Self-assembling α,γ-cyclic peptides that generate cavities with tunable properties.

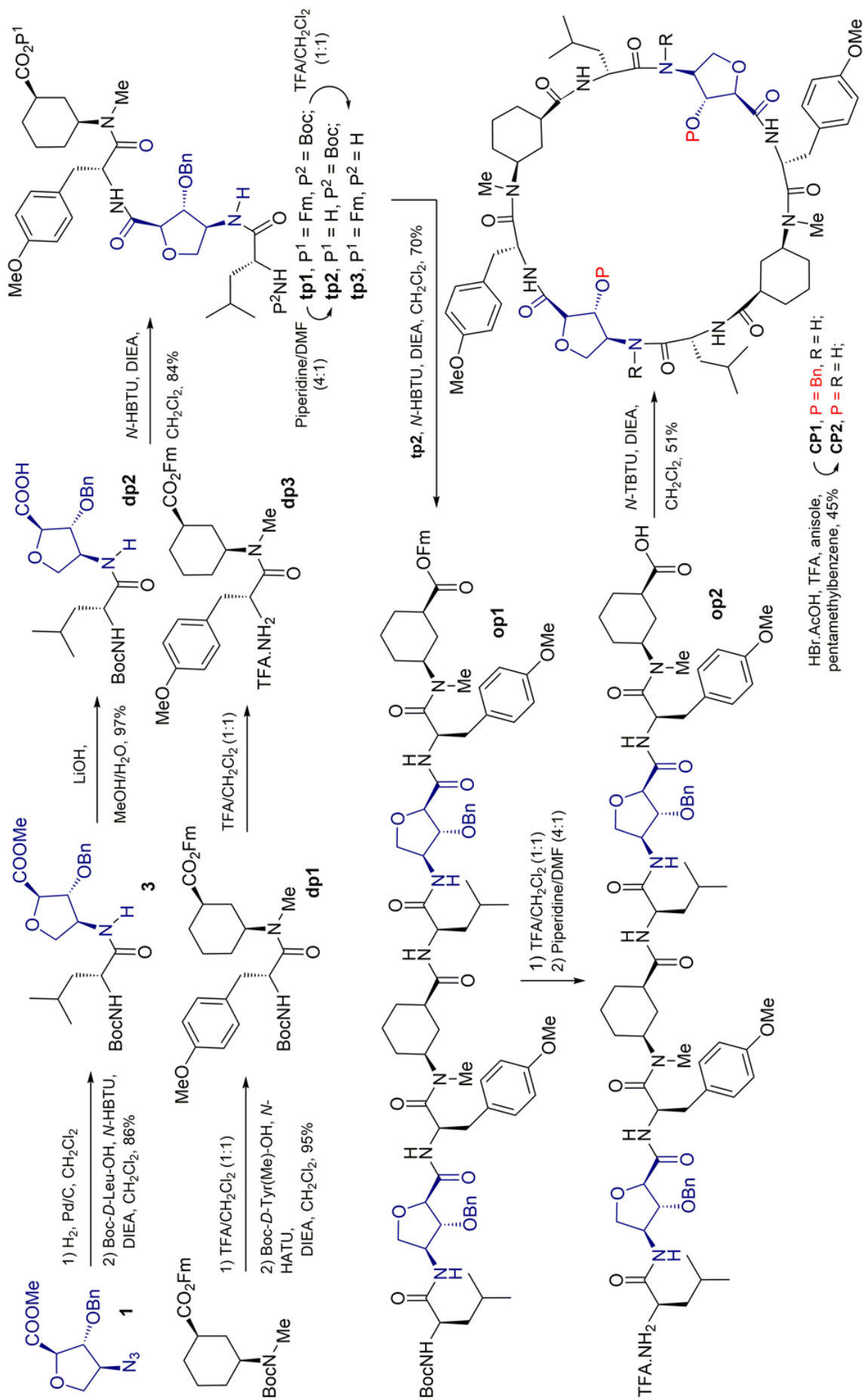**Nuria Rodríguez-Vázquez, Rebeca García-Fandiño, Manuel Amorín,* Juan R. Granja***

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SUPPORTING INFORMATION

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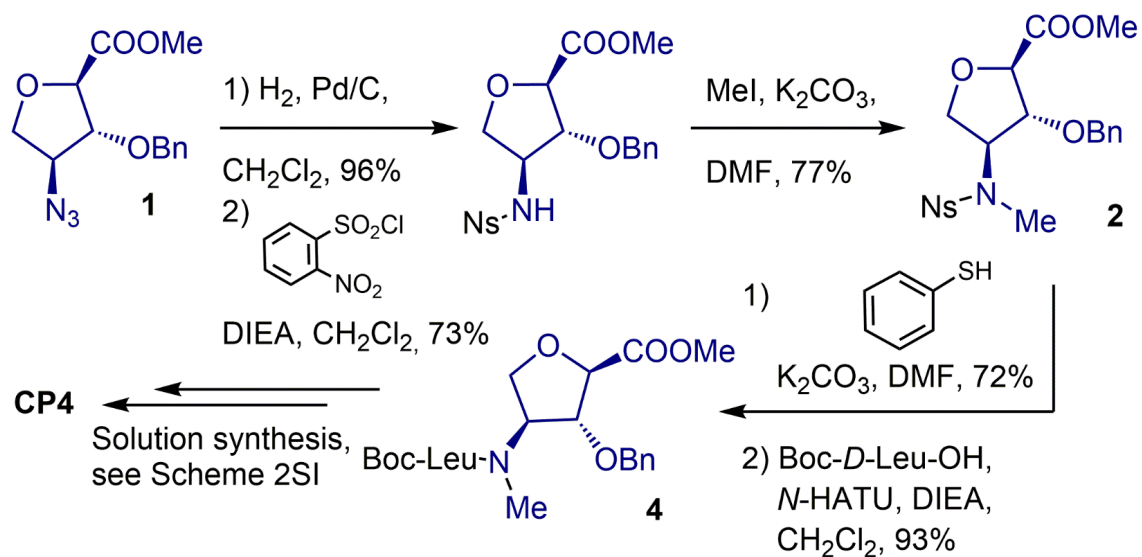
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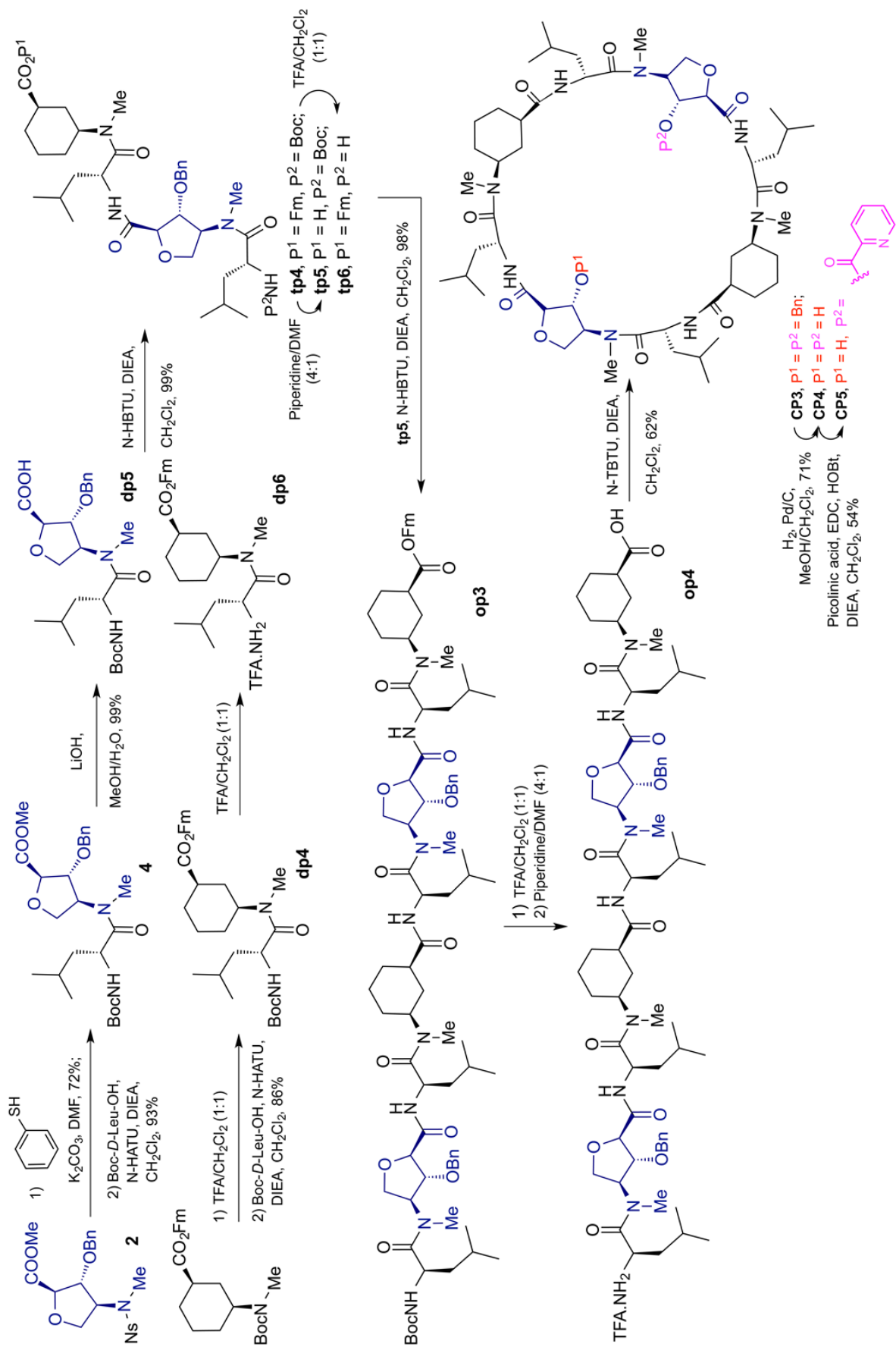
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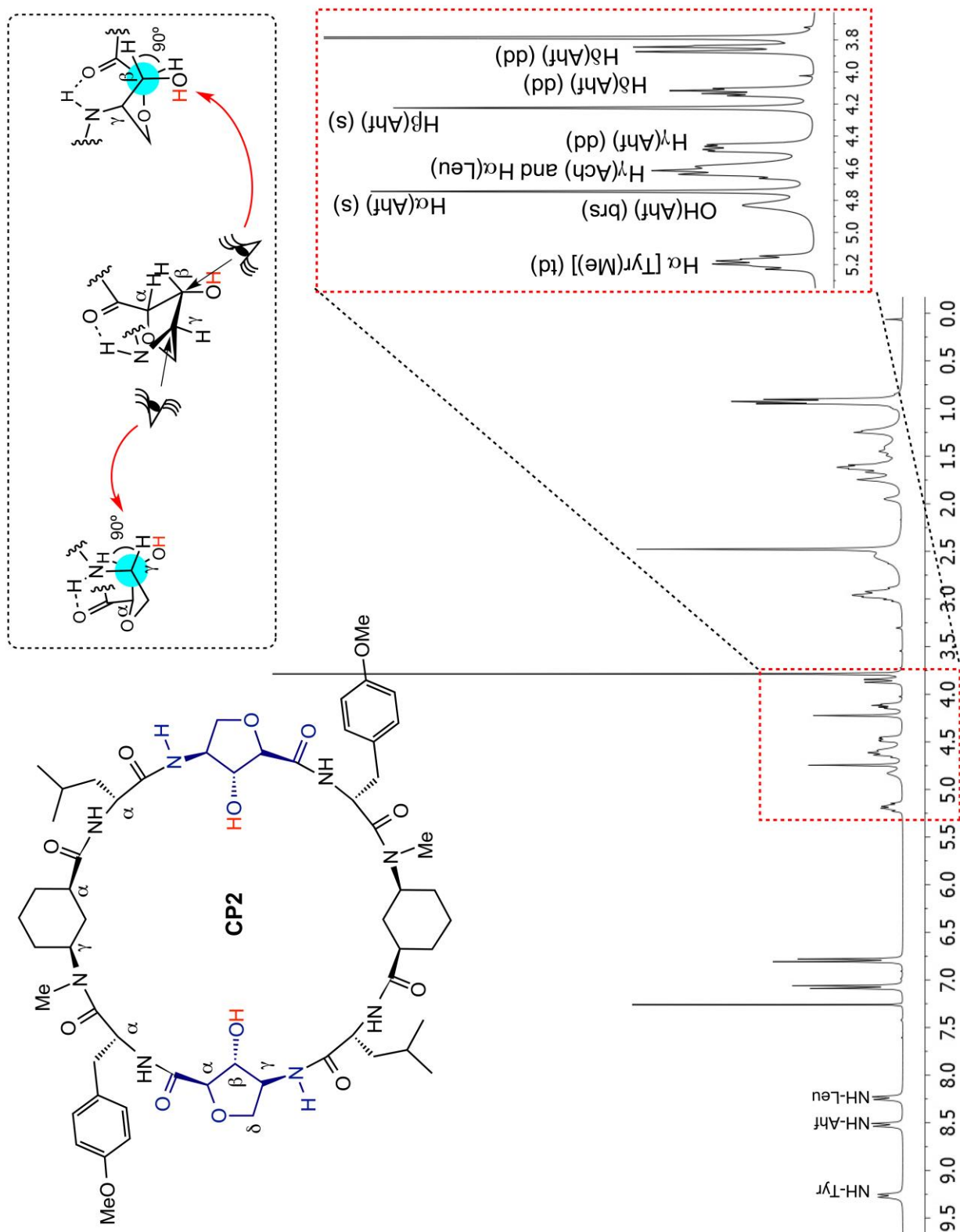
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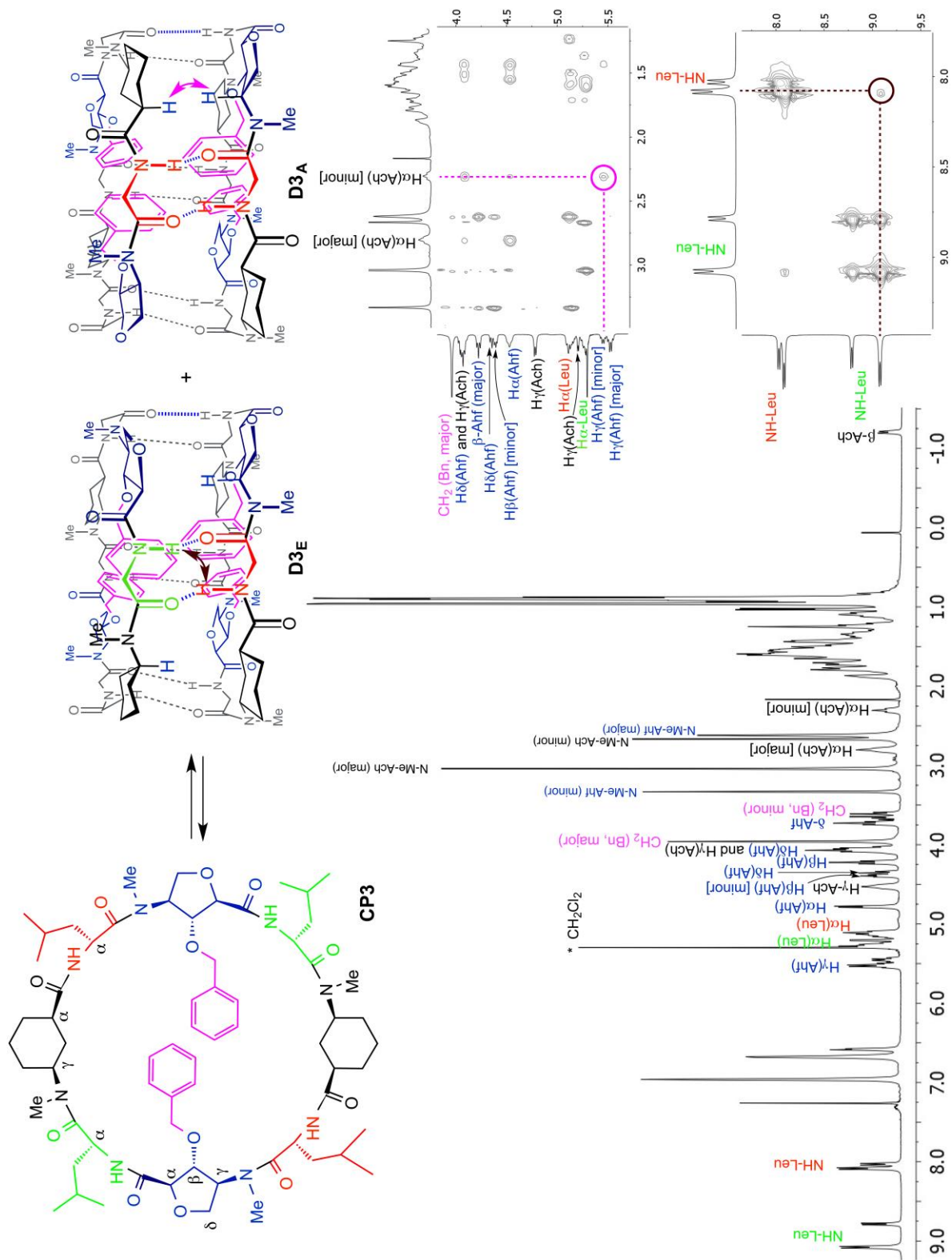
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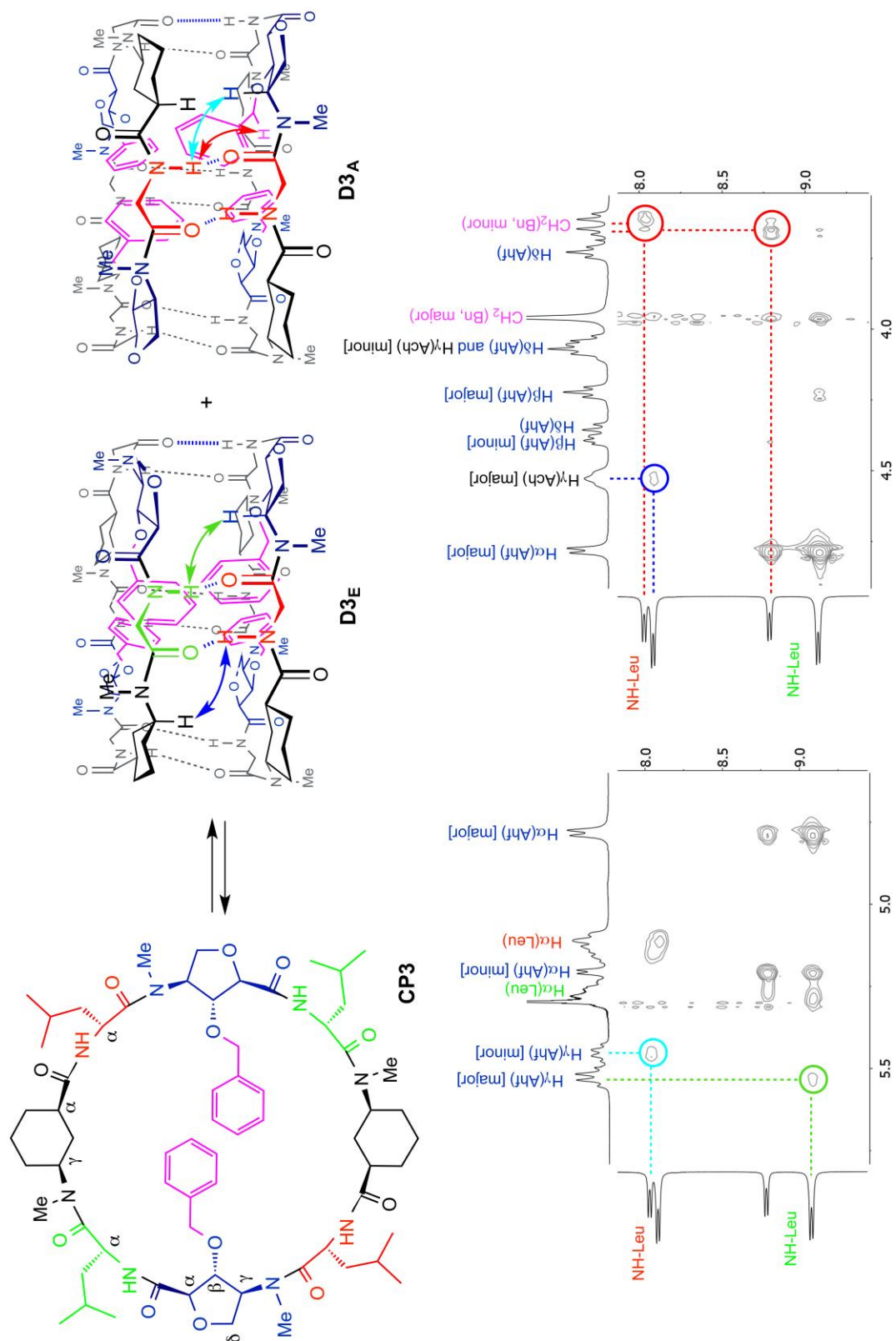
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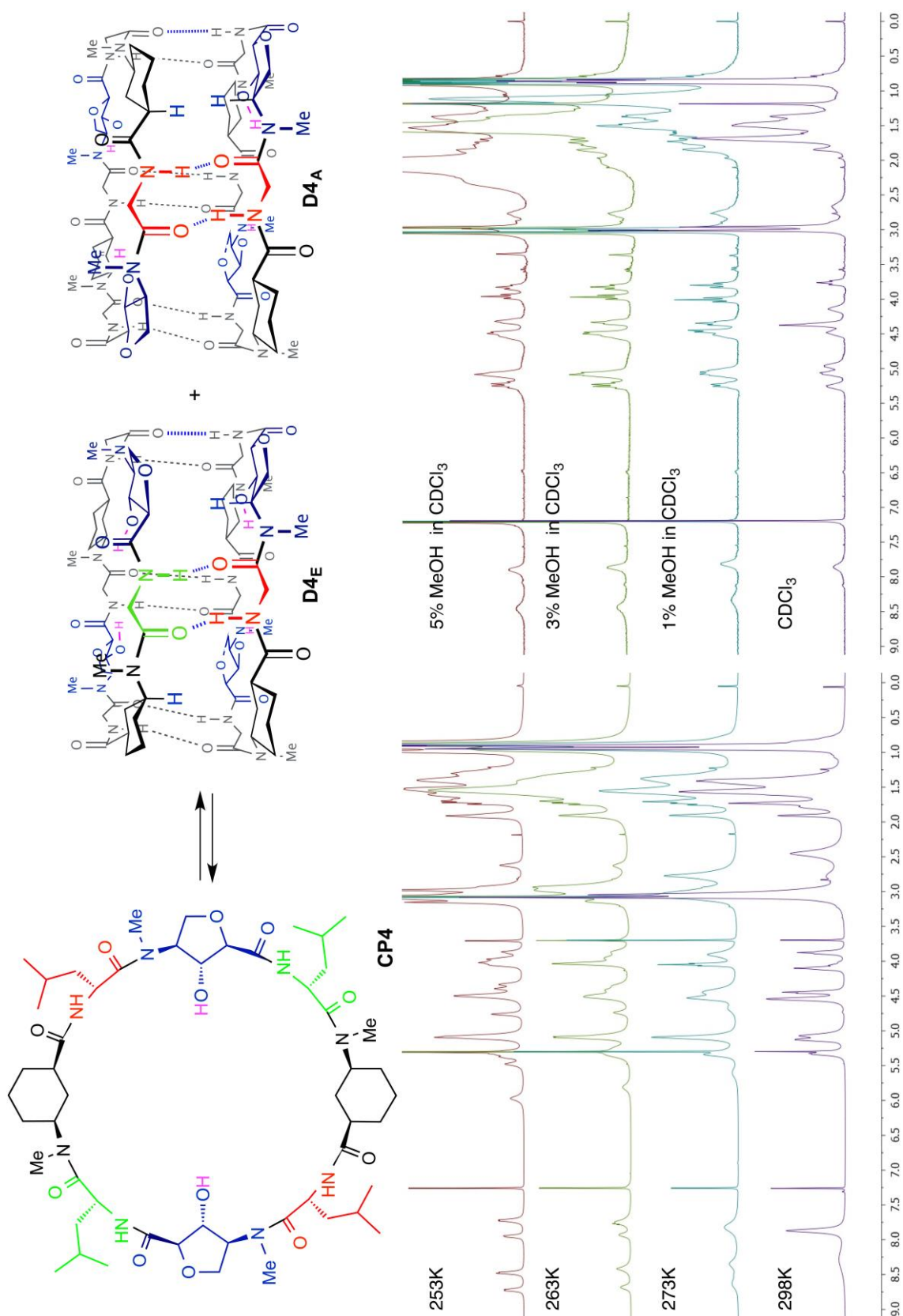
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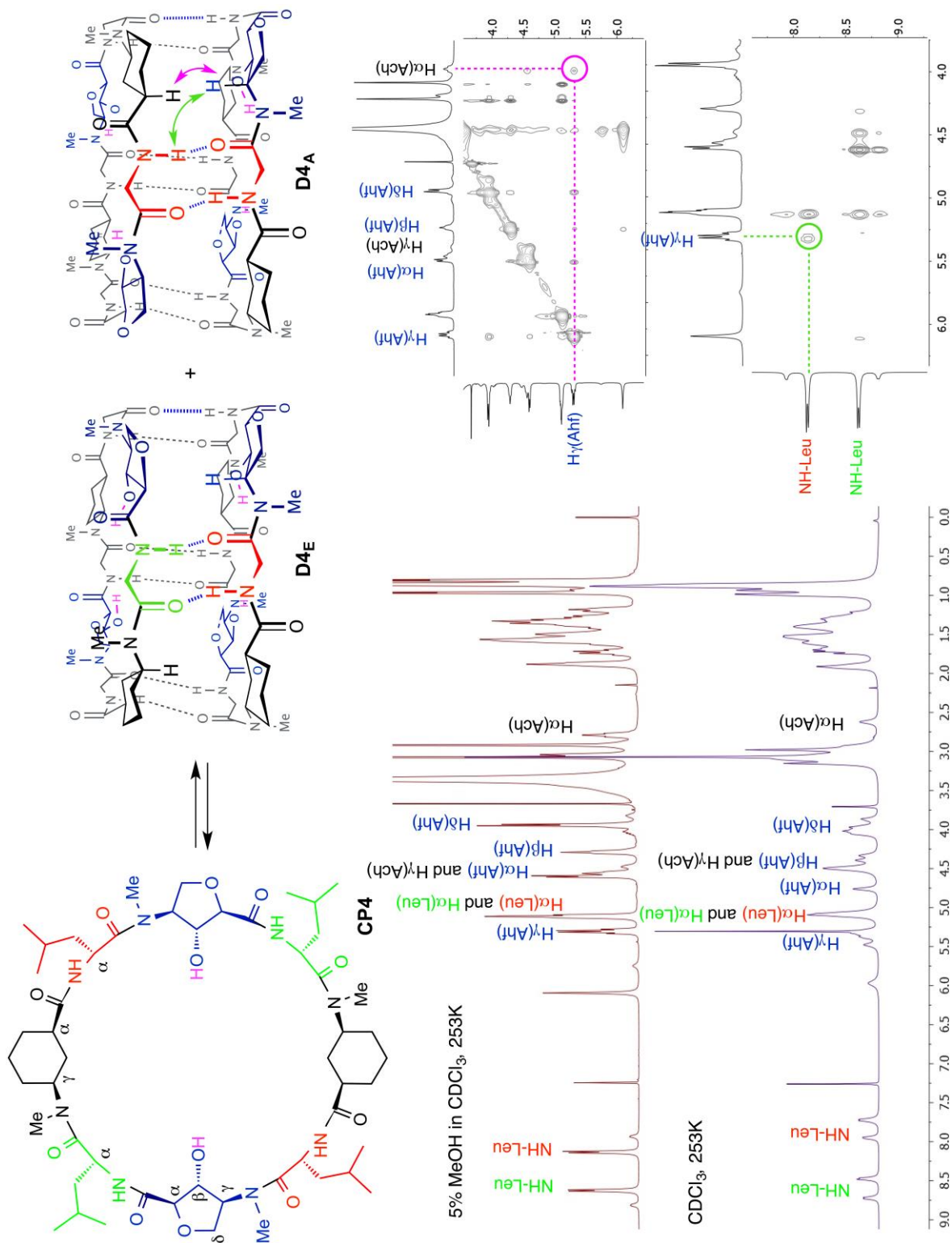
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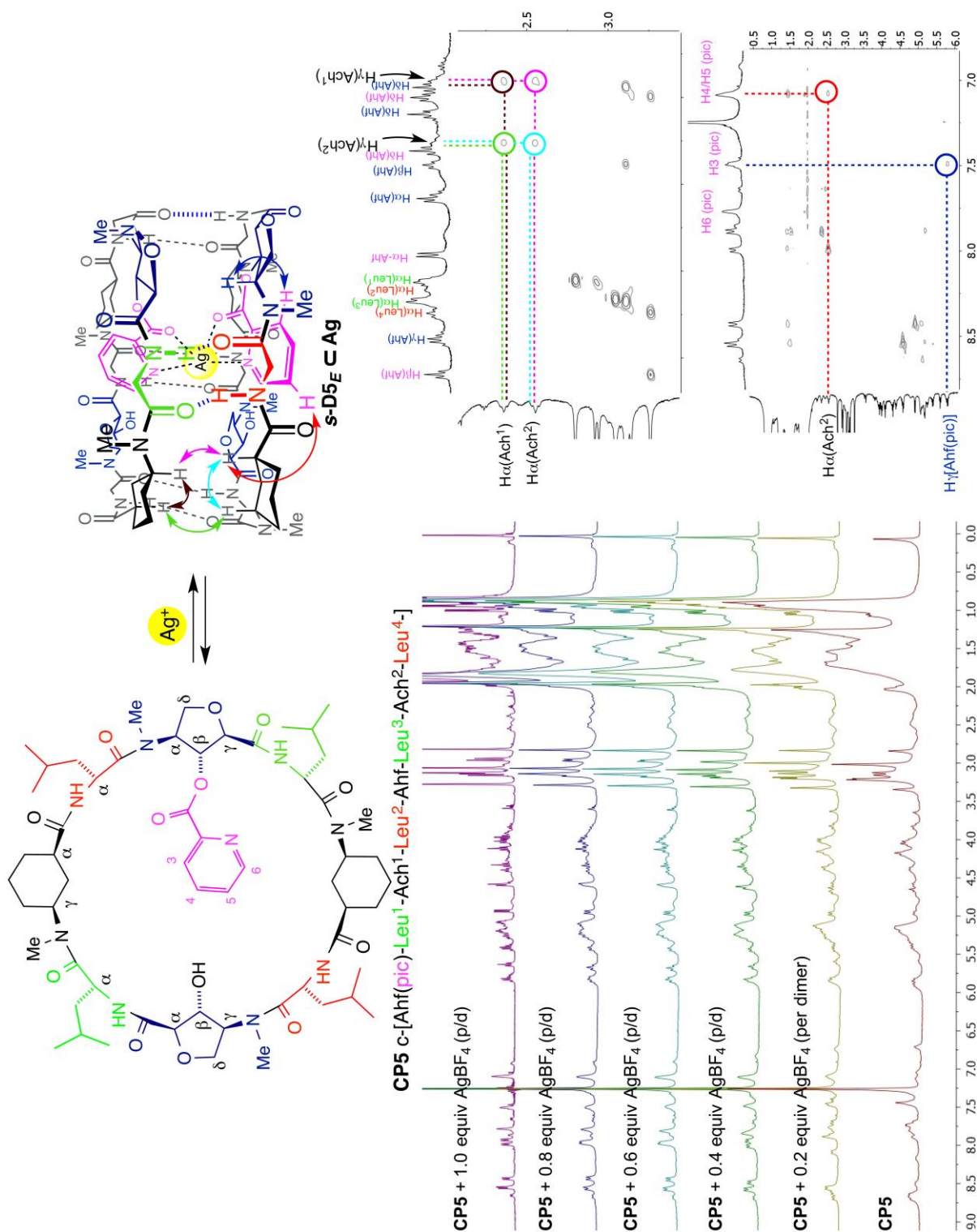
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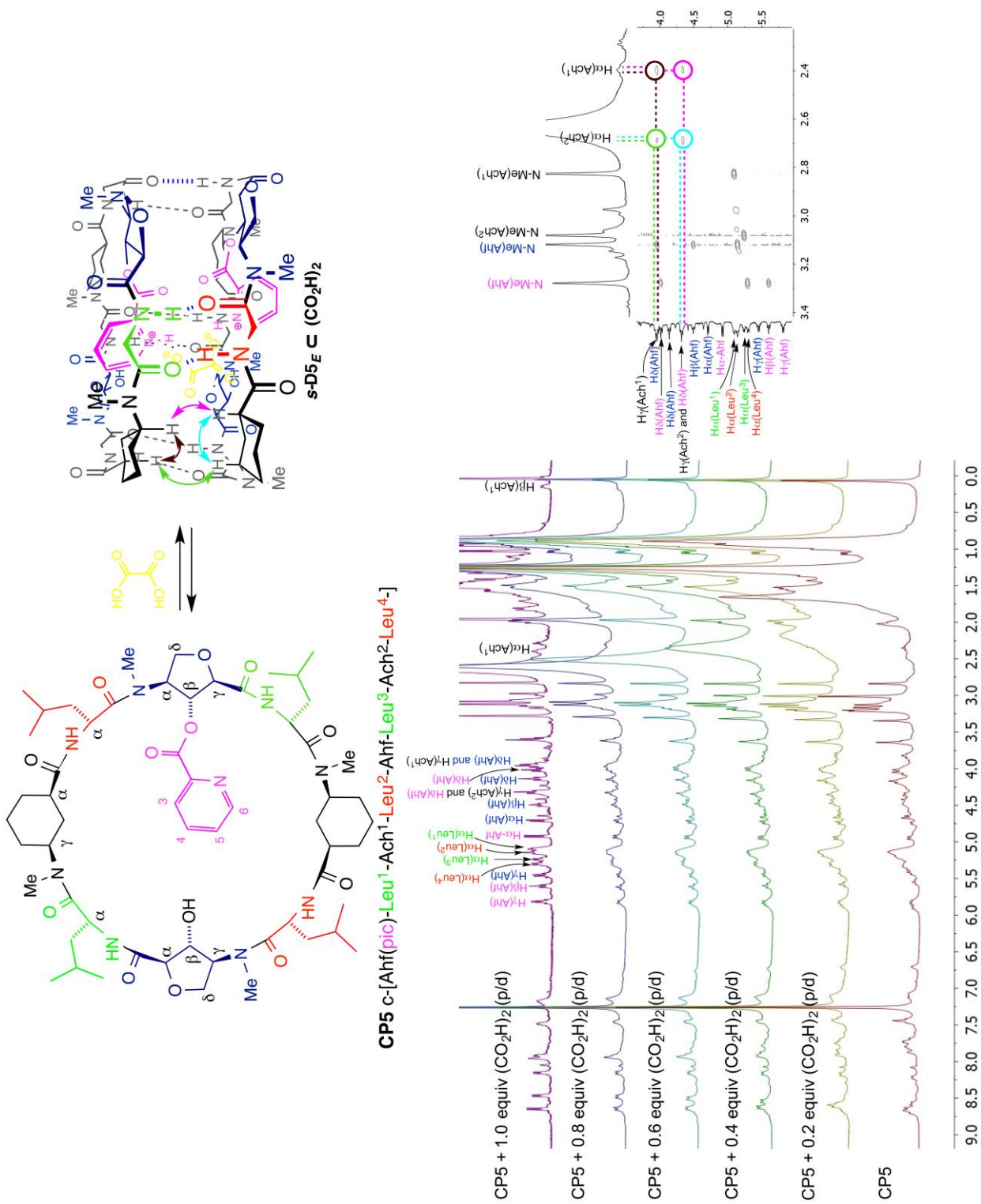
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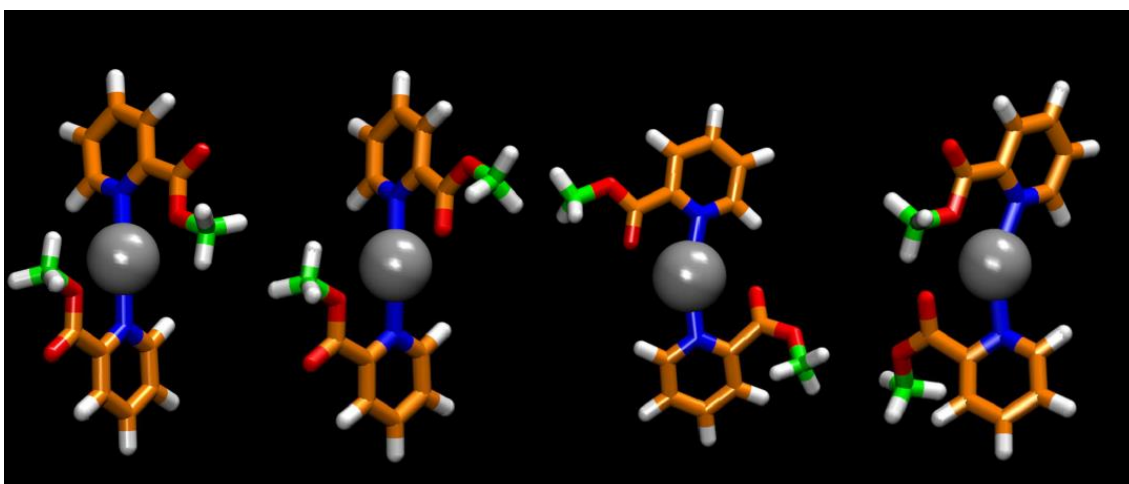
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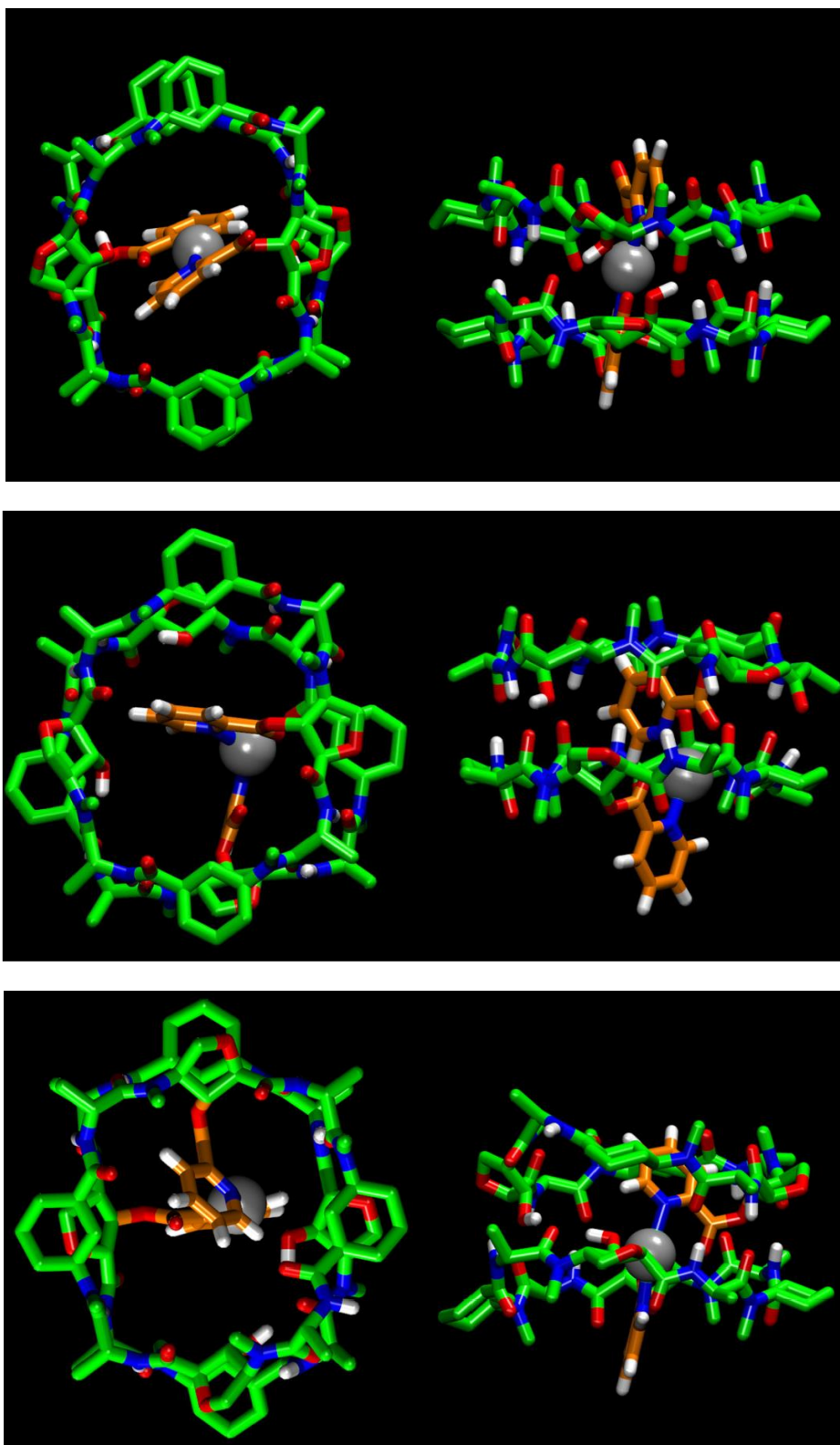
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Materials and Methods:

