

Supplementary Material (ESI) for Soft Matter

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Water-induced gel formation of oleanic acid-adenine conjugate and the effects of uracil derivative on the gel stability

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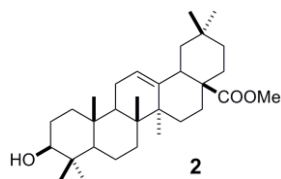
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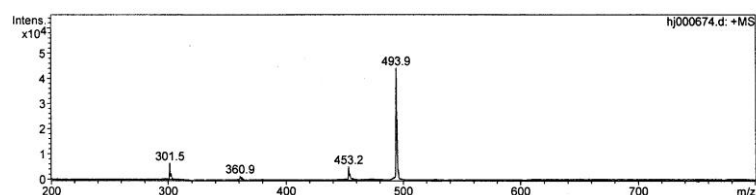
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1. Synthesis of compound **2**

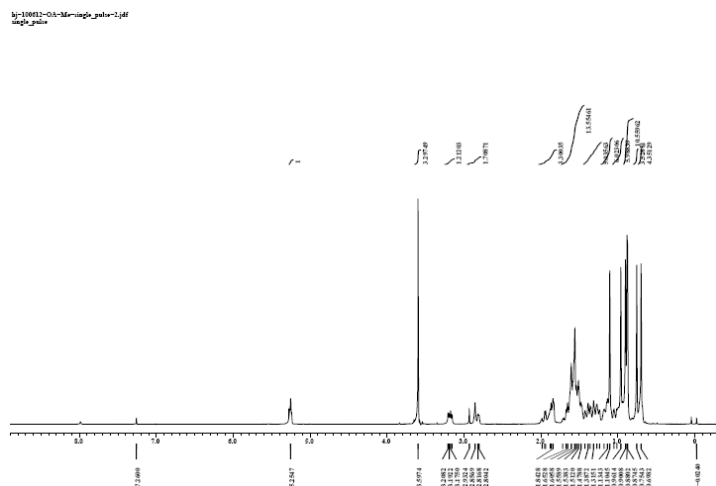


10.1g (21.4 mmol) **1** was dissolved in dry DMF (150 ml). 3.5g K_2CO_3 (25.4 mmol) was added. Then 3.0 ml CH_3I (60 mmol) was added. The mixture stirred for 24 h at rt. The solution was poured into water and the resulting suspension was filtrated to give **2** (solid, 11.5 g, 95%). m. p. 203-205 °C, ESI-MS (+) : $m/z = 493 [M+K]^+$; 1H NMR (300MHz, $CDCl_3$): 5.25 (m, 1H, 12-H), 3.59 (s, 3H, CO_2CH_3), 3.18 (dd, 1H, $J_1=9.96Hz$, $J_2=4.80Hz$, 3-H), 0.69, 0.75, 0.87, 0.88, 0.90, 0.96, 1.10 ($7 \times s$, $7 \times 3H$, 23, 24, 25, 26, 27, 29, 30- CH_3); ^{13}C NMR (75MHz, $CDCl_3$): 178.34 (28-C), 143.84 (13-C), 122.43 (12-C), 79.02 (3-C), 55.31, 51.59, 47.70, 46.78, 45.95, 41.70, 41.36, 39.34, 38.83, 38.52, 37.10, 33.93, 33.19, 32.74, 32.45, 30.76, 28.18, 27.77, 27.26, 26.01, 23.72, 23.47, 23.14, 18.40, 16.90, 15.67, 15.37.

