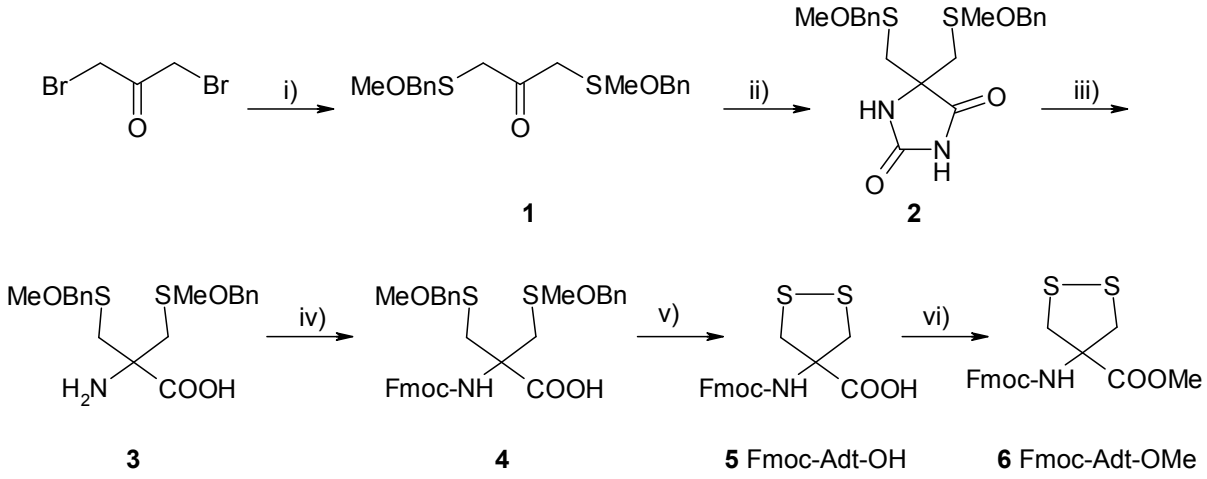
Supplementary Information

1. Synthesis and characterization of the peptide compounds investigated and their synthetic intermediates

The Adt monomer was synthesized by a modified version of the method used by Lucente and coworkers (Morera, E.; Nalli, M.; Pinnen, F.; Rossi, D.; Lucente, G. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1585-1588). Starting from the hydantoin **2** (Comber, R.N.; Reynolds, R.C.; Friedrich, J.D.; Manguikian, R.A.; Buckheit, R.W.; Truss, J.W.; Shannon, W.M.; Secrist, J.A. *J. Med. Chem*. **1992**, *35*, 3567-3572), basic hydrolysis to **3**, Fmoc protection of the amino function to **4**, and thiol deprotection/cyclization furnished Fmoc-Adt-OH **5**. Thionyl chloride-mediated esterification gave the fully protected Fmoc-Adt-OMe **6**.



Synthesis of Fmoc-Adt-OMe **6**. i) *p*-methoxybenzyl thiol (MeOBnSH), 1N NaOH aq., EtOH, rt. ii) KCN, NH_4HCO_3, EtOH, H_2O, 75 °C. iii) 1N NaOH aq., sealed tube, 170°C. iv) Fmoc-OSu, $NaHCO_3$, acetone, H_2O, rt. v) a. TFA, 75°C. b. I_2, MeOH, rt.vi) $SOCl_2$, MeOH, 70°C.

Fmoc-Adt-OH 5 : The partially protected amino acid **4** (2.19g, 3.48 mmol) was dissolved in a mixture of TFA/water/anisole (20mL/1mL/1mL). The solution was stirred at 75 °C for 2 hr. The mixture was allowed to cool and concentrated under reduced pressure. Toluene was added to the residue distilled off twice. The residue was taken up in MeOH (100mL). A 0.1M solution of I_2 in methanol was added dropwise with stirring until a persistently dark yellow color was obtained. The mixture was stirred at rt for 40 min. A saturated solution of $Na_2S_2O_{3(aq.)}$ was added until decolorization of the mixture. The mixture was concentrated under reduced pressure, and the residue was taken up in EtOAc. The resulting solution was washed with saturated aqueous NaCl solution, dried over $MgSO_4$, filtered, and concentrated

under reduced pressure. The residue was purified by column chromatography using CH_2Cl_2/MeOH (95:5, then 90:10) as eluent to give **5** (1.11 g, 82 %) as a foam. R_f =0.45 (CH_2Cl_2/MeOH 95:5). ^{1}H NMR (300 MHz, DMF, 25 °C): δ= 7.94-7.91 (d, J = 7.4 Hz, 2H, ArH); 7.78-7.75 (d, 2H, J = 7.3 Hz, 2H, ArH); 7.46-7.32 (m, 4H, ArH); 5.82 (s, 1H, NH), 4.27 (bs, 3H, CH, CH_2 Fmoc), 3.74 (bs , 4H, 2 SCH_2). ^{13}C NMR (75 MHz, DMF, 25 °C): δ= 156.3, 144.6, 141.4, 127.9, 127.5, 125.9, 120.3, 73.3, 66.5, 55.1, 48.8, 47.5. HRMS (ESI): *m/z* calc. for $[M+H]^+$ $C_{19}H_{18}NO_4S_2$ 388.0677; found 388.0678. FTIR (cm^{-1}): 3351, 3050, 2942, 1684, 1591, 1510.

Fmoc-Adt-OMe 6 : Fmoc-Adt-OH **5** (2.0 g, 5.17 mmol) was dissolved in MeOH (40 mL). The solution was cooled to 0°C and $SOCl_2$ (0.49 mL, 6.72 mmol) was added. The solution was heated at 70 °C for 18 hr. The mixture was allowed to cool and concentrated under reduced pressure. Toluene was added to the residue and distilled off twice to give **6** as a foam (1.93 g, 93%). R_f =0.31 (pentane/EtOAc 80:20). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ= 7.78 (d, J = 7.4 Hz, 2H, ArH); 7.60 (d, , J = 7.4 Hz, 2H, ArH); 7.44-7.31 (m, 4H, ArH); 5.48 (bs, 1H, NH); 4.43-4.46 (m, 2H, CH_2); 4.26-4.21 (m, 1H, CH); 3.79 (s, 3H, OCH_3); 3.65-3.61(b, 2H, SCH_2); 3.42-3.39 (b, 2H, SCH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=170.3, 155.0, 143.6, 141.4, 127.8, 127.1, 125.0, 120.1, 71.2, 67.0, 53.4, 47.4, 47.1. HRMS (ESI): *m/z* calc. for $[M+H]^+$ $C_{20}H_{20}NO_4S_2$ 402.0834; found 402.0832. FTIR (cm^{-1}): 3343, 3019, 2950, 1738, 1711, 1696, 1506.

