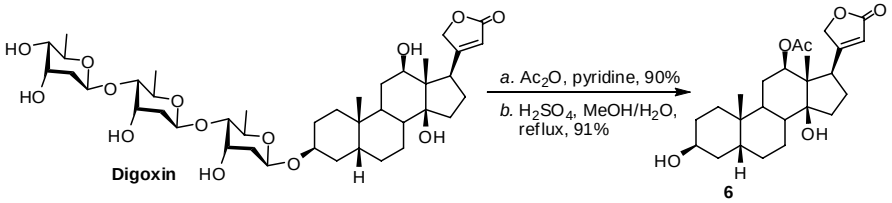
Supporting Information

I. General information

All reactions utilizing air- or moisture-sensitive reagents were carried out in flame-dried glassware under an argon atmosphere, unless otherwise stated. CH_2Cl_2, DMF, DMSO and THF were distilled prior to use according to the standard protocols. Other reagents were purchased and used as received without further purification unless otherwise stated. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with 0.15-0.2 mm pre-coated silica gel (10-40 μm) plate. Compounds were visualized with UV light, 10% sulfuric acid in ethanol and/or ethanolic phosphomolybdic acid (PMA) followed by heating on a hot plate. Flash chromatography was performed with silica gel (300-400 mesh) under pressure. Yields refer to chromatographically homogeneous compounds, unless otherwise stated. NMR spectra were recorded on Varian-300, Bruker-400 and Bruker-500 spectrometers in $CDCl_3$ (or DMSO) with TMS as the internal standard. Chemical shifts (δ) are given in ppm relative to residual chloroform (δ 7.26 for ^{1}H NMR and 77.00 for ^{13}C NMR) and DMSO (δ 1.38 for ^{1}H NMR and 29.8 for ^{13}C NMR), coupling constants (*J*) in Hz. Multiplicity is indicated as follows: s, singlet; d, doublet; t, triplet; q, quattet; m, multiplet; br, broad. High-resolution mass spectra were recorded on IonSpec 4.7 Tesla FTMS or Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS.

II. Experimental Part

12β-Acetoxy-3β,14β-dihydroxy-5β,14β-card-20(22)-enolide (6)

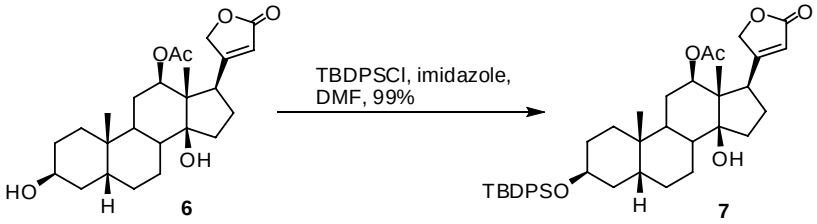


To a solution of digoxin (2.02 g, 2.59 mmol) in pyridine (10 mL) at rt was added

Ac_2O (10 mL). After stirring at 80 °C for 3 h, the reaction was quenched with MeOH (10 mL), and the resulting mixture was concentrated under reduced pressure. The residue was diluted with EtOAc, and the organic phase, after being washed with 1 N HCl, saturated $NaHCO_3$ and water, respectively, was dried over Na_2SO_4 and then concentrated in vacuo. The residue was purified by silica gel column chromatograph (Et_2O/EtOAc, 10:1) to give the digoxin pentacetate (2.32 g, 90%) as a light yellow solid: $[\alpha]_D^{25}$ = 47.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (s, 2 H), 5.32 (dd, *J* = 18.7, 3.9 Hz, 7 H), 4.84 (d, *J* = 18.0 Hz, 3 H), 4.78-4.68 (m, 5 H), 4.65 (d, *J* = 9.1 Hz, 4 H), 4.61-4.51 (m, 3 H), 4.49-4.35 (m, 2 H), 4.05 (dd, *J* = 14.2, 7.1 Hz, 1 H), 3.93 (s, 3 H), 3.86-3.65 (m, 7 H), 3.24 (dd, *J* = 13.9, 6.1 Hz, 5H), 2.84 (d, *J* = 6.4 Hz, 3 H), 2.07 (d, *J* = 8.9 Hz, 12 H), 2.03 (s, 28 H), 1.07 (d, *J* = 6.1 Hz, 6 H), 0.84 (d, *J* = 14.2 Hz, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 173.7, 170.7, 170.2, 170.1, 169.8, 117.6, 98.7, 98.6, 95.8, 85.5, 79.3, 73.2, 72.9, 72.2, 69.9, 69.5, 68.8, 68.8, 67.7, 67.2, 53.9, 45.8, 41.0, 36.1, 35.7, 35.5, 35.0, 32.8, 32.2, 30.0, 27.0, 26.3, 26.2, 23.3, 21.4, 21.2, 21.1, 21.1, 20.8, 20.6, 18.0, 17.8, 17.5, 10.2; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{51}H_{74}O_{19}Na$ 1013.4722, found 1013.4713.

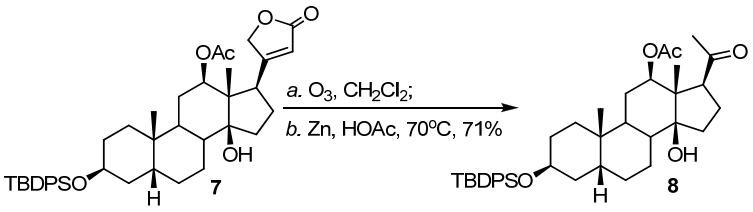
A mixture of the above product (2.32 g, 2.33 mmol) in a mixed solvent of MeOH (200 mL) and H_2SO_4 (0.1 N, 200 mL) was kept refluxed for 1 h. The mixture was neutralized with Et_3N and concentrated under reduced pressure. The residue was diluted with EtOAc, and the organic phase, after being washed with saturated $NaHCO_3$, water and brine, respectively, was dried over Na_2SO_4 and then concentrated in vacuo. The residue was purified by silica gel column chromatograph (Et_2O/EtOAc, 5:1) to give product **6** (910 mg, 91%) as a light yellow solid: $[\alpha]_D^{25}$ = 46.1 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (s, 1 H), 4.92-4.80 (m, 2 H), 4.62 (dd, *J* = 3.9, 12.0 Hz, 1 H), 4.14 (s, 1 H), 2.92-2.87 (m, 1 H), 2.09 (s, 3 H), 0.95 (s, 3 H), 0.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 173.5, 170.8, 117.9, 85.8, 73.3, 66.6, 53.9, 45.9, 41.3, 35.9, 35.3, 33.2, 33.1, 32.1, 29.6, 27.8, 27.2, 26.4, 26.3, 23.5, 21.5, 21.3, 10.3; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{25}H_{36}O_6Na$ 455.2410, found 455.2413.

3β-(*tert*-Butyldiphenylsiloxy)-12β-acetyl-14β-hydroxy-5β,14β-card-20(22)-enolide (7)



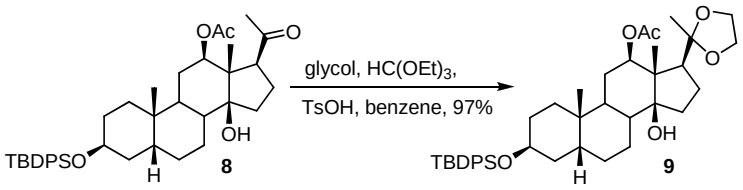
To a solution of **6** (500 mg, 1.16 mmol) in DMF (2 mL) at rt were added imidazole (1.62 g, 23.7 mmol) and TBDPSCl (1.5 mL, 1.16 mmol). After stirring at rt overnight, the mixture was concentrated under reduced pressure. The residue was diluted with EtOAc, and the organic phase, after being washed with saturated $NaHCO_3$, brine and water, respectively, was dried over Na_2SO_4 and then concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 2:1) to give product **7** (750 mg, 99%) as a white solid: $[\alpha]_D^{25}$ = 43.2 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.7 Hz, 4 H), 7.38 (dt, J = 23.0, 7.1 Hz, 6 H), 5.83 (s, 1 H), 4.81 (dt, J = 19.0, 9.5 Hz, 2 H), 4.57 (dd, J = 11.8, 3.6 Hz, 1 H), 4.12 (s, 1 H), 2.87 (dd, J = 9.2, 5.4 Hz, 1 H), 2.08 (s, 4 H), 1.07 (s, 9 H), 0.99 (s, 3 H), 0.88 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 173.7, 170.7, 135.6, 134.6, 134.5, 129.4, 127.4, 117.8, 85.7, 77.4, 77.2, 73.3, 68.1, 53.9, 45.9, 41.3, 36.2, 35.2, 33.6, 32.9, 32.2, 29.9, 29.6, 28.0, 27.1, 27.0, 26.5, 26.4, 23.7, 21.6, 21.2, 19.3, 10.3; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{41}H_{54}O_6SiNa$ 693.3587, found 693.3576.

3β-(*tert*-Butyldiphenylsiloxy)-12β-acetyl-14β-hydroxy-5β,14β-pregn-20-one (8)



A solution of compound **7** (750 mg, 1.12 mmol) in CH_2Cl_2 (30 mL) was cooled to -60 °C in a solid CO_2-acetone-bath. A stream of ozone was passed into the solution until the reaction was complete as monitored by TLC (*cat.* 45 min) and the excess of

ozone was removed by a stream of nitrogen. The solvent was removed under reduced pressure and the residue was dissolved in acetic acid (10 mL). Zinc powder (7.0 g) was added, and the mixture was stirred vigorously at 80 ^{o}C for 3 h. The reaction mixture was filtered and the zinc was washed thoroughly with CH_2Cl_2. The filtrate was washed successively with water and saturated $NaHCO_3$, and was then concentrated. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 8:1) to give **8** (504 mg, 71%) as a white solid: $[\alpha]_D^{25}$ = 43.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, 7.8 Hz, 4 H), 7.41-7.32 (m, 6 H), 4.50 (dd, *J* = 3.9, 11.7 Hz, 1 H), 4.13 (s, 1 H), 4.10 (m, 1 H), 3.04 (t, *J* = 5.1 Hz, 1 H), 2.20 (s, 3 H), 2.11 (s, 3 H), 1.06 (s, 9 H), 0.99 (s, 3 H),0.97 (s, 3 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 216.7, 170.8, 135.7, 134.7, 129.5, 127.5, 85.5, 76.6, 68.3, 57.1, 39.5, 36.4, 35.3, 33.9, 33.7, 33.0, 32.1, 30.0, 28.2, 27.0, 26.6, 26.1, 24.7, 23.9, 21.8, 21.3, 19.3, 9.8; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{39}H_{54}O_5SiNa$ 653.3633, found 653.3661.

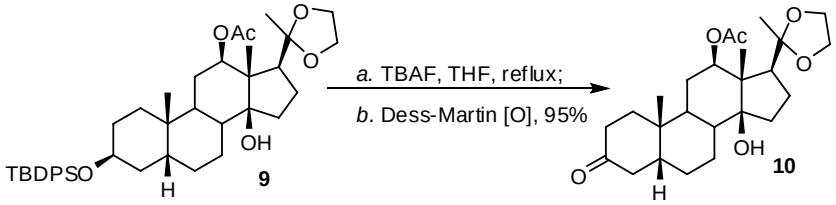


3β-(*tert*-Butyldiphenylsiloxy)-20,20-ethylenedioxy-14β-hydroxy-5β-pregn-12β-acetate (9)

To a solution of compound **8** (200 mg, 0.32 mmol) in benzene (6 mL) at rt were added *p*-TsOH·H_2O (10 mg, 0.052 mmol), ethyleneglycol (0.40 mL, 7.87 mmol) and $HC(OEt)_3$ (0.53 mL, 3.19 mmol). After stirring at rt overnight, the reaction mixture was diluted with EtOAc and washed successively with water and saturated $NaHCO_3$. The organic phase was dried over Na_2SO_4 and concentrated in vacco. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 8:1) to give **9** (207 mg, 97%) as a white solid: $[\alpha]_D^{25}$ = 52.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 4 H), 7.37-7.35 (m, 6 H), 4.46 (dd, *J* = 4.5, 12.0 Hz, 1 H), 4.10-3.96 (m, 6 H), 2.05 (s, 3 H), 1.31 (s, 3 H), 1.12 (s, 3 H), 1.06 (s, 9 H), 1.01 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 135.7, 134.7, 134.7, 129.4, 127.4, 111.7,

84.9, 78.0, 68.3, 64.5, 63.5, 52.7, 52.1, 36.5, 35.3, 39.1, 33.7, 32.1, 31.9, 30.0, 28.1, 27.0, 26.7, 25.7, 23.9, 23.8, 23.2, 21.8, 21.3,19.3, 10.6; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{41}H_{58}O_6SiNa$ 697.3900, found 653.3576.

20,20-Ethylenedioxy-14β-hydroxy-3-oxo-5β-pregn-12β-acetate (10)

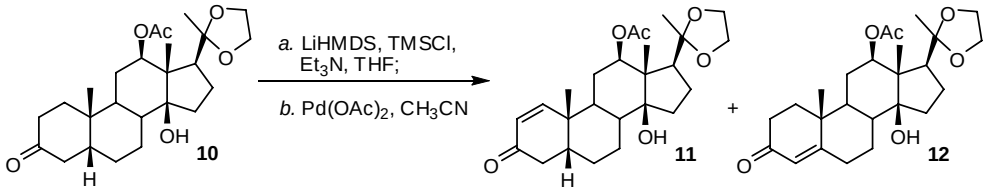


To a solution of compound **9** (207 mg, 0.31 mmol) in THF (10 mL) was added TBAF (5 mL, 1 N in THF). The mixture was refluxed overnight, and then diluted with EtOAc. After washing successively with water and brine, the mixture was dried over Na_2SO_4 and concentrated in vacoo. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 2:1) to give the corresponding 3-ol as a white solid: $[\alpha]_D^{25}$ = 13.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.51 (dd, *J* = 4.2, 12 Hz, 1 H), 4.11 (s, 2 H), 4.02-3.95 (m, 4 H), 2.06 (s, 3 H), 1.32 (s, 3 H), 1.12 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 111.7, 84.9, 77.9, 66.7, 64.4, 63.5, 52.6, 52.0, 39.0, 36.1, 35.3, 33.2, 31.9, 31.8, 29.6, 27.8, 26.4, 25.6, 23.8, 23.6, 23.2, 21.6, 21.3, 10.6; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{25}H_{40}O_6Na$ 459.2723, found 459.2734.

To a solution of the above product in CH_2Cl_2 were added Dess-Martin periodinane (650 mg, 1.53 mmol) and $NaHCO_3$ (129 mg, 1.54 mmol). After stirring at rt overnight, The reaction mixture was filtered and washed thoroughly with CH_2Cl_2. The filtrate was washed successively with water and brine, and then concentrated. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 2:1) to give **10** (127 mg, 95%) as a white solid: $[\alpha]_D^{25}$ = 35.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (dd, *J* = 3.6, 11.4 Hz, 1 H), 4.19 (s, 1 H), 4.05-3.98 (m, 4 H), 2.63 (t, *J* = 14.4 Hz, 1 H), 2.38 (dt, *J* = 5.1, 14.4 Hz, 1 H), 2.26-2.13 (m, 2 H), 2.07 (s, 3 H), 1.33 (s, 3 H)，1.15 (s, 3 H), 1.03 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 171.0, 111.7, 84.6, 77.6, 64.5, 63.5, 52.6, 52.1, 43.9, 42.1, 39.0, 37.1, 36.8, 35.2, 33.1, 32.0, 26.5, 25.7, 23.8, 23.2, 22.4, 21.3, 21.2, 10.6; HRMS (ESI): *m*/*z*

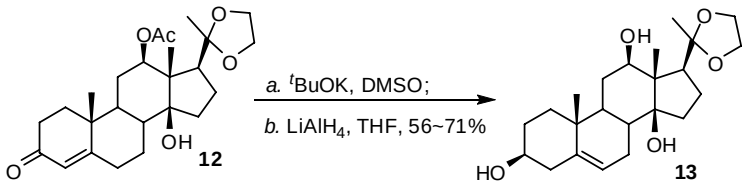
$[M+Na]^+$ calcd for $C_{25}H_{38}O_6Na$ 457.2566, found 457.2625.

20,20-Ethylenedioxy-14β-hydroxy-3-oxo-pregn-4-ene-12β-acetate (12)



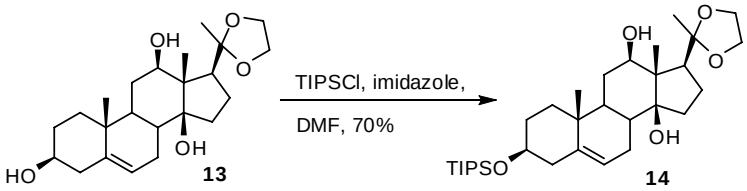
A solution of compound **10** (114 mg, 0.26 mmol) in THF (6 mL) was cooled to -78 °C. Et_3N (0.72 mL, 5.18 mmol), TMSCl (0.65 mL, 5.09 mmol) and LiHMDS (0.79 mL, 2 N in THF) was added under Ar atmasphere. The reaction mixture was stirred at -78 °C for 30 min and then quenched by a pH~7.4 buffer. After warming to rt, the mixture was diluted with EtOAc, the aqueous layer was extracted with EtOAc for 3 times. The organic phase was collected and washed successively with buffer and brine, and then dried over Na_2SO_4, and concentrated in vacuo. The residue was used directly in the next reaction. To a solution of the above residue in CH_3CN (2 mL) at rt was added $Pd(OAc)_2$ (295 mg, 1.31 mmol). After stirring at rt for 1 h, the reaction mixture was filtered and washed thoroughly with CH_2Cl_2. The filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 2:1) to give **11** (9 mg, 8%) and **12** (90 mg, 79%) as white solids. Compound **11**: $[\alpha]_D^{25}$ = 67.2 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, J = 10.2 Hz, 1 H), 5.90 (d, J = 10.2 Hz, 1 H), 4.46 (dd, J = 11.3, 4.7 Hz, 1 H), 4.19 (s, 1H), 4.07-3.92 (m, 5 H), 2.70 (dd, J = 16.5, 14.3 Hz, 1 H), 2.20 (dd, J = 9.1, 5.5 Hz, 1 H), 2.14 (d, J = 4.0 Hz, 1 H), 2.07 (d, J = 2.4 Hz, 3 H), 1.31 (s, 3 H), 1.25 (m, 3 H), 1.19 (s, 3 H), 1.15 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 170.9, 159.8, 127.7, 111.7, 84.3, 77.1, 64.5, 63.5, 52.6, 52.1, 40.7, 38.9, 38.5, 38.2, 32.0, 26.6, 26.5, 23.8, 23.1, 21.5, 21.2, 20.6, 10.6; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{25}H_{36}O_6Na$ 455.2410, found 455.2410. Compound **12**: $[\alpha]_D^{25}$ = 100.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 5.74 (s, 1 H), 4.50 (dd, *J* = 3.9, 11.4 Hz, 1 H), 4.23 (s, 1 H), 4.06-3.98 (m, 4 H), 2.08 (s, 3 H), 1.32 (s, 3 H), 1.19 (s, 3 H), 1.17 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 170.8, 169.9, 123.9, 111.5, 84.0, 77.1, 64.4, 63.4, 52.2, 51.7, 45.7, 38.9, 38.4, 35.6, 33.6, 32.8, 31.8, 27.5, 25.3, 23.6, 22.9, 21.2, 17.3, 10.4; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{25}H_{36}O_6Na$ 455.2410, found 455.2395.

20,20-Ethylenedixoy-pregn-5-ene-3β,12β,14β-triol (13)



To a solution of **12** (1.02 g, 2.36 mmol) in freshly distilled and degassed DMSO (20 mL) was added *t*-BuOK (1.02 g, 9.11 mmol, solid feeder) under Ar atmosphere. The reaction mixture was stirred at rt for 30 min, and then quenched with cold aquous NH_4Cl. After being extracted with cold EtOAc for 3 times, the organic phase was collected and washed successively with aqueous NH_4Cl and brine, and was then dried over Na_2SO_4, and concentrated in vacuo. The residue was used directly in the next reaction. To a solution of the above product at 0 ^oC in THF (10 mL) was added $LiAlH_4$ (500 mg, 1.2 mmol) in portions. The reaction mixture was quenched with EtOAc at 0 ^oC followed by successive addition of water (0.5 mL), NaOH (15%, 0.5 mL) and water (1.5 mL). The suspension was filtered and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatograph (CH_2Cl_2/MeOH, 60:1) to give **13** (518 mg, 56%) as a white solid: $[\alpha]_D^{25}$ = -11.6 (*c* 0.2, DMSO); ^1H NMR (400 MHz, DMSO) δ 5.31 (s, 1 H), 4.59 (d, *J* = 4.5 Hz, 1 H), 4.50 (d, *J* = 5.5 Hz, 1 H), 3.90 (s, 4 H), 3.86 (s, 1 H), 3.34 (s, 1 H), 3.25 (td, *J* = 10.5, 5.4 Hz, 1 H), 3.17 (d, *J* = 5.4 Hz, 1 H), 3.11-3.03 (m, 1 H), 2.55 (dd, *J* = 9.7, 6.6 Hz, 1 H), 2.20-2.03 (m, 3 H), 1.82-1.62 (m, 5 H), 1.58 (dd, *J* = 8.2, 5.5 Hz, 4 H), 1.52-1.39 (m, 3 H), 1.29 (s, 4 H), 0.92 (s, 6 H); ^{13}C NMR (100 MHz, DMSO) δ 130.1, 111.3, 102.0, 74.5, 74.4, 63.3, 60.2, 54.1, 53.4, 43.0, 42.9, 42.2, 33.2, 32.3, 27.2, 26.6, 25.8, 25.8, 22.4, 21.6, 19.2, 17.2, 13.7, 13.1, 9.5; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{23}H_{36}O_5Na$ 415.2460, found 415.2466.

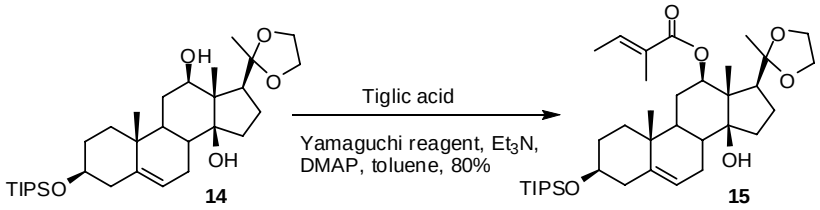
20,20-Ethylenedioxy-pregn-5-ene-3β-triisopropylsiloxy-12β,14β-diol (14)



To a solution of compound **13** (453 mg, 1.16 mmol) in DMF (1 mL) were added

imidazole (396 mg, 5.82 mmol) and TIPSCl (0.5 mL, 3.01 mmol). After stirring at rt overnight, the reaction mixture was diluted with EtOAc and washed successively with saturated $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether /EtOAc, 3:1) to give **14** (445 mg, 70%) as a white solid: $[\alpha]_D^{25}$ = -6.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (d, *J* = 3.6 Hz, 1 H), 4.07 (s, 1 H), 4.04-3.93 (m, 4 H), 3.55 (ddd, *J* = 15.2, 9.8, 4.1 Hz, 1 H), 3.39-3.22 (m, 1 H), 2.64 (dd, *J* = 10.0, 6.9 Hz, 1 H), 2.25 (t, *J* = 12.1 Hz, 3 H), 1.34 (s, 3 H), 1.13-0.94 (m, 30 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 121.5, 112.2, 85.1, 74.7, 72.3, 64.1, 63.4, 53.5, 52.2, 43.4, 42.9, 37.4, 36.8, 35.5, 32.5, 32.2, 29.1, 27.3, 23.5, 23.3, 19.4, 18.1, 12.3, 9.0; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{32}H_{56}O_5SiNa$ 571.3795, found 571.3807.

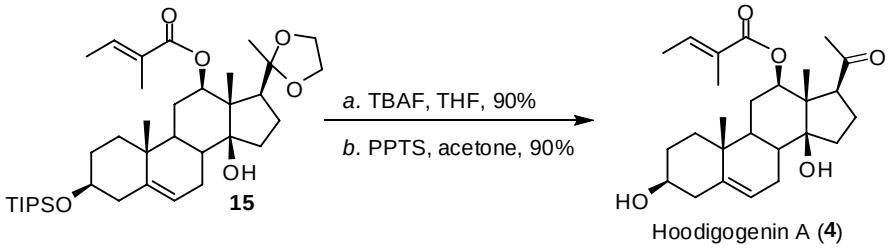
20,20-Ethylenedioxy-14β-hydroxy-pregn-5-ene-3β-triisopropylsiloxy-12β-tiglate (15)



To a solution of tiglic acid (96.4 mg, 0.963 mmol) in toluene (5 mL) were added Et_3N (0.4 mL, 3.0 mmol) and 2,4,6-trichlorobenzoyl chloride (0.15 mL, 0.953 mmol). After stirring at rt for 2 h, a solution of compound **14** (440 mg, 0.803 mmol) and DMAP (44 mg, 0.36 mmol) was added. The reaction mixture was stirred at 60 ^{o}C for addtional 12 h. After cooled to rt, the mixture was diluted with EtOAc and washed successively with saturated $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether /EtOAc, 7:1) to give **15** (485 mg, 80%) as a white solid: $[\alpha]_D^{25}$ = -16.7 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.78 (m, 1 H), 5.37 (d, *J* = 3.7 Hz, 1 H), 4.57 (dd, *J* = 11.8, 4.4 Hz, 1 H), 4.20 (s, 1 H), 4.10-3.92 (m, 4 H), 3.65-3.47 (m, 1 H), 2.26 (d, *J* = 6.5 Hz, 4 H), 1.04 (s, 27 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 139.9, 137.3, 128.8, 121.4, 111.83, 85.0, 77.5, 72.2, 64.5, 63.5, 52.7, 52.1, 43.1, 42.9, 37.4, 36.9, 35.5, 32.4, 32.1, 27.2, 25.6, 23.84, 22.8, 19.4, 18.0, 14.4, 12.3, 12.0, 10.8; LRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{37}H_{62}O_6SiNa$ 653.4,

found 653.2.

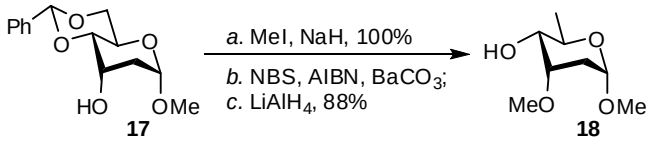
14β-Hydroxy-preg-5-ene-12β-tigloyl-20-one (Hoodigogenin A) (4)



To a solution of compound **15** (476 mg, 0.756 mmol) in THF (5 mL) at 0 °C was added TBAF (10 mL, 1 N in THF). After stirring at 0 °C for 3 h, the reaction mixture was extracted with EtOAc for 3 times. The organic phase was collected and washed successively with water and brine, and was then dried over Na_2SO_4, and concentrated in vacuo. The residue was used directly in the next transformation.

To a solution of the above product in acetone (10 mL) was added PPTS (17 mg, 0.068 mmol). After refluxing for 2 h, the reaction mixture was concentrated in vacuo and then diluted with EtOAc. The solution, after being washed successively with saturated $NaHCO_3$ and brine, was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 7:1) to give **4** (263 mg, 90%) as a white solid: $[\alpha]_D^{25}$ = 5.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.83 (m, 1 H), 5.41 (d, *J* = 4.8 Hz, 1 H), 4.64 (dd, *J* = 11.9, 4.4 Hz, 1 H), 4.27 (s, 1H), 3.63-3.42 (m, 1 H), 3.15 (d, *J* = 4.7 Hz, 1 H), 2.41-2.29 (m, 2 H), 2.20 (s, 3 H), 1.07 (s, 3 H), 1.00 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.9, 167.6, 138.9, 137.7, 128.5, 121.7, 85.6, 75.8, 71.1, 57.0, 53.5, 42.9, 41.8, 37.0, 36.7, 35.6, 34.2, 33.0, 31.2, 27.1, 25.9, 24.2, 19.2, 14.4, 12.0, 9.8; LRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{26}H_{38}O_5Na$ 453.3, found 453.1.

Methyl α-D-cymaropyranoside (18)



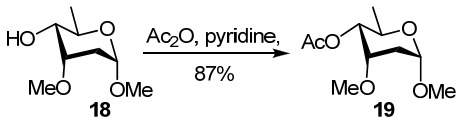
To a solution of compound **17** (12.0 g, 45.1 mmol) in THF (120 mL) cooled in ice-water bath was added NaH (2.70 g, 112 mmol) in portions. After stirring for 30 min, MeI (3.3 mL, 50.8 mmol) was added in ice-water bath. After stirring for additional 4 h, the reaction mixture was quenched carefully with MeOH. The solvent

was removed under reduced pressure. The residue was purified by silica gel column chromatograph (petroleum ether /EtOAc, 5:1) to give the corresponding 3-*O*-methyl derivative as a white solid (12.6 g, 100%): $[\alpha]_D^{25}$ = 120.0 (*c* 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.50 (m, 2 H), 7.35-7.37 (m, 3 H), 5.53 (s, 1 H), 4.69 (d, *J* = 4.2 Hz, 1 H), 4.36-4.27 (m, 2 H), 3.79 (d, *J* = 2.7 Hz, 1 H), 3.73-3.67 (m, 2 H),3.55 (s, 3 H), 3.39 (s, 3 H), 2.22 (dd, *J* = 2.7, 14.4 Hz, 1 H), 1.94 (dt, *J* = 4.2, 13.2 Hz, 1 H), 1.59 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 128.9, 128.2, 126.2, 102.2, 97.8, 80.5, 73.8, 69.5, 59.5, 58.1, 55.5, 34.2. LRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{15}H_{20}O_5Na$ 303.1, found 303.2.

To a solution of the above product (11.6 g, 41.3 mmol) in CCl_4 (120 mL) were added NBS (8.0 g, 44.9 mmol), AIBN (386 mg, 2.35 mmol) and $BaCO_3$ (5.0 g, 25.3 mmol). After refluxing for 1 h, the reaction mixture was cooled to rt and diluted with EtOAc. The mixture, after being washed successively with saturated $NaHCO_3$ and brine, was dried over Na_2SO_4, and concentrated in vacuo. The residue was used directly in the next transformation.

To a solution of the above product in THF (100 mL) in ice-water bath was added $LiAlH_4$ in portions. After stirring at 50 °C for 3 h, the reaction mixture was quenched with EtOAc at 0 °C followed by successive addition of water (2.7 mL), NaOH (15%, 2.7 mL) and water (8.1 mL). The suspension was filtered and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether /EtOAc, 3:1) to give **18** (6.34 g, 88% for 2 steps) as a light yellow syrup: $[\alpha]_D^{25}$ = 128.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.63 (d, *J* = 3.9 Hz, 1 H), 3.84 (dd, *J* = 2.7, 6.6 Hz, 1 H), 3.58 (d, *J* = 3 Hz, 1 H), 3,43 (s, 3 H), 3.34 (s, 3 H), 3.25 (t, *J* = 9.3, 2.4 Hz, 1 H), 2.52 (d, *J* = 10.2, 1 H), 2.26 (d, *J* = 15.0 Hz, 1 H), 1.74 (dt, *J* = 3.9, 15.0 Hz, 1 H), 1.27 (d, *J* = 6.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.4, 75.5, 72.2, 64.4, 57.0, 55.5, 31.0, 17.9; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_8H_{16}O_4Na$ 199.0946, found 199.0945.

