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Fullerene Helical Peptide: Synthesis, Characterization and Formation of Self-Assembled Monolayers on gold surfaces

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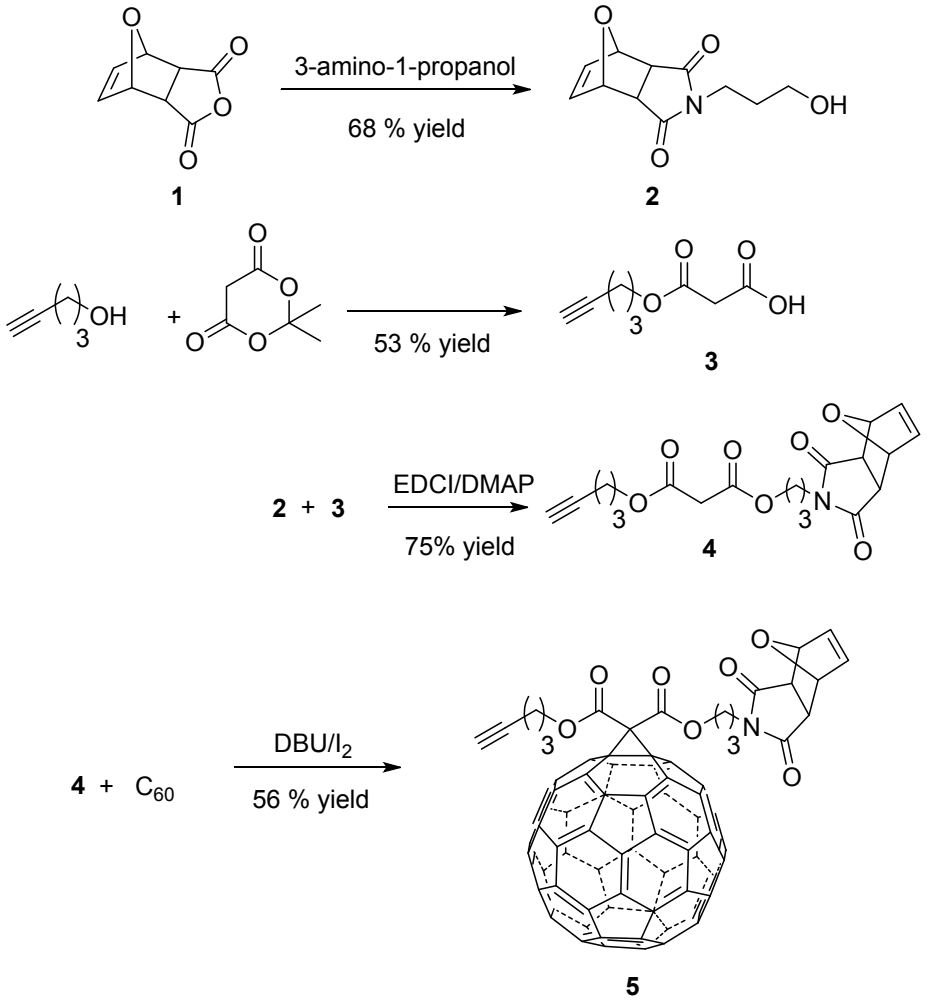
Materials and methods

General methods. All reagents were used directly without further purification. Fullerene C_{60} (purity99.5+%) was purchased from MTR Ltd. Dichloromethane (DCM) was dried and distilled over CaH_2 prior to use. Toluene was distilled over NaH prior to use. All other solvents were used as received. Column chromatography: silica gel 60 (0.040-0.063 mm) was purchased from E. Merck. Thin layer chromatography (TLC) was performed on aluminum sheets coated with silica gel60 F_{254} from E. Merck and visualized by UV light. 1H NMR and ^{13}C NMR spectra were recorded using a Brucker spectrometer at 300MHz or 200MHz (^{1}H) and at 75.5 MHz (^{13}C) in CDCl3 unless otherwise stated. Chemical shifts (δ) were referenced to internal solvent CDCl3 (7.26 for ^{1}H and 77,16 ppm for ^{13}C). High Resolution ESI-MS mass spectra were obtained with a Waters Xevo Qtof. Optical rotations were determined with a Perkin Elmer 341 instrument. Melting points are uncorrected.

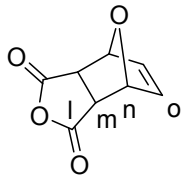
The ligand N,N',N''-tris(2-dibenzylaminoethyl)amine (hexabenzyltren) was synthesized in two steps from tris(2-aminoethyl)amine as described.[1, 2]

Synthesis of compounds 1-5



Scheme S1. Synthesis of compounds **1-5**

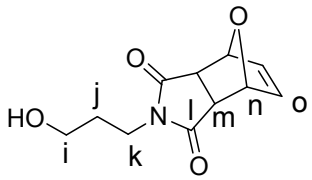
Compound 1[3]:



1

Maleic anhydride (15 g, 150 mmol) and furan (10.2 mL, 140 mmol) were added to diethyl ether (60 mL). The reaction mixture was stirred at room temperature for 48 hours and a white precipitate was observed. The resulting reaction mixture was filtered. The recovered solid was washed with diethyl ether and dried under vacuum to give 14.3 g of **1** as a white solid in 61 % yield. Mp: 118-119°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=3.18 (s, 2H, H_m), 5.46 (t, 2H, J = 0.9 Hz, H_n), 6.58 ppm (s, 2H, H_o).

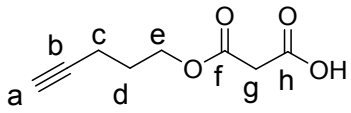
Compound 2[4]:



2

Malonate **1 (**1.11 g, 6.68 mmol) was dissolved in methanol (60 mL) and 3-amino-1-propanol (0.51 mL,6.65 mmol) was then added. The reaction mixture was stirred at 56 °C over a period of 3 days and then concentrated. The residue was purified by column chromatography using DCM/methanol 99/1 as eluent to afford 1.0g of **2** as a white powder in 68% yield. Mp: 120-121 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.76 (dt, 2H, J = 12.1 Hz, J = 6.0 Hz, H_j), 2.53 (bs, 1H, OH), 2.87 (s, 2H, H_m), 3.52 (t, 2H, J = 5.7 Hz, H_k), 3.65 (m, 2H, H_i), 5.27 (s, 2H, H_n), 6.52ppm (s, 2H, H_o).

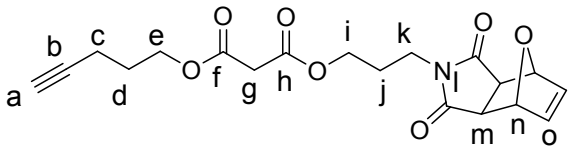
Compound 3:



3

Meldrum's acid (6.07 g, 42 mmol) was added in a round bottomed flask to 4-pentyn-1-ol (3.5 g, 42 mmol). The reaction mixture was stirred overnight at 80°C. After evaporation of the formed acetone, the residue was purified by column chromatography using $CHCl_3$ as eluent to afford 3.83 g of **3** as yellow pasty solid in 53% yield. Mp: 45-49 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.81-1.95 (m, 2H, H_d), 1.97 (t, 1H, J = 2.6 Hz, H_a), 2.30 (td, 2H, J = 7.0 Hz, J = 2.6 Hz, H_c), 3.44 (s, 2H, H_g), 4.29 (t, 2H, J = 6.3 Hz, H_e), 9.07 ppm (bs, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=15.2(C_c), 27.4(C_d), 40.8(C_g), 64.6(C_e), 69.4(C_a), 82.8(C_b), 166.9(C_f), 171.3ppm (C_h); HRMS (ESI+) m/z calcd for $C_8H_{10}O_4Na$: 193.0477 [M +Na^+], found 193.0445.

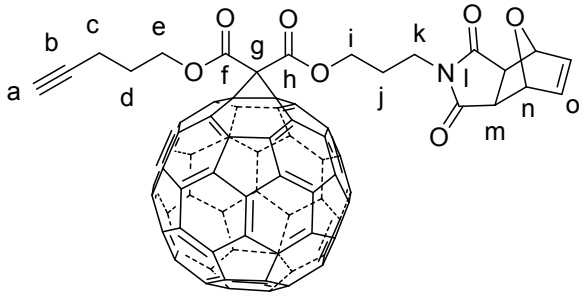
Compound 4:



4

In a round bottomed flask alkyne **3** (1.32 g,8.4 mmol) and maleimide **2** (1.54 g, 6.9 mmol) were dissolved in dry DCM (50 mL) and placed under argon. The resulting solution was cooled to 0 °C, then EDCI.HCl (1.46 g,7.6 mmol) and DMAP (0.84 g,6.9 mmol) were added. The reaction mixture was stirred at 0°C for 30 min, then at room temperature for 3 days and finally concentrated. Purification of the residue by column chromatography (DCM/Et_2O 90/10 as eluent) afforded 2.12 g of **4** as a colorless oil in 82 % yield. ^1H NMR (300 MHz, $CDCl_3$) δ=1.81-1-95 (m, 5H, H_a, H_d, H_j), 2.27 (td, 2H, J = 6.8 Hz, J = 1.9Hz, H_c), 2.82 (s, 2H, H_m), 3.37 (s, 2H, H_g), 3.55 (t, 2H, J = 6.9 Hz, H_k), 4.08 (t, 2H, J = 6.2 Hz, H_e), 4.23 (t, 2H, J = 6.3 Hz, H_i), 5.23 (s, 2H, H_n), 6.48 ppm (s, 2H, H_o); ^{13}C NMR (75 MHz, $CDCl_3$) δ=15.1(C_c), 26.6(C_d), 27.4(C_j), 35.7(C_g), 41.5(C_k), 47.5(C_m), 62.5(C_e), 64.0(C_i), 69.2(C_a), 80.9 (C_n),82.9(C_b),136.5(C_o), 166.37 (C_f), 166.41 (C_h), 176.1 ppm (C_l); HRMS (ESI+) m/z calcd for $C_{19}H_{22}NO_7$: 376.1396 [M + H^+], found 376.1389.

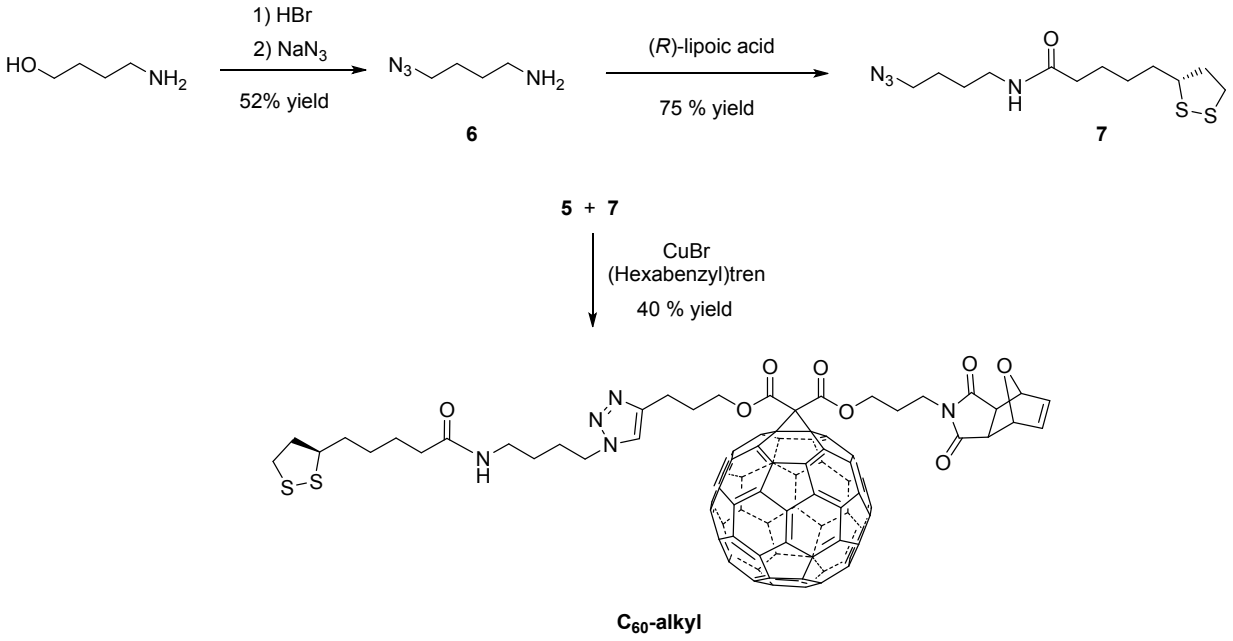
Compound 5:



5

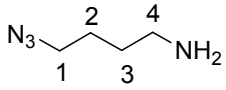
Fullerene C_{60} (600 mg, 0.83 mmol) was dissolved in dry toluene (450 mL). After 3 hours of stirring, malonate **4** (260 mg,0.69 mmol) in dry toluene (5 mL) was added, and argon was then bubbled through the solution for 20 minutes. To the oxygen-free solution were added successively I_2 (210 mg, 0.82 mmol) and DBU (210 µL, 1.40 mmol). The resulting reaction mixture was stirred at room temperature for 19 h under argon and evaporated to dryness. Purification of the brown residue by column chromatography (toluene, then DCM, then DCM/Et_2O 95/5 as eluent) gave 505 mg of **5** as a black solid in 56 % yield. ^1H NMR (300 MHz, $CDCl_3$) δ=2.03-2.14(m, 5H, H_a, H_d, H_j), 2.41 (td, 2H, J = 6.8 Hz, J = 2.2 Hz, H_c), 2.90 (s, 2H, H_m), 3.69 (t, 2H, J = 6.8 Hz, H_k), 4.48 (t 2H, J = 6.2 Hz, H_e), 4.64 (t 2H, J = 6.2 Hz, H_i), 5.29 (s, 2H, H_n), 6.51ppm (s, 2H, H_o); ^{13}C NMR (75 MHz, $CDCl_3$) δ=15.3(C_c), 27.0(C_d), 27.4(C_j), 35.8(C_k), 47.5(C_m), 64.7(C_e), 65.9(C_i), 69.9(C_a, C_g), 81.1(C_n),82.5(C_b),136.6(C_o), 138.8, 139.3, 141.0, 141.9, 142.2, 143.0, 143.1, 143.9, 143.9, 144.66, 144.70, 144.9, 145.0, 145.1, 145.18, 145.2, 145.3, 145.4, (Csp^2 C_{60}),163.57, 163.51 (C_f, C_h), 176.3ppm (C_l); HRMS (ESI+) m/z calcd for $C_{79}H_{19}NO_7Na$: 1116.1059 [M + Na^+], found 1116.1097.

