Supplementary Material (ESI) for New Journal of Chemistry

Tuning aggregation mode induced different chirality in organogels of mono- and bis-triterpenoid derivatives and preparation of gold nanoparticles as a template

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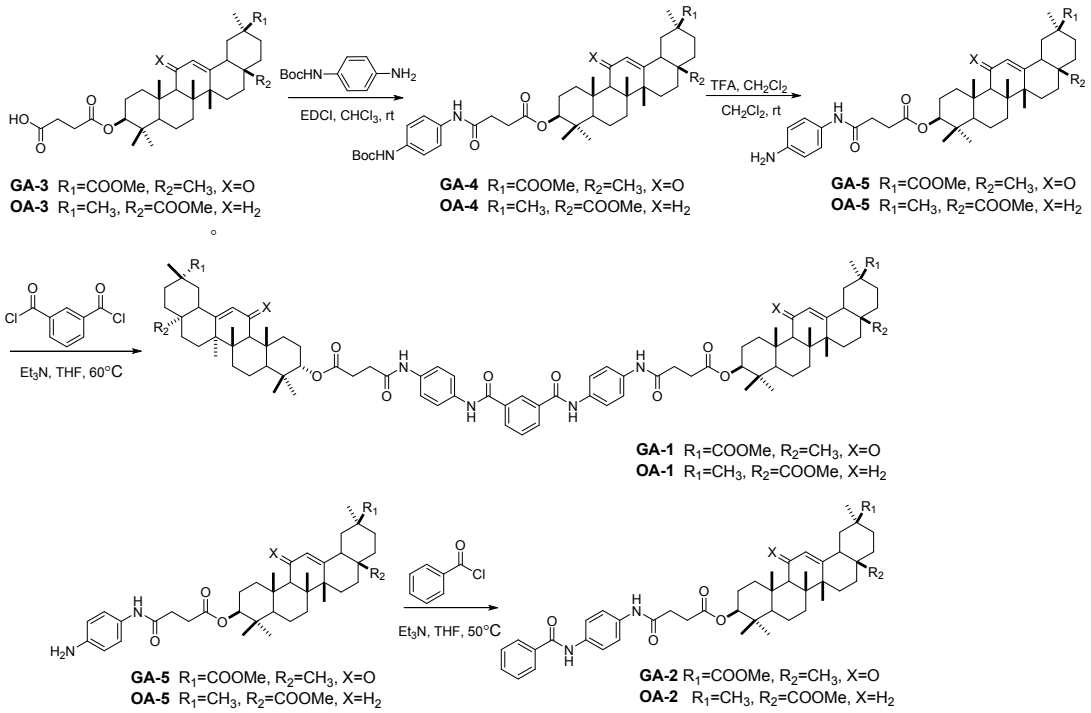


GA-3 and **OA-3** were synthesized as described by the reference.[1]

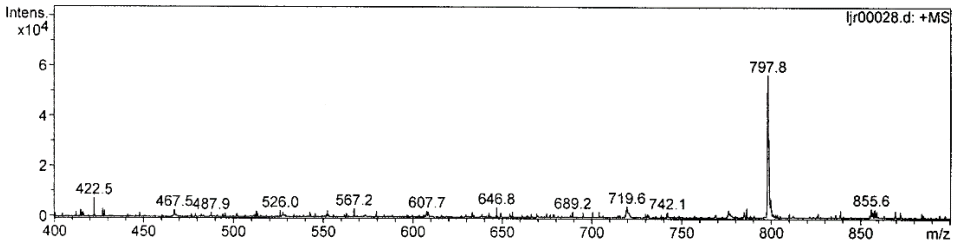
1. Synthesis of compound **GA-4** and **OA-4**

To the solution of 500 mg (0.86 mmol) of **GA-3** in 5 ml of dry $CHCl_3$, 198 mg (1.03 mmol) of EDCI and Boc protected p-Phenylenediamine were added. The reaction mixture was stirred at room temperature for 48 h. The mixture was then washed with water (30 ml) and brine (30 ml), dried by $MgSO_4$ and evaporated. The solid was purified by silica gel column chromatography (PE: $CH_3CO_2C_2H_5$ = 4:1) afforded **GA-4** as a yellow solid (363 mg, 56%). ESI-MS m/z: 797.8 [M+Na]+, ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.54 (s, 1H, -NH), 7.30 (d, 2H, J=8.6 Hz), 7.20(d, 2H, J=7.9 Hz), 5.56 (s, 1H, 12-H), 4.44 (m, 1H, 3-H), 3.60 (s, 3H,30-$COOCH_3$), 1.46 (s, -$(CH_3)_3$, 9H), 0.70, 0.77, 0.79, 1.03, 1.06, 1.08, 1.36 (7×s, 7×3H, 23, 24, 25, 26, 27, 28, 29-CH3). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 200.19 (11-C), 176.94 (30-C), 172.65 (3-OCO-), 169.95 (-NH-COCH2-), 169.75 (13-C), 153.21 (-NH-COO-), 134.69 (benzene-C), 133.43 (benzene-C), 120.73 (12-C), 120.73 (benzene-C), 119.28 (benzene-C), 80.94 (3-C), 77.84(O-$C(CH_3)_3$), 61.63, 60.40, 54.92, 53.61, 51.77, 48.35, 45.38, 43.98, 43.17, 41.00, 38.69, 32.58, 31.77, 31.06, 29.85, 28.50, 28.38, 28.26, 28.00, 26.38, 23.51, 23.31, 21.02, 18.61, 17.30, 16.71, 16.38, 14.18.

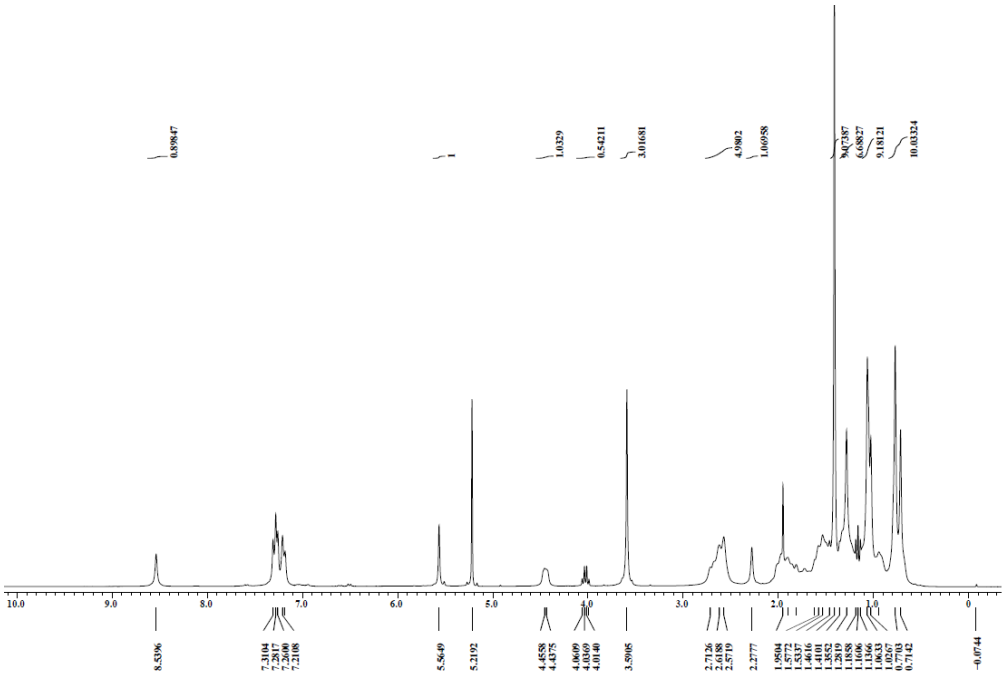
The compound **OA-4** was synthesized by using the same procedure as that described for **GA-4**. ESI-MS *m/z*: 762.0 $[M+H]^+$, 783.8 $[M+Na]^+$, 799.6 $[M+k]^+$, ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.98 (s, 1H, -NH), 6.68 (s, 1H, -NH), 7.23 (d, 2H, J=8.94 Hz), 7.35(d, 2H, J=8.94 Hz), 5.24

(s, 1H, 12-H), 4.50 (m, 1H, 3-H), 3.60 (s, 3H, 28-$COOCH_3$), 1.48 (s, -$(CH_3)_3$, 9H), 1.21, 0.90, 0.88, 0.87, 0.82, 0.82, 0.70 (7×s，7×3H, 23, 24, 25, 26, 27, 29, 30-CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 178.43(28-C), 173.97(3-OCO-), 169.84(-$NHCOCH_2$), 153.03 (-NHCO-), 143.83 (13-C), 134.41 (benzene-C), 133.41(benzene-C), 122.35 (12-C), 120.77 (benzene-C), 119.36 (benzene-C), 81.65 (3-C), 81.20(O-$C(CH_3)_3$), 60.49, 55.38, 51.62, 47.60, 46.79, 45.91, 41.69, 41.35, 39.35, 38.14, 37.83, 36.98, 33.92, 33.18, 32.63, 32.46, 32.11, 30.75, 30.00, 28.45, 28.14, 27.75, 25.98, 23.71, 23.59, 23.46, 23.12, 22.75, 18.26, 16.89, 16.79, 15.41, 14.27.

