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SUPPORTING INFORMATION

Remarkable solvent isotope dependence on gelation strength in low molecular weight hydrogelators

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Contents

Material and analytical methods

General remarks. All amino acids where obtained from Bachem, 1,3,5-*cis,cis*-cyclohexanetricarboxylic acid was obtained from TCI, all other chemicals were from Sigma Aldrich and used without further purification. Solvents were of reagent grade. Water used for gelation studies was doubly distilled. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian AMX400 (operating at 400 and 100 MHz respectively) spectrometer. FTIR spectra were recorded on a Perkin Elmer Spectrum 400 spectrometer. Raman spectra were recorded using a Olympus BX51M upright microscope with excitation at 632.8 nm (Thorlabs Hrr 120-1 HeNe laser, 10 mW at sample, with laser line clean up filter from Semrock). Excitation was delivered using a dichoric mirror (Semrock) and light collected via a round to line multicore fibre (which acted as slit) and delivered to a Shamrock 163 spectrograph and dispersed with a SRT-SHT-9003 grating onto a iDus-418 CCD detector (Andor Technology). Calibration was performed using the spectrum of polystyrene. Dropping ball measurements were carried out using a Thermo Scientific HAAKE DC30 circulator filled with paraffin oil connected to a 6 sample heating block. The temperature of the heating block was recorded using a Amarell Electronic Digital Thermometer and the ball was followed using a Logitech C270-HD webcam. TEM images were recorded on a Phillips CM10 with a LaB_6 emitter. Rheology was carried out using an Anton Paar parallel plate rheometer.

Gelation by heating and cooling cycle. In a typical gelation experiment a weighed amount of the compound under investigation and 1.0 mL of the solvent are placed in a closed 4 mL vial (D 12 mm). The vial was heated using a heating gun for 10 second intervals with shaking until the solid had dissolved. The cap of the vial was wrapped with tissue to check for any leaks during heating. The solution was allowed to cool to room temperature and subsequently examined. Gelation was considered to have occurred when a homogeneous substance was obtained that did not exhibit gravitational flow over 24 h.

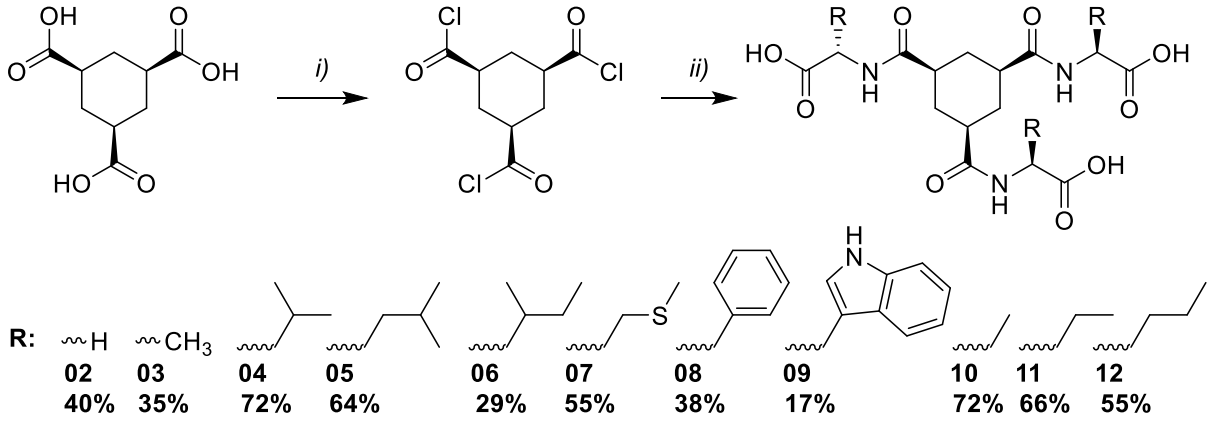
Gelation by pH jumping. In a typical gelation experiment a weighed amount of the compound under investigation was placed in a 4 mL vial (D 12 mm) and 100 μL of 1 M $NaOH_{(aq)}$ solution was added to dissolve the gelator. This solution was diluted with 800 μL of water and acidified by 100 μL of a 1 M $HCl_{(aq)}$ solution for a total of 1.0 mL. Gelation was considered to have occurred when a homogeneous substance was obtained that did not exhibit gravitational flow over 24 h.

Dropping Ball. Gels with a volume of 1.0 mL were prepared as described above. A stainless steel ball (63 mg; d 2.5 mm) was placed on top of the gel and the vial was closed. A series of these samples were placed in a heating block that was heated at a 10 °C h^{-1} while observing the positions of the balls with a video camera and concurrently monitoring the temperature by means of a thermocouple placed in the heating block. The melting temperature of the gel was taken as the temperature at which the steel ball reached the base of the vial. The upper temperature was limited to 130°C.

Rheology. The stress strain behavior of the gels was analyzed using an Anton Paar parallel plate rheometer. Gels were prepared on the bottom plate by pH jumping and the top plate was lowered to a 1 mm gap. Strain scans were performed with a 50 mm plate from 0.1 % to 100 % with a frequency of 1 rad/s. The critical strain was quoted as the point that G' starts to deviate for linearity and ultimately crosses over the G", resulting in gel breakdown.

TEM. Samples were prepared on a carbon coated copper grid by either forming the gel on the grid by pH jumping or by pipetting 4 μL out of heat/cool formed gels on the grid. Both type of samples were blotted off after 1 minute. The grid was stained with 2 μL of Uranylacetate and blotted off after 1 min.

Synthesis of Gelators



Scheme S1: Reagents and conditions *i)* $SOCl_2$, Δ, 20h, 96% yield *ii) a)* The methyl ester hydrochloride salt of the respective amino acid, DCM, trimethylamine, RT, 24 h b) Methanol, water, NaOH, RT, 20 h, 62% yield. Idem indicates that the three side groups are identical, AA: Amino acid side chain.

(1s,3s,5s)-cyclohexane-1,3,5-tricarbonyl trichloride[1] **(01)**

A white suspension of 9.74 g (45.07 mmol) of 1,2,5-*cis*,*cis*-cyclohexane and 26 mL of $SOCl_2$ was heated at reflux for 20 h. The formed clear yellow solution cooled to room temperature (20 °C), and excess $SOCl_2$ was removed by evaporation in vacuo. The resulting liquid was stored at 4 °C overnight, yielding solids which were isolated by filtration, yielding 11.77 g (43.35 mmol, 96%) of a pale yellow powder. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 2.87 (tt, *J* = 12.6, 3.4 Hz, 3H), 2.75 – 2.61 (m, 3H), 1.69 (dt, *J* = 13.7, 12.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 174.2 (COCl), 52.2 (CH), 30.3 (CH_2).

CHex(Gly-OH)[2] **(02)**

9 mL of trimethylamine were added to a cooled (0 °C) solution of 4.28 g (24.05 mmol, 3.1 eq.) of glycine methyl ester hydrochloride in 300 mL of DCM. 3 g (11.05 mmol, 1 eq.) of **2.01** in 30 mL of DCM was added to the solution. Upon mixing the two clear solutions formed an opaque white solution which was stirred at room temperature (20 °C) for 24 h. The solids were isolated by filtration and suspended in 200 mL ethanol. The solids isolated by filtration and dried in vacuo, yielding 5.5 g of the methyl ester as a white powder (80%). The powder was suspended in 60 mL of methanol cooled to 0 °C and 30 mL of 2M $NaOH_{(aq)}$ was added. The suspension was allowed to reach room temperature (20 °C) slowly and stirred for 20 h. A clear solution was obtained and diluted with 100 mL of water. The solution was acidified to pH < 3 using 2M $HCl_{(aq)}$. Gelation was observed and the resulting gel was filtered and washed with 2 x 100 mL water. The solids were dried in vacuo (40 °C, 20 mBar) for 1 h and lyophilized overnight, yielding 1.70 g (4.39 mmol, 50%) of **02** as a white powder. Decomposition above 235 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) 12.47 (s, 3H), 8.13 (t, *J* = 6.0 Hz, 3H), 3.71 (d, *J* = 6.0 Hz, 6H), 2.28 (t, *J* = 12.6 Hz, 3H), 1.94 (d, *J* = 12.6 Hz, 3H), 1.39 (q, *J* = 12.6 Hz, 3H).

^{13}C-APT NMR (101 MHz, DMSO-d_6) δ (ppm) 175.0 (COOH), 171.7 (C=O), 42.7 (CH), 31.8 (CH_2). FTMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}N_3O_9$ 388.1351; Found 388.1348. Anal. Calcd for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46; N, 10.85. Found: C, 38.13; H, 4.89; N, 8.92.

CHex(Ala-OH) **(03)**

The synthesis was analogous to the synthesis of Chex(Gly-OH) (**02**), using 4.76 g (24.05 mmol) of alanine methyl ester hydrochloride, yielding 1.68 g (3.91 mmol, 35%) of **03** as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.41 (s, 3H), 8.04 (d, *J* = 7.4 Hz, 3H), 4.15 (q, *J* = 7.3 Hz, 3H), 2.23 (t, *J* = 12.5, 3H), 1.70 (d, *J* = 12.6 Hz, 3H), 1.37 (q, *J* = 12.6 Hz, 3H), 1.23 (d, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, DMSO-d6) δ (ppm) 174.7, 174.5, 47.7, 42.7, 40.0, 31.7, 17.6. FTMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{28}N_3O_9$ 430.1820; Found 430.1815. Anal. Calcd for $C_{18}H_{27}N_3O_9$: C, 50.35; H, 6.34; N, 9.79. Found: C, 49.72; H, 6.20; N, 9.61. Melting point 150 °C degradation.

CHex(Val-OH) **(04)**

The synthesis was analogous to the synthesis of Chex(Gly-OH) (**02**), using 5.71 g (24.05 mmol) of valine methyl ester hydrochloride, yielding 4.08 g (7.93 mmol, 71%) of **04** as a white powder. Decomposition above 237 °C. ^{1}H-NMR (400 MHz, DMSO-d6) δ (ppm) 12.53 (s, 3H), 7.93 (d, J = 8.7 Hz, 3H), 4.14 (dd, J = 8.6, 5.9 Hz, 3H), 2.44 (t, J = 12.0 Hz, 3H), 2.04 (h, J = 6.7 Hz, 3H), 1.68 (d, J = 12.4 Hz, 3H), 1.42 (q, J = 12.5 Hz, 3H), 0.86 (d, J = 6.8 Hz, 18H). 13C NMR (101 MHz, DMSO-d_6) δ (ppm) 175.1, 173.6, 57.2, 42.4, 32.0, 30.2, 19.6, 18.4. FTMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{40}N_3O_9$ 514.2759; Found 514.2752. Anal. Calcd for $C_{24}H_{40}N_3O_9$; C, 56.13; H, 7.65; N, 8.18. Found; C, 50.34; H, 7.35; N, 7.27.

CHex(Leu-OH) **(05)**

The synthesis was analogous to the synthesis of Chex(Gly-OH) (**02**), using 6.19 g (24.05 mmol) of leucine methyl ester hydrochloride, yielding 3.92 g (7.05 mmol, 64%) of **05** as a white powder. Decomposition above 238 °C. ^{1}H-NMR (400 MHz, DMSO-d6) δ (ppm) 12.45 (s, 3H), 8.02 (d, J = 8.0 Hz, 3H), 4.20 (ddd, J = 10.1, 8.1, 4.9 Hz, 3H), 2.28 (tt, J = 12.5, 3.4 Hz, 3H), 1.74 – 1.65 (m, 3H), 1.65 – 1.33 (m, 13H), 0.85 (dd, J = 22.3, 6.4 Hz, 18H). ^{13}C-APT NMR (101 MHz, DMSO-d_6) δ (ppm) 174.7, 174.6, 50.3, 42.8, 31.8, 24.8, 23.3, 21.6. FTMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{46}N_3O_9$ 556.3220; Found 556.3229. Anal. Calcd for $C_{27}H_{45}N_3O_9$: C, 58.36; H, 8.16; N, 7.56. Found: C,55.66; H, 7.20 ; N, 7.88.

CHex(Ile-OH) (06)

The synthesis was analogous to the synthesis of Chex(Gly-OH) (**02**), using 6.19 g (24.05 mmol) of isoleucine methyl ester hydrochloride, yielding 1.79 g (3.22 mmol, 29%) of **06** as a white powder. Melting point 229-231 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) 12.51 (s, 2H), 7.93 (d, J = 8.6 Hz, 3H), 4.17 (dd, J = 8.6, 6.3 Hz, 3H), 2.40 (t, J = 12.5 Hz, 3H), 1.77 (bs, 3H), 1.67 (d, J = 12.5 Hz, 3H), 1.41 (q, J = 12.5, 11.6 Hz, 6H), 1.17 (h, J = 14.9, 7.5 Hz, 3H), 0.83 (t, J = 7.4 Hz, 18H). ^{13}C-APT NMR (101 MHz, DMSO-d_6) δ (ppm) 175.0, 173.6, 56.4, 42.4, 40.5, 40.3, 39.8, 39.6, 39.4, 36.7, 32.0, 25.1, 16.1, 11.6.FTMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{46}N_3O_9$ 556.3229; Found 556.3221. Anal. Calcd for $C_{27}H_{45}N_3O_9$: C, 58.36; H, 8.16; N, 7.56. Found: C,56.54 ; H, 7.37 ; N, 7.91.

CHex(Met-OH) (07)

The synthesis was analogous to the synthesis of Chex(Gly-OH) (02), using 6.80 g (34.05 mmol) of *L*-methionine methyl ester hydrochloride, yielding 1.86 g (2.86 mmol, 62%) of **07** as a white powder. Decomposition above 214 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) 12.57 (s, 3H), 8.06 (dd, *J* = 7.9, 3.2 Hz, 3H), 4.28 (tt, *J* = 8.2, 3.7 Hz, 3H), 2.45 (dt, *J* = 8.7, 4.6 Hz, 9H), 2.30 (d, *J* = 14.2 Hz, 3H), 2.03 (d, *J* = 3.3 Hz, 3H), 1.95 (dp, *J* = 12.3, 4.0 Hz, 3H), 1.84 (dp, *J* = 13.0, 4.8, 4.0 Hz, 3H), 1.74 (d, *J* = 12.2 Hz, 3H), 1.49 – 1.35 (m, 3H). ^{13}C-APT NMR (101 MHz, DMSO-d_6) δ (ppm) 174.9, 173.8, 51.2, 42.8, 31.8, 31.1, 30.2. FTMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{40}N_3O_9S_3$ 610.1921; Found 610.1911. Anal. Calcd for $C_{24}H_{39}N_3O_9S_3$: C, 47.27; H, 6.45; N, 6.89. Found: C, 46.63; H, 6.39; N, 6.73.

CHex(Phe-OH) (08)

The synthesis was analogous to the synthesis of Chex(Gly-OH) (**02**), using 9.33 g (43 mmol) of *L*-phenylalanine methyl ester hydrochloride and 2.89 g (10.7 mmol) of **01**, yielding 2.68 g (4.1 mmol, 38%) of **08** as a white powder. Decomposition above 245 °C. ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) δ 13.16 – 12.30 (m, 4H), 8.10 (d, 4H), 7.21 (dq, 18H), 4.38 (td, 4H), 3.05 (dd, 4H), 2.84 (dd, 4H), 2.18 (s, 2H), 1.46 (d, 3H), 1.21 (q, 4H). ^{13}C-APT NMR (101 MHz, DMSO-d_6) δ 132.2, 131.2, 129.4, 56.3, 45.2, 43.3, 43.1, 42.9, 42.7 HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{39}N_3O_9Na$ 680.2579; Found 680.2569. Anal. Calcd for $C_{36}H_{39}N_3O_9$: C, 65.74; H, 5.98; N, 6.39. Found: C, 55.90; H, 5.39; N, 5.42.

CHex(Trp-OH)(09)

The synthesis was analogous to the synthesis of Chex(Gly-OH) (**02**), using 5.38 g (21.1 mmol) of *L*-tryptophan methyl ester hydrochloride and 2.03 g (7.05 mmol) of **01**, yielding 0.95 g (1.22 mmol, 17%) of **09** as a white powder. Decomposition above 225 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.56 (s, 3H), 10.91 (s, 3H), 8.06 (s, 3H), 7.50 (s, 3H), 7.31 (s, 3H), 7.10 (s, 3H), 7.03 (s, 3H), 6.95 (s, 3H), 4.42 (s, 3H), 3.13 (s, 3H), 2.99 (s, 3H), 2.23 (s, 3H), 1.59 (s, 3H), 1.29 (s, 3H). ^{13}C-APT NMR (101 MHz, DMSO-d_6) δ 126.51, 123.97, 121.41, 121.23, 114.48, 55.91, 45.22, 43.09, 42.88, 42.67, 42.34, 42.12. HRMS

(ESI) m/z: $[M + Na]^+$ Calcd for $C_{42}H_{42}N_6O_9Na$ 797.2906; Found 797.2896. Anal. Calcd for $C_{36}H_{39}N_3O_9$: C, 65.11; H, 5.46; N, 10.85. Found: C, 54.46; H, 4.83; N, 9.02.

CHex(Abu-OH) **(10)**

The synthesis was analogous to the synthesis of Chex(Gly-OH) (**02**), using 4.79 g (31.18 mmol) of abutaric acid methyl ester hydrochloride and 2.28 g (8.47 mmol) of **01**, yielding 2.84 g of **10** as a white powder. Melting point 229-231 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) 12.50 (s, 3H), 8.04 (d, J = 7.9 Hz, 3H), 4.09 (td, J = 8.3, 5.1 Hz, 3H), 2.33 (s, 3H), 1.79 – 1.66 (m, 6H), 1.58 (dt, J = 14.3, 7.6 Hz, 3H), 1.41 (q, J = 12.6 Hz, 3H), 0.86 (t, J = 7.4 Hz, 9H). ^{13}C-APT NMR (75 MHz, DMSO-d_6) δ (ppm) 175.0, 174.1, 53.5, 42.6, 31.9, 24.8, 10.9. FTMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{34}N_3O_9$ 472.2290; Found 472.2286. Anal. Calcd for $C_{21}H_{33}N_3O_9$: C, 47.27; H, 6.45; N, 6.89. Found: C, 46.63; H, 6.39; N, 6.73; Na, 5.05.

CHex(Nva-OH) **(11)**

The synthesis was analogous to the synthesis of Chex(Gly-OH) (**02**), using 4.95 g (29.53 mmol) of L-norvaline methyl ester hydrochloride and 2.18g (8.03 mmol) of **01**, yielding 2.721 g (5.30 mmol, 66%) of **11** as a white powder. Melting point 229-231 °C. ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) 12.43 (s, 3H), 7.97 (d, J = 7.9 Hz, 3H), 4.14 (td, J = 7.9, 5.2 Hz, 3H), 2.28 (t, J = 12.5 Hz, 3H), 1.72 – 1.58 (m, 6H), 1.58 – 1.47 (m, 3H), 1.39 (q, J = 12.5 Hz, 3H), 1.26 (tt, J = 13.7, 7.3 Hz, 6H), 0.84 (t, J = 7.3 Hz, 9H). ^{13}C-APT NMR (101 MHz, DMSO-d6) δ (ppm) 174.8, 174.3, 51.7, 42.7, 40.0, 33.5, 31.8, 19.2, 13.9. FTMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{39}N_3O_9$ 514.2759; Found 514.2752. Anal. Calcd for $C_{24}H_{39}N_3O_9$: C, 56.13; H, 7.65; N, 8.18. Found: C, 52.51; H, 7.64; N, 7.55.

CHex(Nle-OH) **(12)**

The synthesis was analogous to the synthesis of Chex(Gly-OH) (**02**), using 4.72 g (26 mmol) of *L*-norleucine methyl ester hydrochloride and 2.30 g (8.47 mmol) of **01**, yielding 2.22 g (4.00 mmol, 63%) of **12** as a white powder. Melting point 220-221 °C ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) 12.44 (s, 3H), 7.97 (d, J = 8.0 Hz, 3H), 4.18 – 4.07 (m, 3H), 2.34 – 2.22 (m, 3H), 1.73 – 1.60 (m, 6H), 1.55 (dq, J = 10.3, 6.1, 5.0 Hz, 3H), 1.40 (q, J = 12.6 Hz, 3H), 1.24 (t, J = 6.6, 4.2 Hz, 12H), 0.83 (h, J = 3.7, 3.1 Hz, 9H). ^{13}C-APT NMR (75 MHz, DMSO-d_6) δ (ppm) 174.8, 174.3, 51.9, 42.7, 31.8, 31.1, 28.0, 22.1, 14.2. FTMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{46}N_3O_9$ 556.3229; Found 556.3216. Anal. Calcd for $C_{27}H_{45}N_3O_9$: C, 58.36; H, 8.16; N, 7.56. Found: C, 55.35; H, 7.78; N, 7.17.

Spectroscopic data of all compounds

(1s,3s,5s)-cyclohexane-1,3,5-tricarbonyl trichloride **(01)**

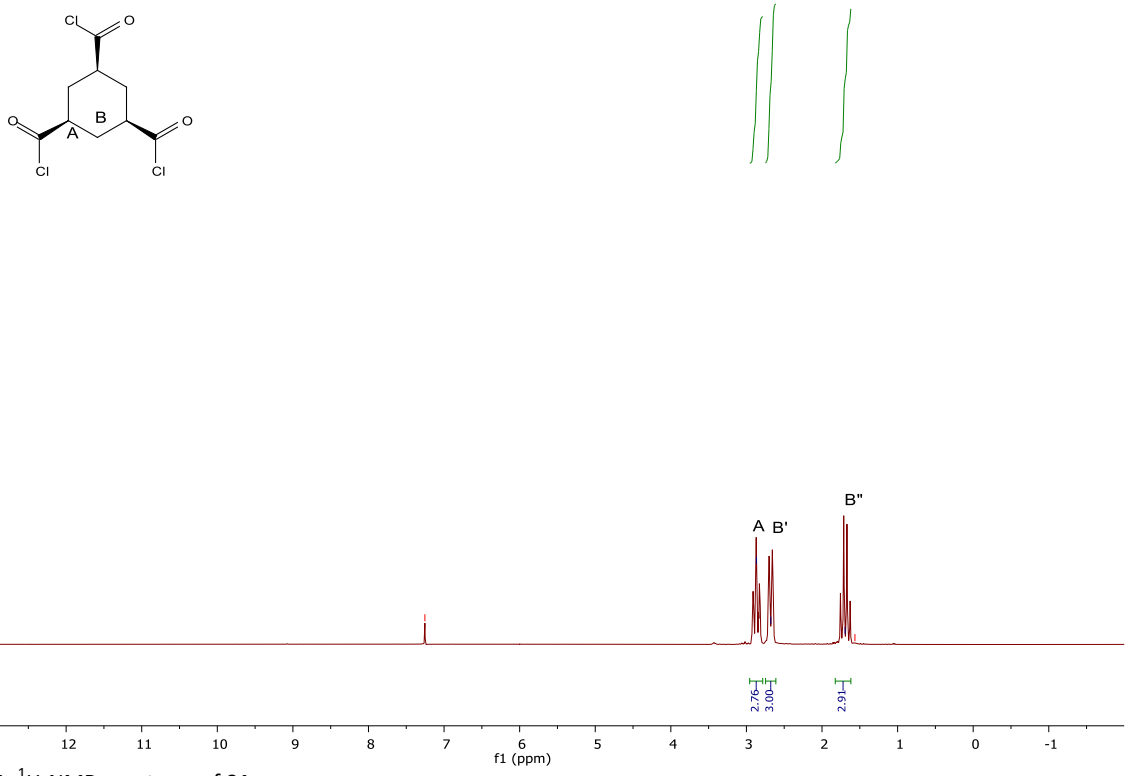


Figure S1: ^{1}H-NMR spectrum of **01**.

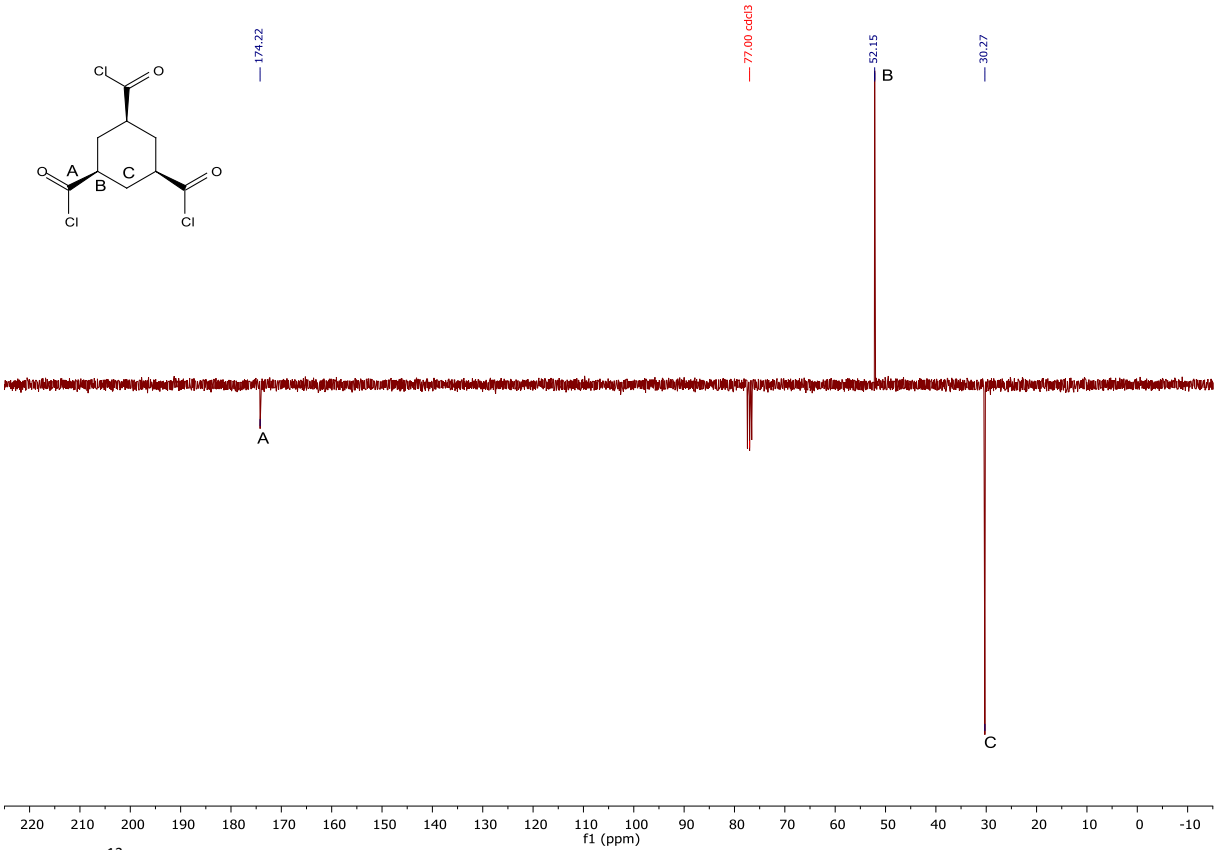


Figure S2: ^{13}C-APT NMR spectrum of **01**.

