Electronic Supplementary Material (ESI) for ChemComm.

Conformational cooperativity between helical domains of differing geometry in oligoamide-oligourea foldamer chimeras

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SUPPORTING INFORMATION

General Information

All solvents were purchased from Sigma-Aldrich and used without purification except THF and CH_2Cl_2 which were obtained by distillation from sodium/benzophenone and calcium hydride respectively.

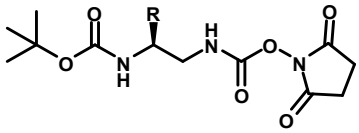
^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 400 or 500 MHz spectrometer. ^1H and ^{13}C spectra were referenced relative to the solvent residual peaks and chemical shifts (δ) reported in ppm downfield of tetramethylsilane (CDCl3 δ H: 7.26 ppm, δ C: 77.16 ppm; CD3OD δ H: 3.31 ppm, δ C: 49.00 ppm). ^1H NMR splitting patterns with observed first-order coupling are designated as singlet (s), doublet (d), triplet (t), or quartet (q). Coupling constants (*J*) are reported in hertz (Hz). In 1H NMR spectra, amide N*H* signals that exchange with deuterated solvent are not reported.

Electrospray (ES) spectra were recorded on a Waters Platform II and high resolution mass spectra (HRMS) were recorded on a Thermo Finnigan MAT95XP and are accurate to ± 0.001 Da. Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 FTIR spectrometer. Melting points were determined on a GallenKamp apparatus and are uncorrected.

Thin layer chromatography (TLC) was performed using commercially available pre-coated plates (Macherey-Nagel alugram. Sil G/UV254) and visualized under UV light at 254 nm and/or by staining with phosphomolybdic acid solution. Flash column chromatography was carried out on Fluorochem Davisil 40-63 µm 60 Å silica with the eluent quoted. Optical rotation measurements were taken on an AA-100 polarimeter using a cell with a path length of 0.25 dm at 24 °C with the solvent and concentration (g/100 mL) stated. Circular dichroism (CD) spectra were recorded on a Jasco J-815 spectrometer using a 1 mm cell at 20 °C with the solvent and concentration stated.

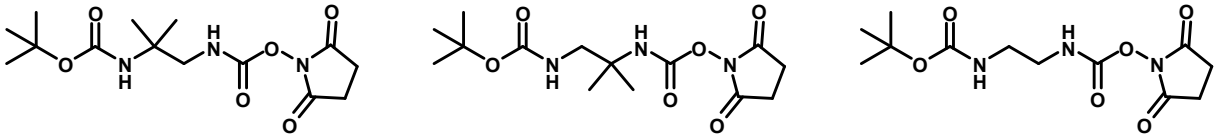
General Procedures

Activated chiral monomers **C** (**a** R= *i*Bu; **b** R= Me; **c** R= *i*Pr), activated achiral monomers **M1** and **M2**, CBzGly-Aib$_4$-OtBu and GlyNH$_2$-Aib$_4$-NHBoc and azlactone **A1**, L-ValNH^{t}Bu and H-PheNH^{t}Bu were prepared using a previously described procedure.[1]



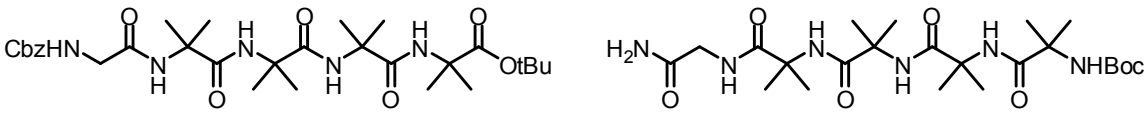
Ca R = *i*Bu
Cb R = Me
Cc R = *i*Pr

Scheme 1: Activated chiral monomers **Ca**, **Cb** and **Cc**



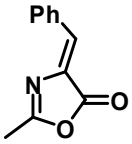
M1 **M2** **M3**

Scheme 2: Activated achiral monomers **M1**, **M2** and **M3**



CBzGly-Aib$_4$-OtBu GlyNH$_2$-Aib$_4$-NHBoc

Scheme 3: Peptides CbzGly-Aib$_4$-OtBu and GlyNH$_2$-Aib$_4$-NHBoc



A1

Scheme 4: Azlactone **A1**

General Procedure A : CbzGly-Aib$_4$-OH (1.00 eq.) and 1-hydroxybenzotriazole hydrate (1.30 eq.) were dissolved in CH_2Cl_2 (60 mL/mmol) and the suspension cooled to 0 °C. *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide (1.1 eq.) was added and the reaction was allowed to warm to room temperature

[1] Activated chiral and achiral monomers: (a) G. Guichard, V. Semetey, C. Didierjean, A. Aubry, J. - P. Briand, M. Rodriguez, *J. Org. Chem.*, 1999, **64**, 8702; (b) J. Fremaux, C. Dolain, B. Kauffmann, J. Clayden and G. Guichard, *Chem. Commun.*, 2013, **49**, 7415. (c) J. Fremaux, L. Fischer, T. Arbogast, B. Kauffmann and G. Guichard, *Angew. Chem. Int. Ed.*, 2011, **50**, 1382. Peptides: J. Solà, M. Helliwell and J. Clayden, *J. Am. Chem. Soc.*, 2010, **132**, 4548. M. De Poli, L. Byrne, R. A. Brown, J. Solà, A. Castellanos, T. Boddaert, R. Wechsel, J. D. Beadle and J. Clayden, *J. Org. Chem.*, 2014, **79**, 4659. Azlactone: B. S. Jursic, S. Sagiraju, D. K. Ancalade, T. Clark and E. D. Stevens, *Synth. Commun.*, 2007, **37**, 1709. Synthesis of L-ValNH^{t}Bu and H-PheNH^{t}Bu: B. A. F. Le Bailly and J. Clayden, *Chem. Commun.,* 2014, **50**, 7949.

and stirred until it was homogenous. The amine[2] (1.5 or 2.5 eq.) and trimethylamine or DIPEA (1.5 or 2 eq.) were added and the reaction mixture was stirred for 72 hours. The solvent was removed *in vacuo* and EtOAc was added. The organic phase was washed with $KHSO_4$ (5%), $NaHCO_3$, brine, dried ($MgSO_4$), filtered and concentrated. The pure oligomer was isolated by column chromatography (CH_2Cl_2:MeOH, 90:10).

General Procedure B : Boc-protected oligomers (1.00 eq) were dissolved in a mixture CH_2Cl_2/TFA (3/1) and stirred for 2 hours. The reaction mixture was then concentrated under reduced pressure and the resulting residue was coevaporated 3 times with cyclohexane. The crude product was then dissolved in DMF. DIPEA (3.00 eq) was then added and the mixture was cooled to 0 °C prior to the dropwise addition of carbamate (1.00 eq) in DMF (0.3 M). The reaction mixture was left to stir at 0 °C for 30 minutes then was allowed to warm to room temperature and stirred for another 18 hours. The reaction mixture was then concentrated and purified by flash chromatography (CH_2Cl_2-MeOH, 90:10) to give the desired compound (If DIPEA remained after column chromatography, the mixture was dissolved in EtOH. $CuSO_4.5H_2O$ was added and the reaction mixture was stirred for 3 hours. A filtration (CH_2Cl_2/MeOH, 90:10) over a short pad of silica gel gave the desired compound).

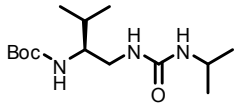
General Procedure C : The Boc-protected oligomer (1.00 eq) was dissolved in a mixture CH_2Cl_2/TFA (3/1) and stirred for 2 hours. The reaction mixture was then concentrated under reduced pressure and the resulting residue was coevaporated 3 times with cyclohexane. The crude product was then dissolved in DMF. DIPEA (3.00 eq) was then added and the mixture was cooled to 0 °C prior to the dropwise addition of Isopropyl isocyanate (2.00 eq) dissolved in DMF. The reaction mixture was left to stir at 0 °C for 30 minutes, then was allowed to warm to room temperature and stirred for another 18 hours. The reaction mixture was then concentrated and purified by flash chromatography (CH_2Cl_2-MeOH, 90:10) to give the desired compound (If DIPEA remained after column chromatography, the mixture was dissolved in EtOH. $CuSO_4.5H_2O$ was added and the reaction mixture was stirred for 3 hours. A filtration (CH_2Cl_2/MeOH, 90:10) over a short pad of silica gel gave the desired compound).

General Procedure D : Boc-protected oligourea (1.00 eq) and DiPEA (1.00 eq) were added to a solution of isopropyl amine (1.30 eq) in DMF (0.26 M) . The reaction was stirred for 30 min, quenched with $NaHCO_3$ aqueous solution and EtOAc was added. The organic phase was washed with $KHSO_4$ (5%), $NaHCO_3$ (sat?), brine, dried ($MgSO_4$), filtered and concentrated.

[2] From deprotection of Boc protected amine [CH_2Cl_2/TFA (3/1), 2h, r.t.]

Experimental Procedures and Characterisation Data

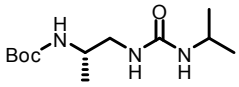
BocVal^{u}-NH(CO)NH*i*Pr U1



$C_{14}H_{29}N_3O_3$
M = 287.40 g.mol^{-1}

U1 was prepared from **Cc** (1.00 g, 2.91 mmol), isopropylamine (310 µL, 3.78 mmol) and DIPEA (537 µL, 2.91 mmol) as described in the general procedure D. The pure oligomer **U1** (794 mg, 95%) was isolated as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.00-4.80 (1H, m, N*H*), 4.79-4.64 (1H, m, N*H*), 4.54-4.35 (1H, m, N*H*), 3.81 (1H, oct, *J* = 6.9, NCH_{iPr}), 3.51-3.38 (1H, m, NCH_{Val}), 3.36-3.23 (1H, m, NCH_AH$_{BVal}$), 3.22-3.12 (1H, m, NCH$_A$$H_{BVal}$), 1.85-1.68 (1H, m, C$H_{Val}$), 1.43 (9H, s, C(C$H_3$)$_3$), 1.13 (6H, d, *J* = 6.5, 2 x CH_{3iPr}), 0.94 (3H, d, *J* = 6.8, CH_{3Val}), 0.92 (3H, d, *J* = 6.9, CH_{3Val}). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.2 (*C*=O), 157.3 (*C*=O), 79.6 (*C*(CH$_3$)$_3$), 56.6 (NC$_\beta$H$_{Val}$), 43.4 (N*C*H$_{iPr}$), 42.5 (NC$_\alpha$H$_{2Val}$), 30.7 (C$_\gamma$H$_{Val}$), 28.5 (C(*C*H$_3$)$_3$), 23.6 (*C*H$_{iPr}$), 23.5 (*C*H$_{iPr}$), 19.5 (C$_\delta$H$_{3Val}$), 18.1 (C$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3311, 2965, 2928, 2871, 1636, 1534; **HRMS** (ESI$^+$): *m/z* calcd for $C_{14}H_{30}N_3O_3$ $[M+H]^+$ 288.2287, found 288.2285.

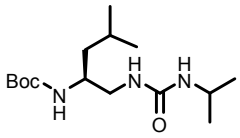
BocAla^{u}-NH(CO)NH*i*Pr U2[1a]



$C_{12}H_{25}N_3O_3$
M = 289.35 g.mol^{-1}

U2 was prepared from **Cb** (1.50 g, 4.76 mmol), isopropylamine (506 µL, 6.18 mmol) and DIPEA (880 µL, 4.76 mmol) as described in the general procedure D. The pure oligomer **U2** (1.16 g, 94.0%) was isolated as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.17 (1H, t, *J* = 4.5, N*H*), 4.94 (1H, d, *J* = 7.5, N*H*), 4.74 (1H, brs, N*H*), 3.82 (1H, oct, *J* = 6.7, NCH_{Ala}), 3.66 (1H, oct, *J* = 7.3, NCH_{iPr}), 3.32-3.17 (1H, m, NCH_AH$_{BAla}$), 3.17-3.03 (1H, m, NCH$_A$$H_{BAla}$), 1.42 (9H, s, C(C$H_3$)$_3$), 1.13 (9H, d, *J* = 6.5, 2 x CH_{3iPr} and CH_{3Ala}). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.3 (*C*=O), 156.5 (*C*=O), 79.6 (*C*(CH$_3$)$_3$), 47.6 (NC$_\beta$H$_{Ala}$), 46.7 (NC$_\alpha$H$_{2Ala}$),42.4 (N*C*H$_{iPr}$), 28.5 (C(*C*H$_3$)$_3$), 23.6 (*C*H$_{iPr}$), 23.5 (*C*H$_{iPr}$), 18.8 (C$_\delta$H$_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3341, 2973, 2932, 2873, 1637, 1563; **HRMS** (ESI$^+$): *m/z* calcd for $C_{12}H_{26}N_3O_3$ $[M+H]^+$ 260.1974, found 260.1986.

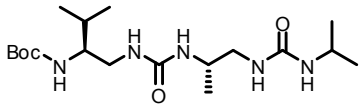
BocLeu^{u}-NH(CO)NH*i*Pr U3



$C_{15}H_{31}N_3O_3$
M = 301.42 g.mol^{-1}

U3 was prepared from **Ca** (2.00 g, 5.60 mmol), isopropylamine (600 µL, 7.27 mmol) and DIPEA (1.03 mL, 5.60 mmol) as described in the general procedure D. The pure oligomer **U3** (1.58 g, 92.7%) was isolated as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.16-4.94 (1H, m, N*H*), 4.81-4.48 (2H, m, N*H*), 3.90-3.75 (1H, m, NCH_{Leu}), 3.70-3.59 (1H, m, NCH_{iPr}), 3.33-3.16 (1H, m, NCH_AH$_{BLeu}$), 3.16-3.02 (1H, m, NCH$_A$$H_{BLeu}$), 1.67 (1H, non, *J* = 6.9, CH_{Leu}), 1.42 (9H, s, C(CH_3)$_3$), 1.28 (2H, t, *J* = 7.3, CH_{2Leu}), 1.13 (6H, d, *J* = 6.5, CH_{3iPr}), 0.91 (3H, d, *J* = 6.5, CH_{3Leu}), 0.90 (3H, d, *J* = 6.5, CH_{3Leu}). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.2 (*C*=O), 156.9 (*C*=O), 79.6 (*C*(CH$_3$)$_3$), 49.8 (NC$_\beta$H$_{Leu}$), 46.2 (NC$_\square$H$_{2Leu}$), 42.4 (C$_\square$H$_{2Leu}$), 42.2 (NCH$_{iPr}$), 28.5 (C(*C*H$_3$)$_3$), 25.0 (C$_\delta$H$_{Leu}$), 23.6 (*C*H$_{iPr}$), 23.5 (*C*H$_{iPr}$), 23.2 (C$_*$H$_{3Leu}$), 22.2 (C$_*$H$_{3Leu}$). **IR** (film, cm^{-1}): ν_{max} = 3341, 2964, 2931, 2870, 1636, 1526;

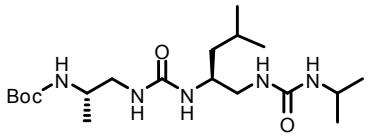
BocVal^{u}-Ala^{u}-NH(CO)NH*i*Pr U4



$C_{18}H_{37}N_5O_4$
M = 387.52 g.mol^{-1}

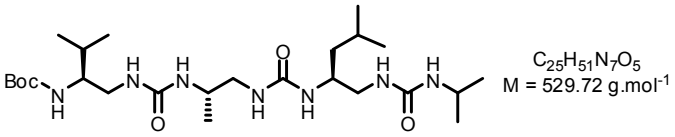
U4 was prepared from **U2** (900 mg, 3.86 mmol), **Cc** (1.33 g, 3.86 mmol) and DIPEA (1.97 mL, 11.58 mmol) as described in the general procedure B2. The pure oligomer **U4** (933 mg, 62.4% in two steps) was isolated as a white solid. **^{1}H NMR** (400 MHz, CD_3OH) δ = 6.39 (1H, d, *J* = 6.7, N*H*), 6.04-5.73 (4H, m, N*H*), 4.88-3.67 (2H, m, NCH_{Ala} and NCH_{iPr}), 3.52-3.38 (1H, m, NCH_{Val}), 3.37-3.15 (2H, m, NCH_AH$_{BVal}$ and NCH_AH$_{BAla}$), 3.01-2.82 (2H, m, NCH$_A$$H_{BVal}$ and NCH$_A$$H_{BAla}$), 1.70 (1H, oct, *J* = 6.6, CH_{Val}), 1.43 (9H, s, C(CH_3)$_3$), 1.11 (3H, d, *J* = 6.5, CH_{3iPr}), 1.10 (3H, d, *J* = 6.5, CH_{3iPr}), 1.07 (3H, d, *J* = 6.7, CH_{3Ala}), 0.93 (3H, d, *J* = 6.8, CH_{3Val}), 0.89 (3H, d, *J* = 6.8, CH_{3Val}). **^{13}C NMR** (100 MHz, CD_3OH) δ = 160.8 (*C*=O), 160.6 (*C*=O), 158.8 (*C*=O), 79.8 (*C*(CH$_3$)$_3$), 57.6 (NC$_\beta$H$_{Val}$), 47.6 (NC$_\beta$H$_{Ala}$), 46.9 (NC$_\square$H$_{2Ala}$), 43.2 (NC$_\square$H$_{2Val}$), 42.9 (NCH$_{iPr}$), 31.7 (C$_\gamma$H$_{Val}$), 28.7 (C(*C*H$_3$)$_3$), 23.5 (*C*H$_{iPr}$), 23.4 (*C*H$_{iPr}$), 19.8 (C$_\delta$H$_{3Val}$), 19.0 (C$_\delta$H$_{3Ala}$), 18.3 (C$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3321, 2969, 2932, 2873, 1630, 1529; **HRMS** (ESI$^+$): *m/z* calcd for $C_{18}H_{38}N_5O_4$ $[M+H]^+$ 388.2924, found 388.2911.

BocAla^{u}-Leu^{u}-NH(CO)NH*i*Pr U5



U5 was prepared from **U3** (1.30 g, 4.98 mmol), **Cb** (1.60 g, 4.98 mmol) and DIPEA (2.54 mL, 14.94 mmol) as described in the general procedure B2. The pure oligomer **U5** (860 mg, 38.4% in two steps) was isolated as a white solid. **^{1}H NMR** (400 MHz, CD_3OH) δ = 6.61-6.42 (1H, m, N*H*), 5.91-5.72 (4H, m, N*H*), 3.85-3.59 (1H, m, NCH_{Ala}, NCH_{Leu} and NCH_{iPr}), 3.28-3.10 (2H, m, NCH_AH$_{BLeu}$ and NCH_AH$_{BAla}$), 3.02-2.81 (2H, m, NCH$_A$$H_{BLeu}$ and NCH$_A$$H_{BAla}$), 1.68 (1H, non, J = 6.9, CH_{Leu}), 1.43 (9H, s, C(CH_3)$_3$), 1.32-1.20 (2H, m, CH_{2Leu}), 1.11 (3H, d, J = 6.5, CH_{3iPr}), 1.10 (3H, d, J = 6.5, CH_{3iPr}), 1.07 (3H, d, J = 6.7, CH_{3Ala}), 0.92 (3H, d, J = 6.7, CH_{3Leu}), 0.90 (3H, d, J = 6.6, CH_{3Leu}). **^{13}C NMR** (100 MHz, CD_3OH) δ = 161.1 (*C*=O), 160.6 (*C*=O), 158.2 (*C*=O), 79.9 (*C*(CH$_3$)$_3$), 49.3 (NC$_\beta$H$_{Leu}$), 47.1(NC$_\beta$H$_{Ala}$), 46.5 (NC$_\alpha$H$_{2Ala}$), 46.3 (NC$_\alpha$H$_{2Leu}$), 43.1 (C$_\alpha$H$_{2Leu}$), 42.9 (NCH$_{iPr}$), 28.7 (C(*C*H$_3$)$_3$), 25.9 (C$_\delta$H$_{Leu}$), 23.6 (*C*H$_{iPr}$), 23.5 (*C*H$_{iPr}$), 23.4 (*C*H$_{3Leu}$), 22.3 (*C*H$_{3Leu}$), 18.5 (C$_\delta$H$_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3331, 2968, 2932, 2872, 1636, 1536; **HRMS** (ESI$^+$): *m/z* calcd for $C_{19}H_{39}N_5O_4Na[M+Na]^+$ 424.2900, found 424.2887.

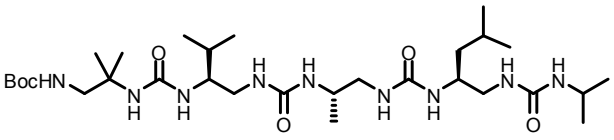
BocVal^{u}-Ala^{u}-Leu^{u}-NH(CO)NH*i*Pr U6



U6 was prepared from **U5** (850 mg, 2.12 mmol), **Cc** (727 mg, 2.12 mmol) and DIPEA (1.08 mL, 6.35 mmol) as described in the general procedure B2. The pure oligomer **U6** (728 mg, 64.9% in two steps) was isolated as a white solid. **^{1}H NMR** (400 MHz, CD_3OH) δ = 6.53 (1H, d, J = 10.0, N*H*), 6.25 (1H, dd, J = 7.2 and 1.7, N*H*), 6.05 (1H, d, J = 7.9, N*H*), 5.96-5.86 (2H, m, N*H*), 5.83 (1H, d, J = 9.3, N*H*), 5.81-5.74 (1H, m, N*H*), 4.04-3.85 (2H, m, NCH_{Ala} and NCH_{Leu}), 3.77-3.68 (1H, oct, J = 7.6, NCH_{iPr}), 3.59-3.39 (4H, m, NCH_{Val}, NCH_AH$_{BVal}$, NCH_AH$_{BLeu}$ and NCH_AH$_{BAla}$), 2.74-2.34 (3H, m, NCH$_A$$H_{BLeu}$, NCH$_A$$H_{BVal}$ and NCH$_A$$H_{BAla}$), 1.76-1.58 (2H, m, C$H_{Leu}$ and CH_{Val}), 1.45 (9H, s, C(CH_3)$_3$), 1.22 (2H, t, J = 7.1, CH_{2Leu}), 1.11 (3H, d, J = 6.5, CH_{3iPr}), 1.10 (3H, d, J = 6.5, CH_{3iPr}), 1.04 (3H, d, J = 6.8, CH_{3Ala}), 0.97-0.85 (12H, m, 2 x CH_{3Val} and 2 x CH_{3Leu}). **^{13}C NMR** (100 MHz, CD_3OH) δ = 161.2 (*C*=O), 160.8 (*C*=O), 160.6 (*C*=O), 159.4 (*C*=O), 80.1 (*C*(CH$_3$)$_3$), 57.5 (NC$_\beta$H$_{Val}$), 49.1 (NC$_\beta$H$_{Leu}$), 48.1 (NC$_\alpha$H$_{2Ala}$), 46.5 (NC$_\beta$H$_{Ala}$), 46.1 (NC$_\alpha$H$_{2Leu}$), 43.9 (NC$_\alpha$H$_{2Val}$), 43.7 (C$_\alpha$H$_{2Leu}$), 42.8 (NCH$_{iPr}$), 31.9 (C$_\gamma$H$_{Val}$), 28.7 (C(*C*H$_3$)$_3$), 25.9 (C$_\delta$H$_{Leu}$), 23.6 (2 x *C*H$_{iPr}$),

23.5 ($C_{\gamma}H_{3Leu}$), 22.4 ($C_{\gamma}H_{3Leu}$), 20.0 ($C_{\delta}H_{3Val}$), 18.6 ($C_{\delta}H_{3Ala}$), 18.4 ($C_{\delta}H_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3319, 2963, 2931, 2872, 1628, 1567, 1530; **HRMS** (ESI^+): *m/z* calcd for $C_{25}H_{52}N_7O_5$ $[M+H]^+$ 530.4030, found 530.4006.

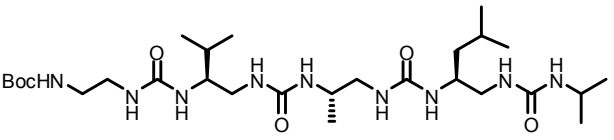
BocAib^{u}-Val^{u}-Ala^{u}-Leu^{u}-NH(CO)NH*i*Pr U7



$C_{30}H_{61}N_9O_6$
M = 643.86 g.mol^{-1}

U7 was prepared from **U6** (150 mg, 0.28 mmol), **M2** (93 mg, 0.28 mmol) and DIPEA (145 µL, 0.85 mmol) as described in the general procedure B2. The pure oligomer **U7** (50 mg, 27.4% in two steps) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OD) δ = 6.87 (1H, t, *J* = 6.9, N*H*), 6.40 (1H, d, *J* = 9.4, N*H*), 6.13 (1H, d, *J* = 9.4, N*H*), 5.93 (1H, d, *J* = 9.0, N*H*), 5.79 (1H, s, N*H*), 5.77 (1H, d, *J* = 10.0, N*H*), 5.61 (1H, d, *J* = 9.8, N*H*), 4.09-3.96 (1H, m, NCH_{Ala}), 3.94-3.85 (1H, m, NCH_{Leu}), 3.77-3.68 (1H, m, NCH_{Val} and NCH_{iPr}), 3.67-3.44 (4H, m, NCH_AH$_{BAib^u}$, NCH_AH$_{BVal}$, NCH_AH$_{BLeu}$ and NCH_AH$_{BAla}$), 2.87-2.76 (1H, m, NCH$_A$$H_{BAib^u}$), 2.70-2.57 (1H, m, NCH$_A$$H_{BLeu}$), 2.53-2.32 (2H, m, NCH$_A$$H_{BVal}$ and NCH$_A$$H_{BAla}$), 1.69 (1H, non, *J* = 6.8, CH_{Leu}), 1.62 (1H, oct, *J* = 6.7, CH_{Val}), 1.46 (9H, s, C(CH_3)$_3$), 1.37 (3H, s, CH_3), 1.22 (2H, t, *J* = 7.2, CH_{2Leu}), 1.14 (3H, s, CH_3), 1.13 (3H, d, *J* = 6.5, CH_{3iPr}), 1.12 (3H, d, *J* = 6.5, CH_{3iPr}), 1.04 (3H, d, *J* = 6.8, CH_{3Ala}), 0.95-0.86 (12H, m, 2 x CH_{3Val} and 2 x CH_{3Leu}). **^{13}C NMR** (125 MHz, CD_3OD) δ = 161.6 (*C*=O), 161.5 (*C*=O), 160.7 (*C*=O), 160.5 (*C*=O), 159.1 (*C*=O), 80.1 (*C*$(CH_3)_3$), 56.0 (N$C_{\beta}H_{Val}$), 54.8 (*C*), 49.3 (N$C_{\beta}H_{Leu}$), 47.9 (NCH_{2Aib^u}), 47.5 (N$C_{\alpha}H_{2Ala}$), 46.5 (N$C_{\beta}H_{Ala}$), 46.0 (N$C_{\alpha}H_{2Leu}$), 44.5 (N$C_{\alpha}H_{2Val}$), 43.8 ($C_{\alpha}H_{2Leu}$), 42.8 (NCH_{iPr}), 31.8 ($C_{\gamma}H_{Val}$), 28.9 (C(CH_3)$_3$), 26.6 (CH_3), 26.0 (CH_3), 25.9 ($C_{\delta}H_{Leu}$), 23.7 (CH_{iPr}), 23.7 (CH_{iPr}), 23.6 ($C_{\gamma}H_{3Leu}$), 22.6 ($C_{\gamma}H_{3Leu}$), 20.3 ($C_{\delta}H_{3Val}$), 18.8 ($C_{\delta}H_{3Ala}$), 18.6 ($C_{\delta}H_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3300, 2970, 1656, 1527; **Mp**: >200 °C; **HRMS** (ESI^+): *m/z* calcd for $C_{30}H_{62}N_9O_6$ $[M+H]^+$ 644.4823, found 644.4826.

BocEDA-Val^{u}-Ala^{u}-Leu^{u}-NH(CO)NH*i*Pr U8

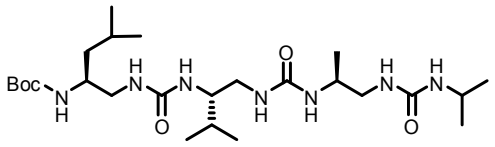


$C_{28}H_{57}N_9O_6$
M = 615.81 g.mol^{-1}

U8 was prepared from **U6** (100mg, 0.16 mmol), **M3** (47 mg, 0.16 mmol) and DIPEA (79 µL, 0.46 mmol) as described in the general procedure B2. The pure oligomer **U8** (50 mg, 52.4% in two steps)

was isolated as a white solid. **^{1}H NMR** (400 MHz, CD_3OH) δ = 6.78-6.66 (1H, m, N*H*), 6.34-6.20 (2H, m, N*H*), 6.17-6.04 (2H, m, N*H*), 5.97 (1H, d, *J* = 9.3, N*H*), 5.91-5.78 (3H, m, N*H*), 4.06-3.94 (1H, m, NCH_{Ala}), 3.93-3.85 (1H, m, NCH_{Leu}), 3.84-3.73 (1H, m, NCH_{iPr}), 3.66-3.42 (4H, m, NCH_{Val}, NCH_AH$_{BVal}$, NCH_AH$_{Bleu}$ and NCH_AH$_{BAla}$), 3.41-3.26 (2H, m, 2 x NCH_AH$_{BEDA}$), 3.07-2.89 (2H, m, 2 x NCH_AH$_{BEDA}$), 2.75-2.37 (3H, m, NCH$_A$$H_{BLeu}$, NCH$_A$$H_{BVal}$ and NCH$_A$$H_{BAla}$), 1.75-1.57 (2H, m, C$H_{Leu}$ and CH_{Val}), 1.45 (9H, s, C(CH_3)$_3$), 1.33-1.16 (2H, m, CH_{2Leu}), 1.12 (3H, d, *J* = 6.5, CH_{3iPr}), 1.11 (3H, d, *J* = 6.5, CH_{3iPr}), 1.04 (3H, d, *J* = 6.7, CH_{3Ala}), 0.97-0.85 (12H, m, 2 x CH_{3Leu} and 2 x CH_{3Val}). **^{13}C NMR** (100 MHz, CD_3OH) δ = 161.5 (*C*=O), 161.4 (*C*=O), 160.6 (*C*=O), 160.6 (*C*=O), 159.0 (*C*=O), 80.2 (*C*(CH$_3$)), 56.5 (NC$_\beta$H$_{Val}$), 49.4 (NC$_\beta$H$_{Leu}$), 48.0 (NC$_\alpha$H$_{2Ala}$), 46.4 (NC$_\beta$H$_{Ala}$), 46.1 (NC$_\alpha$H$_{2Leu}$), 44.5 (NC$_\alpha$H$_{2Val}$), 43.8 (C$_\alpha$H$_{2Leu}$), 42.8 (NCH$_{iPr}$), 41.6 (NCH$_2$), 41.5 (NCH$_2$), 31.8 (C$_\gamma$H$_{Val}$), 28.7 (C(CH$_3$)$_3$), 25.8 (C$_\delta$H$_{Leu}$), 23.7 (CH$_{3iPr}$), 23.6 (CH$_{3iPr}$), 23.5 (C$_\varepsilon$H$_{3Leu}$), 22.5 (C$_\varepsilon$H$_{3Leu}$), 20.2 (C$_\delta$H$_{3Val}$), 18.7 (C$_\delta$H$_{3Ala}$), 18.6 (C$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3310, 2936, 1651, 1538; **Mp**: >200 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{28}H_{57}N_9O_6Na$ [M+Na]$^+$ 638.4330, found 638.4324.

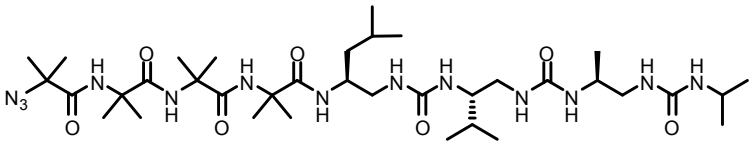
BocLeu^u-Val^u-Ala^u-NH(CO)NH*i*Pr U9



$C_{25}H_{51}N_7O_5$
M = 529.72 g.mol^{-1}

U9 was prepared from **U4** (583 mg, 0.99 mmol), **Ca** (355 mg, 0.99 mmol) and DIPEA (506 µL, 2.98 mmol) as described in the general procedure B2. The pure oligomer **U9** (450 mg, 85.8% in two steps) was isolated as a white solid. **^{1}H NMR** (400 MHz, CD_3OH) δ = 6.59 (1H, d, *J* = 9.6, N*H*), 6.23-6.14 (1H, m, N*H*), 6.12-6.02 (1H, m, N*H*), 6.02-5.87 (2H, m, N*H*), 5.83 (2H, d, *J* = 9.1, N*H*), 3.95-3.76 (3H, m, NCH_{Ala}, NCH_{Leu} and NCH_{iPr}), 3.62-3.55 (2H, m, NCH_{Val} and NCH_AH$_{BVal}$), 3.55-3.45 (1H, m, NCH_AH$_{BLeu}$), 3.45-3.36 (1H, m, NCH_AH$_{BAla}$), 2.80-2.68 (1H, m, NCH$_A$$H_{BLeu}$), 2.67-2.58 (1H, m, NCH$_A$$H_{BAla}$), 2.57-2.44 (1H, m, NCH$_A$$H_{BVal}$), 1.79-1.60 (2H, m, C$H_{Leu}$ and CH_{Val}), 1.48 (9H, s, C(CH_3)$_3$), 1.34-1.18 (2H, m, CH_{2Leu}), 1.14 (6H, d, *J* = 6.5, 2 x CH_{3iPr}), 1.07 (3H, d, *J* = 6.7, CH_{3Ala}), 1.01-0.87 (12H, m, 2 x CH_{3Val} and 2 x CH_{3Leu}). **^{13}C NMR** (100 MHz, CD_3OH) δ = 161.4 (*C*=O), 161.1 (*C*=O), 160.6 (*C*=O), 159.1 (*C*=O), 80.1 (*C*(CH$_3$)$_3$), 56.4 (NC$_\beta$H$_{Val}$), 50.0 (NC$_\beta$H$_{Leu}$), 47.1 (NC$_\beta$H$_{Ala}$), 46.7 (NC$_\alpha$H$_{2Ala}$), 46.5 (NC$_\alpha$H$_{2Leu}$), 44.5 (NC$_\alpha$H$_{2Val}$), 42.8 (NCH$_{iPr}$), 42.4 (C$_\alpha$H$_{2Leu}$), 31.9 (C$_\gamma$H$_{Val}$), 28.9 (C(CH$_3$)$_3$), 26.2 (C$_\delta$H$_{Leu}$), 23.8 (C$_\varepsilon$H$_{3Leu}$), 23.7 (2 x CH$_{iPr}$), 22.5 (C$_\varepsilon$H$_{3Leu}$), 20.1 (C$_\delta$H$_{3Val}$), 19.4 (C$_\delta$H$_{3Ala}$), 18.5 (C$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3339, 2963, 2931, 2871, 1636, 1567; **$[\alpha]_D^{20}$** = +58.8 (c = 1.00; MeOH); **Mp**: 194-196°C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{25}H_{52}N_7O_5$ [M+H]$^+$ 530.4030, found 530.4006.

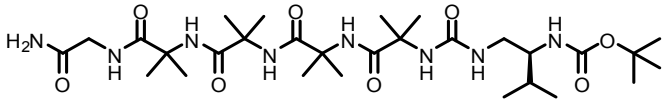
N_3-Aib$_4$-Leu^u-Val^u-Ala^u-NH(CO)NH*i*Pr U10



$C_{36}H_{69}N_{13}O_7$
M = 796.02 g.mol^{-1}

Boc-protected oligourea **U10** (87 mg, 0.16 mmol) was dissolved in TFA (870 µl) and stirred for 45 min. The reaction mixture was then concentrated under reduced. Triethylamine (36 µL, 0.26 mmol) and an azlactone (85 mg, 0.23 mmol)[1] were added to the crude product in acetonitrile (0.58 mL). The reaction stirred at reflux for 3 d. The solvents were removed under reduced pressure and purification by column chromatography (SiO_2; CH_2Cl_2:MeOH; 99:1→90:10) gave the title compound as a white solid (34 mg, 36.8%). **^{1}H NMR** (400 MHz, CD_3OH) δ = 7.73 (1H, s, N*H*), 7.27 (1H, d, *J* = 9.8, N*H*), 6.10 (1H, d, *J* = 9.3, N*H*), 5.97 (1H, d, *J* = 9.8, N*H*), 5.79-5.68 (1H, m, N*H*), 5.60 (1H, d, *J* = 10.0, N*H*), 4.28-4.10 (1H, m, NCH_{Leu}), 3.99-3.87 (1H, m, NCH_{Ala}), 3.86-3.77 (1H, m, NCH_{iPr}), 3.74-3.48 (4H, m, NCH_{Val}, NCH_AH$_{BVal}$, NCH_AH$_{BLeu}$ and NCH_AH$_{BAla}$), 2.77-2.60 (1H, m, NCH$_A$$H_{BAla}$ and NCH$_A$$H_{BLeu}$), 2.46 (1H, dd, *J* = 13.8 and 11.8, NCH$_A$$H_{BVal}$), 1.73-1.58 (2H, m, C$H_{Leu}$ and CH_{Val}), 1.48-1.37 (1H, m, CH$_A$$H_{BLeu}$), 1.56 (3H, s, C$H_3$), 1.53 (9H, s, 3 x C$H_3$), 1.47 (3H, s, C$H_3$), 1.45 (3H, s, C$H_3$), 1.43 (3H, s, C$H_3$), 1.39 (3H, s, C$H_3$), 1.27-1.17 (1H, m, CH$_A$$H_{BLeu}$), 1.14 (6H, d, *J* = 6.5, 2 x CH_{3iPr}), 1.06 (3H, d, *J* = 6.7, CH_{3Ala}), 0.99-0.83 (12H, m, 2 x CH_{3Val} and 2 x CH_{3Leu}). **^{13}C NMR** (100 MHz, CD_3OH) δ = 178.2 (*C*=O), 176.7 (*C*=O), 175.0 (*C*=O), 161.7 (*C*=O), 161.3 (*C*=O), 161.3 (*C*=O), 160.7 (*C*=O), 64.8 (*C*N$_3$), 58.4 (*C*), 57.9 (*C*), 57.8 (*C*), 57.8 (*C*), 56.4 (NC_βH$_{Val}$), 48.7 (NC_βH$_{Leu}$), 47.0 (NC_βH$_{Ala}$), 46.7 (NC_αH$_{2Ala}$), 46.0 (NC_αH$_{2Leu}$), 44.4 (NC_αH$_{2Val}$), 42.8 (NCH$_{iPr}$), 42.3 (C_αH$_{2Leu}$), 32.2 (C_γH$_{Val}$), 28.1 (*C*H$_3$), 27.4 (*C*H$_3$), 26.3 (*C*H$_3$), 25.9 (*C*H$_3$), 24.6 (C_δH$_{Leu}$), 24.5 (*C*H$_3$), 23.8 (*C*H$_{iPr}$), 23.8 (*C*H$_{iPr}$), 23.7 (C_ϵH$_{3Leu}$), 23.6 (*C*H$_3$), 23.4 (*C*H$_3$), 23.1 (*C*H$_3$), 22.4 (C_ϵH$_{3Leu}$), 20.1 (C_δH$_{3Val}$), 19.5 (C_δH$_{3Ala}$), 18.5 (C_δH$_{3Val}$).

GlyNH$_2$-Aib$_4$-(Val^u)$_{rev}$–NHBoc 2a

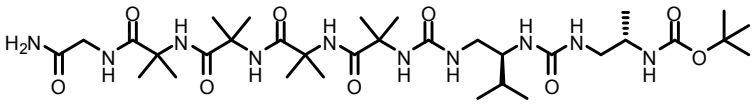


$C_{29}H_{54}N_8O_8$
M = 642.78 g.mol^{-1}

2a was prepared from GlyNH$_2$-Aib$_4$-NH$_2$ (547 mg, 1.32 mmol), **Cc** (453 mg, 1.32 mmol) and DIPEA (673 µL, 3.96 mmol) as described in the general procedure B. The pure oligomer **2a** (500 mg, 58.9%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.60 (1H, s, N*H*), 8.14 (1H, t, *J* = 6.3, NH_{Gly}), 8.07 (1H, s, N*H*), 7.95 (1H, s, N*H*), 7.43 (1H, s, NH_{Val}), 7.22 (1H, s, N*H*), 6.38 (1H, s, N*H*), 6.32

(1H, d, *J* = 9.5, N*H*$_{Val}$), 5.99 (1H, t, *J* = 7.0, N*H*$_{Val}$), 3.94 (1H, dd, *J* = 17.5 and 7.0, NC*H*$_A$CH$_{BGly}$), 3.72 (1H, dd, *J* = 17.5 and 5.7, NC*H*$_A$CH$_{BGly}$), 3.57-3.36 (2H, m, NC*H*$_A$H$_{BVal}$ and NC*H*$_{Val}$), 2.82-2.75 (1H, m, NCH$_A$*H*$_{BVal}$), 1.69 (1H, oct, *J* = 6.9, C*H*$_{Val}$), 1.50 (3H, s, C*H*$_3$), 1.50 (3H, s, C*H*$_3$), 1.47-1.40 (24H, m, C(C*H*$_3$)$_3$ and 5 x C*H*$_3$), 1.34 (3H, s, C*H*$_3$), 0.94 (3H, d, *J* = 6.9, C*H*$_{3Val}$), 0.91 (3H, d, *J* = 6.9, C*H*$_{3Val}$). **^{13}C NMR** (125 MHz, CD_3OH) *δ* = 178.3 (*C*=O), 178.1 (*C*=O), 178.1 (*C*=O), 178.0 (*C*=O), 175.4 (*C*=O), 160.2 (*C*=O), 158.5 (*C*=O), 79.7 (*C*-O), 58.1 (*C*), 58.0 (*C*), 57.8 (*C*), 57.6 (*C*), 57.0 (N*C*$_\beta$H$_{Val}$), 43.7 (N*C*H$_{2Gly}$), 43.4 (N*C*$_\alpha$H$_{2Val}$), 31.5 (N*C*$_\gamma$H$_{Val}$), 28.8 (C(*C*H$_3$)$_3$), 26.7 (*C*H$_3$), 26.5 (*C*H$_3$), 26.5 (*C*H$_3$), 24.8 (*C*H$_3$), 24.6 (*C*H$_3$), 24.3 (*C*H$_3$), 19.9 (*C*$_\delta$H$_{3Val}$), 18.8 (*C*$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3306, 2981, 2935, 1651, 1543; **$[\alpha]_D^{20}$** = + 24.8 (c = 1.00; MeOH); **Mp**: 88-90 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{29}H_{55}N_8O_8$ $[M+H]^+$ 643.4137, found 643.4118.

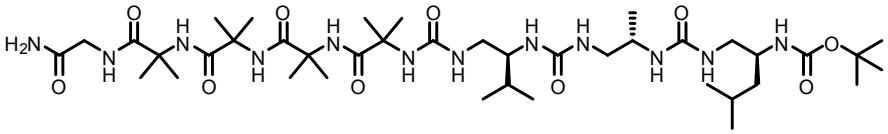
GlyNH$_2$-Aib$_4$-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-NHBoc 2b



$C_{33}H_{62}N_{10}O_9$
M = 742.90 g.mol^{-1}

2b was prepared from **2a** (400 mg, 0.62 mmol), **Cb** (196 mg, 0.62 mmol) and DIPEA (318 µL, 1.87 mmol) as described in the general procedure B. The pure oligomer **2b** (100 mg, 21.6%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) *δ* = 8.57 (1H, s, N*H*), 8.48 (1H, s, N*H*), 8.15 (1H, t, *J* = 6.2, N*H*$_{Gly}$), 7.96 (1H, s, N*H*), 6.60 (1H, s, N*H*$_{Ala}$), 6.59 (1H, s, N*H*), 6.04 (1H, t, *J* = 5.9, N*H*$_{Ala}$), 5.95 (1H, d, *J* = 5.9, N*H*$_{Val}$), 5.78 (1H, d, *J* = 9.1, N*H*$_{Val}$), 3.97 (1H, dd, *J* = 17.6 and 7.1, NC*H*$_A$H$_{BGly}$), 3.94-3.83 (1H, m, NC*H*$_{Val}$), 3.69 (2H, dd, *J* = 17.6 and 5.7, NCH$_A$*H*$_{BGly}$), 3.66-3.53 (2H, m, NC*H*$_{Ala}$ and NC*H*$_A$H$_{BVal}$), 2.77-2.65 (1H, m, NCH$_A$*H*$_{BVal}$), 2.59-2.44 (1H, m, NC*H*$_{2Ala}$), 1.65 (1H, oct, *J* = 6.7, C*H*$_{Val}$), 1.51 (3H, s, C*H*$_3$), 1.50 (3H, s, C*H*$_3$), 1.47-1.40 (24H, m, C(C*H*$_3$)$_3$ and 5 x C*H*$_3$), 1.34 (3H, s, C*H*$_3$), 1.08 (3H, d, *J* = 6.9, C*H*$_{3Ala}$), 0.94 (3H, d, *J* = 6.9, C*H*$_{3Val}$), 0.91 (3H, d, *J* = 6.9, C*H*$_{3Val}$). **^{13}C NMR** (125 MHz, CD_3OH) *δ* = 178.5 (*C*=O), 178.2 (*C*=O), 178.1 (*C*=O), 178.1 (*C*=O), 175.4 (*C*=O), 160.8 (*C*=O), 160.4 (*C*=O), 158.7 (*C*=O), 80.1 (*C*-O), 58.1 (*C*), 57.9 (*C*), 57.8 (*C*), 56.9 (*C*), 56.5 (N*C*$_\beta$H$_{Val}$), 47.6 (N*C*$_\alpha$H$_{2Ala}$), 47.3 (N*C*$_\beta$H$_{Ala}$), 44.7 (N*C*H$_{2Gly}$), 43.8 (N*C*$_\alpha$H$_{2Val}$), 31.6 (N*C*$_\gamma$H$_{Val}$), 28.7 (C(*C*H$_3$)$_3$), 27.1 (*C*H$_3$), 27.0 (*C*H$_3$), 26.9 (*C*H$_3$), 26.7 (*C*H$_3$), 24.7 (*C*H$_3$), 24.3 (*C*H$_3$), 23.9 (*C*H$_3$), 23.8 (*C*H$_3$), 20.1 (*C*$_\delta$H$_{3Val}$), 18.8 (*C*$_\delta$H$_{3Val}$), 18.4 (*C*$_\gamma$H$_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3282, 2981, 2935, 1649, 1544; **$[\alpha]_D^{20}$** = +8.0 (c = 1.00; MeOH); **Mp**: 103-105 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{33}H_{62}N_{10}O_9Na[M+H]^+$ 765.4599, found 765.4586.

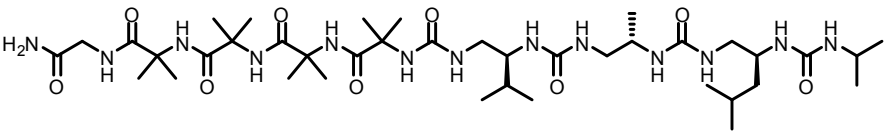
GlyNH$_2$-Aib$_4$-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-(Leu^u)$_{rev}$–NHBoc 2c



$C_{40}H_{76}N_{12}O_{10}$
M = 885.10 g.mol^{-1}

2c was prepared from **2b** (90 mg, 0.12 mmol), **Ca** (43 mg, 0.12 mmol) and DIPEA (21 µL, 0.36 mmol) as described in the general procedure B. The pure oligomer **2c** (80 mg, 74.7%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.57 (1H, s, N*H*), 8.46 (1H, s, N*H*), 8.16 (1H, t, *J* = 6.7, NH_{Gly}), 7.94 (1H, s, N*H*), 7.43 (1H, s, N*H*), 7.22 (1H, s, N*H*), 6.88 (1H, s, N*H*), 6.60 (1H, d, *J* = 10.0, NH_{Leu}), 6.44 (1H, brd, *J* = 9.5, NH_{Val}), 6.08 (1H, t, *J* = 6.7, NH_{Leu}), 5.88 (1H, dd, *J* = 9.4 and 3.4, NH_{Ala}), 5.84 (1H, d, *J* = 9.9, NH_{Ala}), 5.76 (1H, d, *J* = 10.4, NH_{Val}), 4.13-4.02 (1H, m, NCH_{Ala}), 3.98 (1H, dd, *J* = 17.5 and 7.2, NCH_AH$_{BGly}$), 3.89-3.76 (1H, m, NCH_{Leu}), 3.68 (1H, dd, *J* = 17.5 and 5.5, NCH$_A$$H_{BGly}$), 3.74-3.54 (3H, m, NC$H_AH_{BAla}$, NC$H_{Val}$ and NCH_AH$_{BVal}$), 3.44 (1H, ddd, *J* = 14.1, 7.3 and 3.5, NCH_AH$_{BLeu}$), 2.56-2.41 (2H, m, NCH$_A$$H_{BLeu}$ and NCH$_A$$H_{BVal}$), 2.39-2.25 (1H, m, NCH$_A$$H_{BAla}$), 1.76-1.55 (2H, m, C$H_{Val}$ and CH_{Leu}), 1.51 (3H, s, CH_3), 1.50 (3H, s, CH_3), 1.48-1.42 (24H, m, 5 x CH_3 and C(CH_3)$_3$), 1.34 (3H, s, CH_3), 1.31-1.14 (2H, m, CH_{2Leu}), 1.06 (3H, d, *J* = 7.0, CH_{3Ala}), 0.94 (3H, d, *J* = 6.7, CH_{3Val}), 0.93 (3H, d, *J* = 6.9, CH_{3Val}), 0.90 (3H, d, *J* = 6.6, CH_{3Leu}), 0.89 (3H, d, *J* = 6.8, CH_{3Leu}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.6 (*C*=O), 178.3 (*C*=O), 178.2 (*C*=O), 178.1 (*C*=O), 175.4 (*C*=O), 161.4 (*C*=O), 160.9 (*C*=O), 160.7 (*C*=O), 159.2 (*C*=O), 80.1 (*C*-O), 58.1 (*C*), 57.9 (*C*), 57.9 (*C*), 56.9 (*C*), 55.8 (NC$_\beta$H$_{Val}$), 50.0 (NC$_\beta$H$_{Leu}$), 48.5 (NC□H$_{2Ala}$), 46.8 (NC□H$_{2Leu}$), 46.6 (NC$_\beta$H$_{Ala}$), 44.5 (NC□H$_{2Val}$), 43.8 (NCH$_{2Gly}$), 42.3 (C□H$_{2Leu}$), 31.9 (C$_\gamma$H$_{Val}$), 28.8 (C(*C*H$_3$)$_3$), 27.4 (*C*H$_3$), 27.2 (*C*H$_3$), 27.1 (*C*H$_3$), 26.8 (*C*H$_3$), 26.2 (C$_\delta$H$_{Leu}$), 24.5 (*C*H$_3$), 24.3 (*C*H$_3$), 23.8 (*C*H$_3$), 23.7 (*C*H$_3$), 23.5 (C□H$_{3Leu}$), 22.6 (C□H$_{3Leu}$), 20.0 (C$_\delta$H$_{3Val}$), 18.6 (C$_\delta$H$_{3Val}$), 18.4 (C$_\gamma$H$_{3Ala}$ **IR** (film, cm^{-1}): ν_{max} = 3297, 2975, 1659, 1537; $[\alpha]_D^{20}$ = + 30.0 (c = 1.00; MeOH); **Mp**: 138-140 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{40}H_{77}O_{10}N_{12}$ $[M+H]^+$ 885.5880, found 885.5880.

GlyNH$_2$-Aib$_4$-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-(Leu^u)$_{rev}$-NH(CO)NH*i*Pr 2d

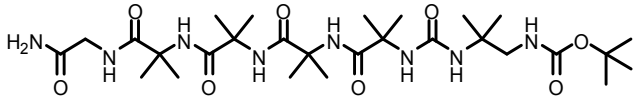


$C_{39}H_{75}N_{13}O_9$
M = 870.09 g.mol^{-1}

2d was prepared from **2c** (60 mg, 0.07 mmol), isopropyl isocyanate (13.3 µL, 0.14 mmol) and DIPEA (28 µL, 0.20 mmol) as described in the general procedure C. The pure oligomer **2d** (56 mg, 94.9%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.58 (1H, s, N*H*), 8.44 (1H, s, N*H*), 8.18

(1H, t, *J* = , N*H*$_{Gly}$), 7.96 (1H, s, N*H*), 7.47 (1H, s, N*H*), 7.26 (1H, s, N*H*), 6.98 (1H, s, N*H*), 6.39 (1H, dd, *J* =, N*H*$_{Val}$), 6.28 (1H, dd, *J* =, N*H*$_{Ala}$), 6.12 (1H, d, *J* =, N*H*$_{Val}$), 6.06 (1H, t, *J* = 6.7, N*H*$_{Leu}$), 5.95 (1H, d, *J* =, N*H*$_{Ala}$), 5.73 (1H, d, *J* =, N*H*$_{iPr}$), 5.57 (1H, d, *J* =, N*H*$_{Leu}$), 4.09-3.90 (2H, m, NC*H*$_{Ala}$ and NC*H*$_{Leu}$), 3.96 (1H, dd, *J* = and, NC*H*$_A$H$_{BGly}$), 3.80 (1H, oct, *J* =, N*H*$_{iPr}$), 3.70 (1H, dd, *J* = and, NCH$_A$*H*$_{BGly}$), 3.67-3.58 (2H, m, NC*H*$_A$H$_{BVal}$ and NC*H*$_{Val}$), 3.57-3.47 (1H, m, NC*H*$_A$H$_{BAla}$), 3.44-3.35 (1H, m, NC*H*$_A$H$_{BLeu}$), 2.64-2.48 (2H, m, NCH$_A$*H*$_{BLeu}$ and NCH$_A$*H*$_{BVal}$), 2.47-2.38 (1H, m, NCH$_A$*H*$_{BAla}$), 1.76-1.55 (2H, m, C*H*$_{Val}$ and C*H*$_{Leu}$), 1.51 (3H, s, C*H*$_3$), 1.50 (3H, s, C*H*$_3$), 1.48-1.42 (24H, m, 5 x C*H*$_3$ and C(C*H*$_3$)$_3$), 1.34 (3H, s, C*H*$_3$), 1.26-1.18 (2H, m, C*H*$_{2Leu}$), 1.13 (6H, d, *J* =, C*H*$_3$), 1.06 (3H, d, *J* =, C*H*$_{3Ala}$), 0.93 (6H, d, *J* =, C*H*$_{3Val}$), 0.89 (6H, d, *J* = 6.9, C*H*$_{3Leu}$). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.6 (*C*=O), 178.4 (*C*=O), 178.2 (*C*=O), 175.5 (*C*=O), 163.1 (*C*=O), 162.8 (*C*=O), 161.8 (*C*=O), 161.0 (*C*=O), 160.7 (*C*=O), 160.5 (*C*=O), 58.1 (*C*), 57.9 (*C*), 57.8 (*C*), 56.9 (*C*), 56.0 (N*C*$_\beta$H$_{Val}$), 48.7 (N*C*$_\beta$H$_{Leu}$), 48.2 (N*C*$_\alpha$H$_{2Ala}$), 47.2 (N*C*$_\alpha$H$_{2Leu}$), 46.8 (N*C*$_\beta$H$_{Ala}$), 44.3 (N*C*$_\alpha$H$_{2Val}$), 43.7 (NCH$_{2Gly}$), 43.0 (NCH$_{iPr}$), 43.0 (*C*$_\alpha$H$_{2Leu}$), 31.9 (*C*$_\gamma$H$_{Val}$), 27.2 (*C*H$_3$), 27.0 (*C*H$_3$), 26.9 (*C*H$_3$), 26.7 (*C*H$_3$), 26.2 (*C*$_\delta$H$_{Leu}$), 24.6 (*C*H$_3$), 24.4 (*C*H$_3$), 23.9 (*C*H$_3$), 23.8 (*C*H$_3$), 23.6 (*C*$_\epsilon$H$_{3Leu}$), 23.5 (*C*H$_{3iPr}$), 23.4 (*C*H$_{3iPr}$), 22.5 (*C*$_\epsilon$H$_{3Leu}$), 20.0 (*C*$_\delta$H$_{3Val}$), 18.8 (*C*$_\delta$H$_{3Val}$), 18.5 (*C*$_\gamma$H$_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3325, 2965, 1648, 1555; **$[\alpha]_D^{20}$** = +28 (c = 1.00; MeOH); **Mp**: > 200 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{39}H_{76}O_9N_{13}$ $[M+H]^+$ 870.5883, found 870.5873.

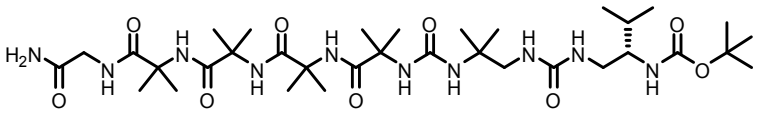
GlyNH$_2$-Aib$_4$-Aib^u-NHBoc 3



$C_{28}H_{52}N_8O_8$
M = 628.76 g.mol^{-1}

3 was prepared from GlyNH$_2$AiB$_4$NHBoc (650 mg, 1.57 mmol), **M2** (517 mg, 1.57 mmol) and DIPEA (800 µL, 4.70 mmol) as described in the general procedure B. The pure oligomer **3** (200 mg, 20.3%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.81 (1H, s, N*H*), 8.20 (1H, s, N*H*), 8.15 (1H, t, *J* = 5.8, N*H*$_{Gly}$), 7.98 (1H, s, N*H*), 7.44 (1H, s, N*H*), 7.27 (1H, s, N*H*), 6.65 (1H, t, *J* = 5.9, N*H*$_{Aibu}$), 6.06 (1H, s, N*H*), 5.75 (1H, s, N*H*), 3.83 (2H, brd, *J* = 17.5 and 7.0, NC*H*$_{2Gly}$), 3.25 (2H, brd, *J* = 4.5, NC*H*$_{2Aibu}$), 1.50 (6H, s, C*H*$_3$), 1.45 (15H, m, C(C*H*$_3$)$_3$ and 2 x C*H*$_3$), 1.43 (6H, s, C*H*$_3$), 1.35 (6H, s, C*H*$_3$), 1.25 (6H, s, C*H*$_3$). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.4 (*C*=O), 178.2 (2 x *C*=O), 178.1 (*C*=O), 175.4 (*C*=O), 159.2 (*C*=O), 158.3 (*C*=O), 79.7 (*C*-O), 58.1 (*C*), 58.1 (*C*), 57.8 (*C*), 56.8 (*C*), 54.6 (*C*), 48.8 (NCH$_{2Aibu}$), 43.7 (NCH$_{2Gly}$), 28.7 (C(*C*H$_3$)$_3$), 26.0 (2 x *C*H$_3$), 25.8 (2 x *C*H$_3$), 25.5 (6 x *C*H$_3$). **IR** (film, cm^{-1}): ν_{max} = 3343, 2982, 29341, 1650, 1542; **Mp**: 103-105 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{28}H_{53}O_8N_8$ $[M+H]^+$ 629.3981, found 629.3974.

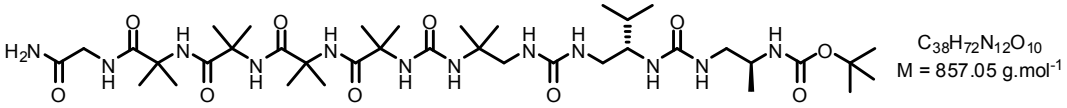
GlyNH_2-Aib$_4$-Aib^u-(Val^u)$_{rev}$–NHBoc 3a



$C_{34}H_{64}N_{10}O_9$
M = 756.93 g.mol^{-1}

3a was prepared from **3** (200 mg, 0.32 mmol), **Cc** (109 mg, 0.32 mmol) and DIPEA (162 µL, 0.95 mmol) as described in the general procedure B. The pure oligomer **3a** (150 mg, 62.3%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.74 (1H, s, N*H*), 8.46 (1H, s, N*H*), 8.15 (1H, t, *J* = 6.1, NH_{Gly}), 7.91 (1H, s, N*H*), 7.45 (1H, s, N*H*), 7.23 (1H, s, N*H*), 6.45 (1H, d, *J* = 9.8, NH_{Val}), 6.38 (1H, s, N*H*), 6.13 (1H, t, *J* = 6.0, NH_{Aibu}), 6.00 (1H, t, *J* = 5.9, NH_{Val}), 5.58 (1H, s, N*H*), 3.91 (1H, dd, *J* = 17.4 and 6.6, NCH_ACH$_{BGly}$), 3.75 (1H, dd, *J* = 17.3 and 5.7, NCH$_A$CH_{BGly}), 3.71-3.59 (1H, m, NCH_AH$_{BAibu}$), 3.58-3.50 (1H, m, NCH_{Val}), 3.49-3.39 (1H, m, NCH_AH$_{BVal}$), 2.95-2.88 (1H, m, NCH$_A$$H_{BAibu}$), 2.79 (1H, ddd, *J* = 6.9, NCH$_A$$H_{BVal}$), 1.68 (1H, oct, *J* = 6.8, CH_{Val}), 1.50 (6H, s, 2 x CH_3), 1.46 (6H, s, 2 x CH_3), 1.45 (9H, s, C(CH_3)$_3$), 1.42 (6H, s, 2 x CH_3), 1.40 (3H, s, CH_3), 1.35 (6H, s, 2 x CH_3), 1.15 (3H, s, CH_3), 0.97 (3H, d, *J* = 6.7, CH_{3Val}), 0.92 (3H, d, *J* = 6.8, CH_{3Val}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.6 (*C*=O), 178.5 (*C*=O), 178.2 (*C*=O), 178.1 (*C*=O), 175.4 (*C*=O), 160.7 (*C*=O), 159.3 (*C*=O), 159.1 (*C*=O), 79.9 (*C*-O), 58.1 (*C*), 58.0 (*C*), 57.8 (*C*), 57.5 (NC$_\beta$H$_{Val}$), 56.8 (*C*), 55.0 (*C*), 48.5 (NCH$_{2Aibu}$), 43.8 (NCH$_{2Gly}$), 43.4 (NC□H$_{2Val}$), 32.0 (NC$_\gamma$H$_{Val}$), 28.8 (C(CH$_3$)$_3$), 26.8 (CH$_3$), 26.3 (3 x CH$_3$), 26.2 (CH$_3$), 25.5 (CH$_3$), 25.0 (CH$_3$), 24.9 (CH$_3$), 24.6 (2 x CH$_3$), 19.9 (C$_\delta$H$_{3Val}$), 18.8 (C$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3295, 2976, 2941, 1654, 1555; **$[\alpha]_D^{20}$** = + 29.0 (c = 1.00; MeOH); **Mp**: 115-117 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{34}H_{64}O_9N_{10}Na$ $[M+Na]^+$ 779.4755, found 779.4684.

GlyNH_2-Aib$_4$-Aib^u-(Val^u)$_{rev}$-(Ala^u)$_{rev}$–NHBoc 3b

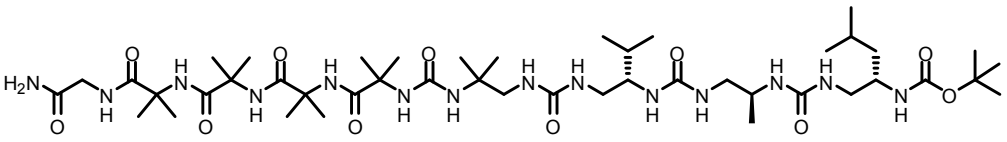


$C_{38}H_{72}N_{12}O_{10}$
M = 857.05 g.mol^{-1}

3b was prepared from **3a** (115 mg, 0.15 mmol), **Cb** (48 mg, 0.15 mmol) and DIPEA (78 µL, 0.46 mmol) as described in the general procedure B. The pure oligomer **3b** (58 mg, 44.5%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.74 (1H, s, N*H*), 8.45 (1H, s, N*H*), 8.16 (1H, t, *J* = 6.3, NH_{Gly}), 7.98 (1H, s, N*H*), 7.47 (1H, s, N*H*), 7.25 (1H, s, N*H*), 6.56 (1H, d, *J* = 8.8, NH_{Ala}), 6.47 (1H, s, N*H*), 6.15-6.05 (2H, m, NH_{Ala} and NH_{Aibu}), 6.04-5.97 (1H, m, NH_{Val}), 5.87 (1H, d, *J* = 9.4, NH_{Val}), 5.78 (1H, s, N*H*), 3.92 (1H, dd, *J* = 17.5 and 6.8, NCH_ACH$_{BGly}$), 3.75 (1H, dd, *J* = 17.2 and 5.7, NCH$_A$CH_{BGly}), 3.83-3.64 (3H, m, NCH_AH$_{BAibu}$, NCH_{Ala} and NCH_{Val}), 3.61-3.48 (1H, m, NCH_AH$_{BVal}$), 3.29-3.22 (1H, m, NCH_AH$_{BAla}$),

2.95-2.78 (2H, m, NCH$_A$*H$_{BAla}$* and NCH$_A$*H$_{BAibu}$*), 2.69-2.55 (1H, m, NCH$_A$*H$_{BVal}$*), 1.67 (1H, oct, *J* = 6.9, C*H$_{Val}$*), 1.50 (6H, s, 2 x C*H$_3$*), 1.46 (6H, s, 2 x C*H$_3$*), 1.44 (9H, s, C(C*H$_3$*)$_3$), 1.43 (6H, s, 2 x C*H$_3$*), 1.40 (3H, s, C*H$_3$*), 1.35 (6H, s, 2 x C*H$_3$*), 1.17 (3H, s, C*H$_3$*), 1.07 (3H, d, *J* = 6.8, C*H$_{3Ala}$*), 0.97 (3H, d, *J* = 6.9, C*H$_{3Val}$*), 0.93 (3H, d, *J* = 6.9, C*H$_{3Val}$*). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.6 (2 x *C*=O), 178.2 (*C*=O), 178.2 (*C*=O), 175.5 (*C*=O), 161.5 (*C*=O), 160.9 (*C*=O), 159.4 (*C*=O), 158.4 (*C*=O), 80.0 (*C*-O), 58.1 (*C*), 58.0 (*C*), 57.8 (*C*), 56.8 (N*C$_\beta$*H$_{Val}$), 56.4 (*C*), 54.8 (*C*), 48.5 (N*C*H$_{2Aibu}$), 48.0 (N*C*□H$_{2Ala}$), 46.8 (N*C$_\beta$*H$_{Ala}$), 44.3 (N*C*□H$_{2Val}$), 43.8 (N*C*H$_{2Gly}$), 31.9 (N*C$_\gamma$*H$_{Val}$), 28.7 (C(*C*H$_3$)$_3$), 26.9 (*C*H$_3$), 26.4 (2 x *C*H$_3$), 26.3 (*C*H$_3$), 26.2 (*C*H$_3$), 25.6 (*C*H$_3$), 24.9 (2 x *C*H$_3$), 24.5 (2 x *C*H$_3$), 20.0 (*C$_\delta$*H$_{3Val}$), 18.7 (*C$_\delta$*H$_{3Val}$), 18.5 (*C$_\gamma$*H$_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3325, 2963, 1648, 1572; **$[\alpha]_D^{20}$** = +25.0 (c = 1.00; MeOH); **Mp**: 130-132 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{38}H_{73}O_{10}N_{12}$ $[M+H]^+$ 857.5567, found 857.5566.

GlyNH$_2$-Aib$_4$-Aib^u-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-(Leu^u)$_{rev}$-NHBoc 3c

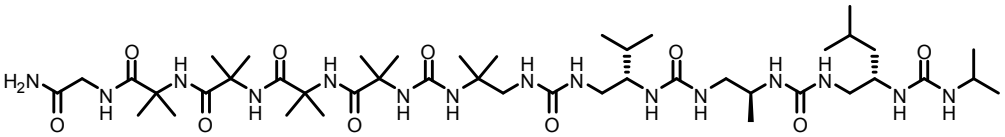


$C_{45}H_{86}N_{14}O_{11}$
M = 999.25 g.mol^{-1}

3c was prepared from **3b** (50 mg, 0.06 mmol), **Ca** (21 mg, 0.06 mmol) and DIPEA (32 µL, 0.18 mmol) as described in the general procedure B. The pure oligomer **3c** (44 mg, 76%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.77 (1H, s, N*H*), 8.43 (1H, s, N*H*), 8.17 (1H, t, *J* = 6.3, N*H$_{Gly}$*), 8.01 (1H, s, N*H*), 7.46 (1H, s, N*H*), 7.24 (1H, s, N*H*), 6.61 (1H, d, *J* = 10.0, N*H$_{Leu}$*), 6.54 (1H, s, N*H*), 6.44 (1H, d, *J* = 8.7, N*H$_{Val}$*), 6.37 (1H, dd, *J* = 8.7 and 3.9, N*H$_{Aibu}$*), 6.07 (1H, t, *J* = 6.4, N*H$_{Leu}$*), 5.93 (1H, s, N*H$_{Ala}$*), 5.91 (1H, s, N*H$_{Val}$*), 5.82 (1H, d, *J* = 9.8, N*H$_{Ala}$*), 5.75 (1H, s, N*H*), 4.09-4.00 (1H, m, NC*H$_{Ala}$*), 3.96 (1H, dd, *J* = 17.5 and 7.0, NC*H$_A$*CH$_{BGly}$), 3.92-3.82 (1H, m, NC*H$_{Leu}$*), 3.81-3.65 (3H, m, NC*H$_A$*H$_{BAibu}$, NC*H$_A$*H$_{BVal}$ and NC*H$_{Val}$*), 3.75 (1H, dd, *J* = 17.5 and 5.9, NCH$_A$C*H$_{B}$*$_{Gly}$), 3.64-3.54 (1H, m, NC*H$_A$*H$_{BAla}$), 3.42 (1H, ddd, *J* = 14.0, 7.1 and 3.6, NC*H$_A$*H$_{BLeu}$), 2.89 (1H, dd, *J* = 14.4 and 3.3, NCH$_A$*H$_{BAibu}$*), 2.63-2.55 (1H, m, NCH$_A$*H$_{BVal}$*), 2.53-2.44 (1H, m, NCH$_A$*H$_{BLeu}$*), 2.40-2.30 (1H, m, NCH$_A$*H$_{BAla}$*), 1.75-1.59 (2H, m, C*H$_{Leu}$* and C*H$_{Val}$*), 1.52 (6H, s, 2 x C*H$_3$*), 1.48 (15H, s, 2 x C*H$_3$* and C(C*H$_3$*)$_3$), 1.45 (6H, s, 2 x C*H$_3$*), 1.42 (3H, s, C*H$_3$*), 1.39 (3H, s, C*H$_3$*), 1.36 (3H, s, C*H$_3$*), 1.32-1.09 (2H, m, C*H$_{2Leu}$*), 1.21 (3H, s, C*H$_3$*), 1.05 (3H, d, *J* = 6.9, C*H$_{3Ala}$*), 0.97 (3H, d, *J* = 6.9, C*H$_{3Val}$*), 0.94 (3H, d, *J* = 7.1, C*H$_{3Leu}$*), 0.93 (3H, d, *J* = 7.3, C*H$_{3Val}$*), 0.90 (3H, d, *J* = 6.7, C*H$_{3Leu}$*). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.6 (2 x *C*=O), 178.2 (*C*=O), 178.1 (*C*=O), 175.4 (*C*=O), 161.8 (*C*=O), 161.1 (*C*=O), 160.6 (*C*=O), 159.4 (*C*=O), 159.2 (*C*=O), 80.1 (*C*-O), 58.1 (*C*), 58.0 (*C*), 57.7 (*C*), 56.8 (*C*), 55.9 (N*C$_\beta$*H$_{Val}$), 54.7 (*C*), 49.8 (N*C$_\beta$*H$_{Leu}$), 48.5 (N*C*H$_{2Aibu}$), 48.0 (N*C*□H$_{2Ala}$), 46.9 (N*C$_\alpha$*H$_{2Leu}$), 46.5 (N*C$_\beta$*H$_{Ala}$), 43.9 (N*C*□H$_{2Val}$), 43.8 (N*C*H$_{2Gly}$), 42.2 (*C*□H$_{2Leu}$), 32.4 (N*C$_\gamma$*H$_{Val}$), 28.8 (C(*C*H$_3$)$_3$), 27.0 (*C*H$_3$), 26.7 (2 x *C*H$_3$), 26.5 (*C$_\delta$*H$_{Leu}$), 26.2 (*C*H$_3$), 26.2 (*C*H$_3$), 25.7 (*C*H$_3$), 24.7 (2 x *C*H$_3$), 24.4 (*C*H$_3$), 24.3 (*C*H$_3$), 23.5

($C_{\delta}H_{3Leu}$), 22.5 ($C_{\delta}H_{3Leu}$), 19.8 ($C_{\delta}H_{3Val}$), 18.7 ($C_{\delta}H_{3Val}$), 18.5 ($C_{\gamma}H_{3Ala}$ **IR** (film, cm^{-1}): ν_{max} = 3287, 2970, 1636, 1549; $[\alpha]_D^{20}$ = + 34.0 (c = 1.00; MeOH); **Mp**: 154-156 °C; **HRMS** (ESI^+): *m/z* calcd for $C_{45}H_{87}O_{11}N_{14}$ $[M+H]^+$ 999.6673, found 999.6655.

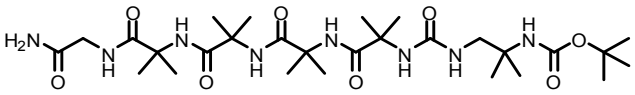
GlyNH$_2$-Aib$_4$-Aib^u-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-(Leu^u)$_{rev}$-NH(CO)NH*i*Pr 3d



$C_{44}H_{85}N_{15}O_{10}$
M = 984.24 g.mol^{-1}

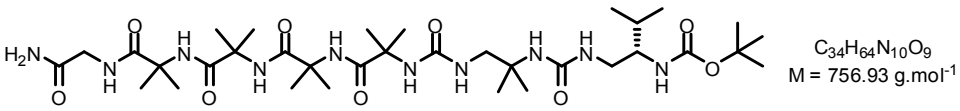
3d was prepared from **3c** (40 mg, 0.04 mmol), isopropyl isocyanate (7.9 µL, 0.08 mmol) and DIPEA (17 µL, 0.12 mmol) as described in the general procedure C. The pure oligomer **3d** (35 mg, 88.9%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.75 (1H, s, N*H*), 8.40 (1H, s, N*H*), 8.16 (1H, t, *J* = 6.3, NH_{Gly}), 7.99 (1H, s, N*H*), 7.45 (1H, s, N*H*), 7.23 (1H, s, N*H*), 6.52 (1H, s, N*H*), 6.45-6.34 (2H, m, NH_{Val} and NH_{Aib^u}), 6.28 (1H, dd, *J* = 9.4 and 3.2, NH_{Ala}), 6.24 (1H, d, *J* = 10.3, NH_{Val}), 5.95 (1H, t, *J* = 7.1, NH_{Leu}), 5.85 (1H, d, *J* = 9.7, NH_{Ala}), 5.75 (1H, s, N*H*), 5.68 (1H, d, *J* = 7.9, NH_{iPr}), 5.50 (1H, d, *J* = 9.5, NH_{Leu}), 4.08-3.96 (2H, m, NCH_{Leu} and NCH_{Ala}), 3.93 (1H, dd, *J* = 17.6 and 7.0, NCH_ACH_{BGly}), 3.80 (1H, oct, *J* = 6.7, NCH_{iPr}), 3.77-3.68 (2H, m, $NCH_AH_{BAib^u}$ and NCH_{Val}), 3.74 (1H, dd, *J* = 17.8 and 6.0, NCH_ACH_{BGly}), 3.67-3.59 (1H, m, NCH_AH_{BVal}), 3.58-3.47 (1H, m, NCH_AH_{BAla}), 3.43-3.35 (1H, m, NCH_AH_{BLeu}), 2.94-2.83 (1H, m, $NCH_AH_{BAib^u}$), 2.63-2.54 (1H, m, NCH_AH_{BVal}), 2.53-2.47 (1H, m, NCH_AH_{BLeu}), 2.46-2.37 (1H, m, NCH_AH_{BAla}), 1.72-1.57 (2H, m, CH_{Leu} and CH_{Val}), 1.50 (6H, s, 2 x CH_3), 1.47 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.34 (3H, s, CH_3), 1.32-1.09 (2H, m, CH_{2Leu}), 1.19 (3H, s, CH_3), 1.13 (6H, d, *J* = 6.6, CH_{3iPr}), 1.03 (3H, d, *J* = 6.9, CH_{3Ala}), 0.95 (3H, d, *J* = 6.9, CH_{3Val}), 0.92 (3H, d, *J* = 6.7, CH_{3Leu}), 0.91 (3H, d, *J* = 6.9, CH_{3Val}), 0.88 (3H, d, *J* = 6.7, CH_{3Leu}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.6 (2 x *C*=O), 178.2 (*C*=O), 178.1 (*C*=O), 175.4 (*C*=O), 162.1 (*C*=O), 161.1 (*C*=O), 160.8 (*C*=O), 160.5 (*C*=O), 159.4 (*C*=O), 58.1 (*C*), 58.0 (*C*), 57.7 (*C*), 56.8 (*C*), 56.1 ($NC_{\beta}H_{Val}$), 54.7 (*C*), 48.7 ($NC_{\beta}H_{Leu}$), 48.5 (NCH_{2Aib^u}), 48.1 ($NC_{\square}H_{2Ala}$), 47.4 ($NC_{\alpha}H_{2Leu}$), 46.6 ($NC_{\beta}H_{Ala}$), 43.9 ($NC_{\square}H_{2Val}$), 43.8 ($C_{\square}H_{2Leu}$), 43.0 (NCH_{2Gly}), 43.0 (NCH_{iPr}), 32.3 ($NC_{\gamma}H_{Val}$), 26.9 (CH_3), 26.6 (2 x CH_3), 26.4 ($C_{\delta}H_{Leu}$), 26.2 (2 x CH_3), 25.7 (CH_3), 24.8 (2 x CH_3), 24.5 (CH_3), 24.4 (CH_3), 23.6 ($C_{\delta}H_{3Leu}$), 23.5 ($C_{\delta}H_{3Leu}$), 23.5 ($C_{\delta}H_{3Leu}$), 22.5 ($C_{\delta}H_{3Leu}$), 19.8 ($C_{\delta}H_{3Val}$), 18.8 ($C_{\delta}H_{3Val}$), 18.7 ($C_{\gamma}H_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3297, 2966, 2930, 2872, 1638, 1546; $[\alpha]_D^{20}$ = +64.8 (c = 1.00; MeOH). **Mp**: 166-168°C; **HRMS** (ESI^+): *m/z* calcd for $C_{44}H_{86}O_{10}N_{15}$ $[M+H]^+$ 984.6677, found 984.6677.

GlyNH_2-Aib$_4$-(Aib^u)$_{rev}$-NHBoc 4



4 was prepared from GlyNH_2-Aib$_4$-NH_2Boc (518 mg, 1.25 mmol), **M1** (4.12 mg, 1.25 mmol) and DIPEA (638 µL, 3.75 mmol) as described in the general procedure B. The pure oligomer **4** (521 mg, 82.9%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.56 (1H, s, N*H*), 8.15 (1H, t, *J* = 6.2, NH_{Gly}), 8.03 (1H, s, N*H*), 8.01 (1H, s, N*H*), 7.44 (1H, s, N*H*), 7.27 (1H, s, N*H*), 6.48 (2H, s, N*H*), 6.26 (1H, t, *J* = 6.3, NH_{Aibu}), 3.83 (2H, brd, *J* = 6.2, NCH_{2Gly}), 3.28 (2H, brd, *J* = 6.2, NCH_{2Aibu}), 1.49 (6H, s, 2 x CH_3), 1.46 (6H, s, 2 x CH_3), 1.40 (9H, s, C(CH_3)$_3$), 1.39 (6H, s, 2 x CH_3), 1.39 (6H, s, 2 x CH_3), 1.23 (6H, s, 2 x CH_3). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.2 (*C*=O), 178.1 (*C*=O), 178.1 (*C*=O), 177.9 (*C*=O), 175.4 (*C*=O), 160.5 (*C*=O), 156.8 (*C*=O), 79.8 (*C*-O), 58.1 (*C*), 58.0 (*C*), 57.5 (*C*), 57.1 (*C*), 54.8 (*C*), 49.5 (N*C*H$_{2Aibu}$), 43.7 (N*C*H$_{2Gly}$), 28.7 (C(*C*H$_3$)$_3$), 25.6 (4 x *C*H$_3$), 25.4 (2 x *C*H$_3$), 25.2 (2 x *C*H$_3$), 25.2 (2 x *C*H$_3$). **IR** (film, cm^{-1}): ν_{max} = 3304, 2982, 2934, 1642, 1539; **HRMS** (ESI$^+$): *m/z* calcd for $C_{28}H_{53}O_8N_8$ $[M+H]^+$ 629.3981, found 629.3971.

