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Note

Determination of substituent distribution in cellulose acetate by means of a ^{13}C NMR study on its propanoated derivative ☆

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Cellulose acetate (**1**) is commercially important, and is produced with various degrees of substitution (DS) suitable for such applications as fibers, plastics, films, and coatings [1]. The final properties of these products may be optimized through control of the distribution pattern of acetyl groups on the glucose residue [2–5], as well as the total DS by acetyl groups. In consequence, a convenient and reliable analytical technique is important for both the elucidation of structure-properties relationships and for quality control in the production process.

Although the total acetyl content in samples of **1** is readily determined by means of a standard titration technique [6,7], the individual DS at O-2, -3, and -6 in the glucose residue is not readily obtainable through chromatographic techniques.

A ^{1}H NMR spectroscopic technique applied with derivatized samples of **1** [4,8] involves conversion of residual hydroxyl groups into the deuterated acetyl groups through reaction with acetyl chloride-d_3. The acetyl proton signals of the resulted cellulose triacetate appear as three lines corresponding to the 2-, 3-, and 6-OAc signals in the glucose residues. Perdeuterioacetylation avoids the spectral complication observed in the acetyl-proton signals of partially substituted **1**.

☆ Part 10 of a series: ^{1}H and ^{13}C NMR Structural Study on Cellulose and Polysaccharide Derivatives with Carbonyl Groups as a Sensitive Probe. For the preceding papers, see ref. [21].

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A ^{13}C NMR technique has been also applied to elucidate the detailed structure of **1** [9–14]. Although chemical shifts of signals due to ring carbons on the glucose residue and those due to acetyl groups were found to be sensitive to their distribution pattern, the exact substituent distribution in **1** over a wide range of DS values is not readily estimated by simple comparison of the relevant peak intensities [13]. Therefore, a convenient and reliable analytical means to provide the substituent distribution in **1** would be of a significant practical importance.

We have recently proposed a new analytical technique for cellulose derivatives, in particular cellulose ethers [15–20], in which unsubstituted hydroxyl groups on the glucose residue (and those at the end of substituent groups in some cases) are peracetylated and examined by ^{13}C NMR. We have also demonstrated recently that the distribution pattern of the two ester substituents of a series of commercial cellulose acetate butanoate samples is readily determined by means of a ^{13}C NMR technique that makes use of the ester carbonyl carbon signals, showing two sets of triplets, as a remarkably sensitive NMR probe [21].

As an extension of the preceding studies, we propose herein a convenient ^{13}C NMR technique to determine the substituent distribution in **1** by using its propanoated derivatives.

Spectra in the ^{13}C NMR carbonyl region of cellulose triesters having acetyl, propanoyl, and butanoyl groups, are shown in Fig. 1. Carbonyl signals of these cellulose esters appear as clearly resolved triplets, corresponding to the substitution position (2, 3, and 6) on the glucose residue. In particular, the propanoyl carbonyl triplet is observed at a position distinctly separated from that of the acetyl carbonyl triplet. The three peaks in the acetyl carbonyl region were previously assigned, namely at the 2 (169.0 ppm), 3 (169.5 ppm), and 6 (170.0 ppm) positions on the glucose residue [7,22–25].

Direct assignment of the three peaks in the propanoyl carbonyl region was achieved in the present study by means of an INAPT technique [21,23], where the H-2 and H-3 proton signals were irradiated by a soft pulse to cause selective long-range polarization transfer to the carbonyl carbon of the propanoyl groups. As shown in Fig. 2, this allowed direct and unambiguous assignment of the three propanoyl carbonyl peaks, namely at the 2 (127.7 ppm), 3 (173.1 ppm), and 6 (173.6 ppm) positions on the glucose residue [26–28].

Complete propanoation reaction of the hydroxyl groups in **1** without the occurrence of ester exchange is a prerequisite for the ^{13}C NMR determination of the substituent distribution of **1** by use of propanoated derivatives. Such a reaction process was realized with a propanoic anhydride–pyridine-4-(dimethylamino)pyridine system for 1 h at 100°C. The complete conversion of the hydroxyl groups in **1** was confirmed through ^{1}H NMR and IR spectroscopic inspection. The possibility of ester exchange reactions was excluded through observing constant total acetyl contents during the propanoation treatment (Table 1), and from the fact that attempted propanoation of cellulose triacetate by this system failed to introduce propanoate groups.