Synthesis of compounds 6-C_{60}-alkyl



Scheme S2. Synthesis of compounds **6-C_{60}-alkyl**

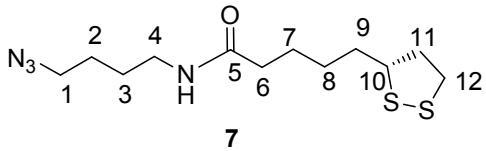
Compound 6[5]:



6

In a round bottomed flask, 4-amino-1-butanol (960 µL, 10.4 mmol) was introduced with 10 mL of HBr 48 %(aq). After 3 hours of stirring at 100 °C, the mixture was concentrated under reduced pressure. The residue was diluted with H_2O (7 mL) and sodium azide (2.8 g, 43 mmol) was added. The reaction mixture was stirred at 80 °C overnight and finally concentrated. A 20 % aq. solution of NaOH was added to the crude product, which was extracted into DCM. The combined extracts were washed with water and dried over $MgSO_4$ to obtain 620 mg of **6** as yellow oil in 52 % yield. ^{1}H NMR (200 MHz, CDCl3) δ=1.48–1.65 (m, 4H, H_2, H_3), 2.74 (t, 2H, J = 6.5 Hz, H_4), 3.29 ppm (t, 2H, J = 6.5 Hz, H_1); HRMS (ESI+) m/z calcd for $C_4H_{11}N_4$: 115.0984 [M+H$^+$], found 115.0981.

Compound 7:

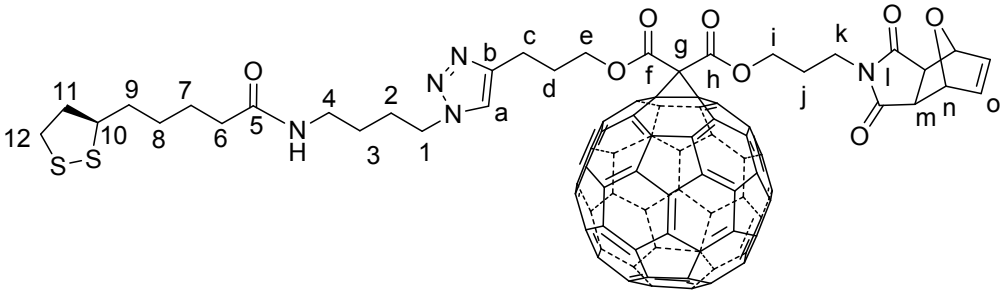


7

Azido derivative **6** (200 mg, 1.75 mmol) was dissolved in THF (10 mL) and (*R*)-lipoic acid (361mg,1.75 mmol) was added. HATU (800 mg, 2.1 mmol) and DIPEA (0.81 mL, 4.7 mmol) were then added at 0 °C. The reaction mixture was stirred overnight at room temperature. The crude product was taken up in DCM and washed successively with aq. HCl 0.5 N, water and aq. $NaHCO_3$ (saturated) and finally dried over $MgSO_4$. Purification of the yellow oily residue was first performed by column chromatography (SiO_2, DCM/MeOH 95/5) then by extraction using Et_2O/H_2O to eliminate residual TMU from the product, and gave 400 mg of **7** as a yellow oil in 75% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.38–1.50 (m, 2H, H_8),1.55-1.79 (m, 8H, H_2, H_3, H_7, H_9), 1.90(td, 1H,

J=13.6Hz, *J* = 6.9 Hz, $H_{11'}$*),* 2.16 (t, 2H, *J* = 7.4 Hz, H_6), 2.44 (td, 1H, $H_{11''}$, *J* = 12.4 Hz, *J* = 6.4 Hz), 3.06-3.35 (m 6H, H_1, H_4,H_{12}), 3.57 (dt, 1H, *J* = 13.6 Hz, *J* = 6.8 Hz, H_{10}), 5.69ppm (bs, 1H, NH).^{13}C NMR (75 MHz, $CDCl_3$) δ=25.4,26.2, 26.9, 28.8, 34.7(C_2, C_3, C_7, C_8, C_9), 36.4(C_6), 38.6(C_{12}), 38.9(C_4), 40.3(C_{11}), 51.0(C_1), 56.3 (C_{10}), 172.9 ppm (C_5). HRMS (ESI+) m/z calcd for $C_{12}H_{23}N_4OS_2$: 303.1313[M+H^+], found 303.1315.

Compound C_{60}-alkyl:

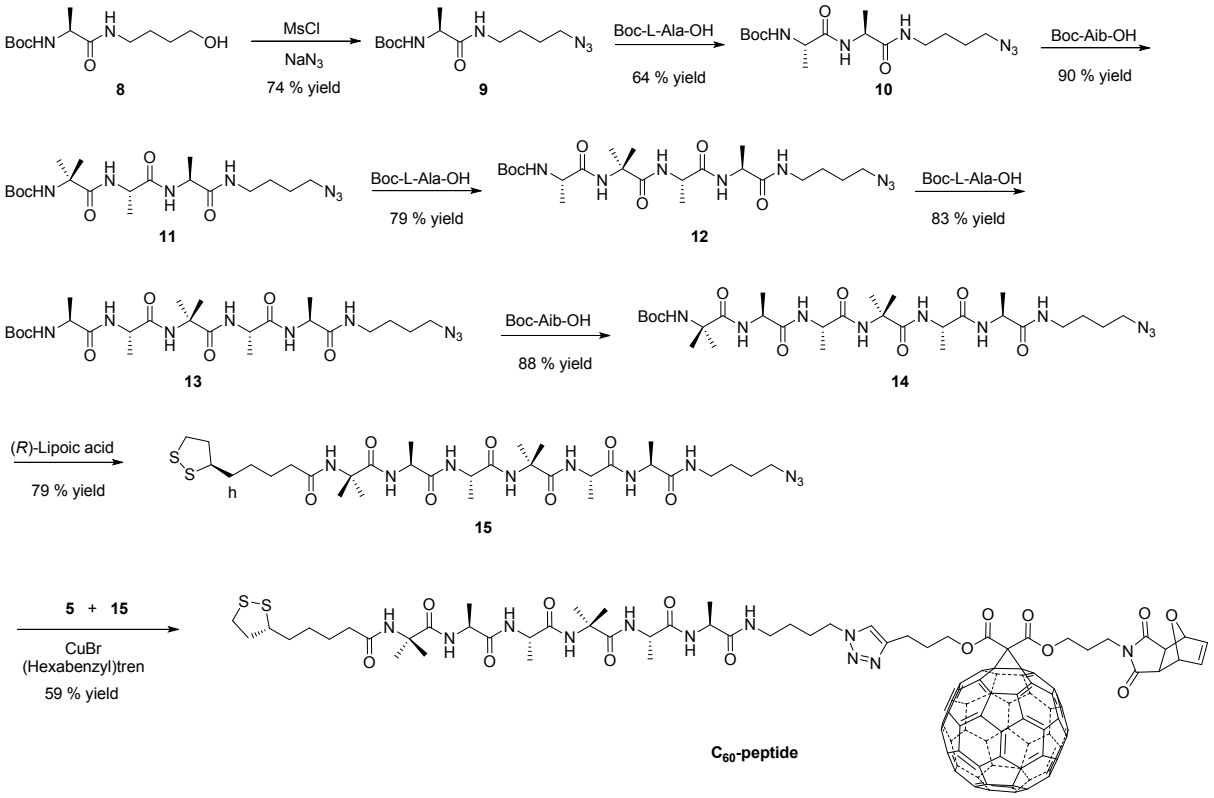


C_{60}-alkyl

Catalyst preparation: an equimolar mixture of CuBr (14mg, 0.096mmol) and hexabenzyltren(66mg, 0.096mmol) were introduced into a dry round bottomed flask under argon with 16 mL of dry and degassed DCM. The reaction mixture was stirred for 6 hours at room temperature.

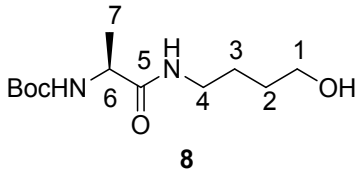
The alkyne **5** (50 mg, 0.045 mmol) and azide **7** (13 mg, 0.04 mol) were introduced into a dry round bottomed flask under argon. Then 3.5 mL of the prepared catalyst solution (0.5 eq) was added and the reaction mixture was stirred at room temperature for 2 days with exclusion of light. The mixture was concentrated under reduced pressure. The purification of the brown residue was performed by column chromatography (SiO_2, DCM/Et2O : 95/5 then DCM/MeOH : 96/4) and afforded 50 mg of **C_{60}-alkyl** as a black solid in 40 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.42-1.97 (m, 12H, H_2,H_3, H_6-H_9,), 2.04–2.36 (m, 6H, H_c, H_d, H_j), 2.44 (m, 1H,$H_{11'}$), 2.90 (m, 4H, H_4, H_m), 3.12 (m, 1H, $H_{11''}$), 3.27 (dd, 1H, *J* = 13.0 Hz, J = 6.8 Hz,H_{12}), 3.55 (m, 1H, H_{10}), 3.69 (t, 2H, *J* = 6.8 Hz, H_k,), 4.36 (t, 2H, *J* = 6.9 Hz, H_1), 4.48 (t 2H, *J* = 6.3 Hz, H_i), 4.58 (t 2H, *J* = 6.2 Hz, H_e), 5.27 (s, 2H, H_n), 5.70 (bs, 1H, NH), 6.52 (s, 2H, H_o), 7.40ppm (s, 1H, H_a); ^{13}C NMR (75 MHz, $CDCl_3$) δ=22.2 (C_c), 25.5, 25.7, 26.8, 27.0, 27.8, 28.2, 29.0, 34.7 (C_2, C_3, C_7, C_8, C_9, C_d,C_j), 35.9 (C_k), 36.6 (C_6), 38.6,38.7 (C_4,C_{12}),40.4 (C_{11}), 47.6 (C_m), 49.8 (C_1), 56.6 (C_{10}), 64.8 (C_e), 66.7 (C_i), 68.1 (C_1), 71.6 (C_g), 81.1 (C_n),136.6 (C_o), 138.8, 139.4, 141.1, 142.0, 142.3, 143.1, 143.2, 144.0,144.8, 145.0, 145.1,145.3,145.4, 146.6(C_b, Csp^2 C_{60}),163.6,163.7 (C_f, C_h), 173.0 (C_5), 176.3 ppm (C_l); HRMS (ESI+) m/z calcd for $C_{91}H_{42}N_5O_8S_2$: 1396.2475 [M +H^+], found 1396.2489.

Synthesis of compounds 8-C_{60}-peptide



Scheme S3. Synthesis of compounds **8-C_{60}-peptide**

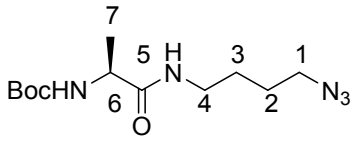
Compound 8:



8

A solution of 4-aminobutanol (600 mg, 6.74 mmol) in DCM (60 mL) was cooled on an ice bath. Boc-L-alanine hydroxysuccinimide ester (2070 mg, 7.25 mmol) and triethylamine (1.0 mL, 7.25 mmol) were added. The mixture was stirred at room temperature for 18 hours. The mixture was diluted with DCM and washed successively with 0.5 N aqueous hydrochloric acid solution, brine and saturated aqueous sodium hydrogen carbonate solution. The organic phase was dried over anhydrous magnesium sulfate, filtered and evaporated. The product **8** was obtained as a colourless oil (yield 1.37 g, 78%) that crystallized on standing in the refrigerator. Mp: 76-78°C; $[\alpha]_{578}^{20}$: -25 (*c* 0.5, DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.35 (d, 3H, *J* = 7.0 Hz, H_7), 1.44 (s, 9H, $BocCH_3$), 1.59-1.61 (m, 4H, H_2, H_3), 2.27 (bs, 1H, OH), 3.27-3.31 (m, 2H, H_4), 3.66 (t, 2H, *J* = 5.8 Hz, H_1), 4.10-4.14 (m, 1H, H_6), 5.16 (d, 1H, *J* = 5.1 Hz, NH), 6.68 ppm (bs, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=18.4 (C_7), 26.1 (C_3), 28.3 ($BocCH_3$), 29.6 (C_2), 39.2 (C_4), 50.2 (C_6), 62.2 (C_1), 80.2 ($BocC_{quat}$), 155.6 ppm (BocCO), 172.9 (C_5); HRMS (ESI+) m/z calcd for $C_{12}H_{24}N_2O_4Na$: 283.1634 [M + Na^+], found 283.1633.

