Supporting Information

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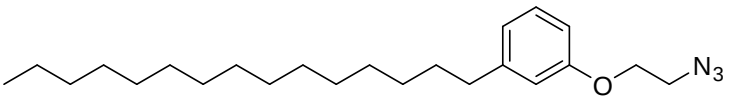
Synthetic procedures and characterizations of glucose-triazole-hydrogenated cardanol conjugate

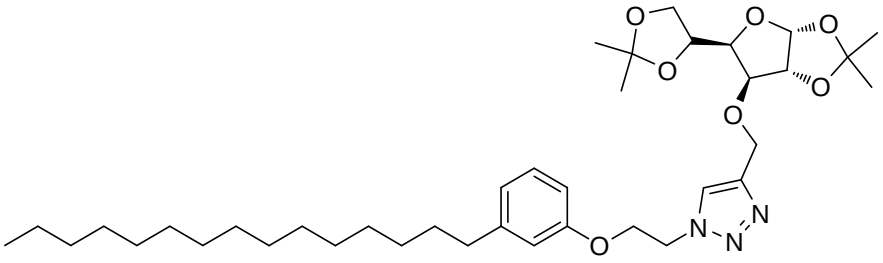
1-(2-Azidoethoxy)-3-pentadecylbenzene 3:



To a stirred solution of 1-(2-bromoethoxy)-3-pentadecylbenzene **2** (0.5 g, 1.21 mmol) in DMSO (5 mL) sodium azide (0.086 g, 1.33 mmol), tetra-*n*-butylammonium bromide (TBAB, 0.04 g, 0.121 mmol) and 18-Crown-6 (0.032 g, 0.121 mmol) were added sequentially. Resulting solution was heated at 70 ^{o}C for 24 h for completion of the reaction by thin layer chromatography (TLC). To the cooled reaction mixture dichloromethane (DCM; 20 mL) and water (20 mL) were added. The aqueous solution was extracted with 20 mL of DCM twice. Combined DCM solutions was washed with water (2 × 10 mL), brine (10 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure resulted in the crude product, which was subjected to column chromatography on silica gel and eluting with hexanes to yield the azide **3** (0.40 g, 88%) as colourless liquid; R_f (hexanes) 0.8; Infrared spectroscopy (IR) (KBr) ν_{max} 2925, 2853, 2104, 1605, 1488, 1258, 1064, 722 cm^{-1}; ^{1}H Nuclear magnetic resonance (NMR) (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.78-6.75 (m, 2H), 4.15 (t, *J* = 4.8 Hz, 2H), 3.59 (t, *J* = 5.2 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.64 (t, *J* = 6.4, 2H), 1.34-1.30 (m, 24H), 0.92 (t, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 144.9, 129.3, 121.6,115.0, 111.5, 66.9, 50.3, 36.1, 32.0,

31.5, 29.83 (3C), 29.81(3C), 29.7, 29.6, 29.5, 29.4, 22.8, 14.2 ppm; HR-Mass Spectra (ESI) Calcd for $C_{23}H_{40}N_3O$ [M + H] 374.3171 amu, found 374.3188 amu.

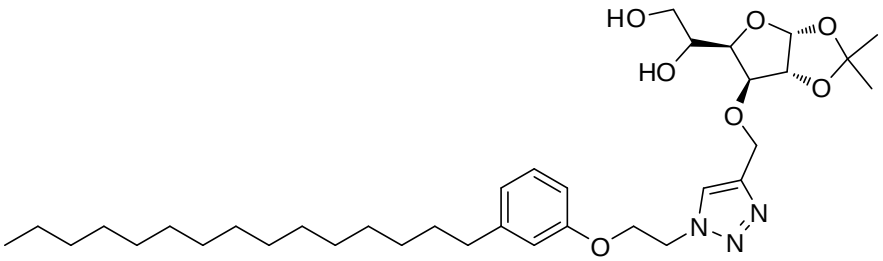
4-((((3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)methyl)-1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazole 5:



To the the propargyl ether **4** (0.4 g, 1.34 mmol) and the azide **3** (0.5 g, 1.34 mmol) taken in biphasic mixture of DCM (5 mL) and H_2O (5 mL) $CuSO_4.5H_2O$ (0.033 g, 0.132 mmol) and sodium ascorbate (0.053 g, 0.267 mmol) were added and stirred at rt for 24 h by which time the cycloaddition was complete (TLC). The reaction mixture was diluted with 30 mL DCM and the aqueous phase was extracted with DCM (10 mL). Combined DCM solutions were washed with (10 mL), brine (10 mL) and dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure resulted in crude product which was subjected to column chromatography on silica gel and eluted with 20% EtOAc in hexanes to yield glucose diacetonide hydrogenated cardanol conjugate **5** (0.825 g, 92%) as faintly yellow paste; $[\alpha]_D$ -10.5^o (c 1, $CHCl_3$); R_f (70% hexanes/EtOAc) 0.5; IR (KBr) ν_{max} 2987, 2925, 2854,1605, 1257, 1077, 849 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.67-6.65 (m, 2H), 5.85 (d, *J* = 3.6 Hz, 1H), 4.80-4.77 (m, 2H), 4.74-4.71 (m, 2H), 4.58 (d, *J* = 5.0 Hz, 1H), 4.34-4.29 (m, 3H), 4.12-3.97(m, 4H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.47 (s, 2H), 1.40 (s, 3H), 1.33 (s, 3H), 1.27 (s, 3H), 1.24 (br s, 27H), 0.86 (t, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 145.0, 144.9, 129.4, 123.7,

121.9,114.7, 111.8, 111.6, 109.0, 105.3, 82.7, 81.8, 81.2, 72.5, 67.4, 66.3, 64.1, 49.9, 36.0, 31.9, 31.4, 29.75 (4C), 29.73 (3C), 29.6, 29.5, 29.4, 26.9, 26.8, 26.2, 25.5, 22.7, 14.1 ppm; HRMS (ESI) Calcd for $C_{38}H_{62}N_3O_7$ [M + H] 672.4588 amu, found 672.4572 amu.

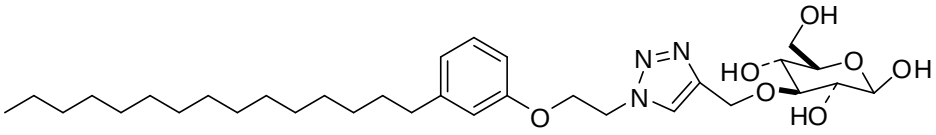
(*R*)-1-((3a*R*,5*R*,6*S*,6a*R*)-2,2-Dimethyl-6-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethane-1,2-diol 6:



To hydrogenated cardanol glucose conjugate **5** (0.5 g, 2.0 mmol) taken in ethanol (5 mL) 1.6 % aqueous sulfuric acid (v/v; 4 mL) was added. Resulting mixture was stirred at rt 12 h by which time the reaction was complete (TLC). Excess acid was neutralized with aqueous 1 N NaOH under ice-cold conditions. The resulting mixture was centrifuged (1000 rpm) and the clear supernatant solution was evaporated under reduced pressure to get crude product. The compound was purified by column chromatography on silica gel using 30% EtOAc in hexanes to yield glucose monoacetonide hydrogenated cardanol conjugate **6** (0.38 g, 82%) as faintly yellow paste; $[\alpha]_D$ -22.0 ^{o} (c 1, $CHCl_3$); R_f (50% hexanes/EtOAc) 0.4; IR (KBr) ν_{max} 2987, 2925, 2854,1605, 1257, 1077, 849 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.67-6.64 (m, 2H), 5.90 (d, *J* = 3.7 Hz, 1H), 4.87-4.84 (m, 1H), 4.72-4.65 (m, 3H), 4.59 (d, *J* = 3.8 Hz, 1H), 4.30 (t, *J* = 5.0 Hz, 2H), 4.14-4.12 (m, 2H), 4.04-4.03 (m, 1H), 3.85-3.82 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.68-3.63 (dd, *J* = 11.6, 6.4 Hz, 1H), 2.54 (t, *J* = 7.5 Hz, 2H),1.57 (t, *J* = 7.1 Hz, 2H), 1.44 (s, 3H), 1.28-1.24 (m, 27H), 0.86 (t, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 144.9, 144.2, 129.4, 123.3, 121.9,114.7, 111.8, 111.5, 105.4, 82.29, 82.25, 80.3, 68.5, 66.1, 64.5,

62.9, 50.0, 36.0, 31.9, 31.4, 29.7 (5C), 29.68, 29.63, 29.5, 29.4, 29.3, 26.7, 26.3, 22.7, 14.1 ppm; HRMS (ESI) Calcd for $C_{35}H_{58}N_3O_7$ [M + H] 632.4275 amu, found 632.4260 amu.

