

Supporting Information File 1

Title: Experimental Data

A simple route for renewable nano-sized arjunolic and asiatic acids and self-assembly of arjuna-bromolactone

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Mixture of Triterpenic acids (from *Terminalia Arjuna*):

The saw-dust used for the extraction of triterpenic acids was from *Terminalia arjuna* timber of approximate age 90 – 100 years (length 4 m and average diameter of 80 cm). Dried and finely powdered saw-dust from *Terminalia arjuna* (1 kg) was initially washed with petroleum ether (24 h) to remove the greasy non-polar materials. Subsequent extraction with refluxing diethyl ether (4 h x 8) using an apparatus designed in our laboratory (see supporting information of [1]) yielded a yellowish solid (40 g). This powdered solid was refluxed with acetone (700 mL) for 1 h and then concentrated to 125 mL and cooled. The precipitate was filtered (through a sintered glass funnel) to afford a whitish solid (22 g). The process was repeated once more to afford a whitish solid (18 g). The crude product was dissolved in methanol (700 mL), decolorized with charcoal and then crystallized to obtain a white crystalline solid (15 g). mp = 298 °C. HPLC (206 nm) t_R = 8.7 min (Fig. 1b). FTIR (neat, cm^{-1}) ν_{max} 3464 (s), 3380 (s), 2925 (s), 1700 (s), 1645 (w), 1454 (m), 1373 (m), 1267 (m), 1188 (m).

Bromolactonization of the mixture of triterpenic acids 1 and 2:

A mixture of the above triterpenic acids (5.00 g, 10.23 mmol) dissolved in 90% acetic acid (100 mL) was treated with solid sodium acetate (2.5 g, 18.37 mmol). The stirred clear solution was then treated with a solution of bromine (0.63 mL, 12.27 mmol) in glacial acetic acid (65 mL) which was added dropwise over a period of 40 min at room temperature. The reaction was then stirred at room temperature for a further 1 h and then poured into an ice/water mixture (1200 mL). The white precipitate that formed was filtered and the residue was washed with distilled water (500 mL). The white solid obtained was initially dried in air and then under reduced pressure to obtain a mixture of **2** and **3** (5.4 g).

Reaction of the mixture of 2 and 3 with CH_2N_2 :

A mixture of **2** and **3** (5.4 g) was suspended in methanol (10 mL) and treated with an excess of ethereal diazomethane repeatedly for complete conversion of asiatic acid (**2**) to methyl asiate (**4**) (as revealed by HPLC analysis). The solvents were removed and the yellowish solid of the mixture of compound **3** and **4** thus obtained (5.4 g) was recrystallized from ethyl acetate. Pure arjuna-bromolactone **3** crystallized from ethyl acetate as a white crystalline solid (3.5 g) and methyl asiate (**4**) (1.1 g) was isolated from the mother liquor. HPLC (206 nm) t_R (arjuna bromolactone) = 10.0 min, (Figure 1d), t_R (methyl asiate) = 20.7 min (Figure 1e).

Selected data of arjuna-bromolactone 3:

MP = 230 – 233 °C. ¹H-NMR (600 MHz, CDCl₃) δ 4.30 (d, 1H), 3.80 (br, m, 1H), 3.70 (s, 1H), 3.65 (dd, 1H, $J_1 = 10.2$ Hz, $J_2 = 3.6$ Hz), 3.46 (dd, 1H, $J_1 = 9.6$ Hz, $J_2 = 3$ Hz), 3.42 (d, 1H), 2.97 (s, 1H), 2.86 (s, 1H), 2.42 - 1.00 (terpenoid protons, 18H), 1.45 (s, 3H), 1.21 (s, 3H), 1.00 (s, 3H), 0.99 (s, 3H), 0.91 (s, 3H), 0.83 (s, 3H). ¹³C-NMR (150 MHz, CDCl₃) δ 178.90, 91.54, 79.36, 69.01, 68.79, 56.03, 52.28, 48.62, 45.92, 45.50, 45.42, 43.43, 42.64, 42.41, 39.88, 37.74, 34.16, 33.81, 33.26, 31.86, 30.53, 29.13, 27.46, 23.55, 21.27, 21.16, 19.04, 18.59, 17.57, 12.78. FTIR (neat, cm⁻¹) ν_{\max} 3407 (s), 2938 (s), 1767 (s), 1465 (m), 1389 (m), 1359 (w), 1246 (w), 1214 (m), 1135 (m), 1107 (s), 1016 (w). $[\alpha]_D^{295} = + 52.63$ (c 0.5, MeOH). HRMS (ESI): m/z calcd (C₃₀H₄₈O₅BrNa) 591.2467, found 591.2467 [M + Na]⁺.

