SUPPORTING INFORMATION

The Self-Assembly of Cystine-Bridged γ-Peptide-Based Cyclic Peptide-Dendron Hybrids

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Contents:

1. General Methods, Instrument Details and Materials:

(1*R*,3*S*)-3-aminocyclohexanecarboxylic acid (γ-Ach) was prepared according to our method.[1] O-(7-azabenzotriazol-1-yl)-1, 1, 3, 3-tetramethyluronium hexafluorophosphate (HATU), 1-Hydroxy-7-azabenzotriazole (HOAT), 1-Hydroxybenzotriazole (HOBt) and N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDCI) were all used as obtained from GL Biochem (Shanghai) Ltd. All other reagents obtained from commercial suppliers were used without further purification unless otherwise noted. Dichloromethane (DCM) was dried and distilled over calcium hydride. Analytical thin-layer chromatography was performed on silica gel GF254 plates from Qingdao Haiyang Chemical Co. Ltd. Silica gel flash chromatography was performed using silica gel (200-300 mesh) from Qingdao Haiyang Chemical Co. Ltd. Melting points were recorded on a BÜCHI Melting Point B-545 apparatus and are uncorrected. Optical rotations were measured with an automatic Perkin-Elmer-341 digital polarimeter; concentrations are given in g/100 mL.

NMR experiments. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker WM-300 MHz or 600 MHz spectrometers. Chemical shifts were reported in parts per million (ppm, δ) from TMS or solvent resonance as the internal standard. ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), 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). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker WM-300 MHz or 600 MHz spectrometers.

Matrix Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) was obtained on a Bruker Autoflex mass spectrometer.

Electrospray (ESI) mass spectra were recorded on a Bruker BioTOF Q mass spectrum.

FT-IR measurements were recorded on a Nicolet MX-1 FT-IR spectrometer or Nicolet MAGNA-IR 560 spectrometer as KBr pellets or liquid film. For the solution state, measurements were performed using a NICOLET 6700 FT-IR Spectrometer. The $CHCl_3$, CH_3CN solution FT-IR measurements placed in a 0.1 mm of KBr solution IR cell and for the D_2O solution, measurements were performed in CaF_2 cell.

Scanning Electron Microscopy (SEM): The sample was placed on a piece of silicon wafers, attached to a stub via carbon tape and coated with ~10 nm of gold. Sample was analyzed using JSM-5900LV at an accelerating voltage of 5 kV.

Transmission Electron Microscopy (TEM): After the sample for TEM was prepared, droplets of 10 μL of the solution were placed onto the specimen holder, a 200 mesh copper grid. After 2 min., the grid was stained with 1% (w/v) phosphotungstic acid for 1 min. and the excess fluid was removed. Samples were viewed using a HITACHI H-600 electron microscope for TEM at an accelerating voltage of 75 kV.

Atom force microscopy (AFM) measurements: After the gels were dispersed in water or water-ethanol (1:1, v/v) mixture, 10 μL of the solution was deposited onto a freshly cleaved piece of

mica and left to adhere for overnight. AFM imaging was performed at room temperature using the tapping mode on a Seiko SPI3800N. According to the manufacturer, the probe used were etched silicon probes with a typical tip radius of < 10 nm, the normal spring constant was 3 N/m. Drive frequency was around 75 kHz.

Analytical HPLC analysis

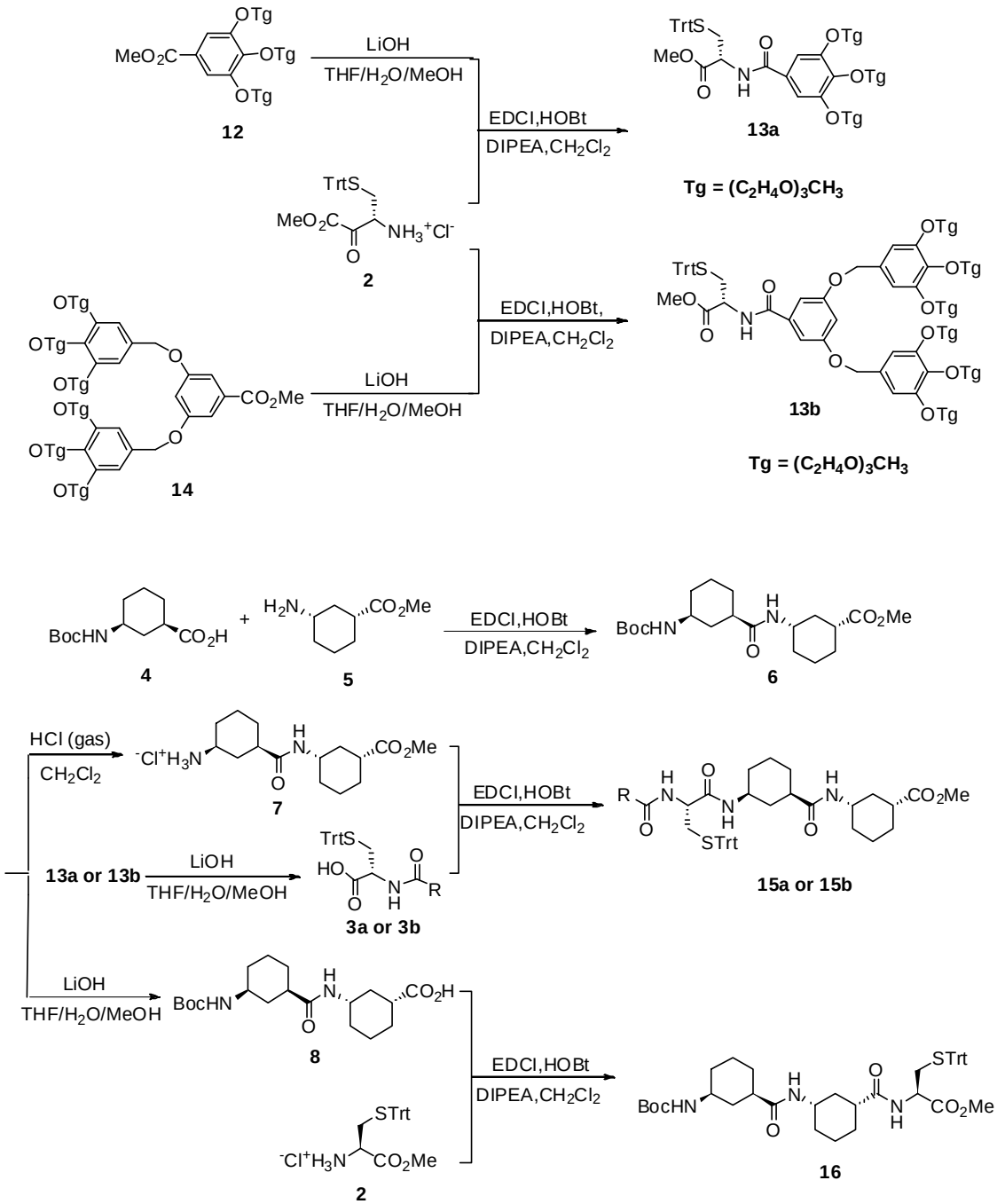
Analytic HPLC was carried out on Ultimate 3100 systems coupled to UV detectors and the data were processed using Chromeleon 6.5 software. Analysis of samples was performed using a reversed-phase HPLC column (Acclaim 120 C18, 5 µm, 120 Å, 4.6 x 150 mm) at 25 °C with an injection volume of 20 µL. All UV traces were obtained by monitoring at 254 nm. The following LC analysis method was used:

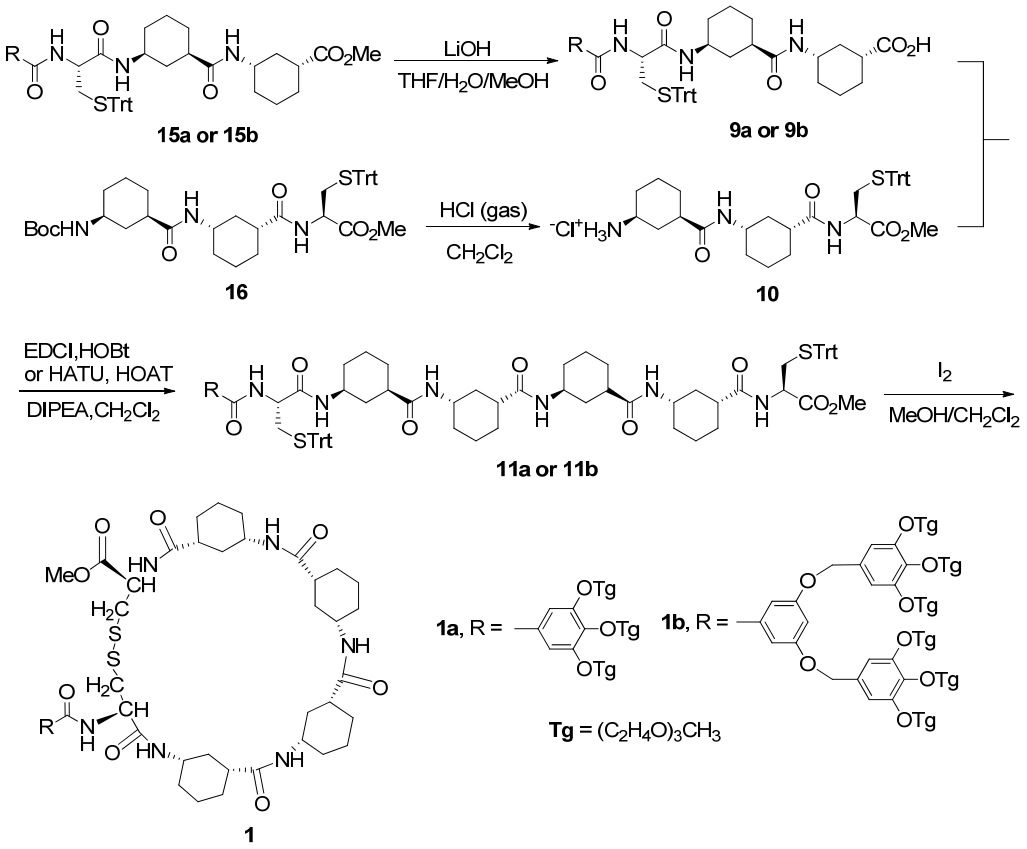
Solvent A: Water; Solvent B: methanol

Flow rate: 1.0 mL/min

Time (min)	B%
0	60
15	60
15	90
30	90

2. Synthesis of Cyclic Peptide-Dendron Hybrids 1a and 1b and Intermolecular Hydrogen-Bonding Model of the Cyclic Peptide of 1a and 1b:





Scheme S1. The synthesis of **1a** and **1b**.

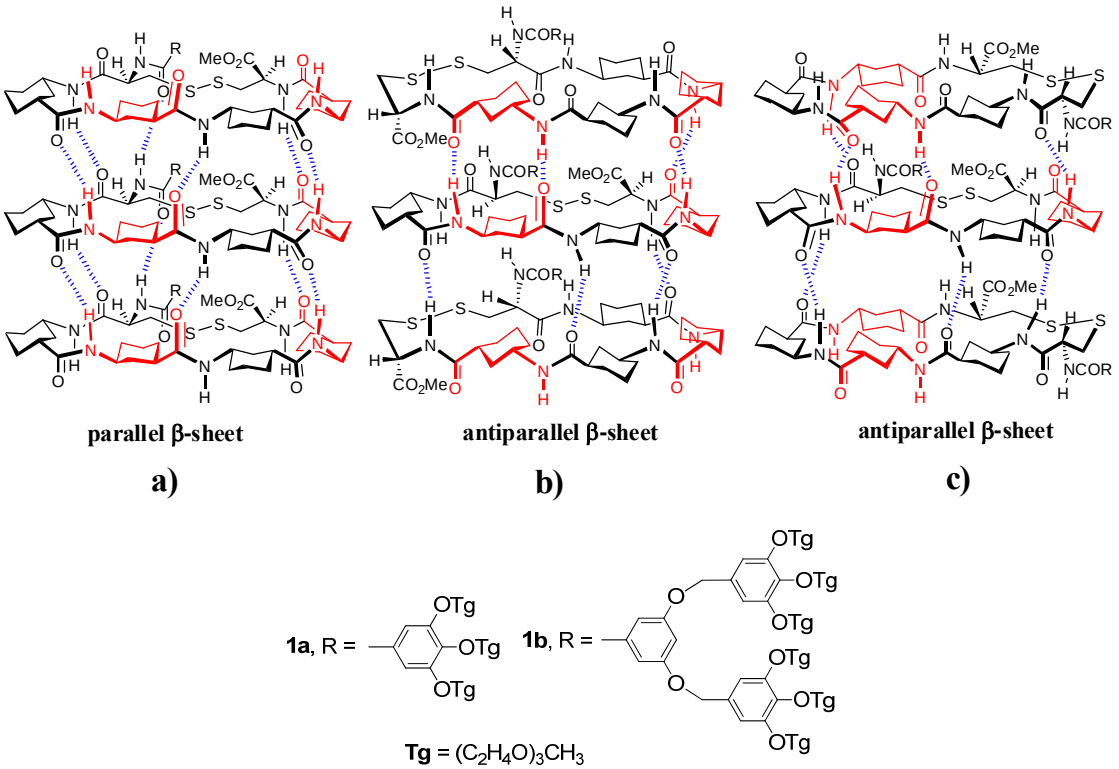
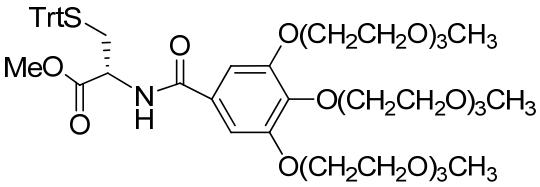


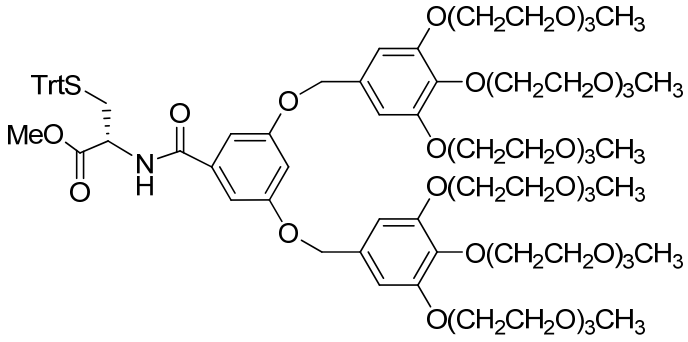
Figure S1. The intermolecular hydrogen-bonding model of the cyclic peptide of **1a** and **1b**. a) Parallel β-sheet; b), c) antiparallel β-sheet.

2.1 (*R*)-2-(3,4,5-Tri(2-(2-(2-methoxy-ethoxy)-ethoxy)-ethoxy)-benzoylamino)-3-tritylsulfanyl propionic acid methyl ester (3Tg-G_1-L-Cys(Trt)-OMe, 13a).



To a solution of benzoate **12**[2] (1.10 g, 1.77 mmol) in THF/H_2O/MeOH (3:1:1, 90mL) LiOH•H_2O (0.74 g, 17.7 mmol) was added at 0 °C. After stirred for 2 hours, the reaction mixture was concentrated and diluted by water. The aqueous solution was acidified by HCl (1 M) to pH 2 and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to give yellow oil (0.81 g, 76%). To a solution of the oil (0.81 g, 1.3 mmol) and *S*-Trityl-L-cysteine methyl ester hydrochloride **2**[3] (0.44 g, 1.0 mmol) in CH_2Cl_2 (20 mL), HOBt (0.18 g, 1.3 mmol), EDCI (0.25 g, 1.3 mmol) and DIPEA (0.17 g, 1.3 mmol) were successively added at 0 °C. After stirred at room temperature for 24 hours, the solution was diluted by CH_2Cl_2 (60 mL) and successively washed with $NaHCO_3$ (sat.), 1 M HCl and brine. The organic layers were dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel ($CHCl_3$/CH_3OH =100:1, v/v) to give **13a** (0.71 g, 77%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ: 2.74 (d, 2H, *J* = 5.3 Hz), 3.35 (s, 6H), 3.36 (s, 3H), 3.52-3.55 (m, 6H), 3.61-3.66 (m, 12H), 3.70-3.72 (m, 9H), 3.78-3.86 (m, 6H), 4.19-4.22 (m, 6H), 4.69-4.75 (m, 1H), 6.71 (d, 1H, *J* = 7.8 Hz), 7.04 (s, 2H), 7.18-7.27 (m, 9H), 7.36-7.38 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm), δ: 33.76, 51.56, 52.55, 58.85, 69.01, 69.54, 70.36, 70.51, 70.61, 71.75, 72.25, 107.27, 126.73, 127.84, 128.64, 129.32, 141.76, 144.11, 152.37, 166.18, 170.88; FT-IR (ν/cm^{-1}): 3277, 3058, 2877, 1744, 1661, 1582, 1538, 1494, 1446, 1339, 1245, 1112, 1033, 744, 701; ESI-HRMS, calculated for $C_{51}H_{73}N_2O_{15}S$ $[M+NH_4]^+$: 985.4732; found 985.4727; $[\alpha]_D^{20}$ = -14.1 (c = 0.5, CH_2Cl_2).

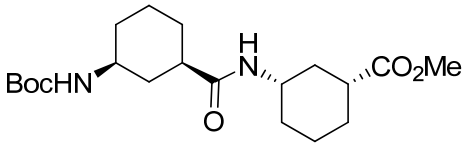
2.2 (*R*)-methyl 2-(3,5-bis(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzyloxy)benzamido)-3-tritylthiopropanoate (6Tg-G_2-L-Cys(Trt)-OMe 13b)



To a solution of methyl ester **14**[2] (5.638 g, 4.26 mmol) in THF/H_2O/MeOH (3:1:1, 100mL) LiOH•H_2O (1.789 g, 42.6 mmol) was added at 0 °C. After stirred for overnight, the reaction mixture was concentrated and diluted by water (50 ml). The aqueous solution was acidified by HCl (1 M) to pH 2 and extracted with CH_2Cl_2 (3 × 80 mL), and washed sequentially with water (2 × 50 mL) and brine (2 × 50 mL). The combined organic layers were dried over Na_2SO_4, and concentrated to afford yellow oil (5.904g). To a solution of the oil (5.904 g, 4.26 mmol) and *S*-Trityl-L-cysteine methyl ester hydrochloride **2** (2.132 g, 4.68 mmol) in CH_2Cl_2 (70 mL), HOBt (632 mg, 4.68 mmol), EDCI (980 mg,

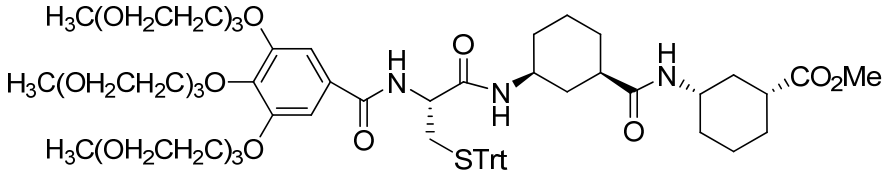
5.11 mmol) and DIPEA (2.20 g, 17.04 mmol) were successively added at 0 °C. After stirred at room temperature for 24 hours, the solution was diluted by CH_2Cl_2 (250 mL) and successively washed with $NaHCO_3$ (sat.), 1 M HCl and brine. The organic layers were dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 40:1, v/v) to give **13b** as yellow oil (4.907 g, 69%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ: 2.74 (d, 2H, J = 5.2 Hz), 3.35, 3.36 (2 × s, 18H), 3.52-3.55 (m, 12H), 3.61-3.66 (m, 24H), 3.70-3.72 (m, 15H), 3.77-3.85 (m, 12H), 4.13-4.18 (m, 12H), 4.72-4.78 (m, 1H), 4.94 (s, 4H), 6.67 (s, 4H), 6.74 (s, 1H), 6.99 (s, 1H), 7.00 (s, 1H), 7.15-7.26 (m, 9H), 7.35-7.38 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm), δ: 33.65, 51.36, 52.46, 58.72, 66.70, 68.66, 69.45, 70.14, 70.26, 70.41, 70.53, 71.64, 71.67, 72.05, 104.95, 106.06, 107.04, 126.63, 127.74, 129.18, 131.44, 135.63, 138.05, 143.98, 152.57, 159.66, 166.18, 170.60; FT-IR (ν/cm^{-1}): 3523，3342，2876，1745，1660，1593，1550，1439，1113, 851, 746, 703; ESI-HRMS, calculated for $C_{86}H_{123}NNa_2O_{29}S$ $[M+2Na]^{2+}$: 855.8839; found 855.8855; $[\alpha]_D^{20}$ = -6.5 (c = 0.5, CH_2Cl_2).

2.3 (1*R*,3*S*)-methyl 3-((1*R*,3*S*)-3-(tert-butoxycarbonylamino)cyclohexanecarboxamido)-cyclohexanecarboxylate (Boc-(γ-Ach)$_2$-CO$_2$Me 6)



To a solution of (1*R*,3*S*)-Boc-3-aminocyclohexanecarboxylic acid (Boc-γ-Ach-OH) **4** (200 mg, 0.83 mmol) and mehtyl (1*R*,3*S*)-3-aminocyclohexanecarboxylate (H-γ-Ach-OMe) **5** (189 mg, 0.83 mmol) in CH_2Cl_2 (20 mL), HOBt (114 mg, 0.85 mmol), EDCI (163 mg, 0.85 mmol) and DIPEA (212 mg, 1.6 mmol) were successsively added at 0 °C and stirred at room temperature for 24 hours. After removal of the solvent in vacuo, the residue was dissolved in $CHCl_3$ (60 mL) and washed with $NaHCO_3$ (sat.), 1 M HCl and brine. The organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3$/ CH_3OH = 100:1, v/v) to give **6** (269 mg, 93%) as a white solid. Mp: 214-216 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ: 1.08-1.12 (m, 2H), 1.20-1.37 (m, 6H), 1.43 (s, 9H), 1.75-1.95 (m, 6H), 2.05-2.20 (m, 3H), 2.39-2.47 (m, 1H), 3.44 (brs, 1H), 3.66 (s, 3H), 3.75-3.79 (m, 1H), 4.46 (d, 1H, NH, J = 7.2 Hz), 5.38 (d, 1H, NH, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm), δ: 23.85, 24.18, 28.05, 28.24, 28.48, 32.10, 32.37, 34.85, 36.03, 41.82, 44.18, 46.97, 48.91, 51.48, 78.89, 155.07, 174.00, 175.38. FT-IR (ν/cm^{-1}): 3445, 3343, 3301, 2935, 2858, 1732, 1680, 1637, 1533, 1438, 1365, 1311, 1276, 1175, 1140, 1052; ESI-HRMS, calculated for $C_{20}H_{34}N_2O_5$ $[M+H]^+$: 383.2540; found 383.2547; $[\alpha]_D^{20}$ = -61 (c = 0.5, MeOH).

2.4 3Tg-G$_1$-L-Cys(Trt)-(γ-Ach)$_2$-OMe (15a)

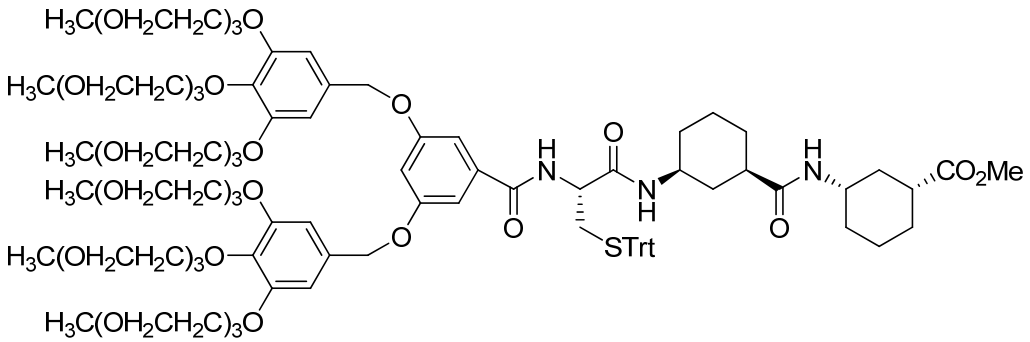


Boc-(γ-Ach)$_2$-OMe **6** (118 mg, 0.31 mmol) was dissolved in CH_2Cl_2 (10 mL), and then HCl gas was introduced over a period of 2 hour. The mixture was stirred for 4 hours at room temperature. The solution was concentrated under reduced pressure, and then added CH_2Cl_2 (2 mL) and removed the

solvents. After repetitive operation three times, the compound of **7** (110 mg, 0.31 mmol) was afforded as a white solid.

