

ELECTRONIC SUPPLEMENTARY INFORMATION.

Green biocatalytic synthesis of panthenyl monoacyl esters in Ionic Liquids and Deep Eutectic Solvents

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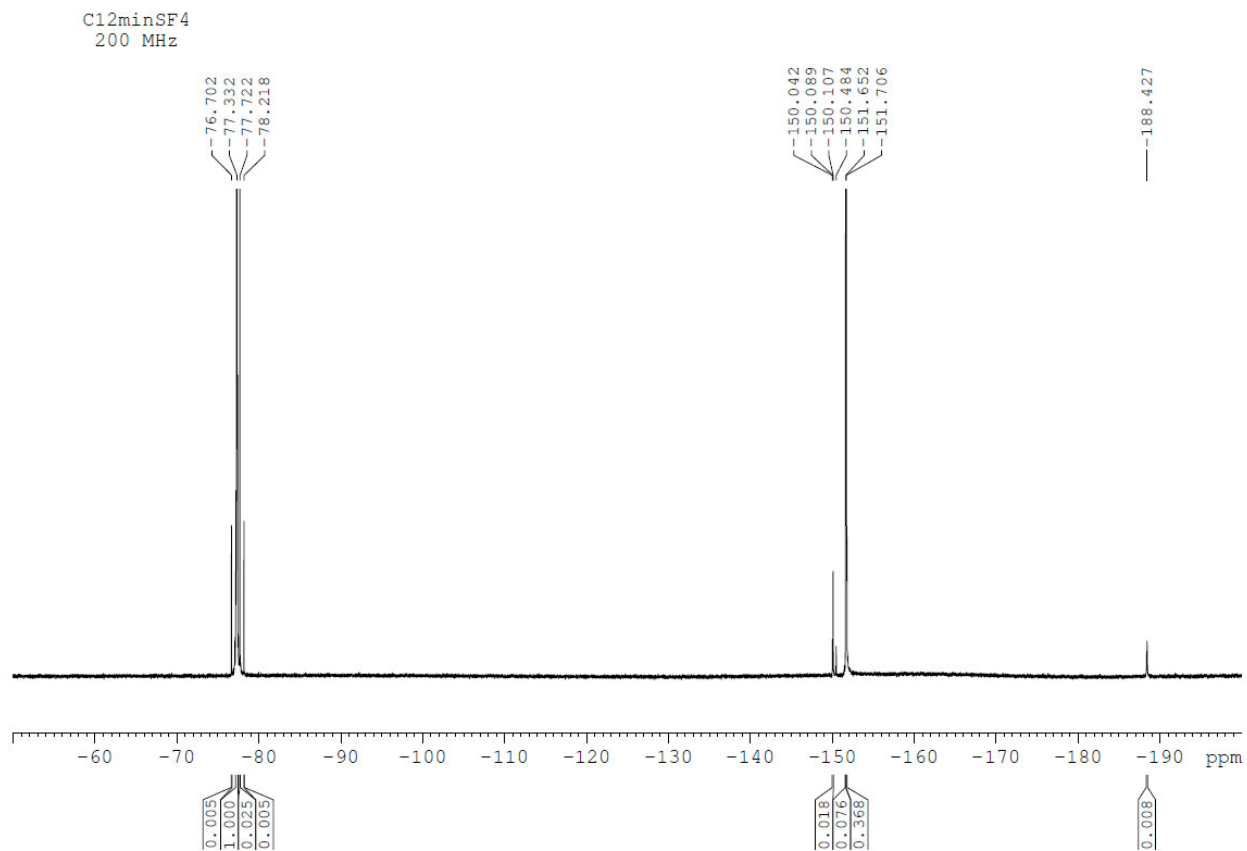
1. ¹⁹F NMR analysis for quantification of residual IL.

Samples preparation from reaction media containing SLILs

As representative example of SLILs in the resulting panthenyl acyl esters products from reaction mixtures reported in Table 1, the synthesis of panthenyl monolaurate in [C₁₂mim][BF₄] (entry 3), was selected for the determination of the residual IL content.