A series of samples of **1** of different total DS values, prepared through the acid hydrolysis of cellulose triacetate, were subsequently propanoated for the ^{13}C NMR measurements. A full-range ^{13}C NMR spectrum of a propanoated derivative and of a starting sample of **1** are shown in Fig. 3. The latter, obtained in Me$_2$SO-d_6 at 100°C,

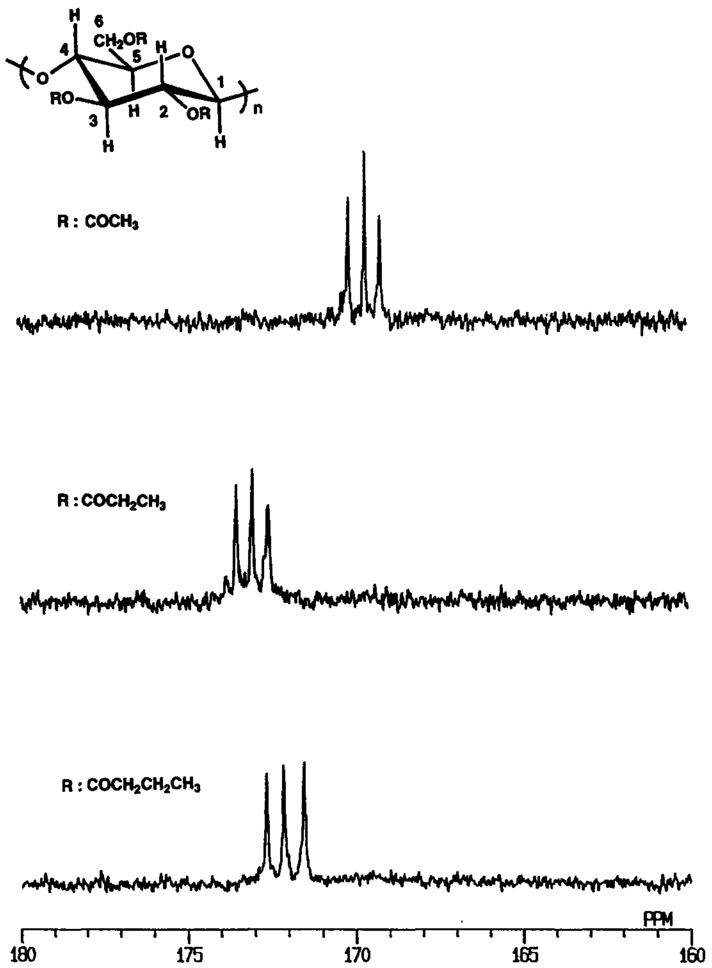

Fig. 1. ^{13}C NMR carbonyl region spectra of cellulose triacetate (top), tripropanoate (middle), and tributanoate (bottom) (100 MHz, normal-mode, $CDCl_3$, 40°C).

showed two broad peaks at the C-1 (99–102 ppm) and C-6 (62–65 ppm) signal regions. These correspond to the substitution patterns at C-2 and C-6, respectively. This permits, in principle, estimation of the individual DS at the 2 and 6 positions by a quantitative-mode ^{13}C NMR measurement. In contrast, the DS at C-3 is not directly obtainable because of the overlapping of signals around 70–80 ppm. In addition, extensive line-broadening of the signals due to ring carbons on the glucose residue is frequently observed in the quantitative-mode ^{13}C NMR measurement, where a relatively long pulse-repetition time must be applied, which in turn, causes T_2 relaxation of the relevant signals. Acetyl methyl (38–41 ppm) and carbonyl (168–170 ppm) signals, on the other hand, appeared as overlapped multiple peaks, reflecting the detailed substitution pattern of acetyl groups and the hydrogen-bond interactions between acetyl groups and hydroxyl groups [13].