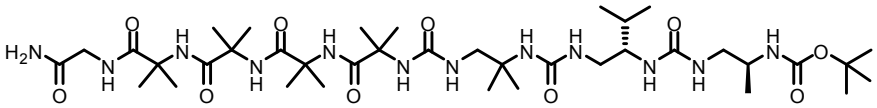
GlyNH_2-Aib$_4$-(Aib^u)$_{rev}$-(Val^u)$_{rev}$-NHBoc 4a



4a was prepared from **4** (474 mg, 0.75 mmol), **Cc** (259 mg, 0.75 mmol) and DIPEA (418 µL, 2.26 mmol) as described in the general procedure B. The pure oligomer **4a** (281 mg, 49.2%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.50 (1H, s, N*H*), 8.14 (1H, t, *J* = 6.3, NH_{Gly}), 7.97 (2H, s, N*H*), 7.46 (1H, s, N*H*), 7.24 (1H, s, N*H*), 6.41 (1H, s, N*H*), 6.36 (1H, d, *J* = 9.8, NH_{Val}), 6.15 (1H, t, *J* = 6.4, NH_{Aibu}), 5.84 (1H, s, N*H*), 5.75 (1H, t, *J* = 5.7, NH_{Val}), 3.85 (1H, dd, *J* = 17.5 and 6.4, NCH_ACH$_{BGly}$), 3.80 (1H, dd, *J* = 17.4 and 6.2, NCH$_A$CH_{BGly}), 3.49 (1H, dd, *J* = 13.5 and 5.8, NCH_AH$_{BAibu}$), 3.45-3.39 (1H, m, NCH_{Val}), 3.39-3.33 (2H, m, NCH_AH$_{BVal}$ and NCH$_A$$H_{BAibu}$), 2.88 (1H, ddd, *J* = 14.8, 9.9 and 5.7, NCH$_A$$H_{BVal}$), 1.70 (1H, oct, *J* = 6.8, CH_{Val}), 1.50 (6H, s, 2 x CH_3), 1.45 (15H, s, C(CH_3)$_3$ and 2 x CH_3), 1.39 (12H, s, 4 x CH_3), 1.25 (3H, s, CH_3), 1.19 (3H, s, CH_3), 0.94 (3H, d, *J* = 6.9, CH_{3Val}), 0.90 (3H, d, *J* = 6.9, CH_{3Val}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.2 (*C*=O), 178.1 (*C*=O), 178.1 (*C*=O), 178.0 (*C*=O), 175.5 (*C*=O), 160.4 (*C*=O), 160.1 (*C*=O), 158.8 (*C*=O), 79.8 (*C*-O), 58.1 (*C*), 58.0 (*C*), 57.6 (*C*), 57.5 (NC_βH$_{Val}$), 57.0 (*C*), 54.4 (*C*), 49.2 (N*C*H$_{2Aibu}$), 43.7 (N*C*H$_{2Gly}$), 42.7 (NC□H$_{2Val}$), 31.9 (NC_γH$_{Val}$), 28.8 (C(*C*H$_3$)$_3$), 26.5

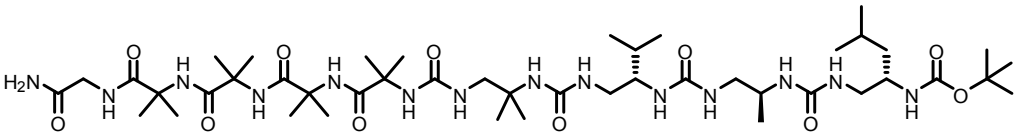
(CH$_3$), 25.9 (CH$_3$), 25.7 (CH$_3$), 25.5 (2 x CH$_3$), 25.4 (2 x CH$_3$), 25.1 (2 x CH$_3$), 25.0 (CH$_3$), 19.8 (C_{δ}H$_{3Val}$), 18.4 (C_{δ}H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3283, 2962, 2938, 1648, 1537; $[\alpha]_D^{20}$ = + 26.0 (c = 1.00; MeOH); **Mp**: 116-118 °C ; **HRMS** (ESI$^+$): *m/z* calcd for $C_{34}H_{65}O_9N_{10}$ $[M+H]^+$ 757.4930, found 757.4928.

GlyNH$_2$-Aib$_4$-(Aib^u)$_{rev}$-(Val^u)$_{rev}$-(Ala^u)$_{rev}$–NHBoc 4b



4b was prepared from **4a** (280 mg, 0.37 mmol), **Cb** (117 mg, 0.37 mmol) and DIPEA (205 µL, 1.11 mmol) as described in the general procedure B. The pure oligomer **4b** (260 mg, 82.0%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.43 (1H, s, NH), 8.14 (1H, t, J = 6.3, NH_{Gly}), 8.00 (1H, s, NH), 7.96 (1H, s, NH), 7.43 (1H, s, NH), 7.22 (1H, s, NH), 6.65 (1H, d, J = 9.3, NH_{Ala}), 6.54 (1H, s, NH), 6.38-6.33 (1H, dd, J = 7.4 and 2.2, NH_{Aib^u}), 6.13 (1H, t, J = 6.0, NH_{Ala}), 6.00 (1H, s, NH), 5.83 (1H, d, J = 10.1, NH_{Val}), 5.78 (1H, dd, J = 8.6 and 3.6, NH_{Val}), 3.95-3.71 (1H, m, NCH_{Ala}), 3.88 (1H, dd, J = 17.4 and 6.7, NCH_ACH$_{BGly}$), 3.77 (1H, dd, J = 17.4 and 6.0, NCH$_A$CH_{BGly}), 3.71-3.50 (3H, m, NCH_AH$_{BAib^u}$, NCH_AH$_{BVal}$ and NCH_{Val}), 3.42-3.33 (2H, m, NCH_AH$_{BAla}$ and NCH$_A$$H_{BAib^u}$), 2.78-2.68 (1H, m, NCH$_A$$H_{BAla}$), 2.54-2.43 (1H, m, NCH$_A$$H_{BVal}$), 1.76-1.59 (1H, m, C$H_{Val}$), 1.50 (6H, s, 2 x C$H_3$), 1.46 (18H, s, 3 x C$H_3$ and C(CH_3)$_3$), 1.40 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.29 (3H, s, CH_3), 1.10 (3H, s, CH_3), 1.10 (3H, d, J = 7.0, CH_{3Ala}), 0.96 (3H, d, J = 6.9, CH_{3Val}), 0.92 (3H, d, J = 6.9, CH_{3Val}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.1 (C=O), 178.1 (C=O), 178.1 (C=O), 178.0 (C=O), 175.4 (C=O), 161.6 (C=O), 160.3 (C=O), 160.2 (C=O), 158.6 (C=O), 80.2 (C-O), 58.1 (C), 58.0 (C), 57.5 (C), 57.0 (NC_{β}H$_{Val}$), 56.2 (C), 54.7 (C), 48.0 (NCH$_{2Aib^u}$), 47.7 (NC_{β}H$_{Ala}$), 47.5 (NC_{α}H$_{2Ala}$), 44.2 (NC_{α}H$_{2Val}$), 43.7 (NCH$_{2Gly}$), 31.8 (NC_{γ}H$_{Val}$), 28.7 (C(CH$_3$)$_3$), 26.9 (CH$_3$), 26.4 (2 x CH$_3$), 26.0 (CH$_3$), 25.9 (CH$_3$), 25.8 (CH$_3$), 25.5 (CH$_3$), 25.0 (CH$_3$), 24.6 (CH$_3$), 24.5 (CH$_3$), 19.9 (C_{δ}H$_{3Val}$), 18.7 (C_{δ}H$_{3Val}$), 18.5 (C_{γ}H$_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3312, 2974, 2944, 1649, 1540; $[\alpha]_D^{20}$ = + 33.0 (c = 1.00; MeOH); **Mp**: 128-130 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{38}H_{73}O_{10}N_{12}$ $[M+H]^+$ 857.5567, found 857.5559.

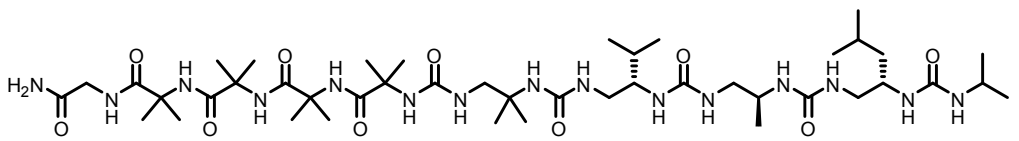
GlyNH$_2$-Aib$_4$-(Aib^u)$_{rev}$-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-(Leu^u)$_{rev}$–NHBoc 4c



$C_{45}H_{86}N_{14}O_{11}$
M = 999.25 g.mol^{-1}

4c was prepared from **4b** (240 mg, 0.28 mmol), **Ca** (100 mg, 0.28 mmol) and DIPEA (109 µL, 0.84 mmol) as described in the general procedure B. The pure oligomer **4c** (215 mg, 76.8%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.38 (1H, s, N*H*), 8.14 (1H, t, *J* = 5.2, NH_{Gly}), 8.04 (1H, s, N*H*), 7.96 (1H, s, N*H*), 7.46 (1H, s, N*H*), 7.24 (1H, s, N*H*), 6.65 (1H, s, N*H*), 6.62 (1H, d, *J* = 10.0, NH_{Leu}), 6.43-6.21 (3H, m, N*H*, NH_{Aib^u} and NH_{Val}), 6.11 (1H, brs, NH_{Leu}), 6.03 (1H, d, *J* = 8.5, NH_{Ala}), 5.89 (1H, s, NH_{Val}), 5.87 (1H, s, NH_{Ala}), 4.03-3.94 (1H, m, NCH_{Ala}), 3.92-3.69 (2H, m, , NCH_{Val} and NCH_{Leu}), 3.89 (1H, dd, *J* = 17.6 and 6.4, NCH_ACH$_{BGly}$), 3.75 (1H, dd, *J* = 16.6 and 4.5, NCH$_A$CH_{BGly}), 3.69-3.62 (1H, m, NCH_AH$_{BAib^u}$), 3.62-3.50 (2H, m, NCH_AH$_{BVal}$ and NCH_AH$_{BAla}$), 3.49-3.37 (1H, m, NCH_AH$_{BLeu}$), 2.30-3.21 (1H, m, NCH$_A$$H_{BAib^u}$), 2.50-2.43 (2H, m, NCH$_A$$H_{BLeu}$ and NCH$_A$$H_{BVal}$), 2.42-2.33 (1H, m, NCH$_A$$H_{BAla}$), 1.73-1.57 (2H, m, C$H_{Leu}$ and CH_{Val}), 1.50 (6H, s, 2 x CH_3), 1.46 (12H, s, 1 x CH_3 and C(CH_3)$_3$), 1.44 (6H, s, 2 x CH_3), 1.39 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.30 (3H, s, CH_3), 1.28-1.15 (2H, m, CH_{2Leu}), 1.08 (3H, s, CH_3), 1.06 (3H, d, *J* = 7.0, CH_{3Ala}), 0.94 (3H, d, *J* = 10.3, CH_{3Val}), 0.93 (3H, d, *J* = 6.8, CH_{3Leu}), 0.89 (3H, d, *J* = 6.6, CH_{3Val}), 0.88 (3H, d, *J* = 7.0, CH_{3Leu}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.1 (3 x *C*=O), 178.0 (2 x *C*=O), 162.3 (*C*=O), 160.6 (*C*=O), 160.5 (*C*=O), 160.2 (*C*=O), 159.3 (*C*=O), 80.1 (*C*-O), 58.1 (*C*), 58.0 (*C*), 57.5 (*C*), 56.9 (*C*), 55.5 (NC$_\beta$H$_{Val}$), 53.8 (*C*), 49.7 (NC$_\beta$H$_{Leu}$), 48.5 (NC□H$_{2Ala}$), 47.9 (NCH$_{2Aib^u}$), 46.8 (NC□H$_{2Leu}$), 46.8 (NC$_\beta$H$_{Ala}$), 43.9 (NCH$_{2Gly}$), 43.8 (NC□H$_{2Val}$), 42.1 (C□H$_{2Leu}$), 31.8 (NC$_\gamma$H$_{Val}$), 28.8 (C(*C*H$_3$)$_3$), 27.0 (*C*H$_3$), 26.6 (C$_\delta$H$_{Leu}$), 26.2 (3 x *C*H$_3$), 26.2 (*C*H$_3$), 25.7 (*C*H$_3$), 25.4 (*C*H$_3$), 24.8 (*C*H$_3$), 24.4 (*C*H$_3$), 24.2 (*C*H$_3$), 23.5 (C$_\delta$H$_{3Leu}$), 22.6 (C$_\delta$H$_{3Leu}$), 19.9 (C$_\delta$H$_{3Val}$), 18.6 (C$_\gamma$H$_{3Ala}$), 18.2 (C$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3290, 2961, 2938, 1635, 1571; **$[\alpha]_D^{20}$** = + 38.0 (c = 1.00; MeOH); **Mp**: 144-146 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{45}H_{87}O_{11}N_{14}$ $[M+H]^+$ 999.6673, found 999.6657.

GlyNH$_2$-Aib$_4$-(Aib^u)$_{rev}$-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-(Leu^u)$_{rev}$-NH(CO)NH*i*Pr 4d

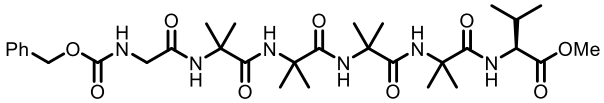


$C_{44}H_{85}N_{15}O_{10}$
M = 984.24 g.mol^{-1}

4d was prepared from **4c** (107 mg, 0.11 mmol), isopropyl isocyanate (21 µL, 0.21 mmol) and DIPEA (44.8 µL, 0.32 mmol) as described in the general procedure C. The pure oligomer **4d** (71 mg, 67.4%)

was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.38 (1H, s, N*H*), 8.14 (1H, t, *J* = 6.2, NH_{Gly}), 8.05 (1H, s, N*H*), 7.96 (1H, s, N*H*), 7.43 (1H, s, N*H*), 7.23 (1H, brs, N*H*), 6.69 (1H, s, N*H*), 6.50-6.40 (2H, m, NH_{Val} and NH_{Aibu}), 6.35 (1H, dd, *J* = 9.2 and 2.0, NH_{Ala}), 6.32-6.22 (2H, m, NH_{Val}), 5.96 (1H, t, *J* = 6.7, NH_{Leu}), 5.86 (1H, d, *J* = 9.9, NH_{Ala}), 5.69 (1H, d, *J* = 7.8, NH_{iPr}), 5.49 (1H, d, *J* = 9.5, NH_{Leu}), 4.10-3.94 (2H, m, NCH_{Leu} and NCH_{Ala}), 3.91 (1H, dd, *J* = 17.5 and 6.7, NCH_ACH_{BGly}), 3.78 (1H, oct, *J* = 6.9, NCH_{iPr}), 3.77-3.72 (1H, m, NCH_{Val}), 3.74 (1H, dd, *J* = 17.2 and 5.5, NCH_ACH_{BGly}), 3.70-3.64 (1H, m, NCH_AH_{BAibu}), 3.63-3.52 (2H, m, NCH_AH_{BVal} and NCH_AH_{BAla}), 3.45 (1H, ddd, *J* = 13.6, 7.4 and 3.4, NCH_AH_{BLeu}), 3.30-3.25 (1H, m, NCH_AH_{BAibu}), 2.56-2.33 (3H, m, NCH_AH_{BVal}, NCH_AH_{BLeu} and NCH_AH_{BAla}), 1.68 (1H, non, *J* = 6.9, CH_{Leu}), 1.61 (1H, oct, *J* = 6.7, CH_{Val}), 1.50 (6H, s, 2 x CH_3), 1.46 (3H, s, CH_3), 1.45 (6H, s, 2 x CH_3), 1.41 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.32 (3H, s, CH_3), 1.21 (2H, t, *J* = 7.4, CH_{2Leu}), 1.13 (6H, d, *J* = 6.6, CH_{3iPr}), 1.09 (3H, s, CH_3), 1.06 (3H, d, *J* = 6.9, CH_{3Ala}), 0.95 (3H, d, *J* = 8.1, CH_{3Val}), 0.93 (3H, d, *J* = 7.2, CH_{3Leu}), 0.89 (6H, d, *J* = 6.8, CH_{3Val} and CH_{3Leu}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.2 (*C*=O), 178.1 (*C*=O), 178.1 (*C*=O), 178.0 (*C*=O), 175.4 (*C*=O), 162.8 (*C*=O), 160.8 (*C*=O), 160.5 (*C*=O), 160.5 (*C*=O), 160.2 (*C*=O), 58.1 (*C*), 58.0 (*C*), 57.5 (*C*), 56.9 (*C*), 55.6 ($NC_\beta H_{Val}$), 53.8 (*C*), 48.5 ($NC_\beta H_{Leu}$), 48.5 ($NC\square H_{2Ala}$), 47.8 (NCH_{2Aibu}), 47.4 ($NC\square H_{2Leu}$), 46.9 ($NC_\beta H_{Ala}$), 43.8 ($NC\square H_{2Val}$), 43.8 (NCH_{2Gly}), 43.1 (NCH_{iPr}), 42.9 ($C\square H_{2Leu}$), 31.9 ($NC_\gamma H_{Val}$), 27.0 (CH_3), 26.7 (2 x CH_3), 26.3 ($C_\delta H_{Leu}$), 26.2 (2 x CH_3), 25.7 (CH_3), 25.4 (CH_3), 24.8 (CH_3), 24.3 (CH_3), 24.1 (CH_3), 23.6 ($C_\delta H_{3Leu}$), 23.5 ($C_\delta H_{3Leu}$), 23.5 ($C_\delta H_{3Leu}$), 22.5 ($C_\delta H_{3Leu}$), 19.9 ($C_\delta H_{3Val}$), 18.9 ($C_\gamma H_{3Ala}$), 18.4 ($C_\delta H_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3310, 2972, 1640, 1563; **$[\alpha]_D^{20}$** = + 28 (c = 1.00; MeOH); **Mp**: >200 °C; **HRMS** (ESI^+): *m/z* calcd for $C_{44}H_{86}O_{10}N_{15}$ $[M+H]^+$ 984.6677, found 984.6661.

Cbz-GlyAib$_4$ValOMe 6a

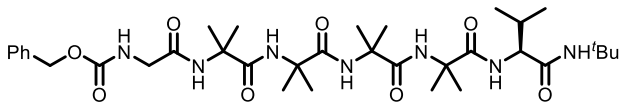


$C_{32}H_{50}N_6O_9$
M = 662.36 g.mol^{-1}

Cbz-GlyAib$_4$OH (71 mg, 0.13 mmol) and HOBt hydrate (27 mg, 0.16 mmol) were dissolved in CH_2Cl_2 (6 mL) and the solution cooled to 0 °C. EDC (22 µL, 0.13 mmol) was added and the reaction mixture was allowed to warm to room temperature and stirred for 2 h. L-Valine methyl ester hydrochloride (169 mg, 1.01 mmol) and NEt_3 (0.20 mL, 1.46 mmol) were added and the solution stirred for 48 h. The solution was then diluted with CH_2Cl_2 (15 mL) and the organic phase washed with HCl (1 M, 2 x 10 mL), $NaHCO_3$ (sat., 2 x 10 mL) and brine (1 x 10 mL). The organic phase was then dried ($MgSO_4$), filtered and concentrated to give a white solid, which was purified by column chromatography (1-5% MeOH in CH_2Cl_2) to give the pure peptide (56 mg, 73%) as a white solid. **^{1}H-NMR** (500 MHz, CD_3OD) δ_H 7.83 (1H, br s, NH), 7.75 (1H, br s, NH), 7.74 (1H, br s, NH), 7.73 (1H, br s, NH), 7.72 (1H, br s, NH), 7.36 (5H, m, ArCH x5), 5.13 (1H, d, *J*=12.5, CH_2O, H^A of AB system),

5.10 (1H, d, *J*=12.5, CH_2O, H^B of AB system), 4.22 (1H, m, CH), 3.77 (1H, d, *J*=17.0 Hz, CH_2-NH, H^A of AB system), 3.70 (1H, d, *J*=18.0, CH_2-NH, H^B of AB system), 3.68 (3H, s, OCH_3), 2.26 (1H, dqq, *J*=7.0, 7.0, 7.0 Hz, C*H*-$(CH_3)_2$), 1.50 (3H, s, CH_3), 1.48 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.02 (3H, d, *J*=7.0, CH_3-CH), 0.97 (3H, d, *J*=7.0, CH_3-CH). **^{13}C-NMR** (126 MHz, CD_3OD) δ_C 178.0 (CO), 177.1 (CO), 176.8 (CO), 176.6 (CO), 173.7 (CO), 172.3 (CO), 159.5 (CO (Cbz)), 138.2 (ArC) 129.7 (ArCH), 129.5 (ArCH), 128.9 (ArCH), 67.9 (CH_2O), 60.3 (CH-NH), 58.2 ($^{\alpha}$C), 57.97 ($^{\alpha}$C), 58.02 ($^{\alpha}$C), 57.7 ($^{\alpha}$C), 52.4 (OCH_3), 45.4 (CH_2-NH), 31.6 (CH), 27.0 (CH_3), 26.5 (CH_3), 26.1 (CH_3), 25.8 (CH_3), 25.1 (CH_3), 24.9 (CH_3), 24.8 (CH_3), 19.8 (*C*H_3-CH), 19.4 (*C*H_3-CH). **IR** (neat) ν_{max}/cm^{-1} = 3324, 2985, 2476, 1658. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ −23.6 (*c* 1.0, MeOH). **Mp** 209-210 °C. **HRMS** (ES^+, MeOH) Calc. for $C_{32}H_{51}N_6O_9$ ($[M+H]^+$) = 663.3718, found 663.3701.

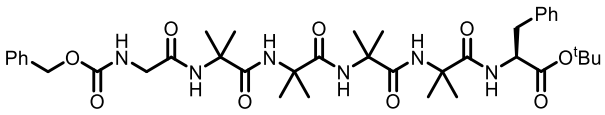
Cbz-GlyAib$_4$ValNH^{t}Bu 6b



$C_{35}H_{57}N_7O_8$
M = 703.43 g.mol^{-1}

Cbz-Gly-Aib$_4$-OH (43 mg, 0.078 mmol) and HOBt hydrate (18 mg, 0.104 mmol) were dissolved in CH_2Cl_2 (4 mL) and the solution cooled to 0 °C. EDC (14 µL, 0.08 mmol) was added and the reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. L-ValNH^{t}Bu (35 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) and NEt_3 (42 µL, 0.3 mmol) were added and the solution stirred for 48 h. The solution was then diluted with CH_2Cl_2 (15 mL) and the organic phase washed with $KHSO_4$ (5%, 2 x 10 mL), $NaHCO_3$ (sat., 2 x 10 mL) and brine (1 x 10 mL). The organic phase was then dried ($MgSO_4$), filtered and concentrated and the crude residue was purified by column chromatography (5% MeOH in CH_2Cl_2) to give the pure peptide (18 mg, 33%) was as a white solid. **^{1}H-NMR** (500 MHz, CD_3OD) δ_H 7.29-7.37 (5H, m, ArCH x5), 7.08 (1H, br s, NH), 5.14 (1H, d, *J*=12.5, CH_2O, H^A of AB system), 5.09 (1H, d, *J*=12.5, CH_2O, H^B of AB system), 3.99 (1H, d, *J*=6.0, CH), 3.80 (1H, d, *J*=18.0, CH_2-NH, H^A of AB system), 3.68 (1H, d, *J*=17.0, CH_2-NH, H^B of AB system), 2.33 (1H, dqq, *J*=7.0, 7.0, 6.5, C*H*-$(CH_3)_2$), 1.49 (6H, s, AibCH_3 x2), 1.44 (3H, s, CH_3), 1.41 (9H, m, CH_3 x3), 1.39 (6H, s, AibCH_3 x2), 1.37 (9H, s, C$(CH_3)_3$). **^{13}C-NMR** (126 MHz, CD_3OD) δ_C 178.1 (CO), 177.2 (CO), 177.1 (CO), 176.7 (CO), 173.5 (CO), 172.3 (CO), 159.6 (CO (Cbz)), 138.3 (ArC), 129.7 (ArCH), 129.3 (ArCH), 128.9 (ArCH), 68.0 (CH_2O), 62.0 (CH-NH), 58.1 ($^{\alpha}$C), 57.92 ($^{\alpha}$C), 57.88 ($^{\alpha}$C) 57.7 ($^{\alpha}$C), 52.6 (CMe_3), 45.5 (CH_2-NH), 31.0 (*C*H-$(CH_3)_2$), 29.2 (C(*C*H_3)$_3$), 28.0 (CH_3), 27.2 (CH_3), 26.9 (CH_3), 26.4 (CH_3), 24.3 (CH_3), 24.2 (CH_3), 24.1 (CH_3), 19.9 (CH_3-CH), 18.5 (CH_3-CH). **IR** (neat) ν_{max}/cm^{-1} = 3305, 2976, 2474, 1644. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ +14.1 (*c* 0.5, MeOH). **Mp** 124-126 °C. **HRMS** (ES^+, MeOH) Calc. for $C_{35}H_{57}N_7NaO_8$ ($[M+Na]^+$) = 726.4166, found 726.4164.

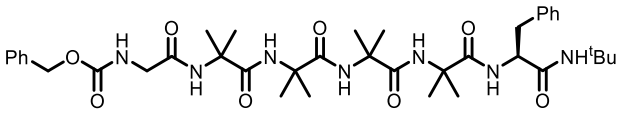
Cbz-GlyAib$_4$PheO^{t}Bu 6c



$C_{39}H_{56}N_6O_9$
M = 752.41 g.mol^{-1}

Cbz-Gly-Aib$_4$-OH (62 mg, 0.113 mmol) and HOBt hydrate (26 mg, 0.147 mmol) were dissolved in CH_2Cl_2 (5 mL) and the solution cooled to 0 °C. EDC (20 μL, 0.113 mmol) was added and the reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. L-PheO^{t}Bu.HCl (117 mg, 0.45 mmol) and NEt_3 (95 µL, 0.88 mmol) were added and the solution stirred for 48 h. The solution was diluted with CH_2Cl_2 (15 mL) and the organic phase washed with $KHSO_4$ (5%, 2 x 10 mL), $NaHCO_3$ (sat., 2 x 10 mL), brine (1 x 10 mL). The organic phase was then dried ($MgSO_4$), filtered and concentrated and the crude residue purified by column chromatography (5% MeOH in CH_2Cl_2) to give the pure peptide (58 mg, 68%) as a white solid. **^{1}H-NMR** (500 MHz, CD_3OD) δ_H 7.29 (10H, m, ArCH x10), 5.13 (1H, d, *J*=12.5, CH_2O, H^A of AB system), 5.10 (1H, d, *J*=12.5, CH_2O, H^B of AB system), 4.44 (1H, dd, *J*=7.5, 7.5 Hz, CH), 3.77 (1H, d, *J*=16.5, C*H*$_2$-NH, H^A of AB system), 3.70 (1H, d, *J*=16.5, C*H*$_2$-NH, H^B of AB system), 3.15 (1H, dd, *J*=14.0, 7.5, CH_2-Ph), 3.09 (1H, dd, *J*=14.0, 7.0, CH_2-Ph) 1.50 (3H, s, CH_3), 1.46 (3H, s, CH_3), 1.44 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.35 (9H, s, $C(CH_3)_3$). **^{13}C-NMR** (126 MHz, CD_3OD) δ_C 177.6 (CO), 177.2 (CO), 176.9 (CO), 176.5 (CO), 172.4 (CO), 172.3 (CO), 159.5 (CO (Cbz)), 139.0 (ArC), 138.3 (ArC), 130.7 (ArCH), 129.7 (ArCH), 129.4 (ArCH), 129.3 (ArCH), 128.9 (ArCH), 127.7 (ArCH), 82.5 (CMe_3), 67.9 (CH_2O), 58.14 ($^{\alpha}$C), 58.10 ($^{\alpha}$C), 57.9 ($^{\alpha}$C), 57.7 ($^{\alpha}$C), 56.9 ($^{\alpha}$C), 45.4 (CH_2-NH), 38.6 (CH_2-Ph), 28.3 ($C(CH_3)_3$), 27.0 (CH_3), 26.6 (CH_3), 26.1 (CH_3), 25.8 (CH_3), 25.0 (CH_3), 24.9 (CH_3), 24.8 (CH_3). **IR** (neat) ν_{max}/cm^{-1} = 3306, 2982, 2934, 1709, 1651. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ −12.0 (*c* 1.0, MeOH). **Mp** 200-202 °C. **HRMS** (ES^+, MeOH) Calc. for $C_{39}H_{57}N_6O_9Na$ ($[M+Na]^+$) = 753.4182, found 753.4178.

Cbz-GlyAib$_4$PheNH^{t}Bu 6d

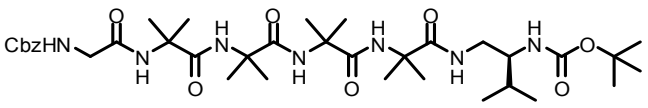


$C_{39}H_{57}N_7O_8$
M = 751.4269 g.mol^{-1}

Cbz-Gly-Aib$_4$-OH (75 mg, 0.136 mmol) and HOBt hydrate (31 mg, 0.177 mmol) were dissolved in CH_2Cl_2 (5 mL) and the solution cooled to 0 °C. EDC (24 µL, 0.136 mmol) was added and the reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. H-PheNH^{t}Bu (75 mg, 0.34 mmol) and NEt_3 (71 µL, 0.51 mmol) were added and the solution stirred for 48 h. The solution was diluted with CH_2Cl_2 (15 mL) and the organic phase washed with $KHSO_4$ (5%, 2 x 10 mL), $NaHCO_3$ (sat., 2 x 10 mL), brine (1 x 10 mL). The organic phase was then dried ($MgSO_4$), filtered and concentrated.

The crude residue was purified by column chromatography (2-5% MeOH in CH_2Cl_2) to give the pure peptide (89 mg, 87%) as a white solid. **^{1}H-NMR** (500 MHz, CD_3OD) δ_H 7.13-7.38 (10H, m, ArCH x10), 5.14 (1H, d, *J*=12.5, CH_2O, H^A of AB system), 5.09 (1H, d, *J*=12.5, CH_2O, H^B of AB system), 4.37 (1H, dd, *J*=11.5, 3.0, C*H*-NH), 3.80 (1H, d, *J*=16.5, CH_2-NH, H^A of AB system), 3.69 (1H, d, *J*=16.5, CH_2-NH, H^B of AB system), 3.41 (1H, m, CH_2-Ph), 2.92 (1H, m, CH_2-Ph), 1.37-1.46 (30H, m, CH_3 x7 and $C(CH_3)_3$), 1.18 (3H, s, CH_3). **^{13}C-NMR** (126 MHz, CD_3OD) δ_C 177.8 (CO), 177.6 (CO), 177.4 (CO), 176.6 (CO), 173.4 (CO), 172.3 (CO), 159.6 (CO (Cbz)), 140.0 (ArC), 138.8 (ArC), 130.3 (ArCH), 129.7 (ArCH), 129.4 (ArCH), 129.3 (ArCH), 128.9 (ArCH), 127.6 (ArCH), 68.0 (CH_2O), 58.1 ($^{\alpha}$C), 57.9 ($^{\alpha}$C), 57.6 ($^{\alpha}$C), 57.5 (CH-NH), 52.8 (CMe_3), 45.4 (CH_2-NH), 38.2 (CH_2-Ph), 29.2 ($C(CH_3)_3$), 27.4 (CH_3), 27.2 (CH_3), 26.9 (CH_3), 26.4 (CH_3), 24.3 (CH_3), 23.9 (CH_3). **IR** (neat) ν_{max}/cm^{-1} = 3303, 2983, 2936, 1729, 1651, 1530, 1455. $[\alpha]_D^{20}$ +12.0 (*c* 1.0, MeOH). **Mp** 122-124 °C. **HRMS** (ES^+, MeOH) Calc. for $C_{39}H_{57}N_6O_9Na$ ($[M+Na]^+$) = 751.4269, found 751.4277.

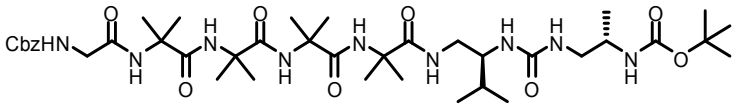
CbzGly-Aib$_4$-(Val^U)$_{rev}$-NHBoc 7a



$C_{36}H_{59}N_7O_9$
M = 733.89 g.mol^{-1}

7a was prepared from CBzGly-Aib-OH (480 mg, 0.87 mmol), HOBt (173 mg, 1.13 mmol), EDC (169 µL, 0.96 mmol), DIPEA (223 µL, 1.31 mmol) and an amine (265 mg, 1.31 mmol)[1] as described in the general procedure A. The pure oligomer **7a** (422 mg, 70%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 7.86 (1H, s, N*H*), 7.76 (1H, s, N*H*), 7.70 (1H, s, N*H*), 7.61 (1H, s, N*H*), 7.50 (1H, s, NH_{Val}), 7.38-7.24 (5H, m, 5 x =CH_{Ar}), 6.62 (1H, d, *J* = 10.1, NH_{Val}), 6.05 (1H, d, *J* = 8.2, N*H*), 5.11 (2H, s, OCH_2), 3.75 (1H, d, *J* = 17.8, A part of AB pattern, NCH_AH$_{BGly}$), 3.72 (1H, d, *J* = 17.1, B part of AB pattern, NCH$_A$$H_{BGly}$), 3.63-3.52 (1H, m, NC$H_AH_{BVal}$), 3.48-3.39 (1H, m, NC$H_{Val}$), 3.17-3.06 (1H, m, NCH$_A$$H_{BVal}$), 1.85 (1H, oct, *J* = 7.5, CH_{Val}), 1.51-1.31 (33H, m, 8 x CH_3 and $C(CH_3)_3$), 0.90 (3H, d, *J* = 7.0, CH_{3Val}), 0.89 (3H, d, *J* = 7.1, CH_{3Val}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 177.8 (*C*=O), 177.6 (*C*=O), 176.6 (*C*=O), 176.4 (*C*=O), 172.1 (*C*=O), 159.3 (*C*=O), 158.1 (*C*=O), 138.1 (=C_{Ar}), 129.4 (2 x =CH_{Ar}), 129.0 (=CH_{Ar}), 128.6 (2 x =CH_{Ar}), 79.7 (*C*-O), 67.7 (OCH_2), 58.3 (*C*), 58.0 (*C*), 57.8 (*C*), 57.5 (*C*), 57.1 (NC_{β}H$_{Val}$), 45.2 (NCH$_{2Gly}$), 42.5 (NC□H$_{2Val}$), 30.4 (NC_{γ}H$_{Val}$), 28.7 ($C(CH_3)_3$), 26.2 (CH_3), 25.6 (CH_3), 25.5 (CH_3), 25.2 (2 x CH_3), 24.9 (CH_3), 19.9 (C_{δ}H$_{3Val}$), 19.2 (C_{δ}H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3344, 2965, 2930, 2907, 1632, 1571; $[\alpha]_D^{20}$ = -76 (c = 1.00; MeOH); **Mp**: 89-91 °C; **HRMS** (ESI^+): *m/z* calcd for $C_{36}H_{60}N_7O_9$ $[M+H]^+$ 734.4447, found 734.4446.

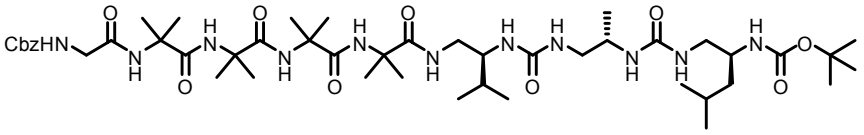
CbzGly-Aib$_4$-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-NHBoc 7b



$C_{40}H_{67}N_9O_{10}$
M = 834.01 g.mol^{-1}

7b was prepared from **7a** (385 mg, 0.52 mmol), **Cb** (164 mg, 0.52 mmol) and DIPEA (172 µL, 1.57 mmol) as described in the general procedure B. The pure oligomer **7b** (300 mg, 69.2%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 7.79 (1H, s, N*H*), 7.74 (1H, s, N*H*), 7.72 (1H, s, N*H*), 7.47 (1H, t, *J* = 5.4, NH_{Val}), 7.38-7.26 (5H, m, 5 x =CH_{Ar}), 6.46 (1H, d, *J* = 7.0, NH_{Ala}), 5.94-5.87 (2H, m, NH_{Val} and NH_{Ala}), 5.10 (2H, s, OCH_2), 3.75 (1H, d, *J* = 17.0, A part of AB pattern, NCH_AH$_{BGly}$), 3.72 (1H, d, *J* = 17.3, B part of AB pattern, NCH$_A$$H_{BGly}$), 3.67-3.52 (2H, m, NC$H_{Val}$ and NCH_{Ala}), 3.41-3.33 (1H, m, NCH_AH$_{BVal}$), 3.32-3.23 (1H, m, NCH$_A$$H_{BVal}$), 3.17-3.05 (2H, m, NC$H_{2Ala}$), 1.88 (1H, oct, *J* = 6.7, CH_{Val}), 1.50-1.35 (33H, m, 8 x CH_3 and C(CH_3)$_3$), 1.07 (3H, d, *J* = 6.7, CH_{3Ala}), 0.93 (3H, d, *J* = 6.8, CH_{3Val}), 0.90 (3H, d, *J* = 6.9, CH_{3Val}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 177.8 (*C*=O), 177.4 (*C*=O), 176.8 (*C*=O), 176.5 (*C*=O), 172.1 (*C*=O), 161.0 (*C*=O), 159.3 (*C*=O), 157.9 (*C*=O), 138.0 (=C_{Ar}), 129.4 (2 x =CH_{Ar}), 129.0 (=CH_{Ar}), 128.6 (2 x =CH_{Ar}), 79.8 (*C*-O), 67.7 (OCH_2), 58.2 (*C*), 57.9 (*C*), 57.8 (*C*), 57.6 (*C*), 56.2 (NC_βH$_{Val}$), 48.5 (NC_βH$_{Ala}$), 46.0 (NC□H$_{2Ala}$), 45.2 (NCH_{2Gly}), 42.4 (NC□H$_{2Val}$), 30.4 (NC_γH$_{Val}$), 28.7 (C(CH_3)$_3$), 26.2 (CH_3), 25.6 (CH_3), 25.4 (CH_3), 25.2 (2 x CH_3), 25.0 (CH_3), 20.1 (C_δH$_{3Val}$), 18.6 (C_δH$_{3Val}$), 18.5 (C_δH$_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3309, 2977, 2938, 1656, 1537; **$[\alpha]_D^{20}$** = -124 (c = 1.00; MeOH); **Mp**: 129-131 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{40}H_{68}N_9O_{10}$ $[M+H]^+$ 834.5084, found 834.5083.

CbzGly-Aib$_4$-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-(Leu^u)$_{rev}$-NHBoc 7c

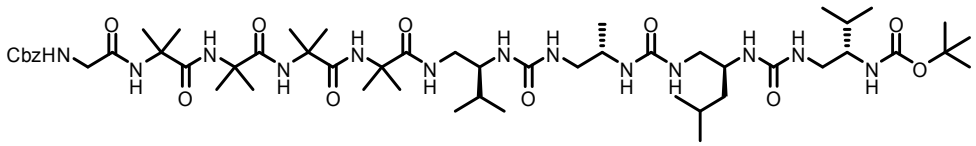


$C_{47}H_{81}N_{11}O_{11}$
M = 976.21 g.mol^{-1}

7c was prepared from **7b** (250 mg, 0.30 mmol), **Ca** (107 mg, 0.30 mmol) and DIPEA (153 µL, 0.90 mmol) as described in the general procedure B. The pure oligomer **7c** (249 mg, 85.1%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.34 (1H, s, N*H*), 7.77 (1H, s, N*H*), 7.74 (1H, s, N*H*), 7.52 (1H, t, *J* = 5.4, NH_{Val}), 7.42 (1H, s, N*H*), 7.37-7.26 (5H, m, 5 x =CH_{Ar}), 6.36 (1H, d, *J* = 6.8, NH_{Leu}), 5.98-5.87 (3H, m, NH_{Leu}, NH_{Ala} and NH_{Ala}), 5.81 (1H, d, *J* = 6.8, NH_{Val}), 5.10 (2H, s, OCH_2), 3.76 (1H, d, *J* = 15.4, A part of AB pattern, NCH_AH$_{BGly}$), 3.71 (1H, d, *J* = 16.9, B part of AB pattern, NCH$_A$$H_{BGly}$), 3.77-3.68 (1H, m, NC$H_{Ala}$), 3.66-3.52 (2H, m, NC$H_{Val}$ and NCH_{Leu}), 3.51-3.39 (1H, m, NCH_AH$_{BVal}$), 3.32-3.22 (2H, m, NCH$_A$$H_{BVal}$ and NCH_AH$_{BAla}$), 3.20-3.16 (1H, m, NCH_AH$_{Bleu}$), 3.07-2.97 (2H, m, NCH$_A$$H_{BLeu}$ and

NCH$_A$*H$_{BAla}$*), 1.90 (1H, oct, *J* = 7.0, C*H$_{Val}$*), 1.65 (1H, non, *J* = 7.1, C*H$_{Leu}$*), 1.50-1.35 (33H, m, 8 x C*H$_3$* and C(C*H$_3$*)$_3$), 1.34-1.28 (1H, m, C*H$_A$*H$_{BLeu}$*), 1.24-1.19 (1H, m, CH$_A$*H$_{BLeu}$*), 1.08 (3H, d, *J* = 6.8, C*H$_{3Ala}$*), 0.93 (3H, d, *J* = 6.8, C*H$_{3Val}$*), 0.92 (3H, d, *J* = 7.2, C*H$_{3Leu}$*), 0.90 (3H, d, *J* = 7.6, C*H$_{3Leu}$*), 0.89 (3H, d, *J* = 6.8, C*H$_{3Val}$*). **^{13}C NMR** (125 MHz, CD_3OH) δ = 177.9 (*C*=O), 177.3 (*C*=O), 176.9 (*C*=O), 176.5 (*C*=O), 172.2 (*C*=O), 161.0 (*C*=O), 160.8 (*C*=O), 159.3 (*C*=O), 158.2 (*C*=O), 138.0 (=*C$_{Ar}$*), 129.4 (2 x =C*H$_{Ar}$*), 129.0 (=C*H$_{Ar}$*), 128.6 (2 x =C*H$_{Ar}$*), 79.7 (*C*-O), 67.7 (OCH$_2$), 58.2 (*C*), 57.9 (*C*), 57.8 (*C*), 57.6 (*C*), 56.3 (NC*$_\beta$*H$_{Val}$), 50.5 (NC*$_\beta$*H$_{Leu}$), 47.5 (NC*$_\beta$*H$_{Ala}$), 46.3 (NC$_\alpha$H$_{2Ala}$), 45.5 (NC$_\alpha$H$_{2Leu}$), 45.3 (NCH$_{2Gly}$), 42.6 (C$_\alpha$H$_{2Leu}$), 41.9 (NC$_\alpha$H$_{2Val}$), 30.0 (C*$_\gamma$*H$_{Val}$), 28.7 (C(CH$_3$)$_3$), 26.5 (CH$_3$), 25.9 (C*$_\delta$*H$_{Leu}$), 25.6 (CH$_3$), 25.4 (CH$_3$), 25.0 (CH$_3$), 24.9 (2 x CH$_3$), 23.5 (C$_\iota$H$_{3Leu}$), 22.4 (C$_\iota$H$_{3Leu}$), 20.2 (C*$_\delta$*H$_{3Val}$), 19.0 (C*$_\delta$*H$_{3Ala}$), 18.6 (C*$_\delta$*H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3304, 2932, 2873, 1655, 1536; **$[\alpha]_D^{20}$** = -14 (c = 1.00; MeOH); **Mp**: 135-136 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{47}H_{82}N_{11}O_{11}$ $[M+H]^+$ 976.6190, found 976.6189.

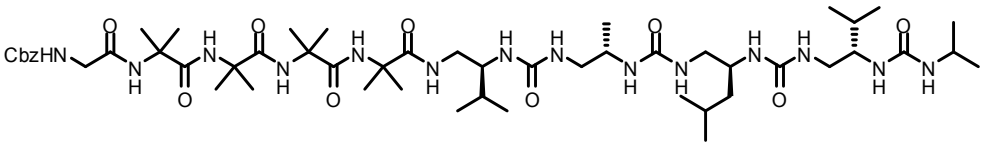
CbzGly-Aib$_4$-(Val^u)$_{rev}$-(Ala^u)$_{rev}$-(Leu^u)$_{rev}$-(Val^u)$_{rev}$-NHBoc 7d



7d was prepared from **7c** (150 mg, 0.15 mmol), **Cc** (53 mg, 0.15 mmol) and DIPEA (79 µL, 0.46 mmol) as described in the general procedure B. The pure oligomer **7d** (40 mg, 21.6%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.35 (1H, s, N*H*), 7.80-7.70 (3H, m, N*H*), 7.62 (1H, t, *J* = 5.4, N*H$_{Val}$*), 7.52 (1H, s, N*H*), 7.43 (1H, t, *J* = 5.4, N*H$_{Gly}$*), 7.42 (1H, s, N*H*), 7.39-7.28 (5H, m, 5 x =C*H$_{Ar}$*), 6.44 (1H, d, *J* = 6.8, N*H$_{Leu}$*), 6.27 (1H, s, N*H$_{Ala}$*), 6.10-5.75 (4H, m, N*H$_{Val}$*, N*H$_{Leu}$*, N*H$_{Val}$* and N*H$_{Ala}$*), 5.12 (2H, s, OC*H$_2$*), 3.96-3.37 (8H, m, NC*H$_{Val}$*, NC*H$_{Leu}$*, NC*H$_{Ala}$*, NC*H$_A$*H$_{BVal}$, NC*H$_A$*H$_{BVal}$, NC*H$_A$*H$_{BAla}$* and NC*H$_A$*H$_{BLeu}$) 3.78 (1H, d, *J* = 19.4, A part of AB pattern, NC*H$_A$*H$_{BGly}$), 3.78 (1H, d, *J* = 19.8, B part of AB pattern, NCH$_A$*H$_{BGly}$*), 3.28-3.11 (1H, m, NCH$_A$*H$_{BVal}$*), 2.99-2.47 (3H, m, NCH$_A$*H$_{BVal}$*, NCH$_A$*H$_{BAla}$* and NCH$_A$*H$_{BLeu}$*), 1.95 (1H, oct, *J* = 7.0, C*H$_{Val}$*), 1.75-1.62 (2H, m, C*H$_{Val}$* and C*H$_{Leu}$*), 1.52-1.35 (35H, m, 8 x C*H$_3$* and C(C*H$_3$*)$_3$ and C*H$_{2Leu}$*), 1.09 (3H, d, *J* = 6.8, C*H$_{3Ala}$*), 0.98-0.86 (18H, m, 4 x C*H$_{3Val}$* and 2 x C*H$_{3Leu}$*). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.0 (*C*=O), 177.3 (*C*=O), 177.0 (*C*=O), 176.6 (*C*=O), 175.0 (*C*=O), 172.3 (*C*=O), 161.1 (*C*=O), 161.0 (*C*=O), 159.4 (*C*=O), 159.1 (*C*=O), 138.2 (=*C$_{Ar}$*), 129.6 (2 x =C*H$_{Ar}$*), 129.1 (=C*H$_{Ar}$*), 128.8 (2 x =C*H$_{Ar}$*), 80.0 (*C*-O), 67.8 (OCH$_2$), 58.3 (*C*), 58.0 (*C*), 57.9 (*C*), 57.7 (*C* and NC*$_\beta$*H$_{Val}$), 56.1 (NC*$_\beta$*H$_{Val}$), 49.5 (NC*$_\beta$*H$_{Leu}$), 47.4 (NC*$_\beta$*H$_{Ala}$), 46.6 (NC$_\alpha$H$_{2Leu}$), 46.5 (NC$_\alpha$H$_{2Ala}$), 45.4 (NCH$_{2Gly}$), 43.4 (NC$_\alpha$H$_{2Val}$), 43.0 (C$_\alpha$H$_{2Leu}$), 42.3 (NC$_\alpha$H$_{2Val}$), 31.9 (C*$_\gamma$*H$_{Val}$), 29.7 (C*$_\gamma$*H$_{Val}$), 28.9 (C(CH$_3$)$_3$), 26.6 (CH$_3$), 26.1 (C*$_\delta$*H$_{Leu}$), 26.0 (CH$_3$), 25.6 (CH$_3$), 25.5 (CH$_3$), 25.1 (2 x CH$_3$), 23.8 (C$_\iota$H$_{3Leu}$), 22.6 (C$_\iota$H$_{3Leu}$), 20.6 (C*$_\delta$*H$_{3Val}$), 20.1 (C*$_\delta$*H$_{3Val}$),

19.2 ($C_{\delta}H_{3Ala}$), 18.8 ($C_{\delta}H_{3Val}$), 18.1 ($C_{\delta}H_{3Val}$).). **IR** (film, cm^{-1}): ν_{max} = 3312, 2945, 1649, 1528; $[\alpha]_D^{20}$ = -16 (c = 1.00; MeOH); **Mp**: 159-161 °C; **HRMS** (ES^+): *m/z* calcd for $C_{53}H_{93}N_{13}O_{12}Na$ $[M+Na]^+$ 1126.99.

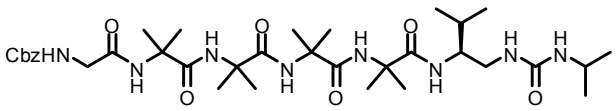
CbzGly-Aib$_4$-(Val^U)$_{rev}$-(Ala^U)$_{rev}$-(Leu^U)$_{rev}$-(Val^U)$_{rev}$-NH(CO)NH*i*Pr 7e



$C_{52}H_{92}N_{14}O_{11}$
M = 1089.37 g.mol^{-1}

7e was prepared from **7d** (36 mg, 0.03 mmol), isopropyl isocyanate (6.4 µL, 0.07 mmol) and DIPEA (13.6 µL, 0.10 mmol) as described in the general procedure C. The pure oligomer **7e** (32 mg, 89.8%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.34 (1H, s, N*H*), 7.80-7.70 (3H, m, N*H*), 7.57 (1H, t, *J* = 6.5, NH_{Val}), 7.40-7.24 (5H, m, 5 x =CH_{Ar}), 6.16 (1H, s, NH_{Leu}), 6.07 (1H, d, *J* = 8.8, NH_{Leu}), 6.03-5.96 (1H, d, *J* = 3.9, NH_{iPr}), 5.96-5.78 (4H, m, NH_{Val}, NH_{Ala}, NH_{Val} and NH_{Ala}), 5.69 (1H, d, *J* = 9.7, NH_{Val}), 5.11 (2H, s, OCH_2), 3.90-3.66 (3H, m, NCH_{Val}, NCH_{Leu}, NCH_{Val}) 3.76 (1H, d, *J* = 16.6, A part of AB pattern, NCH_AH$_{BGly}$), 3.71 (1H, d, *J* = 16.6, B part of AB pattern, NCH$_A$$H_{BGly}$), 3.64-3.38 (6H, m, NC$H_AH_{BVal}$, NC$H_AH_{BVal}$ NCH_AH$_{BAla}$ NCH_AH$_{BLeu}$ NCH_{Val} NCH_{iPr}), 3.22-3.11 (1H, m, NCH$_A$$H_{BVal}$), 2.99-2.88 (1H, m, NCH$_A$$H_{BVal}$), 2.87-2.77 (1H, m, NCH$_A$$H_{BLeu}$), 2.76-2.65 (1H, m, NCH$_A$$H_{BAla}$), 1.93 (1H, oct, *J* = 6.9, CH_{Val}), 1.77-1.59 (2H, m, CH_{Val} and CH_{Leu}), 1.49 (3H, s, CH_3), 1.48 (3H, s, CH_3), 1.47-1.33 (18H, m, 6 x CH_3 and C(CH_3)$_3$), 1.33-1.14 (2H, m, CH_{2Leu}), 1.11 (6H, d, *J* =, NCH(CH_3)$_2$), 1.07 (3H, d, *J* = 6.9, CH_{3Ala}), 0.7-0.86 (18H, m, 4 x CH_{3Val} and 2 x CH_{3Leu}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 177.9 (*C*=O), 177.1 (*C*=O), 176.9 (*C*=O), 176.5 (*C*=O), 175.9 (*C*=O), 175.7 (*C*=O), 172.2 (*C*=O), 161.1 (*C*=O), 161.0 (*C*=O), 160.7 (*C*=O), 159.3 (*C*=O), 138.1 (=C_{Ar}), 129.4 (2 x =CH_{Ar}), 129.0 (=CH_{Ar}), 128.6 (2 x =CH_{Ar}), 67.7 (OCH_2), 58.2 (*C*), 57.9 (*C*), 57.8 (*C*), 57.6 (*C*), 56.3 (NC$_{\beta}$H$_{Val}$), 49.9 (NC$_{\beta}$H$_{Leu}$), 47.3 (NC$_{\beta}$H$_{Ala}$), 45.9 (NC$_{\square}$H$_{2Leu}$), 45.7 (NCH$_{iPr}$), 45.3 (NC$_{\square}$H$_{2Ala}$), 43.3 (NCH$_{2Gly}$), 42.8 (NC$_{\square}$H$_{2Val}$), 42.7 (C$_{\square}$H$_{2Leu}$), 41.9 (NC$_{\square}$H$_{2Val}$), 31.7 (C$_{\gamma}$H$_{Val}$), 29.7 (C$_{\gamma}$H$_{Val}$), 26.6 (*C*H$_3$), 25.9 (C$_{\delta}$H$_{Leu}$), 25.6 (*C*H$_3$), 25.4 (*C*H$_3$), 25.3 (*C*H$_3$), 25.0 (*C*H$_3$), 24.8 (*C*H$_3$), 23.6 (C$_{\cdot}$H$_{3Leu}$), 23.5 (2 x *C*H$_{3iPr}$), 23.5 (C$_{\cdot}$H$_{3Leu}$), 20.4 (C$_{\delta}$H$_{3Val}$), 20.0 (C$_{\delta}$H$_{3Val}$), 18.9 (C$_{\delta}$H$_{3Ala}$), 18.6 (C$_{\delta}$H$_{3Val}$), 18.4 (C$_{\delta}$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3316, 2971, 2871, 1643, 1549; $[\alpha]_D^{20}$ = +49.6 (c = 1.00; MeOH); **Mp**: 190-192 °C; **HRMS** (ES^+): *m/z* calcd for $C_{52}H_{92}N_{14}O_{11}Na$ $[M+H]^+$ 1111.8.

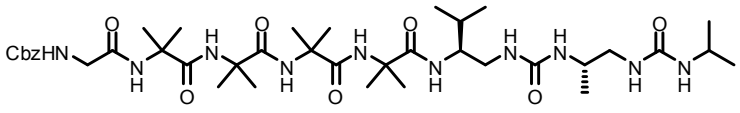
CbzGly-Aib$_4$-(Val^u)-NH(CO)NH*i*Pr 8a



$C_{35}H_{58}N_8O_8$
M = 718.88 g.mol^{-1}

8a was prepared from CBzGly-Aib-OH (200 mg, 0.36 mmol), HOBt (72 mg, 0.47 mmol), EDC.HCl (76 mg, 0.40 mmol), DIPEA (92 µL, 0.55 mmol) and **U1** (250 mg, 0.55 mmol) as described in the general procedure A. The pure oligomer **8a** (176 mg, 68%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 7.82-7.59 (5H, m, N*H*), 7.40-7.26 (5H, m, 5 x =CH_{Ar}), 7.24 (1H, d, *J* = 9.7, CHNH_{Val}), 5.59 (1H, d, *J* = 8.0, NH_{iPr}), 5.54 (1H, d, *J* = 6.5, CH_2NH_{Val}), 5.14 (1H, d, *J* = 12.6, A part of AB pattern, OCH_AH$_B$), 5.08 (1H, d, *J* = 12.6, B part of AB pattern, OCH$_A$$H_B$), 3.80 (1H, d, *J* = 16.5, A part of AB pattern, NCH_AH$_{BGly}$), 3.67 (1H, d, *J* = 16.8, B part of AB pattern, NCH$_A$$H_{BGly}$), 3.89-3.56 (3H, m, NC$H_{iPr}$, NC$H_AH_{BVal}$ and NCH_{Val}), 3.07-2.93 (1H, m, NCH$_A$$H_{BVal}$), 1.75 (1H, oct, *J* = 6.94, CH_{Val}), 1.54-1.47 (6H, m, 2 x CH_3), 1.46-1.30 (18H, m, 6 x CH_3), 1.12 (3H, d, *J* = 6.7, CH_{3iPr}), 1.10 (3H, d, *J* = 6.8, CH_{3iPr}), 0.95 (3H, d, *J* = 6.9, CH_{3Val}), 0.92 (3H, d, *J* = 6.9, CH_{3Val}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 177.7 (*C*=O), 177.5 (*C*=O), 177.3 (*C*=O), 176.6 (*C*=O), 172.2 (*C*=O), 160.4 (*C*=O), 159.3 (*C*=O), 138.0 (=C_{Ar}), 129.4 (2 x =CH_{Ar}), 129.0 (=CH_{Ar}), 128.6 (2 x =CH_{Ar}), 67.7 (OCH_2), 58.4 (*C*), 57.8 (*C*), 57.7 (*C*), 57.6 (*C*), 56.7 (NC$_\beta$H$_{Val}$), 45.3 (NCH_{2Gly}), 42.9 (NCH_{iPr}), 42.5 (NC□H$_{2Val}$), 32.1 (NC$_\gamma$H$_{Val}$), 27.2 (*C*H$_3$), 26.9 (*C*H$_3$), 26.5 (*C*H$_3$), 26.2 (*C*H$_3$), 25.1 (*C*H$_3$), 24.0 (*C*H$_3$), 23.9 (*C*H$_3$), 23.7 (*C*H$_3$), 23.5 (*C*H$_{iPr}$), 23.4 (*C*H$_{iPr}$), 19.9 (C$_\delta$H$_{3Val}$), 19.0 (C$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3304, 2975, 2937, 2873, 1645, 1530; **$[\alpha]_D^{20}$** = +27.6 (c = 1.00; MeOH); **Mp**: 120-122 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{35}H_{59}N_8O_8$ $[M+H]^+$ 719.4456, found 719.4427.

CbzGly-Aib$_4$-Val^u-Ala^u-NH(CO)NH*i*Pr 8b

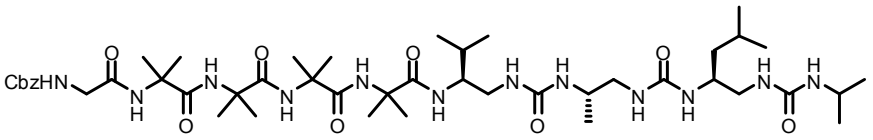


$C_{39}H_{66}N_{10}O_9$
M = 819.00 g.mol^{-1}

8b was prepared from CBzGly-Aib-OH (200 mg, 0.36 mmol), HOBt (72 mg, 0.47 mmol), EDC.HCl (76 mg, 0.40 mmol), DIPEA (92 µL, 0.55 mmol) and **U4** (300 mg, 0.55 mmol) as described in the general procedure A. The pure oligomer **8b** (177 mg, 60%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 7.86 (2H, s, N*H*), 7.80 (2H, s, N*H*), 7.78 (1H, brs, N*H*), 7.42-7.25 (5H, m, 5 x =CH_{Ar}), 7.16 (1H, d, *J* = 10.1, NH_{Val}), 6.07 (1H, d, *J* = 7.9, NH_{iPr}), 5.88 (1H, dd, *J* = 7.9 and 3.4, NH_{Ala}), 5.61 (1H, s, NH_{Ala}), 5.59 (1H, s, NH_{Val}), 5.15 (1H, d, *J* = 12.6, A part of AB pattern, OCH_AH$_B$), 5.08 (1H, d, *J* = 12.5, B part of AB pattern, OCH$_A$$H_B$), 3.98-3.76 (3H, m, NC$H_{iPr}$, NC$H_{Val}$ and NCH_{Ala}), 3.81 (1H, d, *J* = 16.7, A part

of AB pattern, NCH_AH$_{BGly}$), 3.67 (1H, d, *J* = 16.3, B part of AB pattern, NCH$_A$$H_{BGly}$), 3.72-3.59 (1H, m, NC$H_AH_{BVal}$), 3.47 (1H, ddd, *J* = 13.2, 8.1 and 4.1, NCH_AH$_{BAla}$), 2.84 (1H, ddd, *J* = 14.2, 11.3 and 3.2, NCH$_A$$H_{BVal}$), 2.70 (1H, ddd, *J* = 13.4, 9.4 and 3.6, NCH$_A$$H_{BAla}$), 1.73 (1H, oct, *J* = 6.9, CH_{Val}), 1.52 (3H, m, CH_3), 1.50 (3H, m, CH_3), 1.47-1.32 (18H, m, 6 x CH_3), 1.13 (3H, d, *J* = 6.6, CH_{3iPr}), 1.11 (3H, d, *J* = 6.6, CH_{3iPr}), 1.07 (3H, d, *J* = 6.8, CH_{3Ala}), 0.96 (3H, d, *J* = 6.9, CH_{3Val}), 0.91 (3H, d, *J* = 6.9, CH_{3Val}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.1 (*C*=O), 177.9 (*C*=O), 177.4 (*C*=O), 176.6 (*C*=O), 172.2 (*C*=O), 160.8 (*C*=O), 160.6 (*C*=O), 159.3 (*C*=O), 138.0 (=C_{Ar}), 129.4 (2 x =CH_{Ar}), 129.0 (=CH_{Ar}), 128.6 (2 x =CH_{Ar}), 67.7 (OCH_2), 58.3 (*C*), 57.7 (*C*), 57.6 (*C*), 57.5 (*C*), 56.2 (NC$_\beta$H$_{Val}$), 47.2 (NC$_\beta$H$_{Ala}$), 46.7 (NC□H$_{2Ala}$), 45.2 (NCH_{2Gly}), 43.0 (NC□H$_{2Val}$), 42.8 (NCH_{iPr}), 32.0 (NC$_\gamma$H$_{Val}$), 28.1 (*C*H$_3$), 27.2 (*C*H$_3$), 26.8 (*C*H$_3$), 26.4 (*C*H$_3$), 25.0 (*C*H$_3$), 23.8 (*C*H$_3$), 23.6 (*C*H$_{iPr}$), 23.5 (*C*H$_{iPr}$), 23.4 (*C*H$_3$), 23.3 (*C*H$_3$), 20.0 (*C*$_\delta$H$_{3Val}$), 19.2 (*C*$_\delta$H$_{3Ala}$), 19.0 (*C*$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3309, 2961, 2871, 1640, 1538; **$[\alpha]_D^{20}$** = +57.2 (c = 1.00; MeOH); **Mp**: 135-137 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{39}H_{67}N_{10}O_9$ $[M+H]^+$ 819.5092, found 819.5108.

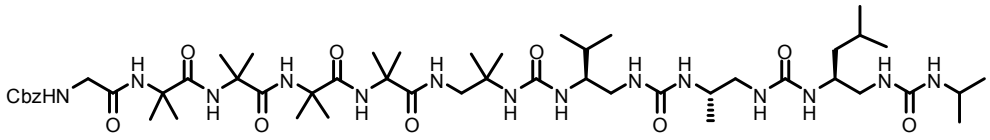
CbzGly-Aib$_4$-Val^u-Ala^u-Leu^u-NH(CO)NH*i*Pr 8c



8c was prepared from CBzGly-Aib-OH (200 mg, 0.36 mmol), HOBt (72 mg, 0.47 mmol), EDC.HCl (76 mg, 0.40 mmol), DIPEA (92 µL, 0.55 mmol) and **U6** (350 mg, 0.55 mmol) as described in the general procedure A. The pure oligomer **8c** (170 mg, 49.1%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 7.80-7.48 (5H, m, N*H*), 7.46-7.25 (5H, m, 5 x =CH_{Ar}), 7.15 (1H, d, *J* = 10.1, NH_{Val}), 6.31 (1H, d, *J* = 8.2, NH_{Leu}), 6.21 (1H, d, *J* = 7.9, NH_{iPr}), 6.04 (1H, d, *J* = 9.7, NH_{Leu}), 5.95 (1H, dd, *J* = 9.0 and 3.6, NH_{Ala}), 5.72 (1H, dd, *J* = 9.1 and 2.9, NH_{Val}), 5.45 (1H, d, *J* = 10.2, NH_{Ala}), 5.15 (1H, d, *J* = 12.6, A part of AB pattern, OCH_AH$_B$), 5.07 (1H, d, *J* = 12.4, B part of AB pattern, OCH$_A$$H_B$), 4.18-4.02 (1H, m, NC$H_{Ala}$), 4.01-3.89 (1H, m, NC$H_{Leu}$), 3.82 (1H, d, *J* = 16.3, A part of AB pattern, NCH_AH$_{BGly}$), 3.88-3.75 (2H, m, NCH_{iPr} and NCH_{Val}), 3.67 (1H, d, *J* = 16.3, B part of AB pattern, NCH$_A$$H_{BGly}$), 3.73-3.65 (1H, m, NC$H_AH_{BVal}$), 3.60 (1H, ddd, *J* = 13.3, 9.5 and 3.7, NCH_AH$_{BLeu}$), 3.53 (1H, ddd, *J* = 13.6, 9.4 and 3.2, NCH_AH$_{BAla}$), 2.80 (1H, ddd, *J* = 14.8, 12.4 and 3.4, NCH$_A$$H_{BVal}$), 2.64 (1H, ddd, *J* = 12.6, 10.4 and 1.5, NCH$_A$$H_{BLeu}$), 2.39 (1H, ddd, *J* = 14.3, 11.9 and 3.4, NCH$_A$$H_{BAla}$), 1.78-1.61 (2H, m, C$H_{Val}$ and CH_{Leu}), 1.54 (3H, s, CH_3), 1.50 (3H, s, CH_3), 1.44 (6H, s, 2 x CH_3), 1.41 (6H, s, 2 x CH_3), 1.39 (6H, s, 2 x CH_3), 1.31-1.16 (2H, m, CH_{2Leu}), 1.12 (3H, d, *J* = 6.6, CH_{3iPr}), 1.11 (3H, d, *J* = 6.6, CH_{3iPr}), 1.05 (3H, d, *J* = 6.9, CH_{3Ala}), 0.98-0.82 (12H, m, 2 x CH_{3Val} and 2 x CH_{3Leu}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.5 (*C*=O), 178.0 (*C*=O), 177.6 (*C*=O), 176.6 (*C*=O), 172.2 (*C*=O), 161.1 (2 x *C*=O), 160.6 (*C*=O), 159.3 (*C*=O), 138.0 (=C_{Ar}), 129.4

(2 x =*C*H$_{Ar}$), 129.0 (=*C*H$_{Ar}$), 128.6 (2 x =*C*H$_{Ar}$), 67.7 (O*C*H$_2$), 58.2 (*C*), 57.7 (*C*), 57.6 (*C*), 57.5 (*C*), 56.2 (N*C*$_\beta$H$_{Val}$), 49.4 (N*C*$_\beta$H$_{Leu}$), 48.1 (N*C*$_\alpha$H$_{2Ala}$), 47.5 (N*C*$_\beta$H$_{Ala}$), 46.1 (N*C*$_\alpha$H$_{2Leu}$), 45.3 (N*C*H$_{2Gly}$), 44.0 (*C*$_\alpha$H$_{2Leu}$), 42.9 (N*C*$_\alpha$H$_{2Val}$), 42.7 (N*C*H$_{iPr}$), 32.2 (*C*$_\gamma$H$_{Val}$), 28.3 (*C*H$_3$), 27.3 (*C*H$_3$), 26.9 (*C*H$_3$), 26.5 (*C*H$_3$), 25.9 (*C*$_\delta$H$_{Leu}$), 23.8 (*C*H$_3$), 23.7 (*C*H$_{iPr}$), 23.6 (*C*$_\gamma$H$_{3Leu}$), 23.5 (*C*H$_{iPr}$), 23.3 (*C*H$_3$), 23.2 (*C*H$_3$), 23.1 (*C*H$_3$), 22.5 (*C*$_\gamma$H$_{3Leu}$), 20.1 (*C*$_\delta$H$_{3Val}$), 19.1 (*C*$_\delta$H$_{3Val}$), 18.7 (*C*$_\delta$H$_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3309, 2962, 2932, 2871, 1641, 1544; $[\alpha]_D^{20}$ = +64.4 (c = 1.00; MeOH); **Mp**: 151-153°C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{46}H_{80}N_{12}O_{10}$ $[M+H]^+$ 960.6120, found 976.6189.

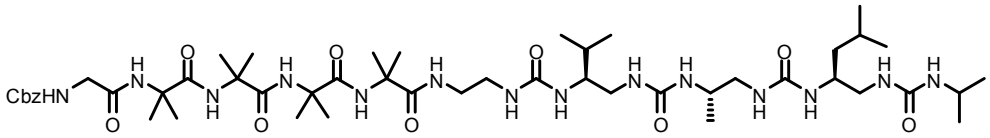
CbzGly-Aib$_4$-(Aib^U)$_{rev}$-Val^u-Ala^u-Leu^u-NH(CO)NH*i*Pr 9c



9c was prepared from CBzGly-Aib-OH (33 mg, 0.06 mmol), HOBt (12 mg, 0.08 mmol), EDC.HCl (13 mg, 0.07 mmol), DIPEA (16 µL, 0.09 mmol) and **U7** (50 mg, 0.08 mmol) as described in the general procedure A. The pure oligomer **9c** (50 mg, 77.9%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD$_3$OH) δ = 8.37 (1H, s, N*H*), 7.88-7.68 (3H, m, N*H*), 7.55-7.40 (2H, m, N*H*$_{Gly}$ and N*H*$_{Aib^u}$), 7.40-7.24 (5H, m, 5 x =C*H*$_{Ar}$), 6.40 (1H, dd, *J* = 9.5 and 3.2, N*H*$_{Ala}$), 6.36 (1H, d, *J* = 9.7, N*H*$_{Leu}$), 6.32 (1H, dd, *J* = 9.4 and 2.2, N*H*$_{Val}$), 6.27 (1H, d, *J* = 8.4, N*H*$_{Leu}$), 6.20 (1H, d, *J* = 7.9, N*H*$_{iPr}$), 5.79 (1H, d, *J* = 10.1, N*H*$_{Ala}$), 5.61 (1H, d, *J* = 10.0, N*H*$_{Val}$), 5.56 (1H, s, N*H*), 5.13 (1H, d, *J* = 12.7, A part of AB pattern, OC*H*$_A$H$_B$), 5.09 (1H, d, *J* = 12.5, B part of AB pattern, OCH$_A$*H*$_B$), 4.14 (1H, dd, *J* = 13.7 and 7.6, NC*H*$_A$H$_{BAib^u}$), 4.09-3.97 (1H, m, NC*H*$_{Ala}$), 3.96-3.86 (1H, m, NC*H*$_{Leu}$), 3.86-3.63 (4H, m, NC*H*$_A$H$_{BVal}$, NC*H*$_{iPr}$ and NC*H*$_{2Gly}$), 3.63-3.45 (3H, m, NC*H*$_{Val}$ and NC*H*$_A$H$_{BLeu}$ and NC*H*$_A$H$_{BAla}$), 2.72 (1H, dd, *J* = 13.5 and 3.6, NCH$_A$*H*$_{BAib^u}$), 2.54-2.51 (1H, m, NCH$_A$*H*$_{BLeu}$), 2.51-2.31 (2H, m, NCH$_A$*H*$_{BVal}$ and NCH$_A$*H*$_{BAla}$), 1.77-1.65 (1H, m, C*H*$_{Leu}$), 1.63-1.52 (1H, m, C*H*$_{Val}$), 1.52 (3H, s, C*H*$_3$), 1.50 (3H, s, C*H*$_3$), 1.45 (3H, s, C*H*$_3$), 1.42-1.35 (18H, m, 6 x C*H*$_3$), 1.25 (3H, s, C*H*$_3$), 1.24-1.17 (2H, m, C*H*$_{2Leu}$), 1.12 (3H, d, *J* = 6.6, C*H*$_{3iPr}$), 1.11 (3H, d, *J* = 6.6, C*H*$_{3iPr}$), 1.03 (3H, d, *J* = 6.9, C*H*$_{3Ala}$), 0.97-0.85 (12H, m, 2 x C*H*$_{3Val}$ and 2 x C*H*$_{3Leu}$). **^{13}C NMR** (125 MHz, CD$_3$OH) δ = 177.8 (*C*=O), 177.3 (*C*=O), 177.1 (*C*=O), 176.6 (*C*=O), 172.2 (*C*=O), 161.8 (*C*=O), 161.5 (*C*=O), 160.6 (*C*=O), 160.3 (*C*=O), 159.3 (*C*=O), 138.0 (=*C*$_{Ar}$), 129.4 (2 x =*C*H$_{Ar}$), 129.0 (=*C*H$_{Ar}$), 128.6 (2 x =*C*H$_{Ar}$), 67.7 (O*C*H$_2$), 58.2 (*C*), 57.8 (*C*), 57.7 (*C*), 57.5 (*C*), 55.9 (N*C*$_\beta$H$_{Val}$), 53.7 (*C*), 49.2 (N*C*$_\beta$H$_{Leu}$), 48.4 (N*C*H$_{2Aib^u}$), 47.8 (N*C*$_\alpha$H$_{2Ala}$), 46.5 (N*C*$_\beta$H$_{Ala}$), 46.2 (N*C*$_\alpha$H$_{2Leu}$), 45.2 (N*C*H$_{2Gly}$), 44.6 (N*C*$_\alpha$H$_{2Val}$), 43.9 (*C*$_\alpha$H$_{2Leu}$), 42.7 (N*C*H$_{iPr}$), 32.0 (*C*$_\gamma$H$_{Val}$), 27.5 (*C*H$_3$), 27.2 (*C*H$_3$), 26.1 (*C*H$_3$), 25.9 (2 x *C*H$_3$), 25.6 (*C*$_\delta$H$_{Leu}$), 25.0 (*C*H$_3$), 24.8 (*C*H$_3$), 24.6 (*C*H$_3$), 23.6 (*C*H$_{iPr}$), 23.6 (*C*H$_{iPr}$), 23.5 (*C*$_\gamma$H$_{3Leu}$), 22.5 (*C*$_\gamma$H$_{3Leu}$), 20.1 (*C*$_\delta$H$_{3Val}$), 18.8 (*C*$_\delta$H$_{3Ala}$), 18.6 (*C*$_\delta$H$_{3Val}$).

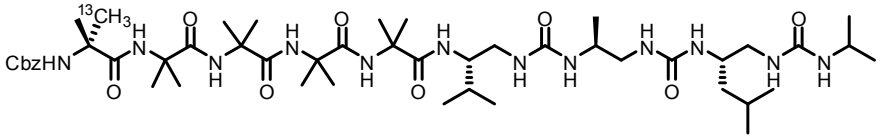
IR (film, cm^{-1}): ν_{max} = 3326, 2970, 2871, 1642, 1551; $[\alpha]_D^{20}$ = +50.4 (c = 1.00; MeOH); **Mp**: > 200°C; **MS** (ES^+): *m/z* calcd for $C_{51}H_{91}N_{14}O_{11}$ $[M+H]^+$ 1076.3.

CbzGly-Aib$_4$-(Aib^U)$_{rev}$-Val^u-Ala^u-Leu^u-NH(CO)NH*i*Pr 10c



10c was prepared from CBzGly-Aib-OH (34 mg, 0.06 mmol), HOBt (12 mg, 0.08 mmol), EDC.HCl (13 mg, 0.07 mmol), DIPEA (16 µL, 0.09 mmol) and **U8** (50 mg, 0.08 mmol) as described in the general procedure A. The pure oligomer **10c** (53 mg, 81.0%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.41 (1H, s, N*H*), 7.83 (1H, s, N*H*), 7.79 (1H, s, N*H*), 7.76 (1H, s, N*H*), 7.51-7.42 (1H, m, NH_{Gly}), 7.39-7.27 (6H, m, 5 x =CH_{Ar} and NH_{EDA}), 6.37 (1H, d, *J* = 8.3, NH_{Leu}), 6.30 (1H, d, *J* = 6.7, NH_{Ala}), 6.18 (1H, d, *J* = 7.9, NH_{iPr}), 6.07 (1H, d, *J* = 8.6, NH_{Val}), 6.02 (1H, d, *J* = 9.8, NH_{Leu}), 5.99-5.88 (2H, m, NH_{EDA} and NH_{Ala}), 5.63 (1H, d, *J* = 10.2, NH_{Val}), 5.15 (1H, d, *J* = 12.6, A part of AB pattern, OCH_AH$_B$), 5.09 (1H, d, *J* = 12.5, B part of AB pattern, OCH$_A$$H_B$), 4.14-3.99 (1H, m, NC$H_{Ala}$), 3.98-3.86 (1H, m, NC$H_{Leu}$), 3.86-3.73 (3H, m, NC$H_AH_{BEDA}$, NC$H_AH_{BGly}$ and NCH_{iPr}), 3.72-3.43 (6H, m, NCH_{Val}, NCH_AH$_{BVal}$, NCH_AH$_{BLeu}$, NCH_AH$_{BAla}$, NCH_AH$_{BEDA}$ and NCH$_A$$H_{BGly}$), 3.11-2.98 (1H, m, NCH$_A$$H_{BEDA}$), 2.95-2.80 (1H, m, NCH$_A$$H_{BEDA}$), 2.70-2.56 (1H, m, NCH$_A$$H_{BLeu}$), 2.56-2.40 (2H, m, NCH$_A$$H_{BVal}$ and NCH$_A$$H_{BAla}$), 1.76-1.65 (1H, m, C$H_{Leu}$), 1.64-1.55 (1H, m, C$H_{Val}$), 1.51 (6H, m, 2 x C$H_3$), 1.47-1.36 (18H, m, 6 x CH_3), 1.28-1.17 (2H, m, CH_{2Leu}), 1.12 (3H, d, *J* = 6.6, CH_{3iPr}), 1.11 (3H, d, *J* = 6.6, CH_{3iPr}), 1.06 (3H, d, *J* = 6.9, CH_{3Ala}), 0.97-0.85 (12H, m, 2 x CH_{3Leu} and 2 x CH_{3Val}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.4 (*C*=O), 177.7 (*C*=O), 176.8 (*C*=O), 172.2 (*C*=O), 161.7 (*C*=O), 161.4 (*C*=O), 161.3 (*C*=O), 160.6 (*C*=O), 160.6 (*C*=O), 159.4 (*C*=O), 138.0 (=C_{Ar}), 129.5 (2 x =CH_{Ar}), 129.0 (=CH_{Ar}), 128.6 (2 x =CH_{Ar}), 67.7 (OCH_2), 58.0 (*C*), 57.8 (*C*), 57.6 (*C*), 57.6 (*C*), 56.4 (NC$_\beta$H$_{Val}$), 49.3 (NC$_\beta$H$_{Leu}$), 48.1 (NC□H$_{2Ala}$), 46.3 (NC$_\beta$H$_{Ala}$), 46.2 (NC□H$_{2Leu}$), 45.3 (NCH$_{2Gly}$), 44.6 (NC□H$_{2Val}$), 44.0 (C□H$_{2Leu}$), 42.8 (NCH_{iPr}), 40.3 (NCH_2), 40.2 (NCH_2), 32.0 (C$_\gamma$H$_{Val}$), 27.6 (*C*H$_3$), 27.0 (*C*H$_3$), 26.5 (*C*H$_3$), 26.1 (*C*H$_3$), 25.8 (C$_\delta$H$_{Leu}$), 24.2 (*C*H$_3$), 23.8 (*C*H$_3$), 23.7 (*C*H$_3$), 23.7 (*C*H$_{3iPr}$), 23.6 (*C*H$_{3iPr}$), 23.6 (C$_\epsilon$H$_{3Leu}$), 23.5 (*C*H$_3$), 22.5 (C$_\epsilon$H$_{3Leu}$), 20.2 (C$_\delta$H$_{3Val}$), 18.7 (C$_\delta$H$_{3Ala}$), 18.6 (C$_\delta$H$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3338, 2960, 2934, 2872, 1639, 1549; $[\alpha]_D^{20}$ = +55.2 (c = 1.00; MeOH); **Mp**: 162-164 °C; **MS** (ES^+): *m/z* calcd for $C_{49}H_{87}N_{14}O_{11}$ $[M+H]^+$ 1047.9.

