Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Aqueous Solutions of Facial Amphiphilic Carbohydrates as Sustainable Media for Organocatalyzed Direct Aldol Reactions

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General Experimental

All reactions were carried out in 10 mL round bottom flasks. The commercially available reagents (3-nitrobenzaldehyde, pyrrolidine, *rac*-pyrrolidinol, (*R*)-3-pyrrolidinol, L-proline, L-prolinol and all cyclohexanones) were purchased from Sigma–Aldrich, TCI and Acros and used without further purification. Nuclear magnetic resonance spectra were recorded on a Bruker Avance DPX-400 instrument. Chemical shifts (δ) are given in parts per million and coupling constants (J) are reported in Hertz. High-resolution mass spectra were performed on a ZabSpec TOF Micromass spectrometer (ESI + mode). Analytical TLC was performed on silica gel 60F-254 plates and visualized with UV light (254 nm) and/or anisaldehyde–H_2SO_4–AcOH as detecting agent. Flash column chromatography was performed on silica gel (Kieselgel 60, EM Reagents, 230–400 mesh). The diastereoselectivity of the reaction was determined by ^{1}H NMR spectroscopy of the crude product (after removal of the ketone excess by column chromatography). Measurement of the integration of the proton signal COCHC*H*(OH) in the two isomers indicated the ratios, while the coupling constant between the protons COCHC*H*(OH) and COC*H*CH(OH) of the products established the *anti*-aldol stereochemistry. In the case of 4-methylcyclohexanone, the 2,4-*trans* relationship was based on NOESY experiments. The enantiomeric excess of aldol products was determined by ^{1}H NMR experiments using Europium tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorate]. All chiral carbonyl compounds were used in racemic forms, except for the 2,2-dimethyl-(*S*)-3-hydroxycyclohexanone.

General procedure for the aldolization reaction

A mixture of 3-nitrobenzaldehyde (75.8 mg, 0.50 mmol), the ketone (2.50 mmol), the catalyst (2 mol%) and water (1.0 mL) was stirred vigorously at RT for the time indicated in Table 2. Once aldehyde consumption was complete (TLC analysis), the reaction mixture was quenched by adding saturated aqueous NH_4Cl solution, and extracted with CH_2Cl_2 several times. The combined organic layers were dried using $MgSO_4$, concentrated, and the residue was purified by flash chromatography on silica gel (cyclohexane/ethyl acetate: 3/1) to give the aldol products (**3**-**7**) as yellow oils.

General procedure for the aldolization reaction in the presence of the sugar media

A mixture of 3-nitrobenzaldehyde (75.8 mg, 0.50 mmol), ketone (2.50 mmol), the catalyst (2 mol%), the sugar derivative (1.0 M) and water (1.0 mL) was stirred vigorously at RT. After the time indicated in Table 2, the reaction mixture was quenched by adding saturated aqueous NH_4Cl solution, and extracted with CH_2Cl_2 several times. The combined organic layers were dried with $MgSO_4$, concentrated, and the residue was purified by flash chromatography on silica gel (cyclohexane/ethyl acetate: 3/1) to give the aldol products (**3**-**7**) as yellow oils.

Analytical data of aldol products 3-7:

2-(Hydroxy-(*m*-nitrophenyl)methyl)cyclohexanone (3)

^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.17-8.14 (dt, 2H, J = 2.0 Hz, Ar*H*), 8.11-8.04 (ddd, 2H, J = 8.4, 2.4, 1.2 Hz, Ar*H*), 7.65-7.62 (m, 2H, Ar*H*), 7.48 (dt, 2H, J = 8.4 Hz, Ar*H*), 5.43 (*syn*; br s, 1H, CHC*H*OH), 4.88 (*anti*; dd, 1H, J = 8.4, 2.0 Hz, CHC*H*OH), 4.15 (*anti*; d, 1H, J = 2.8 Hz, CHCHO*H*), 3.32 (*syn*; d, 1H, J = 3.2 Hz, CHCHO*H*), 2.65-2.57 (*anti* and *syn*; m, 2H, C*H*CHOH), 2.47-2.41 (m, 2H, CH*H*C(O)), 2.39-2.30 (m, 2H, C*H*HC(O)), 2.10-2.02 (m, 2H, cyclohex-*H*), 1.84-1.75 (m, 2H, cyclohex-*H*), 1.72-1.56 (m, 6H, cyclohex-*H*), 1.40-1.29 (m, 2H, cyclohex-*H*) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ= 214.7 (*syn*; *C*(O)), 213. 9 (*anti*; *C*(O)), 148.1 (Ar *C*), 148.0 (Ar *C*), 143.9 (Ar *C*), 143.2 (Ar *C*), 133.1 (Ar *C*H), 131.9 (Ar *C*H), 129.1 (Ar *C*H), 128.9 (Ar *C*H), 122.6 (Ar *C*H), 121.9 (Ar *C*H), 121.8 (Ar *C*H), 120.7 (Ar *C*H), 73.7 (*anti*; CH*C*HOH), 69.7 (*syn*; CH*C*HOH), 56.9 (*anti*; *C*HCHOH), 56.6 (*syn*; *C*HCHOH), 42.5 (CH_2), 42.4 (CH_2), 30.5 (CH_2), 27.6 (CH_2), 27.5 (CH_2), 25.7 (CH_2), 24.5 (CH_2), 24.4 (CH_2) ppm.

HRMS (ESI): calculated for $(C_{13}H_{15}NO_4Na)^+$= $[M+Na]^+$: *m*/*z* = 272.0898, found: *m*/*z* = 272.0897; calculated for $(C_{14}H_{19}NO_5Na)^+$= $[M+Na+CH_3OH]^+$: *m*/*z* = 304.1160; found: *m*/*z* = 304.1160.

2-(Hydroxy-(*m*-nitrophenyl)methyl)-6-methoxycyclohexanone (4)

^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.21 (dd, 1H, J = 2.4, 2.0 Hz, Ar*H*), 8.17 (m, 2H, Ar*H*), 8.14 (ddd, 1H, J = 8.4, 2.0, 0.8 Hz, Ar*H*), 8.11 (ddd, 1H, J = 2.4, 1.2, 0.8 Hz, Ar*H*), 8.09 (ddd, 1H, J = 2.4, 1.2, 0.8 Hz, Ar*H*), 7.70-7.64 (m, 3H, Ar*H*), 7.54-7.49 (m, 3H, Ar*H*), 5.45 (*syn*; br s, 2H, CHC*H*OH), 4.98 (*anti*; d, 1H, J = 8.4Hz, CHC*H*OH), 3.84 (m, 4H, *anti* CHCHO*H* and cyclohex-*H*-6), 3.47 and 3.46 (br s, 9H, CH_3), 3.27 (br s, 2H, CHCHO*H*), 2.69-2.60 (*anti* and *syn*; m, 3H, C*H*CHOH), 2.39 (m, 3H, cyclohex-*H*-5),1.88 (m, 3H, cyclohex-*H*-4), 1.79-1.68 (m, 4H, cyclohex-*H*-3), 1.66-1.61 (m, 5H, cyclohex-*H*-4), 1.36-1.24 (m, 4H, cyclohex-*H*-3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ= 211.7 (*C*(O)), 211.6 (*C*(O)), 148.3 (Ar *C*), 143.6 (Ar *C*), 143.1 (Ar *C*), 133.1 (Ar *C*H), 132.4 (Ar *C*), 131.9 (Ar *C*H), 130.8 (Ar *C*H), 129.3 (Ar *C*H), 129.2 (Ar *C*H), 128.8 (Ar *C*H), 122.9 (Ar *C*H), 122.2 (Ar *C*H), 121.8 (Ar *C*H), 120.7 (Ar *C*H), 84.6 (cyclohex-*C*-6), 84.5 (cyclohex-*C*-6), 73.2 (*anti*; CH*C*HOH), 69.6 (*syn*; CH*C*HOH), 58.1 (O*C*H_3), 58.0 (O*C*H_3), 56.7 (*C*HCHOH), 55.9 (*C*HCHOH), 34.8 (CH_2), 34.7 (CH_2), 31.1 (CH_2), 30.3 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 28.9 (CH_2), 26.1 (CH_2), 23.7 (CH_2), 22.9 (CH_2), 22.6 (CH_2), 22.4 (CH_2) ppm.

HRMS (ESI): calculated for $(C_{14}H_{17}NO_5Na)^+$= $[M+Na]^+$: *m*/*z* = 302.1004; found: *m*/*z* = 302.1004; calculated for $(C_{15}H_{21}NO_6Na)^+$= $[M+Na+CH_3OH]^+$: *m*/*z* = 334.1266; found: *m*/*z* = 334.1277.

2-(Hydroxy-(*m*-nitrophenyl)methyl)-5-methylcyclohexanone (5)

^{1}H NMR (400 MHz, $CDCl_3$): *δ*= 8.17-8.13 (dt, 2H, *J* = 2.0 Hz, Ar*H*), 8.11-8.03 (ddd, 2H, *J* = 8.4, 2.4, 1.2 Hz, Ar*H*), 7.66-7.60 (m, 2H, Ar*H*), 7.50-7.44 (m, 2H, Ar*H*), 5.41 (*syn*; br s, 1H, CHC*H*OH), 4.87 (major *anti*; dd, 1H, *J* = 8.4, 2.4 Hz, CHC*H*OH), 4.84 (minor *anti*; dd, 1H, *J* = 8.4, 2.8 Hz, CHC*H*OH), 4.18 (minor *anti*; br d, 1H, *J* = 3.2 Hz, CHCHO*H*), 4.07 (major *anti*; br d, 1H, *J* = 3.2 Hz, CHCHO*H*), 3.41 (minor *syn*; br d, 1H, *J* = 3.6 Hz, CHCHO*H*), 3.36 (major *syn*; br d, 1H, *J* = 3.2 Hz, CHCHO*H*), 2.61-2.51 (*anti* and *syn*; m, 2H, C*H*CHOH), 2.43-2.36 (m, 2H, cyclohex-*H*), 2.22 (ddd, 1H, *J* = 13.2, 4.0, 1.6 Hz, C*H*HCHHC(O)), 2.05 (m, 1H, cyclohex-*H*), 1.86-1.35 (series of m, 8H, cyclohex-*H*), 1.32-1.16 (series of m, 2H, cyclohex-*H*), 0.98 (d, 3H, *J* = 6.4 Hz, CH_3), 0.97 (d, 3H, *J* = 6.4 Hz, CH_3), 0.92 (major *anti*; d, 3H, *J* = 6.8 Hz, CH_3), 0.88 (d, 3H, *J* = 6.4 Hz, CH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 214.5 (*C*(O)), 214.2 (*C*(O)), 214.1 (*C*(O)), 213.3 (*C*(O)), 148.0 (Ar *C*), 144.0 (Ar *C*), 143.9 (Ar *C*), 143.3 (major *anti*; Ar *C*), 143.2 (Ar *C*), 133.1 (Ar *C*H), 133.0 (major *anti*; Ar *C*H), 131.8 (major *anti*; Ar *C*H), 129.2 (Ar *C*H), 129.1 (Ar *C*H), 129.0 (Ar *C*H), 128.9 (Ar *C*H), 122.7 (major *anti*; Ar *C*H), 122.6 (Ar *C*H), 121.9 (Ar *C*H), 121.8 (Ar *C*H), 121.8 (Ar *C*H), 121.7 (major *anti*; Ar *C*H), 120.7(Ar *C*H), 73.6 (minor *anti*; CH*C*HOH), 73.5 (major *anti*; CH*C*HOH), 69.8 (minor *syn*; CH*C*HOH), 69.5 (major *syn*; CH*C*HOH), 56.6 (major *anti*; *C*HCHOH), 56.1 (*C*HCHOH), 56.0 (*C*HCHOH), 55.7 (*C*HCHOH), 50.5 (CH_2), 50.4 (CH_2), 48.5 (major *anti*; CH_2), 35.4 (CH), 35.3 (CH), 33.1 (CH_2), 33.0 (CH_2), 31.9 (major *anti*; CH), 31.8 (CH), 29.9 (CH_2), 29.7 (major *anti*; CH_2), 29.4 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 25.5 (major *anti*; CH_2), 24.5 (major *anti*; CH_2), 22.1 (CH_3), 22.0 (CH_3), 18.8 (major *anti*; CH_3), 18.4 (CH_3) ppm.

HRMS (ESI): calculated for $(C_{14}H_{17}NO_4Na)^+$= $[M+Na]^+$: *m*/*z* = 286.1055; found: *m*/*z* = 286.1054.

2-(Hydroxy-(*m*-nitrophenyl)methyl)-4-methylcyclohexanone (6)

^{1}H NMR (400 MHz, $CDCl_3$): *δ*= 8.17-8.13 (dt, 2H, *J* = 2.0 Hz, Ar*H*), 8.11-8.03 (ddd, 2H, *J* = 8.4, 2.4, 1.2 Hz, Ar*H*), 7.65-7.58 (m, 2H, Ar*H*), 7.51-7.44 (m, 2H, Ar*H*), 5.41 (*syn*; br s, 1H, CHC*H*OH), 4.91 (major *anti* (2,4-*trans*); dd, 1H, *J* = 8.8, 2.0 Hz, CHC*H*OH), 4.83 (minor *anti* (2,4-*cis*); dd, 1H, *J* = 8.0, 2.0 Hz, CHC*H*OH), 4.20 (minor *anti*; br d, 1H, *J* = 2.8 Hz, CHCHO*H*), 4.06 (major *anti*; br d, 1H, *J* = 3.6 Hz, CHCHO*H*), 3.38 (minor *syn*; br d, 1H, *J* = 3.2 Hz, CHCHO*H*), 3.34 (major *syn*; br d, 1H, *J* = 3.2 Hz, CHCHO*H*), 2.80-2.64 (*anti* and *syn*; m, 2H, C*H*CHOH), 2.54-2.34 (m, 3H, cyclohex-*H*), 2.31 (m, 1H, C*H*CH_3), 2.10-1.66 (series of m, 4H, cyclohex-*H*), 1.58-1.48 (m, 2H, cyclohex-*H*), 1.45-1.26 (m, 4H, cyclohex-*H*), 1.21-1.04 (m, 1H, cyclohex-*H*), 1.00 (major *anti*; d, 3H, *J* = 6.8 Hz, CH_3), 0.99 (minor *anti*; d, 3H, *J* = 7.2 Hz, CH_3), 0.87 (major *syn*; d, 3H, *J* = 6.8 Hz, CH_3), 0.85 (minor *syn*; d, 3H, *J* = 6.4 Hz, CH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 215.0 (*C*(O)), 214.7 (major *anti*; *C*(O)), 214.1 (*C*(O)), 213.9 (*C*(O)), 148.1 (Ar *C*), 144.0 (Ar *C*), 143.9 (Ar *C*), 143.4 (major *anti*; Ar *C*), 143.1 (Ar *C*), 133.2 (Ar *C*H), 133.0 (major *anti*; Ar *C*H), 131.8 (Ar *C*H), 129.2 (major *anti*; Ar *C*H), 129.1 (Ar *C*H), 129.0 (Ar *C*H), 128.9 (Ar *C*H), 122.7 (major *anti*; Ar *C*H), 122.6 (Ar *C*H), 121.9 (Ar *C*H), 121.8 (Ar *C*H), 121.7 (major *anti*; Ar *C*H), 120.7 (Ar *C*H), 120.6 (Ar *C*H), 73.8 (major *anti*; CH*C*HOH), 73.7 (minor *anti*; CH*C*HOH), 70.1 (minor *syn*; CH*C*HOH), 69.4 (major *syn*; CH*C*HOH), 55.8 (*C*HCHOH), 55.5 (*C*HCHOH), 53.0 (major *anti*; *C*HCHOH), 52.1 (*C*HCHOH), 41.7 (CH_2), 41.5 (CH_2), 38.3 (CH_2), 38.1 (CH_2), 38.0 (major *anti*; CH_2), 36.0 (major *anti*; CH_2), 35.4 (CH_2), 35.3 (CH_2), 33.4 (CH_2), 33.0 (major *anti*; CH_2), 32.7 (CH_2), 31.3 (CH), 31.2 (CH), 26.7 (CH_2), 26.5 (major *anti*; CH), 26.4 (CH_2), 21.1 (CH_3), 20.9 (CH_3), 18.3 (major *anti*; CH_3), 18.1 (CH_3) ppm.

HRMS (ESI): calculated for $(C_{14}H_{17}NO_4Na)^+$= $[M+Na]^+$: *m*/*z* = 286.1055; found: *m*/*z* = 286.1053.

2-(Hydroxy-(*m*-nitrophenyl)methyl)-6,6-dimethyl-(*S*)-5-hydroxycyclohexanone (7)

^{1}H NMR (400 MHz, $CDCl_3$): *δ*= 8.22-8.08 (series of m, 8H, Ar*H*), 7.69-7.64 (series of br m, 4H, Ar*H*), 7.51 (ddd, 4H, *J* = 10.8, 4.8, 2.8 Hz, Ar*H*), 5.45 (*syn*; br s, 1H, CHC*H*OH), 5.41 (*syn*; br s, 1H, CHC*H*OH), 4.89 (minor *anti*; dd, 1H, *J* = 8.4, 2.4 Hz, CHC*H*OH), 4.82 (major *anti*; dd, 1H, *J* = 8.4, 2.8 Hz, CHC*H*OH), 4.20 (minor *anti*; br d, 1H, *J* = 2.8 Hz, CHCHO*H*), 4.04 (major *anti*; br d, 1H, *J* = 3.2 Hz, CHCHO*H*), 3.89 (br s, 2H, C*H*(OH)cyclohex), 3.51 (dd, 2H, *J* = 11.2, 4.4 Hz, C*H*(OH)cyclohex), 3.24 (*syn*; br s, 1H, CHCHO*H*), 3.16 (*syn*; d, 1H, *J* = 3.2 Hz, CHCHO*H*), 2.86 (*anti* and *syn*; ddd, 3H, *J* = 8.4, 6.0, 2.4 Hz, C*H*CHOH), 2.20 (*anti*/*syn*; dd, 1H, *J* = 13.6, 4.4Hz, C*H*CHOH), 2.13-2.04 (m, 3H, cyclohex-*H*), 1.96 (m, 5H, cyclohex-*H*), 1.82-1.45 (series of m, 9H, cyclohex-*H*), 1.40 (m, 1H, cyclohex-*H*), 1.26 (s, 3H, CH_3), 1.25 and 1.24 (br s, 6H, CH_3), 1.22 (s, 3H, CH_3), 1.17 and 1.16 (br s, 12H, CH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 217.8 (*C*(O)), 216.9 (*C*(O)), 216.4 (*C*(O)), 215.7 (*C*(O)), 167.8 (C), 148.3 (Ar *C*), 144.0 (Ar *C*), 143.8 (Ar *C*), 143.3 (Ar *C*), 143.1 (Ar *C*), 133.3 (Ar *C*H), 133.1 (Ar *C*H), 132.4 (C), 132.1 (Ar *C*H), 131.9 (Ar *C*H), 130.9 (Ar *C*H), 129.4 (Ar *C*H), 129.2 (2 Ar *C*H), 129.1 (Ar *C*H), 128.8 (Ar *C*H), 122.9 (Ar *C*H), 122.8 (Ar *C*H), 122.2 (Ar *C*H), 122.1 (Ar *C*H), 122.0 (Ar *C*H), 121.9 (Ar *C*H), 120.9 (Ar *C*H), 120.8 (Ar *C*H), 79.1 (*C*H(OH)cyclohex), 78.7 (*C*H(OH)cyclohex), 76.8 (*C*H(OH)cyclohex), 76.6 (*C*H(OH)cyclohex), 74.0 (*anti*; CH*C*HOH), 73.8 (*anti*; CH*C*HOH), 70.1 (*syn*; CH*C*HOH), 69.9 (*syn*; CH*C*HOH), 52.1 (*C*HCHOH), 51.7 (*C*HCHOH), 51.6 (*C*HCHOH), 51.2 (*C*HCHOH), 43.7 (C), 43.6 (C), 43.4 (C), 43.3 (C), 30.3 (CH_2), 30.1 (CH_2), 27.5 (CH_2), 27.4 (CH_2), 26.8 (CH_2), 23.7 (CH_2), 22.9 (CH_2), 21.0 (CH_3), 20.9 (CH_3), 20.6 (CH_3), 20.5 (CH_3), 18.8 (CH_2), 18.6 (CH_3), 18.5 (CH_3), 14.0 (CH_3), 10.9 (CH_3) ppm.

HRMS (ESI): calculated for $(C_{15}H_{19}NO_5Na)^+$= $[M+Na]^+$: *m*/*z* = 316.1160; found: *m*/*z* = 316.1160; calculated for $(C_{15}H_{19}NO_5K)^+$= $[M+Na]^+$: *m*/*z* = 332.0900; found: *m*/*z* = 332.0912.

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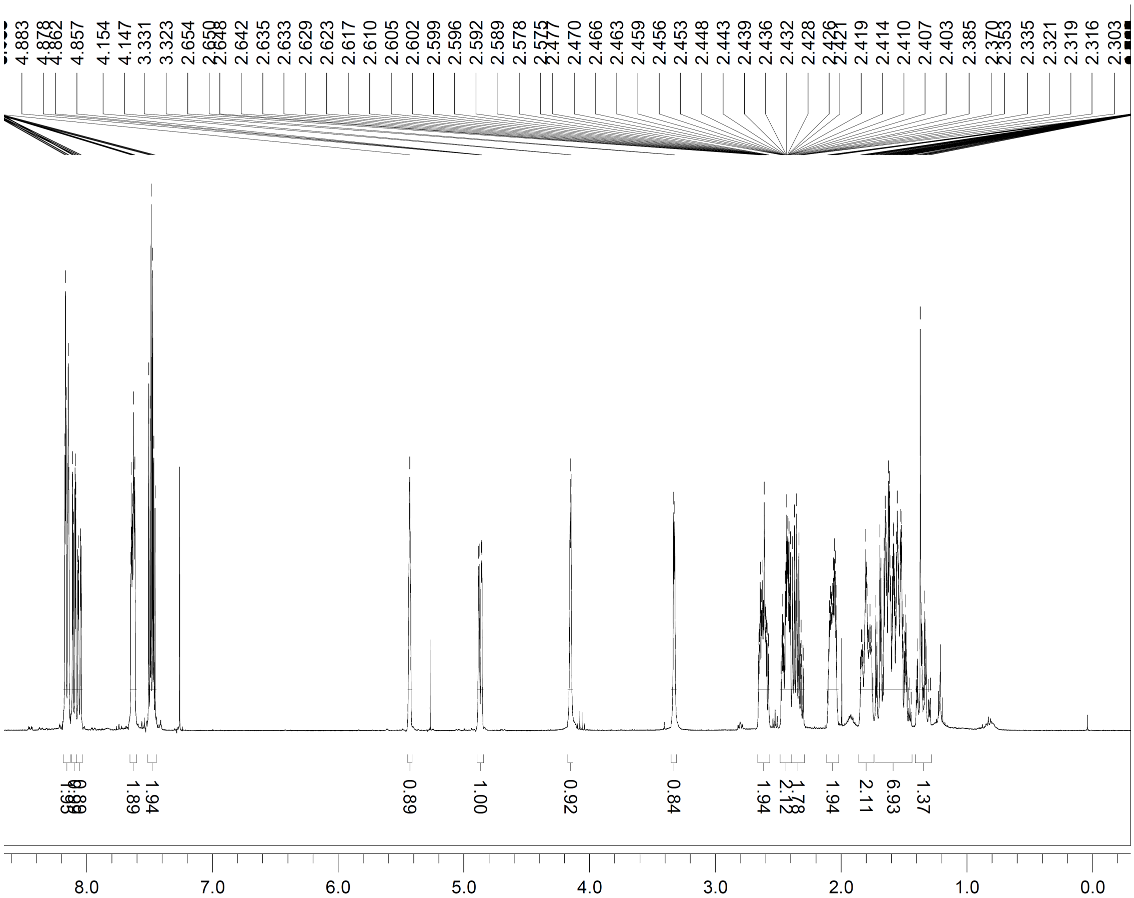
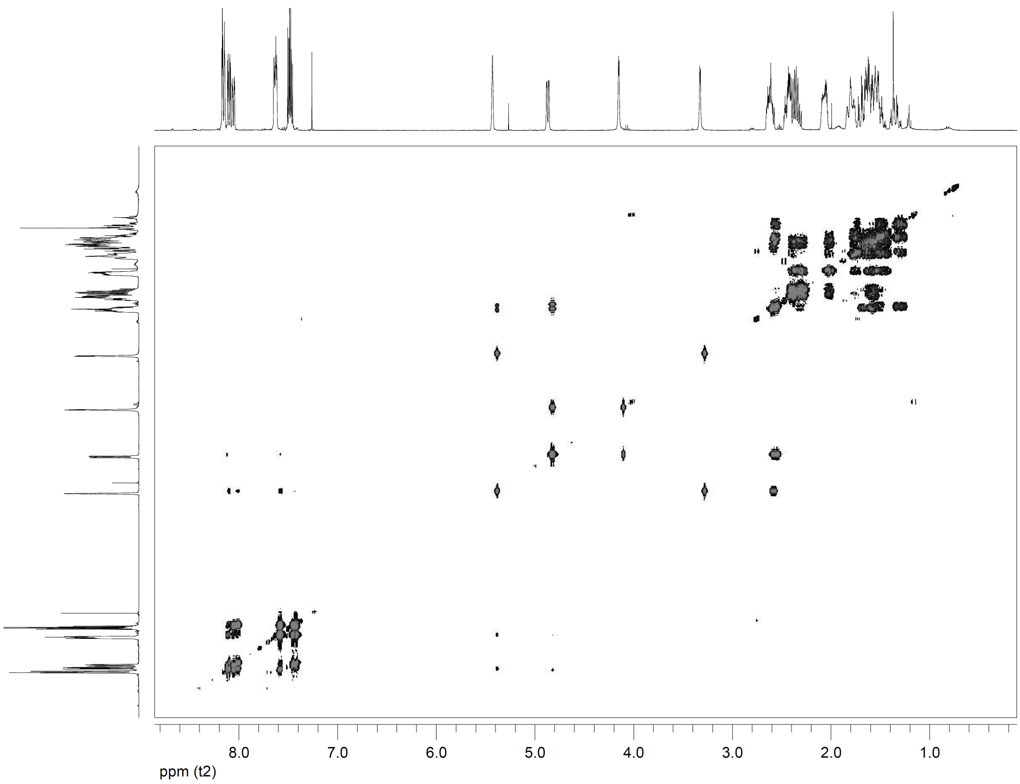
[P3] a) P. Duhamel, D. Cahard, Y. Quesnel, J.-M. Poirier, *J. Org. Chem.* **1996**, *61*, 2232-2235; b) D. E. Ward, M. Sales, P. K. Sasmal, *J. Org. Chem.* **2004**, *69*, 4808-4815; c) B. Schetter, B. Ziemer, G. Schnakenburg, R. Mahrwald, *J. Org. Chem.* **2008**, *73*, 813-819.

