Supplemental Information

A Simple Monoselective C-H Oxygenation Approach for the Synthesis of Ursane Triterpenoids

Wenyi Mei [a], Sisi Fan [a], Yufei Han [a], Cunjian Shi [a], Lijie Qiu [a], Yunheng Shen [b], Zhenjiang Zhao [a*], Yufang Xu [a*], Honglin Li [a*]

[a] Shanghai Key Laboratory of New Drug Design, State Key Laboratory of Bioreactor Engineering, School of Pharmacy, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

[b] Department of Phytochemistry, School of Pharmacy, Naval Medical University, 325 Guohe Road, Shanghai 200433, China

Corresponding author

Yufang Xu, Email: yfxu@ecust.edu.cn. Phone: +86-21-64251399.

Honglin Li, Email: hlli@ecust.edu.cn. Phone: +86-21-64250213.

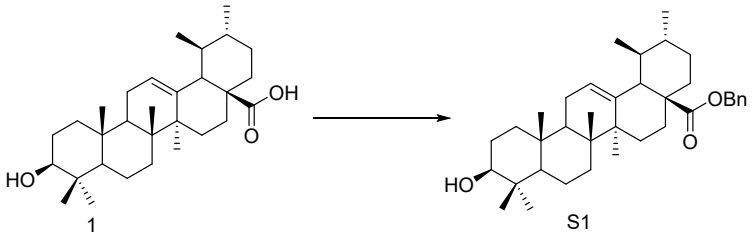
Zhenjiang Zhao, E-mail: zhjzhao@ecust.edu.cn.

Contents

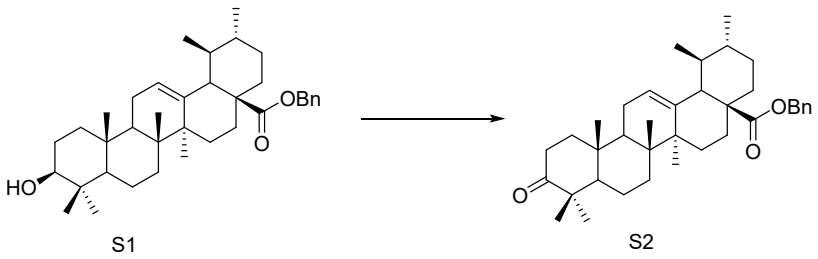
General Information

All the reactions were carried out under nitrogen or argon atmosphere with anhydrous solvents in flame-dried glassware, unless otherwise noted. All reagents and solvents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with Kiese gel F254 with 0.2 mm thickness. Visualization was carried out Phosphomolybdic Acid (PMA) and heat as developing agents. Flash column chromatography was performed on silica gel Sili Flash P60 (40-63 μm). ^{1}H and ^{13}C NMR spectra were recorded using Bruker spectrometers at 300 K with chemical shifts reported as parts per million (ppm) and Me_4Si as the internal standard, residual $CHCl_3$ (^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm), CH_3OH (^{1}H NMR δ = 3.30 ppm, ^{13}C NMR δ = 49.00 ppm) or C_5H_5N (^{1}H NMR δ = 7.20, 7.57, 8.72 ppm, ^{13}C NMR δ = 123.44, 135.43, 149.84 ppm). ^{1}H NMR splitting patterns were designated as broad (b), singlet (s), doublet (d), triplet (t), quartet (q) or combinations thereof, splitting patterns that could not be interpreted were designated as multiplet (m). ESI-MS was run on an Ion Spec Ultra instrument using HP-5989A.

Experimental procedures

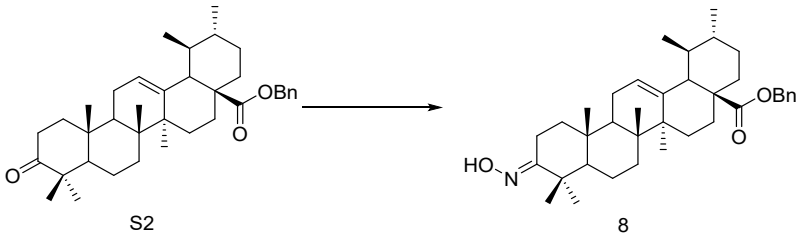


To a solution of ursolic acid (20.00 g, 43.86 mmol) and DMF (100 mL) was added K_2CO_3 (12.00 g, 86.82 mmol) and BnBr (11.00 g, 64.33 mmol). The reaction mixture was warmed to 55 ℃ and stirred for 8 h. After cooling to room temperature and poured into ice water to give a white precipitate, filtered and dried to give the benzyl ester **S1** (22.00 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.23 (t, *J* = 3.5 Hz, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 4.98 (d, *J* = 12.5 Hz, 1H), 3.21 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.27 (d, *J* = 11.3 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.90 – 1.82 (m, 2H), 1.82 – 1.76 (m, 1H), 1.76 – 1.64 (m, 3H), 1.63 – 1.57 (m, 3H), 1.52 – 1.42 (m, 4H), 1.40 – 1.25 (m, 6H), 1.07 (s, 3H), 1.03 (dd, *J* = 13.4, 2.6 Hz, 1H), 0.98 (s, 3H), 0.93 (d, *J* = 6.0 Hz, 3H), 0.90 (s, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.78 (s, 3H), 0.71 (d, *J* = 12.3 Hz, 1H), 0.64 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 167.1, 138.3, 136.5, 128.5, 128.3, 128.1, 125.7, 66.1, 55.9, 53.1, 48.3, 47.2, 42.3, 40.4, 39.7, 39.2, 39.0, 38.7, 37.1, 36.8, 32.9, 30.8, 28.1, 27.5, 24.4, 23.6, 23.5, 23.5, 21.3, 19.2, 17.3, 17.2, 17.2, 15.2. HRMS (ESI-MS, *m*/*z*) $[M + Na]^+$ calc. for $C_{37}H_{54}O_3Na$: 569.3971, found: 569.3972.



S1 S2

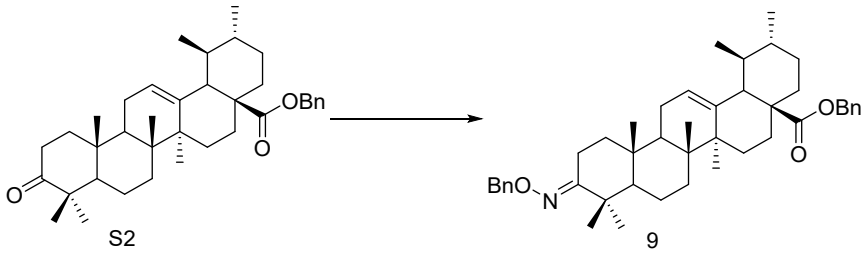
To a solution of benzyl ester **S1** (2.60 g, 4.80 mmol), $NaHCO_3$ (0.61 g, 7.26 mmol) and DCM (50 mL) was added Dess-Martin periodinane (3.10 g, 7.49 mmol) in batches at 0 ℃. The reaction mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ and diluted with DCM (300 mL), the organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated to afford a yellow oil, recrystallization by methanol to gave 3-ketone derivative **S2** (2.50 g, 96%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 5.25 (t, *J* = 3.5 Hz, 1H), 5.11 (d, *J* = 12.5 Hz, 1H), 4.99 (d, *J* = 12.5 Hz, 1H), 2.53 (dd, *J* = 10.9, 7.3 Hz, 1H), 2.37 (dd, *J* = 6.9, 3.7 Hz, 1H), 2.28 (d, *J* = 11.3 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.92 (d, *J* = 3.4 Hz, 1H), 1.92 – 1.85 (m, 2H), 1.80 (dt, *J* = 12.0, 6.0 Hz, 1H), 1.76 – 1.67 (m, 2H), 1.66 – 1.57 (m, 2H), 1.53 (dd, *J* = 19.0, 6.3 Hz, 2H), 1.46 (dd, *J* = 6.2, 2.7 Hz, 2H), 1.45 – 1.39 (m, 2H), 1.36 (dd, *J* = 14.0, 4.5 Hz, 2H), 1.32 – 1.28 (m, 2H), 1.28 – 1.22 (m, 1H), 1.08 (s, 6H), 1.03 (d, *J* = 7.1 Hz, 6H), 0.93 (d, *J* = 6.1 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.68 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 217.9, 177.4, 138.4, 136.5, 128.5, 128.3, 128.1, 125.6, 66.1, 55.4, 53.1, 48.3, 47.5, 46.9, 42.3, 39.6, 39.5, 39.3, 39.0, 36.8, 36.7, 34.3, 32.7, 30.8, 28.1, 26.7, 24.4, 23.6, 23.6, 21.3, 19.7, 17.1, 17.1, 15.4. HRMS (ESI-MS, *m*/*z*) $[M + Na]^+$ calc. for $C_{37}H_{52}O_3Na$: 567.3814, found: 567.3813.



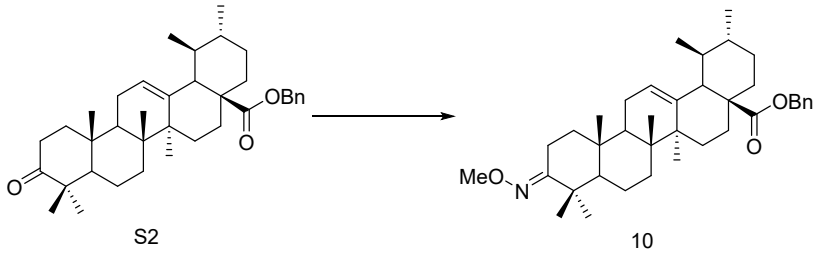
S2 8

To a solution of the 3-ketone **S2** (1.00 g, 1.77 mmol) in pyridine (15 mL), H_2NOH•HCl (0.19 g, 2.73 mmol) was added. The solution was stirred at 50 ℃ for 30 min. Pyridine were removed by evaporation in vacuo, the residue was acidified with 1 mol/L HCl (20 mL) and extracted with DCM, the organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to afford **8** (0.98 g, 95%) as a white solid without further purification. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.29 (s, 1H), 7.41 – 7.27 (m, 5H), 5.15 (t, *J* = 3.5 Hz, 1H), 5.05 (d, *J* = 12.5 Hz, 1H),

4.96 (d, *J* = 12.5 Hz, 1H), 2.89 (ddd, *J* = 15.6, 5.4, 3.2 Hz, 1H), 2.18 (d, *J* = 11.3 Hz, 1H), 2.14 – 1.95 (m, 2H), 1.92 – 1.77 (m, 2H), 1.76 – 1.70 (m, 1H), 1.70 – 1.55 (m, 4H), 1.55 – 1.39 (m, 5H), 1.39 – 1.20 (m, 5H), 1.08 (s, 3H), 1.03 (s, 3H), 0.97 (s, 4H), 0.93 (s, 4H), 0.90 (d, *J* = 4.8 Hz, 3H), 0.86 – 0.83 (m, 2H), 0.81 (d, *J* = 6.4 Hz, 3H), 0.58 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 167.6, 138.3, 136.5, 128.6, 128.3, 128.1, 125.7, 66.1, 60.6, 55.9, 53.1, 48.3, 47.2, 42.3, 40.4, 39.7, 39.2, 39.0, 38.7, 37.1, 36.8, 32.9, 30.8, 29.8, 28.1, 27.5, 24.4, 23.6, 23.5, 23.5, 21.3, 19.2, 17.3, 17.2, 17.2, 15.2, 14.3. HRMS (ESI-MS, *m*/*z*) $[M + H]^+$ calc. for $C_{37}H_{54}NO_3$: 560.4104, found: 560.4107.

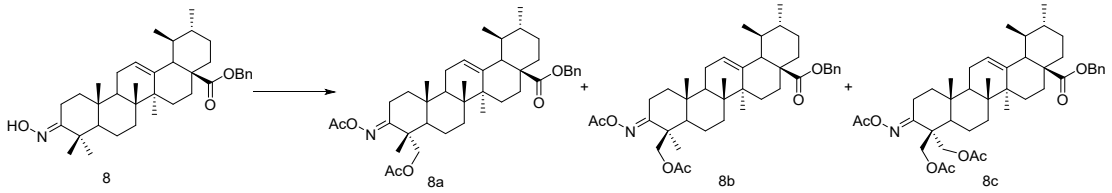


Following the procedure for preparation of 8 afforded 9 (2.0 g, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 10H), 5.24 (t, *J* = 3.7 Hz, 1H), 5.11 (d, *J* = 12.5 Hz, 1H), 5.06 (s, 2H), 4.98 (d, *J* = 12.4 Hz, 1H), 2.98 (ddd, *J* = 15.7, 5.6, 3.5 Hz, 1H), 2.27 (d, *J* = 11.3 Hz, 1H), 2.19 (ddd, *J* = 15.6, 12.2, 6.0 Hz, 1H), 2.00 (dt, *J* = 13.2, 7.0 Hz, 1H), 1.90 – 1.84 (m, 2H), 1.81 (dd, *J* = 13.6, 4.7 Hz, 1H), 1.76 – 1.63 (m, 4H), 1.63 – 1.56 (m, 2H), 1.55 – 1.43 (m, 4H), 1.42 – 1.22 (m, 6H), 1.15 (s, 3H), 1.12 – 1.07 (m, 1H), 1.06 (s, 3H), 1.04 (s, 3H), 1.00 (s, 2H), 0.96 (s, 3H), 0.94 (d, *J* = 6.1 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 166.6, 138.7, 138.3, 136.5, 128.5, 128.3, 128.3, 128.3, 128.1, 127.6, 125.8, 75.4, 66.1, 55.8, 53.1, 48.3, 47.1, 42.3, 40.2, 39.7, 39.2, 39.0, 38.7, 37.0, 36.8, 32.9, 30.8, 30.8, 28.1, 27.7, 24.4, 23.7, 23.6, 23.5, 21.3, 19.2, 18.2, 17.2, 17.1, 15.2. HRMS (ESI-MS, *m*/*z*) $[M + H]^+$ calc. for $C_{44}H_{60}NO_3$: 650.4573, found: 650.4572.



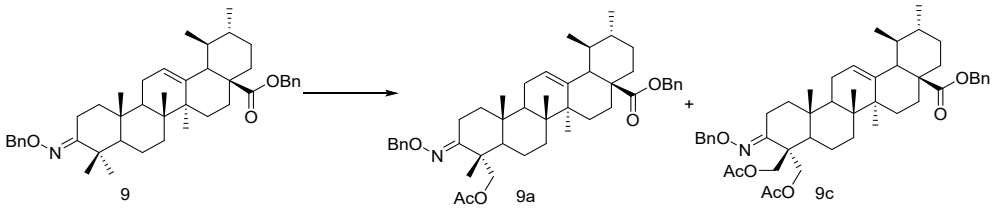
Following the procedure for preparation of 8 afforded 10 (19.80 g, 94%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.24 (t, *J* = 3.7 Hz, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 4.98 (d, *J* = 12.5 Hz, 1H), 3.82 (s, 3H), 2.93 (ddd, *J* = 15.7, 5.6,

3.4 Hz, 1H), 2.26 (d, *J* = 11.3 Hz, 1H), 2.15 (ddd, *J* = 15.8, 12.4, 6.0 Hz, 1H), 2.04 – 1.95 (m, 1H), 1.92 – 1.85 (m, 2H), 1.80 (dd, *J* = 13.9, 4.7 Hz, 1H), 1.77 – 1.66 (m, 5H), 1.62 (dd, *J* = 13.3, 4.2 Hz, 1H), 1.59 – 1.43 (m, 4H), 1.43 – 1.26 (m, 4H), 1.15 (s, 3H), 1.11 – 1.07 (m, 1H), 1.05 (s, 3H), 1.04 (s, 3H), 1.01 (s, 1H), 0.98 (s, 3H), 0.93 (d, *J* = 6.0 Hz, 3H), 0.84 (d, *J* = 6.4 Hz, 3H), 0.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 166.1, 138.3, 136.5, 1286, 128.3, 128.1, 125.8, 66.1, 61.2, 55.9, 53.1, 48.3, 47.2, 42.3, 40.0, 39.7, 39.2, 39.0, 38.8, 37.0, 36.8, 32.9, 30.8, 28.1, 27.6, 24.4, 23.7, 23.6, 23.5, 21.3, 19.2, 17.8, 17.2, 17.1, 15.2. HRMS (ESI-MS, *m*/*z*) [M + Na]$^+$ calc. for $C_{38}H_{56}ON_3$: 574.4260, found: 574.4259.



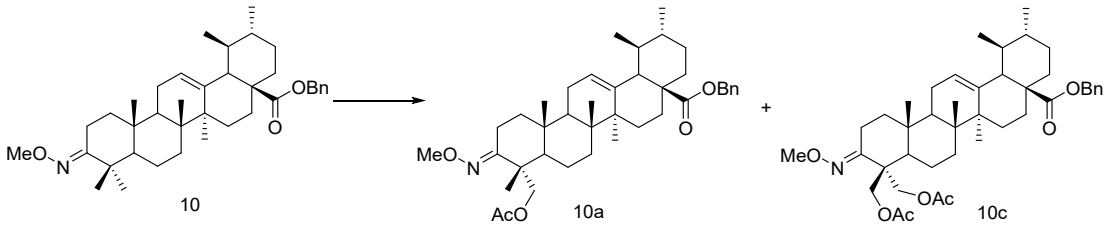
Oxime **8** (12 g, 21.5 mmol) was suspended in Ac_2O (50 mL) and AcOH (50 mL) and stirred for 1.5 h at 50 °C. Then, $Pd(OAc)_2$ (0.72 g, 3.21 mmol) and PIDA (9 g, 27.86 mmol) was added and the reaction mixture was stirred for 8 h at 50 °C. The reaction mixture was cooled to room temperature and concentrated in vacuo, the residue was extracted with DCM, the organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography on silica gel (petroleum : EtOAc = 8 : 1) to afforded **8a-b** (7.21 g, 51%) and **8c** (1.50 g, 10%) as a pale-yellow solid. Major isomer **8a**. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 – 7.29 (m, 5H), 5.16 (q, *J* = 6.3, 4.8 Hz, 1H), 5.05 (d, *J* = 12.5 Hz, 1H), 4.96 (d, *J* = 12.5 Hz, 1H), 4.13 (d, *J* = 11.0 Hz, 1H), 4.00 (d, *J* = 11.0 Hz, 1H), 2.72 – 2.60 (m, 1H), 2.59 – 2.52 (m, 1H), 2.25 (d, *J* = 4.8 Hz, 1H), 2.23 – 2.14 (m, 2H), 2.11 (d, *J* = 1.7 Hz, 3H), 2.02 (dd, *J* = 13.1, 4.1 Hz, 1H), 1.97 (s, 3H), 1.95 (s, 1H), 1.92 – 1.75 (m, 2H), 1.75 – 1.63 (m, 3H), 1.60 (d, *J* = 13.0 Hz, 3H), 1.55 – 1.48 (m, 2H), 1.48 – 1.29 (m, 8H), 1.29 – 1.11 (m, 6H), 1.07 (s, 3H), 1.04 (s, 3H), 1.02 (d, *J* = 6.5 Hz, 2H), 0.91 (s, 3H), 0.89 (s, 3H), 0.84 (dd, *J* = 6.8, 2.6 Hz, 1H), 0.83 – 0.78 (m, 3H), 0.58 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 171.0, 170.6, 169.8, 138.3, 136.3, 128.4, 128.2, 128.0, 125.4, 68.3, 66.0, 53.0, 48.4, 48.2, 48.1, 46.6, 43.8, 42.2, 39.5, 39.4, 39.1, 38.8, 38.8, 37.2, 36.6, 36.4, 32.3, 30.7, 27.9, 24.2, 23.4, 23.4, 21.1, 20.6, 20.4, 20.0, 19.4, 19.3, 17.0, 15.5. HRMS (ESI-MS, m/z) [M + Na] $^+$ calc. for $C_{41}H_{57}NNaO_6$: 682.4084, found: 682.4083. **8c** ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.39 – 7.31 (m, 5H), 5.16 (t, *J* = 3.6 Hz, 1H), 5.05 (d, *J* = 12.6 Hz, 1H), 4.96 (d, *J* = 12.5 Hz, 1H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.37 (d, *J* = 11.4 Hz, 1H), 4.28 (d, *J* = 11.4 Hz, 1H), 4.01 – 3.97 (m,

1H), 2.86 (dd, *J* = 5.7, 3.0 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.21 – 2.17 (m, 1H), 2.11 (s, 3H), 2.02 (dd, *J* = 13.3, 4.5 Hz, 1H), 1.98 (s, 3H), 1.95 (s, 3H), 1.92 – 1.85 (m, 1H), 1.84 – 1.78 (m, 1H), 1.78 – 1.66 (m, 3H), 1.63 – 1.57 (m, 3H), 1.57 – 1.48 (m, 4H), 1.47 – 1.42 (m, 2H), 1.38 (t, *J* = 10.7 Hz, 4H), 1.31 – 1.20 (m, 3H), 1.08 (dq, *J* = 13.4, 6.7, 6.1 Hz, 2H), 1.04 (s, 3H), 0.98 (s, 3H), 0.95 (d, *J* = 7.5 Hz, 1H), 0.91 (d, *J* = 6.0 Hz, 3H), 0.88 – 0.83 (m, 1H), 0.81 (d, *J* = 6.4 Hz, 3H), 0.58 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 176.0, 170.1, 167.0, 168.5, 166.3, 137.8, 136.2, 128.4, 127.9, 127.9, 124.8, 65.3, 63.3, 62.5, 52.6, 49.0, 47.9, 47. 5, 46.3, 41.6, 40.1, 38.9, 38.4, 38.3, 36.8, 36.2, 35.8, 32.3, 30.0, 27.3, 23.8, 23.1, 23.1, 20.9, 20.6, 20.5, 19.6, 19.6, 18.4, 16.9, 16.6, 14.9. HRMS (ESI-MS, m/z) [M + H]$^+$ calc. for $C_{43}H_{60}NO_8$: 718.4319, found: 718.4346.

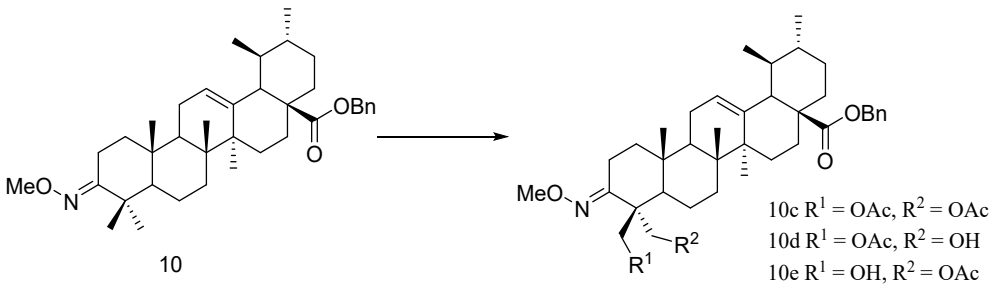


Following the procedure for preparation of **8a-c**, C–H oxidation of **9** with $Pd(OAc)_2$ /PIDA gave **9a** and **9c** as a white solid with 11.5% and 15.2% yields, respectively. **9a** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (tt, *J* = 6.9, 3.7 Hz, 10H), 5.25 (d, *J* = 3.8 Hz, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 5.05 (s, 2H), 4.98 (d, *J* = 12.4 Hz, 1H), 4.15 (d, *J* = 10.7 Hz, 1H), 4.00 (d, *J* = 10.7 Hz, 1H), 2.82 (ddd, *J* = 17.3, 6.7, 2.8 Hz, 1H), 2.35 (td, *J* = 11.2, 10.6, 5.8 Hz, 1H), 2.27 (d, *J* = 11.4 Hz, 1H), 2.00 (dd, *J* = 15.2, 10.8 Hz, 1H), 1.92 (s, 4H), 1.88 (dd, *J* = 11.1, 3.4 Hz, 2H), 1.83 – 1.66 (m, 5H), 1.66 – 1.55 (m, 7H), 1.50 (td, *J* = 11.2, 5.1 Hz, 3H), 1.45 – 1.22 (m, 10H), 1.10 (d, *J* = 6.6 Hz, 2H), 1.06 (s, 3H), 1.04 (s, 3H), 0.93 (d, *J* = 4.1 Hz, 6H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 171.2, 162.0, 138.8, 138.3, 136.49, 128.6, 128.3, 128.2, 128.1, 127.6, 125.8, 75.6, 68.9, 66.1, 53.2, 48.4, 48.3, 46.6, 42.8, 42.3, 39.6, 39.3, 39.0, 37.1, 36.7, 36.5, 32.6, 30.8, 29.9, 28.0, 24.4, 23.5, 21.3, 21.1, 20.1, 19.3, 19.2, 17.2, 17.1, 15.1. HRMS (ESI-MS, *m/z*) [M + H] $^+$ calc. for $C_{46}H_{62}NO_5$: 708.4628, found: 702.4626. **9c** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (h, *J* = 5.7, 4.5 Hz, 11H), 5.27 (d, *J* = 9.7 Hz, 1H), 5.18 – 5.11 (m, 1H), 5.06 (d, *J* = 4.8 Hz, 2H), 5.05 – 4.97 (m, 1H), 4.61 (dd, *J* = 13.3, 9.4 Hz, 1H), 4.54 – 4.44 (m, 1H), 4.19 (dd, *J* = 13.0, 9.0 Hz, 1H), 3.95 (dd, *J* = 13.1, 9.4 Hz, 1H), 3.03 (d, *J* = 16.9 Hz, 1H), 2.26 (dt, *J* = 18.9, 11.0 Hz, 2H), 2.10 – 1.99 (m, 1H), 1.96 (d, *J* = 4.1 Hz, 3H), 1.94 (dd, *J* = 4.9, 3.0 Hz, 2H), 1.90 (d, *J* = 4.0 Hz, 3H), 1.88 – 1.84 (m, 1H), 1.83 – 1.69 (m, 4H), 1.51 (s, 3H), 1.47 – 1.23 (m, 7H), 1.12 (d, *J* = 8.1 Hz, 1H), 1.08 (d, *J* = 5.8 Hz, 3H), 1.04 (d, *J*

= 4.5 Hz, 3H), 1.01 (d, *J* = 4.1 Hz, 1H), 0.96 (t, *J* = 8.1 Hz, 4H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.70 – 0.62 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 171.0, 170.9, 157.5, 138.7, 138.3, 136.5, 128.6, 128.4, 128.3, 128.2, 128.1, 127.6, 125.6, 75.8, 66.2, 64.9, 64.0, 53.1, 49.7, 48.3, 47.1, 47.1, 42.2, 39.5, 39.2, 39.0, 37.4, 36.7, 36.4, 33.0, 30.8, 29.9, 28.0, 24.3, 23.6, 23.5, 21.3, 21.1, 20.9, 19.2, 18.8, 17.1, 17.1, 15.4. HRMS (ESI-MS, *m*/*z*) $[M + H]^+$ calc. for $C_{48}H_{64}NO_7$: 766.4683, found: 766.4681.

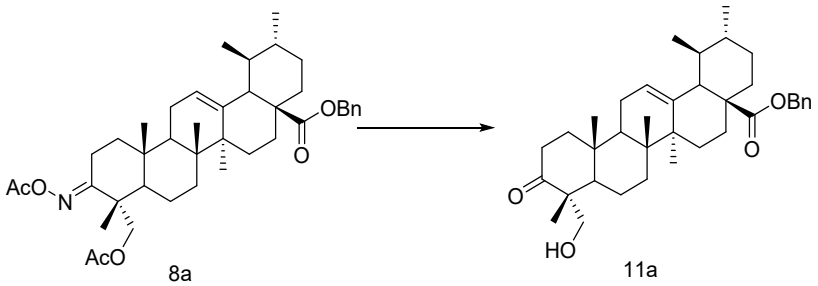


Following the procedure for preparation of **8a-c**, C–H oxidation of **10** with $Pd(OAc)_2$/PIDA gave **10a** and **10c** as a white solid with 18.2% and 9.2% yields, respectively. **10a** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 5.6 Hz, 5H), 5.25 (t, *J* = 3.7 Hz, 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 4.98 (d, *J* = 12.5 Hz, 1H), 4.14 (d, *J* = 10.7 Hz, 1H), 4.06 (d, *J* = 10.7 Hz, 1H), 3.79 (s, 3H), 2.73 (ddd, *J* = 17.2, 6.8, 2.9 Hz, 1H), 2.37 – 2.23 (m, 2H), 2.00 (d, *J* = 4.9 Hz, 1H), 1.96 (d, *J* = 7.0 Hz, 1H), 1.93 – 1.84 (m, 2H), 1.84 – 1.66 (m, 5H), 1.61 (td, *J* = 13.1, 4.0 Hz, 2H), 1.56 – 1.48 (m, 2H), 1.48 – 1.43 (m, 1H), 1.43 – 1.35 (m, 4H), 1.35 – 1.23 (m, 5H), 1.17 – 1.07 (m, 2H), 1.06 (d, *J* = 2.3 Hz, 6H), 1.00 (d, *J* = 12.8 Hz, 2H), 0.94 (s, 3H), 0.93 (d, *J* = 6.1 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 171.1, 161.4, 138.3, 136.5, 128.5, 128.3, 128.1, 125.8, 69.0, 66.1, 61.5, 53.2, 48.5, 48.3, 46.6, 42.6, 42.3, 39.6, 39.2, 39.0, 37.1, 36.7, 36.5, 32.6, 30.8, 28.0, 24.4, 23.5, 21.3, 21.1, 20.0, 19.4, 18.9, 17.2, 17.1, 15.1. HRMS (ESI-MS, *m*/*z*) $[M + H]^+$ calc. for $C_{40}H_{58}NO_5$: 632.4315, found: 632.4317. **10c** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34 (q, *J* = 7.3, 6.7 Hz, 5H), 5.15 (d, *J* = 3.9 Hz, 1H), 5.04 (d, *J* = 12.5 Hz, 1H), 4.95 (d, *J* = 12.5 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.30 (d, *J* = 11.1 Hz, 1H), 4.22 (d, *J* = 11.1 Hz, 1H), 3.91 (d, *J* = 11.6 Hz, 1H), 3.70 (s, 3H), 3.17 (d, *J* = 5.2 Hz, 2H), 2.85 – 2.72 (m, 1H), 2.18 (d, *J* = 11.1 Hz, 2H), 2.14 – 1.99 (m, 4H), 1.98 (s, 3H), 1.96 (s, 3H), 1.88 (d, *J* = 5.3 Hz, 1H), 1.80 (d, *J* = 11.5 Hz, 1H), 1.76 – 1.65 (m, 3H), 1.60 (d, *J* = 13.1 Hz, 5H), 1.54 – 1.20 (m, 14H), 1.03 (s, 4H), 0.96 (s, 4H), 0.91 (d, *J* = 4.7 Hz, 5H), 0.81 (d, *J* = 6.3 Hz, 3H), 0.58 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 176.1, 170.0, 156.9, 137.8, 137.1, 136.2, 130.7, 128.4, 127.9, 127.9, 127.7, 124.9, 94.9, 65.3, 63.9, 62.9, 61.2, 52.6, 49.0, 47.5, 46.7, 46.3, 41.6, 40.1, 38.9, 38.4, 38.3, 36.6, 36.2, 35.7, 32.4, 30.0, 27.3, 23.8, 23.1, 20.9, 20.7, 20.6, 18.4, 18.1, 16.9, 16. 7, 14.7. HRMS (ESI-MS, *m*/*z*) $[M + H]^+$ calc. for $C_{42}H_{60}NO_7$: 690.4370, found: 690.4371.

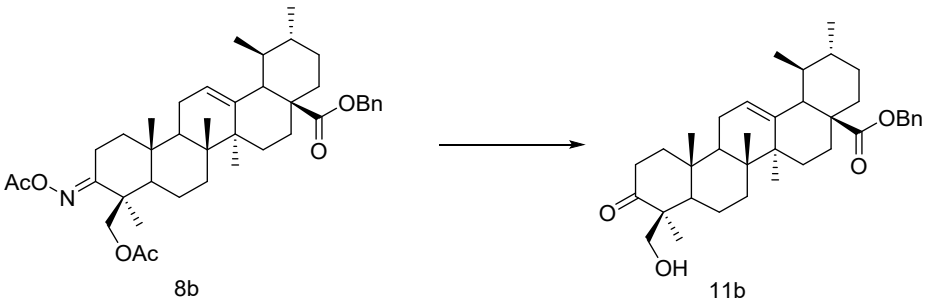


To a solution of the oxime **10** (1.0 g, 1.74 mmol) in AcOH (6 mL), $Pd(OAc)_2$ (59 mg, 0.26 mmol) and PIDA (953 mg, 2.96 mmol) was added and the reaction mixture was stirred for 8 h at 50 °C. The reaction mixture was cooled to room temperature and concentrated in vacuo, the residue was extracted with DCM, the organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography on silica gel (petroleum : EtOAc = 3 : 1) to afforded **10c-e** (0.15 g, 0.28 g and 0.26 g) as a pale-yellow solid with 12.3%, 23.1 and 24.6% yields, respectively. **10d** ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.32 (dp, *J* = 12.2, 7.2 Hz, 5H), 5.16 (d, *J* = 3.9 Hz, 1H), 5.05 (d, *J* = 12.6 Hz, 1H), 4.94 (d, *J* = 12.6 Hz, 1H), 4.43 (t, *J* = 5.9 Hz, 1H), 4.38 (d, *J* = 11.4 Hz, 1H), 3.94 (d, *J* = 11.4 Hz, 1H), 3.72 (s, 3H), 3.70 (d, *J* = 5.5 Hz, 1H), 3.37 (dd, *J* = 10.8, 6.4 Hz, 1H), 2.63 (dd, *J* = 16.6, 6.0 Hz, 1H), 2.20 (dd, *J* = 16.7, 11.3 Hz, 2H), 2.06 – 1.96 (m, 1H), 1.93 (s, 3H), 1.88 (t, *J* = 5.2 Hz, 1H), 1.82 – 1.69 (m, 2H), 1.69 – 1.57 (m, 5H), 1.57 – 1.39 (m, 5H), 1.39 – 1.24 (m, 3H), 1.21 (d, *J* = 12.7 Hz, 2H), 1.04 (s, 3H), 1.01 (dd, *J* = 12.8, 4.4 Hz, 2H), 0.91 (d, *J* = 4.6 Hz, 6H), 0.81 (d, *J* = 6.3 Hz, 3H), 0.60 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 176.1, 170.1, 158.2, 137.9, 137.1, 136.2, 130.7, 128.4, 127.9, 127.7, 125.1, 65.3, 63.9, 61.0, 52.6, 48.0, 47.9, 47.5, 45.7, 41.7, 40.1, 38.9, 38.40, 38.3, 36.2, 36.1, 35.5, 32.3, 30.0, 27.3, 23.8, 23.2, 23.2, 20.9, 20.7, 18.9, 18.6, 16.9, 16.7, 14.6. HRMS (ESI-MS, *m*/*z*) $[M + H]^+$ calc. for $C_{40}H_{58}NO_6$: 648.4264, found: 648.4265. **10e** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 – 7.27 (m, 6H), 5.15 (t, *J* = 3.6 Hz, 1H), 5.04 (d, *J* = 12.5 Hz, 1H), 4.95 (d, *J* = 12.5 Hz, 1H), 4.47 (s, 1H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.15 (d, *J* = 11.2 Hz, 1H), 3.71 (s, 3H), 3.63 (d, *J* = 11.3 Hz, 1H), 3.49 (d, *J* = 11.5 Hz, 1H), 2.87 (dt, *J* = 13.9, 3.8 Hz, 1H), 2.24 – 2.13 (m, 2H), 2.09 – 2.01 (m, 1H), 1.99 (s, 3H), 1.94 – 1.83 (m, 2H), 1.83 – 1.75 (m, 1H), 1.69 (td, *J* = 13.4, 3.5 Hz, 3H), 1.59 (dd, *J* = 13.0, 3.9 Hz, 3H), 1.55 – 1.42 (m, 5H), 1.41 – 1.31 (m, 5H), 1.24 (d, *J* = 9.4 Hz, 4H), 1.02 (s, 3H), 0.98 (d, *J* = 4.5 Hz, 2H), 0.96 – 0.84 (m, 9H), 0.80 (d, *J* = 6.4 Hz, 4H), 0.57 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 176.1, 170.2, 158.6, 137.8, 136.2, 128.4, 127.9, 127.9, 125.0, 65.3, 64.3, 62.1, 60.9, 59.8, 52.6, 49.1, 48.4, 47.5, 46.6, 41.5, 40.1, 39.0, 38.4, 38.3, 37.5, 36.2, 35.9, 32.6, 31.1, 30.0, 29.8, 27.3, 23.8, 23.1,

23.0, 20.9, 20.8, 18.7, 18.0, 16.9, 16.6, 14.9, 14.1. HRMS (ESI-MS, *m*/*z*) $[M + H]^+$ calc. for $C_{40}H_{58}NO_6$: 648.4264, found: 648.4263.