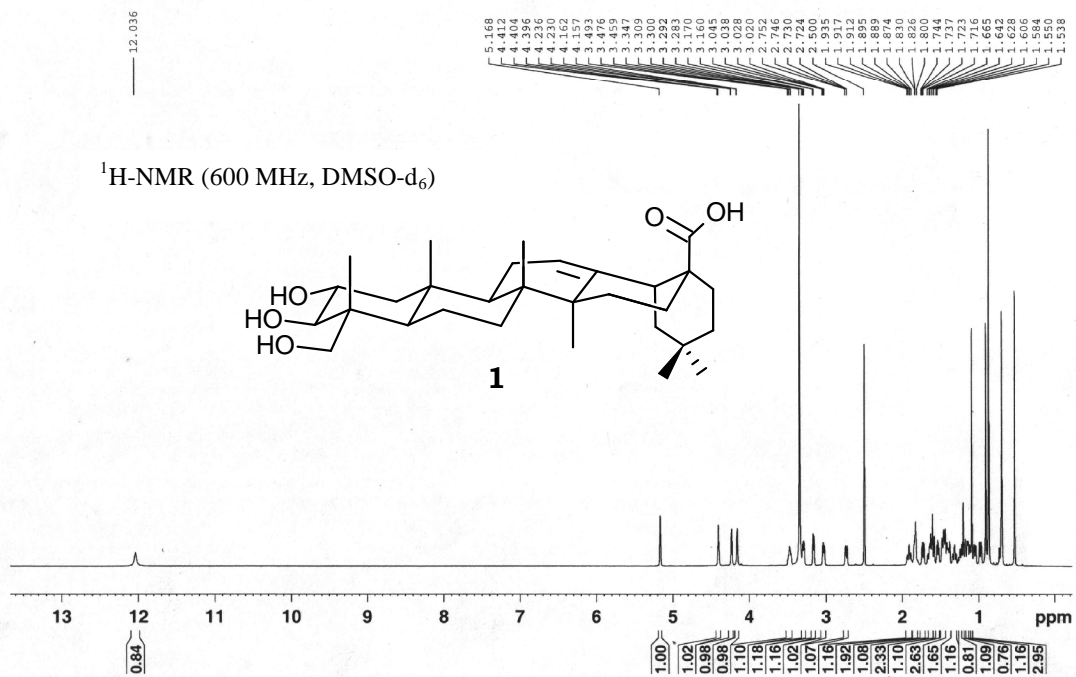
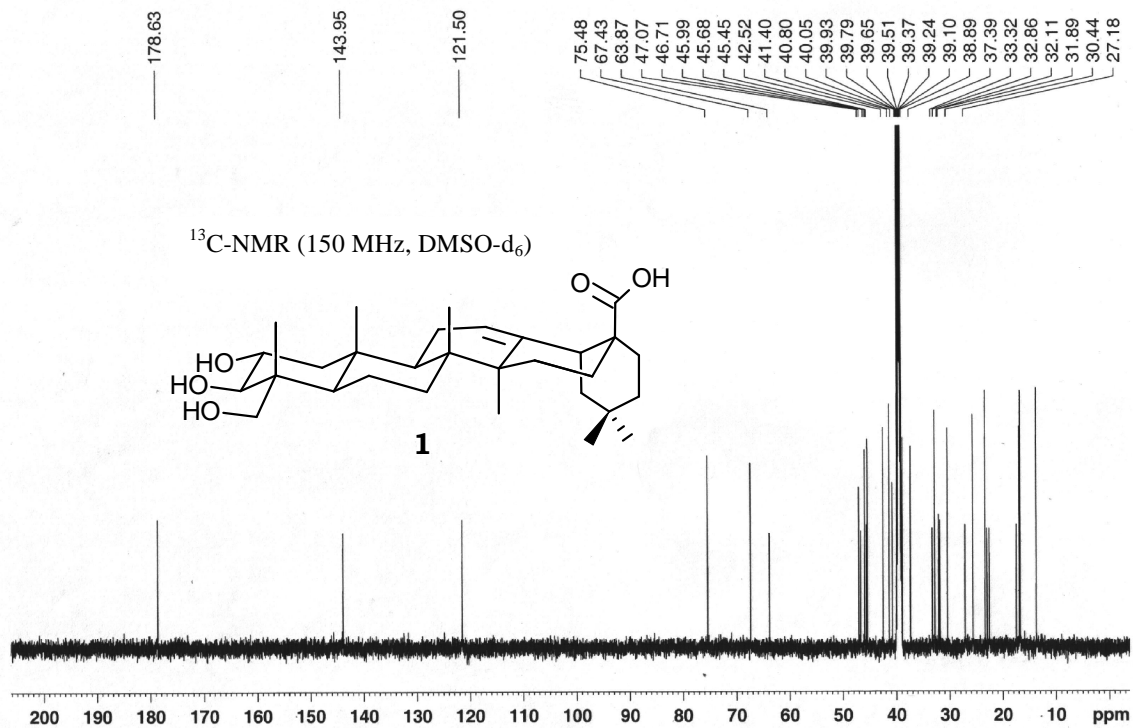
Selected data of methyl asiatate 4: mp = 222 – 224 °C.