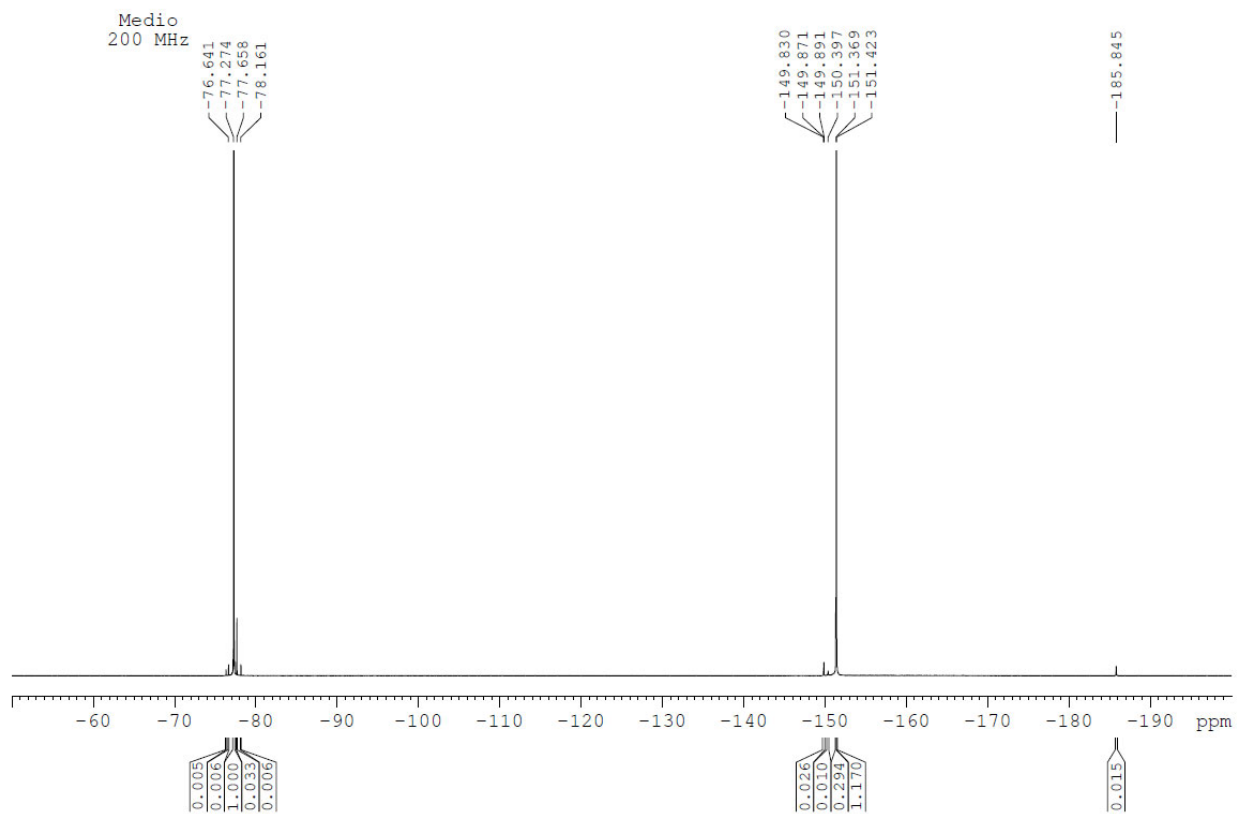
The reaction mixture was placed into a 2-mL vial, and then incubated at 60 °C until a fully clear and homogeneous phase was observed. Then, water (500 μL) and dodecane (500 μL) were added, and the resulting multiphase solution was strongly shaken for 30 min at 60°C, being finally cooled to 0°C into an ice bath. The panthenyl monolaurate/water/[C₁₂mim][BF₄] multiphasic mixture was consecutively centrifuged three times at 15,000 rpm (10 min) and at 0 °C, resulting in three phases, as follows: a dodecane phase containing panthenyl monolaurate product (top phase), an aqueous middle phase and a bottom phase containing the solid IL. Then, an aliquot (50 μL) was taken from the resulting top phase, being dissolved in 0.45 mL acetone-*d*₆ containing 40 μL trifluoroacetic acid (internal standard), and analyzed by 300 MHz ¹⁹F NMR in a Bruker AC 200E spectrometer. As standard reference, a sample (20 mg) of [C₁₂mim][BF₄] dissolved in 0.48 mL acetone-*d*₆, containing 40 μL trifluoroacetic acid, was also analysed to be used as reference.