CHex(Gly-OH) **(02)**

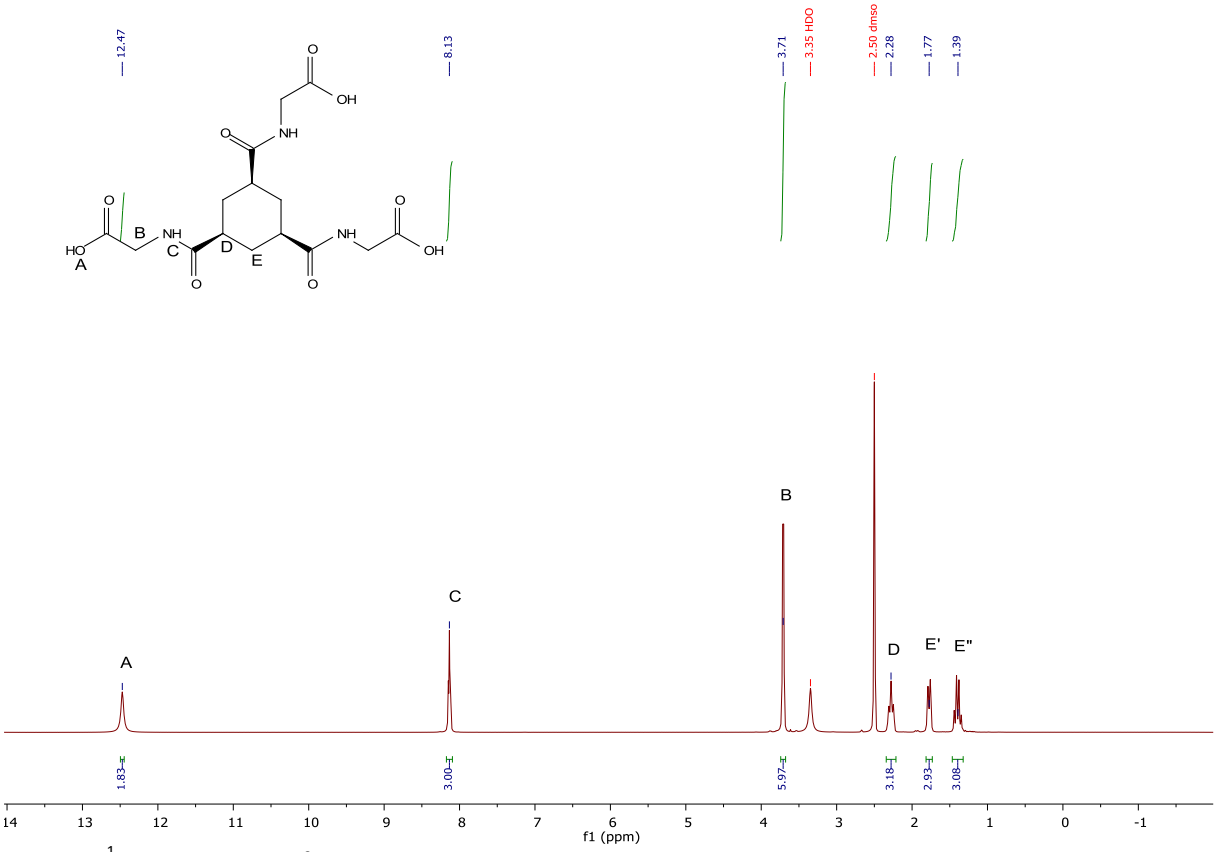


Figure S3: ^{1}H-NMR spectrum of **02**.

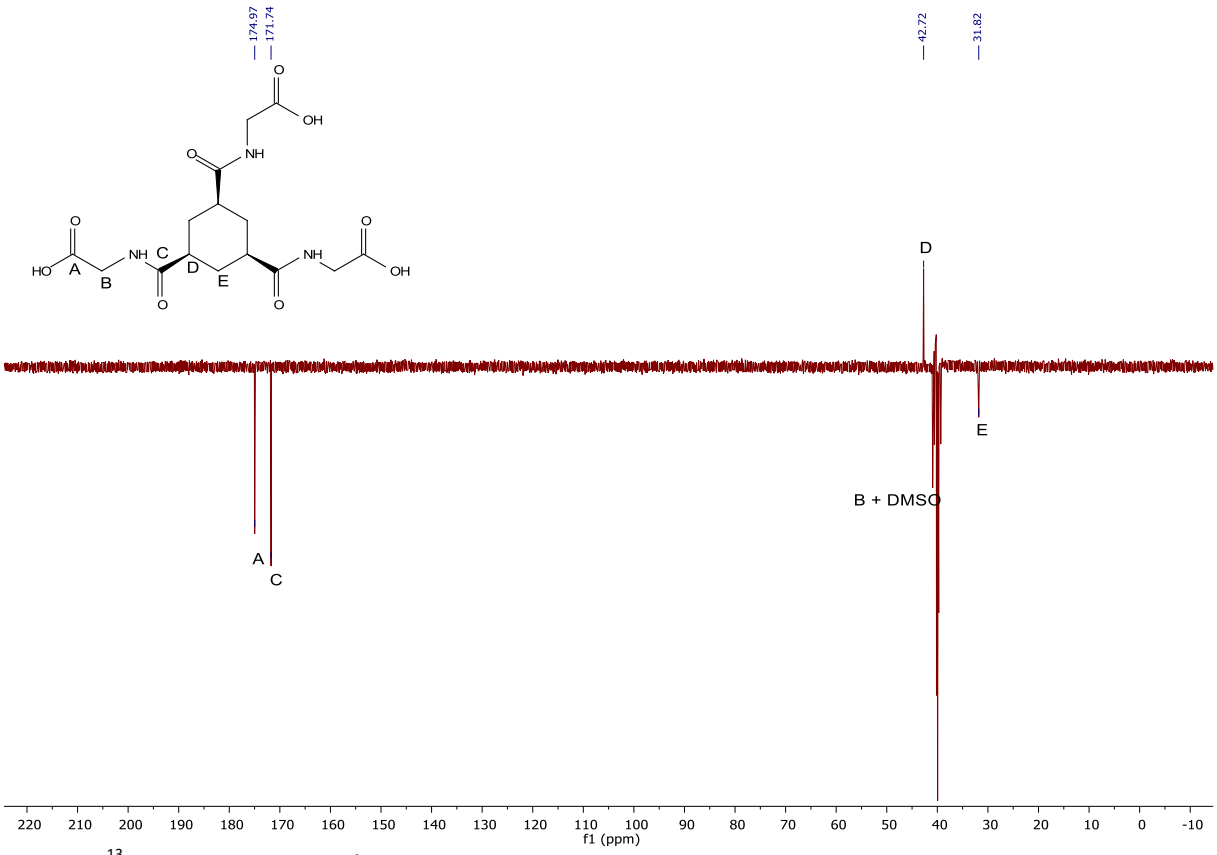


Figure S4: ^{13}C-APT NMR spectrum of **02**.

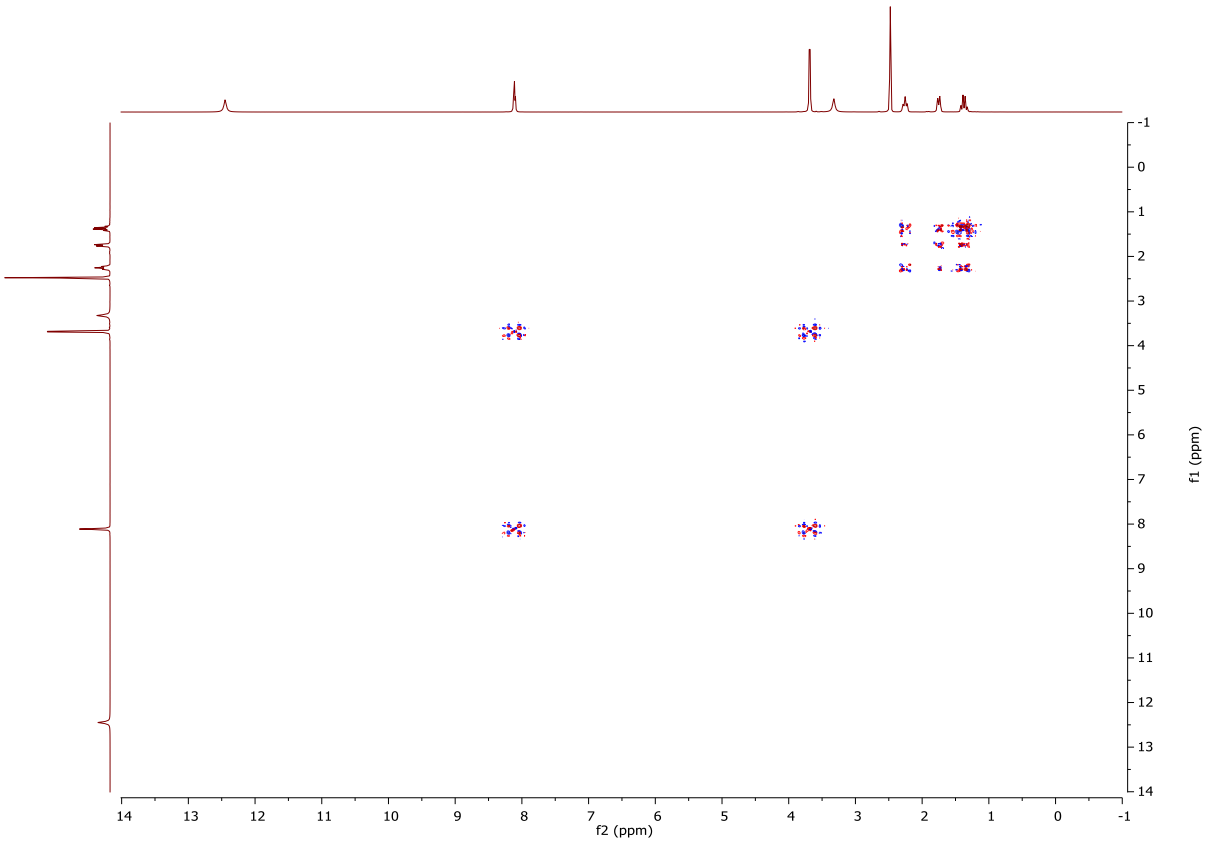


Figure S5: gDQF-COSY spectrum of **02**.

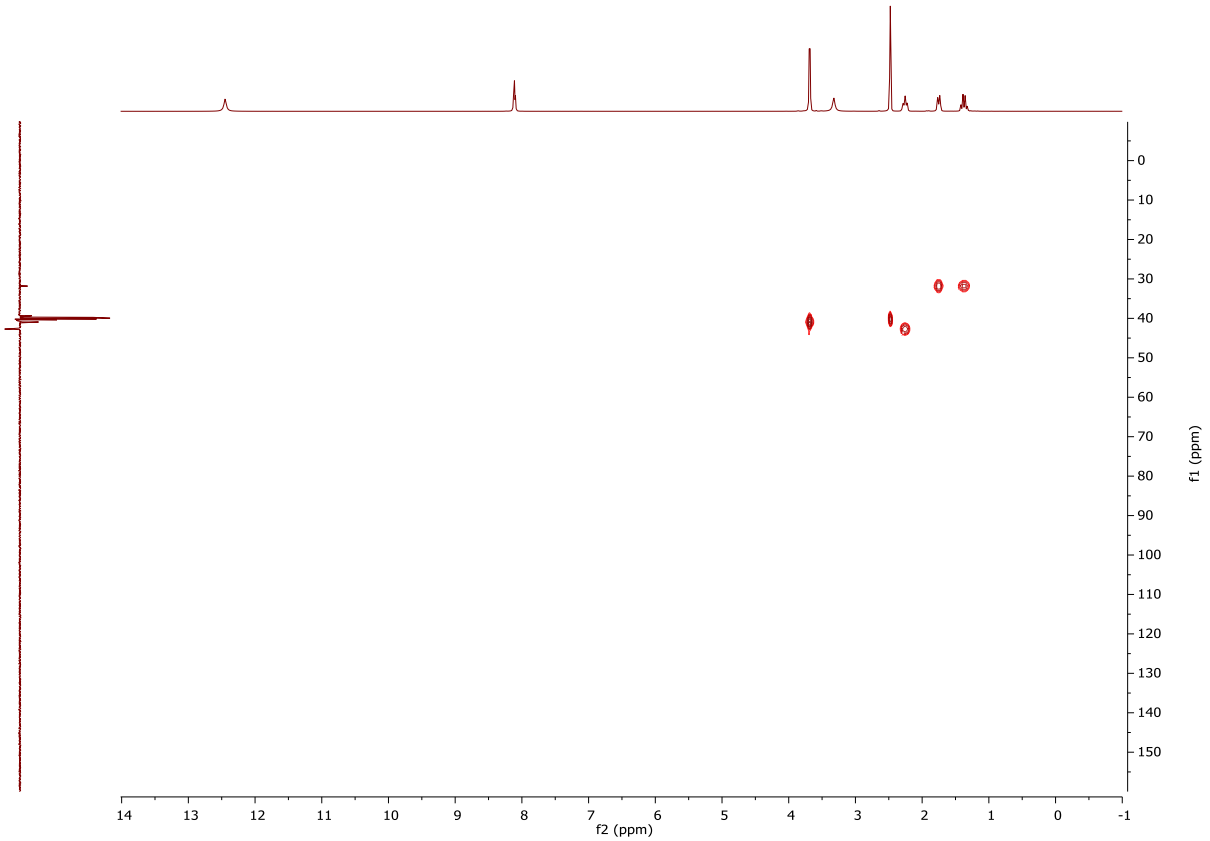


Figure S6: gHSQC spectrum of **02**.

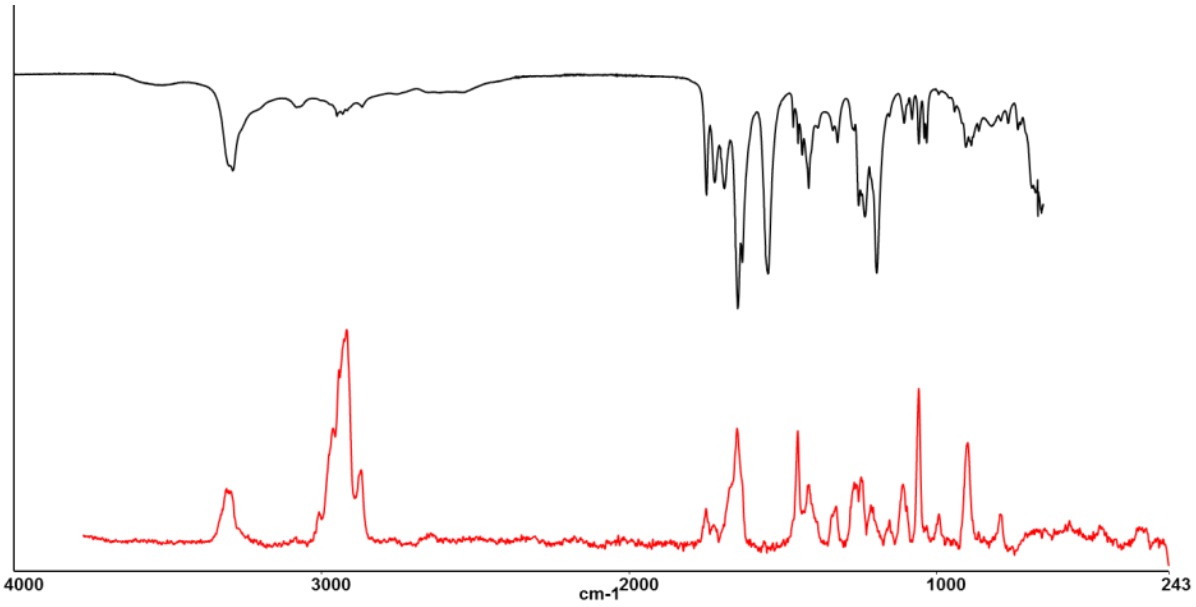


Figure S7: FTIR and Raman (633 nm) spectrum of **02**.

CHex(Ala-OH) (03)

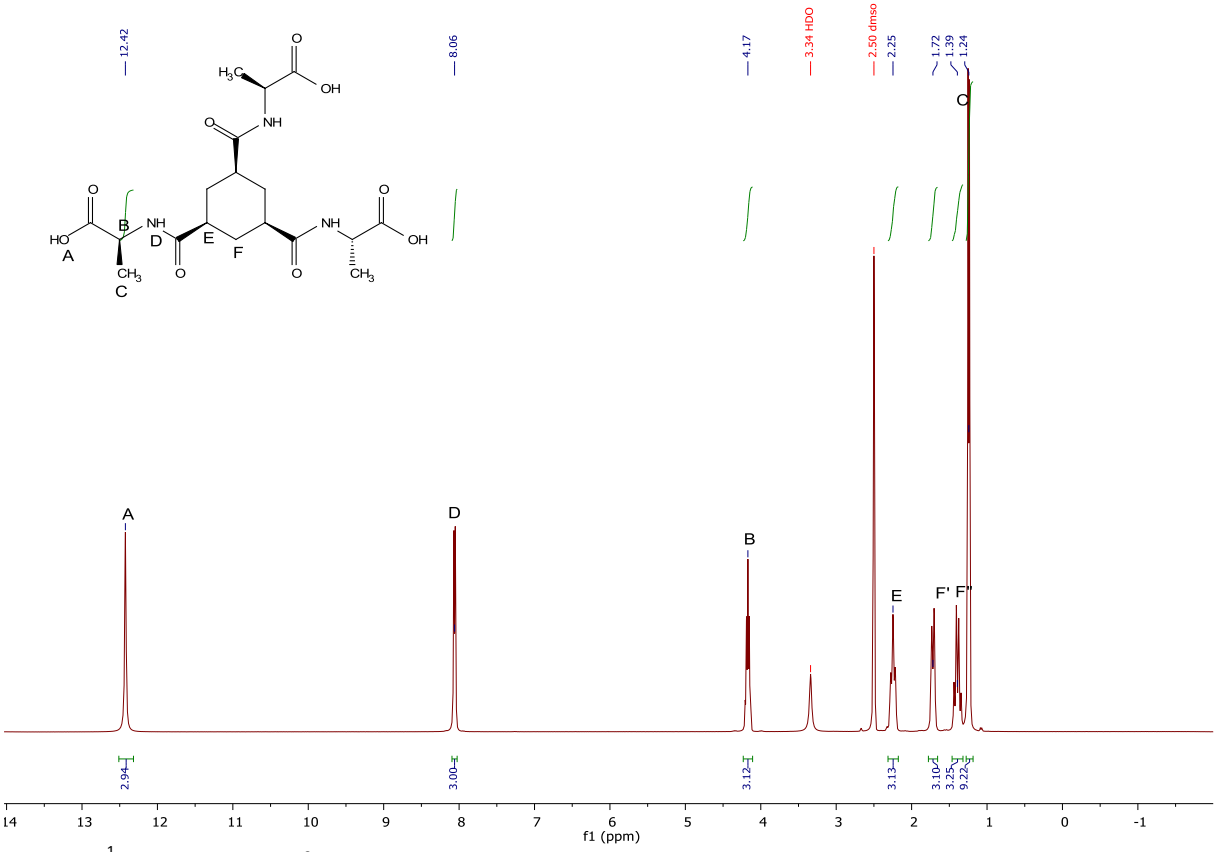


Figure S8: ^{1}H-NMR spectrum of **03**.

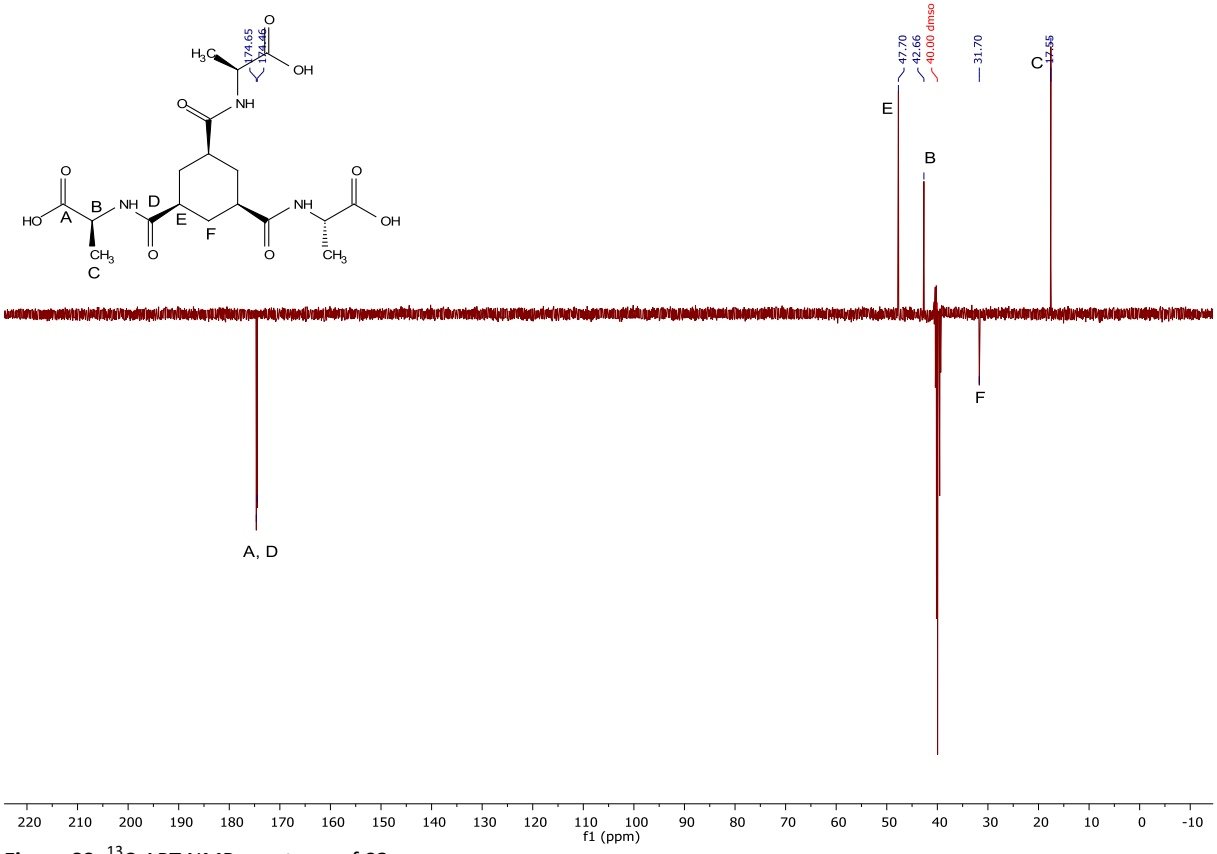


Figure S9: ^{13}C-APT NMR spectrum of **03**.

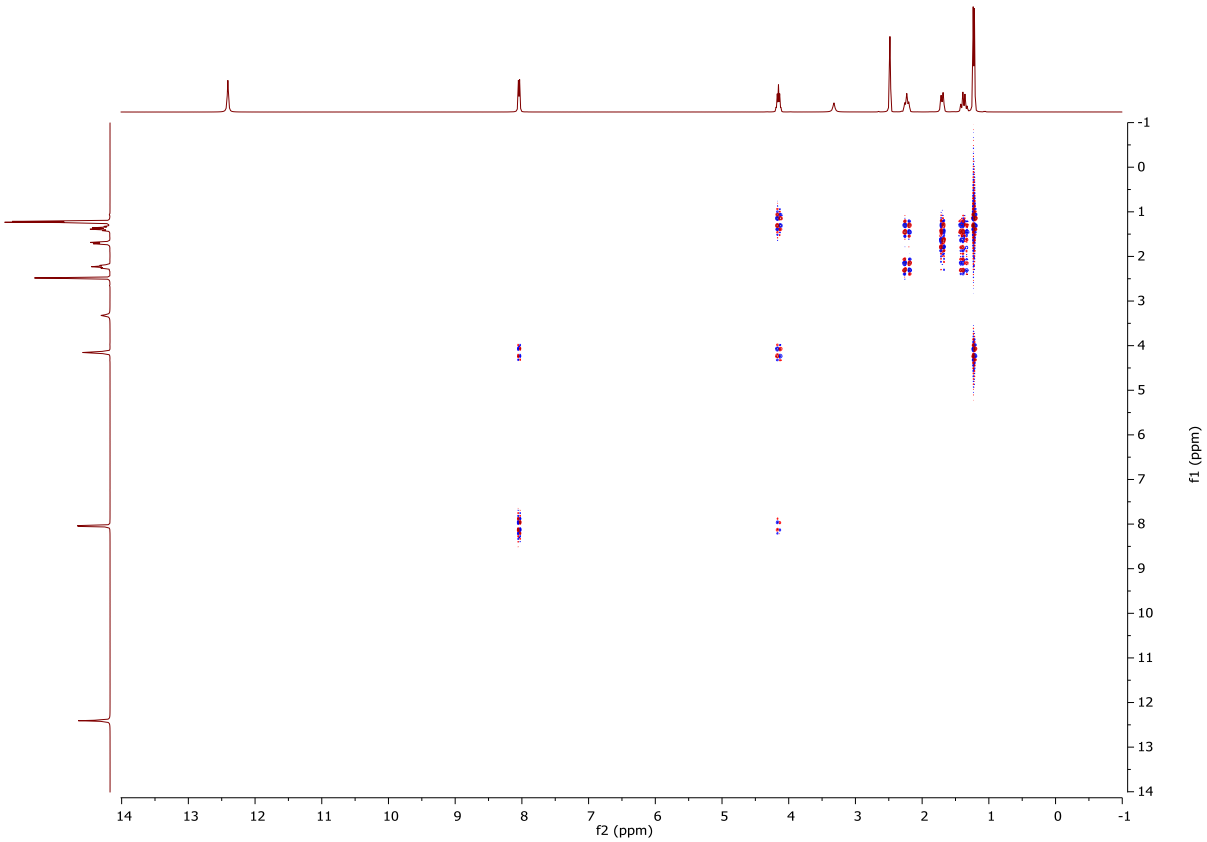


Figure S10: gDQF-COSY spectrum of **03**.