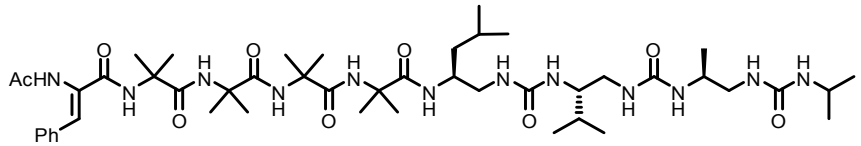
Cbz-Aib*-Aib$_4$-(Aib^U)$_{rev}$-Val^u-Ala^u-Leu^u-NH(CO)NH*i*Pr 11



$C_{47}{}^{13}CH_{84}N_{12}O_{10}$
M = 990.25 g.mol^{-1}

11 was prepared from CBzAib*-Aib-OH (50 mg, 0.09 mmol), HOBt (17 mg, 0.11 mmol), EDC.HCl (18 mg, 0.10 mmol), DIPEA (22 µL, 0.13 mmol) and **U6** (75 mg, 0.11 mmol) as described in the general procedure A. The pure oligomer **11** (70 mg, 82.7%) was isolated as a white solid. **^{1}H NMR** (500 MHz, CD_3OH) δ = 8.11 (1H, s, N*H*), 7.97 (1H, s, N*H*), 7.83 (1H, s, N*H*), 7.72 (1H, s, N*H*), 7.61 (1H, s, N*H*), 7.44-7.25 (5H, m, 5 x =CH_{Ar}), 7.15 (1H, d, *J* = 10.1, NH_{Val}), 6.31 (1H, d, *J* = 7.6, NH_{Leu}), 6.22 (1H, d, *J* = 7.9, NH_{iPr}), 6.04 (1H, d, *J* = 9.7, NH_{Leu}), 5.95 (1H, dd, *J* = 9.1 and 3.8, NH_{Ala}), 5.70 (1H, dd, *J* = 9.4 and 3.4, NH_{Val}), 5.46 (1H, d, *J* = 10.2, NH_{Ala}), 5.22 (1H, d, *J* = 12.9, A part of AB pattern, OCH_AH$_B$), 5.04 (1H, d, *J* = 12.7, B part of AB pattern, OCH$_A$$H_B$), 4.18-4.03 (1H, m, NC$H_{Ala}$), 4.01-3.88 (1H, m, NC$H_{Leu}$), 3.88-3.75 (2H, m, NC$H_{iPr}$ and NCH_{Val}), 3.68 (1H, ddd, *J* = 13.9, 9.6 and 3.8, NCH_AH$_{BVal}$), 3.61 (1H, ddd, *J* = 13.2, 9.6 and 3.6, NCH_AH$_{BLeu}$), 3.53 (1H, ddd, *J* = 13.7, 9.5 and 3.3, NCH_AH$_{BAla}$), 2.80 (1H, ddd, *J* = 14.9, 12.4 and 3.6, NCH$_A$$H_{BVal}$), 2.64 (1H, ddd, *J* = 12.5, 10.0 and 1.3, NCH$_A$$H_{BLeu}$), 2.39 (1H, ddd, *J* = 14.4, 11.7 and 3.6, NCH$_A$$H_{BAla}$), 1.77-1.62 (2H, m, C$H_{Val}$ and CH_{Leu}), 1.56-1.18 (32H, m, 10 x CH_3 and CH_{2Leu}), 1.12 (3H, d, *J* = 6.6, CH_{3iPr}), 1.11 (3H, d, *J* = 6.6, CH_{3iPr}), 1.05 (3H, d, *J* = 6.9, CH_{3Ala}), 0.96-0.86 (12H, m, 2 x CH_{3Val} and 2 x CH_{3Leu}). **^{13}C NMR** (125 MHz, CD_3OH) δ = 178.5 (*C*=O), 178.0 (*C*=O), 177.9 (*C*=O), 177.2 (*C*=O), 177.0 (*C*=O), 161.1 (2 x *C*=O), 160.6 (*C*=O), 157.9 (*C*=O), 138.6 (=C_{Ar}), 129.5 (2 x =CH_{Ar}), 128.9 (=CH_{Ar}), 128.4 (2 x =CH_{Ar}), 67.5 (OCH_2), 58.2 (*C*), 57.8 (d, $^1J_{C\text{-}^{13}C}$ = 39, $^{13}CH_3C$), 57.7 (*C*), 57.6 (*C*), 57.5 (*C*), 56.2 (NC$_\beta$H$_{Val}$), 49.4 (NC$_\beta$H$_{Leu}$), 48.1 (NC$_\alpha$H$_{2Ala}$), 46.2 (NC$_\beta$H$_{Ala}$), 46.1 (NC$_\alpha$H$_{2Leu}$), 44.0 (C$_\alpha$H$_{2Leu}$), 43.0 (NC$_\alpha$H$_{2Val}$), 42.7 (NCH$_{iPr}$), 32.2 (C$_\gamma$H$_{Val}$), 28.3 (*C*H$_3$), 27.4 (*C*H$_3$), 27.0 (*C*H$_3$), 26.8 (*C*H$_3$), 26.2 (^{13}*C*H$_{3minor}$), 25.8 (C$_\delta$H$_{Leu}$), 24.4 (*C*H$_3$), 24.1 (^{13}*C*H$_{3major}$), 23.7 (*C*H$_{iPr}$), 23.6 (C$_\gamma$H$_{3Leu}$), 23.5 (*C*H$_{iPr}$), 23.3 (*C*H$_3$), 23.2 (*C*H$_3$), 23.1 (*C*H$_3$), 22.5 (C$_\gamma$H$_{3Leu}$), 20.1 (C$_\delta$H$_{3Val}$), 19.1 (C$_\delta$H$_{3Val}$), 18.7 (C$_\delta$H$_{3Ala}$). **IR** (film, cm^{-1}): ν_{max} = 3316, 2971, 2871, 1645, 1536; **$[\alpha]_D^{20}$** = +62.4 (c = 1.00; MeOH); **Mp**: 148-150 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{47}H_{85}N_{12}O_{10}$ $[M+H]^+$ 990.6545, found 990.6538.

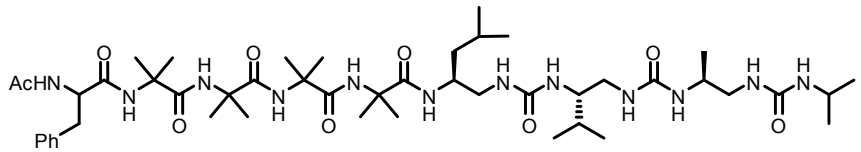
Ac$^{\Delta}$Phe-Aib$_4$-Leu^{u}-Val^{u}-Ala^{u}-NH(CO)NH*i*Pr 12



$C_{47}H_{80}N_{12}O_9$
M = 957.21 g.mol^{-1}

To a stirred solution of H-Aib$_4$-Leu^{u}-Val^{u}-Ala^{u}-NH(CO)NH*i*Pr (34 mg, 0.43 mmol; obtained in quantitative yield by hydrogenolysis of N_3-Aib$_4$-Leu^{u}-Val^{u}-Ala^{u}-NH(CO)NH*i*Pr) and Et_3N (9 μL, 0.06 mmol) in DMF (214 μL) was added **A1** (15 mg, 0.08 mmol) and the reaction stirred at reflux for 5 d. The solvents were removed under reduced pressure and purification by column chromatography (SiO_2; CH_2Cl_2:MeOH; 99:1→90:10) gave the title compound as a white solid (13 mg, 31.8%). **^{1}H NMR** (400 MHz, CD_3OH) δ = 7.95-7.89 (1H, m, N*H*), 7.61-7.53 (2H, m, 2 x =C*H*$_{Ar}$), 7.50-7.43 (2H, m, 2 x =C*H*$_{Ar}$), 7.40-7.34 (1H, m, =C*H*$_{Ar}$), 7.33-7.22 (1H, m, N*H*), 6.90 (1H, s, =C*H*), 5.89-5.80 (1H, m, N*H*), 5.62 (1H, d, *J* = 10.1, N*H*), 4.32-4.15 (1H, m, NC*H*$_{Leu}$), 4.01-3.90 (1H, m, NC*H*$_{Ala}$), 3.89-3.81 (1H, m, NC*H*$_{iPr}$), 3.77-3.47 (4H, m, NC*H*$_{Val}$, NC*H*$_A$H$_{BVal}$, NC*H*$_A$H$_{BLeu}$ and NC*H*$_A$H$_{BAla}$), 2.83-2.62 (2H, m, NCH$_A$*H*$_{BAla}$ and NCH$_A$*H*$_{BLeu}$), 2.57-2.40 (1H, m, NCH$_A$*H*$_{BVal}$), 2.18 (3H, s, C*H*$_3$), 1.76-1.61 (2H, m, C*H*$_{Leu}$ and C*H*$_{Val}$), 1.60-1.47 (24H, m, 8 x C*H*$_3$), 1.46-1.36 (1H, m, C*H*$_A$H$_{BLeu}$), 1.31-1.19 (1H, m, CH$_A$*H*$_{BLeu}$), 1.16 (6H, d, *J* = 6.5, 2 x C*H*$_{3iPr}$), 1.09 (3H, d, *J* = 6.7, C*H*$_{3Ala}$), 1.03-0.84 (12H, m, 2 x C*H*$_{3Val}$ and 2 x C*H*$_{3Leu}$). **^{13}C NMR** (100 MHz, CD_3OH) δ = 178.2 (*C*=O), 178.1 (*C*=O), 176.8 (*C*=O), 176.9 (*C*=O), 173.1 (*C*=O), 161.7 (*C*=O), 161.3 (*C*=O), 161.3 (*C*=O), 160.7 (*C*=O), 135.1 (=*C*), 131.5 (=*C*), 130.6 (2 x =*C*H), 130.0 (=*C*H), 129.9 (2 x =*C*H), 127.3 (=*C*H), 58.4 (*C*), 58.2 (*C*), 58.0 (*C*), 57.7 (*C*), 56.3 (NC$_\beta$H$_{Val}$), 48.7 (NC$_\beta$H$_{Leu}$), 47.0 (NC$_\beta$H$_{Ala}$), 46.7 (NC□H$_{2Ala}$), 45.8 (NC□H$_{2Leu}$), 44.4 (NC□H$_{2Val}$), 42.8 (NCH$_{iPr}$), 42.3 (C□H$_{2Leu}$), 32.2 (C$_\gamma$H$_{Val}$), 28.3 (*C*H$_3$), 27.5 (*C*H$_3$), 26.9 (*C*H$_3$), 26.8 (*C*H$_3$), 26.3 (*C*H$_3$), 23.9 (C$_\delta$H$_{Leu}$), 23.8 (*C*H$_{iPr}$), 23.7 (*C*H$_{iPr}$), 23.7 (C□H$_{3Leu}$), 23.5 (*C*H$_3$), 23.2 (*C*H$_3$), 23.2 (*C*H$_3$), 22.8 (*C*H$_3$), 22.4 (C□H$_{3Leu}$), 20.2 (C$_\delta$H$_{3Val}$), 19.6 (C$_\delta$H$_{3Ala}$), 18.5 (C$_\delta$H$_{3Val}$). 3435, 2972, 2949, 1625, 1493; **$[\alpha]_D^{20}$** = + 41.0 (c = 1.00; MeOH); **Mp**: >200 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{47}H_{80}O_{12}N_9Na$ $[M+Na]^+$ 979.6069, found 979.6024.

AcPhAla-Aib$_4$-Leu^{u}-Val^{u}-Ala^{u}-NH(CO)NH*i*Pr 13

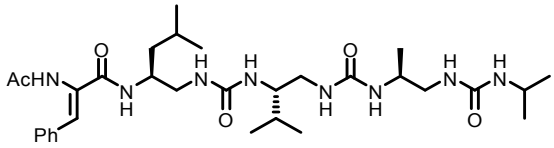


$C_{47}H_{82}N_{12}O_9$
M = 959.23 g.mol^{-1}

A round-bottomed flask was charged with a solution of **12** (12 mg, 0.013 mmol) in EtOH (200 μL) and 10% m. of Pd/C was added carefully. The mixture was stirred under H_2 atmosphere (balloon) for 48 h.

Upon completion, the mixture was filtered through a celite pad and washed with EtOH. The mixture was then concentrated under reduced pressure to give compounds **13a** and **13b** (11 mg, 91.5%, diastereoselecitive ratio 1/3). **^{1}H NMR** (400 MHz, CD_3OH) δ = 7.39-7.16 (5H, m, =CH_{Ar}), 4.45 (0.25H, t, *J* = 7.7, AcNC*H*), 4.35 (0.75H, t, *J* = 8.0, AcNC*H*), 4.27-4.10 (1H, m, NCH_{Leu}), 3.99-3.77 (2H, m, NCH_{Ala} and NCH_{iPr}), 3.75-3.48 (4H, m, NCH_{Val}, NCH_AH$_{BVal}$, NCH_AH$_{BLeu}$, NCH_AH$_{BAla}$), 3.18-2.90 (2H, m, CH_2), 2.76-2.38 (3H, m, NCH$_A$$H_{BLeu}$, NCH$_A$$H_{BVal}$ and NCH$_A$$H_{BAla}$), 1.97 (3H, s, C$H_3$), 1.73-1.58 (2H, m, C$H_{Leu}$ and CH_{Val}), 1.57-1.17 (26H, m, 8 x CH_3 and CH_{2Leu}), 1.13 (6H, d, *J* = 6.6, 2 x CH_{3iPr}), 1.06 (3H, d, *J* = 6.7, CH_{3Ala}), 1.0-0.81 (12H, m, 2 x CH_{3Val} and 2 x CH_{3Leu}).**^{13}C NMR** (100 MHz, CD_3OH) δ = 178.1 (*C*=O), 178.1 (*C*=O), 177.7 (*C*=O), 176.8 (*C*=O), 174.3 (*C*=O), 173.8 (*C*=O), 173.6 (*C*=O), 161.7 (*C*=O), 161.3 (*C*=O), 160.7 (*C*=O), 138.1 (=*C*), 137.8 (=*C*), 130.5 (2 x =*C*H), 130.4 (=*C*H), 129.5 (2 x =*C*H), 128.0 (3 x =*C*H), 127.9 (2 x =*C*H), 58.3 (*C*), 58.2 (*C*), 57.8 (*C*), 57.7 (*C*), 57.7 (*C*), 57.6 (*C*), 57.5 (*C*), 57.3 (*C*), 57.1 (NC_βH$_{Val}$), 56.2 (N*C*H), 48.7 (NC_βH$_{Leu}$), 47.0 (NC_βH$_{Ala}$), 46.7 (NC_αH$_{2Ala}$), 45.8 (NC_αH$_{2Leu}$), 44.4 (NC_αH$_{2Val}$), 42.8 (NCH$_{iPr}$), 42.3 (C_αH$_{2Leu}$), 38.1 (N*C*H), 38.0 (N*C*H), 32.2 (C_γH$_{Val}$), 28.3 (*C*H$_3$), 27.7 (*C*H$_3$), 27.3 (*C*H$_3$), 26.8 (*C*H$_3$), 26.3 (*C*H$_3$), 24.2 (C_δH$_{Leu}$), 23.8 (*C*H$_{iPr}$), 23.8 (*C*H$_{iPr}$), 23.7 (C_γH$_{3Leu}$), 23.4 (*C*H$_3$), 23.2 (*C*H$_3$), 23.2 (*C*H$_3$), 22.4 (*C*H$_3$), 22.4 (C_γH$_{3Leu}$), 20.2 (C_δH$_{3Val}$), 19.5 (C_δH$_{3Ala}$), 18.5 (C_δH$_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3334, 2693, 2930, 1632, 1574, 1472; **HRMS** (ESI$^+$): *m/z* calcd for $C_{47}H_{82}O_{12}N_9Na$ $[M+Na]^+$ 981.6225, found 981.6191.

Ac$^{\Delta}$Phe-Leu^{u}-Val^{u}-Ala^{u}-NH(CO)NH*i*Pr 14

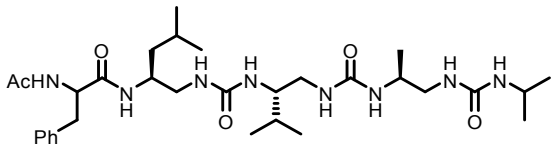


$C_{31}H_{52}N_8O_5$
M = 616.80 g.mol^{-1}

Boc-protected oligourea U9 (80 mg, 0.15 mmol) was dissolved in TFA (800 µl) and stirred for 45 min. The reaction mixture was then concentrated under reduced. Triethylamine (14 µL, 0.14 mmol) and an **A1** (25 mg, 0.13 mmol) were added to the crude product was then dissolved in acetonitrile. The reaction stirred at reflux for 5 d. The solvents were removed under reduced pressure and purification by column chromatography (SiO_2; CH_2Cl_2:MeOH; 99:1→90:10) gave the title compound as a white solid (50 mg, 87%). **^{1}H NMR** (400 MHz, CD_3OH) δ = 7.60-7.51 (2H, m, =CH_{Ar}), 7.47-7.38 (2H, m, =CH_{Ar}), 7.38-7.29 (1H, m, =CH_{Ar}), 6.89 (1H, s, =C*H*), 4.37-4.23 (1H, m, NCH_{Leu}), 3.95-3.87 (1H, m, NCH_{Ala}), 3.86-3.70 (1H, m, NCH_{iPr}), 3.70-3.56 (3H, m, NCH_{Val}, NCH_AH$_{BVal}$ and NCH_AH$_{BAla}$), 3.55-3.44 (1H, m, NCH_AH$_{BLeu}$), 2.70 (1H, dd, *J* = 13.2 and 9.5, NCH$_A$$H_{BLeu}$), 2.62 (1H, t, *J* = 12.2, NCH$_A$$H_{BAla}$), 2.50 (1H, t, *J* = 12.4, NCH$_A$$H_{BVal}$), 2.13 (3H, s, C$H_3$), 1.81-1.69 (1H, m, C$H_{Leu}$), 1.65 (1H, oct, *J* =, CH_{Val}), 1.44 (1H, ddd, *J* = 7.1, CH_AH$_{BLeu}$), 1.26 (1H, ddd, *J* = 7.1, CH$_A$$H_{BLeu}$), 1.14 (6H, d, *J* = 6.5, 2 x CH_{3iPr}), 1.04 (3H, d, *J* = 6.8,

CH_{3Ala}), 1.01-0.86 (12H, m, 2 x CH_{3Val} and 2 x CH_{3Leu}). **^{13}C NMR** (100 MHz, CD_3OH) δ = 173.5 (*C*=O), 168.9 (*C*=O), 161.6 (*C*=O), 161.2 (*C*=O), 160.6 (*C*=O), 135.1 (=*C*), 131.7 (=*C*), 130.5 (2 x =*C*H), 130.0 (=*C*H), 129.9 (2 x =*C*H), 127.9 (=*C*H), 56.3 (N$C_\beta H_{Val}$), 49.7(N$C_\beta H_{Leu}$), 47.0 (N$C_\beta H_{Ala}$), 46.7 (N$C_\alpha H_{2Ala}$), 46.3 (N$C_\alpha H_{2Leu}$), 44.1 (N$C_\alpha H_{2Val}$), 42.8 (N*C*H$_{iPr}$), 42.0 ($C_\alpha H_{2Leu}$), 32.1 ($C_\gamma H_{Val}$), 26.5 ($C_\delta H_{Leu}$), 23.8 ($C_\epsilon H_{3Leu}$), 23.7 (2 x *C*H$_{iPr}$), 22.7 (*C*H$_3$ and $C_\epsilon H_{3Leu}$), 20.1 ($C_\delta H_{3Val}$), 19.4 ($C_\delta H_{3Ala}$), 18.5 ($C_\delta H_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3428, 2962, 2929, 2872, 1619, 1480; **$[\alpha]_D^{20}$** = + 72 (c = 1.00; MeOH); **Mp**: 145-146 °C; **HRMS** (ESI$^+$): *m/z* calcd for $C_{31}H_{52}O_5N_8Na$ $[M+Na]^+$ 639.3958, found 639.3965.

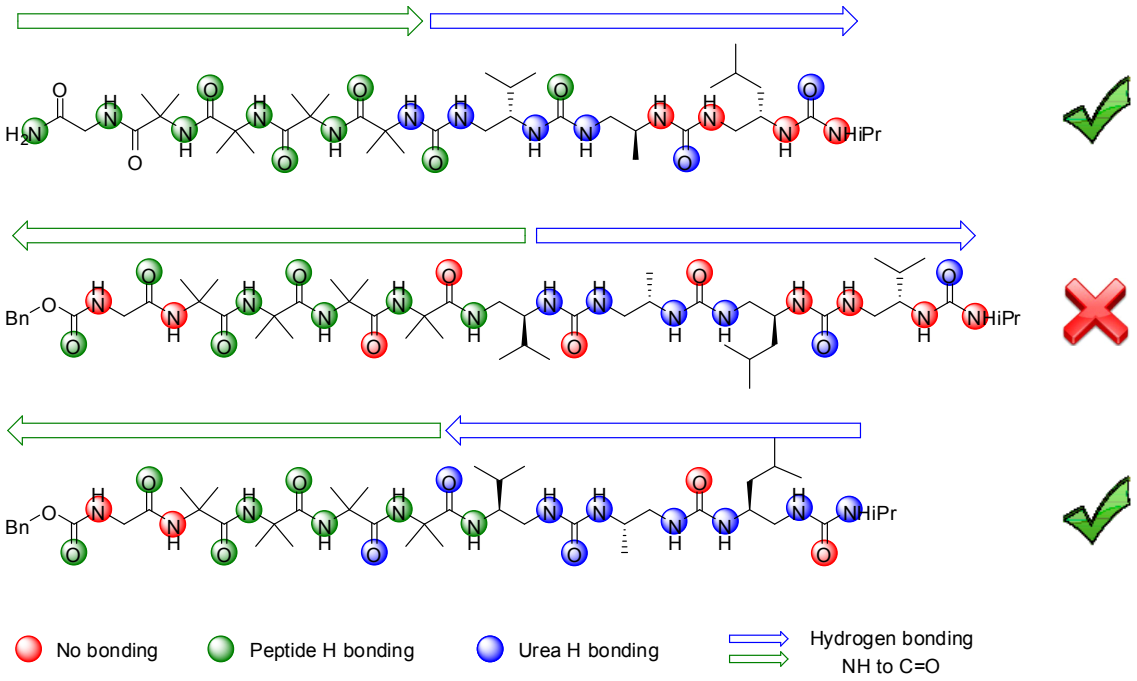
AcPhAla-Leu^u-Val^u-Ala^u-NH(CO)NH*i*Pr 15



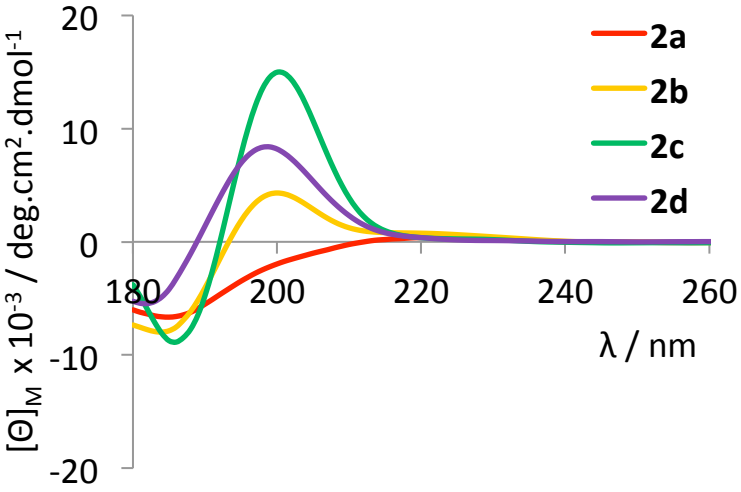
$C_{31}H_{54}N_8O_5$
M = 618.80 g.mol^{-1}

A round-bottomed flask was charged with a solution of **14** (6 mg, 0.01 mmol) in EtOH (200 µL) and 10% m. of Pd/C was added carefully. The mixture was stirred under H_2 atmosphere (balloon) for 48 h. Upon completion, the mixture was filtered through a celite pad and washed with EtOH. The mixture was then concentrated under reduced pressure to give compounds **15a** and **15b** (5 mg, 83%, diastereoselecitive ratio 1/1.3). **^{1}H NMR** (400 MHz, CD_3OH) δ = 7.38-7.12 (5H, m, =CH_{Ar}), 4.56 (0.42H, dd, *J* = 9.5 and 5.5, AcNC*H*), 4.56 (0.58H, t, *J* = 7.9, AcNC*H*), 4.20-4.03 (1H, m, NCH_{Leu}), 3.94-3.75 (2H, m, NCH_{Ala} and NCH_{iPr}), 3.67-3.39 (4H, m, NCH_{Val}, NCH_AH$_{BVal}$, NCH_AH$_{BLeu}$, NCH_AH$_{BAla}$), 3.15 (0.43H, dd, *J* = 14.2 and 5.6, CH_ACH$_B$), 3.00 (1.18H, d, *J* = 7.9, CH_2), 2.94 (0.43H, dd, *J* = 14.1 and 9.5, CH$_A$CH_B), 2.76-2.36 (3H, m, NCH$_A$$H_{BLeu}$, NCH$_A$$H_{BVal}$ and NCH$_A$$H_{BAla}$), 1.97 (1.65H, s, C$H_3$), 1.93 (1.27H, s, C$H_3$), 1.70-1.57 (2H, m, C$H_{Leu}$ and CH_{Val}), 1.41-1.32 (1H, m, CH_AH$_{BLeu}$), 1.26-1.17 (1H, m, CH$_A$$H_{BLeu}$), 1.16-0.70 (21H, m, 2 x CH_{3iPr}, CH_{3Ala}, 2 x CH_{3Val} and 2 x CH_{3Leu}). **^{13}C NMR** (100 MHz, CD_3OH) δ = 174.3 (*C*=O), 174.2 (*C*=O), 173.7 (*C*=O), 173.6 (*C*=O), 162.7 (*C*=O), 161.4 (*C*=O), 161.3 (*C*=O), 161.2 (*C*=O), 161.2 (*C*=O), 160.6 (*C*=O), 138.6 (=*C*), 137.9 (=*C*), 130.3 (2 x =*C*H), 130.2 (2 x =*C*H), 129.6 (2 x =*C*H), 129.5 (2 x =*C*H), 128.0 (=*C*H), 127.9 (=*C*H), 64.3 (N$C_\beta H_{Val}$), 57.7 (N*C*H), 56.9 (N$C_\beta H_{Val}$), 56.2 (N*C*H), 49.2 (N$C_\beta H_{Leu}$), 49.0 (N$C_\beta H_{Leu}$), 47.3 (N$C_\beta H_{Ala}$), 47.2 (N$C_\beta H_{Ala}$), 46.7 (N$C_\alpha H_{2Ala}$), 46.6 (N$C_\alpha H_{2Ala}$), 46.2 (N$C_\alpha H_{2Leu}$), 46.1 (N$C_\alpha H_{2Leu}$), 44.4 (N$C_\alpha H_{2Val}$), 42.8 (N*C*H$_{iPr}$), 42.8 (N*C*H$_{iPr}$), 41.9 ($C_\alpha H_{2Leu}$), 38.8 (CH_2), 38.7 (CH_2), 32.0 ($C_\gamma H_{Val}$), 31.9 ($C_\gamma H_{Val}$), 26.0 ($C_\delta H_{Leu}$), 25.5 ($C_\delta H_{Leu}$), 24.2 ($C_\epsilon H_{3Leu}$), 23.8 ($C_\epsilon H_{3Leu}$), 23.7 (*C*H$_{iPr}$), 23.6 (CH$_{iPr}$), 23.6 (2 x *C*H$_{iPr}$), 22.5 (*C*H$_3$), 22.5 (*C*H$_3$), 22.4 ($C_\epsilon H_{3Leu}$), 22.4 ($C_\epsilon H_{3Leu}$), 20.1 ($C_\delta H_{3Val}$), 20.1 ($C_\delta H_{3Val}$), 19.5 ($C_\delta H_{3Ala}$), 19.4 ($C_\delta H_{3Ala}$), 18.6 ($C_\delta H_{3Val}$), 18.4 ($C_\delta H_{3Val}$). **IR** (film, cm^{-1}): ν_{max} = 3350, 2962, 2929, 1625, 1574, 1480; **HRMS** (ESI$^+$): *m/z* calcd for $C_{31}H_{54}O_5N_8Na$ $[M+Na]^+$ 641.4115, found 641.4101.

Hydrogen Bonding of 2d, 7e and 8c



CD spectra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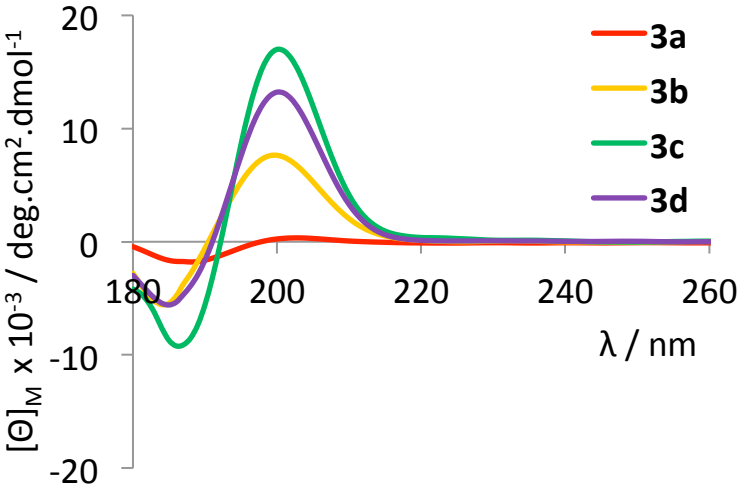
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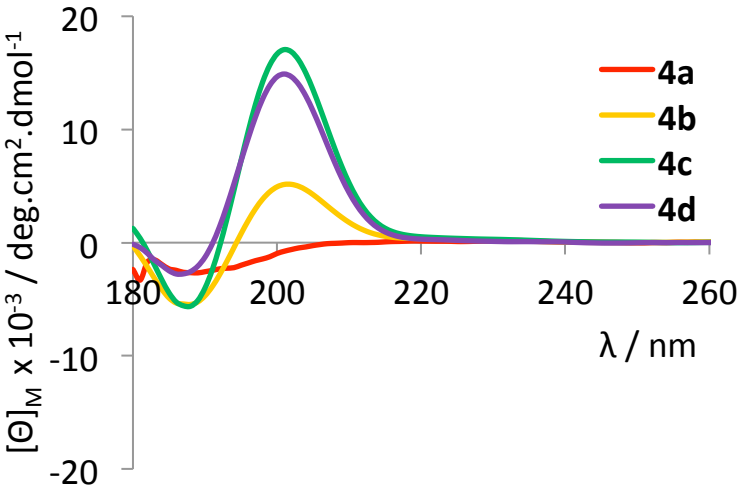
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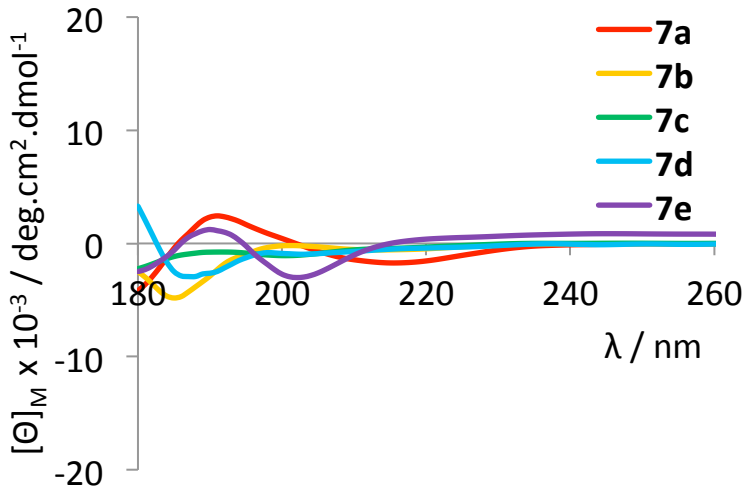
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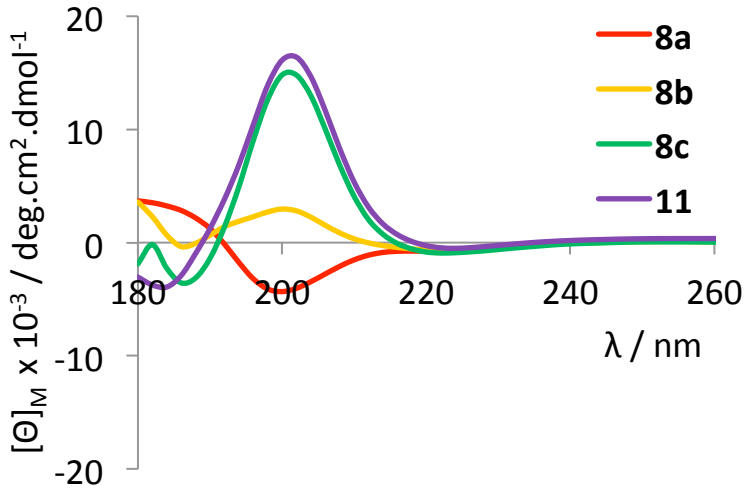
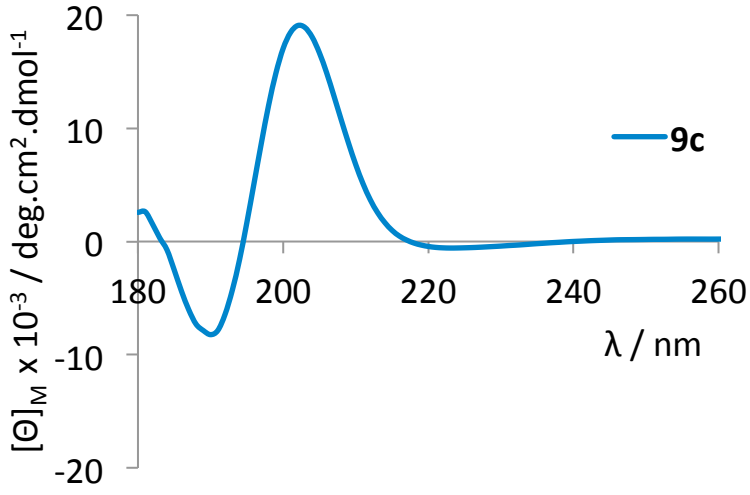
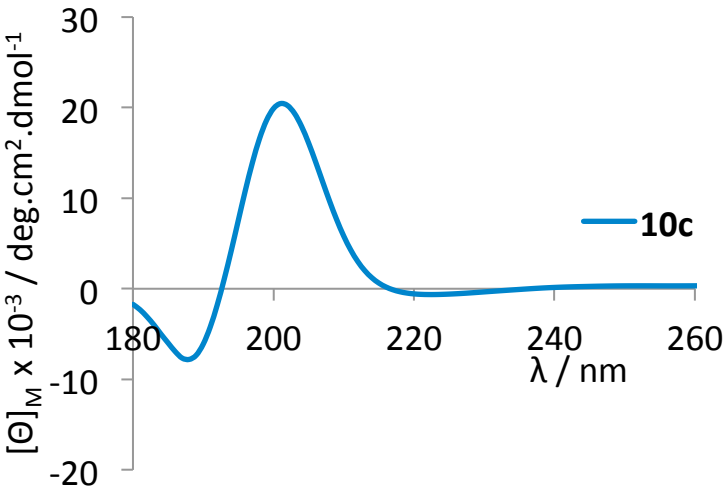
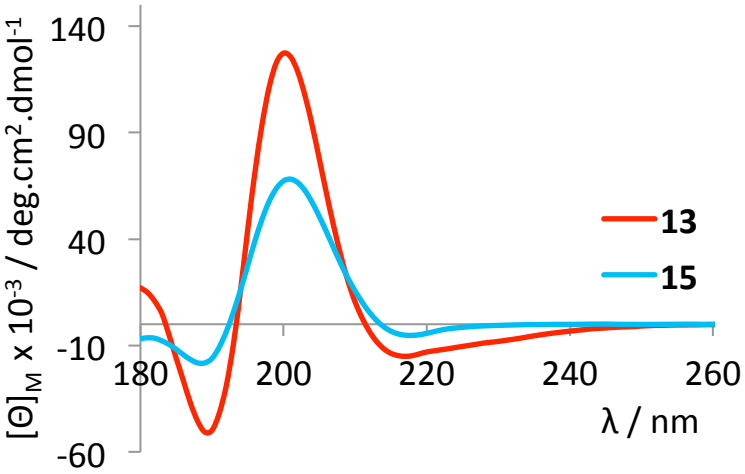
7d
7e

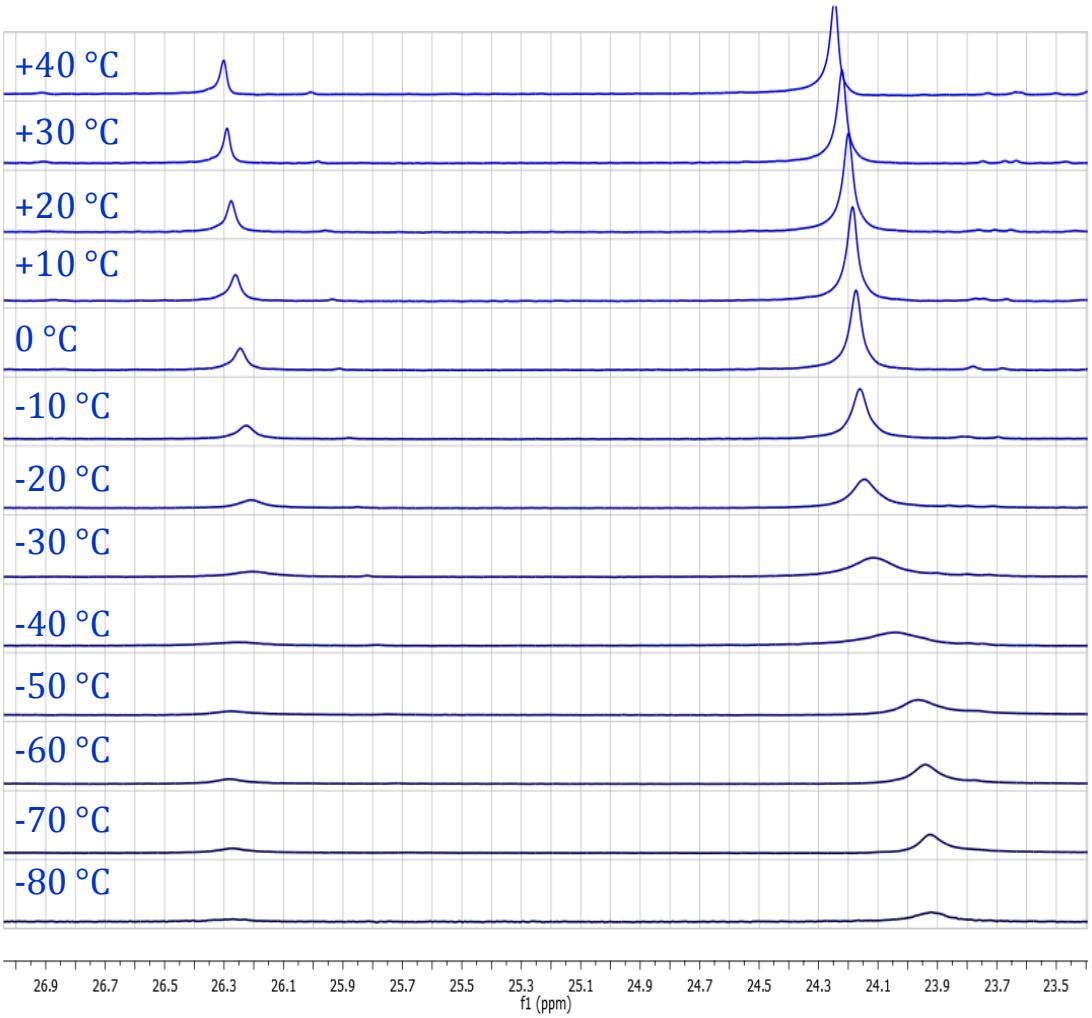

20
10
0
-10
-20
180
200
220
240
260
λ / nm
[Θ]M x 10-3 / deg.cm2.dmol-1
8a
8b
8c
11

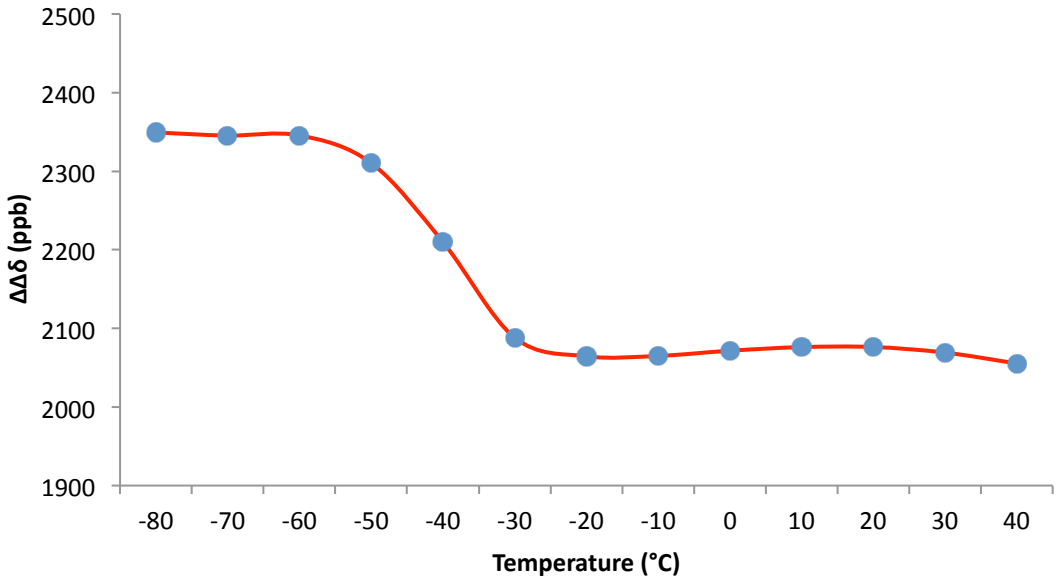

20
10
0
-10
-20
180
200
220
240
260
λ / nm
[Θ]M x 10-3 / deg.cm2.dmol-1
9c


30
20
10
0
-10
-20
180
200
220
240
260
λ / nm
[Θ]M x 10-3 / deg.cm2.dmol-1
10c

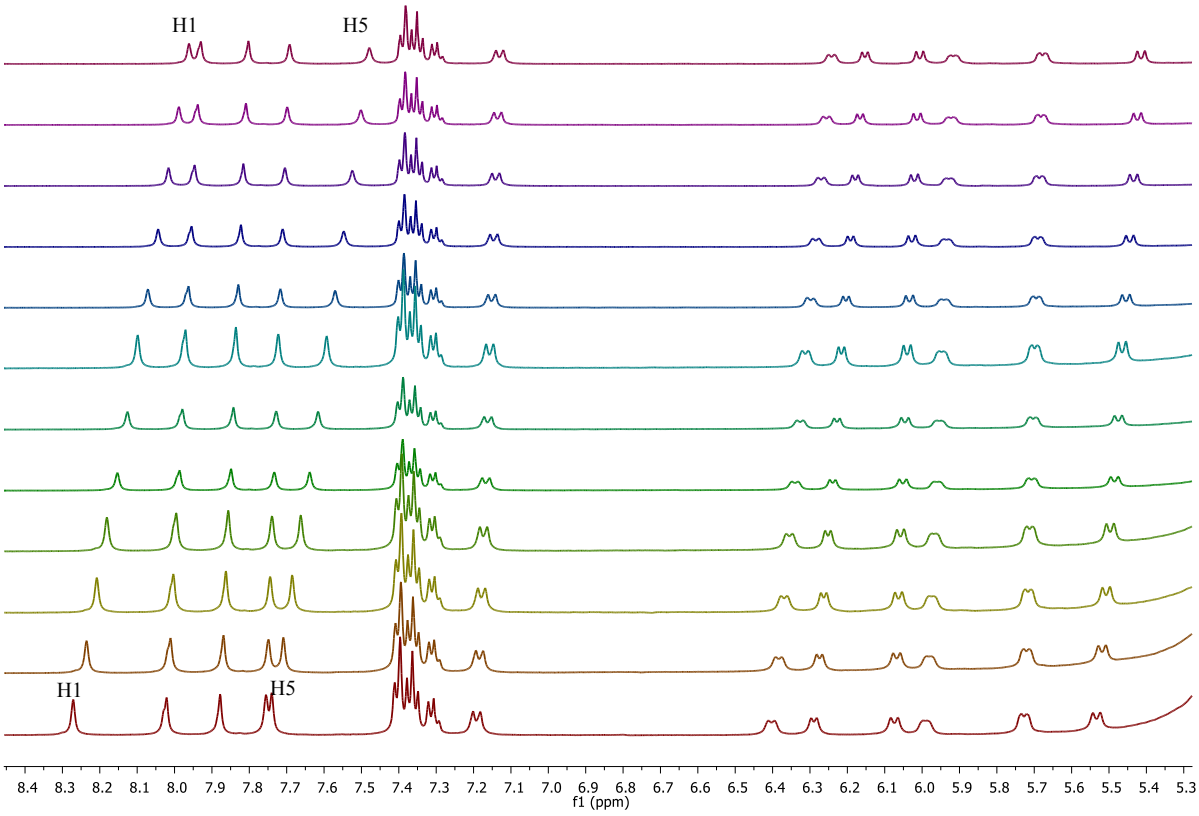

140
90
40
-10
-60
180
200
220
240
260
λ / nm
[Θ]M x 10-3 / deg.cm2.dmol-1
13
15

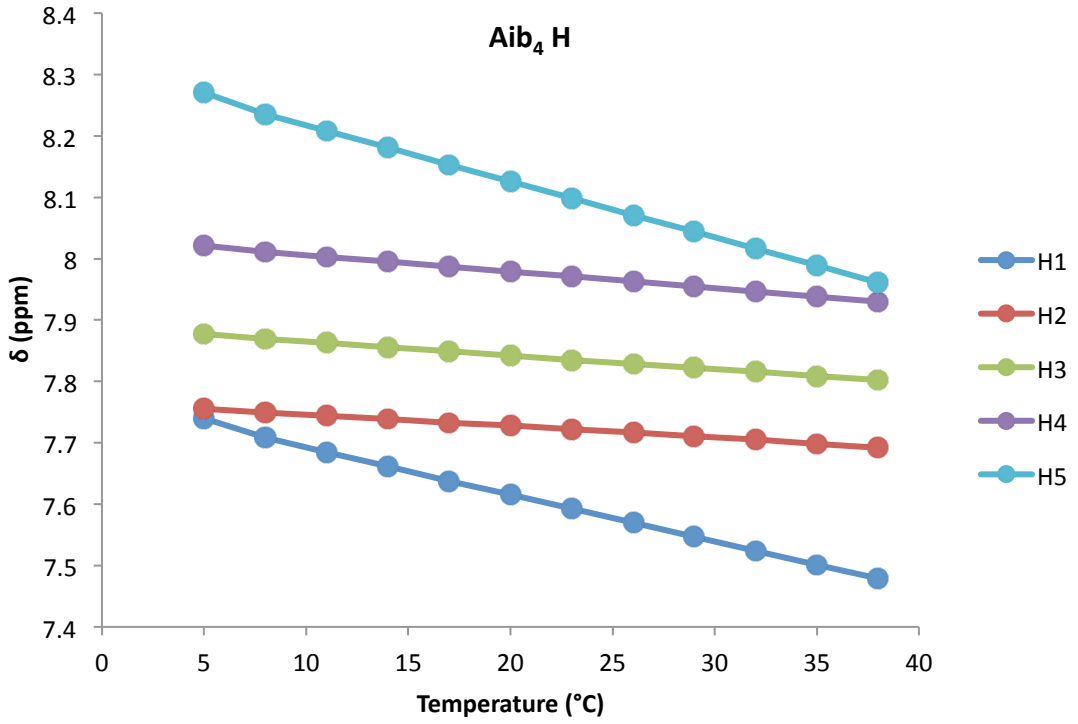
VT-NMR ^{13}C of 11 between -80 and 40°C

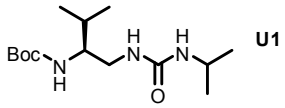


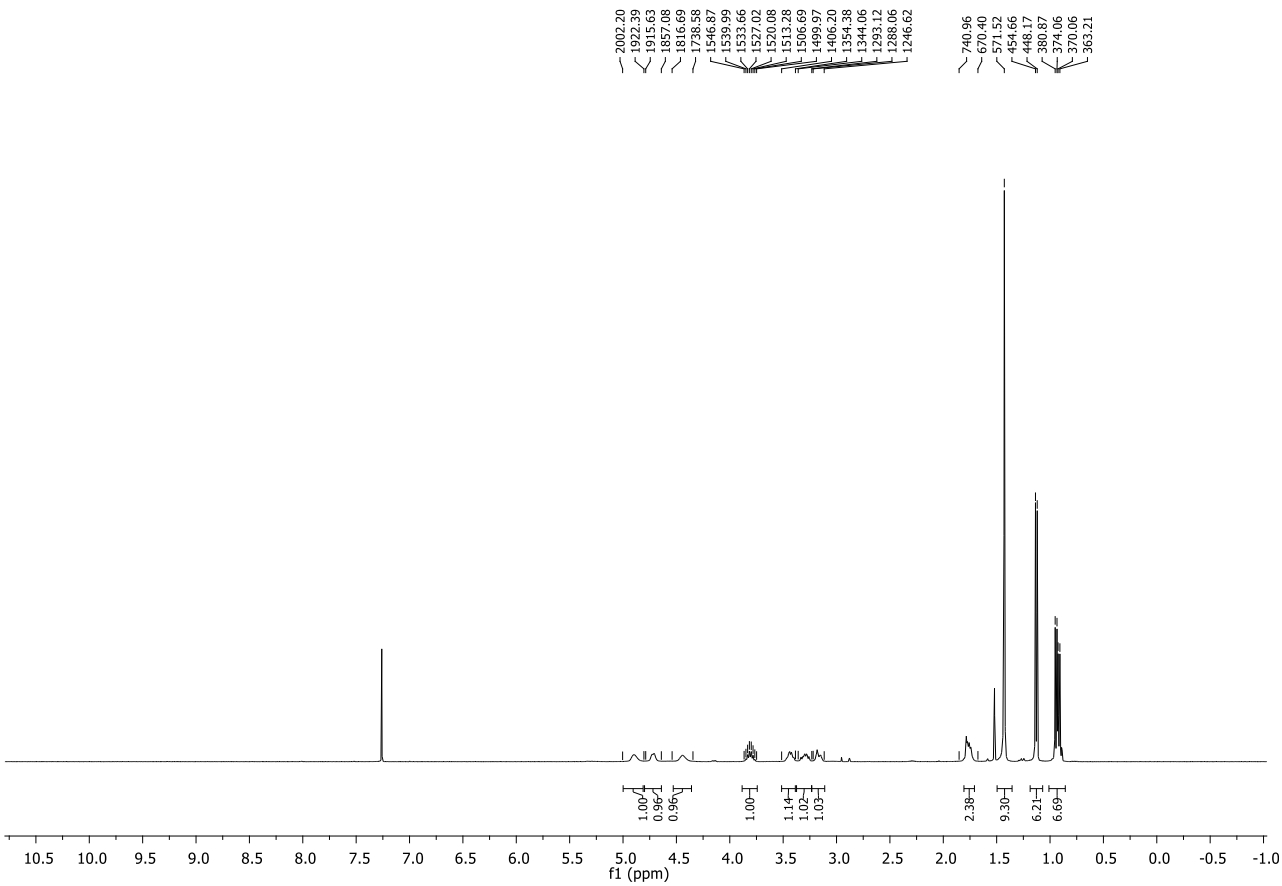


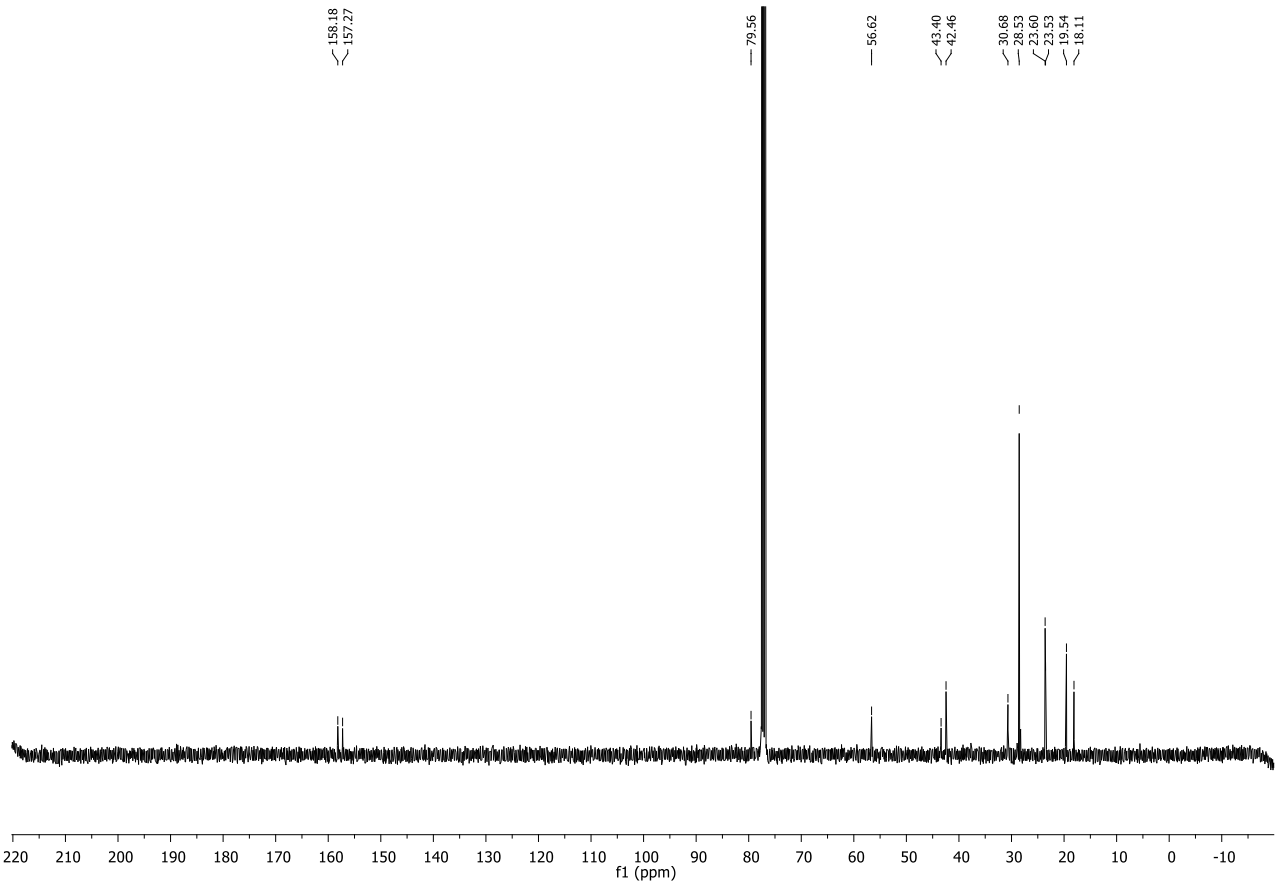
VT-NMR ^{1}H of 11 between 5 and 38 °C

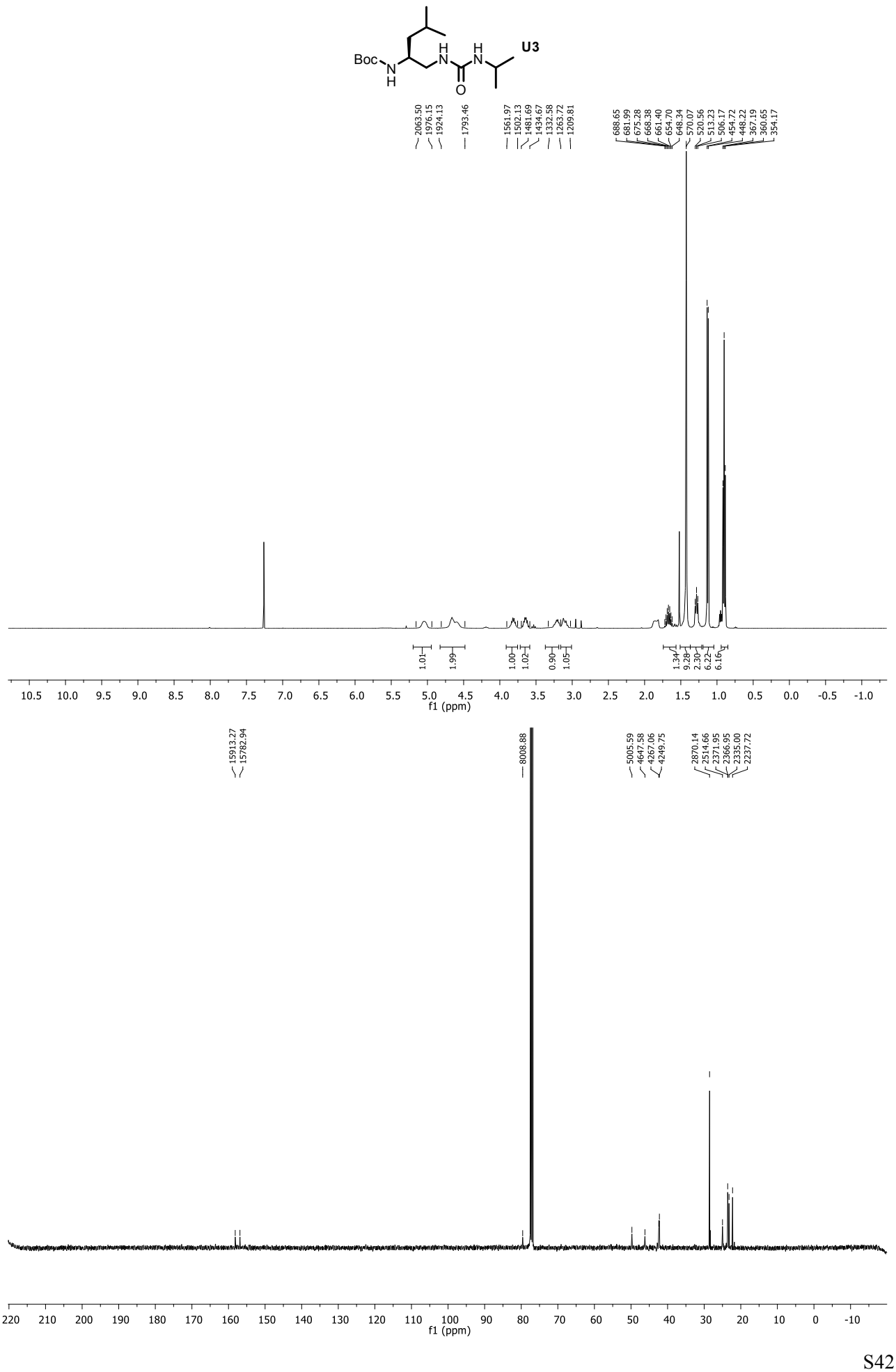


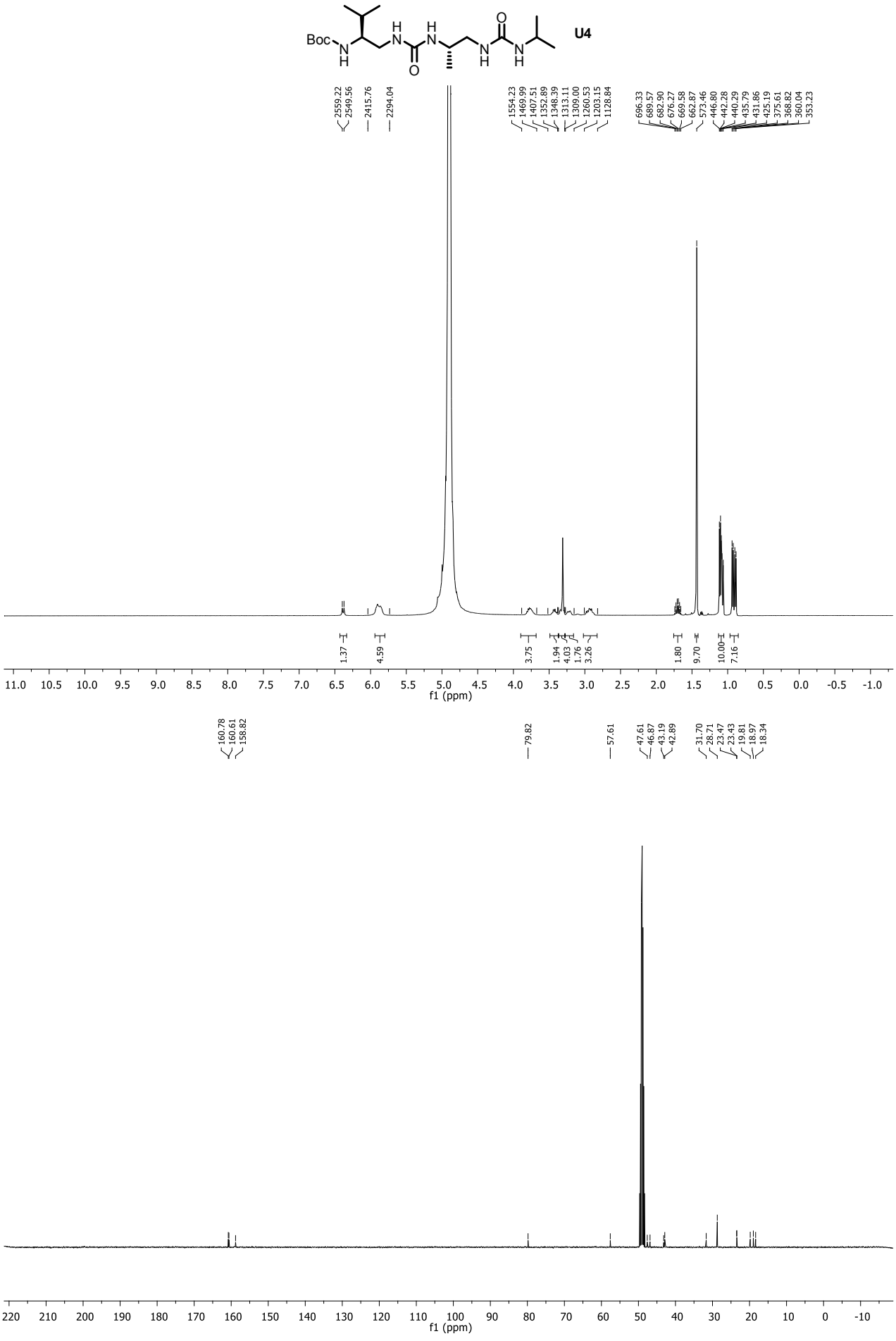


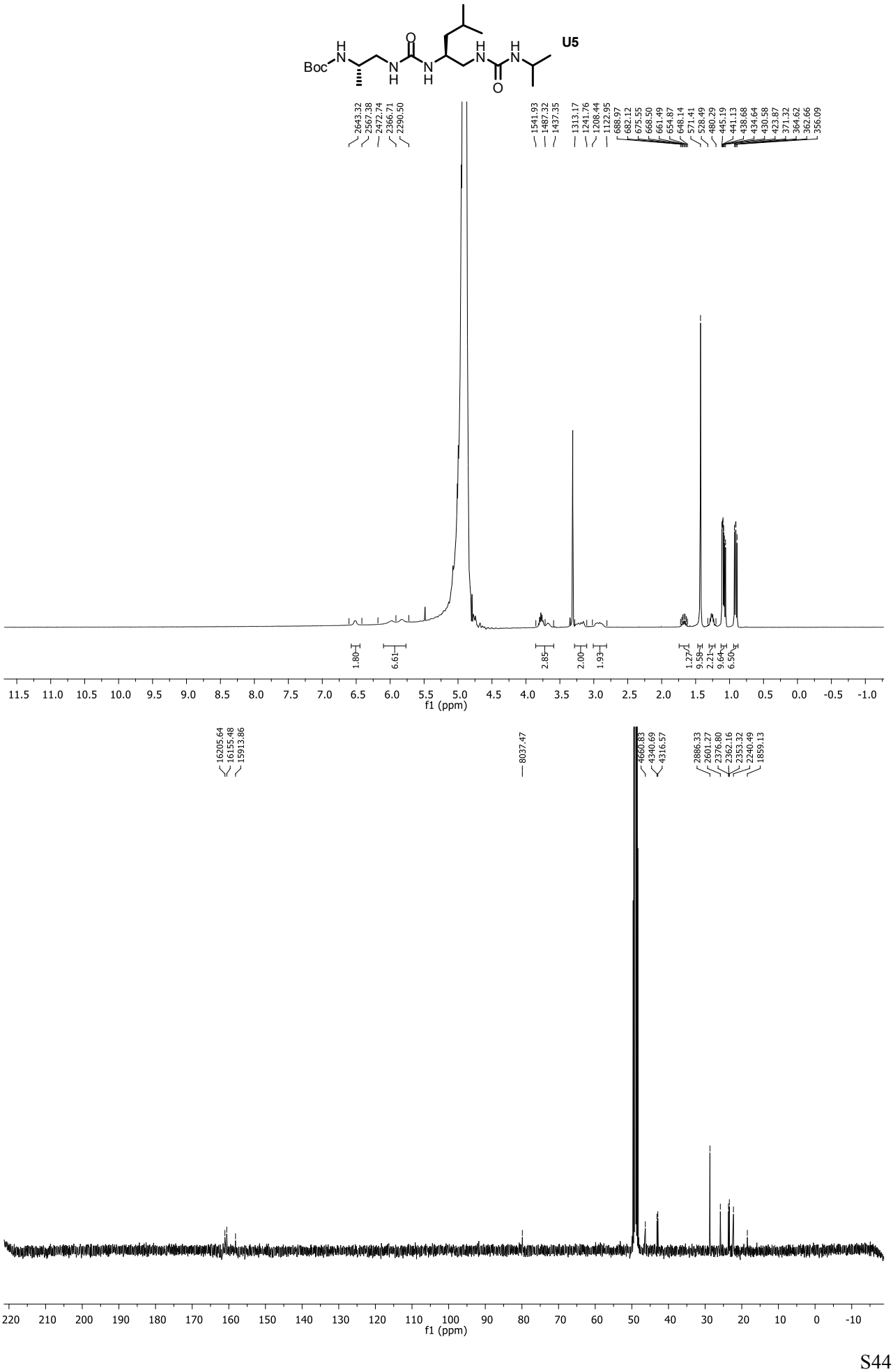

Boc
N
H
H
N
O
H
N
U1

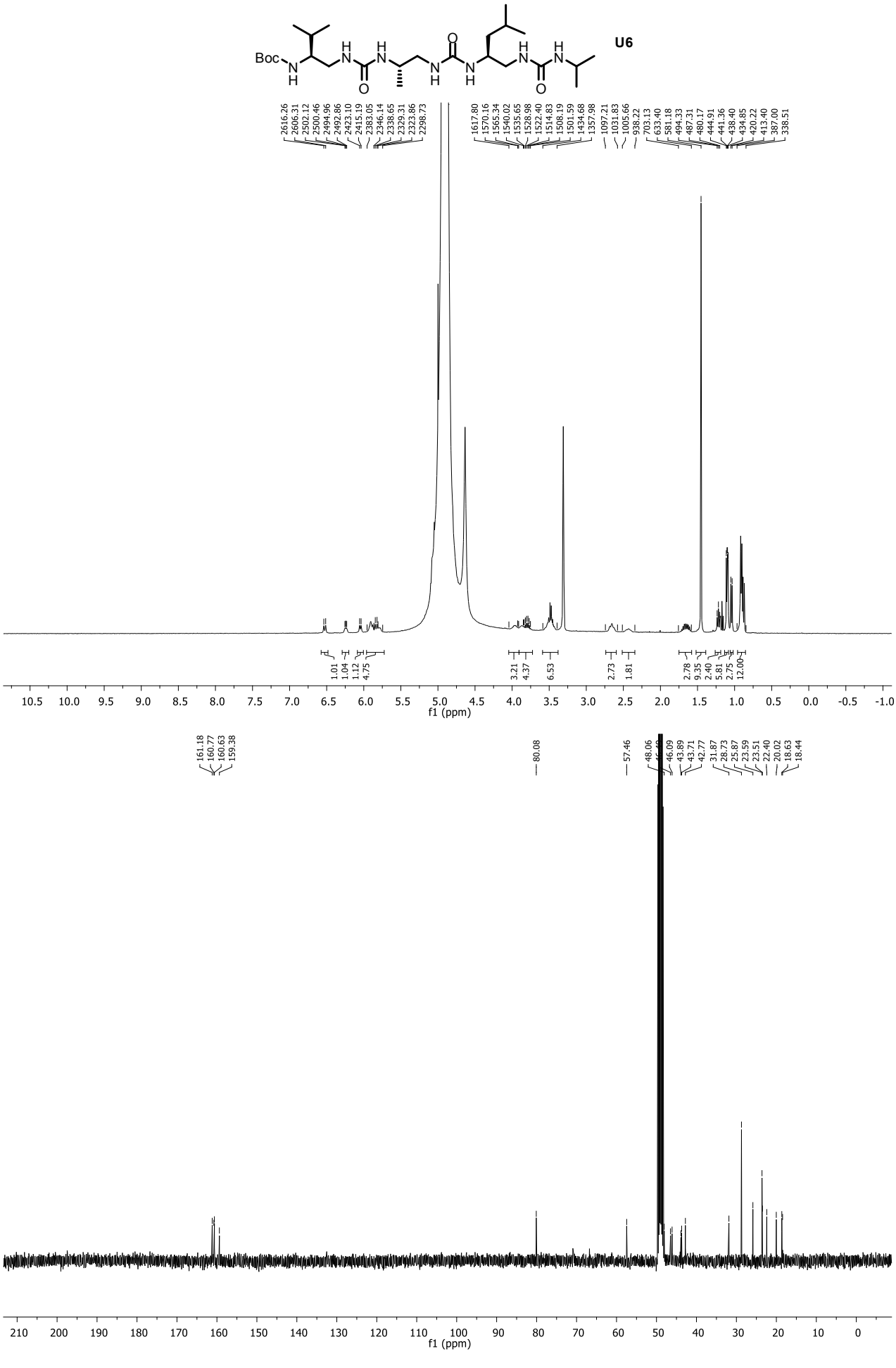

2002.20
1922.39
1915.63
1857.08
1816.69
1738.58
1546.87
1539.99
1533.66
1527.02
1520.08
1513.28
1506.69
1499.97
1406.20
1354.38
1344.06
1293.12
1288.06
1246.62
740.96
670.40
571.52
454.66
448.17
380.87
374.06
370.06
363.21
1.00
0.96
0.96
1.00
1.14
1.02
1.03
2.38
9.30
6.21
6.69
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

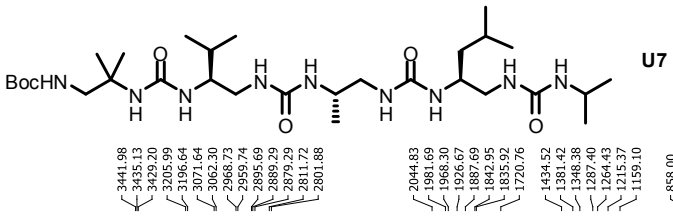

158.18
157.27
79.56
56.62
43.40
42.46
30.68
28.53
23.60
23.53
19.54
18.11
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

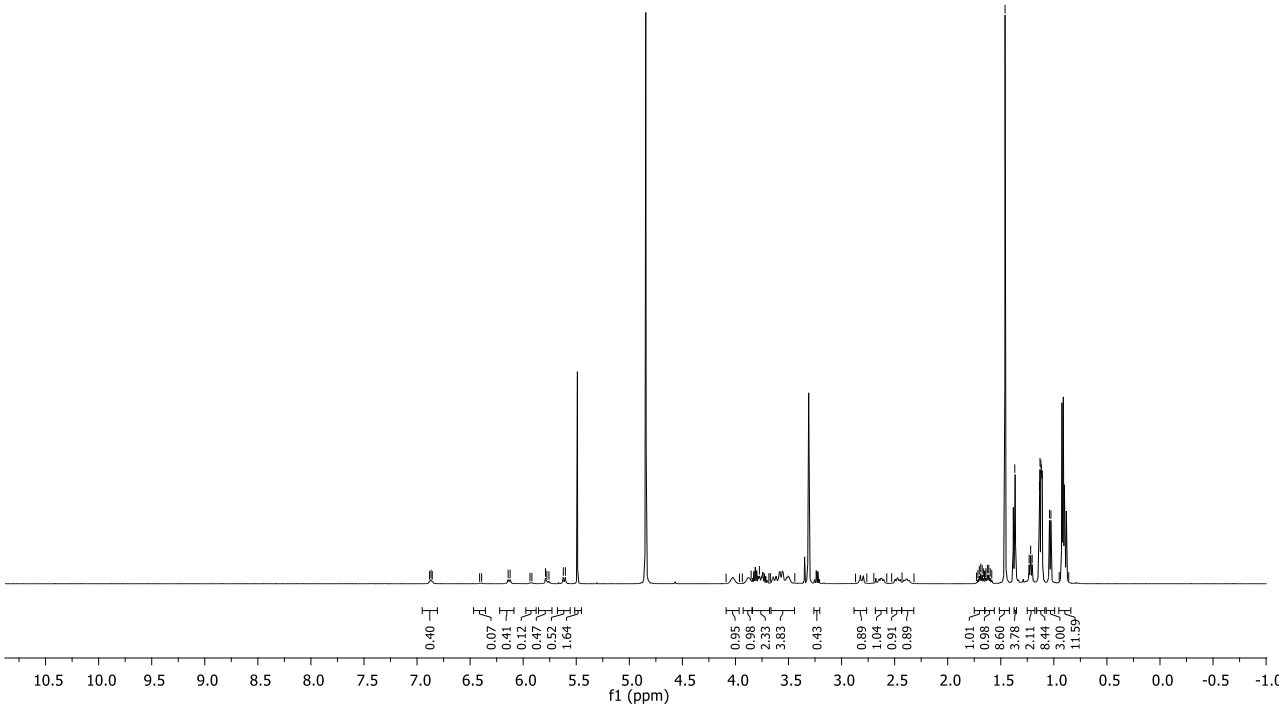

U3
Boc
2063.50
1976.15
1924.13
1793.46
1561.97
1502.13
1491.69
1454.67
1332.58
1263.72
1209.81
688.65
681.99
675.28
668.38
661.40
654.70
648.34
570.07
520.56
513.23
506.17
454.72
448.22
367.19
360.65
354.17
1.01
1.99
1.00
1.02
0.90
1.05
1.34
9.28
2.30
6.22
6.16
f1 (ppm)
15913.27
15782.94
8008.88
5005.59
4647.58
4267.06
4249.75
2870.14
2514.66
2371.95
2366.95
2335.00
2237.72
f1 (ppm)

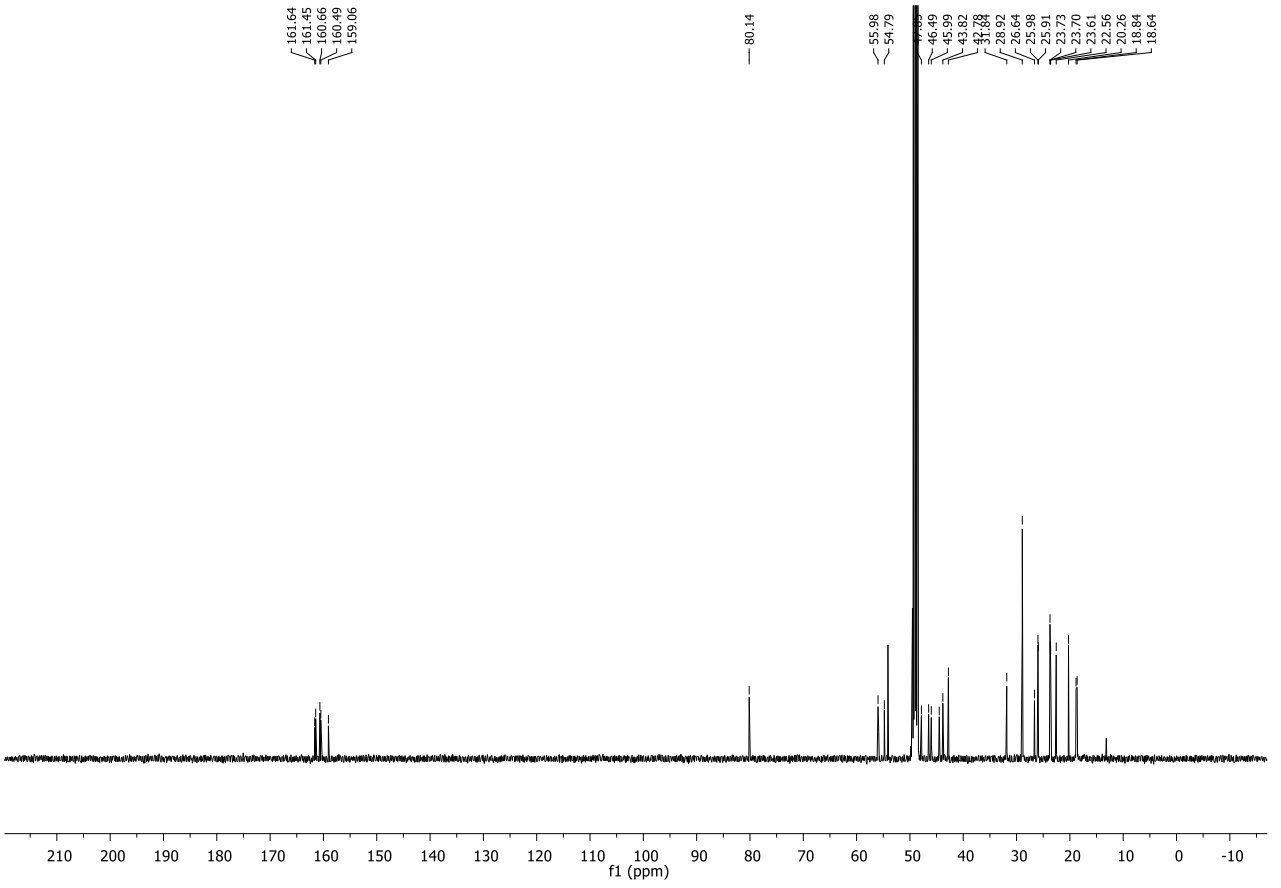

U4
2559.22
2549.56
2415.76
2294.04
1554.23
1469.99
1407.51
1352.89
1348.39
1313.11
1309.00
1260.53
1203.15
1128.84
696.33
689.57
682.90
676.27
669.58
662.87
573.46
446.80
442.28
440.29
435.79
431.86
425.19
375.61
368.82
360.04
353.23
1.37
4.59
3.75
1.94
4.03
1.76
3.26
1.80
9.70
10.00
7.16
f1 (ppm)
160.78
160.61
158.82
79.82
57.61
47.61
46.87
43.19
42.89
31.70
28.71
23.47
23.43
19.81
18.97
18.34
f1 (ppm)

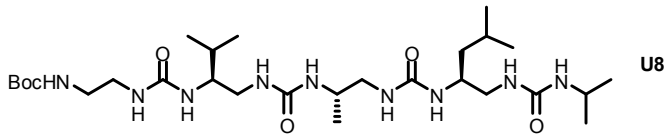

U5
Boc
2643.32
2567.38
2472.74
2366.71
2290.50
1541.93
1487.32
1437.35
1313.17
1241.76
1208.44
1122.95
688.97
682.12
675.55
668.50
661.49
654.87
648.14
571.41
528.49
480.29
445.19
441.13
438.68
434.64
430.58
423.87
371.32
364.62
362.66
356.09
1.80
6.61
2.85
2.00
1.93
1.27
9.58
2.21
9.64
6.50
f1 (ppm)
16205.64
16155.48
15913.86
8037.47
4660.83
4340.69
4316.57
2886.33
2601.27
2376.80
2362.16
2353.32
2240.49
1859.13
f1 (ppm)

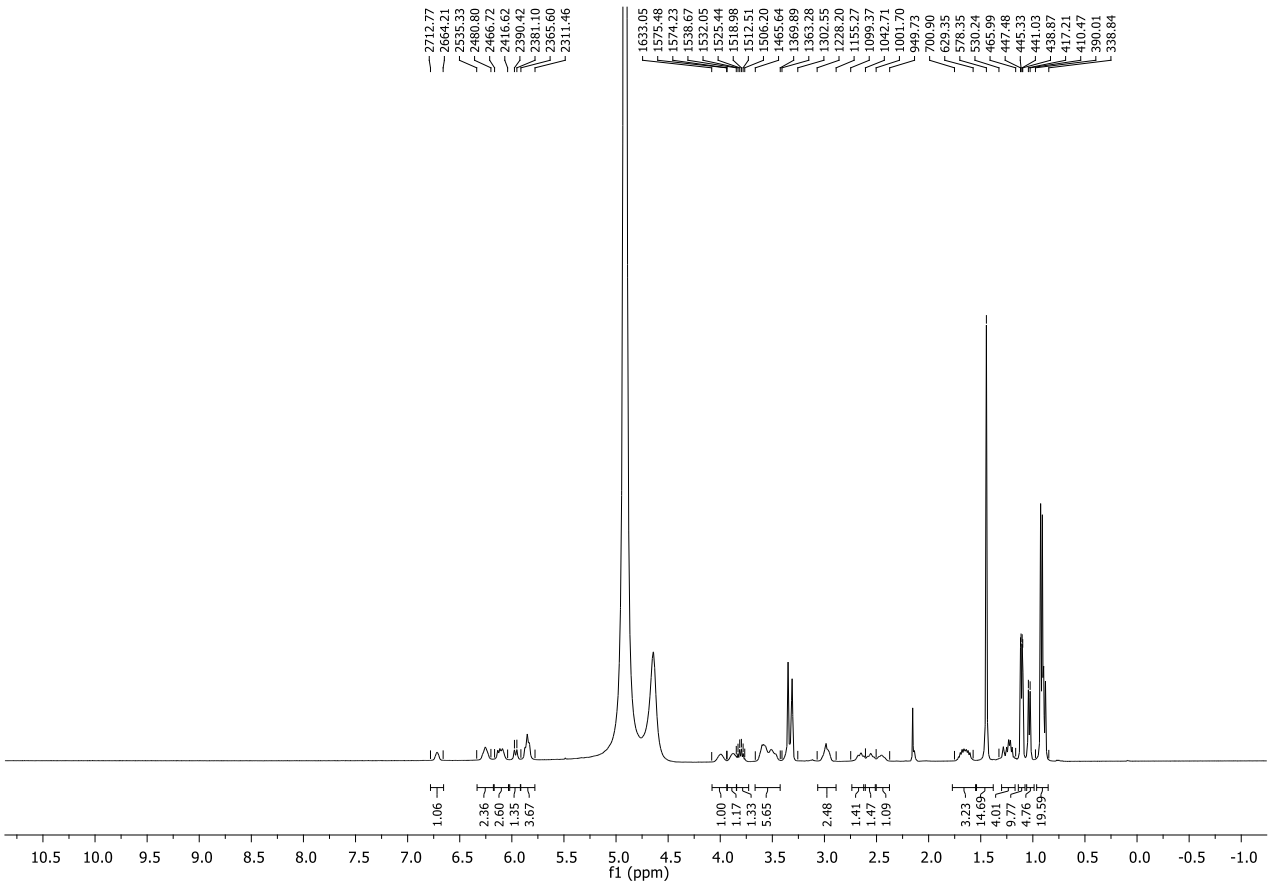

U6
Boc
2616.26
2606.31
2502.12
2500.46
2494.96
2492.86
2423.10
2415.19
2383.05
2346.14
2338.65
2329.31
2323.86
2298.73
1617.80
1570.16
1565.34
1540.02
1535.65
1528.98
1522.40
1514.83
1508.19
1501.59
1434.68
1357.98
1097.21
1031.83
1005.66
938.22
703.13
633.40
581.18
494.33
487.31
480.17
444.91
441.36
438.40
434.85
420.22
413.40
387.00
338.51
1.01
1.04
1.12
4.75
3.21
4.37
6.53
2.73
1.81
2.78
9.35
2.40
5.81
2.75
12.00
f1 (ppm)
161.18
160.77
160.63
159.38
80.08
57.46
48.06
46.09
43.89
43.71
42.77
31.87
28.73
25.87
23.59
23.51
22.40
20.02
18.63
18.44
f1 (ppm)