To a solution of methyl ester **13a** (300 mg, 0.31 mmol) in THF/H_2O/MeOH (2:1:1, 20 mL) LiOH•H_2O (126 mg, 3 mmol) was added at 0 °C. After stirred for 2 hours, the reaction mixture was concentrated and diluted by water. The aqueous solution was acidified by HCl (1 M) to pH 2 and extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were dried over $MgSO_4$, and concentrated to give **3a** as yellow oil (287 mg, 97%). To a solution of the yellow oil **3a** (287 mg, 0.31 mmol) and **7** (110 mg, 0.31 mmol) in CH_2Cl_2 (20 mL), HOBt (42 mg, 0.31 mmol), EDCI (60 mg, 0.31 mmol) and DIPEA (80 mg, 0.63 mmol) were successsively added at 0 °C, and the mixture was stirred at room temperature for 24 hours. After removal of the solvent under reduced pressure, the residue was dissolved in $CHCl_3$ (50 mL) and washed with $NaHCO_3$(sat.), 1 M HCl and brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3$/CH_3OH = 50:1, v/v) to give **15a** (241 mg, 66%) as a white semisolid. ^{1}H NMR ($CDCl_3$, 600 MHz, ppm), δ: 1.03-1.38 (m, 8H), 1.73-2.15 (m, 9H), 2.38-2.42 (m, 1H), 2.58-2.61 (m, 1H), 2.74-2.76 (m, 1H), 3.34 (s, 6H), 3.36 (s, 3H), 3.50-3.53 (m, 6H), 3.61-3.73 (m, 23H), 3.77-3.83 (m, 6H), 4.14-4.19 (m, 7H), 5.51 (d, 1H, J = 8.0 Hz), 6.09, 6.12 (2 × d, 1H, J = 8.3, 8.0 Hz), 6.87 (d, 1H, J = 7.6 Hz), 7.02 (s, 2H), 7.18-7.20 (m, 3H), 7.24-7.26 (m, 6H), 7.38-7.40 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm), δ: 23.87, 28.13, 28.49, 31.94, 32.23, 33.86, 34.91, 35.11, 41.88, 44.08, 47.17, 47.93, 51.55, 52.82, 58.84, 67.03, 69.07, 69.61, 70.37, 70.41, 70.44, 70.54, 70.57, 70.63, 71.83, 71.85, 72.33, 107.36, 126.76, 127.95, 128.62, 129.48, 141.76, 144.37, 152.41, 166.48, 169.20, 173.76, 175.38; FT-IR (ν/cm^{-1}): 3440, 3285, 3076, 2932, 2860, 1731, 1635, 1580, 1544, 1493, 1337, 1215, 1109, 1036, 743, 700; ESI-HRMS, calculated for $C_{65}H_{95}N_4O_{17}S$ $[M+NH_4]^+$: 1235.6413; found 1235.6427; $[\alpha]_D^{20}$ = -16 (c = 0.2, CH_2Cl_2).

2.5 6Tg-G$_2$- L-Cys(Trt)-(γ-Ach)$_2$-CO$_2$Me (15b)

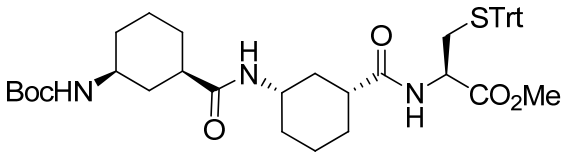


Boc-(γ-Ach)$_2$-CO$_2$Me **6** (115 mg, 0.3 mmol) was dissolved in CH_2Cl_2 (10 mL), and then HCl gas was introduced over a period of 2 hours. The mixture was stirred for 4 hours at room temperature. The solution was concentrated under reduced pressure, and then added CH_2Cl_2 (5mL) and removed the solvents, affored **7** as a white solid (95 mg, 0.3 mmol).

To a solution of methyl ester **13b** (500 mg, 0.3 mmol) in THF/H_2O/MeOH (3:1:1, 50mL) LiOH•H_2O (126 mg, 3 mmol) was added at 0 °C. After stirred for 5 hours, the reaction mixture was concentrated and diluted by water (10 mL). The aqueous solution was acidified by HCl (1 M) to pH 2 and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over Na_2SO_4, and concentrated to give **3b** as yellow oil (609 mg). To a solution of the yellow oil **3b** (490 mg, 0.3 mmol) and **7** (105 mg, 0.3 mmol) in CH_2Cl_2 (20 mL), HATU (136.8 mg, 0.36 mmol), HOAT (52.8 mg, 0.33

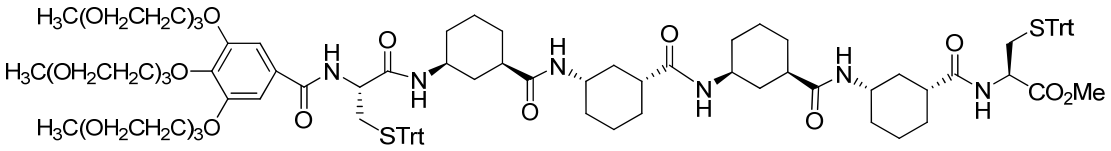
mmol) and DIPEA (154.8 mg, 1.2 mmol) were successsively added at 0 °C, and the mixture was stirred at room temperature for 34 hours, the solution was diluted by CH_2Cl_2 (50 mL) and successively washed with $NaHCO_3$ (sat.) (2 × 25 mL), 1 M HCl (2 × 25 mL), water (1 × 25 mL) and brine (1 × 25 mL). The organic layers were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 40:1, v/v) to give **15b** as a yellow semisolid (328 mg, 57%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm), δ: 0.98-1.36 (m, 8H), 1.72-2.14 (m, 9H), 2.36-2.39 (m, 1H), 2.57-2.60 (m, 1H), 2.67-2.71 (m, 1H), 3.31, 3.33 (2 × s, 18H), 3.48-3.51 (m, 12H), 3.59-3.63 (m, 28H), 3.68-3.70 (m, 13H), 3.75-3.81 (m, 12H), 4.10-4.13 (m, 12H), 4.22-4.24 (m, 1H), 4.88 (s, 4H), 5.62, 5.68 (2 × d, 1H, J = 7.8, 7.9 Hz), 6.31, 6.38 (2 × d, 1H, J = 4.7, 5.5 Hz), 6.62 (s, 4H), 6.68 (s, 1H), 6.84, 6.91 (2 × d, 1H, J = 7.1, 7.7 Hz), 6.94, 6.98 (2 × s, 2H), 7.12-7.23 (m, 9H), 7.34-7.38 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm), δ: 23.95, 28.21, 28.57, 31.92, 32.28, 34.18, 34.96, 35.53, 41.94, 44.13, 47.24, 47.96, 51.65, 52.67, 58.95, 67.02, 68.90, 69.70, 70.37, 70.48, 70.63, 71.76, 71.89, 72.30, 105.33, 106.27, 107.28, 126.83, 128.03, 129.51, 131.75, 135.89, 138.25, 144.37, 152.76, 159.90, 166.67, 169.05, 173.91, 175.46; FT-IR (ν/cm^{-1}): 3507, 3279, 3058, 2934, 2876, 1727, 1636, 1593, 1550, 1440, 1351, 1334, 1252, 1114, 851, 702; ESI-HRMS, calculated for $C_{100}H_{145}N_3Na_2O_{31}S$ $[M+2Na]^{2+}$: 980.9689; found 980.9684; $[\alpha]_D^{20}$ = -16 (c = 0.2, CH_2Cl_2).

2.6 Boc-(γ-Ach)$_2$-L-Cys(Trt)-CO$_2$Me (16)



To a solution of Boc-(γ-Ach)$_2$-OMe **6** (118 mg, 0.31 mmol) in THF/H_2O/MeOH (3:1:1, 20mL) LiOH•H_2O (126 mg, 3 mmol) was added. After stirred for 2 hours, the reaction mixture was concentrated and diluted by water. The aqueous solution was acidified by HCl (1 M) to pH 2 and extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, and concentrated to give a white solid **8** (105 mg, 93%). To a solution of **8** (105 mg, 0.28 mmol) and S-Trityl-L-cysteine methyl ester hydrochloride **2** (162 mg, 0.28 mmol) in CH_2Cl_2 (20 mL), HOBt (39 mg, 0.29 mmol), EDCI (55 mg, 0.29 mmol) and DIPEA (74 mg, 0.51 mmol) were successsively added at 0 °C, and the mixture was stirred at room temperature for 24 hours. After removal of the solvent under reduced pressure, the residue was dissolved in $CHCl_3$ (50 mL) and washed with $NaHCO_3$ (sat.), 1 M HCl and brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3$/CH_3OH = 100:1, v/v) to give **16** (117 mg, 57%) as a white solid. Mp: 182-184 °C; ^{1}H NMR ($CDCl_3$, 600 MHz, ppm), δ: 0.99-1.05 (m, 2H), 1.19-1.32 (m, 6H), 1.36 (s, 9H), 1.68-2.11 (m, 10H), 2.52 (dd, 1H, J = 4.5, 12.5 Hz), 2.61 (dd, 1H, J = 5.9, 12.5 Hz), 3.38 (brs, 1H), 3.62 (s, 3H), 3.74-3.76 (m, 1H), 4.40 (brs, 1H), 4.46-4.50 (m, 1H), 5.43 (d, 1H, J = 7.9 Hz), 5.76 (d, 1H, J = 7.8 Hz), 7.14-7.16 (m, 3H), 7.20-7.23 (m, 6H), 7.31-7.32 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm), δ: 23.89, 24.28, 28.39, 28.55, 28.65, 32.26, 32.64, 33.63, 35.21, 36.23, 43.65, 44.50, 47.04, 49.06, 50.86, 52.52, 66.94, 76.58, 79.17, 126.88, 127.98, 129.44, 144.23, 155.16, 170.85, 173.89, 174.42; FT-IR (ν/cm^{-1}): 3318, 3058, 2934, 2859, 1744, 1679, 1649, 1529, 1445, 1390, 1277, 1172, 1031, 743, 700; ESI-HRMS, calculated for $C_{42}H_{53}N_3O_6S$ $[M+H]^+$:728.3728; found 728.3732; $[\alpha]_D^{20}$ = -11 (c = 0.2, CH_2Cl_2).

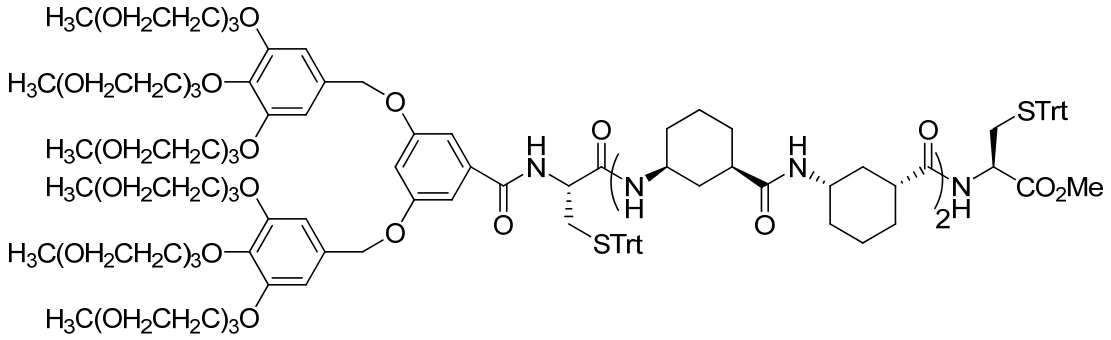
2.7 Linear hexapeptide 3Tg-G$_1$- L-Cys(Trt)-(γ-Ach)$_4$-L-Cys-CO$_2$Me (11a)



To a solution of **16** (76.4 mg, 0.105 mmol) in CH_2Cl_2 (5 mL), and then HCl gas was introduced over a period of 2 hours. The mixture was stirred for 4 hours at room temperature. The solution was concentrated under reduced pressure, and then added CH_2Cl_2 (2 mL) and removed the solvents, afforded **10** as yellow solid and used without further purification.

To a solution of **15a** (121.8 mg, 0.1 mmol) in THF/H_2O/MeOH (3:1:1, 10 mL) LiOH•H_2O (42 mg, 1.0 mmol) was added at 0 °C. After stirred for 4 hours, the reaction mixture was diluted by water (10 mL). The aqueous solution was acidified by HCl (1 M) to pH 2 and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated to give **9a** as yellow oil. To a solution of the yellow oil **9a** (0.1 mmol) and **10** (0.105 mmol) in CH_2Cl_2 (10 mL), HOBt (14.8 mg, 0.11 mmol), EDCI (23 mg, 0.12 mmol) and DIPEA (28.4 mg, 0.22 mmol) were successively added at 0 °C, and then the mixture was stirred at room temperature for 48 hours. After that, the reaction mixture was diluted by CH_2Cl_2 (20 mL), and the solution was washed with $NaHCO_3$ (sat.), 1 M HCl and brine. The organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3$/CH_3OH = 40:1, v/v) to give **11a** (97 mg, 54%) as a white solid. Mp: decomposed at 265 °C; ^{1}H NMR (DMSO-d_6, 600 MHz, ppm), δ: 1.01-1.19 (m, 16H), 1.49-1.77 (m, 16H), 2.07-2.09 (m, 3H), 2.22-2.26 (m, 1H), 2.33-2.53 (m, 4H), 3.20, 3.21 (2 × s, 9H), 3.38-3.40 (m, 6H), 3.47-3.66 (m, 27H), 3.74-3.75 (m, 4H), 4.05-4.14 (m, 7H), 4.48-4.49 (m, 1H), 7.18-7.33 (m, 32H), 7.59-7.62 (m, 3H), 7.81, 7.85 (2 × d, 1H, J = 7.4, 7.7 Hz), 8.20 (d, 1H, J = 7.7 Hz), 8.48 (d, 1H, J = 5.8 Hz); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm), δ: 23.96, 28.30, 31.80, 32.84, 34.19, 35.43, 42.54, 43.05, 46.77, 47.38, 51.10, 51.92, 52.39, 57.96, 68.49, 68.92, 69.55, 69.79, 69.92, 71.22, 71.82, 77.27, 106.91, 126.73, 127.97, 128.99, 144.06, 144.27, 151.69, 165.15, 168.67, 170.64, 173.23, 174.28; FT-IR (ν/cm^{-1}): 3427, 3291, 3059, 2932, 2859, 1746, 1638, 1544, 1489, 1445, 1335, 1218, 1109, 743, 700; ESI-HRMS, calculated for $C_{101}H_{133}N_6O_{20}S_2$ $[M+H]^+$: 1813.9016; found 1813.9032; $[\alpha]_D^{20}$ = -24 (c = 0.2, CH_2Cl_2).

2.8 Linear hexapeptide 6Tg-G_2- L-Cys(Trt)-(γ-Ach)$_4$-L-Cys-CO_2Me (11b)

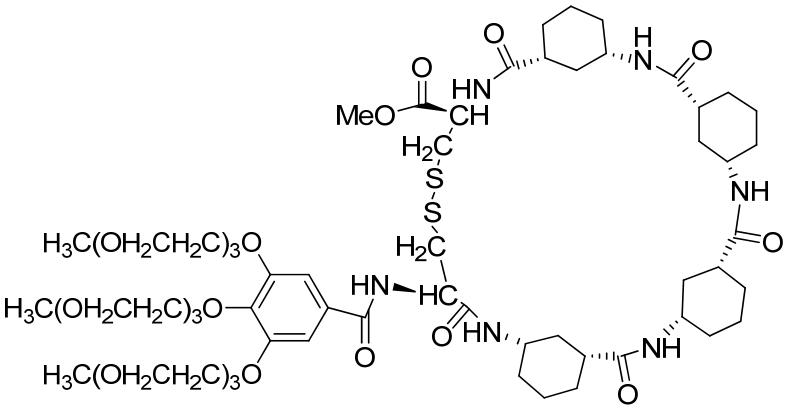


To a solution of **16** (96 mg, 0.132 mmol) in CH_2Cl_2 (10mL) HCl gas was introduced over a period of 2 hours. The mixture was stirred for 4 hours at room temperature. The solution was concentrated under reduced pressure, and then added CH_2Cl_2 (2 mL) and removed the solvents, afforded **10** as yellow solid and used without further purification.

To a solution of **15b** (253 mg, 0.132 mmol) in THF/H_2O/MeOH (3:1:1, 15 mL) LiOH•H_2O (55.4

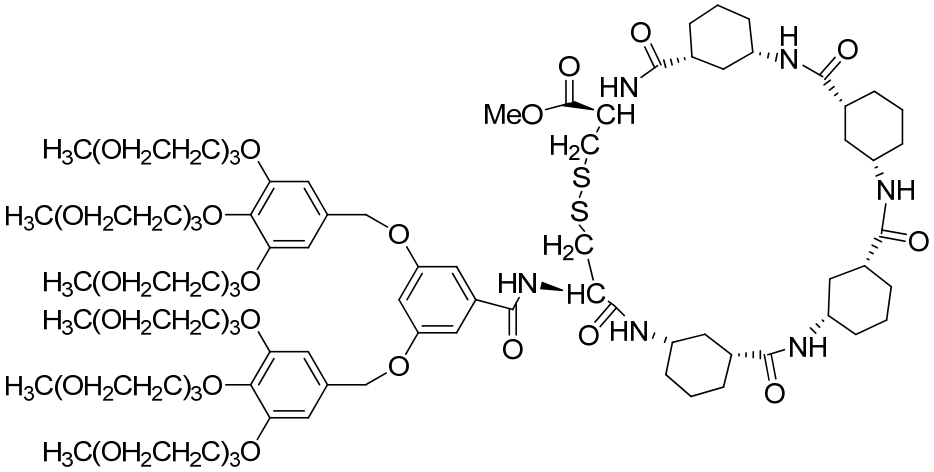
mg, 1.2 mmol) was added at 0 °C. After stirred for 4 hours, the reaction mixture was diluted by water. The aqueous solution was acidified by HCl (1 M) to pH 2 and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated to give **9b** as yellow oil. To a solution of the yellow oil (0.132 mmol) and **10** (0.132 mmol) in CH_2Cl_2 (15 mL), HATU (60.2 mg, 0.158 mmol), HOAT (23.2 mg, 0.145 mmol) and DIPEA (68.1 mg, 0.53 mmol) were successively added at 0 °C, and then the mixture was stirred for 48 hours at room temperature. The solution was diluted by $CHCl_3$ (70 mL) and successively washed with $NaHCO_3$ (sat.) (2 × 25 mL), 1 M HCl (2 × 25 mL) and brine (1 × 25 mL). The organic layers were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 60:1, v/v) to give **11b** (180 mg, 54%) as a white solid. Mp: decomposed at 202 °C; ^{1}H NMR (DMSO-d_6, 600 MHz, ppm), δ: 1.04-1.27 (m, 16H), 1.58-1.80 (m, 16H), 2.12 (brs, 3H), 2.24-2.29 (m, 1H), 2.35-2.47 (m, 3H), 2.54-2.55 (m, 1H), 3.22, 3.24 (2 × s, 18H), 3.40-3.44 (m, 13H), 3.51-3.53 (m, 30H), 3.58-3.60 (m, 12H), 3.67-3.74 (m, 12H), 4.02-4.03 (m, 4H), 4.10-4.11 (m, 9H), 4.45-4.49 (m, 1H), 5.02 (s, 4H), 6.79 (s, 4H), 6.86 (s, 1H), 7.17 (s, 2H), 7.23-7.36 (m, 30H), 7.62-7.66 (m, 3H), 7.85 (d, 1H, J = 8.5 Hz), 8.24 (d, 1H, J = 8.0 Hz), 8.48 (d, 1H, J = 8.1 Hz); ^{13}C NMR (DMSO-d_6, 150 MHz, ppm), δ: 24.00, 24.52, 28.47, 28.83, 32.32, 33.36, 35.96, 43.06, 43.59, 47.18, 47.30, 47.88, 51.62, 52.47, 58.49, 66.35, 66.74, 68.91, 69.49, 70.09, 70.22, 70.33, 70.45, 71.75, 72.28, 107.13, 107.53, 127.19, 127.29, 128.49, 128.55, 129.52, 129.55, 132.47, 137.77, 144.59, 144.78, 152.66, 159.85, 171.19, 173.79, 174.85; FT-IR (ν/cm^{-1}): 3287, 3055, 2931, 2862, 1745, 1637, 1592, 1545, 1505, 1442, 1332, 1111, 851, 745, 702; ESI-HRMS, calculated for $C_{136}H_{186}KN_6O_{34}S_2$ $[M+K]^+$: 2550.2; found 2550.3; $[\alpha]_D^{20}$ = -17 (c = 0.2, CH_2Cl_2).

2.9 Cyclic peptide 3Tg-G$_1$-Cyclo-(L-Cys-(γ-Ach)$_4$-L-Cys) (1a)



To a solution of I_2 (101 mg, 0.4 mmol) in CH_3OH/CH_2Cl_2 (10:90, 120 mL), **11a** (30 mg, 0.017 mmol) in CH_3OH/CH_2Cl_2 (10:90, 30 mL) was added by dropwise at -10 °C, and the resulting mixture was stirred at -10 °C for 20 minutes. After 2 M $Na_2S_2O_3$ (100 mL) was added, the reaction mixture was concentrated. The solution was extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel ($CHCl_3/CH_3OH$ = 30:1, v/v) to give cyclic peptide **1a** (16 mg, 73%) as a white solid. Mp: decomposed at 278 °C; FT-IR(ν/cm^{-1}): 3443, 3296, 2932, 2859, 1747, 1634, 1582, 1546, 1496, 1452, 1397, 1334, 1218, 1112; ESI-HRMS, calculated for $C_{63}H_{102}N_6Na_2O_{20}S_2$ $[M+2Na]^{2+}$: 686.3913; found 686.3187; MS (MALDI-TOF), calculated for $C_{63}H_{102}N_6NaO_{20}S_2$ $[M+Na]^+$: 1349.6; found 1349.8; $[\alpha]_D^{20}$ = -12 (c = 0.2, $CHCl_3$: MeOH, 3:1).

2.10 Cyclic peptide 6Tg-G_2-Cyclo-(L-Cys-(γ-Ach)$_4$-L-Cys) (1b)



To a solution of I_2 (594 mg, 2.34 mmol) in CH_3OH/CH_2Cl_2 (10:90, 400 mL), **11b** (251.3 mg, 0.1 mmol) in CH_3OH/CH_2Cl_2 (10:90, 100 mL) was added by dropwise at -10 °C, and the resulting mixture was stirred at -10 °C for 4 hours. After 2 M $Na_2S_2O_3$ (100 mL) was added, the reaction mixture was concentrated to remove organic solvents. Then, the solution was extracted with $CHCl_3$ (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel ($CHCl_3/CH_3OH$ = 40:1, v/v) to give cyclic peptide **1b** (99 mg, 49%) as a white solid. Mp: decomposed at 271 °C; ^{1}H NMR (DMSO-d_6, 600 MHz, ppm), δ: 1.23-1.35 (m, 16H), 1.64-1.91 (m, 16H), 2.07-2.37 (m, 4H), 2.99-3.16 (m, 4H), 3.20, 3.22 (2 × s, 18H), 3.38-3.42 (m, 12H), 3.48-3.58 (m, 27H), 3.65-3.72 (m, 15H), 4.00 (brs, 4H), 4.09 (brs, 8H), 4.56-4.66 (m, 2H), 5.00 (s, 4H), 6.77 (s, 4H), 6.83 (s, 1H), 7.16 (s, 2H), 7.42-7.43 (m, 2H, NH), 7.65 (brs, 1H, NH), 8.10 (d, 1H, NH, J = 6.5 Hz), 8.32 (d, 1H, NH, J = 7.7 Hz), 8.56 (d, 1H, NH, J = 8.0 Hz); ^{13}C NMR (DMSO-d_6, 150 MHz, ppm), δ: 23.26, 24.08, 24.41, 28.16, 28.29, 30.88, 31.39, 31.74, 32.05, 35.59, 35.72, 36.13, 43.15, 44.23, 44.80, 47.47, 47.72, 48.34, 51.50, 52.53, 53.05, 58.49, 68.91, 69.49, 70.09, 70.21, 70.32, 70.45, 71.75, 72.28, 105.40, 107.06, 107.54, 132.47, 136.33, 137.76, 152.65, 159.83, 166.00, 168.96, 171.33, 173.76, 173.94, 174.37, 174.98; FT-IR(ν/cm^{-1}): 3436, 3307, 3056, 2931, 2863, 1746, 1635, 1593, 1535, 1505, 1439, 1347, 1332, 1296, 1249, 1112, 941, 846; ESI-HRMS, calculated for $C_{98}H_{156}KN_6O_{34}S_2$ $[M+K]^+$: 2064.0; found 2063.9; MS (MALDI-TOF), calculated for $C_{98}H_{156}NaN_6O_{34}S_2$ $[M+Na]^+$: 2048.0; found 2048.5; $[\alpha]_D^{20}$ = -16 (c = 0.2, CH_2Cl_2).

3. Preparation of Peptide Single Crystals for SEM:

25 mg of **1a** was dissolved in $CHCl_3$ (3 mL) and equilibrated by vaporphase diffusion against CH_3OH (5 mL). This resulted in spontaneous crystallization after 7 days.

4. Preparation of Cyclic Peptide Nanotubes and Nanofibers for TEM Analysis:

Method A: The 3 mg of **1a** or **1b** was dissolved in $CHCl_3$ (0.5 mL) and equilibrated via vapor-phase

diffusion against 5 mL of hexane, resulting in a gel phase after 2~4 days. The gels were dispersed in *n*-hexane, water, and water-ethanol (1:1, v/v), respectively, by sonication.

Method B: 1b was dissolved in acetonitrile, water and their mixture (0.1 mg/mL), respectively, and then heated in an oil bath at 100 °C to yield a transparent solution. The resulting solution of **1b** was cooled to room temperature for overnight.

5. FT-IR, SEM and AFM Results:

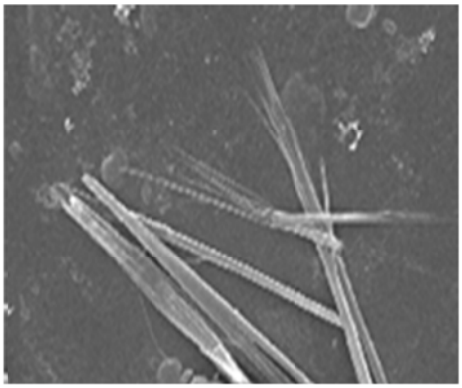


Figure S2 SEM image of the assemblies of **1a**, indicates that each assembly is organized bundle of needle-shaped microcrystals with about 500 nm in diameter and over several microns in length.