(2*S*,3*R*,4*R*,5*R*)-5-((*R*)-1,2-Dihydroxyethyl)-4-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydrofuran-2,3-diol 1:



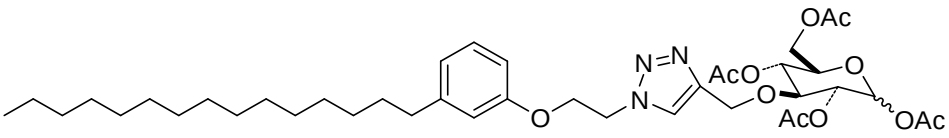
The glucose diacetonide cardnaol conjugate (0.5 g, 0.74 mmol) taken in 6 mL of triflouroacetic acid and water (1:1) was stirred at rt for 10 h by which time deprotection of both the acetonides was complete (TLC). Solid sodium carbonate (1 g) and 25 mL of ethyl acetate (EtOAc) were added to the cooled reaction mixture. The organic layer was decanted followed by washing the inorganic residue with 10 mL of EtOAc. Combined EtOAc layers was washed with brine solution (15 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure resulted in crude product, which was subjected to column chromatography on silica gel and eluted with 3% MeOH in EtOAc. The white solid that was precipitated in the column fractions (20 mg) was collected and analyzed. He compound turned out to be the pure β-anomer. Evaporation of the pooled fractions resulted in the glucose-triazole-hydrogenated cardanol conjugate as a 1:1 mixture of anomers obtained as a colourless solid. Overall yield 0.36 g, (82%); $[\alpha]_D$ +11.0 (c 1, $CHCl_3$); mp 180 ºC; R_f (95% EtOAc /MeOH) 0.5; IR (KBr) ν_{max} 3393, 2923, 2853,1676, 1466, 1039, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.21-7.17 (m,1H), 6.80-6.76 (m, 3H), 6.72 (d, *J* = 6.4 Hz, 1H), 5.16-5.14 (m, 2H), 4.94-4.87 (m, 2H), 4.76 (t, *J* = 4.8 Hz, 2H), 4.55 (t, *J* = 5.7 Hz, 1H), 4.41-4.34 (m, 3H), 3.73-3.69(m, 1H), 3.52-3.45(m, 1H), 3.25-3.21(m, 2H), 3.17-3.14 (m, 1H), 3.11-3.06 (m, 1H), 2.56-2.52 (m, 2H), 1.5 (br s, 2H), 1.26 (br s, 24H), 0.88 (t, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 145.4, 144.1, 129.2, 123.9, 121.0,114.5,

111.7, 96.8, 85.4, 76.6, 74.6, 69.7, 66.0, 65.6, 61.0, 49.0, 35.1, 31.3, 30.8, 29.05 (5C), 29.03 (3C), 28.8, 28.7, 22.1, 13.9 ppm; HRMS (ESI) Calcd for $C_{32}H_{54}N_3O_7$ [M + H] 592.3962 amu, found 592.3981 amu.

Spectral data of the mixture (1:1) of the α- and β-anomers is given below

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.12-7.08 (m,1H), 6.69-6.67 (m, 3H), 4.89 (d, *J* = 3.6 Hz, 1H), 4.85-4.84 (m, 2H), 4.69 (t, *J* = 4.8 Hz, 2H), 4.33-4.27 (m, 3H), 3.59-3.56 (m, 3H), 3.47-3.40 (m, 5H), 3.24-3.16(m, 4H), 3.12-3.0 (m, 2H), 2.47-2.46 (m, 2H), 1.51-1.49 (m, 2H), 1.24-1.20 (m, 24H), 0.84 (t, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 145.6 & 145.4,143.9, 129.0, 123.7 & 123.6, 120.9, 114.4, 111.6, 96.8 & 92.2, 85.3 & 82.3, 76.4 & 74.6, 72.1 & 71.8, 69.9 & 69.7, 65.9, 65.5, 61.1 & 61.0, 49.0, 35.3, 31.3, 30.9, 29.1 (5C), 29.0 (2C), 28.9, 28.8, 28.7, 22.1, 13.9 ppm; HRMS (ESI) Calcd for $C_{32}H_{54}N_3O_7$ [M + H] 592.3962 amu, found 592.3981 amu.

(2*R*,3*R*,4*S*,5*R*,6*RS*)-6-(Acetoxymethyl)-4-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydro-2*H*-pyran-2,3,5-triyl triacetate 7:



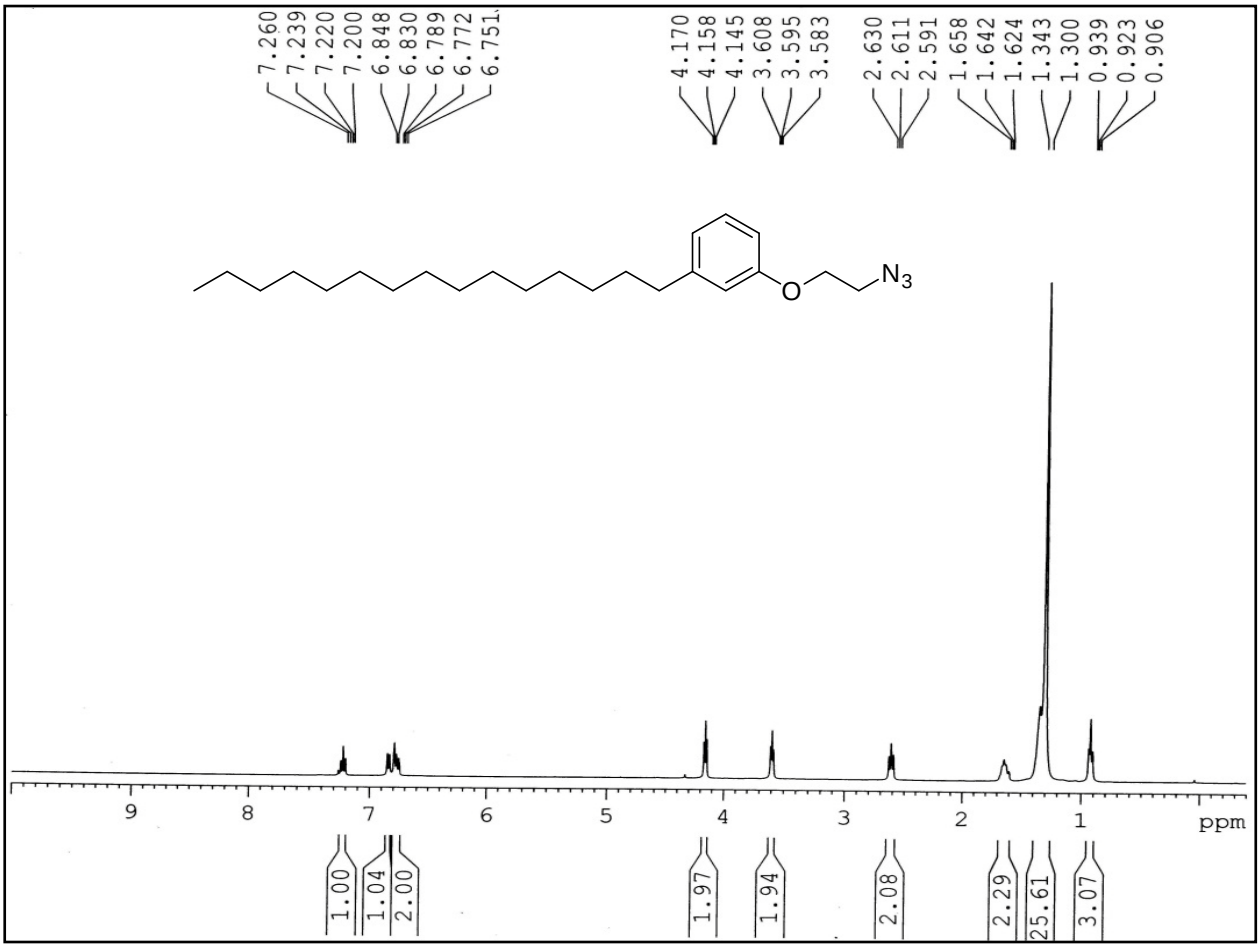
To the cooled (0 ^{o}C) solution of acetic anhydride (0.078 g, 1.52 mmol) in pyridine (0.10 g, 2.53 mmol) glucose-triazole-hydrogenated cardanol (GTHCC) conjugate (0.1 g, 0.168 mmol) was added and the homogeneous solution was stirred at rt for 12 h for completion of reaction (TLC). The reaction mixture was diluted with DCM (20 mL) and water (20 mL). The aqueous layer was further extracted with 10 mL DCM. The combined DCM solutions was washed with water (20 mL), brine (10 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure resulted in the crude product, which

was subjected to column chromatography eluting with 40% EtOAc in hexanes. Removal of solvent from pooled fractions yielded the peracetylation product **7** (0.120 g, 93%) as a mixture (1:1; calculated from ^{13}C spectra) of anomers. Colourless liquid; $[\alpha]_D$ +11.0 (c 1, $CHCl_3$); R_f (40% EtOAc /Hexane) 0.5; IR (KBr) ν_{max} 2925, 2854, 1752,1371, 1225, 1044, 936 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.15 (t, 1H, *J* = 8.0 Hz), 6.78 (d, 1H, *J* = 7.2 Hz), 6.68-6.65 (m, 2H), 6.28 & 5.63 (d, 1H, *J* = 4.0, 8.4 Hz), 5.12-5.06 & 4.75-4.69 (m, 5H), 5.03-4.99 & 4.84-4.81 (m, 1H), 4.32-4.30 (m, 2H), 4.23-4.17 (m, 1H), 4.07-3.99 (m, 2H), 3.86-3.81 & 3.74-3.71 (m, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.15 & 2.07 (s, 3H), 2.05 (d, *J* = 1.6 Hz, 3H), 1.98-1.94 (m, 6H), 1.56 (t, *J* = 7.2 Hz, 2H), 1.27-1.23 (m, 24H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.78 & 170.76, 169.7 & 169.45, 169.43 & 169.27, 169.22 & 168.9, 157.8, 145.2 & 145.04, 145.02 & 144.8, 129.4, 123.7 & 123.5, 121.9, 114.6, 111.6 & 111.5, 91.9 & 89.4, 80.4, 72.9 & 71.6, 71.5 & 70.2, 69.0 & 68.9, 66.5, 66.1 & 66.0, 61.7, 49.9, 36.0, 31.9, 31.4, 29.74 (5C), 29.71, 29.6, 29.5, 29.4 (2C), 22.7, 20.9 & 20.8, 20.77 & 20.76, 20.73 & 20.72, 20.68 & 20.64, 14.1 ppm; HRMS (ESI) Calcd for $C_{40}H_{61}N_3O_{11}$ [M + H] calculated 760.4384 amu, found 760.4361 amu.