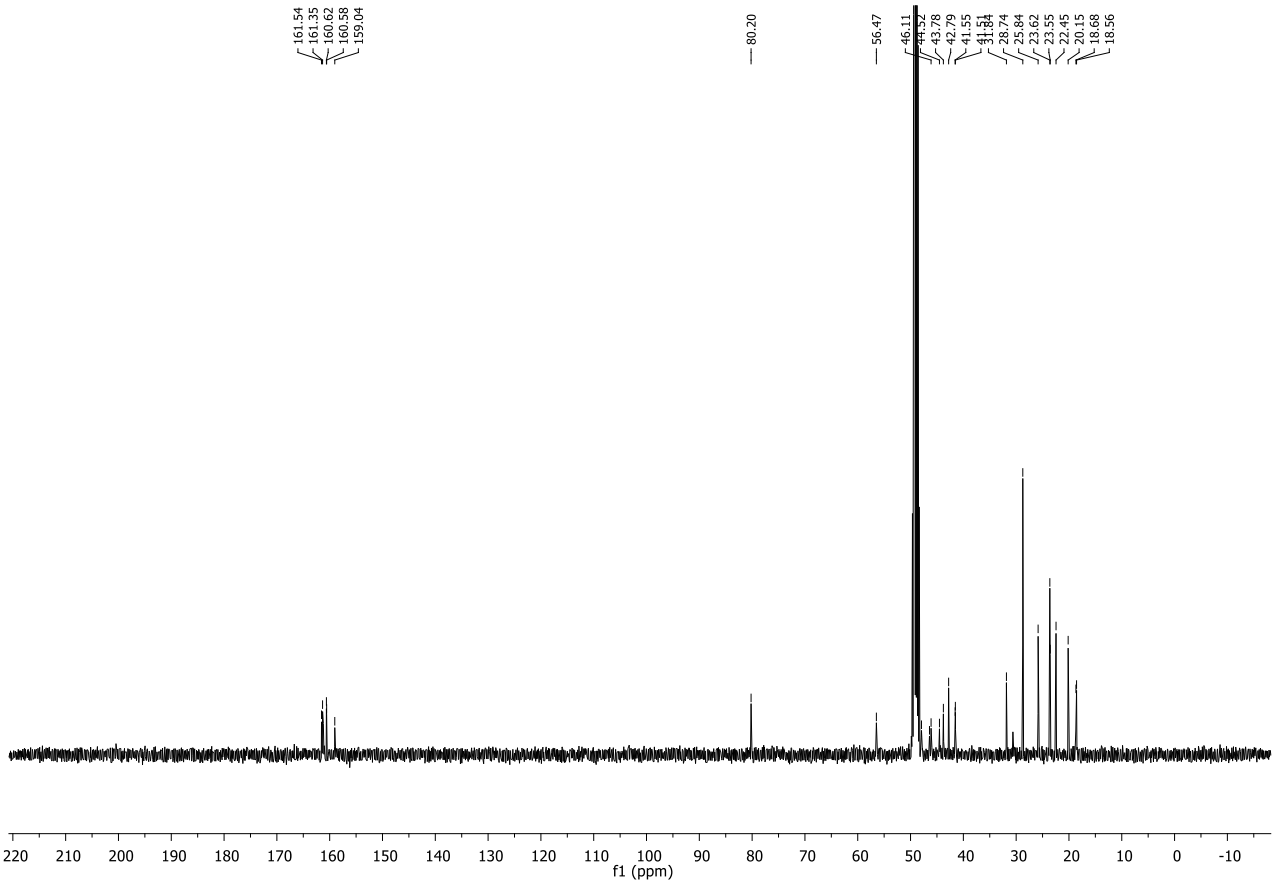

BocHN
U7
3441.98
3435.13
3429.20
3205.99
3196.64
3071.64
3062.30
2968.73
2959.74
2895.69
2889.29
2879.29
2811.72
2801.88
2044.83
1981.69
1968.30
1926.67
1887.69
1842.95
1835.92
1720.76
1434.52
1381.42
1348.38
1287.40
1264.43
1215.37
1159.10
858.00
851.29
844.50
837.72
831.01
820.14
813.41
806.72
800.01
730.05
684.29
616.50
609.28
602.36
568.04
565.37
561.01
558.83
554.50
520.84
514.03

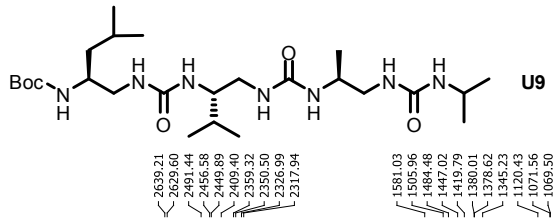

0.40
0.07
0.41
0.12
0.47
0.52
1.64
0.95
0.98
2.33
3.83
0.43
0.89
1.04
0.91
0.89
1.01
0.98
8.60
3.78
2.11
8.44
3.00
11.59
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

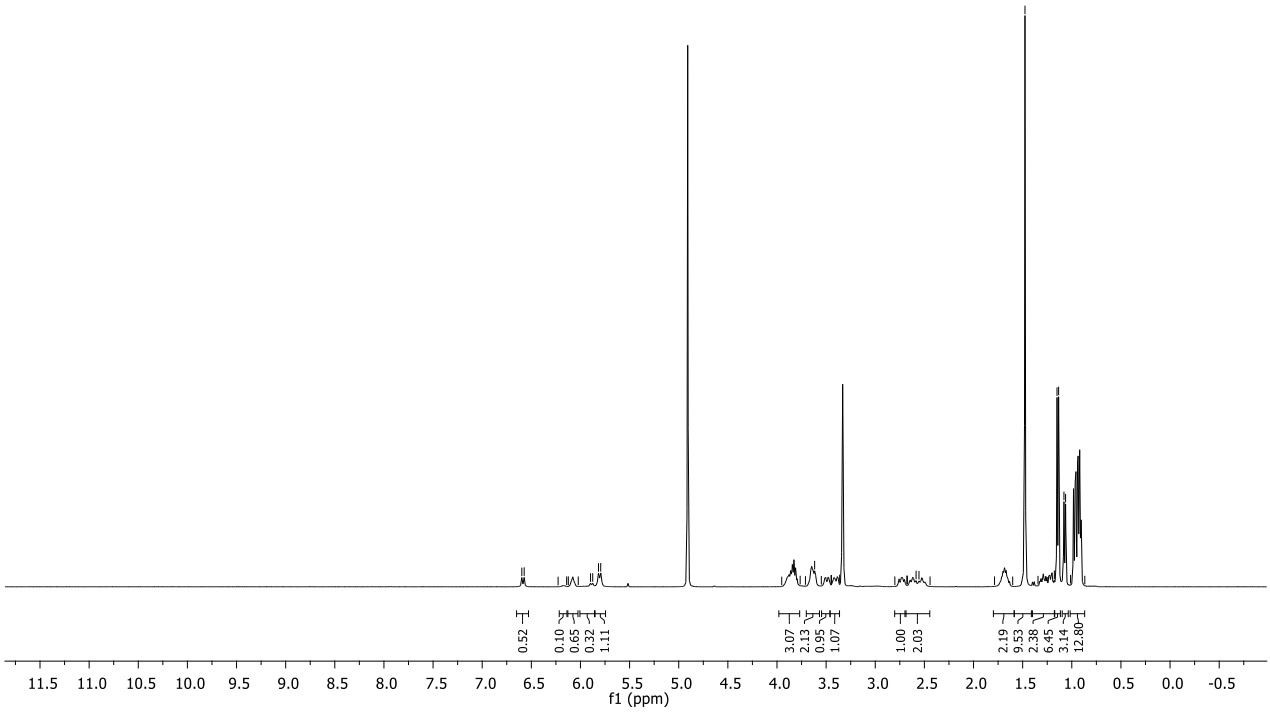

161.64
161.45
160.66
160.49
159.06
80.14
55.98
54.79
46.49
45.99
43.82
28.92
26.64
25.98
25.91
23.73
23.70
23.61
22.56
20.26
18.84
18.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

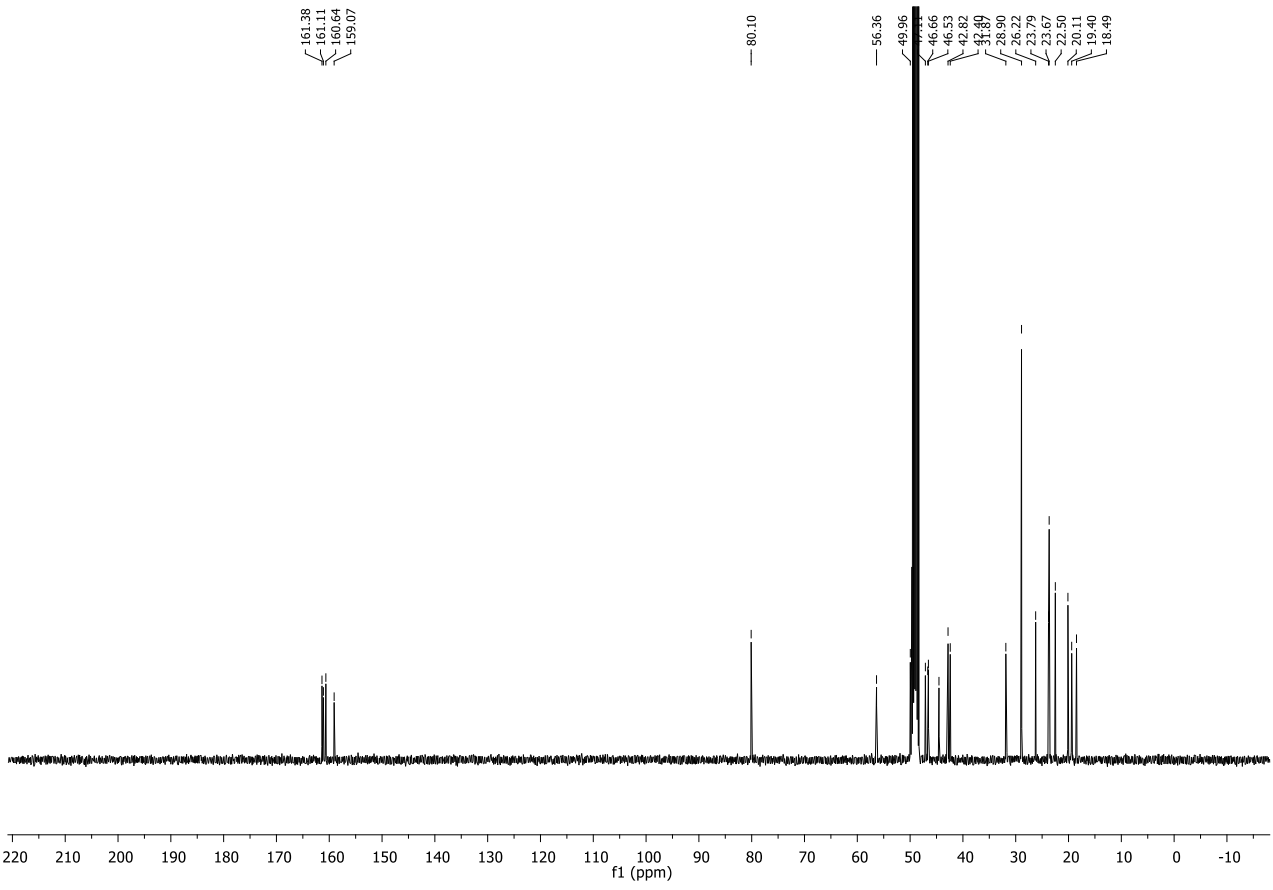

BocHN
U8

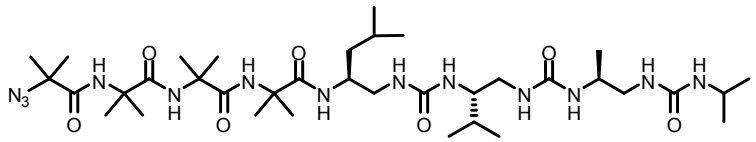

2712.77
2664.21
2535.33
2480.80
2466.72
2416.62
2390.42
2381.10
2365.60
2311.46
1633.05
1575.48
1574.23
1538.67
1532.05
1525.44
1518.98
1512.51
1506.20
1465.64
1369.89
1363.28
1302.55
1228.20
1155.27
1099.37
1042.71
1001.70
949.73
700.90
629.35
578.35
530.24
465.99
447.48
445.33
441.03
438.87
417.21
410.47
390.01
338.84
1.06
2.36
2.60
1.35
3.67
1.00
1.17
1.33
5.65
2.48
1.41
1.47
1.09
3.23
14.69
4.01
9.77
4.76
19.59
f1 (ppm)


161.54
161.35
160.62
160.58
159.04
80.20
56.47
46.11
44.52
43.78
42.79
41.55
41.84
28.74
25.84
23.62
23.55
22.45
20.15
18.68
18.56
f1 (ppm)

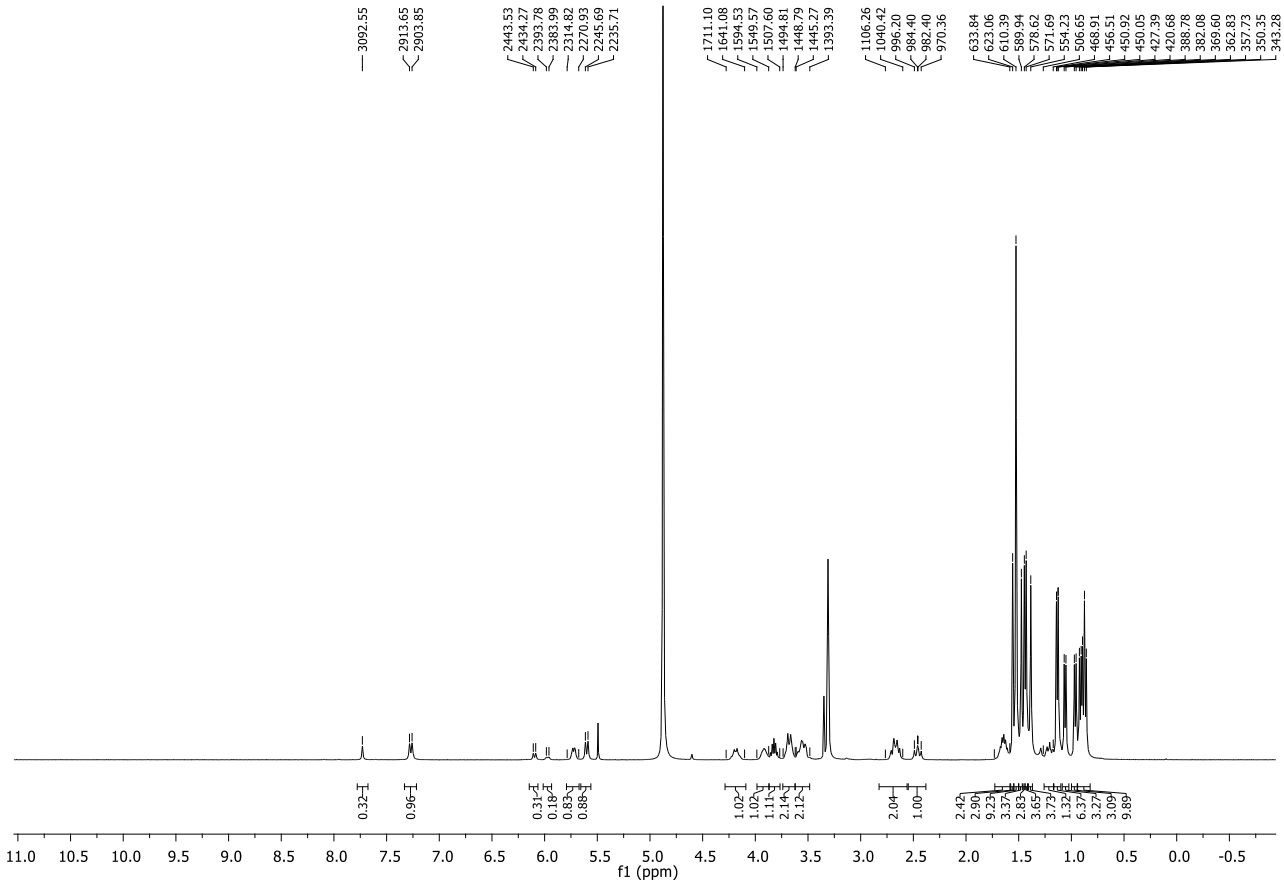

Boc
U9
2639.21
2629.60
2491.44
2456.58
2449.89
2409.40
2359.32
2350.50
2326.99
2317.94
1581.03
1505.96
1484.48
1447.02
1419.79
1380.01
1378.62
1345.23
1120.43
1071.56
1069.50
1034.05
1022.23
977.16
714.56
640.67
590.65
537.68
471.10
460.24
453.75
432.00
425.31
405.08
347.13

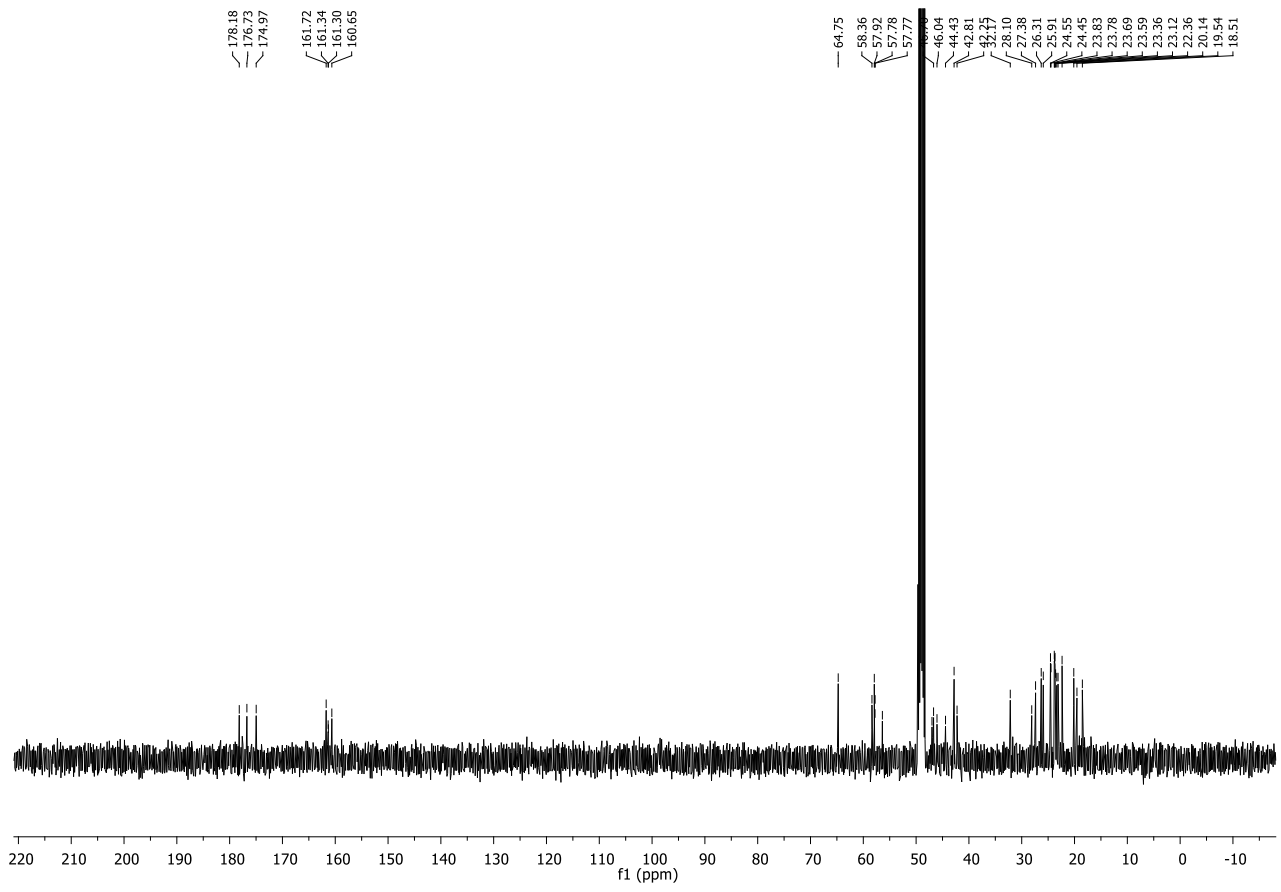

0.52
0.10
0.65
0.32
1.11
3.07
2.13
0.95
1.07
1.00
2.03
2.19
9.53
2.38
6.45
3.14
12.80
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

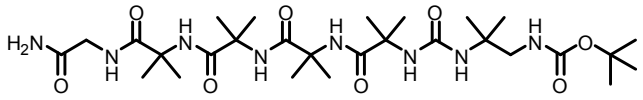

161.38
161.11
160.64
159.07
80.10
56.36
49.96
46.66
46.53
42.82
28.90
26.22
23.79
23.67
22.50
20.11
19.40
18.49
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



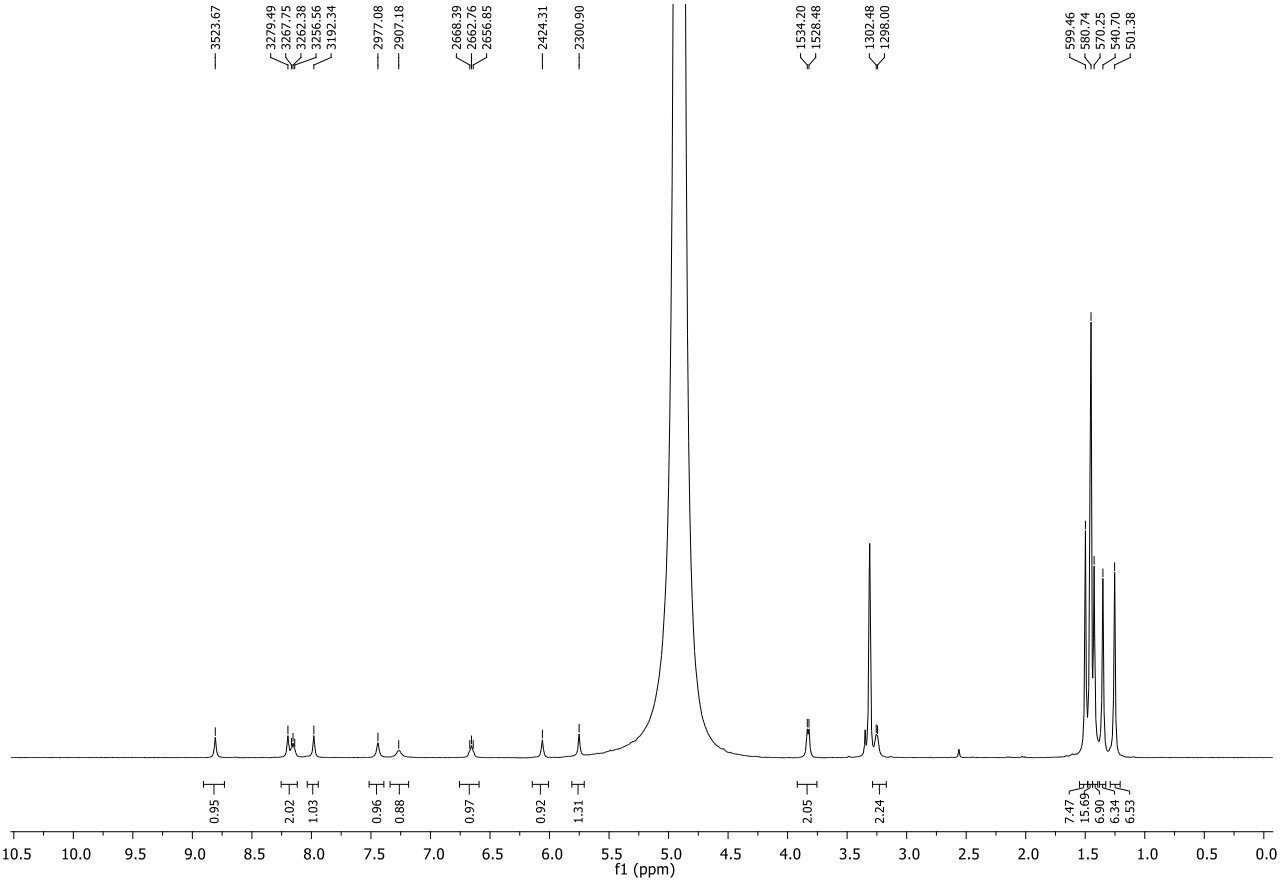
U10

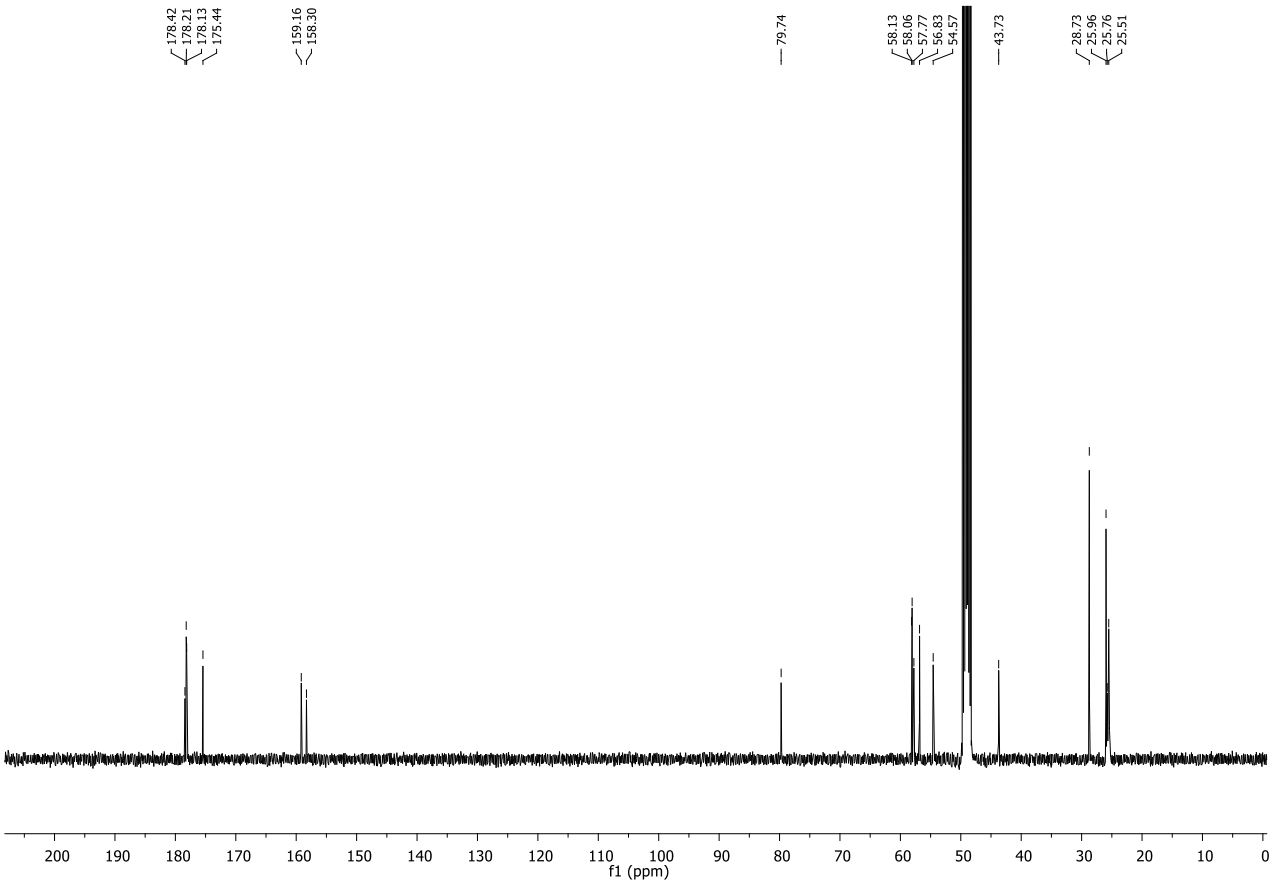


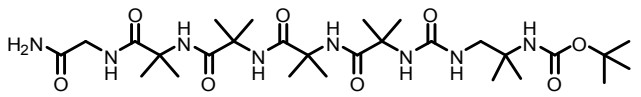




3


3523.67
3279.49
3267.75
3262.38
3256.56
3192.34
2977.08
2907.18
2668.39
2662.76
2656.85
2424.31
2300.90
1534.20
1528.48
1302.48
1298.00
599.46
580.74
570.25
540.70
501.38
0.95
2.02
1.03
0.96
0.88
0.97
0.92
1.31
2.05
2.24
7.47
15.69
6.90
6.34
6.53
f1 (ppm)


178.42
178.21
178.13
175.44
159.16
158.30
79.74
58.13
58.06
57.77
56.83
54.57
43.73
28.73
25.96
25.76
25.51
f1 (ppm)



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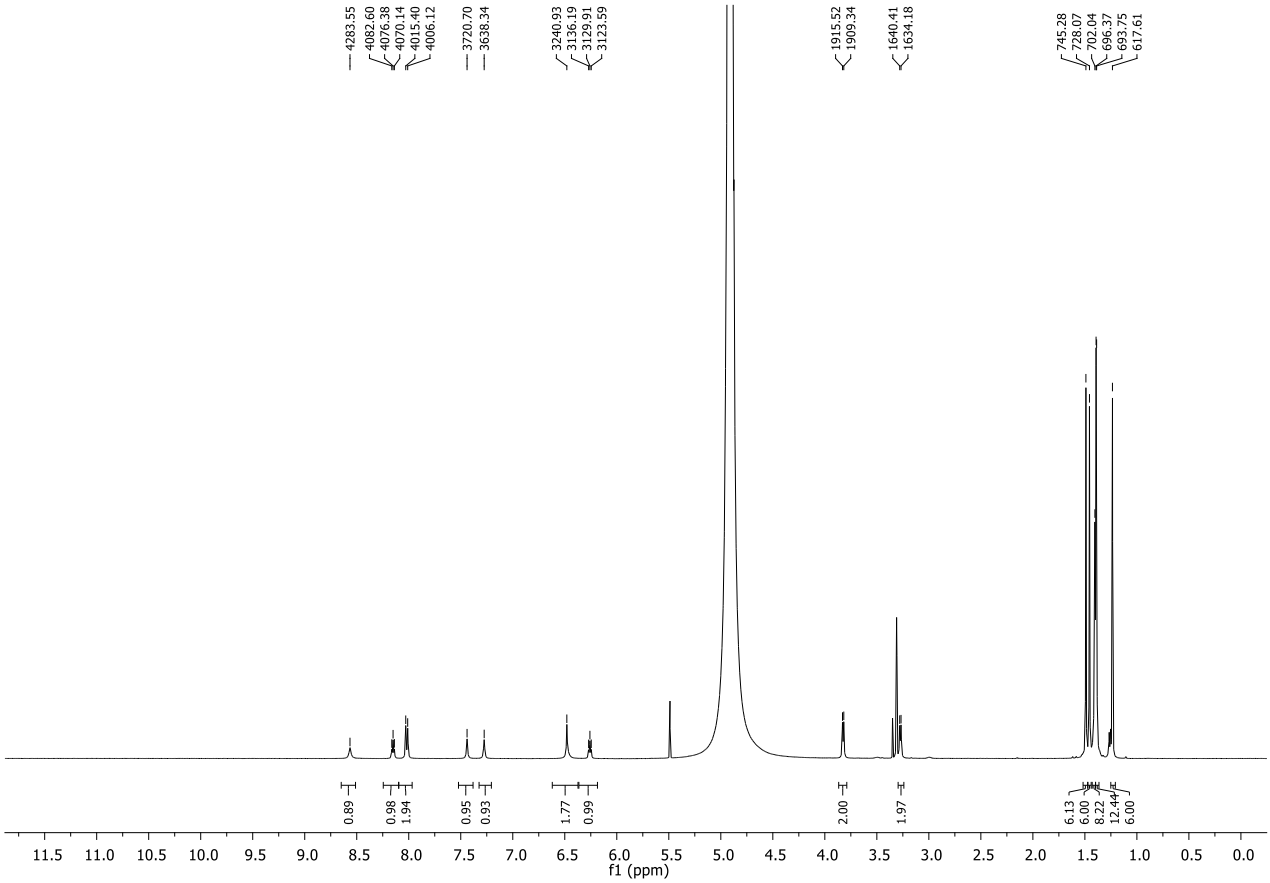
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1634.18
745.28
728.07
702.04
696.37
693.75
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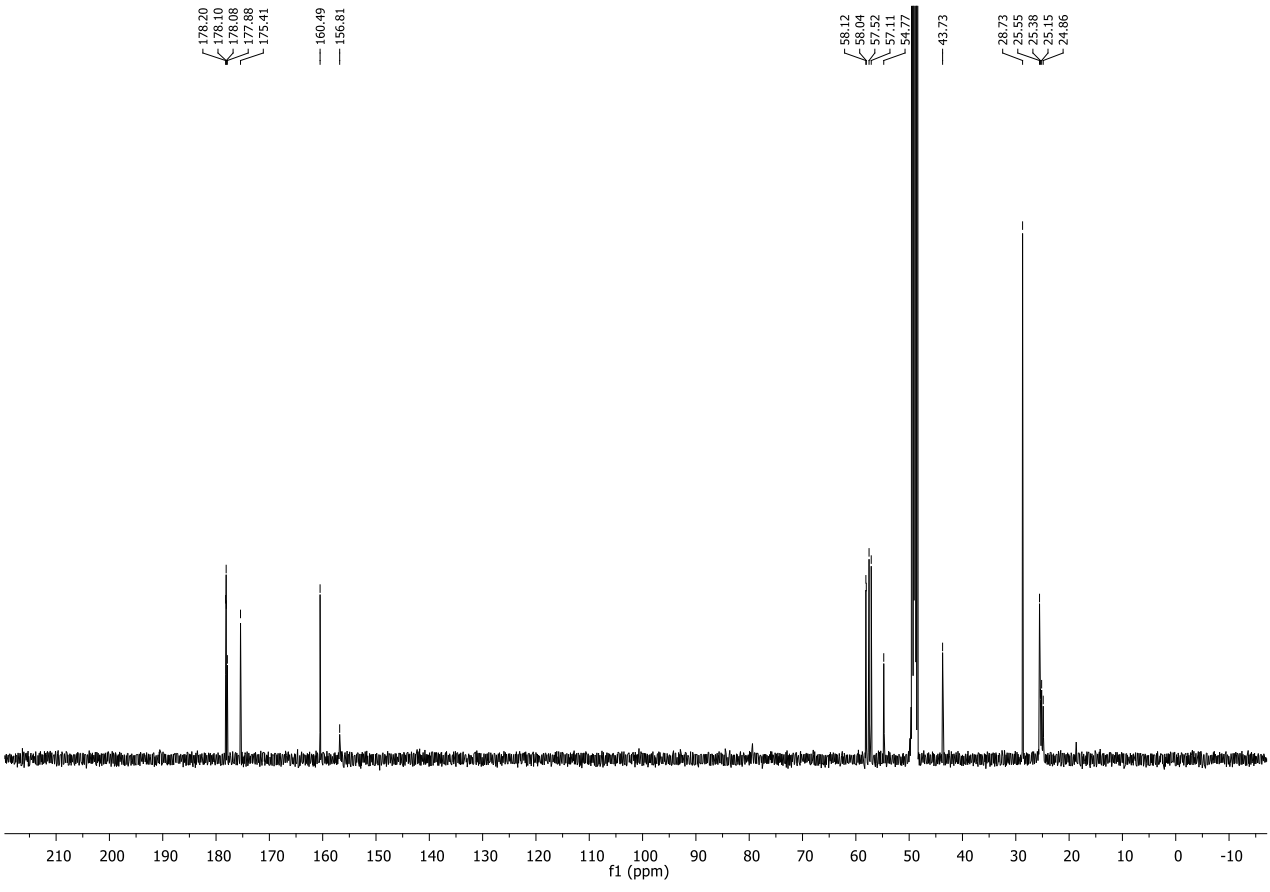
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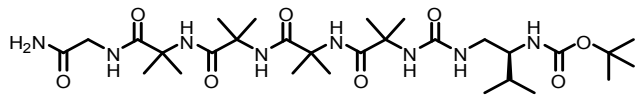
f1 (ppm)



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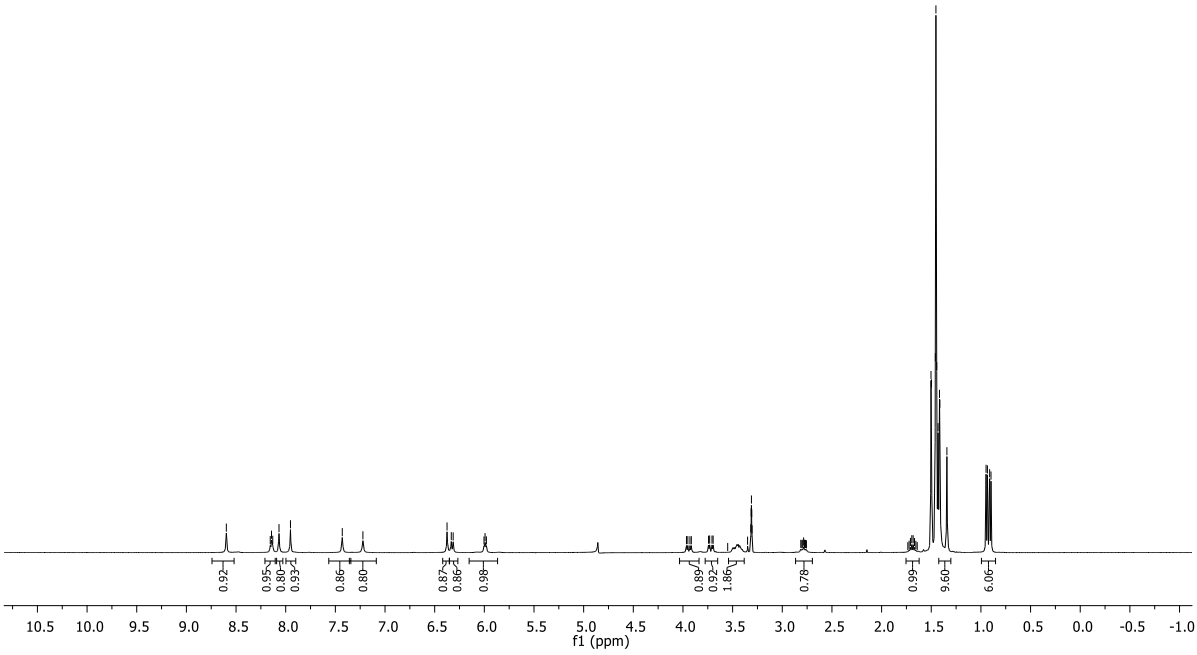

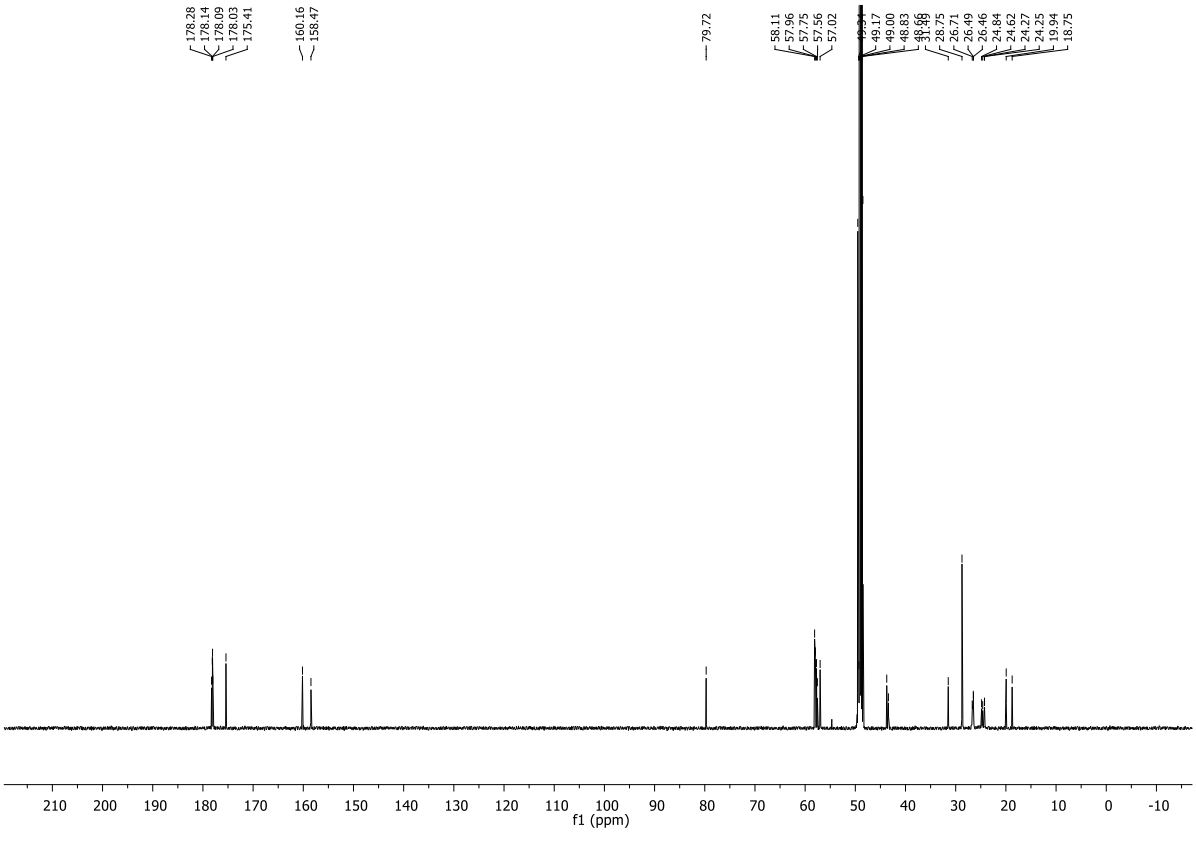

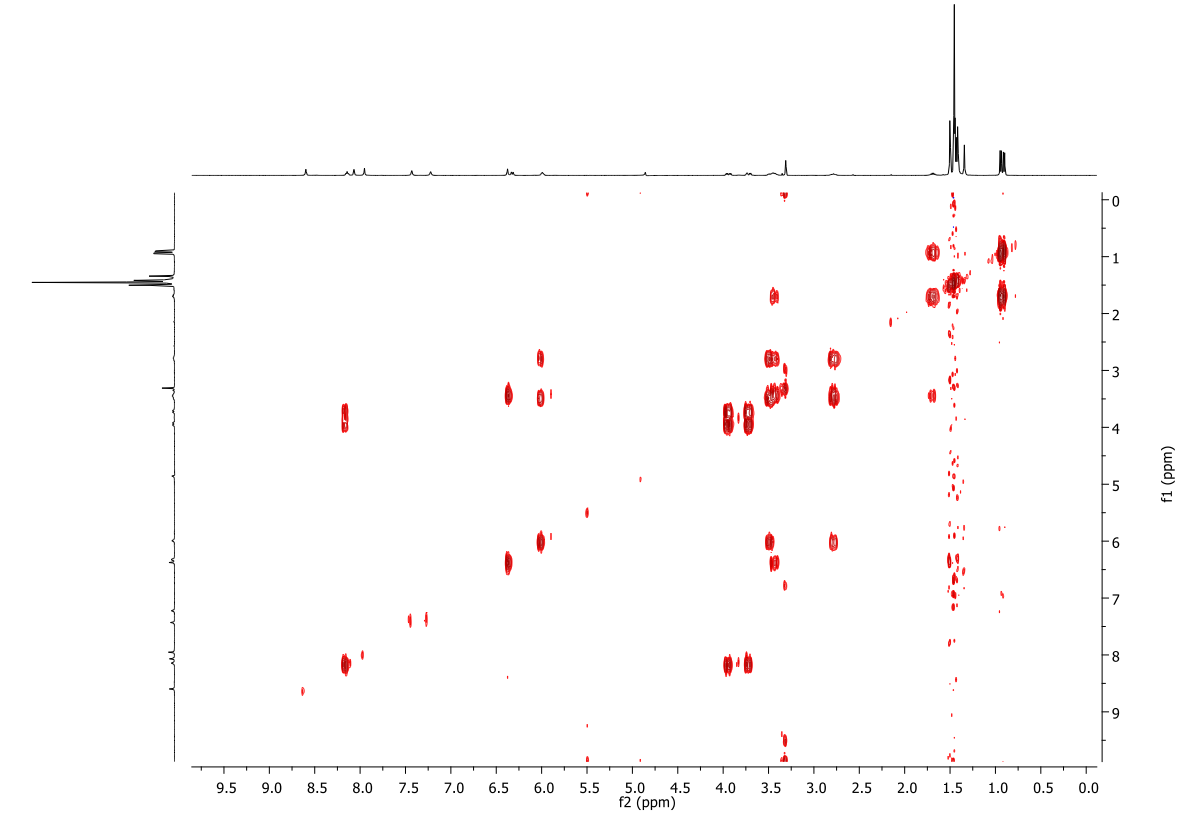
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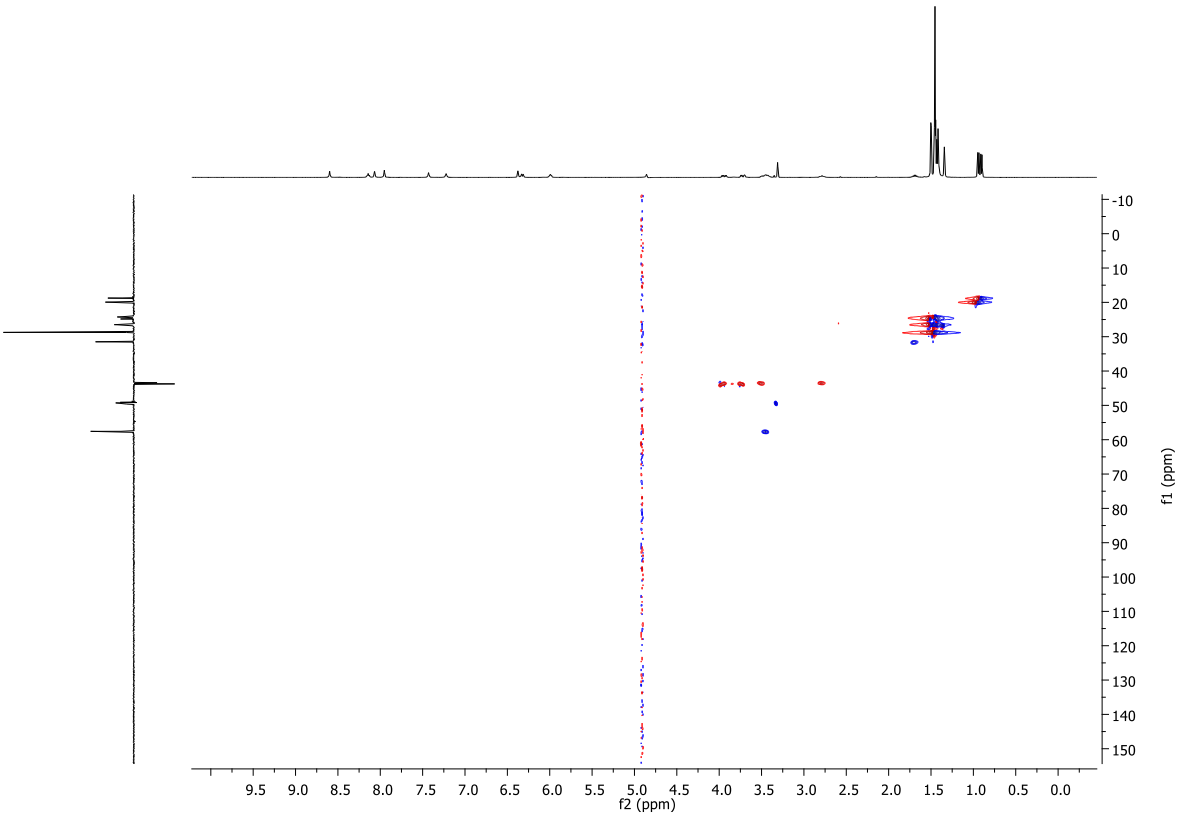
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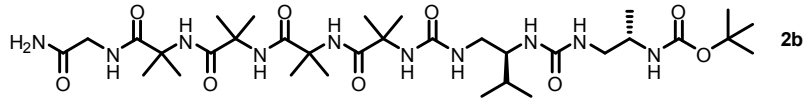

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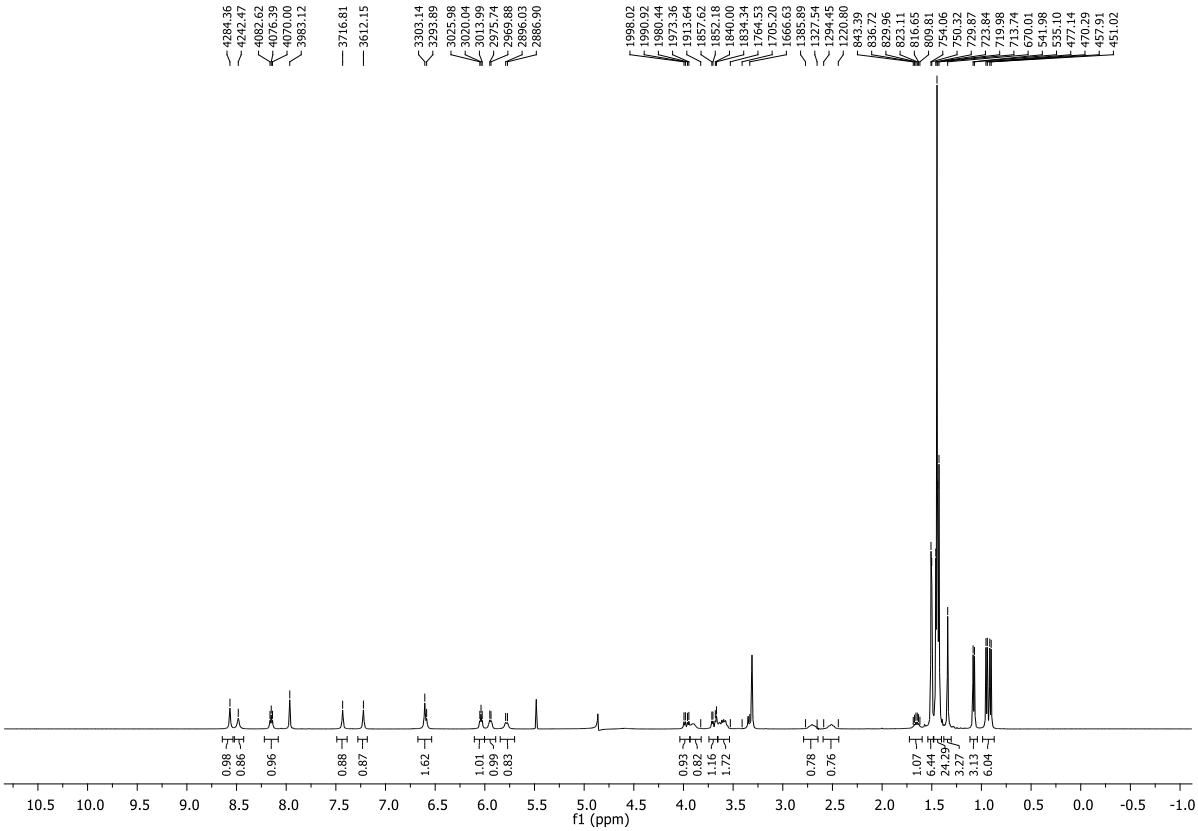
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0.93
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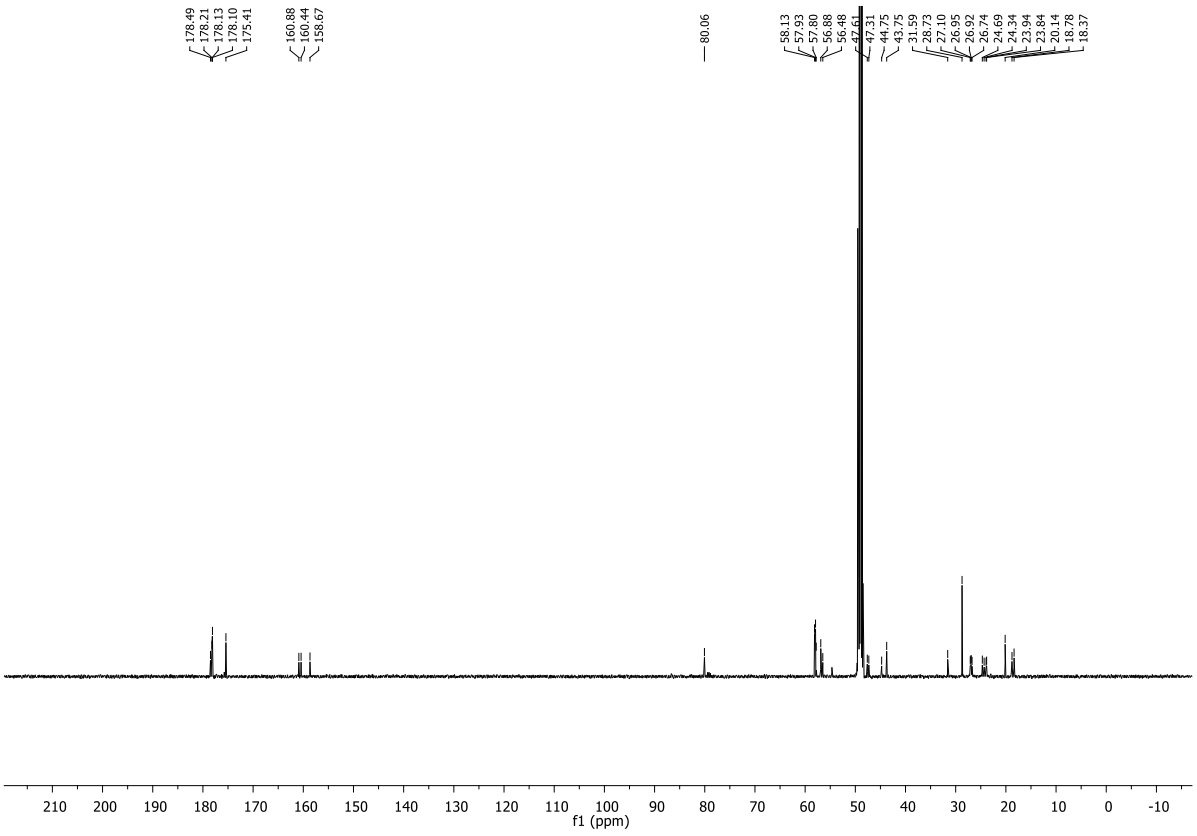
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31.59
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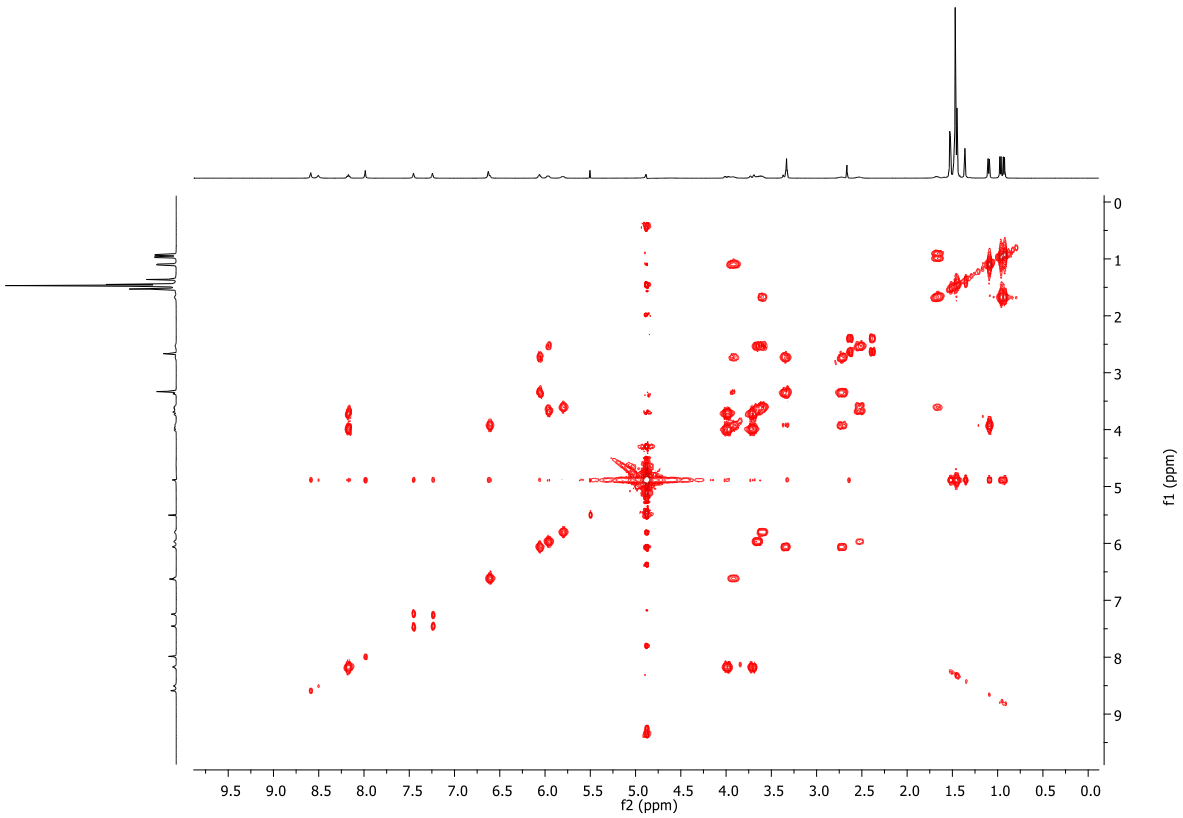
f1 (ppm)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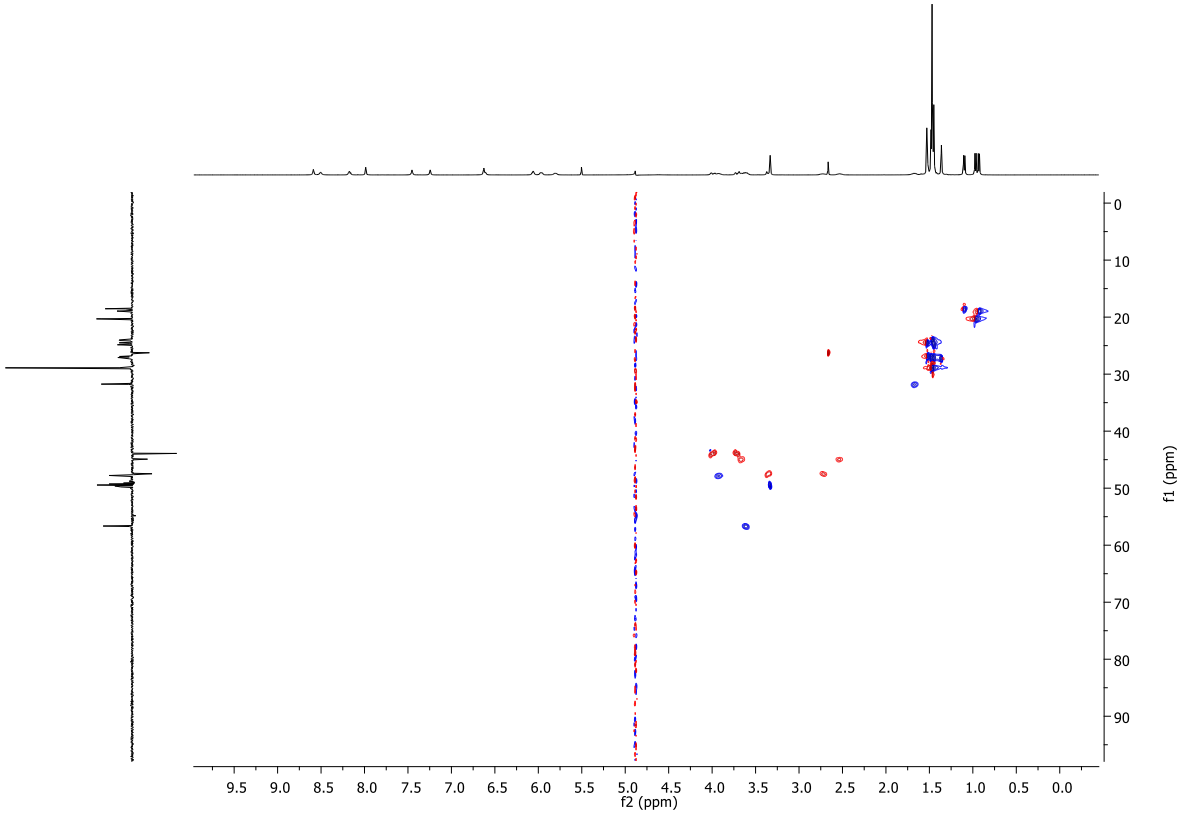
f2 (ppm)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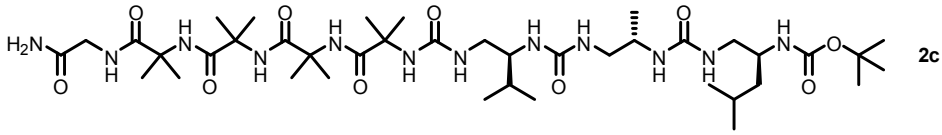
f2 (ppm)



2c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1988.55
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1871.66
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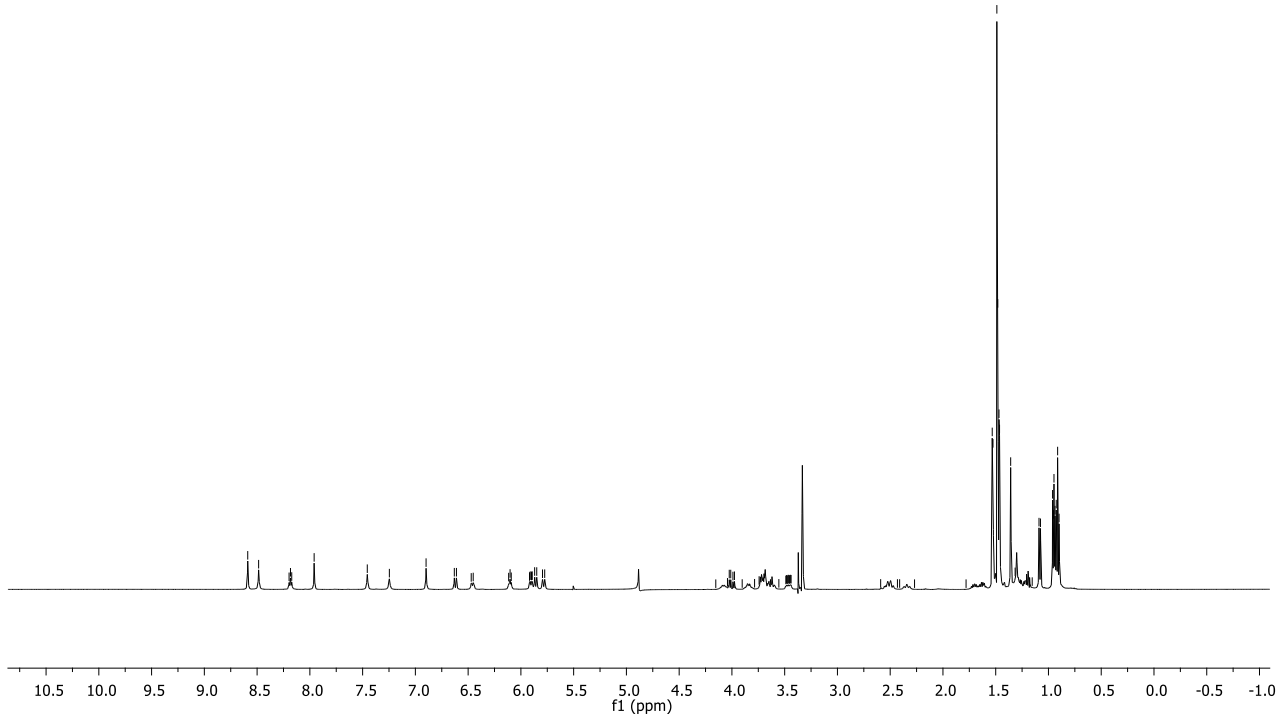
449.93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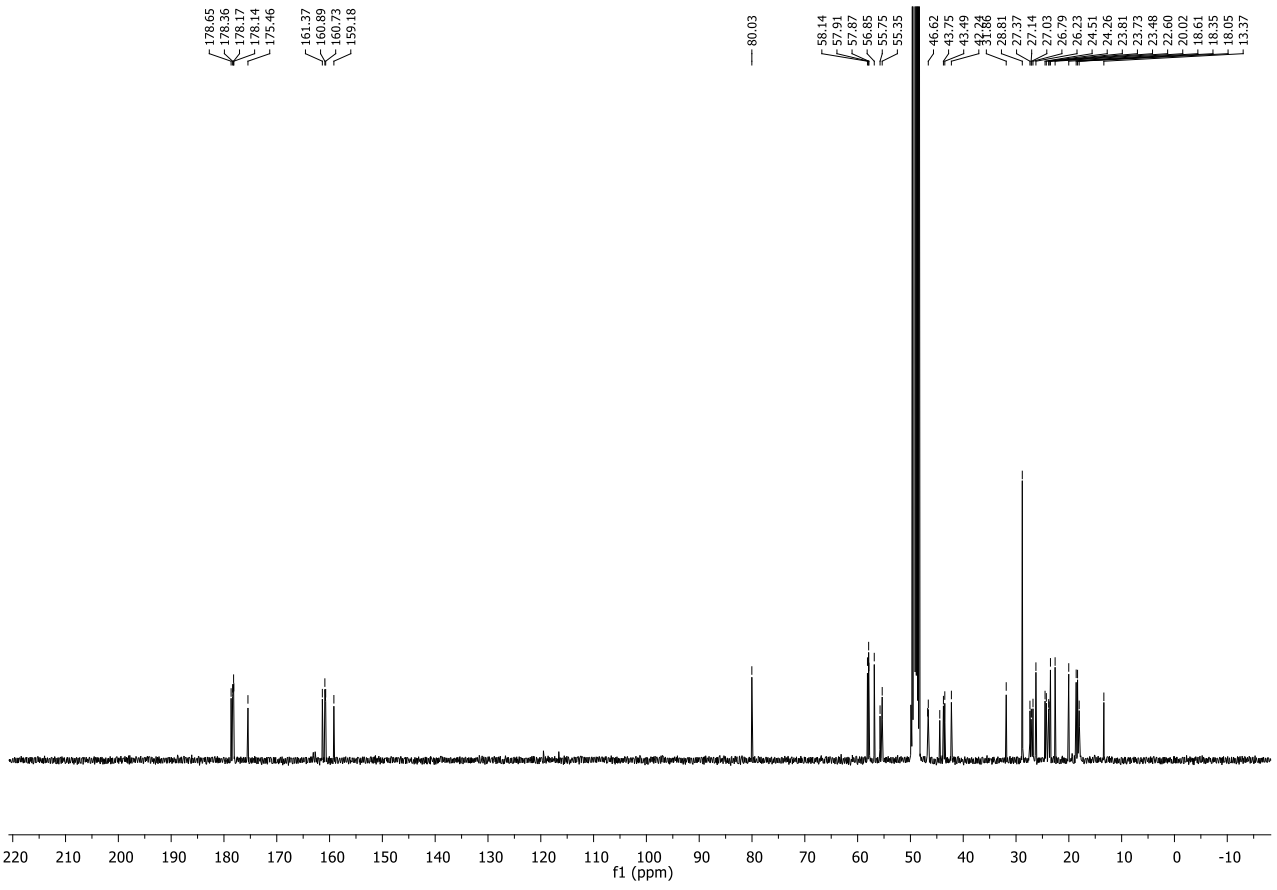
-1.0
f1 (ppm)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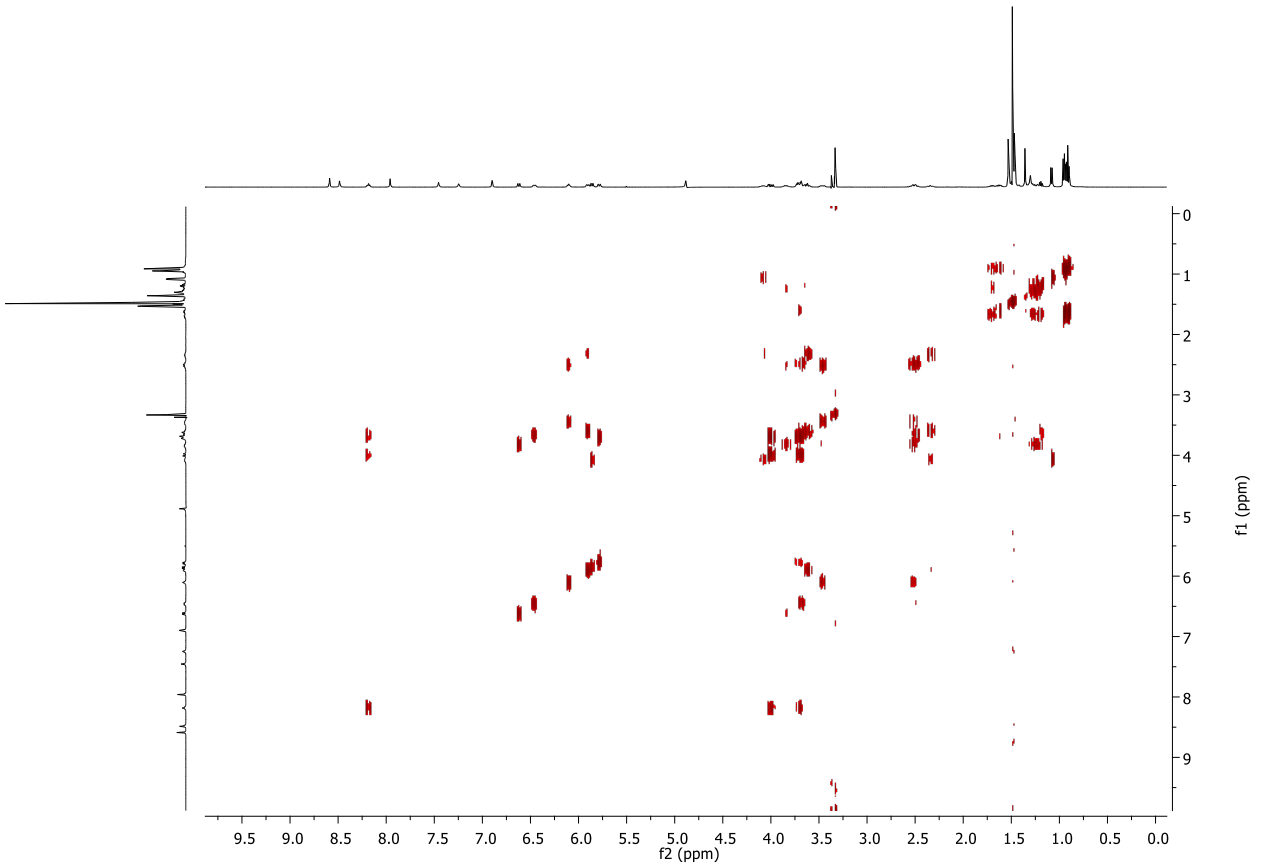
f1 (ppm)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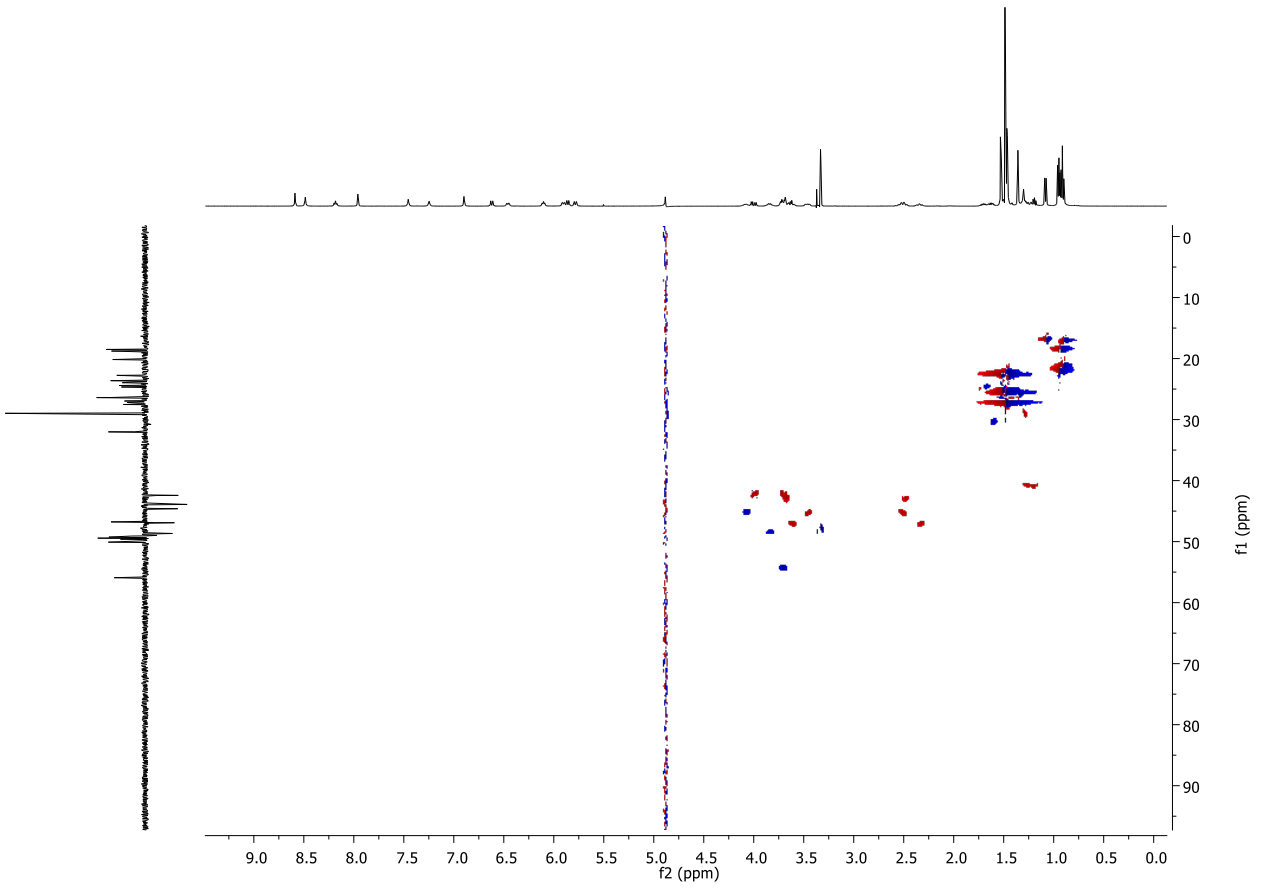
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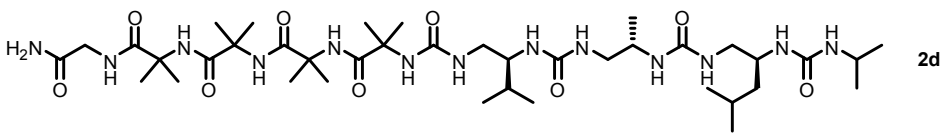