General:

1-[bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo-[4,5-*b*]pyridinium hexafluorophosphate 3-oxide (*N*-HATU), 1-[bis(dimethylamino)methylene]-1*H*-benzotriazolium hexafluorophosphate 3-oxide (*N*-HBTU), 1-[bis(dimethylamino)methylene]-1*H*-benzotriazolium tetrafluoroborate 3-oxide (*N*-TBTU),[1] *N*-(3-dimethylaminopropyl)-*N*´-ethylcarbodiimide hydrochloride (EDC), 1-hydroxybenzotriazole (HOBt), 4-dimethylaminopyridine (DMAP) and α-aminoacids were purchased from Iris Biotech, Aldrich or from Globel Sales Manager, GL Biochem (Shanghai) Ltd, China. All reagents and solvents were used as received unless otherwise noted. CH_2Cl_2 and DIEA to be used as reaction solvents were distilled from CaH_2 over argon immediately prior to use. Analytical thin-layer chromatography was performed on E. Merck silica gel 60 F_{254} plates. Compounds, which were not UV active, were visualized by dipping the plates in a nynhidrin solution and heating. Silica gel flash chromatography was performed using E. Merck silica gel (type 60SDS, 230-400 mesh). Solvent mixtures for chromatography are reported as v/v ratios. HPLC purification was carried out on a HITACHI D-7000 using a Phenomenex Luna 5µ Silica 100 Angstroms column with CH_2Cl_2/MeOH gradients between 96:4 and 87:13. **^{1}H NMR** spectra were recorded on Varian Inova 500 MHz, Varian Mercury 300 MHz or Bruker DPX 250 MHz spectrometers. Chemical shifts (δ) were reported in parts per million (ppm) relative to tetramethylsilane (δ = 0.00 ppm) or by the deuterated solvent. ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), or quartet (q). All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). **^{13}C NMR** spectra were recorded on Varian Mercury 300 MHz spectrometer. Carbon resonances were assigned using distortionless enhancement by polarization transfer (DEPT) spectra obtained with phase angles of 135. **^{1}H NMR Assignments of Cyclic Peptides (CPs).** The signals of the ^{1}H NMR spectra of the peptides were identified from the corresponding double-quantum-filled 2D COSY, TOCSY and NOESY and/or ROESY spectra acquired at concentration and temperature indicated (Mixing times for NOESY and/or ROESY –between 250 and 1000 ms- were not optimized). Electrospray (ESI) mass spectra were recorded on a Bruker BIOTOF II mass spectrometer. FTIR measurements were made on a JASCO FT/IR-400 spectrophotometer placing the sample on a CaF_2 pellet.

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[1] L. A. Carpino, et all., *Angew. Chem. Int. Ed.* **2002**, *41*, 41−445.

Peptide synthesis:
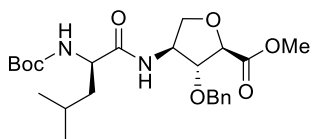
Boc-*D*-Leu-*L*-Ahf(Bn)-OMe (3): A solution of N$_3$-*L*-Ahf(Bn)-OMe[2] (271 mg, 0.97 mmol) and Pd/C (208 mg, 10% in wt) in CH$_2$Cl$_2$ (10 mL) was stirred at rt for 2 h under hydrogen atmosphere (balloon pressure). The resulting mixture was filtered through a Celite pad, the residue was washed with CH$_2$Cl$_2$, and the combined filtrates and washes were concentrated under reduced pressure. The crude was used without further purification. A solution of the resulting NH$_2$-*L*-Ahf(Bn)-OMe in CH$_2$Cl$_2$ (15 mL) was successively treated with DIEA (0.71 mL, 3.9 mmol), Boc-*D*-Leu-OH (225 mg, 1.0 mmol), and *N*-HBTU (405.0 mg, 1.1 mmol), and the mixture was stirred at rt under Argon for 90 min. The solution was washed with aqueous HCl (5%, 3 x 20 mL) and aqueous saturated NaHCO$_3$ (2 x 20 mL). The organic layer was dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The resulting crude was purified by flash chromatography (0-2% MeOH/CH$_2$Cl$_2$) to give 387 mg of dipeptide **3**. [Yellow foam, 86%, R$_f$ = 0.58 (5% MeOH/CH$_2$Cl$_2$)]. **^{1}H NMR** (CDCl$_3$, 250 MHz, δ): 7.51-7.24 (m, 6H), 6.63 (d, *J* = 8.1 Hz, 1H), 4.77 (AB, *J* = 11.8 Hz, 1H), 4.83-4.49 (m, 2H), 4.66 (AB, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 1.6 Hz, 1H), 4.24-3.91 (m, 3H), 3.77 (s, 3H), 1.86-1.51 (m, 3H), 1.43 (s, 9H), 0.93 (d, *J* = 5.7 Hz, 6H). **^{13}C NMR** (CDCl$_3$, 75.4 MHz, δ): 172.8 (CO), 171.7 (CO), 155.4 (CO), 137.3 (C), 128.3 (CH), 127.8 (CH), 127.7 (CH), 86.6 (CH), 82.1 (CH), 79.8 (C), 72.5 (CH$_2$), 71.8 (CH$_2$), 54.7 (CH$_3$), 53.4 (CH), 52.4 (CH), 41.4 (CH$_2$), 28.2 (CH$_3$), 24.7 (CH$_3$), 24.6 (CH$_3$), 23.0 (CH). **MS (ESI)** [m/z(%)]: 487 ([MNa]$^+$), 465 ([MH]$^+$). **HRMS (ESI) calculated** for C$_{24}$H$_{37}$N$_2$O$_7$: 465.2595, **found**: 465.2595.
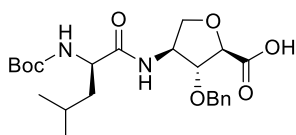
Boc-*D*-Leu-*L*-Ahf(Bn)-OH (dp2): A solution of dipeptide **3** (387 mg, 0.83 mmol) in a mixture of MeOH and water (3:1, 20 mL) was treated with LiOH (100 mg, 4.2 mmol). The solution was stirred at rt for 5 h and then the solvent was removed under reduced pressure. The resulting residue was diluted with water (10 mL) and washed with Et$_2$O (10 mL), and the resulting aqueous solution was acidified to pH 3 with aqueous HCl (5%). The acidic solution was extracted with CH$_2$Cl$_2$ (4 x 10 mL), the combined organic extracts were dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure to give 365 mg of dipeptide **dp2**. [Yellow foam, 97%, R$_f$ = 0.20 (5% MeOH/CH$_2$Cl$_2$)]. **^{1}H RMN** (CDCl$_3$, 300 MHz, δ): 10.1 (br, 1H), 7.56 (d, *J* = 6.8 Hz, 1H), 7.49-7.14 (m, 5H), 6.42 (d, *J* = 7.0 Hz, 1H), 5.35 (d, *J* = 8.4 Hz, 1H), 4.78 (AB, *J* = 11.9 Hz, 1H), 4.69 (AB, *J* = 11.6 Hz, 1H), 4.57-3.91 (m, 5H), 1.74-1.39 (m, 3H), 1.41 and 1.37 (s, 9H), 0.91 (d, *J* = 6.3 Hz,

[2] N. Rodríguez-Vázquez, S. Salzinger, L. F. Silva, M. Amorín, J. R. Granja, *Eur. J. Org. Chem.* **2013**, *17*, 3477–3493.

3H), 0.89 (d, J = 6.3 Hz, 3H). **^{13}C RMN** (CDCl$_3$, 75.4 MHz, δ): 173.7 (CO), 172.6 (CO), 156.5 (CO), 137.4 (C), 128.4 (CH), 127.8 (CH), 127.6 (CH), 87.1 (CH), 82.0 (CH), 81.8 (C), 72.6 (CH$_2$), 71.8 (CH$_2$), 54.9 (CH), 53.5 (CH), 41.2 (CH$_2$), 28.2 (CH$_3$), 24.7 (CH$_3$), 23.0 (CH$_3$), 21.9 (CH). **MS (ESI)** [m/z(%)]: 473 ([MNa]$^+$), 452 ([MH]$^+$). **HRMS (ESI) calculated** for C$_{23}$H$_{35}$N$_2$O$_7$: 452.2425, **found**: 452.2439.
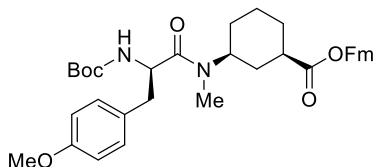
Boc-*D*-Tyr(Me)-*L*-^{Me}*N*-Ach-OFm (dp1): A solution of Boc-*L*-^{Me}*N*-Ach-OFm (811 mg, 1.86 mmol) in mixture of TFA and CH$_2$Cl$_2$ (1:1, 10 mL) was stirred at rt for 10 min. After removal of the solvent under vacuum, the residue was dried under high vacuum for 3 h. The resulting TFA salt was dissolved under Argon in CH$_2$Cl$_2$ (10 mL), then DIEA (1.3 mL, 7.5 mmol), Boc-*D*-Tyr(Me)-OH (550 mg, 1.9 mmol) and *N*-HATU (778 mg, 2.0 mmol) were successively added. After 1 h stirring at rt, the solution was washed with aqueous HCl (5%, 2 x 10 mL) and aqueous saturated NaHCO$_3$ (2 x 10 mL). The organic layer was dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure, providing a yellow oil that was purified by flash chromatography (0-2% MeOH/CH$_2$Cl$_2$) to give 1.0 g of dipeptide **dp1**. [White foam, 95%, R$_f$ = 0.75 (5% MeOH/CH$_2$Cl$_2$)]. **^{1}H NMR** (CDCl$_3$, 300 MHz, δ): 7.71 (m, 2H), 7.61 (d, , J = 7.4 Hz, 1H), 7.54 (m, 2H), 7.43-7.20 (m, 4H), 7.08 (m, 2H), 6.76 (m, 2H), 5.51 (m, 1H), 4.73 (m, 1H), 4.46-4.32 (m, 2H), 4.22-4.04 (m, 1H), 4.14 (AB, J = 6.6 Hz, 1H), 3.95 (AB, J = 6.6 Hz, 1H), 3.73 and 3.60 (s, 3H), 2.89 (m, 1H), 2.70 and 2.46 (s, 3H), 1.96-0.71 (m, 8H), 1.42 and 1.40 (s, 9H). **^{13}C NMR** (CDCl$_3$, 75.4 MHz, δ): 174.6 (CO), 171.3 (CO), 158.5 (C), 155.0 (CO), 144.7 (C), 130.4 (CH), 128.4 (C), 127.7 (CH), 127.0 (CH), 124.8 (CH), 119.9 (CH), 113.7 (CH), 79.5 (C), 65.9 (CH$_2$), 55.1 (CH), 51.5 (CH), 50.3 (CH$_3$), 46.9 (CH), 42.2 (CH), 39.3 (CH$_2$), 38.4 (CH$_3$), 31.3 (CH$_2$), 29.7 (CH$_2$), 28.2 (CH$_3$), 24.2 (CH$_2$). **MS (ESI)** [m/z(%)]: 635.3 ([MNa]$^+$, 62), 613.3 ([MH]$^+$, 38), 557.3 ([MH-^{t}Bu]$^+$, 97), 513.3 ([MH-Boc]$^+$, 100). **HRMS (ESI) calculated** for C$_{37}$H$_{45}$N$_2$O$_6$: 613.3272, **found**: 613.3273.
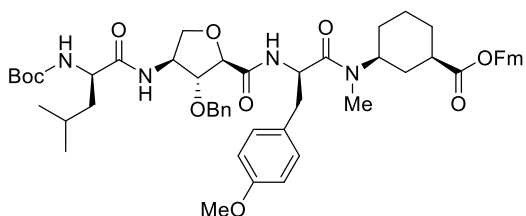
Boc-*D*-Leu-*L*-Ahf(Bn)-*D*-Tyr(Me)-*L*-^{Me}*N*-Ach-OFm (tp1): A solution of dipeptide **dp1** (497.0 mg, 0.81 mmol) in mixture of TFA and CH$_2$Cl$_2$ (1:1, 10.0 mL) was stirred at rt for 30 min. After removal of the solvent under vacuum, the residue was dried under high vacuum for 3 h. The resulting TFA salt (**dp3**) was dissolved under Argon in dry CH$_2$Cl$_2$ (14 mL), then DIEA (560 µL, 3.2 mmol), dipeptide **dp2** (365 mg, 0.81 mmol), and *N*-HBTU (338 mg, 0.89 mmol) were successively added. After 2 h stirring at rt, the solution was washed with aqueous HCl (5%, 2 x 15 mL) and aqueous saturated NaHCO$_3$ (2 x 15 mL). The organic layer was dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The resulting

crude was purified by flash chromatography (0-2% MeOH/CH$_2$Cl$_2$) to give 645 mg of tetrapeptide **tp1**. [White foam, 84%, R$_f$ = 0.42 (5% MeOH/CH$_2$Cl$_2$)]. **MS (ESI)** [m/z(%)]: 967.5 ([MNa]$^+$, 30), 945.5 ([MH]$^+$, 12), 748.4 (100). **HRMS (ESI) calculated** for C$_{55}$H$_{69}$N$_4$O$_{10}$: 945.5008, **found**: 945.5001.
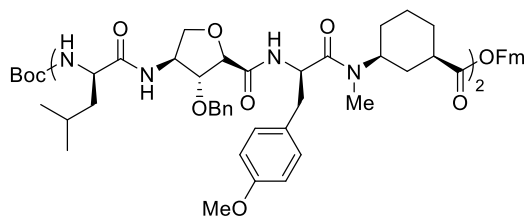
Boc-[D-Leu-L-Ahf(Bn)-D-Tyr(Me)-L-^{Me}N-Ach]$_2$-OFm (op1): A solution of tetrapeptide **tp1** (305 mg, 0.32 mmol) in a mixture of piperidine and CH$_2$Cl$_2$ (1:4, 6 mL) was stirred at rt for 45 min. The solution was washed with aqueous HCl (5%, 4 x 5 mL), dried with anhydrous Na$_2$SO$_4$, filtered and concentrated, to give Boc-D-Leu-L-Ahf(Bn)-D-Leu-L-^{Me}N-Ach-OH (**tp2**), which was used without further purification.

A solution of tetrapeptide **tp1** (305 mg, 0.32 mmol) in mixture of TFA and CH$_2$Cl$_2$ (1:1, 8 mL) was stirred at rt for 15 min. After removal of the solvent under vacuum, the residue was dried under high vacuum for 3 h. The resulting TFA salt (**tp3**) was dissolved in dry CH$_2$Cl$_2$ (12 mL) under Argon, and successively treated with DIEA (222 µL, 1.3 mmol), the previously prepared **tp2** and N-HBTU (134 mg, 0.35 mmol). After 1 h stirring at rt, the solution was washed with aqueous HCl (5%, 2 x 10 mL) and aqueous saturated NaHCO$_3$ (2 x 10 mL). The organic layer was dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The resulting crude was purified by flash chromatography (0-2% MeOH/CH$_2$Cl$_2$) to give 360 mg of octapeptide **op1**. [White foam, 70%, R$_f$ = 0.45 (5% MeOH/CH$_2$Cl$_2$)]. **MS (ESI)** [m/z(%)]: 1593.8 ([MH]$^+$, 8), 845.4 ([tetrapeptide-Boc]$^+$, 100), 747.9 ([MH-Boc]$^{2+}$, 14). **HRMS (ESI) calculated** for C$_{91}$H$_{117}$N$_8$O$_{17}$: 1593.8531, **found**: 1593.8586.
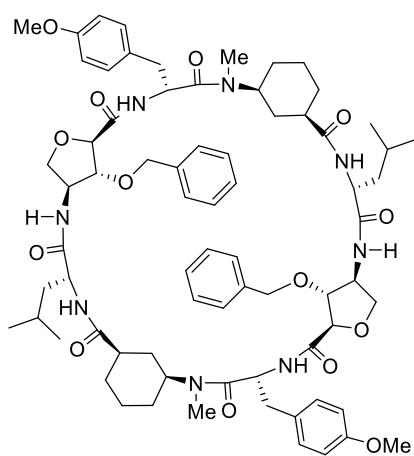
c-{[L-Ahf(Bn)-D-Tyr(Me)-L-^{Me}N-Ach-D-Leu-]$_2$} (CP1): The linear octapeptide **op1** (150.0 mg, 94.1 µmol) was dissolved in a mixture of piperidine and CH$_2$Cl$_2$ (1:4, 5 mL) and stirred at rt for 45 min. The solution was washed with aqueous HCl (5%, 4 x 5 mL), dried with anhydrous Na$_2$SO$_4$, filtered and concentrated to give Boc-[D-Leu-L-Ahf(Bn)-D-Tyr(Me)-L-^{Me}N-Ach]$_2$-OH, which was used without further purification. The resulting C-unprotected octapeptide was dissolved in a mixture of TFA and CH$_2$Cl$_2$ (1:1, 10 mL) and stirred at rt for 30 min. After removal of the solvent under reduced pressure, the residue was dried under high vacuum for 3 h and used without further purification. The

resulting unprotected linear peptide (**op2**) was dissolved in dry CH_2Cl_2 (95 mL) and successively treated with DIEA (66 µL, 0.38 mmol) and *N*-TBTU (39.2 mg, 0.10 mmol). After 12 h, the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 (15 mL), washed with aqueous HCl (10%, 2 x 10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated to dryness. The crude was purified by flash chromatography (0-5% $MeOH/CH_2Cl_2$) to give 62.5 mg of the desired cyclicpeptide. [White solid, 51%, R_f = 0.47 (5% $MeOH/CH_2Cl_2$)]. **^{1}H NMR** (7.5 mM, $CDCl_3$, 300 MHz, δ): 7.29 (m, 12H), 7.09 (d, *J* = 8.6 Hz, 5H), 6.82 (d, *J* = 8.5 Hz, 5H), 6.53 (d, *J* = 8.7 Hz, 1H), 5.59 (d, *J* = 9.3 Hz, 1H), 4.99-3.82 (m, 18H), 3.80 (s, 6H), 3.44 (m, 2H), 2.53 (m, 2H), 2.24 (s, 6H), 2.11-1.08 (m, 26H), 0.90 (d, *J* = 7.5 Hz, 6H), 0.87 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** ($CDCl_3$, 75.4 MHz, δ): 175.2 (CO), 174.0 (CO), 172.7 (CO), 172.0 (CO), 170.0 (C), 159.2 (C), 137.7 (C), 130.5 (CH), 128.5 (CH), 127.4 (CH), 114.2 (CH), 87.7 (CH), 84.9 (CH), 72.4 (CH_2), 72.1 (CH_2), 55.7 (CH), 55.5 (CH_3), 51.9 (CH), 45.0 (CH), 42.1 (CH_2), 39.6 (CH_2), 32.8 (CH_2), 29.6 (CH_3), 28.5 (CH_2), 25.2 (CH), 24.9 (CH_2), 23.3 (CH_3), 21.4 (CH_3). **FTIR** (298 K, $CHCl_3$): 3297 (amide A), 3006, 2958, 2933, 2869, 1655 (amide I_{II}), 1626 (amide I), 1514 cm^{-1} (amide II). **MS (ESI)** [m/z(%)]: 1319.7 ([MNa]$^+$, 19), 1297.7 ([MH]$^+$, 12), 668.3 ([MHK]$^{2+}$, 100), 660.8 ([MHNa]$^{2+}$, 23). **HRMS (ESI) calculated** for $C_{72}H_{97}N_8O_{14}$: 1297.7119, **found**: 1297.7111.
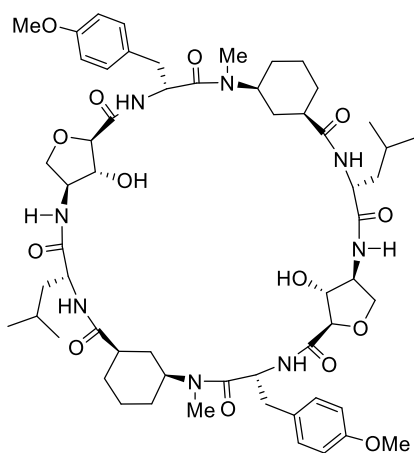
c-{[*L*-Ahf-*D*-Tyr(Me)-*L*-^{Me}*N*-Ach-*D*-Leu-]$_2$} (**CP2**): A solution of **CP1** (42 mg, 0.032 mmol) in TFA (1 mL) was successively treated with pentamethylbenzene (21 mg, 0.13 mmol), anisole (21 µL, 0.18 mmol) and HBr in AcOH (0.5 mL, 33% in wt). The resulting mixture was stirred at rt for 1h. The solvent was removed under reduced pressure and the crude was purified by HPLC (Phenomenex Luna 5µ silica, 4-8% $MeOH/CH_2Cl_2$, 25 min) to give 16.3 mg of the desired cyclic peptide. [White solid, 45%, t_R = 19 min]. **^{1}H NMR** (20 mM, $CDCl_3$, 300 MHz, δ): 9.27 (d, *J* = 9.1 Hz, 2H, NH$_{Tyr}$), 8.52 (d, *J* = 8.9 Hz, 2H, NH$_{Ahf}$), 8.24 (d, *J* = 8.9 Hz, 2H, NH$_{Leu}$), 7.07 (m, 4H, Ar), 6.79 (m, 4H, Ar), 5.19 (m, 2H, Hα_{Tyr}), 4.83 (br, 2H, OH), 4.74 (s, 2H, Hα_{Ahf}), 4.61 (m, 4H, Hα_{Leu} + Hγ_{Ach}), 4.47 (dd, J_1 = 9.7 Hz, J_2 = 3.8 Hz, 2H, Hγ_{Ahf}), 4.22 (s, 2H, Hβ_{Ahf}), 4.13 (dd, J_1 = 9.4 Hz, J_2 = 4.2 Hz, 2H, Hδ_{Ahf}), 3.86 (d, *J* = 8.9 Hz, 2H, Hδ_{Ahf}), 3.79 (s, 6H, OMe$_{Tyr}$), 2.97 (m, 4H, Hβ_{Tyr}), 2.48 (s, 6H, NMe), 1.95 (m, 2H, Hα_{ACH}), 1.85-1.09 (m, 22H, $CH_{2\ Ach}$ + $CH_{2\ Leu}$ + CH_{Leu}), 0.94 (d, *J* = 6.4 Hz, 6H, $CH_{3\ Leu}$), 0.91 (d, *J* = 5.6 Hz, 6H, $CH_{3\ Leu}$). **^{13}C NMR** ($CDCl_3$, 75.4 MHz, δ): 175.0 (CO), 172.2 (CO), 171.4 (CO), 170.4 (CO), 158.9 (C), 130.5 (CH), 128.1 (C), 114.0 (CH), 85.3 (CH), 78.7 (CH), 74.8 (CH_2), 57.9

(CH), 55.5 (CH$_3$), 51.6 (CH), 50.3 (CH), 43.8 (CH$_2$), 43.5 (CH), 39.6 (CH$_2$), 32.8 (CH$_2$), 29.9 (CH$_3$), 28.6 (CH$_2$), 28.1 (CH$_2$), 25.2 (CH), 24.8 (CH$_2$), 22.9 (CH$_3$), 22.8 (CH$_3$). **FTIR** (298 K, CHCl$_3$): 3399, 3299 (amide A), 3006, 2958, 2933, 2865, 1652 (amide I$_{II}$), 1629 (amide I), 1513 cm^{-1} (amide II). **MS (ESI)** [m/z(%)]: 1140.6 ([MNa]$^+$, 7), 1117.6 ([MH]$^+$, 8), 578.3 ([MHK]$^{2+}$, 100), 570.3 ([MHNa]$^{2+}$, 40). **HRMS (ESI) calculated** for C$_{58}$H$_{85}$N$_8$O$_{14}$: 1117.6180, **found**: 1117.6227.
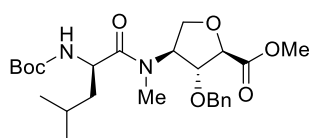
Boc-D-Leu-L-^{Me}N-Ahf(Bn)-OMe (4): A solution of L-^{Me}N-Ahf(Bn)-OMe2 (600 mg, 2.26 mmol) in dry CH$_2$Cl$_2$ (22 mL) was successively treated with DIEA (1.6 mL, 9.0 mmol), Boc-D-Leu-OH (523 mg, 2.3 mmol) and N-HATU (946 mg, 2.5 mmol). The mixture was stirred at rt under Argon for 90 min. The solution was washed with aqueous HCl (5%, 3 x 20 mL) and aqueous saturated NaHCO$_3$ (2 x 20 mL). The organic layer was dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The resulting crude was purified by flash chromatography (0-2% MeOH/CH$_2$Cl$_2$) to give 1.0 g of dipeptide **4**. [Yellow foam, 93%, R$_f$ = 0.53 (5% MeOH/CH$_2$Cl$_2$)]. **¹H NMR** (CDCl$_3$, 300 MHz, δ): 7.44-7.19 (m, 5H), 5.17 (m, 1H), 5.00 (m, 1H), 4.76 (AB, J = 11.9 Hz, 1H), 4.68-4.31 (m, 1H), 4.59 (AB, J = 12.0 Hz, 1H), 4.38 (d, J = 4.5 Hz, 1H), 4.19-3.98 (m, 3H), 3.72 (s, 3H), 2.79 (s, 3H), 1.80-1.25 (m, 3H), 1.42 (s, 9H), 0.98 (d, J = 6.7 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H). **¹³C NMR** (CDCl$_3$, 75.4 MHz, δ): 173.5 (CO), 170.6 (CO), 155.7 (CO), 137.3 (C), 128.3 (CH), 128.0 (CH), 127.8 (CH), 85.5 (CH), 82.4 (CH), 79.5 (C), 71.9 (CH$_2$), 69.3 (CH$_2$), 61.1 (CH), 52.3 (CH$_3$), 49.2 (CH), 42.2 (CH$_2$), 31.5 (CH$_3$), 28.3 (CH$_3$), 24.6 (CH), 23.4 (CH$_3$), 21.6 (CH$_3$). **MS (ESI)** [m/z(%)]: 501.2 ([MNa]$^+$, 100), 423.2 ([MH-^{t}Bu]$^+$, 13), 379.2 ([MH-Boc]$^+$, 6). **HRMS (ESI) calculated** for C$_{25}$H$_{38}$N$_2$NaO$_7$: 501.2571, **found**: 501.2581.
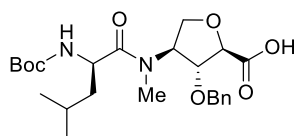
Boc-D-Leu-L-^{Me}N-Ahf(Bn)-OH (dp5): A solution of dipeptide **4** (700 mg, 1.5 mmol) in a mixture of MeOH and water (3:1, 29 mL) was treated with LiOH (175 mg, 7.3 mmol). The solution was stirred at rt for 2 h and then the solvent was removed under reduced pressure. The resulting residue was diluted with water (15 mL), washed with Et$_2$O (10 mL) and the resulting aqueous solution was acidified to pH 3 with aqueous HCl (5%). The acidic solution was extracted with CH$_2$Cl$_2$ (4 x 10 mL) and the combined organic extracts were dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure to give 670 mg of the desired dipeptide. [White foam, 99%, R$_f$ = 0.32 (5% MeOH/CH$_2$Cl$_2$)]. **¹H RMN** (CDCl$_3$, 300 MHz, δ): 9.70 (br, 1H), 7.52-7.10 (m, 5H),

² N. Rodríguez-Vázquez, S. Salzinger, L. F. Silva, M. Amorín, J. R. Granja, *Eur. J. Org. Chem.* **2013**, *17*, 3477–3493.