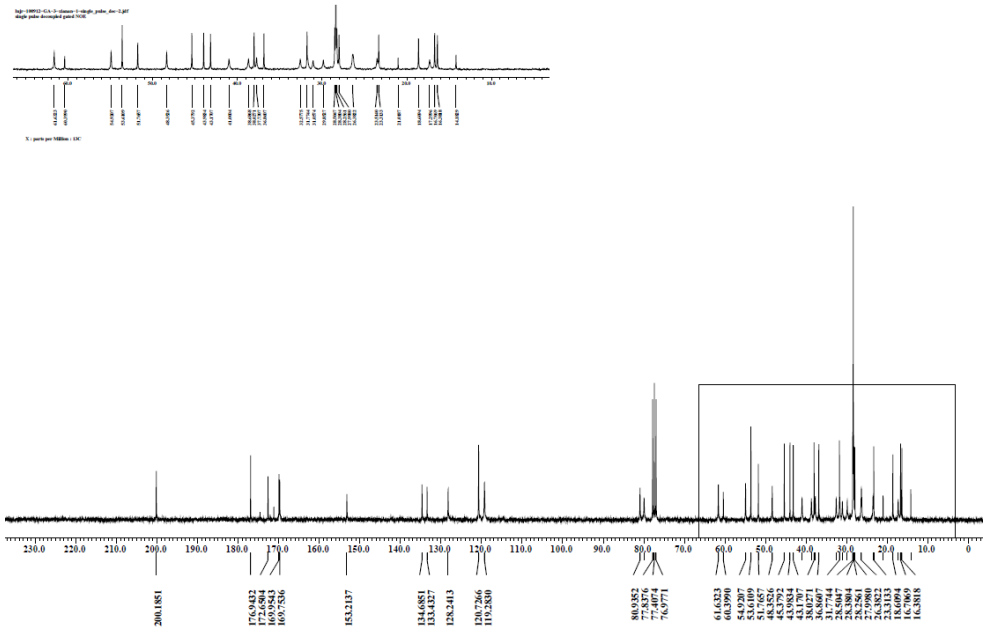
1)ESI-MS (+) Spectra of compound **GA-4**



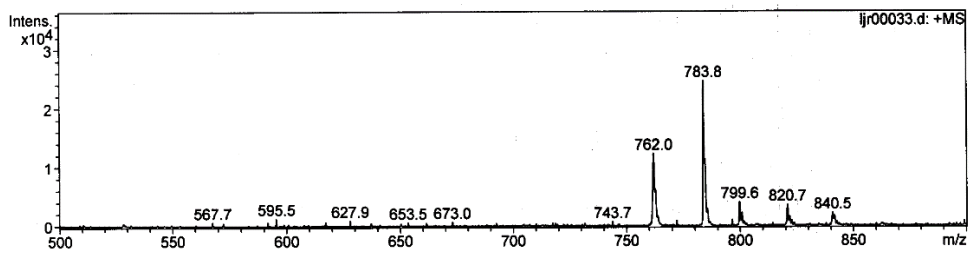
2)^1H NMR Spectra of compound **GA-4** ($CDCl_3$, 300MHz)



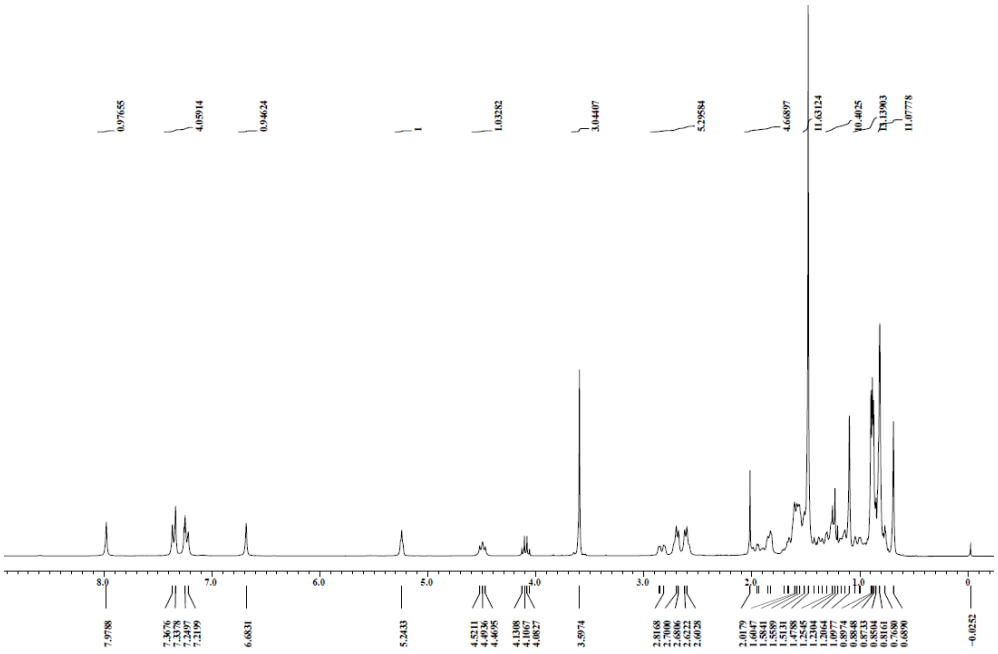
3)^{13}C NMR Spectra of compound **GA-4** ($CDCl_3$, 75MHz)



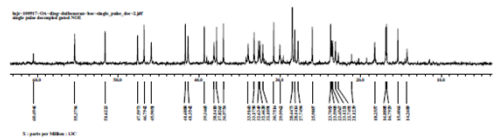
1) ESI-MS (+) Spectra of compound **OA-4**

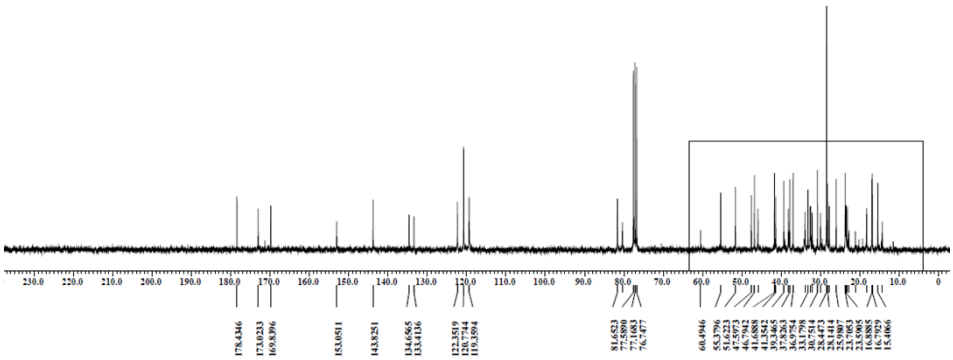


2)[1]H NMR Spectra of compound **OA-4** ($CDCl_3$, 400MHz)



3) [13]C NMR Spectra of compound **OA-4** ($CDCl_3$, 100MHz)





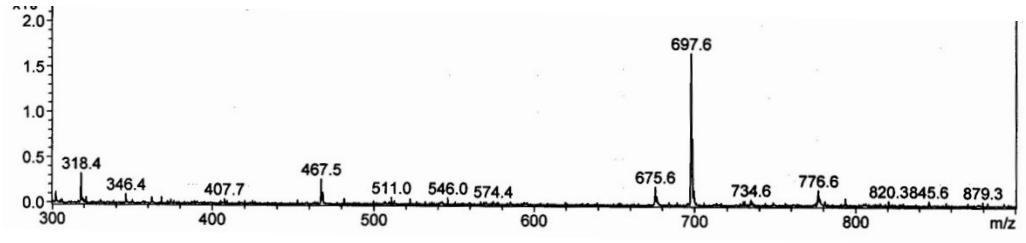
2. Synthesis of compounds **GA-5** and **OA-5**

