Electronic Supplementary Information

"12-Hydroxy stearic acid appended new amphiphilic scaffold for selective capture of hydrogen halides through supramolecular hydrogelation"

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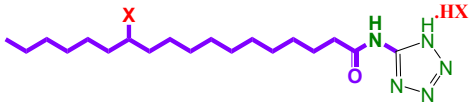
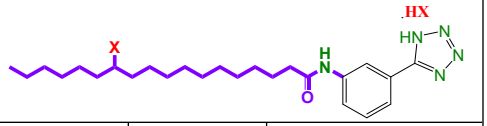
CONTENTS

Table S1: Heats of formation (H_f-s in Kcal/mol)) of the proposed structures of the constructs responsible for driving the gelation mechanism obtained using two semi-empirical methods namely Austin Model 1 (AM1) and Parametric Method 3 (PM3) and DFT are enlisted below.

Hydrogelator I				Hydrogelator II			
Methods	**X=Cl**	**X=Br**	**X=I**	**Methods**	**X=Cl**	**X=Br**	**X=I**
Austin Model 1(AM1) Hf (Kcal/mol)	-70.79 ±0.228	-42.94 ±1.074	-11.39 ±3.540	Austin Model 1(AM1) Hf (Kcal/mol)	-44.68 ±2.234	-16.8 ±0.42	-13.97 ±0.279
Parametric Method 3 (PM3) Hf (Kcal/mol)	-74.69 ±0.097	-40.0 ±3.734	-4.87 ±0.92	Parametric Method 3 (PM3) Hf (Kcal/mol)	-47.51 ±0.252	-24.65 ±2.375	-12.64 ±0.57
DFT B3LYP (Hf (kcal/mol))	-7.205 ±0.360	-3.987 ±0.199	-1.715 ±0.085	DFT B3LYP (Hf (kcal/mol))	-5.224 ±0.261	0.199 ±0.009	0.618 ±0.030

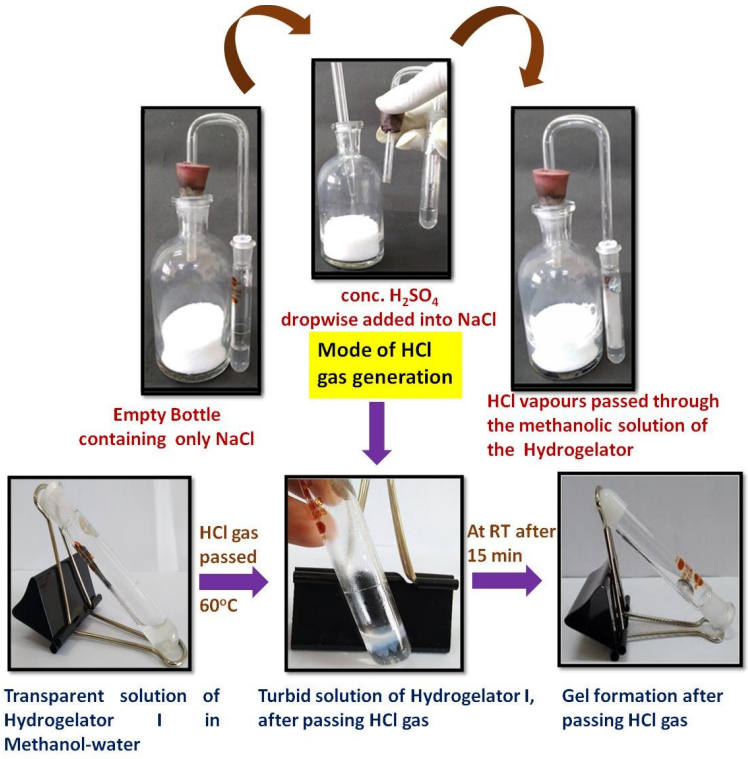


Fig S1 A. The gelation phenomena occurring in the presence of HCl gas, in compound **I.**

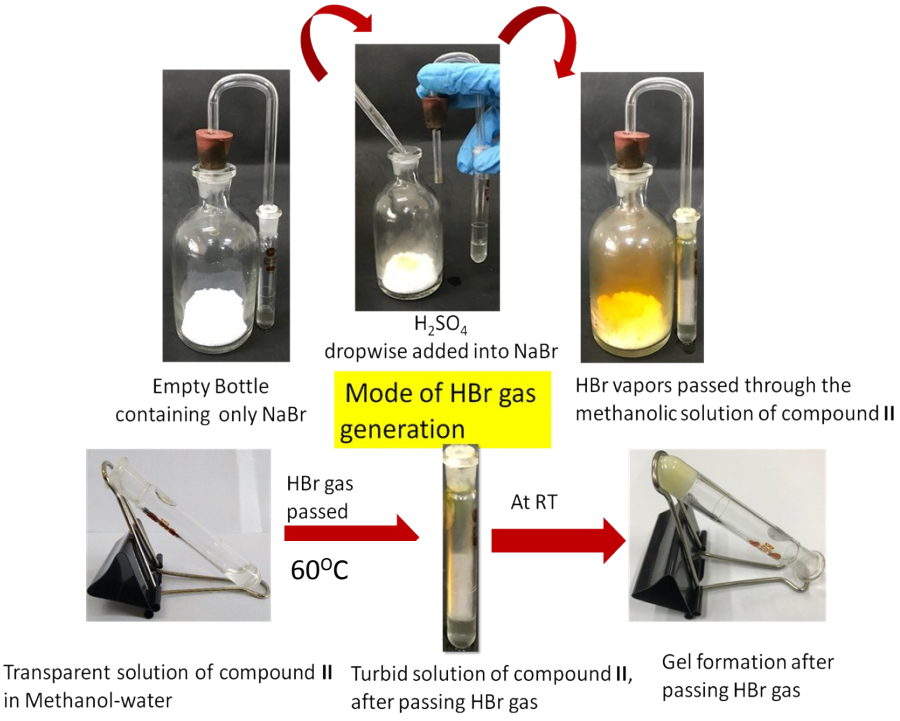


Fig S1 B. The gelation phenomena occurring in the presence of HBr gas, in compound **II**

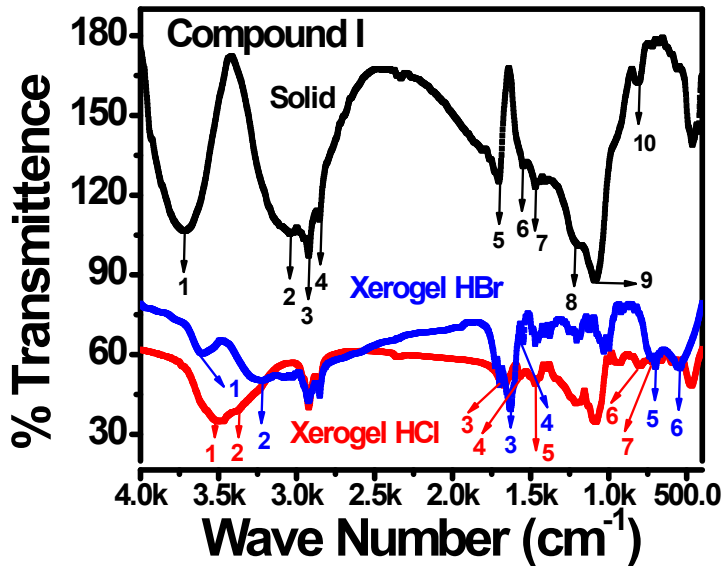


Fig S2. FT-IR spectrum of Compound **I**

Table S2 : IR peak values of Commpound I (solid, xerogel HCl, xerogel HBr)

Peak No.	Peak Value(Solid)	Peak No.	Peak Value(Xerogel-HCl)	Peak No.	Peak Value(Xerogel-HBr)
1	3724	1	3486	1	3608
2	3042	2	3370	2	3370
3	2932	3	1688	3	1656
4	2866	4	1554	4	1550
5	1716	5	1482	5	708
6	1544	6	816	6	538
7	1470	7	794		
8	1190				
9	1082				
10	824				

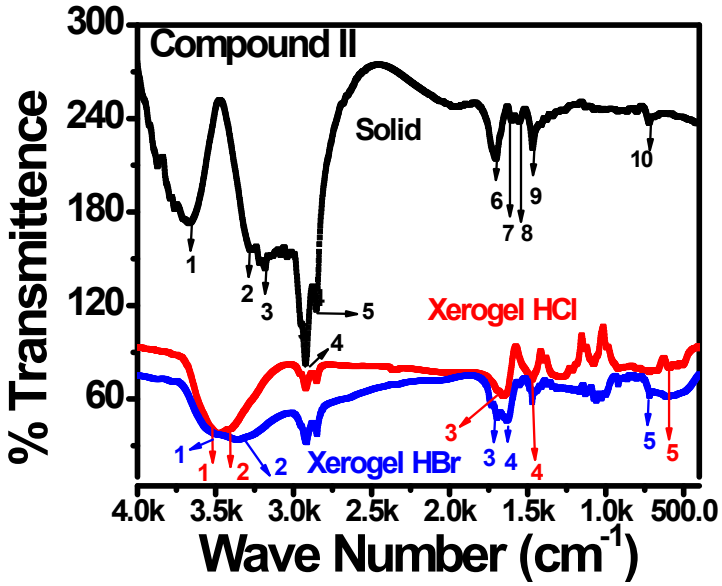


Fig S3. FT-IR spectrum of Compound **II**

Table S3 : IR peak values of Commpound II (solid, xerogel HCl, xerogel HBr)

Peak No.	Peak Value(Solid)	Peak No.	Peak Value(Xerogel-HCl)	Peak No.	Peak Value(Xerogel-HBr)
1	3670	1	3474	1	3486
2	3268	2	3392	2	3364
3	2930	3	1650	3	1650
4	2862	4	1548	4	1556
5	2858	5	662	5	616
6	1712				
7	1630				
8	1568				
9	1472				
10	724				

Table S4: Chemical Shifts (ppm) of Compound I and II in the solid state as well as in xerogels

S. No.		Compound I				
		Solid	Xerogel HCl	Xerogel HBr	Δδ(HCl)	Δδ(HBr)
1.	NH of Tetrazole 	15.78	15.78	----------	----------	----------
2.	Amide NH 	11.95	11.97	11.93	0.2	0.2
3.	12-HSA-OH 	4.21 – 4.19	----------	----------	----------	----------
Compound II						
		Solid	Xerogel HCl	Xerogel HBr	Δδ(HCl)	Δδ(HBr)
1.	NH of Tetrazole 	----------	----------	11.93	----------	----------
2.	Amide NH 	9.90	10.29	10.15	0.39	0.25
3.	12-HSA-OH 	4.23 – 4.22	----------	----------	----------	----------
4.	Aromatic Hs Ha, Hb, Hc,Hd	8.12 (Ha); 7.65 – 7.62 (Hb & Hd); 7.28 – 7.25 (Hc).	8.44 (Ha); 7.78 – 7.74 (Hb & Hd); 7.52 – 7.49 (Hc).	8.23 (Ha); 7.74 – 7.73 (Hb & Hd); 7.55 – 7.45 (Hc).	0.32 (Ha); 0.13 – 0.12 (Hb & Hd); 0.24 – 0.24 (Hc).	0.11 (Ha); 0.09 - 0.11 (Hb & Hd); 0.27 – 0.20 (Hc).

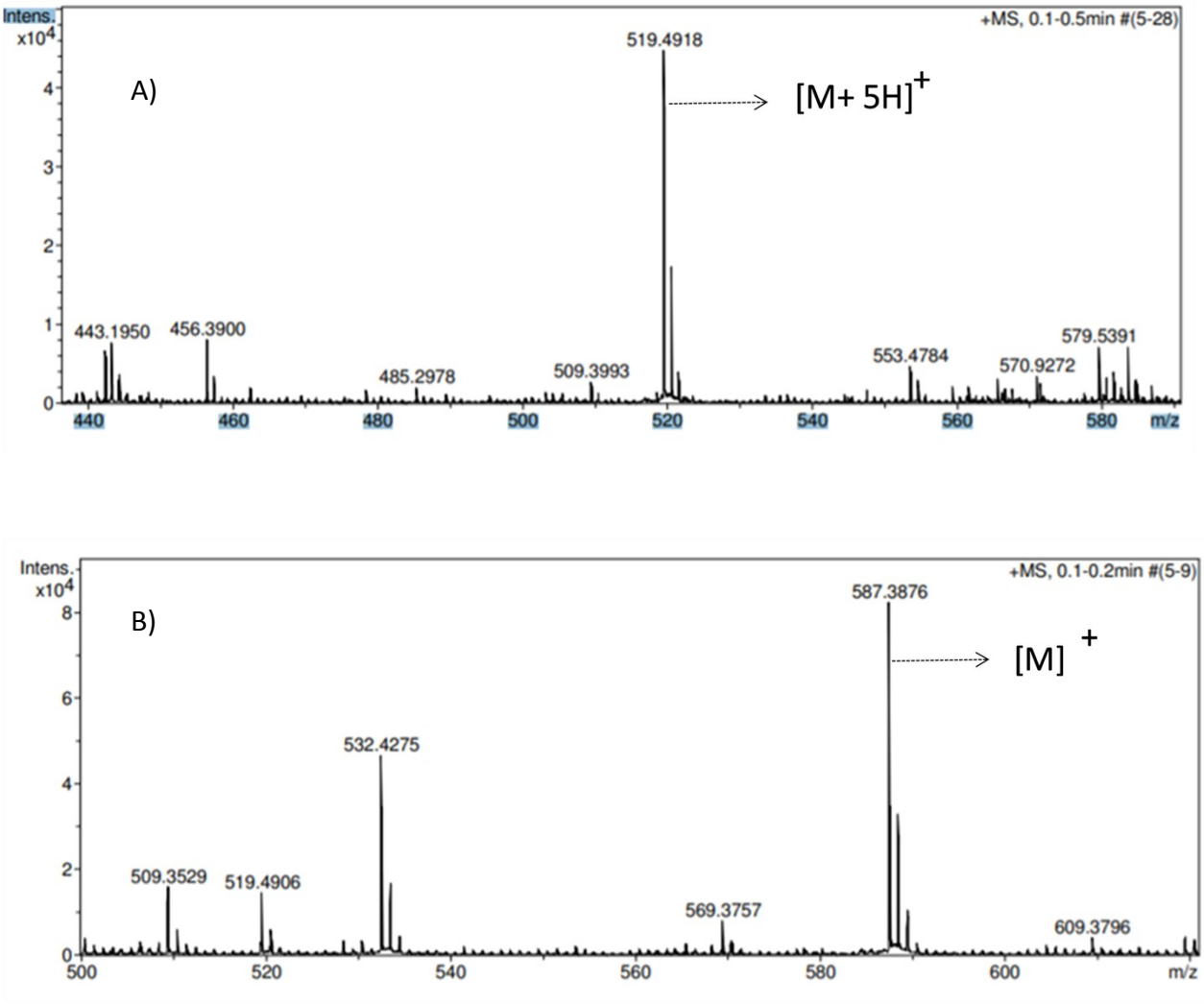


Fig S4. HR-MS spectra of the HBr salt of the bromide derivative of A) Compound **I** (Xerogel HBr); B) Compound **II** (Xerogel HBr).

