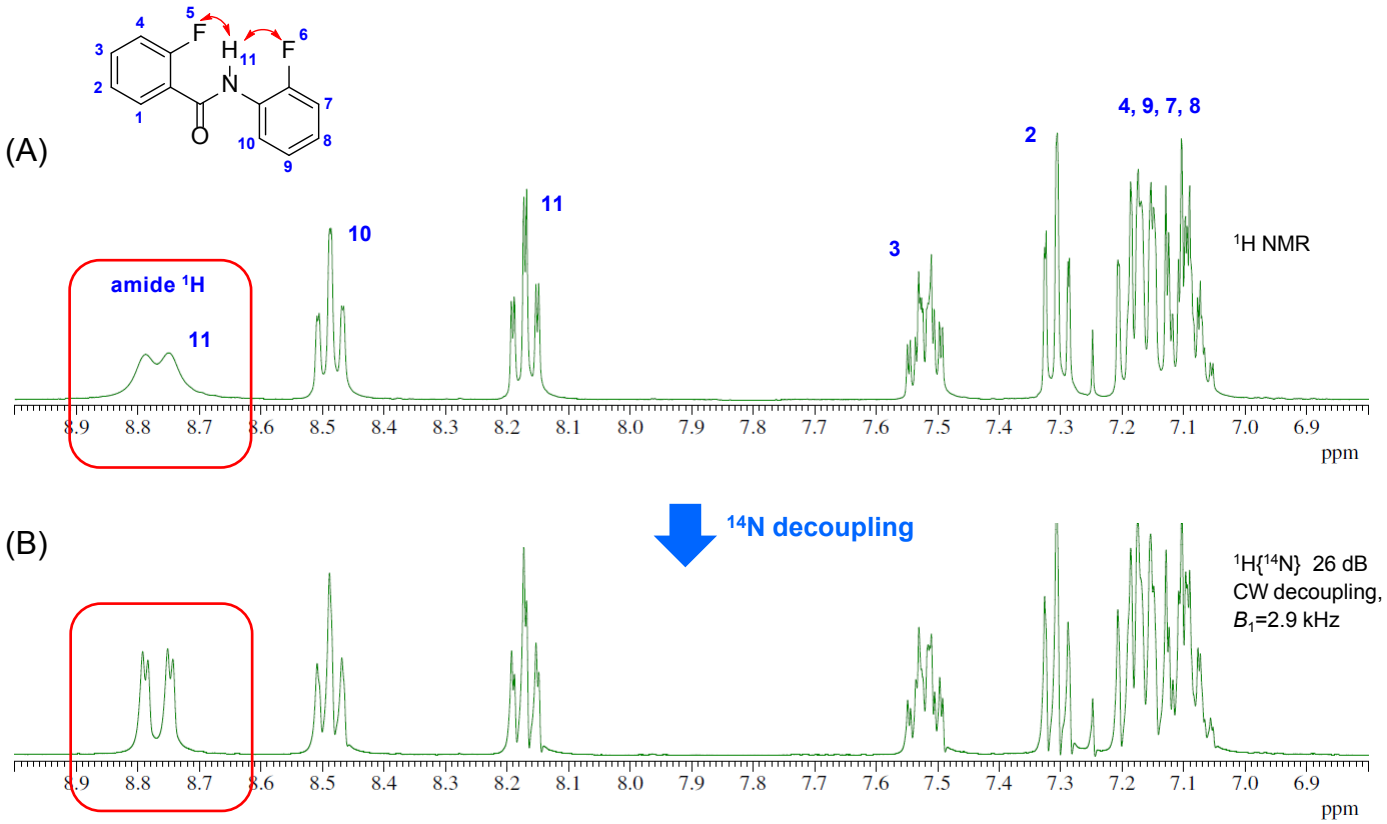


Fig.1 (A) ^{1}H NMR spectrum of **1** (B) ^{1}H{^{14}N} NMR spectrum of **1**

Sample: 36 mg fluorinated benzanilide in chloroform-*d*

Equipment: JNM-ECZ400S with ROYALPROBE™ HFX※

※Special modification for ^{14}N nuclei required.

Measurements of ^{1}H–^{19}F HETCOR with ^{14}N decoupling

In order to confirm two hydrogen bonds between the amide ^{1}H and ^{19}F atoms, we collected ^{1}H–^{19}F HETCOR under the ^{14}N decoupling condition. 1D-HETCOR spectra of **1** are shown in Fig.2. As expected, we could observe cross peaks to amide ^{1}H with both F atoms (F5, F6). Furthermore, by using anti phase signals in 1D-HETCOR spectra, *J* constants were clearly observed as ca. 16 Hz (amide-F5) and 3 Hz (amide-F6), respectively in the case of ^{14}N decoupling conditions. 2D-HETCOR spectrum with ^{14}N decoupling is also available, which is shown in Fig.3.