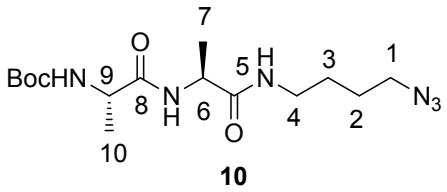
Compound 9:



9

The alcohol **8** (1.37 g, 5.27 mmol) was dissolved in DCM (30 mL). The solution was cooled on an ice bath and triethylamine (0.88 mL, 6.32 mmol) was added. A solution of mesyl chloride (0.45 mL, 5.79 mmol) in DCM (10 mL) was added dropwise over 30 minutes. The resulting mixture was stirred at 0°C for 90 minutes, then diluted with ice-cold DCM and washed successively with ice-cold 0.5 N aqueous hydrochloric acid solution and brine. The organic phase was dried over anhydrous magnesium sulfate, filtered and evaporated. The residue was taken up in dimethylformamide (20 mL) and sodium azide (514 mg, 7.90 mmol) was added. The mixture was stirred at 85 °C for 18 hours and then concentrated under reduced pressure. The residue was taken up in DCM and washed with brine. The organic phase was dried over anhydrous magnesium sulfate, filtered and evaporated. The product **9** was obtained as white solid (yield 1.11 g, 74%). Mp: 49-51°C; $[\alpha]_{578}^{20}$: -20 (*c* 0.45, DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.34 (d, 3H, *J* = 7.0 Hz, H_7), 1.44 (s, 9H, $BocCH_3$), 1.58-1.61 (m, 4H, H_2, H_3), 3.26-3.31 (m, 4H, H_1,H_4), 4.10-4.15 (m, 1H, H_6), 5.09 (d, 1H, *J* = 6.0 Hz, NH), 6.47 ppm (bs, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=18.3 (C_7), 26.1 (C_3), 26.8 (C_2), 28.2 ($BocCH_3$), 38.7 (C_4), 50.1 (C_6), 51.0 (C_1), 80.1 ($BocC_{quat}$), 155.5 (BocCO), 172.7 ppm (C_5); HRMS (ESI+) m/z calcd for $C_{12}H_{23}N_5O_3Na$: 308.1699 [M + Na^+], found 308.1699.

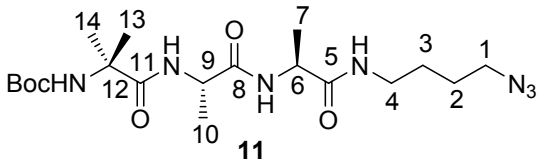
Compound 10:



10

Compound **9** (1.11 g, 3.90 mmol) was dissolved in DCM (15 mL) and trifluoroacetic acid (3 mL) was added. The mixture was stirred at room temperature for 18 hours. The solvent was removed under reduced pressure and toluene was distilled from the residue twice. The residue was dissolved in DCM (10 mL) and cooled on an ice bath. Separately, Boc-L-Ala-OH (884 mg, 4.68 mmol), ethyl (hydroxyimino) cyanoacetate (664 mg, 4.68 mmol), *N*-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (896 mg, 4.68 mmol) and *N*-methyl morpholine (2.2 mL, 20.0 mmol) were dissolved in DCM(30 mL) at 0 °C. This solution was stirred at 0°C for 15 minutes then added to the first solution. The mixture was stirred at room temperature for 3 days. The mixture was diluted with DCM and washed successively with 0.5 N aqueous hydrochloric acid solution, brine and aqueous $NaHCO_3$(sat). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using DCM/MeOH (95:5) as eluent to give the title compound **10** (893 mg, 64 %) as a white solid. Mp: 130-132°C; $[\alpha]_{578}^{20}$: -38 (*c* 0.5, DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.35-1.39 (m, 6H, H_7, H_{10}), 1.45 (s, 9H, $BocCH_3$), 1.58-1.62 (m, 4H, H_2, H_3), 3.21-3.31 (m, 4H, H_1,H_4), 4.11-4.15 (m, 1H, H_9), 4.41-4.50 (m, 1H, H_6), 5.14 (d, 1H, NH, *J* = 5.9 Hz), 6.80-6.83 ppm (m, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=18.0 (C_7, C_{10}), 26.1 (C_3), 26.6 (C_2), 28.2 ($BocCH_3$), 38.8 (C_4), 48.9 (C_6), 50.8 (C_9), 51.0 (C_1), 80.6 ($BocC_{quat}$), 155.8 (BocCO), 172.0, 172.6 ppm (C_5,C_8); HRMS (ESI+) m/z calcd for $C_{15}H_{29}N_6O_4$: 357.2250 [M + H^+], found 357.2255.

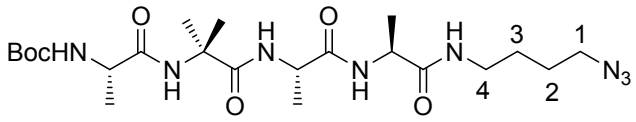
Compound 11:



11

Compound **10** (1.29 g, 3.6 mmol) was dissolved inDCM (18 mL) and a solution of HCl in diethyl ether (appx 2N, 24 mL) was added. The mixture was stirred at room temperature for 18 hours. The solvent was removed under reduced pressure and toluene was distilled from the residue twice. The residue was dissolved in THF (35 mL) and cooled to 0 °C. Boc-Aib-OH (955 mg, 4.7 mmol), HATU (1.78 g, 4.7 mmol) and diisopropylethylamine (1.9 mL, 10.9 mmol) were added. The mixture was stirred at room temperature for 2 days. The solvent was removed under reduced pressure. The residue was taken up in DCM and washed with aqueous HCl 5%, brine, and aqueous $NaHCO_3$(sat). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using DCM/MeOH (95:5) as eluent to give the title compound **11** (1.443 g, 90 %) as a white solid.Mp:111-113 °C; $[\alpha]_{578}^{20}$: +16 (*c* 0.5, DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.42-1.48 (m, 21H, BocCH_3, H_7, H_{10}, H_{13}, H_{14}), 1.61-1.65 (m, 4H, H_2, H_3), 3.21-3.30 (m, 4H, H_1, H_4), 4.10-4.19 (m, 1H, H_9), 4.38-4.49 (m, 1H, H_6), 5.60 (s, 1H, NH), 6.81 (d, 1H, *J* = 4.6 Hz, NH), 7.11 (t, 1H, *J* = 5.4 Hz, NH), 7.76 ppm (d, 1H, *J* = 7.9 Hz, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=17.3 (C_7, C_{10}), 23.2 (C_{13} or C_{14}), 26.0, 26.2 (C_2, C_3), 27.0 (C_{13} or C_{14}), 28.1 (BocCH_3), 38.8 (C_4), 49.4 (C_6), 51.0 (C_1), 51.1 (C_9), 56.6 (C_{12}), 81.1 (BocC_{quat}), 155.8 (BocCO), 172.3, 172.9, 176.0 ppm (C_5, C_8, C_{11}); HRMS (ESI+) m/z calcd for $C_{19}H_{36}N_7O_5$: 442.2778 [M + H^+], found 442.2783.

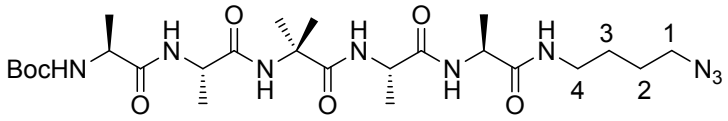
Compound 12:



12

Compound **11** (1.40 g, 3.17 mmol) was dissolved in DCM (10 mL) and a solution of HCl in diethyl ether (appx 2N, 15 mL) was added. The mixture was stirred at room temperature for 18 hours. The solvent was removed under reduced pressure and toluene was distilled from the residue twice. The residue was dissolved in THF (15 mL) and cooled to 0 °C. Boc-L-Ala-OH (780 mg, 4.1 mmol), HATU (1.56 g, 4.1 mmol) and diisopropylethylamine (1.6 mL, 9.2 mmol) were added. The mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure. The residue was taken up in DCM and washed with aqueous HCl 5%, brine, and aqueous $NaHCO_3$(sat). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using DCM/MeOH (95:5) as eluent to give the title compound **12** (1.28 g, 79 %) as a white solid.Mp:73-75 °C; $[\alpha]_{578}^{20}$: +13 (*c* 0.5, DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.37 (d, 3H, *J* = 7.2 Hz, CH_3Ala), 1.43-1.52 (m, 21H, BocCH_3, CH_3Ala, CH_3Aib), 1.59-1.65 (m, 4H, H_2, H_3), 3.23-3.28 (m, 4H, H_1, H_4), 3.82-3.89 (m, 1H, CHAla), 4.11-4.20 (m, 1H, CHAla), 4.36-4.46 (m, 1H, CHAla), 6.03 (bs, 1H, NH), 7.11-7.15 (m, 2H, NH), 7.63-7.65 ppm (m, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=16.6, 16.7, 17.2 (CH_3Ala), 23.0 (CH_3Aib), 26.0, 26.3 (C_2, C_3), 27.6 (CH_3Aib), 28.2 (BocCH_3), 38.8 (C_4), 49.5 (CHAla), 51.1 (C_1), 51.3, 53.0 (CHAla), 56.4 (CAib), 81.0 (BocC_{quat}), 156.9 (BocCO), 173.0, 173.4, 174.3, 175.8 ppm (C=O); HRMS (ESI+) m/z calcd for $C_{22}H_{41}N_8O_6$: 513.3149 [M + H^+], found 513.3154.

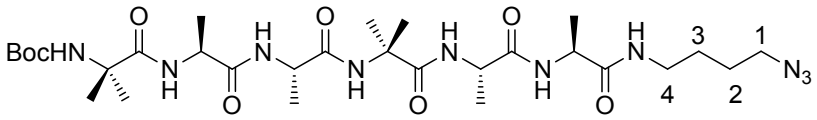
Compound 13:



13

Compound **12** (1.23 g, 2.40 mmol) was dissolved in DCM (5 mL) and a solution of HCl in diethyl ether (appx 2N, 20 mL) was added. The mixture was stirred at room temperature for 7 hours. The solvent was removed under reduced pressure and toluene was distilled from the residue twice. The residue was dissolved in THF (15 mL) and cooled to 0 °C. Boc-L-Ala-OH (590 mg, 3.1 mmol), HATU (1.19 g, 3.1 mmol) and diisopropylethylamine (1.2 mL, 6.9 mmol) were added. The mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure. The residue was taken up in DCM and washed with aqueous HCl 5%, brine, and aqueous $NaHCO_3$(sat). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using DCM/MeOH (95:5) as eluent to give the title compound **13** (1.16 g, 83 %) as a white solid. Mp: 157-159 °C; $[\alpha]_{578}^{20}$: +21 (*c* 0.5, DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.41-1.52 (m, 27H, BocCH_3, CH_3Ala, CH_3Aib), 1.64-1.66 (m, 4H, H_2, H_3), 3.27-3.29 (m, 4H, H_1, H_4), 3.95-4.02 (m, 2H, CHAla), 4.11-4.20 (m, 1H, CHAla), 4.43-4.53 (m, 1H, CHAla), 5.66 (bs, 1H, NH), 7.02 (b, 1H, NH), 7.24 (d, 1H, *J* = 5.6 Hz, NH), 7.32 (d, 1H, *J* = 5.4 Hz, NH), 7.58 (d, 1H, *J* = 7.8 Hz, NH), 7.65 ppm (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=16.7, 16.9, 17.0, 17.2 (CH_3Ala), 23.2 (CH_3Aib), 26.1, 26.3 (C_2, C_3), 27.2 (CH_3Aib), 28.2 (BocCH_3), 38.8 (C_4), 49.6 (CHAla), 51.1 (C_1), 51.3, 51.9, 52.7 (CHAla), 56.7 (CAib), 80.9 (BocC_{quat}), 156.9 (BocCO), 173.3, 173.7, 173.8, 175.4, 176.3 ppm (C=O); NH, HRMS (ESI+) m/z calcd for $C_{25}H_{46}N_9O_7$: 584.3520 [M + H^+], found 584.3521.

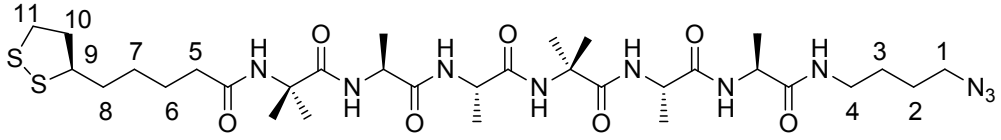
Compound 14:



14

Compound **13** (291 mg, 0.5 mmol) was dissolved in DCM (1 mL) and a solution of HCl in diethyl ether (appx 2N, 9 mL) was added. The mixture was stirred at room temperature for 18 hours. The solvent was removed under reduced pressure and toluene was distilled from the residue twice. The residue was dissolved in THF (5 mL) and cooled to 0°C. Boc-Aib-OH (132 mg, 0.65 mmol), HATU (247 g, 0.65 mmol) and diisopropylethylamine (0.3 mL, 1.7 mmol)) were added. The mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure. The residue was taken up in DCM and washed with aqueous HCl 5%, brine, and aqueous $NaHCO_3$(sat). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using DCM/MeOH (92.5:7.5) as eluent to give the title compound **14** (295 g, 88 %) as a white solid. Mp: 204-206 °C; $[\alpha]_{578}^{20}$: +28 (*c* 0.5, DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ=1.44-1.54 (m, 33H, BocCH_3, CH_3Ala, CH_3Aib), 1.63-1.73 (m, 4H, H_2, H_3), 3.26-3.30 (m, 4H, H_1, H_4), 3.98-4.23 (m, 3H, CHAla), 4.42-4.51 (m, 1H, CHAla), 5.37 (s, 1H, NH), 6.75 (d, 1H, *J* = 3.7 Hz, NH), 7.11 (t, 1H, *J* = 5.6 Hz, NH), 7.19 (d, 1H, *J* = 5.6 Hz, NH), 7.40 (s, 1H, NH), 7.55 (d, 1H, *J* = 7.9 Hz, NH), 7.99 ppm (d, 1H, *J* = 5.2 Hz, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=16.3, 16.8, 17.3 (CH_3Ala), 23.0, 23.3 (CH_3Aib), 26.1, 26.3 (C_2, C_3), 27.1, 27.2 (CH_3Aib), 28.3 (BocCH_3), 38.9 (C_4), 49.5 (CHAla), 51.2 (C_1), 51.3, 51.9, 52.1 (CHAla), 56.6, 56.7 (CAib), 81.3 (BocC_{quat}), 156.0 (BocCO), 173.2, 173.6, 174.4, 174.6, 176.4 ppm (C=O); HRMS (ESI+) m/z calcd for $C_{29}H_{52}N_{10}O_8$: 669.4056 [M + H^+], found 669.4048.