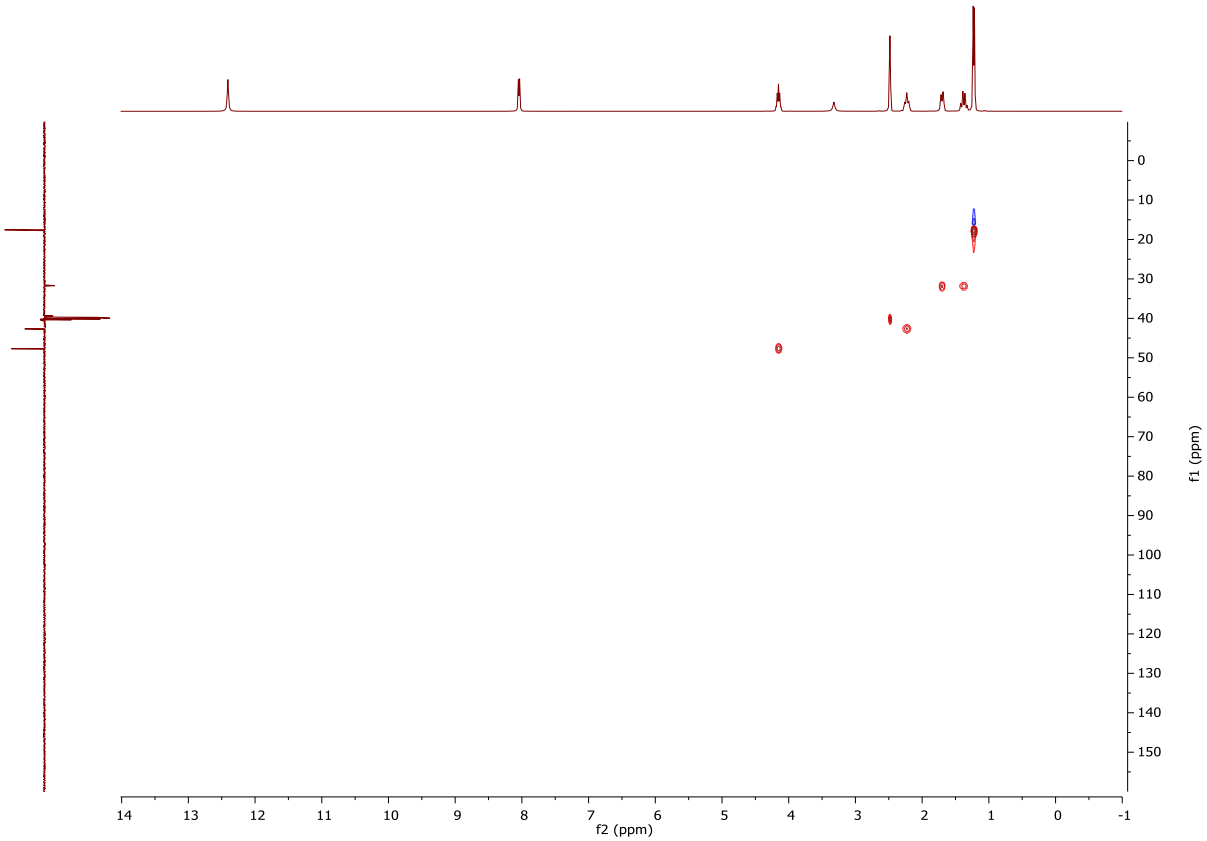


Figure S11: gHSQC spectrum of **03**.

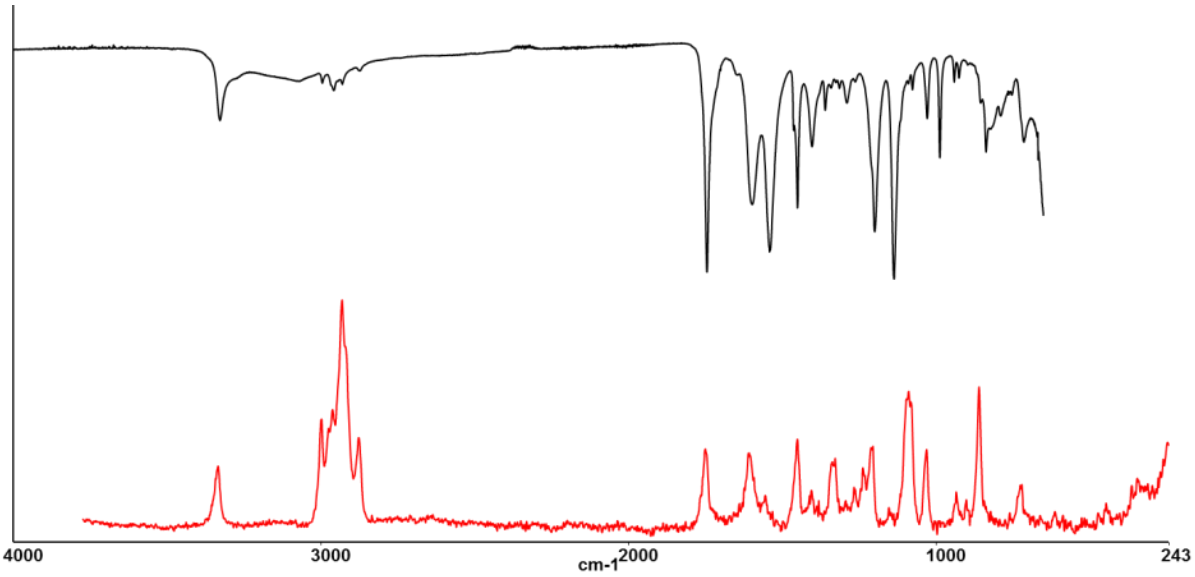


Figure S12: FTIR and Raman (633 nm) spectrum of **03**.

CHex(Val-OH) **(04)**

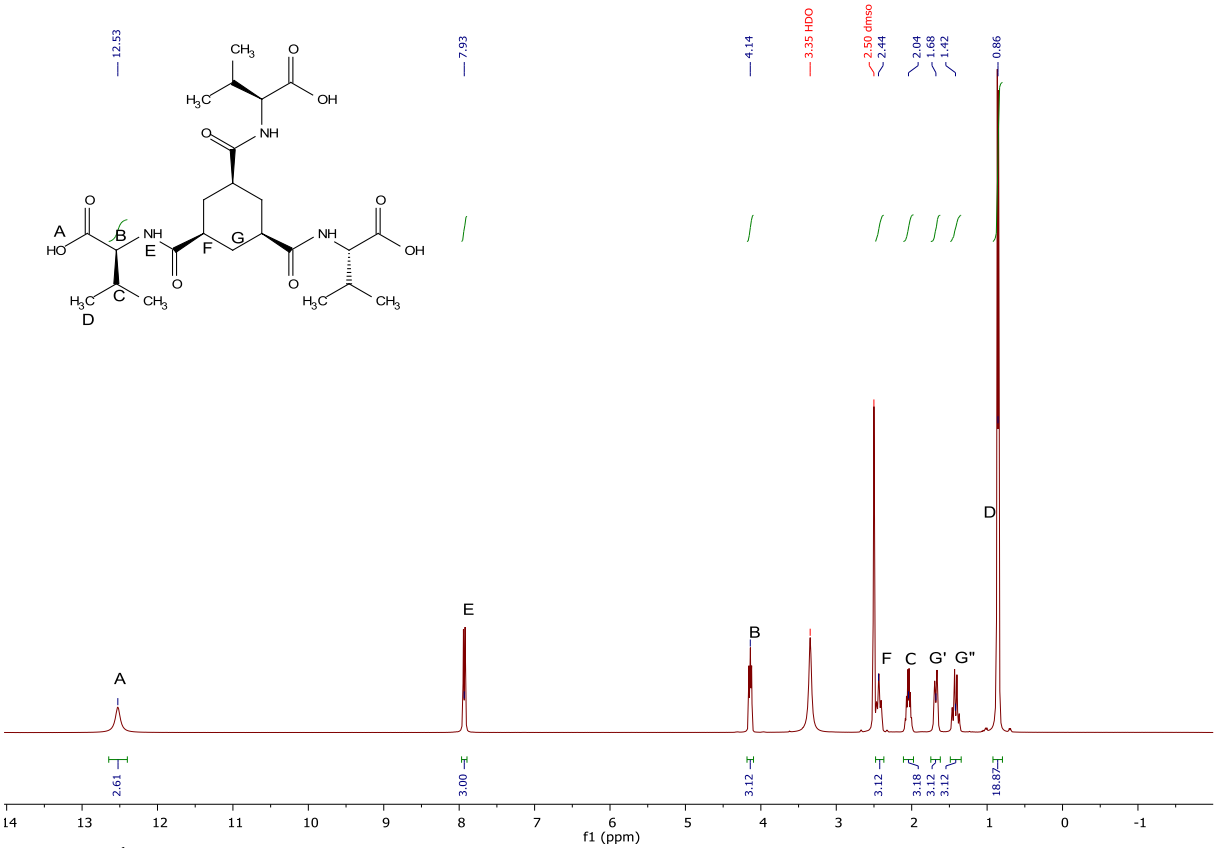


Figure S13: ^{1}H-NMR spectrum of **04**.

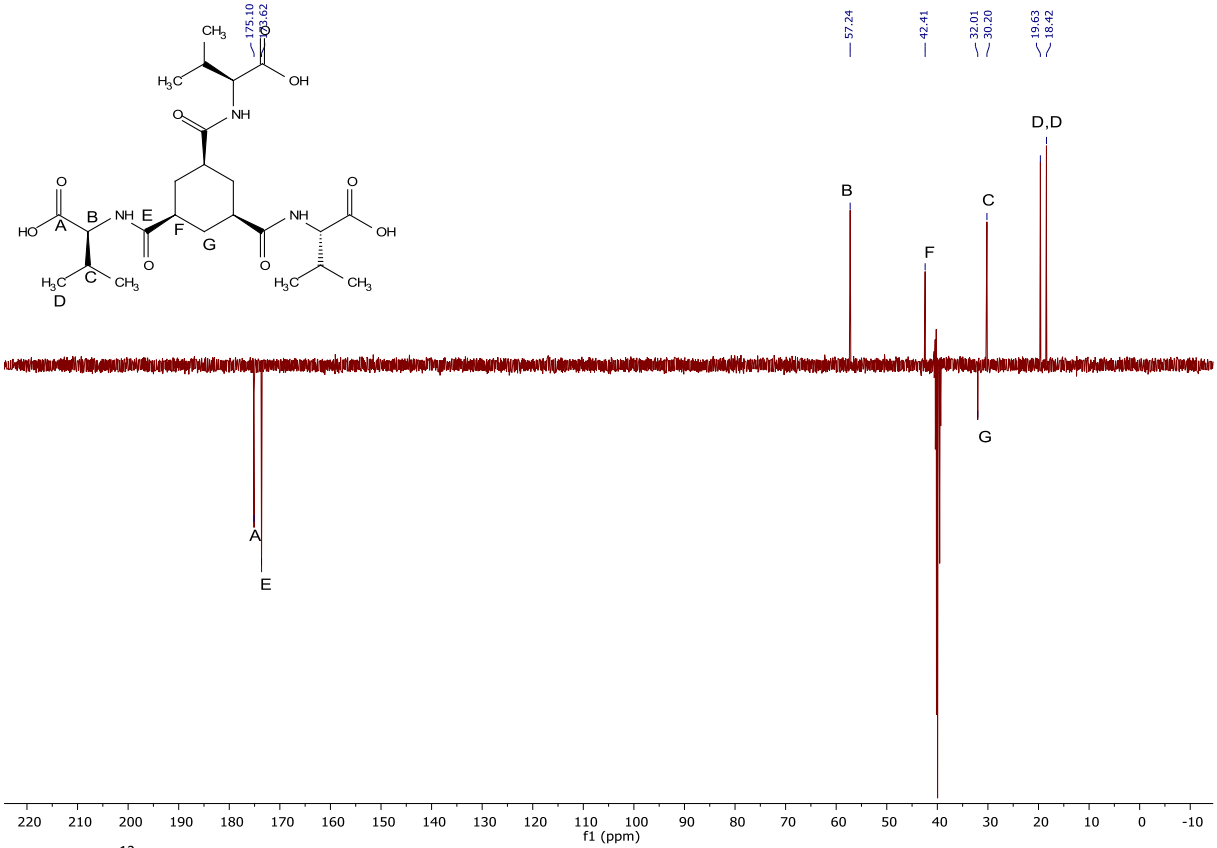


Figure S14: ^{13}C-APT NMR spectrum of **04**.

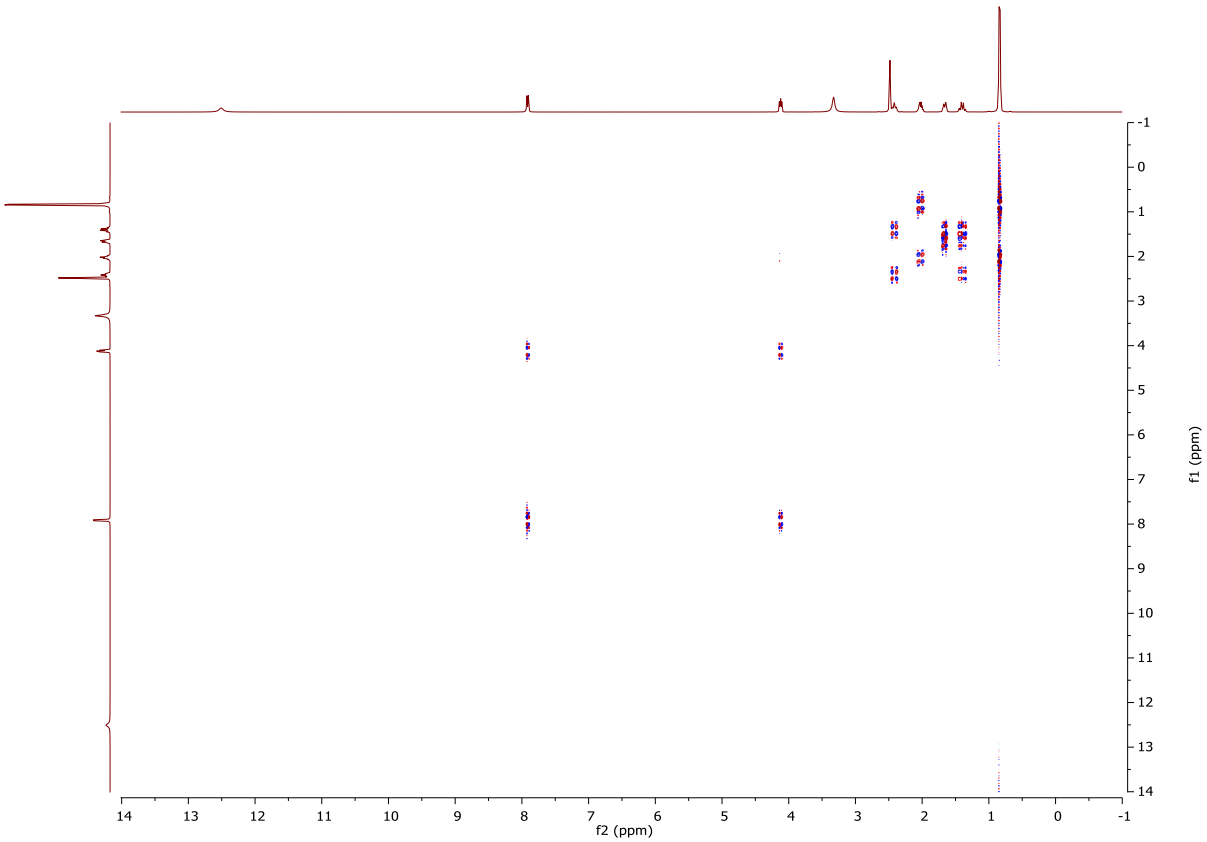


Figure S15: gDQF COSY spectrum of **04**.

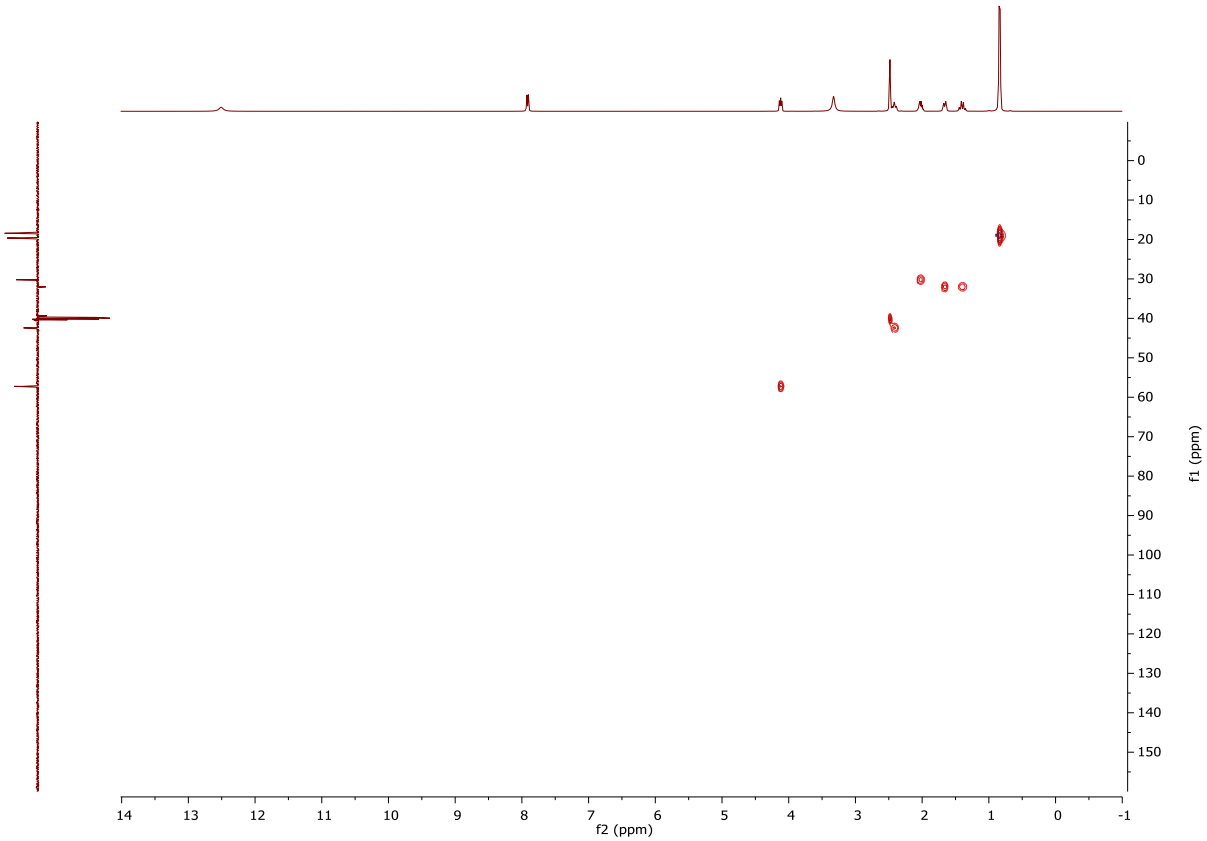


Figure S16: gHSQC spectrum of **04**.

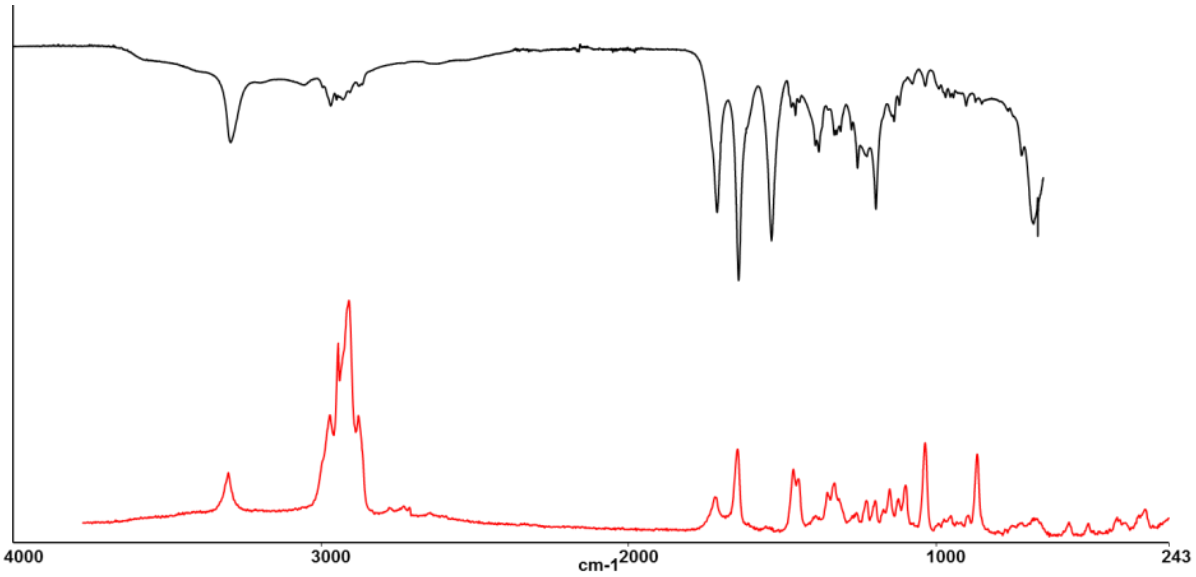


Figure S17: FTIR and Raman (633 nm) spectrum of **04**.

CHex(Leu-OH) **(05)**

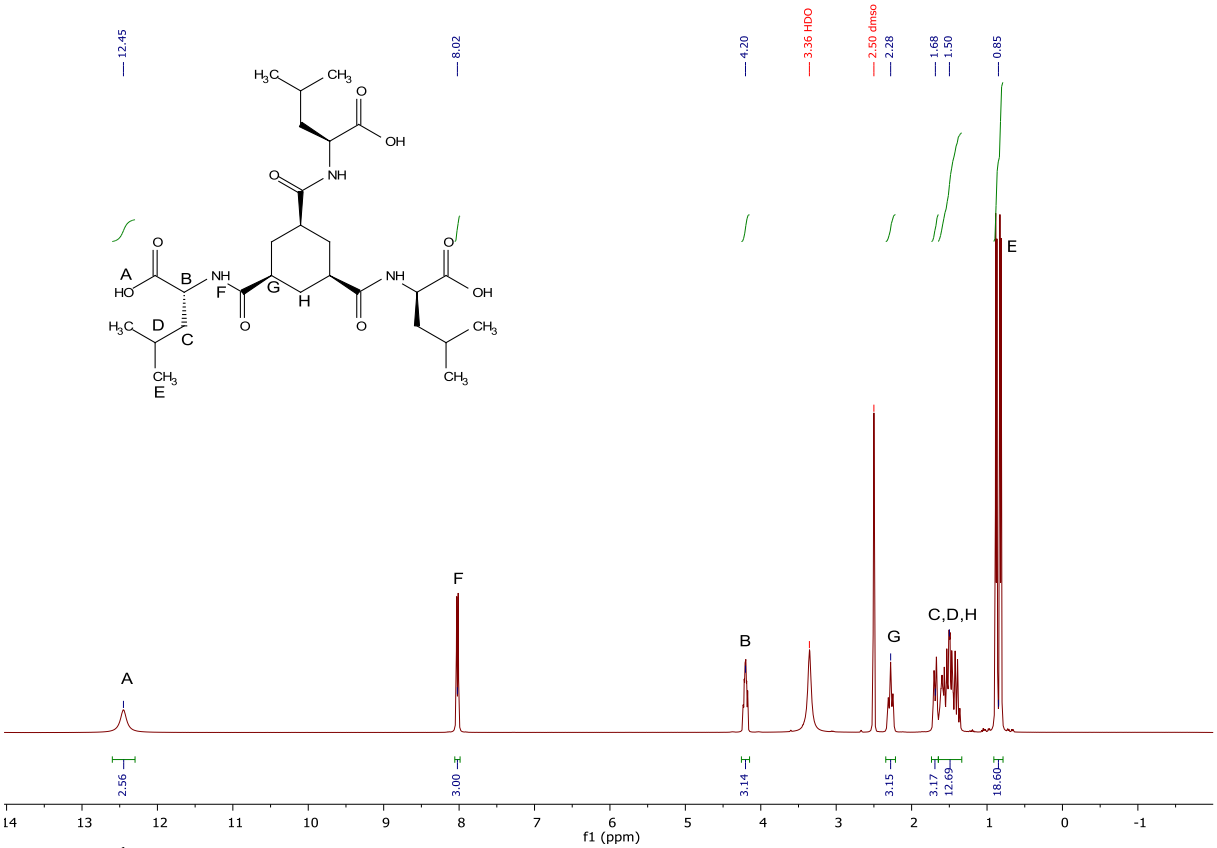


Figure S18: ^{1}H-NMR spectrumof **05**.

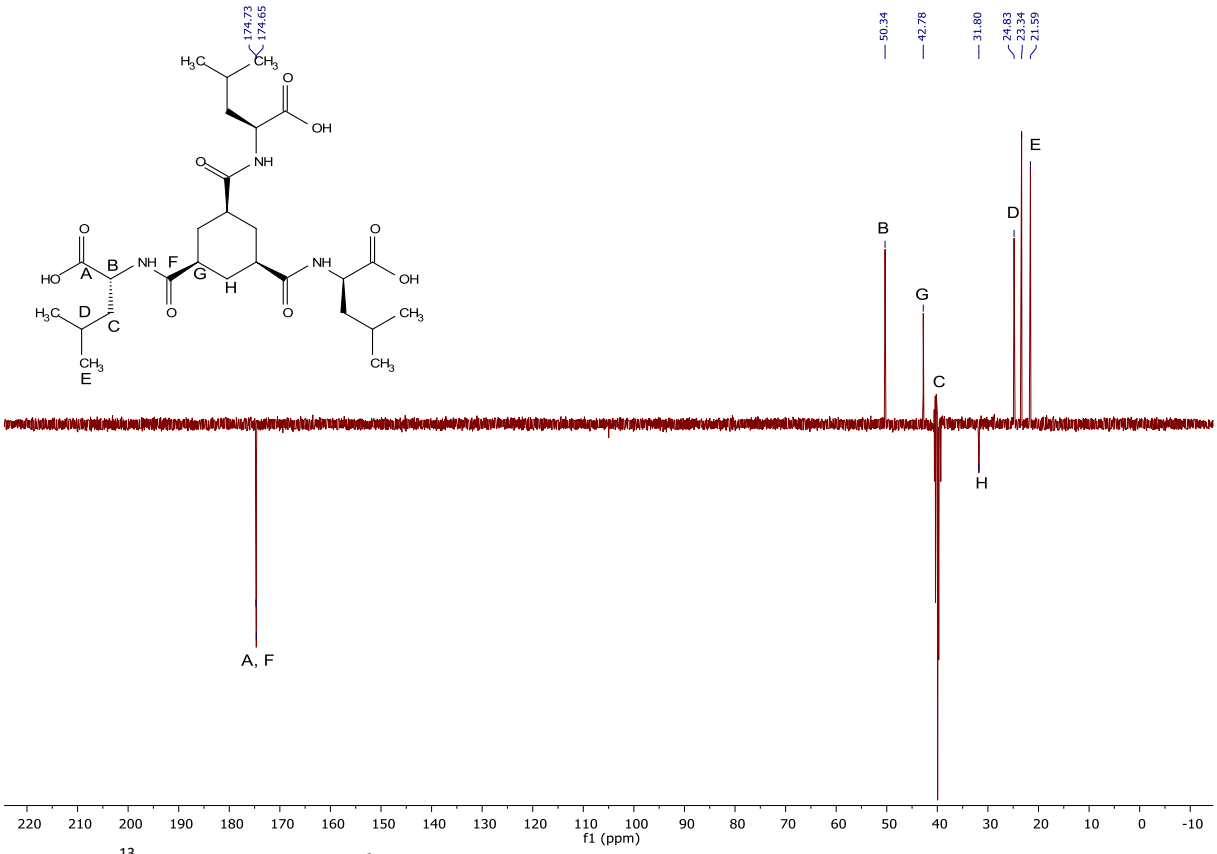


Figure S19: ^{13}C-APT NMR spectrum of **05**.

