Supporting Information for

Self-assembly of sodium glycyrrhetinate into hydrogel: characterisation and properties

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Content **Page**

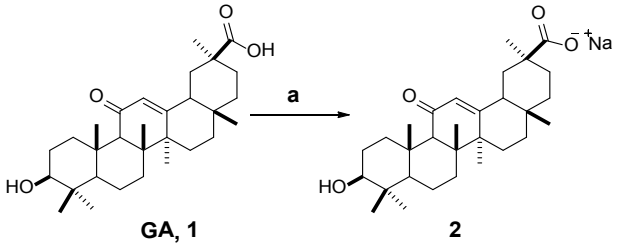
1. Measurements

The *minimum gelation concentration (MGC)* was measured by a weighted amount of gelator and an increasing volume of solvent. The state of the mixture was evaluated by the "stable to inversion of a test tube" method.[1] The *gel-to-sol transition temperatures (T_{gel})* were determined in duplicate by slowly heating in a thermostatted water bath until the gel started to flow.

UV-vis spectra were measured on TU-1901 spectrometers; *NMR spectra* were recorded on JOEL JNM-ECA 300 spectrometers; *Electrospray ionization mass spectrometry (ESI-MS)* was measured on Bruker ESQUIRE-LC spectrometer in positive/negative mode; *IR spectra* were recorded on Nicolet 360 FT-IR spectrophotometer with KBr pellets; *Scanning electron microscopy (SEM)* was performed on a Sirion-200 system; *Rheological experiments* were performed using a TA-AR2000ex rheometer with parallel plate geometry (40 mm in diameter) at 25 ^{o}C.

[1] A. Takahashi, M. Sakai, T. Kato, *Polym. J.*, 1980, **12**, 335-341.

2. Synthesis and structure data



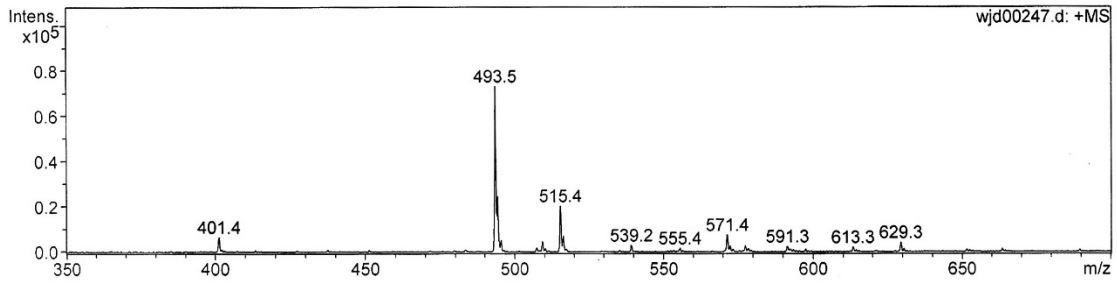
GA, 1 2

Scheme 1 a) NaOH, CH_3OH, H_2O, rt, 40%.

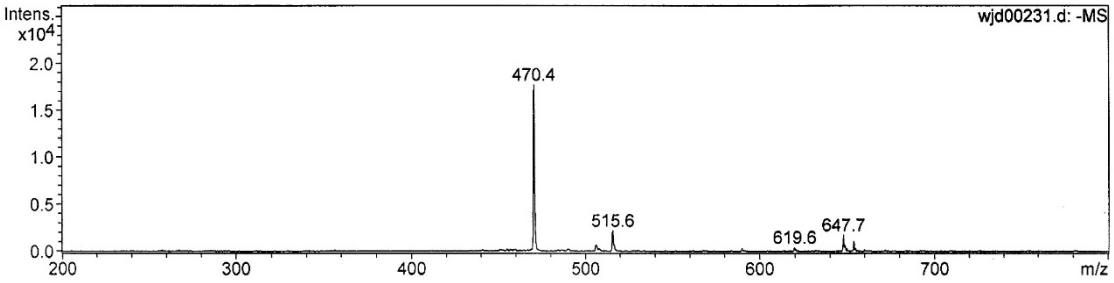
Compound 2

Glycyrrhetinic acid (**GA**, 3 g, 6.37 mmol) and NaOH (256 mg, 6.40 mmol) were dissolved in CH_3OH: H_2O = 40 mL: 10mL. The reaction mixture was stirred at rt for 1h, and then most of the solvent was evaporated. The residue was cooled for 1h after the addition of ethyl acetate. The mixture was filtered, washed with acetone and dried to get **2** as a white solid (1.260 g, 40%). mp. 305-307 ^{o}C; ESI-MS (+): m/z=493.5 $[M+H]^+$, 515.4 $[M+Na]^+$; ESI-MS (-): m/z=470.4 $[M-Na]^-$; ^{1}H NMR (300 MHz, DMSO-d_6): 0.68, 0.71, 0.91, 0.92, 0.97, 1.03, 1.33 (7×s , 21H, 23, 24, 25, 26, 27, 28, 29-CH_3), 3.01 (m, 1H, 3-H), 4.33 (s, 1H, 3-OH), 5.43 (s, 1H, 12-H); ^{13}C NMR (75 MHz, DMSO-d_6): 199.19 (11-C), 180.42 (30-COONa), 171.19 (13-C), 127.16 (12-C), 76.65 (3-C), 61.18, 54.37, 48.03, 44.93, 43.84, 42.91, 42.58, 38.19, 36.71, 32.31, 31.92, 31.56, 29.49, 28.63, 28.26, 27.05, 26.31, 25.19, 23.23, 18.44, 17.31, 16.27, 16.09.