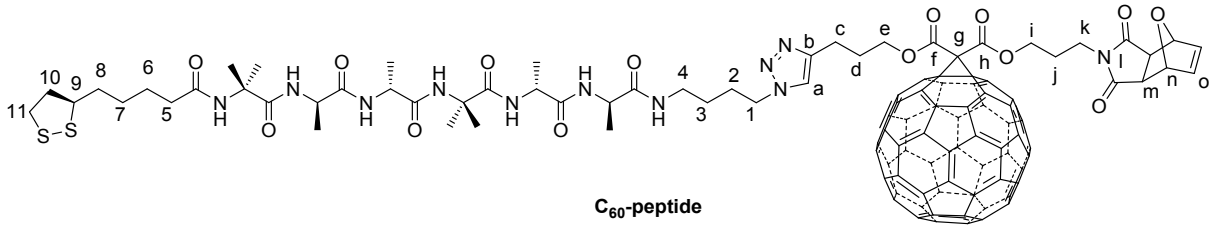
Compound 15:



15

Compound **14** (270 mg, 0.4 mmol) was dissolved inDCM (1 mL) and a solution of HCl in diethyl ether (appx 2N, 9 mL) was added. The mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and toluene was distilled from the residue twice. The residue was dissolved in THF (5 mL) and cooled to 0 °C. (*R*)-Lipoic acid (107 mg, 0.52 mmol), HATU (198 g, 0.52 mmol) and diisopropylethylamine (0.5 mL, 2.8 mmol) were added. The mixture was stirred at room temperature for 3 days. The solvent was removed under reduced pressure. The residue was taken up in DCM and washed with aqueous HCl 5%, brine, and aqueous $NaHCO_3$(sat). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using DCM/MeOH (92.5:7.5) as eluent to give the title compound **15** (239 g, 79 %) as a yellow-white solid. Mp: 157-160 °C; $[\alpha]_{578}^{20}$: +30 (*c* 0.5, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$, [C] = 50 mM) δ=1.45-1.54 (m, 26H, CH_3Ala, CH_3Aib, H_7), 1.61-1.74 (m, 8H, H_2, H_3,H_6,H_8), 1.86-1.97 (m, 1H, $H_{10'}$), 2.22-2.37 (m, 2H, H_5), 2.40-2.51 (m, 1H, $H_{10''}$), 3.06-3.22 (m, 3H, $H_{4'',11}$), 3.26-3.47 (m, 3H, H_1, $H_{4'}$), 3.51-3.60 (m, 1H, H_9), 4.00-4.13 (m, 3H, CHAla), 4.22-4.31 (m, 1H, CHAla), 7.36 (t, 1H, *J* = 5.4 Hz, NH), 7.40 (d, 1H, *J* = 4.3 Hz, NH), 7.49 (s, 1H, NH), 7.68 (d, 1H, *J* = 6.9 Hz, NH), 7.80 (d, 1H, *J* = 6.6 Hz, NH), 7.84 (bs, 1H, NH), 7.96ppm (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=16.1, 16.8, 17.0, 17.3 (CH_3Ala), 22.7, 23.5 (CH_3Aib), 25.2, 26.1 (C_2, C_3,C_6), 26.6, 26.9 (CH_3Aib), 28.7 (C_7), 34.5 (C_8), 35.5 (C_5), 38.4 (C_{11}), 39.0 (C_4), 40.2 (C_{10}), 50.8 (CHAla), 51.1(C_1) , 51.5, 52.2 (CHAla), 56.3 (C_9), 56.4, 56.5 (CAib), 174.3, 174.6, 174.8, 175.3, 175.6, 176.6, 176.7 ppm (C=O);HRMS (ESI+) m/z calcd for $C_{32}H_{57}N_{10}O_7S_2$: 757.3853 [M + H^+], found 757.3849.

Compound C_{60}-peptide:



C_{60}-peptide

Catalyst preparation: a mixture of CuBr (14mg, 0.096mmol) and hexabenzyltren (66mg, 0.096mmol) in dry, degassed DCM (16mL) was stirred for 6 hours at room temperature.

The alkyne **5** (66mg, 0.06 mmol) and lipopeptide azide **15** (50 mg, 0.066 mol) were placed in a dry flask under argon. The prepared catalyst solution (2 mL, 0.2 eq) was added and the reaction mixture was stirred at room temperature for 2 days with exclusion of light. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography using DCM/MeOH (92.5:7.5) as the eluent to give the title compound **C_{60}-peptide** (66 mg, 59 %) as a brown solid.^{1}H NMR (300 MHz, $CDCl_3$, [C] = 30 mM) δ=1.46-1.52 (m, 26H, CH_3Ala, CH_3Aib, H_7), 1.59-1.71 (m, 6H, H_3, H_6, H_8), 1.85-1.99 (m, 3H, H_2, $H_{10'}$), 2.02-2.16 (m, 2H, H_j), 2.19-2.36 (m, 4H, H_5, H_d), 2.39-2.49 (m, 1H, $H_{10''}$), 2.83-2.91 (m, 4H, H_c, H_m), 3.10-3.21 (m, 2H, H_{11}), 3.23-3.33 (m, 2H, H_4), 3.52-3.56 (m, 1H, H_9), 3.68 (t, 2H, *J* = 6.8 Hz, H_k), 4.01-4.10 (m, 3H, CHAla), 4.25-4.30 (m, 1H, CHAla), 4.36 (t, 2H, H_1, *J* = 6.4 Hz), 4.48 (t, 2H, *J* = 6.1 Hz, H_i), 4.59 (t, 2H, *J* = 5.9 Hz, H_e), 5.26 (s, 2H, H_n), 6.51 (s, 2H, H_o), 7.29-7.54 (m, 4H, NH, H_a), 7.59-7.68 (m, 2H, NH), 7.78-7.89 ppm (m, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=16.4, 17.0(CH_3), 17.3, 17.4, 22.2 (C_c), 23.0 (CH_3), 23.8 (CH_3), 25.2, 26.8 (CH_3),

27.0(C_j),27.2(CH_3), 27.2(C_2), 28.3 ($C_d$or C_5), 28.9 (C_7), 34.6, 35.8 (C_d or C_5), 36.0 (C_k), 38.6 ($C_{4,11}$), 40.4 (C_{10}), 47.6 (C_m), 50.0 (C_1), 50.9 (CHAla), 52.2 (CHAla), 56.56, 56.61, 56.7 (C9), 64.4, 64.8 (Ci), 66.9(C_e), 71.6 (C_{sp}3 C_{60}), 81.1 (C_n), 136.7 (C_o), 138.9, 139.3, 141.07, 141.09, 142.3, 143.0, 143.11, 143.15, 143.18, 143.96, 144.00, 144.7, 144.73, 144.75, 144.77, 144.80, 145.0, 145.17, 145.23, 145.27, 145.3, 145.36, 145.37, 145.5(C_b, Csp^2 C_{60}), 163.5, 163.6, 174.2, 174.8, 175.3, 175.2, 175.4, 176.3, 176.7 (C=O); HRMS (ESI+) m/z calcd for $C_{111}H_{75}N_{11}O_{14}S_2Na$: 1872.4834 [M + Na^+], found 1872.4838.

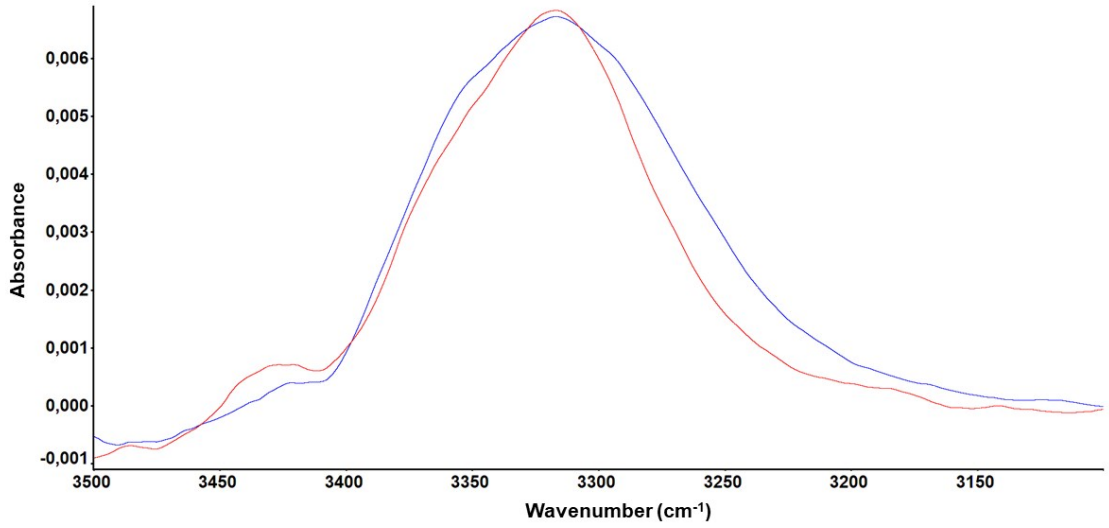


Figure S1. FT-IR absorption spectra (N-H stretching region) of **hexapeptide 15** (red) and **C60-peptide** (blue) at 1 mM in $CDCl_3$ solution. The spectra were normalized with respect to the main N-H band.

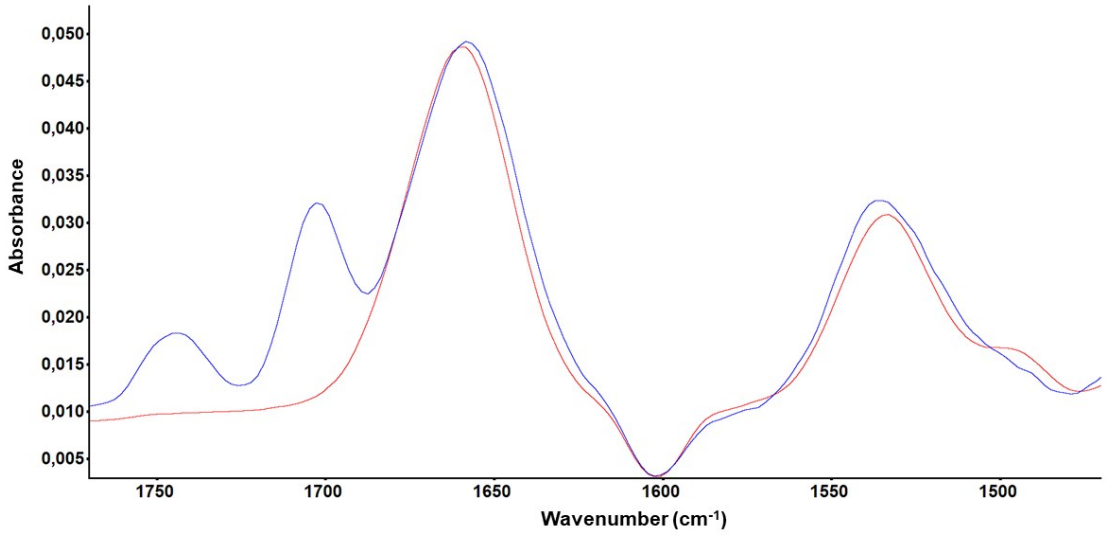


Figure S2. FT-IR absorption spectra (C=O stretching region) of **hexapeptide 15** (red) and **C60-peptide** (blue) at 1 mM in $CDCl_3$ solution. The spectra were normalized with respect to the main C=O band.

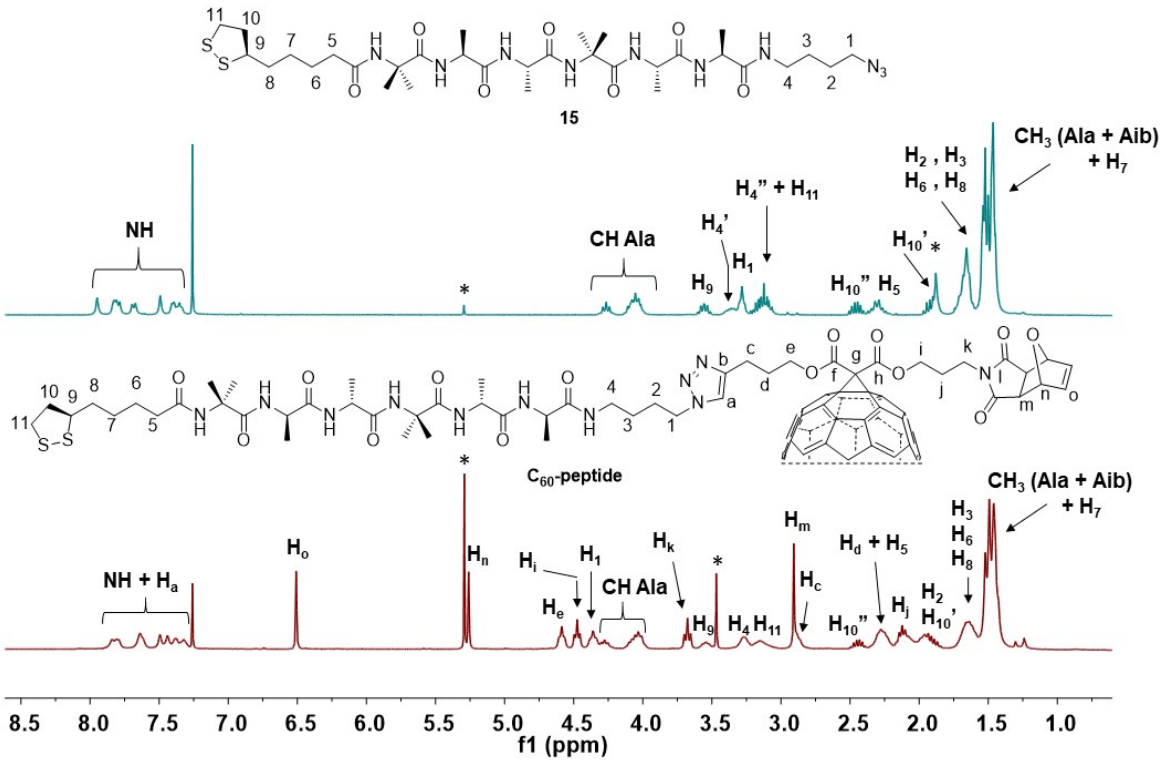


Figure S3. ^{1}H NMR of **15 (**50 mM, 300 MHz, 298K) and **C_{60}-peptide** (30 mM, 300 MHz, 298K) in $CDCl_3$. The peaks labelled with an asterisk are due to solvent residues.