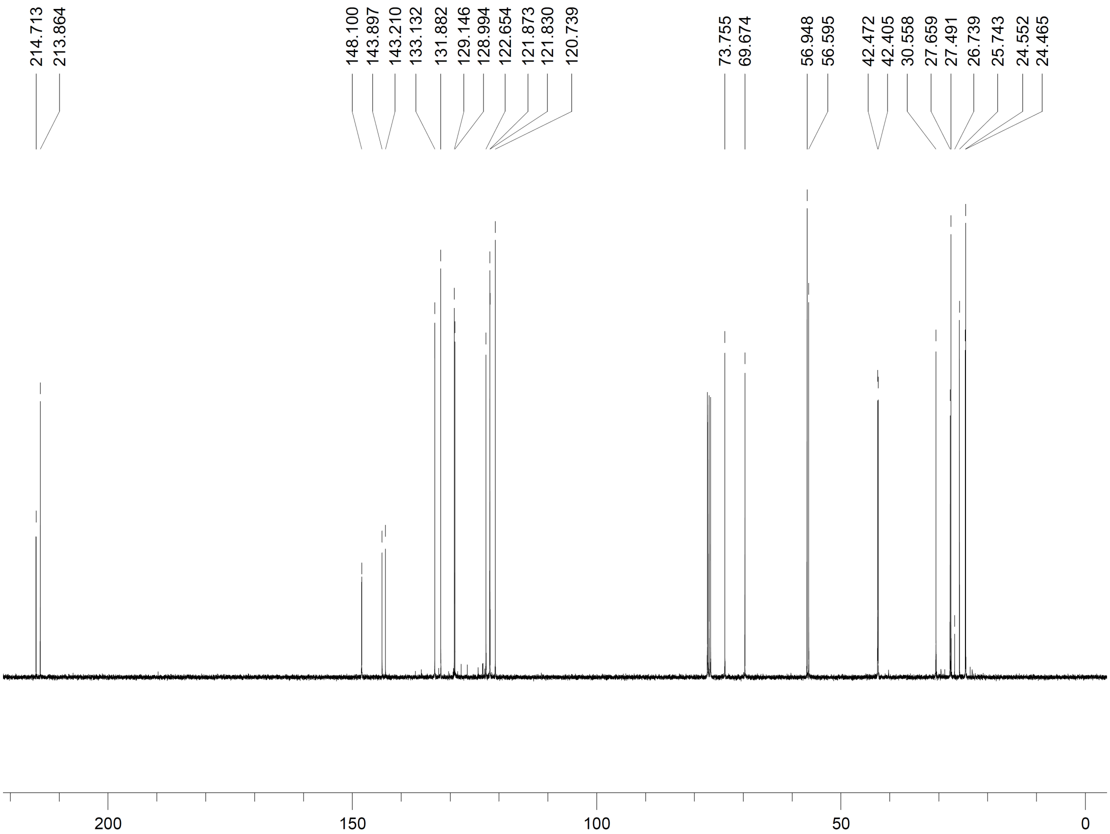
NMR Spectra

Compound 3

Ethanolamine as catalyst in water



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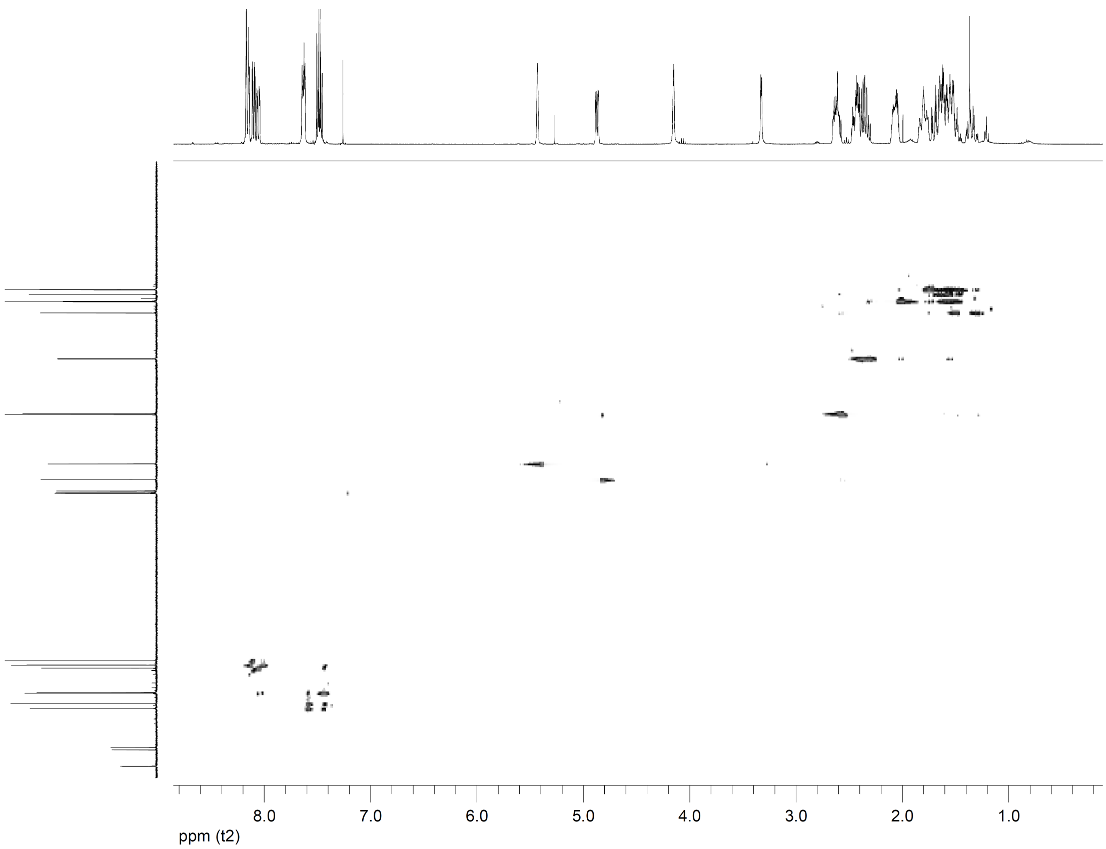
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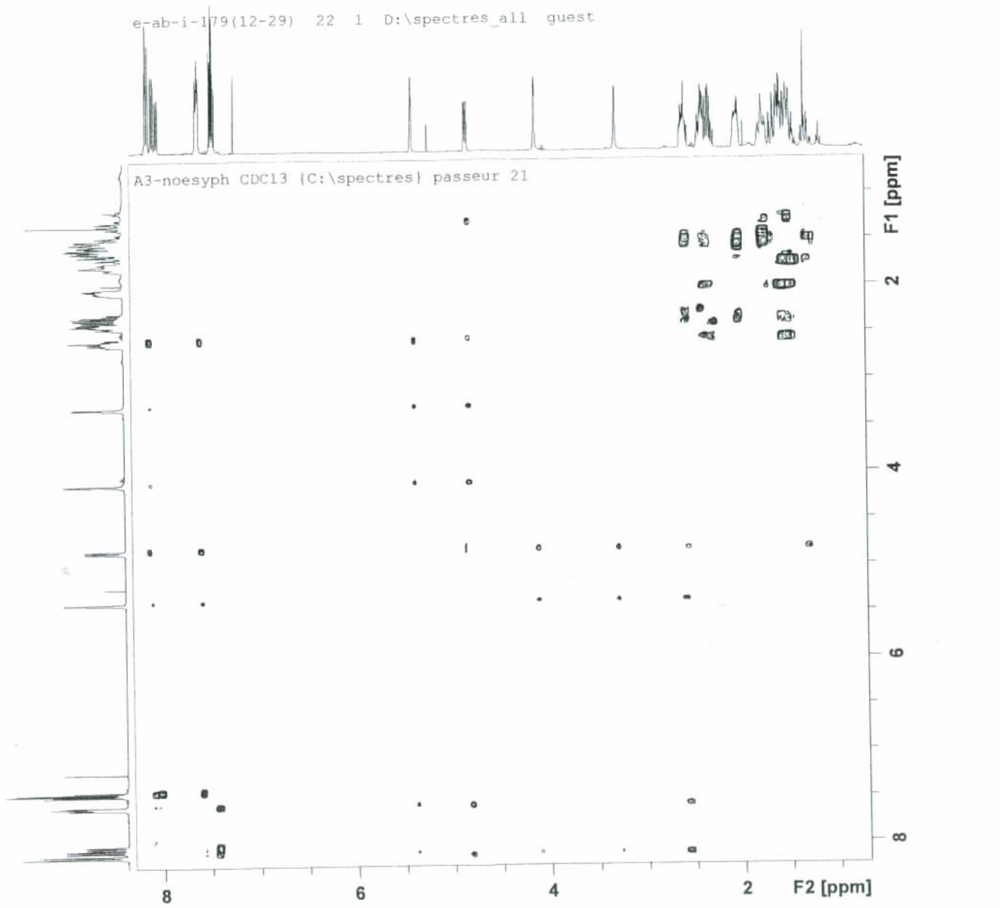
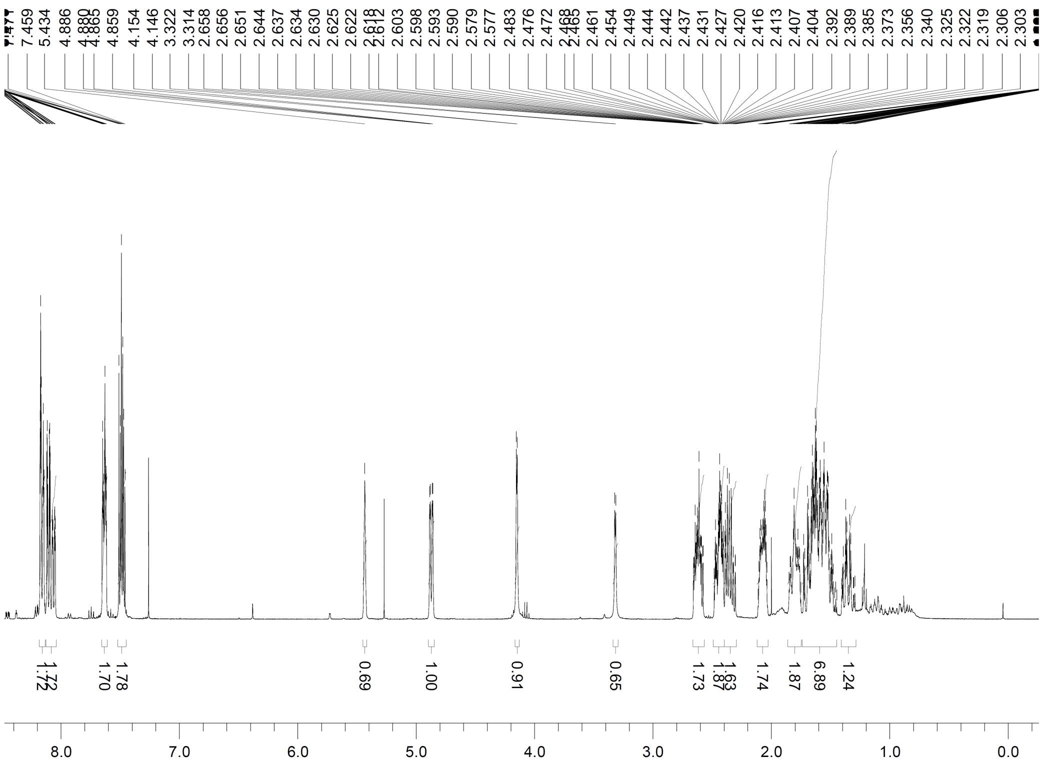
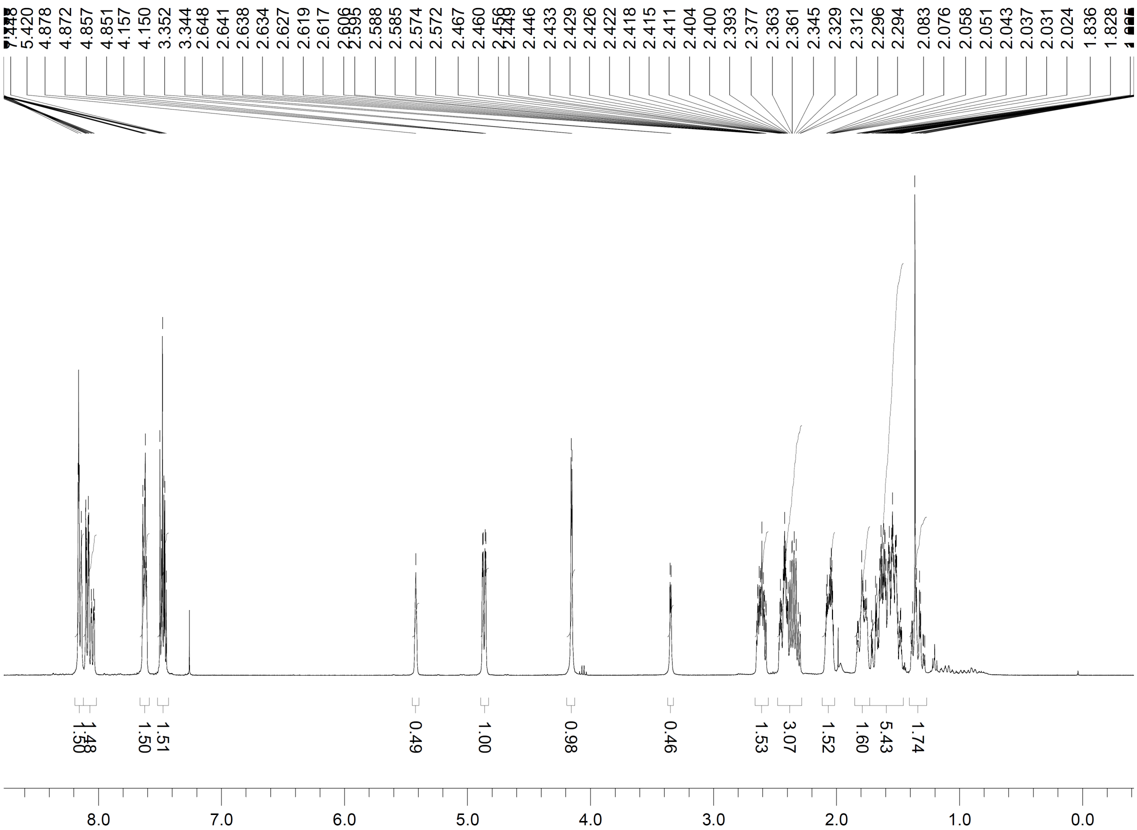


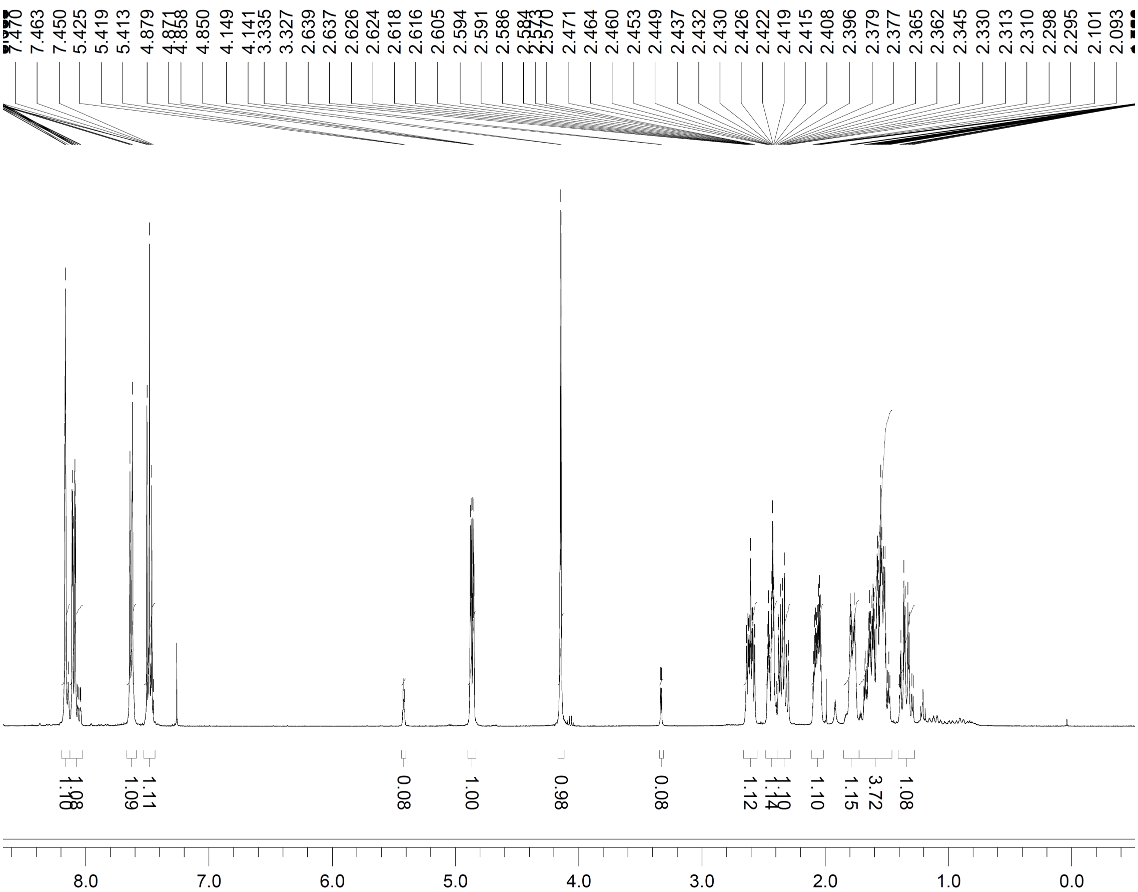
Ethanolamine as catalyst with ethyl sugar 2b

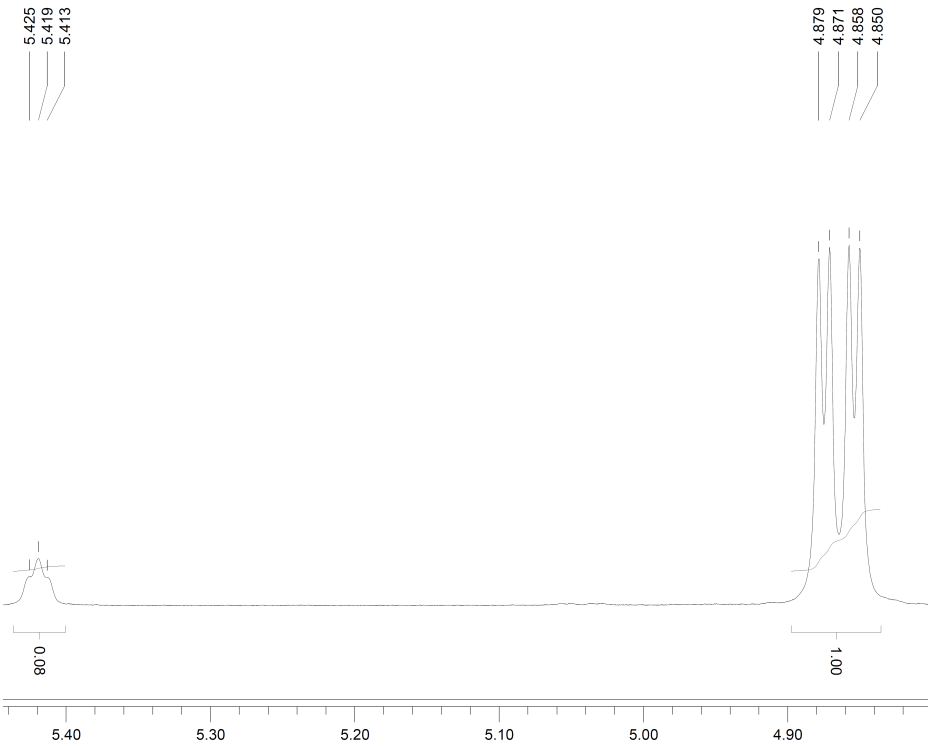


(R)-3-pyrrolidinol as catalyst in water

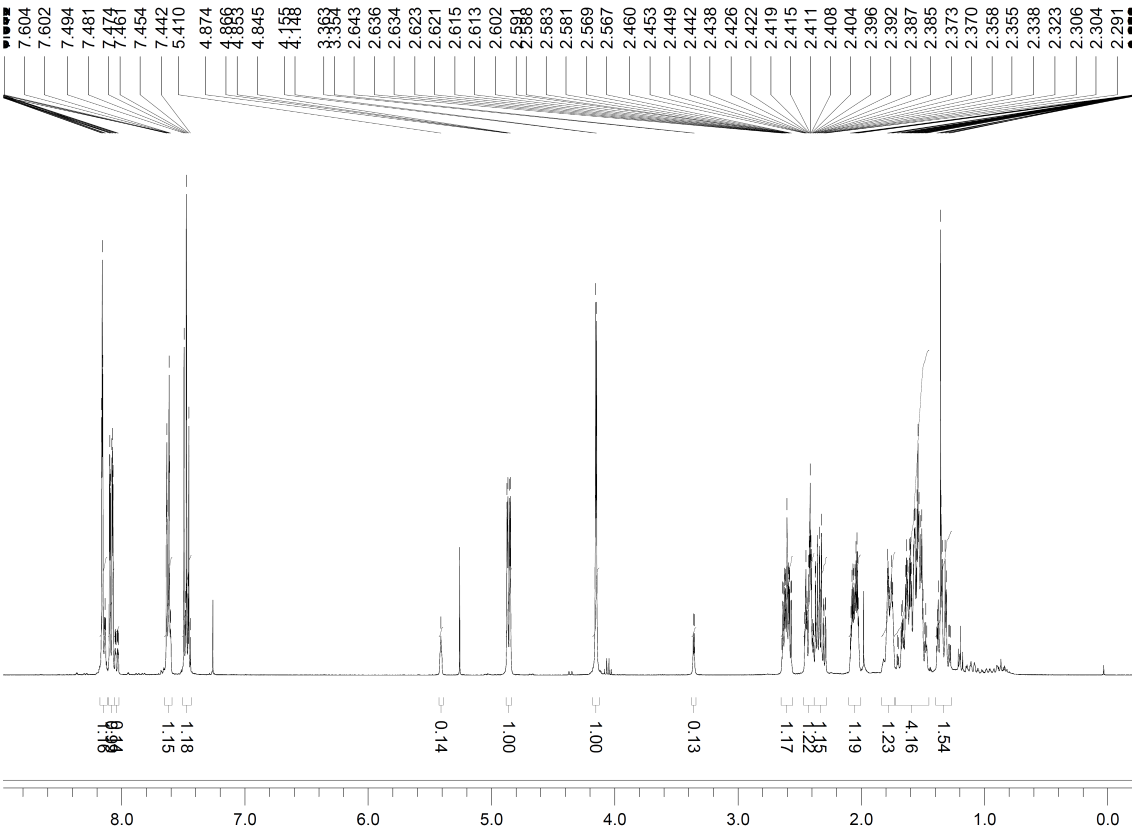


(R)-3-pyrrolidinol as catalyst with ethyl sugar 2b

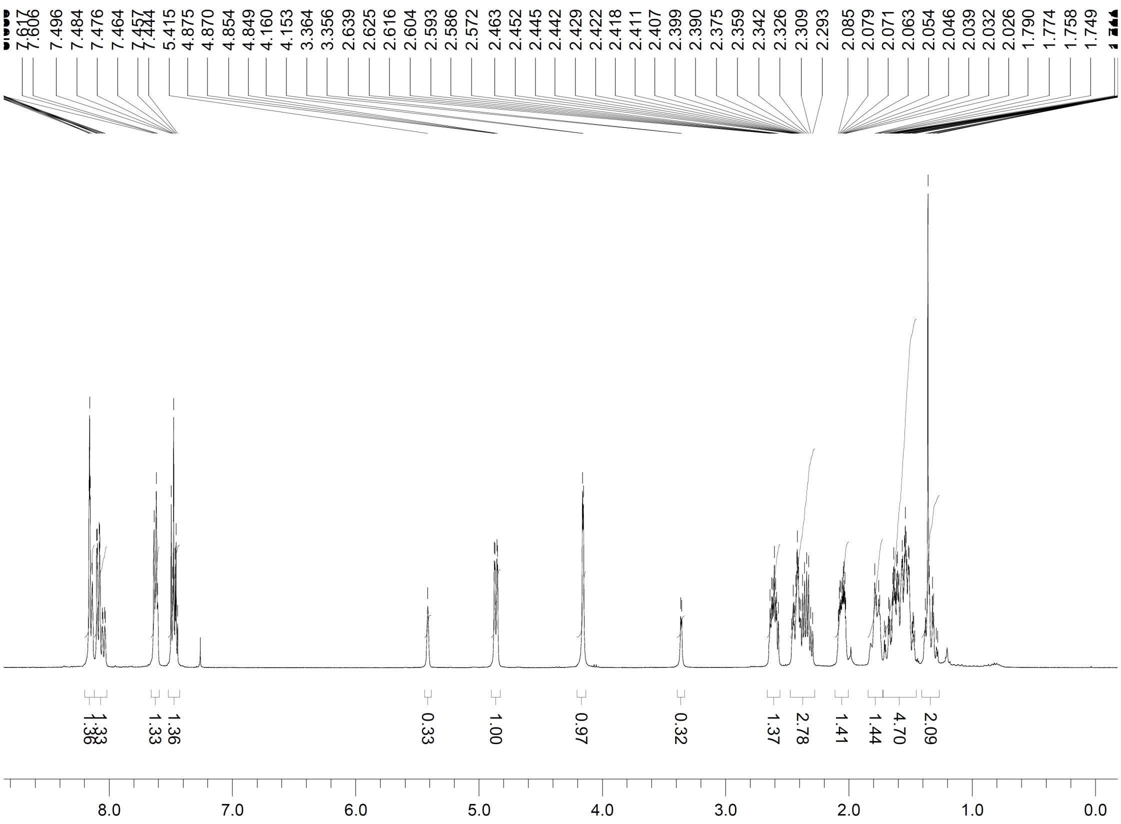




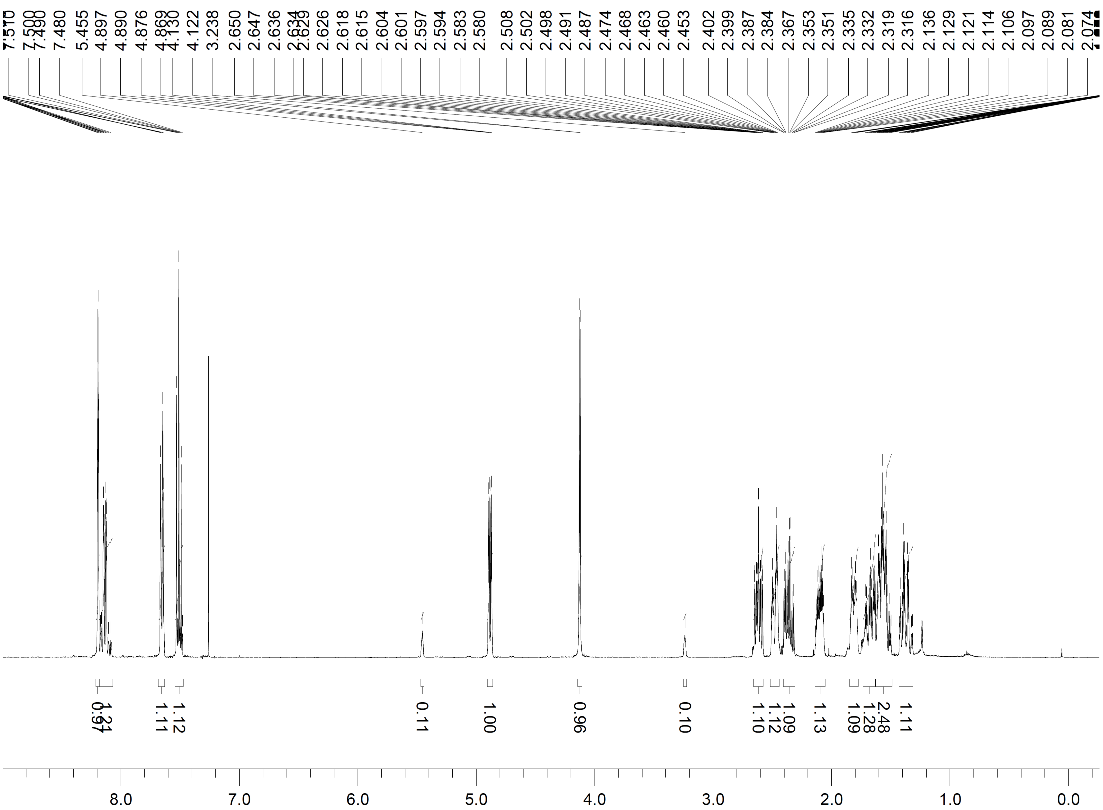
(R)-3-pyrrolidinol as catalyst with sucrose as sugar derivative