Fc-CO-Adt-OMe : Fmoc-Adt-OMe **6** (200 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (4 mL) and diethylamine (1 mL) was added. The mixture was stirred at rt for 6 hr. The mixture was concentrated under reduced pressure. The residue was purified by filtration through a plug of silica gel, eluting with CH_2Cl_2/MeOH (97.5:2.5). The intermediate H-Adt-OMe (89 mg, 0.49 mmol) was dissolved in MeCN (5 mL). Fc-COOH (172 mg, 0.75 mmol), EDC (192 mg, 1.0 mmol), DMAP (92 mg, 0.75 mmol) and NMM (0.11 mL) were added to the solution. The mixture was stirred under argon at 75°C for 18 hr. The mixture was allowed to cool and concentrated under reduced pressure. The residue was taken up in EtOAc and washed with 0.5N aqueous HCl solution, saturated aqueous NaCl solution, then saturated aqueous $NaHCO_3$ solution. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using CH_2Cl_2/EtOAc (95:5) as eluent to give the title compound (112 mg, 58 %) as an orange solid. R_f =0.35 (CH_2Cl_2/EtOAc 95:5). M.p. 185°C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=6.36 (s, 1H,

NH); 4.70 (t, 2H, J = 1.8 Hz; Fc Cp_o); 4.39 (t, 2H, J = 1.8 Hz; Fc Cp_m); 4.27 (s, 5H, Fc Cp); 3.83 (s, 3H, OCH_3); 3.71 (d, J = 12.0 Hz, 2H, SCH_2); 3.52 (d, J = 12.0 Hz, 2H, SCH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=170.3, 169.9, 74.2, 70.9, 70.6, 69.9, 68.3, 53.3, 46.6. HRMS (ESI): *m/z* calc. for $[M+H]^+$ $C_{16}H_{17}FeNO_3S_2$ 392.0077; found 392.0064. FTIR (cm^{-1}): 3282, 2946, 2927, 1738, 1618, 1533.

Fmoc-Adt-L-Ala-Aib-OMe: Boc-L-Ala-Aib-OMe (1.4 g, 4.9 mmol) (Jensen, O. E.; Lawesson, S. O.; Bardi, R.; Piazzesi, A. M.; Toniolo, C. *Tetrahedron*, **1985**, *41*, 5595–5606) was dissolved in a solution of HCl in diethyl ether (2M, 20 mL). The mixture was stirred at rt for 3 hr, then concentrated under reduced pressure. Separately, Fmoc-Adt-OH (1.3 g, 3.4 mmol), ethyl (hydroxyimino)cyanoacetate (480 mg, 3.4 mmol), EDC (668 mg, 3.5 mmol) and DIEA (1.2 mL, 7.0 mmol) were stirred together at 0 °C in CH_2Cl_2 (30 mL) for 10 min, then added to the crude HCl.H-L-Ala-Aib-OMe. The reaction was stirred at rt for five days. The solvent was removed under reduced pressure. The residue was taken up in EtOAc and washed with aqueous HCl 5%, water, aqueous $NaHCO_{3(sat)}$ and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using CH_2Cl_2/MeOH (90:10) as eluent to give the title compound (1.48 g, 78 %) as a solid. R_f =0.32 (CH_2Cl_2/MeOH 95:5). M.p. 92-94 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ= 7.79-7.17 (m, 9H, ArH, Aib NH); 6.99 (d, J = 7.2 Hz, 1H, Ala NH); 5.74 (bs, 1H, Adt NH); 4.57-4.47 (m, 3H, CH_2, CH); 4.24-4.20 (m, 1H, Ala CH); 3.76-3.69 (m, 4H, 1xSCH_2, OCH_3); 3.54 (d, J = 11.6 Hz, 1H, 1xSCH_2); 3.39-3.27 (m, 2H, SCH_2); 1.52 (s, 3H, CH_3); 1.49 (s, 3H, CH_3); 1.37 (d, J = 6.4 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ= 174.6, 170.9, 168.9, 155.6, 143.3, 143.2, 141.3, 128.9, 128.1, 127.9, 127.1, 124.8, 120.1, 71.7, 67.1, 56.3, 52.5, 49.4, 47.0, 46.8, 25.1, 24.5, 17.7. HRMS (ESI): *m/z* calc. for $[M+H]^+$ $C_{27}H_{32}N_3O_6S_2$ 558.1733; found 558.1732. FTIR (cm^{-1}): 3328, 2996, 2946, 1746, 1726, 1645, 1507. $[\alpha]_D^{20}$: + 20 (*c* 1.0, CH_2Cl_2).

Boc-Aib-Adt-L-Ala-Aib-OMe: Fmoc-Adt-L-Ala-Aib-OMe (2.8 g, 5.02 mmol) was dissolved in CH_2Cl_2 (16 mL) and diethylamine (4 mL). The mixture was stirred at rt for 2 hr. The mixture was concentrated under reduced pressure, and toluene was distilled twice from the residue. Separately, Boc-Aib-OH (1.12g, 5.5 mmol) and cyanuric fluoride (0.94 mL, 11 mmol) were dissolved in CH_2Cl_2 (30 mL) containing pyridine (0.9mL, 11 mmol) at -15 °C. The reaction was stirred at -15 °C for 1 hr, then at rt for 1 hr. The mixture was diluted with

CH_2Cl_2 and washed with iced water. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude Boc-Aib-F was dissolved in CH_2Cl_2 (20 mL) and added to the crude residue of H-Adt-Ala-Aib-OMe. The solution was cooled to 0°C, and NMM (1.32 mL, 12 mmol) was added. The reaction was stirred at rt for 3 days. The solvent was removed under reduced pressure. The residue was taken up in EtOAc and washed with aqueous HCl 5%, water, aqueous $NaHCO_{3(sat)}$ and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using pentane/EtOAc/MeOH (90:10:1) as eluent to give the title compound (1.54 g, 59 %) as a solid. R_f =0.47 (CH_2Cl_2/MeOH 97:3). M.p. 85-87 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.98 (d, J = 7.8 Hz, 1H, Ala NH); 7.22 (s, 1H, Aib NH); 6.72 (s, 1H, Adt NH); 5.01 (s, 1H, Aib NH); 4.50-4.40 (m, 1H, Ala CH); 3.98 (d, J = 11.8 Hz, 1H, 1xSCH_2); 3.73-3.69 (m, 4H, 1xSCH_2, OCH_3); 3.52 (d, J = 12.0 Hz, 1H, 1xSCH_2); 3.05 (d, J = 11.8 Hz, 1H, 1xSCH_2); 1.61-1.43 (m, 24H, 8xCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ= 175.1, 174.9, 171.5, 173.9, 168.4, 155.7, 81.4, 70.8, 57.0, 55.9, 52.1, 49.9, 48.0, 45.7, 28.1, 26.4, 25.1, 24.7, 23.4, 17.1. HRMS (ESI): *m/z* calc. for $[M+Na]^+$ $C_{21}H_{40}N_4O_7S_2Na$ 543.1923; found 543.1920. FTIR (cm^{-1}): 3317, 3293, 2981, 2934, 1738, 1661, 1645, 1518. $[\alpha]_D^{20}$: + 77 (*c* 0.54, CH_2Cl_2).