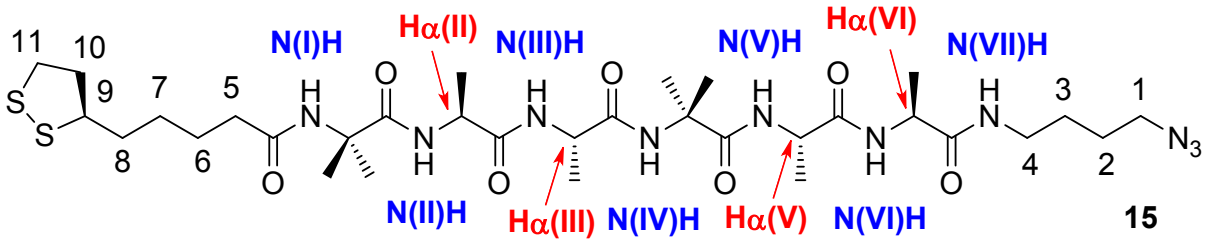


Figure S4. Structure and numbering of **15** used for ^{1}H NMR signals assignments.

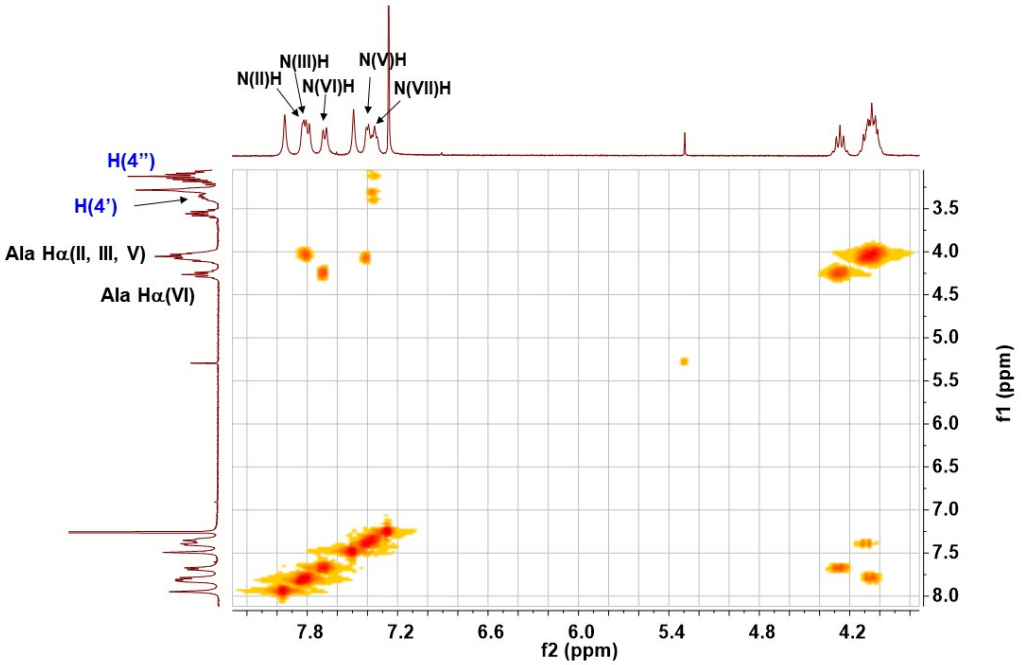


Figure S5. Partial ^{1}H-^{1}H COSY spectrum of **15** in $CDCl_3$ (50 mM, 300 MHz, 298K).

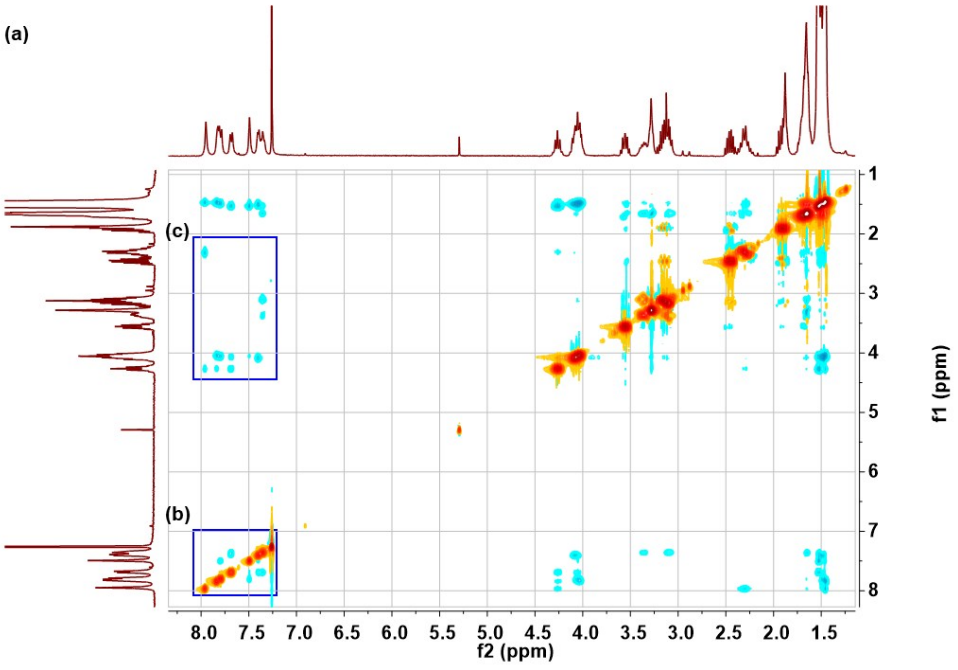


Figure S6. Full ^{1}H-^{1}H ROESY spectrum of **15** in $CDCl_3$ (50 mM, 300 MHz, 298K).

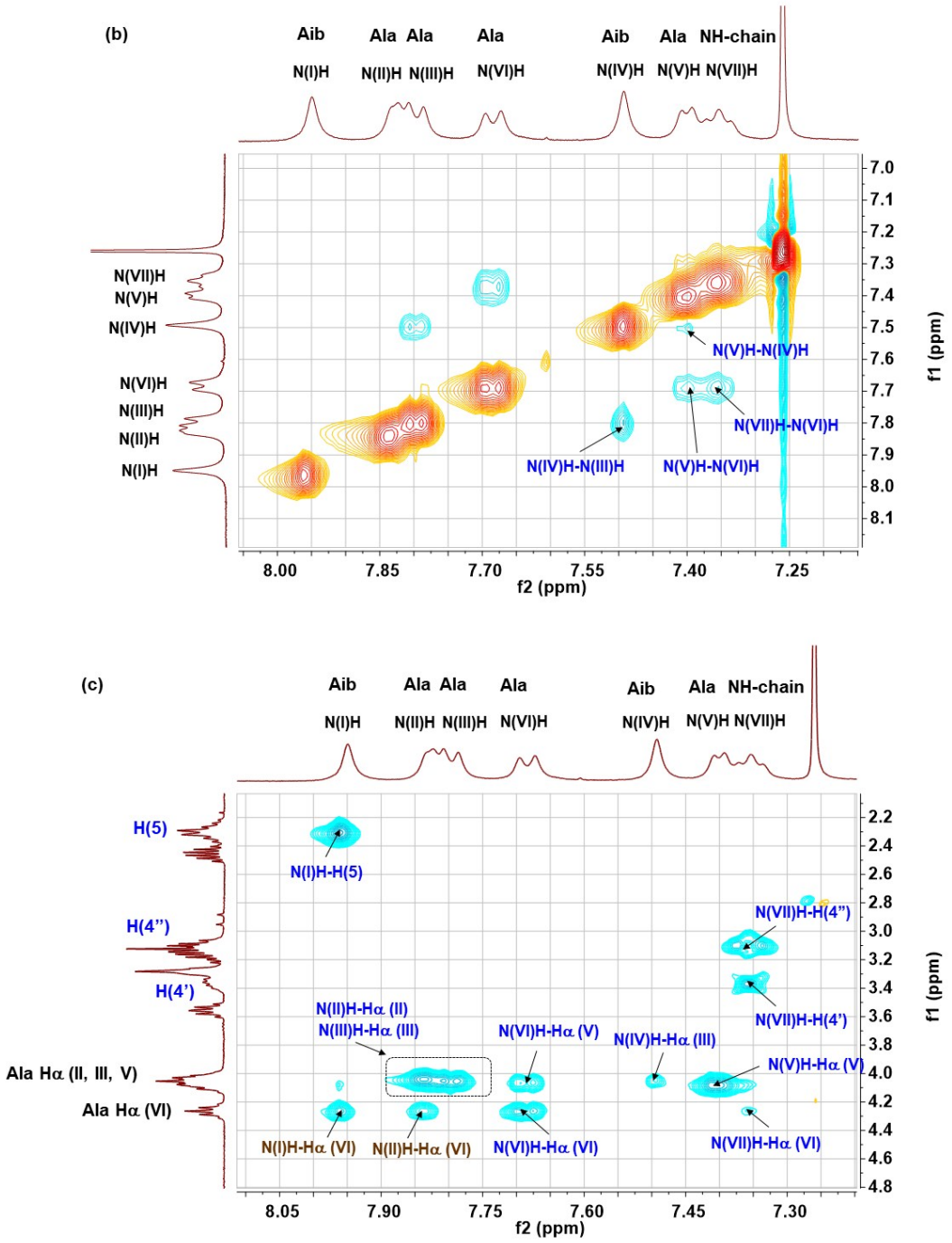


Figure S7. Partial ^{1}H-^{1}H ROESY spectra of **15** in $CDCl_3$ (50 mM, 300 MHz, 298K).

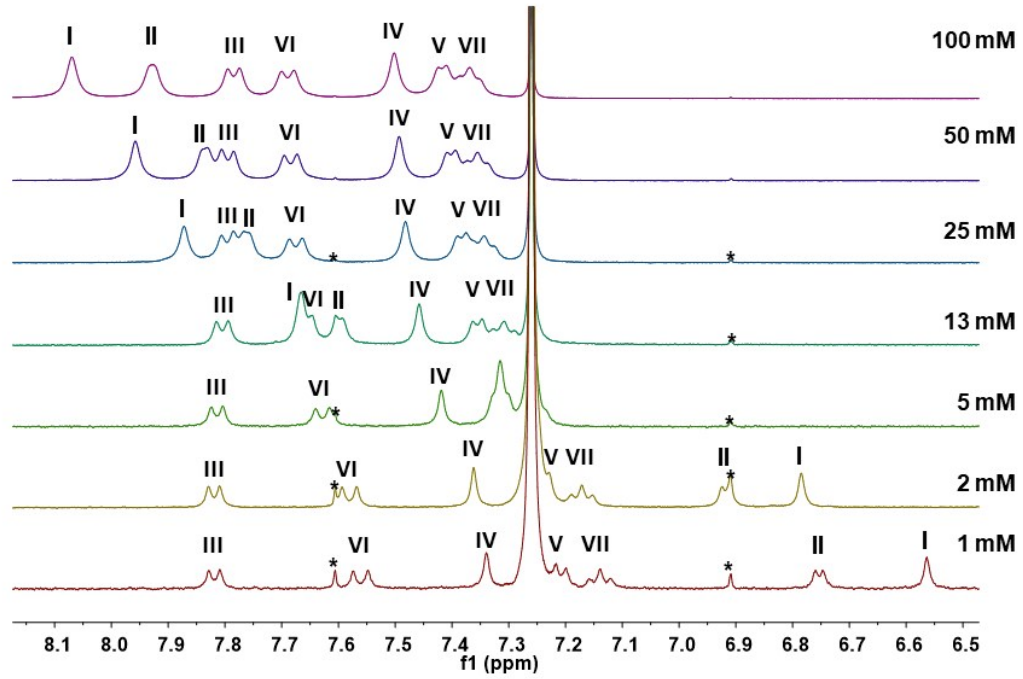


Figure S8. Stack plot of partial ^{1}H NMR spectra of peptide **15** taken at varying concentrations from 1 mM to 100 mM (300 MHz, $CDCl_3$, 298K).

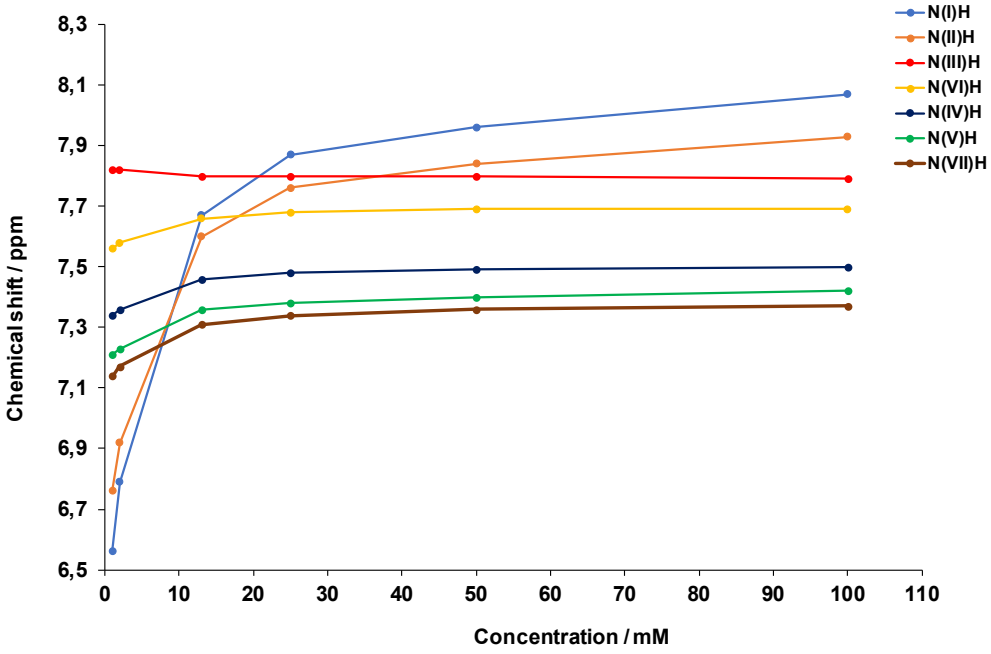


Figure S9. Plot of concentration (mM) *vs* chemical shifts for the NH protons of the peptide **15** (300 MHz, $CDCl_3$, 298K).

