INADEQUATE measurement using SuperCOOL probe

Product used : Nuclear Magnetic Resonance (NMR)

It is often difficult to unambiguously determine structures of molecules, which have many non-protonated carbon atoms. Because such compounds contain quaternary carbons, lack protons and bonding to quaternary carbons each other, HMBC (Heteronuclear Multiple Bond Correlation) experiment cannot provide long-range ^{1}H-^{13}C connectivity. Therefore, INADEQUATE (Incredible Natural Abundance DoublE QUAntum Transfer Experiment), which is ^{13}C-^{13}C correlation experiment at natural ^{13}C abundance, represents a powerful tool for proton-diluted compounds. On the other hand, INADEQUATE is about 200 times less sensitive measurement compared to ordinary ^{13}C measurement in theory. For this reason, INADEQUATE experiment usually requires highly concentrated samples and long experimental times. Experimental time and/or sample amount can be greatly reduced by the use of SuperCOOL probe as shown below.

How to analyze INADEQUATE spectra

^{13}C-^{13}C correlations in INADEQUATE spectra are observed as pairs of doublets symmetrical with respect to the diagonal line of slope 2 Fig.1 shows a correlation between carbons C_B and C_E. Each signal is split into a doublet by the coupling constant $^{1}J(C_BC_E)$.

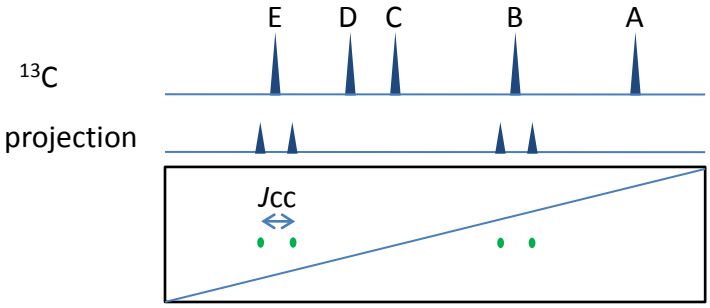


Fig. 1 : Correlation pattern typical of INADEQUATE spectra

Application of INADEQUATE

Genistein is a soy-derived isoflavone and has antioxidant activity. The structure contains eight quaternary carbons and some of these quaternary carbons are bound to others. The INADEQUATE spectrum is shown in Fig. 2. The spectrum was collected on a sample containing 16 mg of Genistein using a SuperCOOL probe at 600 MHz. All one-bond ^{13}C-^{13}C correlations were detected within 18 hours.

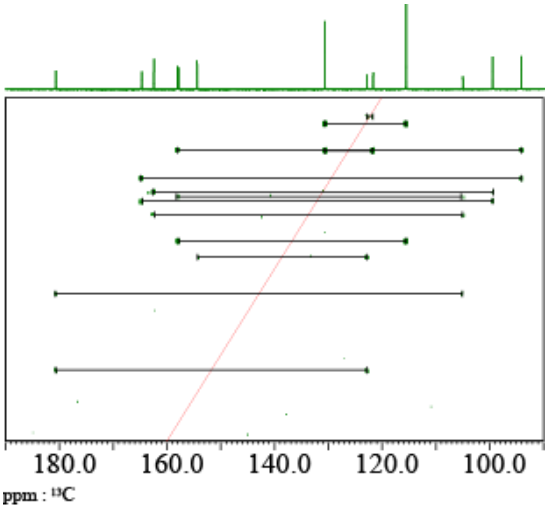
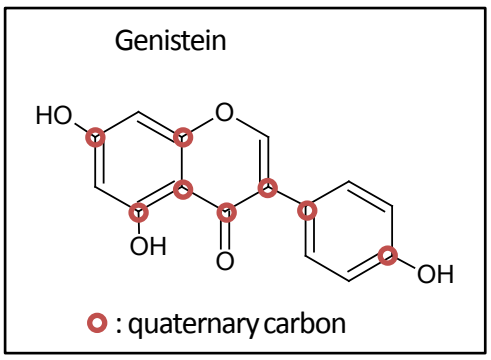


Fig.2 : INADEQUATE spectrum



console : JNM-ECZ600R, SuperCOOL probe
sample : 100mM(16mg) Genistein/DMSO-d_6
measurement time : 18h (standard tube)