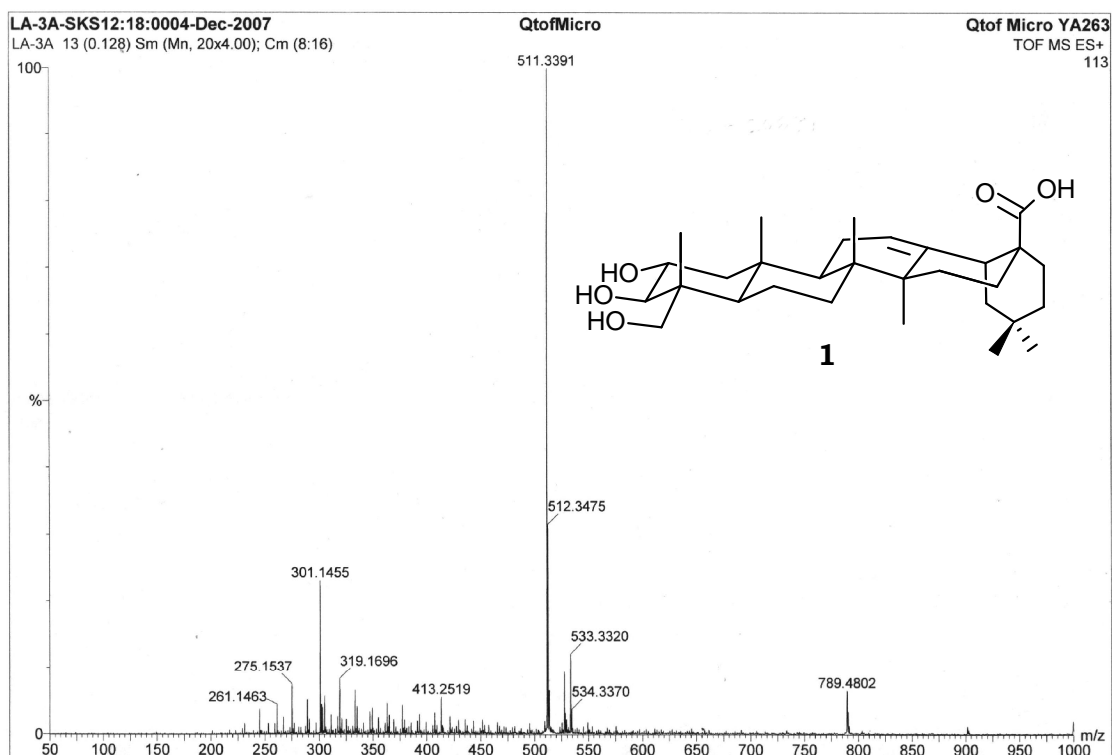
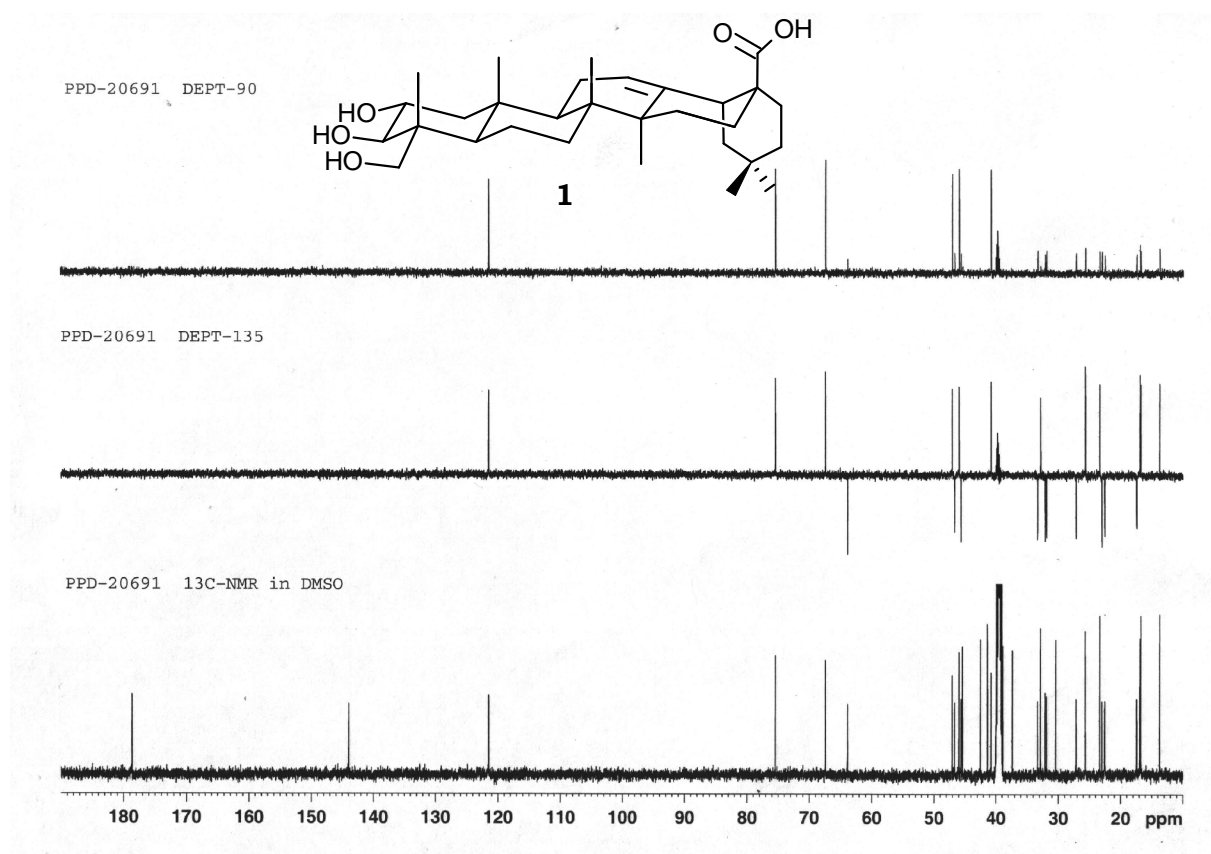
¹H-NMR (600 MHz, CDCl₃) δ 5.25 (s, 1H), 3.76 (m, 1H), 3.64 (m, 1H), 3.60 (s, 3H), 3.42 (m, 2H), 2.23 (d, 1H), 2.02 - 0.80 (terpenoid protons, 20H), 1.07 (s, 3H), 1.03 (s, 3H), 0.87, 0.84 (br, m, 6H), 0.74 (s, 3H). ¹³C-NMR (150 MHz, CDCl₃): δ: 178.07, 138.22, 125.21, 70.59, 68.72, 52.78, 51.48, 49.10, 48.03, 42.40, 42.04, 41.99, 39.46, 39.01, 38.83, 38.12, 36.59, 32.56, 30.60, 29.69, 27.93, 24.15, 23.66, 23.22, 21.17, 18.29, 17.13, 17.03, 16.92, 16.80, 12.76. FTIR (neat, cm⁻¹) ν_{\max} 3401 (s), 2946 (s), 2873 (s), 1722 (s), 1455 (s), 1389 (m), 1241 (w), 1142 (m), 1073 (s), 1048 (w). $[\alpha]_D^{298} = + 52$ (c 0.046, CHCl₃). HRMS (ESI): m/z calcd (C₃₁H₅₀O₅Na) 525.3550, found 525.3556 [M + Na]⁺.