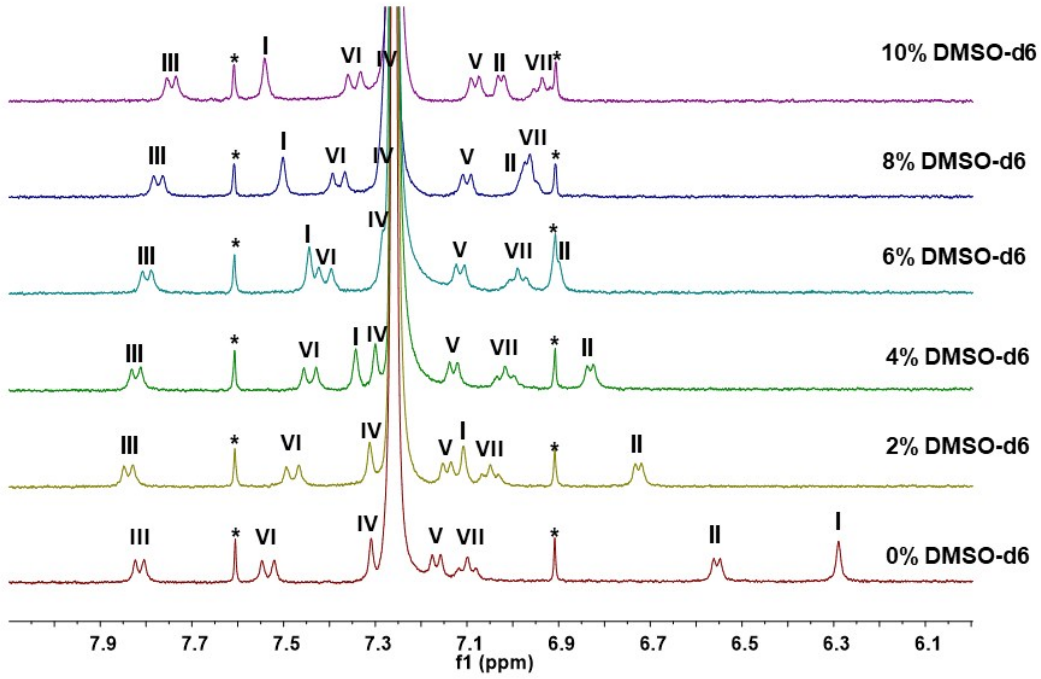


Figure S10. Stack plot of partial ^{1}H NMR spectra in which DMSO-d6 was added to a 1mM solution of the peptide **15** in$CDCl_3$ (300 MHz, 298K).

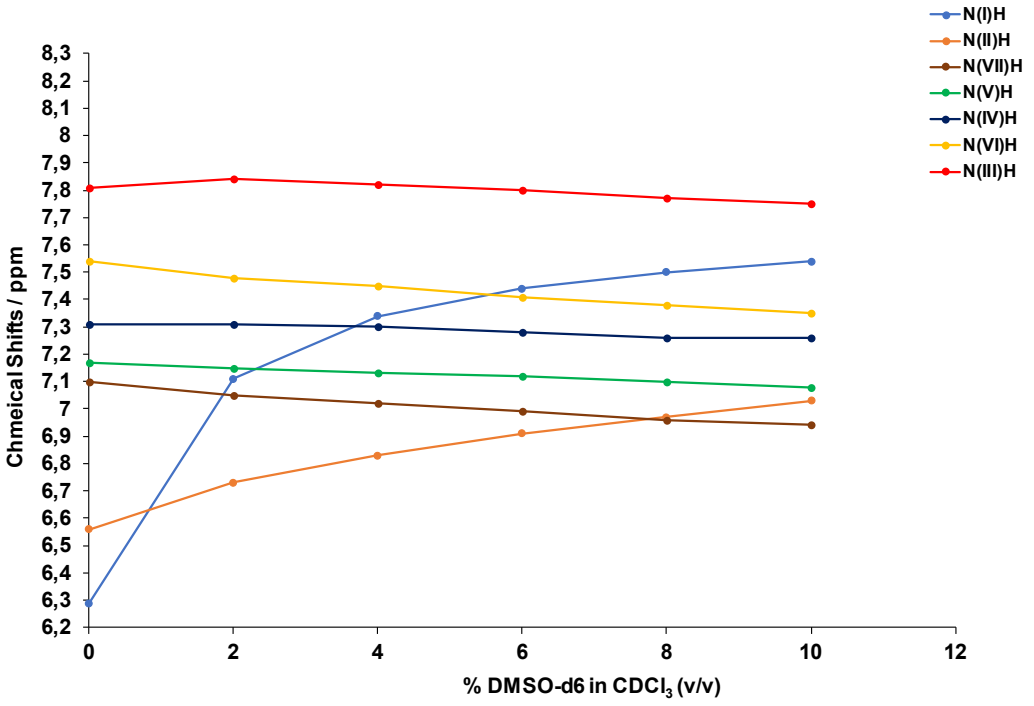


Figure S11. Plot of % of DMSO *vs* chemical shifts for the NH protons of a 1mM solution of the peptide **15**.

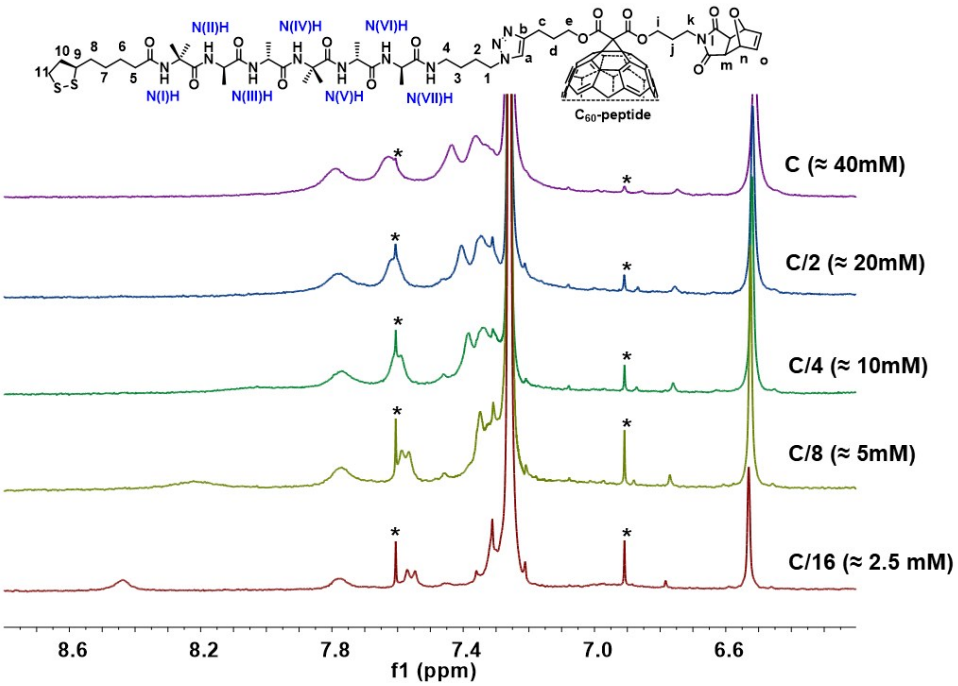


Figure S12. Stack plot of partial ^{1}H NMR spectra of **C_{60}-peptide** taken at varying concentrations (300 MHz, $CDCl_3$, 298K). The stock solution was prepared by dissolving 17.5 mg of **C_{60}-peptide** in 0.5 mL of $CDCl_3$, the solutions were then diluted successively by half. The peaks labelled with an asterisk are due to satellite bands.

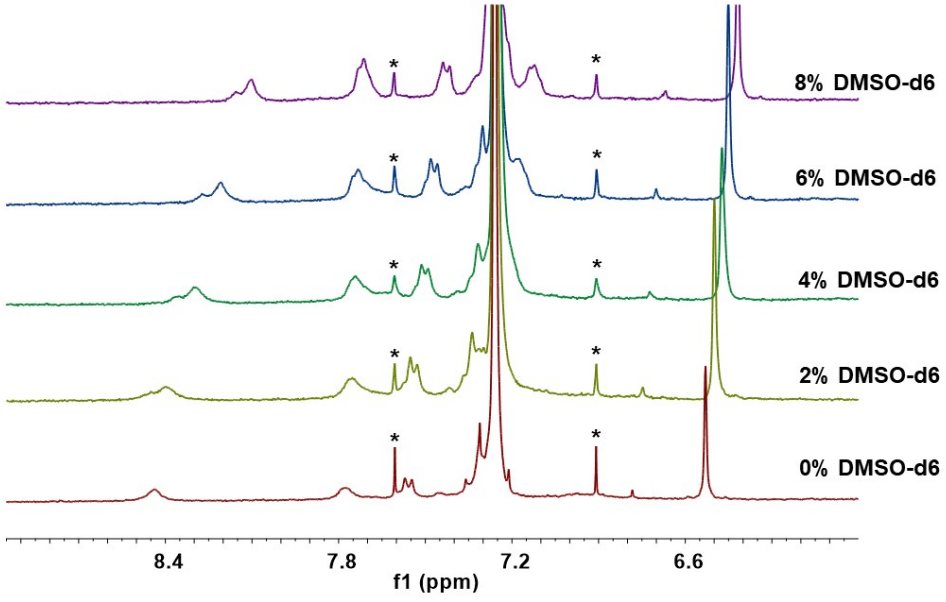


Figure S13. Stack plot of partial ^{1}H NMR spectra in which DMSO-d6 was added to a solution of **C_{60}-peptide** (concentration ≈ 2.5 mM) in $CDCl_3$ (300 MHz, 298K). The peaks labelled with an asterisk are due to satellite bands.

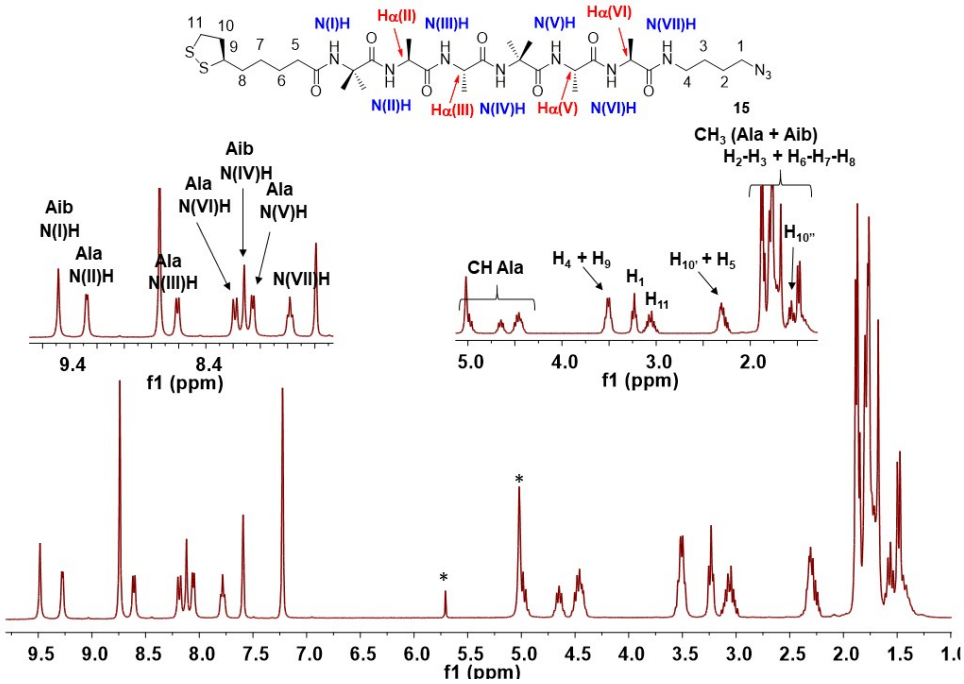


Figure S14. ^{1}H NMR spectrum of **15** in C_5D_5N (300 MHz, 298K). The peaks labelled with an asterisk are due to solvent residues.

