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Supporting Information

The synthesis of oligomers containing alternating C-glycosyl α-amino acids and proteinogenic α-amino acids

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Content

Experimental section

General. All experiments were monitored by analytical thin-layer chromatography (TLC) performed on Merck Kieselgel 60 F254 0.25 mm precoated aluminium plates. After elution, the plate was visualized by staining with *p*-anisaldehyde and charring on a hot plate. *p*-Anisaldehyde solution was prepared by adding added 5 mL of concentrated sulfuric acid, 1.5 mL of glacial acetic acid and 3.7 mL of *p*-anisaldehyde to 135 mL of absolute ethanol. Flash column chromatography was performed on silica gel (Merck, 40−63 μm particle size) using standard techniques eluting with solvents as indicated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 600 MHz equipped with a 5 mm-diameter BBO probe with a z-gradient accessory. Chemical shifts are quoted in ppm and are referenced to the residual nondeuterated solvent peak. Mass spectrometry measurements were performed on a HPLC system coupled with a triple quadrupole mass spectrometer, operating in the positive electrospray ionization (ESI) mode. High-resolution mass spectrometry (HRMS) was performed on a 4800 Plus MALDI TOF/TOF analyser. Unless otherwise indicated, solvents were used as supplied (analytical or HPLC grade) without further purification. “Petrol ether” (PE) refers to the fraction of petroleum ether boiling in the range of 40−60 °C. Where mixtures of solvents are specified, the stated ratios are volume: volume. Unless otherwise indicated, all aqueous solutions used were saturated. Reagents were used directly as supplied by major chemical suppliers.

Synthesis of amino acid-derived isocyanides

General procedure: Amino acid methyl ester (1 equiv.) was dissolved in DCM and solution was cooled to 0°C. Formic acid was added dropwise followed by the addition of *N,N'*-dicyclohexylcarbodiimide (DCC, 1.3 equiv.) and 4-dimethylaminopyridine (DMAP, 0.2 equiv.). The reaction mixture was stirred overnight at room temperature. The reaction was terminated by addition of saturated $NaHCO_3$ solution, extracted with DCM and washed with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4. The product was purified by flash chromatography on a silica gel column in a solvent system: petrol ether/EtOAc (1:1). Isolated product was dissolved in dry THF and cooled to -78 °C. NMM (4 equiv.) was added dropwise followed by the addition of triphosgene (0.5 equiv.) dissolved in dry THF. Reaction mixture was stirred for 3 hours at -78 °C, and then terminated by addition of saturated $NaHCO_3$ solution and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, solvent evaporated and the residue purified by flash chromatography on a silica gel column in a solvent system: petrol ether/EtOAc (1:1). Yields are given over two reaction steps.

***CN-L-Leu-OMe* (*a*)**. Yield: 38% (232 mg; yellow oil; R_f = 0.83 (petrol ether/EtOAc 1:1, v/v); $C_8H_{13}NO_2$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.28 (dd, *J* = 9.9, 4.6 Hz, αLeu, 1H), 3.82 (s, OMe, 3H), 1.96–1.77 (m, ββ'Leu, 2H), 1.75–1.63 (m, γLeu, 1H), 0.98 (dd, *J* = 13.7, 6.6 Hz, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl^3$) δ 167.5, 160.0, 54.9, 53.2, 41.2, 24.7, 22.5, 20.8.

***CN-L-Val-OMe* (*b*).** Yield: 33% (212 mg); yellow oil; R_f = 0.71 (petrol ether/EtOAc 1:1, v/v); $C_7H_{11}NO_2$. ^{1}H NMR (300 MHz, CDCl3) δ 4.18 (d, *J* = 4.3 Hz, αVal, 1H), 3.83 (s, OMe, 3H), 2.45–2.22 (m, βVal 1H), 1.11 (d, *J* = 6.8 Hz, γVal, 3H), 1.02 (d, *J* = 13.0 Hz, γ'Val, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 166.9, 160.5, 62.8, 53.2, 31.2, 19.3, 16.7.

***CN-L-Phe-OMe* (*c*)**. Yield: 54% (345 mg); colourless oil; R_f = 0.78 (petrol ether/EtOAc 1:1, v/v); $C_{11}H_{11}NO_2$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.23 (m, ArPhe, 5H), 4.46 (dd, *J* = 8.4, 4.9 Hz, αPhe, 1H), 3.80 (s, OMe, 3H), 3.34–3.03 (m, ββ'Phe, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 134.5, 129.4, 128.9, 127.9, 53.5, 39.1.

***CN-D-Leu-OMe* (*d*).** Yield: 33% (226 mg); yellow oil; R_f = 0.81 (petrol ether/EtOAc 1:1, v/v); $C_8H_{13}NO_2$. ^{1}H NMR (300 MHz, CDCl3): δ 4.29 (dd, *J* = 9.6, 4.7 Hz, αLeu, 1H), 3.82 (s, OMe, 3H), 1.98–1.81 (m, ββ'Leu, 2H), 1.80–1.64 (m, γLeu, 1H), 0.98 (t, *J* = 6.7 Hz, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 160.1, 55.1, 53.3, 41.3, 24.8, 22.5, 20.9.

***CN-D-Val-OMe* (*e*)**. Yield: 52% (352 mg); colourless oil; R_f = 0.71 (petrol ether/EtOAc 1:1, v/v); $C_7H_{11}NO_2$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.17 (d, *J* = 4.3 Hz, αVal, 1H), 3.82 (s, OMe, 3H),

2.34 (d, *J* = 4.5 Hz, βVal, 1H), 1.10 (d, *J* = 6.9 Hz, γVal, 3H), 1.00 (d, *J* = 6.7 Hz, γ'Val, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 160.5, 62.8, 53.2, 31.2, 19.3, 16.7.

***CN-D-Phe-OMe* (*f*)**. Yield: 76% (475 mg); colourless oil; R_f = 0.78 (petrol ether/EtOAc 1:1, v/v); $C_{11}H_{11}NO_2$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.40–7.21 (m, ArPhe, 5H), 4.46 (dd, *J* = 8.4, 4.9 Hz, 1H), 3.77 (br s, OMe, 3H), 3.23–3.09 (m, ββ'Phe, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 166.7, 160.5, 135.6, 134.5, 129.4, 128.9, 128.8, 127.9, 127.4, 60.5, 53.5, 52.6, 51.9, 39.0, 37.9, 21.2, 14.3.

Synthesis of Passerini products

General procedure: To a flask containing 0.5 M solution of galactose- or sorbose-derived aldehyde (1 equiv.) in dry DCM were added acetic acid (1 equiv.) and the isocyanide component (1 equiv.) dissolved in 200 µL of dry DCM. With all reactants added, the solution was allowed to stir overnight at room temperature. The reactions were concentrated under reduced pressure, and the residue was purified by flash column chromatography on a silica gel column in a solvent system: petrol ether/EtOAc (1:1).

Compound Gal-1a. Yield: 94% (1.51 g); colourless oil; R_f = 0.4 (petrol ether/EtOAc 1:1, v/v); $C_{22}H_{35}NO_{10}$; mixture of two diastereoisomers, d.r. 75:25. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.69 (d, *J* = 7.9 Hz, NHLeu, 1H), 5.55 – 5.48 (m, H1Gal, 1H), 5.35 (d, *J* = 7.2 Hz, αGal, 0.25H), 5.08 (d, *J* = 9.6 Hz, αGal, 0.75H), 4.68 – 4.54 (m, αLeu, Gal, 2H), 4.35 – 4.26 (m, Gal, 2H), 4.24 – 4.17 (m, Gal, 1H), 3.72, 3.70 (s, OMe, 3H), 2.15, 2.14 (s, OAc, 3H), 1.72 – 1.60 (m, ββ'Leu, 2H), 1.57 – 1.53 (m, γLeu, CH_3, 4H), 1.46, 1.44 (s, CH_3, 3H), 1.33-1.29 (m, CH_3, 6H), 0.96 – 0.89 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 172.7, 171.3, 170.5, 169.6, 167.9, 166.9, 109.8, 109.7, 109.6, 109.2, 96.4, 96.3, 73.0, 71.3, 70.9, 70.8, 70.6, 70.5, 70.4, 67.2, 66.9, 60.2, 52.5, 52.2, 51.1, 50.9, 41.5, 41.4, 29.8, 26.2, 26.1, 25.14, 25.10, 24.9, 24.9, 24.5, 24.3, 22.9, 22.8, 22.2, 22.1, 21.2, 21.0, 20.8.

Compound Gal-1b. Yield: 90% (1.50 g); yellow oil; R_f = 0.5 (petrol ether/EtOAc 1:1, v/v); $C_{21}H_{33}NO_{10}$ Chemical shifts are given for major diastereoisomer separated by column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (d, *J* = 8.4 Hz, NHVal, 1H), 5.52 (d, *J* = 4.9 Hz, H1Gal, 1H), 5.05 (d, *J* = 9.7 Hz, αGal, 1H), 4.80 – 4.51 (m, αVal, Gal, 2H), 4.47 – 4.24 (m, Gal, 2H), 4.17 (dd, *J* = 9.8, 1.8 Hz, Gal, 1H), 3.72 (s, OMe, 3H), 2.14 (s, OAc, 3H), 1.78 – 1.65 (m, βLeu, 1H), 1.48, 1.44, 1.32, 1.30 (s, CH_3, 12H), 0.91 (dd, *J* = 6.4, 4.1 Hz, γγ'Leu, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 169.6, 167.8, 109.8, 109.4, 96.3, 70.7, 70.54, 70.47, 67.0, 52.4, 50.9, 42.1, 26.1, 26.0, 25.1, 24.6, 24.5, 23.0, 22.0, 20.8.

Compound Gal-1c. Yield: 75% (1.48 g); colourless oil; R_f = 0.5 (petrol ether/EtOAc 1:1, v/v); $C_{25}H_{33}NO_{10}$; mixture of two diastereoisomers, d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.21 (m, ArPhe, 3H), 7.18–7.15 (m, ArPhe, 1.3H), 7.13–7.07 (m, ArPhe, 0.7H), 6.84 (d, *J* = 7.3 Hz, NHPhe, 0.3H), 6.80 (d, *J* = 7.2 Hz, NHPhe, 0.7H), 5.50 (d, *J* = 4.9 Hz, H1Gal, 0.3H), 5.46 (d, *J* = 4.8 Hz, H1Gal, 0.7H), 5.40 (d, *J* = 6.8 Hz, αGal, 0.3H), 5.04 (d, *J* = 9.6 Hz, αGal, 0.7H), 4.88 – 4.80 (m, αPhe, 1H), 4.62 (dd, *J* = 7.9, 2.6 Hz, Gal, 0.7H), 4.48 (dd, *J* = 7.9, 2.4 Hz, Gal, 0.3H), 4.32 (dd, *J* = 4.9, 2.6 Hz, Gal, 0.7H), 4.30 – 4.26 (m, Gal, 1.3H), 4.20 (dd, *J* = 9.6, 1.8 Hz, Gal, 0.7H), 3.98 (dd, *J* = 8.0, 1.8 Hz, Gal, 0.3H), 3.73 (s, OMe, 1H), 3.67 (s, OMe, 2H), 3.25 – 3.06 (m, ββ'Phe, 2H), 2.14 (s, OAc, 2H), 2.11 (s, OAc, 1H), 1.55, 1.52 (s, CH_3, 3H), 1.44, 1.42 (s, CH_3, 3H), 1.31, 1.30 (br s, CH_3, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 171.4, 170.2, 169.6, 167.8, 166.8, 136.0, 135.9, 129.5, 129.4, 128.7, 128.6, 127.3, 127.1, 109.7, 109.5, 109.1, 96.4, 96.2, 72.7, 71.3, 70.9, 70.8, 70.6, 70.5, 70.4, 66.9, 66.9, 53.8, 53.4, 52.5, 52.3, 37.9, 37.5, 26.2, 26.12, 26.09, 26.0, 25.1, 25.1, 24.6, 24.4, 21.2, 20.9, 20.8.

Compound Gal-1d. Yield: 70% (1.39 g); yellow oil; R_f = 0.44 (petrol ether/EtOAc 1:1, v/v); $C_{22}H_{35}NO_{10}$; mixture of two diastereoisomers, d.r. 80:20. Chemical shifts are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.70 (d, *J* = 8.5 Hz, NHLeu, 1H), 5.51 (d, *J* = 4.9 Hz, H1Gal, 1H), 5.05 (d, *J* = 9.7 Hz, αGal, 1H), 4.70 – 4.56 (m, αLeu, Gal, 2H), 4.33 (dd, *J* = 4.9, 2.6 Hz, Gal, 1H), 4.29 (dd, *J* = 7.9, 1.9 Hz, Gal, 1H), 4.16 (dd, *J* = 9.7, 1.8 Hz, Gal, 1H), 3.71 (s, OMe, 3H), 2.14 (s, OAc, 3H), 1.79 – 1.69 (m, βLeu, 1H), 1.65 – 1.51 (m, β',γLeu, 2H), 1.48 (s, CH_3, 3H), 1.44 (s, CH_3, 3H), 1.32, 1.30 (s, CH_3, 6H), 0.95 – 0.88 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 169.4, 167.5, 109.5, 109.2, 96.1, 76.7, 70.5, 70.3, 70.3, 70.2, 66.8, 52.2, 50.7, 41.9, 25.8, 24.9, 24.3, 24.3, 22.8, 21.7, 20.5.

Compound Gal-1e. Yield: 80% (2.43 g); yellow oil; R_f = 0.46 (petrol ether/EtOAc 1:1, v/v); $C_{21}H_{33}NO_{10}$; mixture of two diastereoisomers, d.r. 80:20. Chemical shifts are given for both diastereoisomers.^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (d, *J* = 8.8 Hz, NHVal, 0.2H), 6.81 (d, *J* = 8.9 Hz, NHVal, 0.8H), 5.54 (d, *J* = 5.0 Hz, H1Gal, 1H), 5.29, (d, *J* = 7.0Hz, αGal, 0.2 H), 5.06 (d, *J* = 9.7 Hz, αGal, 0.8H), 4.64–4.40 (m, αVal, Gal, 2H), 4.35–4.24 (m, Gal, 2H), 4.20–4.14 (m, Gal, 1H), 3.75–3.69 (m, OMe, 3H), 2.15, 2.02 (s, OAc, 3H), 1.75 – 1.65 (m, βVal, 1H), 1.54–1.41 (m, CH_3, 6H), 1.31 (m, CH_3, 6H), 0.97–0.88 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 171.3, 170.5, 169.6, 167.9, 167.3, 109.7, 109.7, 109.6, 109.44, 108.8, 96.4,

96.3, 96.28, 71.7, 71.1, 70.9, 70.8, 70.7, 70.69, 70.6, 70.5, 70.4, 68.2, 66.9, 62.4, 60.5, 57.5, 52.2, 52.18, 31.6, 31.3, 26.12, 26.10, 26.05, 26.0, 25.0, 24.5, 24.4, 21.1, 20.7, 19.0, 17.7.

Compound Gal-1f. Yield: 95% (1.87 g); yellow oil; R_f = 0.52 (petrol ether/EtOAc 1:1, v/v); $C_{25}H_{33}NO_{10}$; mixture of two diastereoisomers, d.r. 80:20. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, ArPhe, 2H), 7.25 – 7.20 (m, ArPhe, 1H), 7.19 - 7.14 (m, ArPhe, 2H), 6.91 (d, *J* = 8.0 Hz, NHPhe, 0.2H), 6.74 (d, *J* = 7.7 Hz, NHPhe, 0.8H), 5.53 – 5.50 (m, H1Gal, 1H), 5.26 (d, *J* = 7.3 Hz, αGal, 0.2H), 5.02 (d, *J* = 6.3 Hz, αGal, 0.8H), 4.91 – 4.80 (m, αPhe, 1H), 4.65 – 4.62 (m, Gal, 0.8H), 4.57 – 4.54 (m, Gal, 0.2H), 4.37 – 4.29 (m, Gal, 1H), 4.29 – 4.25 (m, Gal, 1H), 4.24 – 4.18 (m, Gal, 1H), 3.70, 3.64 (m, OMe, 3H), 3.22 – 3.03 (m, ββ'Phe, 2H), 2.17 – 2.11 (m, OAc, 3H), 1.54 – 1.49 (m, CH_3, 3H), 1.47 – 1.39 (m, CH_3, 3H), 1.36 – 1.29 (m, CH_3, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 171.5, 170.5, 169.6, 167.7, 166.9, 136.2, 135.7, 129.6, 129.6, 128.7, 128.5, 127.3, 127.1, 109.8, 109.6, 109.4, 109.1, 96.3, 71.0, 70.8, 70.8, 70.6, 70.4, 67.3, 67.1, 53.8, 53.1, 52.3, 52.3, 38.4, 37.9, 26.2, 26.1, 26.1, 25.9, 25.1, 25.1, 24.6, 23.9, 20.9, 20.7.

Compound Gal-1g. Yield: 86% (1.67 g); colourless oil; R_f = 0.37 (petrol ether/EtOAc 1:1, v/v); $C_{18}H_{27}NO_{10}$; mixture of two diastereoisomers, d.r. 65:35. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (br t, NHGly, 0.35H), 6.82 (br t, NHGly, 0.65H), 5.54 (d, *J* = 6.9 Hz, H1Gal, 0.35H), 5.52 (d, *J* = 6.9 Hz, H1Gal, 0.65H), 5.38 (d, *J* = 6.8 Hz, αGal, 0.35H), 5.10 (d, *J* = 9.6 Hz, αGal, 0.65H), 4.68 – 4.58 (m, Gal, 1H), 4.43 (dd, *J* = 8.0, 1.7 Hz, Gal, 0.35H), 4.37 – 4.27 (m, Gal, 1.65H), 4.26 – 4.18 (m, Gal, 1.35H), 4.10 – 4.00 (m, Gal, αGly, 1.35H), 3.92 (dd, *J* = 18.3, 4.5 Hz, αGly 0.35H), 3.74 (br s, OMe, 3H), 2.16 (d, *J* = 14.7 Hz, OAc, 3H), 1.54 (d, *J* = 11.7 Hz, CH_3, 3H), 1.45 (d, *J* = 13.8 Hz, CH_3, 3H), 1.38 – 1.29 (m, CH_3, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 169.9, 169.8, 168.3, 167.5, 109.8, 109.8, 109.6, 109.2, 96.4, 96.3, 77.2, 72.9, 71.2, 70.9, 70.8, 70.7, 70.6, 70.6, 70.4, 67.1, 66.9, 52.5, 52.4, 41.5, 41.3, 26.2, 26.1, 26.1, 26.0, 25.1, 24.6, 24.3, 21.1, 20.8.

***Compound Sor-1a*.** Yield: 92% (1.68 g); colourless oil; R_f = 0.38 (petrol ether/EtOAc 1:1, v/v); $C_{22}H_{35}NO_{10}$; mixture of two diastereoisomers, d.r. 90:10. Chemical shifts are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.9 Hz, NHLeu, 1H), 5.34 (s, αSor, 1H), 4.72 – 4.61 (m, H4Sor, 1H), 4.40 (s, H2Sor, 1H), 4.36 (d, *J* = 2.2 Hz, αLeu, 1H), 4.24 – 4.19 (m, Sor, 1H), 4.15 – 4.05 (m, Sor, 2H), 3.72 (s, OMe, 3H), 2.22 (s, OAc, 3H), 1.76 – 1.56 (m, ββ'γLeu, 3H), 1.49, 1.43, 1.42, 1.40 (s, CH_3, 12H), 1.02 – 0.86 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 169.4, 165.2, 113.9, 112.7, 97.7, 85.6, 73.7, 72.8, 72.3, 60.5, 60.4, 52.3, 51.2, 41.9, 29.1, 27.7, 26.4, 24.9, 22.9, 22.5, 21.2, 20.8, 18.8.

Compound Sor-1b. Yield: 42% (669.4mg); colourless oil; R_f = 0.42 (petrol ether/EtOAc 1:1, v/v); $C_{21}H_{33}NO_{10}$; mixture of two diastereoisomers, d.r. 95:5. Chemical shifts are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.5 Hz, NHVal, 1H), 5.37 (s, αSor, 1H), 4.60 (dd, *J* = 8.5, 4.5 Hz, H4Sor, 1H), 4.39 (s, H2Sor, 1H), 4.37 (d, *J* = 2.3 Hz, αVal, 1H), 4.26 – 4.20 (m, Sor, 1H), 4.17 – 4.05 (m, Sor, 2H), 3.72 (s, OMe, 3H), 2.19 (s, OAc, 3H), 2.18 – 2.14 (m, βVal, 1H), 1.53 – 1.35 (m, CH_3, 12H), 1.00 – 0.88 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 169.3, 165.4, 113.9, 112.5, 97.6, 85.5, 73.6, 72.6, 72.1, 60.2, 57.0, 51.9, 31.7, 29.0, 27.6, 26.2, 20.7, 18.8, 18.7, 17.6.

***Compound Sor-1c*.** Yield: 84% (1.64 g); yellow oil; R_f = 0.37 (petrol ether/EtOAc 1:1, v/v); $C_{25}H_{33}NO_{10}$; mixture of two diastereoisomers, d.r. 85:15. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.13 (m, ArPhe, 5H), 7.09 (d, *J* = 7.2 Hz, NHPhe, 0.85H), 7.05 (br d, NHPhe, 0.15H), 5.43 (s, αSor, 0.15H), 5.36 (s, αSor, 0.85H), 5.06 – 4.80 (m, H4Sor, 1H), 4.43 – 4.29 (m, H2Sor, αPhe, 2H), 4.21 – 4.15 (m, Sor, 1H), 4.04 – 3.89 (m, Sor, 2H), 3.69, 3.68 (s, OMe, 3H), 3.27 – 3.07 (m, ββ'Phe, 2H), 2.20, 2.19 (s, OAc, 3H), 1.48, 1.40, 1.40, 1.34 (s, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 171.3, 169.5, 164.9, 136.0, 129.7, 128.5, 127.0, 113.9, 112.6, 97.7, 85.5, 73.8, 72.6, 72.3, 60.5, 60.1, 53.5, 52.3, 37.9, 29.8, 29.1, 27.7, 26.3, 21.2, 20.8, 18.8.

***Compound Sor-1d*.** Yield: 72% (1.43 g); yellow oil; R_f = 0.49 (petrol ether/EtOAc 1:1, v/v); $C_{22}H_{35}NO_{10}$; mixture of two diastereoisomers d.r. 90:10. Chemical shifts are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.0 Hz, NHLeu, 1H), 5.40 (s, αSor, 1H), 4.65 (td, *J* = 8.2, 5.4 Hz, H4Sor, 1H), 4.41 (s, H2Sor, 1H), 4.34 (dd, *J* = 8.5, 1.9 Hz, αLeu, 1H), 4.24 – 4.20 (m, Sor, 1H), 4.12 – 4.06 (m, Sor, 2H), 3.72 (s, OMe, 3H), 2.18 (s, OAc, 3H), 1.76 – 1.63 (m, ββ'γLeu, 3H), 1.46 (s, CH_3, 3H), 1.41 (br s, CH_3, 6H), 1.38 (s, CH_3, 3H), 0.92 (dd, *J* = 7.5, 6.6 Hz, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 169.1, 164.9, 113.6, 112.9, 97.6, 85.4, 73.8, 72.5, 72.3, 60.3, 52.2, 51.1, 41.7, 28.8, 27.5, 26.4, 24.5, 22.8, 22.2, 20.7, 18.7.

Compound Sor-1e. Yield: 76% (1.09 g); yellow oil; R_f = 0.45 (petrol ether/EtOAc 1:1, v/v); $C_{21}H_{33}NO_{10}$; mixture of two diastereoisomers d.r. 90:10. Chemical shifts are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.7 Hz, NHVal, 1H), 5.41 (s, αSor, 1H), 4.59 (dd, *J* = 8.7, 4.6 Hz, H4Sor, 1H), 4.41 (s, H2Sor, 1H), 4.34 (d, *J* = 2.1 Hz, αVal, 1H), 4.22 (s, Sor, 1H), 4.13 – 3.99 (m, Sor, 2H), 3.72 (s, OMe, 3H), 2.18 – 2.14 (m, OAc, 1H), 1.49 (s, CH_3, 3H), 1.43 (br s, CH_3, 6H), 1.41 (s, CH_3, 3H), 0.92 (dd, *J* = 24.0, 6.8 Hz, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 169.2, 164.9, 113.6, 112.9, 97.6, 85.3, 73.8, 72.4, 72.3, 60.3, 57.3, 52.0, 31.7, 28.8, 27.5, 26.3, 20.7, 18.7, 17.5, 14.2.

***Compound Sor-1f*.** Yield: 82% (1.65 g); yellow oil; R_f = 0.39 (petrol ether/EtOAc 1:1, v/v); $C_{25}H_{33}NO_{10}$; mixture of two diastereoisomers d.r. 85:15. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, ArPhe, 6H), 5.43 (s, αSor, 0.85H), 5.36 (s, αSor, 0.15H), 4.95 – 4.87 (m, H4Sor, 1H), 4.41 (br s, H2Sor, 0.85H), 4.38 (br s, H2Sor, 0.15H), 4.34 – 4.29 (m, αPhe, 1H), 4.19 – 4.14 (m, Sor, 1H), 4.03 – 3.97 (m, Sor, 1H), 3.82 (d, *J* = 13.6 Hz, Sor, 1H), 3.71 – 3.64 (m, OMe, 3H), 3.24 – 3.11 (m, ββ'Phe, 2H), 2.24 – 2.16 (m, OAc, 3H), 1.53, 1.45, 1.39, 1.36 (s, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 169.3, 164.9, 136.0, 129.9, 129.7, 128.5, 128.2, 126.9, 113.9, 113.7, 113.0, 97.7, 85.6, 73.9, 73.8, 72.6, 72.33, 72.27, 60.5, 60.3, 53.9, 52.3, 37.9, 29.1, 28.9, 27.8, 27.7, 26.5, 26.3, 21.2, 20.8, 19.1, 18.8.

***Compound Sor-1g*.** Yield: 68% (1.32 g); yellow oil; R_f = 0.5 (petrol ether/EtOAc 1:1, v/v); $C_{18}H_{27}NO_{10}$; mixture of two diastereoisomers, d.r. 90:10. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (t, *J* = 4.2 Hz, NHGly, 0.9H), 6.87 (t, *J* = 4.7 Hz, NHGly, 0.1H), 5.69 (s, αSor, 0.1H), 5.41 (s, αSor, 0.9H), 4.89 (s, H2Sor, 0.1H), 4.42 (s, H2Sor, 0.9H), 4.37 – 4.29 (m, H4Sor, 1H), 4.25 – 4.20 (m, Sor, 1H), 4.19 – 3.95 (m, Sor, Gly, 4H), 3.78 – 3.71 (m, OMe, 3H), 2.23 (s, OAc, 0.3H), 2.20 (s, OAc, 2.7H), 1.55 – 1.31 (m, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 169.9, 169.4, 169.2, 166.4, 165.6, 113.9, 113.4, 112.8, 112.7, 97.8, 97.7, 85.6, 85.5, 74.4, 73.9, 73.4, 73.1, 72.7, 72.3, 60.5, 60.3, 52.5, 52.4, 41.7, 41.2, 29.0, 28.5, 27.8, 27.7, 26.3, 20.9, 20.8, 19.2, 18.8.

Synthesis of α-hydroxy dipeptide esters

General procedure: Passerini product was dissolved in methanol (c = 0.1 M) and solid NaOH was added (5 equiv.) Reaction mixture was stirred at room temperature for 5 hours. Solvent was evaporated and the residue purified by flash column chromatography on a silica gel column in a solvent system: petrol ether/EtOAc (1:1) and EtOAc/EtOH/AcOH/H_2O (70:10:2:2). Isolated hydroxy acid was dissolved in dry DMF (c = 0.2 M), K_2CO_3 (1.5 equiv.) and MeI (3 equiv.) were added, and the reaction mixture was stirred overnight at 75 °C. The reactions were concentrated under reduced pressure, and the residue was dissolved in DCM and extracted with saturated $NaHCO_3$ solution. Organic layer was washed with saturated NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel column in a solvent system: petrol ether/EtOAc (1:1). Yields are given over two reaction steps.

Compound Gal-2a. Yield: 77% (1.06 g); colourless oil; R_f = 0.5 (petrol ether/EtOAc 1:1, v/v); $C_{20}H_{33}NO_9$; mixture of two diastereoisomers d.r. 75:25. Chemical shifts are given for both

diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.08 (m, NHLeu, 1H), 5.61 – 5.46 (m, H1Gal, 1H), 4.67 – 4.55 (m, αLeu, Gal, 2H), 4.53 – 4.44 (m, Gal, 1H), 4.42 – 4.19 (m, Gal, 2H), 4.05 (t, *J* = 6.9 Hz, Gal, 1H), 3.72 (s, OMe, 3H), 1.72 – 1.57 (m, ββ'γLeu, 3H), 1.54 – 1.44 (m, CH_3, 6H), 1.42 – 1.27 (m, CH_3, 6H), 1.01 – 0.89 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 172.6, 172.3, 171.3, 109.9, 109.7, 109.4, 109.4, 96.5, 96.4, 73.5, 72.7, 71.4, 71.0, 70.8, 70.7, 70.6, 70.4, 67.3, 66.7, 60.5, 52.4, 51.1, 51.0, 50.8, 41.4, 41.2, 29.8, 26.2, 25.9, 25.3, 25.1, 24.9, 24.1, 24.0, 22.9, 22.1, 21.9, 14.3.

Compound Gal-2b. Yield: 94% (1.3 g); yellow oil; R_f = 0.4 (petrol ether/EtOAc 1:1, v/v); $C_{19}H_{31}NO_9$; mixture of two diastereoisomers d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, NHVal, 0.70H), 7.30 (d, *J* = 8.7 Hz, NHVal, 0.30H), 5.61 – 5.48 (m, H1Gal, 1H), 4.68 – 4.55 (m, αGal, 1H), 4.54 – 4.40 (m, αVal, Gal, 2H), 4.39 – 4.32 (m, Gal, 1H), 4.30 – 4.19 (m, Gal, 1H), 4.07 (dd, *J* = 7.3, 1.6 Hz, Gal, 1H), 3.76 – 3.70 (m, OMe, 3H), 2.27 – 2.12 (m, βVal, 1H), 1.57 – 1.48 (m, CH_3, 6H), 1.36 – 1.30 (m, CH_3, 6H), 1.02 – 0.89 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5, 171.9, 171.6, 109.9, 109.7, 109.4, 109.3, 96.7, 96.4, 96.4, 71.4, 71.0, 70.8, 70.7, 70.6, 70.4, 68.6, 68.2, 67.3, 66.6, 62.5, 57.8, 57.2, 52.5, 52.2, 31.4, 31.1, 26.2, 26.1, 26.0 25.9, 25.2, 25.1, 24.9, 24.8, 24.11, 24.06, 19.2, 19.0, 18.1, 18.0.

***Compound Gal-2c*.** Yield: 68% (940 mg); yellow oil; R_f = 0.47 (petrol ether/EtOAc 1:1, v/v); $C_{23}H_{31}NO_9$; mixture of two diastereoisomers, d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, CDCl3) δ 7.40– 7.10 (m, ArPhe, NHPhe, 6H), 5.59–5.49 (m, H1Gal, 1H), 4.91–4.78 (m, αGal, 1H), 4.65–4.56 (m, αPhe, 1H), 4.50–4.15 (m, Gal, 3H), 4.06–4.01 (m, Gal, 1H), 3.73–3.64 (m, OMe, 3H), 3.21–3.02 (m, ββ'Phe, 2H), 1.57–1.44 (m, CH_3, 6H), 1.37–1.29 (m, CH_3, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 171.6, 171.5, 171.3, 136.0, 129.7, 129.4, 129.3, 128.7, 128.6, 127.2, 127.2, 109.7, 109.7, 109.4, 109.3, 96.5, 96.3, 72.9, 72.7, 71.5, 67.5, 67.2, 66.9, 66.5, 60.5, 53.8, 53.7, 53.4, 52.1, 52.3, 38.4, 38.1, 37.9, 26.2, 26.1, 26.13, 26.0, 25.9, 25.8, 25.3, 25.2, 25.1, 25.0, 24.3, 24.2, 24.0, 21.2.

Compound Gal-2d. Yield: 46% (599 mg); yellow oil; R_f = 0.54 (petrol ether/EtOAc 1:1, v/v); $C_{20}H_{33}NO_9$; mixture of two diastereoisomers, d.r. 80:20. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.12 (m, NHLeu, 1H), 5.58 (d, *J* = 5.0 Hz, H1Gal, 0.8 H), 5.51 (d, *J* = 4.7 Hz. H1Gal, 0.2H), 4.75 – 4.61 (m, αGal, αLeu, 2H), 4.52 – 4.44 (m, Gal, 1H), 4.34 (dd, *J* = 4.9, 2.4 Hz, Gal, 0.8H), 4.29 (dd, *J* = 4.7, 2.4 Hz, Gal, 0.2H), 4.25 - 4.21 (m, Gal, 1H), 4.09 – 4.02 (m, Gal, 1H), 3.73, 3.72 (s, OMe, 3H), 1.78 – 1.72 (m, βLeu, 1H), 1.70 – 1.61 (m, β'γLeu, 2H), 1.52 – 1.47 (m, CH_3, 6H), 1.42 – 1.30 (m, CH_3, 6H), 1.00 – 0.89 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 172.8, 172.4, 172.1, 109.7,

109.5, 109.5, 109.0, 96.3, 96.1, 73.7, 72.9, 71.0, 70.8, 70.7, 70.6, 70.4, 69.5, 67.6, 66.5, 52.2, 52.1, 50.8, 50.3, 41.8, 41.4, 26.0, 25.9, 25.8, 25.7, 25.1, 24.8, 24.4, 24.3, 24.1, 23.8, 22.9, 22.8, 21.7, 21.5.

Compound Gal-2e. Yield: 58% (1.26 g); yellow oil; R_f = 0.51 (petrol ether/EtOAc 1:1, v/v); $C_{19}H_{31}NO_9$; mixture of two diastereoisomers, d.r. 80:20. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (br d, NHVal, 0.2H), 7.18 (d, *J* = 8.9 Hz, NHVal, 0.8H), 5.58 (d, *J* = 4.9 Hz, H1Gal, 0.8H), 5.51 (d, *J* = 4.7 Hz, H1Gal, 0.2H), 4.68–4.53 (m,αGal, αVal, 2H), 4.49 (m, Gal, 1H), 4.34 (dd, *J* = 4.9, 2.4 Hz, Gal, 0.8H), 4.28 (dd, J = 4.7, 2.3 Hz, Gal, 0.2H), 4.22 (dd, *J* = 8.5, 4.0 Hz, Gal, 1H), 4.07 (d, *J* = 5.1 Hz, Gal, 0.2H), 4.03 (d, *J* = 4.0 Hz, Gal, 0.8H), 3.76– 3.72 (m, OMe, 3H), 2.25–2.12 (m, βVal, 1H), 1.53–1.44 (m, CH_3, 6H), 1.41–1.29 (m, CH_3, 6H), 0.95 (m, $\gamma\gamma$'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 172.1, 171.9, 171.1, 109.8, 109.5, 109.3, 109.1, 96.3, 96.1, 73.6, 73.1, 71.0, 70.9, 70.8, 70.6, 70.3, 70.3, 69.1, 67.8, 66.7, 57.6, 57.0, 52.1, 52.0, 31.6, 31.2, 26.1, 26.0, 25.9, 25.7, 25.2, 24.9, 24.2, 23.9, 19.0, 17.8, 17.6.

Compound Gal-2f. Yield: 70% (1.21 g); yellow oil; R_f = 0.48 (petrol ether/EtOAc 1:1, v/v); $C_{23}H_{31}NO_9$; mixture of two diastereoisomers, d.r. 80:20. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40–7.10 (m, ArPhe, NHPhe, 6H), 5.59–5.49 (m, H1Gal, 1H), 4.91–4.78 (m, αGal, 1H), 4.65–4.56 (m, αPhe, 1H), 4.50–4.15 (m, Gal, 3H), 4.06–4.01 (m, Gal, 1H), 3.73–3.64 (m, OMe, 3H), 3.21–3.02 (m, $\beta\beta$'Phe, 2H), 1.57–1.44 (m, CH_3, 6H), 1.37–1.29 (m, CH_3, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 171.6, 171.5, 171.3, 136.0, 135.9, 129.7, 129.32, 129.31, 128.74, 128.69, 128.5, 127.2, 127.1, 109.9, 109.7, 109.4, 109.2, 96.55, 96.50, 96.4, 96.3, 73.52, 73.48, 72.9, 72.7, 71.5, 71.3, 71.0, 70.8, 70.7, 70.6, 70.5, 67.5, 67.2, 66.9, 66.5, 60.5, 53.8, 53.7, 53.4, 53.3, 52.4, 52.3, 52.2, 38.4, 38.1, 26.2, 26.1, 25.9, 25.8, 25.3, 25.1, 25.0, 24.3, 24.2, 24.0, 21.1.

Compound Gal-2g. Yield: 63% (970 mg); yellow oil; R_f = 0.48 (petrol ether/EtOAc 1:1, v/v); $C_{16}H_{25}NO_9$; mixture of two diastereoisomers, d.r. 65:35. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (t, *J* = 5.2 Hz, NHGly, 0.65H), 5.31 (t, *J* = 5.0 Hz, NHGly, 0.35H), 5.57 (d, *J* = 4.9 Hz, H1Gal, 0.65H), 5.53 (d, *J* = 4.8 Hz, H1Gal, 0.35H), 4.68 – 4.59 (m, αGal, 1H), 4.57 – 4.45 (m, Gal, 1H), 4.33 (dd, *J* = 4.9, 2.4 Hz, Gal, 0.65H), 4.30 (dd, *J* = 4.8, 2.4 Hz, Gal, 0.35H), 4.28 – 4.24 (m, Gal, 1H), 4.20 – 3.93 (m, Gal, Gly, 3H), 3.74, 3.73 (s, OMe, 3H), 1.59 – 1.44 (m, CH_3, 6H), 1.33 (m, CH_3, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 171.3, 170.8, 170.0, 169.7, 109.9, 109.7, 109.4, 109.4, 96.5, 96.4, 73.6, 72.8, 71.3, 71.3, 70.8, 70.7, 70.6, 70.3, 67.5, 66.5, 60.5, 52.4, 52.4, 41.3, 41.2, 26.1, 25.9, 25.8, 25.2, 25.1, 24.3, 24.0, 21.1.

***Compound Sor-2a*.** Yield: 72% (1.14 g); colourless oil; R_f = 0.53 (petrol ether/EtOAc 1:1, v/v); $C_{20}H_{33}NO_9$; mixture of two diastereoisomers, d.r. 85:15. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (br s, NHLeu, 0.85), 6.97 (br d, NHLeu, 0.15H), 4.73 – 4.62 (m, αSor, H4Sor, 1.15H), 4.60 (br s, H4Sor, 0.85H), 4.36, 4.33 (br s, H2Sor, 1H), 4.32 – 4.28 (m, αLeu, 1H), 4.18, 4.16 (br s, Sor, 1H), 4.11 (br s, Sor, 2H), 3.73 (br s, OMe, 3H), 1.70 – 1.59 (m, ββ'γLeu, 3H), 1.46, 1.44 (br s, CH_3,6H), 1.38, 1.37 (br s, CH_3, 6H), 1.00 – 0.89 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 172.8, 171.3, 170.1, 170.0, 114.5, 114.2, 113.6, 113.3, 97.7, 97.6, 85.3, 85.1, 73.5, 73.4, 72.9, 72.8, 70.6, 70.3, 60.6, 60.5, 52.4, 52.3, 51.6, 42.0, 41.2, 29.8, 29.3, 29.2, 27.7, 27.6, 26.5, 26.5, 25.0, 24.7, 22.9, 22.9, 22.3, 21.9, 21.2, 18.7, 18.7.

***Compound Sor-2b*.** Yield: 44% (264 mg); colourless oil; R_f = 0.37 (petrol ether/EtOAc 1:1, v/v); $C_{19}H_{31}NO_9$; mixture of two diastereoisomers, d.r. 85:15. Chemical shifts are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 8.3 Hz, NHVal, 1H), 4.65 – 4.56 (m, αSor, 1H), 4.38 – 4.32 (m, Sor, αVal, 2H), 4.22 – 4.17 (m, Sor, 1H), 4.15 – 4.08 (m, Sor, 2H), 3.92 (d, J = 6.3 Hz, Sor, 1H), 3.73 (s, OMe, 3H), 2.27 – 2.16 (m, βVal, 1H), 1.47, 1.45, 1.39, 1.38 (s, CH_3, 12H), 0.94 (dd, J = 12.7, 6.9 Hz, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 170.4, 114.1, 113.7, 97.6, 85.4, 73.4, 72.9, 70.2, 60.6, 57.8, 52.2, 31.6, 29.3, 27.7, 26.4, 19.0, 18.7, 17.9.

***Compound Sor-2c*.** Yield: 66% (1.02 mg); colourless oil; R_f = 0.53 (petrol ether/EtOAc 1:1, v/v); $C_{23}H_{31}NO_9$; mixture of two diastereoisomers, d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 7.5 Hz, NHPhe, 0.7H), 7.28 – 7.20 (m, NHVal, ArPhe, 4H), 7.13 – 7.09 (m, ArPhe, 1.3H), 4.98 – 4.85 (m, αSor, 1H), 4.63 (s, Sor, 0.3H), 4.56 (s, Sor, 0.7H), 4.38 – 4.25 (m, Sor, αPhe, 2H), 4.14 – 3.88 (m, 3H), 3.70 (s, OMe, 3H), 3.25 – 3.08 (m, ββPhe, 2H), 1.49, 1.46 (s, CH_3, 3H), 1.42, 1.41 (s, CH_3, 3H), 1.40, 1.38 (s, CH_3, 3H), 1.34, 1.33 (s, CH_3, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 171.3, 171.2, 169.2, 169.9, 136.0, 135.7, 129.9, 129.4, 128.6, 128.4, 127.1, 127.1, 97.5, 97.5, 85.2, 85.2, 73.4, 72.8, 72.7, 70.5, 70.2, 60.5, 60.4, 60.3, 54.0, 53.9, 52.4, 52.3, 38.2, 37.9, 29.2, 29.1, 27.7, 27.6, 26.5, 26.4, 21.2, 18.7.

***Compound Sor-2d*.** Yield: 60% (797 mg); colourless oil; R_f = 0.57 (petrol ether/EtOAc 1:1, v/v); $C_{20}H_{33}NO_9$; mixture of two diastereoisomers, d.r. 90:10. Chemical shifts are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.97 (d, J = 7.5 Hz, NHLeu, 1H), 4.64 (br s, αSor, 1H), 4.38 – 4.29 (m, Sor, Leu, 2H), 4.21 – 4.16 (br s, Sor, 1H), 4.13-4.09 (m, Sor, 2H), 4.06 – 4.02 (m, Sor, 1H), 3.74 (s, OMe, 3H), 1.82 – 1.58 (m, ββ'γLeu, 3H), 1.49 – 1.34 (m, CH_3, 12H), 0.99 – 0.90 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 169.8, 114.3,

113.1, 97.4, 84.9, 73.3, 72.6, 70.4, 60.4, 52.2, 51.4, 41.1, 28.9, 27.4, 26.3, 24.5, 22.8, 21.8, 18.5.

***Compound Sor-2e*.** Yield: 58% (571 mg); colourless oil; R_f = 0.55 (petrol ether/EtOAc 1:1, v/v); $C_{19}H_{31}NO_9$; single diastereoisomer separated by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.7 Hz, NHVal, 1H), 4.62 (s, αSor, 1H), 4.57 (dd, *J* = 8.7, 4.8 Hz, Sor, 1H), 4.35 – 4.29 (m, Sor, αVal, 2H), 4.20 – 4.15 (m, Sor, 1H), 4.11 – 4.06 (m, Sor, 1H), 3.99 (br d, 1H), 3.72 (s, OMe, 3H), 2.28 – 2.17 (m, βVal, 1H), 1.42 (br s, CH_3, 6H), 1.36 (br s, CH_3, 6H), 0.94 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 170.0, 114.5, 113.3, 97.6, 85.1, 73.5, 72.8, 70.5, 60.6, 57.9, 52.2, 31.4, 29.1, 27.6, 26.5, 18.9, 18.7, 17.6.

***Compound Sor-2f*.** Yield: 51% (740 mg); colourless oil; R_f = 0.56 (petrol ether/EtOAc 1:1, v/v); $C_{23}H_{31}NO_9$; mixture of two diastereoisomers, d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, NHPhe, 0.3H), 7.31 – 7.18 (m, ArPhe, 5H), 7.12 (d, *J* = 7.0 Hz, NHPhe, 0.7H), 4.97 – 4.87 (m, Sor, 1H), 5.63 (s, Sor, 0.7H), 4.56 (s, Sor, 0.3H), 4.37 – 4.25 (m, Sor, αPhe, 2H), 4.20 - 4.16 (m, Sor, 0.3H), 4.12 – 4.08 (m, Sor, 0.7H), 4.05 – 3.99 (m, Sor, 1.7H), 3.95 (d, *J* = 13.5 Hz, Sor, 0.3H), 3.92 (d, *J* = 6.0 Hz, Sor, 0.3H), 3.80 (d, *J* = 13.6 Hz, Sor, 0.7H), 3.71, 3.72 (s, OMe, 3H), 3.26 – 3.07 (m, ββ'Phe, 2H), 1.52 – 1.31 (m, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.43, 171.38, 169.94, 169.90, 136.1, 135.7, 129.9, 129.5, 128.7, 128.4, 127.2, 127.1, 114.4, 114.1, 113.7, 113.3, 97.5, 85.3, 85.2, 73.5, 73.4, 72.82, 72.78, 70.5, 70.3, 60.5, 60.4, 60.3, 54.0, 53.9, 52.4, 52.4, 38.2, 37.92, 29.3, 29.1, 27.8, 27.7, 26.6, 26.4, 21.2, 18.7, 14.3.

***Compound Sor-2g*.** Yield: 46% (546 mg); colourless oil; R_f = 0.27 (petrol ether/EtOAc 1:1, v/v); $C_{16}H_{25}NO_9$; single diastereoisomer separated by column chromatography. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (br t, NHGly, 1H), 4.65 (s, αSor, 1H), 4.37 – 4.32 (m, Sor, 2H), 4.22 – 4.15 (m, Sor, 2H), 4.11 – 4.09 (m, Gly, 2H), 4.01 (d, *J* = 5.5 Hz, Sor, 1H), 3.76 (s, OMe, 3H), 1.47 (s, CH_3, 3H), 1.44 (s, CH_3, 3H), 1.38 (br d, CH_3, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 170.5, 169.9, 114.3, 113.6, 97.7, 85.3, 73.6, 72.9, 70.4, 60.5, 52.5, 41.9, 29.2, 27.6, 26.4, 21.2, 18.7, 14.3.

Synthesis of azido dipeptide esters

General procedure: α-hydroxy derivative was dissolved in dry DCM (c = 0.04 M) and pyridine (10 equiv.) and trifluoromethanesulfonic anhydride (3 equiv.) were added dropwise to precooled solution (-20 °C). The reaction mixture was stirred under argon for 3 hours, and then extracted with water. The organic layer was washed with 10% solution of $KHSO_4$, saturated $NaHCO_3$ solution and saturated NaCl solution, and then dried over Na_2SO_4. The solvent was evaporated, and the crude product was used in the next step.

Triflate derivative was dissolved in dry DMF (c = 0.2M), cooled to 0 °C and NaN_3 (5 equiv.) was added. The reaction was stirred at room temperature for 12 hours. Solvent was evaporated, residue dissolved in EtOAc and extracted with saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4, solvent evaporated and the residue purified by flash chromatography on a silica gel column in a solvent system: petrol ether/EtOAc (1:1). Yields are given over two reaction steps.

Compound Gal-3a. Yield: 86% (942 mg); yellow oil; R_f = 0.62 (petrol ether/EtOAc 1:1, v/v); $C_{20}H_{32}N_4O_8$; mixture of two diastereoisomers, d.r. nd. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90–6.56 (m, NHLeu, 1H), 5.62–5.51 (m, H1Gal, 1H), 4.71–4.55 (m, αGal, αLeu, 2H), 4.48–4.25 (m, Gal, 2H), 4.21–3.94 (m, Gal, 2H), 3.73 (br s, OMe, 3H), 1.72–1.63 (m, ββ'γLeu, 3H), 1.56 – 1.46 (m, CH_3, 6H), 1.39–1.17 (m, CH_3, 6H), 0.94 (d, *J* = 5.8 Hz, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 172.7, 171.3, 168.2, 167.1, 109.9, 109.8, 109.6, 109.4, 96.6, 96.5, 71.475, 71.1, 70.7, 70.7, 70.6, 70.5, 68.5, 68.3, 67.3, 63.3, 62.9, 61.6, 60.5, 52.6, 52.4, 51.1, 51.0, 41.3, 29.8, 26.1, 26.1, 26.0, 26.0, 25.1, 25.0, 24.9, 24.9, 24.4, 24.4, 22.9, 22.9, 22.0, 21.2.

Compound Gal-3b. Yield: 48% (664 mg); colourless oil; R_f = 0.58 (petrol ether/EtOAc 1:1, v/v); $C_{19}H_{30}N_4O_8$; mixture of diastereoisomers d.r. 65:35. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, *J* = 8.1 Hz, NHVal, 0.35H), 6.70 (d, *J* = 8.6 Hz, NHVal, 0.65H), 5.60 (d, *J* = 5.0 Hz, H1Gal, 0.65H), 5.55 (d, *J* = 4.9 Hz, H1Gal, 0.35H), 4.69 – 4.61 (m, αGal, 1H), 4.60 – 4.52 (m, αVal, 1H), 4.42 – 4.28 (m, Gal, 2H), 4.19 – 4.10 (m, Gal, 2H), 4.06 – 3.99 (m, Gal, 1H), 3.75, 3.73 (s, OMe, 3H), 2.26 – 2.16 (m, βVal, 1H), 1.56, 1.55 (s, CH_3, 3H), 1.50, 1.49 (s, CH_3, 3H), 1.34, 1.33 (br s, CH_3, 6H), 0.99 – 0.92 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 171.8, 171.3, 168.2, 167.2, 109.9, 109.8, 109.5, 109.4, 96.7, 96.6, 71.4, 71.1, 70.8, 70.7, 70.6, 70.5, 68.7, 68.4, 67.4, 63.0, 61.9, 60.5, 57.6, 57.4, 52.4, 52.2, 31.3, 26.1, 26.1, 25.1, 24.5, 24.4, 21.2, 19.1, 17.9, 14.3.

Compound **Gal-3c**. Yield: 93% (921 mg); colourless oil; R_f = 0.66 (petrol ether/EtOAc 1:1, v/v); $C_{23}H_{30}N_4O_8$; mixture of two diastereoisomers, d.r. nd. Chemical shifts are given for both

diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.20 (m, ArPhe, 3H), 7.14 (m, ArPhe, 2H), 6.94–6.69 (m, NHPhe, 1H), 5.59–5.44 (m, H1Gal, 1H), 4.95–4.79 (m, αGal, 1H), 4.69–4.48 (m, αLeu, 1H), 4.44–4.26 (m, Gal, 2H), 4.09–3.95 (m, Gal, 2H), 3.77–3.65 (m, OMe, 3H), 3.27–3.04 (m, ββ'Phe, 2H), 1.67–1.14 (m, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 167.0, 135.8, 129.4, 129.4, 129.3, 128.8, 127.4, 110.0, 109.3, 96.5, 71.3, 71.1, 70.5, 68.3, 62.9, 53.4, 52.6, 37.8, 26.1, 26.0, 25.1, 24.6.

Compound Gal-3d. Yield: 61% (376 mg); yellow oil; R_f = 0.68 (petrol ether/EtOAc 1:1, v/v); $C_{20}H_{32}N_4O_8$; mixture of two diastereoisomers, d.r. 60:40 Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (d, *J* = 8.4 Hz, NHLeu, 0.4H), 6.76 (d, *J* = 8.4 Hz, NHLeu, 0.6H), 5.57 (d, *J* = 4.9 Hz, H1Gal, 0.6H), 5.53 (d, *J* = 8.4 Hz, H1Gal, 0.4H), 4.70 – 4.60 (m, αGal,αLeu, 2H), 4.44 (dd, *J* = 8.0, 1.8 Hz, Gal, 0.6H), 4.39 (dd, *J* = 8.0, 1.7 Hz, αLeu, 0.4H), 4.33 (dd, *J* = 4.9, 2.5 Hz, Gal, 1H), 4.16 (dd, *J* = 7.4, 1.7 Hz, Gal, 0.6H), 4.13-4.11 (m, Gal, 0.4H), 4.04 (d, *J* = 7.4 Hz, Gal, 0.6H), 3.96 (dd, *J* = 9.5, 1.6 Hz, Gal, 0.4H), 3.74 (br s, OMe, 3H), 1.68 – 1.63 (m, βLeu, 1H), 1.59-1.56 (m, β'γLeu, 2H), 1.53-1.47 (m, CH_3, 6H), 1.41 – 1.29 (m, CH_3, 6H), 1.00 – 0.87 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 173.0, 168.4, 167.5, 109.9, 109.8, 109.5, 109.3, 96.5, 71.6, 71.1, 70.8, 70.7, 70.6, 70.6, 68.3, 67.4, 63.3, 61.3, 60.5, 52.5, 51.1, 50.9, 41.7, 41.6, 26.1, 26.1, 25.9, 25.1, 25.1, 24.9, 24.6, 24.4, 24.4, 23.1, 22.9, 22.2, 21.9, 21.2, 14.3.

Compound Gal-3e. Yield: 78% (1.05); colourless oil; R_f = 0.59 (petrol ether/EtOAc 1:1, v/v); $C_{19}H_{30}N_4O_8$; mixture of two diastereoisomers, d.r. 80:20 Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.6 Hz, NHVal, 0.2H), 6.87 (d, *J* = 8.7 Hz, NHVal, 0.8H), 5.57 (d, *J* = 4.9 Hz, H1Gal, 0.8H), 5.53 (d, *J* = 4.9 Hz, H1Gal, 0.2H), 4.69 – 4.61 (m, αGal, 1H), 4.59 (dd, *J* = 8.7, 4.8 Hz, αVal, 0.2H), 4.50 (dd, *J* = 8.8, 4.8 Hz, αVal, 0.8H), 4.44 (dd, *J* = 7.9, 1.8 Hz, Gal, 0.8H), 4.38 (dd, *J* = 7.9, 1.8 Hz, Gal, 0.2H), 4.32 (dd, *J* = 4.9, 2.5 Hz, Gal, 1H), 4.17 – 4.07 (m, Gal, 1H), 4.04 (d, *J* = 7.7 Hz, Gal, 0.8H), 4.01 – 3.94 (m, Gal, 0.2H), 3.77 – 3.70 (m, OMe, 3H), 2.23 – 2.12 (m, βVal, 1H), 1.57 – 1.44 (m, CH_3, 6H), 1.41 – 1.28 (m, CH_3, 6H), 1.00 – 0.87 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 172.0, 168.5, 167.8, 109.9, 109.7, 109.5, 109.3, 96.5, 71.5, 71.0, 70.7, 70.6, 70.6, 68.4, 67.3, 63.3, 61.4, 57.6, 57.4, 52.3, 52.2, 31.4, 31.1, 26.1, 26.1, 26.0, 25.9, 25.1, 25.0, 24.4, 24.3, 19.1, 19.0, 17.8, 17.7.

Compound Gal-3f. Yield: 86% (1.9 mg); colourless oil; R_f = 0.68 (petrol ether/EtOAc 1:1, v/v); $C_{23}H_{30}N_4O_8$; mixture of two diastereoisomers, d.r. nd. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.34 – 7.20 (m, ArPhe, 3H), 7.19 – 7.09 (m, ArPhe 2H), 6.92 – 6.70 (m, NHPhe, 1H), 5.59 – 5.44 (m, H1Gal, 1H), 4.96 – 4.83 (m, αGal,

1H), 4.69 – 4.51 (m, αPhe, 1H), 4.41 – 4.28 (m, Gal, 2H), 4.09 – 3.95 (m, Gal, 2H), 3.78 – 3.67 (m, OMe, 3H), 3.24 – 3.06 (m, ββ'Phe, 2H), 1.66 – 1.30 (m, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.5, 171.4, 167.9, 167.3, 166.9, 135.9, 135.8, 135.6, 129.5, 129.4, 129.3, 128.9, 128.8, 128.6, 127.4, 127.4, 127.2, 109.9, 109.8, 109.3, 109.3, 96.6, 96.5, 71.3, 71.1, 70.9, 70.8, 70.7, 70.6, 70.5, 68.5, 68.3, 63.1, 62.9, 53.8, 53.4, 53.2, 52.6, 52.5, 52.4, 38.1, 37.9, 37.8, 26.2, 26.1, 26.1, 25.8, 25.1, 24.7, 24.4, 24.1.

Compound Gal-3g. Yield: 86% (891 mg); colourless oil; R_f = 0.49 (petrol ether/EtOAc 1:1, v/v); $C_{16}H_{24}N_4O_8$; mixture of two diastereoisomers, d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (t, *J* = 4.2 Hz, NHGly, 0.3H), 6.92 (t, *J* = 4.7 Hz, NHGly, 0.7H), 5.59 (d, *J* = 4.9 Hz, H1Gal, 0.7H), 5.54 (d, *J* = 4.9 Hz, H1Gal, 0.3H), 4.68 –4 .63 (m, αGal, 1H), 4.44 (dd, *J* = 8.0, 1.8 Hz, Gal, 0.7H), 4.40 (dd, *J* = 7.9, 1.7 Hz, Gal, 0.3H), 4.37 – 4.33 (m, Gal, 1H), 4.21 – 4.02 (m, 3H), 3.97 (dd, *J* = 18.3, 4.9 Hz, Gal, 1H), 3.77 (s, OMe, 3H), 1.55, 1.53 (s, CH_3, 3H), 1.49, 1.47 (s, CH_3, 3H), 1.37, 1.36 (s, CH_3, 3H), 1.33, 1.32 (s, CH_3, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.9, 169.8, 168.7, 167.8, 109.9, 109.8, 109.6, 109.4, 96.55, 96.53, 71.5, 71.1, 70.8, 70.7, 70.6, 68.4, 67.4, 63.0, 61.4, 60.5, 52.6, 52.5, 41.5, 41.4, 26.1, 26.1, 26.0, 26.0, 25.1, 24.5, 24.4.

***Compound Sor-3a*.** Yield: 87% (1.05 g); colourless oil; R_f = 0.62 (petrol ether/EtOAc 1:1, v/v); $C_{20}H_{32}N_4O_8$; mixture of two diastereoisomers, d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 6.85 (m, NHLeu, 1H), 5.31, 5.03 (s, αSor, 1H), 4.74 – 4.69 (m, H4Sor, 0.70H), 4.61 – 4.55 (m, H4, Sor, 0.30H), 4.50, 4.48 (s, H2Sor, 1H), 4.44 – 4.38 (m, αLeu, 1H), 4.28 (br s, Sor, 0.70H), 4.17 (br s, Sor, 0.30H), 4.12 – 4.04 (m, Sor, 2H), 3.73, 3.30 (s, OMe, 3H), 1.70 – 1.60 (m, ββ'γLeu, 3H), 1.50, 1.45, 1.39 (s, CH_3, 12H), 0.96-0.90 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 172.5, 165.6, 162.6, 114.9, 114.7, 113.9, 111.6, 97.9, 97.6, 85.4, 85.1, 81.4, 80.8, 74.8, 74.6, 73.1, 72.9, 72.4, 72.2, 67.0, 66.7, 60.3, 52.4, 52.3, 51.5, 50.8, 41.7, 41.7, 31.4, 29.8, 29.5, 29.2, 28.9, 27.9, 27.6, 26.2, 26.0, 24.9, 24.9, 22.9, 22.4, 22.4, 22.2, 18.8, 18.7.

***Compound Sor-3b*.** Yield: 92% (234 mg); colourless oil; R_f = 0.56 (petrol ether/EtOAc 1:1, v/v); $C_{19}H_{30}N_4O_8$; mixture of two diastereoisomers, d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 6.85 (m, NHVal, 1H), 5.31 (br s, αSor, 0.7H), 5.03 (br s, αSor, 0.3H), 4.74 – 4.69 (m, H4Sor, 0.7H), 4.61 – 4.55 (m, H4Sor, 0.3H), 4.51 - 4.46 (m, Sor, 1H), 4.44 – 4.38 (m, αVal, 1H), 4.28 (br s, Sor, 0.7H), 4.17 (br s, Sor, 0.3H), 4.12 – 4.04 (m, Sor, 2H), 3.73, 3.30 (s, OMe, 3H), 2.26 – 2.13 (m, βVal, 1H), 1.50, 1.45, 1.39 (s, CH_3, 12H), 0.96 – 0.90 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 171.6, 171.3, 165.8, 162.9, 114.9, 114.7, 113.8, 111.5, 97.9, 97.7, 85.5, 85.1, 81.4, 80.6, 74.8,

74.5, 72.4, 60.5, 60.3, 57.5, 57.4, 52.3, 52.2, 31.8, 31.5, 29.1, 29.0, 27.9, 27.6, 26.2, 26.0, 21.2, 18.98, 18.88, 18.70, 18.1.

***Compound Sor-3c*.** Yield: 91% (970 mg); yellow oil; R_f = 0.6 (petrol ether/EtOAc 1:1, v/v); $C_{23}H_{30}N_4O_8$; mixture of two diastereoisomers, d.r. 65:35. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.05 (m, ArPhe, NHPhe, 6H), 5.33, 5.31, 5.09, 5.00 (s, αSor, 1H), 4.98 – 4.92 (m, H4Sor, 0.65H), 4.85 – 4.77 (m, H4Sor, 0.35H), 4.55 – 4.36 (m, H2Sor, αPhe, 2H), 4.25 – 4.14 (m, Sor, 1H), 4.08 – 3.89 (m, Sor, 2H), 3.72, 3.69, 3.67 (s, OMe, 3H), 3.37 – 3.00 (m, ββ'Phe, 2H), 1.66 – 1.31 (m, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 171.2, 162.5, 162.4, 135.8, 135.7, 129.9, 129.5, 129.5, 129.4, 128.8, 128.7, 128.6, 128.3, 127.4, 127.2, 114.9, 114.6, 114.5, 113.8, 111.9, 111.5, 97.8, 97.6, 85.5, 85.4, 85.2, 85.0, 81.1, 80.7, 74.7, 74.6, 73.2, 73.0, 72.2, 72.1, 66.9, 66.7, 60.5, 60.2, 60.0, 54.3, 53.8, 53.5, 52.4, 52.4, 38.3, 38.2, 37.8, 37.7, 29.8, 29.1, 28.9, 28.9, 27.9, 27.7, 27.6, 26.2, 26.1, 25.9, 18.8, 18.6.

***Compound Sor-3d*.** Yield: 63% (533 mg); colourless oil; R_f = 0.65 (petrol ether/EtOAc 1:1, v/v); $C_{20}H_{32}N_4O_8$; mixture of two diastereoisomers d.r. 65:35. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$, δ 7.19 (br d, NHLeu, 0.35H), 6.99 (br d, NHLeu, 0.65H), 4.73 – 4.68 (m, Sor, 0.35H), 4.58 (s, Sor, 0.65H), 4.57 – 4.53 (m, Sor, 0.65H), 4.51 (s, Sor, 0.35H), 4.43 – 4.40 (m, αLeu, 1H), 4.29 – 4.27 (m, Sor, 0.35H), 4.19 - 4.17 (m, Sor, 0.65H), 4.13 – 4.09 (m, Sor, 1H), 4.09 – 4.04 (m,Sor, 2H), 3.73 (s, OMe, 3H), 1.77 – 1.63 (m, ββ'γLeu, 3H), 1.47, (br s, CH_3, 3H), 1.44, 1.42 (s, CH_3, 3H), 1.38 (s, CH_3, 3H), 1.27, 1.25 (s, CH_3, 3H), 0.96 – 0.88 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, CDCl3) δ 173.1, 172.8, 165.7, 162.4, 114.9, 114.6, 114.5, 114.0, 112.00, 97.9, 97.6, 97.6, 85.4, 85.1, 81.4, 74.8, 73.1, 73.1, 72.8, 72.2, 67.0, 66.7, 60.6, 60.5, 52.5, 52.5, 51.6, 50.8, 41.6, 41.4, 29.8, 29.2, 28.9, 28.1, 27.5, 26.4, 26.1, 24.7, 24.7, 22.9, 22.3, 22.0, 18.8, 18.7.

Compound Sor-3e. Yield: 95% (569 mg); colourless oil; R_f = 0.66 (petrol ether/EtOAc 1:1, v/v); $C_{19}H_{30}N_4O_8$; mixture of two diastereoisomers d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, NHVal, 0.3H), 7.03 (d, *J* = 8.6 Hz, NHVal, 0.7H), 4.65-4.60 (m, Sor, 1H), 4.57 (br s, Sor, 0.7H), 4.44 – 4.42 (m, Sor, 0.3H), 4.38 - 4.36 (m, Sor, 0.7H), 4.31 – 4.29 (m, αVal, 0.3H), 4.24 – 4.21 (m, αVal, 0.7H), 4.14 – 4.08 (m, Sor, 1H), 4.07 – 4.04 (m, Sor, 1H), 4.02 – 4.00 (m, Sor, 1H), 3.75, 3.74, (s, OMe, 3H), 2.29 – 2.19 (m, βVal, 1H), 1.53 – 1.33 (m, CH_3, 12H), 1.01 – 0.90 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 171.8, 171.6, 166.3, 165.6, 162.4, 114.7, 114.6, 114.4, 113.9, 111.9, 97.6, 97.5, 85.7, 85.0, 81.3, 74.7, 73.9, 72.7, 72.4, 72.1, 66.7, 63.1, 60.4, 60.3, 57.7, 57.5, 57.3, 52.2, 52.1, 31.6, 31.4, 30.8, 29.1, 28.8, 27.7, 27.4, 26.3, 26.0, 21.0, 18.8, 18.7, 18.6, 18.00.

***Compound Sor-3f*.** Yield: 84% (660 mg); colourless oil; R_f = 0.62 (petrol ether/EtOAc 1:1, v/v); $C_{23}H_{30}N_4O_8$; mixture of two diastereoisomers d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2Hz, NHPhe, 0.7H), 7.30 – 7.01 (m, NHPhe, ArPhe, 5.3H), 4.97 – 4.91 (m, Sor, 0.7H), 4.85 – 4.79 (m, Sor, 0.3H), 4.50 (s, Sor, 0.7H), 4.46 (s, Sor, 0.3H), 4.42 – 4.39 (m, αPhe, 1H), 4.23 – 4.20 (m, Sor, 1H), 4.17 – 4.14 (m, Sor, 0.3H), 4.07 – 4.04 (m, Sor, 0.7H), 4.03 – 3.98 (m, Sor, 1H), 3.98 - 3. 94 (br d, 0.3H), 3.85 – 3.89 (br d, 0.7), 3.72, 3.70 (s, OMe, 3H), 3.29 – 3.13 (m, ββ'Phe, 2H), 1.58 – 1.30 (m, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 171.1, 162.5, 162.4, 135.70, 135.68, 129.9, 129.5, 128.6, 128.3, 127.2, 127.1, 114.9, 114.6, 111.9, 111.5, 97.8, 97.6, 85.2, 85.0, 81.1, 80.7, 74.7, 74.6, 73.1, 73.0, 72.2, 72.1, 67.0, 66.7, 60.2, 60.0, 54.3, 53.8, 52.4, 37.8, 37.7, 29.0, 28.9, 27.7, 27.5, 26.1, 26.0, 21.2, 18.7, 18.6, 18.6.

Compound Sor-3g. Yield: 80% (458 mg); yellow oil; R_f = 0.51 (petrol ether/EtOAc 1:1, v/v); $C_{16}H_{24}N_4O_8$; mixture of two diastereoisomers d.r. > 95:5. Chemical shits are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (t, *J* = 4.8 Hz, NHGly, 1H), 5.05 (s, αSor, 1H), 4.54 (s, Sor, 1H), 4.39 (br d, Sor, 1H), 4.19 – 4.16 (m, Sor, 1H), 4.14 – 4.10 (m, Sor, 1H), 4.05 (br d, Sor, Gly, 2H), 3.90 (dd, *J* = 18.2, 4.8 Hz, Gly, 1H), 3.76 (s, OMe, 3H), 1.47, 1.42, 1.37, 1.25 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 169.8, 169.7, 166.1, 163.0, 114.8, 114.6, 113.9, 111.7, 97.9, 97.6, 85.4, 85.1, 81.1, 74.7, 73.2, 72.9, 72.3, 67.0, 60.5, 60.3, 52.6, 52.5, 41.9, 41.2, 29.1, 28.9, 28.0, 27.5, 26.1, 26.0, 21.2, 18.8, 18.6, 14.3.

Synthesis of C-glycosyl dipeptides

General procedure: Azide derivative was dissolved in DCM-MeOH mixture (1:5, v/v, 0.02 M) and $NaBH_4$ (1.5 equiv.) and $NiCl_2 \cdot 6H_2O$ (0.01 equiv.) were added. The reaction mixture was stirred at room temperature until the consumption of the starting compound (typically 12 h). The solvent was evaporated, and the residue was extracted with DCM and a saturated $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and evaporated.

Compound Gal-4a. Yield: 79% (691 mg); yellow oil; R_f = 0.5 (DCM/MeOH 10:1, v/v); $C_{20}H_{34}N_2O_8$; mixture of diastereoisomers d.r. 75:25. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, NHLeu, 0.25H), 7.67 (br d, NHLeu, 0.75H), 5.56 (br d, H1Gal, 0.25H), 5.52 (br d, H1Gal, 0.75H), 4.75 – 4.51 (m, αGal, αLeu, 2H), 4.49 – 4.23 (m, Gal, 2H), 4.16 (br d, Gal, 0.25H), 4.12 (br d, Gal, 0.75H), 3.71 (br s, OMe, 3H), 3.68 – 3.56 (m, Gal, 1H), 1.93 – 1.76 (m, βLeu, 1H), 1.73 – 1.59 (m, β'γLeu, 2H), 1.58 – 1.52 (m, CH_3, 3H), 1.46 (s, CH_3, 3H), 1.35 – 1.27 (m, CH_3, 6H), 1.09 – 0.80 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 173.6, 173.2, 172.5, 172.0, 109.43, 109.41, 109.24,

109.18, 96.6, 96.5, 73.3, 73.1, 71.7, 71.1, 70.9, 70.8, 68.2, 67.8, 67.5, 66.9, 56.1, 55.9, 52.3, 52.3, 50.8, 50.7, 41.6, 41.3, 26.2, 26.1, 26.0, 25.3, 25.1, 25.1, 24.9, 24.3, 24.0, 23.1, 22.9, 22.1, 21.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{34}N_2O_8$ 431.2393; Found 431.2389.

Compound Gal-4b. Yield: 79% (492 mg); colourless oil; R_f = 0.5 (DCM/MeOH 10:1, v/v); $C_{19}H_{32}N_2O_8$; mixture of two diastereoisomers d.r. 60:40. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, NHVal, 0.4H), 7.79 (d, *J* = 9.0 Hz, NHVal, 0.6H), 5.57 (d, *J* = 4.9 Hz, H1Gal, 0.4H), 5.52 (d, *J* = 4.9 Hz, H1Gal, 0.6H), 4.61 – 4.55 (m, αGal, 1H), 4.54 – 4.48 (m, αVal, 1H), 4.44 (dd, *J* = 8.0, 1.5 Hz, Gal, 0.4H), 4.34 (dd, *J* = 8.0, 1.6 Hz, Gal, 0.6H), 4.29 (d, *J* = 5.2, 2.3 Hz, Gal, 1H), 4.18 (dd, *J* = 7.0, 1.3 Hz, Gal, 0.4H), 4.14 (dd, *J* = 5.0, 1.3 Hz, Gal, 0.6H), 3.72 (s, OMe, 3H),3.66 – 3.57 (m, Gal, 1H), 2.04 – 1.68 (m, βVal, 1H), 1.61 – 1.41 (m, CH_3, 6H), 1.39 – 1.25 (m, CH_3, 6H), 1.00 – 0.88 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 172.2, 172.0, 109.4, 109.2, 109.2, 109.1, 96.6, 96.5, 73.2, 71.7, 70.9, 70.8, 67.4, 66.9, 57.2, 56.2, 52.1, 31.5, 31.3, 26.2, 26.1, 25.2, 25.1, 24.3, 24.0, 19.2, 19.11, 17.9, 17.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{33}N_2O_8$ 417.2237; Found 417.2231.

Compound Gal-4c. Yield: 97% (850 mg); colourless oil; R_f = 0.55 (DCM/MeOH 10:1, v/v); $C_{23}H_{32}N_2O_8$; mixture of two diastereoisomers d.r. nd. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.50 (m, NHPhe, 1H), 7.37–7.09 (m, ArPhe, 5H), 5.58 – 5.46 (m, H1Gal, 1H), 4.89 – 4.81 (m, αGal, 1H), 4.63 – 4.52 (m, αPhe, 1H), 4.32–4.18 (m, Gal, 2H), 4.16–4.02 (m, Gal, 1H), 3.74–3.65 (m, OMe, 3H), 3.62–3.52 (m, Gal, 1H), 3.22–3.03 (m, ββ'Phe, 2H), 1.79 (s, CH_3, 3H), 1.60–1.39 (m, CH_3, 6H), 1.38–1.21 (m, CH_3, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 171.8, 171.7, 171.6, 136.2, 135.9, 129.6, 129.5, 129.3, 129.2, 129.1, 128.5, 128.4, 127.0, 126.9, 109.3, 109.2, 109.1, 109.0, 108.9, 96.5, 96.5, 96.3, 73.0, 72.8, 71.6, 71.3, 70.9, 70.9, 70.8, 70.8, 70.7, 70.6, 67.8, 67.7, 67.0, 66.9, 56.1, 55.9, 55.6, 53.5, 53.4, 53.3, 53.2, 53.0, 52.2, 52.1, 38.1, 37.9, 26.1, 26.0, 25.9, 25.1, 25.2, 24.2, 24.2, 23.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{33}N_2O_8$ 465.2237; Found 465.2229.

Compound Gal-4d. Yield: 86% (299 mg); yellow oil; R_f = 0.54 (DCM/MeOH 10:1, v/v); $C_{20}H_{34}N_2O_8$; mixture of two diastereoisomers d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.6 Hz, NHLeu, 0.7H), 7.43 (d, *J* = 8.0 Hz, NHLeu, 0.3H), 5.56 (d, *J* = 4.9 Hz, H1Gal, 0.3H), 5.51 (d, *J* = 4.8 Hz, H1Gal, 0.7H), 4.70–4.53 (m, αGal, αLeu, 2H), 4.48 (d, *J* = 8.0 Hz, Gal, 0.3H), 4.40 (d, *J* = 8.0 Hz, Gal, 0.7H), 4.29 (ddd, *J* = 21.4, 4.8, 2.2 Hz, Gal, 1H), 4.12 (d, *J* = 3.3 Hz, Gal, 0.7H), 3.99 (d, *J* = 7.9 Hz, Gal, 0.7H), 3.72, 3.71 (s, OMe, 3H), 3.60 – 3.58 (m, Gal, 1H), 2.20 – 2.12 (m, βLeu, 1H), 1.85 (br s, β'γLeu, 2H), 1.54 – 1.41 (m, CH_3, 6H), 1.39 – 1.27 (m, CH_3, 6H), 0.93 (d, *J* =

6.4 Hz, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 173.5, 172.8, 172.2, 109.4, 109.3, 109.1, 109.0, 96.6, 96.4, 73.3, 71.5, 71.1, 70.9, 70.8, 68.2, 67.8, 56.5, 55.1, 52.3, 50.9, 50.7, 41.7, 41.5, 26.2, 26.1, 26.1, 25.3, 25.1, 24.8, 24.7, 24.4, 24.2, 23.1, 23.0, 22.0, 21.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{34}N_2O_8$ 431.2393; Found 431.2387.

Compound Gal-4e. Yield: 81% (797 mg); yellow oil; R_f = 0.38 (DCM/MeOH 10:1, v/v); $C_{19}H_{32}N_2O_8$; mixture of two diastereoisomers d.r. 80:20. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.1 Hz, NHVal, 0.8H), 7.47 (d, *J* = 8.6 Hz, NHVal, 0.2H), 5.56 (d, *J* = 5.0 Hz, H1Gal, 0.2H), 5.51 (d, *J* = 4.8 Hz, H1Gal, 0.8H), 4.59 (dd, *J* = 8.0, 2.3 Hz, αGal, 1H), 4.54 (dd, *J* = 8.8, 5.0 Hz, αVal, 0.2H), 4.52 (dd, *J* = 9.1, 5.1 Hz, αVal, 0.8H), 4.48 (dd, *J* = 8.0, 1.8 Hz, Gal, 0.2H), 4.41 (dd, *J* = 8.0, 1.7 Hz, Gal, 0.8H), 4.31 (dd, *J* = 5.0, 2.4 Hz, Gal, 0.2H), 4.27 (dd, *J* = 4.8, 2.3 Hz, Gal, 0.8H), 4.12 (dd, *J* = 4.4, 1.4 Hz, Gal, 0.8H), 3.97 (dd, *J* = 8.3, 1.7 Hz, Gal, 0.2H), 3.72, 3.71 (s, OMe, 3H), 3.64 (d, *J* = 8.5 Hz, Gal, 0.2H), 3.61 (d, *J* = 4.5 Hz, Gal, 0.8H), 2.21 – 2.12 (m, βVal, 1H), 1.82 (br s, NH_3, 3H), 1.54 – 1.43 (m, CH_3, 6H), 1.37 – 1.26 (m, CH_3, 6H), 0.99 – 0.87 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 172.5, 172.5, 172.3, 109.4, 109.3, 109.2, 109.1, 96.5, 96.4, 73.2, 71.4, 71.1, 71.0, 70.7, 68.4, 67.9, 57.5, 57.2, 56.5, 55.0, 52.1, 31.3, 31.2, 26.2, 26.2, 26.1, 25.3, 25.1, 24.34, 24.2, 19.2, 19.1, 17.9, 17.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{33}N_2O_8$ 417.2237; Found 417.2235.