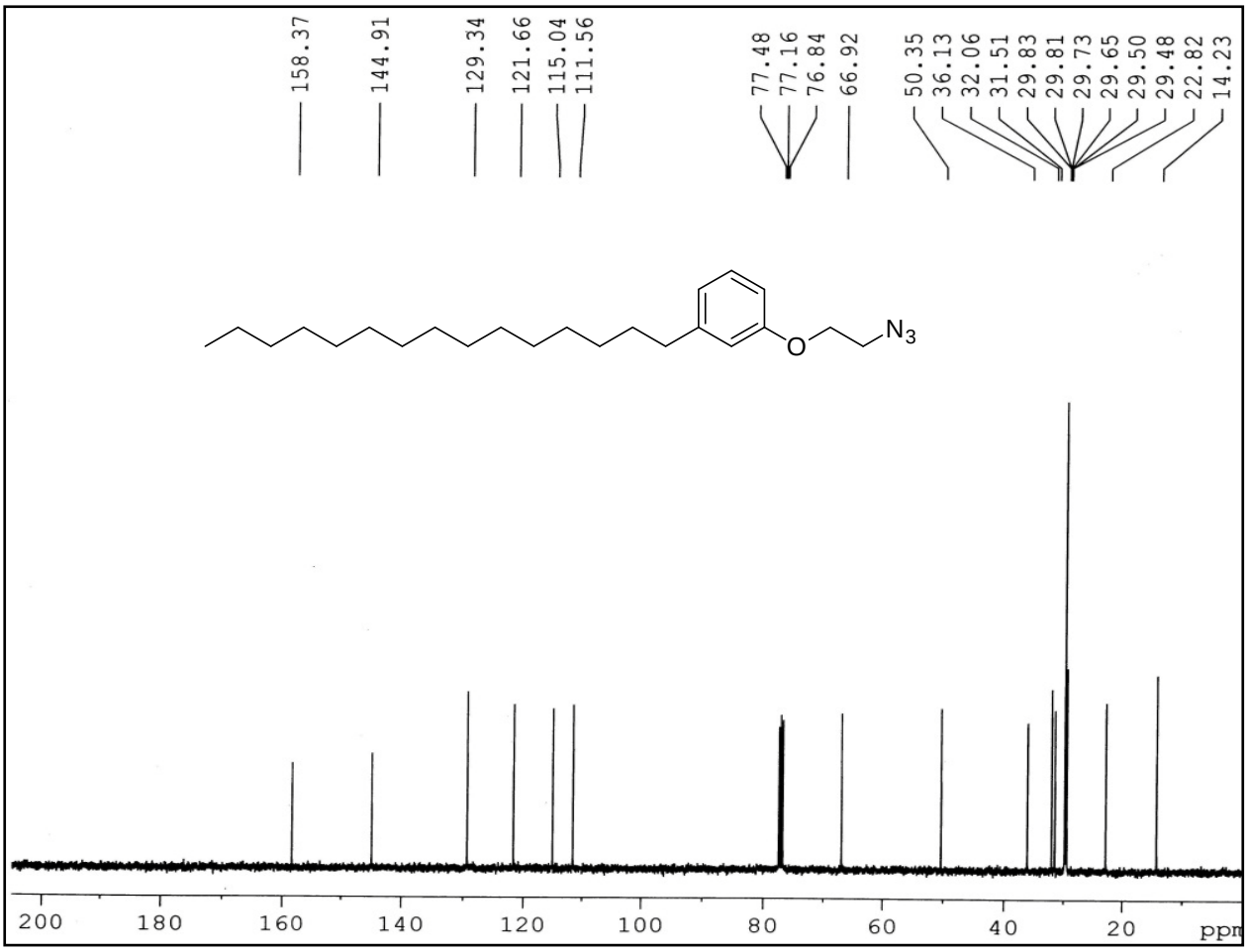
NMR spectra

Index

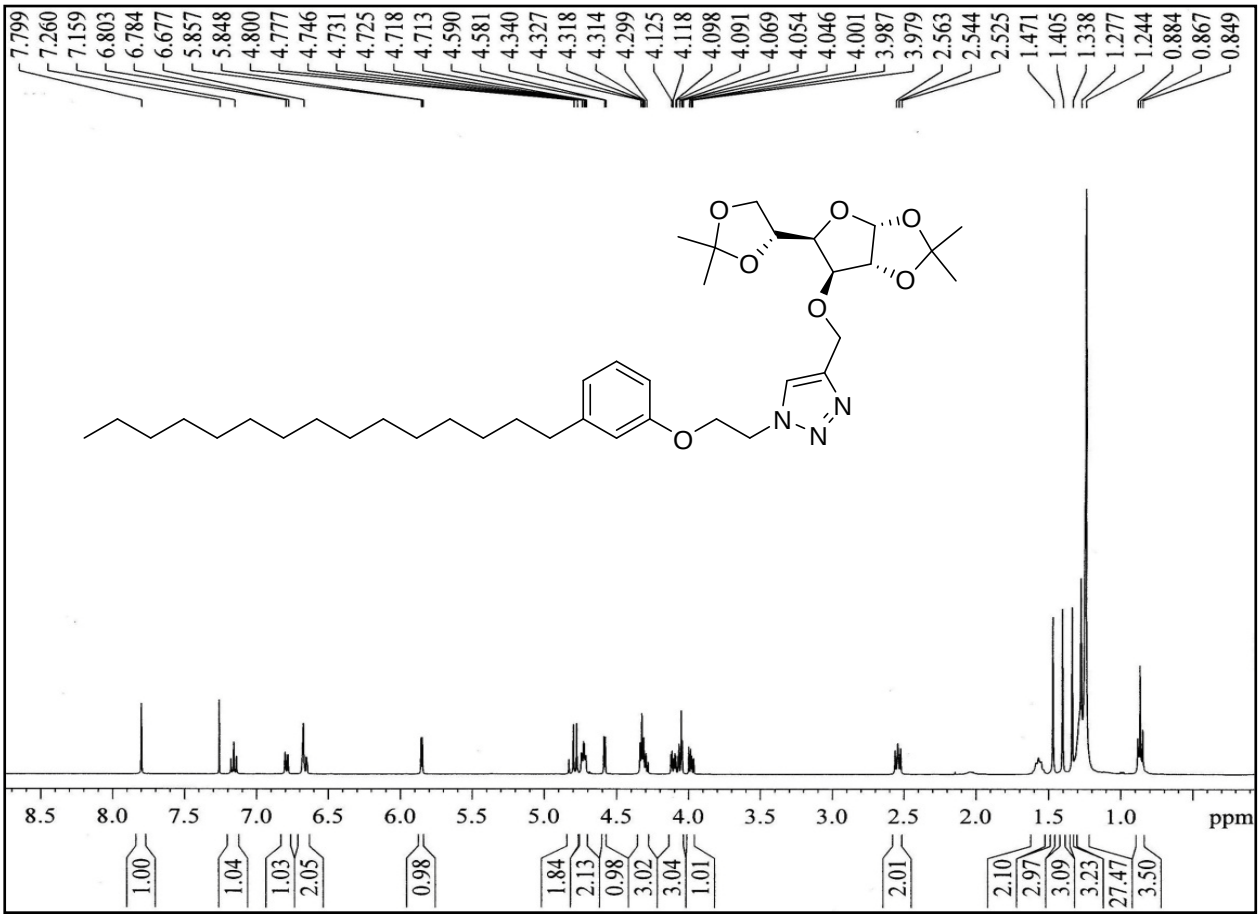
Spectra



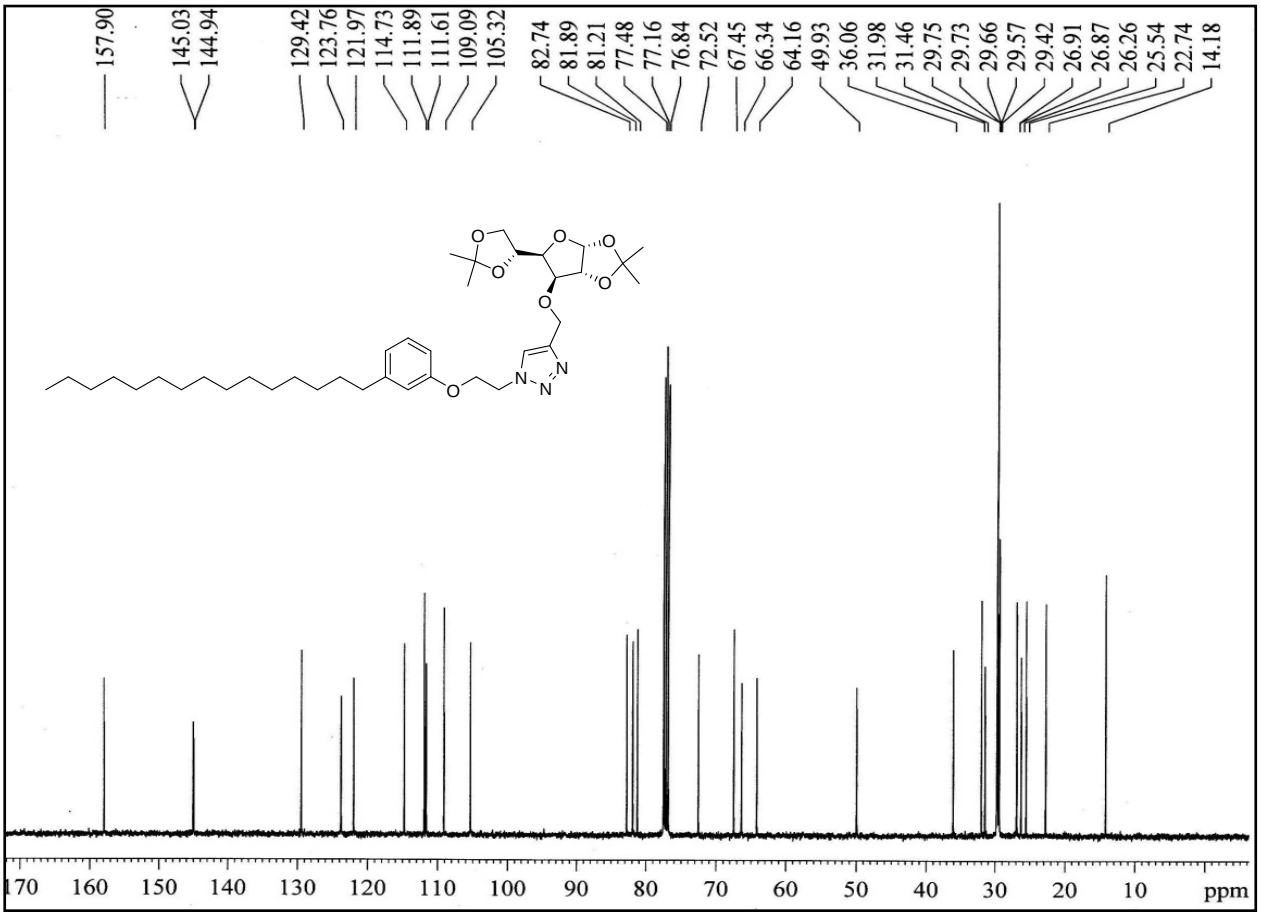
^{1}H (400 MHz, $CDCl_3$) NMR spectrum of 1-(2-azidoethoxy)-3-pentadecylbenzene (**3**).



^{13}C (100 MHz, $CDCl_3$) NMR spectrum of 1-(2-azidoethoxy)-3-pentadecylbenzene (**3**).

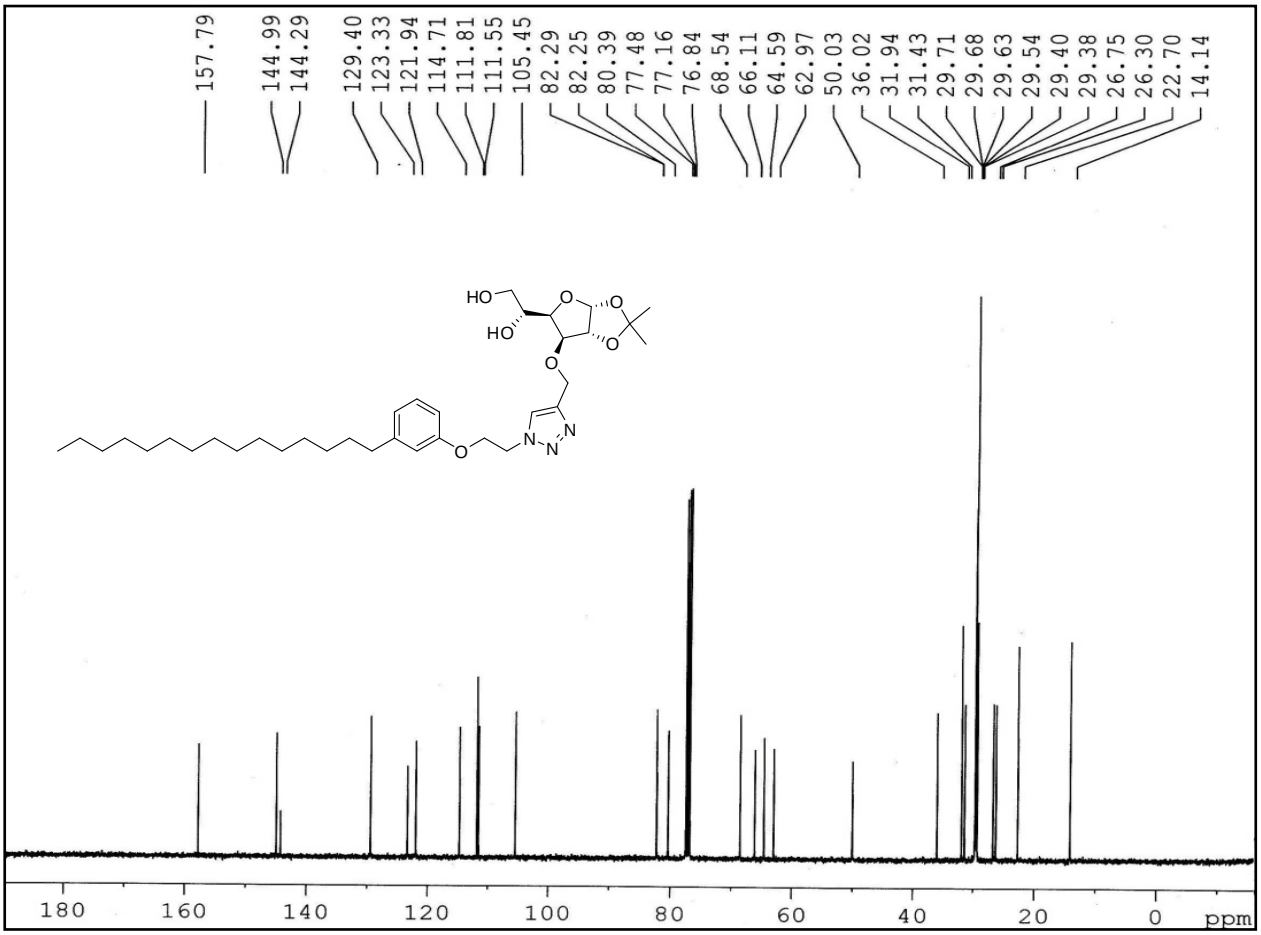