2d


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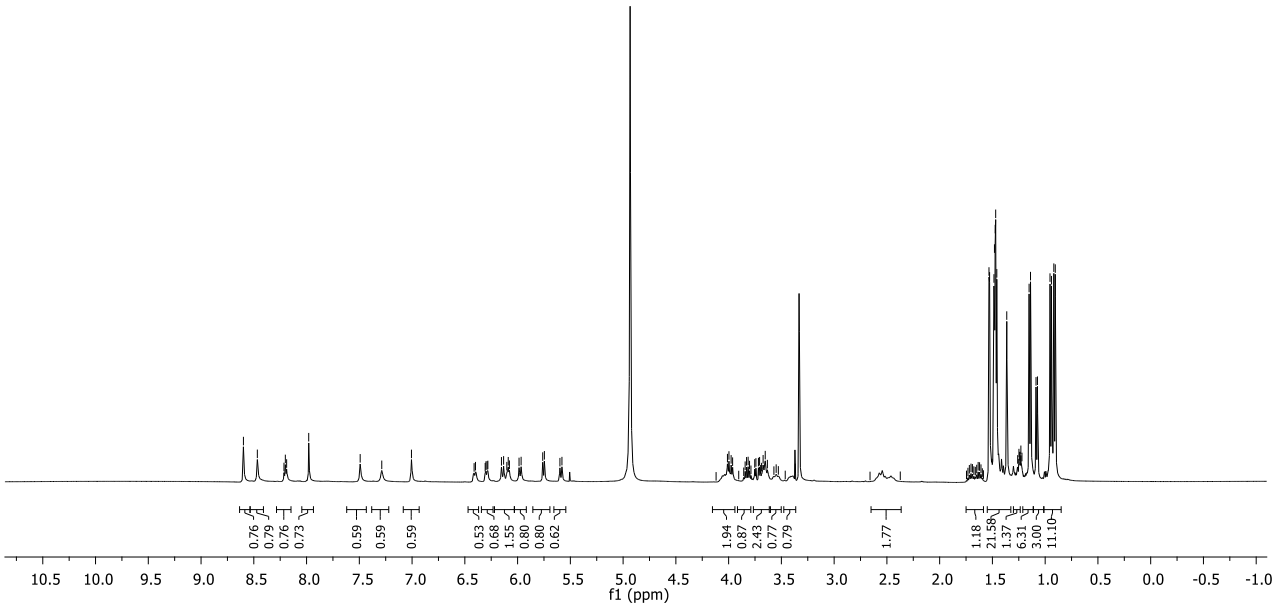
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6.31
3.00
11.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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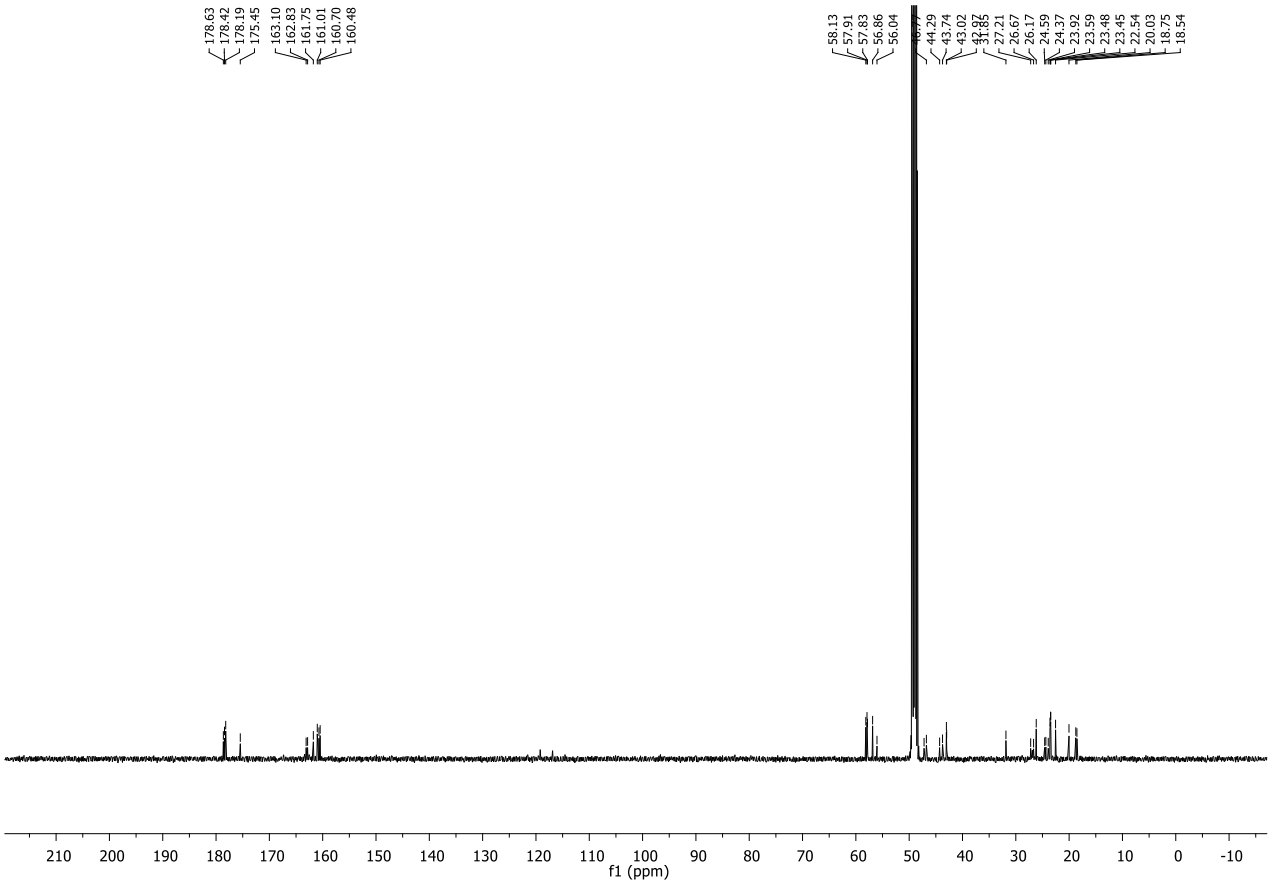
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42.92
31.82
27.21
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26.17
24.59
24.37
23.92
23.59
23.48
23.45
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20.03
18.75
18.54
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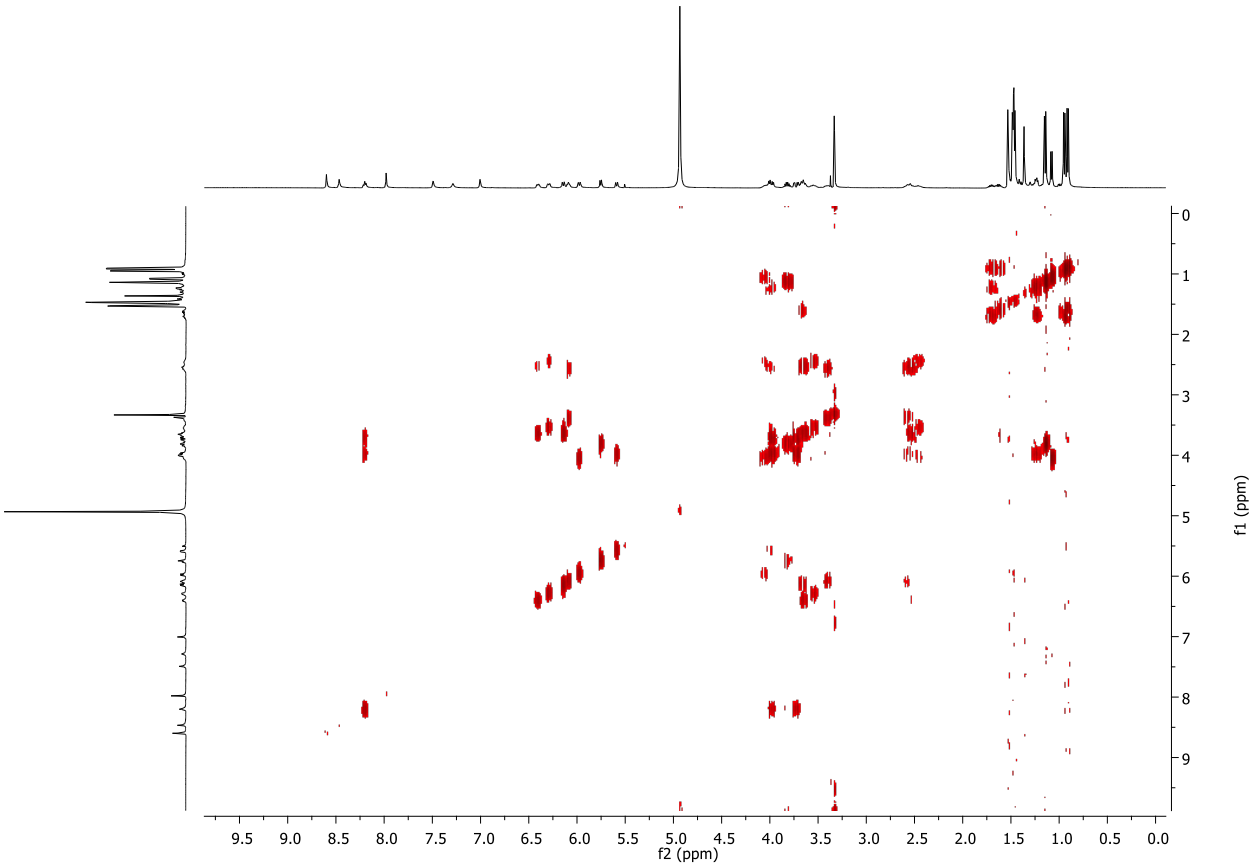
f1 (ppm)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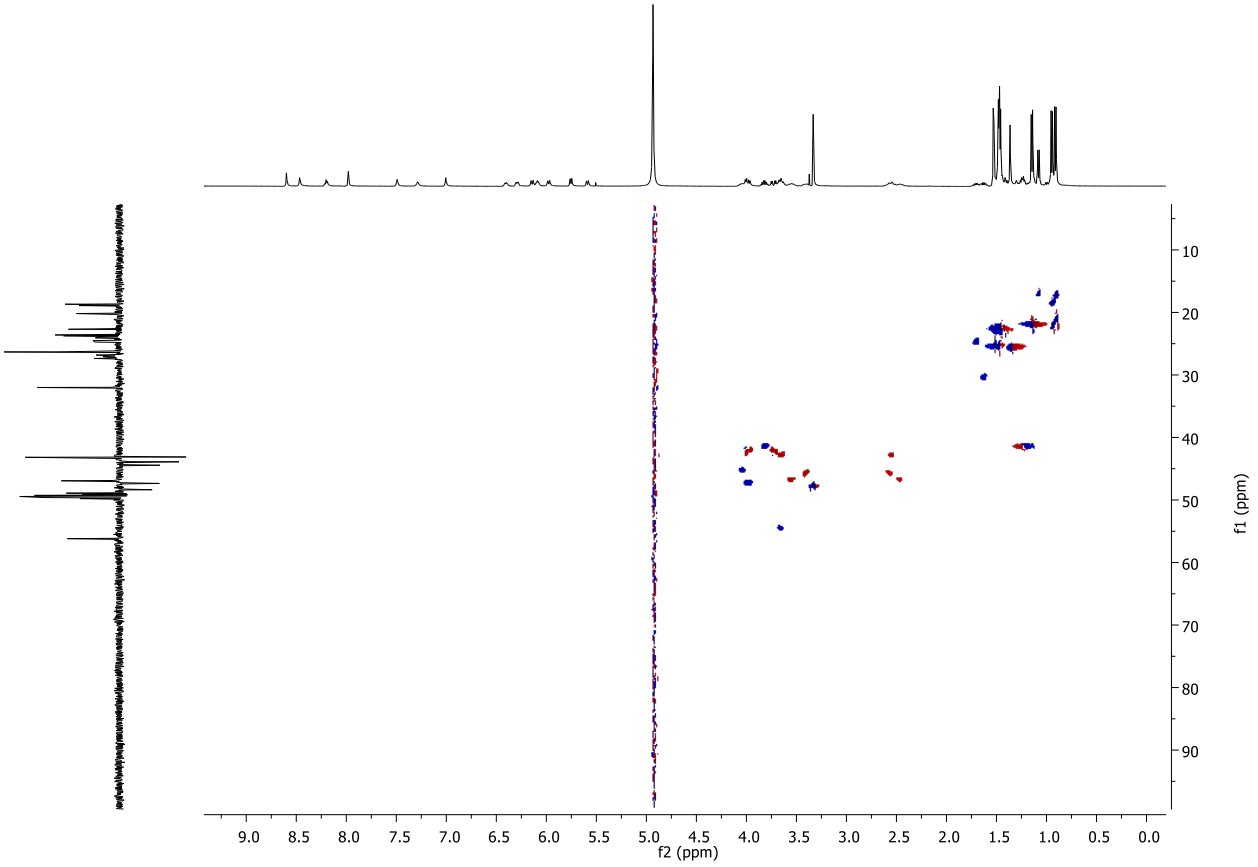
f1 (ppm)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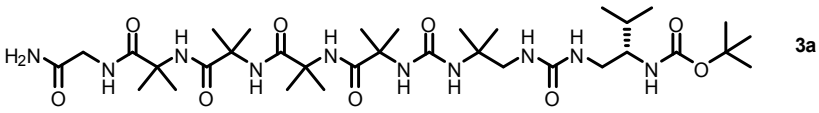
f1 (ppm)



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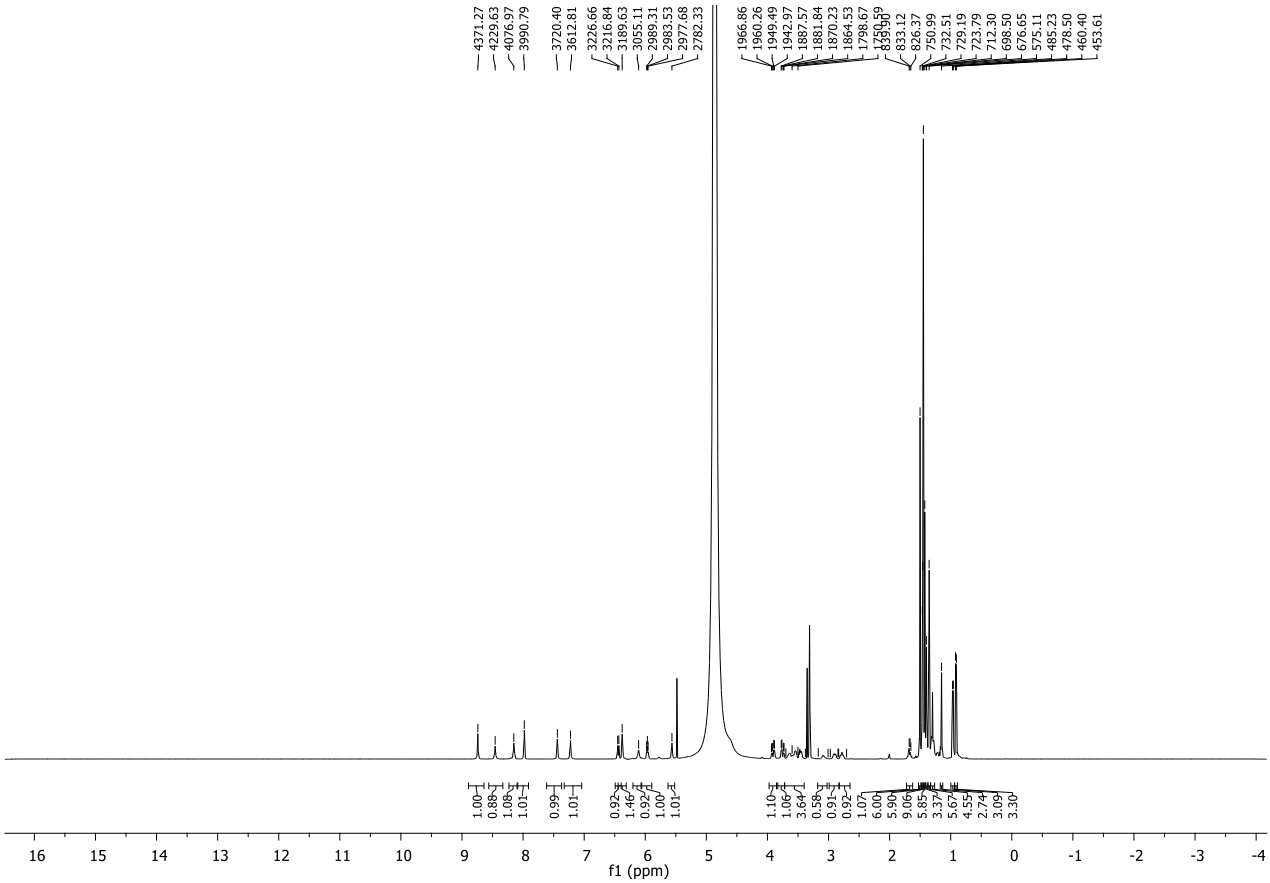
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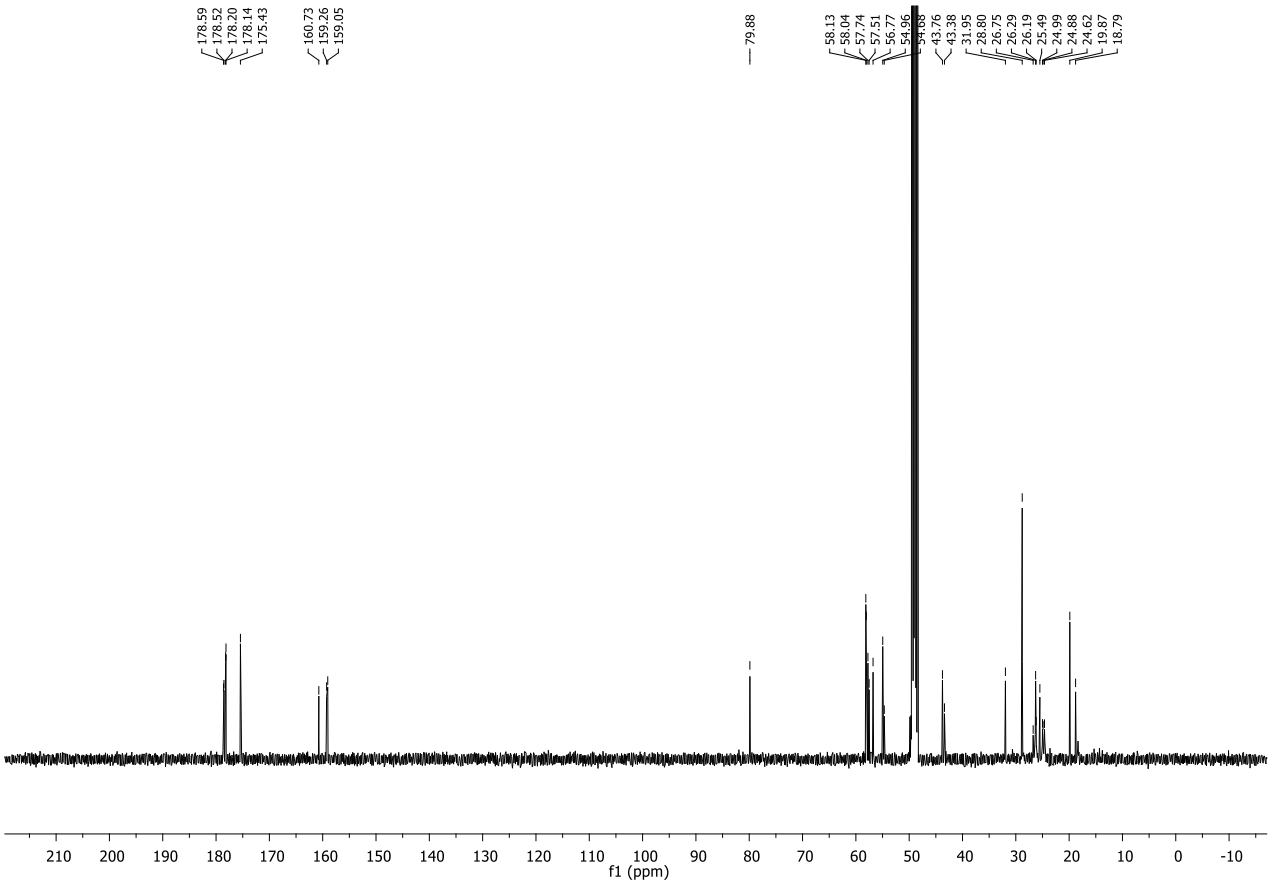
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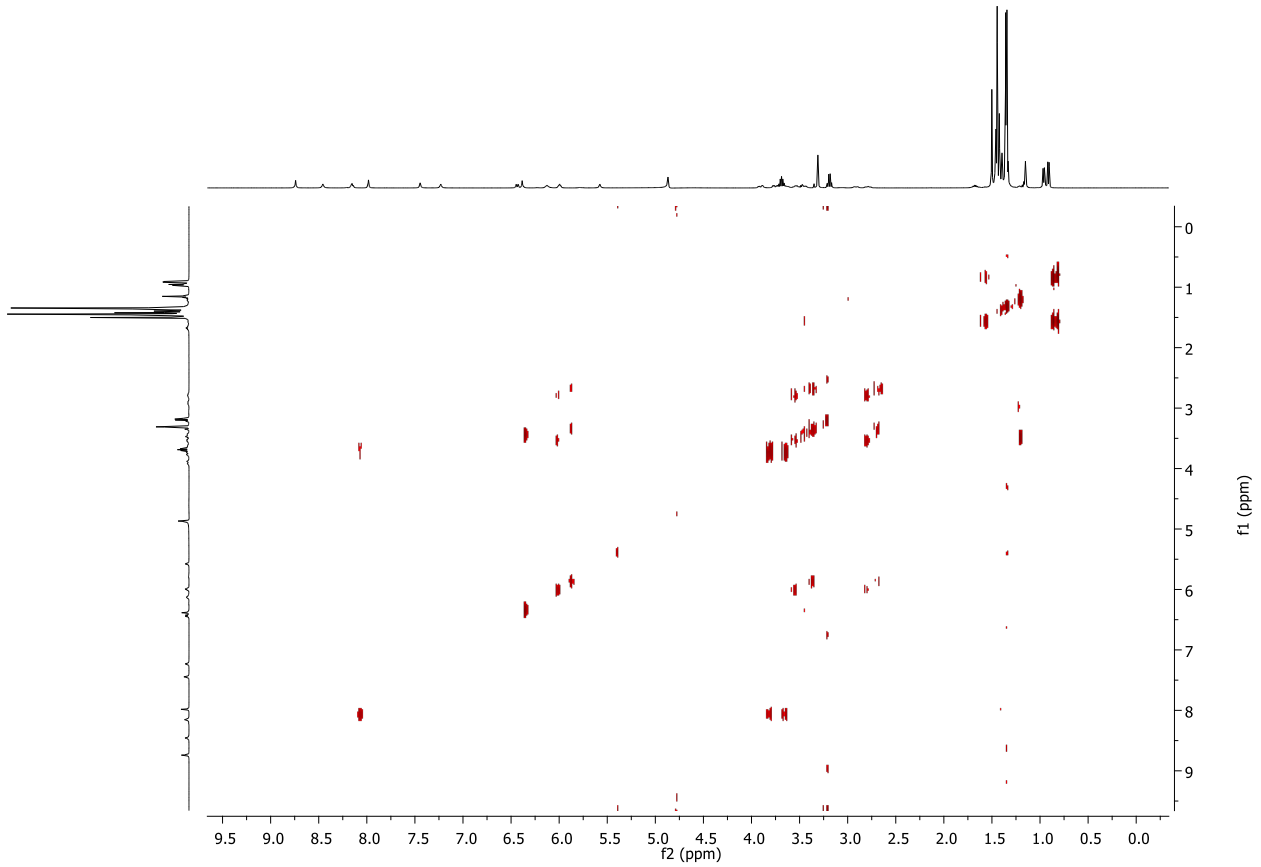
f1 (ppm)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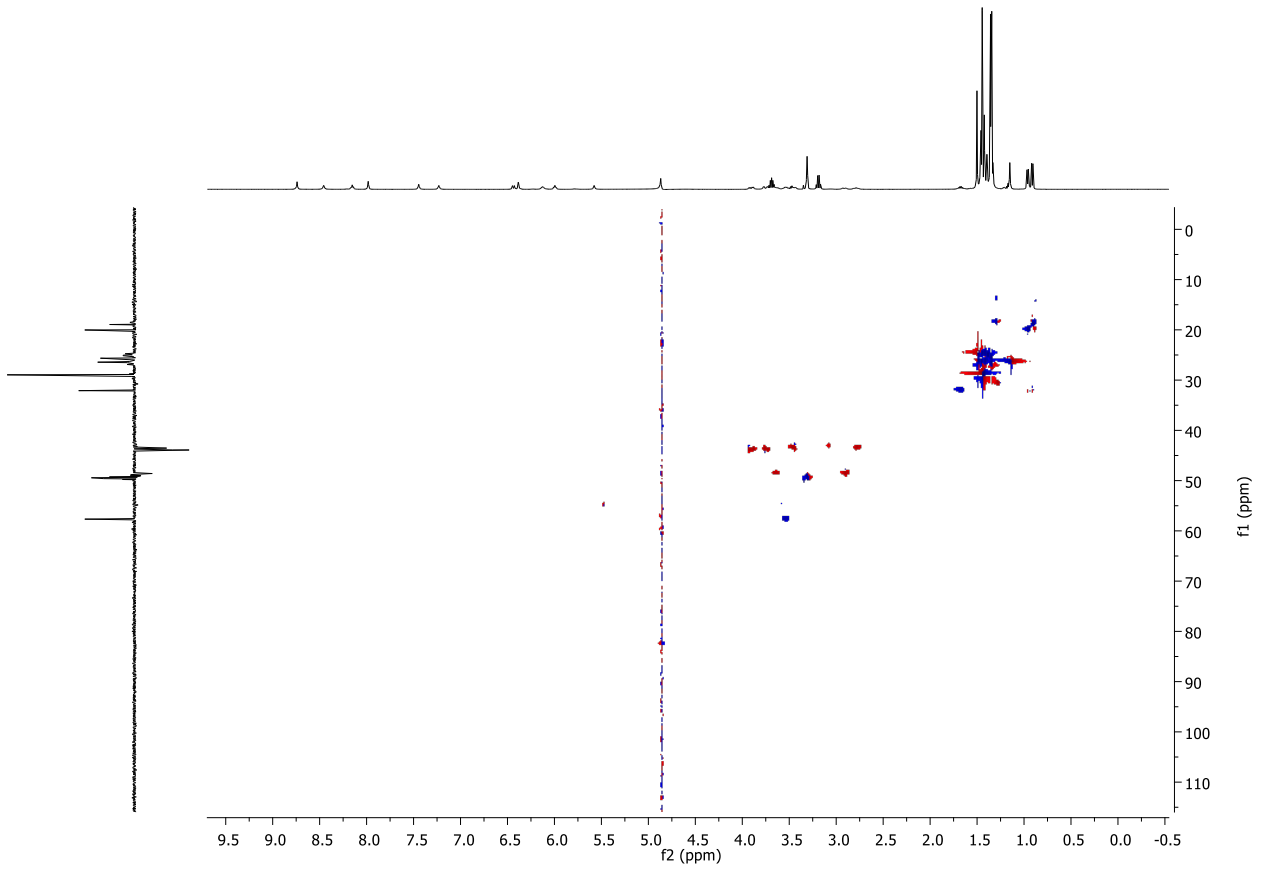
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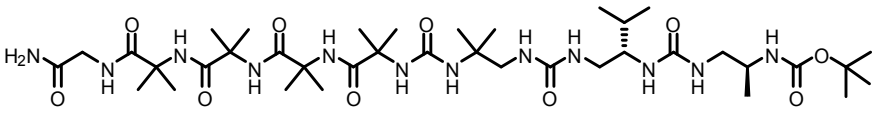
f1 (ppm)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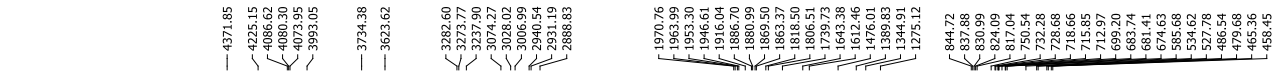
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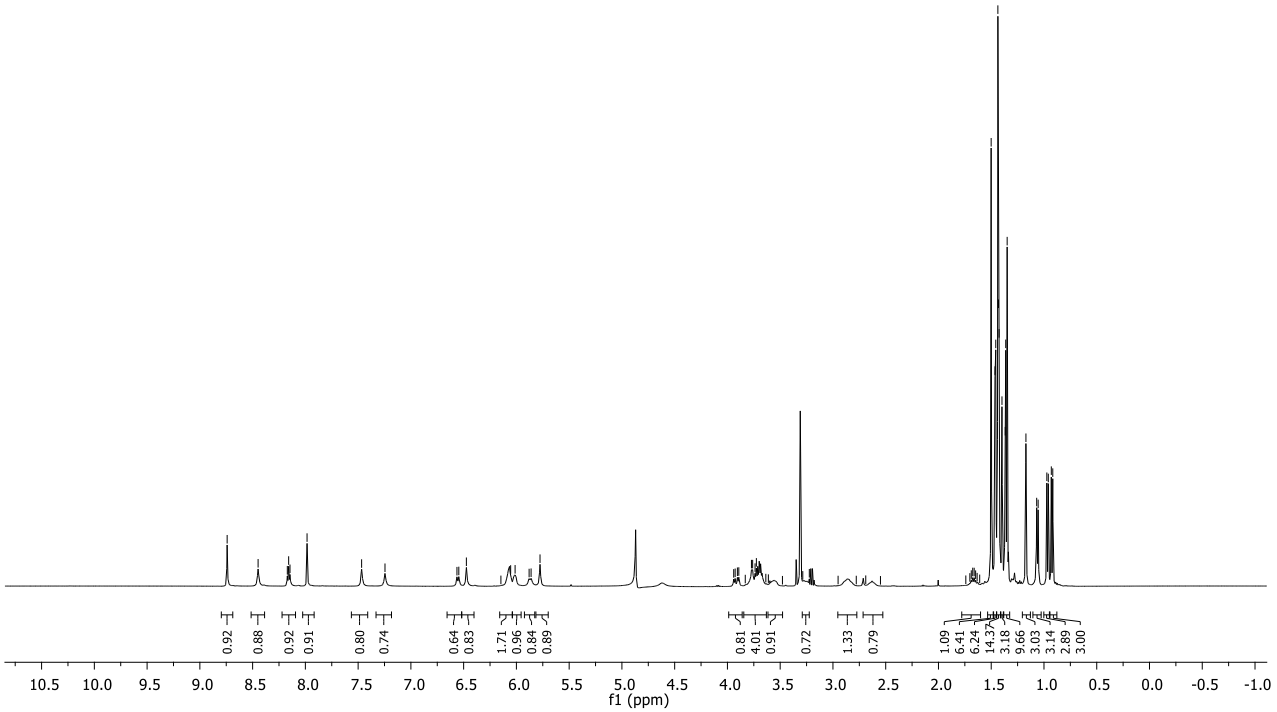
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6.24
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3.18
9.66
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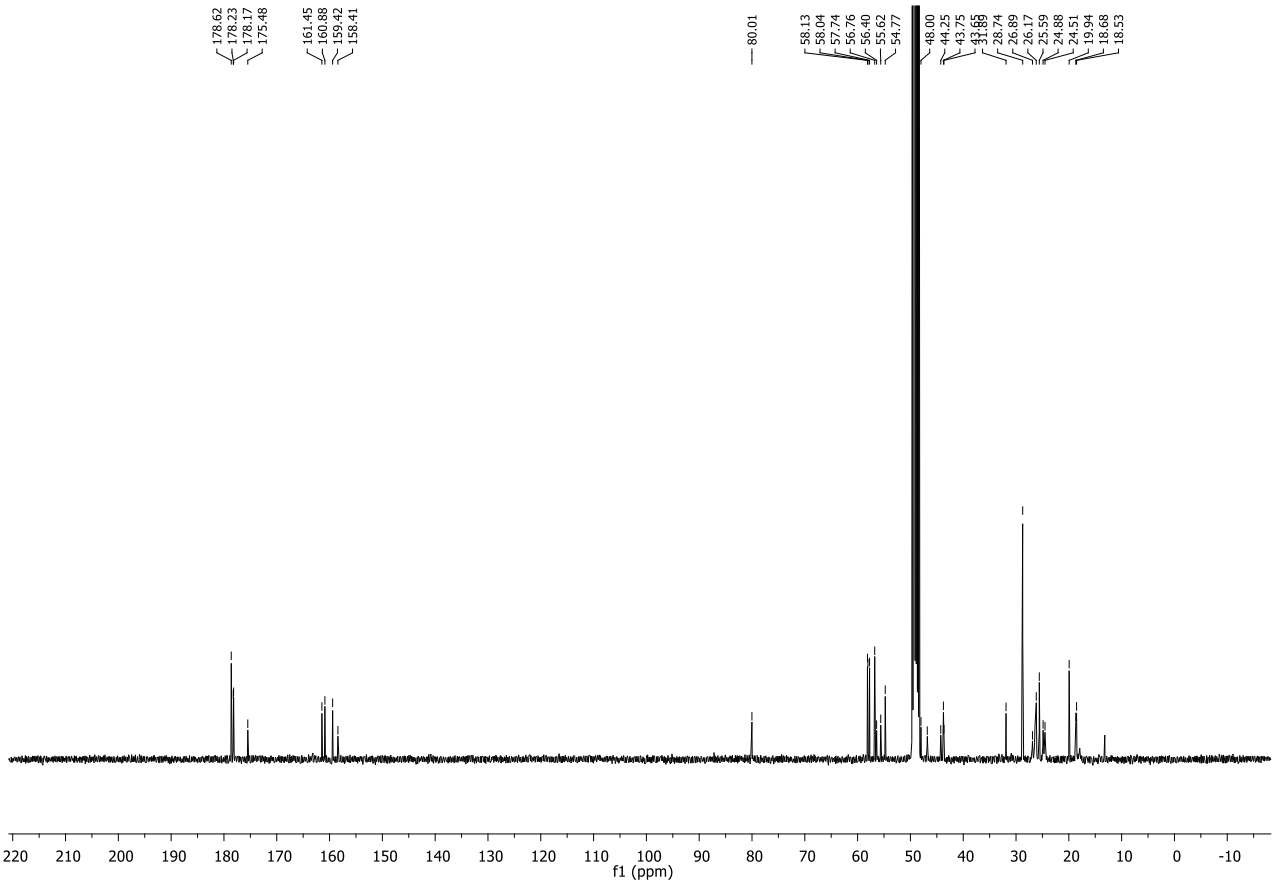
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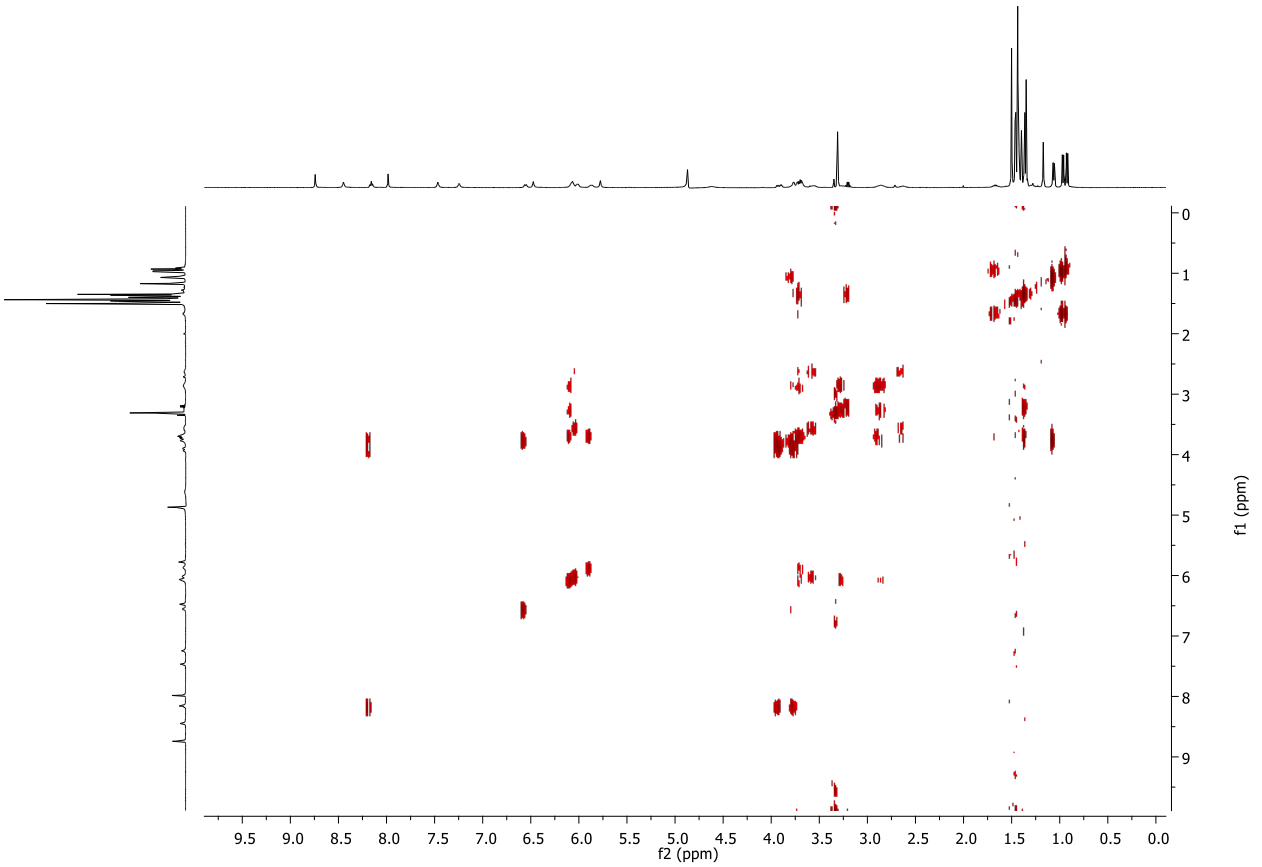
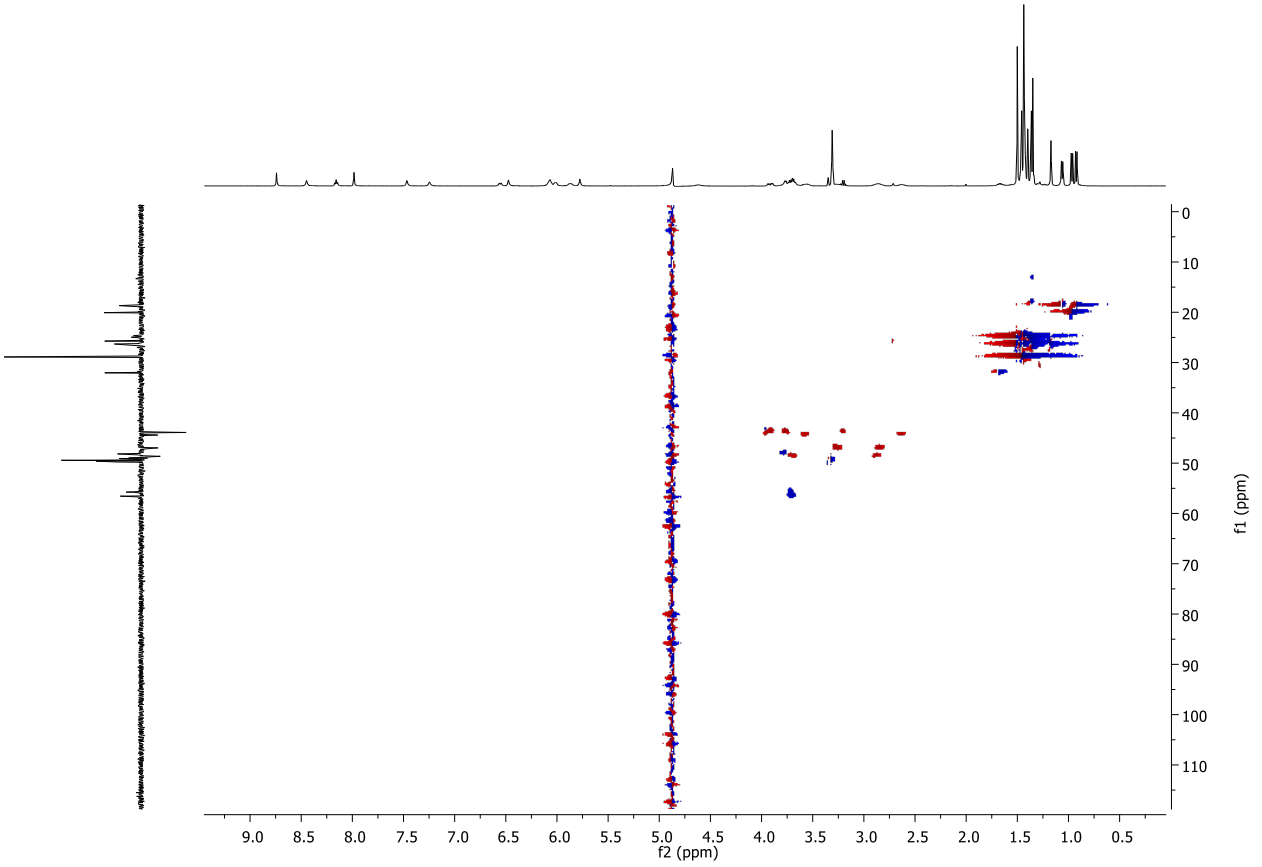
40
30
20
10
0
-10
f1 (ppm)


f2 (ppm)
f1 (ppm)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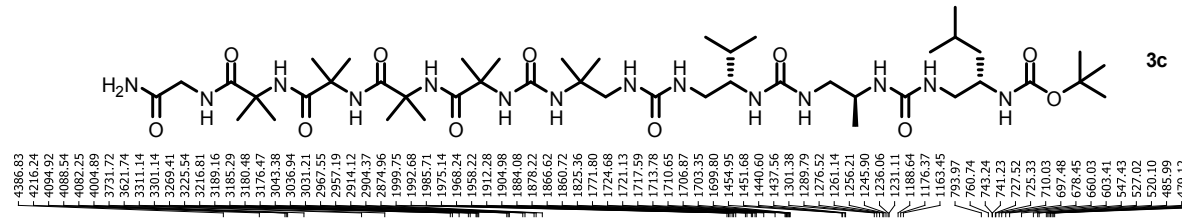
f1 (ppm)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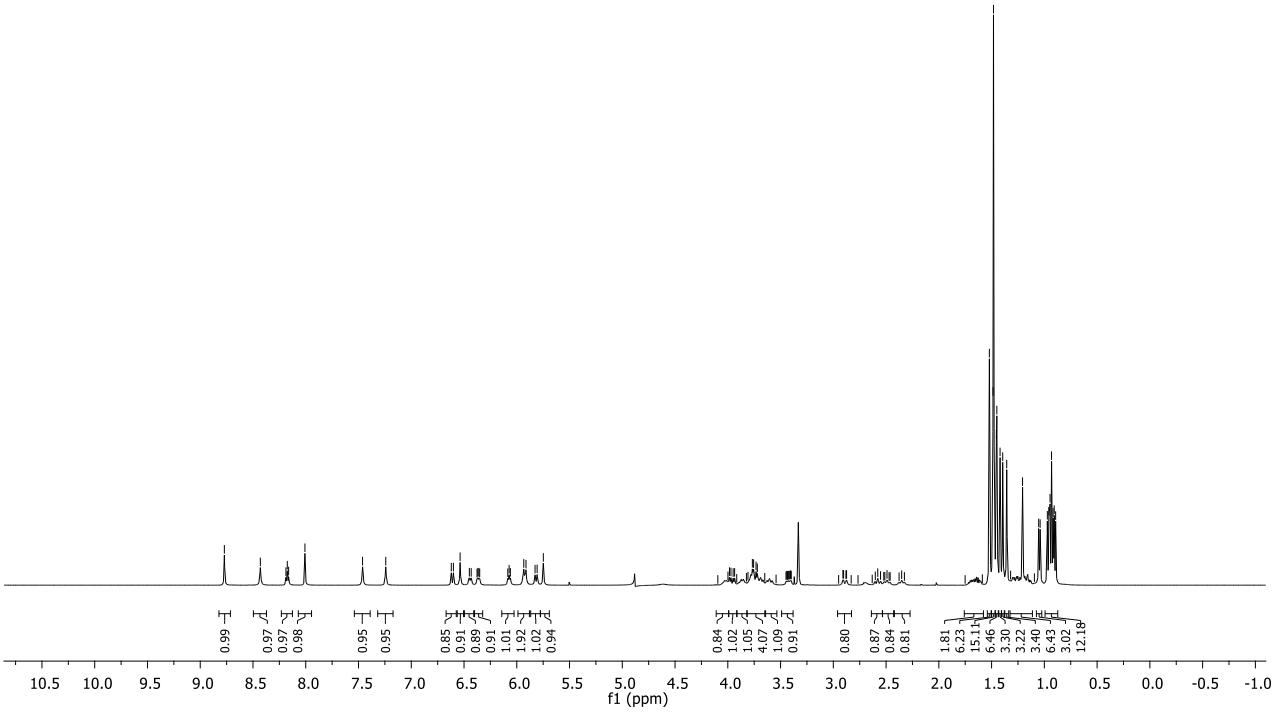
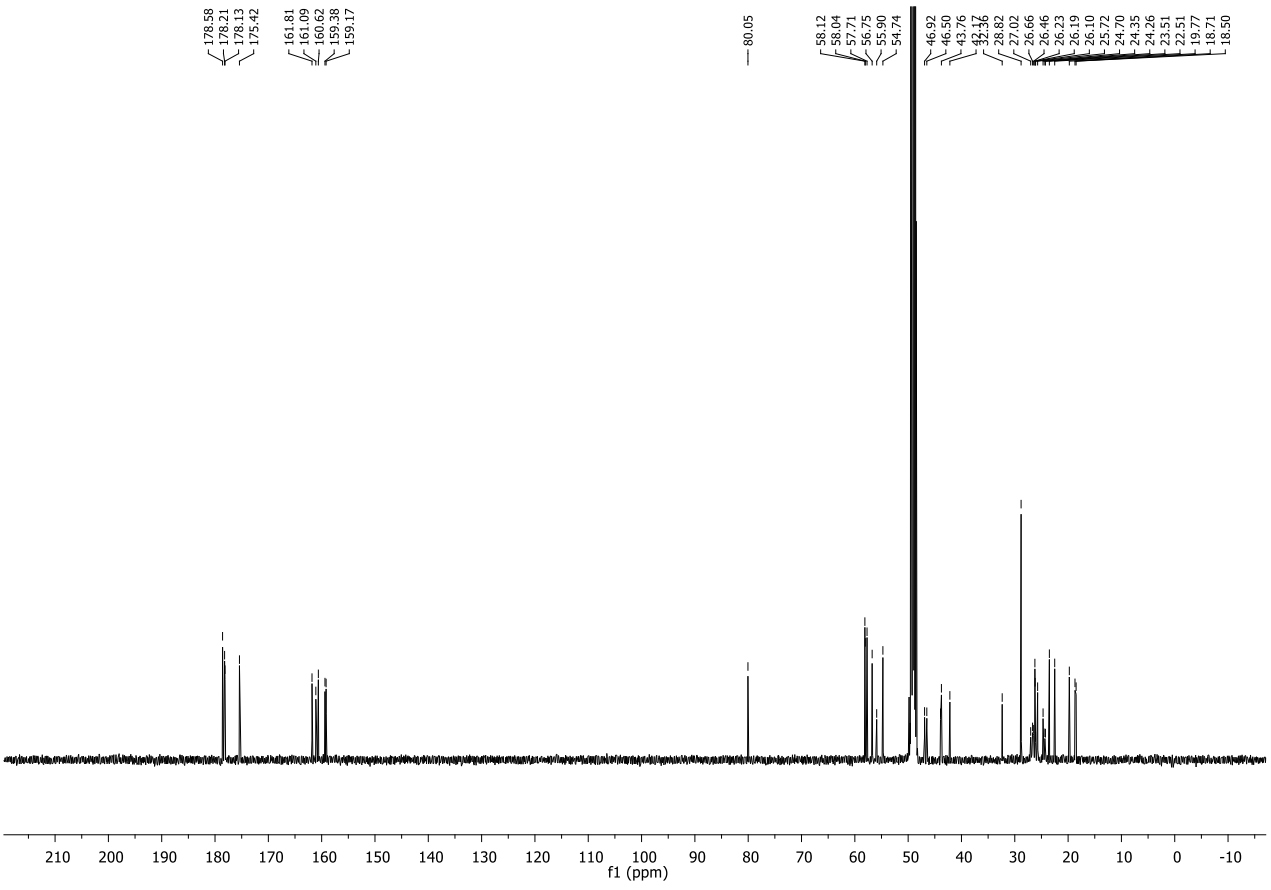

f1 (ppm)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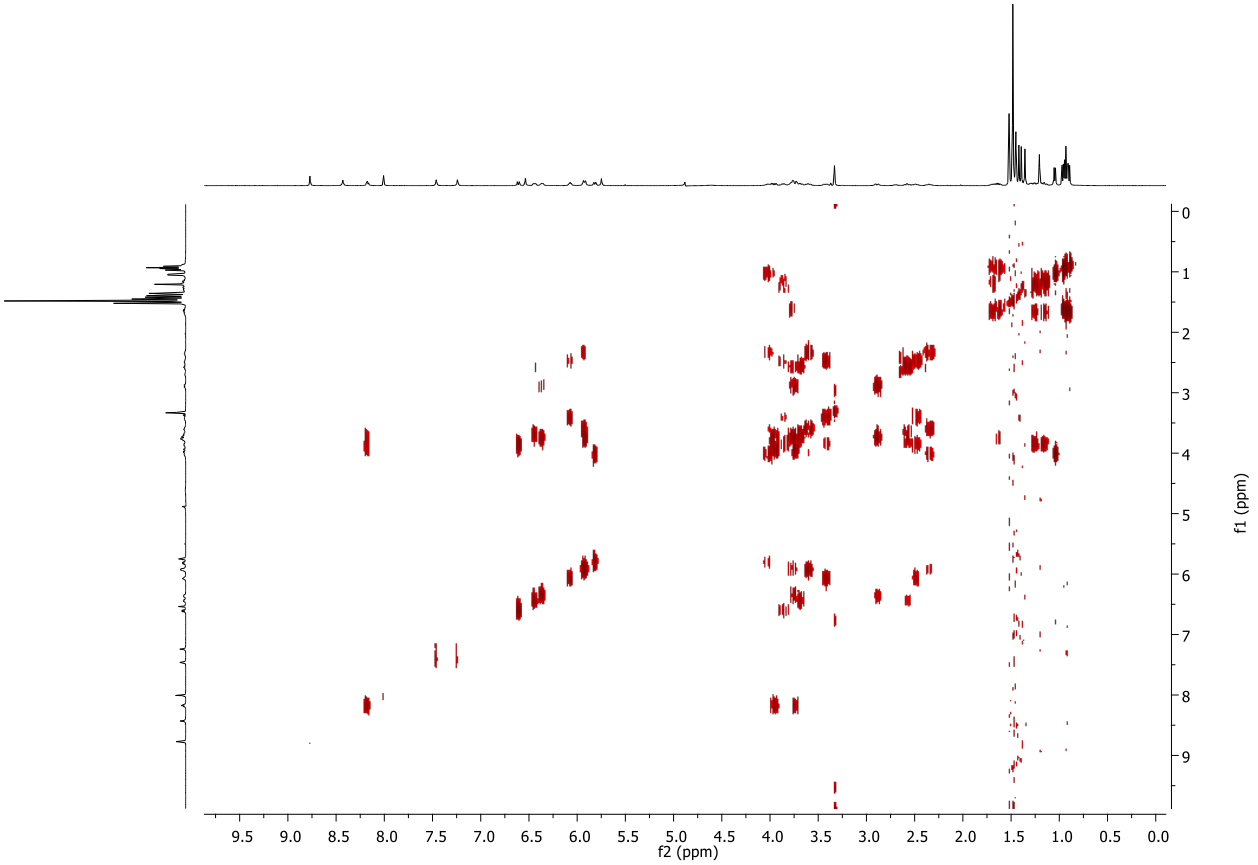
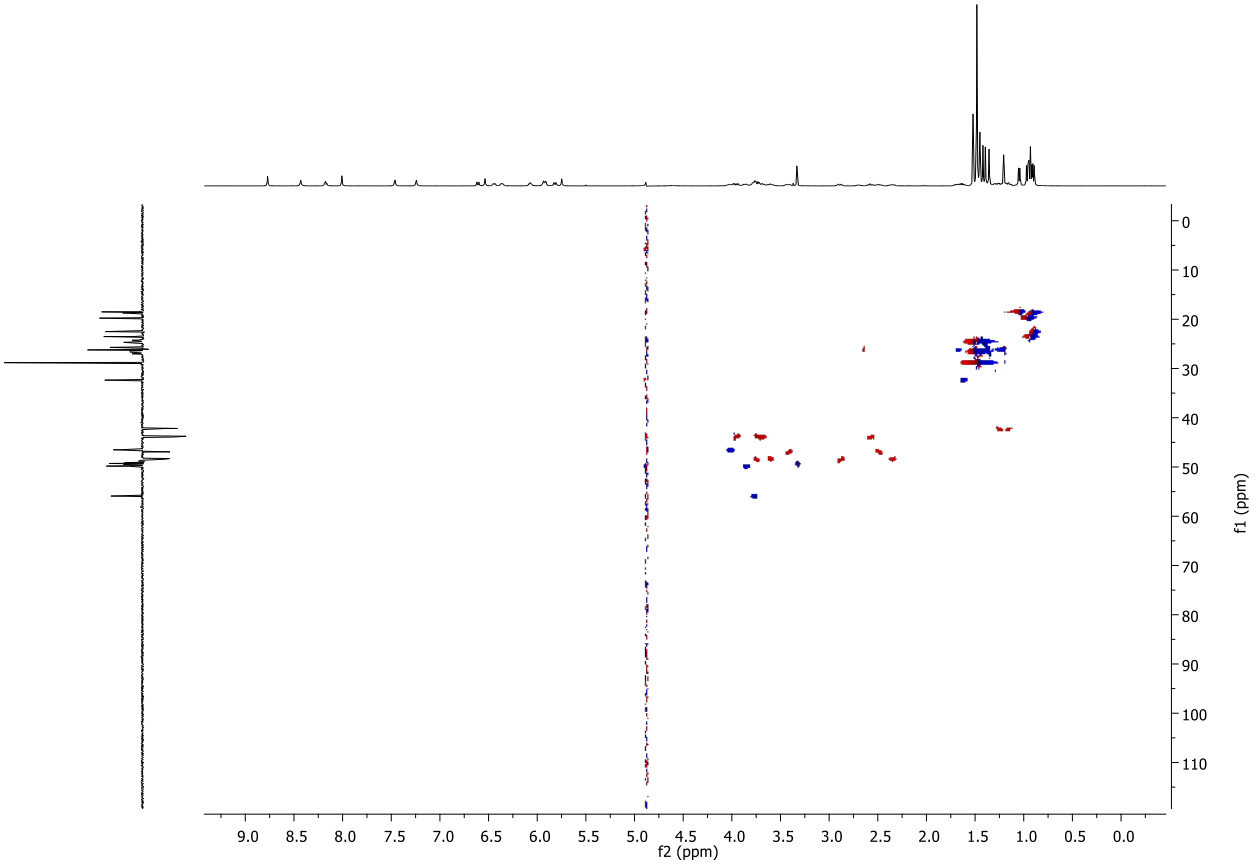

f2 (ppm)
f1 (ppm)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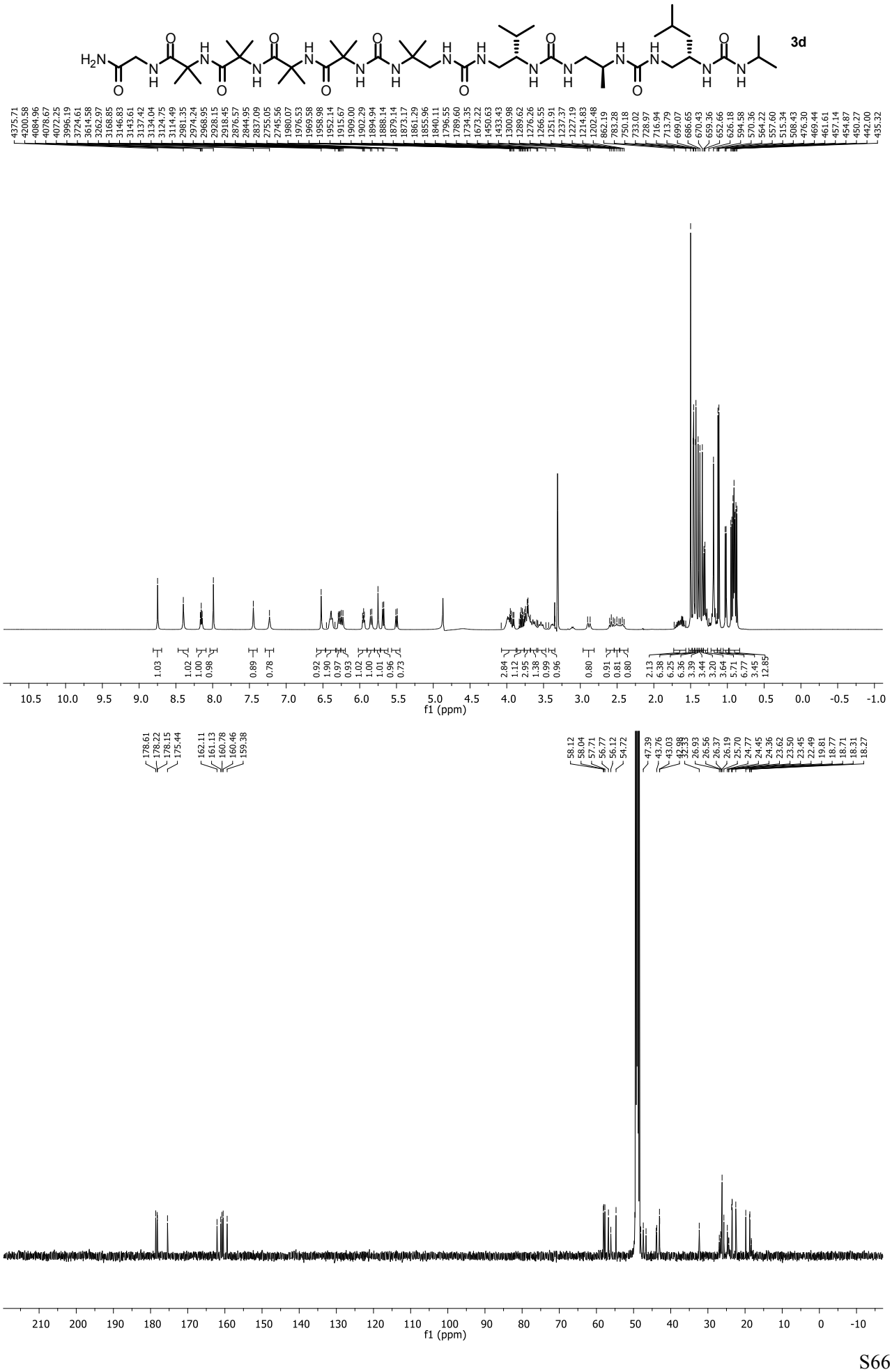
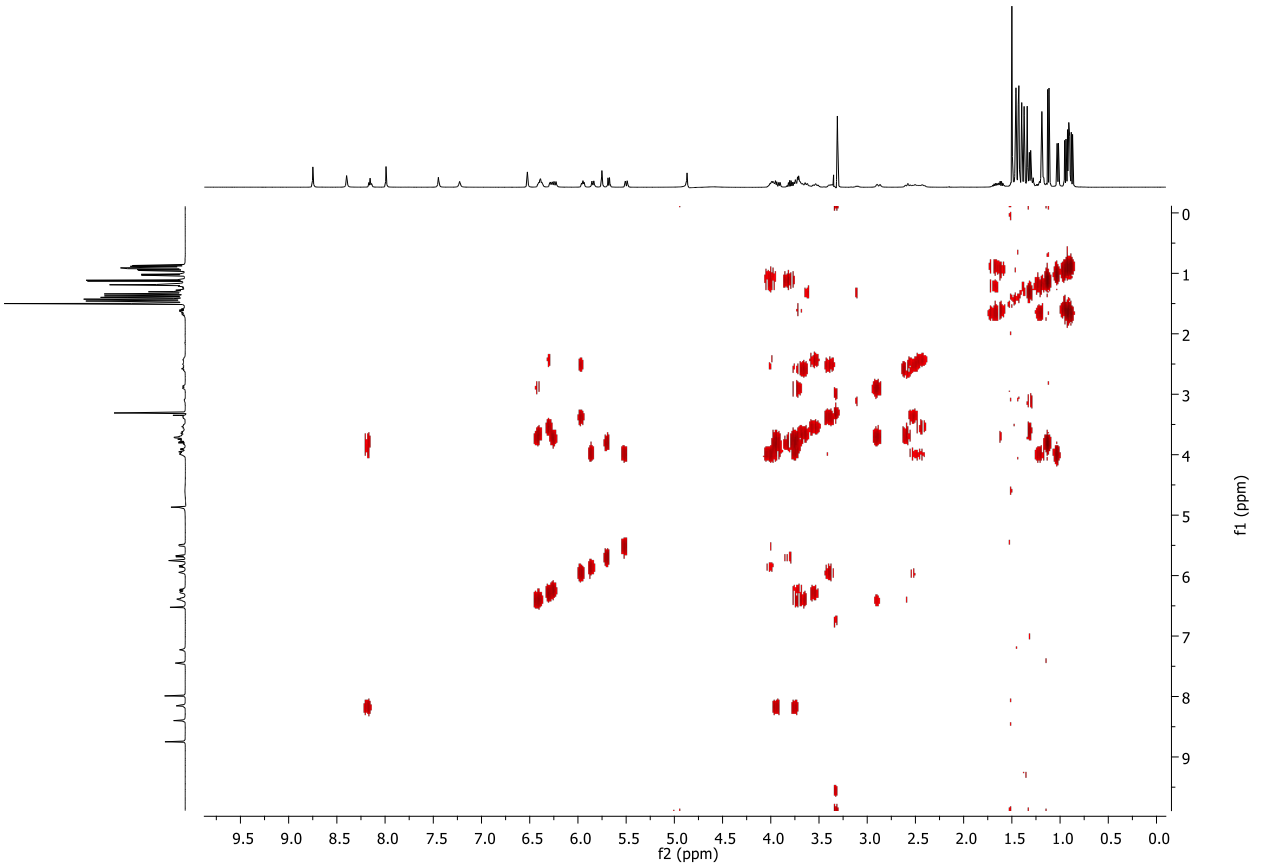
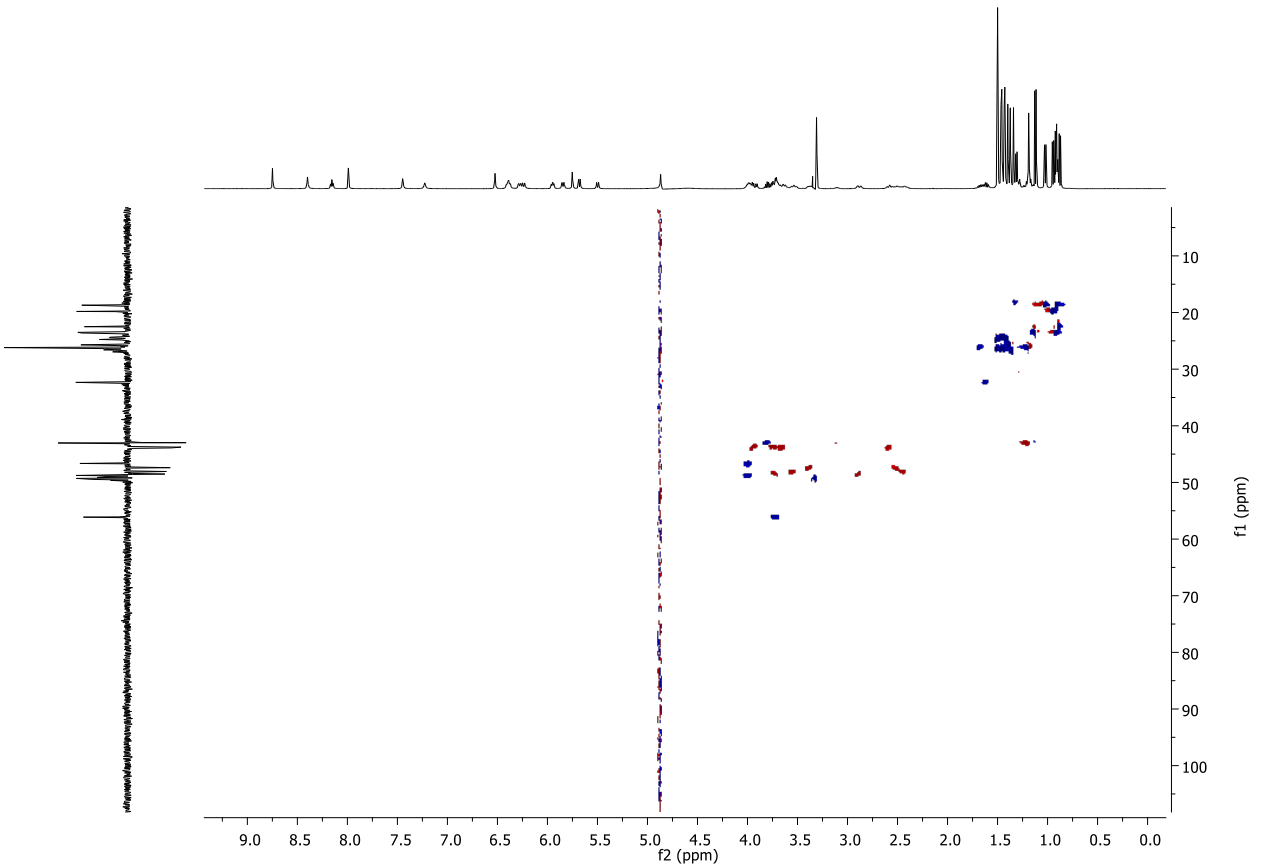
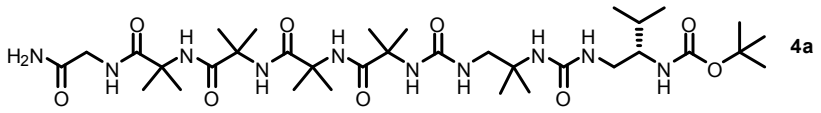
f1 (ppm)


3d
f1 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)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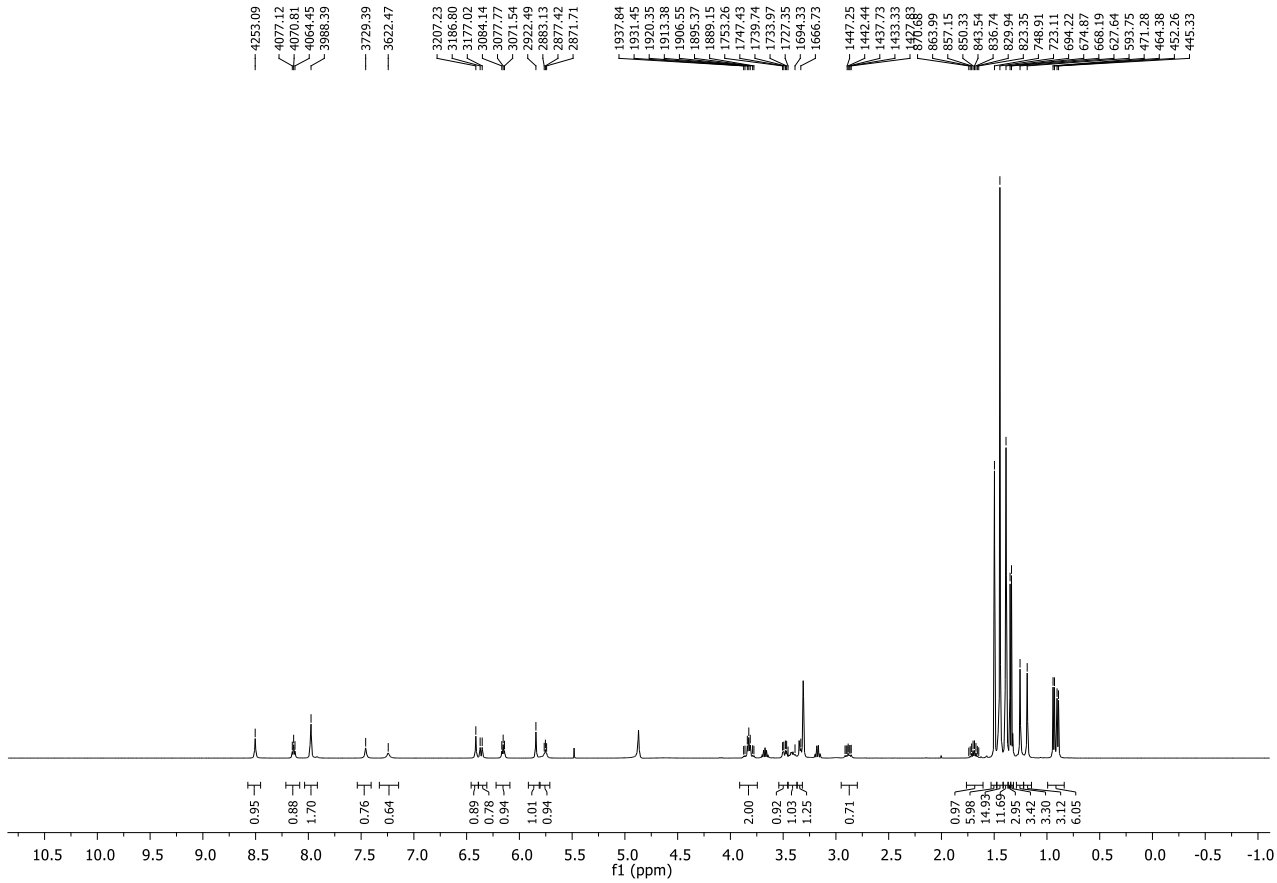
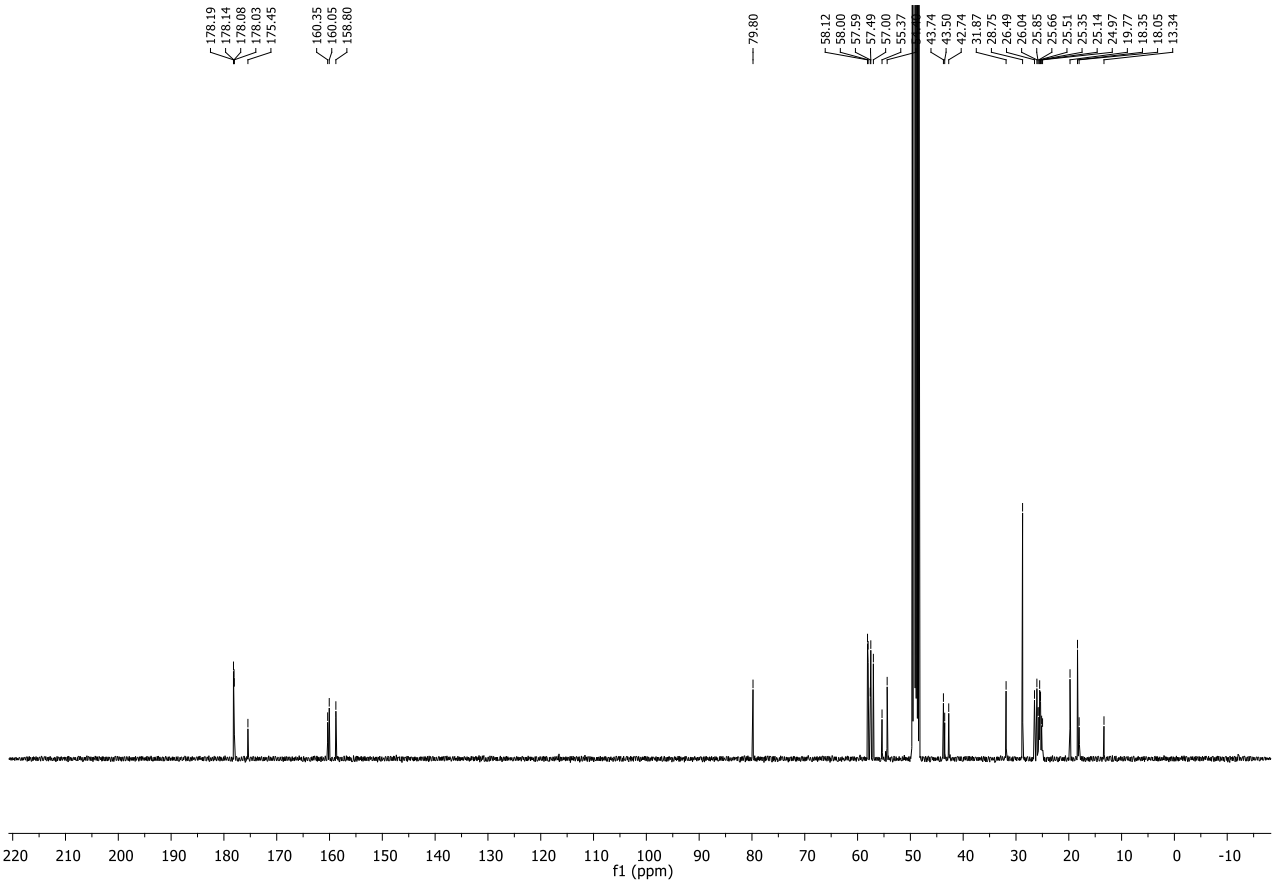
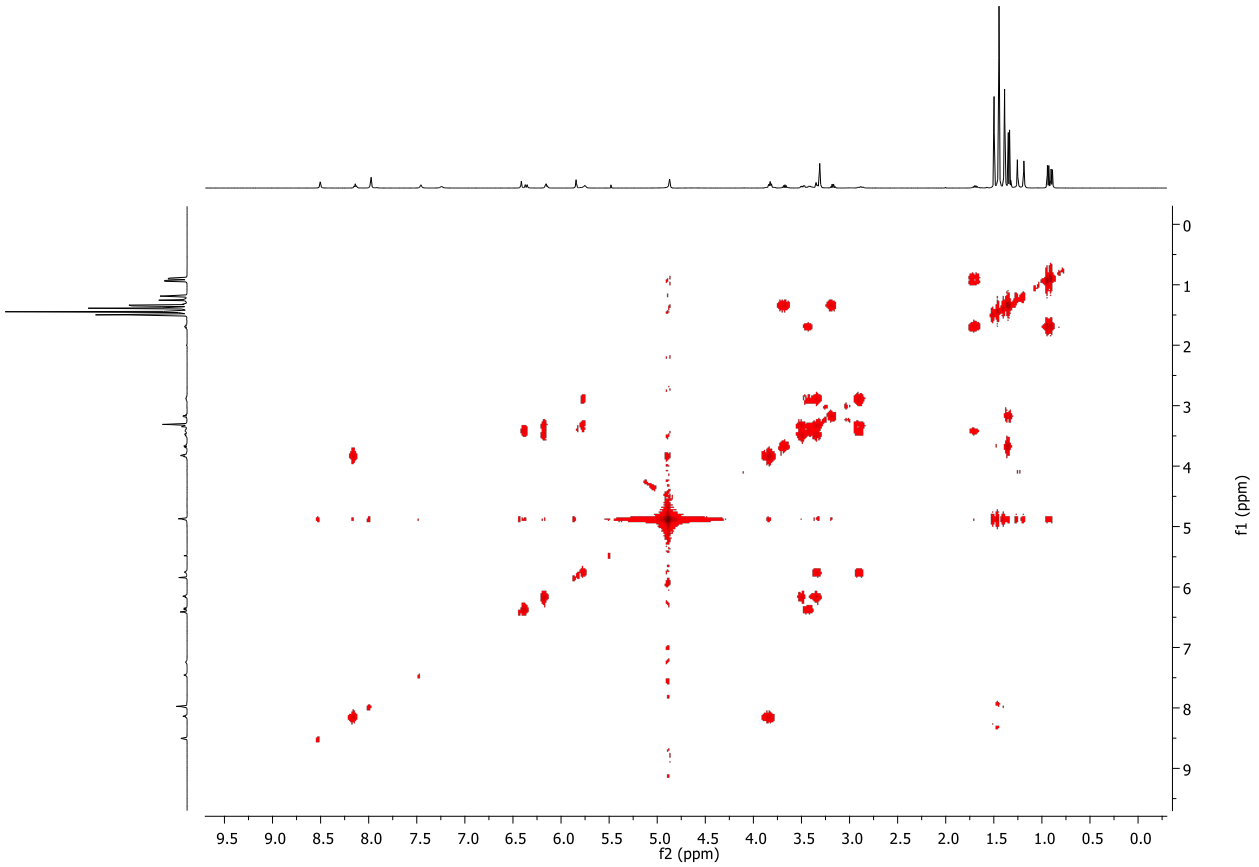
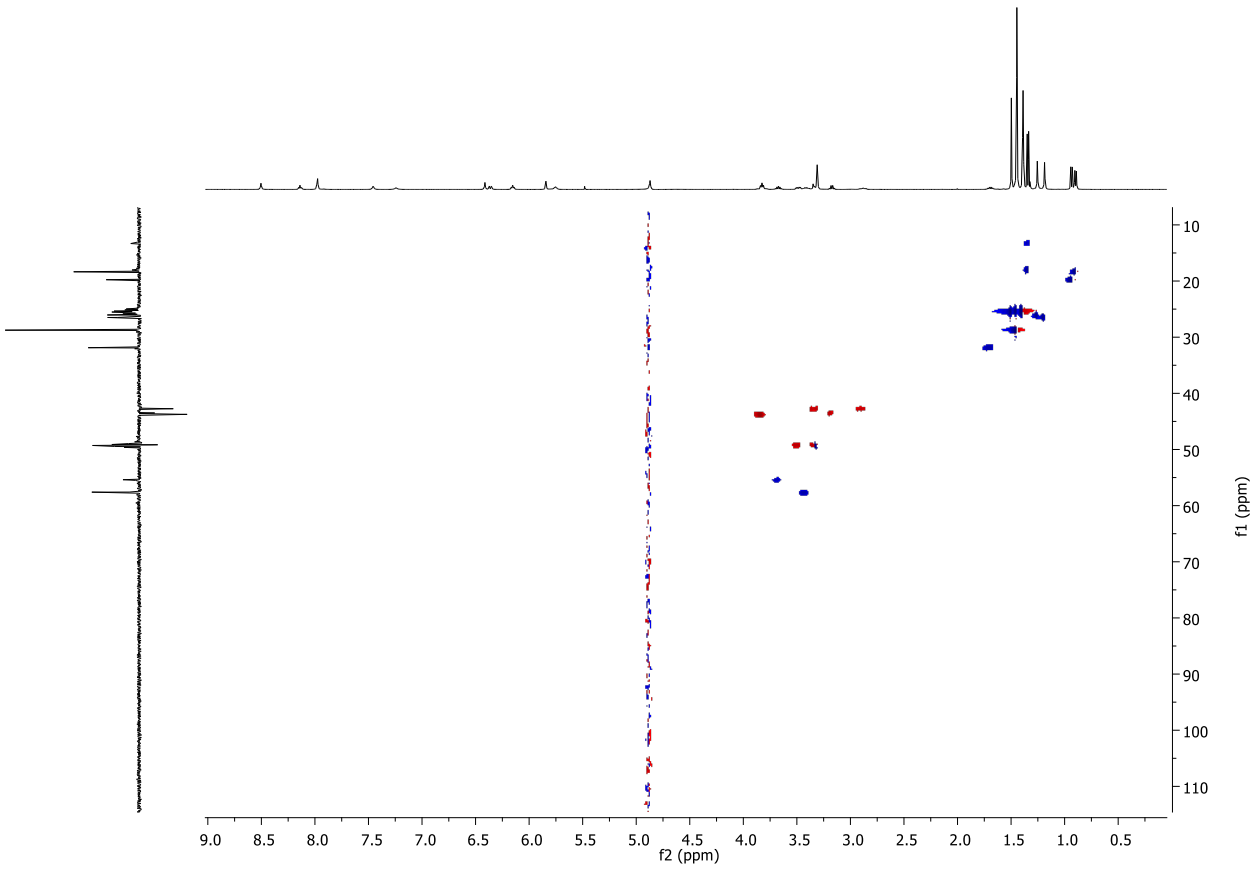
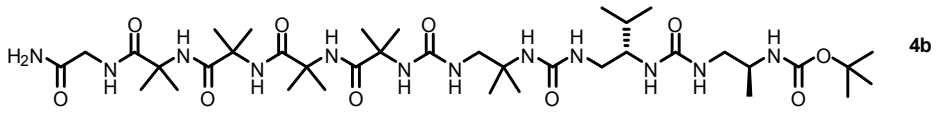

f1 (ppm)


f1 (ppm)