Compound Gal-4f. Yield: 92% (951 mg), colourless oil; R_f = 0.57 (DCM/MeOH 10:1, v/v); $C_{23}H_{32}N_2O_8$; mixture of two diastereoisomers d.r. nd. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.49 (m, NHPhe, 1H), 7.47 – 6.95 (m, ArPhe, 5H), 5.70 – 5.21 (m, H1Gal, 1H), 4.86 (s, αGal, 1H), 4.74 – 4.40 (m, αPhe, Gal 2H), 4.42 – 3.96 (m, Gal, 3H), 3.88 – 3.44 (m, OMe, 3H), 3.30 – 2.94 (m, ββ'Phe, 2H), 1.90 – 1.09 (m, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 171.9, 136.3, 136.1, 129.6, 129.4, 128.6, 127.1, 109.3, 109.1, 96.4, 73.2, 72.9, 71.1, 71.0, 70.8, 67.93, 56.2, 56.0, 53.3, 53.1, 52.3, 38.3, 38.0, 26.3, 26.2, 26.1, 26.0, 25.3, 24.4, 24.3, 24.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{33}N_2O_8$ 465.2237; Found 465.2232.

Compound Gal-4g. Yield: 85% (701 mg); colourless oil; R_f = 0.59 (DCM/MeOH 10:1, v/v); $C_{16}H_{26}N_2O_8$ mixture of two diastereoisomers d.r. 90:10. Chemical shifts are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (br s, NH_3, 3H), 7.88 (br s, NHGly, 1H), 5.55 (d, *J* = 4.9 Hz, H1Gal, 1H), 4.61 (dd, *J* = 8.0, 2.4 Hz, αGal, 1H), 4.49 (dd, *J* = 8.0, 1.6 Hz, Gal, 1H), 4.32 (dd, *J* = 4.9, 2.4 Hz, Gal, 1H), 4.14 (dd, *J* = 7.4, 1.3 Hz, Gal, 1H), 4.06 (dd, *J* = 9.8, 4.7 Hz, Gly, Gal, 2H), 3.85 (d, *J* = 7.4 Hz, Gly 1H), 3.73 (s, OMe, 3H), 1.52, 1.44, 1.32 (s, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 169.9, 109.5, 109.3, 96.5, 96.4, 71.2, 70.7,

70.6, 67.1, 66.4, 60.5, 55.0, 52.3, 44.8, 41.3, 25.9, 25.8, 24.9, 24.1, 21.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{27}N_2O_8$ 375.1767; Found 375.1762.

***Compound Sor-4a*.** Yield: 88% (899 mg); yellow oil; R_f = 0.47 (DCM/MeOH 10:1, v/v); $C_{20}H_{34}N_2O_8$; mixture of two diastereoisomers d.r. nd. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (br d, NHLeu, 1H), 5.32, 5.30 (s, αSor, 1H), 4.85 – 4.58 (m, H4Sor, 1H), 4.49, 4.44 (s, αLeu, Sor, 2H), 4.29 (br s, Sor, 1H), 4.06 - 3.98 (m, Sor, 1H), 3.72 (br s, OMe, 3H), 3.71 – 3.65 (m, Sor, 1H), 1.85 – 1.58 (m, ββ'γLeu, 3H), 1.50, 1.46, 1.39 (s, CH_3, 12H), 1.03 – 0.78 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 162.6, 114.9, 111.6, 97.9, 81.0, 80.8, 74.6, 72.4, 60.3, 52.4, 51.6, 41.7, 28.9, 27.6, 26.0, 25.0, 22.9, 22.4, 18.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{35}N_2O_8$ 431.2393; Found 431.2388.

***Compound Sor-4b*.** Yield: 97% (224 mg); colourless oil; R_f = 0.54 (DCM/MeOH 10:1, v/v); $C_{19}H_{32}N_2O_8$; mixture of two diastereoisomers d.r. nd. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (br d, NHVal, 1H), 5.33 (br d, αSor, 1H), 4.68 – 4.56 (m, H4Sor, 1H), 4.52 – 4.41 (br d, H2Sor, 1H), 4.38 – 4.23 (m, αVal, 1H), 4.17 – 3.88 (m, Sor, 2H), 3.80 – 3.62 (m, Sor, OMe, 4H), 2.28 – 2.03 (m, βVal, 1H), 1.62 – 1.17 (m, CH_3, 12H), 1.06 – 0.81 (m, γγ'Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 162.9, 114.9, 111.5, 97.9, 85.1, 80.6, 74.5, 72.5, 60.3, 57.5, 52.3, 31.8, 29.0, 27.6, 26.0, 18.9, 18.7, 17.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{35}N_2O_8$ 431.2393; Found 431.2388.

***Compound Sor-4c*.** Yield: 86% (824 mg); yellow oil; R_f = 0.49 (DCM/MeOH 10:1, v/v); $C_{23}H_{32}N_2O_8$; mixture of two diastereoisomers d.r. nd. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 6.97 (m, ArPhe, NHPhe, 6H), 5.37 – 5.23 (m, αSor, 0.70H), 5.10 – 5.00 (m, αSor, 0.30H), 4.99 – 4.82 (m, H4Sor, 1H), 4.50 – 4.38 (m, Sor, 1H), 4.33 – 4.19 (m, αPhe, 1H), 4.08 – 3.93 (m, Sor, 2H), 3.78 – 3.57 (m, Sor, OMe, 4H), 3.29 – 3.06 (m, ββ'Phe, 2H), 1.70 – 1.01 (m, CH_3, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 171.1, 162.5, 162.4, 135.7, 135.7, 129.9, 129.5, 128.6, 128.3, 127.2, 127.1, 114.9, 114.6, 111.9, 111.5, 97.8, 85.2, 85.0, 81.1, 80.7, 74.7, 74.6, 72.2, 72.1, 60.2, 60.0, 54.3, 53.8, 52.4, 37.8, 37.7, 28.9, 28.9, 27.7, 27.6, 26.1, 25.9, 18.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{33}N_2O_8$ 465.2237; Found 465.2229.

***Compound Sor-4d*.** Yield: 80% (399 mg); yellow oil; R_f = 0.58 (DCM/MeOH 10:1, v/v); $C_{20}H_{34}N_2O_8$; mixture of two diastereoisomers d.r. 65:35 Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (br d, NHLeu, 0.65H), 7.20 (br d, NHLeu, 0.35H, 5.33 (s, αSor, 0.35H), 5.14 (s, αSor, 0.65H), 4.68–4.52 (m, HSor, 1H), 4.30 –4.27 (m, Sor, 1H), 4.15–3.97 (m, Sor, αLeu, 3H), 3.83–3.67 (m, Sor, OMe, 4H), 1.47–1.56 (m, ββ'γLeu,

3H), 1.46–1.26 (m, CH_3, 12H), 0.95–0.89 (m,δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4, 170.7, 162.3, 114.6, 114.4, 112.6, 112.3, 97.7, 97.3, 85.4, 85.0, 81.2, 74.6, 73.2, 72.1, 60.5, 60.2, 59.7, 52.3, 52.2, 51.5, 50.6, 41.5, 41.4, 29.0, 28.7, 27.8, 26.5, 24.8, 24.6, 24.5, 22.8, 22.7, 22.1, 18.7, 18.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{35}N_2O_8$ 431.2393; Found 431.2392.

***Compound Sor-4e*.** Yield: 86% (457 mg); yellow oil; R_f = 0.6 (DCM/MeOH 10:1, v/v); $C_{19}H_{32}N_2O_8$; mixture of two diastereoisomers d.r. 85:15. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (br s, NHVal, 0.15H), 6.98 (br s, NHVal, 0.85H), 4.65 – 4.56 (m, Sor, 1H), 4.35 – 4.15 (m, Sor, 2H), 4.13 – 3.98 (m, Sor, αVal, 3H), 3.78 – 3.66 (m, Sor, OMe, 4H), 1.77 (br s, βVal, 1H), 1.48 – 1. 34 (m, CH_3, 12H), 0.98 – 0.90 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 171.6, 115.4, 113.2, 97.5, 85.4, 77.0, 76.8, 73.4, 73.2, 72.7, 60.6, 57.6, 57.4, 52.0, 31.2, 29.1, 27.8, 26.8, 18.9, 18.6, 17.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{35}N_2O_8$ 431.2393; Found 431.2386.

***Compound Sor-4f*.** Yield: 84% (542 mg); yellow oil; R_f = 0.47 (DCM/MeOH 10:1, v/v); $C_{23}H_{32}N_2O_8$; mixture of two diastereoisomers d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, NHPhe, 0.30H), 7.39 – 7.15 (m, ArPhe, 5H), 7.11 (d, *J* = 7.1 Hz, NHPhe, 0.70H), 5.34 – 5.30 (m, Sor, 0.70H), 5.05 – 4.80 (m, Sor, 1.30H), 4.52 – 4.26 (m, Sor, αPhe, 2H), 4.05 – 3.93 (m, Sor, 2H), 3.89 – 3.80 (m, Sor, 0.70H), 3.72, 3.70 (s, OMe, 3H), 3.62 – 3.57 (m, Sor, 0.30H), 3.33 – 3.00 (m, ββ'Phe, 2H), 1.55, 1.48 (s, CH_3, 3H), 1.43 – 1.32 (m, CH_3, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 171.1, 162.5, 162.4, 135.7, 135.7, 129.9, 129.5, 128.6, 128.3, 127.2, 127.1, 114.9, 114.6, 111.9, 111.5, 97.8, 97.7, 85.2, 85.0, 81.1, 80.7, 74.7, 74.6, 72.2, 72.1, 60.2, 60.0, 54.3, 53.8, 52.4, 37.8, 37.7, 28.9, 28.8, 27.7, 27.6, 26.1, 25.9, 18.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{33}N_2O_8$ 465.2237; Found 465.2233.

***Compound Sor-4g*.** Yield: 75% (320 mg); colourless oil; R_f = 0.56 (DCM/MeOH 10:1, v/v); $C_{16}H_{26}N_2O_8$; mixture of two diastereoisomers d.r. 80:20. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (br s, NHGly, 1H), 5.29, 5.05 (br s, Sor, 1H), 4.33 – 3.90 (m, Sor, 1H), 3.84 – 3.62 (m, Sor, Gly, 5H), 3.66 – 3.29 (m, Sor, OMe, 4H), 1.94 (br s, NH_3, 3H), 1.51 – 1.28 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 170.4, 114.6, 112.6, 97.5, 85.7, 73.4, 72.3, 60.5, 60.1, 52.4, 41.2, 29.1, 27.8, 26.4, 18.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{27}N_2O_8$ 375.1767; Found 375.1762.

Synthesis of Cbz-protected dipeptides

General procedure: C-glycosyl α-amino acid containing dipeptide was dissolved in dry DCM (c = 0.1 M) and *N,N*-diisopropylethylamine (DIPEA, 3.0 equiv.) was added. The reaction mixture was stirred at room temperature under argon for 15 minutes, and then benzyl chloroformate (1.5 equiv.) was added dropwise. With all reactants added, the solution was allowed to stir under argon overnight at room temperature. The reaction was terminated by addition of saturated $NaHCO_3$, extracted with DCM and washed with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The product was purified by flash chromatography on a silica gel column in a solvent system: DCM/MeOH (10:1). The isolated Cbz-protected product was dissolved in methanol (c = 0.1 M) and solid NaOH was added (5 equiv.) Reaction mixture was stirred at room temperature for 5 hours. The reaction was quenched by adding a 10 % citric acid solution to adjust the pH of the solution to 4. Then, it was extracted with DCM and washed with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4, the solvent was evaporated, and the crude product was used in the next step.

***Compound Gal-5a*.** Yield: 71% (161 mg); yellow oil; R_f = 0.36 (DCM/MeOH 10:1, v/v); $C_{27}H_{38}N_2O_{10}$; mixture of diastereoisomers d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.21 (m, ArCbz, NH, 6H), 7.19 – 6.81 (m, NH, 1H), 5.73 – 5.41 (m, Gal, 2H), 5.27 – 4.99 (m, CH_2Cbz, 2H), 4.63 – 4.53 (m, Gal, αLeu, 2.3H), 4.48 – 4.44 (m, αLeu, 0.7H), 4.31 – 4.25 (m, Gal, 2H), 1.70 – 1.40 (m, ββ'γLeu, CH_3, 6H), 1.40 – 1.22 (m, CH_3, 9H), 1.08 – 0.80 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 175.1, 169.8, 169.7, 157.0, 136.1, 136.0, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 127.0, 109.6, 109.3, 96.5, 96.2, 71.6, 70.9, 70.8, 70.7, 70.4, 67.4, 66.7, 66.5, 65.8, 65.3, 56.5, 56.1, 51.1, 50.9, 47.5, 46.3, 41.3, 40.8, 29.7, 26.1, 26.0, 25.8, 25.8, 25.0, 24.9, 24.9, 24.7, 24.0, 23.9, 22.9, 22.7, 21.9, 21.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{39}N_2O_{10}$ 551.26047; Found 551.26044.

***Compound Gal-5b*.** Yield: 60% (127 mg); yellow oil; R_f = 0.26 (DCM/MeOH 10:1, v/v); $C_{26}H_{36}N_2O_{10}$; mixture of diastereoisomers d.r. 60:40. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, ArCbz, 5H), 7.24 – 6.93 (m, NH, 1H), 6.30 (d, *J* = 8.7 Hz, NH, 0.40H), 5.69 (d, *J* = 6.3 Hz, NH, 0.60H), 5.59 – 5.46 (m, Gal, 1H), 5.13 (d, *J* = 11.4 Hz, CH_2Cbz, 2H), 4.65 – 4.56 (m, Gal, αVal, 1.60H), 4.55 – 4.48 (m, Gal, αVal, 1.4H), 4.43 – 4.32 (m, Gal, 1H), 4.30 – 4.23 (m, Gal, 2H), 2.40 – 2.07 (m, βVal, 1H), 1.55 – 1.36 (m, CH_3, 6H), 1.32 – 1.25 (m, CH_3, 6H), 1.02 – 0.76 (m, γγ+Val, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 174.1, 169.9, 169.7, 157.2, 128.7, 128.65, 128.61, 128.34, 127.8, 127.1, 109.8, 109.7, 109.4, 109.3, 96.7, 96.4, 71.7, 71.0, 70.9, 70.8, 70.6, 67.5, 67.3, 66.7,

65.6, 65.5, 58.2, 57.5, 57.4, 53.6, 31.1, 31.0, 29.8, 26.2, 26.1, 26.0, 25.9, 25.1, 25.0, 24.5, 24.2, 24.0, 19.1, 17.9, 17.8 17.7, 17.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{37}N_2O_{10}$ 537.2448; Found 537.2440.

***Compound Gal-5c*.** Yield: 68% (113 mg); yellow oil; R_f = 0.33 (DCM/MeOH 10:1, v/v); $C_{30}H_{36}N_2O_{10}$; mixture of diastereoisomers d.r. 60:40 Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, ArCbz, ArPhe, NH, 8H), 7.24 – 6.94 (m, ArPhe, 4H), 5.61 (d, *J* = 6.8 Hz, Gal, 0.4H), 5.52 – 5.46 (m, Gal, 0.6H), 5.18 – 5.05 (m, CH_2Cbz, 2H), 4.90 – 4.80 (m, Gal, 1H), 4.57 – 4.39 (m, Gal, αPhe, 2H), 4.33 – 4.04 (m, Gal, 3H), 3.27 – 3.10 (m, ββ'Phe, 2H), 1.56 – 1.50 (m, CH_3, 3H), 1.32 – 1.28 (m, CH_3,6H), 1.27 – 1.22 (m, CH_3, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.5, 173.3, 169.7, 169.6, 140.8, 135.5, 129.6, 129.4, 128.7, 128.6, 128.6, 128.53, 128.49, 128.25, 128.22, 128.0, 127.8, 127.7, 127.2, 127.1, 127.1, 127.0, 109.6, 109.5, 109.3, 109.2, 96.6, 96.5, 96.2, 71.6, 70.9, 70.8, 70.73, 70.68, 70.5, 70.4, 67.3, 66.7, 66.2, 65.4, 53.5, 46.3, 37.3, 37.2, 29.7, 26.1, 26.02, 25.98, 25.8, 25.7, 25.6, 25.0, 24.9, 24.1, 23.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{37}N_2O_{10}$ 585.2448; Found 585.2441.

***Compound Gal-5d*.** Yield: 79% (89 mg); yellow oil; R_f = 0.4 (DCM/MeOH 10:1, v/v); $C_{27}H_{38}N_2O_{10}$; mixture of diastereoisomers d.r. nd Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, ArCbz, NH, 6H), 7.12 – 6.61 (m, NH, 1H), 5.75 – 5.41 (m, Gal, 2H), 5.19 – 5.06 (m, CH_2Cbz, 2H), 4.64 – 4.55 (m, Gal, αLeu, 2H), 4.48 – 4.34 (m, Gal, 1H), 4.33 – 4.19 (m, Gal, 2H), 1.76 – 1.65 (m, ββ'Leu, 2H), 1.55 – 1.44 (m, CH_3, 3H), 1.40 – 1.19 (m, γLeu, CH_3, 10H), 0.99 – 0.85 (m, δδ'Leu, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 169.9, 157.1, 155.3, 136.25, 136.2, 128.7, 128.6, 128.4, 128.1, 127.1, 109.7, 109.4, 96.6, 96.3, 71.6, 70.9, 70.7, 67.44, 67.4, 67.2, 66.8, 65.5, 56.3, 53.6, 51.1, 46.4, 41.3, 40.8, 32.1, 29.8, 29.5, 26.2, 25.9, 25.17, 24.0, 23.1, 22.8, 21.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{39}N_2O_{10}$ 551.26047; Found 551.26041.

***Compound Gal-5e*.** Yield: 49% (60 mg); yellow oil; R_f = 0.34 (DCM/MeOH 10:1, v/v); $C_{26}H_{36}N_2O_{10}$; mixture of diastereoisomers d.r. 60:40. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, ArCbz, 5H), 7.18 – 6.91 (m, NH, 1H), 6.26 (br d, NH, 0.4H), 7.70 (d, *J* = 6.4 Hz, NH, 0.6H), 5.52 (d, *J* = 4.9 Hz, Gal, 0.4H), 5.50 (d, *J* = 4.8 Hz, Gal, 0.6H), 5.13 (br s, CH_2Cbz, 2H), 4.60 – 4.47 (m, Gal, αVal, 3H), 4.38 (br d, Gal, 1H), 4.31 – 4.19 (m, Gal, 2H), 2.37 – 2.07 (m, βVal, 1H), 1.58 – 1.36 (m, CH_3, 6H), 1.34 – 1.23 (m, CH_3, γγ'Val, 6H), 1.06 – 0.75 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 169.8, 156.9, 136.1, 128.6, 128.52, 128.50, 128.2, 128.2, 127.0, 109.6, 109.2, 96.5, 96.2, 71.4, 71.3, 70.8, 70.6, 67.3, 66.9, 65.4, 57.3, 56.2, 31.0, 30.9, 29.7, 26.1, 26.0, 25.8, 25.0,

24.9, 23.9, 19.0, 17.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{37}N_2O_{10}$ 537.2448; Found 537.2443.

***Compound Gal-5f*.** Yield: 46% (154 mg); yellow oil; R_f = 0.29 (DCM/MeOH 10:1, v/v); $C_{30}H_{36}N_2O_{10}$; mixture of diastereoisomers d.r. 70:30. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, ArCbz, ArPhe, NH, 8H), 7.24 – 7.17 (m, ArPhe, 3H), 7.11 – 6.96 (m, NH, 1H), 6.27 (br d, NH, 0.3H), 5.72 – 5.57 (m, NH, 0.7H), 5.55 – 5.40 (m, Gal, 1H), 5.18 – 5.06 (m, CH_2Cbz, 2H), 4.94 – 4.75 (m, Gal, 1H), 4.58 – 4.43 (m, Gal, αPhe, 2H), 4.37 – 4.03 (m, Gal, 3H), 3.29 – 2.93 (m, $\beta\beta$'Phe, 2H), 1.54 – 1.50 (m, CH_3, 3H), 1.34 – 1.27 (m, CH_3, 6H), 1.27 – 1.14 (m, CH_3, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 169.7, 157.0, 140.9, 138.2, 137.6, 136.2, 136.0, 135.8, 135.6, 129.8, 129.6, 128.9, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.3, 127.1, 109.6, 109.4, 96.6, 96.3, 74.8, 71.4, 71.0, 70.9, 67.4, 66.8, 66.4, 65.5, 58.2, 56.1, 53.5, 46.4, 37.2, 26.2, 26.1, 25.9, 25.7, 25.2, 25.1, 24.2, 23.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{37}N_2O_{10}$ 585.2448; Found 585.2445.

***Compound Gal-5g*.** Yield: 37% (86 mg); colourless oil; R_f = 0.25 (DCM/MeOH 10:1, v/v); $C_{23}H_{30}N_2O_{10}$; mixture of diastereoisomers d.r. 55:45. Chemical shifts are given for both diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, ArCbz, 5H), 7.22, 7.12 (br t, NHGly, 1H), 6.34 (d, *J* = 8.1 Hz, NH, 0.55H), 5.73 (d, *J* = 6.5 Hz, NH, 0.45H), 5.55 – 5.48 (m, Gal, 1H), 5.15 – 5.07 (m, CH_2Cbz, 2H), 4.65 – 4.26 (m, Gal, 5H), 4.12 – 4.92 (m, Gly, 2H), 1.53 – 1.46 (m, CH_3, 3H), 1.35 – 1.24 (m, CH_3, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 169.8, 169.7, 140.8, 128.6, 128.5, 128.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.0, 109.6, 109.3, 109.1, 96.6, 96.3, 67.2, 67.1, 66.7, 65.9, 65.4, 64.3, 53.4, 47.5, 43.9, 41.9, 29.7, 26.0, 25.8, 25.7, 25.0, 24.9, 23.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{31}N_2O_{10}$ 495.1979; Found 495.1975.

***Compound Sor-5g*.** Yield: 37% (45 mg); colourless oil; R_f = 0.27 (DCM/MeOH 10:1, v/v); $C_{23}H_{30}N_2O_{10}$; mixture of diastereoisomers d.r. 95:5. Chemical shifts are given for major diastereoisomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, ArCbz, 2H), 7.33 – 7.31 (m, ArCbz, 3H), 7.31 – 7.28 (m, NH, 1H), 7.15 (br t, NHGly, 1H), 6.13 (d, *J* = 8.5 Hz, αSor, 1H), 5.14 – 5.11 (m, CH_2Cbz, 2H), 4.70 (s, Sor, 1H), 4.62 (s, Sor, 1H), 4.24 (d, *J* = 2.1 Hz, Sor, 1H), 4.18 – 4.10 (m, Sor, 2H), 4.07 – 4.04 (m, 2H). 1.52 – 1.44 (m, CH_3, 6H), 1.29, 1.25 (s, CH_3, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 167.9, 156.8, 140.9, 128.7, 128.5, 128.1, 127.8, 127.2, 113.3, 112.7, 98.0, 87.1, 73.6, 72.7, 67.3, 65.5, 59.9, 59.3, 41.9, 29.8, 28.6, 27.1, 26.2, 18.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{31}N_2O_{10}$ 495.1979; Found 495.1971.

Synthesis of oligomers

General procedure: Cbz-protected dipeptide was dissolved in dry DCM (c = 0.05 M). *N*-Methylmorpholine (NMM, 1.1 equiv.) was added dropwise followed by the addition of 1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate (HATU, 1.1 equiv.). The reaction mixture was stirred at room temperature for 30 minutes, and then the amino component (1 equiv.) dissolved in 500 µL of dry DCM, was added dropwise. Reaction mixture was allowed to stir overnight at room temperature. The reaction was quenched by adding a saturated NH_4Cl solution, then extracted with DCM and washed with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4, the solvent evaporated, and the residue purified by flash chromatography on a silica gel column using a solvent system: DCM/MeOH (10:1, v/v).

Tetramer Gal-6a. Yield: 75% (79 mg); yellow oil; R_f = 0.48 (DCM/MeOH 10:1, v/v); $C_{47}H_{70}N_4O_{17}$.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 6.77 (m, 9H), 5.63 – 5.38 (m, 2H), 5.31 – 4.98 (m, 2H), 4.60 – 4.22 (m, 12H), 3.82 – 3.58 (m, 3H), 1.71 – 1.57 (m, 6H), 1.55 – 1.41 (m, 12h), 1.32 – 1.27 (m, 12H), 1.02 – 0.78 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0, 172.9, 172.1, 172.0, 170.1, 169.7, 169.6, 169.3, 169.0, 168.9, 157.1, 156.8, 136.3, 136.1, 128.9, 128.7, 128.6, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 109.5, 109.4, 109.3, 96.7, 96.6, 96.4, 96.3, 96.2, 72.0, 71.9, 71.8, 71.1, 71.0, 70.98, 70.87, 70.8, 67.4, 67.2, 66.8, 66.65, 66.60, 66.24, 66.18, 54.2, 54.1, 52.32, 52.26, 51.3, 51.2, 41.1, 41.0, 40.9, 40.6, 40.4, 26.2, 26.10, 26.07, 26.0, 25.95, 25.90, 25.21, 25.19, 25.1, 24.8, 24.7, 24.6, 24.2, 24.1, 24.04 23.2, 23.1, 23.0, 22.9, 22.9, 22.8, 22.2, 22.14, 22.12, 21.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{47}H_{71}N_4O_{17}$ 963.4814; Found 963.4809.

Tetramer Gal-6b. Yield: 60% (52.3 mg) colourless oil; R_f = 0.53 (DCM/MeOH 10:1, v/v); $C_{45}H_{66}N_4O_{17}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 5H), 7.20 – 5.56 (m, 4H), 5.55 – 5.43 (m, 2H), 5.23 – 5.02 (m, 2H), 4.75 – 4.16 (m, 12H), 3.78 – 3.62 (m, 3H), 2.44 – 2.02 (m, 2H), 1.60 – 1.39 (m, 12H), 1.34 – 1.26 (m, 12H), 1.05 – 0.81 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 171.8, 171.4, 169.5, 168.8, 136.4, 128.6, 128.6, 128.4, 128.1, 128.0, 109.7, 109.3, 109.2, 109.1, 96.4, 96.3, 71.7, 71.6, 71.1, 70.9, 70.8, 67.4, 66.6, 65.2, 59.5, 57.8, 57.6, 56.0, 54.8, 52.2, 52.1, 31.3, 31.1, 30.7, 29.8, 26.2, 26.2, 26.0, 25.1, 24.3, 24.2, 24.1, 23.9, 19.4, 19.3, 19.0, 18.1, 18.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{45}H_{67}N_4O_{17}$ 935.4501; Found 935.4497.

***Tetramer Gal-6c*.** Yield: 78% (41 mg); yellow oil; R_f = 0.55 (DCM/MeOH 10:1, v/v); $C_{53}H_{66}N_4O_{17}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 6-94 (m, 19H), 5.56 – 5.29 (m, 2H), 5.28 – 4.93 (m, 2H), 4.84 – 3.92 (m, 12H), 3.78 – 3.54 (m, 3H), 3.37 – 2.89 (m, 4H), 1.59 – 1.43 (m, 8H), 133 – 1.23 (m, 16H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 170.8, 169.7, 169.1, 168.6,

156.9, 136.6, 136.4, 136.1, 129.6, 129.5, 129.3, 129.2, 128.8, 128.7, 128.5, 128.3, 128.1, 127.2, 127.1, 127.0, 109.7, 109.6, 109.5, 109.3, 109.2, 96.6, 96.4, 96.3, 96.1, 71.8, 71.0, 70.9, 70.7, 70.5, 67.3, 67.1, 66.7, 66.4, 66.1, 56.3, 55.7, 55.2, 54.9, 54.1, 54.0, 53.9, 53.6, 52.4, 52.3, 52.2, 38.7, 38.3, 38.1, 37.9, 37.6, 29.8, 26.2, 26.2, 26.1, 25.9, 25.6, 25.2, 25.1, 24.2, 24.1, 23.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{53}H_{67}N_4O_{17}$ 1031.4501; Found 1031.4999.

***Tetramer Gal-6d*.** Yield: 81% (56.9 mg); yellow oil; R_f = 0.63 (DCM/MeOH 10:1, v/v); $C_{47}H_{70}N_4O_{17}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 5.70 (m, 9H), 5.55 – 5.39 (m, 2H), 5.20 – 5.02 (m, 2H), 4.81 – 4.01 (m, 9H), 3.84 – 3.52 (m, 5H), 1.78 – 1.37 (m, 14H), 1.36 – 1.20 (m, 16H), 0.97 – 0.84 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 172.9, 172.8, 171.8, 171.5, 169.6, 156.8, 136.2, 128.5, 128.5, 128.24, 128.20, 128.1, 127.9, 109.5, 109.4, 109.13, 109.09, 96.5, 96.5, 96.2, 96.1, 71.7, 70.9, 70.8, 70.78, 70.76, 70.6, 67.2, 66.7, 66.4, 56.4, 55.1, 54.9, 54.0, 53.4, 52.6, 52.1, 50.9, 50.9, 46.4, 41.4, 41.2, 41.0, 40.5, 29.7, 26.2, 26.10, 26.07, 25.97, 25.89, 25.8, 25.0, 24.9, 24.64, 24.59, 24.5, 24.4, 24.3, 24.2, 24.1, 23.9, 23.1, 23.0, 22.9, 22.8, 22.7, 21.98, 21.95, 21.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{47}H_{71}N_4O_{17}$ 963.4814; Found 963.4812.

***Tetramer Gal-6e*.** Yield: 73% (51 mg); yellow oil; R_f = 0.48 (DCM/MeOH 10:1, v/v); $C_{45}H_{66}N_4O_{17}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 6.61 (m, 9H), 5.64 – 5.38 (m, 2H), 5.28 – 4.99 (m, 2H), 4.77 – 3.96 (m, 11H), 3.87 – 3.55 (m, 4H), 2.35 – 2.05 (m, 2H), 1.79 – 1.20 (m, 28H), 1.06 – 0.66 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 172.0, 171.9, 171.2, 169.7, 136.4, 128.65, 128.63, 128.61, 128.4, 128.3, 128.1, 109.69, 109.68, 109.4, 109.3, 109.28, 109.26, 96.7, 96.4, 96.3, 71.9, 71.7, 71.1, 70.9, 70.8, 70.7, 67.3, 67.1, 67.0, 66.8, 57.6, 57.5, 52.2, 52.1, 31.6, 31.4, 31.36, 31.30, 29.8, 26.3, 26.26, 26.24, 26.21, 25.9, 25.8, 25.7, 25.2, 25.1, 25.0, 24.1, 24.0, 19.3, 19.1, 18.9, 17.9, 17.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{45}H_{67}N_4O_{17}$ 935.4501; Found 935.4495.

Tetramer Gal-6f. Yield: 76% (40 mg); yellow oil; R_f = 0.55 (DCM/MeOH 10:1, v/v); $C_{53}H_{66}N_4O_{17}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 6.16 (m, 19H), 5.56 – 5.38 (m, 2H), 5.22 – 4.94 (m, 2H), 4.87 – 3.99 (m, 12H), 3.71 – 3.54 (m, 3H), 3.44 – 2.71 (m, 4H), 1.60 – 1.40 (m, 8H), 1.27-1.21 (m, 16H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 171.6, 171.5, 170.8, 169.5, 168.4, 136.6, 136.4, 136.3, 129.7, 129.6, 129.5, 129.4, 128.9, 128.8, 128.7, 128.6, 128.3, 128.0, 127.9, 127.2, 127.1, 127.0, 126.9, 109.6, 109.5, 109.4, 109.3, 109.3, 96.6, 96.5, 96.4, 96.3, 96.2, 71.8, 71.0, 70.9, 70.8, 70.7, 67.3, 67.1, 66.7, 66.5, 66.1, 58.2, 56.2, 55.8, 55.4, 55.1, 54.9, 54.4, 54.0, 53.9, 53.8, 52.3, 52.3, 52.2, 47.6, 46.4, 38.5, 38.1, 37.9, 26.2, 26.1, 25.9, 25.8, 25.7, 25.2, 25.1, 24.1, 23.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{53}H_{67}N_4O_{17}$ 1031.4501; Found 1031.4500.

Tetramer Sor-6g. Yield: 55% (33 mg); colourless oil; R_f = 0.43 (DCM/MeOH 10:1, v/v); $C_{39}H_{54}N_4O_{17}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 6H), 7.12 (br t, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 6.0.9 (br d, 1H), 5.15 – 5.11 (m, 2H), 5.01 (br d, 1H), 4.73 – 4.61 (m, 3H), 4.25 – 4.21 (m, 2H), 4.13 – 4.10 (m, 2H), 4.07 – 4.01 (m, 8H), 3.84 – 3.64 (m, 3H), 1.54 – 1.47 (m, 12H), 1.43 – 1.40 (m, 8H), 1.28 – 1.25 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 169.0, 167.6, 167.0, 156.7, 136.5, 128.5, 128.5, 128.1, 128.0, 128.0, 127.1, 113.7, 113.4, 112.7, 112.5, 98.0, 97.8, 86.9, 86.4, 73.7, 73.6, 72.9, 72.7, 67.1, 60.0, 59.9, 59.4, 57.3, 52.5, 43.5, 41.8, 32.1, 29.8, 29.1, 28.6, 27.2, 27.0, 26.4, 26.2, 18.9, 18.8, 18.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{39}H_{55}N_4O_{17}$ 851.3562; Found 851.3555.

Hexamer Gal-7d. Yield: 95% (32.2 mg); colourless oil; R_f = 0.4 (DCM/MeOH 10:1, v/v); $C_{66}H_{100}N_6O_{24}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.28 (m, 7H), 7.19 – 6.68 (m, 4H), 5.55 – 5.42 (m, 3H), 5.24 – 4.97 (m, 2H), 4.68 – 4.51 (m, 6H), 4.47 – 4.18 (m, 12H), 3.79 – 3.57 (m, 3H), 1.81 – 1.75 (m, 6H), 1.66 – 1.60 (m, 3H), 1.51 – 1.41 (m, 16H), 1.35 – 1.26 (m, 20H), 0.97 – 0.86 (m, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.1, 172.4, 171.89, 171.86, 170.1, 169.9, 169.2, 169.0, 136.3, 128.64, 128.58, 128.4, 128.3, 128.2, 128.1, 109.7, 109.6, 109.5, 109.3, 109.2, 96.7, 96.6, 96.3, 96.2, 72.1, 71.8, 71.6, 71.5, 71.0, 70.93, 70.87, 70.8, 70.7, 67.4, 67.1, 66.7, 66.5, 66.4, 54.8, 54.2, 52.2, 51.1, 41.8, 41.5, 41.4, 41.1, 40.9, 40.7, 38.8, 29.8, 29.5, 26.3, 26.2, 26.1, 26.0, 25.93, 25.90, 25.2, 25.1, 24.7, 24.5, 24.3, 24.2, 24.1, 23.23, 23.20, 23.0, 22.2, 22.1, 22.0, 21.95. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{66}H_{101}N_6O_{24}$ 1361.6867; Found 1361.6862.

Tetramer 8. Yield: 88% (62 mg); colourless oil; R_f = 0.7 (petrol ether-EtOAc 1/1, v/v); $C_{47}H_{70}N_4O_{17}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 – 8.32 (m, 1H), 7.58 – 7.21 (m, 5H), 7.19 – 6.78 (m, 2H), 6.53 – 6.12 (m, 1H), 5.72 – 5.40 (m, 2H), 5.23 – 5.05 (m, 2H), 4.74 – 4.67 (m, 1H), 4.63 – 4.53 (m, 2H), 4.38 – 4.19 (m, 4H), 4.17 – 3.92 (m, 4H), 3.83 – 3.52 (m, 4H), 1.74 – 1.59 (m, 5H), 1.54 – 1.36 (m, 18H), 1.33 – 1.24 (m, 7H), 1.07 – 0.66 (m, 12H). ^{13}C NMR (151 MHz, CDCl3) δ 172.8, 170.7, 169.9, 169.3, 166.8, 162.6, 150.0, 136.3, 136.2, 128.6, 128.6, 128.4, 128.35, 128.32, 128.1, 119.6, 117.5, 114.9, 111.6, 97.9, 96.7, 96.3, 85.1, 80.8, 74.5, 72.4, 71.0, 71.0, 70.9, 70.8, 70.7, 70.55, 67.50, 67.4, 67.3, 67.1, 60.3, 52.4, 51.6, 41.7, 29.0, 27.6, 26.2, 26.0, 26.0, 25.2, 25.0, 24.1, 24.0, 22.9, 22.4, 18.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{47}H_{71}N_4O_{17}$ 963.4814; Found 963.4811.

Tetramer 9. Yield: 91% (48 mg); colourless oil; R_f = 0.64 (petrol ether-EtOAc 1/1, v/v); $C_{53}H_{66}N_4O_{17}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.19 (m, 9H), 7.25 – 6.91 (m, 10H), 5.53 – 5.42 (m, 1H), 5.19 – 5.01 (m, 2H), 4.99 – 4.79 (m, 2H), 4.63 – 4.49 (m, 2H), 4.34 – 4.17 (m, 4H), 4.15 – 3.79 (m, 4H), 3.77 – 3.42 (m, 4H), 3.35 – 3.03 (m, 4H), 1.42 – 1.24 (m, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 171.2, 170.8, 162.5, 162.4, 136.3, 135.7, 129.9, 129.8, 129.6,

129.5, 128.8, 128.71, 128.69, 128.66, 128.60, 128.3, 128.1, 127.21, 127.19, 127.1, 119.6, 117.5, 114.9, 114.6, 111.9, 111.5, 109.6, 109.4, 97.8, 96.6, 96.3, 85.1, 85.0, 81.1, 80.7, 74.7, 74.6, 72.2, 72.1, 71.9, 71.0, 70.9, 70.8, 70.7, 70.5, 67.3, 66.9, 60.2, 60.0, 54.3, 53.8, 52.5, 37.8, 37.7, 29.8, 29.0, 28.9, 27.7, 27.6, 26.2, 26.2, 26.2, 26.1, 26.0, 25.93, 25.92, 25.2, 25.1, 18.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{53}H_{67}N_4O_{17}$ 1031.4501; Found 1031.4997.

Tetramer 10. Yield: 94% (32 mg); colourless oil; R_f = 0.59 (petrol ether-EtOAc 1/1, v/v); $C_{50}H_{68}N_4O_{17}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 7H), 7.24 – 6.97 (m, 7H), 5.52 – 5.41 (m, 1H), 5.14 – 5.07 (m, 2H), 4.75 – 4.67 (m, 1H), 4.63 – 4.50 (m, 2H), 4.34 – 4.22 (m, 4H), 4.15 – 4.03 (m, 4H), 3.74 (s, 3H), 3.70 – 3.66 (m, 2H), 3.26 – 3.02 (m, 2H), 1.70 – 1.62 (m, 3H), 1.52 – 1.37 (m, 24H), 0.96 – 0.91 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 170.9, 169.2, 165.9, 162.6, 136.3, 135.9, 129.7, 129.6, 128.7, 128.6, 128.3, 128.1, 128.0, 127.9, 127.3, 127.2, 127.1, 119.6, 117.5, 114.9, 111.6, 109.3, 97.9, 96.7, 96.3, 85.1, 80.8, 77.4, 77.16, 76.9, 74.5, 72.3, 71.0, 70.9, 70.8, 67.3, 60.3, 41.7, 29.8, 29.0, 27.6, 26.2, 26.0, 25.2, 25.0, 22.9, 22.4, 18.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{50}H_{69}N_4O_{17}$ 997.4658; Found 997.4652.

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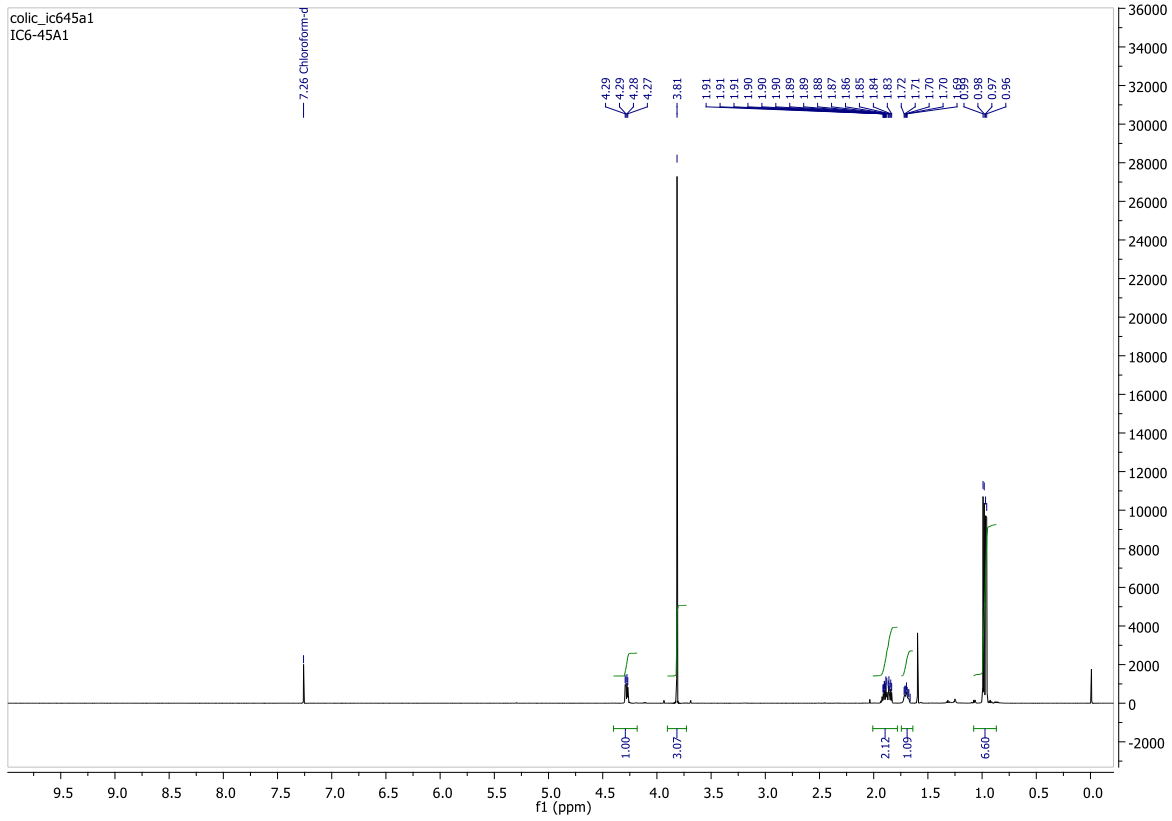
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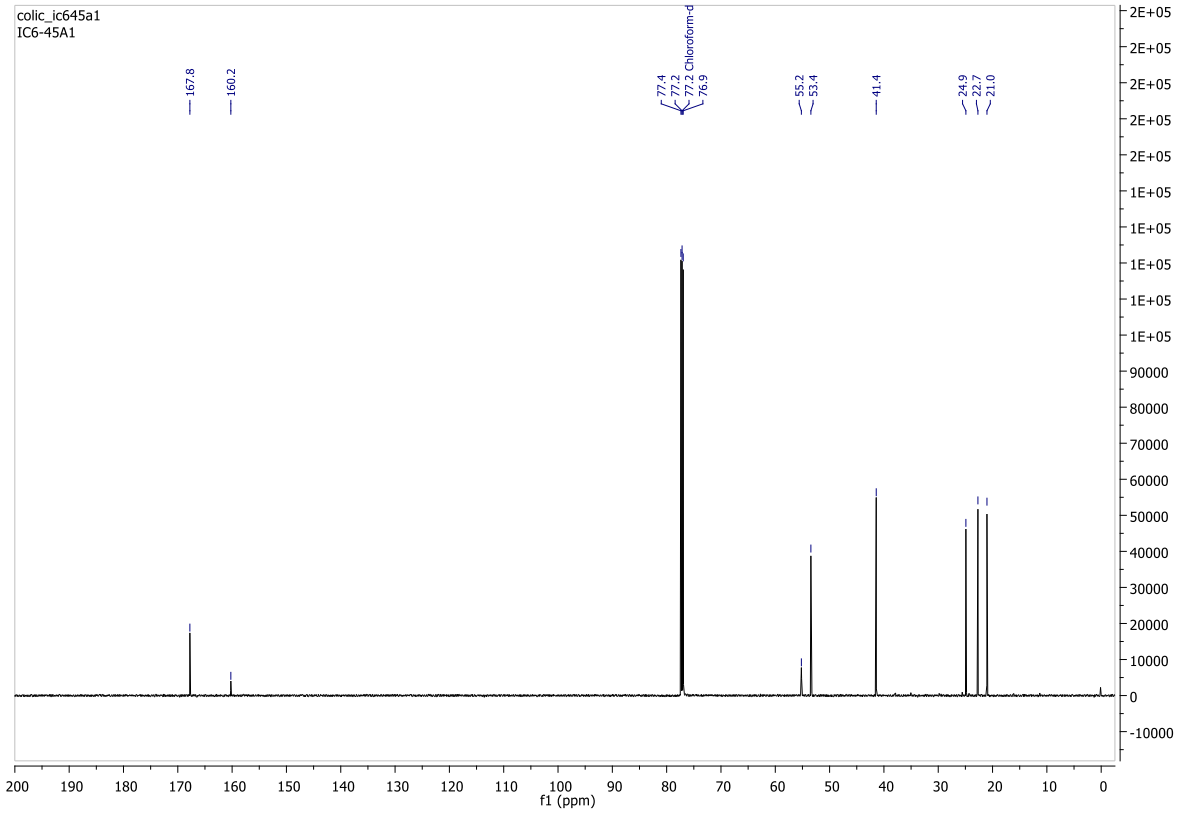
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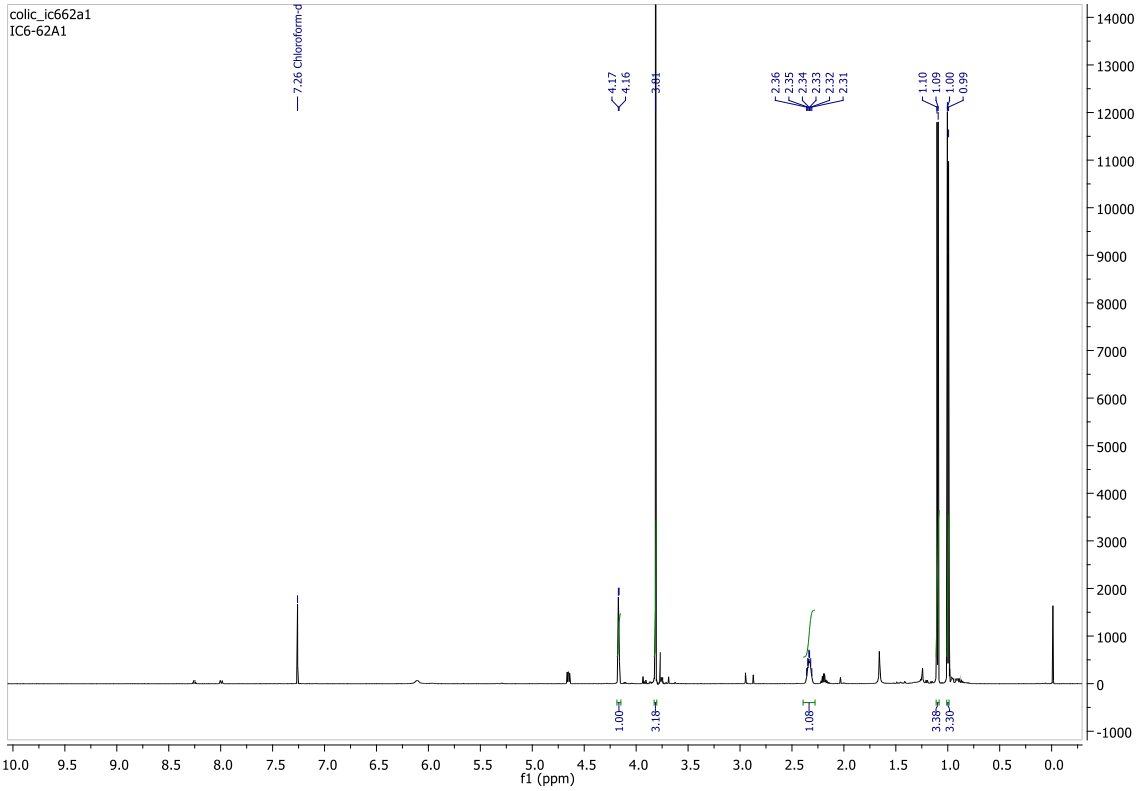
CN-L-Val-OMe (b)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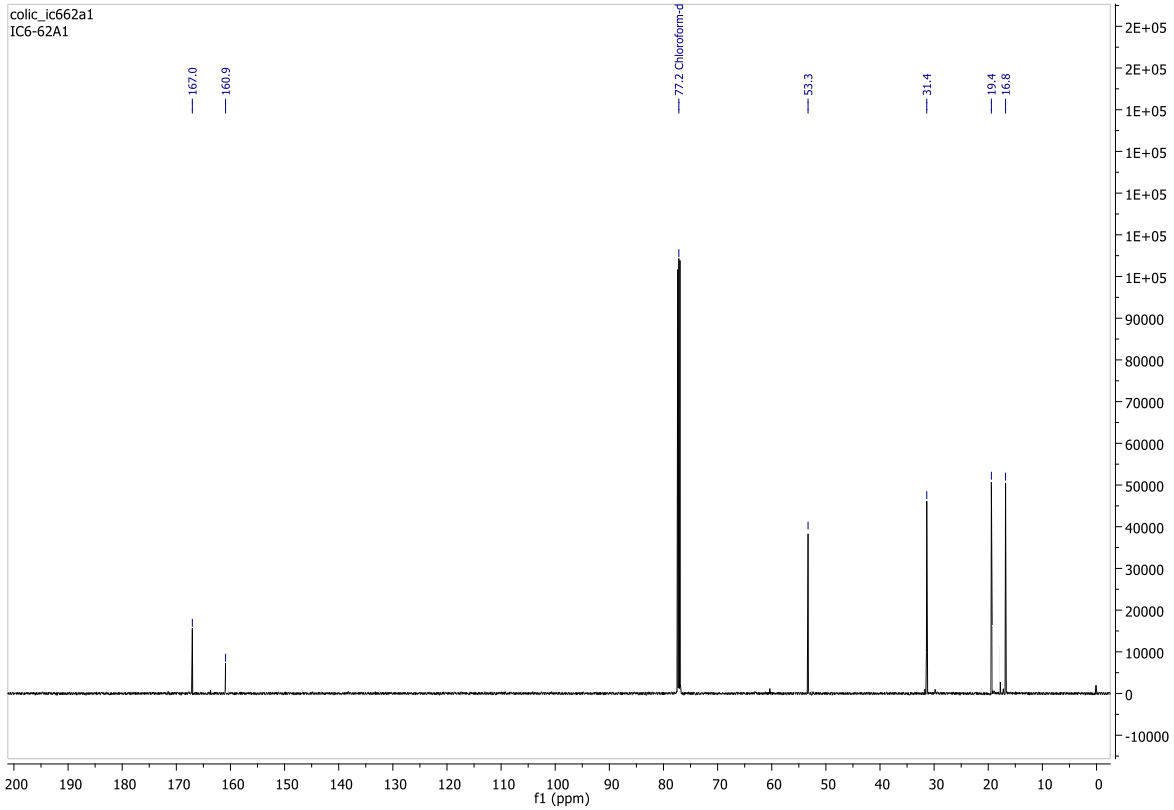
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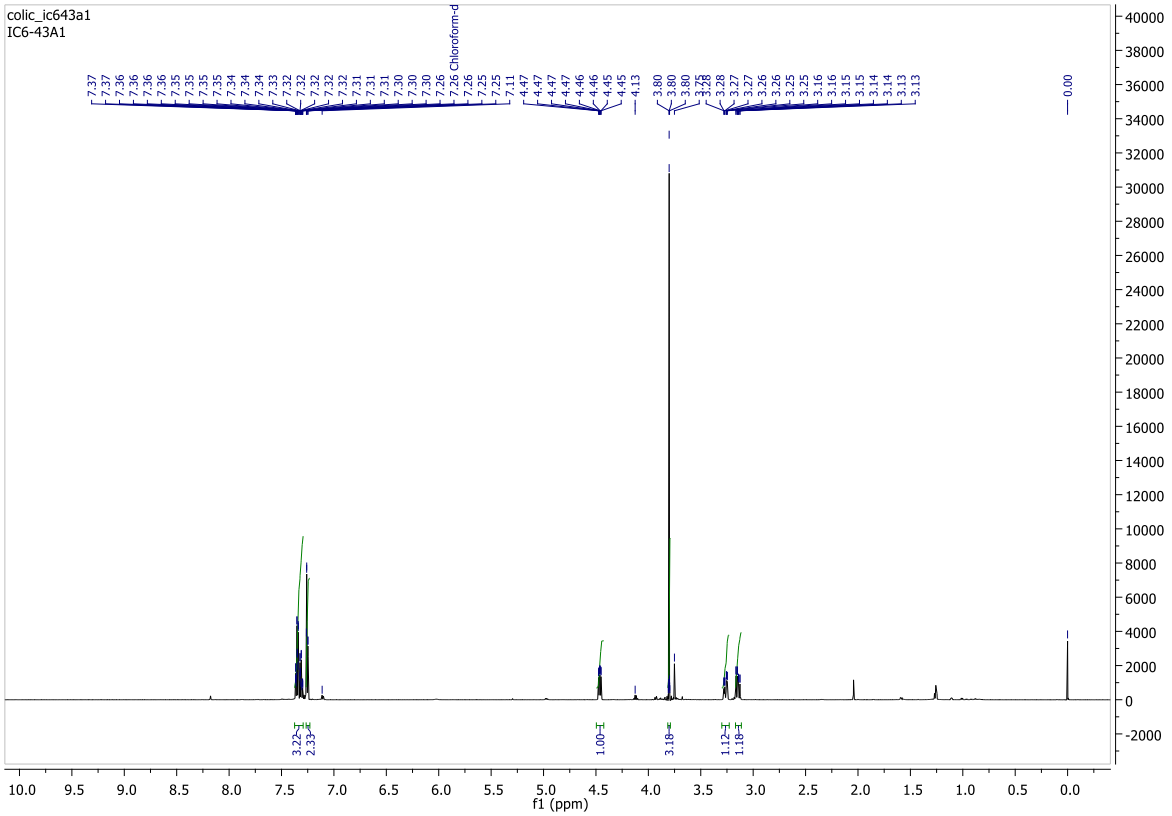
CN-L-Phe-OMe (c)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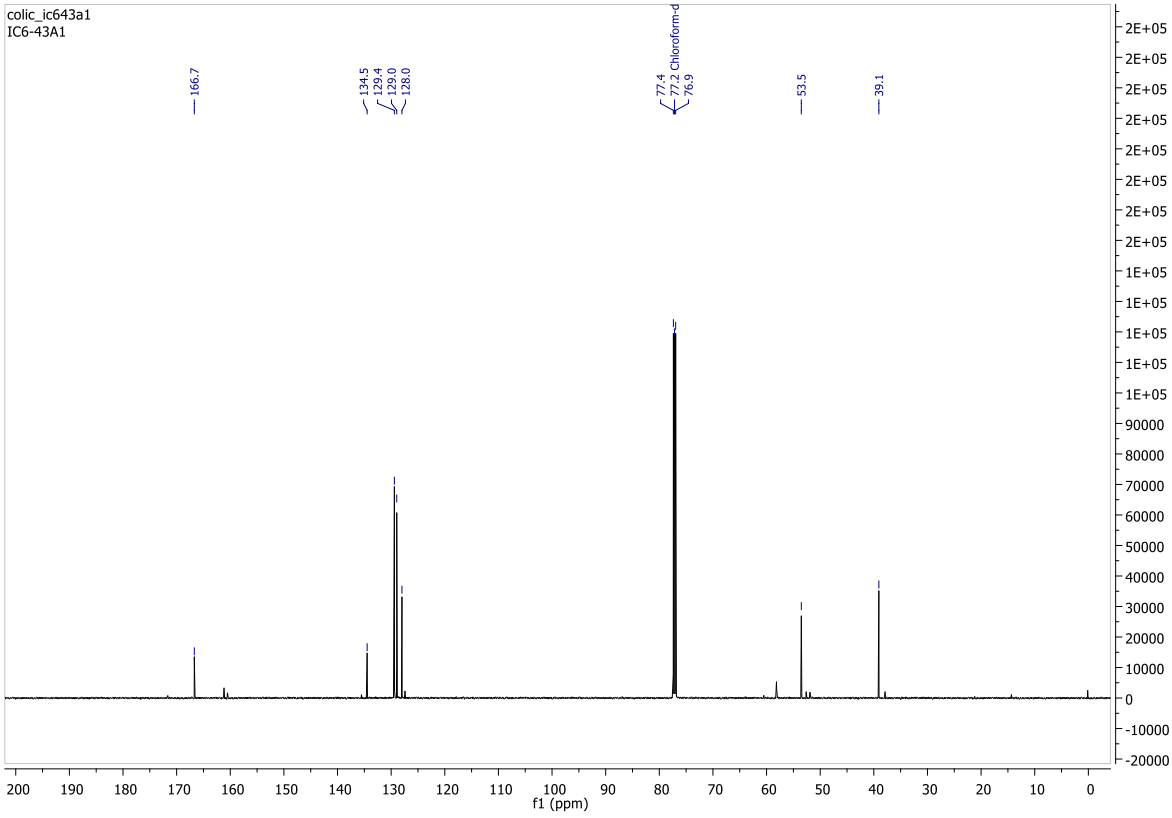
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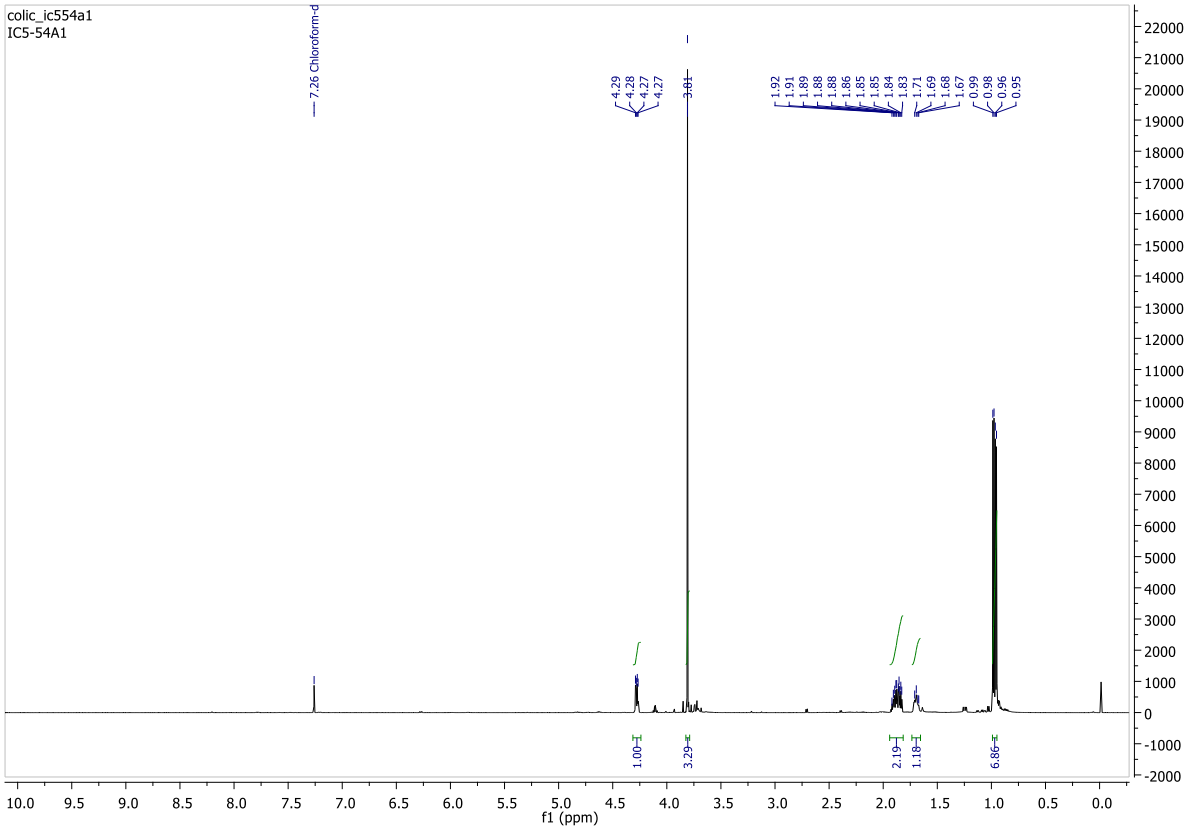
CN-D-Leu-OMe (d)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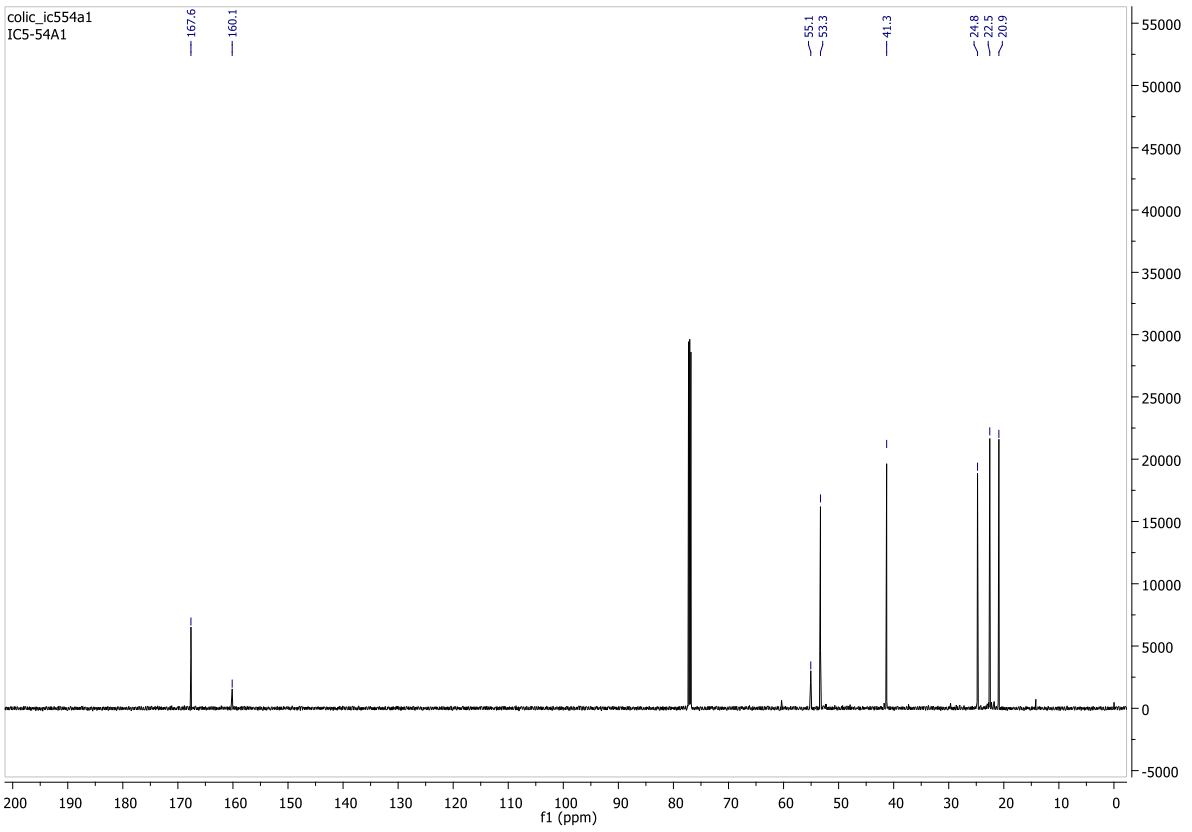
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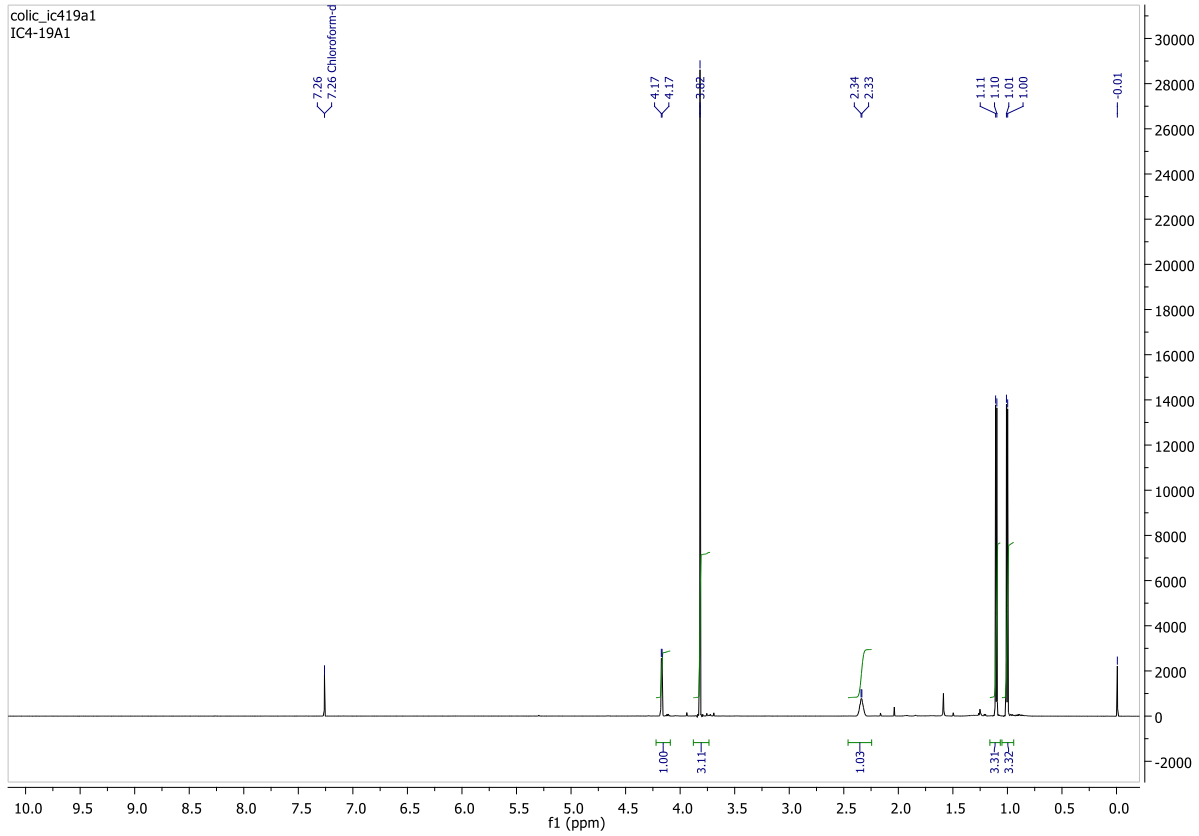
CN-D-Val-OMe (f)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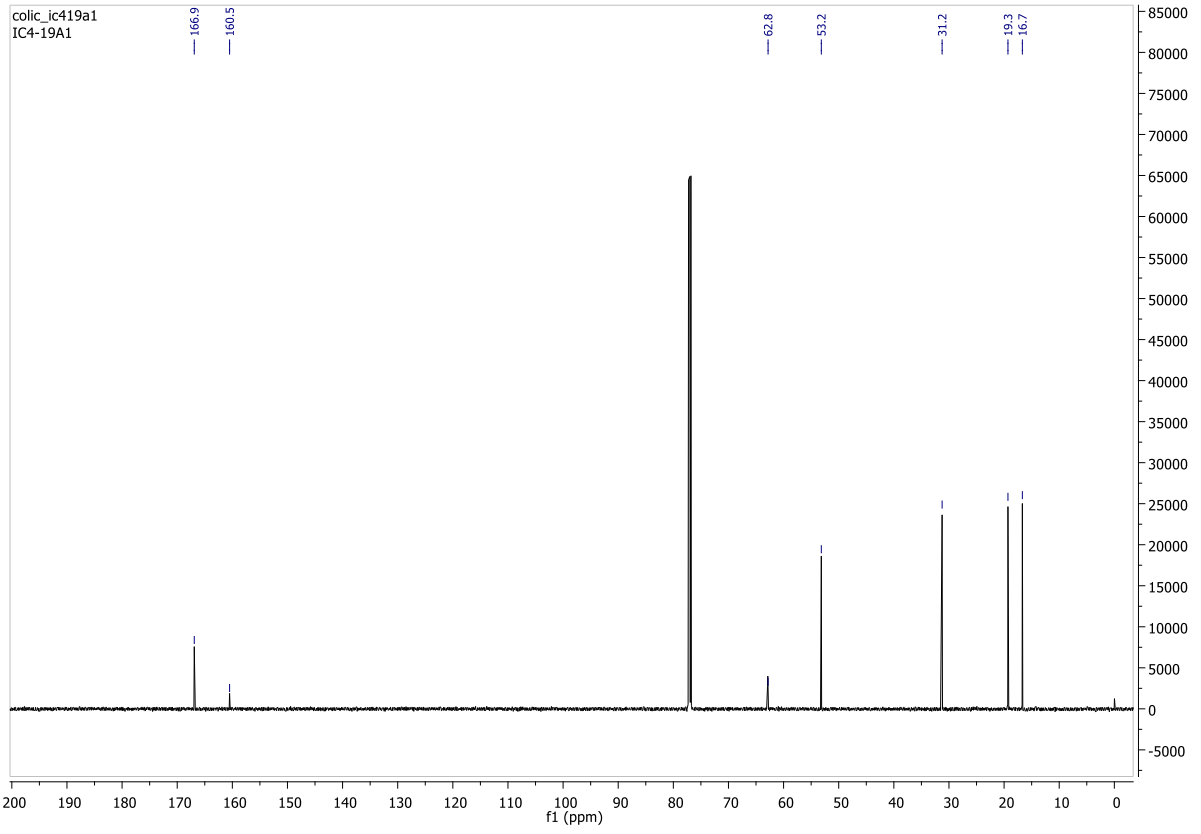
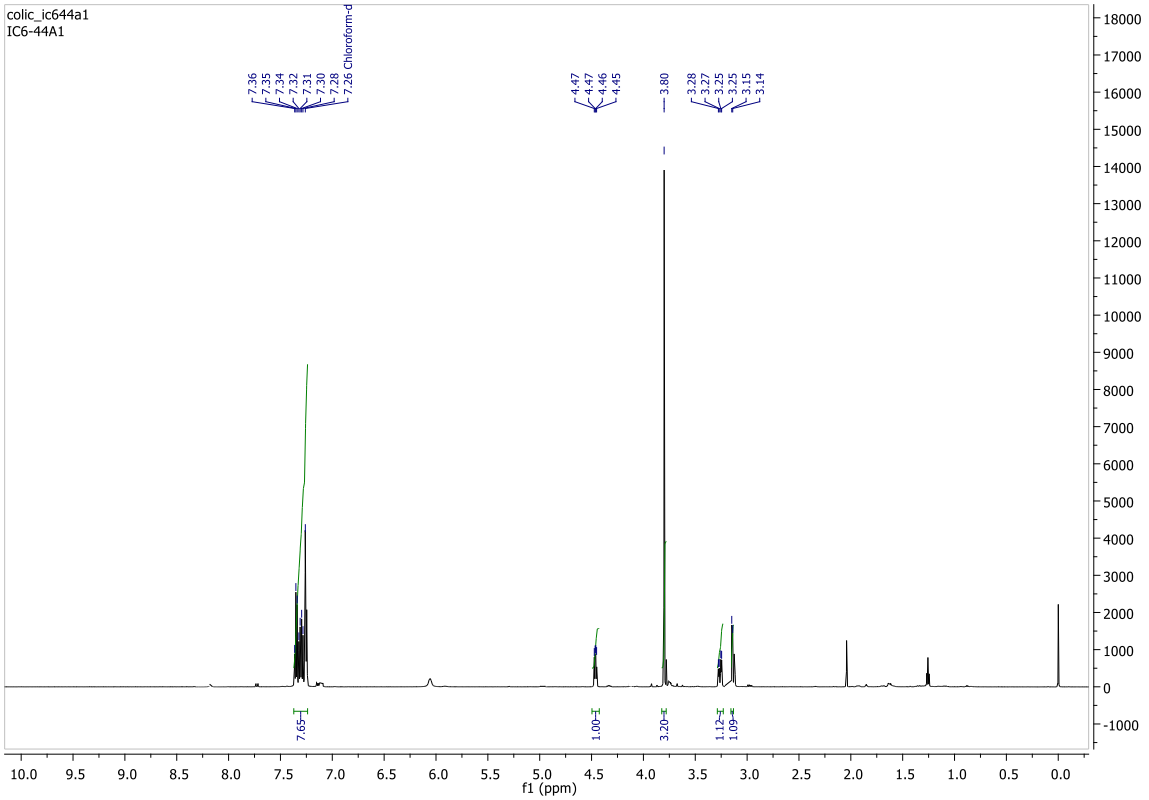
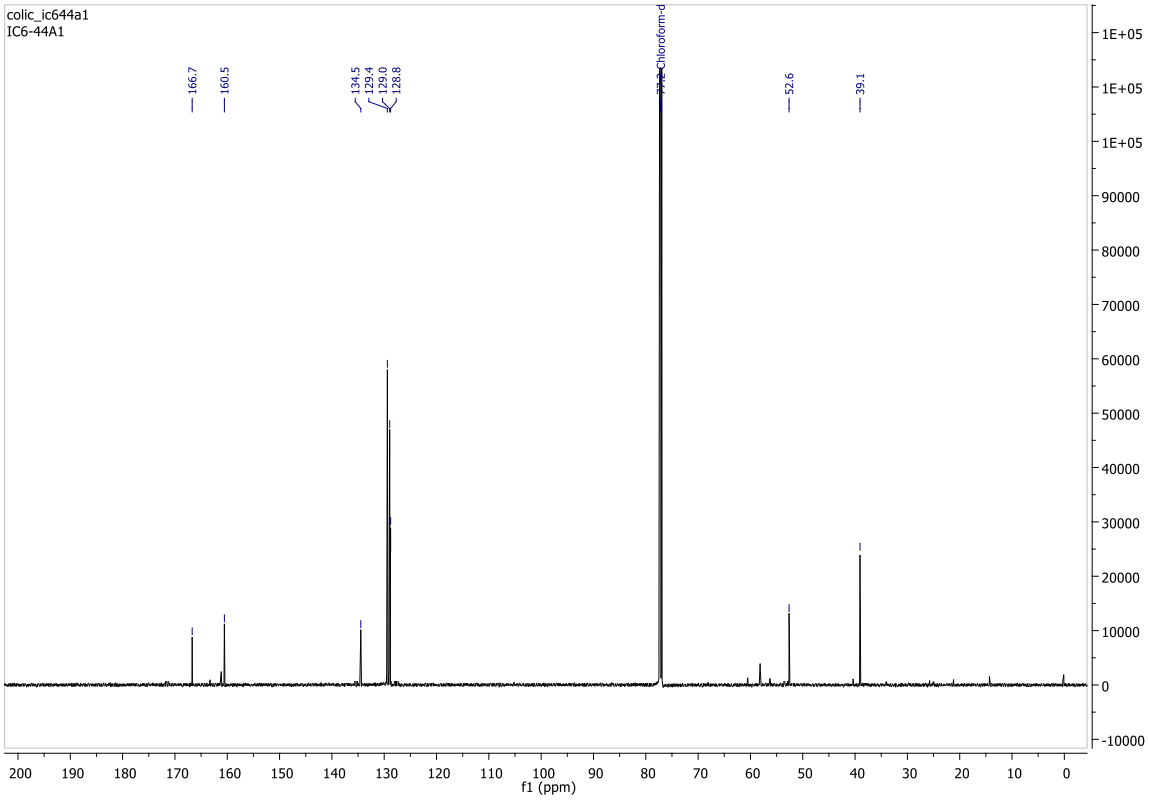
4.17
4.17
3.82
2.34
2.33
1.11
1.10
1.01
1.00
-0.01
1.00
3.11
1.03
3.31
3.32
f1 (ppm)