^{1}H (400 MHz, $CDCl_3$) NMR spectrum of 4-((((3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)methyl)-1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazole (**5**).

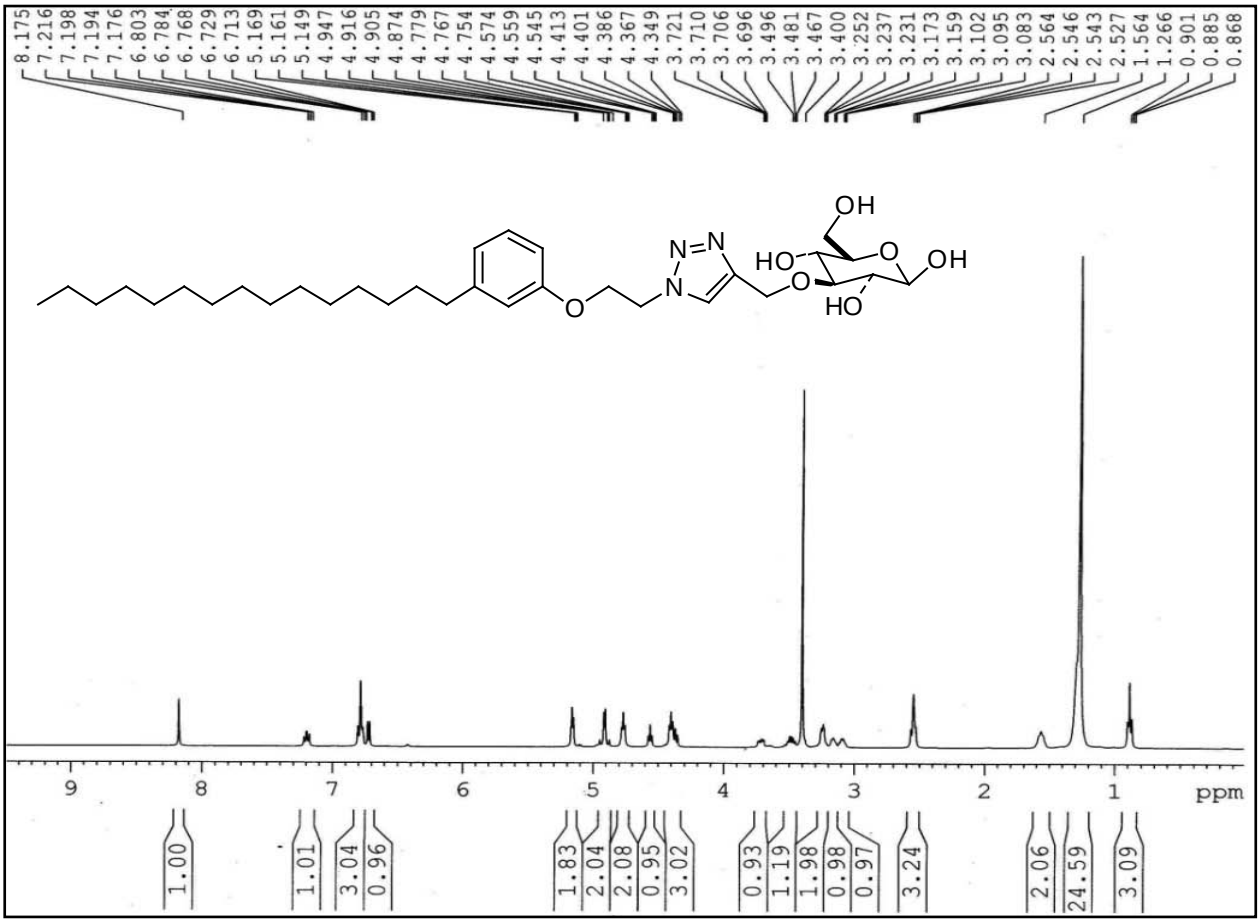


^{13}C (100 MHz, $CDCl_3$) NMR spectrum of 4-((((3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)methyl)-1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazole (**5**).