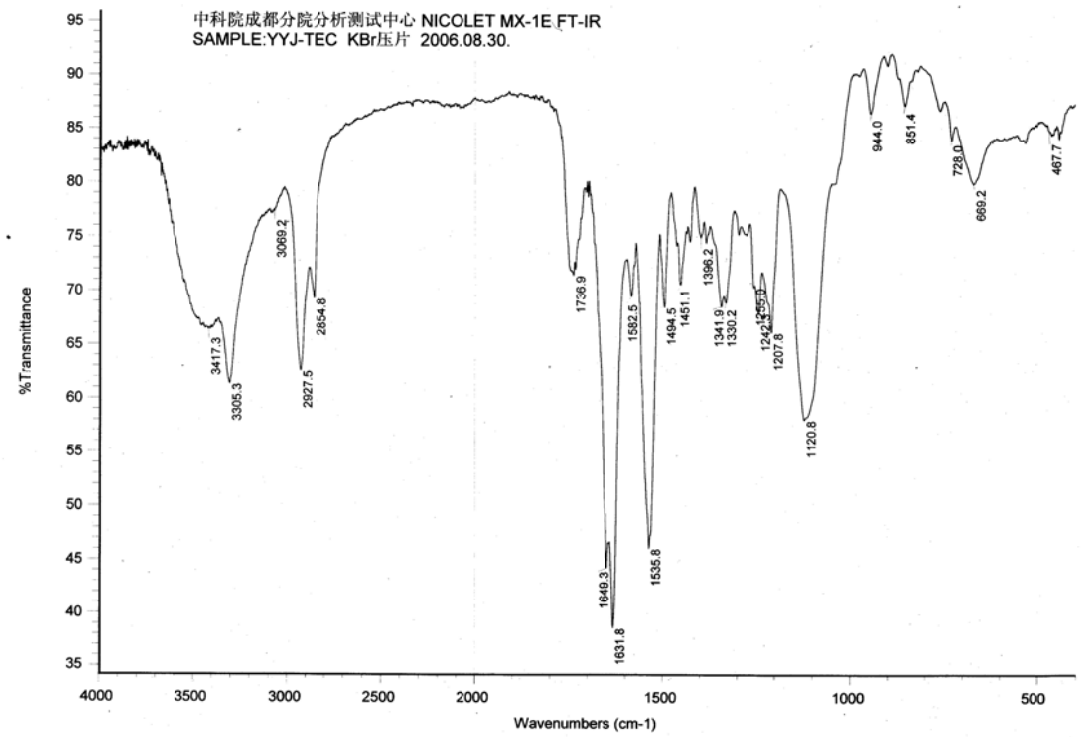


Figure S3. FT-IR Spectrum of 3Tg-G_1-Cyclo-(L-Cys-(γ-Ach)$_4$-L-Cys) (**1a**) in the solid state on KBr pellets.

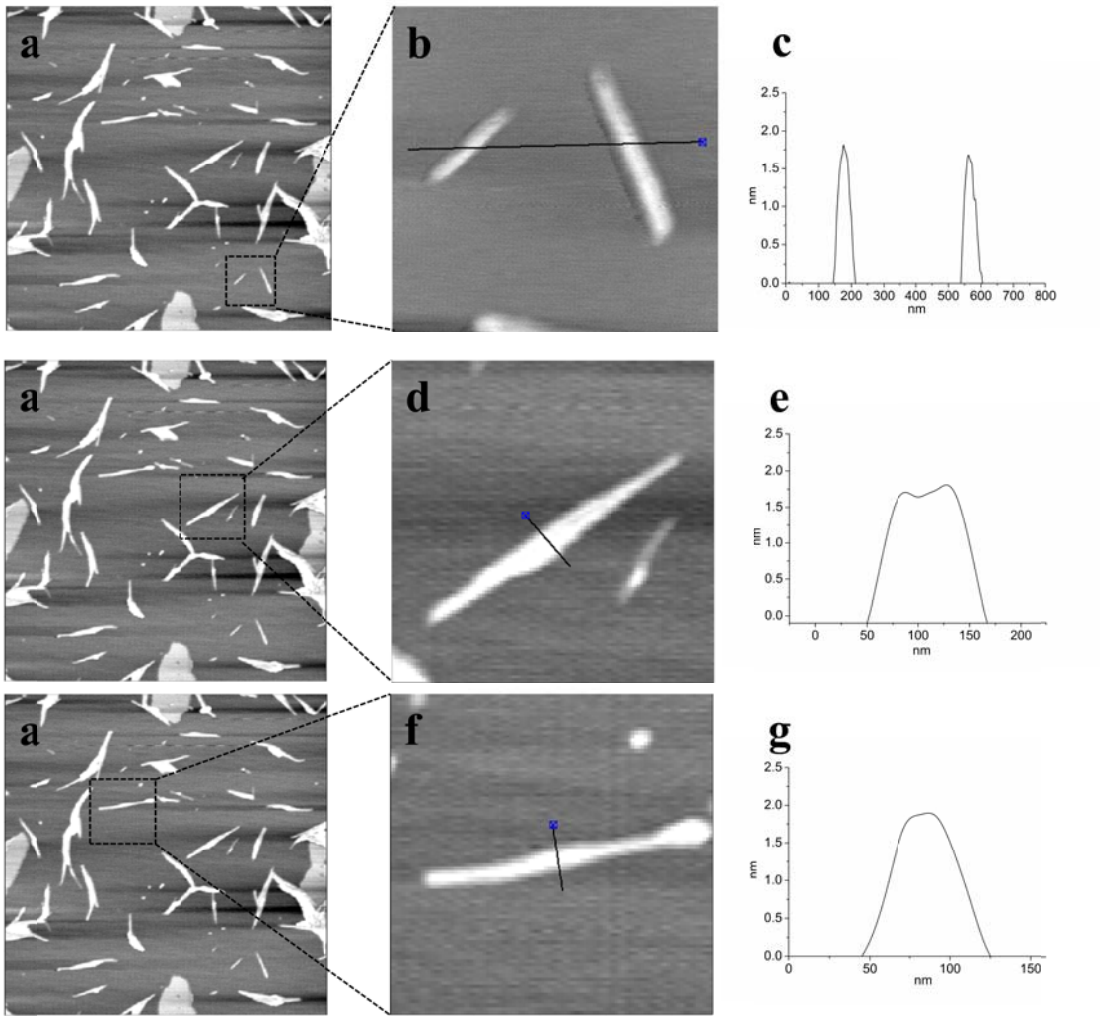


Figure S4 (a) AFM image of the gel of **1a** dispersed in water-ethanol (1:1, v/v); (b,d,f) an enlarged area of the AFM image is shown; (c,e,g) Height profile measured along the line shown respectively in (b,d,f).

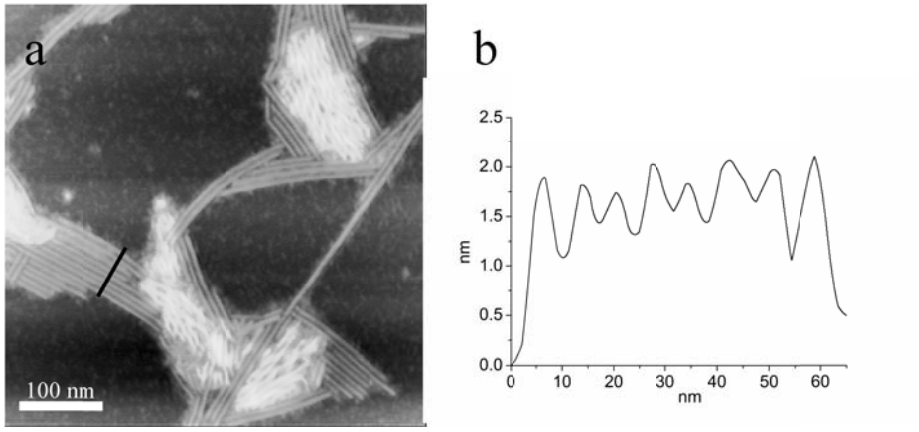


Figure S5 (a) AFM image of the gel of **1b** dispersed in water; (b) Height profile measured along the line shown in (a).

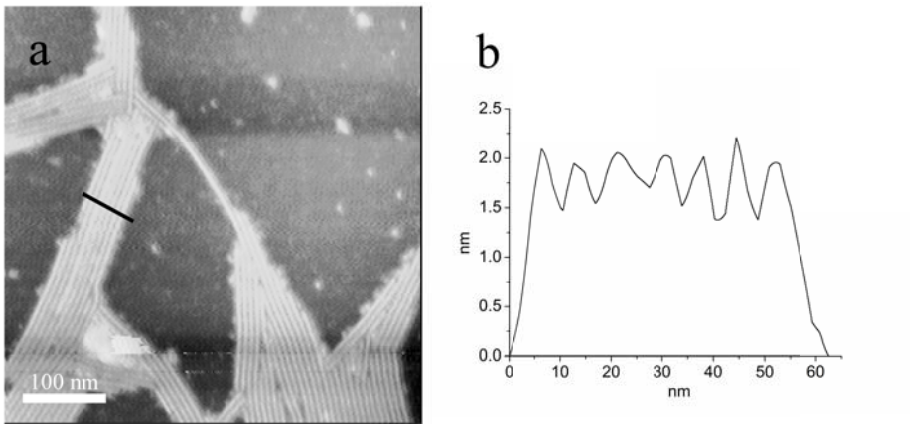


Figure S6 (a) AFM image of the gel of **1b** dispersed in water-ethanol (1:1, v/v); (b) Height profile measured along the line shown in (a).

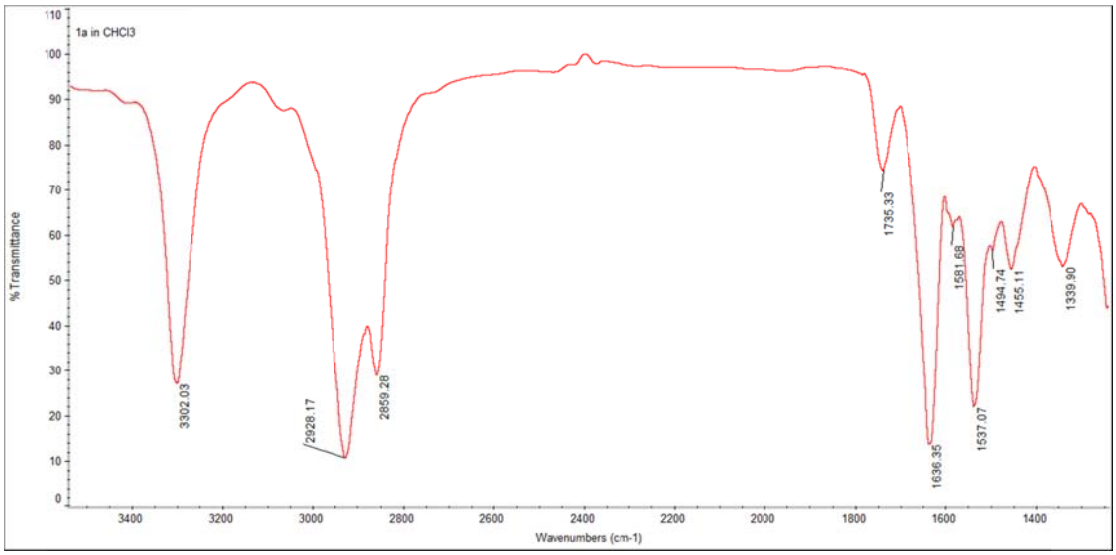


Figure S7. FT-IR spectrum of **1a** in $CHCl_3$.

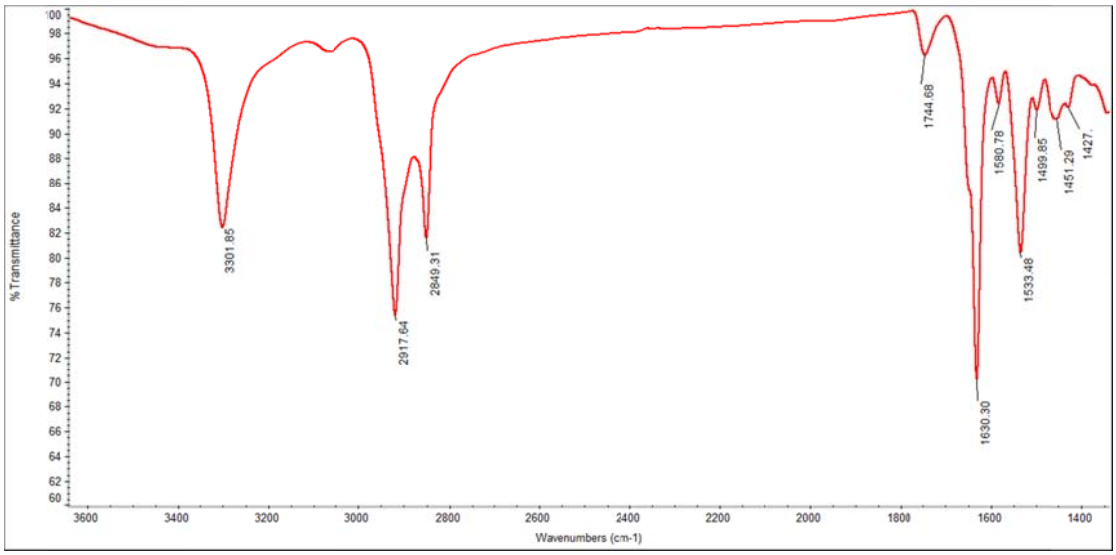


Figure S8. FT-IR spectrum of **1a** in the gel state on KBr pellets .

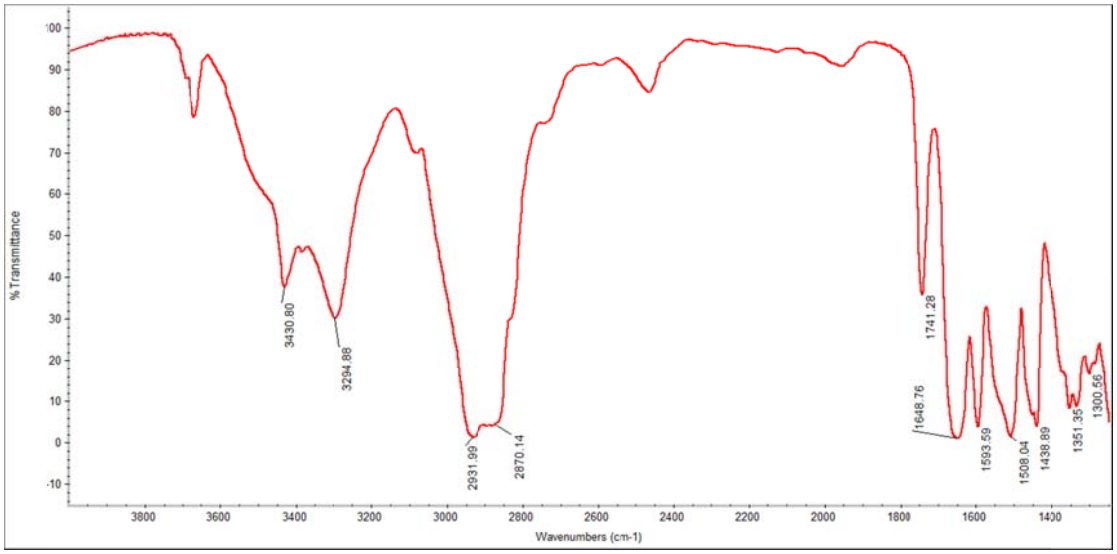


Figure S9. FT-IR spectrum of 6Tg-G_2-Cyclo-(L-Cys-(γ-Ach)$_4$-L-Cys) (**1b**) in $CHCl_3$.

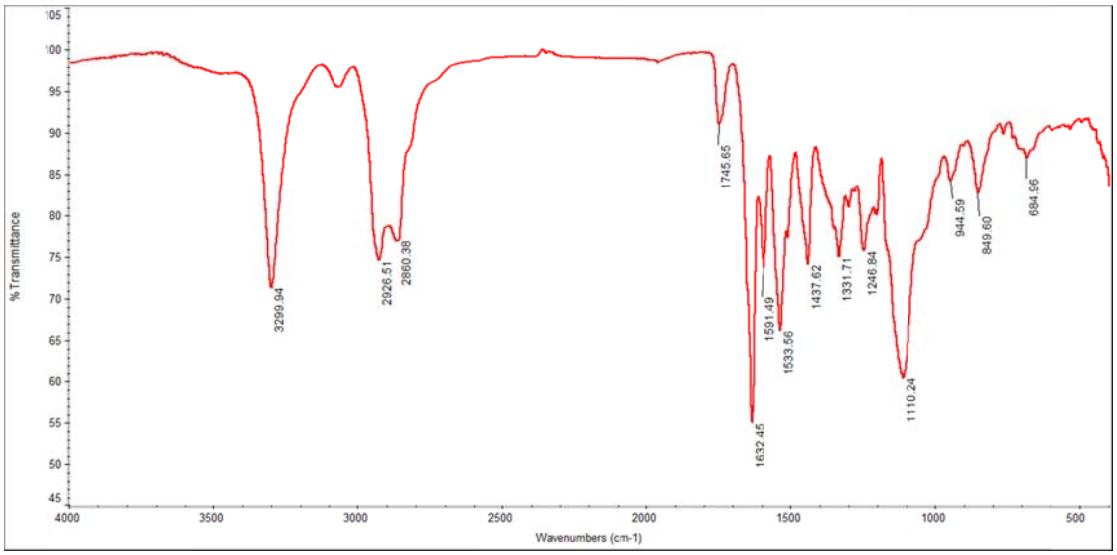


Figure S10. FT-IR spectrum of **1b** in the gel state on KBr pellets .

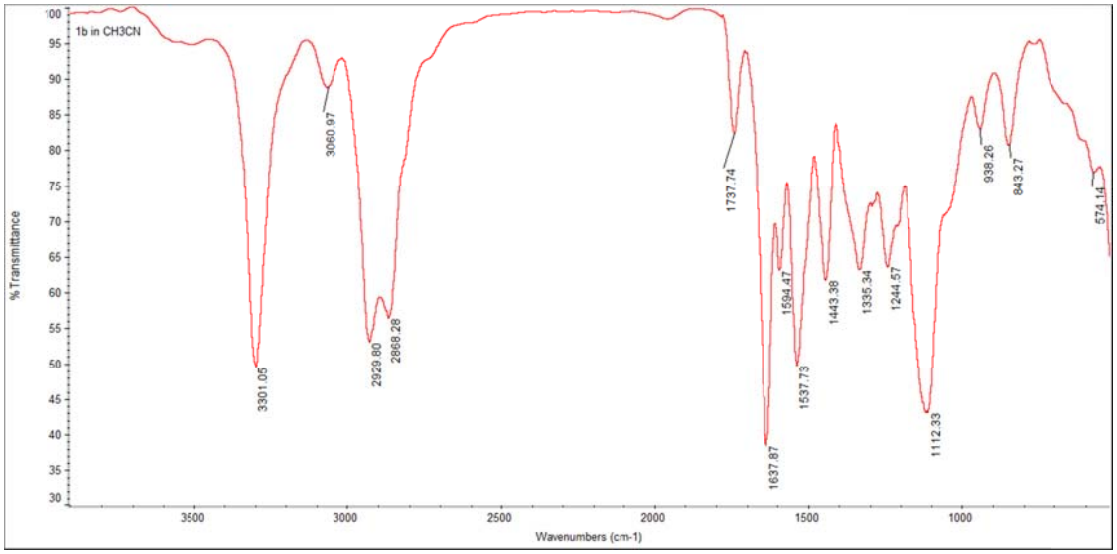


Figure S11. FT-IR spectrum of **1b** in CH_3CN.

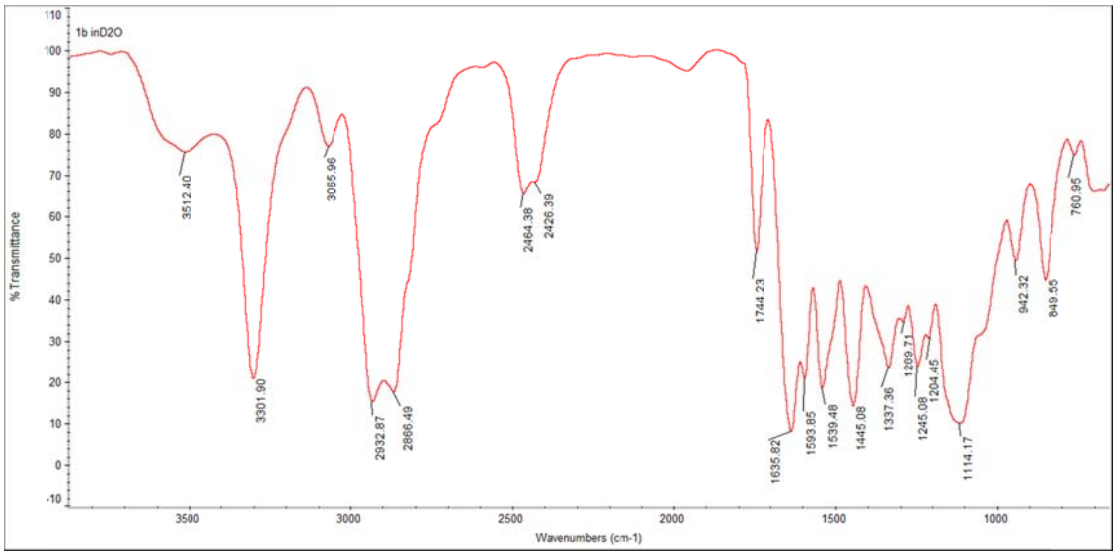


Figure S12. FT-IR spectrum of **1b** in D_2O.

6. NMR Researches:

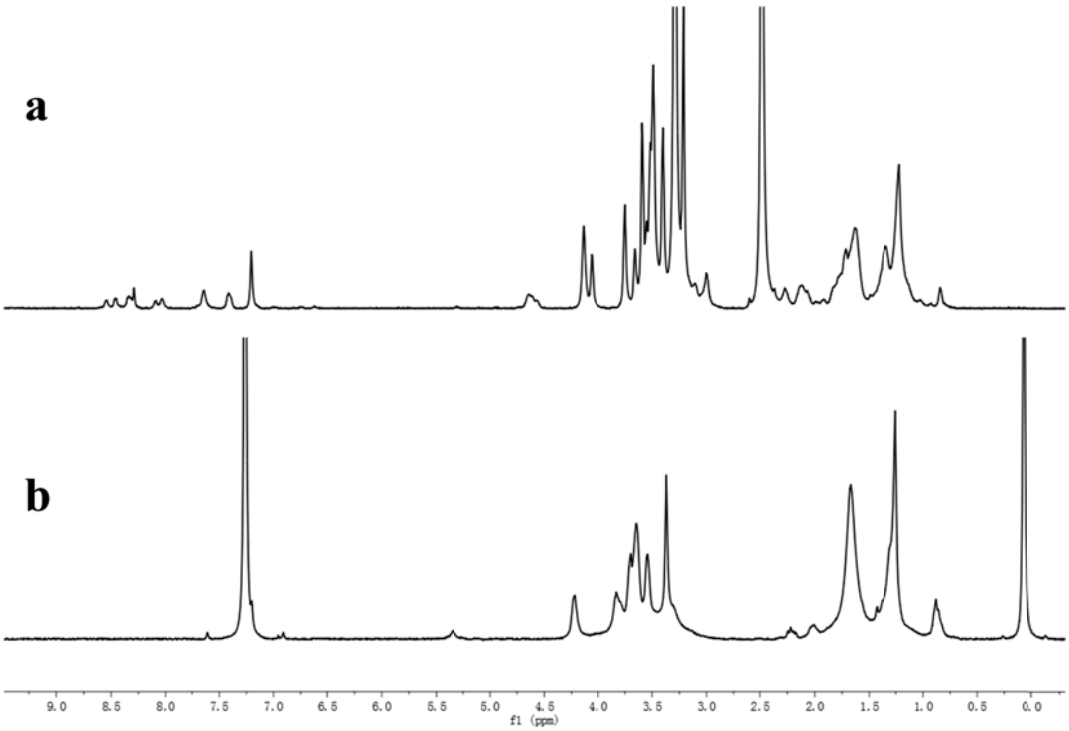


Figure S13. ^{1}H NMR spectrum of **1a** (**a**) in DMSO-d_6, (b) in $CDCl_3$; showing peaks broaden significantly with poor-resolved signals in $CDCl_3$

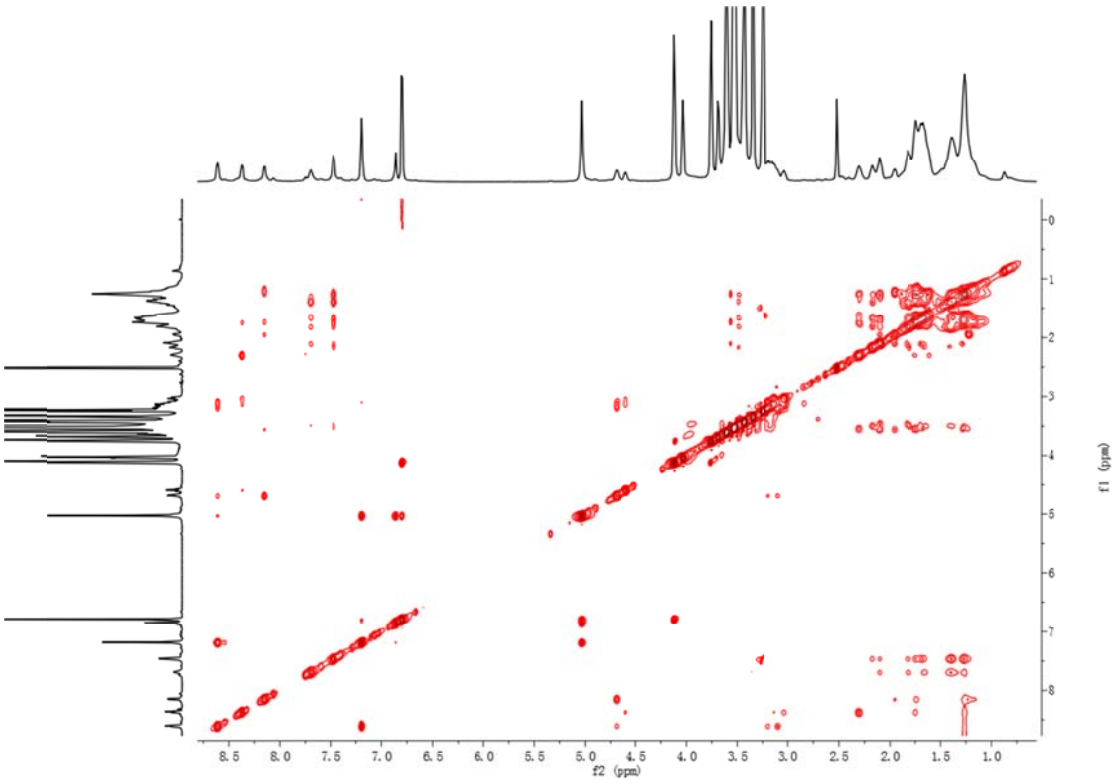


Figure 14. 2D NOESY spectrum of **1b** in DMSO-d_6 (20 mM).