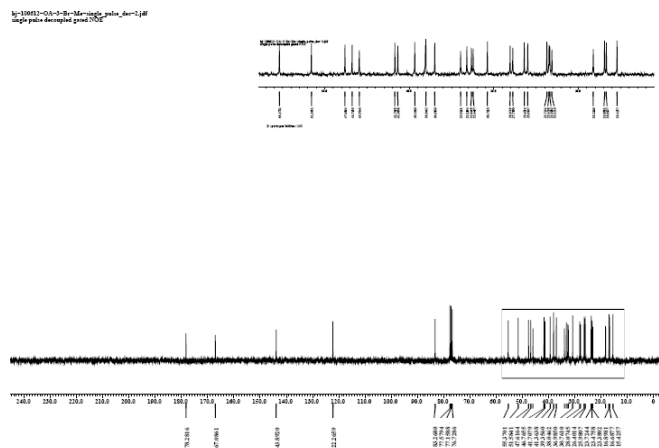
1). ESI-MS (+) Spectra of compound **2**



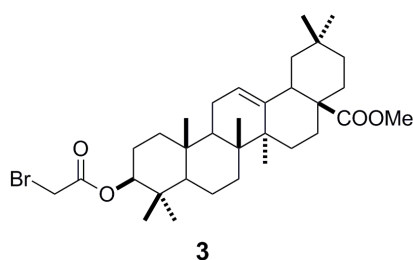
2). 1H NMR Spectra of compound **2**($CDCl_3$, 300MHz)



3). ^{13}C NMR Spectra of compound **2**($CDCl_3$, 75MHz)