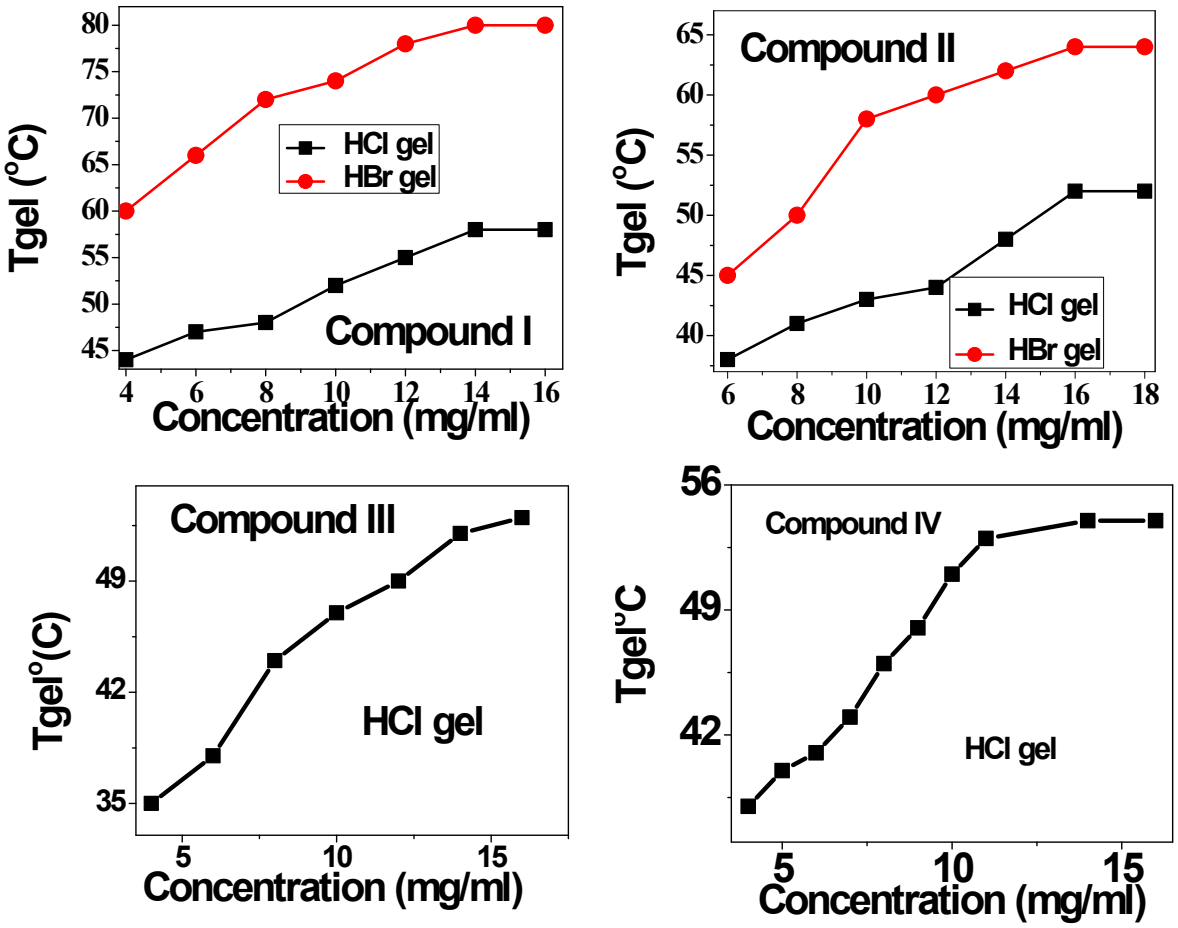
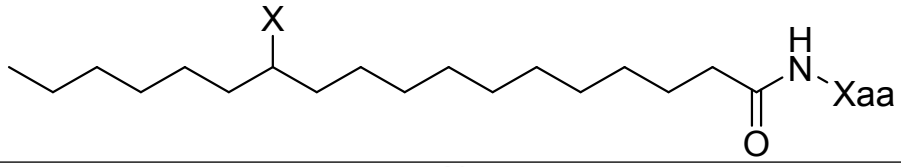
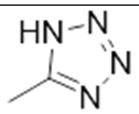
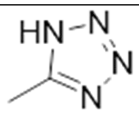
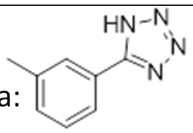
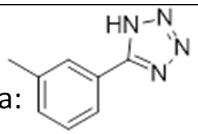
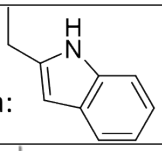
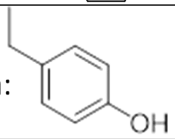


Fig S5. Tgel curves as a function of concentration in compound **I** -**IV**.

Table S5: The regularity of the gelation depending on "X" and "Xaa" groups

	Time taken for Gelation (approximately)
Compound I X: OH; Xaa:  (HCl)	30 (min)
Compound I X: OH; Xaa:  (HBr)	30 (min)
Compound II X: OH; Xaa:  (HCl)	20 (min)
Compound II X: OH; Xaa:  (HBr)	20 (min)
Compound III X: OH; Xaa:  (HCl)	50 (min)
Compound IV X: OH; Xaa:  (HCl)	4 hr

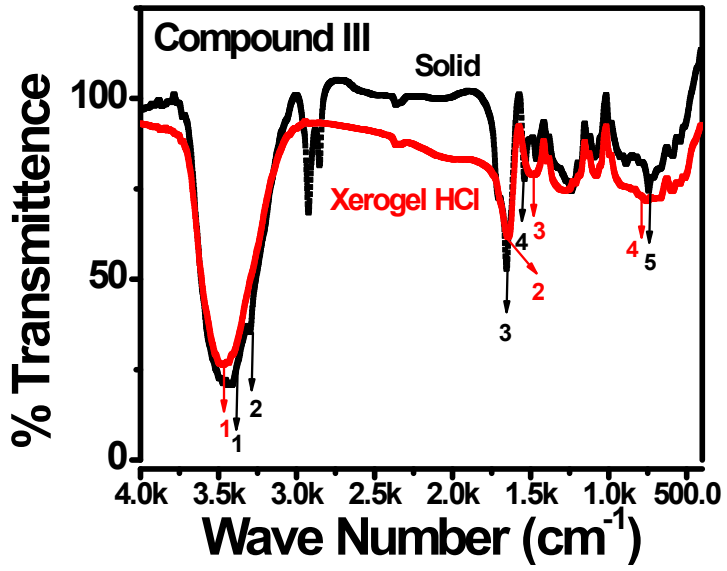


Fig S6. FT-IR spectrum of Compound **III**

Table S6 : IR peak values of Commpound III (solid, xerogel HCl)

Peak No.	Peak Value(Solid)	Peak No.	Peak Value(Xerogel-HCl)
1	3422	1	3456
2	3318	2	1656
3	1668	3	1516
4	1546	4	762
5	766		

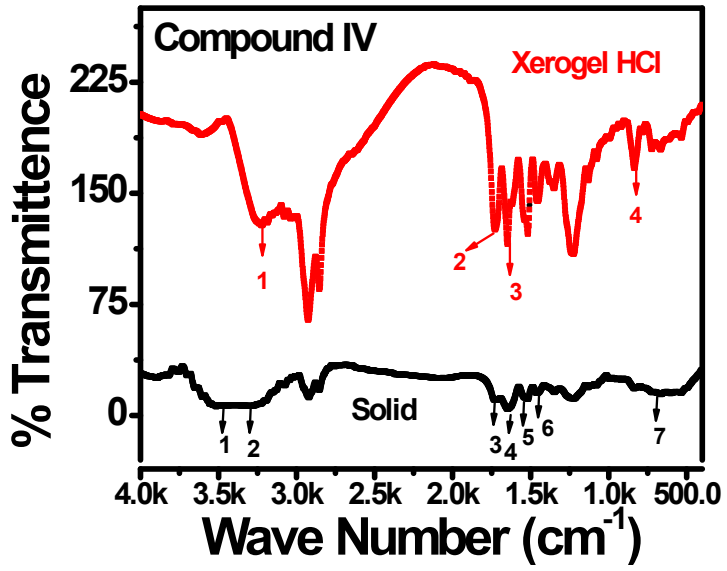


Fig S7. FT-IR spectrum of Compound **IV**

Table S7 : IR peak values of Commpound IV (solid, xerogel HCl)

Peak No.	Peak Value(Solid)	Peak No.	Peak Value(Xerogel-HCl)
1	3488	1	3305
2	3306	2	1656
3	1716	3	1522
4	1640	4	852
5	1512		
6	1468		
7	674		

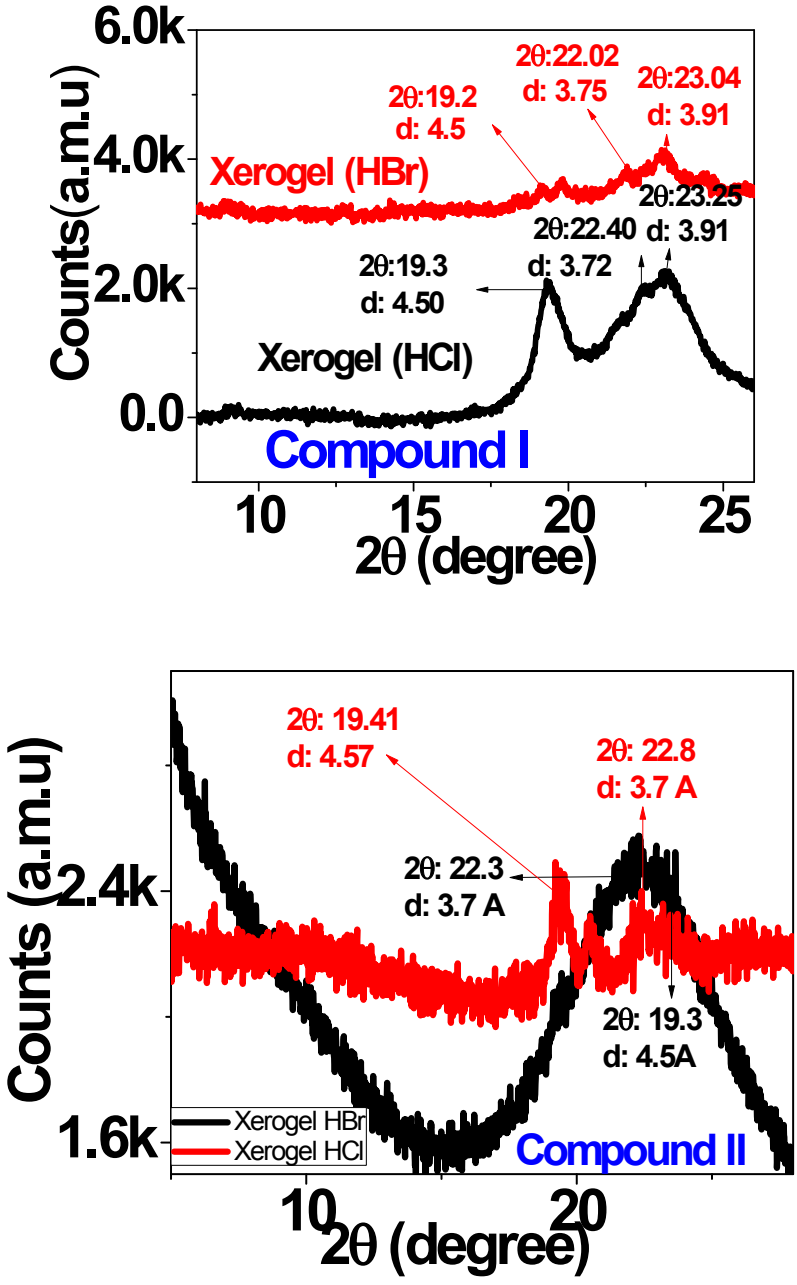


Fig S8. PXRD spectra of the xerogels of compound **I** and **II** (The units of 2θ are ° and d in Å).