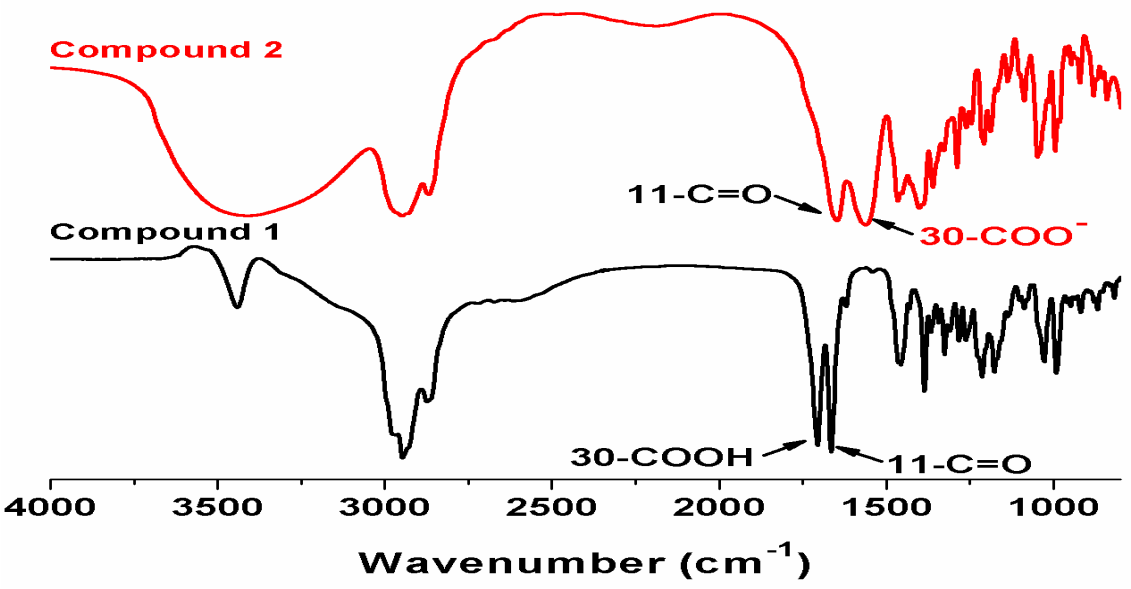
ESI-MS (+) Spectrum of compound **2**



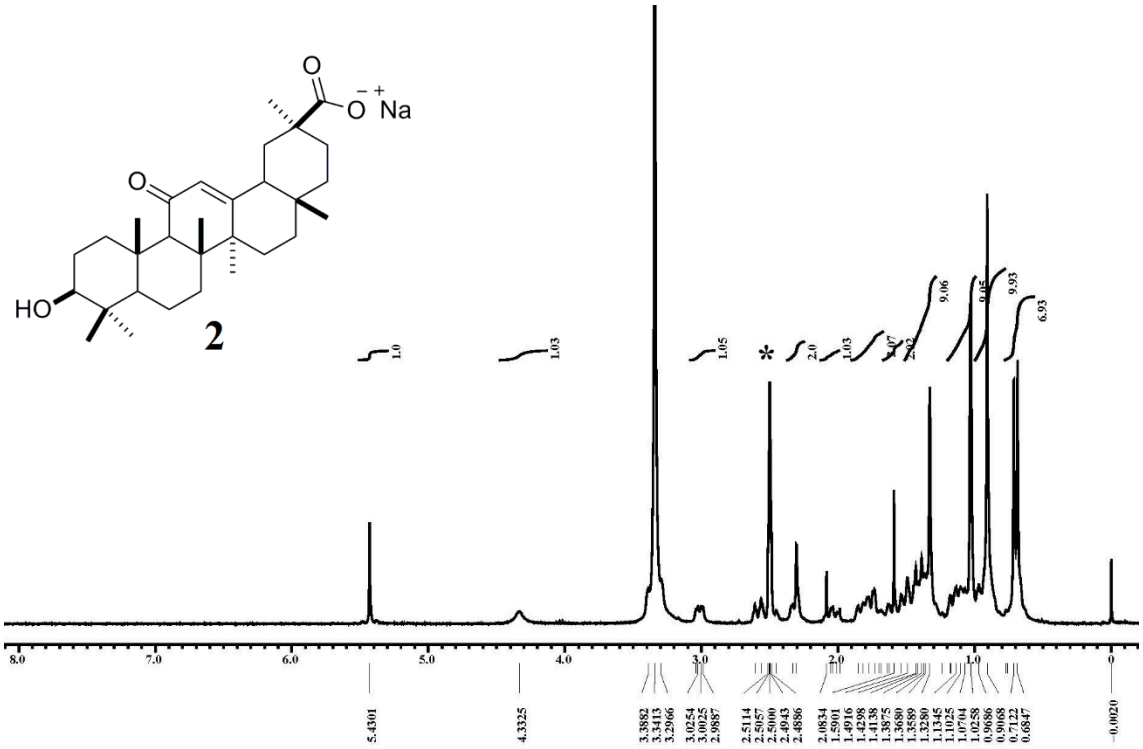
ESI-MS (-) Spectrum of compound **2**



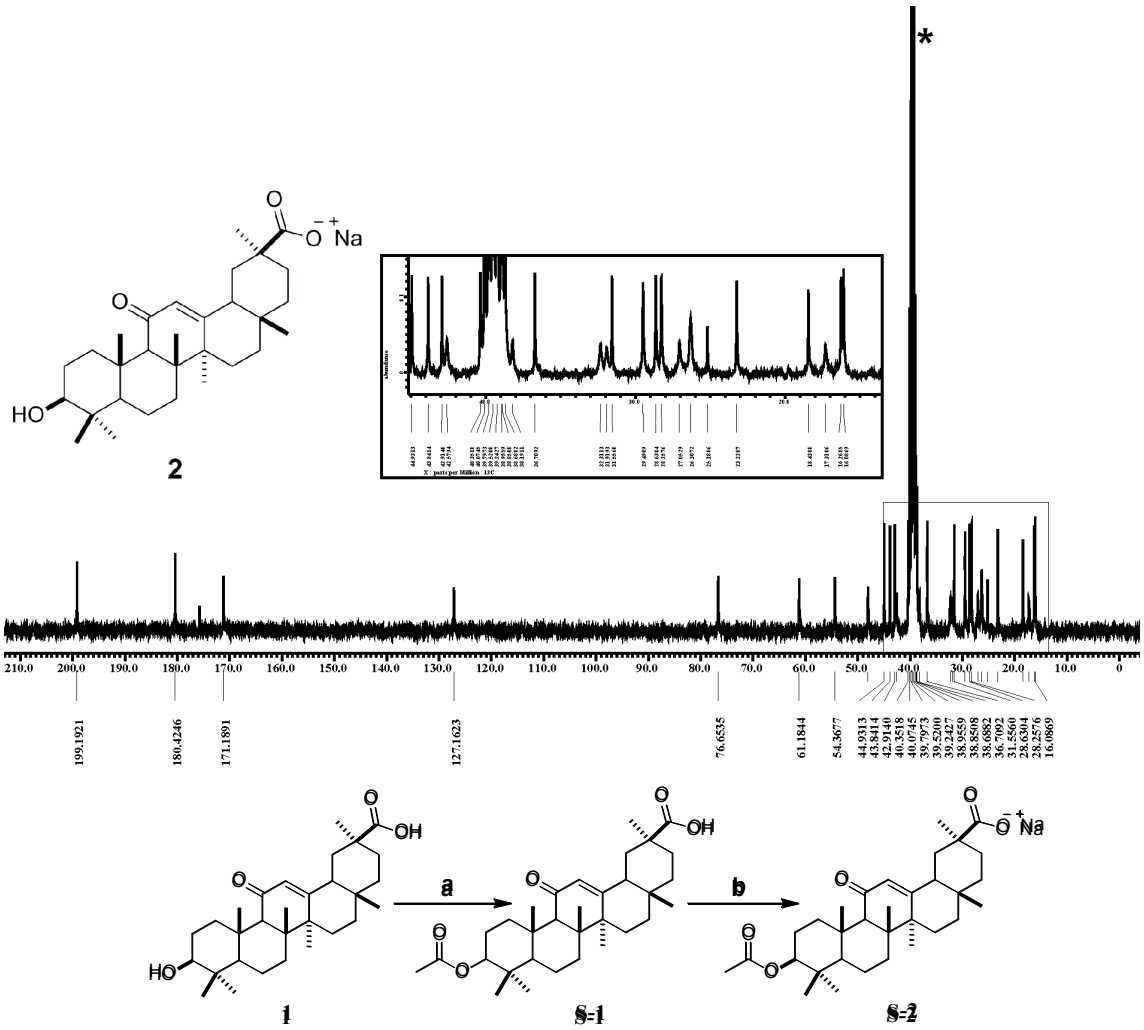
IR spectra of compound **1** and **2**



^{1}H NMR Spectrum of compound **2** (300 MHz, DMSO-d_6, *solvent peak)



^{13}C NMR Spectrum of compound **2** (75 MHz, DMSO-d_6, *solvent peak)

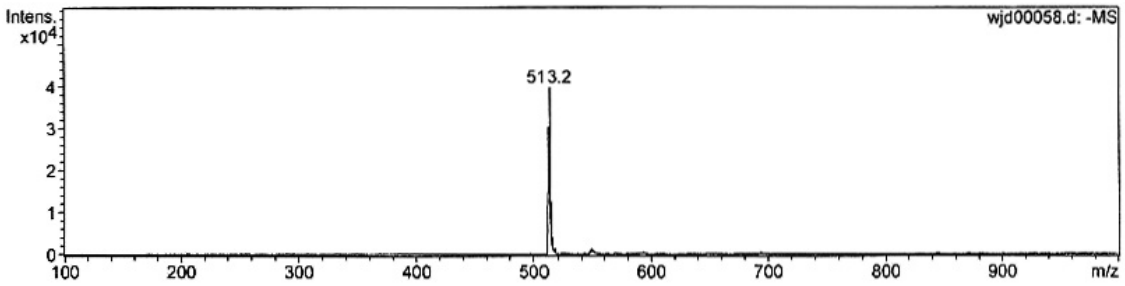


Scheme 2 a) Ac_2O, DMAP, Pyridine, 50 ^oC, 82%; b) Na_2CO_3, THF, H_2O, rt, 48%.

