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Review

NMR spectra of fluorinated carbohydrates

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Abstract

Recent advances in structural and conformational analysis of fluorinated carbohydrates by NMR spectroscopy are reviewed. Characteristic ^{1}H, ^{13}C, and ^{19}F NMR chemical shifts and coupling constants for selected examples are given and the spectral data of a series of fluorinated carbohydrates were collected in continuation of the review of Csuk and Glänzer [*Adv. Carbohydr. Chem. Biochem.*, 46 (1988) 73–177].

Keywords: Fluorinated carbohydrates; NMR; ^{1}H NMR; ^{13}C NMR; ^{19}F NMR

Contents

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1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy has been of primary importance in elucidating the structure and stereochemistry of carbohydrates, proteins, nucleic acids, and other natural or synthetic products [1–4]. The advances in NMR in the last two decades are due to the construction of high-field spectrometers (up to 800 MHz) combined with highly efficient computer systems and the introduction of new NMR techniques, facilitating higher sensitivity as well as increased resolution and correlating power of the experiments. Highlights in this respect were the introduction of two- and higher-dimensional methods with implementation of inverse correlation techniques [5–10] and the use of field-gradient technology, which greatly reduces experiment times [10–15].

Monosaccharides and fluorinated monosaccharides can easily be analyzed in most cases by conventional one-dimensional (1D) NMR techniques using comparative ^{1}H and ^{13}C data of analogous compounds. In complex spectra of oligo- and polysaccharides, unambiguous assignment of signals and extraction of NMR parameters, spin coupling constants and chemical shifts, in general, are only possible if appropriate 2D or multi-dimensional correlation methods determining connections and spatial proximities of atoms are used.

Fluorinated carbohydrates contain a further NMR-active nucleus, fluorine, which possesses favorable NMR properties: 100% natural abundance, high sensitivity ($\gamma_F/\gamma_H = 0.94$), and high chemical-shift resolution [16]. ^{19}F chemical shifts and $^{19}F-^{1}H$, $^{19}F-^{13}C$, or $^{19}F-^{19}F$ couplings are additional parameters that can be immensely helpful in structural and conformational analysis.

Due to their excellent NMR properties, ^{19}F labels can be used as appropriate NMR probes for investigating biologically relevant compounds and various processes in biological and medical systems [17,18]. For this purpose, the substance to be studied is ^{19}F labeled in a specific position to facilitate the assignment of resonances [19]. Another procedure is the introduction of labeled compounds into organisms in order to detect their position, conversion or other interactions by in vivo or in vitro ^{19}F measurements. In this way, the solution structure of *E. coli* tRNA [20], DNA–protein interactions [21], and metabolism of 5-fluorouracil [22–24], which is of special interest in cancer research, have been studied.

The increased importance of fluorinated carbohydrates in chemistry and biochemistry and the new possibilities in structural and conformational analysis given by NMR encouraged us to write this paper as an extension of the prominent review of Csuk and Glänzer [25].

2. ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy

An excellent guide for performance of NMR experiments was delivered by Braun et al. [26]. Experimental aspects of two-dimensional NMR were described in detail by Hull [27].

The structure of fluorinated monosaccharides, and of course non-fluorinated compounds, can easily be analyzed on the basis of standard ^{1}H and ^{13}C and, additionally, ^{19}F NMR spectra. Differentiation between C, CH, CH_2, and CH_3 signals in the ^{13}C NMR spectrum follows from DEPT (distortionless enhancement of polarization transfer) [7,28] or APT (attached proton test) spectra [29]. If comparison of NMR data with those of analogous compounds is unsuccessful, a complete assignment of all ^{1}H and ^{13}C signals, in general, is possible by recording $^{1}H,^{1}H$-COSY (correlation spectroscopy) and $^{13}C,^{1}H$ correlation spectra. $^{1}H,^{1}H$-COSY [7,30,31] correlates coupled protons (vicinal or geminal couplings), whereas $^{13}C,^{1}H$ correlation (HETCOR, heteronuclear correlation) [9,32] or the inverse (proton-detected) variants $^{1}H,^{13}C$-HMQC (heteronuclear multiple quantum coherence) [9,33] and $^{1}H,^{13}C$-HSQC (heteronuclear single quantum coherence) [34], respectively, correlate carbon atoms with directly bound protons.

Furthermore, coupling with fluorine atoms can be helpful in the assignment of signals in

^{1}H and ^{13}C NMR spectra, respectively (see Section 3). The direct extraction of spin coupling constants from ^{1}H NMR spectra might be difficult for complex coupling patterns or if multiplets overlap. The spectra can be simplified by the classical spin decoupling techniques [35–37] or by recording 2D correlation spectra, for example, 2D *J*-resolved ^{1}H NMR spectra [7] or phase-sensitive $^{1}H,^{1}H$-COSY spectra [7,31]. In the case of higher-order coupling, computer-aided spectral analysis of the coupled multiplets has to be performed [38].

Conformational analysis is mainly based on the angular dependence of coupling constants (Karplus relationship [39–41]). The analysis can be greatly supported by classical NOE (nuclear Overhauser enhancement) difference spectroscopy [8,42–45], which allows the spatial proximity of protons to be determined. Recording of 2D NOESY spectra [42,46] supplies NOE information for all protons in a molecule in a single experiment. In connection with TOCSY (total correlation spectroscopy) spectra, NOESY or ROESY (rotating frame Overhauser enhancement spectroscopy) experiments [42,47,48], respectively, are the most important tools for investigating the solution structure of complex carbohydrates, oligo- and polysaccharides, glycoproteins or other carbohydrate containing compounds [49]. Unlike COSY, TOCSY spectra [50] can in principle correlate all protons of a chain with each other. Therefore, they are successfully used for identification of single residues in oligosaccharides [49,51].

Various 1D versions of 2D experiments with selective excitation have been developed, which can alternatively supply necessary information concerning the assignment in a sometimes shorter time. In this respect the 1D TOCSY method [52,53] should be mentioned; it is sometimes preferable, in particular, in complex spectra in which a separate proton signal, e.g., the anomeric proton, can be used as starting point for the magnetization transfer. This method has often been used for the analysis of oligosaccharides or oligonucleotides in which the proton resonances of identical component residues barely differ in their chemical shifts [54,55].

Problems of localization of substituents at the ring atoms or branching of molecules that do not follow from ^{1}H or ^{13}C NMR spectra can be solved by means of long-range heteronuclear ($^{13}C,^{1}H$) COSY spectra: $^{13}C,^{1}H$-COLOC (correlation spectroscopy via long-range coupling) [9,56] or the more sensitive inverse variant $^{1}H,^{13}C$-HMBC (heteronuclear multiple bond correlation) [9,57]. For example, the position of an acetyl group might be indicated by coupling of the CO carbon atom to the corresponding ring proton over three bonds. Furthermore, long-range $^{13}C,^{1}H$ couplings across glycosidic bonds might be important for sequence or conformational analyses [58,59].

Compared with proton and carbon NMR, multi-dimensional NMR spectroscopy including fluorine plays only a secondary role. For fluorinated monosaccharides, the ^{19}F chemical shifts and coupling constants, in general, can easily be extracted from 1D NMR spectra. However, in the case of crowded spectra the use of 2D ^{19}F NMR techniques was found to be a powerful tool in structural and conformational analysis, e.g., of fluorinated oligonucleotides [19].

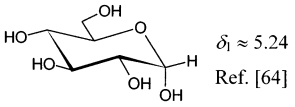
Another means for identification of signals is the determination of relaxation rates of nuclei, particularly the spin–lattice relaxation time T_1 as a molecular mobility parameter [60–62]. An example of this is the assignment of ^{19}F NMR resonances observed for 3-deoxy-3-fluoroglycogen given in Ref. [63].

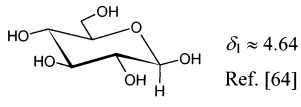
3. NMR chemical shifts and coupling constants

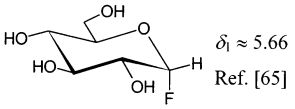
3.1 ^{1}H NMR spectroscopy

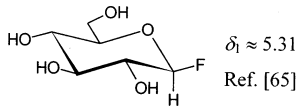
3.1.1 ^{1}H chemical shifts.

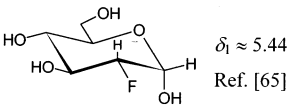
Fluorine substitution in carbohydrates, in general, causes low-field shifts of the signals of adjacent protons. This effect is largest for geminal protons. (For the following structures see Refs. [64,65].)

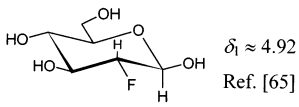

$\delta_1 \approx 5.24$ Ref. [64]


$\delta_1 \approx 4.64$ Ref. [64]


$\delta_1 \approx 5.66$ Ref. [65]


$\delta_1 \approx 5.31$ Ref. [65]

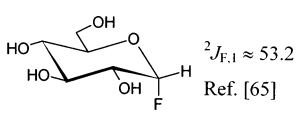

$\delta_1 \approx 5.44$ Ref. [65]

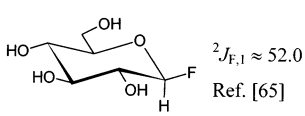

$\delta_1 \approx 4.92$ Ref. [65]

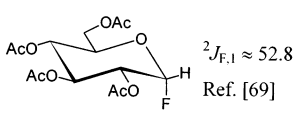
3.1.2 $^{19}F,^{1}H$ coupling constants.

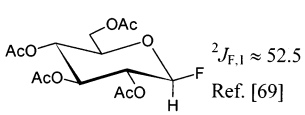
The $^{19}F,^{1}H$ couplings are mainly determined by the Fermi-contact term [66] and are therefore similar to the $^{1}H,^{1}H$ couplings, e.g., the dependence of $^{3}J_{F,H}$ on the dihedral angle as well as the relation $^{2}J_{F,H} > {}^{3}J_{F,H} > {}^{4}J_{F,H}$ for saturated systems.

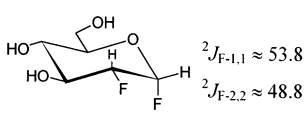
Geminal couplings $^{2}J_{F,H}$. The values of geminal coupling constants for pyranoses are in the range 43–59 Hz, and those for furanoses in the range 49–66 Hz [67]. For fluorinated pyranose derivatives, an increment system has been developed based on substituent effects [68]. (For the following structures see Refs. [65,69–74].)