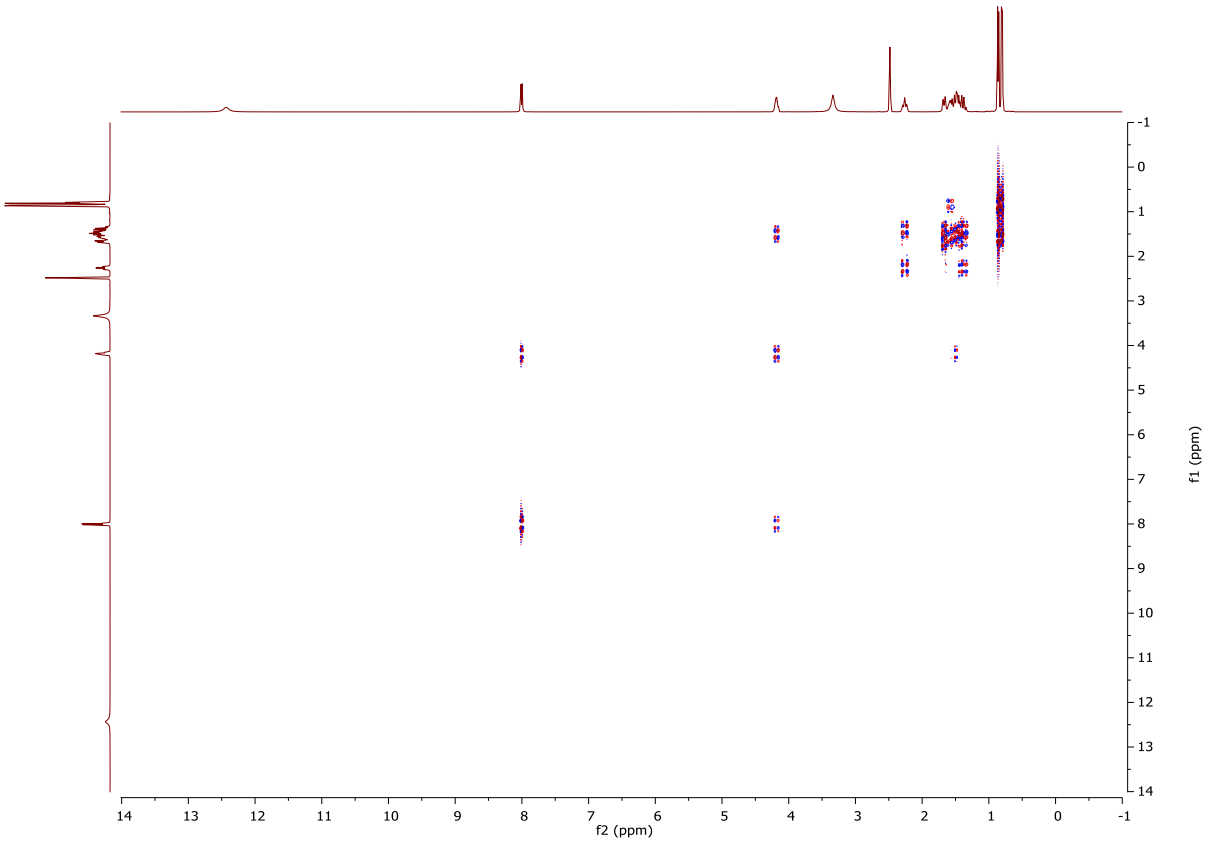


Figure S20: gDQF COSY spectrum of **05**.

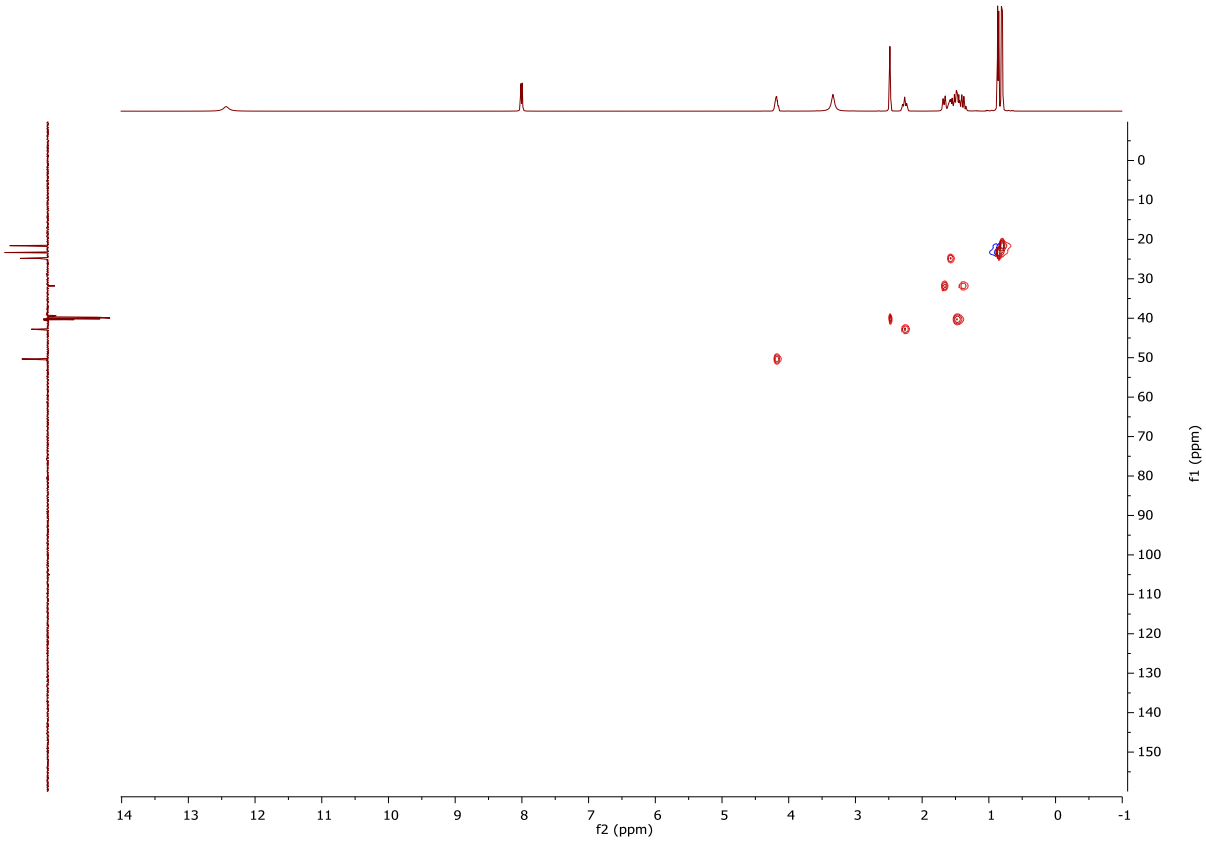


Figure S21: gHSQC spectrum of **05**.

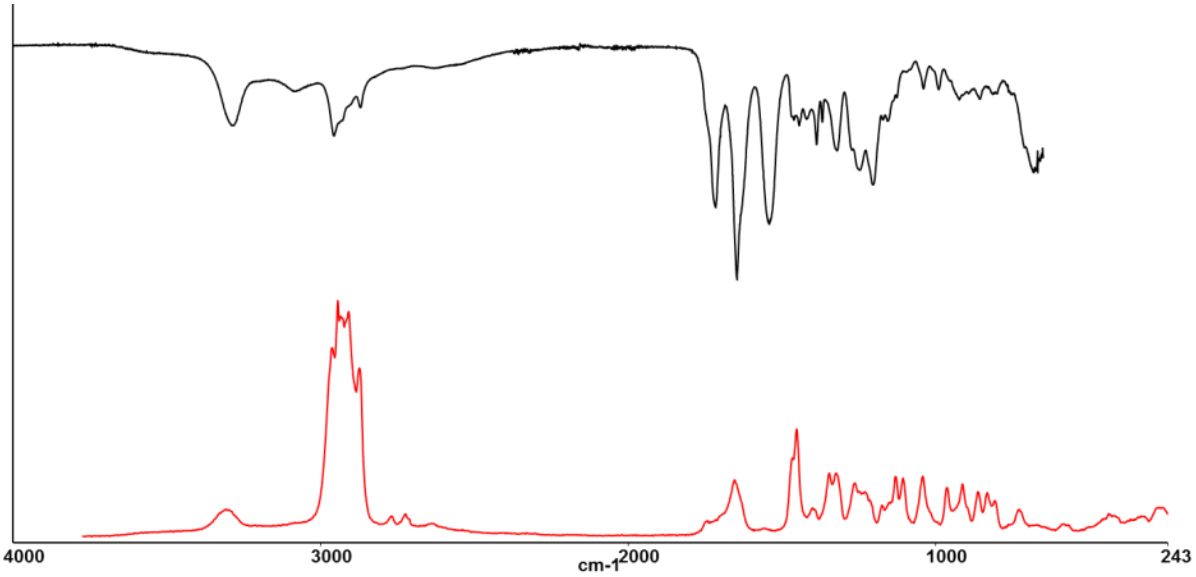


Figure S22: FTIR and Raman (633 nm) spectrum of **05**.

CHex(Ile-OH) **(06)**

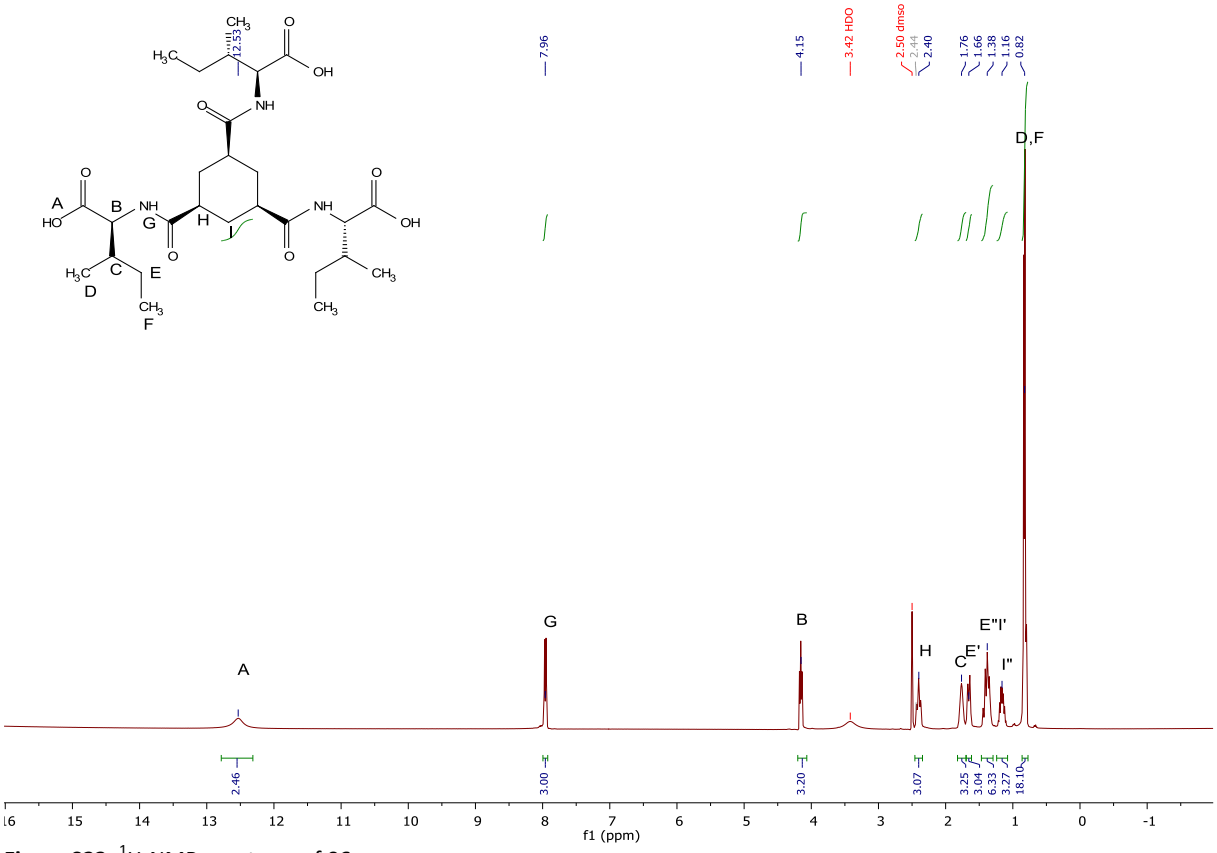


Figure S23: ^{1}H-NMR spectrum of **06**.

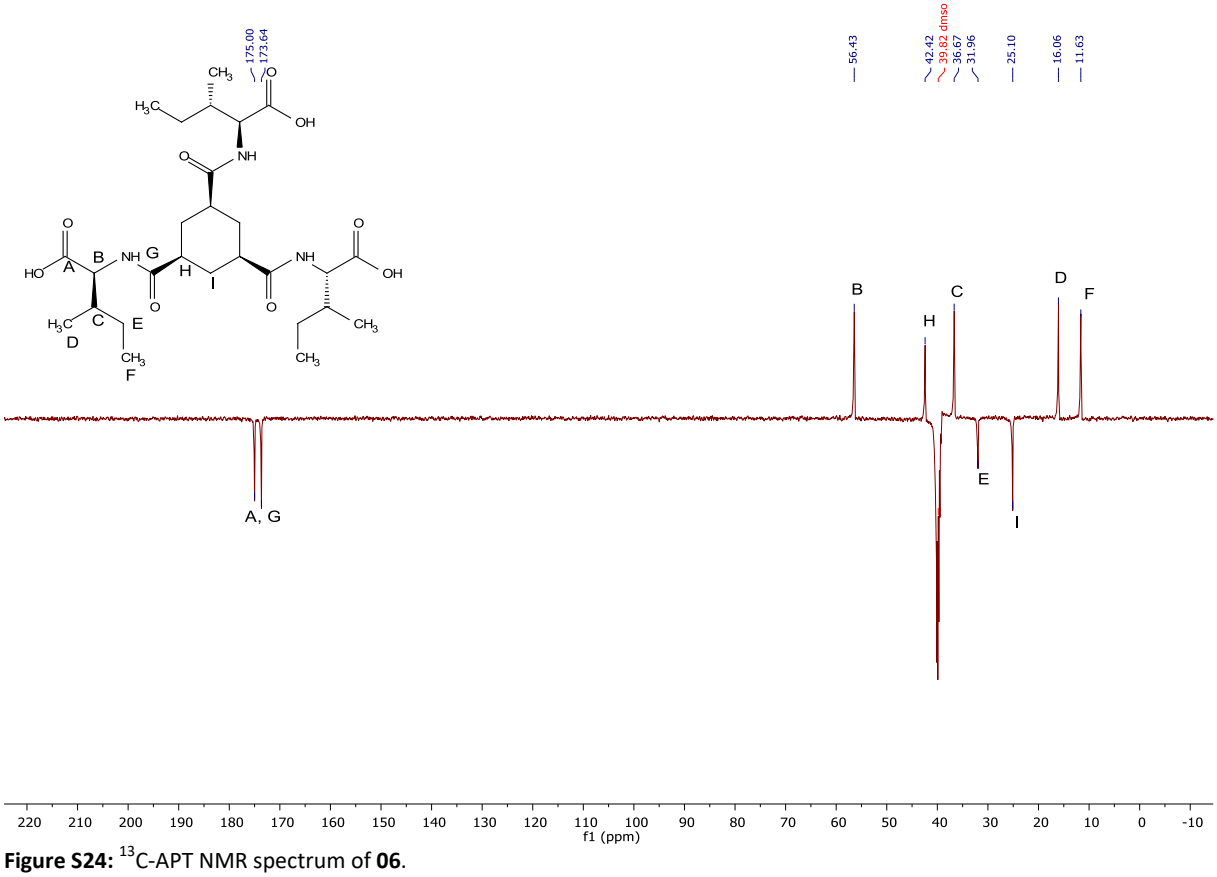


Figure S24: ^{13}C-APT NMR spectrum of **06**.

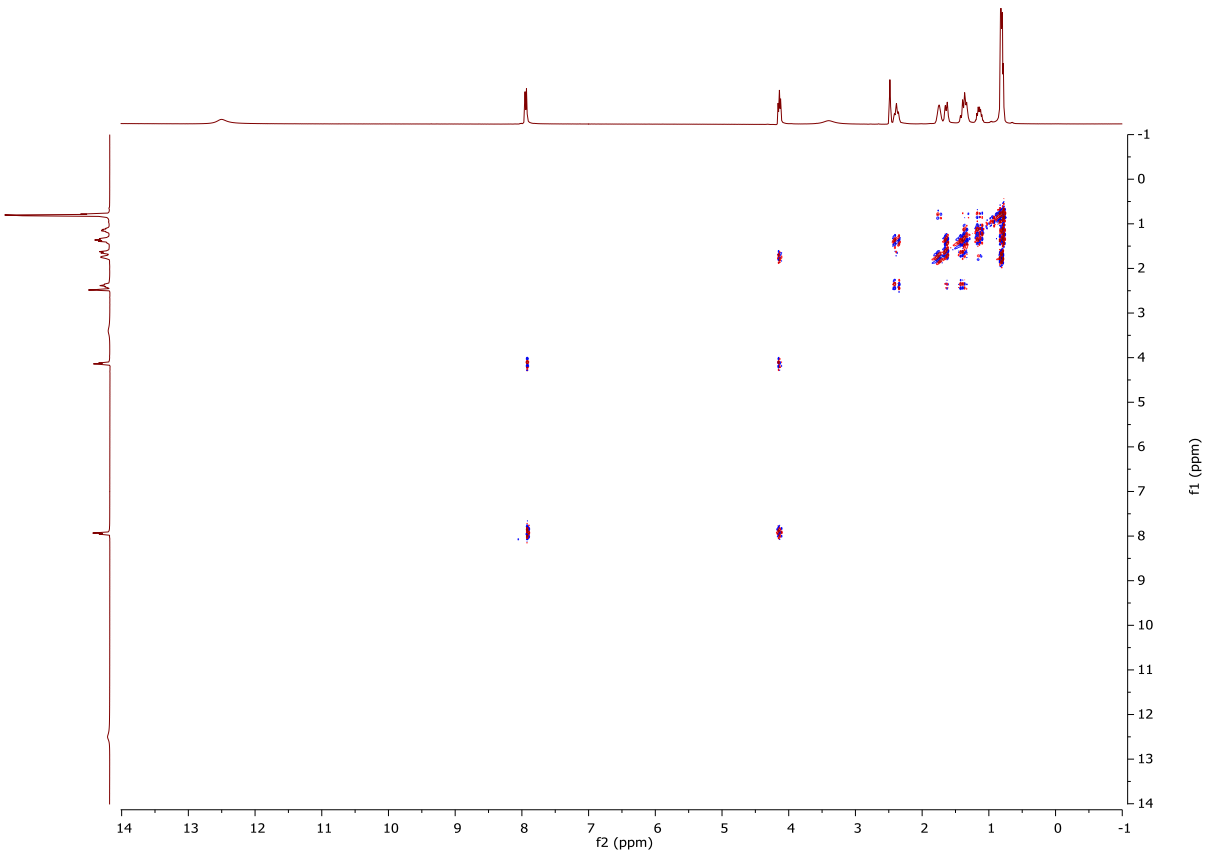


Figure S25: gDQF-COSY spectrum of **06**.

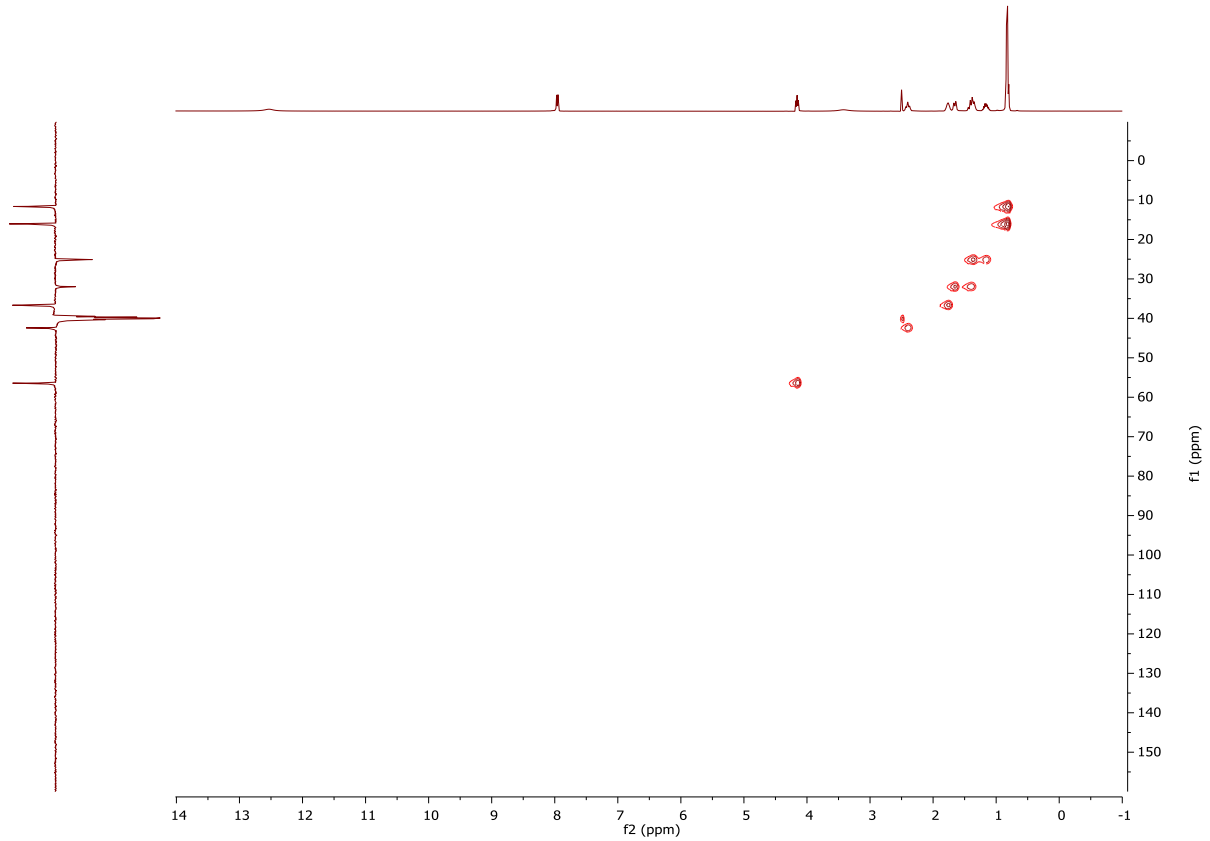


Figure S26: gHSQC spectrum of **06**.

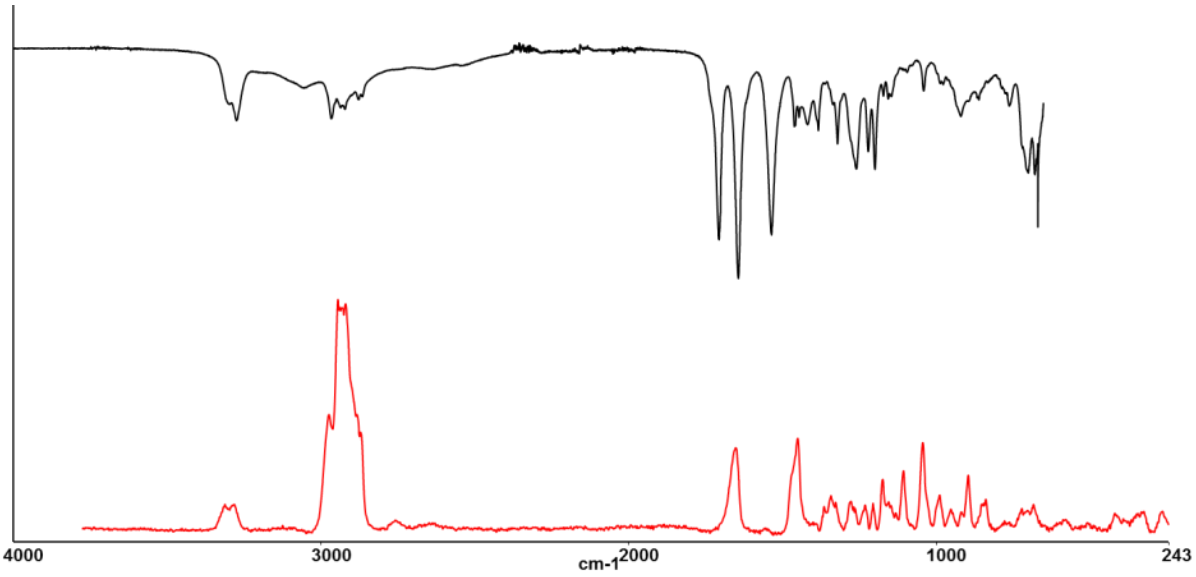


Figure S27: FTIR and Raman (633 nm) spectrum of **06**.

CHex(Met-OH) **(07)**

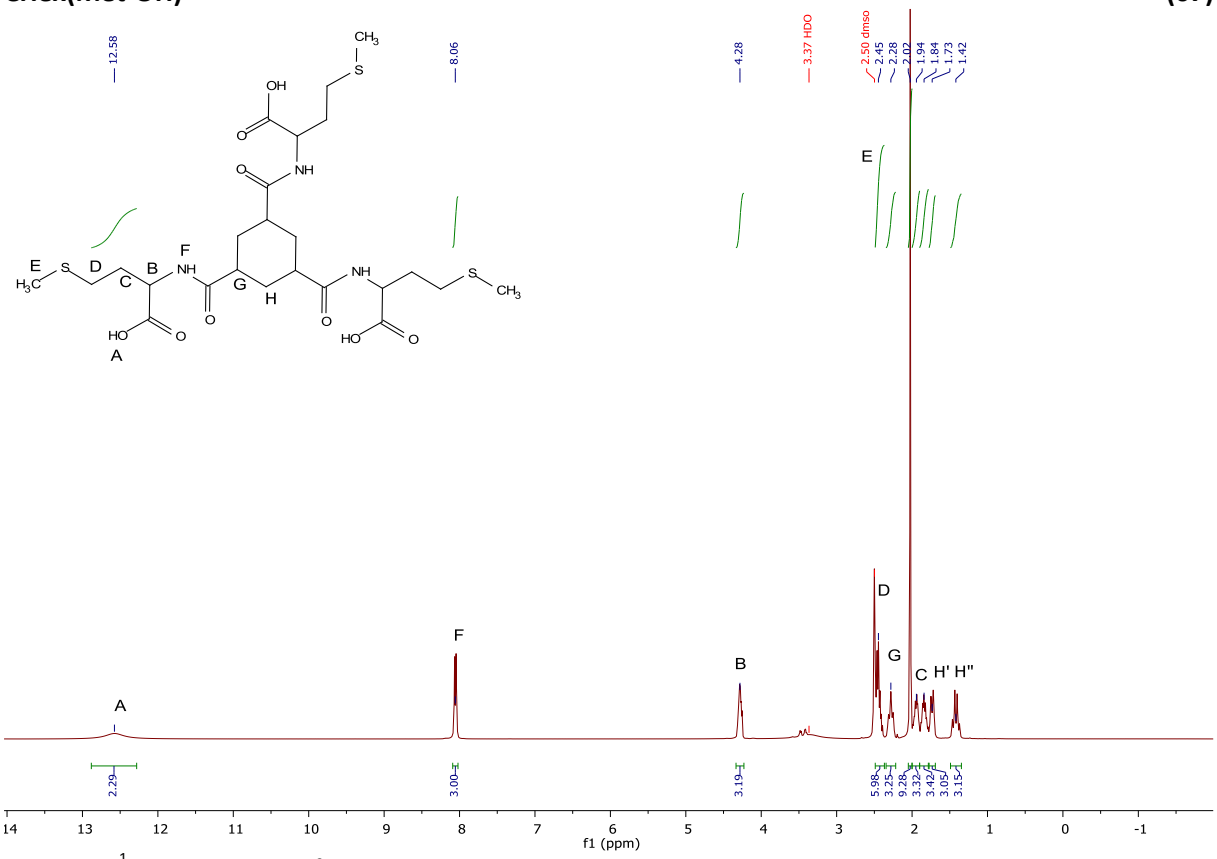


Figure S28: ^{1}H-NMR spectrum of **07**.