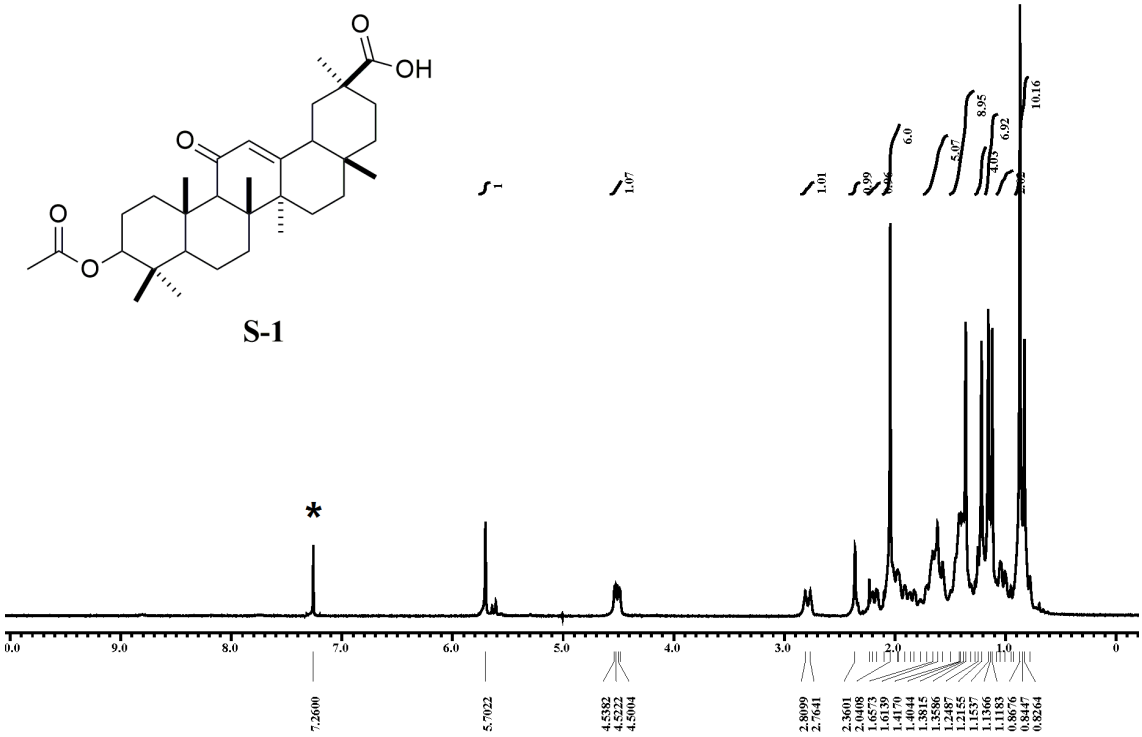
Compound S-1

GA (4.707 g, 10 mmol) and DMAP (25 mg, 0.2 mmol) were dissolved by 30 mL Pyridine. Ac_2O (2.58 mL, 27.3 mmol) was added into the solution and the mixture was stirred at 50 ^oC for 12 h. The crude was poured into water and filtrated. Purification by chromatography (CH_2Cl_2: CH_3OH=50: 1, v/v) afforded **S-1** as a white solid (4.202 g, 82%). mp. 300-301 ^oC; ESI-MS (-): m/z=513.2 $[M-H]^-$; ^1H NMR (300 MHz, $CDCl_3$): 0.78, 0.84, 0.87, 1.12, 1.15, 1.22, 1.36 (7×s , 21H, 23, 24, 25, 26, 27, 28, 29-CH_3), 2.04 (s, 3H, 3-$O_2CC\underline{H}_3$), 4.51 (m, 1H, 3-H), 5.70 (s, 1H, 12-H); ^{13}C NMR (75 MHz, $CDCl_3$): 200.34 (11-C), 181.96 (30-$\underline{C}OOH$), 171.05 (13-C), 169.47 ($CH_3\underline{C}O_2$), 128.42 (12-C), 80.63 (3-C), 61.68, 55.00, 48.22, 45.45, 43.80, 43.18, 40.81, 38.76, 38.03, 37.70, 36.92, 32.69, 31.85, 30.87, 28.52, 28.44, 28.03, 26.44, 23.55, 23.33, 21.29, 18.66, 16.66, 16.39.

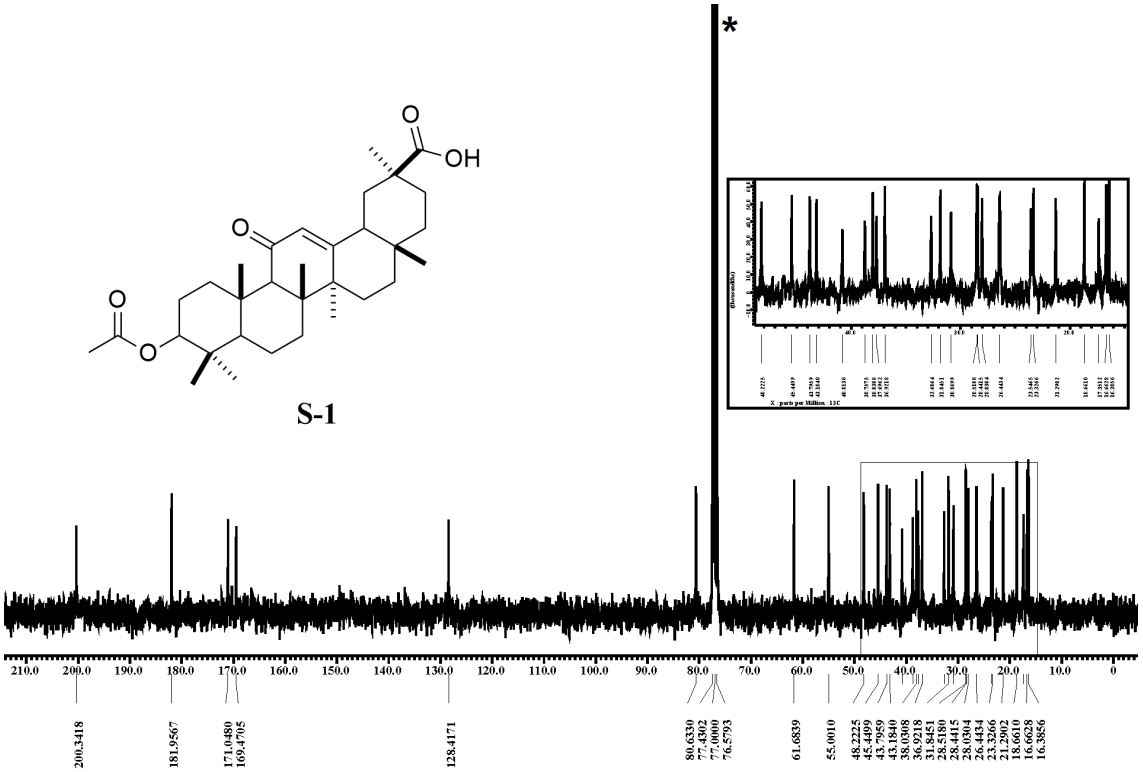
ESI-MS (-) Spectrum of compound **S-1**



^{1}H NMR Spectrum of compound **S-1** (300 MHz, $CDCl_3$, *solvent peak)



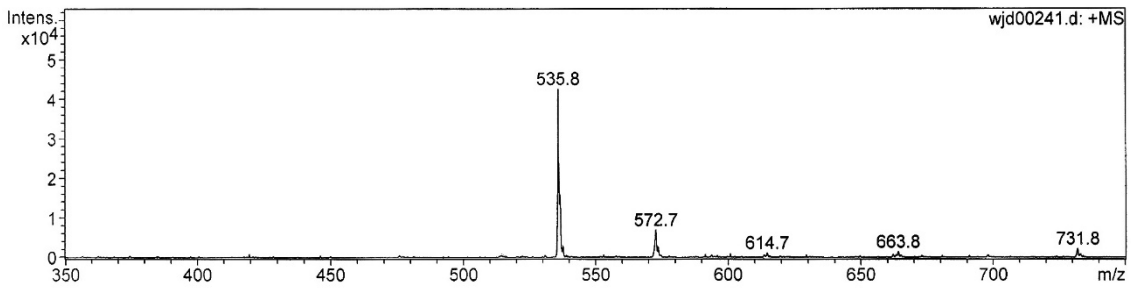
^{13}C NMR Spectrum of compound **S-1** (75 MHz, $CDCl_3$, *solvent peak)



