Reference Data

Carbon-13 NMR Spectra of Isocoumarin, N-Methyl-1(2H)-isoquinolinone and Related Compounds

The ¹³C NMR spectra of isocoumarin, *N*-methyl-1(2*H*)-isoquinolinone and 14 of their 3- and/or 4-substituted derivatives were measured and assigned with the aid of various spectral techniques. The values of the one-bond and some of the long-range ¹³C-¹H coupling constants are reported. The effect of substitution on the ¹³C chemical shifts is discussed.

INTRODUCTION

A number of papers have been published on the ¹³C NMR spectral data of coumarin derivatives, ^{1,2} chromones, flavones and related compounds.³⁻⁷ However, no reports on the ¹³C NMR spectra of isocoumarin, 1(2H)isoquinolinone (isocarbostyril) or their substituted derivatives have been published [except for the ¹³C chemical shifts of four 3and 4-phenyl (or aryl)-substituted isocoumarins⁸]. The ¹H NMR data for such types of compounds are also very scarce.^{9,10}

In this paper the ¹³C chemical shifts, the one-bond and some of the long-range ¹³C-¹H coupling constants for isocoumarin, *N*-methyl-1(2*H*)-isoquinolinone and a series of their 3- and/or 4-methoxycarbonyl, carboxy and —NHCOOCH₃ derivatives have been measured and assigned using broad-band, gated, selective and off-resonance decoupling techniques, ¹³C chemical shift data of model compounds and charge density/ chemical shift correlations.

RESULTS AND DISCUSSION

The ¹³C NMR chemical shifts and one-bond carbon-hydrogen coupling constants are given in Table 1. Some of the long-range ¹³C-¹H coupling constants which could be determined are presented in Table 2. For isocoumarin (1), the assignment of C-3 and C-4 was carried out by comparison of the chemical shifts with those of the 3- and 4-substituted analogues (e.g. 2 and 3). C-3 is also characterized by its large ${}^{1}J(CH)$ value (similar to C-2 in chromone¹¹). The ${}^{3}J(C-4, H-5)$ value is similar to that in coumarins.^{11,12} Of the aromatic CHcarbons, C-5 is the only one which, in addition to the meta-coupling, showed additional vicinal coupling to H-4 (3.5 Hz)¹². An attempt to differentiate between the alpha (C-5,8) and beta (C-6,7) aromatic carbons according to a procedure described in Ref. 13 did not give convincing results for isocoumarin. C-8 was identified by selective decoupling, since H-8 resonates at lower field (8.27 ppm) than the other aromatic protons (7.4-7.7 ppm), as in chromone and

similar structures.14 Of the remaining CH carbons, C-6 is expected to give a signal at lower field than C-7 on the basis of substituent effects in benzenes.14 This assignment is also supported by the larger electron charge density on C-7 as calculated by the INDO method.¹⁵ The assignment of the quaternary carbons C-9,10 was carried out analogously on the basis of chemical shift considerations and their correlation with charge densities. Additional proof was obtained from the proton-coupled spectra, where both carbons appeared as quartets $[{}^{3}J(CH) \approx 6-7 \text{ Hz}]$ in **1**. In the 3-substituted derivative 2, however, C-10 is reduced to a triplet and C-9 remains practically unchanged, whereas for the 4-substituted compound 3 the opposite is true. The signal of C-1 in the proton-coupled spectrum is a complex unresolved multiplet. The spectra of the substituted isocoumarins fully support the above considerations.

The ¹³C NMR spectra of the *N*-methyl-1(2*H*)-isoquinolinones are similar to those of the isocoumarins and the assignment was performed in an analogous manner. In **11**, C-8 was also identified by selective decoupling at 8.43 ppm. The C-3 signal in the proton-coupled spectrum is split into a quintet (separation *ca* 3.8 Hz) by geminal coupling to H-4 and vicinal coupling to the NCH₃ protons.¹¹ For **12**, the exocyclic carbonyl gives a quintet with a separation of *ca* 4.0 Hz.¹¹ In **13**, C-4 is a doublet with a splitting of 3.4 Hz.