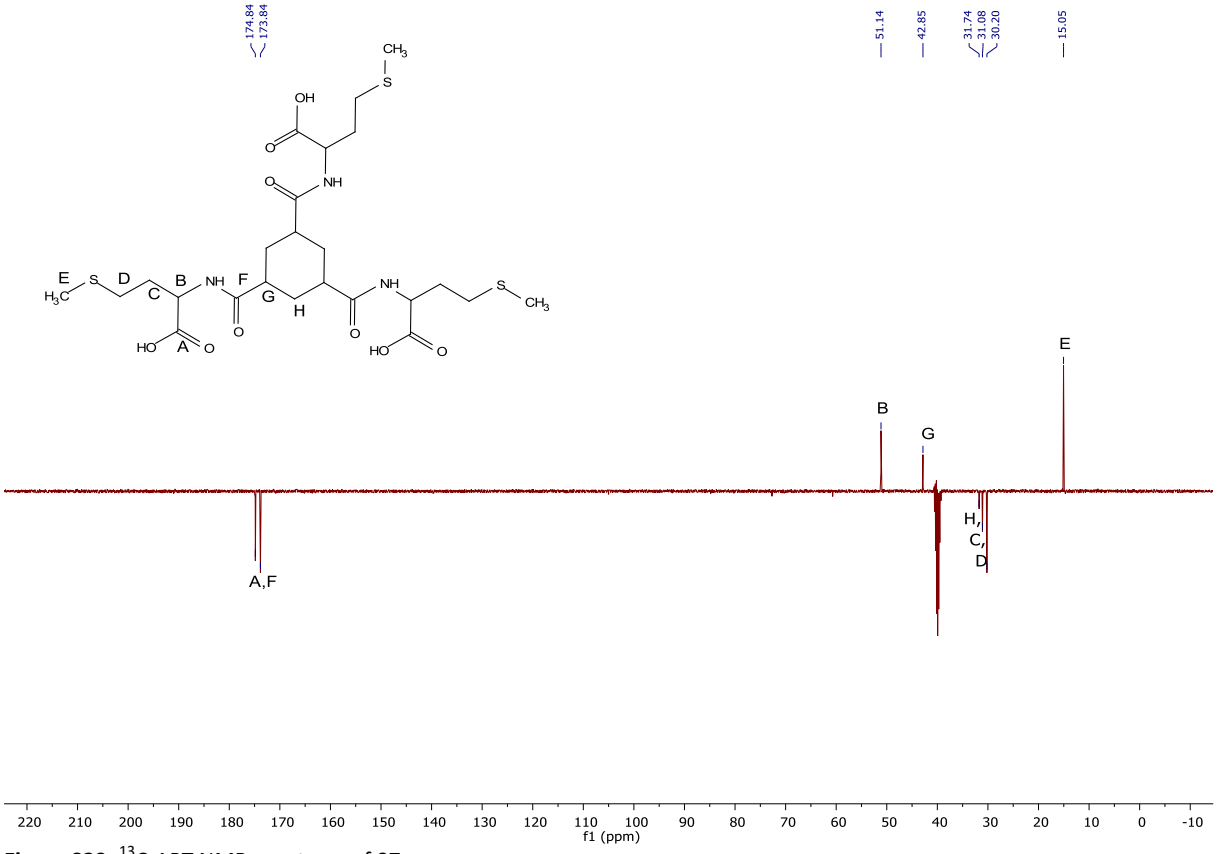


Figure S29: ^{13}C-APT NMR spectrum of **07**.

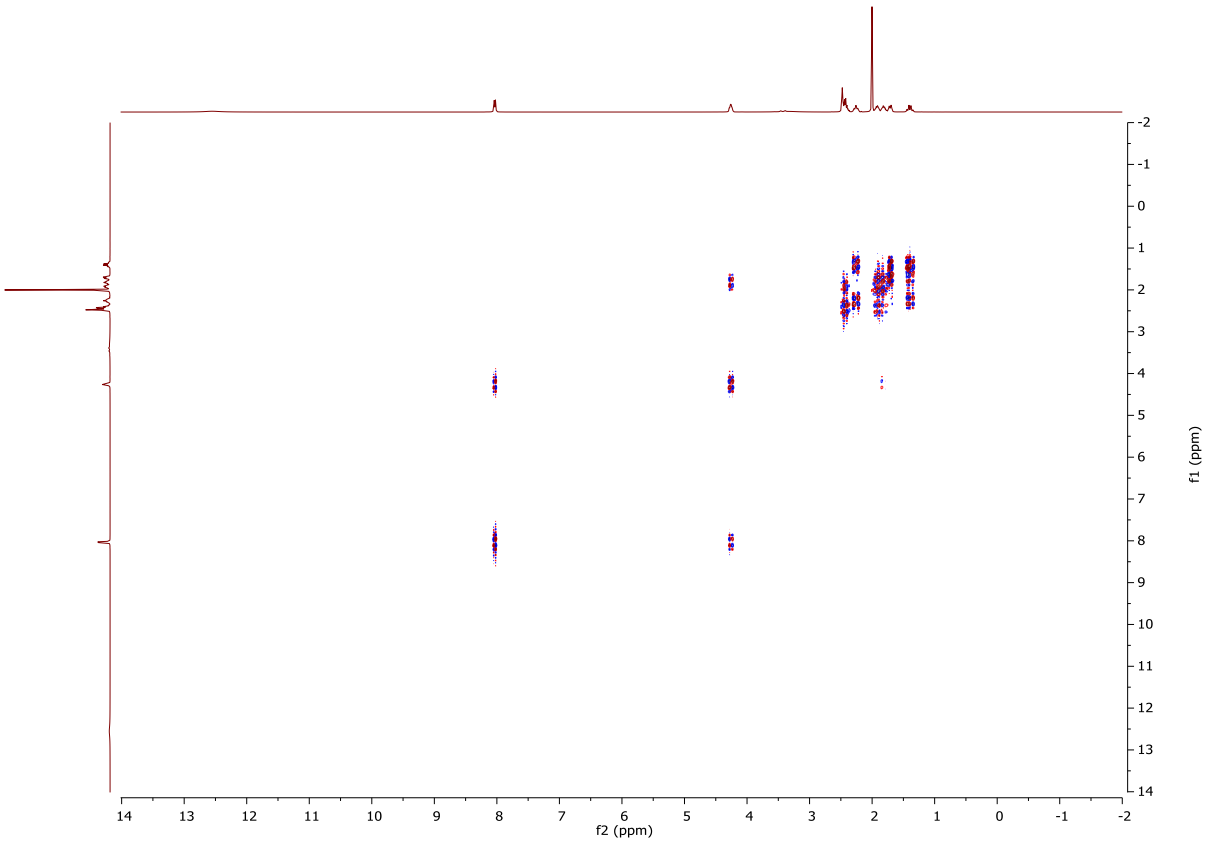


Figure S30: gDQF COSY spectrum of **07**.

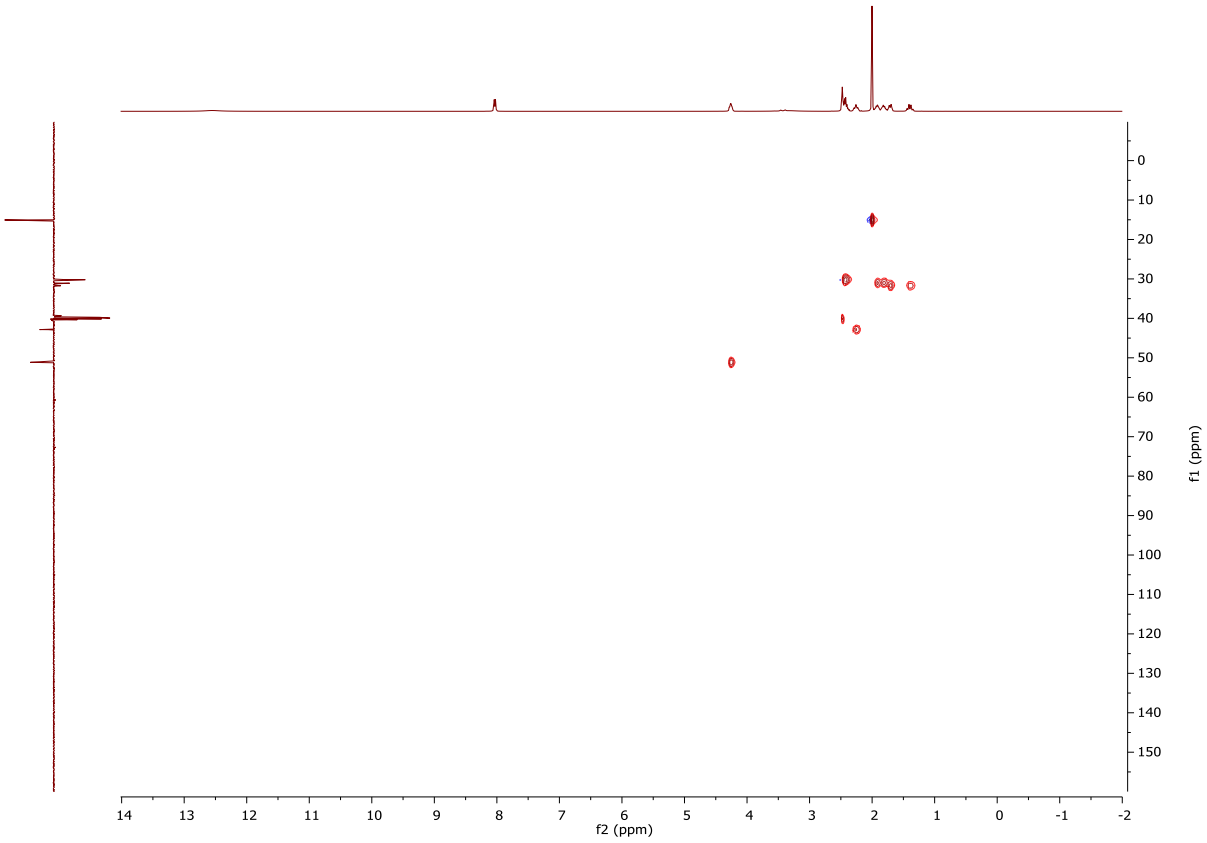


Figure S31: gHSQC spectrum of **07**.

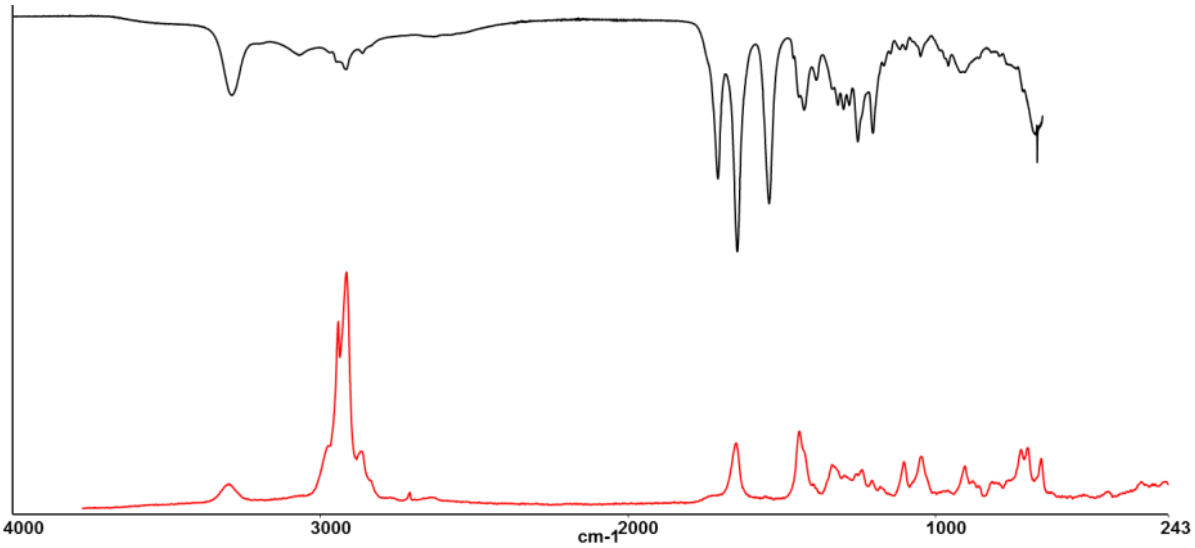


Figure S32: FTIR and Raman (633 nm) spectrum 0f **07**.

Chex(Phe-OH) **(08)**

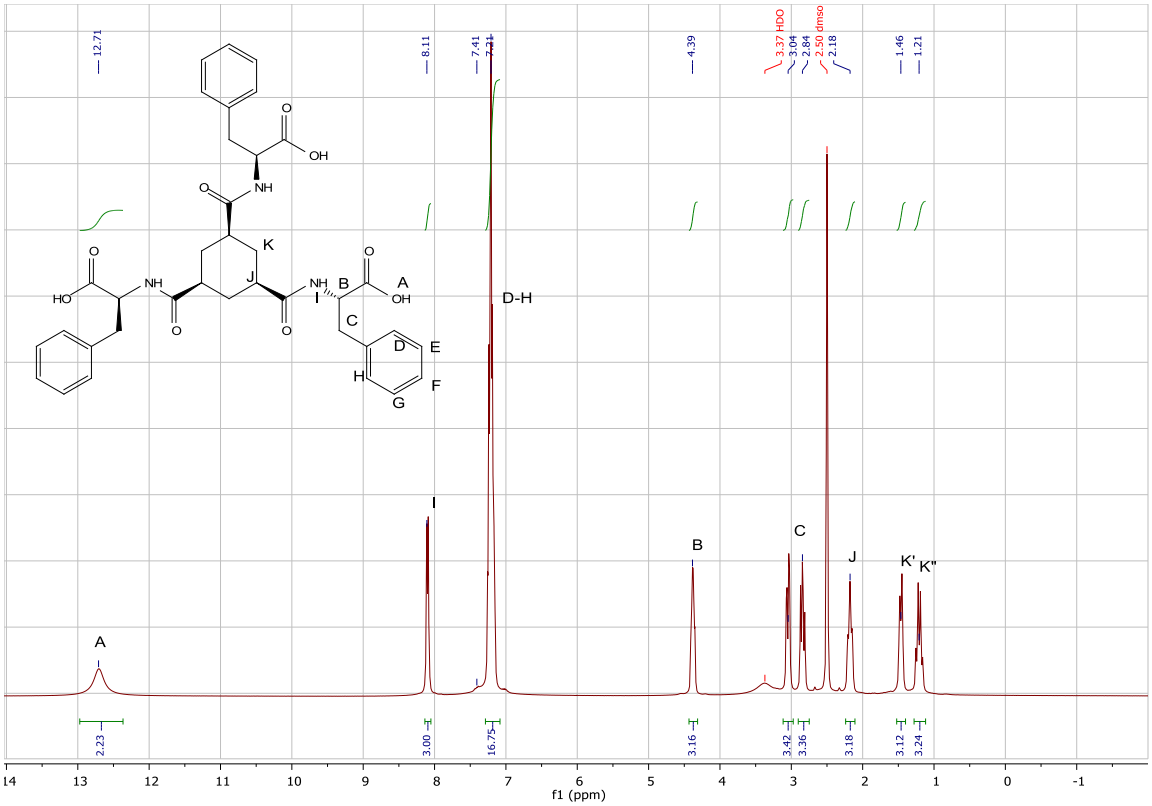


Figure S33: ^{1}H-NMR spectrum of **08**.

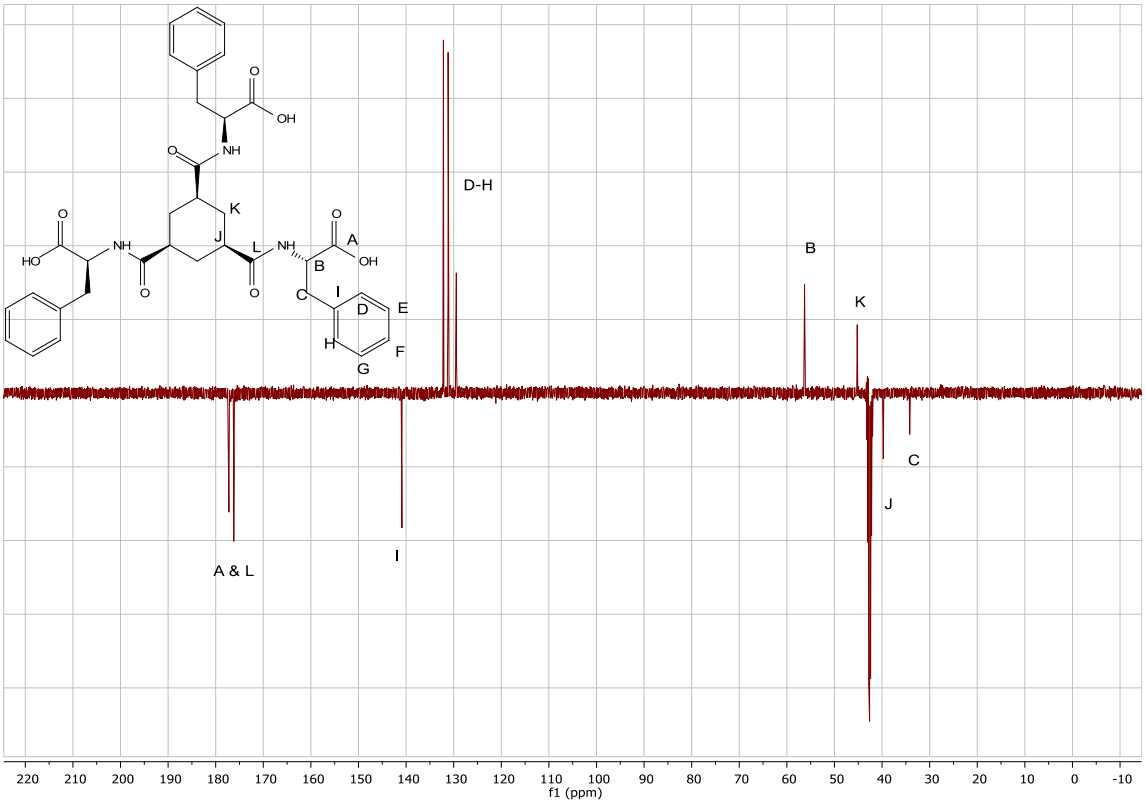


Figure S34: ^{13}C-APT NMR spectrum of **08**.

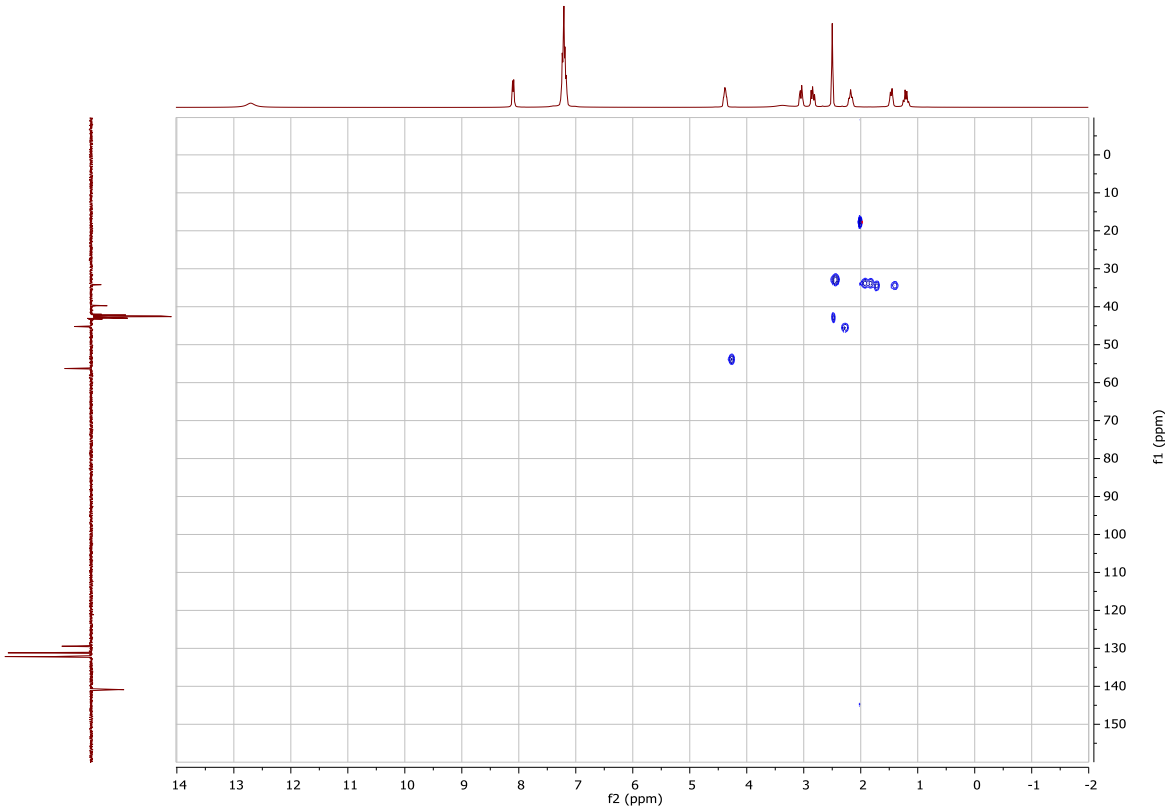


Figure S35: gHSQC spectrum of **08**.

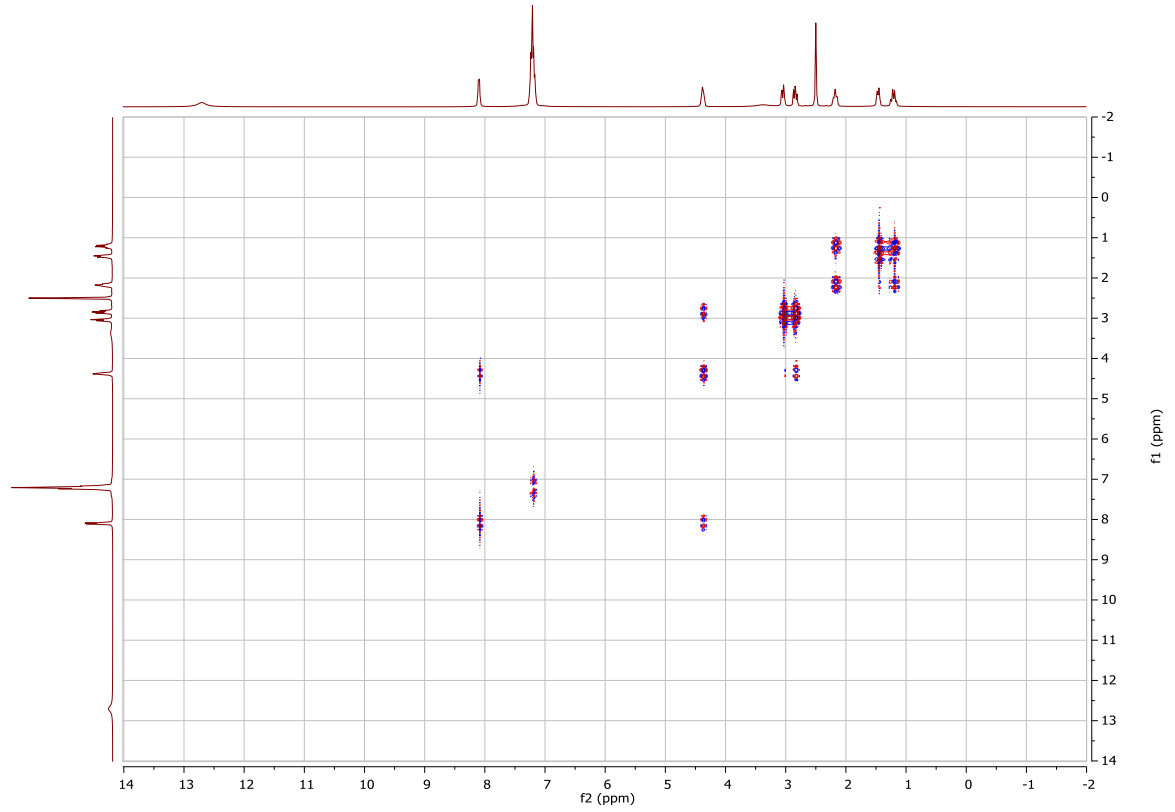


Figure S36: gCosy spectrum of **08**.

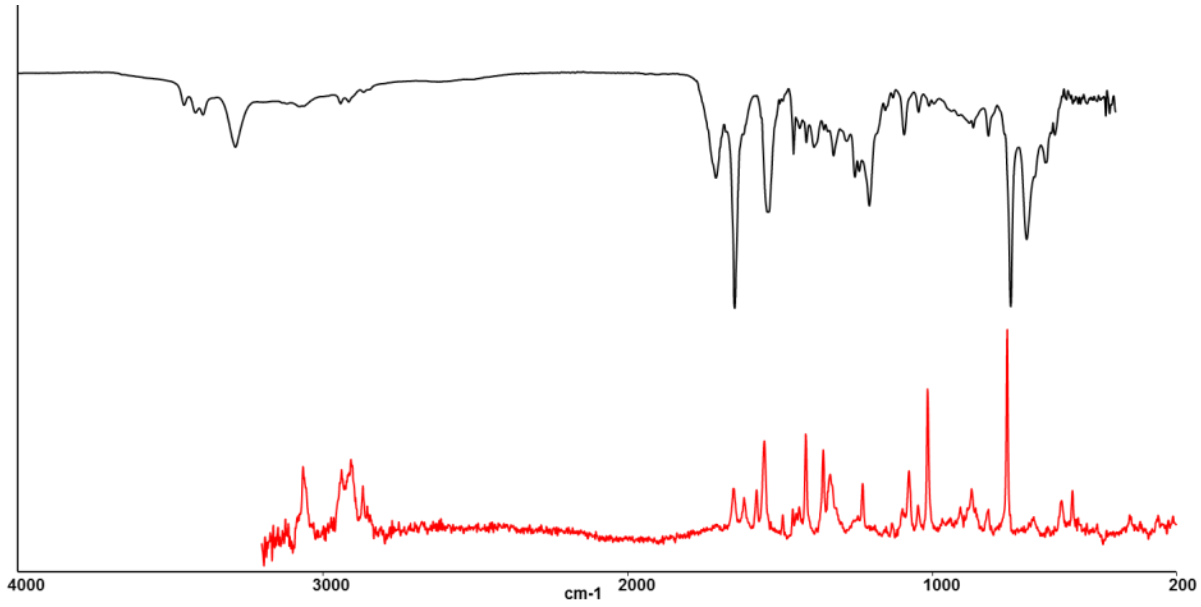


Figure S37: FTIR and Raman (785 nm) spectrum of **08**.