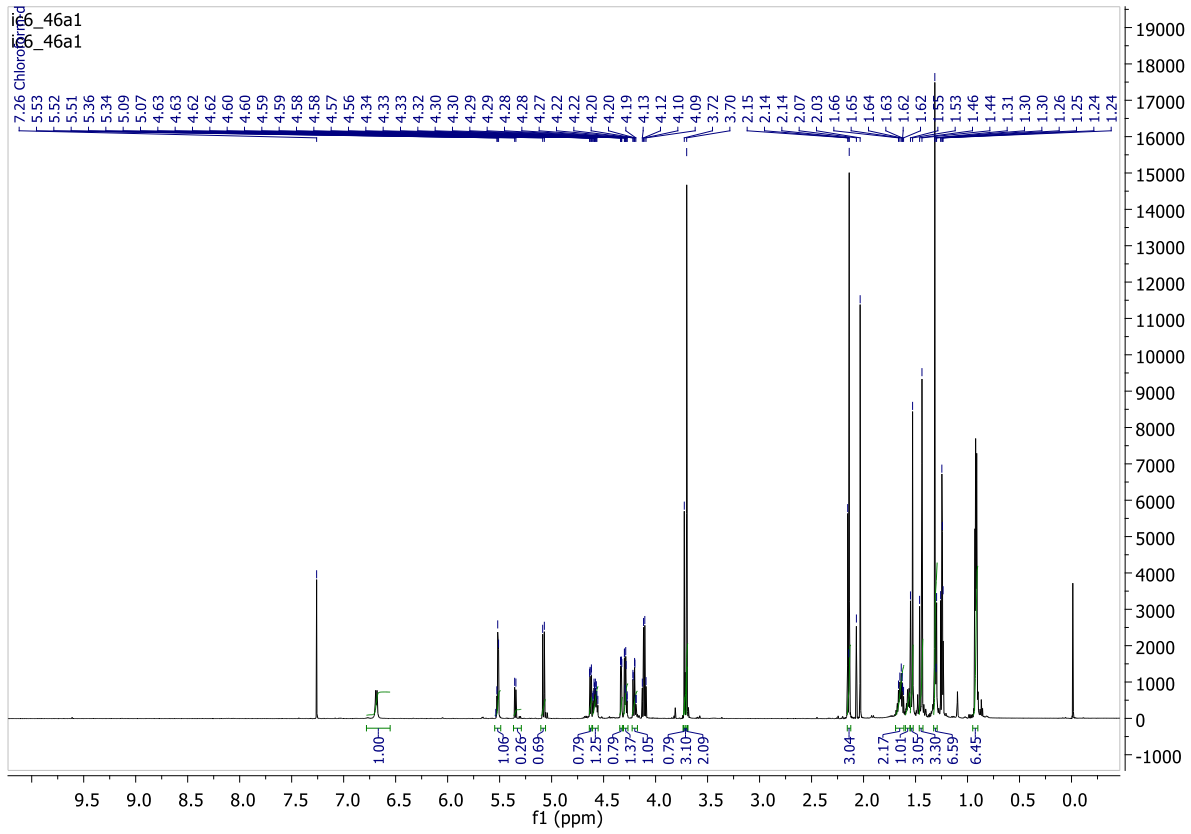

colic_ic419a1
IC4-19A1
166.9
160.5
62.8
53.2
31.2
19.3
16.7
f1 (ppm)

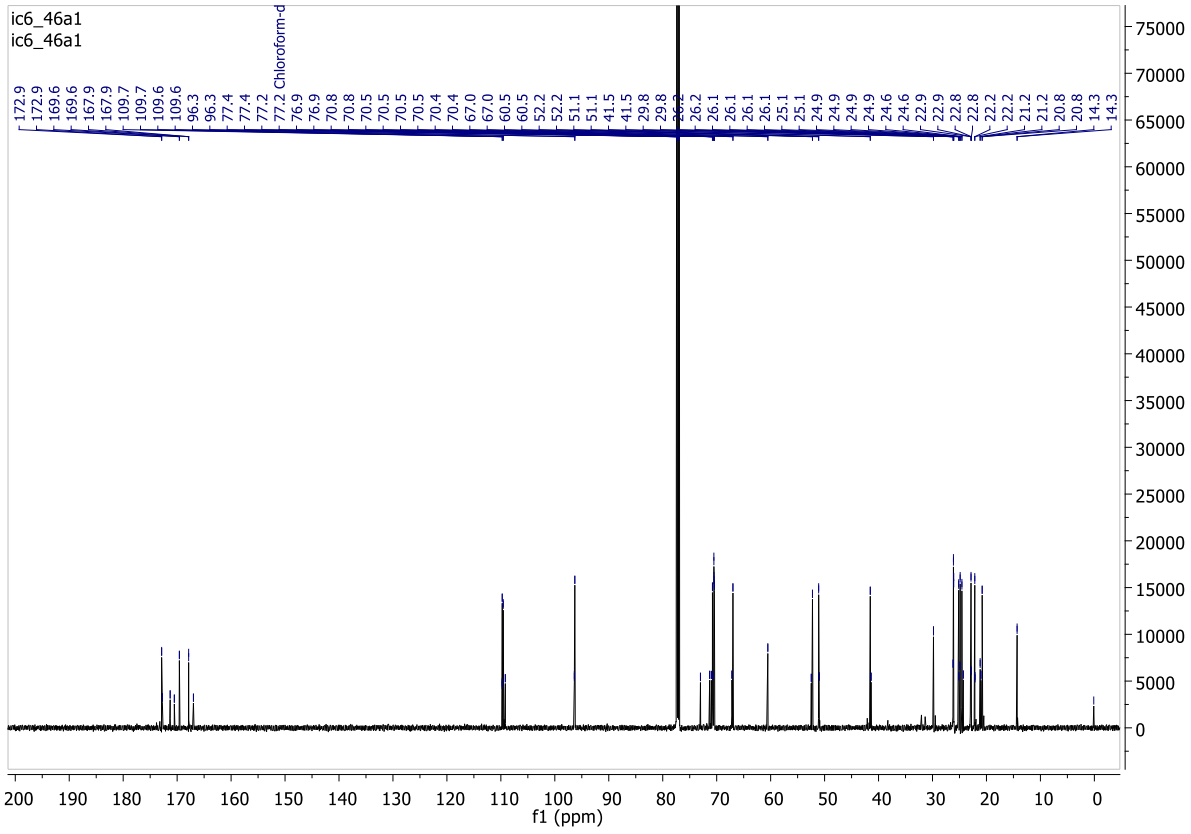
CN-D-Phe-OMe (g)


colic_ic644a1
IC6-44A1
7.36
7.35
7.34
7.32
7.31
7.30
7.28
7.26 Chloroform-d
4.47
4.47
4.46
4.45
3.80
3.28
3.27
3.25
3.25
3.15
3.14
7.65
1.00
3.20
1.12
1.09
f1 (ppm)

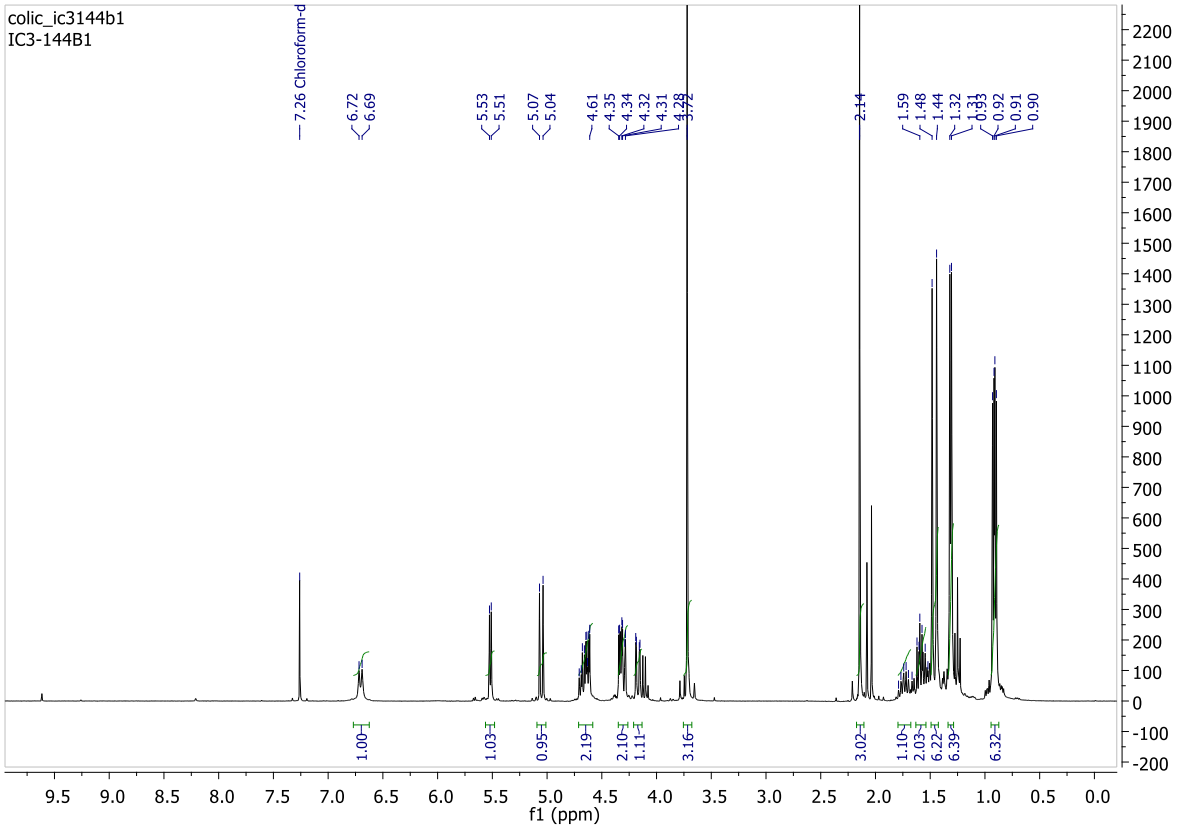

colic_ic644a1
IC6-44A1
166.7
160.5
134.5
129.4
129.0
128.8
77.2 Chloroform-d
52.6
39.1
f1 (ppm)

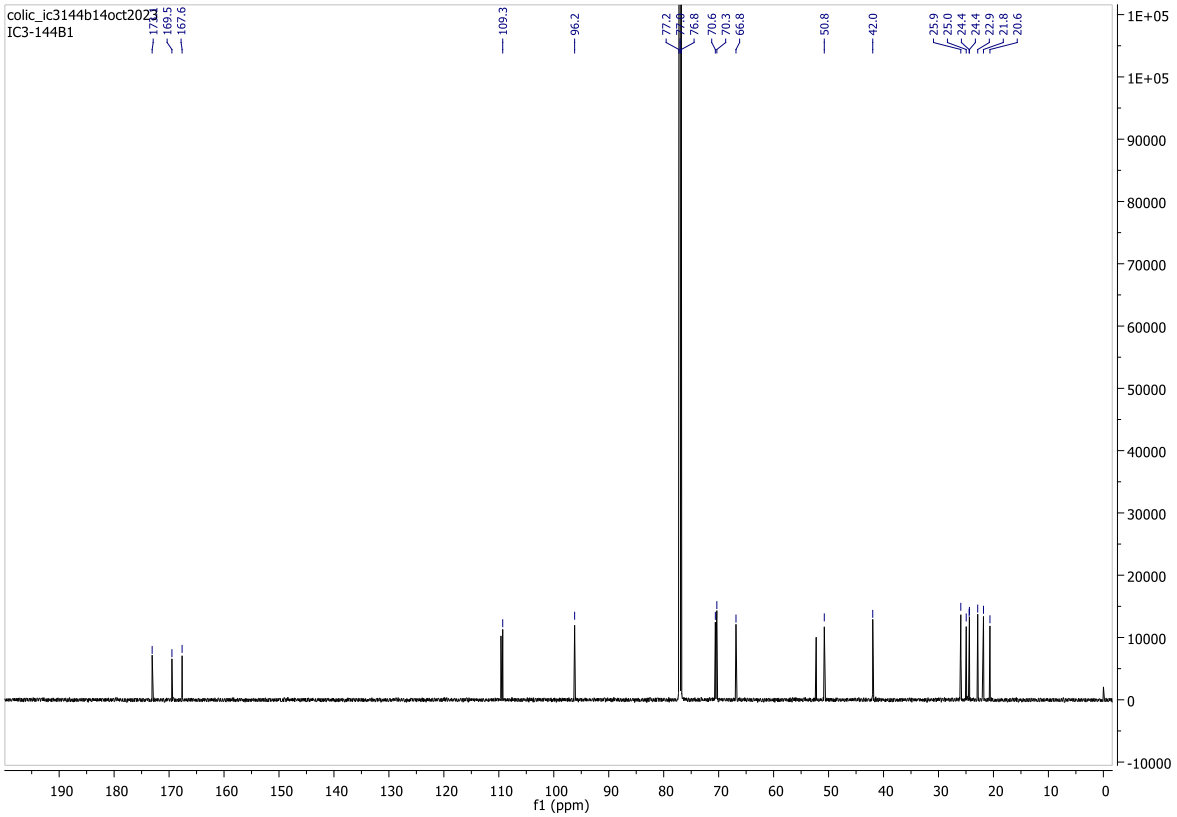
Compound Gal-1a (mixture of diastereoisomers, d.r. 75:25)



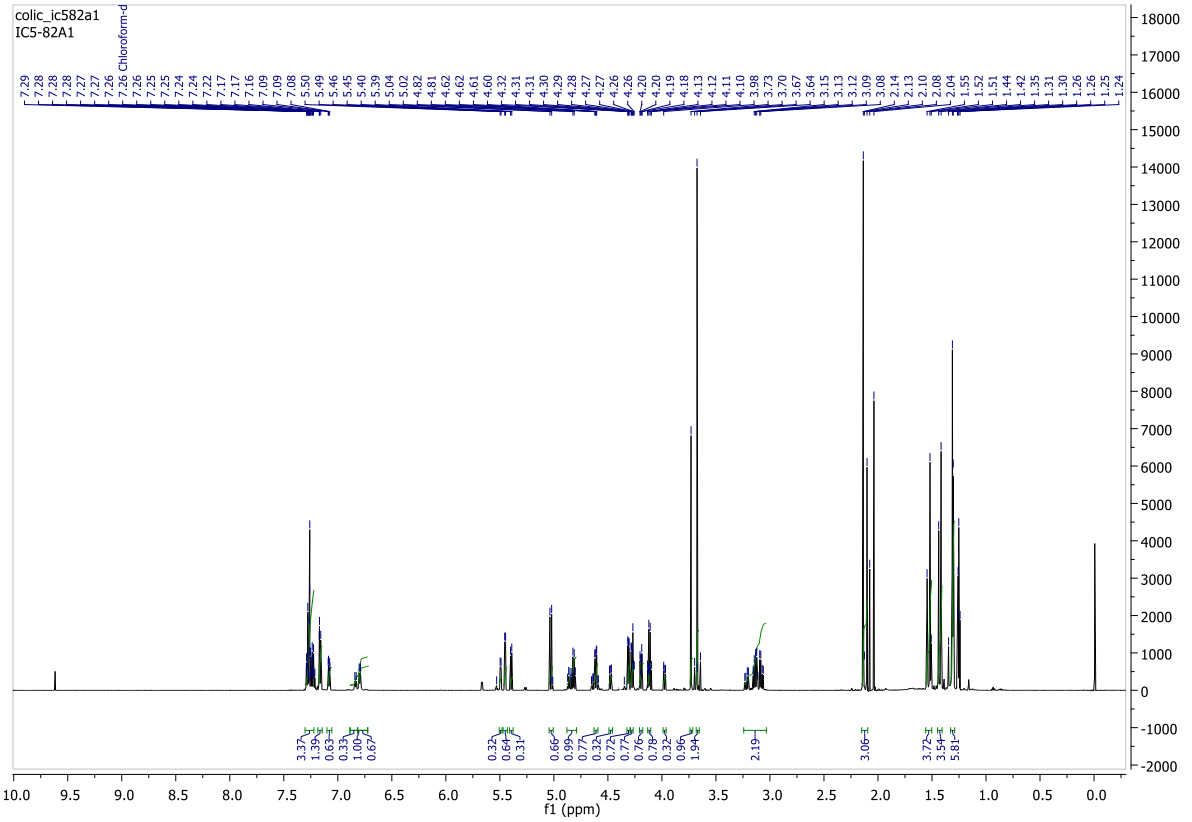


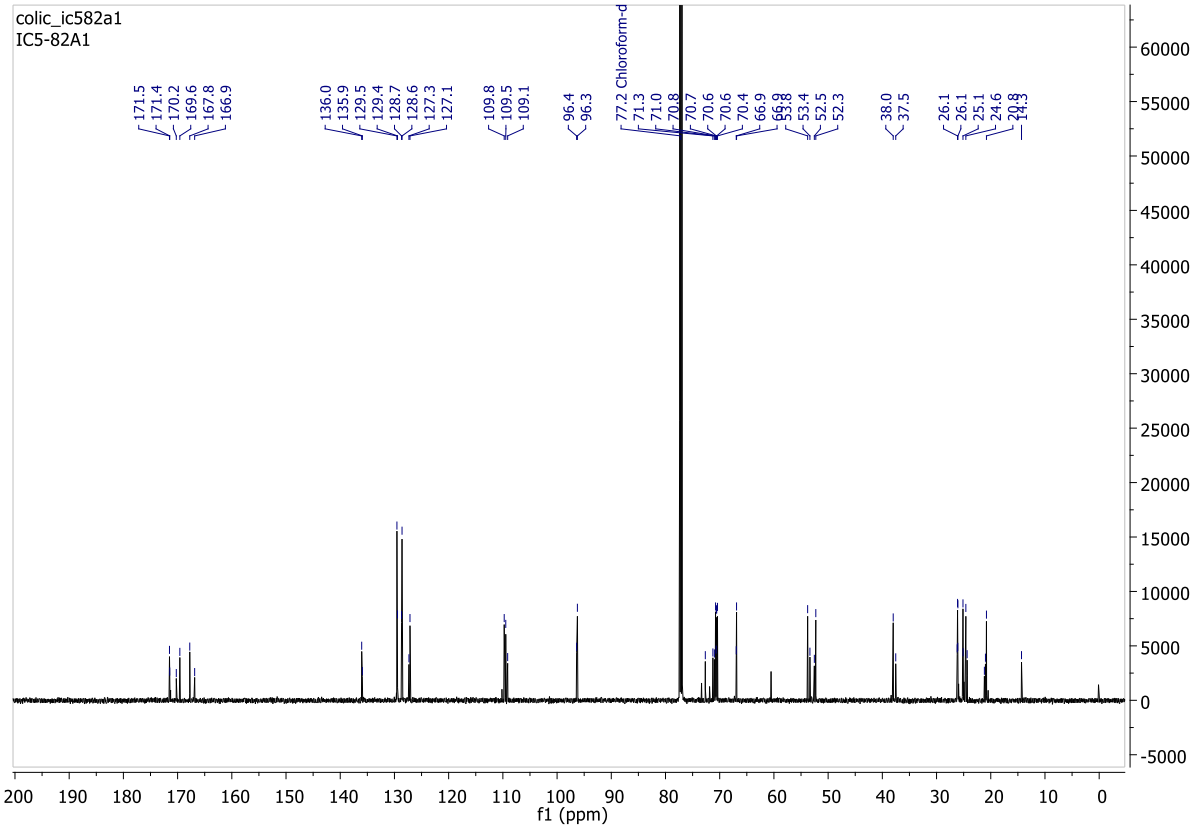
Compound Gal-1b (single diastereoisomer)



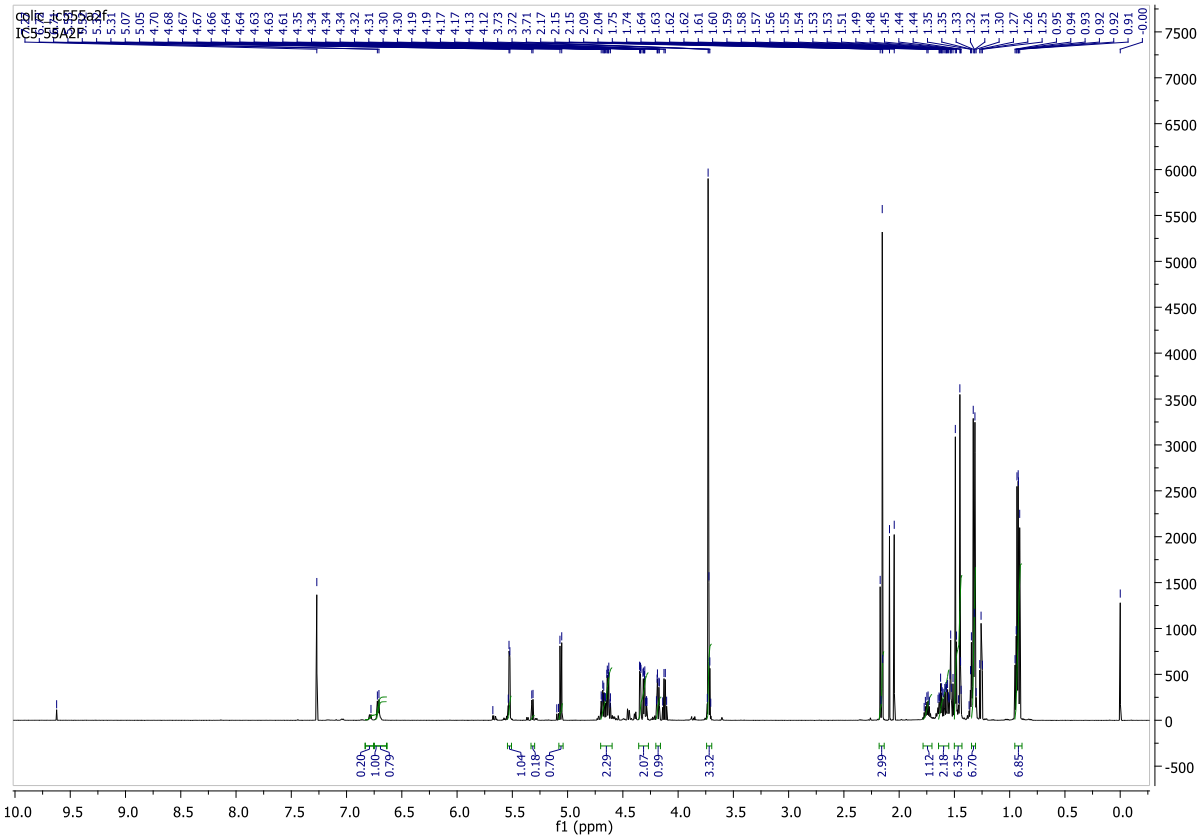


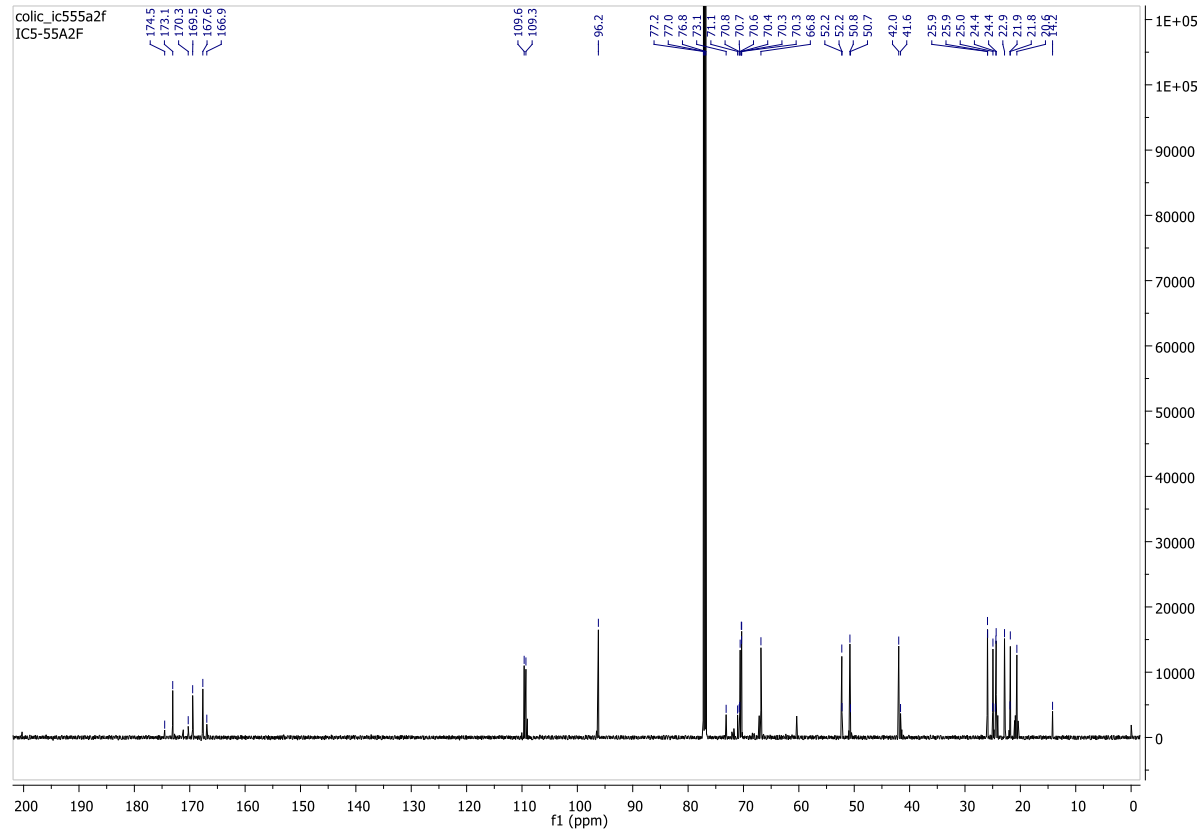
Compound Gal-1c (mixture of diastereoisomers, d.r. 70:30)



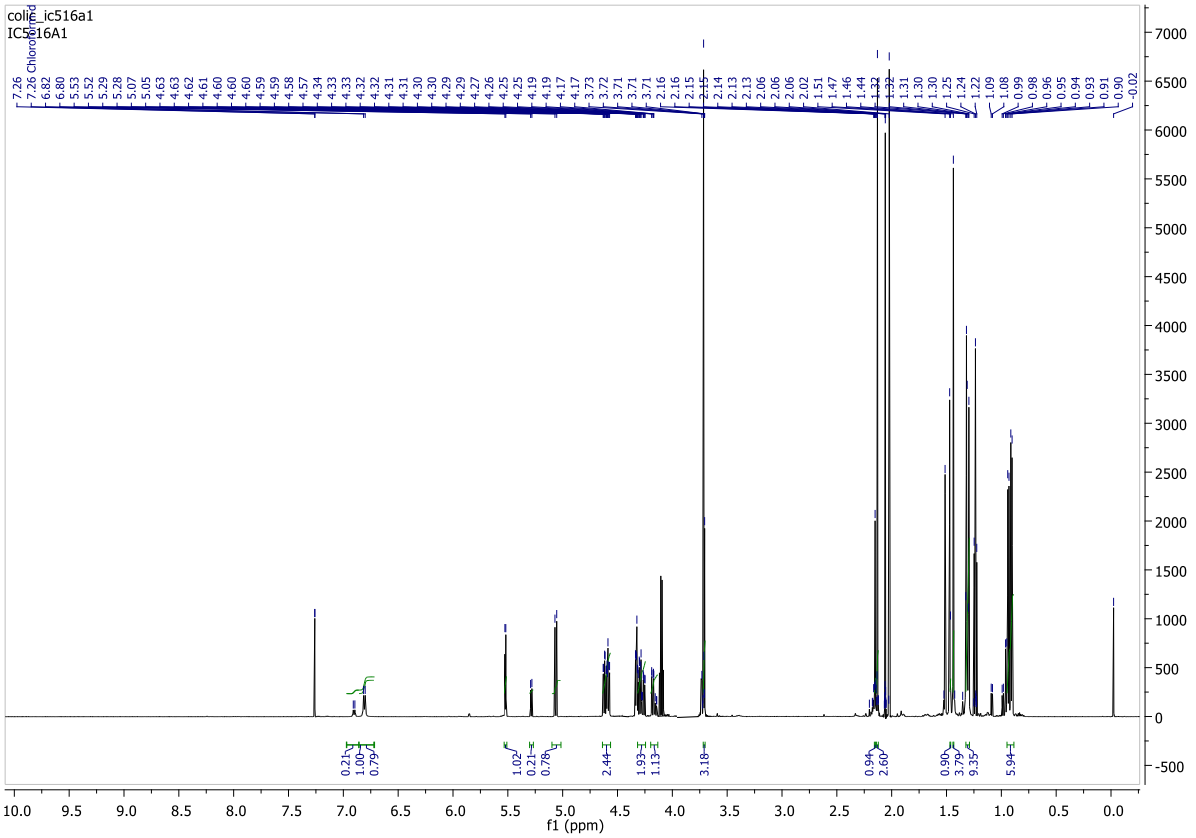


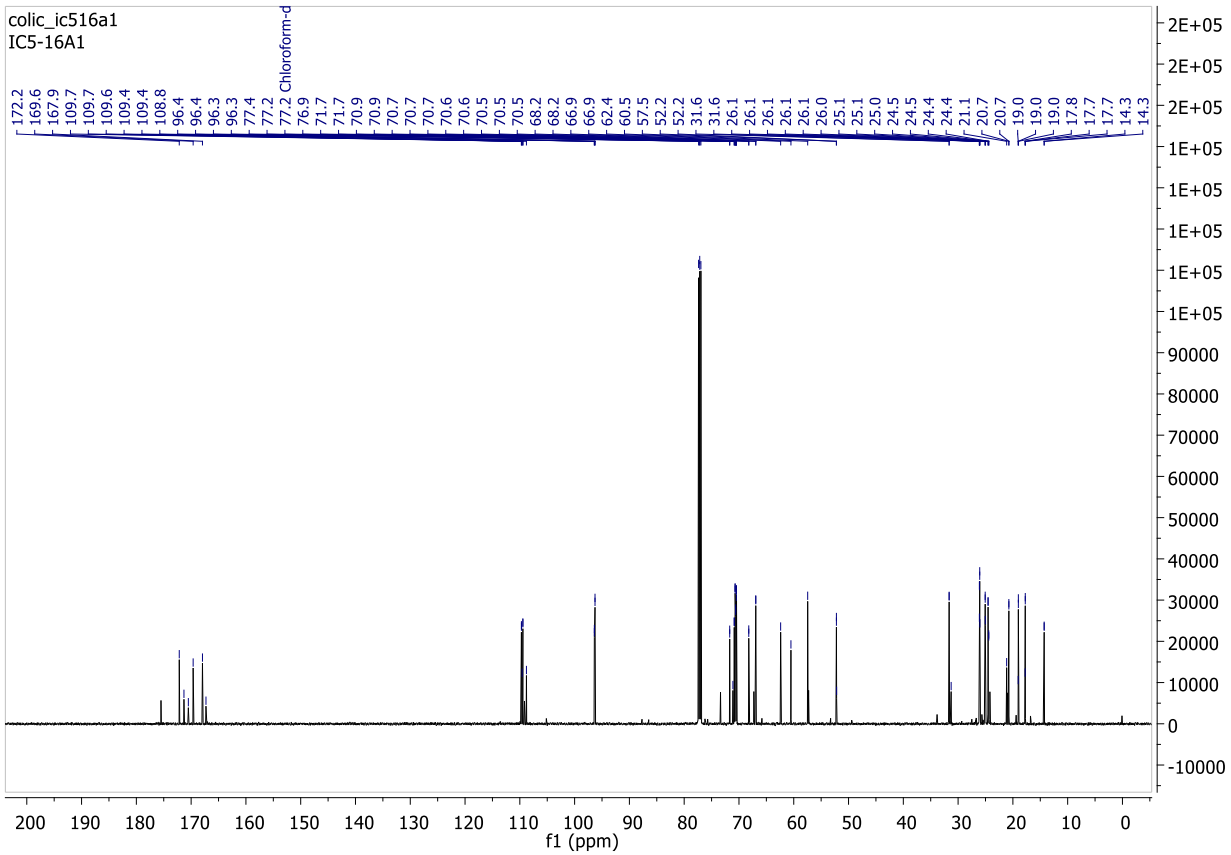
Compound Gal-1d (mixture od diastereoisomers, d.r. 80:20)



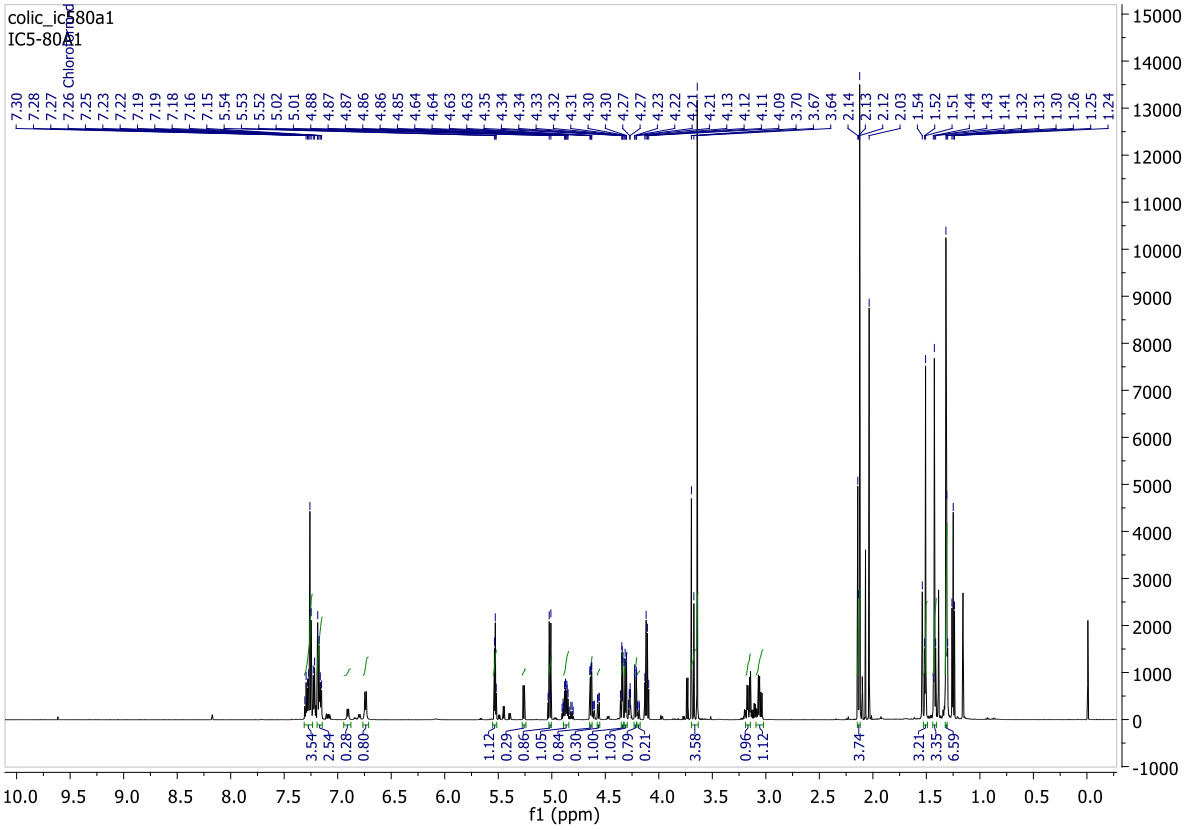


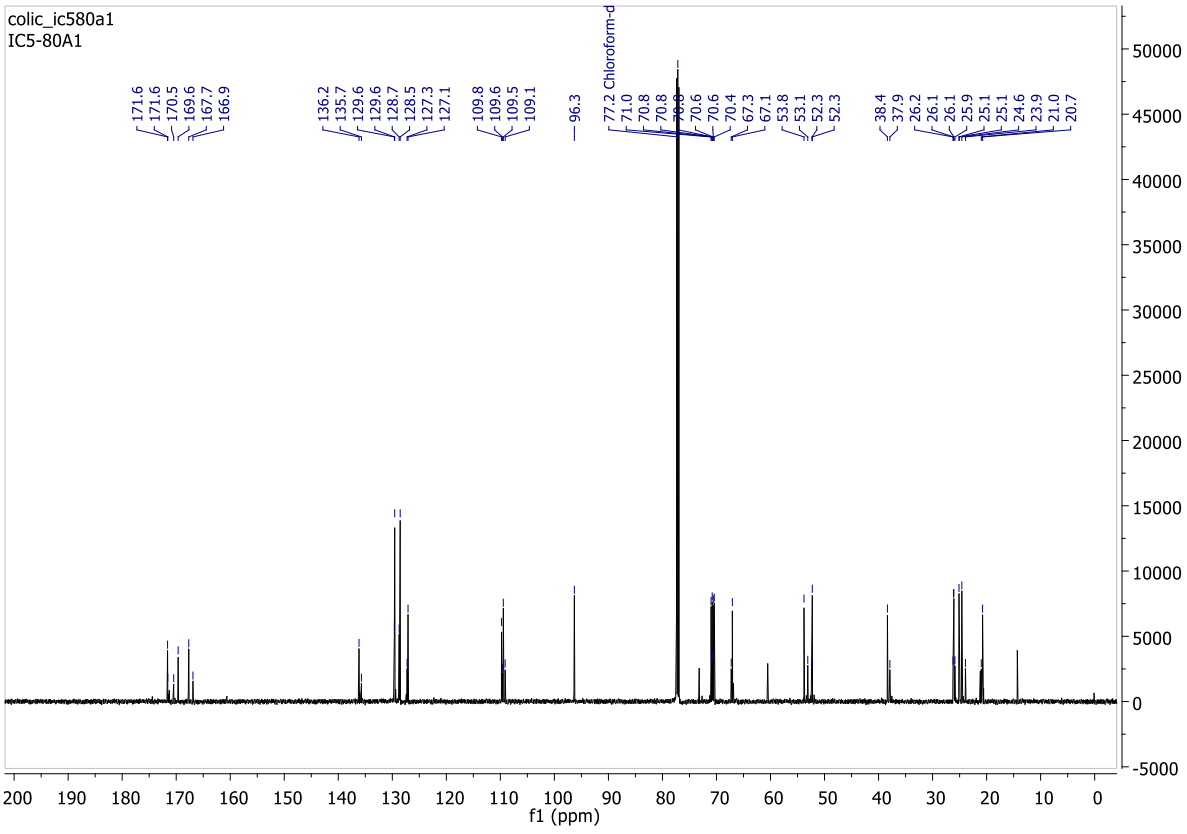
Compound Gal-1e (mixture of diastereoisomers, d.r. 80:20)



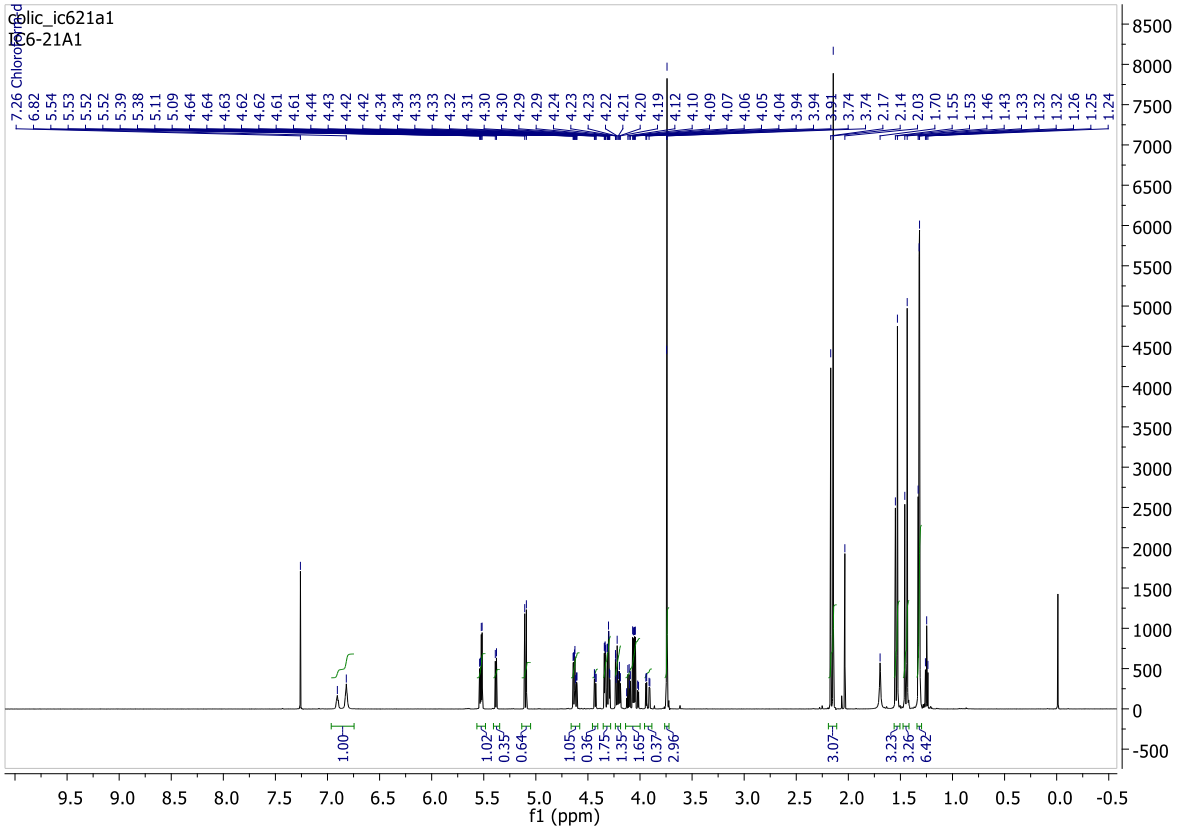


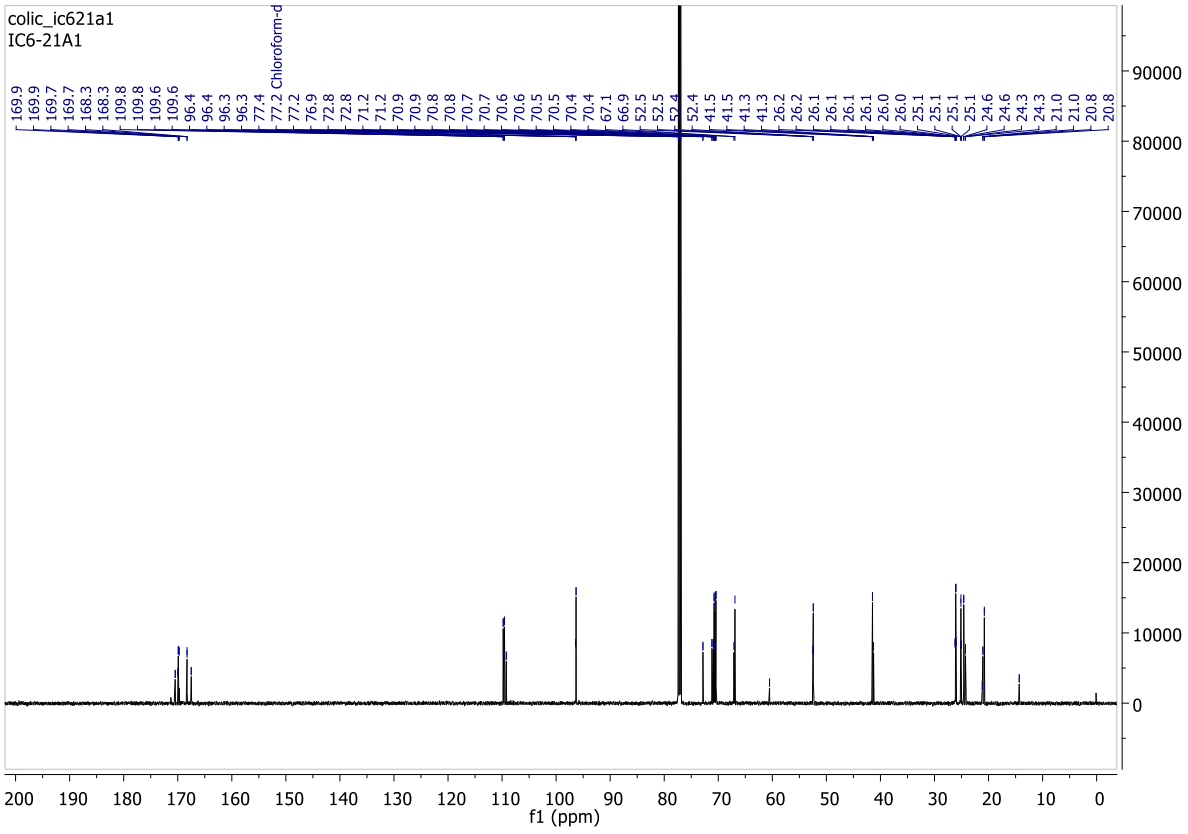
Compound Gal-1f (mixture of diastereoisomers, d.r. 80:20)



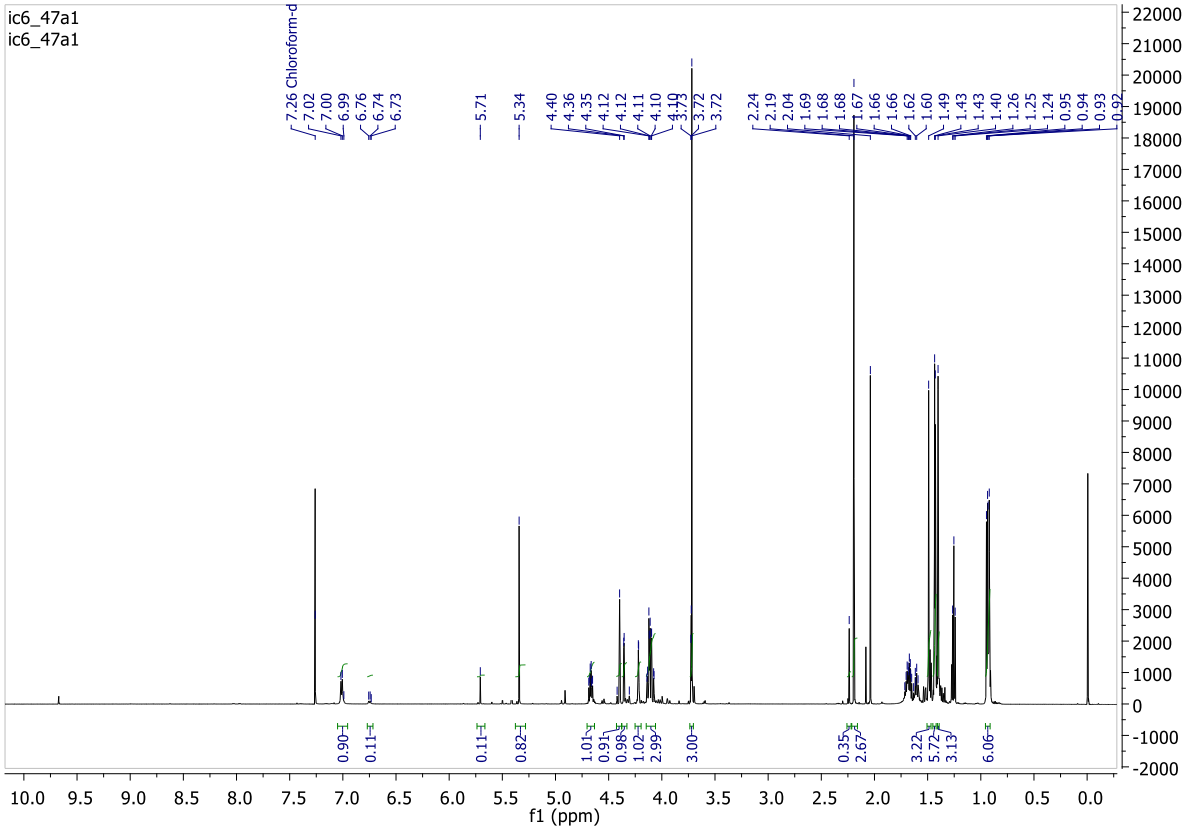


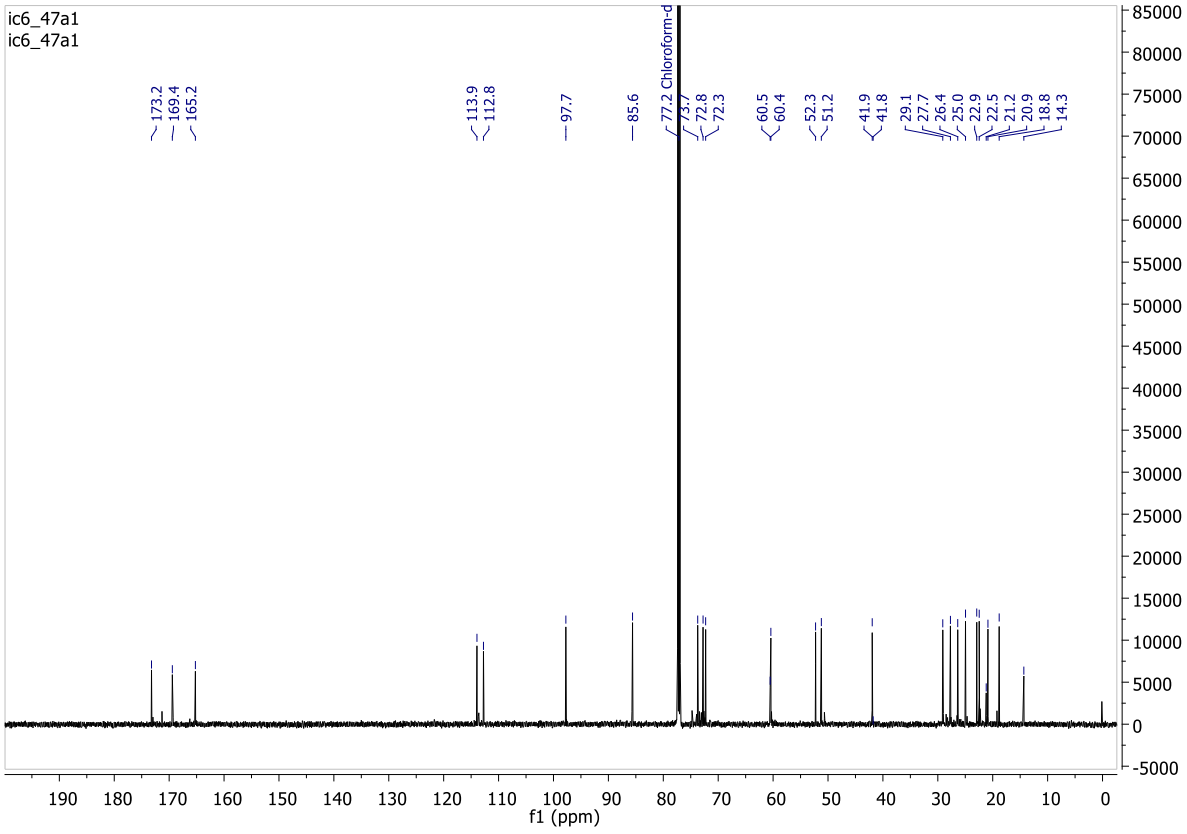
Compound Gal-1g (mixture of diastereoisomers, d.r. 65:35)



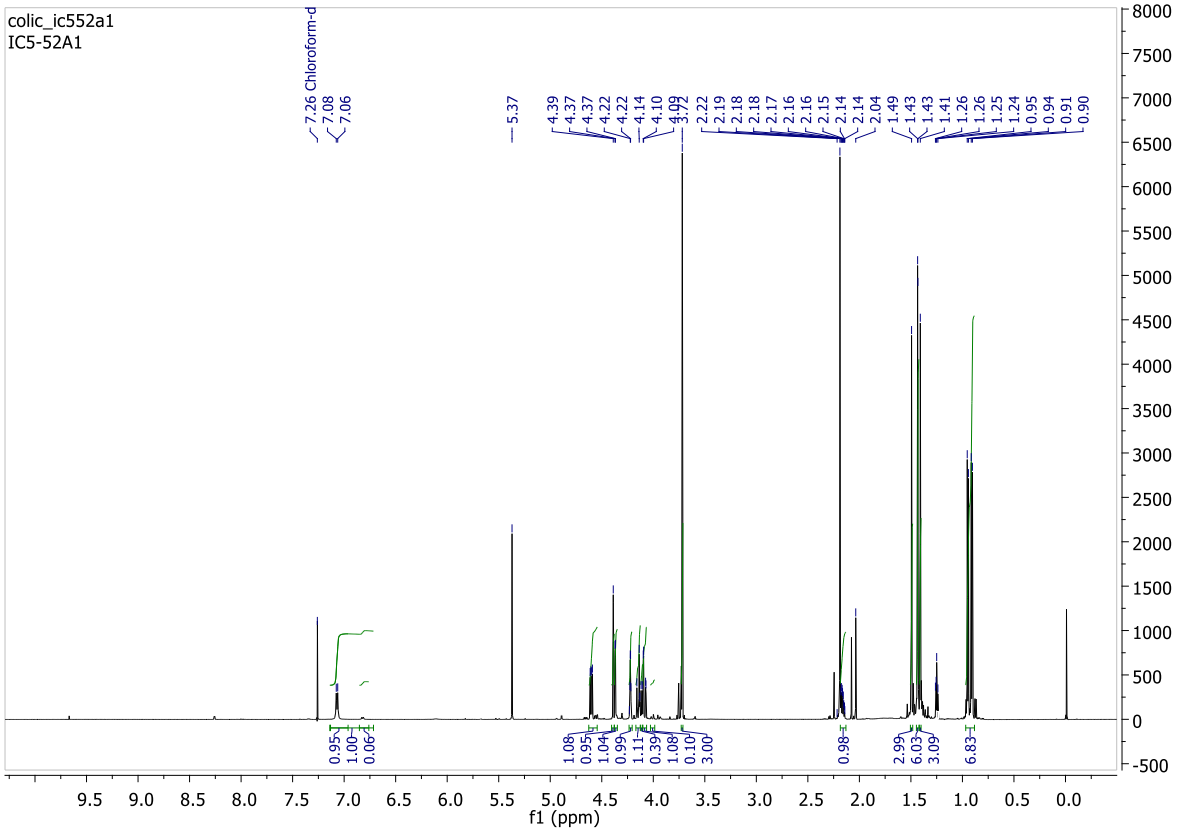


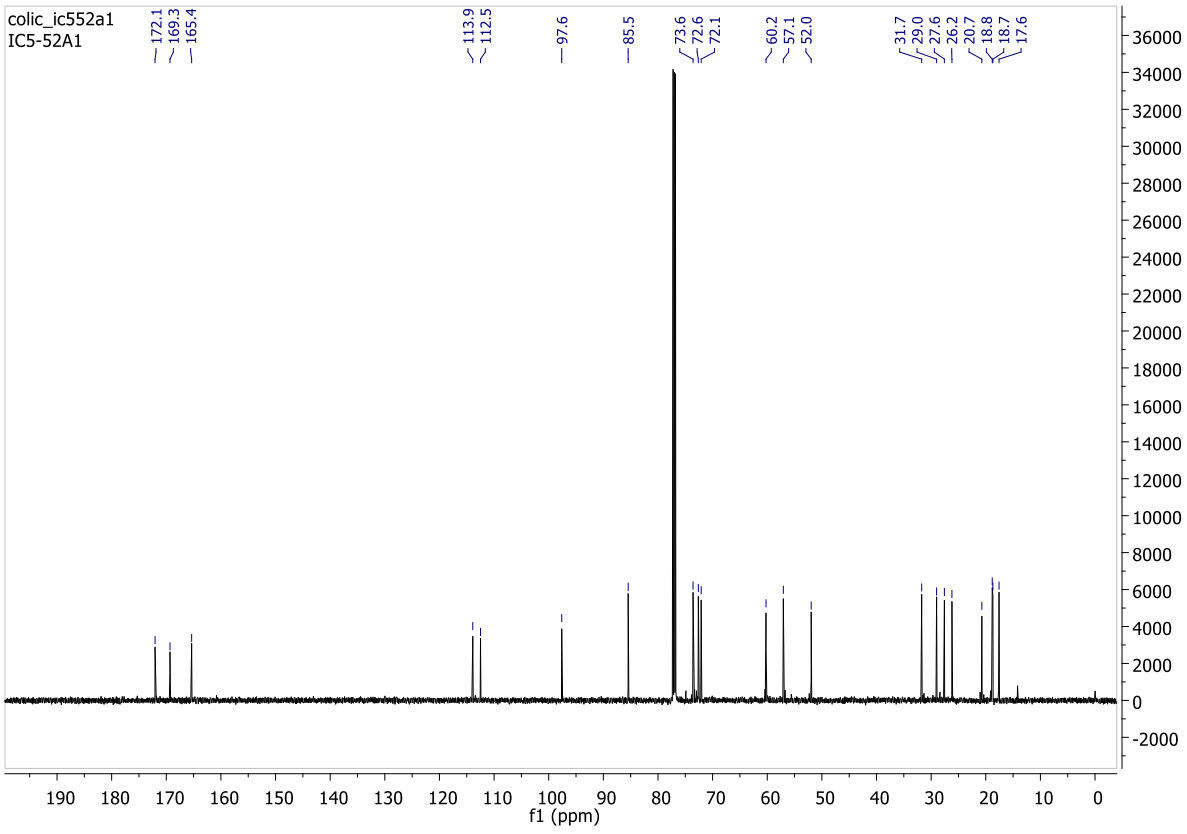
Compound Sor-1a (mixture of diastereoisomers, d.r. 90:10)



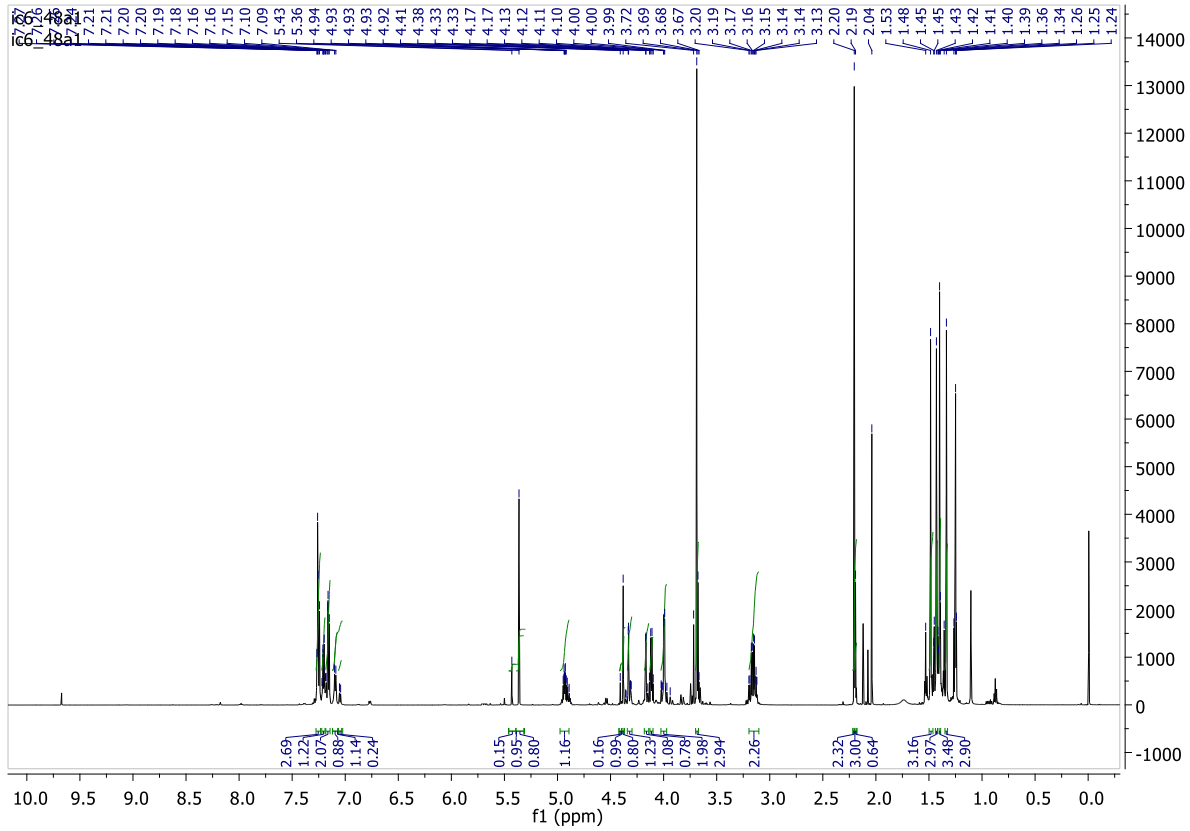


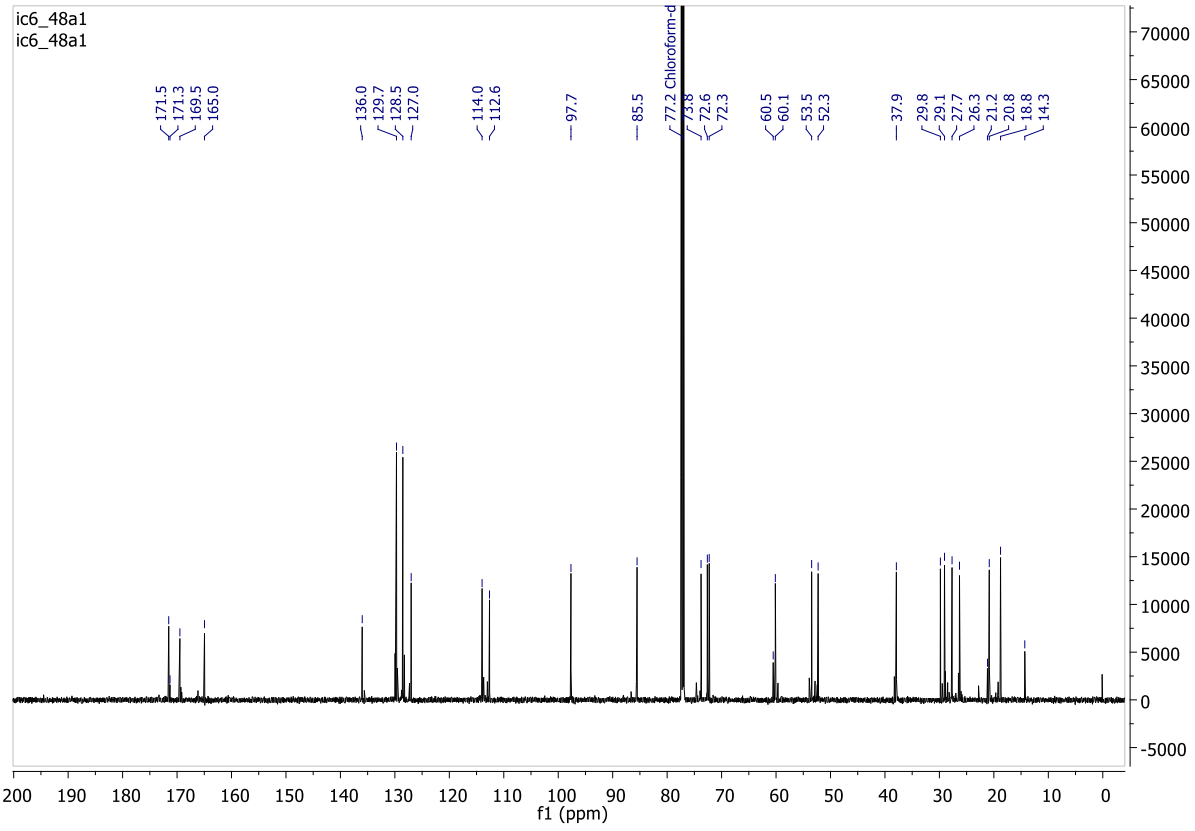
Compound Sor-1b (mixture of diastereoisomers, d.r. 95:5)



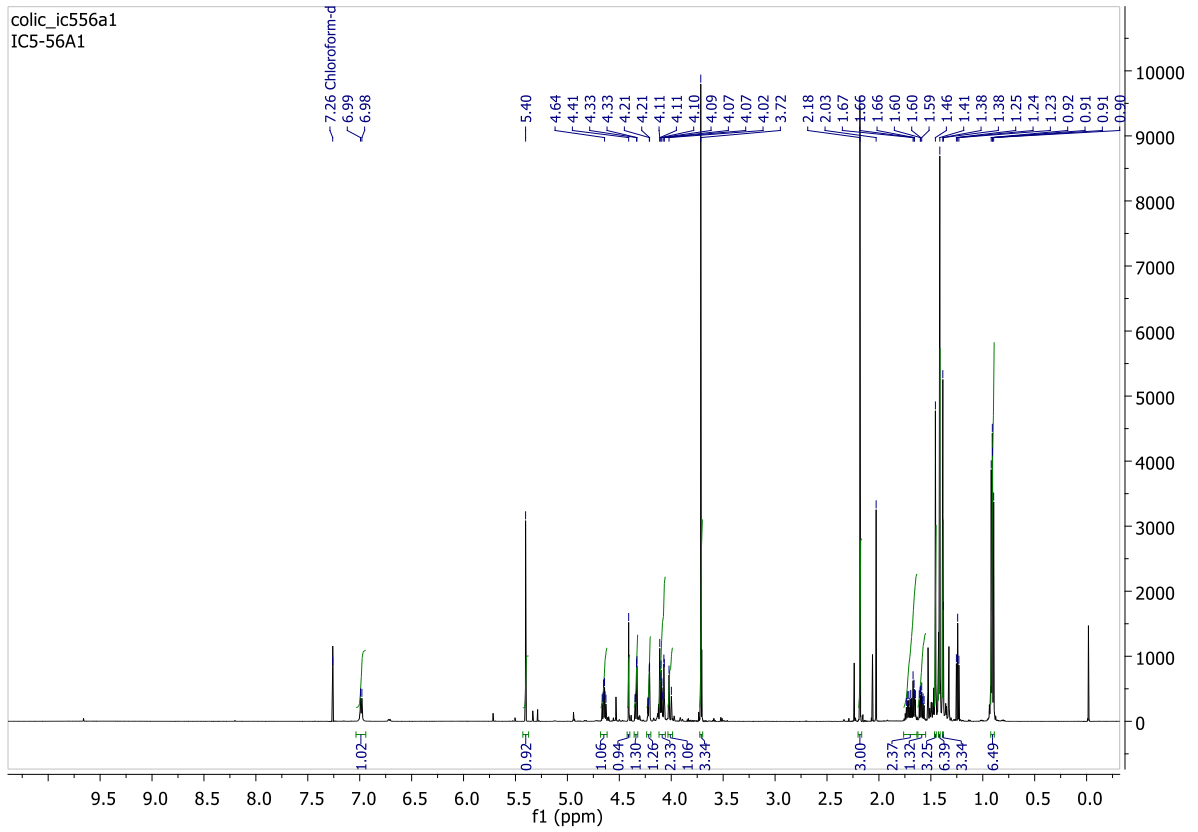


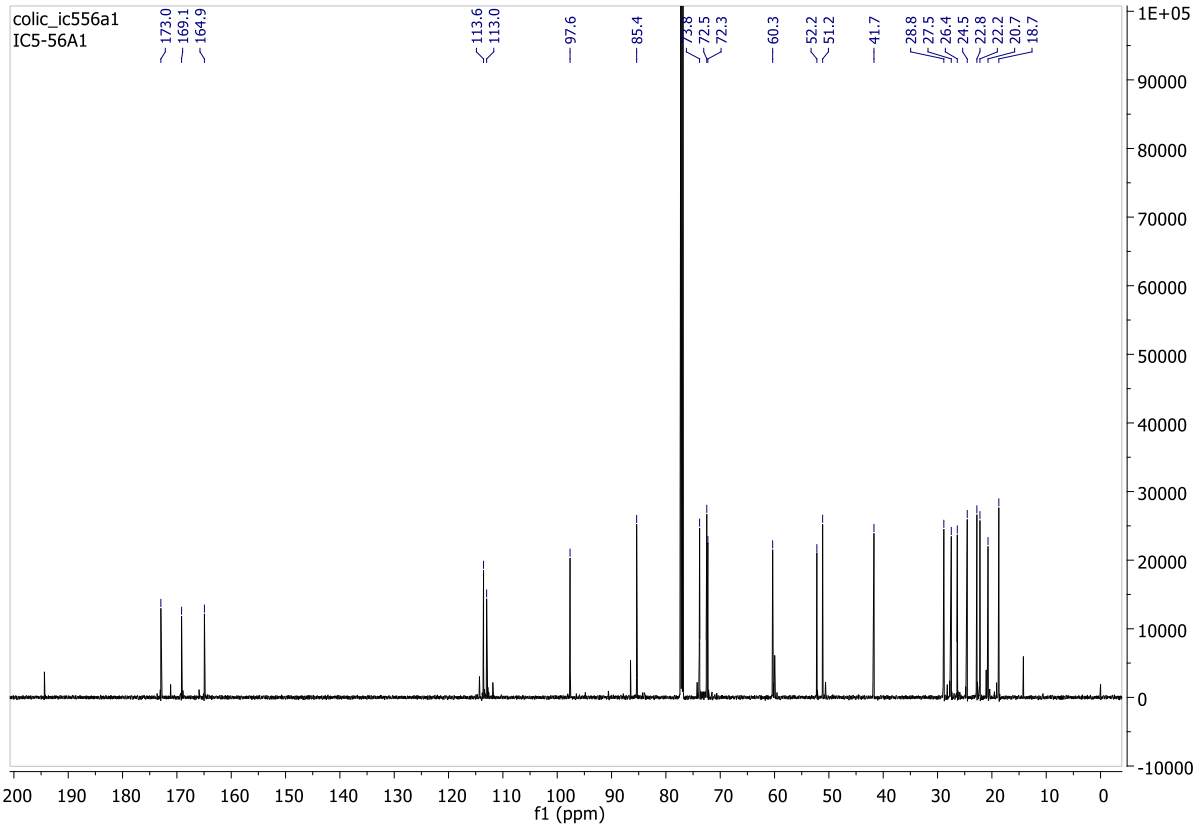
Compound Sor-1c (mixture of diastereoisomers, d.r. 85:15)



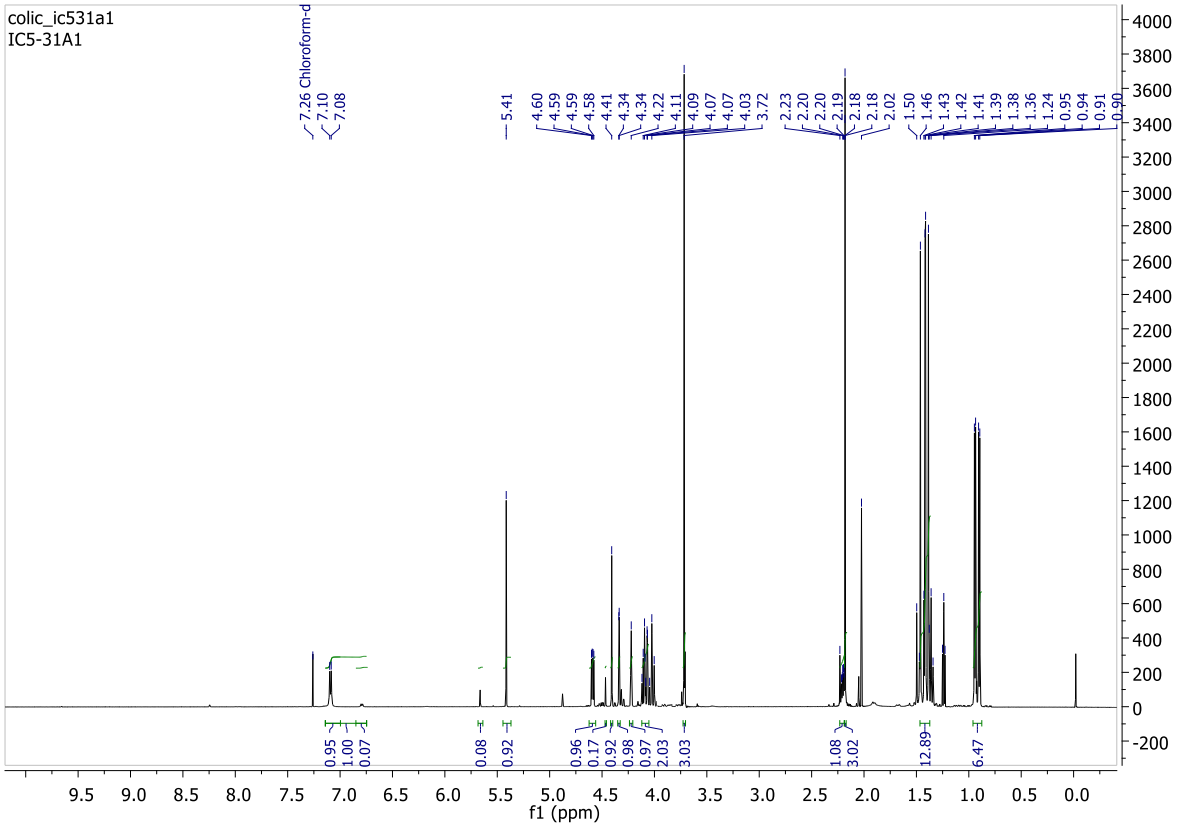


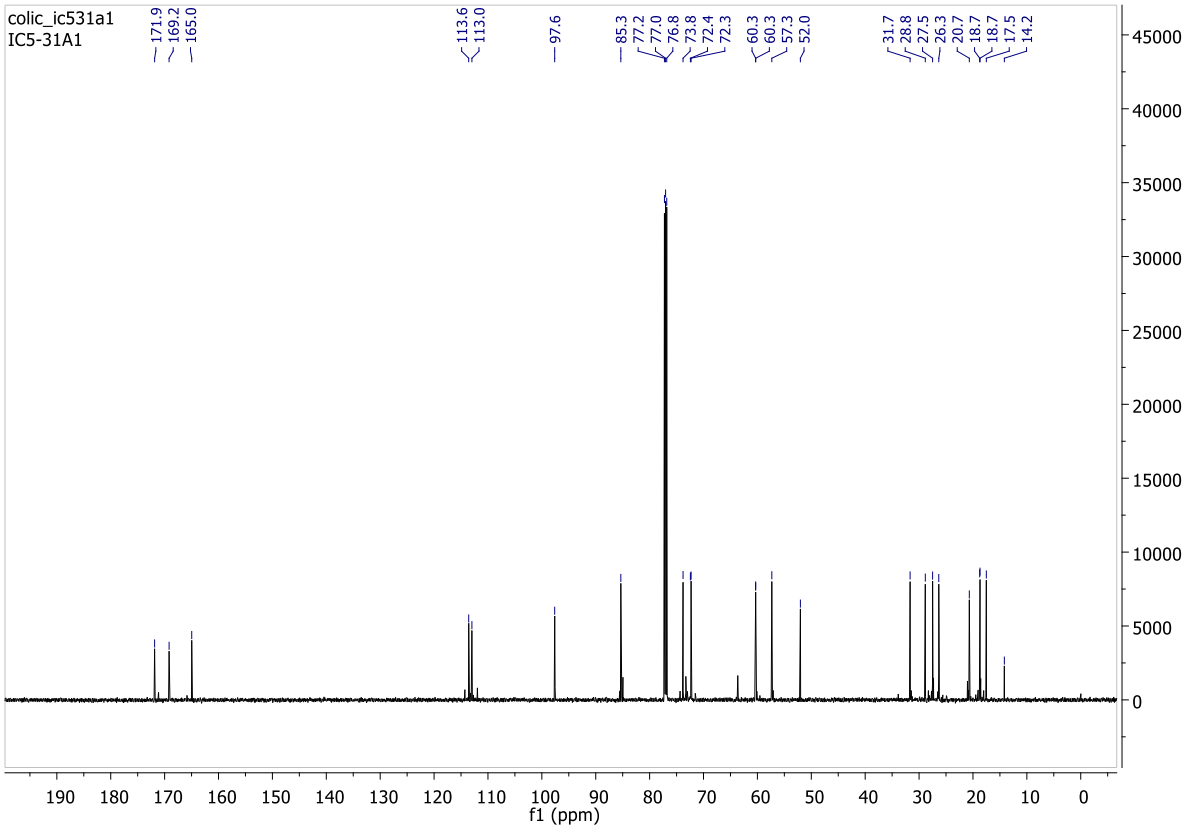
Compound Sor-1d (mixture of diastereoisomers, d.r. 90:10)