***rac*-pyrrolidinol as catalyst in water**



***rac*-pyrrolidinol as catalyst with ethyl sugar 2b**



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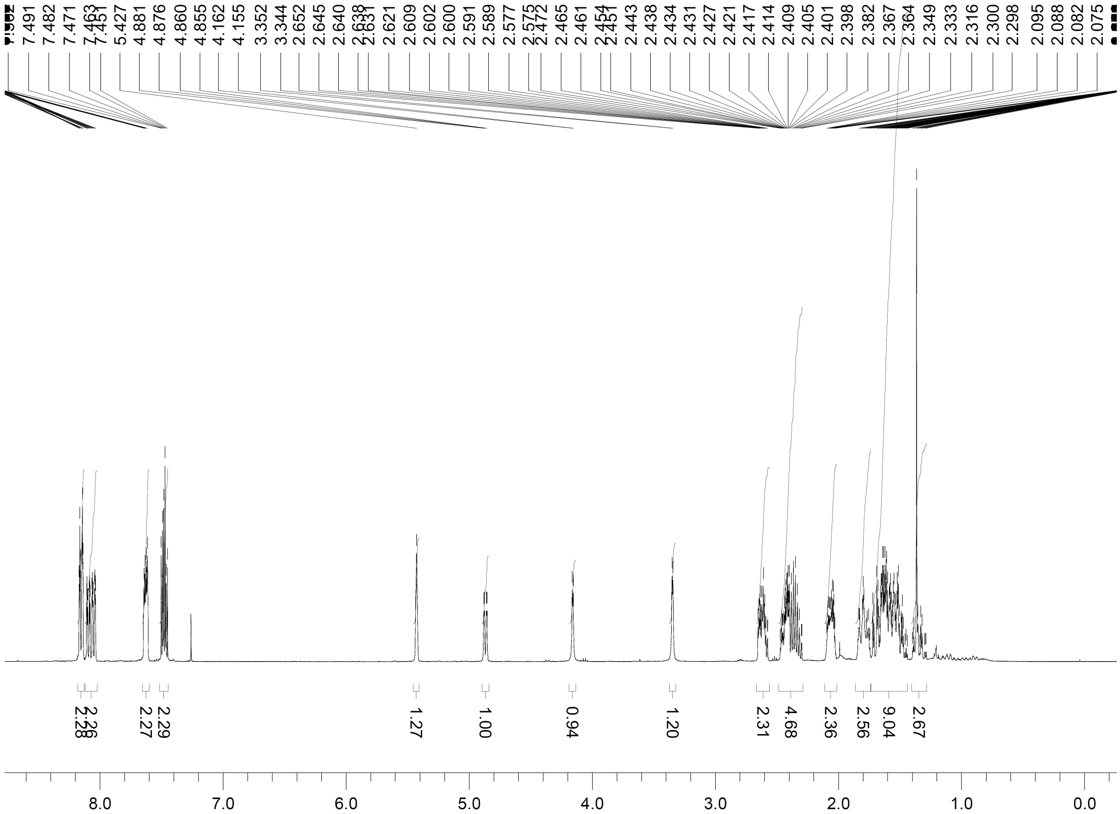
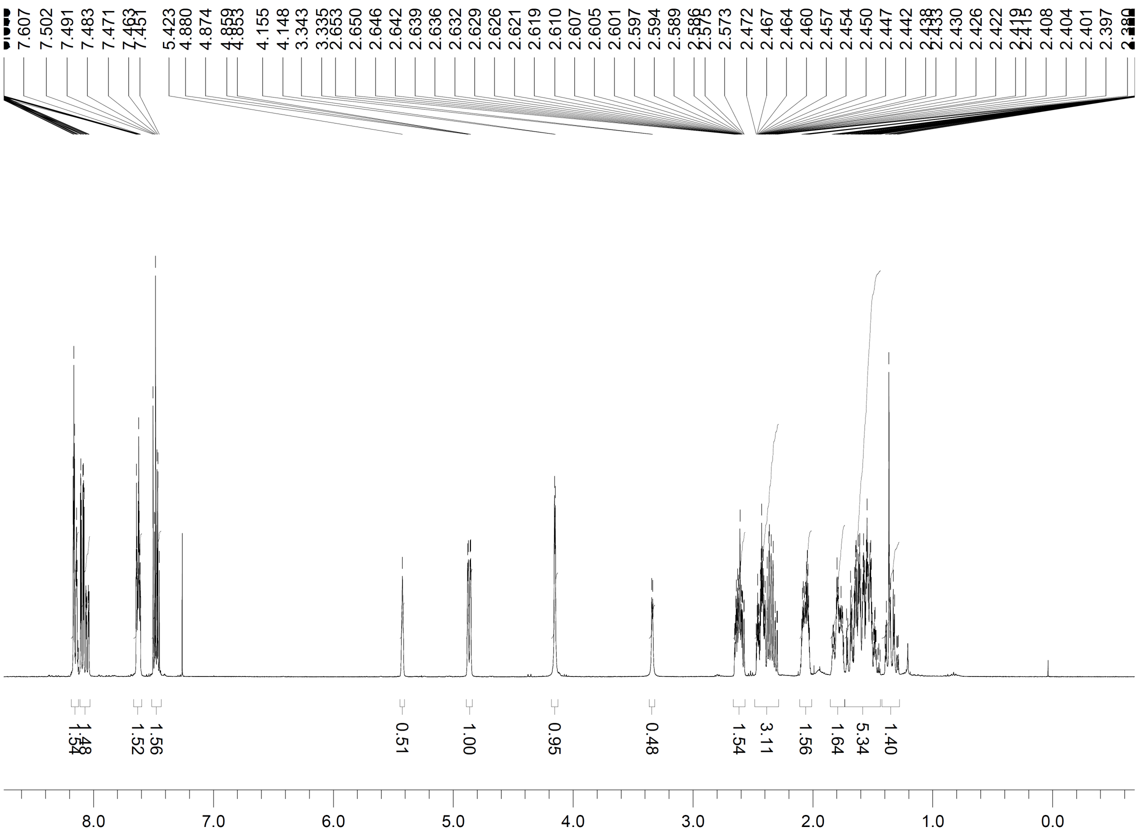
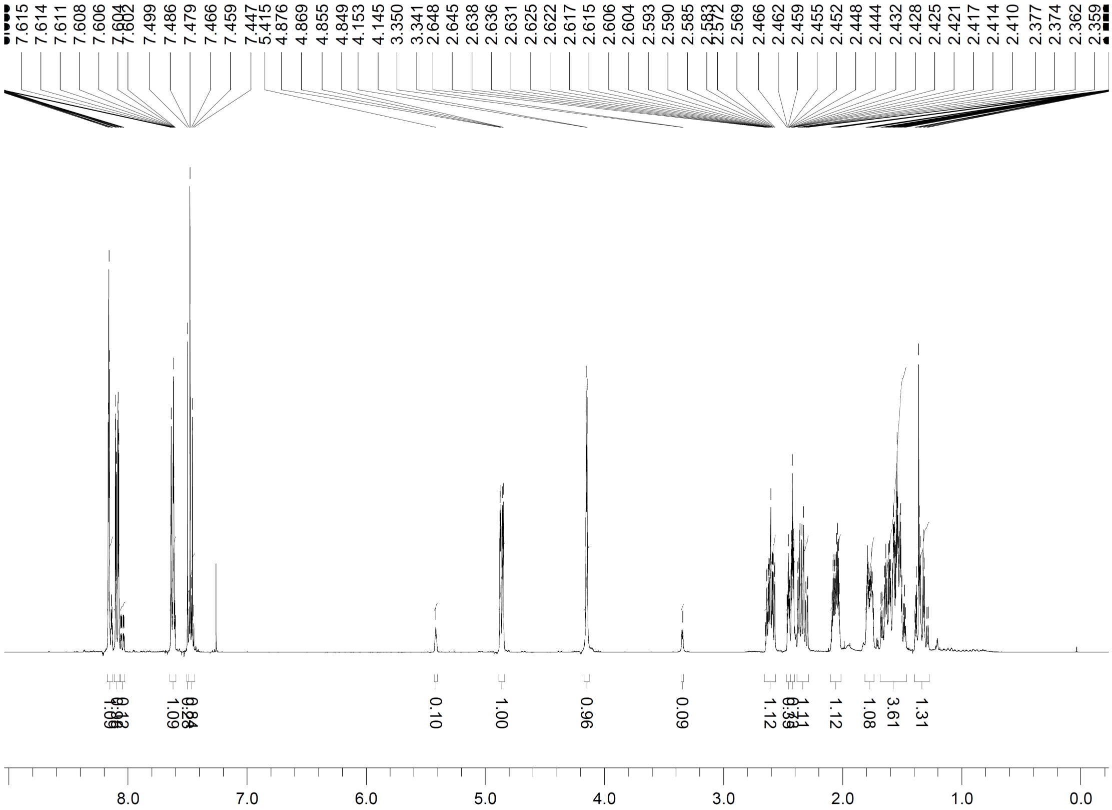
Pyrrolidine as catalyst in water



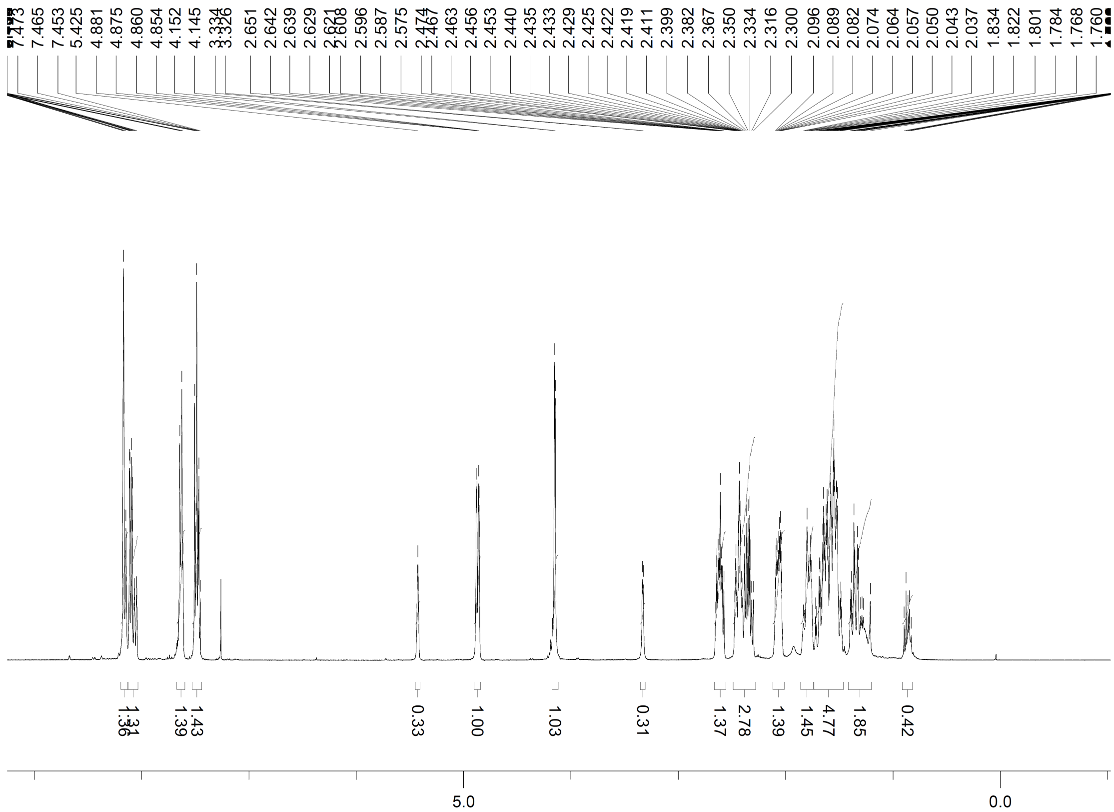
Pyrrolidine as catalyst with ethyl sugar 2b



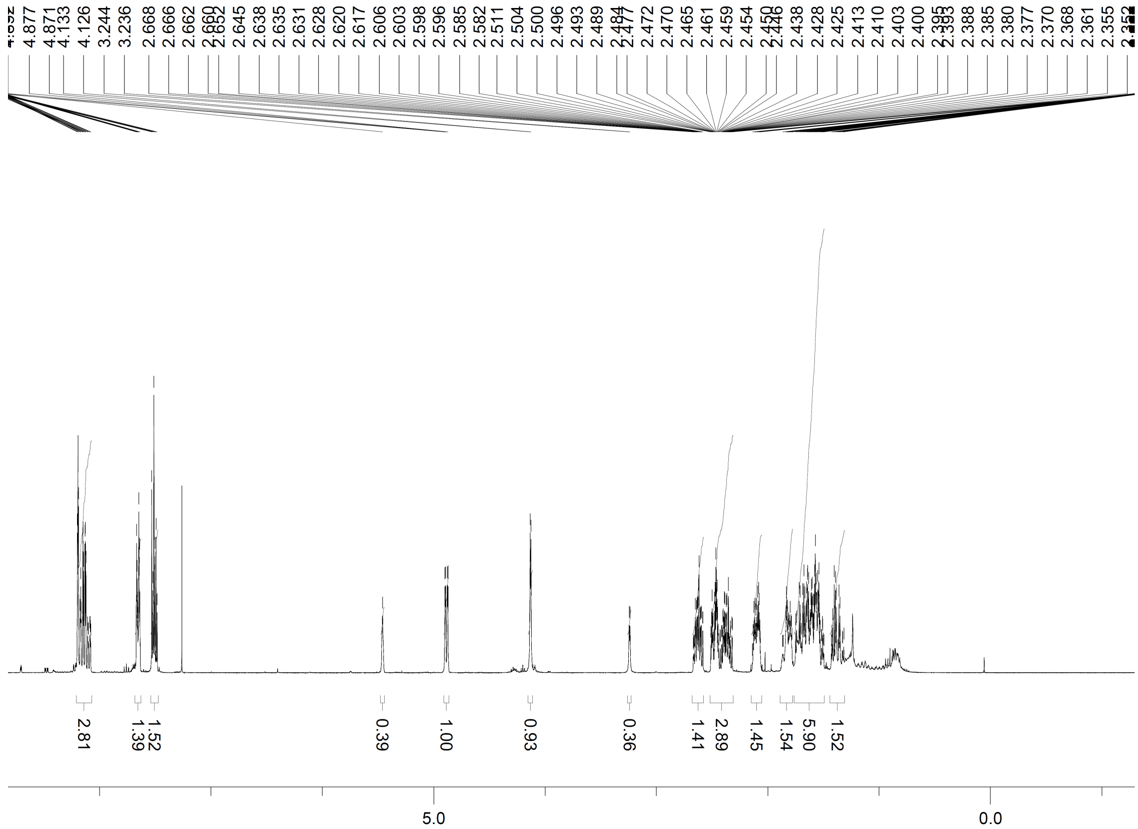
(R)-3-pyrrolidinol as catalyst with ethyl sugar 2b (1.5 equiv. aldehyde)



L-prolinol as catalyst in water



***L*-prolinol as catalyst with ethyl sugar 2b**



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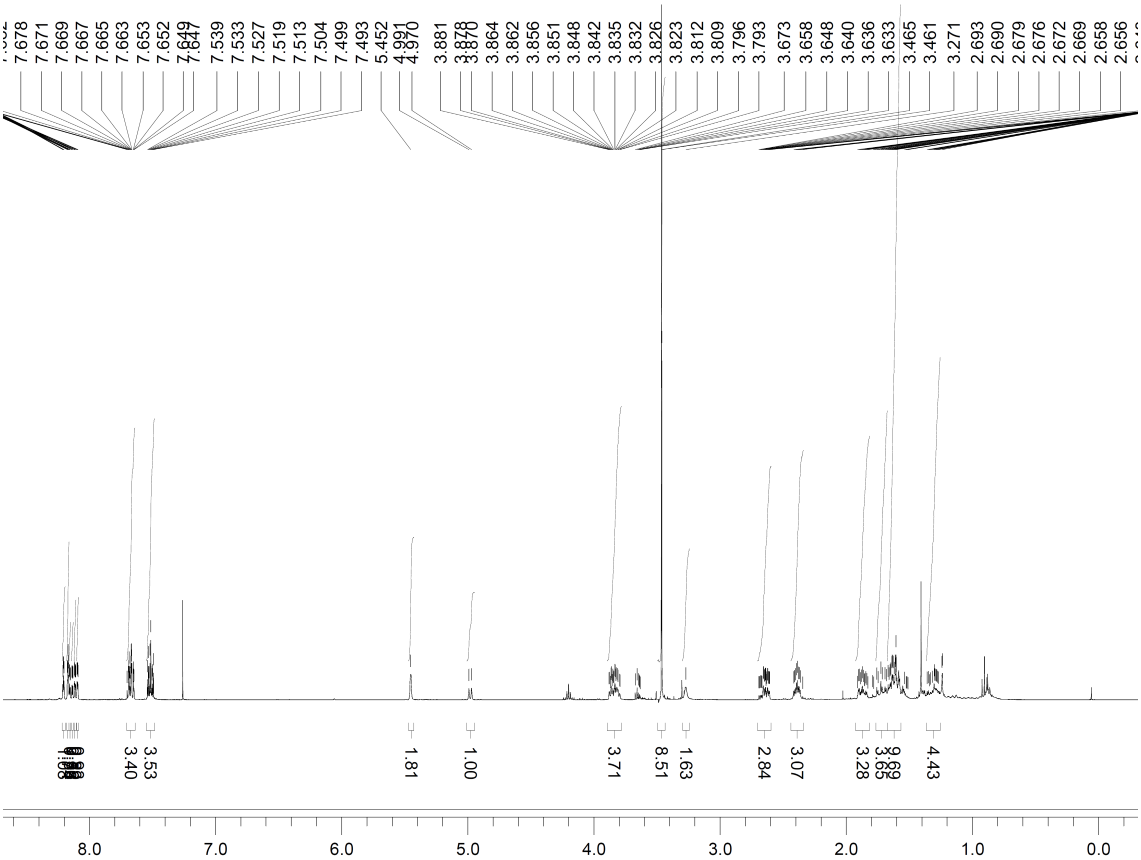
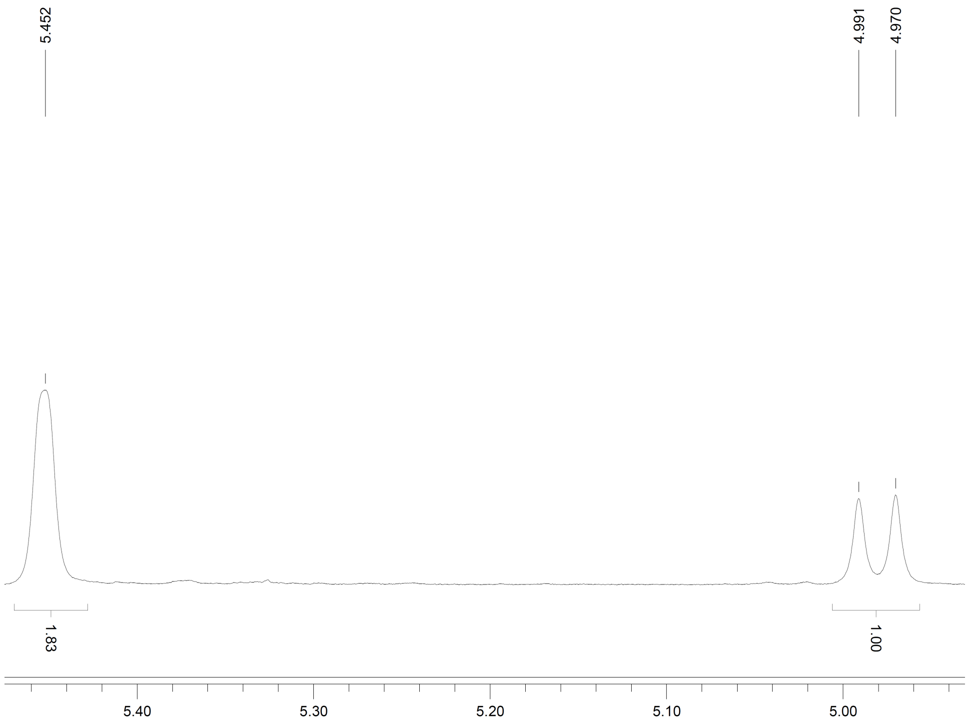
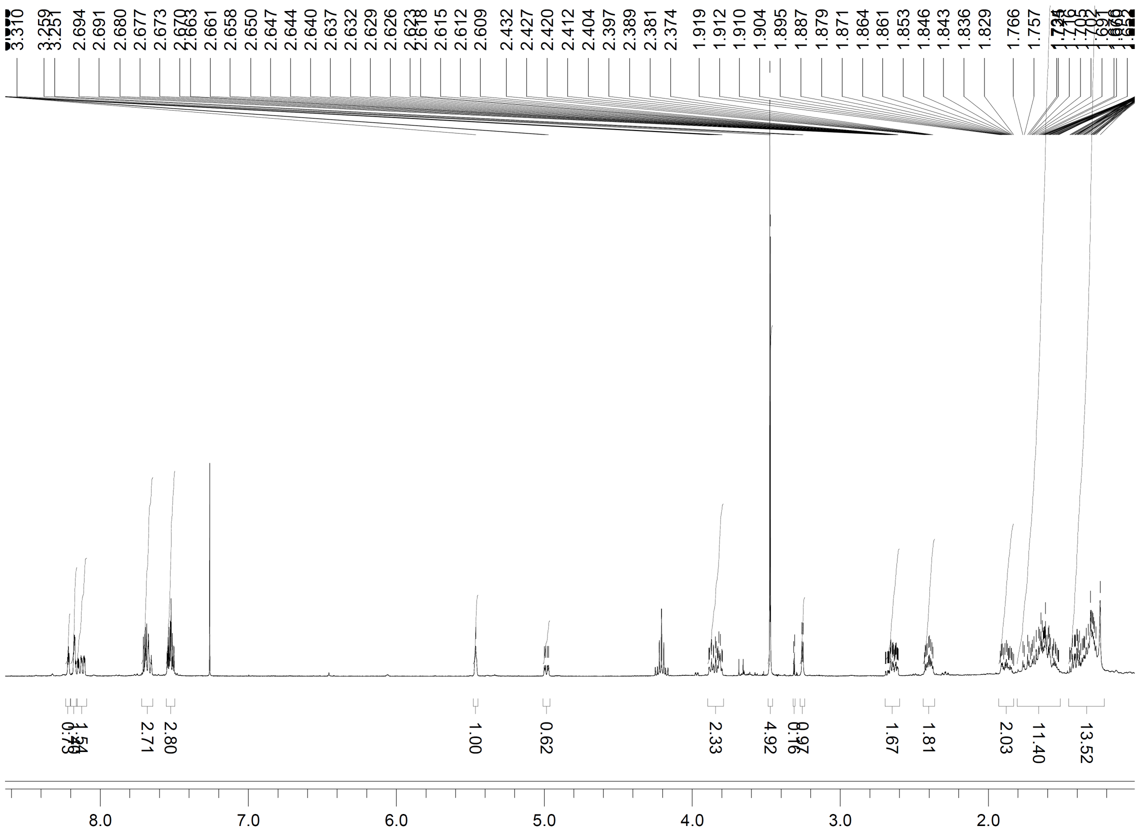
Compound 4