Chex(Trp-OH) **(09)**

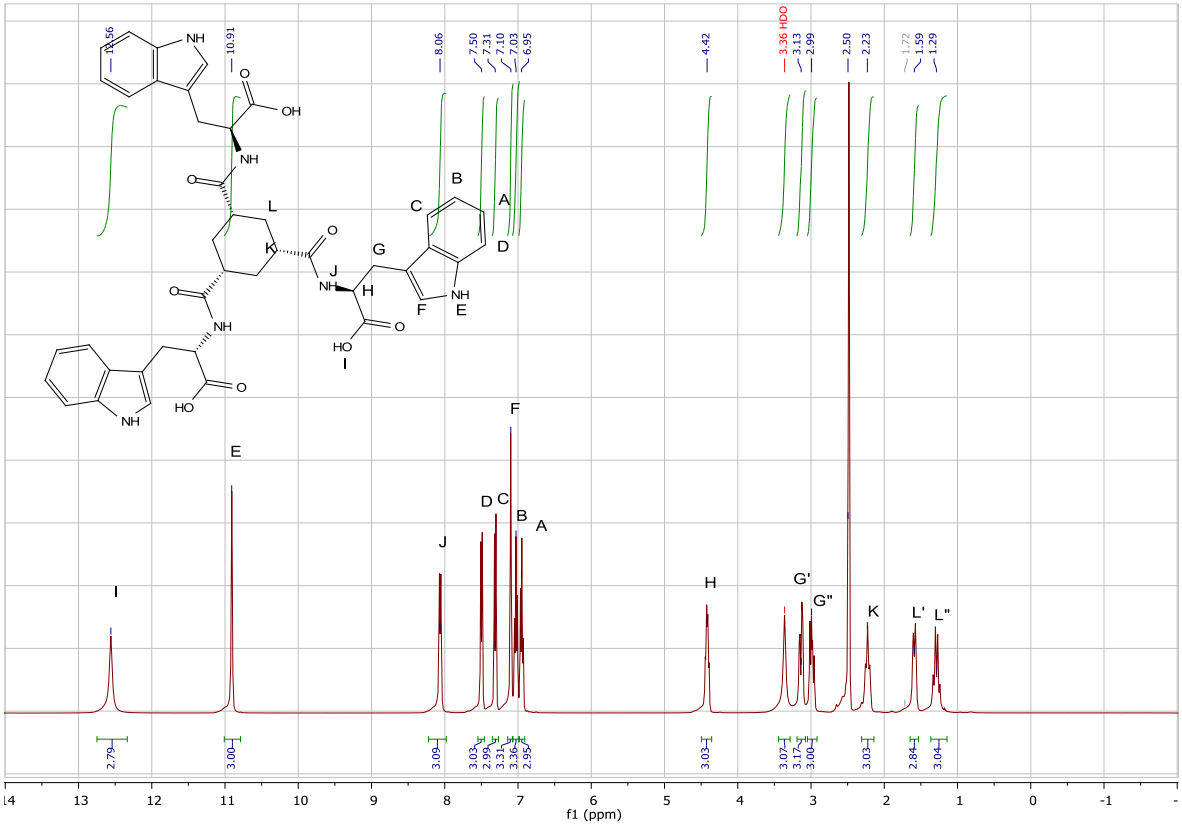


Figure S38: ^{1}H-NMR spectrum 0f **09**.

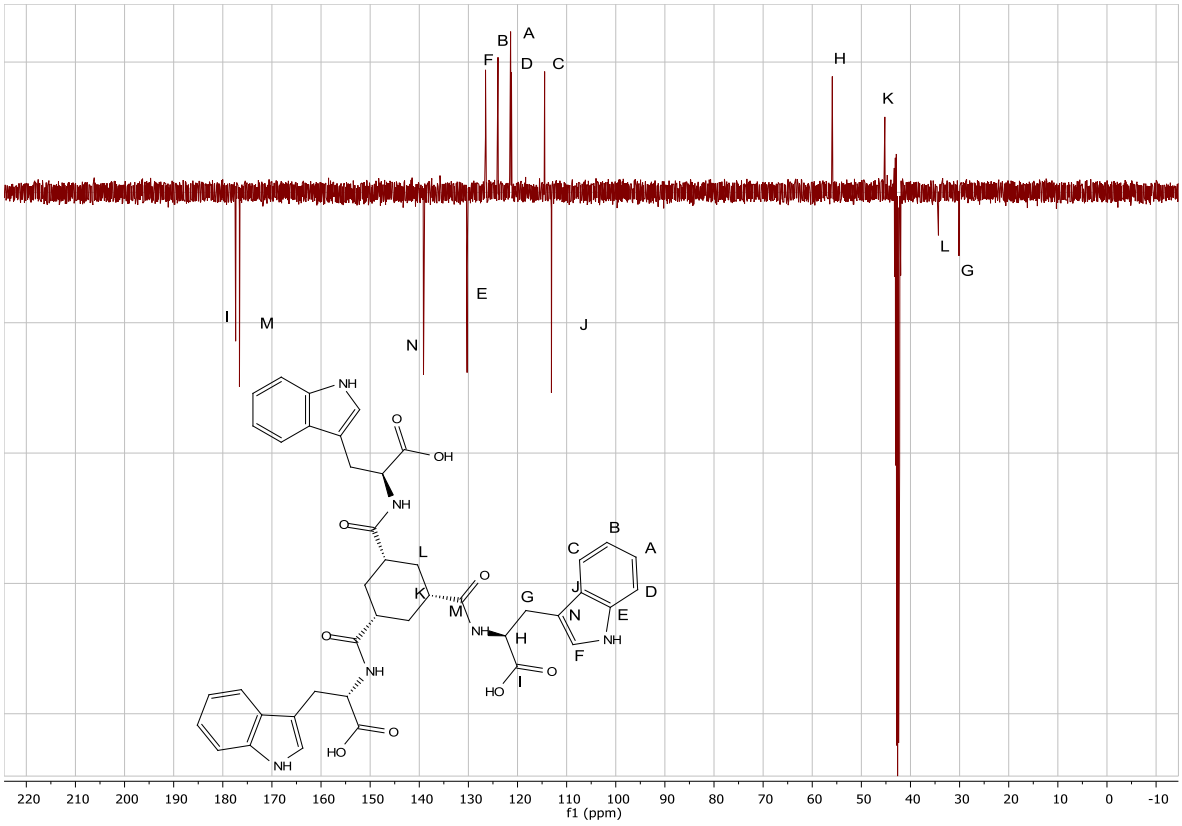


Figure S39: ^{13}C-APT NMR spectrum of **09**.

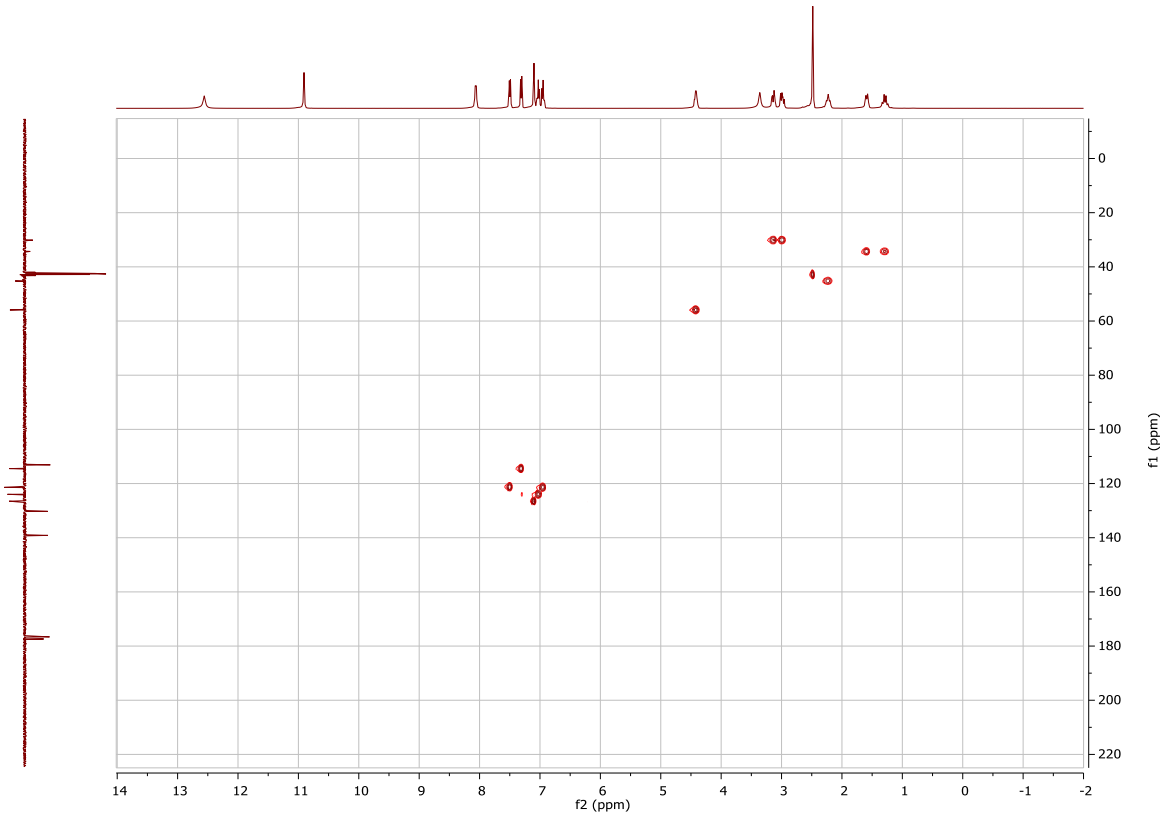


Figure S40: gHSQC spectrum of **09**.

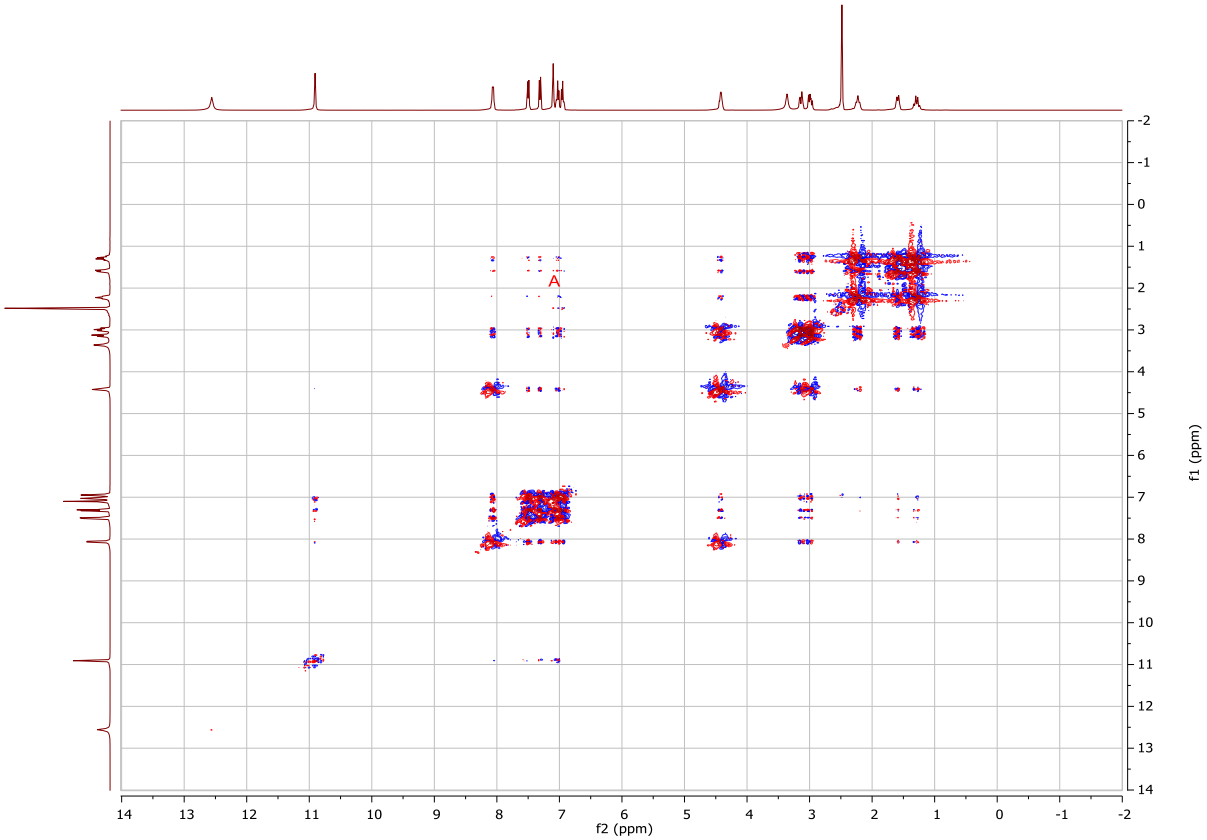


Figure S41: gCosy spectrum of **09**.

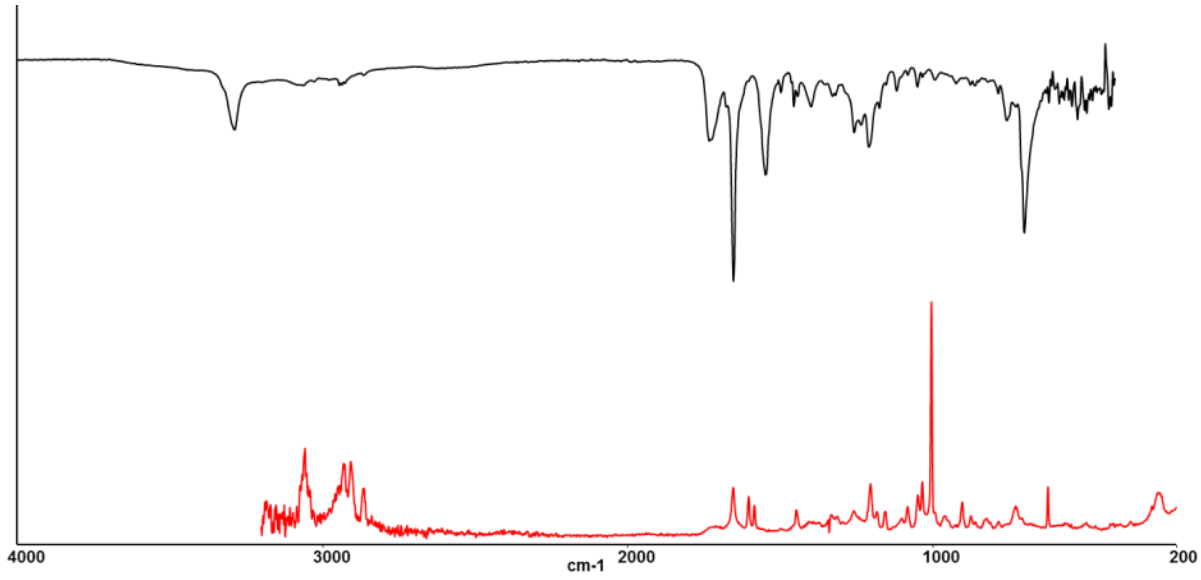


Figure S42: FTIR and Raman (785 nm) spectrum of **09**.

CHex(Abu-OH) **(10)**

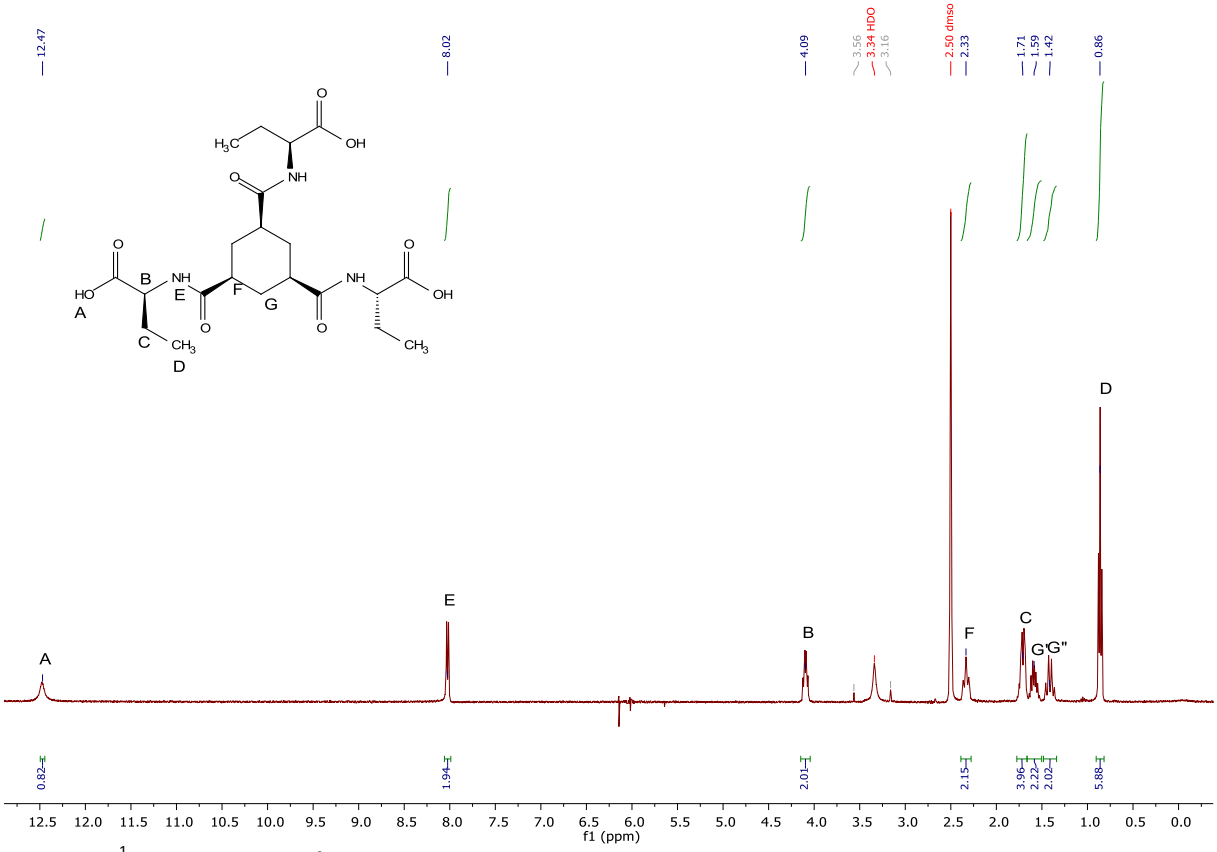


Figure S43: ^{1}H-NMR spectrum of **10**.

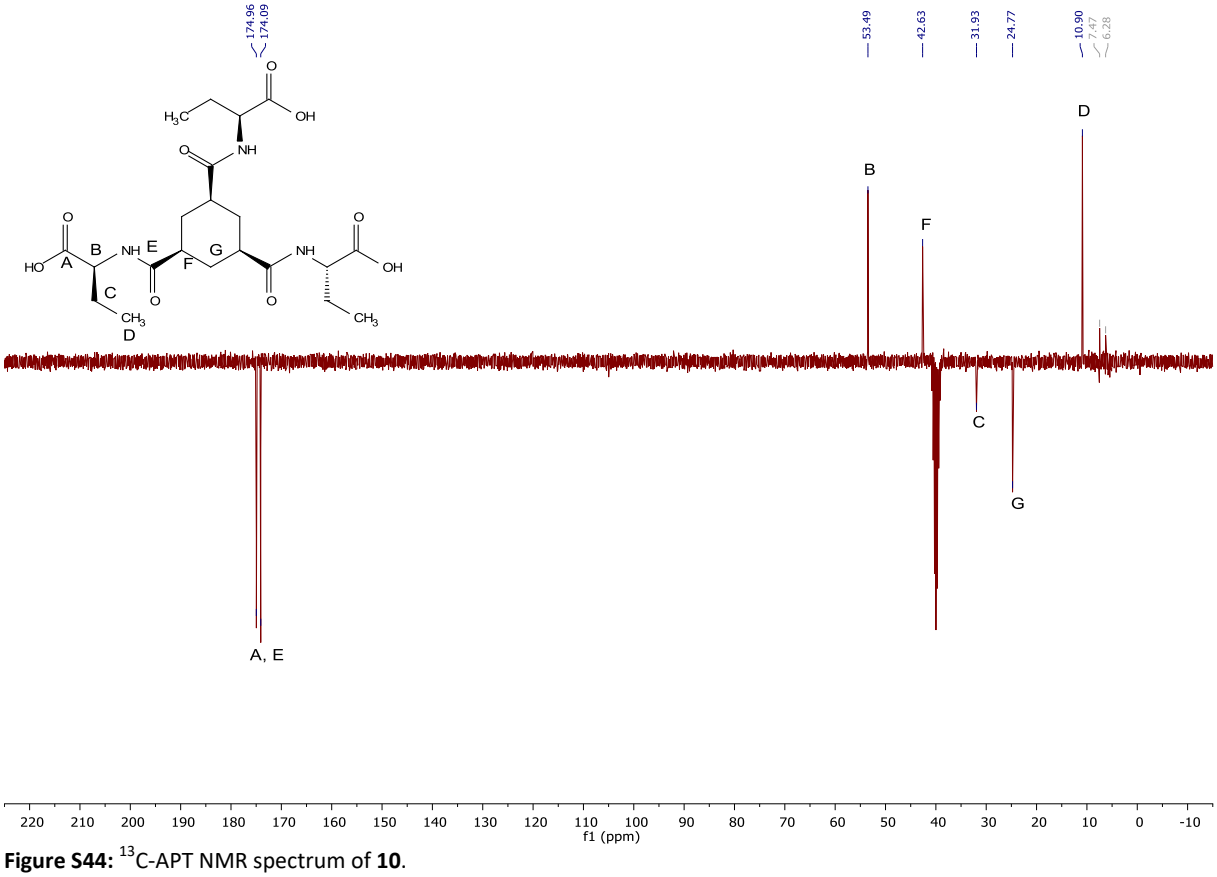


Figure S44: ^{13}C-APT NMR spectrum of **10**.

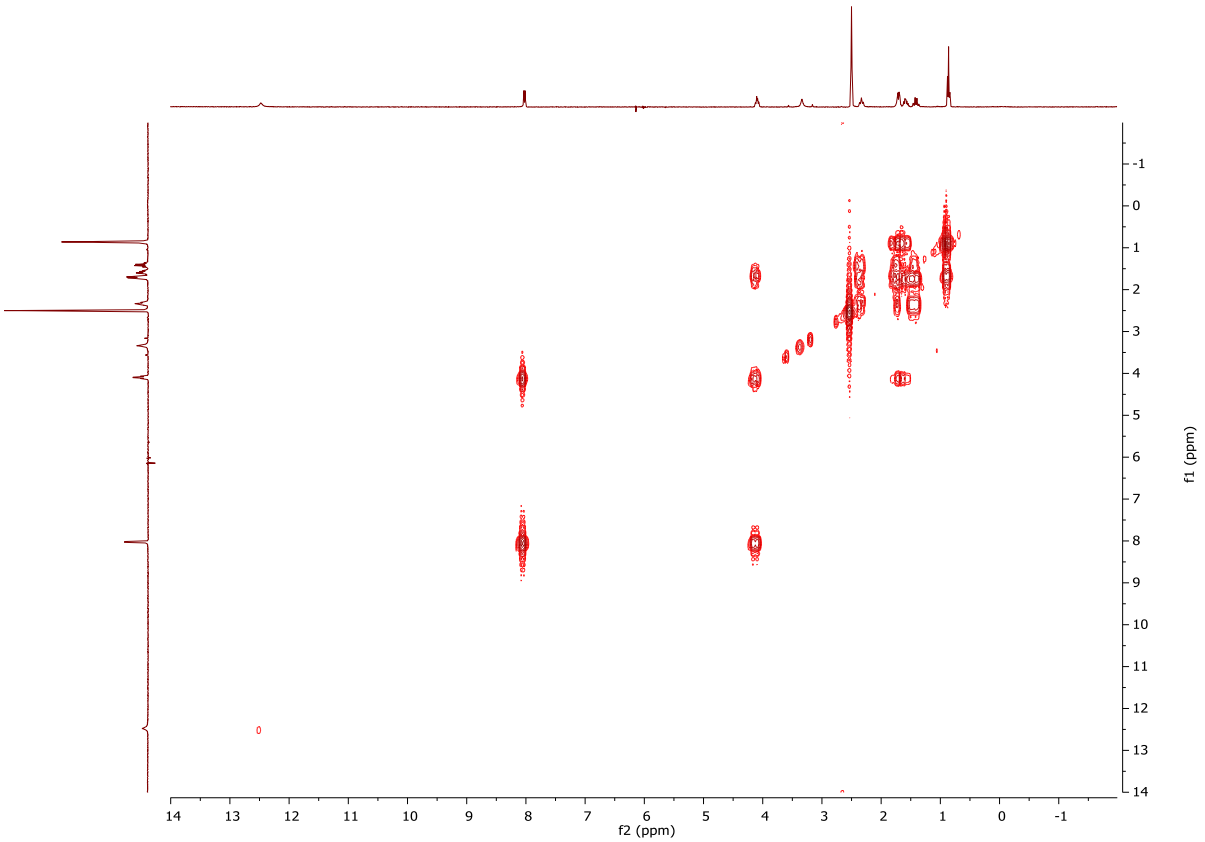


Figure S45: gCOSY spectrum of **10**.