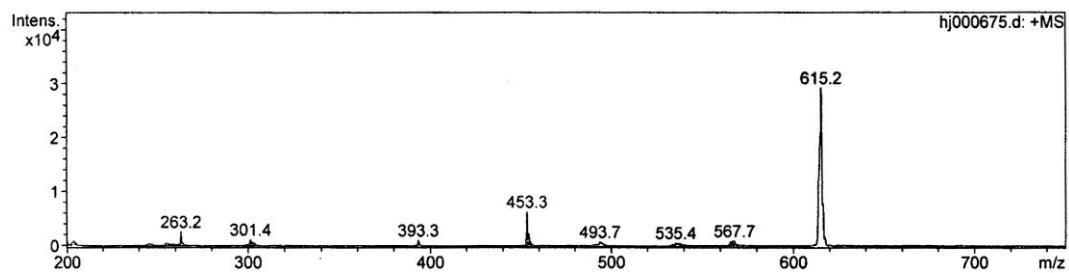


2. Synthesis of compound **3**

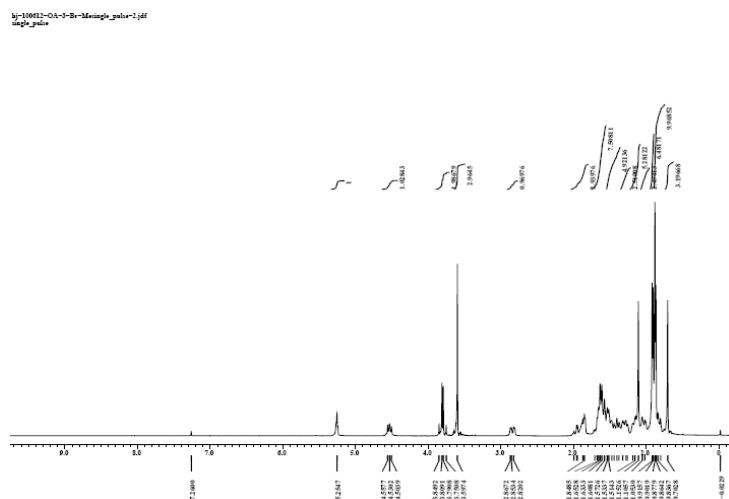


Compound **2** (1.0 g, 2.01 mmol) and K_2CO_3 (300 mg, 2.17 mmol) was dissolved in dry $CHCl_3$ (30 ml). The mixture was cooled to $0^\circ C$. Then 2.41 mmol of bromoacetyl bromide (2.4 ml) was added to the mixture. This reaction mixture was stirred at room temperature ($18^\circ C$) for 24 h. Then the precipitates were filtered and washed with CH_2Cl_2 (10 ml). The filtrates were successively washed with citric acid (10%) for three times (30 ml \times 3). Joined the aqueous-phase were extracted with CH_2Cl_2 (30 ml). The extracts was dried over $MgSO_4$ and solvents were removed under reduced pressure to get pale yellow crude solid (1.344 g). The solid was purified by silica gel column chromatography (CH_2Cl_2 : CH_3OH = 60:1) afforded **3** as a white solid (1.197 g, 98%). m. p. $181-182^\circ C$, ESI-MS (+) : m/z = 615 [$M+Na$] $^+$; 1H NMR (300MHz, $CDCl_3$): 5.25 (m, 1H, 12-H), 4.53 (t, 1H, $J_1=8.25Hz$, $J_2=7.89Hz$, 3-H), 3.89 (dd, 2H, $J_1=17.52Hz$, $J_2=12.03Hz$, $COCH_2Br$), 3.59 (s, 3H, CO_2CH_3), 0.70, 0.86, 0.87, 0.90, 0.91, 1.10 (6xs , 7 \times 3H, 23, 24, 25, 26, 27, 29, 30-CH3); ^{13}C NMR (75MHz, $CDCl_3$): 178.28 (28-C), 167.08 ($COCH_2Br$), 143.89 (13-C), 122.26 (12-C), 83.26 (3-C), 55.37, 51.58, 47.61, 46.76, 45.91, 41.70, 41.36, 39.35, 38.04, 36.98, 33.93, 33.18, 32.64, 32.44, 30.76, 28.07, 27.75, 26.40, 25.98, 23.72, 23.47, 23.38, 23.13, 18.23, 16.89, 16.68, 15.42.

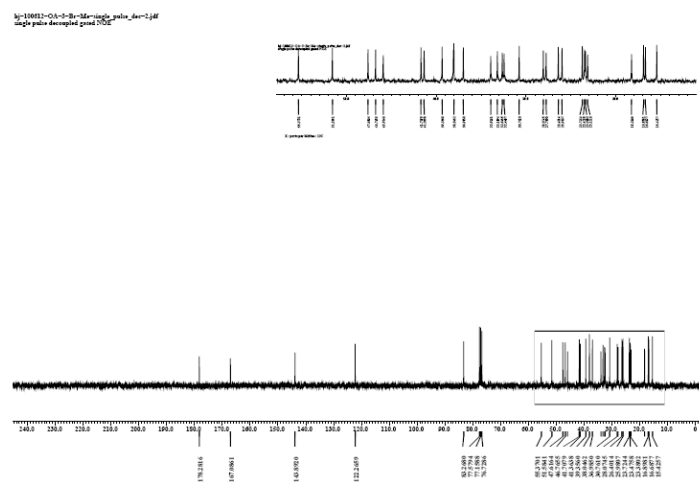
1). ESI-MS (+) Spectra of compound **3**



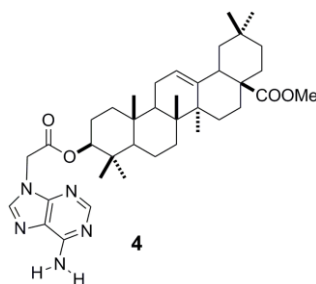
2). ¹H NMR Spectra of compound 3(CDCl₃, 300MHz)



3). ¹³C NMR Spectra of compound 3(CDCl₃, 75MHz)