Methyl 4-*O*-acetyl-α-D-cymaropyranoside (19)

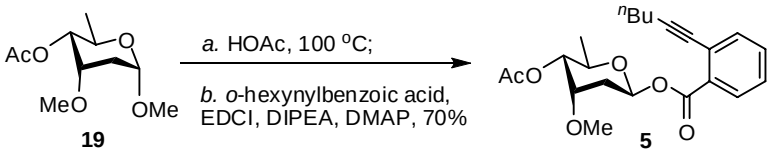


18 **19**

To a solution of **18** (6.34 g, 36.5 mmol) in pyridine (100 mL) was added Ac_2O (13.0 mL). After stirring at rt overnight, the reaction was carefully quenched with

MeOH. The solvent was removed under reduced pressure. The residue was disolved in EtOAc and washed successively with 1 N HCl, saturated $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 2:1) to give **19** (263 mg, 90%) as a colorless syrup: $[\alpha]_D^{25}$ = 169.9 (*c* 0.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.66 (dd, *J* = 3.6, 1.8 Hz, 1 H), 4.62 (d, *J* = 3 Hz, 1 H), 4.25-4.20 (m, 1 H), 3.73 (dd, *J* = 9.0, 3.3 Hz, 1 H), 3.39 (s, 3 H), 3.36 (s, 3 H), 2.20-2.13 (m, 1H), 2.11 (s, 1 H), 1.85 (dt, *J* = 4.2, 14.4 Hz, 1 H), 1.18 (d, *J* = 6.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 97.5, 74.3, 73.8, 62.3, 58.0, 55.4, 32.4, 21.1, 17.4; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{10}H_{18}O_5Na$ 241.1052, found 241.1047.

4-*O*-Acetyl-D-cymaropyranosyl *ortho*-hexynylbenzoate (5)

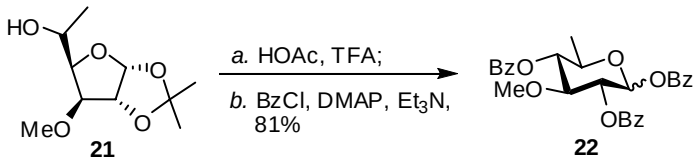


A solution of **19** (300 mg) in HOAc (50 mL, 80%) was stirred at 100 °C for 2 h. The solvent was removed under reduced pressure, and the residue was diluted with EtOAc. The resulting solution, after being washed successively with saturated $NaHCO_3$ and brine, was dried over Na_2SO_4, and concentrated in vacuo. The residue was used directly in the next transformation.

To a solution of the above residue in CH_2Cl_2 (10 mL) were added 2'-(hex-1-ynyl)benzoic acid (446 mg, 2.21 mmol), DMAP (336 mg, 2.75 mmol), EDCI (424 mg, 2.21 mmol) and DIPEA (0.70 mL, 4.00 mmol). After stirring at rt for 12 h, the reaction mixture was diluted with EtOAc and washed successively with 1 N HCl, saturated $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether /EtOAc, 7:1) to give **5** (374 mg, 70% for 2 steps) as a light yellow syrup. **5β**: $[\alpha]_D^{25}$ = 47.3 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1 H), 7.50 (d, *J* = 7.5 Hz, 1 H), 7.42 (t, *J* = 7.5 Hz, 1 H), 7.30 (t, *J* = 7.3 Hz, 1 H), 6.29 (d, *J* = 8.3 Hz, 1 H), 4.70 (dd, *J* = 8.5, 2.2 Hz, 1 H), 4.28-4.15 (m, 1 H), 3.92 (d, *J* = 2.4 Hz, 1 H), 3.43 (s, 3 H), 2.47 (t, *J* = 7.0 Hz, 2 H), 2.42-2.29 (m, 1 H), 2.13 (s, 3 H), 1.93 (dd, *J* = 12.4, 9.7 Hz, 1 H), 1.71-1.57 (m, 4 H), 1.49 (dd, *J* = 14.8, 7.3 Hz, 2 H), 1.25 (d, *J* = 6.4 Hz, 3 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 164.4, 134.4, 131.8, 131.0, 130.4, 127.0, 125.0, 96.5, 91.9, 79.2, 73.7,

73.6, 69.8, 57.6, 32.8, 30.7, 22.1, 21.0, 19.5, 18.2, 13.6; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{22}H_{28}O_6Na$ 411.1784, found 411.1784.

2,4-Di-*O*-benzoyl-D-thevetopyranosyl benzoate (22)

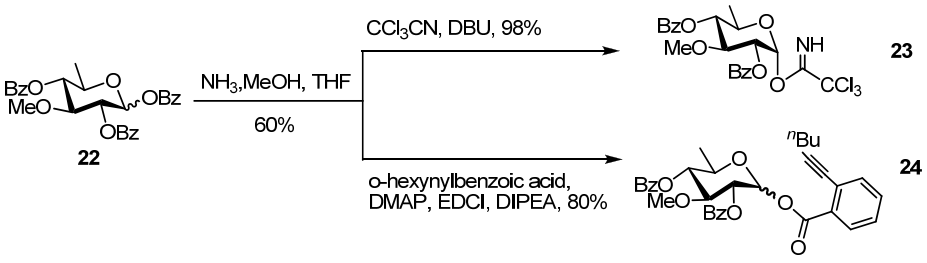


21 **22**

To a solution of compound **21** (241 mg, 1.10 mmol) in HOAc (10 mL, 80%) was added TFA (60 μL, 0.81 mmol). After stirring at 70 °C for 1 h, the solvent was removed under reduced pressure. The residue was used directly in the next transformation.

To a solution of the above residue in CH_2Cl_2 (5 mL) were added TEA (1.7 mL), BzCl (0.7 mL, 12.0 mmol) and DMAP (10 mg, 0.082 mmol). The mixture was stirred at rt for 5 h, and was then diluted with CH_2Cl_2. The mixture, after being washed successively with 1 N HCl, saturated $NaHCO_3$ and brine, was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 8:1) to give **22** (437 mg, 81% for 2 steps; α:β = 1.6:1, inseparable) as a white solid: ^{1}H NMR (400 MHz, CDCl3) δ 8.06 (m, 7 H), 7.84-7.32 (m, 10 H), 6.71 (d, J = 3.7 Hz, 0.60 H), 6.11 (d, J = 8.3 Hz, 0.39 H), 5.66 (t, J = 8.8 Hz, 0.42 H), 5.46 (dd, J = 9.9, 3.8 Hz, 0.69 H), 5.27 (td, J = 9.5, 3.3 Hz, 0.80 H), 4.40-4.22 (m, 0.76 H), 4.21-4.05 (m, 0.83 H), 3.96 (dt, J = 18.6, 7.8 Hz, 1 H), 3.50 (s, 2 H), 3.44 (s, 1.30 H), 3.27 (s, 0.47 H), 1.33 (dd, J = 20.3, 6.1 Hz, 4 H); HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{28}H_{26}O_8Na$ 513.1525, found 513.1517.

2,4-Di-*O*-benzoyl-α-D-thevetopyranosyl trichloroacetimidate (23) and 2,4-Di-*O*-benzoyl-D-thevetopyranosyl *ortho*-hexynylbenzoate (24)



22

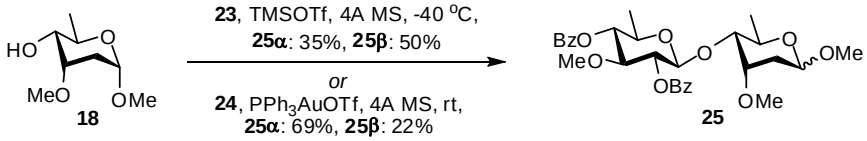
A solution of compound **22** (1.52 g, 3.12 mmol) in THF/MeOH (35 mL/15 mL) was cooled in ice-water bath. A stream of NH_3 was passed into the solution for 30 min.

After stirring in NH_3 atmosphere at rt for additional 12 h, the reaction mixture was concentrated. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 6:1) to give the corresponding lactol as a white solid (723 mg, 60%), which was used directly in the next transformations.

To a solution of the above lactol (700 mg, 1.81 mmol) in CH_2Cl_2 (10 mL) were added CCl_3CN (1 mL, 10 mmol) and DBU (cat.). After stirring at rt for 30 min, the mixture was concentrated. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 10:1) to give **23** (942 mg, 98%; α anomer predominantly) as a white solid. The α isomer: $[\alpha]_D^{25}$ = 53.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03-8.13 (m, 4 H), 7.41-7.61 (m, 6 H), 6.61 (d, *J* = 3.6 Hz, 1 H), 5.35 (dd, *J* = 3.9, 9.6 Hz, 1 H), 5.23 (t, *J* = 9.6 Hz, 1 H), 4.18-4.25 (m, 1 H), 4.10 (t, *J* = 9.6 Hz, 1 H), 3.46 (s, 3 H), 1.30 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 160.6, 133.5, 129.9, 129.8, 129.5, 129.3, 128.6, 128.5, 93.7, 91.1, 78.8, 74.7, 72.5, 68.8, 60.7, 17.5; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{23}H_{22}Cl_3NO_7Na$ 552.0360, found 552.0372.

Compound **24** (594 mg, 80%, α:β = 1:2, inseparable) was prepared from the lactol following a procedure similar to that for **19→5**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 2 H), 8.06-7.91 (m, 3 H), 7.71-7.33 (m, 9 H), 7.32-7.23 (m, 1 H), 6.72 (d, *J* = 3.8 Hz, 0.34H), 6.12 (d, *J* = 8.3 Hz, 0.68 H), 5.77-5.54 (m, 0.68 H), 5.46 (dd, *J* = 9.9, 3.8 Hz, 0.34 H), 5.34-5.11 (m, 1 H), 4.32 (dd, *J* = 10.0, 6.2 Hz, 0.34 H), 4.14 (dd, *J* = 18.0, 8.4 Hz, 0.68 H), 4.01-3.80 (m, 1 H), 3.47 (s, 1 H), 3.42 (s, 2 H), 2.45 (dt, *J* = 18.6, 7.1 Hz, 2 H), 1.72-1.39 (m, 5 H), 1.39-1.18 (m, 4 H), 0.93 (m, 3 H); HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{34}H_{34}O_8Na$ 593.2151, found 593.2146.

Methyl 4-*O*-(2,4-di-*O*-benzoyl-D-thevetopyranosyl)-α-D-cymaropyranoside (25)

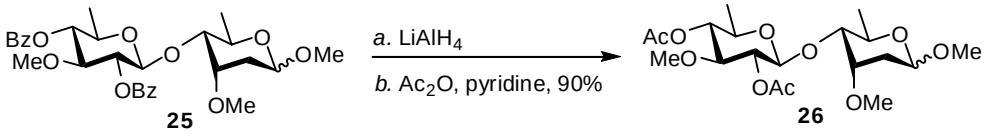


Procedure I: To a mixture of **18** (201 mg, 1.41 mmol), **23** (726 mg, 1.69 mmol) and 4Å MS in dry CH_2Cl_2 (10 mL) at -40 °C was added TMSOTf (25 μL, 0.14 mmol). The mixture was kept at -40 °C for 2 h, which was then filtered through Celite. The filtrate was concentrated to give a residue, which was purified by silica gel column chromatograph (petroleum ether/EtOAc, 5:1~3:1) to provide **25α** (269 mg, 35%) and

25β (384 mg, 50%) as white solids.

Procedure II: To a mixture of **18** (145 mg, 1.02 mmol), **24** (695 mg, 1.22 mmol) and 4Å MS in dry CH_2Cl_2 (10 mL) at rt was added PPh_3AuOTf (4 mL, 0.05 mM). After stirring at rt for 2 h, the mixture was filtered through Celite. The filtrate was concentrated to give a residue, which was purified by silica gel column chromatograph (petroleum ether/EtOAc, 5:1~3:1) to provide **25α** (382 mg, 69%) and **25β** (122 mg, 22%) as white solids. **25α**: $[\alpha]_D^{25}$ = 139.6 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 6.3, 2.1 Hz, 4 H), 7.57 (dd, *J* = 14.8, 7.2 Hz, 2 H), 7.45 (dd, *J* = 13.5, 6.8 Hz, 4 H), 5.33 (t, *J* = 8.7 Hz, 1 H), 5.15 (t, *J* = 9.4 Hz, 1 H), 4.73 (d, *J* = 7.9 Hz, 1 H), 4.57 (d, *J* = 4.2 Hz, 1 H), 4.08 (dd, *J* = 9.1, 6.4 Hz, 1 H), 3.87-3.62 (m, 3 H), 3.50 (s, 3 H), 3.34 (s, 3 H), 3.29 (d, *J* = 9.5 Hz, 1 H), 3.25 (s, 3 H), 2.13 (d, *J* = 14.9 Hz, 1 H), 1.85-1.72 (m, 1 H), 1.30 (d, *J* = 6.0 Hz, 3 H), 0.98 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.7, 133.3, 133.1, 129.7, 129.7, 129.6, 129.5, 128.5, 128.4, 102.4, 97.4, 83.5, 81.6, 75.8, 74.5, 73.2, 70.3, 61.9, 59.1, 59.0, 55.2, 33.8, 17.6, 17.4; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{29}H_{36}O_{10}Na$ 567.2206, found 567.2190. **25β**: $[\alpha]_D^{25}$ = 29.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-7.95 (m, 4 H), 7.58 (dd, *J* = 15.7, 7.7 Hz, 2 H), 7.46 (dd, *J* = 15.5, 7.8 Hz, 4 H), 5.33 (dd, *J* = 17.5, 8.1 Hz, 1 H), 5.15 (dd, *J* = 18.3, 8.8 Hz, 1 H), 4.70 (d, *J* = 8.0 Hz, 1 H), 4.60 (d, *J* = 7.8 Hz, 1 H), 3.90-3.65 (m, 4 H), 3.48 (s, 3 H), 3.42 (s, 3 H), 3.35 (s, 3 H), 3.32 (d, *J* = 3.6 Hz, 1 H), 3.21 (dd, *J* = 9.5, 2.7 Hz, 1 H), 2.13 (d, *J* = 12.4 Hz, 1 H), 1.31 (d, *J* = 6.1 Hz, 3 H), 0.98 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.9, 164.2, 134.2, 131.6, 131.0, 130.2, 126.8, 124.8, 101.8, 96.2, 91.6, 82.4, 81.0, 79.0, 77.3, 77.0, 76.7, 75.3, 73.5, 72.2, 70.0, 69.5, 58.2, 57.7, 33.5, 30.5, 21.9, 20.7, 20.7, 19.3, 17.8, 17.3, 13.5; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{29}H_{36}O_{10}Na$ 567.2206, found 567.2189.

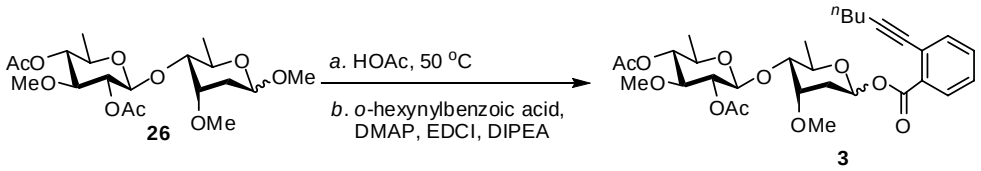
Methyl 4-*O*-(2,4-di-*O*-acetyl-D-thevetopyranosyl)-α-D-cymaropyranoside (26)



To a solution of compound **25** (357 mg, 0.85 mmol) in THF (10 mL) at 0 ^{o}C was added $LiAlH_4$ (50 mg, 1.32 mmol) in portions. After stirring ar rt for 5 h, the mixture was quenched carefully with EtOAc followed by successive addition of water (0.05 mL), NaOH (15%, 0.05 mL) and water (0.15 mL). The suspension was filtered and the filtrate was concentrated in vacuo. The residue was used directly in the next transformation.

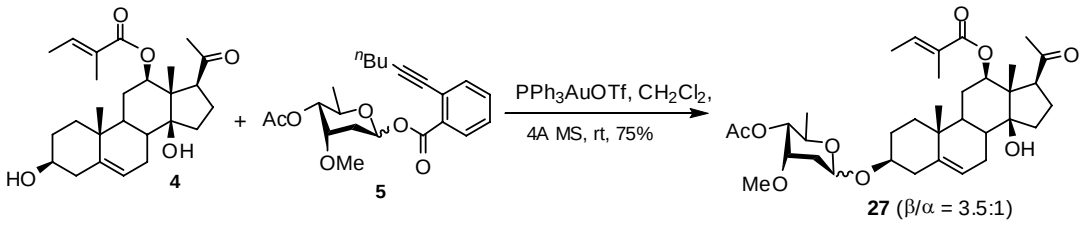
To a solution of the above product in pyridine (5 mL) was added Ac_2O (0.5 mL, 5.0 mmol). After stirring at rt overnight, the reaction was quenched with MeOH, and the solvent was then removed under reduced pressure. The residue was dissolved in EtOAc. The solution, after being washed successively with 1 N HCl, saturated $NaHCO_3$ and brine, was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatograph (petroleum ether/EtOAc, 8:1) to provide **26** (279 mg, 90%) as a white solid. **26α**: $[\alpha]_D^{25}$ = 40.4 (*c* 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (dd, *J* = 9.6, 8.0 Hz, 1 H), 4.74 (t, *J* = 9.5 Hz, 1 H), 4.54 (d, *J* = 4.3 Hz, 1 H), 4.41 (d, *J* = 7.9 Hz, 1 H), 4.17-4.01 (m, 1 H), 3.64 (d, *J* = 3.0 Hz, 1 H), 3.43-3.36 (m, 4 H), 3.31 (s, 3 H), 3.25 (s, 3 H), 3.20 (dd, *J* = 9.5, 2.8 Hz, 1 H), 2.14-2.06 (m, 1 H), 2.03 (d, *J* = 6.1 Hz, 6 H), 1.72 (dt, *J* = 14.7, 4.0 Hz, 1 H), 1.24-1.06 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.8, 102.1, 97.3, 83.1, 81.0, 75.5, 73.5, 72.2, 69.9, 61.9, 58.8, 58.2, 55.1, 33.5, 20.7, 20.7, 17.3, 17.2; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{19}H_{32}O_{10}Na$ 443.1893, found 443.1879. **26β**: $[\alpha]_D^{25}$ = 16.4 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (dd, *J* = 9.6, 8.0 Hz, 1 H), 4.82 (t, *J* = 9.5 Hz, 1 H), 4.64 (dd, *J* = 9.4, 1.7 Hz, 1 H), 4.44 (d, *J* = 7.9 Hz, 1 H), 3.96-3.81 (m, 1 H), 3.76 (d, *J* = 2.9 Hz, 1 H), 3.46 (s, 3 H), 3.43 (s, 3 H), 3.37 (s, 3 H), 3.18 (dd, *J* = 9.4, 2.7 Hz, 1 H), 2.19-2.12 (m, 1 H), 2.10 (s, 3 H), 2.08 (s, 3 H), 1.60-1.48 (m, 1 H), 1.21 (dd, *J* = 6.0, 4.5 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.0, 102.4, 99.0, 84.0, 81.1, 76.3, 73.5, 72.3, 70.1, 68.1, 58.3, 58.1, 56.5, 35.3, 20.9, 20.9, 17.8, 17.5; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{19}H_{32}O_{10}Na$ 443.1893, found 443.1889.

Disaccharide *ortho*-hexynylbenzoate 3



Compound **3** (426 mg, 85% for 2 steps) was prepared from the metyl glycoside **26** following a procedure similar to that for **19**→**5**. (NOTE: The hydrolysis should be kept at 50 °C for about 5 h). **3β**: $[\alpha]_D^{25}$ = 11.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05-7.82 (m, 1 H), 7.53-7.50 (m, 1 H), 7.46-7.41 (dt, *J* = 1.2, 7.2 Hz, 1 H), 7.33-7.28 (dt, *J* = 1.5, 7.5 Hz, 1 H), 6.29 (dd, *J* = 2.4, 8.4 Hz, 1 H), 5.05-4.95 (m, 1 H), 4.82 (t, *J* = 9.5 Hz, 1 H), 4.60 (dd, *J* = 9.6, 1.9 Hz, 1 H), 4.47 (d, *J* = 7.9 Hz, 1 H), 4.24-4.10 (m, 1 H), 3.70 (d, *J* = 3.0 Hz, 1 H), 3.46 (s, 3 H), 3.37 (s, 3 H), 2.14 (dd, *J* = 14.8, 2.7 Hz, 1 H), 3.33 (s, 3 H), 3.25 (dd, *J* = 9.5, 2.7 Hz, 1 H), 3.25 (dd, *J* = 9.5, 2.7 Hz, 1 H), 2.20-2.06 (m, 1 H), 2.11 (d, *J* = 7.2 Hz, 3 H), 2.08 (s, 3 H), 1.79 (dt, *J* = 14.8, 4.1 Hz, 2 H), 1.39-1.13 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 168.9, 164.2, 134.2, 131.6, 131.0, 130.2, 126.8, 124.8, 101.8, 96.2, 91.6, 82.4, 81.0, 79.0, 75.3, 73.5, 72.2, 70.0, 69.5, 58.2, 57.7, 33.5, 30.5, 21.9, 20.7, 20.7, 19.3, 17.8, 17.3, 13.5; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{31}H_{42}O_{11}Na$ 615.2625, found 615.2620.

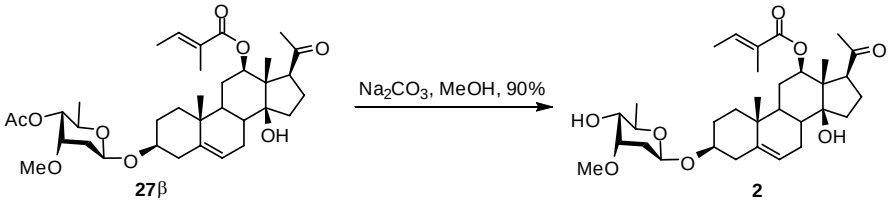
3β-*O*-(4-*O*-Acetyl-β-D-cymaropyranoside)-12β-tigloyl-14β-hydoxy-5α-pregn-20-one (27)



To a mixture of **4** (50 mg, 0.116 mmol), **5** (47 mg, 0.139 mmol) and 4Å MS in dry CH_2Cl_2 (10 mL) at rt was added PPh_3AuOTf (0.4 mL, 0.05 mM). After stirring at rt for 4 h, the mixture was filtered through Celite. The filtrate was concentrated to give a residue, which was purified by silica gel column chromatograph (petroleum ether/EtOAc, 5:1) to provide **27** (77 mg, 75%, β/α = 3.4:1) as a white solid. Compound **27β**: $[\alpha]_D^{25}$ = 24.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ

6.96-6.86 (m, 1 H), 5.40 (d, *J* = 5.0 Hz, 1 H), 4.88 (dd, *J* = 9.3, 1.9 Hz, 1 H), 4.63 (dd, *J* = 11.9, 4.4 Hz, 1 H), 4.52 (dd, *J* = 9.6, 2.9 Hz, 1 H), 4.26 (s, 1 H), 3.83-3.71 (m, 1 H), 3.53 (dt, *J* = 15.8, 5.5 Hz, 1 H), 3.13 (t, *J* = 5.6 Hz, 1 H), 2.19 (s, 3H), 2.09 (s, 3 H), 1.88 (s, 3 H), 1.26 (d, *J* = 12.3 Hz, 3 H), 1.18 (d, *J* = 6.3 Hz, 3 H), 1.05 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.0, 170.3, 167.7, 138.9, 137.8, 128.7, 122.0, 95.7, 85.7, 77.5, 75.9, 75.0, 74.9, 67.8, 58.0, 57.2, 53.7, 43.0, 38.5, 37.2, 37.1, 35.7, 35.1, 34.4, 33.1, 29.7, 29.4, 27.3, 26.0, 24.3, 21.0, 19.3, 18.1, 14.5, 12.1, 9.9; HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{27}H_{43}O_4$ 639.3509, found 639.3569. Compound **27α**: $[\alpha]_D^{25}$ = 58.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-6.85 (m, 1 H), 5.39 (d, *J* = 4.5 Hz, 1 H), 4.92 (dd, *J* = 4.1, 2.6 Hz, 1 H), 3.80 (dd, *J* = 7.3, 2.8 Hz, 1 H), 3.73 (dd, *J* = 8.0, 3.4 Hz, 1 H), 3.39 (s, 3 H), 2.42-2.25 (m, 3 H), 2.19 (s, 3 H), 2.11 (s, 3 H), 1.21 (d, *J* = 6.3 Hz, 3 H), 1.17 (d, *J* = 6.5 Hz, 3 H), 1.06 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.0, 170.5, 167.7, 139.2, 137.8, 128.7, 121.8, 94.2, 85.7, 76.0, 74.1, 73.4, 68.4, 63.2, 57.2, 56.9, 53.7, 43.0, 39.9, 37.1, 37.0, 35.7, 34.4, 33.1, 32.2, 31.4, 30.2, 29.7, 27.6, 27.3, 26.1, 24.4, 21.1, 19.3, 17.4, 14.5, 12.1, 9.9; HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{27}H_{43}O_4$ 639.3509, found 639.3572.

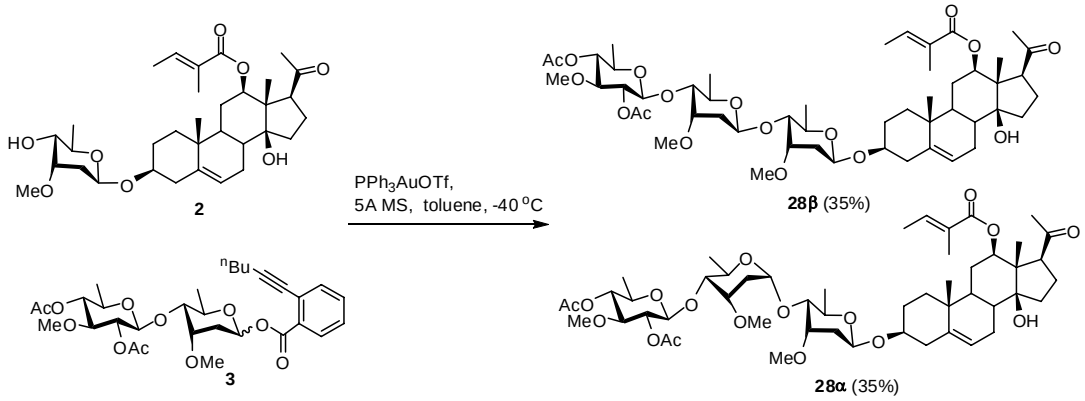
3β-*O*-(β-D-Cymaropyranoside)-14β-hydroxy-pregn-5-ene-12β-tigloyl-20-one (2)



To a solution of compound **27β** (30 mg, 0.049 mmol) in MeOH (5 mL) was added Na_2CO_3 (13 mg, 0.12 mmol). After stirring at rt for 5 h, the mixture was neutralized and concentrated in vacuo. The residue was purified by silica gel column chromatograph (CH_2Cl_2/MeOH, 80:1) to provide **2** (25 mg, 90%) as a white solid: $[\alpha]_D^{25}$ = 17.7 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.86 (m, 1H), 5.41 (d, *J* = 4.7 Hz, 1 H), 4.78 (dd, *J* = 9.6, 1.6 Hz, 1 H), 4.64 (dd, *J* = 11.9, 4.3 Hz, 1 H), 4.27 (s, 1 H), 3.66-3.60 (m, 1 H), 3.60-3.50 (m, 2 H), 3.39 (s, 3 H), 3.21 (s, 1H), 3.14 (t, *J* = 5.5 Hz, 1 H), 2.44-2.25 (m, 3 H), 2.23-2.14 (m, 5 H), 1.06 (s, 3 H), 0.98 (s, 3

H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.1, 167.7, 139.0, 137.8, 128.7, 122.0, 95.5, 85.7, 77.5, 75.9, 72.5, 70.7, 57.2, 57.2, 53.7, 43.0, 38.6, 37.2, 37.1, 35.7, 34.4, 34.1, 33.1, 31.9, 31.4, 30.2, 29.7, 29.4, 29.3, 27.4, 26.1, 24.4, 22.7, 19.3, 18.3, 14.5, 14.09, 12.1, 9.9; LRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{33}H_{50}O_8Na$ 597.3, found 597.6.