5.61 (m, 1H), 4.90 (m, 1H), 4.75 (AB, J = 11.9 Hz, 1H), 4.68-4.40 (m, 1H), 4.63 (AB, J = 11.6 Hz, 1H), 4.43 (dd, J_1 = 4.3 Hz, J_2 = 1.4 Hz, 1H), 4.26 (m, 1H), 4.11 (m, 2H), 3.04 (s, 3H), 1.78-1.23 (m, 3H), 1.41 (s, 9H), 0.96 (d, J = 6.5 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H). **^{13}C RMN** (CDCl$_3$, 75.4 MHz, δ): 174.3 (CO), 172.8 (CO), 156.2 (CO), 137.4 (C), 128.5 (CH), 128.0 (CH), 127.9 (CH), 86.4 (CH), 82.5 (CH), 80.1 (C), 72.2 (CH$_2$), 69.4 (CH$_2$), 62.3 (CH), 49.6 (CH), 41.9 (CH$_2$), 32.3 (CH$_3$), 28.4 (CH$_3$), 24.7 (CH), 23.5 (CH$_3$), 21.7 (CH$_3$). **MS (ESI)** [m/z(%)]: 487.2 ([MNa]$^+$, 100), 409.2 ([MH-^{t}Bu]$^+$, 21), 365.2 ([MH-Boc]$^+$, 16). **HRMS (ESI) calculated** for C$_{24}$H$_{36}$N$_2$NaO$_7$: 487.2415, **found**: 487.2395.
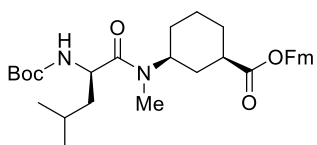
Boc-D-Leu-L-^{Me}N-Ach-OFm (dp4): A solution of Boc-L-^{Me}N-Ach-OFm (700 mg, 1.6 mmol) in a mixture of TFA and CH$_2$Cl$_2$ (1:1, 8 mL) was stirred at rt for 15 min. After removal of the solvent under vacuum, the residue was dried under high vacuum for 3 h. The resulting TFA salt was dissolved under Argon in dry CH$_2$Cl$_2$ (16 mL), and DIEA (1.1 mL, 6.4 mmol), Boc-D-Leu-OH (372 mg, 1.6 mmol), and N-HATU (669 mg, 1.8 mmol) were successively added. After 1 h stirring at rt, the solution was washed with aqueous HCl (5%, 2 x 15 mL) and aqueous saturated NaHCO$_3$ (2 x 15 mL). The organic layer was dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure, providing a yellow oil that was purified by flash chromatography (30% EtAcO/hexanes) to give 755 mg of the dipeptide. [White foam, 86%, R$_f$ = 0.65 (50% EtAcO/hexanes)]. **^{1}H NMR** (CDCl$_3$, 300 MHz, δ): 7.76 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.6 Hz, 2H), 7.36 (td, J_1 = 25.0 Hz, J_2 = 7.6 Hz, 4H), 5.31 (d, J = 9.2 Hz, 1H), 4.64 (m, 1H), 4.53-4.35 (m, 3H), 4.19 (t, J = 6.7 Hz, 1H), 2.90 and 2.79 (s, 3H), 2.08-1.12 (m, 11H), 1.42 (s, 9H), 0.99 (dd, J = 6.5 Hz, J = 1.9 Hz, 3H), 0.91 (dd, J = 6.7 Hz, J = 1.4 Hz, 3H). **^{13}C NMR** (CDCl$_3$, 75.4 MHz, δ): 174.9 (CO), 172.8 (CO), 155.7 (CO), 143.8 (C), 141.4 (C), 127.9 (CH), 127.2 (CH), 125.1 (CH), 120.1 (CH), 79.5 (C), 66.2 (CH$_2$), 55.1 (CH), 51.7 (CH), 49.2 (CH), 47.1 (CH), 42.9 (CH$_2$), 42.6 (CH), 32.8 (CH$_2$), 31.6 (CH$_2$), 29.3 (CH$_3$), 29.0 (CH$_2$), 28.5 (CH$_3$), 24.8 (CH), 24.5 (CH$_2$), 23.6 (CH$_3$), 21.8 (CH$_3$). **MS (ESI)** [m/z(%)]: 571.3 ([MNa]$^+$, 24), 549.3 ([MH]$^+$, 11), 493.3 ([MH-^{t}Bu]$^+$, 100), 449.3 ([MH-Boc]$^+$, 100). **HRMS (ESI) calculated** for C$_{33}$H$_{45}$N$_2$O$_5$: 549.3323, **found**: 549.3323.
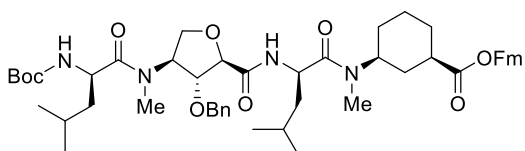
Boc-D-Leu-L-^{Me}N-Ahf(Bn)-D-Leu-L-^{Me}N-Ach-OFm (tp4): A solution of dipeptide **dp4** (700 mg, 1.2 mmol) in a mixture of TFA and CH$_2$Cl$_2$ (1:1, 10 mL) was stirred at rt for 30 min. After removal of the solvent under vacuum, the residue was dried under high vacuum for 3 h. The resulting TFA salt (**dp6**) was dissolved in dry CH$_2$Cl$_2$ (12 mL) under Argon, then DIEA (850 µL, 4.8 mmol), dipeptide **dp5** (562 mg, 1.2 mmol) and N-HBTU (504 mg, 1.3 mmol) were successively added. After 2 h stirring at rt, the solution was washed with

aqueous HCl (5%, 2 x 10 mL) and aqueous saturated NaHCO$_3$ (2 x 10 mL). The organic layer was dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The resulting crude was purified by flash chromatography (0-2% MeOH/CH$_2$Cl$_2$) to give 1.1 g of the tetrapeptide **tp4**. [White foam, 99%, R$_f$ = 0.41 (2% MeOH/CH$_2$Cl$_2$)]. **MS (ESI)** [m/z(%)]: 933.4 ([MK]$^+$, 3), 917.5 ([MNa]$^+$, 82), 895.5 ([MH]$^+$, 100), 795.5 ([MH-Boc]$^+$, 4). **HRMS (ESI) calculated** for C$_{52}$H$_{71}$N$_4$O$_9$: 895.5216, **found**: 895.5204.
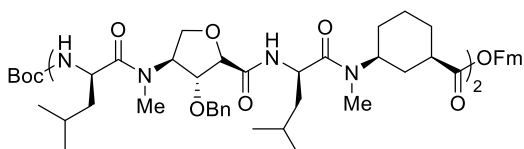
Boc-[*D*-Leu-*L*-^{Me}*N*-Ahf(Bn)-*D*-Leu-*L*-^{Me}*N*-Ach]$_2$-OFm (op3): A solution of tetrapeptide **tp4** (515 mg, 0.46 mmol) in a mixture of piperidine and CH$_2$Cl$_2$ (1:4, 5 mL) was stirred at rt for 45 min. The solution was washed with aqueous HCl (5%, 4 x 10 mL), dried with anhydrous Na$_2$SO$_4$, filtered and concentrated, to give Boc-*D*-Leu-*L*-^{Me}*N*-Ahf(Bn)-*D*-Leu-*L*-^{Me}*N*-Ach-OH (**tp5**), which was used without further purification.

A solution of tetrapeptide **tp4** (515 mg, 0.46 mmol) in a mixture of TFA and CH$_2$Cl$_2$ (1:1, 6 mL) was stirred at rt for 30 min. After removal of the solvent under vacuum, the residue was dried under high vacuum for 3 h. The resulting TFA salt (**tp6**) was dissolved in dry CH$_2$Cl$_2$ (5 mL) under Argon, and successively treated with DIEA (320 μL, 1.9 mmol), the previously prepared **tp5** and *N*-HBTU (193 mg, 0.51 mmol). After 2 h stirring at rt, the solution was washed with aqueous HCl (5%, 2 x 10 mL) and aqueous saturated NaHCO$_3$ (2 x 10 mL). The organic layer was dried with anhydrous Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The resulting crude was purified by flash chromatography (0-5% MeOH/CH$_2$Cl$_2$) to give 683 mg of the desired octapeptide (**op3**). [White foam, 98%, R$_f$ = 0.35 (2% MeOH/CH$_2$Cl$_2$)]. **MS (ESI)** [m/z(%)]: 1531.8 ([MK]$^+$, 1), 1516.9 ([MNa]$^+$, 24), 1493.9 ([MH]$^+$, 10), 774.7 (100), 769.9 ([MNa]$^{2+}$, 24), 697.4 ([MH-Boc]$^{2+}$, 97). **HRMS (ESI) calculated** for C$_{85}$H$_{121}$N$_8$O$_{15}$: 1493.8946, **found**: 1493.8971.
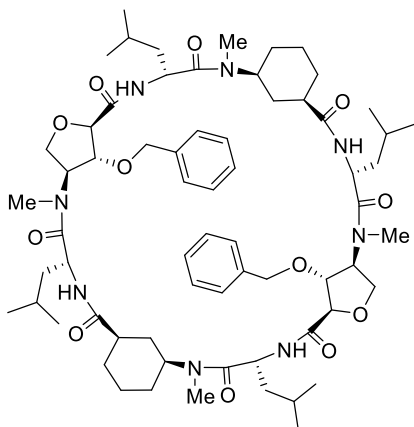
c-{[*L*-^{Me}*N*-Ahf(Bn)-*D*-Leu^1-*L*-^{Me}*N*-Ach-*D*-Leu^2-]$_2$} (CP3): The linear octapeptide **op3** (400 mg, 0.27 mmol) was dissolved in a mixture of piperidine and CH$_2$Cl$_2$ (1:4, 5 mL) and stirred at rt for 45 min. The solution was washed with aqueous HCl (5%, 4 x 10 mL), dried with anhydrous Na$_2$SO$_4$, filtered and concentrated to dryness to give Boc-[*D*-Leu-*L*-^{Me}*N*-Ahf(Bn)-*D*-Leu-*L*-^{Me}*N*-Ach]$_2$-OH, which was used without further purification. The resulting octapeptide was dissolved in a mixture of TFA and CH$_2$Cl$_2$ (1:1, 6 mL) and stirred at rt for 20 min. After removal of the solvent under reduced pressure, the residue was dried under high vacuum for 3 h and used without

further purification. The resulting unprotected linear peptide (**op4**) was dissolved in dry CH_2Cl_2 (268 mL) and successively treated with DIEA (280 μL, 1.6 mmol) and *N*-TBTU (112 mg, 0.29 mmol). After 12 h, the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (25 mL), washed with aqueous HCl (10%, 2 x 20 mL), dried with anhydrous Na_2SO_4, filtered and concentrated to dryness. The crude was purified by flash chromatography (0-6% $MeOH/CH_2Cl_2$) to give 200 mg of **CP3**. [White solid, 62%, R_f = 0.37 (5% $MeOH/CH_2Cl_2$)]. **^{1}H NMR** (16 mM, $CDCl_3$, 500 MHz, δ): 9.08 (d, *J* = 9.4 Hz, 1.33H, $NH_{Leu1-D3E}$), 8.79 (d, *J* = 9.4 Hz, 0.66H, $NH_{Leu1-D3A}$), 8.08 (d, *J* = 9.2 Hz, 1.33H, $NH_{Leu2-D3E}$), 8.03 (d, *J* = 9.6 Hz, 0.66H, $NH_{Leu2-D3A}$), 6.96 (br, 4.66H, Bn), 6.68 (br, 4H, Bn), 6.58 (m, 1.33H, Bn), 5.53 (m, 1.33H, $Hγ_{Ahf-D3E}$), 5.45 (m, 0.66H, $Hγ_{Ahf-D3A}$), 5.29 (m, 2H, $Hα_{Leu1}$), 5.21 (d, *J* = 5.4 Hz, 0.66H, $Hα_{Ahf-D3A}$), 5.13 (m, 2H, $Hα_{Leu2}$), 4.78 (d, *J* = 8.3 Hz, 1.33H, $Hα_{Ahf-D3E}$), 4.53 (m, 1.33H, $Hγ_{Ach-D3E}$), 4.37 (m, 1.33H, $Hβ_{Ahf-D3A}$ + $Hδ_{Ahf-D3A}$), 4.22 (dd, J_1 = 10.2 Hz, J_2 = 8.8 Hz, 1.33H, $Hβ_{Ahf-D3E}$), 4.06 (m, 2.66H, $Hδ_{Ahf-D3E}$ + $Hγ_{Ach-D3A}$ + $Hδ_{Ahf-D3A}$), 3.96 (br, 2.66H, $Hβ_{Bn-D3E}$), 3.73 (dd, J_1 = 10.7 Hz, J_2 = 9.3 Hz, 1.33H, $Hδ_{Ahf-D3E}$), 3.66 (AB, *J* = 9.9 Hz, 0.66H, $Hβ_{Bn-D3A}$), 3.60 (AB, *J* = 9.8 Hz, 0.66H, $Hβ_{Bn-D3A}$), 3.33 (s, 2H, $NMe_{Ahf-D3A}$), 3.04 (s, 4H, $NMe_{Ach-D3E}$), 2.80 (m, 1.33H, $Hα_{Ach-D3E}$), 2.67 (s, 2H, $NMe_{Ach-D3A}$), 2.62 (s, 4H, $NMe_{Ahf-D3E}$), 2.31 (m, 0.66H, $Hα_{Ach-D3A}$), 1.91-1.05 (m, 27.33H, $CH_{2\ Ach}$ + $CH_{2\ Leu}$ + CH_{Leu}), 1.04-0.80 (m, 24H, $CH_{3\ Leu}$), -1.20 (d, *J* = 11.5 Hz, 0.66H, $Hβ_{Ach-D3A}$). **^{13}C NMR** ($CDCl_3$, 75.4 MHz, δ): 175.2 (CO), 175.0 (CO), 174.4 (CO), 173.8 (CO), 172.4 (CO), 171.8 (CO), 171.4 (CO), 169.5 (CO), 136.8 (C), 136.0 (C), 128.7 (CH), 128.4 (CH), 128.1 (CH), 127.3 (CH), 127.0 (CH), 82.8 (CH), 82.3 (CH), 79.9 (CH), 77.1 (CH), 72.2 (CH_2), 71.8 (CH_2), 67.9 (CH_2), 66.2 (CH_2), 59.6 (CH), 57.7 (CH), 51.5 (CH), 51.1 (CH), 47.0 (CH), 46.6 (CH), 46.5 (CH), 43.9 (CH_2), 43.5 (CH_2), 31.4 (CH), 30.7 (CH_2), 30.1 (CH_2), 29.8 (CH), 29.3 (CH), 29.0 (CH), 28.7 (CH_2), 25.4 (CH_2), 25.0 (CH_2), 24.7 (CH_3), 24.6 (CH_3), 24.5 (CH_3), 23.7 (CH_3), 23.4 (CH_3), 23.2 (CH_3), 22.5 (CH), 22.1 (CH_3), 21.7 (CH_3). **FTIR** (298 K, $CHCl_3$): 3307 (amide A), 3066, 2954, 2925, 2866, 1678 (amide I_{II}), 1626 (amide I), 1526 cm^{-1} (amide II). **MS (ESI)** [m/z(%)]: 1219.7 ($[MNa]^+$, 10), 1197.7 ($[MH]^+$, 100), 945.6 (30), 683.6 (60), 599.4 ($[MH]^{2+}$, 9). **HRMS (ESI) calculated** for $C_{66}H_{101}N_8O_{12}$: 1197.7533, **found**: 1197.7556.

X-Ray Crystallographic Determination of D3$_A$

Preparation of single crystals for X-Ray analysis: In a typical experiment, 1.0 mg of pure **CP3** was dissolved in 900 μL of $CHCl_3$, and equilibrated by vapour-phase diffusion against 3.0 mL of hexanes. The corresponding dimer crystallized spontaneously after 7 days.

X-Ray Crystallographic Analysis: Data were collected at 100 K, using Bruker X8 APEXII CCD diffractometer. All calculations were performed on a PC compatible computer using the programs: SORTAV (Blessing, 1995), SHELXT-2014 (Sheldrick, 2014), SHELXL204/7 (Sheldrick,

2014), ORTEP-3 (Farrugia, 2012), WinGX (Farrugia, 2012). Supplementary crystallographic data for D3$_A$ (CIF format) can be obtained free of charge from the journal.

The crystal structure was deposited at the Cambridge Crystallographic Data Centre, and the data was assigned to the following deposition number: CCDC 1400134.
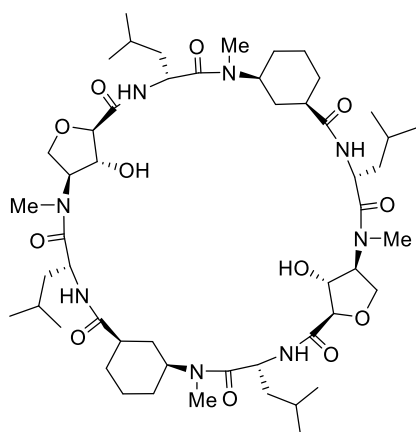
c-{[L-^{Me}N-Ahf-D-Leu^1-L-^{Me}N-Ach-D-Leu^2-]$_2$} **(CP4):** A solution of **CP3** (50 mg, 0.042 mmol) and Pd/C (36 mg, 10% in wt) in a mixture of MeOH and CH$_2$Cl$_2$ (3:1, 20 mL) was stirred at rt for 20 h under hydrogen atmosphere (balloon pressure). The resulting mixture was filtered through a Celite pad, the residue was washed with CH$_2$Cl$_2$, and the combined filtrates and washes were concentrated under reduced pressure. The crude was purified by HPLC (Phenomenex Luna 5µ silica, 6-13% MeOH/CH$_2$Cl$_2$, 30 min) to give 30 mg of the cyclic peptide **CP4**. [White solid, 71%, t_R = 22 min]. **^{1}H NMR** (5 mM, CDCl$_3$, 298 K, 300 MHz, δ): 7.92 (br, 2H), 5.31 (br, 2H), 5.08 (m, 4H), 4.47 (m, 6H), 4.23 (br, 2H), 3.83 (dd, J_1 = 10.7 Hz, J_2 = 9.0 Hz, 2H), 3.08 (s, 6H), 3.03 (s, 6H), 2.79 (m, 2H), 2.01-1.10 (m, 28H), 1.03-0.80 (m, 24H). **^{1}H NMR** (32 mM, CDCl$_3$, 253 K, 500 MHz, δ): 8.72 (d, J = 9.1 Hz, 0.8H, NH$_{Leu1}$), 8.47 (d, J = 9.1 Hz, 1.2H, NH$_{Leu1-D4A}$), 7.95 (d, J = 8.6 Hz, 0.8H, NH$_{Leu2}$), 7.72 (d, J = 9.4 Hz, 1.2H, NH$_{Leu2-D4A}$), 5.97 (br, 0.8H, OH), 5.48 (br, 1.2H, OH), 5.32 (m, 2H, Hγ$_{Ahf}$), 5.09 (m, 4H, Hα$_{Leu}$), 4.76 (br, 1H, Hα$_{Ahf-D4A}$), 4.45 (m, 5H, Hγ$_{Ach}$ + Hβ$_{Ahf}$ + Hα$_{Ahf}$), 3.98 (m, 4H, Hδ$_{Ahf}$), 3.13 (s, 2H, NMe), 3.07 (s, 7H, NMe$_{Ahf}$ + Hα$_{Ach}$), 2.98 (s, 4H, NMe$_{Ach}$), 2.62 (m, 1H, Hα$_{Ach}$), 2.07-1.14 (m, 28H, CH$_{2\ Ach}$ + CH$_{2\ Leu}$ + CH$_{Leu}$), 1.07-0.68 (m, 24H, CH$_{3\ Leu}$). **^{1}H NMR** (32 mM, 5% CD$_3$OH/CDCl$_3$, 253 K, 500 MHz, δ): 8.83 (d, J = 9.3 Hz, 0.2H, NH$_{Leu1}$), 8.64 (d, J = 8.9 Hz, 1.8H, NH$_{Leu1-D4A}$), 8.15 (d, J = 9.5 Hz, 1.8H, NH$_{Leu2-D4A}$), 7.94 (d, J = 8.0 Hz, 0.2H, NH$_{Leu2}$), 6.11 (s, 1.8H, OH), 5.76 (s, 0.2H, OH), 5.31 (m, 2H, Hγ$_{Ahf}$), 5.13 (m, 4H, Hα$_{Leu}$), 4.62 (d, J = 7.9 Hz, 2H, Hα$_{Ahf}$), 4.57 (m, 2H, Hγ$_{Ach}$), 4.31 (dd, J_1 = 9.7 Hz, J_2 = 8.7 Hz, 2H, Hβ$_{Ahf}$), 4.05 (m, 0.2H, Hδ$_{Ahf}$), 3.96 (d, J = 9.6 Hz, 3.6H, Hδ$_{Ahf-D4A}$), 3.84 (m, 0.2H, Hδ$_{Ahf}$), 3.37 (s, CH$_3$OH), 3.09 (s, 5.4H, NMe$_{Ahf-D4A}$), 3.06 (s, 0.6H, NMe$_{Ahf}$), 2.93 (s, 6H, NMe$_{Ach}$), 2.78 (m, 2H, Hα$_{Ach}$), 1.97-1.15 (m, 28H, CH$_{2\ Ach}$ + CH$_{2\ Leu}$ + CH$_{Leu}$), 0.98 (d, J =6.3 Hz, 4H, CH$_{3\ Leu}$), 0.87 (dd, J_1 =8.1 Hz, J_2 = 6.8 Hz, 16H, CH$_{3\ Leu}$), 0.82 (d, J =6.9 Hz, 4H, CH$_{3\ Leu}$). **FTIR** (298 K, CHCl$_3$): 3437, 3298 (amide A), 2955, 2931, 2867, 1676 (amide I$_{II}$), 1621 (amide I), 1537 cm^{-1} (amide II). **MS (ESI)** [m/z(%)]: 1017.6 ([MH]$^+$, 16), 536.8 (32), 528.3 ([MK]$^{2+}$, 21), 509.3 ([MH]$^{2+}$, 9), 381.3 (100). **HRMS (ESI) calculated** for C$_{52}$H$_{89}$N$_8$O$_{12}$: 1017.6594, **found**: 1017.6556.
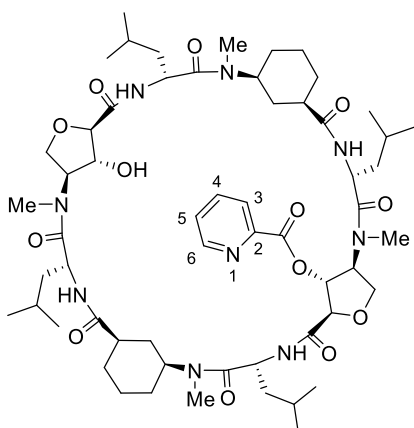
***c*-[*L*-^MeN-Ahf(pic)-*D*-Leu¹-*L*-^MeN-Ach¹-*D*-Leu²-*L*-^MeN-Ahf-*D*-Leu³-*L*-^MeN-Ach²-*D*-Leu⁴-] (CP5):** A solution of **CP4** (5.5 mg, 5.4 µmol) in CH_2Cl_2 (1 mL) was treated with 2-picolinic acid (0.73 mg, 5.9 µmol), EDC·HCl (1.1 mg, 5.9 µmol), HOBt (0.79 mg, 5.9 µmol) and DMAP (0.72 mg, 5.9 µmol). Each 12 h, additional 2-picolinic acid (1.5 mg, 11.8 µmol), EDC (2.2 mg, 11.8 µmol) and DMAP (1.4 mg, 11.8 µmol) was added during 3-4 days. Then, the solution was washed with aqueous saturated $NaHCO_3$ (2 x 5 mL) and aqueous

HCl (5%, 2 x 5 mL). The organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated to dryness. The crude was purified by HPLC (Phenomenex Luna 5µ silica, 7-11% $MeOH/CH_2Cl_2$, 30 min) to give 3.2 mg of the cyclic peptide **CP5**. [White solid, 54%, t_R = 20 min]. **¹H NMR** ($CDCl_3$, 300 MHz, δ): 8.80-8.15 (m, 3H), 7.99-7.56 (m, 3H), 7.43 (m, 1H), 7.11 (m, 0.5H), 6.72 (m, 0.5H), 6.06-3.67 (m, 17H), 3.35 (s, 1.5H), 3.21 (s, 1H), 3.20 (s, 2H), 3.17 (s, 1H), 3.13 (s, 1H), 3.01 (s, 4H), 2.84 (s, 1.5H), 2.37 (m, 2H), 2.12-0.54 (m, 52H). **FTIR** (298 K, $CHCl_3$): 3298 (amide A), 3068, 3003, 2956, 2929, 2868, 1747 (C=O), 1683 (amide I_{II}), 1623 (amide I), 1540 cm⁻¹ (amide II). **MS (ESI)** [m/z(%)]: 1144.7 ([MNa]⁺, 23), 1122.7 ([MH]⁺, 32), 572.8 ([MNa]²⁺, 8), 511.3 (34), 500.3 (100). **HRMS (ESI) calculated** for $C_{58}H_{92}N_9O_{13}$: 1122.6809, **found**: 1122.6807.

ADDITION EXPERIMENT OF AgBF₄:

CP5 (2.2 mg, 1.9 µmol) was dissolved in $CDCl_3$ (400 µL) in a NMR tube. In a flask under Ar and protected from light, AgBF₄ (15.8 mg, 0.081 mmol) (dry box) was dissolved in CD_3CN (2.0 mL). Then, different portions (0.1, 0.2, 0.3, 0.4 and 0.5 equiv) of the solution of AgBF₄ (24 µL, 0.95 µmol) were added to the NMR tube to form mainly the complex ***s*-D5$_E$⊃Ag**. **¹H NMR** (4.5 mM, $CDCl_3$, 500 MHz, δ): 8.66 (d, *J* = 9.1 Hz, 0.25H, NH$_{minor}$), 8.55 (d, *J* = 9.2 Hz, 1H, NH$_{Leu3(major)+minor}$), 8.43 (d, *J* = 9.6 Hz, 0.75H, NH$_{Leu1(major)}$), 7.99 (d, *J* = 9.1 Hz, 0.75H, NH$_{Leu4(major)}$), 7.93 (d, *J* = 9.2 Hz, 0.75H, NH$_{Leu2(major)}$), 7.87 (d, *J* = 4.3 Hz, 0.25H, Pic$_{minor}$), 7.78 (s, 1H, NH$_{minor}$+ H6-Pic$_{major}$), 7.65 (d, *J* = 9.1 Hz, 0.25H, NH$_{minor}$), 7.51 (m, 1H, H3-Pic$_{major}$+Pic$_{minor}$), 7.23 (m, 0.25H, Pic$_{minor}$), 7.10 (m, 1.50H, H4/H5-Pic$_{major}$), 6.93 (m, 0.25H, Pic$_{minor}$), 5.82 (m, 1.50 H, Hγ$_{Ahf(pic)}$), 5.63 (dd, J_1 = 9.7 Hz, J_2 = 9.2 Hz, 0.75H, Hβ$_{Ahf(pic)}$), 5.41 (m, 1H, Hγ$_{Ahf}$), 5.27 (m, 1.25H, Hα$_{Leu4}$), 5.19 (m, 1.5H, Hα$_{Leu3}$ + Hα$_{Ahf(pic)(minor)}$), 5.12 (m, 1.25H, Hα$_{Leu2}$), 5.07 (m, 1.5H, Hα$_{Leu1}$), 4.93 (d, *J* = 9.0 Hz, 0.75H, Hα$_{Ahf(pic)}$), 4.81 (br, 0.25H), 4.59 (d, *J* = 8.5 Hz, 1.50H, Hα$_{Ahf}$), 4.40 (dd, J_1 = 10.6 Hz, J_2 = 8.9 Hz, 0.75H, Hβ$_{Ahf}$), 4.33 (dd, J_1 = 11.7 Hz, J_2 = 9.6 Hz, 0.75H, Hδ$_{Ahf(pic)}$), 4.27 (m, 0.75H, Hγ$_{Ach2}$), 4.12 (dd, J_1 = 9.3 Hz, J_2 = 8.8 Hz, 0.75H, Hδ$_{Ahf}$), 4.02 (dd, J_1 = 9.8 Hz, J_2 = 8.3 Hz, 0.75H, Hδ$_{Ahf(pic)}$), 3.97 (dd, J_1 = 10.2 Hz, J_2 = 9.7 Hz, 0.75H, Hδ$_{Ahf}$), 3.92 (m, 0.75H, Hγ$_{Ach1}$), 3.82 (m, 0.5H), 3.28 (s, 2.25H, NMe$_{Ahf(pic)}$), 3.16 (s,

0.75H, NMe), 3.14 (s, 0.75H, NMe), 3.13 (s, 2.25H, NMe$_{Ahf}$), 3.06 (s, 2.25H, NMe$_{Ach2}$), 2.96 (s, 0.75H), 2.94 (s, 0.75H), 2.82 (s, 2.25H, NMe$_{Ach1}$), 2.57 (m, 0.75H, Hα$_{Ach2(major)}$), 2.48 (m, 0.25H, Hα$_{Ach(minor)}$), 2.35 (m, 0.75H, Hα$_{Ach1(major)}$), 2.26 (m, 0.25H, Hα$_{Ach(minor)}$), 2.02-1.17 (m, 27H, CH$_2$ $_{Ach}$ + CH$_2$ $_{Leu}$ + CH$_{Leu}$), 1.04-0.77 (m, 24H, CH$_3$ $_{Leu}$), 0.11 (d, J = 9.0 Hz, 0.75H, Hβ$_{Ach1(major)}$). **MS (ESI)** [m/z(%)]: 2957.6 (35), 2546.2 (Dimer+Ag+AgBF$_4$, 71), 2352.3 (Dimer+Ag, 100), 2247.2 (Dimer, 28), 2057.3 (28), 1230.6 (CP+Ag, 19), 942.1 (17). **HRMS (ESI) calculated** for C$_{116}$H$_{182}$AgN$_{18}$O$_{16}$: 2350.2518, **found**: 2350.2604.

ADDITION EXPERIMENT OF OXALIC ACID:

CP5 (2.5 mg, 2.3 μmol) was dissolved in CDCl$_3$ (400 μL) in a NMR tube. In another flask, (CO$_2$H)$_2$ · 2H$_2$O (7.9 mg, 0.063 mmol) was dissolved in CD$_3$CN (1.0 mL). Then, different portions (0.1, 0.2, 0.3, 0.4 and 0.5 equiv) of the solution of (CO$_2$H)$_2$ · 2H$_2$O (17.8 μL, 1.15 μmol) were added to the NMR tube to form mainly the complex *s*-D5$_E$⊃(CO$_2$H)$_2$. **^{1}H NMR** (5mM, CDCl$_3$, 500 MHz, δ): 8.65 (d, J = 9.2 Hz, 1H, NH$_{Leu3}$), 8.47 (d, J = 9.5 Hz, 1H, NH$_{Leu1}$), 8.15 (d, J = 9.4 Hz, 1H, NH$_{Leu4}$), 7.96 (S, 1H, H6-Pic), 7.92 (d, J = 10.0 Hz, 1H, NH$_{Leu2}$), 7.48 (br, 1H, H3-Pic), 7.18 (br, 2H, H4/H5-Pic), 5.82 (m, 1H, Hγ$_{Ahf(pic)}$), 5.60 (dd, J_1 = 10.3 Hz, J_2 = 9.4 Hz, 1H, Hβ$_{Ahf(pic)}$), 5.46 (m, 1H, Hγ$_{Ahf}$), 5.30 (m, 1H, Hα$_{Leu4}$), 5.23 (m, 1H, Hα$_{Leu3}$), 5.14 (m, 2H, Hα$_{Leu2}$ + OH), 5.08 (m, 1H, Hα$_{Leu1}$), 4.92 (d, J = 9.1 Hz, 1H, Hα$_{Ahf(pic)}$), 4.71 (d, J = 8.5 Hz, 1H, Hα$_{Ahf}$), 4.49 (dd, J_1 = 11.0 Hz, J_2 = 8.7 Hz, 1H, Hβ$_{Ahf}$), 4.32 (m, 2H, Hδ$_{Ahf(pic)}$ + Hγ$_{Ach2}$), 4.14 (m, J_1 = 11.5 Hz, J_2 = 9.0 Hz, 1H, Hδ$_{Ahf}$), 4.02 (dd, J_1 = 10.1 Hz, J_2 = 8.9 Hz, 1H, Hδ$_{Ahf(pic)}$), 3.96 (dd, J_1 = 11.1 Hz, J_2 = 9.6 Hz, 1H, Hδ$_{Ahf}$), 3.92 (m, 1H, Hγ$_{Ach1}$), 3.28 (s, 3H, NMe$_{Ahf(pic)}$), 3.12 (s, 3H, NMe$_{Ahf}$), 3.08 (s, 3H, NMe$_{Ach2}$), 2.83 (s, 3H, NMe$_{Ach1}$), 2.65 (m, 1H, Hα$_{Ach2}$), 2.40 (m, 1H, Hα$_{Ach1}$), 1.88-1.07 (m, 27H, CH$_2$ $_{Ach}$ + CH$_2$ $_{Leu}$ + CH$_{Leu}$), 1.06-0.70 (m, 24H, CH$_3$ $_{Leu}$), 0.15 (d, J = 11.8 Hz, 1H, Hβ$_{Ach1}$).

NMR and FTIR Spectra:

Boc-*D*-Leu-*L*-Ahf(Bn)-OMe (3): **¹H NMR** (CDCl₃, 298 K, 250 MHz), **DEPT** and **¹³C NMR** (CDCl₃, 298 K, 75.4 MHz).
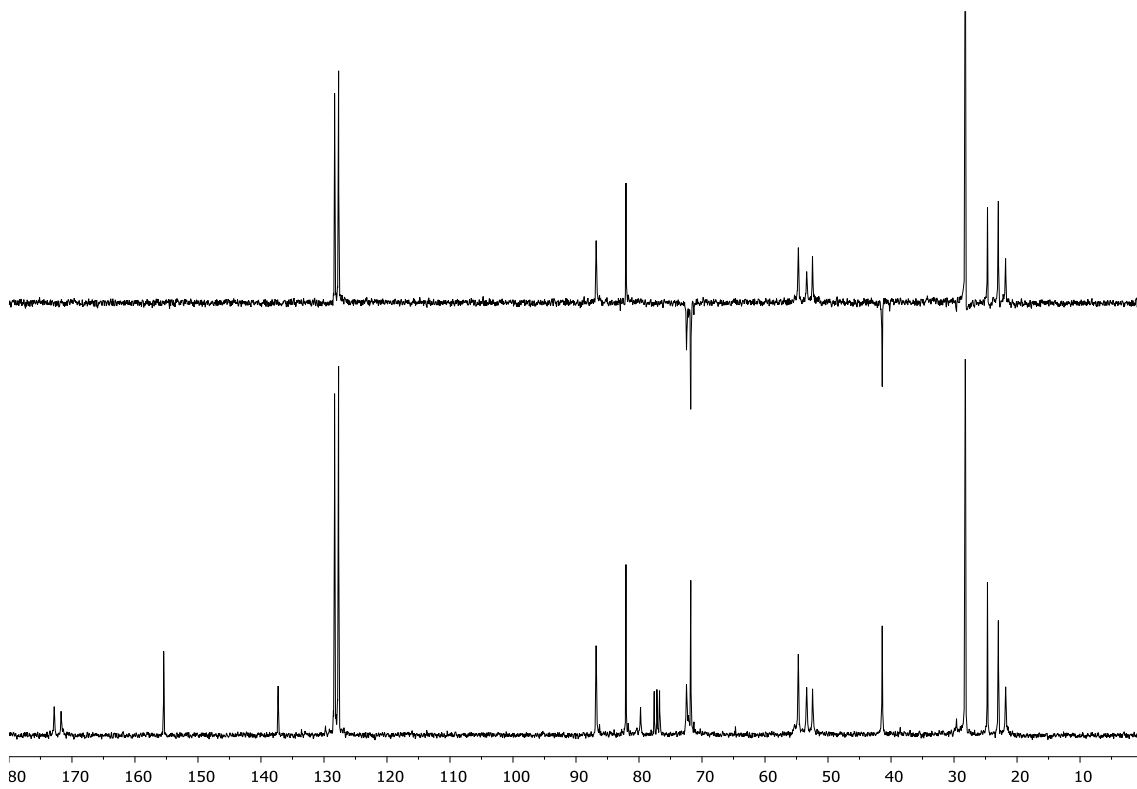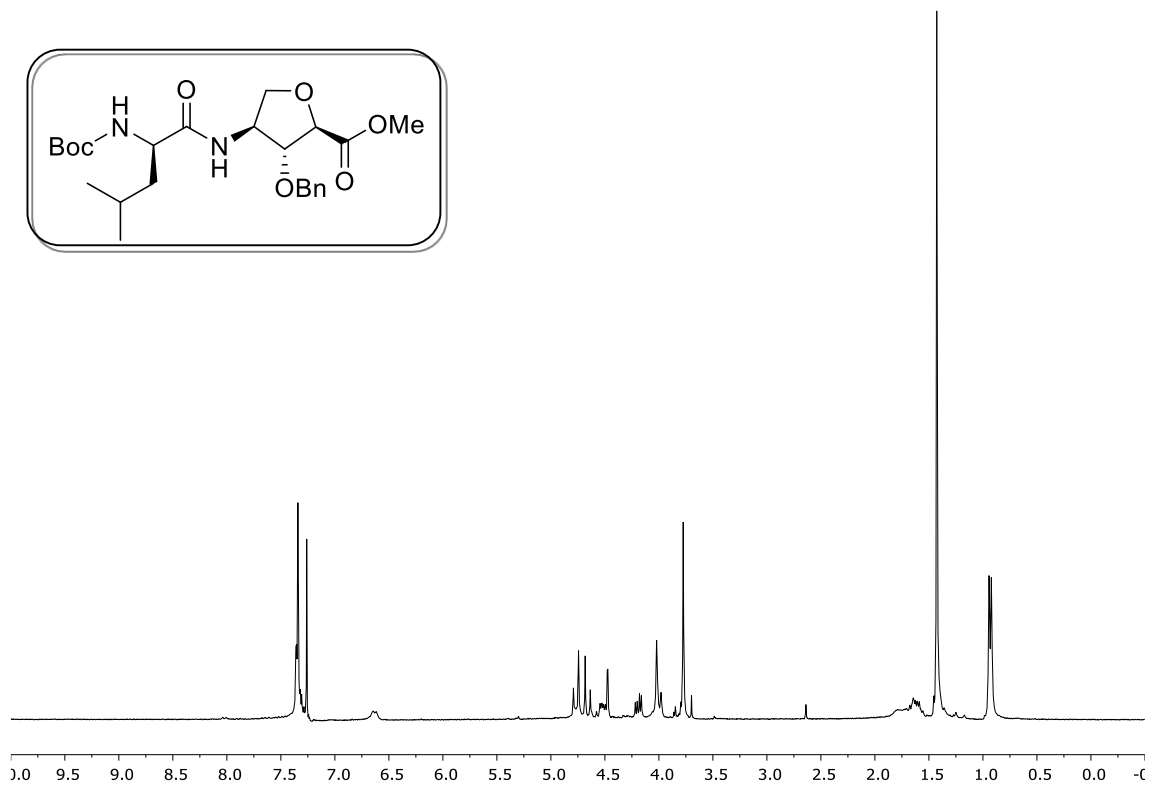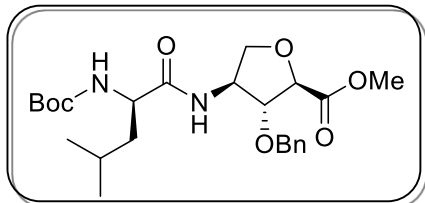
Boc-*D*-Leu-*L*-Ahf(Bn)-OH (dp2): **¹H NMR** (CDCl$_3$, 298 K, 300 MHz), **DEPT** and **¹³C NMR** (CDCl$_3$, 298 K, 75.4 MHz).
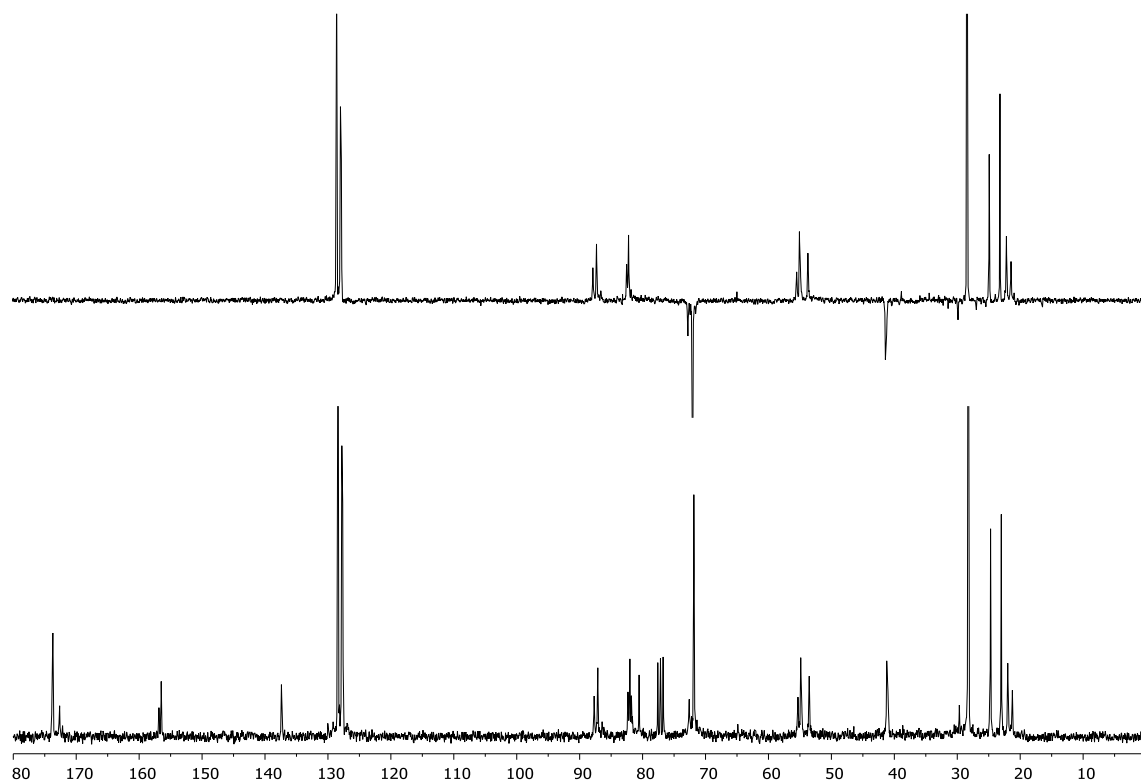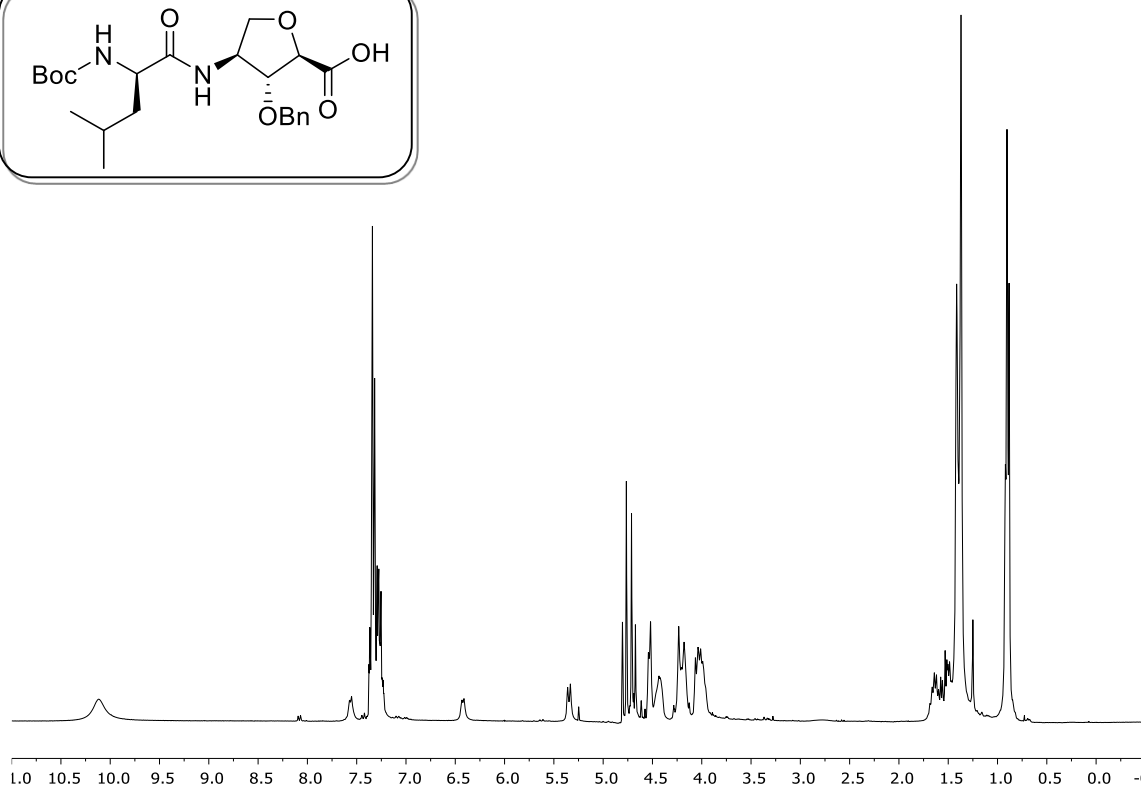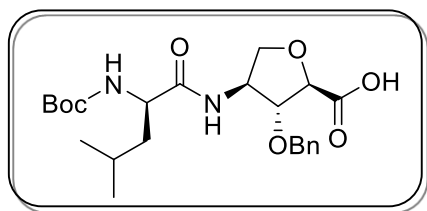
Boc-*D*-Tyr(Me)-*L*-*Me*N-Ach-OFm (dp1): **¹H NMR** (CDCl₃, 298 K, 300 MHz), **DEPT** and **¹³C NMR** (CDCl₃, 298 K, 75.4 MHz).
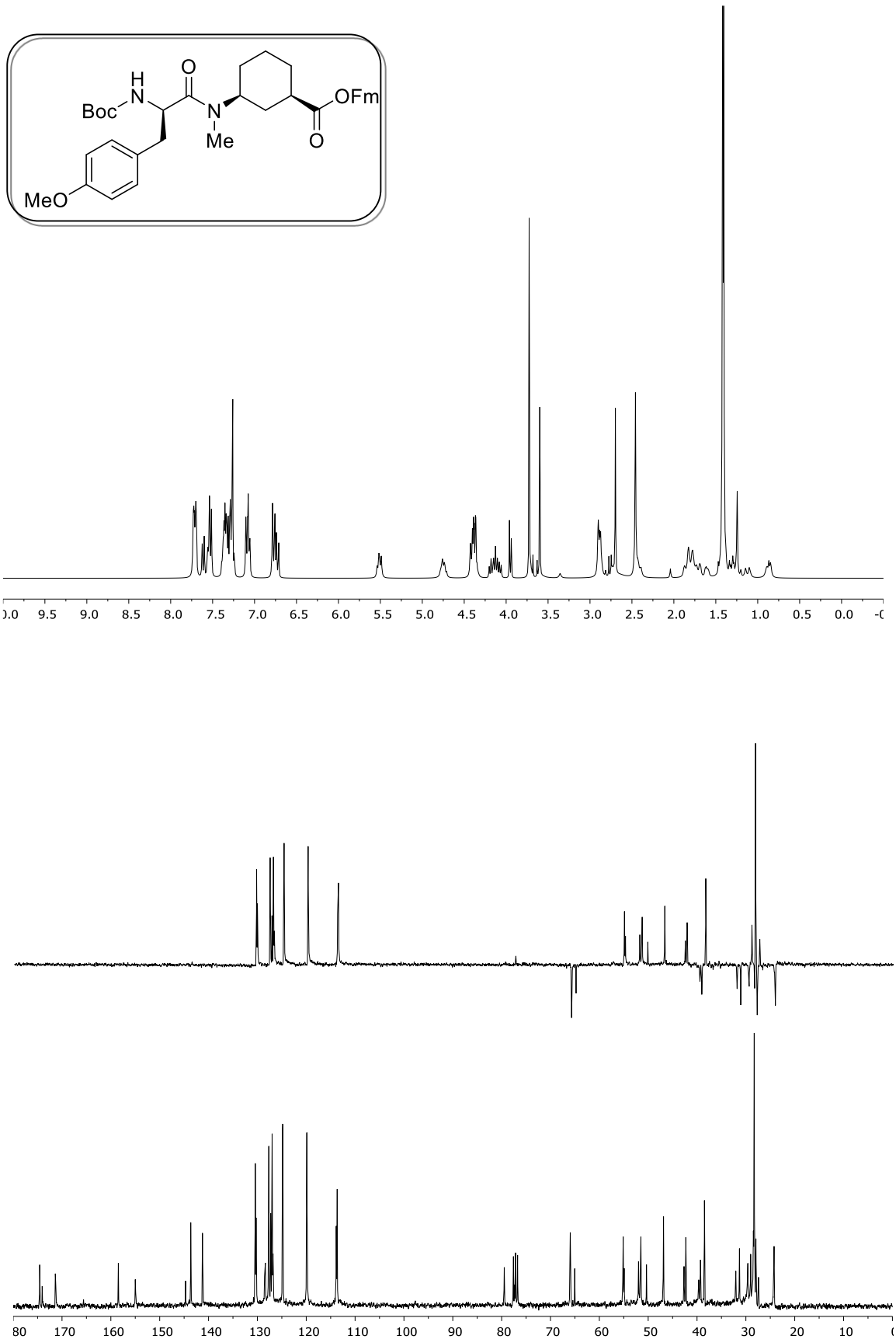
***c*-{[*L*-Ahf(Bn)-*D*-Tyr(Me)-*L*-^{Me}*N*-Ach- *D*-Leu-]₂} (CP1): ¹H NMR** (7.5 mM, CDCl₃, 298 K, 300 MHz) and **¹³C NMR** (CDCl₃, 298 K, 75.4 MHz).
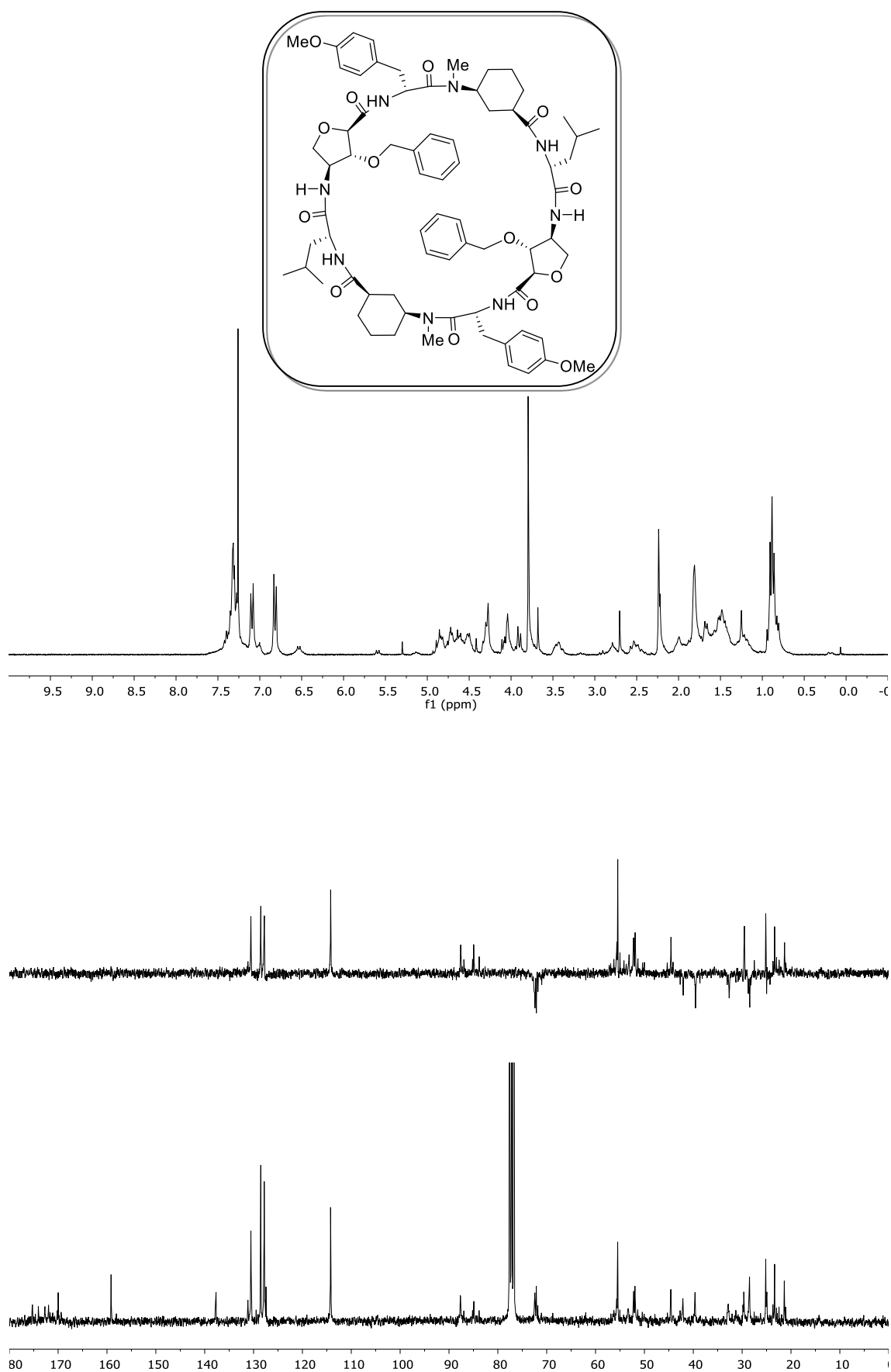
FTIR (298 K, CHCl$_3$):
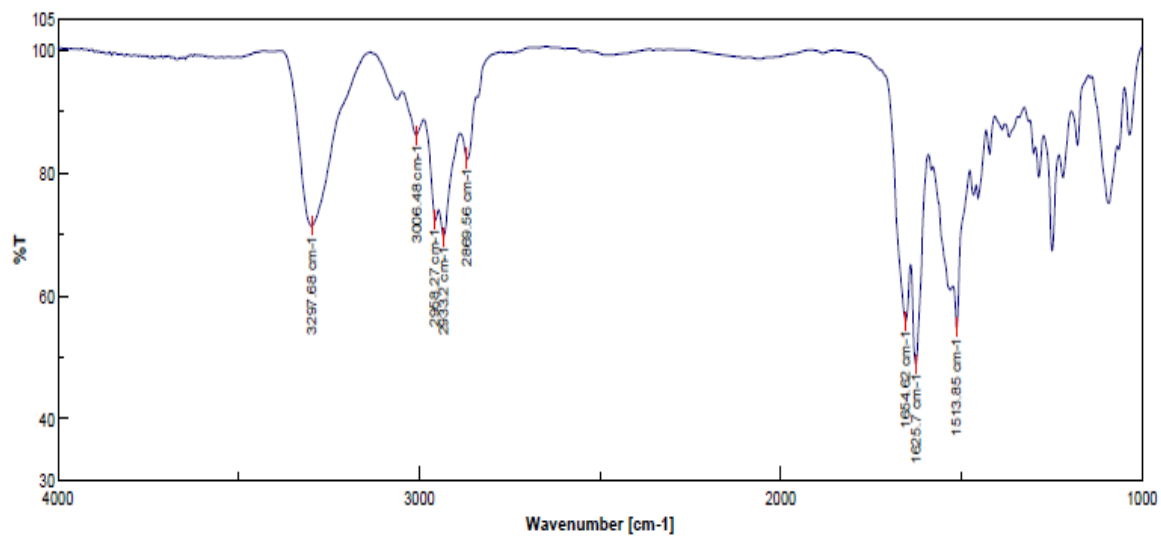
c-{[*L*-Ahf-*D*-Tyr(Me)-*L*-^{Me}*N*-Ach-*D*-Leu-]₂} (CP2): **¹H NMR** (20 mM, CDCl₃, 298 K, 300 MHz), **DEPT** and **¹³C NMR** (CDCl₃, 298 K, 75.4 MHz).
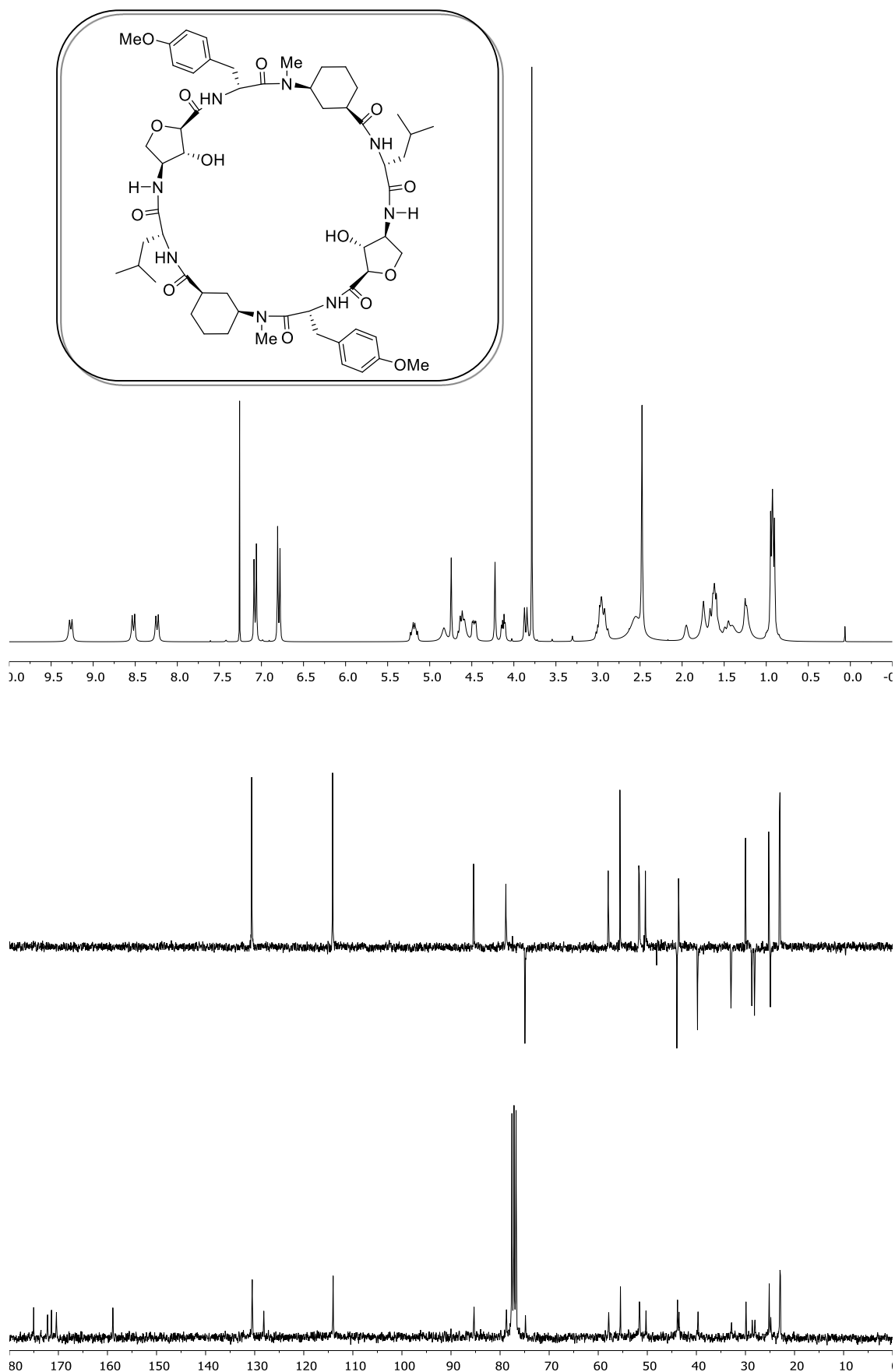
COSY (20 mM, CDCl$_3$, 298 K, 500 MHz).
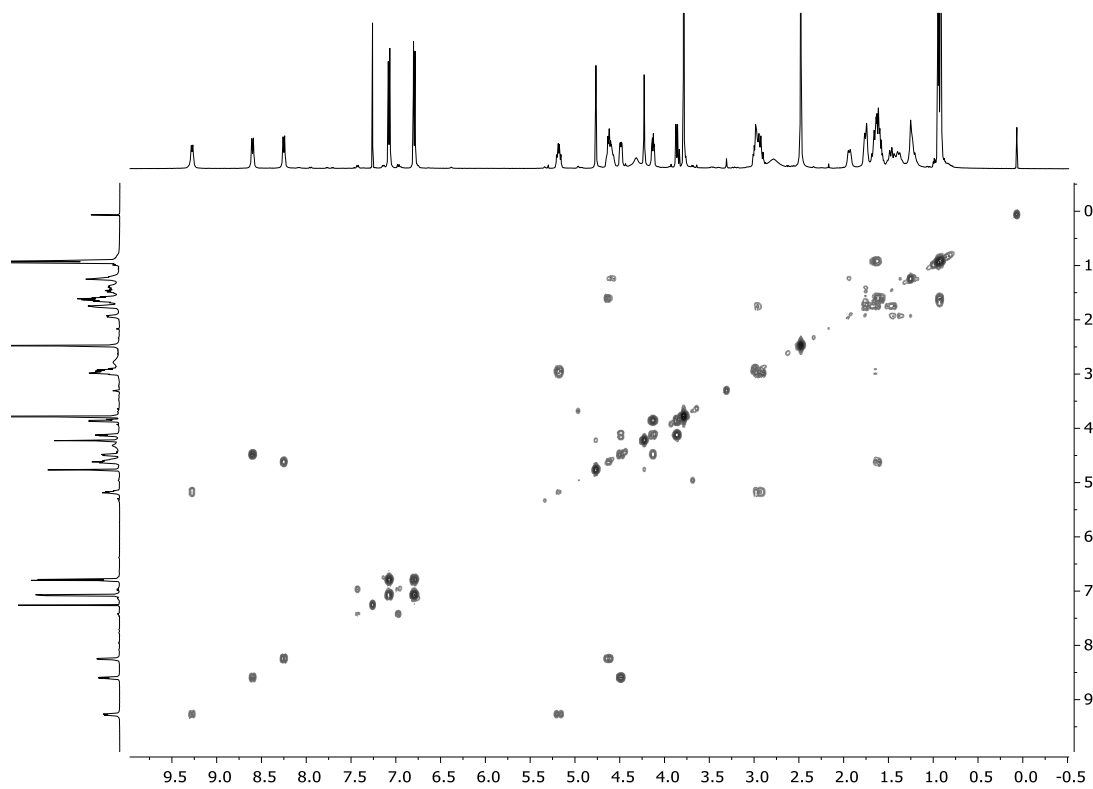
TOCSY (20 mM, CDCl$_3$, 298 K, 500 MHz).
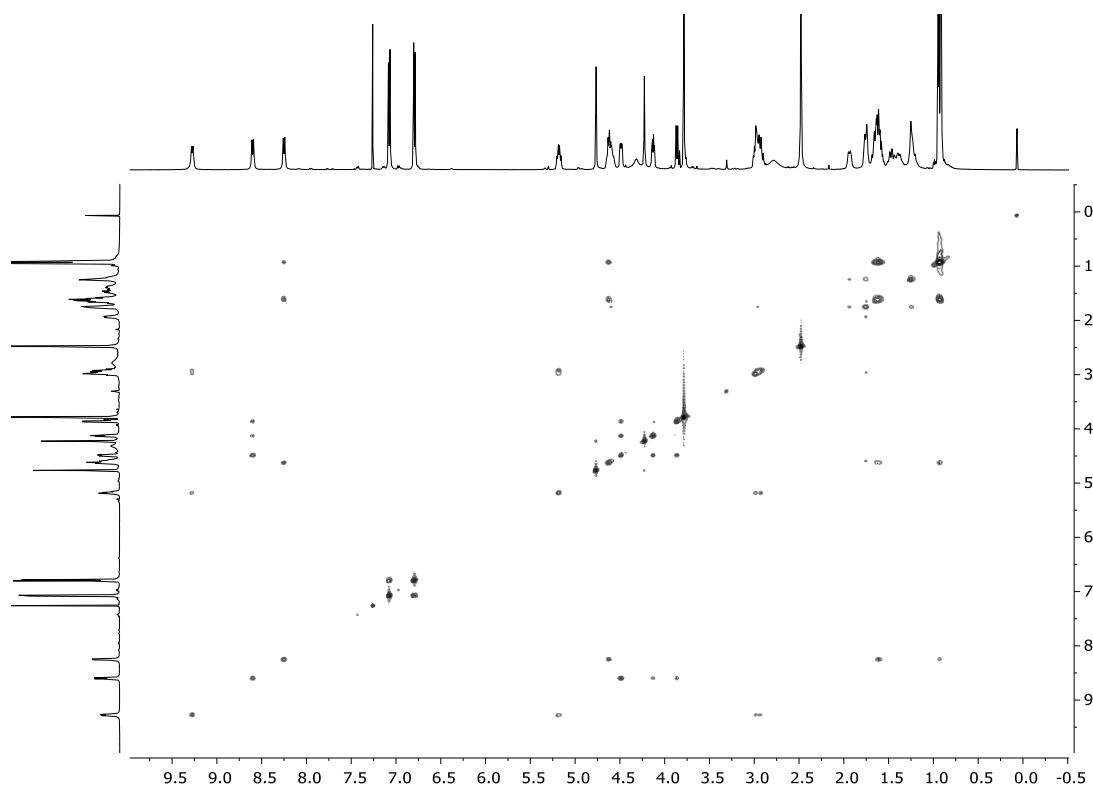
NOESY (20 mM, CDCl₃, 298 K, 500 MHz).
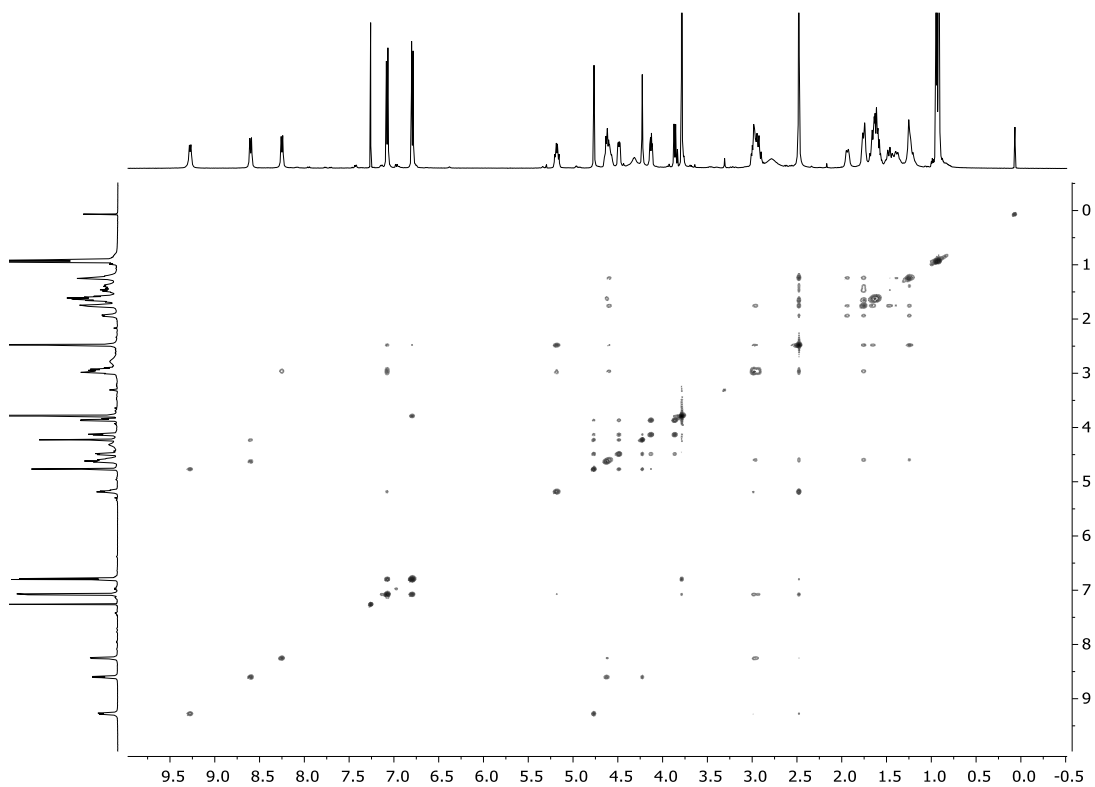
FTIR (298 K, CHCl₃):
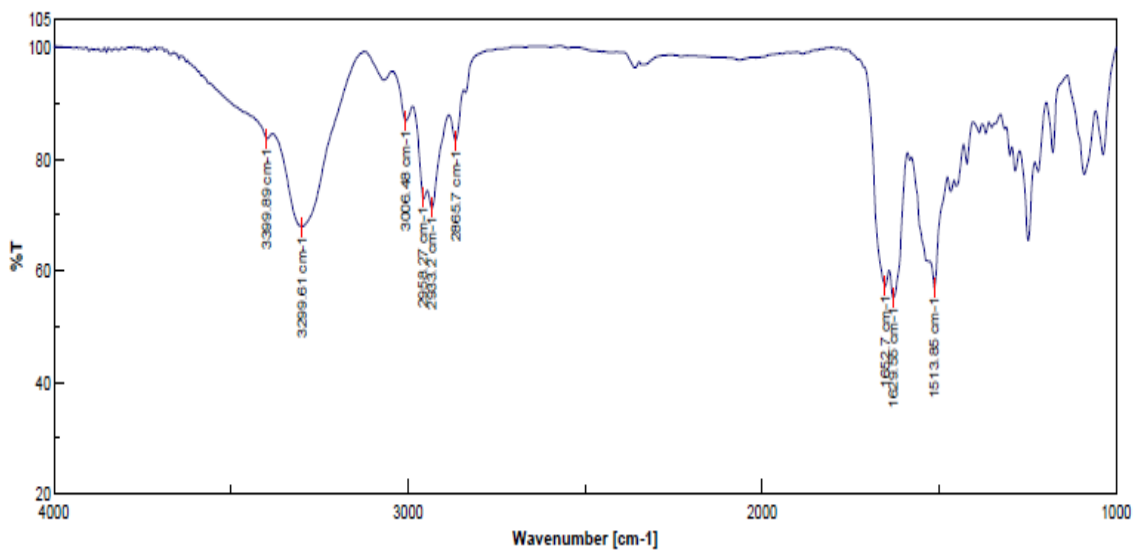
Boc-*D*-Leu-*L*-^{Me}*N*-Ahf(Bn)-OMe (4): **¹H NMR** (CDCl₃, 298 K, 300 MHz), **DEPT** and **¹³C NMR** (CDCl₃, 298 K, 75.4 MHz).
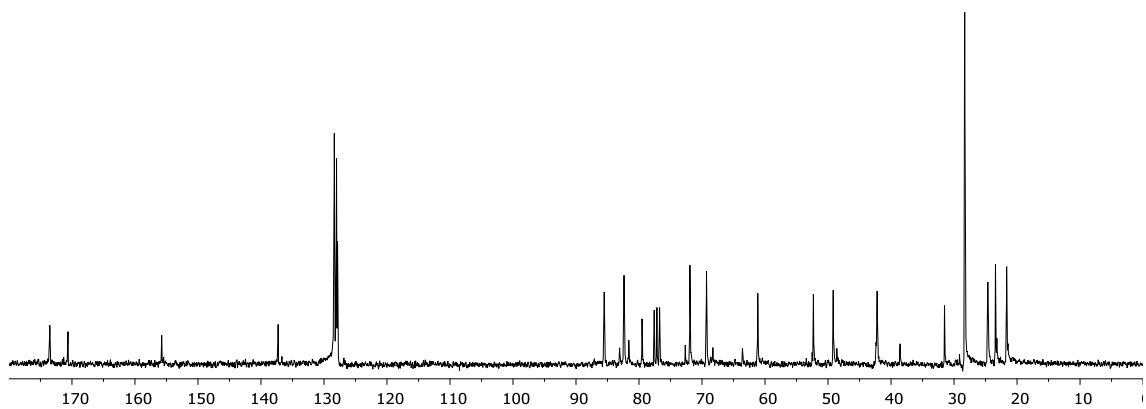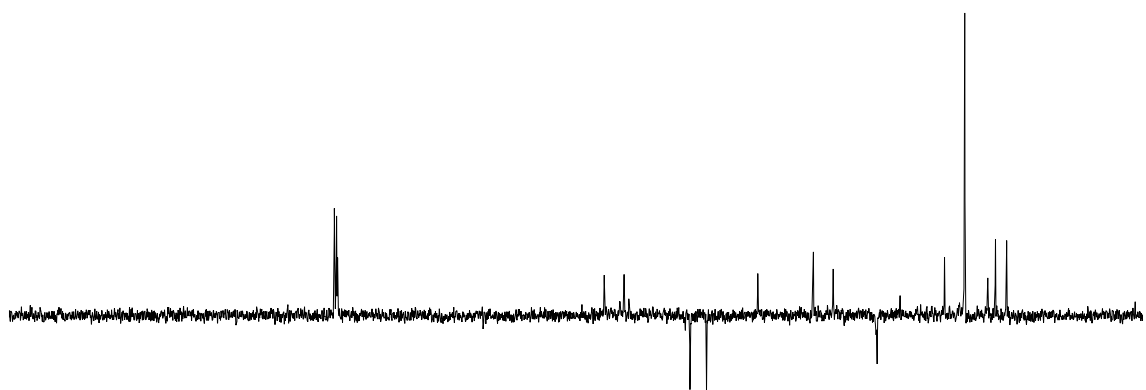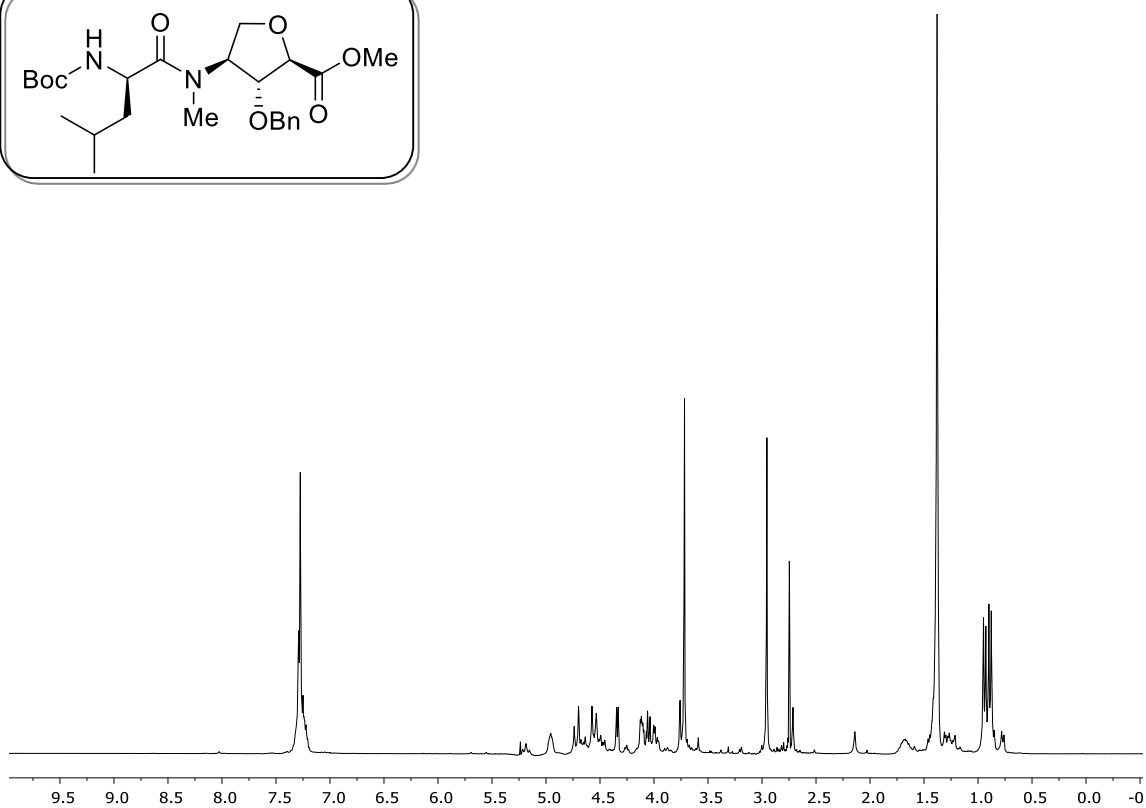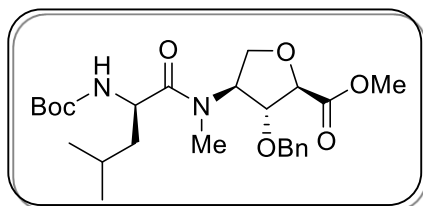
Boc-*D*-Leu-*L*-^{Me}*N*-Ahf(Bn)-OH (dp5): **¹H NMR** (CDCl₃, 298 K, 300 MHz), **DEPT** and **¹³C NMR** (CDCl₃, 298 K, 75.4 MHz).
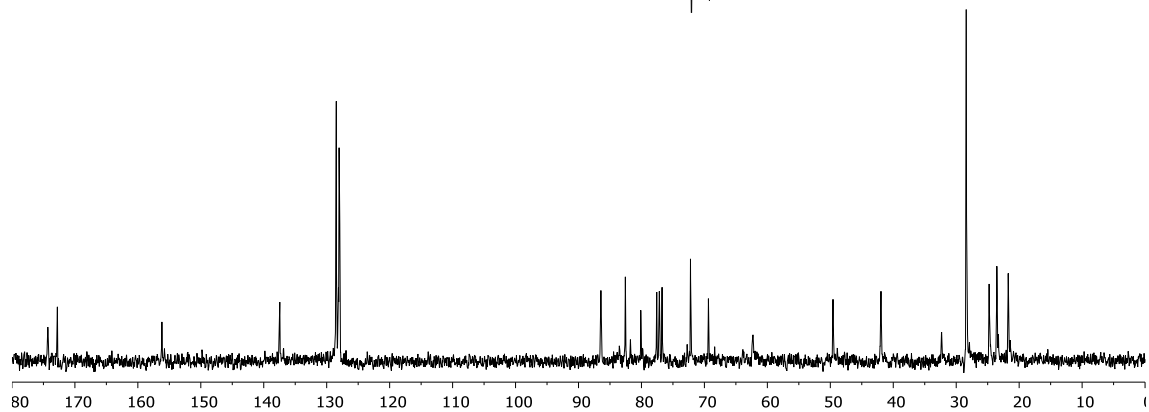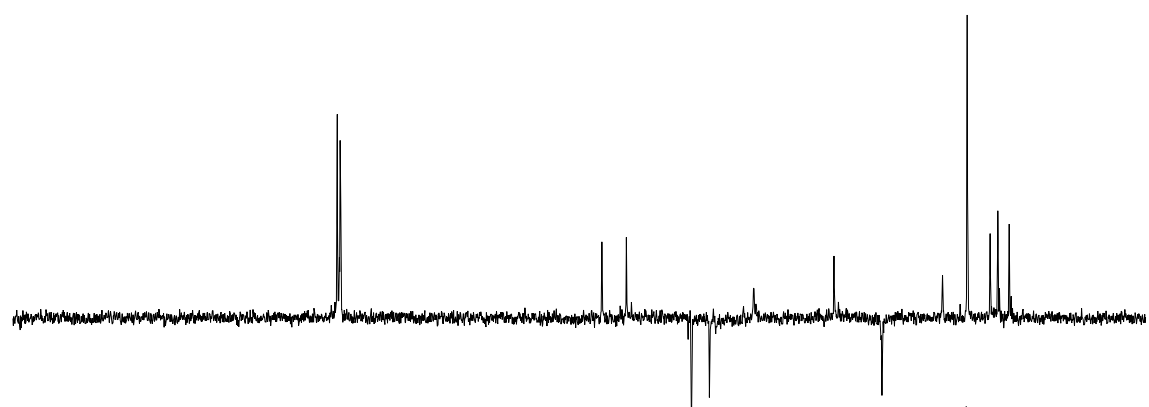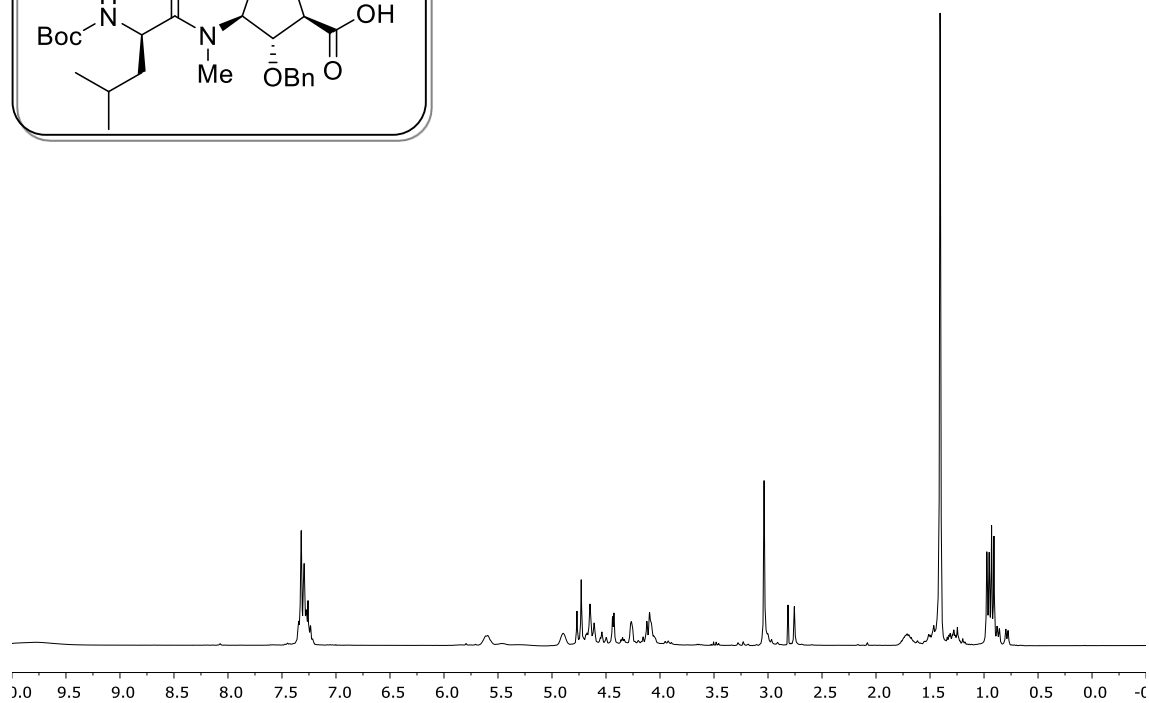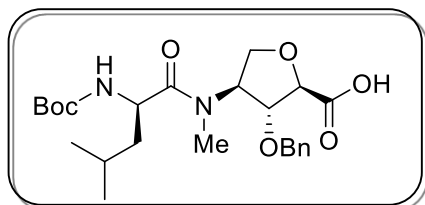
Boc-*D*-Leu-*L*-^{Me}*N*-Ach-OFm (dp4): **¹H NMR** (CDCl₃, 298 K, 300 MHz), **DEPT** and **¹³C NMR** (CDCl₃, 298 K, 75.4 MHz).
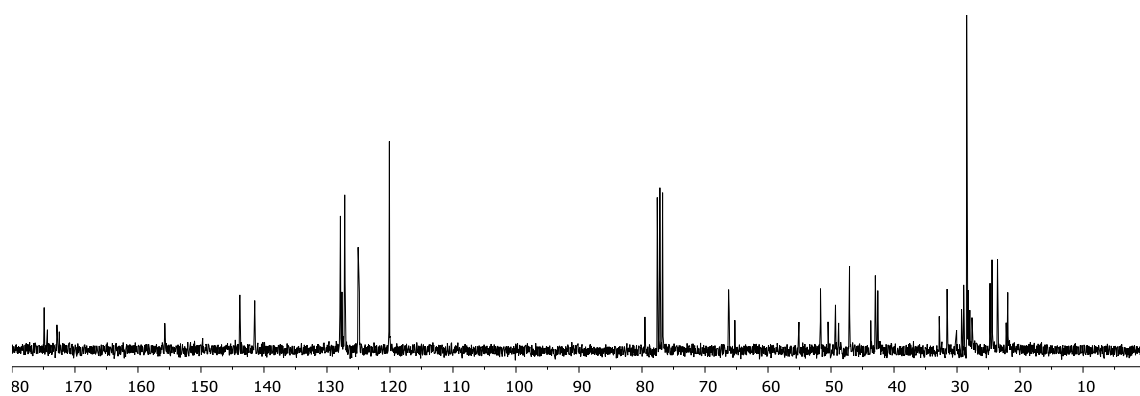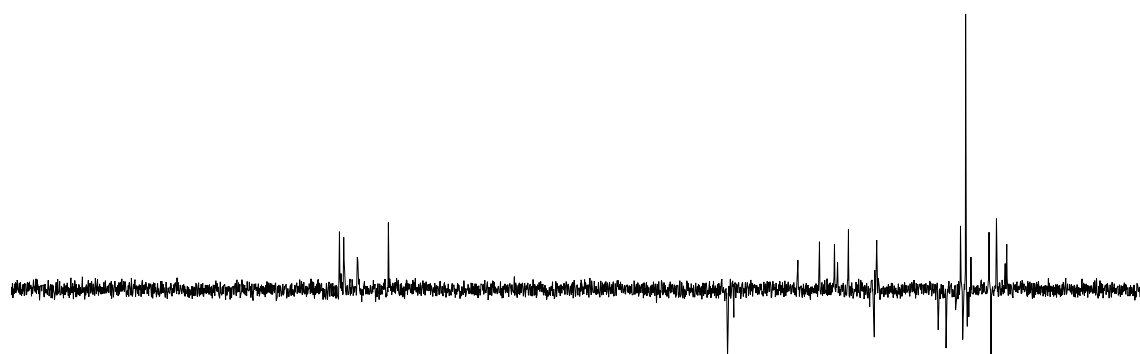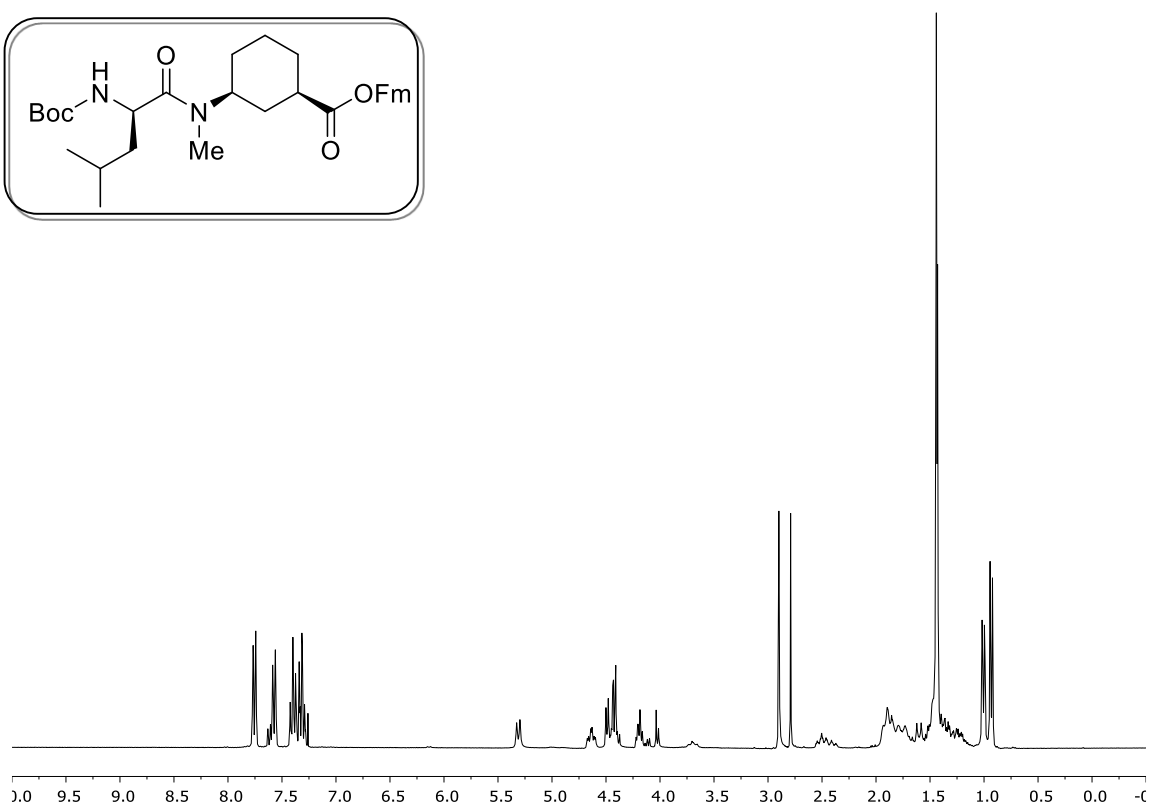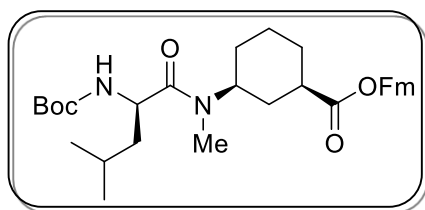
***c*-{[*L*-^{Me}*N*-Ahf(Bn)-*D*-Leu¹-*L*-^{Me}*N*-Ach-*D*-Leu²-]₂} (CP3): ¹H NMR** (16 mM, CDCl₃, 298 K, 500 MHz), **DEPT** and **¹³C NMR** (CDCl₃, 298 K, 75.4 MHz).
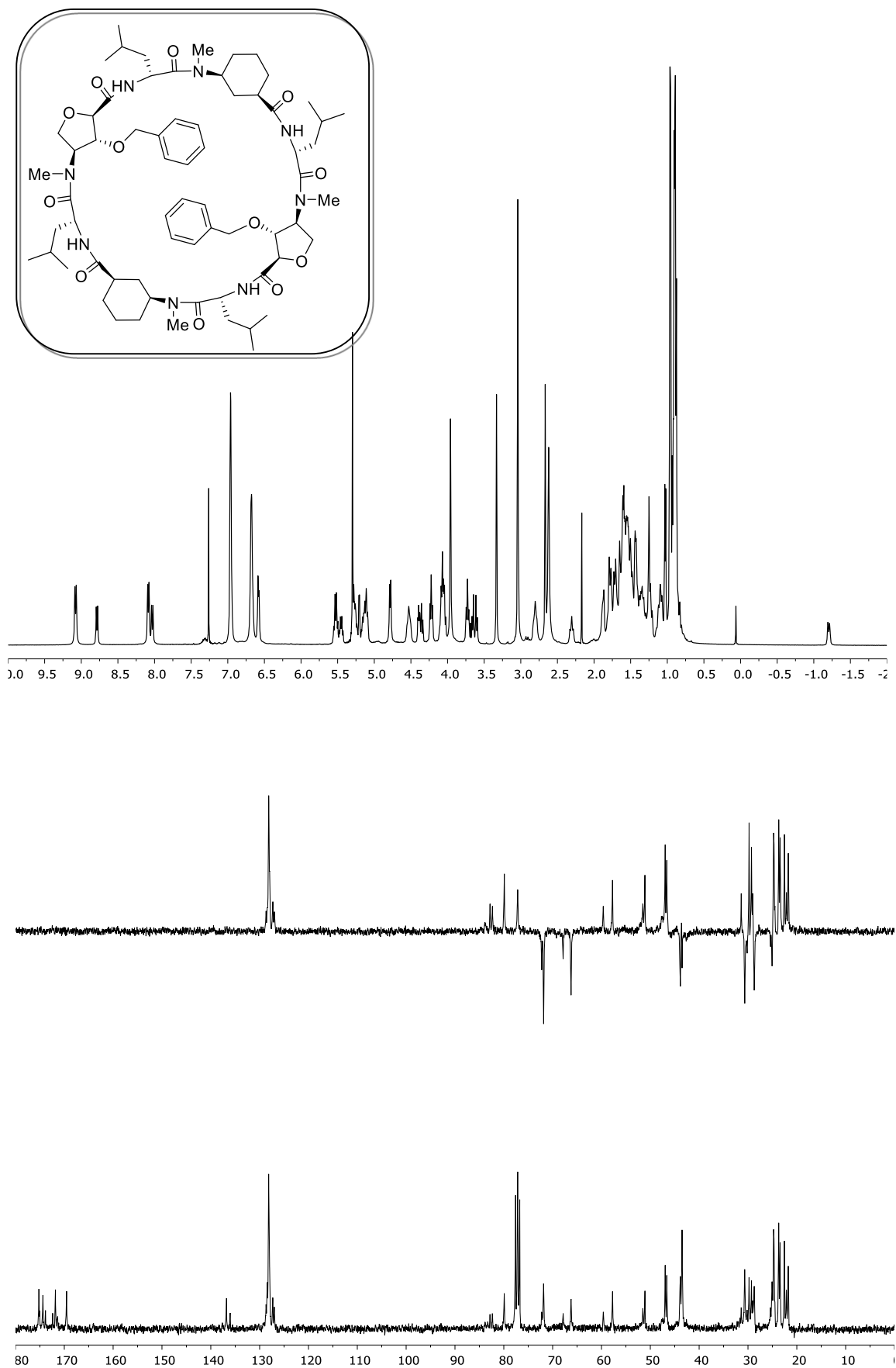
COSY (16 mM, CDCl₃, 298 K, 500 MHz).
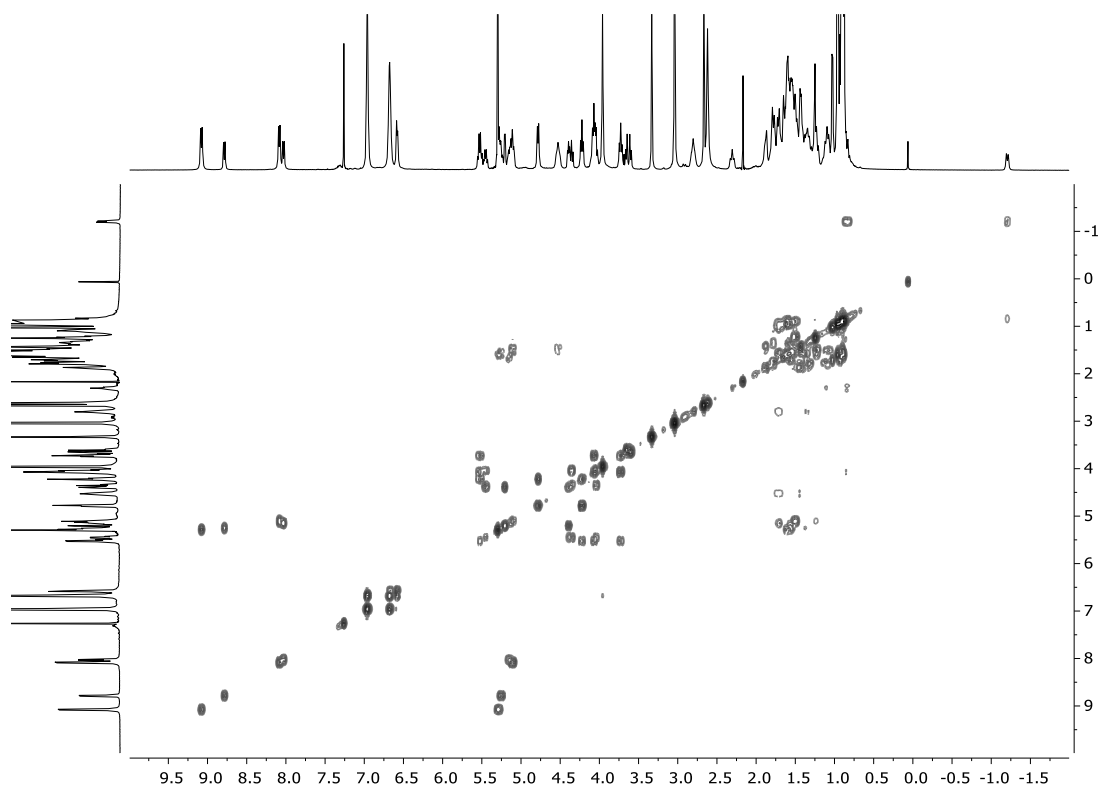
TOCSY (16 mM, CDCl₃, 298 K, 500 MHz).
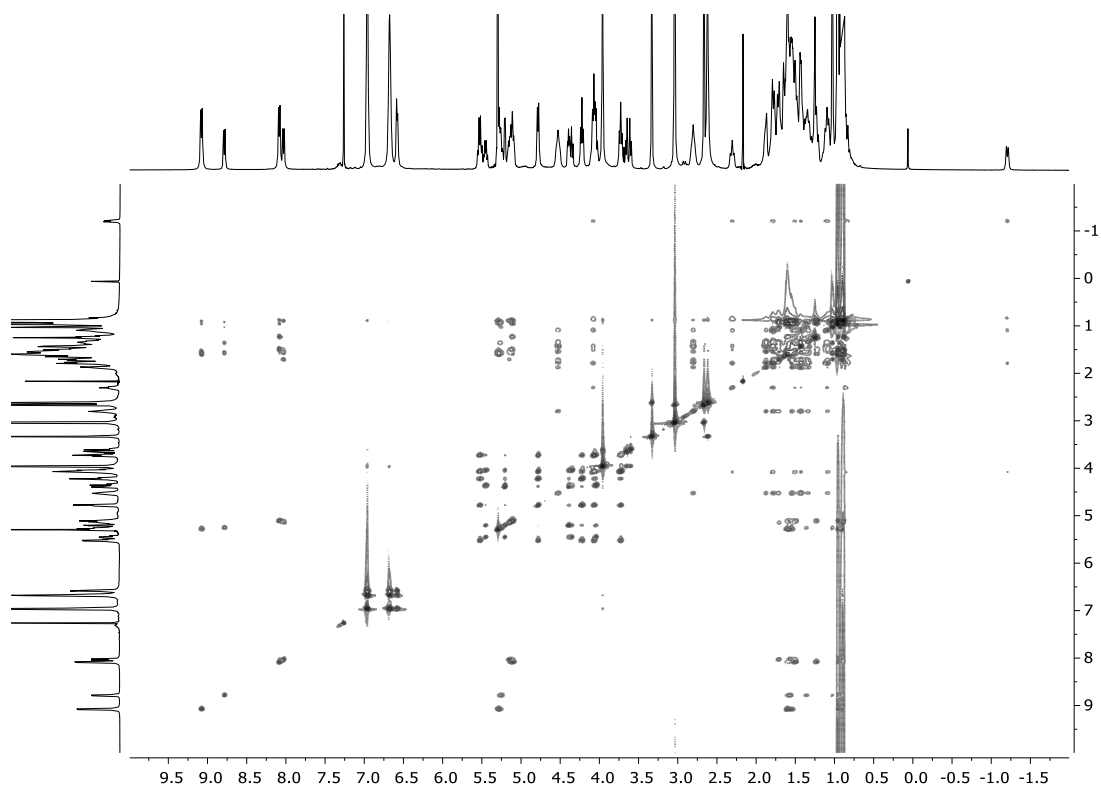
NOESY (16 mM, CDCl₃, 298 K, 500 MHz).
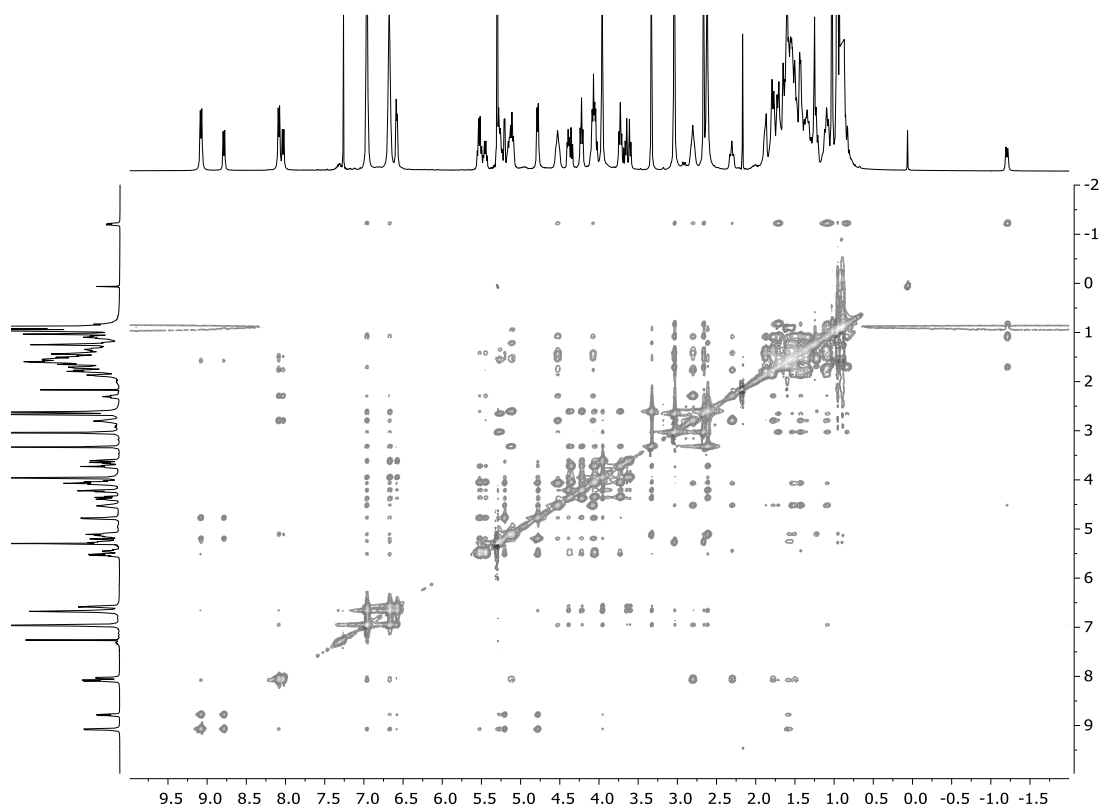
ROESY (16 mM, CDCl₃, 298 K, 500 MHz).