Considering the influence of substituents on the ¹³C chemical shifts of isocoumarins, the rather unusual α shielding effect (ca 1.5 ppm) of the carboxyl and methoxycarbonyl groups in the 3-position should be noted (compounds 4 and 2, respectively). The α effect of the 4-NHCOOCH₃ group in isocoumarin and N-methyl-1(2H)-isoquinolinone is similar (+9–10 ppm). The β effect of the COOH and COOCH3 substituents in both types of heterocycles is larger (+5-10 ppm) than the corresponding α effects. The γ steric effect of 4-COOH or COOCH₃ groups on C-5 is small (<1 ppm), whereas that of 4-NHCOOCH₃ is significant (ca -3 ppm). Steric shifts of a similar order are also observed for the NCH₃ carbon in the 3-substituted compounds 12 and 14.

The chemical shifts of the carbonyl groups are also of importance for assignment purposes, in addition to the long-range C-H coupling data. The C-1 signal of the substituted isocoumarins studied appears at 159-161 ppm, except in **8** (steric effect) and isocoumarin itself (probably an electronic effect). For the N-methyl-1(2H)-isoquinolinones the range for C-1 is 161.5-162.7 ppm. In isocoumarins the 3-COOR signal ($R = H, CH_3$) appears at ca 160 ppm, and that of 4-COOR around 165 ppm. For the isoquinolinones the distinction is not so clear, both signals being at 163.3– 166.4 ppm (Table 1). The characteristic one-bond carbon-proton coupling constants are the high values for C-3 (200-204 Hz for isocoumarins and 178–183 Hz for isoquinolinones) and, to some extent, also those for C-4 (167–174 Hz for both types of compounds). Practically all the ${}^{1}J(CH)$ values for the aromatic carbons fall in the range 161–167 Hz.

EXPERIMENTAL

Natural abundance FT ¹³C NMR spectra were obtained at ambient temperature (297 K) on a Bruker WM-250 spectrometer operating at 62.896 MHz. Typical conditions were: memory size, 16 K; pulse width, *ca* 30°; relaxation delay, 2 s; and digital resolution, 2 Hz (0.5 Hz for the protoncoupled spectra). The concentrations of the solutions were 0.5–1 M using TMS as internal (CDCl₃ solutions) or external (DMSO d_6 solutions) standard. The C-H coupling constants were estimated by first-order analysis and their signs were not determined.

The 1 H NMR spectra were measured at 60 MHz (unless indicated otherwise) and referenced to internal TMS.

The preparative methods and the physical properties of most of the compounds studied are summarized in Table 3.

3-Carboxy-4-methoxycarbonylisocoumarin (7)

A solution of dimethyl homophthalate (1.2 g) in benzene (19 ml) and diethyl oxalate (0.9 g) was added to cooled dry sodium methylate (prepared from 0.15 g of sodium) and the mixture left overnight. After treatment with water, the aqueous layer was acidified with hydrochloric acid and extracted with diethyl ether. The solvent was removed and the residue heated at 105 °C for 2 h (negative reaction with aqueous FeCl₃). After addition of 10 ml of concentrated hydrochloric acid the mixture was heated at 80 °C for 2 h, then poured into water to yield 1.6 g (85%) of the product (7). Calculated for $C_{12}H_8O_6$ (248.18):C 58.07, H 3.25%. Found: C 58.18, H 3.57%.