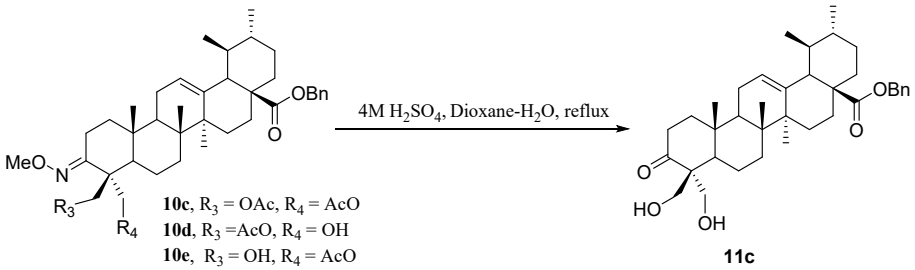


To a solution Oxime **8a** (8.2 g, 12.6 mmol) in MeOH (126 mL), K_2CO_3 (870 mg, 6.3 mmol) was added and the mixture was stirred for 1.5 h at 60 °C. Then, AcOH (720 µL, 12.6 mmol) was added. The mixture was stirred until gas evolution deceased. Then, a solution of $CuSO_4$•$5H_2O$ (15.7g, 62.8 mmol) in water (126 mL) and THF (126 mL) was added. The mixture was stirred at 60 °C for 9 h. After the reaction mixture was cooled to room temperature and extracted with DCM (3 x 500 mL), the organic layer was washed H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography on silica gel (petroleum : EtOAc = 5 : 1) afforded **11a** (4.2 g, 59%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 – 7.27 (m, 5H), 5.18 (t, *J* = 3.5 Hz, 1H), 5.05 (d, *J* = 12.5 Hz, 1H), 4.96 (d, *J* = 12.5 Hz, 1H), 4.83 (t, *J* = 5.4 Hz, 1H), 3.18 (dd, *J* = 10.3, 5.1 Hz, 1H), 2.32 (dd, *J* = 9.0, 5.9 Hz, 2H), 2.20 (d, *J* = 11.2 Hz, 1H), 2.01 (td, *J* = 13.2, 4.1 Hz, 1H), 1.91 (td, *J* = 9.8, 7.9, 4.0 Hz, 2H), 1.78 (tdd, *J* = 27.4, 14.5, 8.0 Hz, 4H), 1.60 (td, *J* = 11.4, 4.4 Hz, 5H), 1.56 – 1.47 (m, 3H), 1.50 – 1.41 (m, 3H), 1.39 (s, 4H), 1.35 – 1.19 (m, 9H), 1.08 (s, 4H), 1.05 (d, *J* = 12.9 Hz, 4H), 0.99 – 0.92 (m, 2H), 0.93 (d, *J* = 7.1 Hz, 5H), 0.85 (s, 8H), 0.86 – 0.79 (m, 9H), 0.78 (s, 4H), 0.61 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 216.2, 176.1, 137.8, 136.2, 128.4, 127.9, 127.9, 125.2, 67.0, 65.4, 52.7, 51.5, 47.5, 45.9, 45.4, 41.8, 40.1, 39.0, 38.4, 38.4, 37.1, 36.2, 35.6, 35.5, 31.8, 27.4, 23.8, 23.2, 23.1, 20.9, 19.1, 17.3, 16.9, 16.6, 15.1. HRMS (ESI-MS, *m*/*z*) $[M + Na]^+$ calc. for $C_{37}H_{52}O_3Na$: 583.3763, found: 583.3762.



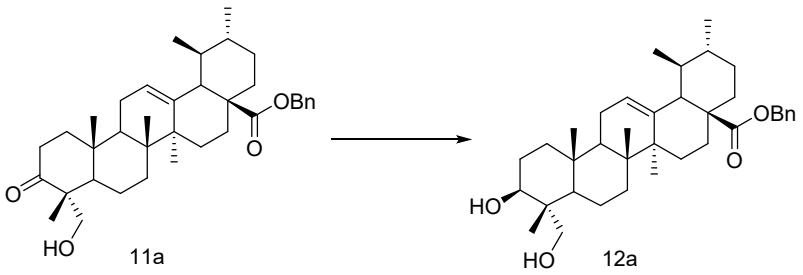
Oxime **8b** (2.0 g, 3.1 mmol) was dissolved in MeOH (31 mL) and K_2CO_3 (210

mg, 1.5 mmol) was added and the reaction mixture was stirred for 1.5 h at 60 °C. Then, AcOH (180 μL, 3.1 mmol) was added. The reaction mixture was stirred until gas evolution deceased. Then, a solution of $CuSO_4$•$5H_2O$ (3.9 g, 15.4 mmol) in water (31 mL) and THF (31 mL) was added. The reaction mixture was stirred at 60 °C for 9 h. After the reaction mixture was cooled to room temperature and extracted with DCM (3 x 100 mL), the organic layer was washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography on silica gel (petroleum : EtOAc = 5 : 1) afforded **11b** (0.20 g, 12%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 – 7.31 (m, 6H), 5.15 (t, J = 3.9 Hz, 1H), 5.05 (d, J = 12.5 Hz, 1H), 4.96 (d, J = 12.5 Hz, 1H), 4.45 (d, J = 5.8 Hz, 1H), 3.84 (dd, J = 11.0, 4.4 Hz, 1H), 3.33 (s, 1H), 2.69 (td, J = 14.3, 6.1 Hz, 1H), 2.29 – 2.13 (m, 2H), 2.11 – 1.96 (m, 3H), 1.95 – 1.80 (m, 3H), 1.72 (dd, J = 16.0, 11.2 Hz, 2H), 1.60 (d, J = 13.2 Hz, 3H), 1.56 – 1.37 (m, 8H), 1.34 (s, 3H), 1.30 (s, 6H), 1.26 (s, 7H), 1.23 (s, 5H), 1.21 – 1.12 (m, 4H), 1.08 (s, 4H), 1.03 (s, 4H), 1.00 (s, 4H), 0.91 (s, 5H), 0.88 – 0.85 (m, 1H), 0.81 (d, J = 6.3 Hz, 3H), 0.58 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 213.7, 176.1, 137.9, 136.2, 128.4, 127.9, 124.8, 65.3, 63.8, 56.9, 54.1, 52.5, 47.4, 46.5, 43.7, 41.6, 40.1, 39.1, 38.4, 38.3, 36.3, 36.2, 35.8, 34.8, 32.8, 30.0, 27.4, 23.5, 23.2, 23.2, 20.9, 20.0, 19.2, 16.9, 16.9, 16.6, 15.3, 14.8. HRMS (ESI-MS, m/z) [M + Na] $^+$ calc. for $C_{37}H_{52}O_3Na$: 583.3763, found: 583.3762.

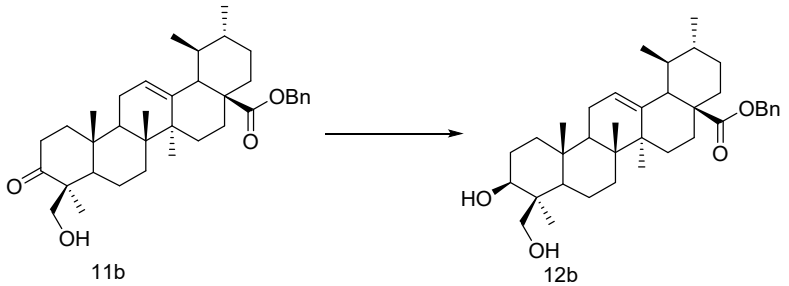


To a solution of the oxime **10d-e** (100 mg, 0.16 mmol) in dioxane (5 mL) and H_2O (5 mL), 4M H_2SO_4 was added and the mixture was stirred at 60 °C for 0.5 h. Then, the mixture was stirred at 80 °C for 1.5 h. After the reaction mixture was cooled to room temperature and extracted with DCM (3 x 500 mL), the organic layer was washed H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography on silica gel (petroleum : EtOAc = 2 : 1) afforded **11c** (65 mg, 71%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 – 7.29 (m, 5H), 5.17 (t, J = 3.6 Hz, 1H), 5.05 (d, J = 12.5 Hz, 1H), 4.96 (d, J = 12.6 Hz, 1H), 4.48 (t, J = 5.4 Hz, 1H), 4.32 (t, J = 5.5 Hz, 1H), 3.74 (dd, J = 10.5, 5.3 Hz, 1H), 3.59 (dd, J = 11.2, 5.3 Hz, 1H), 3.41 (dd, J = 11.2, 5.7 Hz, 1H), 3.21 (dd, J = 10.5, 5.6 Hz, 1H), 2.42 (ddd, J = 16.7, 12.2, 7.2 Hz, 1H), 2.24 – 2.11 (m, 3H), 2.08 – 1.94 (m, 2H), 1.92 (t, J = 4.0 Hz, 1H),

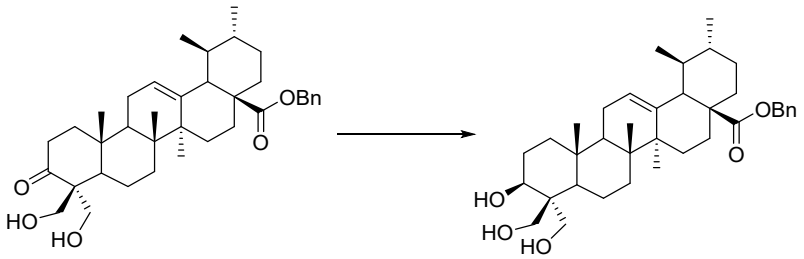
1.88 – 1.66 (m, 4H), 1.66 – 1.52 (m, 4H), 1.47 (dd, *J* = 18.2, 12.9 Hz, 4H), 1.41 – 1.18 (m, 7H), 1.06 (s, 3H), 1.04 – 0.99 (m, 1H), 0.97 (s, 3H), 0.91 (d, *J* = 5.1 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H), 0.60 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 213.4, 176.1, 137.9, 136.2, 128.4, 128.0, 127.9, 125.1, 65.4, 62.9, 61.7, 57.7, 52.6, 47.7, 47.5, 45.8, 41.7, 40.1, 39.0, 38.4, 38.3, 37.6, 36.2, 35.8, 35.5, 32.4, 30.0, 27.4, 23.8, 23.3, 21.0, 18.8, 17.0, 16.7, 15.0. HRMS (ESI-MS, *m*/*z*) [M + Na] $^+$ calc. for $C_{37}H_{52}O_5Na$: 599.3707, found: 599.3711.



Compound **11a** (3.0 g, 5.4 mmol) was dissolved in MeOH (30 mL). $NaBH_4$ (240 mg, 6.4 mmol) was added in 0 °C. The reaction solution was stirred for 2 h at room temperature. The reaction solution was quenched by saturated NH_4Cl and extracted with EA (3 x 100 mL), the organic layer was wished with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography on silica gel (petroleum : EtOAc = 3 : 1) afforded **12a** (2.2 g, 74%) as a white solid. ^{1}H NMR (600 MHz, MeOD-d_4) δ 5.23 (d, *J* = 3.7 Hz, 1H), 3.61 (d, *J* = 11.6, 4.9 Hz, 1H), 3.53 (d, *J* = 10.9 Hz, 1H), 3.29 (d, overlapped, 1H), 2.20 (d, *J* = 11.3 Hz, 1H), 2.04 (d, *J* = 4.3 Hz, 1H), 1.92 (dd, *J* = 10.4, 4.0 Hz, 3H), 1.65 (d, *J* = 11.5 Hz, 9H), 1.54 – 1.41 (m, 3H), 1.37 (d, *J* = 11.2 Hz, 4H), 1.30 (d, *J* = 9.7 Hz, 8H), 1.27 (s, 3H), 1.15 (d, *J* = 11.4 Hz, 2H), 1.13 (s, 3H), 1.09 (dt, *J* = 13.6, 3.4 Hz, 1H), 1.01 (d, *J* = 10.5 Hz, 1H), 0.99 (s, 3H), 0.96 (d, *J* = 5.6 Hz, 3H), 0.91 (d, *J* = 6.2 Hz, 1H), 0.89 (d, *J* = 6.3 Hz, 3H), 0.85 (s, 3H), 0.71 (s, 3H). ^{13}C NMR (151 MHz, MeOD-d_4) δ 181.6, 139.7, 126.9, 73.9, 67.4, 54.4, 49.4, 49.3, 49.1, 49.0, 48.9, 48.7, 48.6, 43.3, 43.3, 40.7, 40.4, 39.7, 38.1, 37.9, 33.8, 32.2, 31.8, 30.8, 30.8, 30.1, 29.2, 27.5, 25.3, 24.4, 24.1, 21.6, 19.1, 17.8, 17.7, 16.4, 12.8. HRMS (ESI-MS, *m*/*z*) [M + Na] $^+$ calc. for $C_{37}H_{52}O_3Na$: 585.3920, found: 585.3917.

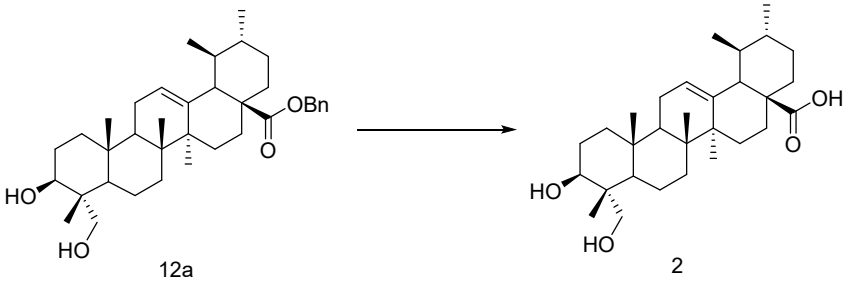


Following the procedure for preparation of **12a**, reduction of **11b** with $NaBH_4$ gave **12b** as a white solid (75% yield). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.38 – 7.28 (m, 5H), 5.13 (t, *J* = 3.7 Hz, 1H), 5.03 (d, *J* = 12.5 Hz, 1H), 4.95 (s, 1H), 4.93 (d, *J* = 6.8 Hz, 1H), 4.05 (dd, *J* = 7.5, 2.9 Hz, 1H), 3.81 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.24 (dd, *J* = 11.0, 7.5 Hz, 1H), 3.15 (dt, *J* = 11.6, 4.6 Hz, 1H), 2.17 (d, *J* = 11.3 Hz, 1H), 1.98 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.84 (dt, *J* = 18.2, 5.5 Hz, 1H), 1.71 (d, *J* = 12.4, 3.9 Hz, 2H), 1.61 – 1.57 (m, 2H), 1.53 (dd, *J* = 13.5, 4.4 Hz, 2H), 1.51 – 1.48 (m, 2H), 1.42 (td, *J* = 11.9, 4.9 Hz, 2H), 1.35 (d, *J* = 6.5 Hz, 2H), 1.30 – 1.25 (m, 2H), 1.22 (d, *J* = 4.6 Hz, 2H), 1.20 – 1.10 (m, 2H), 1.05 (s, 3H), 1.02 (s, 3H), 0.90 (s, 3H), 0.81 (d, *J* = 6.9 Hz, 6H), 0.51 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 176.5, 138.2, 136.7, 128.8, 128.4, 125.5, 79.1, 65.8, 63.5, 55.8, 53.0, 47.9, 47.5, 42.6, 42.0, 41.3, 40.5, 38.9, 38.8, 38.6, 36.7, 36.7, 33.5, 32.0, 30.5, 29.9, 29.0, 27.8, 27.7, 24.3, 23.7, 23.5, 23.4, 23.0, 21.4, 20.4, 19.8, 19.7, 19.0, 17.4, 17.0, 16.0, 11.7. HRMS (ESI-MS, *m/z*) $[M + Na]^+$ calc. for $C_{37}H_{52}O_3Na$: 585.3920, found: 585.3925.



11c 12c

Following the procedure for preparation of **12a**, reduction of **11c** with $NaBH_4$ gave **12c** as a white solid (70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 5.22 (t, *J* = 3.7 Hz, 1H), 5.09 (d, *J* = 12.4 Hz, 1H), 4.97 (d, *J* = 12.4 Hz, 1H), 4.32 (d, *J* = 11.7 Hz, 1H), 4.16 (d, *J* = 11.3 Hz, 1H), 3.74 (dt, *J* = 30.9, 12.1 Hz, 3H), 2.25 (dd, *J* = 11.3, 1.7 Hz, 1H), 1.99 (td, *J* = 13.4, 12.9, 4.5 Hz, 1H), 1.89 (dd, *J* = 6.3, 4.3 Hz, 1H), 1.80 (ddd, *J* = 20.9, 11.0, 4.4 Hz, 2H), 1.73 (dt, *J* = 14.6, 5.1 Hz, 3H), 1.70 – 1.65 (m, 2H), 1.65 – 1.61 (m, 1H), 1.60 (d, *J* = 4.3 Hz, 1H), 1.59 – 1.53 (m, 1H), 1.47 (dq, *J* = 10.3, 5.9, 4.9 Hz, 2H), 1.42 (dd, *J* = 12.8, 4.1 Hz, 1H), 1.30 (dd, *J* = 9.3, 6.4 Hz, 6H), 1.05 (s, 3H), 1.03 – 0.99 (m, 1H), 0.99 – 0.95 (m, 1H), 0.93 (d, *J* = 6.3 Hz, 3H), 0.90 – 0.86 (m, 2H), 0.85 (s, 3H), 0.84 (d, *J* = 6.4 Hz, 3H), 0.59 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 138.2, 136.5, 128.5, 128.3, 128.1, 125.5, 78.0, 71.2, 64.0, 53.0, 51.7, 48.2, 47.7, 45.9, 42.1, 39.6, 39.2, 39.0, 38.4, 36.7, 36.7, 33.2, 30.8, 29.8, 28.0, 26.9, 24.3, 23.7, 23.6, 21.3, 18.9, 17.1, 17.0, 15.8. HRMS (ESI-MS, m/z) $[M + Na]^+$ calc. for $C_{37}H_{54}O_5Na$: 601.3869, found: 601.3871.

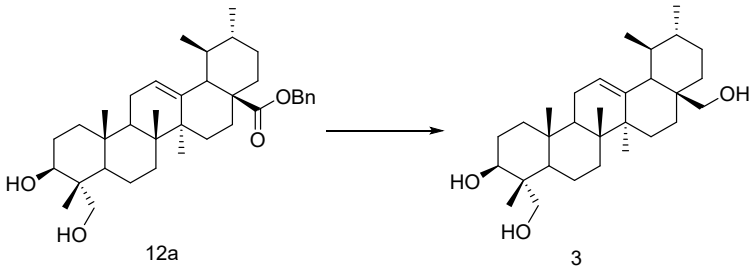


Compound **12a** (0.50 g, 0.88 mmol) was dissolved in THF (20 mL). 10% Pd/C (50 mg) was added. The reaction mixture was stirred overnight at room temperature under H_2 at atmospheric pressure. The reaction mixture was filtered through Celiteand and washed with THF; the organic layer was concentrated in vacuo. Purification by column chromatography on silica gel (DCM : MeOH = 20 : 1) afforded **2** (0.41 g, 99%) as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.93 (s, 1H), 5.13 (t, J = 3.6 Hz, 1H), 4.40 (s, 1H), 4.15 (s, 1H), 3.44 (dd, J = 11.4, 5.2 Hz, 1H), 3.33 (s, 1H), 3.07 (d, J = 10.5 Hz, 1H), 2.11 (d, J = 11.3 Hz, 1H), 1.92 (qd, J = 12.1, 10.9, 3.4 Hz, 1H), 1.88 – 1.75 (m, 3H), 1.65 – 1.35 (m, 10H), 1.36 – 1.15 (m, 4H), 1.11 (d, J = 11.4 Hz, 1H), 1.04 (s, 3H), 1.02 – 0.96 (m, 1H), 0.91 (d, J = 5.3 Hz, 3H), 0.89 (s, 3H), 0.82 (d, J = 6.4 Hz, 3H), 0.75 (s, 3H), 0.54 (s, 3H). ^{13}C NMR (151 MHz, MeOD-d_4) δ 181.8, 139.9, 127.1, 74.1, 67.6, 54.6, 43.5, 43.5, 41.0, 40.6, 39.9, 38.3, 38.1, 34.0, 32.4, 32.0, 31.0, 31.0, 30.3, 29.4, 27.7, 25.5, 24.6, 24.4, 21.8, 19.3, 18.1, 17.9, 16.6, 13.0. HRMS (ESI-MS, m/z) [M + Na] $^+$ calc. for $C_{30}H_{47}O_4Na$: 495.3450, found: 495.3448. The NMR spectrograms are almost same with that of reported isolated natural product [1].

Table S1. Comparison of ^{13}C NMR data of isolated and herein prepared 3β, 23-dihydroxyurs-12-en-28-oic acid

Carbon No.	**Synthetic** δ_c (ppm)	**Natural** δ_c (ppm)	**Err** (Natural- Synthetic) $\Delta\delta_c$ (ppm)
1	38.8	38.8	0
2	27.6	27.6	0
3	73.3	73.5	0.2
4	42.4	42.4	0
5	48.0	48.0	0
6	18.5	18.5	0
7	33.2	33.2	0
8	39.9	39.9	0
9	48.0	48.0	0
10	37.0	37.0	0
11	23.5	23.6	0.1
12	125.6	125.6	0
13	139.2	139.2	0
14	42.8	42.7	-0.1
15	28.6	28.6	0
16	24.8	24.8	0
17	48.4	48.6	0.2

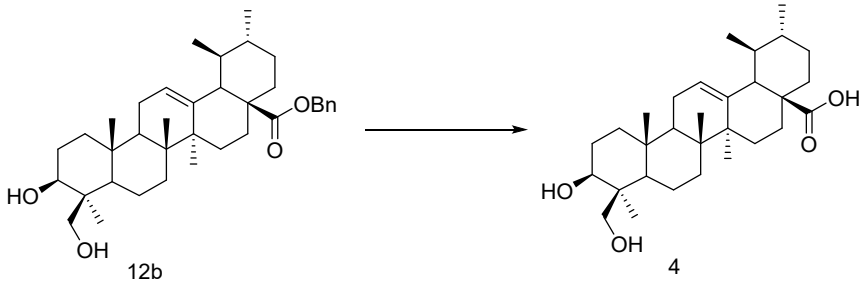
18	53.5	53.5	0
19	39.4	39.4	0
20	39.3	39.3	0
21	31.0	31.0	0
22	37.4	37.3	-0.1
23	67.8	68.1	0.3
24	13.1	13.0	-0.1
25	16.0	16.0	0
26	17.4	17.4	0
27	23.8	23.8	0
28	179.8	179.7	-0.1
29	17.4	17.4	0
30	21.3	21.2	-0.1



To a solution of **12a** (200 mg, 0.36 mmol) in dry THF (10 mL). $LiAlH_4$ (21 mg, 0.54 mmol) was added at 0°C. The reaction mixture was stirred at 65 °C for 1.5 h under N_2 atmosphere. At this point, the $LiAlH_4$ was quenched with MeOH and water was added, and then the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography on silica gel (DCM : MeOH = 30 : 1) afforded **3** (140 mg, 86% yield) as white solid. ^{1}H NMR (400 MHz, Pyridine-d_5) δ 4.26 – 4.20 (m, 2H), 4.08 (q, J = 7.1 Hz, 1H), 3.94 (d, J = 10.6 Hz, 1H), 3.75 (d, J = 10.4 Hz, 1H), 3.50 (d, J = 10.6 Hz, 1H), 2.08 (td, J = 13.0, 12.6, 4.1 Hz, 1H), 2.03 – 1.98 (m, 2H), 1.97 – 1.92 (m, 3H), 1.76 – 1.70 (m, 3H), 1.69 – 1.61 (m, 3H), 1.57 – 1.51 (m, 3H), 1.46 – 1.36 (m, 2H), 1.34 – 1.25 (m, 2H), 1.19 (s, 3H), 1.10 (s, 3H), 1.06 (s, 3H), 1.03 (s, 3H), 0.98 – 0.95 (m, 6H).^{13}C NMR (151 MHz, Pyridine-d_5) δ 139.4, 124.8, 73.1, 68.9, 67.6, 54.4, 48.2, 47.9, 42.7, 42.2, 40.1, 39.6, 39.5, 38.8, 38.5, 36.8, 36.0, 32.7, 31.0, 27.5, 26.3, 23.6, 23.5, 23.4, 21.4, 18.3, 17.5, 16.8, 16.1, 12.9. HRMS (ESI-MS, m/z) [M + Na] $^+$ calc. for $C_{30}H_{49}O_3Na$: 481.3658, found: 481.3655. The NMR spectrograms are almost same with that of reported isolated natural product [2].

Table S2. Comparison of ^{13}C NMR data of isolated and herein prepared 3β,23,28-Trihydroxy-12-ursene [2].

Carbon No.	**Synthetic** δ_c (ppm)	**Natural** δ_c (ppm)	**Err** (Natural- Synthetic) $\Delta\delta_c$ (ppm)
1	39.4	39.3	-0.1
2	28.1	27.9	-0.2
3	73.7	73.7	0
4	40.7	40.6	-0.1
5	48.8	48.7	-0.1
6	18.9	18.8	-0.1
7	33.3	33.2	-0.1
8	39.1	38.9	-0.2
9	48.5	48.4	-0.1
10	37.3	37.2	-0.1
11	24.0	23.9	-0.1
12	125.4	125.3	-0.1
13	140.0	140.0	0
14	42.7	42.6	-0.1
15	26.9	26.8	-0.1
16	24.2	24.0	-0.2
17	43.3	43.1	-0.2
18	55.0	54.9	-0.1
19	40.1	40.0	-0.1
20	40.2	40.1	-0.1
21	31.6	31.5	-0.1
22	36.6	36.4	-0.2
23	68.2	68.2	0
24	13.5	13.4	-0.1
25	16.7	16.0	-0.7
26	17.4	17.3	-0.1
27	23.9	23.8	-0.1
28	69.5	69.4	-0.1
29	18.1	18.0	-0.1
30	22.0	21.8	-0.2



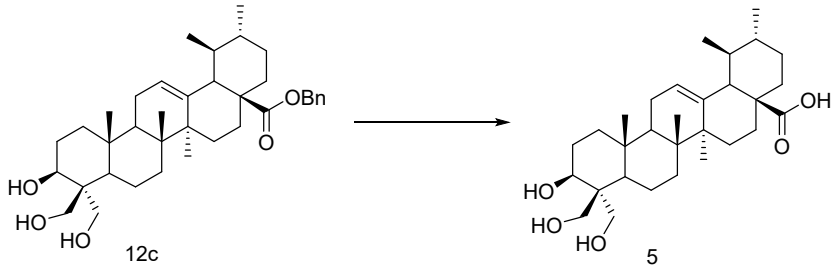
12b 4

Following the procedure for preparation of **2**, hydrogenolysis of **12b** with Pd/C-H_2 gave **4** as a white solid (91% yield). ^{1}H NMR (600 MHz, Pyridine-d_5) δ 5.50 (t, J = 3.7 Hz, 1H), 4.52 (s, 1H), 3.70 – 3.66 (m, 2H), 2.68 (d, J = 11.3 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.13 (td, J = 13.1, 4.2 Hz, 1H), 2.05 – 2.01 (m, 2H), 1.98 (dt, J = 17.8, 3.6 Hz, 3H), 1.94 – 1.89 (m, 2H), 1.69 (s, 1H), 1.64 (dd, J = 11.2, 6.5 Hz, 1H), 1.60 (s, 2H), 1.58 (s, 3H), 1.49 (dt, J = 14.3, 4.2 Hz, 2H), 1.43 – 1.37 (m, 2H), 1.25 (s, 3H), 1.21 (dq, J = 13.6, 2.5 Hz, 1H), 1.03 (d, J = 5.8 Hz, 6H), 0.98 (d, J = 6.3 Hz, 4H), 0.89 (s, 3H).^{13}C NMR (151 MHz, Pyridine-d_5) δ 179.8, 139.2, 125.5, 80.1, 64.5, 56.3, 53.5, 48.0, 48.0, 43.1, 42.4, 39.9, 39.4, 39.3, 38.8, 37.4, 37.0, 33.8, 31.0, 28.6, 28.4, 24.8, 23.8, 23.8, 23.6, 21.4, 19.0, 17.5, 17.2, 16.1. HRMS (ESI-MS, m/z) [M + Na] $^+$ calc. for $C_{30}H_{47}O_4Na$: 495.3450, found: 495.3449. The NMR spectrograms are almost same with that of reported isolated natural product [3].

Table S3. Comparison of ^{13}C NMR data of isolated and herein prepared 3β, 24-dihydroxyurs-12-en-28-oic acid

Carbon No.	**Synthetic** δ_c (ppm)	**Natural** δ_c (ppm)	**Err** (Natural- Synthetic) $\Delta\delta_c$ (ppm)
1	38.8	38.9	0.1
2	28.6	28.7	0.1
3	80.1	80.2	0.1
4	43.1	43.2	0.1
5	56.3	56.4	0.1
6	19.0	19.1	0.1
7	33.8	32.9	-0.9
8	39.9	40.0	0.1
9	48.0	48.1	0.1
10	36.9	37.0	0.1
11	23.8	23.8	0.1
12	125.4	125.5	0.1
13	139.1	139.2	0.1
14	42.3	42.2	-0.1
15	28.3	28.4	0.1
16	24.8	24.9	0.1
17	48.0	48.2	0.2
18	53.4	53.5	0.1
19	39.3	39.4	0.1
20	39.4	39.5	0.1
21	31.0	31.1	0.1

22	37.3	37.4	0.1
23	23.6	22.9	-0.7
24	64.5	64.5	0
25	16.0	16. 1	0.1
26	17.2	17.3	0.1
27	23.6	23.6	0
28	179.8	179.9	0.1
29	17.5	17.5	0
30	21.3	21.4	0.1

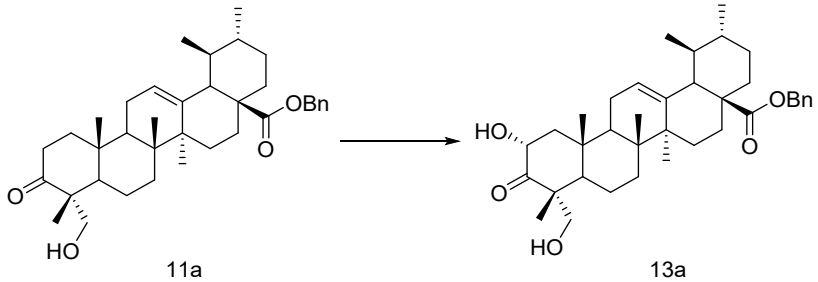


Following the procedure for preparation of **2**, hydrogenolysis of **12c** with Pd/C-H_2 gave **5** as a white solid (91% yield). ^{1}H NMR (600 MHz, MeOD-d_4) δ 5.22 (t, J = 3.6 Hz, 1H), 4.12 (d, J = 11.5 Hz, 1H), 4.06 (d, J = 11.4 Hz, 1H), 3.75 (dd, J = 11.8, 4.6 Hz, 1H), 3.65 (d, J = 11.3 Hz, 1H), 3.54 (d, J = 11.6 Hz, 1H), 2.20 (dd, J = 11.4, 1.9 Hz, 1H), 2.04 (td, J = 13.5, 4.6 Hz, 1H), 1.92 (tdd, J = 18.6, 12.3, 5.6 Hz, 3H), 1.83 – 1.75 (m, 1H), 1.74 – 1.55 (m, 9H), 1.51 (dt, J = 13.3, 3.5 Hz, 1H), 1.12 (s, 3H), 1.08 (ddd, J = 13.8, 4.5, 2.6 Hz, 1H), 1.06 – 0.99 (m, 1H), 0.99 – 0.94 (m, 7H), 0.89 (t, J = 6.8 Hz, 4H), 0.83 (s, 3H). ^{13}C NMR (151 MHz, MeOD-d_4) δ 181.6, 139.7, 126.7, 74.8, 63.7, 63.2, 54.3, 49.1, 48.9, 48.7, 47.2, 43.2, 40.7, 40.4, 40.4, 39.5, 38.1, 37.6, 34.2, 31.8, 29.2, 28.0, 25.3, 24.6, 24.1, 21.6, 19.7, 17.7, 17.7, 16.4. HRMS (ESI-MS, m/z) $[M + Na]^+$ calc. for $C_{30}H_{48}O_5Na$: 511.3399, found: 511.3397. The NMR spectrograms are almost same with that of reported isolated natural product [4].