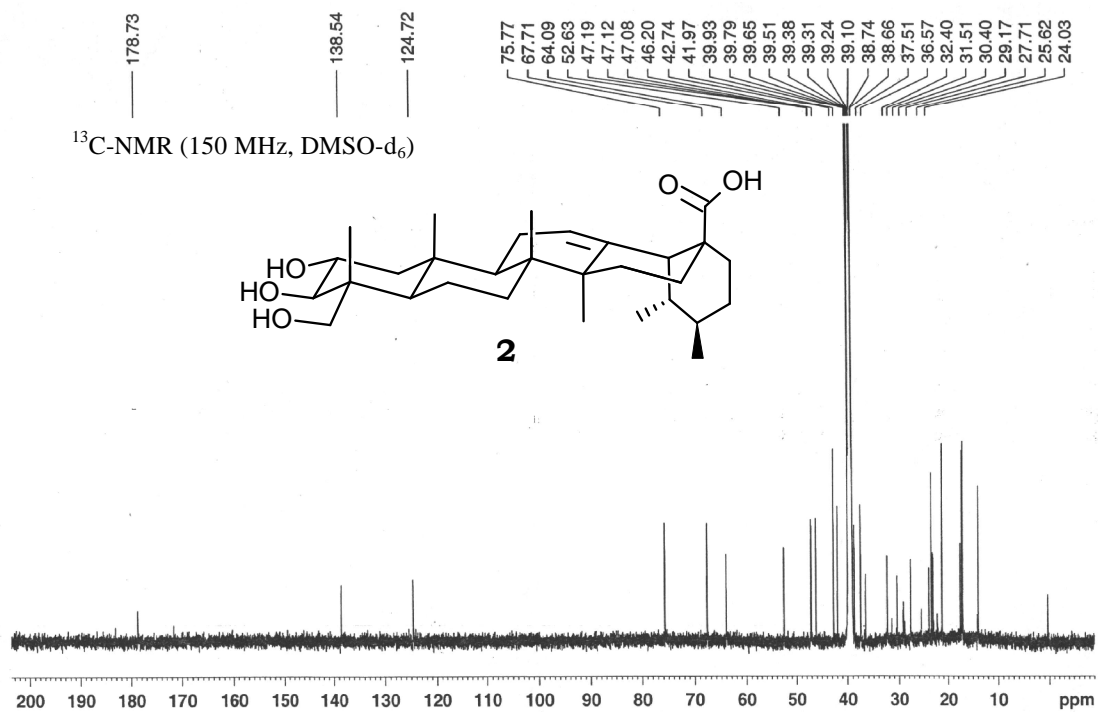
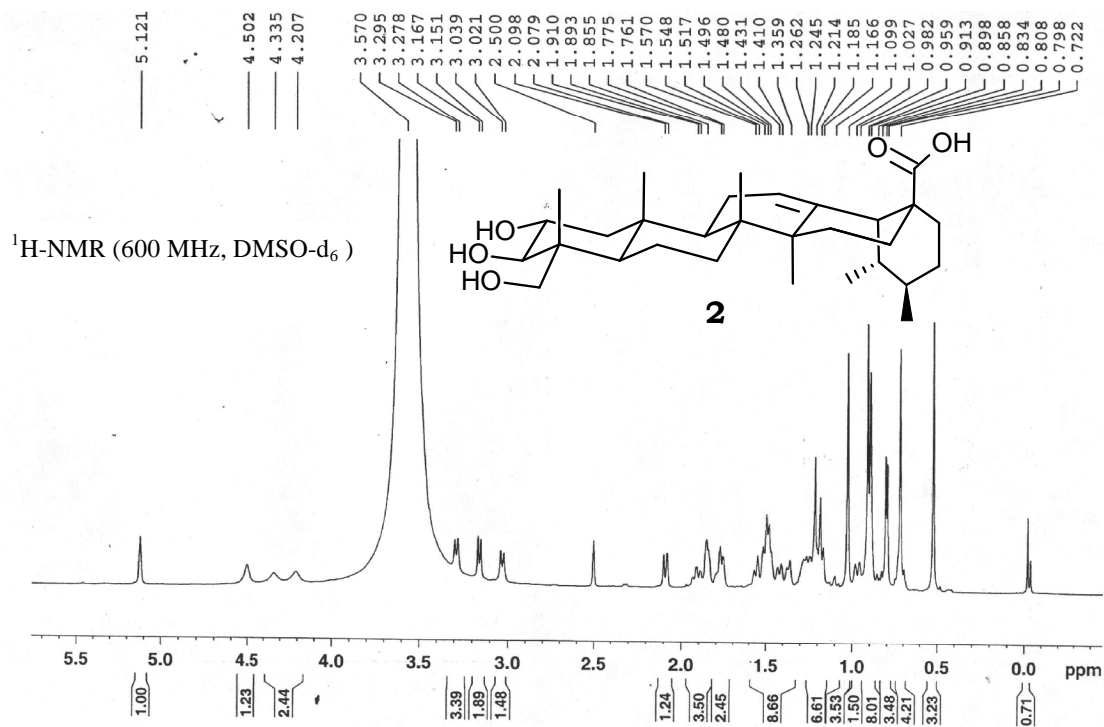
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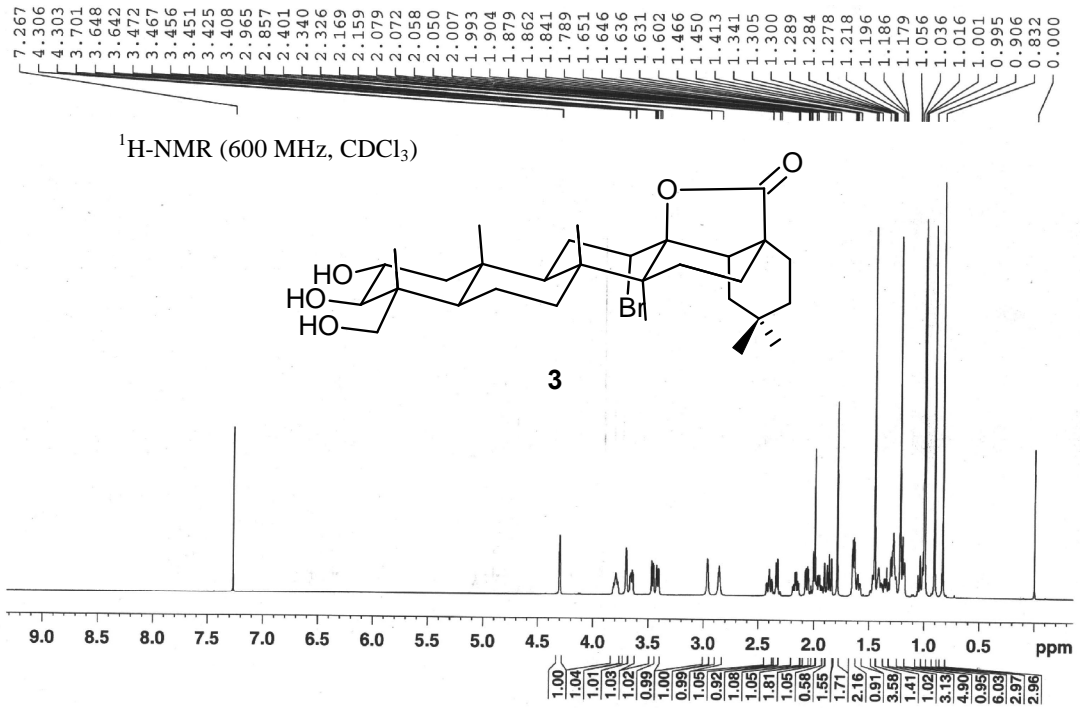
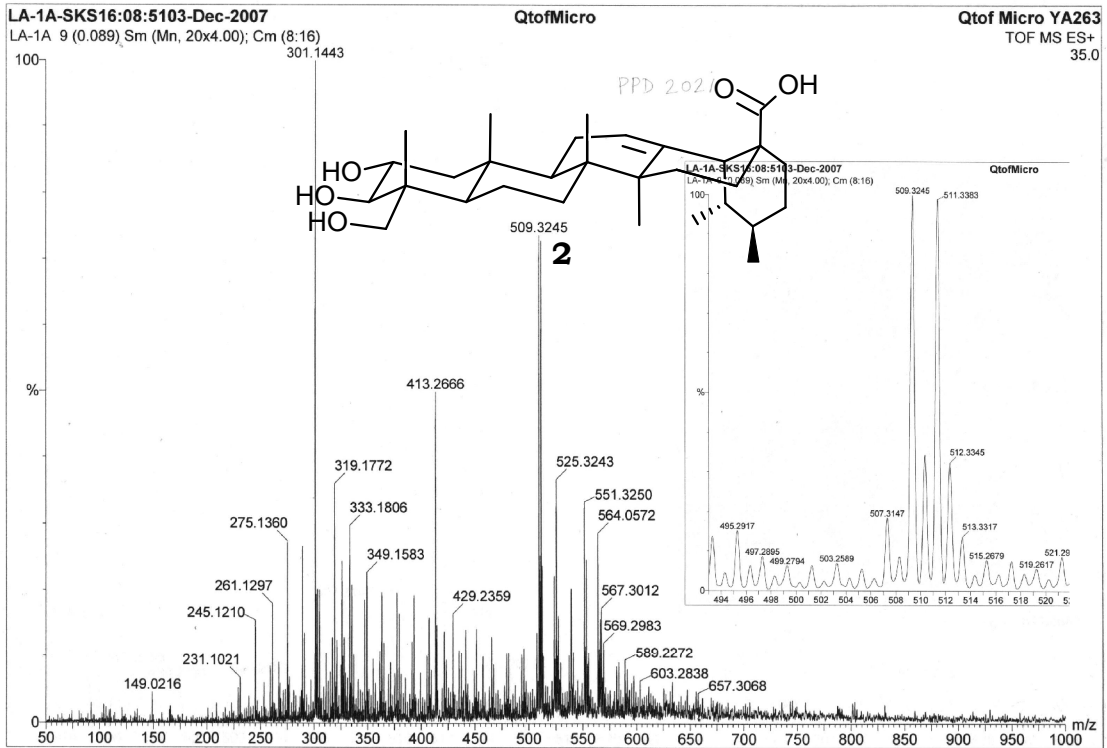
1. Bag, B. G.; Pramanik, S. R.; Maity, G. C. *Supramol. Chem.* **2005**, *17*, 297–302.

