Supporting Information

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1. General

Solvents were dried and distilled before use. Millipore water was obtained with a Micropure from *TKA*. All reactions were carried out in oven dried glassware. Lyophilization was carried out with an Alpha 1-4 2D plus freeze drying apparatus from *Christ*. Analytical TLC was carried out on SiO_2 aluminum foils ALUGRAM SIL G/UV_{254} from *Macherey-Nagel*. Reversed phase column chromatography was done with an *Armen Instrument* Spot Flash Liquid Chromatography MPLC apparatus with *RediSep* C-18 Reversed-Phase columns. The analytical "High Performance Liquid Chromatography" (HPLC) was done with the following parameters: reversed phase, Dionex HPLC system: P680 pump, ASI-100 automated sample injector, UVD-340U UV detector, UltiMate 3000 Column Compartment; Software: Dionex Chromeleon 6.80; Column: YMC-Pack ODSA,150 mm length, 3.0 mm diameter, 5 µm, 12 nm; type: AA12S05-1503QT. ^{1}H- and ^{13}C-NMR spectra were recorded on a DRX 500 MHz spectrometer from *Bruker* at ambient temperature. The chemical shifts are reported in parts per million (ppm) relative to the deuterated solvent DMSO-d_6. The following abbreviations are used for peak multiplicities: s, singlet; d, doublet, m, multiplet; br, broad. MALDI-TOF-mass spectra were received by using a *Bruker* BioTOF III. Determination of pH values was carried out with a pH-Meter 766 Calimatic from *Knick*. Isothermal Titration Calorimetry (ITC) experiments were conducted on a Microcal VP-ITC

microcalorimeter. Origin 7.0 software, supplied by the manufacturer, was used for data acquisition and analysis. Microwave assisted SPPS was carried out with a CEM Discover. GCP group was synthesized as previous report.[1]

2. Peptide Synthesis

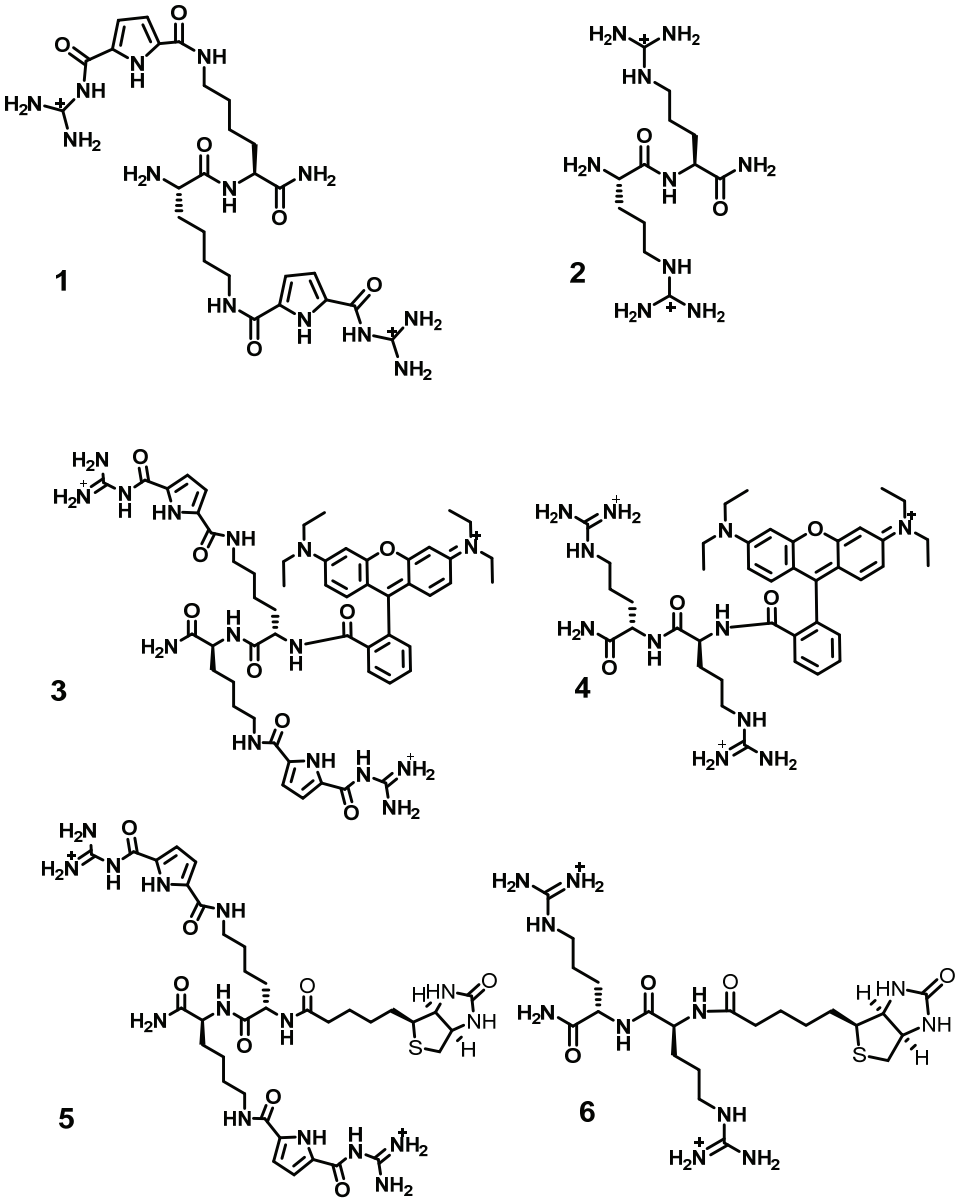


Fig. S1. Chemical structures of peptide **1- 6**

Microwave Assisted Solid-Phase Peptide Synthesis of (1):

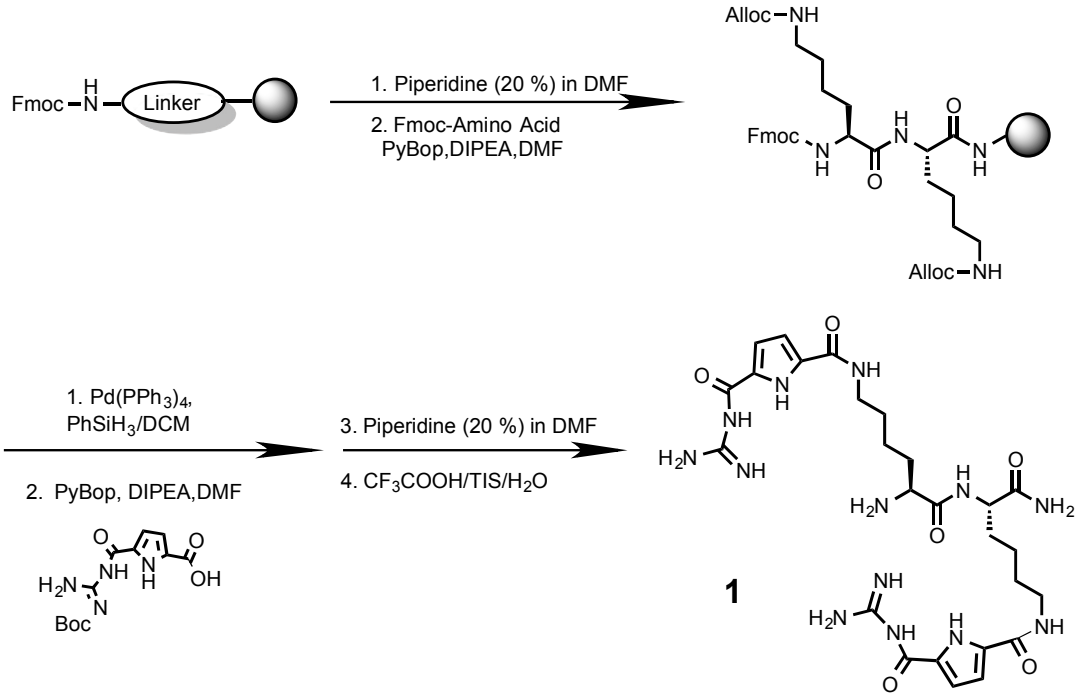


Fig. S2. Solid phase synthesis of **1**.

The reaction was carried out in a microwave-transparent 25 ml polyethylene column with a CEM Discover microwave apparatus. Rink-Amide MBHA resin was swollen in for 2 h. Fmoc removal was achieved by irradiating the resin in 20 % piperidine/DMF for 1 min and 5 min at 20 W and a maximum temperature of 60° C followed. Fmoc-Alloc-Lys-OH was attached to the resin by microwave irradiation for 20 min at 20 W and a maximum temperature of 60° C under argon atmosphere with PyBOP and DIPEA in DMF and consequent washing with DMF. Coupling and washing steps were repeated. After Fmoc deprotection the second Fmoc-Alloc-Lys-OH was attached to the resin as described above. Alloc removal was achieved by $Pd(PPh_3)_4$ and $PhSiH_3$ in

DCM for 30 min at room temperature under argon bubbling. The deprotection and washing process was repeated. GCP moiety was synthesized according to previous literature.[1] The GCP groups were attached to the resin by microwave irradiation for 30 min at 20 W with PyBOP and DIPEA in DMF and consequent washing with DMF. The coupling process was repeated until *Kaiser Test* showed negative result. After Fmoc deprotection the resin was washed with DCM and methanol and dried under reduced pressure for one hour. To cleave the product, the resin was transferred to a flask equipped with a frit onto a Heidolph Rotamax 120 shaker. There it was shaken under argon atmosphere in a mixture containing 95 % TFA, 2.5 % water and 2.5 % TIS for three hours and washed twice with the cleavage mixture. The filtrates were combined and concentrated in high vacuum at room temperature. Diethyl ether was added and the resulting suspension was centrifuged. The supernatant solvent was decanted and the solid was washed with diethyl ether and centrifuged again. After decanting, the raw product was dissolved in water and the mixture was freeze-dried in vacuum. The resulting solid was purified by MPLC on C18 reversed-phase silica gel (10 % to 50 % methanol/water in 45 min, 0.1 % TFA) to obtain **1** as white solid (20 mg, 25 %) with 96 % purity determined by analytical RP-HPLC.