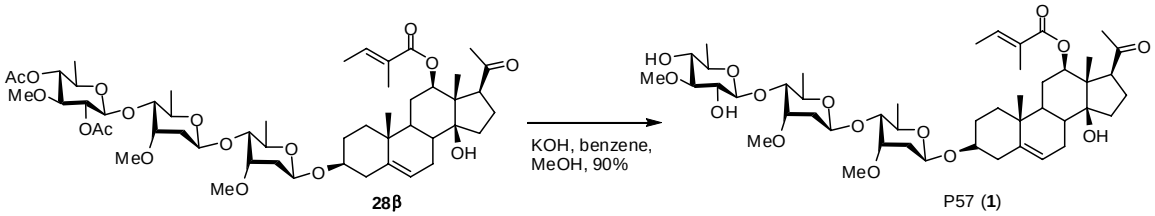
14β-Hydroxy-pregn-5-ene-12β-tigloyl-20-one-3β-*O*-(2,4-di-*O*-acetyl-β-D-thevetopyranosyl)-(1→4)-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside (28)



Compounds **28β** (11 mg, 35%) and **28α** (11 mg, 35%) were prepared from **2** and **3** following a procedure similar to that for **4**→**27**. (NOTE: 5Å MS was used instead of the 4Å MS, and the reaction was conducted in toluene at -40 °C). **28α**: $[\alpha]_D^{25}$ = 67.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.85 (m, 1 H), 5.41 (s, 1 H), 5.00 (dd, *J* = 9.7, 8.0 Hz, 1 H), 4.82 (t, *J* = 9.6 Hz, 2 H), 4.75 (d, *J* = 7.9 Hz, 1 H), 4.63 (dd, *J* = 11.9, 4.4 Hz, 1 H), 4.43 (d, *J* = 7.9 Hz, 1 H), 4.27 (s, 1 H), 3.92-3.69 (m, 4 H), 3.43 (s, 3 H), 3.37 (s, 3 H), 3.20 (dd, *J* = 9.9, 2.8 Hz, 1 H), 3.17-3.08 (m, 2 H), 2.10 (s, 3 H), 2.08 (s, 3 H), 1.88 (s, 3 H), 1.06 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.0, 169.5, 168.9, 167.7, 139.1, 137.7, 128.8, 122.0, 102.3, 95.79, 91.2, 85.7, 83.7, 81.1, 75.9, 74.7, 74.6, 73.4, 72.4, 72.2, 70.2, 69.0, 62.6, 57.7, 57.5, 57.2, 57.1, 53.8, 43.1, 38.7, 37.3, 37.1, 35.8, 34.8, 34.4, 33.1, 31.9, 29.7, 29.5, 27.4, 26.1, 24.4, 20.9, 20.9, 19.3, 18.4, 17.5, 17.4, 14.4, 12.1, 9.9; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{51}H_{78}O_{17}Na$ 985.5137, found 985.5126. **28β**: $[\alpha]_D^{25}$ = 38.4 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (q, *J* = 6.5 Hz, 1 H), 5.40 (s, 1 H), 5.09 -4.93 (m, 1 H), 4.88-4.70 (m, 3 H), 4.63 (dd, *J* = 11.8, 4.0 Hz, 1 H), 4.42 (d, *J* = 7.9 Hz, 1 H),

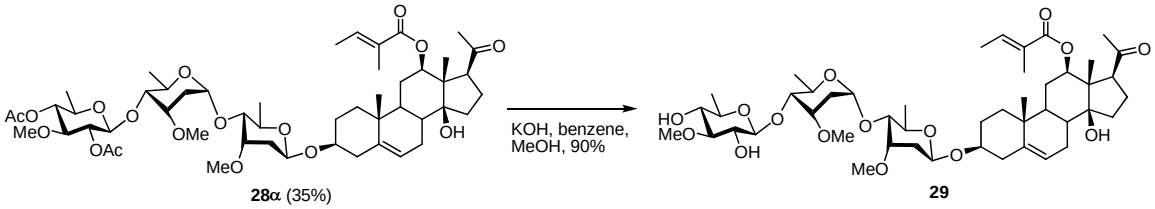
4.26 (s, 1 H), 3.94-3.67 (m, 4 H), 3.42 (s, 9 H), 3.36 (s, 3 H), 2.19 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 1.87 (s, 3 H), 1.31-1.13 (m, 12 H), 1.05 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.1, 169.6, 169.0, 167.6, 138.9, 137.8, 128.6, 121.9, 102.3, 99.5, 95.8, 85.7, 83.8, 82.5, 81.0, 77.2, 76.4, 75.8, 73.4, 72.2, 70.0, 68.5, 67.9, 58.4, 58.1, 57.7, 57.1, 53.7, 43.0, 38.6, 37.2, 37.0, 35.7, 35.6, 35.3, 34.4, 33.2, 29.7, 29.4, 27.3, 26.0, 24.3, 20.9, 20.9, 19.3, 18.2, 17.9, 17.5, 14.5, 12.1, 9.9; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{51}H_{78}O_{17}Na$ 985.5137, found 985.5121.

14β-Hydroxy-pregn-5-ene-12β-tigloyl-20-one-3β-*O*-(β-D-thevetopyranosyl)-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside (P57, 1)



A solution of **28β** (11.0 mg, 0.011 mmol) in benzene (2 mL) was treated with a solution of KOH (2.2 mg, 0.039 mmol) in MeOH (0.2 mL). After stirring at rt for 30 min, the reaction mixture was neutralized and concentrated in vacuo. The residue was purified by silica gel column chromatograph (CH_2Cl_2/MeOH, 40:1) to provide **1** (9.0 mg, 90%) as a white solid: $[\alpha]_D^{25}$ = 14.7 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.86 (m, 1 H), 5.41 (d, *J* = 4.8 Hz, 1 H), 4.84 (d, *J* = 8.2 Hz, 1H), 4.76 (d, *J* = 8.1 Hz, 1 H), 4.64 (dd, *J* = 11.9, 4.3 Hz, 1 H), 4.30 (d, *J* = 7.7 Hz, 1 H), 4.25 (s, 1 H), 3.95-3.75 (m, 4 H), 3.65 (s, 3 H), 3.52 (dd, *J* = 15.4, 6.0 Hz, 2 H), 3.44 (s, 3 H), 3.43 (s, 3 H), 2.35 (t, *J* = 18.0 Hz, 4 H), 2.19 (s, 3 H), 1.87 (d, *J* = 7.3 Hz, 3 H), 1.31 (d, *J* = 6.1 Hz, 4 H), 1.29-1.24 (m, 6 H), 1.21 (d, *J* = 6.2 Hz, 3 H), 1.06 (s, 3 H), 0.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.0, 167.8, 139.0, 137.7, 128.8, 122.0, 104.4, 99.6, 95.9, 85.7, 85.3, 82.8, 82.6, 77.0, 76.9, 75.9, 74.7, 74.7, 71.7, 68.5, 68.3, 60.6, 58.0, 57.9, 57.2, 53.8, 43.1, 38.7, 37.3, 37.1, 35.7, 35.6, 35.2, 34.4, 33.1, 29.7, 29.5, 27.4, 26.1, 24.4, 19.31, 18.4, 18.2, 17.8, 14.5, 12.1, 9.9; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{47}H_{74}O_{15}Na$ 901.4925, found 901.4922.

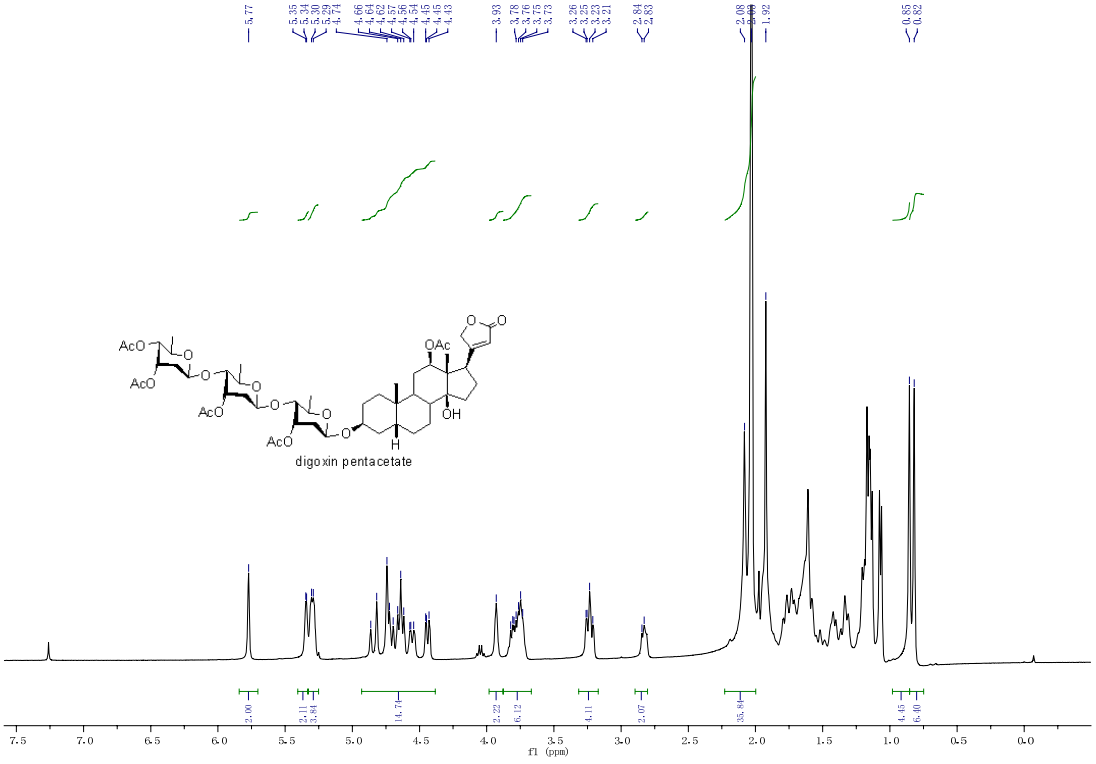
14β-hydroxy-pregn-5-ene-12β-tigloyl-20-one-3-*O*-(β-D-thevetopyranosyl)-(1→4)-α-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside (29)

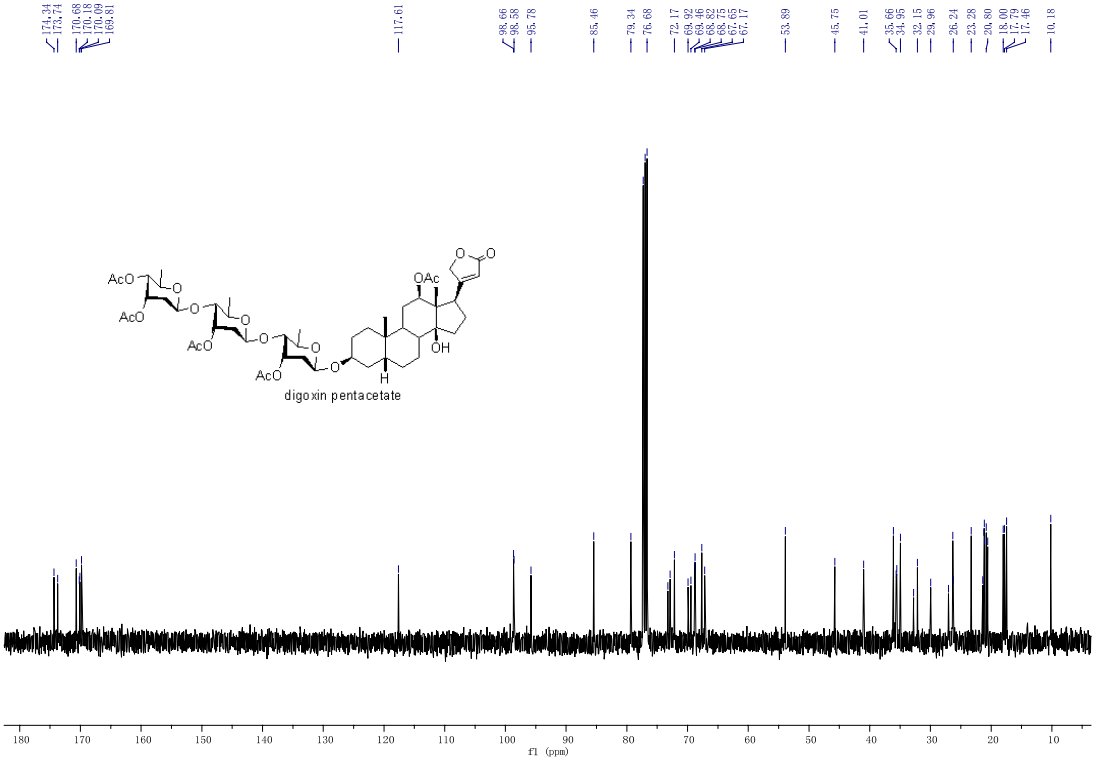


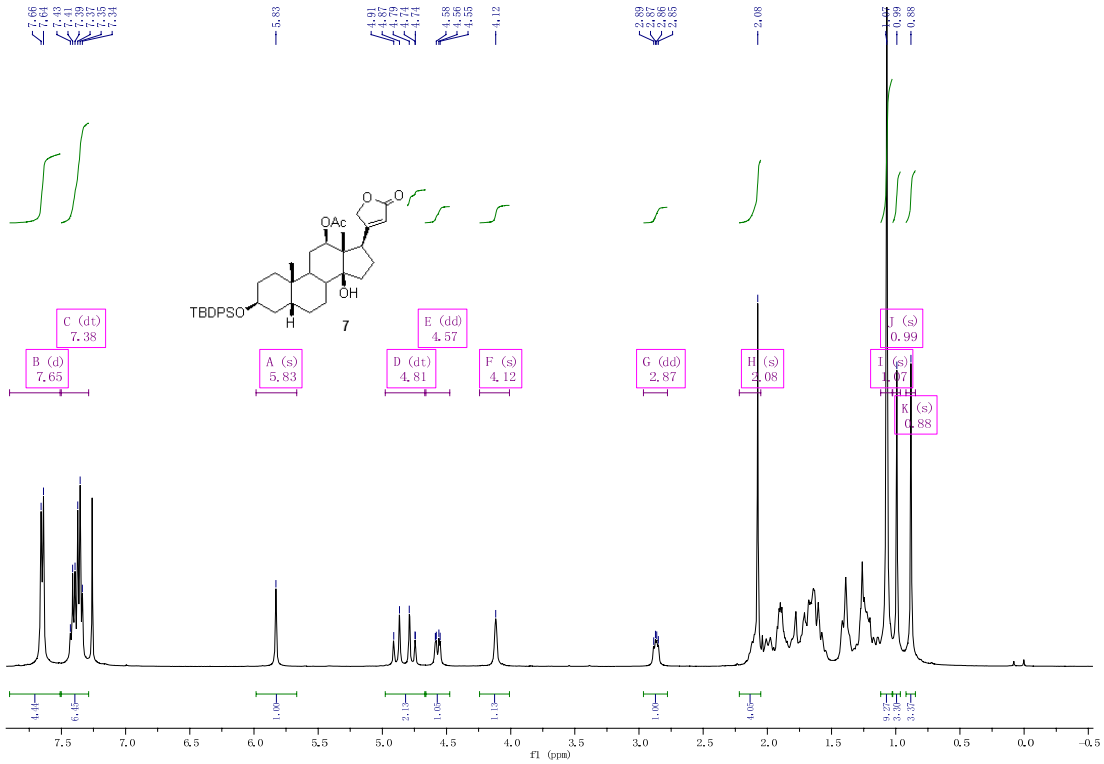
28α (35%) **29**

Compound **29** (8.1 mg, 85%) was prepared from **28α** following a procedure similar to that for **28β→1**. $[\alpha]_D^{25}$ = 56.0 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (br d, *J* = 7.6 Hz, 1 H), 5.40 (br, 1 H), 4.91 (d, *J* = 4 Hz, 1 H), 4.85 (dd, *J* =1.6, 9.6 Hz , 1 H), 4.64 (dd, *J* = 11.6, 4.4 Hz, 1 H), 4.33 (d, *J* = 7.6 Hz, 1 H), 4.27 (s, 1 H), 4.22 (dd, *J* = 6.8, 9.2 Hz, 1 H), 3.83-3.86 (m, 2 H), 3.75 (d, *J* = 3.6 Hz, 1 H), 3.64 (s, 3 H), 3.52-3.58 (m, 2 H), 3.40 (s, 3 H), 3.39 (s, 3 H), 3.40-3.52 (m, 3 H), 3.19 (t, *J* = 9.2 Hz, 1 H), 3.08-3.15 (m, 2 H), 2.53 (s, 1 H), 2.45 (s, 1 H), 2.27-2.34 (m, 2 H), 2.19-2.24 (m, 1 H) 2.19 (s, 1 H), 1.88 (s, 3 H), 1.27-1.31 (m, 7 H), 1.22-1.25 (m, 5 H), 1.05 (3 H) 0.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.1, 167.7, 138.0, 137.8, 128.7, 122.0, 104.2, 95.7, 91.2, 85.7, 85.2, 77.0, 76.9，75.9, 75.1, 74.7, 74.5, 74.4, 72.4, 71.7, 68.9, 63.3, 60.6, 57.4, 57.2, 56.6, 53.7, 43.0, 38.6, 37.2, 37.1, 35.7, 34.6, 34.4, 33.1, 31.2, 29.5, 27.3, 26.0, 24.4, 19.3, 18.5, 17.8, 17.7, 14.5, 12.1, 9.9; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{47}H_{74}O_{15}Na$ 901.4925, found 901.4920.

III. NMR spectra of new compounds



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H
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B (d) 7.65
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D (dt) 4.81
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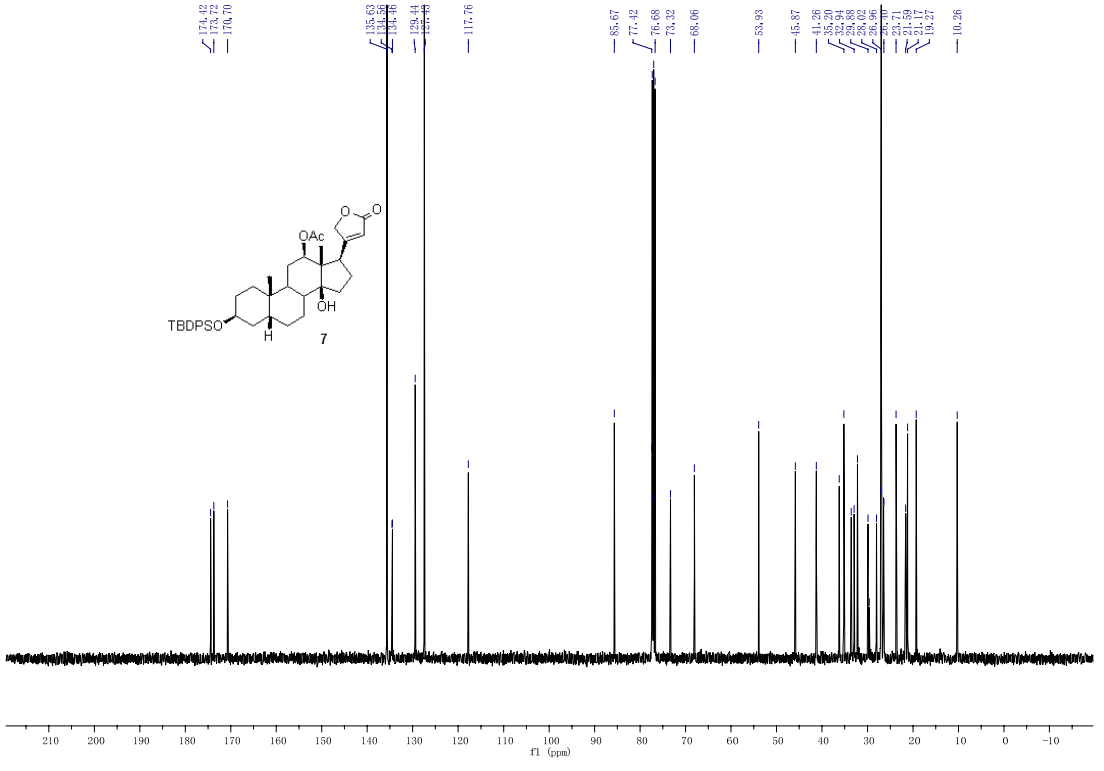
J (s) 0.99
K (s) 0.88
f1 (ppm)


OAc
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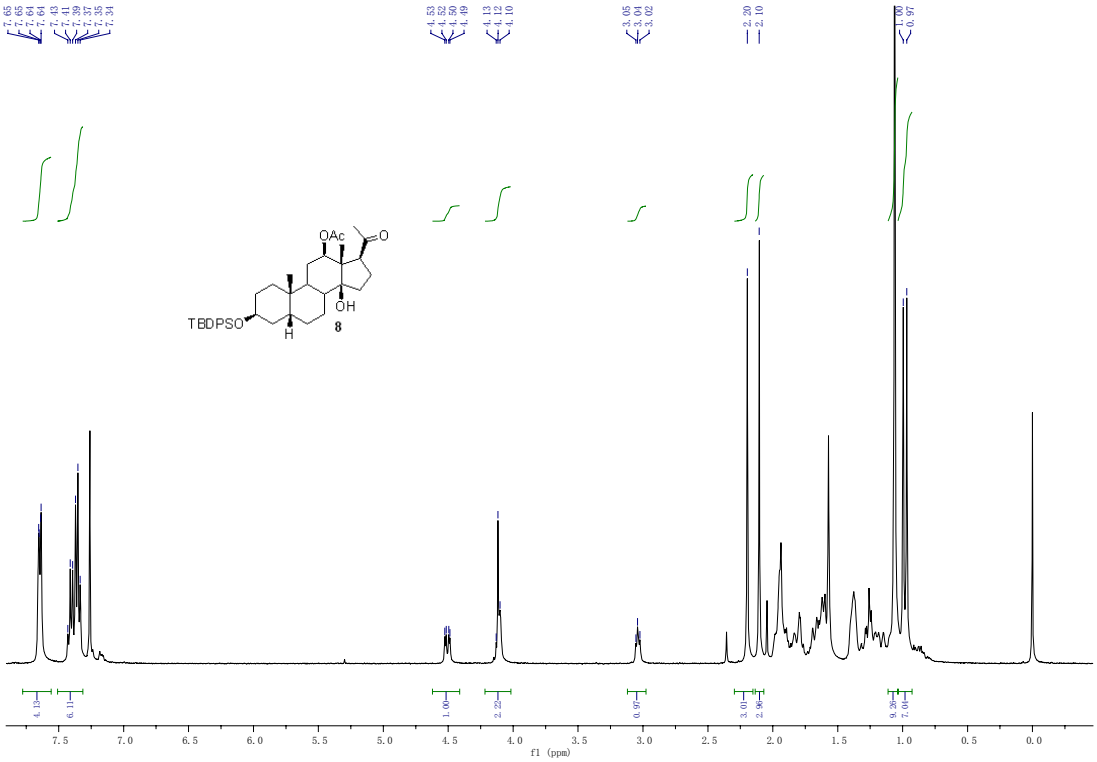
f1 (ppm)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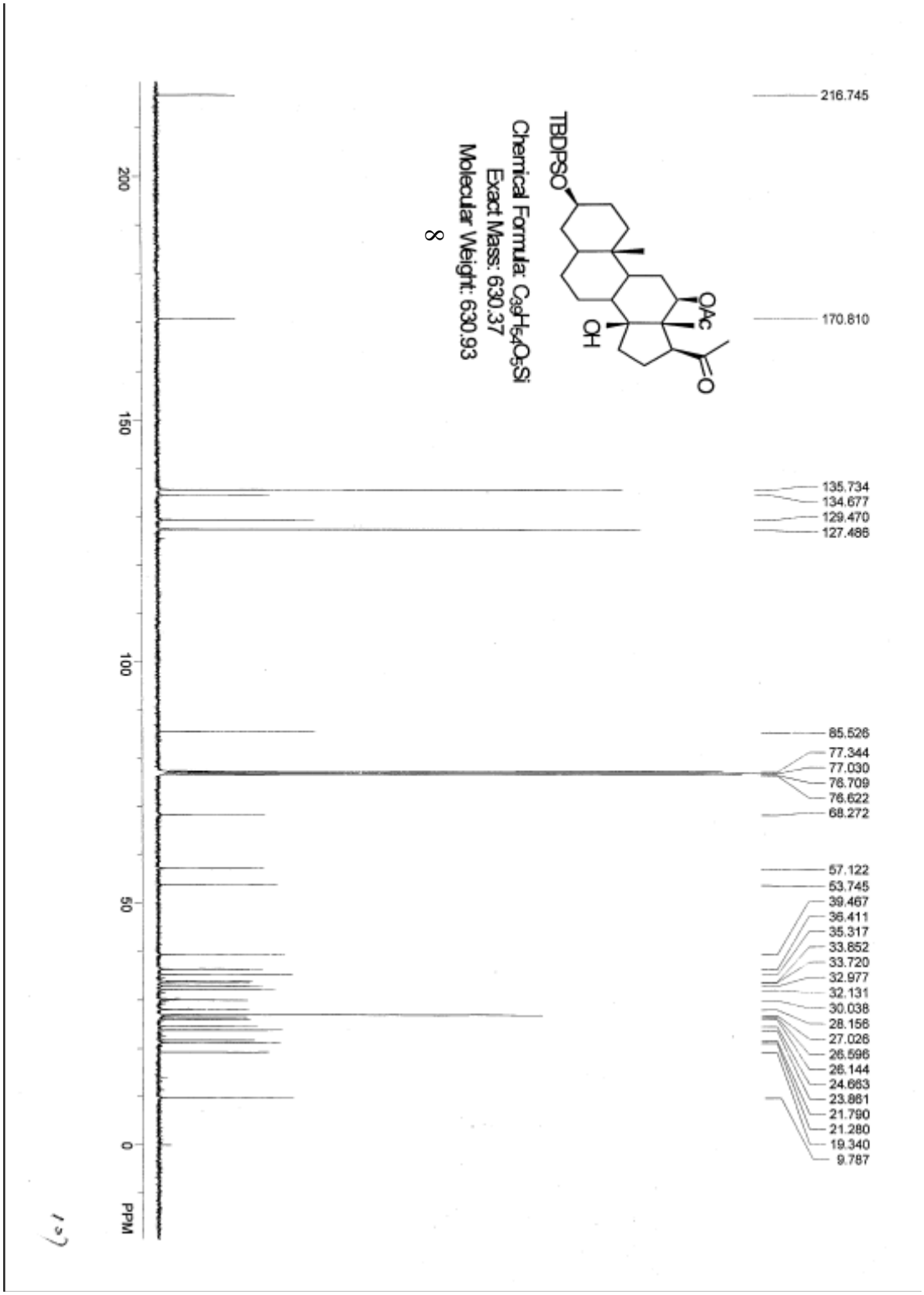
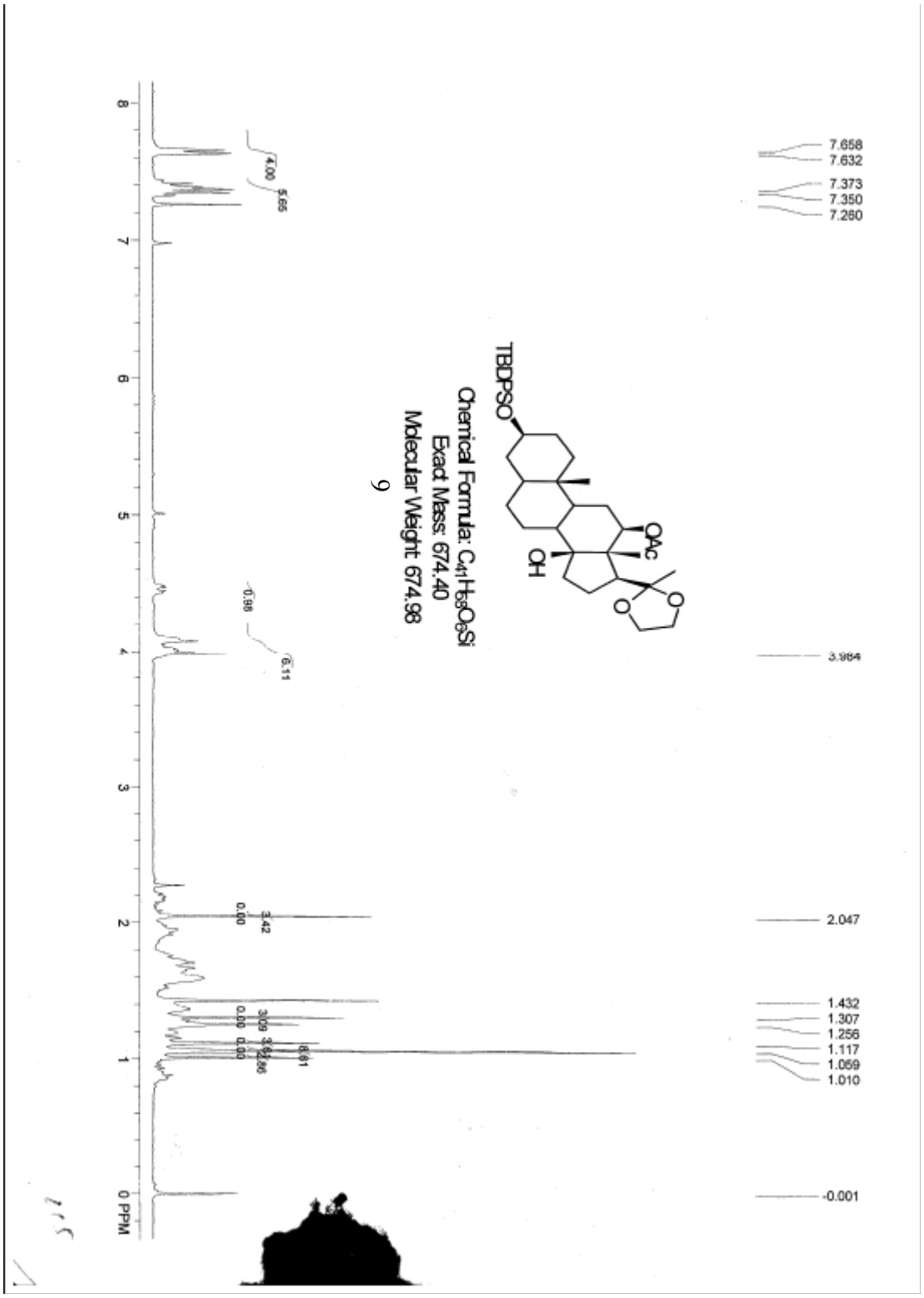
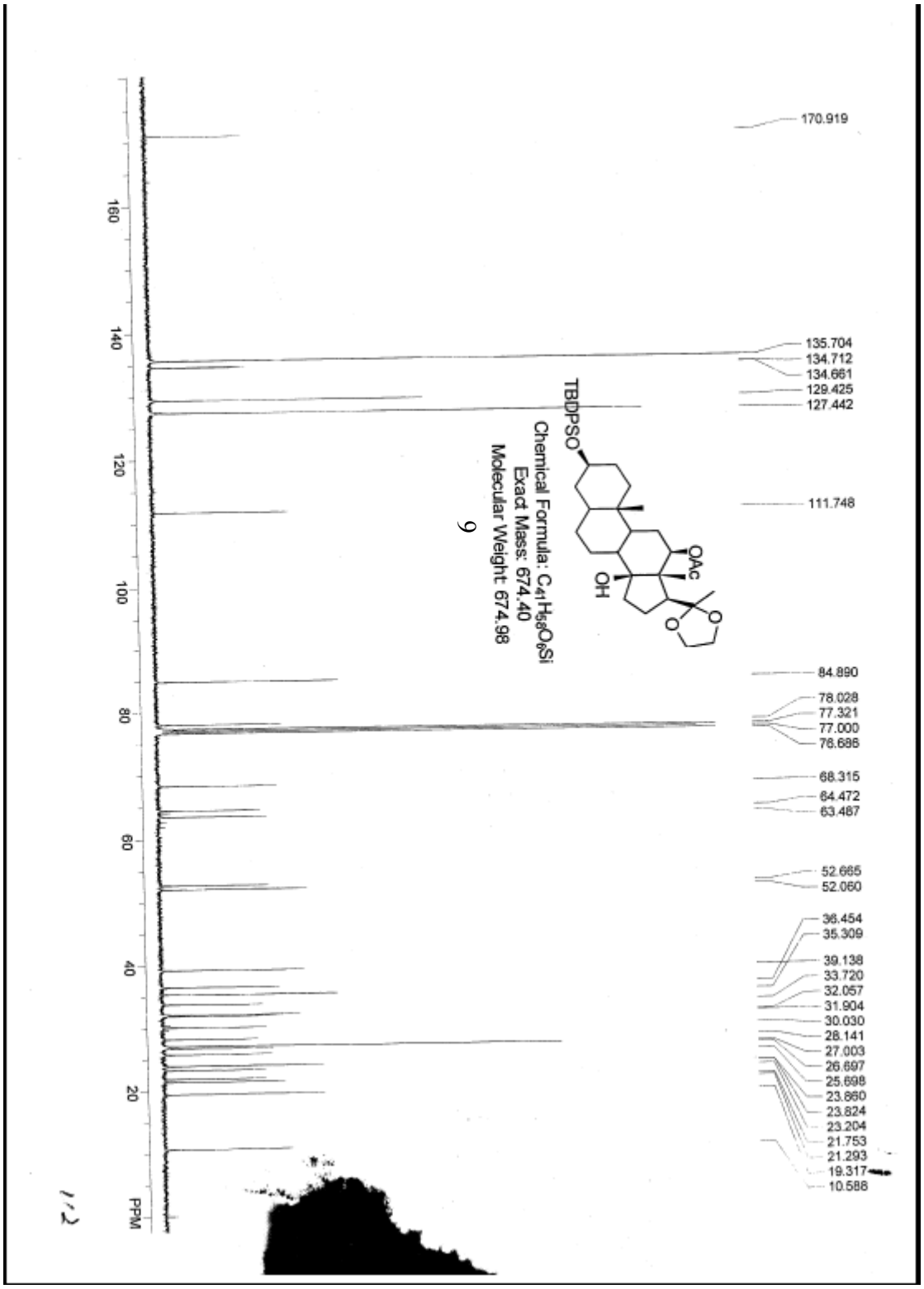
2.96
9.26
7.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