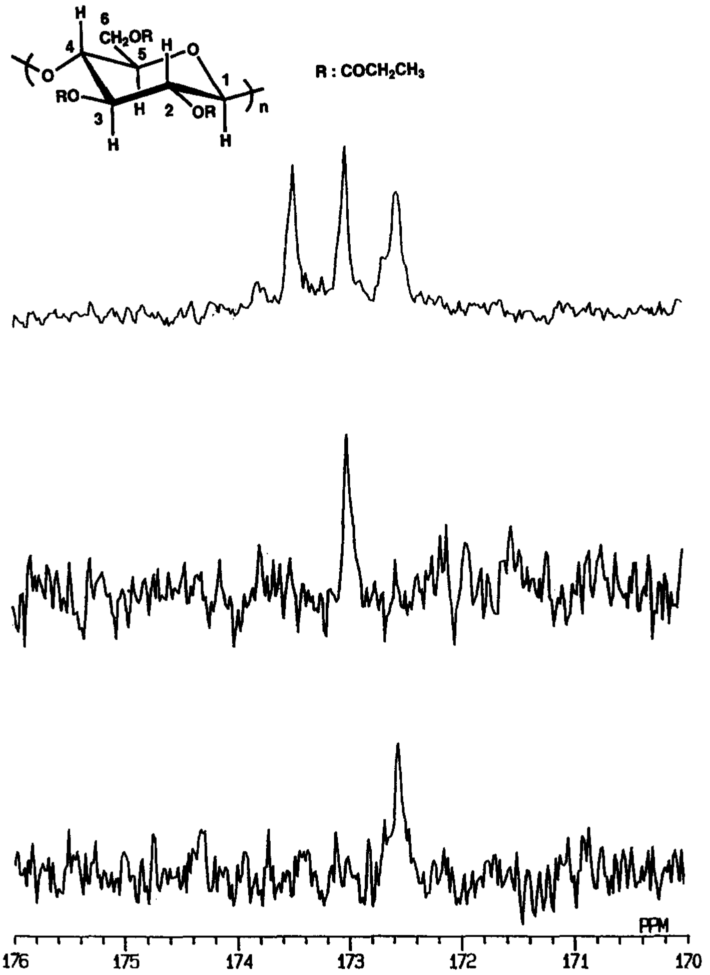

Fig. 2. A normal proton-decoupled ^{13}C NMR carbonyl region spectrum of cellulose tripropanoate (top) and the INAPT spectra with the irradiation of H-3 (middle) and of H-2 (bottom) (100 MHz, CDCl$_3$, 40°C).

Table 1
Distribution of acetyl groups in cellulose acetate samples

Sample	Total DS					Individual position		
	Cellulose acetate		Propanoated derivative			2	3	6
	^{1}H NMR	Titration	^{1}H NMR	^{13}C NMR				
				(CH$_3$)	(C=O)			
1	0.83	1.00	0.98	0.98	1.00	0.25	0.14	0.61
2	1.50	1.07	1.43	1.43	1.42	0.42	0.34	0.64
3	1.98	1.87	1.90	1.90	1.93	0.60	0.64	0.69
4	2.66	2.25	2.42	2.42	2.41	0.84	0.81	0.76