^{1}H-NMR (500 MHz, d^6-DMSO): δ [ppm] = 1.33-1.39 (m, 4H, Lys-CH_2), 1.49-1.51 (m, 4H, Lys-CH_2), 1.67-1.75 (m, 4H, Lys-CH_2), 3.20-3.24 (t, 4H, J = 5 Hz, Lys-CH_2), 3.80-3.81 (m, 1H, Lys-CH), 4.22-4.26 (m, 1H, Lys-CH), 6.85-6.86 (m, 2H, pyrrole-CH), 7.06 (s, 1H, pyrrole -NH),

7.37-7.38 (m, 2H, pyrrole-CH), 7.51 (s, 1H, pyrrole -NH), 8.13 (s, 3H, amide-NH), 8.39-8.52 (m, 10H, guanidine-NH), 11.70 (s, 1H, amine-NH), 12.31 (s, 2H, amide-NH_2).

^{13}C-NMR (125 MHz, d^6-DMSO): δ [ppm] = 21.7 (Lys-CH_2), 22.9 (Lys-CH_2), 28.6 (Lys-CH_2), 28.8 (Lys-CH_2), 31.0 (Lys-CH_2), 31.9 (Lys-CH_2), 38.6 (Lys-CH_2), 38.7 (Lys-CH_2), 52.1 (Lys-CH), 52.7 (Lys-CH), 112.4 (pyrrole-CH), 115.9 (pyrrole-CH), 125.4 (Cq), 132.9 (Cq), 155.4 (Cq), 159.1 (Cq), 159.2 (Cq), 159.7 (Cq), 168.5 (Cq), 173.2 (Cq).

MALDI-TOF-MS (pos.) m/z calculated for $C_{26}H_{39}N_{13}O_6$ $[M + H]^+$ 630.31, found 630.33

Microwave Assisted Solid-Phase Peptide Synthesis of (2):

Peptide 2 was synthesized using the above mention procedure of solid phase peptide synthesis with rink-Amide MBHA resin. The final product was purified by MPLC on C18 reversed-phase silica gel (5 % to 50 % methanol/water in 45 min, 0.1 % TFA) to obtain **2** as colorless solid (10 mg, 25 %).

^{1}H-NMR (500 MHz, D_2O): δ [ppm] = 1.65-1.67 (m, 4H, Arg-CH_2), 1.79-1.94 (m, 4H, Arg-CH_2), 3.18-3.24 (m, 4H, Arg-CH_2), 4.10 (s, 1H, Arg-CH), 4.29-4.33 (m, 1H, Arg-CH).

^{13}C-NMR (125 MHz, D_2O): δ [ppm] = 23.4 (Arg-CH_2), 24.4 (Arg-CH_2), 28.0 (Arg-CH_2), 28.1 (Arg-CH_2), 40.4 (Arg-CH_2), 40.6 (Arg-CH_2), 52.6 (Arg-CH), 53.6 (Arg-CH), 156.8 (guanidine-C), 169.8(Cq), 175.9 (Cq).

ESI-MS (pos.) m/z calculated for $C_{12}H_{28}N_9O_2$ $[M + H]^+$ 330.2, found 330.2

Synthesis of Rhodamine labeled peptide (Rh-1):

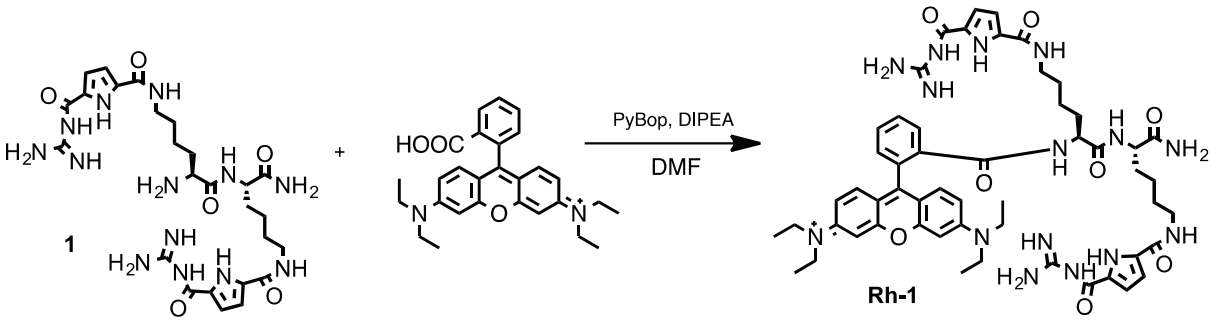


Fig. S3. Synthesis of peptide **Rh-1**

To a reaction mixture of rhodamine B (9.6 mg, 0.02 mmol) in 10 mL DMF, PyBop (12 mg, 0.024 mmol) and DIPEA (4.1 µl, 0.024 mmol) were added under argon atmosphere at room temperature avoid of light. The solution was stirred for 30 minutes and peptide **1** (12 mg, 0.02mmol) was added subsequently. The reaction solution was stirred for overnight at room temperature. Afterwards, DMF was removed under reduced pressure. 20 mL water was then added to the residue oil and lyophilized. The crude product was purified with MPLC on C18 reversed-phase silica gel (10 % to 100 % methanol/water in 45 min, 0.1 % TFA) to obtain **Rh-1** as red solid (8 mg, 38%).

^{1}H-NMR (500 MHz, d^6-DMSO): δ [ppm] = 1.01-1.09 (m, 8H, Lys-CH_2), 1.15-1.23 (m, 12H, Lys-CH_2, Rhodamine-CH_3), 1.43-1.45 (m, 4H, Lys-CH_2), 2.83-2.89 (m, 2H, Lys-CH_2), 3.13-3.33 (m, 10H, Lys-CH_2, Rhodamine-CH_2), 3.89-3.93 (m, 1H, Lys-CH), 4.08-4.10 (m, 1H, Lys-CH),

6.33-6.37 (m, 2H, pyrrole-CH), 6.81-6.86 (m, 2H, pyrrole-CH), 6.91 (m, 1H, pyrrole-NH), 7.00-7.11 (m, 6H, amide-NH), 7.28-7.29 (m, 2H, amide-NH), 7.39-7.44 (m, 2H, amide-NH), 7.52-7.54 (m, 2H, amide-NH), 7.75-7.81 (m, 2H, amide-NH), 8.23-8.40 (m, 10H, guanidine-NH), 11.14-11.25 (m, 2H, amide-NH), 12.29-12.33 (m, 2H, amide-NH_2).

^{13}C-NMR (125 MHz, d^6-DMSO): δ [ppm] = 12.3 (Rhodamine-CH_3), 12.4 (Rhodamine-CH_3), 13.9 (Rhodamine-CH_3), 22.1 (Lys-CH_2), 28.1 (Lys-CH_2), 28.4 (Lys-CH_2), 28.7 (Lys-CH_2), 29.0 (Lys-CH_2), 31.2 (Lys-CH_2), 32.3 (Lys-CH_2), 38.6 (Lys-CH_2), 43.7 (Rhodamine-CH_2), 45.2 (Rhodamine-CH_2), 45.3 (Rhodamine-CH_2), 51.6 (Lys-CH), 52.1 (Lys-CH), 112.3 (pyrrole-CH), 114.4 (pyrrole-CH), 115.4 (pyrrole-CH), 125.3 (Rhodamine-CH), 132.8 (Rhodamine-CH), 152.6 (Rhodamine-CH), 155.0 (Rhodamine-CH), 158.0 (Cq), 158.7 (Cq), 158.9 (Cq), 159.5 (Cq), 167.3 (Cq),172.9 (Cq).

MALDI-TOF-MS (pos.) m/z calculated for $C_{54}H_{69}N_{15}O_8$ $[M + H]^+$ 1056.54, found 1056.47

Microwave Assisted Solid-Phase Peptide Synthesis of (Rh-2):

The di-arginine scaffold was synthesized through solid phase peptide synthesis with rink-Amide MBHA resin. After Fmoc deprotection, rhodamine B (3eq) was attached onto the resin using PyBOP (3eq) and DIPEA (6eq) and consequent washing with DMF. The resin was then washed with methanol and DCM and dried under reduced pressure for one hour. After cleavage

and ether precipitation, the resulting solid was purified by MPLC on C18 reversed-phase silica gel (10 % to 100 % methanol/water in 45 min, 0.1 % TFA) to obtain **Rh-2** as red solid (20 mg, 21%).

^{1}H-NMR (500 MHz, D_2O): δ [ppm] = 1.09-1.27 (m, 14H, Arg-CH_2, Rhodamine-CH_3), 1.55-1.68 (m, 6H, Arg-CH_2), 2.94-2.97 (t, 2H, J = 5 Hz, Arg-CH_2), 3.19-3.21 (t, 2H, J = 5 Hz, Arg-CH_2), 3.55-3.72 (m, 8H, Rhodamine-CH_2), 3.94-3.97 (m, 1H, Arg-CH), 4.03-4.11 (m, 1H, Arg-CH), 6.73-6.74 (d, 1H, J = 5 Hz, Rhodamine-CH), 6.89-6.91 (d, 1H, J = 5 Hz, Rhodamine-CH), 7.09-7.13 (m, 2H, Rhodamine-CH), 7.26-7.28 (m, 2H, Rhodamine-CH), 7.58 (s, 1H, Rhodamine-CH), 7.66 (s, 1H, Rhodamine-CH), 7.76-7.78 (m, 1H, Rhodamine-CH), 8.06-8.08 (d, 1H, J = 5 Hz, Rhodamine-CH).

^{13}C-NMR (125 MHz, D_2O): δ [ppm] = 10.4 (Rhodamine-CH_3), 11.1 (Rhodamine-CH_3), 13.3 (Rhodamine-CH_3), 25.5 (Arg-CH_2), 27.1 (Arg-CH_2), 28.1 (Arg-CH_2), 29.3 (Arg-CH_2), 29.4 (Arg-CH_2), 30.3 (Arg-CH_2), 41.5 (Arg-CH_2), 41.8 (Arg-CH_2), 47.1 (Rhodamine-CH_2), 53.8 (Arg-CH), 54.2 (Arg-CH), 54.9 (Arg-CH), 55.0 (Arg-CH), 61.0 (Arg-CH), 67.1 (Arg-CH), 97.3 (Rhodamine-CH), 112.8-158.4 (Rhodamine-CH), 171.9 (Cq), 173.5 (Cq), 176.2 (Cq),177.1 (Cq).