216.745
170.810
135.734
134.677
129.470
127.486
85.526
77.344
77.030
76.709
76.622
68.272
57.122
53.745
39.467
36.411
35.317
33.852
33.720
32.977
32.131
30.038
28.156
27.026
26.596
26.144
24.663
23.861
21.790
21.280
19.340
9.787
200
150
100
50
0
PPM
TBDPSO
OAc
OH
O
Chemical Formula: C39H54O3Si
Exact Mass: 630.37
Molecular Weight: 630.93
8


9
Chemical Formula: C41H58O6Si
Exact Mass: 674.40
Molecular Weight: 674.98
TBDPSO
OAc
OH
7.658
7.632
7.373
7.350
7.260
3.984
2.047
1.432
1.307
1.256
1.117
1.059
1.010
-0.001
4.00
5.65
0.89
6.11
0.90
3.42
0.00
3.09
0.00
0.00
8.61
0 PPM


170.919
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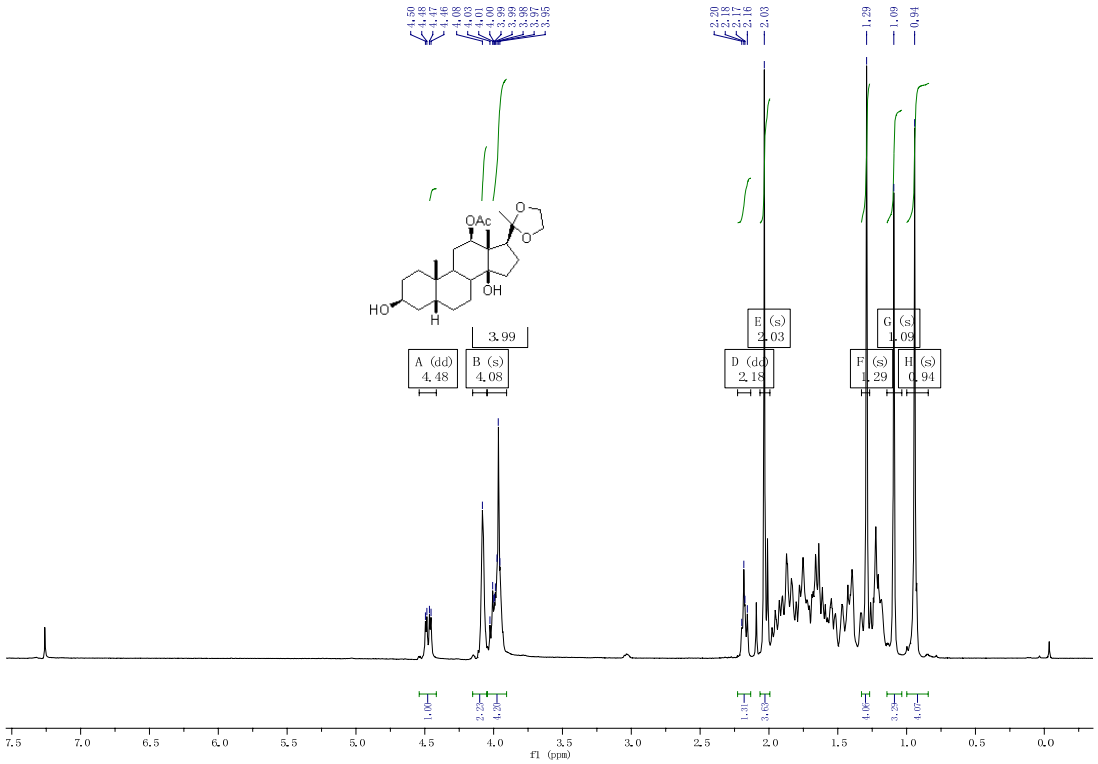
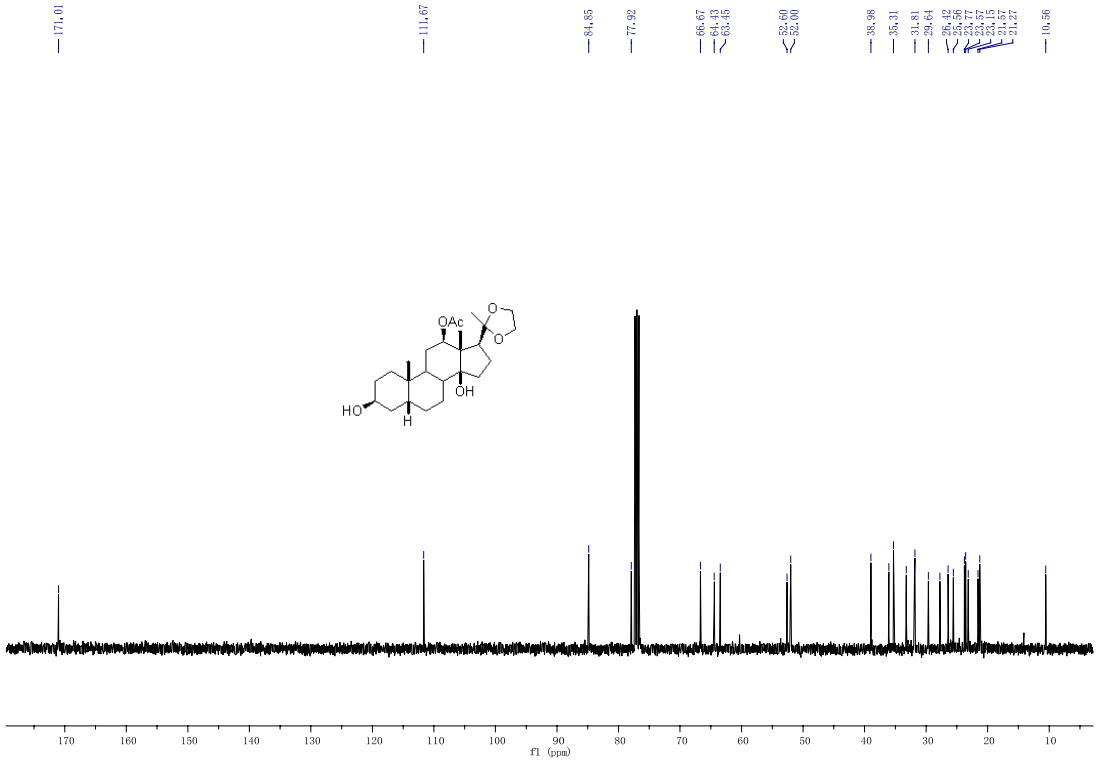
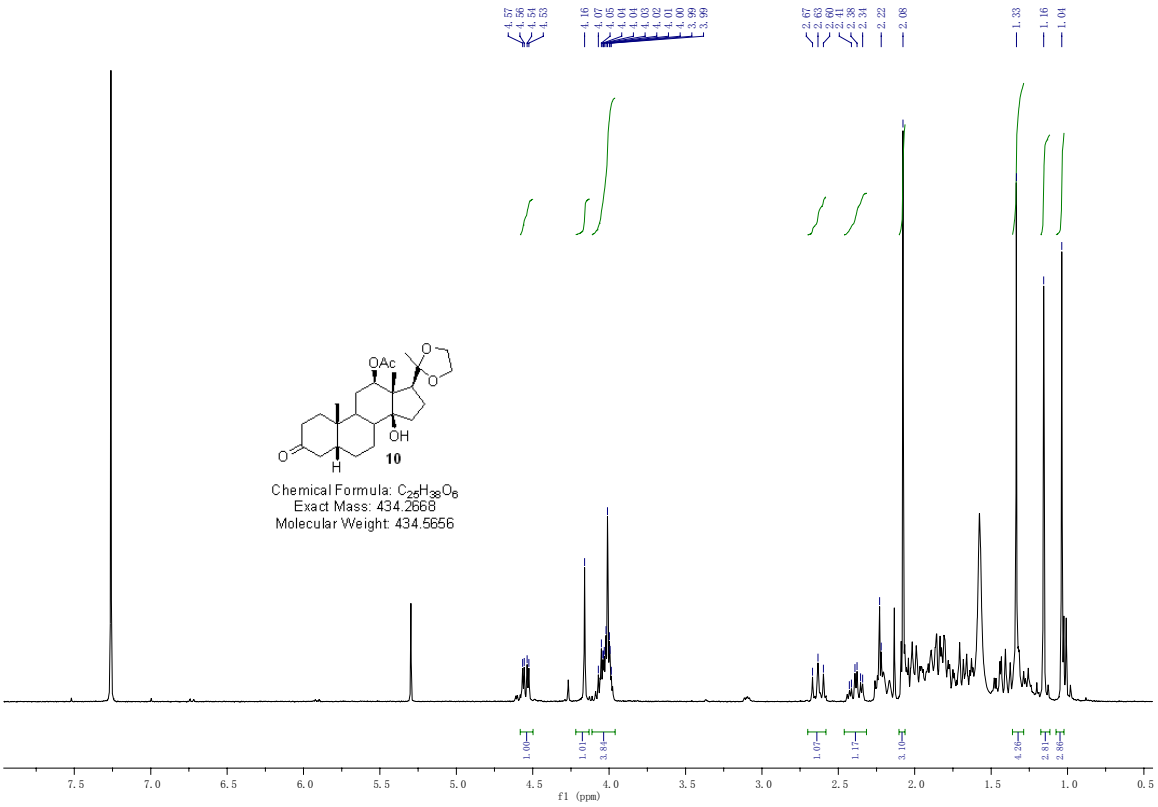
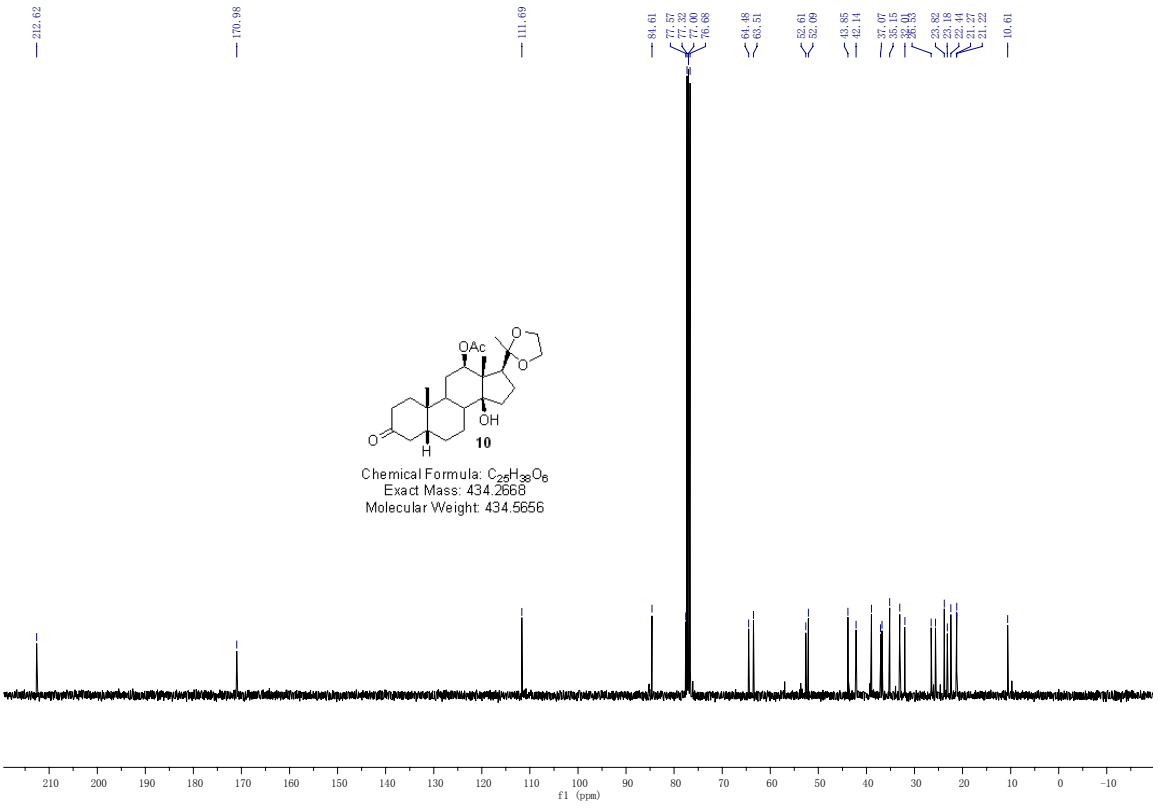
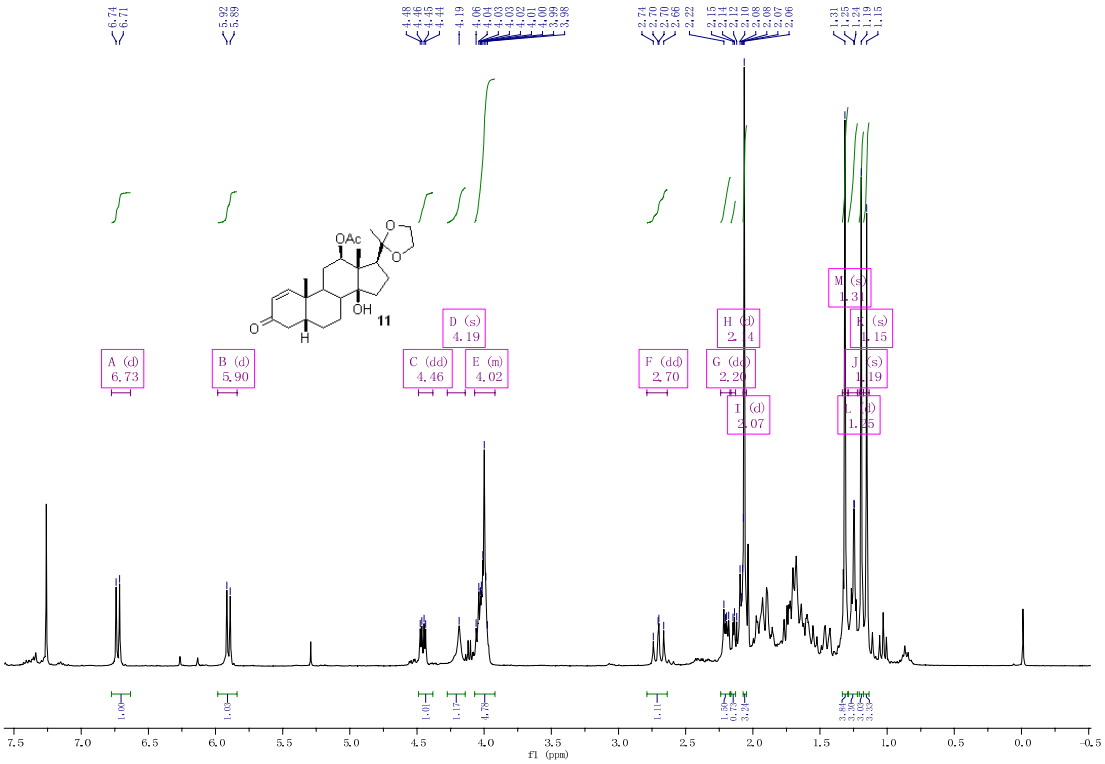
134.712
134.661
129.425
127.442
111.748
84.890
78.028
77.321
77.000
76.686
68.315
64.472
63.487
52.665
52.060
36.454
35.309
39.138
33.720
32.057
31.904
30.030
28.141
27.003
26.697
25.698
23.860
23.824
23.204
21.753
21.293
19.317
10.588
160
140
120
100
80
60
40
20
PPM
TBDPSO
OAc
OH
O
O
O
Chemical Formula: C41H58O6Si
Exact Mass: 674.40
Molecular Weight: 674.98
9

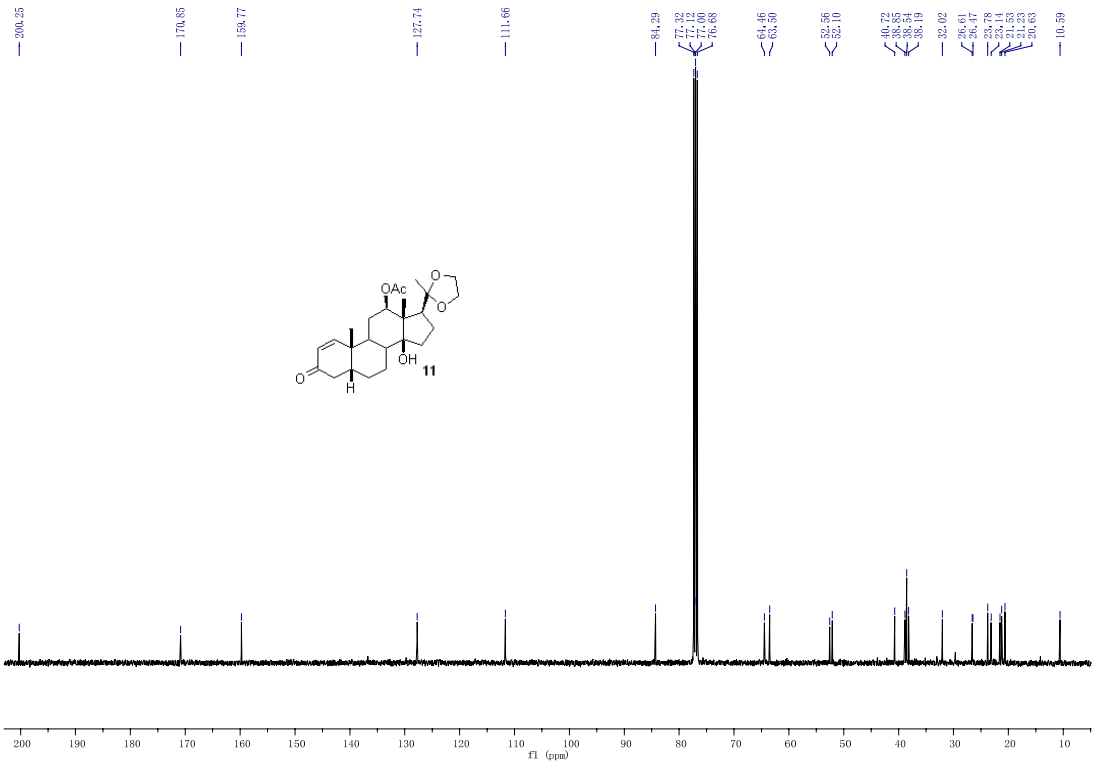

OAc
O
O
OH
HO
H
3.99
A (dd) 4.48
B (s) 4.08
D (dd) 2.18
E (s) 2.03
F (s) 1.29
G (s) 1.09
H (s) 0.94
f1 (ppm)

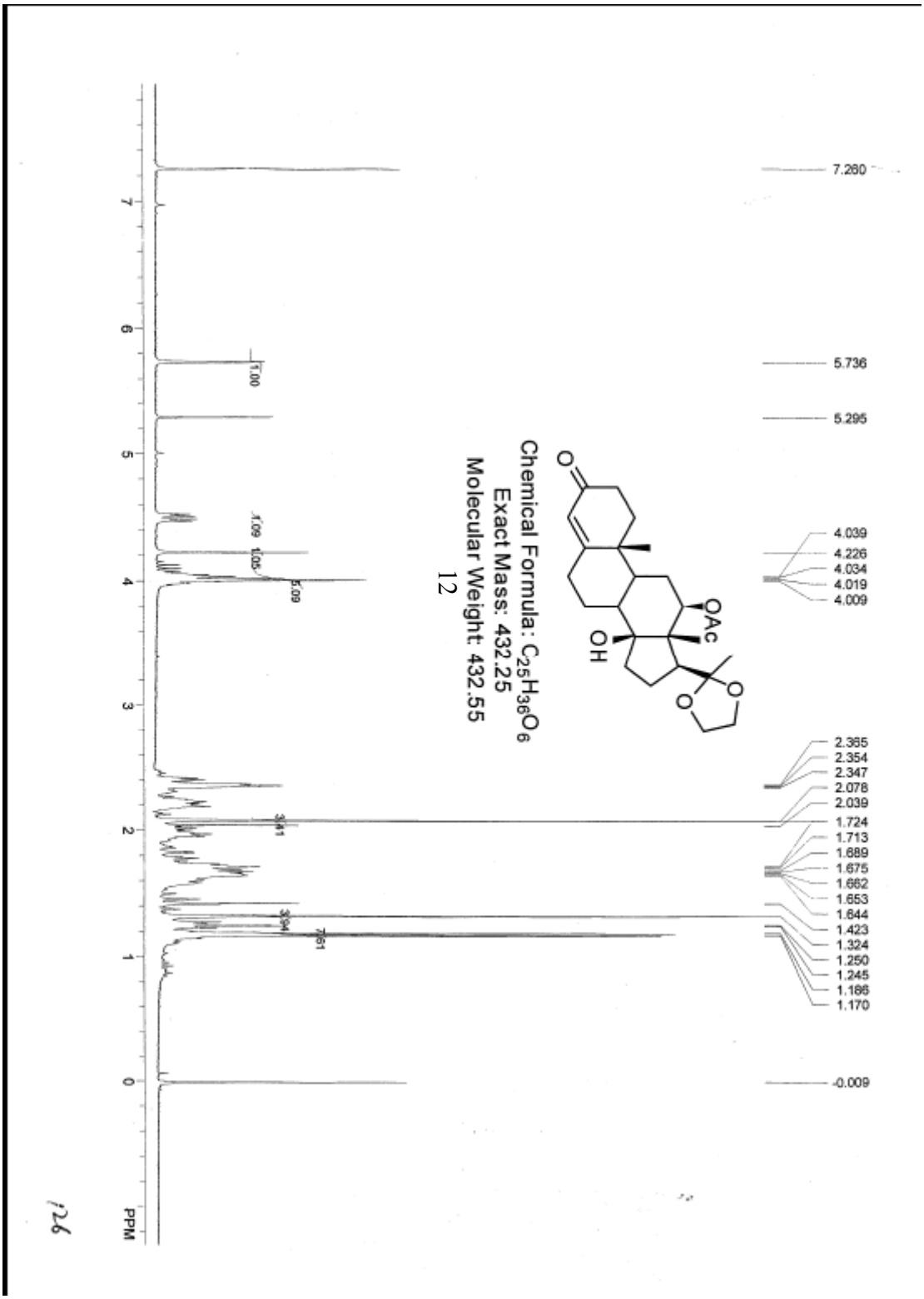

OAc
O
O
OH
HO
H
f1 (ppm)

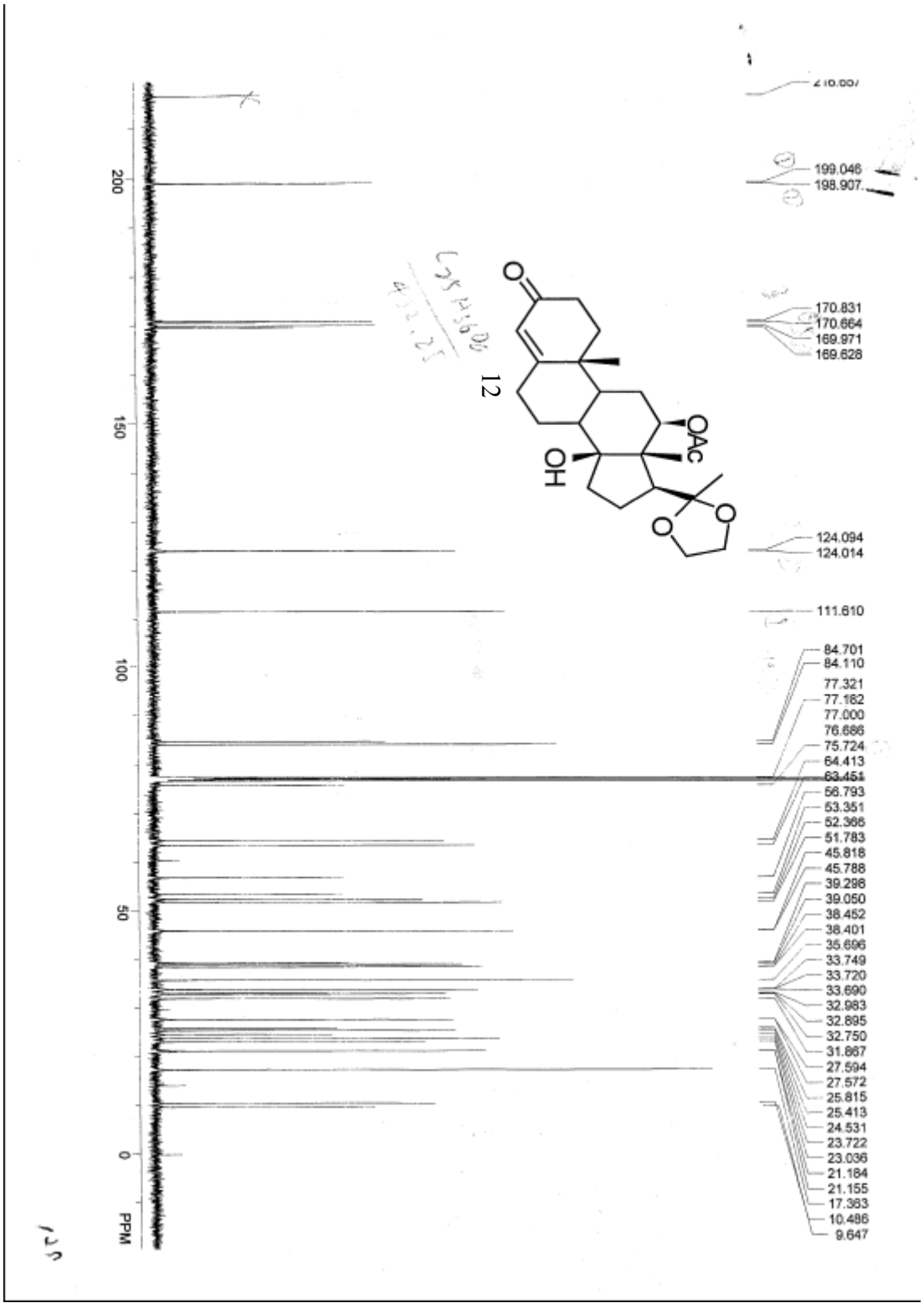

OAc
O
O
OH
O
H
10
Chemical Formula: C25H38O6
Exact Mass: 434.2668
Molecular Weight: 434.5656
f1 (ppm)

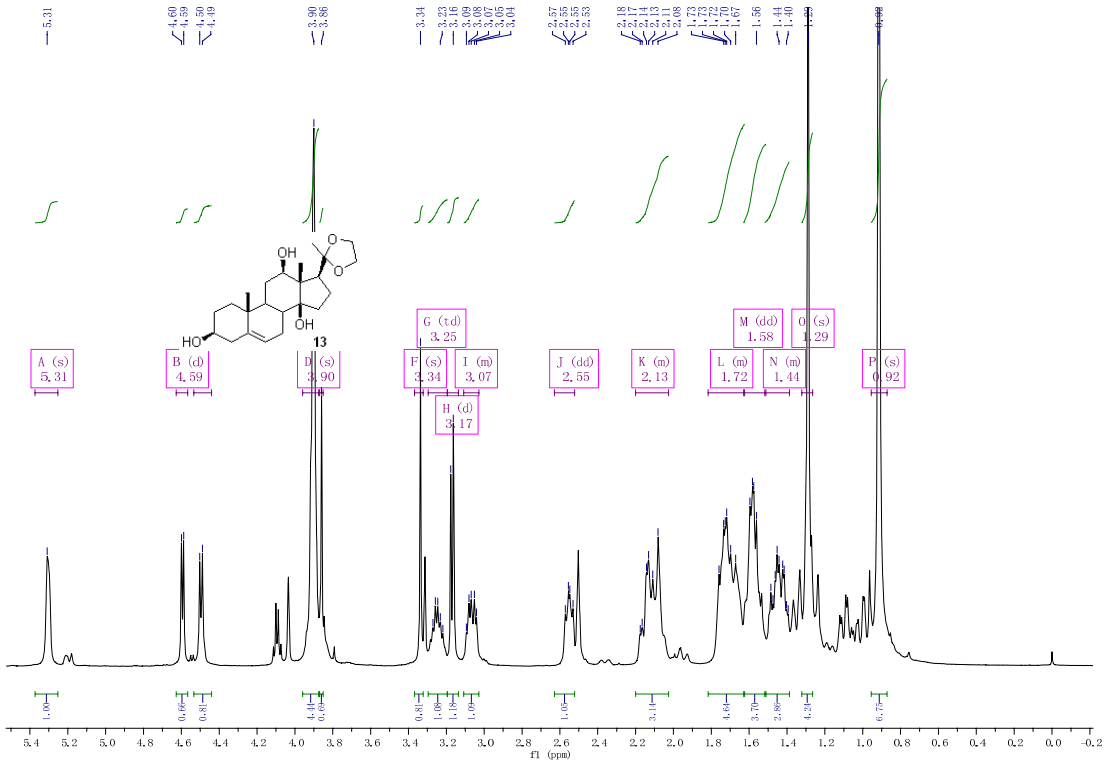

OAc
O
O
OH
O
H
10
Chemical Formula: C25H38O6
Exact Mass: 434.2668
Molecular Weight: 434.5656
f1 (ppm)