Table S4. Comparison of ^{13}C NMR data of isolated and herein prepared 3β, 23, 24-trihydroxyurs-12-en-28-oic acid

Carbon No.	**Synthetic** δ_c (ppm)	**Natural** δ_c (ppm)	**Err** (Natural- Synthetic) $\Delta\delta_c$ (ppm)
1	39.5	39.5	0
2	28.0	28.0	0
3	74.8	74.8	0
4	47.2	47.2	0
5	49.1	49.0	0.1
6	19.7	19.7	0
7	34.1	34.2	0.1

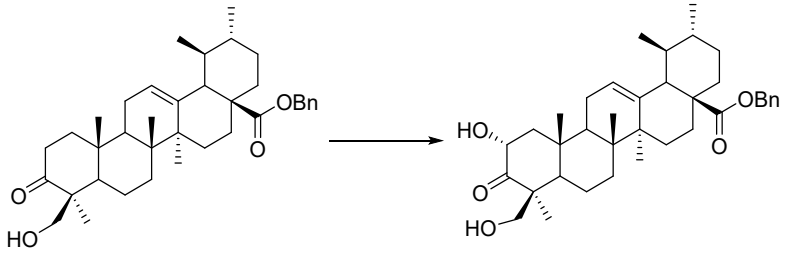
8	40.7	40.8	0.1
9	48.7	48.8	0.1
10	37.6	37.6	0
11	24.6	25.0	0.4
12	126.7	126.7	0
13	139.7	139.8	0.1
14	43.3	43.3	0
15	29.2	29.2	0
16	25.3	25.4	0.1
17	48.9	48.9	0
18	54.3	54.3	0
19	40.4	40.4	0
20	40.4	40.2	-0.2
21	31.8	31.6	-0.2
22	38.1	38.2	0.1
23	63.2	63.4	0.2
24	63.7	63.7	0
25	16.4	16.4	0
26	17.7	17.7	0
27	24.1	24.1	0
28	181.6	182.0	0.4
29	17.7	17.6	-0.1
30	21.6	21.6	0



11a 13a

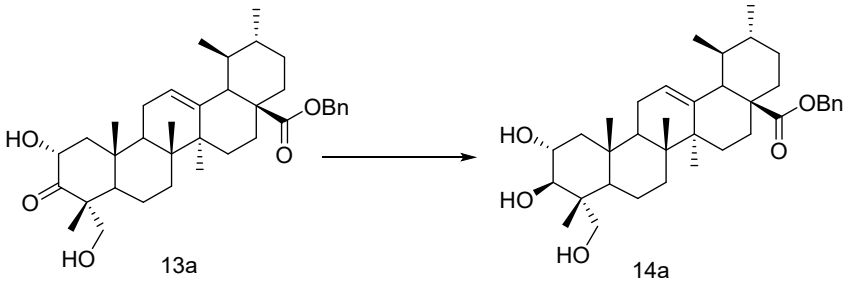
Compound **11a** (1.0 g, 1.8 mmol) was dissolved in MeOH-DCM (30 mL, V / V = 1 : 1), m-CPBA (620 mg, 2.7 mmol) and concentrated H_2SO_4 (cat.) was added at 0 °C. Then, the reaction mixture was stirred for 12 h at room temperature in darkness. Excess $NaHSO_3$ was added to the reaction mixture and stirred for 0.5 h. After most organic solvents were removed by evaporation in vacuo, the residue was extracted with DCM (3 x 50 mL), the organic layer was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vavco. Purification by column chromatography on silica gel (petroleum : EtOAc = 5 : 1) afforded **13a** (0.78 g, 76%) as white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46 – 7.27 (m, 5H), 5.17 (s, 1H), 5.05 (d, J = 12.5 Hz, 1H), 4.96 (dd, J = 12.5, 7.0 Hz, 1H), 4.73 (d, J = 4.6 Hz, 1H), 4.48 (t, J = 5.4 Hz, 1H), 4.35 – 4.26 (m, 1H), 3.69 (dd, J = 10.8, 5.2 Hz, 1H), 3.09 (dd, J = 10.8, 5.5 Hz, 1H), 2.19 (d, J = 11.2 Hz, 1H), 2.11 (dd, J = 12.4, 6.5 Hz, 1H), 2.02 (dd, J = 13.7, 9.3 Hz, 2H), 1.94 – 1.88 (m, 1H),

1.74 (d, *J* = 9.4 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.55 (d, *J* = 12.2 Hz, 2H), 1.52 – 1.41 (m, 3H), 1.37 (d, *J* = 13.2 Hz, 2H), 1.32 (d, *J* = 7.9 Hz, 2H), 1.26 – 1.20 (m, 2H), 1.15 (s, 3H), 1.04 (s, 3H), 0.92 (s, 3H), 0.82 (s, *J* = 6.4 Hz, 3H), 0.81 (s, *J* = 7.1 Hz, 3H), 0.61 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 213.8, 176.1, 138.0, 136.2, 128.4, 127.9, 124.9, 68.6, 65.3, 63.4, 52.5, 51.9, 47.6, 47.4, 47.3, 46.4, 41.7, 40.1, 38.4, 38.3, 36.5, 36.2, 31.9, 30.0, 27.3, 23.8, 23.3, 23.0, 21.0, 18.1, 17.4, 17.0, 16.9, 16.0. HRMS (ESI-MS, *m*/*z*) [M + Na]$^+$ calc. for $C_{37}H_{51}O_5Na$: 599.3712, found: 599.3713.



11b 13b

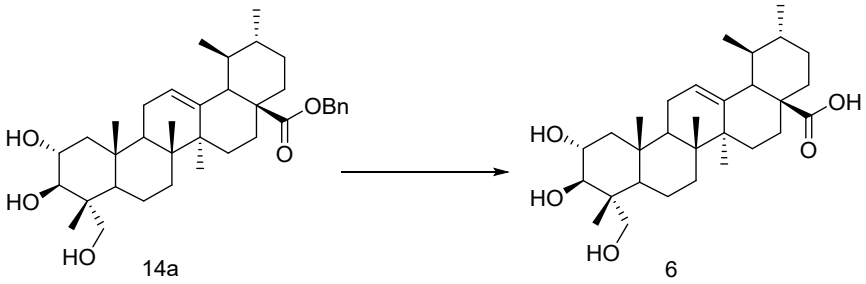
Following the procedure for preparation of **13a**, hydroxylation of **11b** with m-CPBA gave **13b** as a white solid (66% yield). ^{1}H NMR (400 MHz, DMSO-d_6) ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 – 7.29 (m, 5H), 5.14 (d, *J* = 3.8 Hz, 1H), 5.04 (d, *J* = 12.6 Hz, 1H), 4.96 (d, *J* = 12.6 Hz, 1H), 4.58 (t, *J* = 6.4 Hz, 2H), 4.47 (dt, *J* = 12.0, 5.7 Hz, 1H), 3.90 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.30 (s, 1H), 2.22 – 2.09 (m, 2H), 1.99 (dt, *J* = 13.2, 6.7 Hz, 1H), 1.87 (q, *J* = 4.2, 3.7 Hz, 2H), 1.71 (dt, *J* = 17.0, 8.7 Hz, 1H), 1.58 (t, *J* = 8.4 Hz, 2H), 1.54 – 1.37 (m, 6H), 1.35 – 1.27 (m, 2H), 1.26 – 1.20 (m, 2H), 1.17 (s, 3H), 1.06 (s, 3H), 1.01 (s, 3H), 0.91 (s, 3H), 0.80 (d, *J* = 6.4 Hz, 3H), 0.56 (s, 3H).^{13}C NMR (151 MHz, DMSO-d_6) δ 214.0, 176.5, 138.3, 136.7, 131.1, 129.3, 128.3, 125.1, 69.5, 65.8, 64.5, 58.1, 55.1, 52.9, 50.5, 47.8, 47.2, 42.0, 40.5, 38.8, 38.7, 37.6, 36.6, 33.2, 30.4, 27.8, 24.2, 23.7, 21.4, 20.1, 19.6, 17.4, 17.1, 17.0. HRMS (ESI-MS, *m*/*z*) [M + Na]$^+$ calc. for $C_{37}H_{51}O_5Na$: 599.3712, found: 599.3713.



13a 14a

Following the procedure for preparation of **11a**, reduction of **13a** with $NaBH_4$ gave **14a** as a white solid (88% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (h, *J* = 7.4 Hz, 5H), 5.22 (d, *J* = 3.6 Hz, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 5.01 (d, *J* = 12.5 Hz, 1H), 4.47 (s, 1H), 4.28 (s, 1H), 4.24 (s, 1H), 3.54 (q, *J* = 7.6, 5.2 Hz, 1H), 3.36 (d, *J* = 10.4 Hz, 1H), 3.23 (d, *J* = 9.4 Hz, 1H), 3.09 (d, *J* = 10.5 Hz, 1H), 2.24 (d, *J* = 11.2 Hz,

1H), 2.06 (dt, *J* = 13.1, 6.8 Hz, 1H), 1.84 (d, *J* = 8.6 Hz, 4H), 1.70 – 1.61 (m, 2H), 1.54 (m, 4H), 1.47 – 1.28 (m, 4H), 1.23 (q, *J* = 13.0, 11.0 Hz, 3H), 1.11 (s, 3H), 1.05 (d, *J* = 14.1 Hz, 2H), 0.98 (s, 3H), 0.96 (s, 3H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.79 (t, *J* = 12.0 Hz, 1H), 0.61 (s, 3H), 0.59 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 138.3, 136.5, 128.6, 128.3, 128.1, 125.5, 80.5, 70.5, 68.9, 66.1, 53.0, 49.1, 48.2, 47.6, 46.4, 42.2, 39.6, 39.2, 39.0, 38.3, 36.7, 32.8, 30.8, 28.0, 24.3, 23.8, 23.4, 21.3, 18.4, 17.3, 17.2, 13.0. HRMS (ESI-MS, *m*/*z*) [M + Na] $^+$ calc. for $C_{37}H_{54}O_5Na$: 601.3869, found: 601.3871.

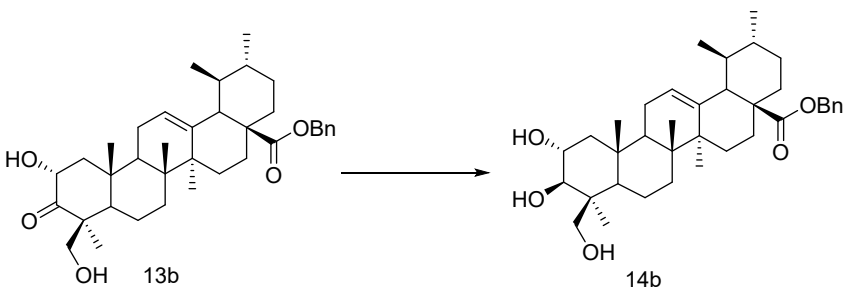


Compound **14a** (0.40 g, 0.68 mmol) was dissolved in THF (10 mL). 10% Pd/C (40 mg) was added. The reaction mixture was stirred overnight at room temperature under H_2 at atmospheric pressure. The reaction mixture was filtered through Celiteand and washed with THF; the organic layer was concentrated in vacuo. Purification by column chromatography on silica gel (CH_2Cl_2 : MeOH = 15 : 1) afforded **6** (324 mg, 96% yield) as white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.88 (s, 1H), 5.14 (t, *J* = 3.4 Hz, 1H), 4.39 (s, 1H), 4.21 (d, *J* = 11.4 Hz, 1H), 4.15 (s, 1H), 3.48 (t, *J* = 7.8 Hz, 1H), 3.29 (d, *J* = 4.2 Hz, 1H), 3.17 (d, *J* = 9.4 Hz, 1H), 3.03 (dd, *J* = 10.4, 3.6 Hz, 1H), 2.11 (d, *J* = 11.3 Hz, 1H), 1.93 (td, *J* = 13.3, 4.1 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.82 – 1.74 (m, 2H), 1.57 (dd, *J* = 9.7, 3.2 Hz, 1H), 1.54 – 1.51 (m, 2H), 1.49 (d, *J* = 7.8 Hz, 2H), 1.44 – 1.37 (m, 2H), 1.32 – 1.26 (m, 2H), 1.25 – 1.22 (m, 2H), 1.19 (d, *J* = 11.5 Hz, 2H), 1.04 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H), 0.82 (s, *J* = 6.4 Hz, 3H), 0.74 (s, *J* = 4.6 Hz, 3H), 0.54 (s, 3H). ^{13}C NMR (151 MHz, Pyridine-d_5) δ 179.9, 139.1, 125.3, 77.9, 68.6, 66.2, 53.3, 47.8, 47.8, 47.7, 47.6, 43.4, 42.3, 39.8, 39.2, 39.2, 38.1, 37.2, 32.9, 30.9, 28.4, 24.7, 23.7, 23.5, 21.2, 18.3, 17.3, 17.3, 17.3, 14.2. HRMS (ESI-MS, *m*/*z*) [M + Na] $^+$ calc. for $C_{30}H_{48}O_5Na$: 511.3399, found: 511.3398. The NMR spectrograms are almost same with that of reported isolated natural product [5].

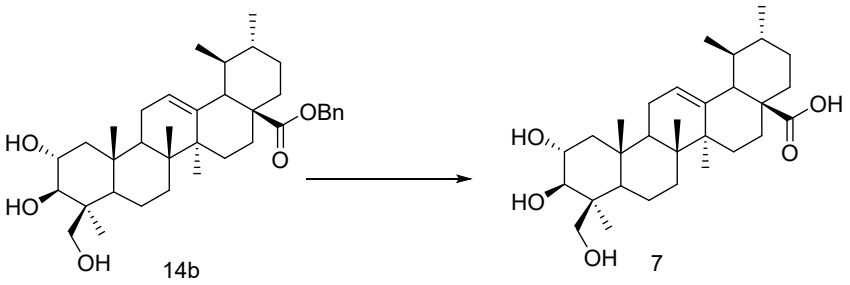
Table S5. Comparison of ^{13}C NMR data of isolated and herein prepared asiatic acid

Carbon No.	**Synthetic** δ_c (ppm)	**Natural** δ_c (ppm)	**Err** (Natural- Synthetic) $\Delta\delta_c$ (ppm)
1	47.8	47.8	0
2	66.3	66.5	0.2

3	78.1	78.2	0.1
4	43.6	43.6	0
5	48.0	48.0	0
6	18.4	18.5	0.1
7	33.1	33.1	0
8	39.9	40.0	0.1
9	47.8	47.8	0
10	38.2	38.3	0.1
11	23.8	23.8	0
12	125.5	125.5	0
13	139.2	139.3	0.1
14	42.5	42.5	0
15	28.6	28.6	0
16	24.8	24.8	0
17	47.9	48.0	0.1
18	53.4	53.5	0.1
19	39.4	39.4	0
20	39.3	39.3	0
21	31.0	31.0	0
22	37.4	37.4	0
23	68.8	68.9	0.1
24	14.3	14.3	0
25	17.5	17.5	0
26	17.4	17.4	0
27	23.7	23.7	0
28	179.9	179.9	0
29	17.4	17.4	0
30	21.3	21.3	0



Following the procedure for preparation of **11a**, reduction of **13b** with $NaBH_4$ gave **14b** as a white solid (85% yield). which was used directly in the next step without further purification.



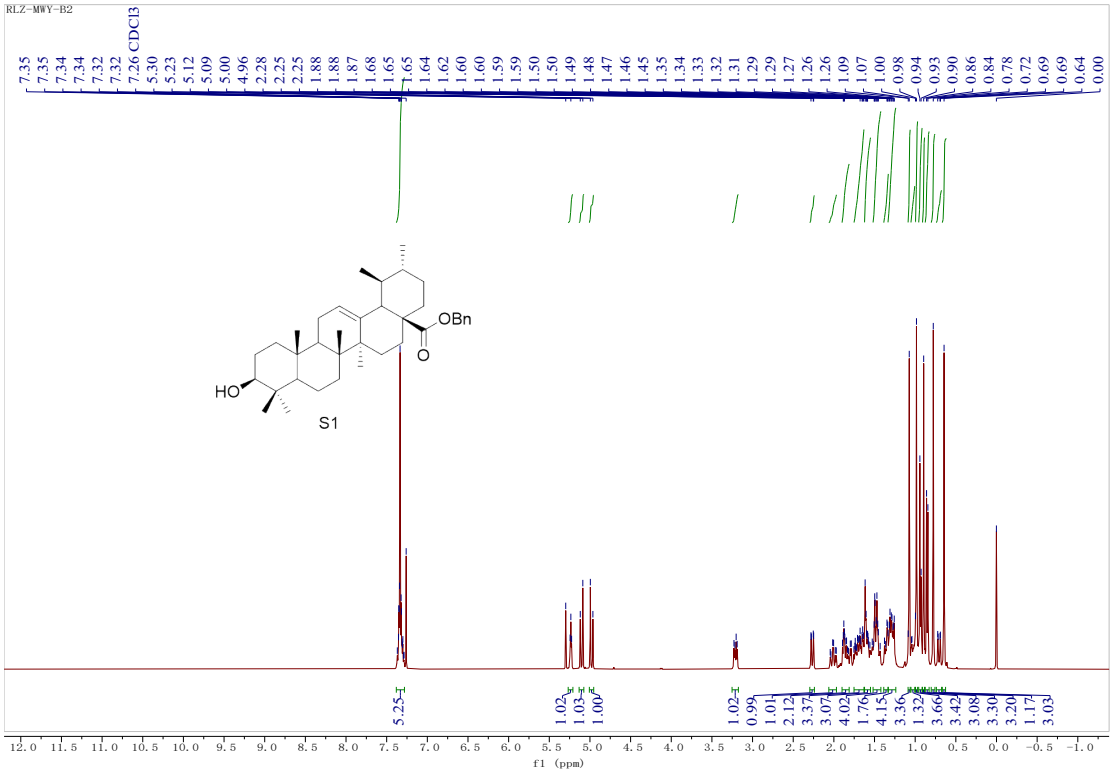
Following the procedure for preparation of **6**, hydrogenolysis of **14b** with Pd/C-H_2 gave **7** a s a white solid (99% yield). ^{1}H NMR (600 MHz, Pyridine-d_5) δ 5.47 (t, J = 3.6 Hz, 1H), 4.47 (d, J = 10.9 Hz, 1H), 4.32 (ddd, J = 11.2, 9.4, 4.4 Hz, 1H), 3.73 (d, J = 11.0 Hz, 1H), 3.59 (d, J = 9.4 Hz, 1H), 2.64 (d, J = 13.0 Hz, 1H), 2.32 (td, J = 13.6, 5.0 Hz, 1H), 2.27 (dd, J = 12.6, 4.4 Hz, 1H), 2.13 (td, J = 13.3, 4.5 Hz, 1H), 2.09 – 1.91 (m, 5H), 1.76 (dd, J = 11.3, 6.3 Hz, 1H), 1.71 (dd, J = 10.2, 6.5 Hz, 1H), 1.61 (s, 3H), 1.59 – 1.53 (m, 1H), 1.53 – 1.45 (m, 3H), 1.45 – 1.34 (m, 3H), 1.30 (td, J = 13.3, 3.8 Hz, 4H), 1.22 (s, 3H), 1.20 – 1.14 (m, 2H), 1.04 (s, 1H), 1.03 (s, 3H), 1.00 (d, J = 6.2 Hz, 6H), 0.96 (d, J = 6.3 Hz, 3H).^{13}C NMR (151 MHz, Pyridine-d_5) δ 179.8, 139.2, 125.4, 85.6, 68.6, 65.6, 56.4, 53.4, 48.1, 47.9, 47.9, 43.9, 42.4, 39.9, 39.4, 39.3, 38.2, 37.4, 33.8, 31.0, 28.5, 24.8, 24.1, 23.9, 23.8, 21.3, 19.2, 17.4, 17.3, 17.2. HRMS (ESI-MS, m/z) [M + Na] $^+$ calc. for $C_{30}H_{47}O_5Na$: 511.3399, found: 511.3400. The NMR spectrograms are almost same with that of reported isolated natural product [5].

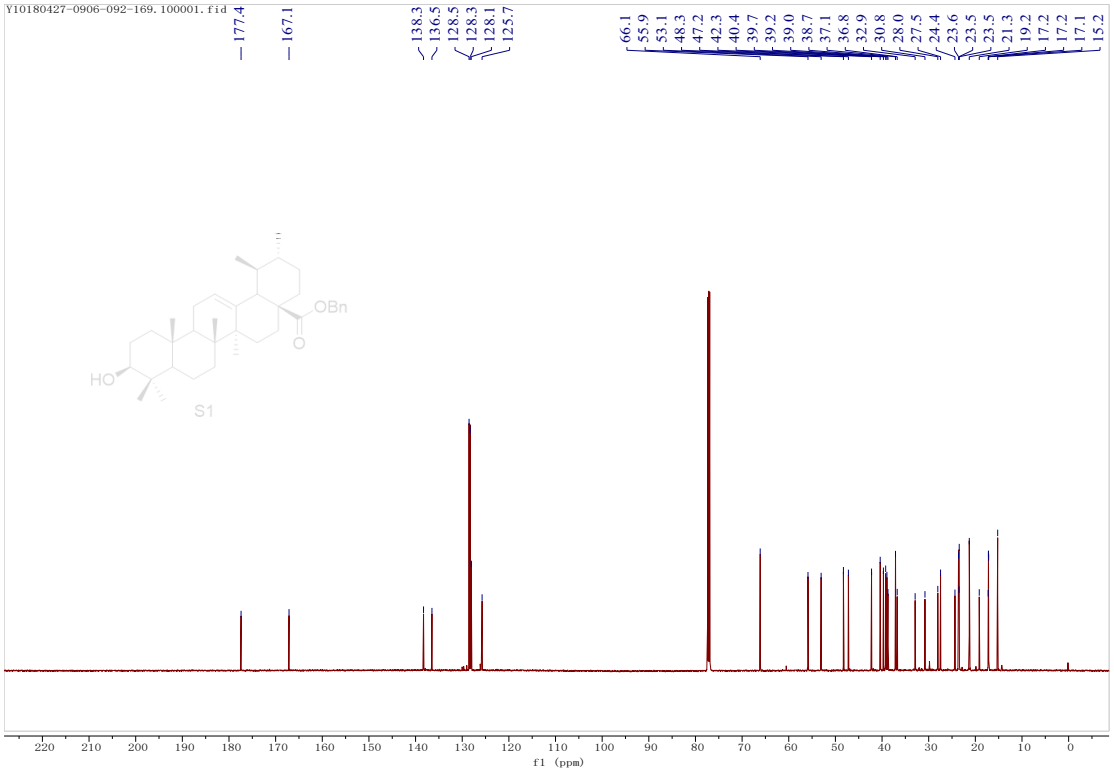
Table S6. Comparison of ^{13}C NMR data of isolated and herein prepared 2α, 3β, 24-trihydroxyurs-12-en-28-oic acid

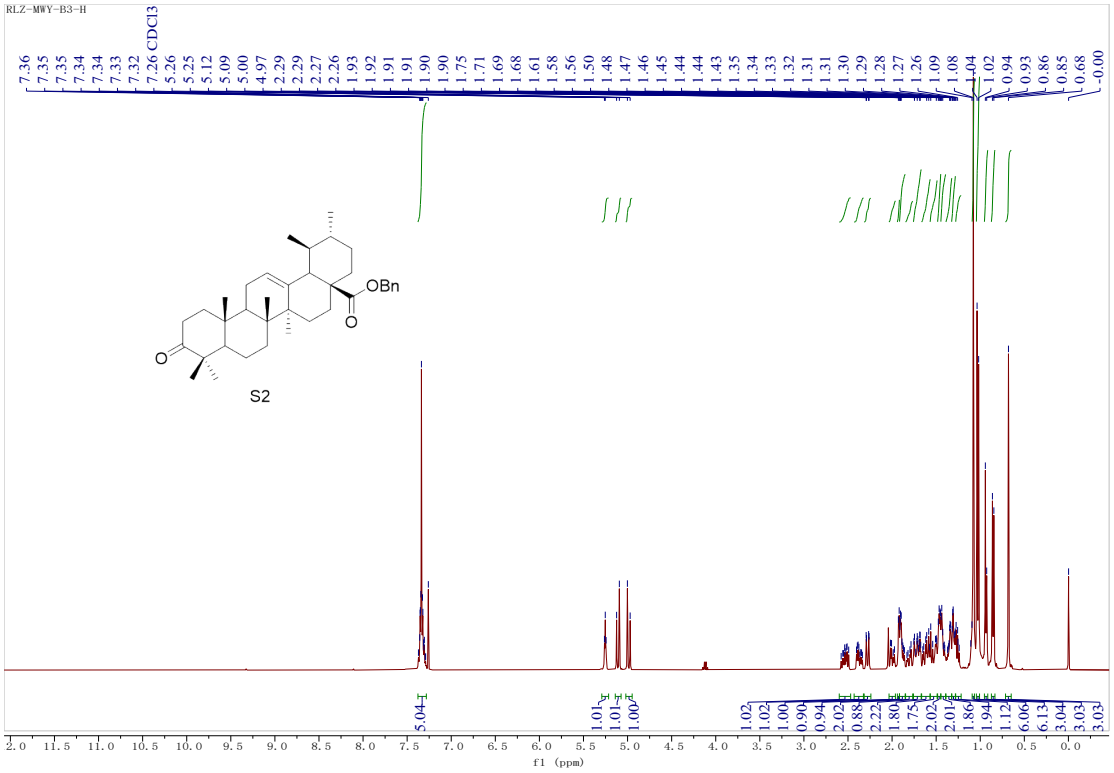
Carbon No.	**Synthetic** δ_c (ppm)	**Natural** δ_c (ppm)	**Err** (Natural- Synthetic) $\Delta\delta_c$ (ppm)
1	47.8	47.9	0.1
2	68.6	68.7	0.1
3	85.6	85.8	0.2
4	43.9	44.0	0.1
5	56.4	56.5	0.1
6	19.2	19.3	0.1
7	33.8	33.9	0.1
8	39.9	40.1	0.2
9	48.1	48.2	0.1
10	38.2	38.3	0.1
11	23.9	24.0	0.1
12	125.4	125.5	0.1
13	139.2	139.3	0.1
14	42.4	42.5	0.1

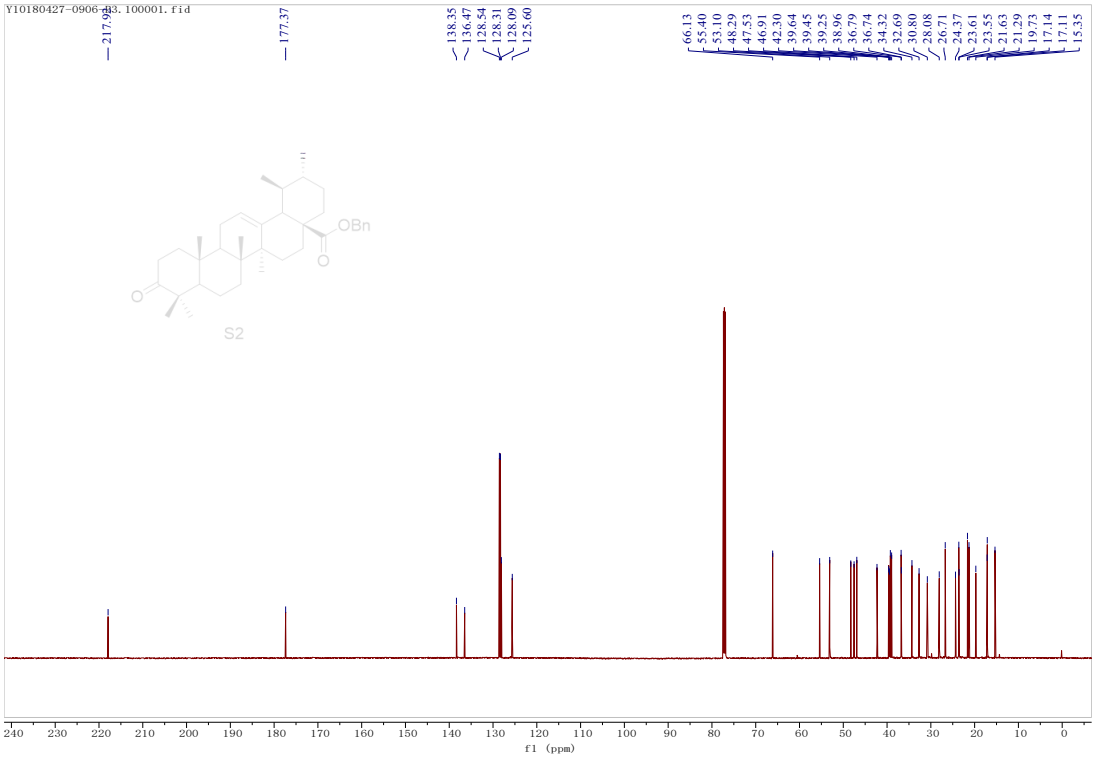
15	28.5	28.7	0.2
16	24.8	24.9	0.1
17	47.9	48.1	0.2
18	53.4	53.6	0.2
19	39.3	39.4	0.1
20	39.4	39.5	0.1
21	31.0	31.1	0.1
22	37.4	37.4	0
23	24.1	24.2	0.1
24	65.6	65.7	0.1
25	17.4	17.5	0.1
26	17.3	17.4	0.1
27	23.8	23.9	0.1
28	179.8	179.9	0.1
29	17.2	17.4	0.2
30	21.3	21.4	0.1

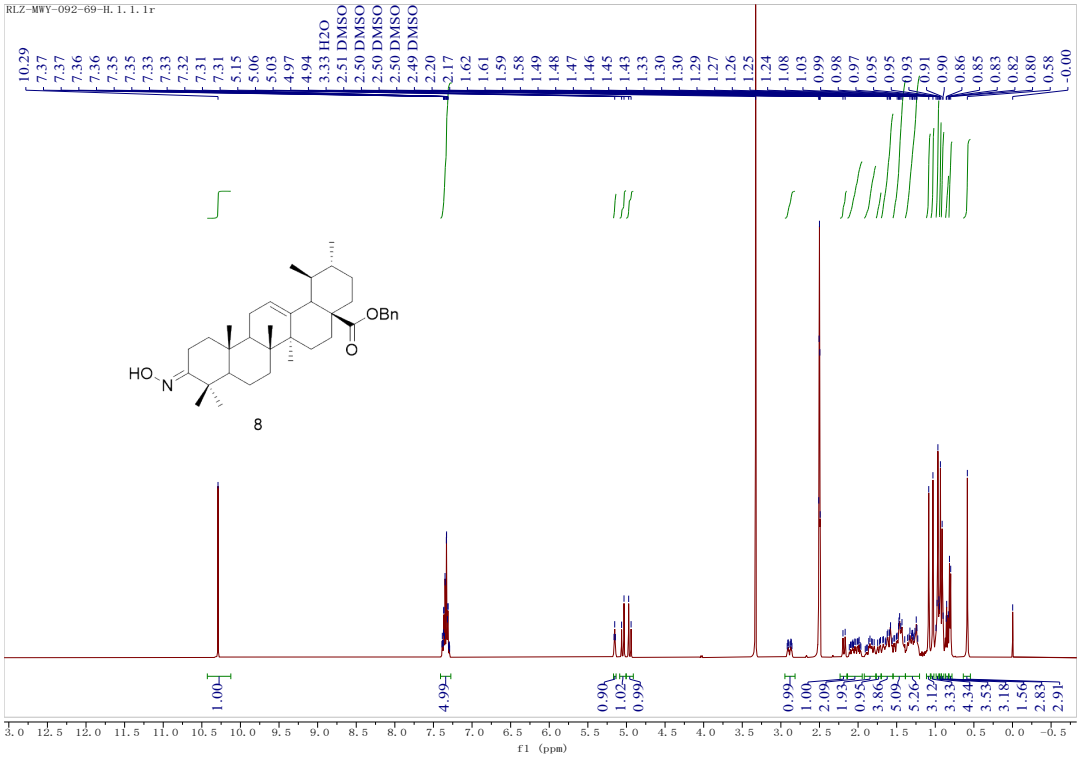
^{1}H and ^{13}C NMR spectra

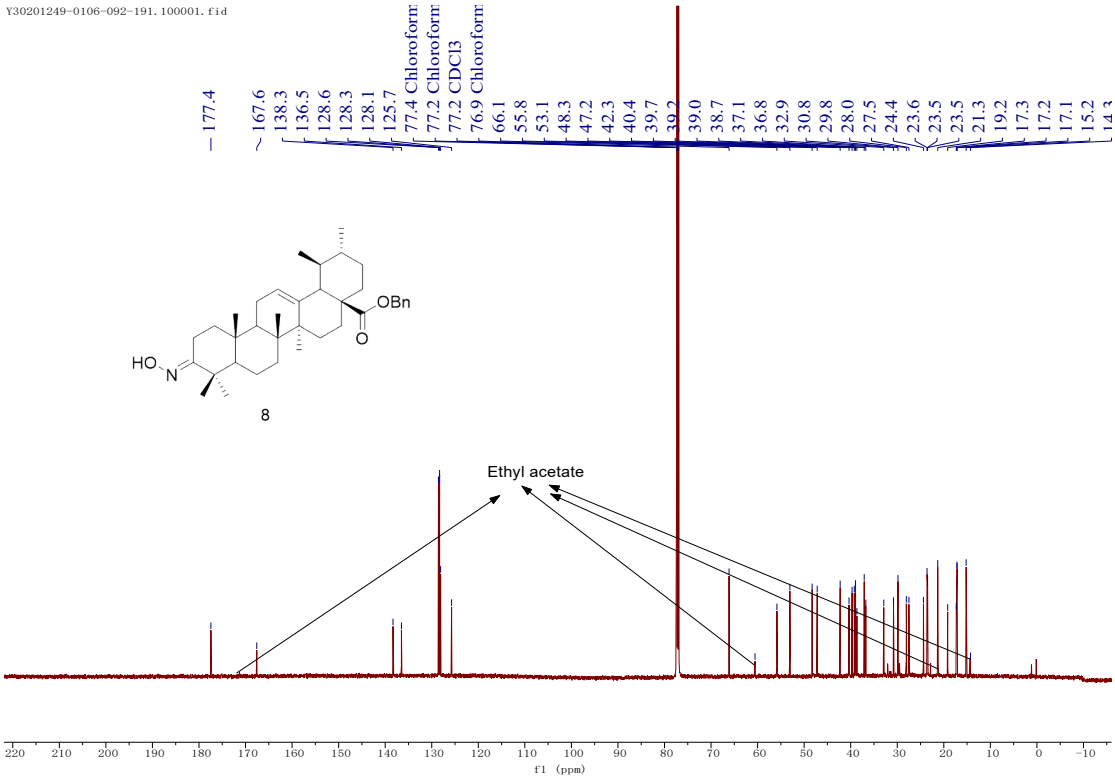


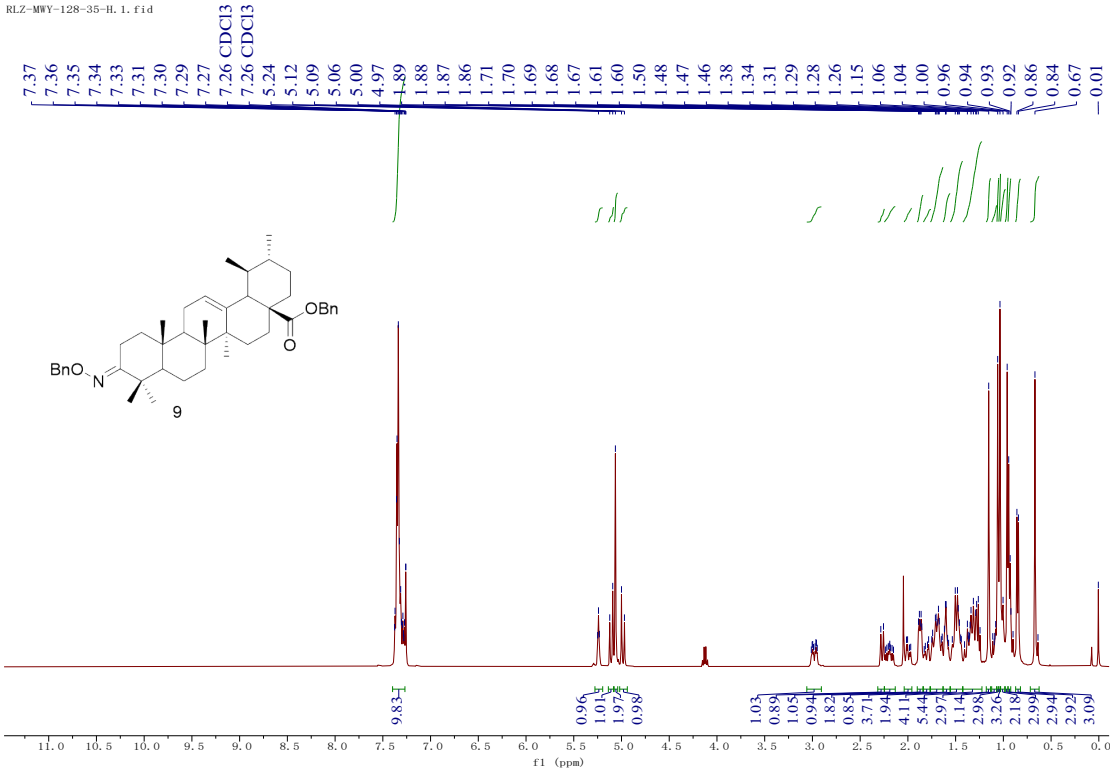

Y10180427-0906-092-169.100001.fid
177.4
167.1
138.3
136.5
128.5
128.3
128.1
125.7
66.1
55.9
53.1
48.3
47.2
42.3
40.4
39.7
39.2
39.0
38.7
37.1
36.8
32.9
30.8
28.0
27.5
24.4
23.6
23.5
23.5
21.3
19.2
17.2
17.2
17.1
15.2
OBn
O
HO
S1
f1 (ppm)