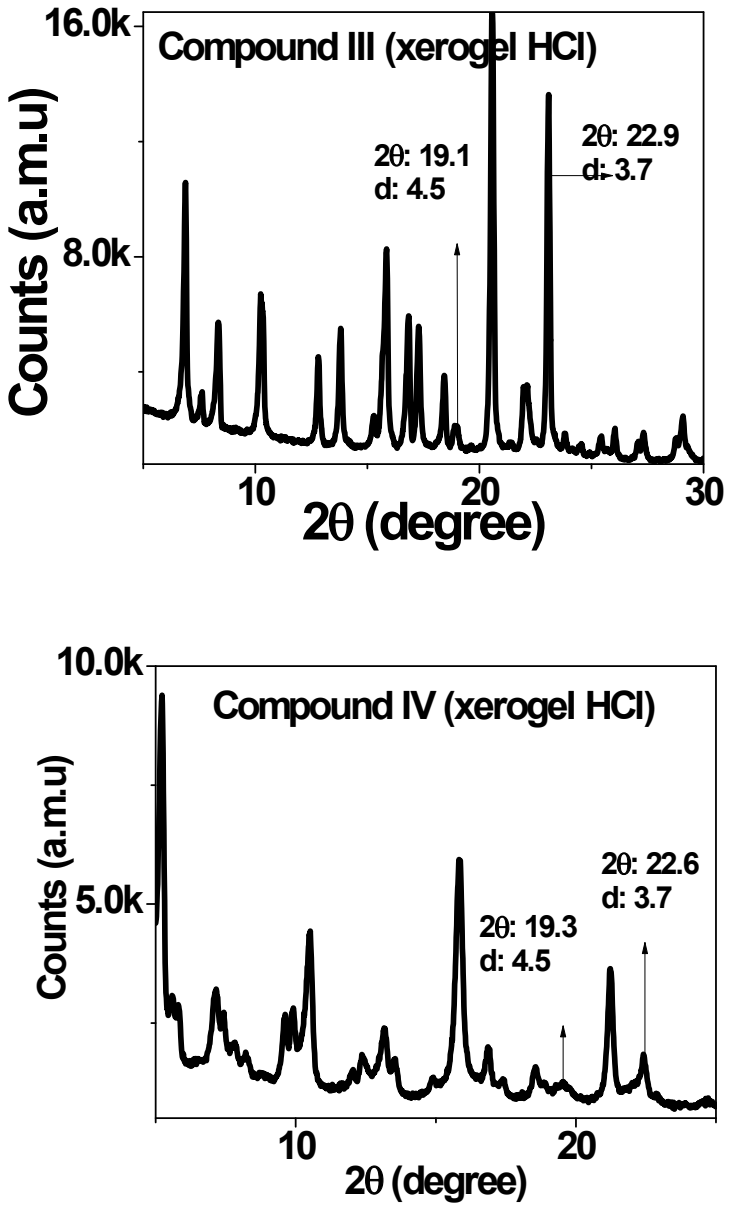


Fig S9. PXRD spectrum of the xerogel of compound **III - IV** (The units of 2θ are ° and d in Å).

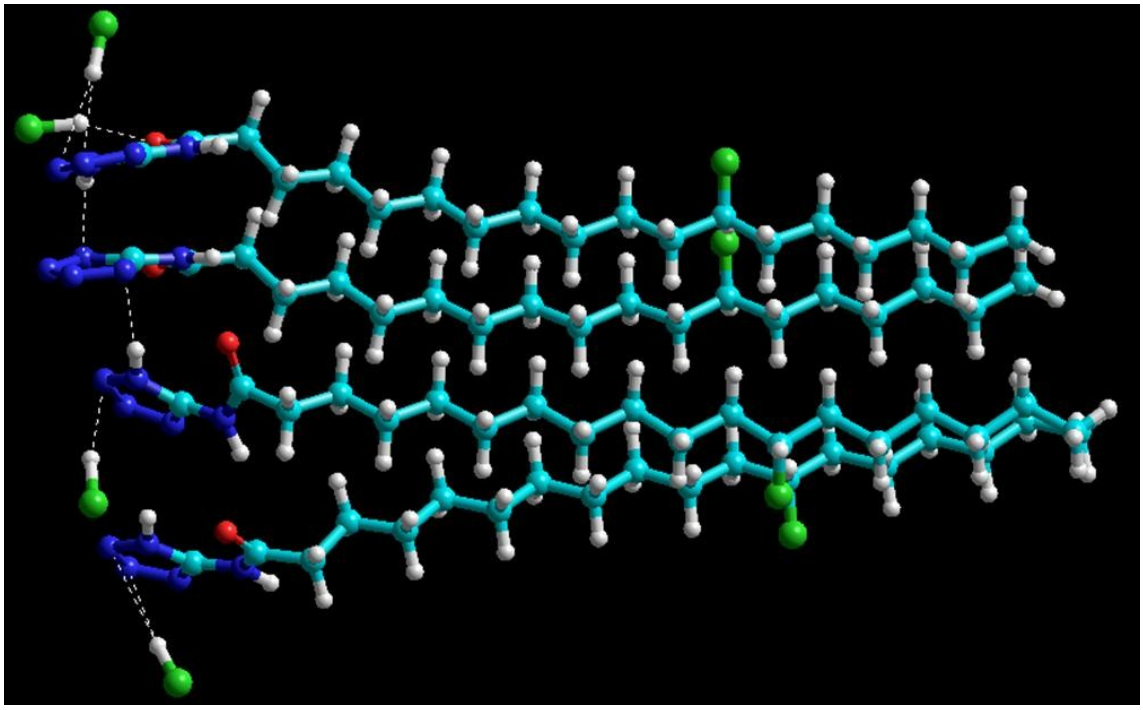


Fig S10A. Enlarged packing diagram of Compound **I** in parallel orientation.

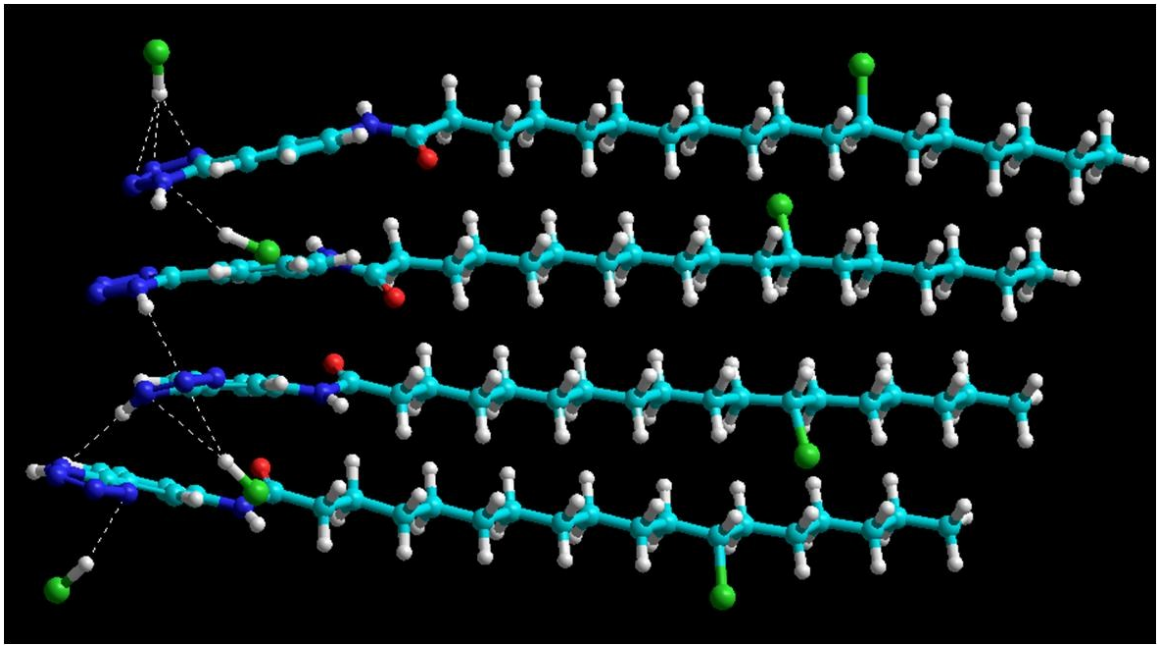


Fig S10B. Enlarged packing diagram of Compound **II** in parallel orientation.

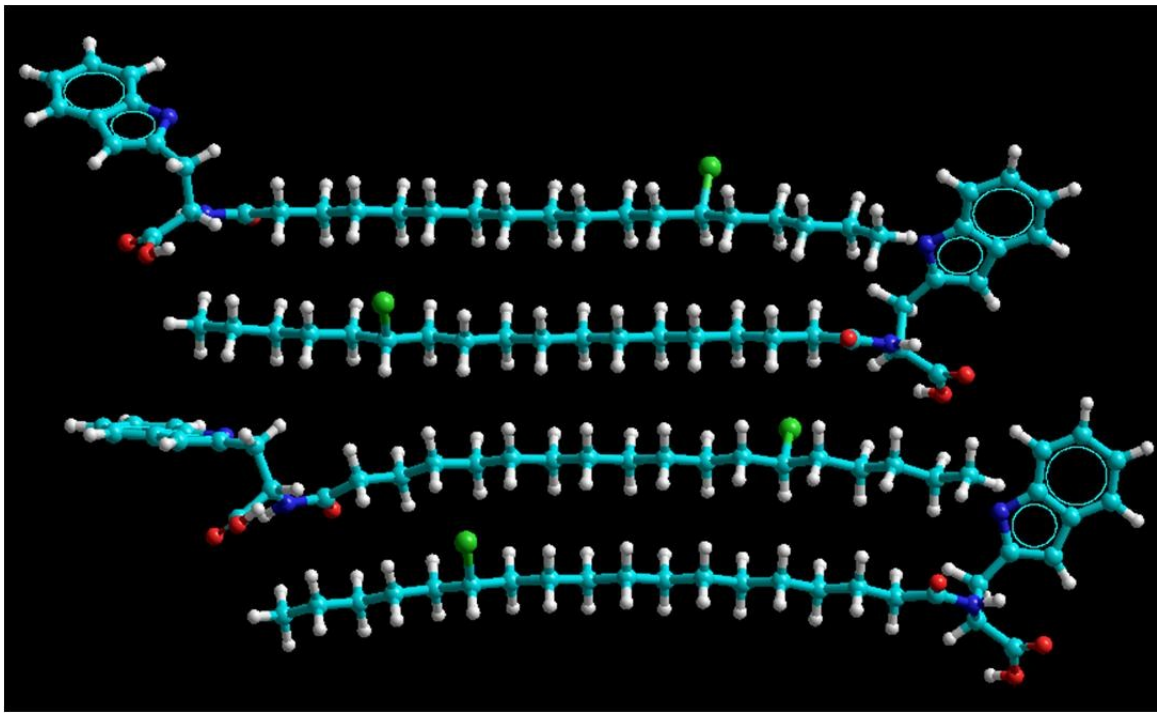


Fig S10C. Enlarged packing diagram of Compound **III** in anti-parallel orientation.

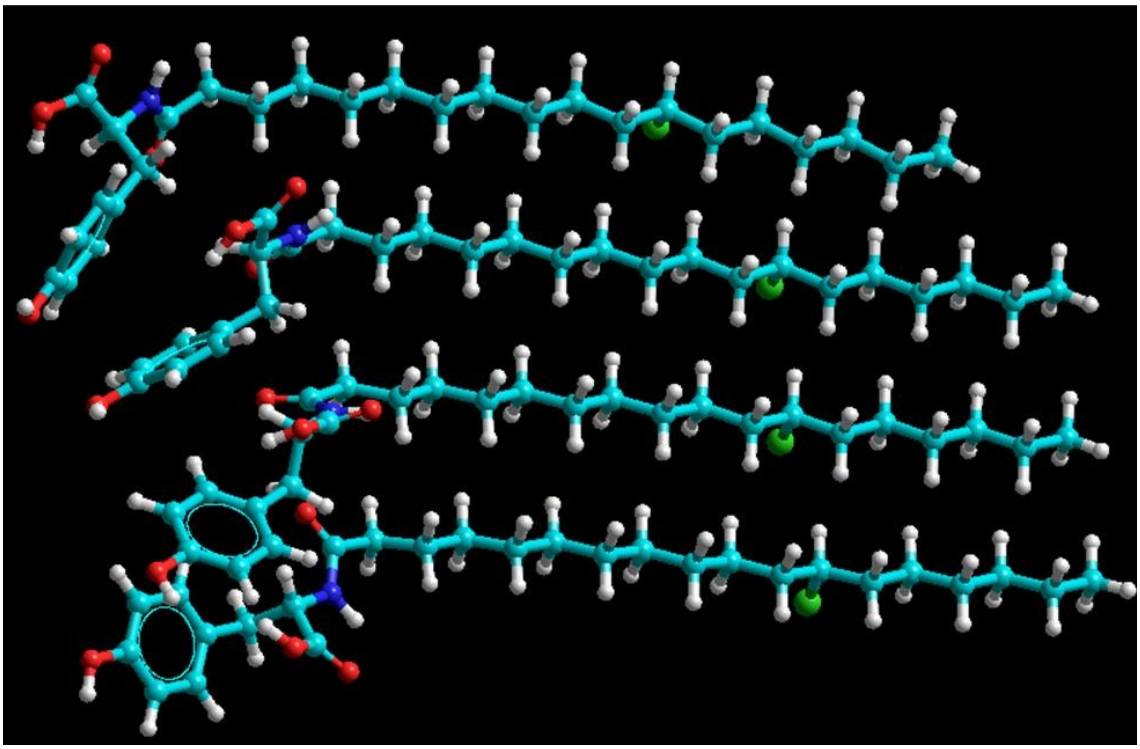


Fig S10D. Enlarged packing diagram of Compound **IV** in parallel orientation.