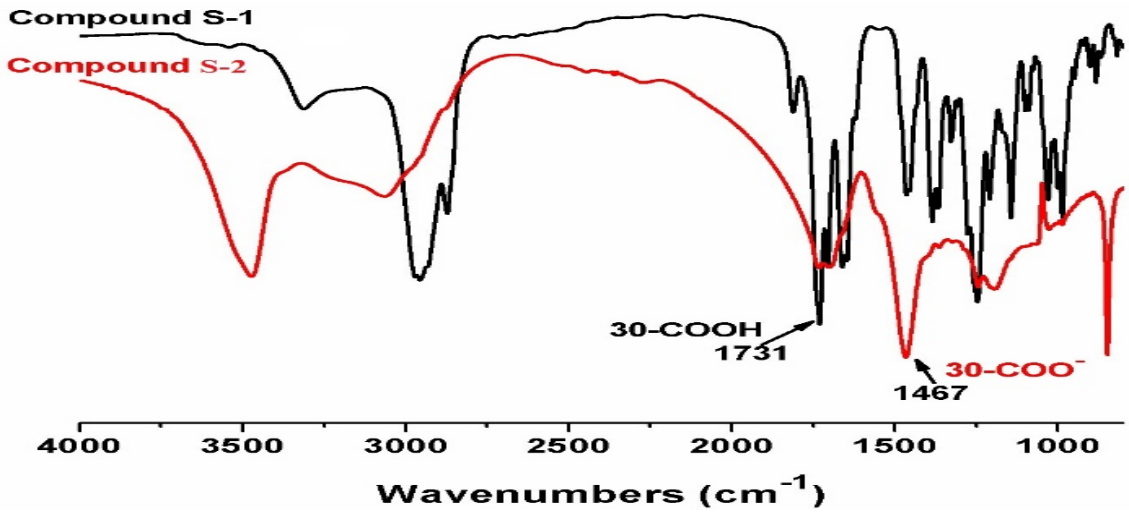
Compound S-2

S-1 (2.050 g, 4 mmol) was dissolved in 60 mL THF and a 10 mL aqueous solution containing Na_2CO_3 (435 mg, 4.1 mmol) was added. The reaction mixture was stirred at rt for 1h, and then most of the solvent was evaporated. The residue was cooled for 1h after the addition of ethyl acetate. The mixture was filtered, washed with acetone and dried, leaving **S-2** as a white solid (1.026 g, 48%). mp. >300 ^{o}C; ESI-MS (+): m/z=535.8 $[M+H]^+$, 572.7 $[M+K]^+$; ^{1}H NMR (300 MHz, DMSO-d_6): 0.72, 0.78, 0.82, 0.93, 1.04, 1.06, 1.35 (7×s , 21H, 23, 24, 25, 26, 27, 28, 29-CH_3), 2.04 (s, 3H, 3-OCOC$\underline{H}_3$), 4.42 (m, 1H, 3-H), 5.43 (s, 1H, 12-H); ^{13}C NMR (75 MHz, DMSO-d_6): 199.00 (11-C), 178.92 (30-$\underline{C}$OONa), 171.82 (13-C), 170.12 (3-O$\underline{C}$OCH$_3$), 126.78 (12-C), 79.69 (3-C), 60.76, 53.76, 44.83, 43.58, 42.97, 42.73, 38.12, 37.93, 37.56, 36.49, 31.96, 31.46, 29.35, 28.62, 27.66, 26.25, 26.14, 23.21, 23.09, 20.95, 18.35, 16.93, 16.56, 16.13.

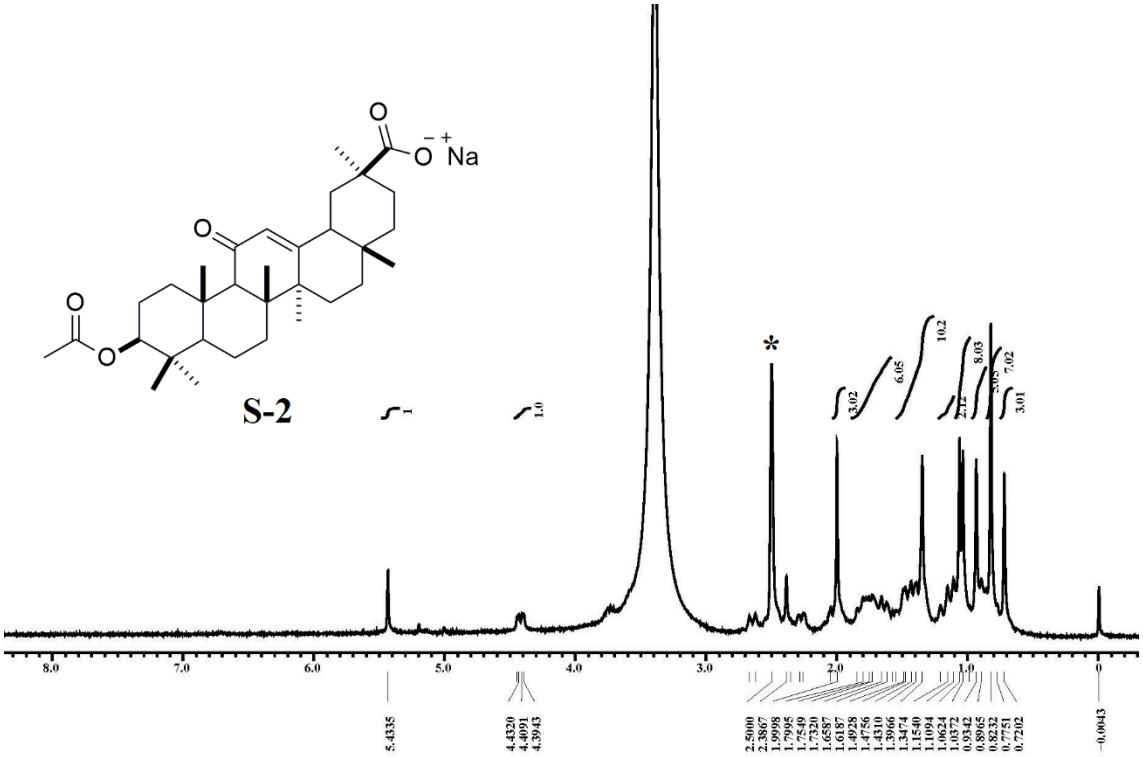
ESI-MS (+) Spectrum of compound **S-2**



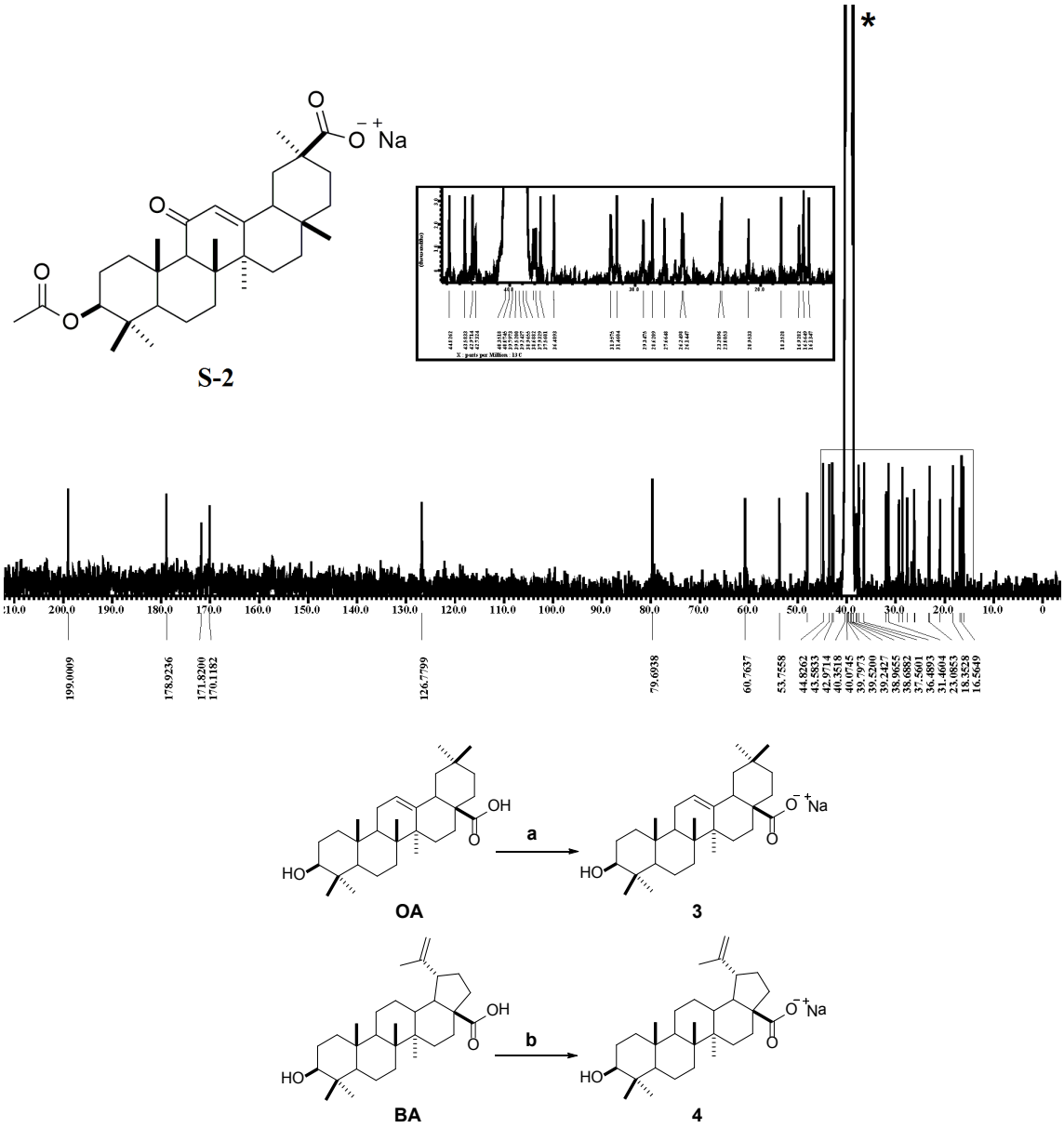
IR spectra of compound **S-1** and **S-2**