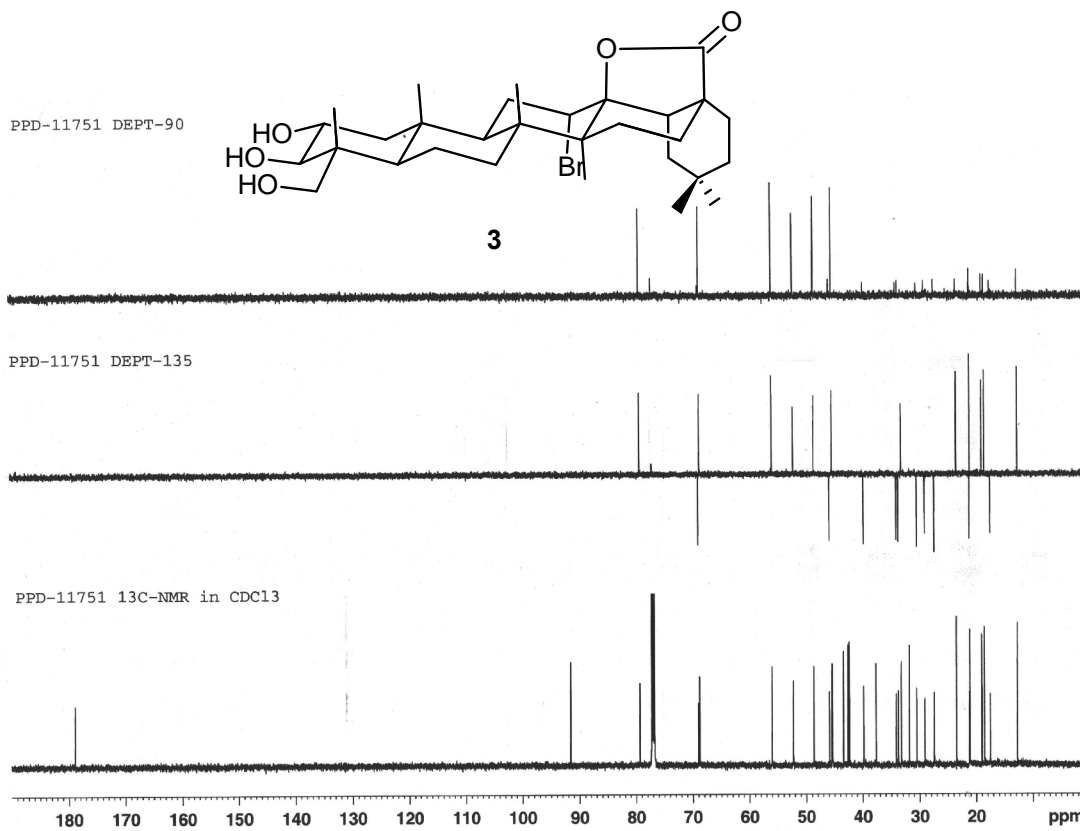
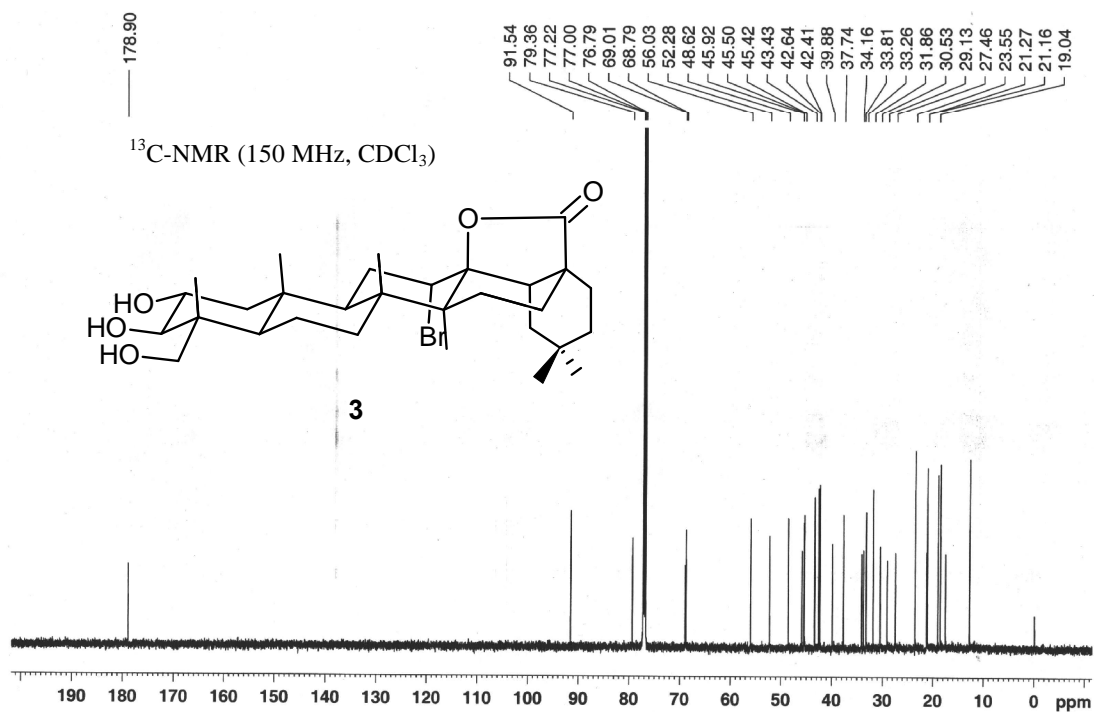
doi:10.1080/10610270500067822