f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)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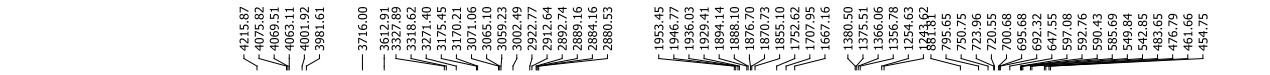
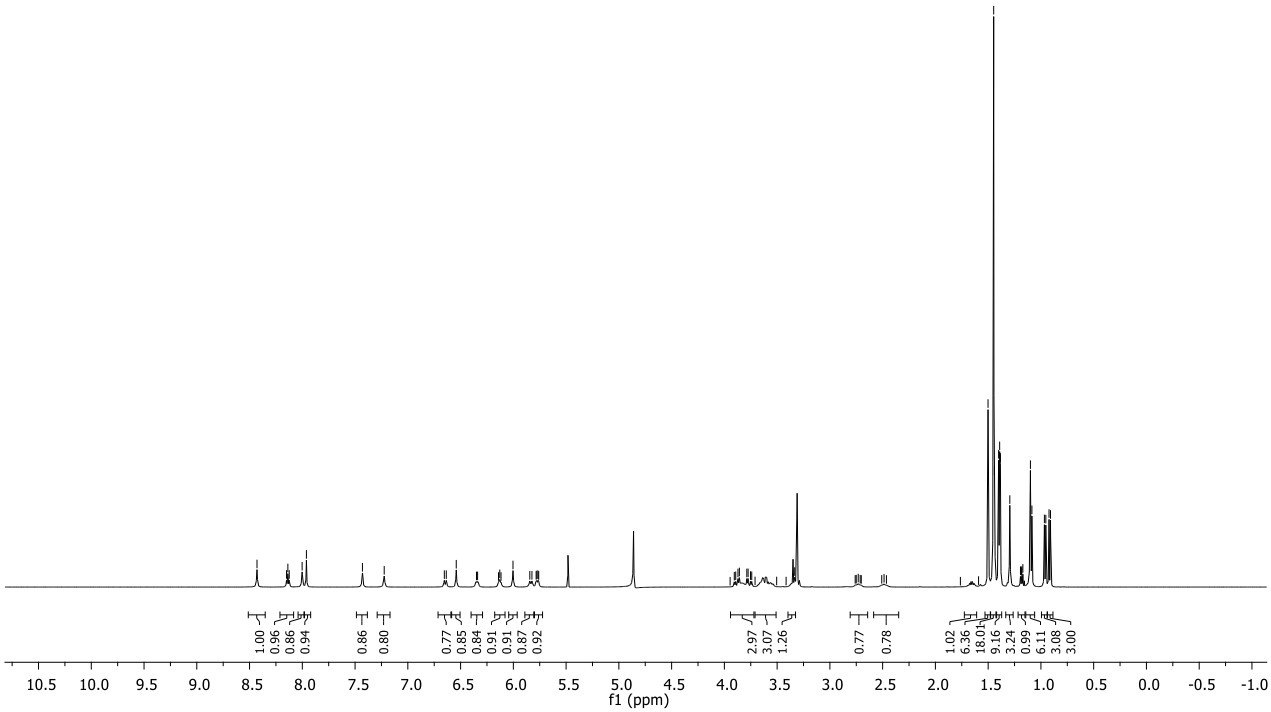
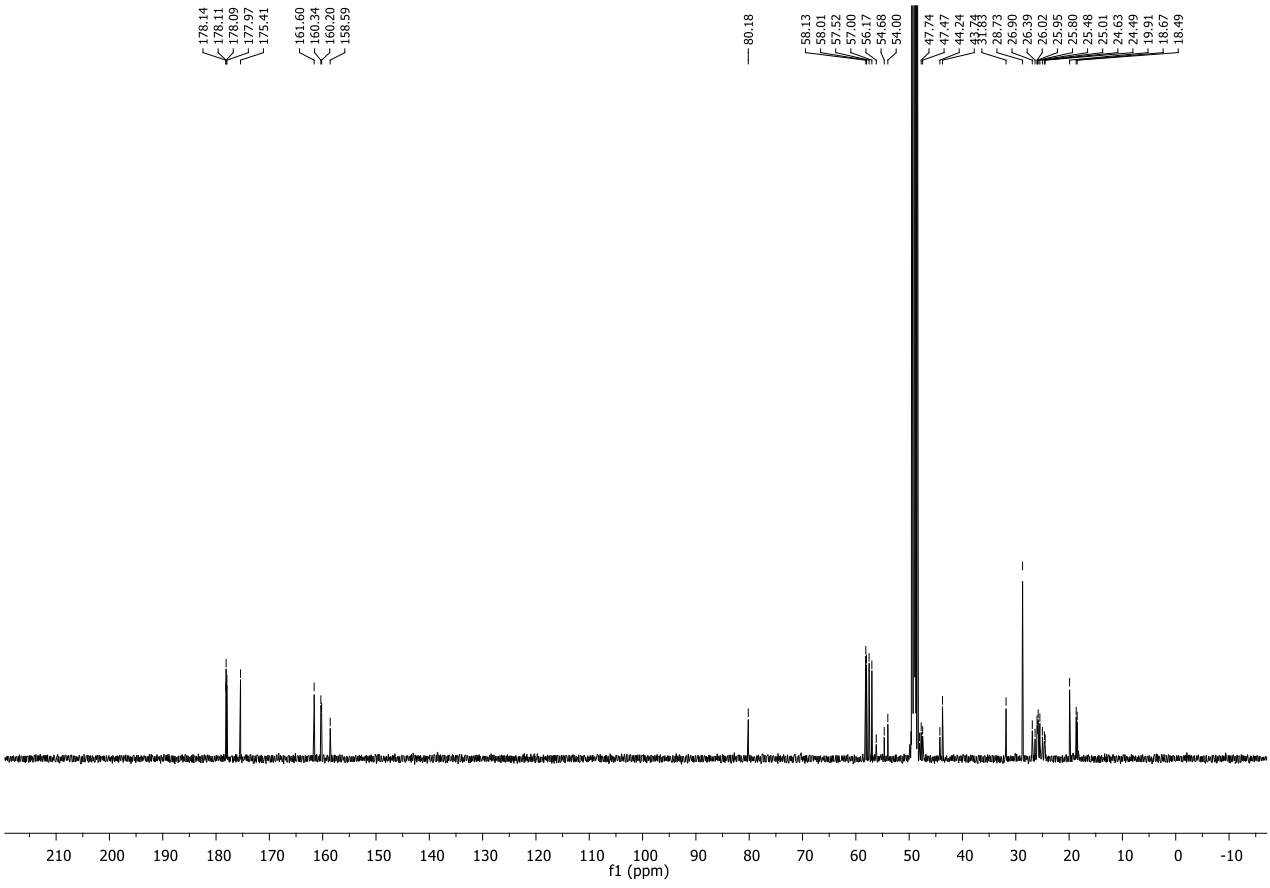
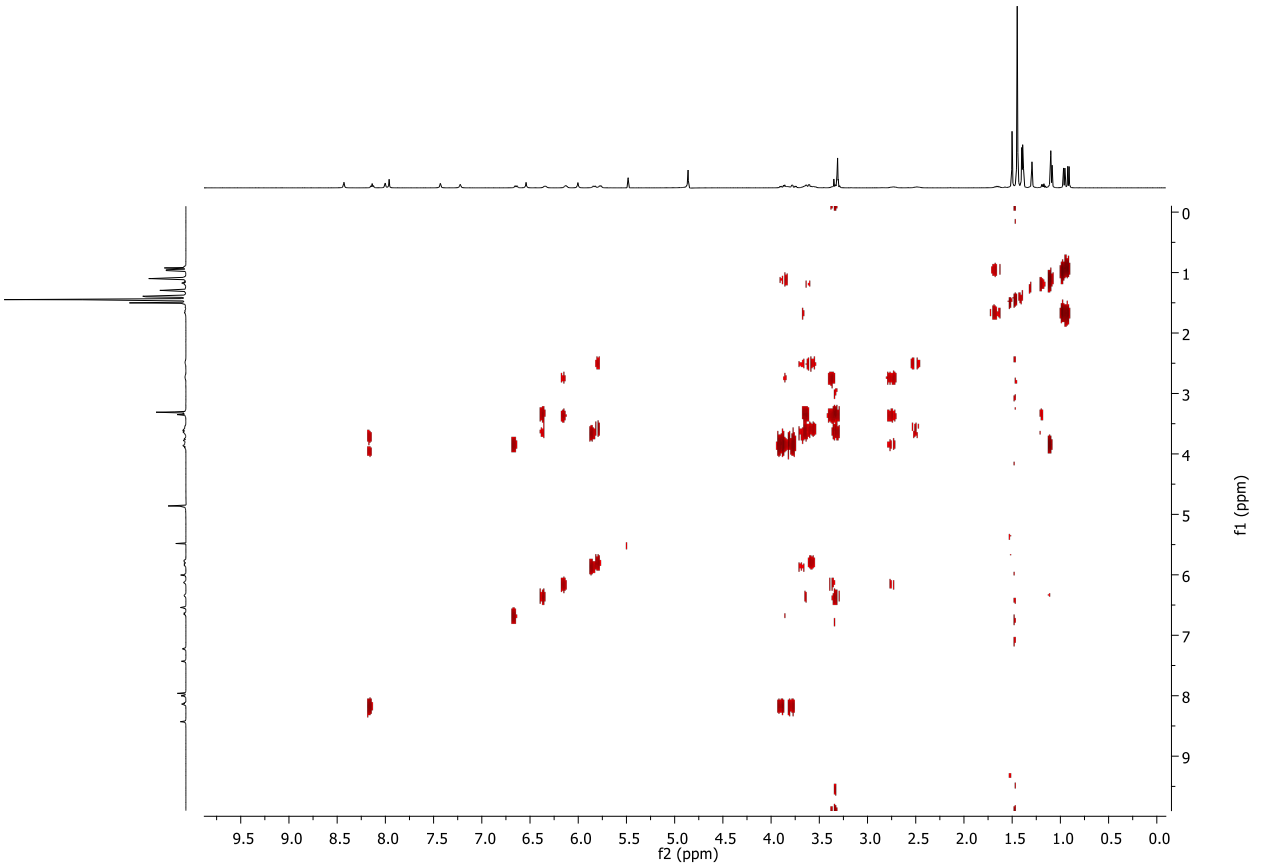
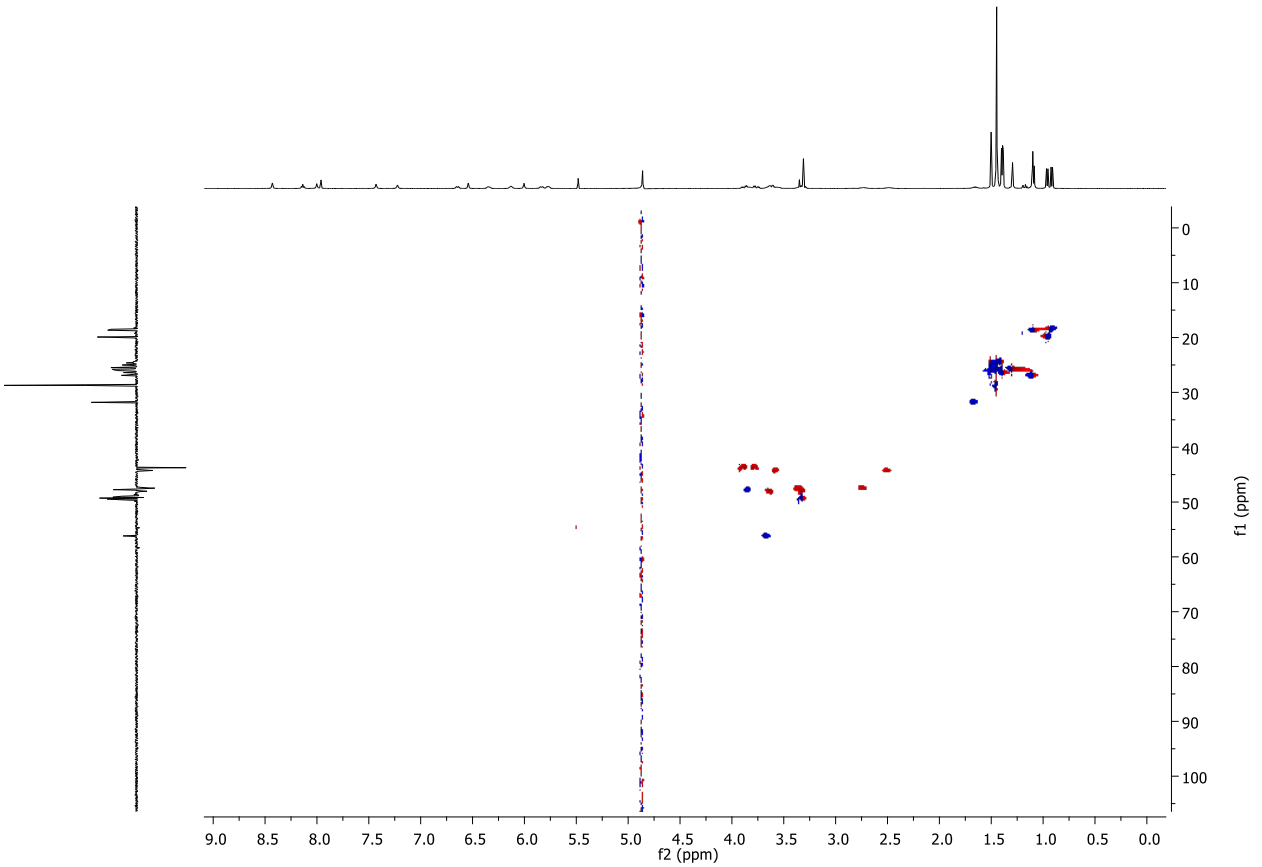
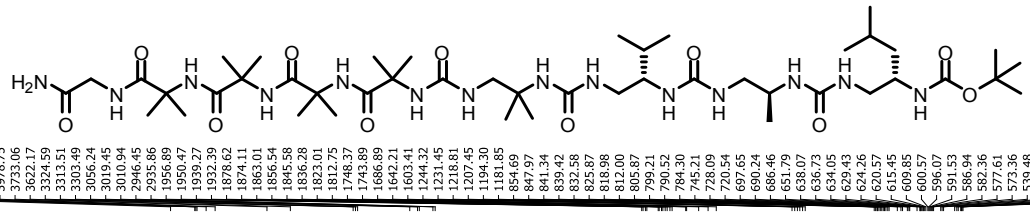







f1 (ppm)
f2 (ppm)


f1 (ppm)
f2 (ppm)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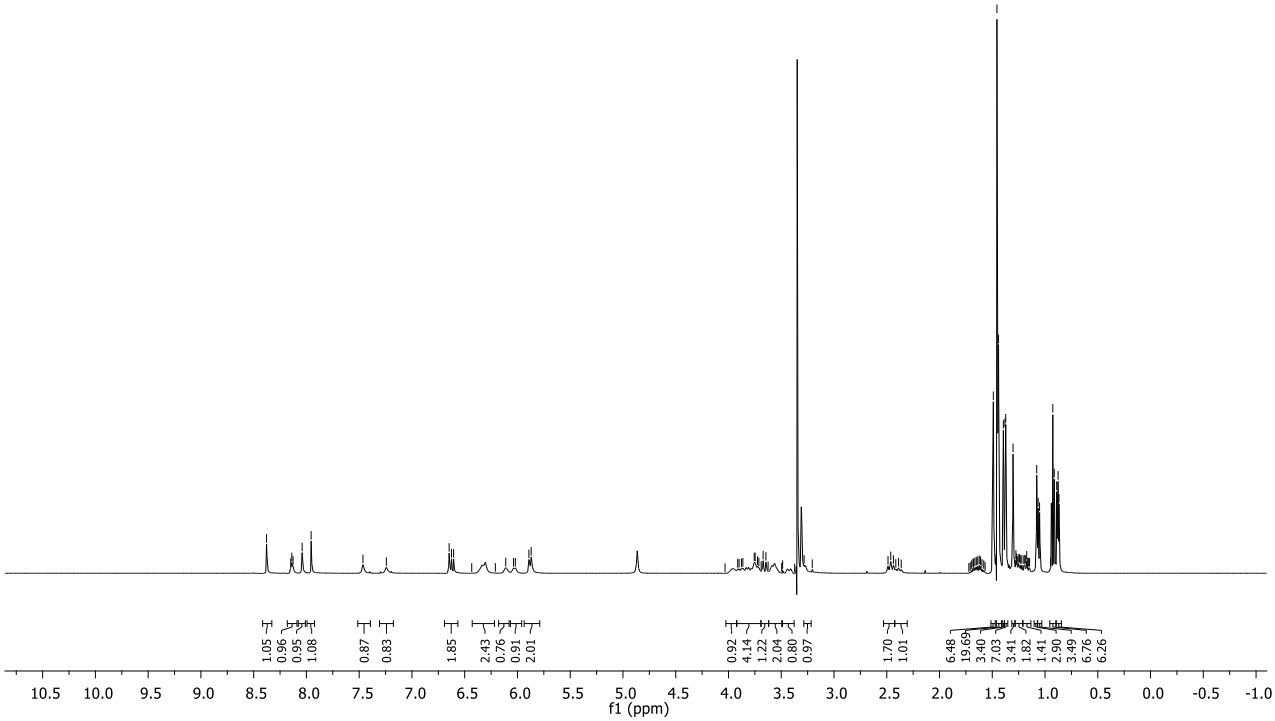
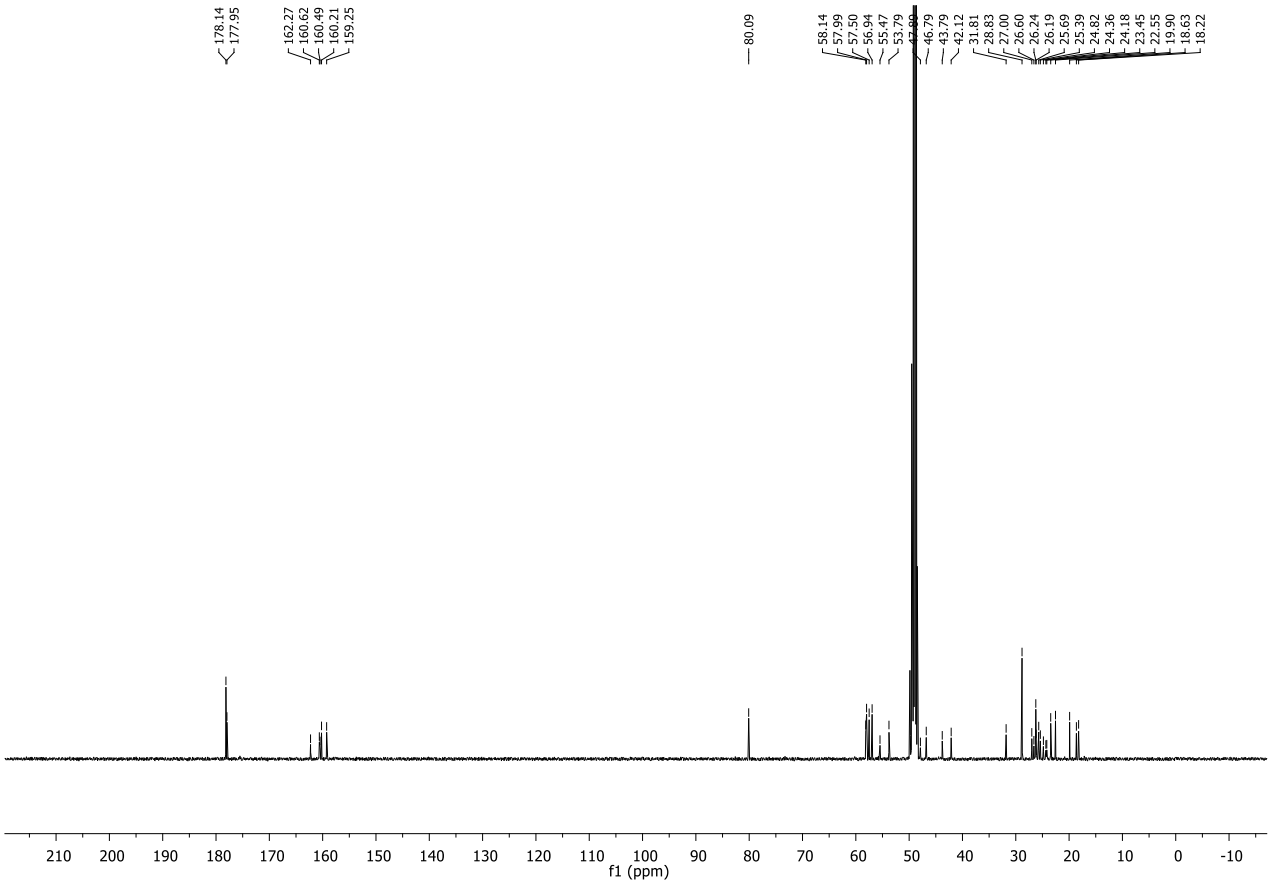
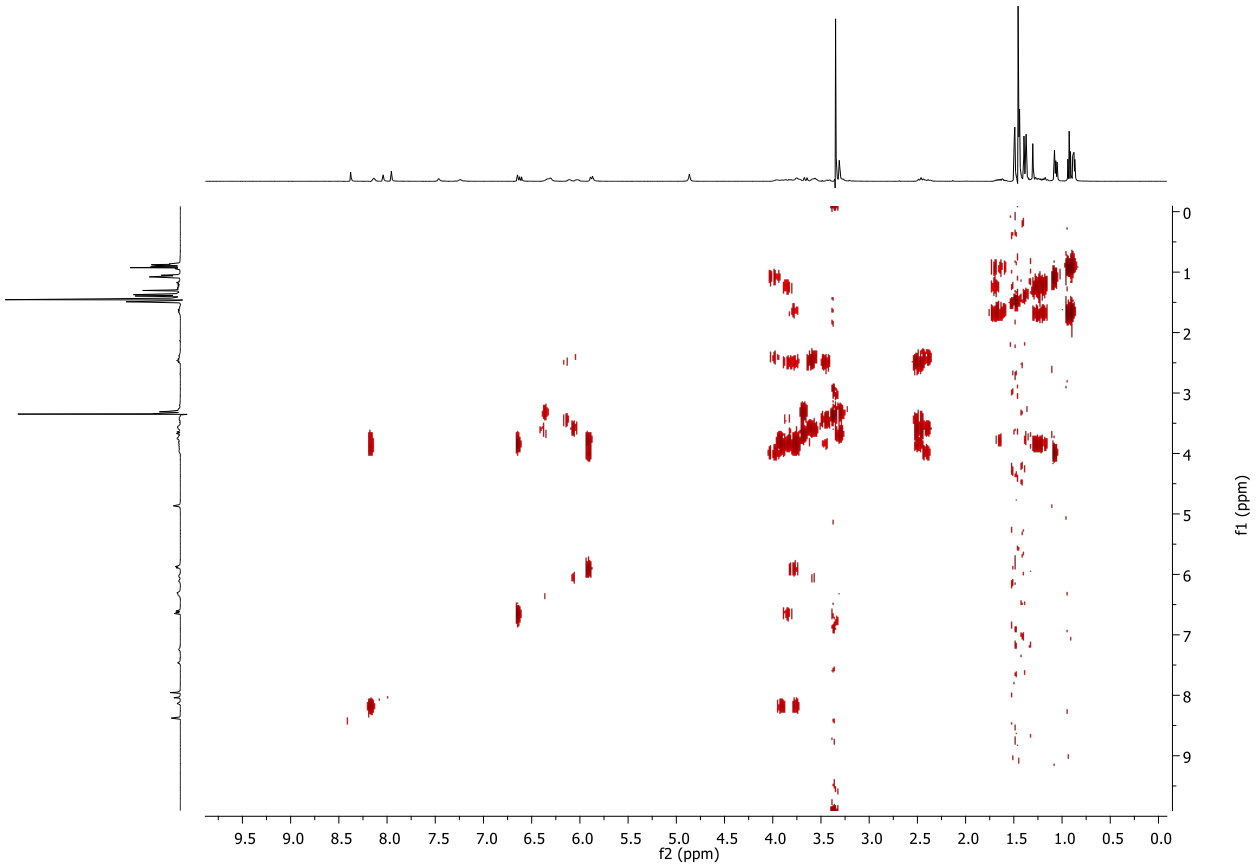
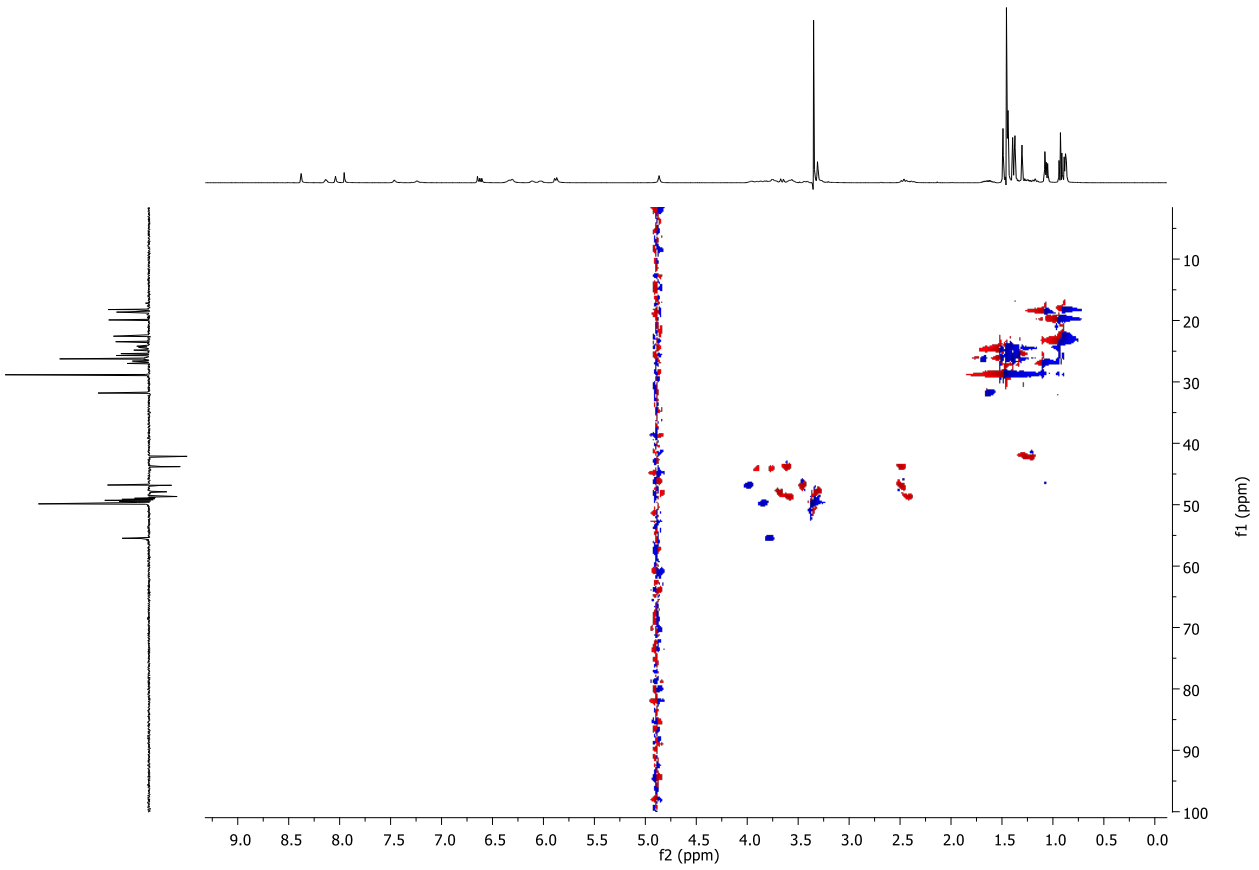
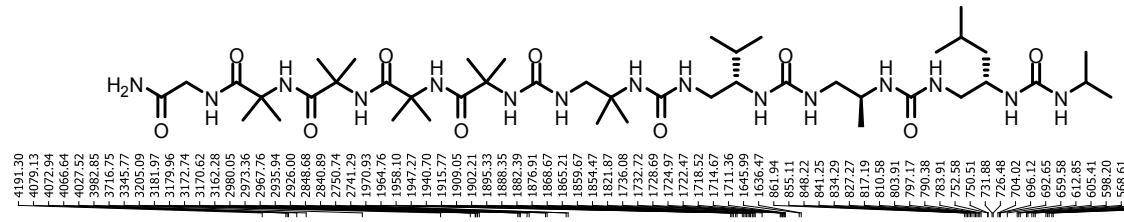
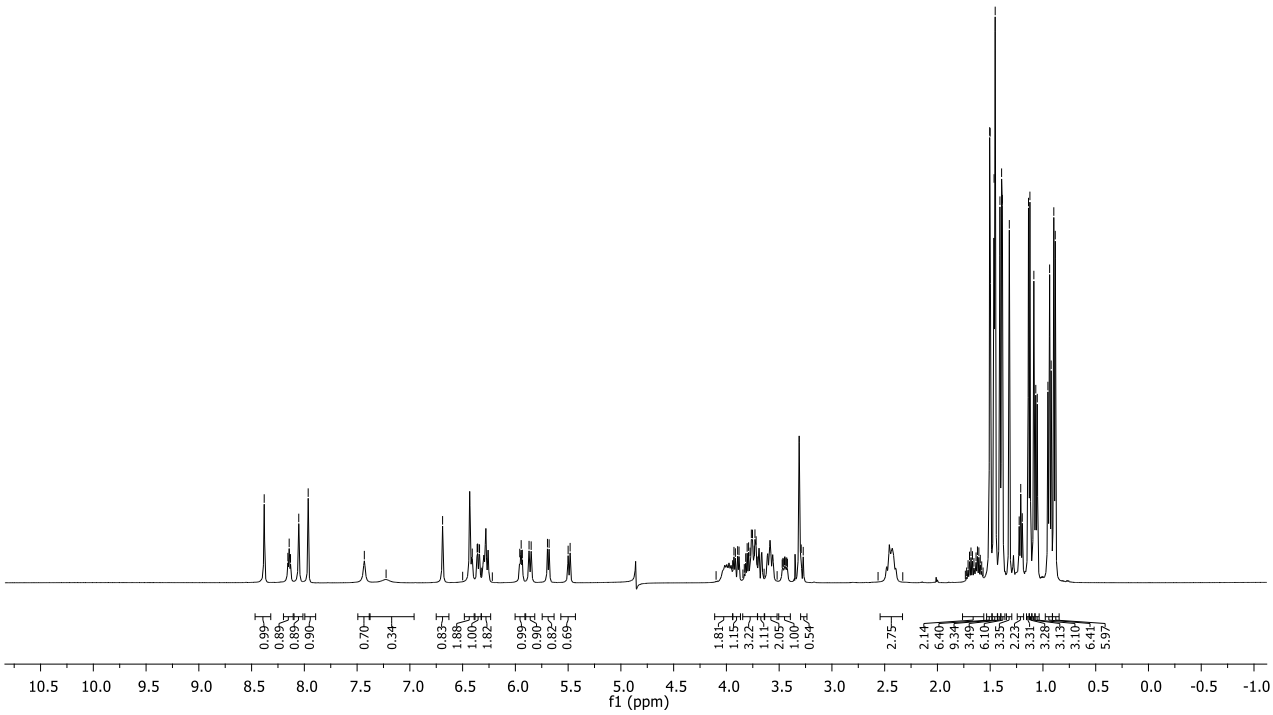

f1 (ppm)

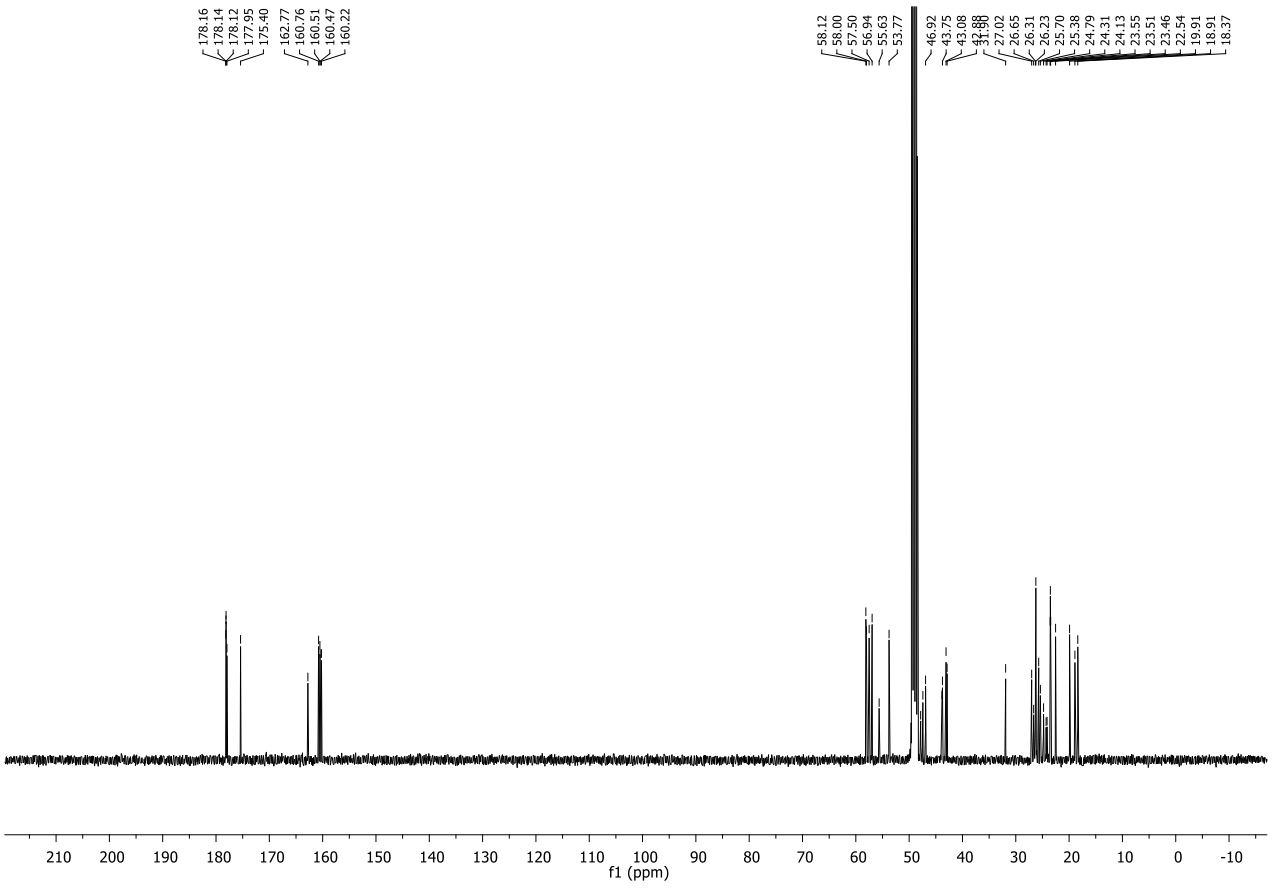

f1 (ppm)

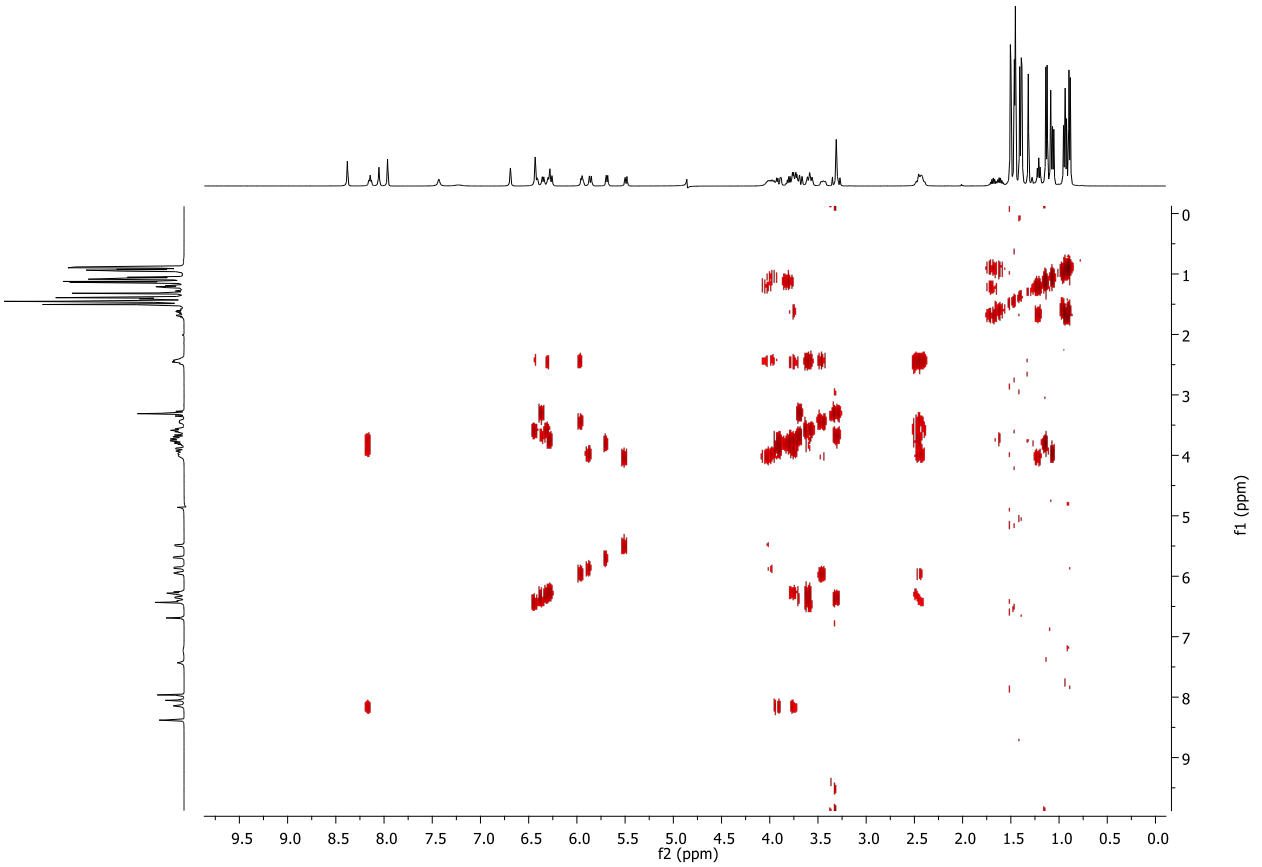

f2 (ppm)
f1 (ppm)

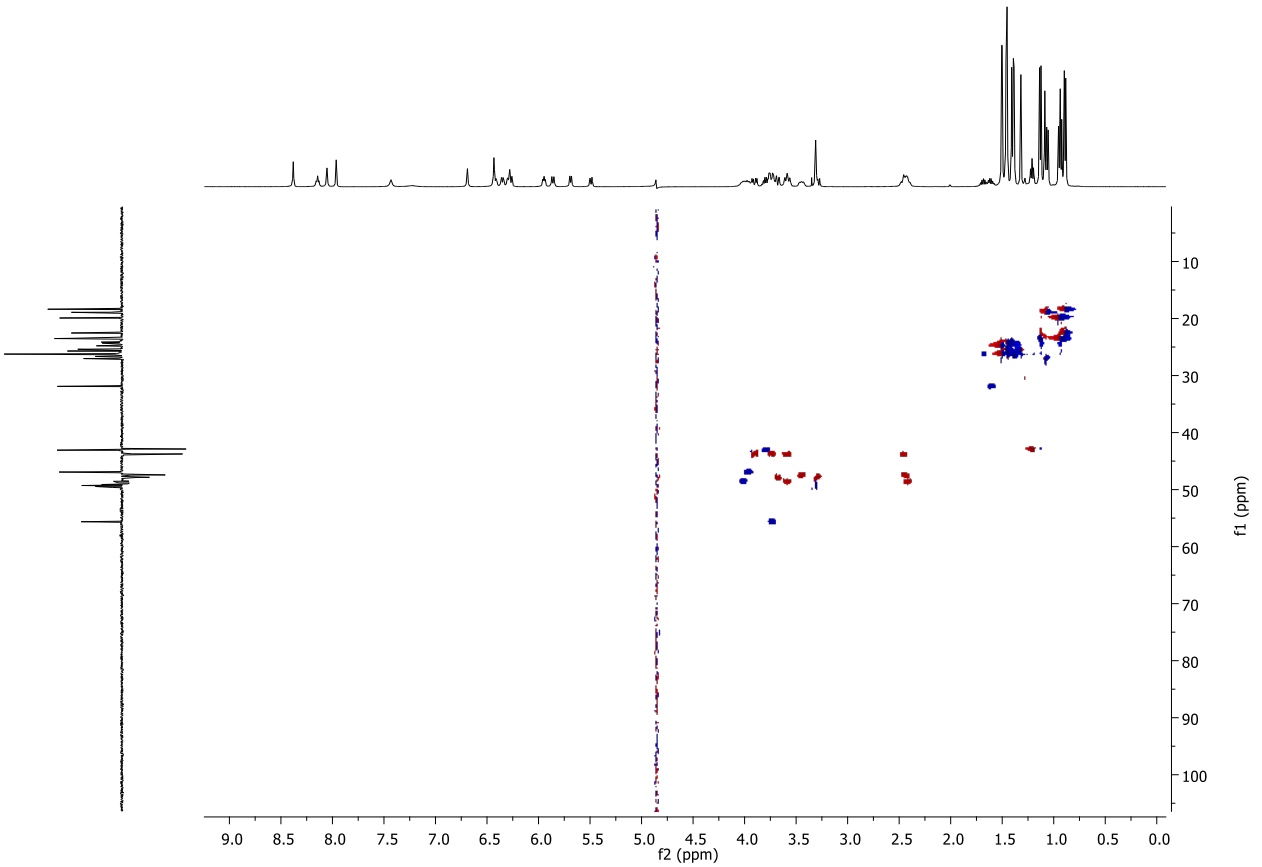

f2 (ppm)
f1 (ppm)

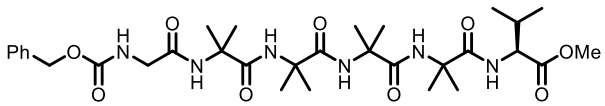

4d


f1 (ppm)

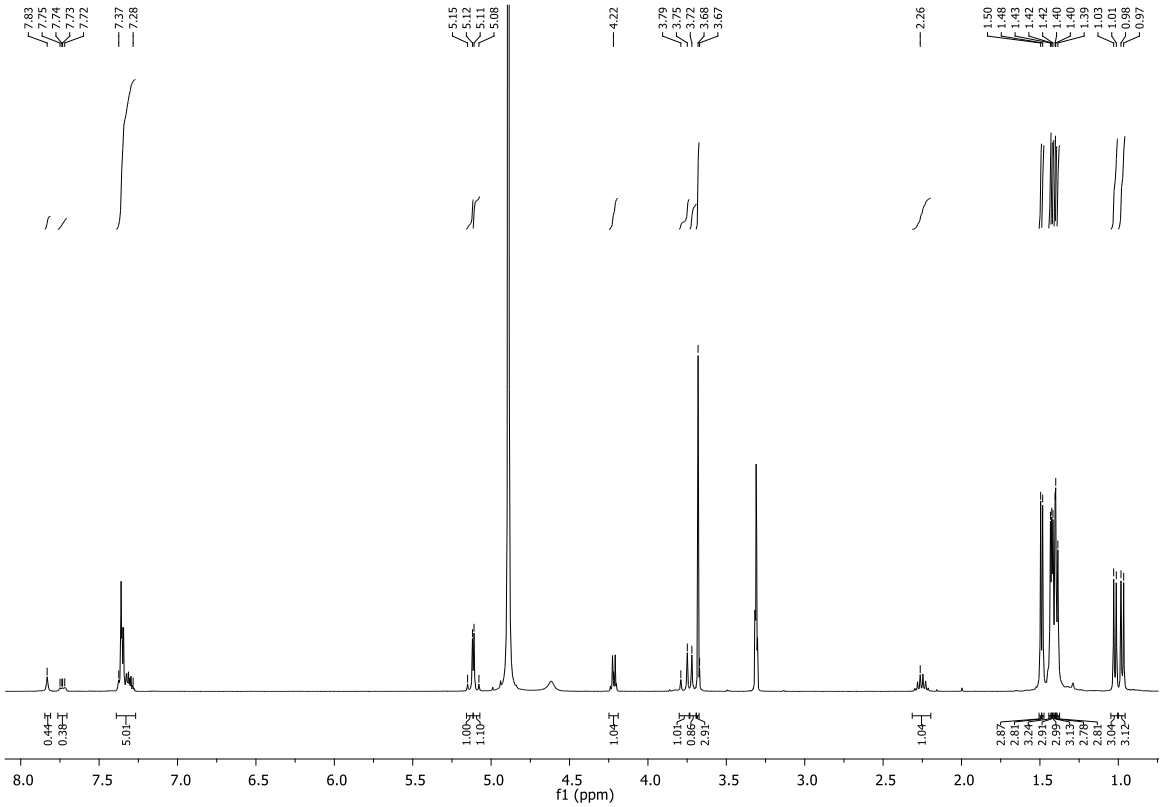

f1 (ppm)

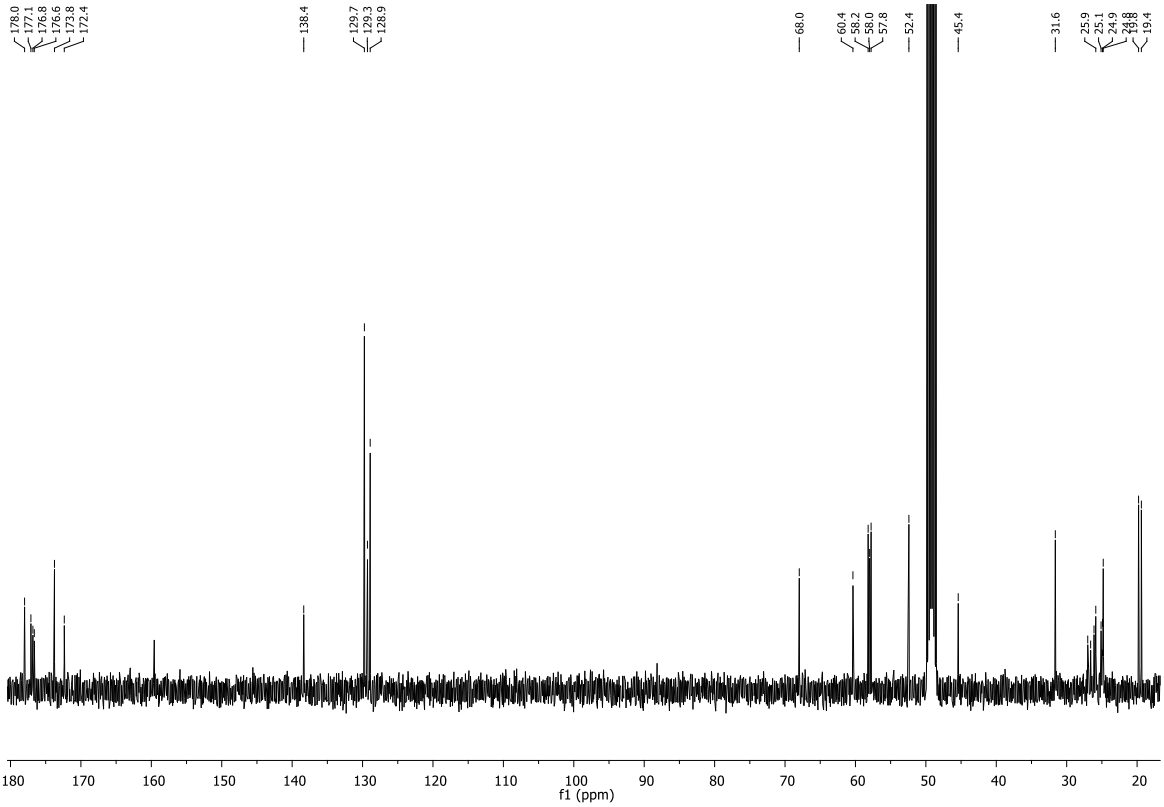

0
1
2
3
4
5
6
7
8
9
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)

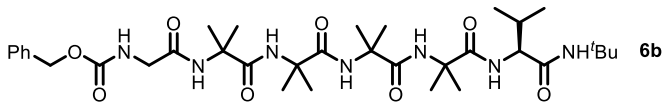

10
20
30
40
50
60
70
80
90
100
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)


Ph
O
H
N
O
O
H
N
O
H
N
O
H
N
O
OMe
O

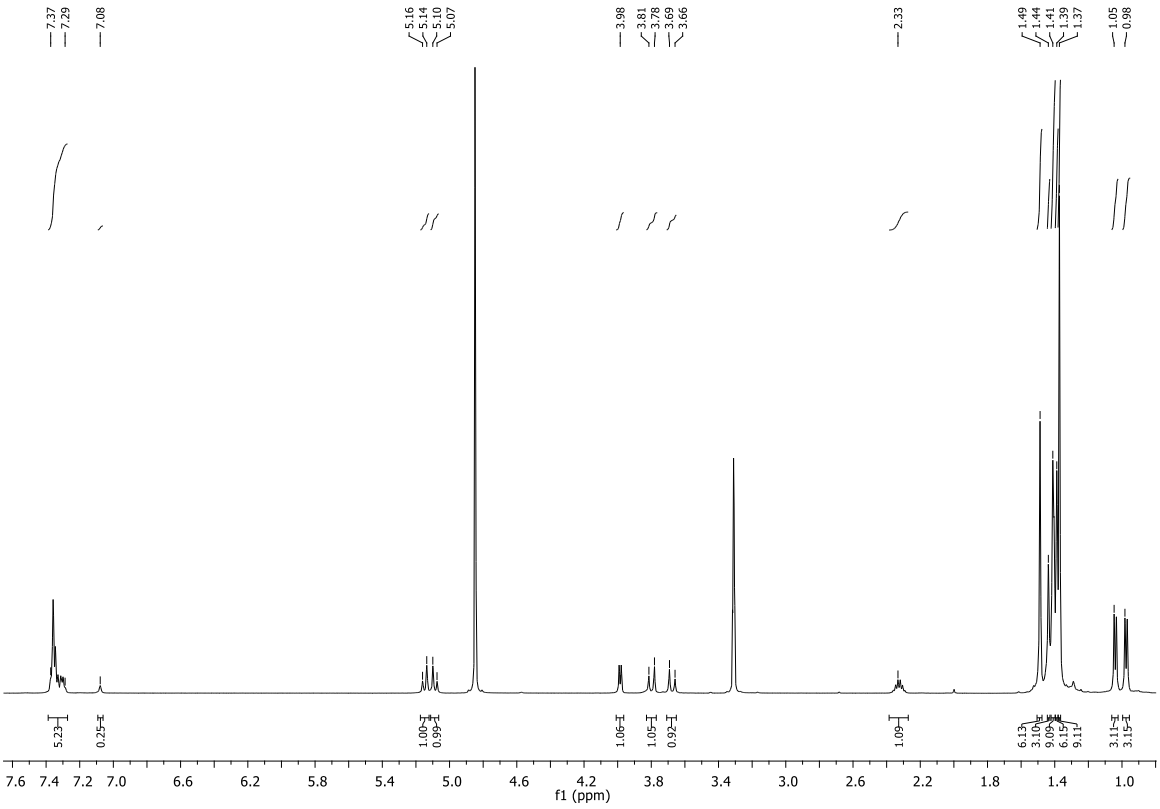
6a

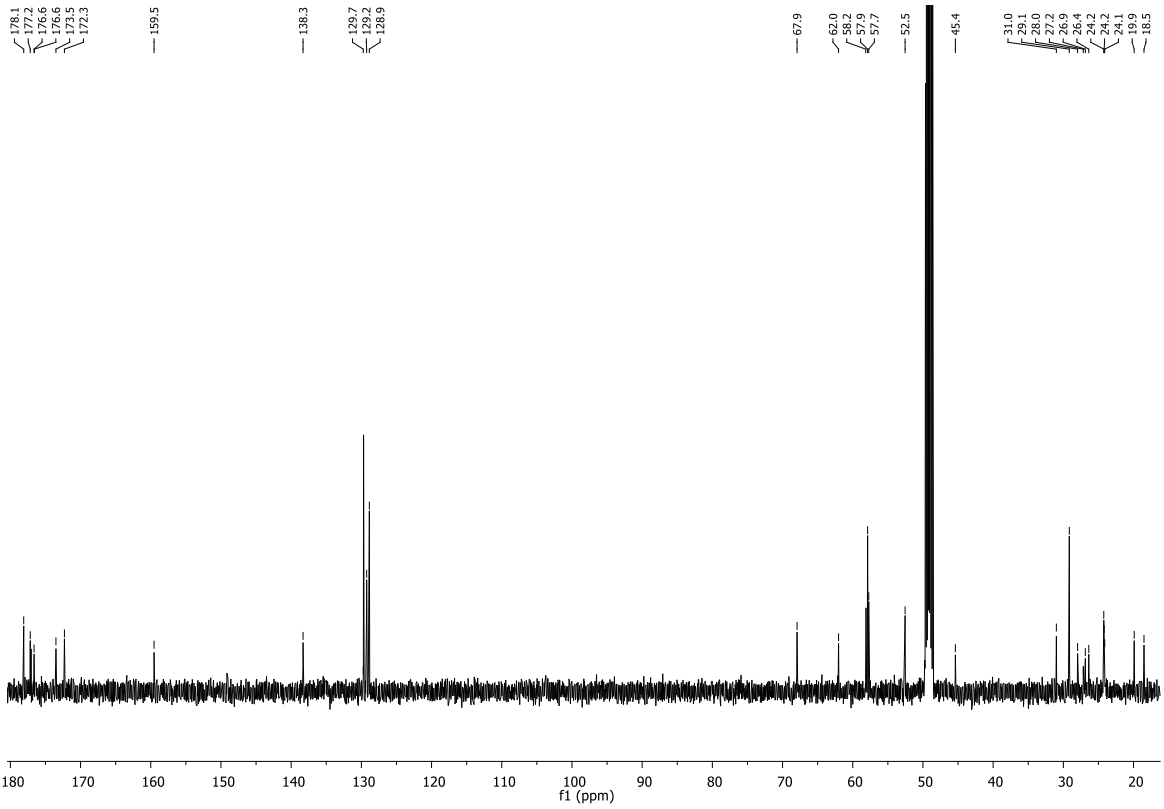

7.83
7.75
7.74
7.73
7.72
7.37
7.28
5.15
5.12
5.11
5.08
4.22
3.79
3.75
3.72
3.68
3.67
2.26
1.50
1.48
1.43
1.42
1.42
1.40
1.40
1.39
1.03
1.01
0.98
0.97
0.44
0.38
5.01
1.00
1.10
1.04
1.01
0.86
2.91
1.04
2.87
2.81
3.24
2.91
2.99
3.13
2.78
2.81
3.04
3.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

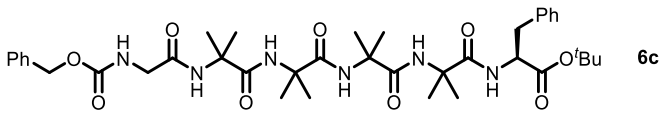

178.0
177.1
176.8
176.6
173.8
172.4
138.4
129.7
129.3
128.9
68.0
60.4
58.2
58.0
57.8
52.4
45.4
31.6
25.9
25.1
24.9
19.4
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


Ph
O
O
H
N
O
N
H
O
H
N
O
N
H
O
H
N
O
N
H
O
H
N
O
NH^{t}Bu

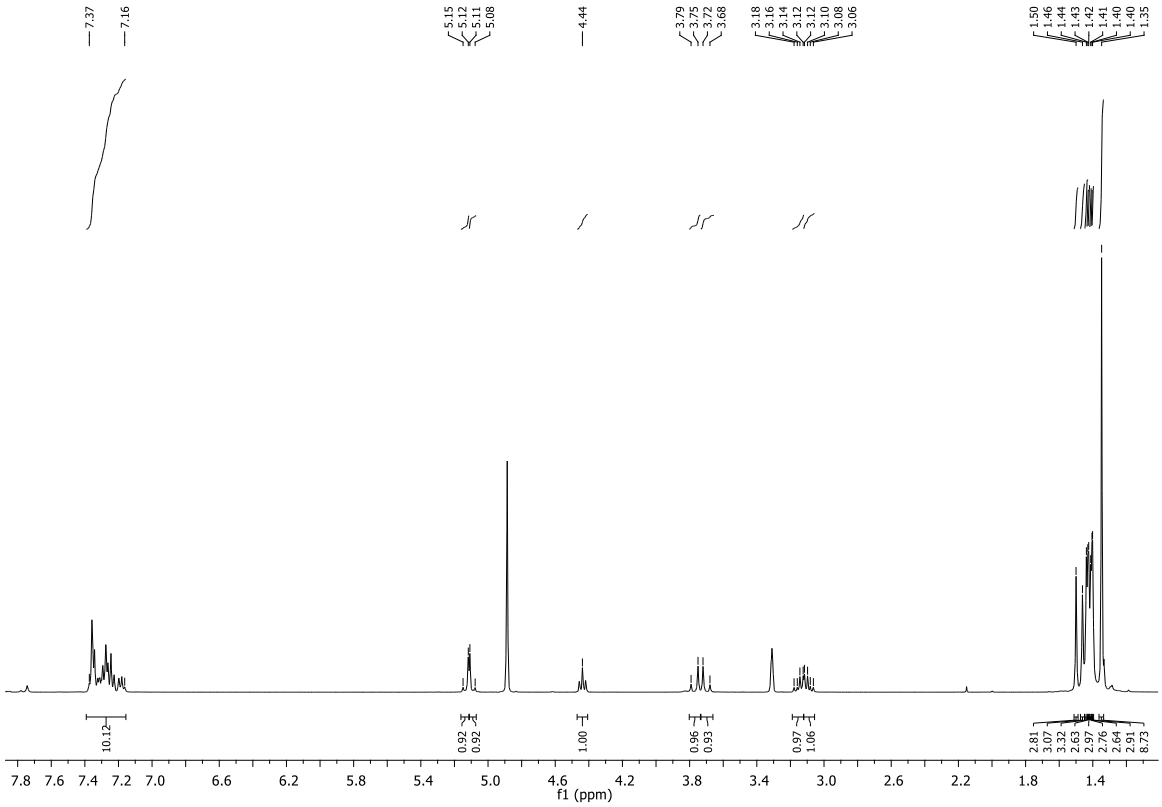
6b

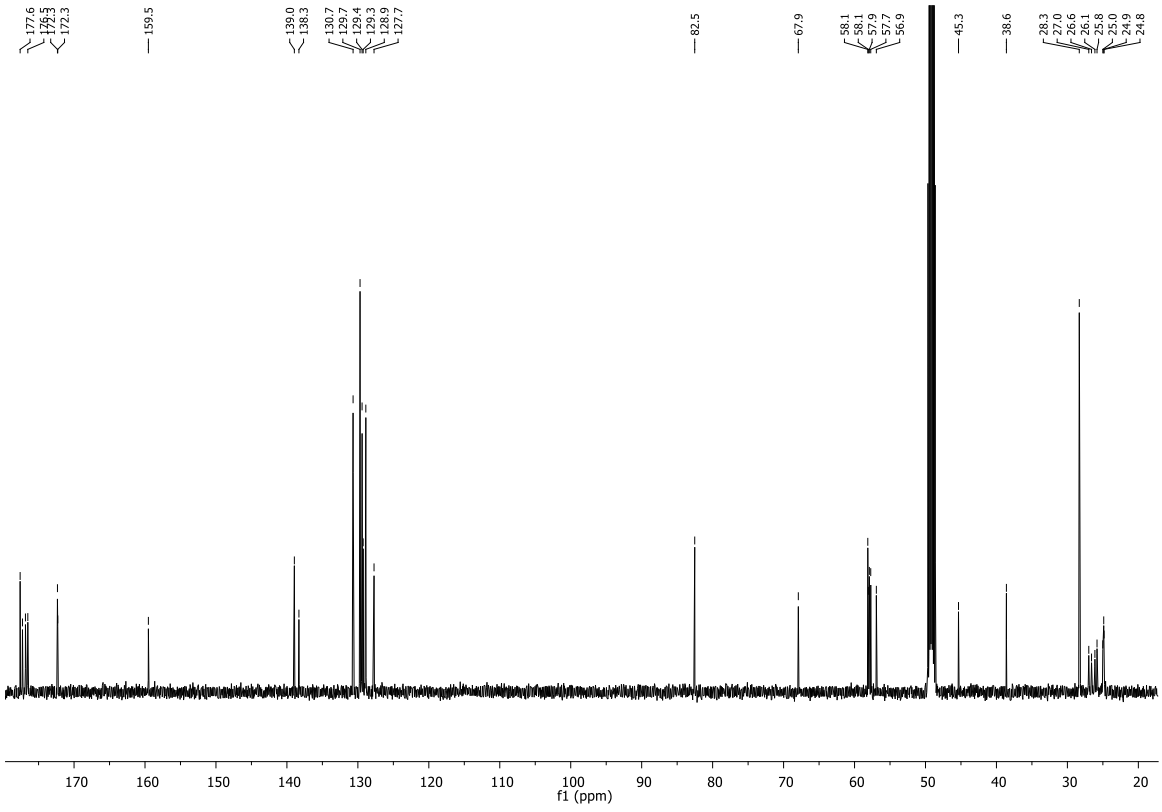

7.37
7.29
7.08
5.16
5.14
5.10
5.07
3.98
3.81
3.78
3.69
3.66
2.33
1.49
1.44
1.41
1.39
1.37
1.05
0.98
5.23
0.25
1.00
0.99
1.06
1.05
0.92
1.09
6.13
3.10
9.06
6.15
9.11
3.11
3.15
7.6 7.4 7.2 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4 1.0
f1 (ppm)

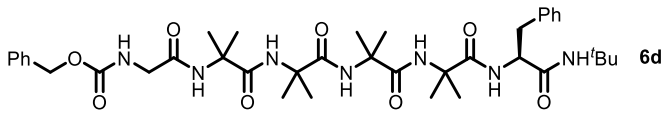

178.1
177.2
176.6
176.6
176.6
173.5
172.3
159.5
138.3
129.7
129.2
128.9
67.9
62.0
58.2
57.9
57.7
52.5
45.4
31.0
29.1
28.0
27.2
26.9
26.4
24.2
24.2
24.1
19.9
18.5
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Ph
O
H
N
O
N
H
O
H
N
O
N
H
O
H
N
O
N
H
O
Ph
O
O
tBu

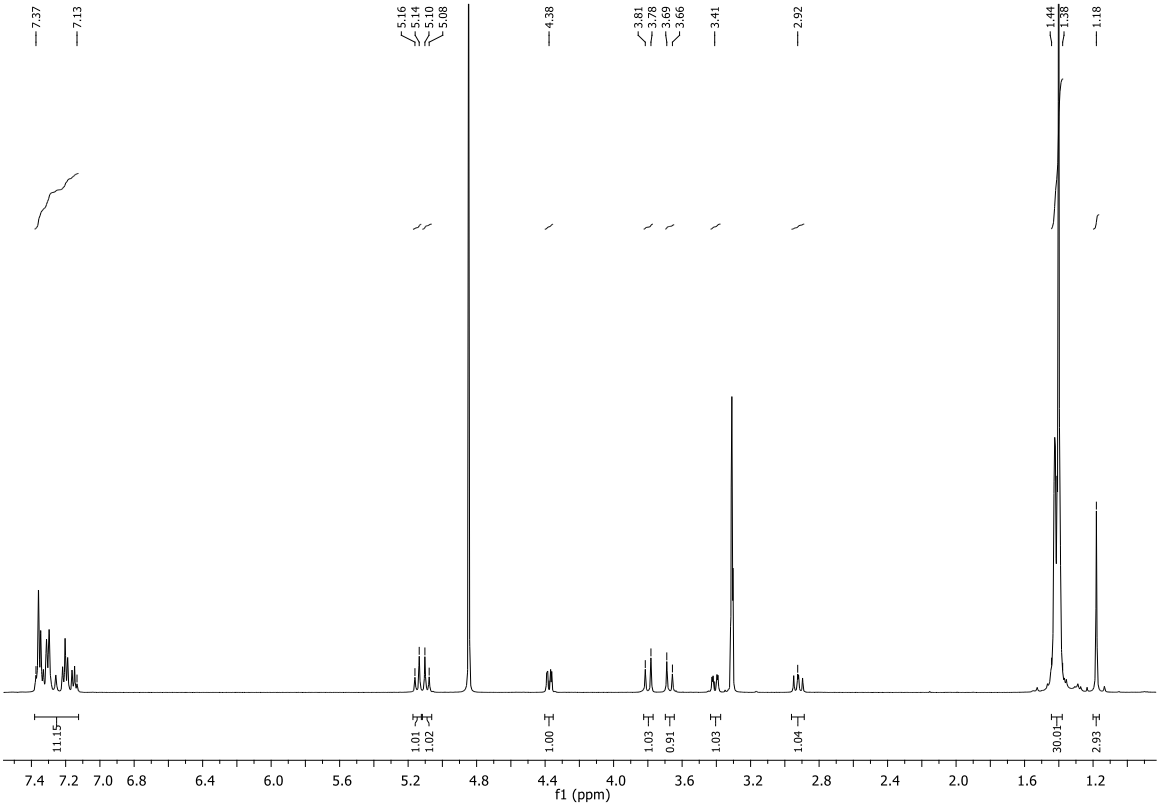
6c

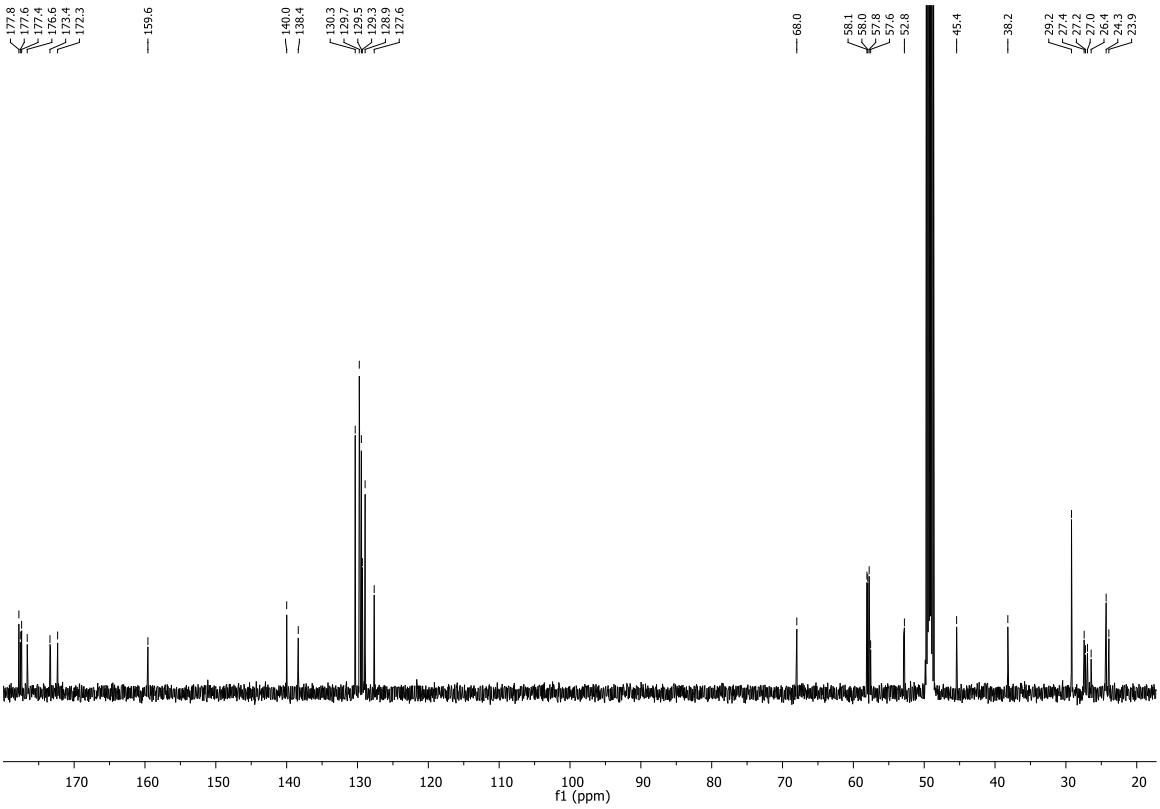

7.37
7.16
5.15
5.12
5.11
5.08
4.44
3.79
3.75
3.72
3.68
3.18
3.16
3.14
3.12
3.12
3.10
3.08
3.06
1.50
1.46
1.44
1.43
1.42
1.41
1.40
1.40
1.35
10.12
0.92
0.92
1.00
0.96
0.93
0.97
1.06
2.81
3.07
3.32
2.63
2.97
2.76
2.64
2.91
8.73
7.8 7.6 7.4 7.2 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4
f1 (ppm)

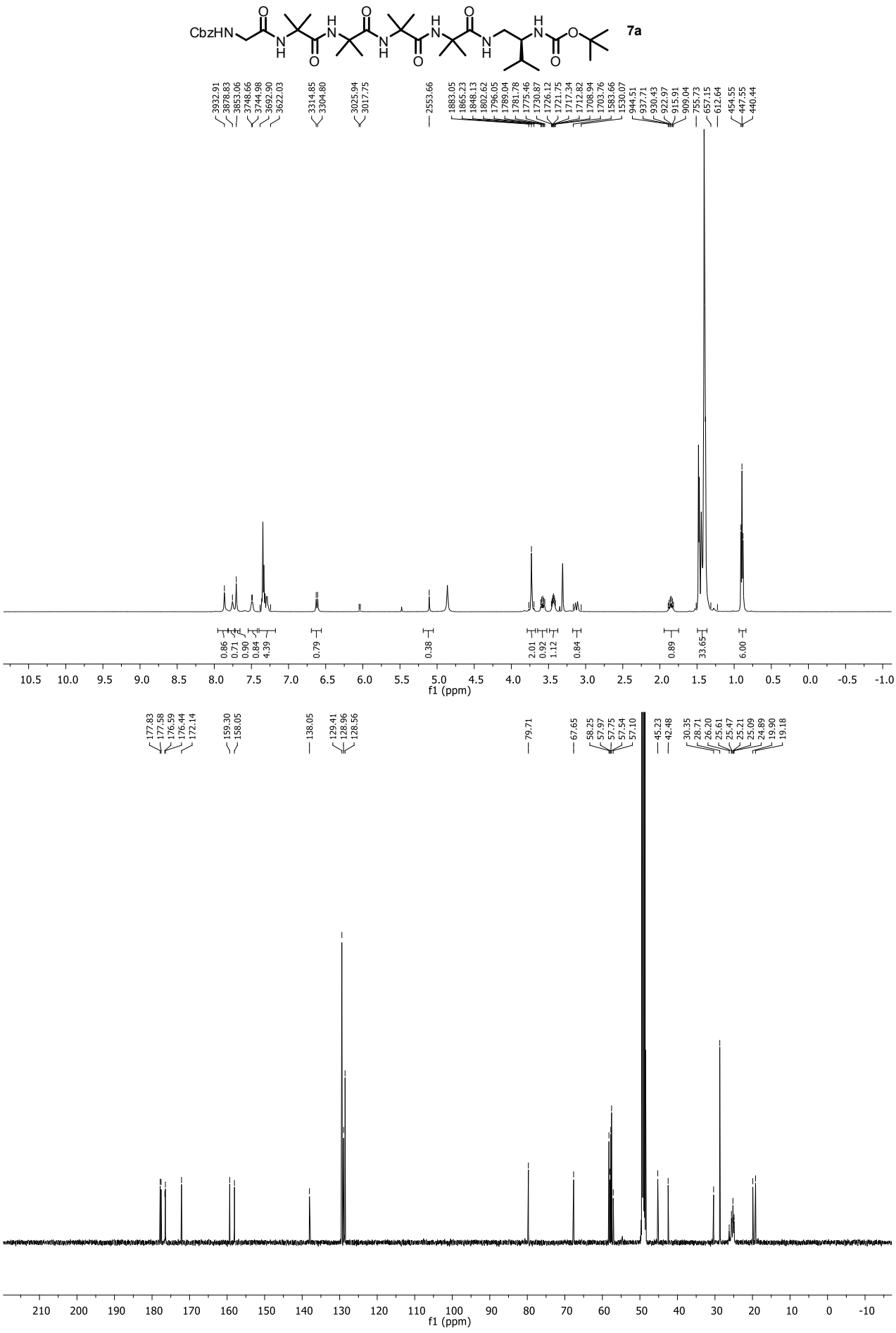

177.6
175.3
172.3
172.3
159.5
139.0
138.3
130.7
129.7
129.4
129.3
128.9
127.7
82.5
67.9
58.1
58.1
57.9
57.7
56.9
45.3
38.6
28.3
27.0
26.6
26.1
25.8
25.0
24.9
24.8
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Ph
O
H
N
O
N
H
O
H
N
O
N
H
O
H
N
O
N
H
O
Ph
NH^{t}Bu

6d


7.37
7.13
5.16
5.14
5.10
5.08
4.38
3.81
3.78
3.69
3.66
3.41
2.92
1.44
1.38
1.18
11.15
1.01
1.02
1.00
1.03
0.91
1.03
1.04
30.01
2.93
f1 (ppm)