MALDI-TOF-MS (pos.) m/z calculated for $C_{40}H_{56}N_{11}O_4$ $[M + H]^+$ 754.45, found 754.55

Microwave Assisted Solid-Phase Peptide Synthesis of (1-biotin):

The di-GCP modified peptide scaffold was synthesized through solid phase peptide synthesis with rink-Amide MBHA resin using the same procedure as in **1**. After Fmoc deprotection, biotin (3eq) was attached onto the resin using PyBOP (3eq) and DIPEA (6eq) and consequent washing with DMF. The resin was then washed with methanol and DCM and dried under reduced pressure for one hour. After cleavage and ether precipitation, the resulting solid was purified by MPLC on C18 reversed-phase silica gel (10 % to 100 % methanol/water in 45 min, 0.1 % TFA) to obtain **1-biotin** as white solid (25 mg, 23%) with 99 % purity determined by analytical RP-HPLC.

^{1}H-NMR (500 MHz, d^{6}-DMSO): δ [ppm] = 1.26-1.34 (m, 6H, Lys-CH_2, Biotin-CH_2), 1.44-1.68 (m, 12H, Lys-CH_2, Biotin-CH_2), 2.10-2.13 (t, 2H, J = 5 Hz, Biotin-CH_2), 2.80-2.83 (m, 1H, Biotin-CH), 3.07-3.08 (m, 2H, Biotin-CH_2), 3.19-3.23 (m, 4H, Lys-CH_2), 4.11-4.20 (m, 3H, Lys-CH, Biotin-CH), 4.28-4.31 (m, 1H, Biotin-CH), 6.47-6.48 (s, 2H, pyrrole-NH), 6.85 (s, 2H, pyrrole-CH), 7.05 (s, 1H, biotin-NH), 7.33 (s, 1H, biotin-NH), 7.40-7.43 (m, 2H, pyrrole-CH), 7.77-7.78 (m, 1H, amide-NH), 7.97-7.98 (m, 1H, amide-NH), 8.38-8.53 (m, 10H, guanidine-NH), 11.73-11.81 (m, 2H, amide-NH), 12.32 (s, 2H, amide-NH_2).

^{13}C-NMR (125 MHz, d^{6}-DMSO): δ [ppm] = 22.7 (Lys-CH_2), 22.9 (Lys-CH_2), 25.3 (Biotin-CH_2), 27.9 (Biotin-CH_2), 28.0 (Biotin-CH_2), 28.7 (Lys-CH_2), 31.3 (Lys-CH_2), 31.8 (Lys-CH_2), 38.6 (Lys-CH_2), 38.7 (Lys-CH_2), 40.1 (Biotin-CH_2), 52.1 (Lys-CH), 52.6 (Lys-CH), 53.8 (Biotin-

CH), 59.2 (Biotin-CH), 60.9 (Biotin-CH), 112.3 (pyrrole-CH), 115.8 (pyrrole-CH), 125.2 (Cq), 132.9 (Cq), 155.3 (Cq), 158.9 (Cq), 159.6 (Cq), 162.8 (Cq), 171.7 (Cq), 172.4 (Cq), 173.5 (Cq).

MALDI-TOF-MS (pos.) m/z calculated for $C_{36}H_{54}N_{15}O_8S$ $[M + H]^+$ 856.39, found 856.50

Microwave Assisted Solid-Phase Peptide Synthesis of (2-biotin):

The di-arginine peptide scaffold was synthesized through solid phase peptide synthesis with rink-Amide MBHA resin using the same procedure as in **2**. After Fmoc deprotection, biotin (3eq) was attached onto the resin using PyBOP (3eq) and DIPEA (6eq) and consequent washing with DMF. The resin was then washed with methanol and DCM and dried under reduced pressure for one hour. After cleavage and ether precipitation, The resulting solid was purified by MPLC on C18 reversed-phase silica gel (5 % to 50 % methanol/water in 45 min, 0.1 % TFA) to obtain **2-biotin** as colorless solid (15 mg, 22 %).

^{1}H-NMR (500 MHz, D_2O): δ [ppm] = 1.35-1.37 (m, 2H, Biotin-CH_2), 1.58-1.76 (m, 12H, Arg-CH_2, Biotin-CH_2), 2.28-2.30 (t, 3H, J = 5 Hz, Biotin-CH_2), 2.73-2.75 (m, 1H, Biotin-CH_2), 2.94-2.97 (m, 1H, Biotin-CH_2), 3.17-3.19 (m, 4H, Arg-CH_2), 3.28-3.29 (m, 1H, Biotin-CH_2), 4.27-4.30 (m, 2H, Arg-CH), 4.37-4.39 (m, 1H, Biotin-CH), 4.56-4.58 (m, 1H, Biotin-CH).

^{13}C-NMR (125 MHz, D_2O): δ [ppm] = 24.5 (Arg -CH_2), 24.6 (Biotin-CH_2), 25.1 (Arg-CH_2), 27.7 (Biotin-CH_2), 27.8 (Biotin-CH_2), 28.0 (Arg-CH_2), 28.1 (Arg-CH_2), 28.2 (Biotin-CH_2), 35.0

(Biotin-CH_2), 39.8 (Biotin-CH_2), 40.5 (Arg-CH_2), 40.6 (Arg-CH_2), 52.2 (Arg-CH), 53.1 (Arg-CH), 53.4 (Arg-CH),55.4 (Biotin-CH), 60.4 (Biotin-CH), 62.1 (Biotin-CH), 156.7 (guanidine-C), 165.3(Cq), 174.0 (Cq), 176.1 (Cq), 177.0 (Cq).

MALDI-TOF-MS (pos.) m/z calculated for $C_{22}H_{42}N_{11}O_4S$ $[M + H]^+$ 556.31, found 556.32

3. Biological studies

Cell lines and heparin: The Human cervix carcinoma cell line HeLa Kyoto, Chinese hamster ovary CHO-K1 and CHO pgsA-745 cells were obtained from the American Type Culture Collection and maintained as recommended, for HeLa cells in complete Dulbecco`s Modified Eagle Medium (DMEM) as well as for CHO cells in F-12K Medium, each supplemented with 10 % fetal bovine serum and 1 % Antibiotic-Antimycotic (*Invitrogen*) at 37 °C in a humidified atmosphere of 5% CO_2. Heparin was obtained from Aldrich, dissolved in sodium cacodylate buffer (0.05 M, pH 7.4).

1-avidin and 2-avidin preparation: Peptide **1-biotin** and **2-biotin** was prepared in a 1 mM stock solution in PBS buffer containing 20 % DMSO. FITC-avidin (*Thermo fisher*) was prepared in a 250 µM stock solution in PBS. For the generation of **1-avidin** and **2-avidin**, 25 µL **1-biotin** or **2-biotin** were mixed with 25 µL avidin solution. The resulting mixture was

incubated at room temperature for 30 min protected from light to obtain the desired product. The final stock solution of **1-avidin** and **2-avidin** was determined to be 125 µM.

3.1 Cellular Uptake Study

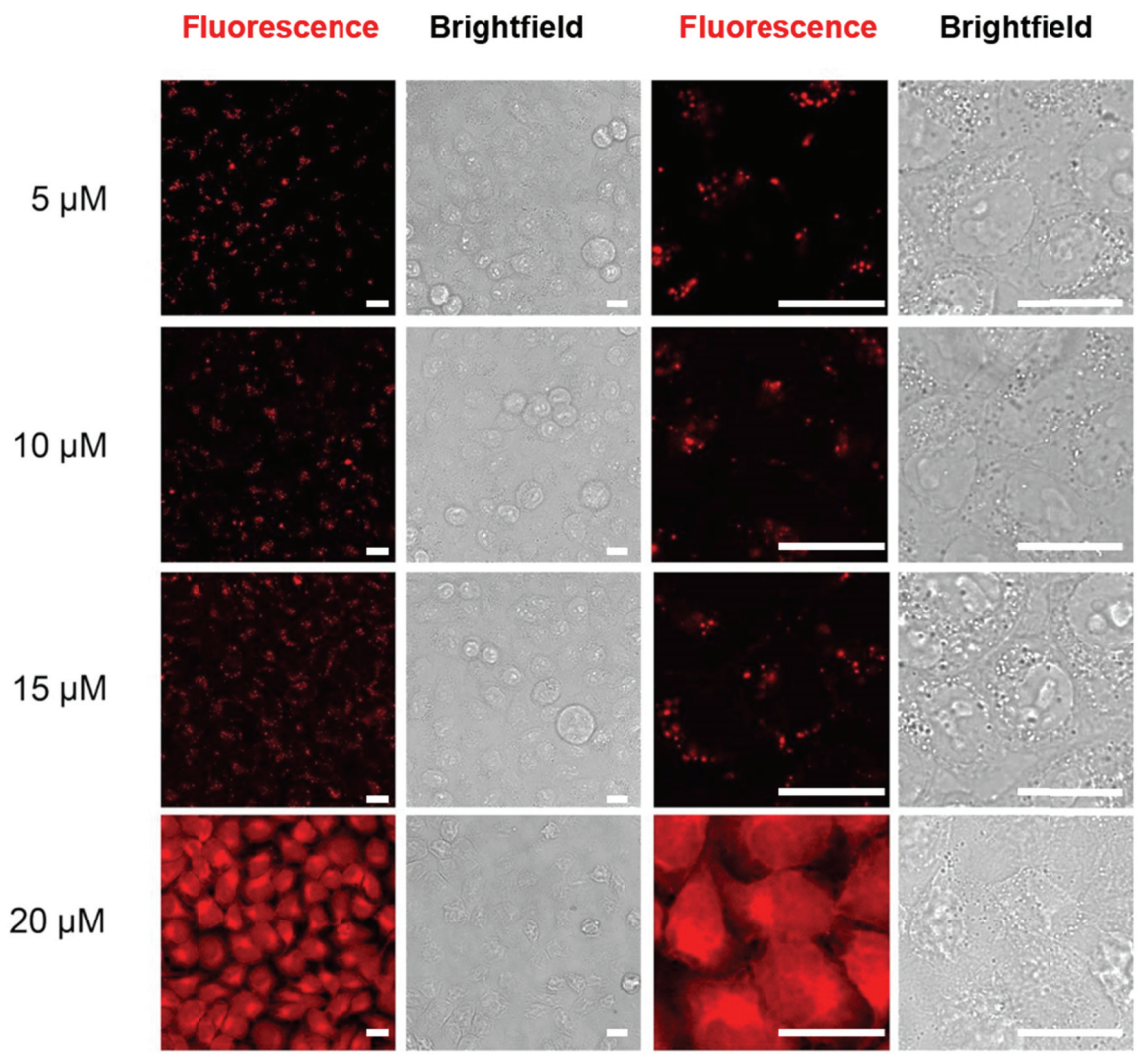


Fig. S4. Confocal microscopy images of HeLa cells treated with different concentrations of peptide **Rh-1**. Scale bar 25 µm.