To the solution of 300 mg (0.86 mmol) of **GA-4** in 7 ml of CH_2Cl_2, 1.4 mL TFA was added at 0 ºC. The reaction mixture was stirred at room temperature for 10 h. The mixture was then washed with saturated $NaHCO_3$ solution, water (30 ml) and brine (30 ml), dried by $MgSO_4$ and evaporated. The solid was purified by silica gel column chromatography (CH_2Cl_2: CH_3OH = 100:1) afforded **GA-5** as a yellow solid (233 mg, 89%). ESI-MS *m/z*: 675.6 $[M+H]^+$, 697.6 $[M+Na]^+$, ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.69 (s, 1H, -NH), 7.22 (d, 2H, J=8.58 Hz) 6.59(d, 2H, J=8.58Hz), 5.64 (s, 1H, 12-H), 4.52 (m, 1H, 3-H), 3.66 (s, 3H,30-$COOCH_3$), 3.26 (s, -NH_2, 2H) 1.34, 1.13, 1.13, 1.10, 0.85, 0.85, 0.78 (7×s，7×3H, 23, 24, 25, 26, 27, 28, 29-CH_3), ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm) 200.19 (11-C), 177.04 (30-C), 173.01 (3-OCO-), 169.63 (-$NHCOCH_2$-), 169.48 (13-C), 143.26 (benzene-C), 129.45 (benzene-C), 128.52 (benzene-C), 122.03 (12-C), 115.46 (benzene-C), 81.29 (3-C), 61.78, 55.10, 51.86, 48.49, 45.49, 44.12, 43.29, 41.15, 38.84, 38.19, 37.82, 37.00, 32.74, 32.08, 31.91, 31.20, 30.14, 28.60, 28.40, 28.15, 26.54, 23.64, 23.43, 18.74, 17.42, 16.79, 16.48.

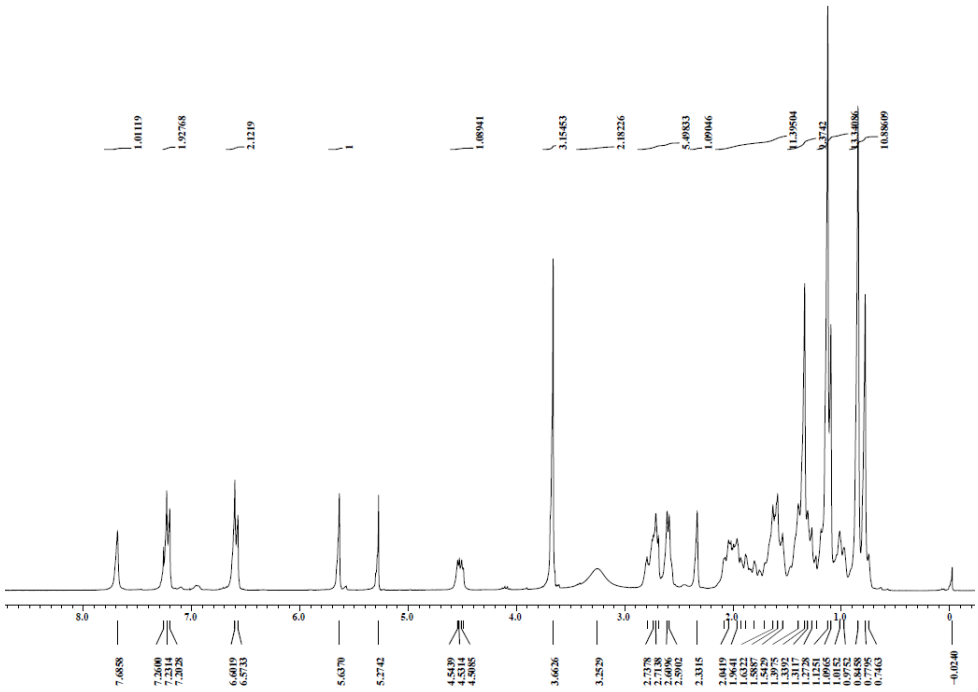
The compound **OA-5** was synthesized by using the same procedure as that described for **GA-5**. ESI-MS *m/z*: 661.8 $[M+H]^+$, 683.7 $[M+Na]^+$, 699.6 $[M+k]^+$, ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.87 (s, 1H, -NH), 7.20 (d, 2H, J=8.94 Hz), 6.55(d, 2H, J=8.58 Hz), 4.50 (m, 1H, 3-H), 3.62 (s, 3H, 28-$COOCH_3$), 1.21, 0.88, 0.87, 0.86, 0.83, 0.82, 0.71(7×s, 7×3H, 23, 24, 25, 26, 27, 29, 30-CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 177.51(28-C), 173.09(3-OCO-), 169.72(-NHCO-), 143.313 (13-C), 138.22 (benzene-C), 129.46(benzene-C), 127.95(benzene-C), 122.07 (12-C), 115.38 (benzene-C), 81.56 (3-C), 55.49, 51.65, 48.58, 44.40, 41.46, 41.24, 38.57, 37.89, 37.29, 36.96, 35.79, 34.93, 33.19, 32.71, 32.20, 31.96, 28.15, 27.14, 25.22, 24.22, 23.72, 22.76, 24.72,

21.13, 18.27, 17.42, 16.75, 16.49

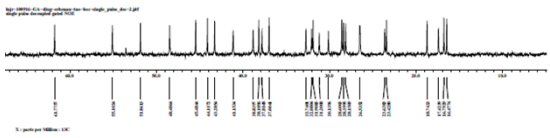
1) ESI-MS (+) Spectra of compound **GA-5**

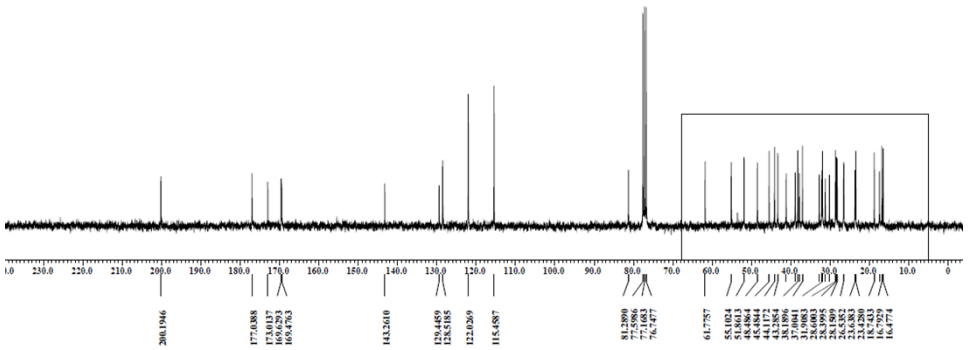


2) ^{1}H NMR Spectra of compound **GA-5** ($CDCl_3$, 300MHz)

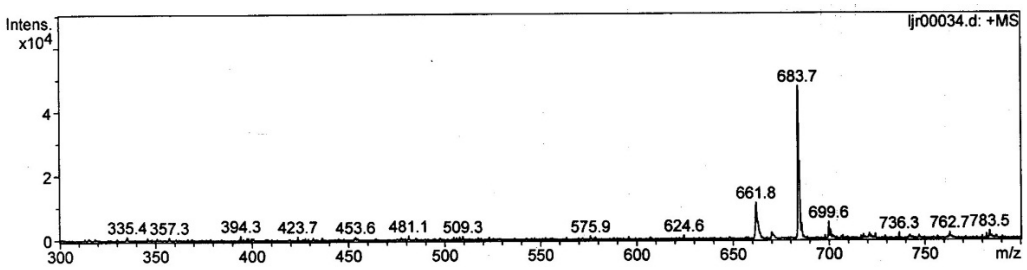


3) ^{13}C NMR Spectra of compound **GA-5** ($CDCl_3$, 75MHz)