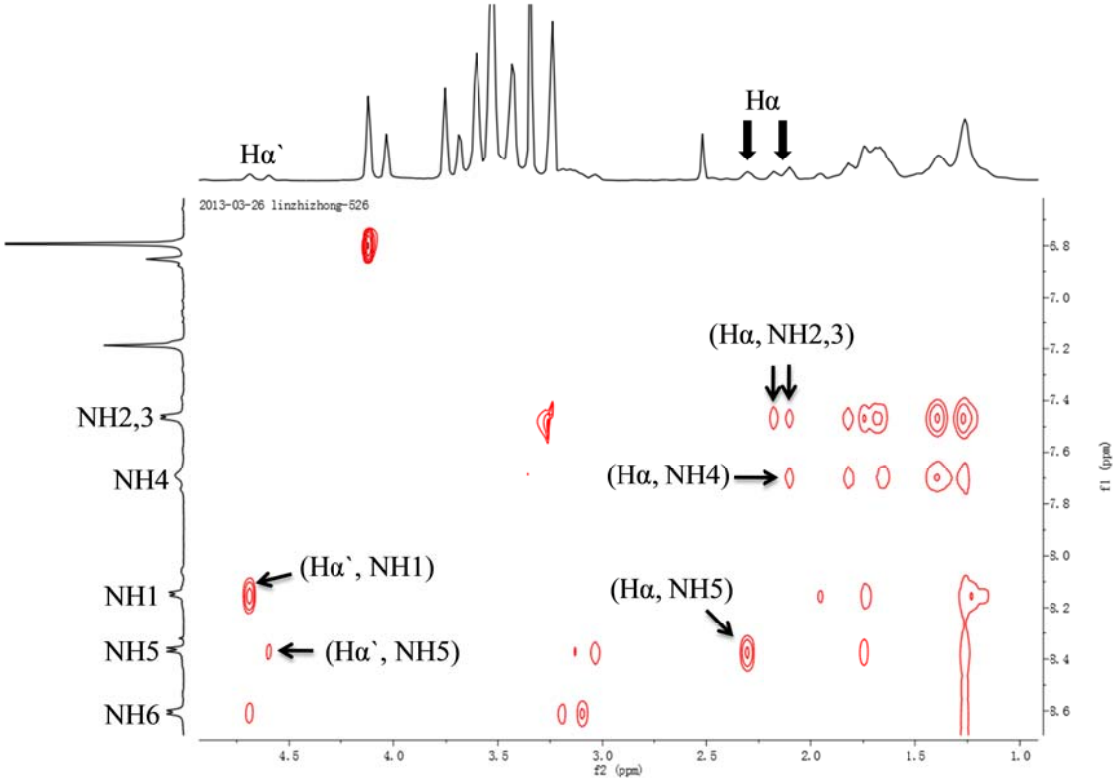


Figure S15. Expand 2D NOESY spectrum of **1b** in DMSO-d_6. Hα is the proton of γ-Achs, while Hα` is the proton of cysteine residues.

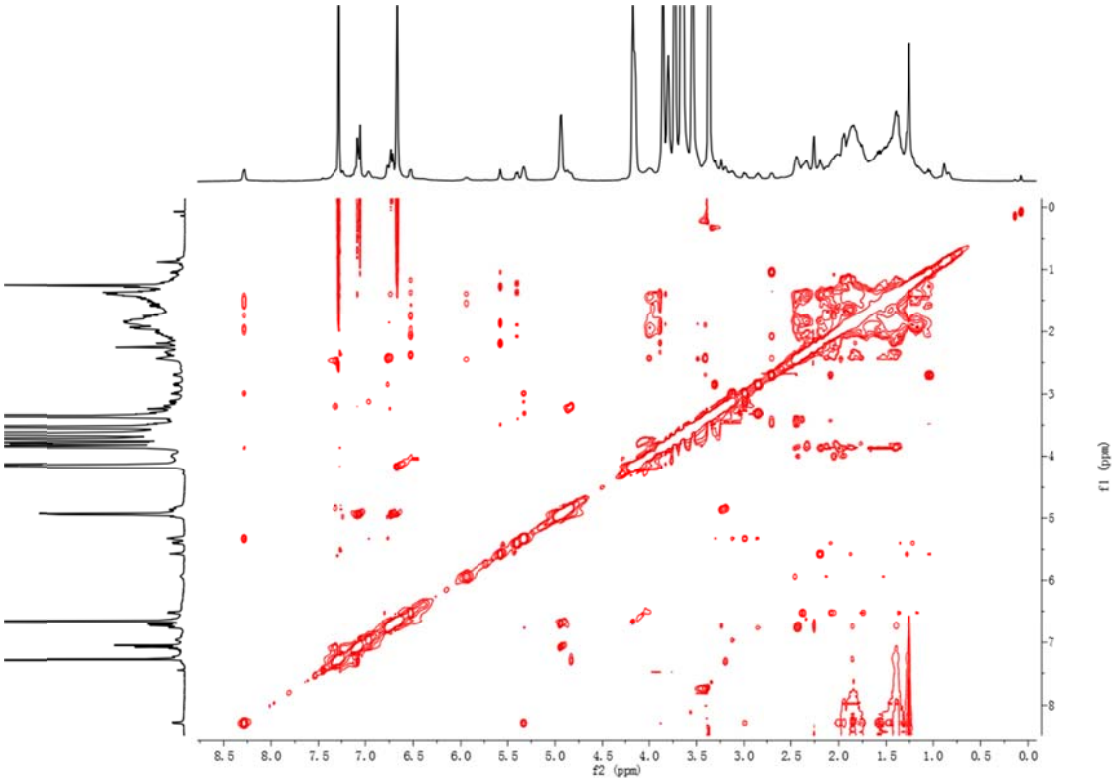


Figure S16. 2D NOESY spectrum of **1b** in $CDCl_3$ (20 mM).

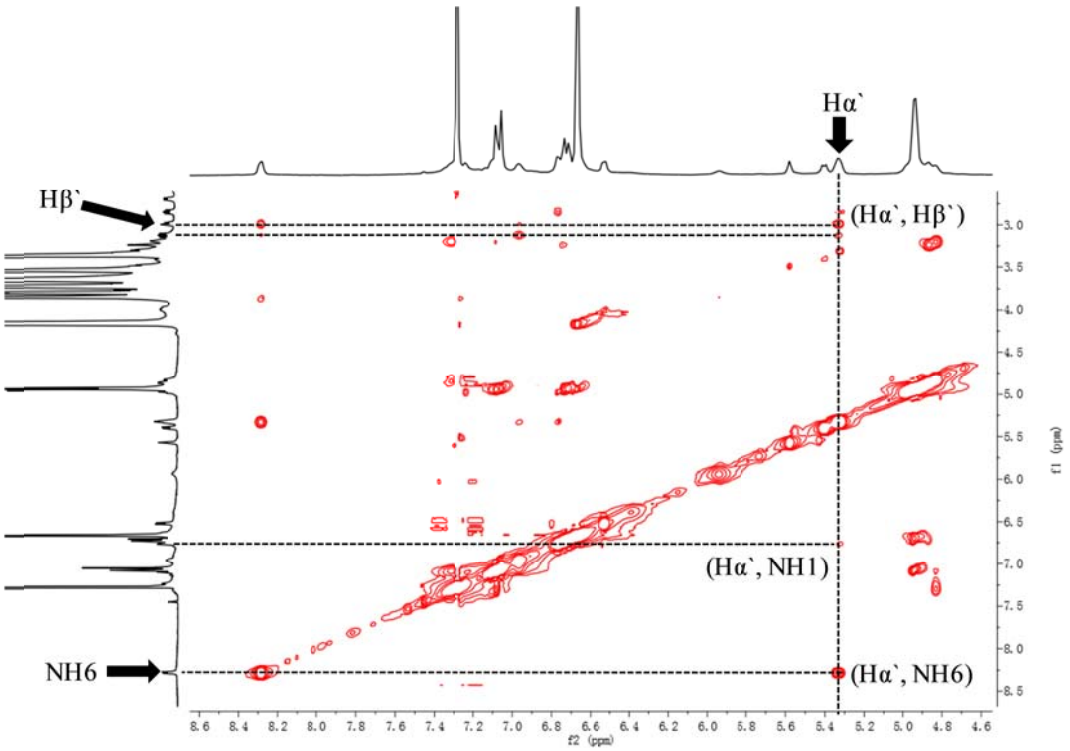


Figure S17. Expand 2D NOESY spectrum of **1b** in $CDCl_3$. Hα` and Hβ` are the proton of cysteine residues.

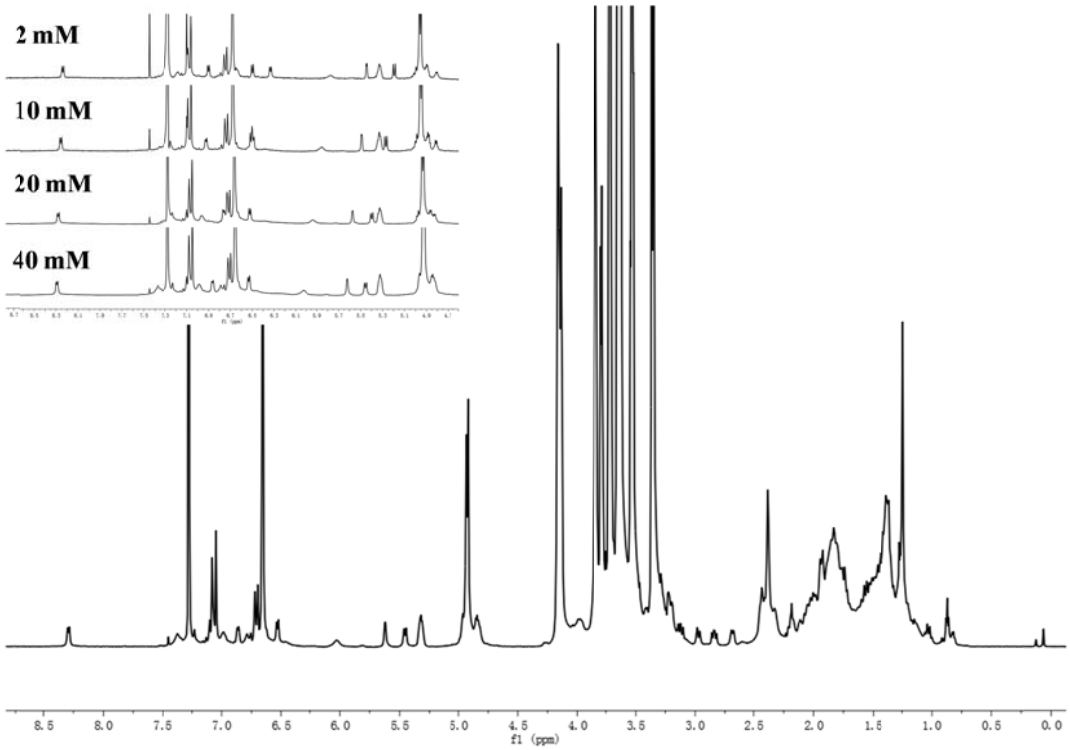


Figure S18. ^{1}H NMR spectrum of **1b** in $CDCl_3$ (40 mM). Inset is the selected region of (4.7-8.7 ppm) of the spectrum of **1b** in $CDCl_3$ at 2, 10, 20, and 40 mM concentration, showing the downfield shifted of the N-H signals.

7. MALDI-TOF and HPLC Results:

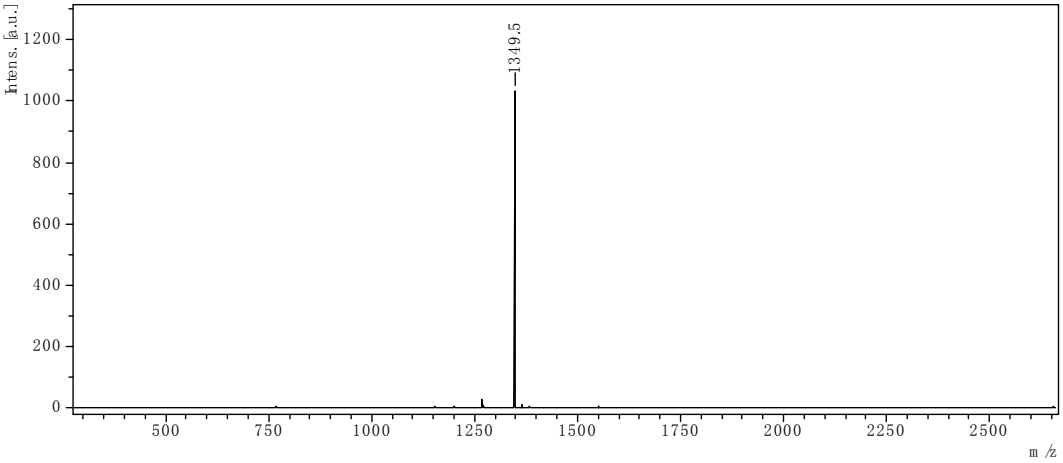


Figure S19. MALDI–TOF mass spectra of a gel sample prepared from **1a**.

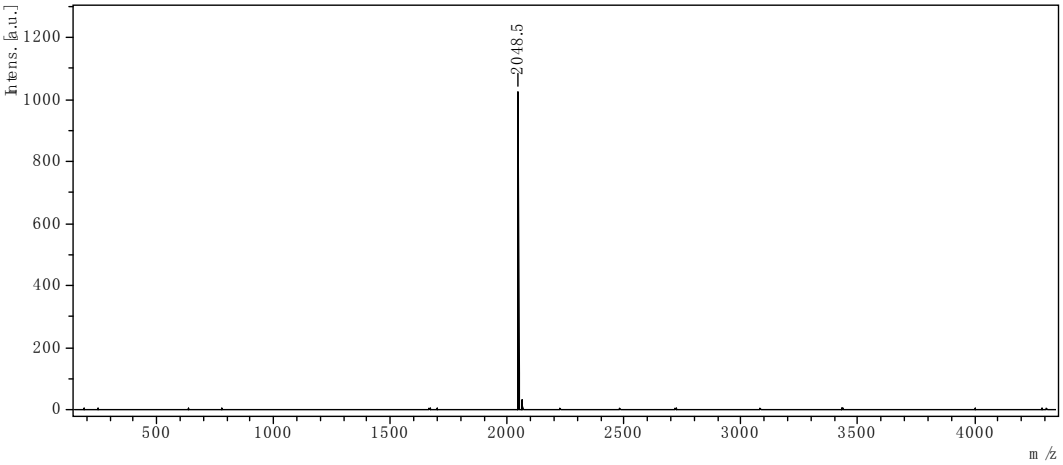
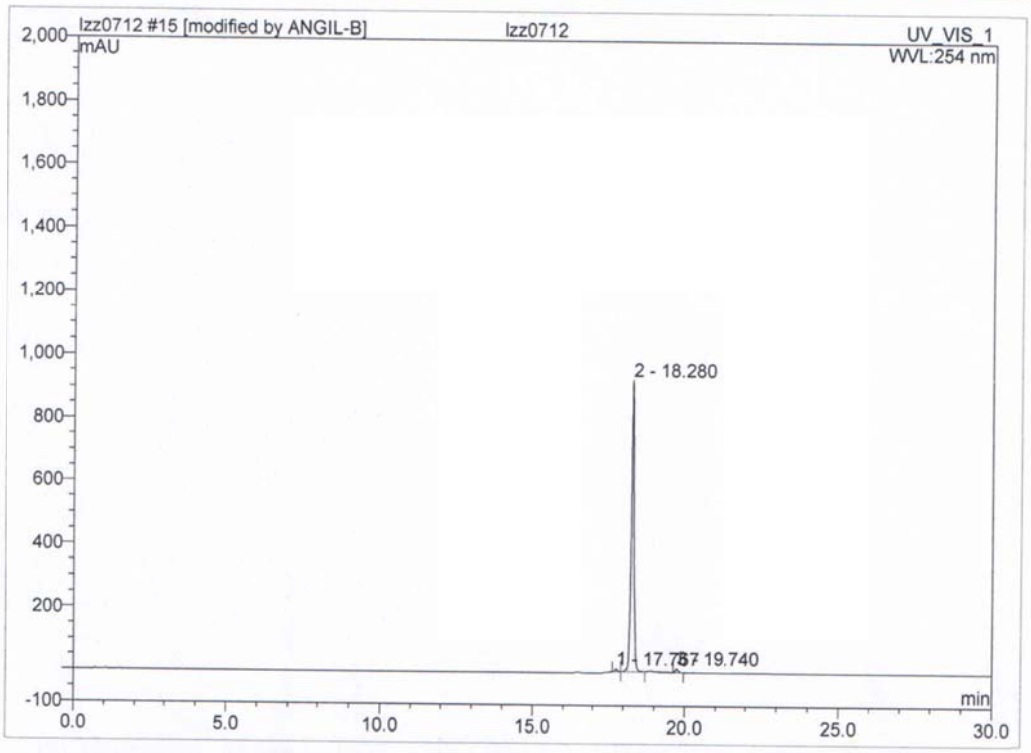


Figure S20. MALDI–TOF mass spectra of a gel sample prepared from **1b**.

15 lzz0712

Sample Name:	**lzz0712**	*Injection Volume:*	**20.0**
Vial Number:	**RA2**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**254**
Control Program:	**lzz0712**	*Bandwidth:*	**n.a.**
Quantif. Method:	**method**	*Dilution Factor:*	**1.0000**
Recording Time:	**2013/7/17 21:33**	*Sample Weight:*	**1.0000**
Run Time (min):	**30.00**	*Sample Amount:*	**1.0000**

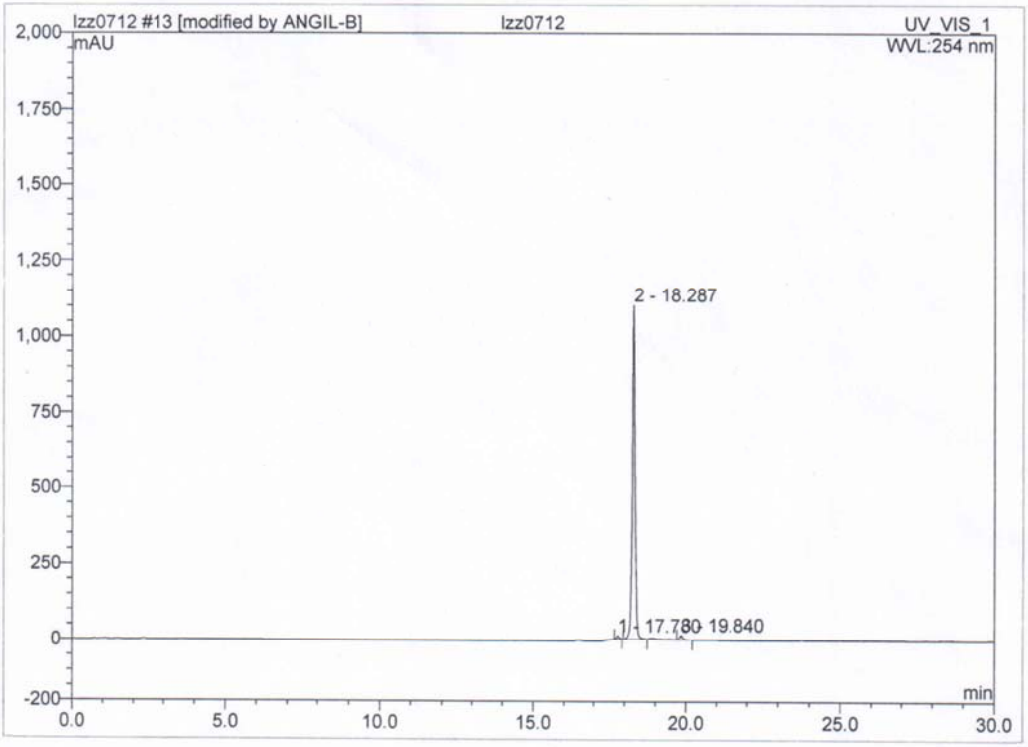


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.77	n.a.	9.336	0.826	0.86	n.a.	BMb*
2	18.28	n.a.	924.535	94.413	97.92	n.a.	bMB*
3	19.74	n.a.	11.613	1.174	1.22	n.a.	BMB
Total:			945.485	96.414	100.00	0.000	

Figure S21. HPLC analysis of a sample of **1b** which was purified by column chromatography (silica gel).

13 lzz0712

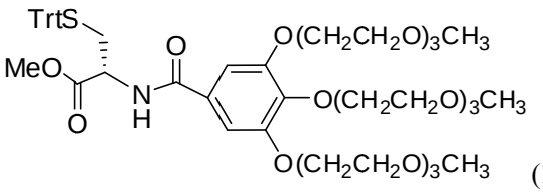
Sample Name:	**lzz0712**	*Injection Volume:*	**20.0**
Vial Number:	**RA1**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**254**
Control Program:	**lzz0712**	*Bandwidth:*	**n.a.**
Quantif. Method:	**method**	*Dilution Factor:*	**1.0000**
Recording Time:	**2013/7/17 19:45**	*Sample Weight:*	**1.0000**
Run Time (min):	**30.00**	*Sample Amount:*	**1.0000**



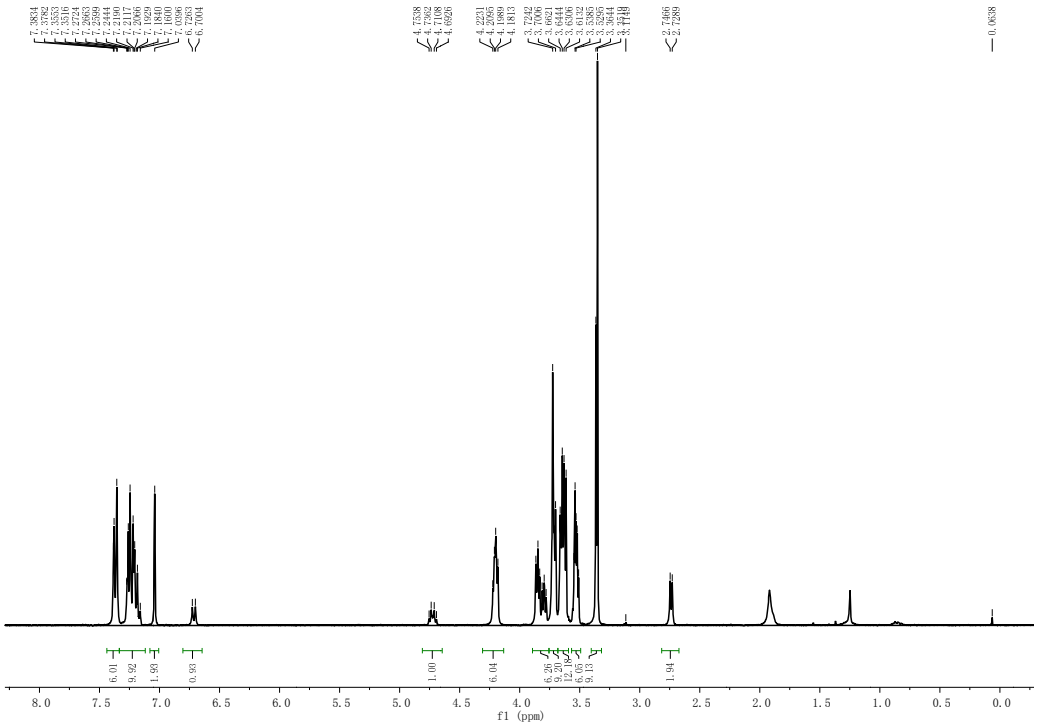
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.78	n.a.	10.455	0.937	0.81	n.a.	BMB*
2	18.29	n.a.	1100.342	113.277	97.82	n.a.	BMB*
3	19.84	n.a.	14.160	1.589	1.37	n.a.	BMB
Total:			1124.956	115.804	100.00	0.000	

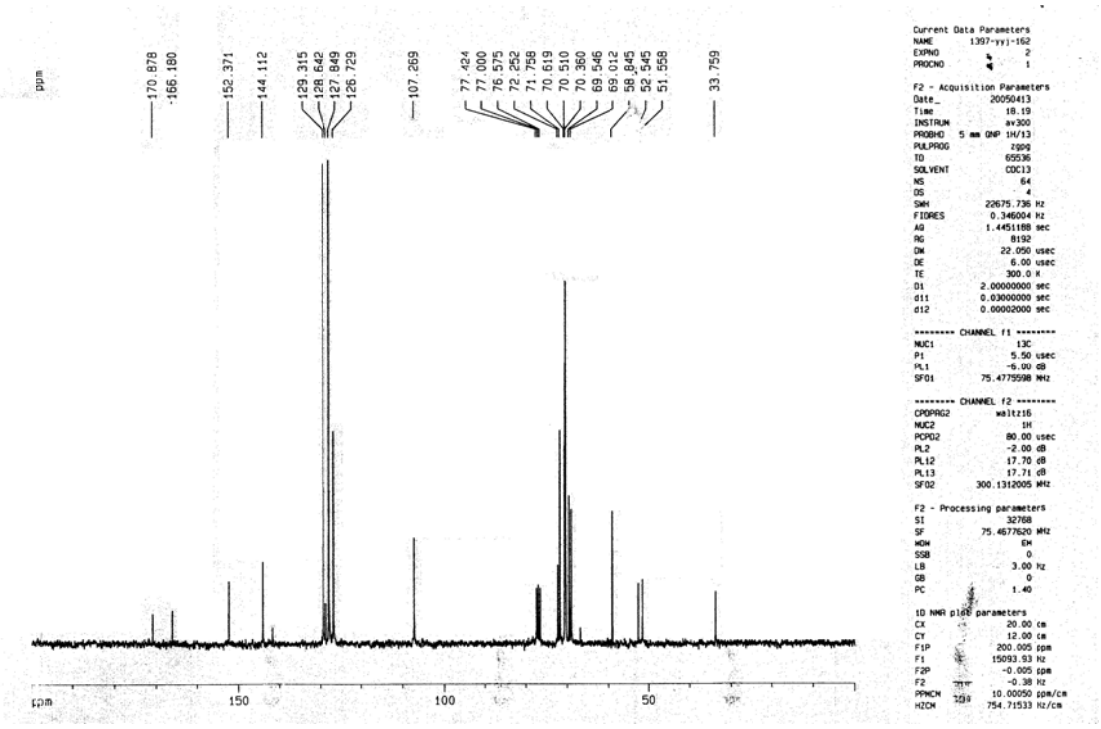
Figure S22. HPLC analysis of a sample of **1b** from formed gels.