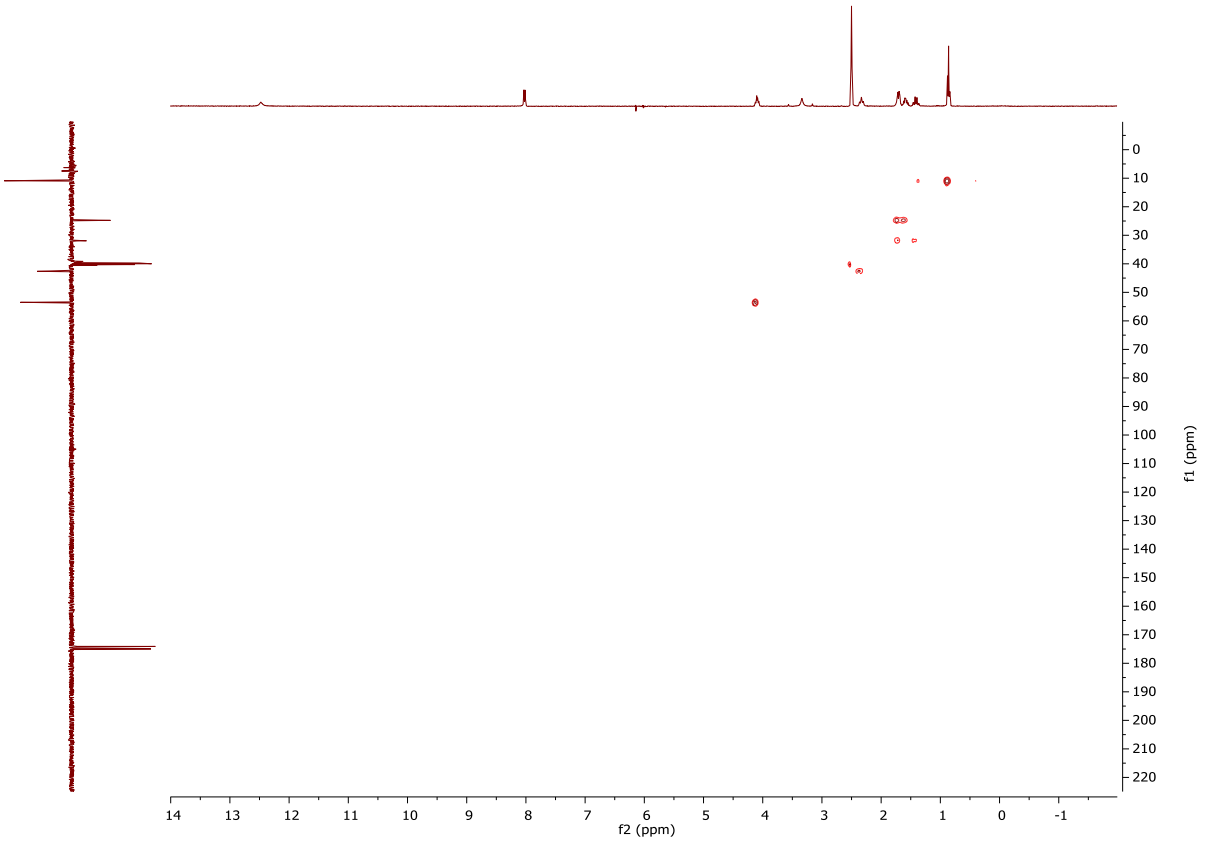


Figure S46: gHSQC spectrum of **10**.

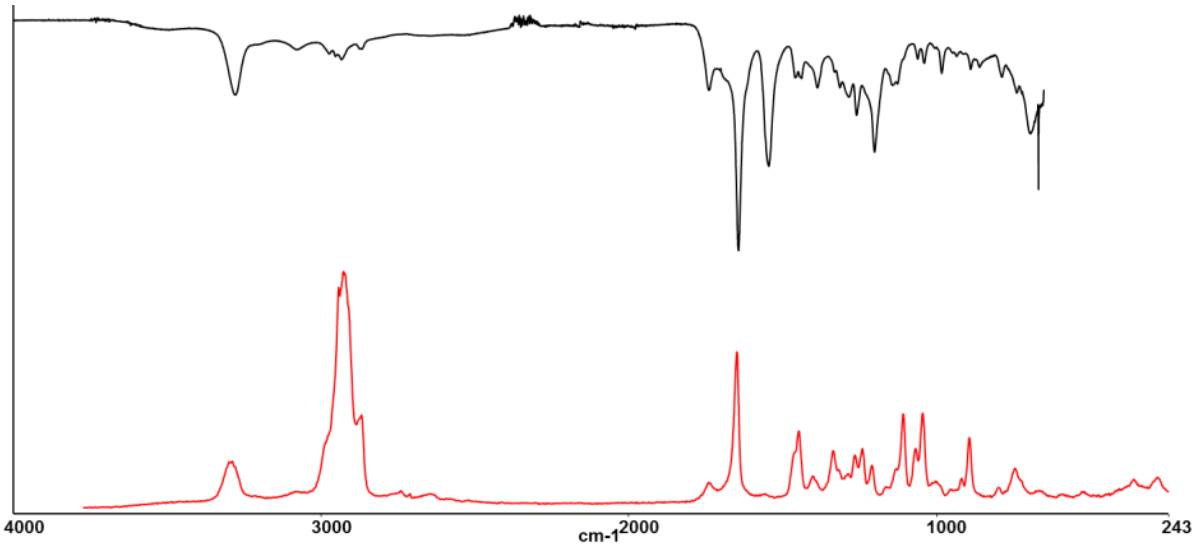


Figure S47: FTIR and Raman (633nm) spectrum of **10**.

CHex(Nva-OH) **(11)**

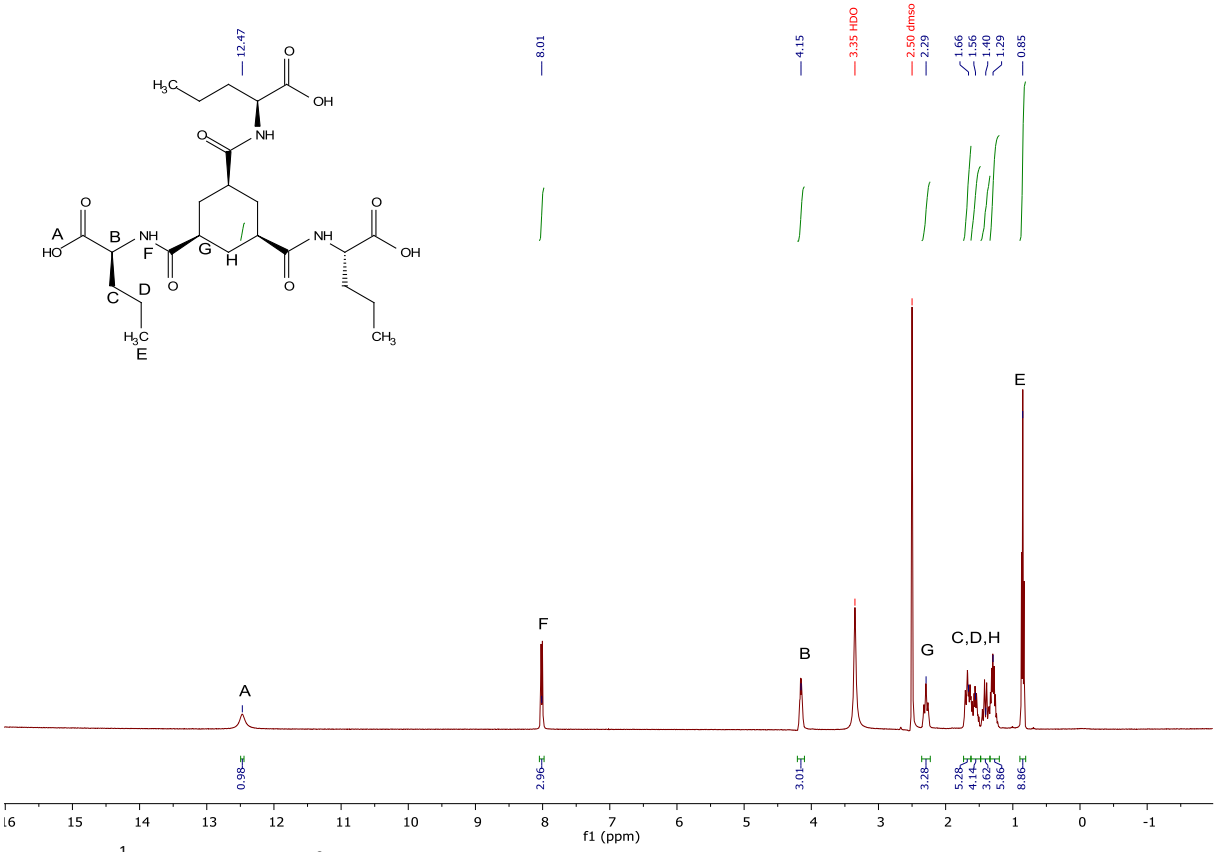


Figure S48: ^{1}H-NMR spectrum of **11**.

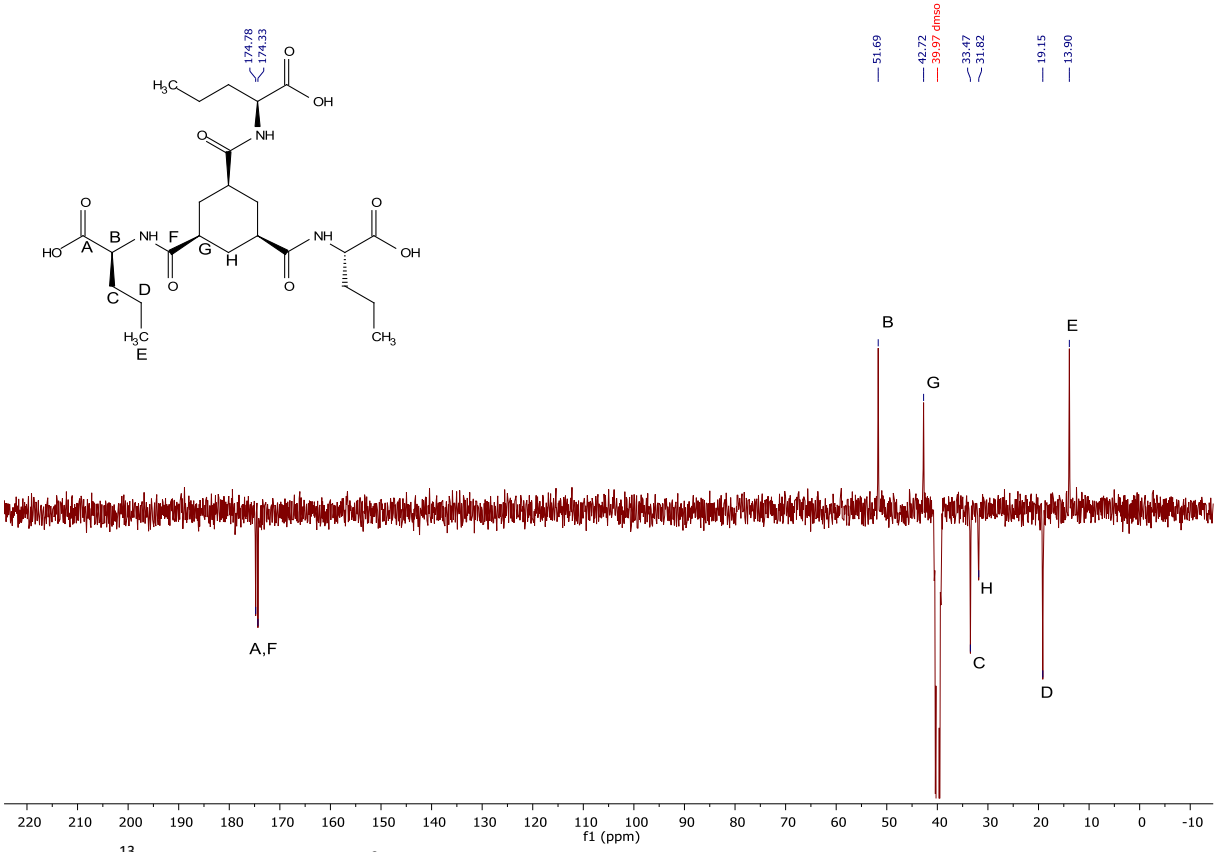


Figure S49: ^{13}C-APT NMR spectrum of **11**.

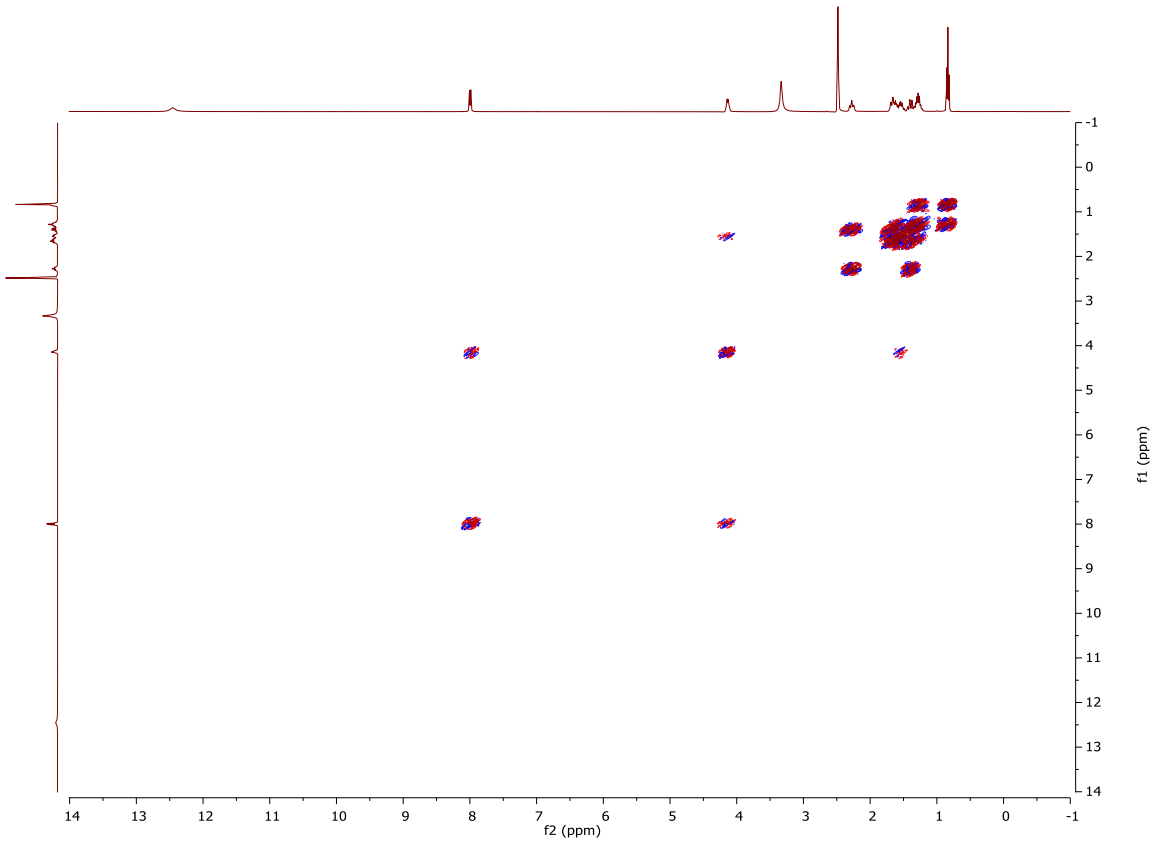


Figure S50: gDQF COSY spectrum of **11**.

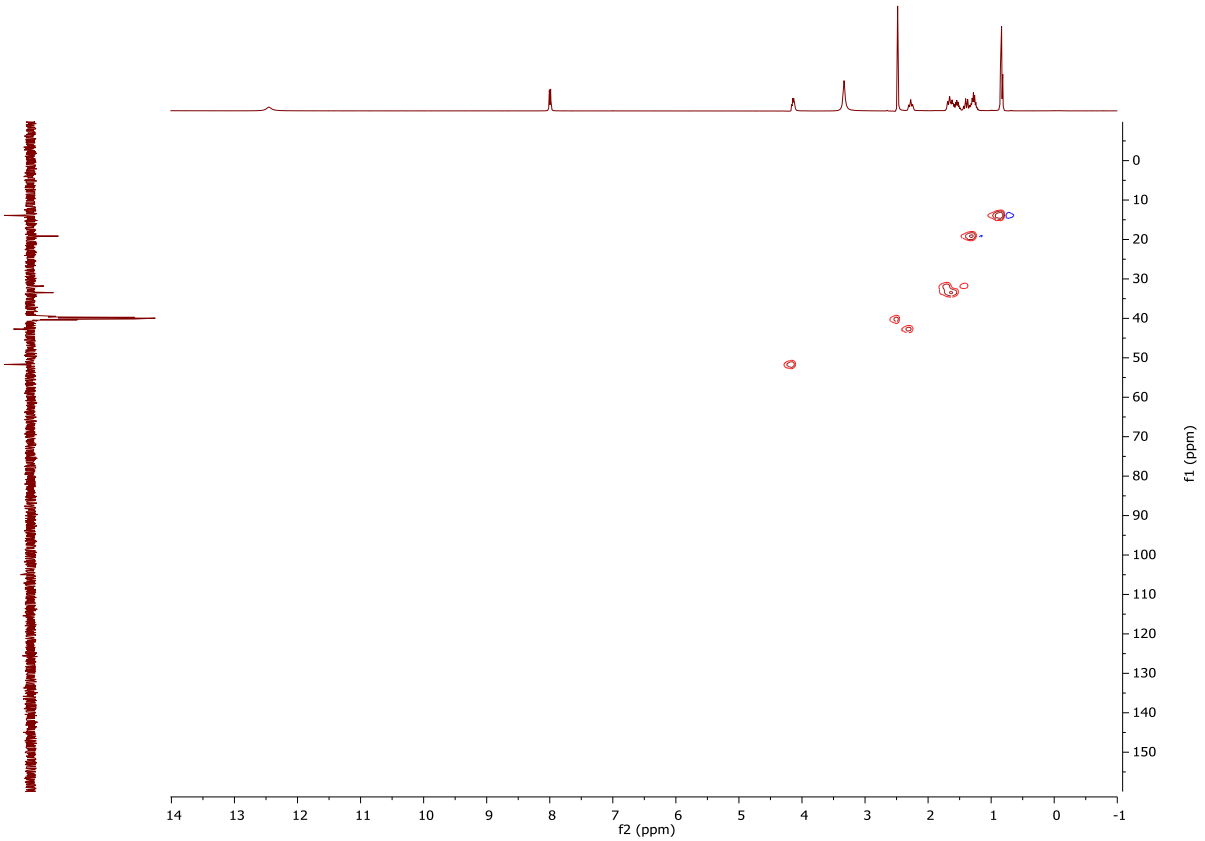


Figure S51: gHSQC spectrum of **11**.

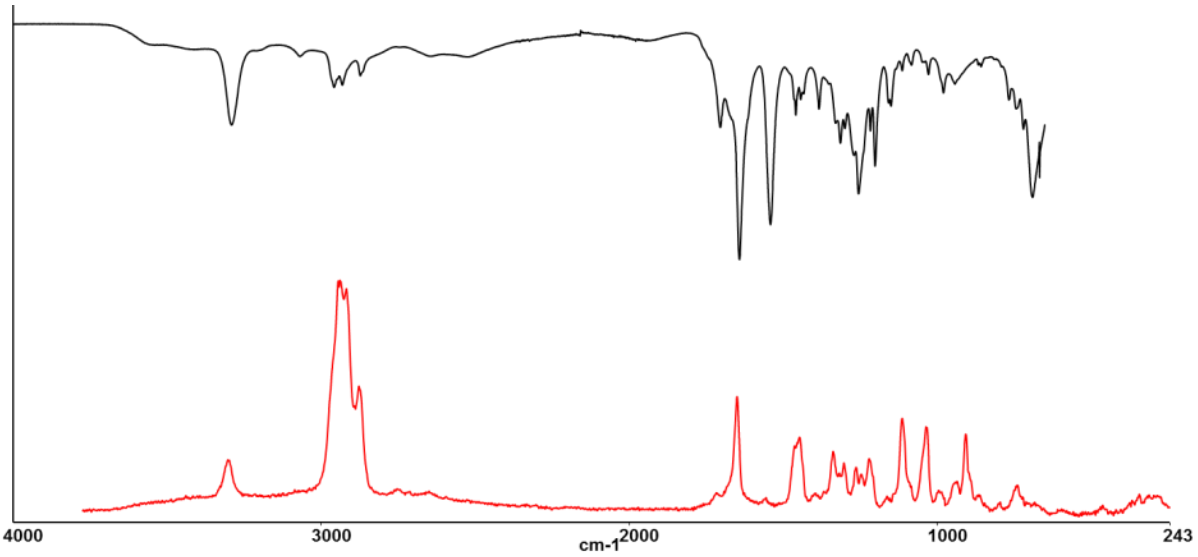


Figure S52: FTIR and Raman (633nm) spectrum of **11**.

CHex(Nle-OH) **(12)**

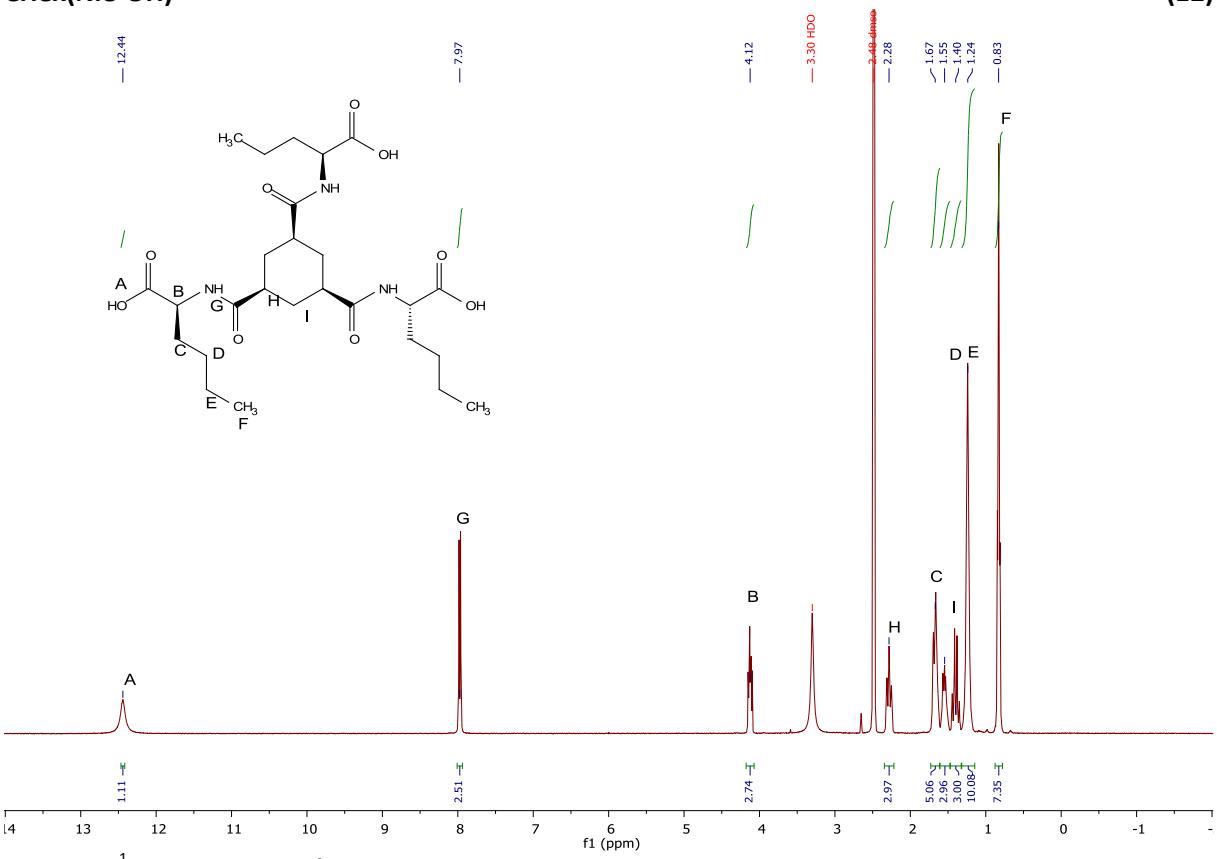


Figure S53: ^{1}H-NMR spectrum of **12**.

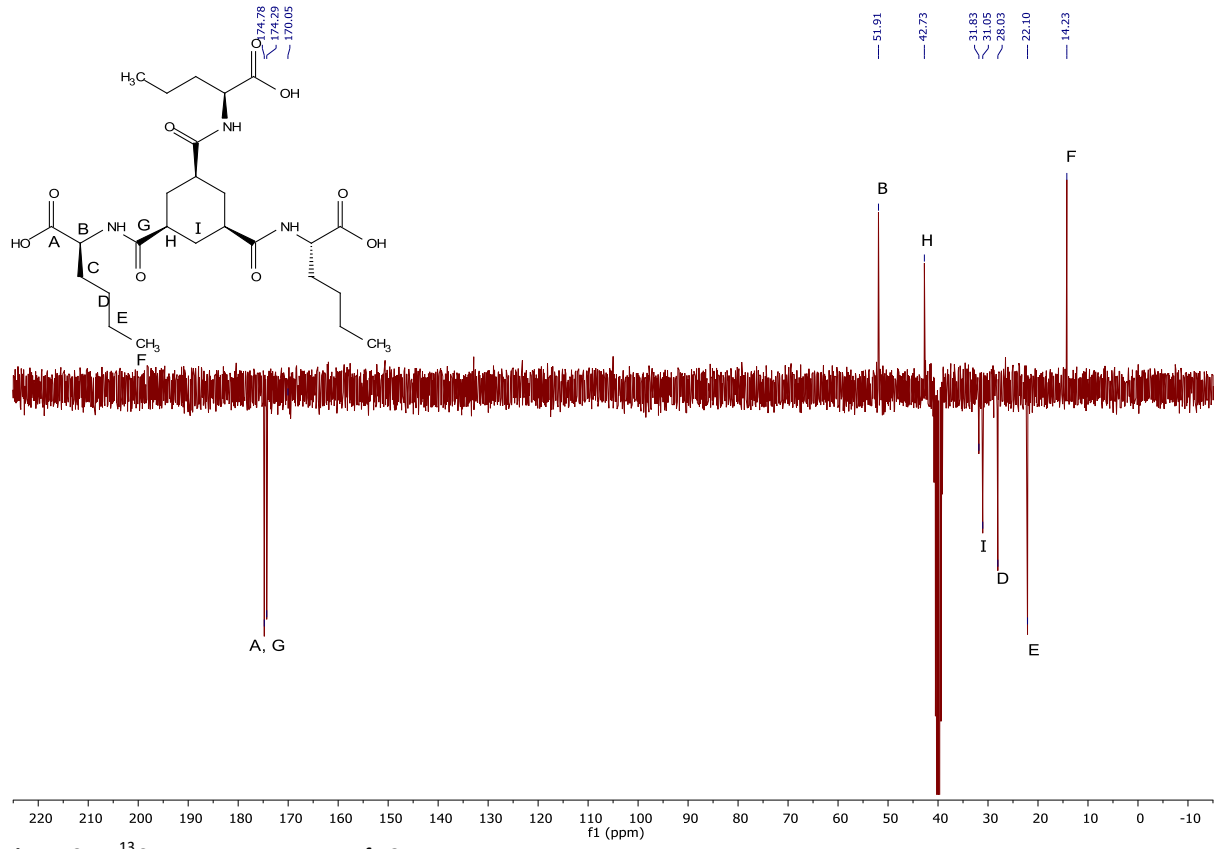


Figure S54: ^{13}C-APT NMR spectrum of **12**.