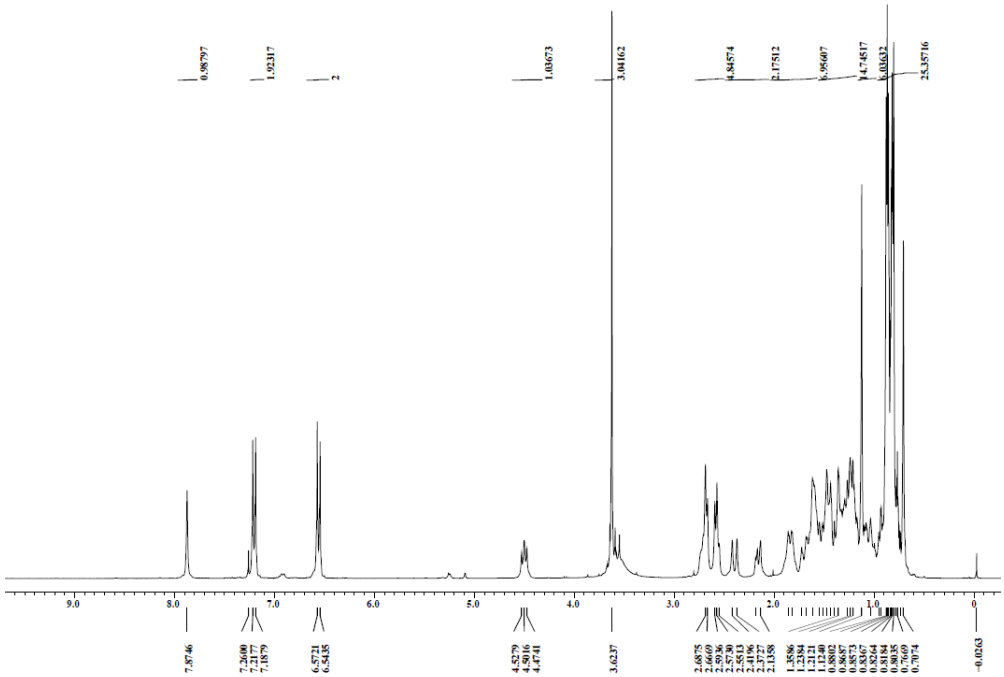




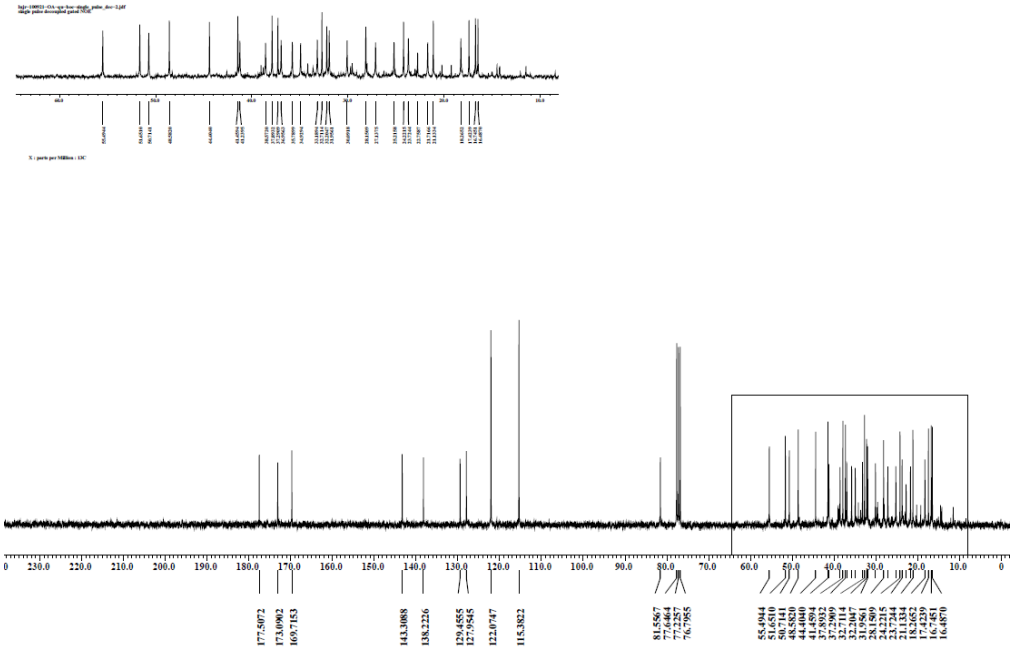
1) ESI-MS (+) Spectra of compound **OA-5**



2) ^{1}H NMR Spectra of compound **OA-5** ($CDCl_3$, 300MHz)



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

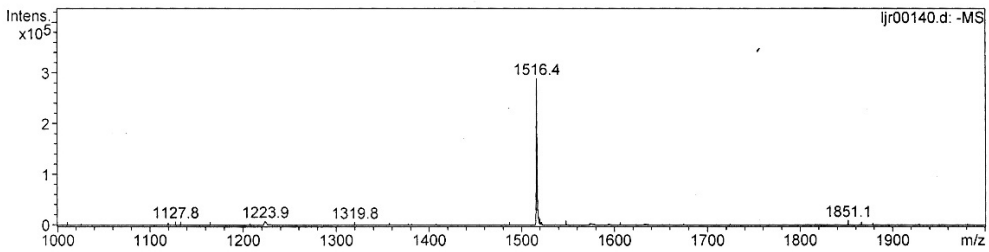


3. Synthesis of compound **GA-1** and **OA-1**

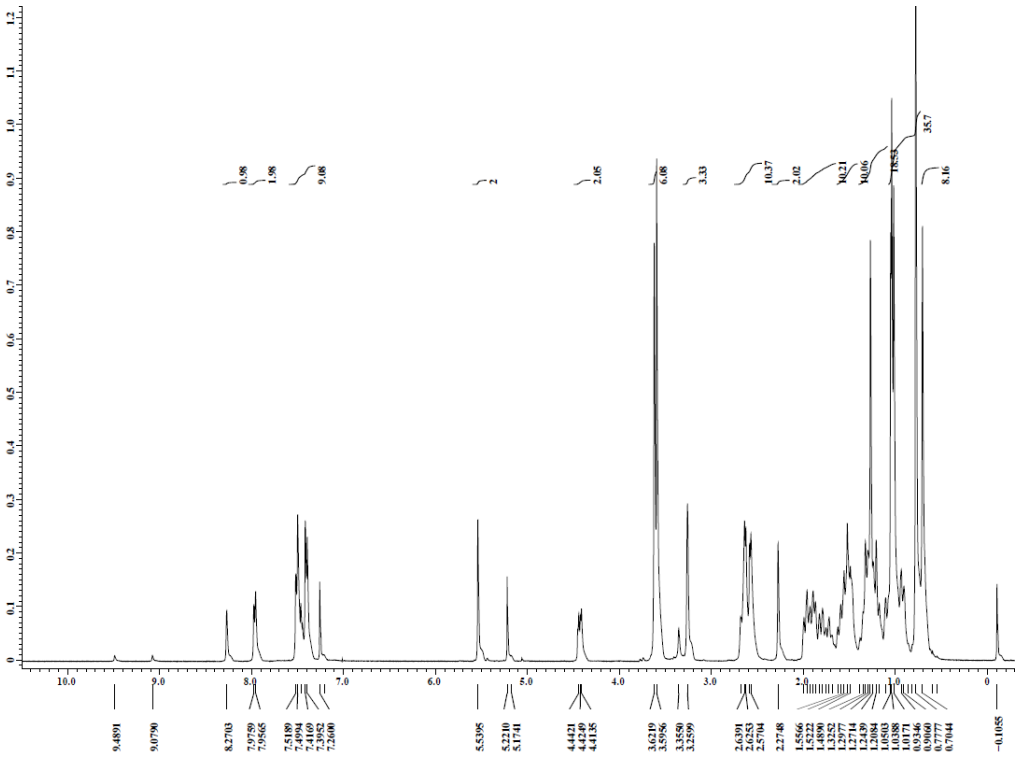
430 mg (0.63 mmol) **GA-5** and Et_3N (100 μL) were dissolved in 15 ml dry THF and cooled in ice bath. 69 mg (0.32 mmol) isophthaloyl dichloride was added to the reaction mixture. The reaction mixture was stirred at 60 ºC for 5 h. The reaction mixture was filtered and evaporated in vacuum to solid. Purification was done by silica gel column (100-200 mesh) using CH_2Cl_2: CH_3OH =30:1 as eluent to give **GA-1** as a white solid (450 mg，48%). ESI-MS *m/z*: 1516.4 $[M+Cl]^-$, ^1H NMR ($CDCl_3$: CD_3OD=4:1, 400 MHz, δ ppm): 9.49, 9.08 (2×d, 2H, -NH), 8.27 (s, 1H, benzene), 7.96 (d, 2H, benzene), 7.52~7.40 (m, 9H, benzene), 5.54(s, 1H, 12-H), 4.44~4.41 (m, 2H, 3-H), 3.62 (s, 6H, 30-$COOCH_3$), 1.27, 1.05, 1.04, 1.02, 0.78, 0.78, 0.70 (7×s, 7×3H, 23, 24, 25, 26, 27, 28, 29-CH_3) ^{13}C NMR ($CDCl_3$ and CD_3OD, 100 MHz, δ ppm): 200.81(11-C), 177.39(-$COOCH_3$), 173.21(-COO-), 170.50(13-C) 170.37, 165.96(-CONH-), 135.01, 134.92, 134.11, 130.85, 129.07, 128.18, 125.63, 121.27, 120.45, 81.40, 61.71, 54.97, 53.44, 45.47, 44.09, 43.27, 41.00, 38.69, 38.06, 37.70, 36.91, 32.60, 31.81, 31.48, 31.03, 29.79, 28.46, 28.21, 27.95, 26.40, 26.31, 23.44, 23.27, 18.59, 17.29, 16.59, 16.32.