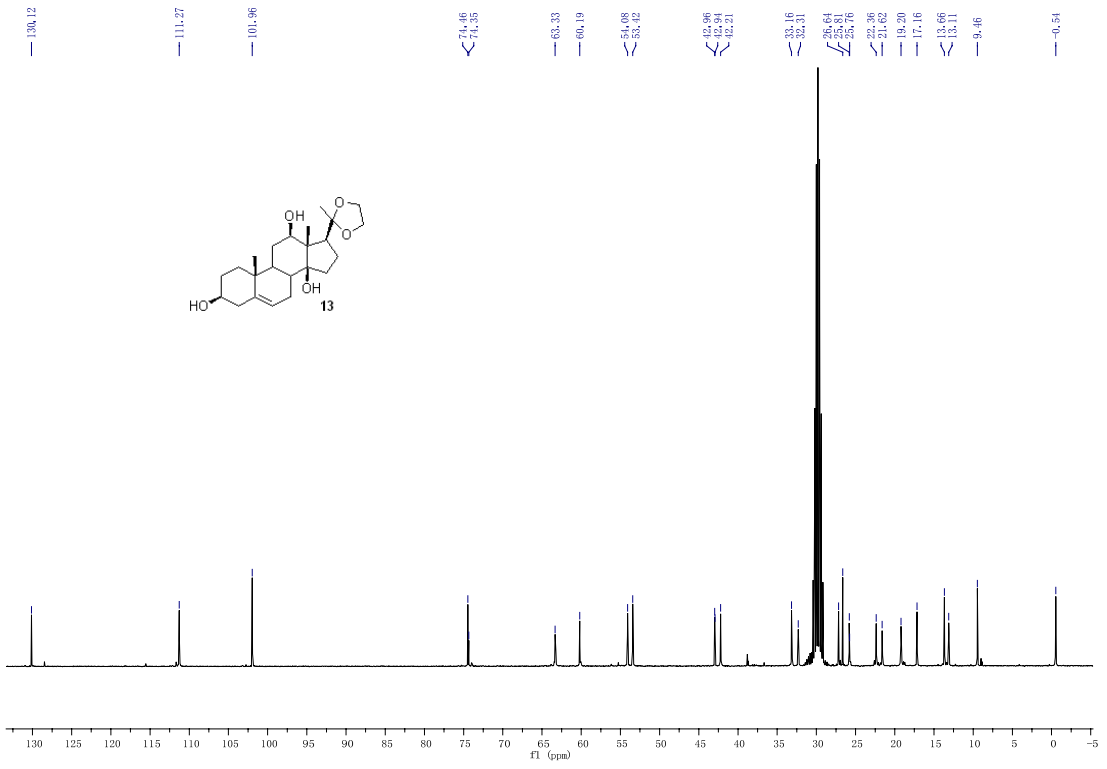

OAc
OH
11
A (d) 6.73
B (d) 5.90
C (dd) 4.46
D (s) 4.19
E (m) 4.02
F (dd) 2.70
G (dd) 2.20
H (d) 2.14
I (d) 2.07
J (s) 1.19
K (s) 1.15
M (s) 1.31
f1 (ppm)

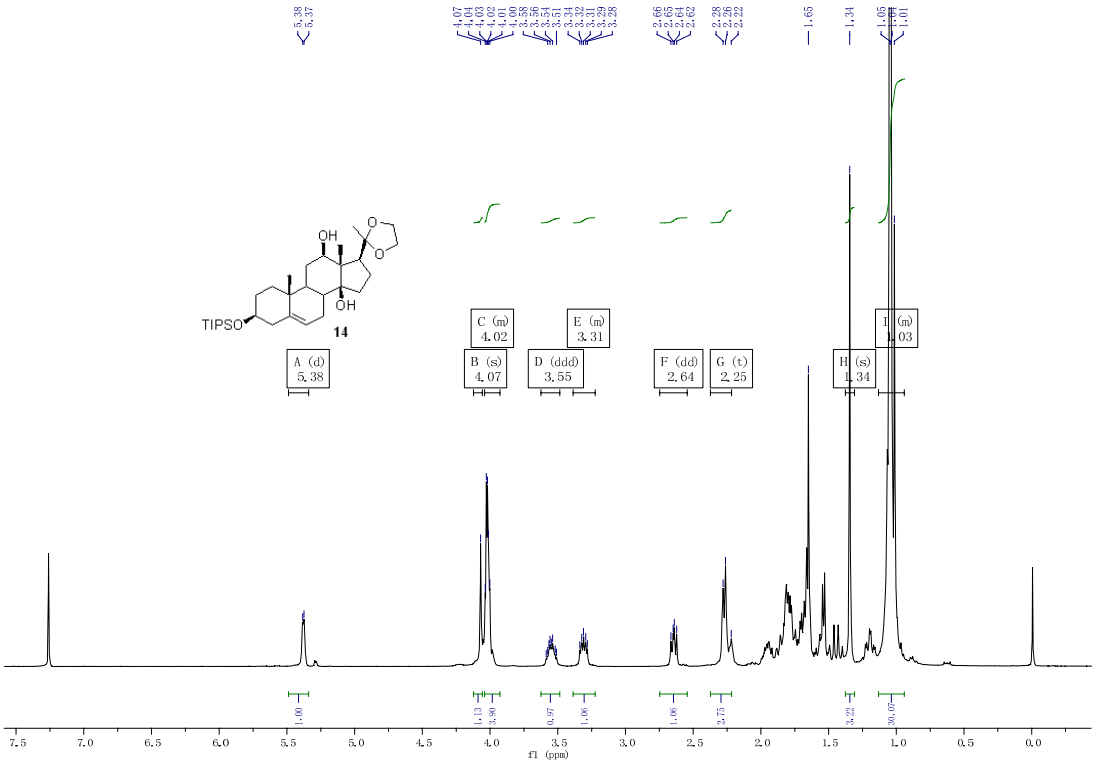

OAc
OH
11
f1 (ppm)

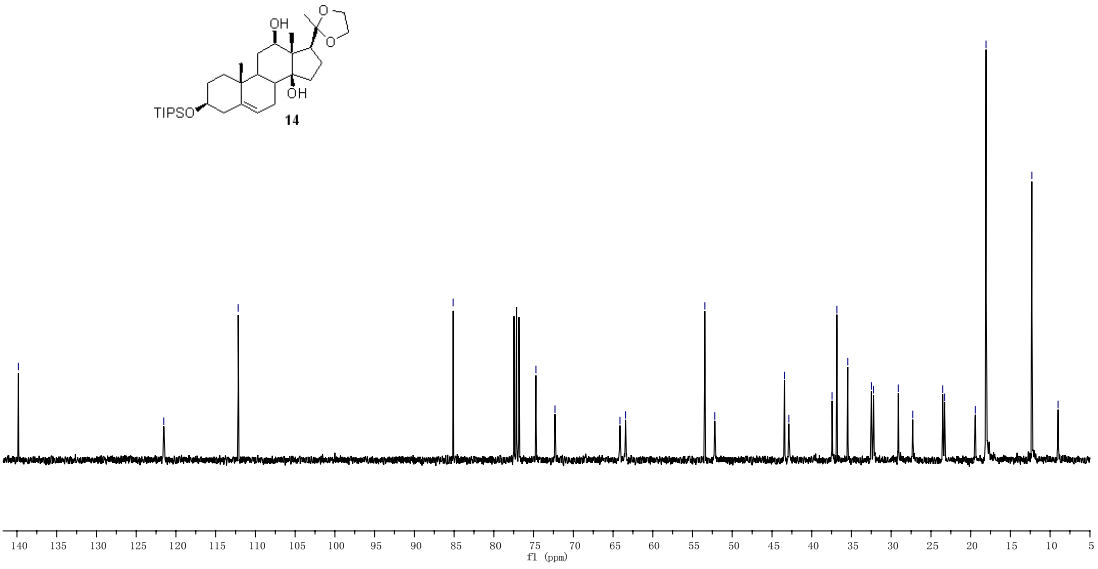

Chemical Formula: C25H36O6
Exact Mass: 432.25
Molecular Weight: 432.55
12
OAc
OH
O
O
O
7.260
5.736
5.295
4.039
4.226
4.034
4.019
4.009
2.365
2.354
2.347
2.078
2.039
1.724
1.713
1.689
1.675
1.662
1.653
1.644
1.423
1.324
1.250
1.245
1.186
1.170
-0.009
1.00
1.09
1.05
5.09
3.41
3.04
7.61
PPM

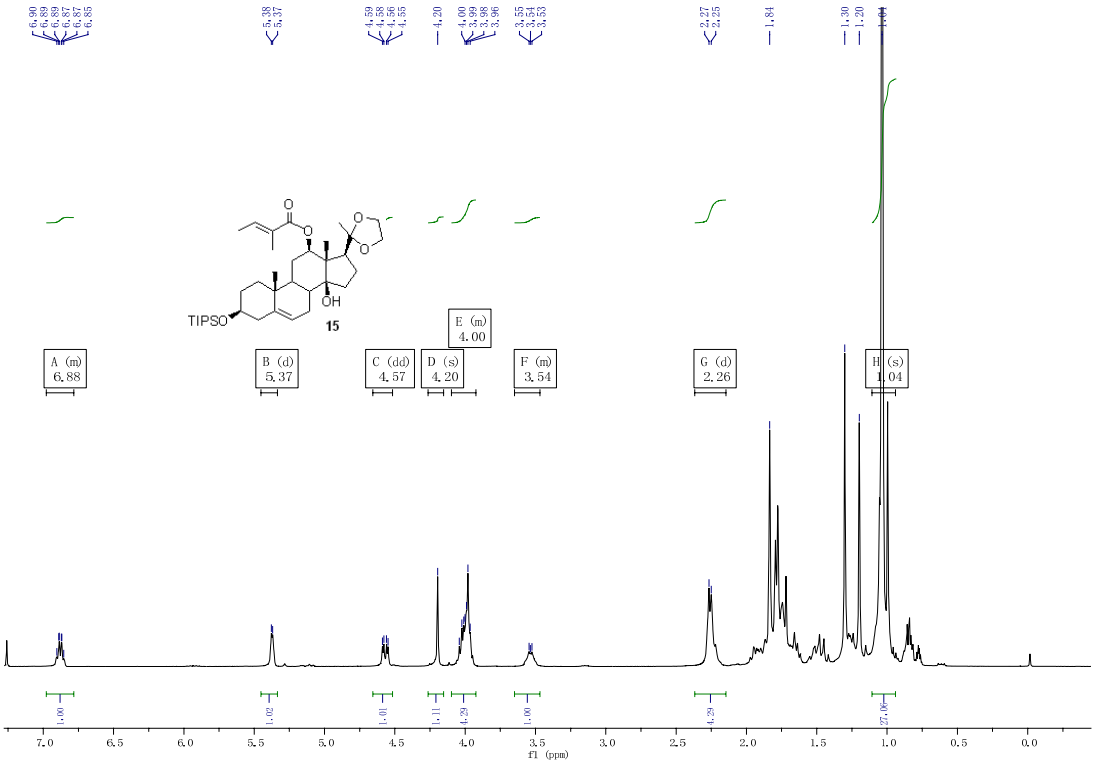

199.046
198.907
170.831
170.664
169.971
169.628
124.094
124.014
111.610
84.701
84.110
77.321
77.162
77.000
76.686
75.724
64.413
63.451
56.793
53.351
52.366
51.783
45.818
45.788
39.296
39.050
38.452
38.401
35.696
33.749
33.720
33.690
32.983
32.695
32.750
31.867
27.594
27.572
25.815
25.413
24.531
23.722
23.036
21.184
21.155
17.383
10.486
9.647
200
150
100
50
0
PPM
OAc
OH
O
O
O
12

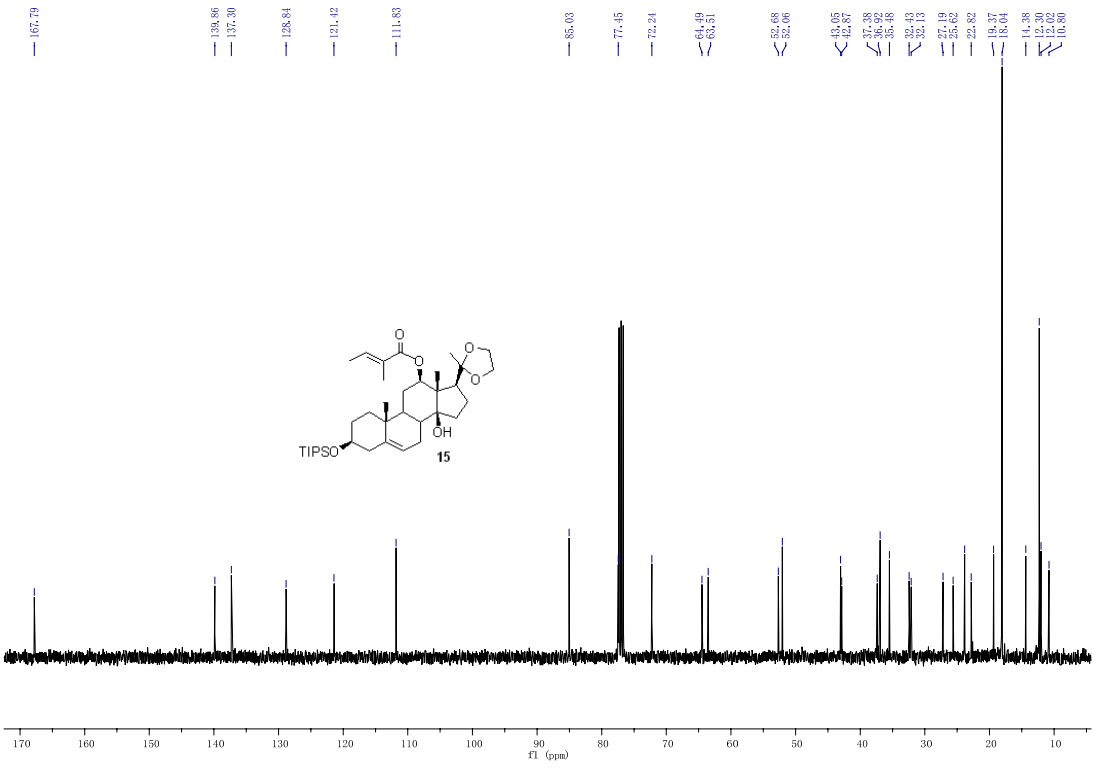

OH
O
O
OH
HO
13
A (s) 5.31
B (d) 4.59
D (s) 3.90
G (td) 3.25
F (s) 3.34
I (m) 3.07
H (d) 3.17
J (dd) 2.55
K (m) 2.13
L (m) 1.72
N (m) 1.44
M (dd) 1.58
O (s) 1.29
P (s) 0.92
f1 (ppm)

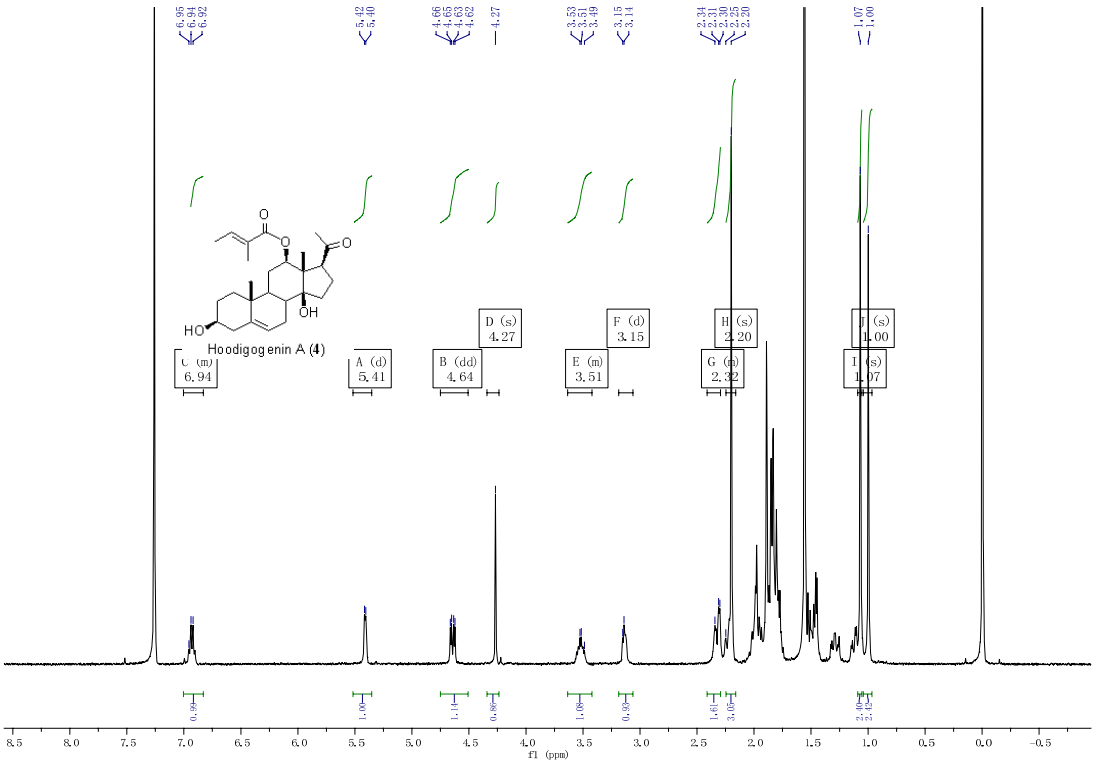

OH
O
O
OH
HO
13
f1 (ppm)

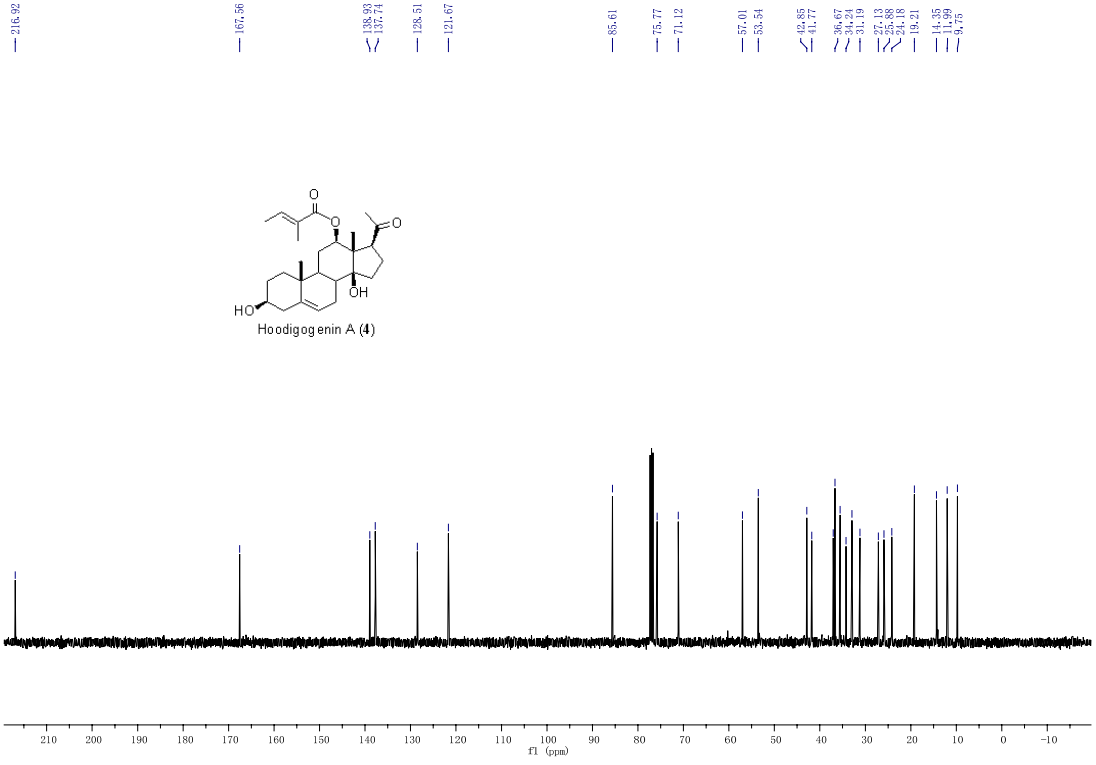

TIPSO
OH
OH
O
O
14
A (d) 5.38
B (s) 4.07
C (m) 4.02
D (ddd) 3.55
E (m) 3.31
F (dd) 2.64
G (t) 2.25
H (s) 1.34
I (m) 1.03
f1 (ppm)

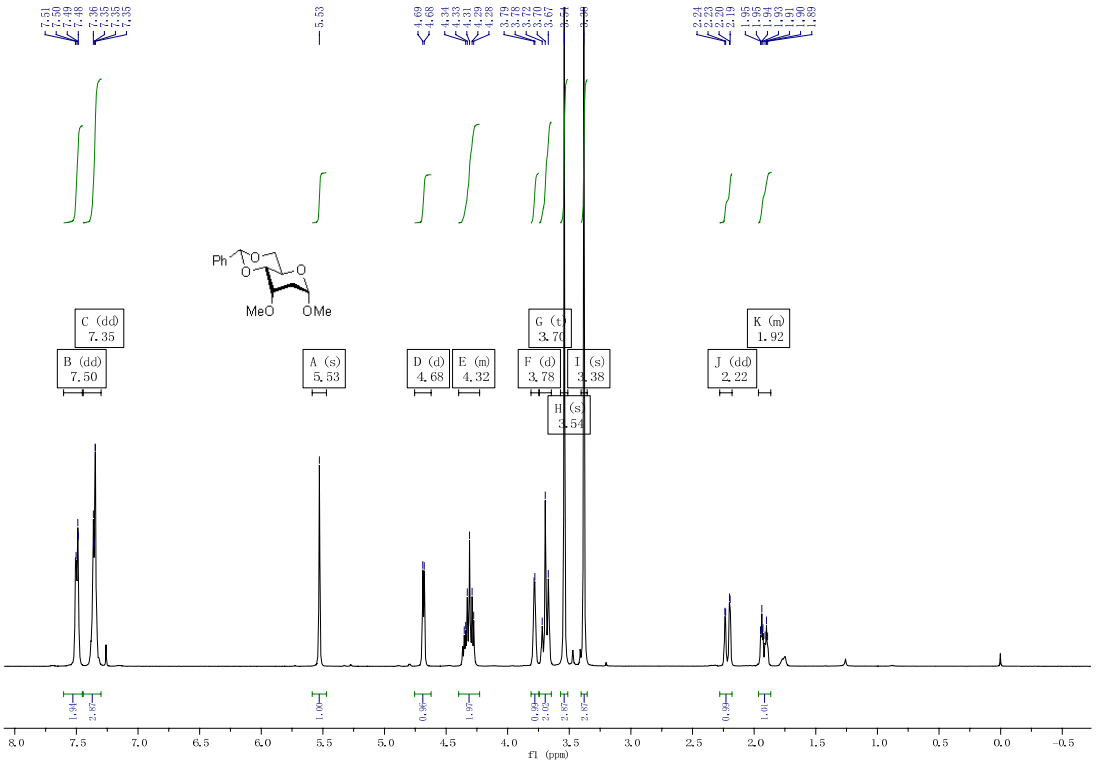

TIPSO
OH
OH
O
O
14
f1 (ppm)

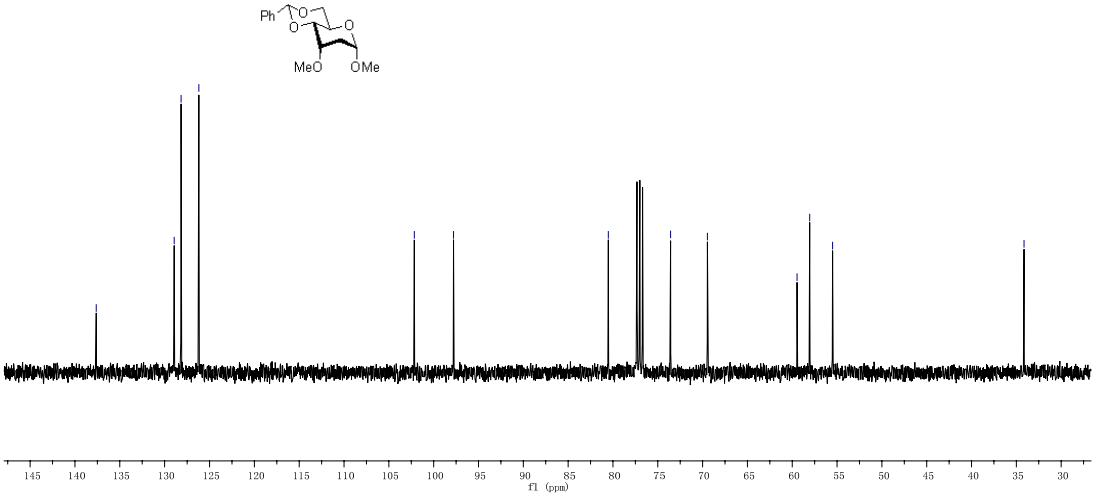

TIPSO
OH
15
A (m) 6.88
B (d) 5.37
C (dd) 4.57
D (s) 4.20
E (m) 4.00
F (m) 3.54
G (d) 2.26
H (s) 1.04
f1 (ppm)

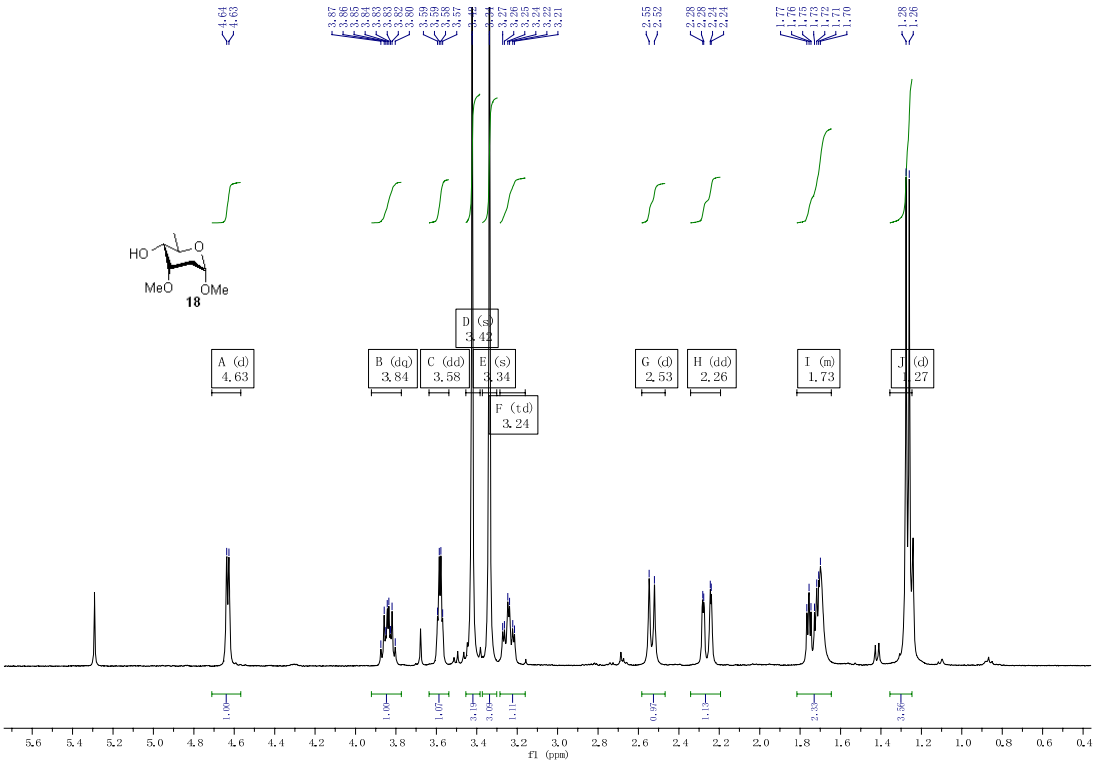

TIPSO
OH
15
f1 (ppm)

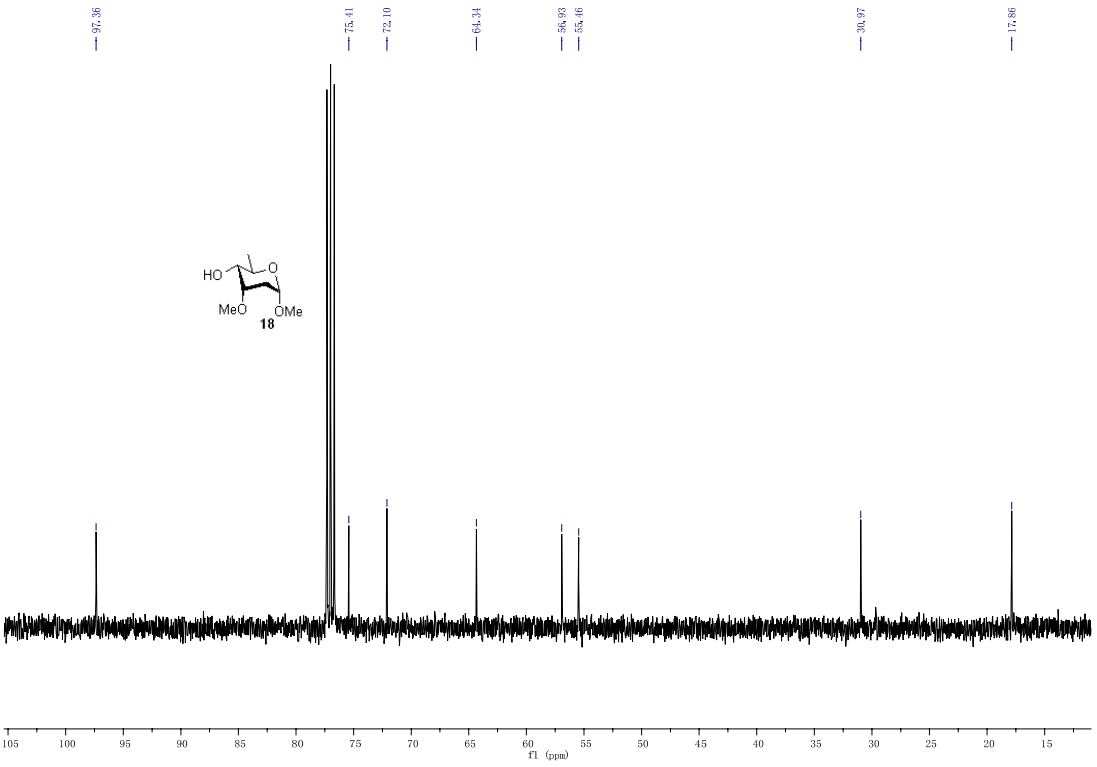

Hoodigogenin A (4)
C (m) 6.94
A (d) 5.41
B (dd) 4.64
D (s) 4.27
E (m) 3.51
F (d) 3.15
G (m) 2.32
H (s) 2.20
I (s) 1.07
J (s) 1.00
f1 (ppm)