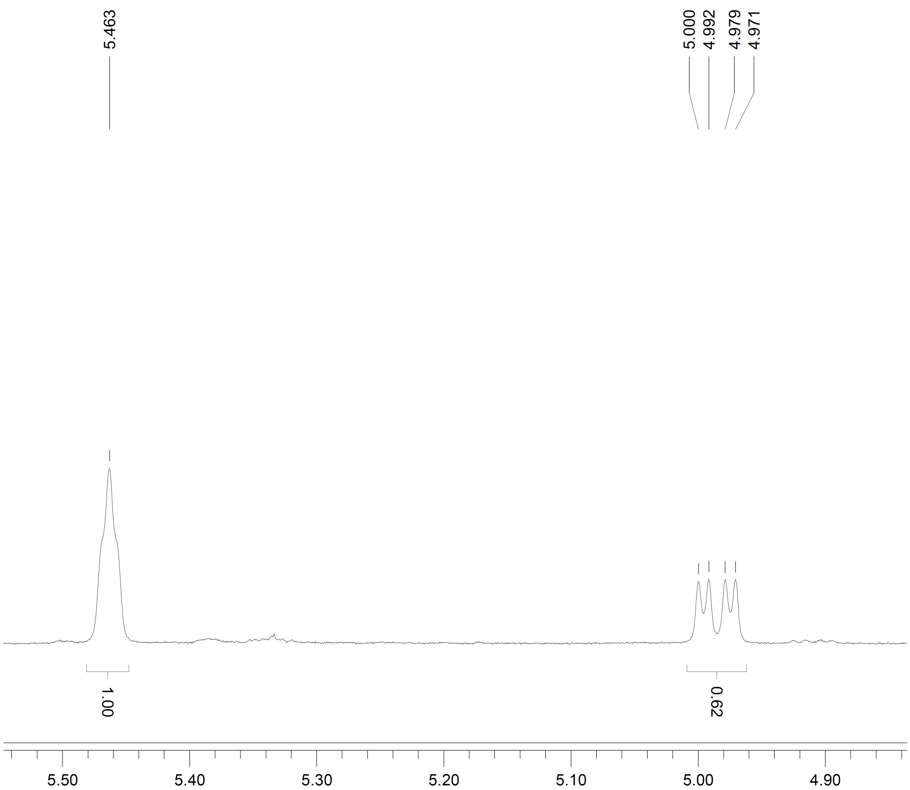
(R)-3-pyrrolidinol as catalyst in water

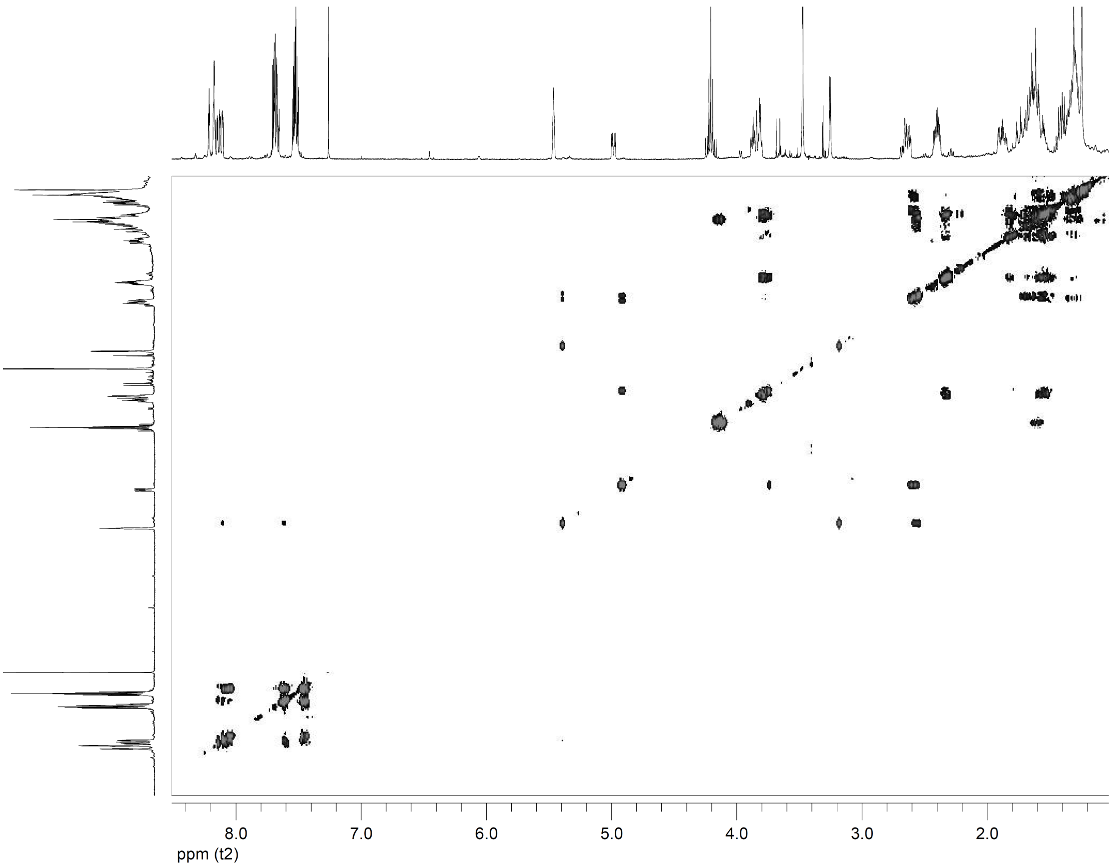


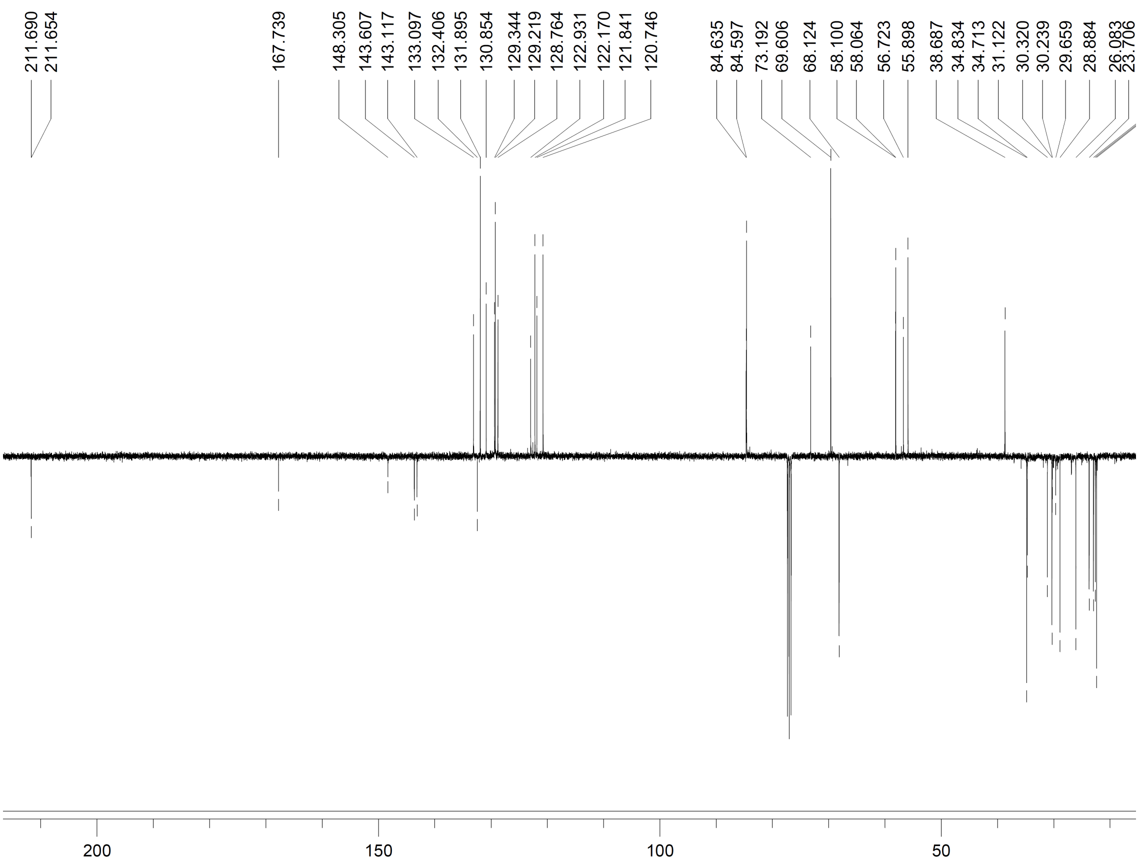


(R)-3-pyrrolidinol as catalyst with ethyl sugar 2b






8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t2)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211.654
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148.305
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143.117
133.097
132.406
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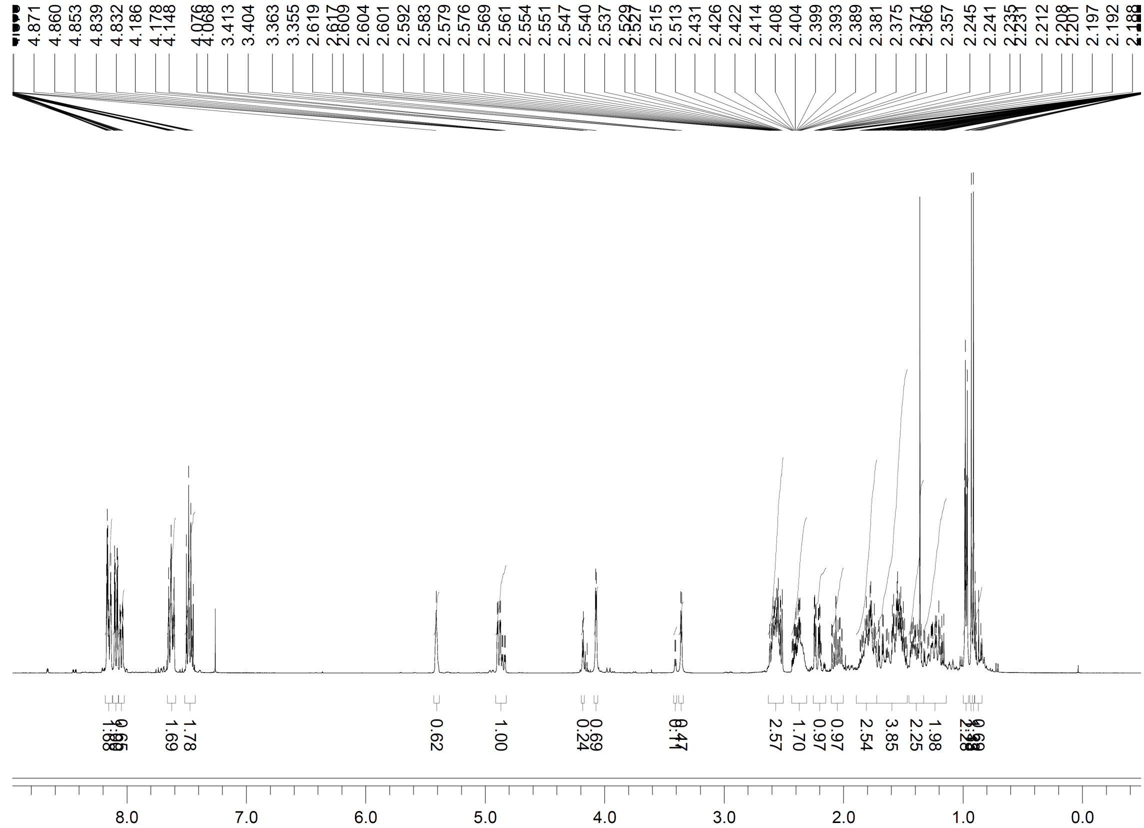
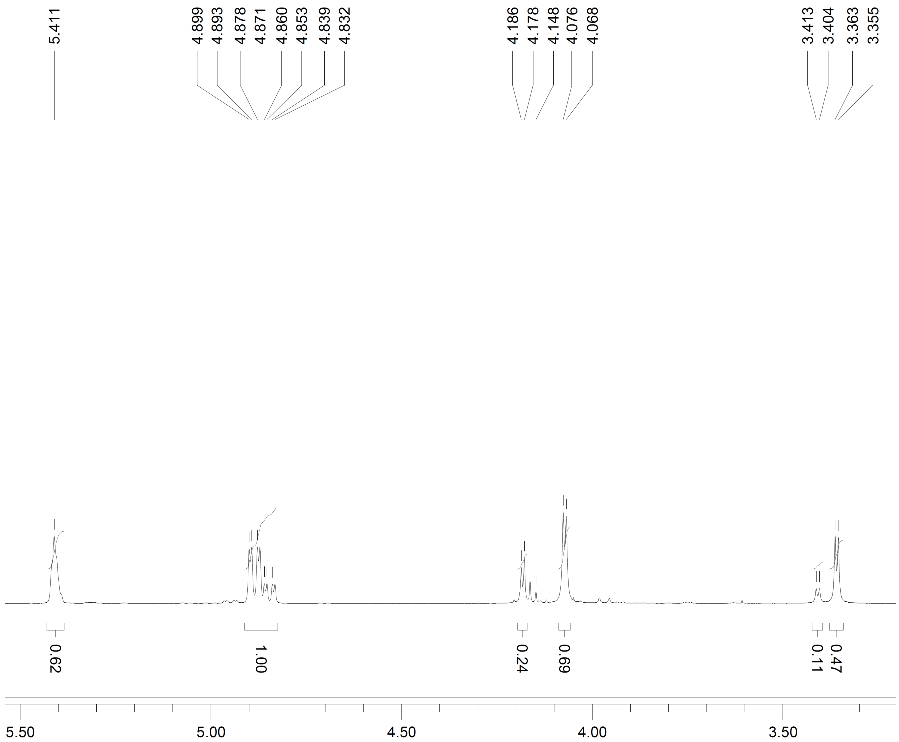
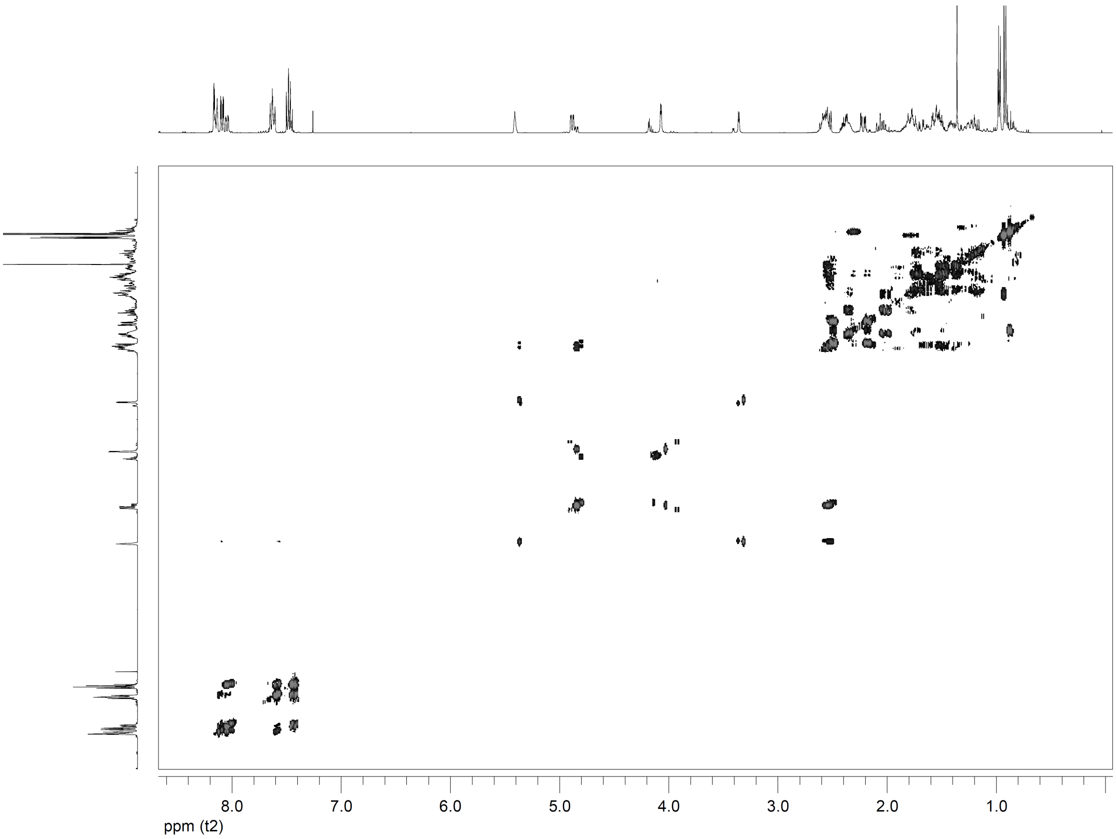
122.931
122.170
121.841
120.746
84.635
84.597
73.192
69.606
68.124
58.100
58.064
56.723
55.898
38.687
34.834
34.713
31.122
30.320
30.239
29.659
28.884
26.083
23.706
200
150
100
50

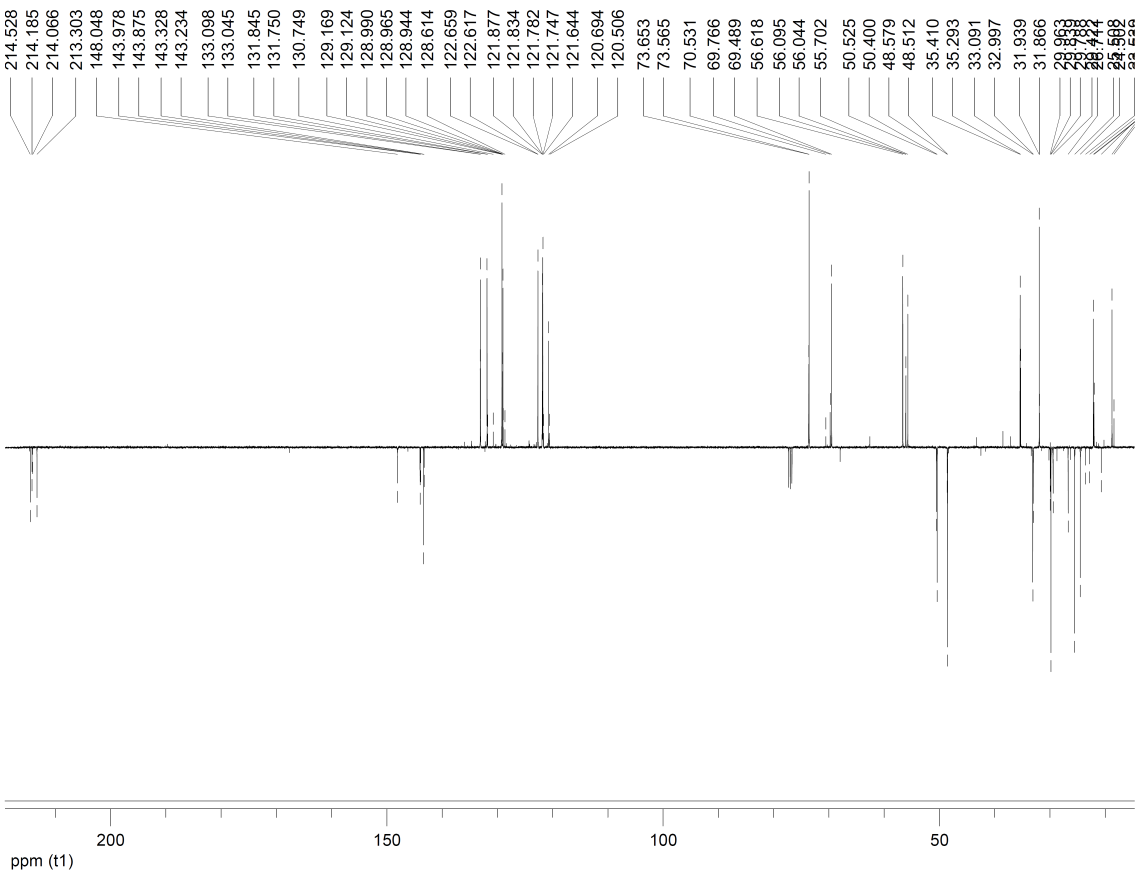
Compound 5

(R)-3-pyrrolidinol as catalyst in water






8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t2)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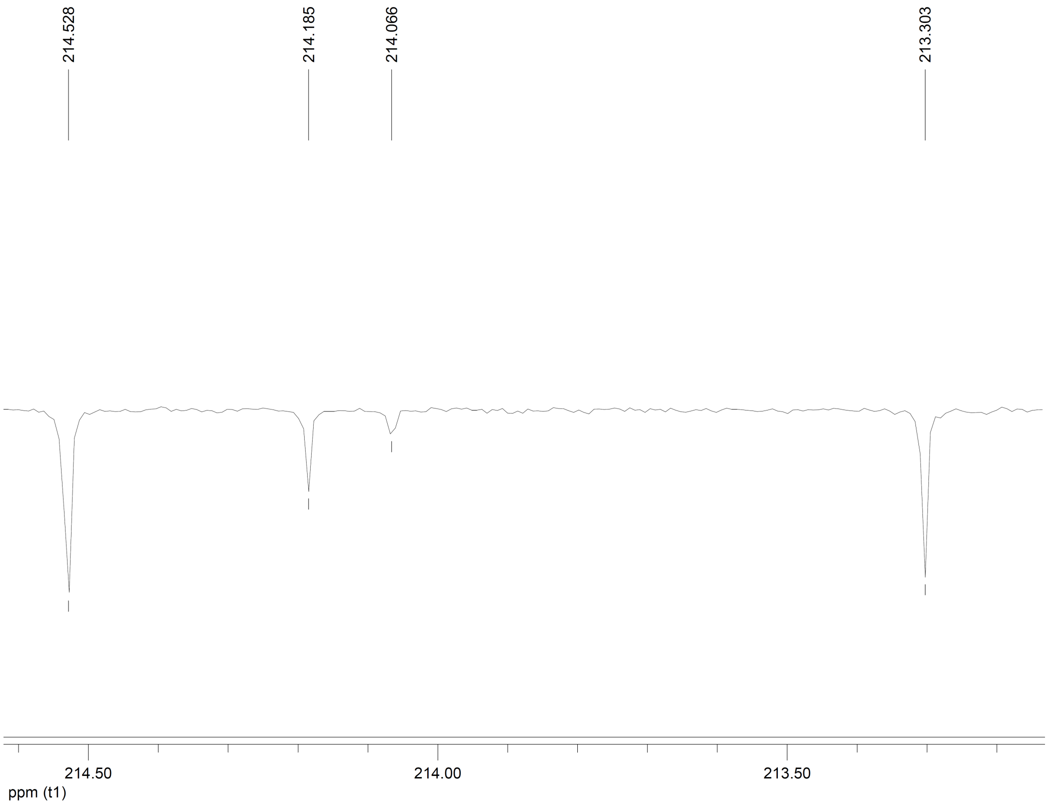
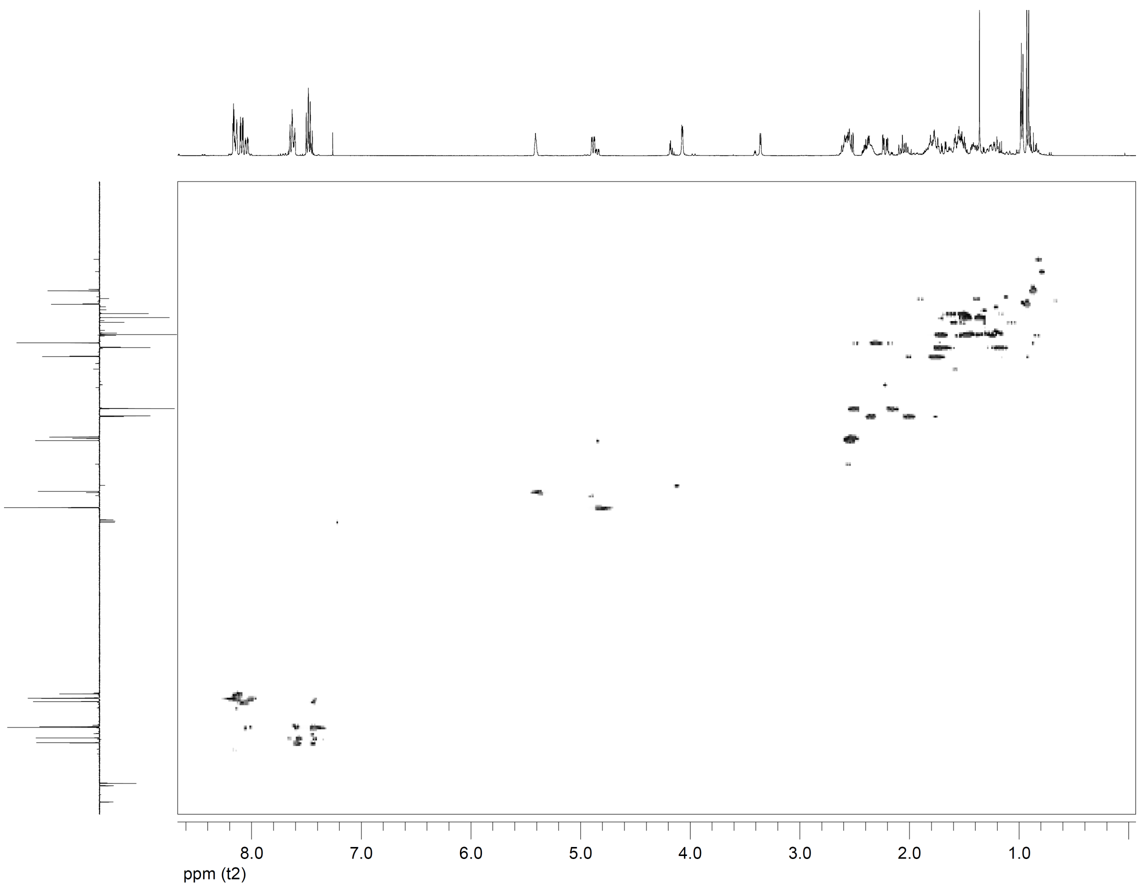
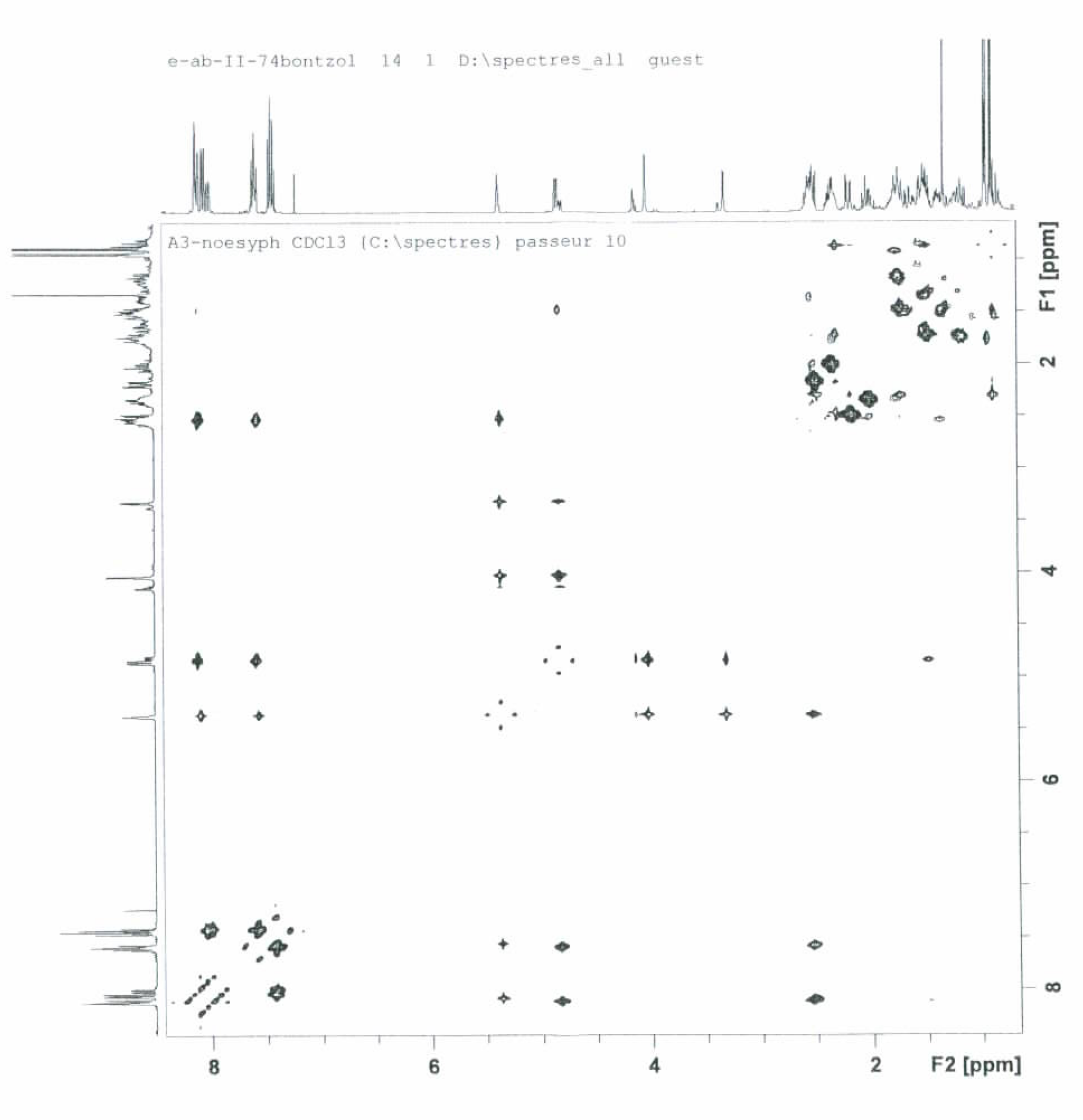
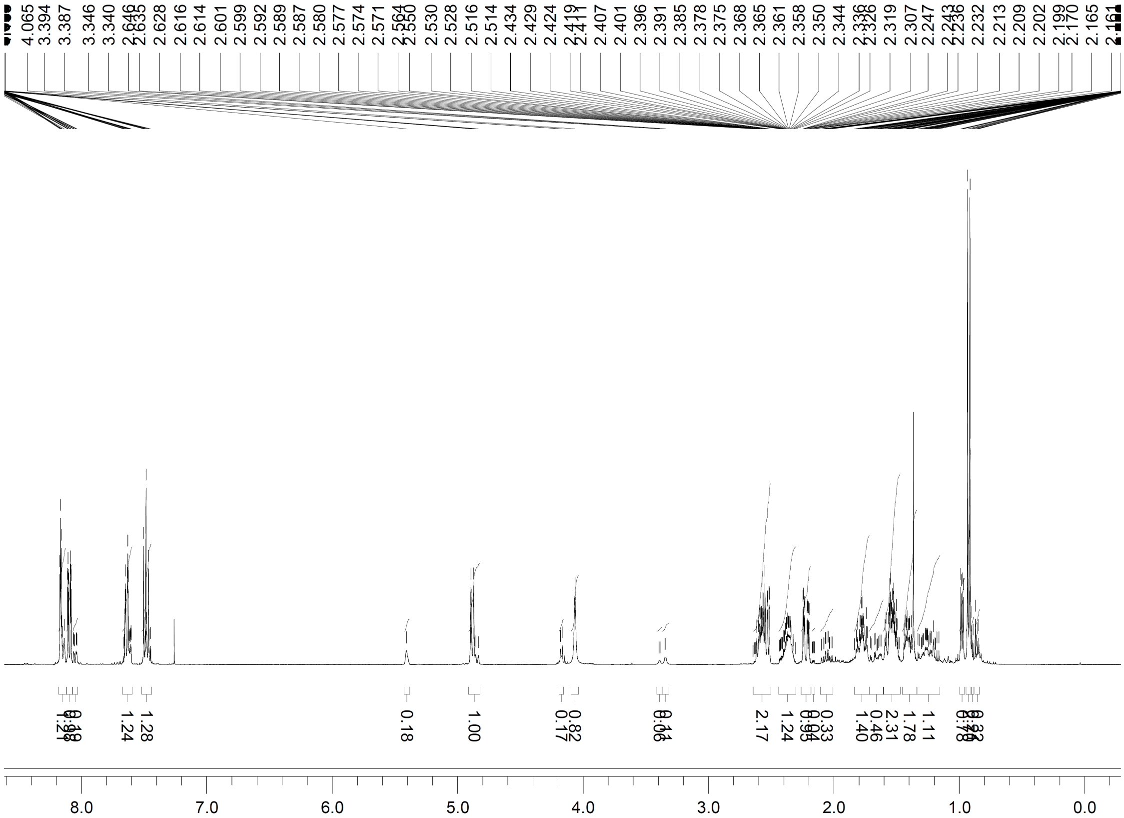
214.185
214.066
213.303
148.048
143.978
143.875
143.328
143.234
133.098
133.045
131.845
131.750
130.749
129.169
129.124
128.990
128.965
128.944
128.614
122.659
122.617
121.877
121.834
121.782
121.747
121.644
120.694
120.506
73.653
73.565
70.531
69.766
69.489
56.618
56.095
56.044
55.702
50.525
50.400
48.579
48.512
35.410
35.293
33.091
32.997
31.939
31.866
29.963
200
150
100
50
ppm (t1)