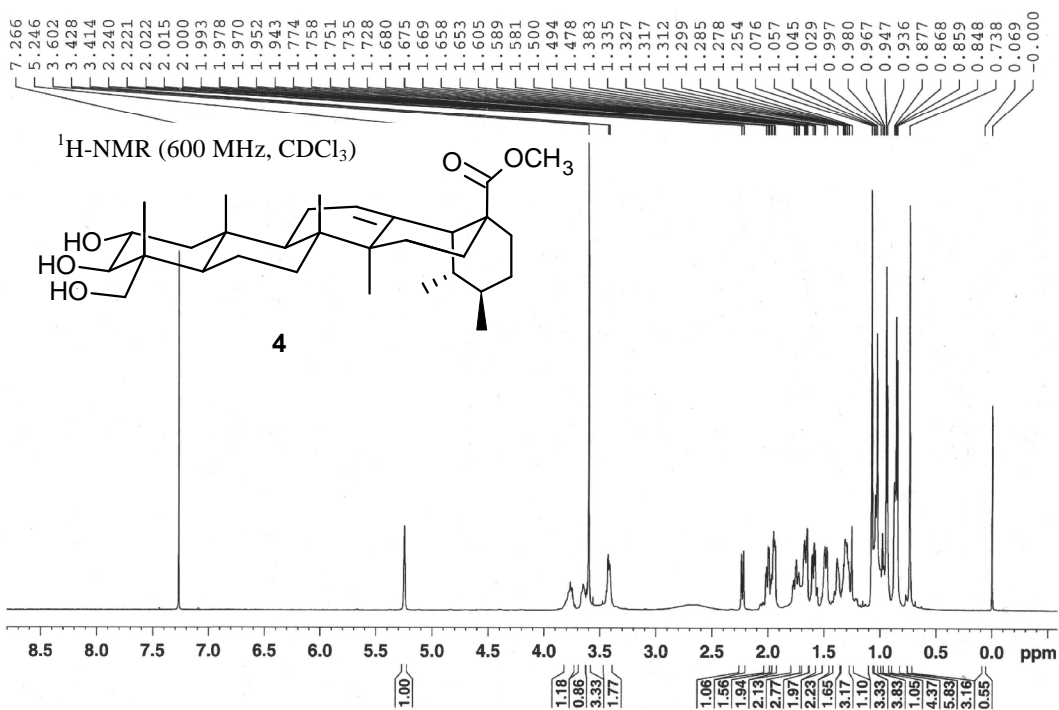
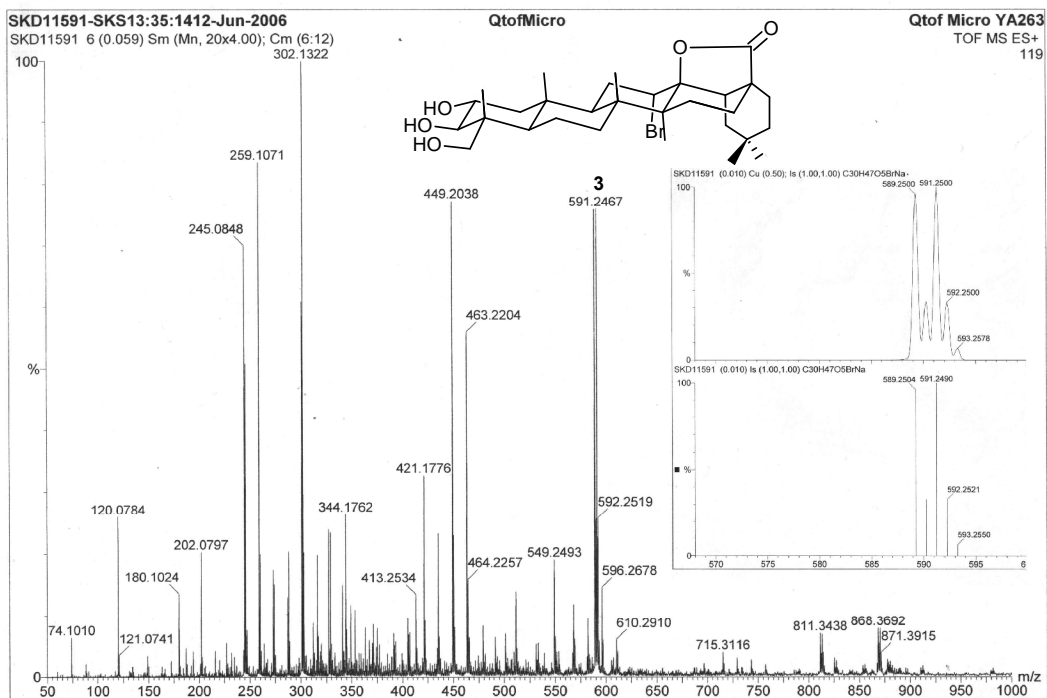
PPD-20691 $^1\text{H-NMR}$ in DMSOPPD-20691 $^{13}\text{C-NMR}$ in DMSO