N-Methyl-1(2H)-isoquinolinone (11)

To 0.725 g (5 mmol) of 1(2H)-isoquinolinone suspended in 20 ml of methylene chloride were added 1.55 ml (25 mmol) of methyl iodide, 1.140 g (5 mmol) of benzyltriethylammonium chloride and 5 ml of 50% aqueous sodium hydroxide solution. The reaction mixture was vigorously stirred at room Table 1. ¹³C NMR data for isocoumarins (1-10) and N-methyl-1(2H)-isoquinolinones (11-16)

| R |
|-------------|
| |
| v o o |
| |

| | | | | | | U ¹³ r chamical chiffe | o pue (muu) | ne hond ¹³ r | ailanos u ¹ . | a constants (| H- in narent | hacac) | | | |
|----------------------|--------------------|-------------------------------|----------------------|---------------------|--|--------------------------------------|-------------|-------------------------|--------------------------|-------------------|-------------------|-------------------|--------------------|--------|--------------|
| Compound | × | ų | R | Solvent | сн ₃ | COR | C-1 | C-3 | C.4 | C-5 | C-6 | C-1 | C-8 | 6-3 | C-10 |
| ٦ | 0 | I | I | cDCL | | | 162.06 | 144.77 | 107.00 | 125.61 | 134.77 | 128.58 | 129.62 | 122.02 | 136.56 |
| | (| | : | | 50 | | | (199.5) | (168.3) | (167.1) | (162.7) | (163.8) | (165.2) | | 10 |
| N | þ | cooch3 | r | വവം | 997.7G | 200.001 | -0G'N01 | 143.11 | 112.38 | (163.6) | 153.24 | 123.31 | (28.051 | 69.771 | 5 |
| m | 0 | I | соосн, | cDCI | 52.06 | 164.51 | 160.69 | 152.70 | 110.05 | 125.48 | 135.35 | 129.04 | 130.01 | 120.64 | 133.62 |
| | | | 0 | 0 | | | | (202.6) | | (169.2) | (161.9) | (164.1) | (166.2) | | |
| 4 | 0 | соон | I | DMSO-d ₆ | | 160.98 | 160.43 | 143.38 | 111.69 | 127.97 | 135.22 | 128.93 | 130.64 | 121.85 | 134.98 |
| 1 | C | : | 1000 | | | | | | (173.2) | (~165) 125.00 | (163.8) 127.27 | (165.5) 120.01 | (165.6) | 00055 | 1 |
| ß | c | I | HOOD | UMSO-a6 | | 12.691 | 160.23 | (204.2) | 10.601 | (166.1) | (163.5) | 128.84 (165.3) | (165.3) (165.3) | 119.89 | 33.4/ |
| 9 | 0 | соосн | COOCH | cDCI | 53.26(2 OCH ₃) | 160.15(3-COOCH ₃) | 159.13 | 141.21 | 118.77 | 125.49 | 135.49 | 130.31 | 131.13 | 121.97 | 32.77 |
| | | 7 | 0 | , | | 164.93(4-COOCH ₃) | | | | (165.3) | (165.2) | (164.7) | (165.7) | | |
| 7 | 0 | соон | coocH ₃ | DMSO-d ₆ | 52.89 | 160.40(3-COOH) | 159.02 | 141.52 | 117.53 | 125.06 | 135.76 | 129.43 | 131.14 | 121.21 | 132.21 |