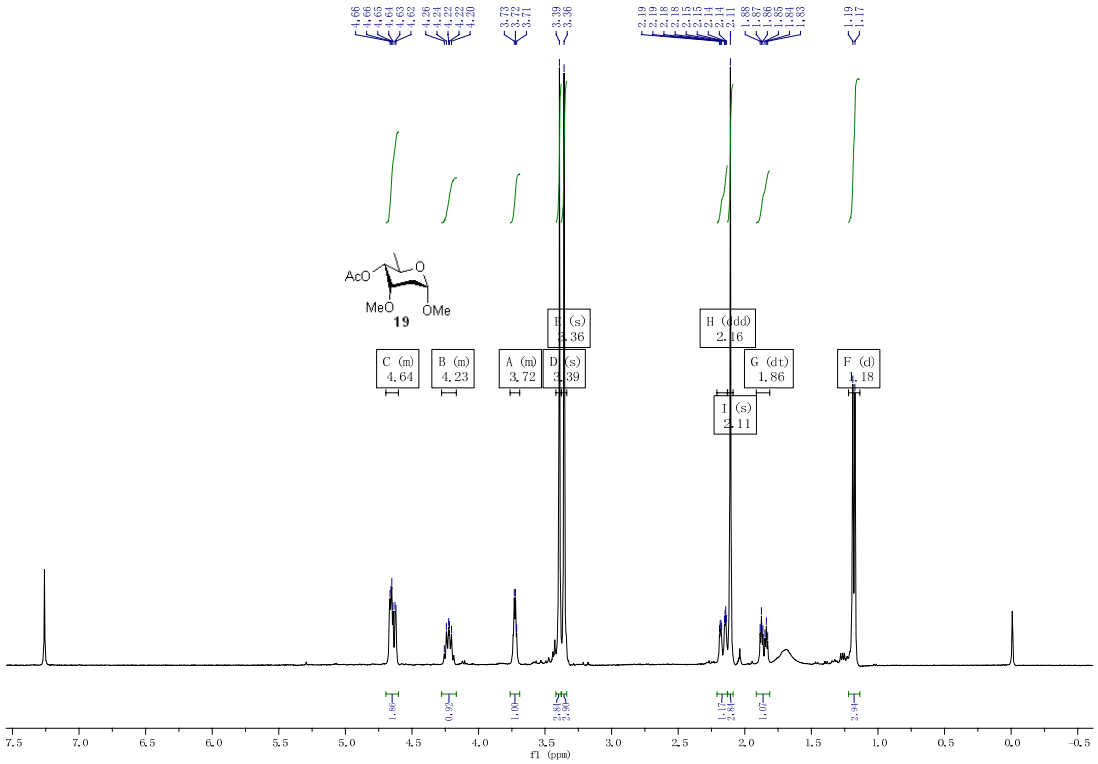

Hoodigogenin A (4)
f1 (ppm)

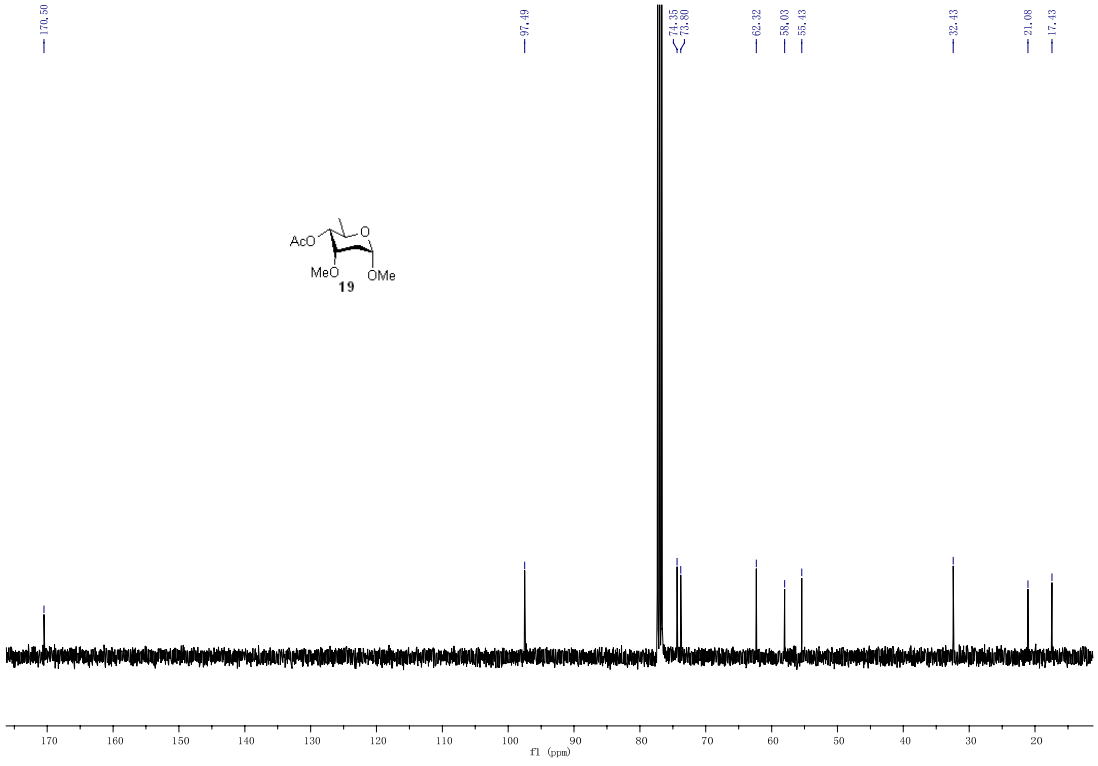

Ph
MeO
OMe
C (dd) 7.35
B (dd) 7.50
A (s) 5.53
D (d) 4.68
E (m) 4.32
G (t) 3.70
F (d) 3.78
I (s) 3.38
H (s) 3.54
K (m) 1.92
J (dd) 2.22
f1 (ppm)

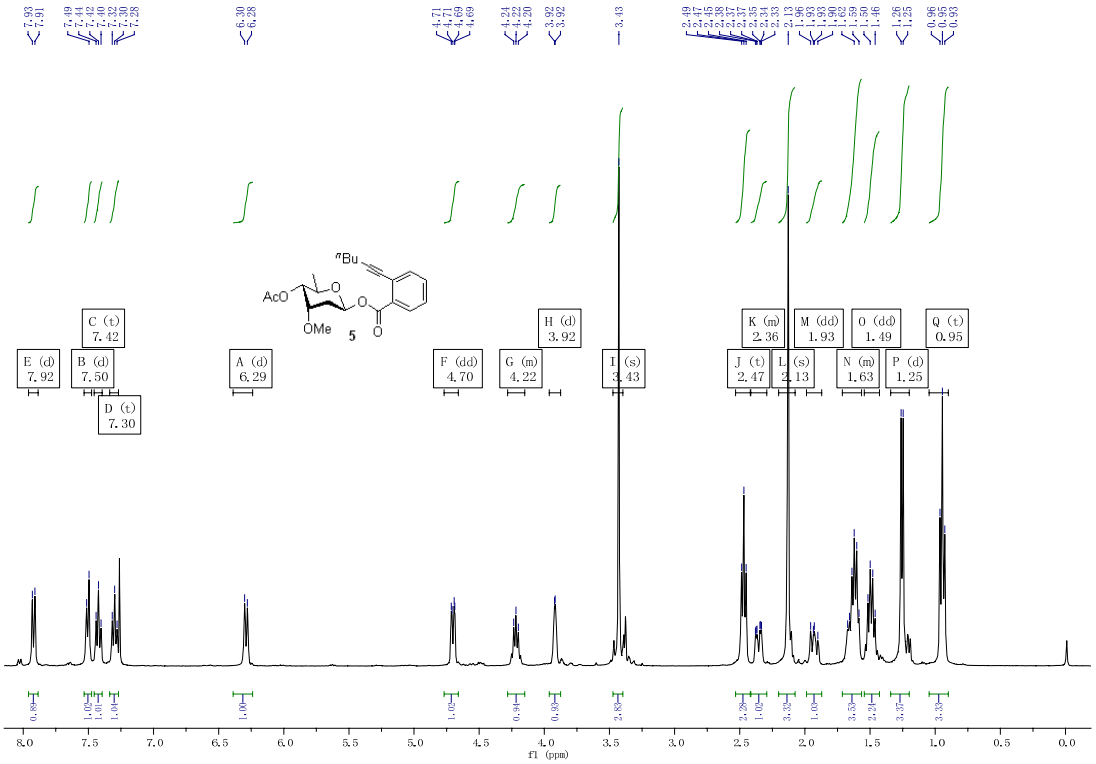

Ph
MeO
OMe
f1 (ppm)

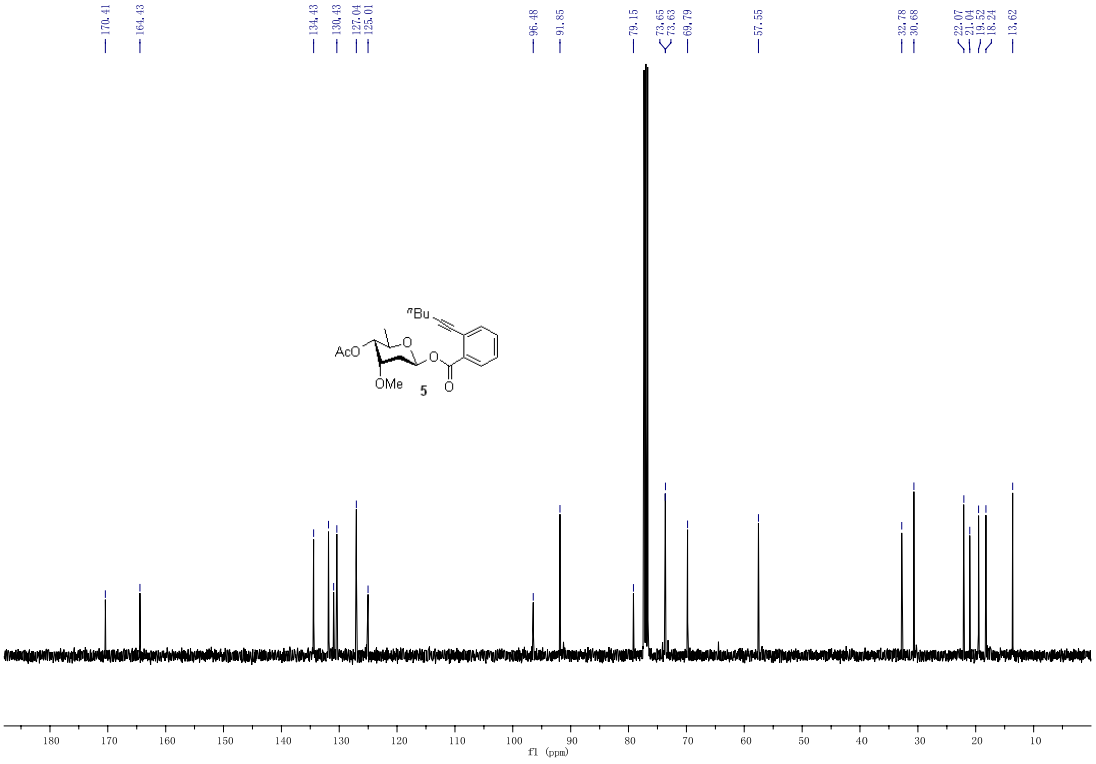

HO
O
MeO
OMe
18
A (d) 4.63
B (dq) 3.84
C (dd) 3.58
D (s) 3.42
E (s) 3.34
F (td) 3.24
G (d) 2.53
H (dd) 2.26
I (m) 1.73
J (d) 1.27
f1 (ppm)

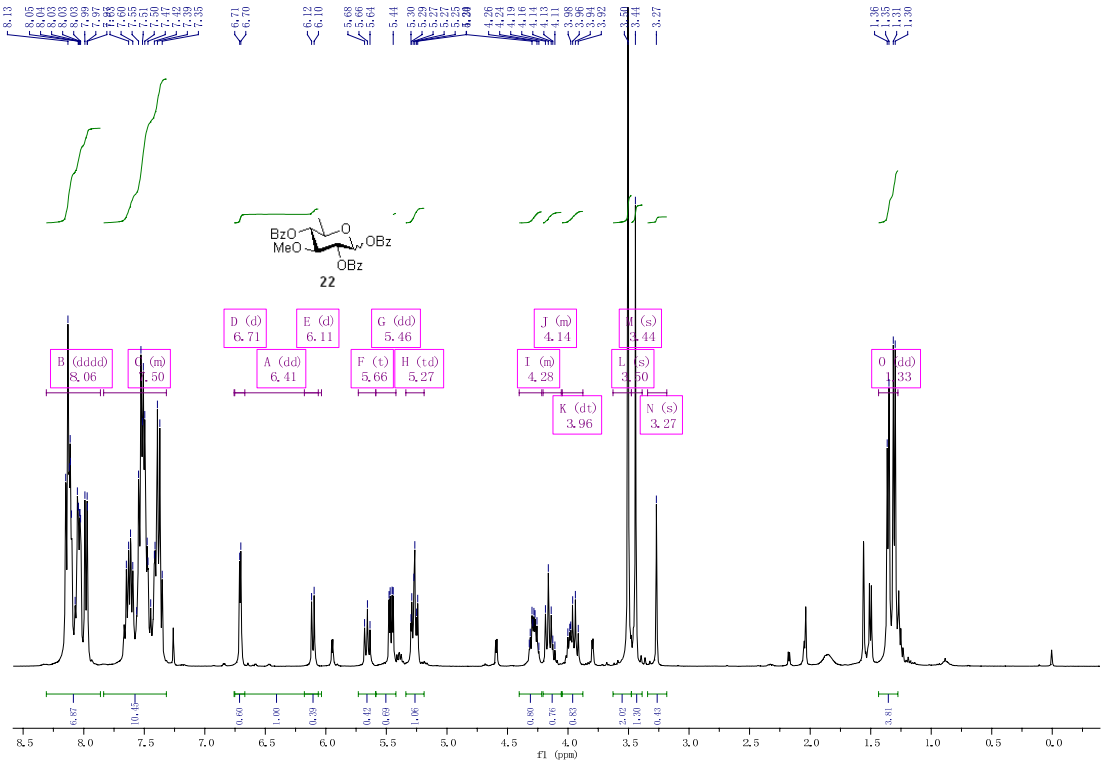

97.36
75.41
72.10
64.34
56.93
55.46
30.97
17.86
HO
O
MeO
OMe
18
f1 (ppm)

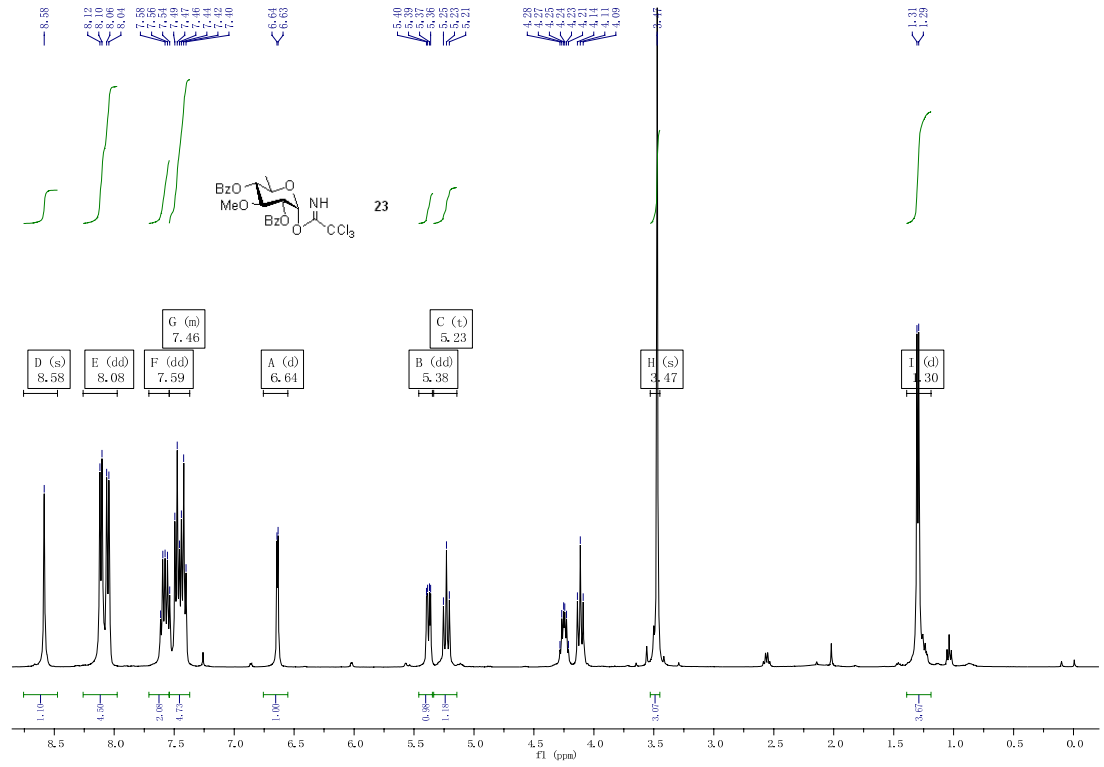

AcO
MeO
OMe
19
C (m) 4.64
B (m) 4.23
A (m) 3.72
D (s) 3.39
E (s) 3.36
H (ddd) 2.16
G (dt) 1.86
I (s) 2.11
F (d) 1.18
f1 (ppm)

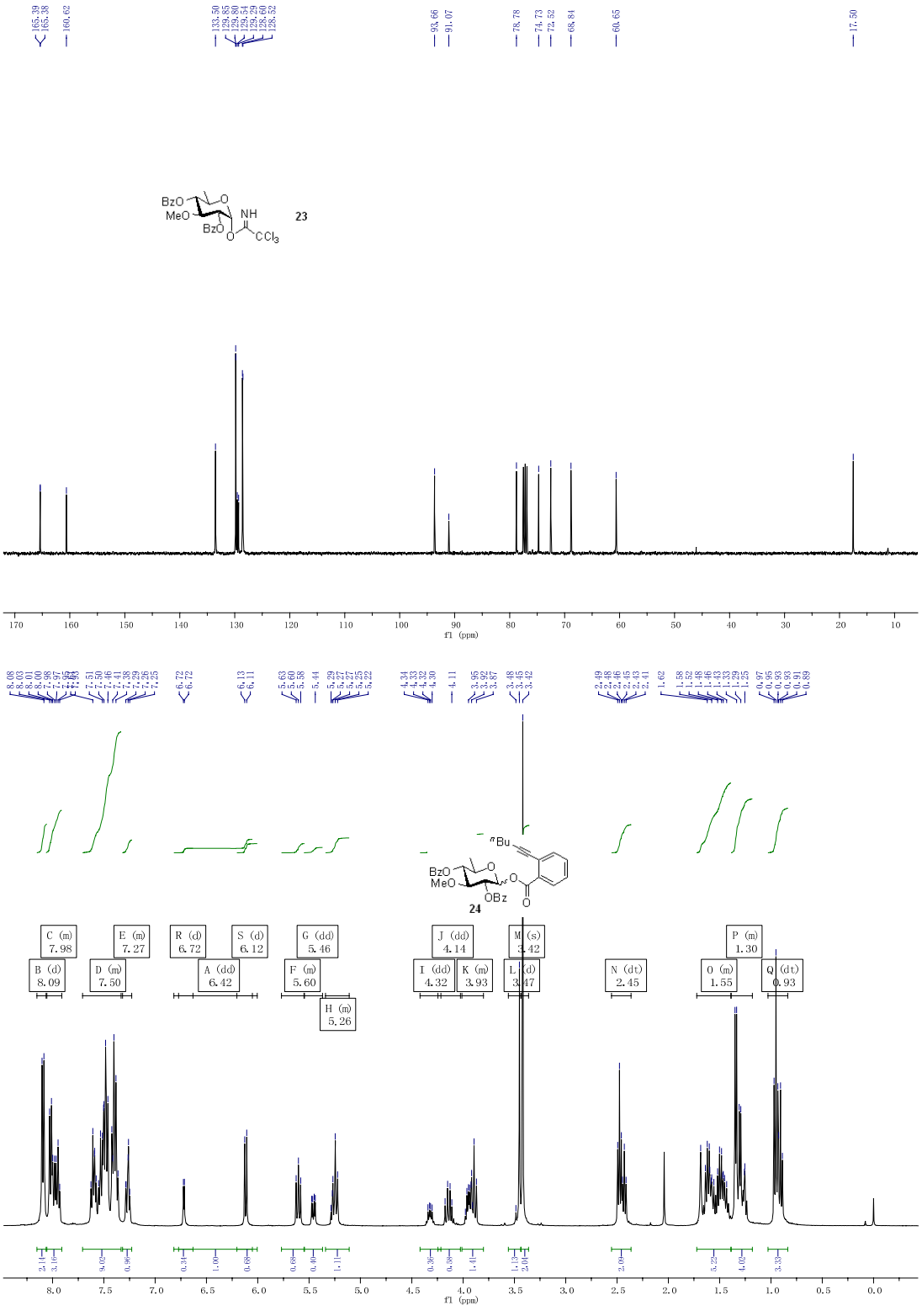

170.50
97.49
74.35
73.80
62.32
58.03
55.43
32.43
21.08
17.43
AcO
MeO
OMe
19
f1 (ppm)

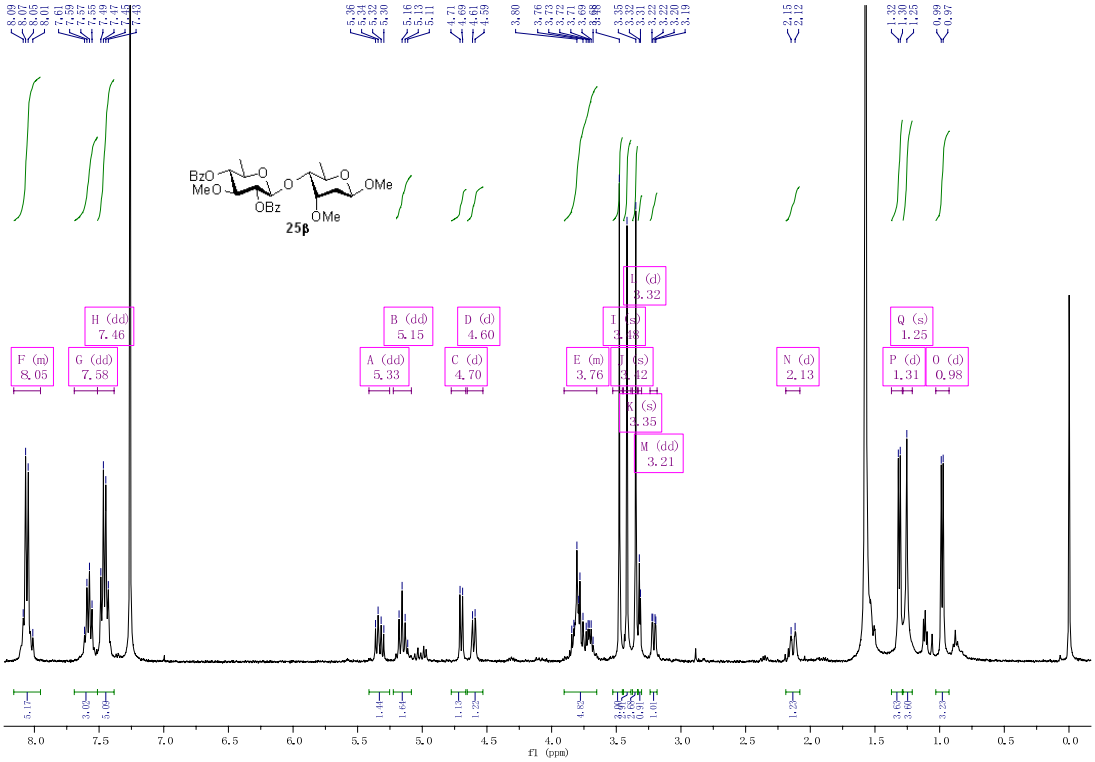

nBu
AcO
OMe
5
E (d) 7.92
C (t) 7.42
B (d) 7.50
D (t) 7.30
A (d) 6.29
F (dd) 4.70
G (m) 4.22
H (d) 3.92
I (s) 3.43
K (m) 2.36
J (t) 2.47
L (s) 2.13
M (dd) 1.93
N (m) 1.63
O (dd) 1.49
P (d) 1.25
Q (t) 0.95
f1 (ppm)

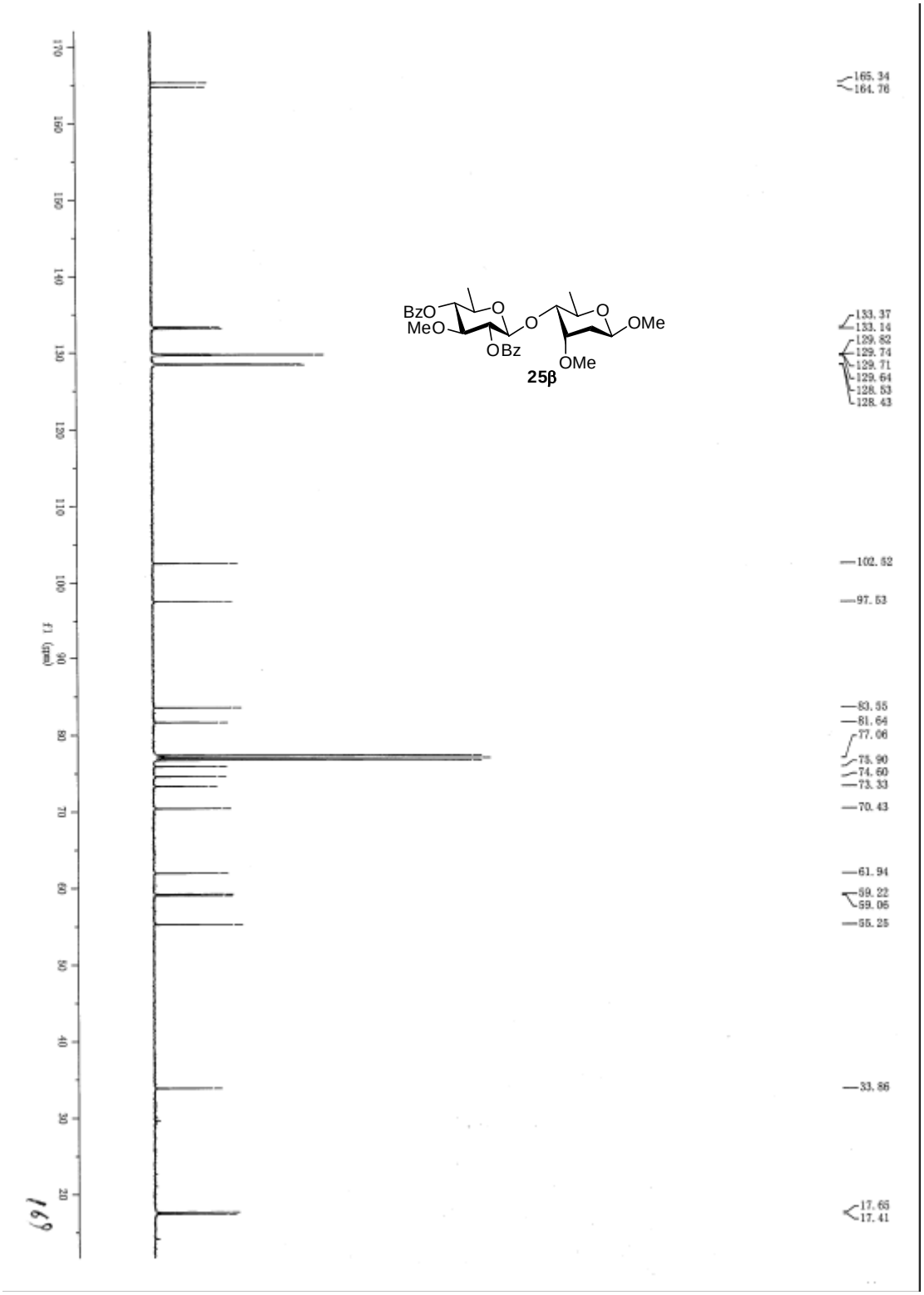

nBu
AcO
OMe
5
f1 (ppm)


BzO
MeO
OBz
OBz
22
D (d) 6.71
E (d) 6.11
G (dd) 5.46
J (m) 4.14
M (s) 3.44
B (dddd) 8.06
C (m) 7.50
A (dd) 6.41
F (t) 5.66
H (td) 5.27
I (m) 4.28
L (s) 3.50
O (dd) 1.33
K (dt) 3.96
N (s) 3.27
f1 (ppm)


BzO
MeO
BzO
NH
CCl3
23
G (m) 7.46
C (t) 5.23
D (s) 8.58
E (dd) 8.08
F (dd) 7.59
A (d) 6.64
B (dd) 5.38
H (s) 3.47
I (d) 1.30
f1 (ppm)


23
24


BzO
MeO
OBz
OMe
OMe
25β
F (m) 8.05
G (dd) 7.58
H (dd) 7.46
A (dd) 5.33
B (dd) 5.15
C (d) 4.70
D (d) 4.60
E (m) 3.76
I (d) 3.32
J (s) 3.42
K (s) 3.35
M (dd) 3.21
N (d) 2.13
P (d) 1.31
Q (s) 1.25
O (d) 0.98
f1 (ppm)