Sample 1. Standard reference [C₁₂mim][BF₄]
¹⁹F-NMR spectrum

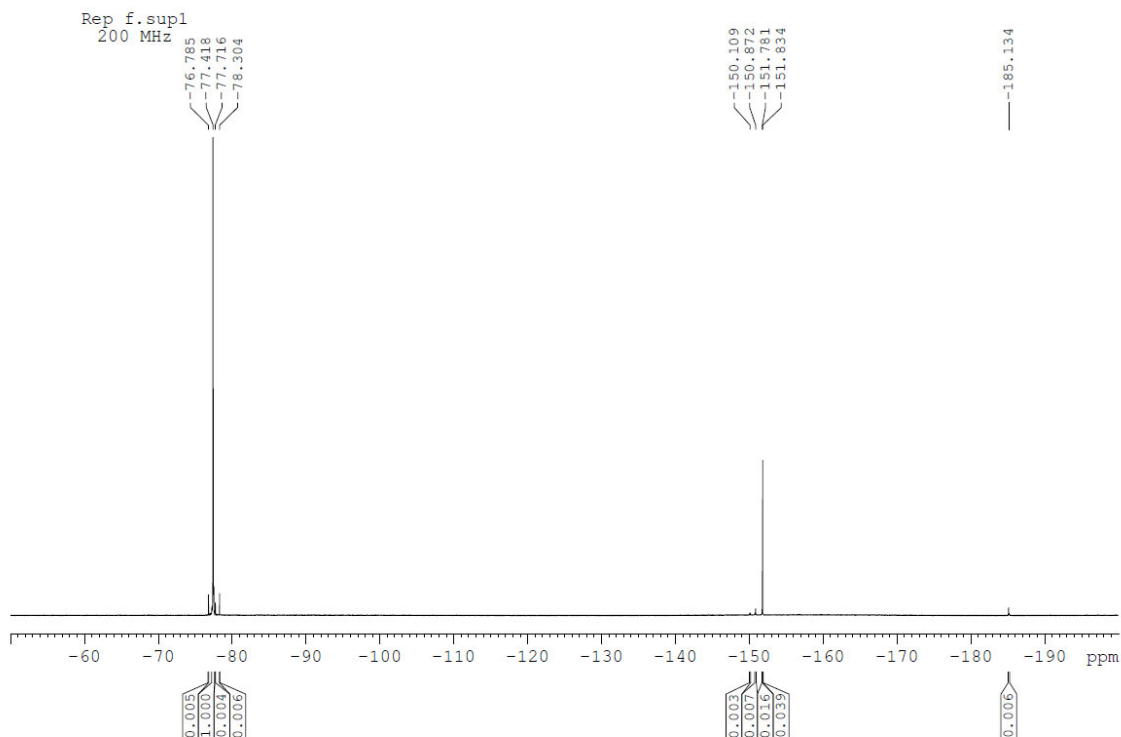


Sample 2. Reaction medium of Entry 3, Table 1(from [C₁₂mim][BF₄])

¹⁹F-NMR spectrum



Sample 3. Top-phase after the IL extraction from the reaction medium of Entry 3, Table 1 (from [C₁₂mim][BF₄])
¹⁹F-NMR spectrum