FTIR (298 K, CHCl₃):

Spectrum peaks: 3307.32 cm-1, 3066.26 cm-1, 2954.41 cm-1, 2925.18 cm-1, 2865.7 cm-1, 1677.77 cm-1, 1625.7 cm-1, 1526.38 cm-1
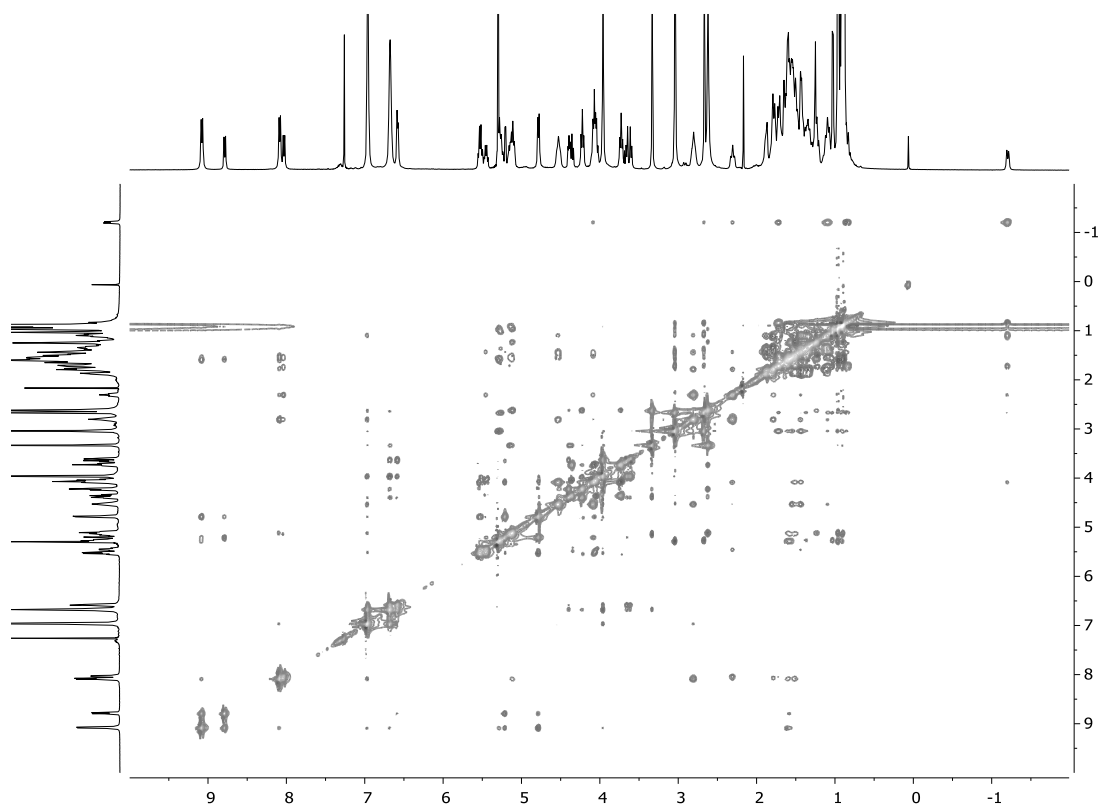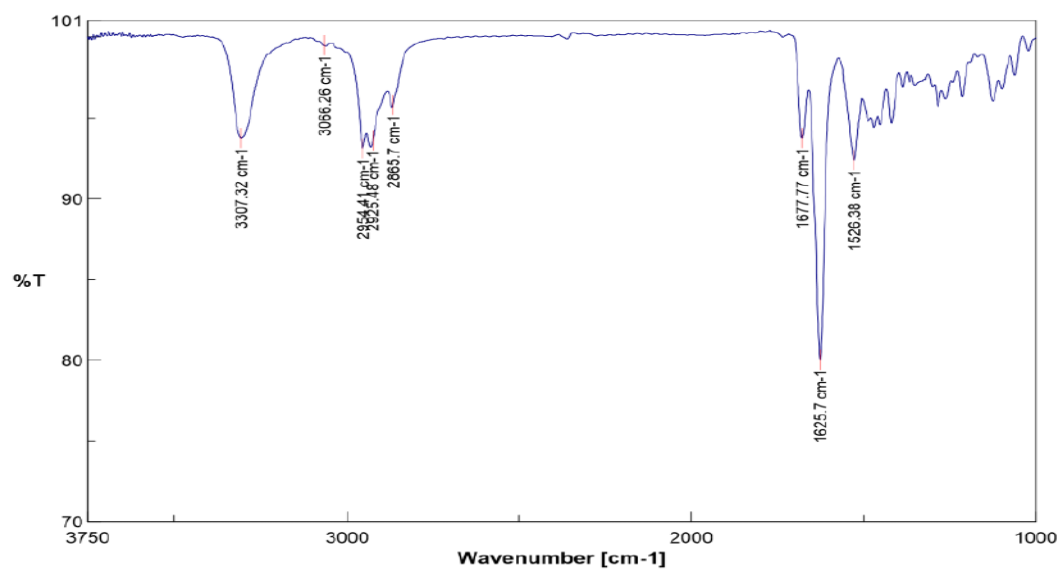
***c*-{[*L*-Me*N*-Ahf-*D*-Leu1-*L*-MeN-Ach-*D*-Leu2-]2} (CP4):**