Boc-L-Ala-Aib-Adt-L-Ala-Aib-OMe: Boc-Aib-Adt-L-Ala-Aib-OMe (740 mg, 1.4 mmol) was dissolved in CH_2Cl_2 (10 mL) and TFA (1 mL) was added. The mixture was stirred at rt for 4 hr. The solvent was removed under reduced pressure and toluene was distilled from the residue twice. Separately, Boc-L-Ala-OH (265 mg, 1.4 mmol), HATU (528 mg, 1.39 mmol) and DIEA (0.73 mL, 4.2 mmol) were dissolved in THF (10 mL) at 0 °C. This solution was directly added to the crude H-Aib-Adt-L-Ala-Aib-OMe. The mixture was stirred at rt for 3 days. The solvent was removed under reduced pressure. The residue was taken up in EtOAc and washed with aqueous HCl 5%, water, aqueous $NaHCO_{3(sat)}$ and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using CH_2Cl_2/MeOH (95:5) as eluent to give the title compound (430 mg, 52 %) as a solid. R_f =0.45 (CH_2Cl_2/MeOH 97.5:2.5). M.p. 191-193 °C ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ= 7.86 (d, J = 7.8 Hz, 1H, Ala NH), 7.39 (s, 1H, Aib NH), 7.25 (s, 1H, Adt NH), 6.76 (s, 1H, Aib NH), 5.25 (bs, 1H, Ala NH), 4.47-4.36 (m, 1H, Ala CH), 4.06 (d, J = 12.0 Hz, 1H, 1xSCH_2), 3.95-3.87 (m, 1H, Ala CH), 3.70-3.66 (m, 4H, 1xSCH_2, OCH_3), 3.52 (d, J = 11.9 Hz, 1H, 1xSCH_2), 3.37 (d, J = 11.9 Hz, 1H, 1xSCH_2),

1.63-1.37 (m, 27H, 9CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=: 175.1, 174.9, 173.9, 172.1, 169.7, 156.8, 81.6, 71.7, 56.5, 55.8, 52.6, 52.1, 50.1, 48.6, 47.8, 28.3, 26.8, 25.3, 24.7, 23.3, 16.9, 16.6. HRMS (ESI): *m/z* calc. for $[M+Na]^+$ $C_{24}H_{41}N_5O_8S_2Na$ 614.2294; found 614.2294. FTIR (cm^{-1}): 3289, 2977, 2930, 1738, 1665, 1653, 1522**.** $[\alpha]_D^{20}$: + 65 (*c* 0.32, CH_2Cl_2).

Fc-CO-Adt-L-Ala-Aib-Adt-L-Ala-Aib-OMe: Boc-L-Ala-Aib-Adt-L-Ala-Aib-OMe (20 mg, 0.034 mmol) was dissolved in a solution of HCl in diethyl ether (2M, 4 mL). The mixture was stirred at rt for 3 h, then concentrated under reduced pressure. Separately, Fc-CO-Adt-OMe (25 mg, 0.063 mmol) was dissolved in THF (0.5 mL) and MeOH (0.3 mL) and aqueous NaOH solution (2M, 0.06 mL) was added. The mixture was stirred at rt for 6 hr. The mixture was acidified by the addition of aqueous HCl 5%, and extracted three times with EtOAc. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue of crude Fc-CO-Adt-OH was dissolved in THF (2 mL) and added to the residue of crude HCl·H-L-Ala-Aib-Adt-L-Ala-Aib-OMe. The mixture was cooled on an ice bath and HATU (27 mg, 0.071 mmol) and DIEA (25 µL) were added. The mixture was then stirred at rt for 6 days. The mixture was concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 and washed with aqueous HCl 0.5N, water, aqueous $NaHCO_{3(sat.)}$ and brine. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using CH_2Cl_2/MeOH (95:5) as eluent to give the title compound (11 mg, 38 %) as an orange solid. R_f =0.48 (CH_2Cl_2/EtOAc 92.5:7.5). M.p. 134-136°C. NMR (^{1}H 300 MHz CD_3CN) δ (ppm): 7.76 (d, *J* = 7.4 Hz, 1H, Ala^5 NH), 7.62 (s, 1H, Aib^3 NH), 7.59 (b, 1H, Ala^2 NH), 7.53 (s, 1H, Adt^4 NH), 7.23 (s, 1H, Aib^6 NH), 7.19 (s, 1H, Adt^1 NH), 4.88, 4.82 (2s, 2H, 2H Fc ring), 4.48 (s, 2H, 2H Fc ring) 4.30 (s, 5H, Fc ring), 4.16 (m, 2H, Ala^5 α-CH, 1xSCH_2), 3.96 (m, 2H, Ala^2 α-CH, 1xSCH_2), 3.78 (d, *J* = 12.0 Hz, 1H, 1xSCH_2), 3.62-3.54 (m, 6H, 3xSCH_2, OCH_3), 3.38 (d, *J* = 12.4 Hz, 1H, 1xSCH_2), 3.25 (d, *J* = 12.0 Hz, 1H, 1xSCH_2), 1.52-1.27 (m, 18H, Aib^3 β-CH_3, Aib^6 β-CH_3, Ala^2 β-CH_3, Ala^5 β-CH_3). ^{13}C NMR (75 MHz, CD_3CN, 25 °C): δ 177.1, 175.7, 175.4, 173.3, 172.9, 170.8, 167.8, 75.8, 73.0, 72.7, 72.4, 72.3, 70.8, 70.0, 69.7, 57.7, 56.5, 53.8, 52.5, 51.1, 50.4, 49.0, 48.9, 48.5, 28.8, 26.9, 25.7, 25.4, 23.7, 17.6, 16.7. HRMS (ESI): *m/z* calc. for $[M+H]^+$ $C_{34}H_{47}FeN_6O_8S_4$ 851.1687; found 851.1659. FTIR (cm^{-1}): 3286, 3027, 2950, 2927, 2849, 2336, 1715, 1487, 1406. $[\alpha]_D^{20}$: + 115 (*c* 0.12, CH_2Cl_2).