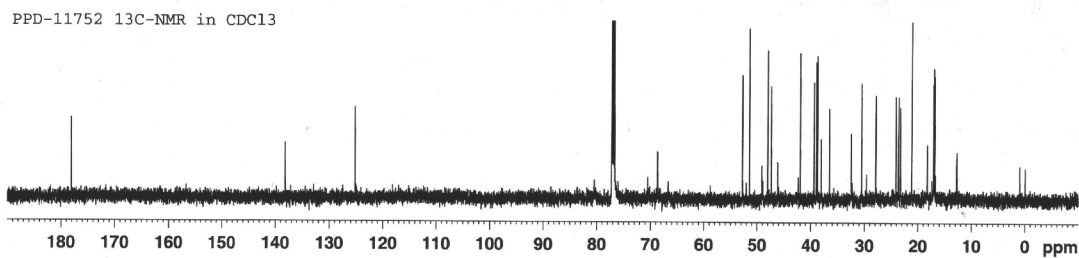
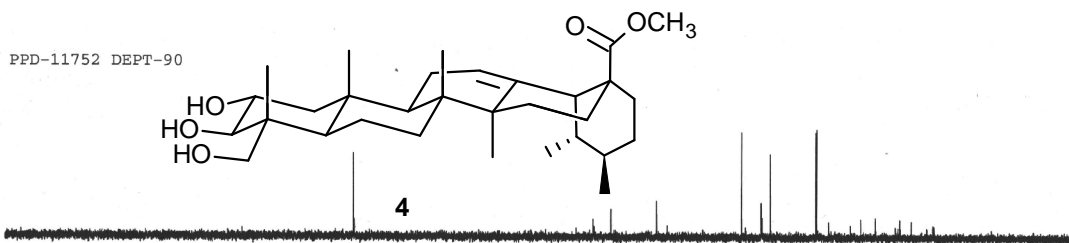
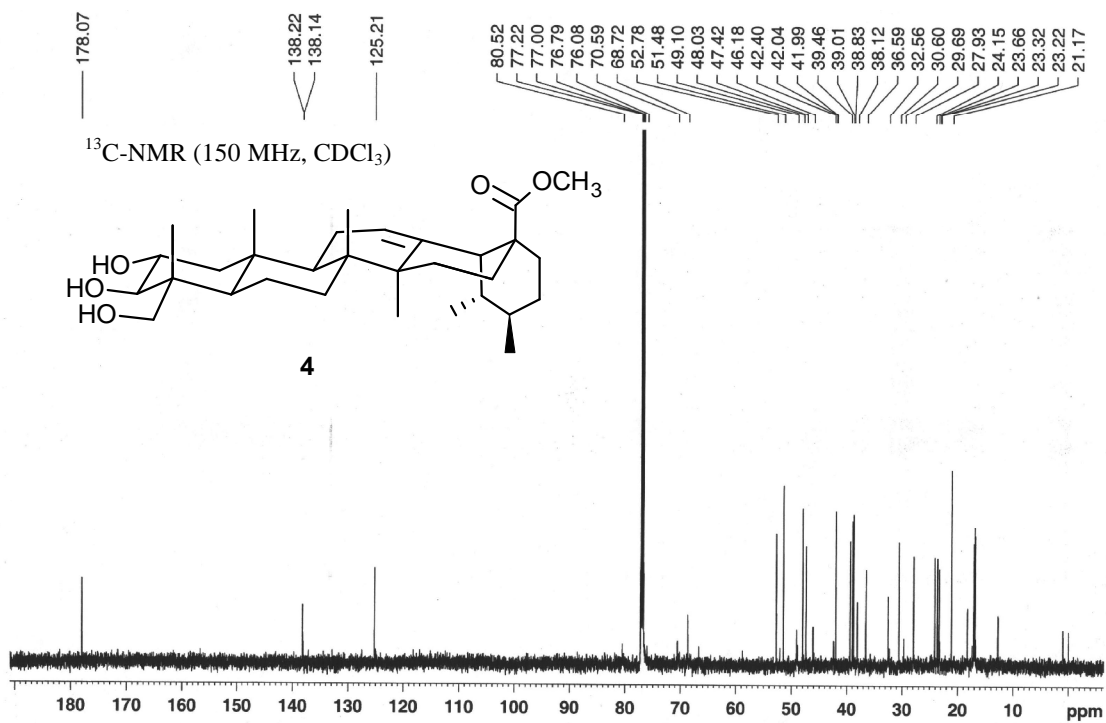