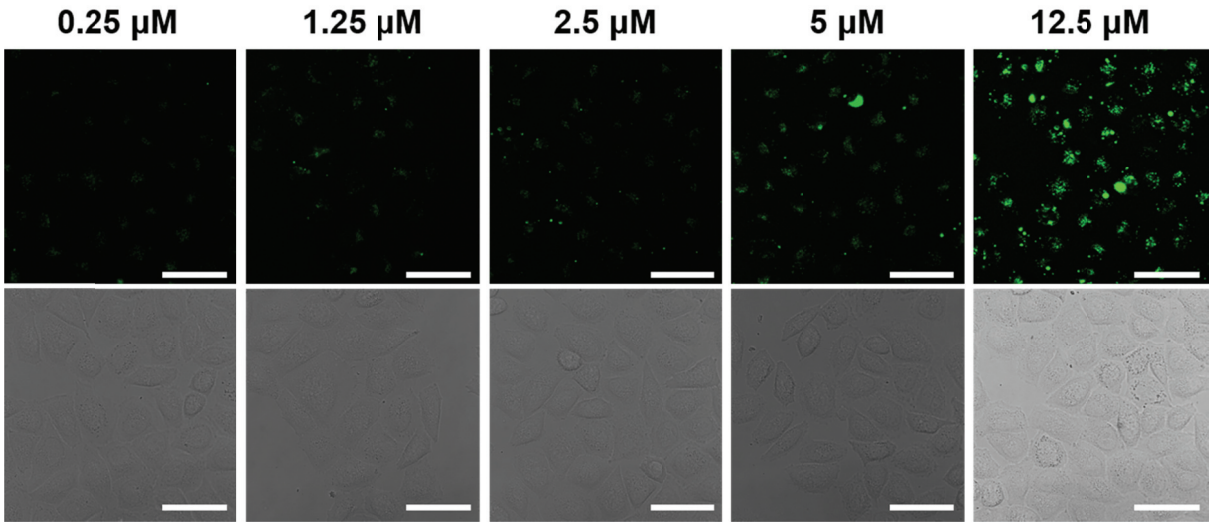


Fig. S5. Confocal microscopy images of HeLa cells treated with different concentrations of **1-avidin**. Scale bar 50 µm.

3.2 Cellular Co-localization Study

Golgi-apparatus

Hela cells were seeded in 8-well chamber slides, grown for 24 h and transfected with 50 ng pEYFP-Golgi (encodes a fusion protein consisting of EYFP and a sequence encoding the N-terminal 81 amino acids of human beta 1,4-galactosyltransferase)with Lipofectamine 2000 according to the manufacturer´s instructions (*Invitrogen*). After an additional incubation of 24 h, cells were treated with 10 µM **Rh-1** for 1 h. Afterwards, Hoechst 33342 was added to stain nuclear DNA and incubated for 5 minutes. Cells were then thoroughly washed with PBS buffer for three times and examined under a confocal fluorescence microscope (SP8 LCSM, *Leica*). Images were processed using LAS AF software (*Leica*) and Adobe Photoshop CS2.

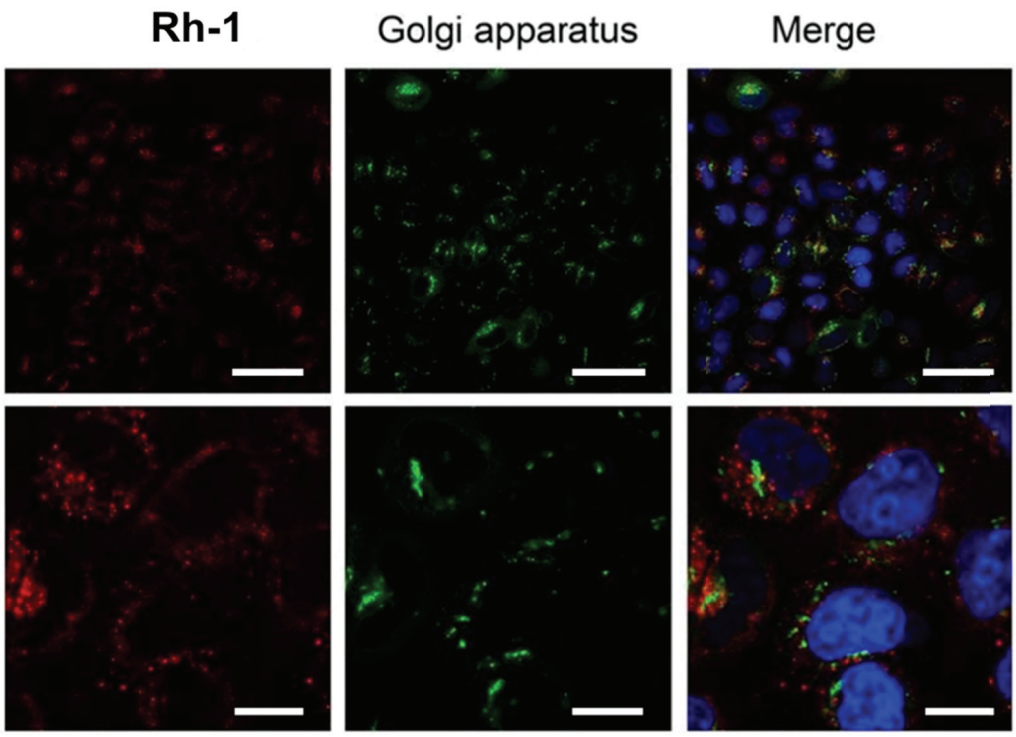


Fig. S6. Co-localization with cellular organelles. Hela cells were treated with 10 μM **Rh-1** (red) and incubated at 37 ℃ for 1 h. Golgi apparatus (green) were stained with GFP marker and cell nuclei (blue) were stained with Hoechst 33342. Scale bar: upper row 50 μm, lower row 10 μm.

Endosome and lysosome (immunostaining)

Hela cells were seeded in 8-well plates, grown for 24 h and incubated with 10 μM **Rh-1** or 12.5 μM **1-avidin** for 1 h, respectively. Cells were then washed with PBS buffer and then fixed with 4 % paraformaldehyde for 20 min at RT. After permeabilization with 0,1 % Triton X-100/PBS for 10 min the cells were blocked in 5 % BSA (bovine serum albumin)/PBS for 30 min. Followed by an incubation step with a mouse monoclonal anti-LAMP1 antibody (*Santa Cruz* sc-20011, lysosome marker) or an mouse anti-EEA1 antibody (BD 610457, endosome marker) for 1 h at RT in 5 % BSA/PBS. Incubation with anti-mouse antibody conjugated with Alexa

Fluor 488 (*Thermo Fisher Scientific*) and Hoechst 33342. Cells were washed between each step for 3 times with PBS and examined under a confocal fluorescence microscope (SP8 LCSM, *Leica*). Images were processed using LAS AF software (*Leica*) and Adobe Photoshop CS2.

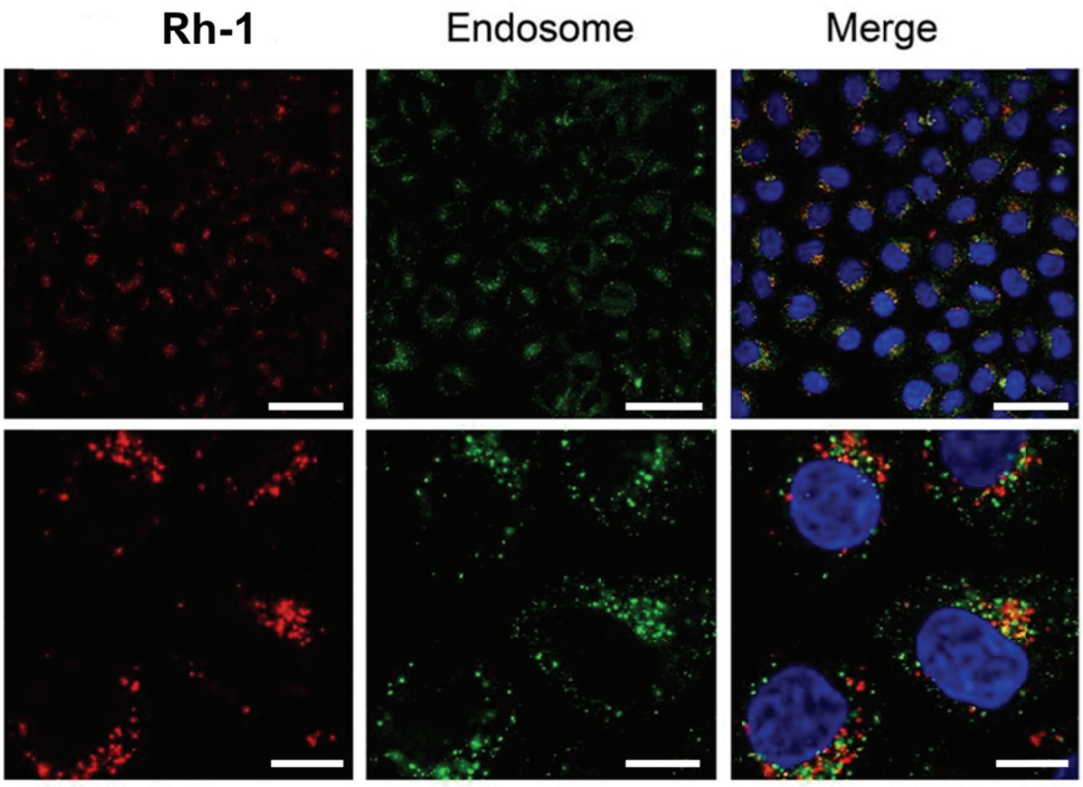


Fig. S7. Co-localization with cellular organelles. Hela cells were treated with 10 μM **Rh-1** (red) and incubated at 37 ℃ for 1 h. Endosomes (green) were stained with an antibody marker, and the cell nuclei (blue) were stained with Hoechst 33342. Scale bar: upper row 50 μm, lower row 10 μm.