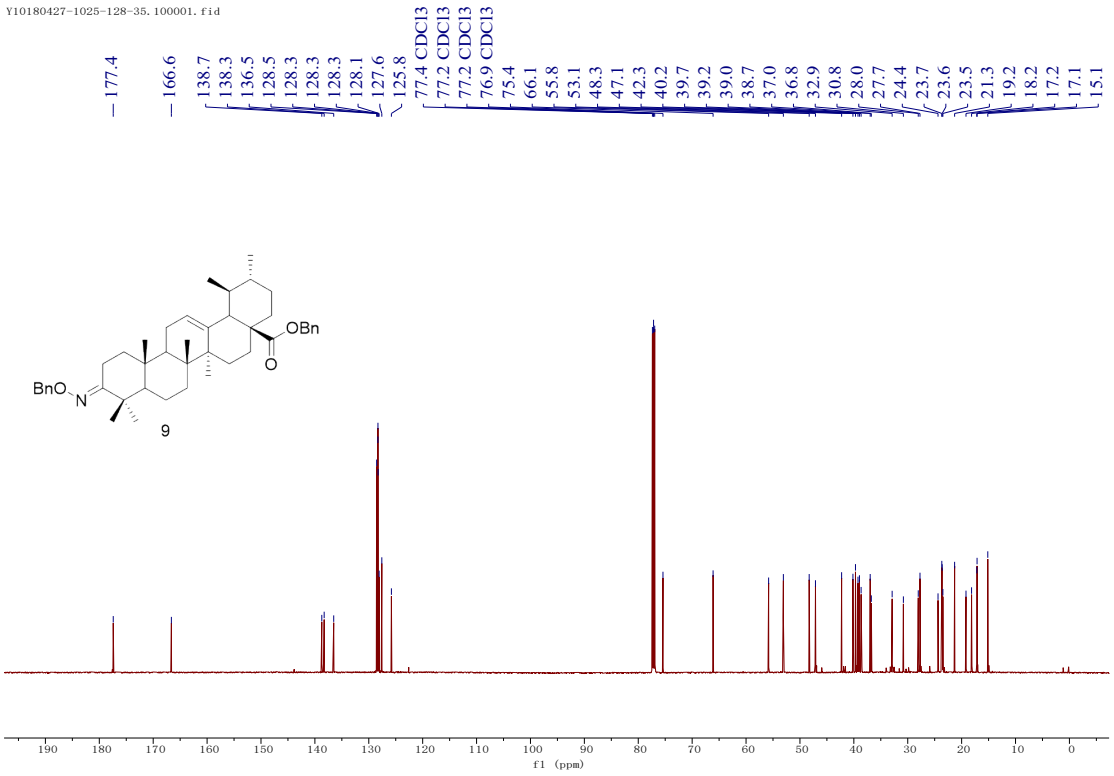

RLZ-MWY-B3-H
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.26 CDCl3
5.26
5.25
5.12
5.09
5.00
4.97
2.29
2.29
2.27
2.26
1.93
1.92
1.91
1.91
1.90
1.90
1.75
1.71
1.69
1.68
1.61
1.58
1.56
1.50
1.48
1.47
1.46
1.45
1.44
1.44
1.43
1.35
1.34
1.33
1.32
1.31
1.31
1.30
1.29
1.28
1.27
1.26
1.09
1.08
1.04
1.02
0.94
0.93
0.86
0.85
0.68
-0.00
OBn
O
O
S2
5.04
1.01
1.01
1.00
1.02
1.02
1.00
0.90
0.94
2.02
0.88
2.22
1.80
1.75
2.02
2.01
1.86
1.94
1.12
6.06
6.13
3.04
3.03
3.03
f1 (ppm)

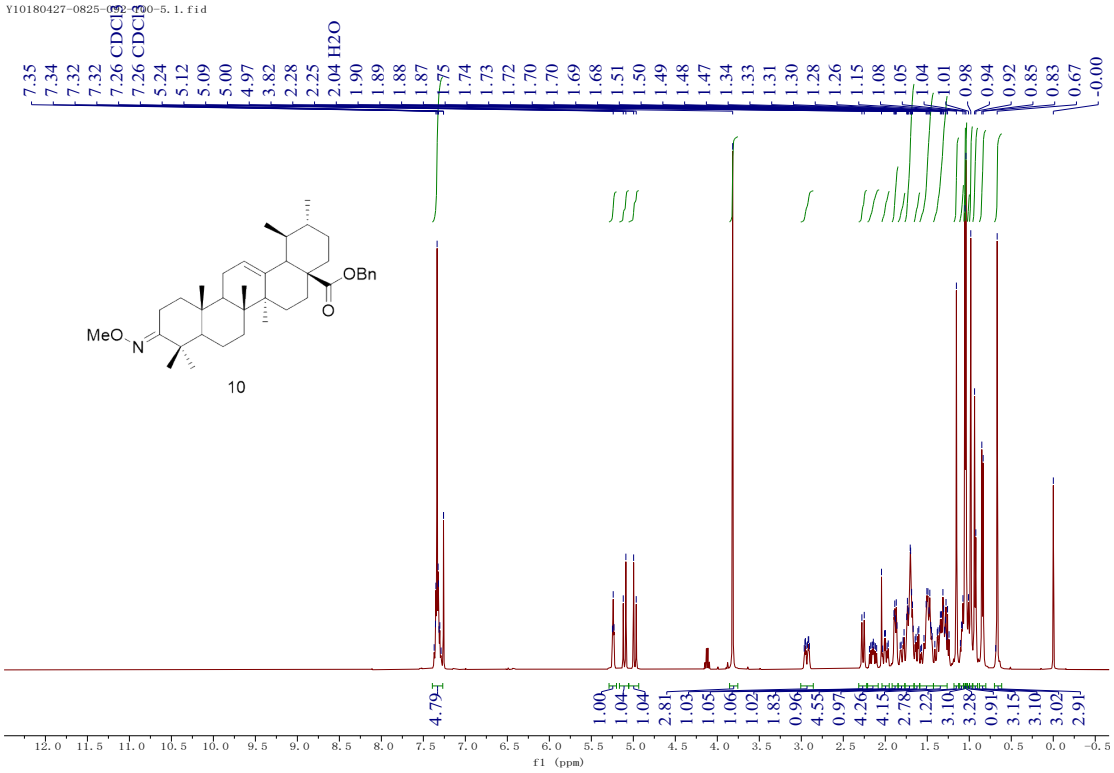

Y10180427-0906-13. 100001. fid
217.94
177.37
138.35
136.47
128.54
128.31
128.09
125.60
66.13
55.40
53.10
48.29
47.53
46.91
42.30
39.64
39.45
39.25
38.96
36.79
36.74
34.32
32.69
30.80
28.08
26.71
24.37
23.61
23.55
21.63
21.29
19.73
17.14
17.11
15.35
OBn
O
O
S2
f1 (ppm)

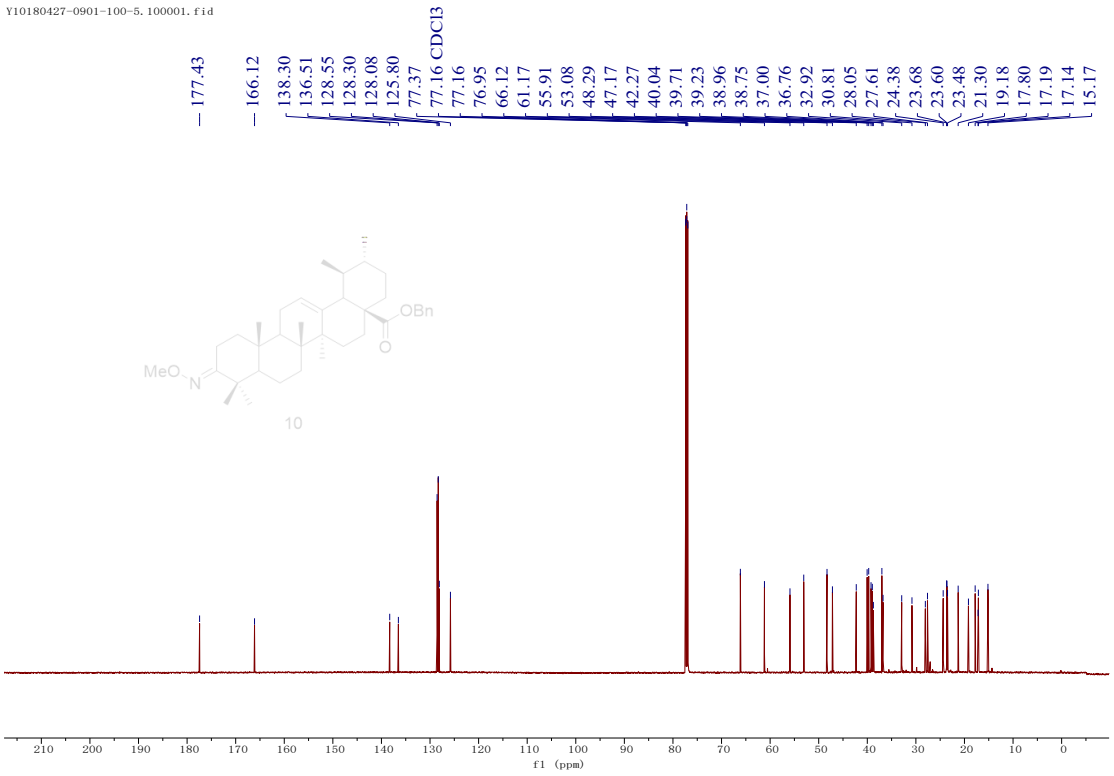

RLZ-MWY-092-69-H. 1. 1. 1r
10.29
7.37
7.37
7.36
7.36
7.35
7.35
7.33
7.33
7.32
7.31
7.31
5.15
5.06
5.03
4.97
4.94
3.33 H2O
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.20
2.17
1.62
1.61
1.59
1.58
1.49
1.48
1.47
1.46
1.45
1.43
1.33
1.30
1.30
1.29
1.27
1.26
1.25
1.24
1.08
1.03
0.99
0.98
0.97
0.95
0.95
0.93
0.91
0.90
0.86
0.85
0.83
0.82
0.80
0.58
-0.00
OBn
O
HO
N
8
1.00
4.99
0.90
1.02
0.99
0.99
1.00
2.09
1.93
0.95
3.86
5.09
5.26
3.12
3.33
4.34
3.53
3.18
1.56
2.83
2.91
f1 (ppm)

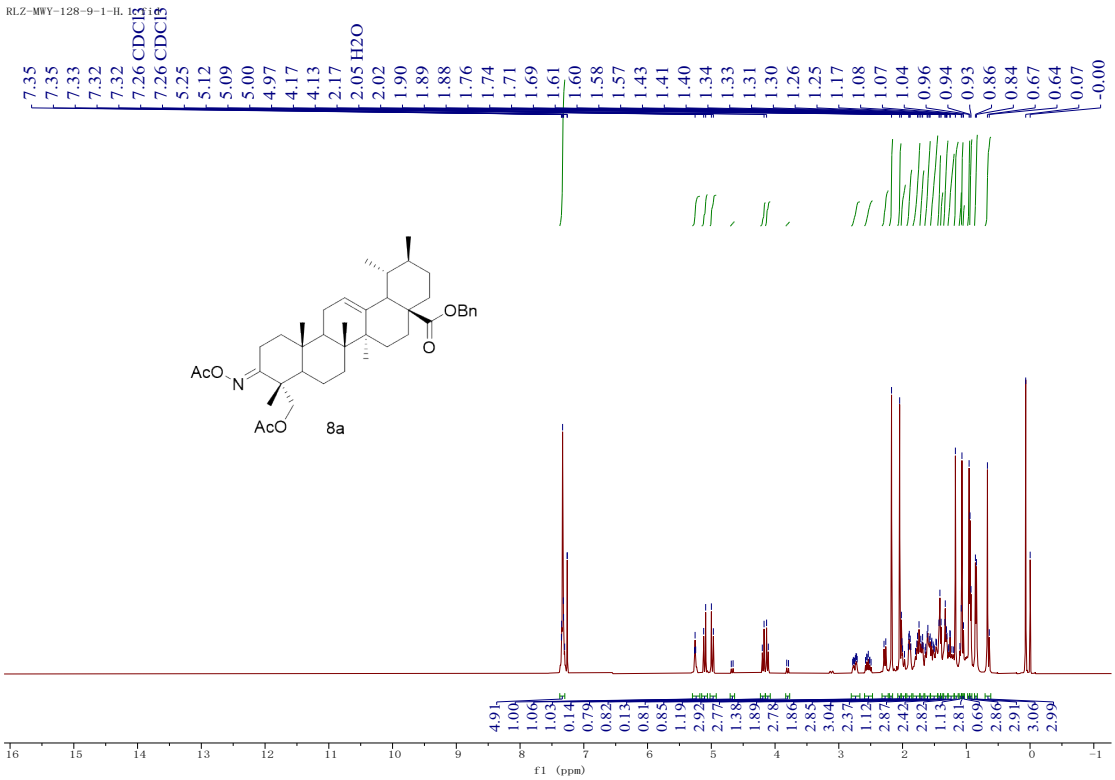

Y30201249-0106-092-191.100001.fid
177.4
167.6
138.3
136.5
128.6
128.3
128.1
125.7
77.4 Chloroform
77.2 Chloroform
77.2 CDCl3
76.9 Chloroform
66.1
55.8
53.1
48.3
47.2
42.3
40.4
39.7
39.2
39.0
38.7
37.1
36.8
32.9
30.8
29.8
28.0
27.5
24.4
23.6
23.5
23.5
21.3
19.2
17.3
17.2
17.1
15.2
OBn
O
HO
N
8
Ethyl acetate
f1 (ppm)

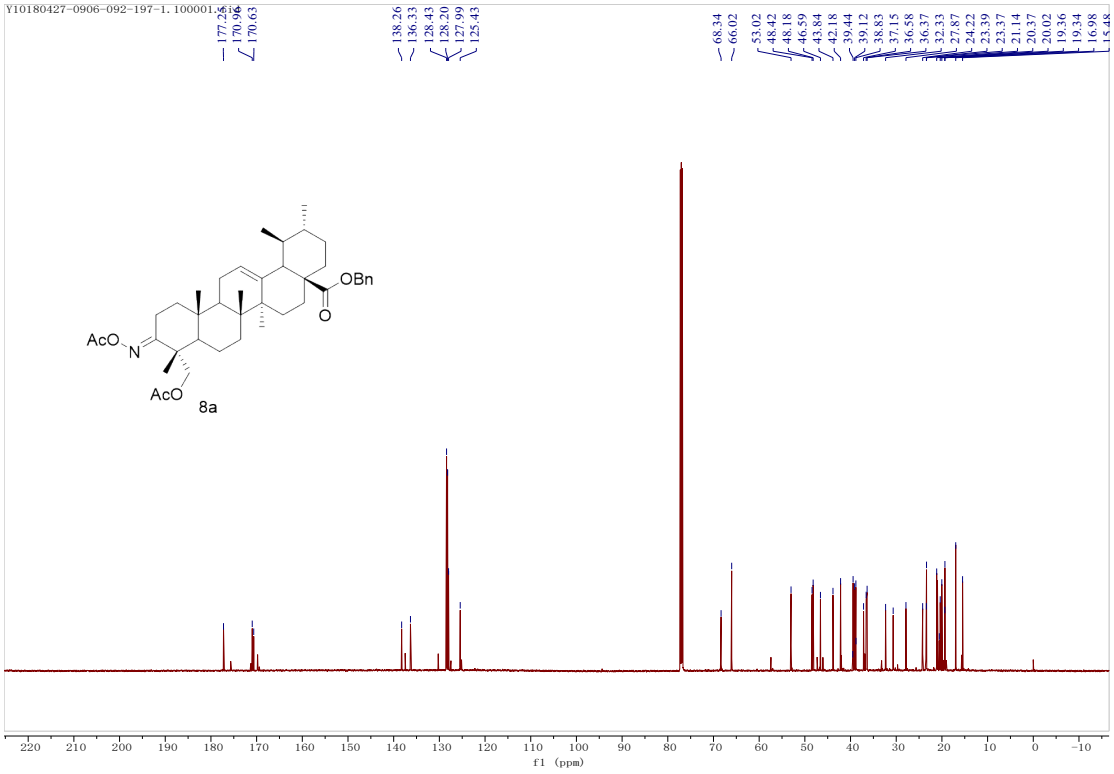

RLZ-MWY-128-35-H.1.fid
7.37
7.36
7.35
7.34
7.33
7.31
7.30
7.29
7.27
7.26 CDCl3
7.26 CDCl3
5.24
5.12
5.09
5.06
5.00
4.97
1.89
1.88
1.87
1.86
1.71
1.70
1.69
1.68
1.67
1.61
1.60
1.50
1.48
1.47
1.46
1.38
1.34
1.31
1.29
1.28
1.26
1.15
1.06
1.04
1.00
0.96
0.94
0.93
0.92
0.86
0.84
0.67
0.01
OBn
O
BnO
N
9
9.83
0.96
1.01
1.97
0.98
1.03
0.89
1.05
0.94
1.82
0.85
3.71
1.94
4.11
5.44
2.97
1.14
2.98
3.26
2.18
2.99
2.94
2.92
3.09
f1 (ppm)

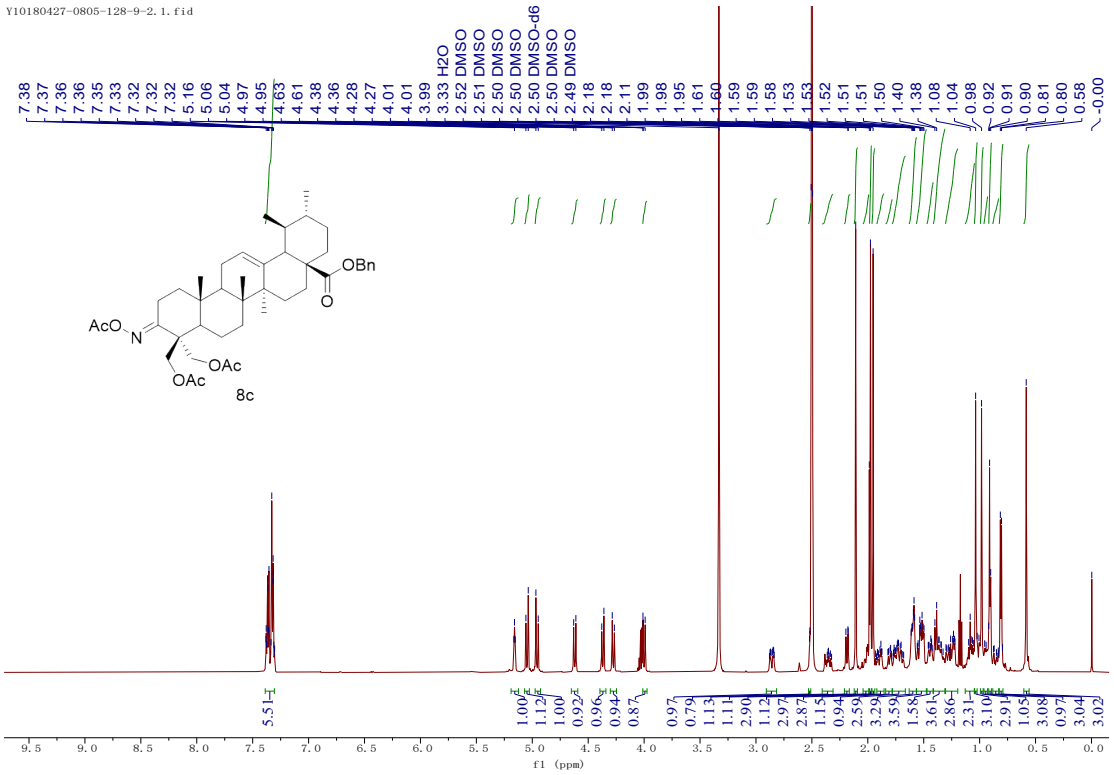

Y10180427-1025-128-35.100001.fid
177.4
166.6
138.7
138.3
136.5
128.5
128.3
128.3
128.3
128.1
127.6
125.8
77.4 CDCl3
77.2 CDCl3
77.2 CDCl3
76.9 CDCl3
75.4
66.1
55.8
53.1
48.3
47.1
42.3
40.2
39.7
39.2
39.0
38.7
37.0
36.8
32.9
30.8
28.0
27.7
24.4
23.7
23.6
23.5
21.3
19.2
18.2
17.2
17.1
15.1
OBn
O
BnO
N
9
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

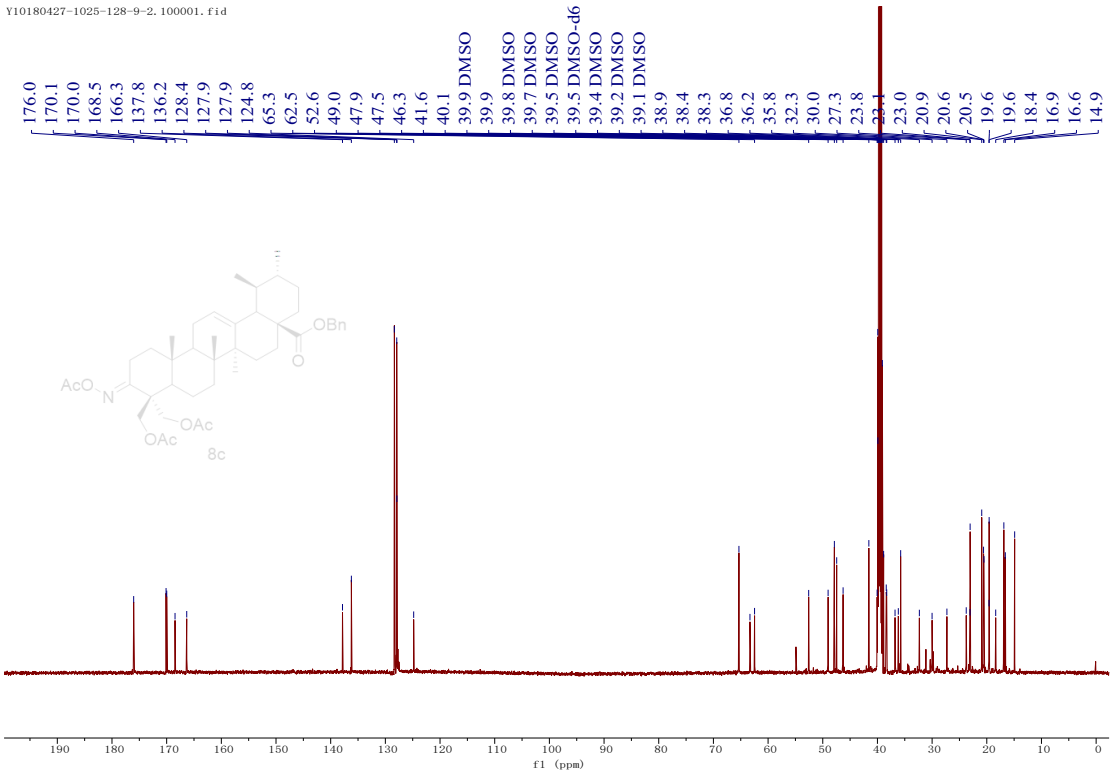

Y10180427-0825-002-200-5.1.fid
7.35
7.34
7.32
7.32
7.26 CDCl3
7.26 CDCl3
5.24
5.12
5.09
5.00
4.97
3.82
2.28
2.25
2.04 H2O
1.90
1.89
1.88
1.87
1.75
1.74
1.73
1.72
1.70
1.70
1.69
1.68
1.51
1.50
1.49
1.48
1.47
1.34
1.33
1.31
1.30
1.28
1.26
1.15
1.08
1.05
1.04
1.01
0.98
0.94
0.92
0.85
0.83
0.67
-0.00
OBn
O
MeO
N
10
4.79
1.00
1.04
1.04
2.81
1.03
1.05
1.06
1.02
1.83
0.96
4.55
0.97
4.26
4.15
2.78
1.22
3.10
3.28
0.91
3.15
3.10
3.02
2.91
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

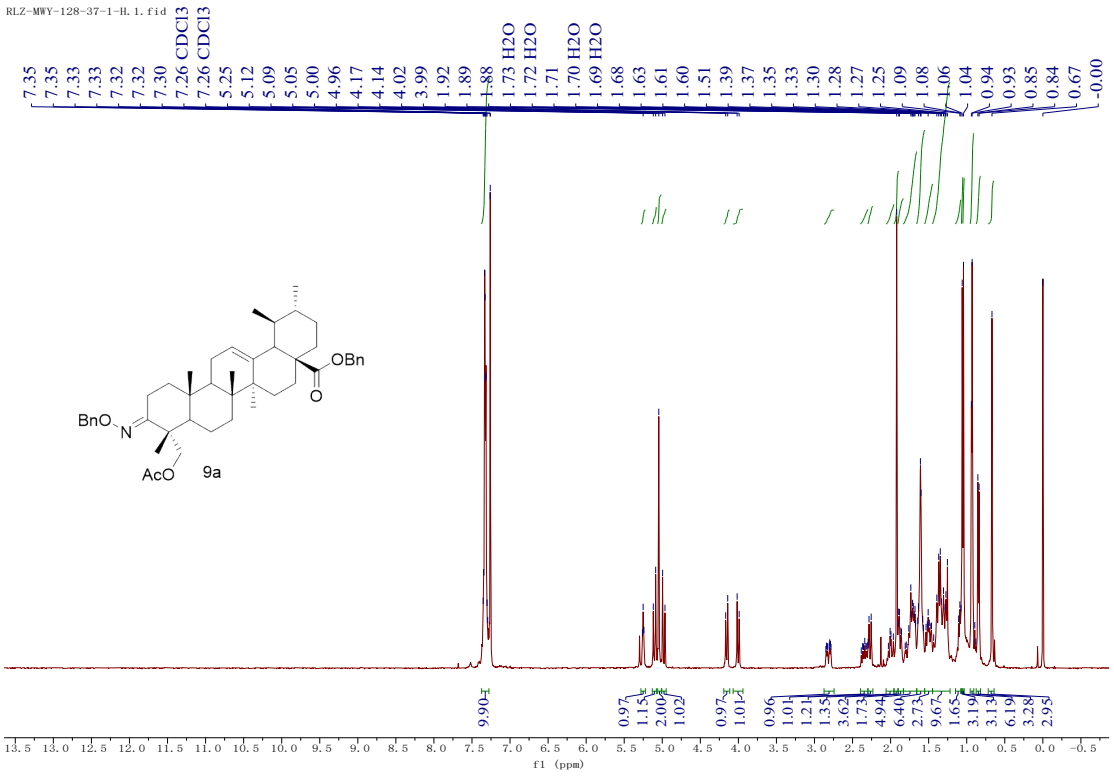

Y10180427-0901-100-5.100001.fid
177.43
166.12
138.30
136.51
128.55
128.30
128.08
125.80
77.37
77.16 CDCl3
77.16
76.95
66.12
61.17
55.91
53.08
48.29
47.17
42.27
40.04
39.71
39.23
38.96
38.75
37.00
36.76
32.92
30.81
28.05
27.61
24.38
23.68
23.60
23.48
21.30
19.18
17.80
17.19
17.14
15.17
OBn
O
MeO
N
10
f1 (ppm)

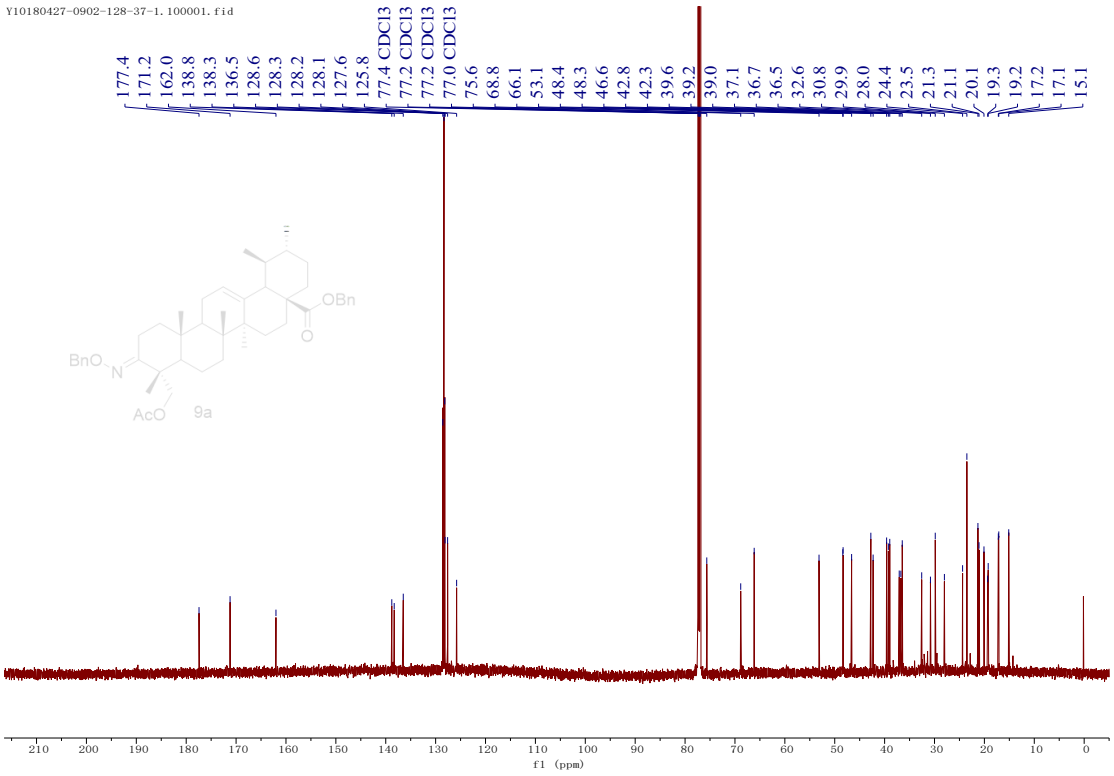

RLZ-MWY-128-9-1-H.fid
7.35
7.35
7.33
7.32
7.32
7.26 CDCl3
7.26 CDCl3
5.25
5.12
5.09
5.00
4.97
4.17
4.13
2.17
2.05 H2O
2.02
1.90
1.89
1.88
1.76
1.74
1.71
1.69
1.61
1.60
1.58
1.57
1.43
1.41
1.40
1.34
1.33
1.31
1.30
1.26
1.25
1.17
1.08
1.07
1.04
0.96
0.94
0.93
0.86
0.84
0.67
0.64
0.07
-0.00
OBn
O
AcO
N
AcO
8a
4.91
1.00
1.06
1.03
0.14
0.79
0.82
0.13
0.81
0.85
1.19
2.92
2.77
1.38
1.89
2.72
1.86
2.85
3.04
2.37
1.12
2.87
2.42
2.82
1.13
2.81
0.69
2.86
2.91
3.06
2.99
f1 (ppm)

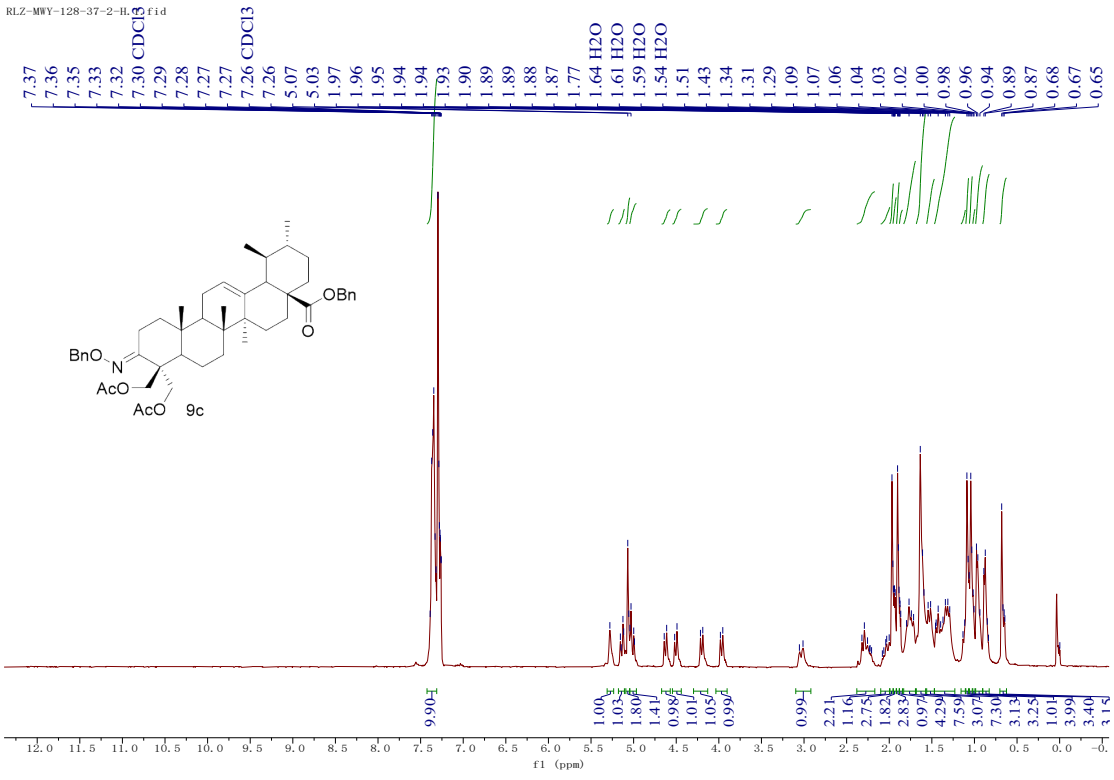

Y10180427-0906-092-197-1.100001.fid
177.25
170.96
170.63
138.26
136.33
128.43
128.20
127.99
125.43
68.34
66.02
53.02
48.42
48.18
46.59
43.84
42.18
39.44
39.12
38.83
37.15
36.58
36.37
32.33
27.87
24.22
23.39
23.37
21.14
20.37
20.02
19.36
19.34
16.98
15.48
OBn
O
AcO
N
AcO
8a
f1 (ppm)