2. Extraction of unreacted panthenol and PME_s from DES.

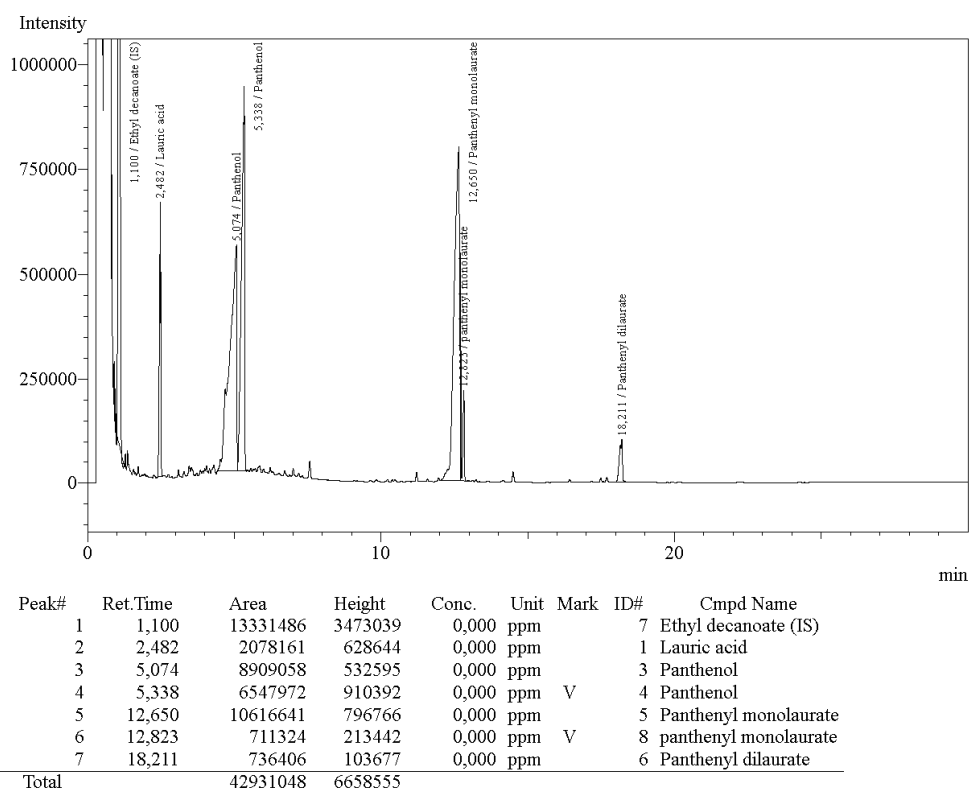
Samples preparation from reaction media based on DES_s for GC analysis

The reaction mixture resulted from the synthesis of panthenyl monolaurate in DES (see Table 2, entry 3) was selected as representative example. In agreement with the separation protocol reported in Experimental section 2.4, the following experimental procedure was carried out:

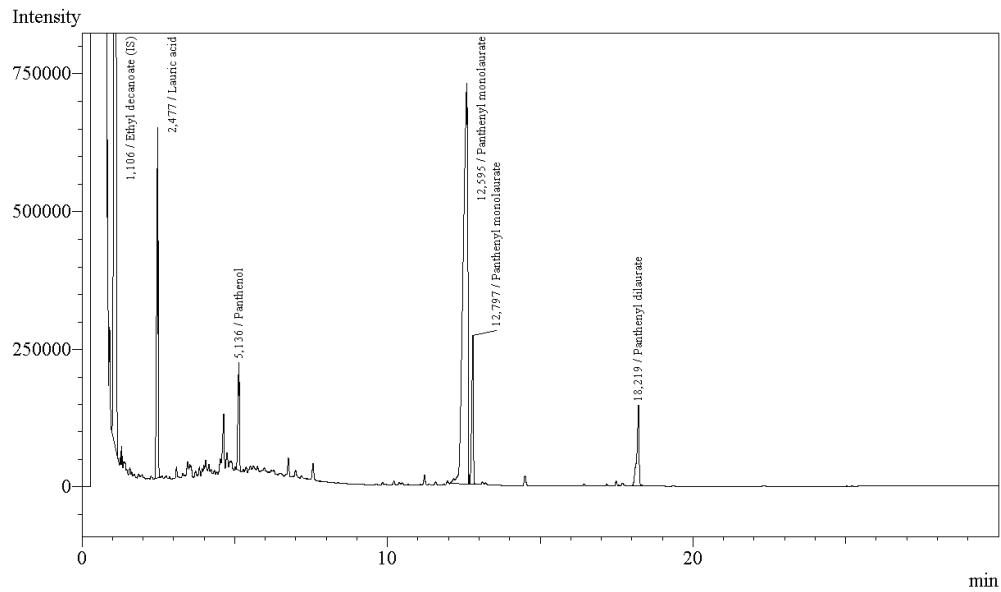
Into a 1 mL vial, a sample (20 μ L) of the PME_s reaction medium was dissolved in limonene (480 μ L), and the resulting mixture was strongly shaken for 60 min at 60°C. Then, the solution was cooled into an ice bath for 30 min, and followed by centrifugation (15,000 rpm, 10 min) at 0°C, resulting in a limonene phase containing the panthenyl monolaurate product (liquid top-phase), and a precipitated gel phase, consisting of unreacted panthenol (bottom-phase). For GC analysis, an aliquot (400 μ L) of the PME_s solution in limonene, obtained before and after the cooling/centrifugation protocol, was mixed with 200 μ L of the BSTFA+TMCS (99:1 v/v) reagent into a 2 mL screw-capped tubes with teflon-lined septa, and then incubated for 1 h at 70°C to carry out the trimethylsilylation of alcohols groups of panthenol and PME_s, as described in Experimental section 2.6. The derivatized samples (200 μ L) were diluted in 300 μ L

