Supporting Information

Total Synthesis of Astrosterioside A, an Anti-inflammatory Asterosaponin

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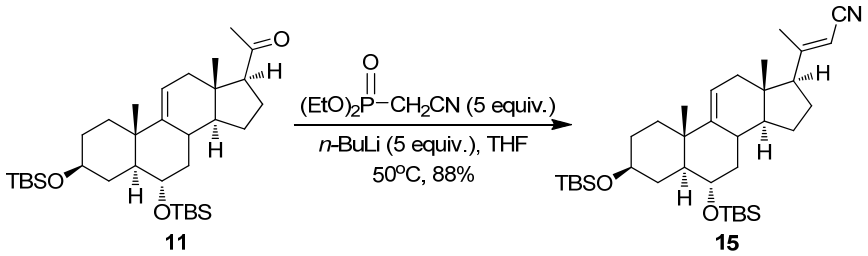
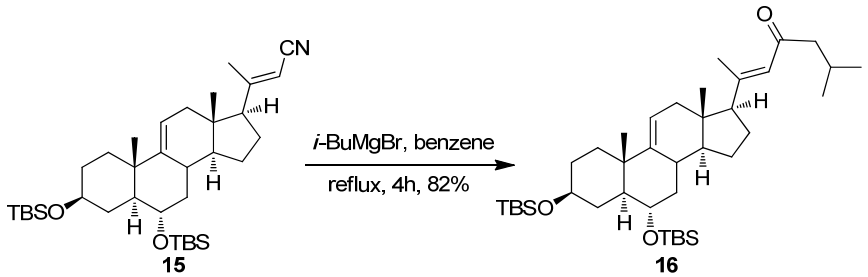
General Remarks. All reactions were carried out under nitrogen or argon with anhydrous solvents in flame-dried glassware, unless otherwise noted. All glycosylation reactions were performed in the presence of 4Å or 5Å molecular sieves, which were flame-dried immediately before use in the reaction under high vacuum. Glycosylation solvents were dried using a solvent purification system and used directly without further drying. The chemicals used were reagent grade as supplied, except where noted. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates. Compound spots were visualized by UV light (254 nm) and by heating with a solution with 10% H_2SO_4 in ethanol. Flash column chromatography was performed on silica gel. NMR spectra were referenced using Me_4Si (0 ppm), residual $CHCl_3$ (^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.00 ppm), CD_3OD (^{1}H NMR δ = 3.30 ppm, ^{13}C NMR δ = 49.00 ppm), or D_2O (^{1}H NMR δ = 4.67 ppm). Peak and coupling constant assignments are based on ^{1}H NMR, ^{1}H–^{1}H COSY, and ^{1}H–^{13}C HSQC experiments. Splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), and brs (broad singlet) for ^{1}H NMR data. ESI-MS and MALDI-MS were run on an IonSpec Ultra instrument using HP5989A or VG Quattro MS. Optical rotations were measured using a Perkin-Elmer 241 polarimeter.

3β,6α-Di-(*tert*-butyldimethylsiloxy)-5α-chol-9(11),20(22)-ene-23-nitrile (15)



To a solution of *n*-butyllithium (1.22 mL, 2.674 mmol, 2.2 M in cyclohexane) in THF (3 mL) was added dropwise diethyl cyanomethylphosphonate[1] (0.433 mL, 2.674 mmol) at room temperature. The mixture was stirred at room temperature for 1 h. A solution of ketone **11**[2] (300 mg, 0.5347 mmol) in THF (3 mL) was added dropwise, and the mixture was stirred at 50°C for 12 h. It was then quenched with a saturated NH_4Cl solution. The aqueous layer was extracted with EtOAc, and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash column chromatography on silica gel (hexane/EtOAc, 80:1) gave **15** (274 mg, 88%) as a white solid: $[\alpha]_D^{25}$ = +4.8 (*c* 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (d, *J* = 4.9 Hz, 1H), 5.15 (s, 1H), 3.52 (dtd, *J* = 25.7, 10.0, 4.6 Hz, 2H), 2.28 (t, *J* = 9.5 Hz, 1H), 2.13 (d, *J* = 11.7 Hz, 1H), 2.09 (s, 3H), 2.03 (dd, *J* = 19.2, 7.5 Hz, 3H), 1.92–1.85 (m, 1H), 1.78 (dd, *J* = 16.2, 8.8 Hz, 3H), 1.65 (d, *J* = 12.9 Hz, 1H), 1.60–1.47 (m, 2H), 1.45–1.21 (m, 7H), 1.16–1.06 (m, 2H), 1.01–0.95 (m, 1H), 0.94 (s, 3H), 0.87 (dd, *J* = 16.5, 3.5 Hz, 18H), 0.50 (s, 3H), 0.07 (s, 3H), 0.06–0.05 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.36, 146.43, 117.51, 115.48, 95.58, 72.11, 69.84, 58.07, 53.31, 49.79, 43.30, 42.49, 40.42, 38.26, 35.90, 33.57, 31.77, 25.92, 25.89, 25.31, 25.07, 22.49, 19.30, 18.33, 18.07, 12.51, 1.02, -4.05, -4.63, -4.71, -4.72; HRMS (ESI) calcd for $C_{35}H_{62}O_2Si_2$ $[M+H]^+$ 584.4319, found 584.4325.

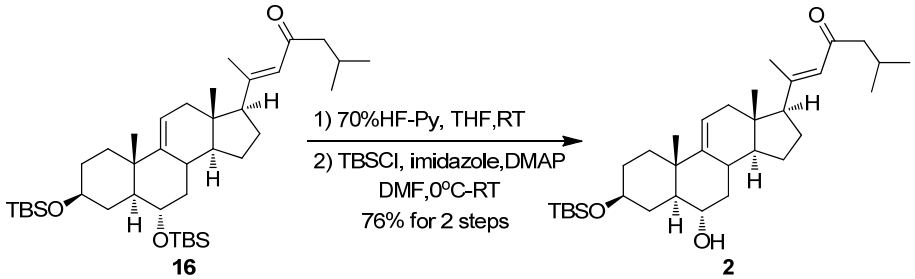
3β,6α-Di-(*tert*-butyldimethylsiloxy)-5α-cholest-9(11),20(22)-ene-23-one (16)



To a solution of **15** (81 mg, 0.137 mmol) in benzene (4 mL) at room temperature was added a solution of *iso*-butylmagnesium bromide (0.35 mL, 2 M in ether).[3] The reaction mixture was brought to reflux and stirred for 4 h. After cooling to room temperature, it was quenched with a saturated NH_4Cl solution. The aqueous layer was extracted with EtOAc, and the combined organic layers were dried over $MgSO_4$ and

condensed under vacuum. Purification of the residue by flash column chromatography on silica gel (hexane/EtOAc, 60:1) gave **16** (72 mg, 82%) as a white solid: $[\alpha]_D^{25}$ = +0.6 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 5.31 (d, *J* = 5.5 Hz, 1H), 3.54 (dd, *J* = 18.2, 10.2 Hz, 2H), 2.30 (d, *J* = 7.0 Hz, 2H), 2.25 (dd, *J* = 12.0, 8.2 Hz, 1H), 2.15 (d, *J* = 7.4 Hz, 3H), 2.13–1.97 (m, 6H), 1.96–1.45 (m, 14H), 1.32 (ddd, *J* = 35.5, 24.7, 14.0 Hz, 11H), 1.13 (t, *J* = 9.6 Hz, 3H), 0.99 (dd, *J* = 19.6, 12.8 Hz, 2H), 0.92 (s, 3H), 0.88 (d, *J* = 0.5 Hz, 18H), 0.50 (s, 2H), 0.07 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.03, 146.26, 123.83, 115.87, 77.32, 72.16, 69.94, 60.03, 53.83, 53.36, 49.81, 43.34, 42.57, 40.50, 38.23, 35.98, 35.91, 33.58, 31.79, 29.69, 29.61, 25.92, 25.89, 25.33, 25.29, 25.16, 22.66, 20.82, 19.28, 18.34, 18.07, 12.59, 1.00, -4.04, -4.64, -4.72, -4.73; HRMS (ESI) calcd for $C_{39}H_{71}O_3Si_2$ $[M+H]^+$ 643.4936, found 643.4938.

3β-*tert*-Butyldimethylsiloxy-6α-hydroxy-5α-cholest-9(11),20(22)-ene-23-one (2)

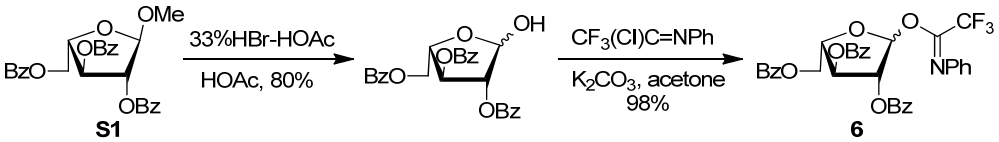


To a solution of **16** (170 mg, 0.265 mmol) in THF (5 mL), 70% HF•pyridine (0.5 mL) was added dropwise. The mixture was stirred at room temperature for 10 h and was then quenched with saturated $NaHCO_3$ (2 mL) and diluted with EtOAc. The mixture was washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4 and concentrated in vacuo.

The residue was dissolved in DMF (4 mL) and the solution was cooled to 0°C. Imidazole (68 mg, 0.96 mmol), DMAP (19 mg, 0.15 mmol), and TBSCl (49 mg, 0.32 mmol) were added to the solution. The mixture was stirred and allowed to warm to room temperature overnight. The suspension was then diluted with EtOAc. The organic layer was washed with water, saturated $NaHCO_3$ solution, and brine, respectively, and was then dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 6:1) to afford **2** (106 mg, 76%) as a white solid. The diol (27 mg, 0.065 mmol) was recovered by using CH_2Cl_2/MeOH (10:1) as the eluant. **2:** $[\alpha]_D^{25}$ = -4.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 5.33 (d, *J* = 5.5 Hz, 1H), 3.56 (dtd, *J* = 20.5, 10.7, 4.5 Hz, 2H), 2.30 (d, *J* = 7.0 Hz, 2H), 2.28–2.16 (m, 3H), 2.14 (s, 3H), 2.13–1.99 (m, 5H), 1.96–1.19 (m, 16H), 1.07 (ddd, *J* = 13.3, 8.1, 2.9 Hz, 1H), 0.94 (d, *J* = 4.3 Hz, 7H), 0.91 (s, 3H), 0.88 (s, 10H), 0.50 (s, 3H), 0.06 (s, 6H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 201.38, 157.88, 145.97, 123.86, 116.32, 77.32, 71.83, 69.27, 59.99, 53.83, 53.37, 49.82, 43.31, 42.20, 40.49, 38.21, 35.95, 35.75, 32.96, 31.70, 25.92, 25.33, 25.28, 25.20, 22.67, 20.84, 19.25, 18.21, 12.61, -4.56, -4.58; HRMS (ESI) calcd for $C_{33}H_{57}O_3Si$ $[M+H]^+$ 529.4071, found 529.4073.

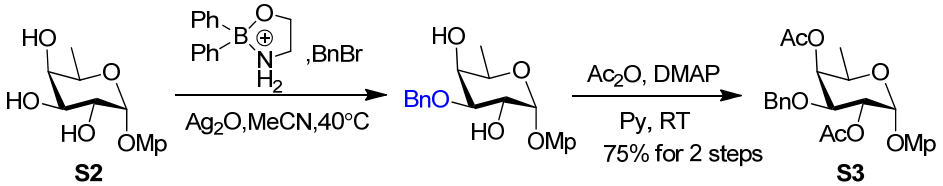
Tri-*O*-benzoyl-α/β-L-arabinofuranosyl *N*-phenyl trifluoroacetimidate (6)



To a solution of compound **S1**[4] (0.44 g, 0.92 mmol) in acetic acid (3 mL), was added 33% HBr•HOAc (2.5 mL). The mixture was stirred for 4 h at room temperature. After TLC showed complete consumption of the starting material, the mixture was diluted with EtOAc, washed three times with brine, then with water, dried over Na_2SO_4, and was concentrated in vacuo. The crude product was purified by flash column chromatography (hexane/EtOAc, 10:1→5:1) to afford the corresponding hemiacetal (0.34 g, 80%) a pale yellow foam.

The above hemiacetal (0.25 g, 0.54 mmol) was dissolved in acetone, K_2CO_3 (0.3 g, 2.17 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.15 g, 0.7 mmol) were added. The resulting suspension was vigorously stirred under argon at room temperature for 4 h. The reaction mixture was filtered through Celite. The filtrate was concentrated in vacuo, and the crude product was purified by flash chromatography (petroleum ether/EtOAc, 10:1 with 1% Et_3N) to afford compound **6** (0.33 g, 98%, α/β = 2:1) as a white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (ddd, *J* = 4.9, 2.8, 1.6 Hz, 7H), 8.07 – 8.03 (m, 4H), 7.99 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.65 – 7.38 (m, 19H), 7.29 (dd, *J* = 8.2, 7.6 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.17 (dd, *J* = 10.7, 5.0 Hz, 3H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 4.7 Hz, 1H), 6.82 (s, 2H), 6.70 (d, *J* = 7.4 Hz, 2H), 6.58 (d, *J* = 7.6 Hz, 3H), 6.10 (dd, *J* = 6.5, 5.5 Hz, 1H), 6.04 – 5.96 (m, 2H), 5.92 (s, 2H), 5.82 (dd, *J* = 6.6, 4.7 Hz, 1H), 4.81 (ddd, *J* = 11.6, 4.2, 2.4 Hz, 3H), 4.74 (dd, *J* = 11.7, 6.8 Hz, 2H), 4.69 – 4.58 (m, 3H).

***p*-Methoxyphenyl 3-*O*-benzyl-2,4-di-*O*-acetyl-α-D-fucopyranoside (S3)**

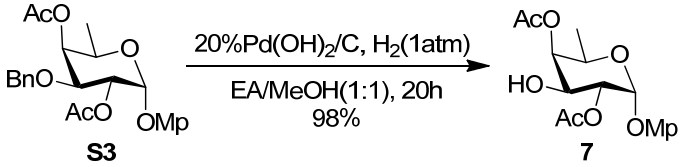


To a solution of compound **S2**[5] (1.49 g, 5.5 mmol) in dry acetonitrile (35 mL), were added 2-aminoethyl diphenylborinate (0.25 g, 1.1 mmol), benzyl bromide (0.9 mL, 8.3 mmol) and Ag_2O (1.2 g, 8.3 mmol). The mixture was stirred vigorously (750-1000

rpm) for 48 h at 40°C. The resulting mixture was diluted with CH_2Cl_2, filtered through celite and concentrated to dryness.

The resulting crude material was dissolved in dry pyridine (25 mL), DMAP (0.15 g, 1.2 mmol) and acetic anhydride (3.0 mL, 21 mmol) were then added. After stirring for 12 h at room temperature, the solution was quenched with saturated $NaHCO_3$ solution, then extracted with CH_2Cl_2, dried over Na_2SO_4, and was concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 5:1) to give compound **S3** (1.83 g, 75% for two steps) as a white foam: $[\alpha]_D^{25}$ = +154.5 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.15 (m, 5H), 7.02–6.91 (m, 2H), 6.88–6.75 (m, 2H), 5.60 (d, *J* = 3.7 Hz, 1H), 5.48 (d, *J* = 3.2 Hz, 1H), 5.19 (dd, *J* = 10.5, 3.7 Hz, 1H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.22 (q, *J* = 6.5 Hz, 1H), 4.15 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.76 (s, 3H), 2.18 (s, 3H), 2.08 (s, 3H), 1.15 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.77, 170.44, 155.13, 150.75, 137.79, 128.32, 127.66, 117.98, 114.58, 96.07, 73.45, 71.69, 70.23, 69.92, 65.40, 55.59, 20.86, 20.79, 16.12; HRMS (ESI) calcd for $C_{24}H_{28}O_8Na$ $[M+Na]^+$ 467.1676, found 467.1681.