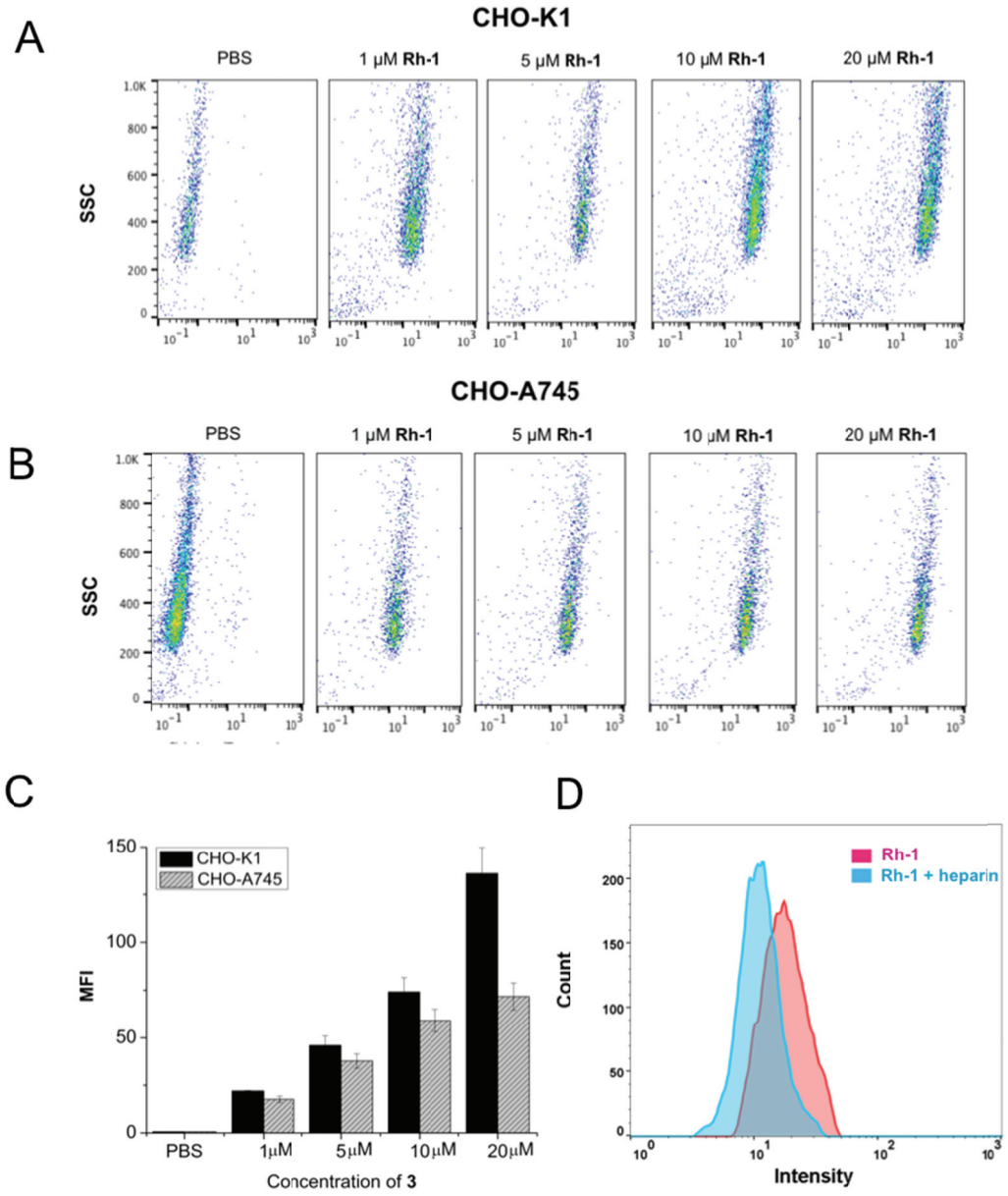
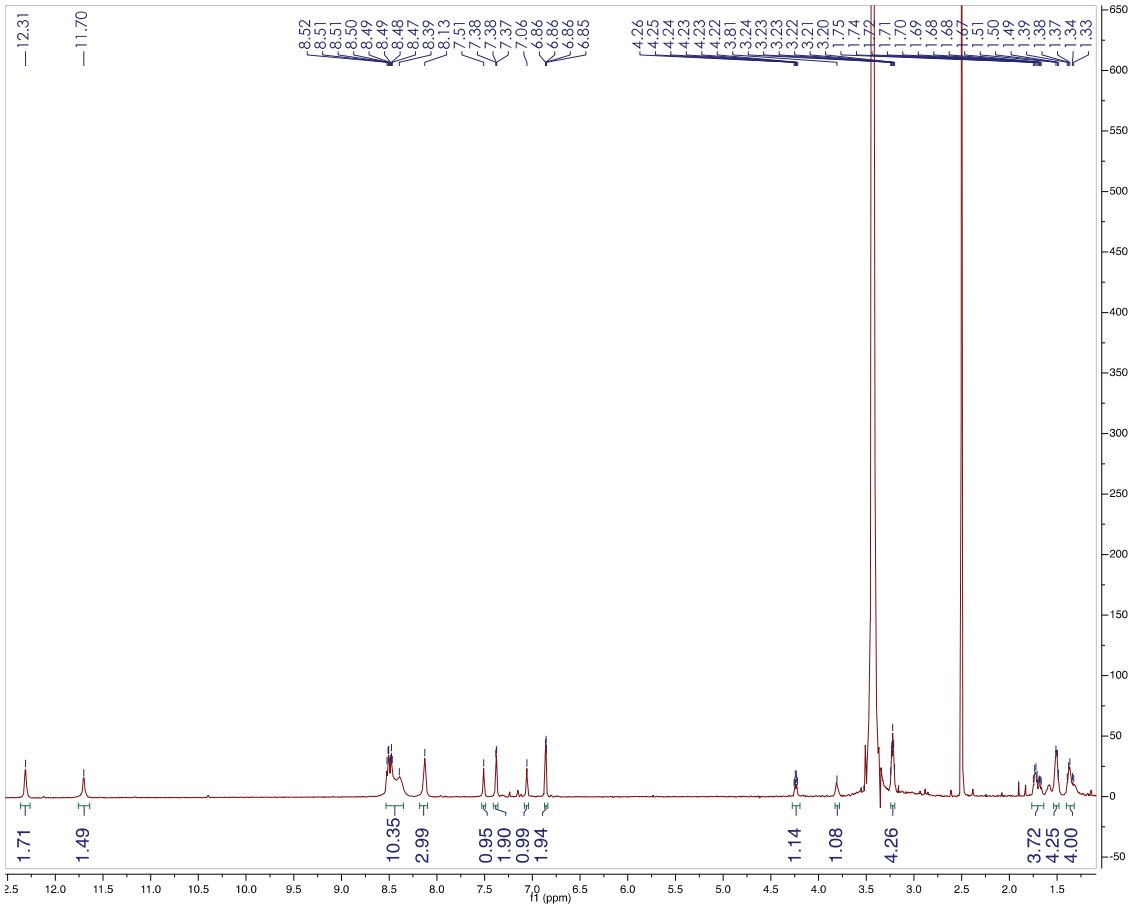


Fig. S8. Glycosaminoglycan dependency of the cellular uptake of peptide **Rh-1.** (A and B) Flow cytometry analysis of the cellular uptake of **Rh-1** in CHO-K1 (A) and CHO-pgsA745 cells (B); (C) Mean fluorescence intensity of the two cell lines treated with different concentration of **Rh-1**; (D) Histogram of the cellular uptake of 10 μM peptide **Rh-1** and its mixture with heparin (1 eq) in HeLa cells obtained from flow cytometry analysis.

(1) Schmuck, C.; Bickert, V.; Merschky, M.; Geiger, L.; Rupprecht, D.; Dudaczek, J.; Wich, P.; Rehm, T.; Machon, U. *Eur. J. Org. Chem.* **2008**, *2*, 324.

4. Spectra of all compounds

Fig.S9. ^{1}H-NMR of **1** in DMSO-d^{6} recorded at 500 MHz.



^{13}C-NMR of **1** in DMSO- d^{6} recorded at 125 MHz.