177.8
177.6
177.4
176.6
173.4
172.3
159.6
140.0
138.4
130.3
129.7
129.5
129.3
128.9
127.6
68.0
58.1
58.0
57.8
57.6
52.8
45.4
38.2
29.2
27.4
27.2
27.0
26.4
24.3
23.9
f1 (ppm)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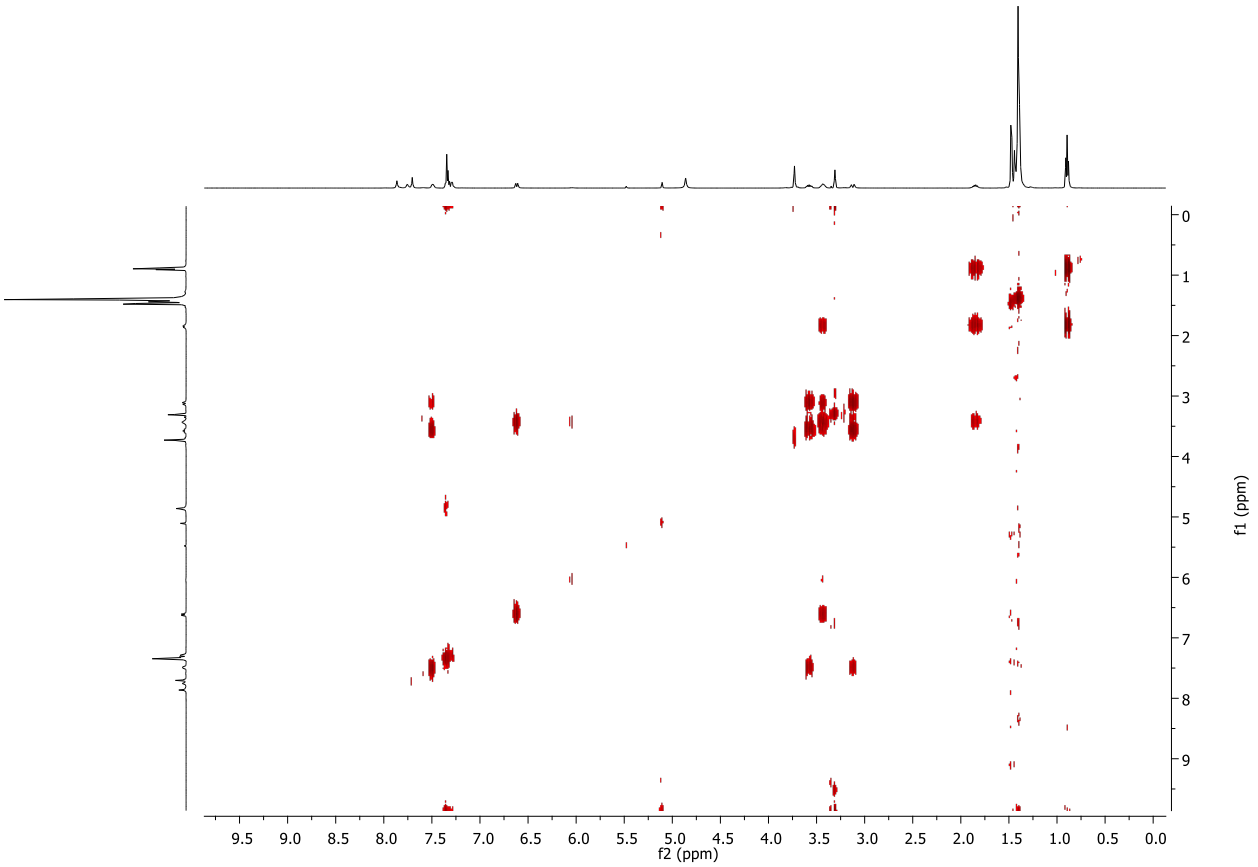
f1 (ppm)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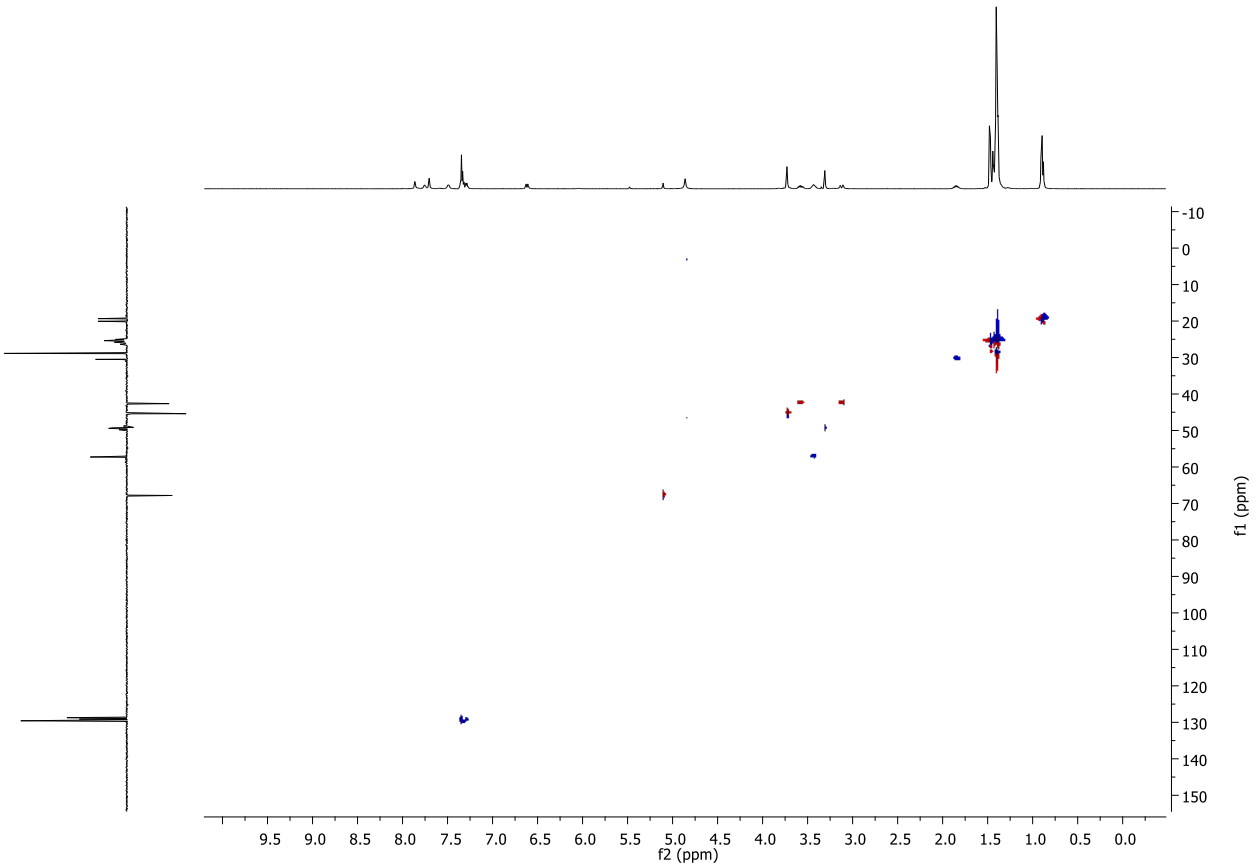
f2 (ppm)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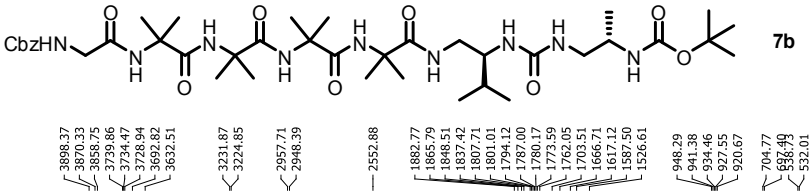
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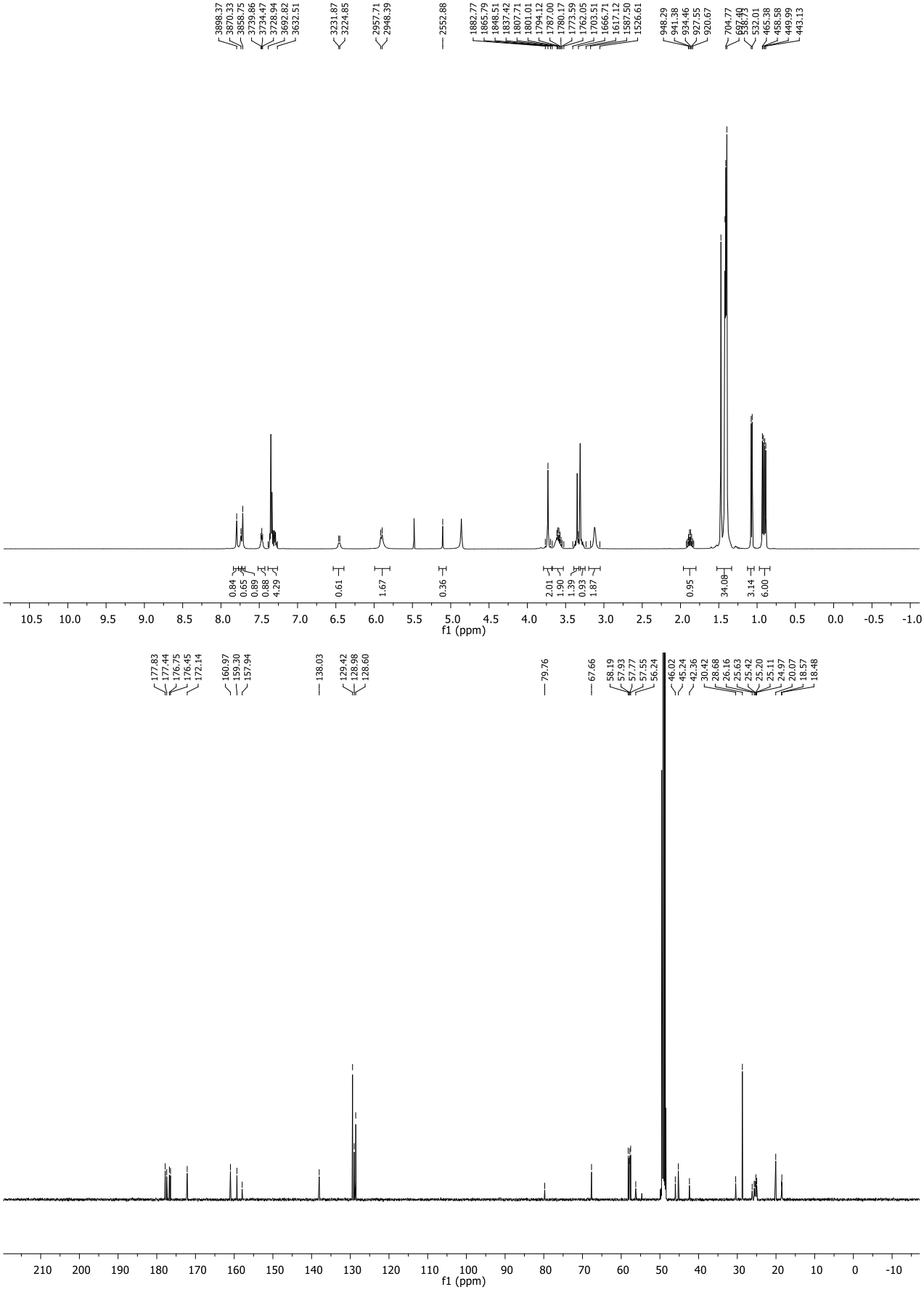
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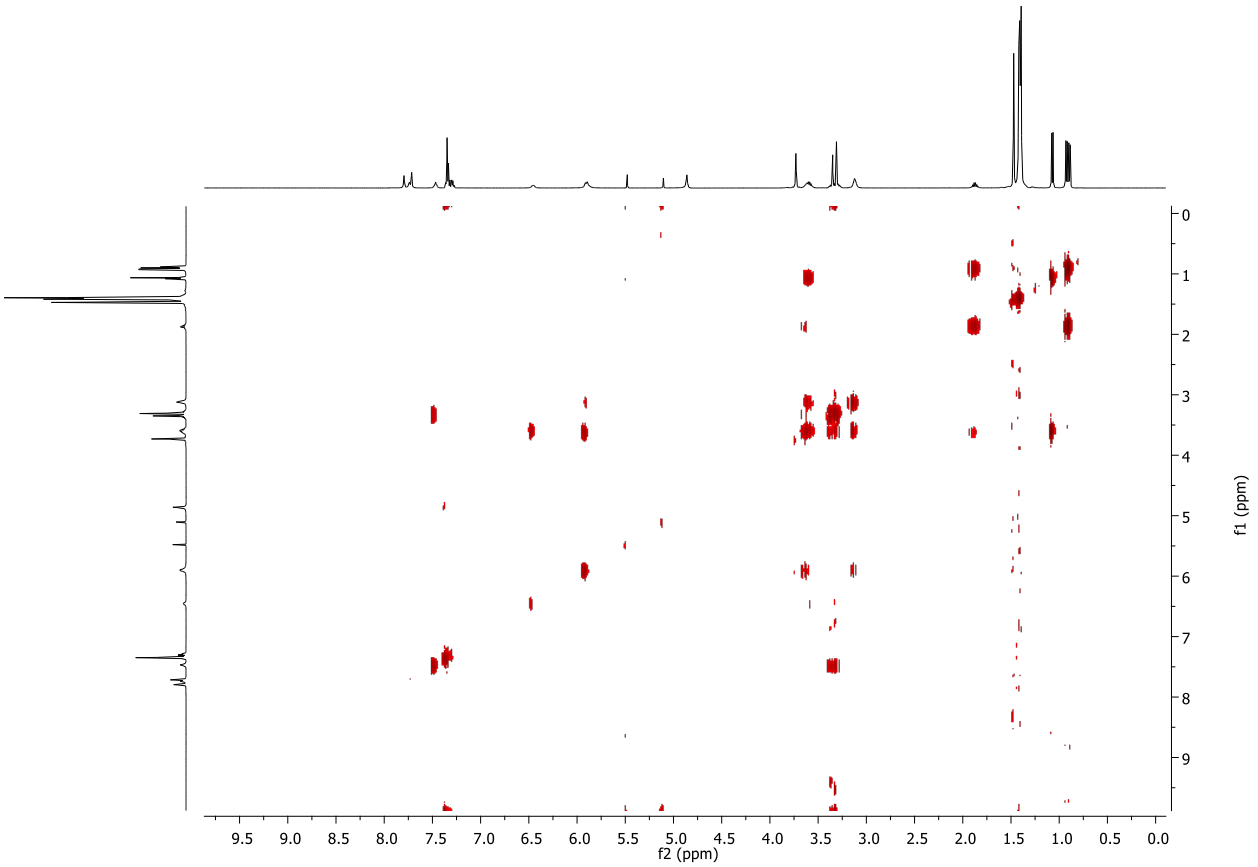
f1 (ppm)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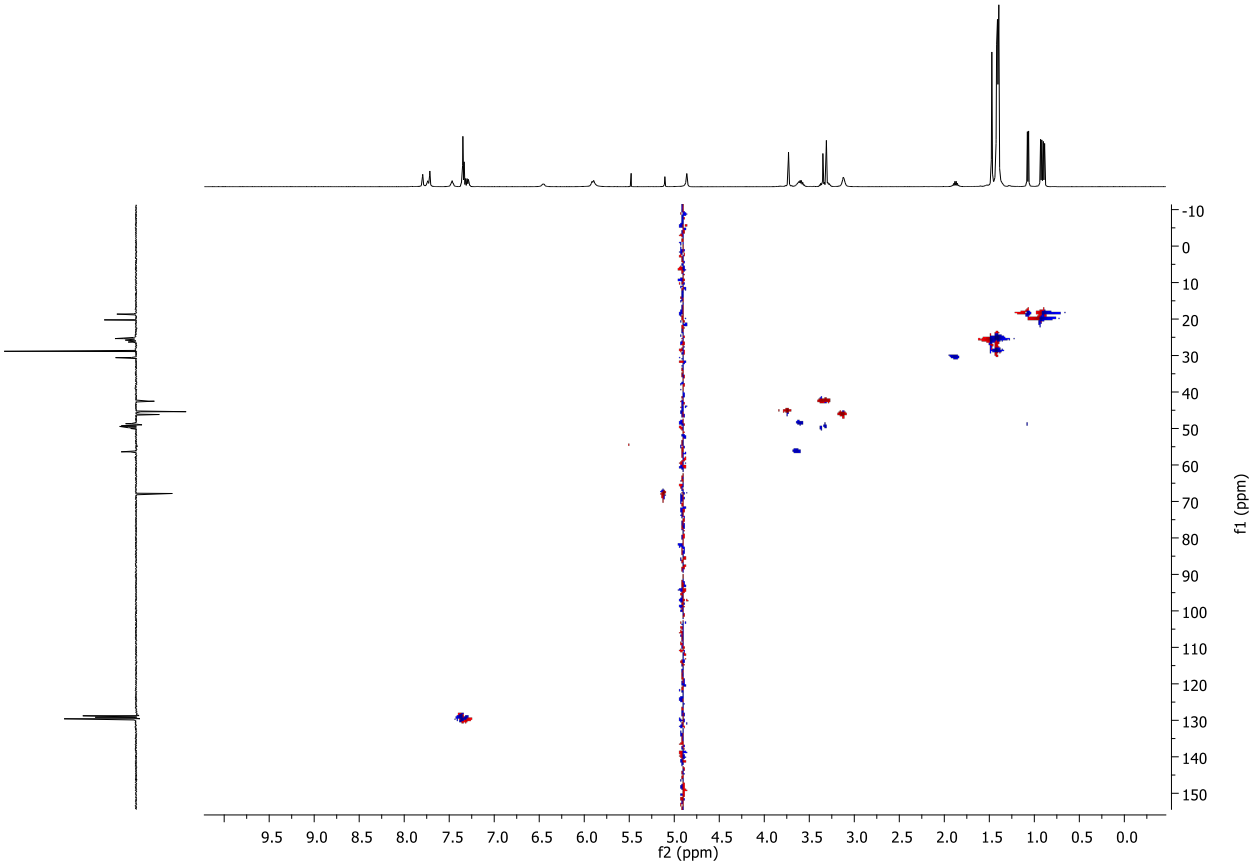
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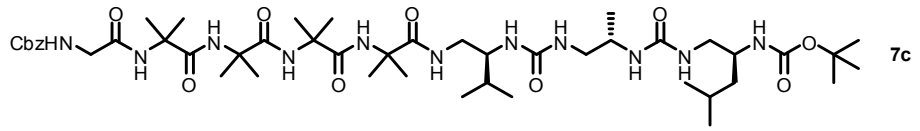
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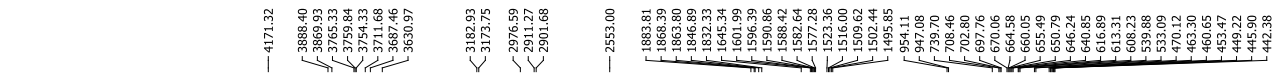
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2553.00
1883.81
1868.39
1863.80
1846.89
1832.33
1645.34
1601.99
1596.39
1590.86
1588.42
1582.64
1577.28
1523.36
1516.00
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702.80
697.76
670.06
664.58
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655.49
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640.85
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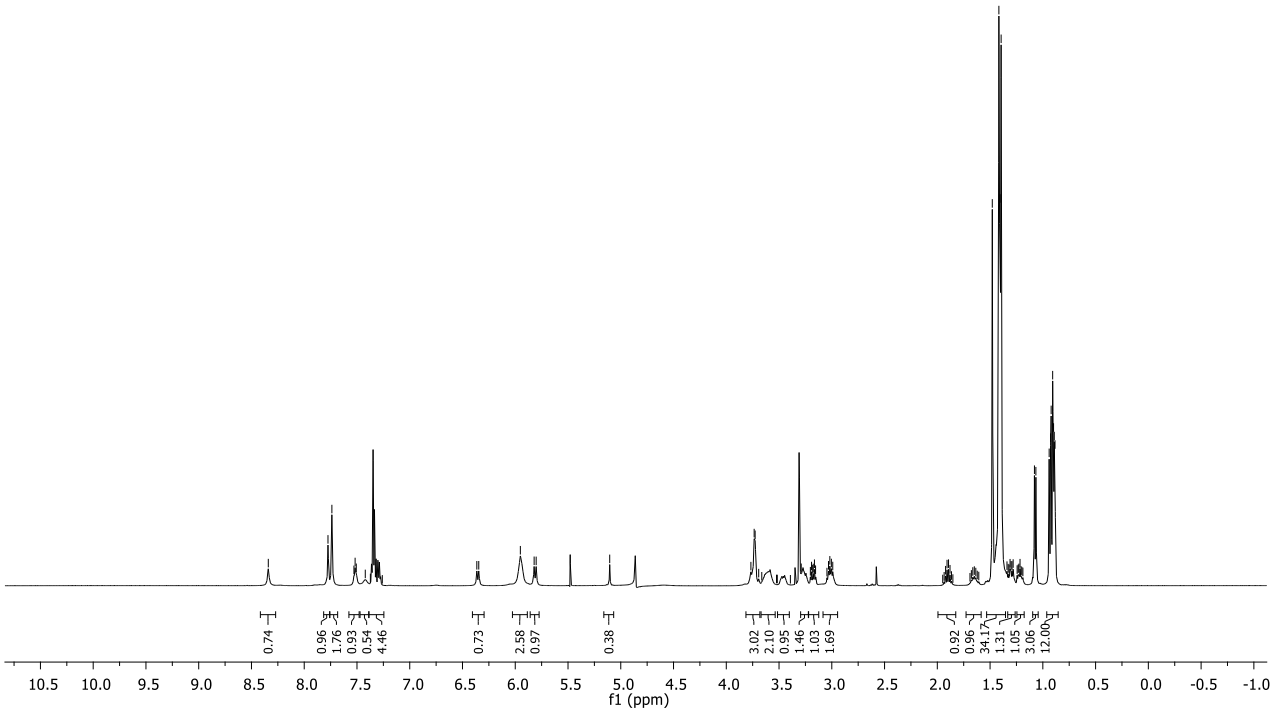
442.38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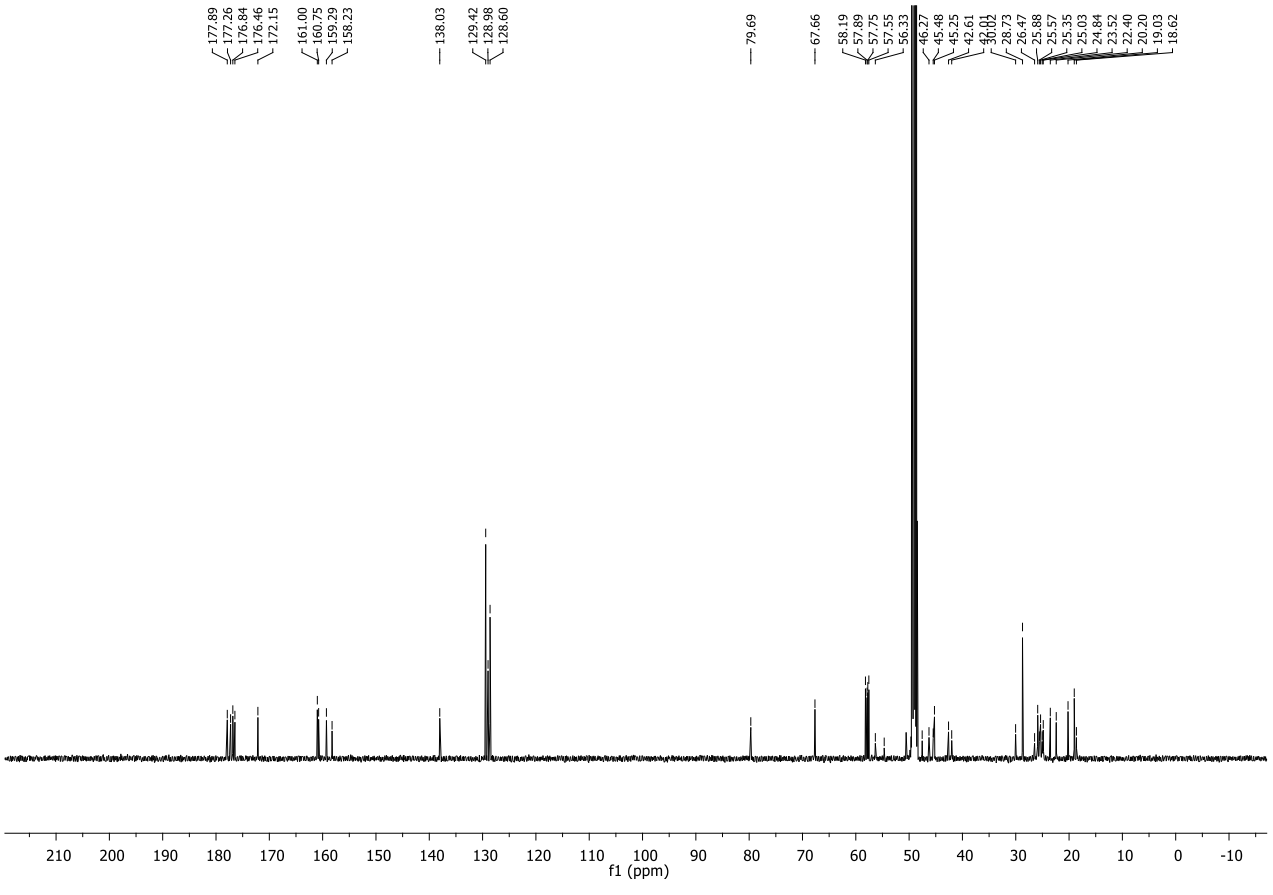
3.02
2.10
0.95
1.46
1.03
1.69
0.92
0.96
34.17
1.31
1.05
3.06
12.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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159.29
158.23
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128.60
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67.66
58.19
57.89
57.75
57.55
56.33
46.27
45.48
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42.61
42.01
30.02
28.73
26.47
25.88
25.57
25.35
25.03
24.84
23.52
22.40
20.20
19.03
18.62
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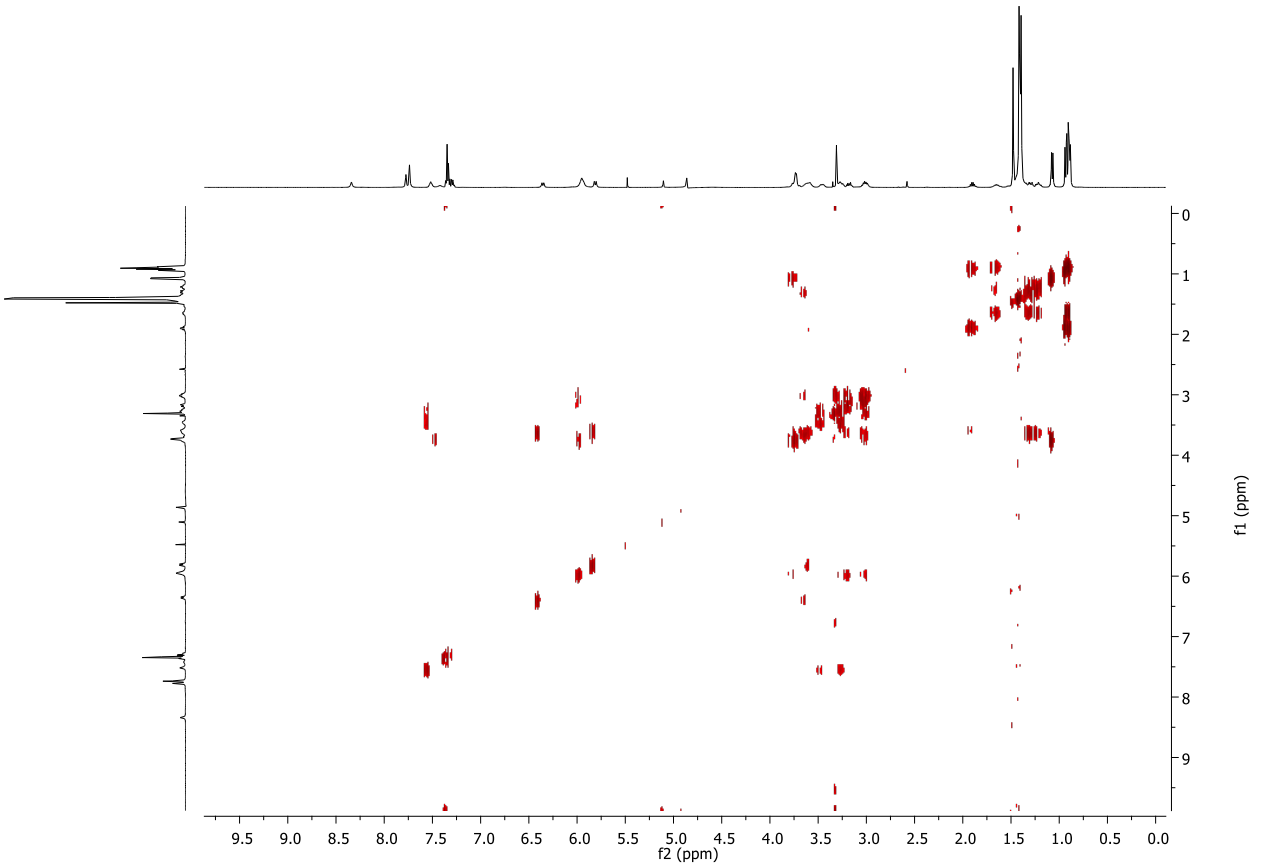
f1 (ppm)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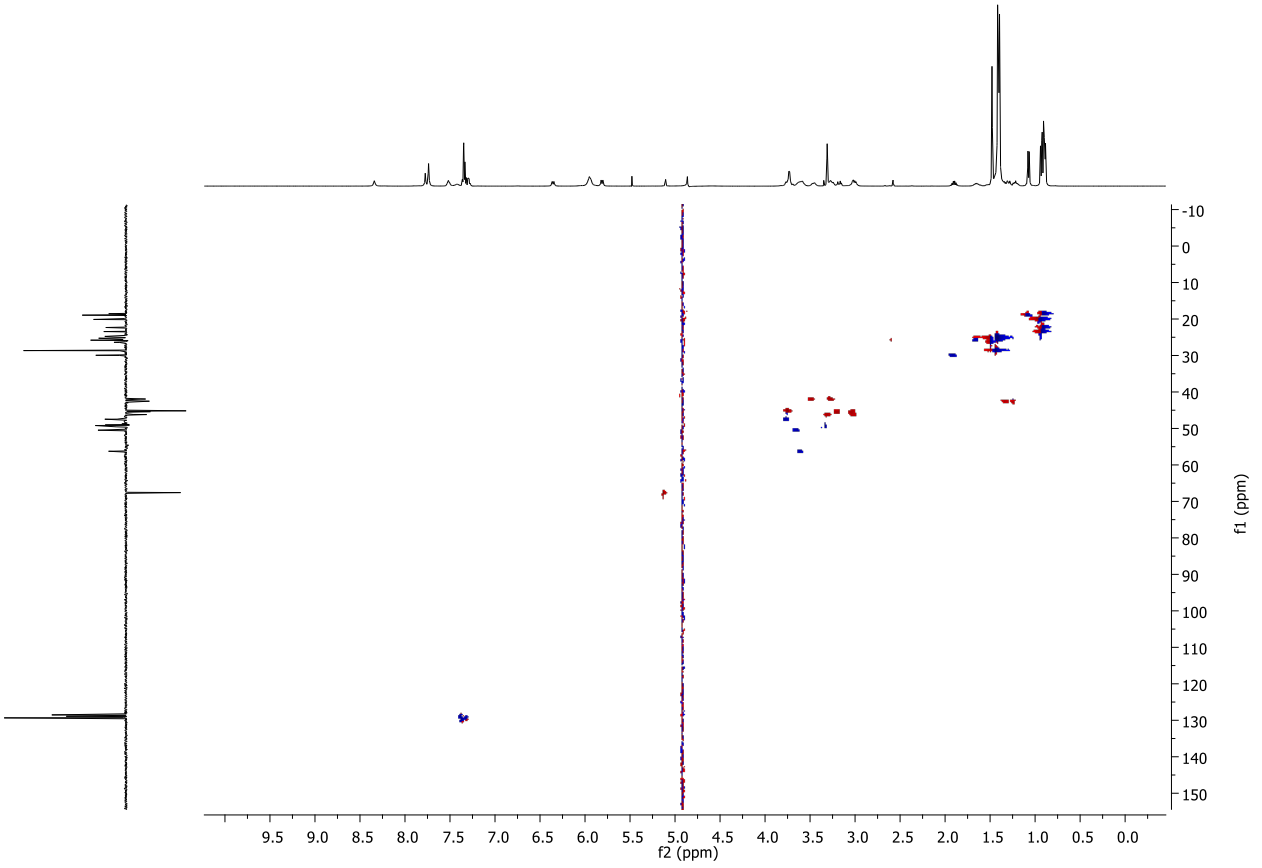
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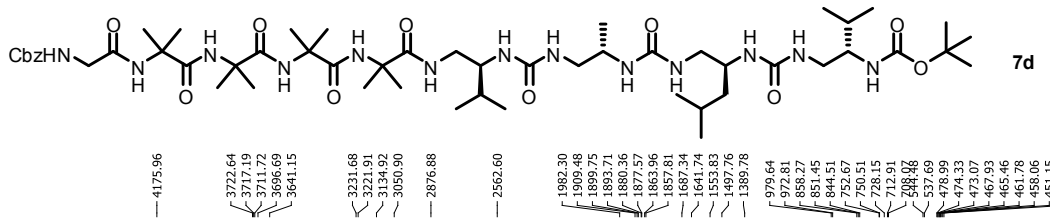
f1 (ppm)


CbzHN
7d

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1909.48
1899.75
1893.71
1880.36
1877.57
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1857.81
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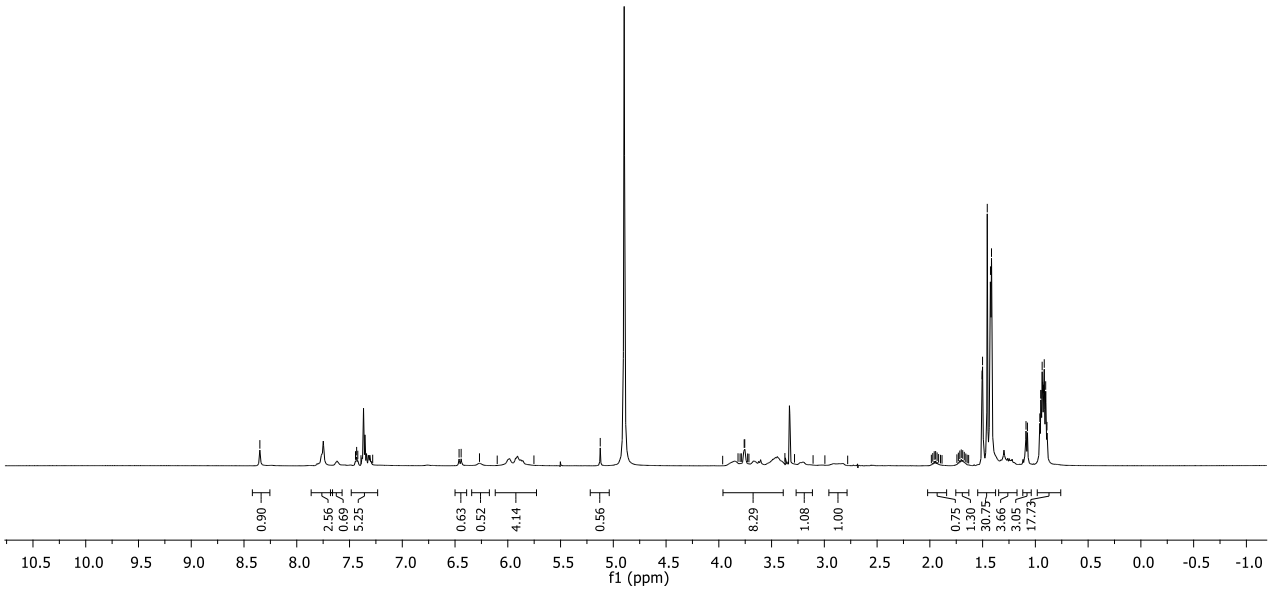
445.18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0.52
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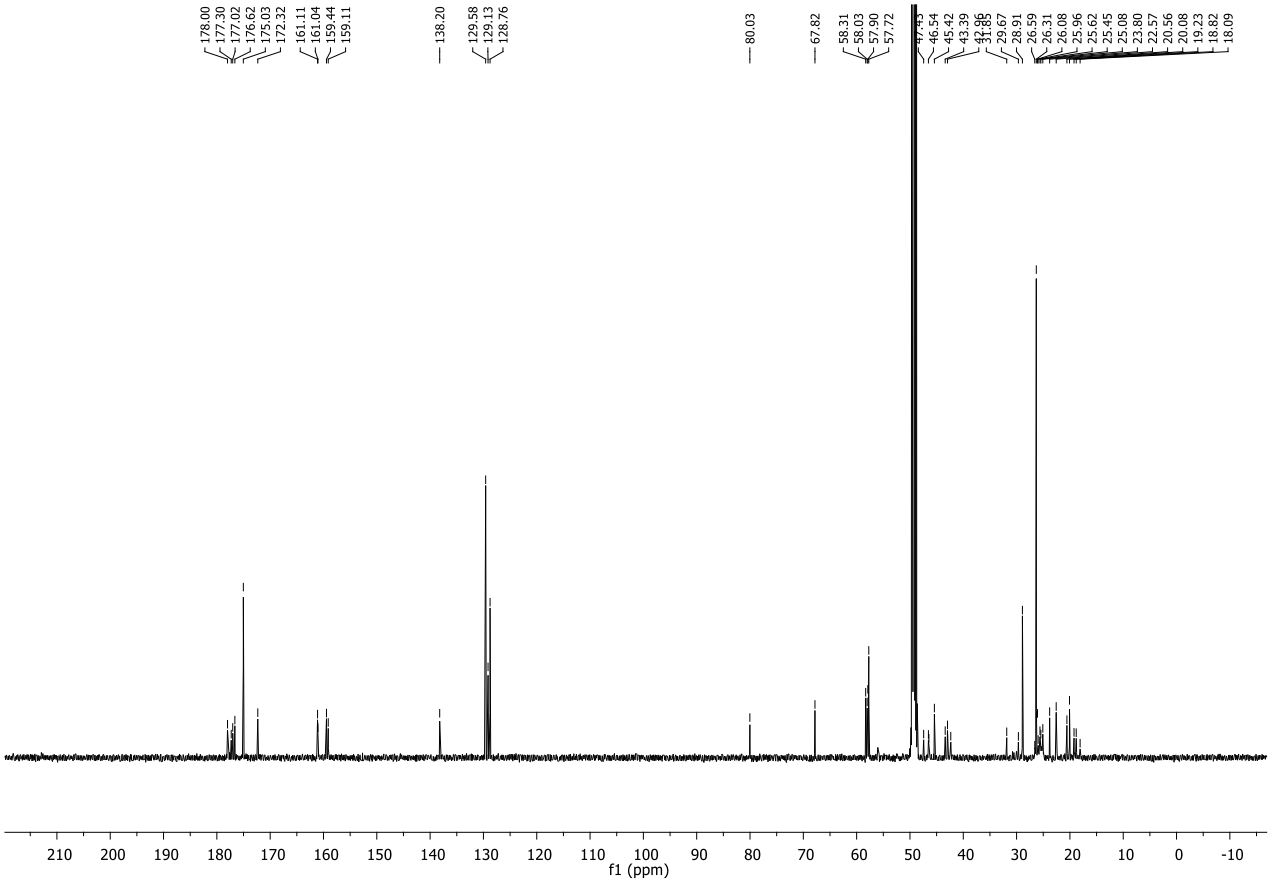
0.56
8.29
1.08
1.00
0.75
1.30
30.75
3.66
3.05
17.73
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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80.03
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46.54
45.42
43.39
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26.31
26.08
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25.08
23.80
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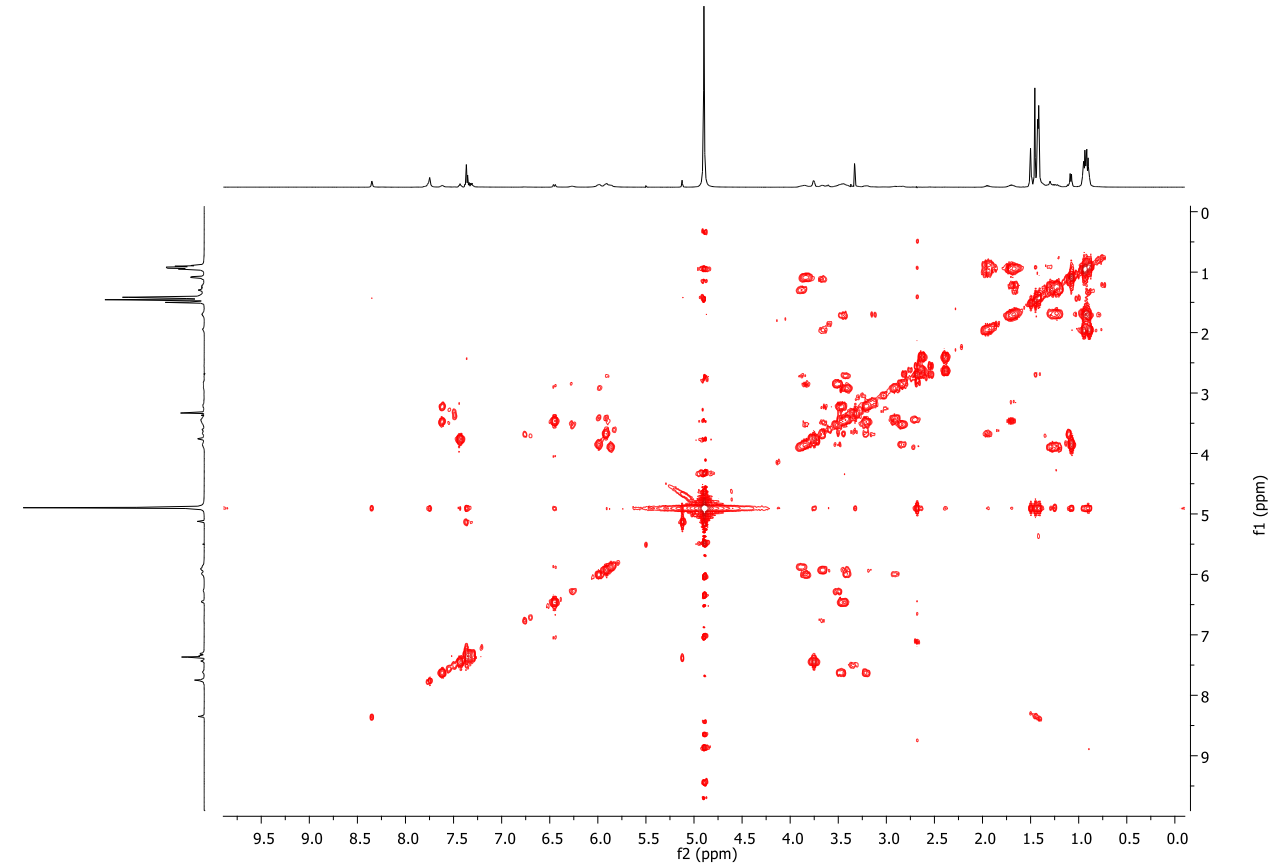
19.23
18.82
18.09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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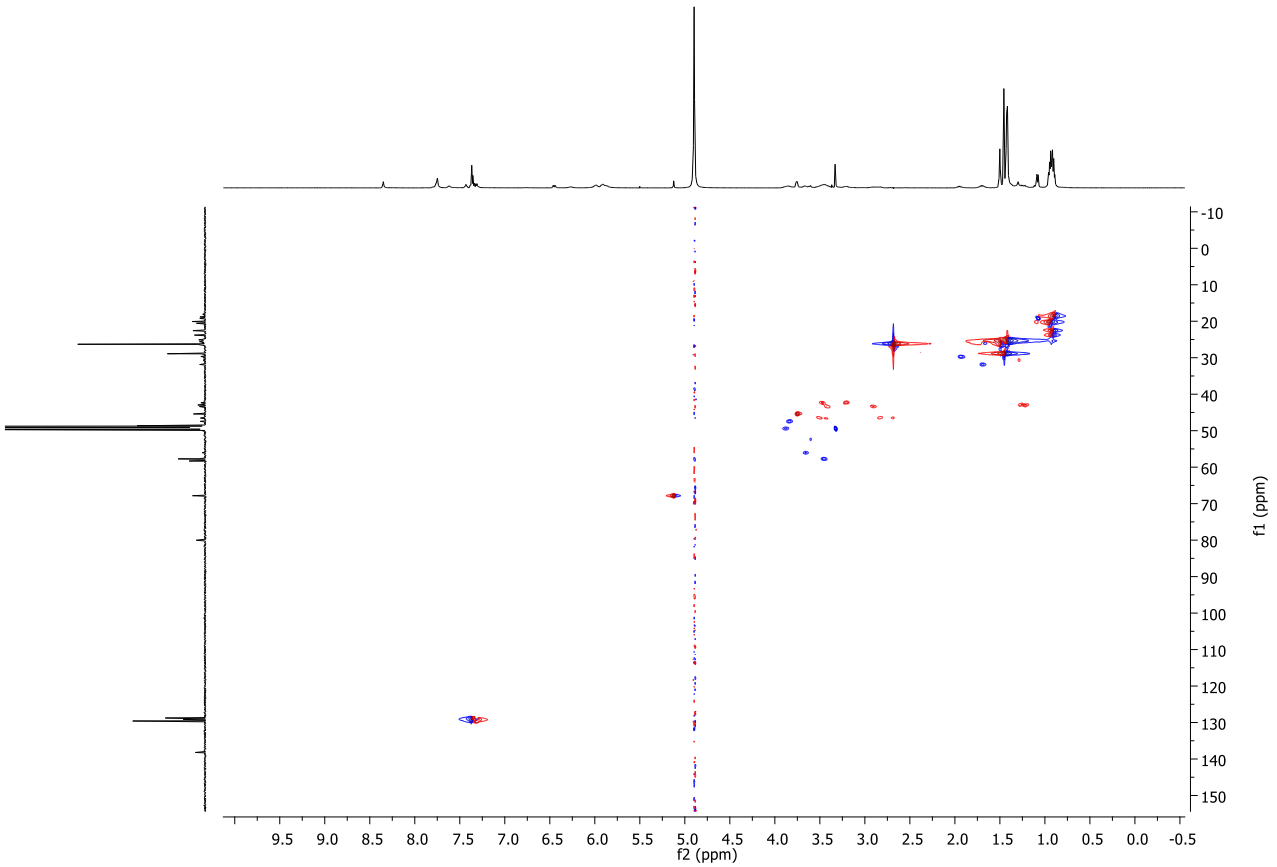
f1 (ppm)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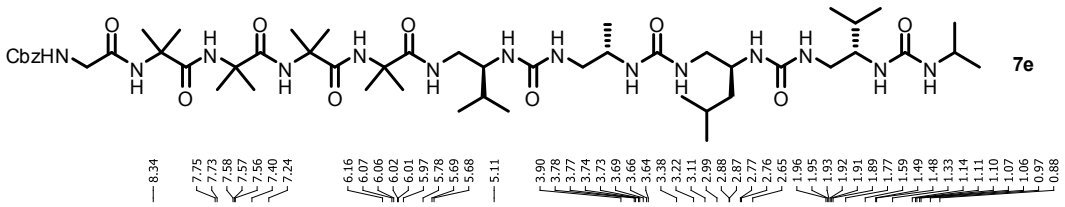
f1 (ppm)


CbzHN
7e

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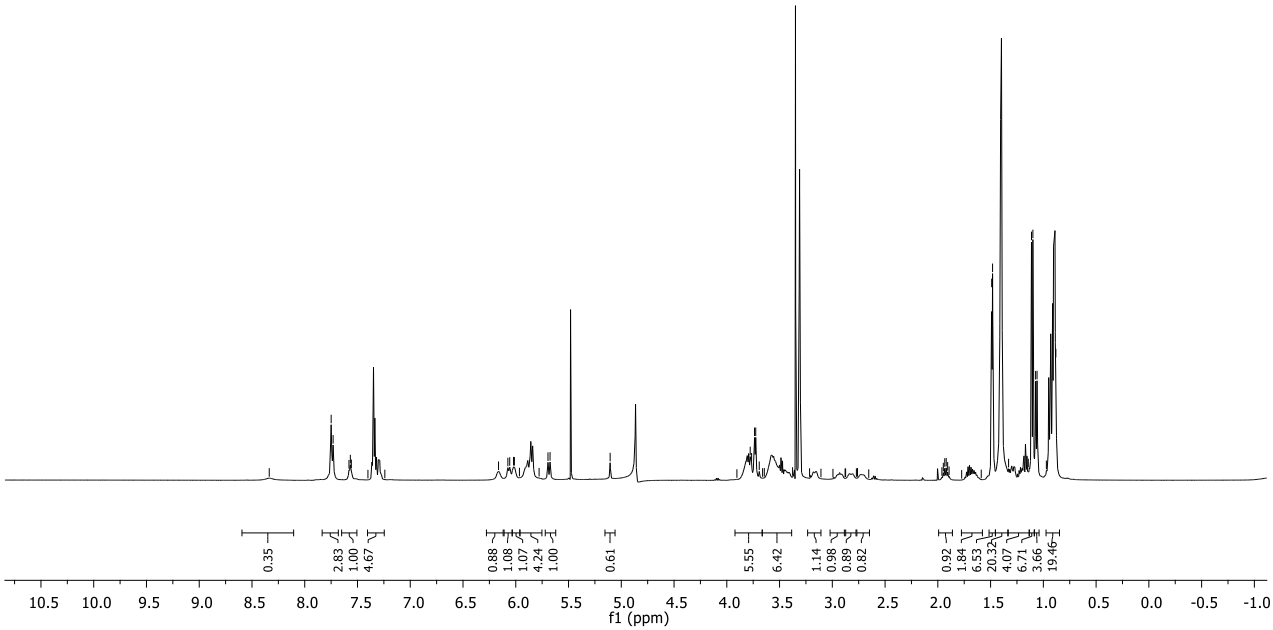
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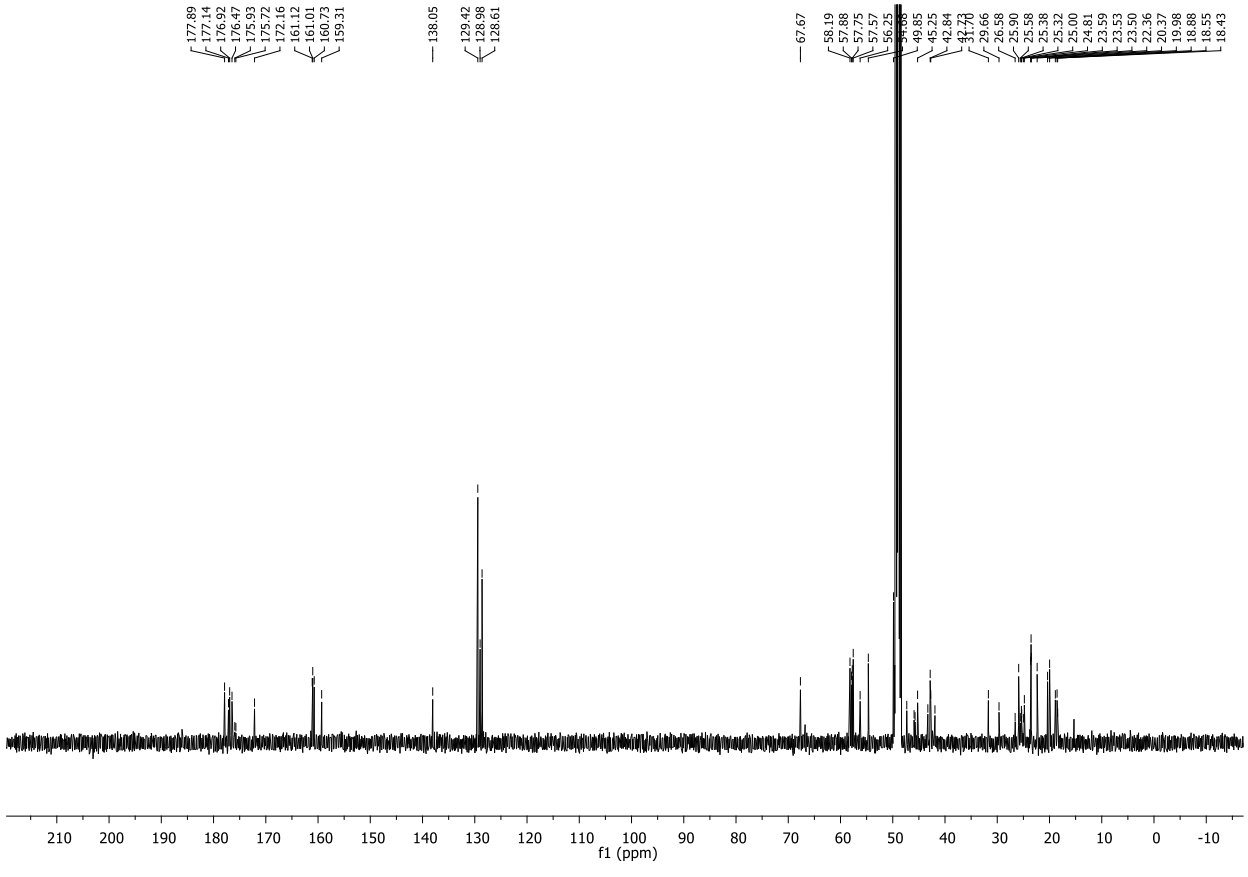
1.14
0.98
0.89
0.82
0.92
1.84
6.53
20.32
4.07
6.71
3.66
19.46
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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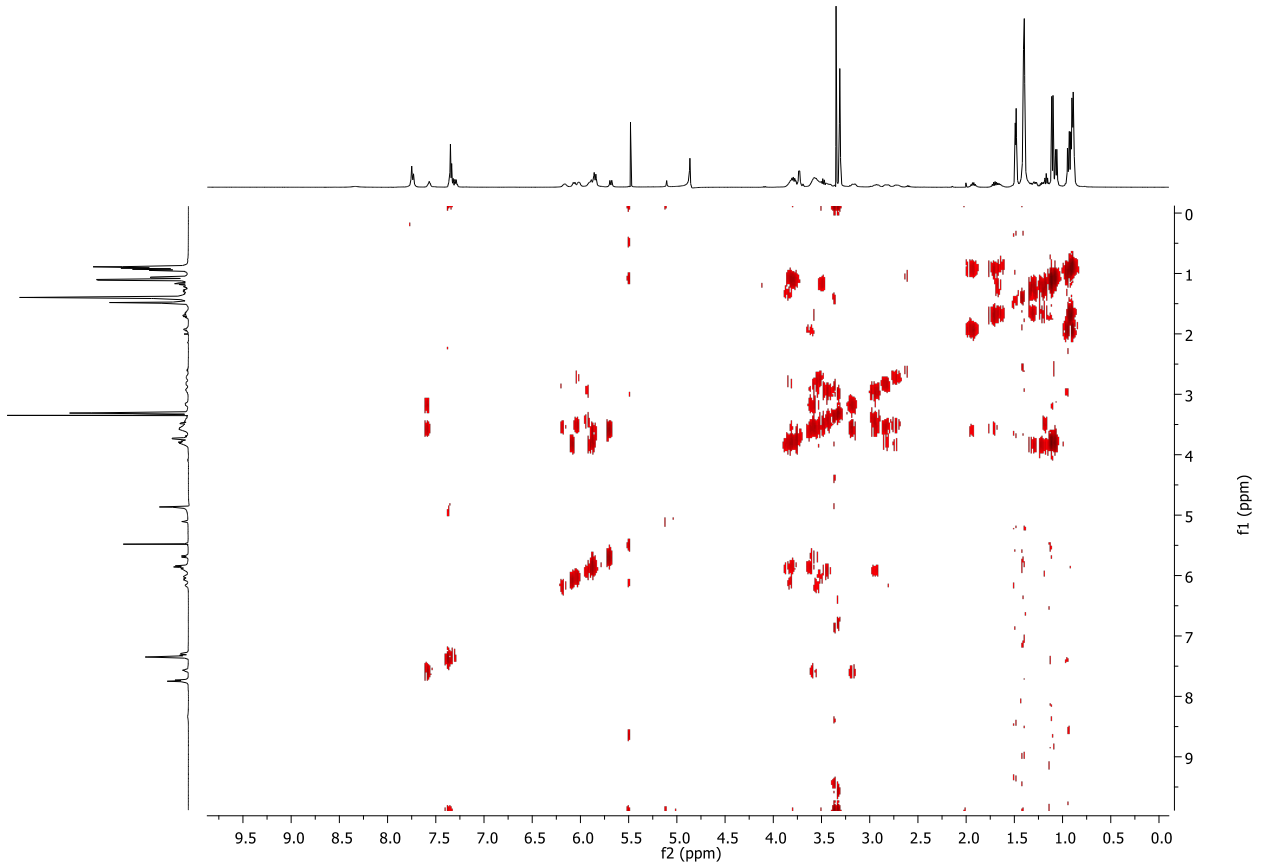
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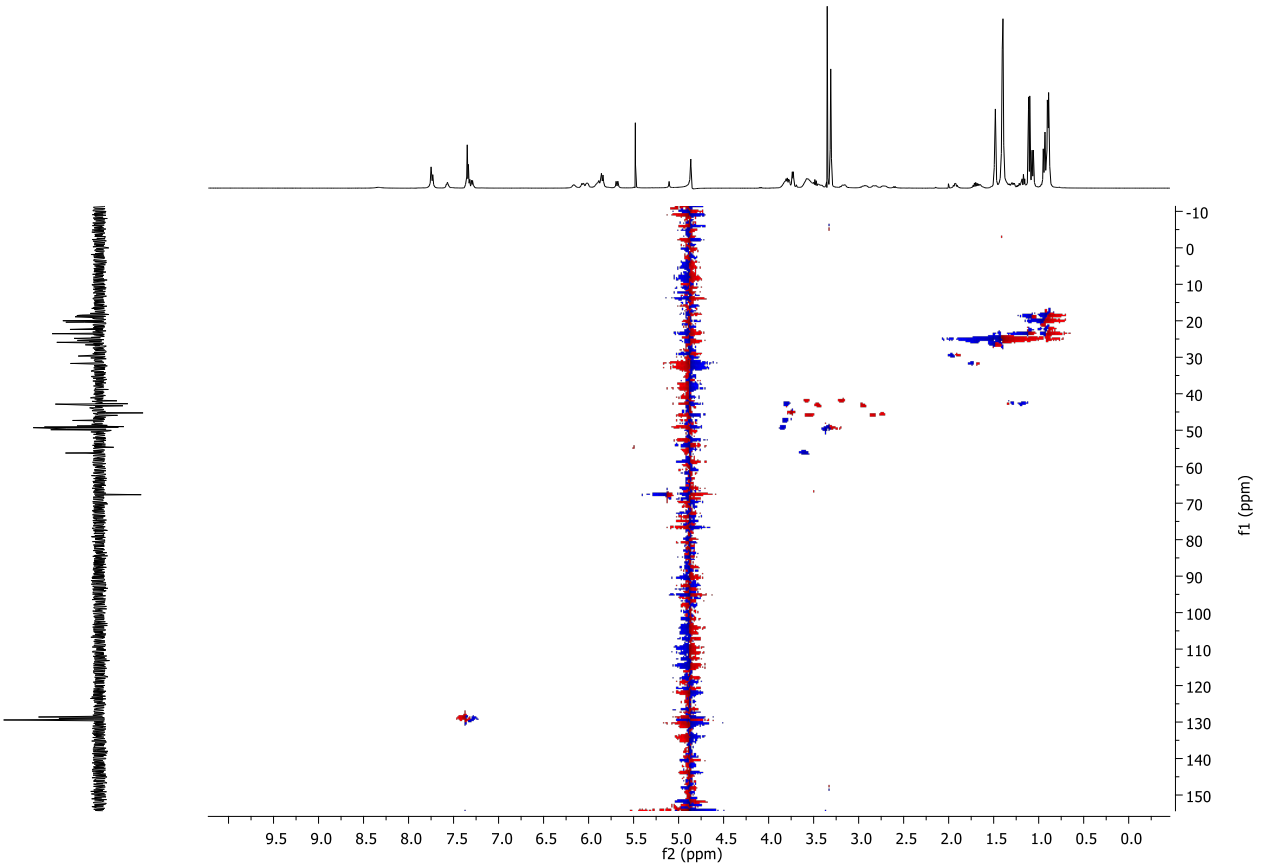
f1 (ppm)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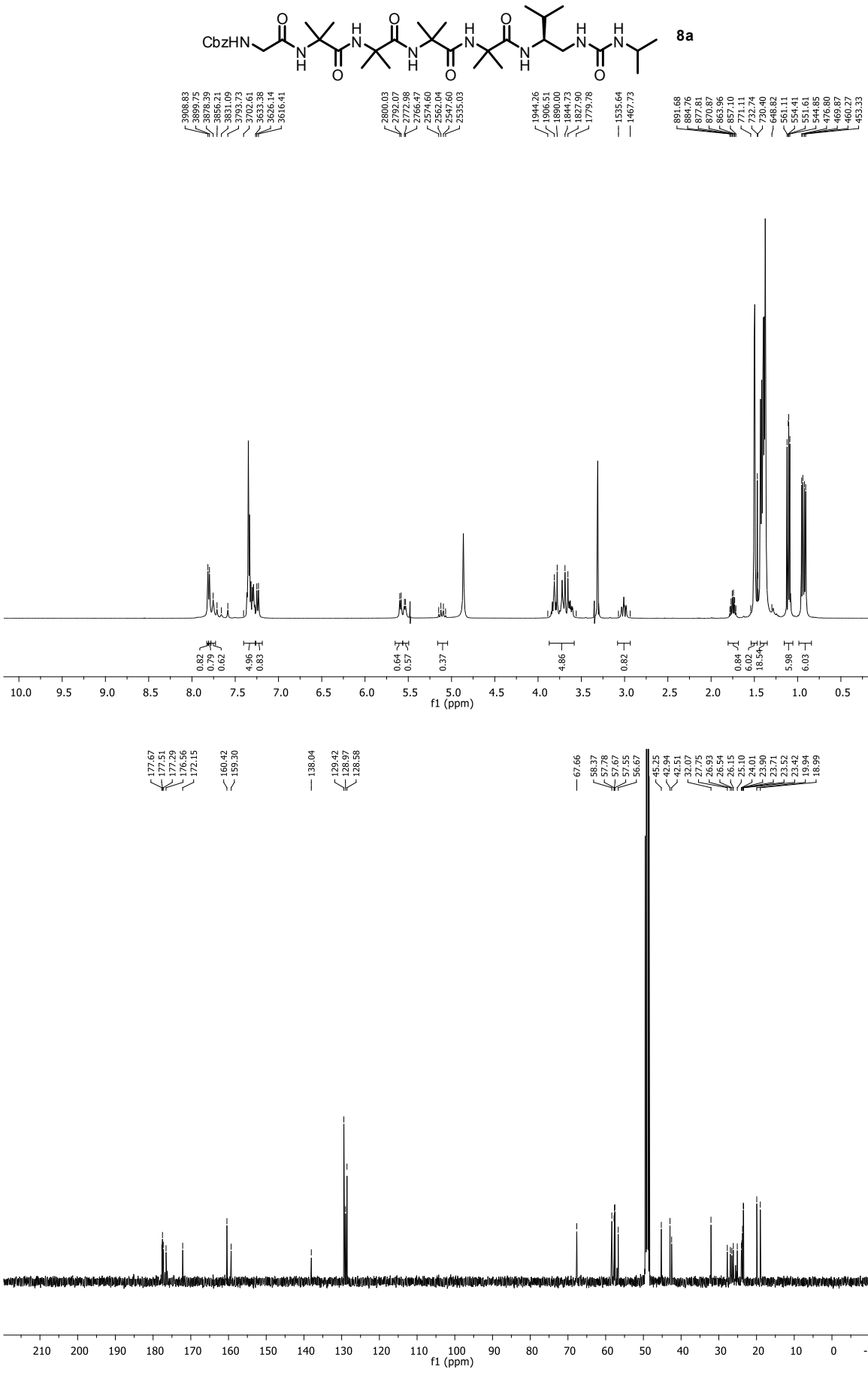
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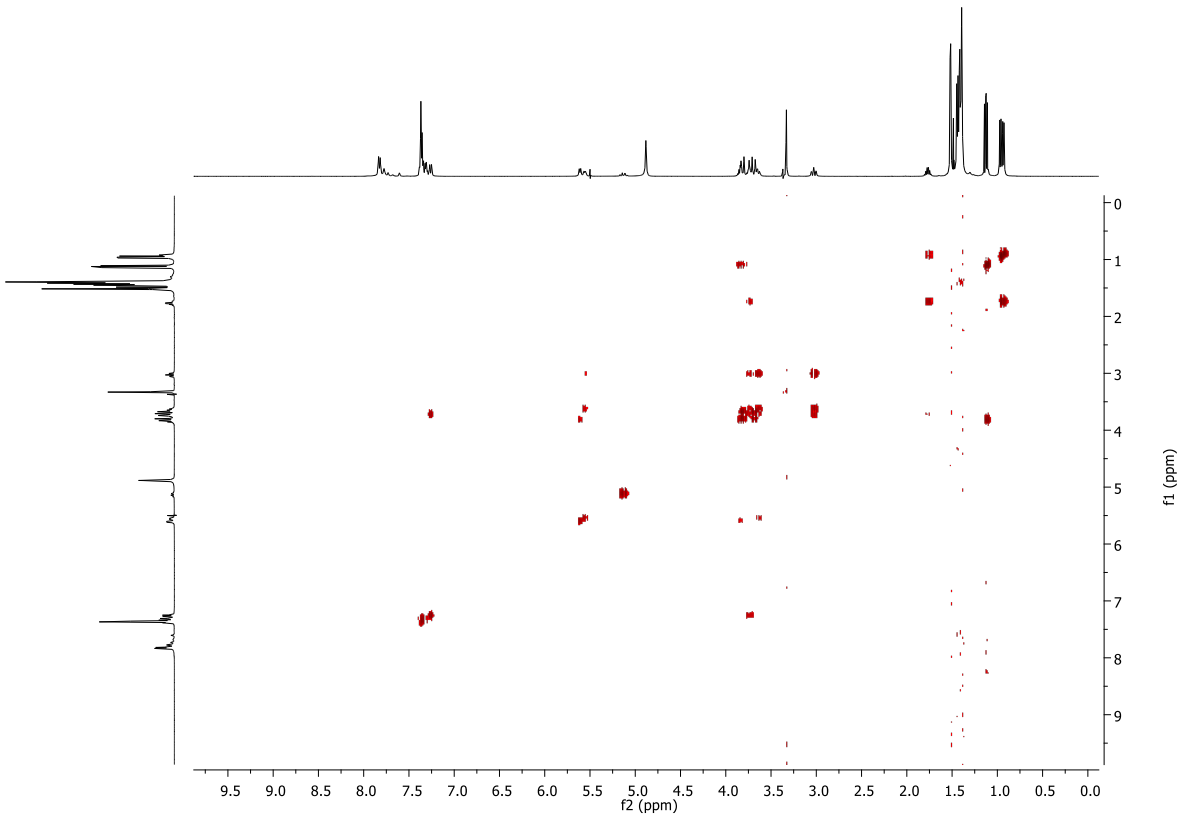
f1 (ppm)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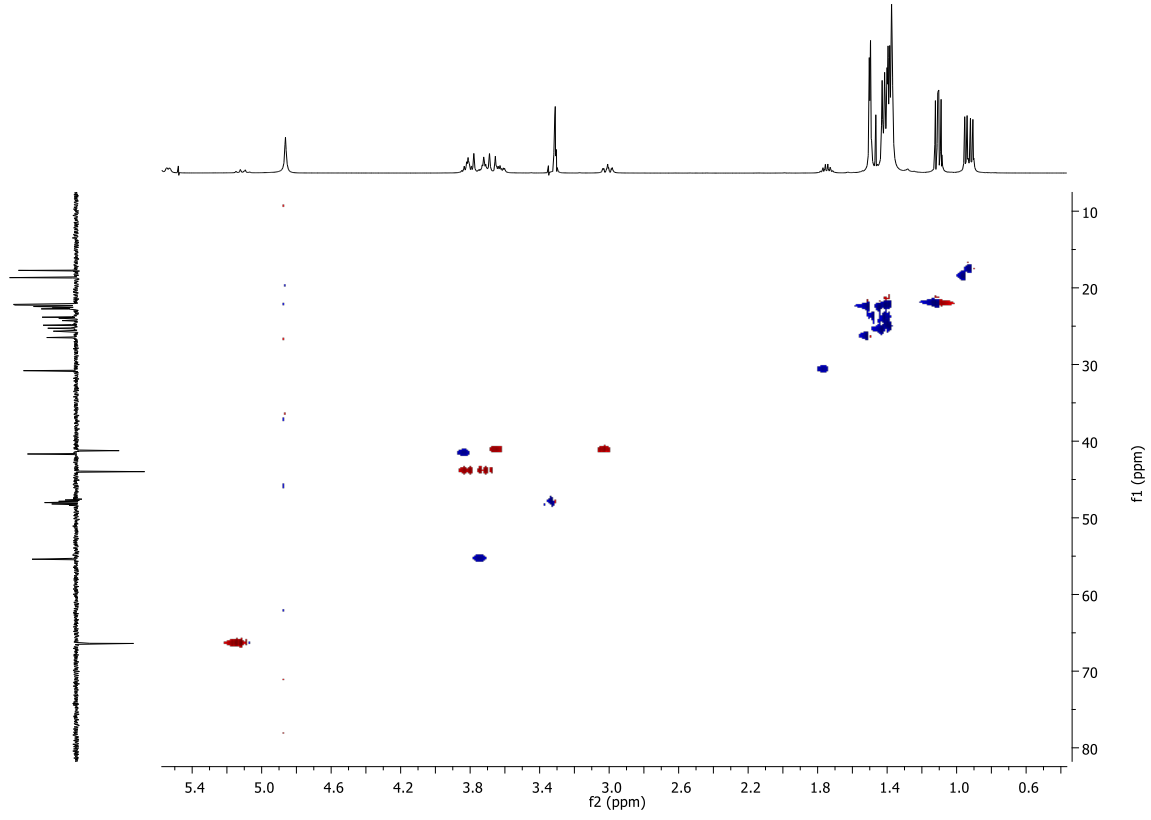
f2 (ppm)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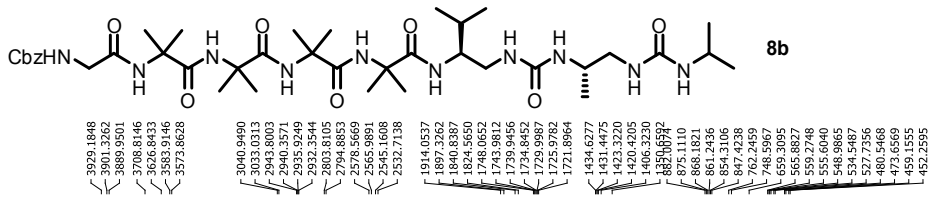
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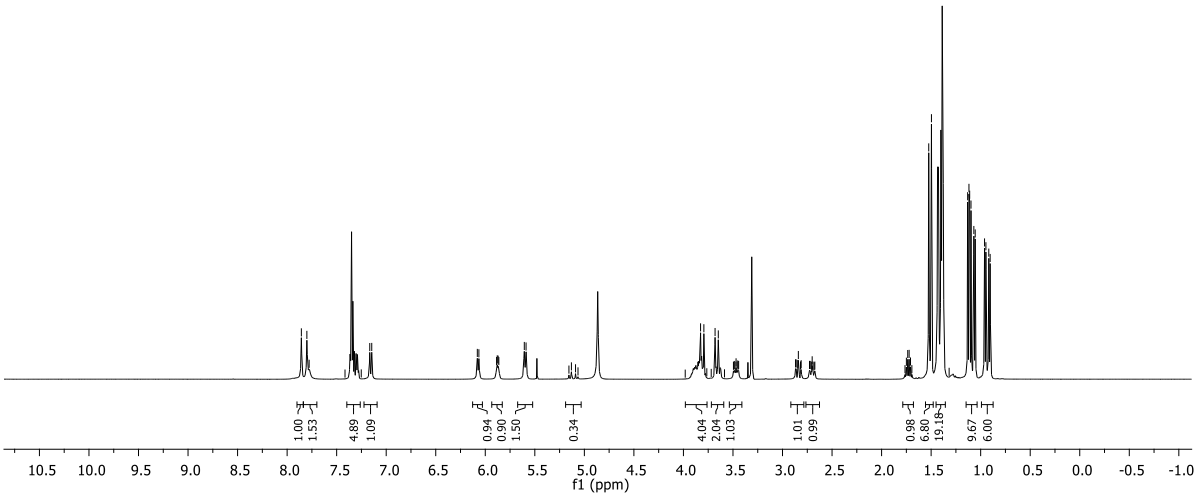
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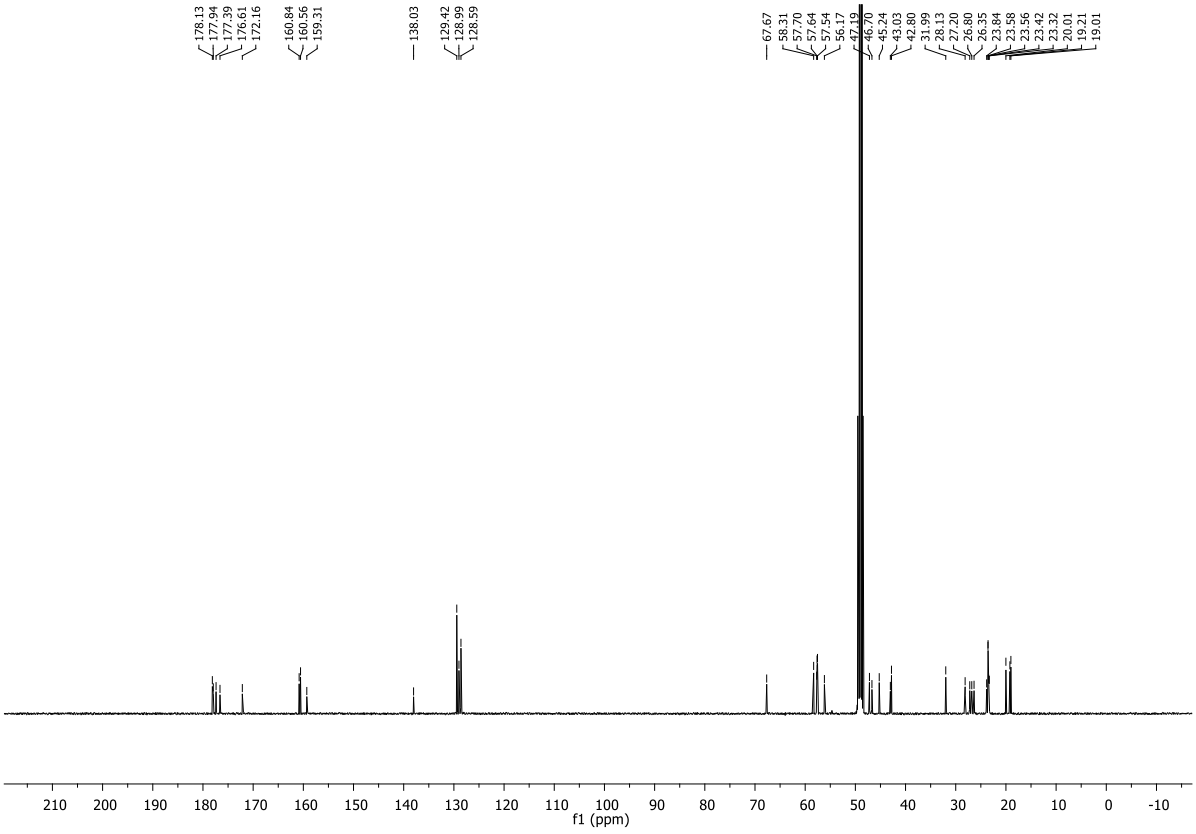
f1 (ppm)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23.42
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20.01
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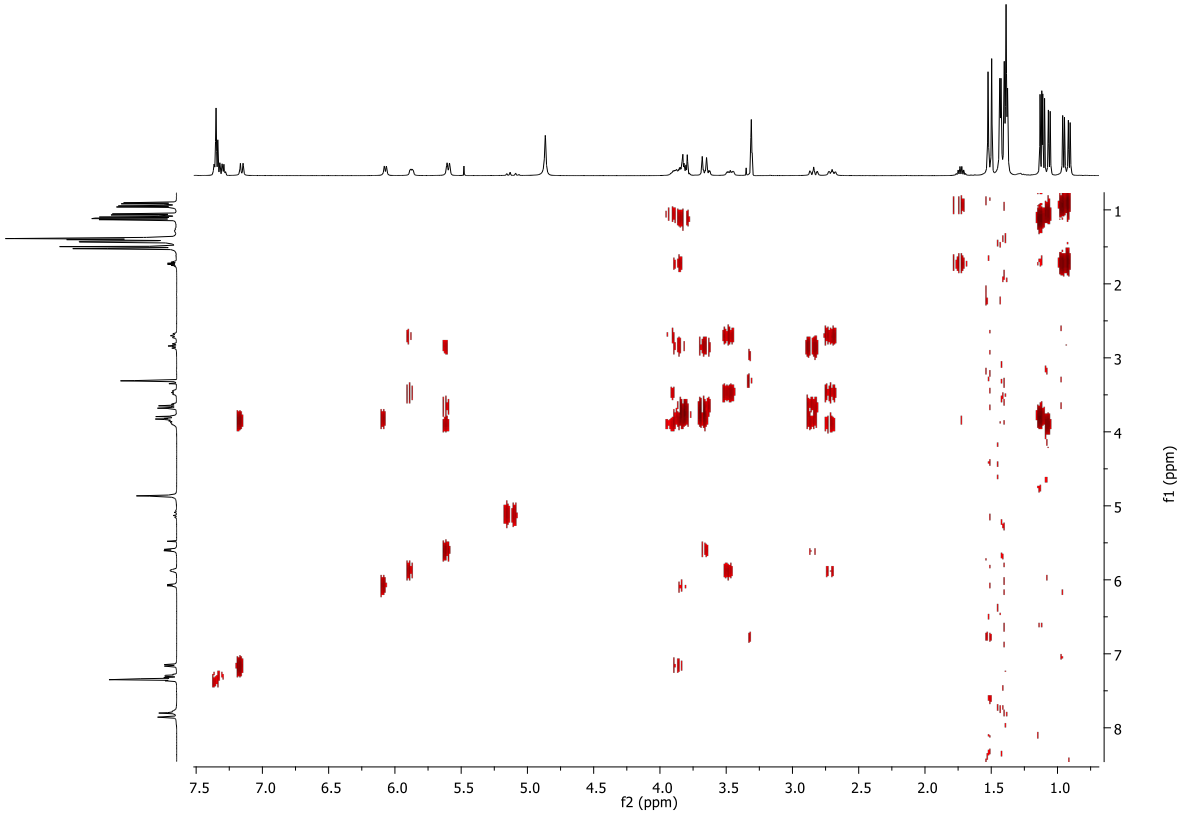
19.01
f1 (ppm)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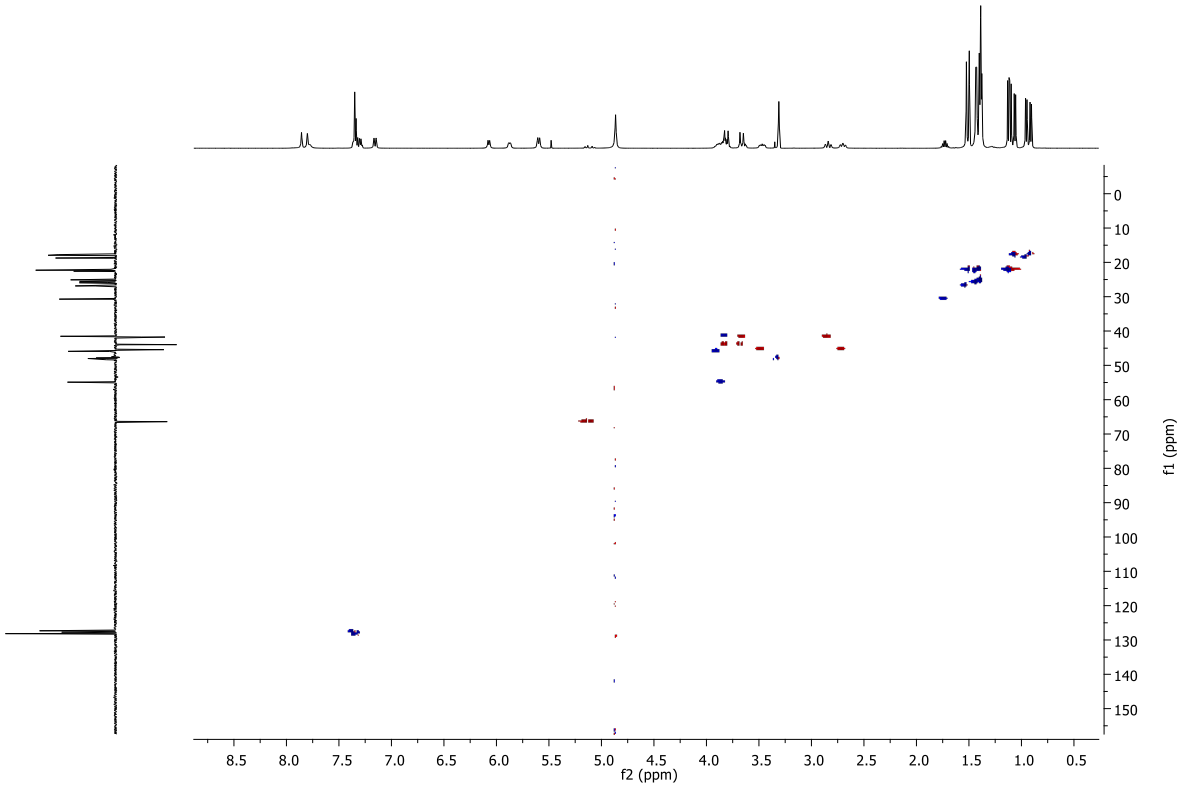
f1 (ppm)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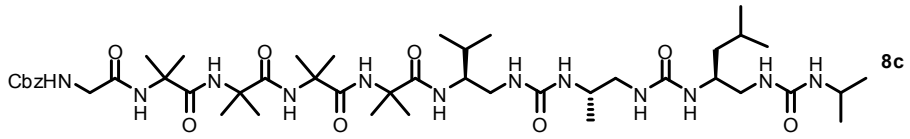
CbzHN
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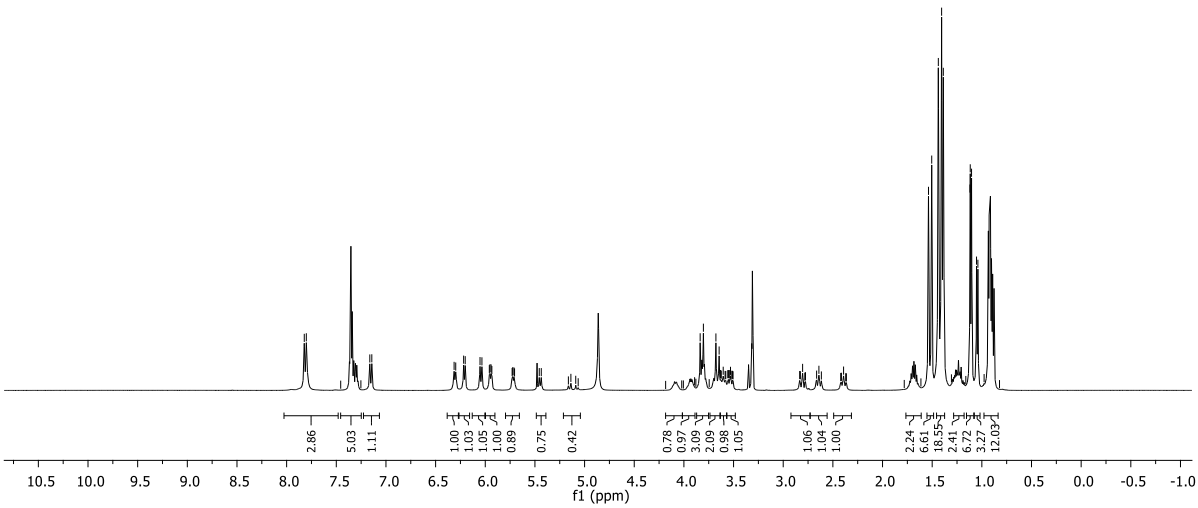

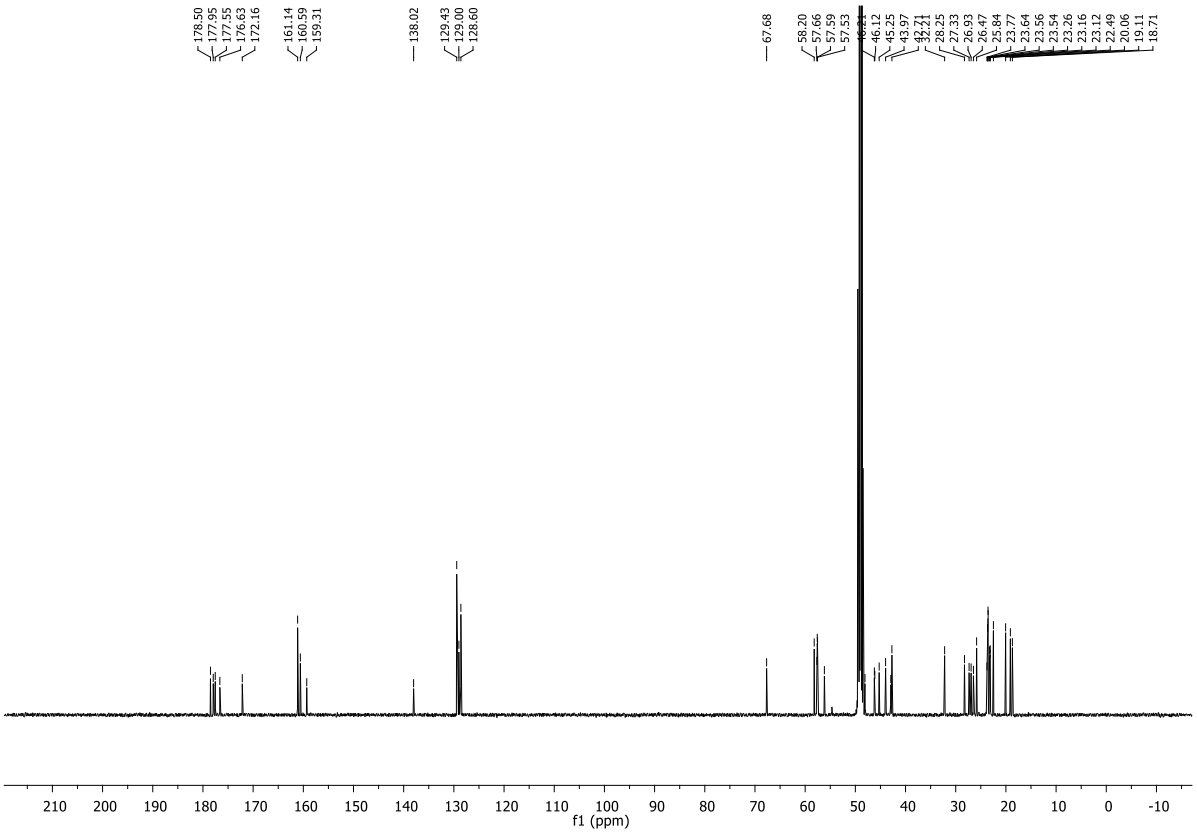

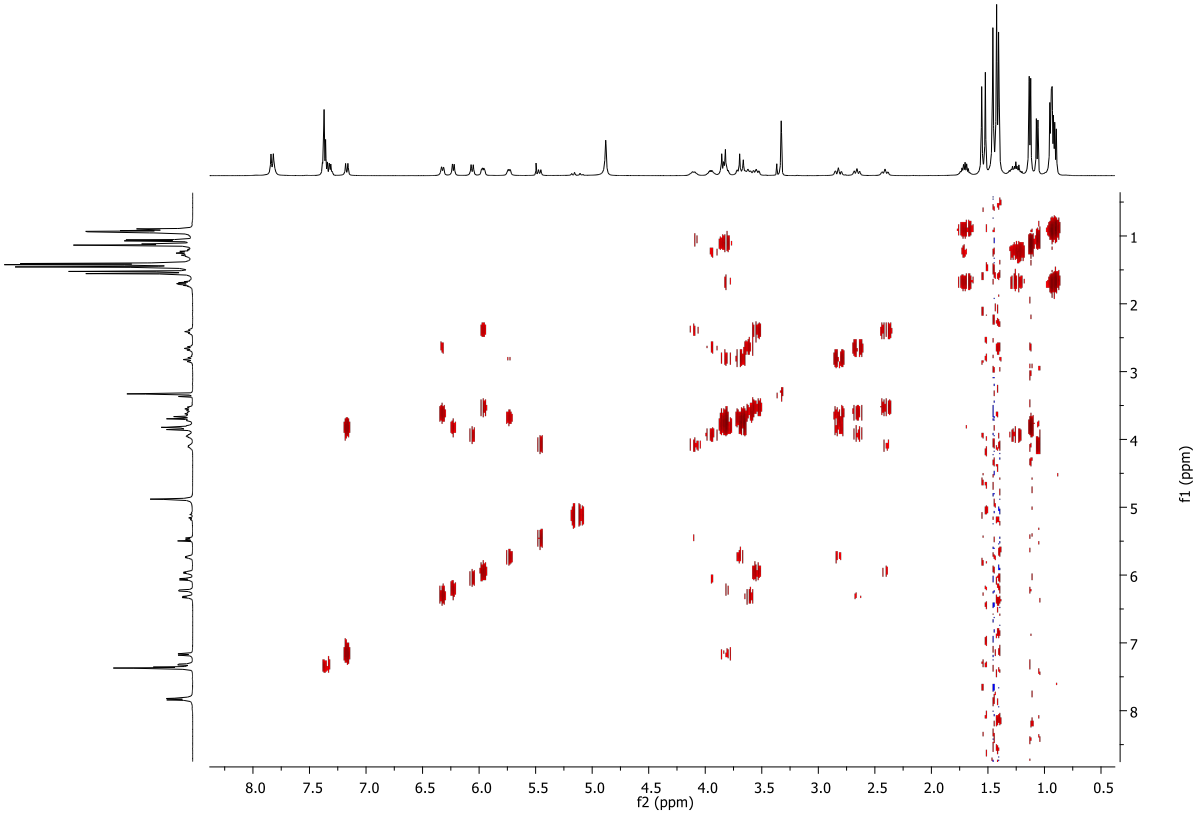
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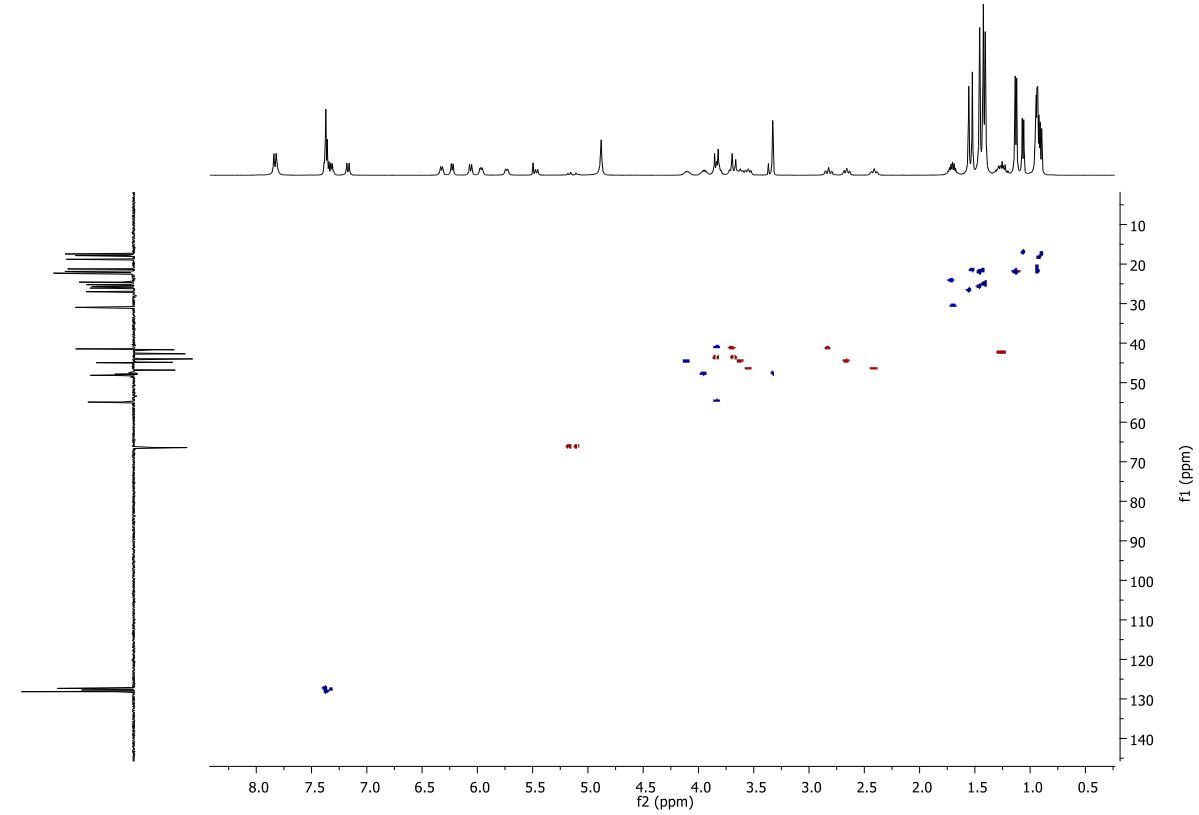
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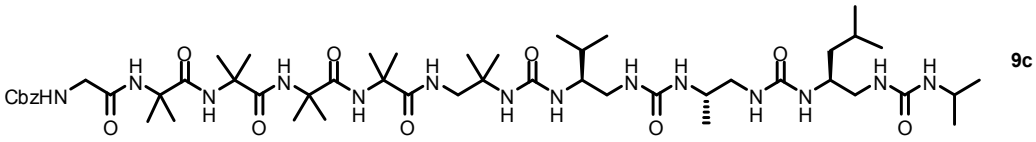
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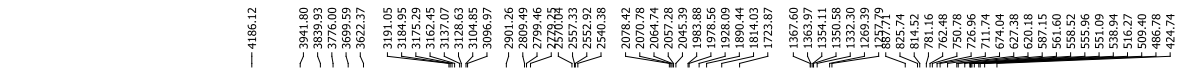