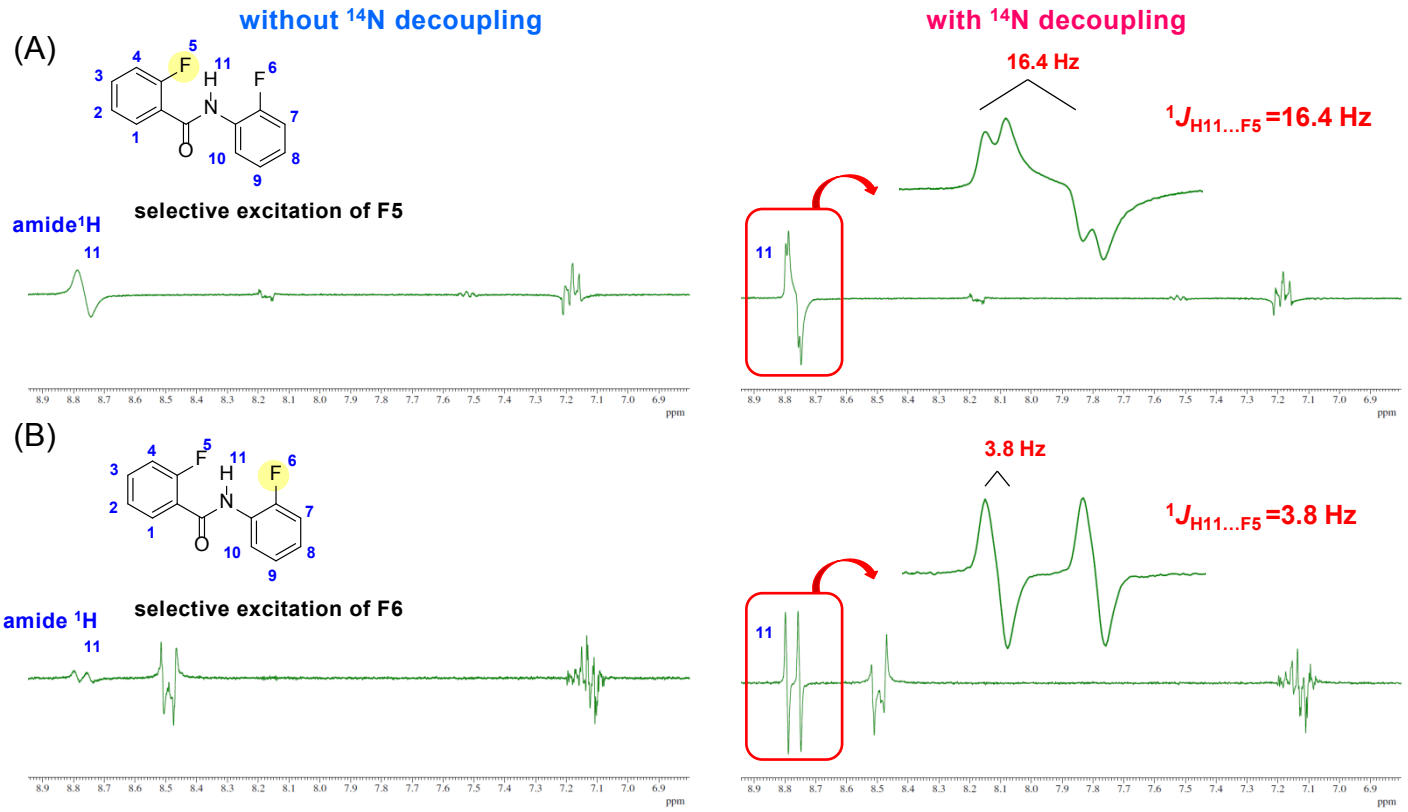
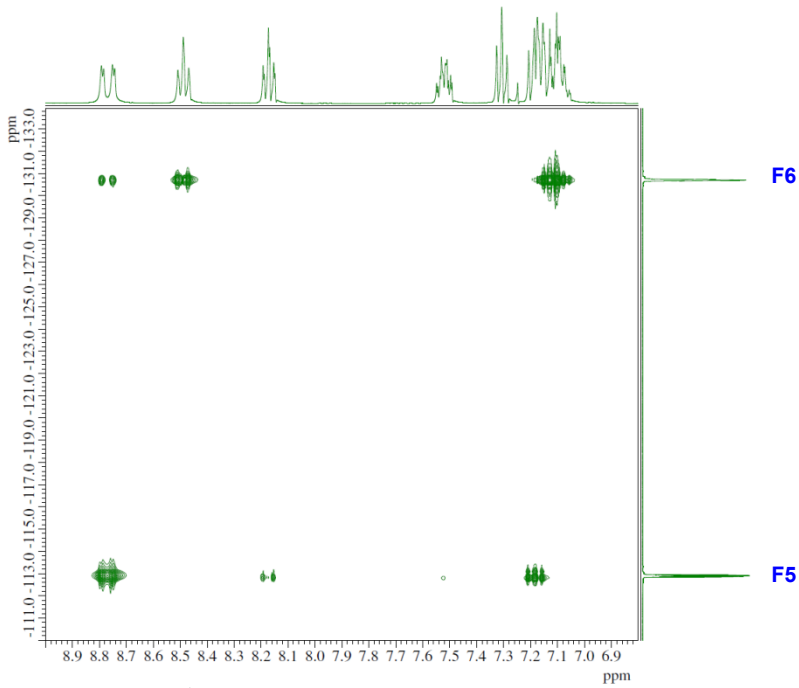


Fig.2 1D-HETCOR spectra of **1** *with* or *without* ^{14}N decoupling
(A: selective excitation at F5; B: selective excitation at F6).

Scans: 4



x points: 1024
y points: 128
Scans: 1

Fig.3 ^{14}N decoupling 2D-HETCOR spectrum of **1**

Reference

G. N. Manjunatha Reddy, M. V. Vasantha Kumar, T. N. Guru Row, N. Suryaprakash, *Phys. Chem. Chem. Phys.*, **12**, 13232–13237 (2010).

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