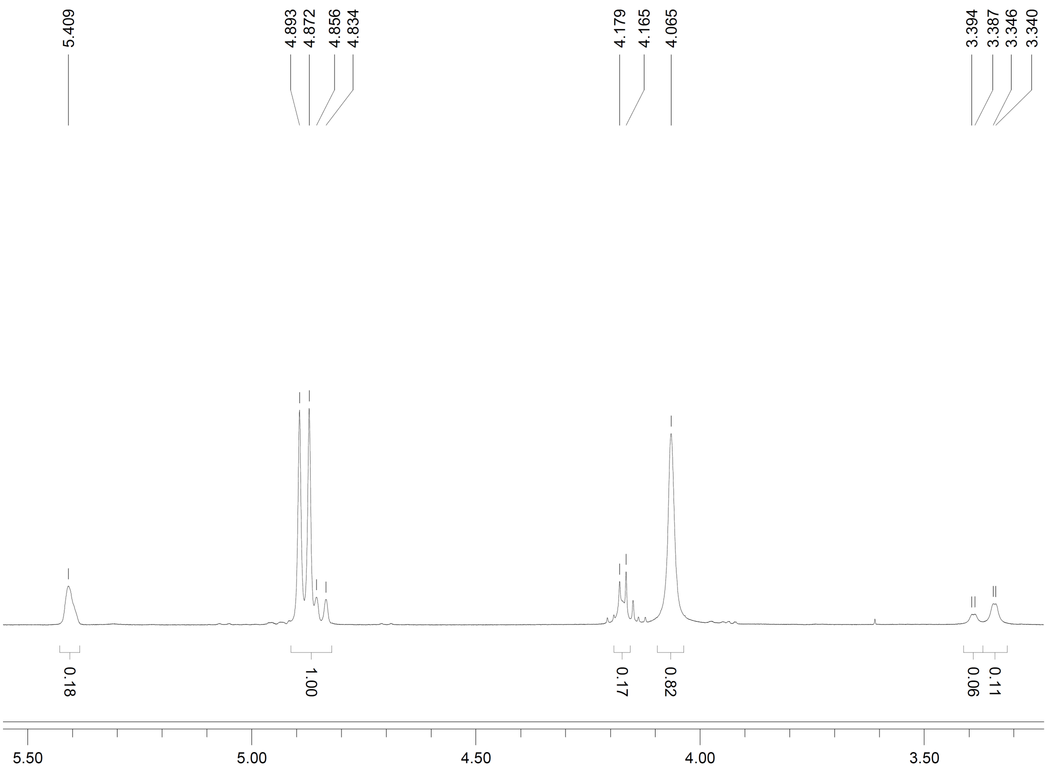

214.528
214.185
214.066
213.303
214.50
214.00
213.50
ppm (t1)


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t2)


e-ab-II-74bontzol 14 1 D:\spectres_all guest
A3-noesyph CDCl3 (C:\spectres) passeur 10
F1 [ppm]
F2 [ppm]
8
6
4
2

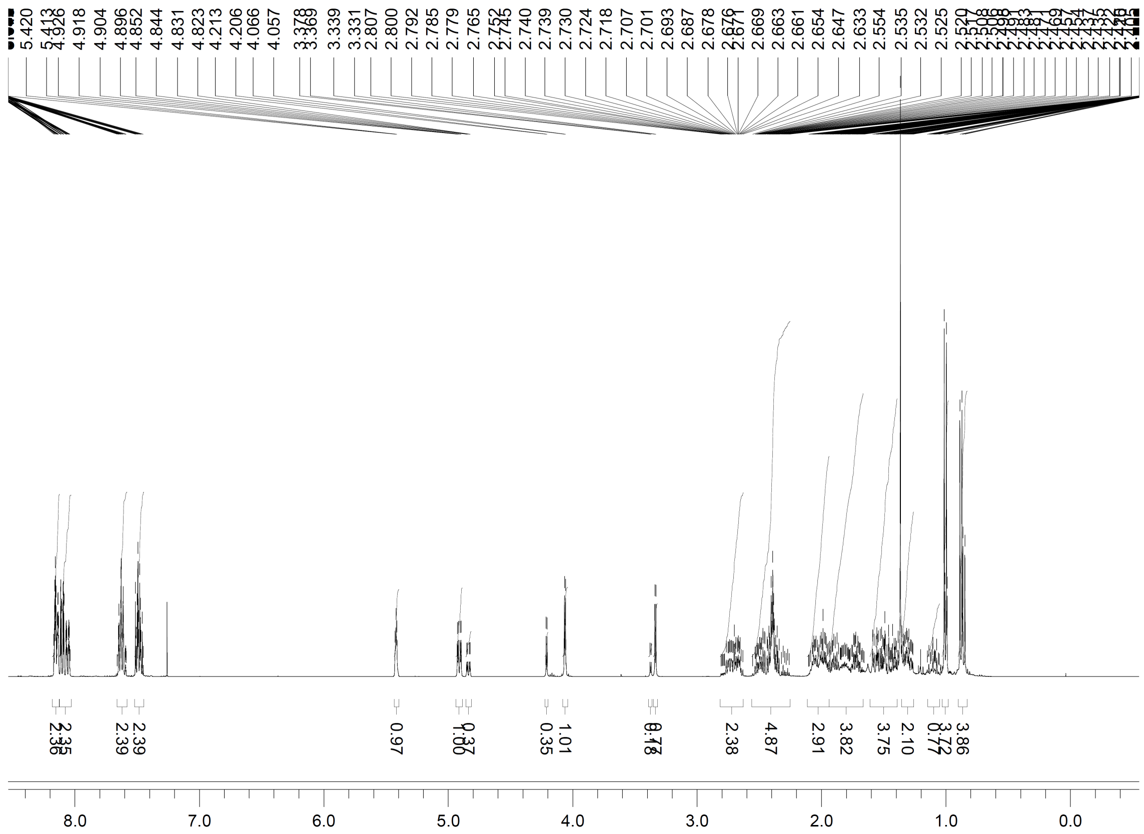
(R)-3-pyrrolidinol as catalyst with ethyl sugar 2b

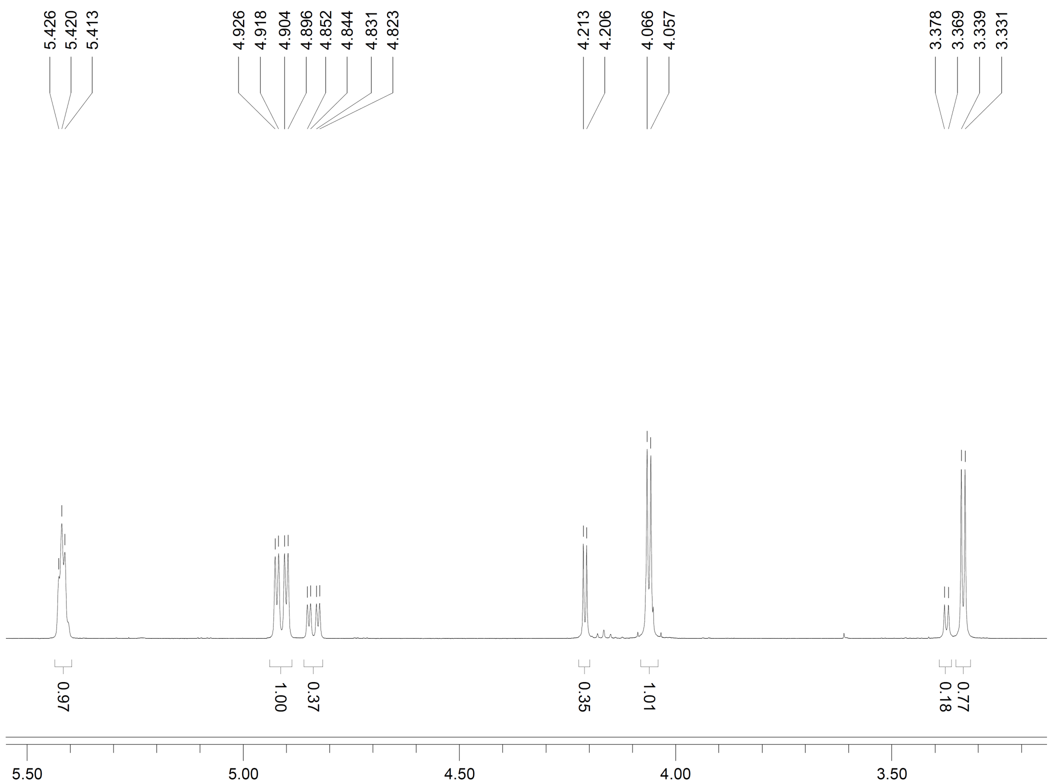




Compound 7

(R)-3-pyrrolidinol as catalyst in water





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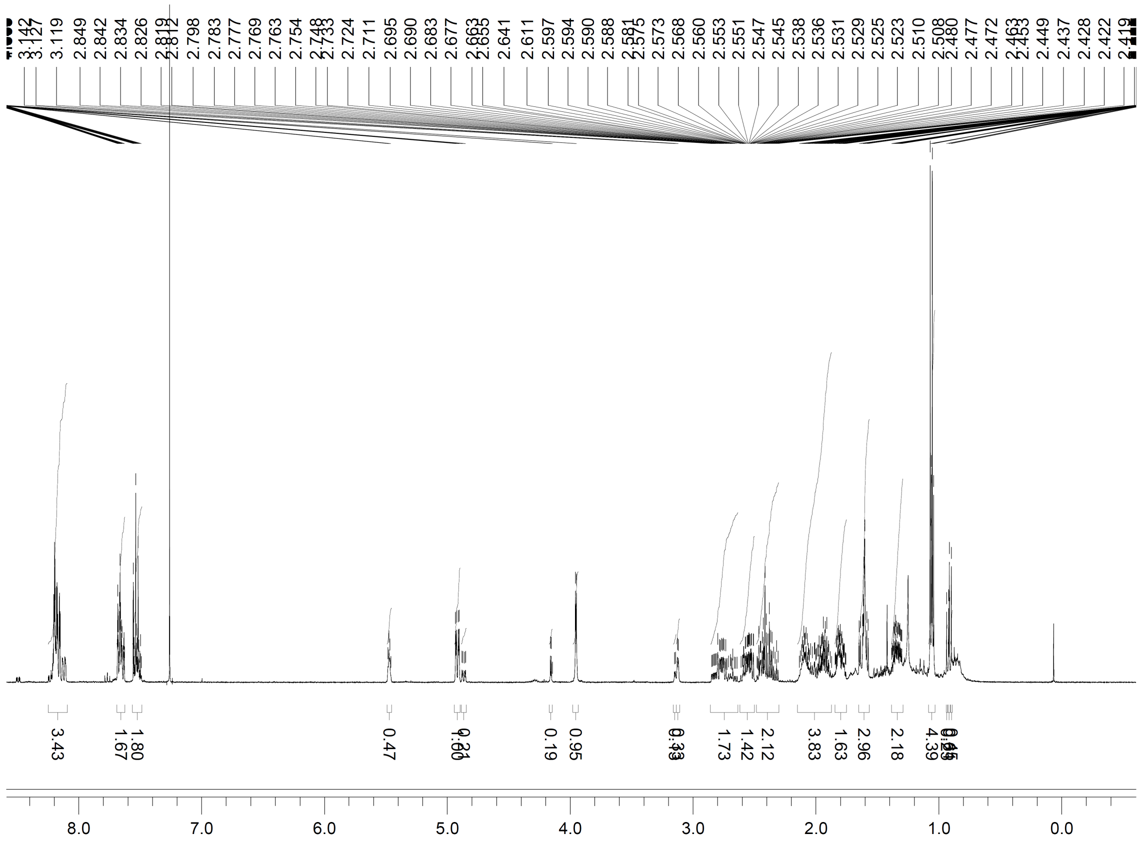
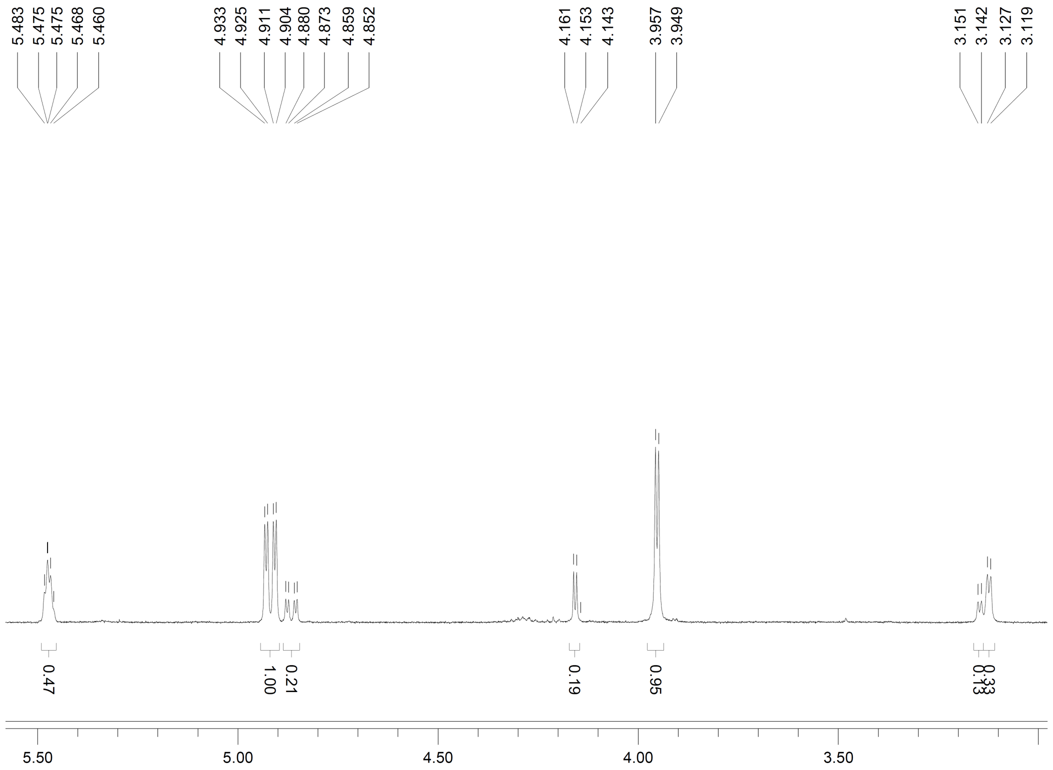
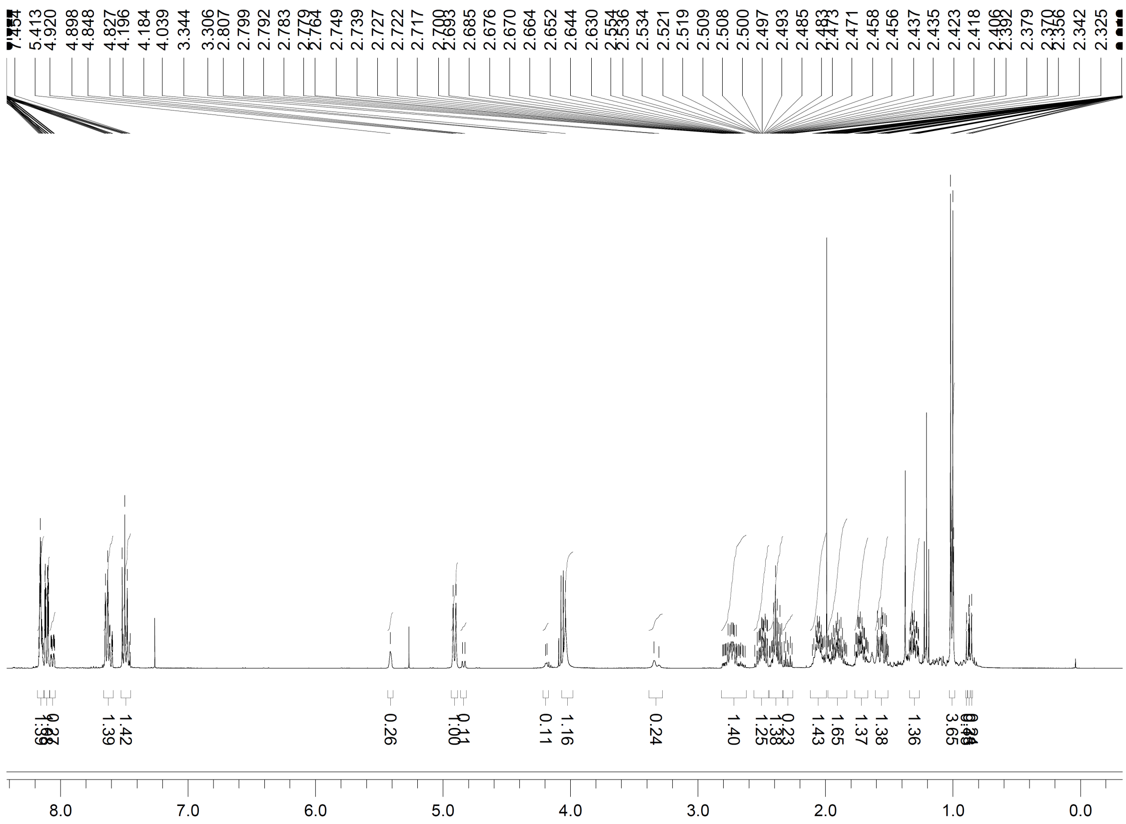
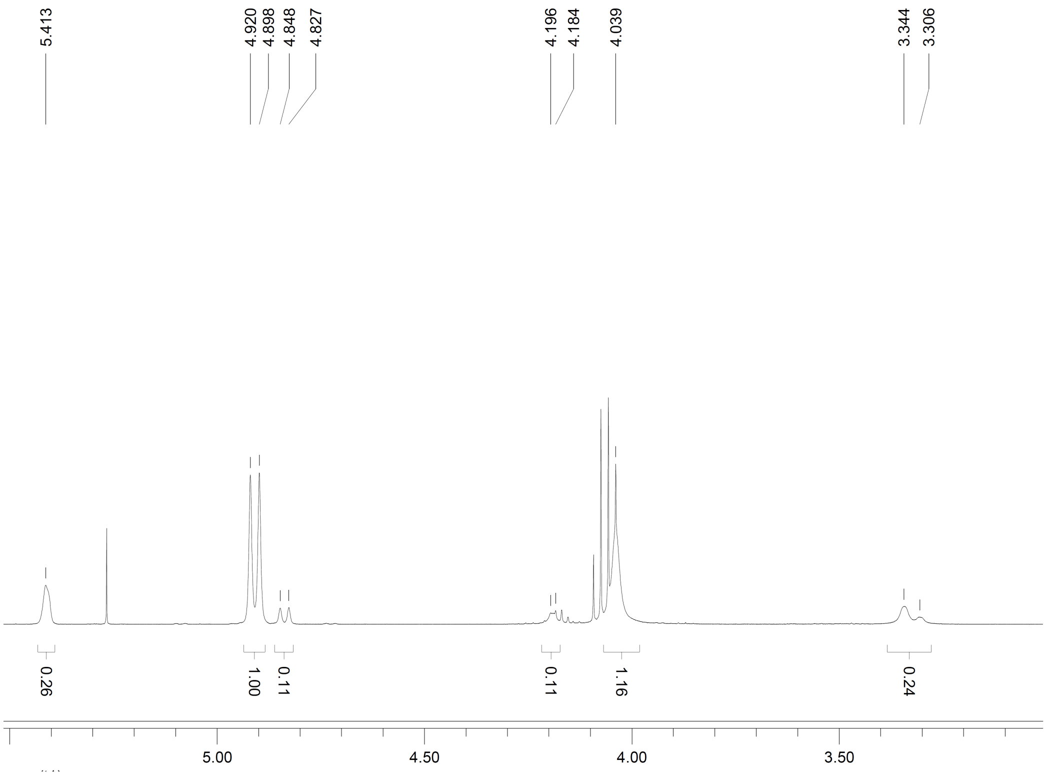
(R)-3-pyrrolidinol as catalyst with methyl sugar 2a



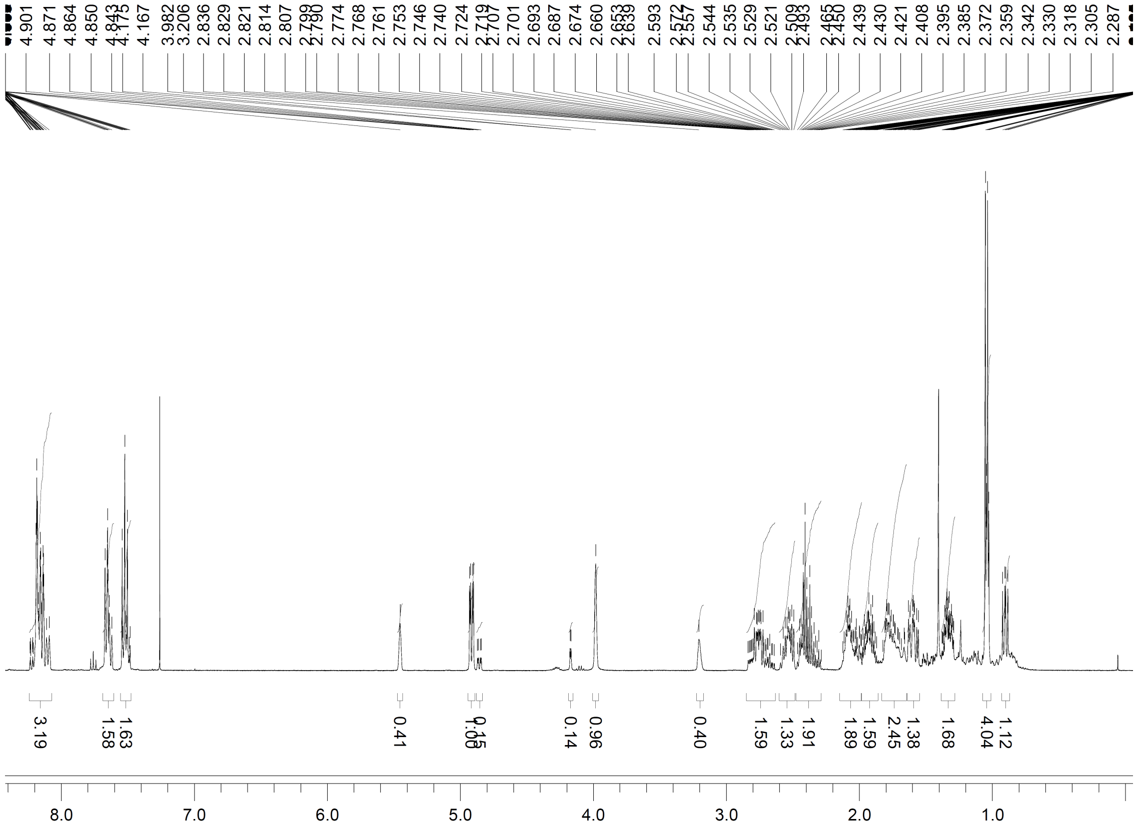


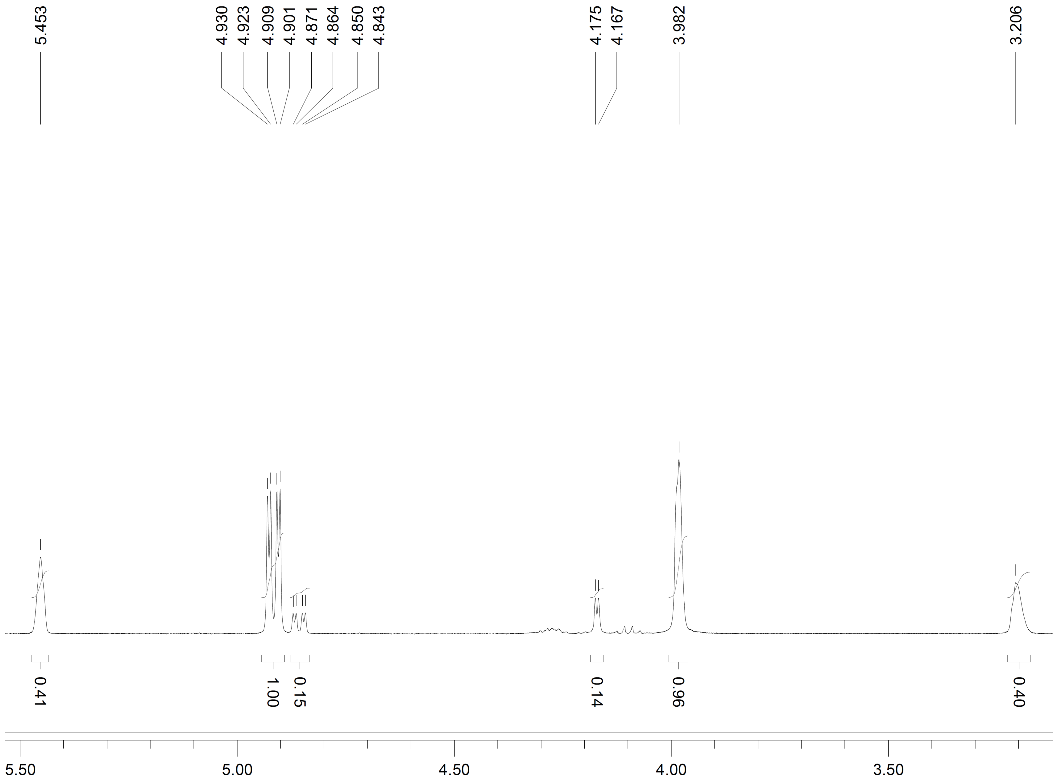
(R)-3-pyrrolidinol as catalyst with ethyl sugar 2b