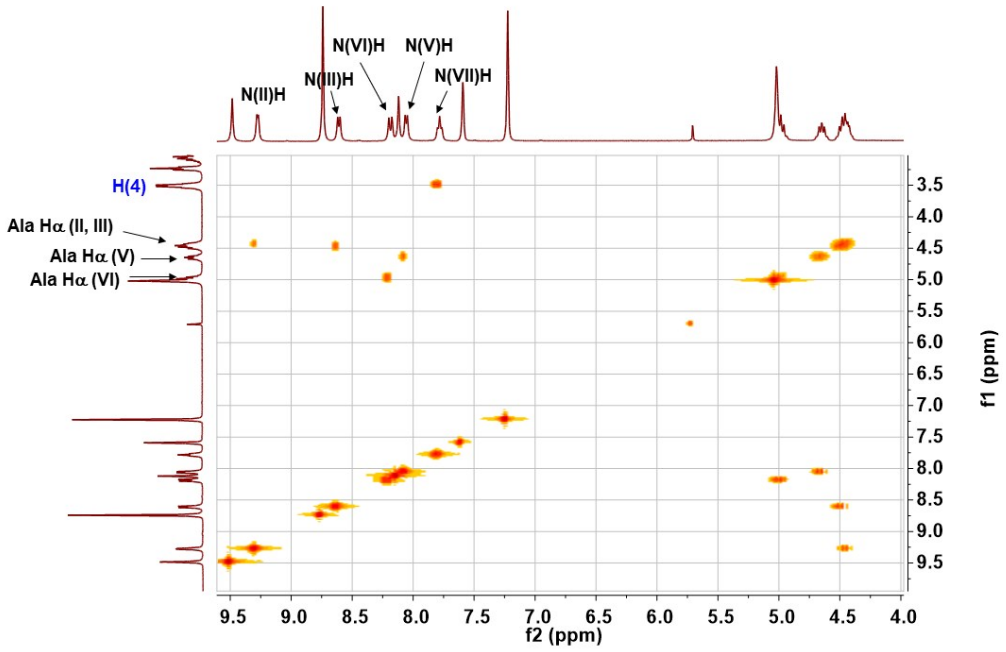


Figure S15. Partial ^{1}H-^{1}H COSY spectrum of **15** in C_5D_5N (300 MHz, 298K).

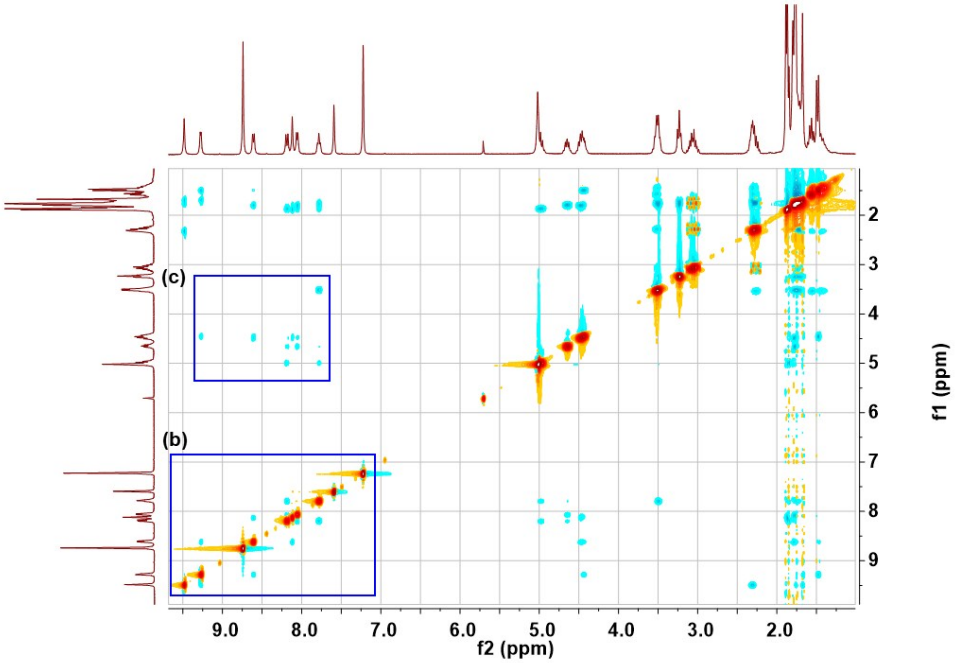


Figure S16. Full ^{1}H-^{1}H NOESY spectrum of **15** in C_5D_5N (300 MHz, 298K).

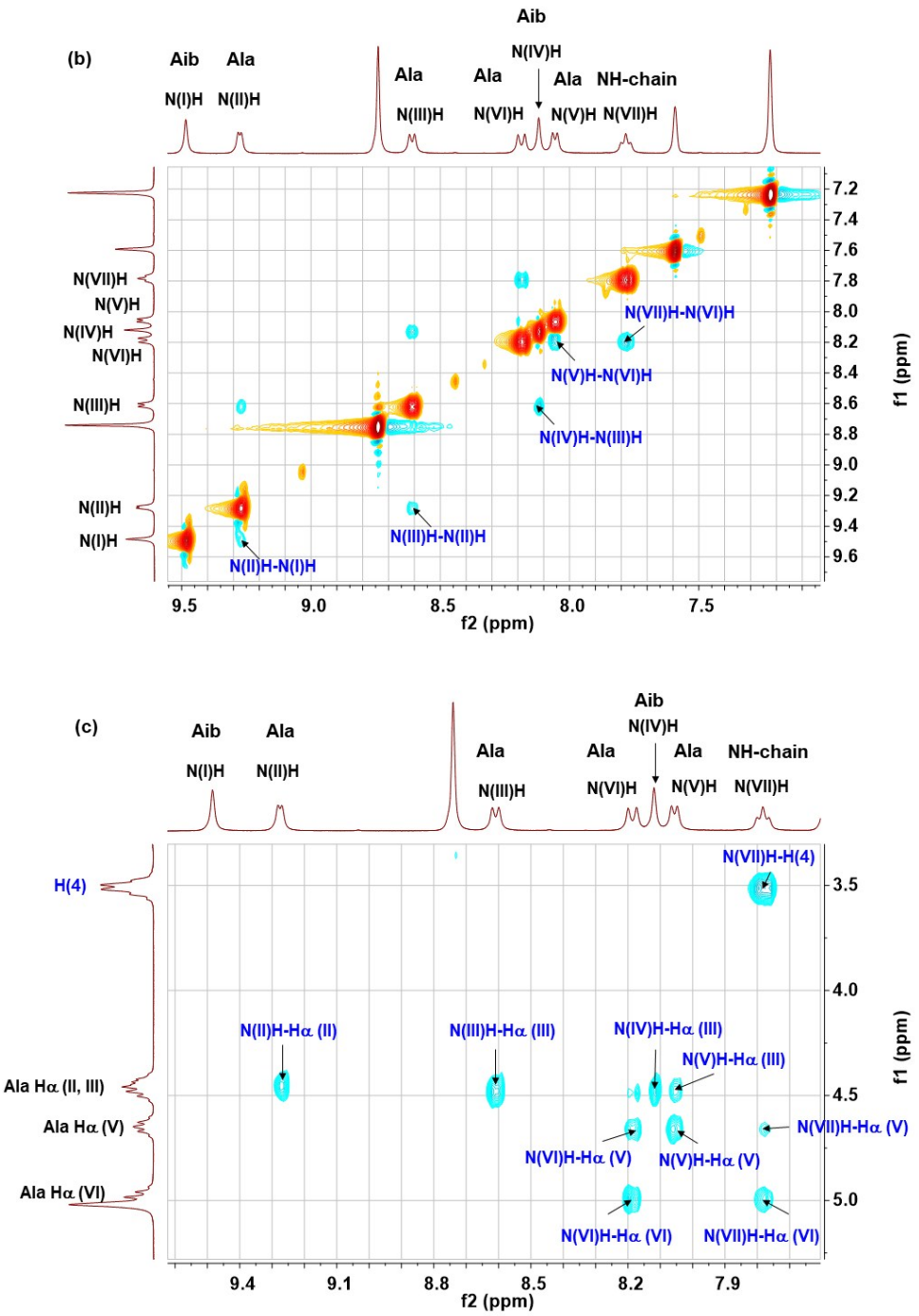


Figure S17. Partial ^{1}H-^{1}H NOESY spectra of **15** in C_5D_5N (300 MHz, 298K).

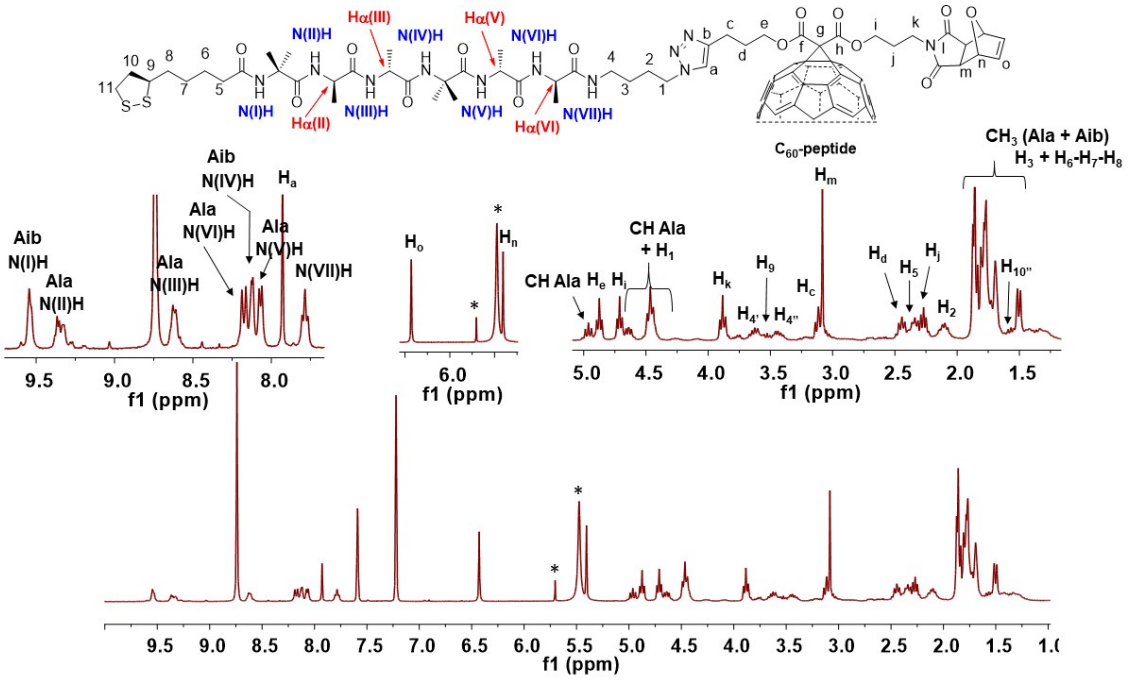


Figure S18. ^{1}H NMR spectrum of **C_{60}-peptide** in C_5D_5N (300 MHz, 298K). The peaks labelled with an asterisk are due to solvent residues.

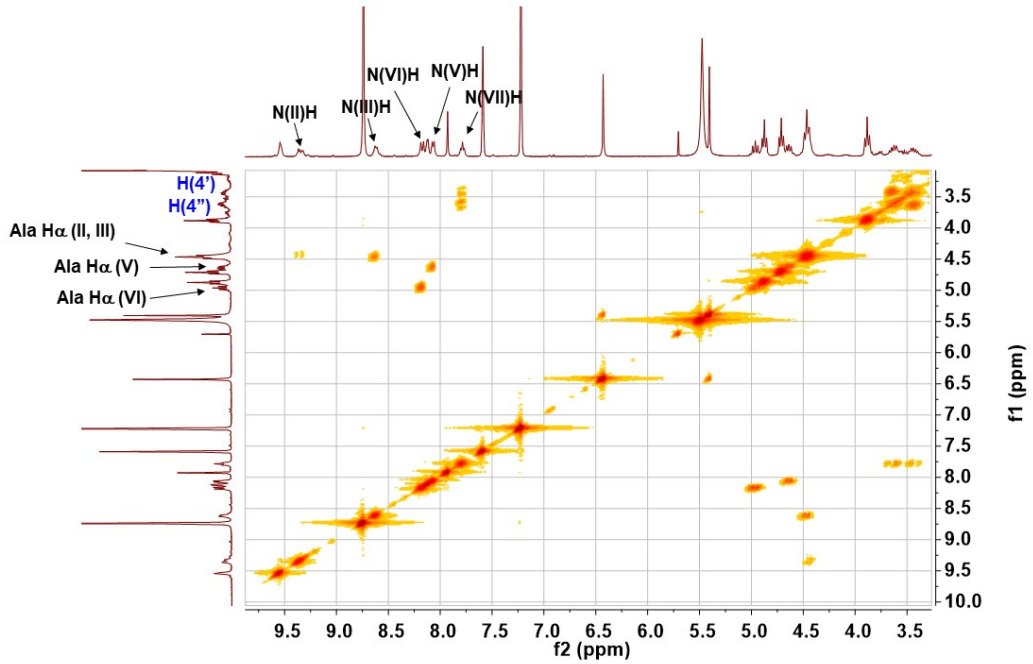


Figure S19. Partial ^{1}H-^{1}H COSY spectrum of **C_{60}-peptide** in C_5D_5N (300 MHz, 298K).

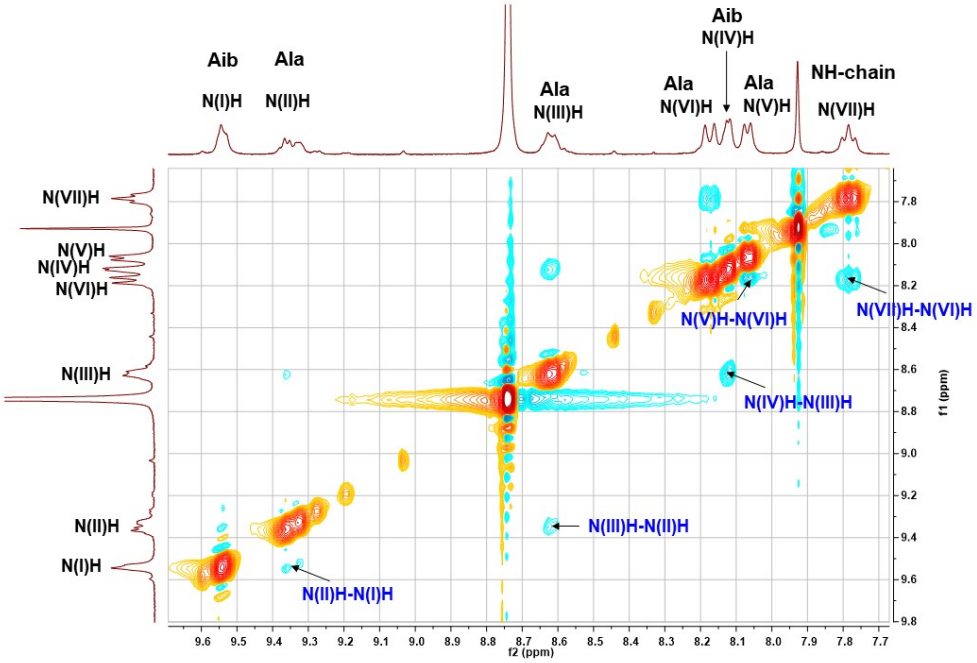


Figure S20. Partial ^{1}H-^{1}H ROESY spectra of **C_{60}-peptide** in C_5D_5N (300 MHz, 298K).