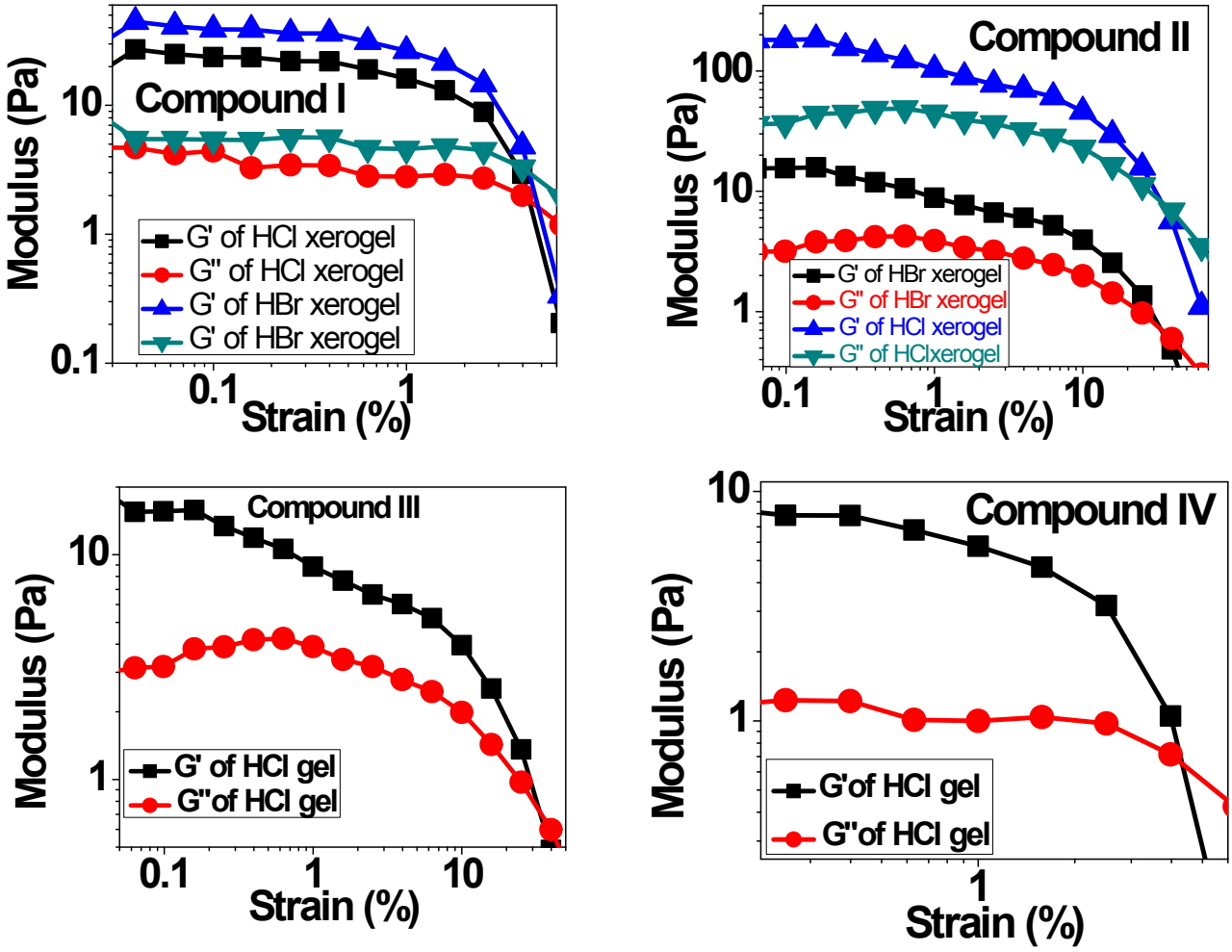


Fig S11. Rheological measurements of compounds **I - IV** showing the variation of G' and G'' with variation in strain

Experimental Section

Abbreviations:

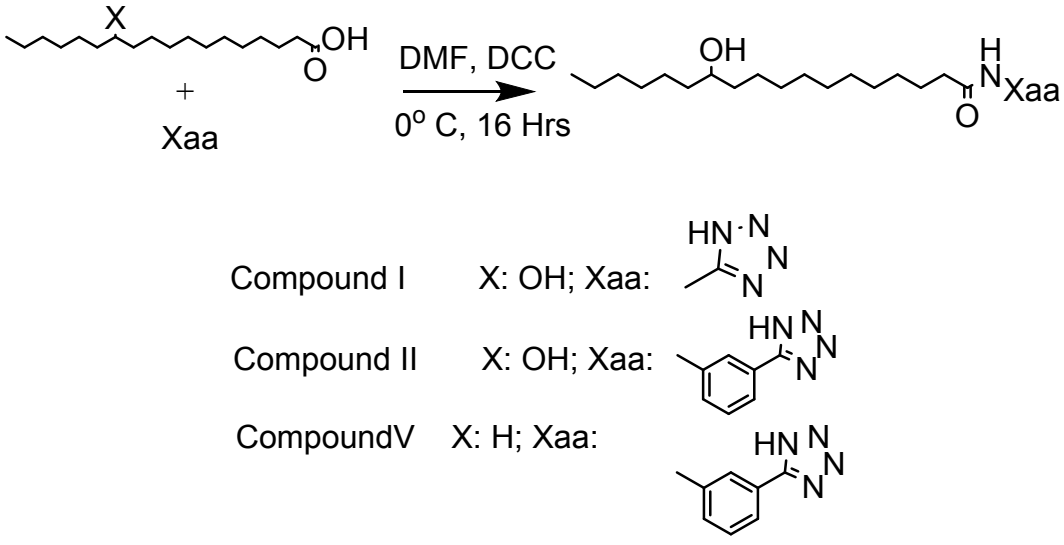
DCC, Dicyclohexyl-carbodiimide; 12 HSA,12 Hydroxy Stearic acid; SA: Stearic Acid; DMF, Dimethyl Formamide

Materials and methods:

All chemicals and solvents were purchased from Spectrochem. The Compounds I –III were synthesized using conventional solution phase methodology, with racemization free techniques. All the intermediates obtained were checked for purity by thin layer chromatography (TLC) on silica gel. The final molecules were purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and ethyl acetate and petroleum ether mixture as the eluent. The compounds were finally characterized by NMR, IR spectroscopy and mass spectrometry.

Instrumentation:

- All ^{1}H NMR studies were recorded on a Bruker Advance 400 model spectrometer operating at 400 MHz respectively. The peptide concentrations were in the range 10 mM in d_6-DMSO for ^{1}H NMR spectroscopy for both the solid compounds as synthesized as well as xerogels.
- Mass spectra were recorded in ESI-MS mode on MicroTOF-Q-II instrument manufactured by Bruker Daltonics;



Scheme 1. Synthesis strategy for the preparation of Compounds **I-III**

Synthesis of the compounds

Compound I: The Amino tetrazole (1.691 gm, 8.333 mmol) was added to an ice cold solution of 12-HSA (1 gm, 3.333 mmol) in 8 ml of DMF. Then to the reaction mixture DCC (0.824 gm, 4mmol: 1, 3-dicyclohexylcarbodiimide) was added to it and the reaction was stirred for 18 hours at room temperature. The progress of the reaction was monitored by TLC. The residue was taken up in ethyl acetate and the DCU was filtered off. The organic layer was washed with 2 M HCl / 1 M Sodium carbonate and brine (2 × 100 ml), dried over anhydrous sodium sulphate and evaporated in *vacuo* to obtain a white solid material. The crude peptide was used without further purification.

Yield: 1.10 gm, (90%, 3.0 mmol); Mp=175 - 173 ˚C; IR data (Solid): 3724, 3042, 2932, 2866, 1716, 1544, 1470, 1190, 1082, 824; $C_{19}H_{37}N_5O_2$: 366.9 $[M-H]^+$; MS (calculated) m/z: 367.5 $[M]^+$;

Compound I (solid): ^{1}H NMR (d_6-DMSO, ppm): 15.78 (NH of tetrazole, 1H, s); 11.95 (Amide NH of Aminotetrazole, 1H, s); 4.21 - 4.19 (OH of 12-HSA, 1H, broad peak); 2.45 - 2.42 (CH_2-H of 12-HSA adjacent to carbonyl, 1H, m) ; 2.20 - 2.17 (CH_2-H of 12-HSA adjacent to carbonyl, 1H, m) ; 1.61 - 1.59 (C_{12}-H of 12-HSA , 1H, m); 1.50 - 1.47 (C_{12}-H of 12-HSA , 1H, m); 1.34 - 1.25 (14 CH_2-Hs 12HSA , 28 H, m); 0.86 (CH_3 s of 12-HSA, 3H, t, *J* = 8Hz).

Xerogel (HCl): ^{1}H NMR (d_6-DMSO, ppm): 15.78 (NH of tetrazole, 1H, s); 11.97 (Amide NH of Aminotetrazole, 1H, s); 2.45 - 2.42 (CH_2-H of 12-HSA adjacent to carbonyl, 1H, m) ; 2.30 - 2.27 (CH_2-H of 12-HSA adjacent to carbonyl, 1H, m) ; 1.61 - 1.59 (C_{12}-H of 12-HSA , 1H, m); 1.51 - 1.47 (C_{12}-H of 12-HSA , 1H, m); 1.34 - 1.24 (14 CH_2-Hs 12HSA , 28 H, m); 0.86 (CH_3 s of 12-HSA, 3H, t, *J* = 8Hz); (Xerogel-HCl): IR: 3486, 3370, 1688, 1554, 1482, 816, 794.

Xerogel (HBr) ^{1}H NMR (d_6-DMSO, ppm): 11.93 (Amide NH of Aminotetrazole, 1H, s); 2.45 - 2.42 (CH_2-H of 12-HSA adjacent to carbonyl, 1H, m) ; 2.30 - 2.27 (CH_2-H of 12-HSA adjacent to carbonyl, 1H, m) ; 1.61 - 1.58 (C_{12}-H of 12-HSA , 1H, m); 1.52 - 1.47 (C_{12}-H of 12-HSA , 1H, m); 1.33 - 1.24 (14 CH_2-Hs 12HSA , 28 H, m); 0.85 (CH_3 s of 12-HSA, 3H, t, *J* = 8Hz); Xerogel-HBr: IR: 3608, 3370, 1656, 1550,708, 538.

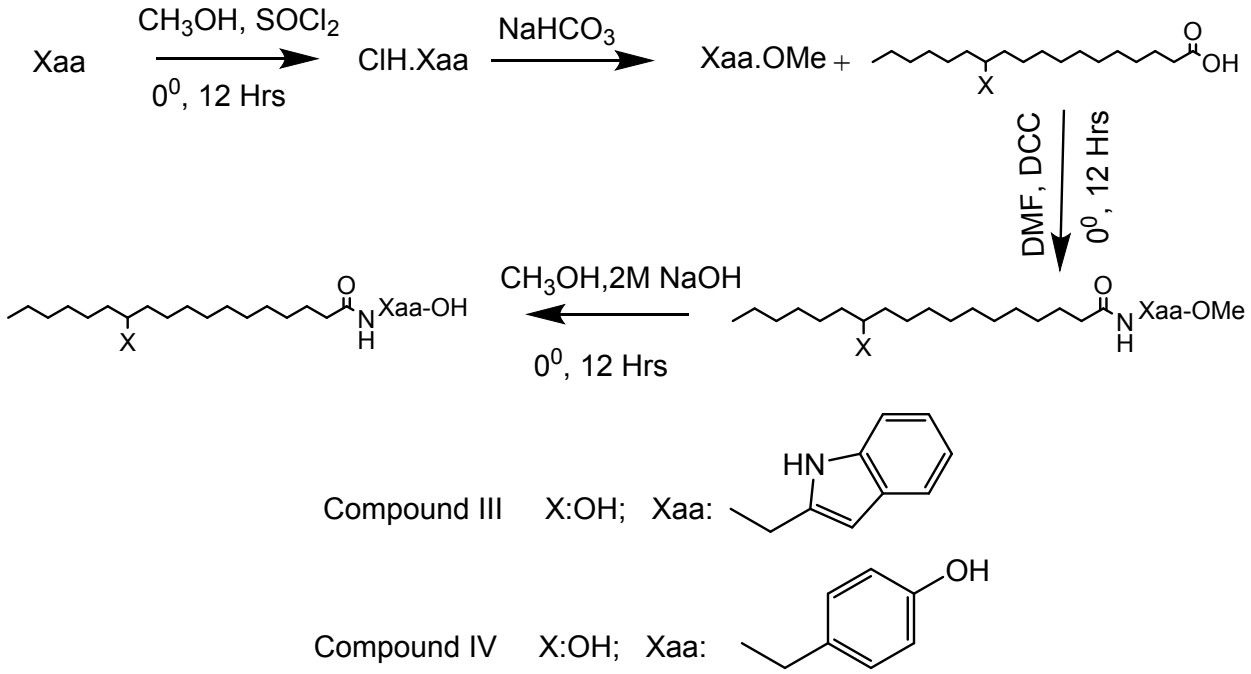
Compound II: This compound was prepared using the same synthetic procedure as that of compound **I**.

Yield: 1.25 gm, (85%, 4.16 mmol); Mp=76-74˚c; IR data (Solid) 3670, 3268, 2930, 2862, 2858, 1712, 1630, 1568, 1474, 724; $C_{25}H_{41}N_5O_2$: 443.0 $[M]^+$; MS (calculated) m/z: 443.33 $[M]^+$; ^{1}H NMR (d_6-DMSO, ppm): 9.90 (Amide NH of Anilinetetrazole, 1H, s); 8.12 (Ha of of Anilinetetrazole, 1H, s); 7.65 - 7.62 (Hb & Hd of Anilinetetrazole, 2H, m) ; 7.28 - 7.25 (Hc of Anilinetetrazole, 1H, m); 4.23 - 4.22 (OH of 12-HSA, 1H, broad peak); 2.32-2.29 (CH_2-Hs of 12-HSA adjacent to carbonyl, 2H, m); 1.65 -1.58 (CH_2-Hs of 12-HSA, 2H, m); 1.30-1.25 (14 CH_2-Hs 12HSA , 28 H, m); 0.86 (CH_3 s of 12-HSA, 3H, t, *J* = 8Hz).

Xerogel (HCl) ^{1}H NMR (d_6-DMSO, ppm): 10.29 (Amide NH of Anilinetetrazole, 1H, s); 8.44 (Ha of Anilinetetrazole, 1H, s); 7.78 -7.74 (Hb & Hd of Anilinetetrazole, 2H, m); 7.52-7.49 (Hc of Anilinetetrazole, 1H, m); 2.36 - 2.33 (CH_2-H of 12-HSA adjacent to carbonyl, 1H, m) ; 2.19 - 2.16 (CH_2-H of 12-HSA adjacent to carbonyl, 1H, m) ; 1.61 - 1.57 (C_{12}-H of 12-HSA , 1H, m); 1.49 - 1.46 (C_{12}-H of 12-HSA , 1H, m); 1.31 - 1.23 (14 CH_2-Hs 12HSA , 28 H, m); 0.84 (CH_3 s of 12-HSA, 3H, t, *J* = 8Hz; (Xerogel-HCl) IR: 3474, 3392, 1650, 1548, 662.