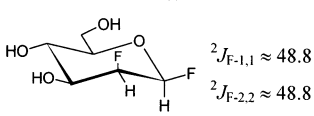

$^{2}J_{F,1} \approx 53.2$ Ref. [65]

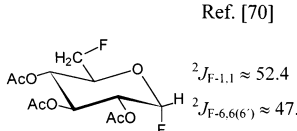

$^{2}J_{F,1} \approx 52.0$ Ref. [65]

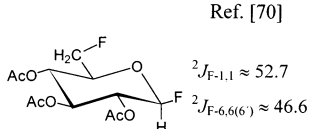

$^{2}J_{F,1} \approx 52.8$ Ref. [69]

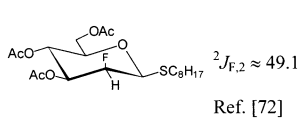

$^{2}J_{F,1} \approx 52.5$ Ref. [69]

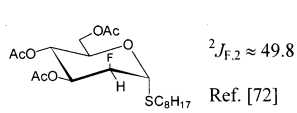

$^{2}J_{F-1,1} \approx 53.8$
$^{2}J_{F-2,2} \approx 48.8$
Ref. [70]

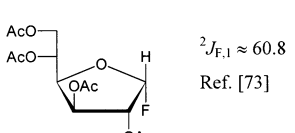

$^{2}J_{F-1,1} \approx 48.8$
$^{2}J_{F-2,2} \approx 48.8$
Ref. [70]

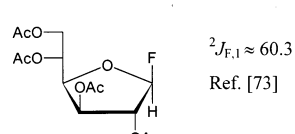

$^{2}J_{F-1,1} \approx 52.4$
$^{2}J_{F-6,6(6')} \approx 47.0$
Ref. [71]

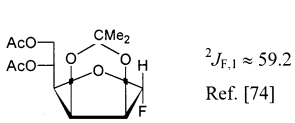

$^{2}J_{F-1,1} \approx 52.7$
$^{2}J_{F-6,6(6')} \approx 46.6$
Ref. [71]

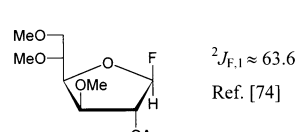

$^{2}J_{F,2} \approx 49.1$ Ref. [72]


$^{2}J_{F,2} \approx 49.8$ Ref. [72]

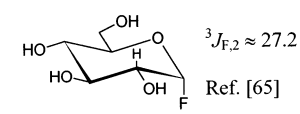

$^{2}J_{F,1} \approx 60.8$ Ref. [73]

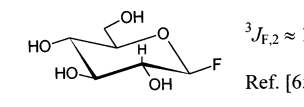

$^{2}J_{F,1} \approx 60.3$ Ref. [73]

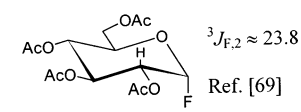

$^{2}J_{F,1} \approx 59.2$ Ref. [74]

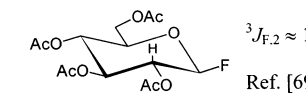

$^{2}J_{F,1} \approx 63.6$ Ref. [74]

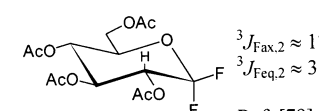
Vicinal couplings $^{3}J_{F,H}$. An angular dependence is characteristic for this type of coupling [75–80]. In addition, the coupling constants are found to depend on the electronegativity of neighboring substituents [67]. In general, for aliphatic compounds, the dependence can be stated analogously to $^{3}J_{H,H}$: $^{3}J_{F,H\ trans} > {}^{3}J_{F,H\ cis} > {}^{3}J_{F,H\ gauche}$. However, this range is valid only for structurally similar systems, since electronic substituent effects may exert a strong influence. (For the following structures see Refs. [65,69–74,76,79,81].)

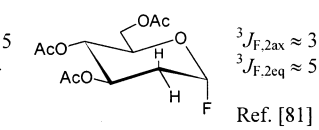

$^{3}J_{F,2} \approx 27.2$ Ref. [65]

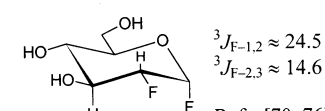

$^{3}J_{F,2} \approx 12.0$ Ref. [65]

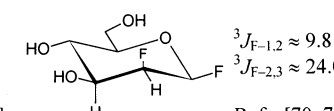

$^{3}J_{F,2} \approx 23.8$ Ref. [69]

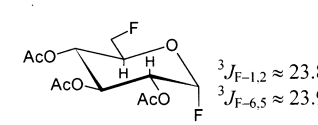

$^{3}J_{F,2} \approx 12.0$ Ref. [69]

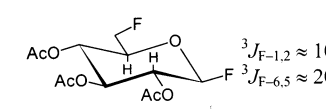

$^{3}J_{Fax,2} \approx 17.5$
$^{3}J_{Feq,2} \approx 3.4$
Ref. [79]

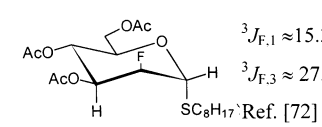

$^{3}J_{F,2ax} \approx 38.0$
$^{3}J_{F,2eq} \approx 5.0$
Ref. [81]

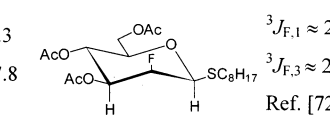

$^{3}J_{F-1,2} \approx 24.5$
$^{3}J_{F-2,3} \approx 14.6$
Refs. [70, 76]

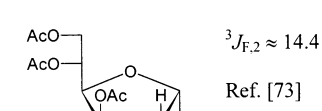

$^{3}J_{F-1,2} \approx 9.8$
$^{3}J_{F-2,3} \approx 24.0$
Refs. [70, 76]

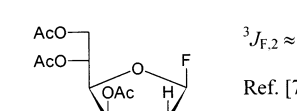

$^{3}J_{F-1,2} \approx 23.8$
$^{3}J_{F-6,5} \approx 23.9$
Ref. [71]

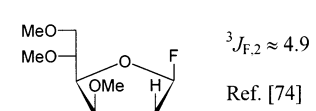

$^{3}J_{F-1,2} \approx 10.4$
$^{3}J_{F-6,5} \approx 20.6$
Ref. [71]

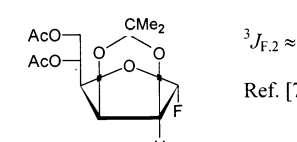

$^{3}J_{F,1} \approx 15.3$
$^{3}J_{F,3} \approx 27.8$
Ref. [72]


$^{3}J_{F,1} \approx 26.3$
$^{3}J_{F,3} \approx 26.8$
Ref. [72]


$^{3}J_{F,2} \approx 14.4$ Ref. [73]

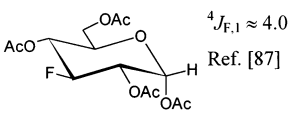

$^{3}J_{F,2} \approx 4.4$ Ref. [73]

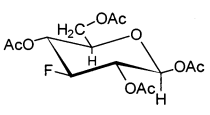

$^{3}J_{F,2} \approx 4.9$ Ref. [74]

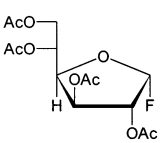

$^{3}J_{F,2} \approx 6.2$ Ref. [74]

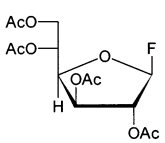
Long-range $^{19}F,^{1}H$ couplings. Couplings over four and five bonds are relatively frequent. The largest magnitude is observed when the coupled nuclei adopt a coplanar 'W' arrangement [65,67,82].

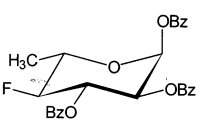
2′,3′-Dideoxy-4′-fluoroalkylnucleotides exhibit long-range $^{7}J_{H,F}$ and $^{6}J_{C,F}$ couplings, which are mainly transmitted via a through-space mechanism [83]. Through-space couplings can always occur if the nuclei concerned are in spatial proximity [84,85]. Generally, long-range couplings transmitted either via through bond or through space are highly sensitive to the steric environment of the coupled atoms [86], therefore, their general applicability as a tool for stereochemical studies is questionable. (For the following structures see Refs. [73,83,87–89].)

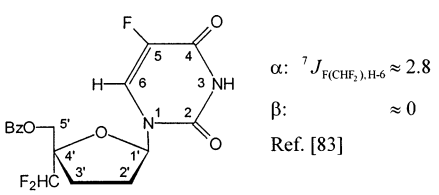








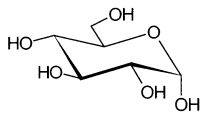


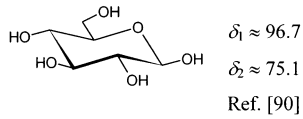


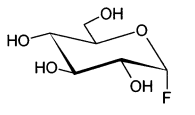
3.2 ^{13}C NMR spectroscopy

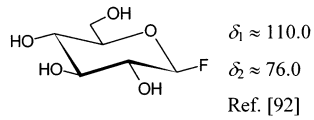
3.2.1 ^{13}C chemical shifts.

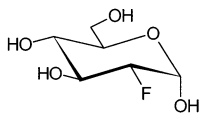
An excellent review on ^{13}C NMR data of monosaccharides has been published by Bock and Pedersen [90]. Introduction of fluorine into a carbohydrate molecule causes a significant low-field shift of the signals of the adjacent carbon atoms (α effect) [91]. (For the following structures see Refs. [90,92,93].)

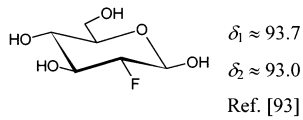








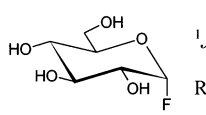


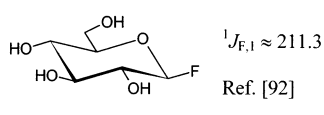


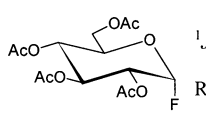
3.2.2 $^{19}F,^{13}C$ coupling constants.

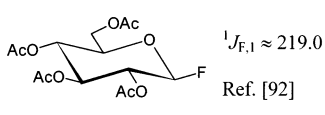
The $^{19}F,^{13}C$ coupling constants can be directly taken from the proton broad-band decoupled ^{13}C NMR spectra. They represent a useful tool for assigning the ^{13}C NMR signals. In spectra of polyfluorinated carbohydrates higher-order couplings may require computer analysis [38,93,94].

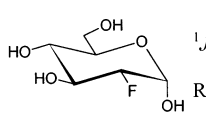
Couplings over one bond $^{1}J_{F,C}$. The couplings, ranging between 160 and 250 Hz, are influenced by the steric and electronic effects of substituents attached to the coupled carbon atom, as well as by the orientation of the fluorine atom. Increasing electronegativity of the substituent causes an increase in the cou-

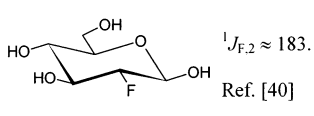


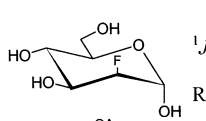


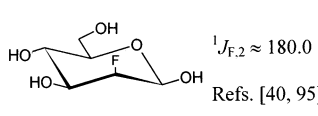


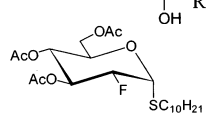


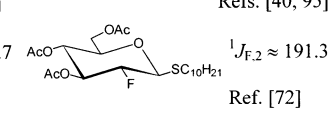


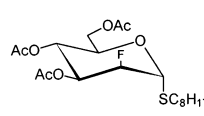


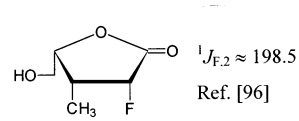


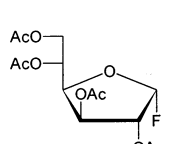


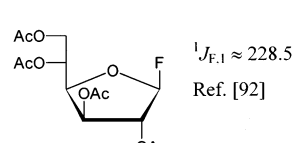






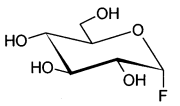


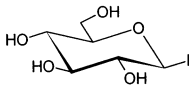


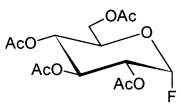


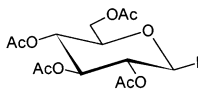
pling constant. (For the following structures see Refs. [40,72,92,95,96].)

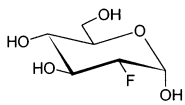
Geminal couplings $^{2}J_{F,C}$. These coupling constants are in the range 15–40 Hz. They are found to be dependent on the orientation of electronegative substituents attached to the coupled carbon atom with respect to the fluorine [67]. (For the following structures see Refs. [40,72,92,95,96].)