^{1}H (400 MHz, $CDCl_3$) NMR spectrum of (*R*)-1-((3a*R*,5*R*,6*S*,6a*R*)-2,2-dimethyl-6-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydrofuro[2,3-*d*][1,3]dioxol-5-yl)ethane-1,2-diol (**6**).



^{13}C (100 MHz, $CDCl_3$) NMR spectrum of (*R*)-1-((3a*R*,5*R*,6*S*,6a*R*)-2,2-dimethyl-6-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethane-1,2-diol (**6**).



^{1}H (400 MHz, DMSO-D_6) NMR spectrum of (2*S*,3*R*,4*R*,5*R*)-5-((*R*)-1,2-dihydroxyethyl)-4-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydrofuran-2,3-diol (**1**).

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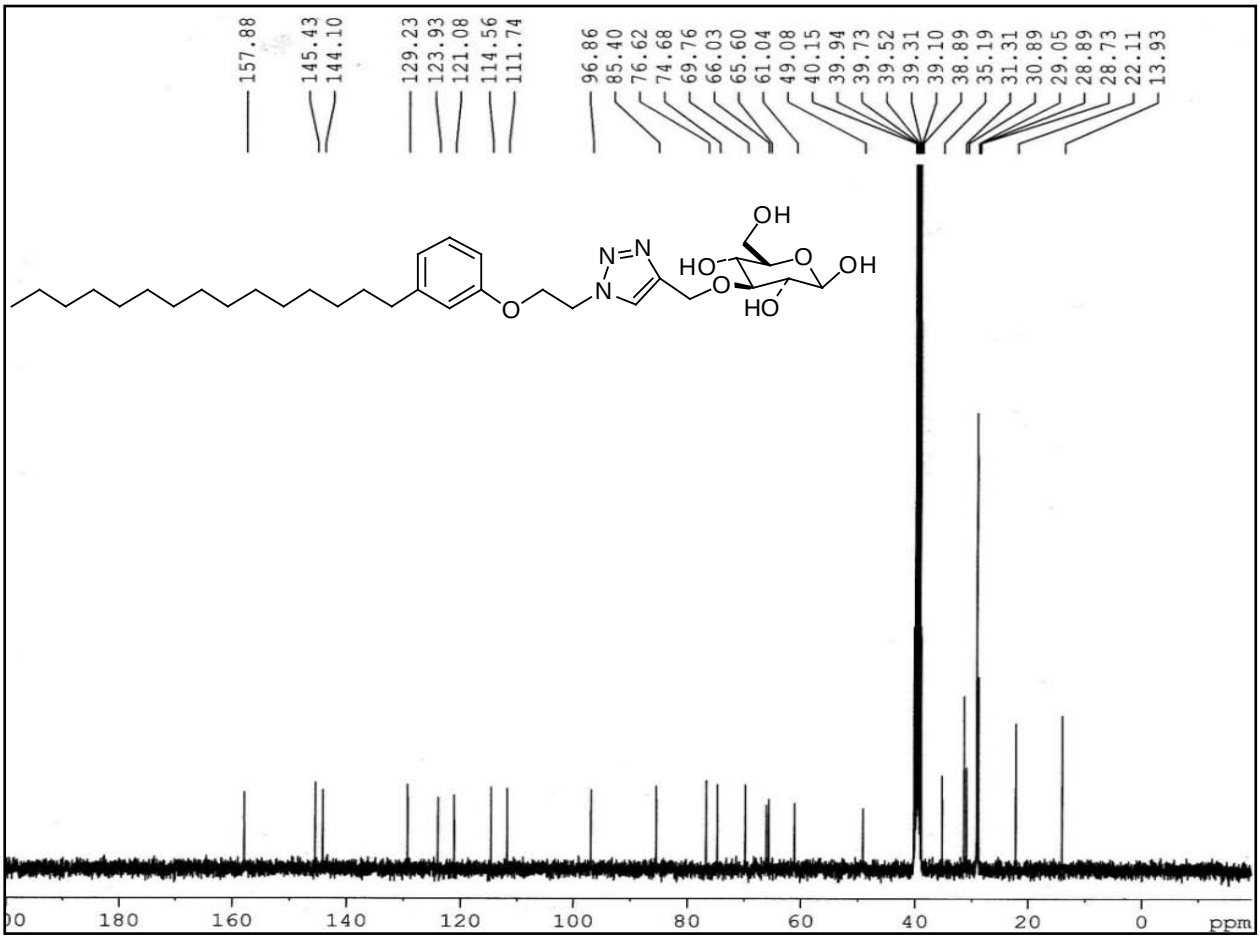
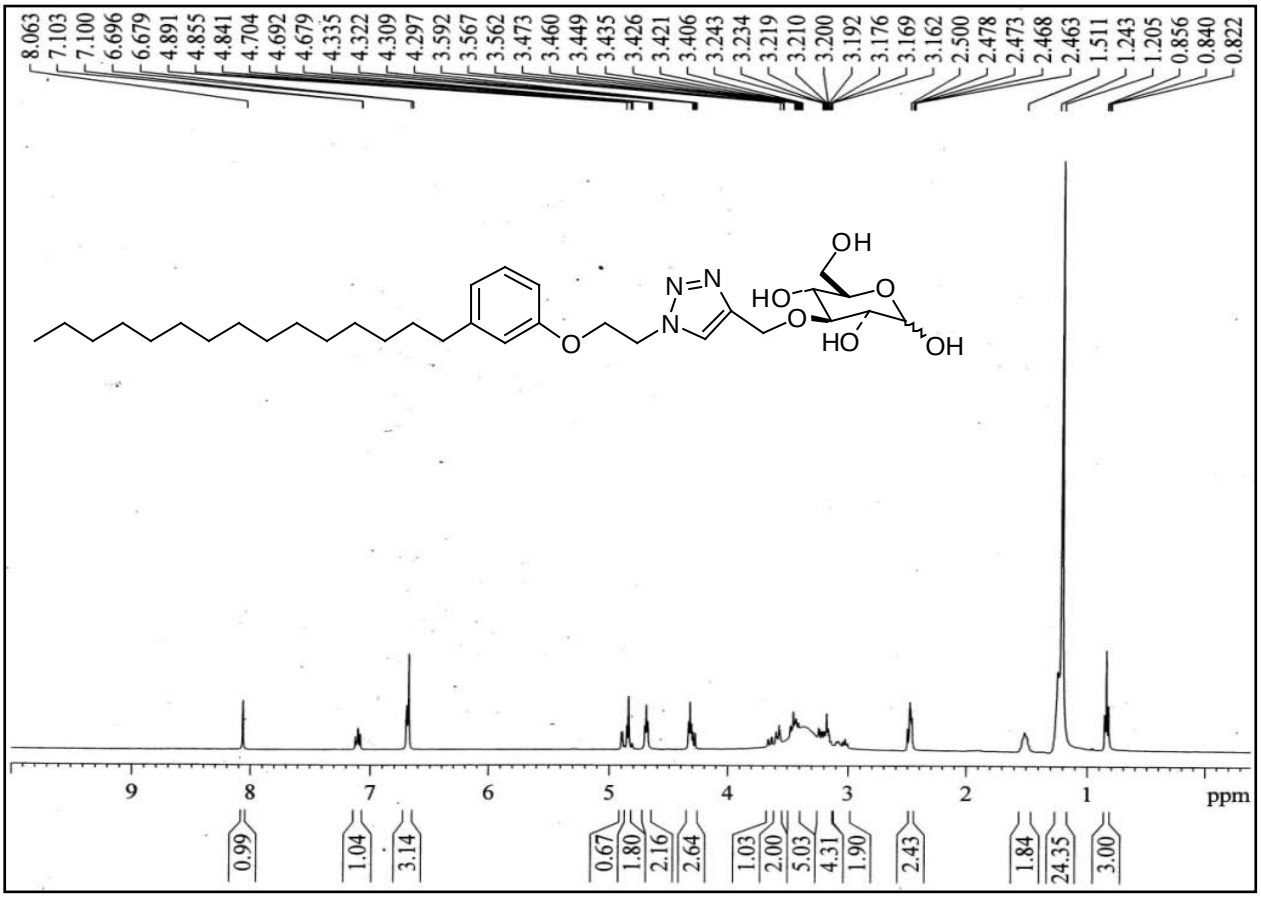
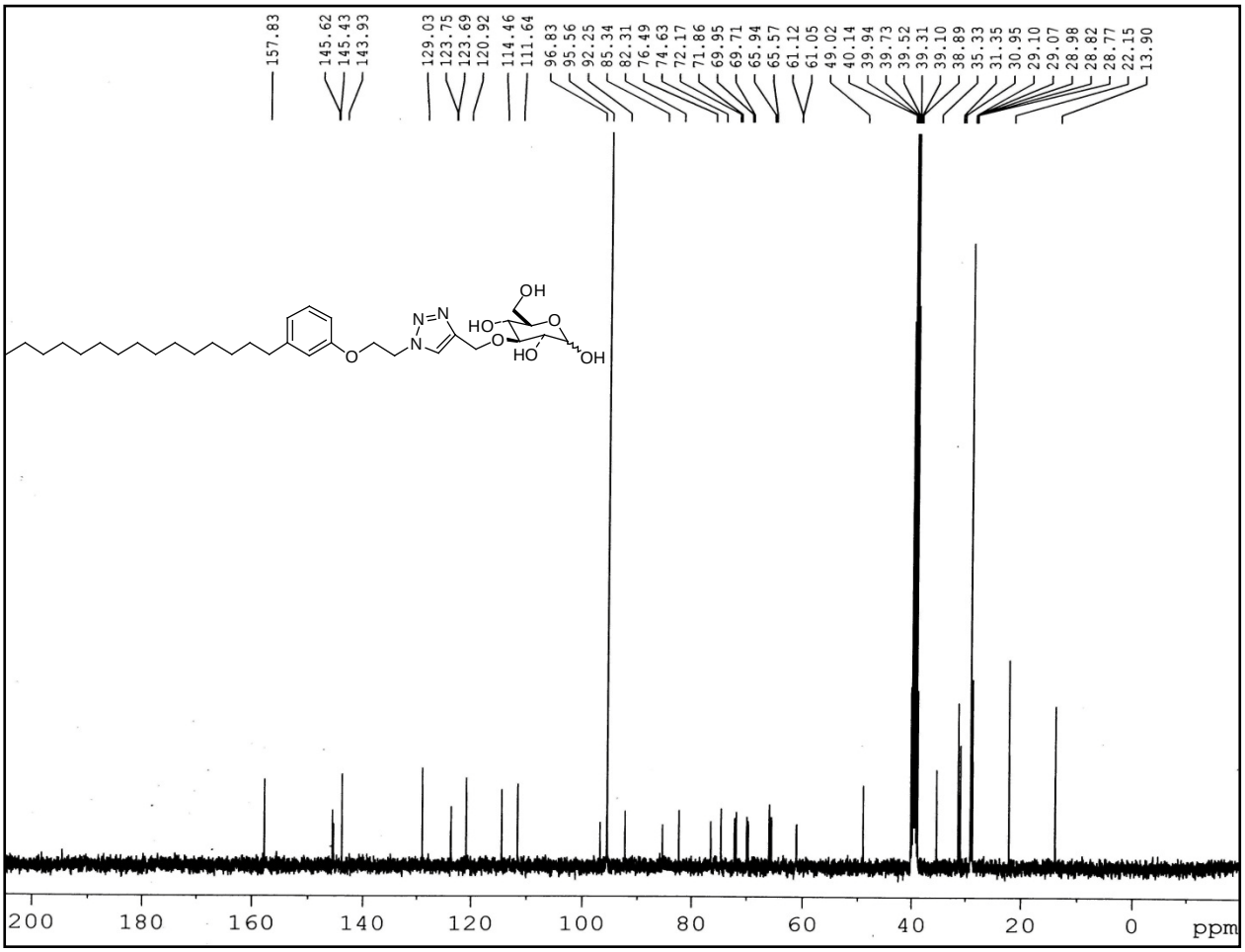