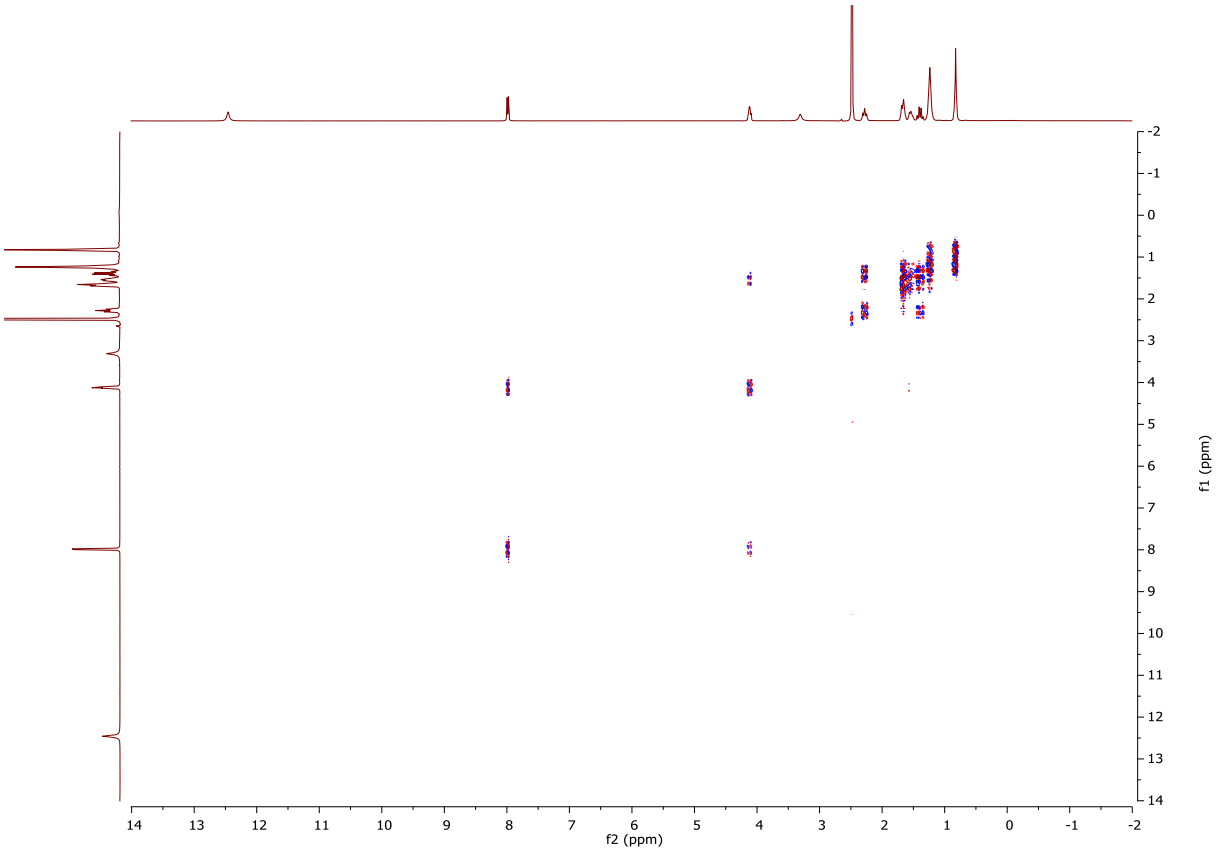


Figure S55: gCOSY spectrum of **12**.

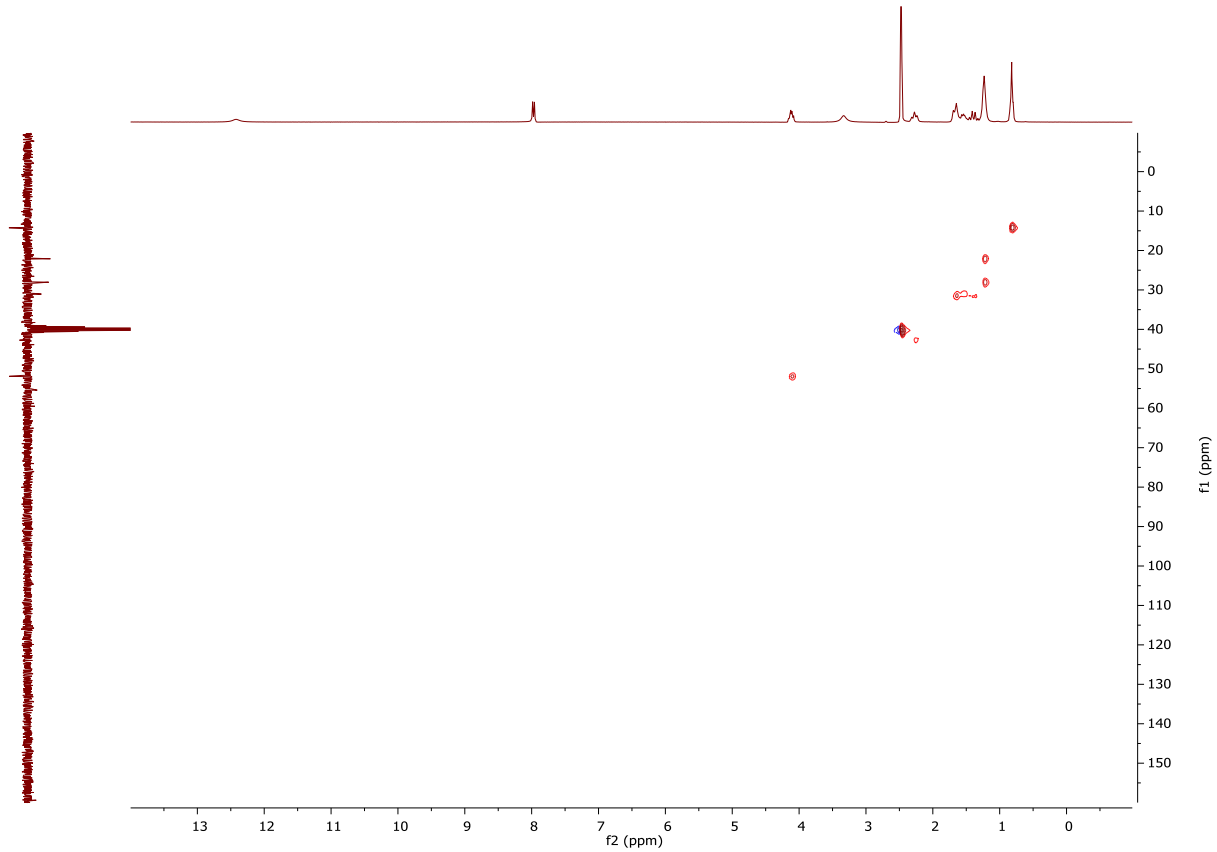


Figure S56: gHSQC spectrum of **12**.

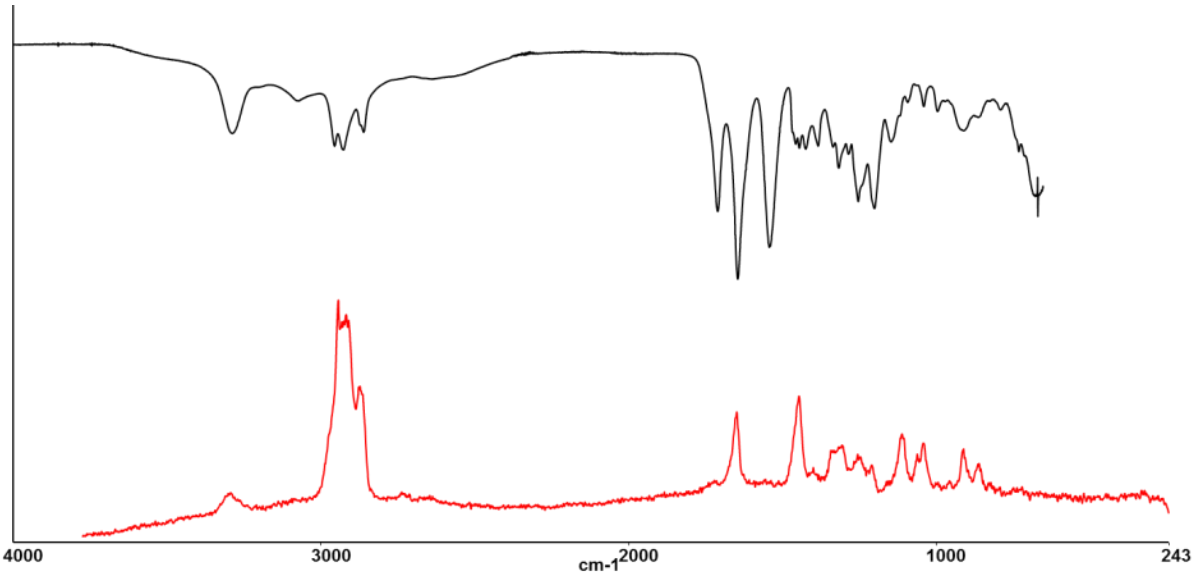


Figure S57: FTIR and Raman (633 nm) spectrum of **12**.

Elemental Analysis

The elemental analysis of the compounds is not as expected due to incomplete removal of NaCl during purification, however the C/N and C/H ratios are as expected showing that the only additional component is inorganic. The sodium content for Chex(Abu-OH) was determined to be 5.05% by ICP-AA (Perkin Elmer). FTIR spectroscopy shows that the carboxylic acid groups are partially in the carboxylate form, consistent with salt formation. Hence the significant, but minor, deviations between expected and found elemental analyses is due to residual sodium content (typically one equivalent).

Table S1: calculated versus found CHN analysis of compounds **2-12**.

Compound	calculated				found			Ratio	
	C	H	N	Na	C	H	N	C/H	C/N
02 CHex(Gly-OH)	46.51	5.46	10.85		38.13	4.89	8.92	1.09	1.00
03 CHex(Ala-OH)	50.35	6.34	9.79		49.72	6.2	9.61	0.99	0.99
04 CHex(Val-OH)	56.13	7.65	8.18		50.34	7.35	7.27	1.07	0.99
05 CHex(Leu-OH)	58.36	8.16	7.56		55.66	7.2	7.88	0.93	1.09
06 CHex(Ile-OH)	58.36	8.16	7.56		56.54	7.37	7.91	0.93	1.08
07 CHex(Met-OH)	47.27	6.54	6.89		46.63	6.39	6.73	0.99	0.99
08 CHex(Phe-OH)	65.74	5.98	6.39		55.9	5.39	5.42	1.06	1.00
09 CHex(Trp-OH)	65.11	5.46	10.85		54.56	4.83	9.02	1.06	0.99
10 CHex(Abu-OH)	47.27	6.45	6.89	5.05	46.63	6.39	6.73	1.00	0.99
11 CHex(Nva-OH)	56.13	7.65	8.18		52.51	7.64	7.55	1.07	0.99
12 CHex(Nle-OH)	58.36	8.16	7.56		55.35	7.78	7.17	1.01	1.00

Rheology

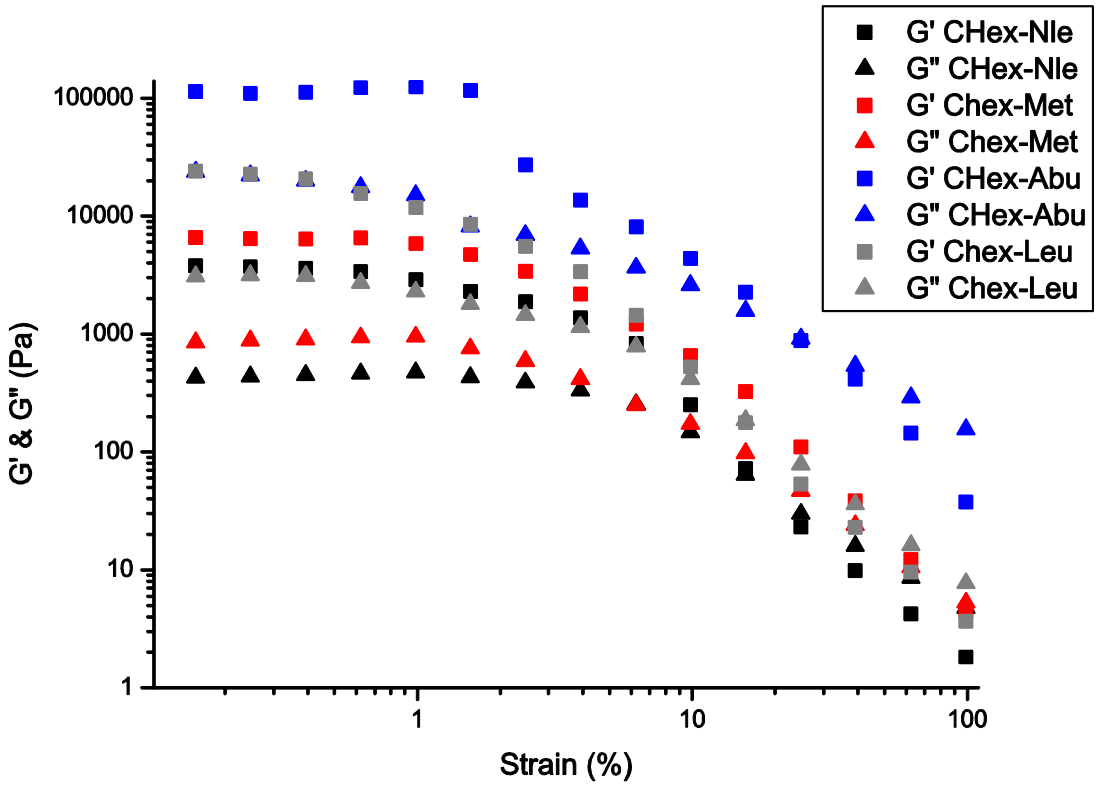


Figure S58: Loss (G') and Storage (G") modulus of CHex(Ile-OH), CHex(Met-OH), CHex(Abu-OH) and CHex(Nle-OH) prepared by pH jumping.

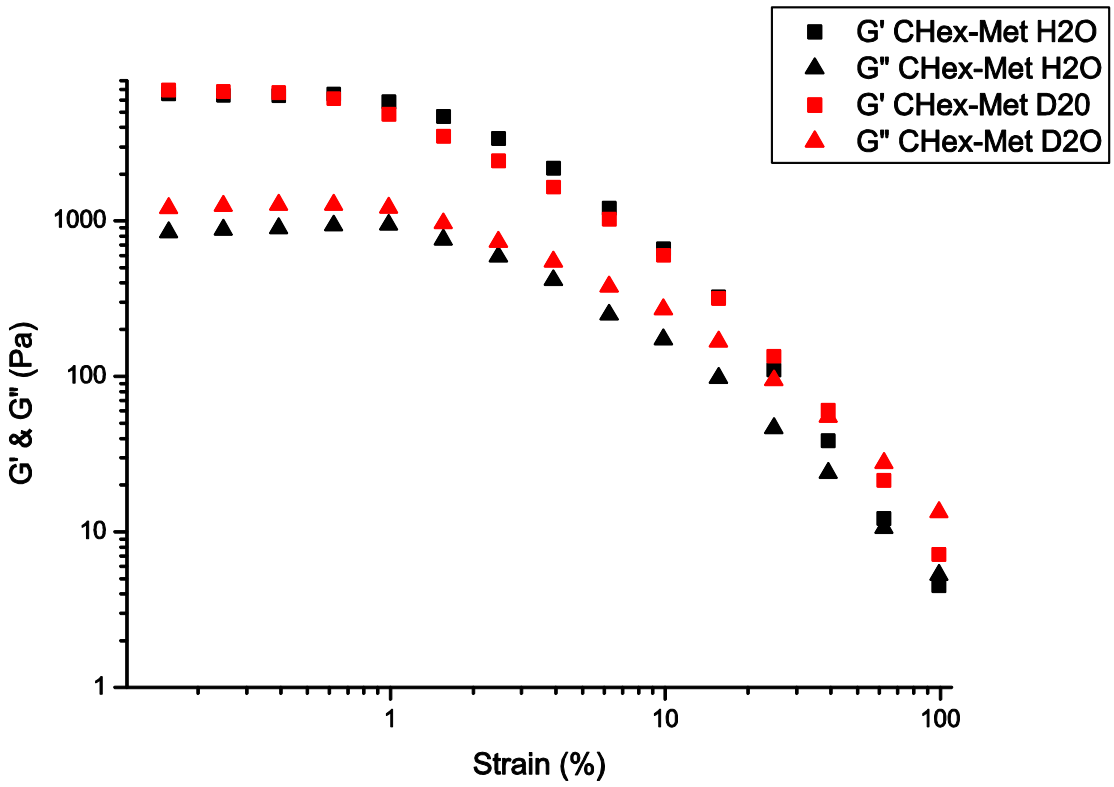


Figure S59: Loss (G') and Storage (G") modulus of Chex(Met-OH) prepared by pH jumping in H_2O and D_2O.

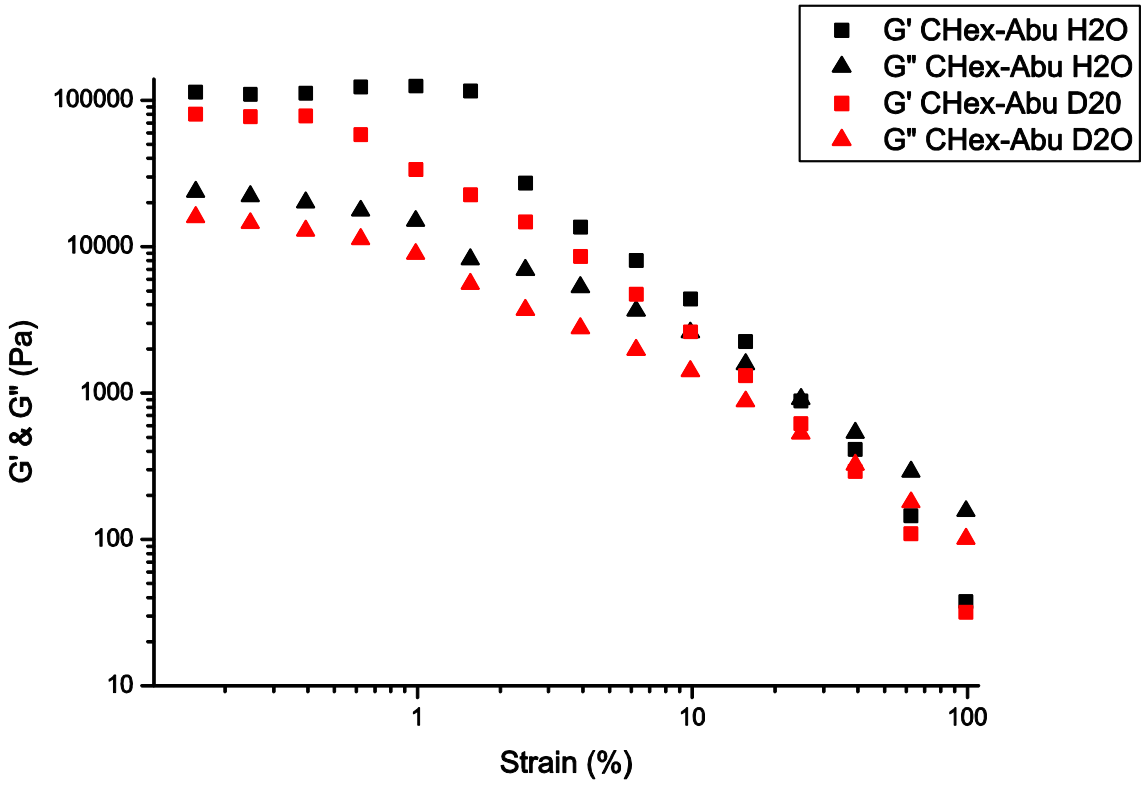


Figure S60: Loss (G') and Storage (G") modulus of Chex(Abu-OH) prepared by pH jumping in H_2O and D_2O.

Deuteration studies

Gels were prepared by replacing H_2O by D_2O with the heating and cooling cycles, the resulting gel was lyophilized and analyzed by FTIR. The FTIR spectrum was compared with the ones obtained from H_2O by the C-H stretches as internal standard.

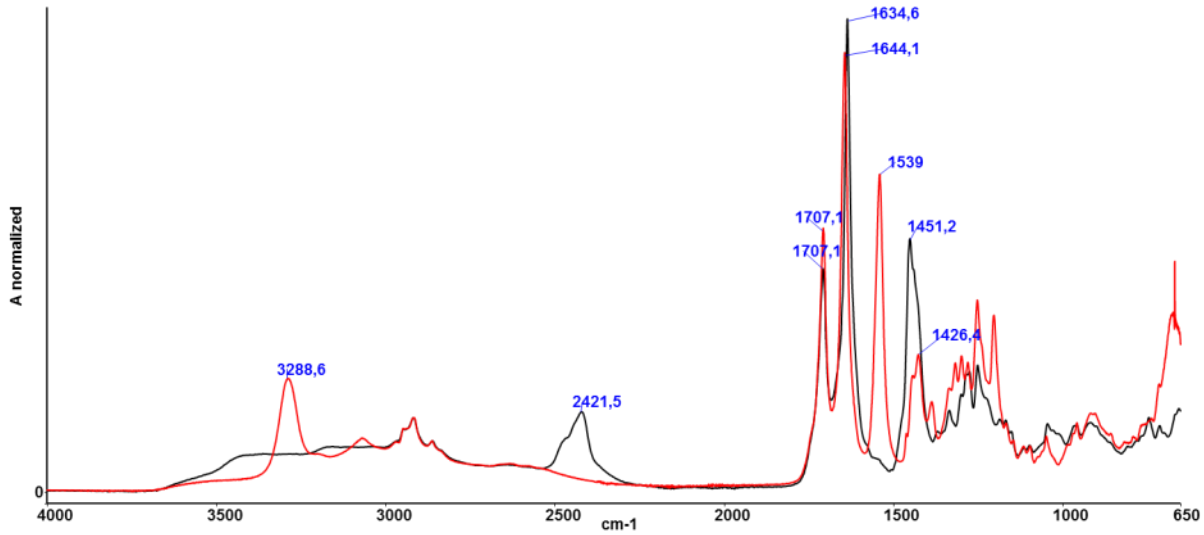


Figure S61: FTIR Spectrum of Chex(Met-OH) (black) and deuterated form (red).

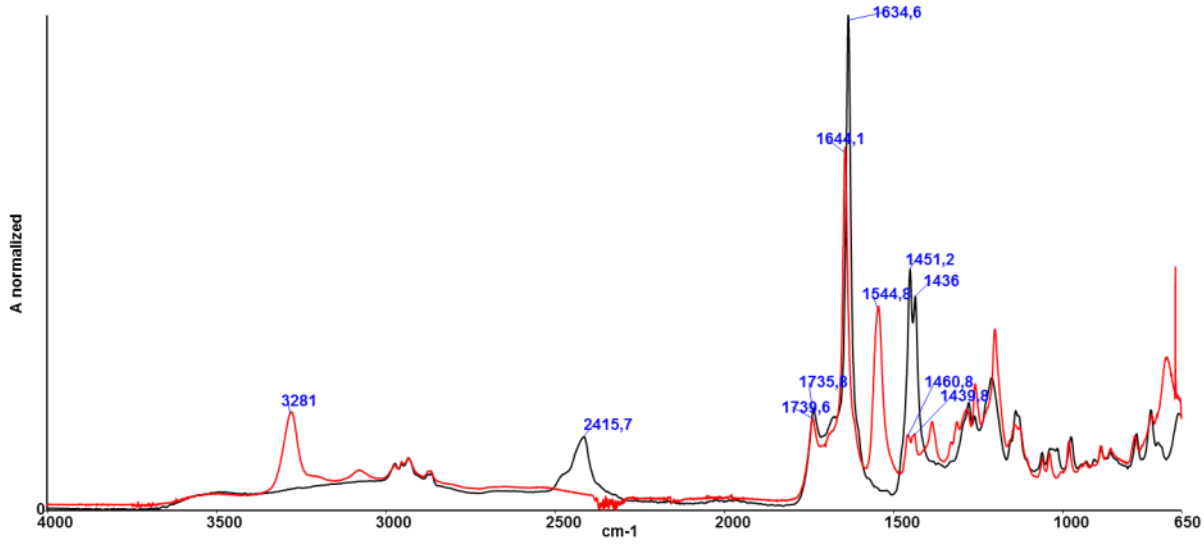


Figure S62: FTIR Spectrum of Chex(Abu-OH) (black) and deuterated form (red).

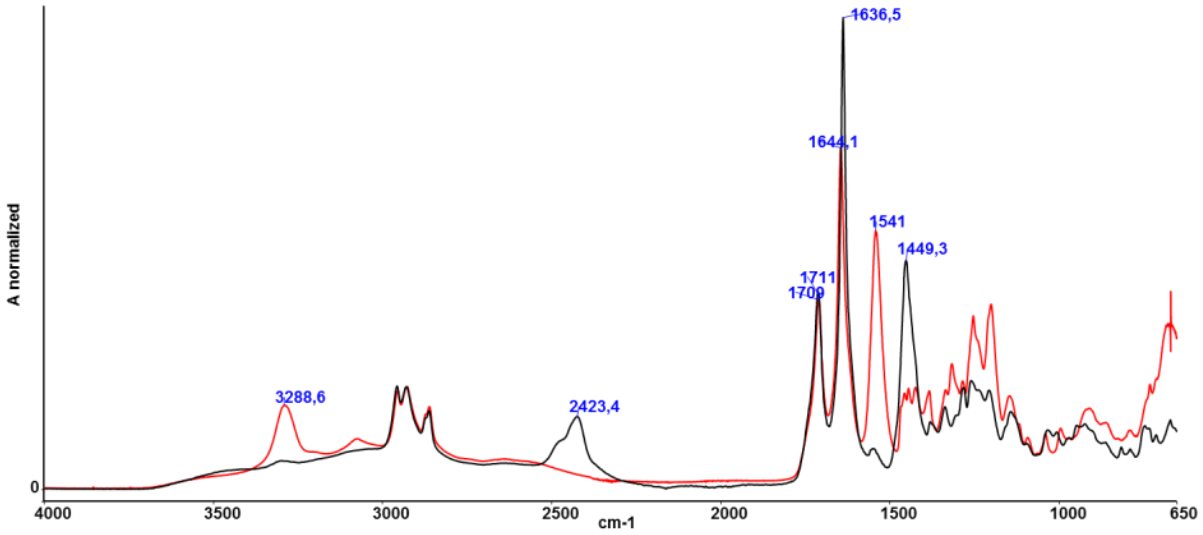


Figure S63: FTIR Spectrum of Chex(Nle-OH) (black) and deuterated form (red).

FTIR spectrum of a gel obtained from of D_2O solution showed total deuteration of the compounds exchangeable sites with the bands at 3288 (N-H stretch) and 1539 (amide II) cm^{-1} shifted to 2421 cm^{-1} and 1451 cm^{-1}, respectively, and the band at 1634 cm^{-1} (amide I) shifted to 1624 cm^{-1}.

References

1 M. de Loos, J. H. van Esch, R. M. Kellogg and B. L. Feringa, *Tetrahedron*, 2007, **63**, 7285–7301.

2 K. J. C. Van Bommel, C. Van Der Pol, I. Muizebelt, A. Friggeri, A. Heeres, A. Meetsma, B. L. Feringa and J. Van Esch, *Angew. Chemie - Int. Ed.*, 2004, **43**, 1663–1667.