The compound **OA-1** was synthesized by using the same procedure as that described for **GA-1**. ESI-MS *m/z*: 1488.2 $[M+Cl]^-$, ^1H NMR (DMSO-d_6, 400 MHz, δ ppm): 10.34, 9.96 (2×d, 4H, -NH), 8.50 (s, 1H, benzene), 8.12 (d, 2H, benzene), 7.71~7.54 (m, 9H, benzene), 4.45~4.40 (m, 2H, 3-H), 3.57 (s, 6H, 28-$COOCH_3$), 1.13, 0.93, 0.84, 0.83, 0.80, 0.80, 0.71(7×s, 7×3H, 23, 24, 25, 26, 27, 29, 30-CH_3) ^{13}C NMR (DMSO-d_6, 100 MHz, δ ppm):176.67 (30-$COOCH_3$), 172.42 (3-COO-), 170.07 (13-C), 165.25, 162.60 (-CONH-), 138.24, 135.80, 135.72, 134.68, 133.24, 131.01, 130.15, 129.11, 127.86, 127.39, 121.30, 119.67, 80.50, 61.03, 55.17, 52.05, 50.32, 48.42, 44.45, 41.38, 41.27, 37.91, 37.26, 36.96, 35.72, 34.87, 32.83, 32.42, 31.86, 28.23, 27.11, 25.94, 24.36, 23.55, 21.31, 18.28, 17.69, 17.07, 16.64.

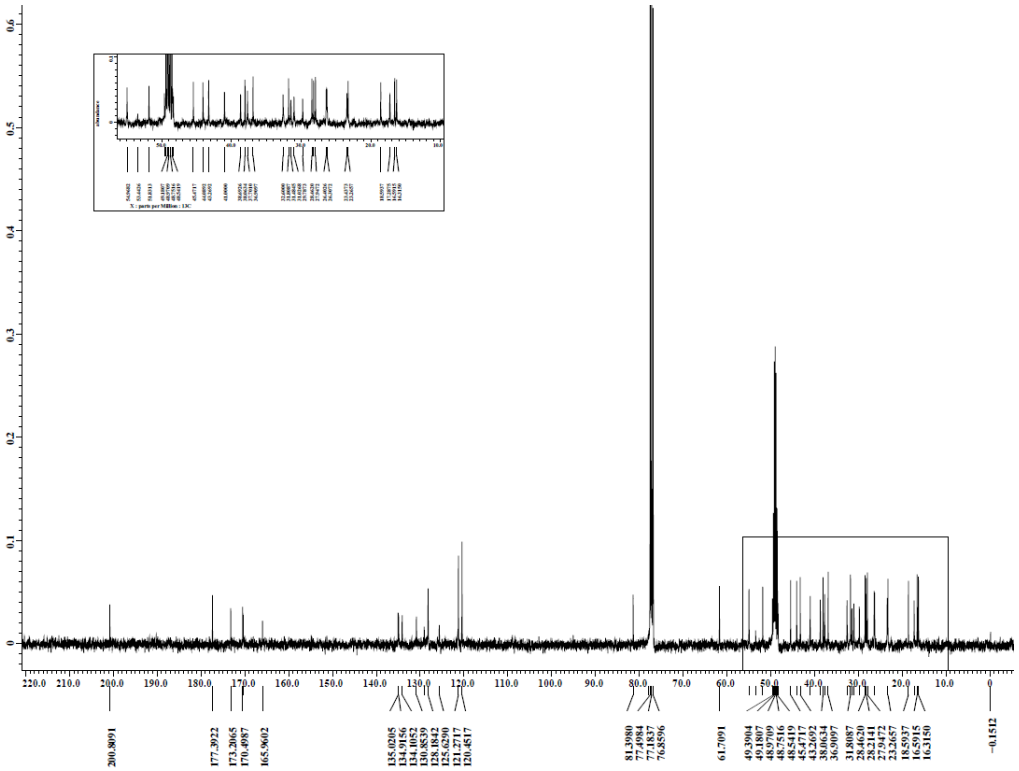
1) ESI-MS (-) Spectra of compound **GA-1**



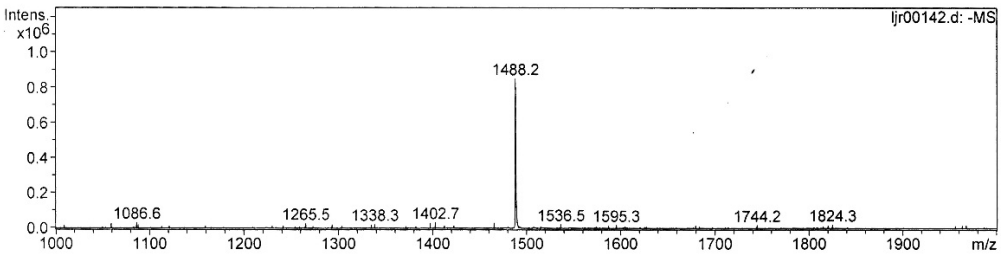
2) ^1H NMR Spectra of compound **GA-1** ($CDCl_3$ and CD_3OD, 400 MHz)



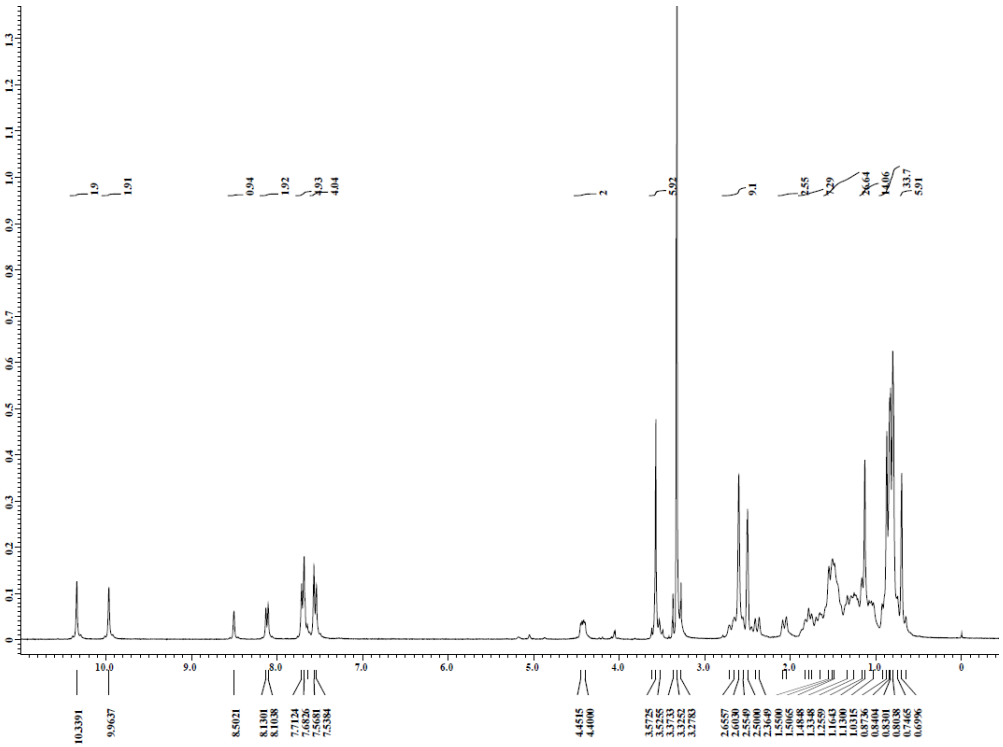
3) ^{13}C NMR Spectra of compound **GA-1**($CDCl_3$ and CD_3OD, 100 MHz)