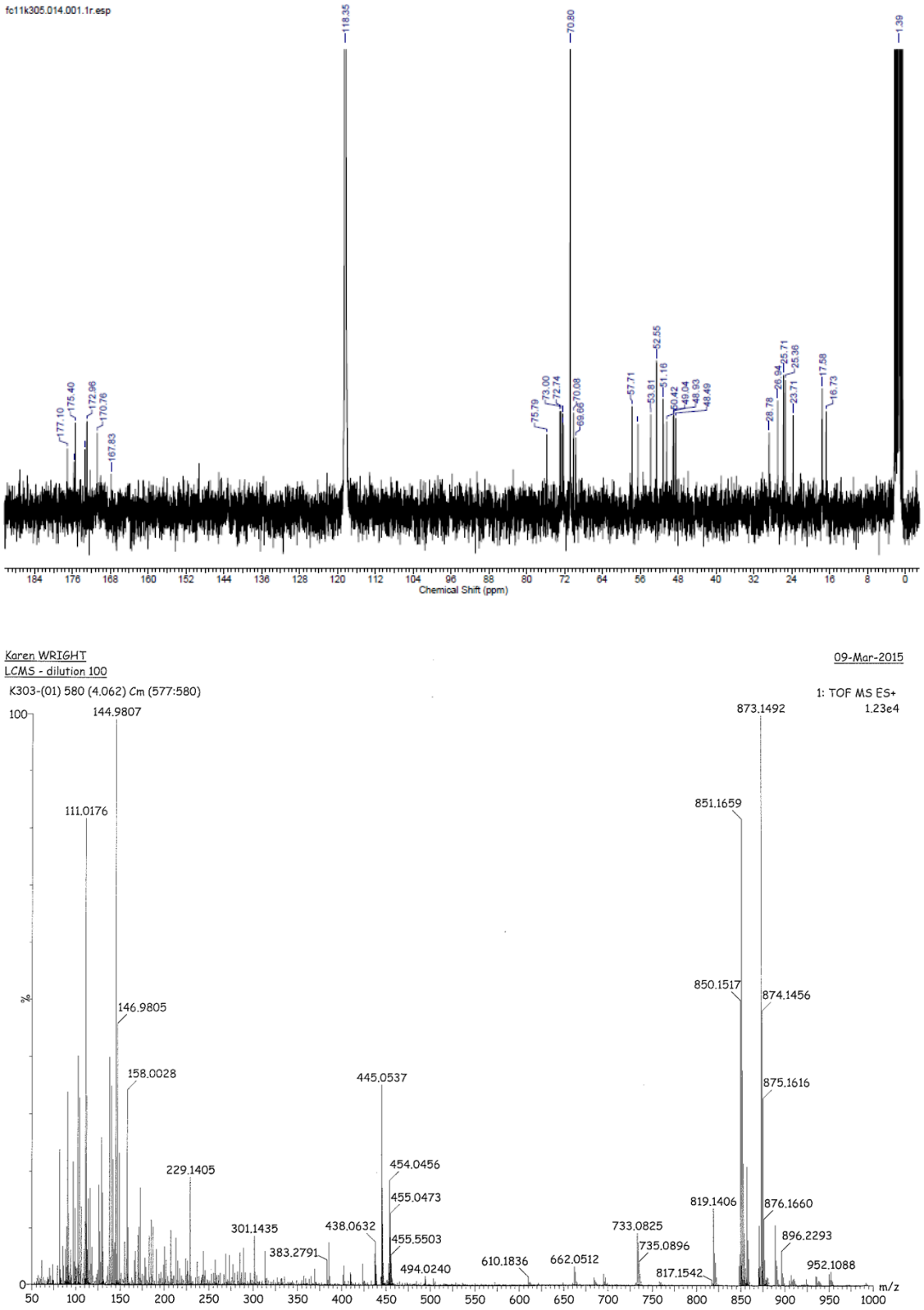


Figure S1. ^{13}C NMR spectrum (top) and HRMS (ESI) spectrum (bottom) of Fc-CO-Adt-L-Ala-Aib-Adt-L-Ala-Aib-OMe.

2. 2D-NMR (TOCSY and ROESY) spectra of Fc-CO-6Adt2 in 7:3 (*v/v*) CD_3CN/CD_3Cl 70/30 (v/v).

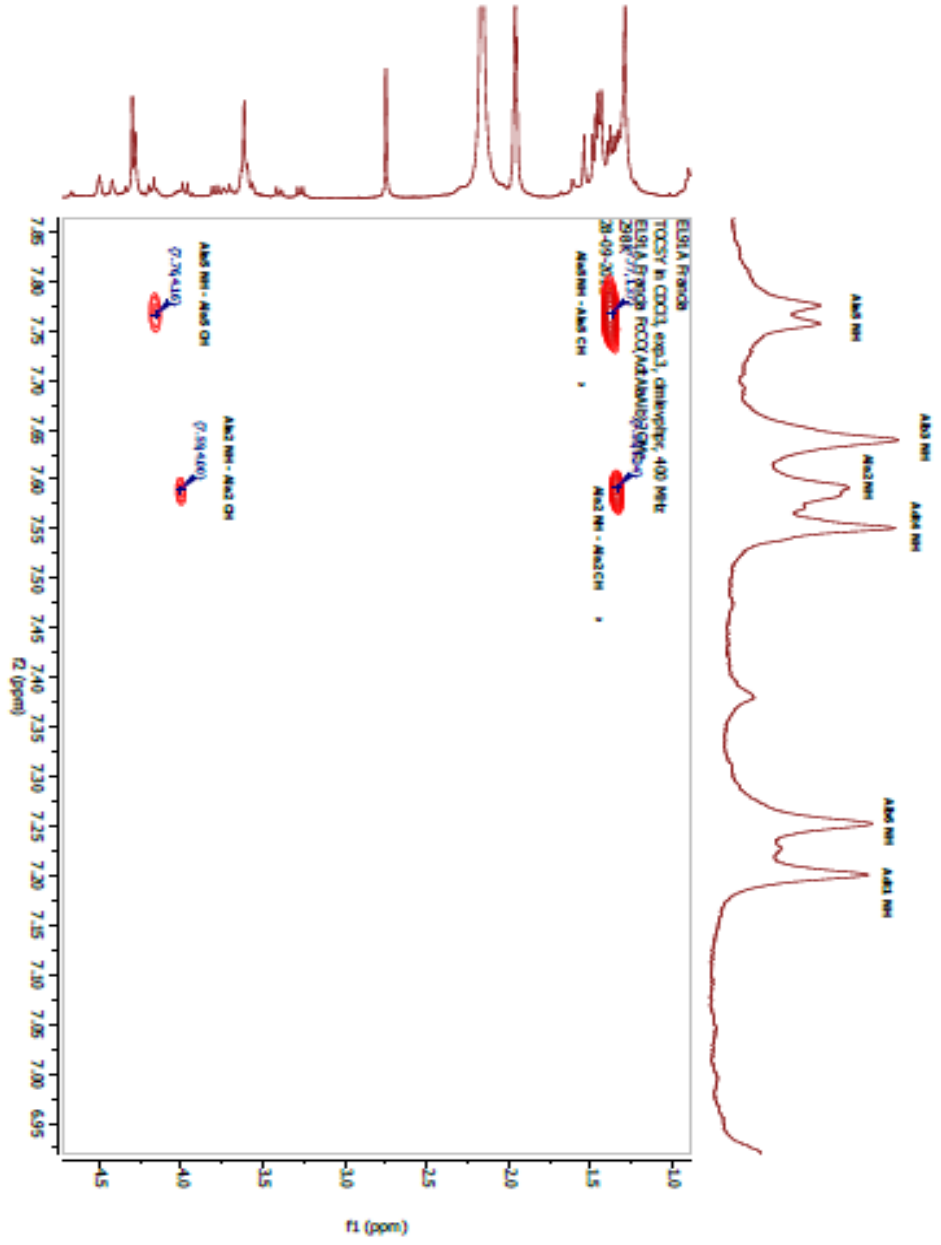


Figure S2. TOCSY spectrum of Fc-CO-6Adt2 in the $NH_i \rightarrow CH_i$ and $NH_i \rightarrow CH_{3,i}$ regions. The two Ala spin systems have been assessed by means of these cross-couplings.