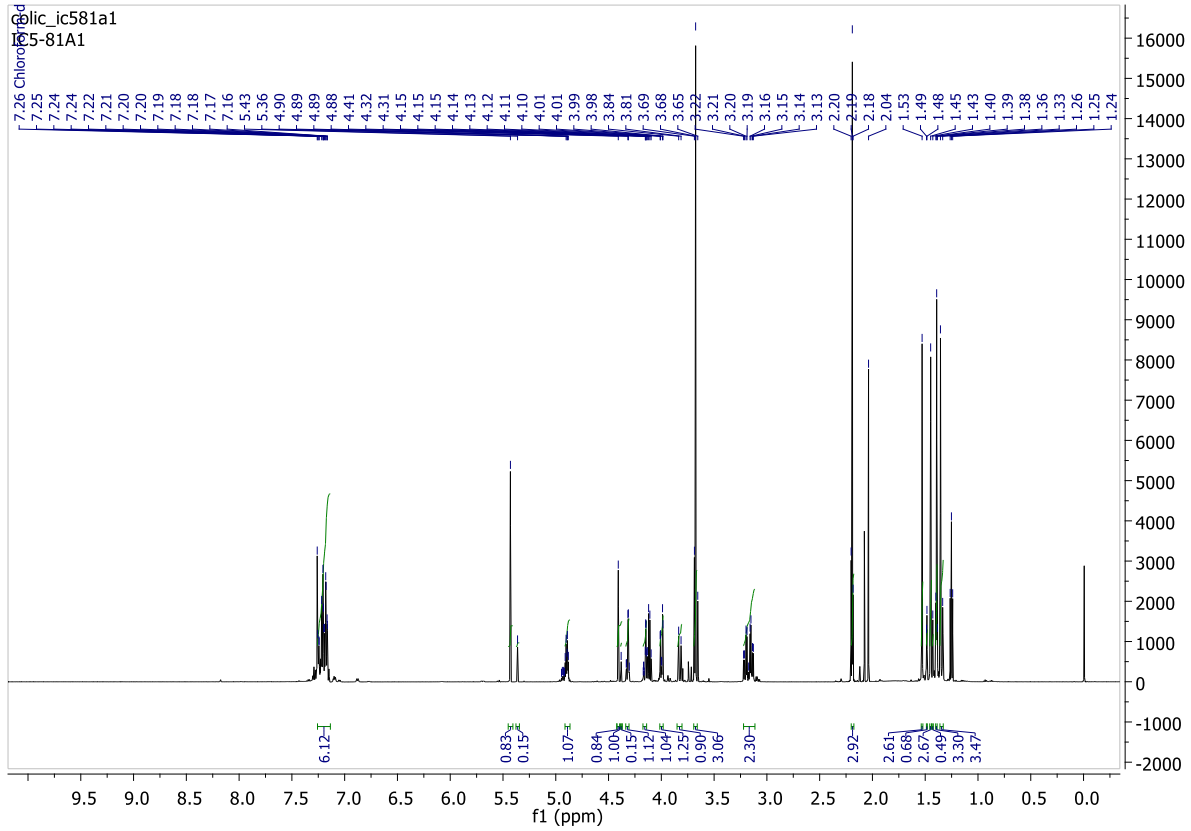


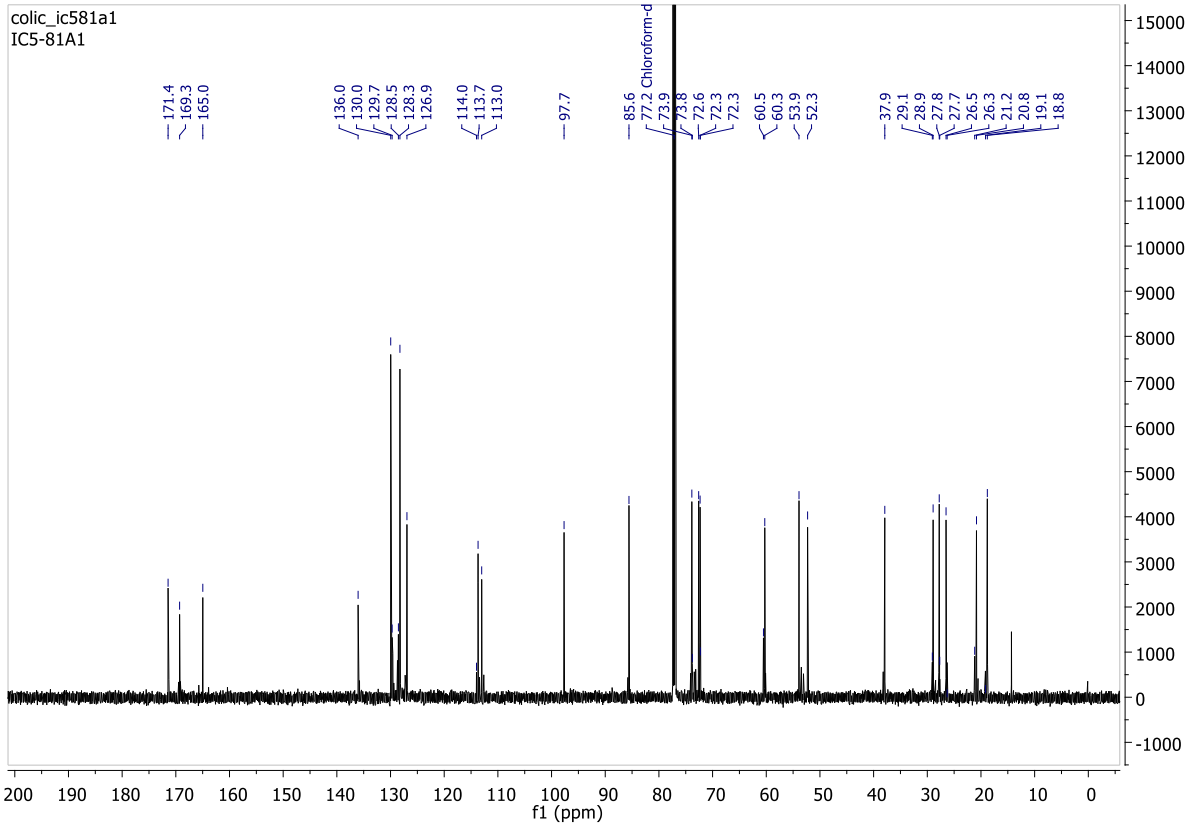
Compound Sor-1e (mixture of diastereoisomers, d.r. 90:10)



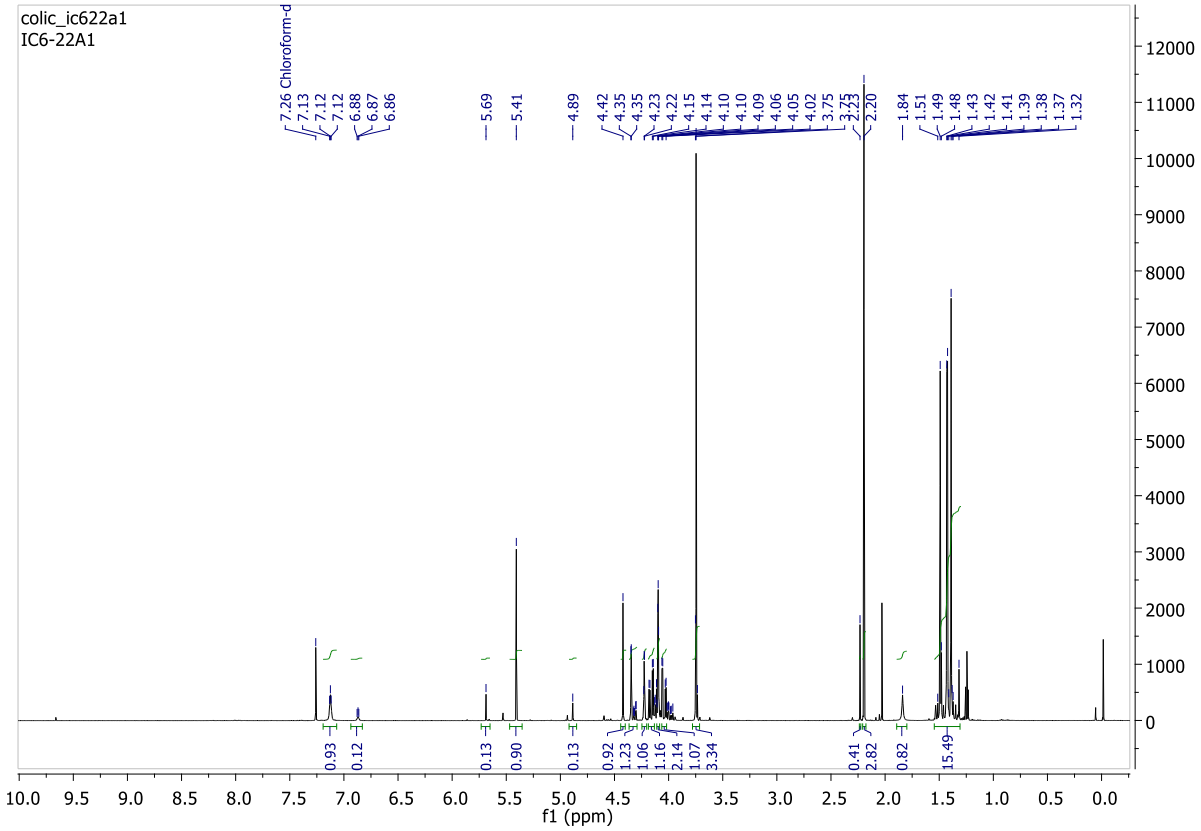


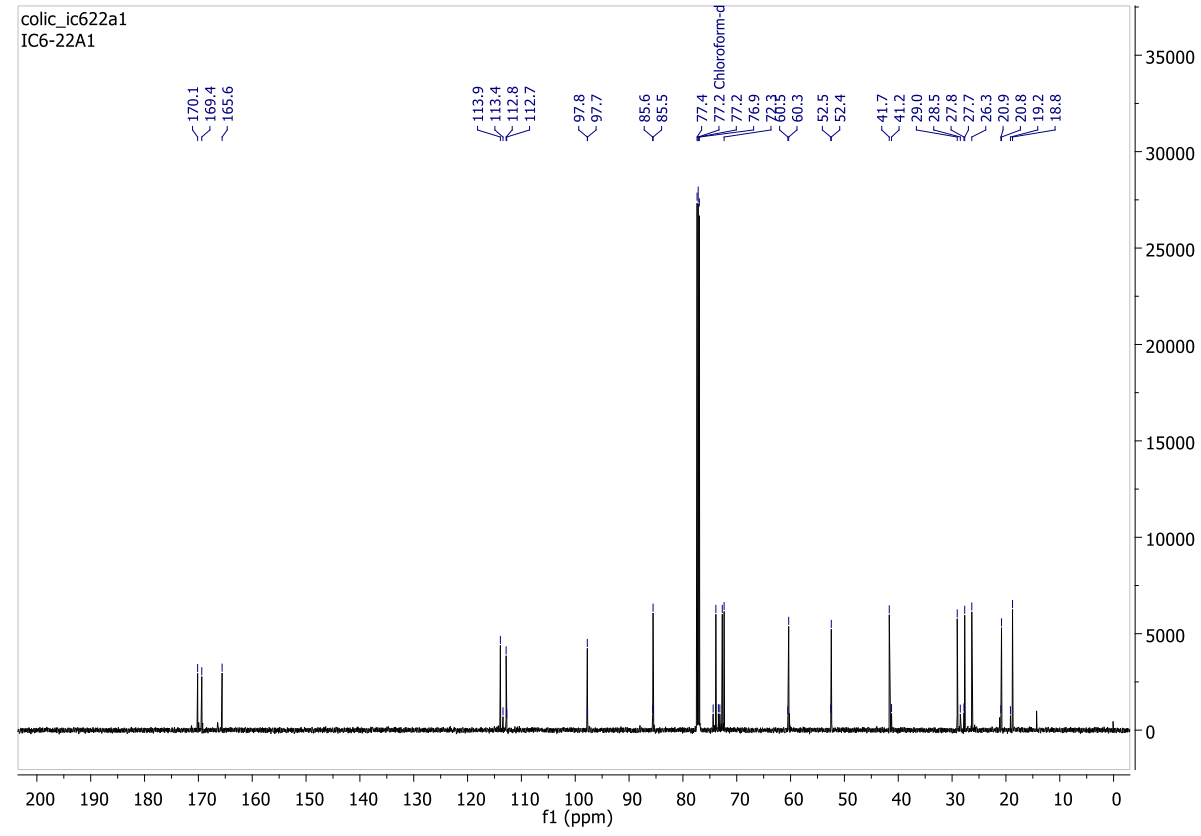
Compound Sor-1f (mixture of diastereoisomers, d.r. 85:15)



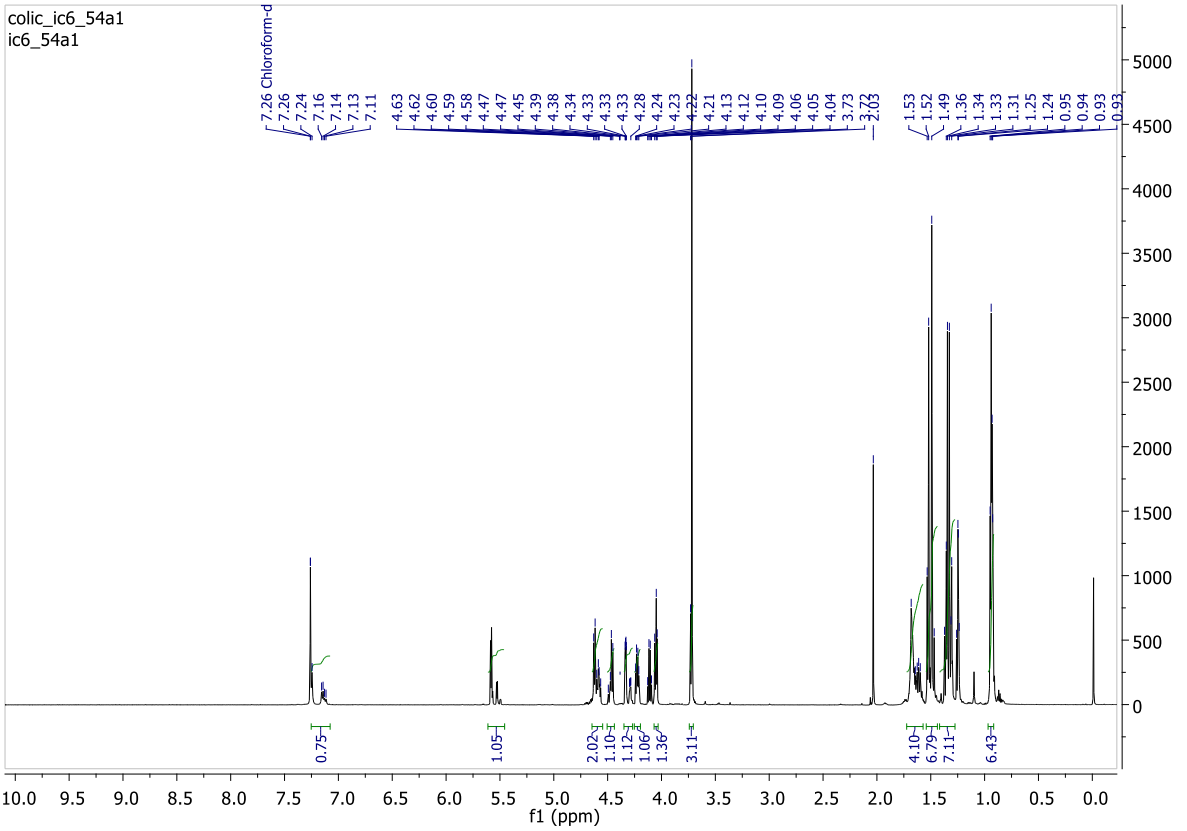


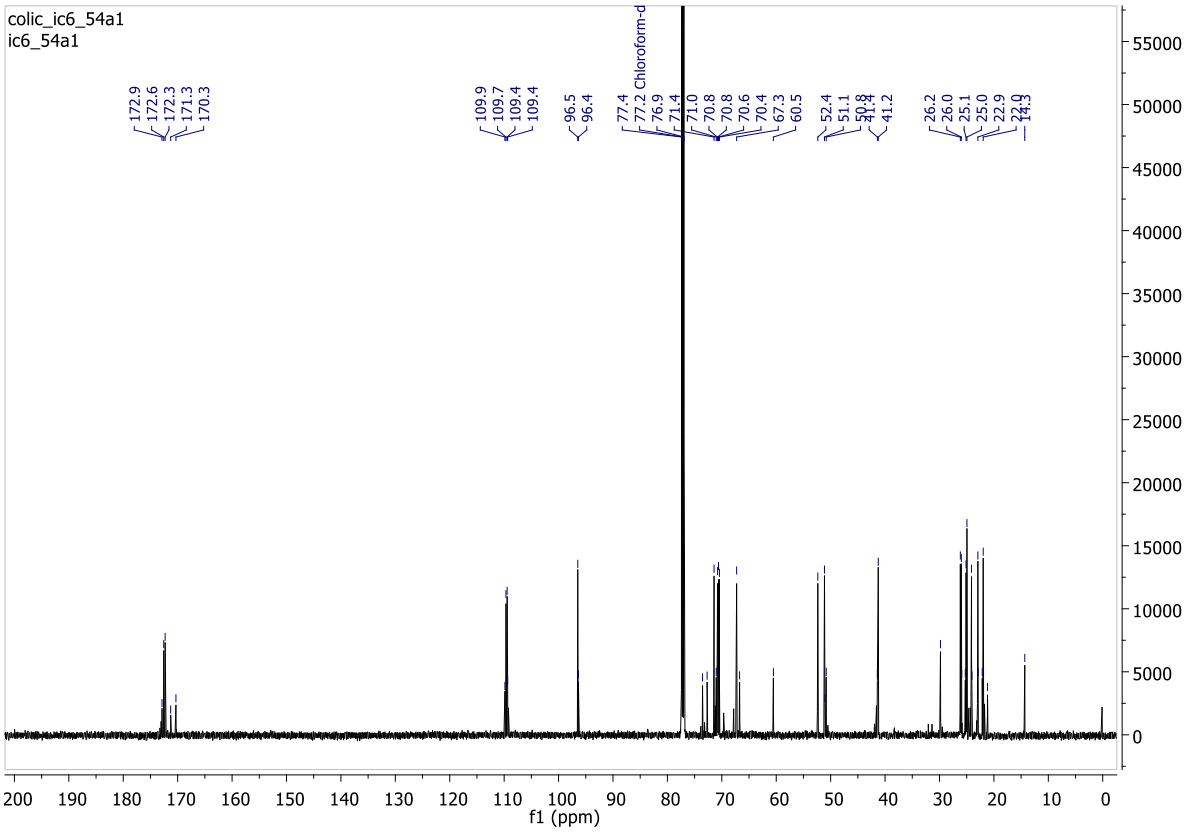
Compound Sor-1g (mixture of diastereoisomers, d.r. 90:10)



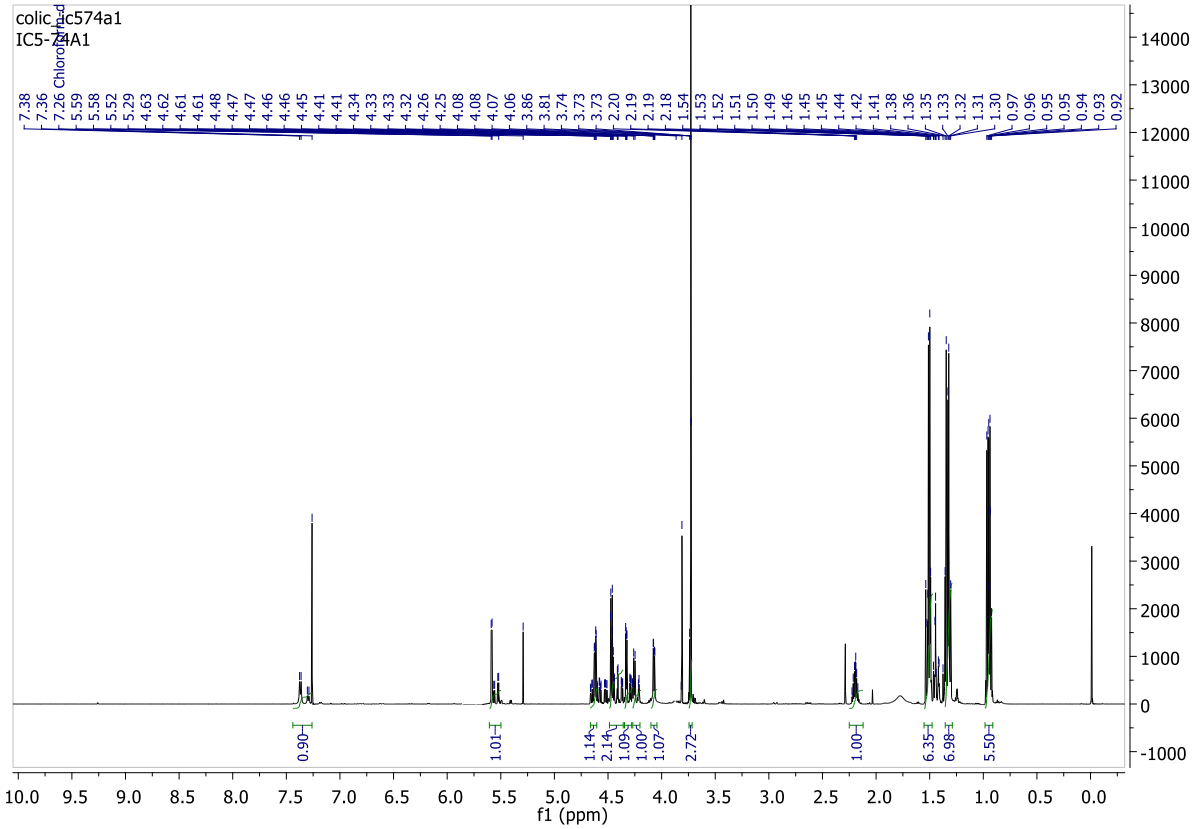


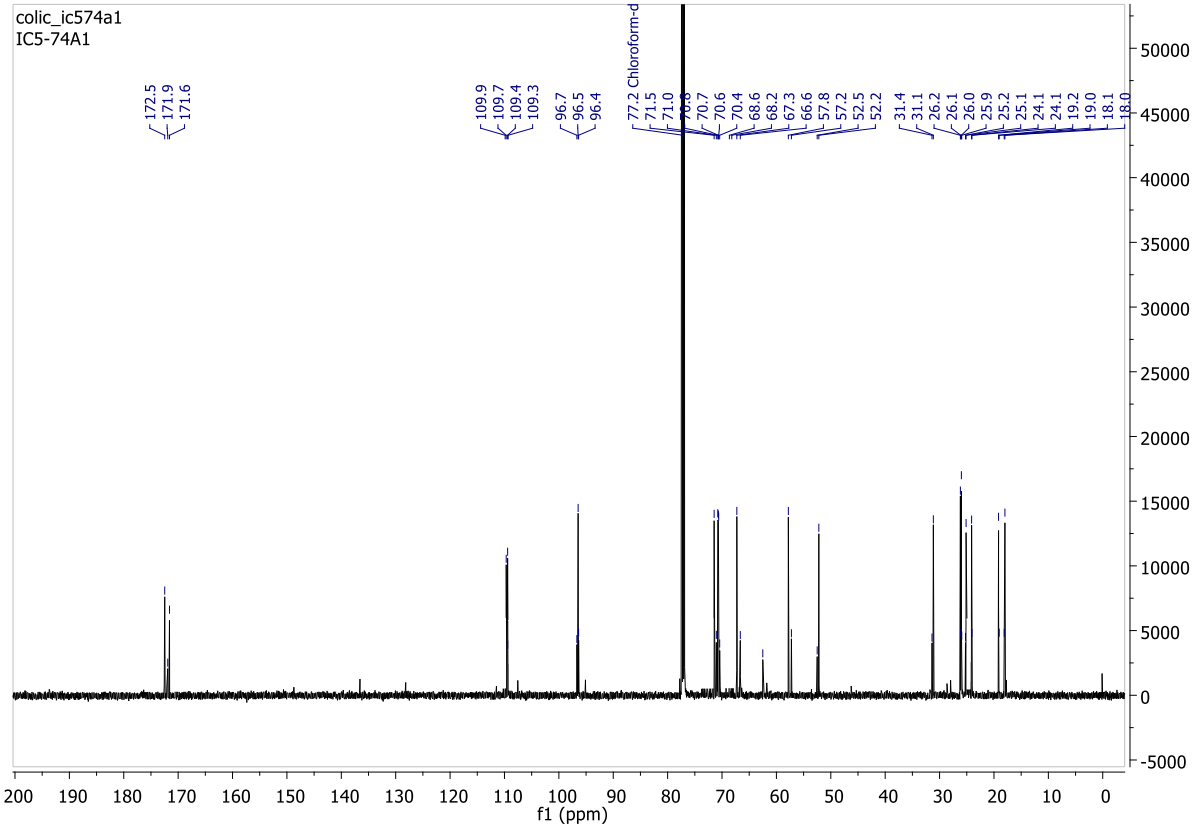
Compound Gal-2a (mixture of diastereoisomers, d.r. 75:25)



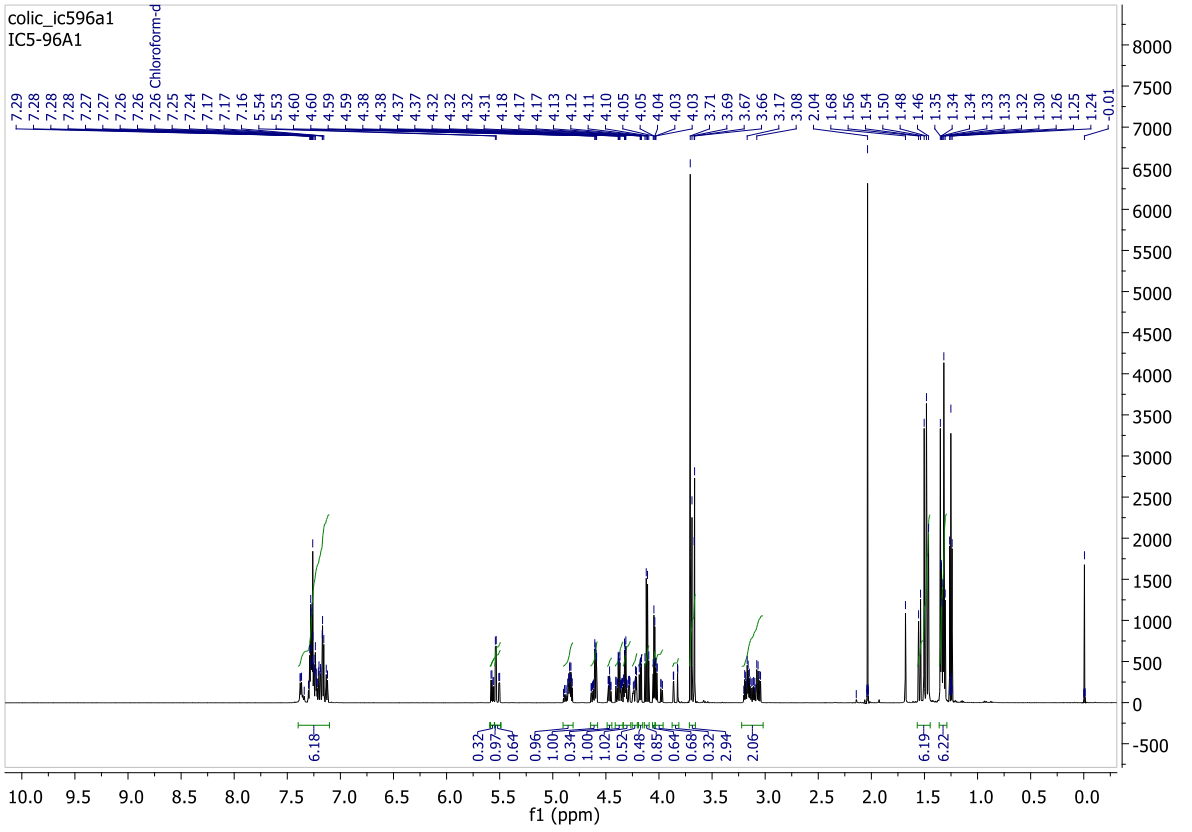


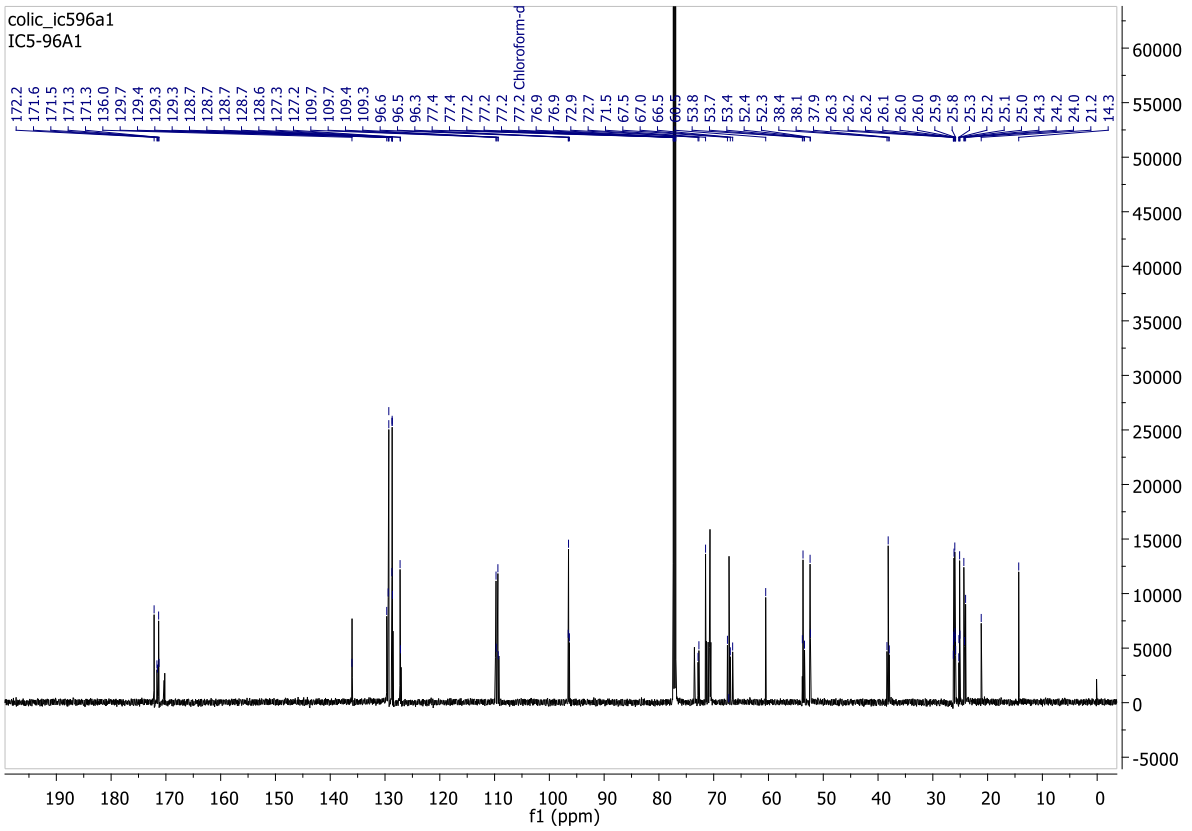
Compound Gal-2b (mixture of diastereoisomers, d.r. 70:30)



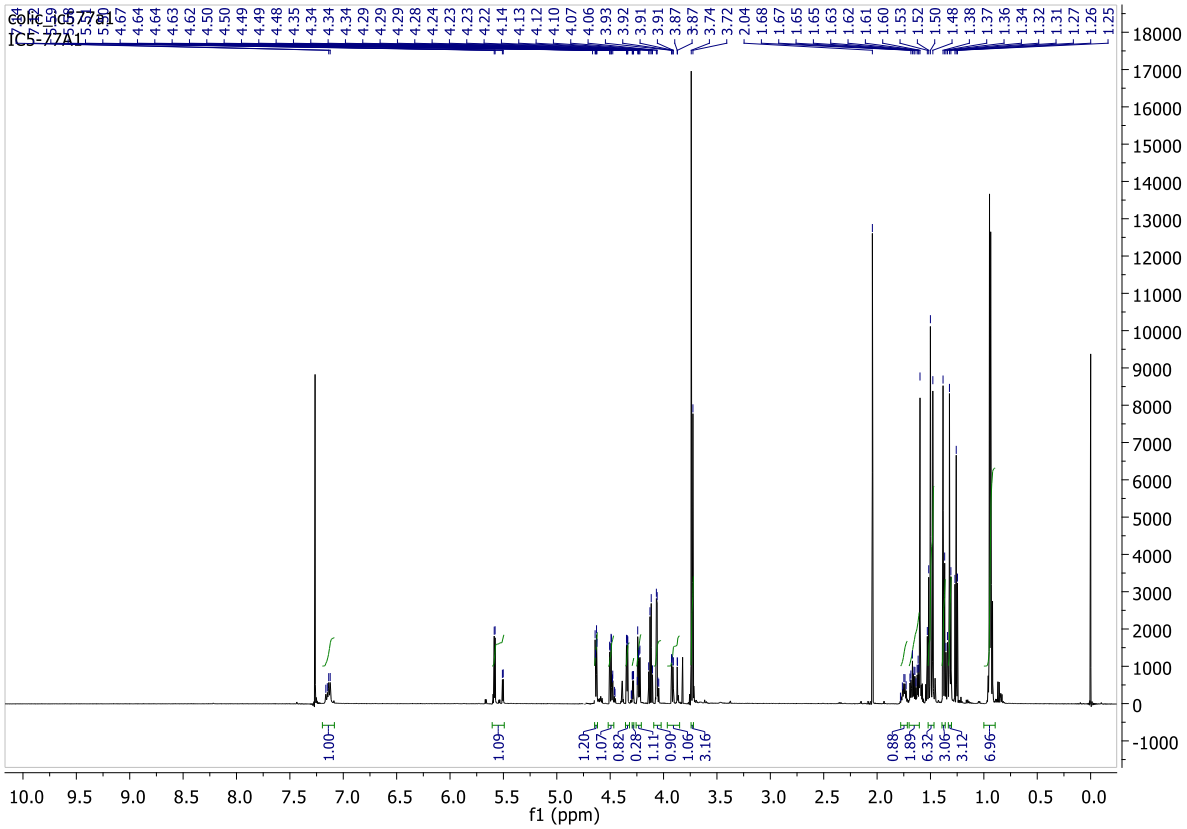


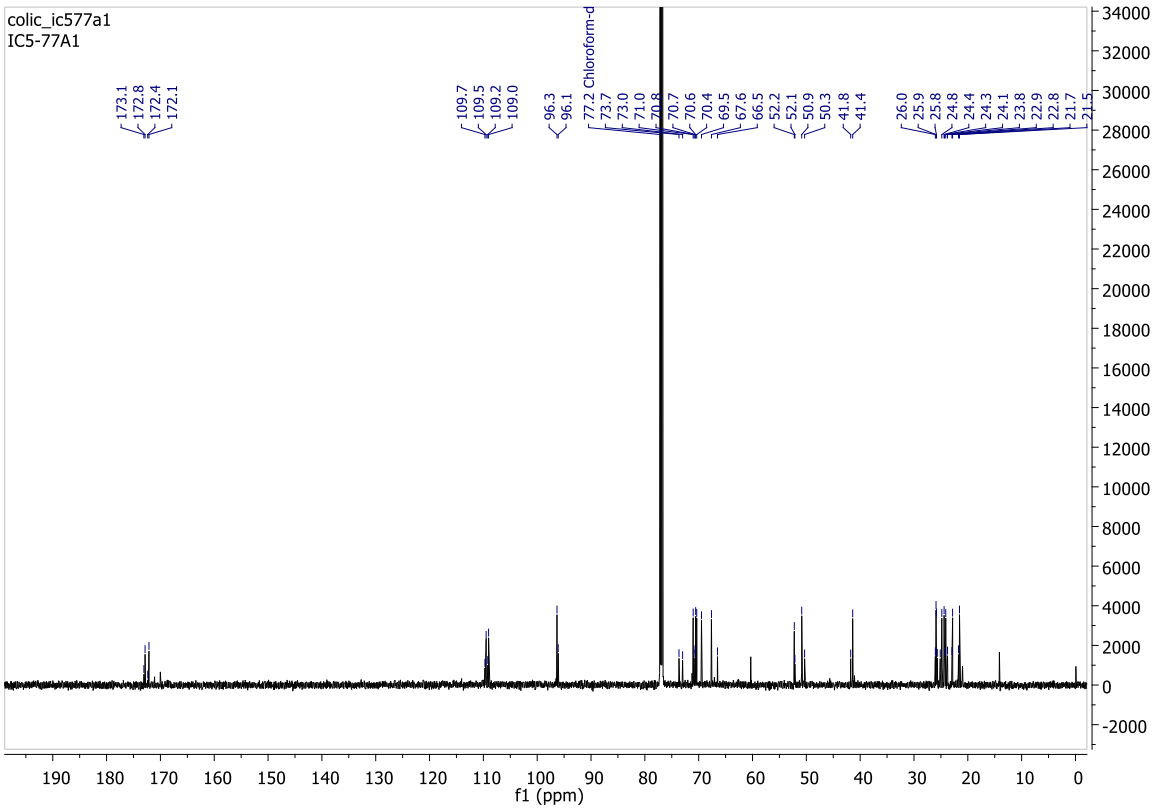
Compound Gal-2c (mixture of diastereoisomers, d.r. 70:30)



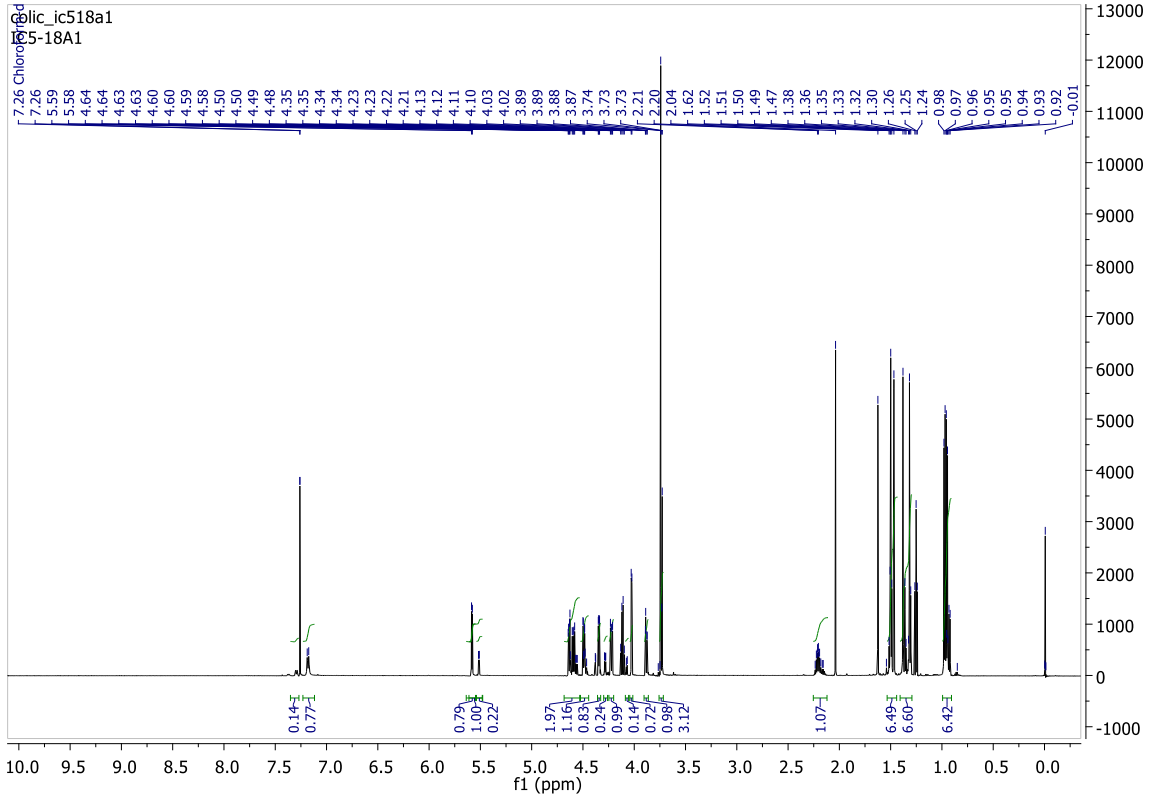


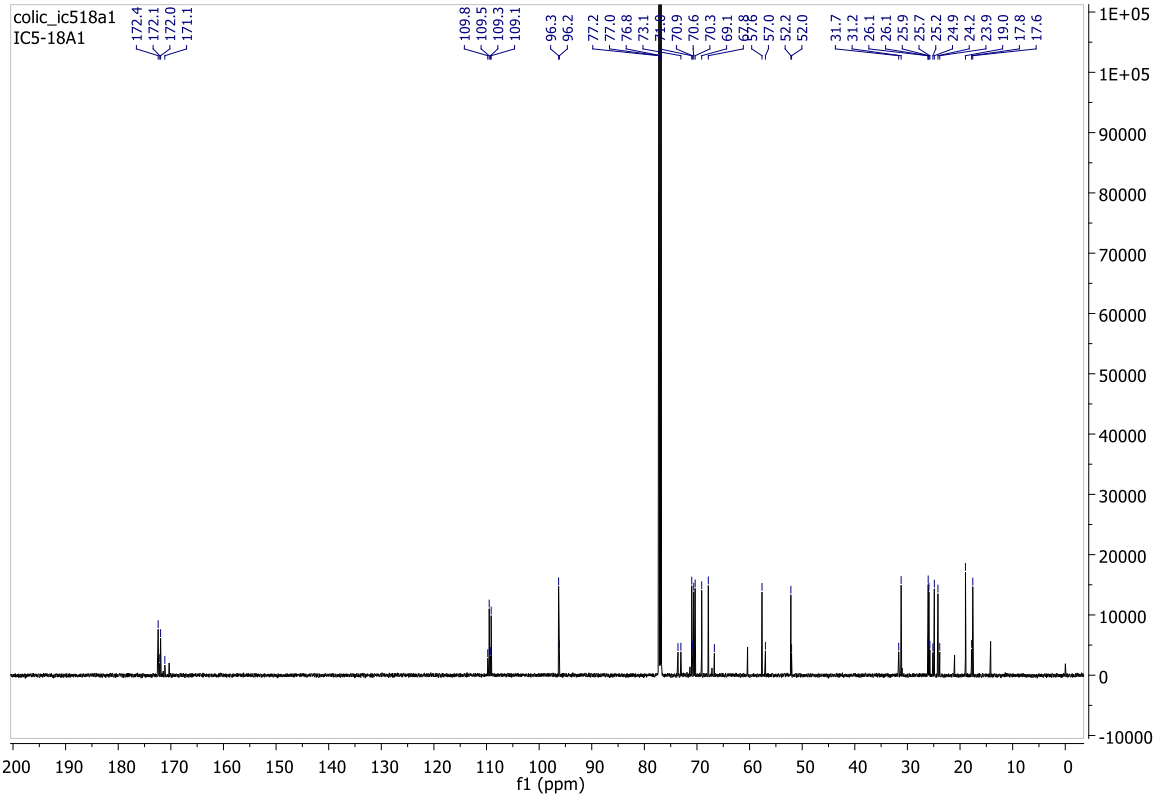
Compound Gal-2d (mixture of diastereoisomers, d.r. 80:20)



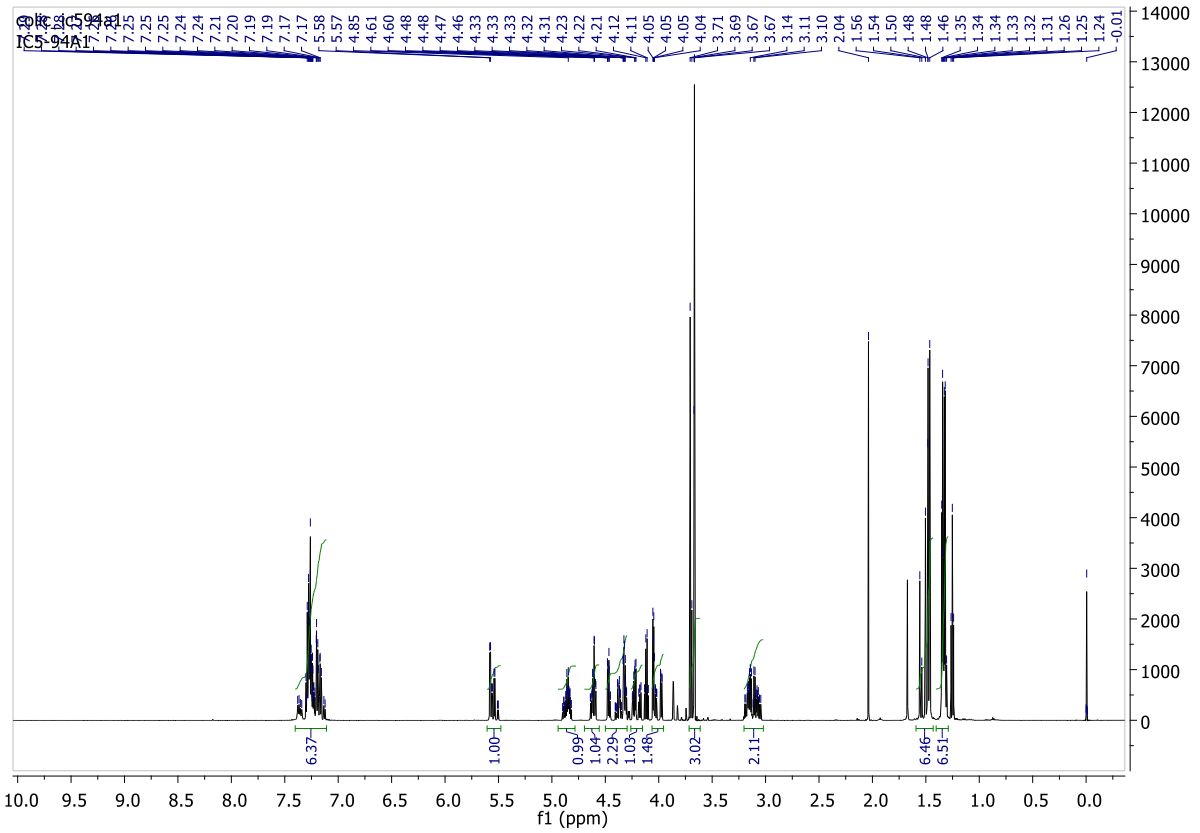


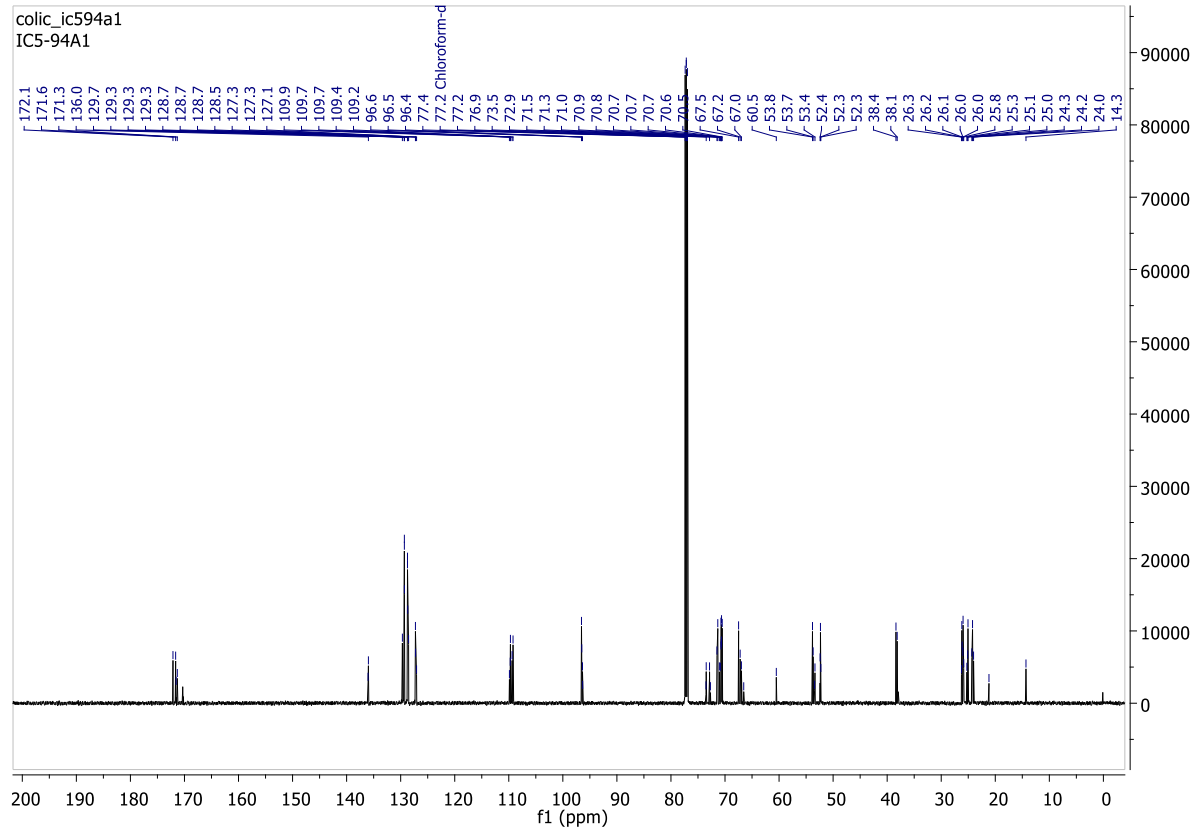
Compound Gal-2e (mixture of diastereoisomers, d.r. 80:20)



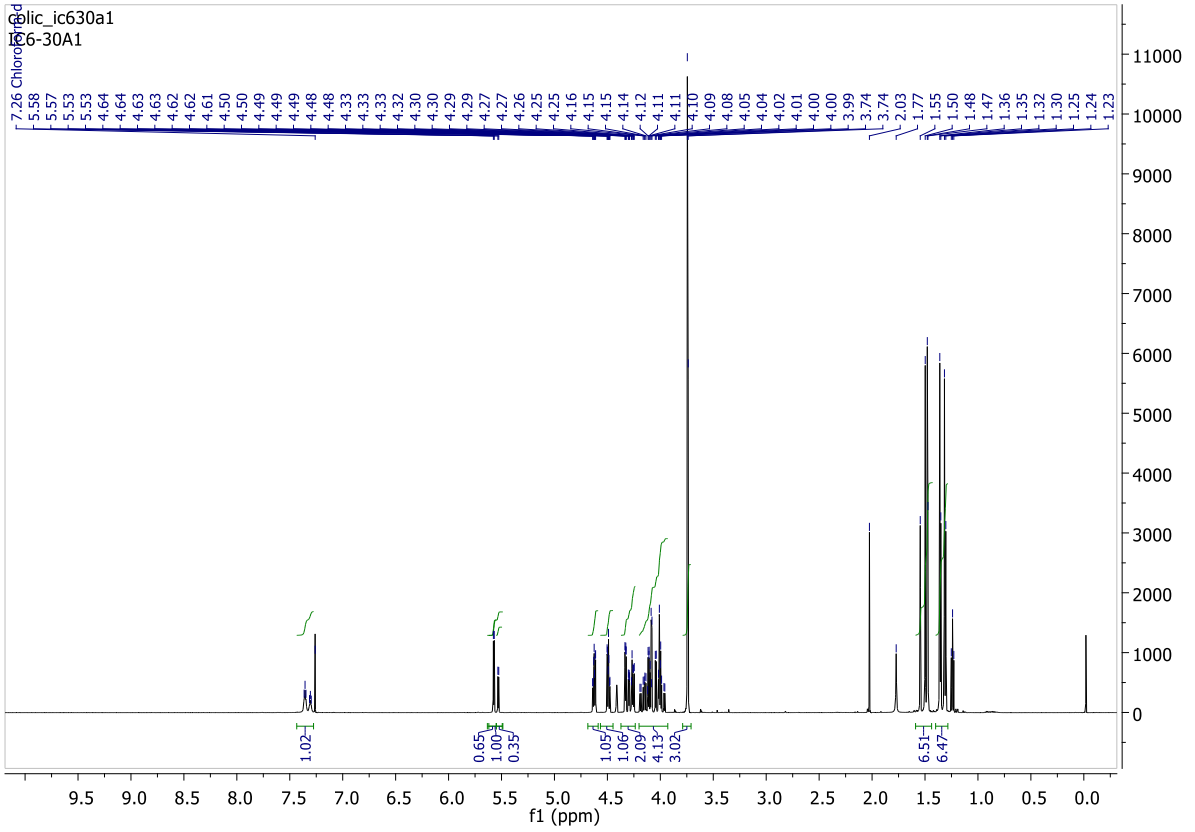


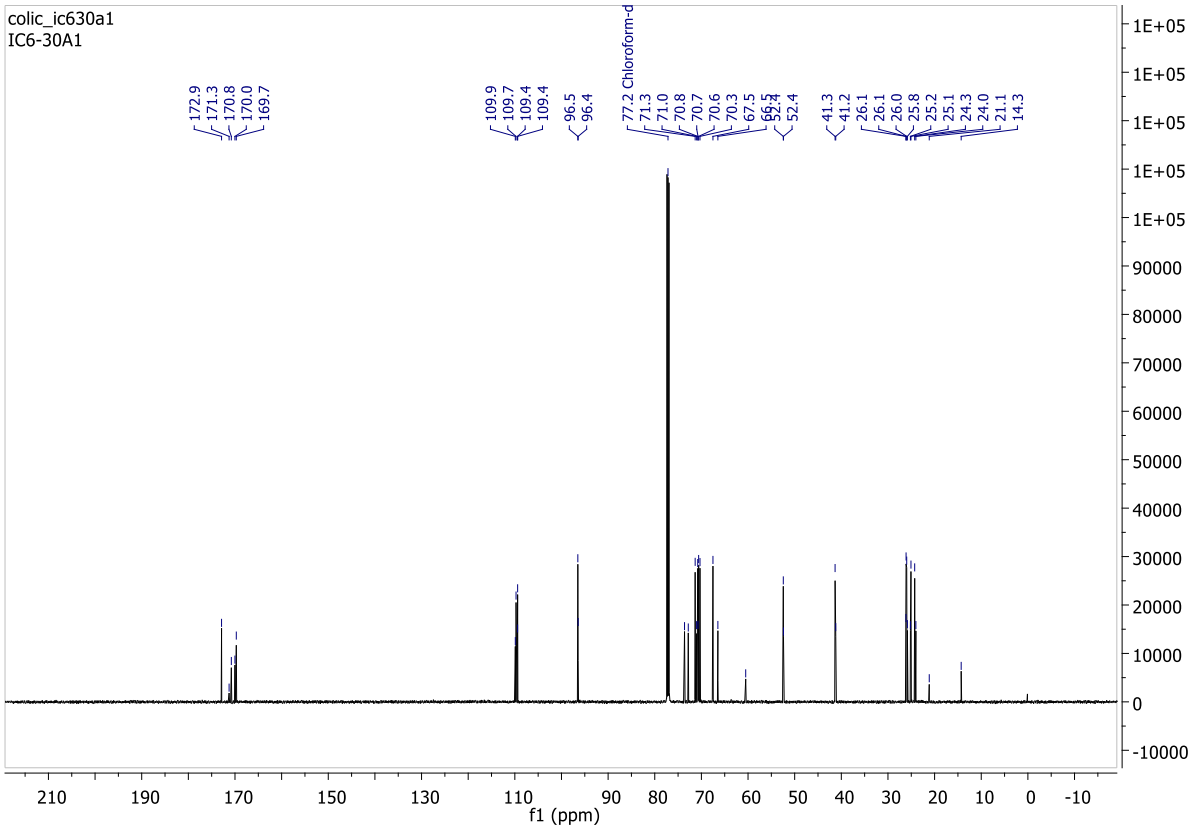
Compound Gal-2f (mixture of diastereoisomers, d.r. 80:20)



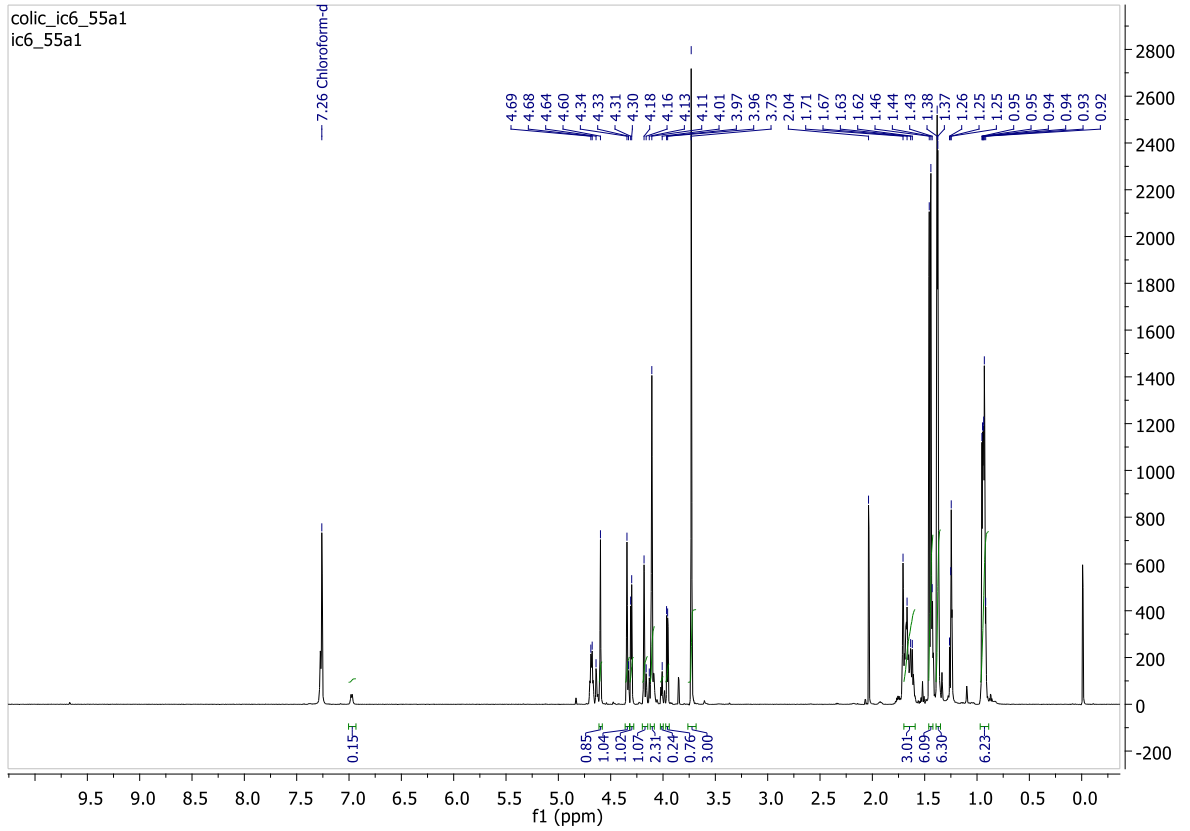


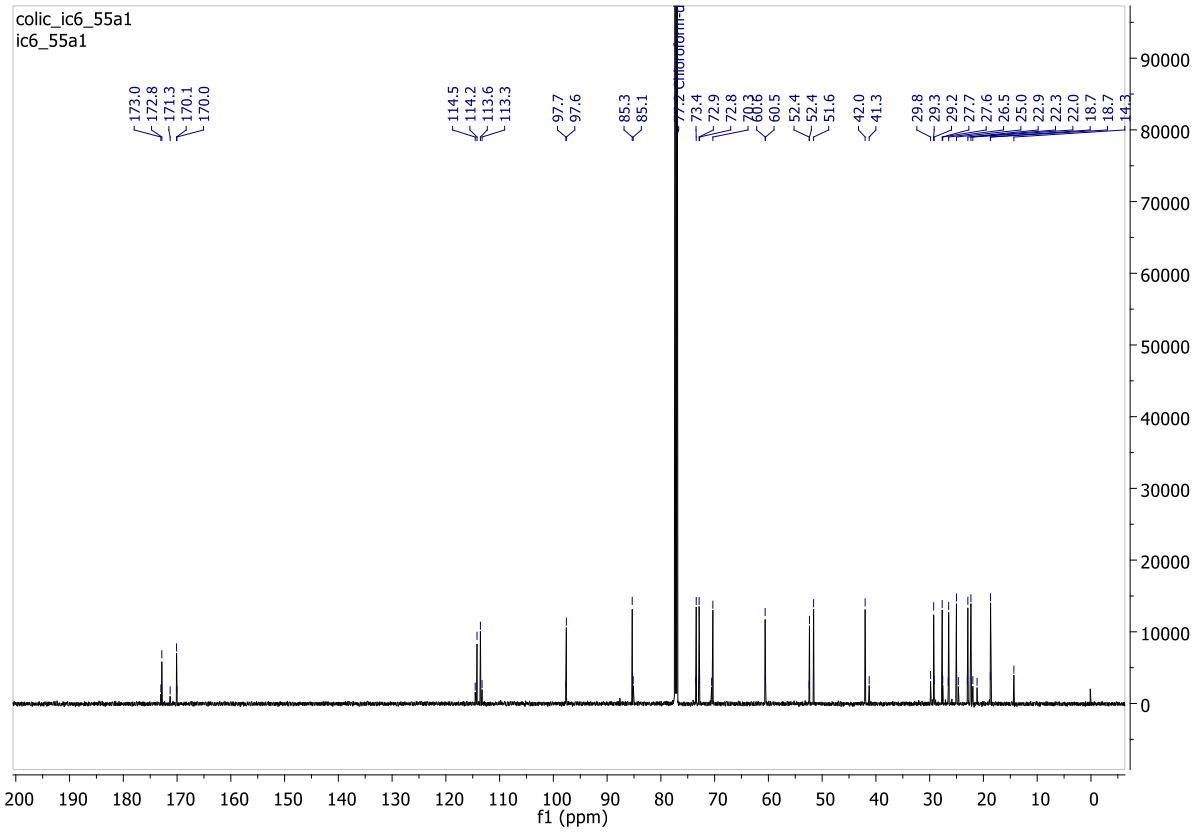
Compound Gal-2g (mixture of diastereoisomers, d.r. 65:35)



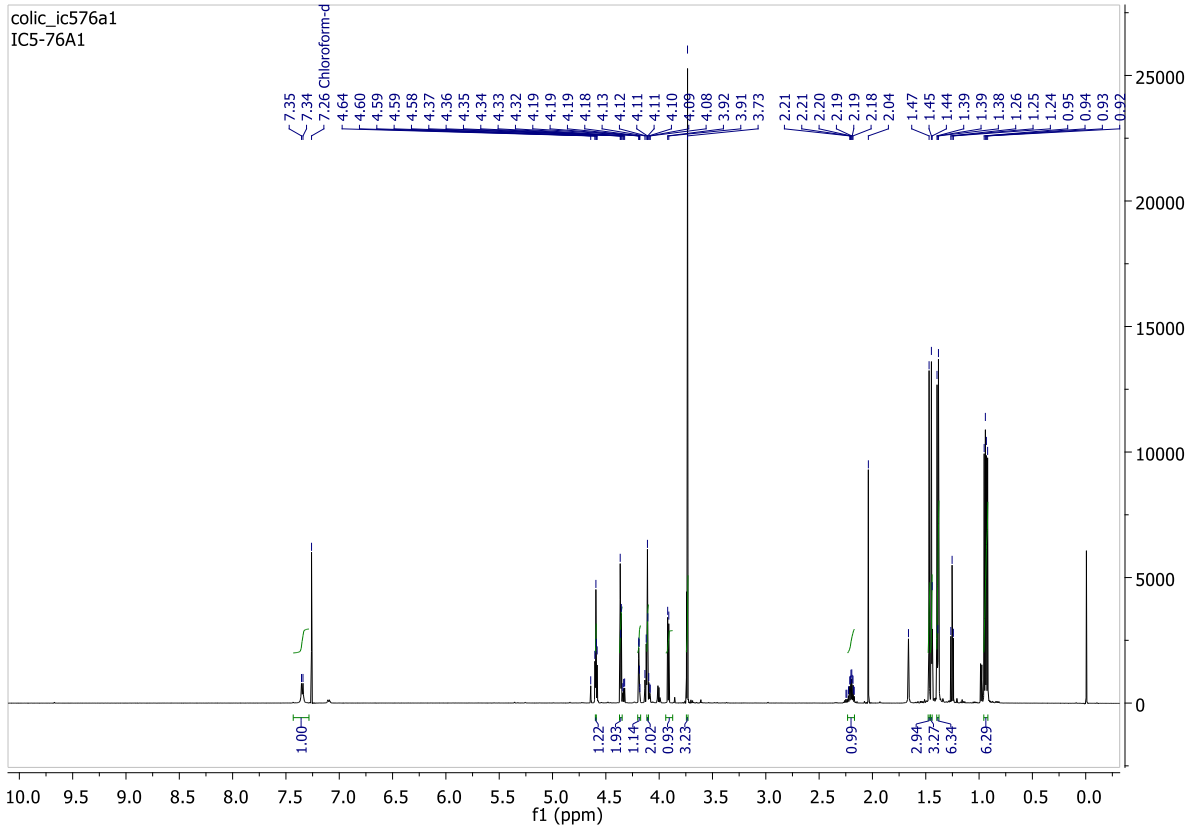


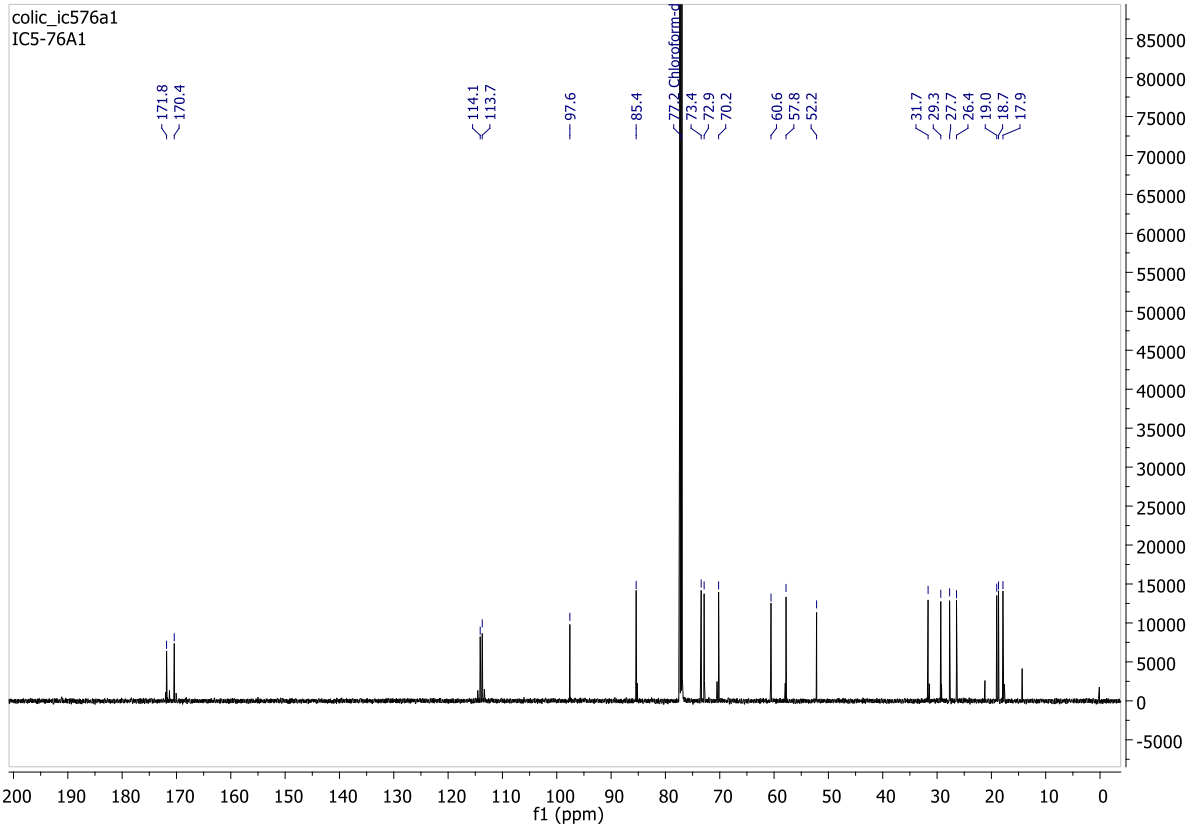
Compound Sor-2a (mixture of diastereoisomers, d.r. 85:15)



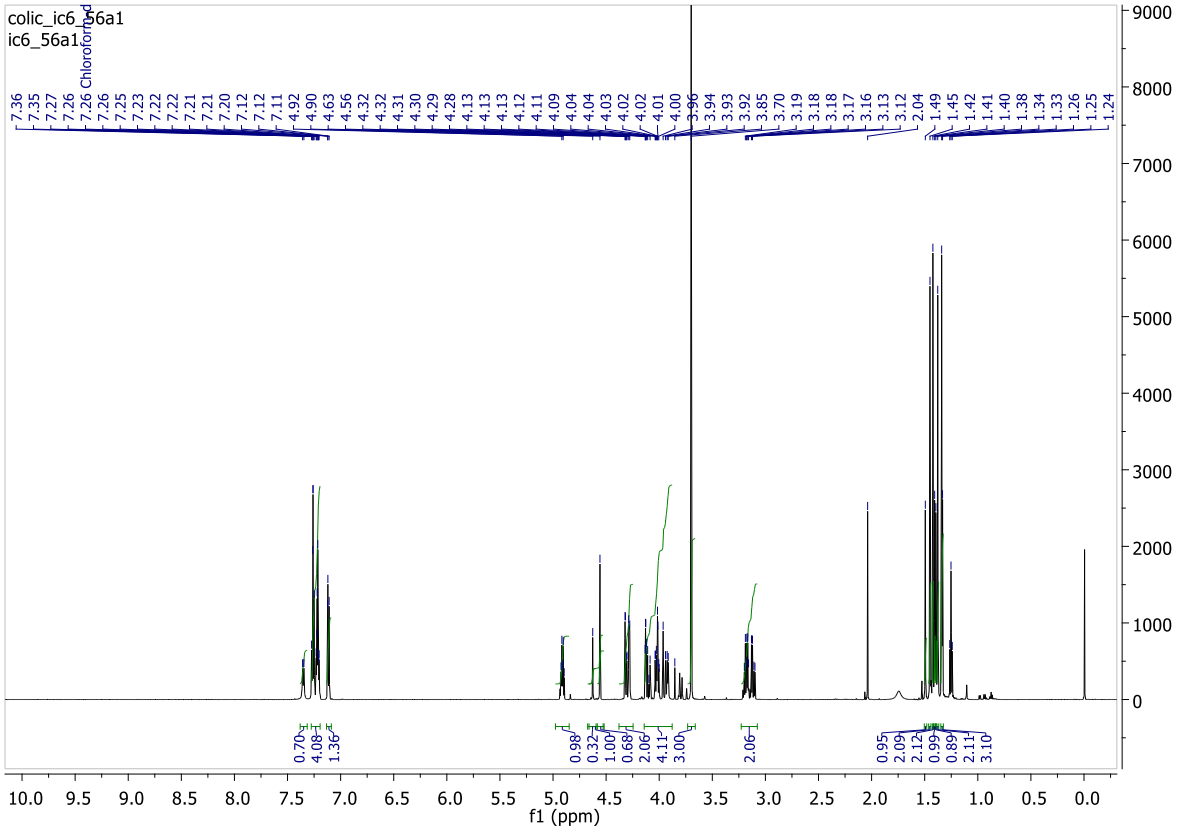


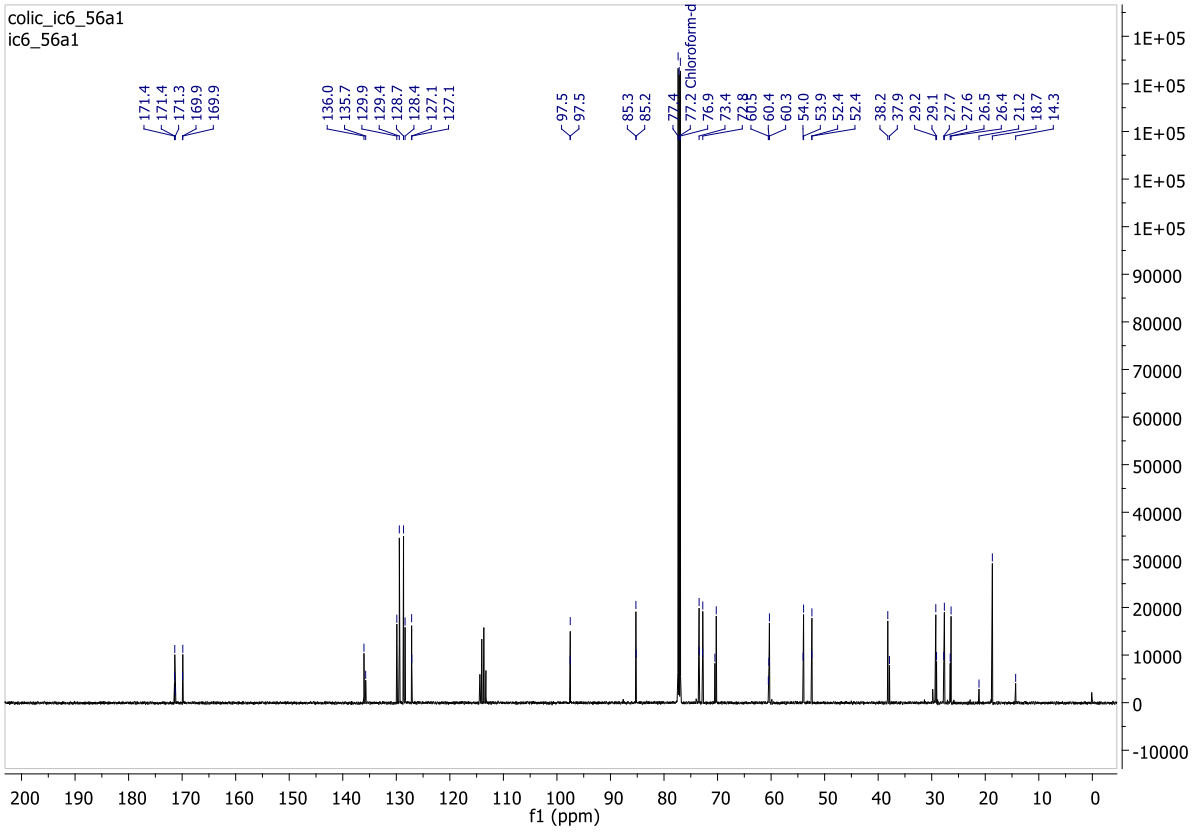
Compound Sor-2b (mixture of diastereoisomers, d.r. 85:15)



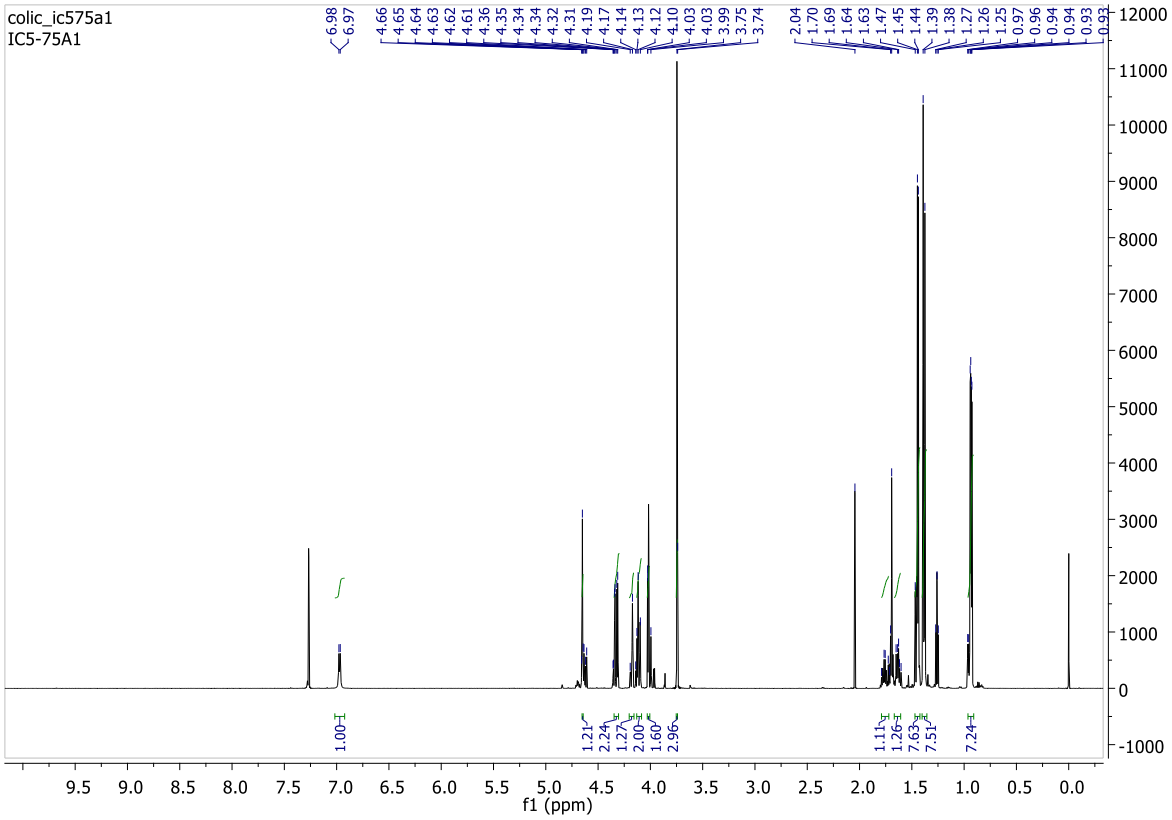


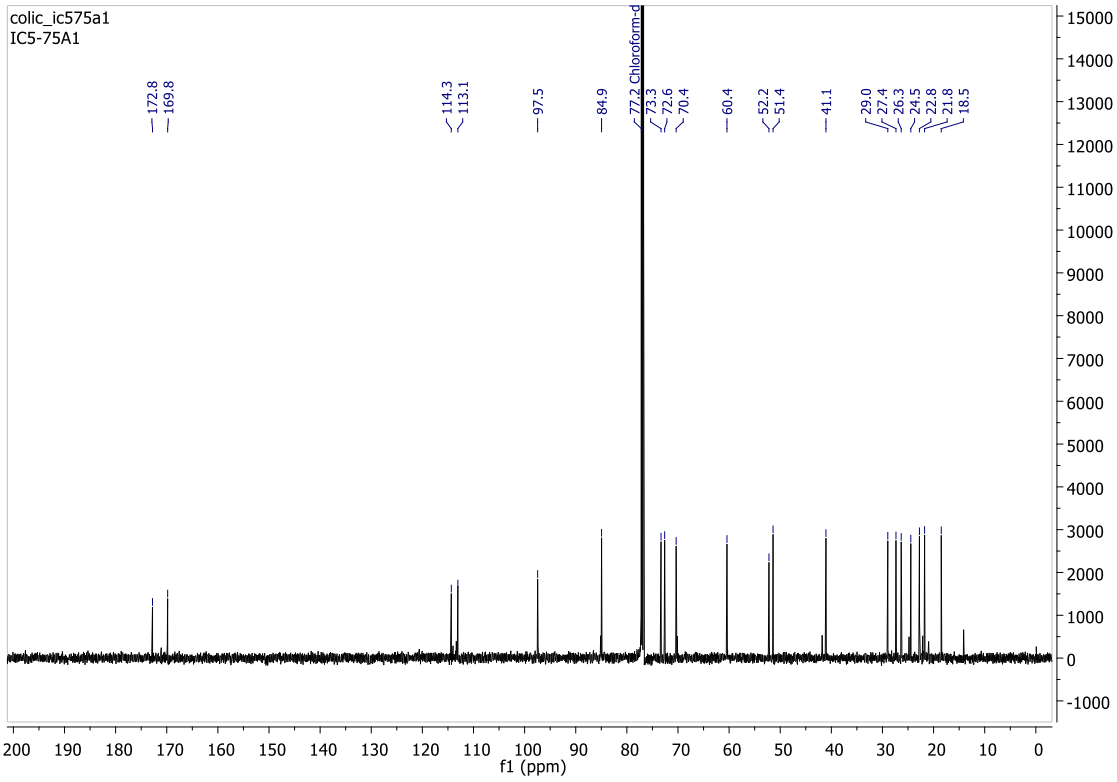
Compound Sor-2c (mixture of diastereoisomers, d.r. 70:30)