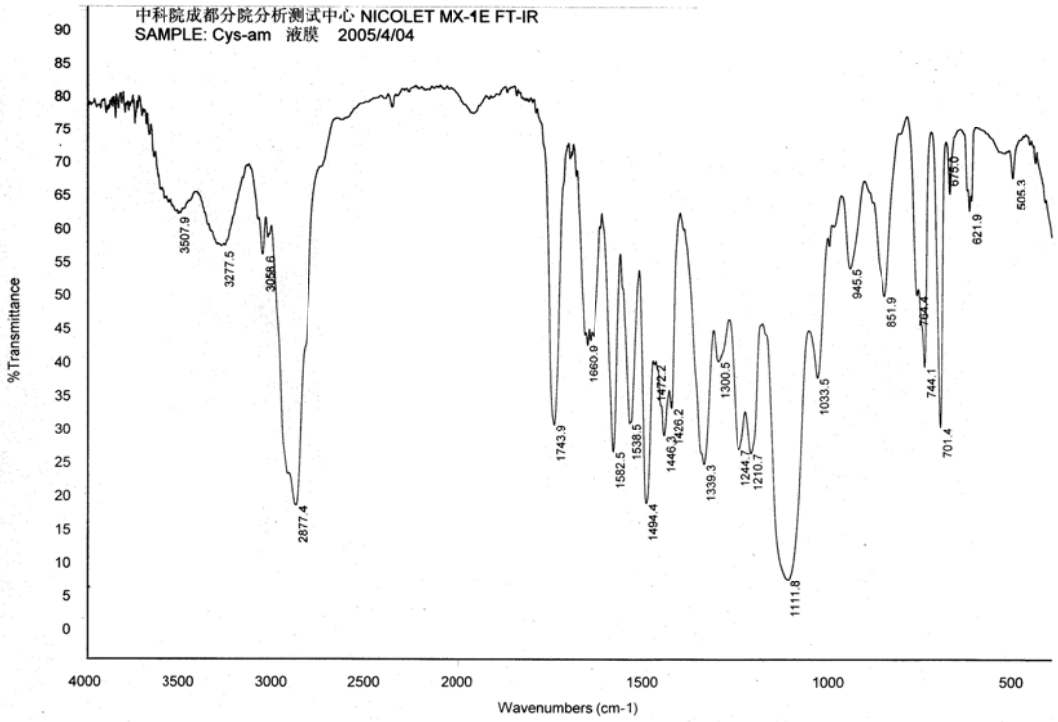
8. Spectral Data:

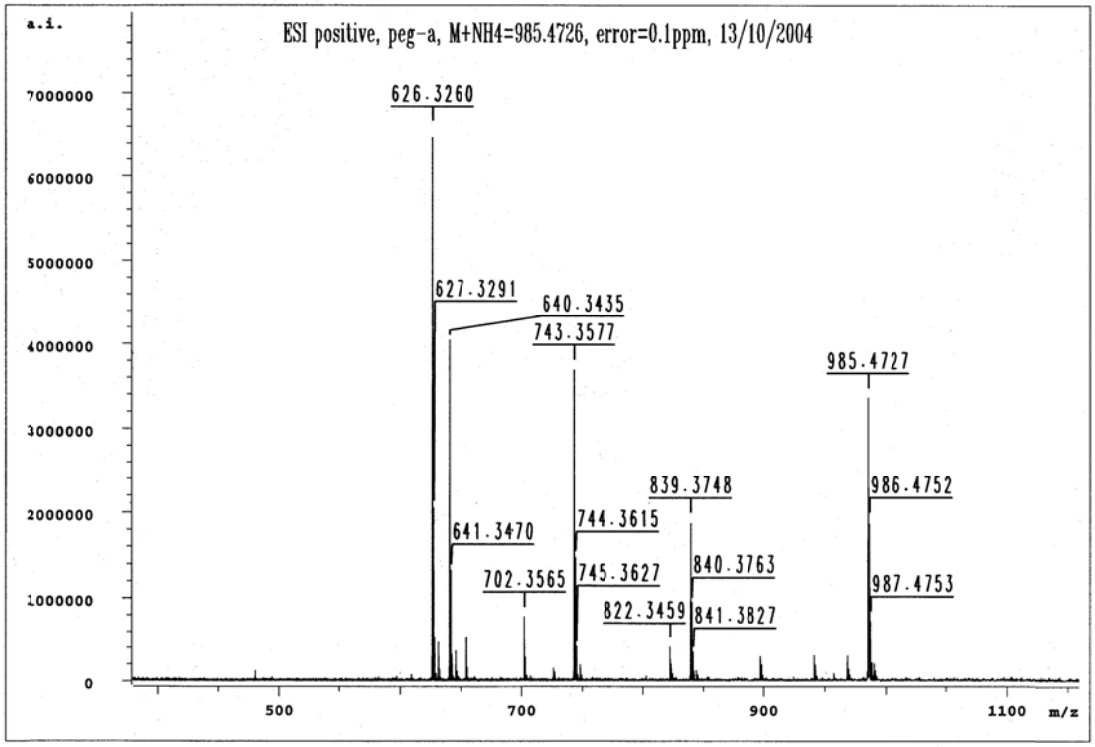


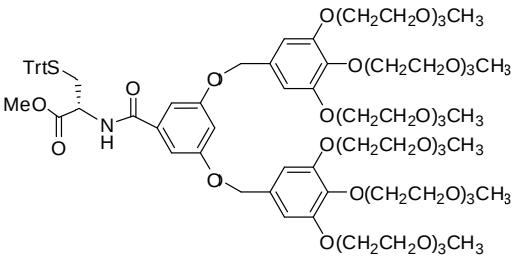
(**13a**)



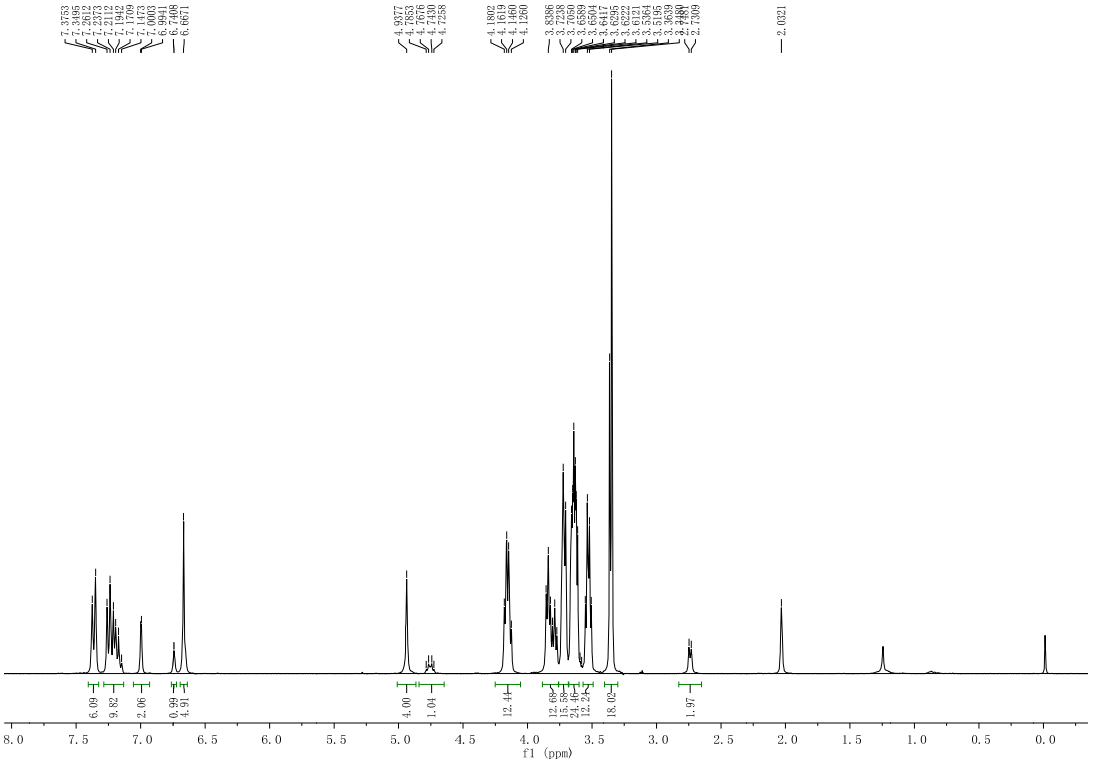


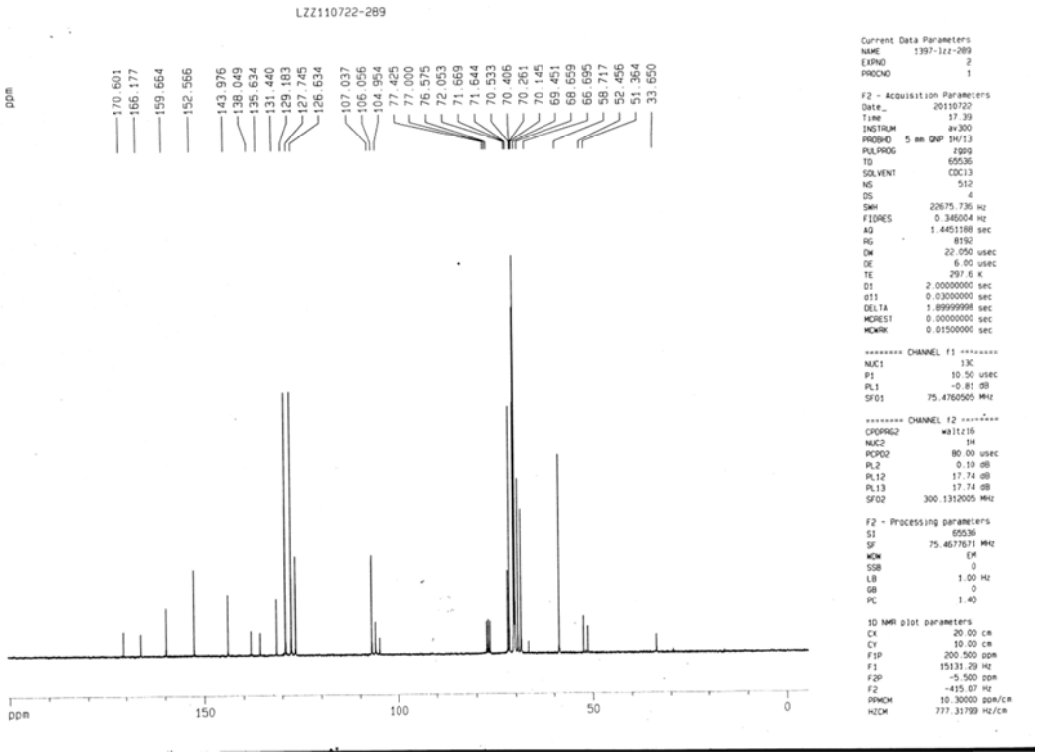


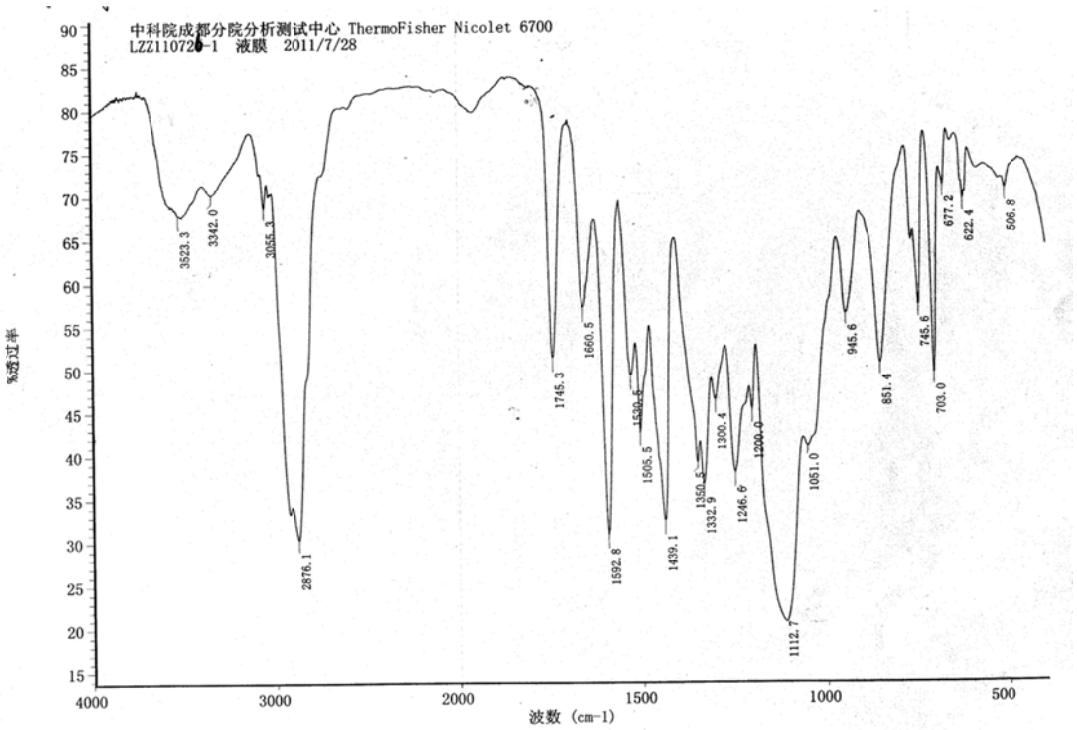




(**13b**)







Mass Spectrum SmartFormula Report

Analysis Info

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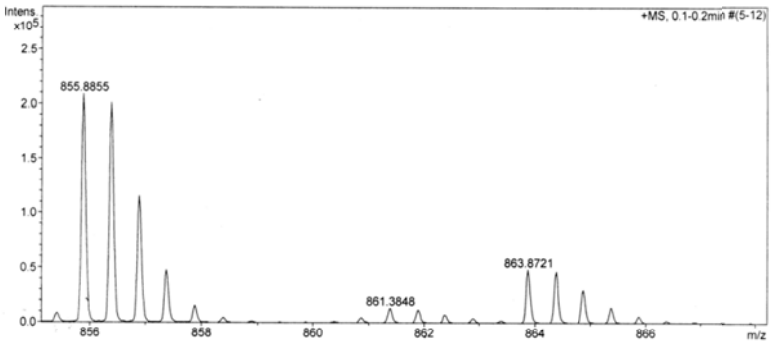
Sample Name	LZZ110726-7	Operator	Ma
Comment		Instrument / Ser#	micrOTOF-Q II 10203

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



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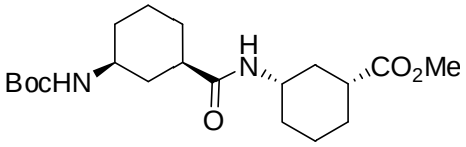
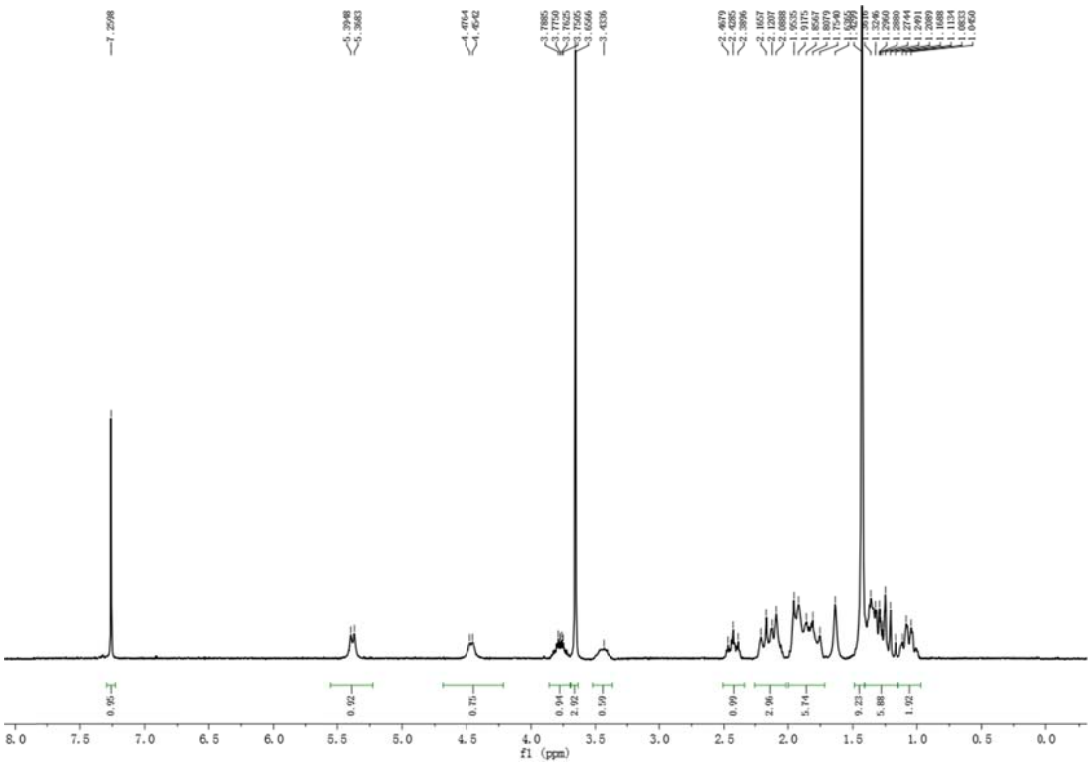
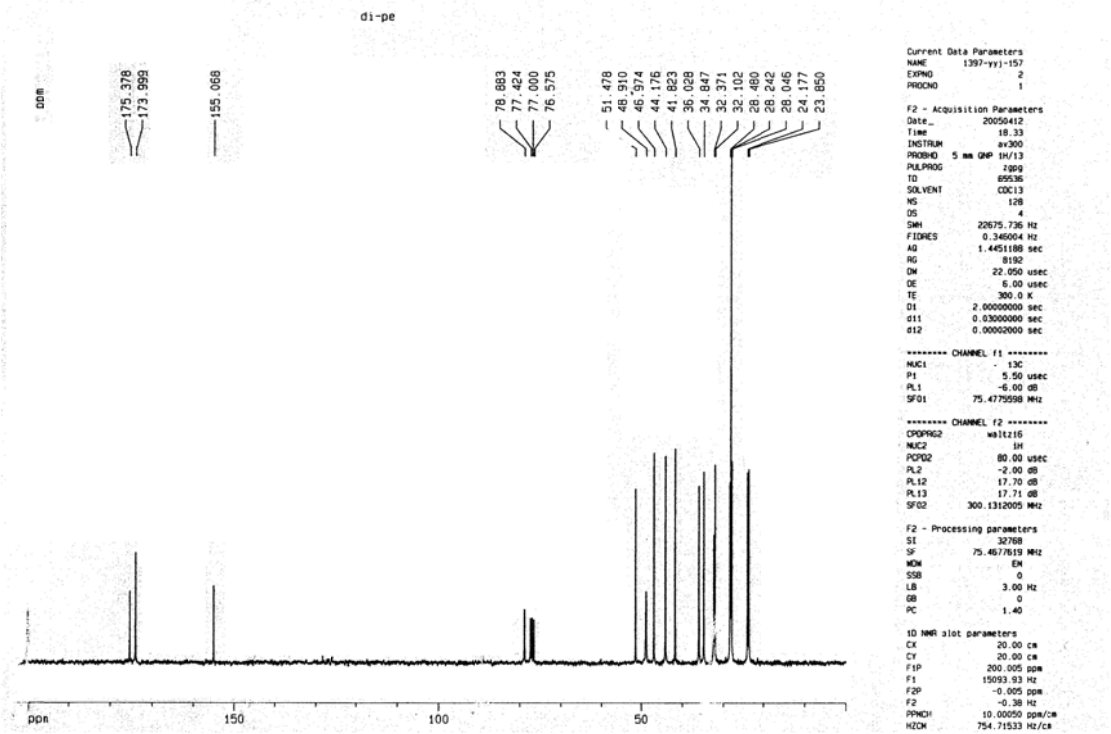
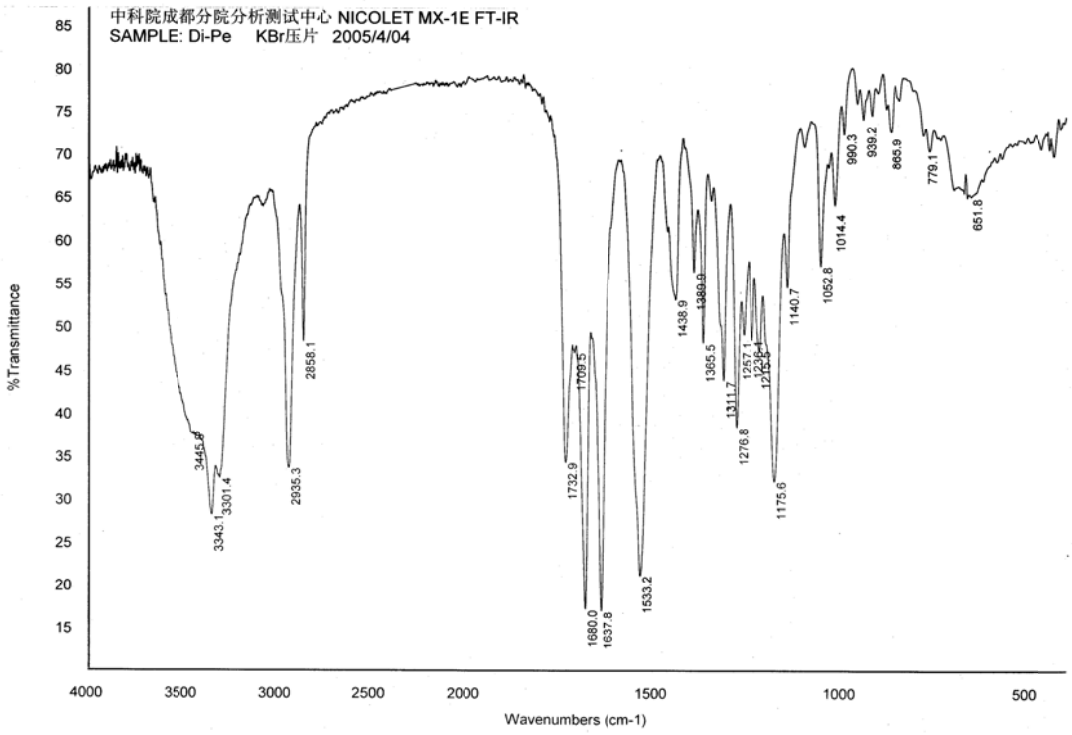
856.8878	1	C 99 H 120 N Na O 21 S	100.00	856.8980	12.0	13.4	330.8	40.0	even	ok