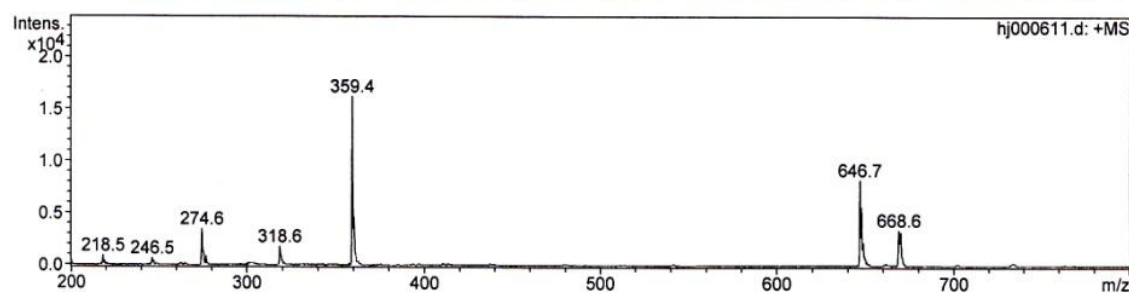


3. Synthesis of compound 4

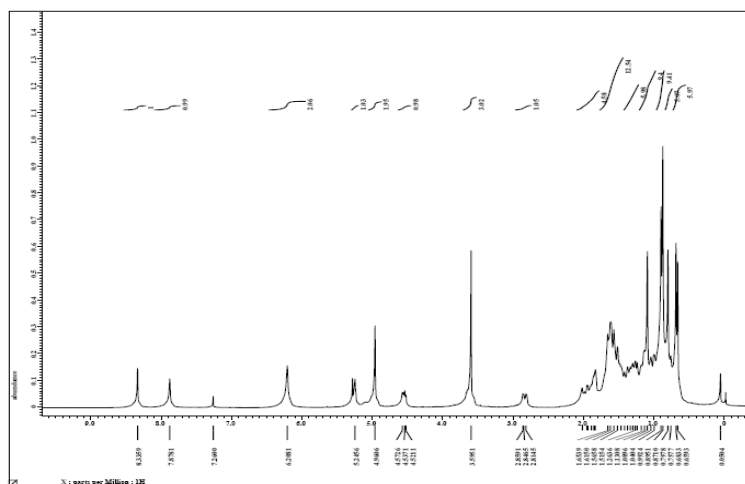


The solution of compound **3** (300 mg, 0.50 mmol) in 15mL dry DMF was added slowly to the solution of adenine(89 mg, 0.66 mmol) in 8ml dry DMF in the presence of K_2CO_3 (91 mg, 0.66 mmol). This mixture solution were stirred for 9 h at rt (15°C). The mixture was poured into water, and then was extracted with CH_2Cl_2 (30 ml \times 3). Joined the organic extracts were washed with H_2O and brine, dried by anhydrous MgSO_4 and evaporated, affording the pale yellow solid (395 mg). The solid was purified by silica gel column chromatography (CH_2Cl_2 : CH_3OH = 60:1-20:1) afforded **4** as a white solid (210 mg, 60%). m. p. 302-305 °C, ESI-MS (+) : m/z = 646 $[\text{M}+\text{H}]^+$, 668 $[\text{M}+\text{Na}]^+$; ^1H NMR (300MHz, CDCl_3): 8.33 (s, 1H, adenine-H), 7.78 (s, 1H, adenine-H), 6.20 (s, 2H, NH_2), 5.24 (s, 1H, 12-H), 4.96 (s, 2H, OCH_2 -adenine), 4.54 (dd, $J_1=12.00\text{Hz}$, $J_2=6.00\text{Hz}$, 1H, 3-H), 3.59 (s, 3H, CO_2CH_3), 0.65, 0.68, 0.79, 0.87, 0.89, 1.08 (7 \times s, 7 \times 3H, 23, 24, 25, 26, 27, 29, 30- CH_3); ^{13}C NMR (75MHz, CDCl_3): 178.32 (30-C), 166.89 (OCOCH_2), 155.60 (adenine-C), 153.08 (adenine-C), 150.31 (adenine-C), 143.89 (13-C), 140.97 (adenine-C), 122.21 (2C, 12-C, adenine-C), 83.73 (3-C), 72.03 (OCH_2), 55.27, 51.60, 47.56, 46.76, 45.90, 44.56, 41.68, 41.33, 39.31, 38.02, 37.77, 36.92, 33.91, 33.17, 32.58, 32.42, 30.75, 28.13, 27.73, 25.97, 23.70, 23.48, 23.11, 18.21, 16.87, 16.53, 15.36.