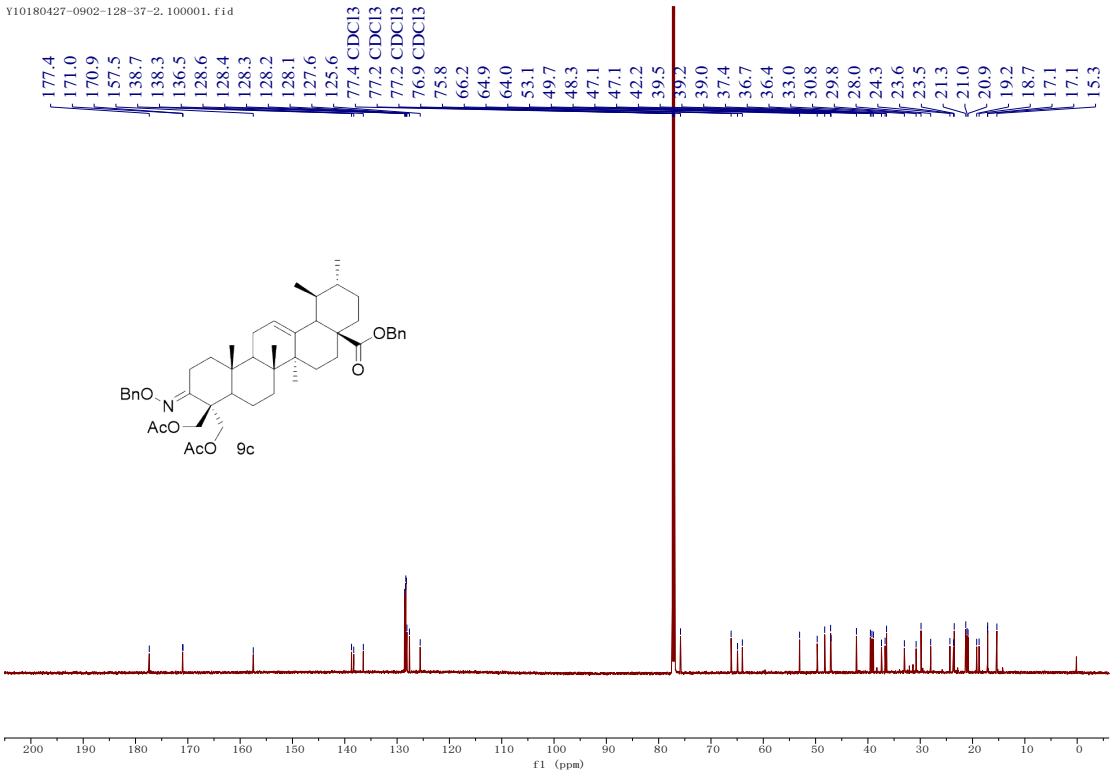

Y10180427-0805-128-9-2.1.fid
7.38
7.37
7.36
7.36
7.35
7.33
7.32
7.32
7.32
5.16
5.06
5.04
4.97
4.95
4.63
4.61
4.38
4.36
4.28
4.27
4.01
4.01
3.99
3.33 H2O
2.52 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO-d6
2.50 DMSO
2.49 DMSO
2.18
2.18
2.11
1.99
1.98
1.95
1.61
1.60
1.59
1.59
1.58
1.53
1.53
1.52
1.51
1.51
1.50
1.40
1.38
1.08
1.04
0.98
0.92
0.91
0.90
0.81
0.80
0.58
-0.00
OBn
O
AcO
N
OAc
OAc
8c
5.51
1.00
1.12
1.00
0.92
0.96
0.94
0.87
0.97
0.79
1.13
1.11
2.90
1.12
2.97
2.87
1.15
0.94
2.59
3.29
3.59
1.58
3.61
2.86
2.31
3.10
2.91
1.05
3.08
0.97
3.04
3.02
f1 (ppm)

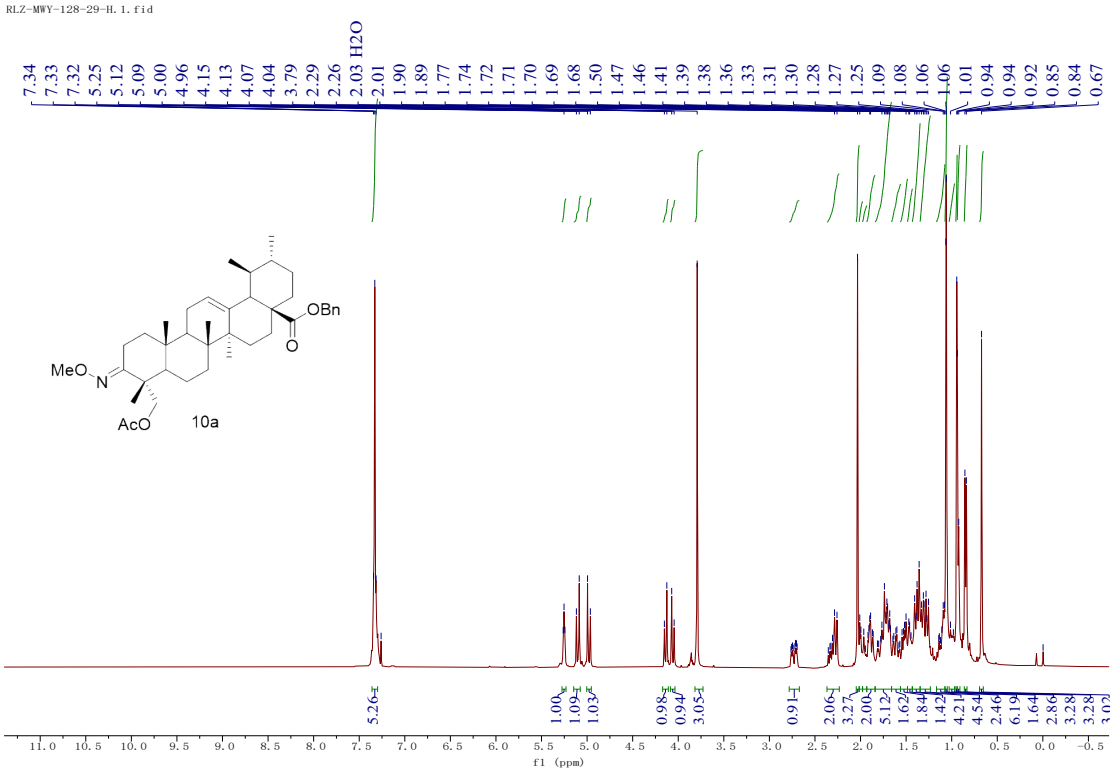

Y10180427-1025-128-9-2.100001.fid
176.0
170.1
170.0
168.5
166.3
137.8
136.2
128.4
127.9
127.9
124.8
65.3
62.5
52.6
49.0
47.9
47.5
46.3
41.6
40.1
39.9 DMSO
39.9
39.8 DMSO
39.7 DMSO
39.5 DMSO
39.5 DMSO-d6
39.4 DMSO
39.2 DMSO
39.1 DMSO
38.9
38.4
38.3
36.8
36.2
35.8
32.3
30.0
27.3
23.8
23.1
23.0
20.9
20.6
20.5
19.6
19.6
18.4
16.9
16.6
14.9
OBn
O
AcO
N
OAc
OAc
8c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

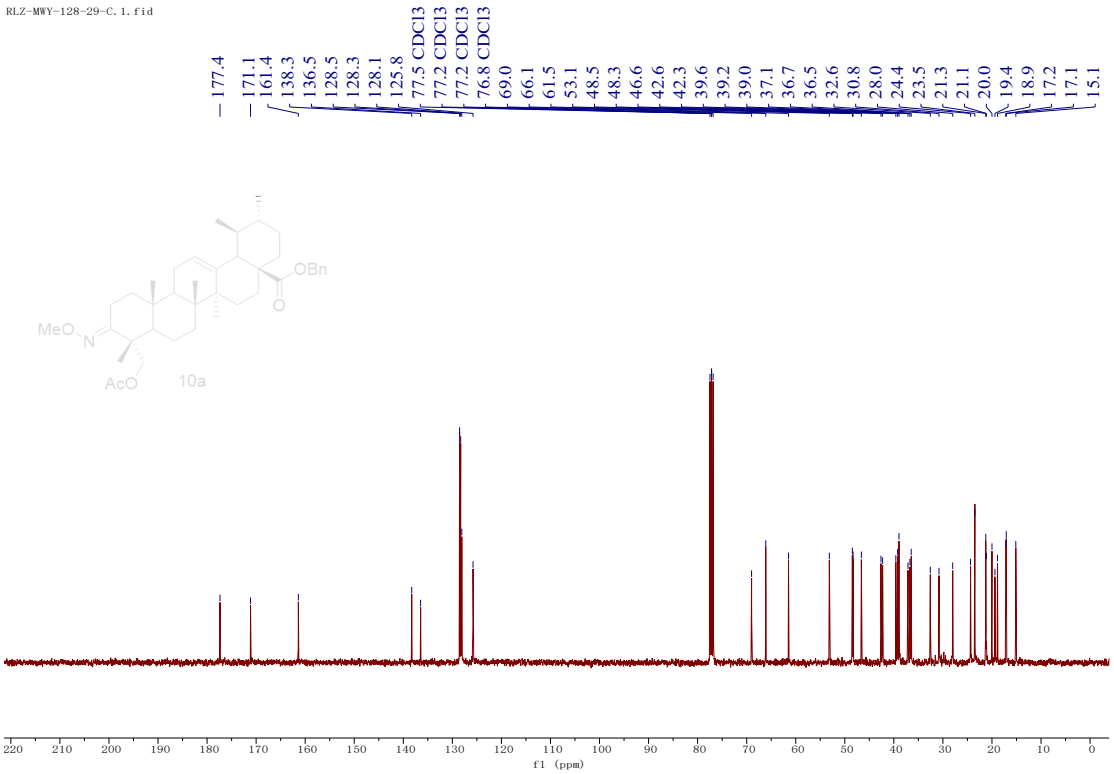

RLZ-MWY-128-37-1-H.1.fid
7.35
7.35
7.33
7.33
7.32
7.32
7.30
7.26 CDCl3
7.26 CDCl3
5.25
5.12
5.09
5.05
5.00
4.96
4.17
4.14
4.02
3.99
1.92
1.89
1.88
1.73 H2O
1.72 H2O
1.71
1.70 H2O
1.69 H2O
1.68
1.63
1.61
1.60
1.51
1.39
1.37
1.35
1.33
1.30
1.28
1.27
1.25
1.09
1.08
1.06
1.04
0.94
0.93
0.85
0.84
0.67
-0.00
OBn
O
BnO
N
AcO
9a
9.90
0.97
1.15
2.00
1.02
0.97
1.01
0.96
1.01
1.21
1.35
3.62
1.73
4.94
6.40
2.73
9.67
1.65
3.19
3.13
6.19
3.28
2.95
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

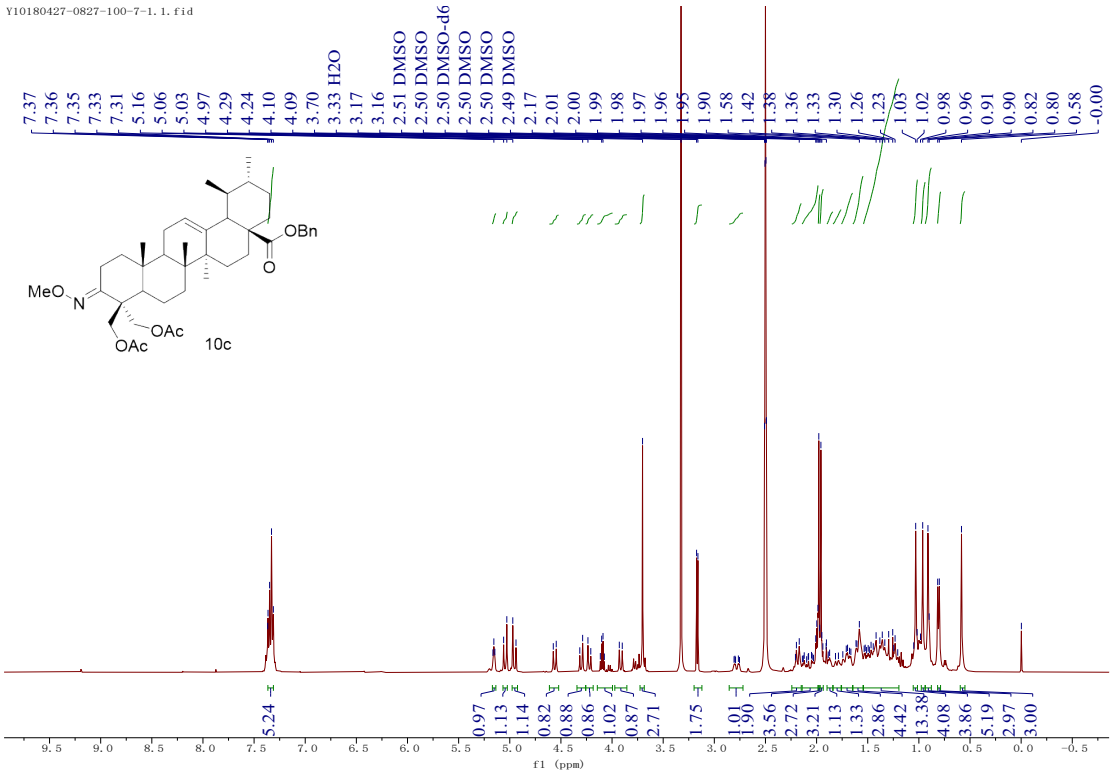

Y10180427-0902-128-37-1.100001.fid
177.4
171.2
162.0
138.8
138.3
136.5
128.6
128.3
128.2
128.1
127.6
125.8
77.4 CDCl3
77.2 CDCl3
77.2 CDCl3
77.0 CDCl3
75.6
68.8
66.1
53.1
48.4
48.3
46.6
42.8
42.3
39.6
39.2
39.0
37.1
36.7
36.5
32.6
30.8
29.9
28.0
24.4
23.5
21.3
21.1
20.1
19.3
19.2
17.2
17.1
15.1
OBn
O
BnO
N
AcO
AcO
9a
f1 (ppm)

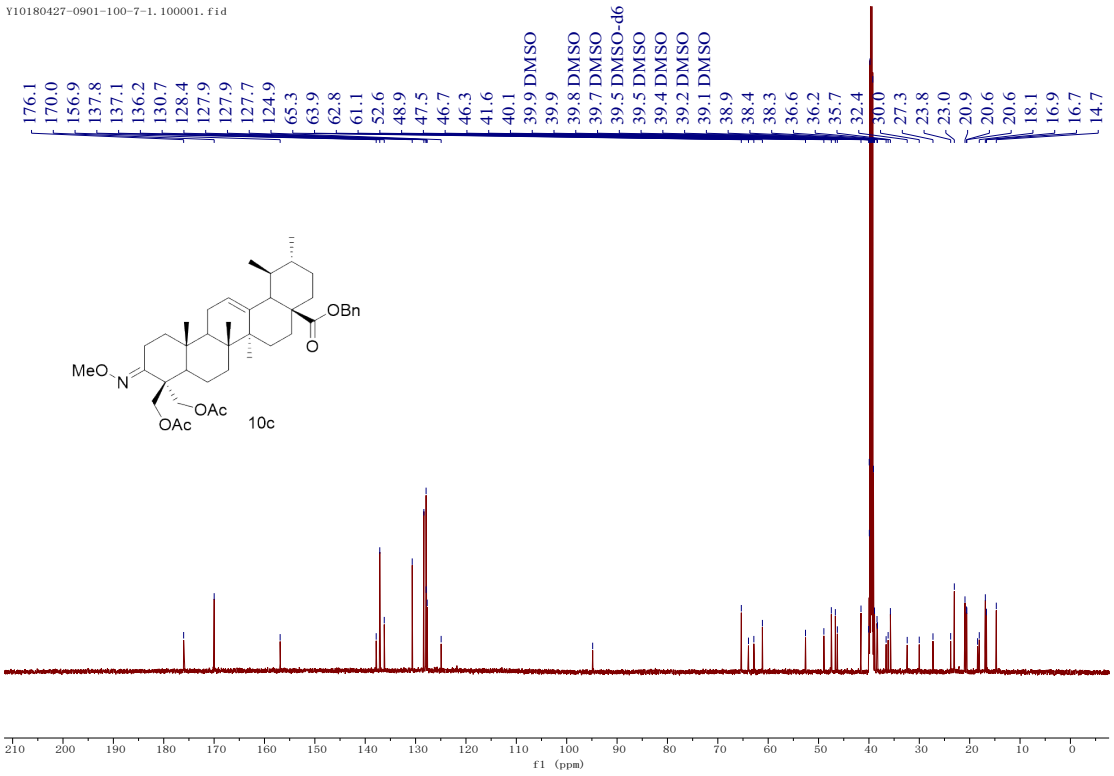

RLZ-MWY-128-37-2-H1.10.fid
7.37
7.36
7.35
7.33
7.32
7.30 CDCl3
7.29
7.28
7.27
7.27
7.26 CDCl3
7.26
5.07
5.03
1.97
1.96
1.95
1.94
1.94
1.93
1.90
1.89
1.89
1.88
1.87
1.77
1.64 H2O
1.61 H2O
1.59 H2O
1.54 H2O
1.51
1.43
1.34
1.31
1.29
1.09
1.07
1.06
1.04
1.03
1.02
1.00
0.98
0.96
0.94
0.89
0.87
0.68
0.67
0.65
OBn
O
BnO
N
AcO
AcO
9c
9.90
1.00
1.03
1.80
1.41
0.98
1.01
1.05
0.99
0.99
2.21
1.16
2.75
1.82
2.83
0.97
4.29
7.59
3.07
7.30
3.13
3.25
1.01
3.99
3.40
f1 (ppm)

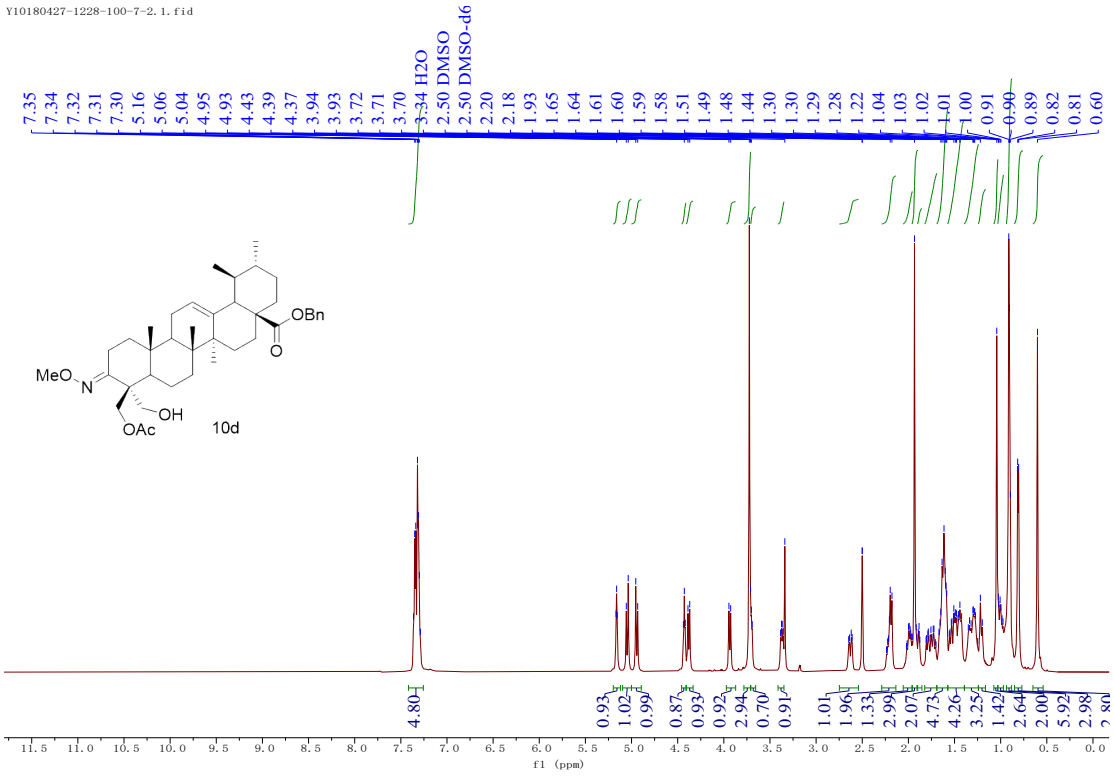

Y10180427-0902-128-37-2.100001.fid
177.4
171.0
170.9
157.5
138.7
138.3
136.5
128.6
128.4
128.3
128.2
128.1
127.6
125.6
77.4 CDCl3
77.2 CDCl3
77.2 CDCl3
76.9 CDCl3
75.8
66.2
64.9
64.0
53.1
49.7
48.3
47.1
47.1
42.2
39.5
39.2
39.0
37.4
36.7
36.4
33.0
30.8
29.8
28.0
24.3
23.6
23.5
21.3
21.0
20.9
19.2
18.7
17.1
17.1
15.3
OBn
O
BnO
N
AcO
AcO
9c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

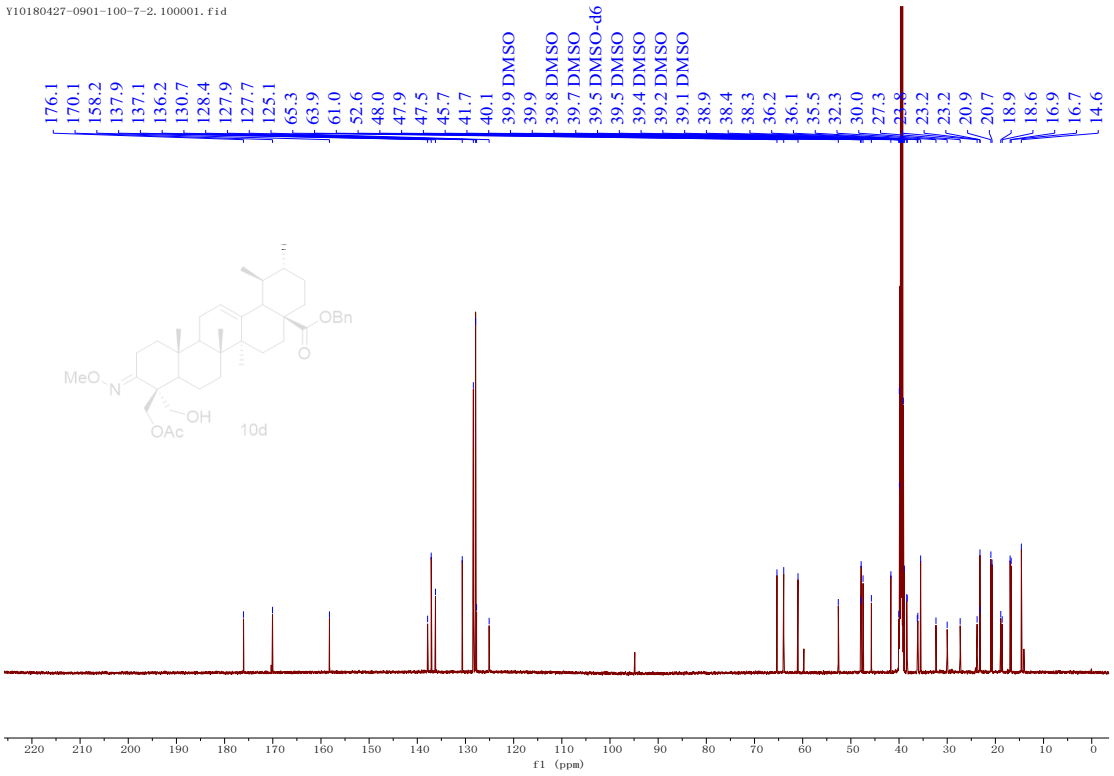

RLZ-MWY-128-29-H.1.fid
7.34
7.33
7.32
5.25
5.12
5.09
5.00
4.96
4.15
4.13
4.07
4.04
3.79
2.29
2.26
2.03 H2O
2.01
1.90
1.89
1.77
1.74
1.72
1.71
1.70
1.69
1.68
1.50
1.47
1.46
1.41
1.39
1.38
1.36
1.33
1.31
1.30
1.28
1.27
1.25
1.09
1.08
1.06
1.06
1.01
0.94
0.94
0.92
0.85
0.84
0.67
OBn
O
MeO
N
AcO
10a
5.26
1.00
1.09
1.03
0.98
0.94
3.05
0.91
2.06
3.27
2.00
5.12
1.62
1.84
1.42
4.21
4.54
2.46
6.19
1.64
2.86
3.28
3.28
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

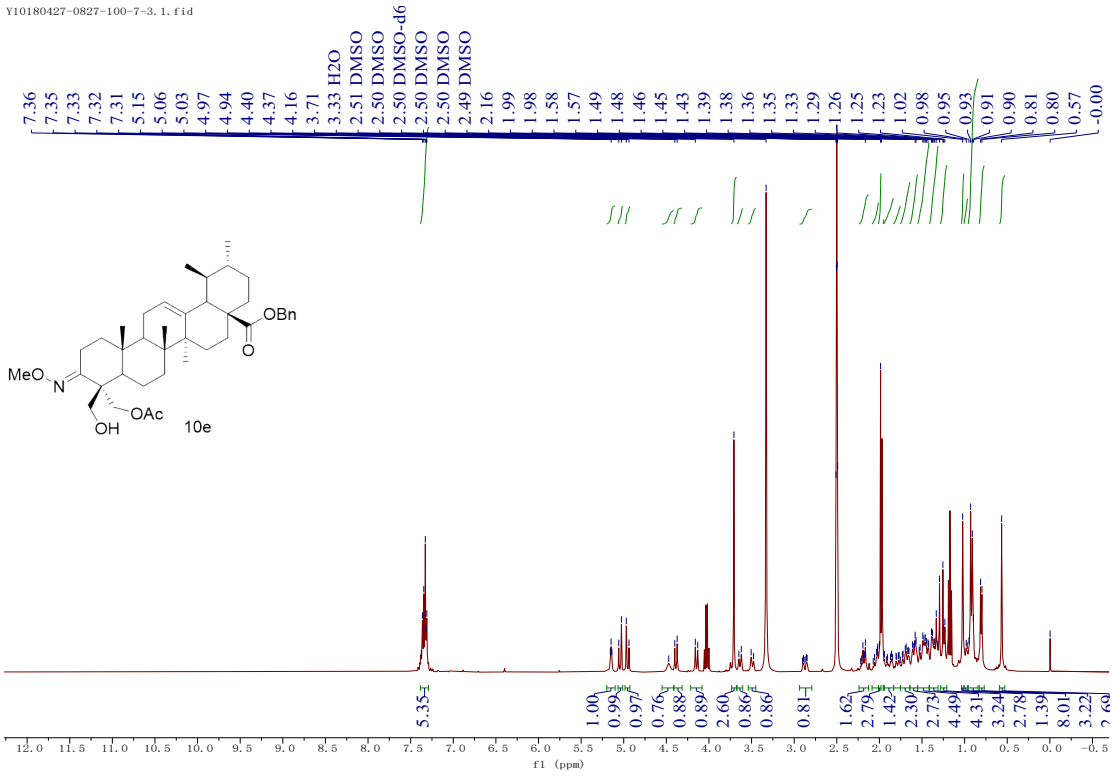

RLZ-MWY-128-29-C.1.fid
177.4
171.1
161.4
138.3
136.5
128.5
128.3
128.1
125.8
77.5 CDCl3
77.2 CDCl3
77.2 CDCl3
76.8 CDCl3
69.0
66.1
61.5
53.1
48.5
48.3
46.6
42.6
42.3
39.6
39.2
39.0
37.1
36.7
36.5
32.6
30.8
28.0
24.4
23.5
21.3
21.1
20.0
19.4
18.9
17.2
17.1
15.1
OBn
MeO
N
O
AcO
10a
f1 (ppm)

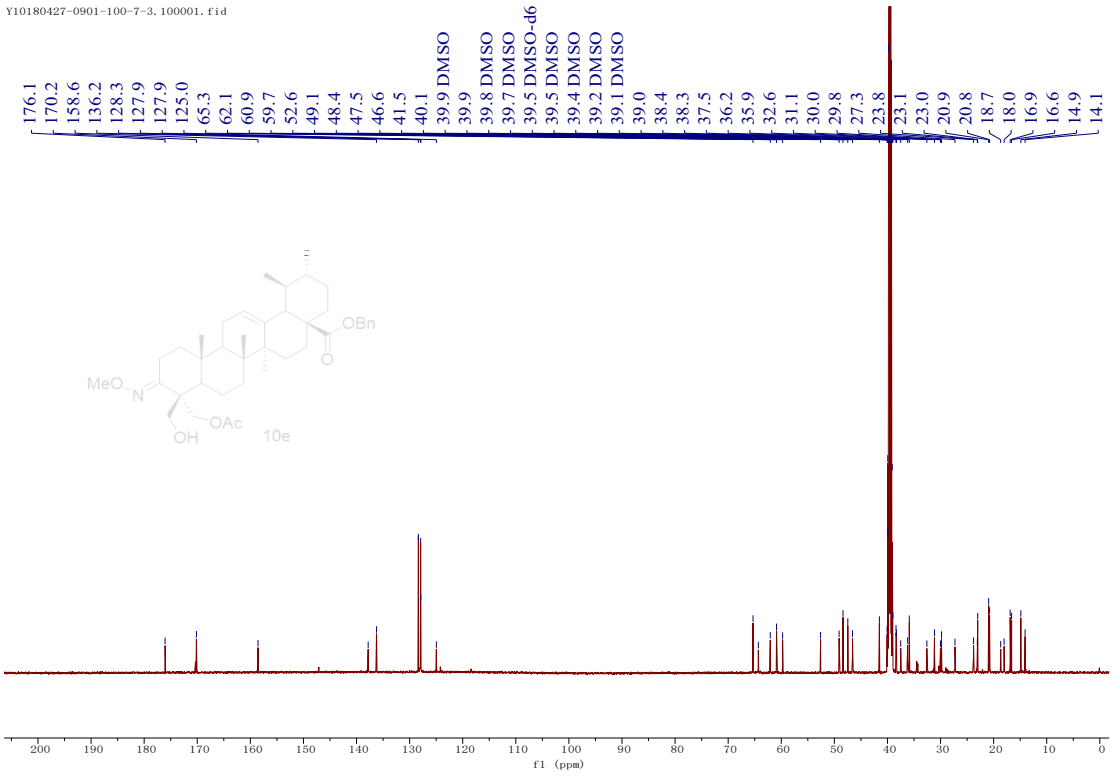

Y10180427-0827-100-7-1.1.fid
7.37
7.36
7.35
7.33
7.31
5.16
5.06
5.03
4.97
4.29
4.24
4.10
4.09
3.70
3.33 H2O
3.17
3.16
2.51 DMSO
2.50 DMSO
2.50 DMSO-d6
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.17
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.90
1.58
1.42
1.38
1.36
1.33
1.30
1.26
1.23
1.03
1.02
0.98
0.96
0.91
0.90
0.82
0.80
0.58
-0.00
OBn
MeO
N
O
OAc
OAc
10c
5.24
0.97
1.13
1.14
0.82
0.88
0.86
1.02
0.87
2.71
1.75
1.01
1.90
3.56
2.72
3.21
1.13
1.33
2.86
4.42
13.38
4.08
3.86
5.19
2.97
3.00
f1 (ppm)

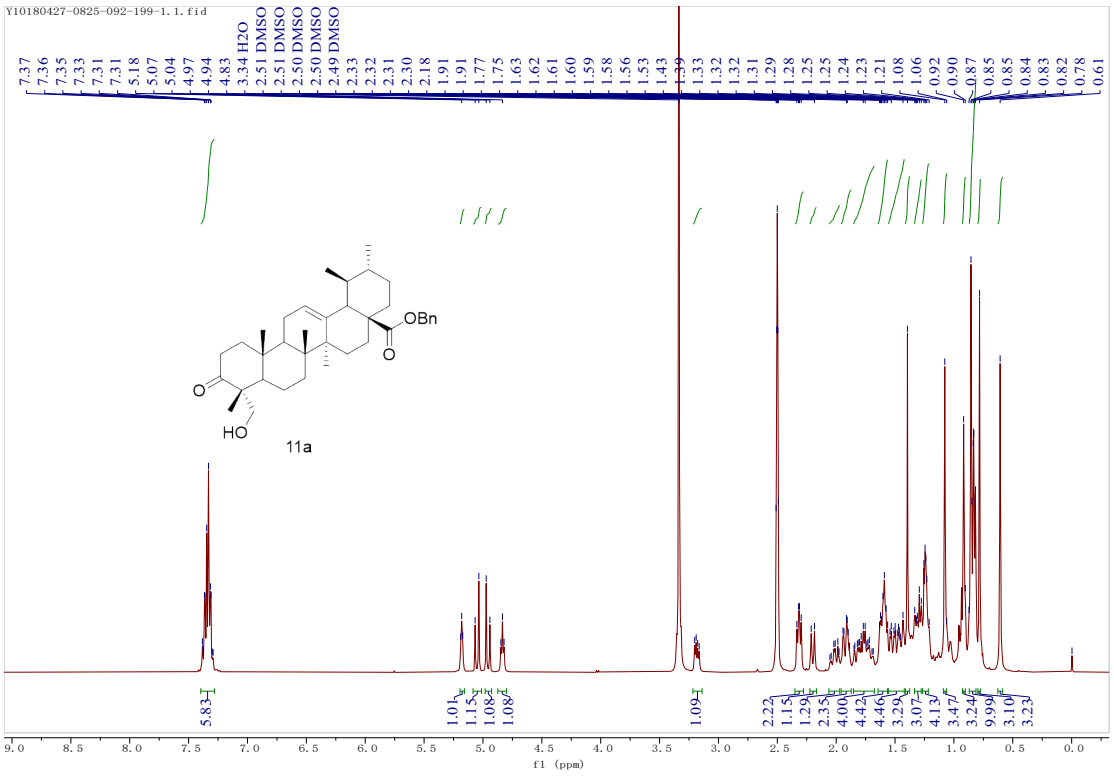

Y10180427-0901-100-7-1.100001.fid
176.1
170.0
156.9
137.8
137.1
136.2
130.7
128.4
127.9
127.9
127.7
124.9
65.3
63.9
62.8
61.1
52.6
48.9
47.5
46.7
46.3
41.6
40.1
39.9 DMSO
39.9
39.8 DMSO
39.7 DMSO
39.5 DMSO-d6
39.5 DMSO
39.4 DMSO
39.2 DMSO
39.1 DMSO
38.9
38.4
38.3
36.6
36.2
35.7
32.4
30.0
27.3
23.8
23.0
20.9
20.6
20.6
18.1
16.9
16.7
14.7
OBn
O
MeO
N
OAc
OAc
10c
f1 (ppm)