limonene: tetrahydrofuran (50:50 v/v), containing ethyl decanoate (50 mM, v/v as internal standard, IS) for GC analysis in a Shimadzu GC-2010 (Shimadzu Europe, Germany) equipped with an FID detector and automatic injector. Each sample (1 μ L injection volume) was analysed by using a TRB-biodiesel capillary column (10 m x 0.28 mm x 0.1 μ m, Teknokroma, Spain), in the following conditions: carrier gas (He) at 28.6 kPa (40 mL/min total flow), temperature injector, 290°C; temperature programme: 100°C, 10°C min⁻¹, 200 °C, 15 °C min⁻¹, 370°C, variable split ratio (80:1 to 10:1); detector temperature, 370°C (see section 2.6). The quantification of unreacted panthenol was calculated by comparison of panthenol/IS area ratio for samples obtained before and after the cooling/centrifugation protocol.

2.1. GC chromatogram: Sample of reaction medium in limonene (before the cooling / centrifugation protocol)



2.2. GC chromatogram: Sample of reaction medium in limonene (after the cooling/centrifugation protocol)

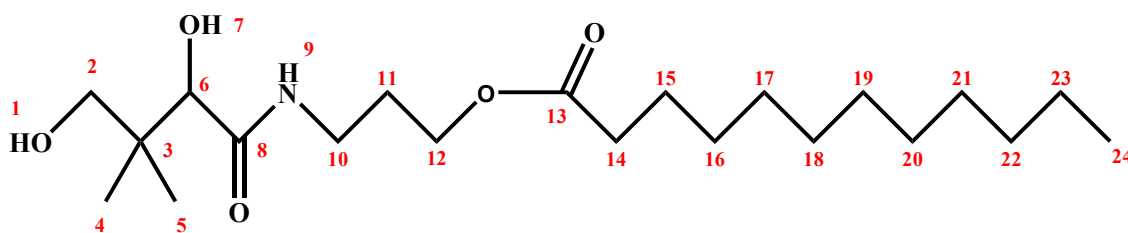


Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1,106	13748103	3383557	0,000	ppm		6	Ethyl decanoate (IS)
2	2,477	1997544	628120	0,000	ppm		1	Lauric acid
3	5,136	655476	192991	0,000	ppm		3	Panthenol
4	12,595	7585308	727058	0,000	ppm		4	Panthenyl monolaurate
5	12,797	988193	268024	0,000	ppm	V	4	Panthenyl monolaurate
6	18,219	728729	145194	0,000	ppm		5	Panthenyl dilaurate
Total		25703353	5344944					