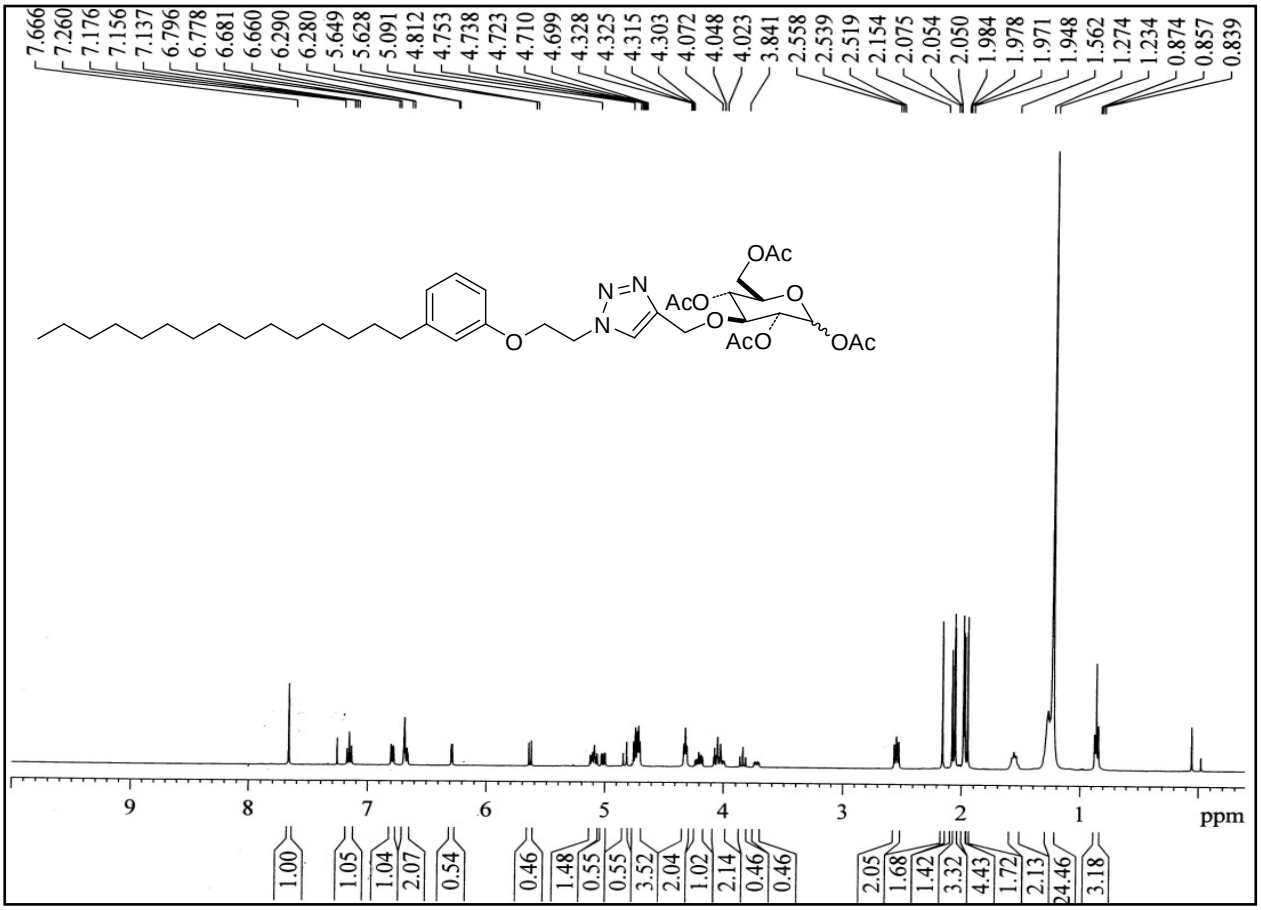
^{13}C (100 MHz, DMSO-D_6) NMR spectrum of (2*S*,3*R*,4*R*,5*R*)-5-((*R*)-1,2-dihydroxyethyl)-4-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydrofuran-2,3-diol (**1**).



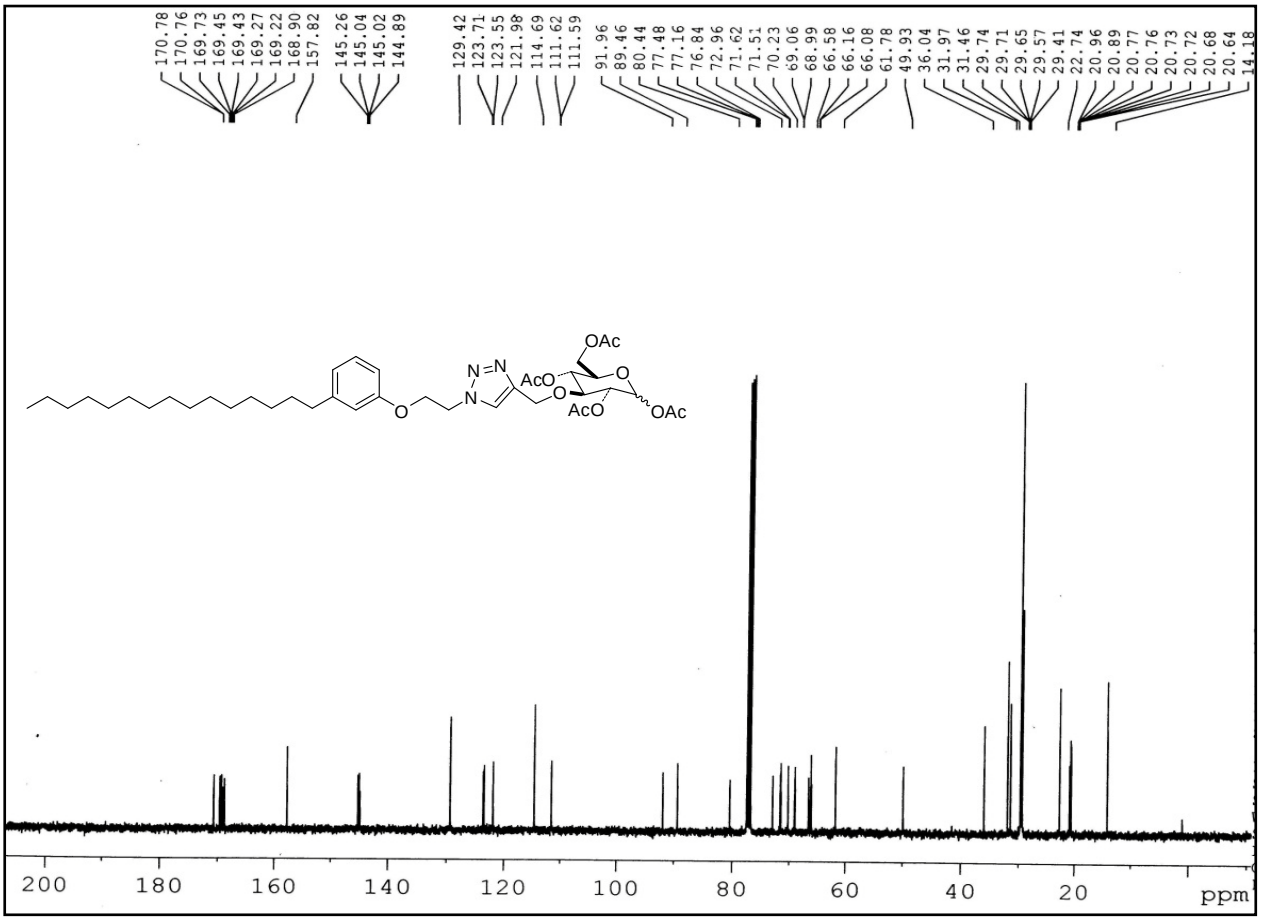
^{1}H (400 MHz, DMSO-D_6 + CCl_4, 1:1) NMR spectrum of (2*S*,3*R*,4*R*,5*R*)-5-((*R*)-1,2-dihydroxyethyl)-4-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4 yl)methoxy)tetrahydrofuran-2,3-diol (**1**).