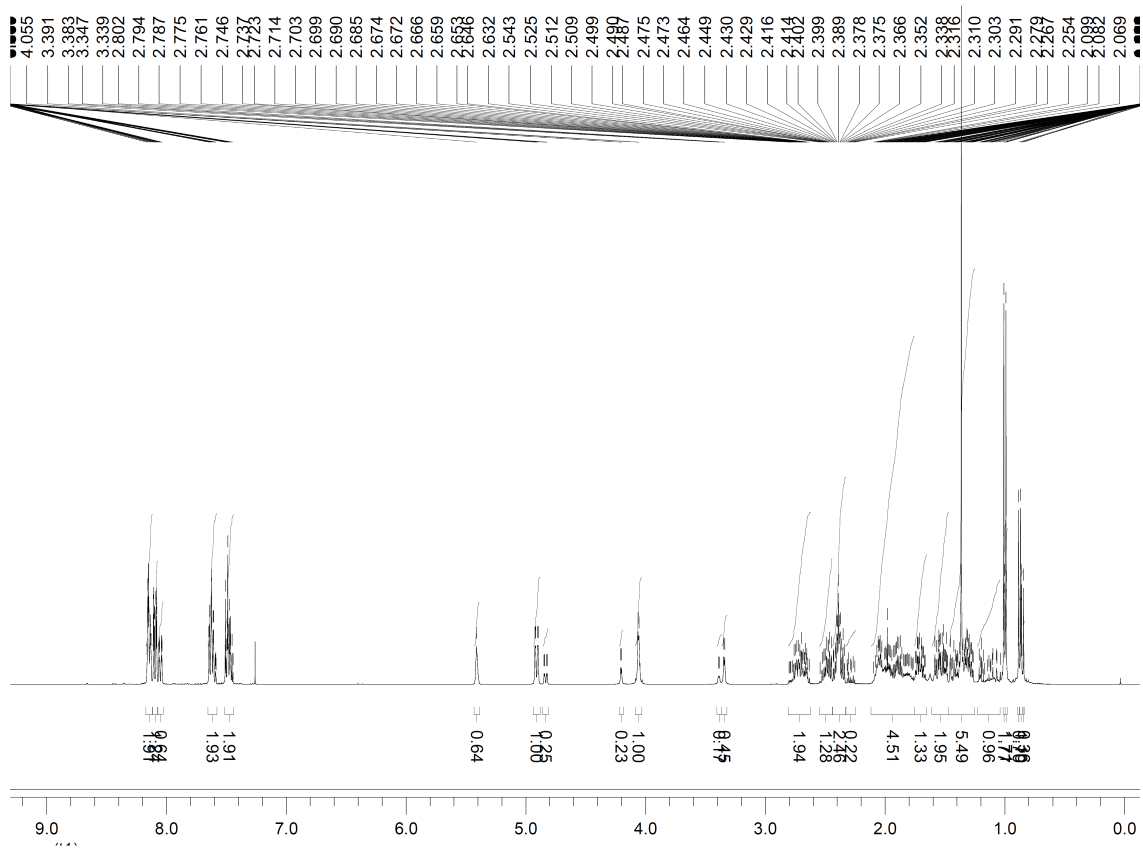


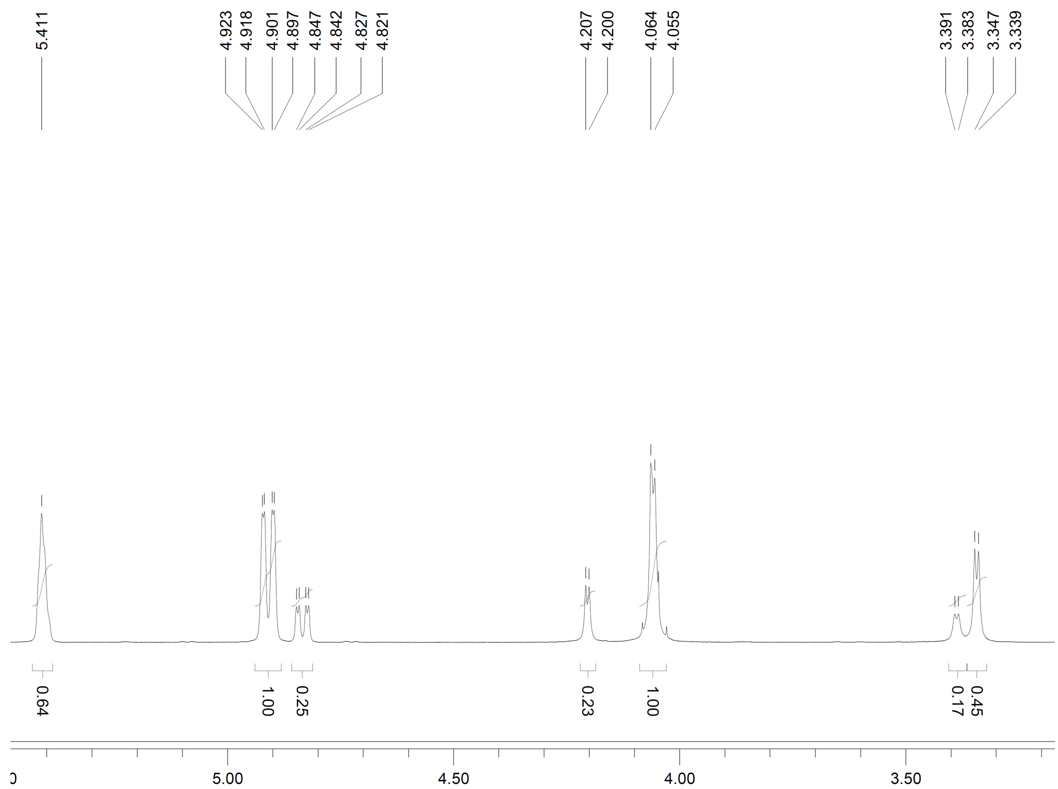
(R)-3-pyrrolidinol as catalyst with propyl sugar 2c





(R)-3-pyrrolidinol as catalyst with allyl sugar 2d





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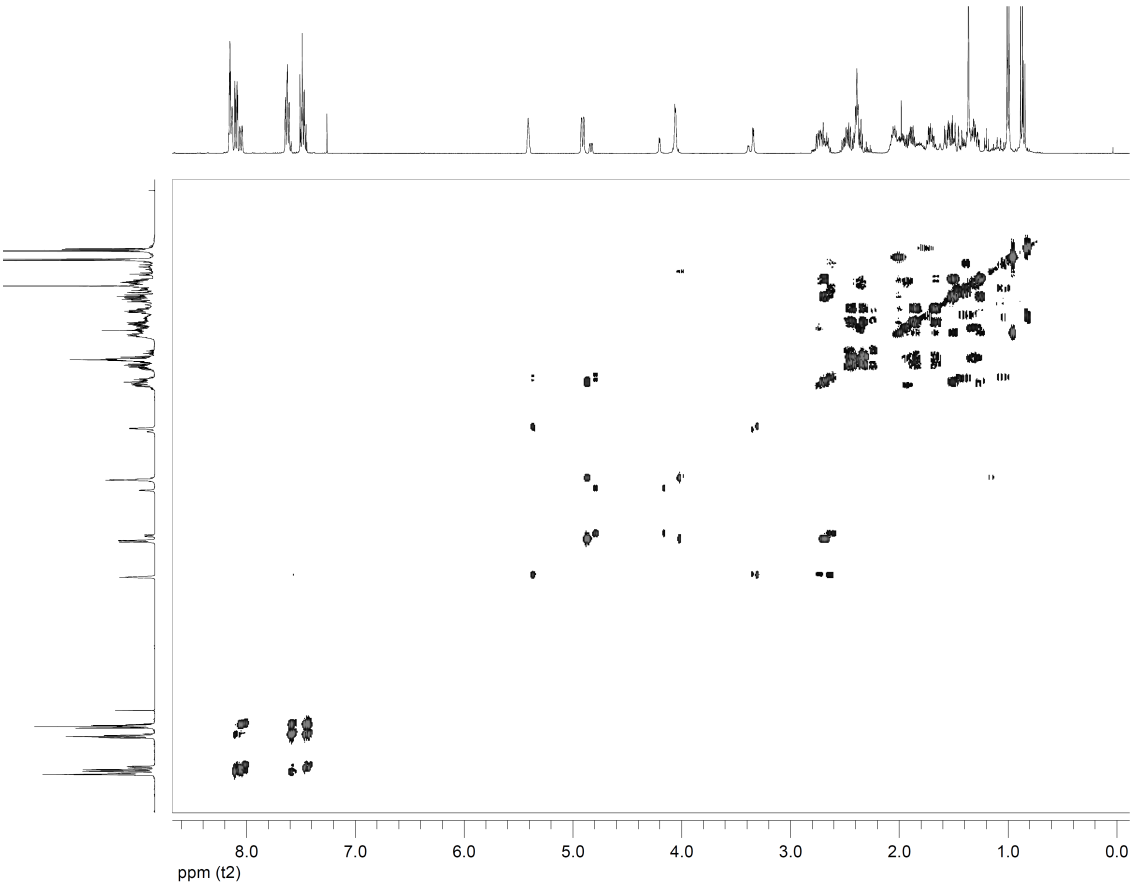

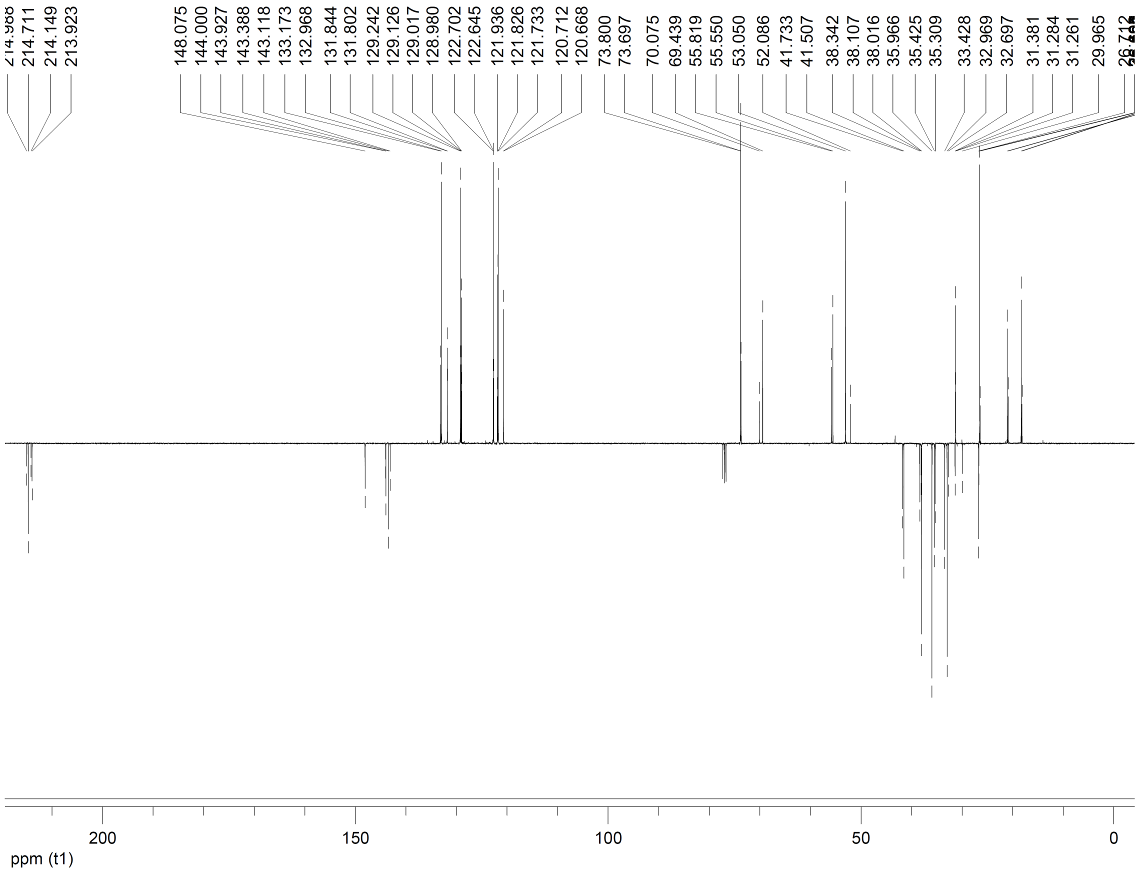

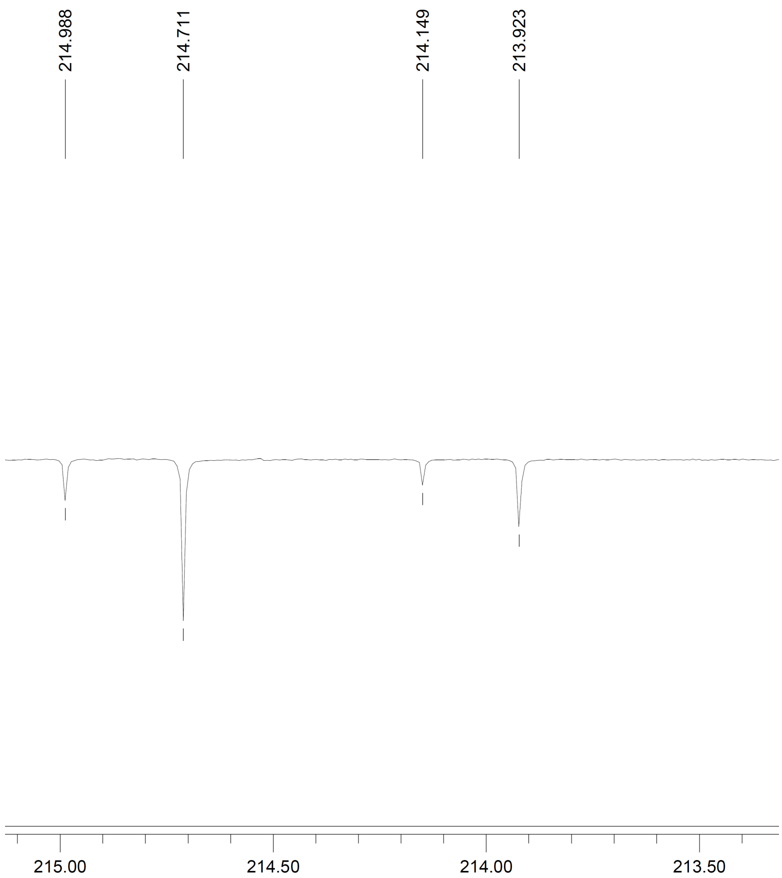
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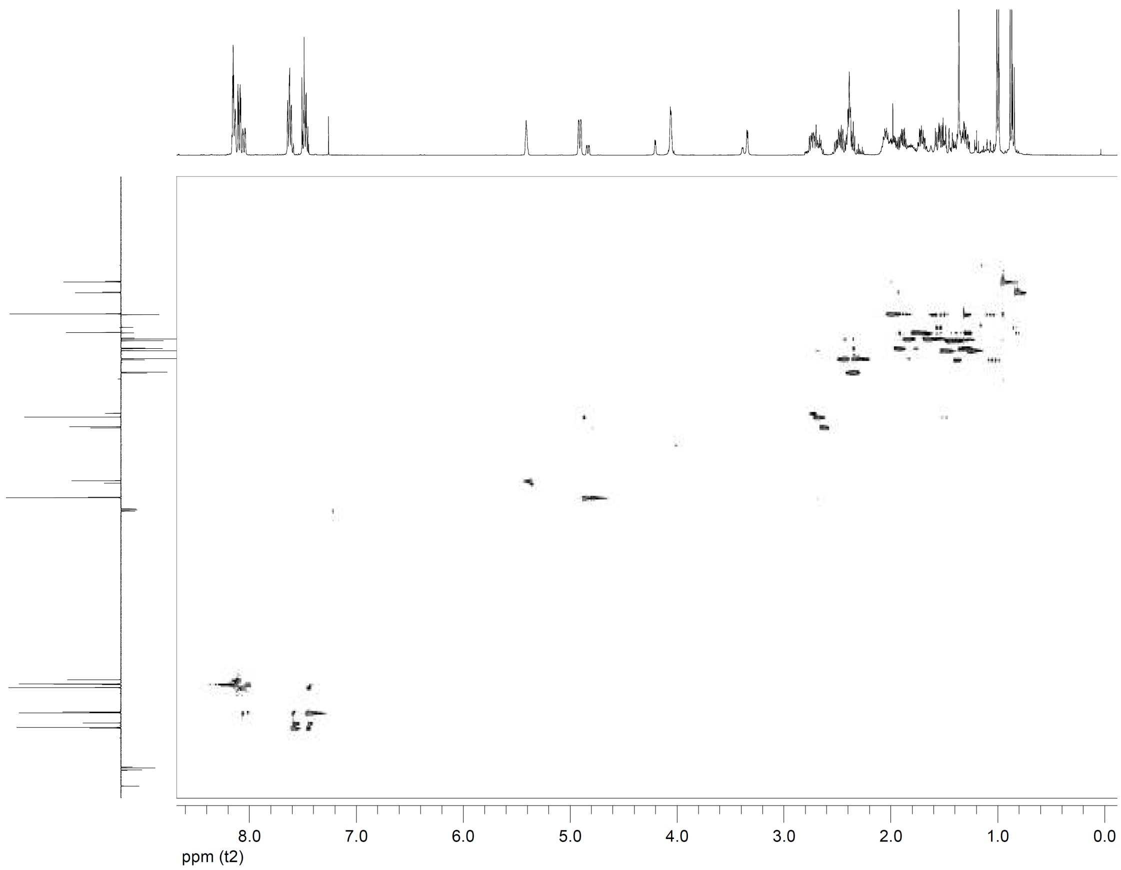
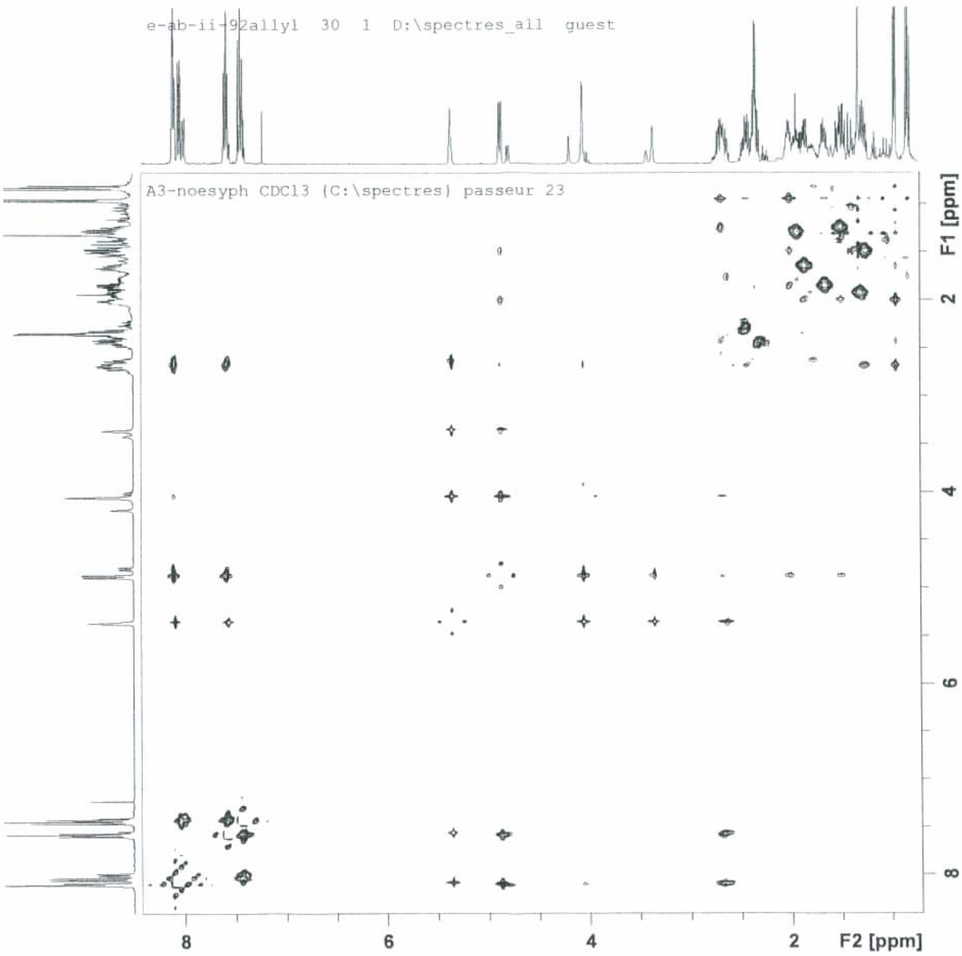
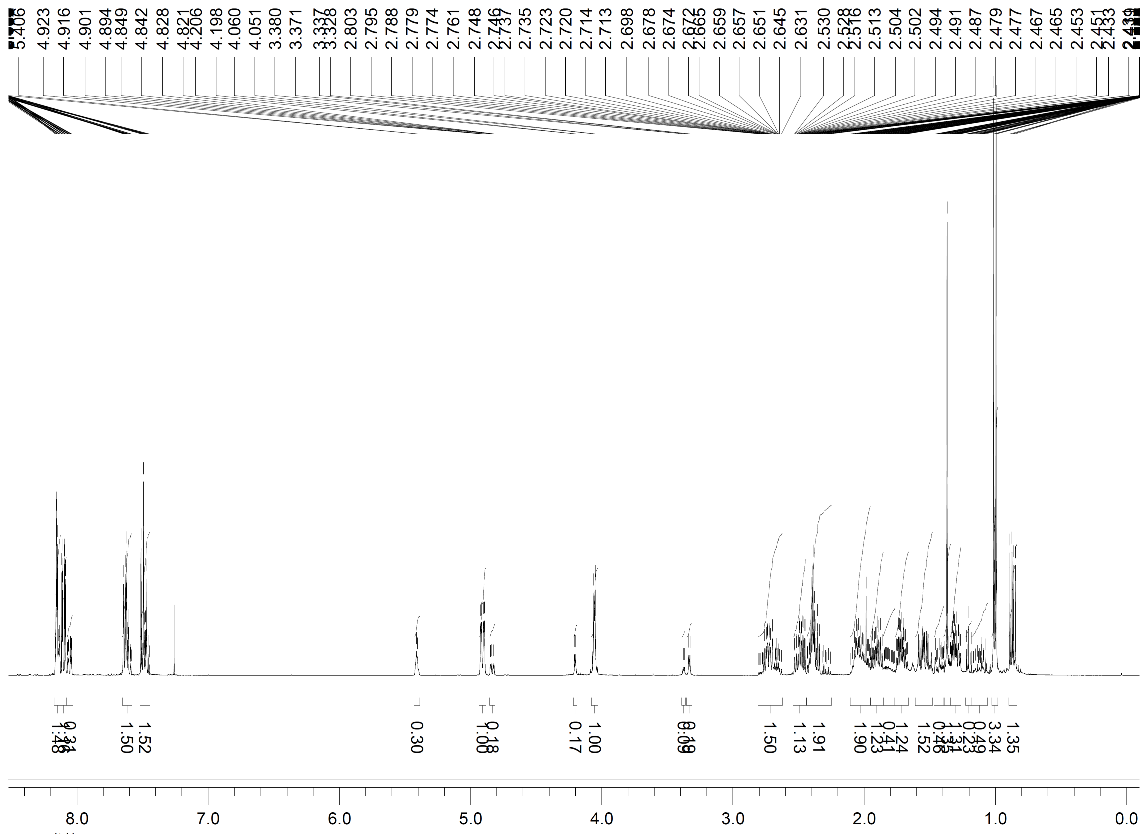
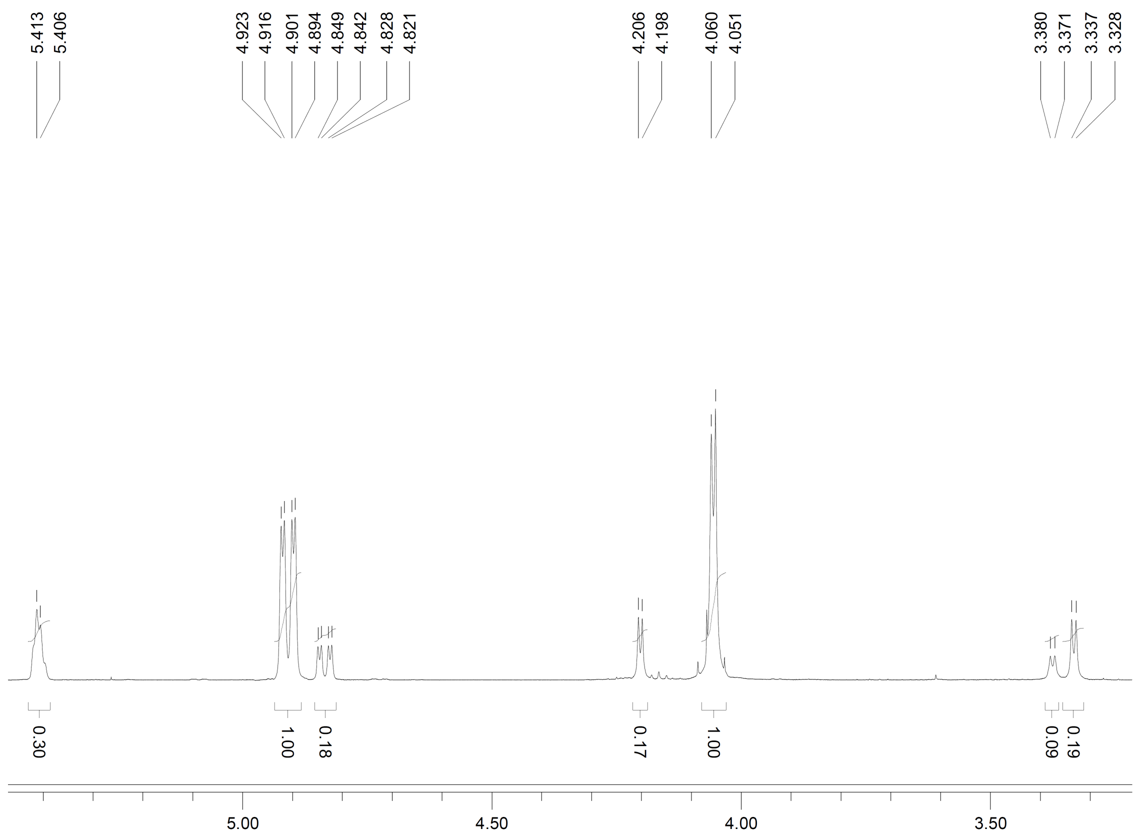
214.149
213.923
215.00
214.50
214.00
213.50