3. ^1H NMR and ^{13}C NMR analysis of panthenyl monolaurate

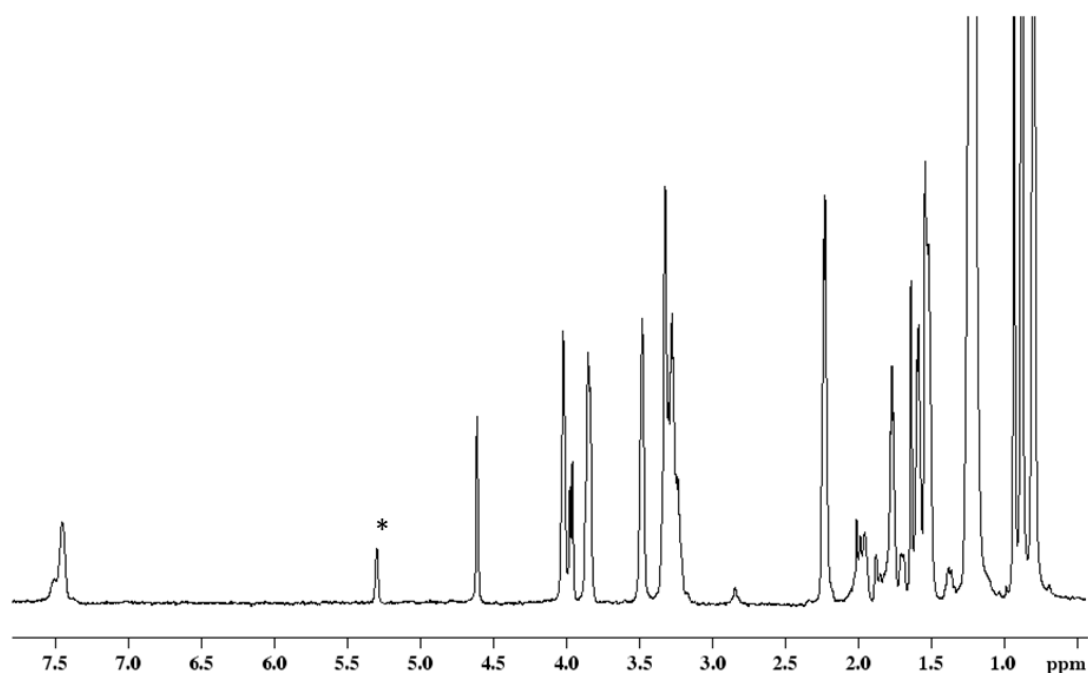
Panthenyl monolaurate was identified from ^1H NMR and ^{13}C NMR spectra. ^1H homonuclear correlation experiments as well as $^1\text{H},^{13}\text{C}$ heteronuclear experiments were performed on a Bruker Avance 600 MHz. Panthenyl monolaurate samples, collected from the limonene phase (see section 2.4), were dissolved in acetone- δ_6 (1 mL). The assignment of almost the totality of protons and carbons was achieved using TOCSY and NOESY homonuclear experiments, as well as $^1\text{H},^{13}\text{C}$ HSQC spectra. ^1H NMR $\delta(\text{ppm})$: 0.88 (s, 3H, H₄ or H₅); 0.89 (t, 3H, H₂₄); 0.96 (s, 3H, H₄ or H₅); 1.27-1.33 (from H₁₇ to H₂₃, indistinguishable); 1.59 (m, 2H, H₁₆); 1.69 (m, 2H, H₁₁); 2.05 (m, 2H, H₁₅); 2.31 (t, 2H, H₁₄); 3.38 (m, 2H, H₁₀); 3.43 (d, 2H, H₂); 3.96 (d, 1H, H₆); 4.11 (t, 2H, H₁₂); 4.18 (t, 1H, H₁); 4.83 (d, 1H, H₇); 7.64 (d, 1H, H₉). ^{13}C NMR $\delta(\text{ppm})$: 13.7 (C₂₄); 20.1 (C₅); 20.8 (C₄); 25.5 (C₁₆); 29.6-32.3 (from C₁₇ to C₂₃, indistinguishable); 30.0 (C₁₅); 33.1 (C₁₁); 34.1 (C₁₄); 36.0 (C₁₀); 61.9 (C₁₂); 70.0 (C₂); 75.4 (C₆).