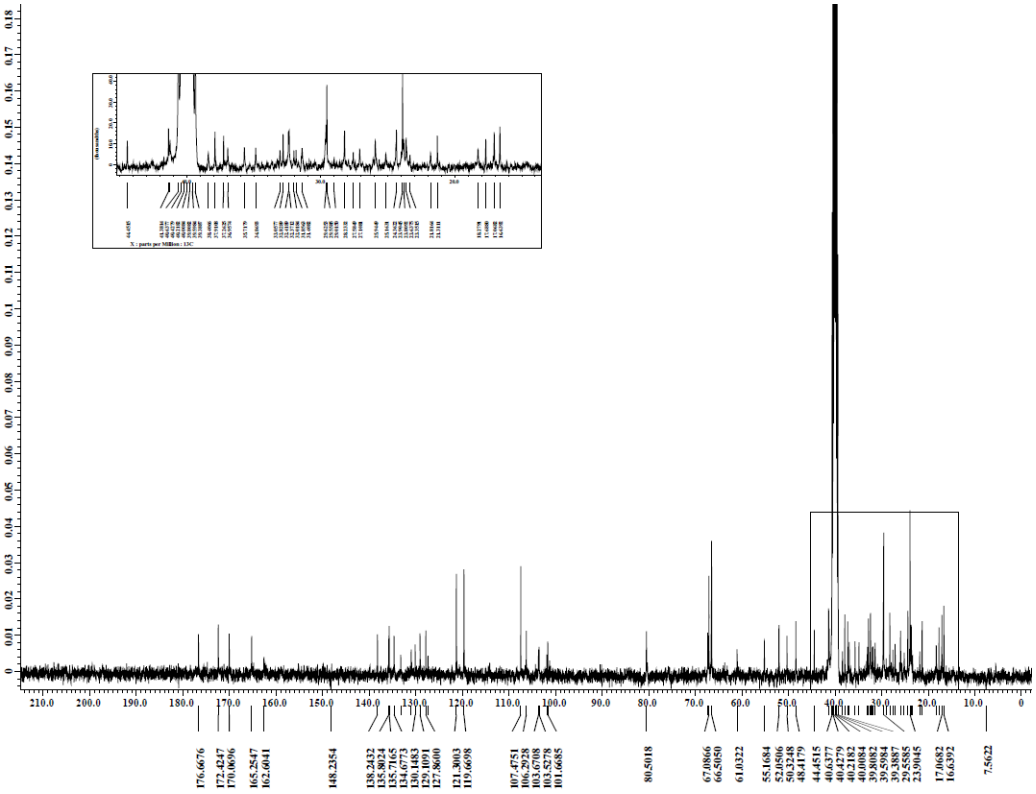
1) ESI-MS (-) Spectra of compound **OA-1**



2) ^{1}H NMR Spectra of compound **OA-1**(DMSO-d_6, 400 MHz)



3) ^{13}C NMR Spectra of compound **OA-1**(DMSO-d_6, 100 MHz)



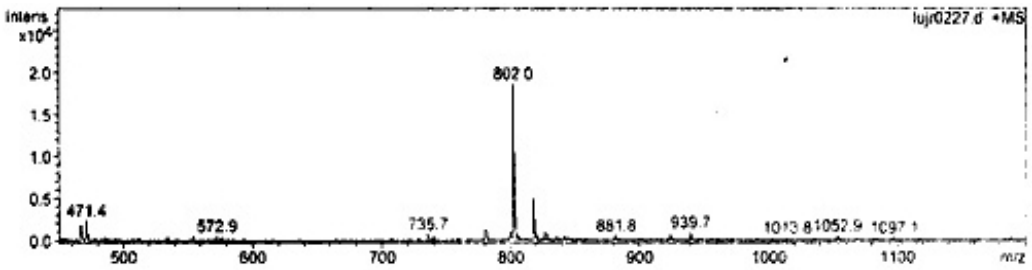
4. Synthesis of compound **GA-2** and **OA-2**

100 mg (0.14 mmol) **GA-5** and Et_3N (25 μL) were dissolved in 10 ml dry THF and cooled in ice bath. 20 μL (0.16 mmol) benzoyl chloride was added to the reaction mixture. The reaction mixture was stirred at 50 ºC for 1.5 h. The reaction mixture was filtered and evaporated in vacuum to solid. Purification was done by silica gel column (100-200 mesh) using CH_2Cl_2: CH_3OH =40:1 as eluent to give **GA-2** as a white solid (110 mg，95%). ESI-MS *m/z*: 802.0$[M+Na]^+$, 817.8 $[M+K]^+$, ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.25, 8.12 (2×s, 2H, -NH), 7.86 (d, 2H, benzene-H), 7.51~7.41 (m, 7H, benzene-H), 5.64(s, 1H, 12-H), 4.57 (dd, J1=4.6 Hz, J2=11.48Hz, 1H, 3-H), 3.67 (s, 3H, 30-$COOCH_3$), 1.34, 1.13, 1.13, 1.10, 0.85, 0.85, 0.79 (7×s, 7×3H,23, 24, 25, 26, 27, 28, 29-CH_3) ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.30(11-C), 177.07(-30$COOCH_3$), 173.07(-COO-), 170.05(13-C) 169.63, 166.01(-CONH-), 134.91, 134.11, 131.86, 130.18, 128.77, 128.50, 127.25, 121.42, 120.74, 81.42, 61.78, 55.08, 51.89, 48.48, 45.49, 44.10, 43.29, 41.13, 38.82, 38.20, 37.82, 36.99, 32.73, 31.91, 31.20, 30.00, 28.61, 28.40, 28.16, 26.53, 26.47, 26.53, 26.47, 23.65, 23.44, 18.74, 17.41, 16.80, 16.49.

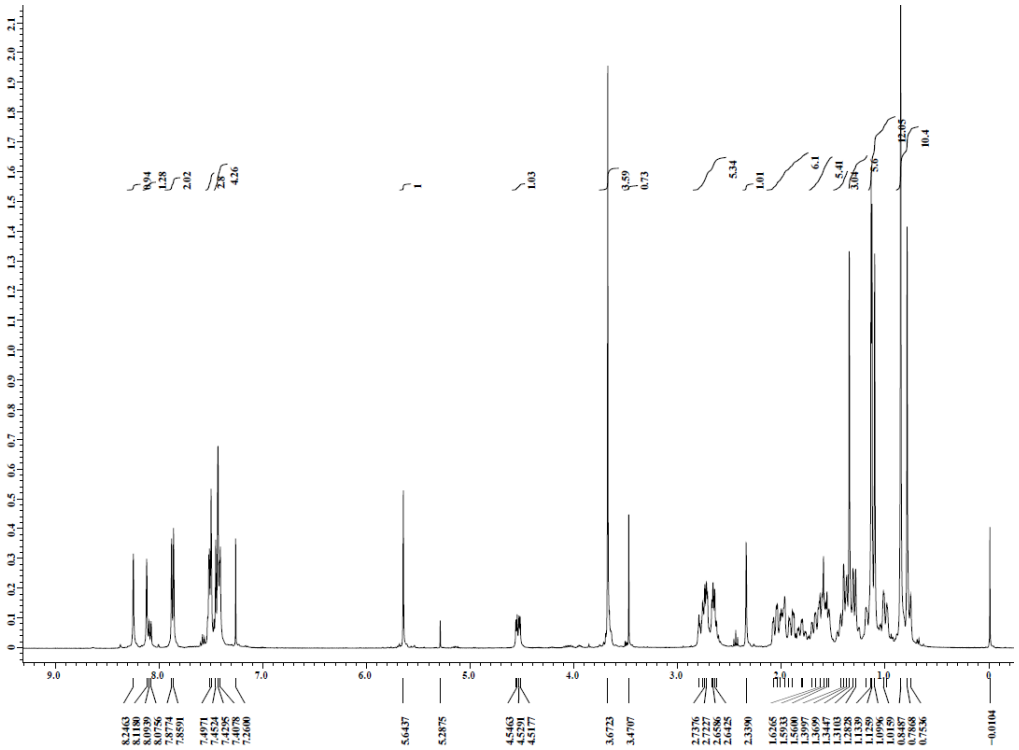
The compound **OA-2** was synthesized by using the same procedure as that described for **GA-2**. ESI-MS *m/z*: 766.1$[M+H]^+$, 788.1 $[M+Na]^+$, 800.4 $[M+Cl]^-$ ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.25, 8.12 (2×s, 2H, -NH), 7.86 (d, 2H, benzene-H), 7.53~7.37 (m, 7H, benzene-H), 5.25(s,