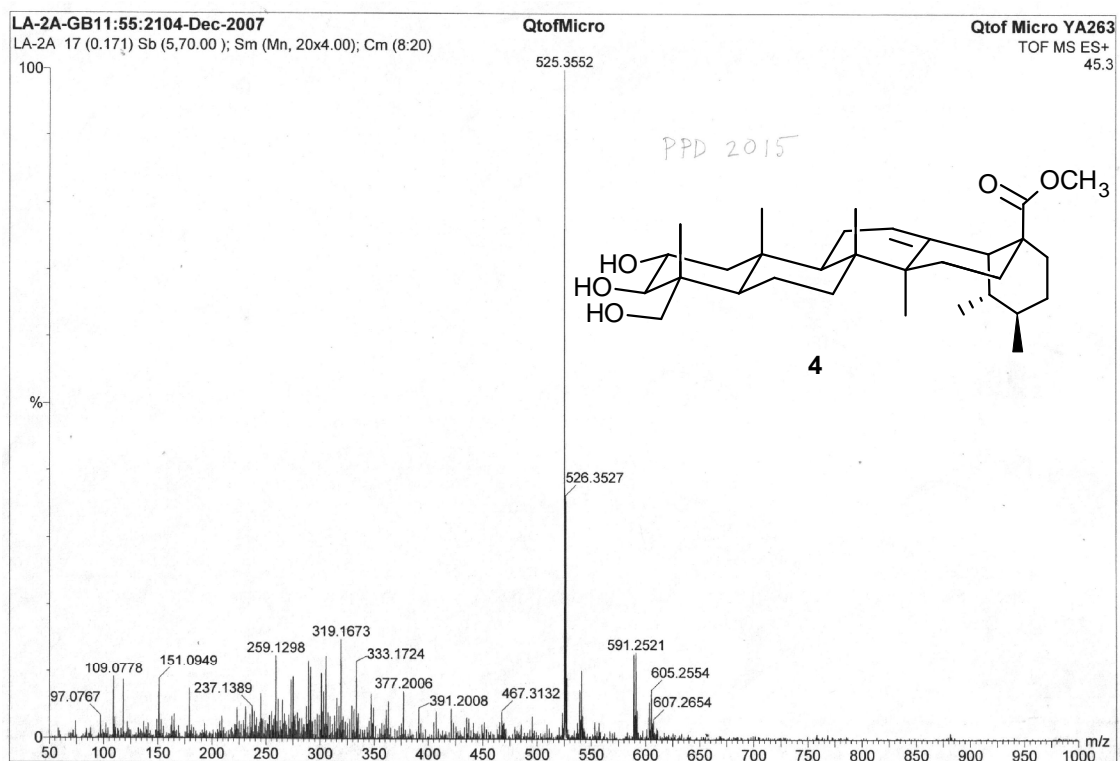












Gelation Tests: The arjuna-bromolactone **3** (ca. 5 mg) was dissolved by heating with an organic solvent in a vial. The clear solution thus obtained was allowed to cool to RT and examined visually. When the vial could be turned upside down without significant flow of the medium, we called it a gel. Minimum gel concentration (mgc) was measured by repeating the gelation experiments at different initial concentrations and allowing the solutions to cool to room temperature. The minimum concentration needed for gelation at room temperature was termed as the minimum gel concentration (mgc). The gel to sol transition temperature (T_{gel}) was measured by the ball drop method.



Figure 1: Inverted vial containing a gel of compound **3** in mesitylene (0.65% w/v). Photograph was taken after 4 h of cooling at RT).

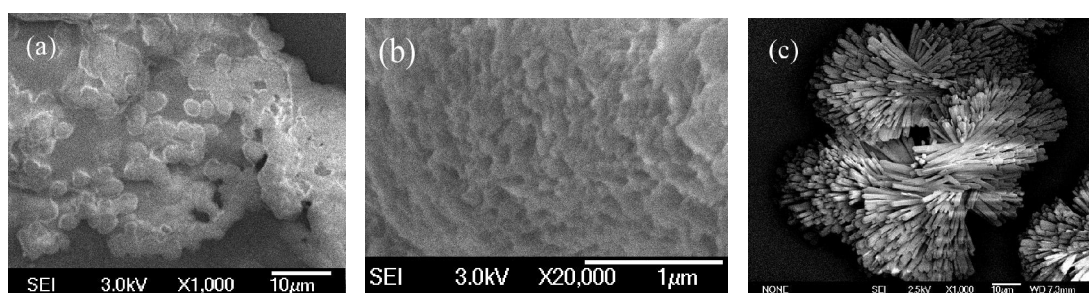


Figure 2: Scanning electron micrographs of the dried gels in mesitylene (2.25% w/v, (a) and (b)) and *o*-xylene (1.6% w/v, (c)) after sputter coating with Pt.