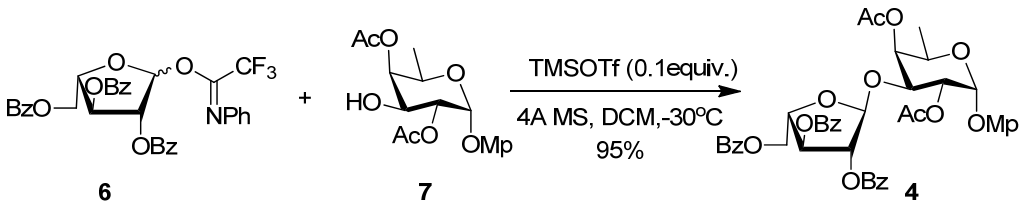
p-Methoxyphenyl 2,4-di-*O*-acetyl-α-D-fucopyranoside (7)



S3 **7**

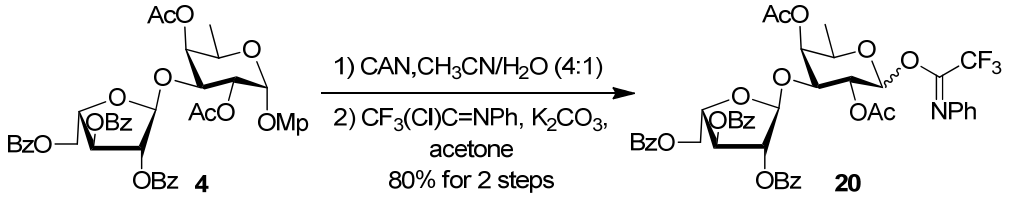
To a solution of compound **S3** (200 mg, 0.45 mmol) in EtOAc (5 mL) and methanol (5 mL), was added $Pd(OH)_2$/C (20 wt%; 80 mg). The resulting suspension was vigorously stirred under hydrogen pressure (1 atm) for 20 h at room temperature. The reaction mixture was filtered through a pad of celite. The filtrate was concentrated to dryness to give, without further purification, compound **7** (156 mg, 98%) as a pale yellow foam: $[\alpha]_D^{25}$ = +30.8 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03–6.92 (m, 2H), 6.87–6.75 (m, 2H), 5.57 (d, *J* = 3.6 Hz, 1H), 5.32 (d, *J* = 2.5 Hz, 1H), 5.09 (dd, *J* = 10.5, 3.7 Hz, 1H), 4.43 (dd, *J* = 10.5, 3.6 Hz, 1H), 4.26 (q, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 2.21 (s, 3H), 2.14 (s, 3H), 1.15 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.31, 171.22, 155.19, 150.76, 117.91, 114.65, 95.99, 73.45, 71.23, 67.05, 65.57, 55.66, 20.95, 20.80, 16.14; HRMS (ESI) calcd for $C_{17}H_{22}O_8Na$ $[M+Na]^+$ 377.1207, found 377.1210.

p-Methoxyphenyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,4-di-*O*-acetyl-α-D-fucopyranoside (4)



A mixture of acceptor **7** (0.15 g, 0.24 mmol), donor **6** (0.32 g, 0.50 mmol), and 4Å molecular sieves (0.8 g) in dry CH_2Cl_2 (10 mL) was stirred for 30 min under an argon atmosphere. The mixture was cooled to –30°C, and TMSOTf (15 μL, 0.05 mmol) was slowly added. After being stirred for another 3 h, the reaction was quenched with triethylamine (0.5 mL) and filtered through a pad of Celite. The solvent was evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 5:1) to give disaccharide **4** (0.32 g, 95%) as a white foam: $[\alpha]_D^{25}$ = +77.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 4H), 8.00–7.82 (m, 2H), 7.68–7.21 (m, 9H), 6.95 (dd, *J* = 7.4, 5.2 Hz, 2H), 6.82 (dd, *J* = 9.9, 3.0 Hz, 2H), 5.61 (t, *J* = 5.0 Hz, 2H), 5.51 (s, 1H), 5.44 (s, 2H), 5.27 (dd, *J* = 10.6, 3.6 Hz, 1H), 4.98 (dd, *J* = 12.1, 2.8 Hz, 1H), 4.86–4.80 (m, 1H), 4.73 (dd, *J* = 12.1, 3.7 Hz, 1H), 4.54 (dd, *J* = 10.6, 3.4 Hz, 1H), 4.27 (q, *J* = 6.4 Hz, 1H), 3.76 (s, 3H), 2.16 (s, 3H), 1.96 (s, 3H), 1.11 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.84, 170.51, 166.20, 165.93, 165.38, 155.08, 150.67, 133.51, 133.41, 133.02, 129.93, 129.86, 129.81, 129.70, 129.17, 128.94, 128.44, 128.43, 128.33, 117.66, 114.63, 107.37, 95.79, 82.50, 81.10, 77.85, 73.05, 71.84, 70.09, 65.67, 63.16, 55.62, 20.76, 20.58, 15.87; HRMS (ESI) calcd for $C_{43}H_{42}O_{15}Na$ $[M+Na]^+$ 821.2416, found 821.2415.

2,3,5-Tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,4-di-*O*-acetyl-α-D-fucopyranosyl *N*-phenyl trifluoroacetimidate (20)

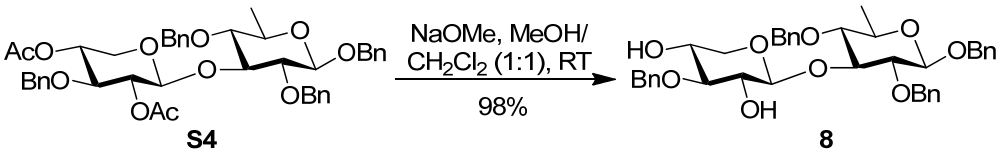


Compound **4** (300 mg, 0.38 mmol) was dissolved in acetonitrile/water (4:1, 5 mL). Cerium ammonium nitrate (620 mg, 1.14 mmol) was added, and the mixture stirred for 3 h at room temperature. After TLC showed complete consumption of the starting material, the mixture was diluted with EtOAc. The organic layer was washed two times with brine and water, dried over Na_2SO_4, and concentrated in vacuo to give the corresponding lactol as a syrup.

The above syrup was dissolved in acetone (7 mL), then K_2CO_3 (300 mg, 2.17 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (95 mg, 0.46 mmol) were

added. The mixture was vigorously stirred under argon at room temperature for 4 h, and was then filtered through Celite. The filtrate was concentrated to dryness and the crude product was purified by flash chromatography (petroleum ether/EtOAc, 6:1 with 1% Et_3N) to afford compound **20** (0.26 g, 80% for two steps, α/β = 2.3:1) as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 11.4, 4.2 Hz, 7H), 7.89 – 7.81 (m, 3H), 7.48 (dddd, *J* = 28.7, 15.4, 8.0, 1.4 Hz, 9H), 7.31 – 7.16 (m, 12H), 7.04 (dt, *J* = 15.0, 7.7 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 5.52 (t, *J* = 5.5 Hz, 2H), 5.41 – 5.20 (m, 6H), 4.86 (ddd, *J* = 19.6, 12.0, 2.7 Hz, 2H), 4.69 (tdd, *J* = 15.5, 9.9, 5.7 Hz, 4H), 4.26 (d, *J* = 8.6 Hz, 2H), 1.08 (d, *J* = 6.2 Hz, 9H).

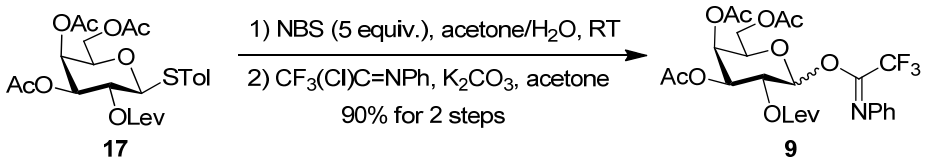
Benzyl 3-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (8)



S4 **8**

Disaccharide **S4**[2] (2.2 g, 2.97 mmol) was dissolved in dichloromethane (3 mL) and methanol (3 mL). The solution was treated with sodium methoxide (160 mg, 2.97 mmol) at room temperature for 4 h. The mixture was neutralized with an ion-exchange resin (Amberlite IR 120, H^+) and filtrated. The filtrate was concentrated. The residue was purified by flash column chromatography (CH_2Cl_2/MeOH, 50:1) to give **8** (1.85 g, 95%) as a white solid: $[\alpha]_D^{25}$ = -25.3 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–6.93 (m, 20H), 5.02 (d, *J* = 10.5 Hz, 1H), 4.97 (dd, *J* = 11.1, 5.5 Hz, 2H), 4.91 (d, *J* = 11.4 Hz, 1H), 4.70 (d, *J* = 10.5 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.60 (dd, *J* = 10.9, 3.4 Hz, 2H), 4.55 (d, *J* = 7.4 Hz, 1H), 4.49 (d, *J* = 7.8 Hz, 1H), 3.93–3.86 (m, 1H), 3.86–3.81 (m, 1H), 3.69–3.64 (m, 1H), 3.63 (d, *J* = 1.9 Hz, 1H), 3.57–3.51 (m, 1H), 3.44 (d, *J* = 7.4 Hz, 1H), 3.41–3.35 (m, 1H), 3.23 (t, *J* = 6.7 Hz, 1H), 3.20 (t, *J* = 7.0 Hz, 1H), 3.02 (t, *J* = 10.9 Hz, 1H), 2.19 (s, 1H), 1.37 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.66, 138.28, 137.38, 137.20, 129.00, 128.61, 128.58, 128.42, 128.24, 128.21, 128.05, 127.95, 127.85, 105.70, 102.21, 83.34, 83.10, 81.35, 75.86, 75.20, 75.15, 74.34, 71.29, 69.12, 65.64, 17.94; HRMS (ESI) calcd for $C_{39}H_{44}O_9Na$ $[M+Na]^+$ 679.2883, found 679.2877.

3,4,6-Tri-*O*-acetyl-2-*O*-levulinoyl-1-thio-β-D-galactopyranosyl *N*-phenyl trifluoroacetimidate (9)

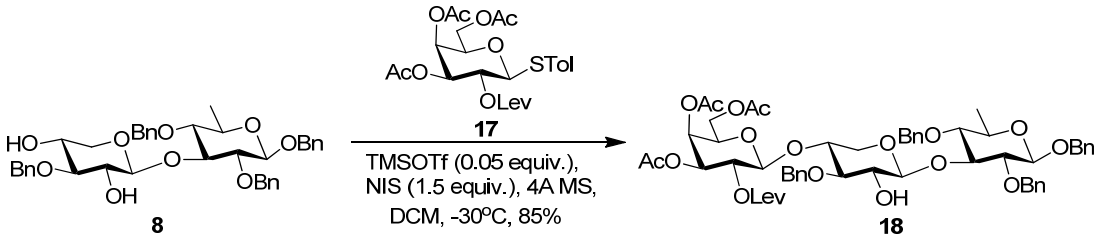


To a stirred solution of thiogalacoside **17**[6] (2.0 g, 3.91 mmol) in acetone/H_2O (9:1, 30 mL) was added *N*-bromosuccinimide (NBS, 3.49 g, 19.58 mmol). The mixture was stirred at room temperature for 1.5 h, and TLC (petroleum ether/EtOAc, 2:1) showed complete conversion of the starting material to a slower moving component. The mixture was diluted with EtOAc (150 mL) and washed with 10% $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and concentrated to a syrup.

The crude lactol was then dissolved in acetone (20 mL), K_2CO_3 (2.5 g, 18.09 mmol) was added followed by addition of 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.8 mL, 4.31 mmol). The mixture was stirred at room temperature for 4 h.[7,8] The reaction mixture was filtered through Celite. The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (petroleum ether/EtOAc, 5:1 with 1% Et_3N) to afford compound **20** (1.62 g, 90% for two steps, α/β = 1.4:1) as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 15.1, 7.4 Hz, 4H), 7.13 (dt, *J* = 13.6, 6.7 Hz, 2H), 6.84 (t, *J* = 8.3 Hz, 4H), 5.60 – 5.29 (m, 5H), 5.10 (s, 1H), 4.35 (s, 1H), 4.23 – 4.02 (m, 4H), 2.90 – 2.45 (m, 8H), 2.16 (dd, *J* = 5.7, 2.2 Hz, 11H), 2.05 (dd, *J* = 4.2, 2.9 Hz, 10H).

Benzyl
3,4,6-Tri-*O*-acetyl-2-*O*-levulinoyl-β-D-galactopyranosyl-(1→4)-3-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (18)

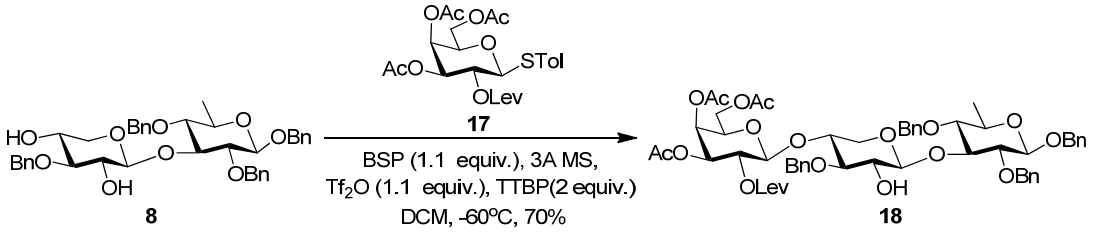
Procedure 1:



A mixture of disaccharide **8** (502 mg, 0.76 mmol) and 4Å MS (1.5 g) in dry CH_2Cl_2 (20 mL) was stirred at room temperature for 20 min under an argon atmosphere. Then the solution was cooled to -30 °C, NIS (136 mg, 0.77 mmol) and TMSOTf (9 μL, 0.026 mmol) were added. Five minutes later, a solution of thiogalacoside **17** in CH_2Cl_2 (260 mg, 0.51 mmol, 0.1 M) was slowly added. After being stirred for another 1 h, the mixture was quenched with triethylamine (0.5 mL) and filtered through Celite. The filtrates were concentrated in vacuo to give a residue, which was purified by flash column chromatography (toluene/EtOAc, 15:1 to 4:1) to recover acceptor **8** (250 mg,

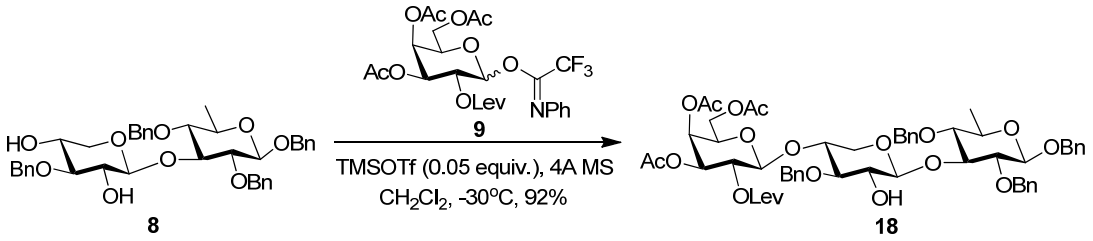
0.38 mmol) and afford **18** (451 mg, 85% based on **17**) as a white solid: $[\alpha]_D^{25}$ = -21.9 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–6.93 (m, 20H), 5.35 (d, *J* = 3.3 Hz, 1H), 5.16 (dd, *J* = 10.5, 7.9 Hz, 1H), 5.01 (dd, *J* = 10.5, 3.4 Hz, 1H), 4.97–4.88 (m, 3H), 4.79 (d, *J* = 5.8 Hz, 1H), 4.76 (d, *J* = 7.8 Hz, 1H), 4.70 (d, *J* = 10.2 Hz, 1H), 4.63 (d, *J* = 11.8 Hz, 1H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.51 (d, *J* = 10.9 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.11 (dd, *J* = 11.2, 7.5 Hz, 1H), 4.03 (dd, *J* = 11.2, 6.1 Hz, 1H), 3.90–3.85 (m, 1H), 3.85–3.80 (m, 2H), 3.78 (dd, *J* = 9.3, 6.1 Hz, 1H), 3.50 (ddd, *J* = 17.4, 11.3, 5.1 Hz, 3H), 3.37 (tt, *J* = 12.3, 6.1 Hz, 1H), 3.24 (d, *J* = 4.0 Hz, 1H), 3.14 (t, *J* = 9.2 Hz, 1H), 3.07 (dd, *J* = 12.0, 8.6 Hz, 1H), 2.70 (ddd, *J* = 14.4, 8.7, 5.3 Hz, 1H), 2.61–2.48 (m, 2H), 2.41–2.33 (m, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.31 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.80, 171.49, 170.30, 170.26, 170.13, 138.60, 138.37, 137.48, 137.19, 129.00, 128.44, 128.44, 128.28, 128.23, 128.06, 128.02, 127.89, 127.84, 127.83, 127.64, 127.58, 103.84, 102.13, 100.24, 82.50, 81.72, 81.49, 80.25, 77.32, 76.51, 74.96, 74.93, 73.86, 73.27, 71.17, 70.85, 70.49, 69.32, 66.91, 61.97, 61.01, 37.59, 29.61, 27.77, 20.61, 20.53, 17.83; HRMS (ESI) calcd for $C_{56}H_{66}O_{19}Na$ $[M+Na]^+$ 1065.4091, found 1065.4110.