The numeration of protons and carbons of the following structure was used for the assignment:



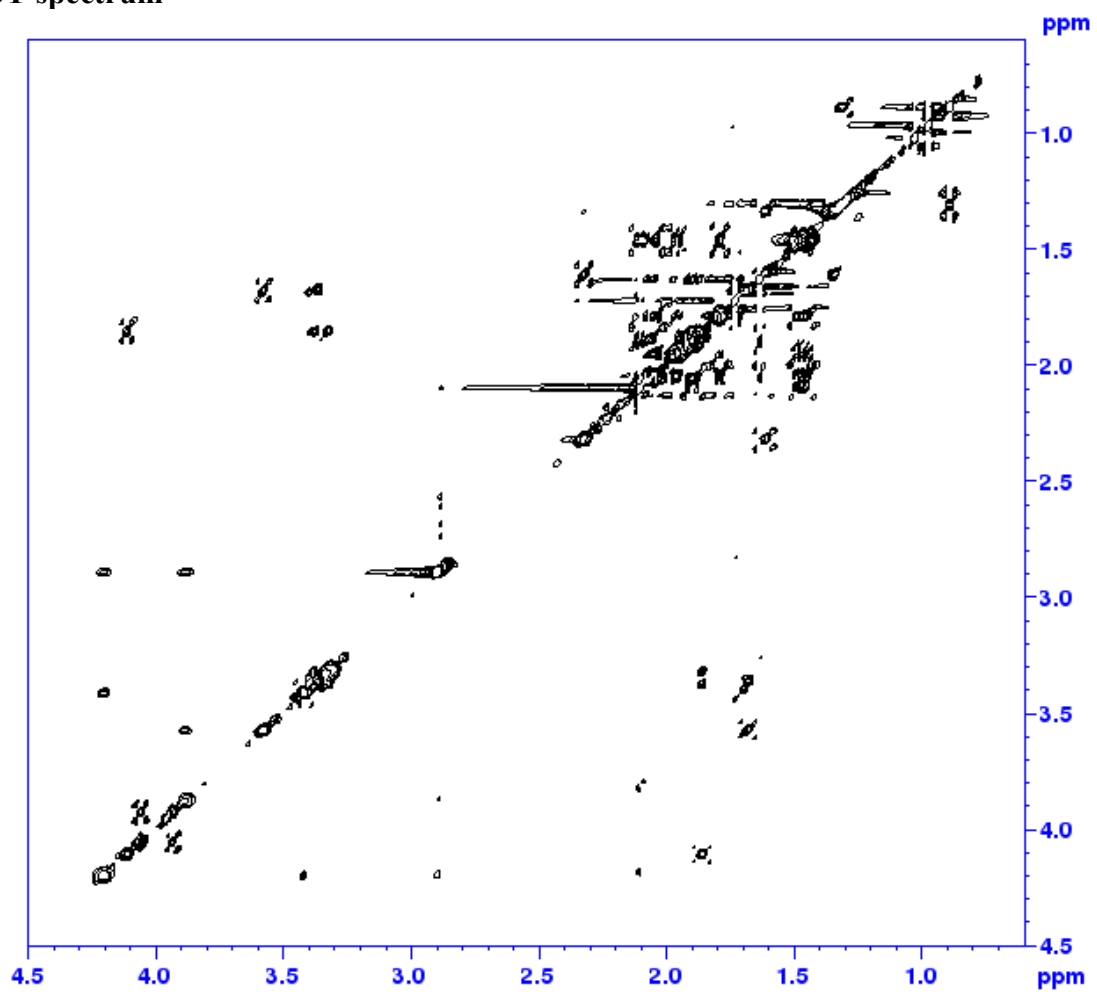
The ^1H and $^1\text{H},^{13}\text{C}$ experiments were recorded in acetone- δ_6 .