1H, 12-H), 4.51 (m, 1H, 3-H) 3.61(s, 3H, 28-$COOCH_3$), 1.11, 0.91, 0.90, 0.89, 0.83, 0.83, 0.71 (7×s, 7×3H, 23, 24, 25, 26, 27, 29, 30-CH_3) ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 178.45(-28$COOCH_3$), 173.08(-COO-), 170.69(13-C), 168.94, 166.02(-CONH-), 143.86, 134.87, 134.09, 131.86, 128.77, 127.27, 122.33, 121.53, 120.82, 81.72, 55.36, 51.66, 47.60, 46.80, 45.90, 41.70, 41.34, 39.33, 38.13, 37.83, 36.99, 33.93, 33.19, 32.63, 32.25, 30.77, 29.97, 28.17, 27.75, 26.00, 23.72, 23.61, 18.27, 16.90, 16.82, 15.43.

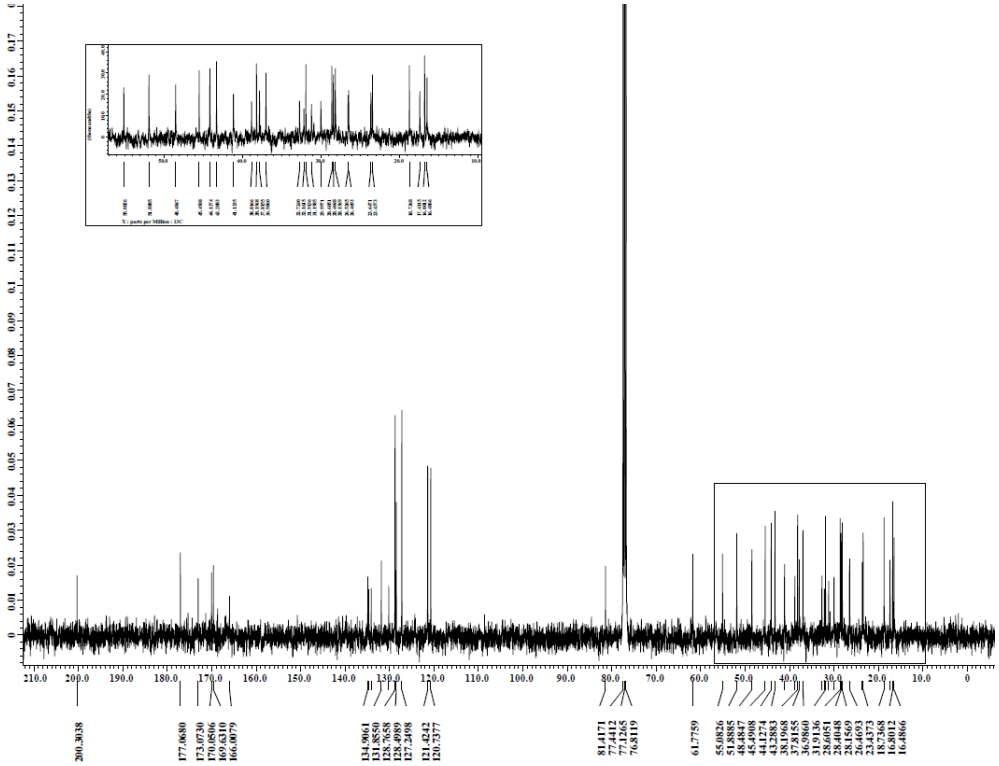
1) ESI-MS (+) Spectra of compound **GA-2**



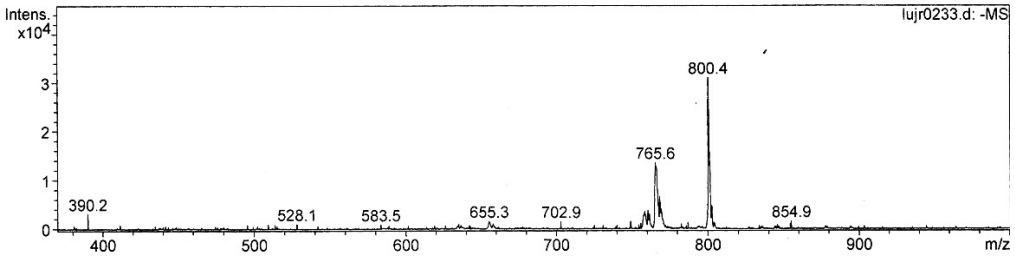
2) ^1H NMR Spectra of compound **GA-2** ($CDCl_3$, 400MHz)



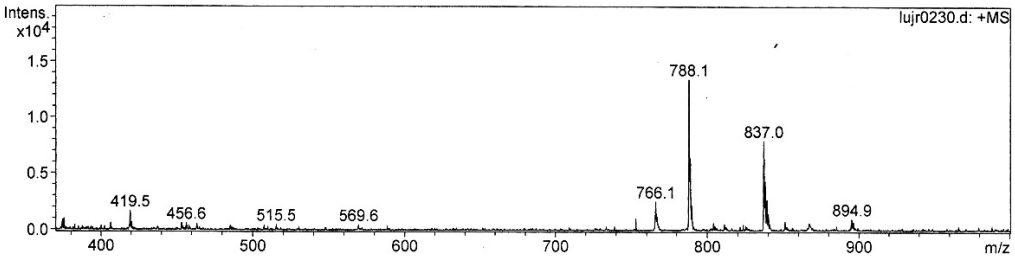
3) ^{13}C NMR Spectra of compound **GA-2**($CDCl_3$, 100MHz)



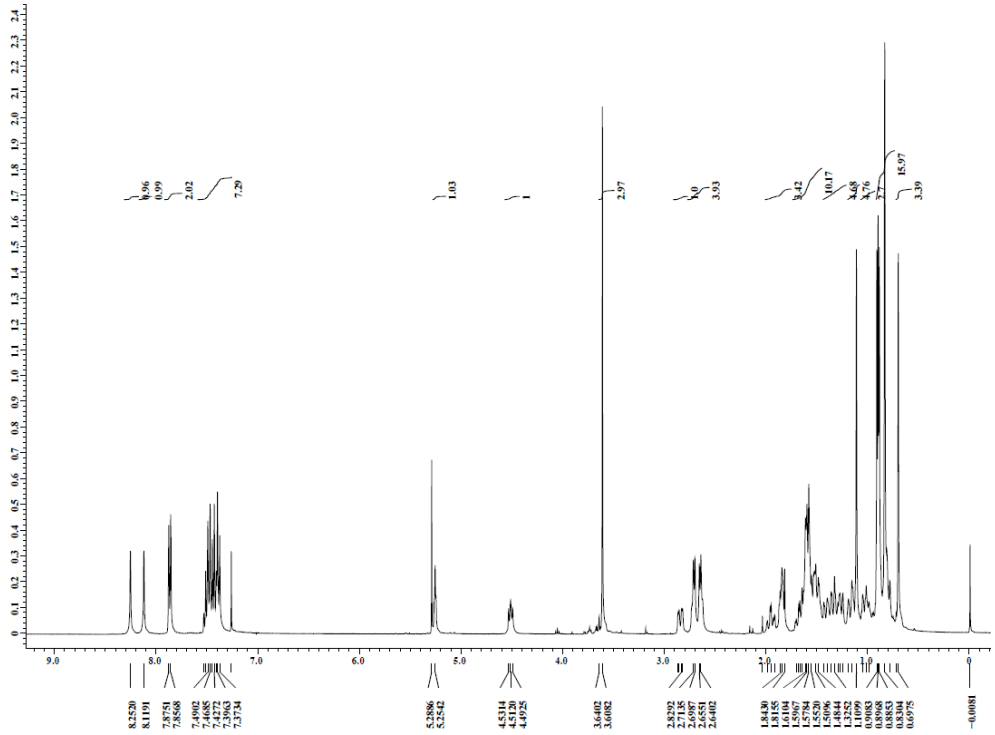
1) ESI-MS (-) Spectra of compound **OA-2**