Procedure 2:



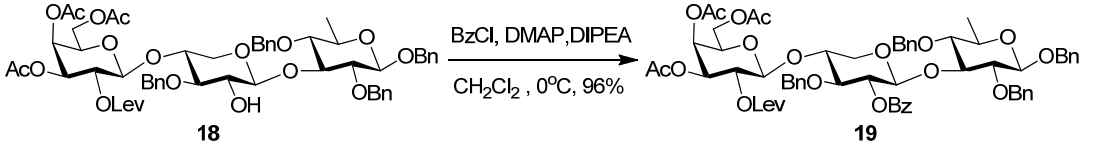
To a stirred dry CH_2Cl_2 solution (4 mL) containing thiogalactoside **17** (97 mg, 0.19 mmol), 1-benzenesulfinyl piperidine (BSP) (44 mg, 0.21 mmol), 2,4,6-tri-*tert*-butylpyrimidine (TTBP) (92 mg, 0.38 mmol), and activated 3Å powdered sieves (300 mg) at -60 °C under an argon atmosphere, trifluoromethanesulfonic anhydride (Tf_2O) (59 mg, 0.21 mmol) was added.[9] After 5 min, a solution of the disaccharide acceptor **8** (184 mg, 0.28 mmol) in dichloromethane (2 mL) was added. The reaction mixture was stirred for 30 min at -60 °C and was then warmed to room temperature. The mixture was filtered, the filtrate was washed with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (toluene/EtOAc, 15:1 to 4:1) to afford **18** (138 mg, 70%) as a white solid.

Procedure 3:



A mixture of disaccharide acceptor **8** (250 mg, 0.38 mmol) and 4Å MS (800 mg) in dry CH_2Cl_2 (8 mL) was stirred at room temperature for 20 min under an argon atmosphere. Then, the solution was cooled to -30 ^oC, TMSOTf (4 μL, 0.012 mmol) was added. Five minutes later, a solution of imidate **9** (120 mg, 0.26 mmol) in CH_2Cl_2 (1 mL) was slowly added. After being stirred for another 1 h, the mixture was quenched with triethylamine (0.5 mL) and filtered through Celite. The filtrates were concentrated in vacuo to give a residue, which was purified by flash column chromatography (toluene/EtOAc, 15:1 to 4:1) to recover **8** (86 mg, 0.13 mmol) and afford **18** (248 mg, 92% based on **9**) as a white solid.

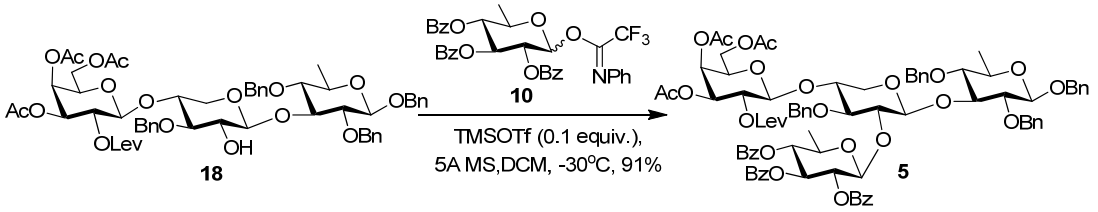
Benzyl 3,4,6-tri-*O*-acetyl-2-*O*-levulinoyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (19)



To a solution of compound **18** (20 mg, 0.019 mmol) in dry CH_2Cl_2 (2 mL) were added BzCl (0.46 mL, 4.0 mmol), DMAP (12 mg, 0.08 mmol) and DIPEA (20 μL, 0.15 mmol) under an argon atmosphere. The solution was stirred for 3 h at room temperature. Solvents were evaporated in vacuo to give a residual syrup, which was diluted with EtOAc (20 mL). The solution was washed with 1 M HCl and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 2:1) to give compound **19** (21 mg, 96%) as a white solid: $[\alpha]_D^{25}$ = -3.8 (*c* 1.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.00–7.86 (m, 2H), 7.76–6.67 (m, 23H), 5.33 (d, *J* = 3.2 Hz, 1H), 5.27–5.15 (m, 3H), 5.05–5.00 (m, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.86 (d, *J* = 11.8 Hz, 1H), 4.82 (d, *J* = 11.4 Hz, 1H), 4.77 (d, *J* = 10.7 Hz, 1H), 4.70 (d, *J* = 11.4 Hz, 1H), 4.59–4.49 (m, 3H), 4.44–4.33 (m, 2H), 4.06–3.97 (m, 2H), 3.96–3.90 (m, 2H), 3.85 (ddd, *J* = 16.1, 12.8, 7.1 Hz, 2H), 3.74 (t, *J* = 7.3 Hz, 1H), 3.35 (dd, *J* = 9.5, 6.2 Hz, 1H), 3.31 (dd, *J* = 11.0, 6.1 Hz, 1H), 3.21 (dd, *J* = 12.1, 8.2 Hz, 1H), 3.09 (t, *J* = 9.2 Hz, 1H), 2.74 (ddd, *J* = 18.2, 8.2, 5.1 Hz, 1H), 2.64–2.51 (m, 2H), 2.40 (ddd, *J* = 17.2, 6.6, 5.2 Hz, 1H), 2.11 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.27–1.24 (m, 3H); ^{13}C NMR (126

MHz, $CDCl_3$) δ 205.68, 171.17, 170.28, 170.25, 170.05, 165.28, 138.44, 138.22, 137.95, 137.24, 132.97, 129.83, 129.78, 128.31, 128.29, 128.27, 128.17, 128.12, 128.02, 127.93, 127.72, 127.69, 127.56, 127.52, 102.08, 101.01, 100.11, 82.89, 81.23, 79.53, 77.98, 77.68, 75.01, 74.30, 73.73, 71.89, 71.07, 71.03, 70.86, 70.60, 69.15, 66.92, 61.83, 61.02, 37.62, 29.63, 27.77, 20.59, 20.57, 20.53, 17.87; HRMS (ESI) calcd for $C_{63}H_{70}O_{20}Na$ $[M+Na]^+$ 1169.4353, found 1169.4366.

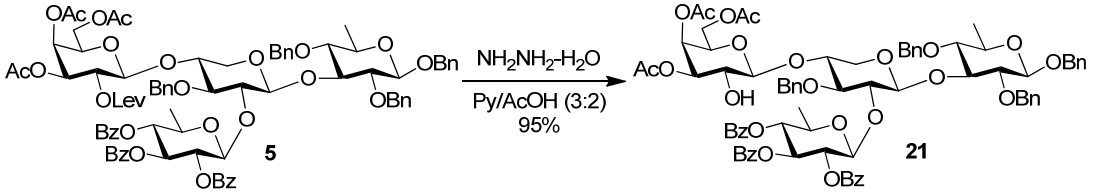
Benzyl 3,4,6-tri-*O*-acetyl-2-*O*-levulinoyl-β-D-galactopyranosyl-(1→4)–[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (5)



A mixture of trisaccharide acceptor **18** (0.35 g, 0.34 mmol), donor **10**[6] (0.27 g, 0.41 mmol) and 5Å molecular sieves (1.1 g) in dry CH_2Cl_2 (20 mL) was stirred for 30 min under an argon atmosphere. The mixture was cooled to –30 °C, then TMSOTf (15 μL, 0.05 mmol) was slowly added. After being stirred for another 3 h, the reaction mixture was quenched with triethylamine (0.5 mL) and filtered through a pad of Celite. The solvents were evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 2:1) to give tetrasaccharide **5** (0.47 g, 92%) as a white foam: $[\alpha]_D^{25}$ = -29.1 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.78 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.72 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.54–7.13 (m, 30H), 5.80 (t, *J* = 9.7 Hz, 1H), 5.60 (dd, *J* = 9.8, 8.0 Hz, 1H), 5.37 (dd, *J* = 16.9, 8.7 Hz, 3H), 5.10 (dd, *J* = 10.5, 7.9 Hz, 1H), 4.92 (d, *J* = 9.8 Hz, 1H), 4.87 (d, *J* = 10.2 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.61 (d, *J* = 11.1 Hz, 1H), 4.47 (dd, *J* = 13.0, 5.2 Hz, 3H), 4.07 (dd, *J* = 11.1, 7.8 Hz, 1H), 3.96 (dt, *J* = 11.1, 7.4 Hz, 2H), 3.88–3.73 (m, 5H), 3.71–3.64 (m, 1H), 3.43 (t, *J* = 8.8 Hz, 1H), 3.38 (dt, *J* = 12.3, 6.1 Hz, 1H), 3.17 (t, *J* = 9.1 Hz, 1H), 2.91 (t, *J* = 10.5 Hz, 1H), 2.71 (ddd, *J* = 19.1, 9.0, 5.0 Hz, 1H), 2.59–2.45 (m, 2H), 2.36–2.25 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.35 (d, *J* = 6.1 Hz, 3H), 1.29 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.52, 171.06, 170.26, 170.19, 169.98, 165.82, 165.36, 164.84, 138.47, 138.45, 138.38, 137.50, 133.21, 132.94, 129.71, 129.62, 129.61, 129.05, 128.48, 128.34, 128.33, 128.19, 128.18, 128.16, 128.13, 127.92, 127.89, 127.65, 127.63, 102.21, 100.62, 100.47, 100.36, 83.14, 82.80, 81.25, 79.75, 78.42, 78.04, 74.94, 74.88, 74.02, 73.27, 72.56, 71.08, 70.80, 70.73, 70.50, 70.30, 69.11, 66.80, 62.65, 60.74, 37.54,

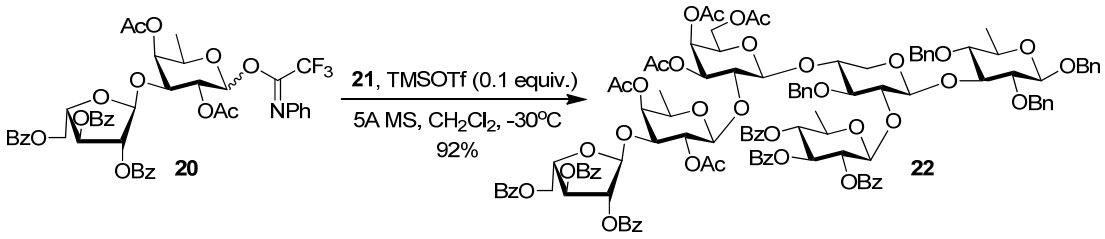
29.54, 27.68, 20.57, 20.53, 20.48, 17.93, 17.66; HRMS (MALDI) calcd for $C_{83}H_{88}O_{26}Na$ $[M+Na]^+$ 1523.5456, found 1523.5496.

Benzyl 3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)–[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (21)



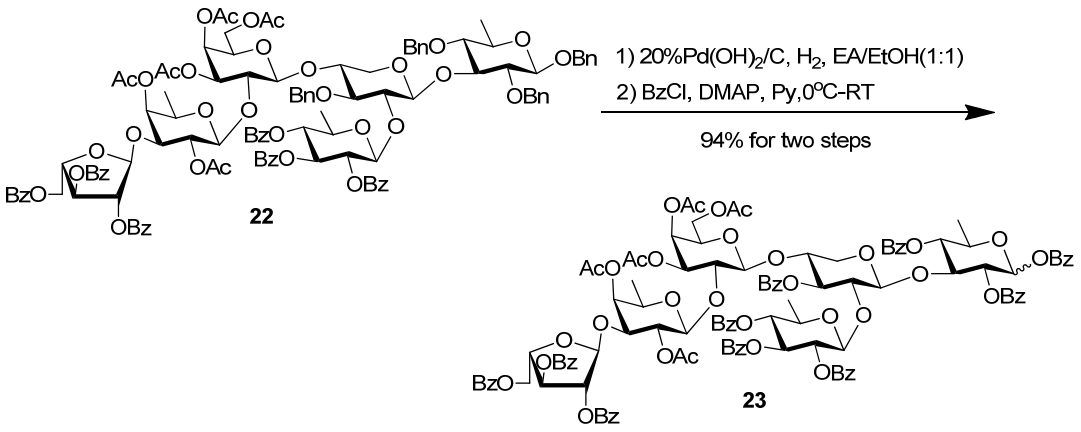
Tetrasaccharide **5** (390 mg, 0.26 mmol) was dissolved in pyridine/acetic acid (3:2, 5 mL), then N_2H_2•H_2O (60 μL, 0.11 mmol) was added. The reaction mixture was stirred for 5 h at room temperature, and was then quenched with acetone (0.5 mL) and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 3:1) to give compound **21** (346 mg, 95%) as a white foam: $[\alpha]_D^{25}$ = +6.9 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.88 (m, 2H), 7.78 (dd, *J* = 12.0, 4.2 Hz, 4H), 7.52 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.47–7.27 (m, 21H), 7.26–7.19 (m, 7H), 5.77 (t, *J* = 9.7 Hz, 1H), 5.56 (dd, *J* = 9.8, 8.0 Hz, 1H), 5.39–5.31 (m, 2H), 5.21 (d, *J* = 8.0 Hz, 1H), 5.12 (d, *J* = 6.7 Hz, 1H), 4.91–4.83 (m, 2H), 4.73 (d, *J* = 10.7 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.59 (d, *J* = 11.0 Hz, 1H), 4.53 (d, *J* = 10.7 Hz, 1H), 4.49 (d, *J* = 7.9 Hz, 1H), 4.35 (d, *J* = 7.7 Hz, 1H), 4.09 (dd, *J* = 11.1, 7.6 Hz, 1H), 4.01–3.85 (m, 4H), 3.80 (dd, *J* = 14.7, 7.7 Hz, 2H), 3.69 (ddd, *J* = 20.5, 11.5, 6.5 Hz, 3H), 3.46–3.37 (m, 2H), 3.17 (t, *J* = 9.1 Hz, 1H), 3.03 (dd, *J* = 11.5, 8.7 Hz, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.32 (d, *J* = 6.2 Hz, 3H), 1.29 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.31, 170.27, 170.02, 165.89, 165.39, 164.91, 138.65, 138.48, 138.08, 137.51, 133.28, 133.01, 132.96, 129.75, 129.70, 129.68, 129.35, 129.18, 128.93, 128.81, 128.39, 128.29, 128.23, 128.00, 127.98, 127.85, 127.71, 127.66, 127.50, 102.27, 101.23, 100.67, 100.48, 83.17, 81.78, 81.50, 79.68, 78.21, 75.61, 74.84, 73.95, 74.42, 73.95, 73.19, 72.74, 72.42, 71.14, 70.90, 70.84, 70.43, 68.70, 66.97, 61.95, 61.00, 20.71, 20.62, 20.56, 17.98, 17.68; HRMS (MALDI) calcd for $C_{78}H_{82}O_{24}Na$ $[M+Na]^+$ 1425.5088, found 1425.5066.

Benzyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,4-di-*O*-acetyl-β-D-fucopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-benzyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranoside (22)



A mixture of tetrasaccharide acceptor **21** (0.17 g, 0.122 mmol), disaccharide donor **20** (0.14 g, 0.16 mmol) and molecular sieves (5 Å; 0.6 g) in dry CH_2Cl_2 (6 mL) was stirred for 30 min under an argon atmosphere. The mixture was cooled to –30 °C, and TMSOTf (6 μL, 0.02 mmol) was slowly added. After being stirred for another 3 h at room temperature, the reaction mixture was quenched with triethylamine (0.5 mL) and filtered through a pad of Celite. The solvents were evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 2:1) to give hexasaccharide **22** (0.23 g, 91%) as a white foam: $[\alpha]_D^{25}$ = -21.9 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.07 (m, 2H), 7.98–7.87 (m, 6H), 7.81–7.74 (m, 2H), 7.70–7.63 (m, 2H), 7.59–7.49 (m, 5H), 7.46–7.17 (m, 36H), 7.13 (t, *J* = 7.2 Hz, 2H), 5.76 (t, *J* = 9.6 Hz, 1H), 5.63 (dd, *J* = 9.8, 8.0 Hz, 1H), 5.58 (d, *J* = 4.7 Hz, 1H), 5.38 (dd, *J* = 11.8, 5.1 Hz, 2H), 5.31–5.24 (m, 2H), 5.23–5.12 (m, 3H), 5.07 (dd, *J* = 8.9, 7.5 Hz, 2H), 5.04–4.98 (m, 2H), 4.98–4.77 (m, 5H), 4.76–4.71 (m, 2H), 4.67 (dd, *J* = 11.0, 7.9 Hz, 2H), 4.52 (dd, *J* = 13.1, 9.1 Hz, 2H), 4.43 (t, *J* = 8.2 Hz, 2H), 4.28 (dd, *J* = 12.0, 5.5 Hz, 1H), 3.98–3.86 (m, 3H), 3.85–3.80 (m, 1H), 3.80–3.73 (m, 2H), 3.70 (dd, *J* = 14.3, 6.1 Hz, 2H), 3.57–3.51 (m, 1H), 3.48 (dd, *J* = 10.4, 5.6 Hz, 1H), 3.45–3.36 (m, 2H), 3.30 (dd, *J* = 9.4, 6.1 Hz, 1H), 3.18 (t, *J* = 9.1 Hz, 1H), 3.06–2.95 (m, 1H), 2.12 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.90 (s, 3H), 1.67 (s, 3H), 1.36 (t, *J* = 6.1 Hz, 6H), 0.90 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.72, 170.08, 169.96, 169.81, 169.48, 166.20 (s), 165.91, 165.83, 165.48, 165.40, 164.84, 138.65, 138.47, 137.58, 133.49, 133.32, 133.24, 133.04, 133.00, 132.93, 129.87, 129.81, 129.76, 129.73, 129.66, 129.28, 128.93, 128.80, 128.49, 128.43, 128.39, 128.38, 128.36, 128.34, 128.21, 12817, 127.90, 127.74, 127.72, 127.61, 127.39, 126.80, 107.56, 102.78, 102.26, 100.69, 100.46, 100.39, 84.27, 82.69, 81.43, 79.52, 79.38, 78.32, 77.56, 76.32, 75.34, 75.01, 74.66, 74.42, 74.07, 73.32, 72.74, 72.61, 71.82, 71.26, 71.11, 71.02, 70.73, 70.45, 69.28, 66.97, 63.27, 60.51, 20.77, 20.61, 20.52, 18.01, 17.72, 15.98; HRMS (MALDI) calcd for $C_{114}H_{116}O_{37}Na$ $[M+Na]^+$ 2099.7087, found 2099.7071.

2,3,5-Tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,4-di-*O*-acetyl-β-D-fucopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl benzoate (23)

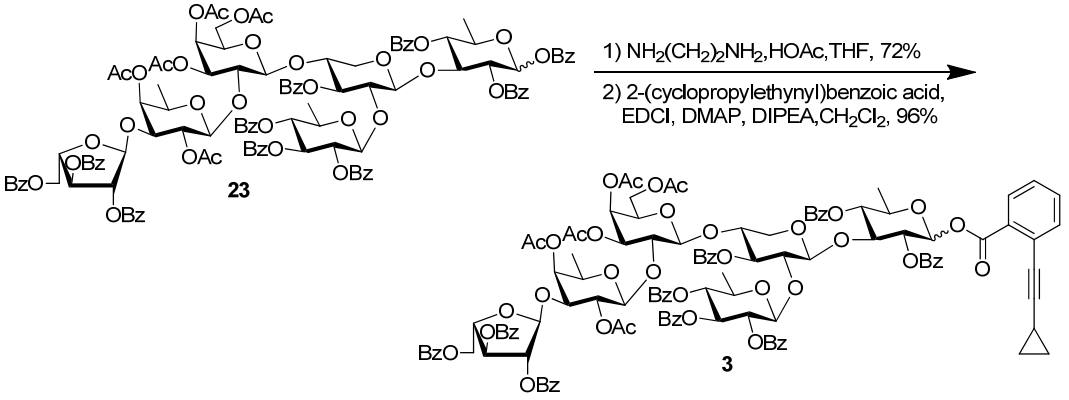


To a solution of **22** (260 mg, 0.125 mmol) in EtOAc/ethanol (1:1, 14 mL) at room temperature was added $Pd(OH)_2$ (20 wt.%; 75 mg). The suspension was stirred under hydrogen pressure (1 atm) for 24 h, and was then filtered through Celite. The filtrate was concentrated in vacuo to give a residue.

The residue was dissolved in dry pyridine (6 mL). DMAP (110 mg, 0.9 mmol) was added. The mixture was stirred and cooled to 0 °C, then BzCl (0.55 mL, 4.5 mmol) was slowly added. The mixture was allowed to warm to room temperature. After being stirred for 14 h, the mixture was diluted with EtOAc, washed with 1 M HCl, saturated $NaHCO_3$ solution, and brine, respectively. The organic layer was dried over Na_2SO_4, filtered, and then concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 2.5:1 to 1.5:1) to give compound **23** as a white solid (250 mg, 94% for two steps; α/β = 2.5:1). **23α**: $[\alpha]_D^{25}$ = +18.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.14 (m, 2H), 8.13–8.02 (m, 8H), 7.98–7.91 (m, 2H), 7.88–7.80 (m, 2H), 7.72–7.41 (m, 22H), 7.41–7.11 (m, 14H), 6.74 (d, *J* = 3.6 Hz, 1H), 5.59 (d, *J* = 4.8 Hz, 1H), 5.42 (dd, *J* = 9.9, 3.7 Hz, 1H), 5.38 (d, *J* = 9.7 Hz, 1H), 5.36–5.33 (m, 1H), 5.31–5.23 (m, 3H), 5.15–5.05 (m, 3H), 4.97 (d, *J* = 4.8 Hz, 1H), 4.90 (dd, *J* = 11.7, 2.7 Hz, 1H), 4.84 (t, *J* = 9.6 Hz, 1H), 4.76 (ddd, *J* = 15.8, 9.4, 4.4 Hz, 2H), 4.69 (dd, *J* = 10.3, 3.4 Hz, 1H), 4.60 (d, *J* = 7.9 Hz, 1H), 4.57–4.44 (m, 3H), 4.26 (dd, *J* = 9.9, 6.2 Hz, 1H), 3.91 (d, *J* = 7.5 Hz, 1H), 3.80 (dd, *J* = 7.7, 4.9 Hz, 1H), 3.72 (dt, *J* = 8.1, 4.2 Hz, 2H), 3.68–3.58 (m, 2H), 3.55–3.45 (m, 4H), 3.44–3.38 (m, 1H), 3.16 (dd, *J* = 13.0, 8.5 Hz, 1H), 3.10 (tt, *J* = 7.3, 3.7 Hz, 2H), 2.08 (s, 3H), 1.98 (s, 6H), 1.94 (s, 3H), 1.88 (s, 3H), 1.31 (d, *J* = 6.2 Hz, 3H), 1.26 (d, *J* = 3.9 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.62, 170.12, 169.85, 169.40, 166.20, 165.89, 165.57, 165.55, 165.46, 165.40, 165.14, 164.77, 164.67, 164.53, 133.71, 133.66, 133.56, 133.50, 133.48, 133.12, 132.98, 132.53, 129.97, 129.81, 129.76, 129.73, 129.65, 129.56, 129.51, 129.48, 129.40, 129.23, 129.14, 129.05, 128.99, 128.96, 128.65, 128.48, 128.32, 128.22, 128.08, 127.99, 109.99, 107.81, 102.56, 101.08, 100.92, 100.58, 90.08, 82.70, 81.26, 77.90, 77.67, 75.33, 74.51, 74.19, 74.14, 73.19, 73.06, 72.65, 72.31, 72.11, 71.55, 70.23,

70.05, 69.46, 68.56, 66.79, 63.43, 61.44, 60.43, 45.78, 20.86, 20.64, 20.62, 20.49, 20.37, 17.61, 16.95, 16.25; HRMS (MALDI) calcd for $C_{114}H_{108}O_{41}Na$ $[M+Na]^+$ 2155.6266, found 2155.6226.

2,3,5-Tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,4-di-*O*-acetyl-α-D-fucopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (3)

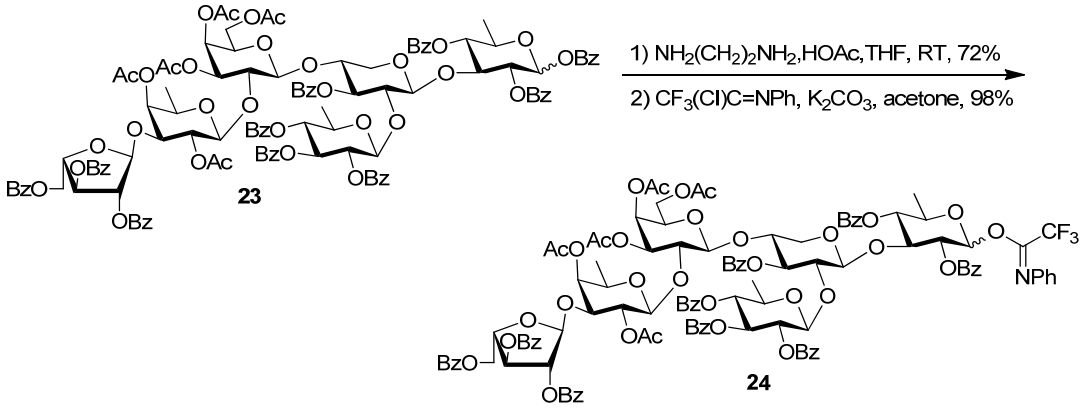


HOAc (0.34 mL, 5.5 mmol) was added dropwise and with stirring to a solution of ethylenediamine (0.72 mL, 11.0 mmol) in THF (1.2 mL) under an argon atmosphere.[10] Then compound **23** (102 mg, 0.0477 mmol) in THF (1.5 mL) was added. The mixture was stirred at room temperature for 24 h, and was then quenched with water (2 mL). The resulting mixture was extracted with EtOAc. The organic phase, after being washed sequentially with 1 M HCl, saturated $NaHCO_3$ solution, and brine, was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 1.5:1) to give the corresponding lactol (69 mg, 72%) as a white foam and recover **23** (17 mg).

The above lactol (69 mg, 0.034 mmol), *ortho*-cyclopropylethynylbenzoic acid (14 mg, 0.07 mmol), EDC•HCl (27 mg, 0.11 mmol), and DMAP (16 mg, 0.12 mmol) were dissolved in CH_2Cl_2 (2 mL), then DIPEA (20 μL, 0.26 mmol) was added under an argon atmosphere.[11,12] The mixture was stirred overnight, then diluted with CH_2Cl_2, washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 2:1) to give **3** (72 mg, 96%; α/β= 4.2:1, which are inseparable) as a white foam: **3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.14 (m, 2H), 8.14–8.02 (m, 10H), 7.95 (d, *J* = 7.1 Hz, 2H), 7.85–7.81 (m, 2H), 7.74–7.28 (m, 47H), 7.25–7.15 (m, 5H), 6.77 (d, *J* = 3.6 Hz, 1H), 6.11 (d, *J* = 8.3 Hz, 1H), 5.59 (d, *J* = 4.7 Hz, 2H), 5.45–5.32 (m, 4H), 5.27 (dt, *J* = 9.6, 3.0 Hz, 4H), 5.16–5.03 (m, 4H), 4.95–4.87 (m, 3H), 4.84 (d, *J* = 9.6 Hz, 1H), 4.80–4.66 (m, 5H), 4.63–4.47 (m, 5H), 4.36 (dd, *J* = 10.0, 6.3 Hz, 1H), 4.06 (t, *J* = 6.7 Hz, 1H), 3.92 (d, *J* = 7.5 Hz, 1H),

3.83–3.40 (m, 15H), 3.13 (dd, *J* = 11.9, 7.6 Hz, 1H), 2.08 (d, *J* = 2.8 Hz, 3H), 2.04 (s, 2H), 1.98 (d, *J* = 2.2 Hz, 6H), 1.93 (d, *J* = 5.2 Hz, 3H), 1.87 (d, *J* = 2.5 Hz, 3H), 1.60 (d, *J* = 7.9 Hz, 1H), 1.39 (ddd, *J* = 15.8, 13.0, 10.0 Hz, 4H), 1.32 (d, *J* = 6.2 Hz, 3H), 1.25 (d, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 6.4 Hz, 3H), 0.90–0.79 (m, 5H); HRMS (MALDI) calcd for $C_{119}H_{112}O_{41}Na$ $[M+Na]^+$ 2219.6571, found 2219.6566.

2,3,5-Tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,4-di-*O*-acetyl-β-D-fucopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-6-deoxy-D-glucopyranosyl *N*-phenyl trifluoroacetimidate (24)



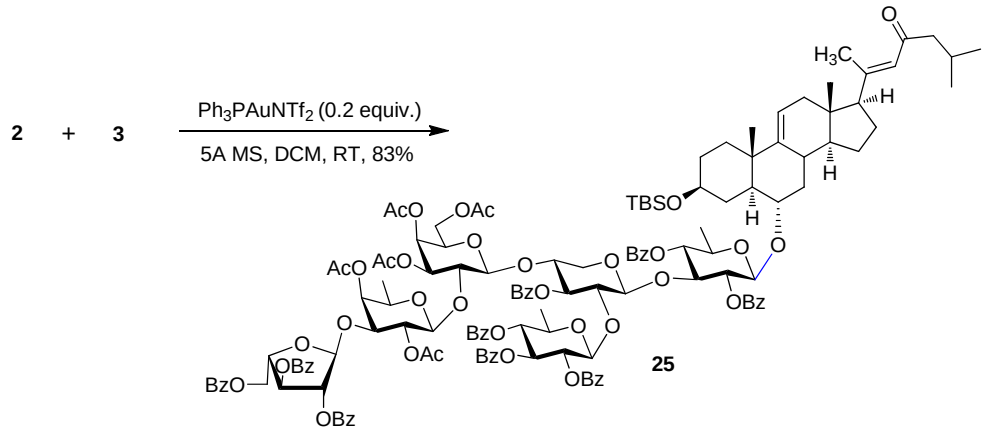
HOAc (0.34 mL, 5.5 mmol) was added dropwise and with stirring to a solution of ethylenediamine (0.72 mL, 11.0 mmol) in THF (2 mL) under an argon atmosphere. Then compound **23** (102 mg, 0.0477 mol) in THF (1.5 mL) was added. The mixture was stirred at room temperature for 24 h, then quenched with water (2 mL). The resulting mixture was extracted with EtOAc. The organic phase, after being washed sequentially with 1 M HCl, saturated $NaHCO_3$ solution, and brine, was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether-EtOAc, 1.5:1) to give the corresponding lactol as a white foam (69 mg, 72%) and recover **23** (17 mg).

The above lactol (69 mg, 0.034 mmol) was dissolved in acetone (3 mL), then K_2CO_3 (200 mg, 1.45 mmol) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (0.1 mL, 0.25 mmol) were added under an argon atmosphere.[7,8] After being stirred for 4 h, the mixture was diluted with EtOAc, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 4:1, with 1% Et_3N) to give **24** (74 mg, 98%; α/β = 1.5:1) as a white foam, which was used without further detailed characterization.