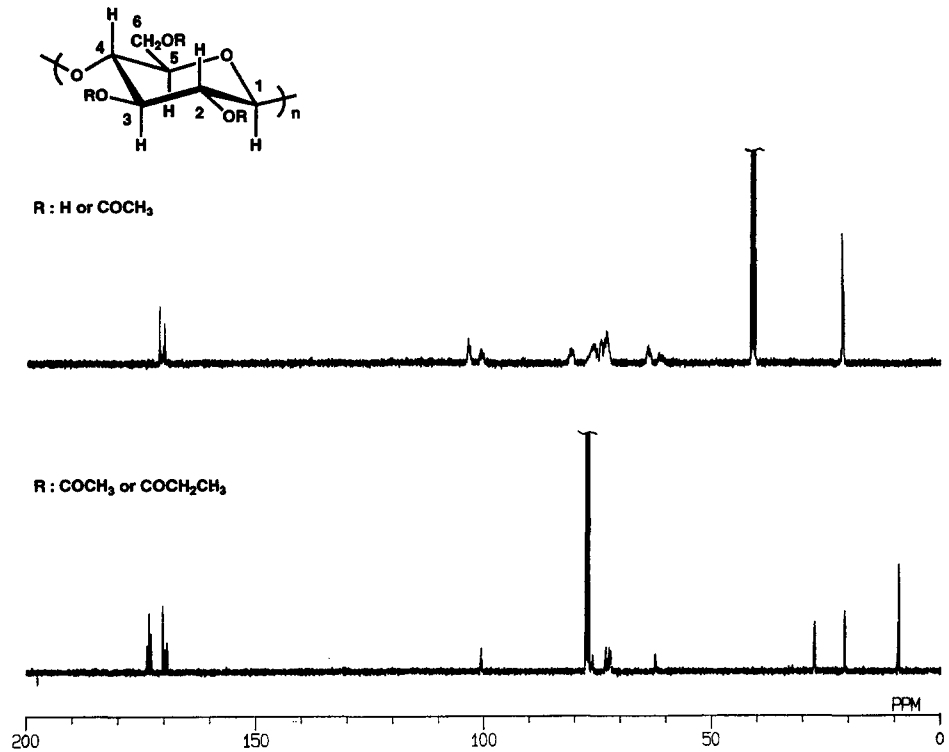

Fig. 3. ^{13}C NMR full-range spectra of cellulose acetate in Me_2SO-d_6 at 100°C (top) and of its propanoated derivative in $CDCl_3$ at 40°C (bottom) (sample 2 in Table 1, 100 MHz, normal-mode).

In contrast, the former spectrum obtained in $CDCl_3$ at 40°C showed, besides the signals for C-1–C-6 in the glucose residue, signals for the acetyl methyl (doublet at 20.5 and 20.7 ppm) and the propanoyl methyl (doublet at 8.9 and 9.1 ppm) and methylene (doublet at 27.3 and 27.4 ppm) signals. The relative contents of the two ester groups, and subsequently the total acetyl contents in the starting **1**, were determined by quantitative ^{13}C NMR. The values obtained agree with those obtained from the carbonyl-region analysis (Table 1). The complete propanoation of the hydroxyl groups in **1** was confirmed by comparison of the peak area of the C-1 signal with that of the sum of the relevant acetyl and propanoyl signals. In the quantitative-mode ^{13}C NMR operation, a long instrumental time (up to 24 h) was required to obtain a spectrum with a high enough S/N ratio for rigorous peak analysis. On the other hand, a routine ^{13}C NMR measurement with a shorter pulse-repetition time of up to 3 s, and with an instrumental time of up to ~ 1 h, also gave a good quality spectrum. Since quantitative calibration factors of the relative peak intensities in the latter spectrum can be obtained by making reference to those of the former spectrum, such an indirect, but convenient analytical procedure should be of use for the quality control of **1** during production process.

