

EXPERIMENTAL SECTION

General procedure for derivatization of amines:

Acetyl-d₃ chloride (78 μ L, 1.1 equiv.) was added at 0°C to a stirred solution of the studied amine (1 mmole) and triethylamine (167 μ L, 1.2 equiv.) in dry ether (0.1-0.2M) under argon atmosphere. The reaction mixture was stirred for 10 min, and the formed triethylamine hydrochloride precipitate was eliminated by filtration. Evaporation of the solvent followed, if necessary, by column chromatography on silica gel (elution with 1:1 AcOEt/cyclohexane) afforded the corresponding acetamide-d₃ (commonly 90-95% yield).

General procedure for diderivatization of amino acids:

Thionyl chloride (88 μ L, 1.2 equiv.) was added at -10°C to a stirred solution of the studied amino acid (1 mmole) in 1 mL of methanol-d₄. The reaction mixture was stirred for 1 h at -10°C then overnight at room temperature. After evaporation of the solvent, the crude aminoester hydrochloride was dissolved in dry dichloromethane (0.1-0.2M). After addition of triethylamine (306 μ L, 2.2 equiv.) at room temperature followed by addition of acetyl-d₃ chloride (78 μ L, 1.1 equiv.) at 0°C, the reaction mixture was stirred for 1 h. After filtration of the triethylamine hydrochloride precipitate, evaporation of the solvent followed, if necessary, by column chromatography on silica gel (elution with AcOEt) afforded the corresponding doubly derivatized amidoester (commonly 90-95% yield).

General procedure for preparation of ²H NMR samples:

Samples were prepared in 5 mm o.d. NMR tubes. PBLG was purchased from Sigma (degree of polymerization : 1352, mol. weight: 150000-350000). It should be noted that any degree of polymerization of PBLG up to 500 is efficient for the obtention of a liquid-crystalline phase.

PBLG (72 mg, 12% w/w ration in CH₂Cl₂) was introduced in the NMR tube. 0.15 mmole of amide or amido ester dissolved in dry dichloromethane (400 μ L) was added. The sample was mixed by centrifugation (2 min, 2000 rpm) of the tube alternatively placed in both directions (commonly 6 times up and down), until an homogeneous and birefringent solution was obtained.

General procedure for NMR spectra record:

Deuterium NMR spectra were recorded on a DSX 300 Bruker spectrometer, equipped with a multinuclear 10 mm probe operating at 46.01 MHz without field-frequency lock. Temperature was held at 300 K, using the Bruker BVT 3000 temperature regulation system (\pm 0.2 K). Samples were spun during acquisition.

Proton broad-band decoupling was achieved through the WALTZ composite pulse scheme. Typically, 2-4 Kwords interferograms were acquired using a 90° pulse and a small relaxation delay (0.5s). Under such conditions, 400 scans were enough to obtain a good signal-to-noise ratio. Zero filling was used to achieve good digital resolution but no apodization was applied.