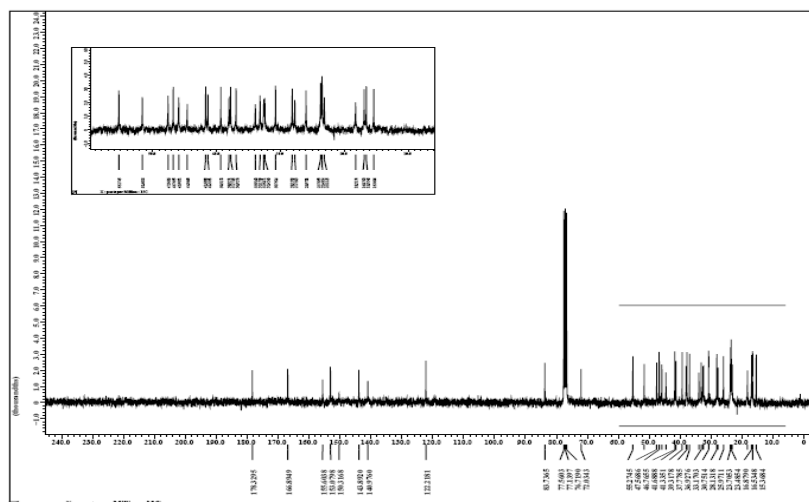
1). ESI-MS (+) Spectra of compound **4**



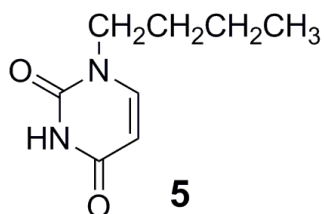
2). ^1H NMR Spectra of compound **4**(CDCl_3 , 300MHz)



3). ^{13}C NMR Spectra of compound **4**(CDCl_3 , 75MHz)