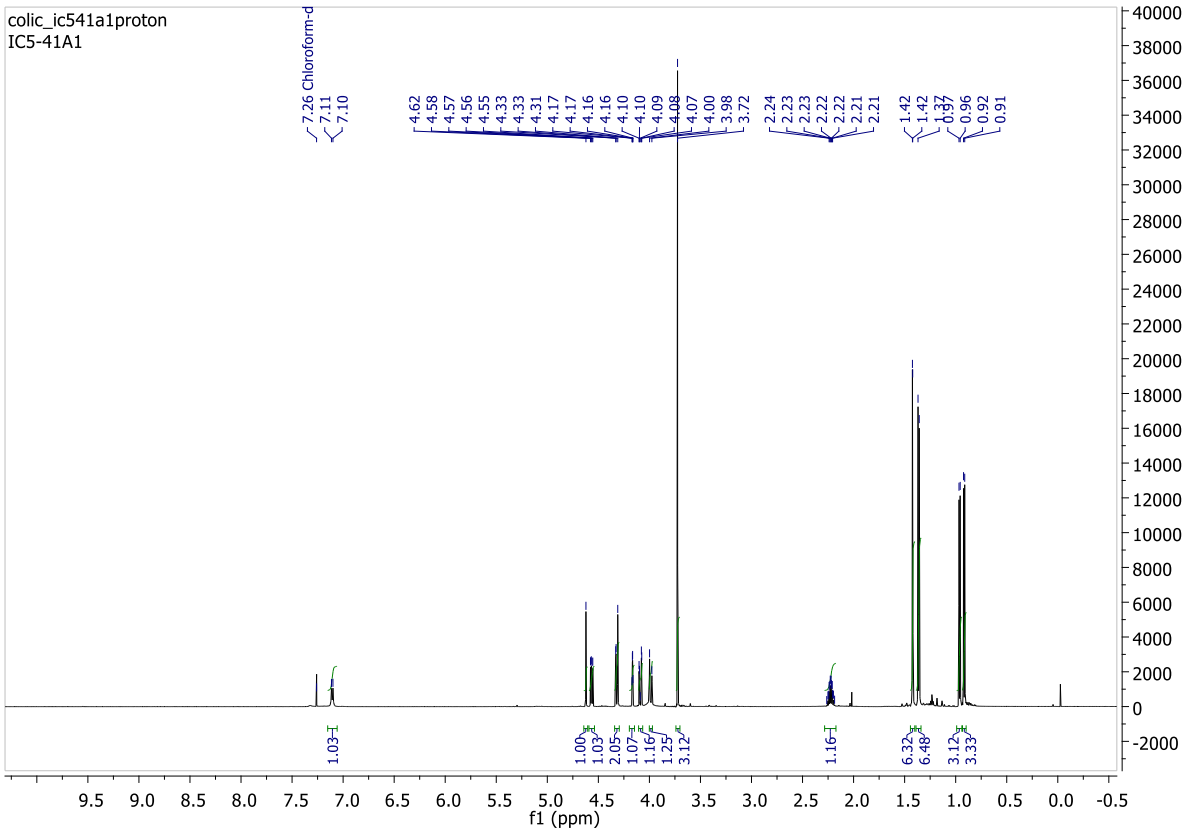


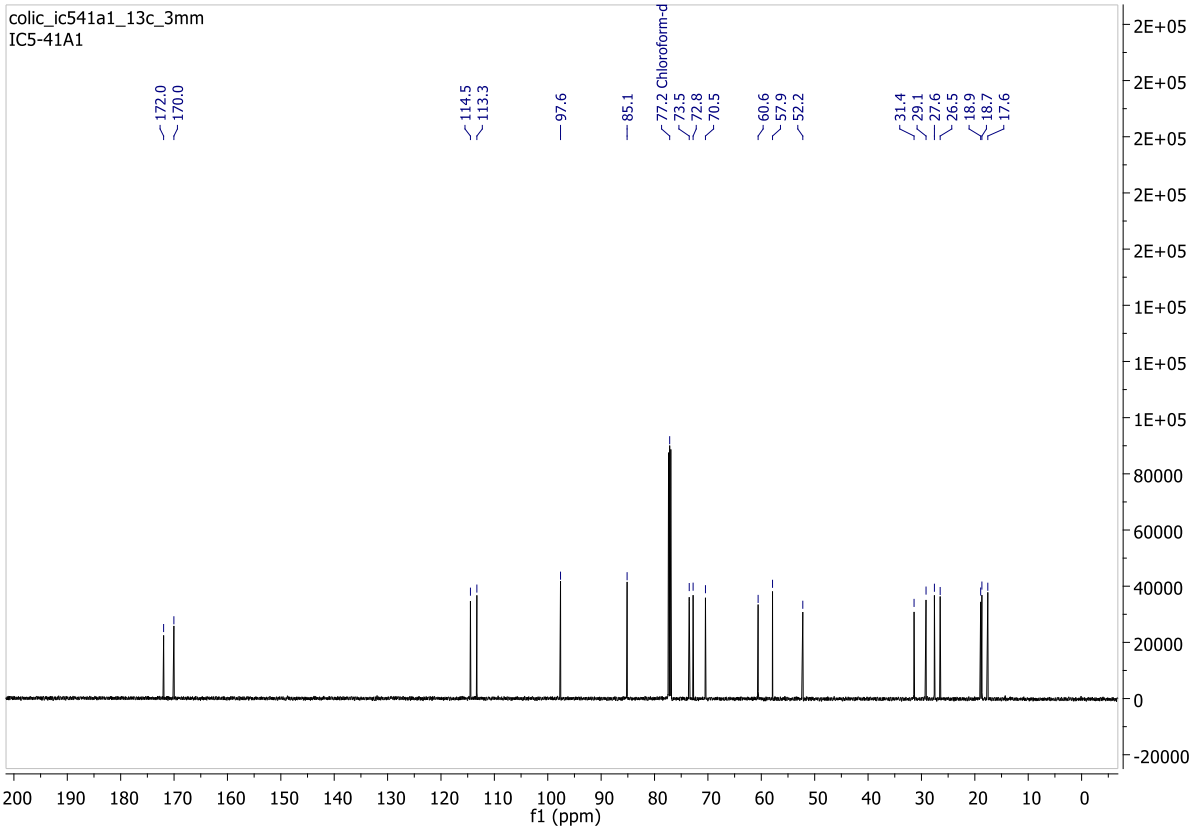
Compound Sor-2d (mixture of diastereoisomers, d.r. 90:10)



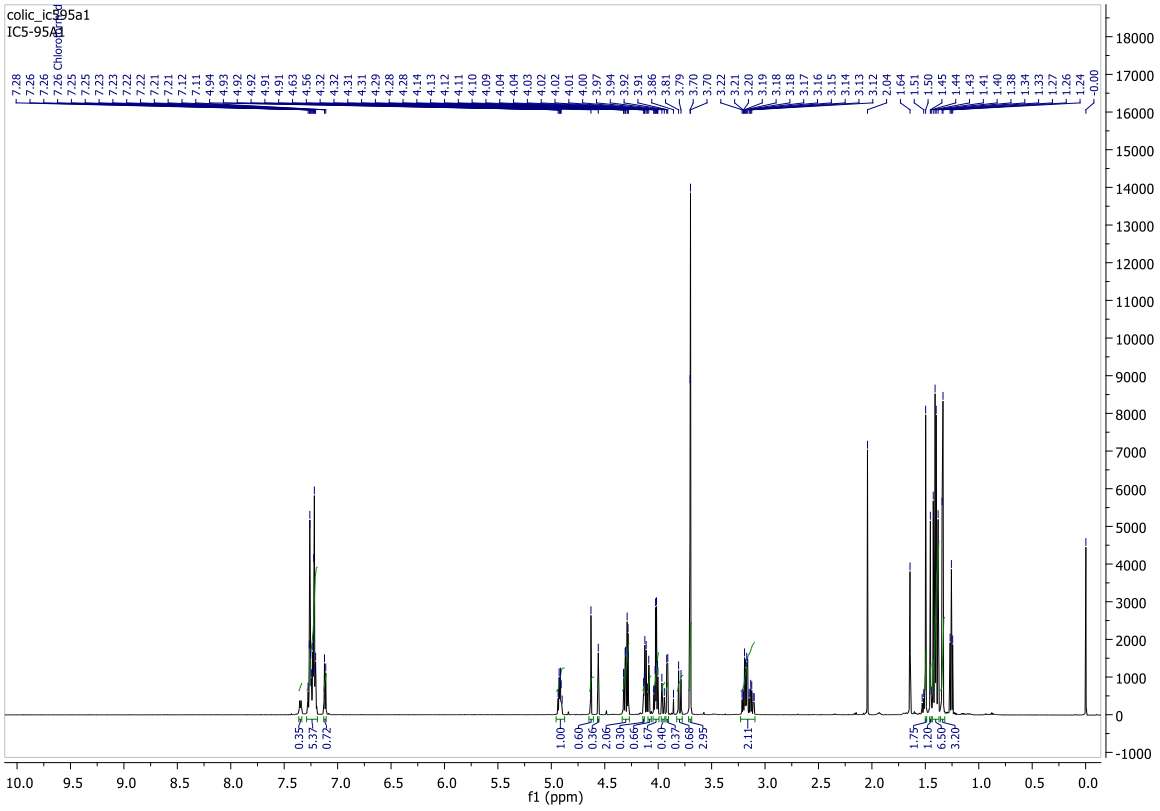


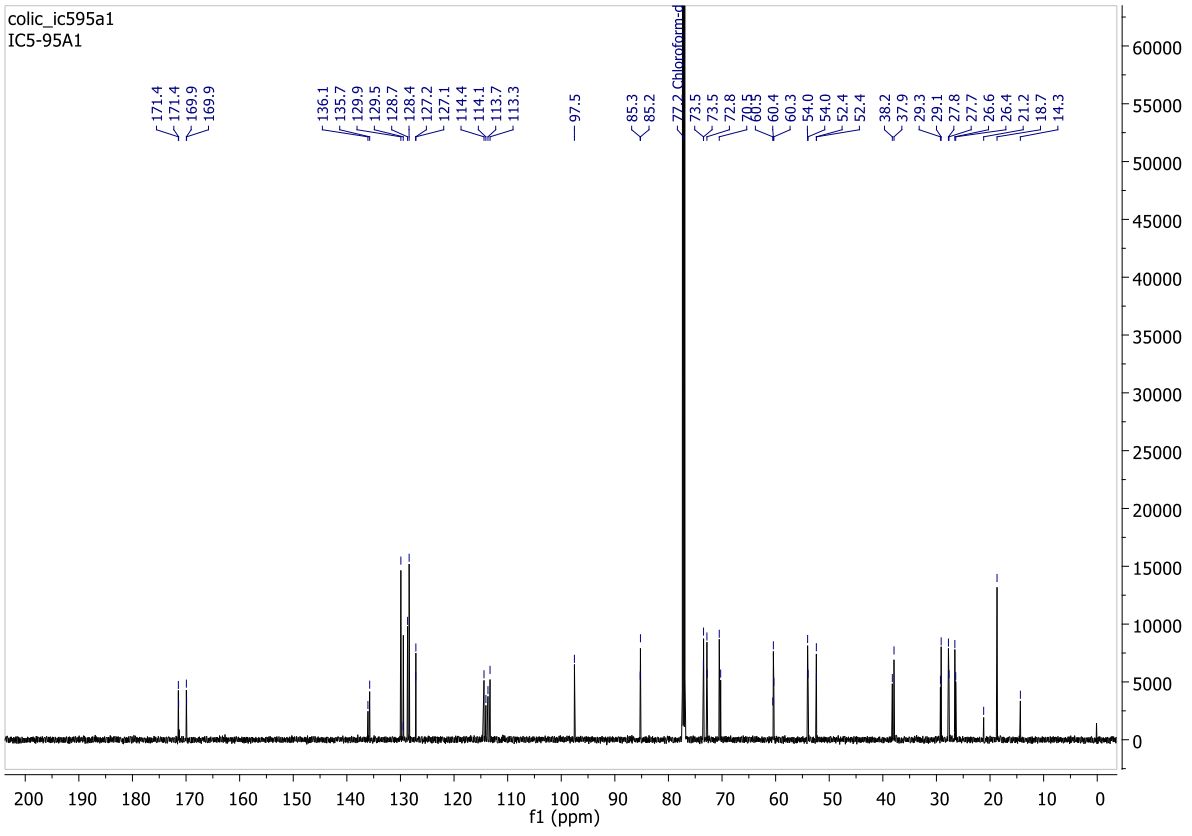
Compound Sor-2e (single diastereoisomers)



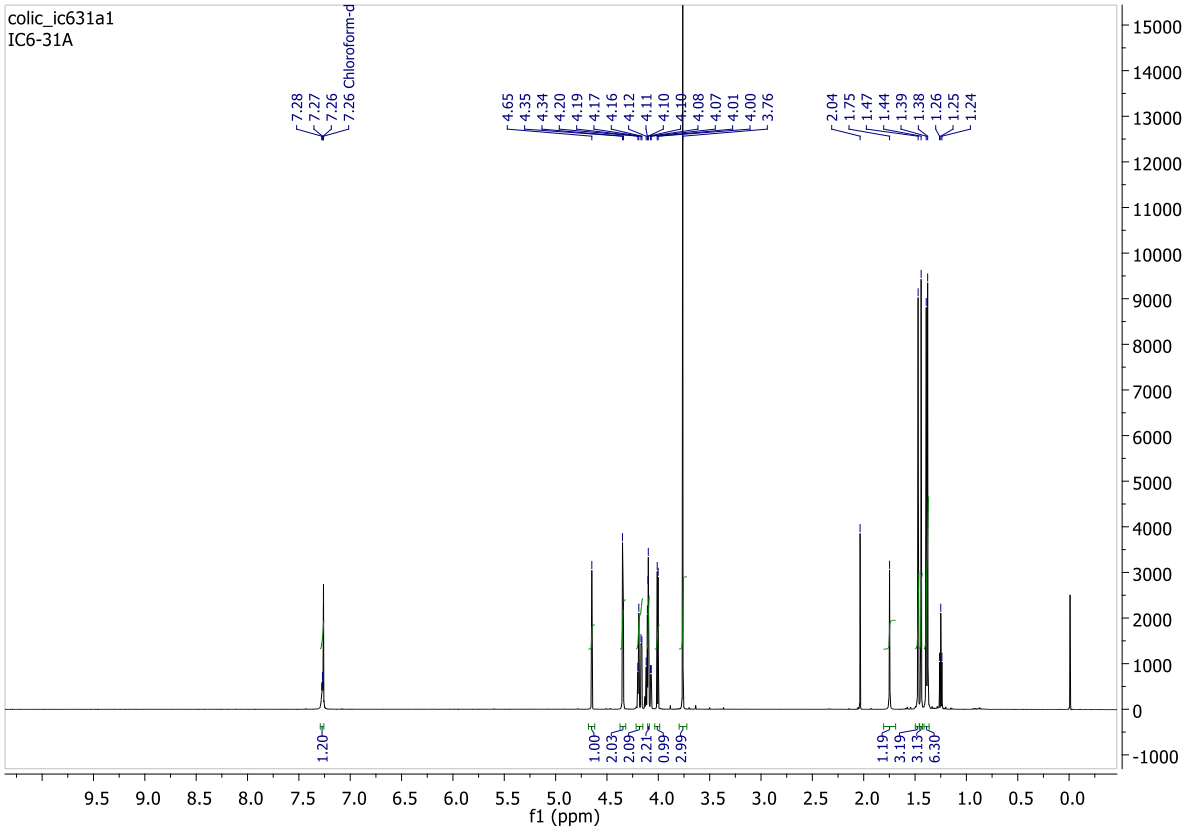


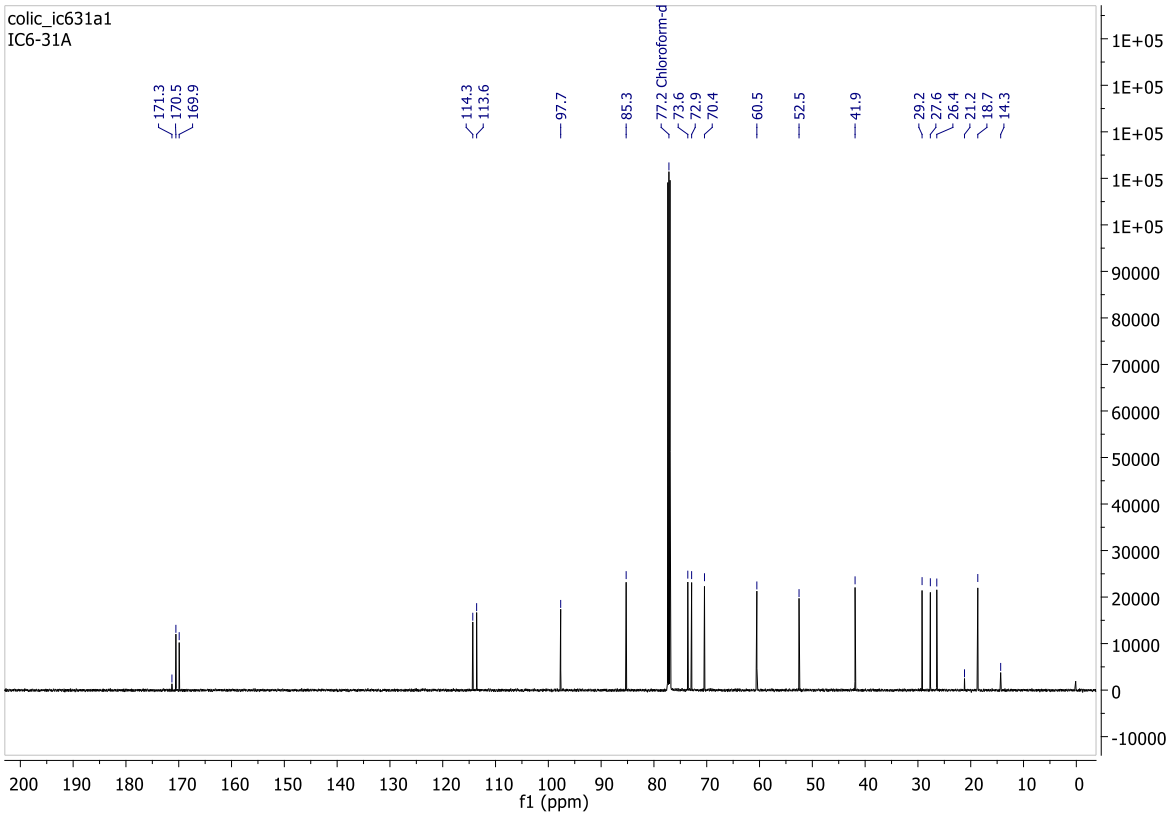
Compound Sor-2f (mixture of diastereoisomers, d.r. 70:30)



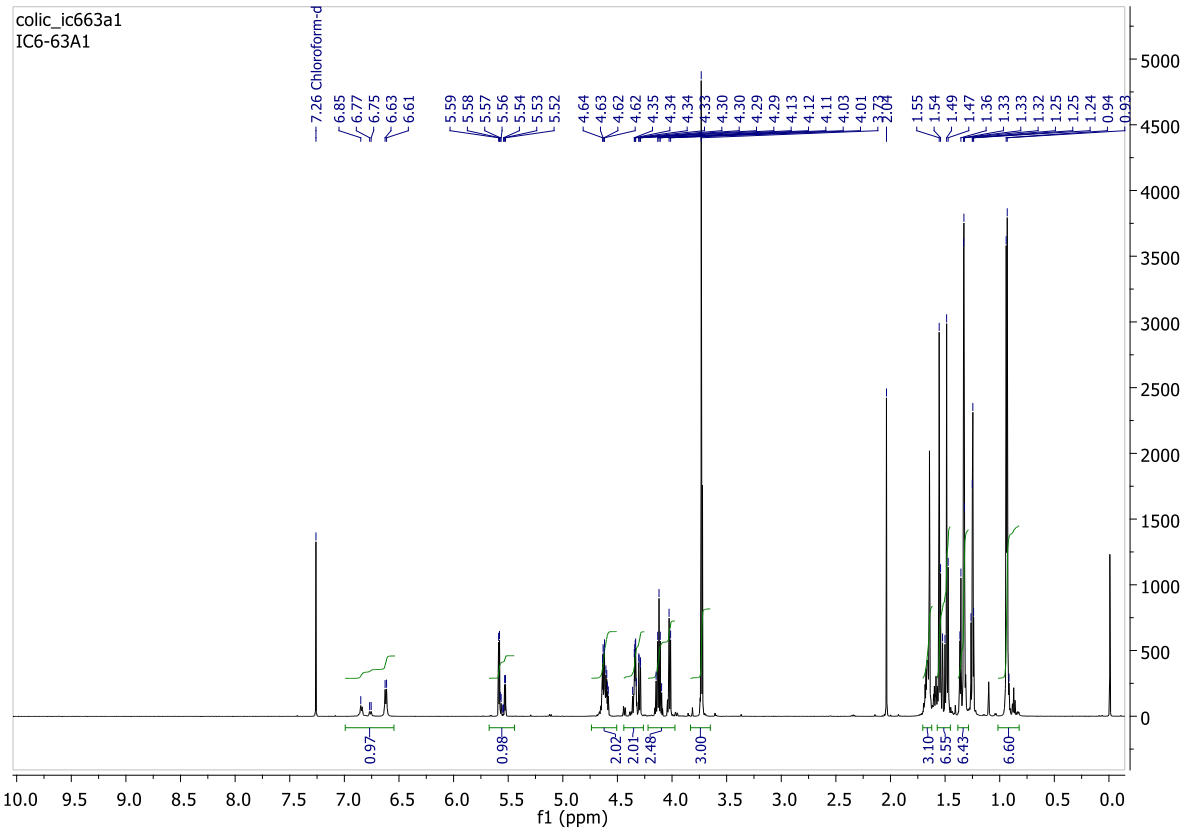


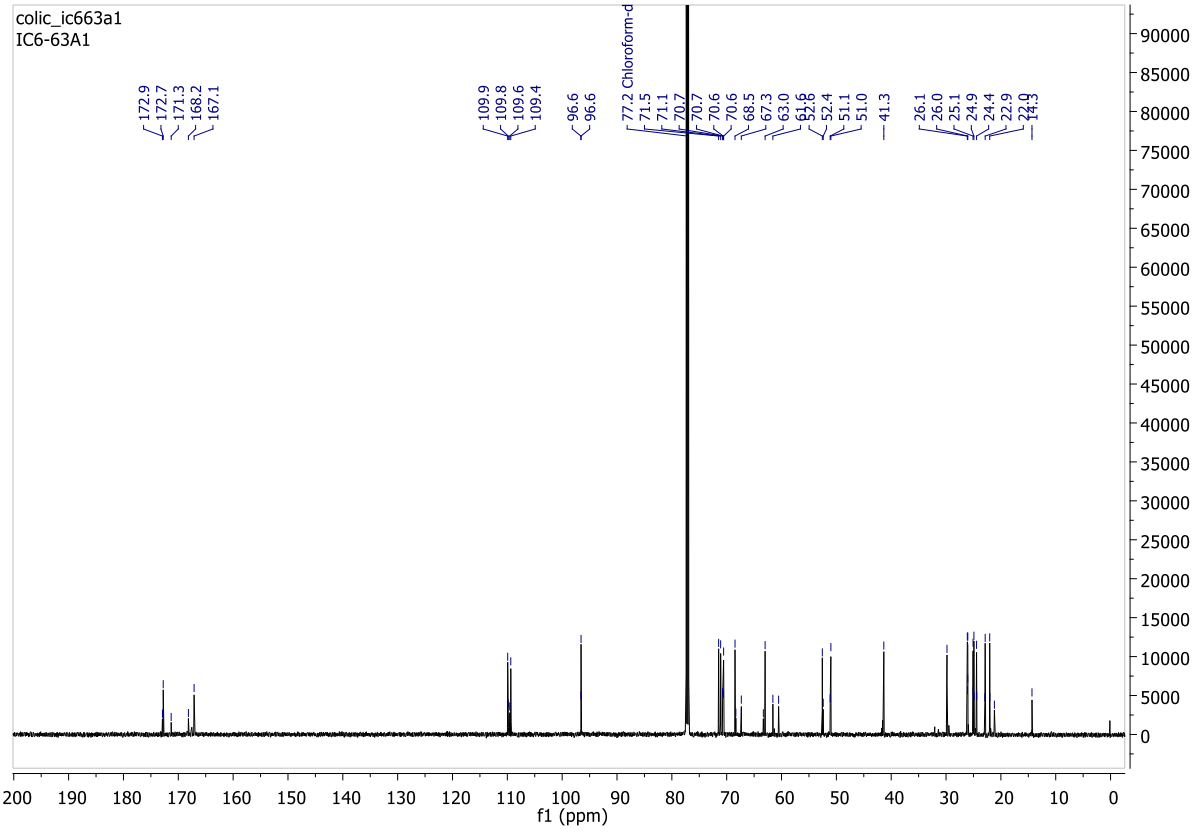
Compound Sor-2g (single diastereoisomer)



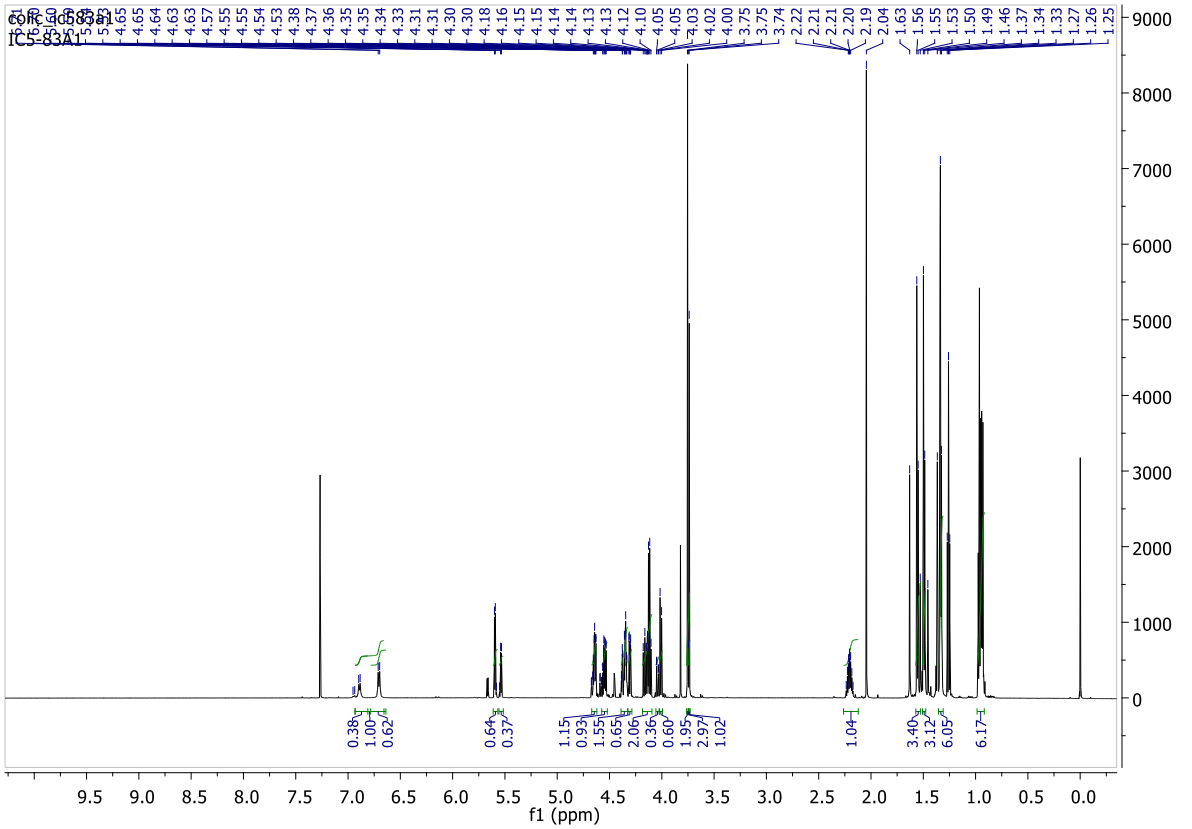


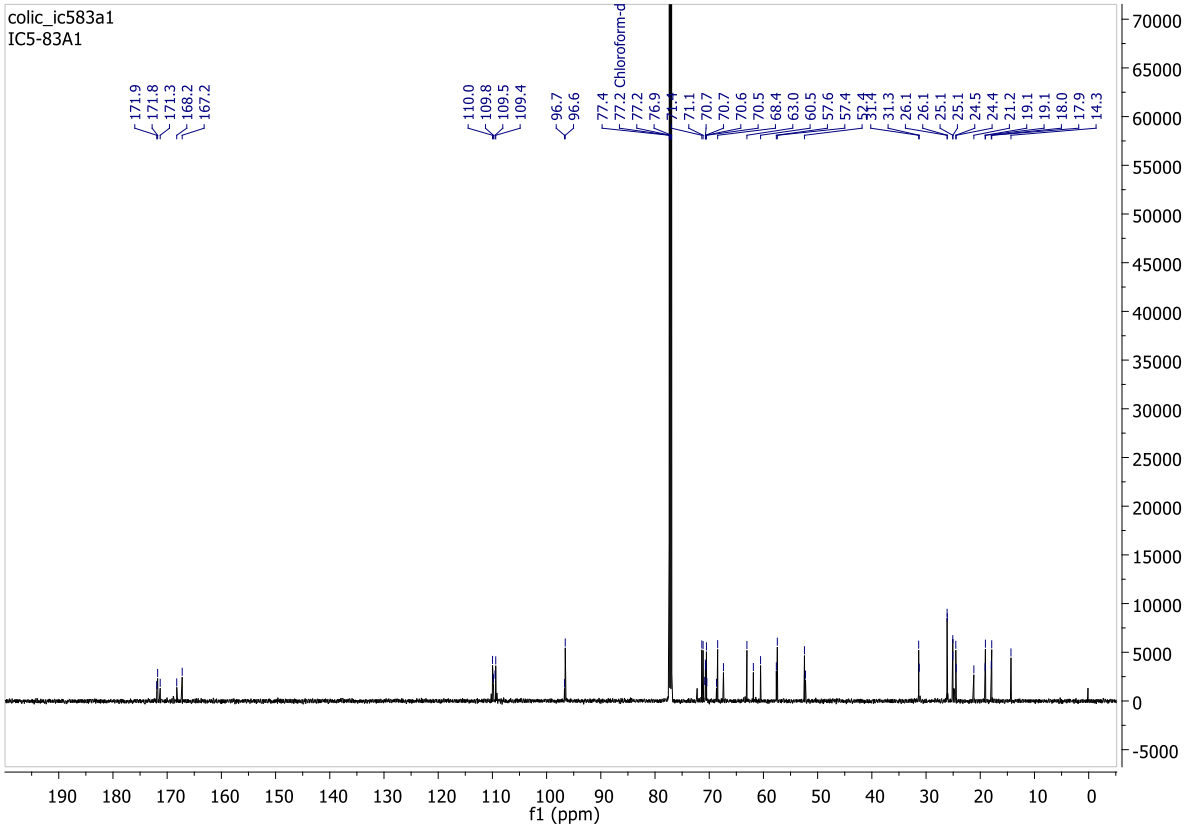
Compound Gal-3a (mixture of diastereoisomers, d.r. nd)



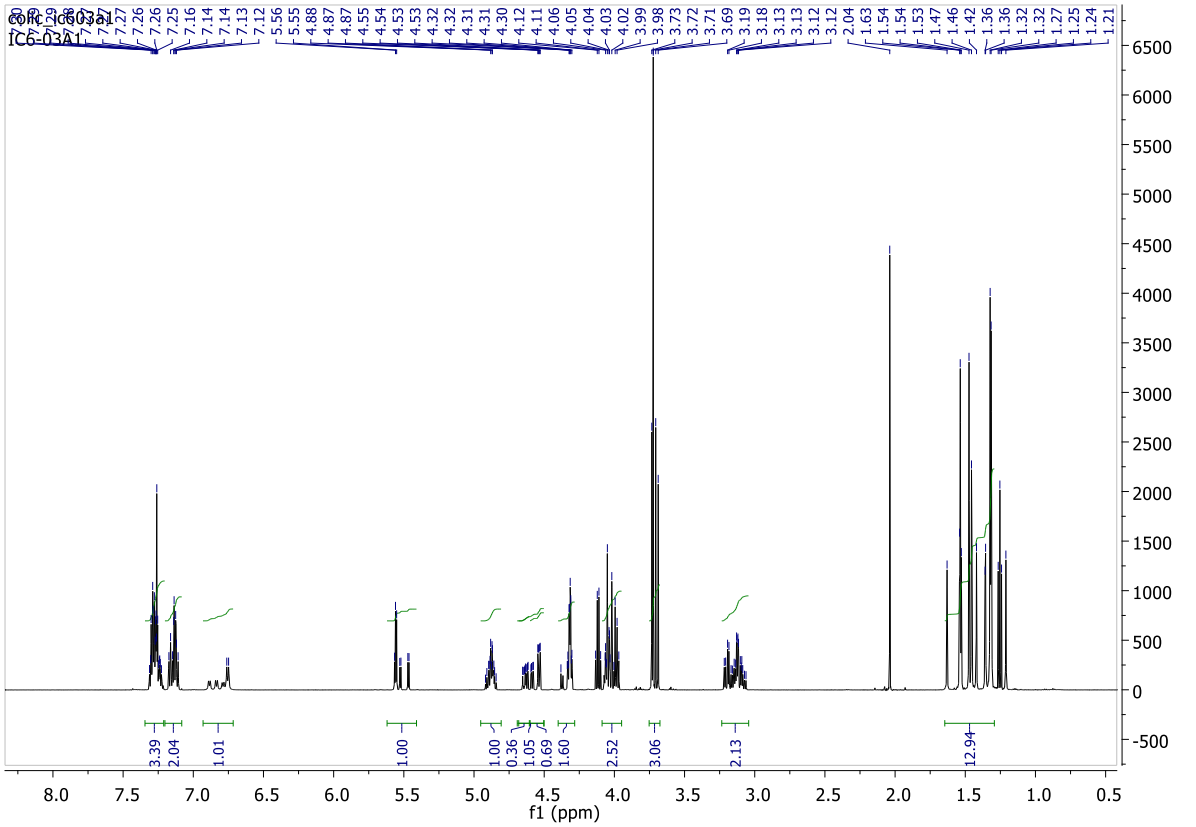


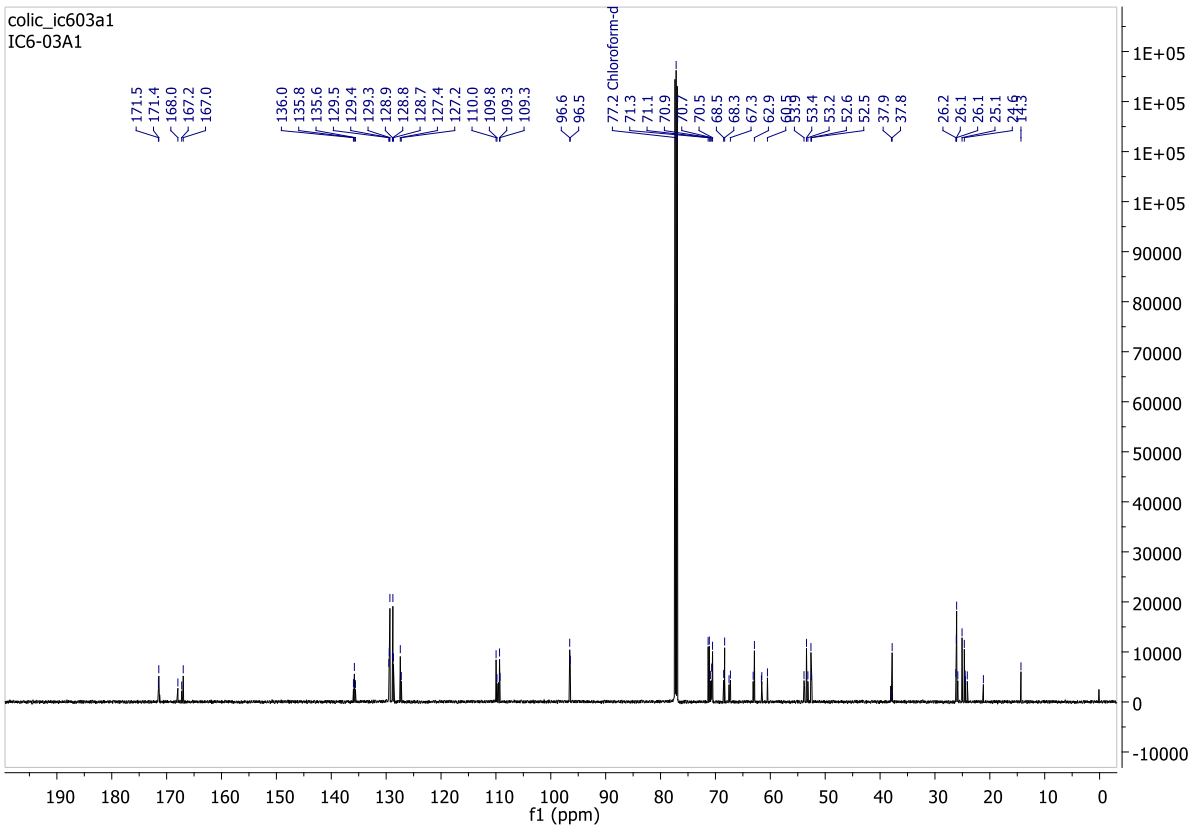
Compound Gal-3b (mixture of diastereoisomers, d.r. 65:35)



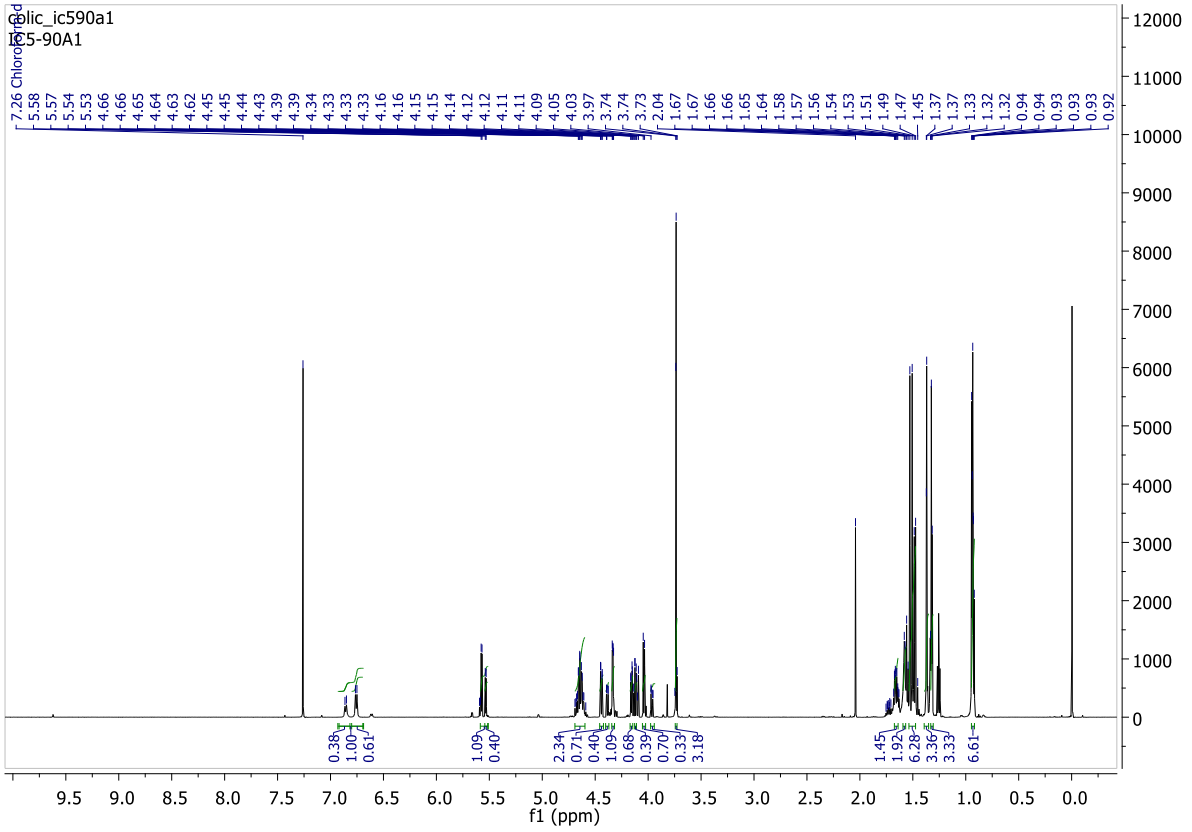


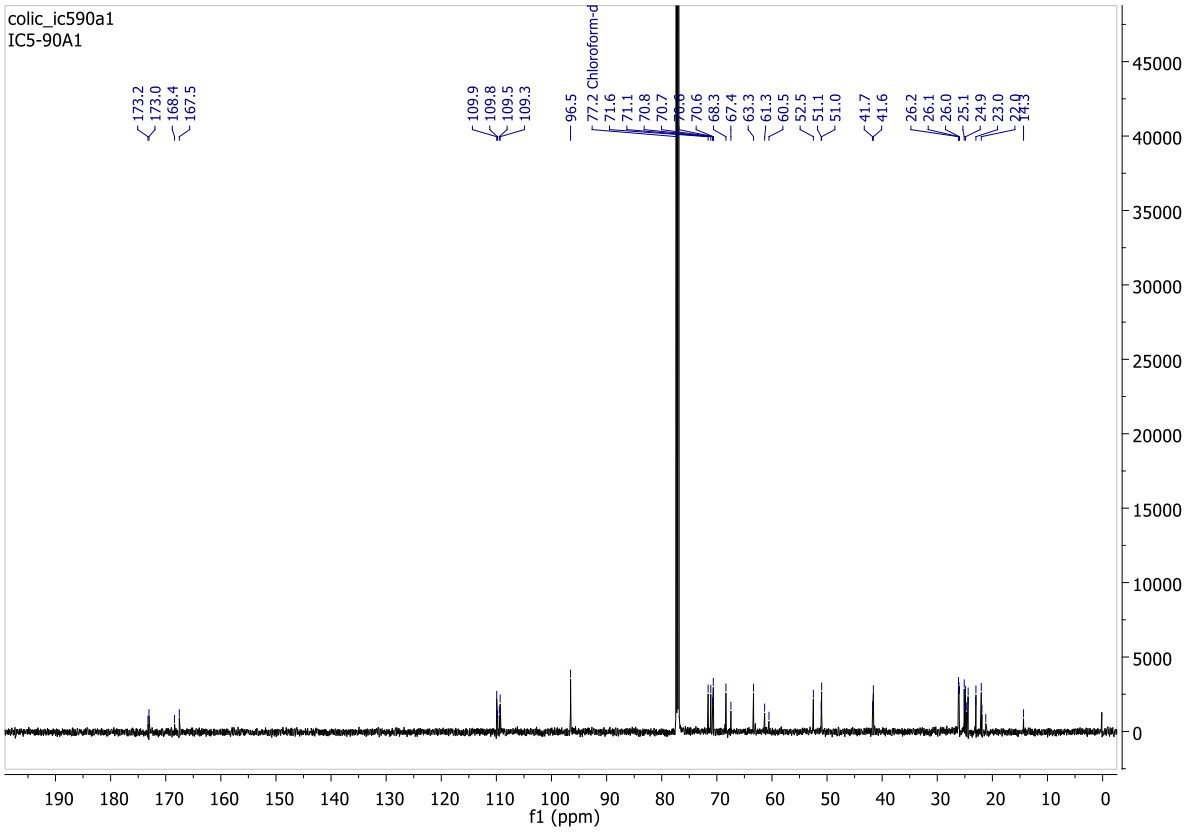
Compound Gal-3c (mixture of diastereoisomers, d.r. nd)



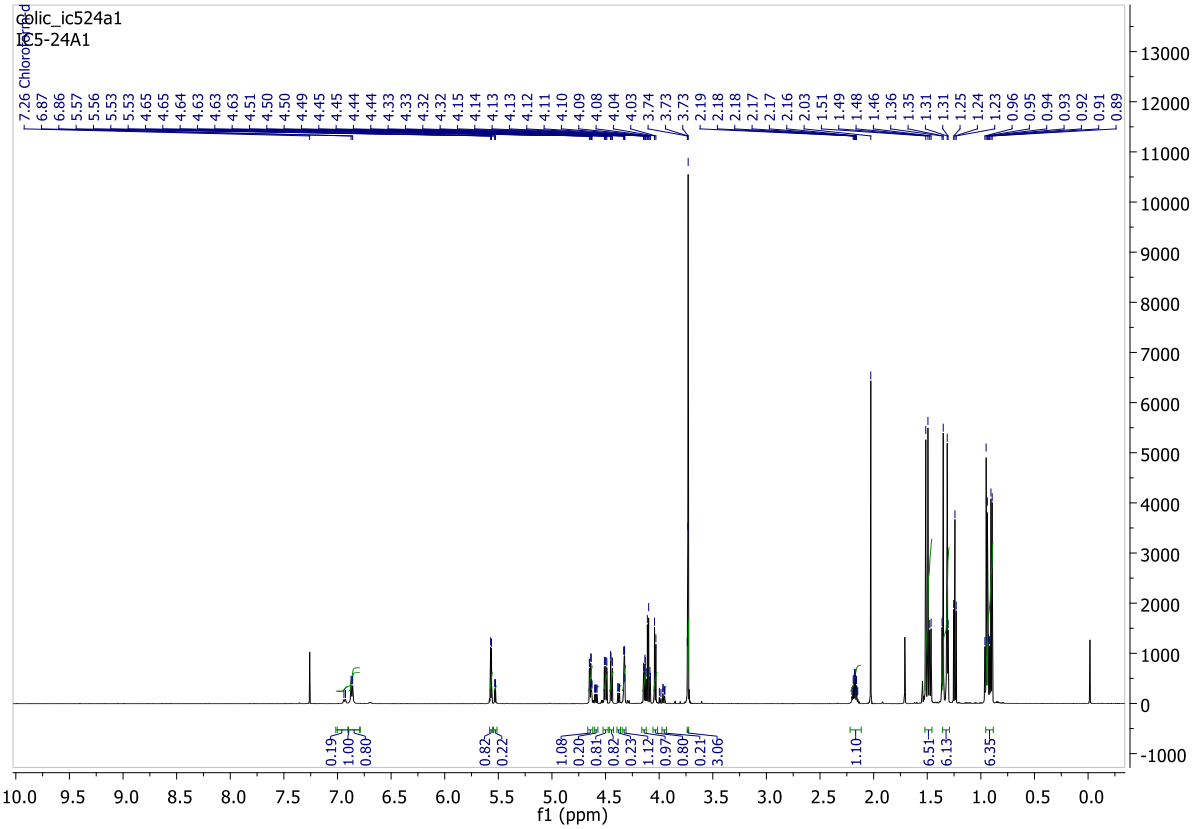


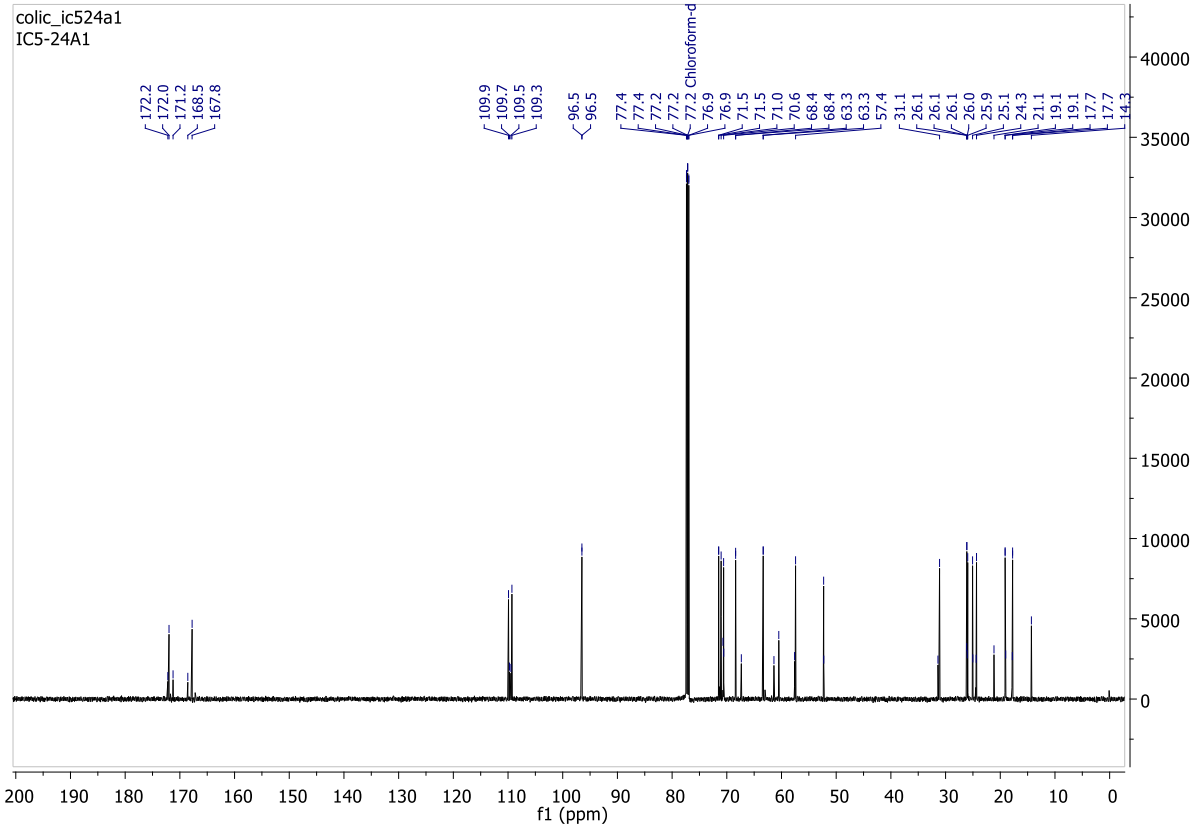
Compound Gal-3d (mixture of diastereoisomers, d.r. 60:40)



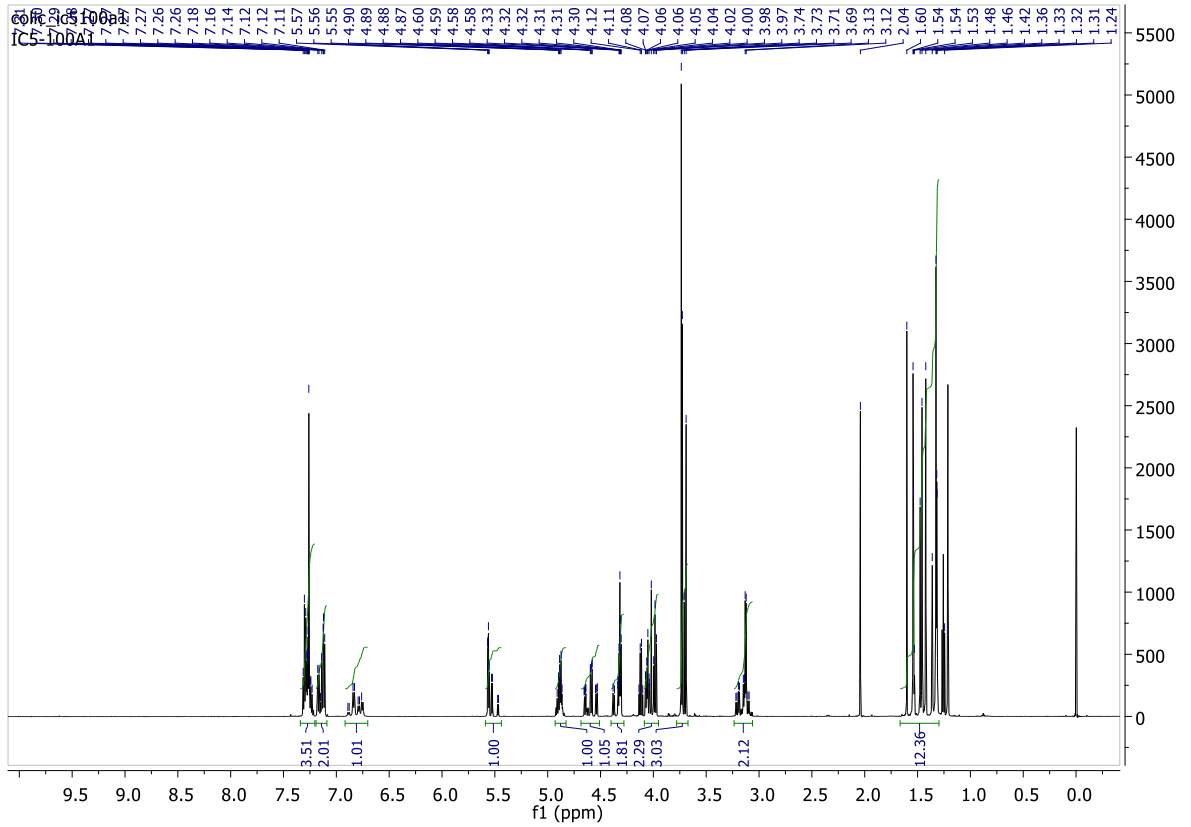


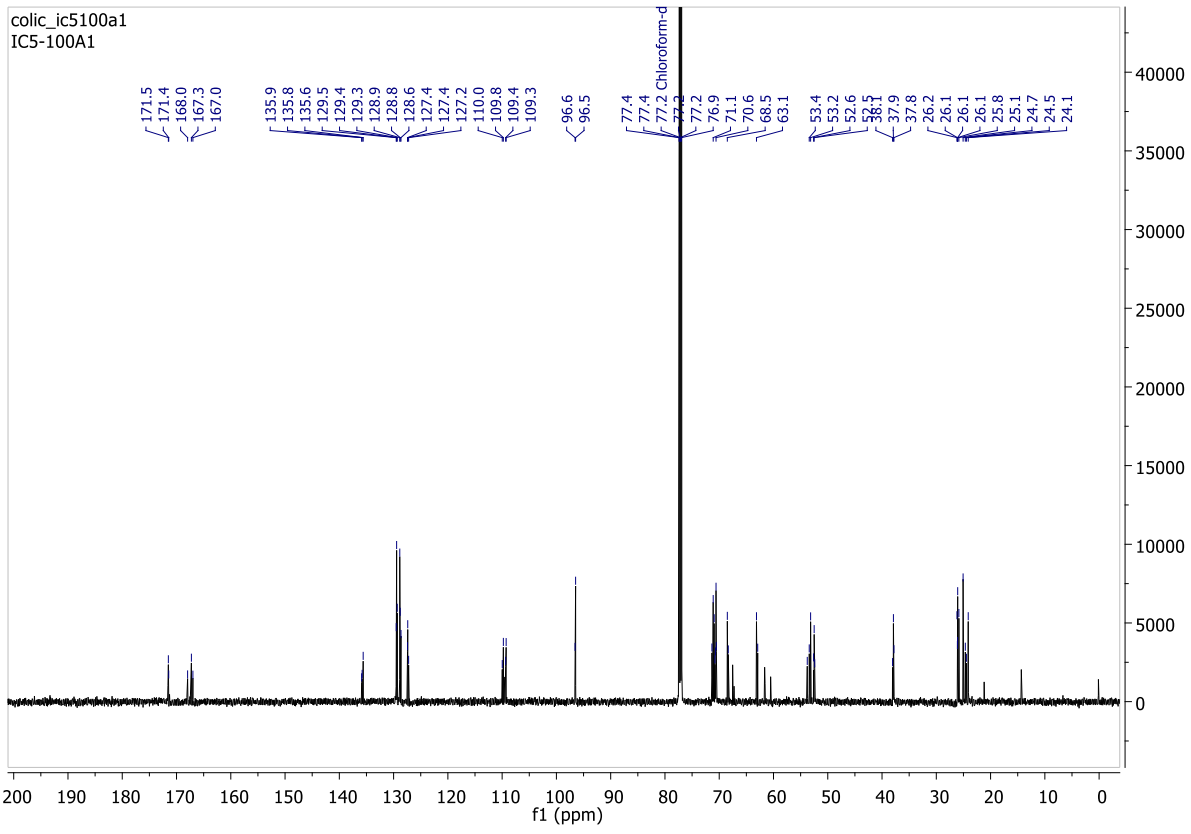
Compound Gal-3e (mixture of diastereoisomers, d.r. 80:20)



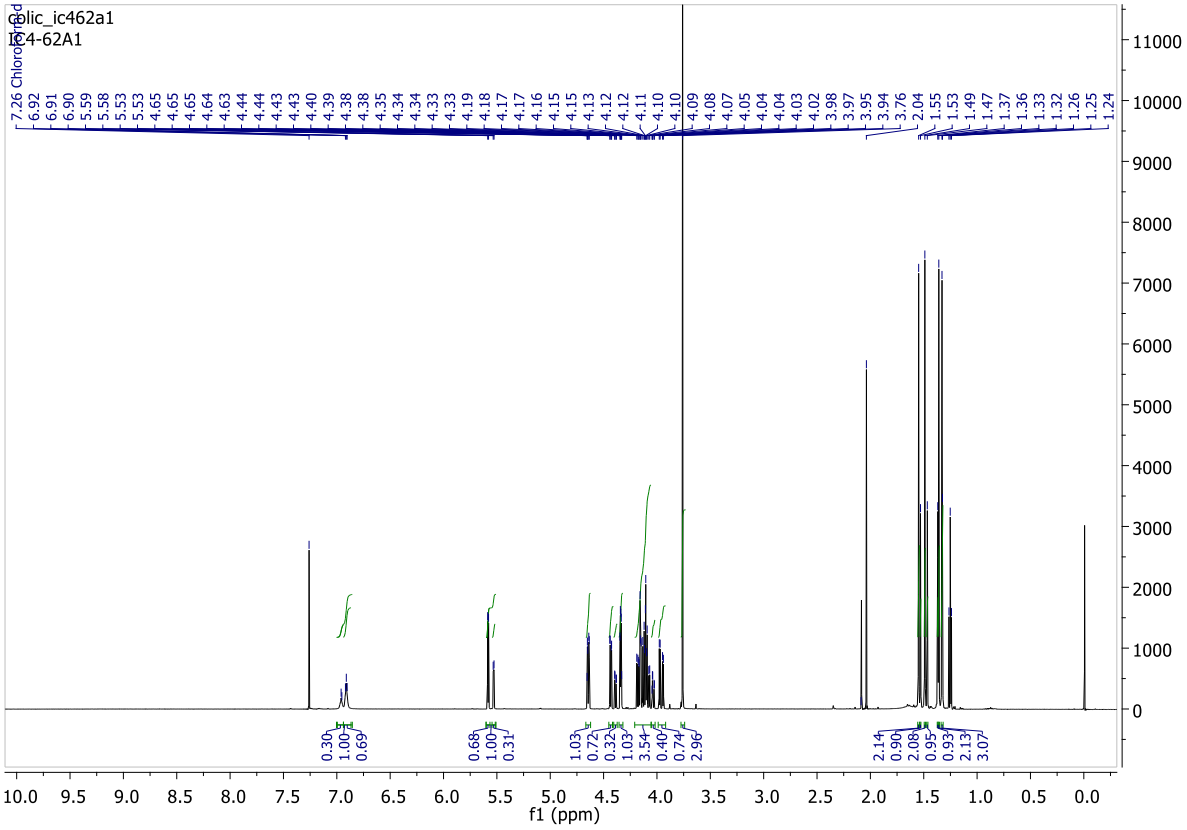


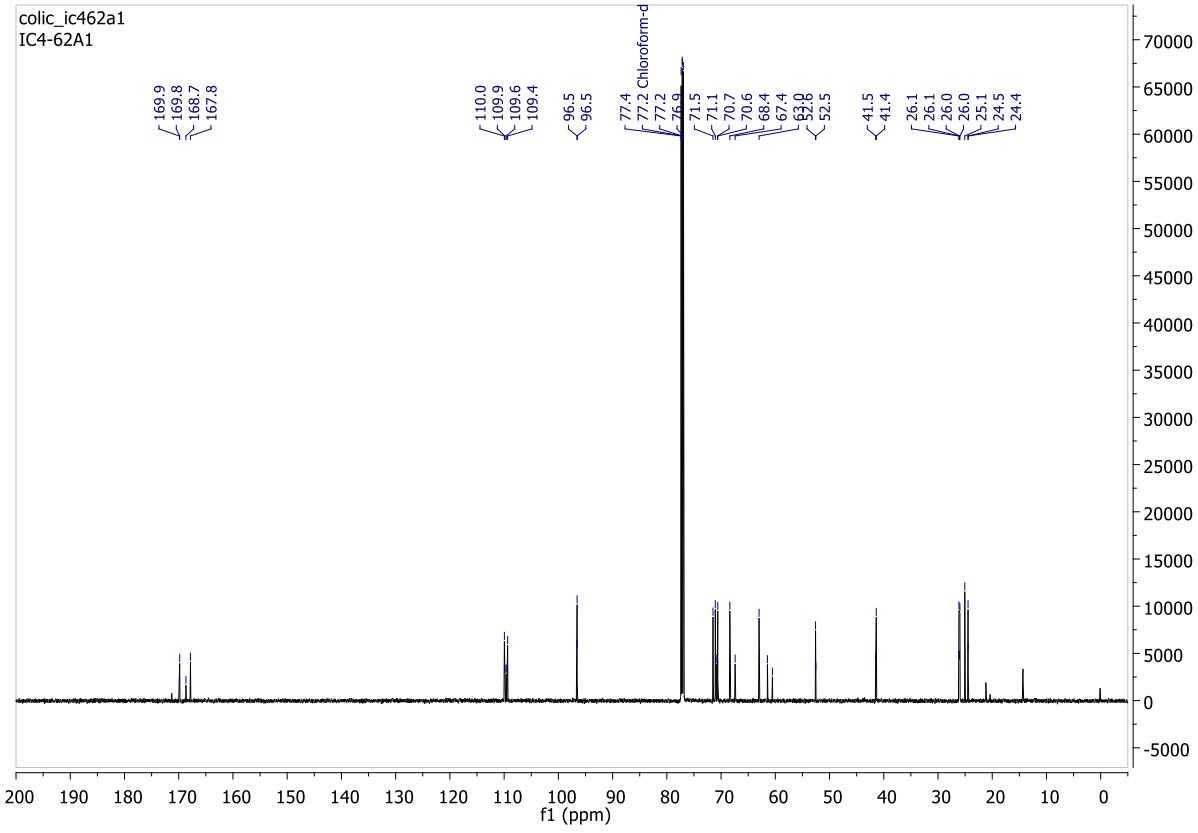
Compound Gal-3f (mixture of diastereoisomers, d.r. nd)



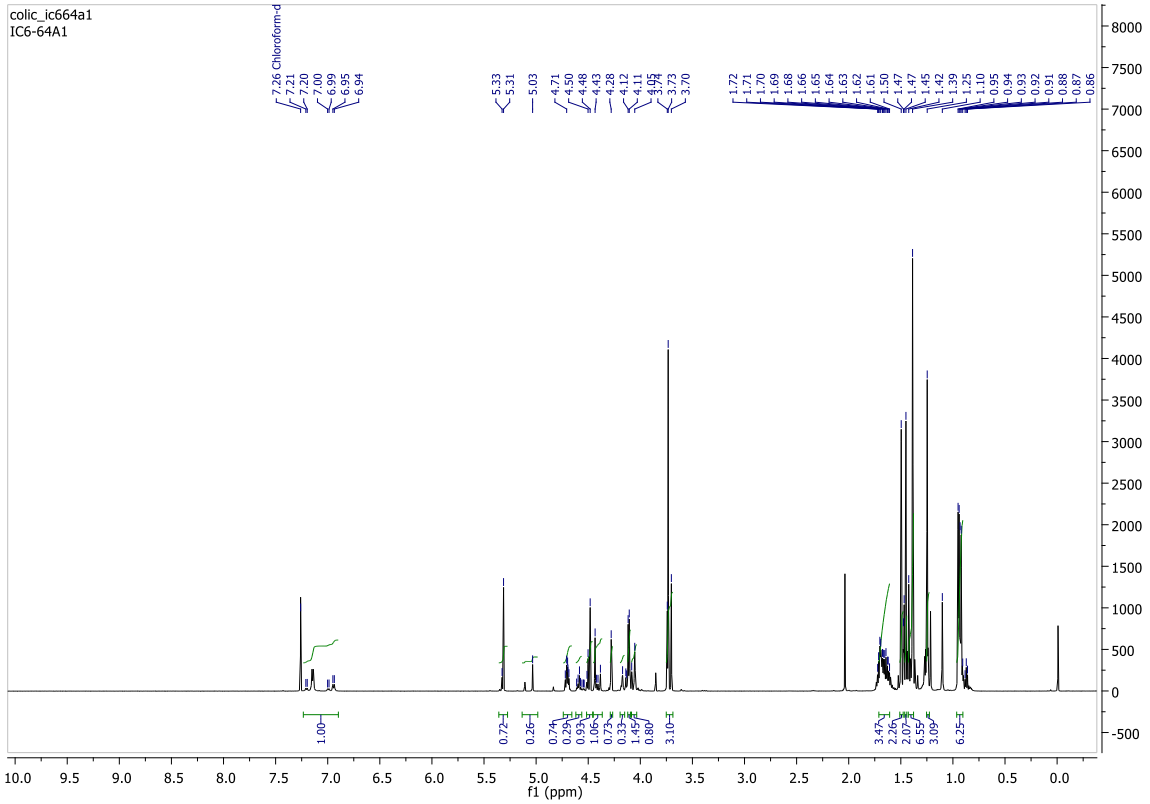


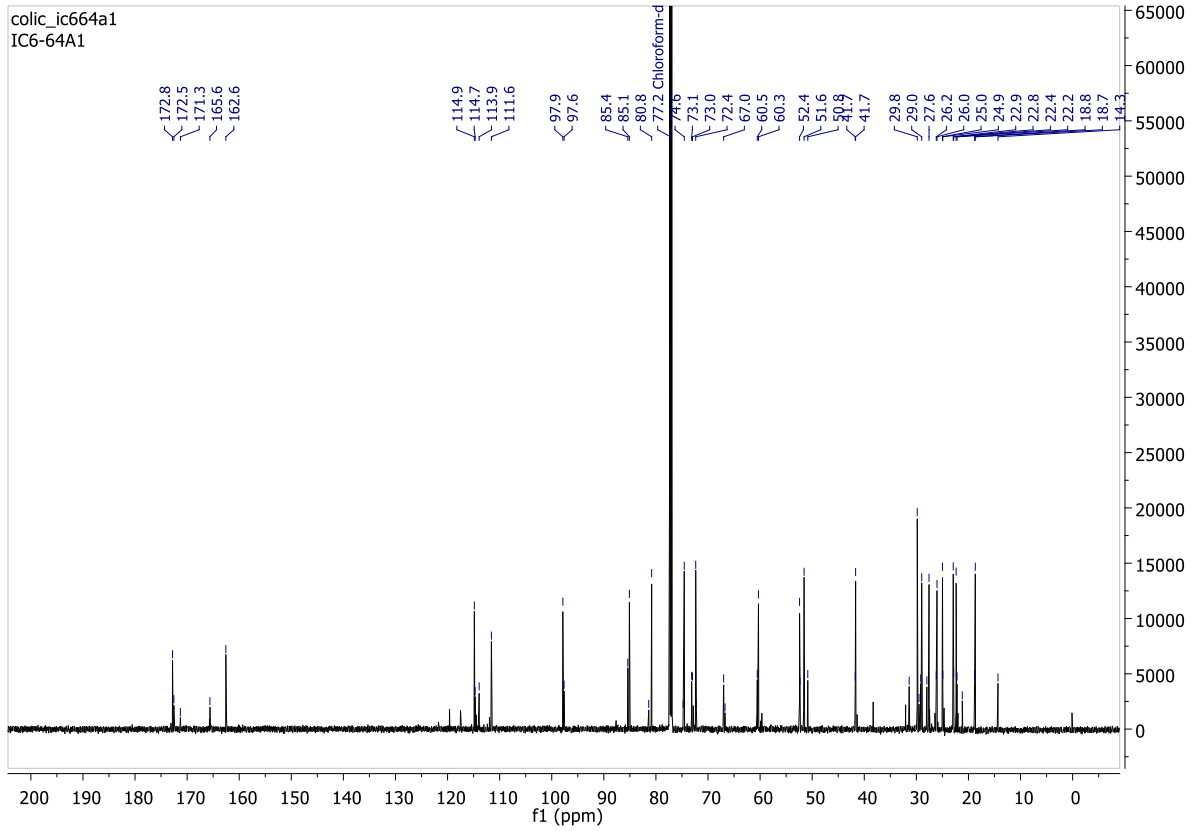
Compound Gal-3g (mixture of diastereoisomers, d.r. 70:30)



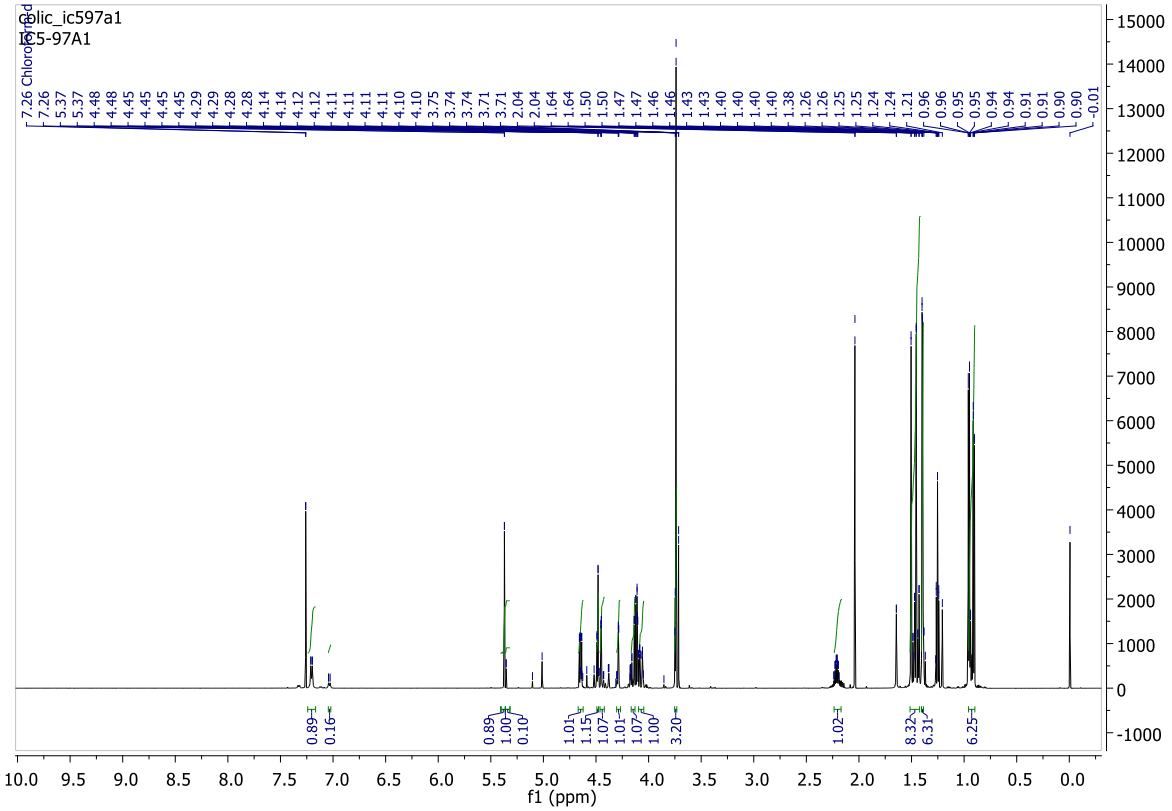


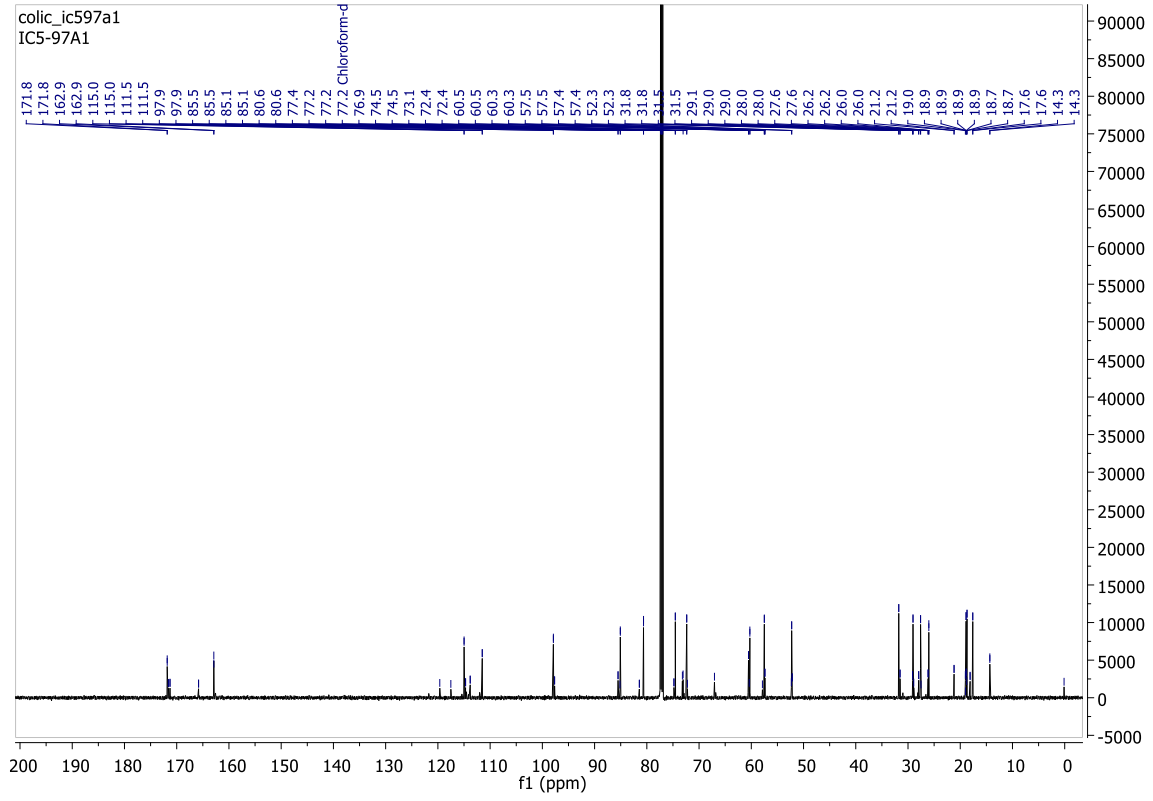
Compound Sor-3a (mixture of diastereoisomers, d.r. 70:30)