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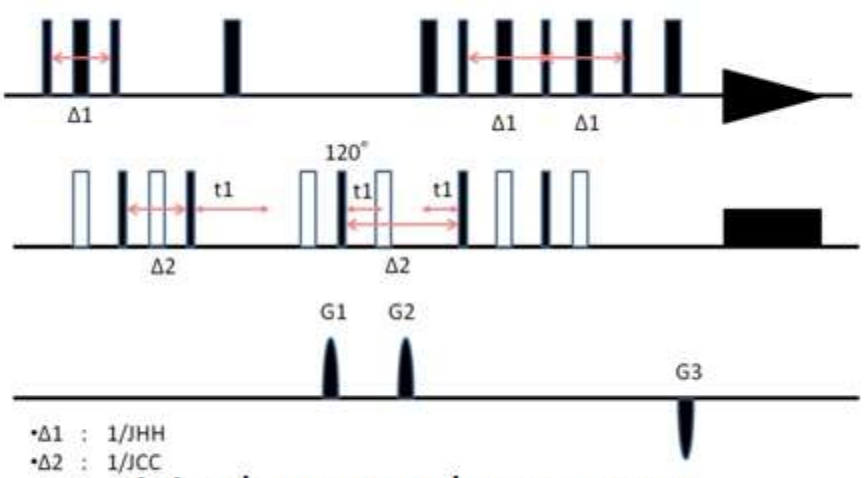
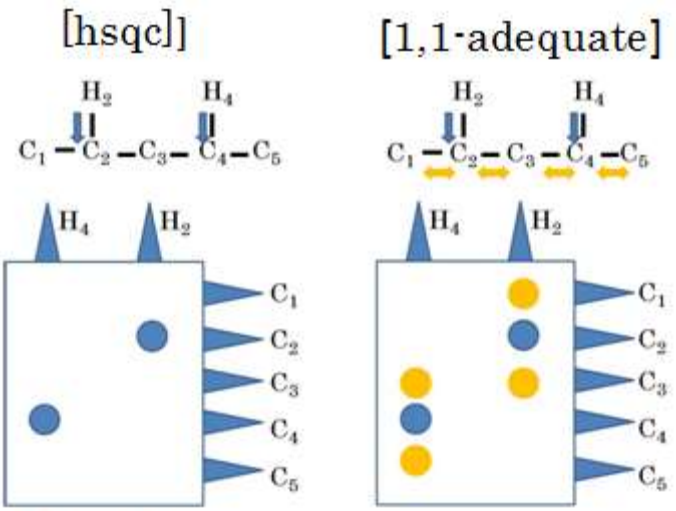
1,1-adequate is a technique to obtain heteronuclear correlation similarly to hmbc. While correlation signals from hmbc do not separate $^{2}J_{CH}$ from $^{3}J_{CH}$, 1,1-adequate, which exclusively observes $^{1}J_{CH}$ amd $^{2}J_{CH}$, can be combined with hsqc to identify $^{2}J_{CH}$. 1,1-adequate uses $^{1}J_{CH}$ and $^{1}J_{CC}$ coupling for signal observation. This technique is effective for compounds rich in quaternary carbon and for aromatic ring identification.



1,1-adequate pulse sequence



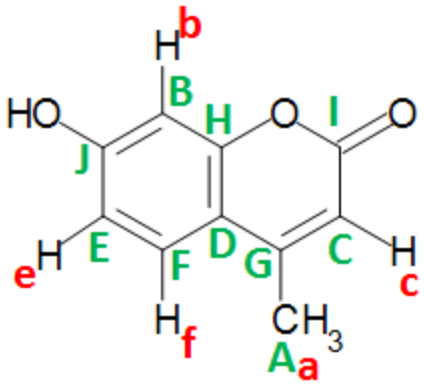
1,1-adequate signal emergence

1,1-adequate is not high in sensitivity because it uses $^{1}J_{CC}$ for signal observation. However, being an inverse analysis on the ^{1}H side, 1,1-adequate is capable of higher sensitivity analysis than inadequate.