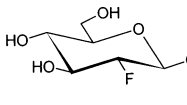

$^{2}J_{F,2} \approx 24.9$ Ref. [92]

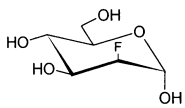

$^{2}J_{F,2} \approx 22.1$ Ref. [92]

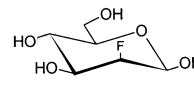

$^{2}J_{F,2} \approx 24.3$ Ref. [92]

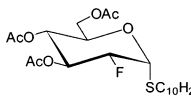

$^{2}J_{F,2} \approx 22.3$ Ref. [92]

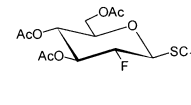

$^{2}J_{F,1} \approx 21.4$
$^{2}J_{F,3} \approx 17.5$
Ref. [40]

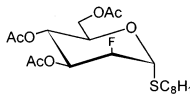

$^{2}J_{F,1} \approx 23.0$
$^{2}J_{F,3} \approx 17.3$
Ref. [40]

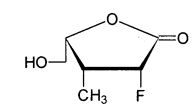

$^{2}J_{F,1} \approx 29.6$
$^{2}J_{F,3} \approx 17.5$
Refs. [40, 95]

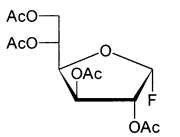

$^{2}J_{F,1} \approx 15.8$
$^{2}J_{F,3} \approx 17.6$
Refs. [40, 95]

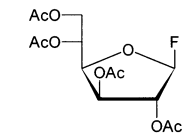

$^{2}J_{F,1} \approx 21.4$
$^{2}J_{F,3} \approx 19.2$
Ref. [72]


$^{2}J_{F,1} \approx 23.2$
$^{2}J_{F,3} \approx 20.3$
Ref. [72]

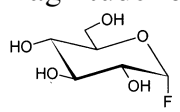

$^{2}J_{F,1} \approx 22.6$
$^{2}J_{F,3} \approx 17.5$
Ref. [72]

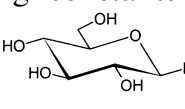

$^{2}J_{F,1} \approx 22.2$
$^{2}J_{F,3} \approx 18.3$
Ref. [96]

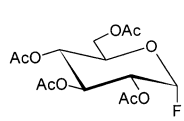

$^{2}J_{F,2} \approx 19.6$ Ref. [92]

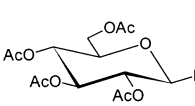

$^{2}J_{F,2} \approx 35.4$ Ref. [92]

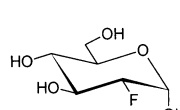
Vicinal couplings $^{3}J_{F,C}$. The angular dependence of vicinal F,C couplings, ranging from 0 to 20 Hz, parallels that of $^{3}J_{F,H}$ and $^{3}J_{H,H}$ [39] (Karplus-type relationship [40,41]). Furthermore, the influence of electronegative substituents, attached directly or adjacent to the coupled carbon atom, has been found on the magnitude of coupling constants [40]. (For the following structures see Refs. [40,72,-74,92,95,96].)

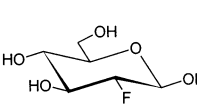

$^{3}J_{F,5} \approx 2.9$ Ref. [92]

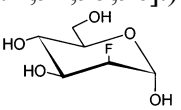

$^{3}J_{F,3} \approx 2.2$
$^{3}J_{F,5} \approx 4.3$
Refs. [40, 92]

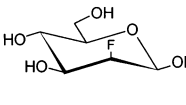

$^{3}J_{F,5} \approx 4.4$ Ref. [92]

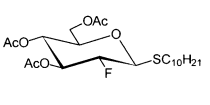

$^{3}J_{F,3} \approx 3.8$
$^{3}J_{F,5} \approx 2.1$
Ref. [92]

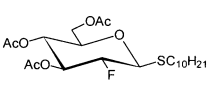

$^{3}J_{F,4} \approx 8.0$ Ref. [40]

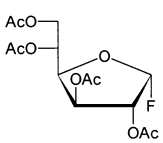

$^{3}J_{F,4} \approx 8.2$ Ref. [40]

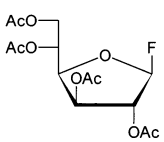

$^{3}J_{F,4} \approx 1.4$ Refs. [40, 95]


$^{3}J_{F,4} \approx 1.5$ Refs. [40, 95]

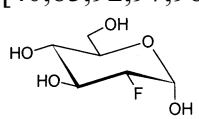

$^{3}J_{F,4} \approx 6.7$ Ref. [74]

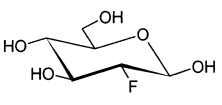

$^{3}J_{F,4} \approx 7.0$ Ref. [72]

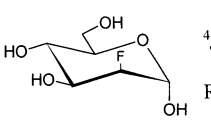

$^{3}J_{F,4} \approx 1.2$ Ref. [92]

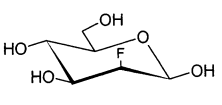

$^{3}J_{F,4} \approx 2.5$ Ref. [92]

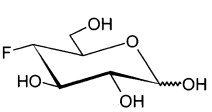
Long-range couplings $^{n}J_{F,C}$. $^{19}F,^{13}C$ couplings over four bonds, $^{4}J_{F,C}$ may often be detected; their magnitude is found to depend on the orientation of the coupled nuclei [40,92]. Couplings over five or six bonds are also known [83,97]. (For the following structures see Refs. [40,83,92,97,98].)

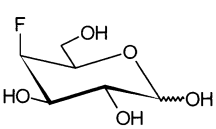

$^{4}J_{F,5} \approx 1.3$ Ref. [40]

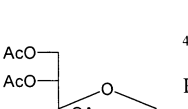

$^{4}J_{F,5} \approx 1.2$ Ref. [40]

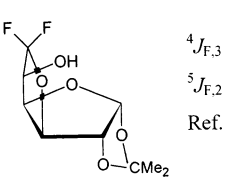

$^{4}J_{F,5} \approx 0$ Ref. [40]

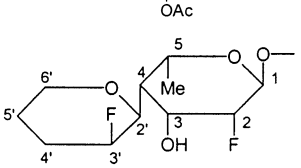

$^{4}J_{F,5} \approx 0$ Ref. [40]

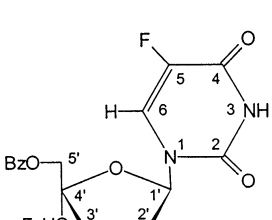

$^{4}J_{F,1} \approx 1.4$ Ref. [40]


$^{4}J_{F,1} \approx 0$ Ref. [40]


$^{4}J_{F,5} \approx 0.7$ Ref. [92]


$^{4}J_{F,3} \approx 2.0$
$^{5}J_{F,2} \approx 1.8$
Ref. [97]


$^{4}J_{F\text{-}3',6'} \approx 7.0$ $^{2}J_{F\text{-}2,1} \approx 32.3$
$^{3}J_{F\text{-}3',5'} \approx 8.4$ $^{2}J_{F\text{-}2,3} \approx 17.2$
$^{2}J_{F\text{-}3',4'} \approx 18.9$ $^{1}J_{F\text{-}2,2} \approx 179.3$
$^{2}J_{F\text{-}3',2'} \approx 22.4$ $^{1}J_{F\text{-}3',3'} \approx 184.0$
Ref. [98]


α: $^{6}J_{F(CHF_2),C\text{-}6} \approx 7.9$
β: ≈ 0
Ref. [83]

3.3 ^{19}F NMR spectroscopy.

^{19}F NMR data of fluorinated carbohydrates have been reviewed in Refs. [25,67]; those of

specifically fluorinated compounds are in compounds are included in a series of articles [99–104].

3.3.1 ^{19}F chemical shifts.

There are characteristic ^{19}F chemical shift ranges for different types of CF groups (see Table 1).

In the case of aldohexopyranosyl fluorides, α anomers show characteristic high-field shifts with regard to β anomers, due to the higher shielding of the axially positioned F atom compared with the equatorially positioned fluorine. For the α and β anomers of deoxy-monofluorohexopyranoses, there are no such significant differences. The corresponding shifts in furanosyl fluorides depend greatly on the configuration at the other ring atoms. (For the following structures see Refs. [65,69–71,73, 76,81,105].)

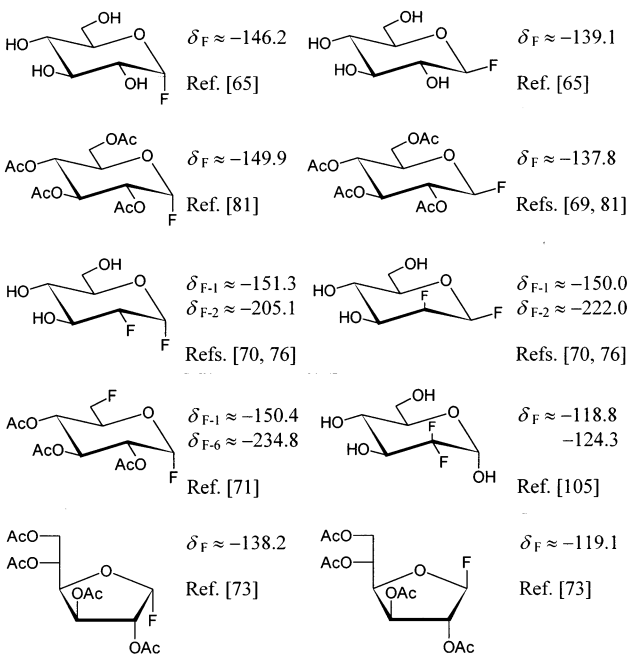


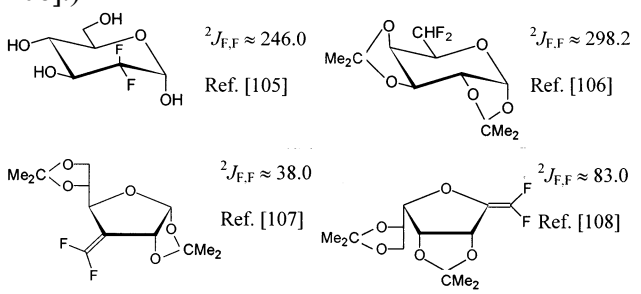
Table 1
Characteristic ^{19}F chemical shift ranges (Hz) for the different types of CF groups

Range	Group	Examples
−65 to −90	$OCRF_2$	3,6-anhydro-2,2-difluoro-D-glucofuranoses
−110 to −140	CR_2F_2	2-deoxy-2,2-difluorohexopyranoses;
	OC(R)F	hexofuranosylfluorides
−135 to −150	OCHF	glycosylfluorides
−180 to −220	RCHF	2-deoxy-2-fluorohexopyranoses
−225 to −245	CH_2F	6-deoxy-6-fluorohexopyranoses

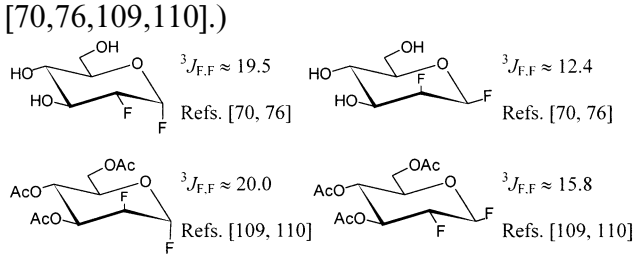
3.3.2 $^{19}F,^{19}F$ coupling constants.

The $^{19}F,^{19}F$ couplings can be extracted from the $^{19}F\{^1H\}$ NMR spectra. For complex spectra, e.g., of polyfluorinated compounds, simplifications may be obtained, for instance, by using selective decoupling or recording two-dimensional correlation spectra [16,19,26]. If necessary, computer simulations for complete spectra analysis can be used [38,94].

Geminal couplings $^2J_{F,F}$. The coupling constants $^2J_{F,F}$ for aliphatic CF_2 groups range from 200 to 350 Hz, and for $=CF_2$ from 10 to 100 Hz. (For the following structures see Refs. [105–108].)



Vicinal couplings $^3J_{F,F}$. For 1,2-difluoropyranoses, vicinal F,F coupling constants are found in the range 10–20 Hz. Generally, in contrast to $^3J_{H,H}$ and $^3J_{F,H}$, there is no correlation with the dihedral angle (Karplus relationship [41]) for $^3J_{F,F}$ because of dominating substituent effects. (For the following structures see Refs. [70,76,109,110].)



Long-range couplings $^nJ_{F,F}$. Long-range couplings over four and five bonds have been reported [111,112]. They are of special interest, because the coupling constants may be enlarged by the spatial proximity of coupled nuclei (through-space couplings [84] (see F,H couplings)). (For the following structures see Refs. [71,111–113].)