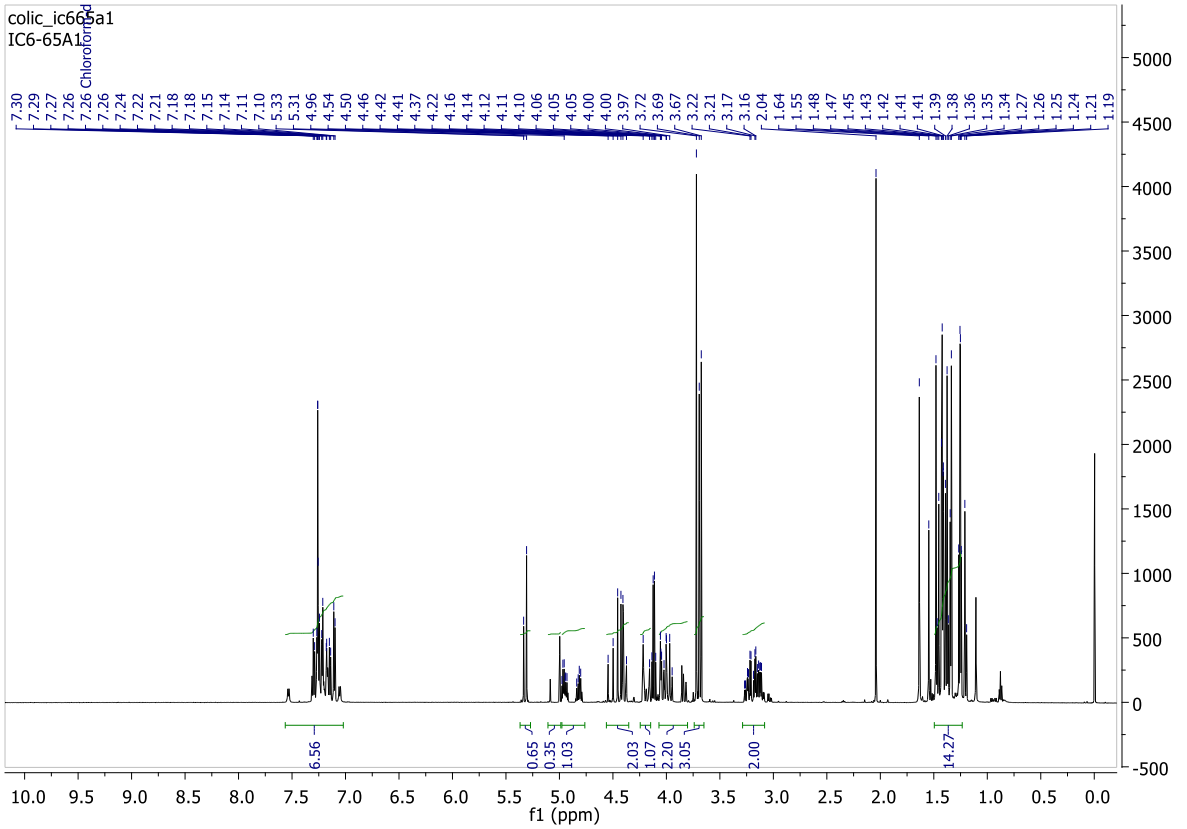


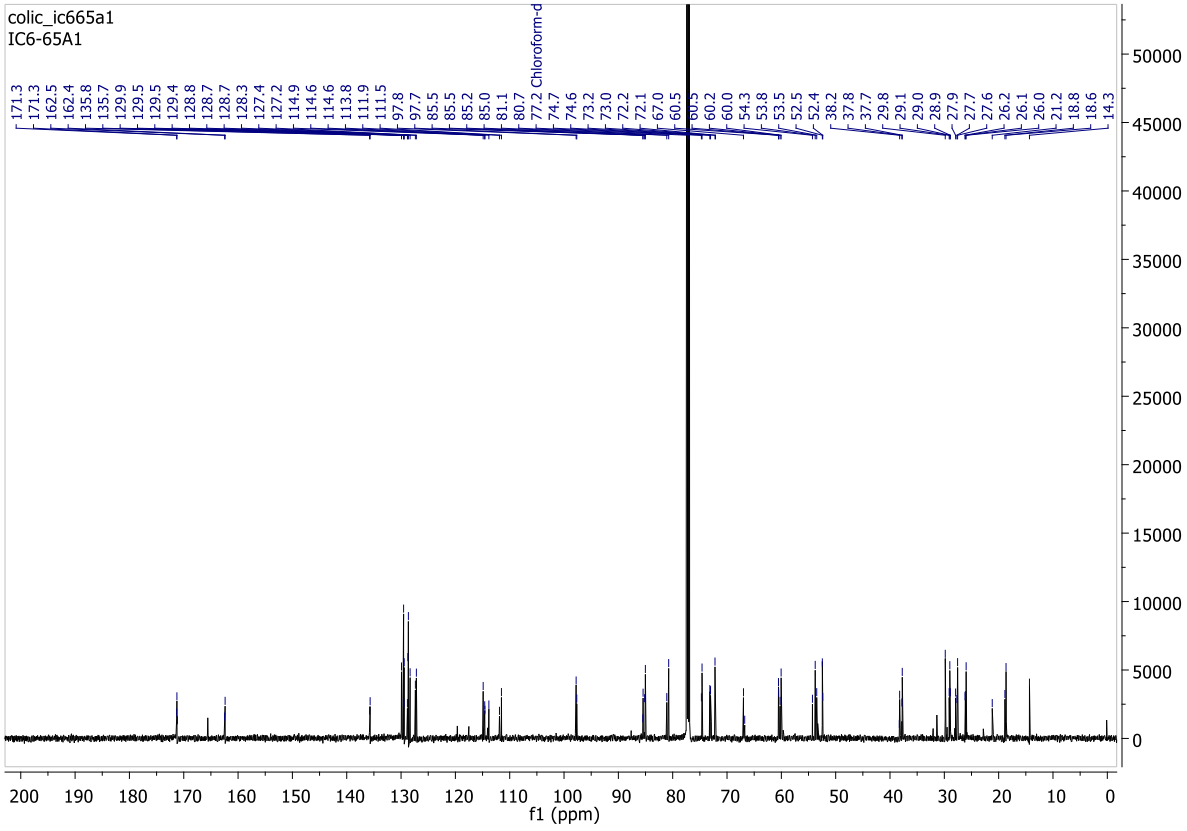
Compound Sor-3b (mixture of diastereoisomers, d.r. 70:30)



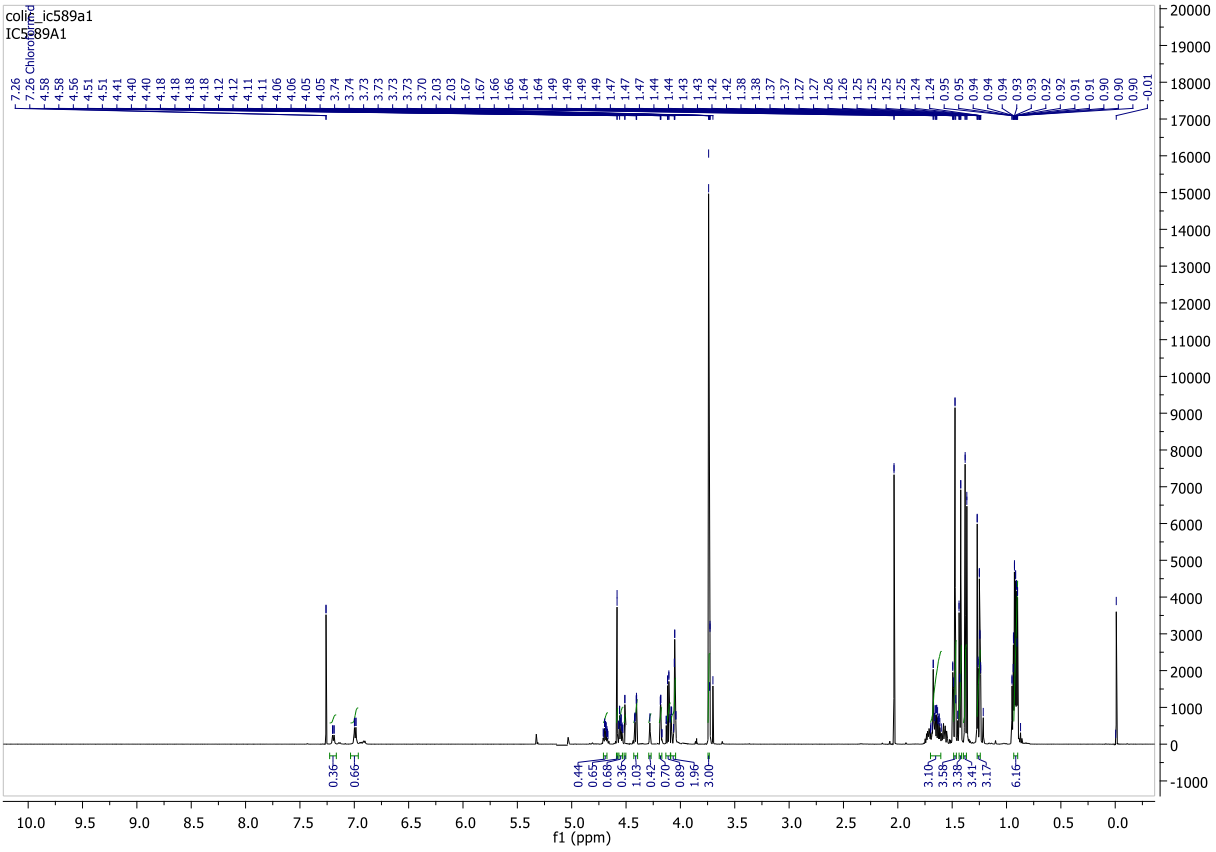


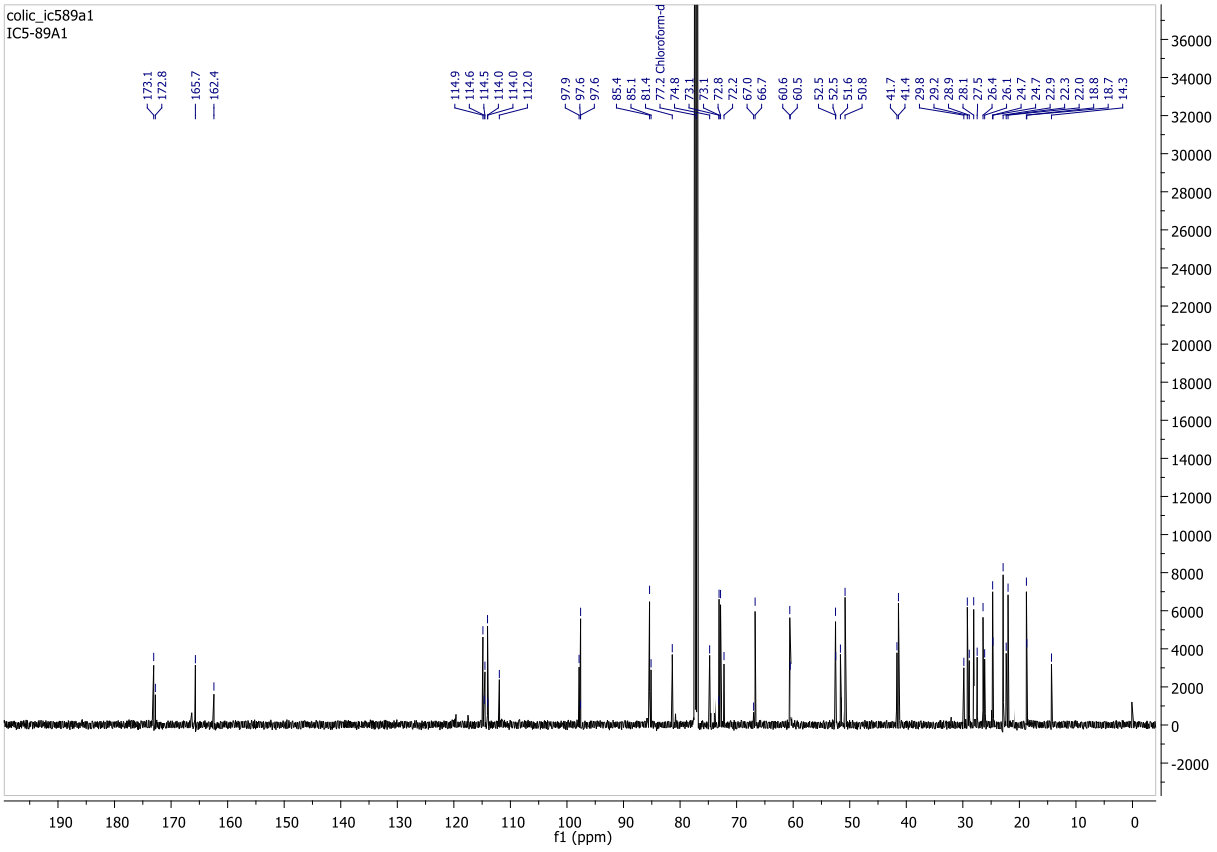
Compound Sor-3c (mixture of diastereoisomers, d.r. 65:35)



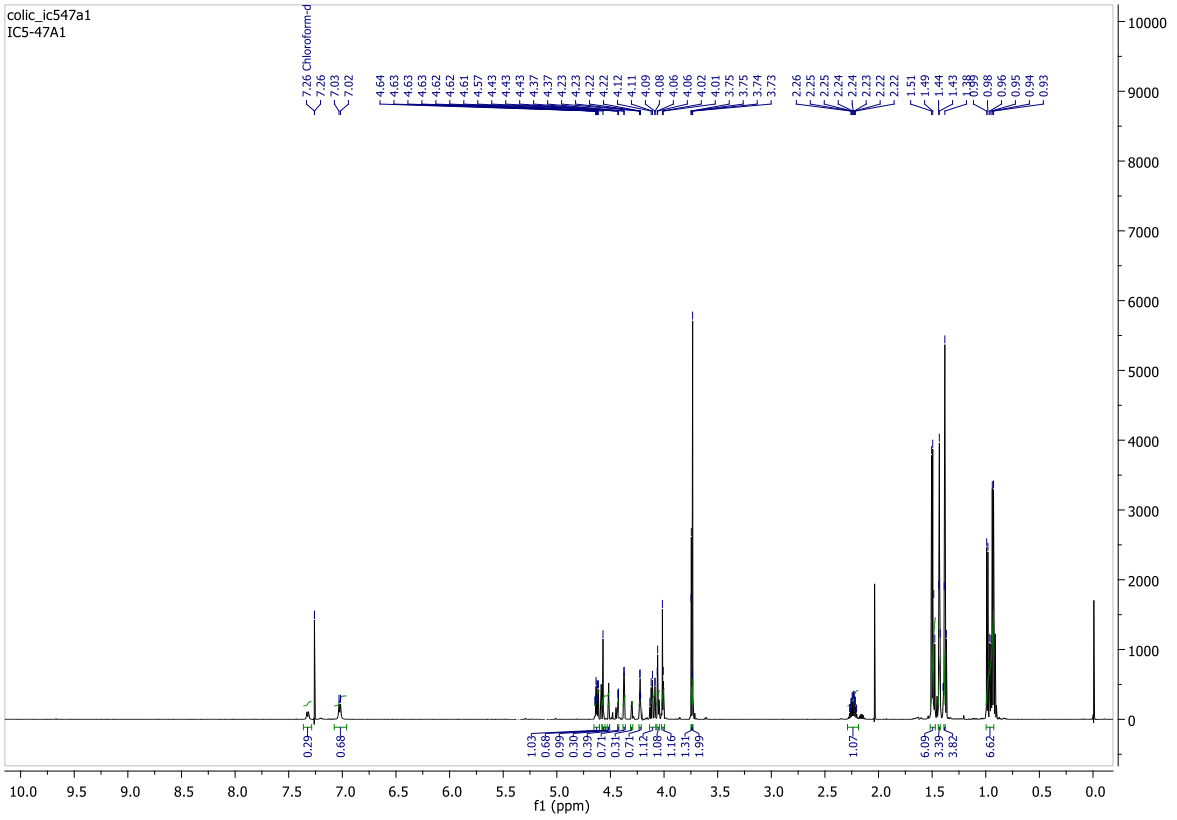


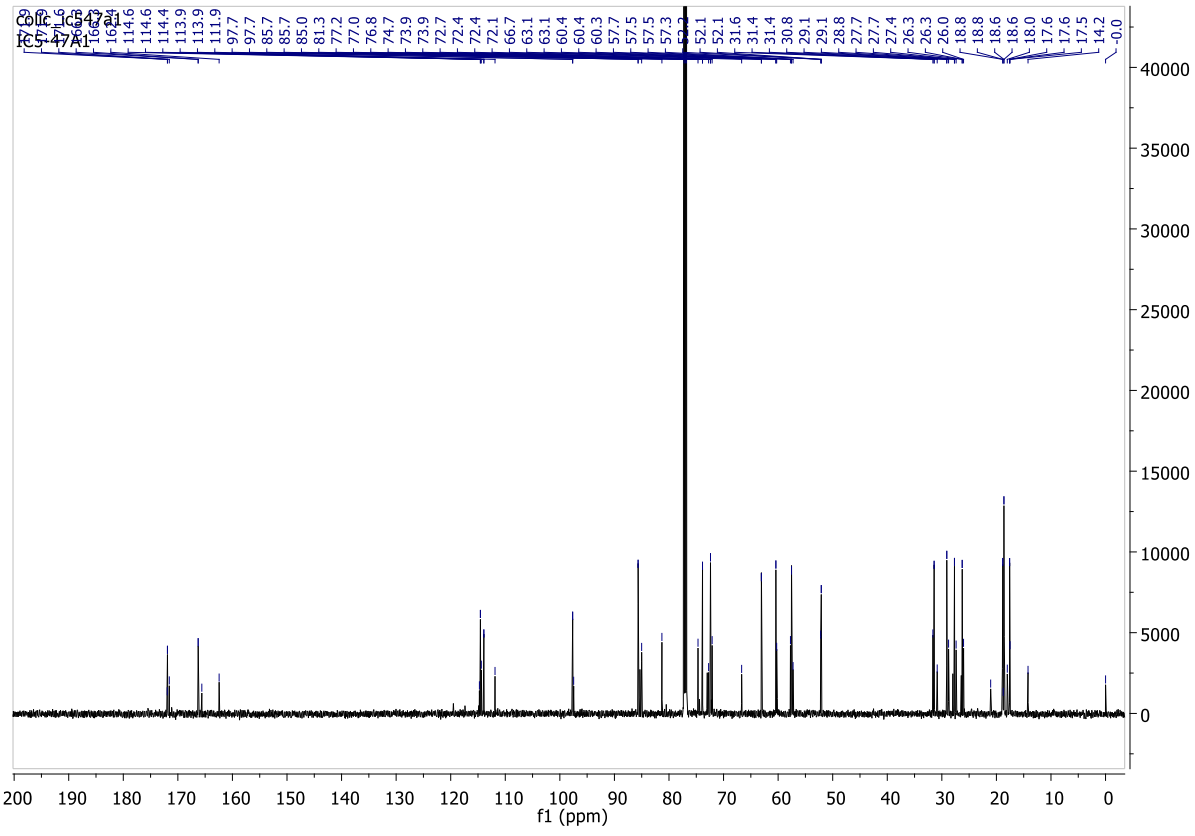
Compound Sor-3d (mixture of diastereoisomers, d.r. 65:35)



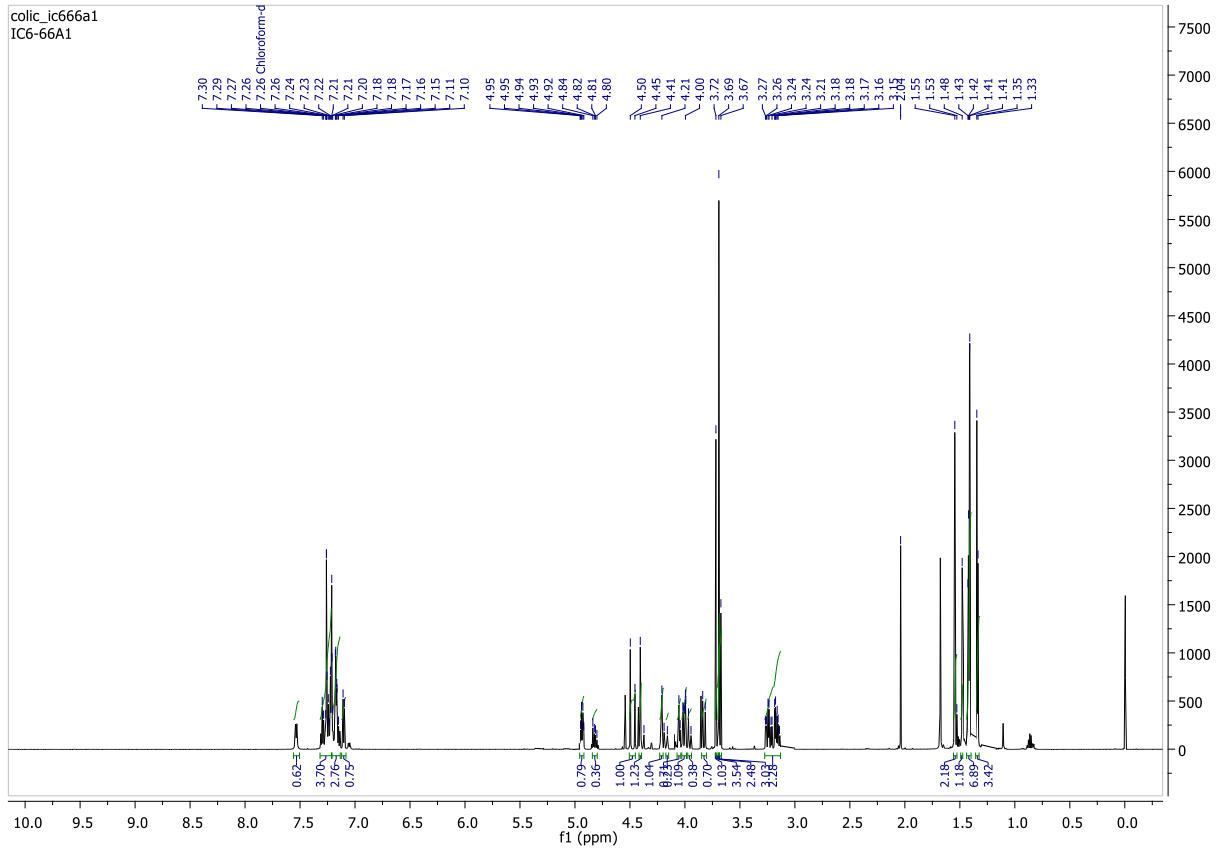


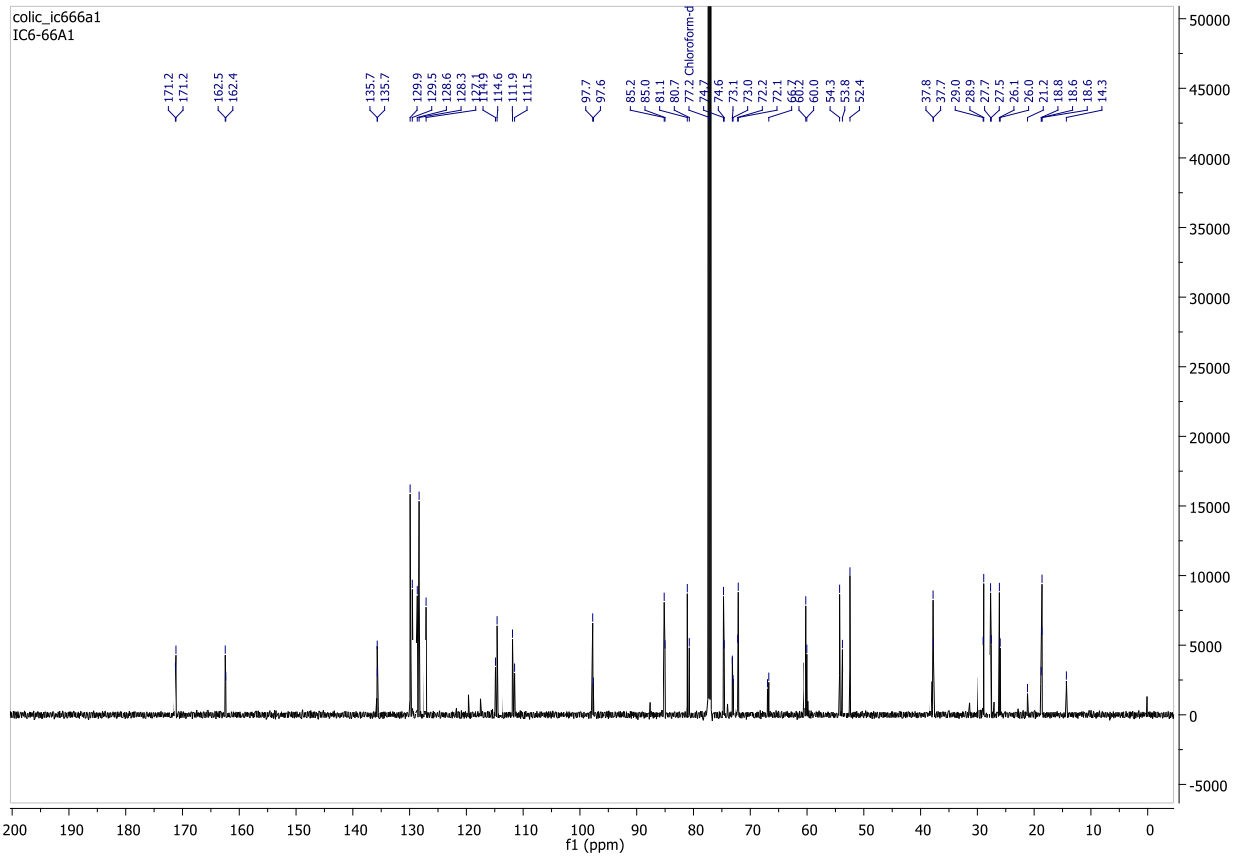
Compound Sor-3e (mixture of diastereoisomers, d.r. 70:30)



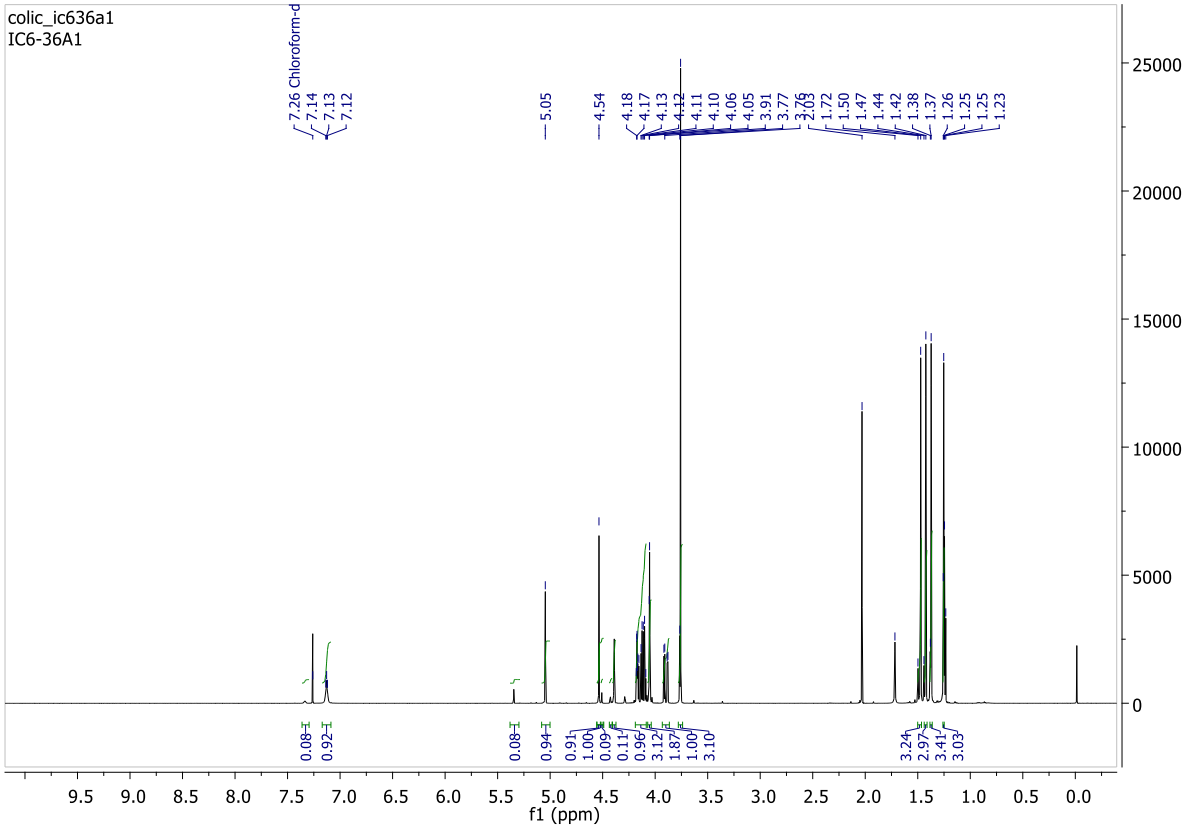


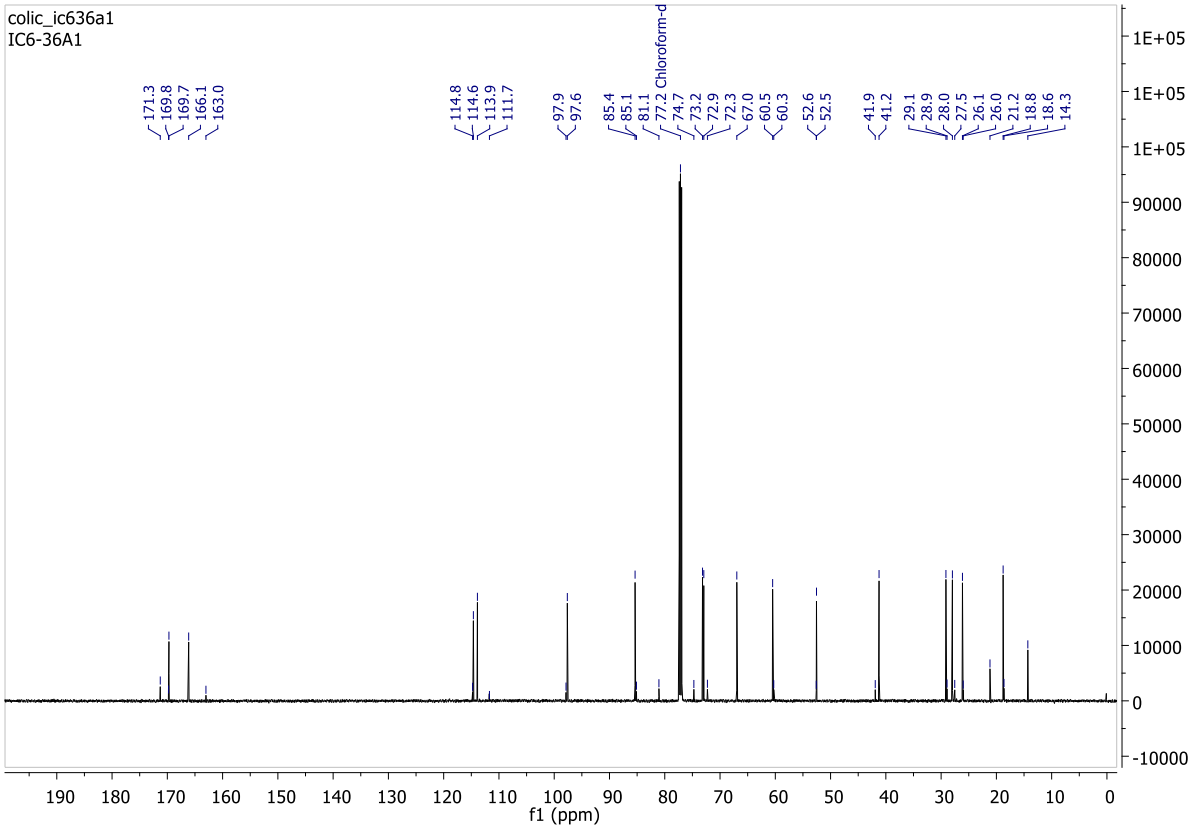
Compound Sor-3f (mixture of diastereoisomers, d.r. 70:30)



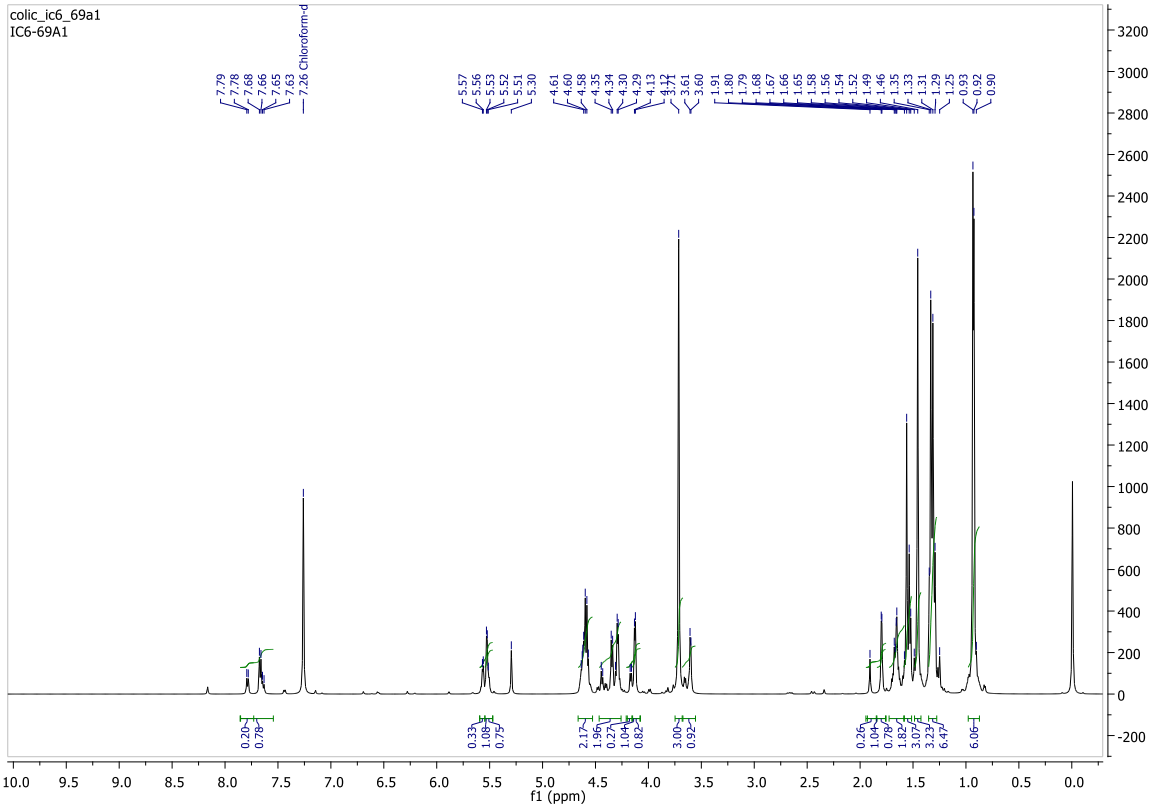


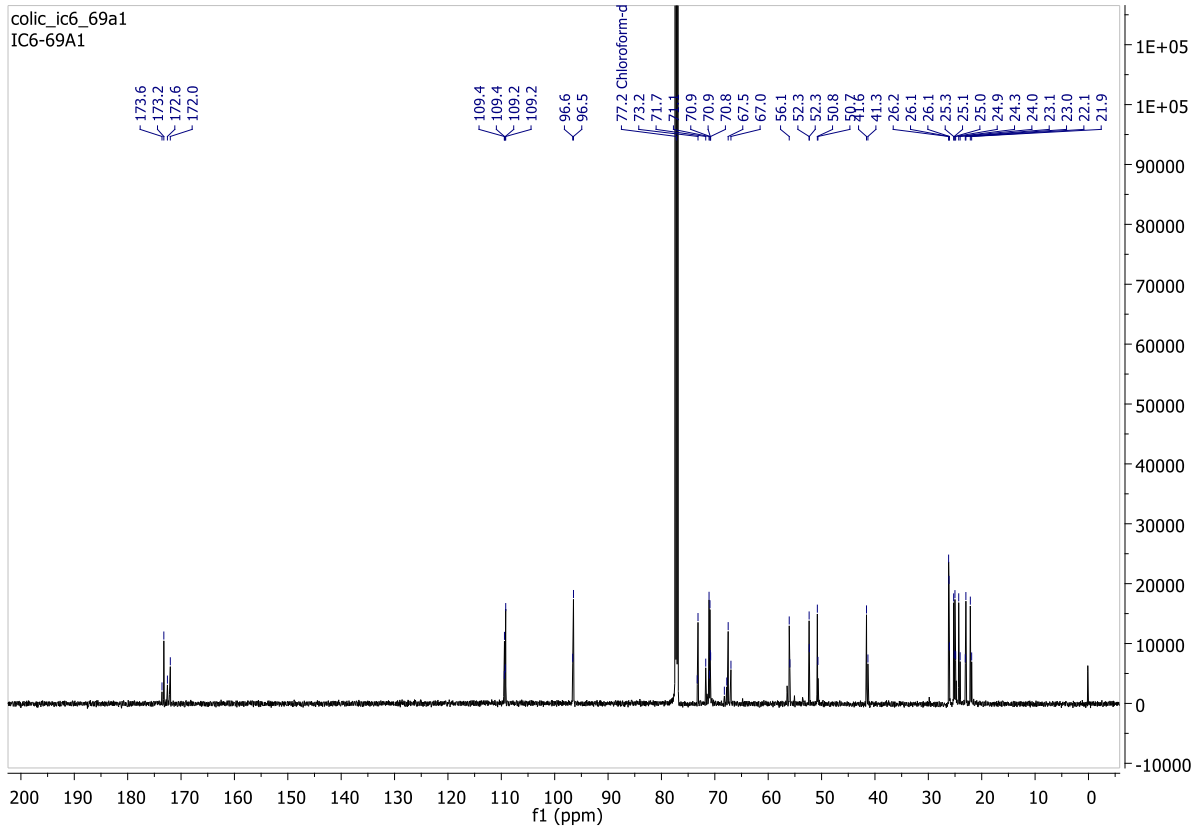
Compound Sor-3g (mixture of diastereoisomers, d.r. >95:5)



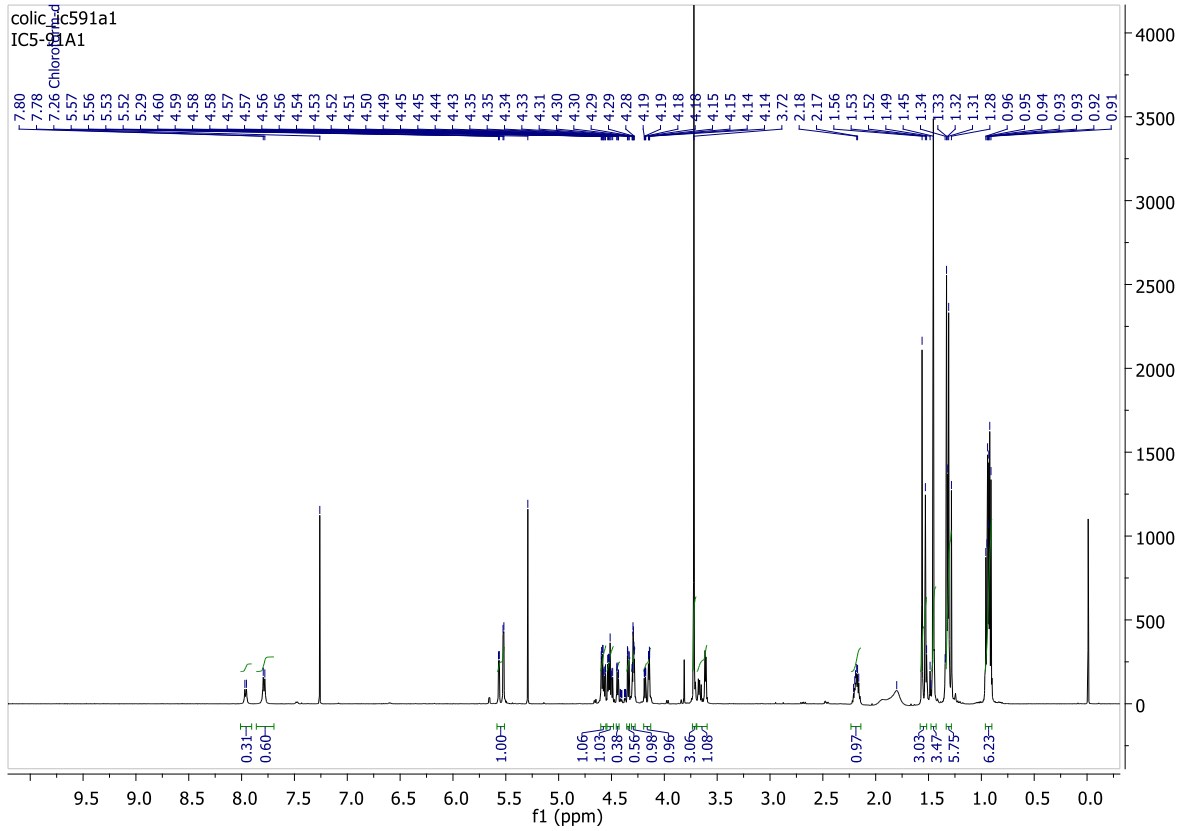


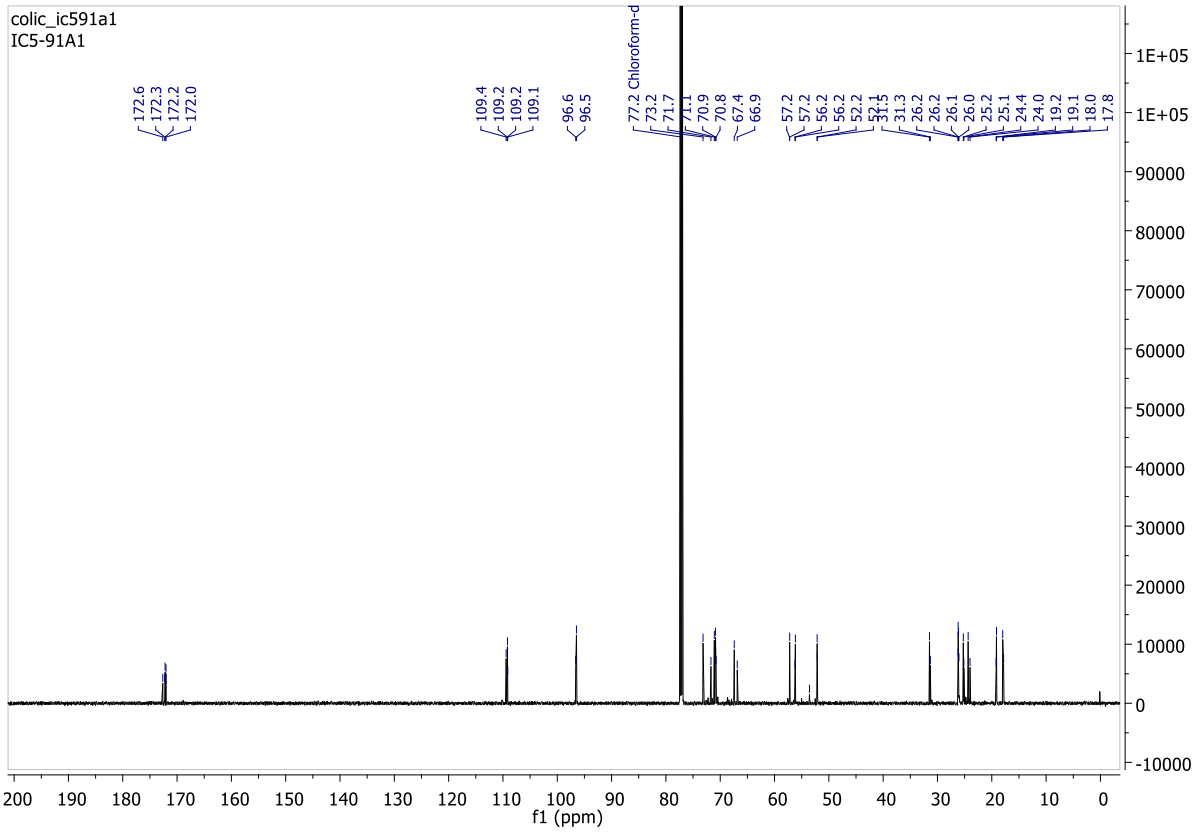
Compound Gal-4a (mixture of diastereoisomers d.r. 75:25)



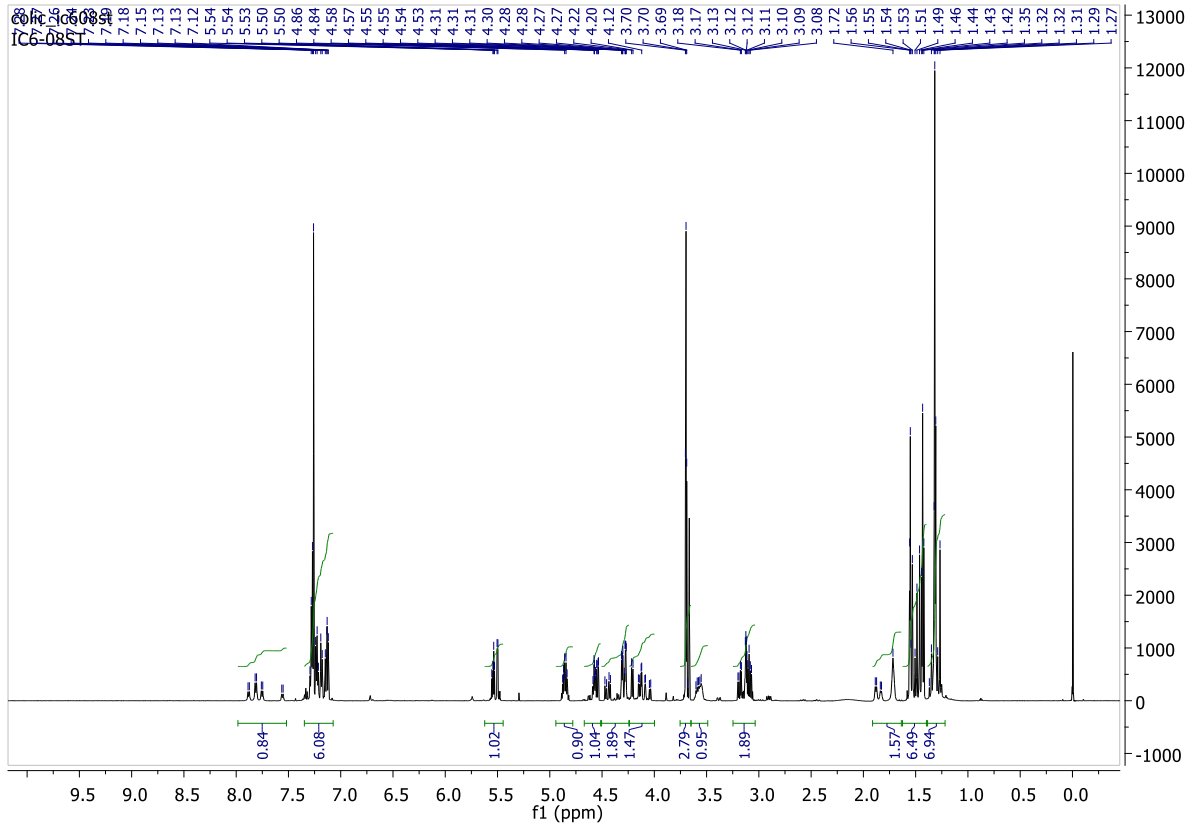


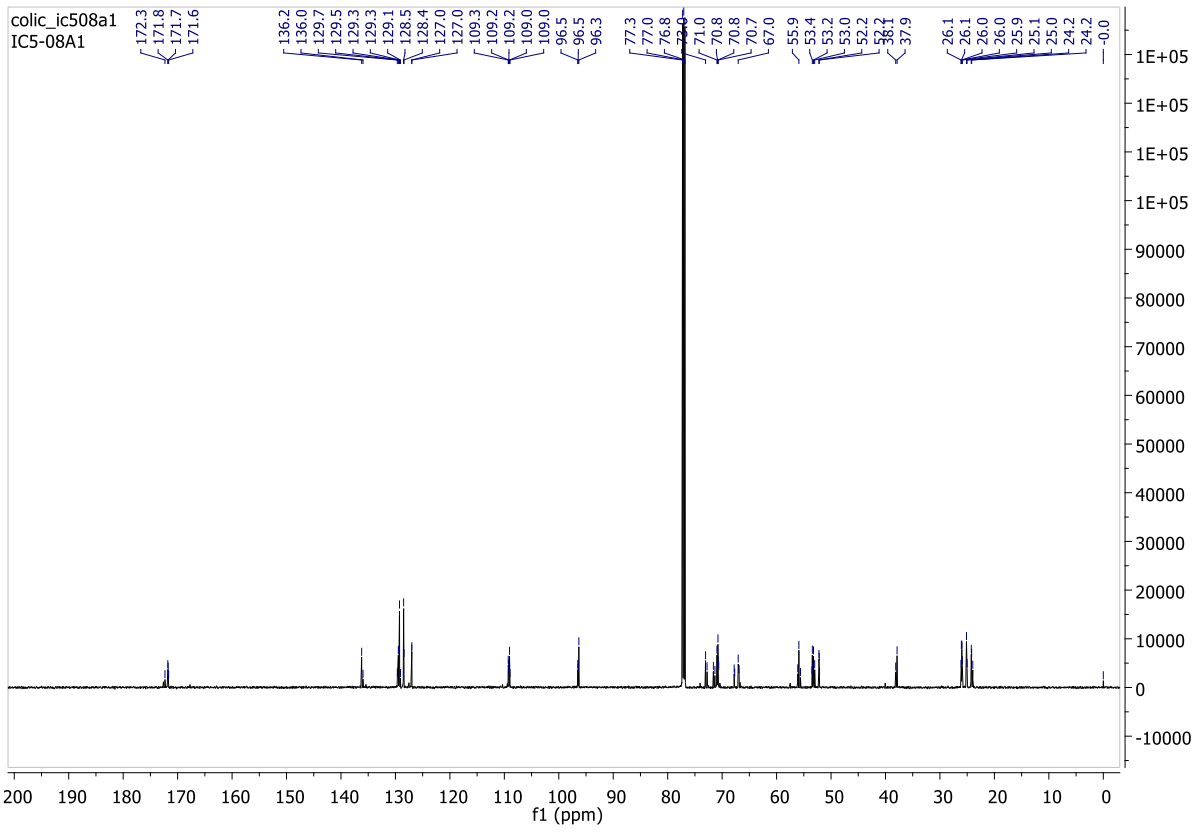
Compound Gal-4b (mixture of diastereoisomers d.r. 60:40)



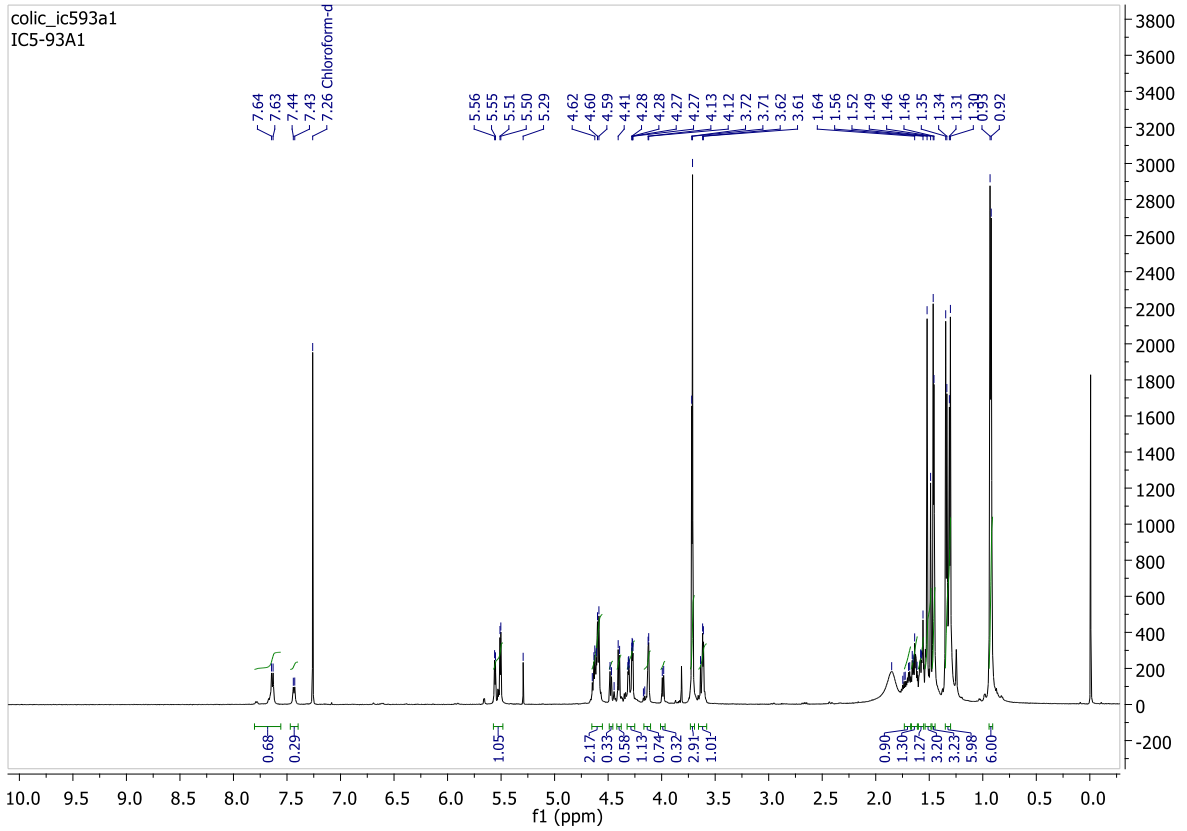


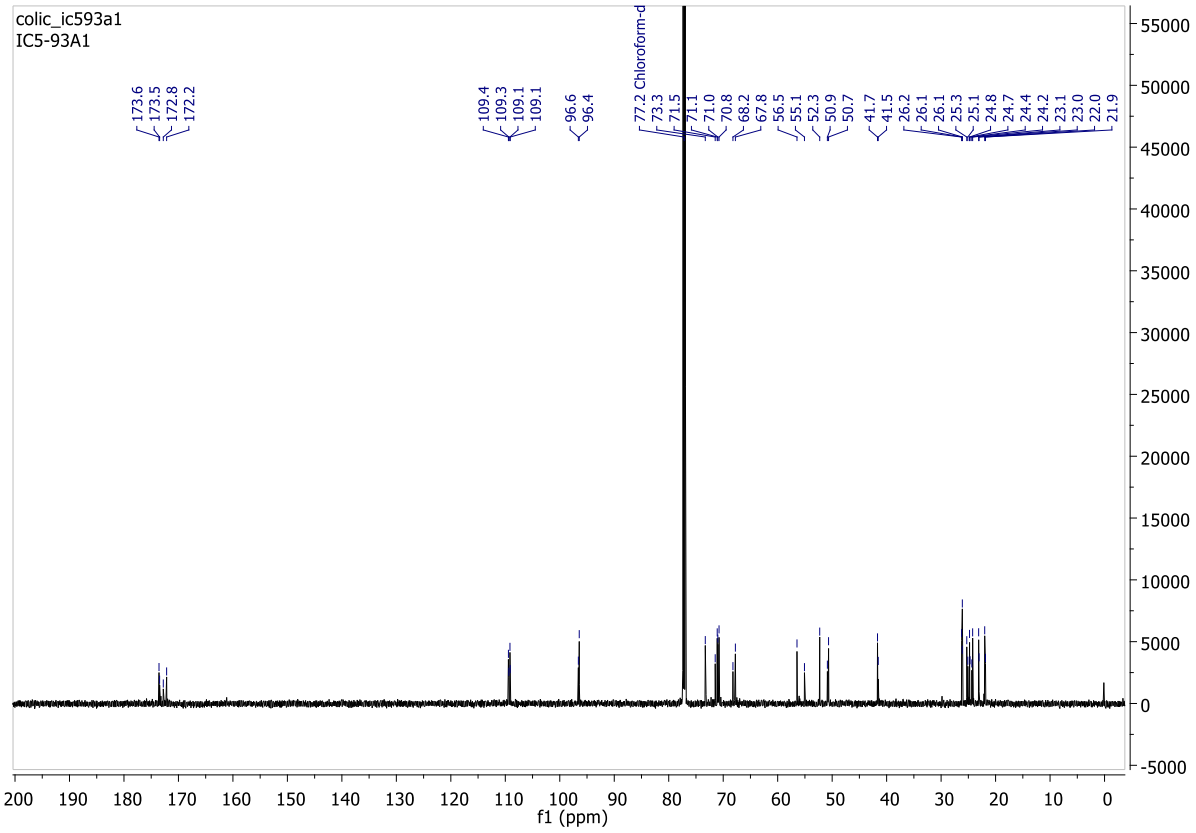
Compound Gal-4c (mixture of diastereoisomers d.r. nd)



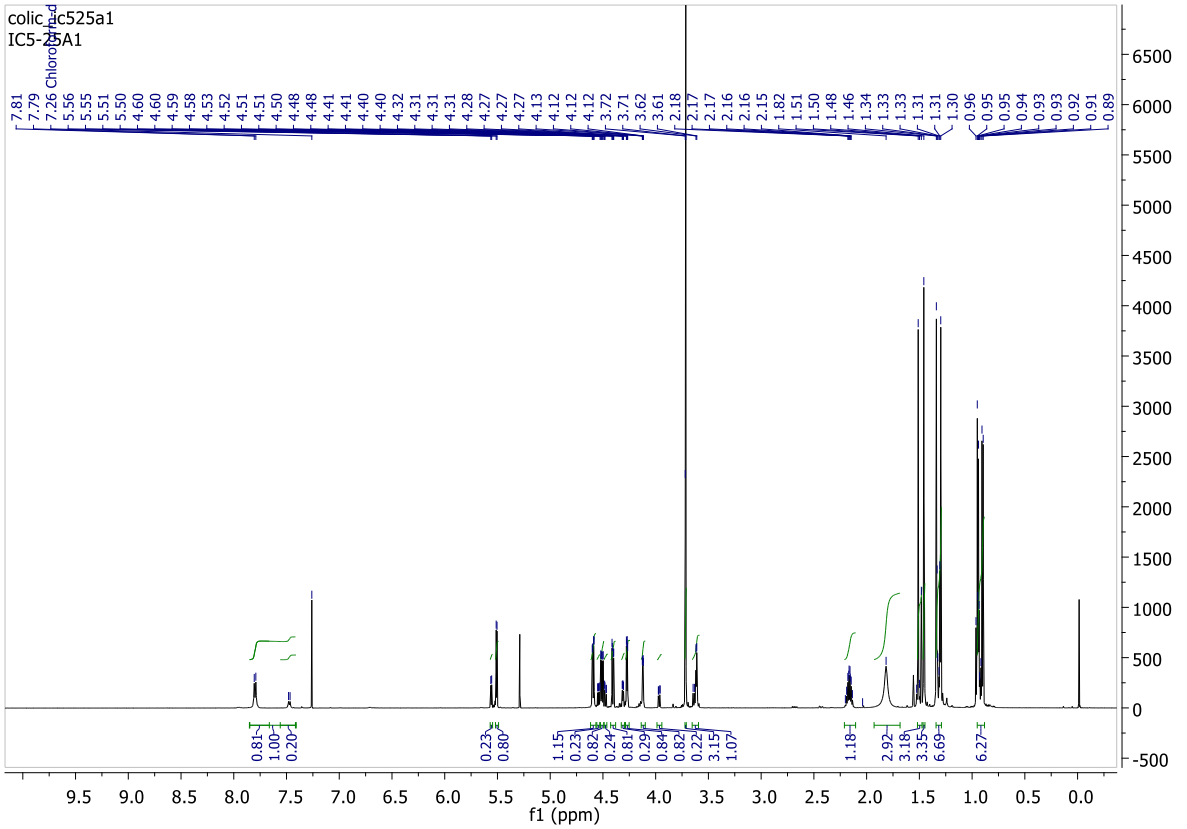


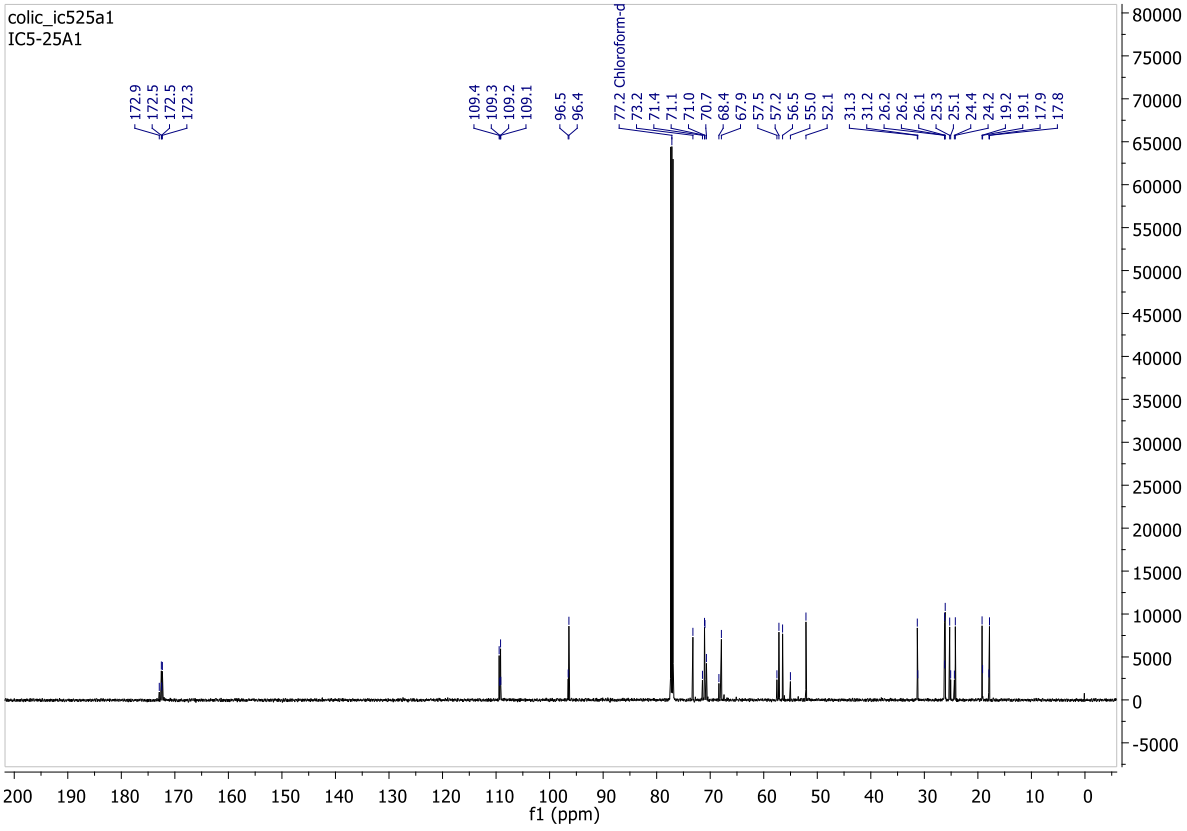
Compound Gal-4d (mixture of diastereoisomers d.r. 70:30)



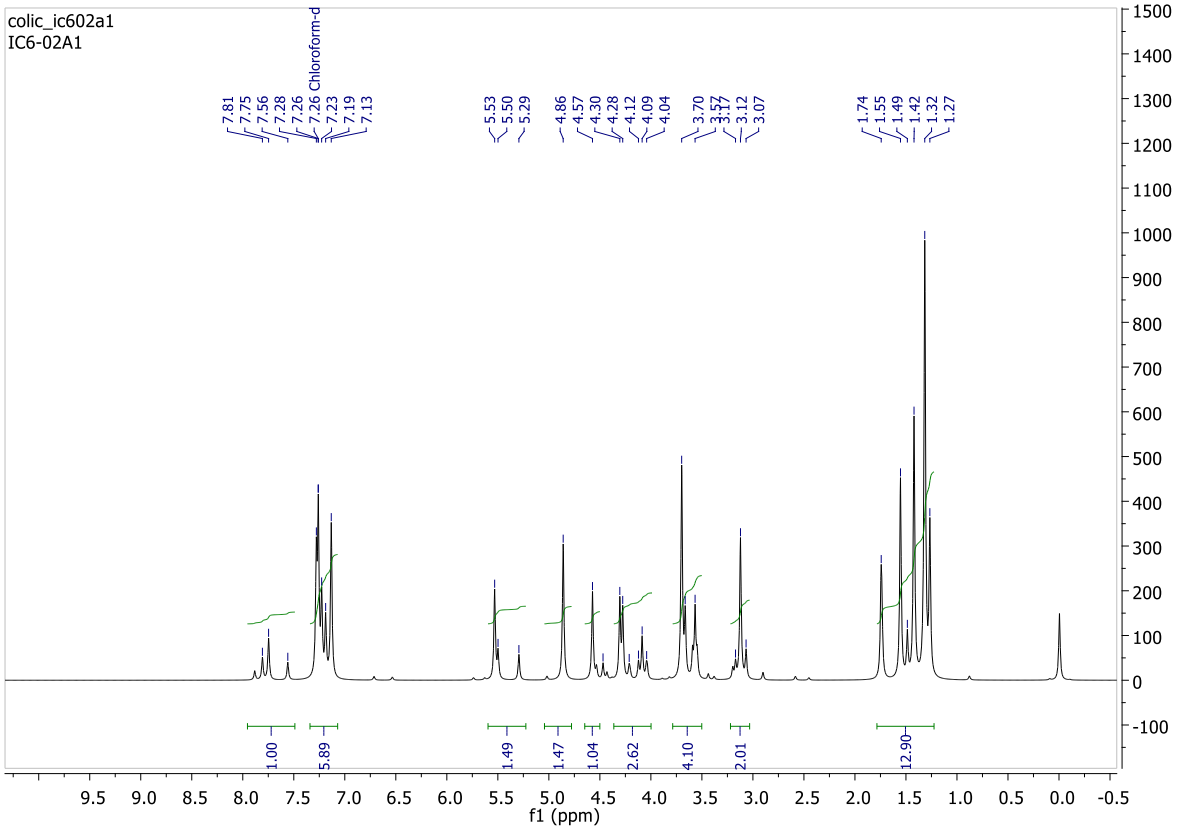


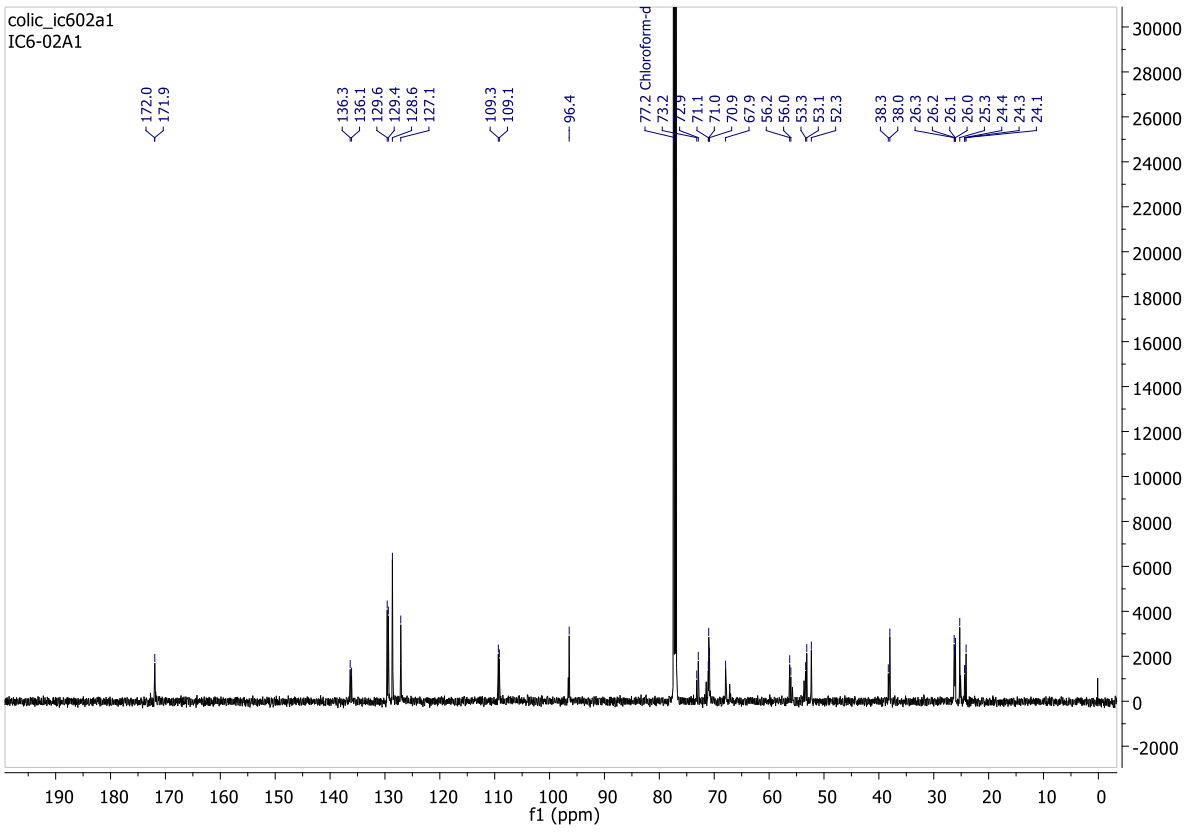
Compound Gal-4e (mixture of diastereoisomers d.r. 80:20)



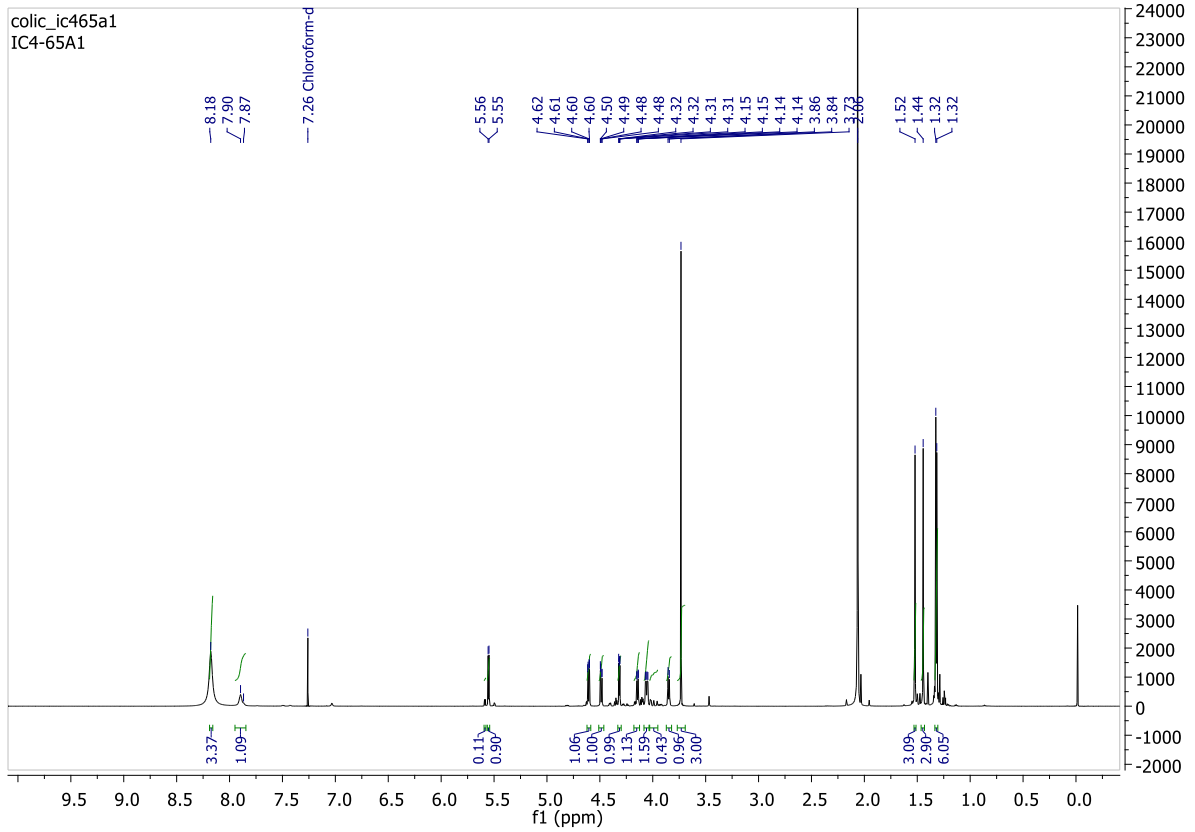


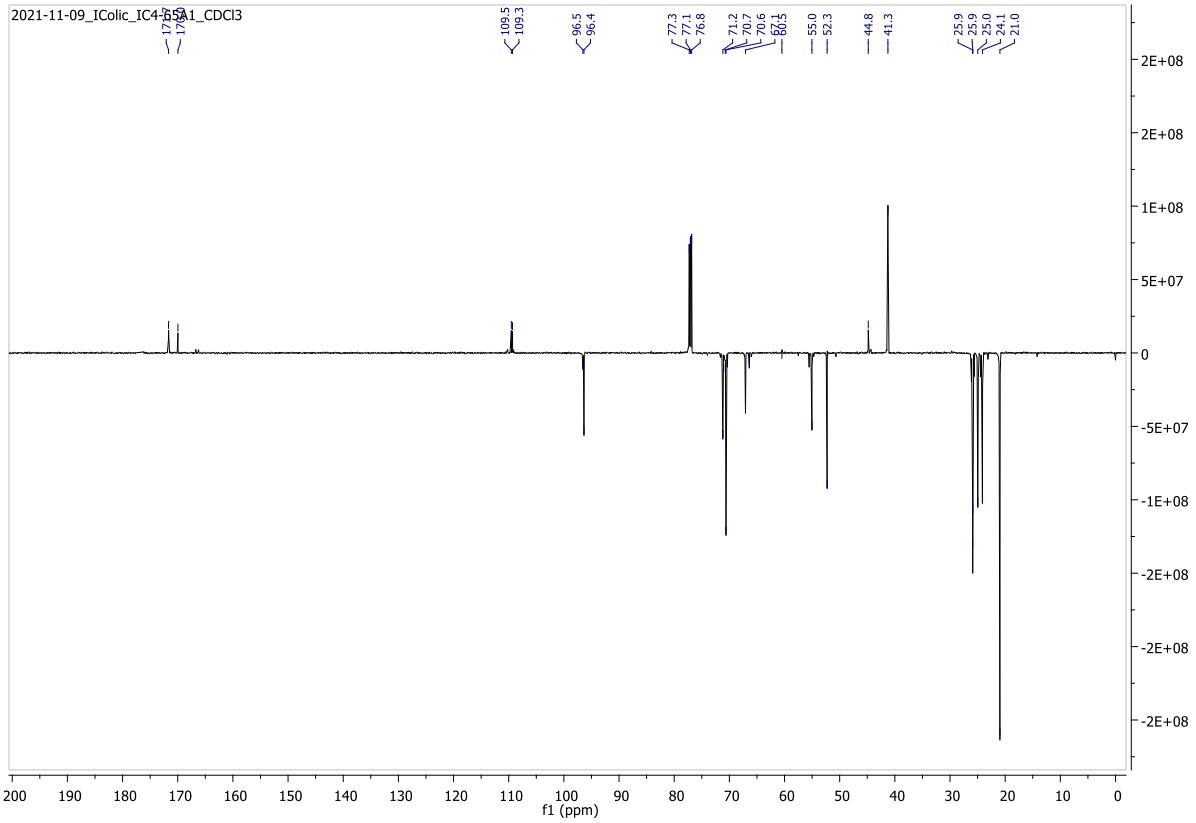
Compound Gal-4f (mixture of diastereoisomers d.r. nd)