Xerogel (HBr) ^{1}H NMR (d_6-DMSO, ppm): 11.93 (NH of Anilinetetrazole, 1H, s); 10.15 (Amide NH of Anilinetetrazole, 1H, s); 8.23 (Ha of Anilinetetrazole, 1H, s); 7.74 -7.73 (Hb & Hd of Anilinetetrazole, 2H,

m); 7.55-7.45 (Hc of Anilinetetrazole, 1H, m); 2.45 - 2.42 (CH_2-H of 12-HSA adjacent to carbonyl, 2H, m) ; 1.61 - 1.58 (C_{12}-H of 12-HSA , 1H, m); 1.49 - 1.47 (C_{12}-H of 12-HSA , 1H, m); 1.33 - 1.24 (14 CH_2-Hs 12HSA , 28 H, m); 0.86 (CH_3 s of 12-HSA, 3H, t, *J* = 8Hz); (Xerogel - HBr) IR: 3486 , 3364, 1650, 1556, 616.



Scheme 2. Synthesis strategy for the preparation of Compounds **III and IV**

12-HSA-Trp-OMe (1): The Trp-OMe obtained from its hydrochloride (2.120 gm, 8.33 mmol) was added to an ice cold solution of 12 hydroxy stearic acid (1 gm, 3.33 mmol) in 8 ml of DMF. Then DCC (0.824 gm, 4mmol: 1, 3- Dicyclohexyl- carbodiimide) was added to the cold mixture, and stirred for 18 hours at room temperature. The progress of the reaction was monitored by TLC. The residue was taken into ethyl acetate and the DCU was filtered off. The organic layer was washed with 2 M HCl (3 × 100), 1 M Sodium carbonate (3 × 100 ml) and brine (2 × 100 ml), dried over anhydrous sodium sulphate and evaporated in vacuo to obtain a white solid material. The crude peptide was used without further purification.

Yield: 1.42 gm, (85%, 4.72mmol).

Compound III: The compound **1** (1.42 g, 4.72 mmol) was dissolved in methanol (20 mL) and 2 N NaOH (8.86 mL) was dropwise added to it. The progress of the reaction was monitored by TLC. After completion of the reaction the methanol was evaporated. The residue obtained was diluted with water and washed with diethylether. The aqueous layer was cooled, neutralized with 2 N HCl and extracted with ethyl acetate. The solvent was evaporated in vacuo to give a white solid.

Yield: 1.296 gm (80%, 2.66 mmol); Mp = 115-113˚C; IR data (Solid): 3422, 3318, 1668, 1546, 766; $C_{29}H_{46}N_2O_4$: 485.3 $[M-H]^+$; MS (calculated) m/z: 486.35 $[M]^+$.

Compound III (solid): ^{1}H NMR (d_6-DMSO, ppm): 12.52 (OH of Acid, 1H, s); 10.81 (NH of indole ring of Trp, 1H, broad peak); 8.01(Amide NH of Trp ,1H,d, *J* = 8Hz); 7.51- 6.92 (Aromatic protons of indole ring, 5H, m); 4.47 - 4.41 (C^α of Trp,1H, m); 4.17 (OH of 12-HSA, 1H,m) 3.15 – 2.93 (CH_2-Hs of 12-HSA adjacent

to carbonyl and C^{β}-Hs of Trp , 6H, m) ; 2.04 - 1.99 (C_{12}-H of 12-HSA , 1H, m); 1.41-1.07 (14 CH_2-Hs12HSA , 28 H, m); 0.83 (CH_3 s of 12-HSA, 3H, t, *J* = 8Hz).

Xerogel (HCl): ^{1}H NMR (d_6-DMSO, ppm): 10.82 (NH of indole ring of Trp, 1H, broad peak); 8.05(Amide NH of Trp ,1H,d, *J* = 8Hz); 7.51-6.92 (Aromatic protons of indole ring, 5H, m); 4.48 - 4.43 (C^{α} of Trp,1H, m); 4.28 (OH of 12-HSA,1H,broad) 3.17 - 2.96 (CH_2-Hs of 12-HSA adjacent to carbonyl and C^{β} of Hs of Trp, 6H, m) ; 2.06-2.01 (C_{12}-H of 12-HSA , 1H, m); 1.42-1.13 (14 CH_2-Hs12HSA , 28 H, m); 0.85 (CH_3 s of 12-HSA, 3H, t, *J* = 8Hz).(xerogel-HCl) IR: 3456, 1656,1516,762.

Compound IV: This compound was synthesized following the same experimental procedures as that of Compound **III** starting from 12-HSA-Tyr-OMe **(2).**

Yield: 1.222 g (88%, 2.63 mmol) Mp=81-79˚C; IR data (Solid) : 3488, 3306, 1716,1640,1512,674; $C_{27}H_{45}NO_5$: 462.3 $[M-H]^+$; MS (calculated) m/z: 463.33 $[M]^+$.

Compound IV (solid): ^{1}H NMR (d_6-DMSO, ppm): 12.54 (OH of Acid, 1H, s); 9.21 (OH of Tyr,1H,s); 8.00 (Amide NH of Tyr, 1H, d, *J* = 8Hz); 6.97(Ha proton of Tyr, 1H,d, *J* = 8Hz); 6.62 (Hb proton of Tyr, 1H,d, *J* = 8Hz); 4.32-4.27 (C^{α} of Tyr and OH of 12-HSA, m); 2.90-2.66 (CH_2-Hs of 12-HSA adjacent to carbonyl and C^{β}-Hs of Trp , 6H, m); 2.03-1.94 (C_{12}-H of 12-HSA , 1H, m); 1.40-1.06 (14 CH_2-Hs12HSA , 28 H, m); 0.83 (CH_3 s of 12-HSA, 3H, t, *J* = 8Hz).

Xerogel (HCl): ^{1}H NMR (d_6-DMSO, ppm): 8.05 (Amide NH of Tyr, 1H, d, *J* = 8Hz); 6.99 (Ha proton of Tyr, 1H,d, *J* = 8Hz); 6.63 (Hb proton of Tyr, 1H,d, *J* = 8Hz); 4.33-4.29 (C^{α} of Tyr and OH of 12-HSA, m); 2.92-2.68 (CH_2-Hs of 12-HSA adjacent to carbonyl and C^{β}-Hs of Trp , 6H, m); 2.03-1.96 (C_{12}-H of 12-HSA , 1H, m); 1.42-1.05 (14 CH_2-Hs12HSA , 28 H, m); 0.83-0.819 (CH_3 s of 12-HSA, 3H, m).(Xerogel-HCl)IR: 3305, 1522,1656,852.

Compound V: This compound was synthesized following the same experimental procedures as that of Compound **I** and **II**.

Yield: gm, (85%, 6.27 mmol) Mp = 198 - 200^{o}c; LC-MS: $C_{25}H_{41}N_5O$: 423.3 $[M]^+$; MS (calculated) m/z: 423.3 $[M]^+$; IR :(Solid) 3479, 1659,1547,1470,1419; ^{1}H NMR (d_6-DMSO, ppm): 9.90 (Amide NH of Anilinetetrazole, 1H, s); 8.10 (Ha of of Anilinetetrazole, 1H, s); 7.61 -7.57 (Hb & Hd of Anilinetetrazole, 2H, m) ; 7.24 - 7.20 (Hc of Anilinetetrazole, 1H, m); 2.30 - 2.26 (CH_2-Hs of SA, 2H, m) ; 1.58 -1.55(CH_2-Hs of SA, 2H, m); 1.26 - 1.21 (14 CH_2-Hs of SA,28 H, m) 0.84 - 0.81 (CH_3-Hs of SA, 3H, *t* , J=8Hz).

Preparation of the Hydrogel: For preparation of the hydrogels, 6 mg of each of the compounds were dissolved in methanolic water medium and dropwise concentrated hydrohalic acids (HCl /HBr /HI) were added (MeOH: Water: Hydrohalic acids: 3:1:1). Initially a clear solution was produced, but gradual addition of hydrohalic acids led to complete immobilization of the solution instantaneously resulting in the formation of an opaque gel for HCl / HBr. The formation of the hydrogels were confirmed by the inverted vial method.

Thermal Stability Studies (Tgel): Gel melting studies were performed by heating the hydrogels in a digital water bath having temperature ranging from 25 to 99.9^{o}C and temperature stability of (±)0.5^{o}C. The temperature was increased at the above range in steps of 2^{o}C and the hydrogels were stabilized for

10 min at each temperature. The Tgel temperature was assessed by investigating the final material using an inverted vial method. The process was repeated on three samples and the average value is reported.

Fourier –transform infrared (FT-IR) Spectroscopy: The FT-IR spectra were recorded using a KBr pellet method. A freeze dried sample of the gel was mixed with KBr to make the pellet. The spectrum was recorded from 500 to 4000 cm^{-1} and 20 accunulations were averaged to obtain single spectra on an Agilent CARY 620 FTIR spectrophotometer. The background was collected using a blank KBr pellet. Spectra were background substracted to correct for atmospheric interference.

Powdered X-ray Diffraction: The hydrogel was freeze dried by using liquid nitrogen at first and it was further dried in lyophilizer to get xerogel for X-ray diffraction study. The dried powder was then placed on a glass plate and the experiment was carried out by using an X-ray diffractometer (Bruker AXS, Model No. D8Advance). The instrument was operated at a 40 kV voltages and 40 mA current using Ni-filtered Cu-Karadiation and the instrument was calibrated with a standard Al_2O_3 (corundum) sample before use. For scan, the Lynx Eye superspeed detector was used with scan speed 0.3 s and step size 0.028.

Field Emission scanning electron microscopic study (FESEM)

The morphology of the xerogels obtained from the compounds **I – IV** were gold coated and observed under a FESEM microscope (JEOL JSM - 6700F).

Rheology

Rheological measurements were carried out using a Rheoplus MCR302 (Anton paar) rotational rheometer with parallel plate geometry and the data were processed using start rheometer software. For the oscillatory shear measurements, a parallel top plate with a 25 mm diameter and 1.0 mm gap distance were used. Gels for the rheological experiments were prepared on the bottom plate of the rheometer. The concentrations of the all the hydrogels were 6 mg/ml.

Computation Methodologies

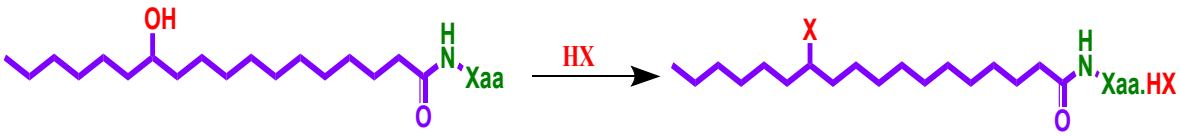
All computational studies were performed using AM1 (Austin Model 1) and PM3 (Parametric Method 3) molecular models, implemented through Heperchem 8.0 trial version software package (Hypercube Inc. USA). The Model Build function of the software package was first used to generate the starting structures of the -halo derivatives of Compounds **I** - **IV** prior to performing their energy minimization using Polak-Ribiere conjugate gradient algorithm (with RMS gradient as 0.1). The optimized structures thus obtained, were merged with a HX molecule and energy minimised once again to obtain the final Hydrogelator-HX complex structure (where applicable) and calculate the corresponding H_f values. To obtain the plausible self-assembly conformations of these hydrogelator complexes, at least four units of the above-mentioned structures were merged together to be used as the starting points for the subsequent calculations. These structural units were energy minimised using molecular mechanics with AMBER99 forcefield and reported.

DFT

For this the models were created using Spartan08 software. DFT Calculation was done using a molecule of Hydrogelator I and a HX molecule. B3LYP method was used along with Ahlrichs and co-workers type SVP basis set. Optimization and frequency calculation was done and tight convergence criteria was used. Optimization of reactant, hydrogen halide, product and water molecule was done.

The heat of formation was calculated using the formula:

ΔH_f= (Enthalpy of Hydrogelator 1 + Enthalpy of H_2O) – (Enthalpy of Reactant + (2*(Enthalpy of HX))



For Compound **I**:

For Compound **II**:

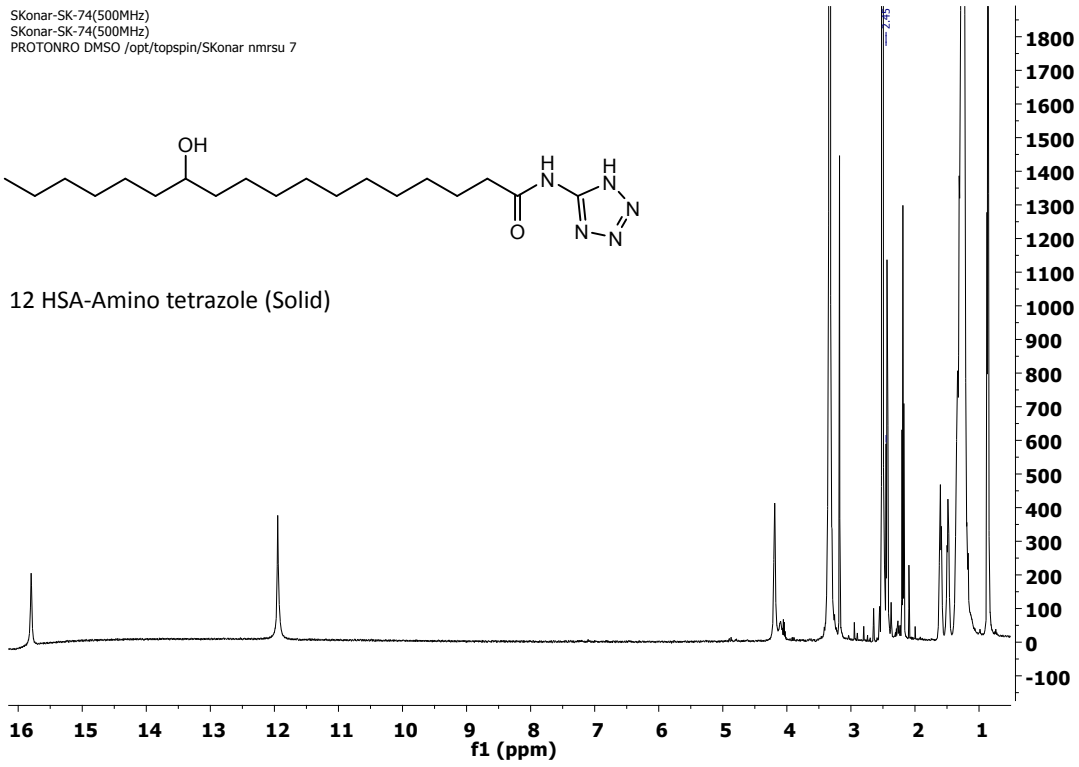


Fig S12 . NMR Spectrum of Compound **I** (Solid)