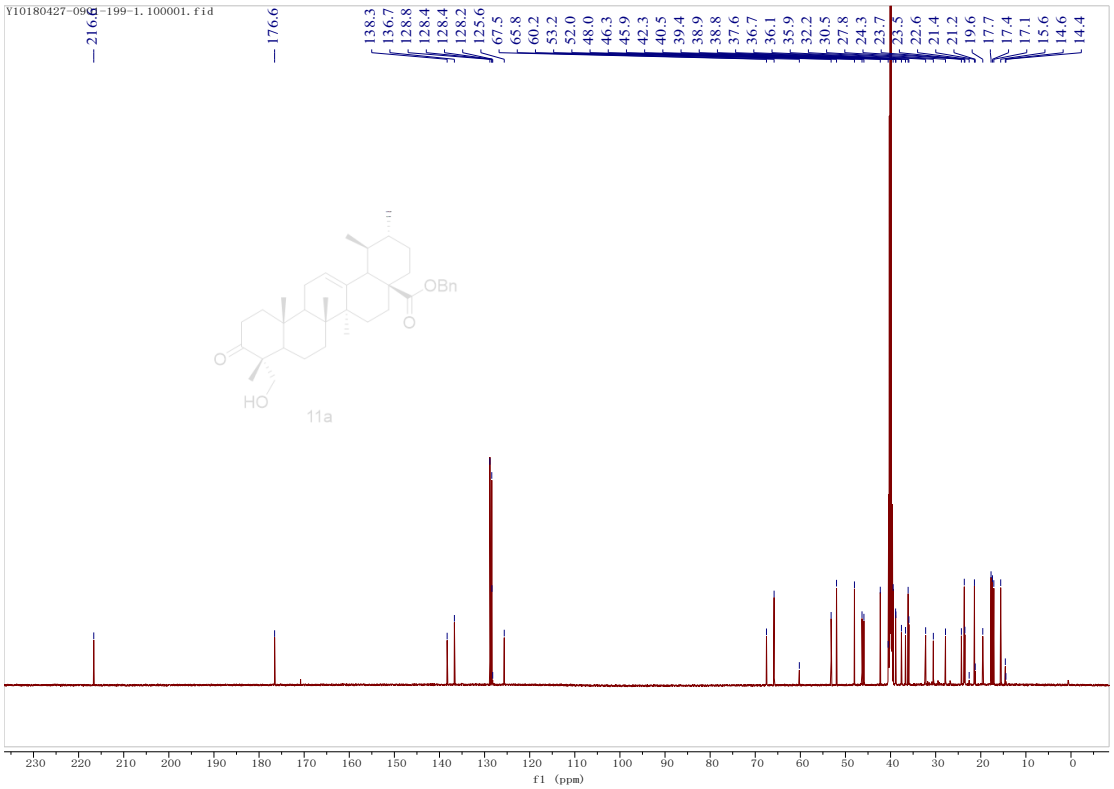

Y10180427-1228-100-7-2.1.fid
7.35
7.34
7.32
7.31
7.30
5.16
5.06
5.04
4.95
4.93
4.43
4.39
4.37
3.94
3.93
3.72
3.71
3.70
3.34 H2O
2.50 DMSO
2.50 DMSO-d6
2.20
2.18
1.93
1.65
1.64
1.61
1.60
1.59
1.58
1.51
1.49
1.48
1.44
1.30
1.30
1.29
1.28
1.22
1.04
1.03
1.02
1.01
1.00
0.91
0.90
0.89
0.82
0.81
0.60
OBn
O
MeO
N
OH
OAc
10d
4.80
0.93
1.02
0.99
0.87
0.93
0.92
2.94
0.70
0.91
1.01
1.96
1.33
2.99
2.07
4.73
4.26
3.25
1.42
2.64
2.00
5.92
2.98
f1 (ppm)

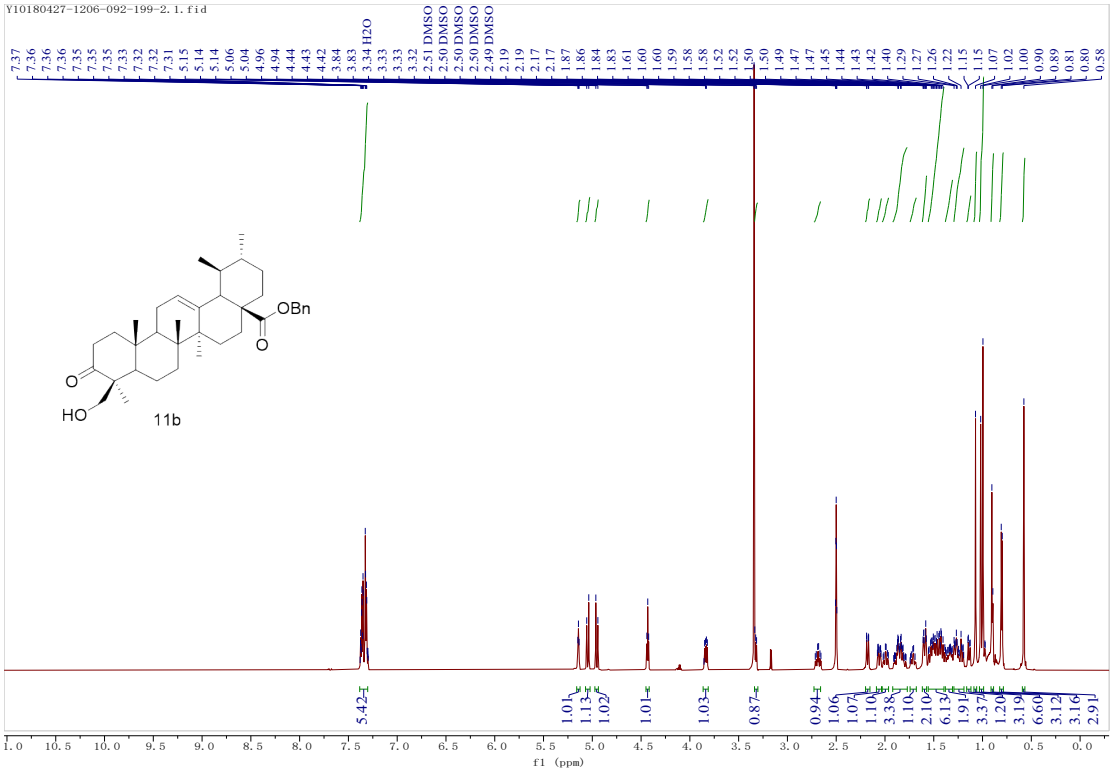

Y10180427-0901-100-7-2.100001.fid
176.1
170.1
158.2
137.9
137.1
136.2
130.7
128.4
127.9
127.7
125.1
65.3
63.9
61.0
52.6
48.0
47.9
47.5
45.7
41.7
40.1
39.9 DMSO
39.9
39.8 DMSO
39.7 DMSO
39.5 DMSO-d6
39.5 DMSO
39.4 DMSO
39.2 DMSO
39.1 DMSO
38.9
38.4
38.3
36.2
36.1
35.5
32.3
30.0
27.3
23.8
23.2
23.2
20.9
20.7
18.9
18.6
16.9
16.7
14.6
OBn
O
MeO
N
OH
OAc
10d
f1 (ppm)

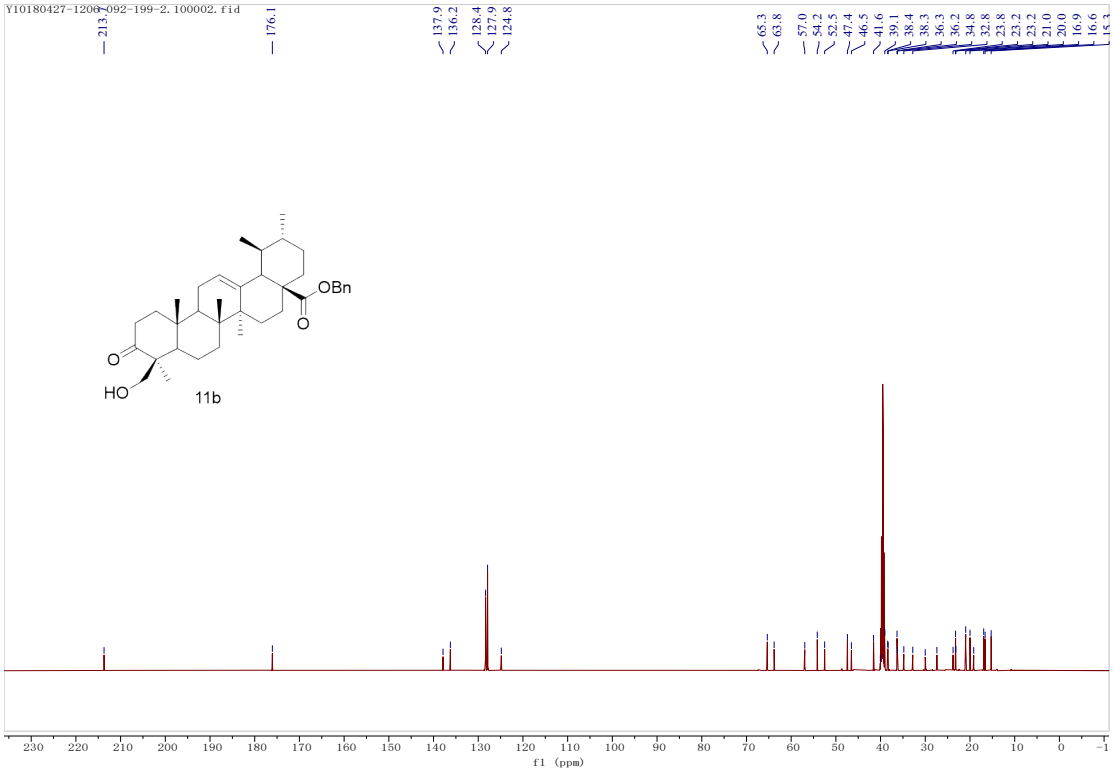

Y10180427-0827-100-7-3.1.fid
7.36
7.35
7.33
7.32
7.31
5.15
5.06
5.03
4.97
4.94
4.40
4.37
4.16
3.71
3.33 H2O
2.51 DMSO
2.50 DMSO
2.50 DMSO-d6
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.16
1.99
1.98
1.58
1.57
1.49
1.48
1.46
1.45
1.43
1.39
1.38
1.36
1.35
1.33
1.29
1.26
1.25
1.23
1.02
0.98
0.95
0.93
0.91
0.90
0.81
0.80
0.57
-0.00
OBn
O
MeO
N
OH
OAc
10e
5.35
1.00
0.99
0.97
0.76
0.88
0.89
2.60
0.86
0.86
0.81
1.62
2.79
1.42
2.30
2.73
4.49
4.31
3.24
2.78
1.39
8.01
3.22
f1 (ppm)

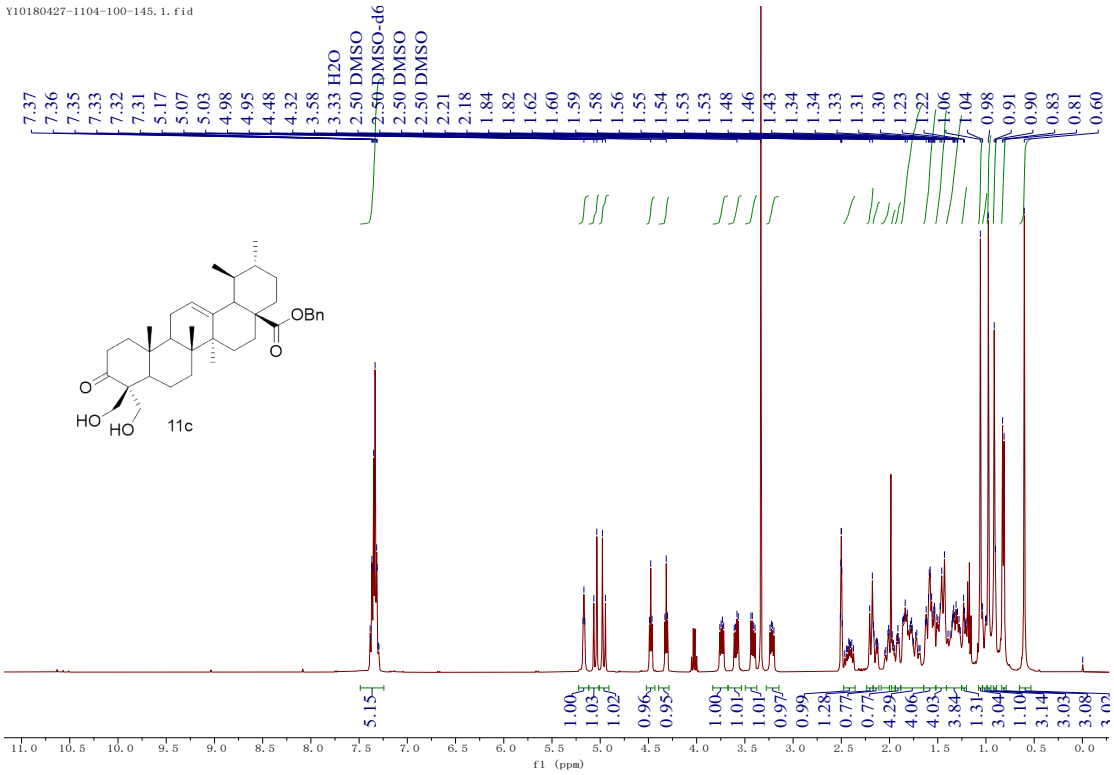

Y10180427-0901-100-7-3.100001.fid
176.1
170.2
158.6
136.2
128.3
127.9
127.9
125.0
65.3
62.1
60.9
59.7
52.6
49.1
48.4
47.5
46.6
41.5
40.1
39.9 DMSO
39.9
39.8 DMSO
39.7 DMSO
39.5 DMSO-d6
39.5 DMSO
39.4 DMSO
39.2 DMSO
39.1 DMSO
39.0
38.4
38.3
37.5
36.2
35.9
32.6
31.1
30.0
29.8
27.3
23.8
23.1
23.0
20.9
20.8
18.7
18.0
16.9
16.6
14.9
14.1
OBn
O
MeO
N
OAc
OH
10e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

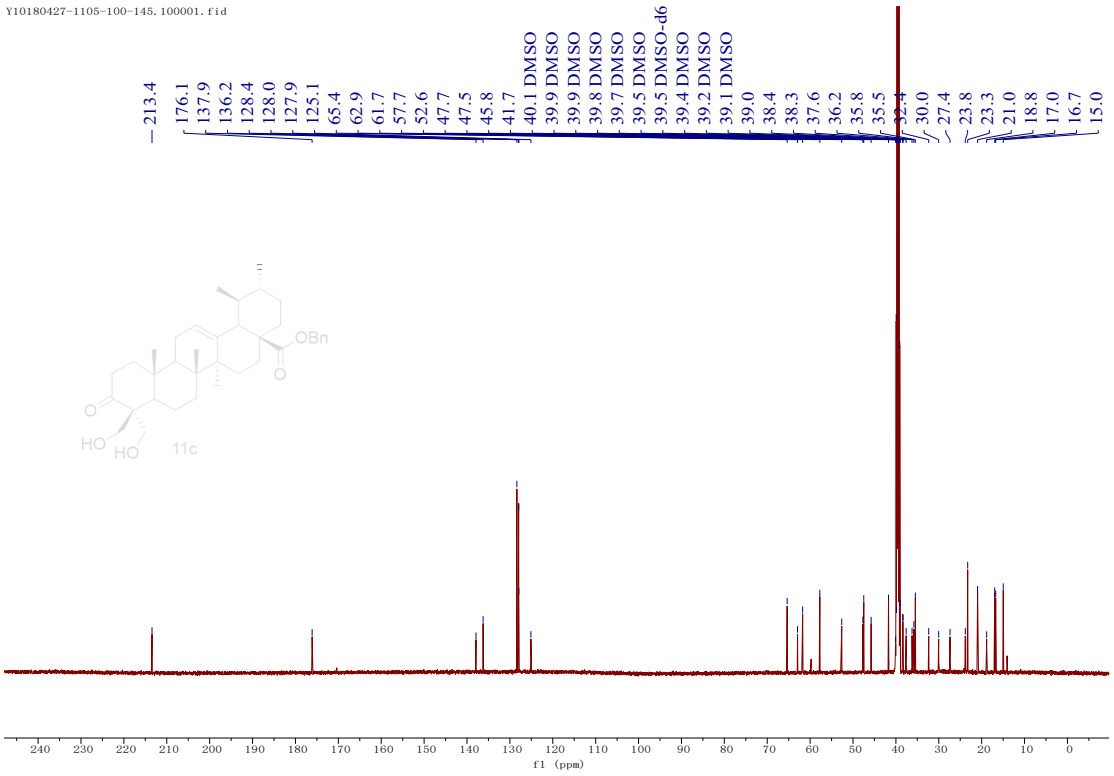

Y10180427-0825-092-199-1.1.fid
7.37
7.36
7.35
7.33
7.31
7.31
5.18
5.07
5.04
4.97
4.94
4.83
3.34 H2O
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.33
2.32
2.31
2.30
2.18
1.91
1.91
1.77
1.75
1.63
1.62
1.61
1.60
1.59
1.58
1.56
1.53
1.43
1.39
1.33
1.32
1.32
1.31
1.29
1.28
1.25
1.25
1.24
1.23
1.21
1.08
1.06
0.92
0.90
0.87
0.85
0.85
0.84
0.83
0.82
0.78
0.61
OBn
O
O
HO
11a
5.83
1.01
1.15
1.08
1.08
1.09
2.22
1.15
1.29
2.35
4.00
4.42
4.46
3.29
3.07
4.13
3.47
3.24
9.99
3.10
3.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

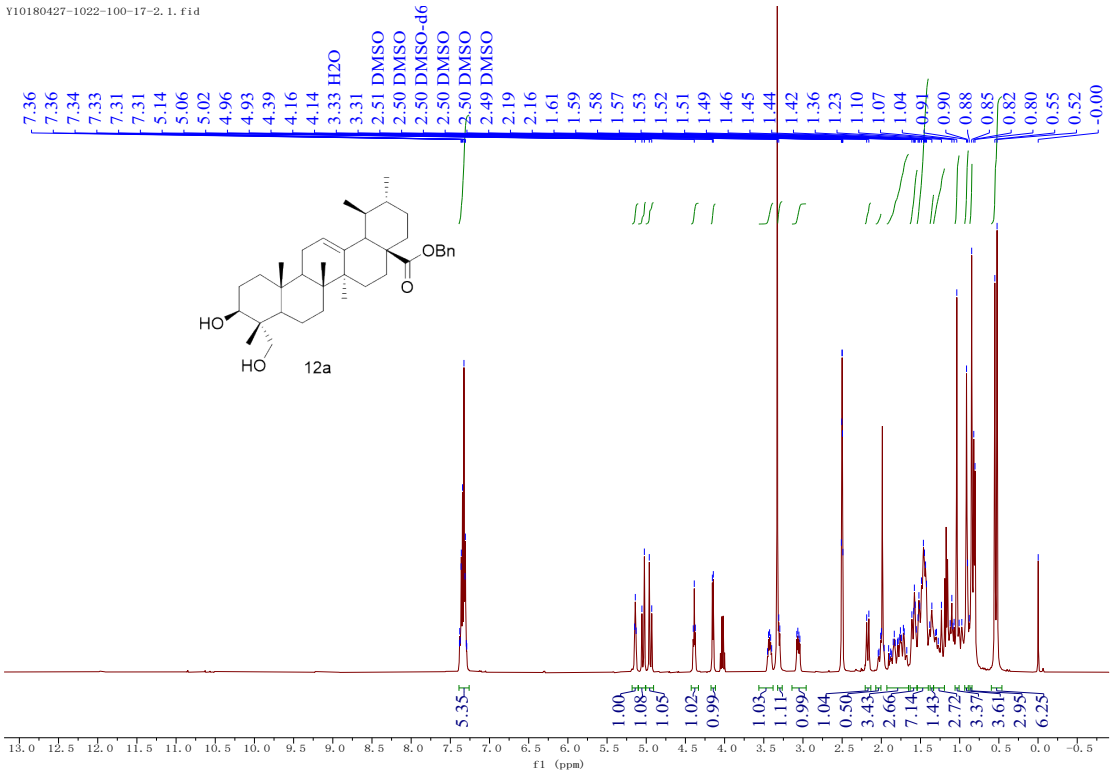

Y10180427-0906-199-1.100001.fid
216.6
176.6
138.3
136.7
128.8
128.4
128.4
128.2
125.6
67.5
65.8
60.2
53.2
52.0
48.0
46.3
45.9
42.3
40.5
39.4
38.9
38.8
37.6
36.7
36.1
35.9
32.2
30.5
27.8
24.3
23.7
23.5
22.6
21.4
21.2
19.6
17.7
17.4
17.1
15.6
14.6
14.4
OBn
O
O
HO
11a
f1 (ppm)

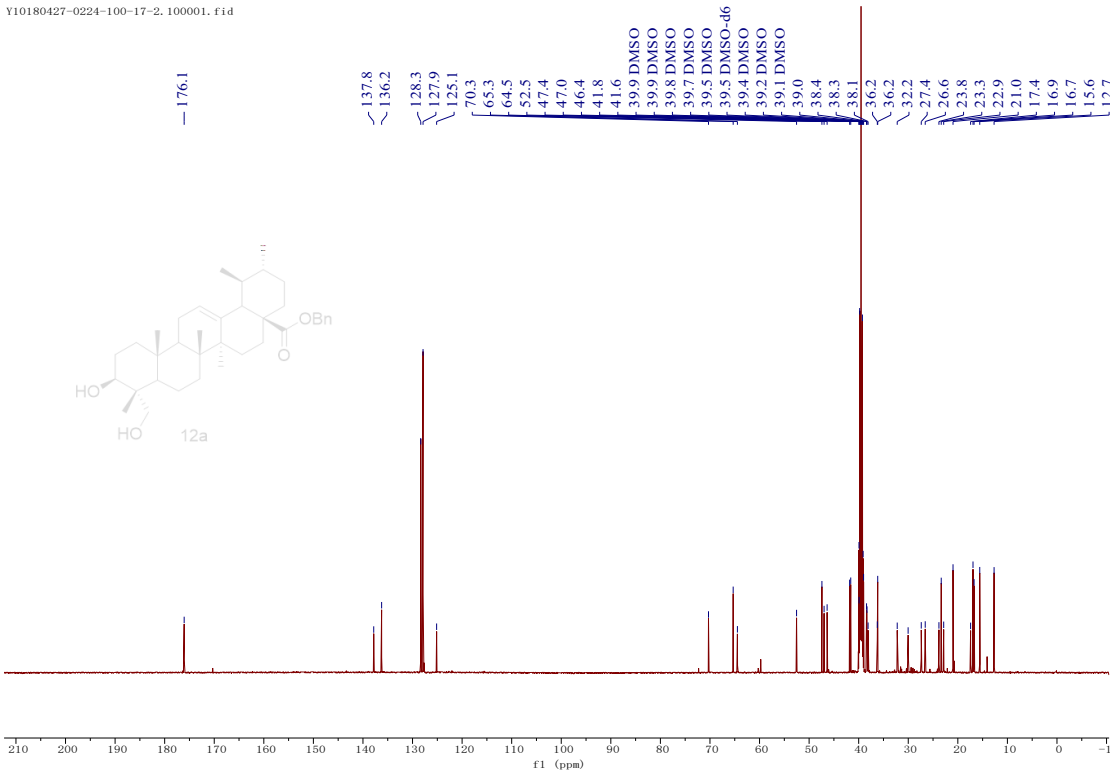

Y10180427-1206-092-199-2.1.fid
7.37
7.36
7.36
7.36
7.35
7.35
7.35
7.33
7.32
7.32
7.31
5.15
5.14
5.14
5.06
5.04
4.96
4.94
4.44
4.43
4.42
3.84
3.83
H2O
3.34
3.33
3.33
3.32
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.19
2.19
2.17
2.17
1.87
1.86
1.84
1.83
1.61
1.60
1.60
1.59
1.58
1.58
1.52
1.52
1.50
1.50
1.49
1.47
1.47
1.45
1.44
1.43
1.42
1.40
1.29
1.27
1.26
1.22
1.15
1.15
1.07
1.02
1.00
0.90
0.89
0.81
0.80
0.58
OBn
O
O
HO
11b
5.42
1.01
1.13
1.02
1.01
1.03
0.87
0.94
1.06
1.07
1.10
3.38
1.10
2.10
6.13
1.91
3.37
1.20
3.19
6.60
3.12
3.16
2.91
f1 (ppm)

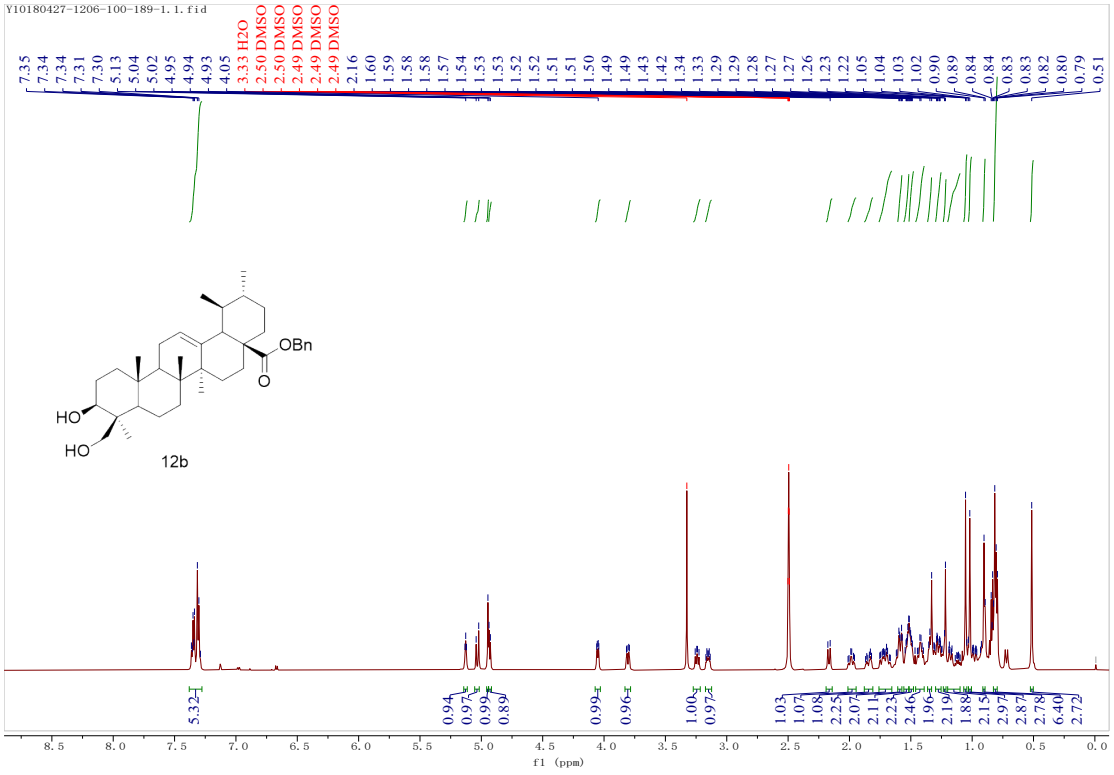

Y10180427-1206-092-199-2.100002.fid
213.3
176.1
137.9
136.2
128.4
127.9
124.8
65.3
63.8
57.0
54.2
52.5
47.4
46.5
41.6
39.1
38.4
38.3
36.3
36.2
34.8
32.8
23.8
23.2
23.2
21.0
20.0
16.9
16.6
15.3
OBn
O
O
HO
11b
f1 (ppm)

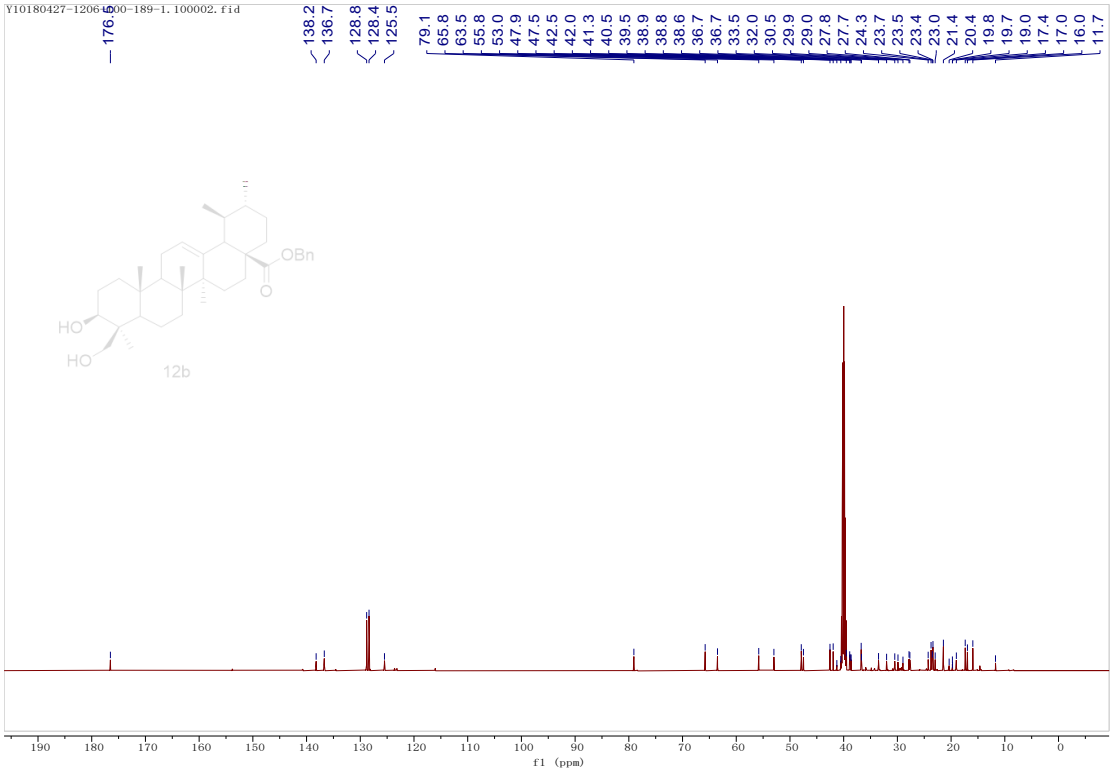

Y10180427-1104-100-145.1.fid
7.37
7.36
7.35
7.33
7.32
7.31
5.17
5.07
5.03
4.98
4.95
4.48
4.32
3.58
3.33 H2O
2.50 DMSO
2.50 DMSO-d6
2.50 DMSO
2.50 DMSO
2.21
2.18
1.84
1.82
1.62
1.60
1.59
1.58
1.56
1.55
1.54
1.53
1.53
1.48
1.46
1.43
1.34
1.34
1.33
1.31
1.30
1.23
1.22
1.06
1.04
0.98
0.91
0.90
0.83
0.81
0.60
OBn
O
O
HO
HO
11c
5.15
1.00
1.03
1.02
0.96
0.95
1.00
1.01
1.01
0.97
0.99
1.28
0.77
0.77
4.29
4.06
4.03
3.84
1.31
3.04
1.10
3.14
3.03
3.08
f1 (ppm)

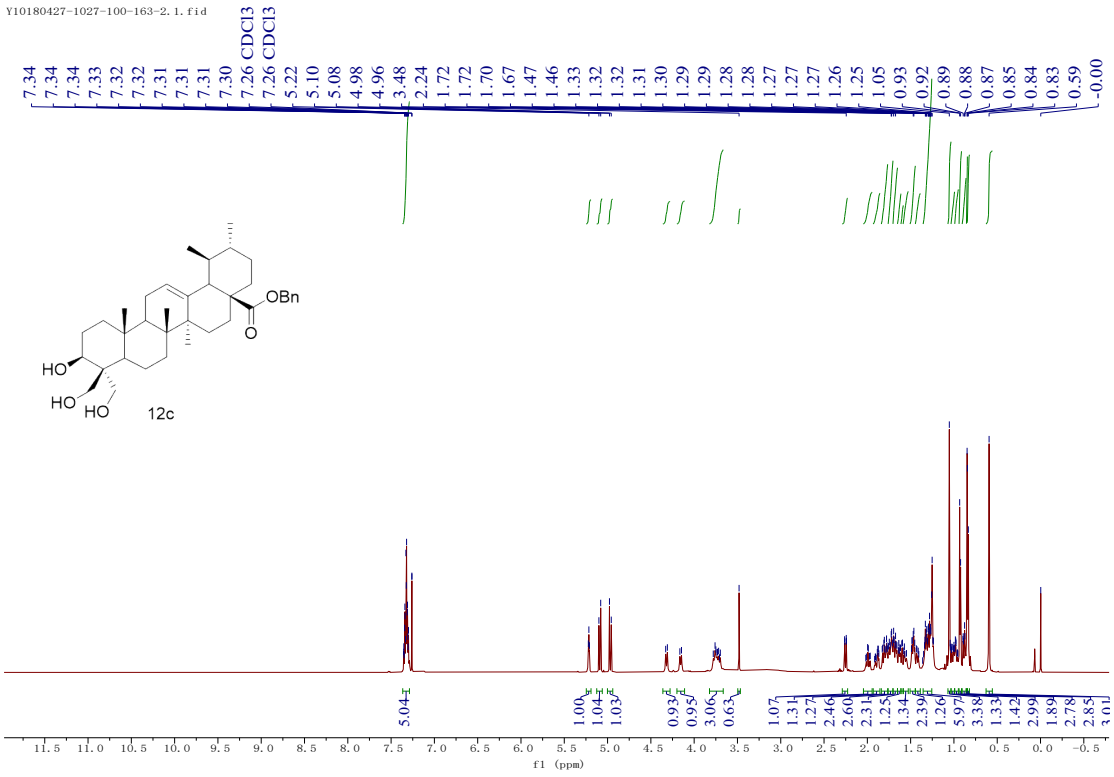

Y10180427-1105-100-145.100001.fid
213.4
176.1
137.9
136.2
128.4
128.0
127.9
125.1
65.4
62.9
61.7
57.7
52.6
47.7
47.5
45.8
41.7
40.1 DMSO
39.9 DMSO
39.9 DMSO
39.8 DMSO
39.7 DMSO
39.5 DMSO
39.5 DMSO-d6
39.4 DMSO
39.2 DMSO
39.1 DMSO
39.0
38.4
38.3
37.6
36.2
35.8
35.5
32.4
30.0
27.4
23.8
23.3
21.0
18.8
17.0
16.7
15.0
OBn
O
O
HO
HO
11c
f1 (ppm)