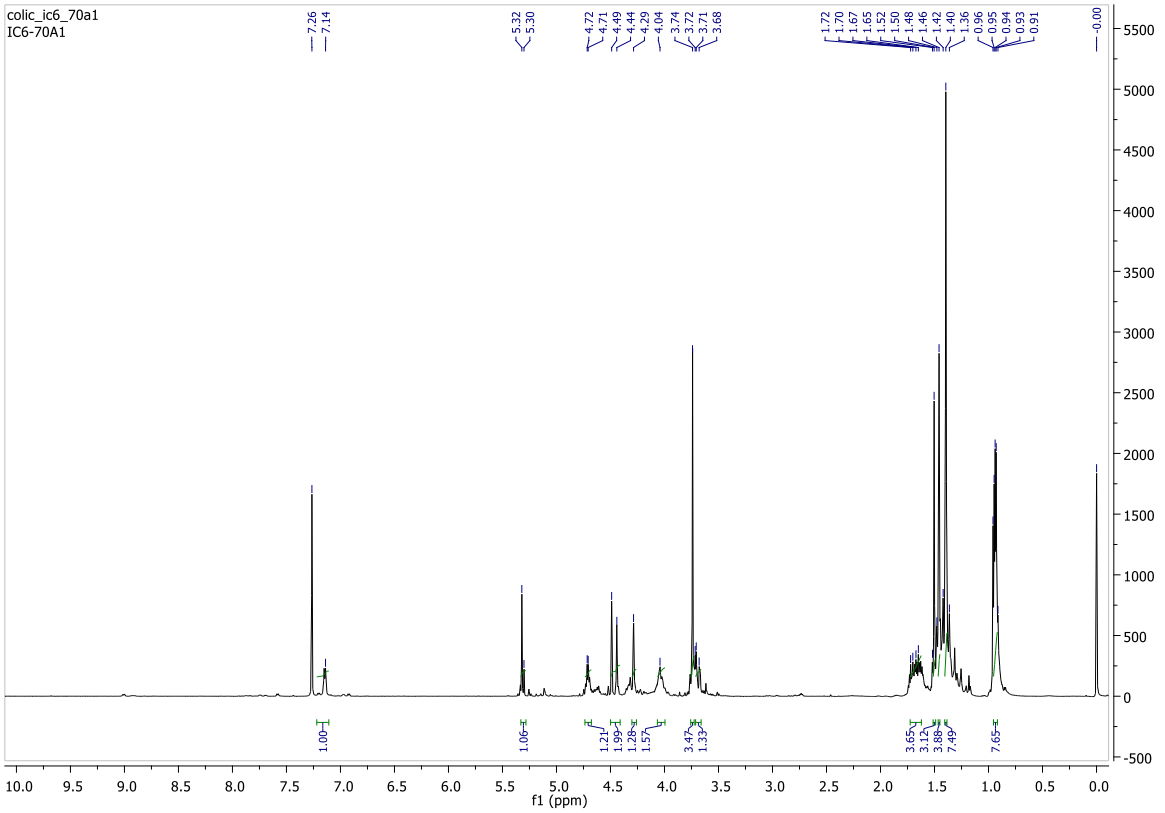


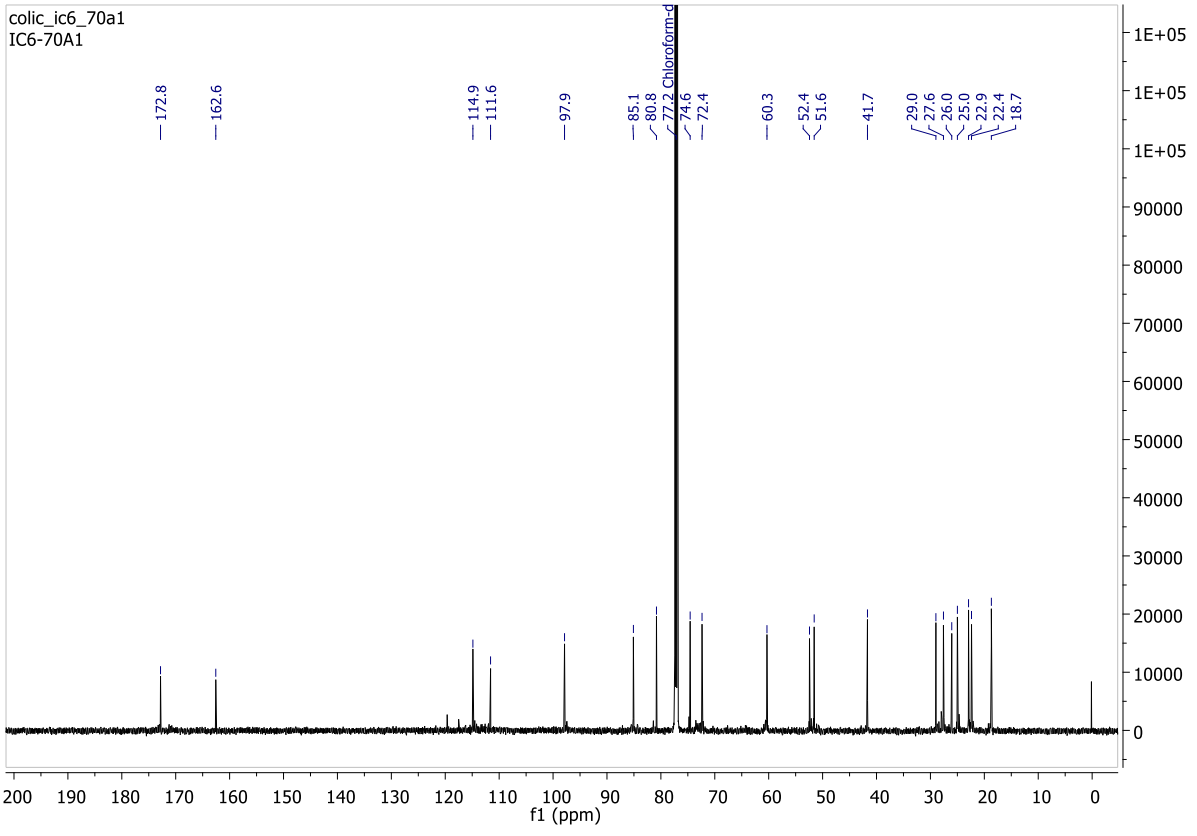
Compound Gal-4g (mixture of diastereoisomers d.r. 90:10)



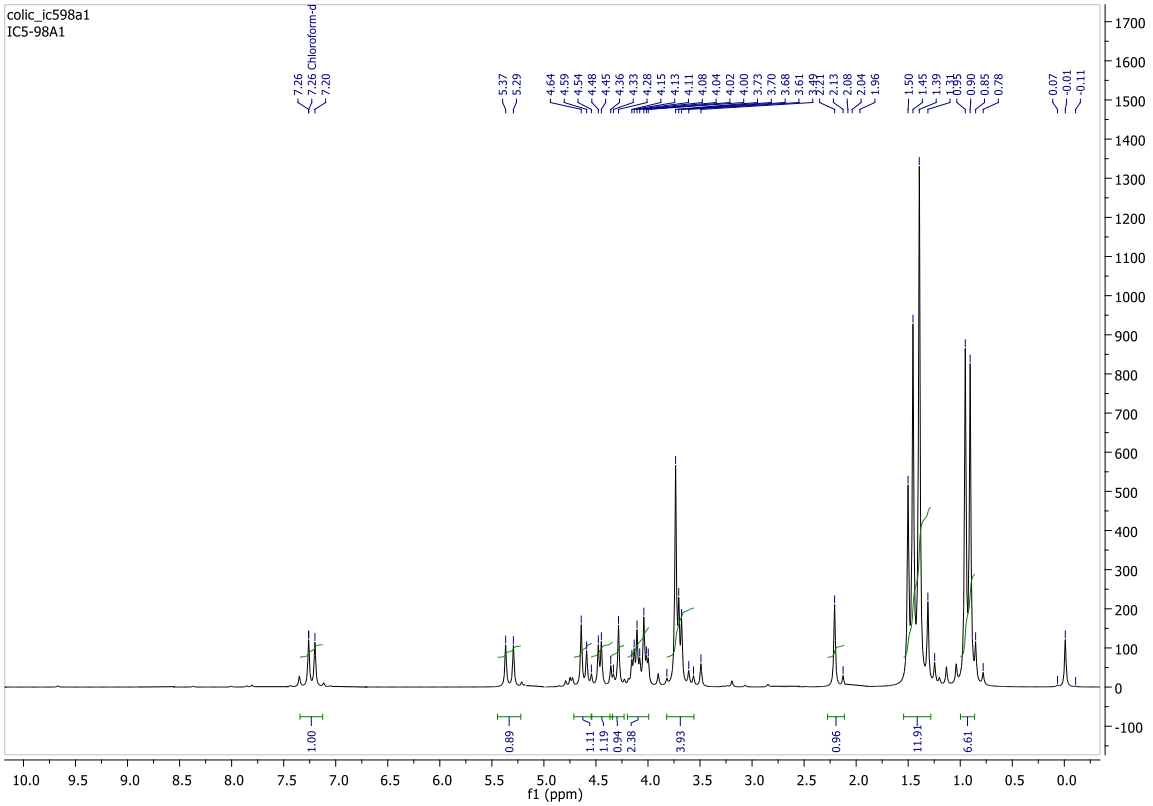


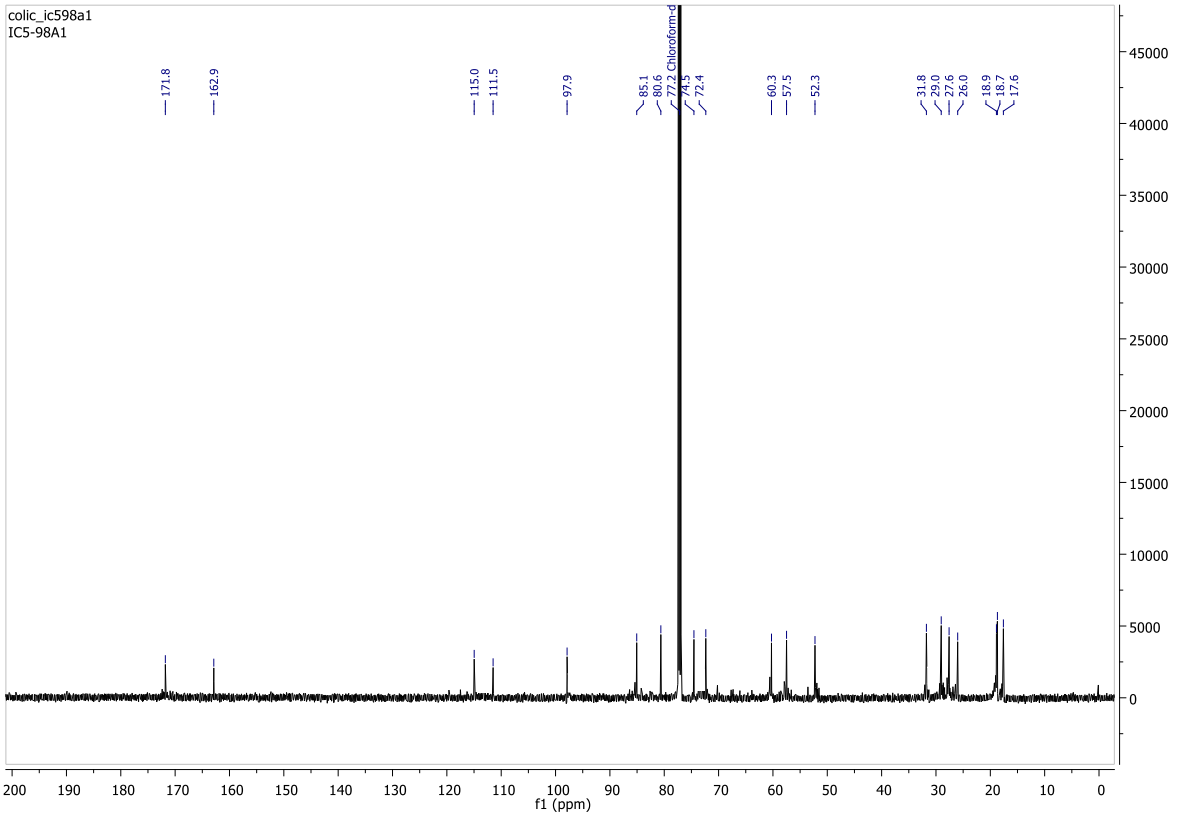
Compound Sor-4a (mixture of diastereoisomers d.r. nd)



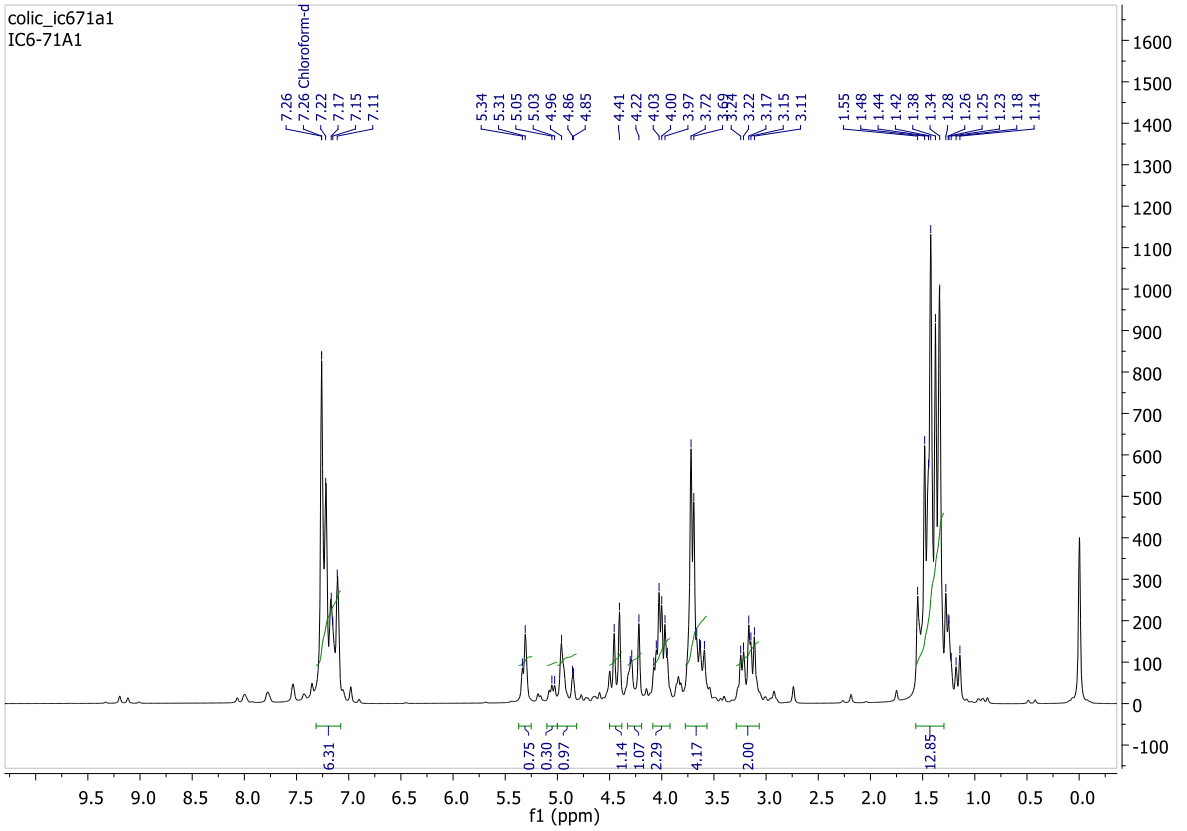


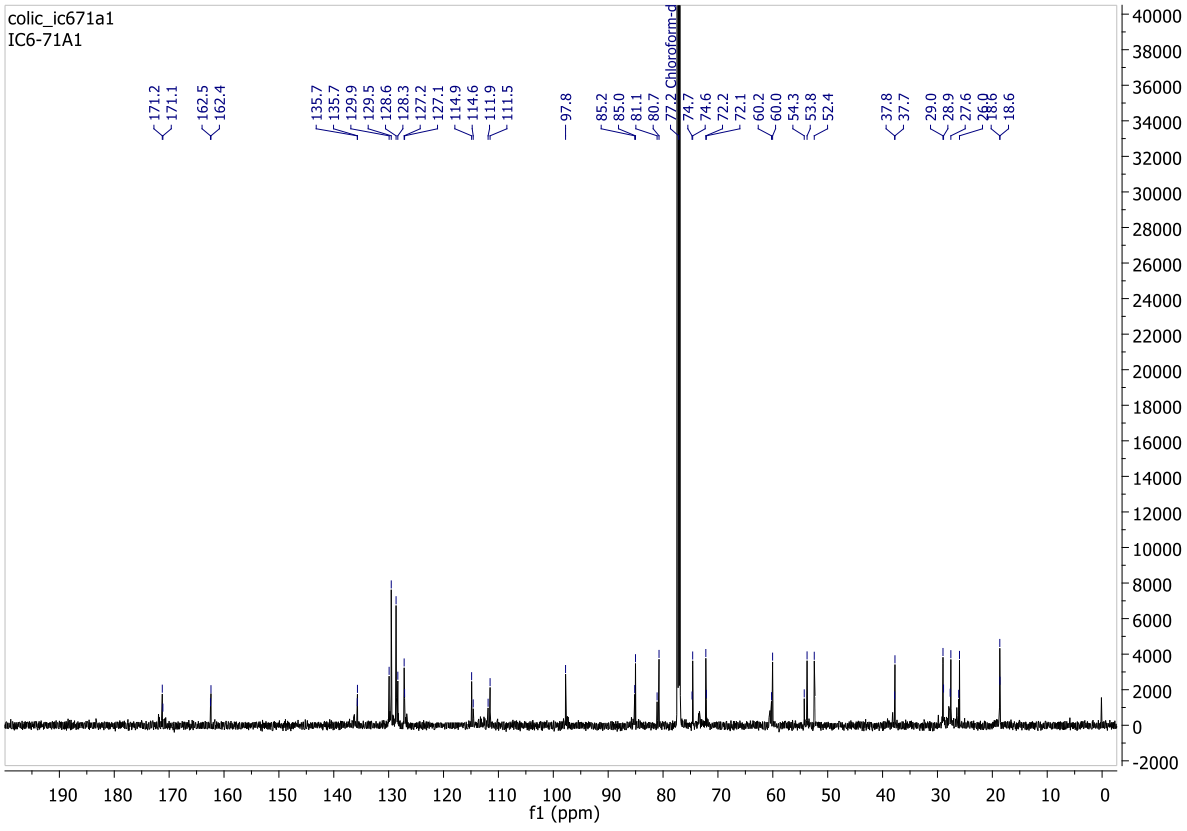
Compound Sor-4b (mixture of diastereoisomers d.r. nd)



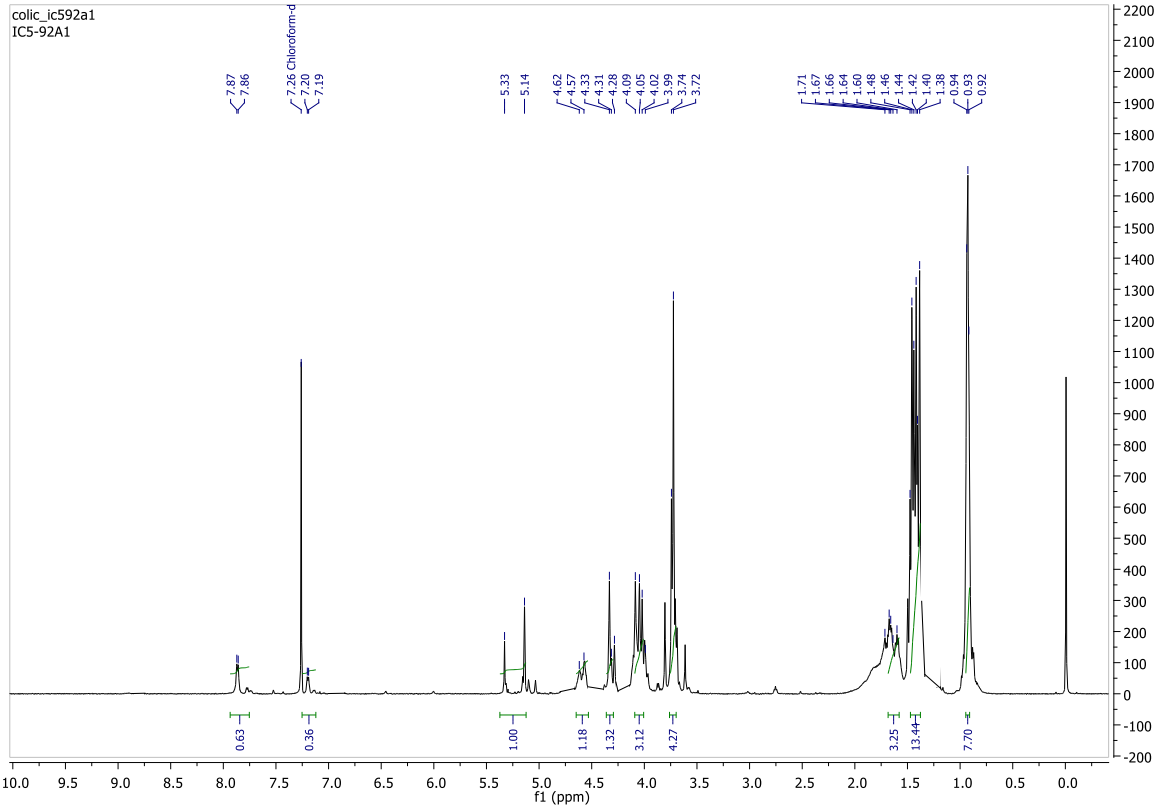


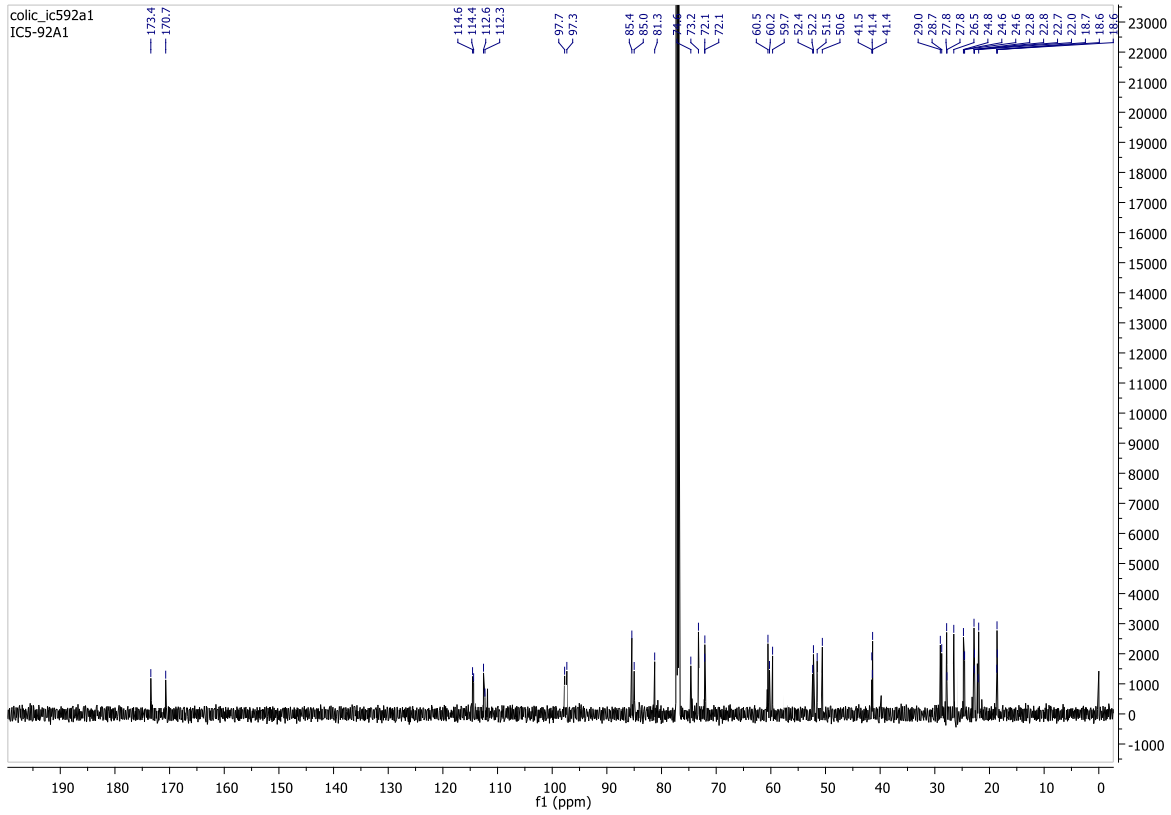
Compound Sor-4c (mixture of diastereoisomers d.r. nd)



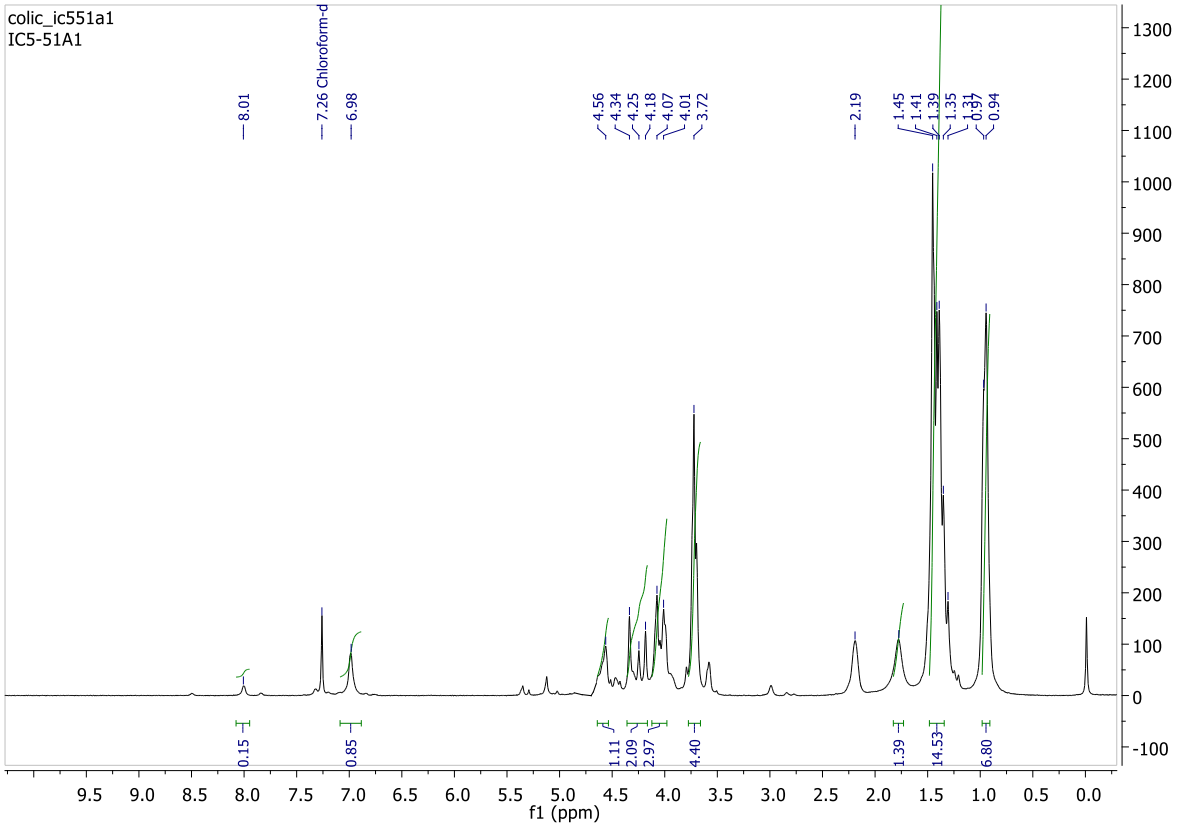


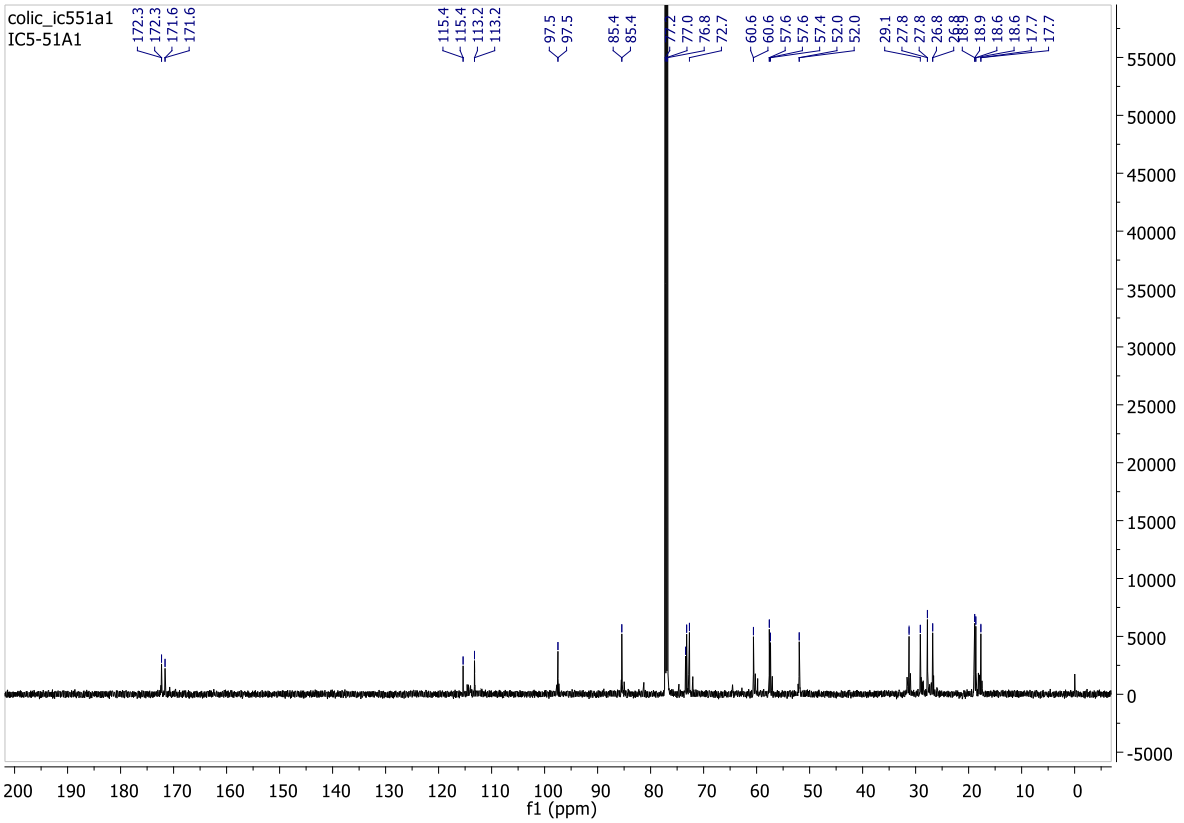
Compound Sor-4d (mixture of diastereoisomers d.r. 65:35)



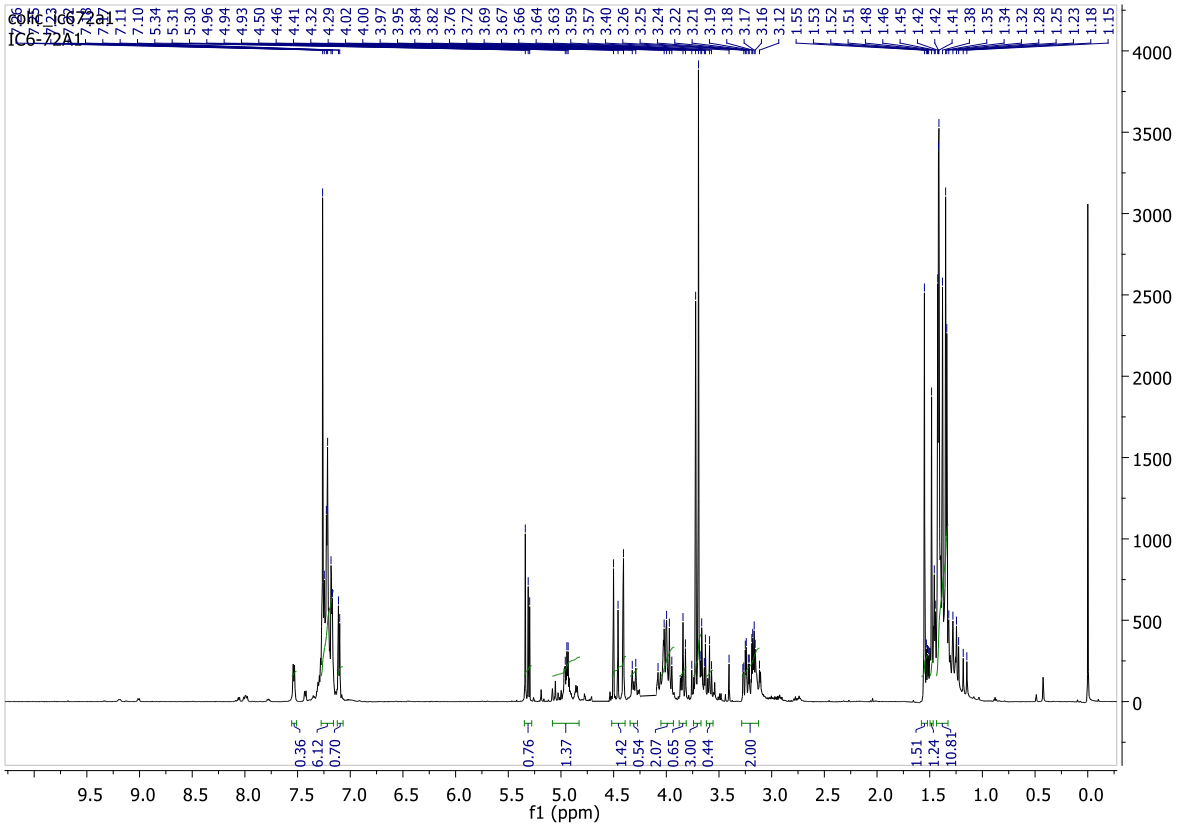


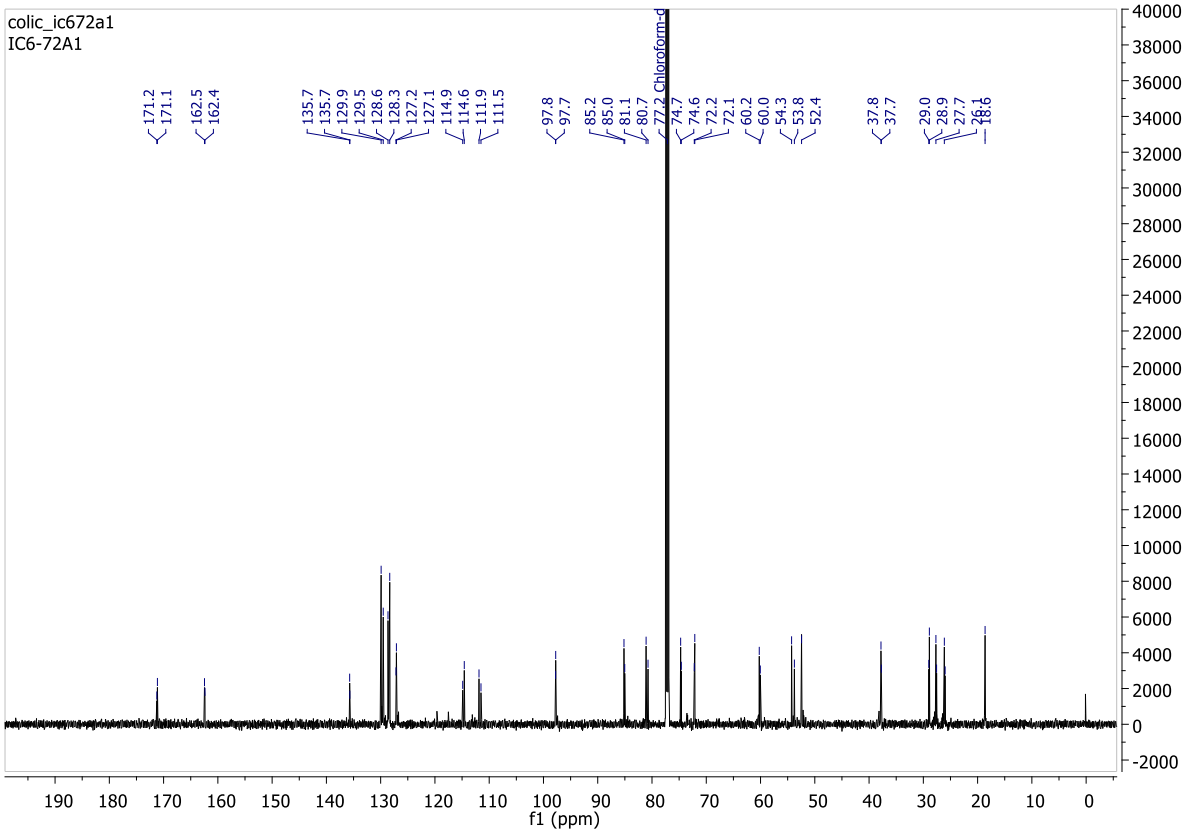
Compound Sor-4e (mixture of diastereoisomers d.r. 85:15)



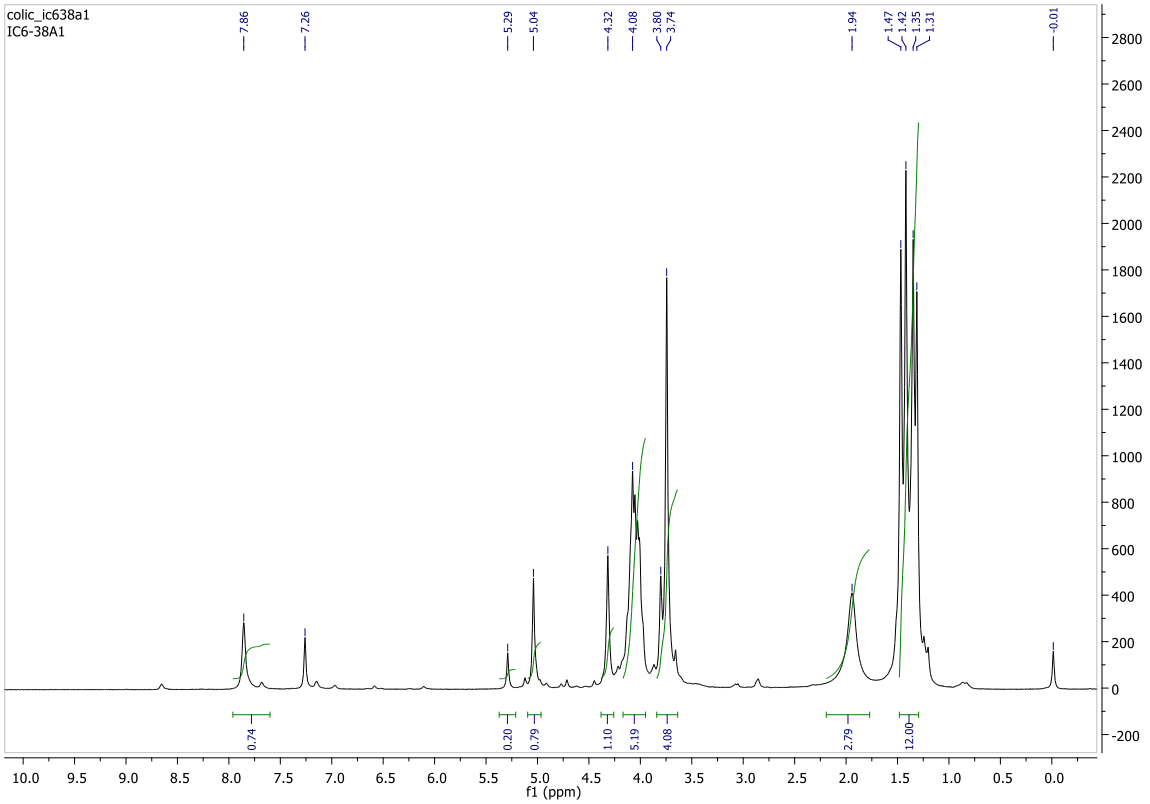


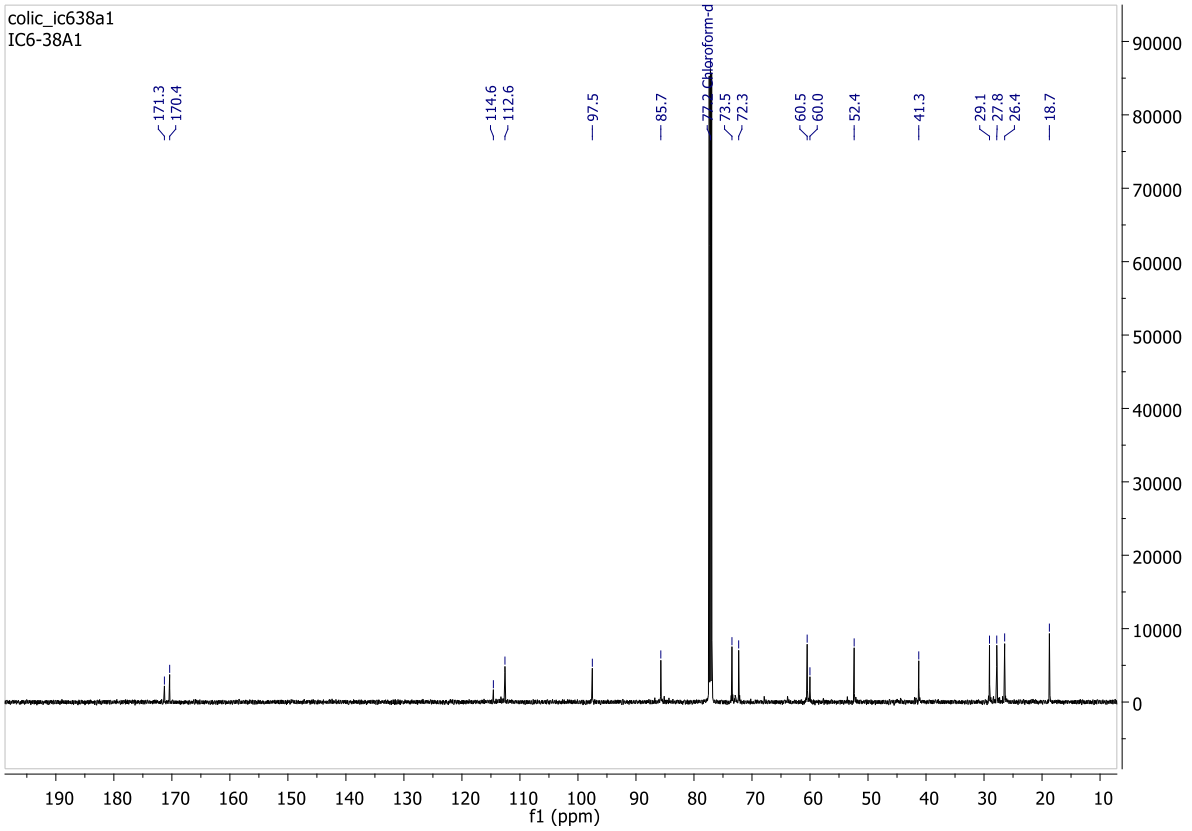
Compound Sor-4f (mixture of diastereoisomers d.r. 70:30)



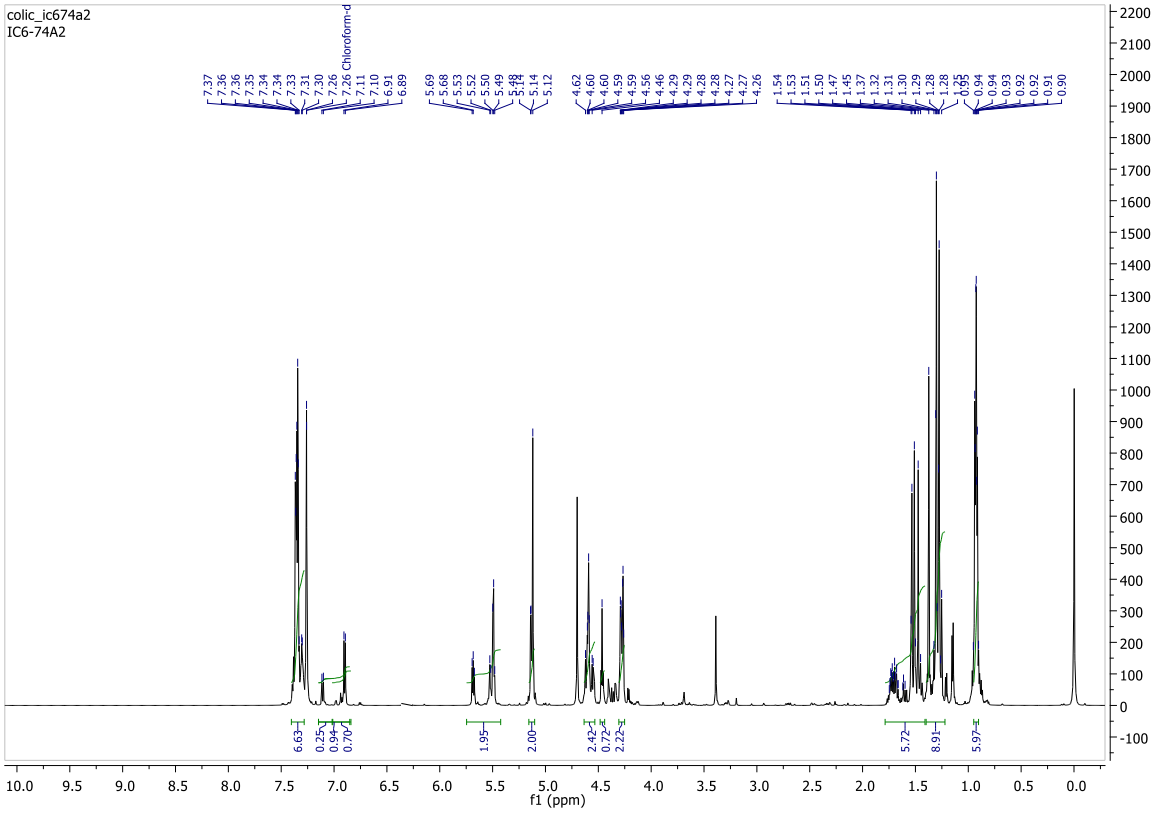


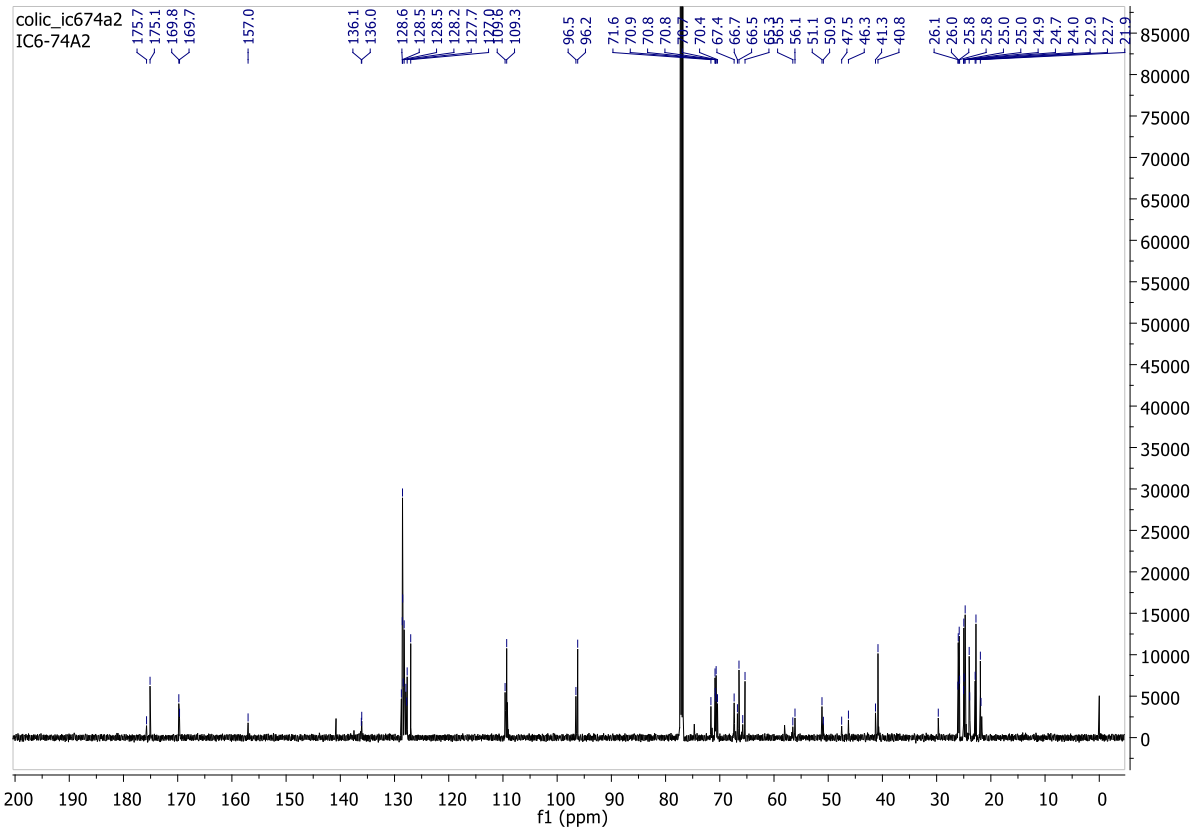
Compound Sor-4g (mixture of diastereoisomers d.r. 80:20)



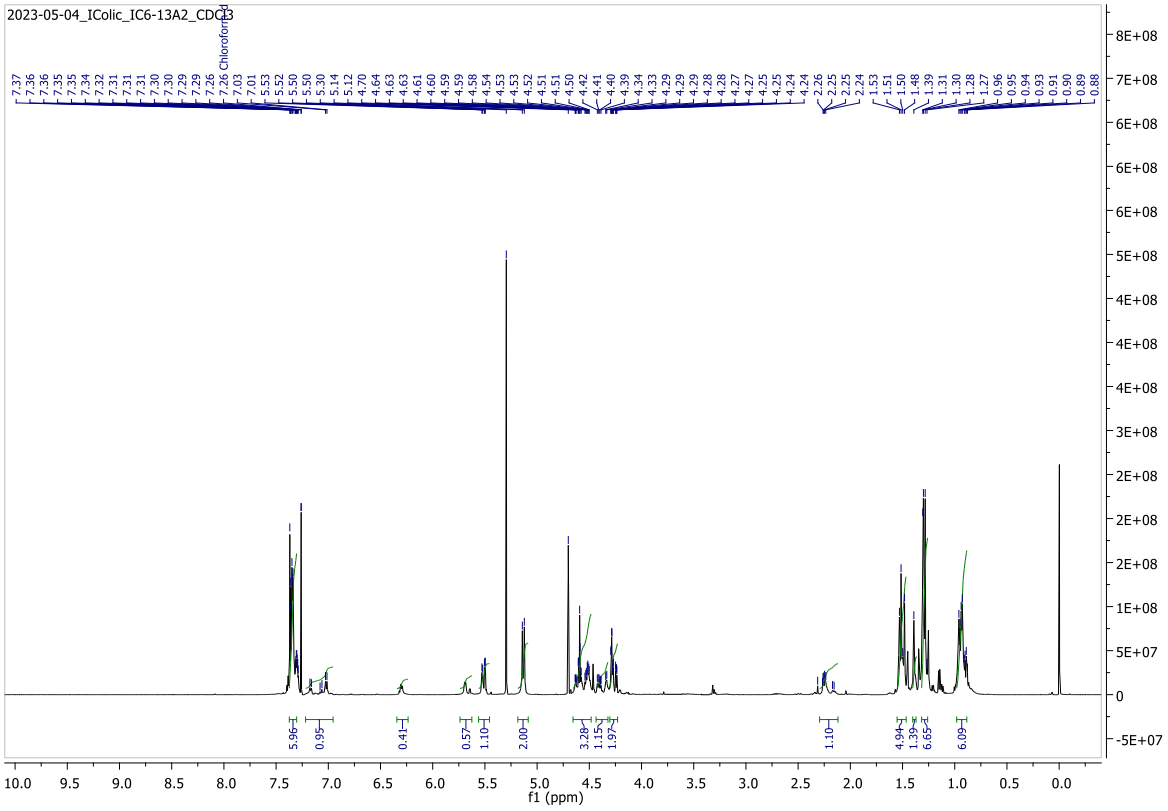


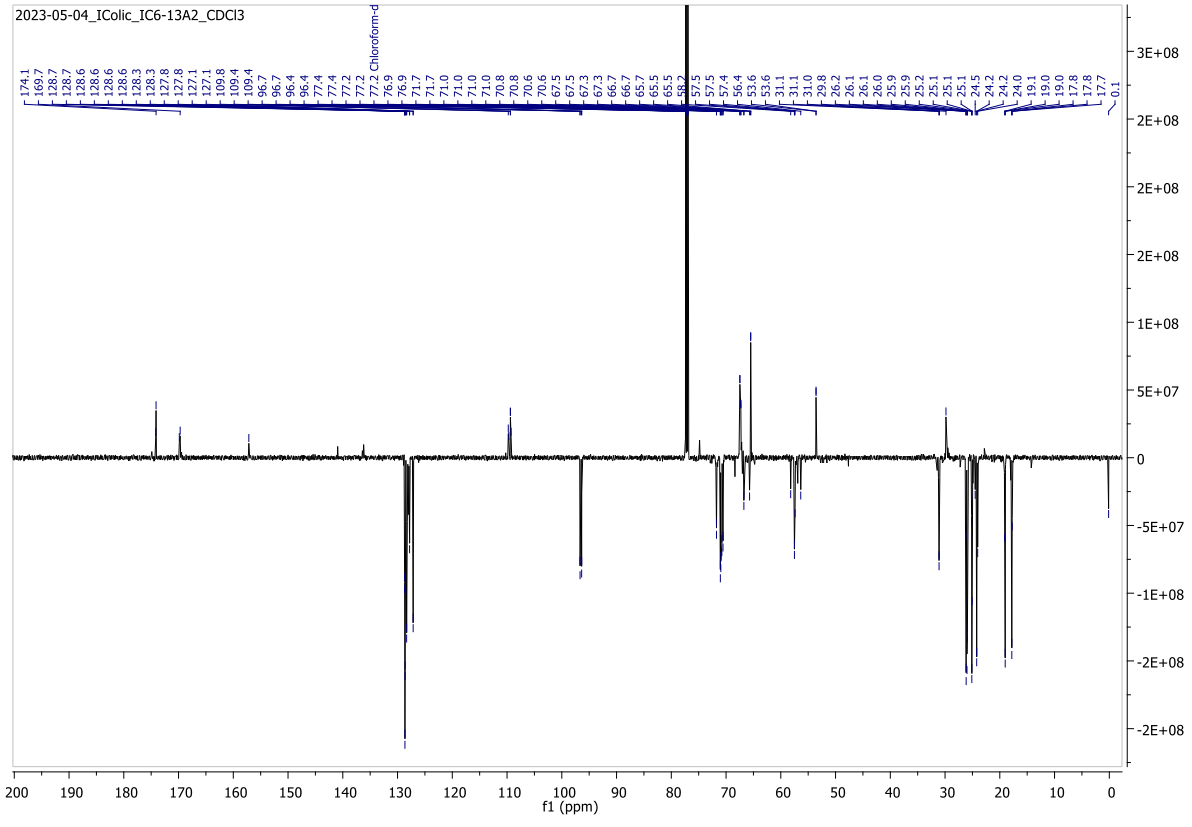
Compound Gal-5a (mixture of diastereoisomers d.r. 70:30)



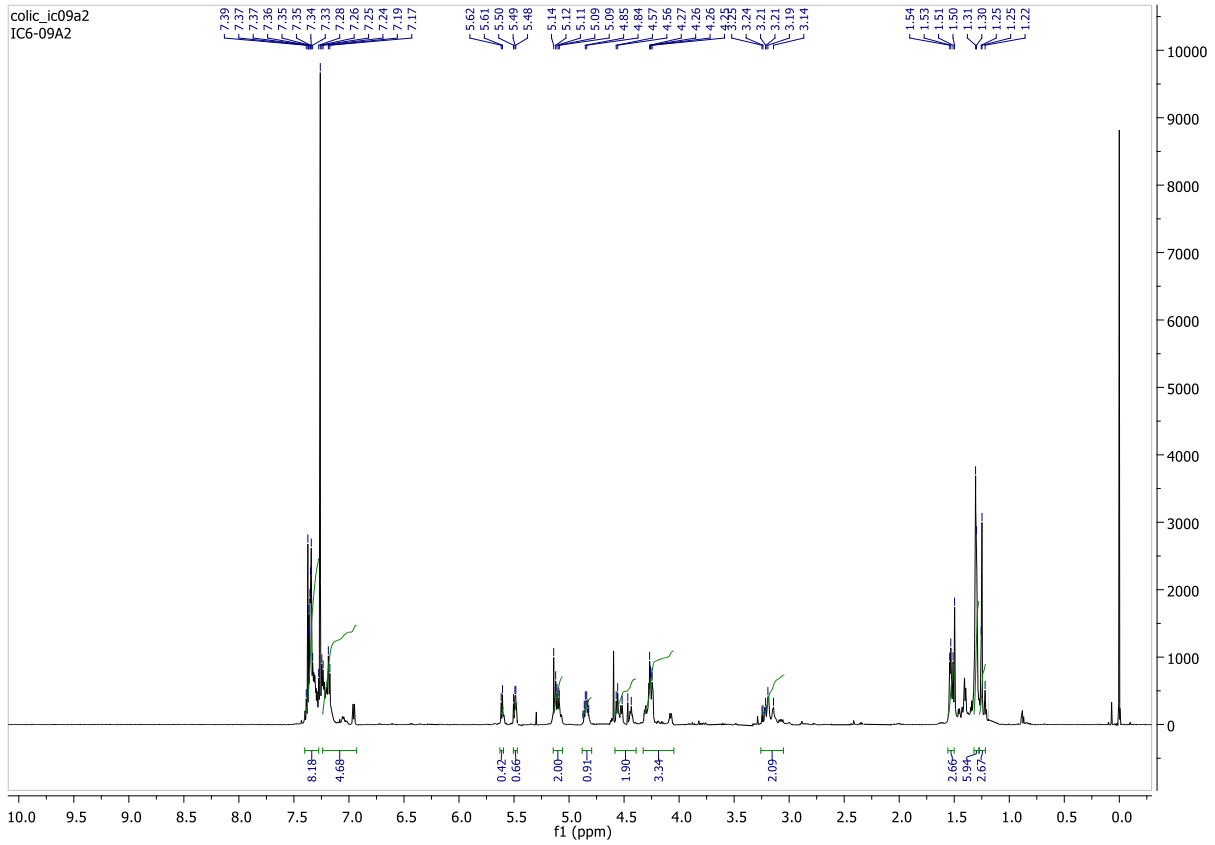


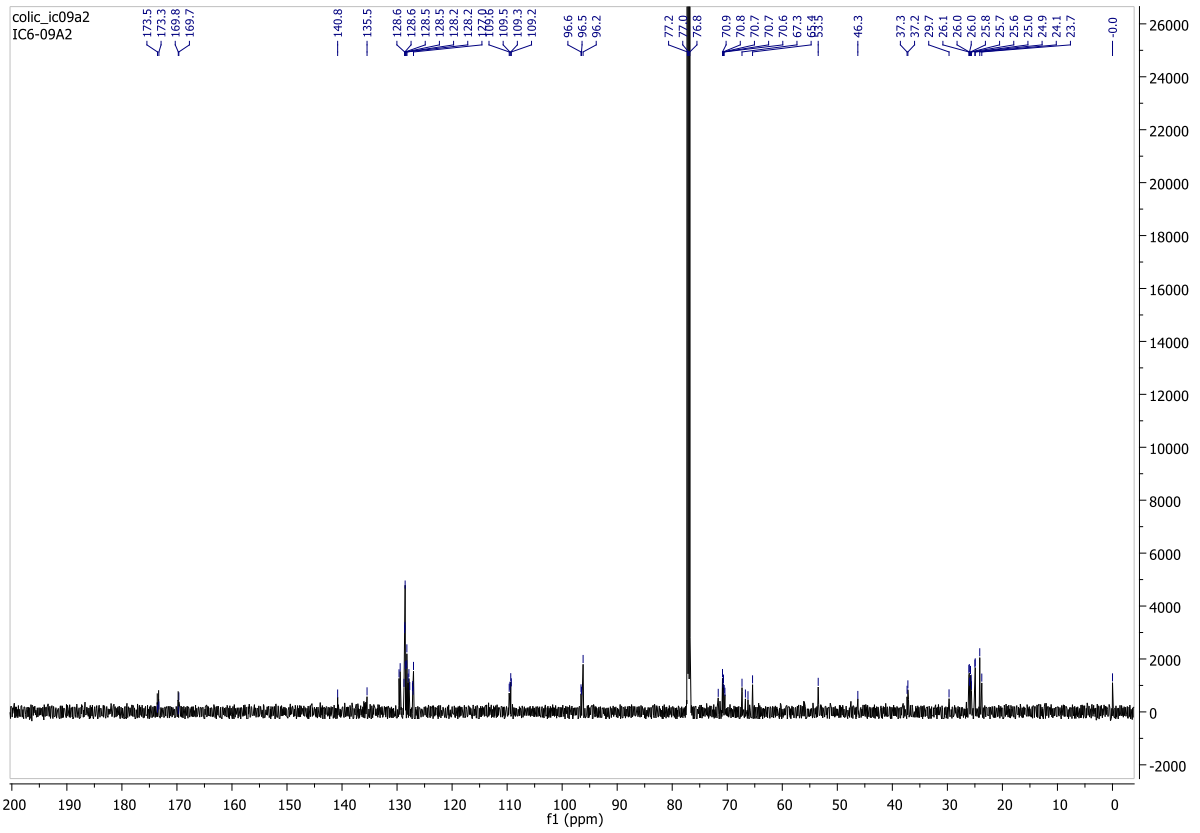
Compound Gal-5b (mixture of diastereoisomers d.r. 60:40)



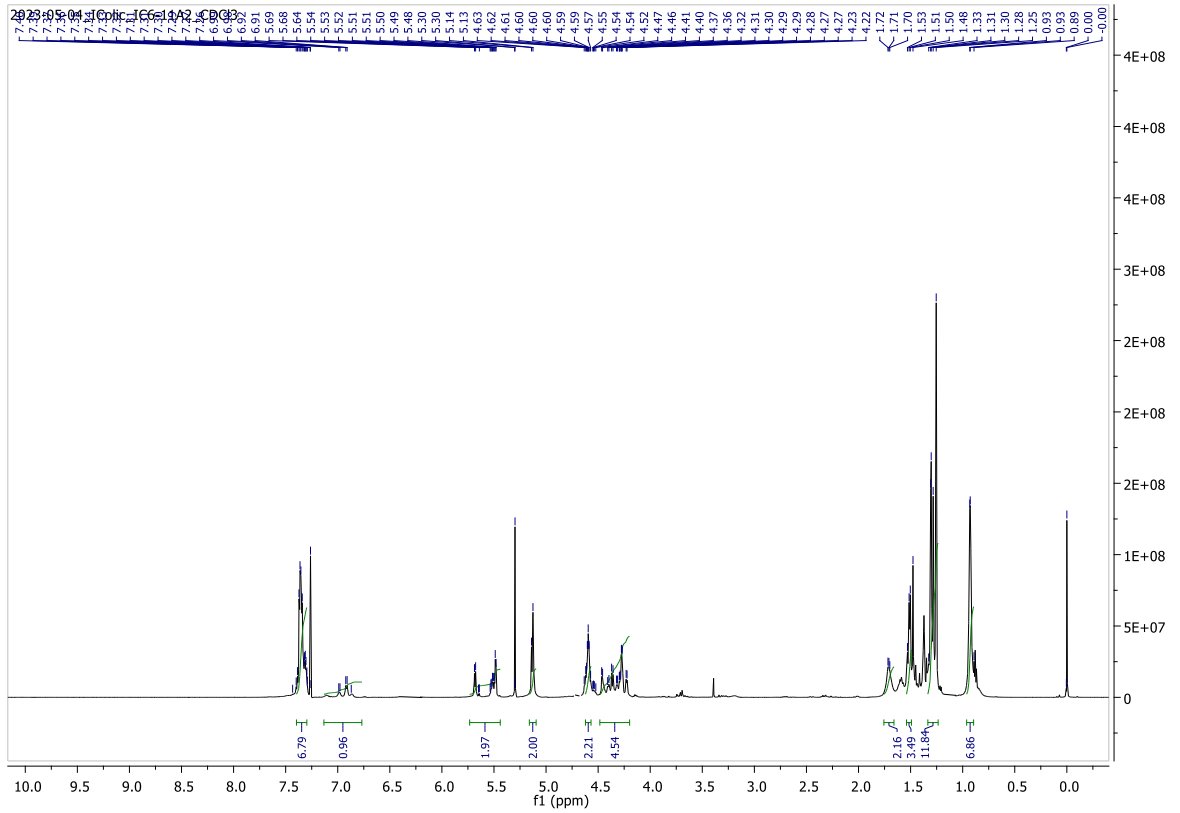


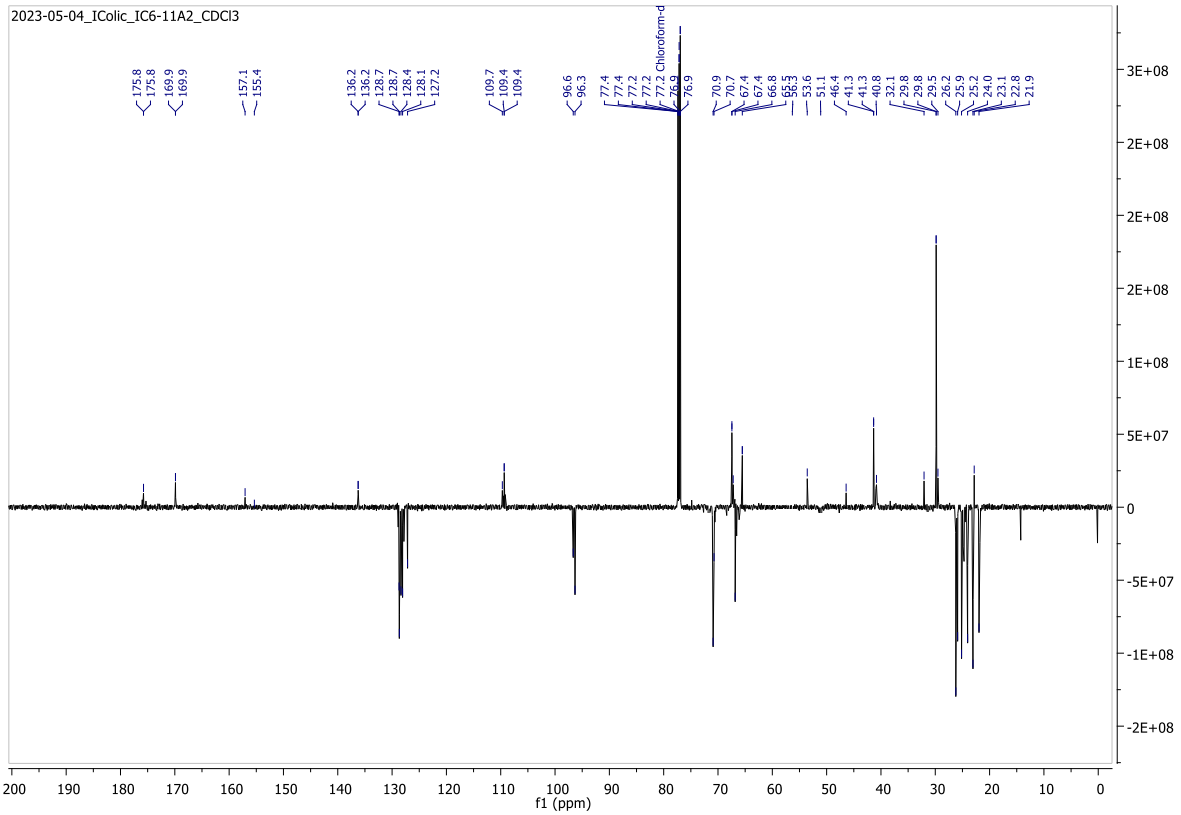
Compound Gal-5c (mixture of diastereoisomers d.r. 60:40)



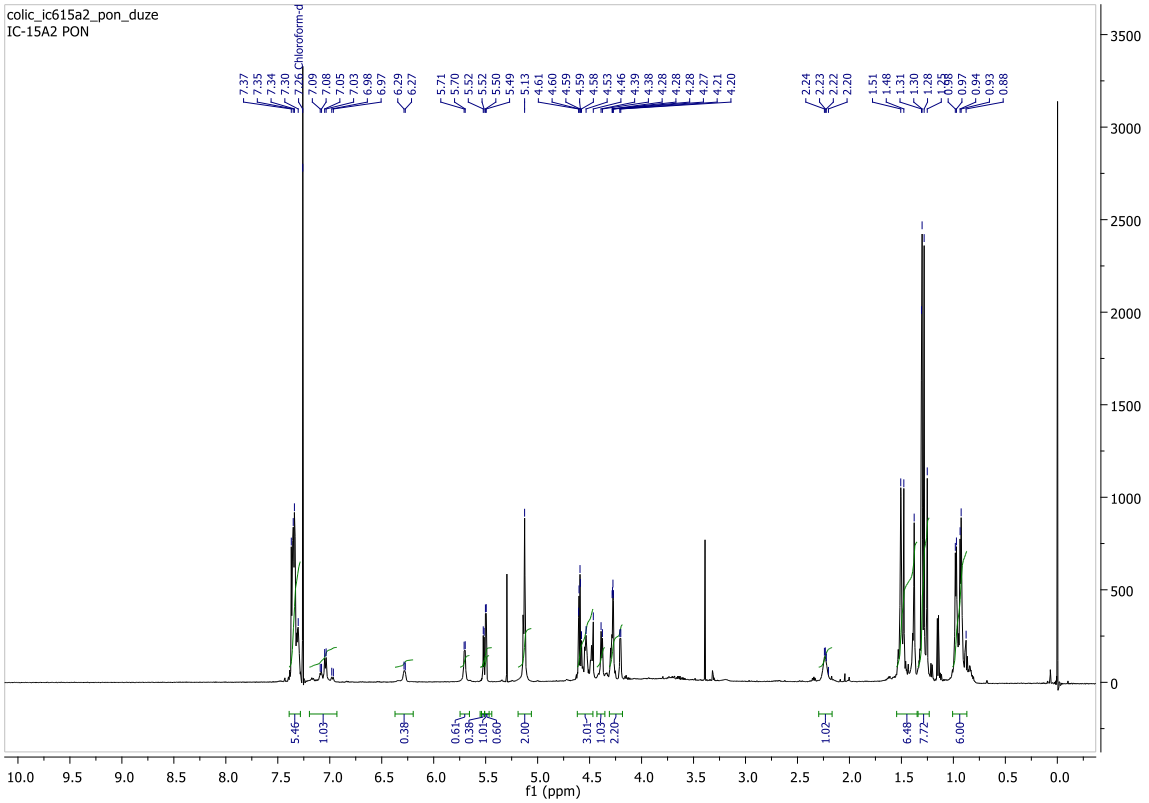


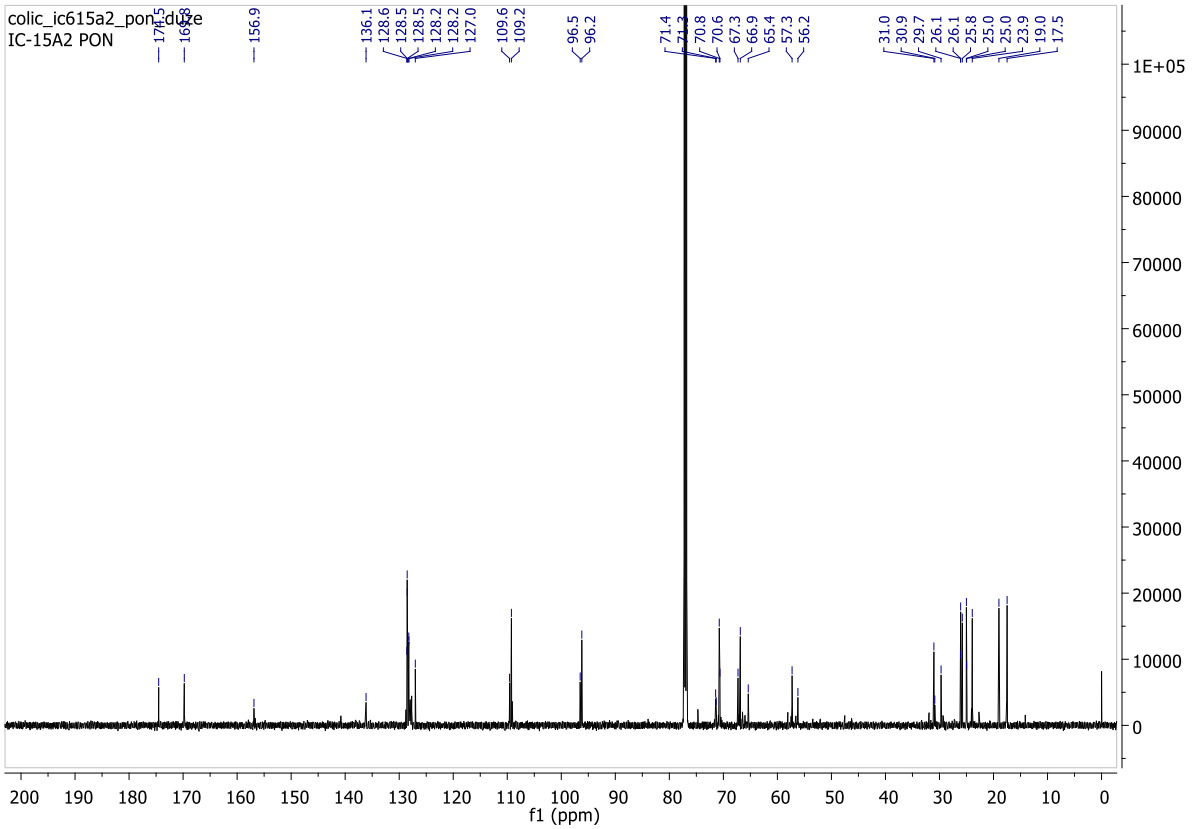
Compound Gal-5d (mixture of diastereoisomers d.r. nd)



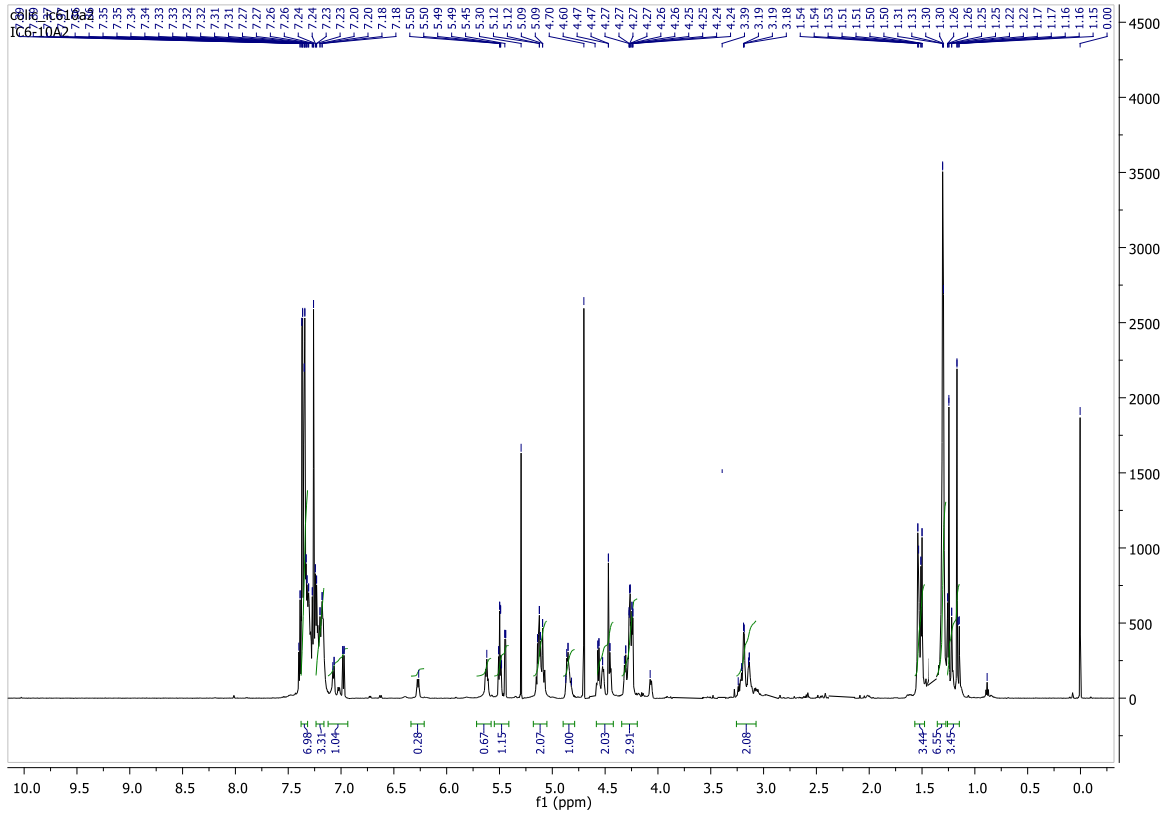


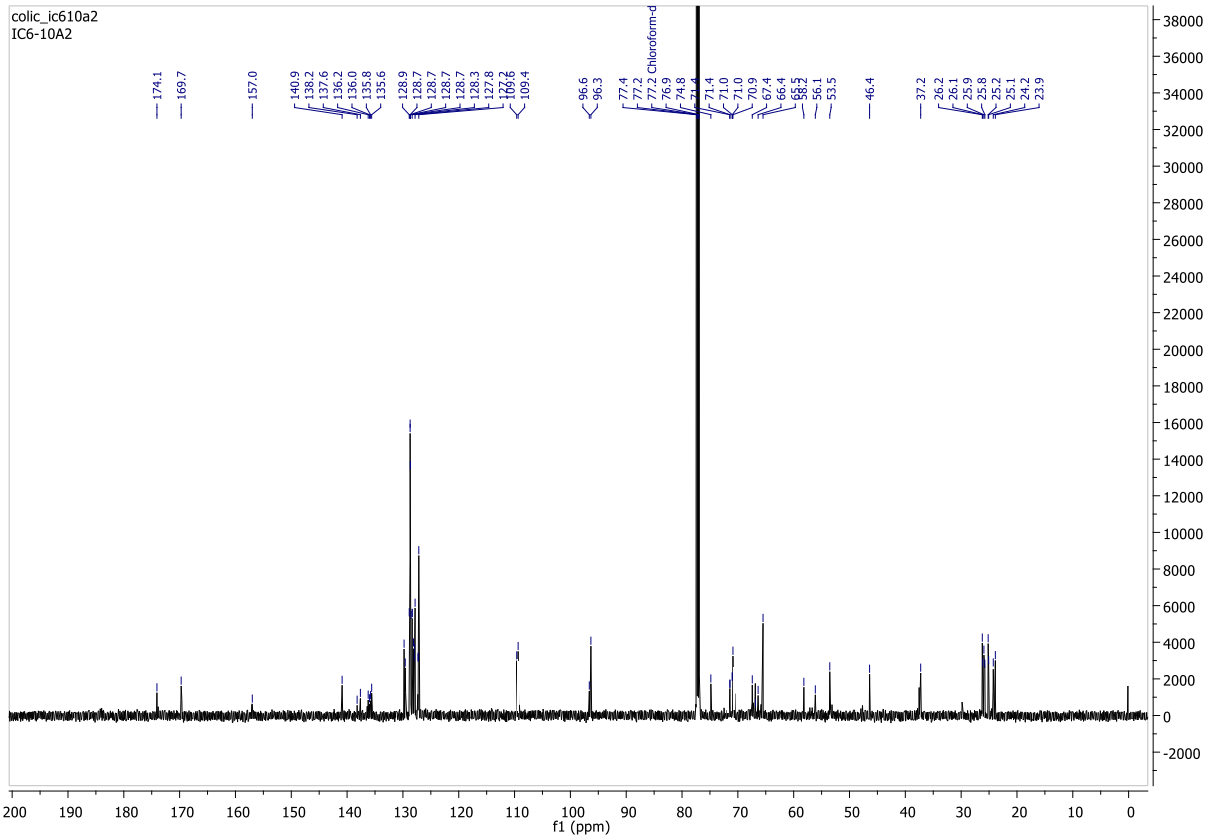
Compound Gal-5e (mixture of diastereoisomers d.r. 60:40)