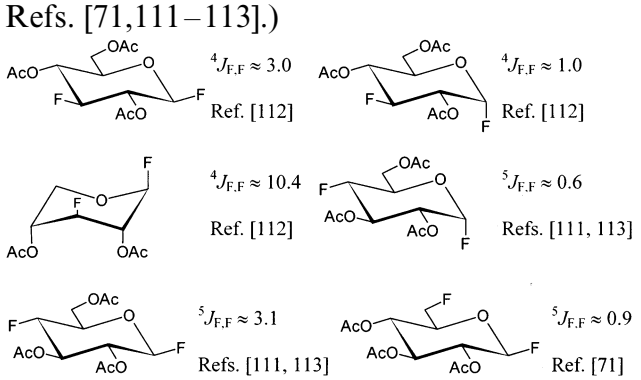


Table 2
NMR data for pyranoses with fluorine atom at C-1 [a]

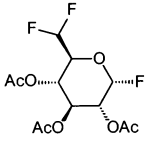
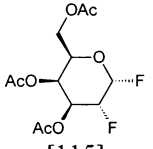
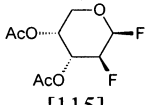
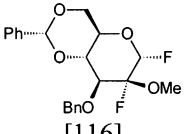
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [114]		5.80	4.94	5.54	5.32	4.21	5.84	103.2	69.7	68.7	66.0	69.5	112.8	-128.3 (F6b) -132.0 (F6a) -150.8 (F1)	$CDCl_3$
		2.8	10.1	9.7	9.8	2.7		230.7 (F1,C1)	24.3 (F1,C2)		4.1, 1.9 (F6a,b, C4)	23.6 (F6a,b, C5) 4.3 (F1,C5)	246.5 (F6a,b, C6)	295.0 (F6a, F6b)	
		52.4 (F1,1)	24.1 (F1,2)			11.0 (F6a,5) 10.1 (F6b,5)	54.1 (F6a,b,6)								
 [115]		5.84	4.77	5.40	5.53	4.40	4.0-4.2 (6a,b)	104.1	84.4	67.7	67.8	69.0	61.1	-152.6 (F1) -211.3 (F2)	$CDCl_3$
		2.9	10.1	3.3	1.1	6.2 (5,6a) 6.2 (5,6b)		23.5 (F2,C) 230.5 (F1,C)	191.2 (F2,C) 25.3 (F1,C)	25.1 (F2,C)	1.6 (F2,C)	3.2 (F1,C)		18.0	
		53.1 (F1,1)	48.8 (F2,2) 23.3 (F1,2)	11.1 (F2,3)	3.3 (F2,4)										
 [115]		5.82	4.79	5.3-5.45	5.3-5.45	4.11 (5a) 3.77 (5b)		104.7	85.0	67.3	68.8	62.6		-155.2 (F1) -209.3 (F2)	$CDCl_3$
		2.7	10.0		1.6 (4,5b)	13.2 (5a,5b)		23.3 (F2,C) 229.5 (F1,C)	190.8 (F2,C) 25.6 (F1,C)	18.9 (F2,C)	7.7 (F2,C)	3.3 (F1,C)		18.0	
		53.1 (F1,1)	48.5 (F2,2) 23.3 (F1,2)			1.6 (F1,5b)									
 [116]		5.65		3.90-4.10	3.90-4.10	3.90-4.10	3.81 (6a) 4.36 (6b)	104.0	109.7	78.7	78.5	65.2	68.2	-137.0 (F2) -145.7 (F1)	$CDCl_3$
						10.0 (5,6a) 5.5 (5,6b)	10.0	229.0 (F1,C) 50.6 (F2,C)	225.5 (F2,C) 33.6 (F1,C)	31.0 (F2,C)		3.4			
		50.5 (F1,1) 2.0 (F2,1)													

Table 2 (Continued)

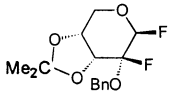
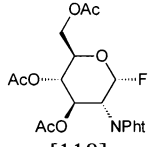
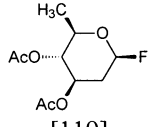
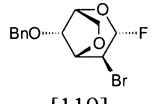
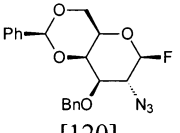
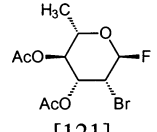
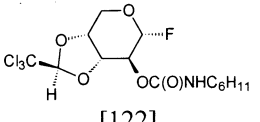
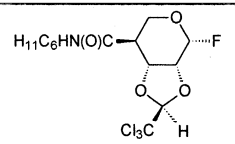
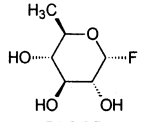
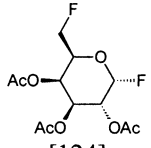
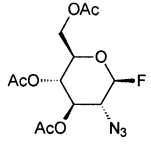
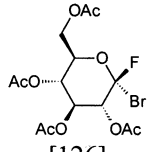
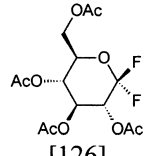
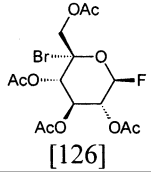
 [117]	5.31	4.60-4.93	4.60-4.93	4.60-4.93	4.13-4.22 (5a,b)		106.8	112.2	79.3	78.3	72.4		-123.5 (F2) -143.7 (F1)	$CDCl_3$
							223.0 (F1,C) 45.0 (F2,C)	239.9 (F2,C) 28.0 (F1,C)	19.6 (F2,C)				3.1	
	63.9 (F1,1)													
 [118]	5.91	4.62	6.29	5.15	4.10-4.35	4.10-4.35 (6a,b)	105.1	52.0	68.5	69.6	66.2	61.3		Me_2SO-d_6
	2.6	10.4	9.2				230.0	29.4						
	51.8	30.3												
 [119]	5.41	2.43 (2b) 1.82 (2a)	4.96	4.80	3.61	1.26								$CDCl_3$
	7.7 (1,2a) 2.6 (1,2b)	13.3 (2a,2b) 5.1 (2b,3) 7.4 (2a,3)	8.7	8.9	6.2									
	51.8	7.8 (F,2b) 12.8 (F,2a)												
 [119]	5.75	4.41	4.33	4.61	4.0	4.15 (6a) 4.0 (6b)	109.2	49.8	77.5	73.8	77.8	69.5		$CDCl_3$
	6.8	0.7				11.0	216.0	23.0	7.0					
	55.4	14.8												
 [120]	5.00	3.98	3.44	4.09	3.41	4.02 (6a) 4.33 (6b)	102.2	62.0	66.7	68.6 or 71.6	77.4	68.6 or 71.6		$CDCl_3$
	7.7	10.3				12.5	213.6	20.8	6.1		9.8			
	52.8	12.5												
 [121]	5.77	4.57	5.10	5.24	4.09	1.27	106.9	47.6	70.0	68.4	69.4	17.4		$CDCl_3$
	1.6	3.8	9.8	9.2	6.2		224.0	35.8			3.4			
	50.7	2.7												
 [122]	5.48	5.10	4.64	4.81	3.98 (5a,b)		104.1	67.6	75.5	72.5	60.2		-132.2	$CDCl_3$
	2.7	4.0	6.7	5.5 (4.5a) 5.8 (4,5b)			228.8	35.0	1.5					
	54.0	7.0												

Table 2 (Continued)

 [122]	6.89	4.85	4.60	5.02	3.69 (5a) 4.01 (5b)		104.5	72.1	66.4; 74.2		58.7		-93.0	Me_2SO-d_6 (^1H, ^{13}C) $CDCl_3$ (^{19}F)
	4.0	5.8	3.7	3.4 (4,5a) 3.1 (4,5b)	12.5 (5a,5b)		226.5	23.3						
	55.2	25.3												
 [123]	5.56	3.08-3.90	3.08-3.90	3.08-3.90	3.08-3.90	1.24	107.7	71.7	70.9	74.5; 72.6		17.0		D_2O
	2.5				6.0		222.0	25.0	5.0					
	53.0													
 [124]	5.75	5.13	5.31	5.51	4.36	4.36 (6a) 4.43 (6b)	104.3	67.4	66.9	67.3	69.4	80.6	-150.7 (F1) -232.1 (F6)	$CDCl_3$
	2.7	11.0	3.3	1.2	3.7 (5,6a) 6.1 (5,6b)	9.2 (6a,6b)	228.9 (F1,C)	24.0 (F1,C)		5.2 (F6,C)	3.8 (F1,C) 23.8 (F6,C)	172.6 (F6,C)		
	53.4 (F1,1)	23.5 (F1,2)			15.2 (F6,5)	42.4 (F6,6a,b)								
 [125]	5.17	3.67	5.03-5.12	5.03-5.12	3.81	4.30 (6a) 4.18 (6b)	107.8	63.9	72.3	67.9	72.0	61.8	-139.4	$CDCl_3$
	7.4				4.9 (5,6a) 2.5 (5,6b)	12.6	218.0	23.3	5.8					
	51.5	12.1												
 [126]		5.11	5.38	5.25	4.15-4.45	4.15-4.45 (6a,b)	120.3	72.5	71.2	66.4	74.9	60.3	-68.9	$CDCl_3$
		10.0	9.5	12.2			281.3	23.7	8.6		2.5			
		8.3												
 [126]		5.37	5.37	5.26	4.19	4.19 (6a) 4.32 (6b)	120.3	68.7	70.7	66.8	72.6	60.6	-86.4 -82.8	$CDCl_3$
			9.2	9.2	4.3 (5,6b)	13.3	256.0 271.7 (Fa,b,C)	30.6 (Fa,b,C)	9.4		2.8, 4.0 (Fa,b,C)		148.8	
		17.5 (Fa,2) 3.4 (Fb,2)												
 [126]	5.68	5.27	5.53	5.29		4.56 (6a) 4.41 (6b)	106.6	70.4	70.4	67.9	94.7	65.5	-150.2	$CDCl_3$
	7.3	9.5	10.0			12.6	222.8	24.6	10.6		7.2			
	52.1	14.0												

[a] For further examples (fluorine atom in anomeric position) see Refs. [126–130].

Table 3
NMR data for pyranoses with fluorine atom at C-2 [a]

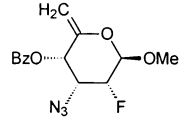
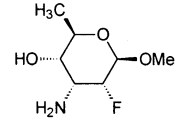
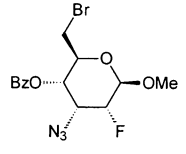
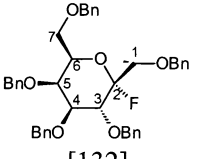
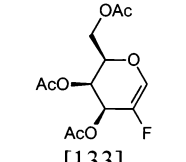
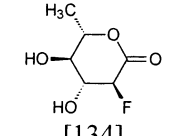
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [131]		5.05	4.82	3.76	5.84		4.94 (6a) 4.92 (6b)	99.3	87.0	55.9	69.2	149.8	103.7		$CDCl_3$
		2.7	2.8	3.8			1.3	29.3	186.0	16.4	0				
		7.1	48.7	30.1											
 [131]		4.63	4.26	3.30	3.5-3.6	3.5-3.6	1.30	98.5	89.7	52.0	71.9	70.2	17.7		$CDCl_3$
		7.6	4.4	1.0		6.3		23.5	186.0	18.2	4.2				
		2.0	48.1	9.2											
 [131]		4.83	4.46	4.60	5.04	4.17	3.57 (6a) 3.44 (6b)	99.0	87.6	61.1	70.0	71.1	31.4		$CDCl_3$
		7.7	3.8	3.2	9.5	2.7 (5,6a) 6.6 (5,6b)	11.3	23.3	194.5	16.7	4.4				
		1.4	46.8	7.4	1.5										
 [132]		3.38 (1a) 3.87 (1b)		4.31	3.98	4.09	4.14	69.4	113.5	74.8	72.4; 73.9; 79.9				$CDCl_3$
		11.0 (1a,1b)		10.1	2.7			38.1	225.7	23.4					
		2.0 (F,1a) 7.3 (F,1b)		23.4											
 [133]		6.68		5.82	5.38	4.10-4.30	4.10-4.30 (6a,b)							-168.7	$CDCl_3$
				5.2											
		4.4													
 [134]			4.92	4.03	3.61	4.40	1.43	167.3	89.6	73.5	73.4	78.1	19.8		acetone-d_6
			9.4	9.2	9.2	6.0		20.0	189.0						
			48.0	16.0											

Table 3 (Continued)