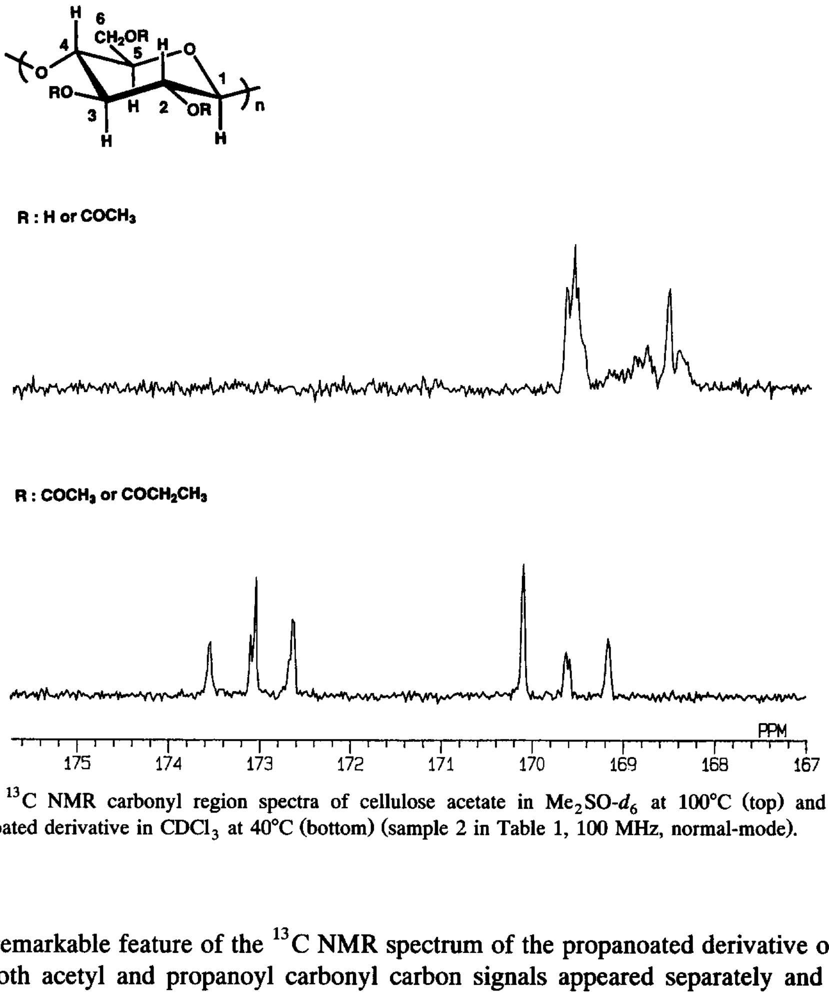

Fig. 4. ^{13}C NMR carbonyl region spectra of cellulose acetate in Me_2SO-d_6 at 100°C (top) and of its propanoated derivative in $CDCl_3$ at 40°C (bottom) (sample 2 in Table 1, 100 MHz, normal-mode).

A remarkable feature of the ^{13}C NMR spectrum of the propanoated derivative of **1** is that both acetyl and propanoyl carbonyl carbon signals appeared separately and were resolved into two sets of three peaks corresponding to their substitution positions on the glucose residue. The expanded carbonyl-region spectrum of a propanoated derivative of **1** is shown in Fig. 4, together with that of the starting **1**, where the carbonyl-carbon signal appears as overlapped multiple peaks, which reflect the detailed substitution pattern of acetyl groups and the hydrogen-bond interaction between acetyl groups and hydroxyl groups.

A series of samples of **1** having different acetyl contents were subjected to the quantitative-mode ^{13}C NMR measurement after the specific propanoation treatment already described. The expanded carbonyl-region spectra of a series of propanoated derivatives of **1** are listed in Fig. 5. The two sets of triplets observed for each propanoated derivative of **1** permitted estimation of the distribution of acetyl groups in the starting **1**. It must be stressed also that it provides the additional information on the distribution of propanoyl groups, which is considered to be complementary to that of acetyl groups. This information can facilitate the calculation of the individual DS of **1**

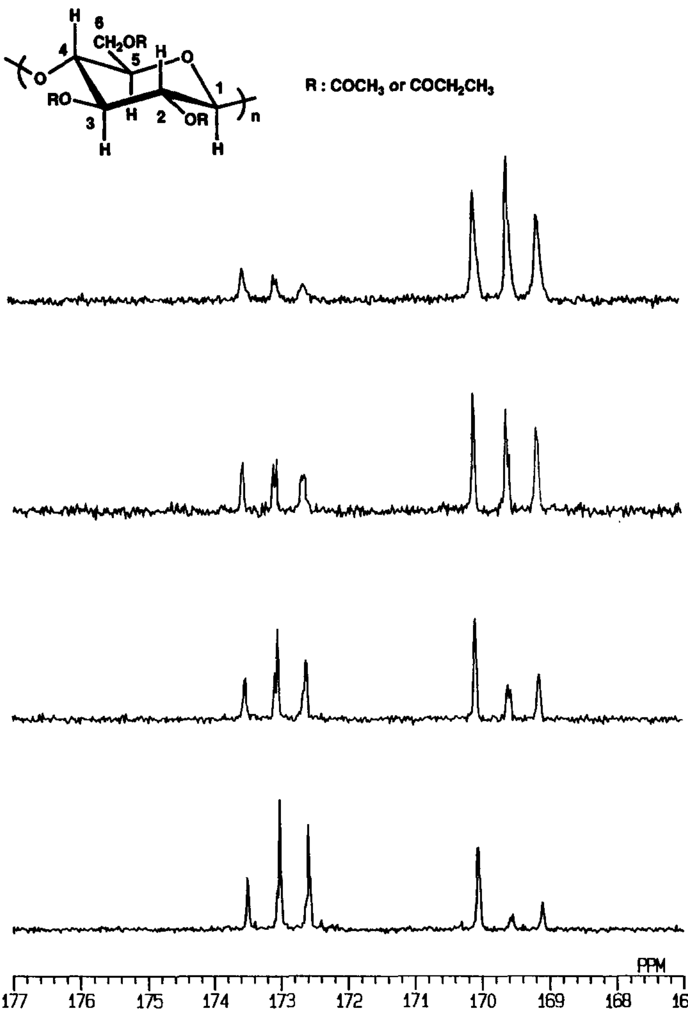

Fig. 5. ^{13}C NMR carbonyl region spectra of propanoated cellulose acetate samples having different acetyl contents (samples 1–4 in Table 1, from the bottom to the top, 100 MHz, quantitative-mode, $CDCl_3$, 40°C).

having low acetyl contents, in comparison with the previous ^1H NMR technique [8] by use of the perdeuterioacetylated derivative of **1**, where the decrease in the acetyl contents of samples of **1** inherently causes a decrease of the absolute signal intensities.