3β-*tert*-Butyldimethylsilyloxy-5α-cholest-9(11),20(22)-ene-23-on-6α-oxyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,4-di-*O*-acetyl-β-D-fucopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-

deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-6-deoxy-β-D-glucopyranoside (25)

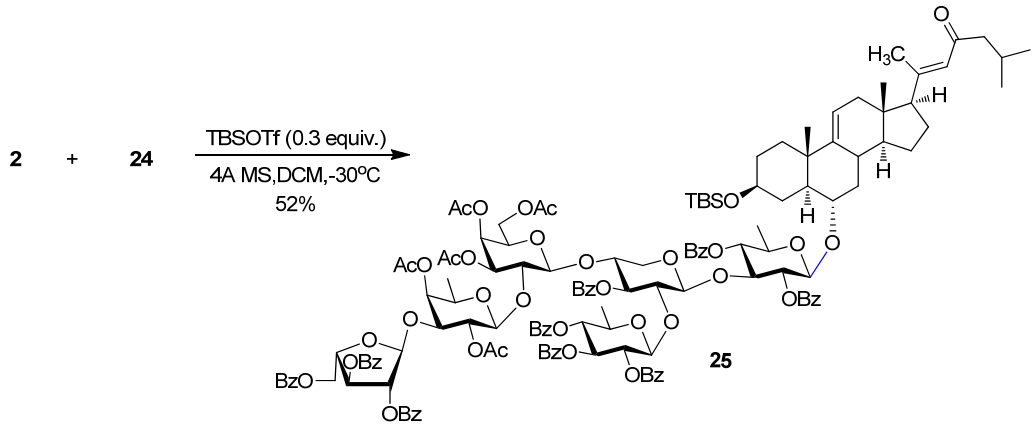
Procedure 1:



PPh_3AuNTf_2 (2 mg, 0.003 mmol) in dry CH_2Cl_2 (0.2 mL) was added to a mixture of donor **3** (21 mg, 0.0092 mmol), acceptor **2** (15 mg, 0.028 mmol), and 5Å molecular sieves (100 mg) in dry CH_2Cl_2 (2 mL) under an argon atmosphere.[11,13,14] After stirring at room temperature for another 5 h, the mixture was filtered through a pad of celite. The filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 6:1 to 2:1) to recover acceptor **2** (10 mg, 0.189 mmol) and afford compound **25** (19 mg, 83%) as a white solid: $[\alpha]_D^{25}$ = +6.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.03 (m, 9H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.72 (t, *J* = 6.6 Hz, 3H), 7.66–7.36 (m, 21H), 7.33–7.20 (m, 10H), 6.07 (s, 1H), 5.59 (d, *J* = 5.1 Hz, 1H), 5.40 (t, *J* = 9.7 Hz, 1H), 5.35 (s, 1H), 5.29 (s, 1H), 5.25 (d, *J* = 2.9 Hz, 1H), 5.17 (ddd, *J* = 27.3, 19.3, 8.7 Hz, 5H), 5.08–5.03 (m, 1H), 5.00 (t, *J* = 9.6 Hz, 1H), 4.88–4.73 (m, 7H), 4.69 (dd, *J* = 11.9, 4.0 Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 7.9 Hz, 1H), 4.13 (t, *J* = 9.1 Hz, 1H), 4.07 (d, *J* = 7.5 Hz, 1H), 3.89–3.60 (m, 9H), 3.60–3.49 (m, 4H), 3.32 (s, 1H), 3.16 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.10 (dd, *J* = 11.6, 7.4 Hz, 1H), 2.30 (d, *J* = 7.0 Hz, 2H), 2.29–2.21 (m, 2H), 2.14 (s, 6H), 2.11 (d, *J* = 7.3 Hz, 1H), 2.06 (s, 4H), 2.00 (s, 3H), 1.98 (s, 3H), 1.93 (d, *J* = 4.2 Hz, 6H), 1.86 (dd, *J* = 14.5, 5.3 Hz, 2H), 1.79–1.63 (m, 6H), 1.62–1.53 (m, 2H), 1.47–1.33 (m, 4H), 1.31 (d, *J* = 6.0 Hz, 3H), 1.30–1.20 (m, 8H), 1.15 (d, *J* = 6.1 Hz, 3H), 1.09 (dd, *J* = 24.1, 11.4 Hz, 2H), 0.98 (d, *J* = 6.3 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H), 0.91–0.87 (m, 2H), 0.84 (s, 3H), 0.80 (s, 11H), 0.49 (s, 3H), -0.08 (s, 3H), -0.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.31, 170.73, 170.20, 170.15, 169.99, 169.47, 166.14, 165.87, 165.57, 165.55, 165.45, 164.95, 164.91, 164.78, 164.51, 157.82, 145.52, 133.51, 133.40, 133.24, 133.03, 132.92, 132.74, 129.95, 129.91, 129.87, 129.74, 129.64, 129.57, 129.54, 129.19, 129.16, 129.08, 128.88, 128.45, 128.37, 128.24, 128.08, 126.88, 123.86, 116.26, 107.70, 101.38, 101.36, 101.28, 100.57, 100.32, 82.75, 80.88, 79.37, 77.69,

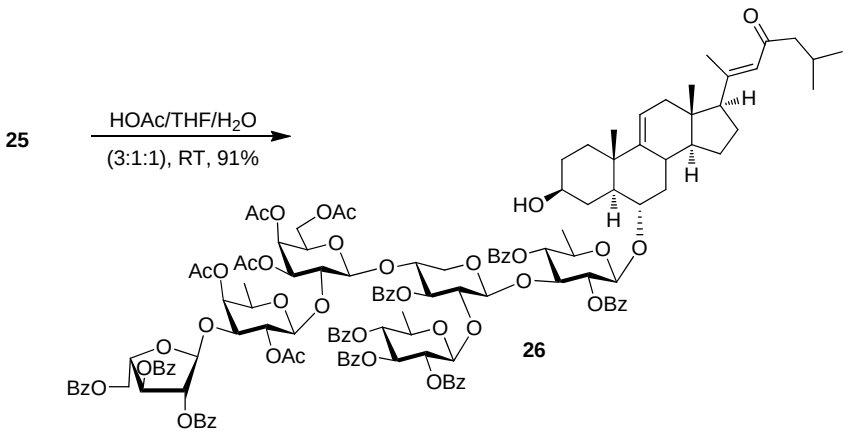
75.16, 74.57, 73.14, 72.86, 72.38, 72.05, 71.77, 71.61, 71.45, 70.35, 70.12, 70.06, 69.36, 66.92, 63.41, 60.59, 59.91, 53.79, 53.22, 47.69, 43.27, 40.41, 39.89, 38.13, 35.69, 32.25, 31.51, 29.65, 25.94, 25.22, 22.64, 22.57, 20.77, 20.75, 20.61, 20.54, 20.46, 20.40, 19.20, 18.06, 17.34, 16.10, 12.58, -4.49, -5.09; HRMS (MALDI) calcd for $C_{140}H_{158}O_{42}SiNa$ $[M+Na]^+$ 2563.0031, found 2563.0068.

Procedure 2:



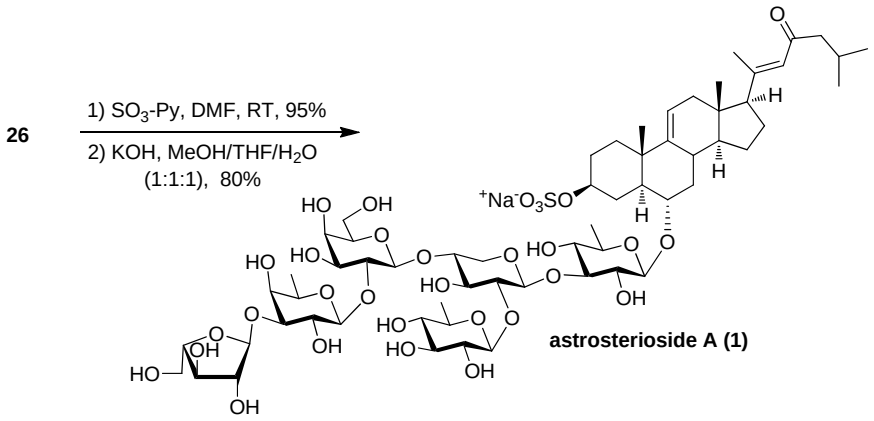
A mixture of donor **24** (12 mg, 0.0077 mmol), acceptor **2** (8 mg, 0.015 mmol) and 4Å molecular sieves (50 mg) in dry CH_2Cl_2 (1 mL) was stirred for 30 min under an argon atmosphere. The mixture was cooled to –30 °C, and TBSOTf (2 μL, in 0.2 mL CH_2Cl_2) was slowly added. After being stirred for another 3 h, the reaction was quenched with triethylamine (0.1 mL) and filtered through a pad of Celite. The solvents were evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc, 6:1 to 2:1) to give compound **25** (7 mg, 52%) as a white solid. Meanwhile, the 6α-*O*-TBS derivative **16** (1.8 mg, 19%) was isolated as a byproduct.

3β-Hydroxy-5α-cholest-9(11),20(22)-en-23-on-6α-oxyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→3)-2,4-di-*O*-acetyl-α-D-fucopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl-(1→4)-[2,3,4-tri-*O*-benzoyl-6-deoxy-β-D-glucopyranosyl-(1→2)]-3-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-6-deoxy-β-D-glucopyranoside (26)



Compound **25** (37 mg, 0.0146 mmol) was dissolved in HOAc/THF/H_2O (5 mL, 3:1:1).[15] The solution was stirred at room temperature for 20 h, then concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 1.5:1) to afford **26** (33 mg, 91%) as a white solid: $[\alpha]_D^{25}$ = +6.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.6 Hz, 2H), 8.07 (t, *J* = 6.8 Hz, 6H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.78 (t, *J* = 7.3 Hz, 4H), 7.68 (t, *J* = 7.5 Hz, 5H), 7.61 (dd, *J* = 13.5, 6.9 Hz, 4H), 7.56–7.36 (m, 13H), 7.31 (dd, *J* = 13.7, 7.8 Hz, 6H), 7.25–7.20 (m, 3H), 6.06 (s, 1H), 5.59 (d, *J* = 5.1 Hz, 1H), 5.37 (dd, *J* = 15.7, 6.1 Hz, 1H), 5.33 (d, *J* = 8.8 Hz, 2H), 5.27 (dd, *J* = 16.5, 5.0 Hz, 3H), 5.14 (dt, *J* = 17.7, 9.4 Hz, 3H), 5.01 (t, *J* = 9.6 Hz, 1H), 4.93 (t, *J* = 7.0 Hz, 1H), 4.86 (t, *J* = 11.6 Hz, 2H), 4.77 (dd, *J* = 10.1, 4.3 Hz, 2H), 4.74–4.65 (m, 3H), 4.57 (dd, *J* = 17.1, 7.9 Hz, 2H), 4.19 (t, *J* = 9.1 Hz, 1H), 4.00 (d, *J* = 7.5 Hz, 1H), 3.75 (dd, *J* = 13.0, 8.7 Hz, 5H), 3.60–3.50 (m, 4H), 3.49–3.40 (m, 2H), 3.32 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.13–3.00 (m, 2H), 2.34 (d, *J* = 12.4 Hz, 1H), 2.30 (d, *J* = 7.0 Hz, 2H), 2.27–2.21 (m, 1H), 2.13 (s, 3H), 2.11 (s, 3H), 2.07–2.04 (m, 2H), 2.01 (d, *J* = 4.6 Hz, 1H), 1.99 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H), 1.90 (s, 3H), 1.90–1.67 (m, 7H), 1.60 (d, *J* = 7.2 Hz, 2H), 1.40 (dd, *J* = 18.4, 5.8 Hz, 3H), 1.29 (dt, *J* = 25.1, 6.9 Hz, 13H), 1.22 (d, *J* = 6.2 Hz, 3H), 1.13 (dd, *J* = 22.1, 11.4 Hz, 3H), 1.02 (d, *J* = 6.1 Hz, 3H), 0.91 (t, *J* = 6.8 Hz, 8H), 0.88 (s, 3H), 0.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.35, 170.69, 170.14, 170.12, 169.92, 169.45, 166.17, 165.88, 165.58, 165.53, 165.45, 165.09, 164.77, 164.65, 164.42, 157.92, 145.25, 133.59, 133.35, 133.08, 133.03, 132.96, 132.64, 130.13, 130.02, 129.96, 129.85, 129.82, 129.77, 129.75, 129.71, 129.64, 129.61, 129.52, 129.20, 129.13, 129.06, 128.65, 128.47, 128.43, 128.29, 128.08, 128.02, 123.86, 116.40, 107.73, 102.49, 101.94, 101.08, 100.94, 100.43, 82.73, 81.14, 80.44, 75.26, 74.66, 74.31, 73.75, 73.37, 73.19, 72.31, 72.15, 71.60, 70.32, 70.28, 70.17, 70.06, 69.36, 66.81, 63.39, 61.05, 60.47, 59.90, 53.80, 53.27, 47.63, 43.29, 40.40, 38.11, 35.83, 35.24, 32.63, 31.60, 29.67, 29.64, 25.31, 25.19, 25.14, 22.65, 20.82, 20.76, 20.66, 20.62, 20.48, 20.39, 19.06, 17.86, 17.16, 16.19, 12.62; HRMS (MALDI) calcd for $C_{134}H_{144}O_{42}Na$ $[M+Na]^+$ 2447.9030, found 2448.9067.

Astrosterioside A (1)



Compound **26** (30 mg, 0.0124 mmol) was dissolved in dry DMF (2 mL). Sulfur trioxide-pyridine complex (15 mg, 0.124 mmol) was added. The mixture was stirred at room temperature for 5 h, then quenched with methanol (0.5 mL). The mixture was stirred for 15 min and concentrated in vacuo. The residue was dissolved in CH_2Cl_2. The solution was washed with ice-water, dried over Na_2SO_4, filtered, and then concentrated in vacuo. The residue was purified by flash column chromatography (CH_2Cl_2/MeOH, 10:1) to give a white solid (29 mg, 95%).

The above white solid (29 mg, 0.0115 mmol) was dissolved in MeOH/THF/H_2O (1:1:1, 3 mL) and treated with potassium hydroxide (50 mg, 0.89 mmol) at room temperature for 24 h. The mixture was neutralized with the weakly acidic ion-exchange resin (amberlite IRC 76, H^+ form). The resin was filtered and the filtrate was concentrated in vacuo. The residue was dissolved in methanol (5 mL). The solution was passed through an ion-exchange resin (amberlite IR 120, Na^+ form) to give a solid. The solid was purified by RP-18 column chromatography (methanol/water, 1.5:1) to afford astrosterioside A (**1**) (12.6 mg, 80%) as a white solid: $[\alpha]_D^{25}$ = -3.7 (*c* 0.5, MeOH); ^{1}H NMR (500 MHz, pyridine-d5) δ 6.30 (s, 1H), 6.08 (s, 1H), 5.23 (d, *J* = 5.3 Hz, 1H), 5.18 (d, *J* = 7.4 Hz, 1H), 5.13 (d, *J* = 7.5 Hz, 1H), 4.96 (d, *J* = 7.7 Hz, 1H), 4.93 (s, 1H), 4.92–4.82 (m, 3H), 4.79 (dd, *J* = 4.9, 2.9 Hz, 1H), 4.46 (ddd, *J* = 29.5, 15.0, 8.8 Hz, 4H), 4.36–4.16 (m, 6H), 4.07 (tdd, *J* = 24.9, 16.3, 8.4 Hz, 5H), 3.95 (dd, *J* = 15.5, 8.8 Hz, 2H), 3.88–3.80 (m, 2H), 3.79–3.68 (m, 2H), 3.64–3.53 (m, 2H), 3.40 (d, *J* = 11.3 Hz, 1H), 2.85–2.61 (m, 3H), 2.40 (dd, *J* = 12.7, 6.9 Hz, 2H), 2.39–2.29 (m, 3H), 2.28–2.19 (m, 2H), 2.16–1.88 (m, 5H), 1.85 (t, *J* = 9.3 Hz, 3H), 1.73 (dd, *J* = 25.8, 13.4 Hz, 3H), 1.62 (dd, *J* = 13.1, 8.2 Hz, 3H), 1.45 (t, *J* = 10.0 Hz, 3H), 1.41–1.10 (m, 10H), 1.06–0.73 (m, 10H), 0.57 (s, 3H); ^{13}C NMR (151 MHz, pyridine-d5) δ 200.95, 157.64, 146.02, 124.26, 116.19, 110.84, 106.73, 105.41, 104.64, 104.03, 102.05, 89.34, 87.10, 82.92, 82.70, 82.58, 80.88, 79.84, 78.72, 78.51, 77.52, 76.81, 76.14, 75.53, 74.64, 74.07, 73.77, 72.42, 71.97, 71.80, 71.54, 69.26, 64.25, 62.85, 61.86, 59.89, 53.67, 53.46, 49.10, 43.37, 41.35, 40.48, 38.28,

35.93, 35.86, 32.00, 30.64, 29.85, 29.79, 29.48, 29.29, 25.33, 25.21, 22.82, 22.62, 22.53, 20.89, 19.15, 18.50, 18.07, 16.98, 12.80; HRMS (ESI, negative) calcd for $C_{61}H_{97}O_{31}S$ $[M\text{-}Na]^+$ 1357.5740, found 1357.5730.