1H NMR (5 mM, CDCl3, 298 K, 500 MHz).
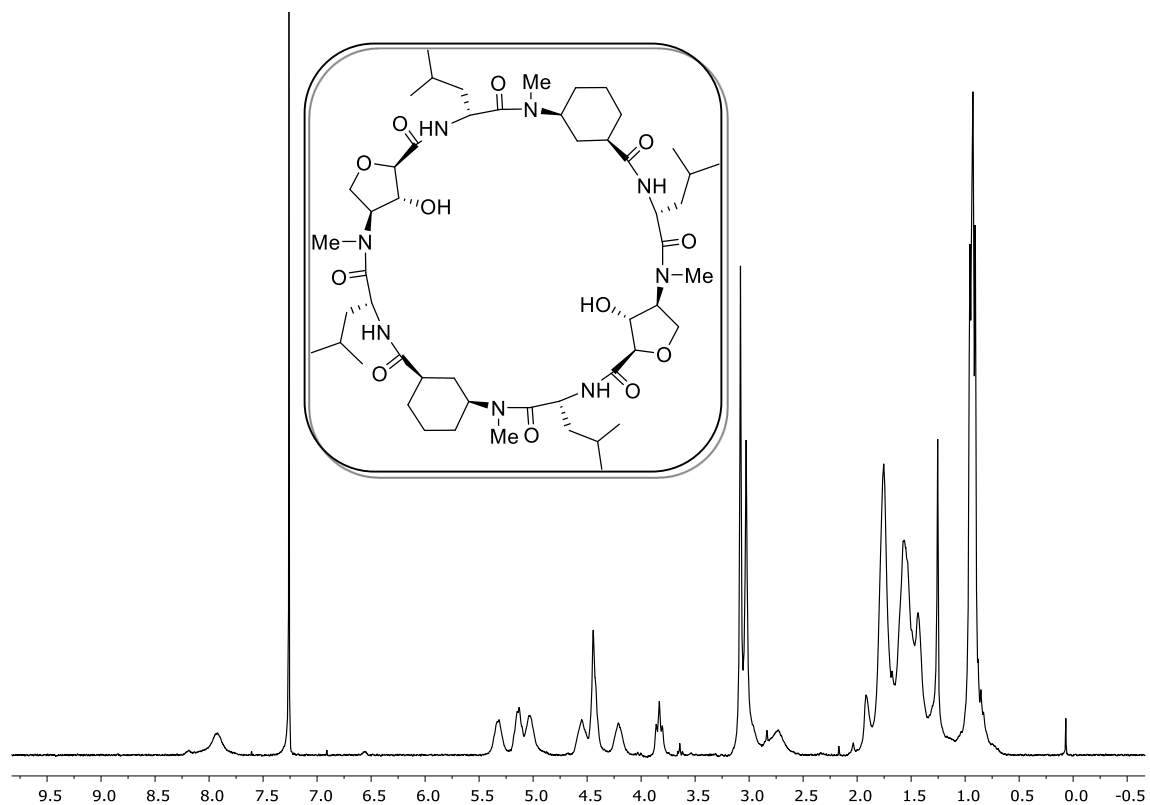
1H NMR (32 mM, CDCl3, 253 K, 500 MHz).
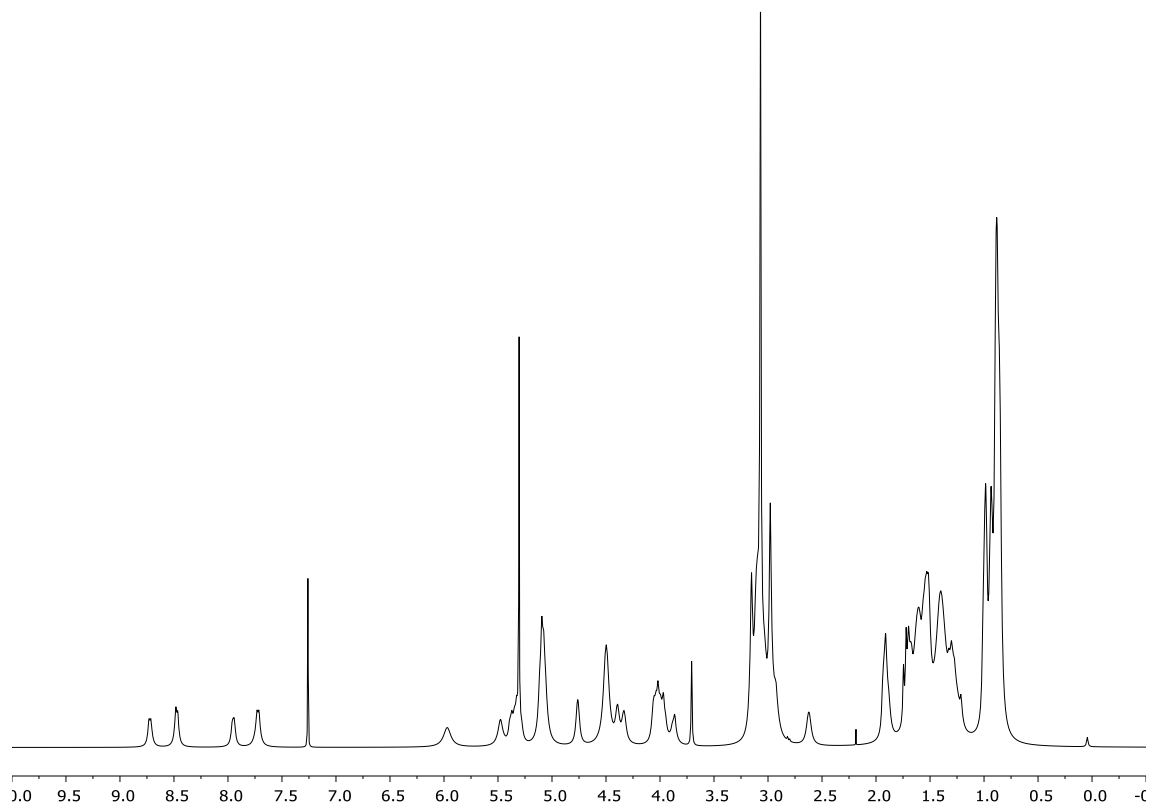
COSY (16 mM, CDCl$_3$, 253 K, 500 MHz).
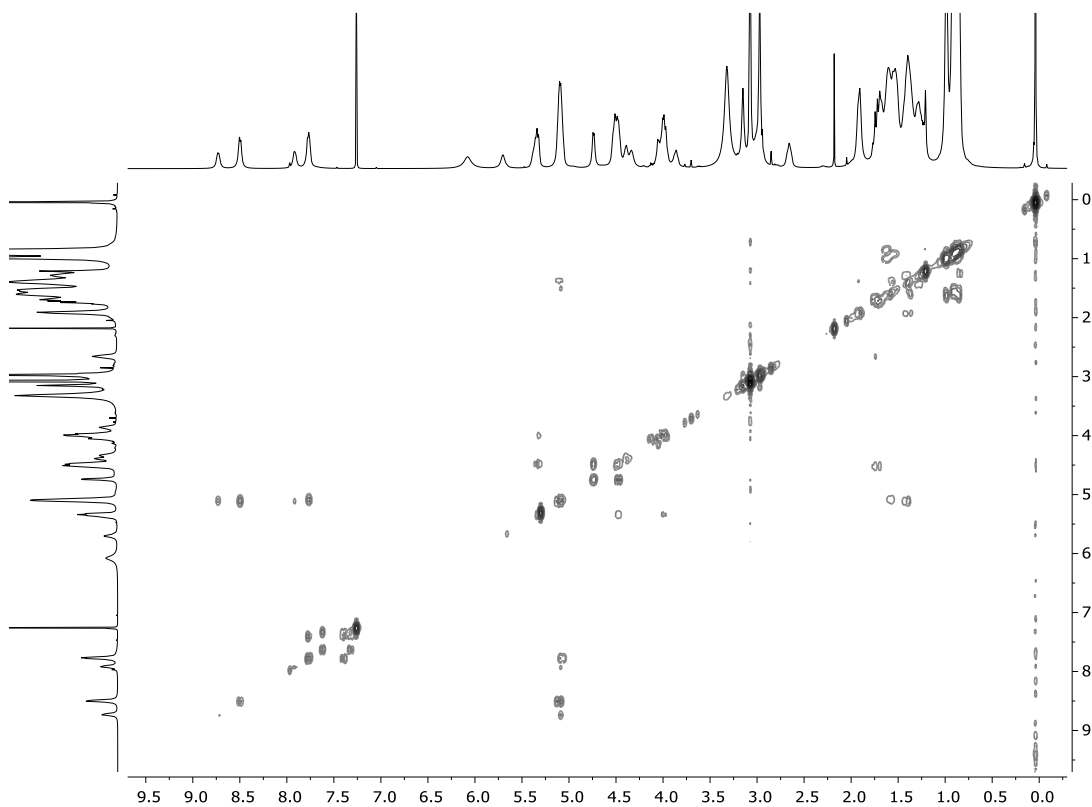
TOCSY (16 mM, CDCl$_3$, 253 K, 500 MHz).
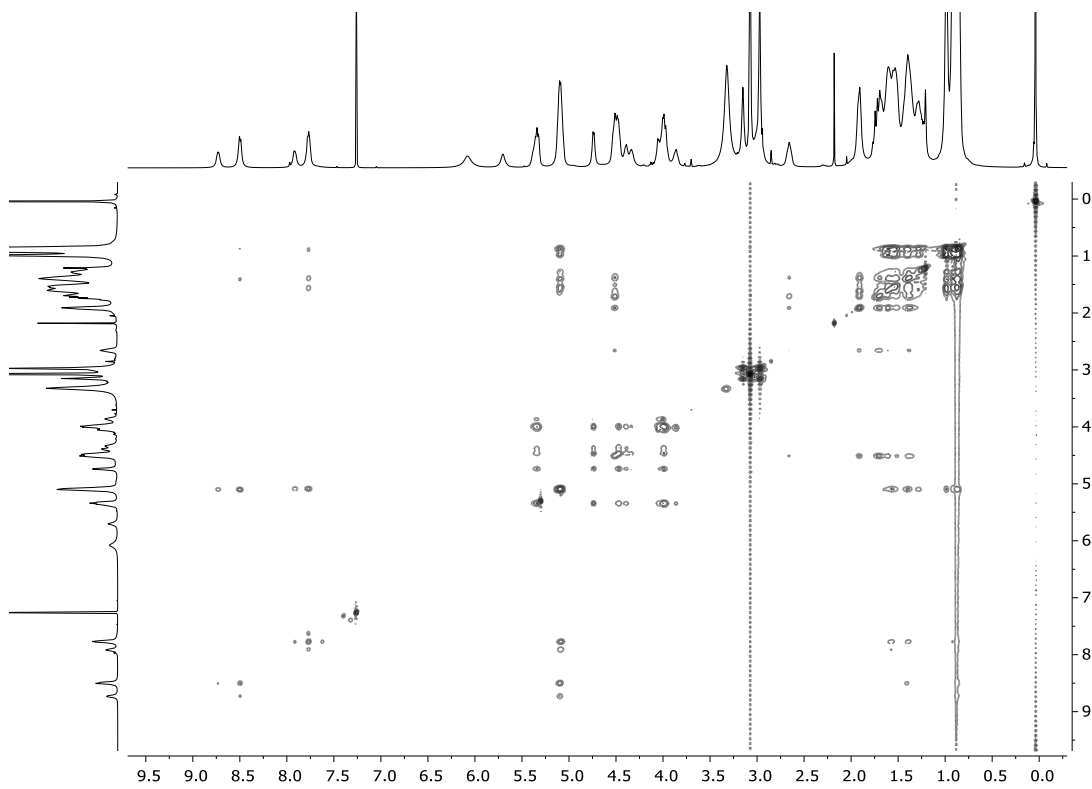
ROESY (16 mM, CDCl$_3$, 253 K, 500 MHz).
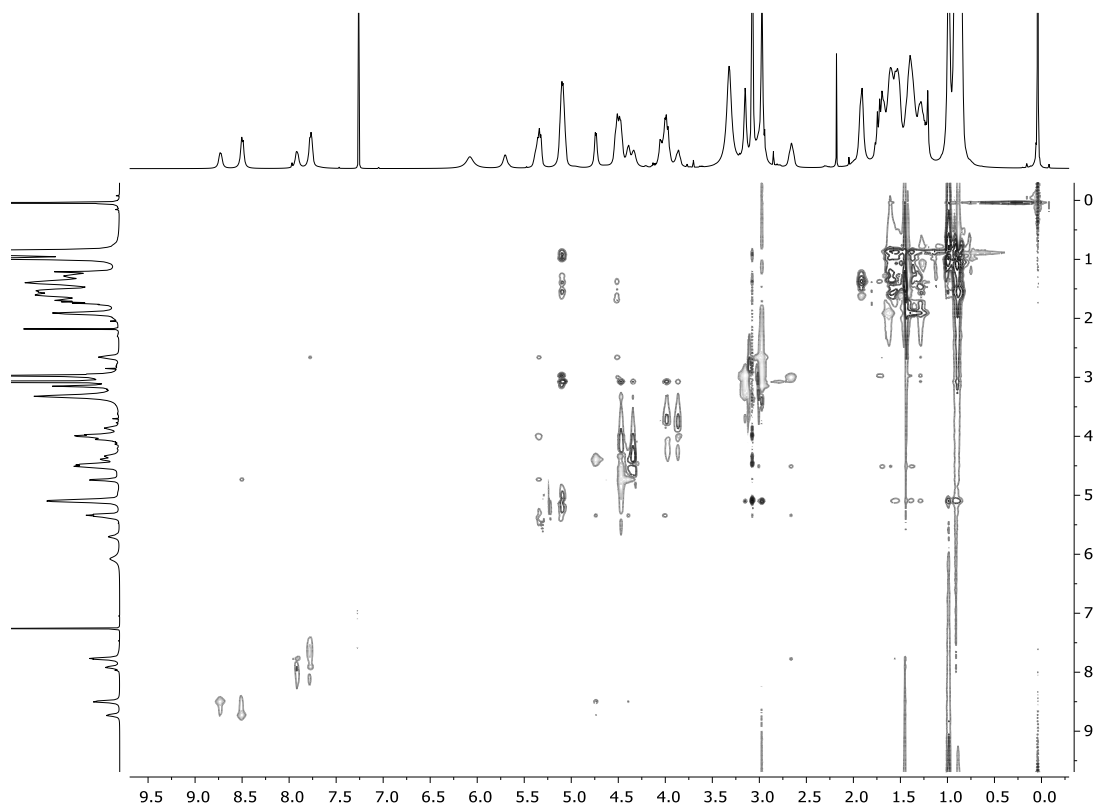
^{1}H NMR (32 mM, 5% CD$_3$OH/CDCl$_3$, 253 K, 500 MHz).
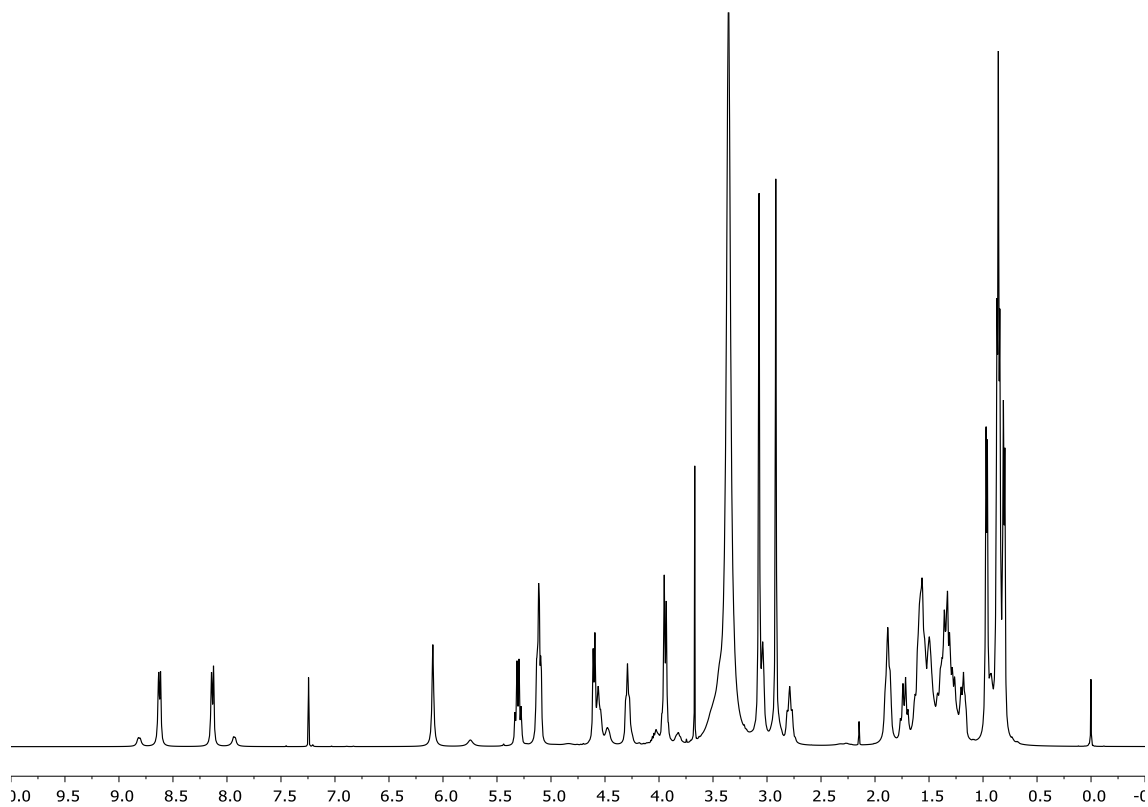
COSY (32 mM, 5% CD$_3$OH/CDCl$_3$, 253 K, 500 MHz).
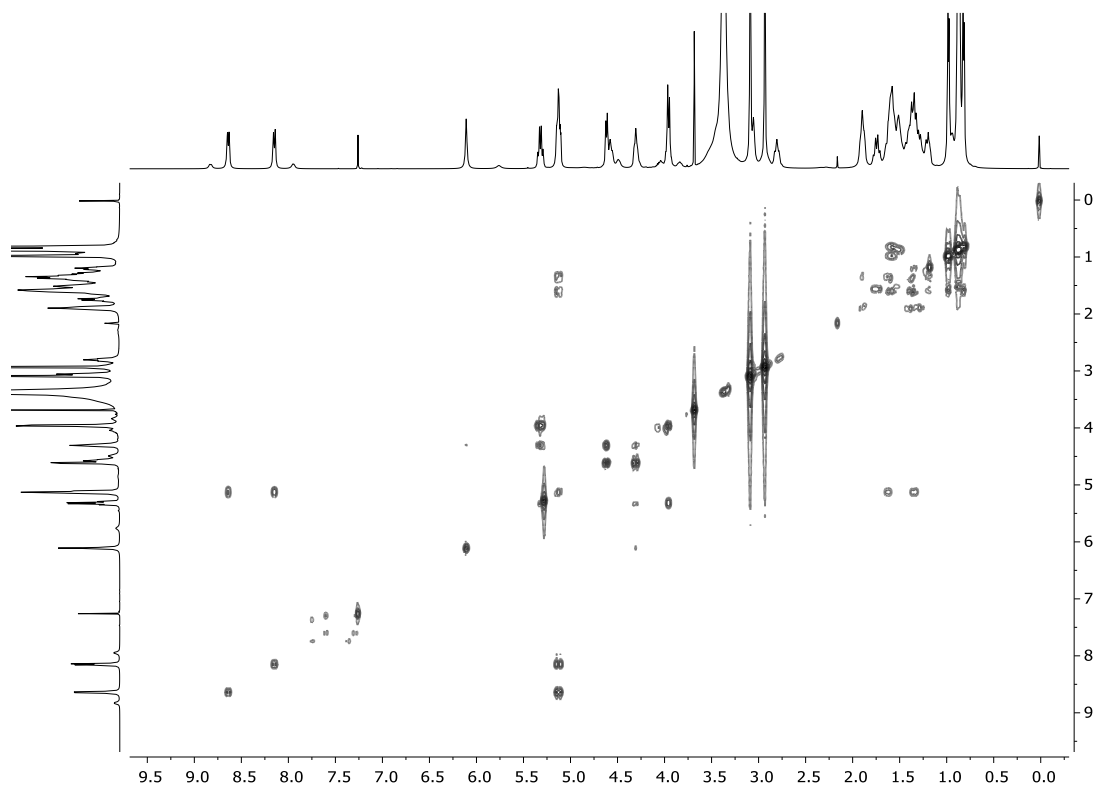
TOCSY (32 mM, 5% CD$_3$OH/CDCl$_3$, 253 K, 500 MHz).
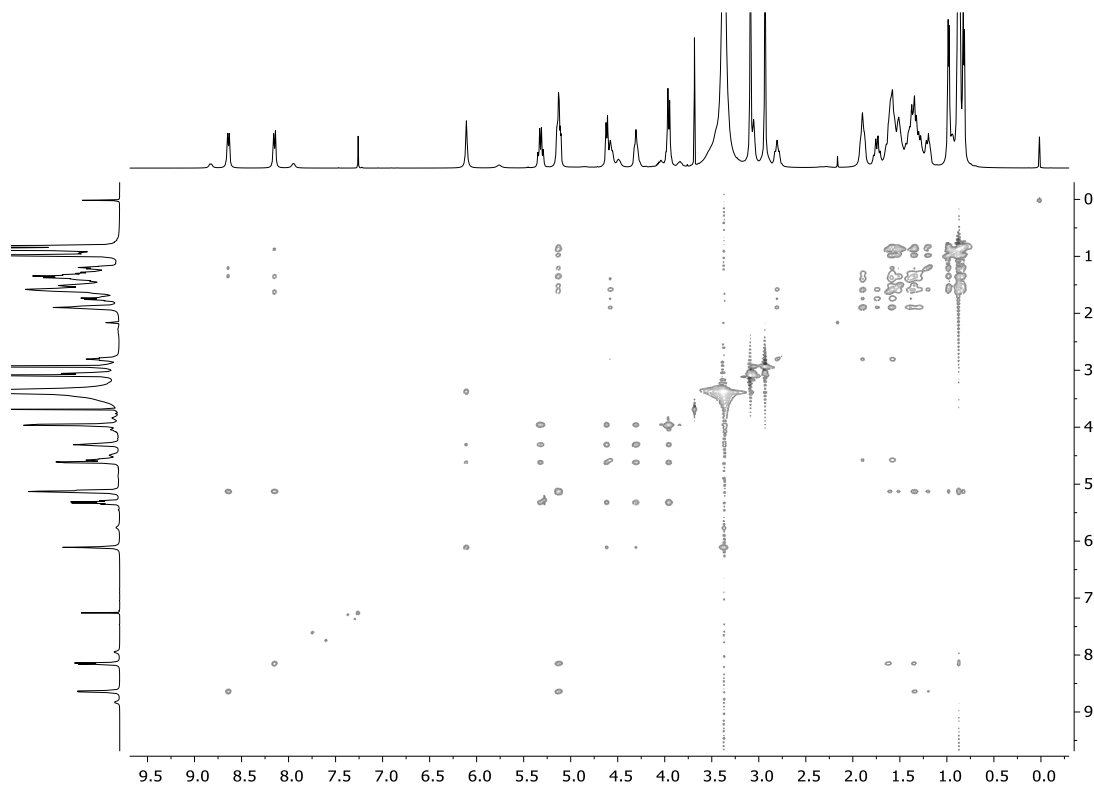
ROESY (32 mM, 5% CD$_3$OH/CDCl$_3$, 253 K, 500 MHz).
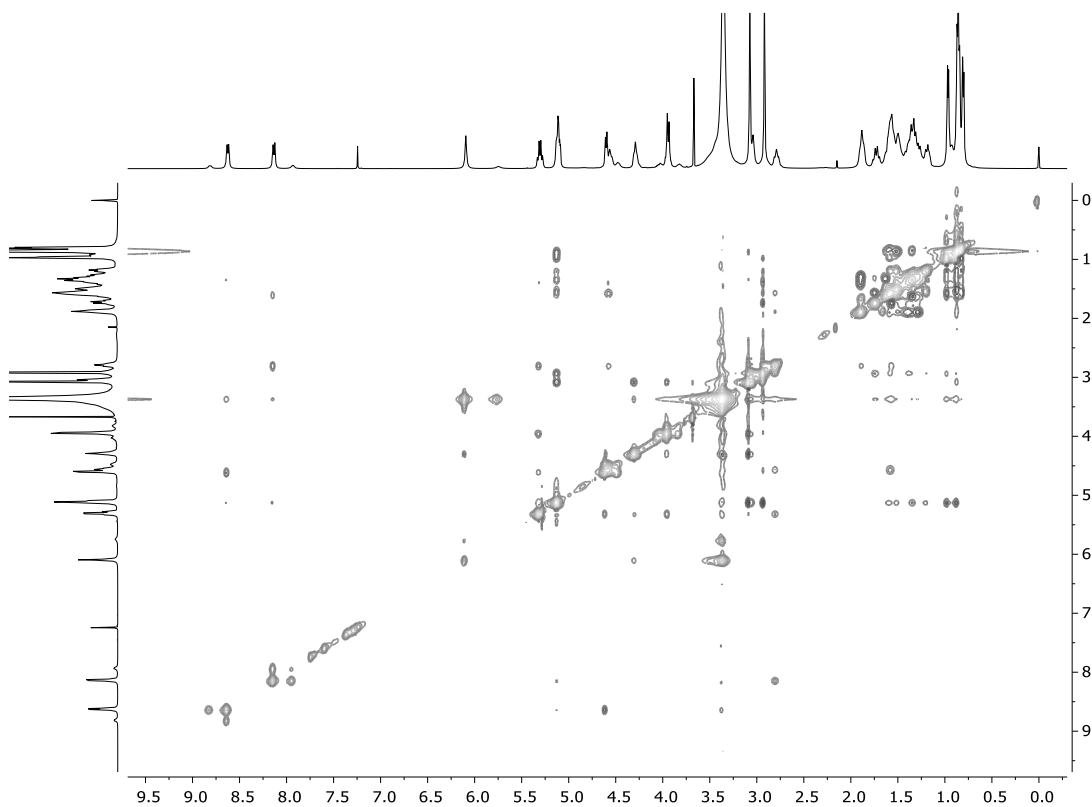
FTIR (298 K, CHCl$_3$):
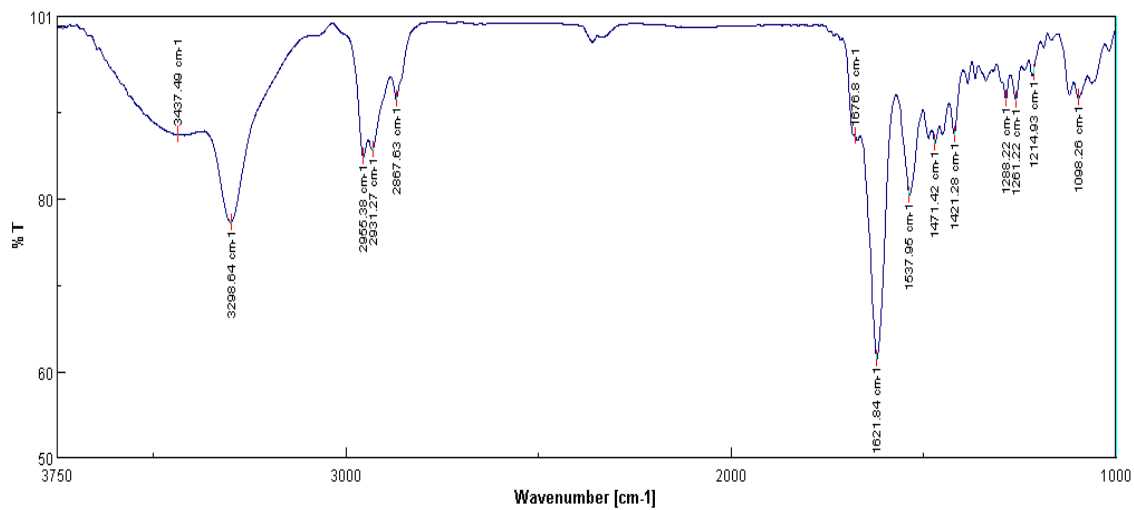
c-[*L*-^{Me}*N*-Ahf(pic)-*D*-Leu¹-*L*-^{Me}*N*-Ach¹-*D*-Leu²-*L*-^{Me}*N*-Ahf-*D*-Leu³-*L*-^{Me}*N*-Ach²-*D*-Leu⁴-] (CP5):

^{1}H NMR (CDCl$_3$, 298 K, 300 MHz).
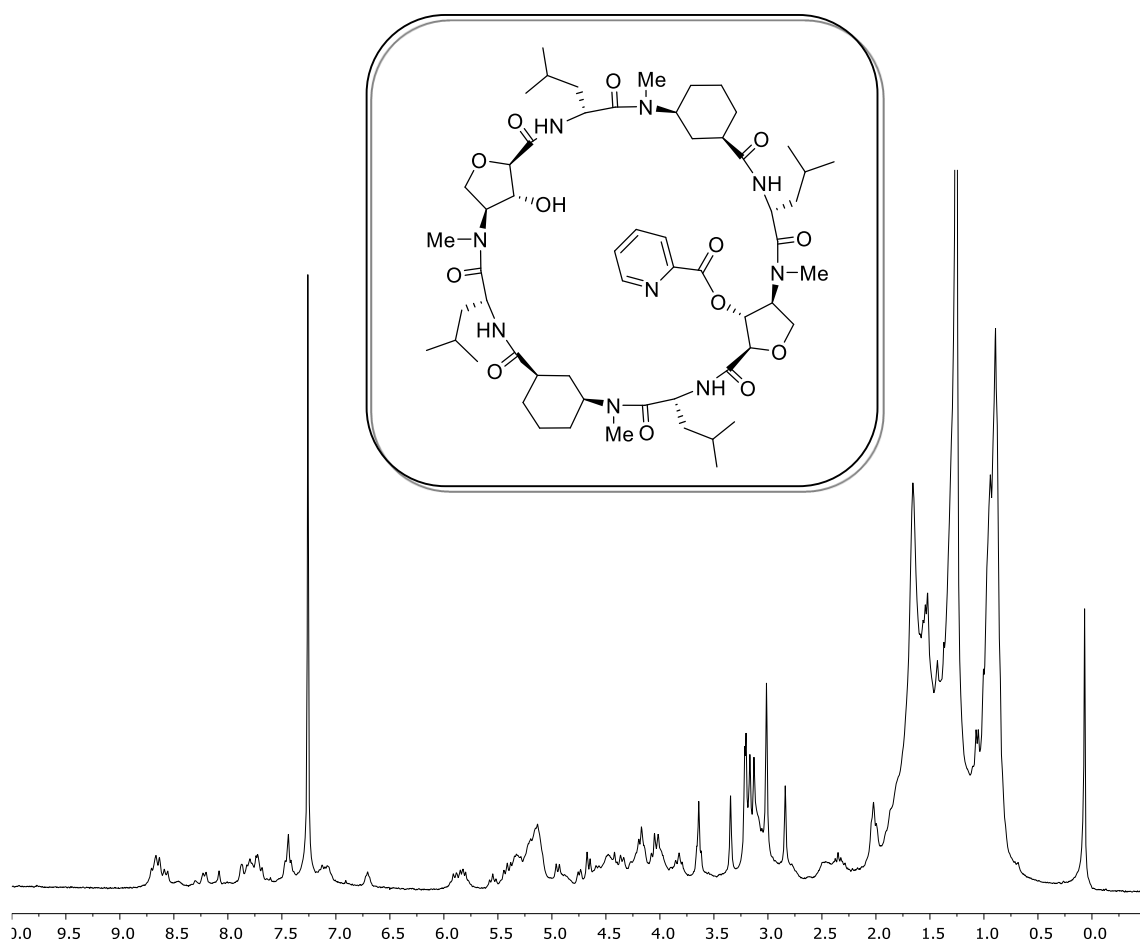
FTIR (298 K, CHCl$_3$):
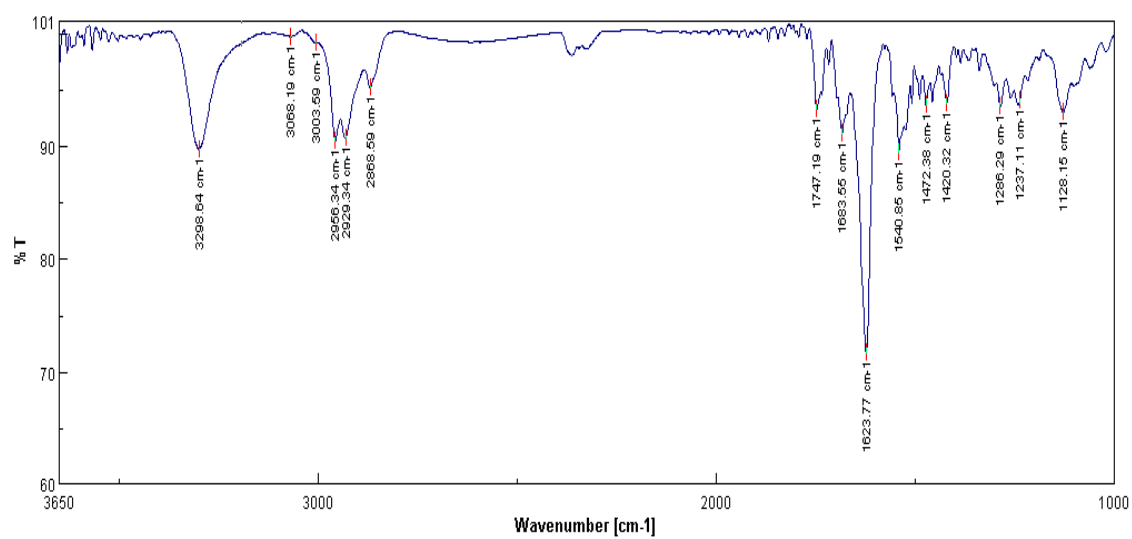
c-[*L*-^{Me}*N*-Ahf(pic)-*D*-Leu¹-*L*-^{Me}*N*-Ach¹-*D*-Leu²-*L*-^{Me}*N*-Ahf-*D*-Leu³-*L*-^{Me}*N*-Ach²-*D*-Leu⁴-] + 0.5 equiv of AgBF₄ (*s*-D5ₑ⊃Ag): ¹H NMR (4.5 mM, CDCl₃, 298 K, 500 MHz).
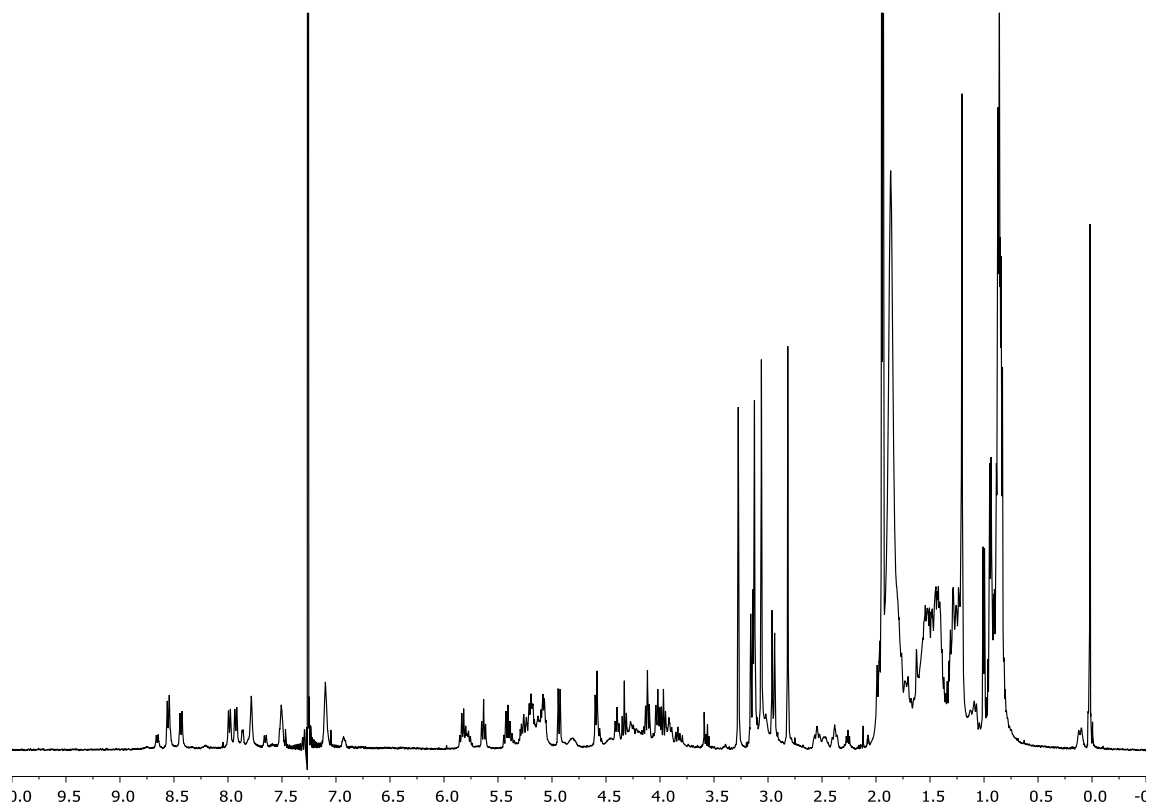
COSY (4.5 mM, CDCl₃, 298 K, 500 MHz).