^{1}H NMR Spectrum of compound **S-2** (300 MHz, DMSO-d_6, *solvent peak)



^{13}C NMR Spectrum of compound **S-2** (75 MHz, DMSO-d_6, *solvent peak)



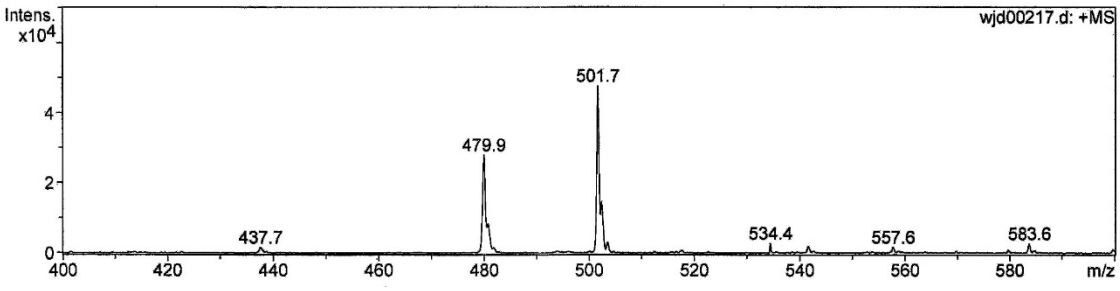
Scheme 3 a) NaOH, THF, H_2O, rt, 90%; b) NaOH, CH_3OH, H_2O, rt, 78%.

Compound 3

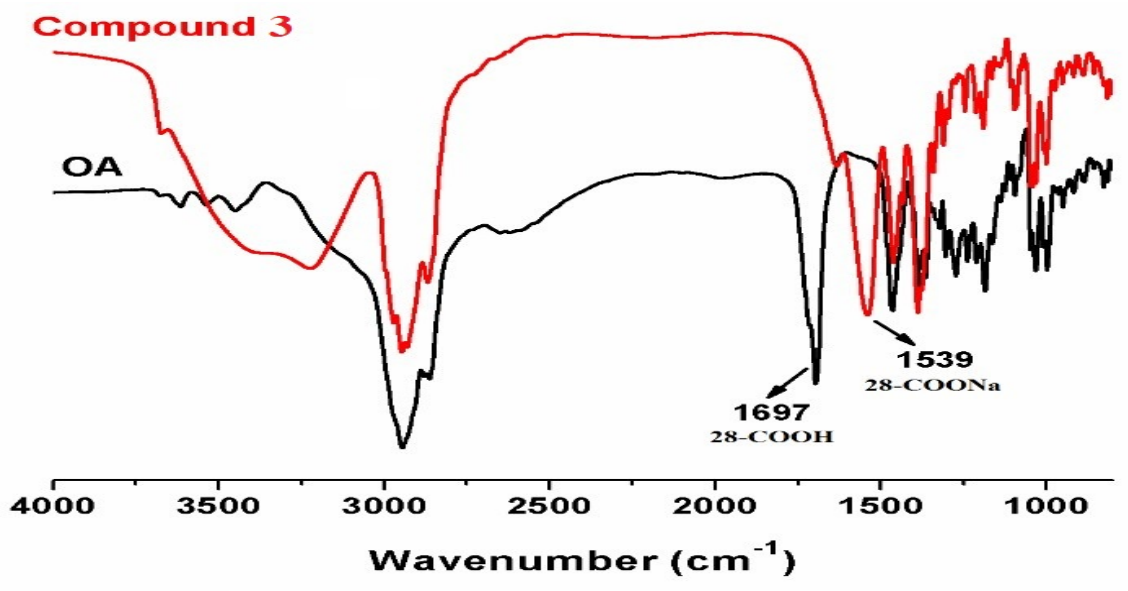
Oleanic acid (**OA**, 3 g, 6.57 mmol) was dissolved in 40 mL THF and a 10 mL aqueous solution containing NaOH (263 mg, 6.57 mmol) was added. The reaction mixture was stirred at rt for 1h, and then the solution was evaporated. The solid was purified by recrystallization from CH_3OH to get **3** as a white crystalline solid (2.832 g, 90%). mp. 294-295 ^oC; ESI-MS (+): m/z=479.9 $[M+H]^+$, 501.7 $[M+Na]^+$; ^1H NMR (300 MHz, DMSO-d_6): 0.67, 0.73, 0.83, 0.84, 0.86, 0.88, 1.04 (7×s , 21H, 23, 24, 25, 26, 27, 29, 30-CH_3), 2.99 (m, 1H, 3-H), 4.40 (s, 1H, 3-O<u>H</u>), 5.02 (s, 1H, 12-H); ^{13}C NMR (75 MHz, DMSO-d_6): 181.30 (28-<u>C</u>OONa), 146.24 (13-C), 119.60 (12-C), 76.85 (3-C), 54.96, 47.38, 47.01, 45.56, 41.81, 41.49, 40.35, 40.07, 39.80, 39.52, 39.23, 38.96,

38.79, 38.69, 38.39, 38.14, 36.67, 34.41, 33.41, 33.06, 32.76, 30.74, 28.28, 27.70, 27.01, 25.68, 23.77, 23.53, 22.97, 18.15, 17.41, 16.07, 15.15.