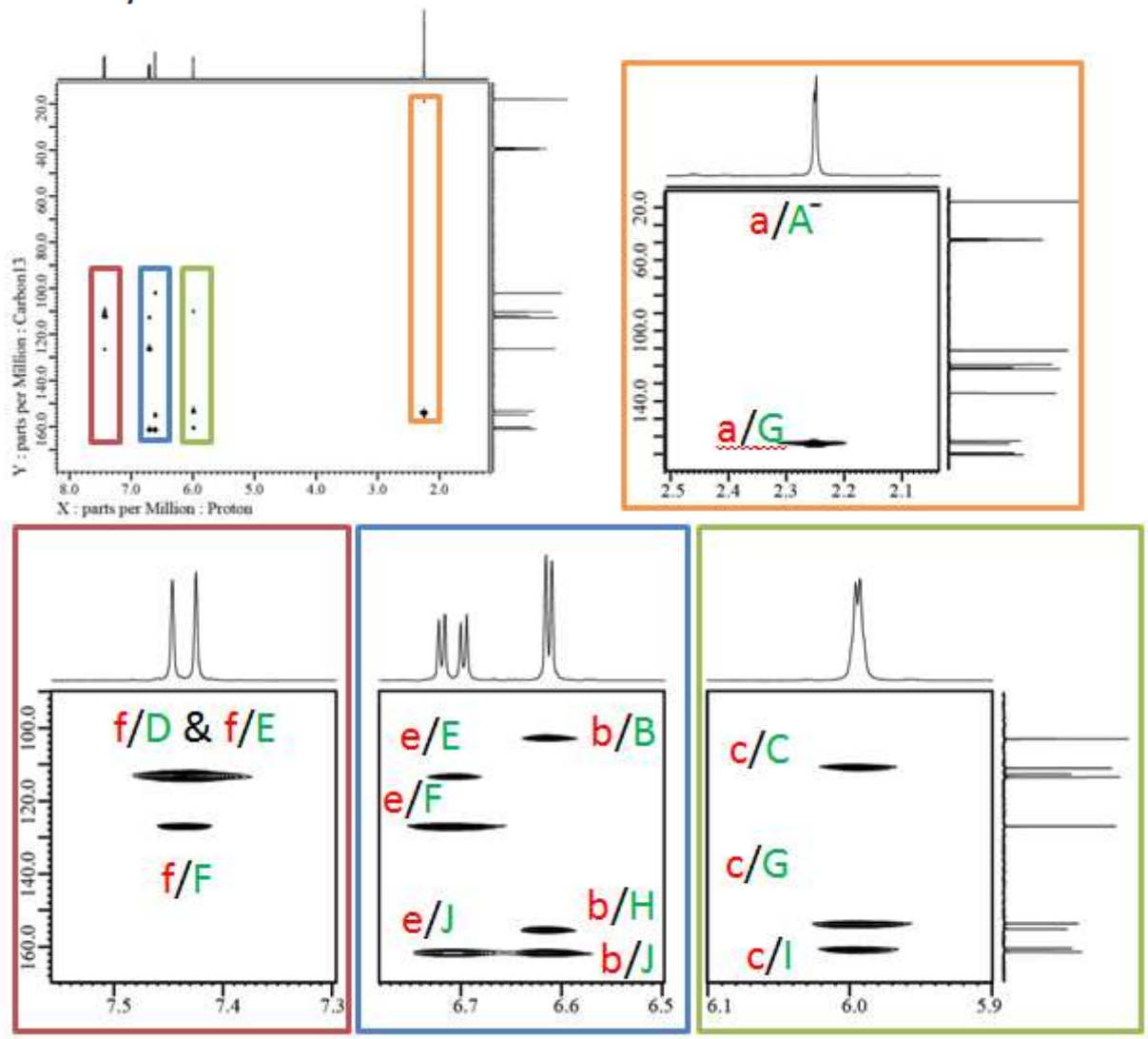
For measurement conditions, parameters for $^{1}J_{CH}$ and $^{1}J_{CC}$ are defined.

100 mg 4-methylumbelliferone/DMSO-d_6

Shown below are total and magnified views of 1,1-adequate.



4-methylumbelliferone



Instruments used: JNM-ECZ400S+ROYAL probe
Measuring conditions: 48 scans (7h), J_constant=140 Hz, JCC=60 Hz

Reference

B. Reif, M. Kock, R. Kerssebaum, H. Kang, W. Fenical, C. Griesinger, JMR ser-A 1996, 118, 282-285 M. Kock, R. Kerssebaum, W. Bermel, MRC 2003, 41, p65-69