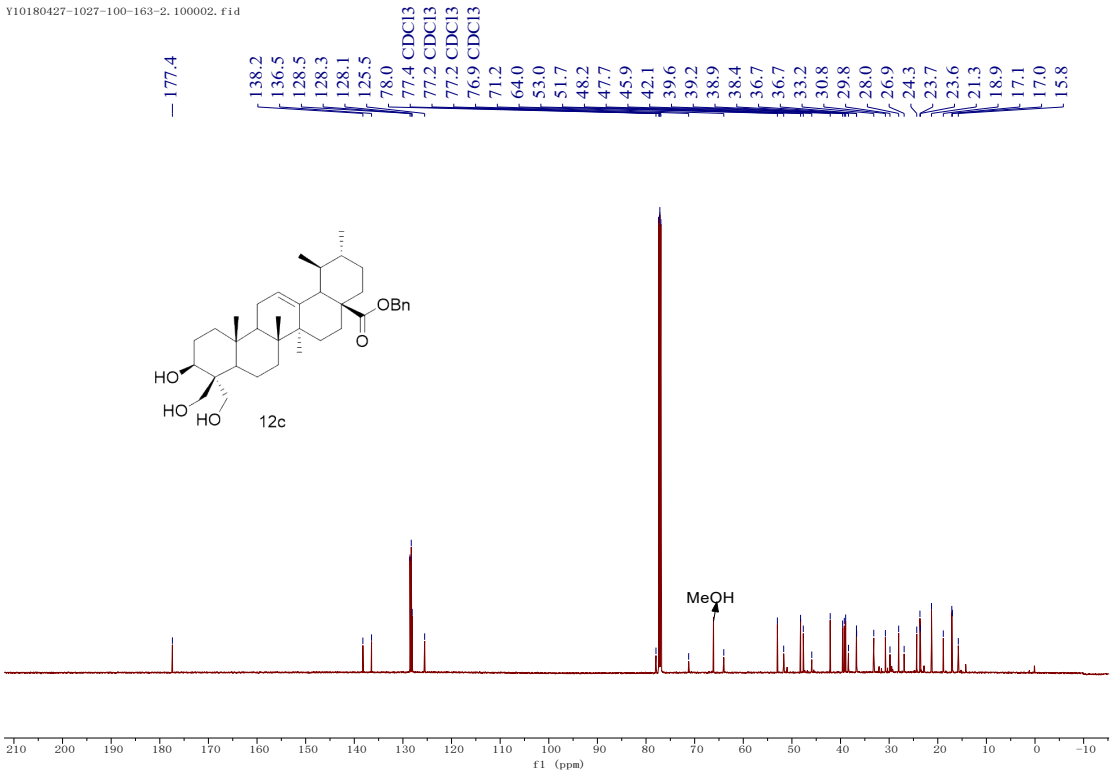

Y10180427-1022-100-17-2.1.fid
7.36
7.36
7.34
7.33
7.31
7.31
5.14
5.06
5.02
4.96
4.93
4.39
4.16
4.14
3.33 H2O
3.31
2.51 DMSO
2.50 DMSO
2.50 DMSO-d6
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.19
2.16
1.61
1.59
1.58
1.57
1.53
1.52
1.51
1.49
1.46
1.45
1.44
1.42
1.36
1.23
1.10
1.07
1.04
0.91
0.90
0.88
0.85
0.82
0.80
0.55
0.52
-0.00
OBn
O
HO
HO
12a
5.35
1.00
1.08
1.05
1.02
0.99
1.03
1.11
0.99
1.04
0.50
3.43
2.66
7.14
1.43
2.72
3.37
3.61
2.95
6.25
f1 (ppm)

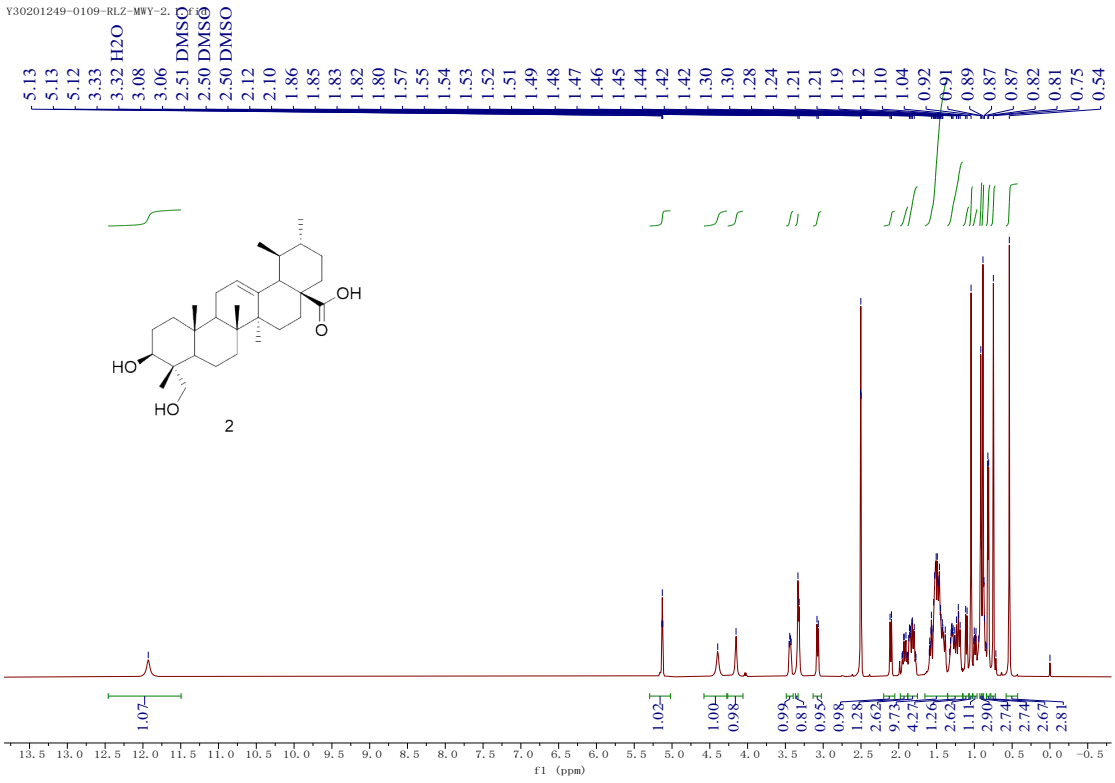

Y10180427-0224-100-17-2.100001.fid
176.1
137.8
136.2
128.3
127.9
125.1
70.3
65.3
64.5
52.5
47.4
47.0
46.4
41.8
41.6
39.9 DMSO
39.9 DMSO
39.8 DMSO
39.7 DMSO
39.5 DMSO
39.5 DMSO-d6
39.4 DMSO
39.2 DMSO
39.1 DMSO
39.0
38.4
38.3
38.1
36.2
36.2
32.2
27.4
26.6
23.8
23.3
22.9
21.0
17.4
16.9
16.7
15.6
OBn
O
HO
HO
12a
f1 (ppm)

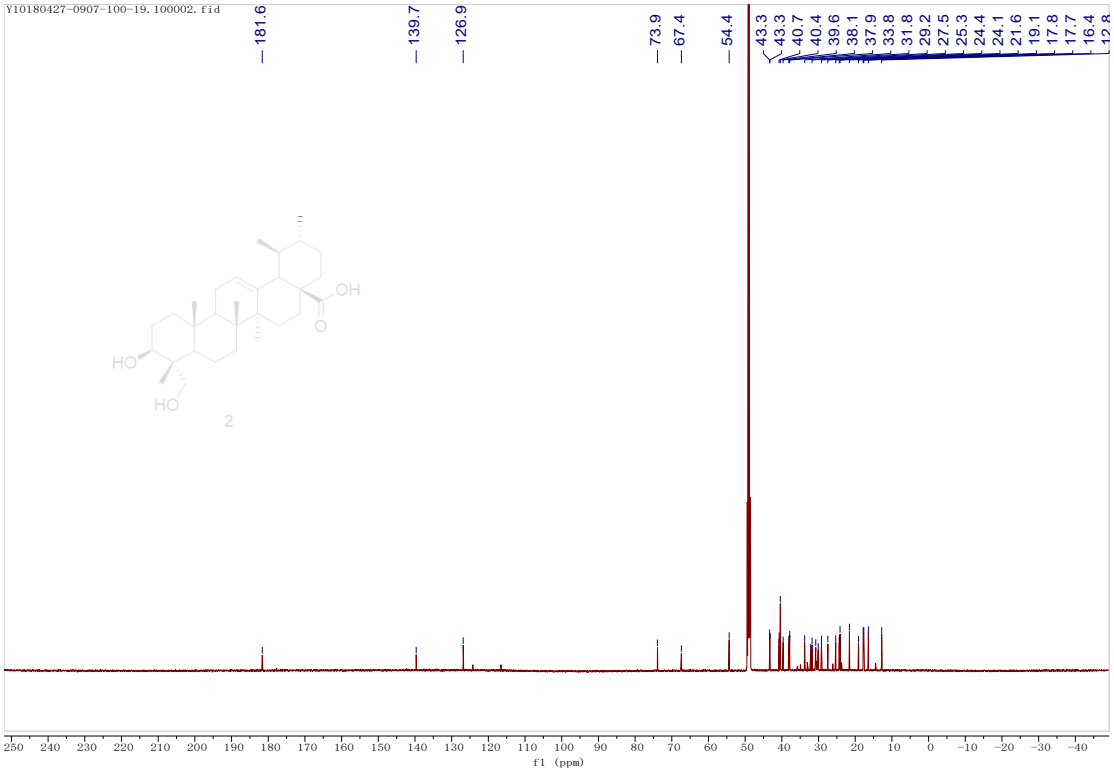

Y10180427-1206-100-189-1.1.fid
7.35
7.34
7.34
7.31
7.30
5.13
5.04
5.02
4.95
4.94
4.93
4.05
3.33 H2O
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
2.49 DMSO
2.16
1.60
1.59
1.58
1.58
1.57
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.50
1.49
1.49
1.43
1.42
1.34
1.33
1.29
1.29
1.28
1.27
1.27
1.26
1.23
1.22
1.05
1.04
1.03
1.02
0.90
0.89
0.84
0.84
0.83
0.83
0.82
0.80
0.79
0.51
OBn
O
HO
HO
12b
5.32
0.94
0.97
0.99
0.89
0.99
0.96
1.00
0.97
1.03
1.07
1.08
2.25
2.07
2.11
2.23
2.46
1.96
2.19
1.88
2.15
2.97
2.87
2.78
6.40
2.72
f1 (ppm)

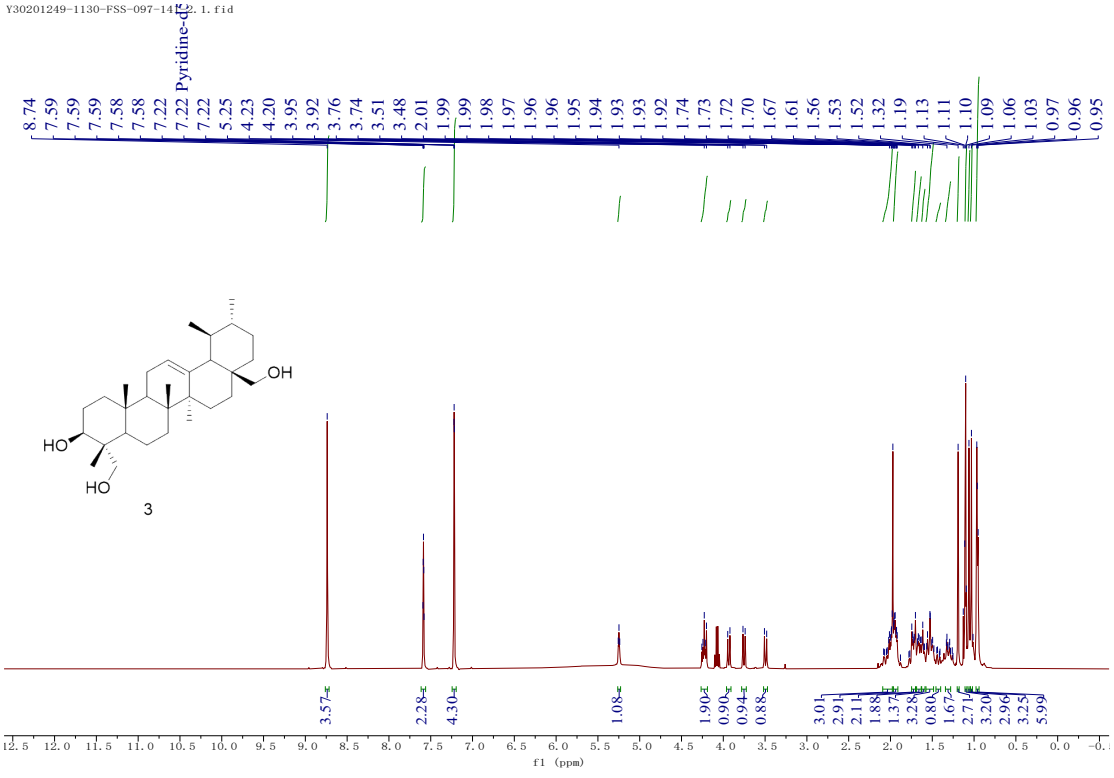

Y10180427-1206-100-189-1.100002.fid
176.5
138.2
136.7
128.8
128.4
125.5
79.1
65.8
63.5
55.8
53.0
47.9
47.5
42.5
42.0
41.3
40.5
39.5
38.9
38.8
38.6
36.7
36.7
33.5
32.0
30.5
29.9
29.0
27.8
27.7
24.3
23.7
23.5
23.4
23.0
21.4
20.4
19.8
19.7
19.0
17.4
17.0
16.0
11.7
OBn
O
HO
HO
12b
f1 (ppm)

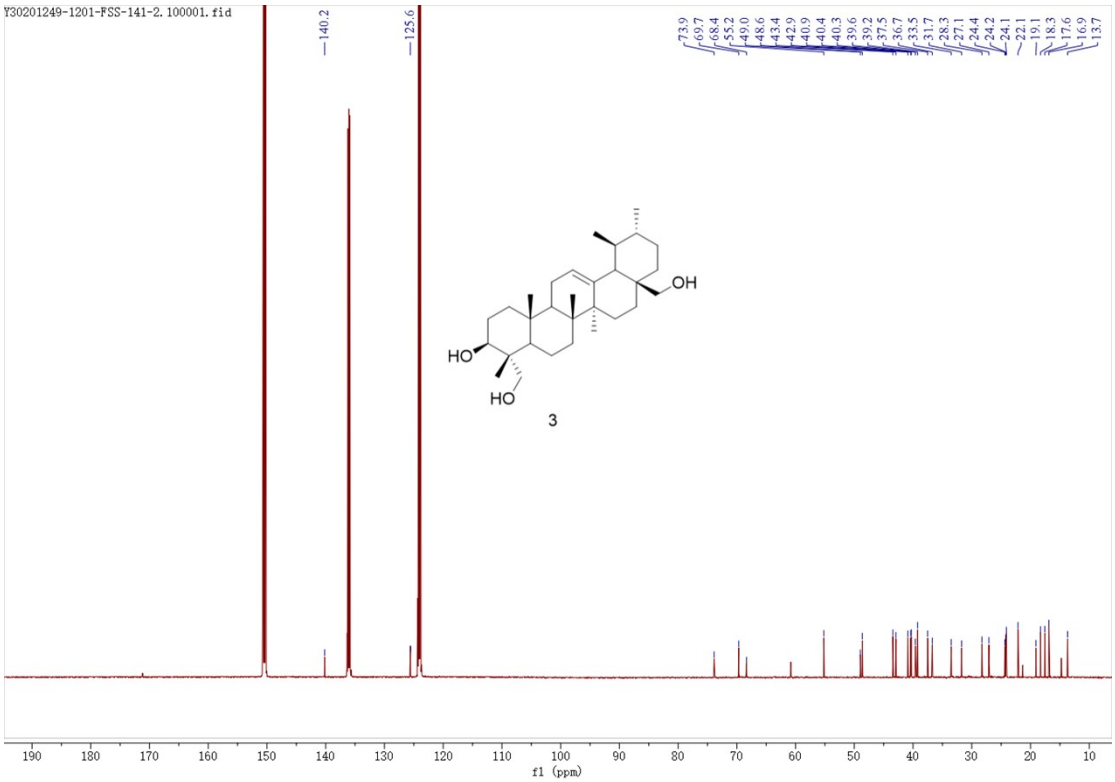

Y10180427-1027-100-163-2.1.fid
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.26 CDCl3
7.26 CDCl3
5.22
5.10
5.08
4.98
4.96
3.48
2.24
1.72
1.72
1.70
1.67
1.47
1.46
1.33
1.32
1.32
1.31
1.30
1.29
1.29
1.28
1.28
1.27
1.27
1.27
1.26
1.25
1.05
0.93
0.92
0.89
0.88
0.87
0.85
0.84
0.83
0.59
-0.00
OBn
O
HO
HO
HO
12c
5.04
1.00
1.04
1.03
0.93
0.95
3.06
0.63
1.07
1.31
1.27
2.46
2.60
2.31
1.25
1.34
2.39
1.26
5.97
3.38
1.33
1.42
2.99
1.89
2.78
2.85
f1 (ppm)

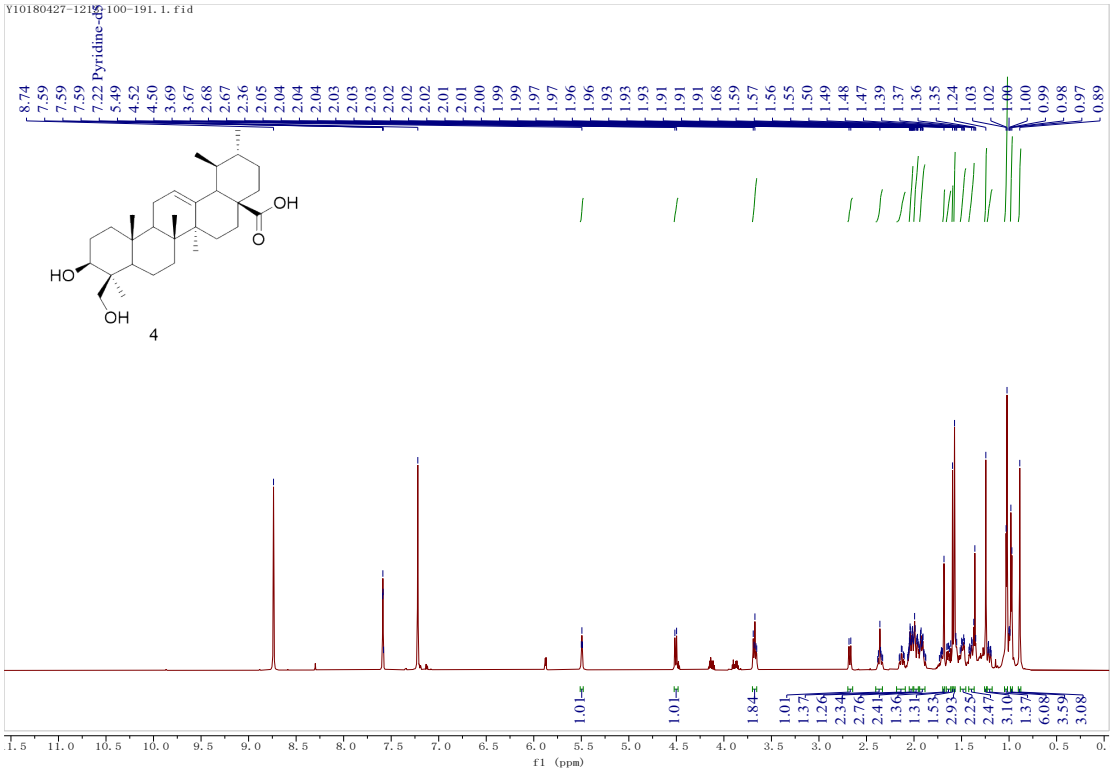

Y10180427-1027-100-163-2.100002.fid
177.4
138.2
136.5
128.5
128.3
128.1
125.5
78.0
77.4 CDCl3
77.2 CDCl3
77.2 CDCl3
76.9 CDCl3
71.2
64.0
53.0
51.7
48.2
47.7
45.9
42.1
39.6
39.2
38.9
38.4
36.7
36.7
33.2
30.8
29.8
28.0
26.9
24.3
23.7
23.6
21.3
18.9
17.1
17.0
15.8
OBn
O
HO
HO
HO
12c
MeOH
f1 (ppm)

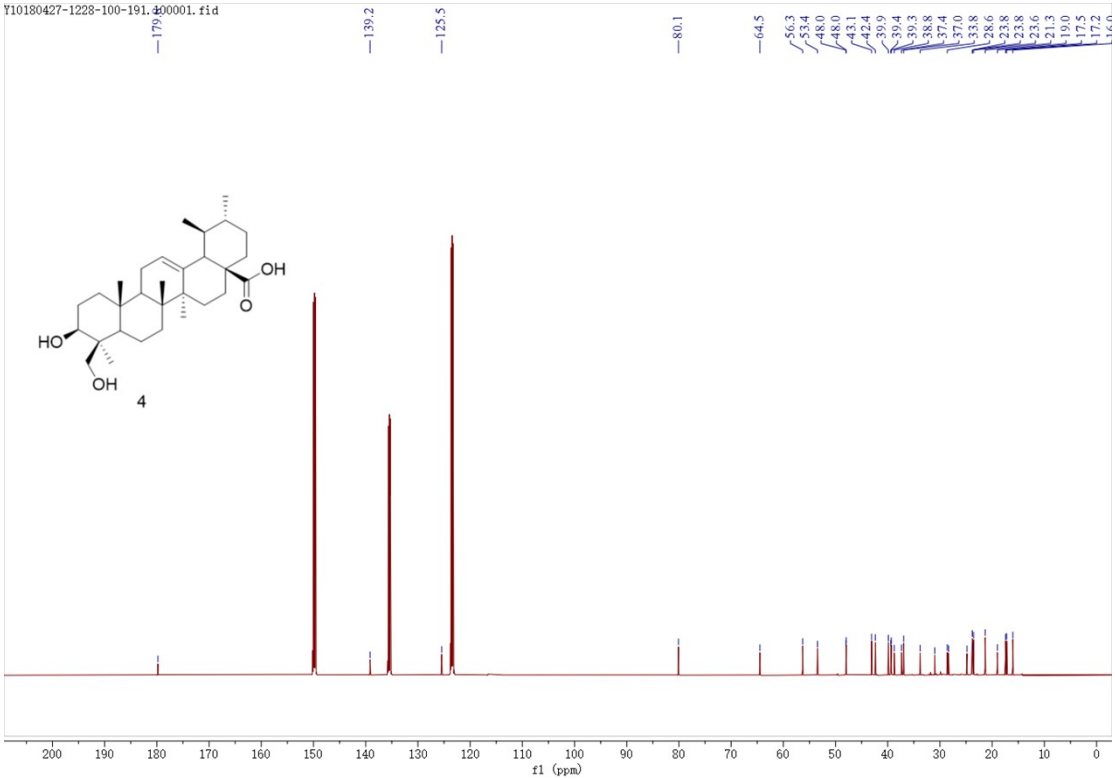

Y30201249-0109-RLZ-MWY-2.fid
5.13
5.13
5.12
3.33
3.32 H2O
3.08
3.06
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.12
2.10
1.86
1.85
1.83
1.82
1.80
1.57
1.55
1.54
1.53
1.52
1.51
1.49
1.48
1.47
1.46
1.45
1.44
1.42
1.42
1.30
1.30
1.28
1.24
1.21
1.21
1.19
1.12
1.10
1.04
0.92
0.91
0.89
0.87
0.87
0.82
0.81
0.75
0.54
OH
O
HO
HO
2
1.07
1.02
1.00
0.98
0.99
0.81
0.95
0.98
1.28
2.62
9.73
4.27
1.20
2.62
1.11
2.90
2.74
2.74
2.67
2.81
f1 (ppm)

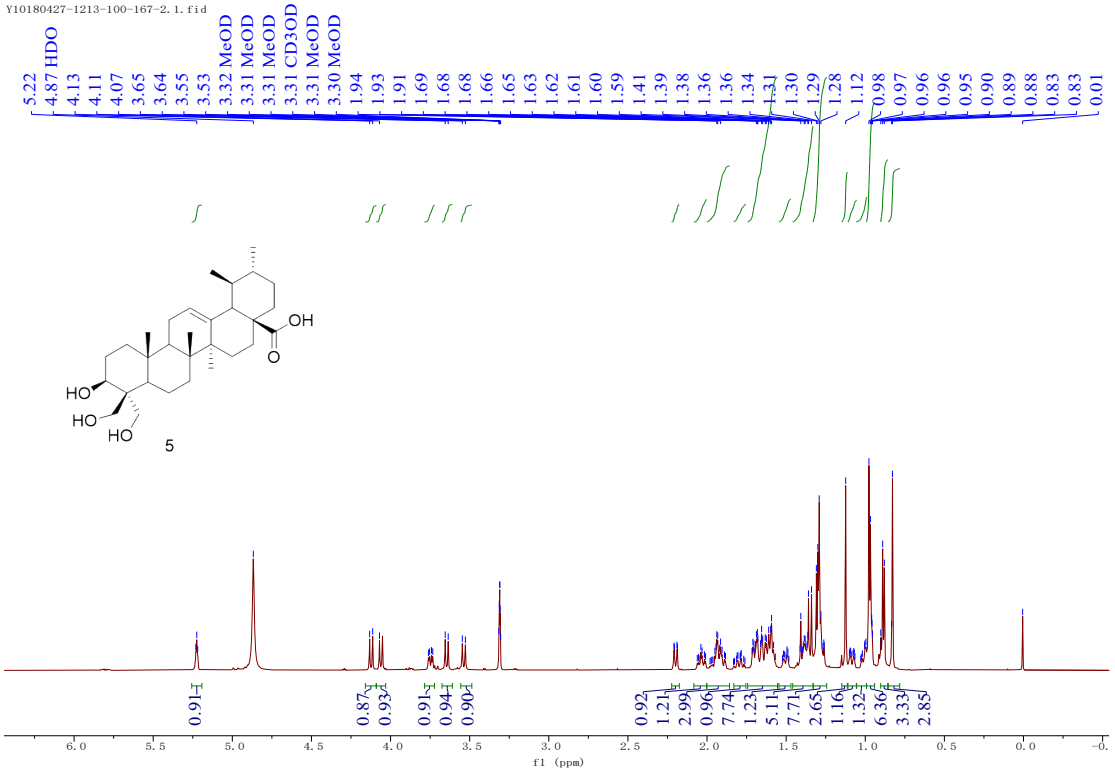

Y10180427-0907-100-19.100002.fid
181.6
139.7
126.9
73.9
67.4
54.4
43.3
43.3
40.7
40.4
39.6
38.1
37.9
33.8
31.8
29.2
27.5
25.3
24.4
24.1
21.6
19.1
17.8
17.7
16.4
OH
O
HO
HO
2
f1 (ppm)

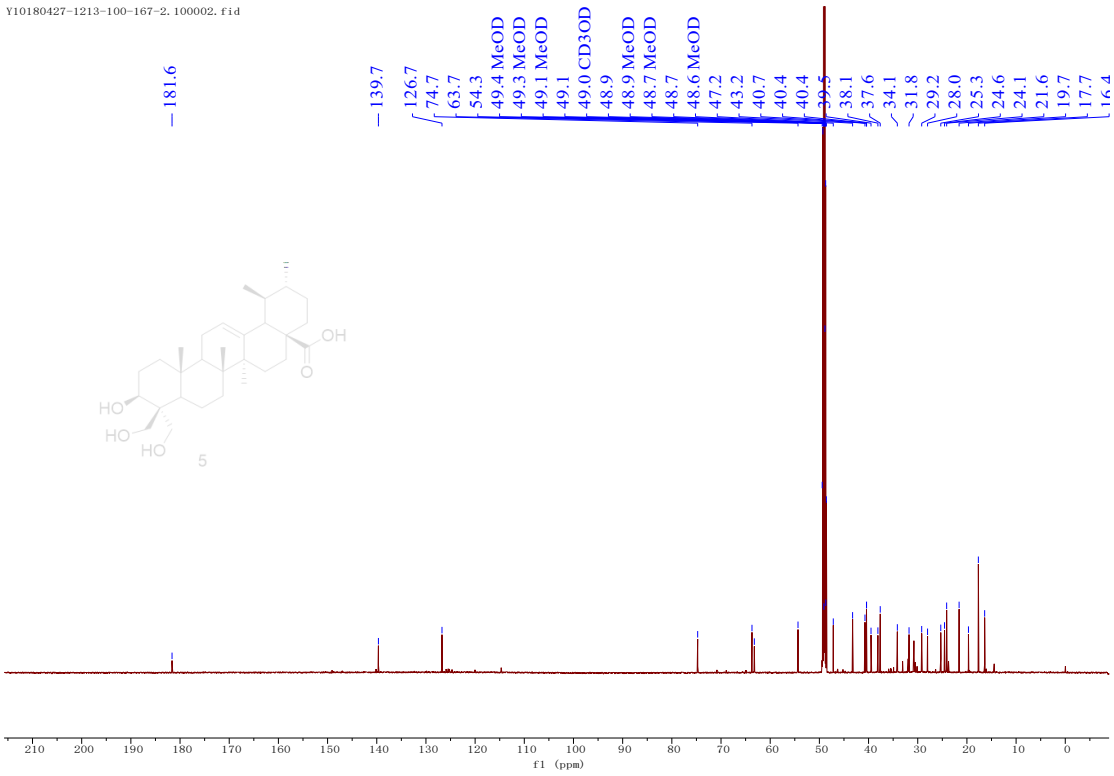

Y30201249-1130-FSS-097-14
8.74
7.59
7.59
7.59
7.58
7.58
7.22
7.22 Pyridine-d5
7.22
5.25
4.23
4.20
3.95
3.92
3.76
3.74
3.51
3.48
2.01
1.99
1.99
1.98
1.97
1.96
1.96
1.95
1.94
1.93
1.93
1.92
1.74
1.73
1.72
1.70
1.67
1.61
1.56
1.53
1.52
1.32
1.19
1.13
1.11
1.10
1.09
1.06
1.03
0.97
0.96
0.95
OH
HO
HO
3
3.57
2.28
4.30
1.08
1.90
0.90
0.94
0.88
3.01
2.91
2.11
1.88
1.37
3.28
0.80
1.67
2.71
3.20
2.96
3.25
5.99
f1 (ppm)

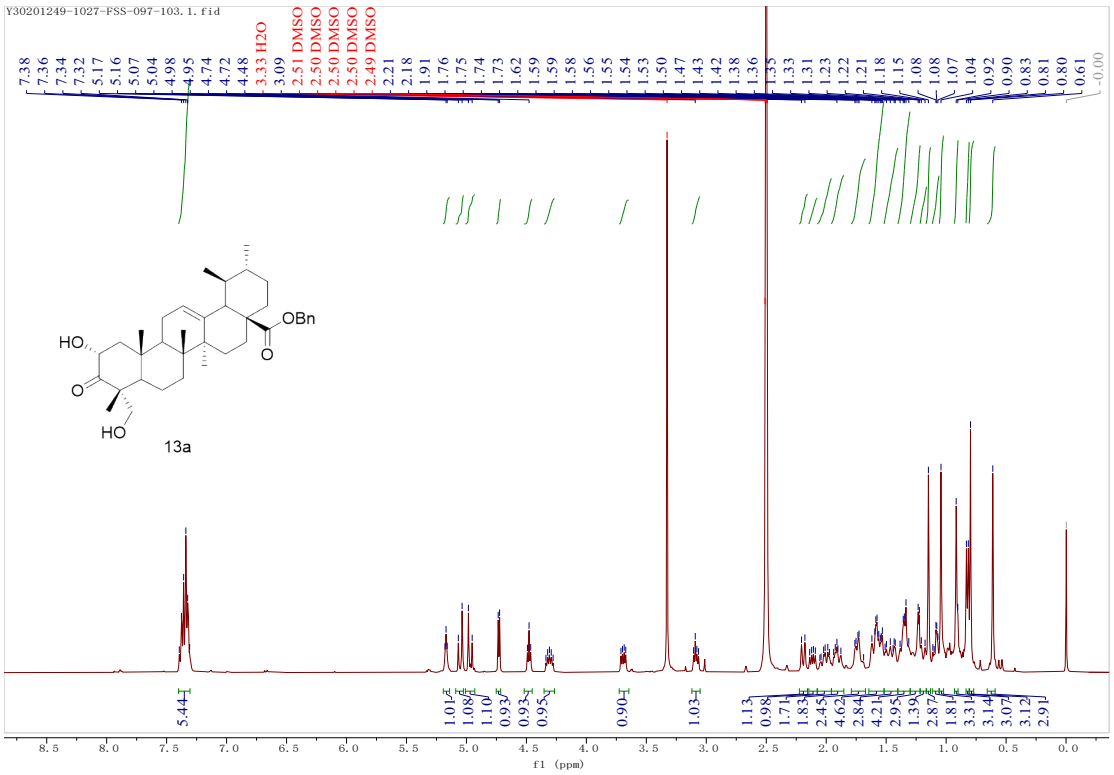

Y30201249-1201-FSS-141-2.100001.fid
140.2
125.6
73.9
69.7
68.4
55.2
49.0
48.6
43.4
42.9
40.9
40.4
40.3
39.6
39.2
37.5
36.7
33.5
31.7
28.3
27.1
24.4
24.2
24.1
22.1
19.1
18.3
17.6
16.9
13.7
OH
HO
HO
3
f1 (ppm)