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t2)


e-ab-ii-92allyl 30 1 D:\spectres_all guest
A3-noesyph CDCl3 (C:\spectres) passeur 23
F1 [ppm]
2
4
6
8
8
6
4
2
F2 [ppm]

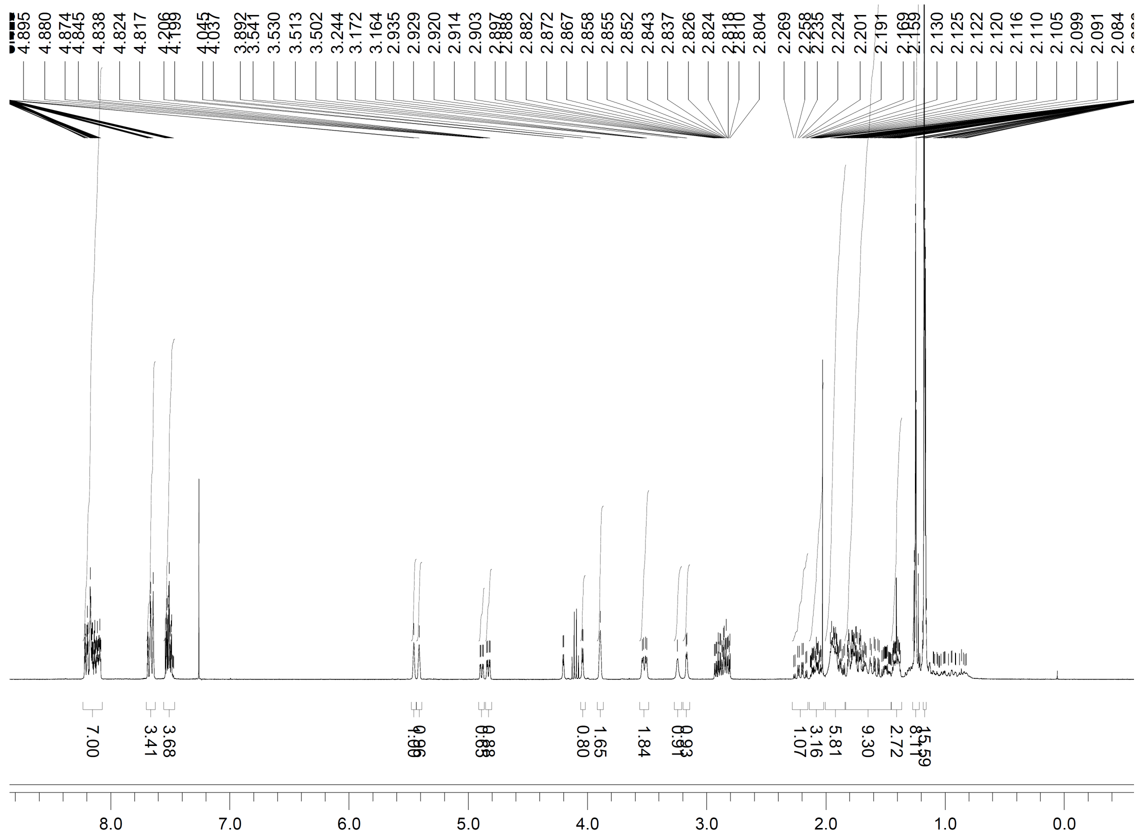
(R)-3-pyrrolidinol as catalyst with pentenyl sugar 2e

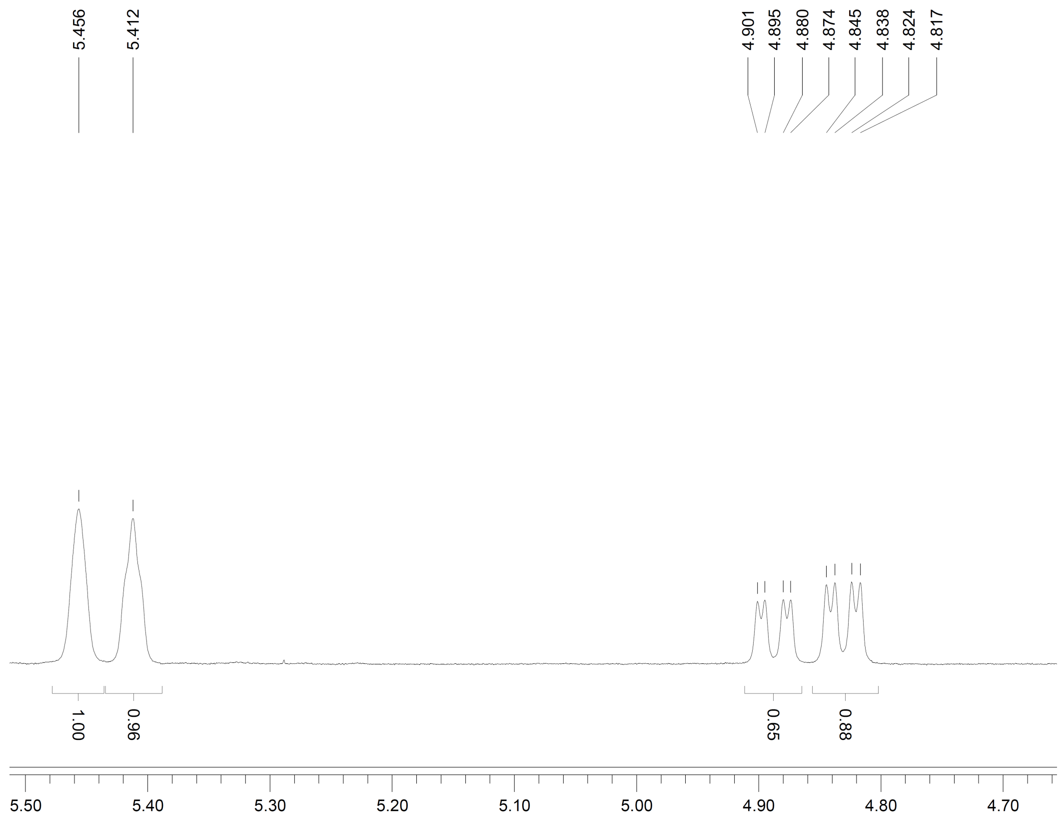




Compound 7

(R)-3-pyrrolidinol as catalyst in water





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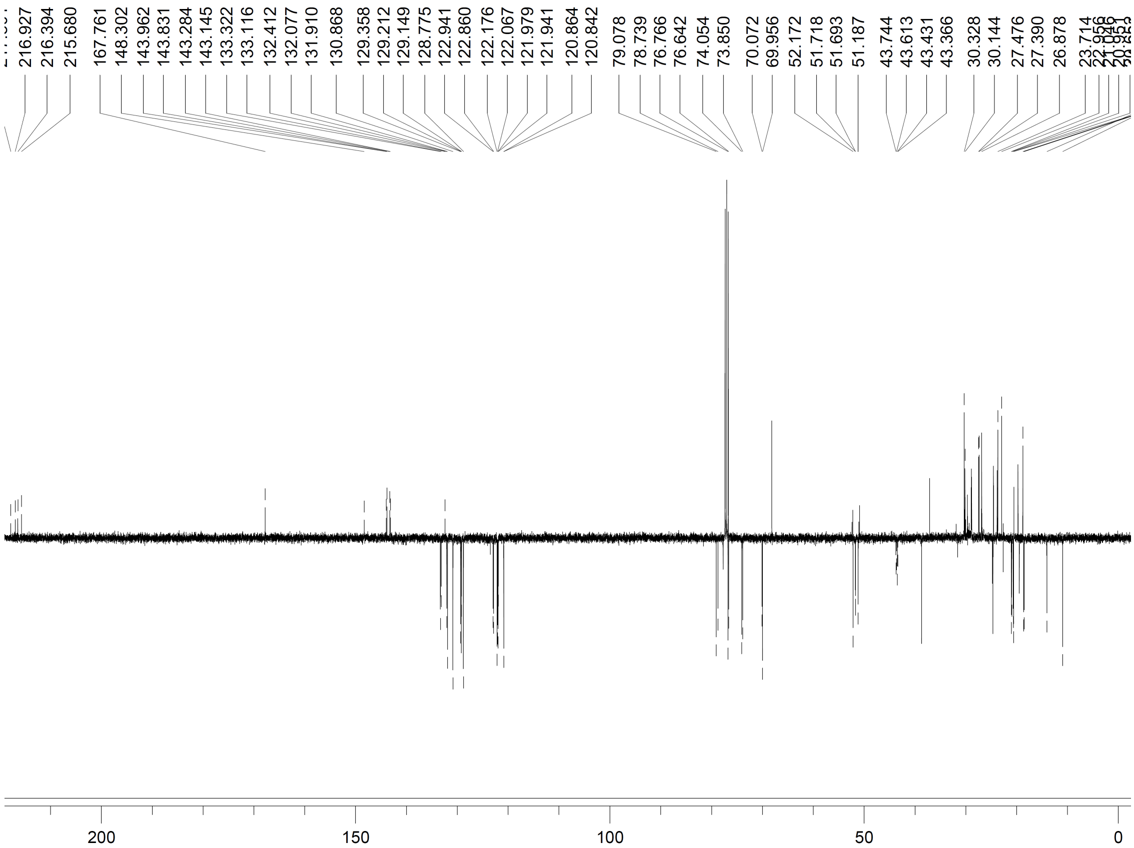
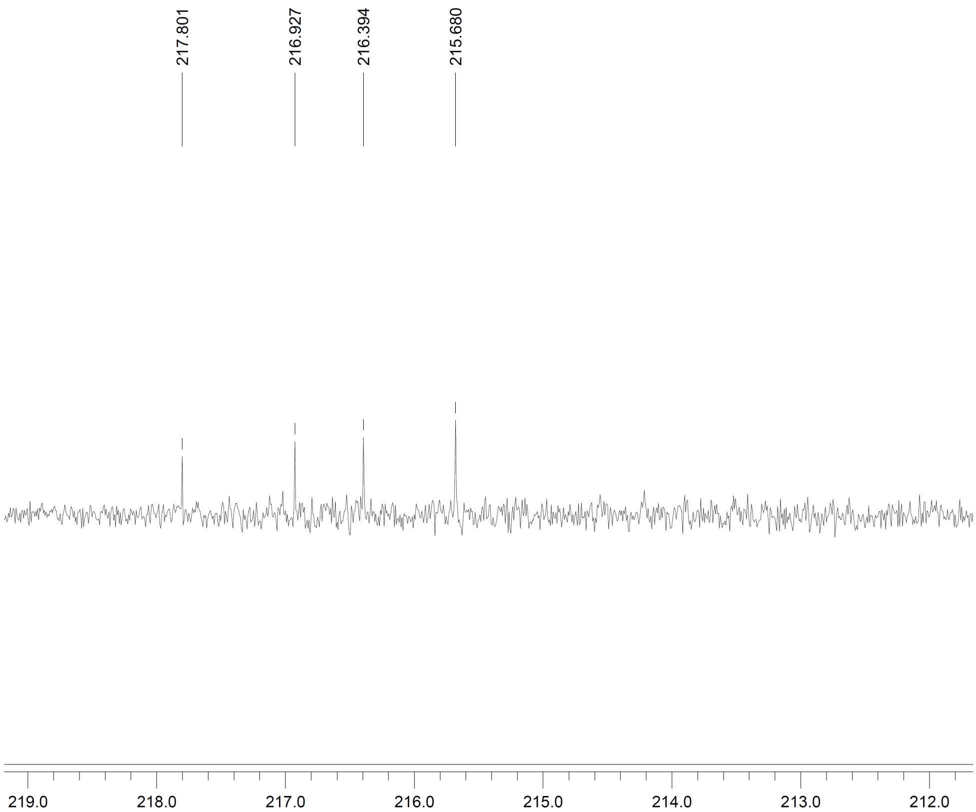
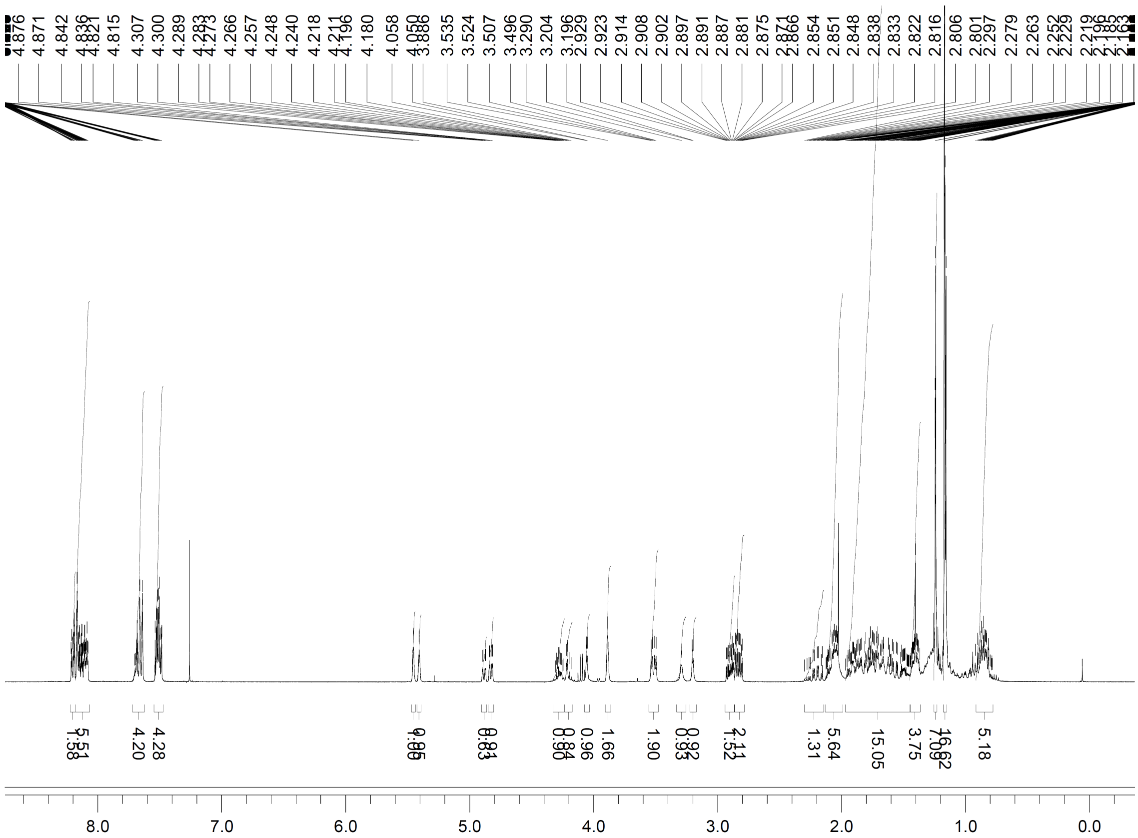
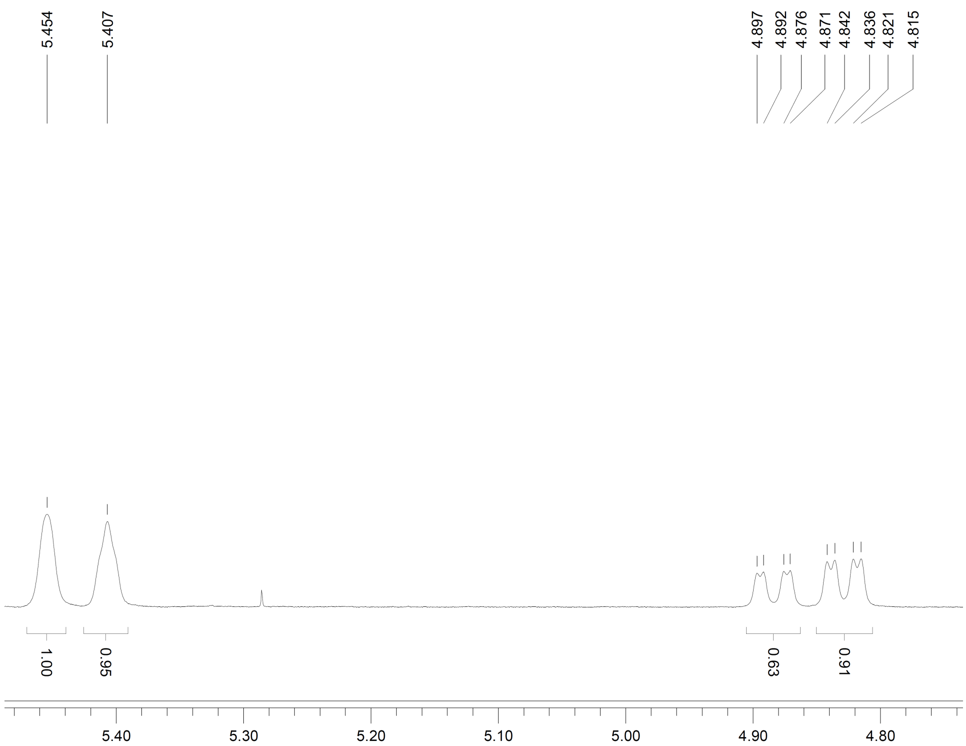




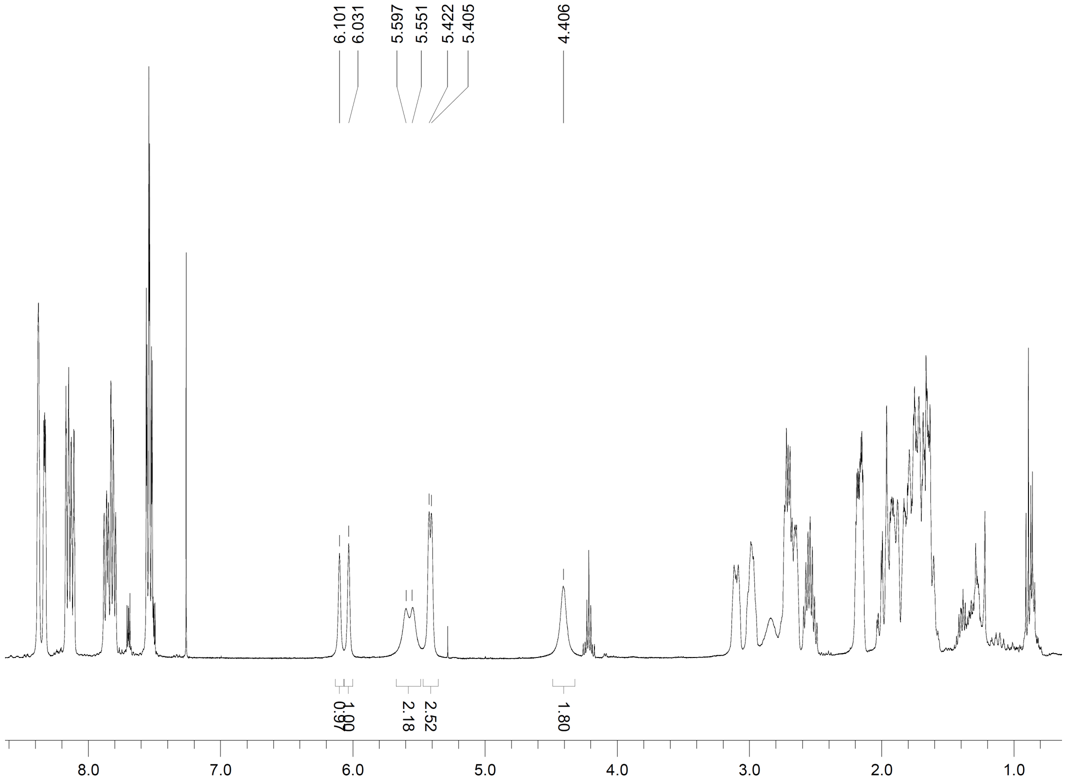
(R)-3-pyrrolidinol as catalyst with ethyl sugar 2b



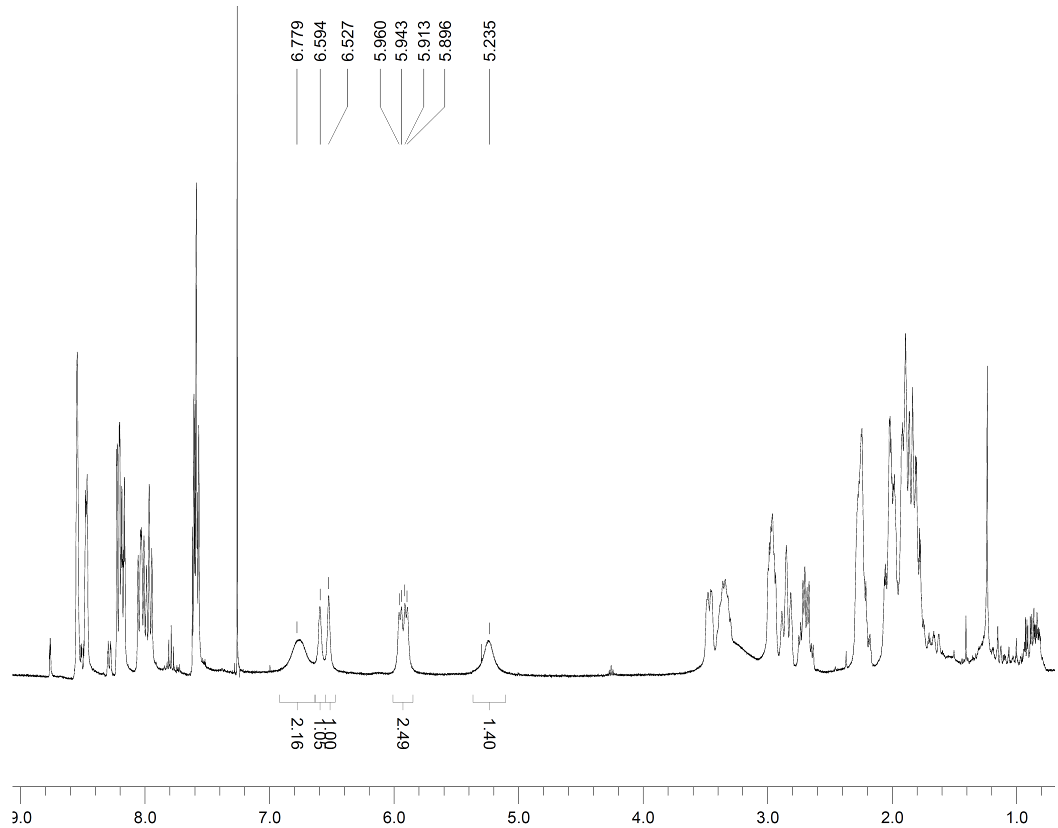


Europium experiments

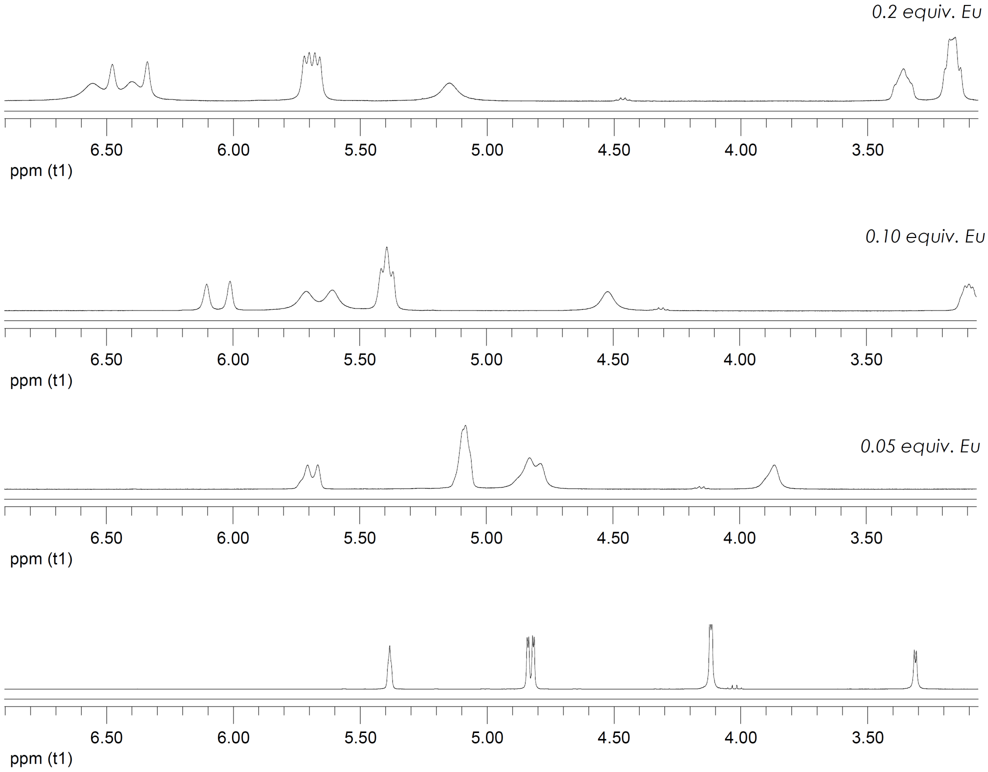
Compound 3 - Ethanolamine as catalyst in water