| | | | | | | 164.59(4-COOCH ₃) | | | | (164.6) | (163.7) | (166.5) | (166.3) | | |
| 8 | 0 | соосн | н | cociª | 52.55(COOCH ₃) | 160.81 | 157.00 | 141.28 | 112.25 | 123.77 | 119.50 | 154.96 | 151.39 | 116.79 | 128.91 |
| | | | | | 56.46(8-OCH ₃) 61.55(7-OCH ₃) | | | | (171.7) | (165.1) | (161.0) | | | | |
| ő | 0 | NHCOOCH ₃ | I | DMSO-d ₆ | 52.27 | 152.60 | 160.23 | 147.49 | 113.65 | 125.39 | 135.32 | 126.21 | 128.70 | 117.30 | 39.02 |
| | | | | | | | | | (174.2) | (164.5) | (163.4) (| ~165) | (164.5) | | |
| 10° | 0 | I | NHCOOCH ₃ | DMSO-d ₆ | 51.98 | 155.68 | 160.43 | 142.35 | 117.22 | 122.16 | 135.07 | 128.91 | 129.19 | 119.97 | 35.28 |
| | | | | | | | | (202.8) | | (166.4) | (165.3) | (165.6) | (164.8) | | |
| 11 | NCH ₃ | т | т | cocis | 36.85 | | 162.62 | 132.44 | 105.90 | 125.88 | 131.98 | 126.78 | 127.73 | 126.31 | 37.25 |
| | | | | | | | | (177.9) | (167.0) | (161.3) | (160.5) | (162.1) | (164.1) | | |
| 12 | NCH ₃ | coocH ₃ | т | cDCI3 | 52.85(OCH ₃) | 163.29 | 162.71 | 133.01 | 112.47 | 127.19 | 132.46 | 128.07 | 129.04 | 127.07 | 34.40 |
| : | | : | | | 33.57(NCH ₃) | | | | (169.9) | (162.0) | (161.4) | (164.7) | (162.6) | | |
| 13 | NCH3 | I | cooch | cncia | 51.69(OCH ₃) 37 52(NCH ₂) | 165.39 | 162.42 | 140./4 (180.5) | 100.10 | 125.19 (165.8) | 132.83 (160.8) | (162.7) | 127.08 (163.9) | 90.621 | 5 |
| 14 | NCH | соон | н | DMSO-d ₆ | 34.17 | 165.00 | 162.62 | 135.41 | 111.34 | 128.39 | 133.50 | 128.05 | 129.62 | 126.91 | 35.41 |
| |) | | |) | | | | | (170.8) | (163.8) | (161.7) | (163.4) | (163.2) | | |
| 15 | NCH ₃ | I | соон | DMSO-d ₆ | 36.78 | 166.43 | 161.58 | 141.72 | 105.36 | 124.99 | 132.50 | 126.62 | 127.06 | 124.51 | 34.45 |
| | | : | | | | | | (182.2) | | (165.6) | (161.4) | (163.5) | (163.4) | | |
| 16 | NCH3 | T | NHCOOCH | DMSO-d ₆ | 52.88(OCH ₃) | 157.21 | 161.54 | 132.64 | 114.94 | 123.02 | 133.07 | 12/.81 | 128.24 | 125.88 | 36.32 |
| | | | | | 37.23(NCH ₃) | | | (183.1) | | (93.5) | (162.3) | (163.8) | (163.6) | | |
| ^a Upon ad | dition c | of benzene-d ₆ , 1 | the two carbo | nyls give sig | nals at 160.28 and | 160.34 ppm. | | | | | | | | | |
| | etnoxy al signs | compound. Me prohably di | ue to a minor | rotamer aho | ut the N-CO hon | d are also ohserved | | | | | | | | | |
| -> | | - firmania (oli | | | | a, are aree eree. | | | | | | | | | |