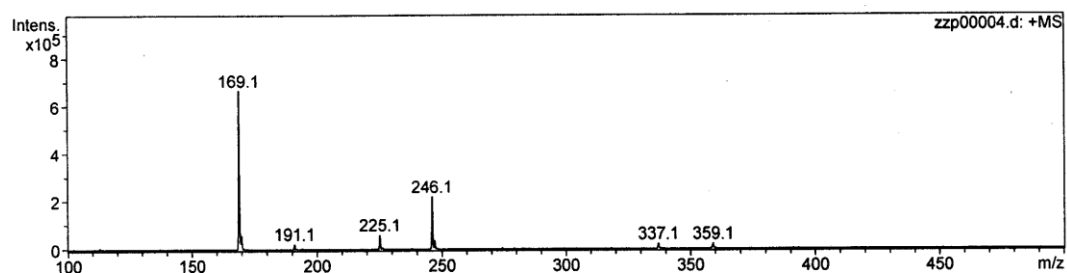


4. Synthesis of compound **5**

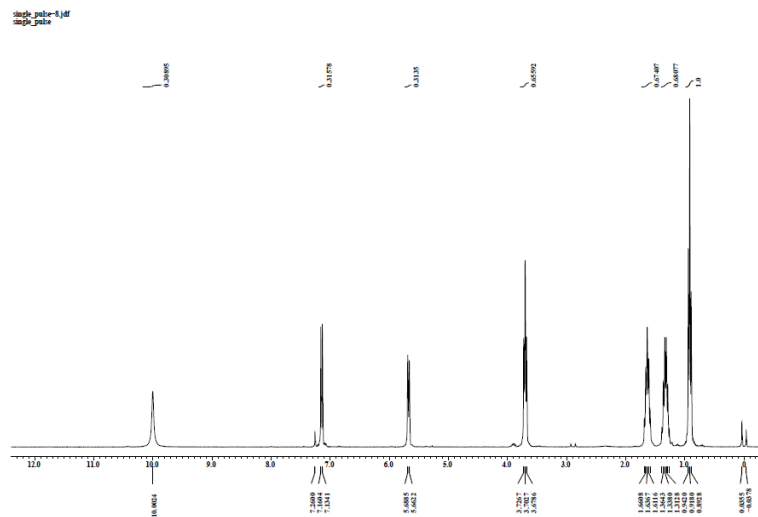


In a typical procedure, uracil (1.005 g, 8.9 mmol) was treated with n-butyl bromide (0.97 ml, 9.0mmol) in the presence of anhydrous K_2CO_3 (1.240 g, 9.0 mmol) in dry DMF (50 ml) for 18 h at room temperature (22 °C). Then the precipitates was filtered and washed with CH_2Cl_2 . DMF was evaporated under vacuo. The crude product obtained was dissolved in chloroform (30 ml) and washed with brine (20 ml), dried with Mg_2SO_4 and evaporated to dryness under vacuum. The impure product was then purified by silica gel column chromatography (elution with CH_2Cl_2 : CH_3OH = 50:1) to give 700 mg of **5** (50%). m. p. 108-111 °C, ESI-MS: m/z 169.1 $[M+H]^+$, 191.1 $[M+Na]^+$. 1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.92(t, - CH_3 , 2H, $J=7.2$ Hz). 1.39(m, - CH_2CH_2 , 2H) 1.64(m, - CH_2CH_2 , 2H) 3.70(t, - CH_2 , 2H, $J=7.2$ Hz) 5.52(d, uracil-5-H, 1H, $J=7.89$ Hz) 7.14(d, uracil-6-H, 1H, $J=7.89$ Hz) ^{13}C NMR (75MHz, $CDCl_3$) δ (ppm): 164.39 (uracli-1-C) 151.22 (uracil-4-C) 144.63 (uracil-6-C) 102.16 (uracil-5-C) 48.68, 31.12, 19.71, 13.70.

1). ESI-MS (+) Spectra of compound **5**

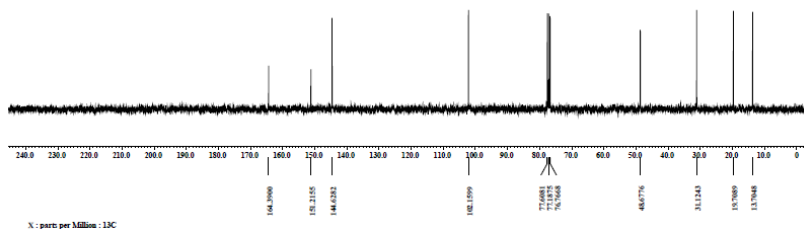


2). 1H NMR Spectra of compound **5**($CDCl_3$, 300MHz)

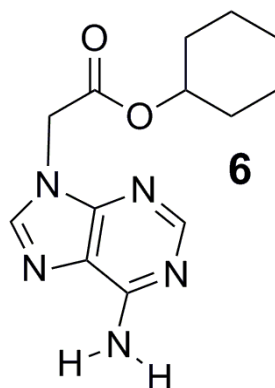


3). ^{13}C NMR Spectra of compound **5**(CDCl_3 , 75MHz)

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single pulse decoupled gated NOE