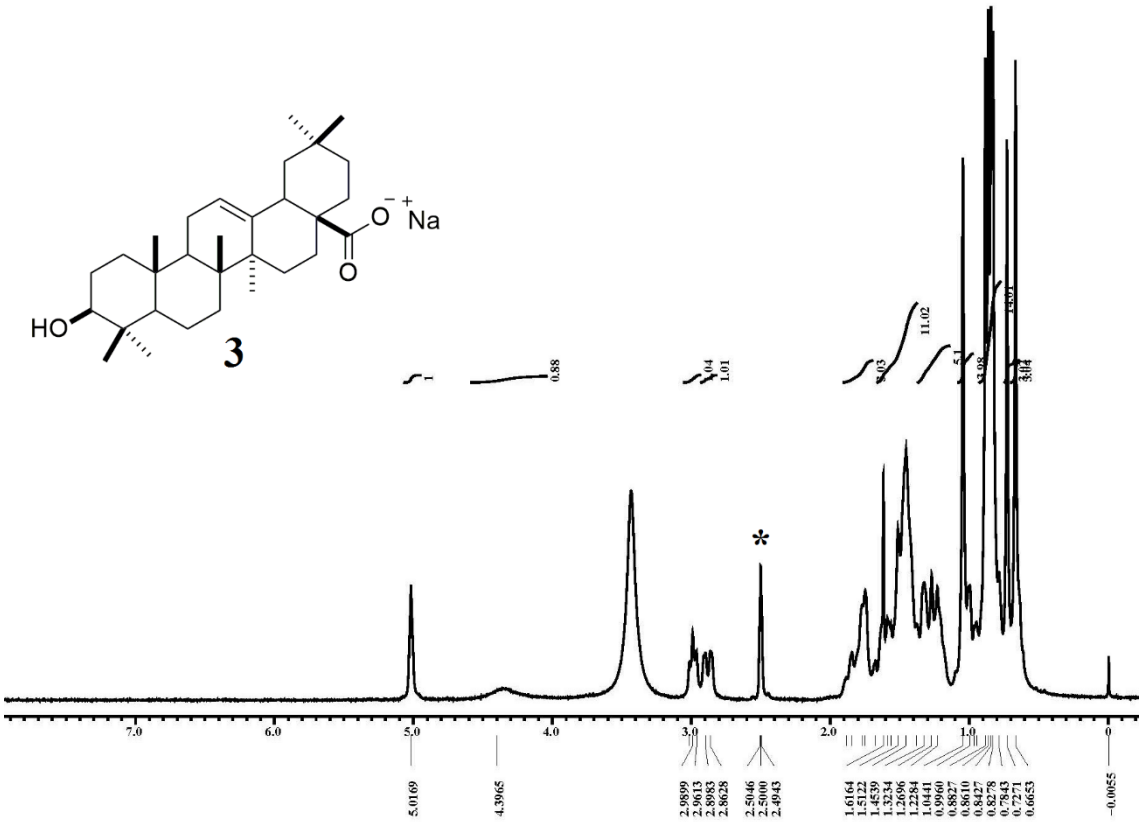
ESI-MS (+) Spectrum of compound **3**



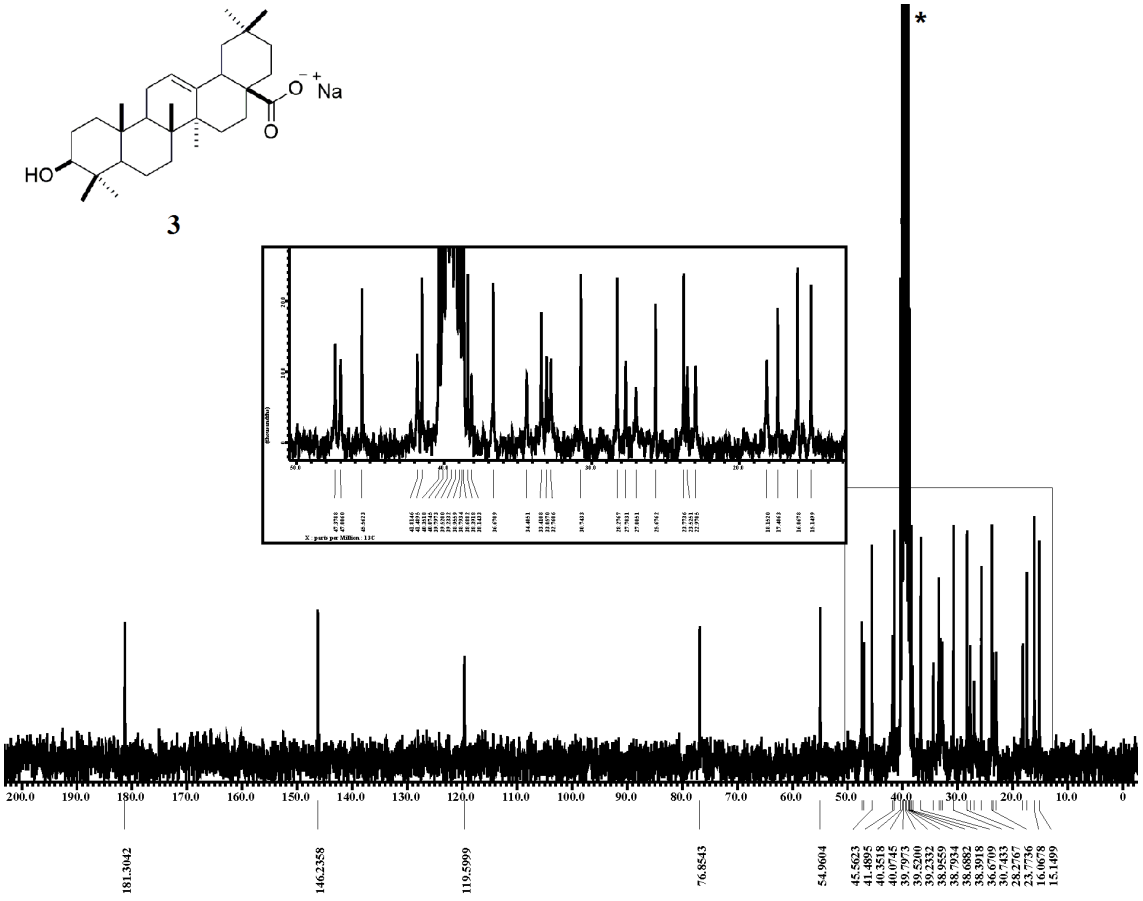
IR spectra of compound **3** and **OA**



^{1}H NMR Spectrum of compound **3** (300 MHz, DMSO-d_6, *solvent peak)



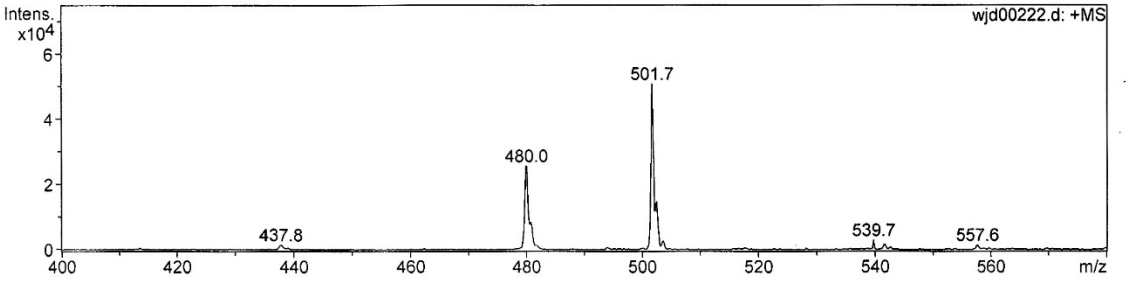
^{13}C NMR Spectrum of compound **3** (75 MHz, DMSO-d_6, *solvent peak)



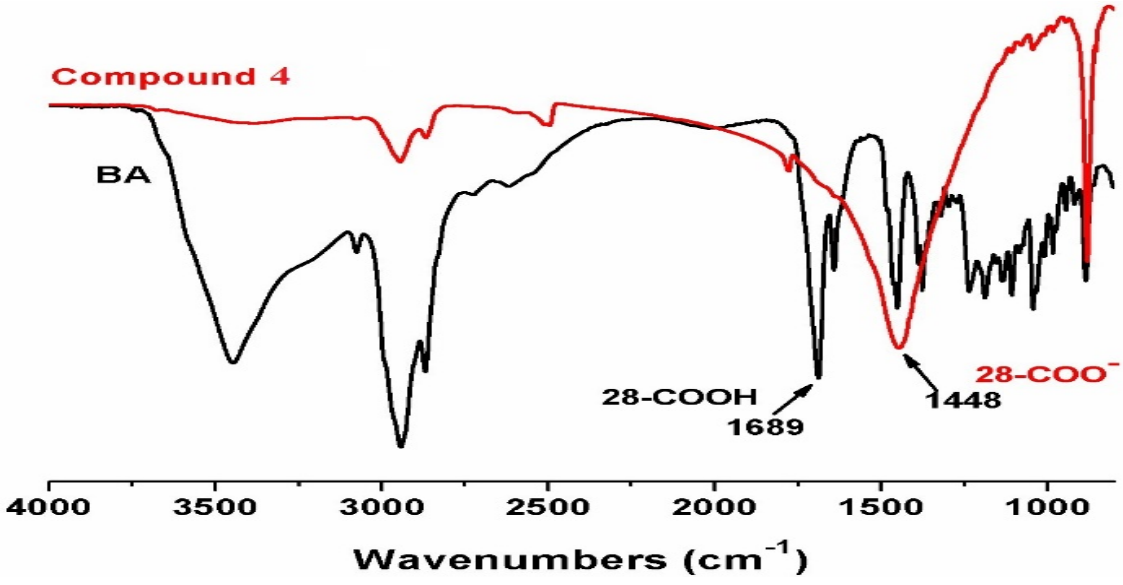
Compound 4

Betulinic acid (**BA**, 200 mg, 0.44 mmol) was dissolved in 40 mL CH_3OH and a 10 mL aqueous solution containing NaOH (18 mg, 0.45 mmol) was added. The reaction mixture was stirred at rt for 1h, and then the solution was evaporated to get crude product. The solid product was washed with acetone, filtered and dried to give **4** as white solid (164 mg, 78%). mp. >300 ^{o}C; ESI-MS (+): m/z=480.0 $[M+H]^+$, 501.7 $[M+Na]^+$; ^{1}H NMR (300 MHz, DMSO-d_6): 0.64, 0.76, 0.86, 0.88, 0.93, 1.62 (6×s , 18H, 23, 24, 25, 26, 27, 30-CH_3), 3.17 (m, 1H, 3-H), 4.48 (s, 1H, 29-CH), 4.60 (s, 1H, 29-CH); ^{13}C NMR (75 MHz, DMSO-d_6): 179.22 (28-COONa), 151.98 (20-C), 108.56 (29-C), 76.80 (3-C), 56.02, 55.00, 50.19, 49.17, 46.93, 42.06, 38.50, 38.33, 37.75, 37.25, 36.77, 34.18, 33.51, 30.81, 29.52, 28.13, 27.20, 25.40, 20.70, 19.13, 18.05, 16.24, 16.00, 15.81, 14.39.