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| Table 2. S | ome long-r | ange ¹³ C- ¹ F | I coupling | constants (| Hz) for con | npounds 1- | 5 and 7-1 | 6 |
|------------|------------|--------------------------------------|------------|-------------|-------------|------------|-----------|---|
| Compound | C-1 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | Others |
| 1 | | 7.0 H-4 | 8.5 H-3 | 3.5 H-4 | 8.1 H-8 | 7.9 H-5 | 7.2 H-6 | |
| | | | 5.3H-5 | 7.2 H-7 | | | | |
| 2 | | 3.3 H-4 | 5.3 H-5 | 4.0 H-4 | 8.1 H-8 | 7.7 H-5 | 7.7 H-6 | |
| | | | | 7.3 H-7 | | | | |
| 3 | | | 4 H-3 | 6.7 H-7 | 8.1 H-8 | 8.0 H-5 | 7.2 H-6 | |
| | | | 5 H-5 | | | | | |
| 4 | 3.1 H-8 | 3.3 H-4 | 4.2 H-5 | 3,5 H-4 | 7.9 H-8 | 5.8 H-5 | 7.2 H-6 | |
| | | | | 6.7 H-7 | | | | |
| 5 | 6.5 H-3 | | | 6.1 H-7 | 7.9 H-8 | 7.7 H-5 | 7.3H-6 | |
| | 4.5 H-8 | | | | | | | |
| 7 | 3.5 H-8 | | 4.7 H-5 | 7.2 H-7 | 7.9 H-8 | 7.2 H-5 | 7.4 H-6 | ³ J(COOCH ₃) = 4.1 |
| 8 | | 3.7 H-4 | 5.2 H-5 | | | | | ³ J(C-10, H-6) = 8.5 |
| 9 | 3.9 H-8 | 1.8 H-4 | | 3.8 H-4 | 8.2 H-8 | 8.1 H-5 | 6.9 H-6 | $^{3}J(COOCH_{3}) = 4.0$ |
| | | | | 7.0 H-7 | | | | |
| 10 | | | | 7.2 H-7 | 7.8 H-8 | 8.0 H-5 | 7.1 H-6 | |
| 11 | | | 3.0 H-3 | 3.9 H-4 | 8.3 H-8 | 7.9 H-5 | 7.2 H-6 | |
| | | | 4.5 H-5 | 6.5 H-7 | | | | |
| 12 | | | 4.9 H-5 | 4.2 H-4 | 8.1 H-8 | 7.0 H-5 | 7.7 H-6 | |
| | | | | 7.2 H-7 | | | | |
| 13 | | | | 7.2 H-7 | 8.2 H-8 | 8.1 H-5 | 7.5 H-6 | |
| 14 | | | 4.2 H-5 | | 8.1 H-8 | | 7.2 H-6 | ³ J(COOH, H-4) = 4.1 |
| 15 | | 3.6 NCH ₃ | | 4.1 H-4 | 8.4 H-8 | 8.3 H-5 | 7.6 H-6 | ³ J(COOH, H-3) = 4.1 |
| 16 | | | | 7.0 H-7 | 8.3 H-8 | 7.6 H-5 | 7.4 H-6 | ³ J(COOCH ₃) = 3.6 |