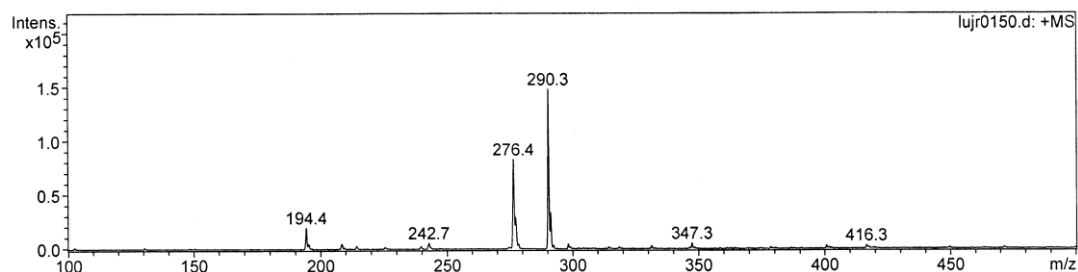
5. Synthesis of compound **6**



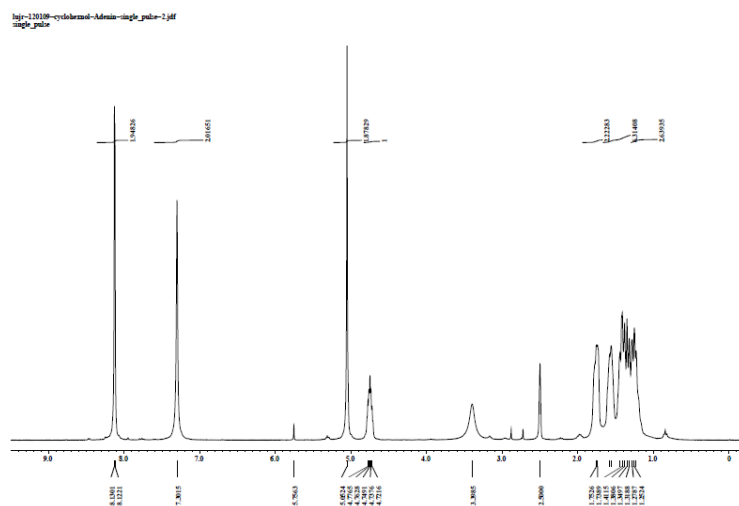
This compound was synthesized by using the same procedure as that described for **4**. m. p. 227-233 °C, ESI-MS (+) : $m/z = 276.4$ $[\text{M}+\text{H}]^+$, 290.3 $[\text{M}+\text{Na}]^+$; ^1H NMR (300MHz, $\text{DMSO}-d_6$): 8.13 (s, 1H, adenine-H), 8.12 (s, 1H, adenine-H), 7.30 (s, 2H, NH_2), 5.05 (s, 2H,

OCH₂-adenine), 4.75 (m, 1H); ¹³C NMR (75MHz, DMSO-*d*₆): 167.83 (OCOCH₂), 156.45 (adenine-C), 153.11 (adenine-C), 150.26 (adenine-C), 141.82 (adenine-C), 118.78 (adenine-C), 73.95, 44.65, 31.38, 25.25, 23.36.

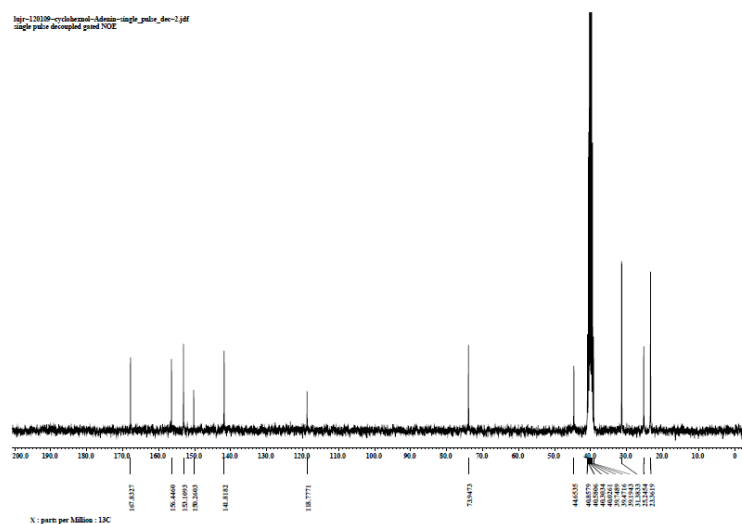
1). ESI-MS (+) Spectra of compound **6**



2). ¹H NMR Spectra of compound **6**(DMSO-*d*₆, 300MHz)



3). ¹³C NMR Spectra of compound **6**(DMSO-*d*₆, 75MHz)



6. ¹H NMR spectra at different temperatures of the organogel of **4**

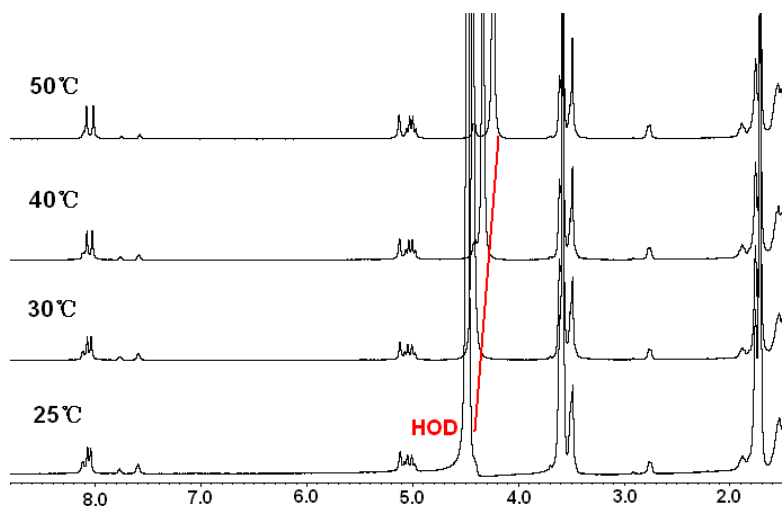


Figure S1. ^1H NMR spectra at different temperatures of the organogel of **4** in $\text{THF-}d_8$ solvent containing D_2O .