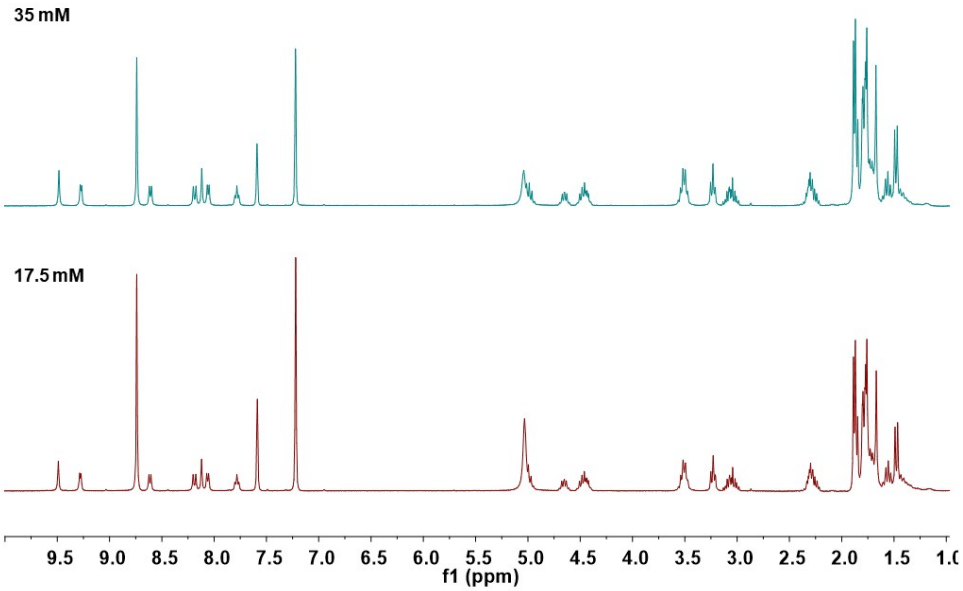


Figure S21.^{1}H NMR spectra of peptide **15** taken at different concentrations in C_5D_5N (300 MHz, 298K).

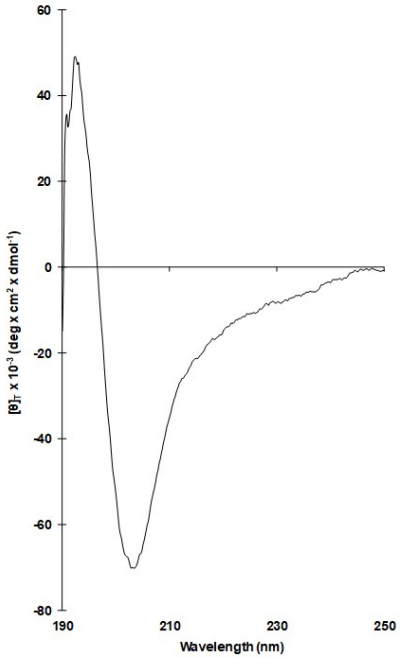


Figure S22. Circular dichroism spectra of the hexapeptide **15** in MeOH solution (peptide concentration 0.2 mM).

The ECD spectra were measured on a Jasco model J-810 spectropolarimeter. Baselines were corrected by subtracting the solvent contribution. The values are expressed in terms of $[\theta]_T$, the total molar ellipticity (deg × cm^2 × $dmol^{-1}$).

Preparation of Fullerene derivatives on Gold Substrates

For the IRRAS, XPS and electrochemistry experiments, we used 11 mm × 11 mm Arrandee™ (Werther, Germany) gold plates, which consist of a borosilicate glass substrate (0.7 +/- 0.1 mm), a thin chromium interlayer (2.5 +/- 1.5 nm) and a gold layer (250 +/- 50 nm). The gold coated substrates were cleaned by annealing in a butane flame to ensure good crystallinity of the topmost layers and rinsed in a bath of absolute ethanol for 15 min before adsorption.

The gold plates were placed in a 25 mL 2-necked vessel and the system was flushed through with argon. A freshly prepared oxygen-free solution of fullerene or peptide derivative in dichloromethane (10^{-4} M) was then introduced under argon to the vessel containing the gold substrates. After standing for 18 h in the dark under inert atmosphere, the gold plates were then rinsed once. After 18 h in the dark under an inert atmosphere, the gold plates were rinsed once with a CH_2Cl_2 spray, then immersed 10 minutes in CH_2Cl_2, washed once with a water-spray, then immersed 5 minutes in water (MilliQ) and once again in CH_2Cl_2 (5 min), and finally dried under a nitrogen flow.

Electrochemical methods

Cyclic Voltammetry measurements were performed with an Autolab (PGSTAT302N, Metrohm) at room temperature, using a saturated calomel reference electrode, a Pt counter-electrode and a gold substrate modified by a chemisorbed fullerene or peptide derivative layer, placed in a home-made polymer cell, as the working electrode. KCl 1M in water (20 ml) was used as a supporting electrolyte. $K_3[Fe(CN)_6]$ 1 mM was used as redox probe. The applied over-potential was changed from negative (0.7 V) to positive (-0.4 V) values with steps of 100 mV.

Infra-red

The amide I/II absorbance ratios were determined to be 1.74 and 1.54 for the hexapeptide **15** and **C60-peptide** respectively from the ATR analysis of the solid phase spectra. These ratios were used in the calculations of the helix tilt angles obtained from the infrared reflection-absorption spectra of the SAMs, described later.

PM-RAIRS analyses were performed in air with the crystal placed in the external beam of a Fourier transform infrared Nicolet 5700 spectrometer. The experimental setup was described in a previous paper.[6] All reported spectra were recorded at 8 cm^{-1} resolution by co-addition of 128 scans; using a modulation of polarization enabled us to perform rapid analyses of the samples after immersion without purging the atmosphere or requiring a reference spectrum.

The molecular orientation of the helical peptide was determined from the Amide I/Amide II ratio in the RAIRS spectrum under the assumption of uniform orientation of the helix axis around the surface normal[7] according to the following formula[8]:

$$\frac{I_1}{I_2} = K\frac{\left(3cos^2\gamma - 1\right)\left(3cos^2\theta_1 - 1\right) + 2}{\left(3cos^2\gamma - 1\right)\left(3cos^2\theta_2 - 1\right) + 2}$$

Where Ii, γ, and θi (i = 1 or 2 corresponding to amide I or amide II) represent the observed absorbance, the tilt angle of the helical axis from the surface normal, and the angle between the transition moment and the helix axis, respectively. The value of θ_1 was set to be 39° while θ_2 was taken between 75° for an α-helix and 83° for a 3_{10}-helix, according to the literature.[9]

K is the scaling factor related to the intrinsic "oscillator strength" of the amide I and amide II vibrational mode. K was set to be 1.74 and 1.54 for the hexapeptide **15** and **C60-peptide** respectively, which account for the amide I/II absorbance ratios experimentally determined for the respective helical peptides in the solid phase.

XPS

XPS analyses were collected on a Thermo Scientific ESCALAB 250 Xi and Omicron Argus X-ray photoelectron spectrometers. The X-ray source was Al Kα radiation (1486.6 eV) monochromatized radiation with a pass energy of 20 eV. The emissions of photoelectrons from the sample were analyzed at a take-off angle of 90° under UHV conditions. After collection, the binding energies (BE) were calibrated against the Au4f7/2 BE at 84.0 eV. The accuracy of the reported binding energies can be estimated to be ± 0.1 eV. The XPS peak areas were determined after subtraction of a background. Element peak intensities were corrected by Scofield factors.[10] All spectrum processing was carried out using Thermo Scientific™ Avantage Data System software or Casa XPS v.2.3.15 (Casa Software Ldt., UK). The spectral decomposition was performed by using Gaussian-Lorentzian (70%/30%) functions.

QCM-D measurements

Quartz crystal microbalance with dissipation measurements were performed with AT-cut gold- or silicon-coated quartz crystal electrodes with nominal frequency of 5 MHz (Lot-Oriel, France) in the flow-through mode (flow rate = 50 µL/min) on a quartz crystal microbalance with dissipation monitoring QCM-D (E4 model, Q-sense, Sweden) at 22°C. Before use, sensors were washed in ethanol and dried by a nitrogen gas flow. Experiments were run using dichloromethane as solvent. Mass uptakes Δm were calculated with the Sauerbrey equation (1) assuming the deposited films behave as an elastic mass

(1) $\Delta F = -N \times \Delta m / C_f$

where ΔF is the frequency shift at the 9th overtone, C_f (= -17.7 ng/cm^2/Hz at F = 5 MHz) the mass sensitivity factor and N (= 1,3, 5, 7 …) the overtone number.

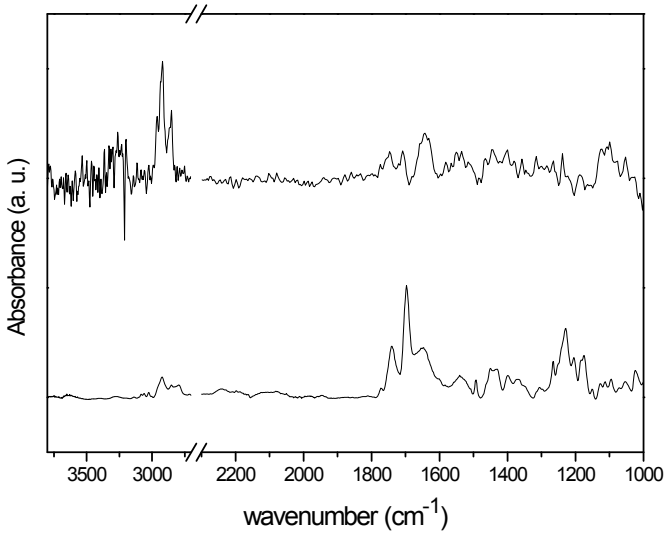


Figure S23. IR spectra of **C_{60}-alkyl** in bulk (solid state) (bottom) and adsorbed on gold (top).

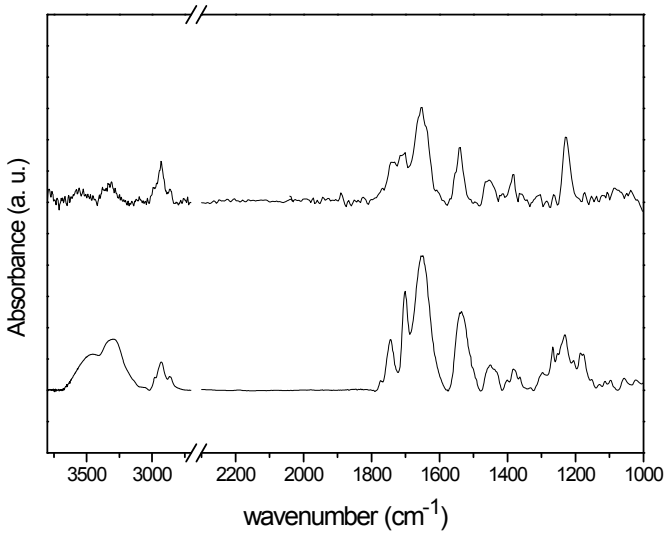


Figure S24. IR spectra of **C_{60}-peptide** in bulk (solid state) (bottom) and adsorbed on gold (top).

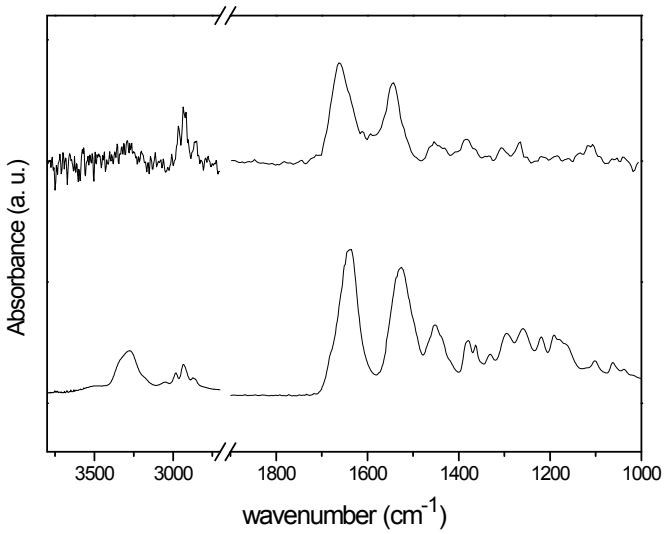


Figure S25. IR spectra of **hexapeptide 15** in bulk (solid state) (bottom) and adsorbed on gold (top).

Table S1. I.R. absorption data of **hexapeptide 15**, **C_{60}-peptide** and **C_{60}-alkyl** in bulk (solid state) and adsorbed on gold.

	Hexapeptide**15**		**C_{60}-peptide**		**C_{60}-alkyl**	
	SAM	bulk	SAM	bulk	SAM	bulk
νasym N=N-N	2093	2093				
νc=o malonate			1740	1742	1747	1740
νc=o maleimide			1699	1699	1708	1697
Amide I	1658	1636	1658	1647	1644	1647
Amide II	1542	1525	1542	1527	1542	1540
triazole ring			1429	1434	1423	1430
νCN maleimide			1399	1399	1402	1398
CH3 sym bending	1382	1379	1382	1377		
νC-O malonate	1295	1306	1267	1295	1266	
νN-N			1224	1228	1238	1228
Azide N=N-N	1216	1219				
$\omega_3 C_{60}$			1181	1175	1187	1175

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