Table 3. Methods of preparation, melting points and ¹H NMR data for compounds 1-8 and 11-15

| Compound | Method of preparation and (lit. m.p., °C) | M.p. (°C) (solvent) | ¹ H NMR data |
|----------|--|------------------------|--|
| 1 | Lit. ¹⁶ (45-46) | 4446 | 250 MHz, in CDCl ₂ : 6.50 d ($J = 5.6$, H-4), 7.27 d ($J = 5.6$, H-4), 7.27 d ($J = 5.6$, |
| | • • | (hexane) | H-3), 7.4–7.7 m (H-5, 6, 7), 8.27 m (H-8). |
| 2 | From 4 and CH ₂ N ₂ | 173-174 | In CDCl ₃ : 3.80 s (OCH ₃), 7.2–8.3 m (H-4,5,6,7,8). |
| | (172–173) ¹⁷ | (benzene-hexane) | |
| 3 | Lit. ¹⁶ (97–98) | 98-99 | In CDCl ₃ : 3.86 s (OCH ₃), 7.3-7.8 m (H-6, 7), 8.13 s (H-3), 8.23 m (H-8), 8.57 (H-5). |
| | | (benzene-hexane) | |
| 4 | Lit. ¹⁸ (236-237) | 236-237 | In DMSO-d ₆ : 7.62 s (H-4), 7.5–8.0 m (H-5, 6, 7), 8.19 m (H-8). |
| | | (ethanol) | · |
| 5 | Lit. ¹⁶ (244) | 243-244 | In DMSO-d ₆ :7.5–8.1 m (H-6, 7), 8.22 m (H-8), 8.37 s (H-3), 8.66 m (H-5). |
| | | (acetic acid) | |
| 6 | From 7 and CH ₂ N ₂ | 133134 | In CDCl ₃ : 3.96 s and 4.01 s (2 OCH ₃), 7.2–7.9 m (H-5, 6, 7), 8.32 m (H-8). |
| | (130.5–131.7) ¹⁹ – | (diethyl ether) | |
| 7 | See text | 218-219 | In DMSO-d ₆ : 3.99 s (OCH ₃), 7.2–8.0 m (H-6,7), 8.00 m (H-8), 8.32 m (H-5). |
| | | (chloroform) | |
| 8 | Lit. ²⁰ (174–176) | 175–176 | In CDCl ₃ : 3.93 s, 3H, and 3.96 s, 6H(3 OCH ₃), 7.3–7.4 m (H-4, 5, 6). |
| | | (benzene-hexane) | |
| 11 | See text | 54–55 | 250 MHz, in $CDCl_3$: 3.58 s (NCH ₃), 6.45d (J = 7.3, H-4), 7.04d (J = 7.3, H-3), |
| | (55.5-56) ²¹ | (diethyl ether-hexane) | 7.4–7.6 m (H-5, 6, 7), 8.43 m (H-8). |
| 12 | From 14 and CH ₂ N ₂ | 130–131 | In CDCl ₃ : 3.70 s (NCH ₃), 3.88 s (OCH ₃), 7.13 s (H-4), 7.3–7.6 m (H-5, 6, 7), 8.32 m |
| | (132–133) ²² | (benzene-hexane) | (H-8). |
| 13 | Lit. ²³ (131–131.5) | 131–132 | In CDCl ₃ : 3.53 s (NCH ₃), 3.80 s (OCH ₃), 7.2–7.7 m (H-6,7), 8.02 s (H-3), 8.29 m |
| | | (benzenehexane) | (H-8), 8.66 m (H-5). |
| 14 | Lit. ²⁴ (238) | 236-239 | In DMSO-d ₆ : 3.74 s (NCH ₃), 7.36 s (H-4), 7.5–8.0 m (H-5, 6, 7), 8.29 m (H-8). |
| | | (acetic acid) | |
| 15 | Lit. ²⁵ (262–263) | 260-263 | In DMSO-d ₆ : 3.66 s (NCH ₃), 7.4–7.9 m (H-6, 7), 8.29 m (H-8), 8.39 s (H-3), 8.82 m |
| | | (acetic acid) | (H-5). |

temperature and the process was controlled by thin-layer chromatography (silica gel G, diethyl ether-hexane 2:1). The organic layer yielded 0.500 g (63%) of the product (**11**).

The preparation and properties of compounds 9, 10 and 16 will be reported elsewhere.²⁶

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¹H NMR Spectra of the 2-Trifluoroacetyl Derivatives of Benzo[b]furan and Benzo[b]thiophene

The ¹H NMR spectra of the 2-trifluoroacetyl derivatives of benzo[b]furan and benzo[b]thiophene were recorded at 200 MHz in two solvents, chloroform and acetone. A long-range coupling constant, ⁵J(HF), between the fluorine nuclei of the trifluoroacetyl group and H-3, of a value higher than 1 Hz, was measured. From the comparison of the ¹H chemical shifts of, and the solvent effects on, the trifluoroacetvl compounds and those of the corresponding 2-acetyl derivatives, and on the basis of an empirical interpretation of the ⁵J(HF) coupling constant, a predominant Z conformation was tentatively assigned to these derivatives.

INTRODUCTION

Acetyl derivatives of aromatic and heteroaromatic systems have been extensively studied by NMR, especially in connection with their properties related to E, Z stereoisomerism.¹⁻¹¹ In this context the effect of the acetyl substituent on ¹H and

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 13 C chemical shifts and on 1 H¹H long-range coupling constants has been extensively studied^{2-6,8,10,11} and lanthanide-induced shifts on several acetyl derivatives of heterocyclic compounds followed.^{3,5,9,11} Less attention has been paid to the corresponding trifluoroacetyl derivatives.