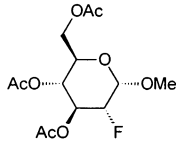
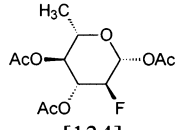
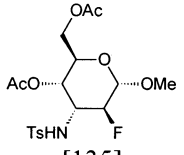
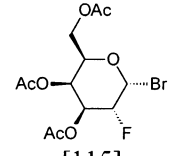
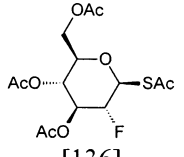
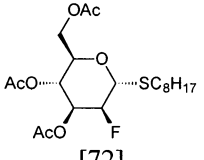
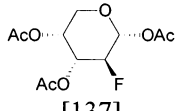
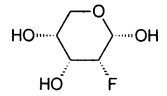
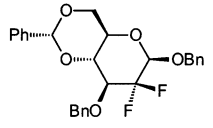
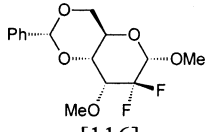
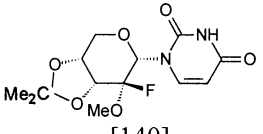
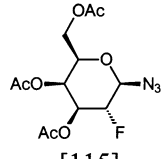
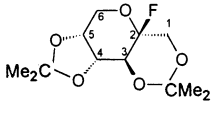
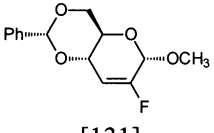
 [131]	4.95	4.49	5.53	5.00	3.99	4.25 (6a) 4.08 (6b)	96.9	87.3	70.6	68.1	67.2	61.3		$CDCl_3$
	3.9	9.6	9.5	9.5	4.6 (5,6a) 2.4 (5,6b)	12.4	20.4	194.5	19.5	7.2				
	<0.5	49.2	12.1	<0.5										
 [134]	5.76	4.42	5.32	4.79	3.73	.1.24	91.1	88.5	72.6	70.9; 72.7		17.1		$CDCl_3$
	8.2	9.0	9.4	9.8	6.2		24.0	192.0	14.0					
	3.2	51.0	14.0											
 [135]	5.01	4.90	4.67	5.51	4.50	4.47 (6a) 4.57 (6b)	99.2	89.0	52.1	66.1	66.5	63.1	-188.2	pyridine-d_5
	2.0	4.5	4.5	8.5	2.0 (5,6a) 5.5 (5,6b)	12.5	31.6	178.1	26.7					
	10.5	46.0	9.0	2.0										
 [115]	6.60	4.74	5.45	5.50	4.49	4.15 (6a) 4.09 (6b)	86.9	84.2	68.9	67.5	71.3	60.7	-195.3	$CDCl_3$
	4.2	9.6	3.3	1.2	6.2 (5,6a) 6.8 (5,6b)	11.4	25.6	195.0	18.0	7.6				
		50.0	13.4	3.5										
 [136]	5.27	4.37	5.33	4.99	3.81	4.21 (6a) 4.04 (6b)	79.3	87.0	73.7	67.5	76.1	61.4		$CDCl_3$
	10.2	8.8	9.8	9.8	4.6 (5,6a) 2.2 (5,6b)	12.5	24.0	191.0	20.0	7.0				
	2.0	49.6	14.1											
 [72]	5.40	4.87	5.14	5.32	4.34	4.29 (6a) 4.08 (6b)	82.3	88.7	70.3	68.9	66.0	62.1	-189.4	$CDCl_3$
	1.8	2.5	10.0	9.8	4.9 (5,6a) 2.5 (5,6b)	12.2	22.6	187.5	17.5					
	15.3	49.8	27.8											
 [137]	5.74	4.67	5.20	5.34	4.1, 3.8 (5a,b)		91.7	86.5	70.1	68.0	64.2			$CDCl_3$
	7.5	9.2	3.5		13 (5a,5b)		25	186	20					
	4.8	50.9	12.4											

Table 3 (Continued)

 [138]	5.01	4.44	4.26	3.70	3.79 (5a) 3.46 (5b)		92.1	87.2	71.6	67.1	59.0		-201.1	acetone-d_6
	3.1	3.1		9.8 (4,5a) 4.8 (4,5b)	11.1 (5a,5b)			197.0	10.0					
	3.1	46.6	3.1											
 [139]	4.56		3.72-3.94	3.72-3.94	3.42	3.72-3.94 (6a) 4.38 (6b)	97.4	116.1	77.5	79.2	66.5	68.3	-118.3 (Fb) -136.0 (Fa)	$CDCl_3$
				10.0	5.0 (5,6b)	10.5	28, 20 (Fa,b,C)	255.0 (Fa,b,C)	19.3 (Fa,b,C)	8.7 (F,C)			251.5	
	15.0 (Fa,1)		15.0 (Fa,3) 4.2 (Fb,3)											
 [116]	4.60		3.84	3.77	4.25	3.69 (6a) 4.30 (6b)	100.0	115.8	78.2	78.5	62.4	69.6	-107.1 (Fb) -116.9 (Fa)	$CDCl_3$
				10.0	10.0 (5,6a) 5.5 (5,6b)	10.0	40, 28 (Fa,b,C)	268, 240 (Fa,b,C)	32, 21 (Fa,b,C)	7.0 (F,C)			271.0	
	9.0 (Fa,1) 1.0 (Fb,1)													
 [140]	5.69		4.75	4.88	4.21-4.24 (5a,b)		84.5	113.6	81.6	78.2	72.4		-127.8	$CDCl_3$
			6.6				27.3	246.9	21.5					
	13.2		13											
 [115]	4.81	4.42	5.12	5.42	3.88-4.18	3.88-4.18 (6a,b)	88.0	87.4	70.9	67.5	72.8	61.1	-205.5	$CDCl_3$
	8.5	9.7	3.5	1.0			23.1	188.7	18.8	8.2				
	4.0	50.8	13.0	2.6										
 [141]	3.82 (1a) 3.76 (1b)		3.89	4.30	4.30	4.16 (6a) 4.02 (6b)	64.1	104.7	71.6	72.8	72.4	62.4		$CDCl_3$
	15.1 (1a,1b)		7.5		3.5 (5,6a) 2.4 (5,6b)	13.0	26.1	228.0	26.5			3.5		
	23.0 (F,1a) 2.3 (F,1b)		25.4			2.4 (F,6b)								
 [131]	4.86		5.64	4.25-4.32	3.93	3.81 (6a) 4.25-4.32 (6b)	95.5	156.5	107.3	75.6	65.4	69.5		$CDCl_3$
			1.8	8.7	4.5 (5,6b) 10.0 (5,6a)	10.0 (6a,6b)	34.2	272.0	12.9	7.7				
	0.5		13.5	6.5										

[a] For further examples (fluorine atom at C-2) see Refs. [142–144].

Table 4
NMR data for pyranoses with fluorine atom at C-3 [a]

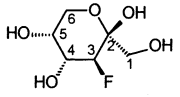
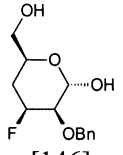
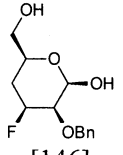
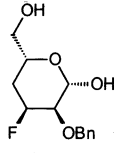
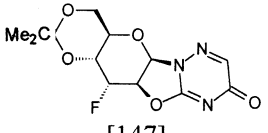
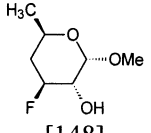
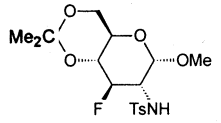
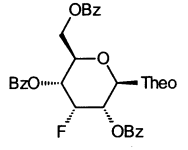
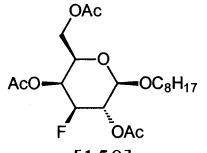
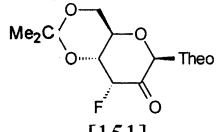
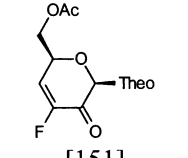
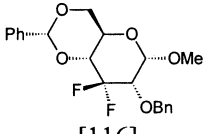
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [145]		3.88 (1a) 3.55 (1b)		4.51	3.98	3.89	3.53 (6a) 3.41 (6b)	64.4 or 64.3	97.1	89.2	68.9	70.5	64.4 or 64.3	-209.4	D_2O
		12.9 (1a,1b)		9.8	3.6	1.6 (5,6a) 1.5 (5,6b)	12.1		19.1	183.1	17.5	8.4			
		1.2 (F,1a) 2.0 (F,1b)		50.3	13.3										
 [146]		5.23	3.80	5.02	2.08 (4a) 1.79 (4b)	4.05	3.63 (6a) 3.60 (6b)	94.2	74.3	88.4	28.7	68.9	65.3	-192.3	$CDCl_3$ + D_2O
		2.0	3.0	12.0 (3,4a) 5.0 (3,4b)	12.0 (4a,4b) 12.0 (4a,5) 2.5 (4b,5)	6.5 (5,6a) 3.3 (5,6b)	12.0	9.0	15.0	182.0	20.0	11.0	3.0		
		5.5	6.0	47.0	8.5 (F,4a) 5.5 (F,4b)										
 [146]		4.60	3.89	4.73	2.04 (4a) 1.81 (4b)	3.48	3.68 (6a) 3.63 (6b)	93.4	75.5	90.9	27.6	71.5	64.8	-186.6	$CDCl_3$ + D_2O
		1.5	3.0	12.0 (3,4a) 5.0 (3,4b)	12.0 (4a,4b) 12.0 (4a,5) 2.3 (4b,5)	3.5 (5,6a) 6.0 (5,6b)	12.0	10.7	15.0	185.0	20.0	11.0	3.0		
		2.3	6.5	46.5	8.5 (F,4a) 5.0 (F,4b)										
 [146]		5.14	3.20	5.02	1.69 (4a) 1.94 (4b)	4.00	3.71 (6a) 3.53 (6b)	94.4	77.8	88.3	32.1	70.9	64.7	-201.0	$CDCl_3$ + D_2O
		8.0	2.5	2.1 (3,4a) 3.5 (3,4b)	13.4 (4a,4b) 11.7 (4a,5) 2.3 (4b,5)	3.0 (5,6a) 6.0 (5,6b)	12.0	3.0	17.0	175.5	20.0				
		1.1	28.5	50.4	43.5 (F,4a) 11.0 (F,4b)										
 [147]		6.28	5.30	5.46	4.02	3.70-3.94	3.70-3.94							-193.6	Me_2SO-d_6
		3.3			9.5										
			11.2	46.3	30.5										
 [148]		4.79	3.65	4.66	1.54 (4a) 2.15 (4b)		1.24							-188.4	$CDCl_3$
		4.0	9.0	11.5 (3,4a) 5.5 (3,4b)											
		4.0	13.5	53.0	12.0 (F,4a) 5.0 (F,4b)										

Table 4 (Continued)

 [135]	4.85	4.17	4.93	4.06	3.78	3.93 (6a) 4.01 (6b)	100.8	57.5	90.0	73.4	63.3	62.4	-195.8	pyridine-d_5 (^{13}C, ^{19}F) pyridine-d_5 / D_2O 14:1 (^{1}H)
	3.5	10.0	9.5	9.5	10.5 (5,6a) 6.0 (5,6b)	10.5	8.9	17.2	189.6	16.7	7.4			
	3.5	11.0	54.0	11.0										
 [149]	5.64	4.80	5.50	4.80	4.49	3.92 (6a) 3.53 (6b)	80.7	69.7	87.8	67.2	72.2	62.4	-211.0	$CDCl_3$
	6.9	0.5	0.5	9.2	3.8 (5,6a)	12.1	7.4	9.1	177.6	14.8				
		28.9	53.7	28.9										
 [150]	4.40	5.28	4.61	5.55	3.83	4.17 (6a,b)	100.8	70.0	89.0	67.0	69.9	61.4	-200.3	$CDCl_3$
	8.0	9.5	3.5	1.0	6.5 (5,6a,b)		10.6	25.7	194.0	16.6		2.4		
		12.0	47.0	6.0	1.0									
 [151]	6.07		4.73	4.17	3.89-4.05	3.89-4.05 (6a,b)							-199.4	$CDCl_3$
				9.8										
			51.9	28.8										
 [151]	6.57			6.67	5.10	4.37 (6a,b)							-202.4	$CDCl_3$
				1.7										
				11.2	7.5									
 [116]	4.54	3.50-3.70			4.00	4.23 (6b) 3.50-3.70 (6a)	99.0	74.8	118.5	77.8	60.3	68.7	-115.3 -130.2	$CDCl_3$
	4.0			10.2	5.0 (5,6b) 10.2 (5,6a)	10.3 (6a,6b)	3.0	18.5 (Fa,b,C)	245 (Fa,b,C)	18.5 (Fa,b,C)			236.7	
	4.0	18.5 (Fa,2)		18.5 (Fa,4)		2.5 (F,6b)								

[a] For further examples (fluorine atom at C-3) see Refs. [152–156].