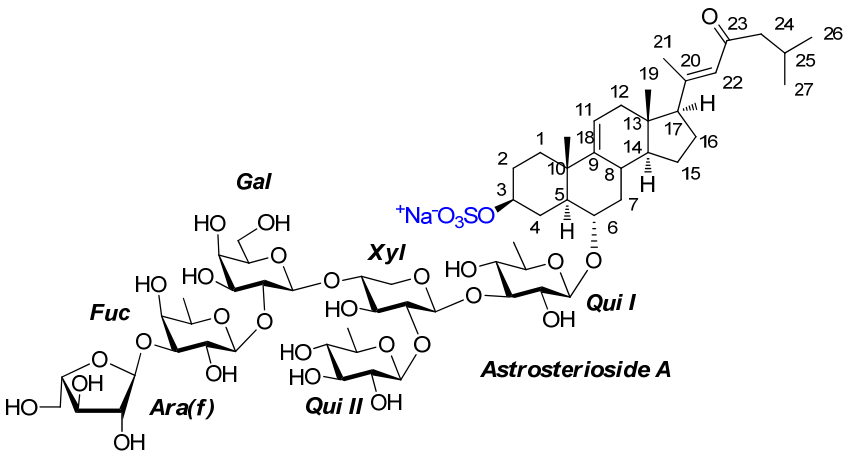


Table 1. Comparison of the NMR data of the synthetic **1** with those reported for natural astrosterioside A.[16,a]

position	δ ^{1}H natural	δ ^{1}H synthetic	Δ	δ ^{13}C natural	δ ^{13}C synthetic	Δ
1	1.35, m 1.68, m	1.33, m 1.67, m	-0.02 -0.01	35.9	35.9	0.0
2	1.83, m 2.75, m	1.83, m 2.75, m	0.00	29.4	29.5	+0.1
3	4.85, m	4.86, m	+0.01	77.7	77.6	-0.1
4	1.68, m 3.42, m	1.67, m 3.42, m	-0.01	30.7	30.7	0.0
5	1.45, m	1.44, m	-0.01	49.3	49.2	-0.1
6	3.79, m	3.78, m	-0.01	80.1	79.9	-0.2
7	1.27, m 2.68, m	1.27, m 2.68, m	0.00	41.6	41.4	-0.2
8	2.10, m	2.08, m	-0.02	36.1	36.0	-0.1
9	-	-	-	146.2	146.1	-0.1
10	-	-	-	38.4	38.3	-0.1
11	5.22, d (4.5)	5.24, d (4.5)	+0.02	116.3	116.2	-0.1
12	1.98, m	1.98, m	0.00	40.6	40.5	-0.1
13	-	-	-	43.4	43.4	0.0
14	1.33, m	1.33, m	0.00	53.6	53.5	-0.1
15	1.30, m	1.31, m	+0.01	25.4	25.4	0.0

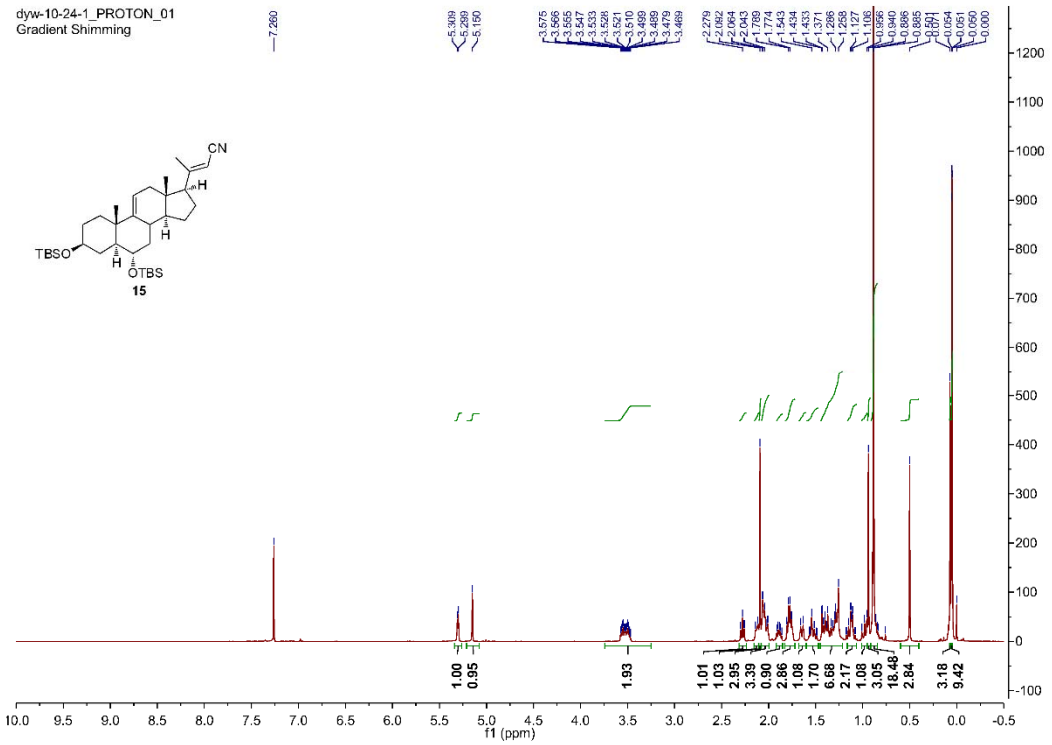
	1.80, m	1.80, m				
16	1.65, m 1.93, m	1.65, m 1.92, m	-0.01	25.4	25.4	0.0
17	2.19, m	2.18, m	-0.01	59.9	59.9	0.0
18	0.57, s	0.54, s	-0.03	13.1	12.8	-0.3
19	0.91, s	0.92, s	+0.01	19.3	19.2	-0.1
20	-	-	-	157.4	157.7	+0.3
21	2.28, s	2.26, s	-0.02	20.9	20.9	0.0
22	6.23, s	6.24, s	+0.01	124.4	124.3	-0.1
23	-	-	-	200.6	201.0	+0.3
24	2.37, m	2.37, m	0.00	53.8	53.7	-0.1
25	2.25, m	2.26, m	+0.01	25.4	25.3	-0.1
26	0.92, d (6.0)	0.92, d (6.0)	0.00	22.7	22.7	0.0
27	0.92, d (6.0)	0.92, d (6.0)	0.00	22.7	22.7	0.0
Qui I						
1	4.80, d (7.0)	4.81, d (7.0)	+0.01	105.0	104.7	-0.3
2	4.00[b]	4.00[b]	0.00	74.5	74.3	-0.2
3	3.85[b]	3.85[b]	0.00	89.8	89.4	-0.4
4	3.57[b]	3.57[b]	0.00	74.2	74.1	-0.1
5	3.70[b]	3.69[b]	-0.01	72.0	72.0	0.0
6	1.59, d (6.0)	1.59, d (6.0)	0.00	18.6	18.5	-0.1
Xyl						
1	5.07, d (7.5)	5.05, d (7.5)	-0.02	104.2	104.1	-0.1
2	4.05[b]	4.05[b]	0.00	82.5	82.6	+0.1
3	4.21[b]	4.21[b]	0.00	75.7	75.7	0.0
4	4.21[b]	4.22[b]	+0.01	79.1	78.9	-0.2
5	3.78/4.45[b]	3.78/4.44[b]		64.5	64.3	-0.2
Qui II						
1	5.22, d (7.0)	5.24, d (7.0)	+0.02	105.3	105.4	+0.1
2	4.05[b]	4.05[b]	0.00	76.3	76.2	-0.1
3	4.10[b]	4.08[b]	-0.02	76.9	76.9	0.0
4	3.97[b]	3.98[b]	+0.01	75.6	75.6	0.0
5	3.70[b]	3.69[b]	-0.01	73.7	73.6	-0.1
6	1.77 d (6.0)	1.76 d (6.0)	-0.01	18.0	18.1	+0.1
Gal						
1	4.97, d (7.5)	4.95, d (7.5)	-0.02	102.3	102.1	-0.2
2	4.43[b]	4.42[b]	-0.01	83.3	83.0	-0.3

3	4.15[b]	4.14[b]	-0.01	74.9	74.7	-0.2
4	4.47[b]	4.47[b]	0.00	69.4	69.3	-0.1
5	4.07[b]	4.07[b]	0.00	76.8	76.9	+0.1
6	4.32/4.40[b]	4.31/4.40[b]	-0.01	62.0	61.9	-0.1
Fuc						
1	4.85, d (7.0)	4.86, d (7.0)	+0.01	107.0	106.8	-0.2
2	4.47[b]	4.47[b]	0.00	72.5	72.4	-0.1
3	4.08[b]	4.07[b]	-0.01	80.9	80.9	0.0
4	4.20[b]	4.19[b]	-0.01	72.0	72.0	0.0
5	3.53[b]	3.53[b]	0.00	71.6	71.6	0.0
6	1.38 d (6.0)	1.39 d (6.0)	+0.01	17.1	17.0	-0.1
Ara(f)						
1	6.07, br s	6.07, s	0.00	110.9	110.9	0
2	4.87[b]	4.86[b]	-0.01	82.4	82.6	+0.2
3	4.79[b]	4.79[b]	0.00	78.8	78.8	0.0
4	4.85[b]	4.85[b]	0.00	87.5	87.1	-0.4
5	4.21/4.28[b]	4.22/4.28[b]	+0.01	63.0	62.9	-0.1

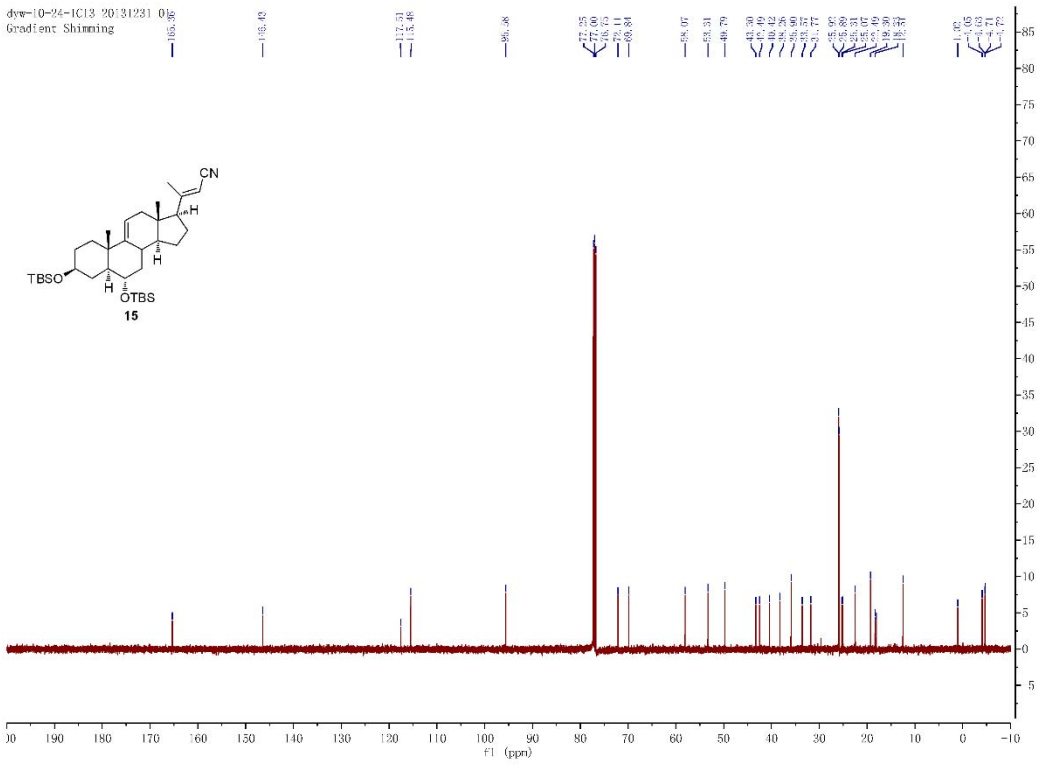
[a] All the spectra were measured in pyridine-d_5, with 500 MHz for ^{1}H NMR and 151 MHz for ^{13}C NMR; listed in parentheses are coupling constants in Hz. [b] Overlapped signals.

References:

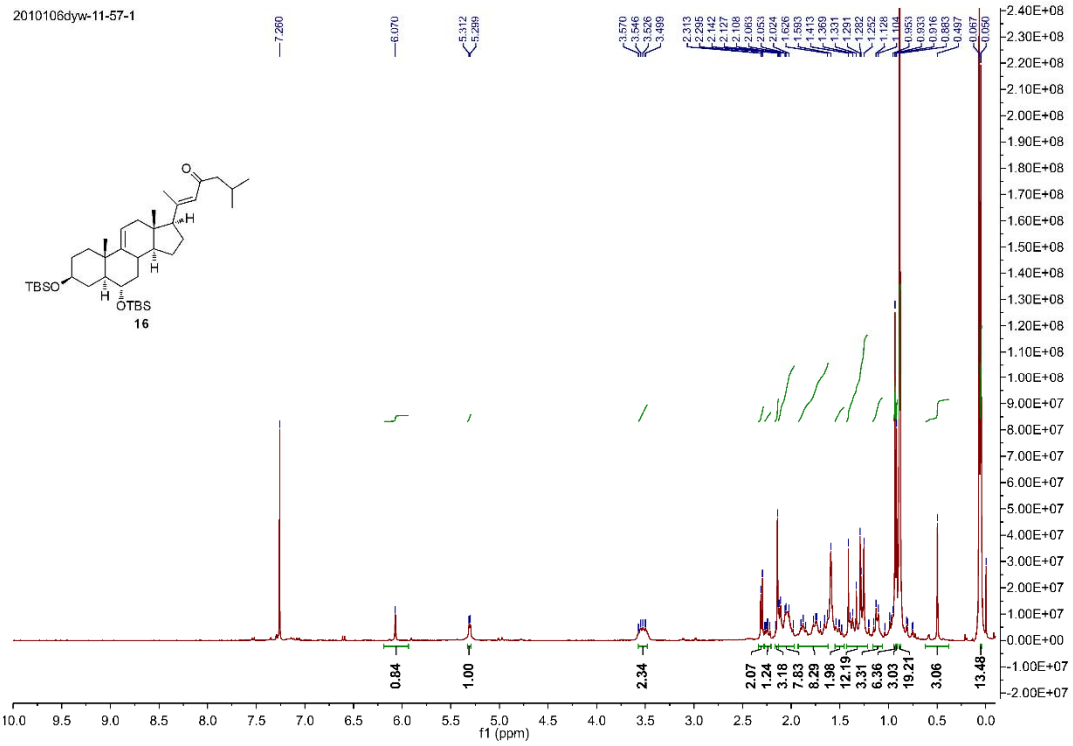
1. D. Comins, A. Jacobine, J. Marshall and M. Turnbull, *Synthesis*, 1978, **4**, 309-311.
2. G. Xiao and B. Yu, *Chem. Eur. J.*, 2013, **19**, 7708-7712.
3. P. Canonne, S. Foscolos and F. Lemay, *Tetrahedron Lett.*, 1980, 155-160.
4. P. I. Abronina, K. G. Fedina, N. M. Podvalnyy, A. I. Zinin, A. O. Chizhov, N. N. Kondakov, V. I. Torgov and L. O. Kononov, *Carbohydr. Res.*, 2014, **396**, 25-36.
5. D. B. Werz and P. H. Seeberger, *Angew. Chem. Int. Ed.*, 2005, **44**, 6315-6318.
6. J. Xiong, Z. Lu, N. Ding, S. Ren and Y. Li, *Eur. J. Org. Chem.*, 2013, **2013**, 6158-6166.
7. B. Yu and H. Tao, *Tetrahedron Lett.*, 2001, **42**, 2405-2407.
8. B. Yu and H. Tao, *J. Org. Chem.*, 2002, **67**, 9099-9102.
9. D. Crich and M. Smith, *J. Am. Chem. Soc.*, 2001, **123**, 9015-9020.
10. J. Zhang and P. Kováč, *J. Carbohydr. Chem.*, 1999, **18**, 461-469.
11. Y. Li, Y. Yang and B. Yu, *Tetrahedron Lett.*, 2008, **49**, 3604-3608.
12. Y. Ma, Z. Li, H. Shi, J. Zhang and B. Yu, *J. Org. Chem.*, 2011, **76**, 9748-9756.
13. Y. Yang, Y. Li and B. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 12076-12077.
14. Y. Zhu and B. Yu, *Angew. Chem. Int. Ed.*, 2011, **50**, 8329-8332.
15. Z. H. Jiang, X. B. Han and R. R. Schmidt, *Liebigs Ann. Chem.*, 1993, 1179-1184.
16. N. P. Thao, N. X. Cuong, B. T. Luyen, N. V. Thanh, N. X. Nhiem, Y. S. Koh, B. M. Ly, N. H. Nam, P. V. Kiem, C. V. Minh and Y. H. Kim, *J. Nat. Prod.*, 2013, **76**, 1764-1770.