BzO
MeO
OBz
O
O
O
OMe
OMe
25β
165.34
164.76
133.37
133.14
129.82
129.74
129.71
129.64
128.53
128.43
102.52
97.53
83.55
81.64
77.06
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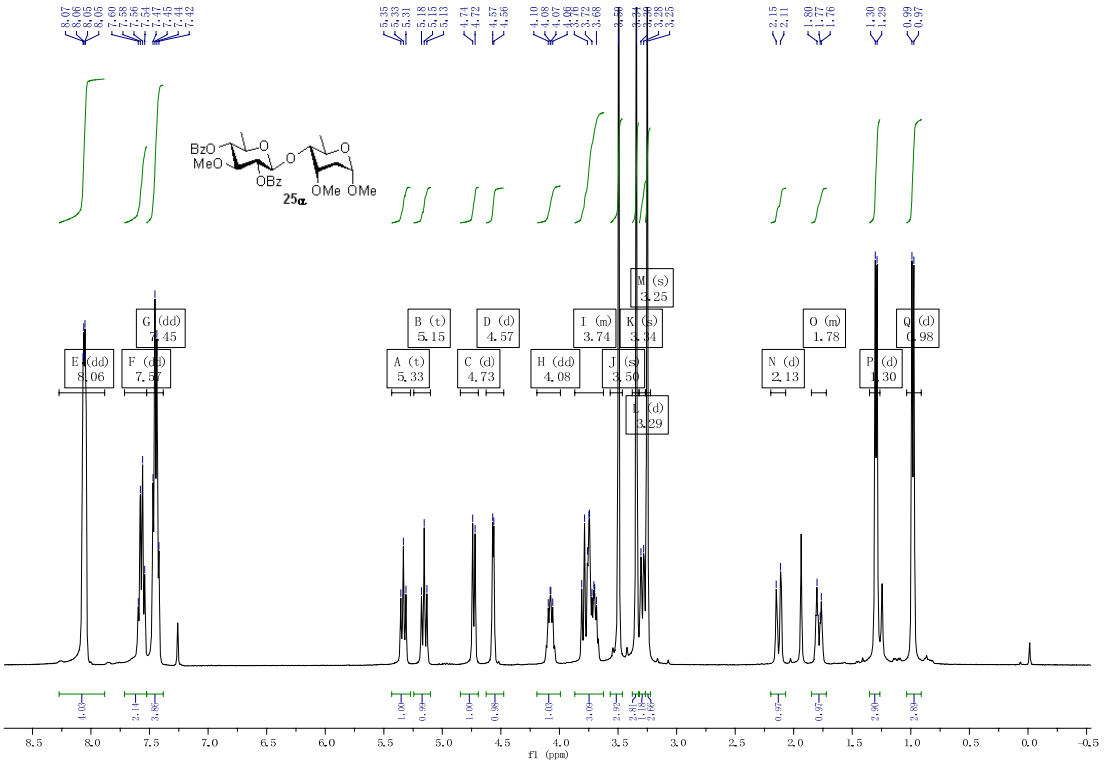
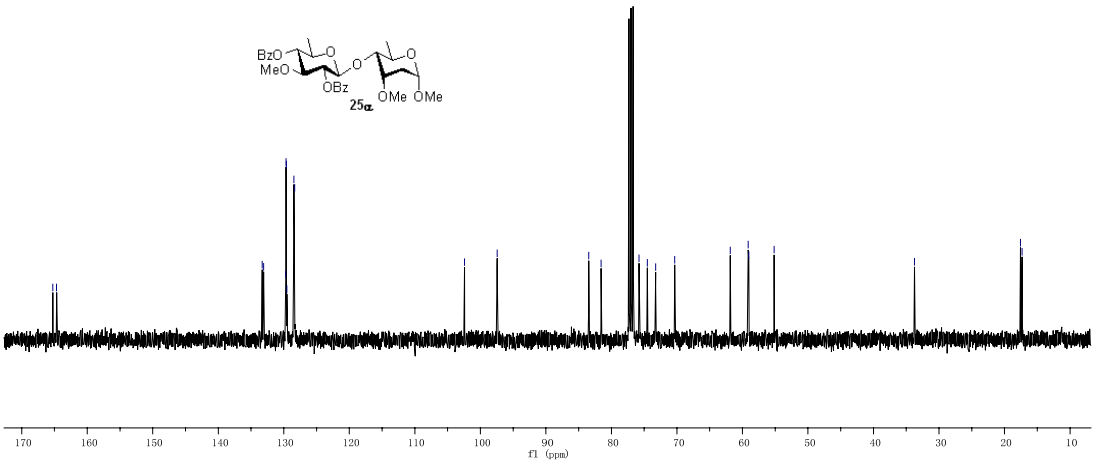
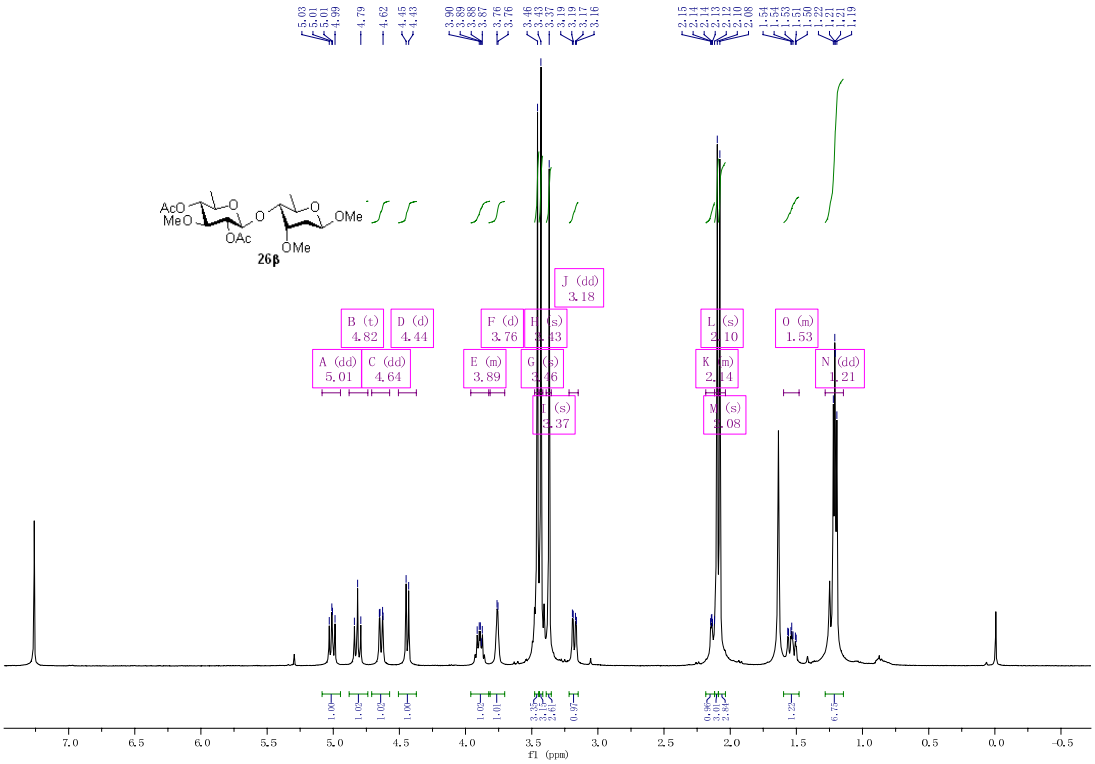
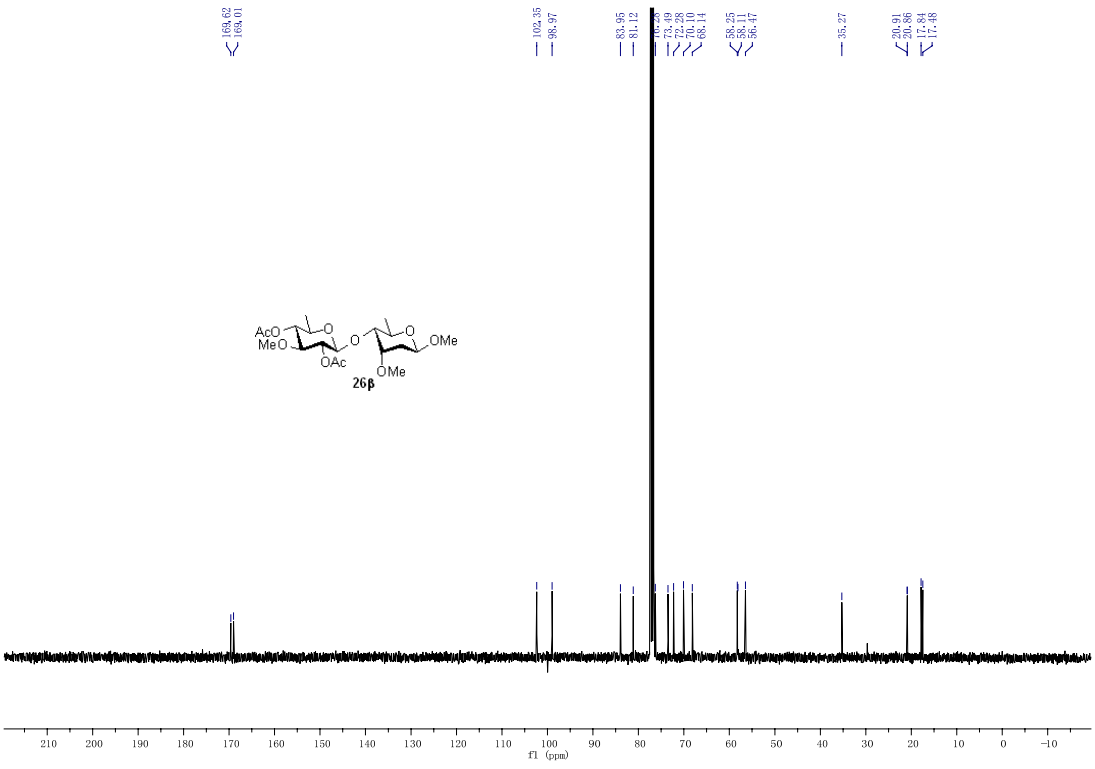
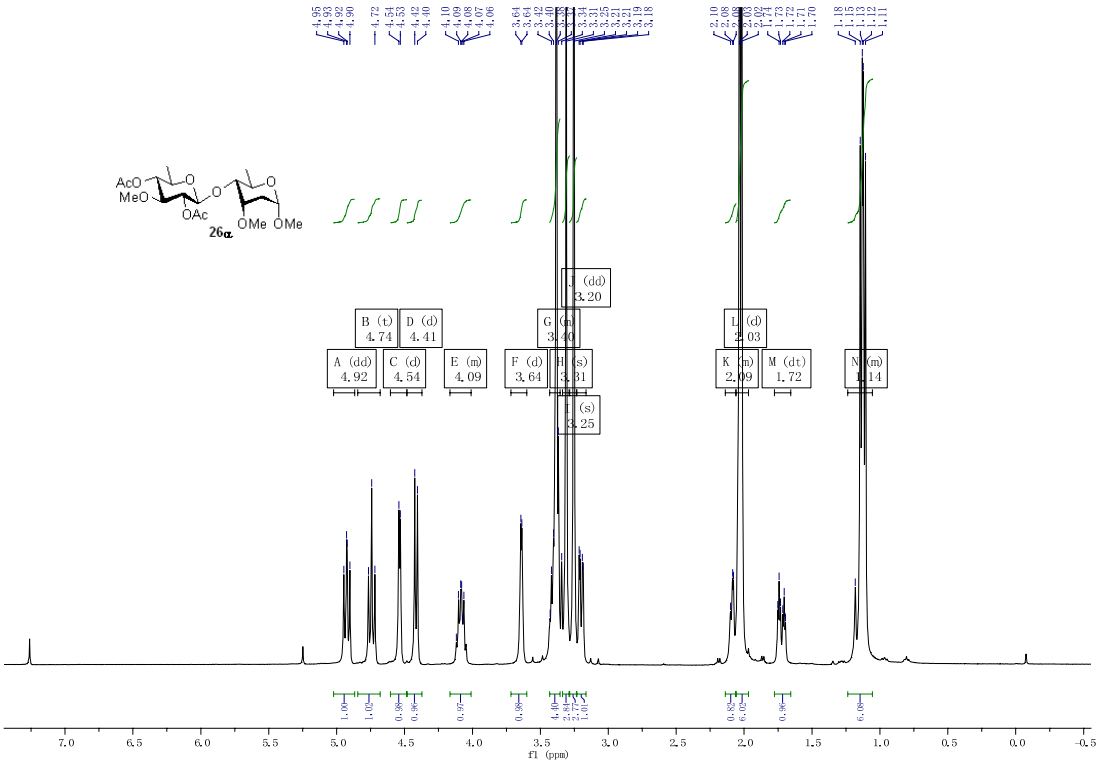
70.43
61.94
59.22
59.06
55.25
33.86
17.66
17.41
f1 (ppm)

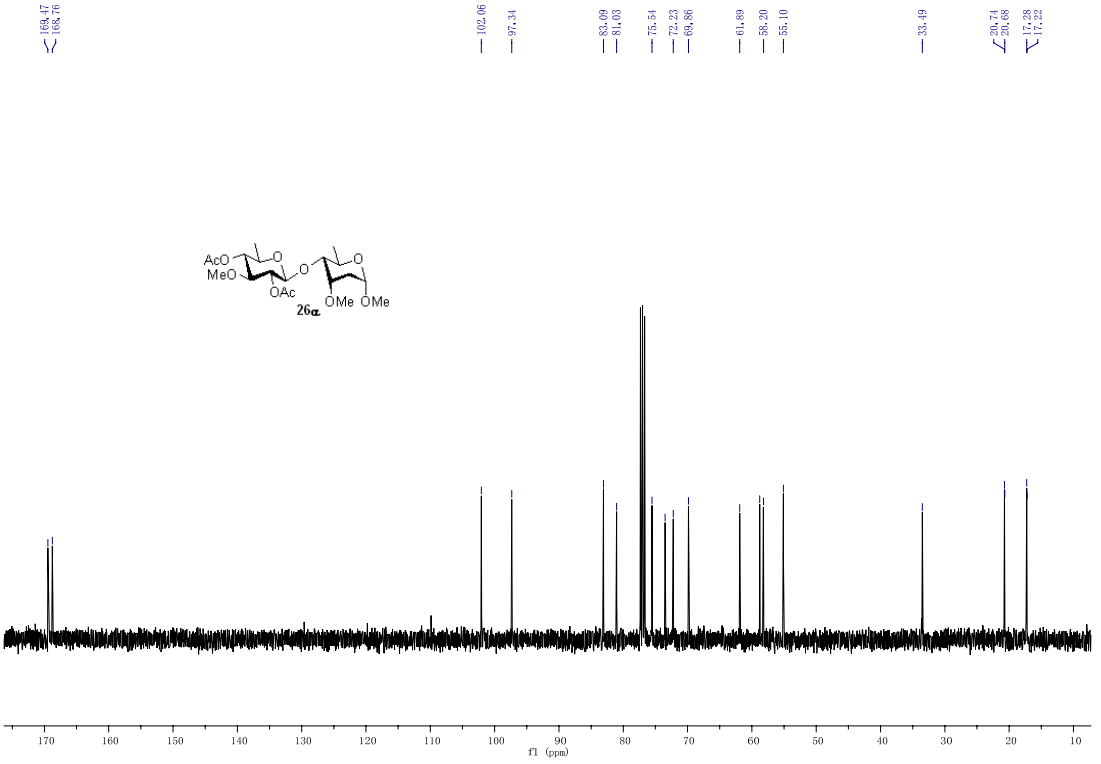

BzO
MeO
OBz
OMe OMe
25α
A (t) 5.33
B (t) 5.15
C (d) 4.73
D (d) 4.57
E (dd) 8.06
F (dd) 7.57
G (dd) 7.45
H (dd) 4.08
I (m) 3.74
J (s) 3.50
K (s) 3.34
L (d) 3.29
M (s) 3.25
N (d) 2.13
O (m) 1.78
P (d) 1.30
Q (d) 0.98
f1 (ppm)

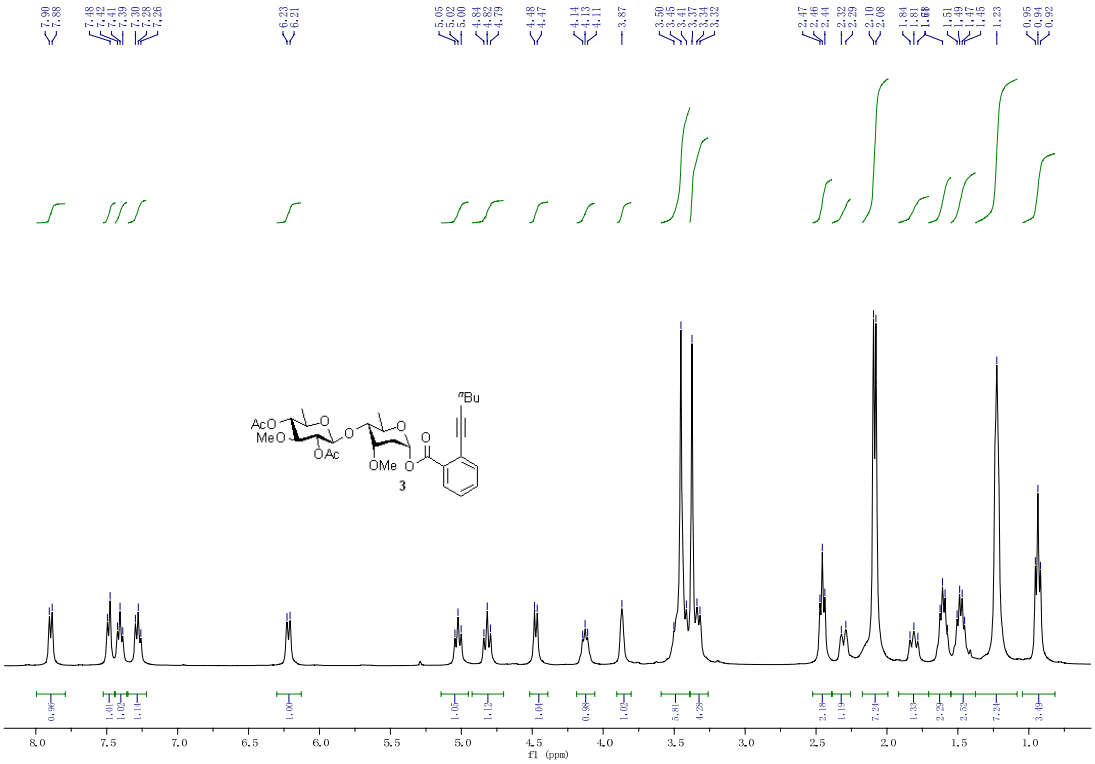

BzO
MeO
OBz
OMe OMe
25α
f1 (ppm)

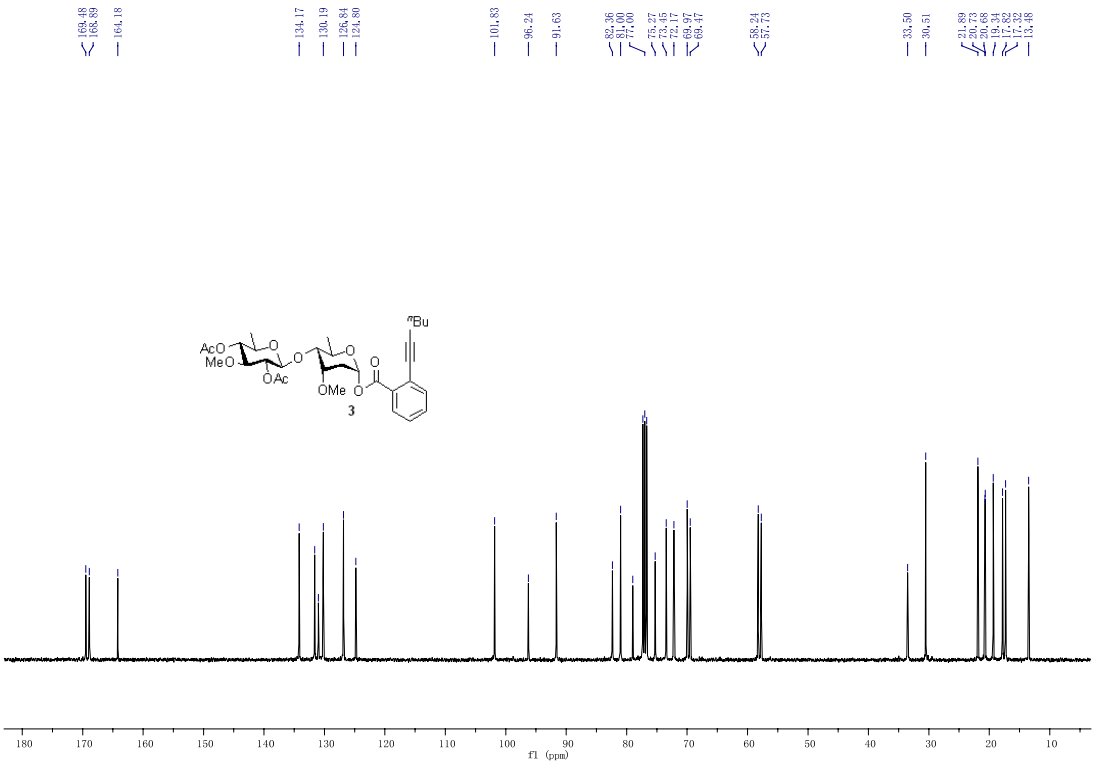

26β
A (dd) 5.01
B (t) 4.82
C (dd) 4.64
D (d) 4.44
E (m) 3.89
F (d) 3.76
G (s) 3.46
H (s) 3.43
I (s) 3.37
J (dd) 3.18
K (m) 2.14
L (s) 2.10
M (s) 2.08
N (dd) 1.21
O (m) 1.53
f1 (ppm)

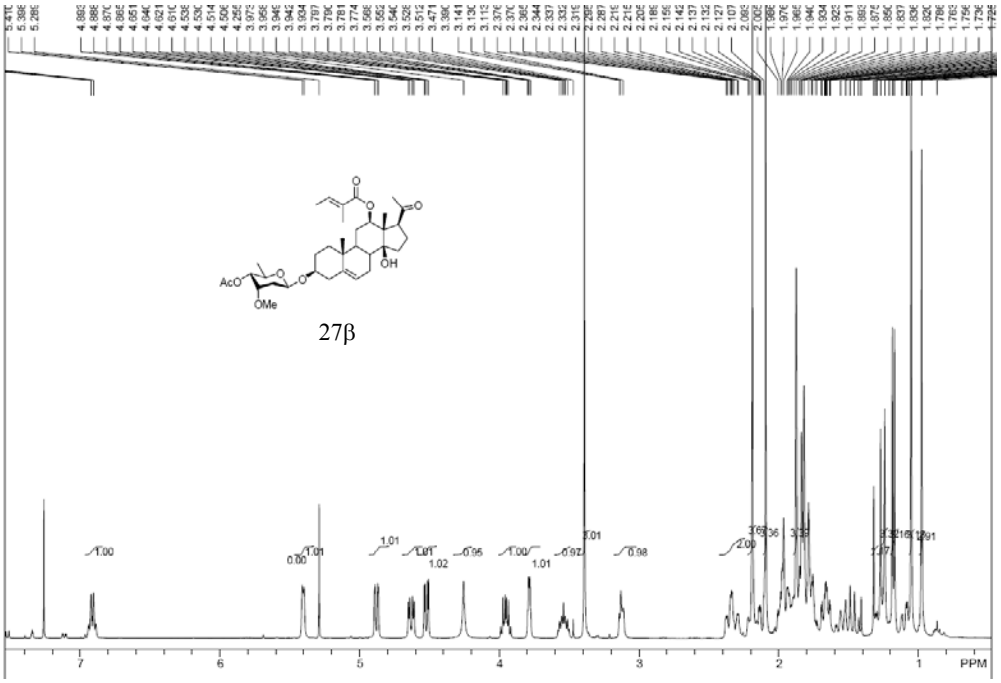

26β
f1 (ppm)


AcO
MeO
OAc
OMe OMe
26α
A (dd) 4.92
B (t) 4.74
C (d) 4.54
D (d) 4.41
E (m) 4.09
F (d) 3.64
G (m) 3.40
H (s) 3.31
I (dd) 3.20
J (s) 3.25
K (m) 2.09
L (d) 2.03
M (dt) 1.72
N (m) 1.14
f1 (ppm)

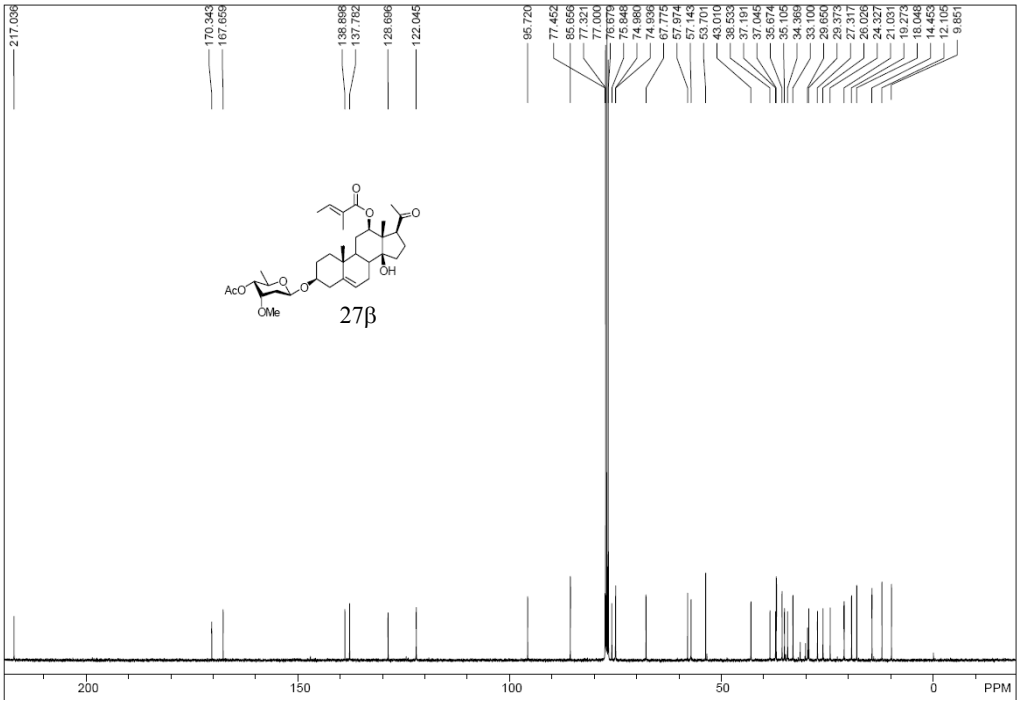

AcO
MeO
OAc
OMe OMe
26α
f1 (ppm)


7.90
7.88
7.48
7.42
7.41
7.39
7.30
7.28
7.26
6.23
6.21
5.05
5.02
5.00
4.84
4.82
4.79
4.48
4.47
4.14
4.13
4.11
3.87
3.50
3.45
3.41
3.37
3.34
3.32
2.47
2.46
2.44
2.32
2.29
2.10
2.08
1.84
1.83
1.68
1.51
1.49
1.47
1.45
1.23
0.95
0.94
0.92
AcO
MeO
OAc
OMe
O
nBu
3
f1 (ppm)

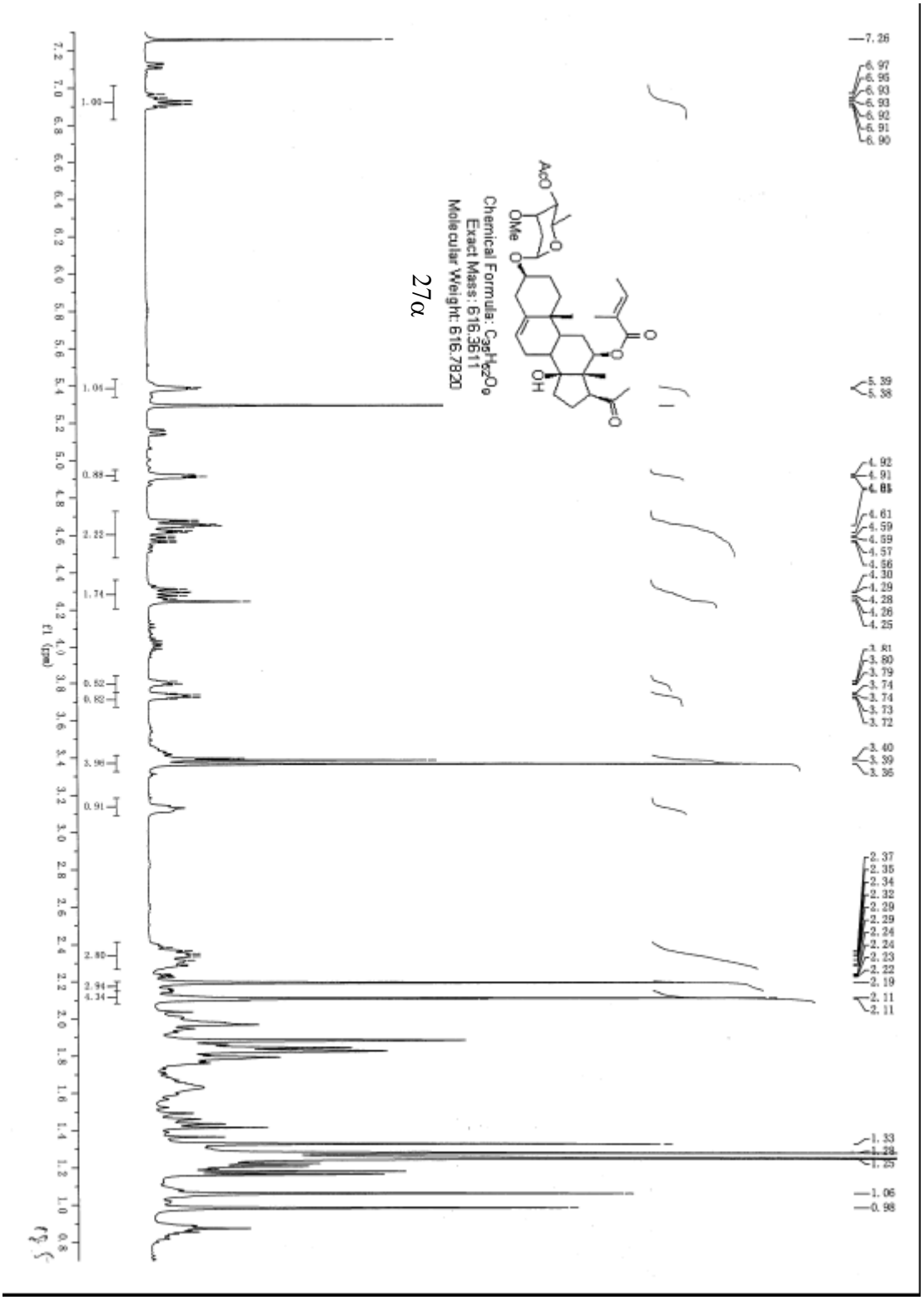

169.48
168.89
164.18
134.17
130.19
126.84
124.80
101.83
96.24
91.63
82.36
81.00
77.00
75.27
73.45
72.17
69.97
69.47
58.24
57.73
33.50
30.51
21.89
20.73
20.68
19.34
17.82
17.32
13.48
AcO
MeO
OAc
OMe
O
nBu
3
f1 (ppm)