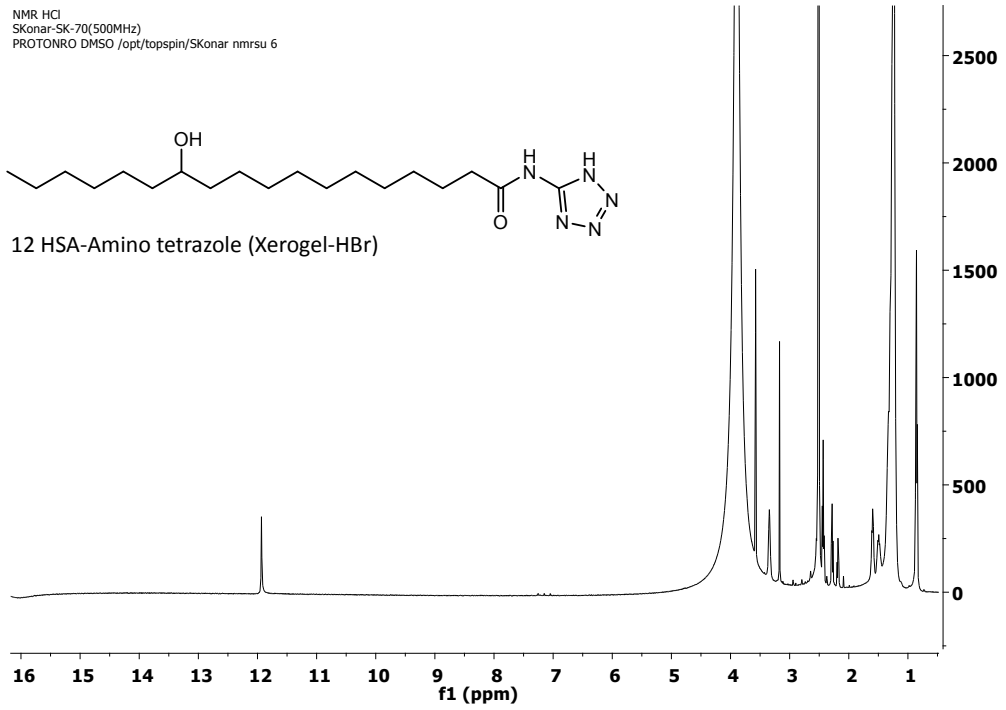


Fig S13. NMR Spectrum of Compound **I** (Xerogel HBr)

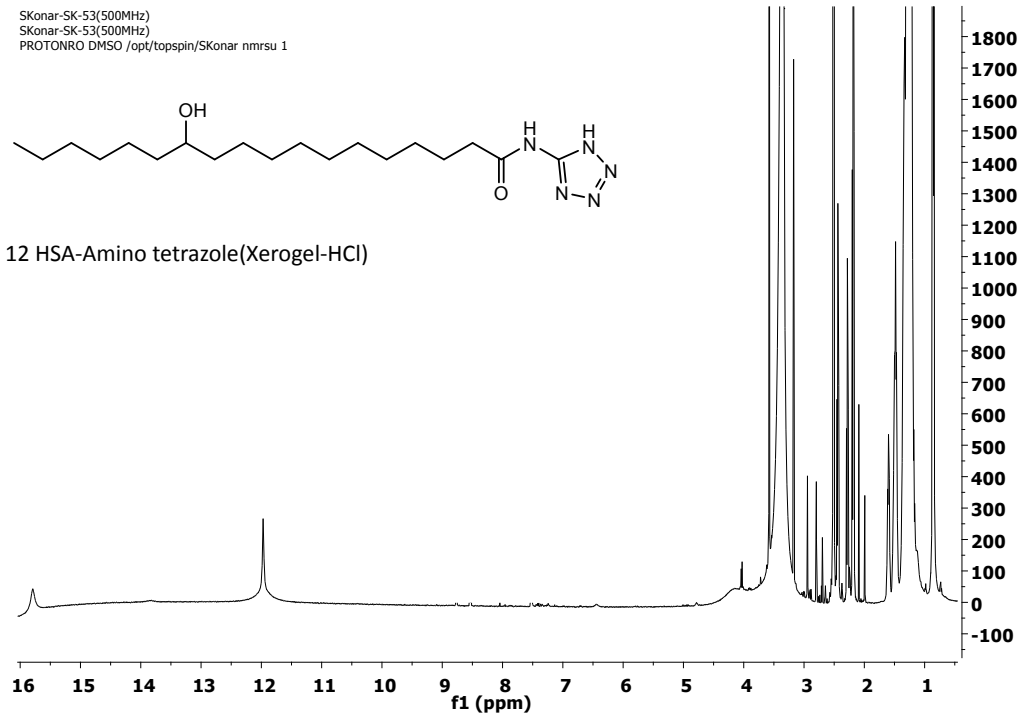


Fig S14. NMR Spectrum of Compound **I** (Xerogel-HCl)

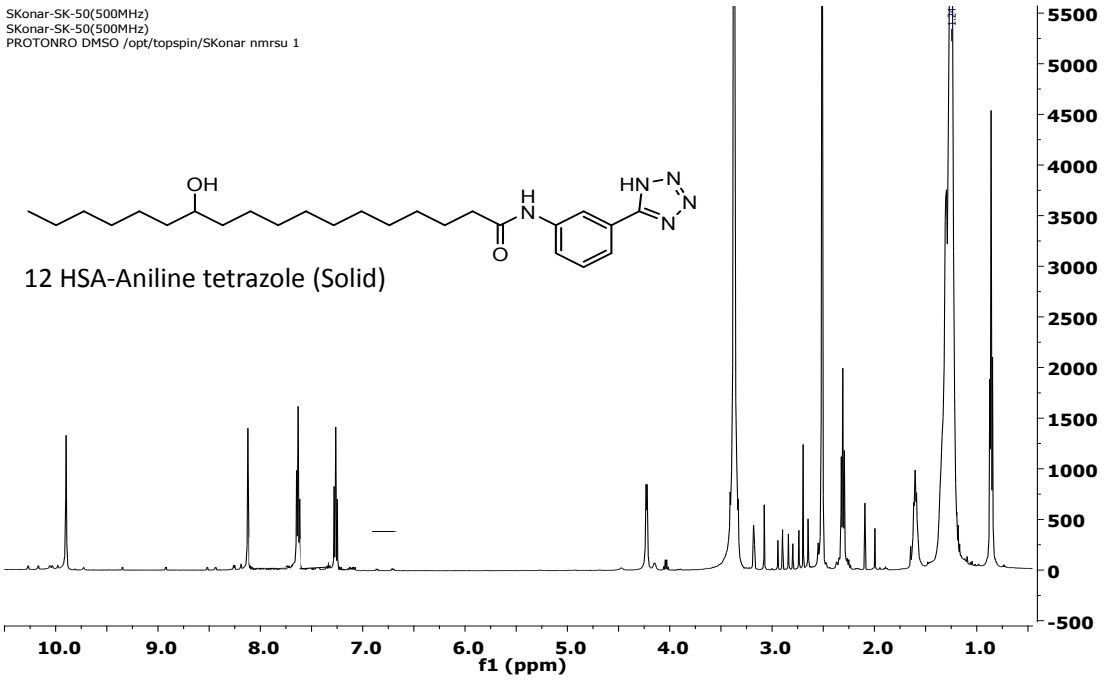


Fig S15. NMR Spectrum of Compound **II** (Solid)

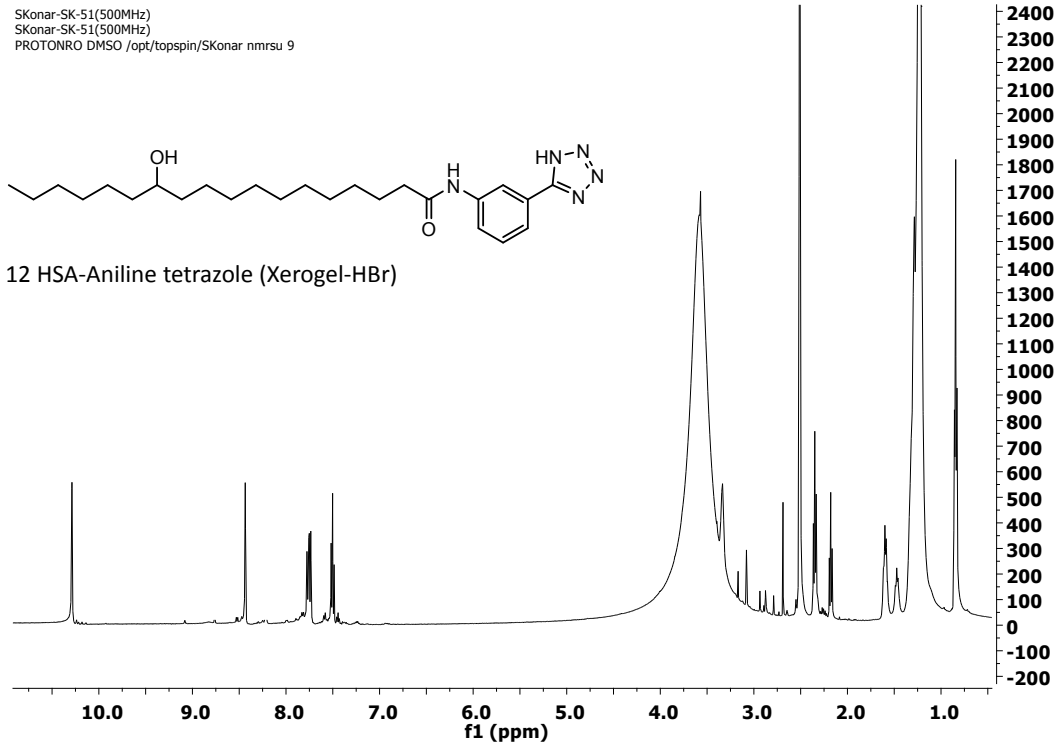


Fig S16. NMR Spectrum of Compound **II** (Xerogel-HBr)

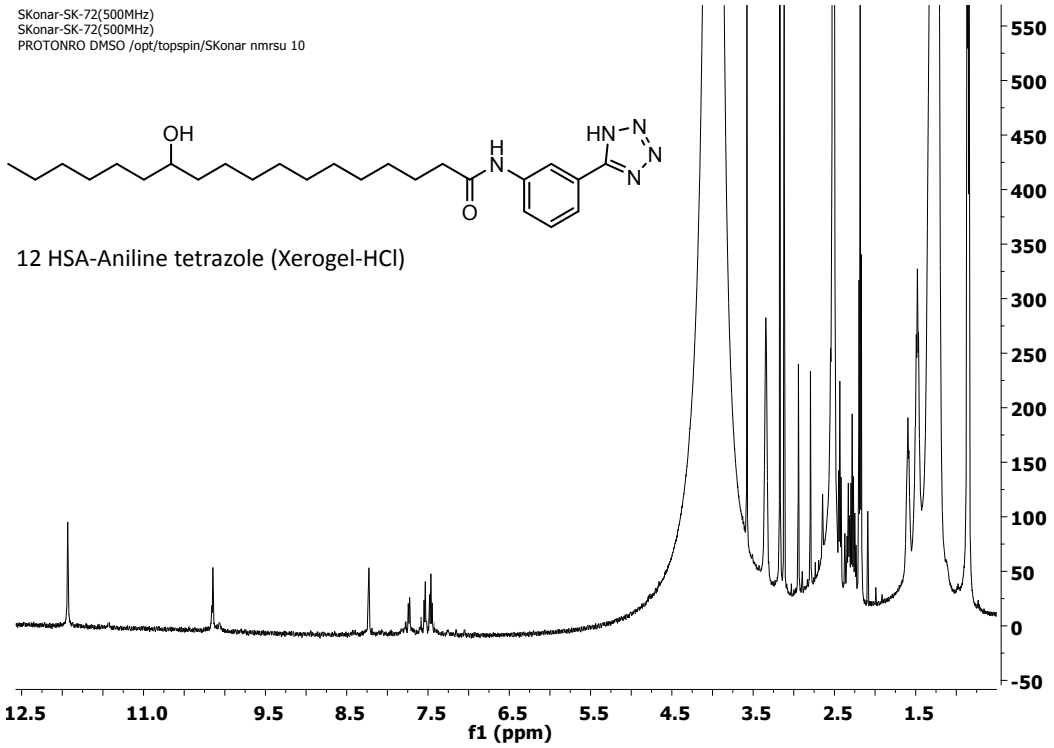


Fig S17. NMR Spectrum of Compound **II** (Xerogel-HCl)