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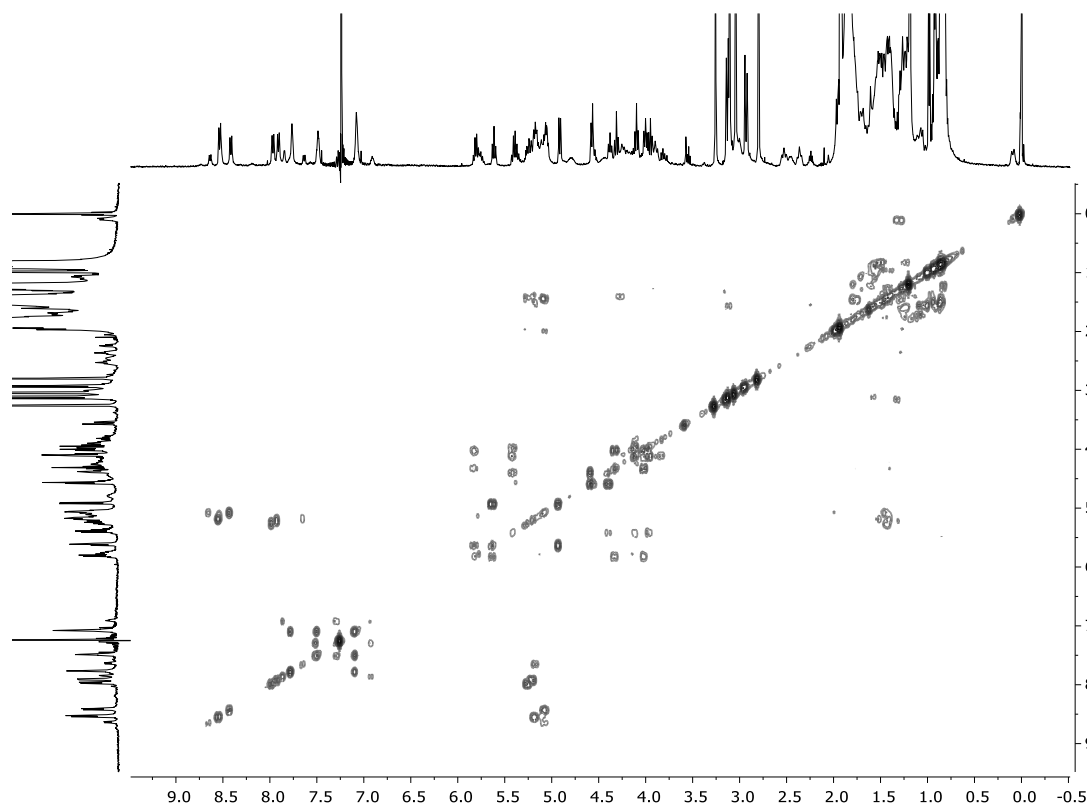
TOCSY (4.5 mM, CDCl$_3$, 298 K, 500 MHz).
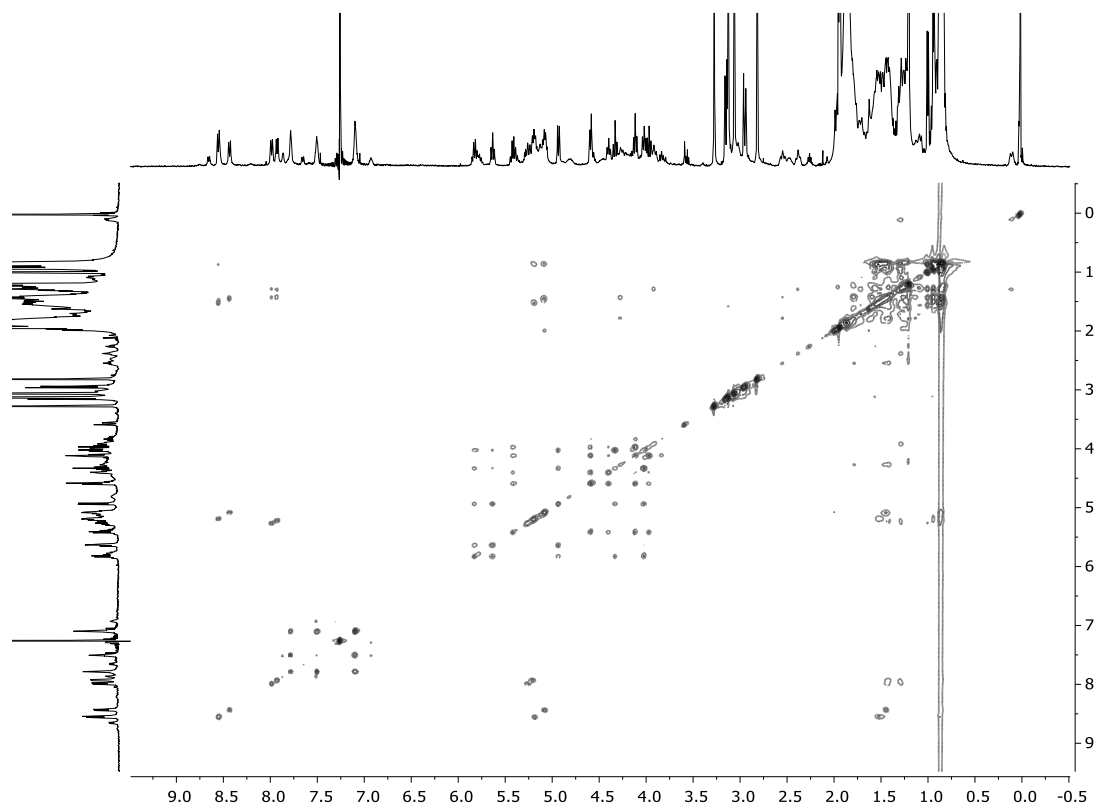
NOESY (4.5 mM, CDCl$_3$, 298 K, 500 MHz).
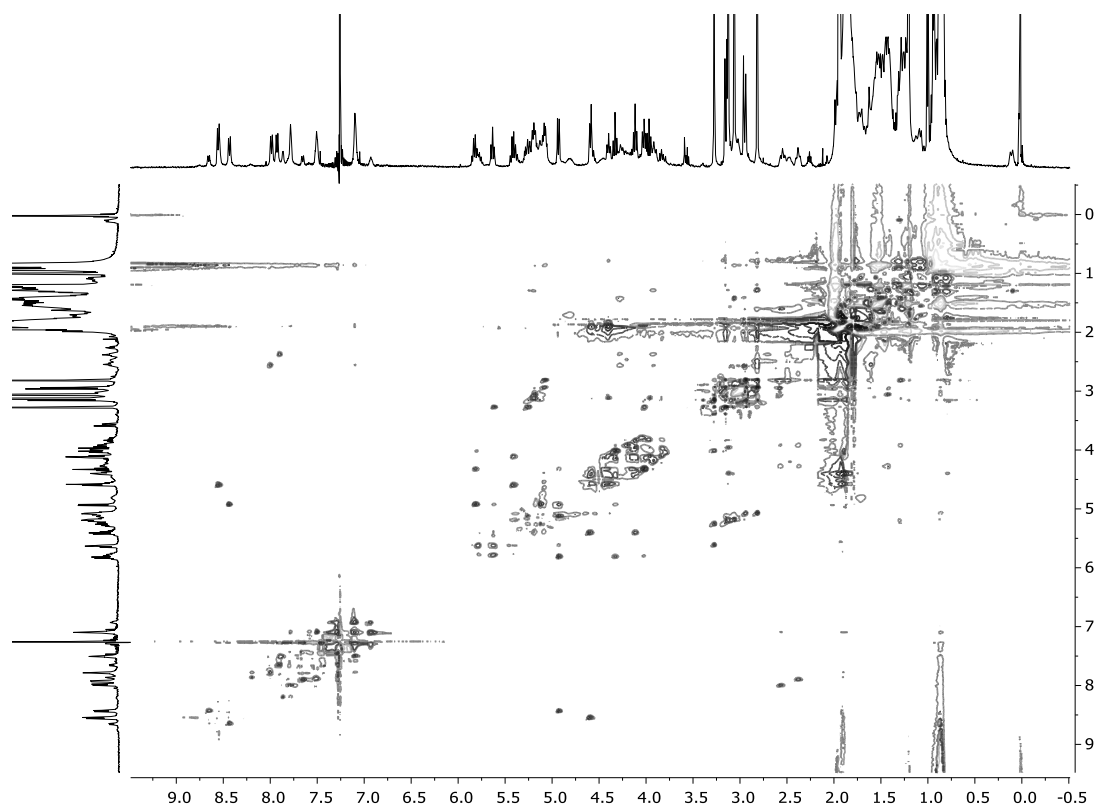
ROESY (4.5 mM, CDCl$_3$, 298 K, 500 MHz).
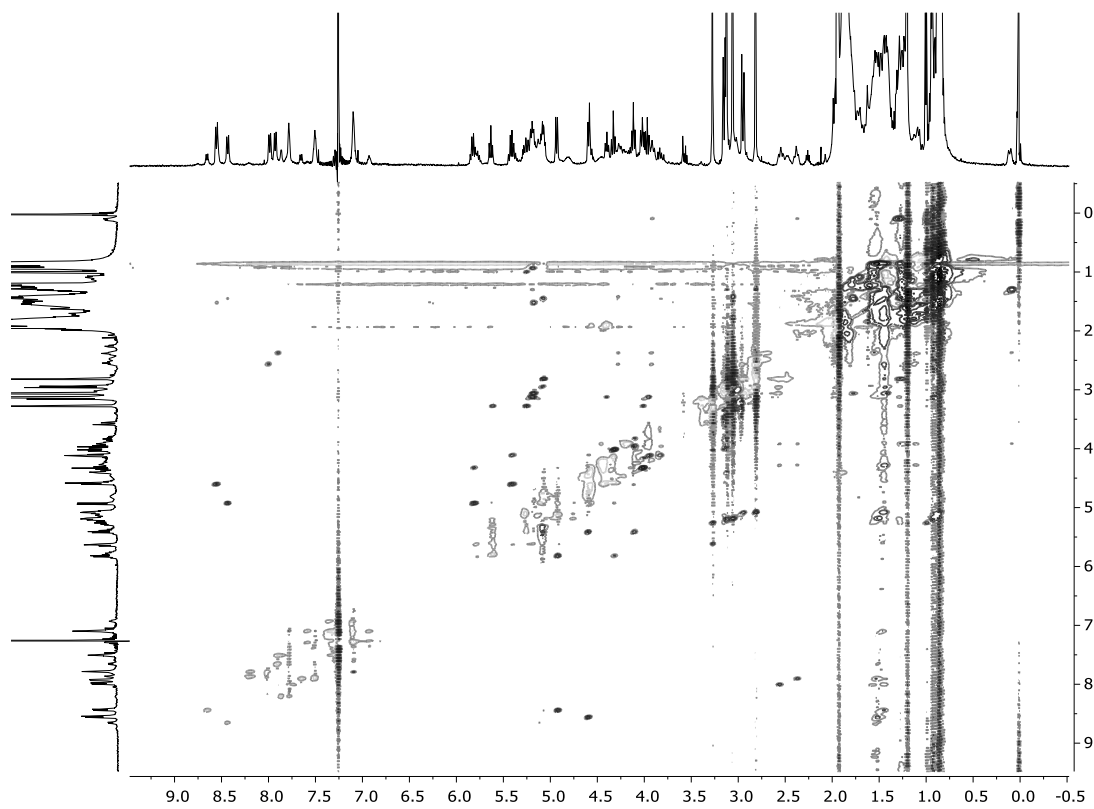
c-[*L*-Me*N*-Ahf(pic)-*D*-Leu[1]-*L*-Me*N*-Ach[1]-*D*-Leu[2]-*L*-Me*N*-Ahf-*D*-Leu[3]-*L*-Me*N*-Ach[2]-*D*-Leu[4]-] + 0.5 equiv of (CO₂H)₂ · 2H₂O (*s*-D5$_E$⊃(CO₂H)₂): ¹H NMR (5 mM, CDCl₃, 298 K, 500 MHz).
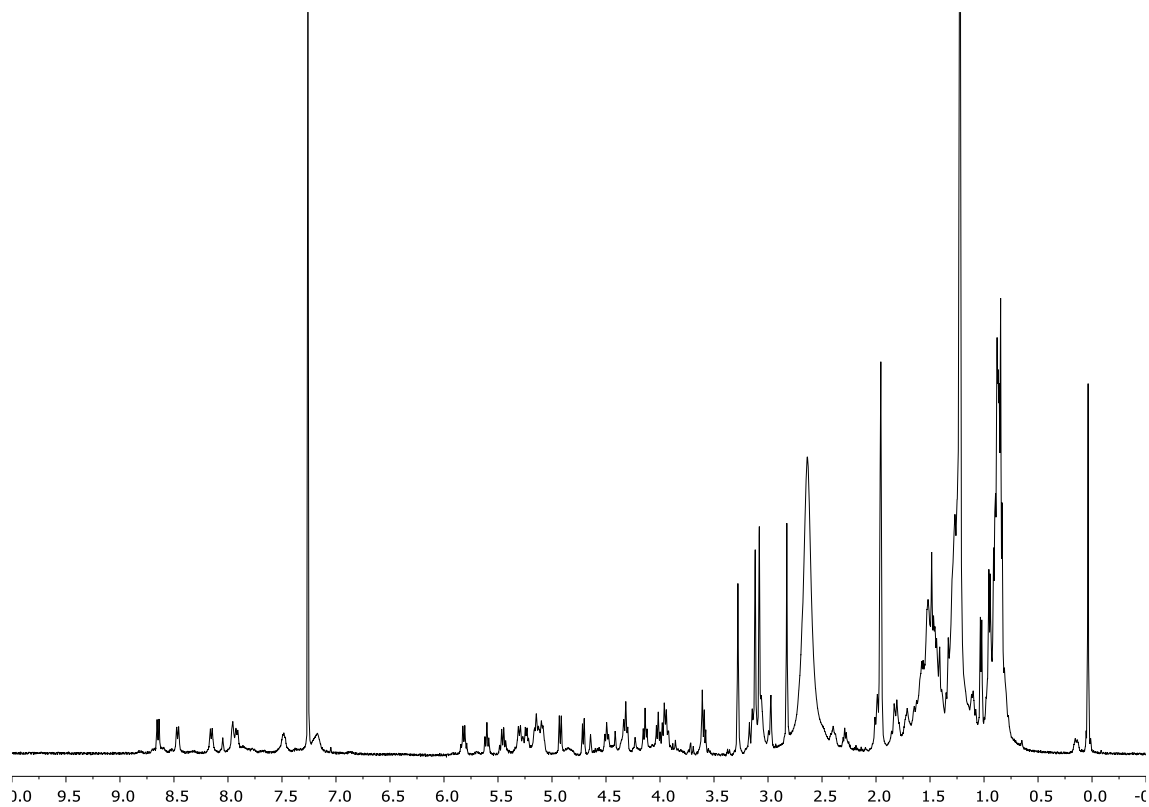
COSY (5 mM, CDCl₃, 298 K, 500 MHz).

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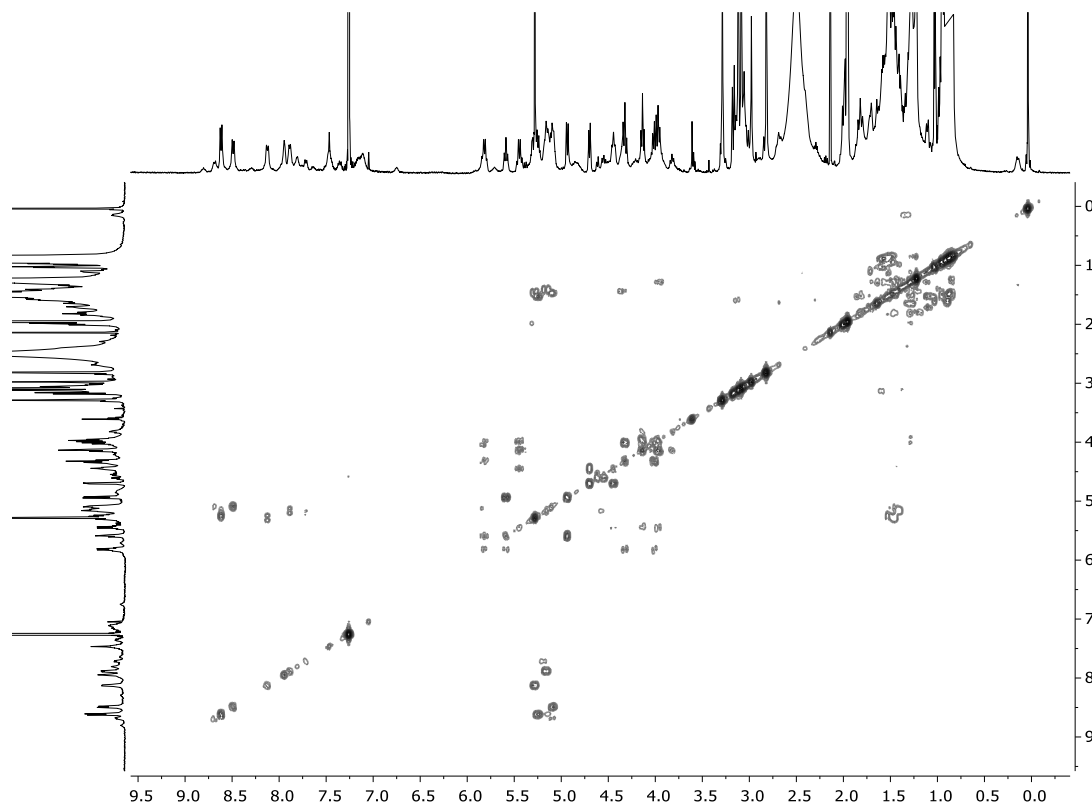
TOCSY (5 mM, CDCl$_3$, 298 K, 500 MHz).
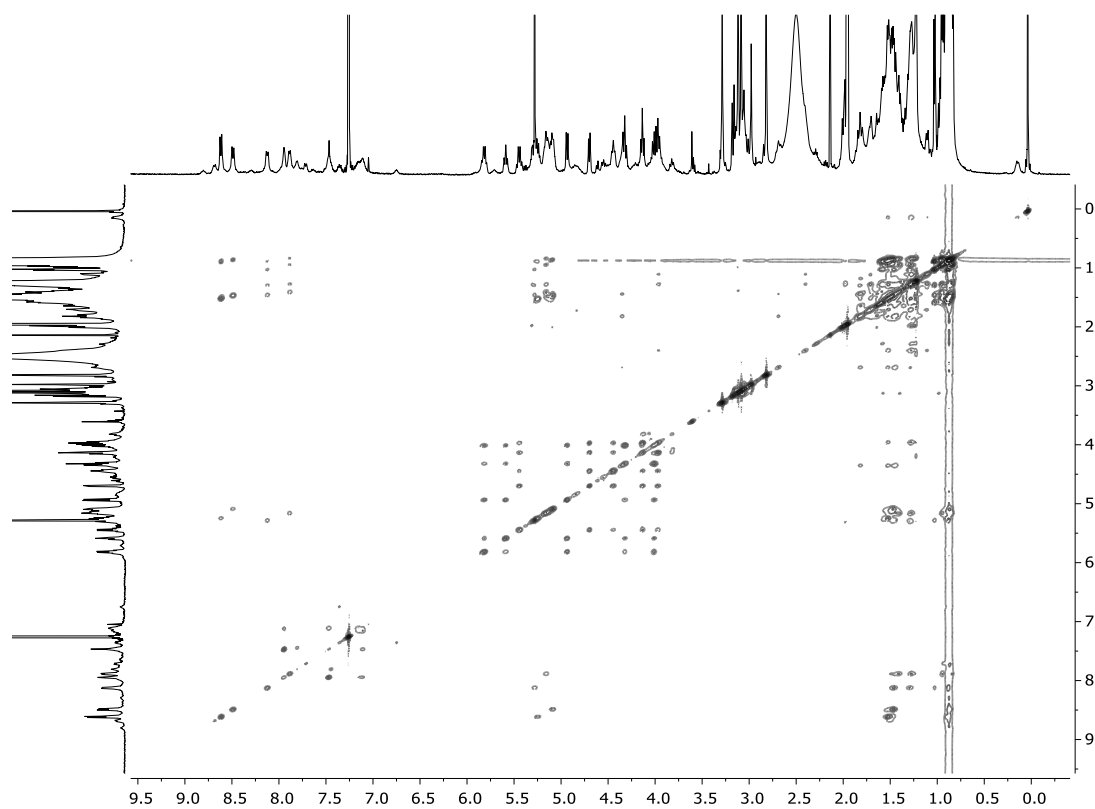
NOESY (5 mM, CDCl$_3$, 298 K, 500 MHz).
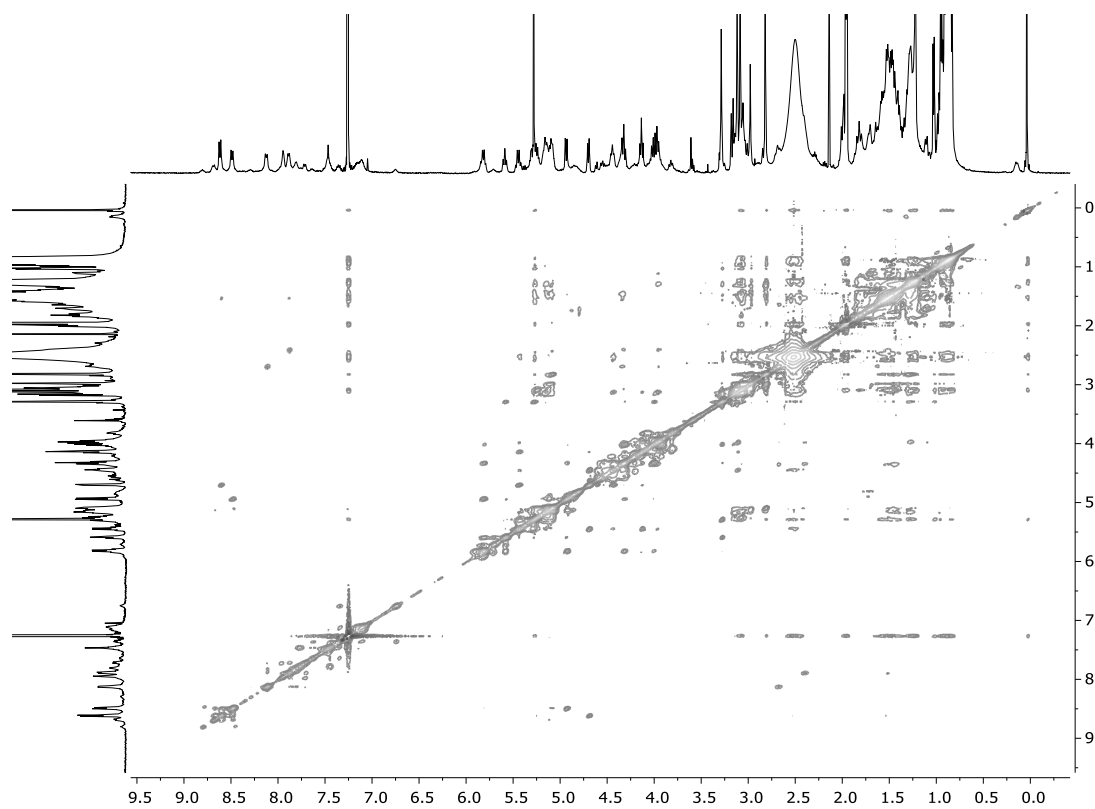
ROESY (5 mM, CDCl$_3$, 298 K, 500 MHz).
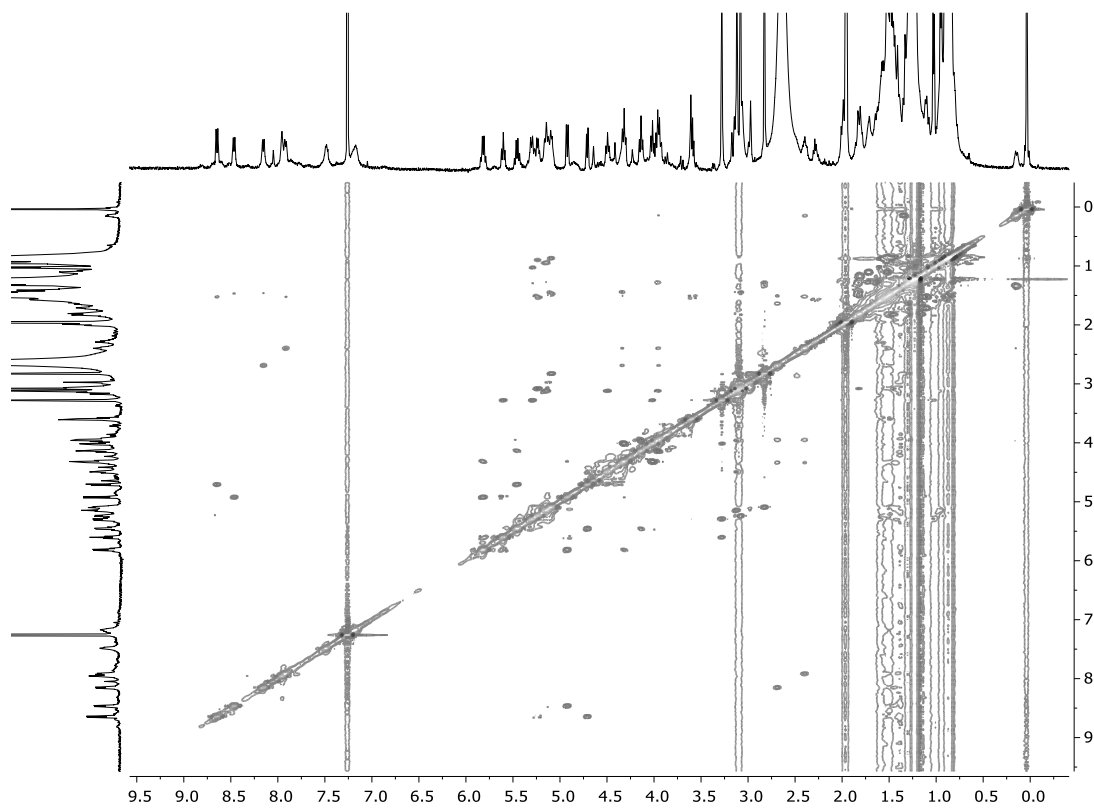
Computational methods:

The starting geometries of the cyclic peptides investigated in this work were constructed from X-ray crystallographic data of related compounds: *c*-[(*D*-Phe-*L*-^{Me}N-γ-Ach-)4][1] and previous simulations carried out with related systems[2]. The silver complex from these dimers was built using the optimized structures of bis(methyl picolinate) silver(I) complexes. All DFT calculations were carried out using the B3LYP[3] functional with the standard 6-31G(d) basis set for C, N, O and H[4] and Lanl2dz pseudopotential basis set for Ag[5], as implemented in the Gaussian 09[6] program package.

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[3] Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys*. **1993**, *98*, 5648-52.

[4] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, 1st ed.; Wiley: New York, 1986.

[5] Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations - potentials for the transition-metal atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270-83.

[6] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. et al., *Gaussian 09, Revision A.01, Gaussian Inc.*, Wallingford, CT, USA, **2009**.

Geometries

Cartesian coordinates (Å) of conformations optimized at the B3LYP/6-31G(d) basis set for C, N, O and H and Lanl2dz pseudopotential basis set for Ag

Square planar bis(methyl picolinate) silver(I) complex

```
---------------------------------------------------------------
Center     Atomic     Atomic        Coordinates (Angstroms)
Number     Number      Type         X          Y          Z
---------------------------------------------------------------
   1          6          0       4.129494   -3.235475   0.341259
   2          6          0       3.326356    3.043674  -0.277417
   3          6          0       2.106282    2.367067  -0.224799
   4          7          0       2.023797    1.035051  -0.100148
   5          6          0       3.164118    0.318997  -0.020096
   6          6          0       4.423229    0.918155  -0.065254
   7          6          0       4.503849    2.305581  -0.196990
   8          6          0       2.998973   -1.171098   0.123802
   9          8          0       4.169768   -1.796073   0.196482
  10          8          0       1.917643   -1.736553   0.169547
  11          6          0      -4.133667    3.233334   0.341120
  12          8          0      -4.172184    1.793882   0.196269
  13          6          0      -3.322343   -3.044836  -0.277613
  14          6          0      -2.103201   -2.366545  -0.224914
  15          7          0      -2.022628   -1.034423  -0.100252
  16          6          0      -3.163919   -0.319958  -0.020261
  17          6          0      -4.422205   -0.920830  -0.065500
  18          6          0      -4.500866   -2.308371  -0.197258
  19          6          0      -3.000653    1.170314   0.123702
  20          8          0      -1.919984    1.737045   0.169578
  21         47          0      -0.000048    0.001765  -0.022877
  22          1          0       3.606483   -3.502706   1.261834
  23          1          0       3.622283   -3.682319  -0.516340
  24          1          0       5.171958   -3.546543   0.381762
  25          1          0       3.340425    4.123593  -0.379162
  26          1          0       1.164464    2.903538  -0.282526
  27          1          0       5.313111    0.305151   0.002105
  28          1          0       5.471180    2.796775  -0.234872
  29          1          0      -5.176512    3.543130   0.381553
  30          1          0      -3.611049    3.501150   1.261746
  31          1          0      -3.626926    3.680825  -0.516419
  32          1          0      -3.334935   -4.124773  -0.379366
  33          1          0      -1.160595   -2.901643  -0.282567
  34          1          0      -5.312946   -0.309063   0.001815
  35          1          0      -5.467507   -2.800917  -0.235219
---------------------------------------------------------------
```

Perpendicularly oriented bis(methyl picolinate) silver(I) complex

```
---------------------------------------------------------------------
Center     Atomic      Atomic          Coordinates (Angstroms)
Number     Number       Type          X           Y           Z
---------------------------------------------------------------------
   1          6           0        4.129494   -3.235475    0.341259
   2          6           0        3.326356    3.043674   -0.277417
   3          6           0        2.106282    2.367067   -0.224799
   4          7           0        2.023797    1.035051   -0.100148
   5          6           0        3.164118    0.318997   -0.020096
   6          6           0        4.423229    0.918155   -0.065254
   7          6           0        4.503849    2.305581   -0.196990
   8          6           0        2.998973   -1.171098    0.123802
   9          8           0        4.169768   -1.796073    0.196482
  10          8           0        1.917643   -1.736553    0.169547
  11          6           0       -4.133667    3.233334    0.341120
  12          8           0       -4.172184    1.793882    0.196269
  13          6           0       -3.322343   -3.044836   -0.277613
  14          6           0       -2.103201   -2.366545   -0.224914
  15          7           0       -2.022628   -1.034423   -0.100252
  16          6           0       -3.163919   -0.319958   -0.020261
  17          6           0       -4.422205   -0.920830   -0.065500
  18          6           0       -4.500866   -2.308371   -0.197258
  19          6           0       -3.000653    1.170314    0.123702
  20          8           0       -1.919984    1.737045    0.169578
  21         47           0       -0.000048    0.001765   -0.022877
  22          1           0        3.606483   -3.502706    1.261834
  23          1           0        3.622283   -3.682319   -0.516340
  24          1           0        5.171958   -3.546543    0.381762
  25          1           0        3.340425    4.123593   -0.379162
  26          1           0        1.164464    2.903538   -0.282526
  27          1           0        5.313111    0.305151    0.002105
  28          1           0        5.471180    2.796775   -0.234872
  29          1           0       -5.176512    3.543130    0.381553
  30          1           0       -3.611049    3.501150    1.261746
  31          1           0       -3.626926    3.680825   -0.516419
  32          1           0       -3.334935   -4.124773   -0.379366
  33          1           0       -1.160595   -2.901643   -0.282567
  34          1           0       -5.312946   -0.309063    0.001815
  35          1           0       -5.467507   -2.800917   -0.235219
---------------------------------------------------------------------
```

Syn-eclipsed dimer

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	47	0	0.745805	-0.189113	0.018908
2	6	0	-5.781976	4.035521	-2.455178
3	6	0	0.647979	-2.253207	2.460937
4	6	0	-3.405474	4.624260	-2.630207
5	6	0	-2.272957	5.455639	-2.009179
6	6	0	-0.877064	4.831939	-2.179156
7	6	0	-0.027689	6.051546	-2.563265
8	6	0	1.329090	0.479310	5.006467
9	6	0	2.300218	5.571976	-2.195236
10	6	0	1.065067	-0.785365	4.478265
11	6	0	1.468979	5.508053	-4.546469
12	6	0	-1.017468	6.816821	-3.450465
13	6	0	0.939188	-0.923988	3.096730
14	6	0	1.319744	1.331999	2.765445
15	6	0	1.456522	1.558029	4.138536
16	6	0	-6.989822	4.890436	-2.048098
17	6	0	-6.009968	1.833796	-4.315361
18	6	0	-6.493472	0.237385	-2.408727
19	6	0	-5.433062	-0.813506	-2.782735
20	6	0	-7.896283	-0.156542	-2.902799
21	6	0	-8.281680	-1.546866	-2.377667
22	6	0	-7.244069	-2.603020	-2.777485
23	6	0	-5.821626	-2.220519	-2.295758
24	6	0	-4.834493	-3.267035	-2.820879
25	6	0	-6.489187	5.548111	2.166710
26	6	0	-3.941318	-5.519573	-2.516439
27	6	0	-4.562574	-6.865384	-2.109915
28	6	0	-2.524364	-5.402980	-1.928425
29	6	0	-5.431138	4.529140	2.610385
30	6	0	-5.717505	2.109857	2.956237
31	6	0	-1.602232	-6.181953	-4.104641
32	6	0	-0.131209	-5.589836	-2.142933
33	6	0	0.792498	-4.631379	-2.903513
34	6	0	-6.324012	0.825256	2.384819
35	6	0	0.783948	-6.817004	-2.013568
36	6	0	-7.814384	0.784817	2.808564
37	6	0	2.089633	-4.851865	-2.121011
38	6	0	3.344518	-4.384599	-2.867927
39	6	0	-8.494707	-0.525145	2.393972
40	6	0	-7.743104	-1.744072	2.946925
41	6	0	5.745795	-3.923297	-2.633005
42	6	0	6.888473	-4.840089	-2.182931
43	6	0	6.003468	-2.480723	-2.142935
44	6	0	-5.567177	-0.413473	2.903777
45	6	0	-6.272573	-1.720488	2.495847
46	6	0	5.818542	-1.712929	-4.497032
47	6	0	6.361428	-0.106622	-2.614725
48	6	0	5.285726	0.933644	-2.985386
49	6	0	7.754631	0.300028	-3.126537
50	6	0	8.137781	1.691247	-2.604435
51	6	0	7.085724	2.738230	-2.988136
52	6	0	5.670663	2.342168	-2.492718
53	6	0	4.691944	3.398841	-3.007341

54	6	0	-5.330387	-3.107485	4.399790
55	6	0	-5.231753	-3.888442	2.046524
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57	6	0	4.381673	6.931777	-2.082390
58	6	0	-1.790729	1.149927	-3.466505
59	6	0	-0.959267	1.110087	-2.343485
60	6	0	-0.330709	-1.071866	-2.793510
61	6	0	-1.162239	-1.126287	-3.911450
62	6	0	-1.900279	0.006926	-4.253386
63	6	0	0.552492	-2.226962	-2.402762
64	6	0	4.958803	3.841854	1.888014
65	6	0	4.378042	5.168722	2.418406
66	6	0	1.945053	5.169256	2.778485
67	6	0	0.592597	5.591710	2.190575
68	6	0	-0.558892	4.620081	2.504466
69	6	0	-1.746620	5.601758	2.475401
70	6	0	-5.314404	-6.410550	2.063315
71	6	0	-4.049475	4.969195	2.094086
72	6	0	-4.537982	-5.177096	2.539251
73	6	0	-3.122948	4.730823	4.400495
74	6	0	-1.146676	6.814965	3.198777
75	6	0	-2.094715	-5.103035	2.859728
76	6	0	-0.752301	-5.038015	2.113174
77	6	0	1.037548	-6.568666	1.903663
78	6	0	5.272745	6.329859	1.963141
79	6	0	0.417383	-4.607065	3.007636
80	6	0	1.593450	-5.170796	2.205046
81	6	0	5.279757	3.109209	4.236991
82	6	0	6.110870	1.716989	2.291824
83	6	0	5.418304	0.403584	2.698595
84	6	0	7.587607	1.749960	2.723104
85	6	0	8.341347	0.531730	2.171850
86	6	0	7.673443	-0.779029	2.603692
87	6	0	6.183575	-0.828054	2.180807
88	6	0	5.569873	-2.117947	2.732450
89	6	0	3.148088	-5.195001	4.231549
90	6	0	3.946442	-4.836971	1.900460
91	6	0	5.360682	-4.541858	2.428545
92	6	0	6.334306	-5.630798	1.963397
93	6	0	-5.994518	2.591769	-1.951863
94	7	0	1.306777	5.749712	-3.104538
95	7	0	-5.746149	3.190137	2.123346
96	7	0	-6.118990	1.595078	-2.869871
97	7	0	-5.544711	-2.926243	2.956773
98	7	0	-4.757912	-4.406090	-2.068247
99	7	0	-3.168088	-5.159575	2.034423
100	7	0	-1.461199	-5.795016	-2.697746
101	7	0	4.461932	-4.370735	-2.105674
102	7	0	2.930400	-5.082450	2.783155
103	7	0	6.006560	-1.473279	-3.057666
104	7	0	5.768741	-3.224308	1.955273
105	7	0	4.499786	4.464125	-2.171511
106	7	0	5.383968	2.911998	2.784396
107	7	0	-0.243000	0.025169	-2.011761
108	7	0	-4.548841	4.594381	-1.910826
109	7	0	3.006789	5.346694	1.950860
110	7	0	-3.021298	5.102782	2.981060
111	7	0	1.070402	0.120601	2.249939
112	8	0	4.196730	3.349267	-4.135638