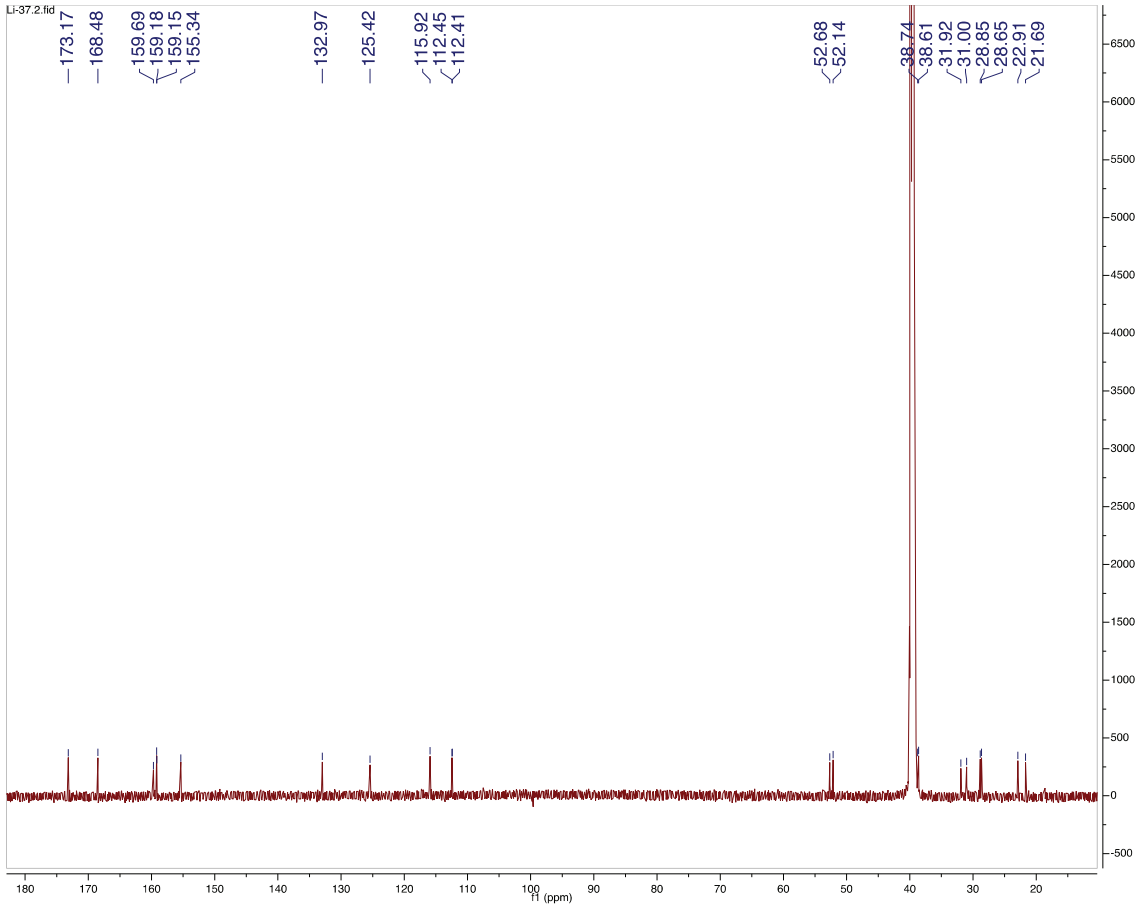
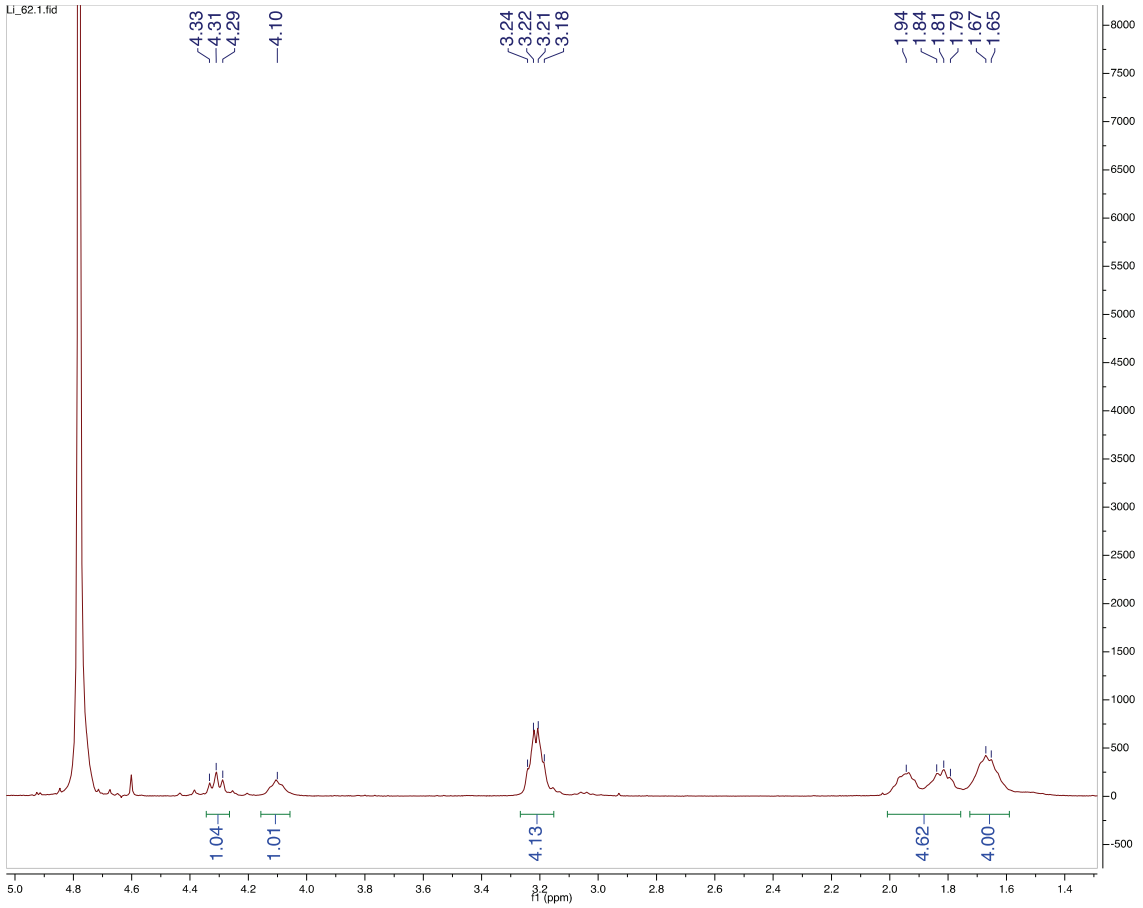


Fig.S10. ^{1}H-NMR of **2** in DMSO- d^{6} recorded at 500 MHz.



^{13}C-NMR of **2** in DMSO- d^{6} recorded at 125 MHz.

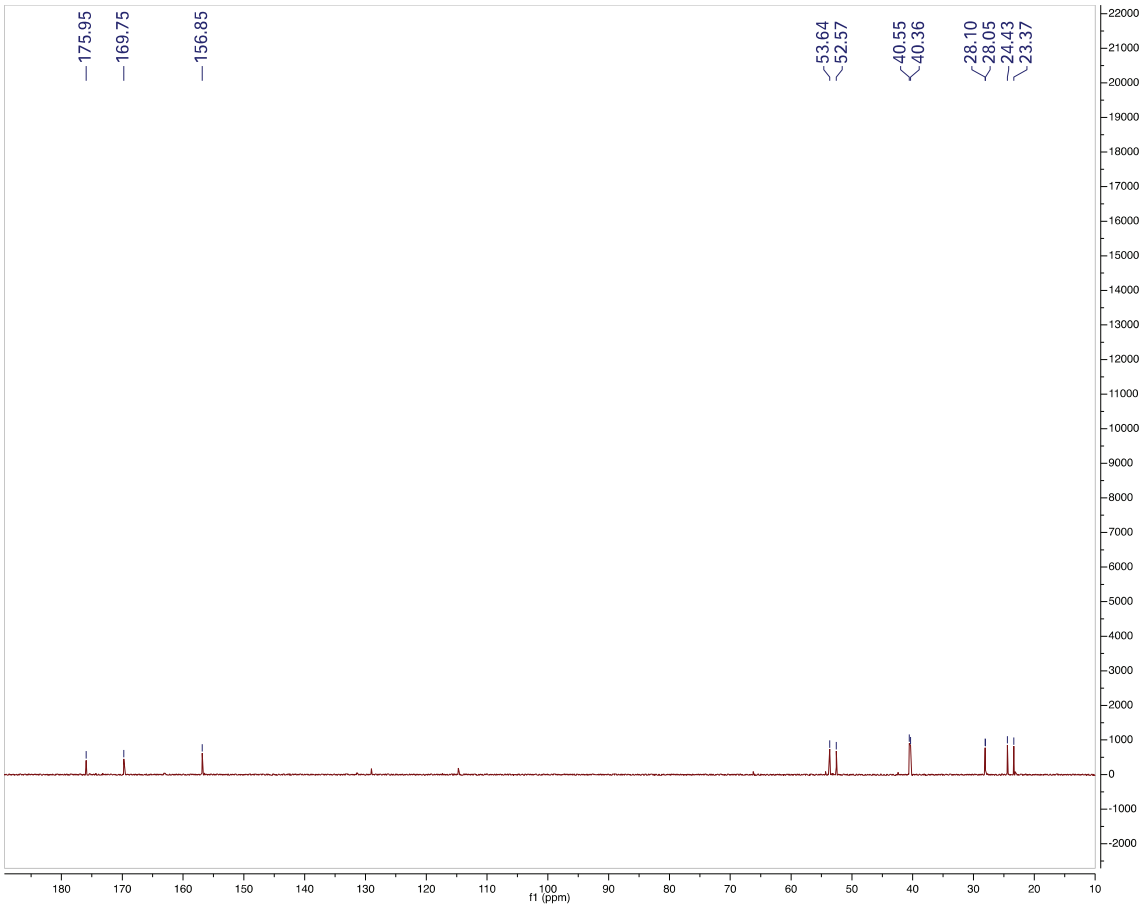
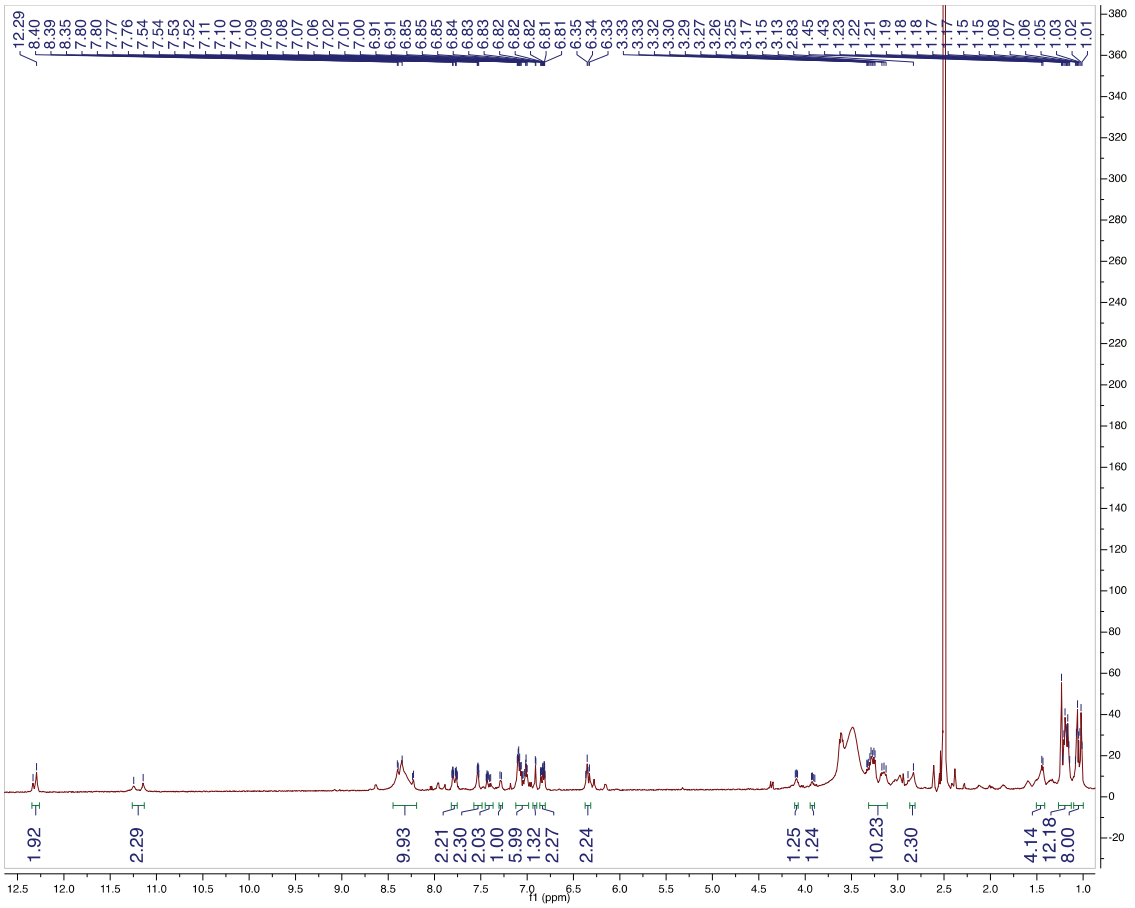


Fig.S11. ^{1}H-NMR of **Rh-1** in DMSO- d^{6} recorded at 500 MHz.