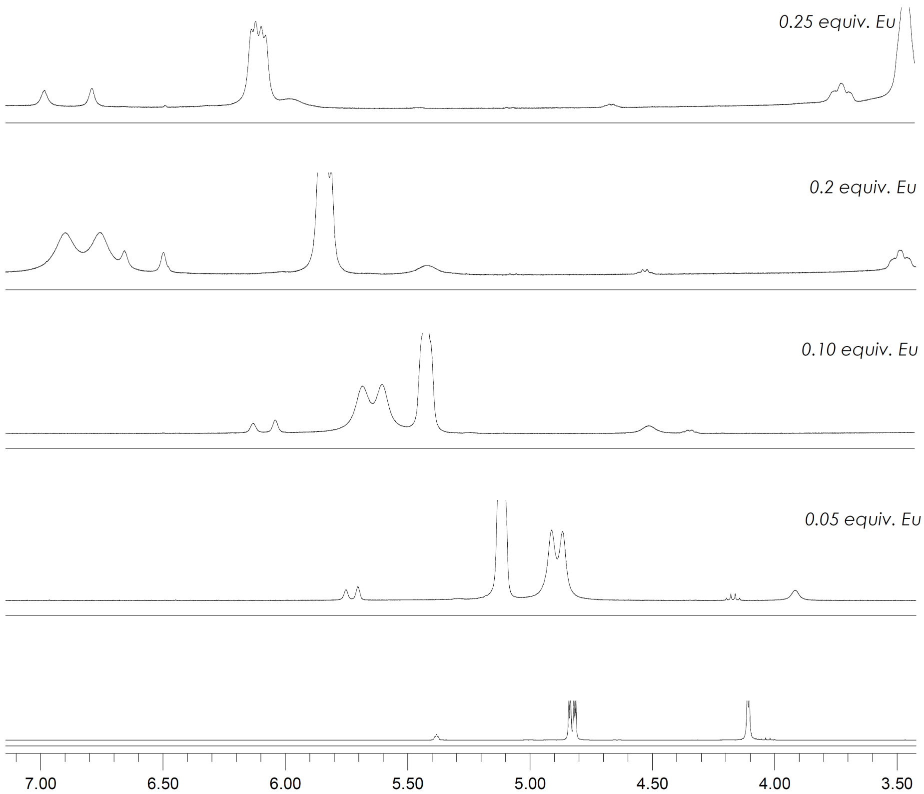
Compound 3 - Ethanolamine as catalyst with ethyl sugar 2b



Compound 3 - (R)-3-pyrrolidinol as catalyst in water



Compound 3 - (R)-3-pyrrolidinol as catalyst with ethyl sugar 2b



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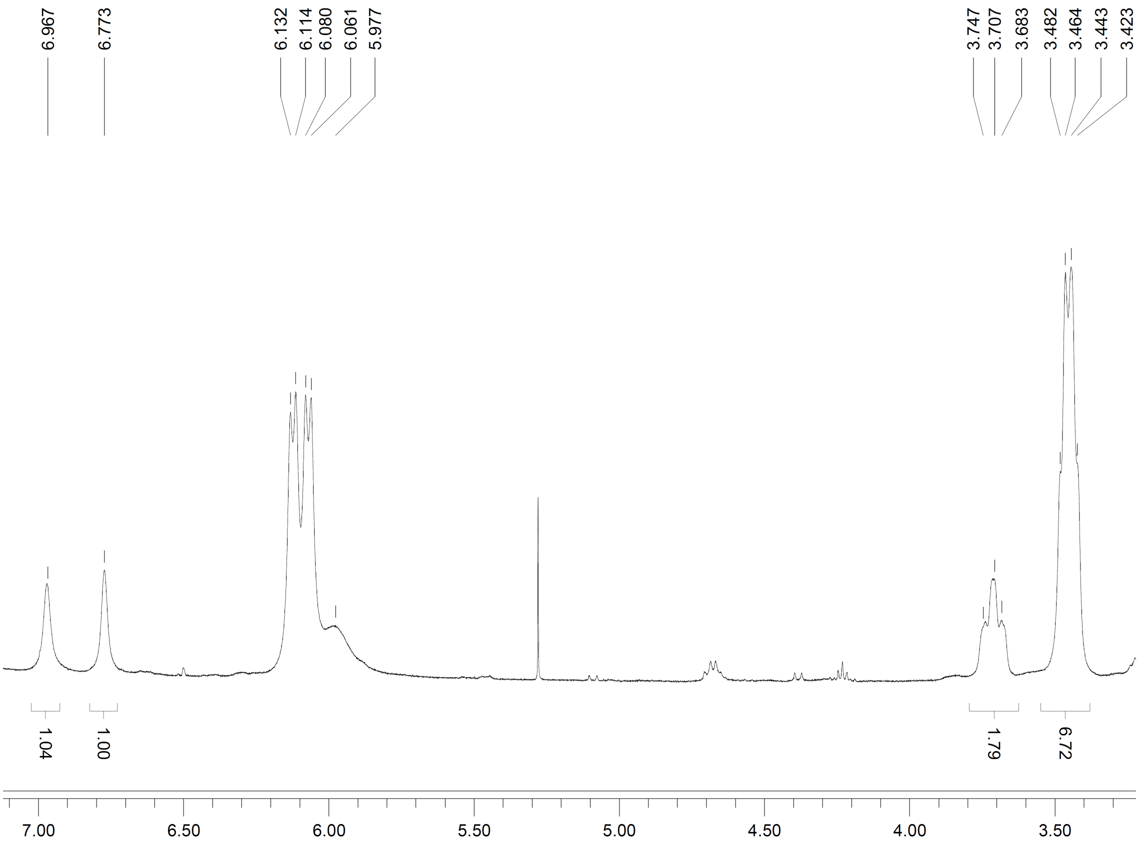
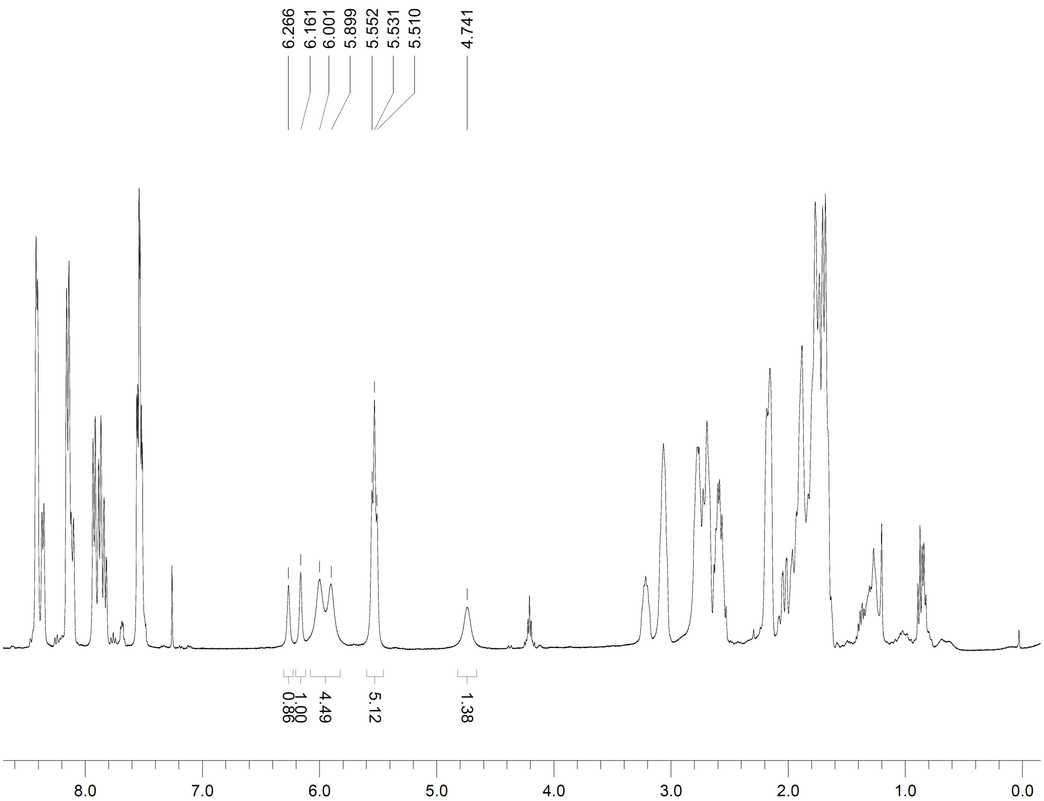
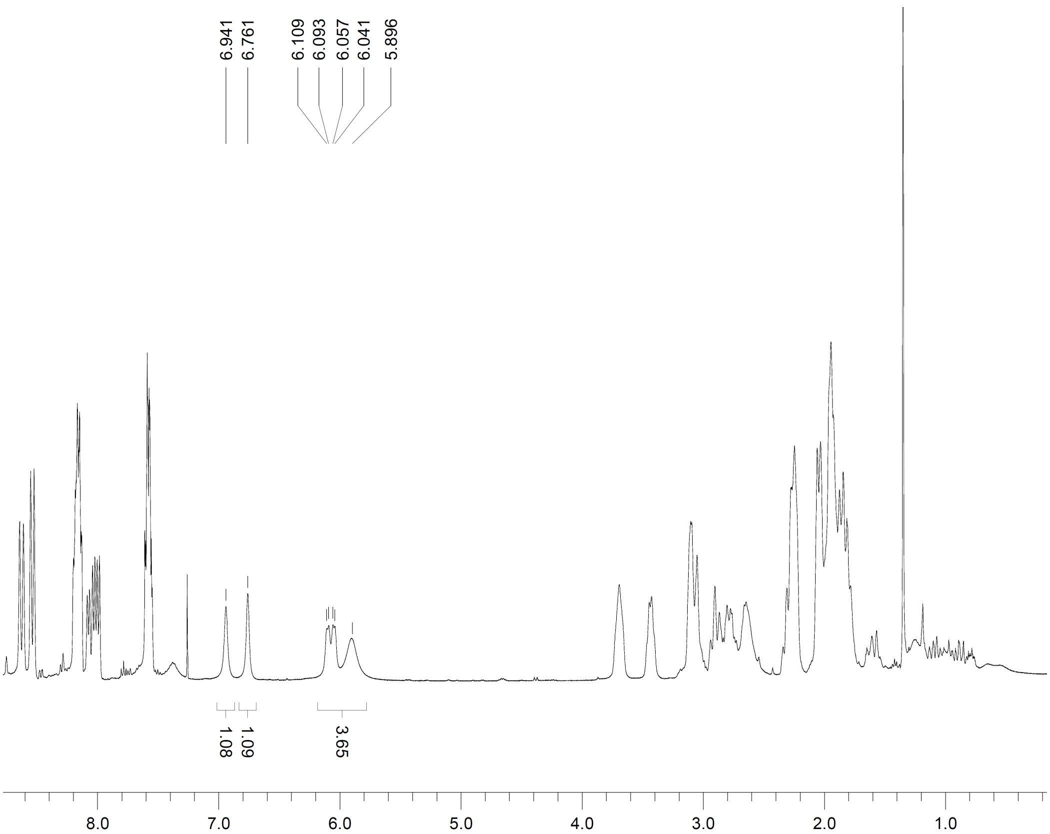
Compound 3 - (R)-3-pyrrolidinol as catalyst with saccharose 1



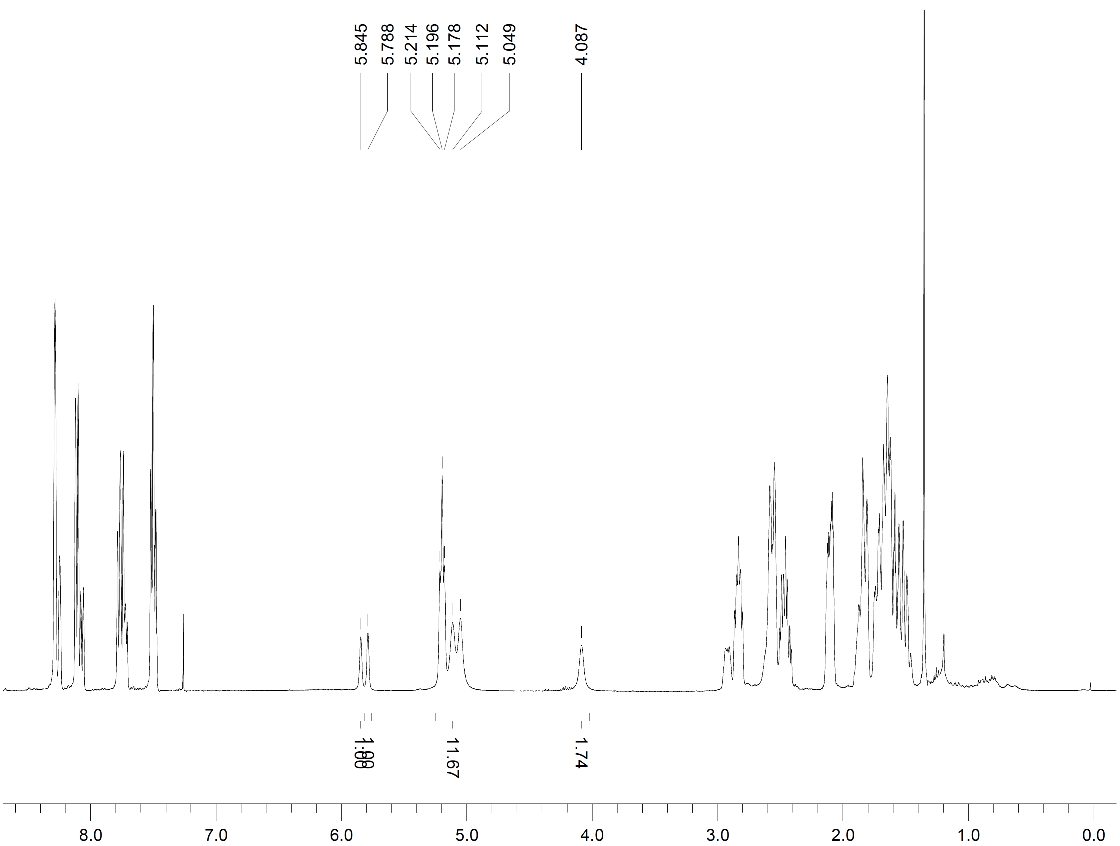
Compound 3 - L-prolinol as catalyst in water



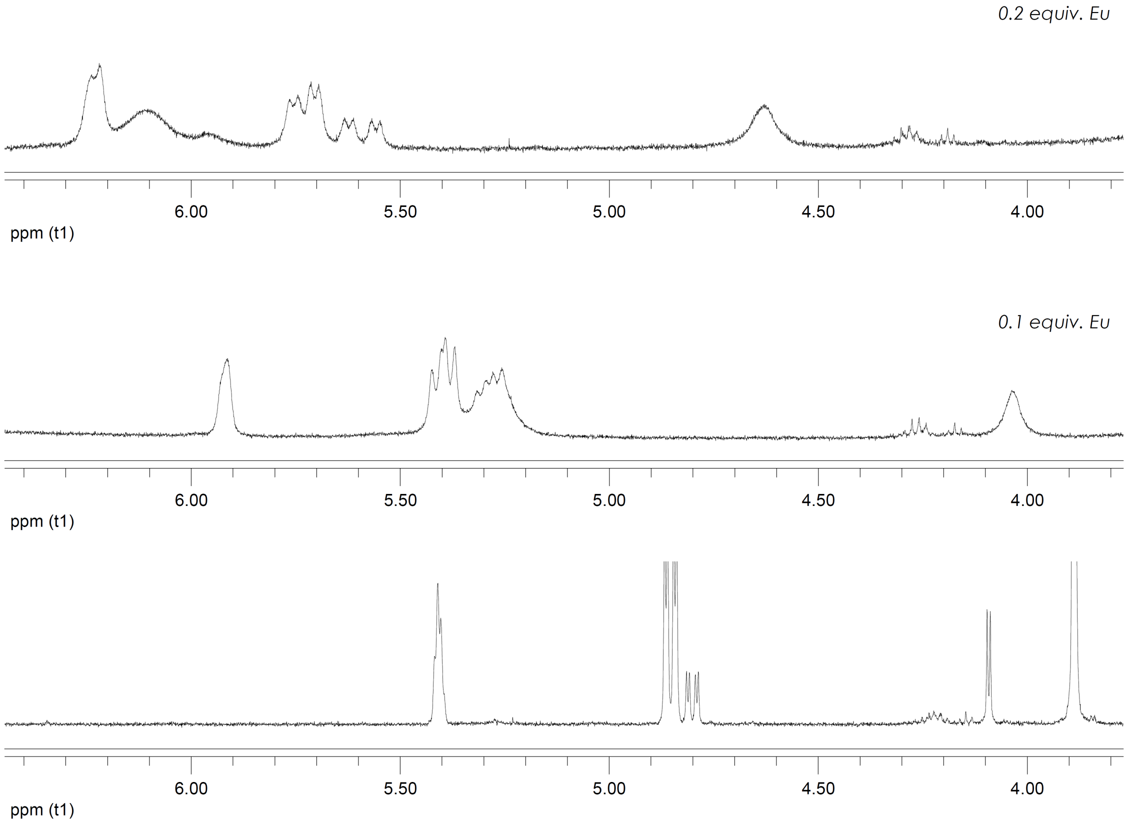
Compound 3 - Pyrrolidine as catalyst in water



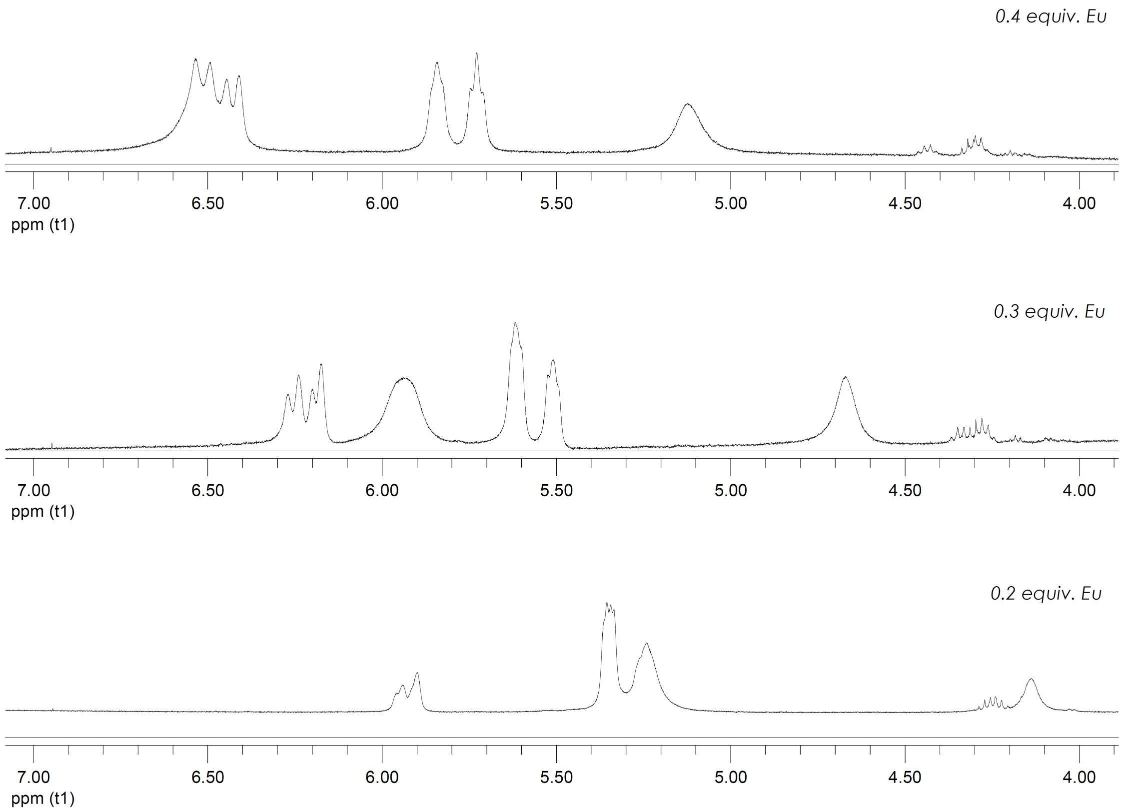
Compound 3 - rac-pyrrolidinol as catalyst in water



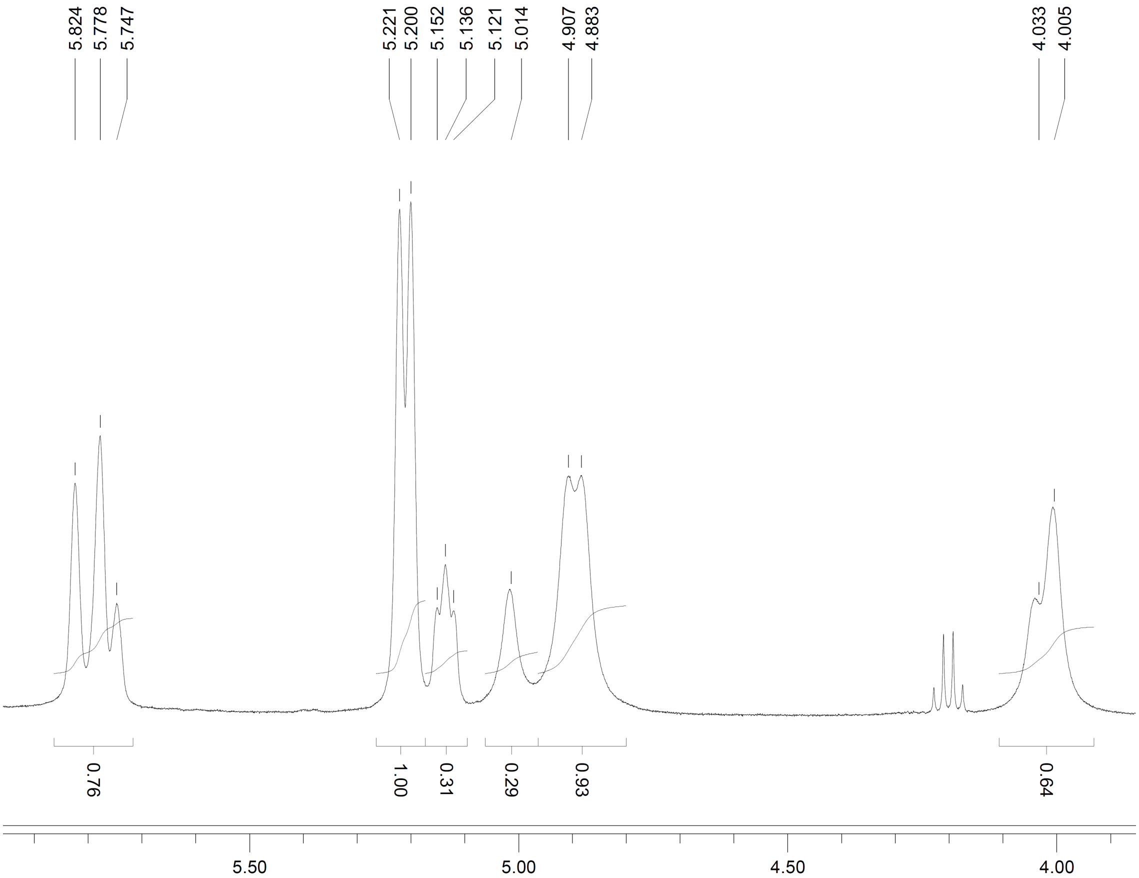
Compound 6 -(R)-3-pyrrolidinol as catalyst with methyl sugar 2a



Compound 6 -(R)-3-pyrrolidinol as catalyst with ethyl sugar 2b



***Compound 6 -(R)-3-pyrrolidinol as catalyst with allyl sugar* 2e**



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NMR Study for Interaction of 2d, Cyclohexanone and the Catalyst

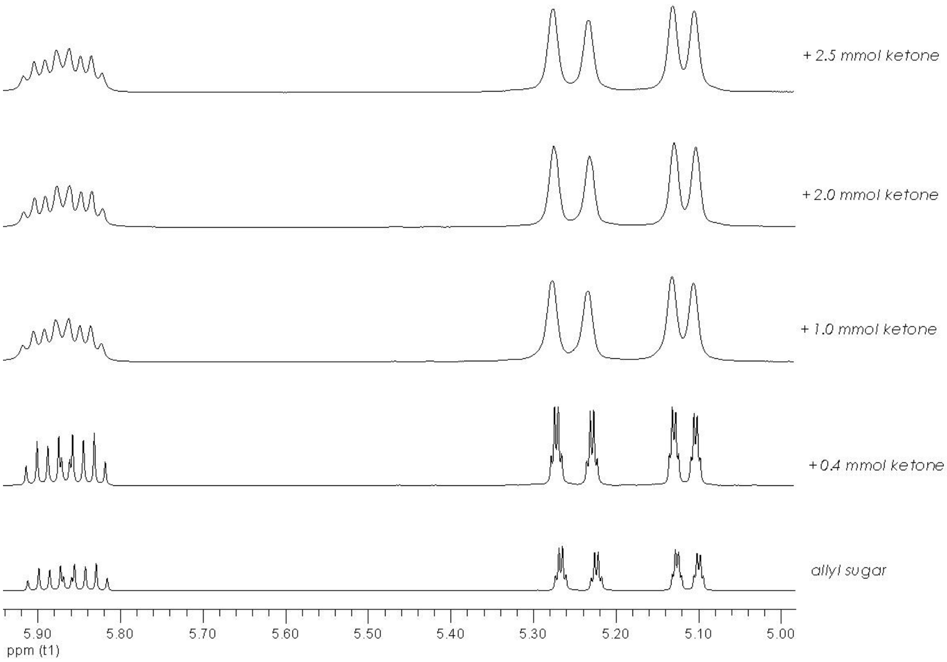

Figure S1. NMR study for the interaction between the sugar and (*R*)-3-pyrrolidinol (10 mol%) in the presence of increasing amounts of cyclohexanone. Only the signals of the allyl group in the sugar **2d** are shown.

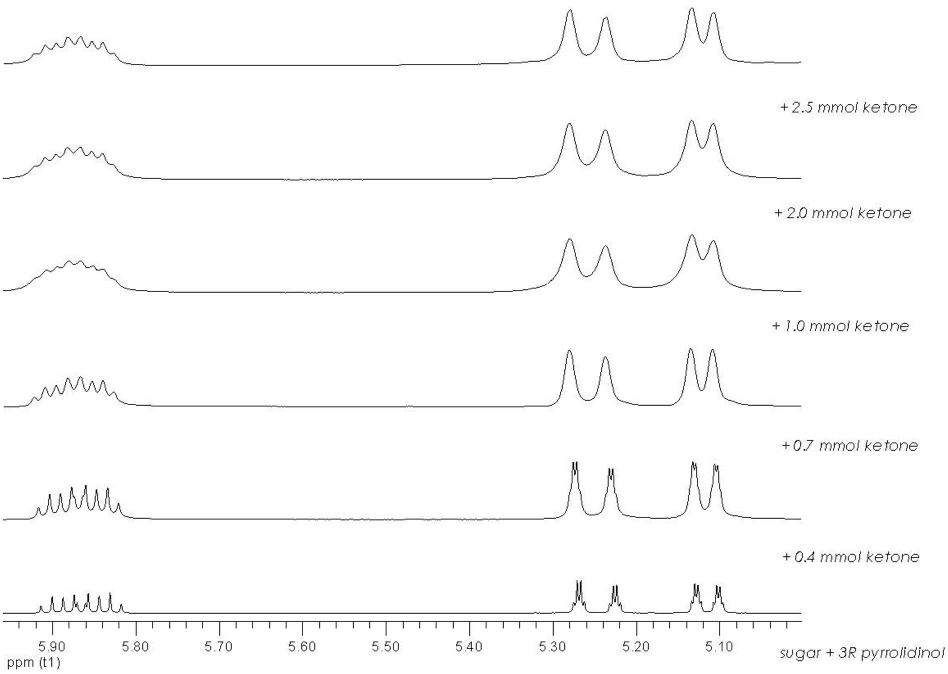

Figure S2. NMR study for the interaction between the sugar and different amounts of cyclohexanone. Only the signals of the allyl group in the sugar **2d** are shown.