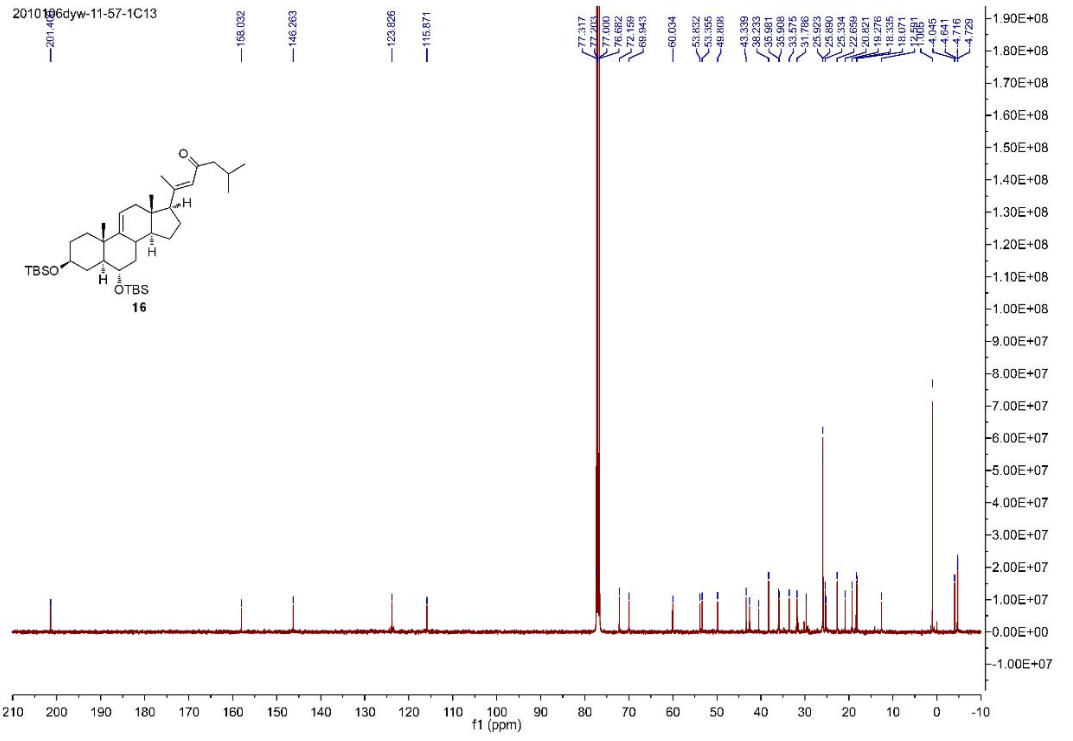
^{1}H NMR of compound **15** (500 Hz, $CDCl_3$)



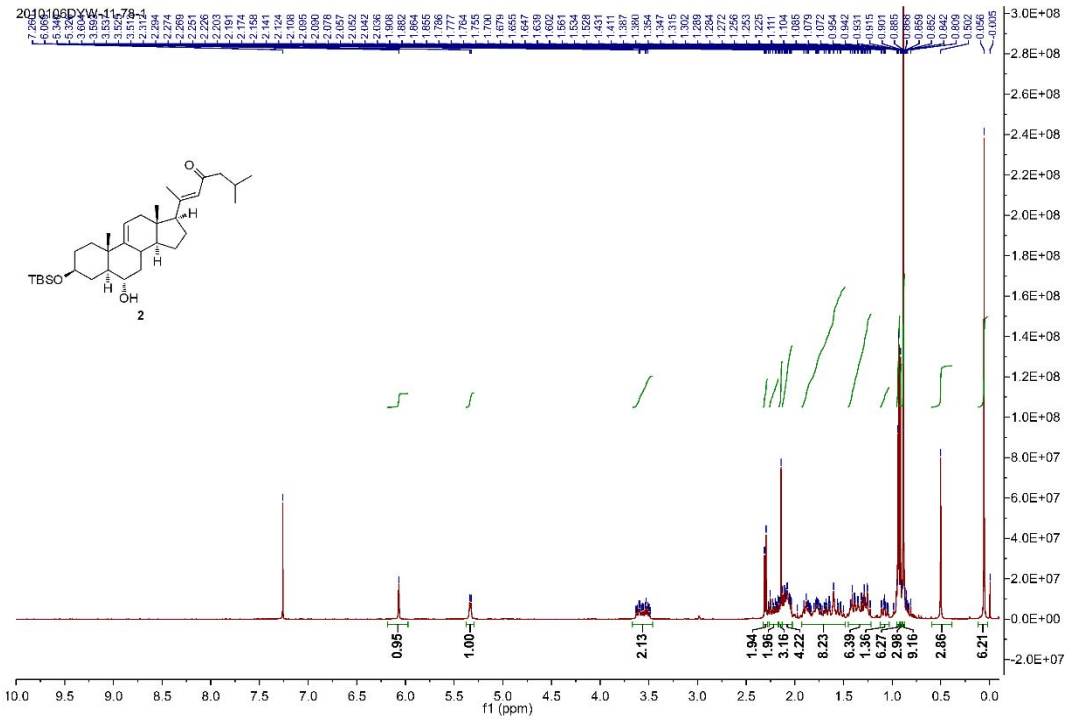
^{13}C NMR of compound **15** (126 Hz, $CDCl_3$)



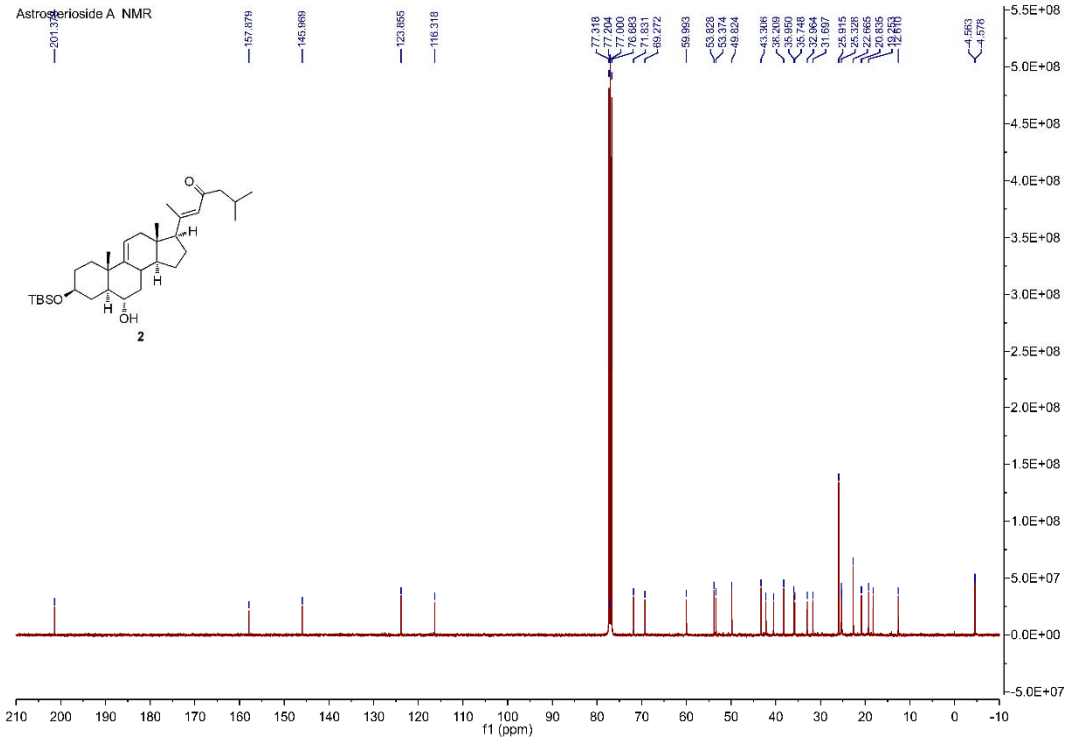
^{1}H NMR of compound **16** (400 Hz, $CDCl_3$)



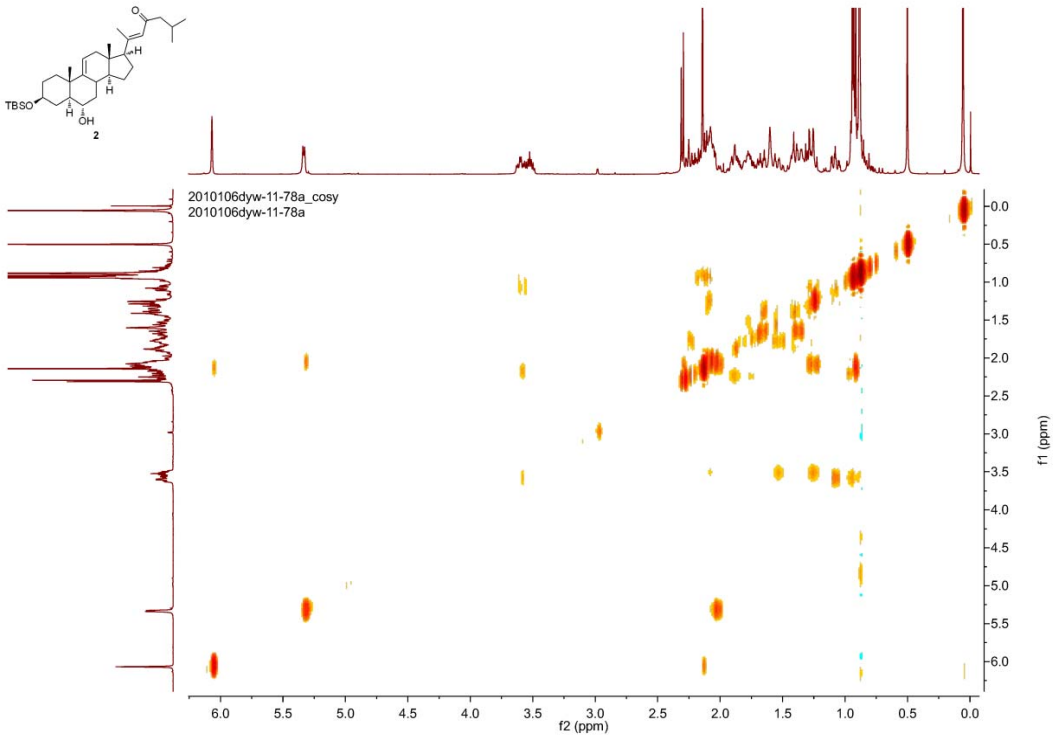
^{13}C NMR of compound **16** (101 Hz, $CDCl_3$)



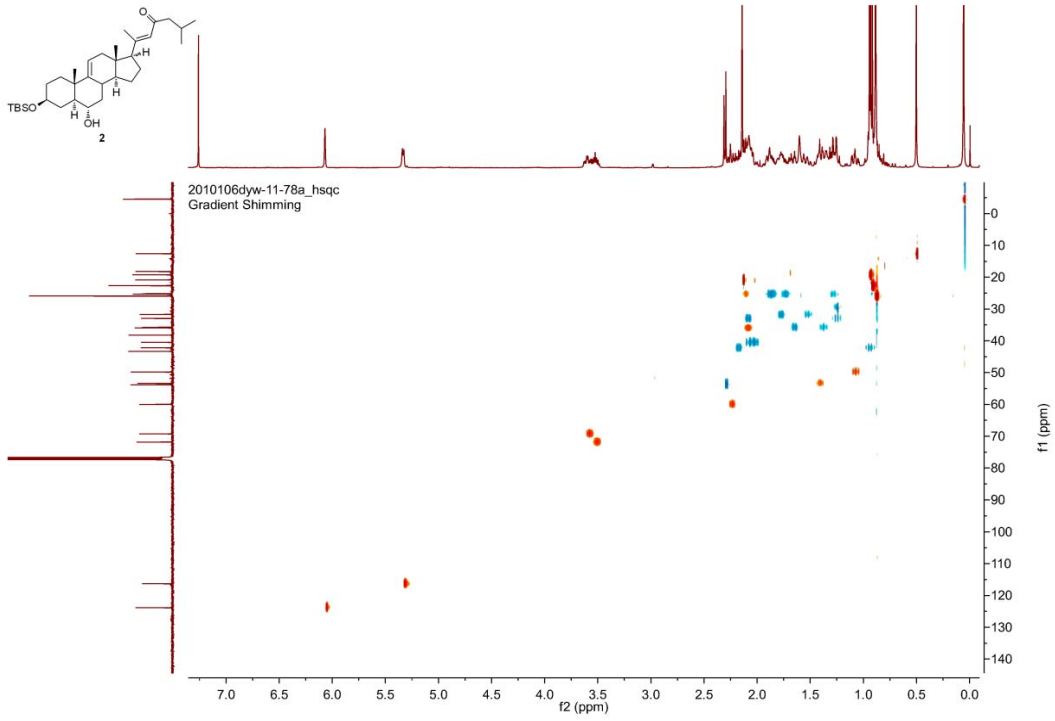
^{1}H NMR of compound **2** (400 Hz, $CDCl_3$)



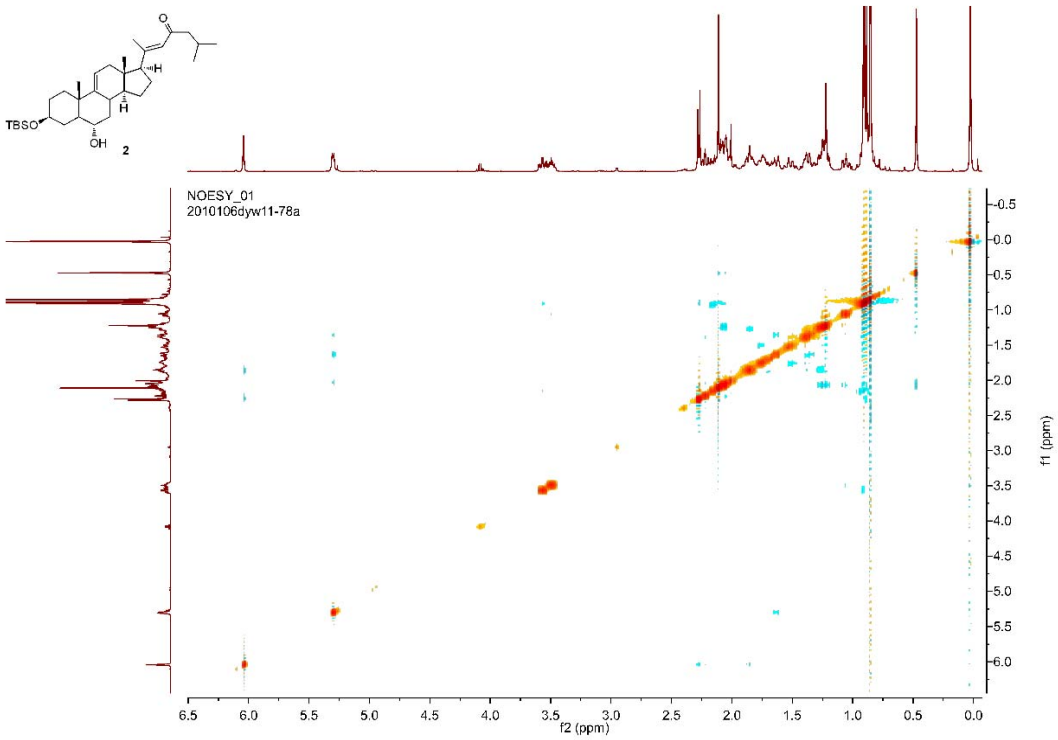
^{13}C NMR of compound **2** (101 Hz, $CDCl_3$)