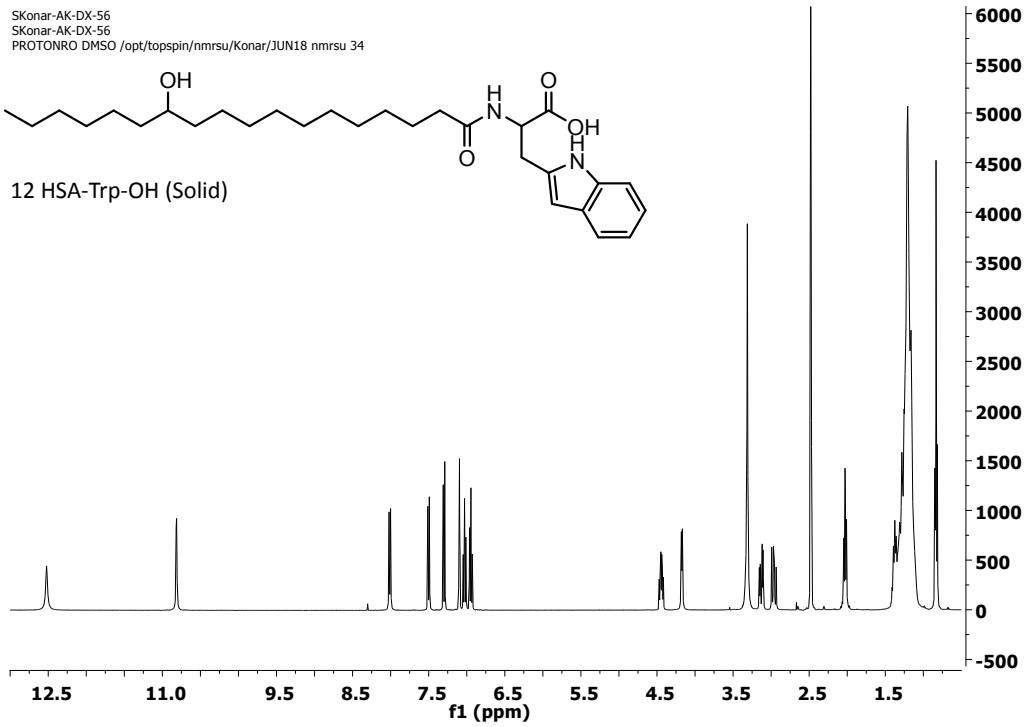


Fig S18 . NMR Spectrum of Compound **III** (Solid)

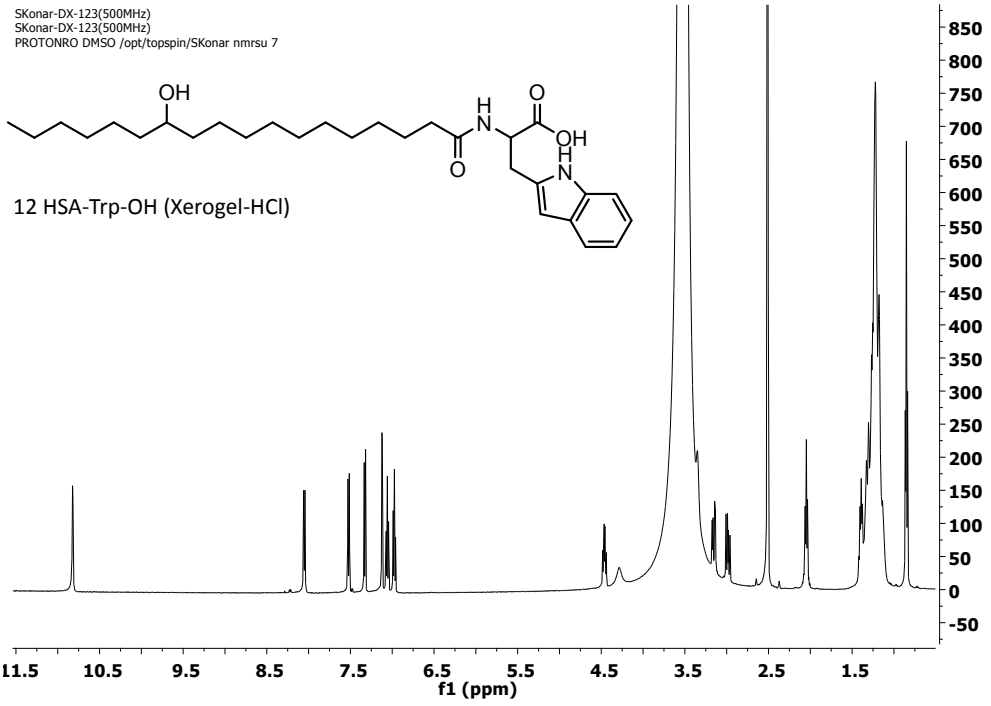


Fig S19 . NMR Spectrum of Compound **III** (Xerogel-HCl)

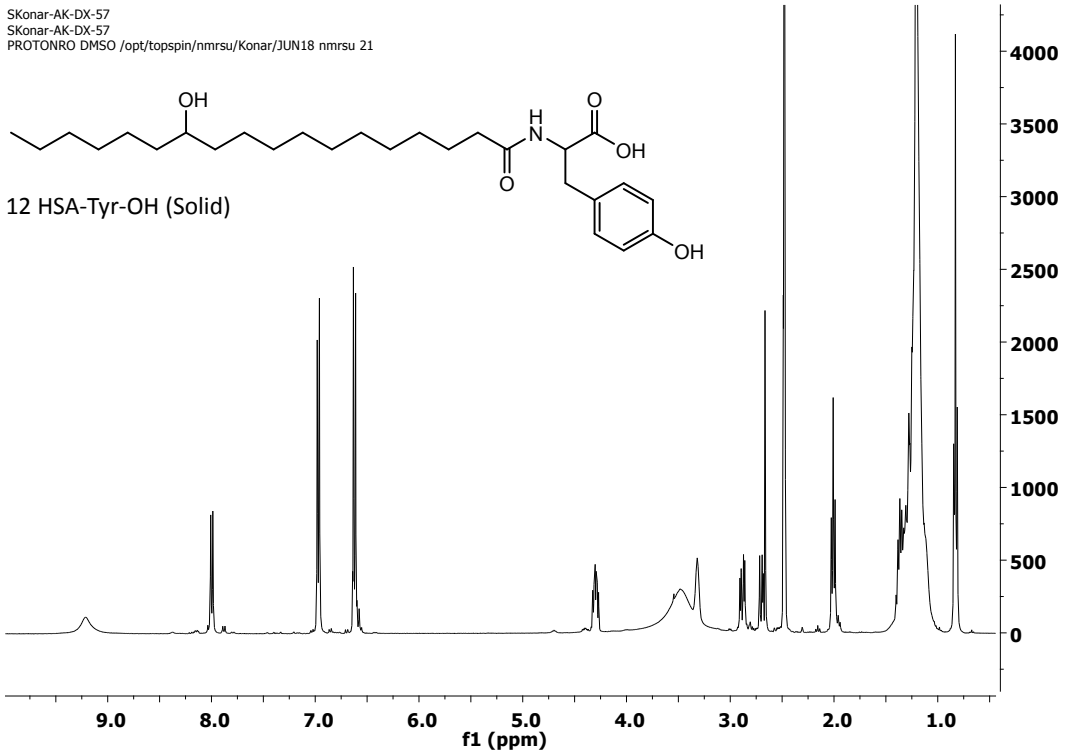


Fig S20. NMR Spectrum of Compound **IV** (Solid)

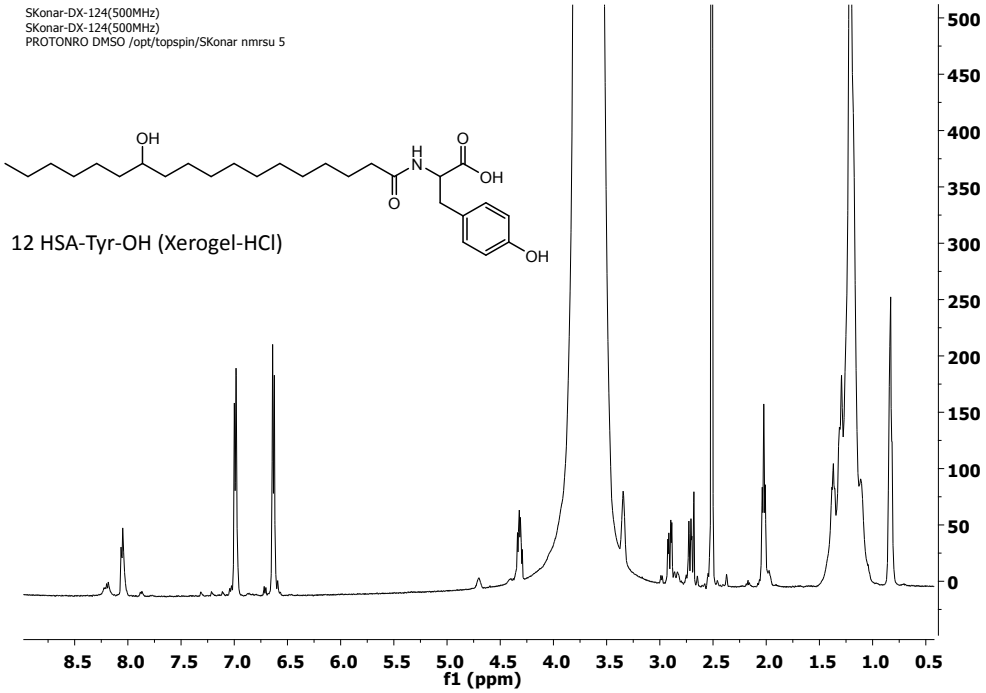


Fig S21. NMR Spectrum of Compound **IV** (Xerogel-HCl)