^{13}C (100 MHz, DMSO-D_6 + CCl_4, 1:1) NMR spectrum of (2*S*,3*R*,4*R*,5*R*)-5-((*R*)-1,2-dihydroxyethyl)-4-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydrofuran-2,3-diol (**1**).



^{1}H (400 MHz, $CDCl_3$) NMR spectrum of (2*R*,3*R*,4*S*,5*R*,6*RS*)-6-(acetoxymethyl)-4-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydro-2*H*-pyran-2,3,5-triyl triacetate (**7**).



^{13}C (100 MHz, $CDCl_3$) NMR spectrum of (2*R*,3*R*,4*S*,5*R*,6*RS*)-6-(acetoxymethyl)-4-((1-(2-(3-pentadecylphenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)tetrahydro-2*H*-pyran-2,3,5-triyl triacetate (**7**).

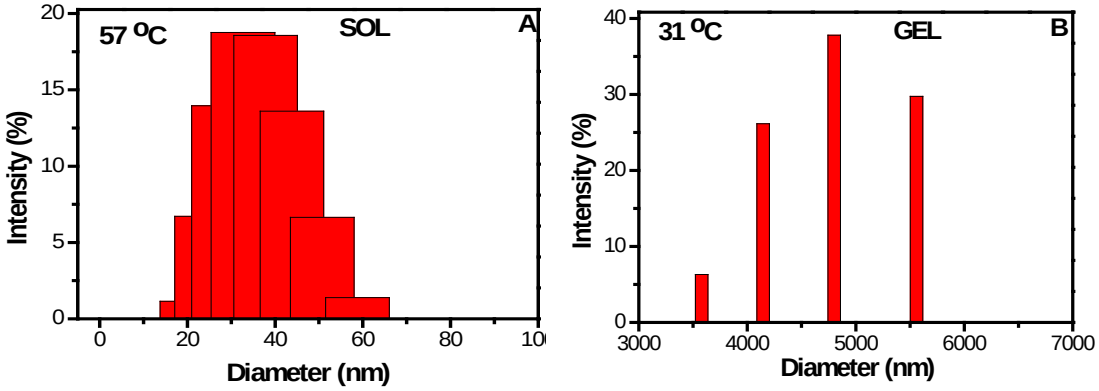
Gelation test table

SITable 1 Result for the gelation test of GTHCC in different fraction of water/methanol and water/ethanol solvent (at 2 mg/mL) at 20 ^{o}C

Fraction of Water : Methanol	State
10 : 90	P
20 : 80	S
30 : 70	PG
40 : 60	G (CGC=0.1%, 1 mg/mL)
50 : 50	G (CGC=0.025%,0.25 mg/mL)
60 : 40	G (CGC=0.1%, 1 mg/mL)
70 : 30	PG
80 : 20	S
90 : 10	P
Fraction of Water : Ethanol	**State**
10 : 90	P
20 : 80	P
30 : 70	S
40 : 60	PG
50 : 50	G (CGC=0.08%, 0.8 mg/mL)
60 : 40	PG
70 : 30	S
80 : 20	P
90 : 10	P

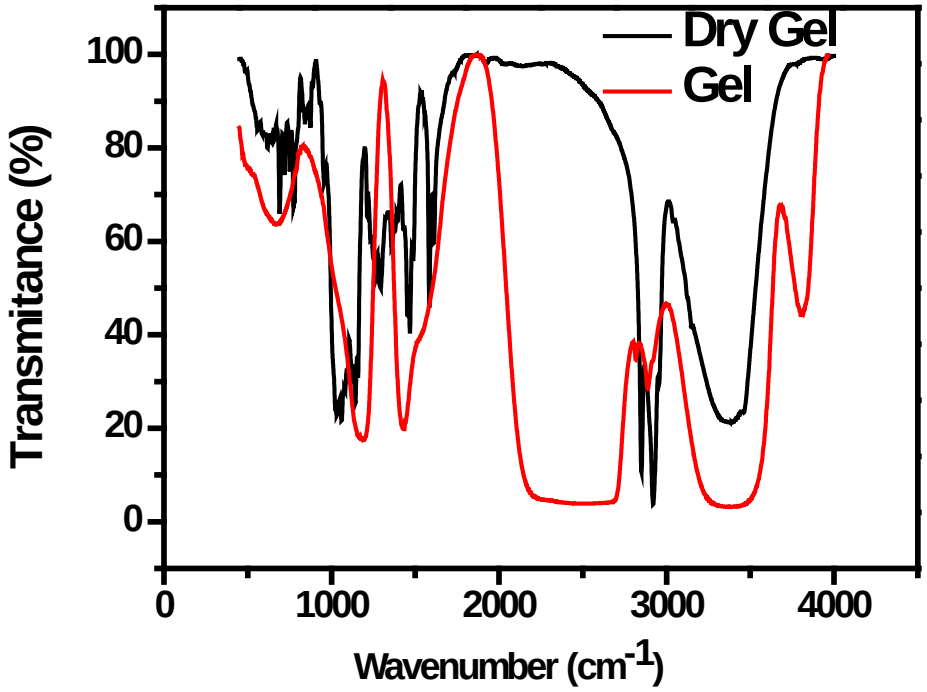
G = gel; S = solution; P = precipitate; PG=partially gel CGC=Critical Gelation concentration at 20 ^{o}C are given.

Dynamic Light Scattering Plot



SI Figure 1. (A, B) DLS histogram plots for GTHCC hydrogel in water/methanol (1:1) solvent at Sol state (57 ^{o}C) and GEL state (31 ^{o}C), ([GTHCC] =2mg/mL).