7. ^1H NMR Spectra titration and calculation of binding constant of compound **4** for **5**^[1]

^1H NMR spectra were recorded at 300 MHz for protons on JOEL JNM-ECA 300 spectrometers. Chemical shifts (δ) are given in ppm relative to TMS ($\delta=0.0$).

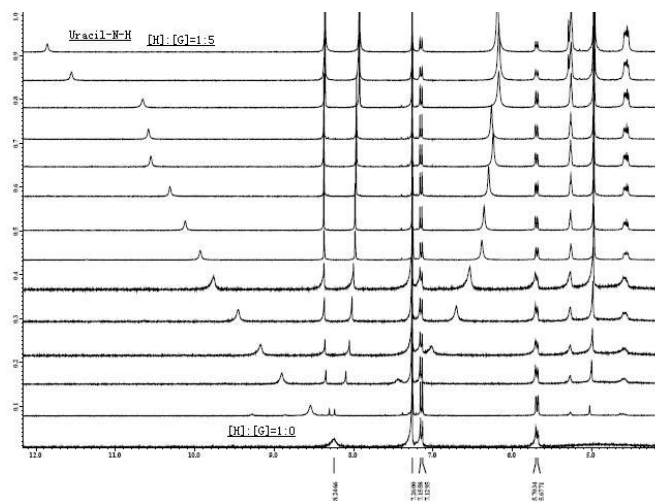


Figure S2. Partial ^1H NMR spectra of the uracil derivative **5**(=[H]) (5 mM) in CDCl_3 upon the addition of the compound **4**(=[G]).

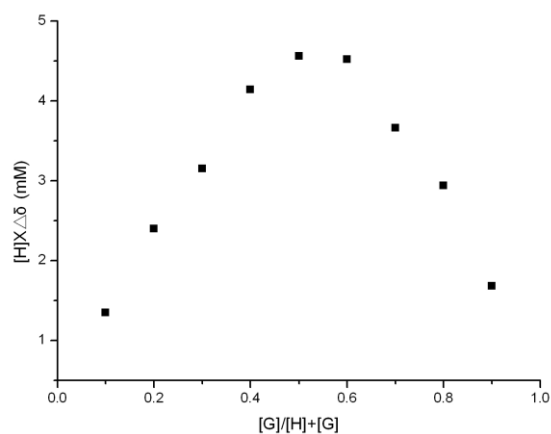


Figure S3. Job's plot showing 1:1 complex formation for compound **4** and **5**

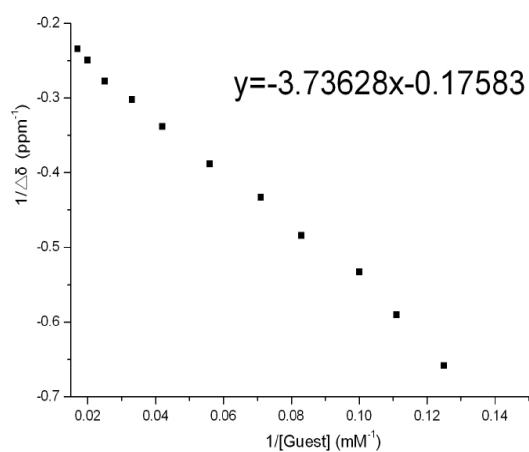


Figure S4. Hildebrand - Benesi plot based on the 1:1 for compound **4** and **5**

$$1/\Delta\delta = 1/(K_a\Delta\delta_{\max}[G]) + 1/\Delta\delta_{\max}$$

$$1/\Delta\delta_{\max} = -0.17583$$

$$1/K_a\Delta\delta_{\max} = -3.73628$$

$$K_a = 47.1 \text{ M}^{-1}$$