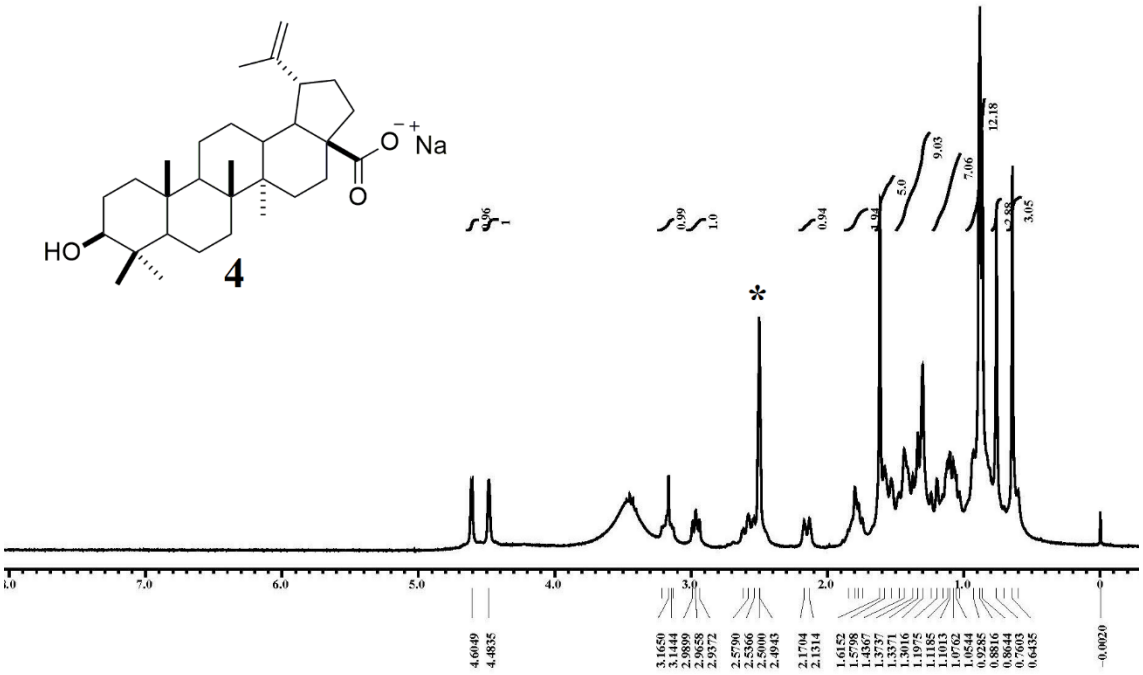
ESI-MS (+) Spectrum of compound **4**



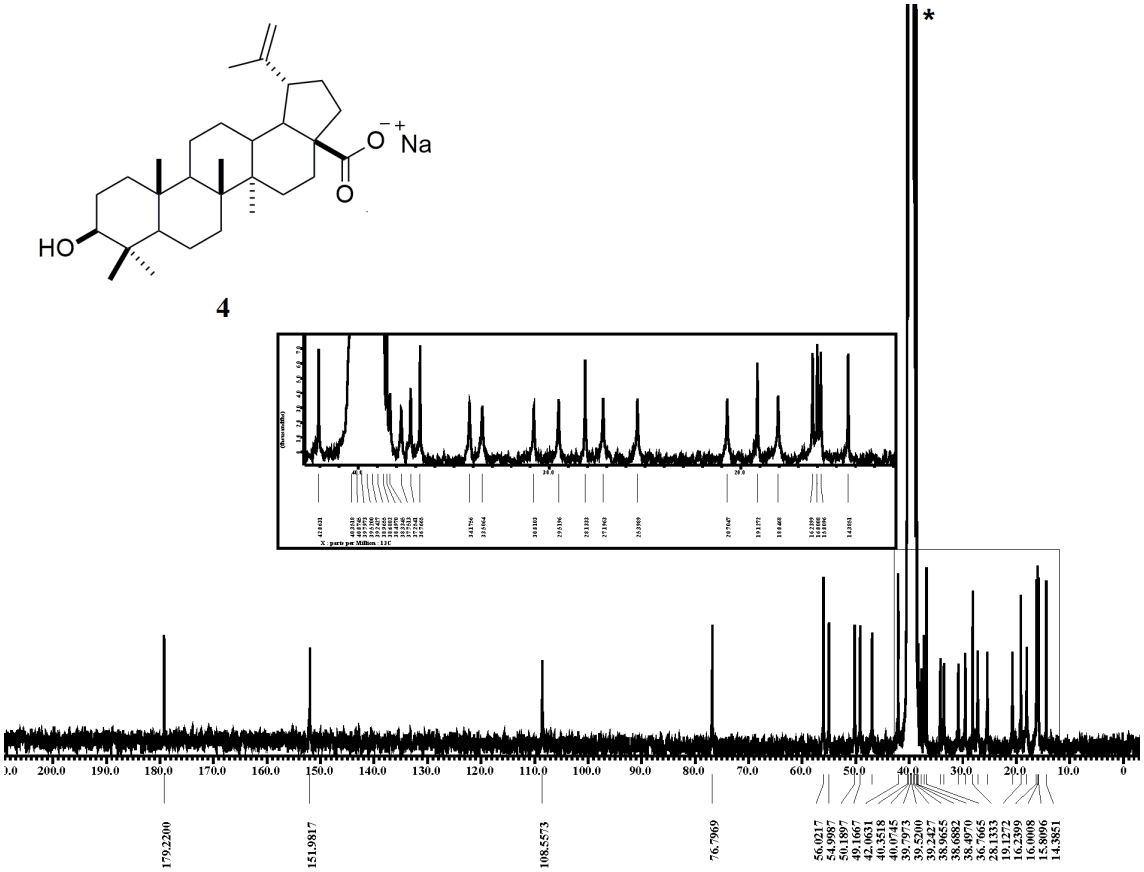
IR spectra of compound **4** and **BA**



^{1}H NMR Spectrum of compound **4** (300 MHz, DMSO-d_6, *solvent peak)



^{13}C NMR Spectrum of compound **4** (75 MHz, DMSO-d_6, *solvent peak)



3. Thermodynamic parameters of the hydrogel[2]

The Gibbs free energy change (ΔG) during the gel-to-sol transition can be expressed as:

$$\Delta G = -RT\ln K = \Delta H - T\Delta S$$

That is, $= -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$, where *K* is the equilibrium constant of the thermoreversible gel-to-sol transition. For one component gel, $K = \frac{[Gelator]}{[Gel]}$, assuming unit activity of the gel and taking concentration of the solution to be equal to the dissolved concentration of the gelator, the equilibrium constant can be expressed as: $K = [Gelator]$.

According to the above, a plot of ln*K* versus 1/T can allow us to calculate the thermodynamic parameters.

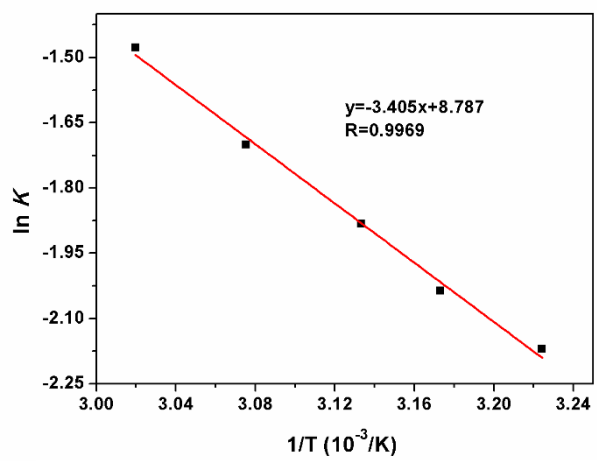


Fig. S1 Plot of ln*K versus* 1/T for the hydrogel of **2**.

y=-3.405x +8.787

ΔH/R=3405K, ΔH=28.3 kJ/mol;

ΔS/R=8.787, ΔS=73.1 J/(mol•K);

T=298 K, ΔG= ΔH-T ΔS=6.52 kJ/mol.