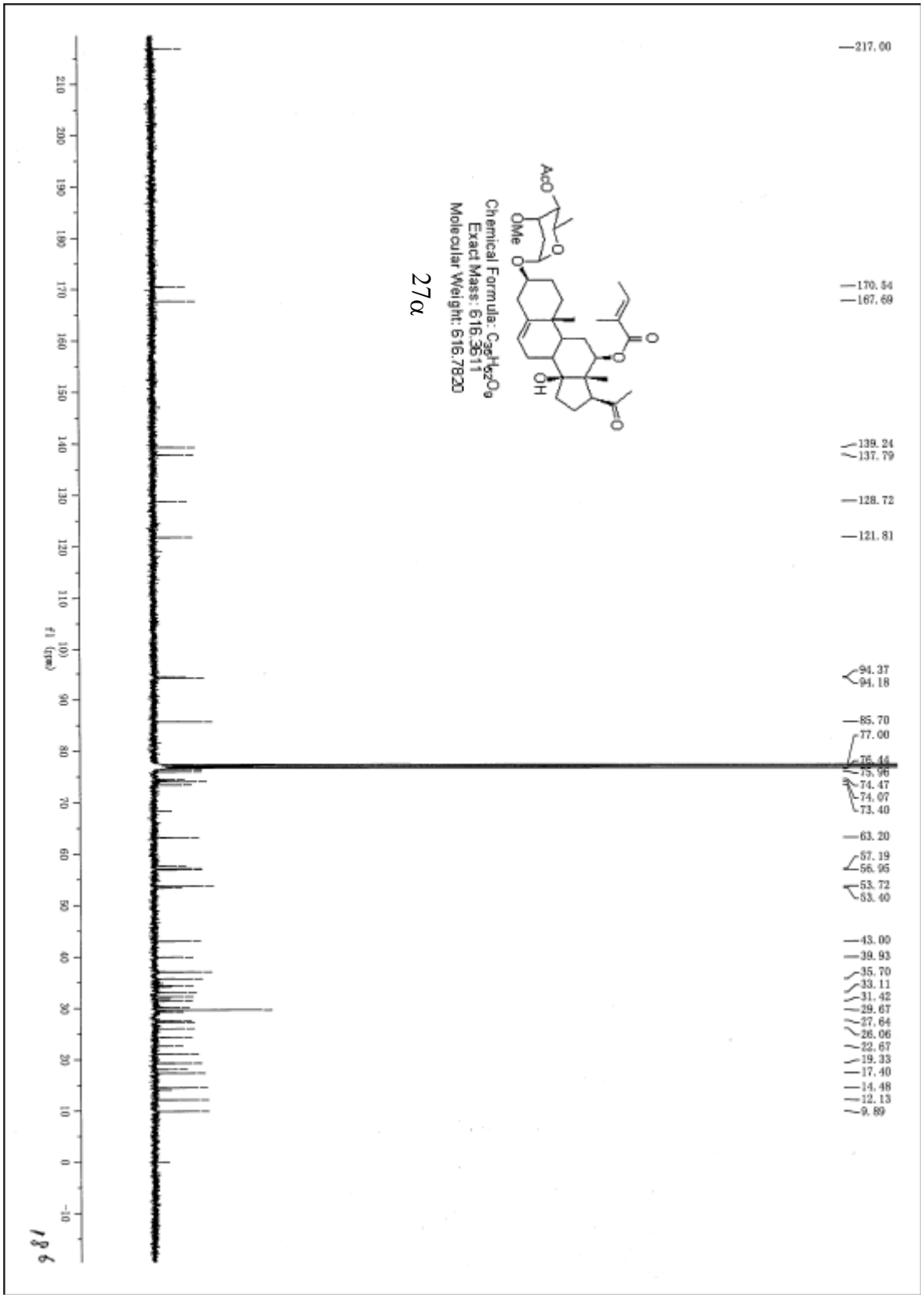

AcO
OMe
OH
O
O
O
O
O
1.00
0.00
1.01
1.01
1.01
1.02
0.95
1.00
1.01
0.97
1.01
0.98
2.00
7
6
5
4
3
2
1
PPM

27β

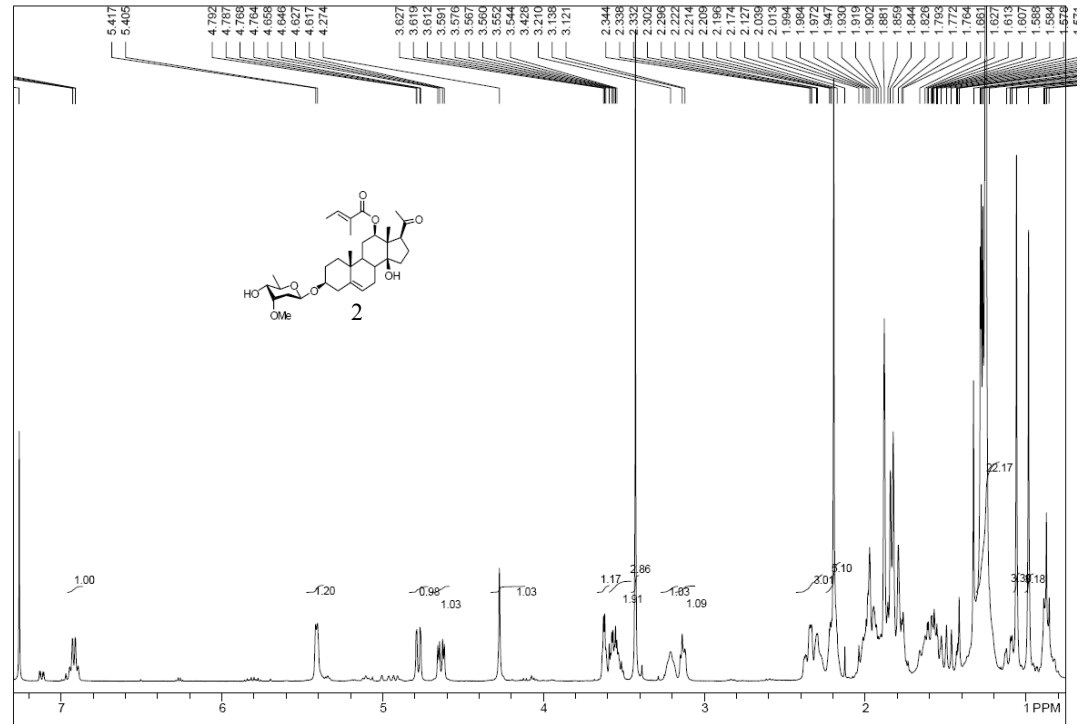

217.006
170.343
167.669
138.898
137.782
128.696
122.045
95.720
77.452
85.656
77.321
77.000
76.679
75.848
74.980
74.936
67.775
57.974
57.143
53.701
43.010
38.533
37.191
37.045
35.674
35.105
34.369
33.100
29.650
29.373
27.317
26.026
24.327
21.031
19.273
18.048
14.453
12.105
9.851
AcO
OMe
OH
O
O
O
O
O
200
150
100
50
0
PPM

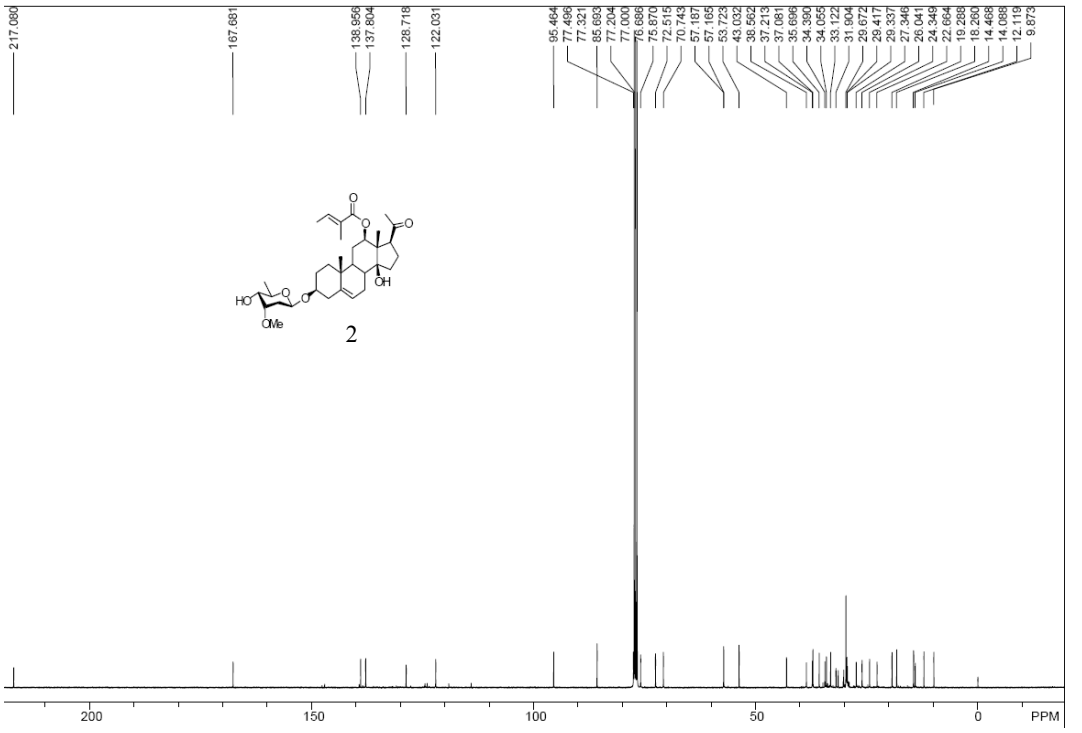
27β

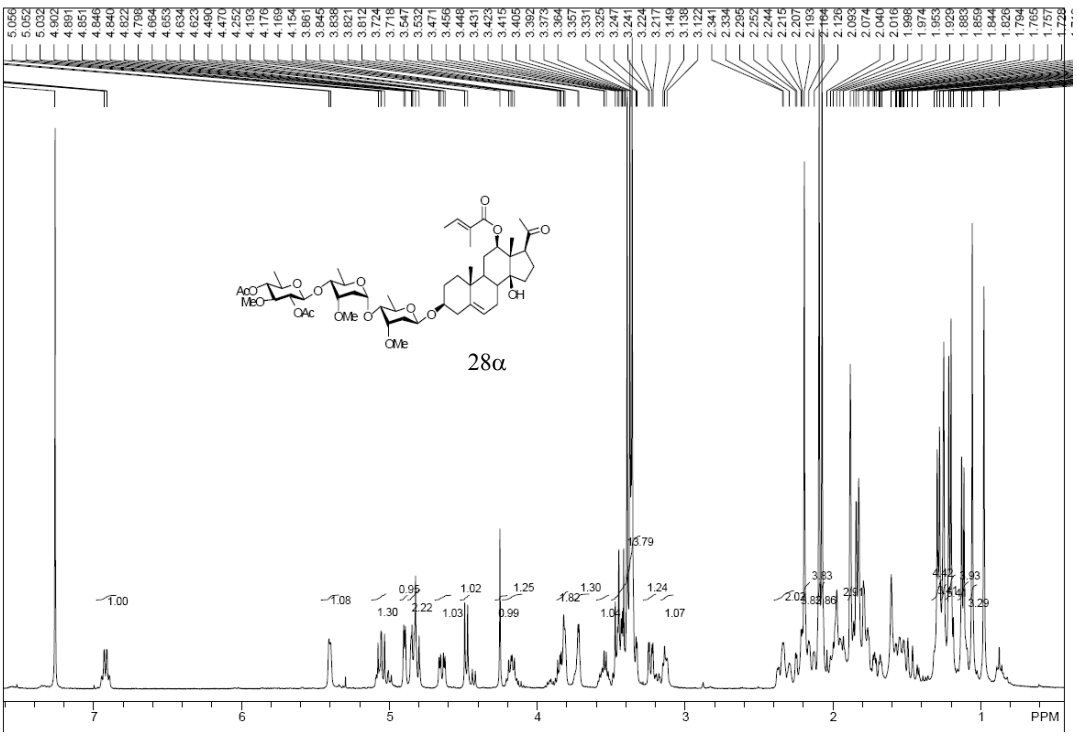

27α
Chemical Formula: C36H48O9
Exact Mass: 616.3611
Molecular Weight: 616.7820
AcO
OMe
OH
O
f1 (ppm)

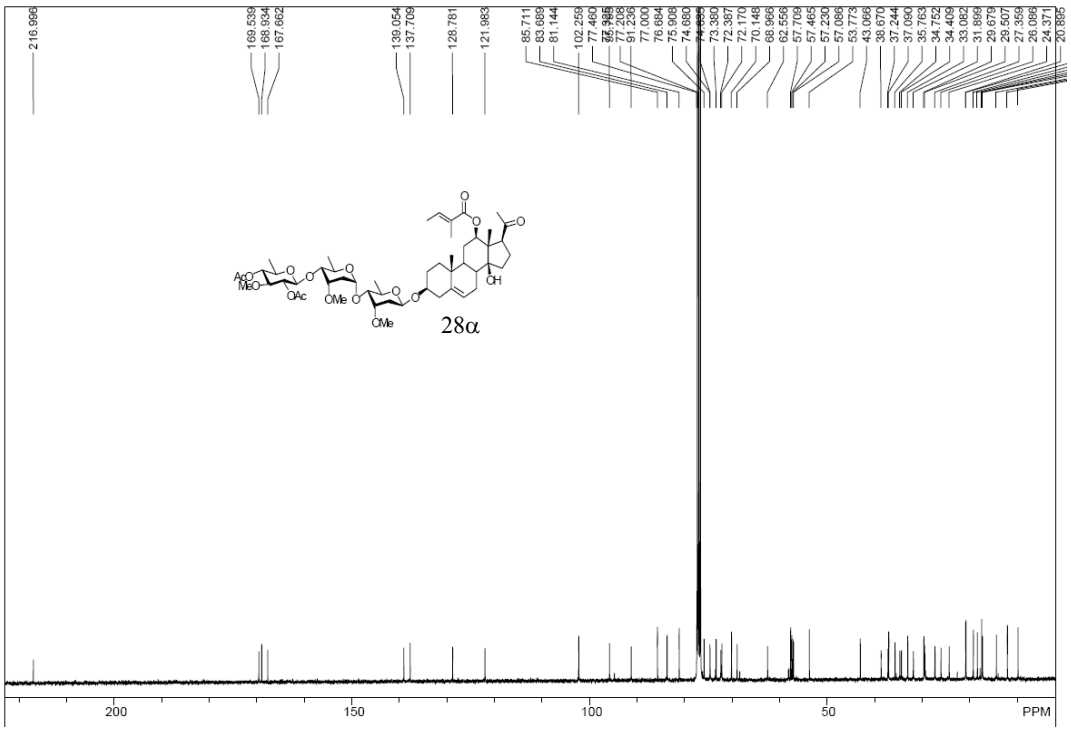

217.00
170.54
167.69
139.24
137.79
128.72
121.81
94.37
94.18
85.70
77.00
76.44
75.96
74.47
74.07
73.40
63.20
57.19
56.95
53.72
53.40
43.00
39.93
35.70
33.11
31.42
29.67
27.64
26.06
22.67
19.33
17.40
14.48
12.13
9.89
f1 (ppm)
AcO
OMe
OH
O
Chemical Formula: C36H42O9
Exact Mass: 618.3611
Molecular Weight: 618.7820

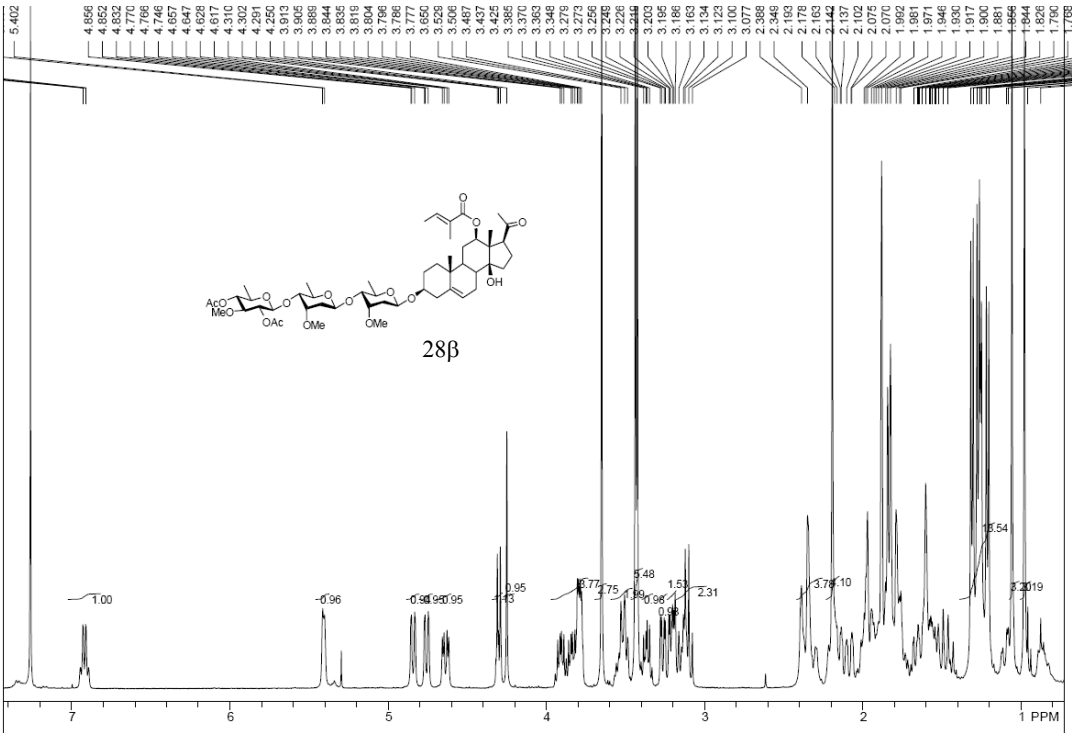
27α

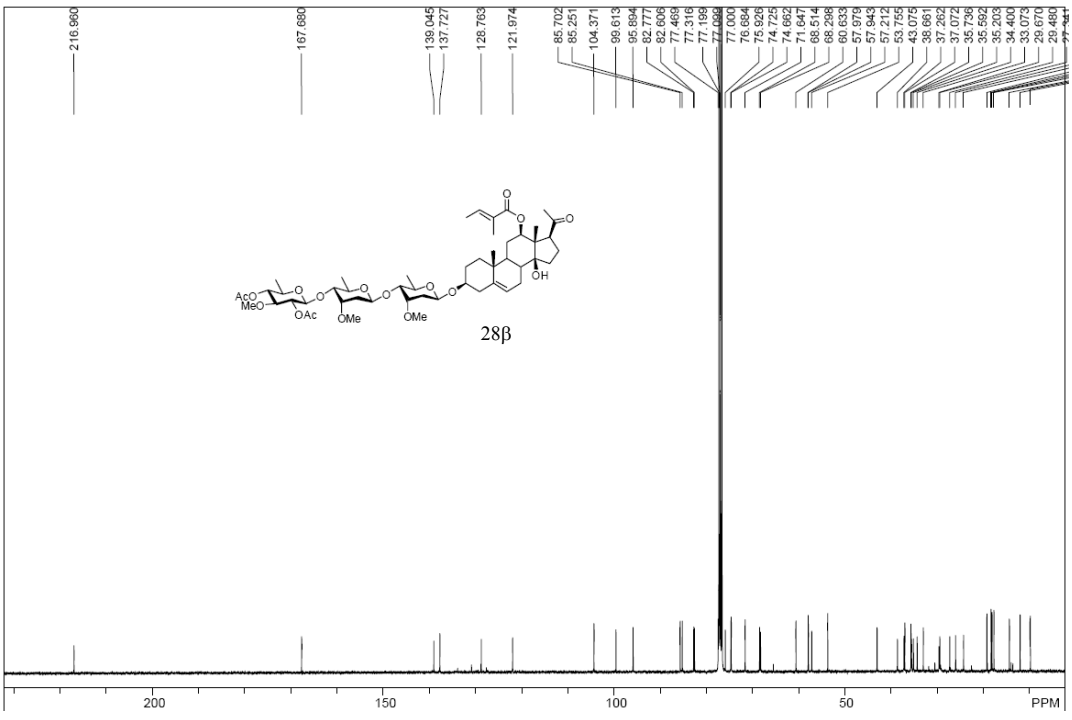

5.417
5.405
4.792
4.787
4.768
4.764
4.658
4.646
4.637
4.617
4.274
3.627
3.619
3.612
3.591
3.576
3.567
3.560
3.552
3.544
3.428
3.210
3.138
3.121
2.344
2.338
2.332
2.302
2.296
2.222
2.214
2.209
2.196
2.174
2.127
2.039
2.013
1.994
1.984
1.972
1.947
1.930
1.919
1.902
1.891
1.859
1.844
1.828
1.793
1.772
1.764
1.681
1.627
1.613
1.607
1.588
1.584
1.579
HO
O
O
OMe
O
O
O
OH
2
1.00
1.20
0.98
1.03
1.03
1.17
2.86
1.91
1.03
1.09
3.01
3.10
22.17
3.30
3.18
7
6
5
4
3
2
1 PPM


217.080
167.681
138.956
137.804
128.718
122.031
95.464
77.496
77.321
85.693
77.204
77.000
76.686
75.670
72.515
70.743
57.187
57.165
53.723
43.032
38.562
37.213
37.081
35.696
34.390
34.055
33.122
31.904
29.672
29.417
29.337
27.346
26.041
24.349
22.664
19.288
18.260
14.468
14.088
12.119
9.873
HO
O
O
OMe
O
O
O
OH
2
200
150
100
50
0
PPM

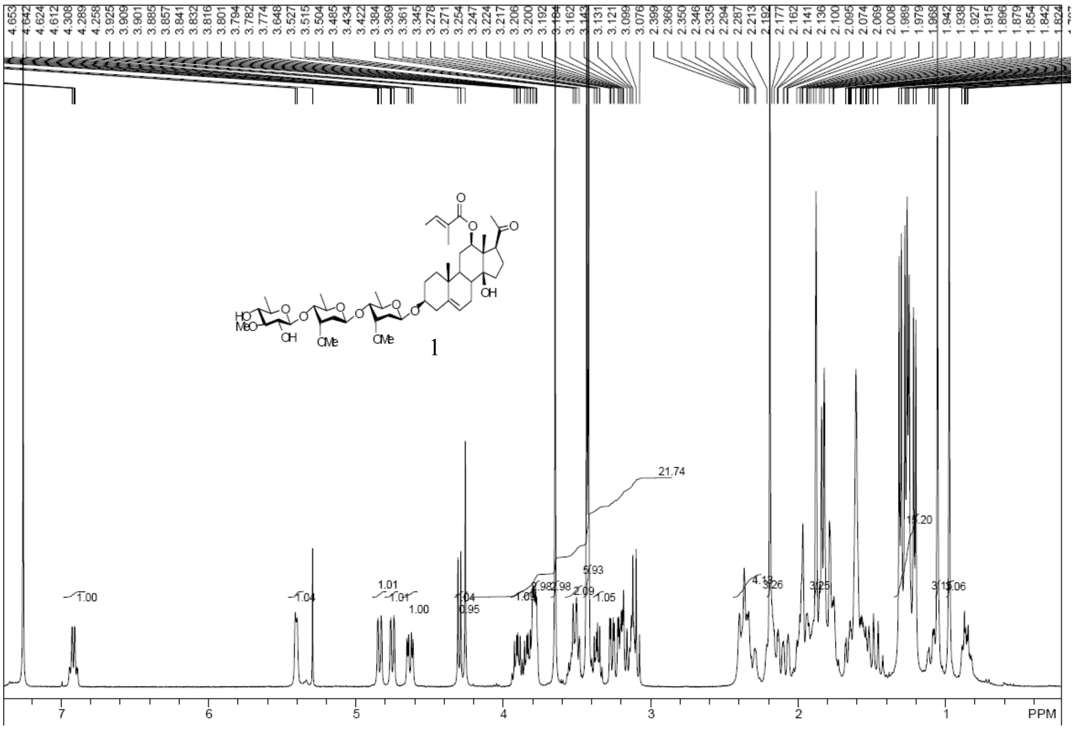

28α
PPM

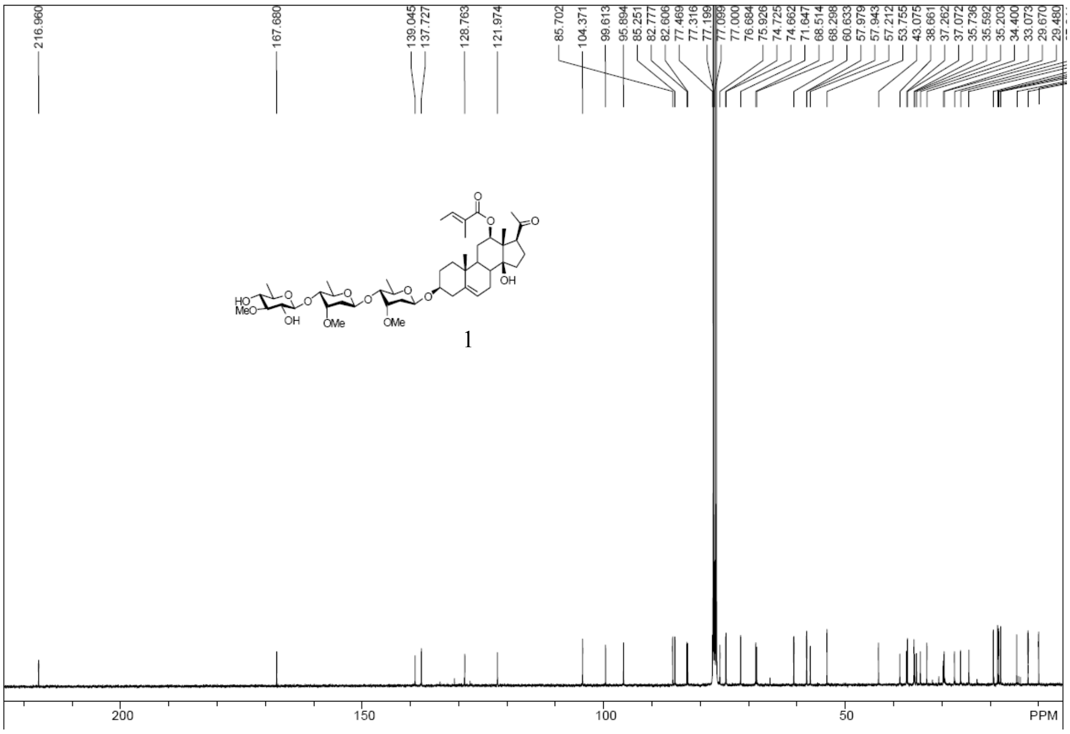

28α
PPM

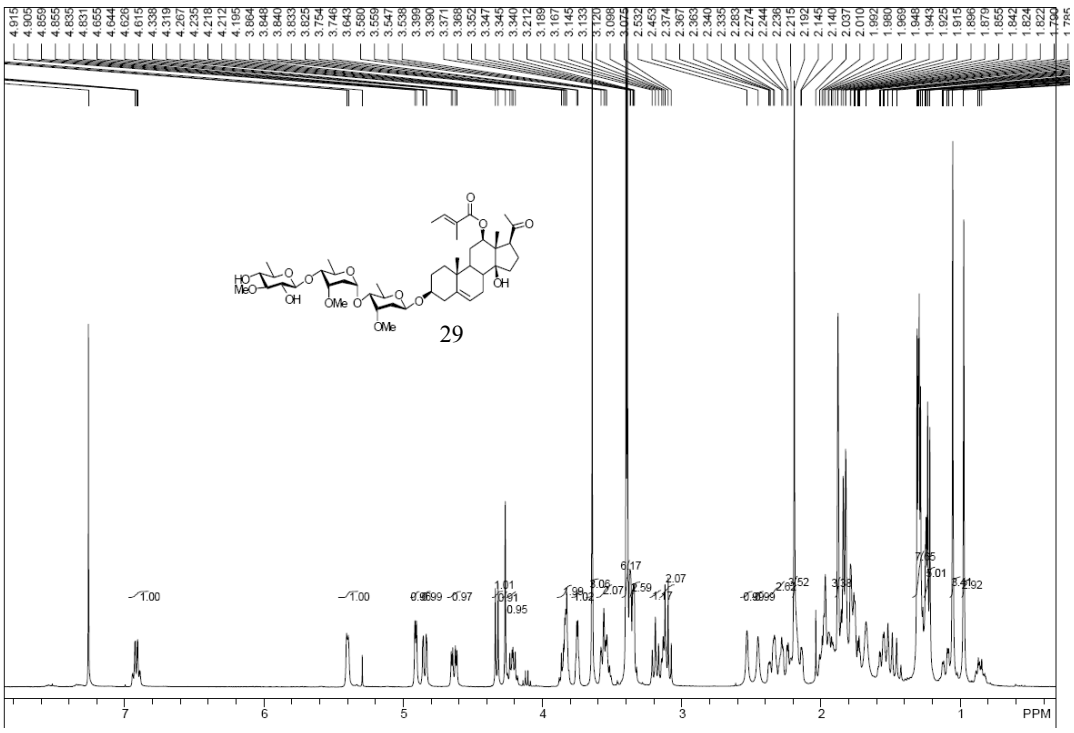

28β
1.00
0.96
0.95
0.95
0.95
0.95
1.43
0.77
2.75
5.48
1.99
0.98
0.98
1.53
2.31
3.78
4.10
13.54
3.2019
7
6
5
4
3
2
1 PPM

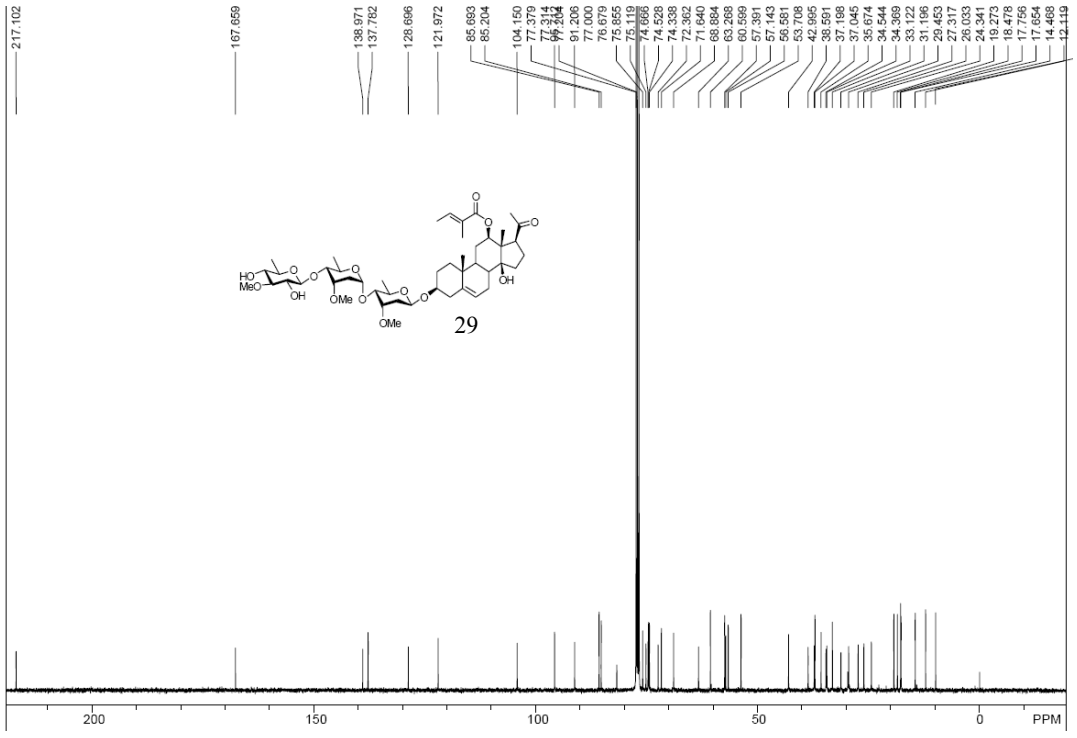

28β
216.960
167.690
139.045
137.727
128.763
121.974
85.702
85.251
104.371
99.613
95.894
82.777
82.606
77.489
77.316
77.199
77.000
76.684
75.926
74.725
74.662
71.647
68.514
68.298
60.633
57.979
57.943
57.212
53.755
43.075
38.661
37.282
37.072
35.736
35.592
35.203
34.400
33.073
29.670
29.480
200
150
100
50
PPM

Electronic Supplementary Material (ESI) for Chemical Communications






29
PPM


29
PPM