FT-IR Data

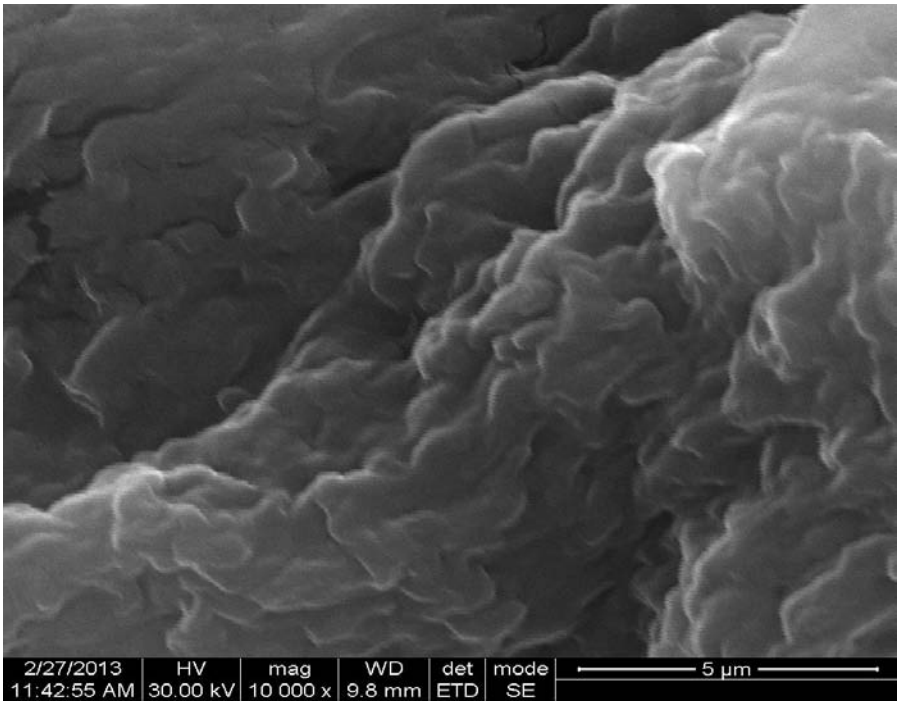


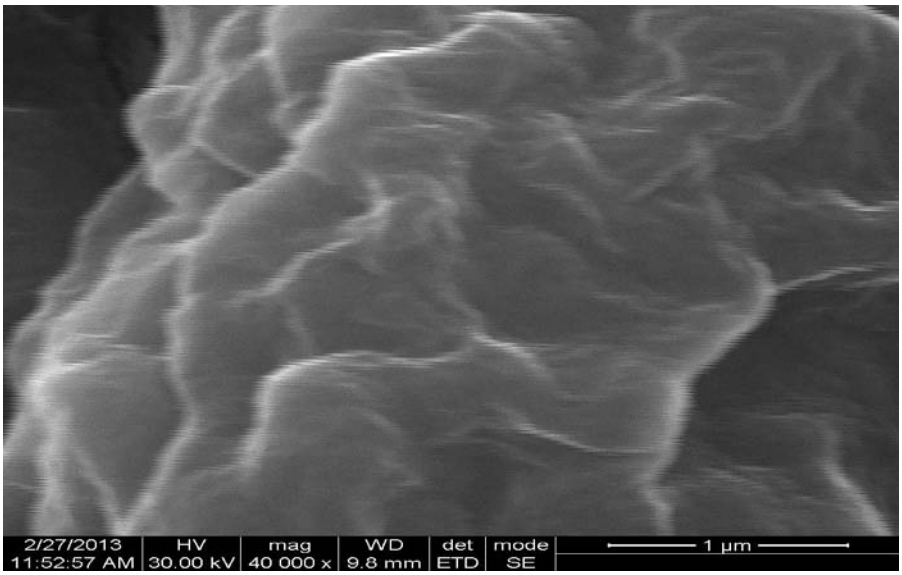
SI Figure 2. FT-IR Spectrum for dryg gel and wet gel of GTHCC conjugate in deuterated water/methanol (1:1) solvent, ([GTHCC]=2mg/mL).

SI Figure 2 is the plot for IR spectra of Dry and wet gel of GTHCC in deuterated water/methanol (1:1) mixture. The band observed at 1467cm^{-1} is due to long alkanes chain. The band observed from 1050-1250 cm^{-1} is due to CO stretching frequency. The broad band observed at 3450cm^{-1} is due to intermolecular hydrogen bonding between –OH groups of GTC conjugate. For alkyl group -CH_2 the asymmetric and symmetric stretching were observed at 2950cm^{-1} and 2853cm^{-1} respectively. A broad band observed from 2350-2650 cm^{-1} is due to -OD stretching frequency.

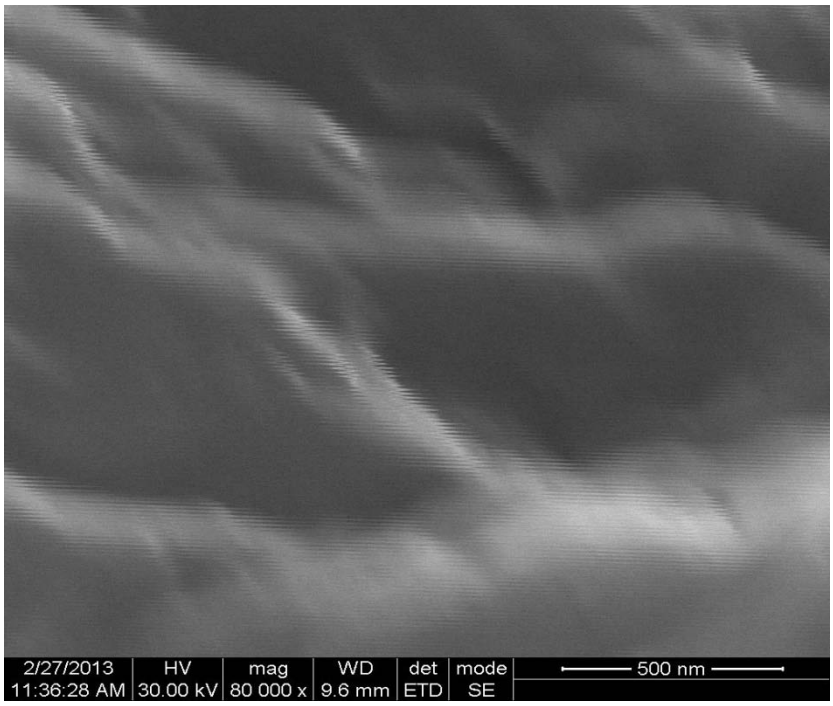
HR-SEM Images

A)



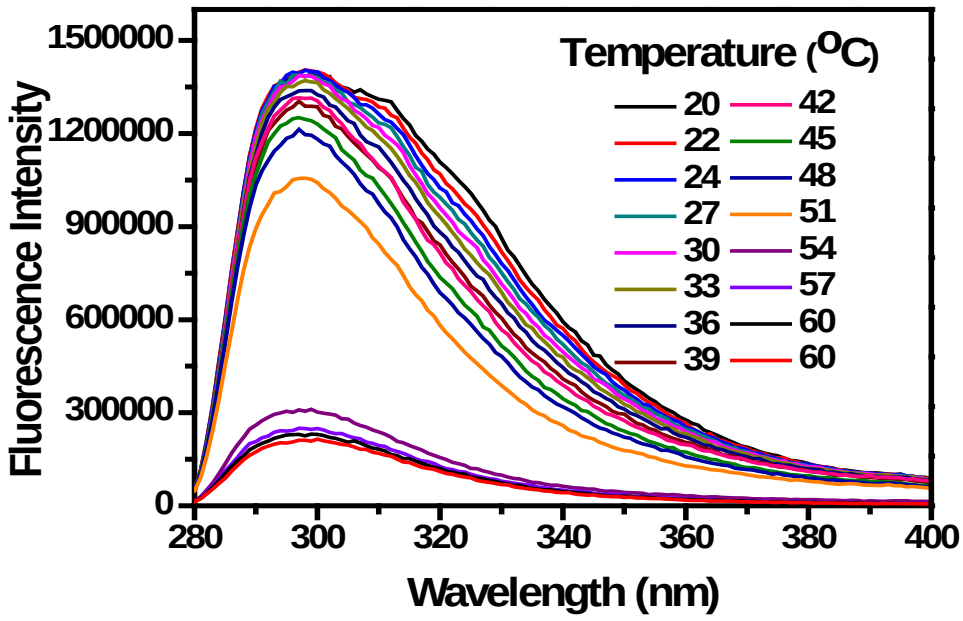


(B)



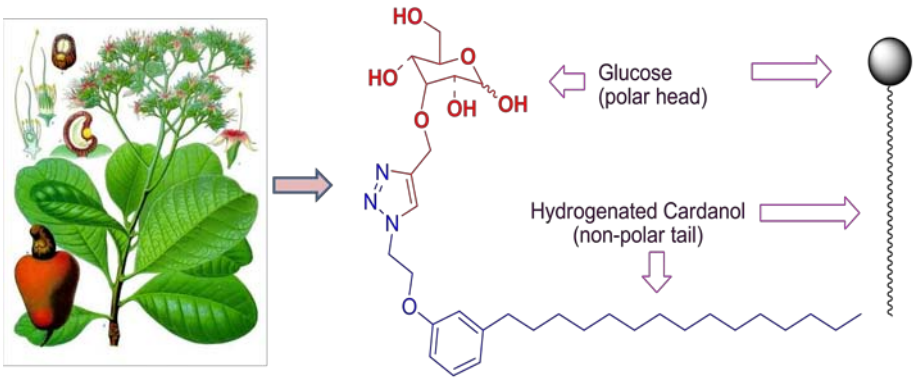
SI Figure 3. HR-SEM images of GTHCC gel (A) water/methanol (1:1) solvent (B) Cyclohexane solvent.

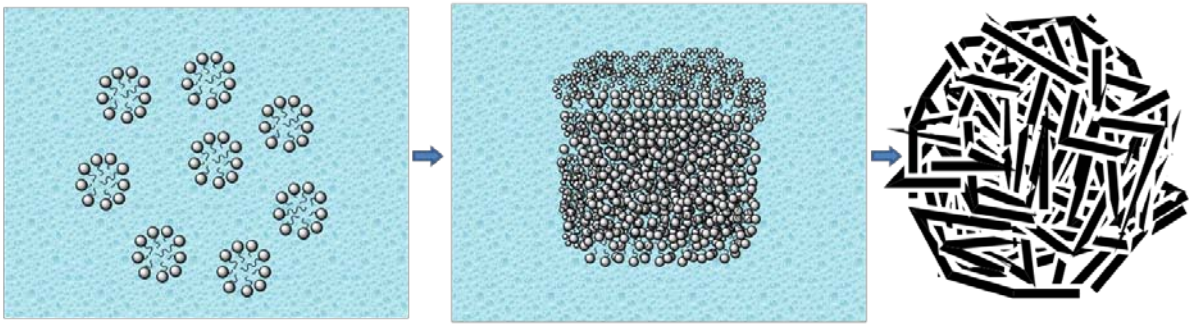
Fluorescence Emission Spectra



SI Figure 4. Plot for fluorescence emission spectra of GTHCC hydrogel with variation of temperature in water/methanol (1:1) solvent ([GTHCC]= 2mg/mL)

Schematic representation of Gelation process





Above 50 °C
Size= 22-50 nm
Micellar Phase(SOL)

From 38-44 °C
Size=200-700 nm
Phase of Higher Micellar Aggregate

Below 27 °C
Size =2-7 µM
GEL Phase