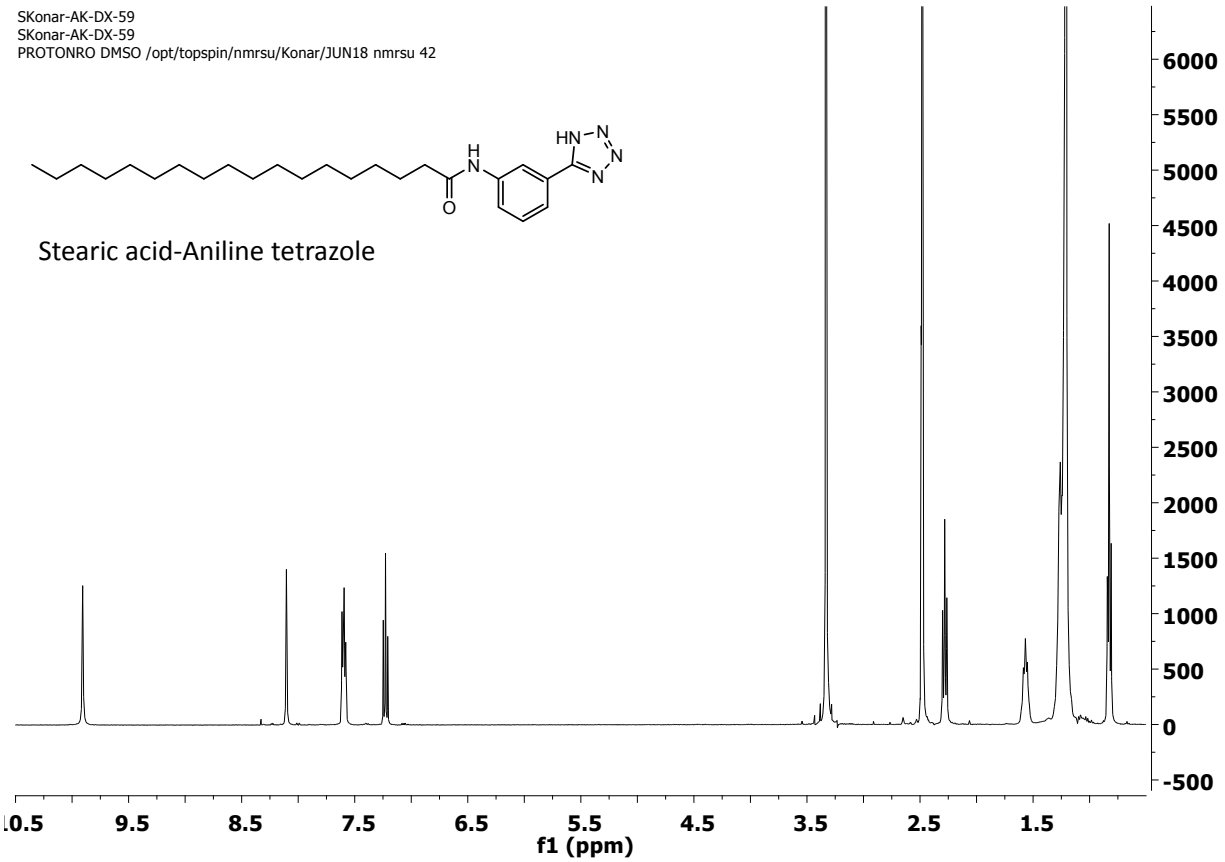
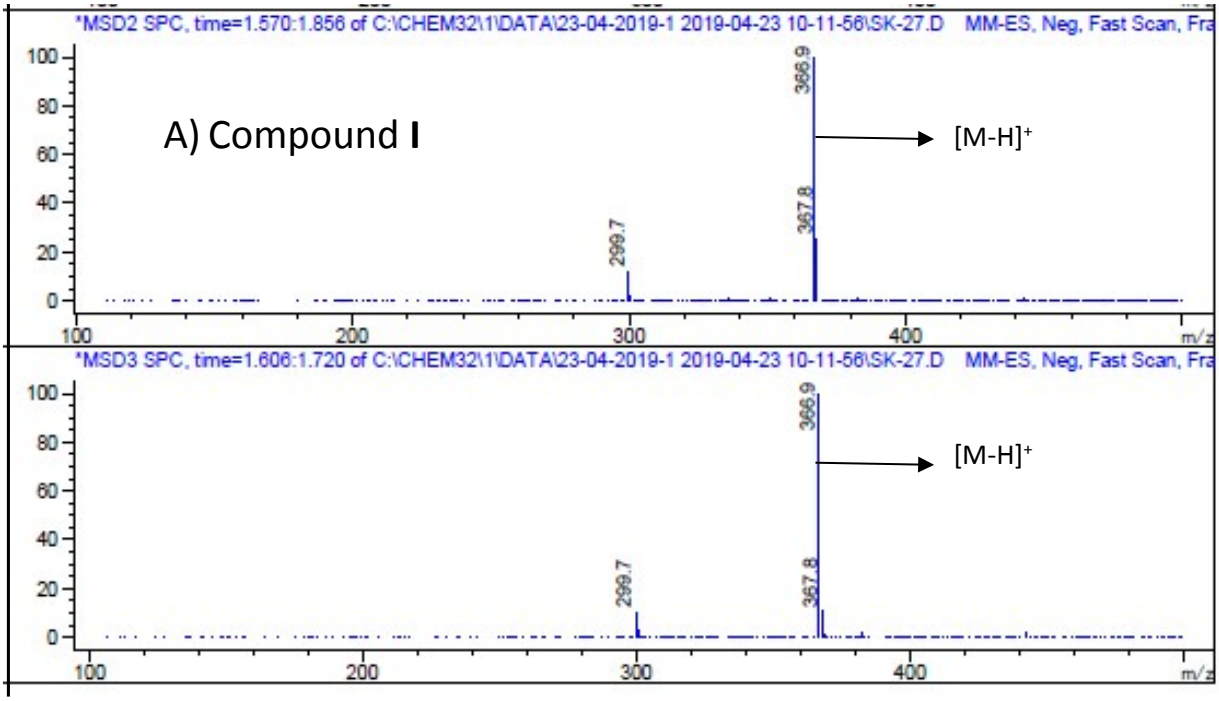
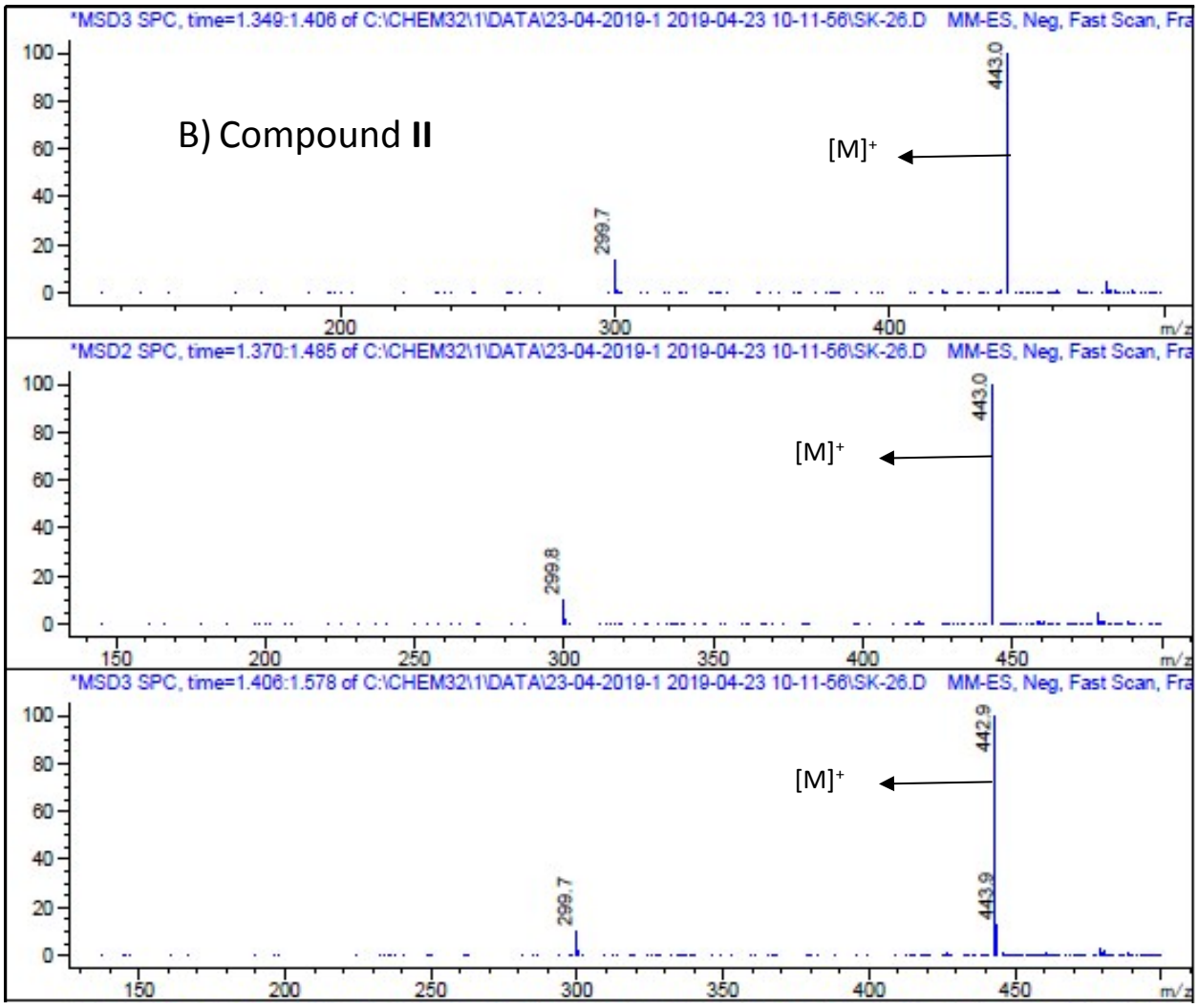
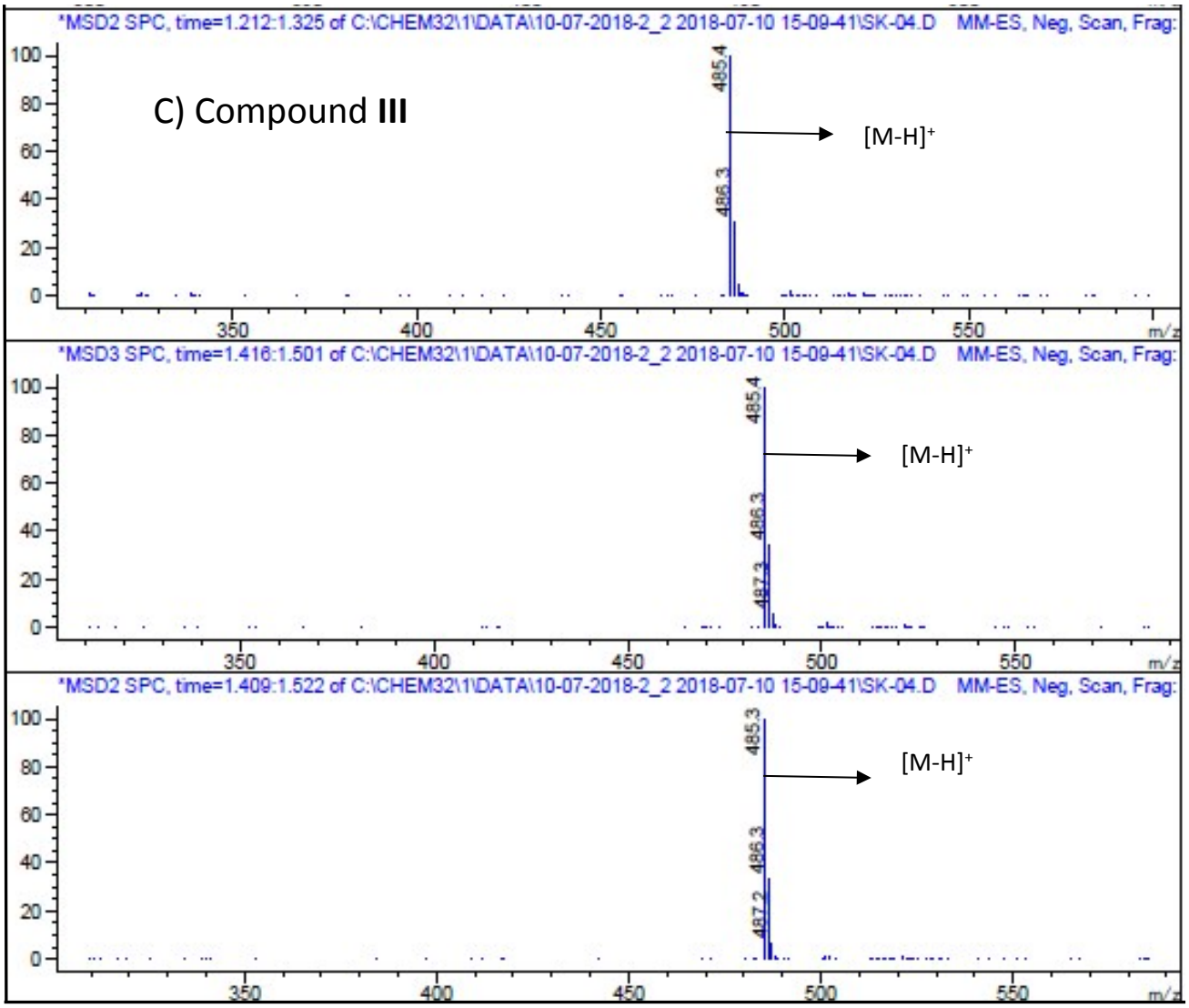


Fig S22. NMR Spectrum of Compound **V** (solid)


*MSD2 SPC, time=1.570:1.856 of C:\CHEM32\1\DATA\23-04-2019-1 2019-04-23 10-11-56\SK-27.D MM-ES, Neg, Fast Scan, Fra
A) Compound I
[M-H]+
366.9
367.8
299.7
*MSD3 SPC, time=1.606:1.720 of C:\CHEM32\1\DATA\23-04-2019-1 2019-04-23 10-11-56\SK-27.D MM-ES, Neg, Fast Scan, Fra
[M-H]+
366.9
367.8
299.7
100
200
300
400
m/z


*MSD3 SPC, time=1.349:1.406 of C:\CHEM32\1\DATA\23-04-2019-1 2019-04-23 10-11-56\SK-26.D MM-ES, Neg, Fast Scan, Fra
B) Compound II
[M]+
443.0
299.7
*MSD2 SPC, time=1.370:1.485 of C:\CHEM32\1\DATA\23-04-2019-1 2019-04-23 10-11-56\SK-26.D MM-ES, Neg, Fast Scan, Fra
[M]+
443.0
299.8
*MSD3 SPC, time=1.406:1.578 of C:\CHEM32\1\DATA\23-04-2019-1 2019-04-23 10-11-56\SK-26.D MM-ES, Neg, Fast Scan, Fra
[M]+
442.9
443.9
299.7
m/z

C) Compound **III**



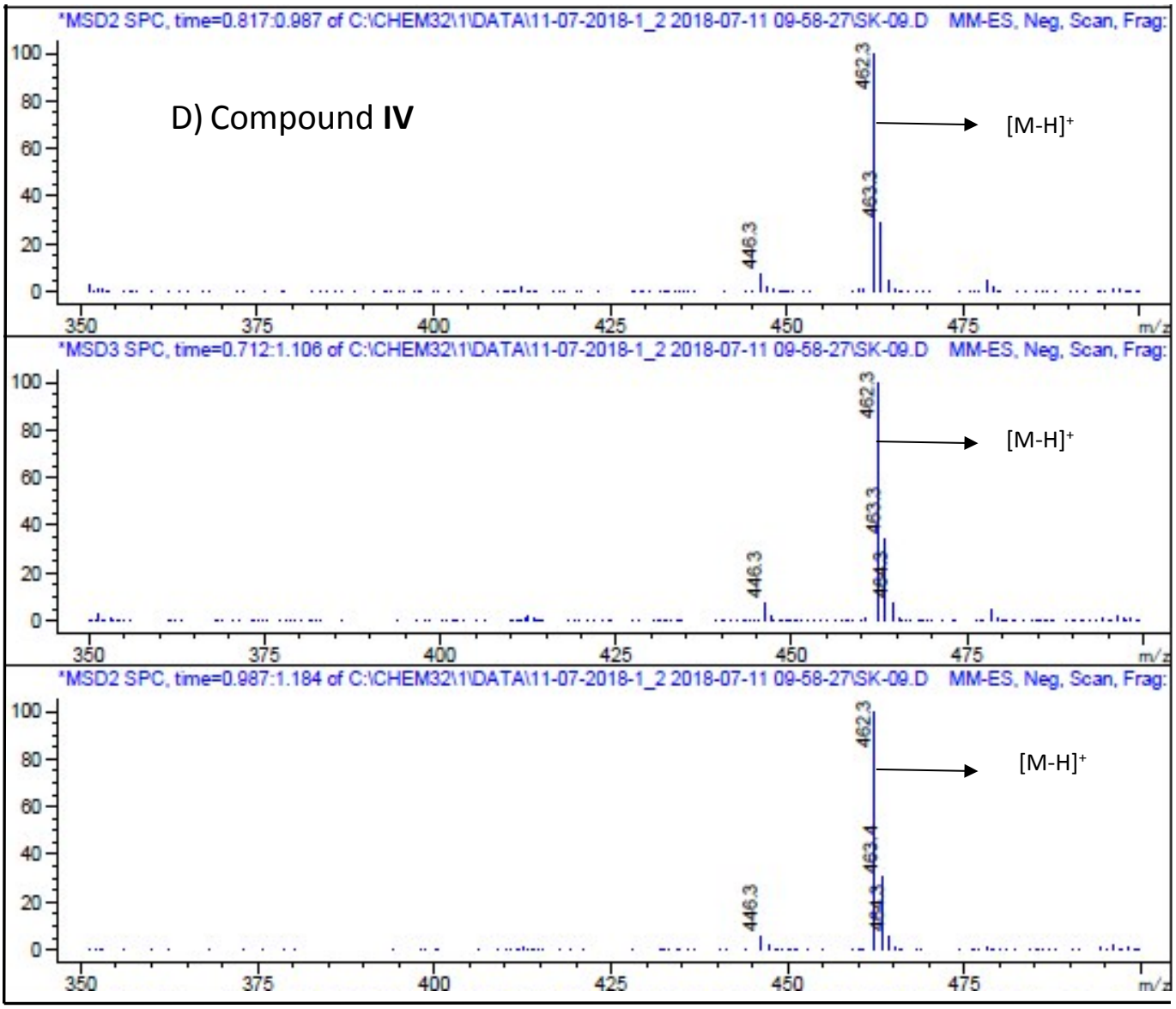


Fig S23. Mass Spectra of A) Compound I; B) Compound II; C) Compound III; D) Compound **IV**