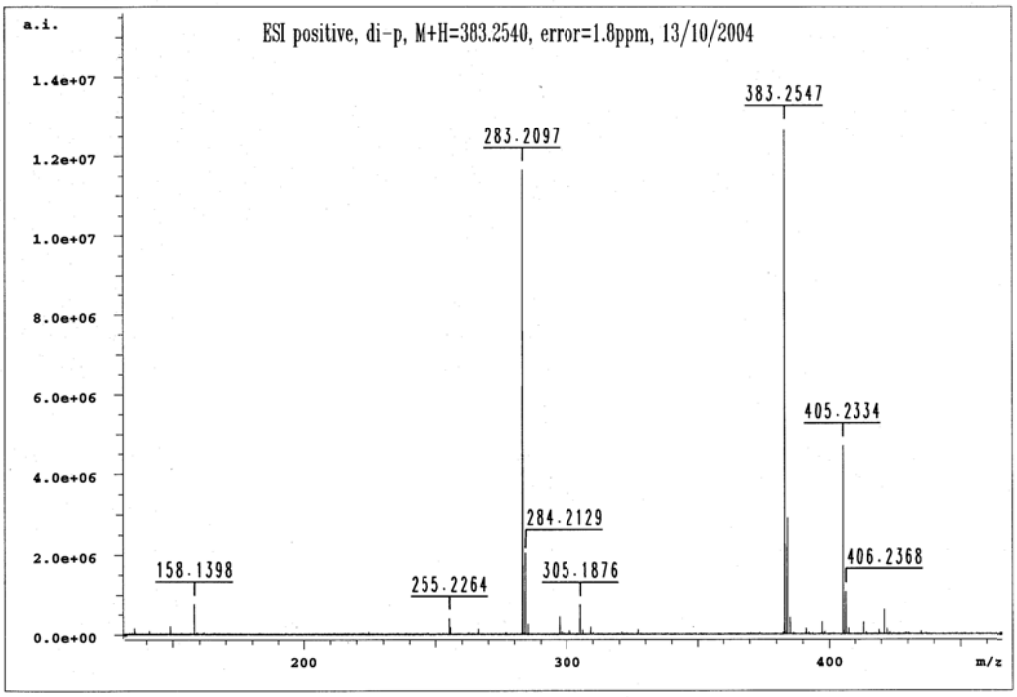


(6)









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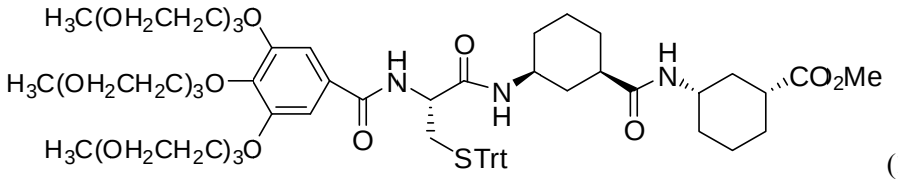
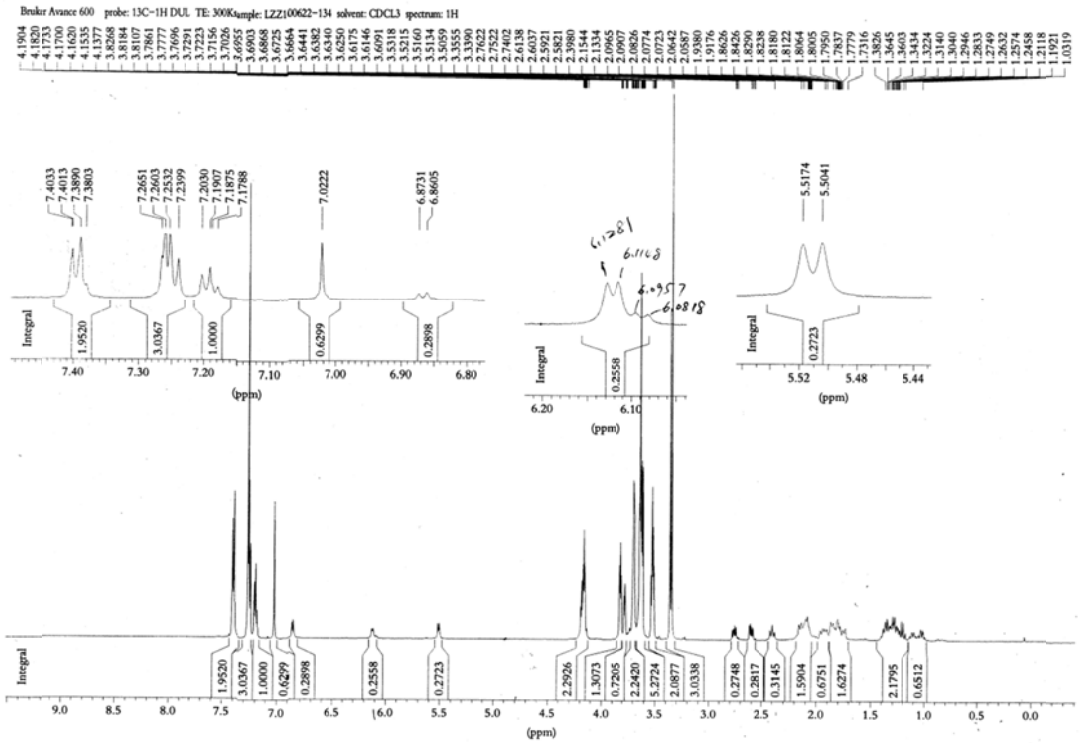
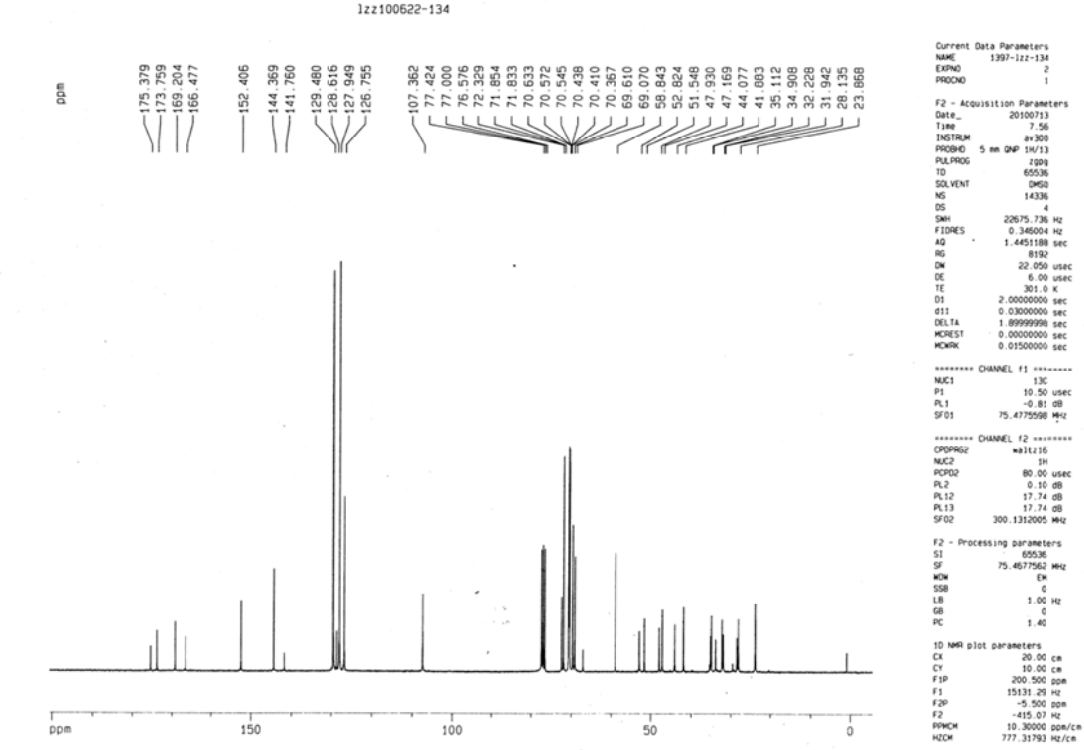
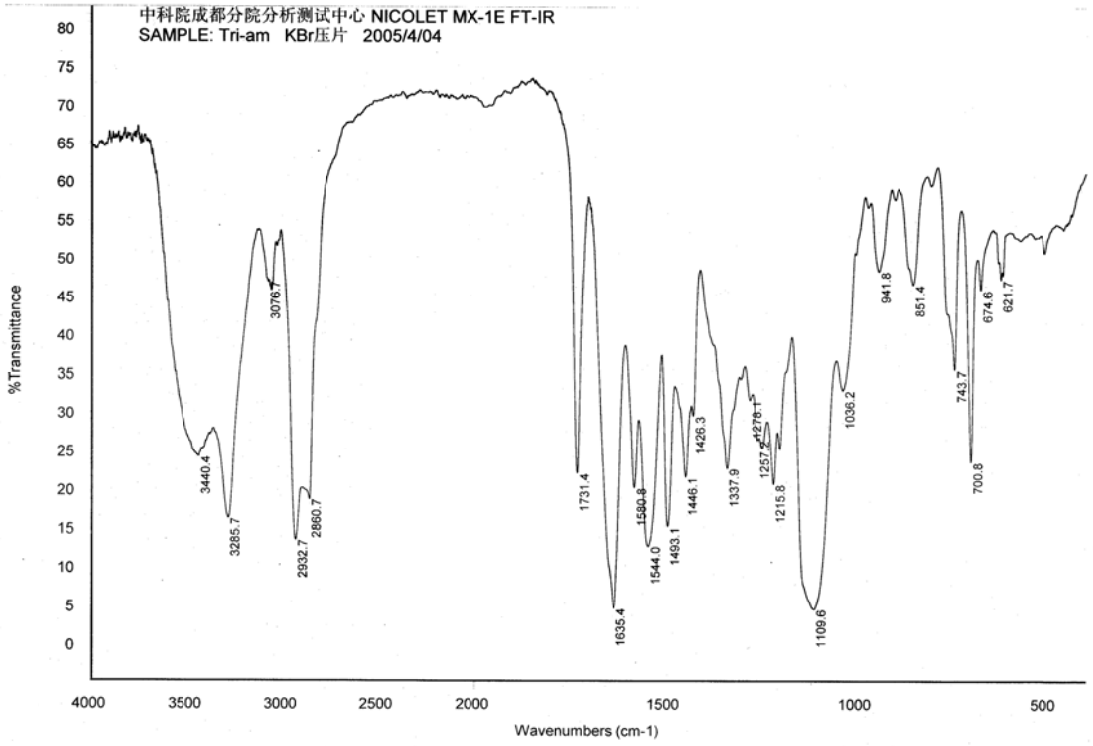
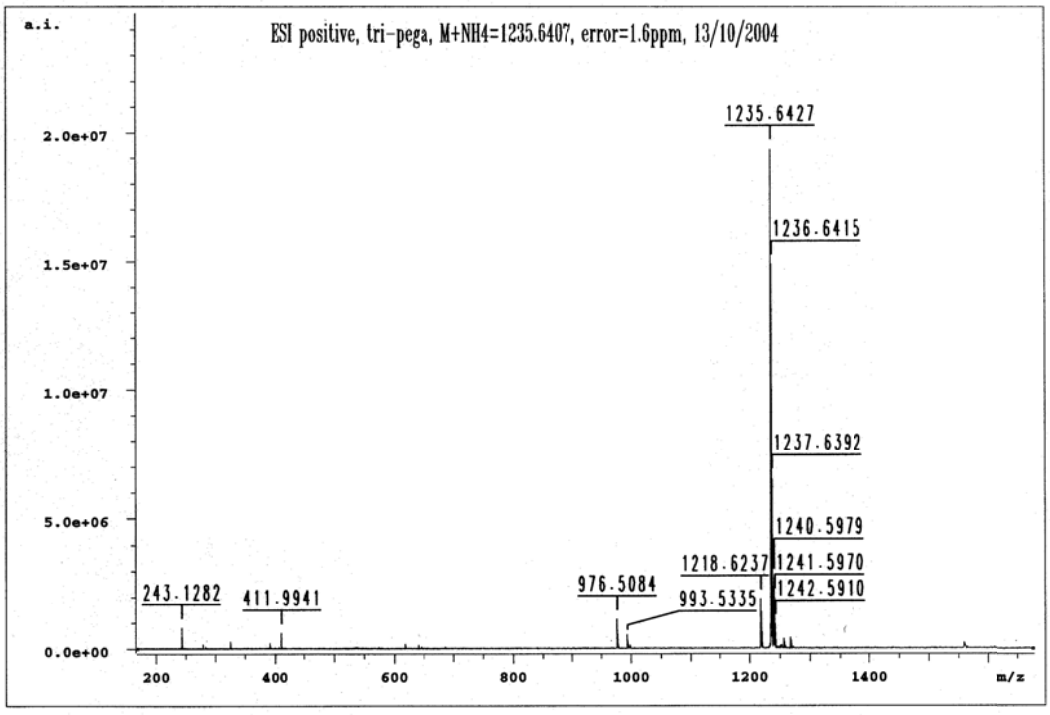


(**15a**)









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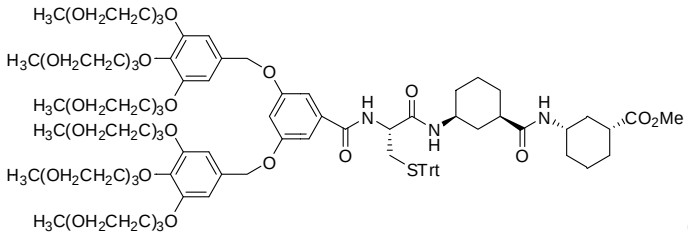
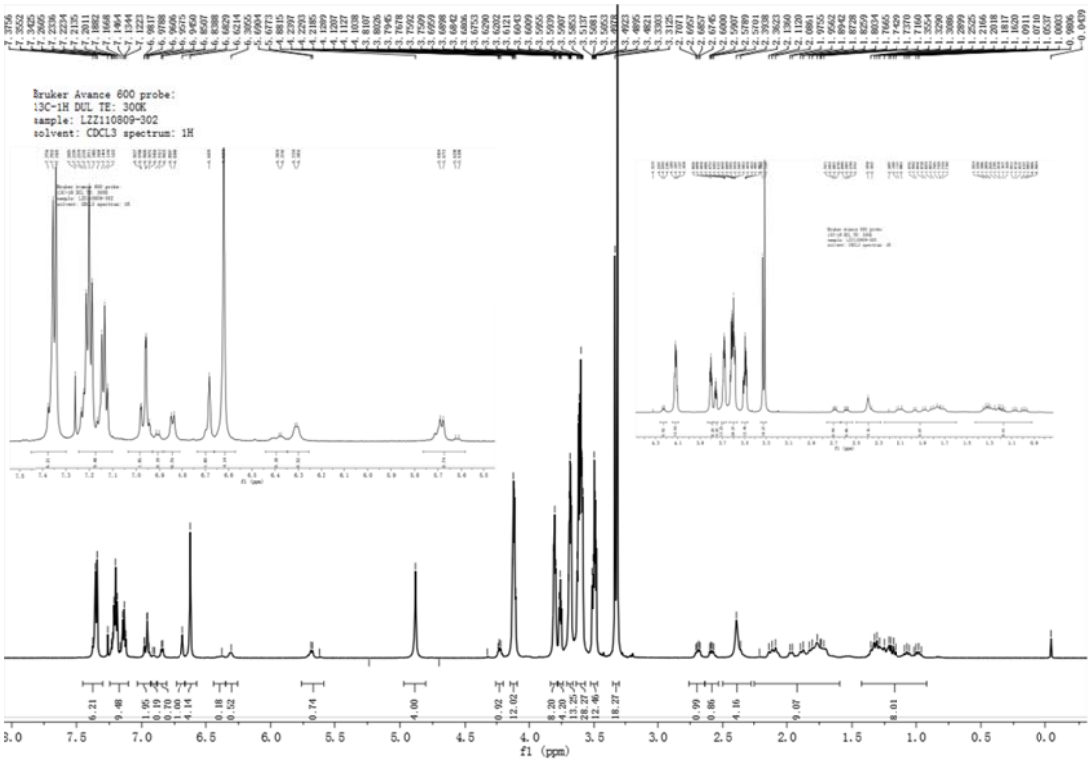
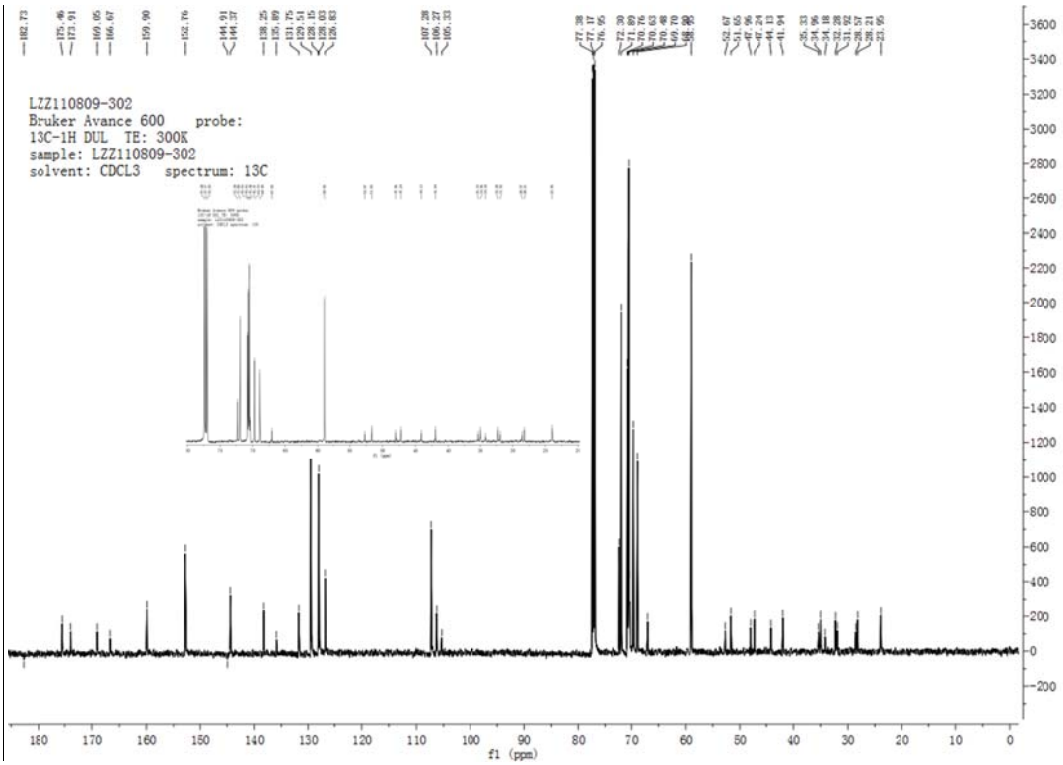
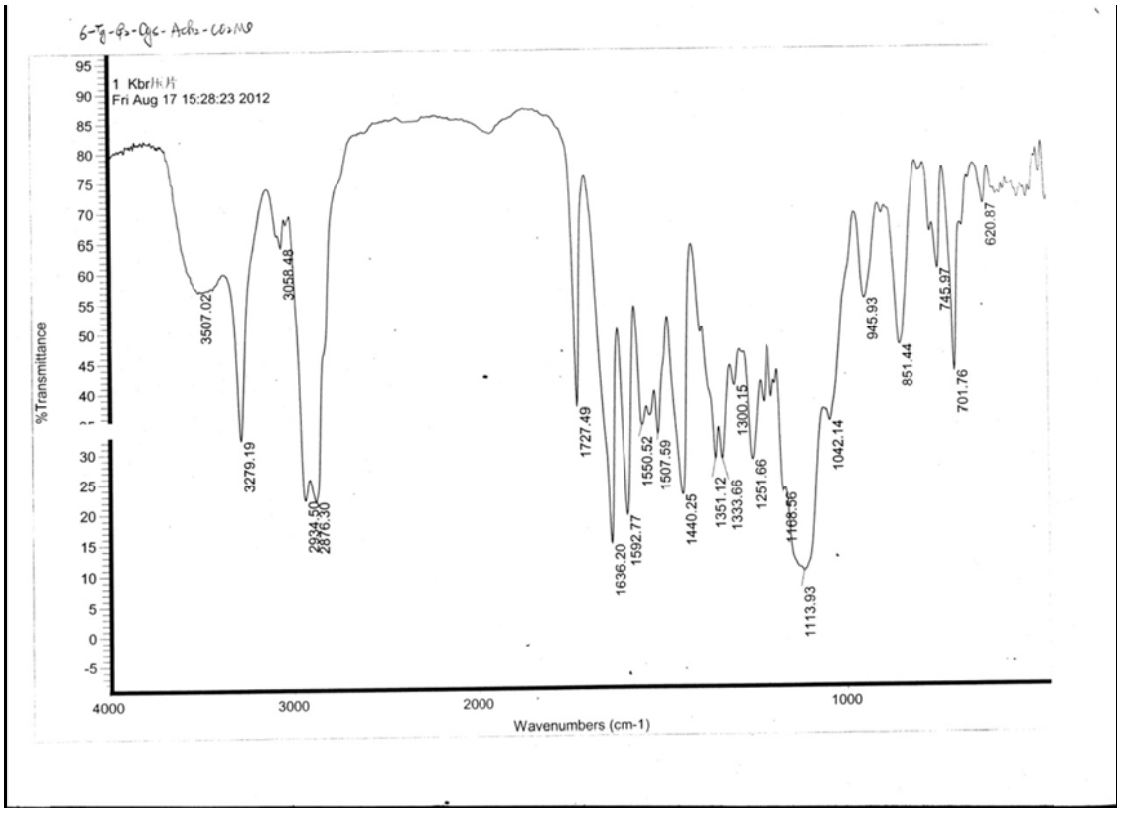


(15b)







Mass Spectrum SmartFormula Report

Analysis Info

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Method	WU_tune_low_20101108.m	Operator	Ma
Sample Name	LZZ110721-6	Instrument / Ser#	micrOTOF-Q II 10203
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
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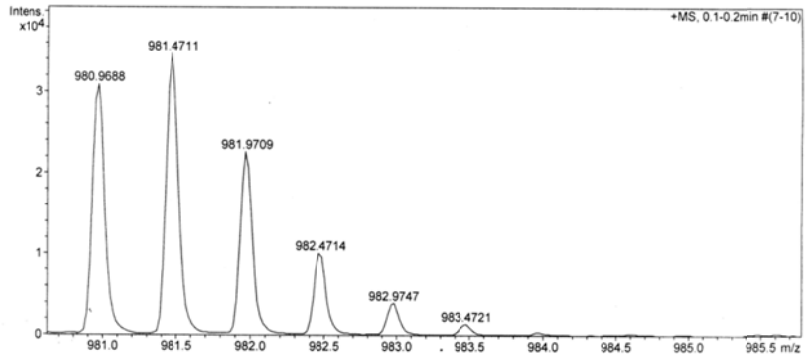
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