Table 5
NMR data for pyranoses with fluorine atom at C-4 [a]

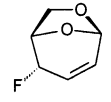
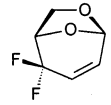
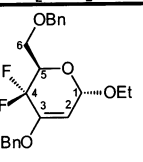
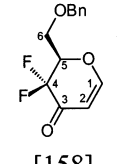
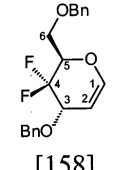
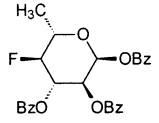
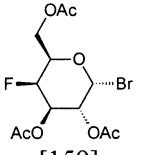
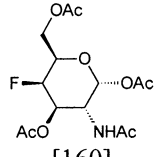
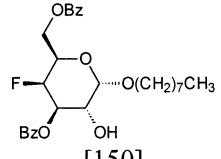
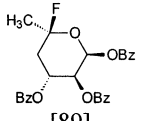
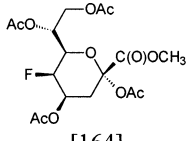
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [157]		5.53	6.71	5.83	4.40	4.80	3.34 (6a) 3.88 (6b)	95.2	133.6	121.7	83.8	74.2	61.3	-171.5	$CDCl_3$
		3.4	9.6	4.5	1.5	6.7 (5,6a) 1.8 (5,6b)	8.0								
					47.2										
 [157]		5.57	6.24	5.78		4.65	3.83 (6a) 3.95 (6b)	95.6	135.1	122.0	163.0	75.5	75.5	-95.4 -117.8	$CDCl_3$
														280.0	
 [158]		5.26	5.13			4.45	3.76 (6a) 3.95 (6b)							-126.1 (Fa) -119.5 (Fb)	$CDCl_3$
		3.5				8.0 (5,6a) 3.0 (5,6b)	11.3							275.0	
						22.5 (Fb,5) 3.0 (Fa,5)									
 [158]		7.45	5.59			4.65	3.97 (6a,b)							-124.4 (Fa) -123.5 (Fb)	$CDCl_3$
		6.4												282.8	
			3.0 (Fa,b,2)			18.6 (Fa,5) 9.8 (Fb,5)									
 [158]		6.52	4.94	3.85		4.41	3.81 (6a) 3.95 (6b)							-125.1 (Fa) -121.4 (Fb)	$CDCl_3$
		5.6	5.6			7.7 (5,6a) 2.2 (5,6b)	11.0							256.3	
			5.6	8.0 (Fb,3)		23.7 (Fb,5)									

Table 5 (Continued)

 [89]	6.61	5.44	6.10	4.41	4.21	1.38	89.6	70.1	70.5	91.8	67.9	17.3		$CDCl_3$
	4.0	10.4	9.3	10.0	6.1			7.7	19.8	188.3	23.7			
	3.4	0.9	13.0	50.0	4.0	1.0								
 [159]	6.68	5.07	5.32	5.00	4.29	4.29 (6a,b)	87.8	67.5	68.5	85.8	71.3	60.9	-216	$CDCl_3$
	3.9	10.7	2.6	2.6					17.1	185.6	18.1			
			26.5	47.5										
 [160]	6.25						91.0	46.9	68.8	85.8	68.1	61.4	-219.4	$CDCl_3$
	4.0							2.4	18.6	186.6	18.6	6.1		
			26.4	50.3	26.4									
 [150]	4.45	3.90-4.12	5.19	5.02	3.90-4.12	4.64 (6a) 4.51 (6b)	103.1	69.4	71.2	86.3	73.5	61.9	-216.4	$CDCl_3$
	7.5	10.5	3.0		6.5 (5,6a) 7.5 (5,6b)	11.0			17.2	186.0	18.8	5.7		
	1.0		27.0	50.0	27.0	1.0 (F,6a)								

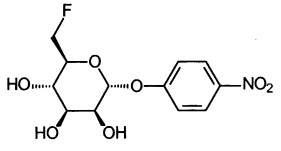
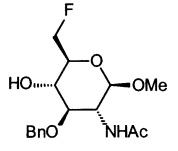
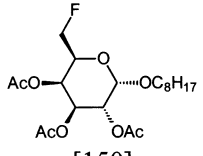
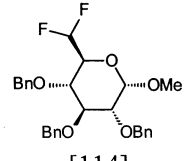
[a] For further examples (fluorine atom at C-4) see Refs. [161–163].

Table 6
NMR data for pyranoses with fluorine atom at C-5 [a]

Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [89]		6.80	5.66	6.15	2.93 (4b) 2.15 (4a)		1.64	90.1	70.3	65.3	39.5	112.8	26.5		$CDCl_3$
		4.0	10.4	5.1 (3,4b) 11.5 (3,4a)	13.6 (4a,4b)						30.5	225.6	25.7		
					34.8 (F,4a) 5.0 (F,4b)		17.8								
 [164]				2.27 (3a) 2.32 (3b)	5.24	4.83	4.07								$CDCl_3$
				13.3 (3a,3b) 11.5 (3a,4) 5.9 (3b,4)	2.1		9.5 (6,7)								
					21.3	50.9	27.8								

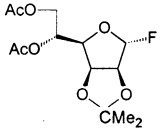
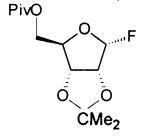
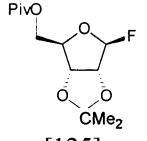
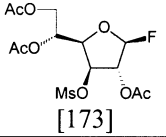
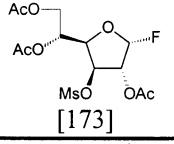
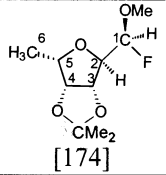
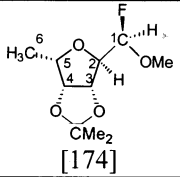
[a] For further examples (fluorine atom at C-5) see Refs. [165,166].

Table 7
NMR data for pyranoses with fluorine atom at C-6 [a]

Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F'}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [167]		5.60						98.5	70.4	69.6	75.2	73.4	82.4	-230.8	Me_2SO-d_6
		1.0									6.8	17.3	169.8		
						25.7	47.9 (F,6a,b)								
 [168]		4.87	3.21	4.13	3.58	3.54	4.68, 4.62 (6a,b)	103.7	57.5 or 56.0	84.1	71.0	76.2	84.1	-235.2	$CDCl_3$ (^1H, ^{19}F) CD_3CN (^{13}C)
		8.5	10.0	8.5		2.5 (5,6a) 4.5 (5,6b)	10.5				7.6	17.4	169.8		
						22.5	47.0 (F,6a,b)								
 [150]		4.48	5.22	5.03	5.44	3.87-4.01	4.51 (6a) 4.43 (6b)	101.4	69.0	70.9	67.2	71.6	80.9	-230.9	$CDCl_3$
		8.0	10.5	3.5	1.0	6.5 (5,6a) 5.5 (5,6b)	10				6.0	23.5	172.0		
						12.5	46.5 (F,6a,b)								
 [114]		4.63	3.53	4.01	3.58	3.84	5.76	97.9	79.4	81.5	76.6	68.6	113.6	-132.6 -135.2	$CDCl_3$
		3.6	9.7	8.7	8.4	1.1					4.8	19.9	243.8	283.7	
						18.4 (Fa,5) 8.7 (Fb,5)	54 (Fa,b,6)								

[a] For further examples (fluorine atom at C-6) see Refs. [169–172].

Table 8
NMR data for furanoses with fluorine atom at C-1 [a]

Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [74]		5.68	4.74	4.78	4.34	5.28	4.59 (6a) 4.16 (6b)	113.3	84.3	78.3; 80.0		68.6	62.7		$CDCl_3$
		0	5.9	3.8	8.1	5.1 (5,6b) 2.5 (5,6a)	12.5	222.7	41.8						
		59.2	6.2		<1.0										
 [125]		5.63	4.58-4.80	4.58-4.80	4.58-4.80	4.30 (5a) 4.17 (5b)		107.8	80.8	81.5	79.1	63.2		-130.0	$CDCl_3$
		3.5			3.5 (4,5a) 3.5 (4,5b)	12.1 (5a,5b)		236	20.6	2.2					
		64.5	15.1												
 [125]		5.76	4.72	4.80	4.52	4.05-4.20 (5a,b)		115.6	85.3	86.6	81.1	64.4		-116.4	$CDCl_3$
			6.0	6.0				223	40.6	2.7					
		61.9													
 [173]		5.76	5.39	5.18	4.75	5.30	4.21 (6b) 4.65 (6a)	111.6	78.8	76.0	80.1	68.0	62.5		$CDCl_3$
		0	0	5.1	10.1	2.2 (5,6a) 3.8 (5,6b)	12.6	229.3	35.6		2.3				
		61.0	3.8		5.4										
 [173]		6.00	5.26	5.30	4.66	5.31	4.13 (6b) 4.60 (6a)	106.9	78.1	76.2	77.7	67.2	62.3		$CDCl_3$
		3.8	3.5	5.0		2.5 (5,6a) 4.7 (5,6b)	12.3	235.5	19.4						
		61.6	14.6												
 [174]		5.16	4.09	4.92	4.57	4.16	1.28	111.8	83.4	81.4	82.3	78.4	14.4		$CDCl_3$
		2.7	1.1	6.1	4.0	6.4		221.5	29.2						
		63.3	8.0												
 [174]		5.20	4.00	4.92	4.58	4.10	1.28	111.8	83.9	81.5	82.3	78.5	14.4		$CDCl_3$
		2.3	1	6.1	3.6	6.3		221.5	21.4	3.3					
		67.2	25												

[a] For further examples (fluorine atom in anomeric position) see Refs. [175–179].

Table 9
NMR data for furanoses with fluorine atom at C-2 [a]

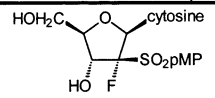
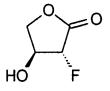
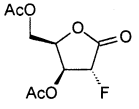
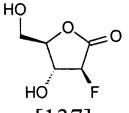
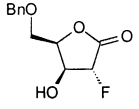
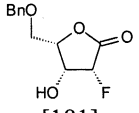
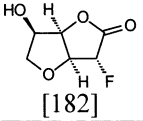
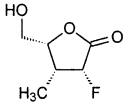
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [180]		6.46		4.65	3.58	3.78 3.72 (5a,b)		87.1	108.3	69.0	80.5	58.4		-171.0	Me_2SO-d_6
				9.0	2.0 (4,5a) 2.5 (4,5b)	13.0 (5a,5b)		38.8	229.0	16.2					
		22.5		21.5											
 [137]			5.12	4.78	4.54 (4a) 4.09 (4b)			170.6	90.9	70.7	69.1				$CDCl_3$
			7.0	7.0 (3,4a) 7.0 (3.4b)	9.5 (4a,4b)			22.0	194.0	21.0	11.0				
			51.0	17.0	1.0 (F,4a)										
 [137]			5.41	5.64	5.04	4.30 (5a) 4.26 (5b)		167.0	86.7	72.8	74.6	60.2			$CDCl_3$
			7.5	7.5	3.0 (4,5a) 3.0 (4,5b)	13.0 (5a,5b)		22.0	196.0	23.0	8.0				
			52.0	21.0		1.5 (F,5b)									
 [137]								172.6	92.8	71.7	81.8	60.1			D_2O
								22.0	196.0	21.0	10.0				
 [181]			5.32	4.73	4.64	3.89 3.89 (5a,b)		169.7	95.4	73.0	73.9	66.8		-198.7	$CDCl_3$
			7.4	8.1	1.8 (4,5a) 1.8 (4,5b)	11.2 (5a,5b)			192.8	21.7					
			52.8	22.0		2.2 (F,5b)									
 [181]			5.14	4.52-4.60	4.48-4.51	3.81-3.88 (5a,b)		170.2	86.5	68.3	73.8	67.5		-216.8	$CDCl_3$
			4.4						202.8	18.8					
			48.4												
 [182]			5.36	4.97	5.33			170.8	91.3	80.9	80.6	69.2	74.8	-189.3	acetone-d_6
			4.1	7.8	4.4			27.0	191.0	24.6	5.8				
			50.9	20.5											
 [96]			5.24		4.58	3.89 (5a) 3.80 (5b)		171.8	87.8	35.8	79.8	61.3		-208.5	$CDCl_3$
			7.0		7.2 (4,5a) 3.7 (4,5b)	12.1 (5a,5b)		22.2	198.5	18.3	5.6				
			51.0	11.0											