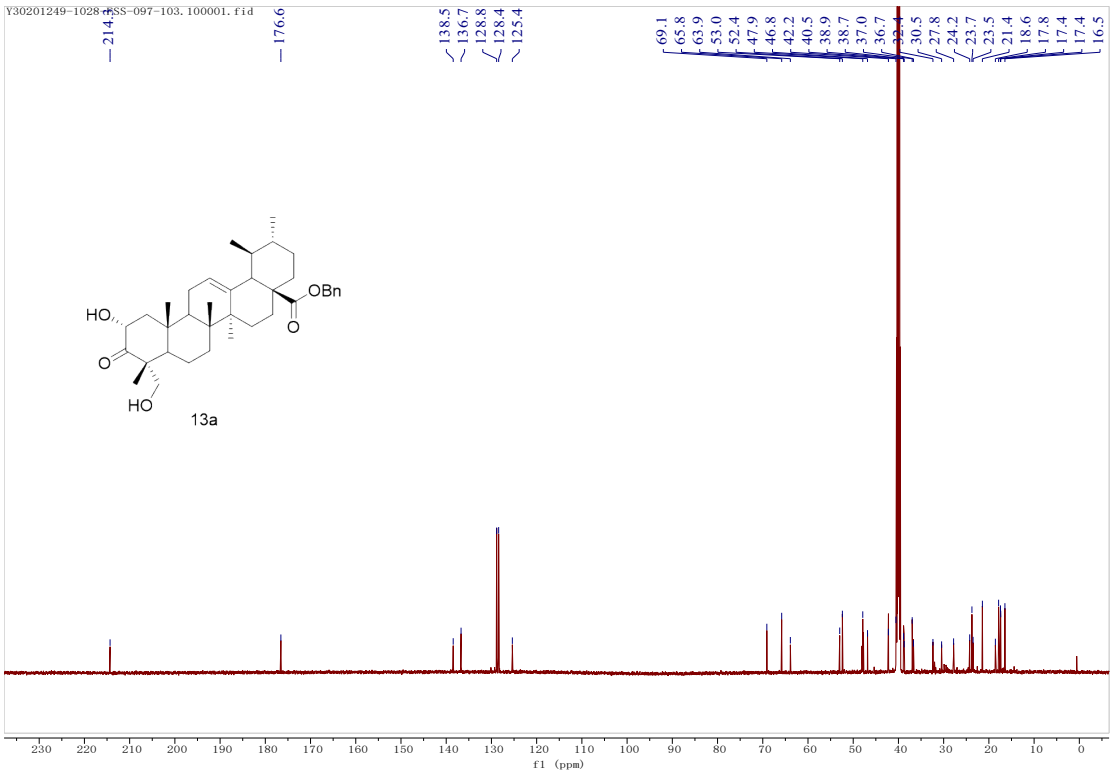

Y10180427-1215-100-191.1.fid
Pyridine-d5
8.74
7.59
7.59
7.59
7.22
5.49
4.52
4.50
3.69
3.67
2.68
2.67
2.36
2.05
2.04
2.04
2.04
2.03
2.03
2.03
2.02
2.02
2.02
2.01
2.01
2.00
1.99
1.99
1.97
1.97
1.96
1.96
1.93
1.93
1.93
1.91
1.91
1.91
1.68
1.59
1.57
1.56
1.55
1.50
1.49
1.48
1.47
1.39
1.37
1.36
1.35
1.24
1.03
1.02
1.00
1.00
0.99
0.98
0.97
0.89
OH
O
HO
OH
4
1.01
1.01
1.84
1.01
1.37
1.26
2.34
2.76
2.41
1.36
1.31
1.53
2.93
2.25
2.47
3.10
1.37
6.08
3.59
3.08
f1 (ppm)

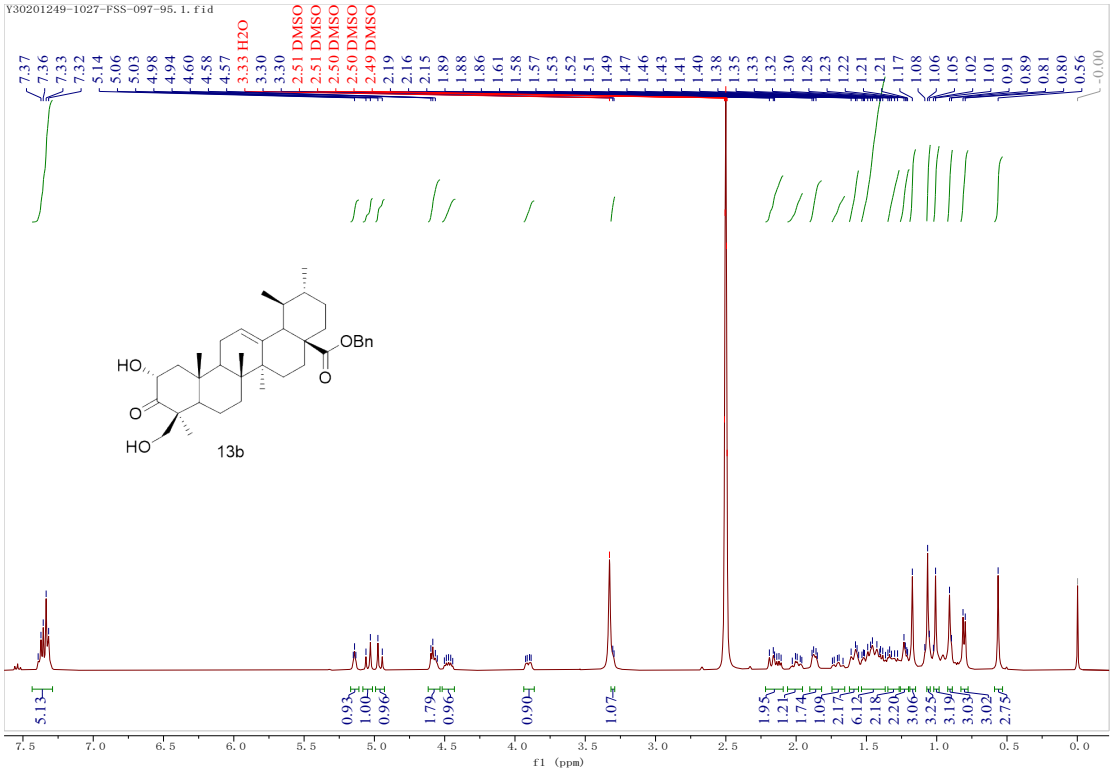

Y10180427-1228-100-191.400001.fid
179.4
139.2
125.5
80.1
64.5
56.3
53.4
48.0
48.0
43.1
42.4
39.9
39.4
39.3
38.8
37.4
37.0
33.8
28.6
23.8
23.8
23.6
21.3
19.0
17.5
17.2
OH
O
HO
OH
4
f1 (ppm)

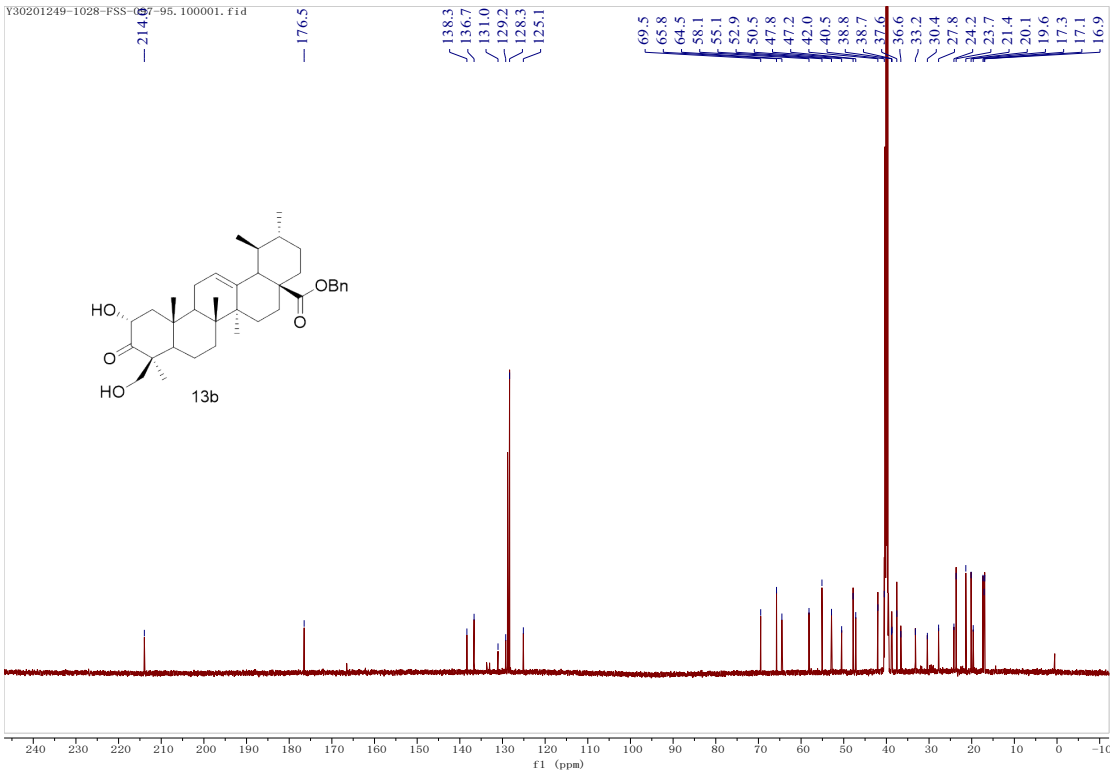

Y10180427-1213-100-167-2.1.fid
5.22
4.87 HDO
4.13
4.11
4.07
3.65
3.64
3.55
3.53
3.32 MeOD
3.31 MeOD
3.31 MeOD
3.31 CD3OD
3.31 MeOD
3.30 MeOD
1.94
1.93
1.91
1.69
1.68
1.68
1.66
1.65
1.63
1.62
1.61
1.60
1.59
1.41
1.39
1.38
1.36
1.36
1.34
1.31
1.30
1.29
1.28
1.12
0.98
0.97
0.96
0.96
0.95
0.90
0.89
0.88
0.83
0.83
0.01
OH
O
HO
HO
HO
5
0.91
0.87
0.93
0.91
0.94
0.90
0.92
1.21
2.99
0.96
7.74
1.23
5.11
7.71
2.65
1.16
1.32
6.36
3.33
2.85
f1 (ppm)

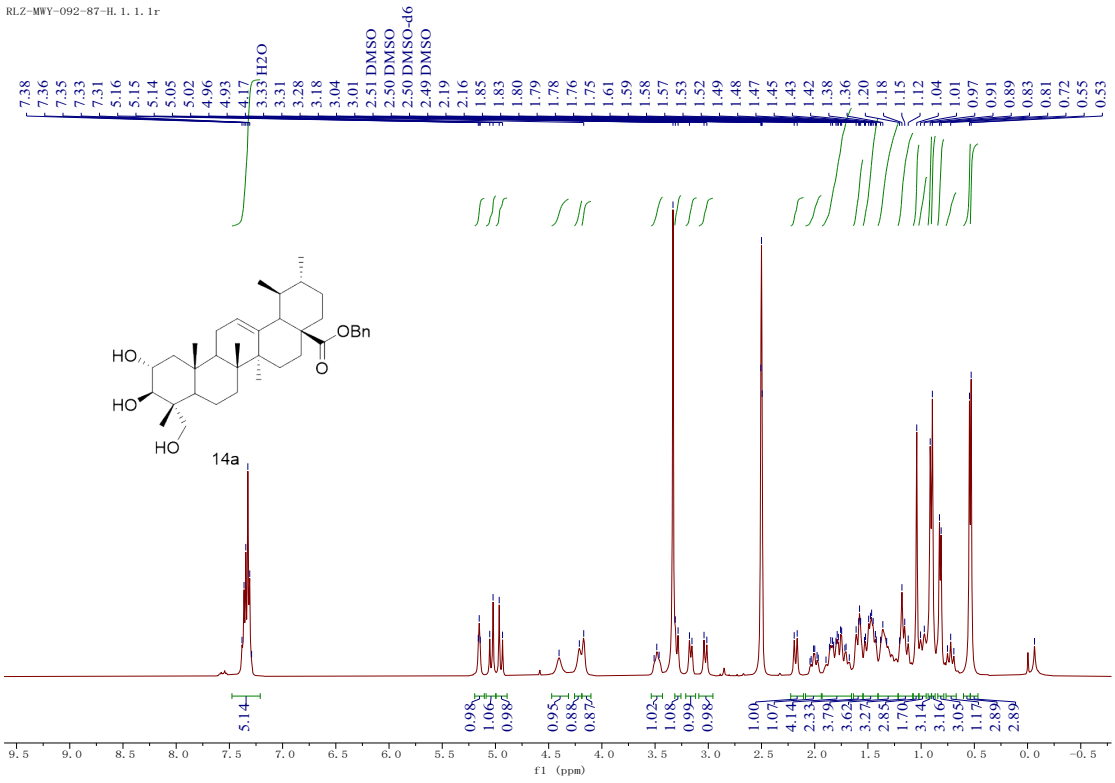

Y10180427-1213-100-167-2.100002.fid
181.6
139.7
126.7
74.7
63.7
54.3
49.4 MeOD
49.3 MeOD
49.1 MeOD
49.1
49.0 CD3OD
48.9
48.9 MeOD
48.7 MeOD
48.7
48.6 MeOD
47.2
43.2
40.7
40.4
40.4
39.5
38.1
37.6
34.1
31.8
29.2
28.0
25.3
24.6
24.1
21.6
19.7
17.7
16.4
OH
O
HO
HO
HO
5
f1 (ppm)

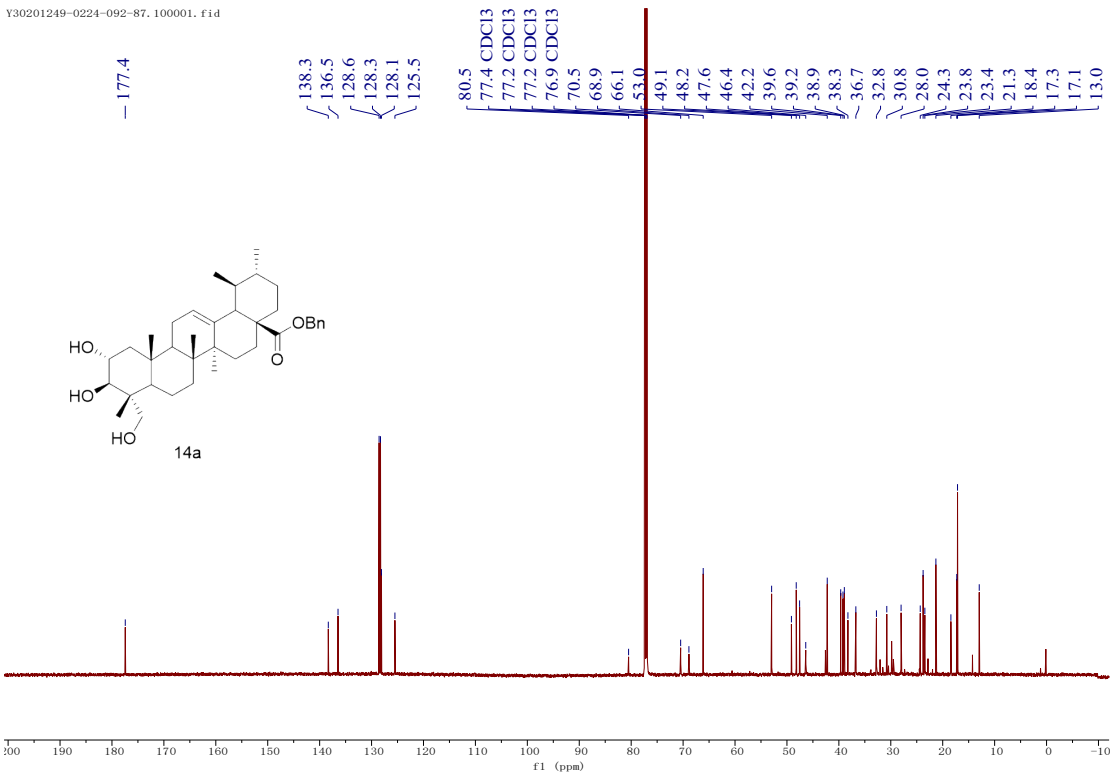

Y30201249-1027-FSS-097-103.1.fid
7.38
7.36
7.34
7.32
5.17
5.16
5.07
5.04
4.98
4.95
4.74
4.72
4.48
3.33 H2O
3.09
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.21
2.18
1.91
1.76
1.75
1.74
1.73
1.62
1.59
1.59
1.58
1.56
1.55
1.54
1.53
1.50
1.47
1.43
1.42
1.38
1.36
1.35
1.33
1.31
1.23
1.22
1.21
1.18
1.15
1.08
1.08
1.07
1.04
0.92
0.90
0.83
0.81
0.80
0.61
-0.00
OBn
O
HO
O
HO
13a
5.44
1.01
1.08
1.10
0.93
0.95
0.90
1.03
1.13
0.98
1.71
1.83
2.45
4.62
2.84
4.21
2.95
1.39
2.87
1.81
3.11
3.14
3.07
3.12
2.91
f1 (ppm)

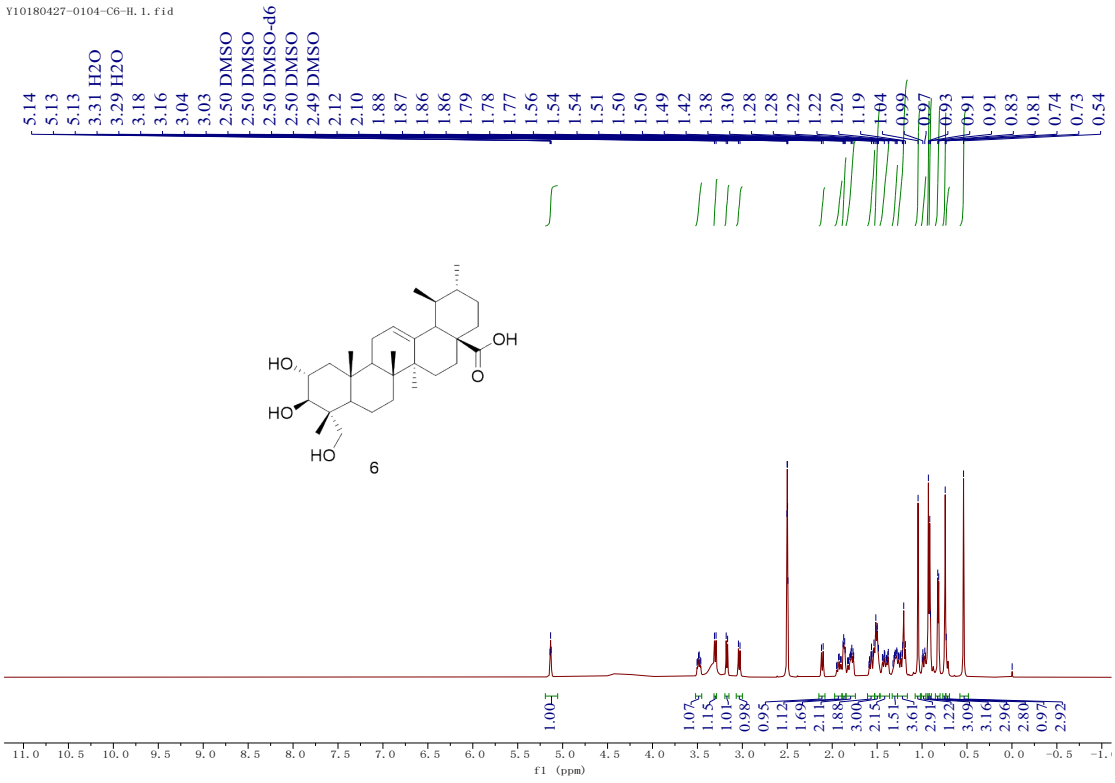

Y30201249-1028-FSS-097-103.100001.fid
214.7
176.6
138.5
136.7
128.8
128.4
125.4
69.1
65.8
63.9
53.0
52.4
47.9
46.8
42.2
40.5
38.9
38.7
37.0
36.7
32.4
30.5
27.8
24.2
23.7
23.5
21.4
18.6
17.8
17.4
17.4
16.5
HO
O
HO
OBn
O
13a
f1 (ppm)

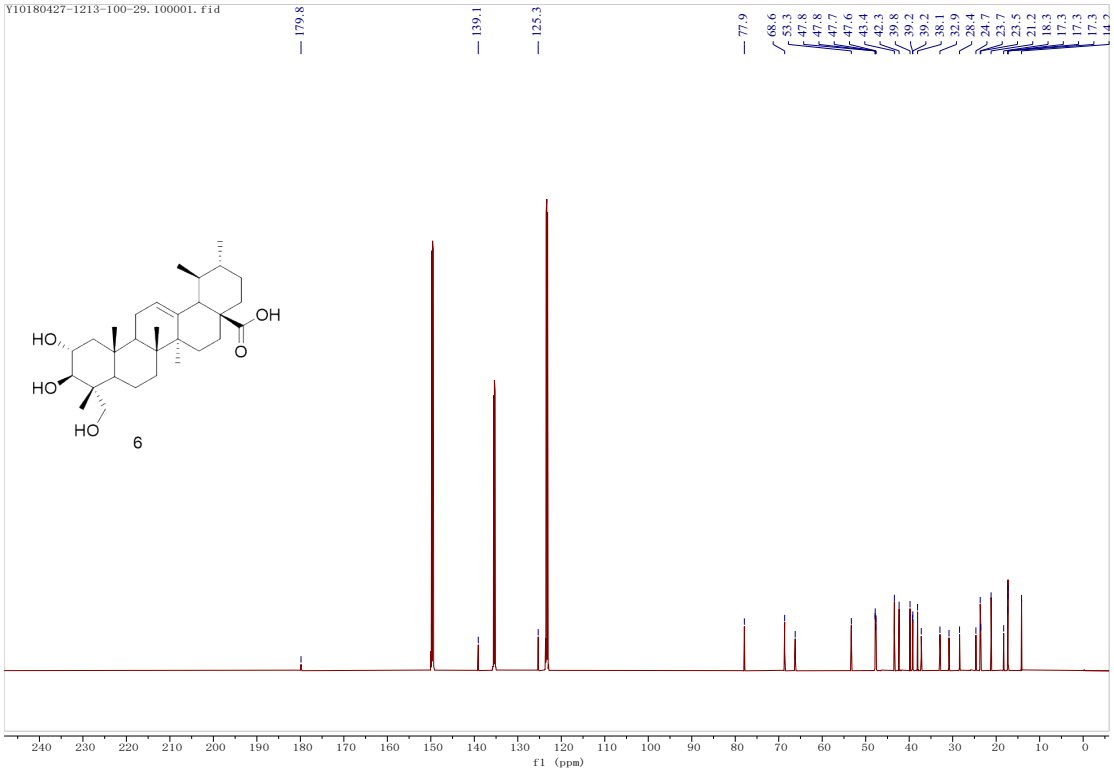

Y30201249-1027-FSS-097-95.1.fid
7.37
7.36
7.33
7.32
5.14
5.06
5.03
4.98
4.94
4.60
4.58
4.57
3.33 H2O
3.30
3.30
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.19
2.16
2.15
1.89
1.88
1.86
1.61
1.58
1.57
1.53
1.52
1.51
1.49
1.47
1.46
1.43
1.41
1.40
1.38
1.35
1.33
1.32
1.30
1.28
1.23
1.22
1.21
1.21
1.17
1.08
1.06
1.05
1.02
1.01
0.91
0.89
0.81
0.80
0.56
-0.00
HO
O
HO
OBn
O
13b
5.13
0.93
1.00
0.96
1.79
0.96
0.90
1.07
1.95
1.21
1.74
1.09
2.17
6.12
2.18
2.20
3.06
3.25
3.19
3.03
3.02
2.75
f1 (ppm)

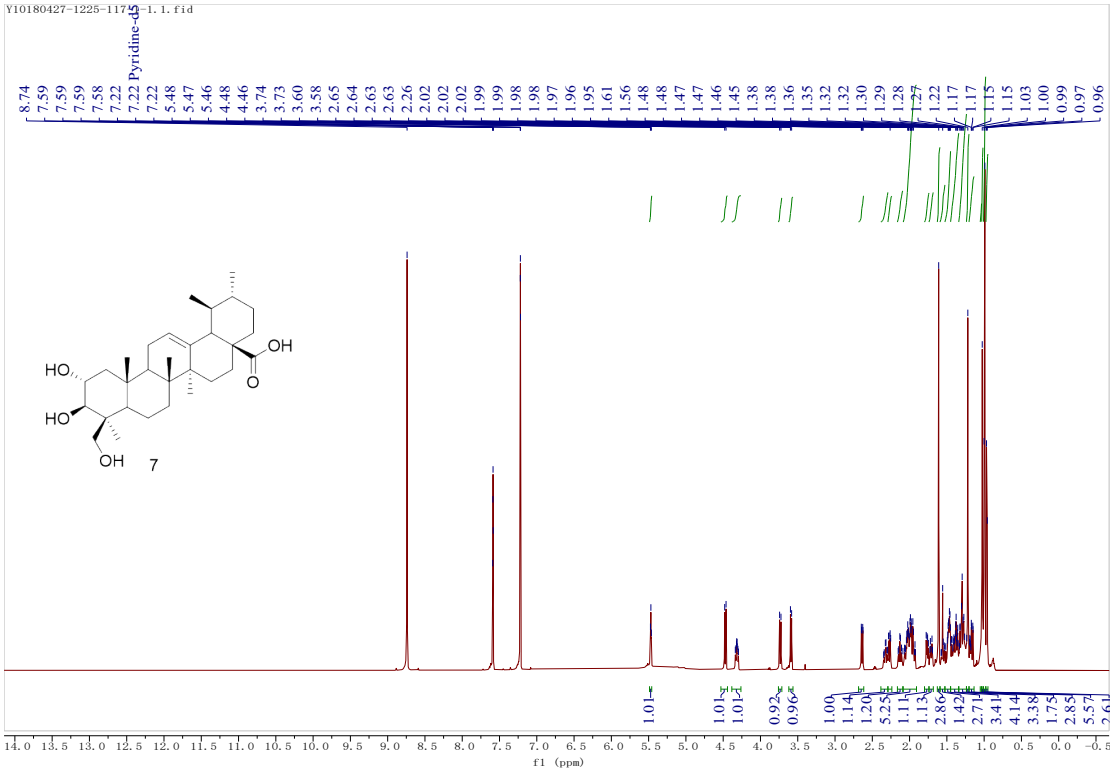

Y30201249-1028-FSS-07-95.100001.fid
214.4
176.5
138.3
136.7
131.0
129.2
128.3
125.1
69.5
65.8
64.5
58.1
55.1
52.9
50.5
47.8
47.2
42.0
40.5
38.8
38.7
37.6
36.6
33.2
30.4
27.8
24.2
23.7
21.4
20.1
19.6
17.3
17.1
16.9
HO
O
HO
OBn
O
13b
f1 (ppm)

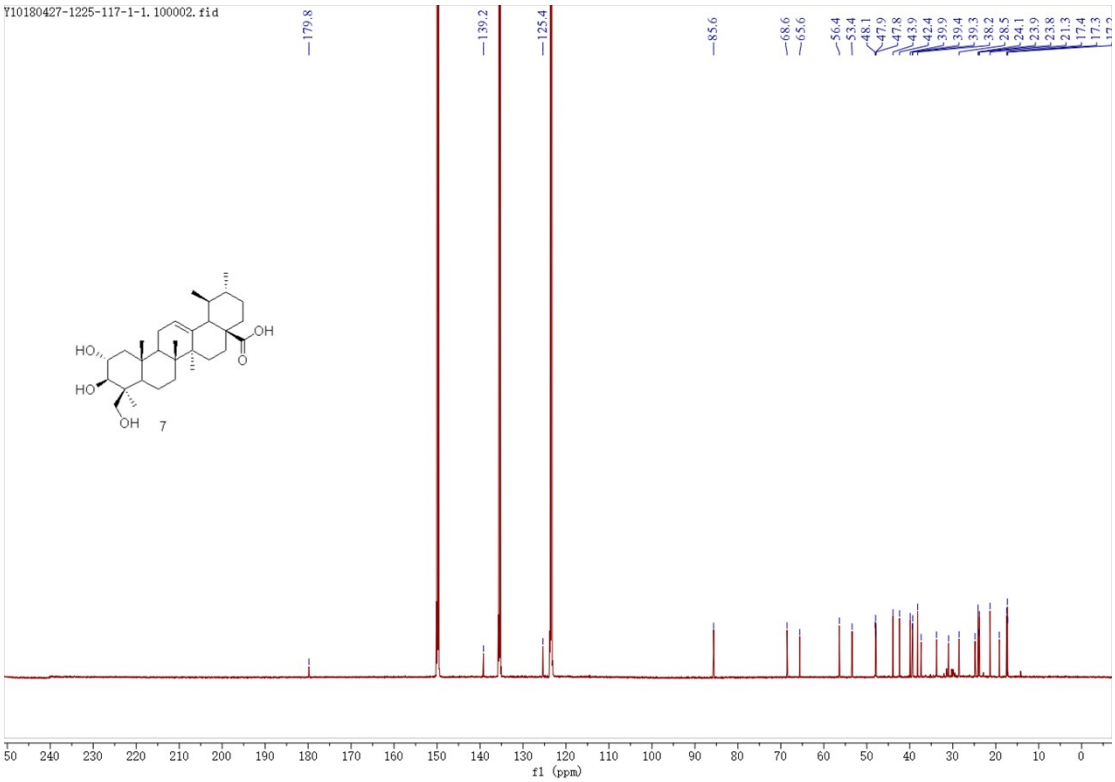

RLZ-MWY-092-87-H.1.1.1r
7.38
7.36
7.35
7.33
7.31
5.16
5.15
5.14
5.05
5.02
4.96
4.93
4.17
3.33 H2O
3.31
3.28
3.18
3.04
3.01
2.51 DMSO
2.50 DMSO
2.50 DMSO-d6
2.49 DMSO
2.19
2.16
1.85
1.83
1.80
1.79
1.78
1.76
1.75
1.61
1.59
1.58
1.57
1.53
1.52
1.49
1.48
1.47
1.45
1.43
1.42
1.38
1.36
1.20
1.18
1.15
1.12
1.04
1.01
0.97
0.91
0.89
0.83
0.81
0.72
0.55
0.53
HO
HO
HO
OBn
O
14a
5.14
0.98
1.06
0.98
0.95
0.88
0.87
1.02
1.08
0.99
0.98
1.00
1.07
4.14
2.33
3.79
3.62
3.27
2.85
1.70
3.14
3.16
3.05
1.17
2.89
2.89
f1 (ppm)


Y30201249-0224-092-87.100001.fid
177.4
138.3
136.5
128.6
128.3
128.1
125.5
80.5
77.4 CDCl3
77.2 CDCl3
77.2 CDCl3
76.9 CDCl3
70.5
68.9
66.1
53.0
49.1
48.2
47.6
46.4
42.2
39.6
39.2
38.9
38.3
36.7
32.8
30.8
28.0
24.3
23.8
23.4
21.3
18.4
17.3
17.1
13.0
HO
HO
HO
OBn
O
14a
f1 (ppm)


Y10180427-0104-C6-H.1.fid
5.14
5.13
5.13
3.31 H2O
3.29 H2O
3.18
3.16
3.04
3.03
2.50 DMSO
2.50 DMSO
2.50 DMSO-d6
2.50 DMSO
2.49 DMSO
2.12
2.10
1.88
1.87
1.86
1.86
1.79
1.78
1.77
1.56
1.54
1.54
1.51
1.50
1.50
1.49
1.42
1.38
1.30
1.28
1.28
1.22
1.22
1.20
1.19
1.04
0.99
0.97
0.93
0.91
0.91
0.83
0.81
0.74
0.73
0.54
HO
HO
HO
OH
O
6
1.00
1.07
1.15
1.01
0.98
0.95
1.12
1.69
2.11
1.88
3.00
2.15
1.51
3.61
2.91
1.22
3.09
3.16
2.96
2.80
0.97
2.92
f1 (ppm)


Y10180427-1213-100-29.100001.fid
179.8
139.1
125.3
77.9
68.6
53.3
47.8
47.8
47.7
47.6
43.4
42.3
39.8
39.2
39.2
38.1
32.9
28.4
24.7
23.7
23.5
21.2
18.3
17.3
17.3
17.3
HO
HO
HO
OH
O
6
f1 (ppm)


Y10180427-1225-1174-1.1.fid
8.74
7.59
7.59
7.59
7.58
7.22
7.22 Pyridine-d5
7.22
5.48
5.47
5.46
4.48
4.46
3.74
3.73
3.60
3.58
2.65
2.64
2.63
2.63
2.26
2.02
2.02
2.02
1.99
1.99
1.98
1.98
1.97
1.96
1.95
1.61
1.56
1.48
1.48
1.47
1.47
1.46
1.45
1.38
1.38
1.36
1.35
1.32
1.32
1.30
1.29
1.28
1.27
1.22
1.17
1.17
1.15
1.15
1.03
1.00
0.99
0.97
0.96
HO
HO
OH
OH
7
1.01
1.01
1.01
0.92
0.96
1.00
1.14
1.20
5.25
1.11
1.13
2.86
1.42
2.71
3.41
4.14
3.38
1.75
2.85
5.57
f1 (ppm)



References

1. A Inada, M. Y., H Murata, M Kobayashi, H Toya, Y Kato, T Nakanishi, Phytochemical studies of seeds of medicinal plants. I. Two sulfated triterpenoid glycosides, sulfapatrinosides I and II, from seeds of Patrinia scabiosaefolia FISCHER. *Chemical and Pharmaceutical Bulletin* **1988,** *36* (11), 4269-4274.
2. José A. Guerrero-Analco, L. M., Ammar Saleem, Padma Madiraju, Asim Muhammad, Tony Durst, Pierre Haddad, John Thor Arnason, Bioassay-Guided Isolation of the Antidiabetic Principle from Sorbus decora (Rosaceae) Used Traditionally by the Eeyou Istchee Cree First Nations. *J. Nat. Prod.* **2010,** *73* (9), 1519–1523.
3. Yutaka Sashida, K. O., Tsuyoshi Yamanouchi, Hiroyuki Tanaka, Yukihiro Shoyama, Itsuo Nishioka, Triterpenoids from callus tissue of Actinidia polygama. *Phytochemistry* **1994,** *35* (2), 377-380.
4. Viet Cuong, L. C.; Anh, L. T.; Huu Dat, T. T.; Anh, T. T. P.; Lien, L. Q.; Kim, Y. H.; Tuan Anh, H. L., Cytotoxic and anti-inflammatory activities of secondary metabolites from Ophiorrhiza baviensis growing in Thua Thien Hue, Vietnam. *Nat Prod Res* **2019,** *35* (22), 4218-4224.
5. Sashida, Y. O., Kazunori; Mori, Noriaki; Yamanouchi, Tsuyoshi., Triterpenoids from the fruit galls of Actinidia polygama. *Phytochemistry* **1992,** *31* (8), 2801-2804.