The results obtained for a series of samples of **1** are collected in Table 1. The total DS values of the starting **1** estimated either by the ^1H NMR or the titration techniques before the propanoation treatment agree in most cases with those obtained by the ^1H and ^{13}C NMR analysis of propanoated derivatives of **1**. It may be noted that the deacetylation of cellulose triacetate took place indiscriminately at the 2, 3, and 6 positions in the initial stage, but proceeded predominantly at the 2 and 3 positions in the later stage under the hydrolytic conditions used.

In conclusion, the distribution pattern of acetyl groups in **1** having a wide range of DS is readily determined by means of a ^{13}C NMR technique by the use of their propanoated derivatives. This novel technique may offer a significantly improved analytical means to provide the detailed structural parameters in **1** of commercial importance.

1. Experimental

Samples.—A series of cellulose acetate samples (**1**) having different DS values were prepared by acid hydrolysis of cellulose triacetate [13]. Thus in a 300-mL round-botton flask, 7 g of cellulose triacetate (Aldrich) was suspended in 140 mL of AcOH (Nacalai Tesque) with stirring overnight at ambient temperature, and then the mixture was heated at 80°C after adding H_2SO_4 (0.168 g of concd H_2SO_4 acid was diluted with 21 mL of distilled water). Hydrolysis was performed for the prescribed reaction times, namely 10, 20, 54, and 83 h, and the products were isolated by pouring the mixture into either water, MeOH, or acetone, and drying the precipitate in vacuo. The yields of the products were 4.80 g (10 h), 3.62 g (20 h), 1.30 g (54 h) and 1.90 g (83 h), respectively. The titration of a series of samples of **1** was performed by a standard titration method reported before [6,7].

Propanoation of a series of **1** was carried out by a propanoic anhydride–pyridine-4-(dimethylamino)pyridine system. A preliminary experiment on the propanoation of cellulose (Avicel) by this system proceeded satisfactorily during 1 h at 100°C, which failed to produce cellulose tripropanoate in the absence of 4-(dimethylamino)pyridine even during at 3 h at 130°C. Thus in a 100-mL round-bottom flask 1 g of **1**, 10 mL of pyridine, 15 mL of propanoic anhydride, and 0.5 g of 4-(dimethylamino)pyridine were charged and the mixture was heated at 100°C for 1 h. The reaction solution turned homogeneous over the course of the reaction. The reaction product was isolated by pouring the mixture into MeOH and was dried in vacuo. The isolated yields of propanoated derivatives of **1** were generally no less than 70%.

NMR spectra.—^{1}H and ^{13}C NMR measurements were performed with a Jeol EX-400 spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C, respectively, with a 5 mm wide C-H dual probe, with solutions in $CDCl_3$ at 40°C or in Me_2SO-d_6 at 100°C. Chemical shifts were referenced from the residual proton signal of $CDCl_3$ (7.30 ppm for ^{1}H and 77.0 ppm for ^{13}C) or of Me_2SO-d_6 (2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C), respectively. Quantitative-mode ^{13}C NMR measurements were performed by a non-NOE gated-decoupling technique with a pulse-repetition time of 50 s, and with up to 1500 transients. INAPT (selective INEPT) measurements were performed with the delays $\Delta_{1/2}$ and $\Delta_{2/2}$ being set to 40 ms, and with the pulse width of the selective soft 90° ^{1}H pulse being set to 10 ms. Calibration of this 90° pulse was performed as reported before [21] with incrementation of the attenuation by using 90% ethylbenzene in CD_3COCD_3. The optimum value of the present system was found for an attenuation value of 390. Broad-band decoupling was applied during data acquisition and a pulse delay of 1.5 s was used between scans. Each of the INAPT spectra was obtained with ~ 10,000 transients.

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