113	8	0	5.023159	-2.170172	3.836835
114	8	0	5.042791	3.684720	0.659529
115	8	0	3.748295	-4.822554	0.680014
116	8	0	-0.655258	3.501359	1.658595
117	8	0	0.229044	6.842290	2.790867
118	8	0	-3.915652	5.218711	0.885495
119	8	0	6.194626	-2.295336	-0.929732
120	8	0	-0.367494	-6.359553	1.672542
121	8	0	3.299725	-4.066699	-4.058314
122	8	0	2.122417	-6.289660	-2.001796
123	8	0	0.176148	-3.334989	-3.037377
124	8	0	-2.153093	-5.082498	4.089763
125	8	0	-2.379959	-4.992368	-0.771972
126	8	0	-5.460233	-3.769517	0.832285
127	8	0	-4.231942	-3.134168	-3.888508
128	8	0	-5.323155	2.175340	4.123470
129	8	0	-6.081664	2.397732	-0.730472
130	8	0	-3.269230	4.100109	-3.743846
131	8	0	-0.419769	4.170983	-1.001865
132	8	0	-2.235252	6.716116	-2.716045
133	8	0	2.041995	5.438246	-0.978679
134	8	0	0.525204	-3.216347	3.375511
135	8	0	1.476319	-2.125502	-1.616478
136	8	0	2.043067	4.746617	3.934315
137	8	0	0.535385	-2.418770	1.257974
138	1	0	-5.667373	4.070418	-3.535771
139	1	0	-2.474092	5.660288	-0.954487
140	1	0	-0.889338	4.120886	-3.015277
141	1	0	0.130760	6.645076	-1.658373
142	1	0	1.428108	0.613072	6.079438
143	1	0	0.953845	-1.652594	5.115956
144	1	0	0.581042	4.989977	-4.918346
145	1	0	1.585674	6.443702	-5.105185
146	1	0	2.323743	4.853414	-4.722098
147	1	0	-1.125326	6.370663	-4.448078
148	1	0	-0.777359	7.877930	-3.558330
149	1	0	1.373788	2.154452	2.064372
150	1	0	1.647194	2.568912	4.485364
151	1	0	-7.903047	4.509850	-2.518751
152	1	0	-7.135558	4.864521	-0.964615
153	1	0	-6.841213	5.926367	-2.366615
154	1	0	-5.960914	0.870835	-4.823449
155	1	0	-5.098477	2.388376	-4.550890
156	1	0	-6.876981	2.375382	-4.712313
157	1	0	-6.528305	0.317381	-1.320674
158	1	0	-4.466978	-0.519897	-2.355129
159	1	0	-5.292671	-0.868412	-3.868208
160	1	0	-7.921492	-0.168856	-4.001516
161	1	0	-8.623042	0.596228	-2.573595
162	1	0	-9.270648	-1.829382	-2.758095
163	1	0	-8.366164	-1.513398	-1.281673
164	1	0	-7.228711	-2.707225	-3.871657
165	1	0	-7.517797	-3.581684	-2.367979
166	1	0	-5.814678	-2.252909	-1.198506
167	1	0	-7.476363	5.230222	2.514744
168	1	0	-6.507262	5.647253	1.078357
169	1	0	-6.274124	6.536191	2.588938
170	1	0	-3.908028	-5.438070	-3.602477
171	1	0	-3.980192	-7.704297	-2.506939

172	1	0	-5.582865	-6.936582	-2.497717
173	1	0	-4.592762	-6.967504	-1.020607
174	1	0	-5.443385	4.455784	3.695703
175	1	0	-1.888302	-5.329760	-4.731304
176	1	0	-0.646890	-6.570993	-4.460774
177	1	0	-2.340538	-6.978886	-4.223433
178	1	0	-0.300987	-5.174461	-1.149503
179	1	0	0.971443	-4.943638	-3.935069
180	1	0	-6.274710	0.861139	1.289393
181	1	0	0.587493	-7.370525	-1.089376
182	1	0	0.683738	-7.508237	-2.860468
183	1	0	-7.867317	0.896917	3.900078
184	1	0	-8.340761	1.642837	2.373811
185	1	0	2.057042	-4.395626	-1.129750
186	1	0	-9.534151	-0.534176	2.743654
187	1	0	-8.534126	-0.588827	1.296480
188	1	0	-7.800412	-1.737694	4.044654
189	1	0	-8.212685	-2.674445	2.605293
190	1	0	5.654166	-3.972695	-3.715177
191	1	0	6.677951	-5.871656	-2.480010
192	1	0	7.832244	-4.530454	-2.645763
193	1	0	7.019442	-4.797634	-1.098484
194	1	0	-4.540933	-0.417433	2.514951
195	1	0	-5.493063	-0.317889	3.992529
196	1	0	-6.254892	-1.793149	1.406596
197	1	0	4.918413	-2.303847	-4.680744
198	1	0	5.698004	-0.751937	-4.995968
199	1	0	6.684237	-2.215356	-4.945294
200	1	0	6.409527	-0.175165	-1.526055
201	1	0	4.324211	0.629428	-2.552355
202	1	0	5.139304	0.992156	-4.069397
203	1	0	7.763167	0.311451	-4.225539
204	1	0	8.490171	-0.448113	-2.807030
205	1	0	9.118486	1.984284	-2.998267
206	1	0	8.238391	1.655658	-1.509686
207	1	0	7.054484	2.845459	-4.081048
208	1	0	7.354995	3.718994	-2.578635
209	1	0	5.671271	2.365788	-1.395760
210	1	0	-5.536182	-2.163619	4.903012
211	1	0	-6.000340	-3.865534	4.822410
212	1	0	-4.295981	-3.384213	4.618205
213	1	0	3.852312	5.635977	-3.715700
214	1	0	5.435562	6.987370	-2.369663
215	1	0	4.307852	6.974622	-0.992400
216	1	0	3.863975	7.806280	-2.491304
217	1	0	-2.340278	2.058877	-3.696020
218	1	0	-0.855737	1.972070	-1.691395
219	1	0	-1.231401	-2.037633	-4.490037
220	1	0	-2.551965	-0.011791	-5.121146
221	1	0	4.312933	5.176967	3.503215
222	1	0	0.677520	5.723521	1.104013
223	1	0	-0.407640	4.227549	3.515330
224	1	0	-1.929852	5.871765	1.434555
225	1	0	-4.782540	-7.320725	2.355385
226	1	0	-5.437878	-6.397546	0.977459
227	1	0	-6.313275	-6.431857	2.514035
228	1	0	-4.448985	-5.210703	3.622357
229	1	0	-2.117478	4.559496	4.788473
230	1	0	-3.583728	5.527780	4.996738

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231      1      0      -3.692188      3.806924      4.521318
232      1      0      -1.208194      6.719461      4.291466
233      1      0      -1.614493      7.760439      2.906534
234      1      0      -0.849799     -4.384444      1.242596
235      1      0       1.182919     -7.256214      2.749065
236      1      0       1.491170     -7.003550      1.008882
237      1      0       6.277711      6.227019      2.387446
238      1      0       5.370806      6.343680      0.874197
239      1      0       4.850724      7.281393      2.299587
240      1      0       0.285369     -5.093412      3.975437
241      1      0       1.650157     -4.628396      1.262380
242      1      0       5.490239      2.161638      4.732111
243      1      0       6.000147      3.848639      4.606817
244      1      0       4.270241      3.417514      4.516874
245      1      0       6.072618      1.800942      1.204055
246      1      0       5.340247      0.311544      3.787558
247      1      0       4.392664      0.399928      2.308348
248      1      0       8.048220      2.681378      2.371419
249      1      0       7.659802      1.750109      3.819656
250      1      0       8.369338      0.584062      1.073717
251      1      0       9.383784      0.552336      2.511719
252      1      0       8.203032     -1.636608      2.174019
253      1      0       7.733552     -0.880071      3.696614
254      1      0       6.143119     -0.861143      1.084854
255      1      0       3.898854     -5.957436      4.458687
256      1      0       2.218703     -5.506991      4.707888
257      1      0       3.462989     -4.236524      4.655780
258      1      0       5.369506     -4.476329      3.514901
259      1      0       7.349105     -5.390202      2.293486
260      1      0       6.054845     -6.604042      2.382737
261      1      0       6.325912     -5.722458      0.873553
262      1      0      -5.932267      3.057748      1.129089
263      1      0      -5.030654     -4.362519     -1.086321
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265      1      0       4.375677     -4.535119     -1.102101
266      1      0       5.989668     -3.099211      0.966631
267      1      0       4.729940      4.375251     -1.181495
268      1      0      -4.530701      4.896151     -0.935128
269      1      0       2.845941      5.546768      0.965665
270      1      0      -0.850610      3.799046      0.745923
271      1      0       0.511407      4.459131     -0.857415
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Anti-eclipsed dimer

1	6	0	-5.387776	-0.955010	-3.136076
2	6	0	5.480198	3.116242	4.348196
3	6	0	3.662393	-4.386280	-3.029401
4	6	0	2.351676	-4.727118	-2.295421
5	6	0	1.123014	-4.294475	-3.098874
6	6	0	0.045984	-5.193872	-2.490481
7	6	0	-3.299278	4.828267	4.232950
8	6	0	-2.310339	-5.553279	-2.278560
9	6	0	-5.196808	-3.275313	4.121662
10	6	0	0.837204	-6.516682	-2.467108
11	6	0	1.490320	1.157781	-3.736160
12	6	0	1.341026	-0.217391	-3.544760
13	6	0	0.760354	-0.669921	-2.359696
14	6	0	7.175486	-4.813252	-2.240769
15	6	0	6.289164	-2.449338	-2.196173
16	6	0	0.431975	1.489087	-1.600166
17	6	0	1.014555	2.018878	-2.754446
18	6	0	6.553516	-0.049735	-2.601221
19	6	0	7.891437	0.499800	-3.123281
20	6	0	8.150248	1.903071	-2.556186
21	6	0	7.000750	2.862128	-2.888793
22	6	0	5.379964	0.899246	-2.910225
23	6	0	5.636235	2.324463	-2.385770
24	6	0	4.545858	3.288820	-2.862538
25	6	0	3.213977	-4.956738	4.081913
26	6	0	-0.565997	1.979656	2.845839
27	6	0	3.503995	5.474887	-2.487132
28	6	0	4.207389	6.818941	-2.224282
29	6	0	2.147537	5.483096	-1.763056
30	6	0	-1.419992	-0.474277	5.619783
31	6	0	-1.118267	0.726349	4.974003
32	6	0	-0.221859	6.060808	-1.734840
33	6	0	-0.918215	7.402655	-2.085649
34	6	0	-0.861966	0.712210	3.602446
35	6	0	-1.329518	5.005132	-2.033467
36	6	0	-2.594063	5.885451	-2.164042
37	6	0	-3.680743	5.239806	-3.025815
38	6	0	-1.185757	-1.575422	3.504091
39	6	0	-1.459702	-1.645328	4.871839
40	6	0	-5.720393	3.881281	-2.990583
41	6	0	-7.051305	4.654059	-2.903442
42	6	0	-5.904650	2.489090	-2.366768
43	6	0	-6.393542	0.100876	-2.641590
44	6	0	-7.850836	-0.323762	-2.895794
45	6	0	-8.133207	-1.700178	-2.277074
46	6	0	-7.148802	-2.759117	-2.788844
47	6	0	0.647443	-2.133131	-2.060204
48	6	0	-5.679400	-2.341371	-2.533343
49	6	0	-4.757289	-3.400316	-3.142589
50	6	0	6.430380	-5.529553	1.809184
51	6	0	-3.747954	-5.622363	-2.823220
52	6	0	-4.406945	-6.939057	-2.396994
53	6	0	-1.438632	-5.055791	-4.567257
54	6	0	6.146156	-1.635235	-4.538279
55	6	0	1.036073	6.062794	-3.922683
56	6	0	5.462940	-4.438430	2.290393
57	6	0	-6.126927	1.598000	-4.667647

58	6	0	6.049864	-3.887068	-2.711591
59	6	0	-4.347967	-5.314492	2.241791
60	6	0	5.781664	-2.045622	2.698181
61	6	0	-1.910339	-5.194146	2.537743
62	6	0	-0.558601	-5.527724	1.890354
63	6	0	0.582804	-4.602181	2.323002
64	6	0	1.788603	-5.525482	2.071786
65	6	0	6.419358	-0.750736	2.187844
66	6	0	4.055958	-4.745360	1.749185
67	6	0	5.657334	0.474084	2.727355
68	6	0	1.245847	-6.868958	2.587145
69	6	0	7.901432	-0.728057	2.638510
70	6	0	8.589076	0.590229	2.263082
71	6	0	7.837370	1.797155	2.842092
72	6	0	-5.223218	-6.479023	1.759499
73	6	0	-4.960062	-3.983394	1.752566
74	6	0	6.370324	1.793554	2.379052
75	6	0	5.212833	3.920244	2.013759
76	6	0	-6.141977	-1.890669	2.225653
77	6	0	-7.592646	-1.943276	2.736813
78	6	0	-8.395313	-0.743138	2.215300
79	6	0	-7.727632	0.583680	2.595712
80	6	0	-5.452314	-0.562817	2.591761
81	6	0	-6.261222	0.653284	2.099765
82	6	0	-5.651778	1.958359	2.615561
83	6	0	-5.373481	4.360606	2.211362
84	6	0	-6.242417	5.440555	1.555726
85	6	0	-3.898038	4.565393	1.832939
86	6	0	5.217665	6.441457	2.044580
87	6	0	-1.580868	4.880714	2.340787
88	6	0	-1.077131	6.305011	2.063521
89	6	0	4.515894	5.183408	2.568528
90	6	0	-0.429309	4.388134	3.227812
91	6	0	2.109639	4.867031	3.020170
92	6	0	0.739189	4.832179	2.335615
93	1	0	-2.158518	4.129232	-0.474399
94	1	0	-2.833591	-5.686533	0.768422
95	1	0	-4.704481	-4.405545	-1.335266
96	1	0	-5.944512	2.877475	0.784105
97	1	0	-4.564199	4.494772	-1.300130
98	1	0	4.674783	4.342891	-1.088438
99	1	0	2.904585	5.219597	1.162384
100	1	0	6.138009	-2.968269	0.880324
101	1	0	4.615318	-4.440279	-1.211254
102	1	0	0.799662	4.218590	1.431637
103	1	0	-0.349611	4.936813	4.167971
104	1	0	4.508339	5.203027	3.655716
105	1	0	-1.340373	6.993414	2.878610
106	1	0	-1.469298	6.709186	1.125003
107	1	0	-1.521377	4.321597	1.410560
108	1	0	5.250122	6.439667	0.951695
109	1	0	6.249515	6.485463	2.410755
110	1	0	4.688145	7.334901	2.388017
111	1	0	-6.135515	5.424332	0.467434
112	1	0	-7.292659	5.272113	1.810715
113	1	0	-5.956150	6.437180	1.909523
114	1	0	-5.510833	4.387054	3.290620
115	1	0	-6.267855	0.675540	1.001944
116	1	0	-5.331437	-0.460567	3.676109

117	1	0	-4.444886	-0.546438	2.156720
118	1	0	-8.293375	1.428222	2.185397
119	1	0	-7.730609	0.697920	3.688396
120	1	0	-8.484371	-0.809818	1.121338
121	1	0	-9.416802	-0.775136	2.612699
122	1	0	-8.056562	-2.884691	2.418220
123	1	0	-7.606299	-1.933982	3.835580
124	1	0	-6.162200	-1.976473	1.137497
125	1	0	6.359248	1.915290	1.294072
126	1	0	-5.323135	-6.466335	0.670812
127	1	0	-6.228150	-6.406494	2.189862
128	1	0	-4.781328	-7.430620	2.069001
129	1	0	7.887498	1.758743	3.939221
130	1	0	8.314188	2.734995	2.531925
131	1	0	9.625719	0.587804	2.620996
132	1	0	8.637069	0.680253	1.167869
133	1	0	7.938388	-0.865165	3.728174
134	1	0	8.432265	-1.576540	2.191477
135	1	0	1.685845	-7.726767	2.067836
136	1	0	0.690841	-3.445503	0.725804
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138	1	0	6.154982	3.876196	4.759993
139	1	0	4.450152	3.366149	4.613276
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141	1	0	2.366226	-4.263551	-1.302979
142	1	0	1.322770	-4.525490	-4.145857
143	1	0	-0.126742	-4.883816	-1.463108
144	1	0	-3.882707	5.727281	4.457724
145	1	0	-3.854116	3.936388	4.534979
146	1	0	-2.377123	4.878029	4.810440
147	1	0	-5.362854	-2.324498	4.628499
148	1	0	-4.178973	-3.601603	4.344308
149	1	0	-5.910715	-4.002135	4.527930
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151	1	0	0.465885	-7.204419	-1.702793
152	1	0	1.990784	1.549322	-4.614524
153	1	0	1.689546	-0.933200	-4.278572
154	1	0	6.962150	-5.843129	-2.541557
155	1	0	8.128848	-4.511215	-2.688721
156	1	0	7.288706	-4.770562	-1.154770
157	1	0	0.042064	2.141889	-0.829083
158	1	0	1.104791	3.092646	-2.857541
159	1	0	6.634096	-0.155853	-1.517806
160	1	0	8.700836	-0.185321	-2.843549
161	1	0	7.878564	0.551756	-4.220975
162	1	0	9.093440	2.299015	-2.951486
163	1	0	8.270801	1.839781	-1.464847
164	1	0	6.942343	3.001317	-3.977399
165	1	0	7.188809	3.848409	-2.449572
166	1	0	5.203078	0.971660	-3.989259
167	1	0	4.462403	0.492724	-2.466689
168	1	0	5.653387	2.325282	-1.288285
169	1	0	3.690889	-4.006215	4.332107
170	1	0	2.221513	-4.966839	4.535261
171	1	0	3.789233	-5.783762	4.514549
172	1	0	3.378053	5.334631	-3.559436
173	1	0	3.611847	7.654726	-2.608651
174	1	0	4.354436	6.976358	-1.150944
175	1	0	5.182537	6.831422	-2.719612

176	1	0	-1.619389	-0.484384	6.687081
177	1	0	-1.078888	1.661521	5.516482
178	1	0	0.045723	6.014389	-0.679836
179	1	0	-0.329035	8.059053	-2.729813
180	1	0	-1.157032	7.954197	-1.162983
181	1	0	-1.134535	4.550273	-3.012155
182	1	0	-2.988167	6.107027	-1.159100
183	1	0	-1.180984	-2.469068	2.897929
184	1	0	-1.686312	-2.612508	5.306850
185	1	0	-5.410118	3.827135	-4.033003
186	1	0	-7.844600	4.141314	-3.460310
187	1	0	-7.372840	4.746021	-1.860796
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189	1	0	-6.260366	0.225336	-1.565058
190	1	0	-8.526974	0.433692	-2.481015
191	1	0	-8.047417	-0.371020	-3.975966
192	1	0	-9.162904	-2.005732	-2.498339
193	1	0	-8.056442	-1.631092	-1.182017
194	1	0	-7.291222	-2.905092	-3.868677
195	1	0	-7.344305	-3.724183	-2.307464
196	1	0	-5.415507	-1.053316	-4.226759
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201	1	0	6.434278	-5.598370	0.718158
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203	1	0	-3.874886	-7.793639	-2.829845
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205	1	0	-4.392398	-7.053341	-1.310185
206	1	0	-2.329998	-4.460095	-4.774298
207	1	0	-0.582148	-4.506379	-4.957240
208	1	0	-1.497356	-6.014206	-5.096941
209	1	0	5.265467	-2.241971	-4.762273
210	1	0	7.032505	-2.109729	-4.975693
211	1	0	6.017741	-0.665586	-5.018725
212	1	0	1.595869	6.964522	-4.196911
213	1	0	0.004332	6.192245	-4.255690
214	1	0	1.460930	5.209316	-4.458311
215	1	0	5.471756	-4.410080	3.377509
216	1	0	-6.859347	2.344608	-4.988822
217	1	0	-5.141938	1.874377	-5.057378
218	1	0	-6.408690	0.647721	-5.119148
219	1	0	5.983247	-3.927580	-3.795982
220	1	0	-4.276166	-5.350096	3.325967
221	1	0	-0.664862	-5.515471	0.796621
222	1	0	0.465889	-4.394551	3.390978
223	1	0	1.946570	-5.598802	0.993438
224	1	0	6.396561	-0.753302	1.090526
225	1	0	5.556551	0.346965	3.810781
226	1	0	4.639418	0.494865	2.317598
227	7	0	4.743233	-4.318028	-2.218405
228	7	0	5.890452	-3.116012	1.858652
229	7	0	-1.275291	-5.240381	-3.116703
230	7	0	5.636696	2.973280	2.892740
231	7	0	0.325411	0.168255	-1.396007
232	7	0	3.116658	5.142348	2.158577
233	7	0	6.294866	-1.424275	-3.090432
234	7	0	4.323423	4.358047	-2.046053

235	7	0	1.032290	5.834093	-2.470169
236	7	0	-2.960573	4.748435	2.802409
237	7	0	-4.643584	4.585271	-2.310036
238	7	0	-5.784056	3.029985	1.780304
239	7	0	-6.112263	1.439933	-3.207332
240	7	0	-5.371076	-3.072204	2.677341
241	7	0	-4.488326	-4.464830	-2.330885
242	7	0	-2.981485	-5.451624	1.750463
243	7	0	3.068839	-5.092171	2.624833
244	7	0	-0.888642	-0.428020	2.879645
245	8	0	-4.354707	-3.329133	-4.306004
246	8	0	-5.086125	-3.803876	0.531472
247	8	0	-1.422809	3.954167	-1.095253
248	8	0	-5.166050	2.052577	3.746007
249	8	0	0.620922	-3.342266	1.690348
250	8	0	3.870563	-4.720088	0.523526
251	8	0	-0.166076	-6.838320	2.322202
252	8	0	-5.905137	2.376518	-1.130490
253	8	0	-3.600038	4.542821	0.623215
254	8	0	-3.648794	5.288412	-4.248653
255	8	0	-2.119419	7.067593	-2.780269
256	8	0	0.350641	6.177563	1.978065
257	8	0	2.106933	5.230817	-0.553289
258	8	0	-0.518025	3.024586	3.676558
259	8	0	3.978690	3.155850	-3.952431
260	8	0	2.239804	4.647404	4.225204
261	8	0	6.443018	-2.280590	-0.976338
262	8	0	5.348114	3.813224	0.783956
263	8	0	3.677406	-4.164819	-4.242329
264	8	0	0.912960	-2.866276	-3.137779
265	8	0	2.189338	-6.145726	-2.148489
266	8	0	-2.120557	-5.765349	-1.071716
267	8	0	5.284806	-2.130704	3.824062
268	8	0	-1.991237	-4.752890	3.690027
269	8	0	0.361046	-2.573422	-0.955897
270	8	0	-0.402850	2.037634	1.640282
271	47	0	-0.302711	-0.482973	0.691518

Clockwise alternating dimer

```
-----------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number     Type         X           Y           Z
-----------------------------------------------------------------
    1        47         0        0.510593   -1.809849   -2.080444
    2         6         0        4.279597    5.271016    2.563575
    3         6         0       -2.602003   -1.373810   -3.099635
    4         6         0        1.827602    5.307668    2.532936
    5         6         0        0.616626    5.930012    1.826648
    6         6         0       -0.661736    5.071284    1.874243
    7         6         0       -1.715448    6.093595    2.341645
    8         6         0       -1.586243   -1.725562   -6.745955
    9         6         0       -3.917427    5.187518    2.001785
   10         6         0       -2.380163   -1.488472   -5.623746
   11         6         0       -3.034200    5.266145    4.340110
   12         6         0       -0.881451    6.991000    3.264789
   13         6         0       -1.790521   -1.541231   -4.359047
   14         6         0        0.270078   -2.066596   -5.265624
   15         6         0       -0.239173   -2.026371   -6.565402
   16         6         0        5.285399    6.383582    2.220859
   17         6         0        5.060153    3.312063    4.544868
   18         6         0        6.282239    1.987359    2.762456
   19         6         0        5.770023    0.589042    3.154662
   20         6         0        7.685662    2.259188    3.331688
   21         6         0        8.670837    1.185988    2.845125
   22         6         0        8.185675   -0.224279    3.200021
   23         6         0        6.759105   -0.498718    2.673879
   24         6         0        6.323398   -1.884471    3.160156
   25         6         0       -7.041655    4.497414   -2.222015
   26         6         0        5.781995   -4.205023    2.457188
   27         6         0        6.789673   -5.067499    1.691870
   28         6         0        4.337246   -4.591565    2.068855
   29         6         0       -5.734862    3.749051   -2.520687
   30         6         0       -3.532140    4.727903   -3.005708
   31         6         0        3.446678   -3.629295    4.229416
   32         6         0        1.968067   -4.588928    2.446018
   33         6         0        0.829357   -3.669915    2.888254
   34         6         0        1.395248   -5.934695    2.914117
   35         6         0       -2.407452    5.628814   -2.491747
   36         6         0       -0.417855   -4.487952    2.522176
   37         6         0       -1.566562   -4.246048    3.521121
   38         6         0       -2.695525    7.076110   -2.960595
   39         6         0       -1.573692    8.033507   -2.542667
   40         6         0       -3.977514   -4.468695    3.863220
   41         6         0       -4.825744   -5.741779    3.989906
   42         6         0       -4.796249   -3.357886    3.172443
   43         6         0       -0.211876    7.556315   -3.065187
   44         6         0       -1.037244    5.141505   -3.006921
   45         6         0       -5.029573   -2.272107    5.387057
   46         6         0       -6.076759   -1.275135    3.300561
   47         6         0       -5.459850    0.118887    3.527288
   48         6         0       -7.548461   -1.330235    3.745540
   49         6         0       -8.369306   -0.237470    3.045145
   50         6         0       -7.772157    1.154927    3.286992
   51         6         0       -6.287906    1.230323    2.852970
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54	6	0	1.651994	5.511002	-4.505831
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59	6	0	2.448380	5.648707	-2.168189
60	6	0	1.064289	-0.553264	0.842157
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62	6	0	1.346244	1.714050	1.588241
63	6	0	0.909542	-2.027383	1.087336
64	6	0	-2.919110	-6.093947	-0.711255
65	6	0	-4.426093	-5.957671	-1.028912
66	6	0	-4.717276	-3.657497	-1.797556
67	6	0	-4.931445	-2.209230	-1.364634
68	6	0	-4.979065	-1.196150	-2.520470
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79	6	0	4.967804	1.011768	-1.376603
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82	6	0	0.194807	-5.480420	-1.925876
83	6	0	-0.065572	-8.015726	-1.750357
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88	6	0	5.977354	-0.140446	-1.654658
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192	1	0	-0.210534	7.603192	-4.163618
193	1	0	0.587925	8.220229	-2.714481
194	1	0	-0.816043	4.148962	-2.595907
195	1	0	-1.114881	5.031908	-4.094140
196	1	0	-5.569848	-1.417970	5.793894
197	1	0	-5.397699	-3.166078	5.900579
198	1	0	-3.966306	-2.141997	5.613623
199	1	0	-6.037687	-1.510755	2.234090
200	1	0	-4.432412	0.127342	3.141855
201	1	0	-5.399886	0.357471	4.595023
202	1	0	-7.620466	-1.190735	4.833504
203	1	0	-7.956902	-2.322558	3.520931
204	1	0	-9.407150	-0.264105	3.398472
205	1	0	-8.403652	-0.444347	1.965783
206	1	0	-7.830223	1.402564	4.355080
207	1	0	-8.351202	1.917805	2.752031
208	1	0	-6.233245	1.118813	1.762619
209	1	0	0.144630	6.105122	-1.512934
210	1	0	0.685813	5.397310	-4.996071
211	1	0	2.158979	6.371714	-4.958362
212	1	0	2.233694	4.605409	-4.694302
213	1	0	-5.448656	5.053003	3.549210
214	1	0	-6.069911	6.914801	2.010470
215	1	0	-7.335773	5.670223	2.074012
216	1	0	-6.237824	5.766652	0.673401
217	1	0	1.431290	3.150027	-0.032687
218	1	0	1.173599	1.395394	-1.783157
219	1	0	1.206445	0.005844	2.913016
220	1	0	1.454009	2.445066	2.384851
221	1	0	-4.642019	-6.172362	-2.073206
222	1	0	-4.146360	-1.949209	-0.644780
223	1	0	-5.750671	-1.541558	-3.212711
224	1	0	-4.645159	0.319315	-1.041239
225	1	0	4.103429	7.692600	-2.939531
226	1	0	5.642876	6.819740	-2.779512
227	1	0	4.612575	7.101204	-1.351261
228	1	0	3.923728	5.320007	-3.753431
229	1	0	-5.429768	0.881919	-4.529295
230	1	0	-7.009277	0.319221	-3.923523

231	1	0	-6.735051	2.035549	-4.178440
232	1	0	-7.542185	-0.558541	-1.429998
233	1	0	-6.685888	-0.175908	0.082816
234	1	0	6.237811	2.761659	-1.145290
235	1	0	-6.305799	-6.762686	-0.315766
236	1	0	-4.980545	-7.946692	-0.358644
237	1	0	-5.020082	-6.720286	0.916969
238	1	0	7.609339	-0.009603	-3.161715
239	1	0	7.930529	0.825710	-1.621209
240	1	0	4.045683	0.828866	-1.945242
241	1	0	-1.587047	-6.707346	-3.709519
242	1	0	-3.118496	-5.885818	-3.413568
243	1	0	-2.989760	-7.661968	-3.217619
244	1	0	-0.590321	-6.575378	-0.248497
245	1	0	-0.208573	-4.539549	-1.538074
246	1	0	0.086441	-5.446360	-3.016634
247	1	0	-0.172401	-8.167330	-2.833258
248	1	0	-0.639061	-8.810302	-1.258133
249	1	0	1.820537	-9.085843	-1.705895
250	1	0	1.531719	-8.083377	-0.288622
251	1	0	2.210035	-7.065483	-3.104707
252	1	0	3.292941	-7.073108	-1.713686
253	1	0	1.833929	-5.505841	-0.505201
254	1	0	6.278714	-0.576085	-0.705561
255	1	0	5.540040	-1.524723	-4.548360
256	1	0	3.899435	-1.181778	-3.942296
257	1	0	5.108559	0.107299	-4.013689
258	1	0	4.216267	-3.274728	-3.561342
259	1	0	5.598834	-5.336955	-3.747914
260	1	0	6.497624	-4.885344	-2.278953
261	1	0	6.657402	-3.909038	-3.749942
262	1	0	-4.431503	4.732271	-1.137671
263	1	0	6.012816	-2.510504	1.208376
264	1	0	4.878315	4.526238	-1.073822
265	1	0	-2.848732	-5.077905	2.145722
266	1	0	-5.750255	3.209767	1.249148
267	1	0	4.134271	-4.874003	-1.070590
268	1	0	2.999928	5.786340	0.916655
269	1	0	-4.917917	-4.241795	0.160941
270	1	0	4.702916	2.035452	0.292626
271	1	0	-1.902681	4.504347	0.497769

Counter-clockwise alternating dimer

```
-------------------------------------------------------------------------
Center      Atomic      Atomic              Coordinates (Angstroms)
Number      Number      Type          X            Y            Z
-------------------------------------------------------------------------
    1          47          0       0.401803     0.752274     1.247958
    2           6          0       5.743129    -3.010519     2.560316
    3           6          0       7.752657    -1.564778     3.017026
    4           6          0       5.409451    -0.590945     3.144499
    5           6          0       6.011837     0.823458     3.089755
    6           6          0       7.420446     0.866189     3.704125
    7           6          0       8.336335    -0.144540     2.992686
    8           6          0       4.665231     2.864323     2.905375
    9           6          0       3.683901     3.885799     3.509438
   10           6          0       1.341269     4.226080     2.863905
   11           6          0       0.374650     4.563515     1.717652
   12           6          0      -0.950600     3.781834     1.825576
   13           6          0      -2.016638     4.887973     1.718805
   14           6          0      -1.277021     6.080692     2.342948
   15           6          0      -4.171368     3.837853     1.475655
   16           6          0      -5.688900     3.915334     1.698220
   17           6          0      -6.280779     1.816941     2.809319
   18           6          0      -7.005766     0.481061     2.675483
   19           6          0      -6.044774    -0.702221     2.913098
   20           6          0      -6.810065    -2.036876     2.831577
   21           6          0      -8.189228     0.441749     3.666013
   22           6          0      -7.981163    -2.083409     3.828185
   23           6          0      -8.931882    -0.899015     3.595073
   24           6          0      -5.598247    -3.918980     1.863282
   25           6          0      -4.839845    -5.255972     2.020337
   26           6          0      -2.415399    -4.946225     2.162011
   27           6          0      -1.112331    -4.793612     1.366278
   28           6          0       0.104699    -4.589587     2.272287
   29           6          0       1.241848    -4.877982     1.289884
   30           6          0       0.652895    -6.141569     0.620646
   31           6          0       3.599224    -5.044575     0.919619
   32           6          0       5.071842    -5.081517     1.384317
   33           6          0       5.910537    -5.964433     0.457106
   34           6          0       4.662836     1.655334     5.065589
   35           6          0       4.445566     5.162455     3.910116
   36           6          0       2.777765    -5.254120     3.286589
   37           6          0      -5.660915    -6.384229     1.385199
   38           6          0      -5.407125    -3.520383     4.318463
   39           6          0      -3.658773     4.892837     3.666691
   40           6          0      -6.281170     4.800056     0.586220
   41           6          0       5.442475    -0.935664    -4.420780
   42           6          0       5.537556     6.547114    -0.812487
   43           6          0       3.130144     6.335595    -3.652960
   44           6          0      -5.178286     5.063418    -5.455824
   45           6          0      -4.348093     1.325703    -4.731879
   46           6          0      -5.447181    -5.614369    -2.707338
   47           6          0      -2.588564    -4.210414    -4.957256
   48           6          0       6.276132    -4.905761    -3.769292
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   50           6          0      -4.998160     3.422746    -3.567266
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   53           6          0      -5.142296     0.436430    -1.753226
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55	6	0	-5.196304	-1.970130	-2.620572
56	6	0	-4.655908	-4.318574	-2.928004
57	6	0	-3.176079	-4.570918	-2.574922
58	6	0	0.583036	-7.163576	-3.696435
59	6	0	-0.766862	-6.516133	-4.027448
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61	6	0	0.242323	-4.205971	-3.627612
62	6	0	1.746975	-6.224424	-4.030738
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66	6	0	5.751340	-2.706933	-2.662185
67	6	0	7.347541	0.574861	-2.519600
68	6	0	6.255577	-0.417295	-2.093648
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70	6	0	5.949402	1.761731	-1.098008
71	6	0	5.458169	3.026818	-1.813287
72	6	0	4.845501	5.379308	-1.532890
73	6	0	3.322796	5.494843	-1.331384
74	6	0	-0.716868	7.929755	-1.781901
75	6	0	-2.119178	4.586004	-3.374776
76	6	0	-1.663029	7.047071	-2.613893
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78	6	0	0.229226	5.384989	-2.961737
79	6	0	1.134239	6.263140	-2.081606
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81	6	0	-0.067484	-2.153144	2.577366
82	6	0	3.169448	-0.088736	-0.213047
83	6	0	1.310257	-0.146948	-3.541241
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236        1        0       5.044580   -3.363520   -4.627667
237        1        0       8.344268    0.127331   -2.539584
238        1        0       7.141931    1.048497   -3.487705
239        1        0       6.630460   -0.985956   -1.242792
240        1        0       4.438937    0.788974   -2.336700
241        1        0       5.905810    1.876541   -0.014582
242        1        0       5.113198    5.381779   -2.587950
243        1        0      -0.817612    7.671414   -0.718216
244        1        0      -1.009874    8.981336   -1.881098
245        1        0      -2.686881    7.178303   -2.237622
246        1        0      -1.655828    7.391620   -3.657800
247        1        0      -1.349714    5.213632   -1.522482
248        1        0       0.344950    5.652308   -4.021803
249        1        0       0.508188    4.332645   -2.863745
250        1        0       0.988040    5.967326   -1.041338
251        1        0       1.403883    8.346721   -1.547828
252        1        0       0.893422    8.107415   -3.222406
253        1        0       1.353868   -0.644255   -4.505090
254        1        0       3.084523   -1.126719   -2.798983
255        1        0      -0.448702    1.067767   -3.945183
256        1        0      -0.514198    1.996415   -1.649427
257        1        0      -1.016305   -1.080650    7.024381
258        1        0      -0.796979   -2.717894    5.127700
259        1        0      -0.492366    1.339987    6.570117
260        1        0       6.375834   -1.333030    1.360182
261        1        0       0.182894    2.014388    4.282468
262        1        0      -6.446639    2.145739    0.797211
263        1        0      -3.439521   -5.094071    0.389417
264        1        0       2.930876    4.400817    1.568257
265        1        0       5.783146   -3.284042    0.500646
266        1        0       5.272486    3.956901   -0.000962
267        1        0       3.947701   -4.762585   -2.255493
268        1        0      -5.483102   -3.409841   -1.162865
269        1        0      -3.581913    5.987338   -3.657560
270        1        0      -4.625371    1.739653   -0.346397
271        1        0      -2.004509    2.727344    0.576385
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