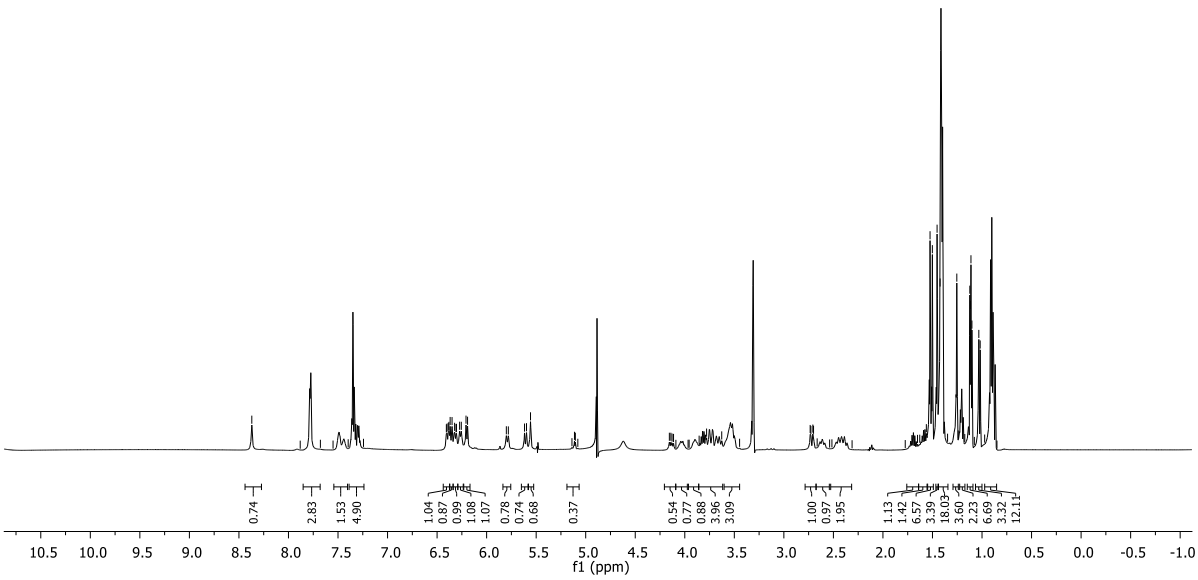
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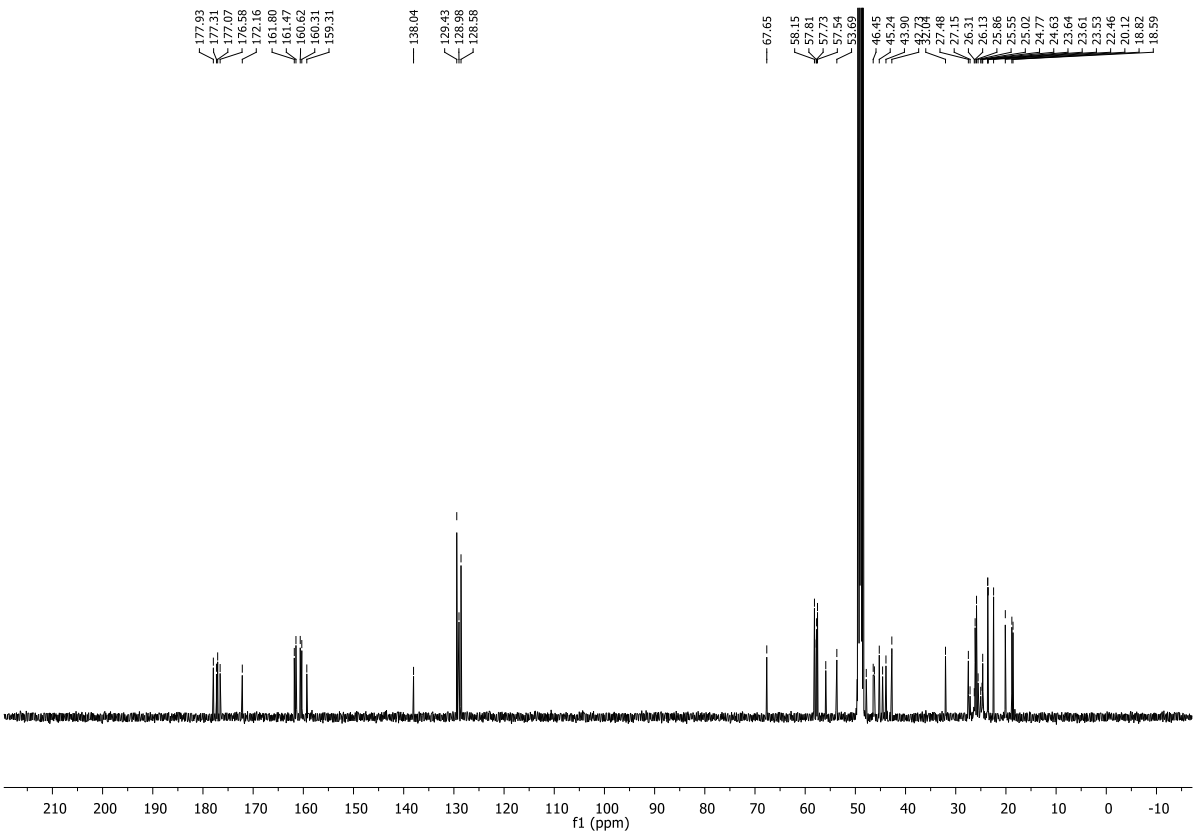
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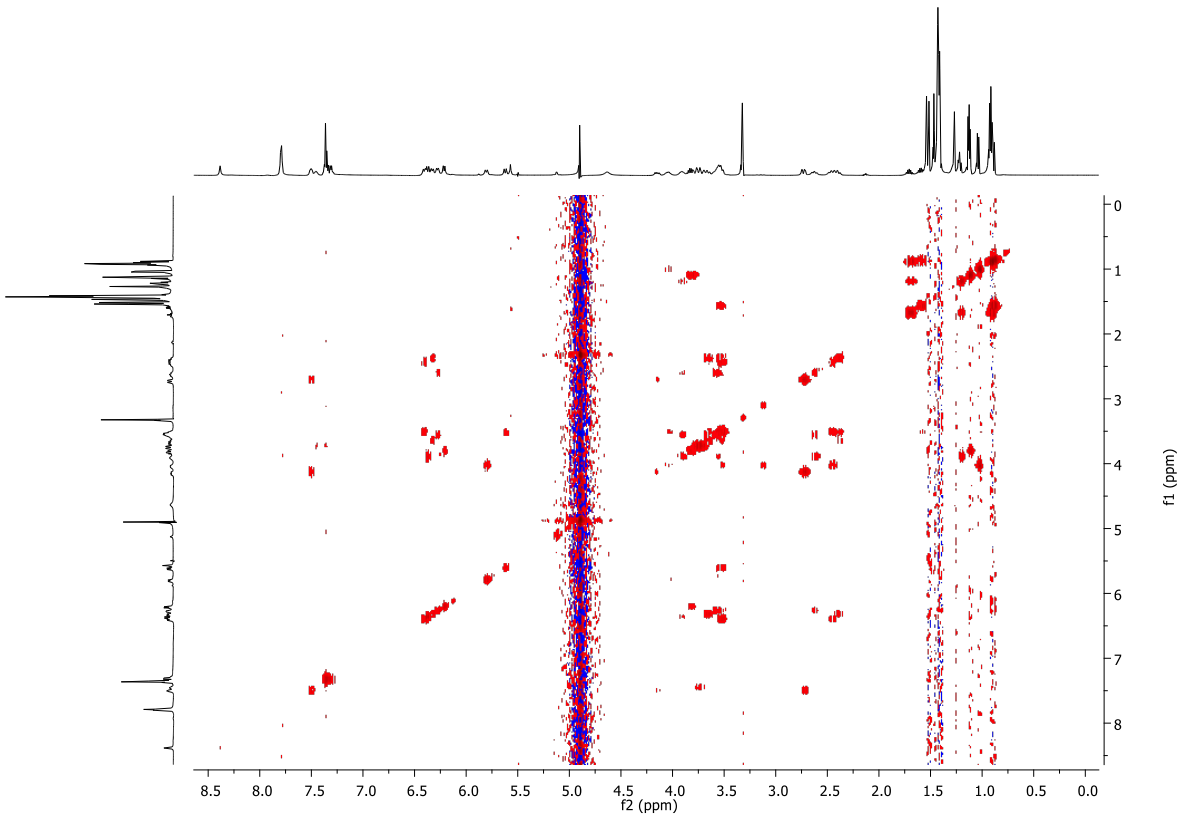
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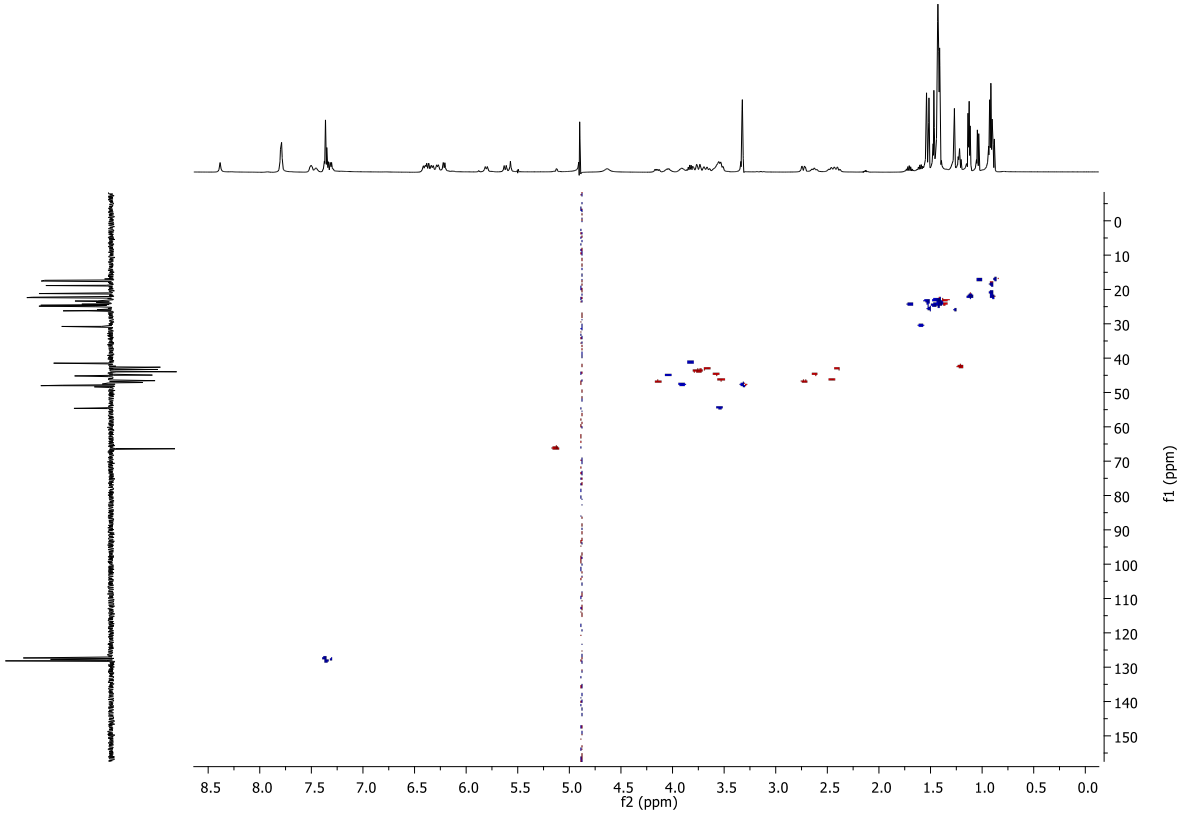
f2 (ppm)
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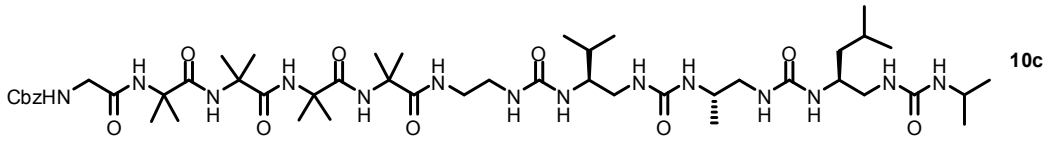
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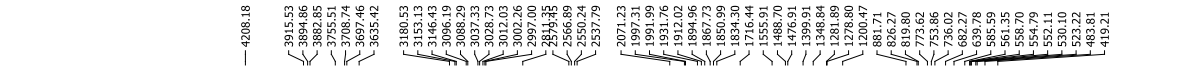

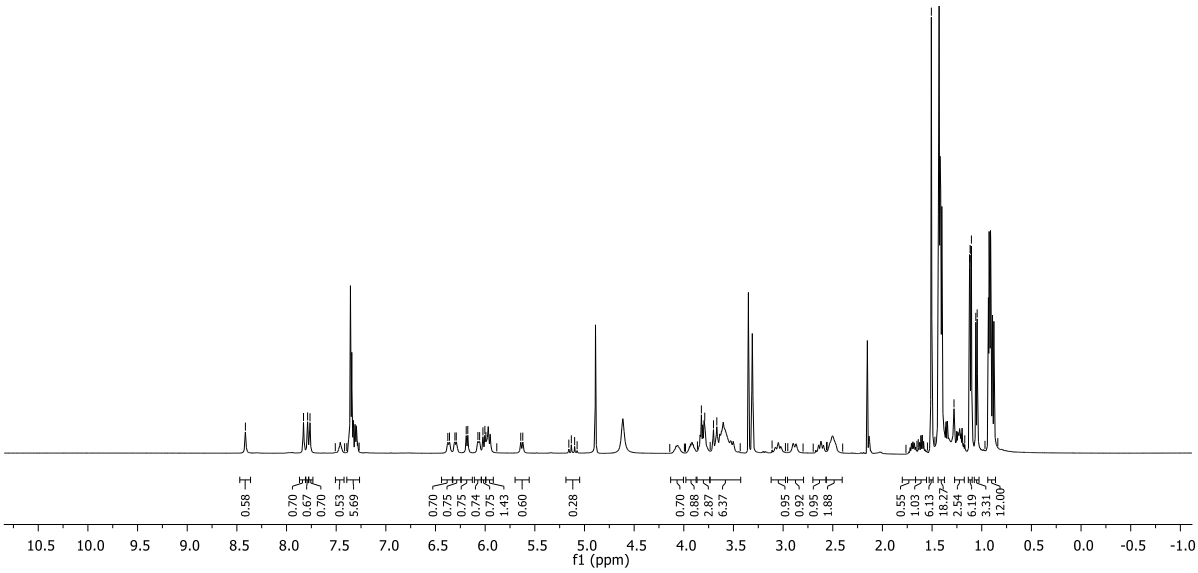
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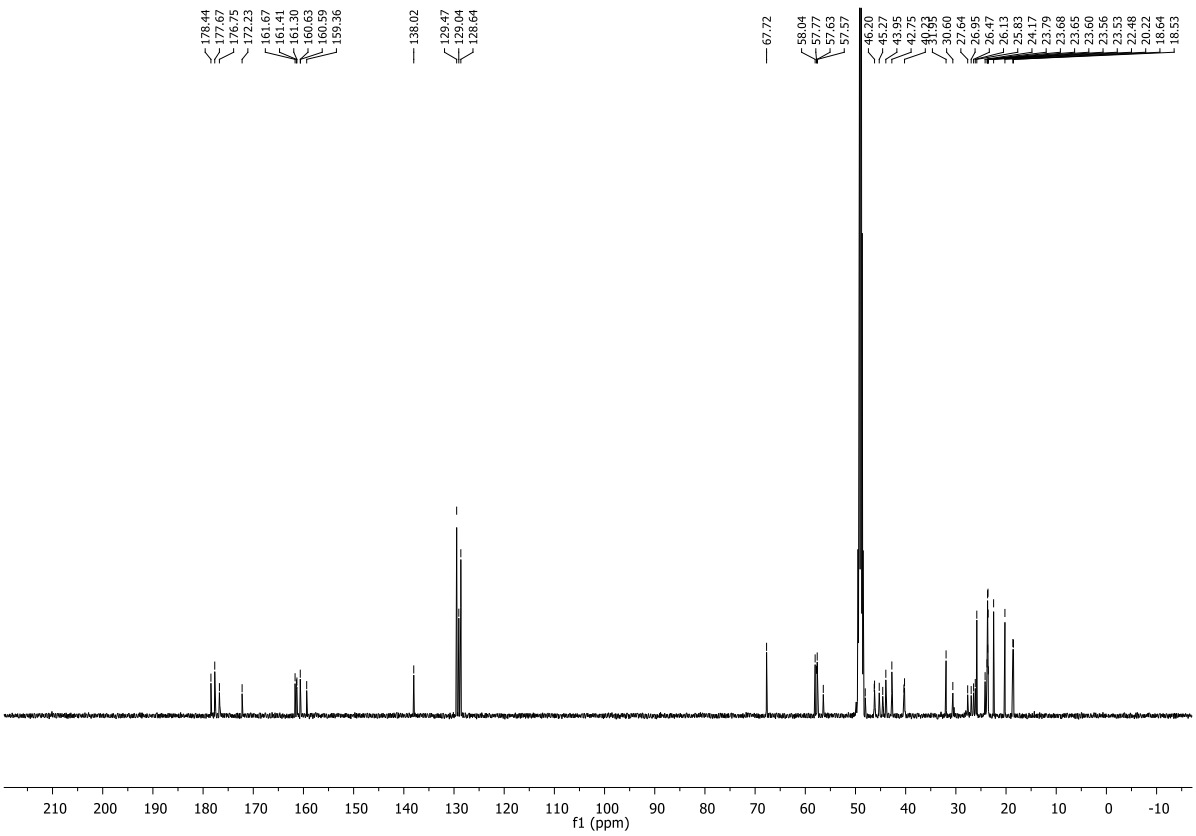
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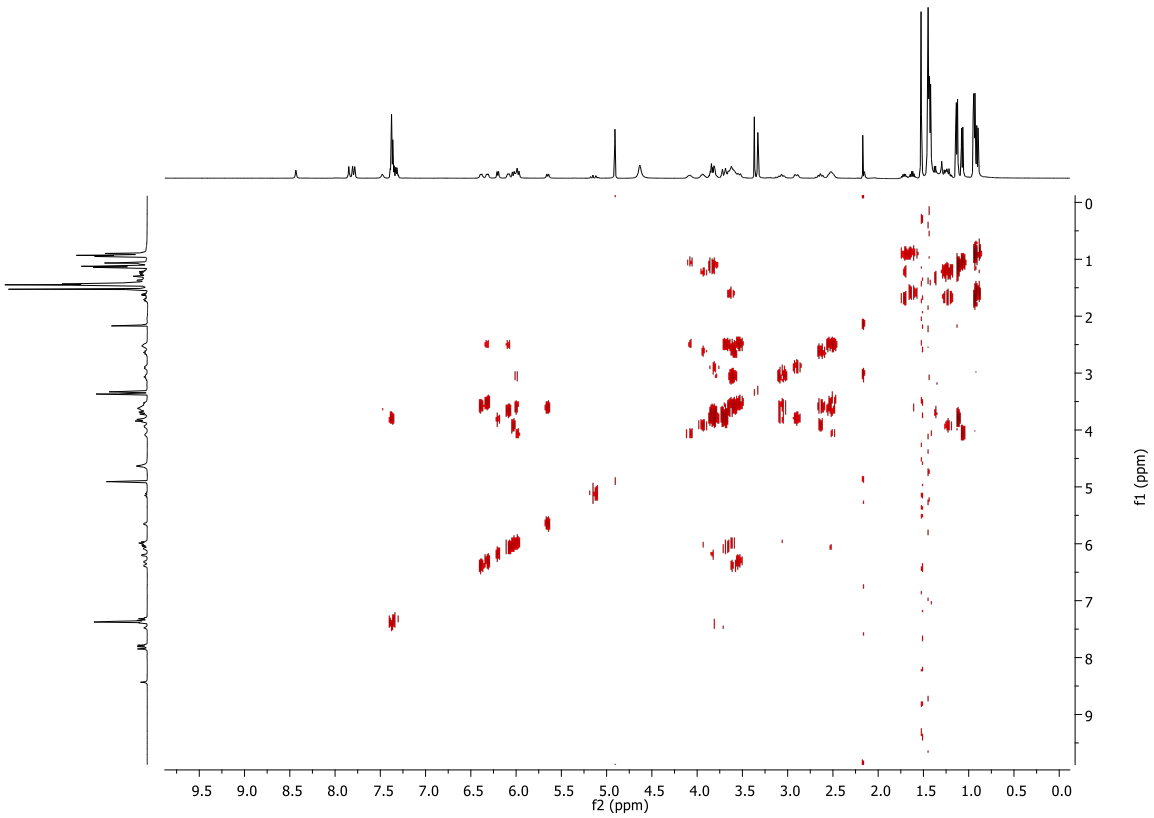
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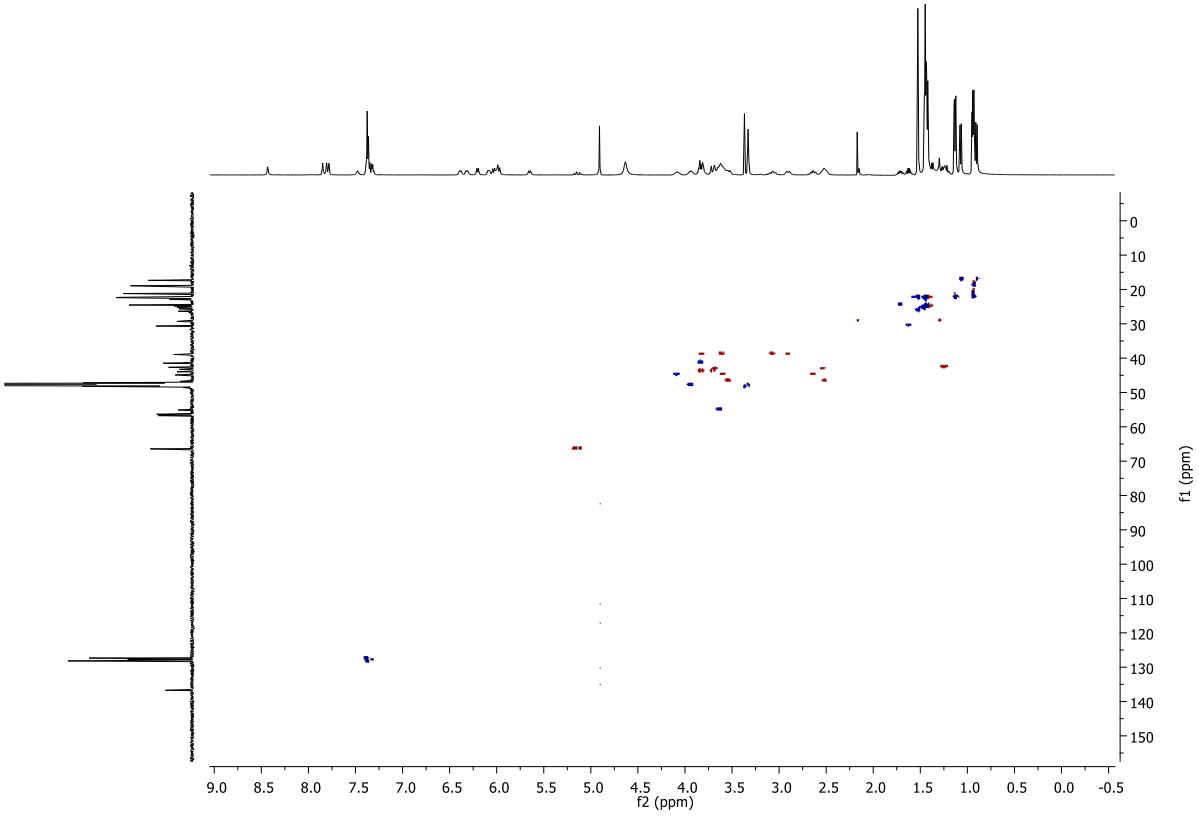
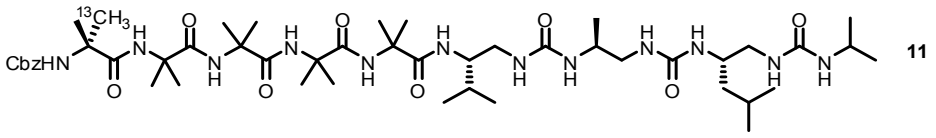
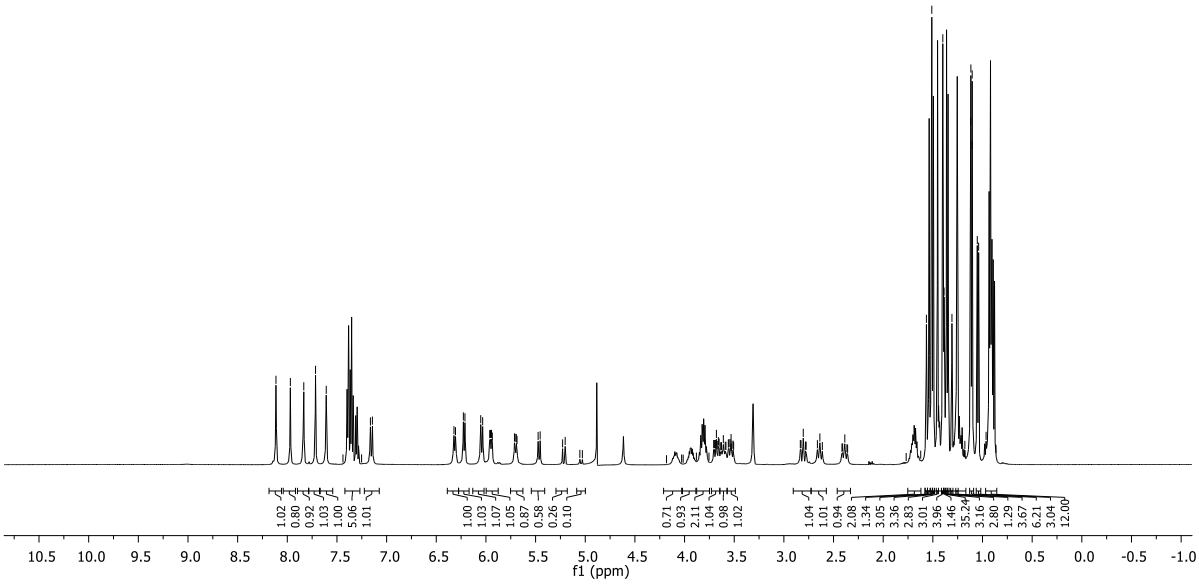
f1 (ppm)


f2 (ppm)
f1 (ppm)


$^{13}CH_3$
CbzHN
11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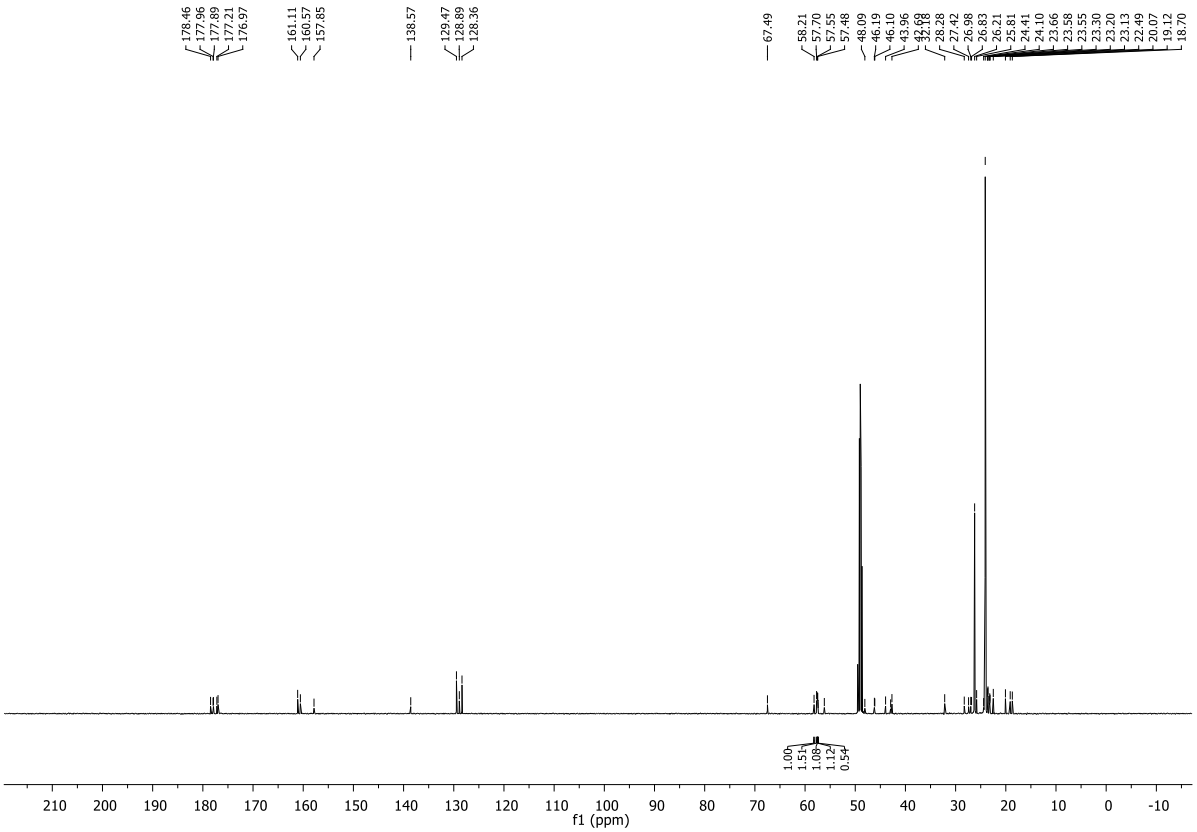
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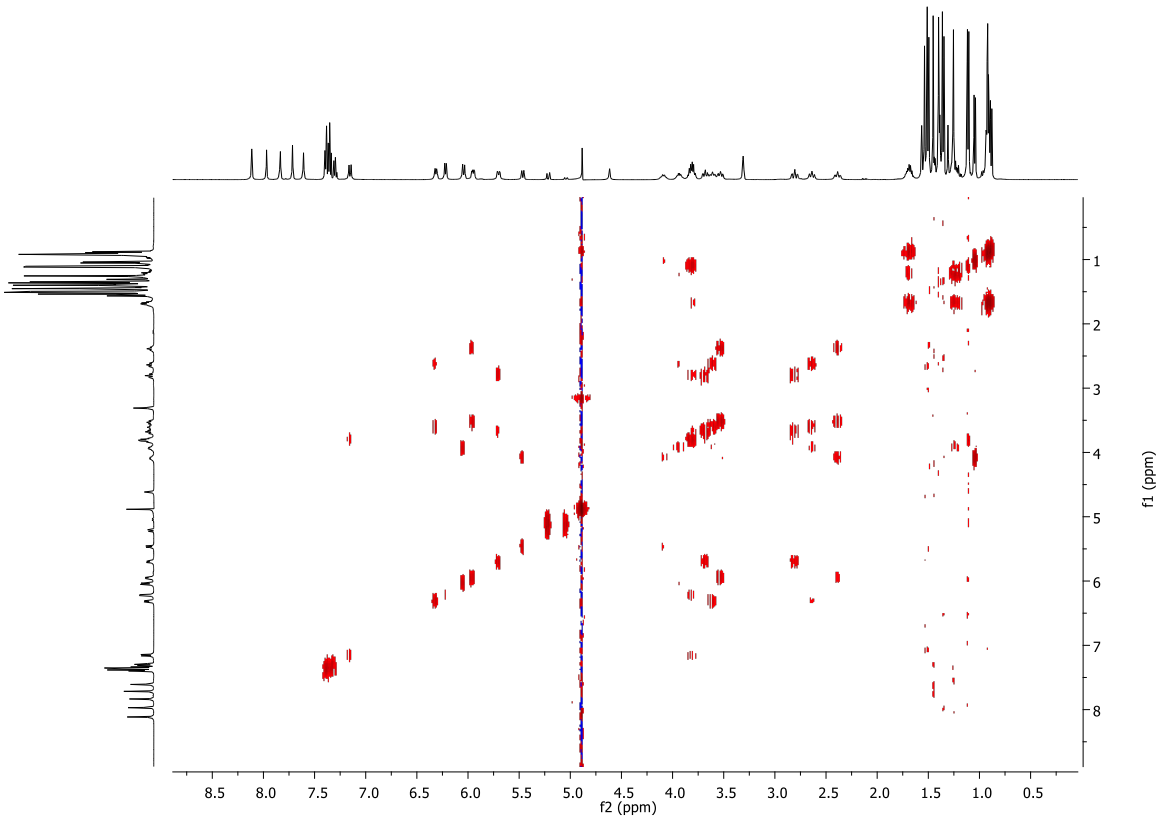
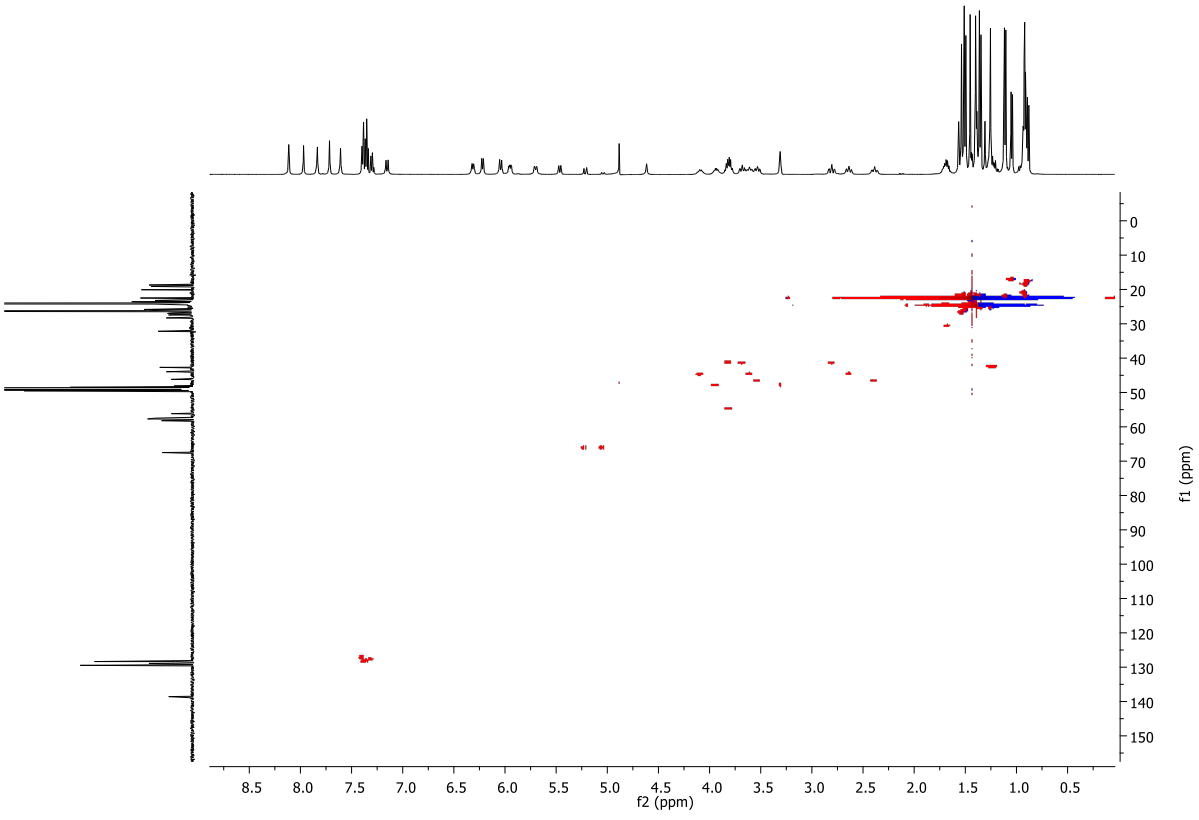
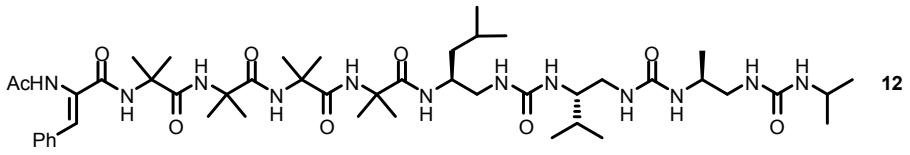
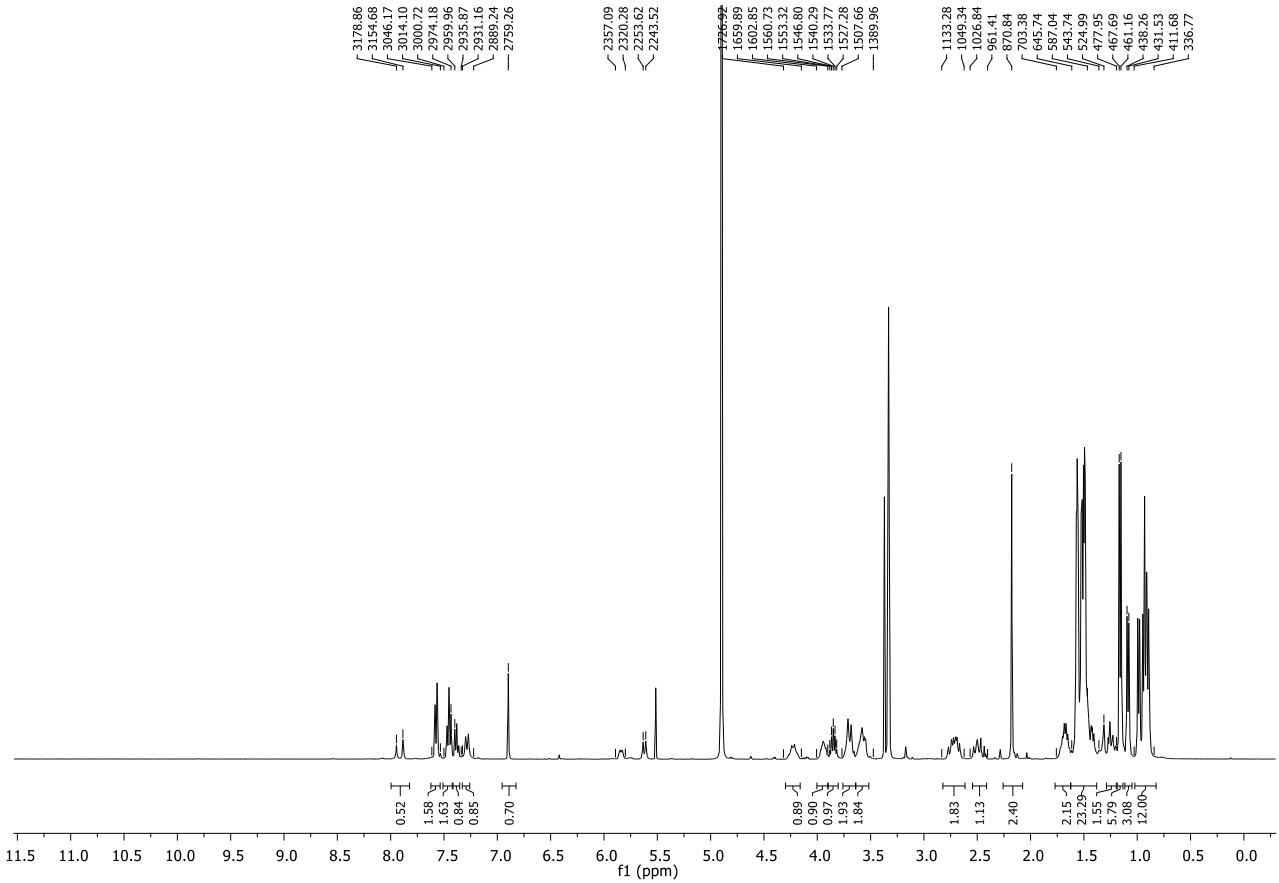

f1 (ppm)
f2 (ppm)


f1 (ppm)
f2 (ppm)


AcHN
Ph
12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3000.72
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2959.96
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2931.16
2889.24
2759.26
2357.09
2320.28
2253.62
2243.52
1726.92
1659.89
1602.85
1560.73
1553.32
1546.80
1540.29
1533.77
1527.28
1507.66
1389.96
1133.28
1049.34
1026.84
961.41
870.84
703.38
645.74
587.04
543.74
524.99
477.95
467.69
461.16
438.26
431.53
411.68
336.77
0.52
1.58
1.63
0.84
0.85
0.70
0.89
0.90
0.97
1.93
1.84
1.83
1.13
2.40
2.15
23.29
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5.79
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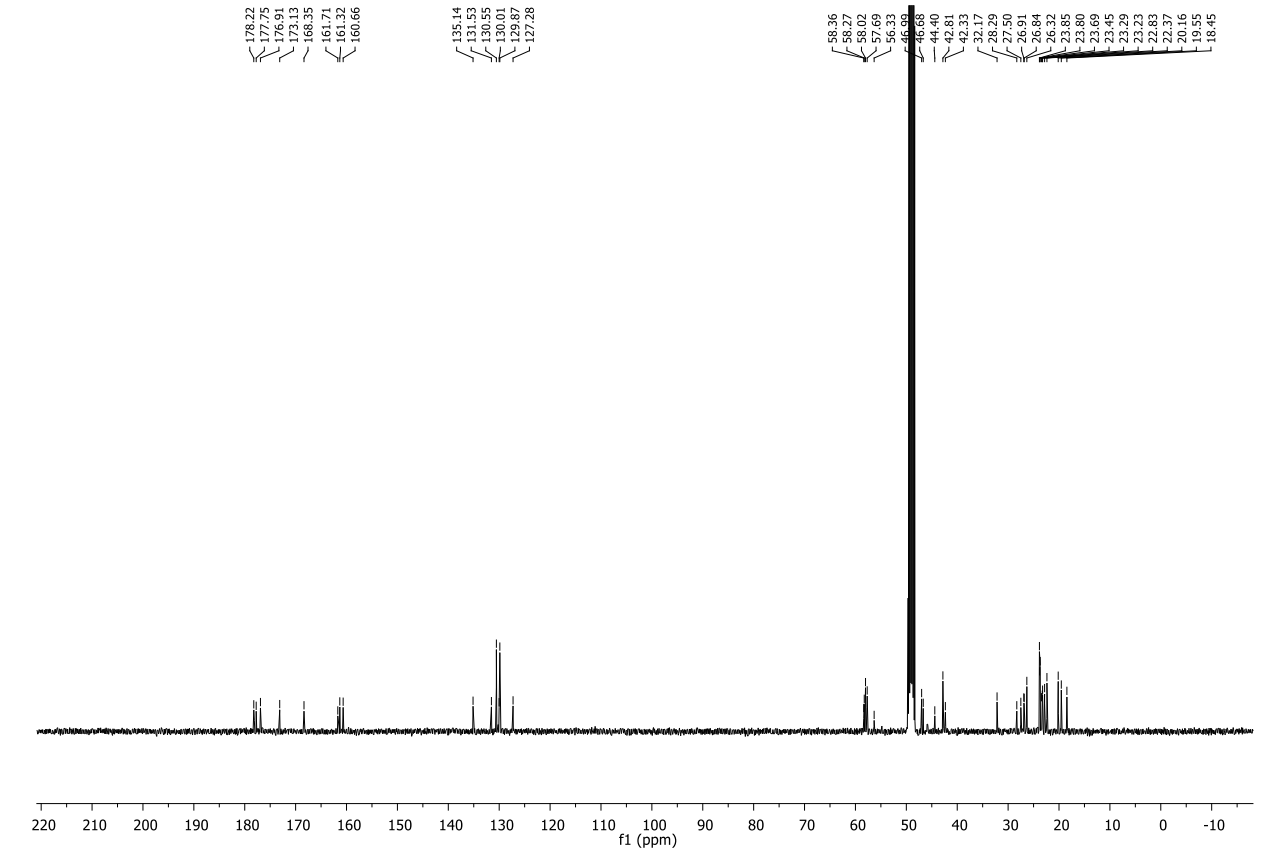
12.00
f1 (ppm)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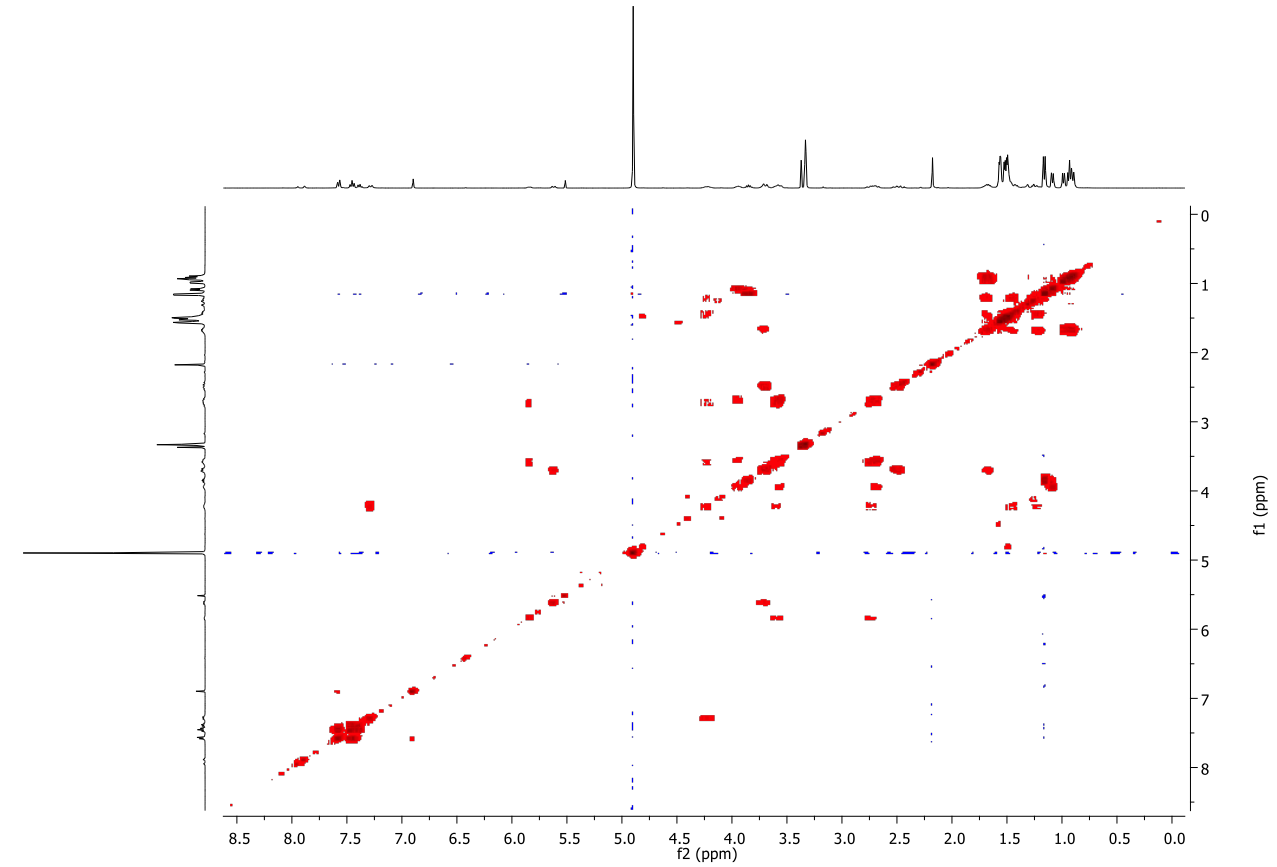
130.01
129.87
127.28
58.36
58.27
58.02
57.69
56.33
46.99
46.68
44.40
42.81
42.33
32.17
28.29
27.50
26.91
26.84
26.32
23.85
23.80
23.69
23.45
23.29
23.23
22.83
22.37
20.16
19.55
18.45
f1 (ppm)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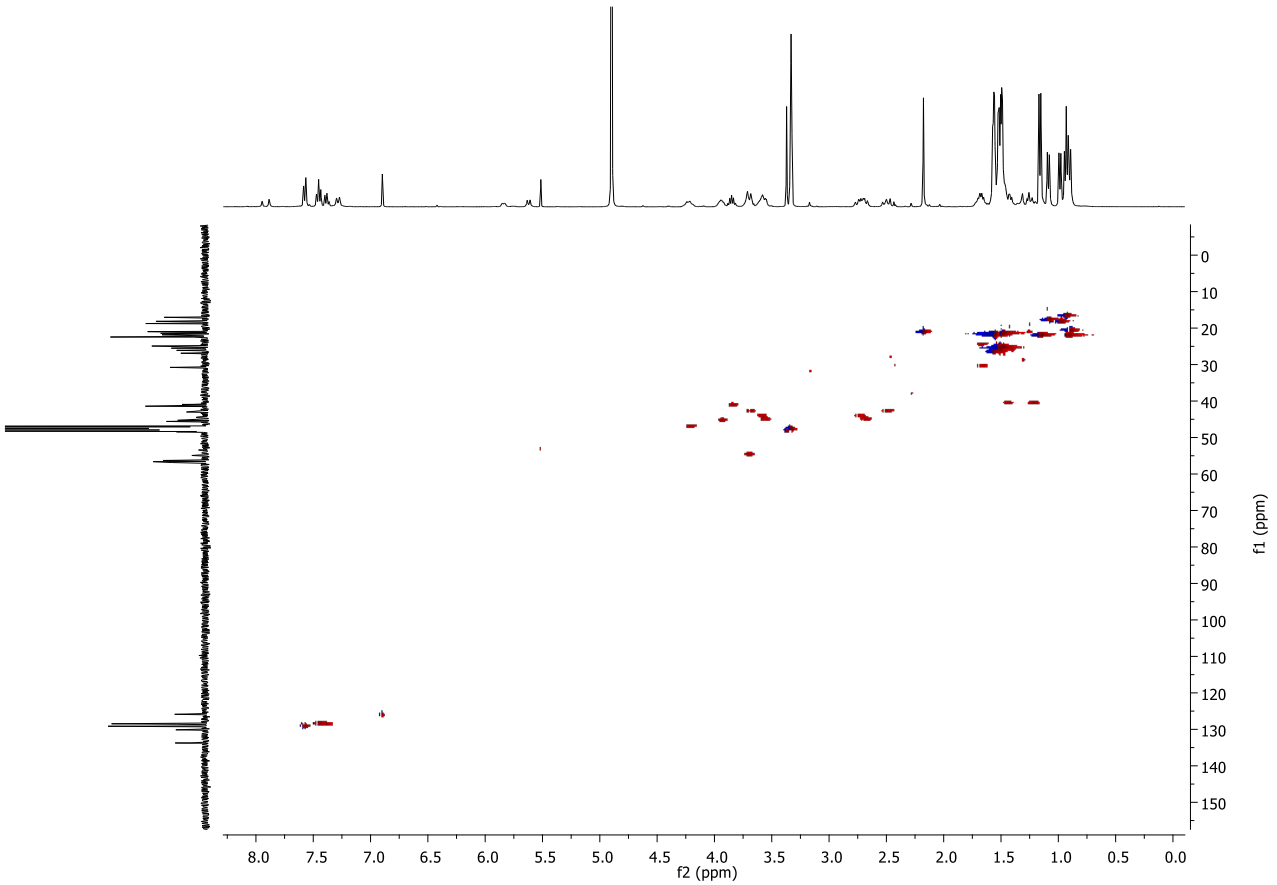
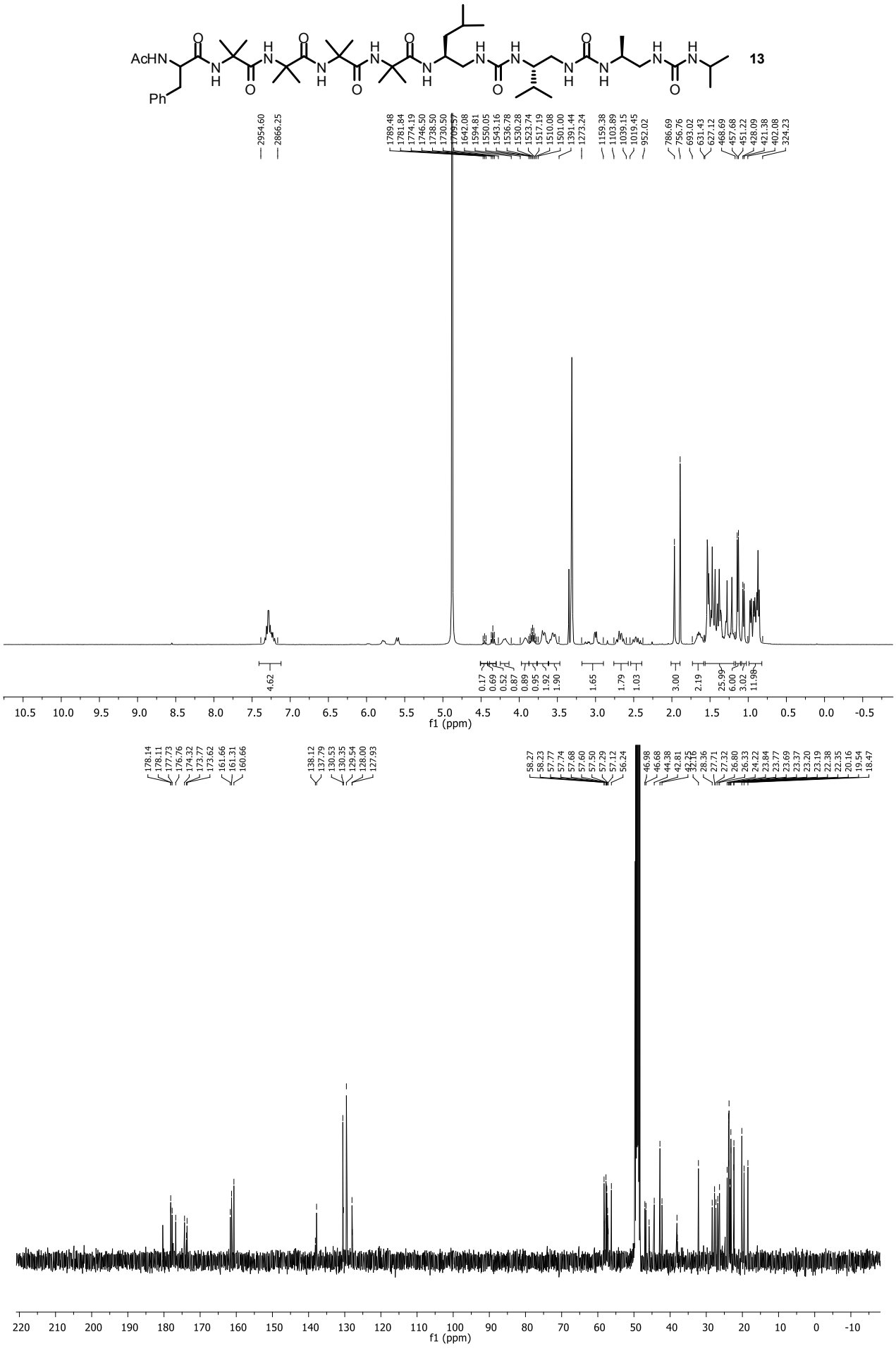
f1 (ppm)


f2 (ppm)
f1 (ppm)


AcHN
Ph
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1550.05
1543.16
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1501.00
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1273.24
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1103.89
1039.15
1019.45
952.02
786.69
756.76
693.02
631.43
627.12
468.69
457.68
451.22
428.09
421.38
402.08
324.23
4.62
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0.69
0.52
0.87
0.89
0.95
1.92
1.90
1.65
1.79
1.03
3.00
2.19
25.99
6.00
3.02
11.98
f1 (ppm)
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178.11
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173.62
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129.54
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57.60
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46.68
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42.81
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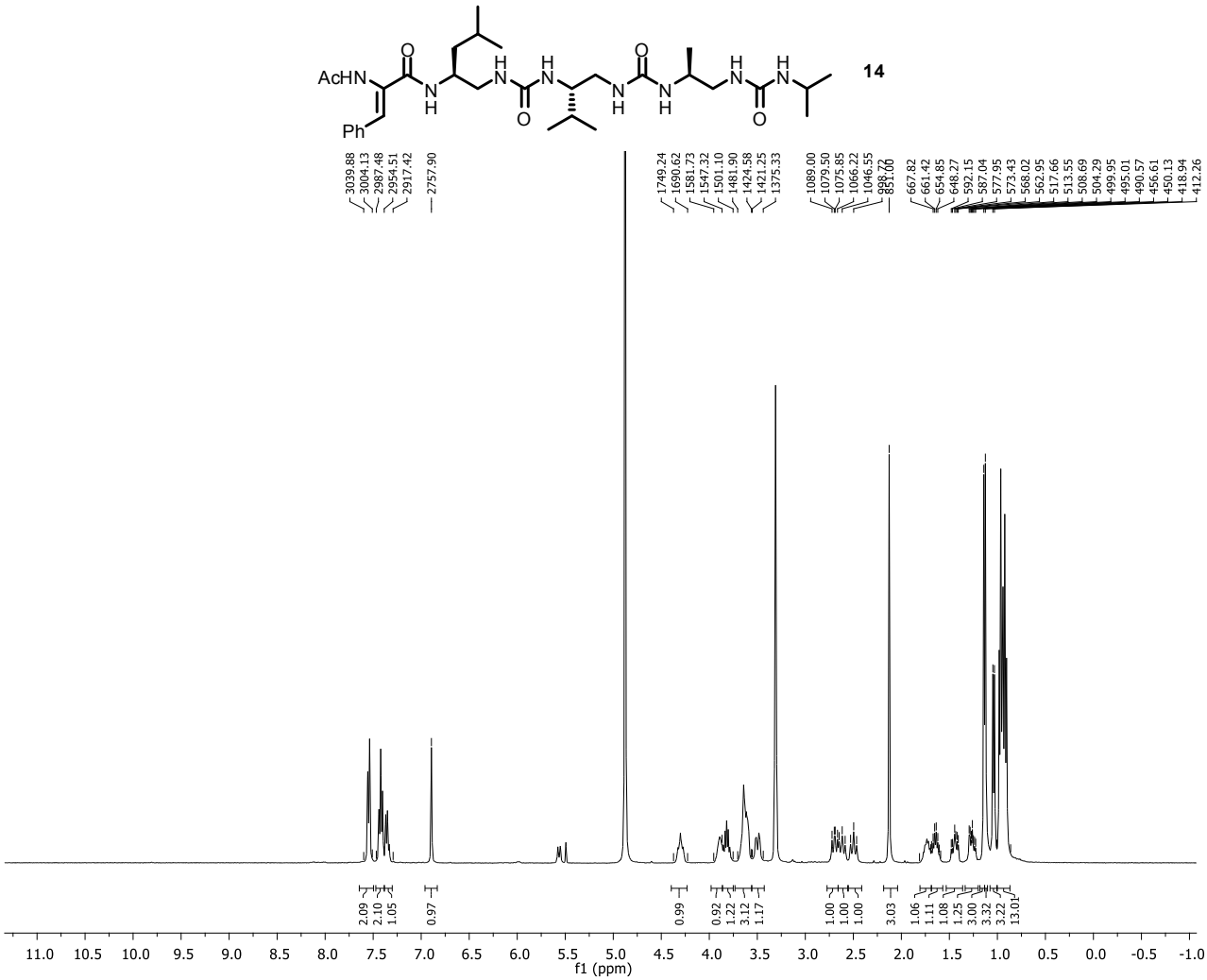
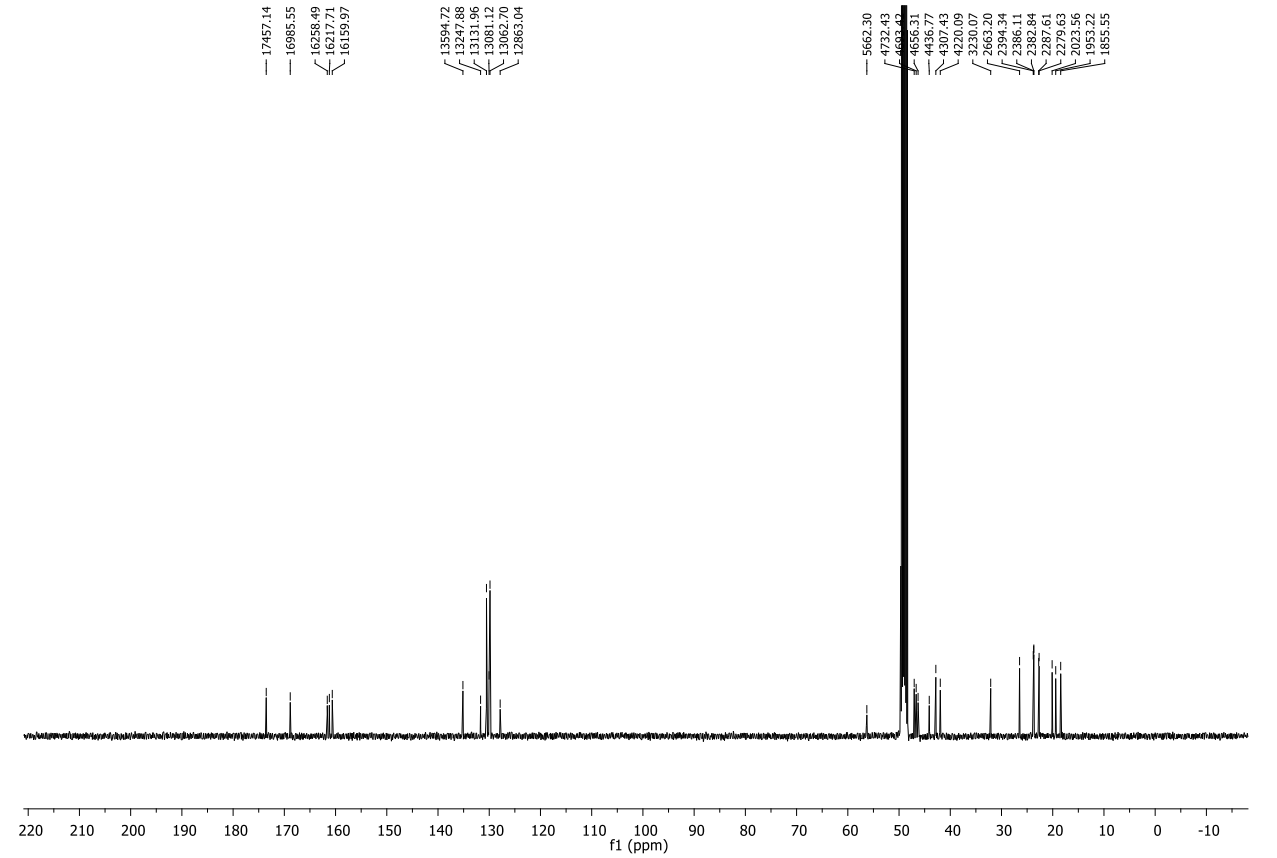
18.47
f1 (ppm)


AcHN
Ph
14
f1 (ppm)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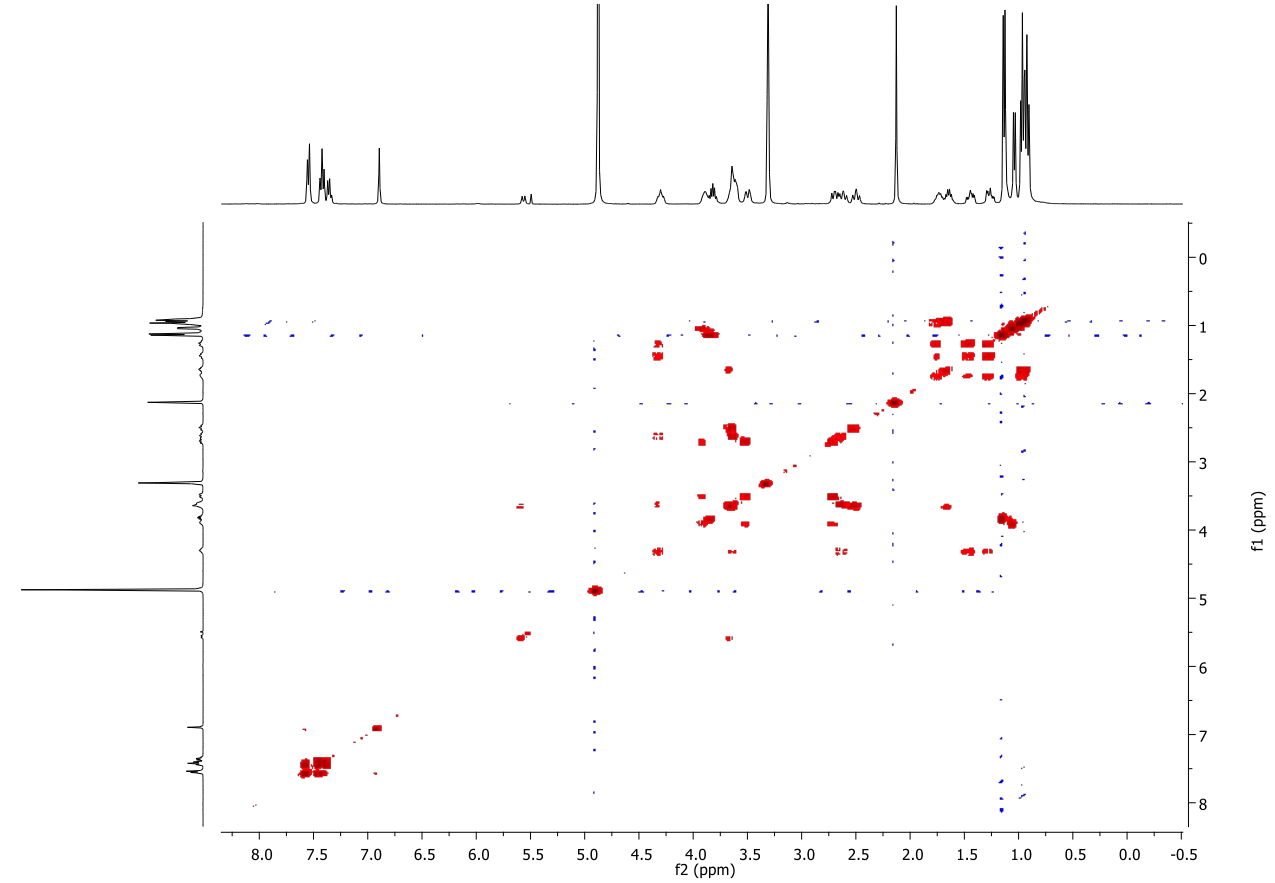
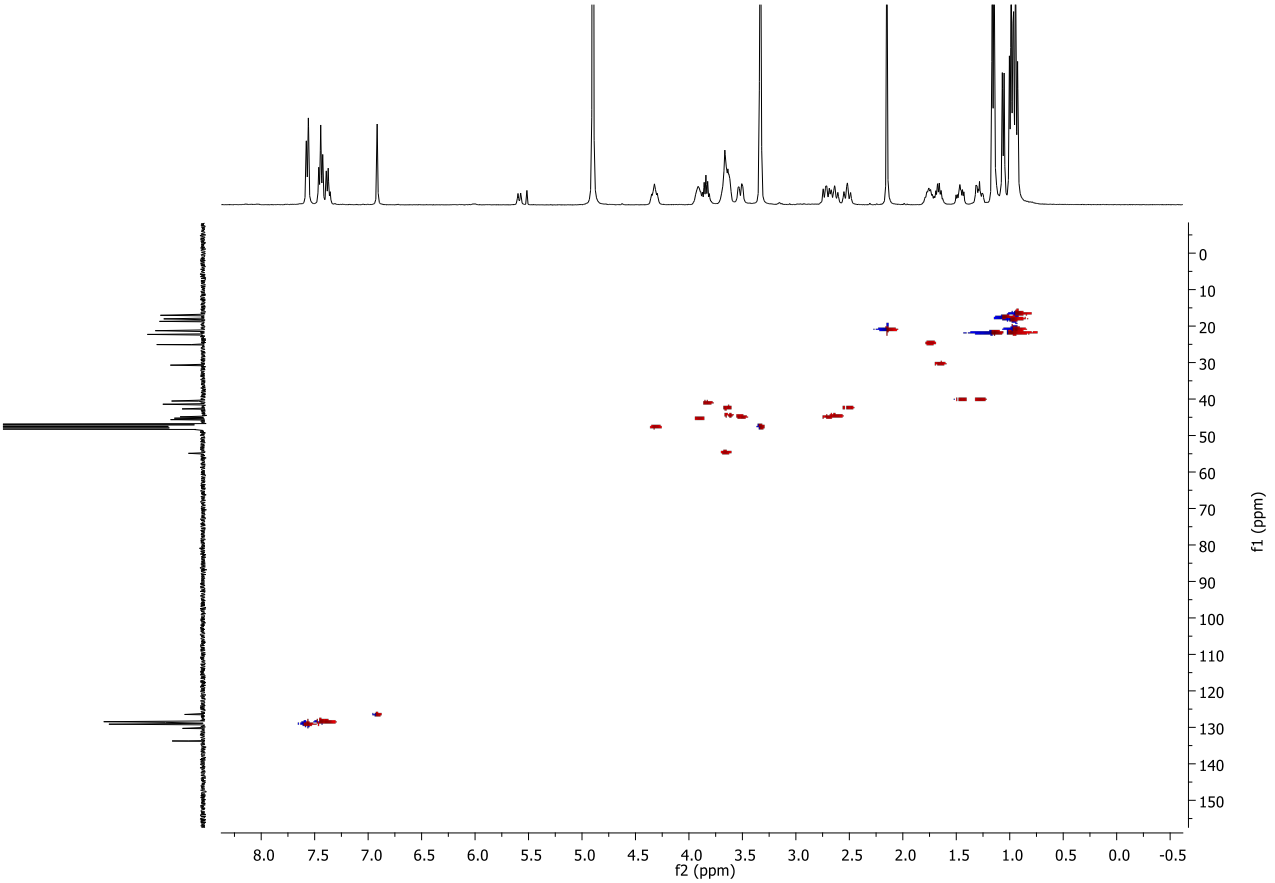

f2 (ppm)
f1 (ppm)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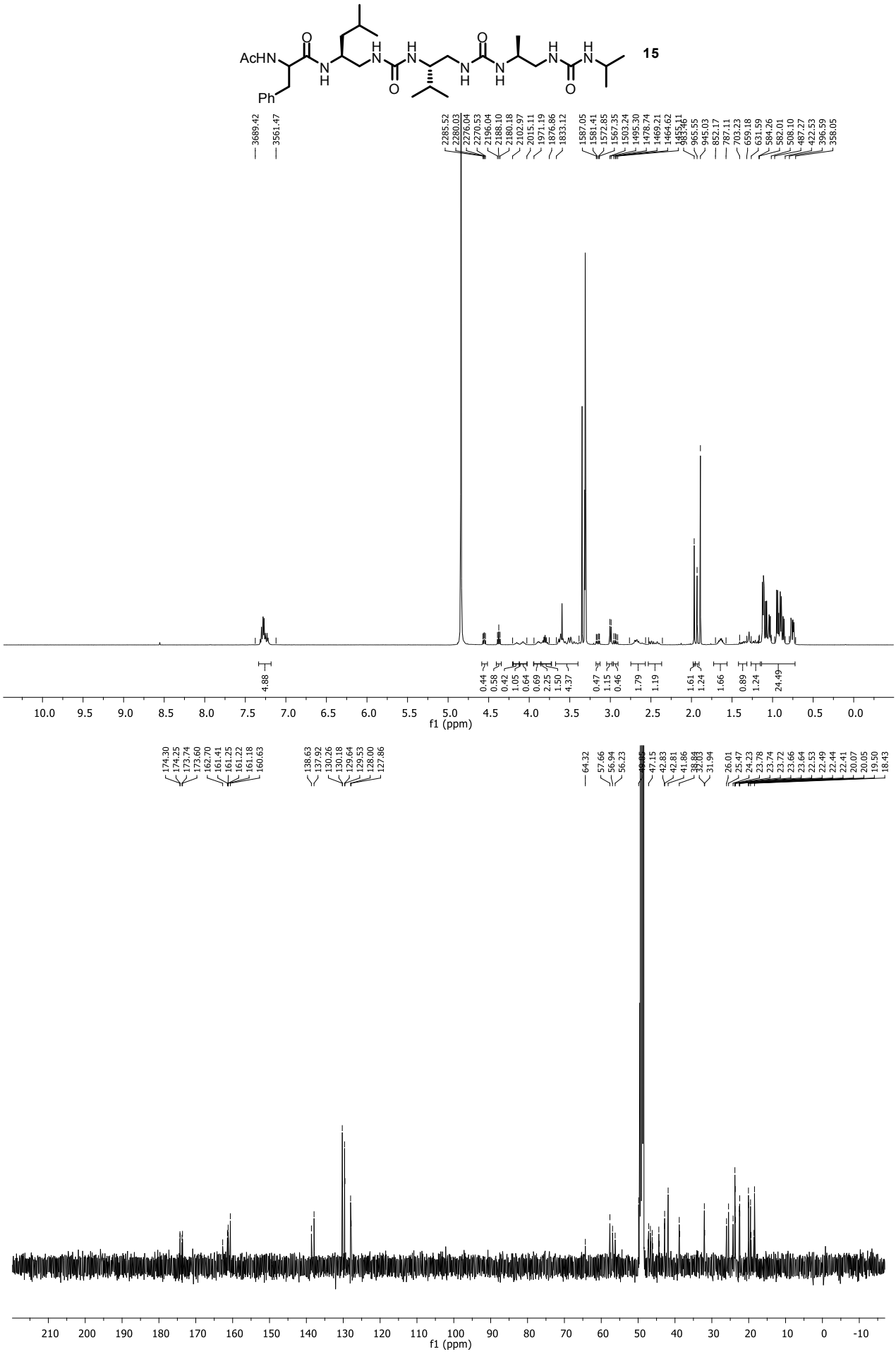
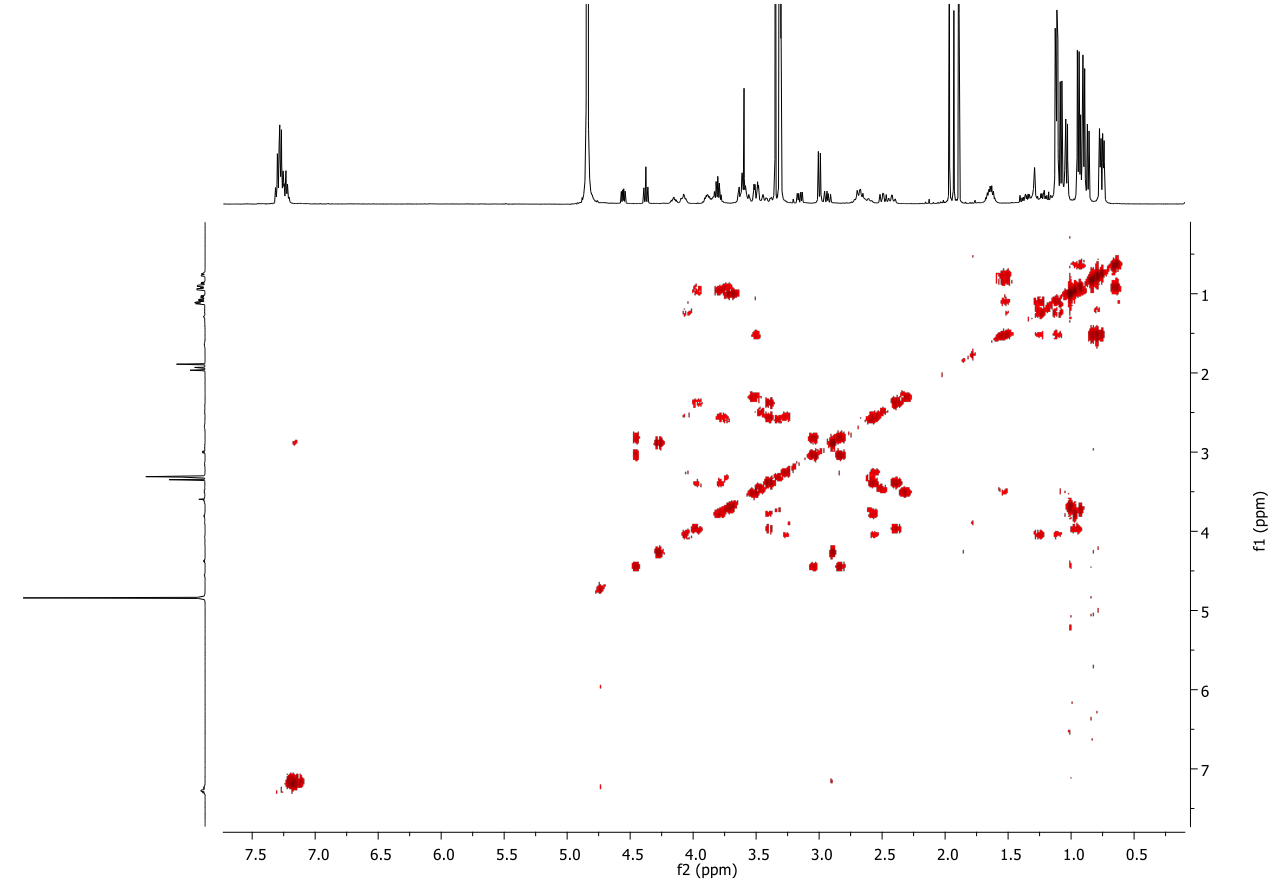
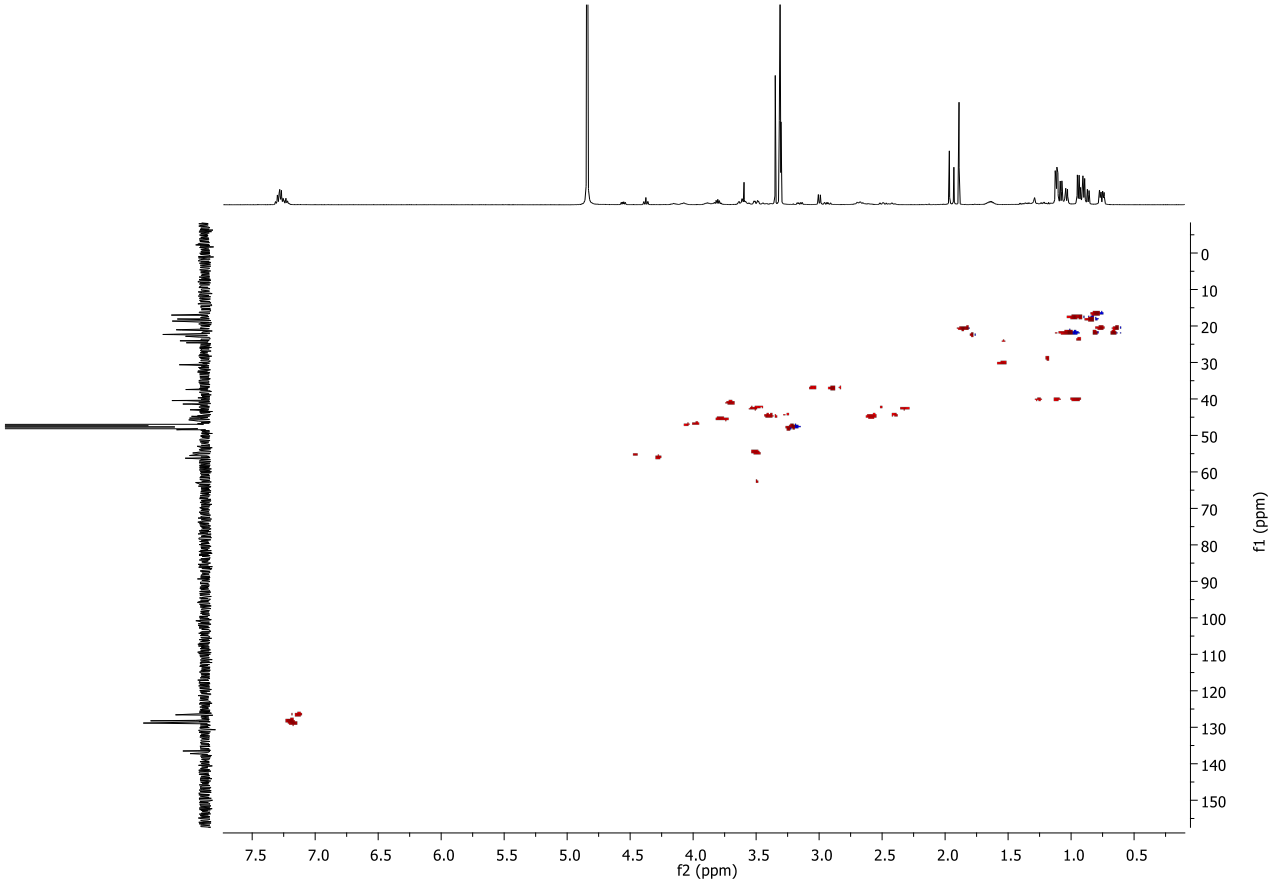
f1 (ppm)


15
AcHN
Ph
f1 (ppm)
f1 (ppm)


f1 (ppm)
f2 (ppm)


f1 (ppm)
f2 (ppm)