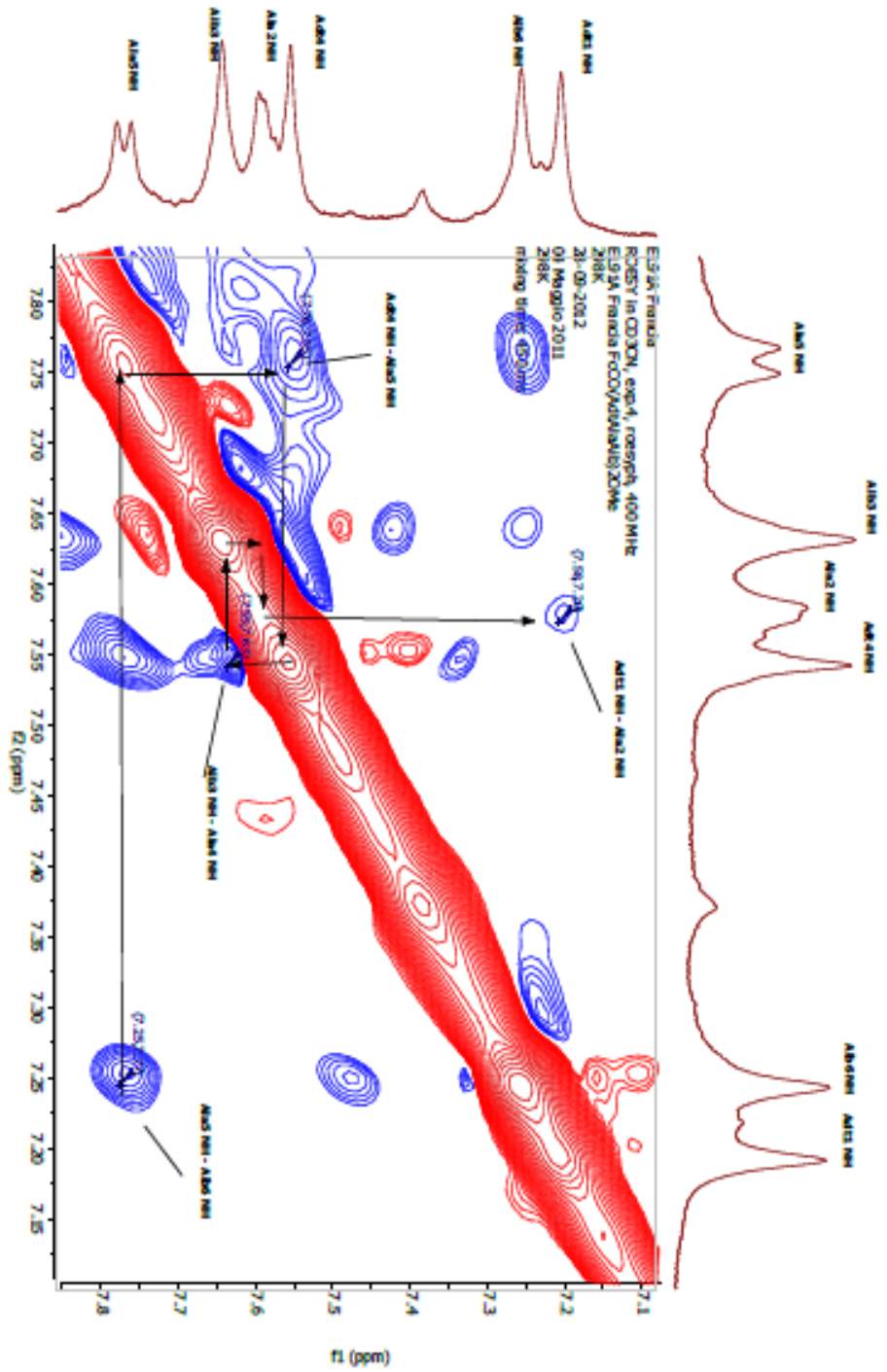


Figure S3. ROESY spectrum of Fc-CO-6Adt2 in the $NH_i \rightarrow NH_{i+1}$ cross-coupling region.

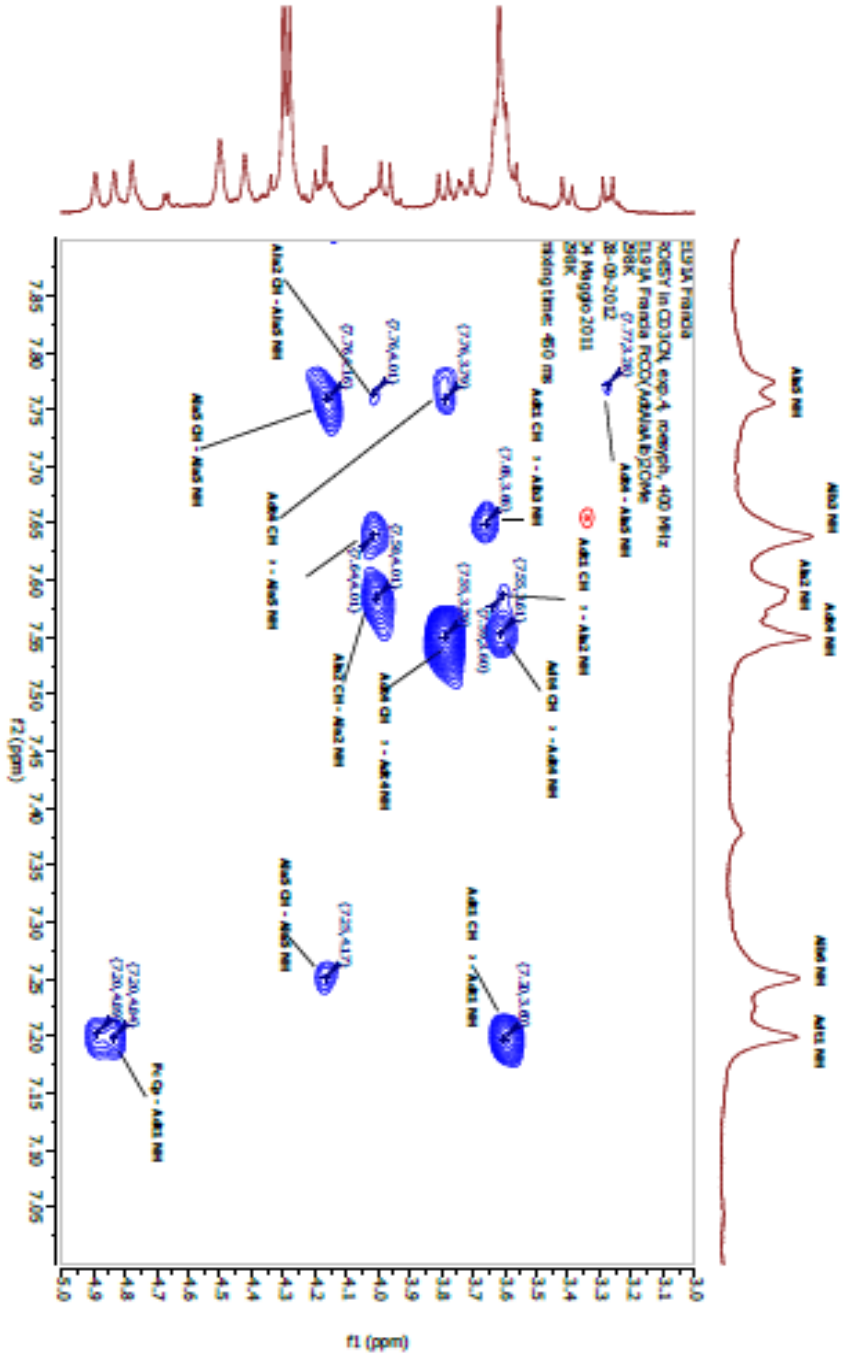


Figure S4. ROESY spectrum of Fc-CO-6Adt2 in the $CH_i/CH_{2,i} \rightarrow NH_{i+n}$ (n=0, 1, 2, 3, 4) cross-coupling region.