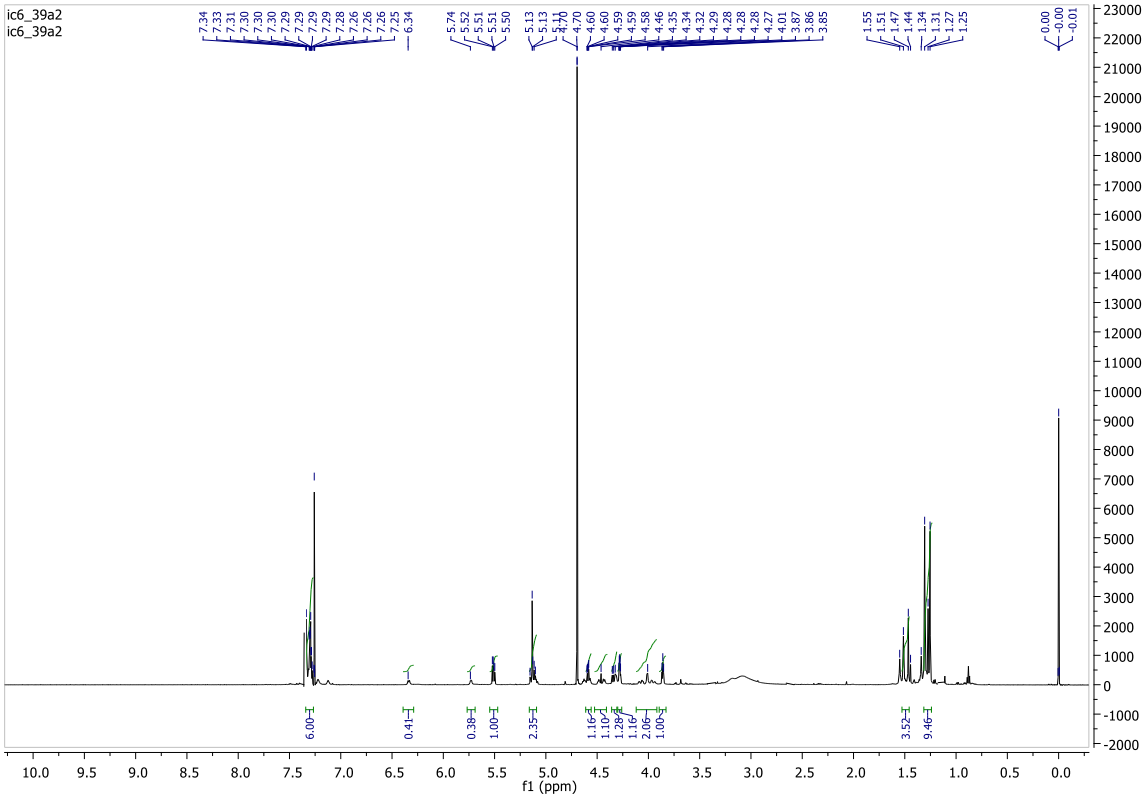


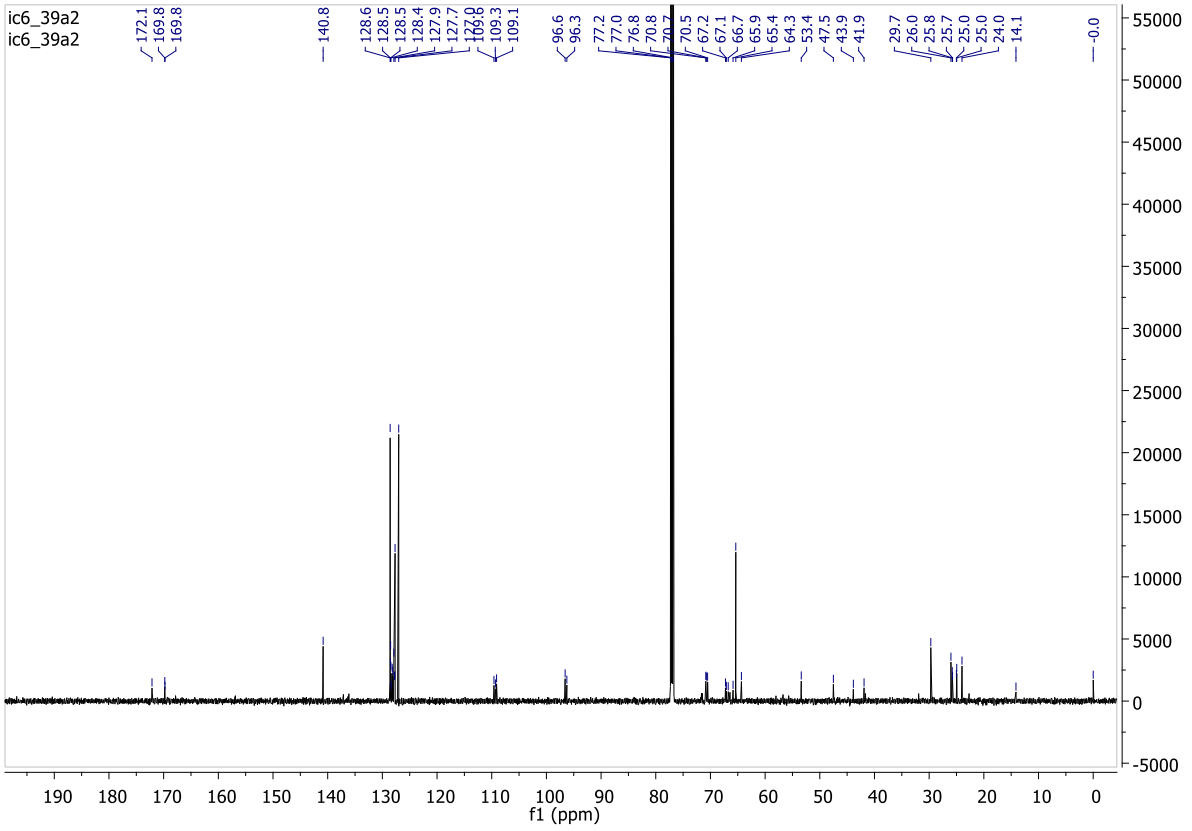
Compound Gal-5f (mixture of diastereoisomers d.r. 70:30)



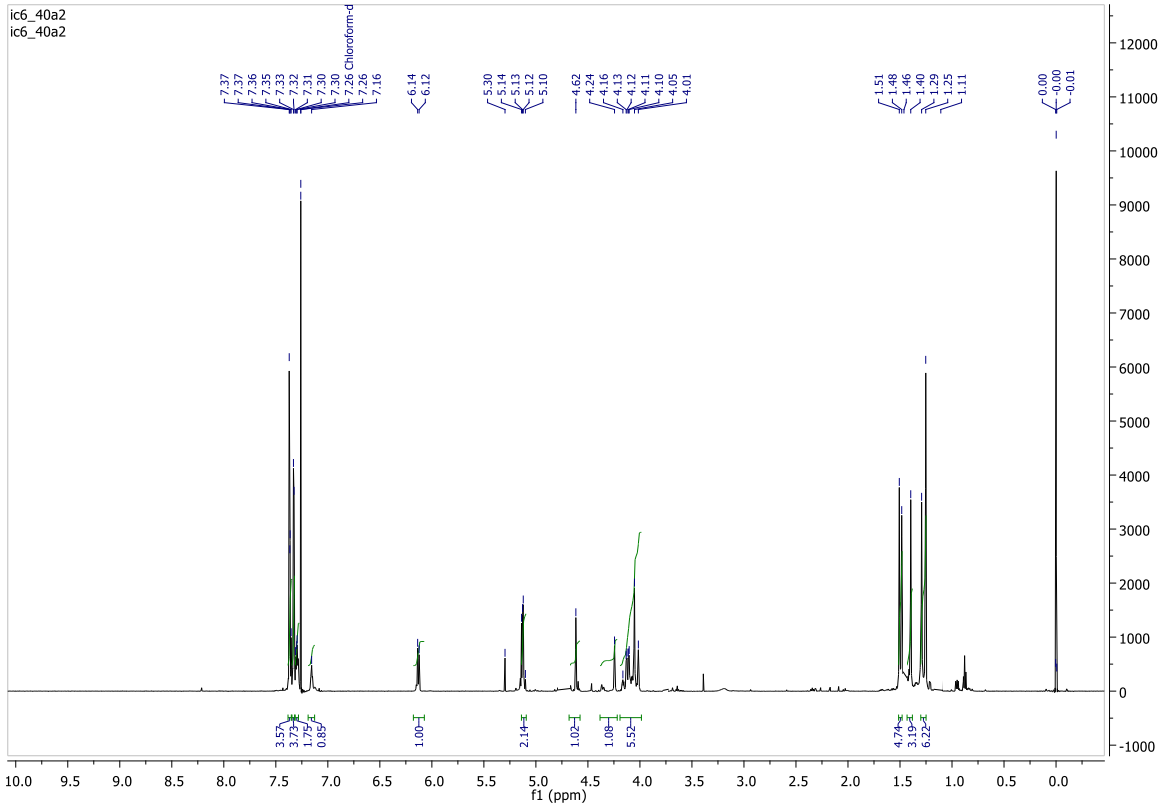


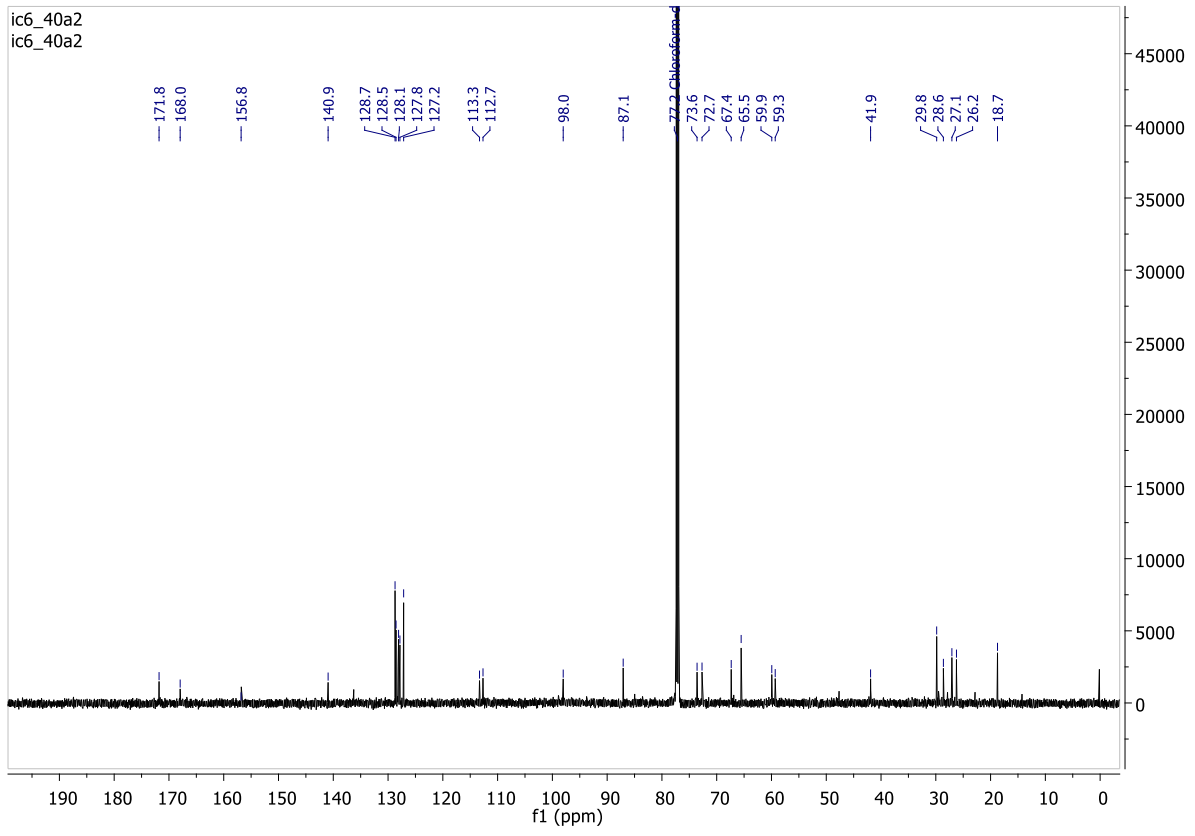
Compound Gal-5g (mixture of diastereoisomers d.r. 55:45)



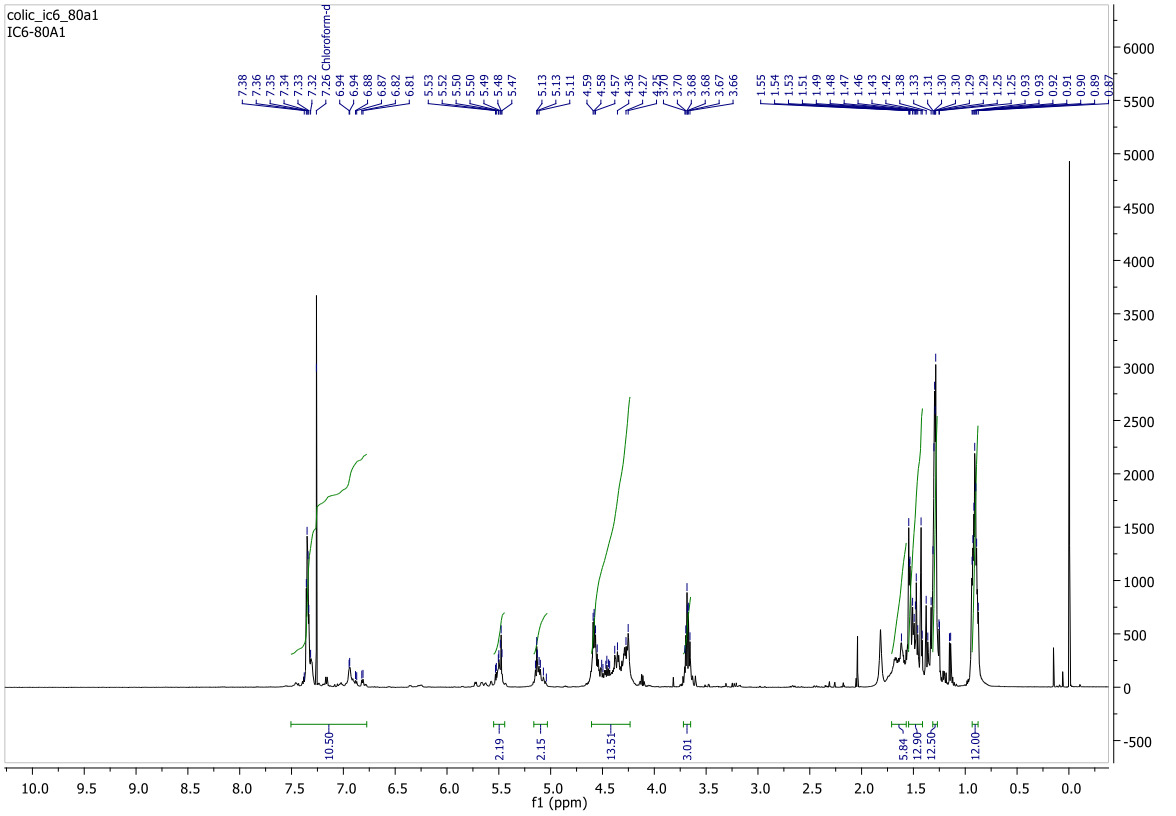


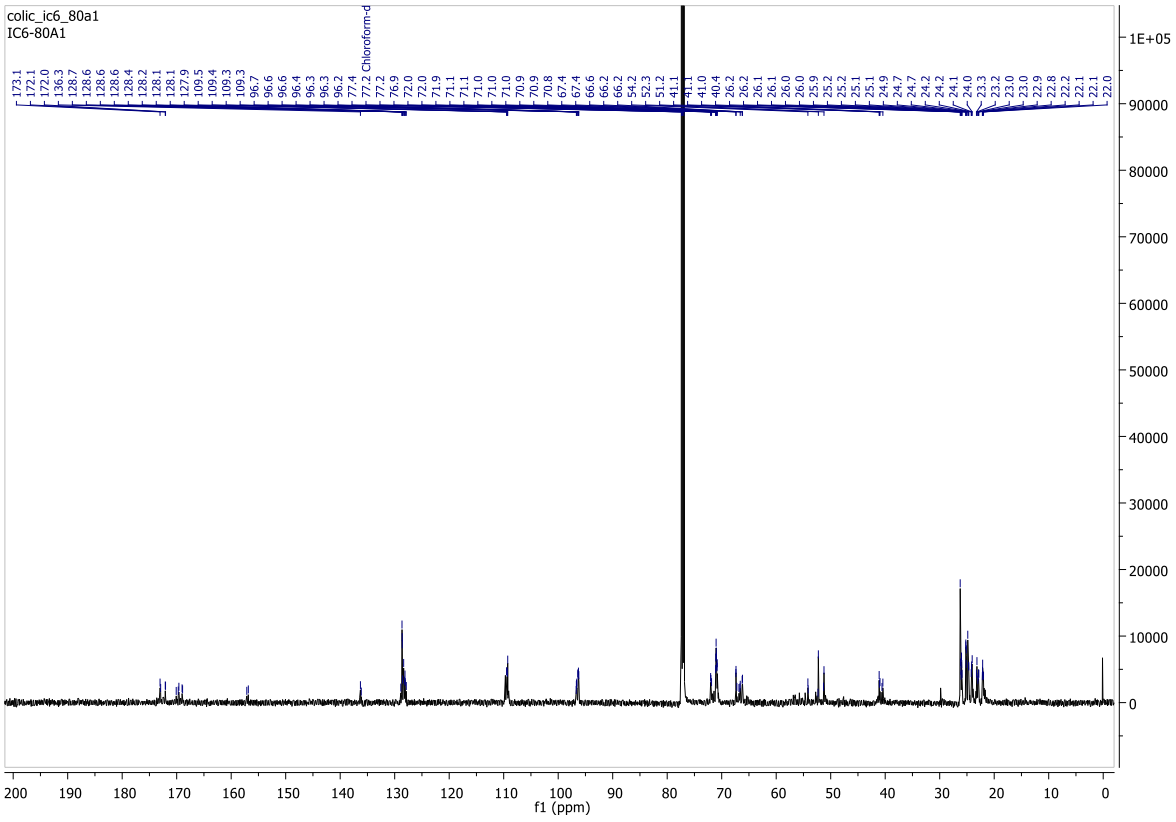
Compound Sor-5g (mixture of diastereoisomers d.r. 95:5)



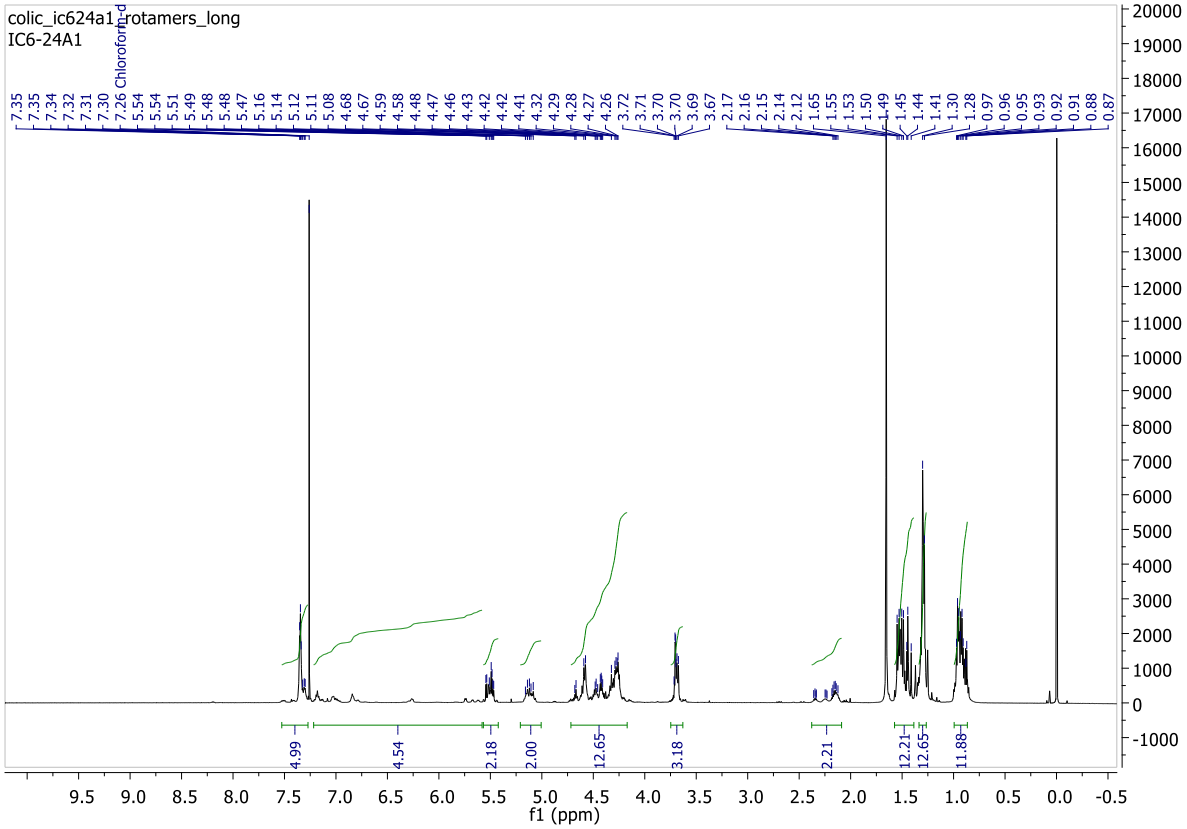


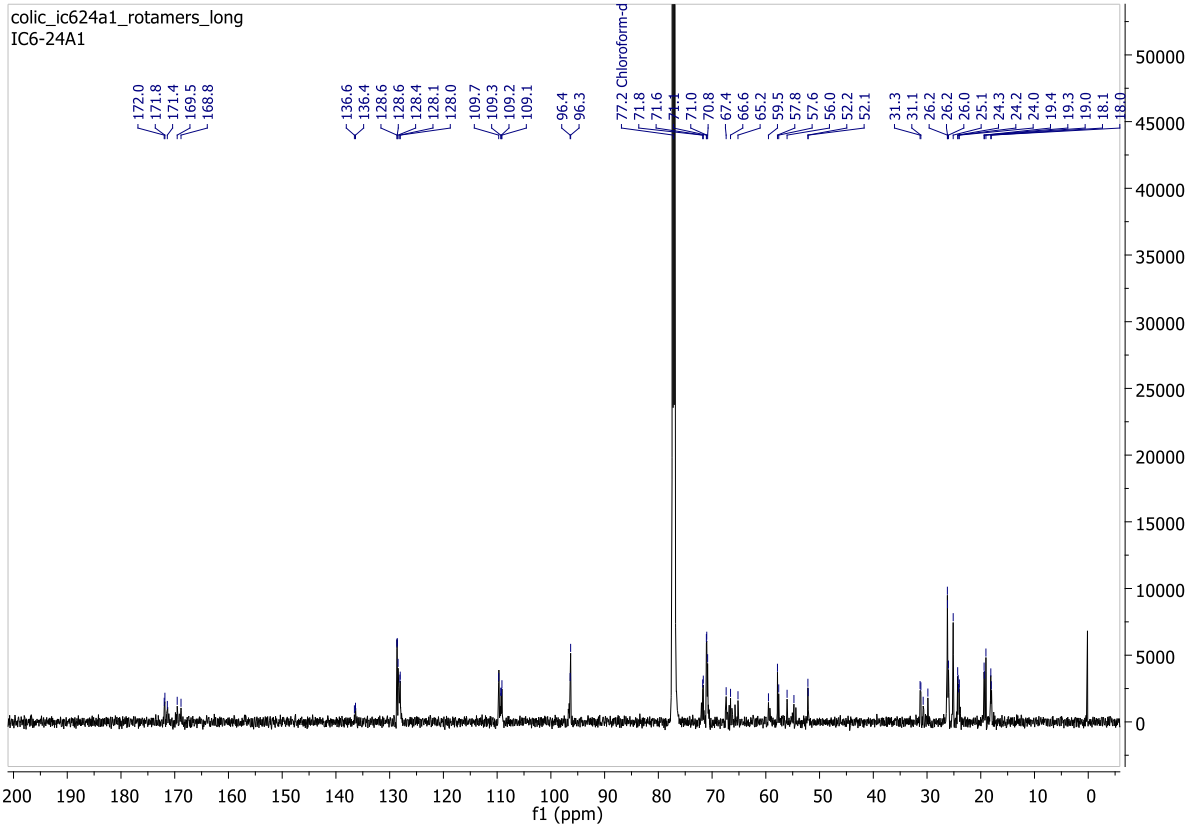
Tetramer Gal-6a (mixture of diastereoisomers)



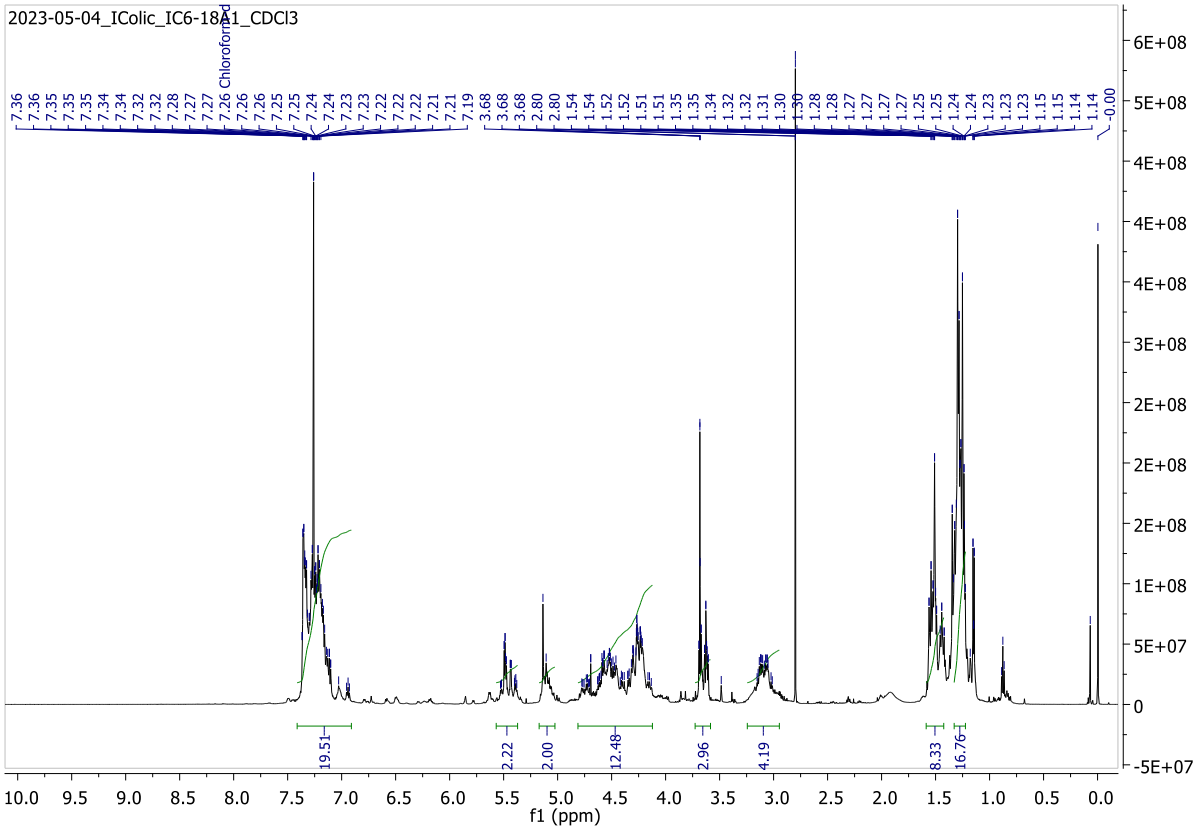


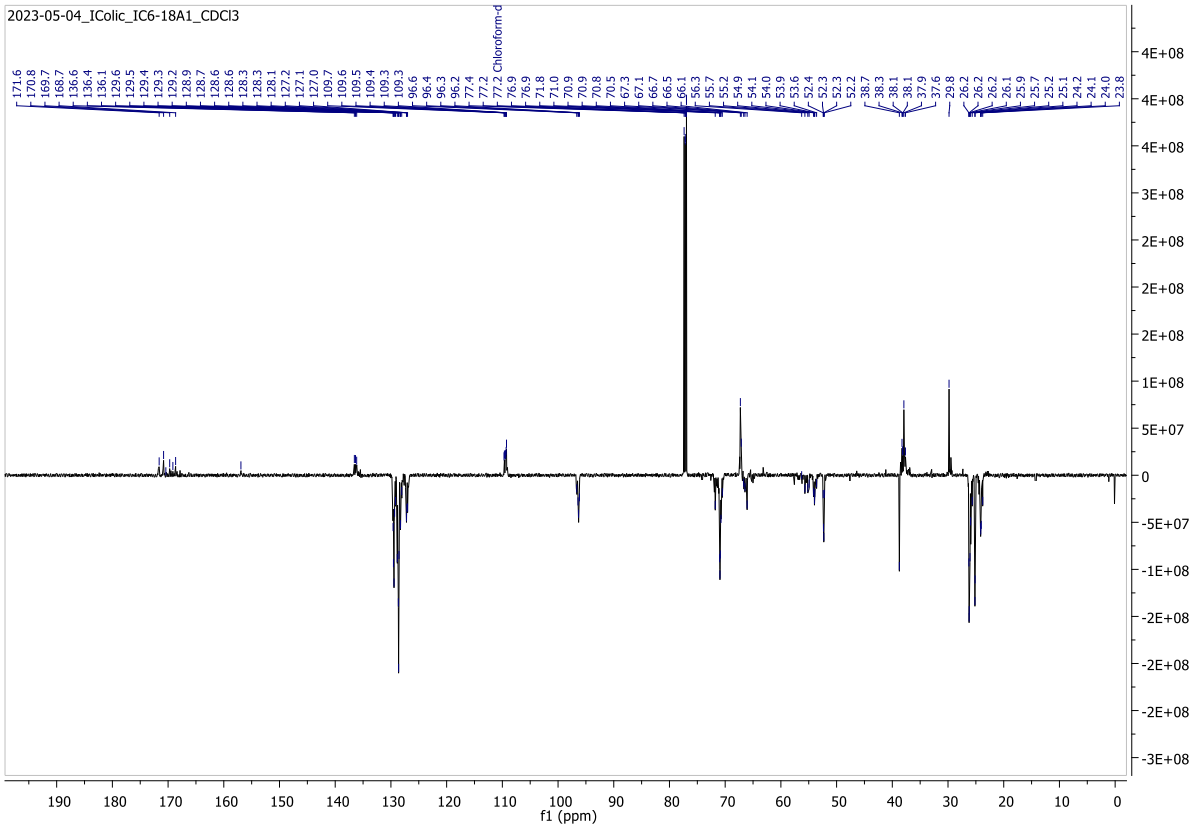
Tetramer Gal-6b (mixture of diastereoisomers)



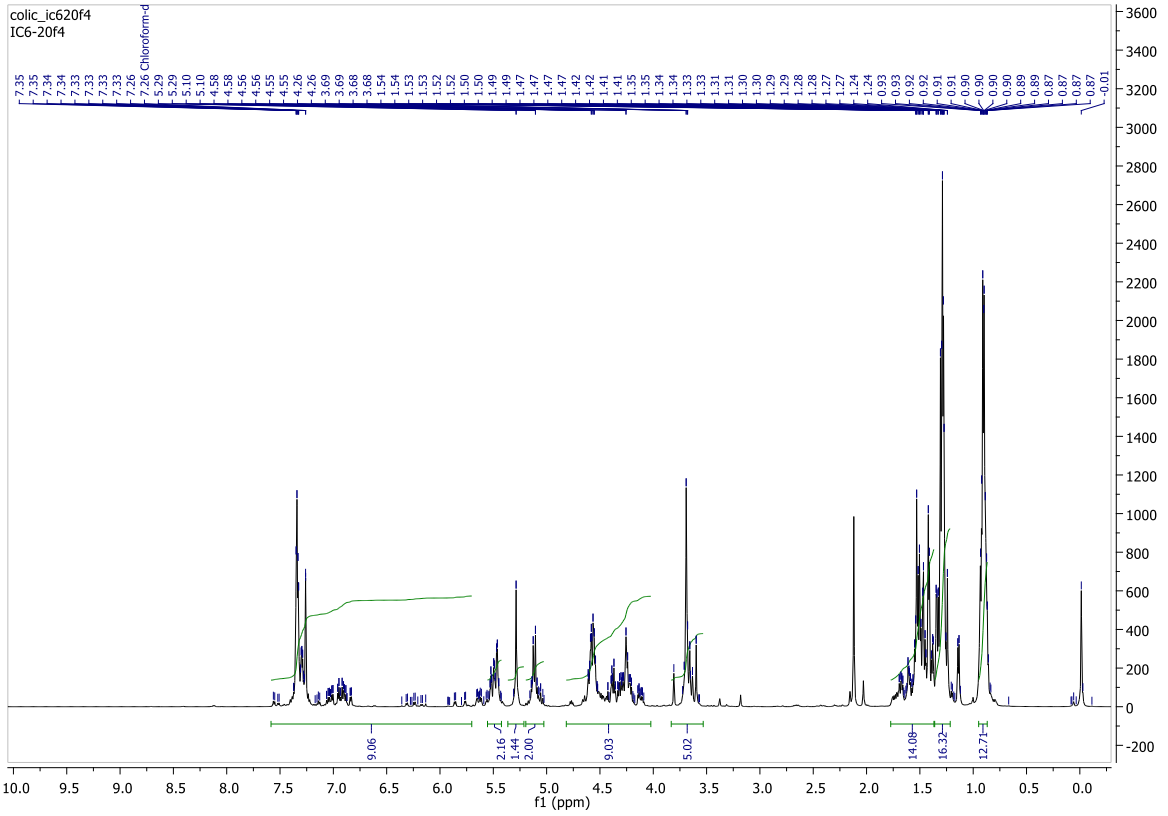


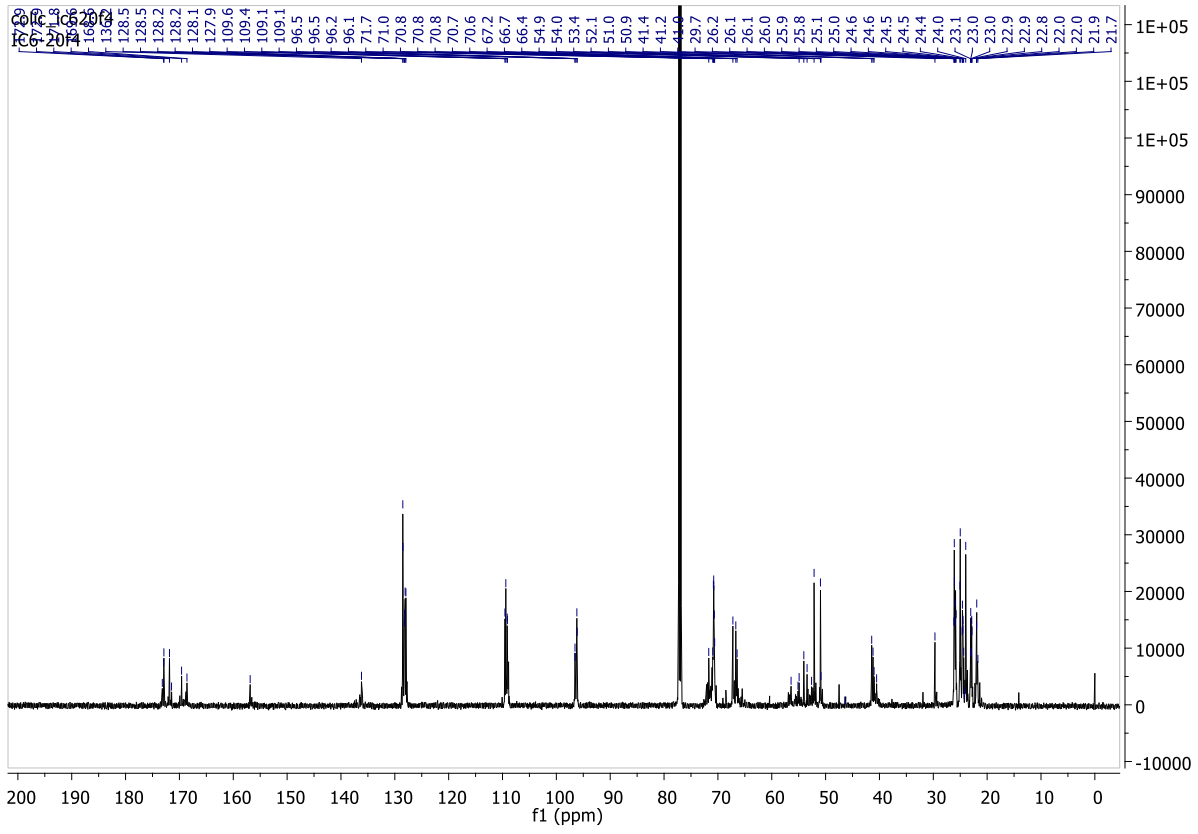
Tetramer Gal-6c (mixture of diastereoisomers)



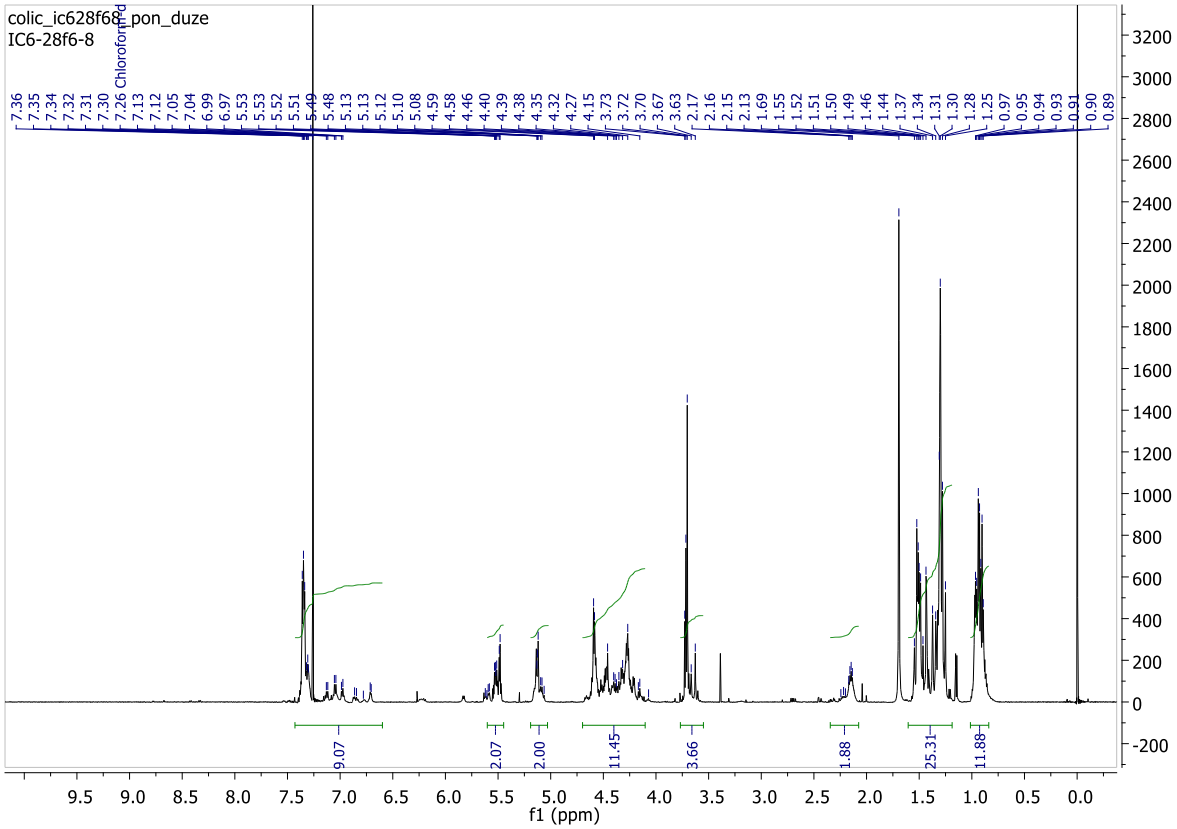


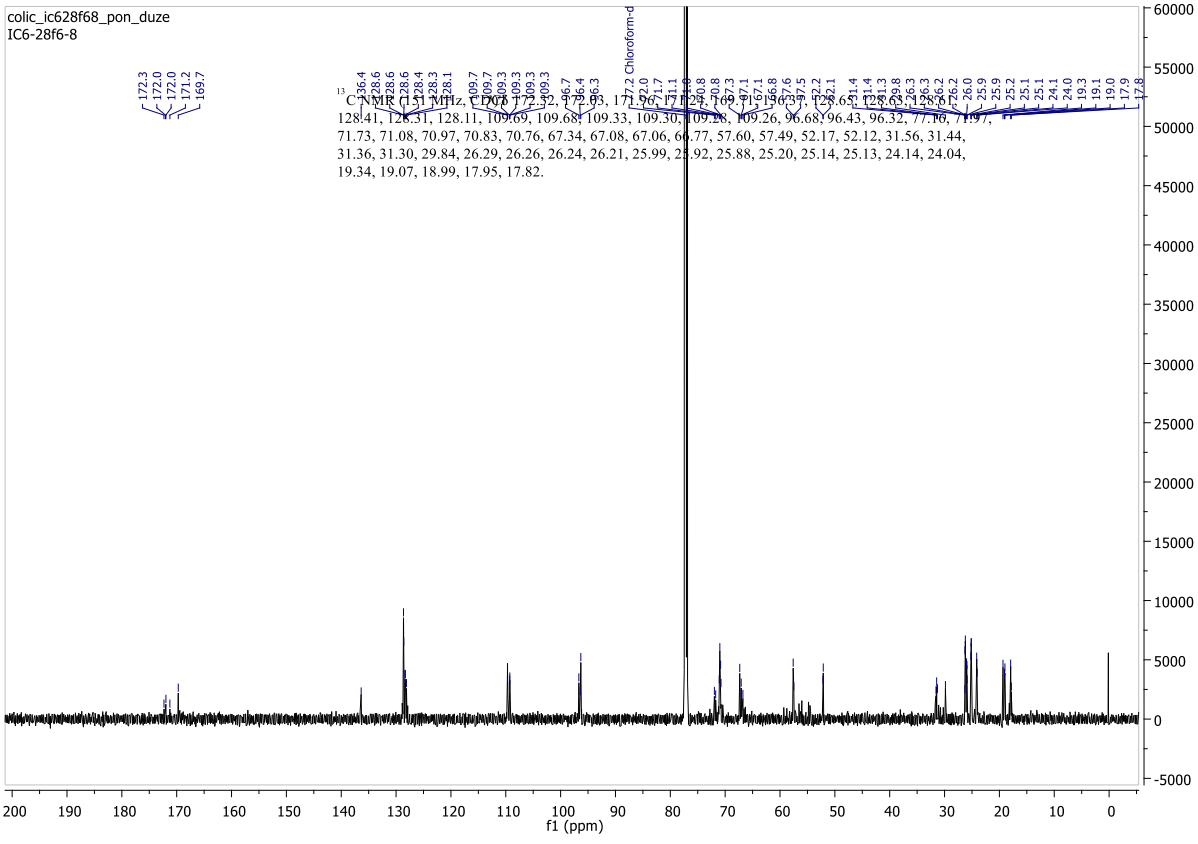
Tetramer Gal-6d (mixture of diastereoisomers)





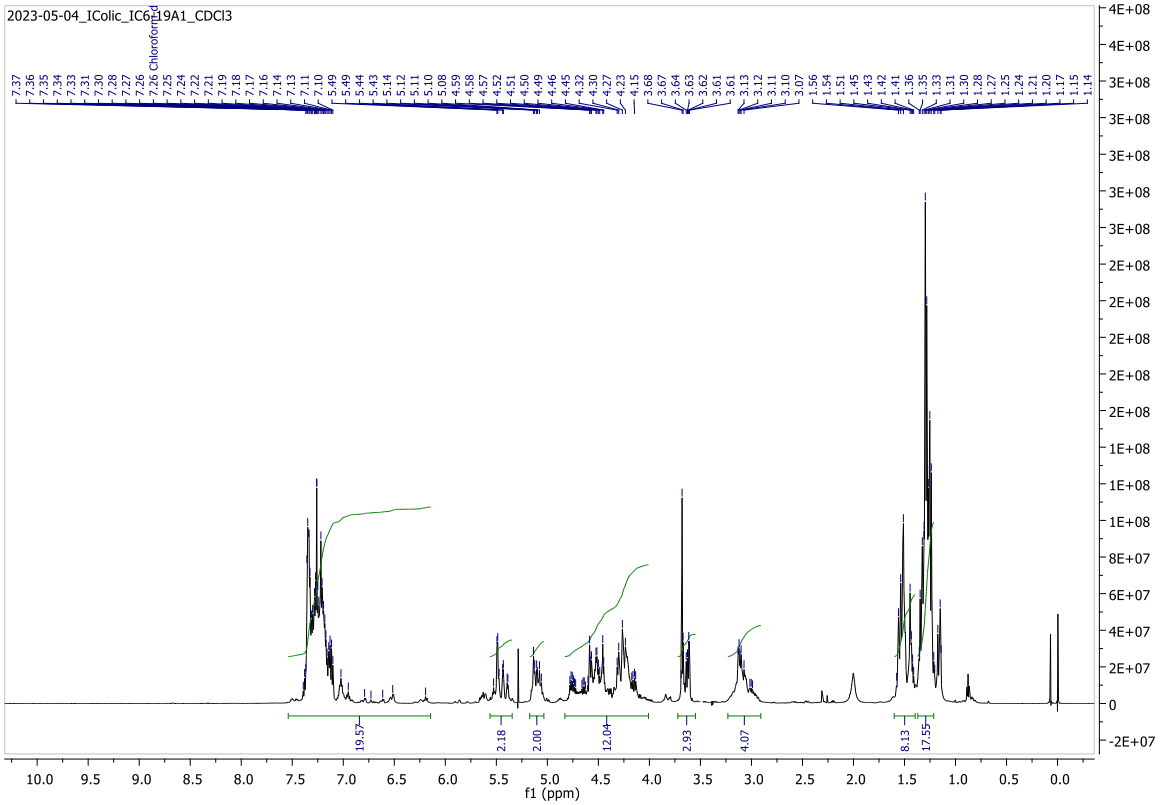
Tetramer Gal-6e (mixture of diastereoisomers)

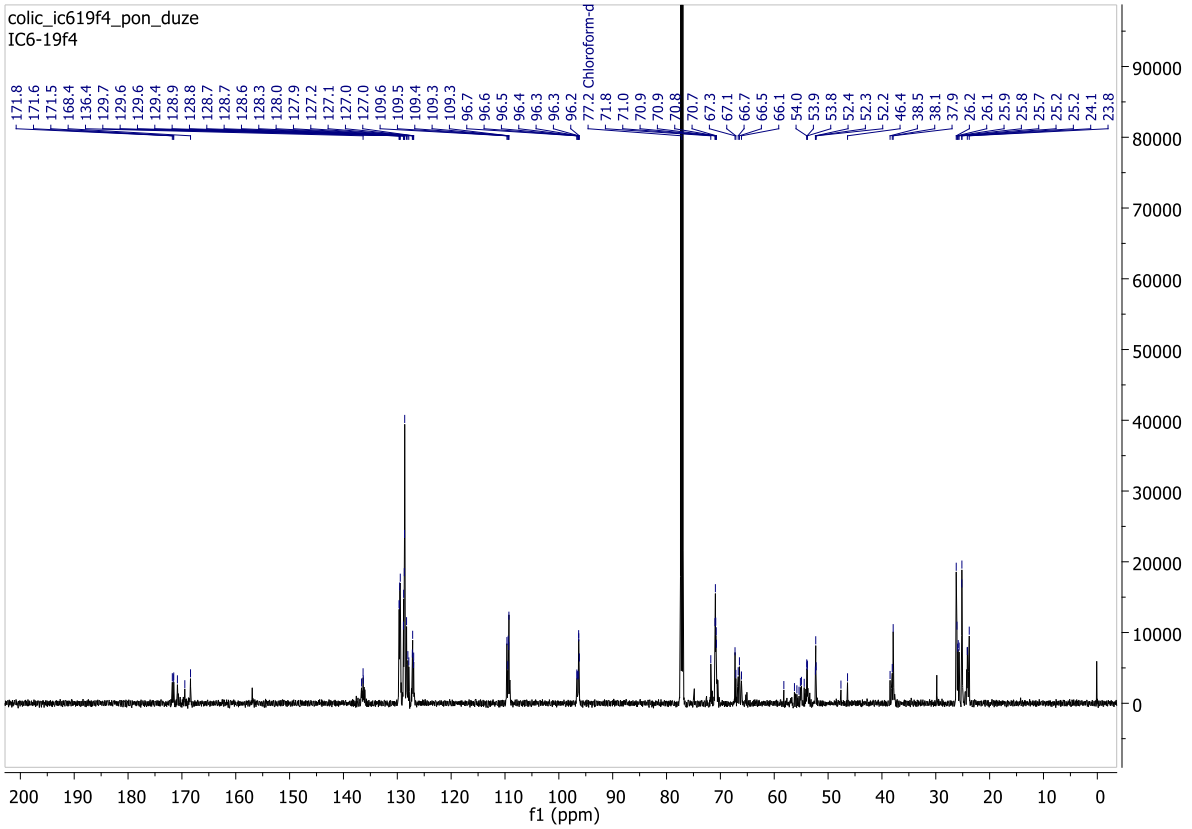




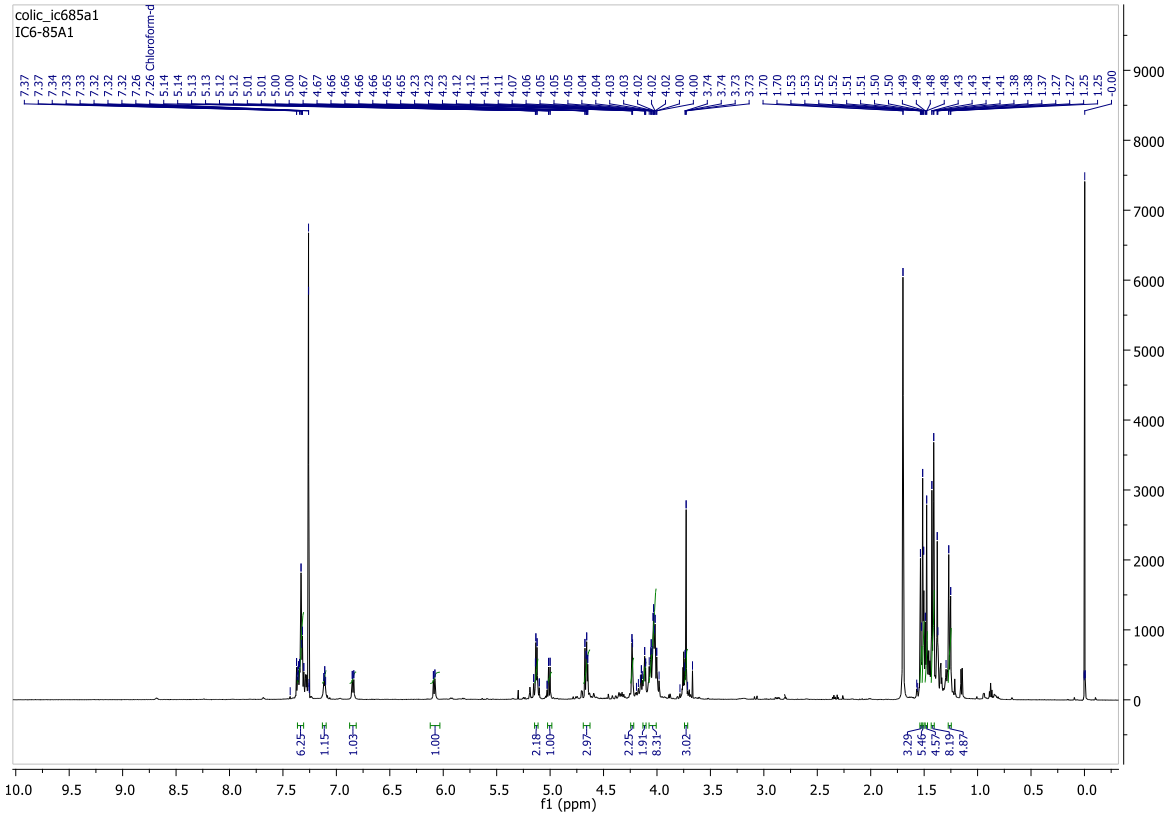
^{13}C NMR (151 MHz, CDCl$_3$) 172.32, 172.03, 171.96, 171.29, 169.71, 156.37, 128.65, 128.63, 128.61, 128.41, 128.31, 128.11, 109.69, 109.68, 109.33, 109.30, 109.28, 109.26, 96.68, 96.43, 96.32, 77.36, 71.97, 71.73, 71.08, 70.97, 70.83, 70.76, 67.34, 67.08, 67.06, 66.77, 57.60, 57.49, 52.17, 52.12, 31.56, 31.44, 31.36, 31.30, 29.84, 26.29, 26.26, 26.24, 26.21, 25.99, 25.92, 25.88, 25.20, 25.14, 25.13, 24.14, 24.04, 19.34, 19.07, 18.99, 17.95, 17.82.

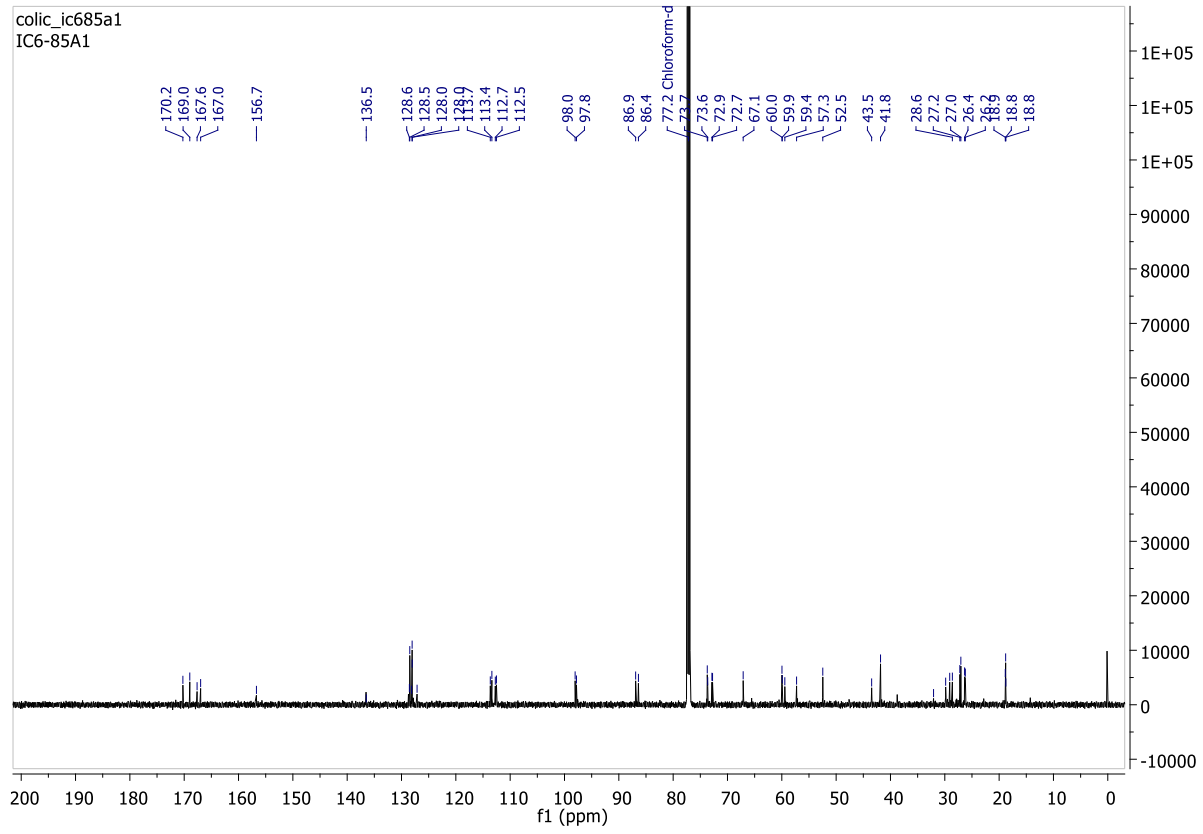
Tetramer Gal-6f (mixture of diastereoisomers)



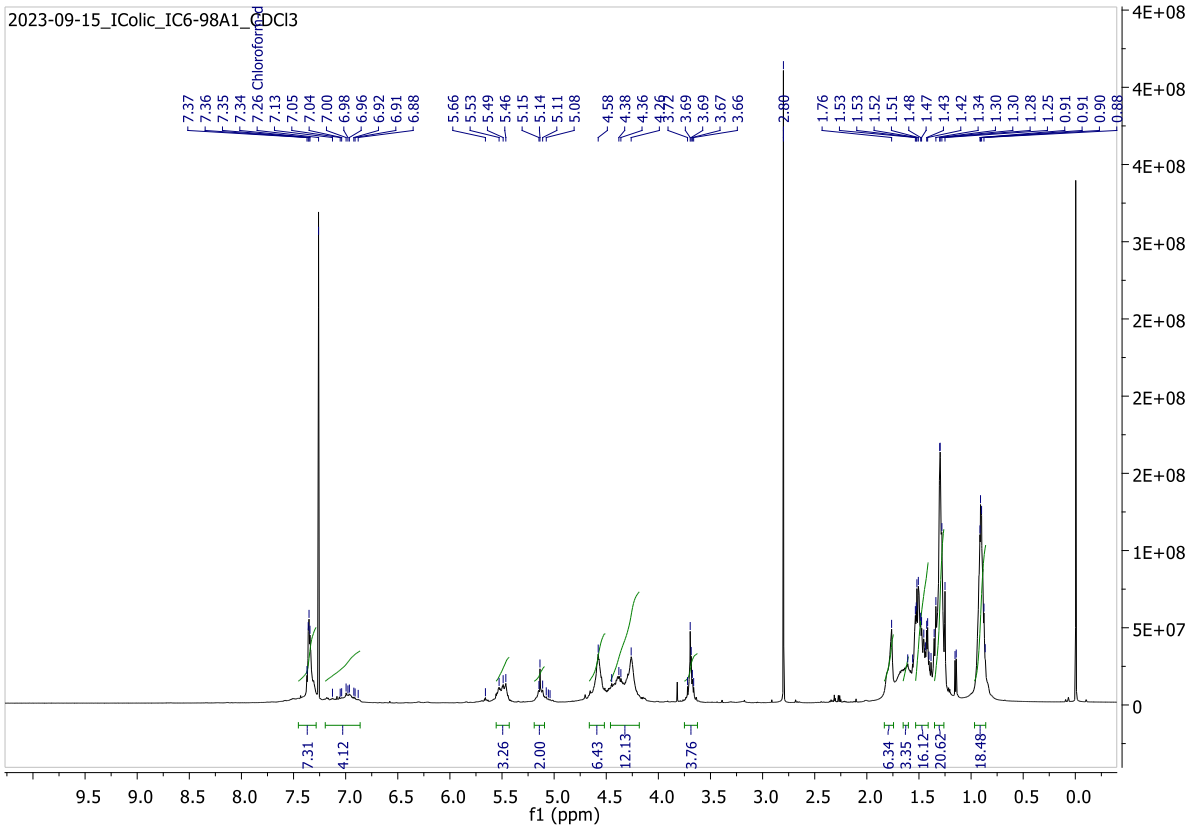


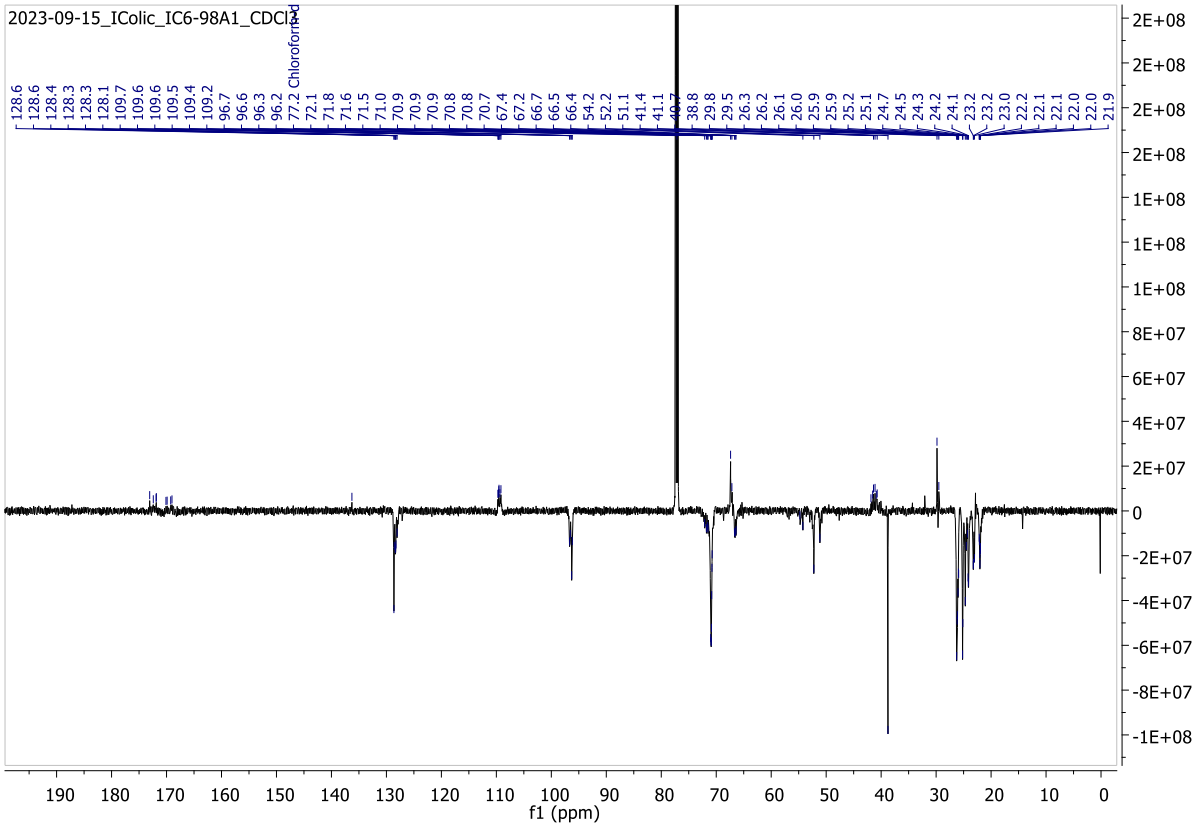
Tetramer Sor-6g (mixture of diastereoisomers)



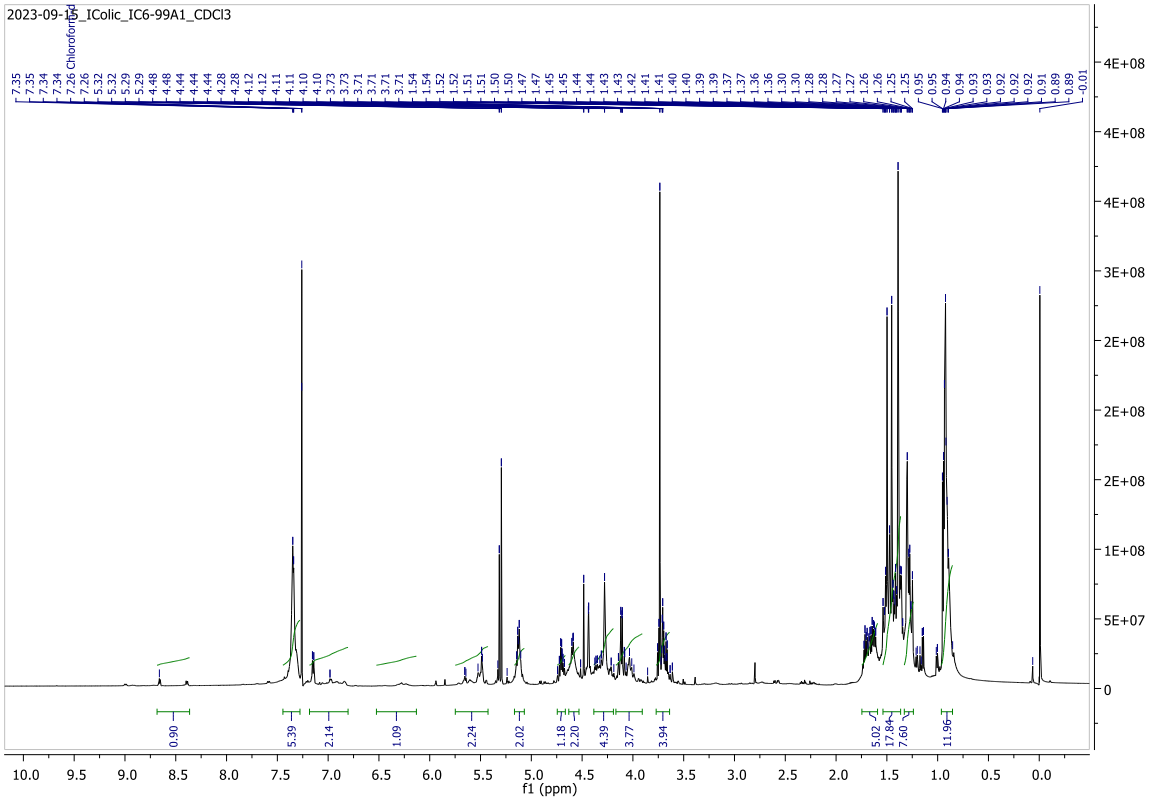


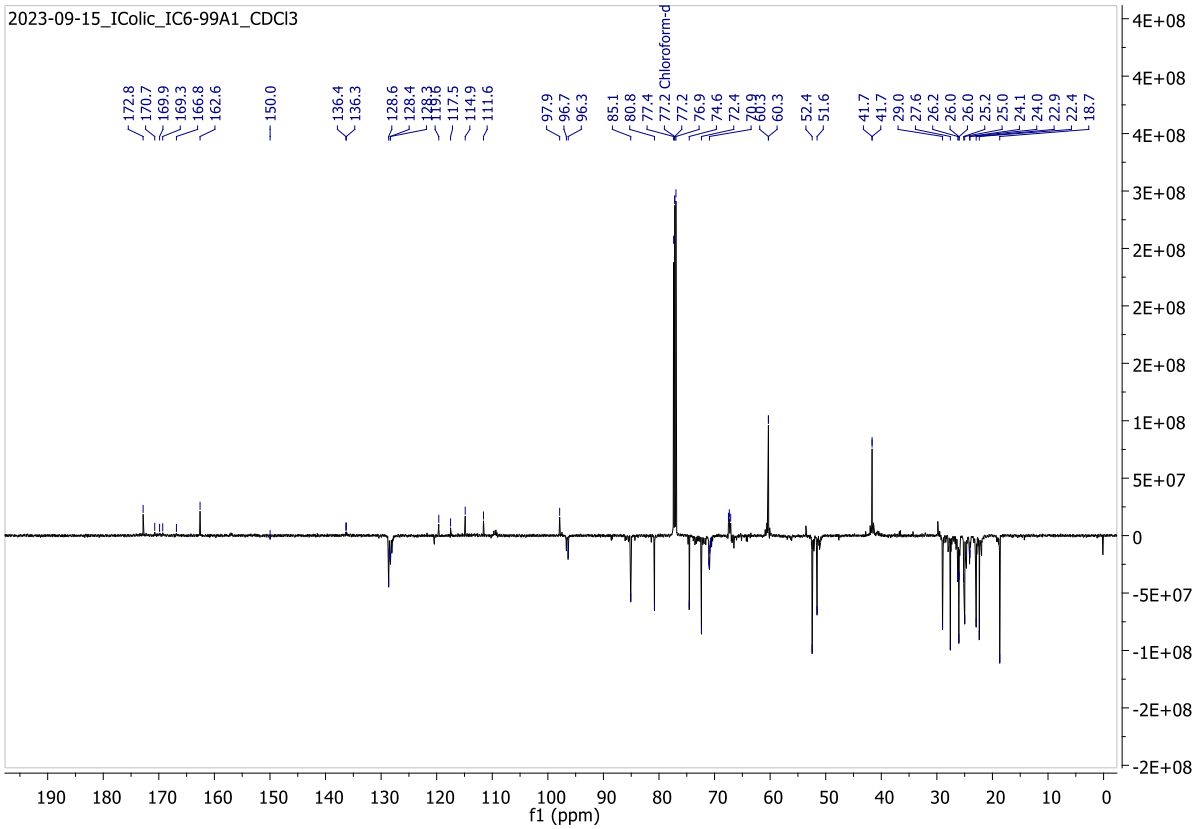
Hexamer Gal-7d (mixture of diastereoisomers)



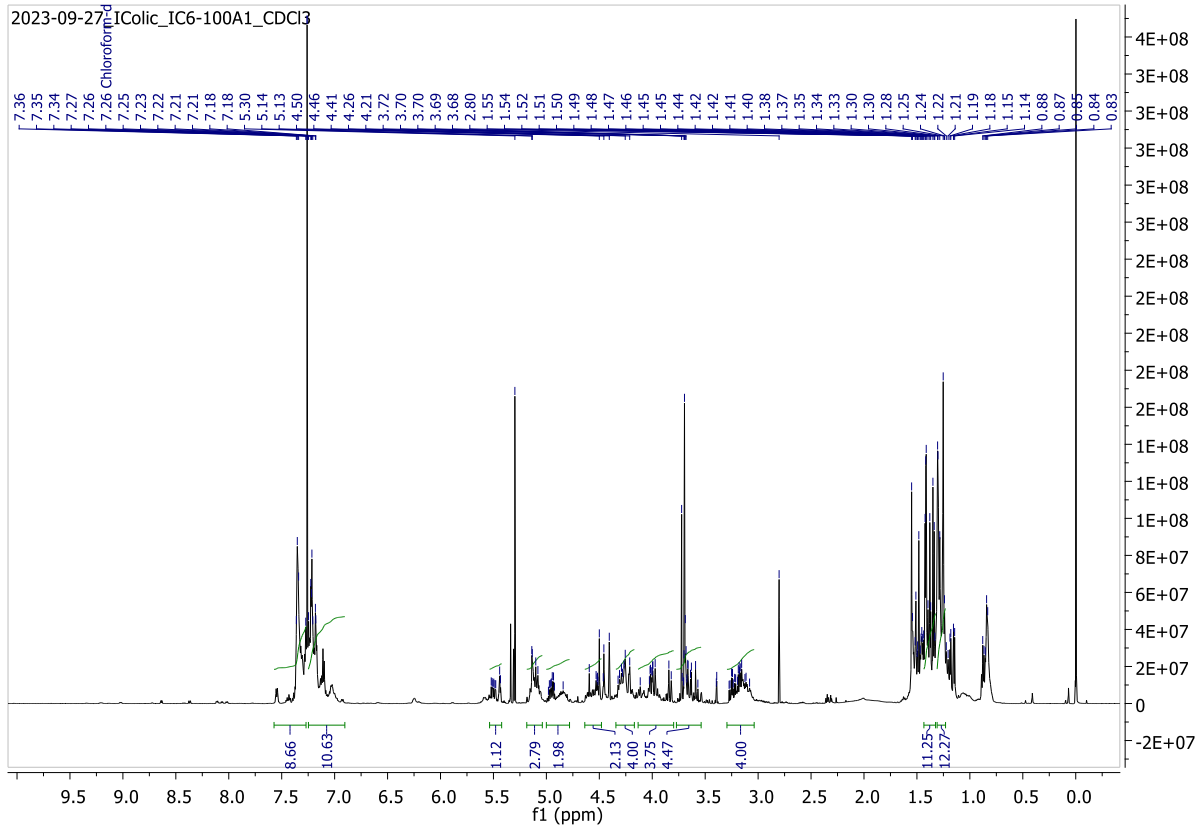


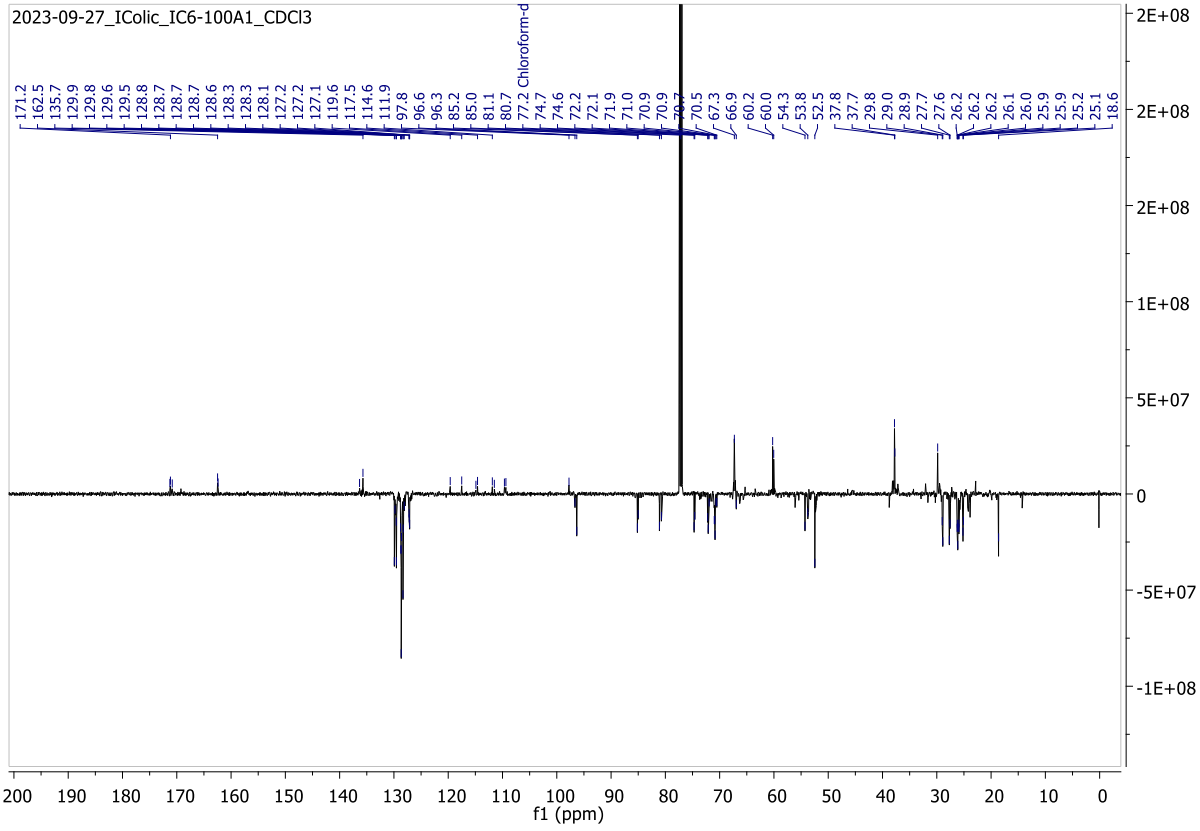
Tetramer 8 (mixture of diastereoisomers)





Tetramer 9 (mixture of diastereoisomers)





Tetramer 10 (mixture of diastereoisomers)