^{13}C-NMR of **Rh-1**in DMSO- d^{6} recorded at 125 MHz.

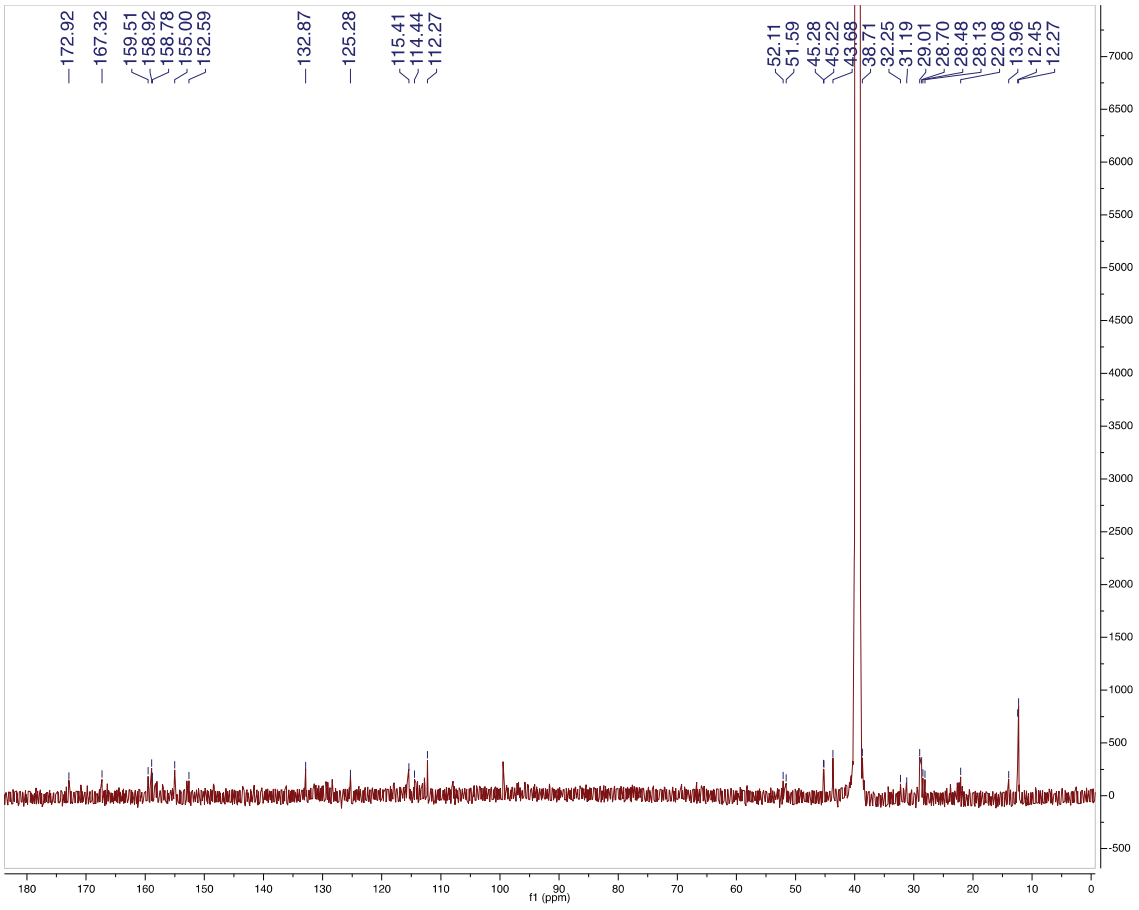
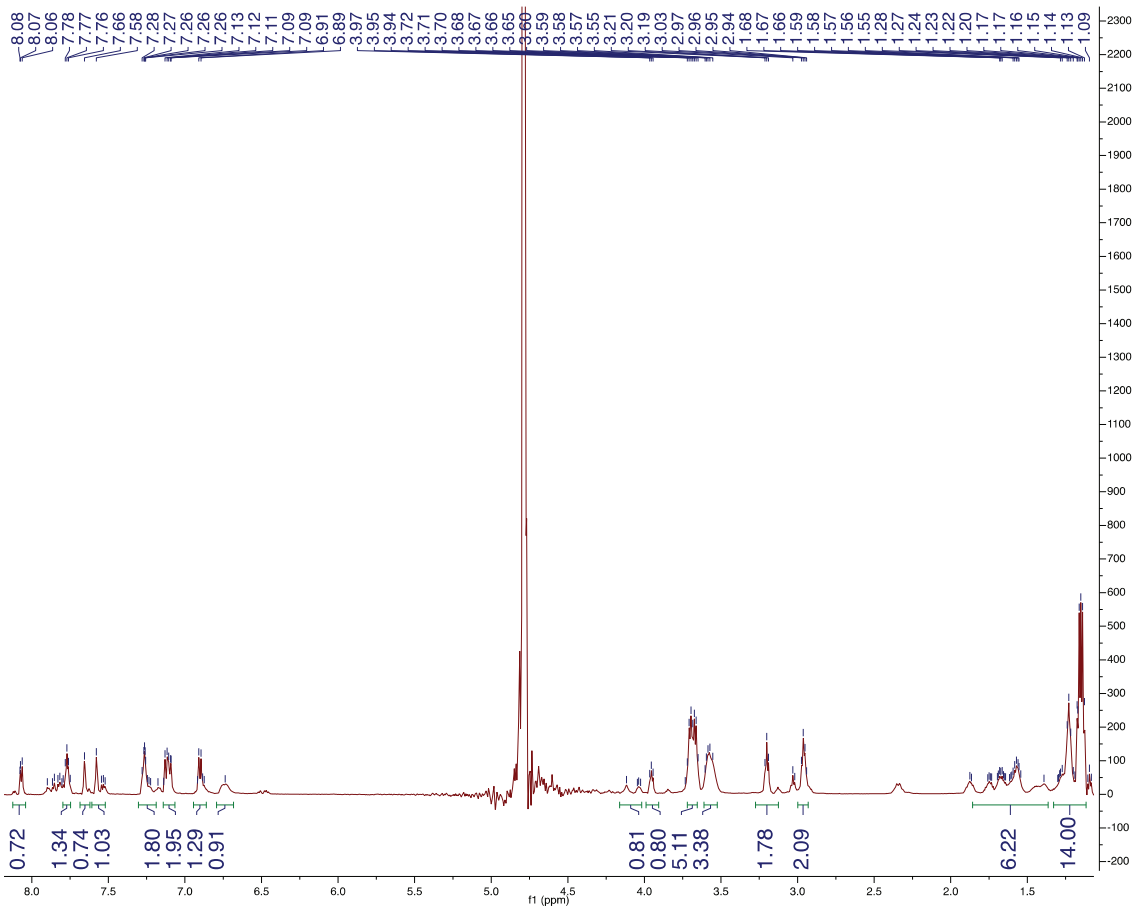


Fig.S12. ^{1}H-NMR of **Rh-2** in D_2O recorded at 500 MHz.



^{13}C-NMR of **Rh-2** in D_2O recorded at 125 MHz.