Table 9 (Continued)

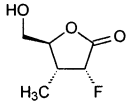
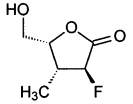
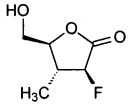
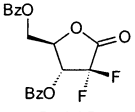
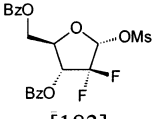
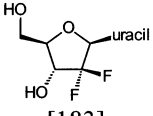
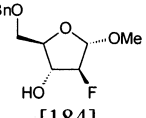
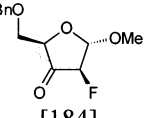
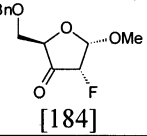
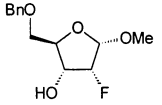
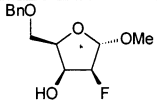
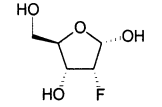
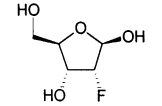
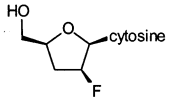
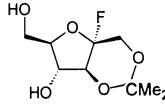
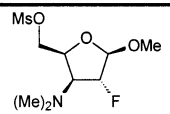
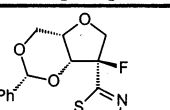
 [96]		5.25	2.6-2.85	4.32	3.98 (5a) 3.70 (5b)		172.5	87.6	35.5	85.8	61.8		-207.7	$CDCl_3$
		6.6		2.4 (4,5a) 3.0 (4,5b)	12.7 (5a,5b)		20.8	191.2	19.3					
		52.5	20.4											
 [96]		5.13	2.7-2.9	4.48	3.90 (5a) 3.72 (5b)			90.3	39.6	80.2	60.4		-194.5	$CDCl_3$
		10.0	8.2	2.4 (4,5a) 1.4 (4,5b)	12.7 (5a,5b)			190.3	19.2	8.0				
		53.4	26.0											
 [96]		4.84	2.6-2.8	4.05	3.92 (5a) 3.64 (5b)		171.2	91.7	37.4	82.2	60.8		-200.2	$CDCl_3$
		10.2	9.8	2.4 (4,5a) 4.6 (4,5b)	13.2 (5a,5b)		22.5	197.8	19.4	7.6				
		52.0	21.9											
 [183]			5.76	4.99	4.69 4.76 (5a,b)		162.5	111.6	69.5	78.5	62.3			$CDCl_3$
							32.1 33.6 (Fa,b,C)	258 263 (Fa,b,C)	15.7 30.7 (Fa,b,C)	5.6				
 [183]	6.13		5.57	4.84	4.66 4.76 (5a,b)		99.6	122.2	71.0	82.8	62.5			$CDCl_3$
							25.5 48.3 (Fa,b,C)	259 286 (Fa,b,C)	18.3 38.5 (Fa,b,C)					
 [183]	6.17		4.36	4.04	3.83 3.98 (5a,b)		86.8	124.9	72.1	83.4	62.2			D_2O
							24.4 40.0 (Fa,b,C)	257 261 (Fa,b,C)	19.3 27.2 (Fa,b,C)	7.1				
 [184]	5.06	4.82	4.00-4.20	4.00-4.20	3.62 (5a,b)		106.1	99.3	76.3	83.9	70.0			$CDCl_3$
	<1.0	<1.0		5.0 (4,5a) 5.0 (4,5b)			34.4	181.8	17.3	<2.0				
	10.0	50.0												
 [184]	5.32	4.58		4.30	3.84 (5a) 3.78 (5b)		103.2	88.4	205.9	78.1	69.0			$CDCl_3$
	1.5			1.5 (4,5a) 2.5 (4,5b)	10.0 (5a,5b)		28.9	189.2	13.4	<2.0				
	9.0	50.5		3.5										
 [184]	5.30	5.16		4.14	3.75 (5a,b)		98.2	89.4	205.1	76.5	68.0			$CDCl_3$
	4.5			2.5 (4,5a) 2.5 (4,5b)			14.6	209.9	27.3	3.7				
	<1.0	49.5		<1.0										

Table 9 (Continued)

 [184]	5.06	4.91	4.17	4.26	3.62 (5a,b)		101.5	88.5	70.1	84.3	69.7			$CDCl_3$
	4.0	5.5		3.0 (4,5a) 3.0 (4,5b)			16.5	201.0	15.9	2.1				
	<1.0	50.0												
 [184]	5.08	4.77	-	4.27	3.84 (5a) 3.75 (5b)		104.7	93.5	71.3	77.8	69.0			$CDCl_3$
	<1.0	4.5	6.5	3.5 (4,5a) 4.0 (4,5b)	11.0 (5a,5b)		30.0	185.1	16.0	<2.0				
	10.0	52.5												
 [138]	5.28	4.79	4.20	4.06	3.65 (5a) 3.56 (5b)								-217.5	acetone-d_6
	3.4	4.6	8.5	4 (4,5a) 3 (4,5b)	11.4 (5a,5b)									
	12.5	53.3	20.6											
 [138]	5.29	4.62	4.36	3.94	3.72 (5a) 3.59 (5b)		99.5	96.0	70.5	83.4	62.5		-207.9	acetone-d_6
	0.6	4.1	7.3	3.5 (4,5a) 3.5 (4,5b)			28	174	18					
	10.8	54.1	25.2											
 [185]	5.96	5.25	1.80-2.60 (3a,b)	4.25	3.65 (5a,b)		85.9	91.1	32.8	77.5	63.0			D_2O (^1H) Me_2SO-d_6 (^{13}C)
	3.0						16.0	185.0	20.0					
	19.0	53.0												
 [141]	3.98 (1a) 3.87 (1b)		4.25	4.12	4.35	3.80 (6a,b)	62.2	113.2	80.0			62.3		$CDCl_3$
	15.2 (1a,1b)		0.0				37.9	226	33.5					
	6.3 (F,1a) 5.2 (F,1b)		4.7											
 [186]	5.10	4.98	2.99	4.55	4.32 (5a) 4.21 (5b)		109.2	100.7	73.0	80.1	71.3		-190.3	CD_3CN
	2.6	7.1	7.2	2.8 (4,5a) 8.9 (4,5b)	11.3 (5a,5b)		35.9	181.0	20.4	8.6				
	15.6	53.6	28.2											
 [187]	4.74 (1a) 4.44 (1b)		4.94	4.26	4.29 (5a) 4.24 (5b)		74.1	102.2	78.7	73.3	61.0		-91.1	Me_2SO-d_6
	11.0 (1a,1b)		2.5	1.5 (4,5b)	12.5 (5a,5b)		22.0	177.1	34.5					
	41.0 (F,1a) 26.0 (F,1b)		8.0	3.8										

[a] For further examples (fluorine atom at C-2) see Refs. [188–190].

Table 10
NMR data for furanoses with fluorine atom at C-3 [a]

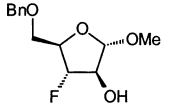
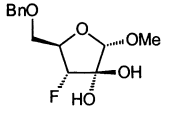
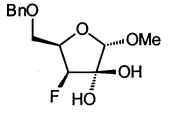
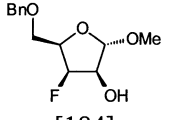
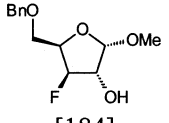
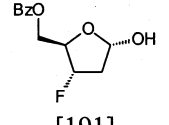
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [184]		4.87	4.04	4.77	4.33	3.66 (5a) 3.61 (5b)		110.1	77.7	97.3	83.2	69.3			$CDCl_3$
		<1.0	<1.0	1.8	2.4 (4,5a) 2.4 (4,5b)	10.8 (5a,5b)		<2.0	24.4	187.4	27.1	9.1			
			12.9	51.6	26.1										
 [184]		4.67		4.49	4.40	3.69 (5a,b)		106.0	99.2	93.7	81.5	69.3			$CDCl_3$
				1.8	3.6 (4,5a) 3.6 (4,5b)			<2.0	18.3	191.6	26.0	8.1			
				54.0	26.4										
 [184]		4.86		4.70	4.48	3.74 (5a) 3.68 (5b)		98.1	99.2	86.7	76.4	67.6			$CDCl_3$
				2.8	5.5 (4,5a) 6.0 (4,5b)	10.0 (5a,5b)		<2.0	18.3	195.8	26.0	<2.0			
		1.2		54.0	27.2	1.8 (F,5b)									
 [184]		4.86	4.10	5.26	4.35	3.75 (5a) 3.63 (5b)		108.1	74.8 or 76.6	91.2	74.8 or 76.6	67.1			$CDCl_3$
		1.8	5.1	5.7	4.2 (4,5a) 3.6 (4,5b)	10.8 (5a,5b)		<2.0	15.8 or 14.0	192.2	15.8 or 14.0	9.2			
		1.8	7.2	53.7	15.9	1.8 (F,5a) 1.8 (F,5b)									
 [184]		5.07	4.36	4.94	4.38	3.71 (5a) 3.64 (5b)		101.7	76.5 or 77.3	97.1	76.5 or 77.3	67.4			$CDCl_3$
		4.9	2.4	3.7	4.9 (4,5a) 6.7 (4,5b)	10.5 (5a,5b)		4.5	28.9 or 20.4	181.2	28.9 or 20.4	10.4			
			19.6	52.8	25.0	1.2 (F,5b)									
 [191]		5.67	2.30 (2a) 2.36 (2b)	5.24	4.79	4.38 (5a) 4.41 (5b)		99.1	40.3	94.5	82.2	63.8		-173.6	$CDCl_3$
		5.2 (1,2a) <0.3 (1,2b)	5.5 (2a,3) <0.9 (2b,3) 15.0 (2a,2b)	1.2	5.0 (4,5a) 4.5 (4,5b)	11.6 (5a,5b)			20.7	177.4	25.8	10.0			
			39.0 (F,2a) 23.0 (F,2b)	55.0	25.1										

Table 10 (Continued)

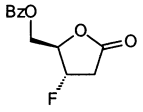
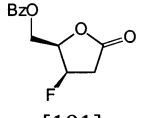
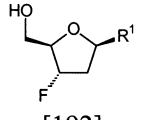
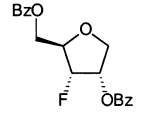
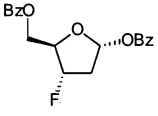
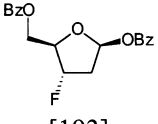
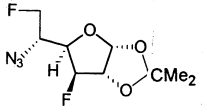
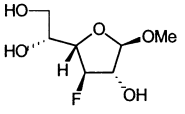
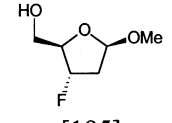
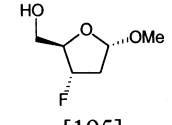
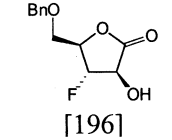
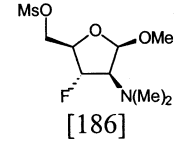
 [191]		2.84 (2a) 3.00 (2b)	5.36	5.01	4.52 (5a) 4.65 (5b)		173.2	35.8	90.0	82.5	63.1			$CDCl_3$
		19.0 (2a,2b) 1.4 (2a,3) 5.8 (2b,3)		3.9 (4,5a) 3.1 (4,5b)	12.5 (5a,b)			23.9	182.4	27.0	10.7			
		27.0 (F,2a) 33.0 (F,2b)	53.0		1.5 (F,5a)									
 [191]		2.91 (2a,b)	5.48	4.85	4.62 (5a) 4.80 (5b)			36.5	88.8	81.0	61.7		-195.9	$CDCl_3$
								25.0	186.0	20.0	14.0			
			53.0											
 [192]	6.33	2.50 (2a,b)	5.34	4.10	3.53 (5a,b)		82.3	37.0	95.2	84.5	61.2		-177.1	Me_2SO-d_6
								20.4	173.3	22.2	11.6			
			53.9	27.9										
 [193]	4.40-4.64 (1a) 4.06 (1b)	5.48	5.28	4.40-4.64	4.40-4.64 (5a,b)		69.2	71.7	90.4	80.2	63.8			$CDCl_3$
	9.5 (1a,1b) 6.5 (1b,2)	5.0	3.5				< 1.0	14.6	192.0	24.8	7.3			
	1.5 (F,1b)	13	53.5											
 [193]	6.74	2.60 (2a) 2.50 (2b)	5.32	4.84	4.52 (5a) 4.43 (5b)		98.7	39.4	93.1	84.1	63.6			$CDCl_3$
	<1.0 (1,2a) 5.4 (1,2b)	15.6 (2a,2b) 1.2 (2a,3) 5.4 (2b,3)	1.2	4.2 (4,5a,b)	12.0 (5a,5b)		<1.0	21.0	180.8	26.9	10.0			
		38.4 (F,2b) 22.8 (F,2a)	55.2	27.6										
 [193]	6.73	2.64, 2.78 (2a,b)	5.43	4.70	4.50 (5a) 4.46 (5b)		99.2	39.4	93.5	83.3	63.6			$CDCl_3$
	3.5, 5.5 (1,2a,b)	15.6 (2a,2b) 3.5, 5.5 (2a,b,3)	2.0	5.4 (4,5a,b)	12.0 (5a,5b)		<1.0	21.8	181.5	25.2	8.9			
		27.6, 25.8 (F,2a,b)	54.6	21.6										