[2] D. Rizkov, J. Gun, O. Lev, R. Sicsic and A. Melman, *Langmuir*, 2005, **21**, 12130-12138.

4. IR spectra of compound 2 and xerogel

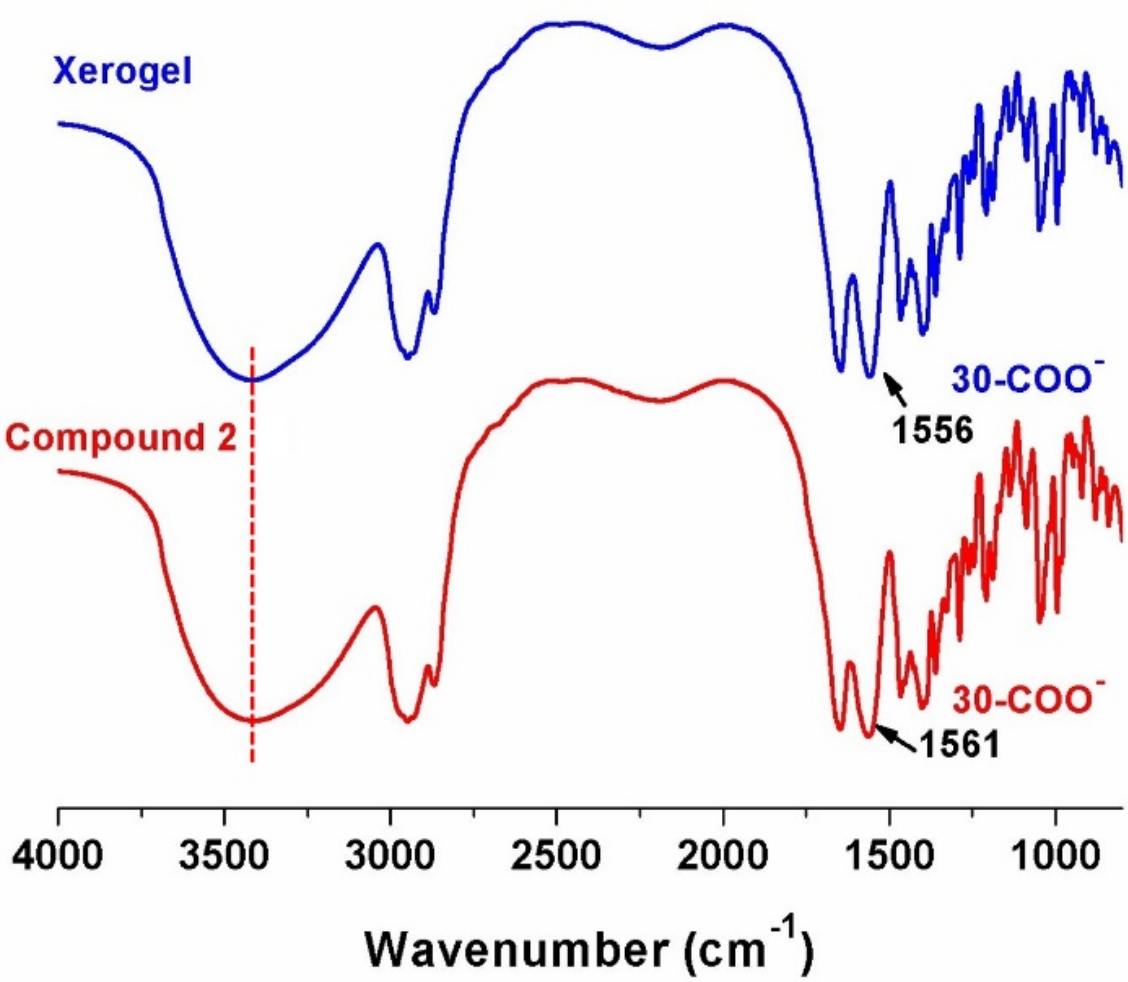


Fig. S2 IR spectra of compound **2** and xerogel.

The wavenumber of C=O stretching vibration of 30-COO^- was changed from 1561 cm^{-1} to 1556 cm^{-1}, while the wavenumber of 3-OH stretching vibration remained the same, indicating the dipole-dipole interaction between sodium carboxylates was the driving force.

5. Dye adsorption properties in dilute solutions

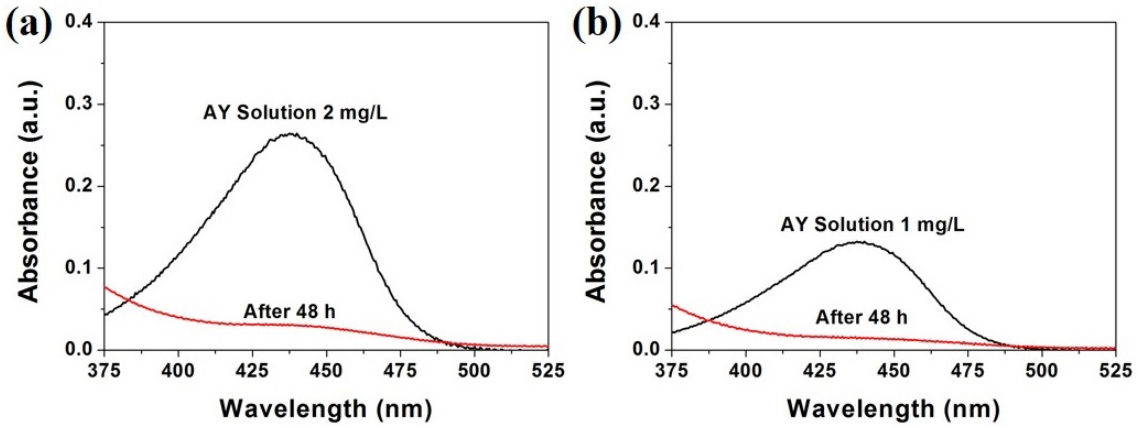


Fig. S3 UV-vis spectra of Acridine Yellow (AY) solutions before and after the addition of the hydrogels (1 cm^3 containing 90 mg of compound **2**): (a) [AY] = 2 mg/L; (b) [AY] = 1 mg/L.

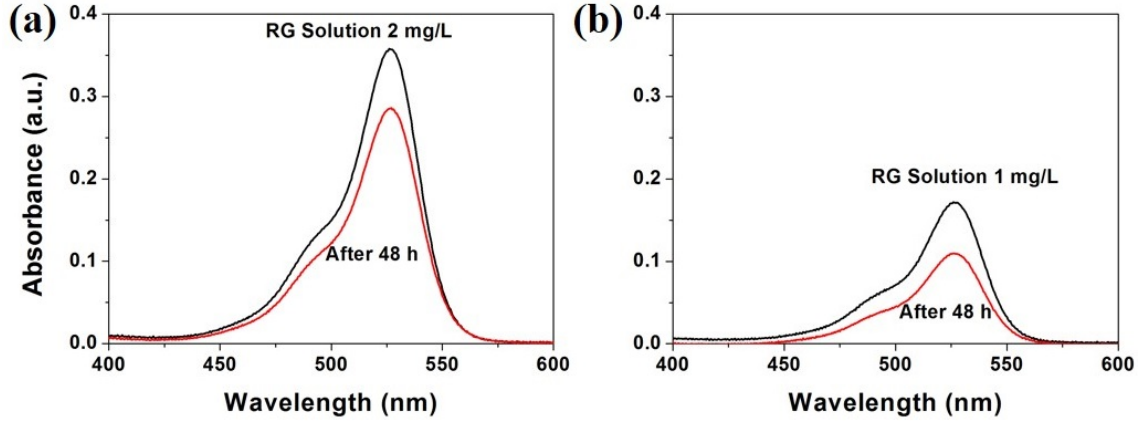


Fig. S4 UV-vis spectra of Rhodamine 6G (RG) solutions before and after the addition of the hydrogels (1 cm^3 containing 90 mg of compound **2**): (a) [RG] = 2 mg/L; (b) [RG] = 1 mg/L.

According to the experiment data, the hydrogel was found efficient for the adsorption of AY from dilute dye solutions. While, the adsorption of RG was not significant in dilute solutions.

6. Gelation properties of control molecules

Table S1 Gelation properties of control molecules

Compound	Solvents	State*
S-2	H_2O	Transparent gel
3	H_2O	Insoluble
4	H_2O	Insoluble

*Determined with 60.0 mg of the tested substances and 1.00 mL H_2O.