^1H ^1D NMR spectrum

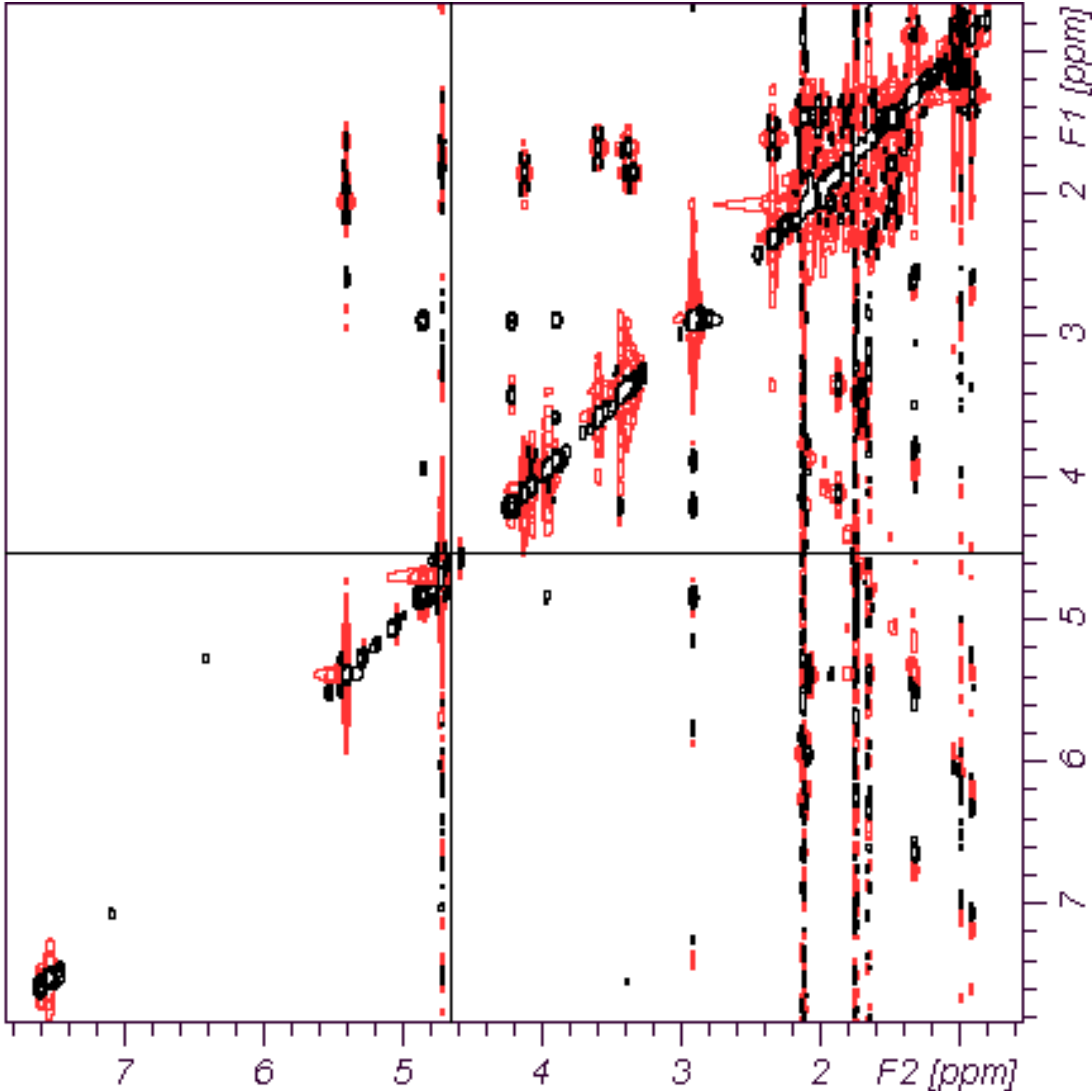


* Signal of limonene molecule, see sections 2.4 and 2.7 for details of sample preparation).

NOESY spectrum



TOCSY spectrum



$^1\text{H}, ^{13}\text{C}$ HSQC spectrum