Table 10 (Continued

 [194]	5.96	4.72	5.06	4.08	3.8-3.9	4.60 (6a) 4.79 (6b)	104.2	81.1	92.7	78.0	57.8	82.5		$CDCl_3$
	3.7	0	2.1	10.0	6.5 (5,6a) 2.4 (5,6b)	9.9		32.4 (F3,C)	185.5 (F3,C)	19.7 (F3,C)	7.2 (F3,C) 18.4 (F6,C)	173.3 (F6,C)		
	0	10.5 (F3,2)	49.9 (F3,3)	27.4 (F3,4)		47.1 (F6,6a) 46.6 (F6,6b)								
 [162]	4.48	3.80	4.42	3.78	3.39	3.22 (6a) 3.14 (6b)	109.3	83.7	98.3	79.1	71.8	63.4	-188.9	D_2O
		1.9	4.0	4.6	4.2; 6.8 (5,6a,b)	11.8	4.3	27.4	182.4	25.3	6.4			
		16.6	54.8	24.5										
 [195]	5.16	2.18 (2a) 2.34 (2b)	5.21	4.17	3.47 (5a) 3.56 (5b)		106.3	40.4	95.6	86.3	63.2			acetone-d_6
	3.4 (1,2a) 5.7 (1,2b)	15.0 (2a,2b) 5.9 (2a,3) 2.5 (2b,3)	1.2	7.1 (4,5a) 5.1 (4,5b)	11.4 (5a,5b)			21.6	175.6	22.6	10.0			
		29.0 (F,2a) 29.6 (F,2b)	55.0	23.6	5.8 (F,5a) 6.2 (F,5b)									
 [195]	5.06	2.06 (2a) 2.24 (2b)	5.08	4.19	3.53 (5a) 3.63 (5b)		105.8	40.1	94.6	85.5	62.4			acetone-d_6
	0.8 (1,2a) 5.5 (1,2b)	14.9 (2a,2b) 1.0 (2a,3) 6.7 (2b,3)	2.1	4.2 (4,5a) 4.2 (4,5b)	11.8 (5a,5b)			21.1	177.6	23.6	9.6			
		26.1 (F,2a) 35.9 (F,2b)	56.4	26.2	5.5 (F,5a) 6.2 (F,5b)									
 [196]		4.50-4.70	5.17	4.50-4.70	3.79 (5a,b)		173.6	91.8 or 95.5	76.2	91.8 or 95.5	67.8			$CDCl_3$
		4.4	4.2						379.2					
			53.2											
 [186]	4.92	2.81	5.05	4.21-4.40	4.21-4.40 (5a,b)		105.6	74.9 or 80.7	97.7	74.9 or 80.7	71.6		-186.4	CD_3CN
	4.4	7.0	4.4				10.7	18.7 or 29.1	182.0	18.7 or 29.1	5.7			
	0	25.8	57.6	25.2										

[a] For further examples (fluorine atom at C-3) see Refs. [197–201].

Table 11
NMR data for furanoses with fluorine atom at C-4

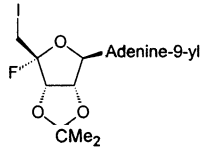
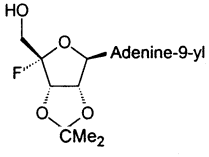
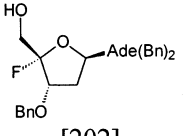
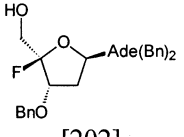
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [202]		6.30	5.29	5.49		3.46-3.65 (5a,b)								-103.7	$CDCl_3$
		1.0	6.4												
				12.2		13.5 16.5 (F,5a,b)									
 [202]		6.26	5.16	5.50		3.90 (5a,b)								-114.9	$CDCl_3$ (^1H) CD_3OD (^{19}F)
		2.5	7.0												
				9.0		12.2 12.2 (F,5a,b)									
 [202]		6.46-6.54	2.90-3.03 (2a) 2.57-2.68 (2b)	4.84-4.96		4.02 (5a) 3.87 (5b)								-124.5	$CDCl_3$
		6.2 (1,2a) 6.8 (1,2b)	5.1 (2b,3) 7.1 (2a,3) 13.2 (2a,2b)			11.9 (5a,5b)									
		1.8		8.6		1.6 (F,5a) 1.5 (F,5b)									
 [202]		6.86-6.92	2.80-2.90 (2a) 2.59-2.70 (2b)	4.47		3.96-4.06 (5a,b)								-107.5	$CDCl_3$
		6.5 (1,2a) 7.5 (1,2b)	4.4 (2b,3) 14.2 (2a,2b)												
		7.5		4.4											

Table 12
NMR data for furanoses with fluorine atom at C-5

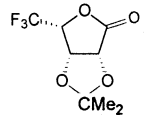
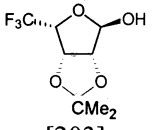
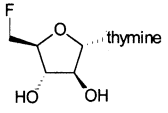
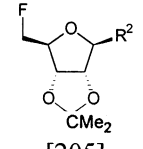
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [203]			4.93	5.01	4.78			171.7	75.6 or 74.3	75.6 or 74.3	75.1	121.7		-72.5	$CDCl_3$
			5.4	4.1							35.0	279.8			
					5.8										
 [203]		5.55	4.68	4.96	4.47			101.5	84.9	78.6	77.6	123.0		-71.2	$CDCl_3$
			5.8	4.2						0.6	32.4	279.0			
					6.3										
 [204]		5.89	4.39	4.18	4.52	4.63 (5a,b)		92.8	81.0	76.0	85.8	83.3			CD_3OD
		4.6	4.6							6.4	19.2	170.3			
					21.4	48.2									
 [205]		6.17	5.26	4.91	4.26	4.62 (5a,b)		91.5	82.7	79.7	85.1	81.8			Me_2SO-d_6
		2.0								7.5	18.7	167.0			

Table 13
NMR data for furanoses with fluorine atom at C-6

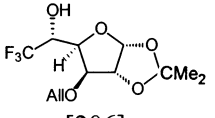
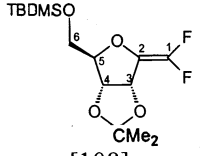
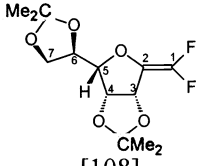
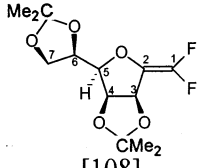
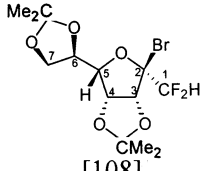
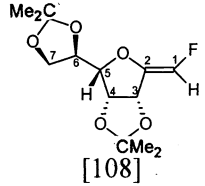
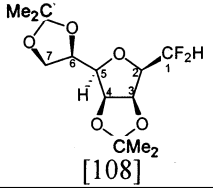
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [206]		5.72	4.30	3.75	4.26	4.21		105.2	82.4	82.9	76.8	68.7	124.4	-78.0	C_6D_6
		3.8	0	3.4	5.3							31.0	281.6		
						6.5									

Table 14
NMR data for furanoses with fluorine atom in 1′-position

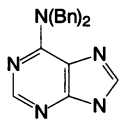
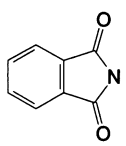
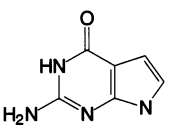
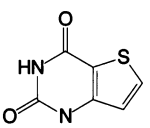
Structure	δ [ppm]	H-1	H-2	H-3	H-4	H-5	H-6	C-1	C-2	C-3	C-4	C-5	C-6	F	Solvent
	J [Hz]	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6a,6b}$	$J_{F,C-1}$	$J_{F,C-2}$	$J_{F,C-3}$	$J_{F,C-4}$	$J_{F,C-5}$	$J_{F,C-6}$	$J_{F,F}$	
		$J_{F,1}$	$J_{F,2}$	$J_{F,3}$	$J_{F,4}$	$J_{F,5}$	$J_{F,6}$								
 [108]				5.28	4.81	4.45	3.77 3.72 (6a,b)	149.9	121.4					-105.6 -122.6	$CDCl_3$
				6.1			11.2	285 270 (Fa,b,C)	19.0 13.0 (Fa,b,C)						
														98.0	
 [108]				5.34	4.71	3.96	4.42	150.4	118.8					-100.4 -117.5	$CDCl_3$
				6.1	4.2	8.4	6.7 (6,7a) 7.0 (6,7b)	290 274 (Fa,b,C)	49.0 14.0 (Fa,b,C)						
														83.0	
 [108]				5.35	4.86	3.92	4.46	150.4	118.8					-102.0 -118.0	$CDCl_3$
				6.0	3.8	7.8	5.6 (6,7a) 4.9 (6,7b)	288 274 (Fa,b,C)	49.0 14.0 (Fa,b,C)					83.0	
 [108]		5.88		5.22	4.86	4.29	4.45	110.9	103.6					-123.8 -129.6	$CDCl_3$
				5.6	4.2	8.3	6.6 (6,7a) 6.6 (6,7b)	250 244 (Fa,b,C)	35.0 22.0 (Fa,b,C)					293.0	
		56.9, 53.7 (Fa,b,1)													
 [108]		6.37		5.10	4.69	4.07	4.42							-160.0	$CDCl_3$
				6.1	4.4	8.3	6.7 (6,7a) 6.7 (6,7b)								
		74.7													
 [108]		5.90	3.69	4.83	4.83	3.60	4.41	114.5	80.1					-127.8	$CDCl_3$
		6.6			3.2	7.8	5.8 (6,7a) 4.6 (6,7b)	243 238 (Fa,b,C)	23.0 23.0 (Fa,b,C)						
		57.4, 53.5 (Fa,b,1)													

4. NMR tables

Table 2 [114–126], Table 3 [72,115,116,131–141], Table 4 [116,135,145–151], Table 5 [89,150,157–160], Table 6 [89,164], Table 7 [114,150,167,168], Table 8 [74,125,173,174], Table 9 [96,137,138,141,180–187], Table 10 [162,184,186,191–196], Table 11 [202], Table 12 [203–205], Table 13 [206], and Table 14 [108] give NMR data of selected examples of fluorinated carbohydrates, which include the most common pyranoses and furanoses available in the literature since 1989. The chemical shifts are referred to TMS (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F).

Glossary

List of used abbreviations:

Ade(Bn)$_2$		Piv	2,2-Dimethylpropanoyl
NPht		R^1	
pMP	4-Methoxyphenyl	R^2	
		Theo	Theophylline

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