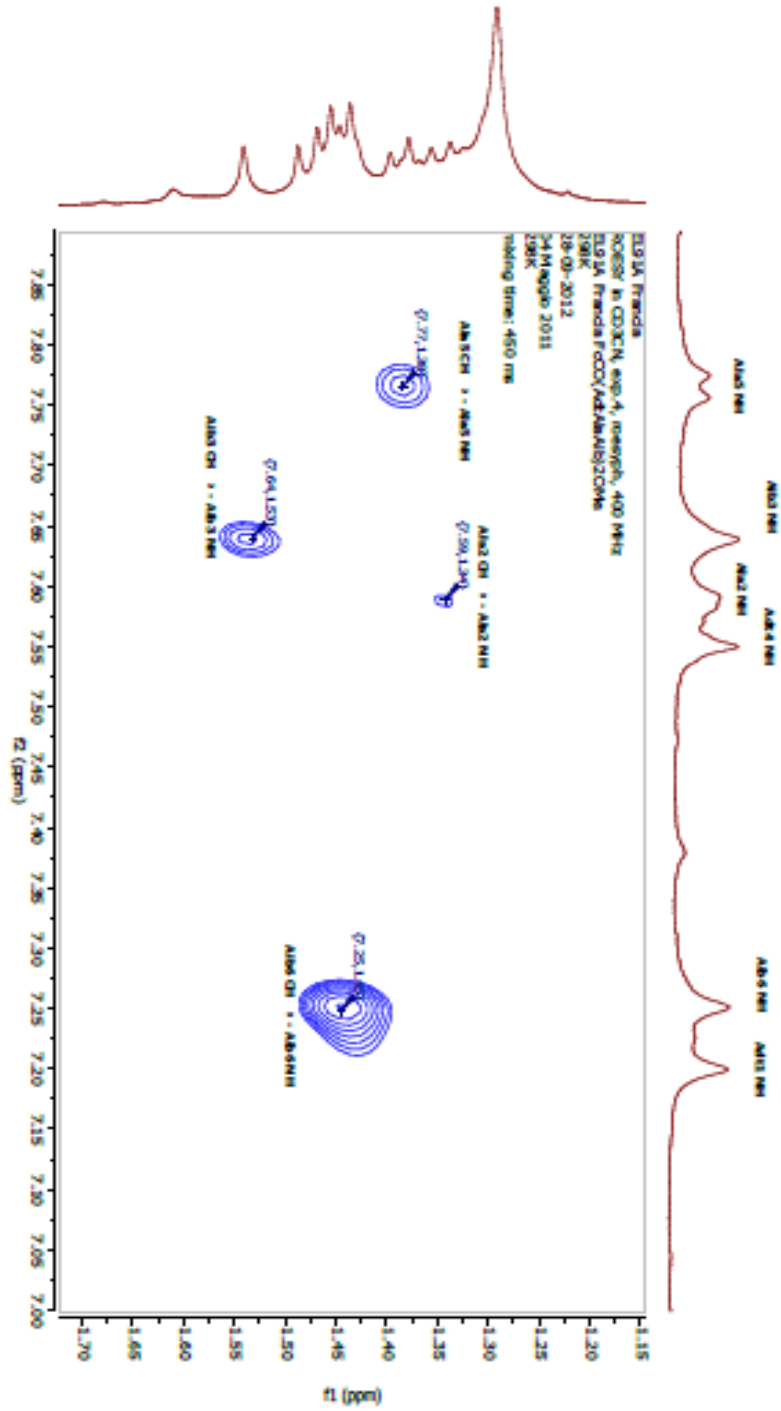


Figure S5. ROESY spectrum of Fc-CO-6Adt2 in the $CH_{3,i} \rightarrow NH_{i+n}$ (n=0, 1, 2, 3) cross-coupling region.

3. X-Ray diffraction data for BOC-L-Ala-Aib-Adt-L-Ala-Aib-OMe

Table S1. Crystal data and structure refinement for Boc-L-Ala-Aib-Adt-L-Ala-Aib-OMe monohydrate (mc212f)

Identification code	mc212f	
Empirical formula	$C_{24}H_{43}N_5O_9S_2$	
Formula weight	609.75	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.3683(2) Å	α = 90°.
	b = 13.2976(2) Å	β = 103.835(2)°.
	c = 11.9762(2) Å	γ = 90°.
Volume	1603.30(5) $Å^3$	
Z	2	
Density (calculated)	1.263 Mg/m^3	
Absorption coefficient	1.962 mm^{-1}	
F(000)	652	
Crystal size	0.44 × 0.18 × 0.06 mm^3	
Theta range for data collection	3.80 to 70.96°.	
Index ranges	$-11 \le h \le 12$, $-16 \le k \le 16$, $-14 \le l \le 14$	
Reflections collected	25756	
Independent reflections	6118 [*R*(int) = 0.0367]	
Completeness to theta = 70.96°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.39179	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6118 / 1 / 361	
Goodness-of-fit on F^2	1.032	
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0590$, $wR_2 = 0.1707$	
R indices (all data)	$R_1 = 0.0623$, $wR_2 = 0.1761$	
Absolute structure parameter	0.02(3)	
Largest diff. peak and hole	0.723 and -0.334 e.$Å^{-3}$	

Table S2. Selected torsion angles [°] for Boc-L-Ala-Aib-Adt-L-Ala-Aib-OMe monohydrate

C01-OU-C0-N1	-170.1(3)
OU-C0-N1-C1A	173.1(3)
C0-N1-C1A-C1	-55.3(4)
N1-C1A-C1-N2	-23.7(3)
C1A-C1-N2-C2A	177.1(2)
C1-N2-C2A-C2	-52.0(3)
N2-C2A-C2-N3	-30.3(3)
C2A-C2-N3-C3A	179.5(2)
C2-N3-C3A-C3	-53.9(3)
N3-C3A-C3B1-S3G1	-98.3(3)
C3B2-C3A-C3B1-S3G1	23.5(3)
C3A-C3B1-S3G1-S3G2	7.9(3)
C3B1-S3G1-S3G2-C3B2	-30.15(18)
N3-C3A-C3B2-S3G2	71.1(3)
C3B1-C3A-C3B2-S3G2	-49.1(3)
S3G1-S3G2-C3B2-C3A	47.3(2)
N3-C3A-C3-N4	-30.4(3)
C3A-C3-N4-C4A	-176.3(2)
C3-N4-C4A-C4	-88.5(3)
N4-C4A-C4-N5	3.5(4)
C4A-C4-N5-C5A	-176.6(3)
C4-N5-C5A-C5	-44.4(5)
N5-C5A-C5-OT	-48.5(5)
C5A-C5-OT-CT	-176.9(6)

Table S3. Intra- and intermolecular hydrogen bond parameters for Boc-L-Ala-Aib-Adt-L-Ala-Aib-OMe monohydrate

Donor (D-H)	Acceptor (A)	Distance (Å) D … A	Distance (Å) H … A	Angle (°) D-H … A	Symmetry equivalence of A
N3-H3	O0	3.054(3)	2.22	164	*x, y, z*
N4-H4	O1	2.902(3)	2.08	160	*x, y, z*
N5-H5	O2	2.999(3)	2.16	164	*x, y, z*
N1-H1	O3	2.942(3)	2.10	168	1+*x, y, z*
N2-H2	O1W	2.909(4)	2.11	154	*x, y, z*
O1W-H1WA	O3	2.958(4)	2.23	154	1+*x, y, z*
O1W-H1WB	O4	2.781(4)	2.00	159	1-*x,* 1/2+*y,* 1-*z*