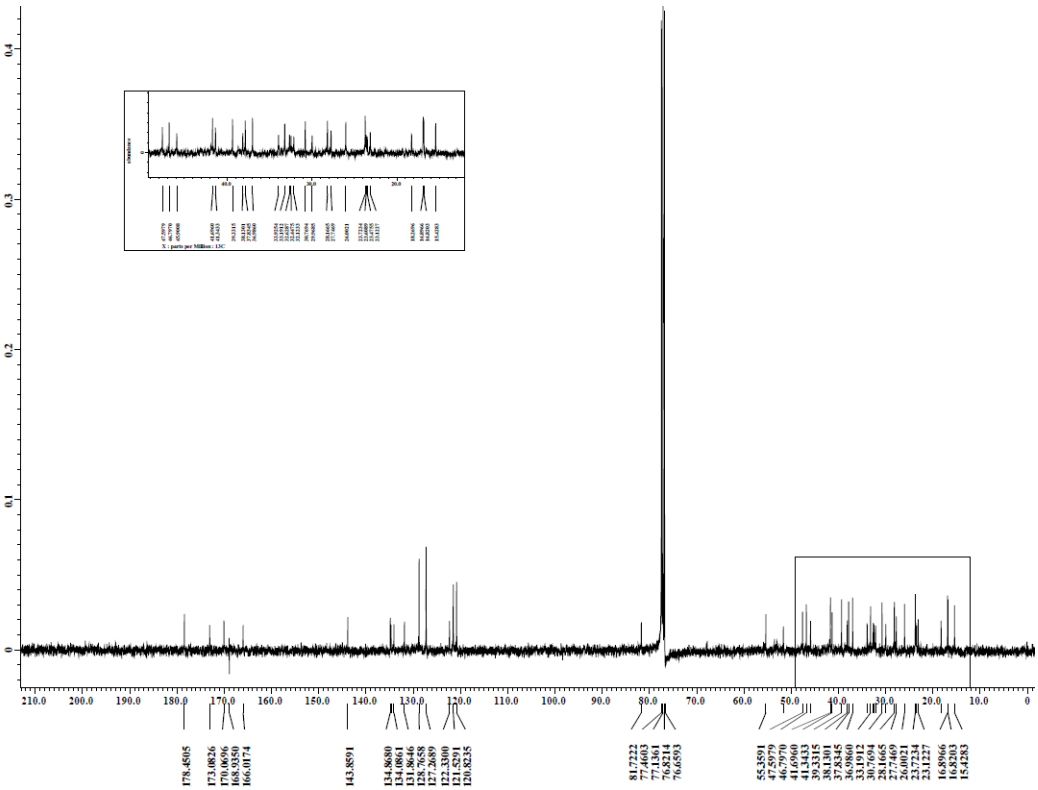
ESI-MS (+) Spectra of compound **OA-2**



2) ^{1}H NMR Spectra of compound **OA-2**($CDCl_3$, 400MHz)



3) ^{13}C NMR Spectra of compound **OA-2**($CDCl_3$, 100MHz)



5. The photographs of gels formed by **GA-1** and **OA-1**

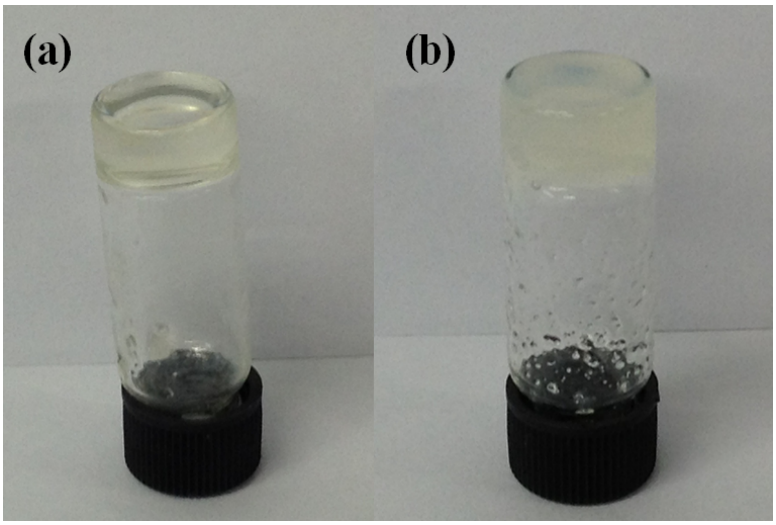


Figure S1. Gels containing (a) **OA-1** bromobenzene (b) **GA-1** in DMSO

6. The morphology of gel formed by **OA-1** observed by SEM images

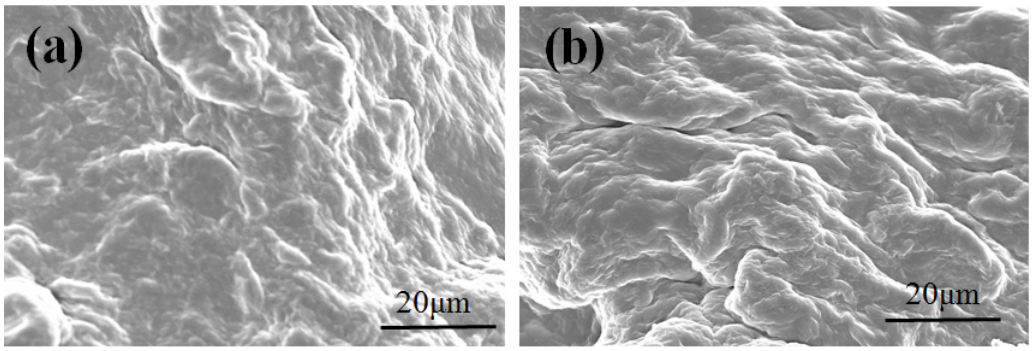


Figure S2. Morphology observed from the dried gel of **OA-1** (a) Bromobenzene (b) in Dichlorobenzene by SEM.

7. Temperature-dependent ^{1}H NMR spectroscopy of gel of **OA-2** in benzene

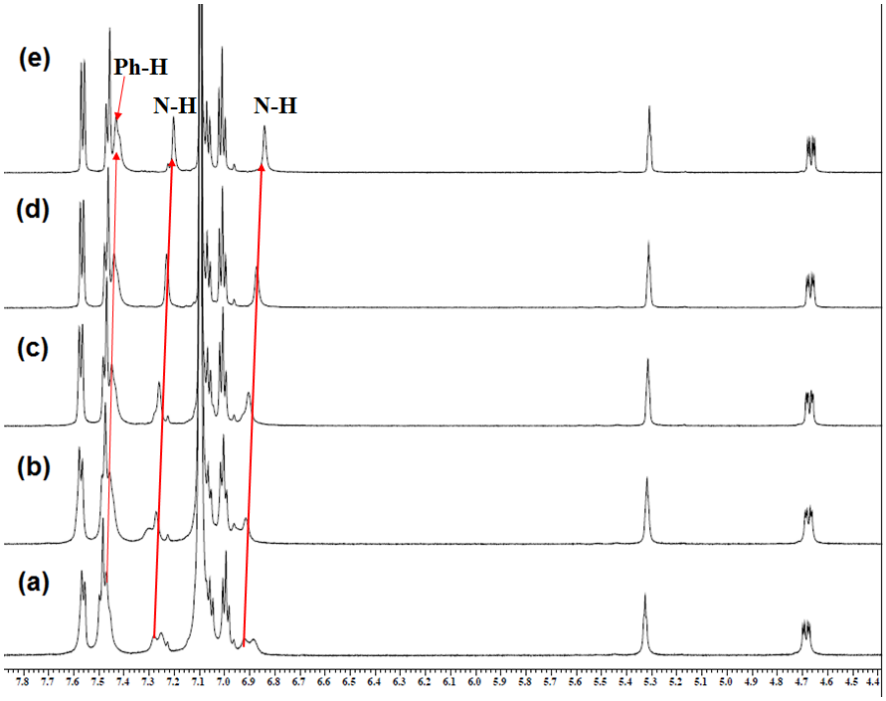


Figure S3. Variable temperature ^{1}H NMR (600 MHz) of gel **OA-2** from C_6D_6