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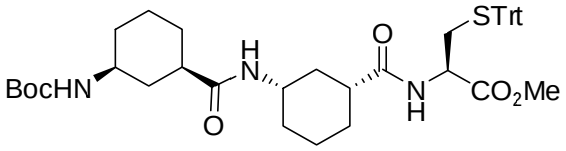
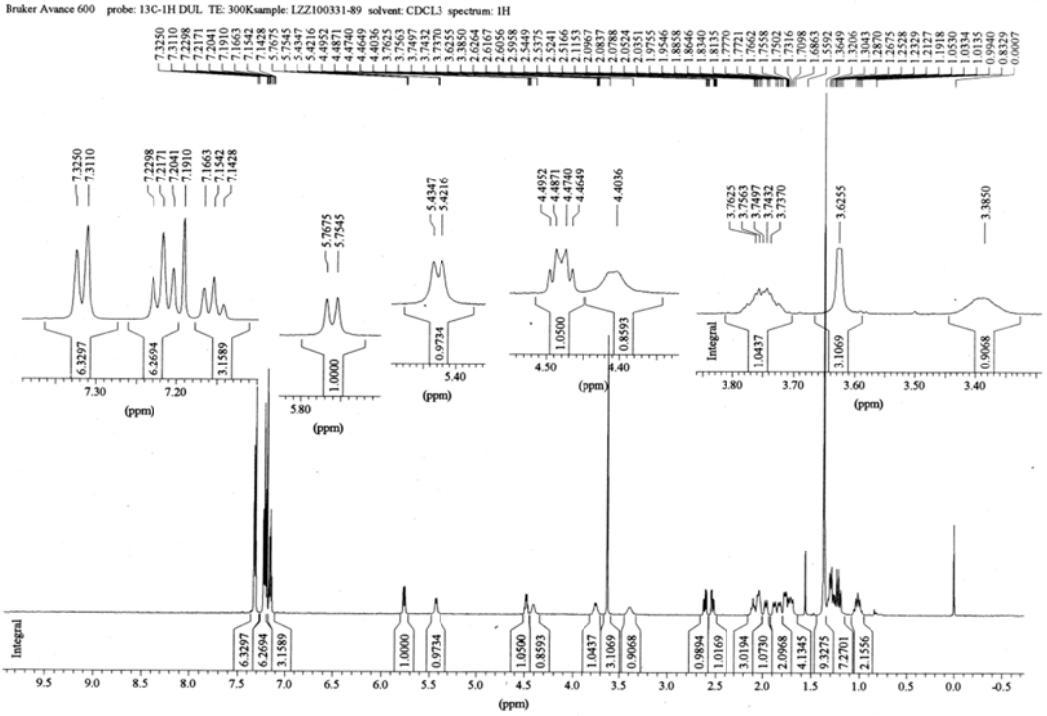
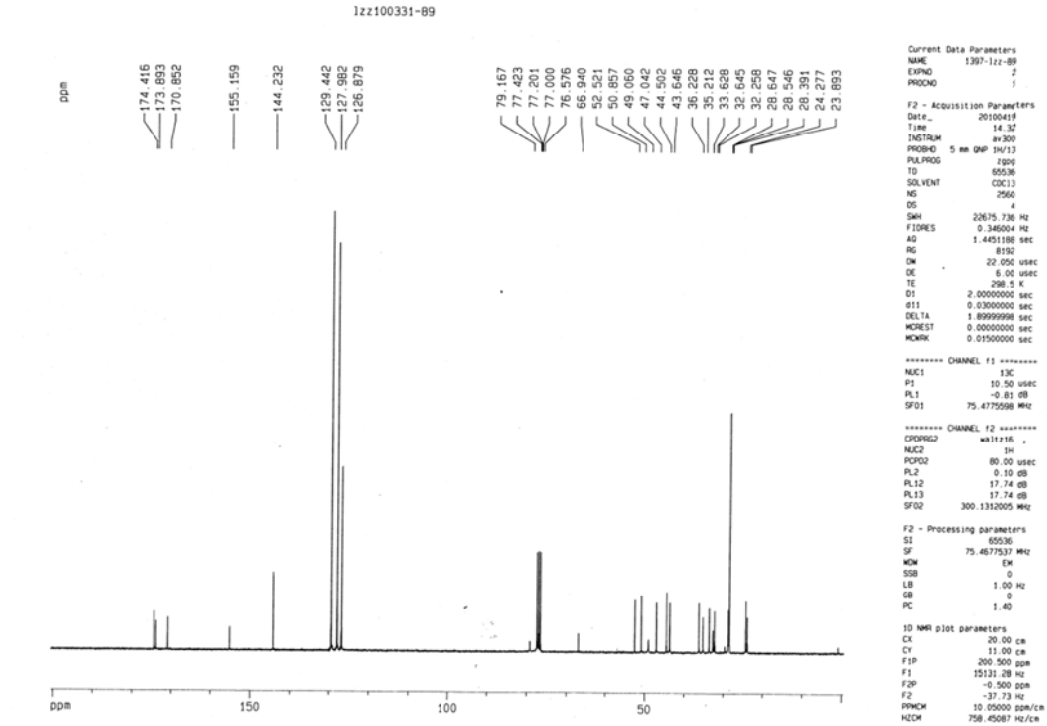
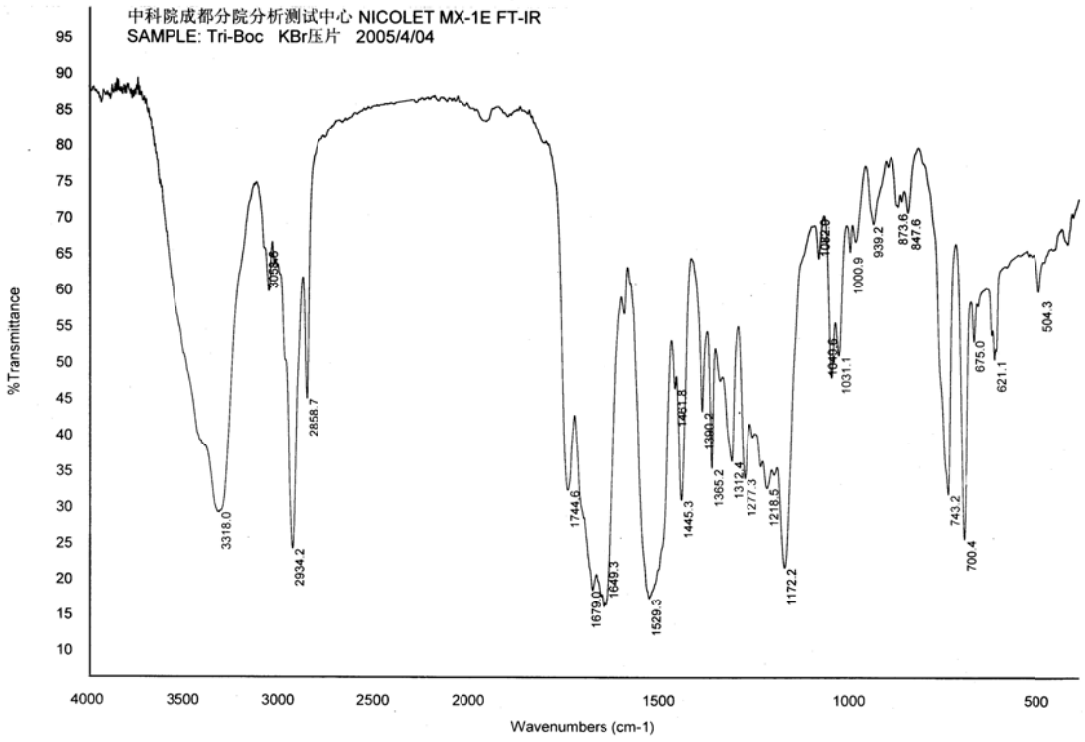
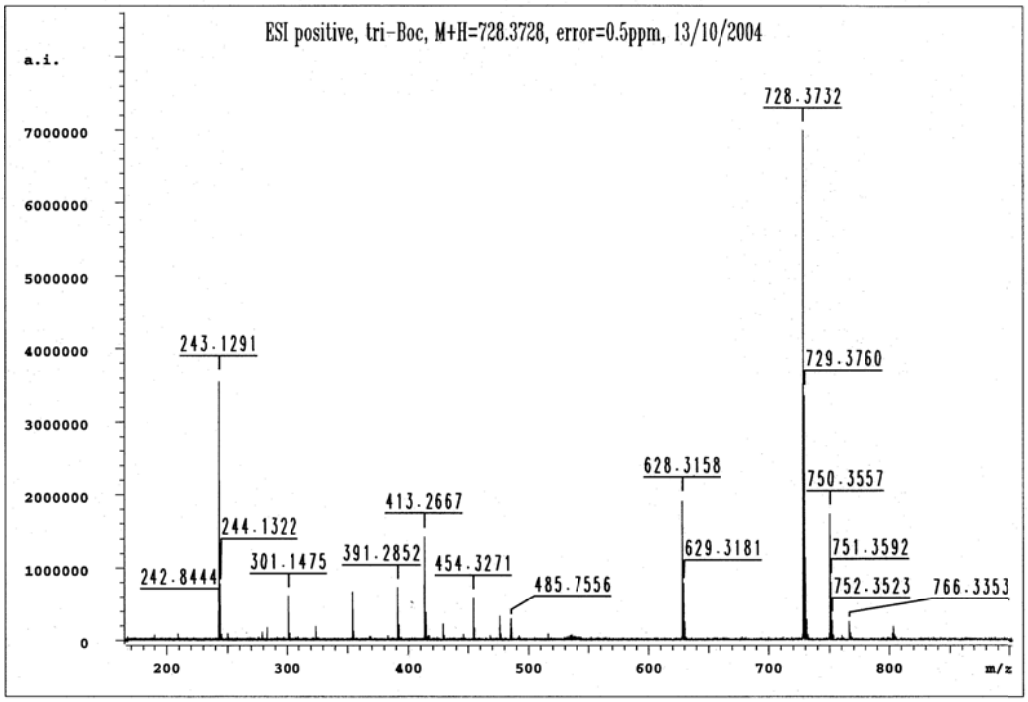


(16)









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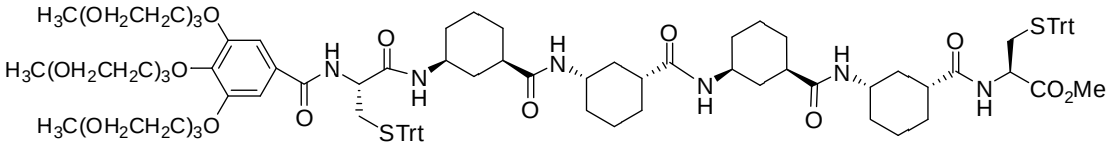
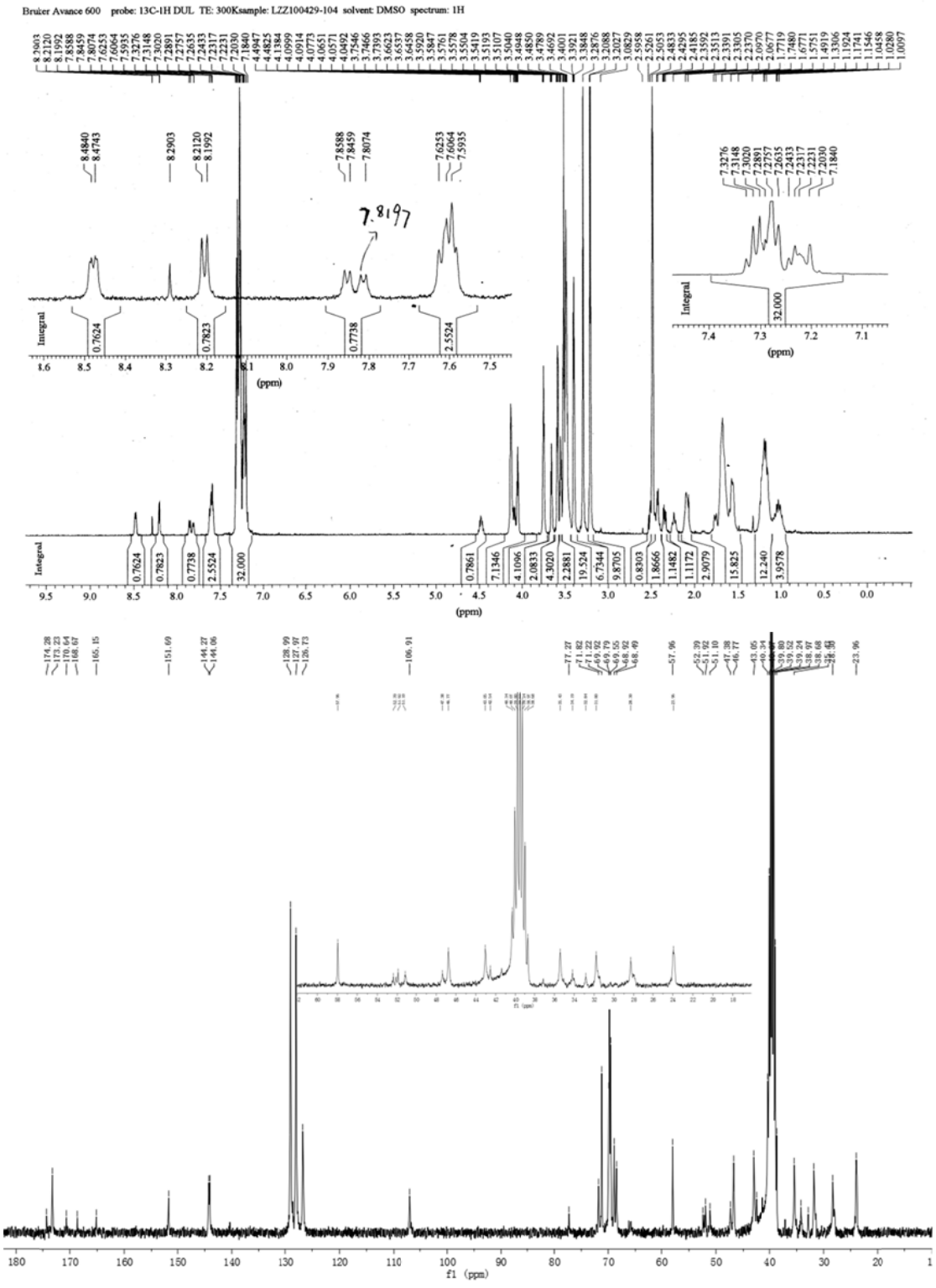
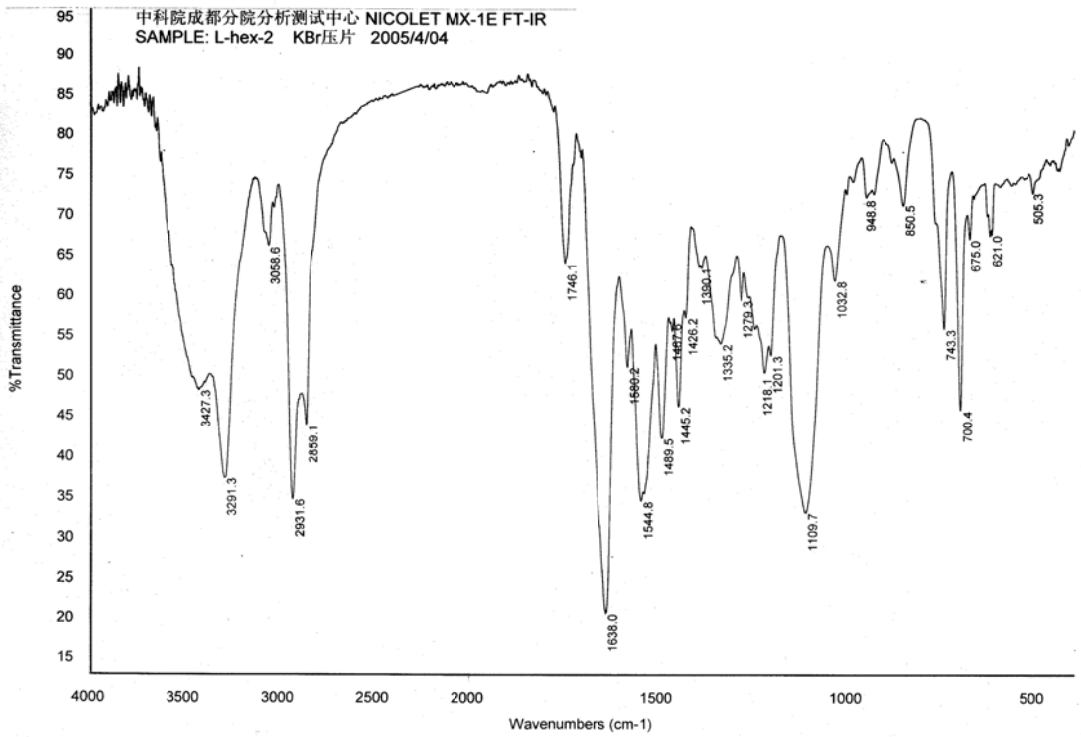
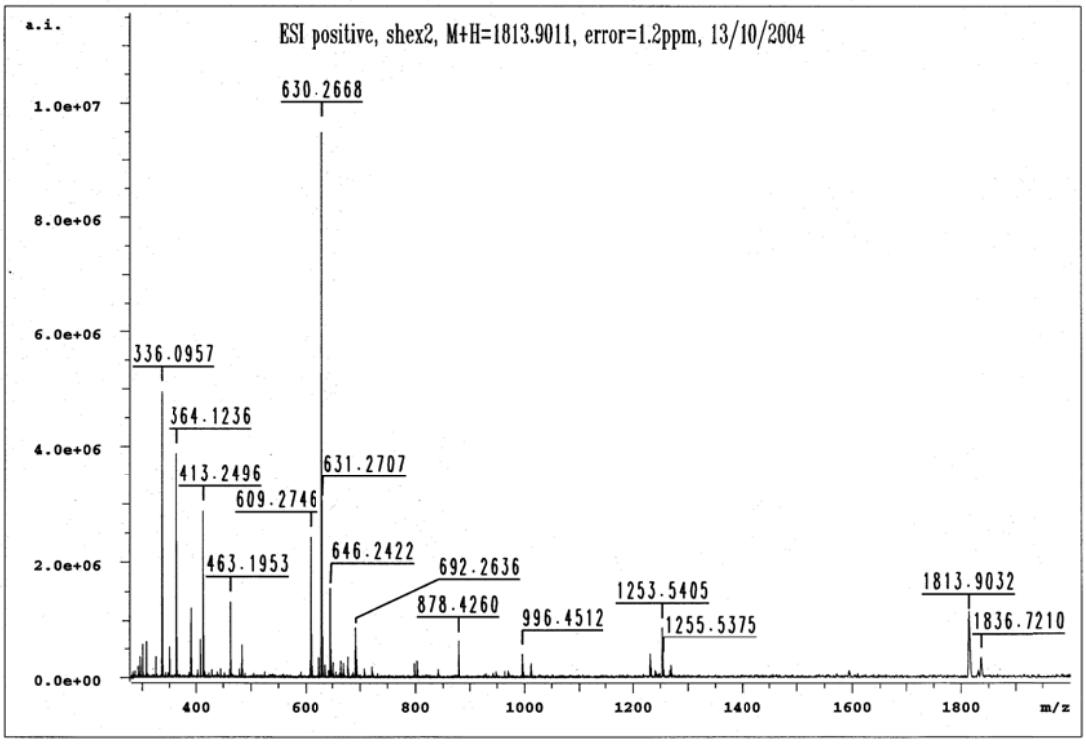
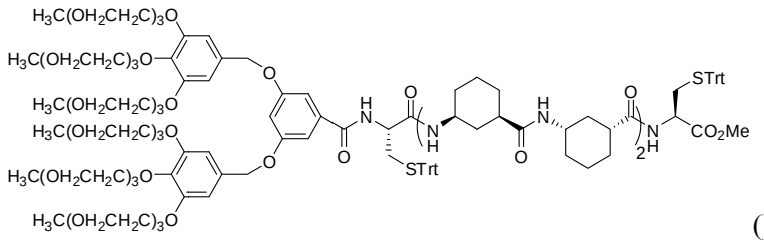


(**11a**)

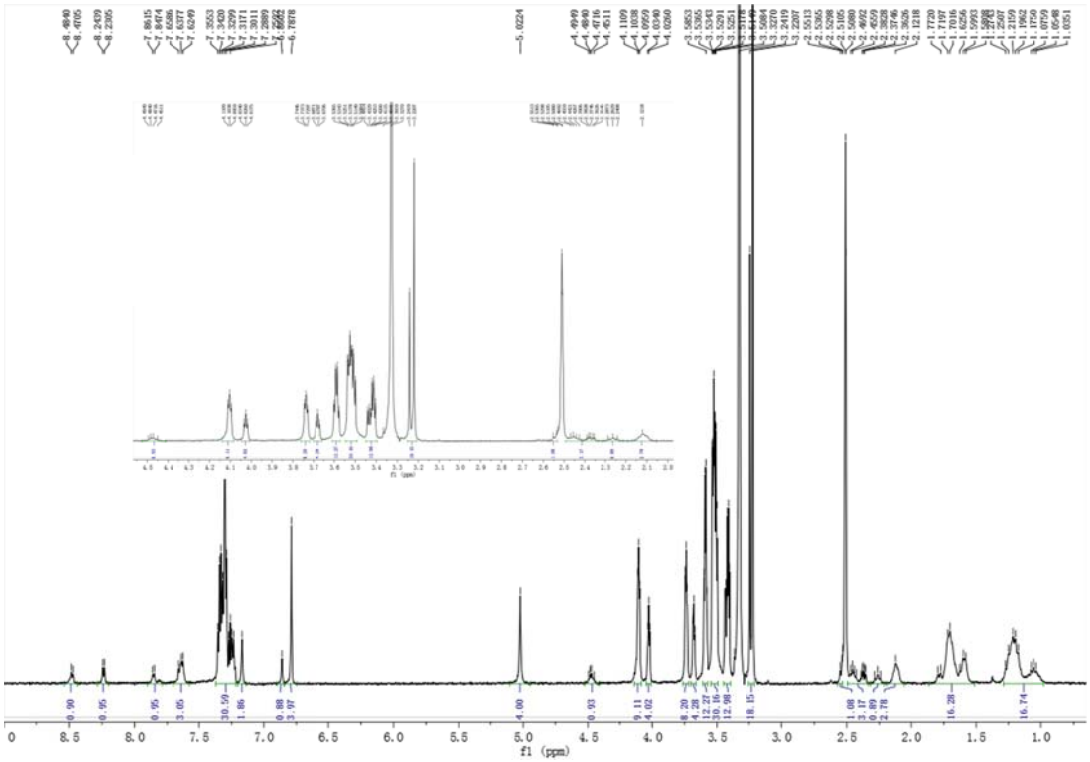


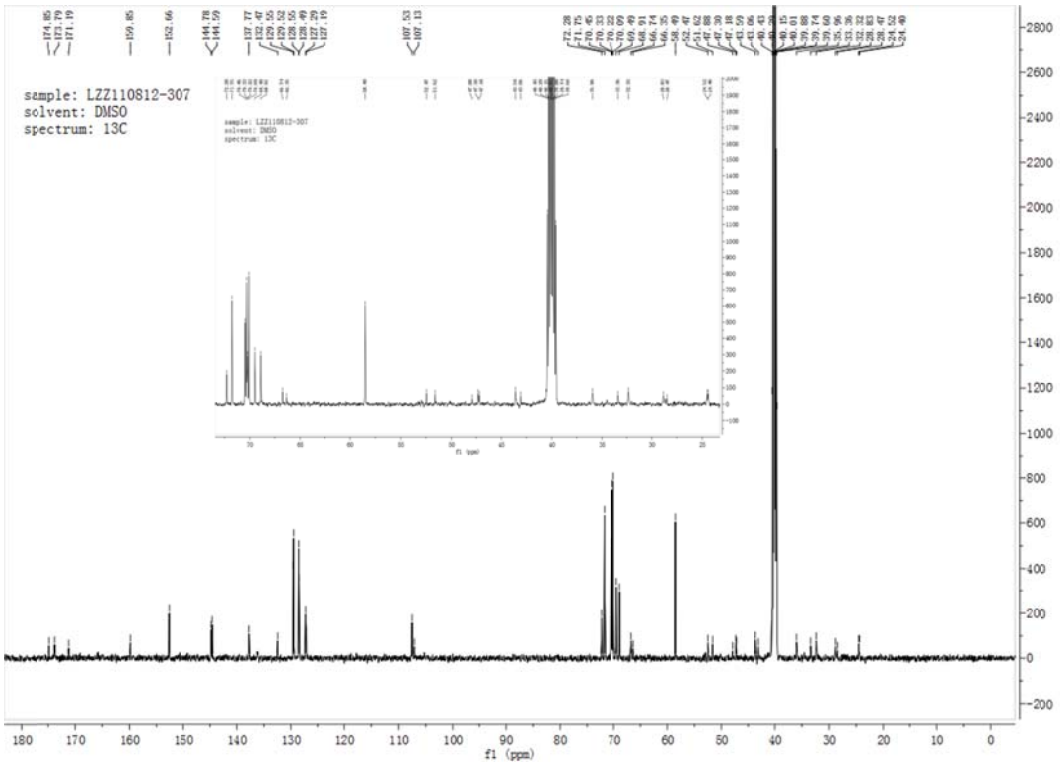


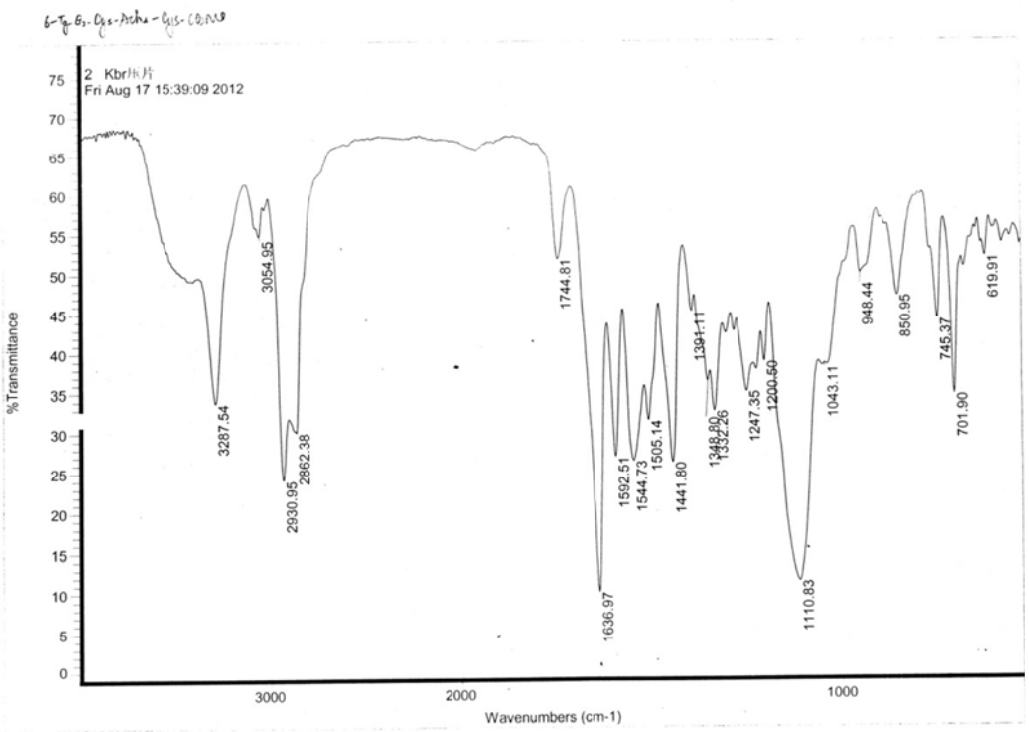




(**11b**)







Mass Spectrum SmartFormula Report

Analysis Info

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Method	tune_wide_20110309.m	Operator	Ma
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Comment			