Recently we explored the conformational properties of several organic carbonyl compounds^{5,8,12} and we have now studied the perturbation induced by the trifluoroacetyl group on the ¹H NMR parameters (chemical shifts and coupling constants) of heterocyclic compounds and the conformational properties of this group.

RESULTS AND DISCUSSION

We report results on the trifluoroacetyl derivatives of benzo[b]furan and benzo[b]thioAbstr. 83, 79080w (1975).

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phene, and compare them with those of the corresponding acetyl derivatives. From the parameters (Table 1) it appears that interring coupling constants are present: ${}^{5}J(37)$ is observed both in the benzo[b]furan and benzo[b]thiophene derivatives, and ${}^{4}J(34)$ only in **3** and **4**, i.e. in the benzo[b]thiophene ring. [This coupling constant was also found in the 2-CHO derivative, with a value of 0.22 Hz (chloroform- d_1 solution).] From the width of the experimental spectral lines it is assessed that this coupling in **1** and **2** should be not higher than 0.10 Hz.

These inter-ring coupling constants have been previously identified in benzo[b]heterocycles.^{13,14} The values of ${}^{5}J(37)$ have the same order of magnitude¹⁵ as those found in other benzo[b]heterocycles and in naphthalene.

A long-range ${}^{5}J(HF)$ is observed in 1 and

H-4 H-5 H-5 H-6 H-7 H-7 H-7

 $---R \qquad \begin{array}{c} 1 \quad X = 0 \quad R = COCF_3 \\ 2 \quad X = 0 \quad R = COCH_3 \\ 3 \quad X = S \quad R = COCF_3 \\ 4 \quad X = S \quad R = COCH_3 \end{array}$

Table 1. Chemical shifts (in ppm) relative to TMS and coupling constants (in Hz) for derivatives 1-4

| Compound | Solvent | Н-З | H-4 | H-5 | H-6 | H-7 | J(34) | J(37) | J (45) | J (46) | J(47) | J (56) | J(57) | J(67) | J(3F) |
|----------|---------------------------|-------|-------|-------|-------|-------|-------|-------|--------|--------|-------|--------|-------|-------|-------|
| 1 | Chloroform-d | 7.849 | 7.790 | 7.389 | 7.593 | 7.638 | | 0.952 | 8.035 | 1.261 | 0.803 | 7.108 | 0.939 | 8.531 | 1.396 |
| | Acetone-de | 8.178 | 7.964 | 7.471 | 7.703 | 7.744 | _ | 0.895 | 8.037 | 1.265 | 0.775 | 6.987 | 1.017 | 8.543 | 1.360 |
| 2 | Chloroform-d1 | 7.492 | 7.695 | 7.301 | 7.466 | 7.568 | | 0.921 | 7.925 | 1.248 | 0.792 | 7.211 | 0.851 | 8.464 | |
| | Acetone-d ₆ | 7.709 | 7.806 | 7.350 | 7.529 | 7.625 | | 0.962 | 7.954 | 1.264 | 0.804 | 7.258 | 0.841 | 8.474 | |
| 3 | Chloroform-d1 | 8.230 | 7.974 | 7.473 | 7.563 | 7.908 | 0.311 | 0.833 | 8.175 | 1.156 | 0.789 | 7.123 | 1.014 | 8.291 | 1.578 |
| | Acetone-d ₆ | 8.509 | 8.180 | 7.549 | 7.655 | 8.100 | 0.336 | 0.828 | 8.194 | 1.197 | 0.798 | 7.126 | 1.005 | 8.314 | 1.627 |
| 4 | Chloroform-d ₁ | 7.926 | 7.879 | 7.399 | 7.453 | 7.855 | 0.292 | 0.779 | 8.107 | 1.217 | 0.768 | 7.180 | 1.029 | 8.222 | — |
| | Acetone-d ₆ | 8.195 | 7.993 | 7.450 | 7.509 | 7.981 | 0.317 | 0.825 | 8.103 | 1.187 | 0.799 | 7.134 | 1.020 | 8.254 | _ |