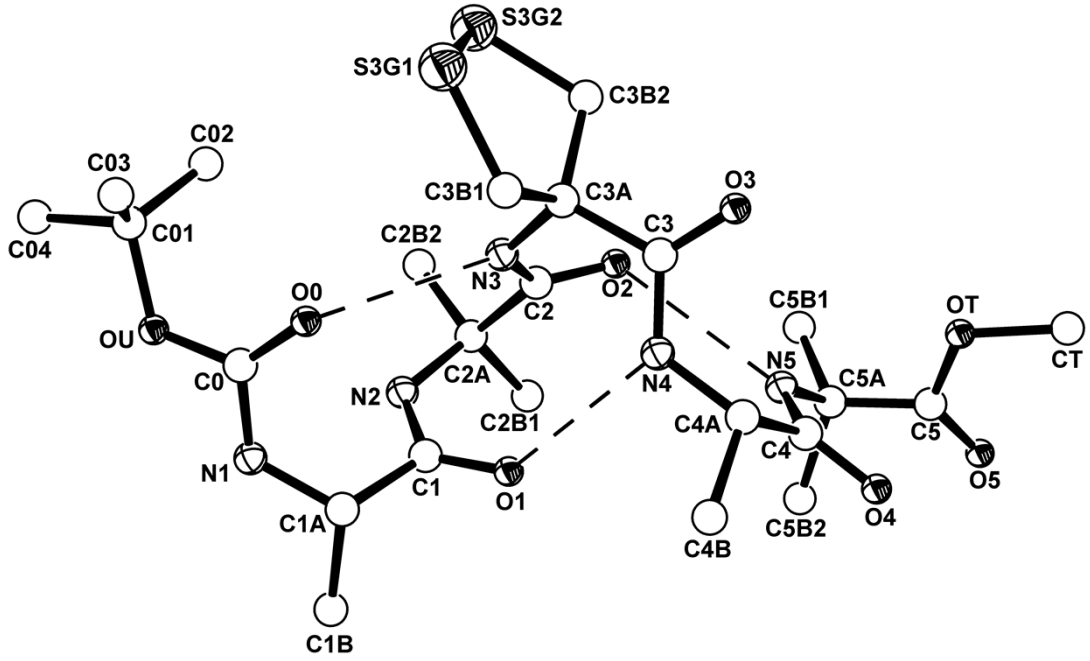


Figure S6. X-Ray diffraction structure of Boc-L-Ala-Aib-Adt-L-Ala-Aib-OMe with atom numbering. Intramolecular H-bonds are indicated by dashed lines.

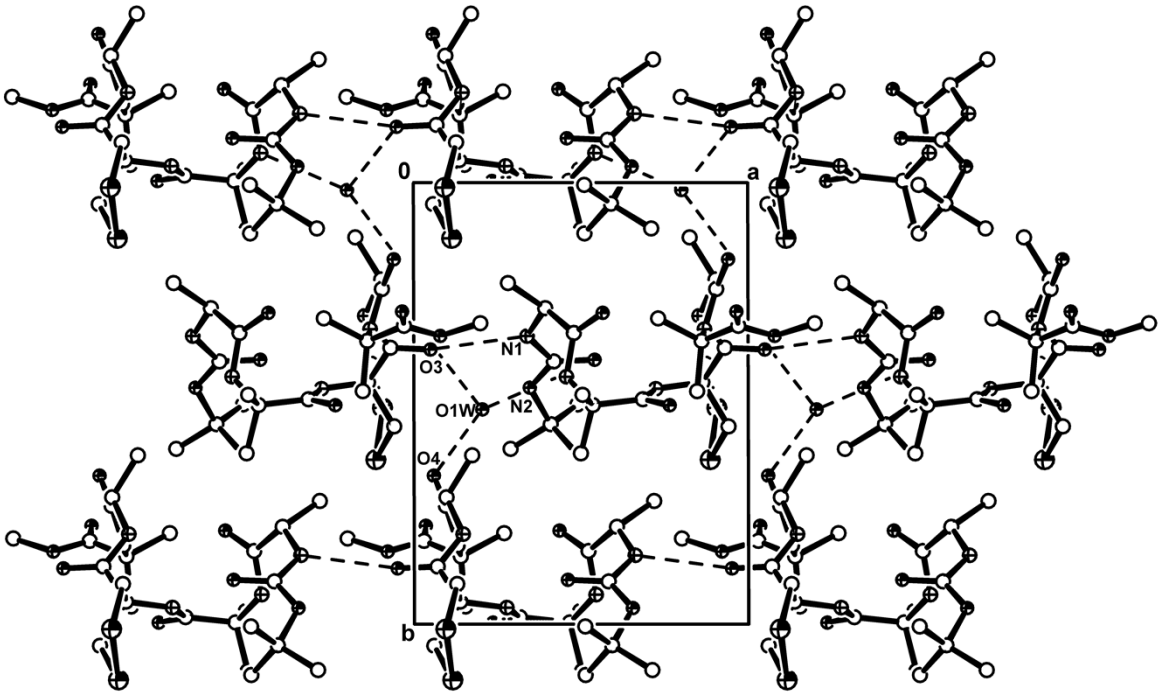


Figure S7. Packing mode of the molecules of Boc-L-Ala-Aib-Adt-L-Ala-Aib-OMe monohydrate as viewed down the *c* axis. Intermolecular H-bonds are indicated by dashed lines.

4**. X-Ray Photoelectron spectrum of Fc-CO-6Adt2 in the C1s region.**

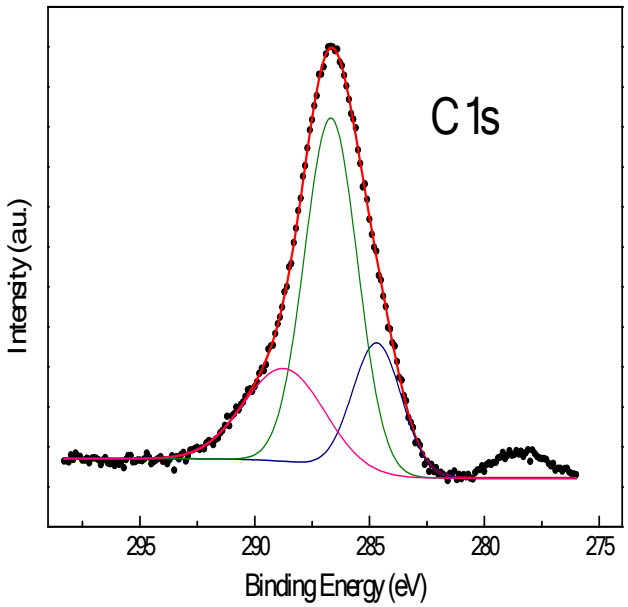


Figure S8. X-Ray photoelectron spectrum of Fc-CO-6Adt2 in the C1s region.