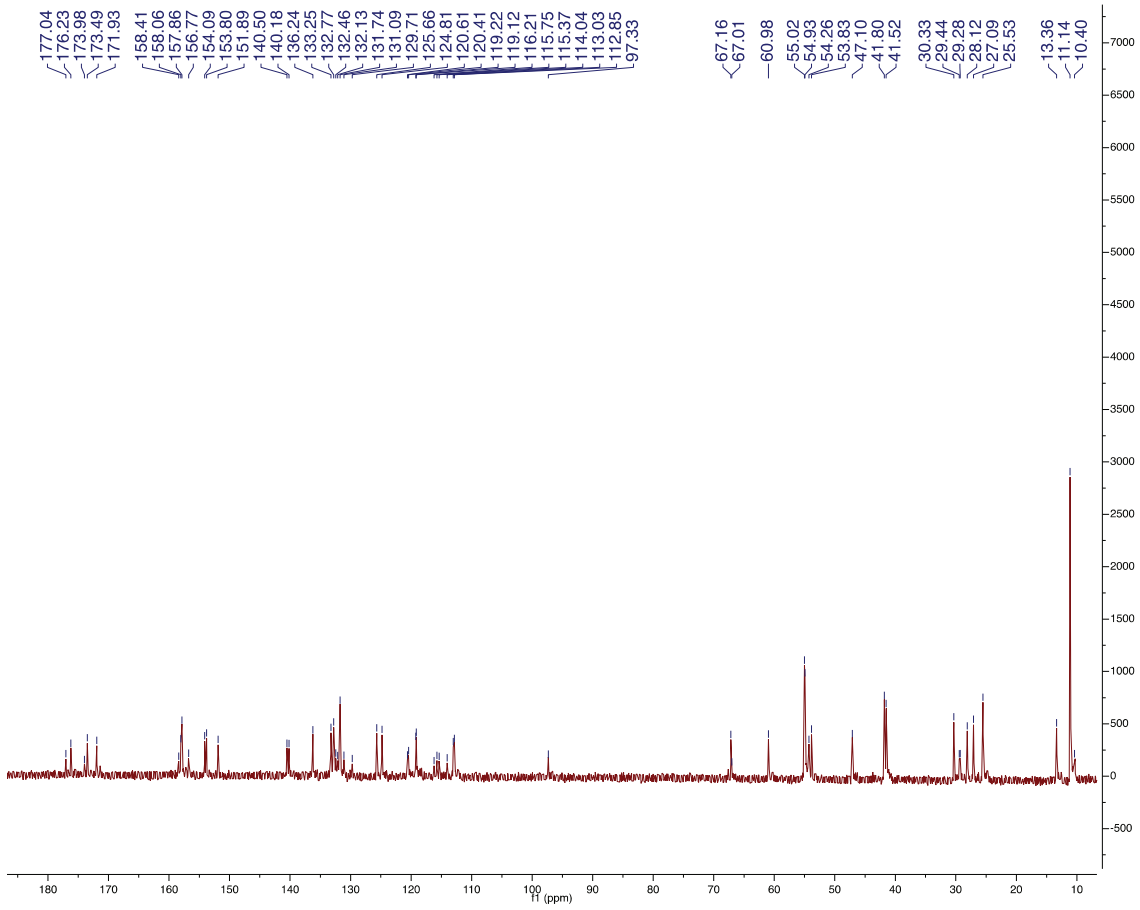
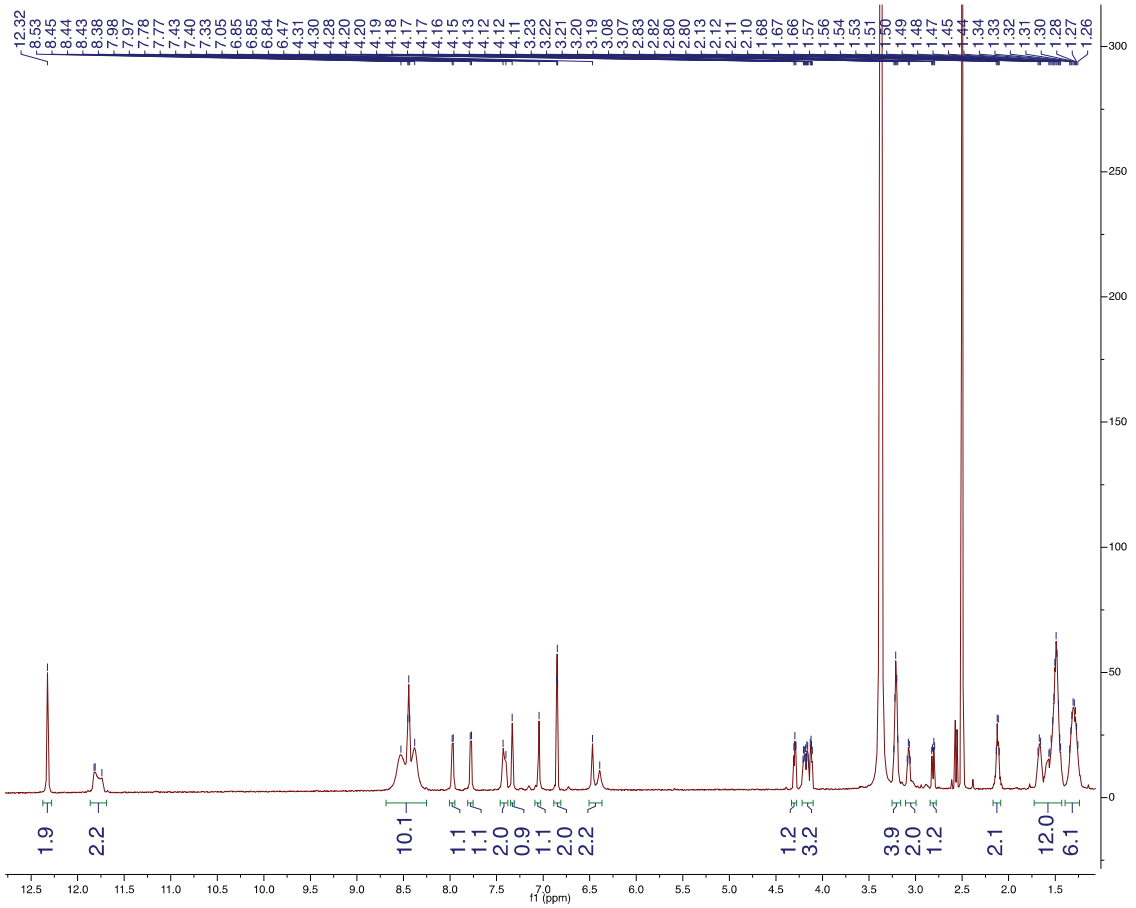


Fig.S13. ^{1}H-NMR of **1-biotin** in DMSO- d^{6} recorded at 500 MHz.



^{13}C-NMR of **1-biotin** in DMSO- d^{6} recorded at 125 MHz.

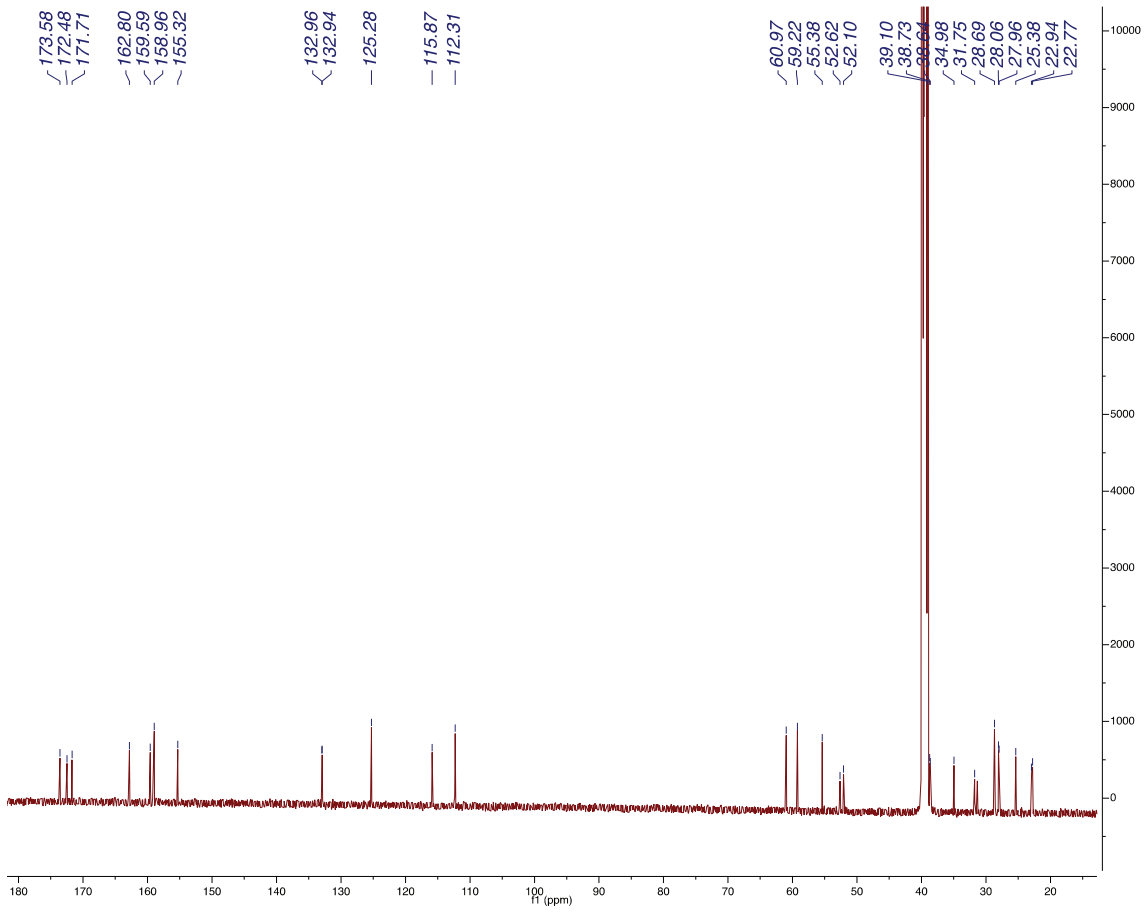
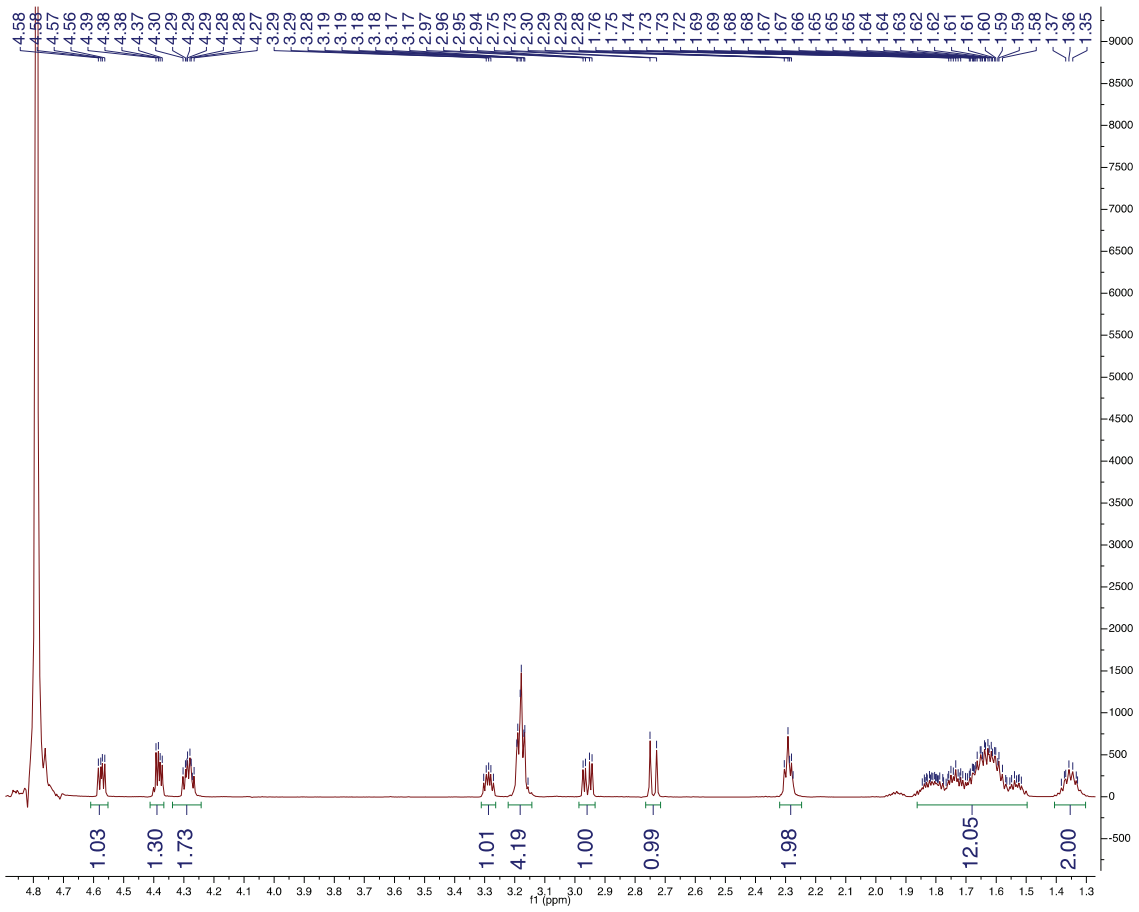


Fig.S14. ^{1}H-NMR of **2-biotin** in D_2O recorded at 500 MHz.



^{13}C-NMR of **2-biotin** in D_2O recorded at 125 MHz.