Acquisition Parameter

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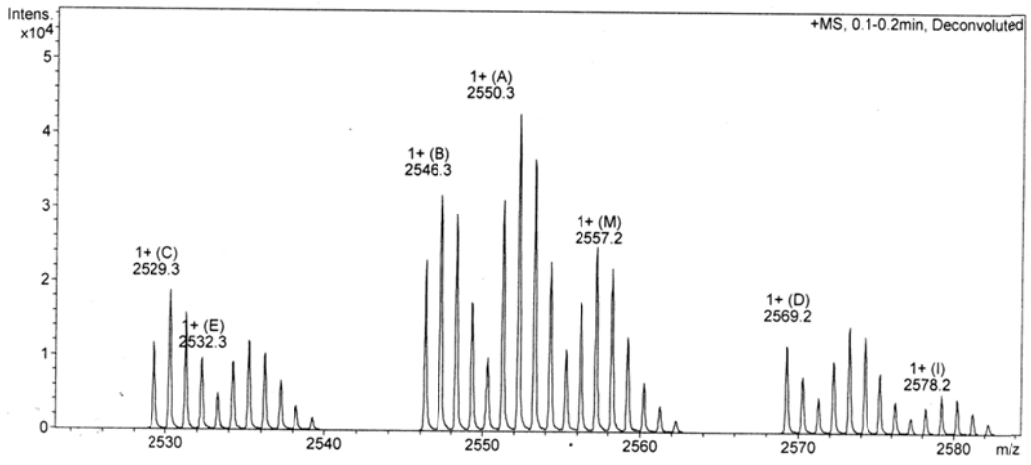
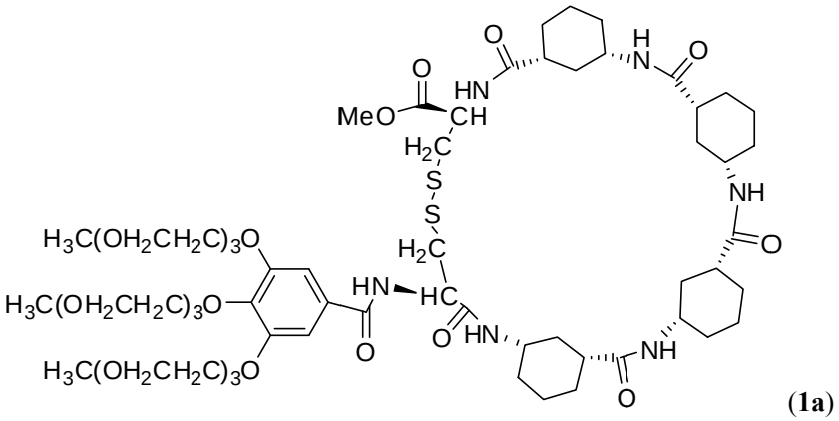
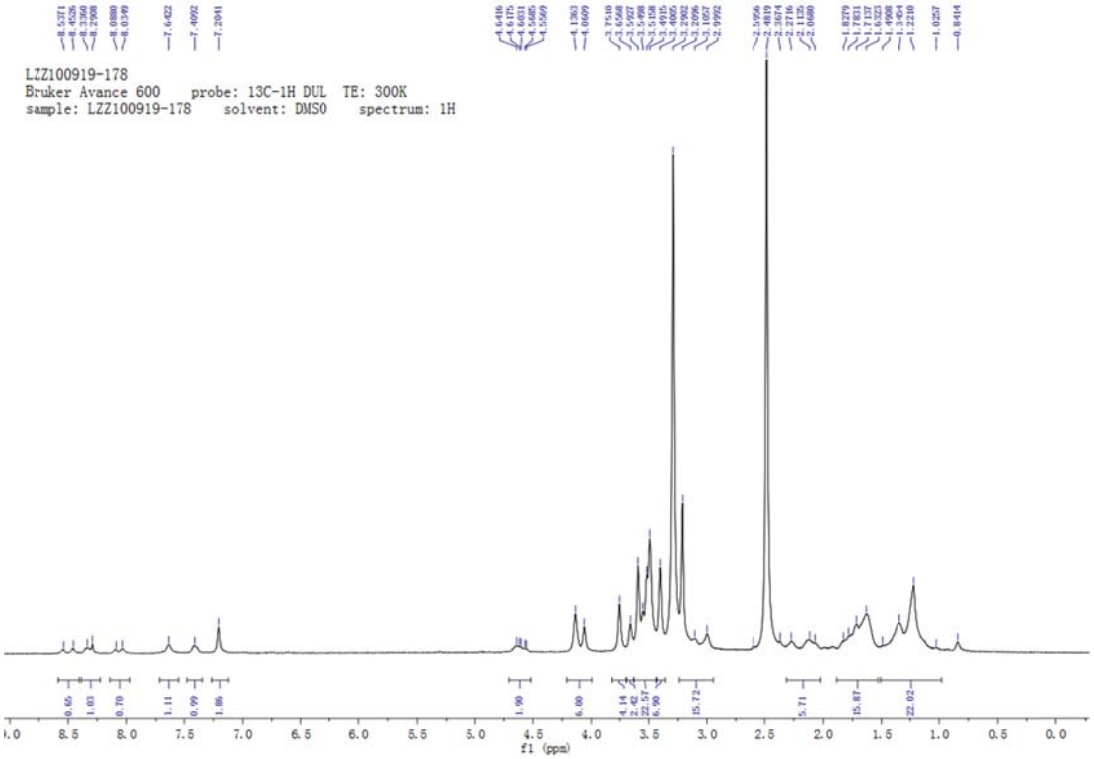
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	550.0 Vpp	Set Divert Valve	Source

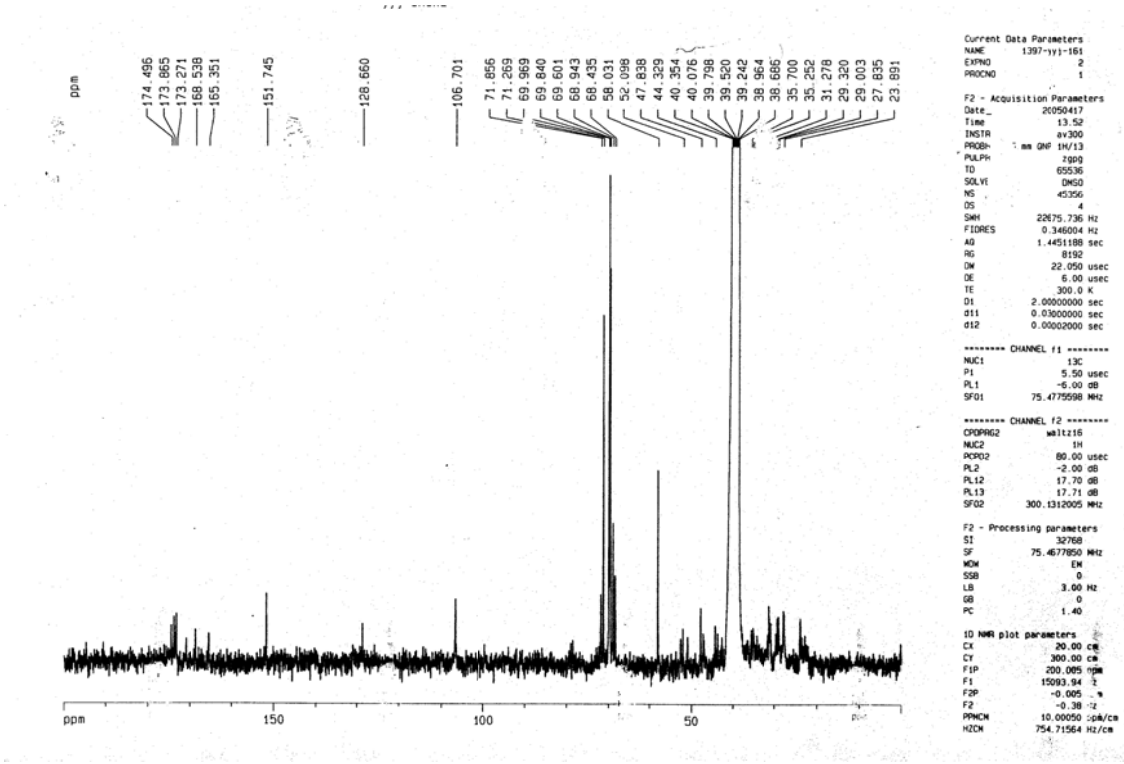


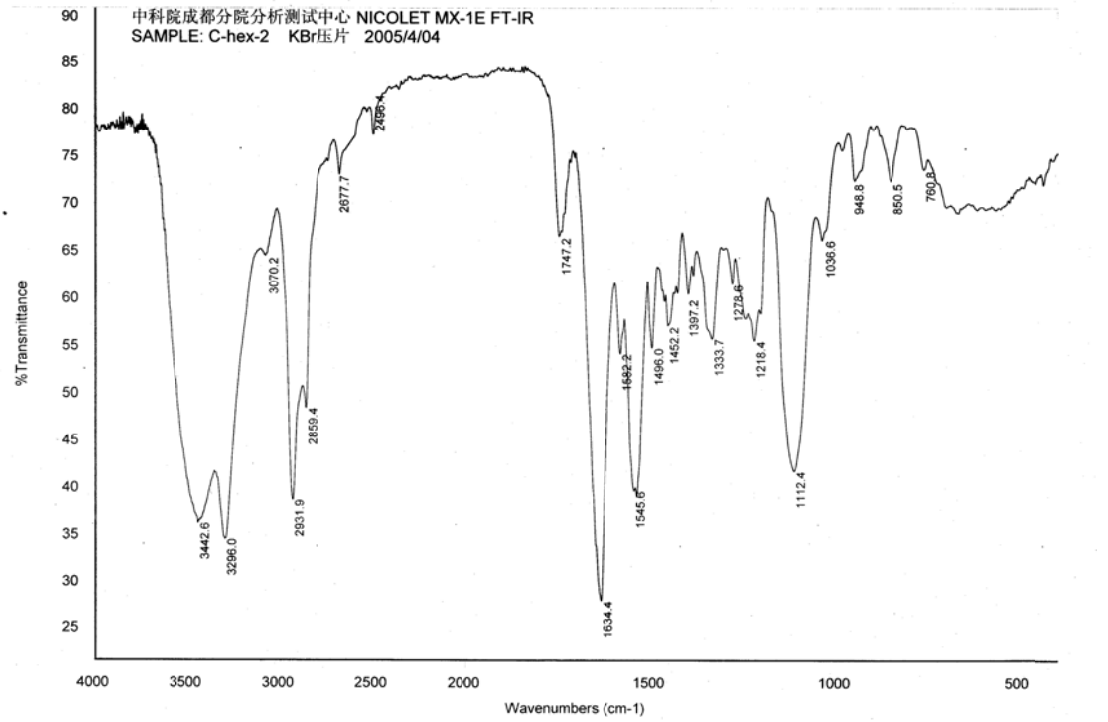
Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule



(1a)







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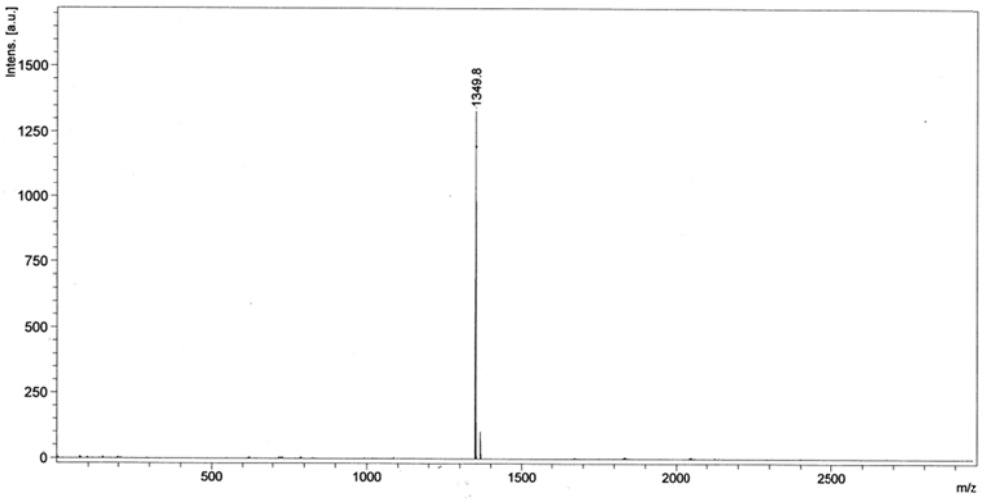
MALDI-TOF,CCA,1,2010,05,18



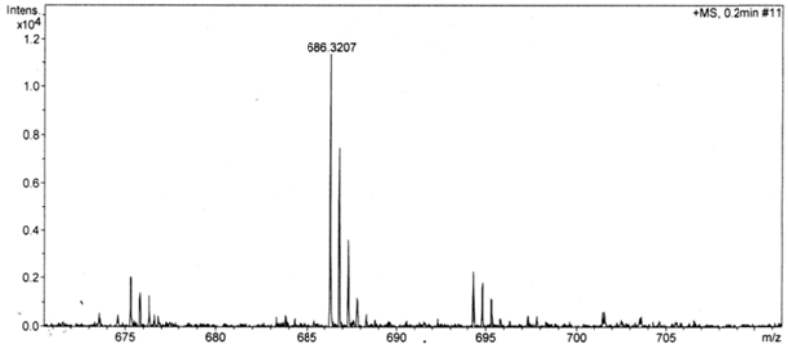
Mass Spectrum SmartFormula Report

Analysis Info

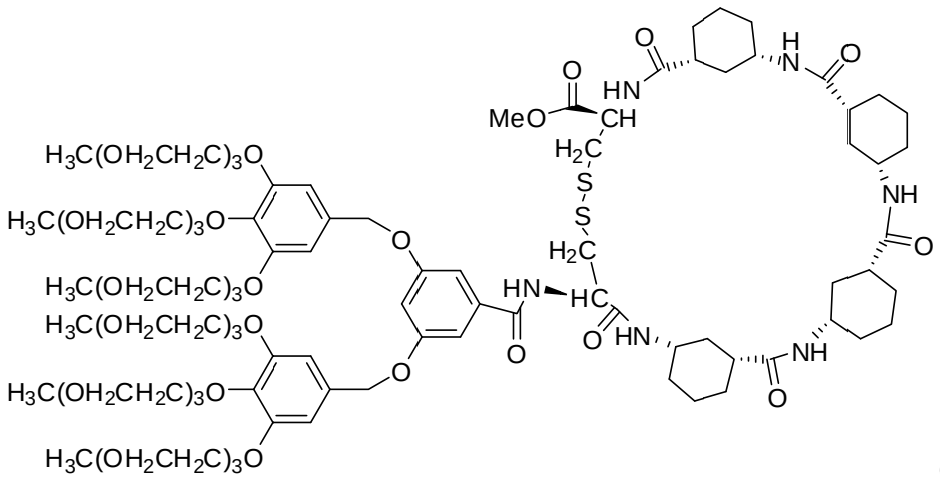
Analysis Name	D:\Data\User\lzz101101-2.d	Acquisition Date	11/3/2010 3:12:16 PM
Method	tune_wide_20101102.m	Operator	Ma
Sample Name	lzz101101-2	Instrument / Ser#	micrOTOF-Q II 10203
Comment	1:100 Dilution		

Acquisition Parameter

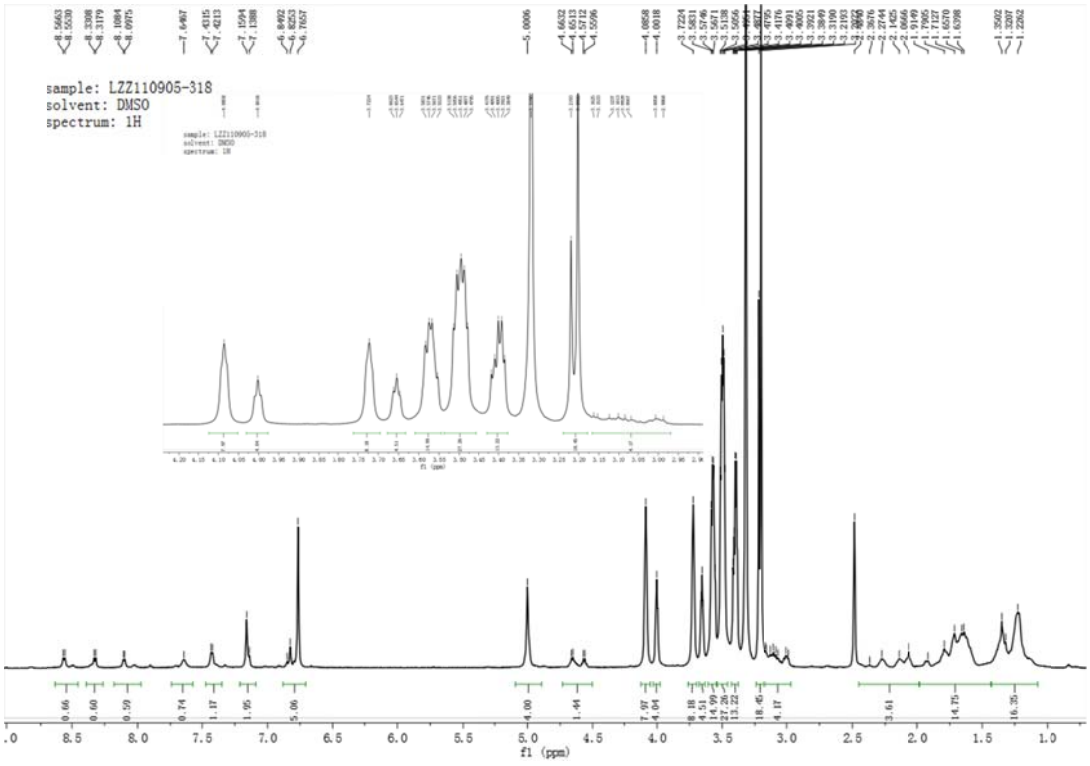
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

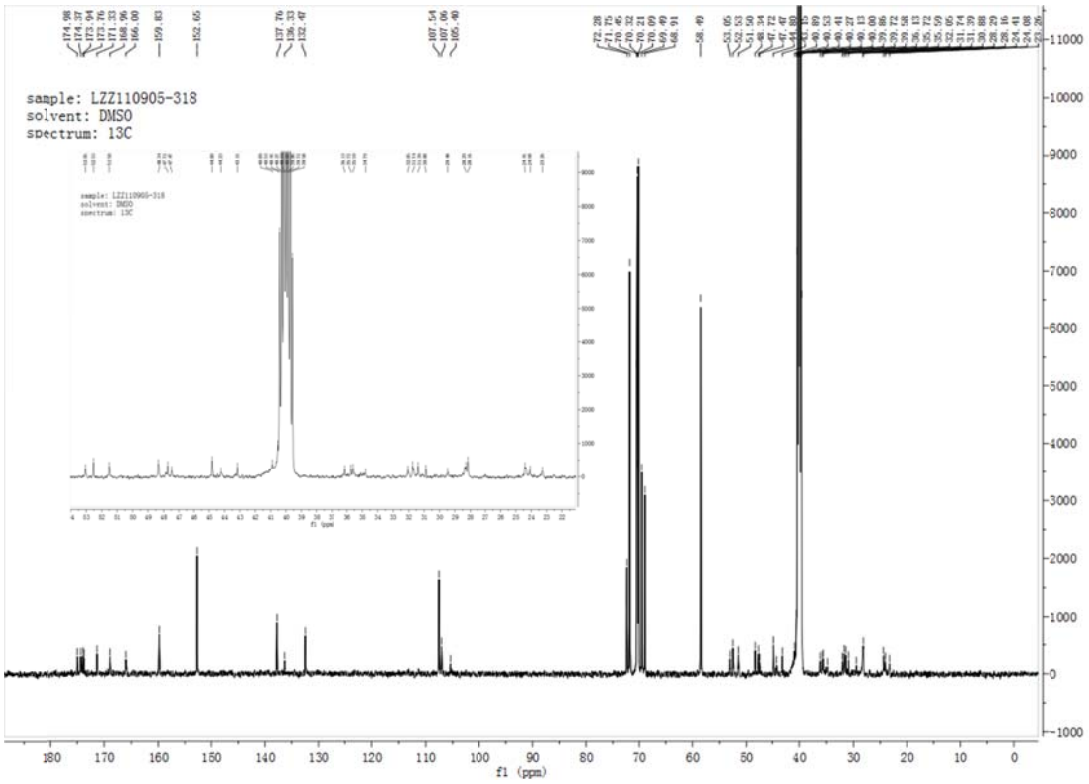


Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
686.3207	1	C 56 H 106 N 6 Na 2 O 25 S 2	100.00	686.3217	1.4	3.0	67.7	6.0	even	ok
	2	C 63 H 102 N 6 Na 2 O 20 S 2	27.06	686.3187	-2.9	-1.3	83.3	15.0	even	ok
	3	C 81 H 94 N 6 Na 2 O 7 S 2	0.58	686.3205	-0.4	1.3	169.0	37.0	even	ok



(**1b**)





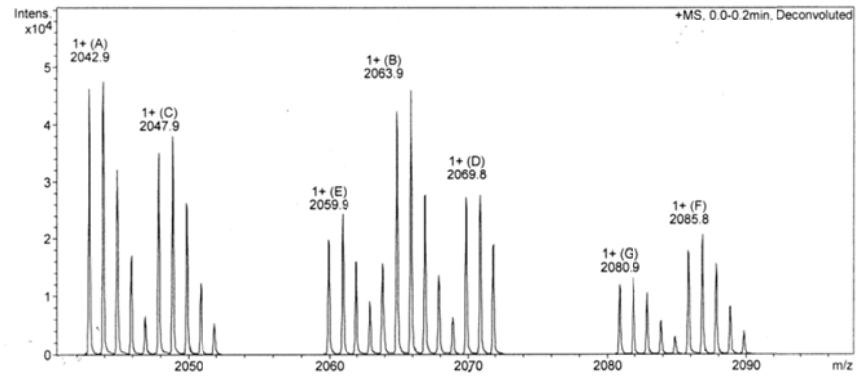
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\User\LZZ110807-11.d	Acquisition Date	9/5/2011 9:30:14 AM
Method	tune_wide_20110309.m	Operator	Ma
Sample Name	LZZ110807-11	Instrument / Ser#	micrOTOF-Q II 10203
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	550.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule

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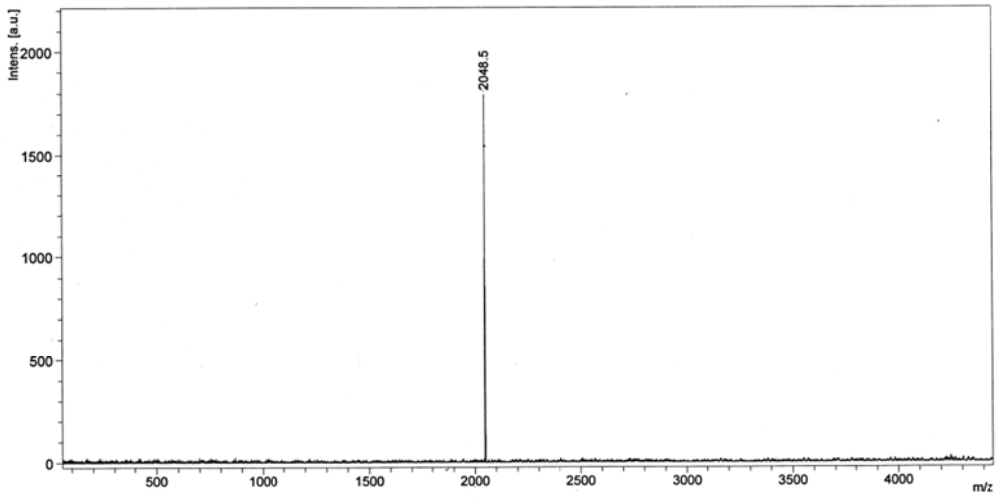
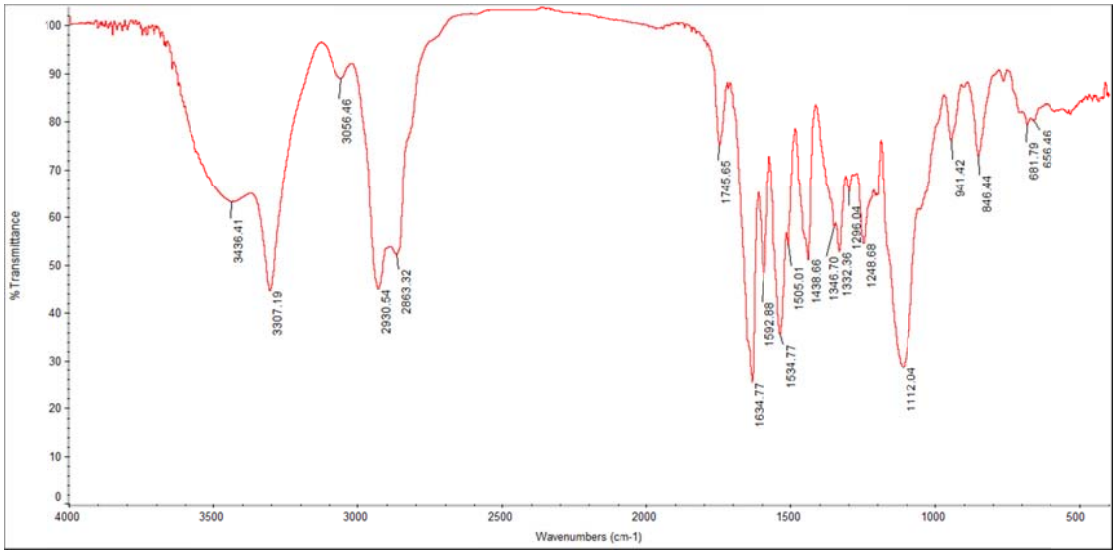
MALDI-TOF,CCA,LZZ110819-9,2011,08,25





9. References:

1. Y. Hu, S. L. Yu, Y. J. Yang, J. Zhu and J. G. Deng, *Chin. J. Chem.*, 2006, **24**, 795-799.
2. L. Xu, L. Shao, L. Chen, M. Hu and Y. Bi, *Chem. Lett.*, 2010, **39**, 1177-1179.
3. J. Rudolph, H. Theis, R. Hanke, R. Endermann, L. Johannsen and F.-U. Geschke, *J. Med. Chem.*, 2001, **44**, 619-626.