5. STM imaging of the bare and Fc-CO-6Adt2-modified gold surface

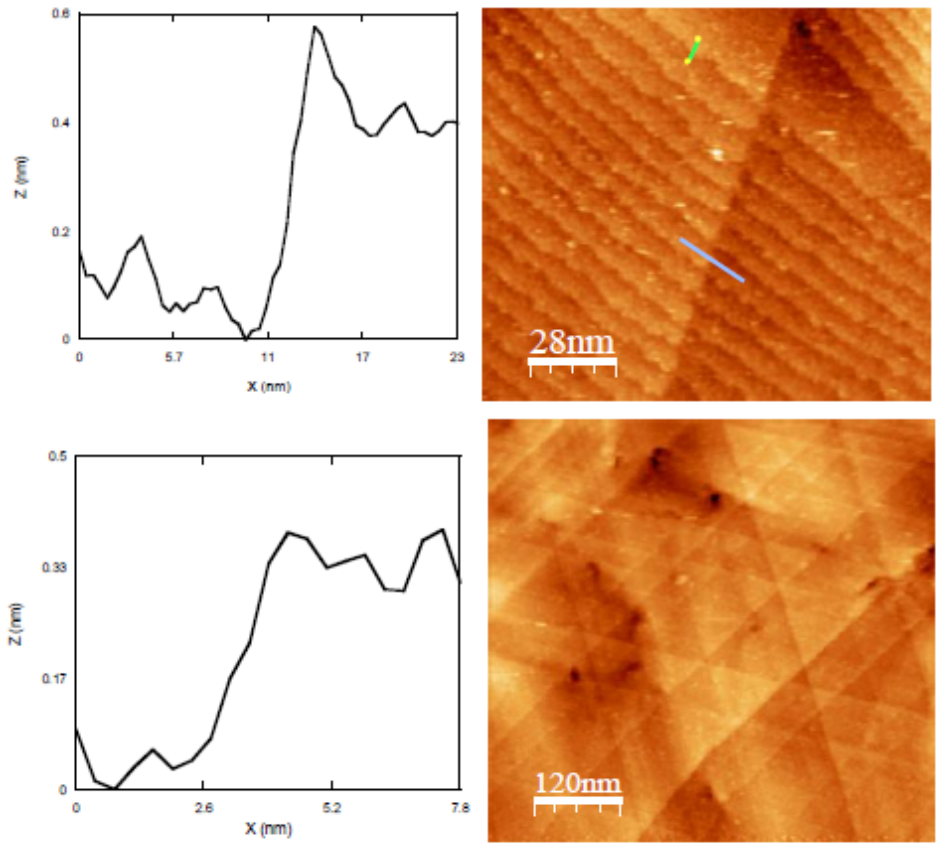


Figure S9. Scanning tunneling microscopy imaging of the bare gold substrate under ultra-high vacuum conditions. The images show wide atomically-flat regions of the bare gold substrate (right). The profiles reported on the left, corresponding to the green (upper left) and pale blue (lower left) bars on the upper right figure, show that the gold terraces are separated by Au(111) atomic steps (0.24 nm) or slight dislocations during the gold growth.

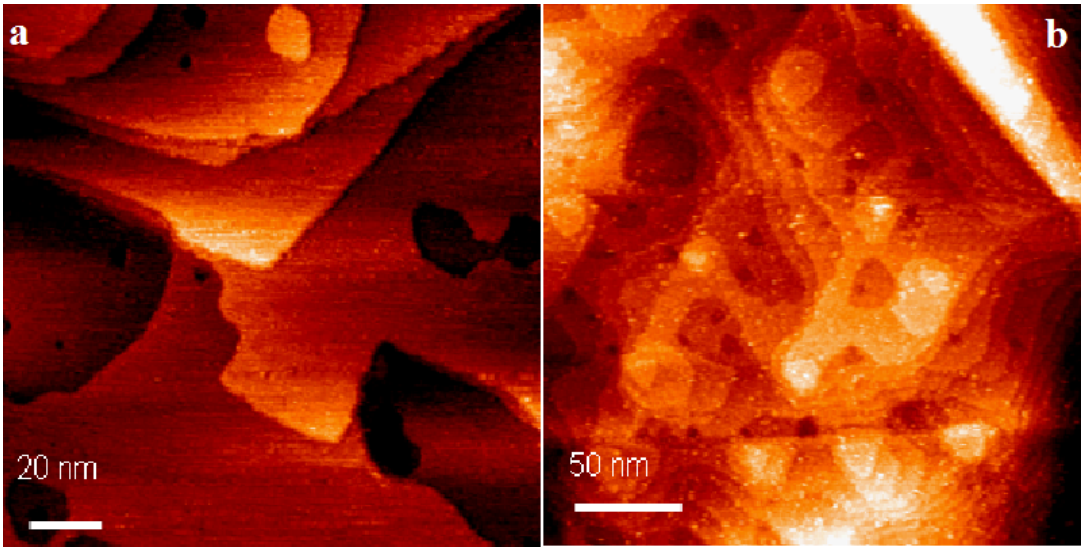


Figure S10. Scanning tunneling microscopy imaging of the bare gold substrate (a) and the gold substrate modified by deposition of a millimolar solution of Fc-CO-6Adt2 (b).

6. Cathodic and anodic overpotential as a function of the scan velocity (Cyclic Voltammetry)

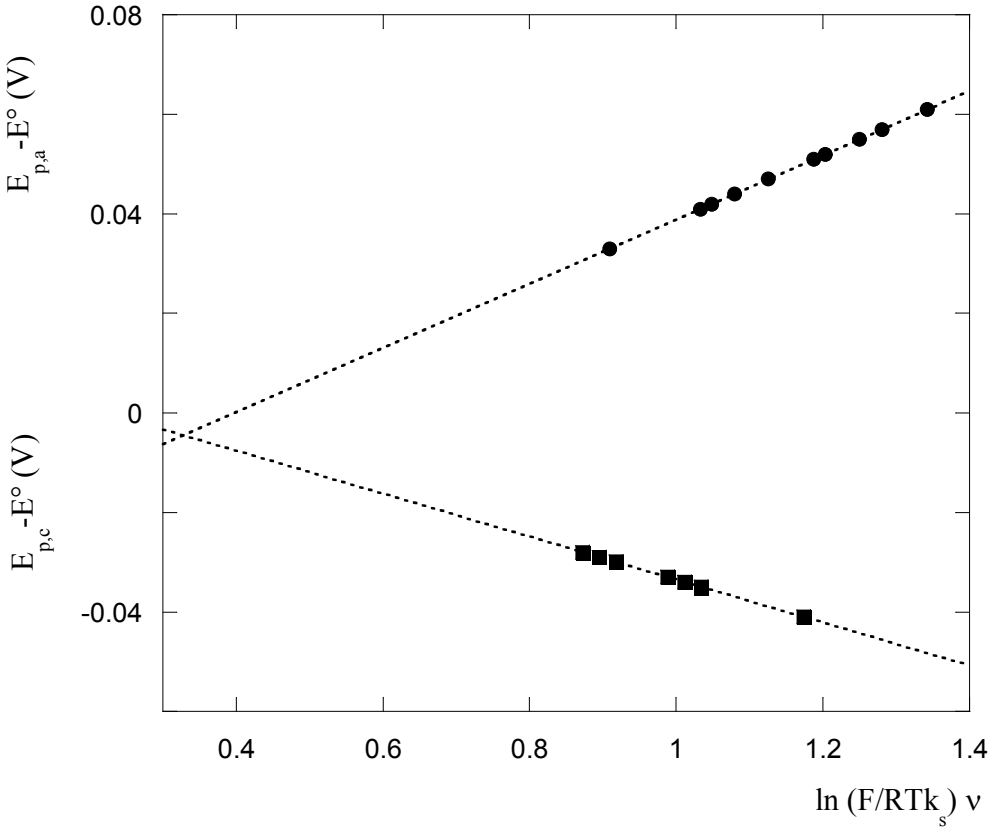


Figure S11. Dependence of the difference between the anodic ($E_{p,a}$; filled circles) and cathodic ($E_{p,c}$; filled squares) peak potentials and the formal potential E° with respect to the natural logarithm of the scan velocity ν from Cyclic Voltammetry experiments using an Fc-CO-6Adt2 modified gold electrode.