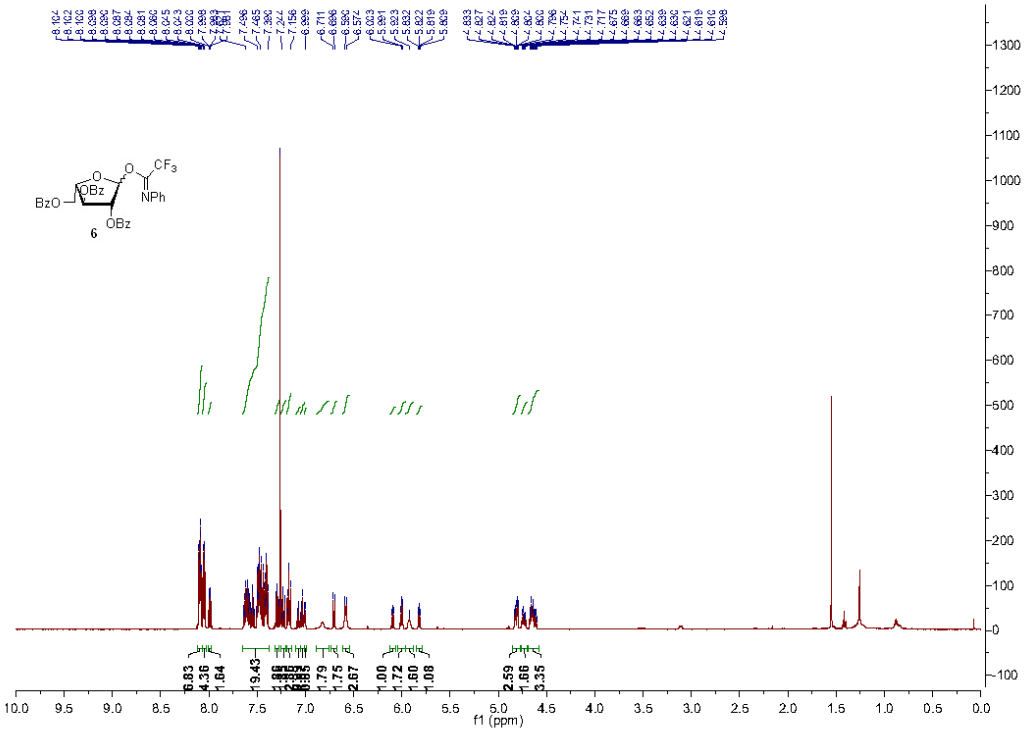
COSY of compound **2**



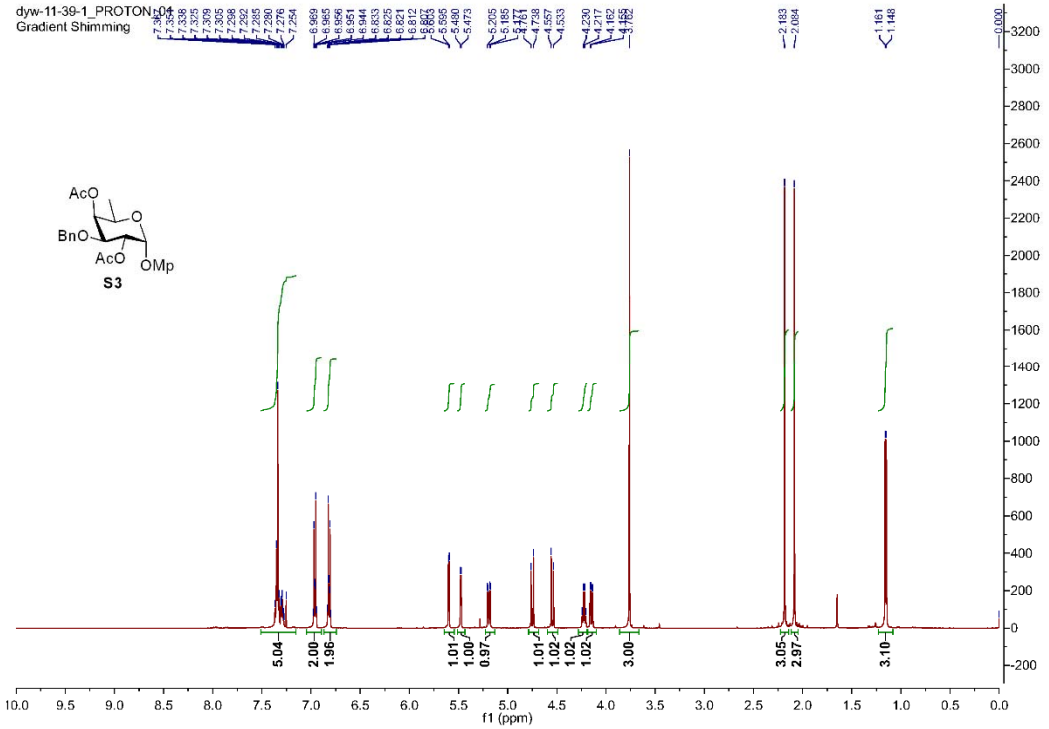
HSQC of compound **2**



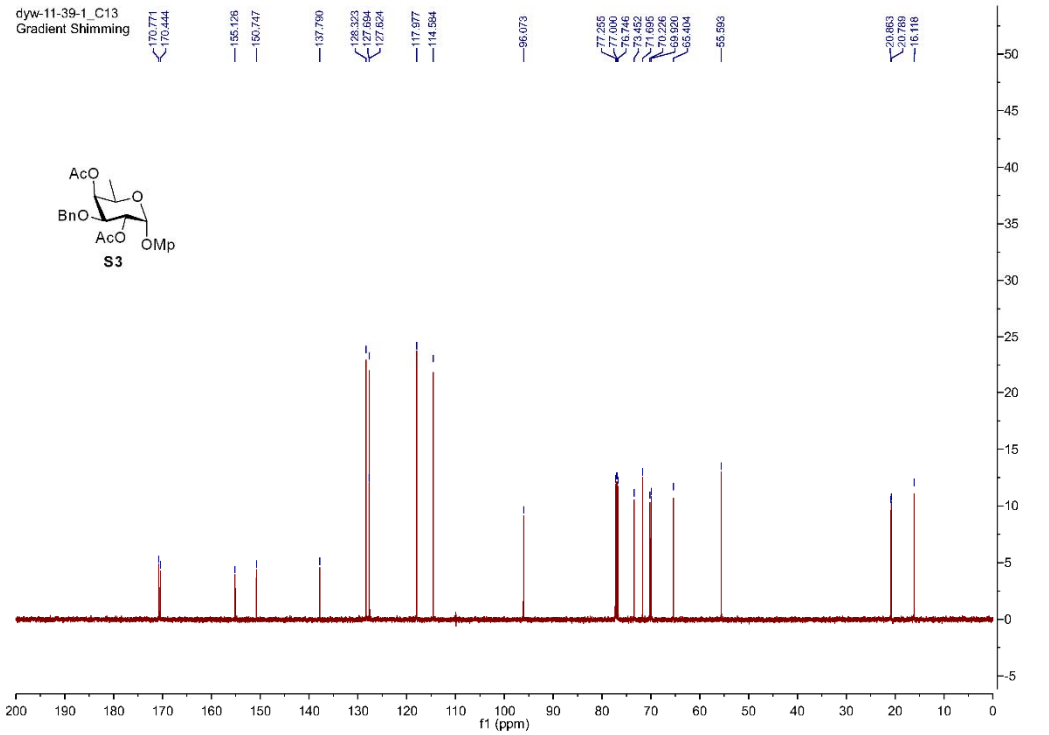
NOESY of compound **2**



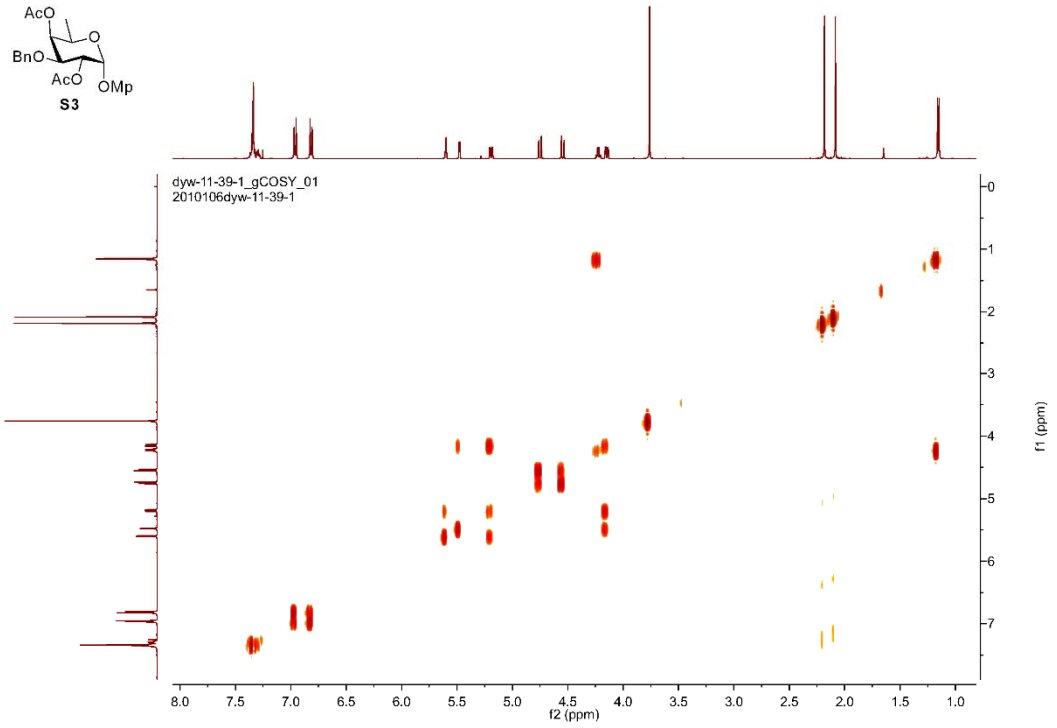
^{1}H NMR of compound **6** (500 Hz, $CDCl_3$)



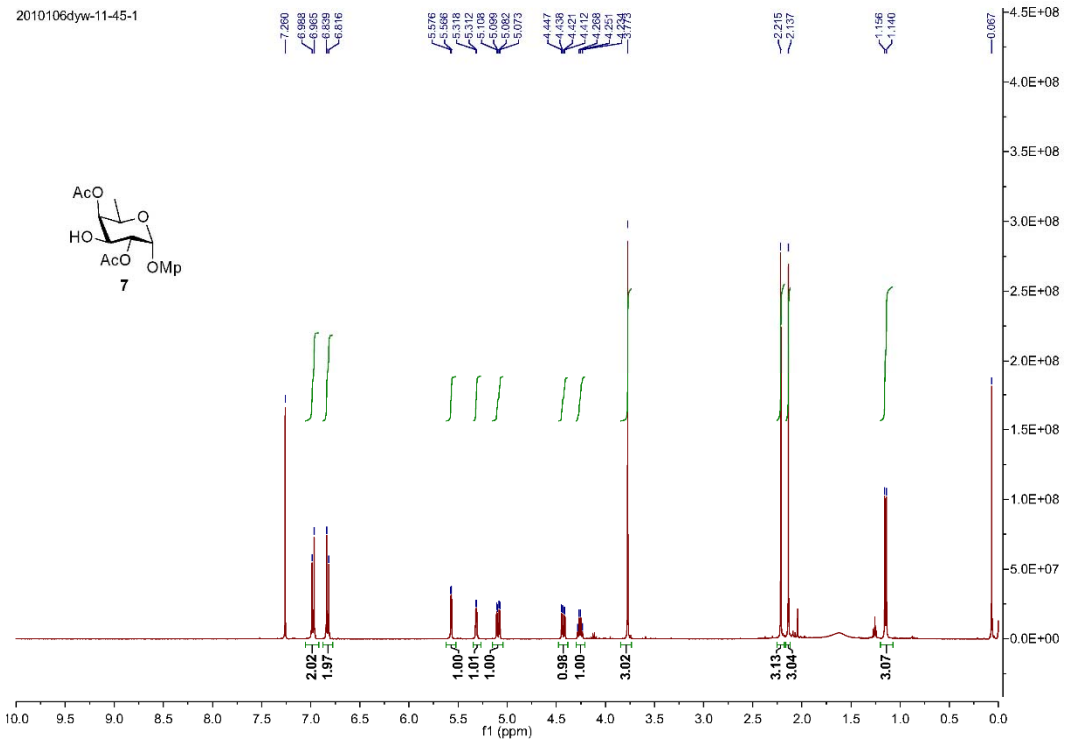
^{1}H NMR of compound **S3** (500 Hz, $CDCl_3$)



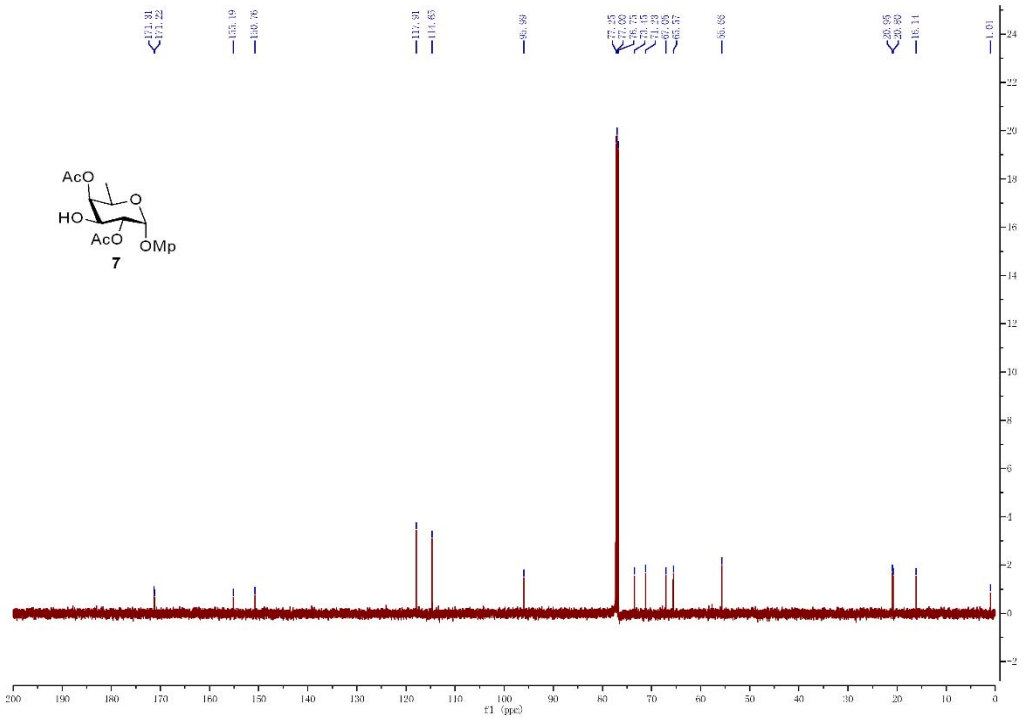
^{13}C NMR of compound **S3** (126 Hz, $CDCl_3$)



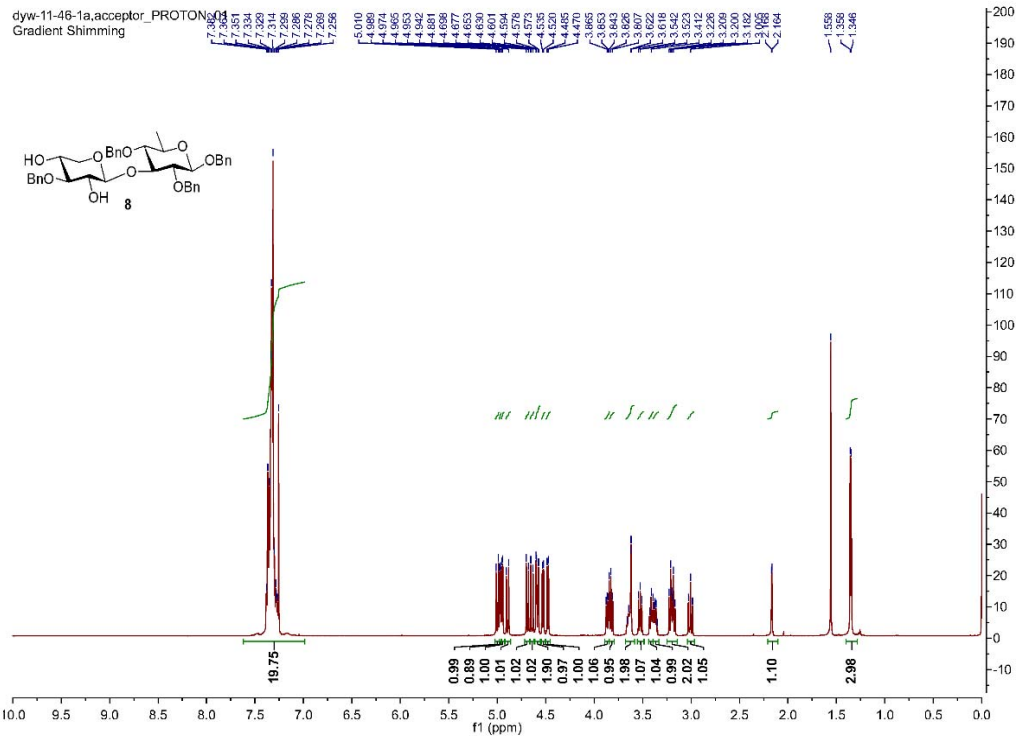
COSY of compound **S3**



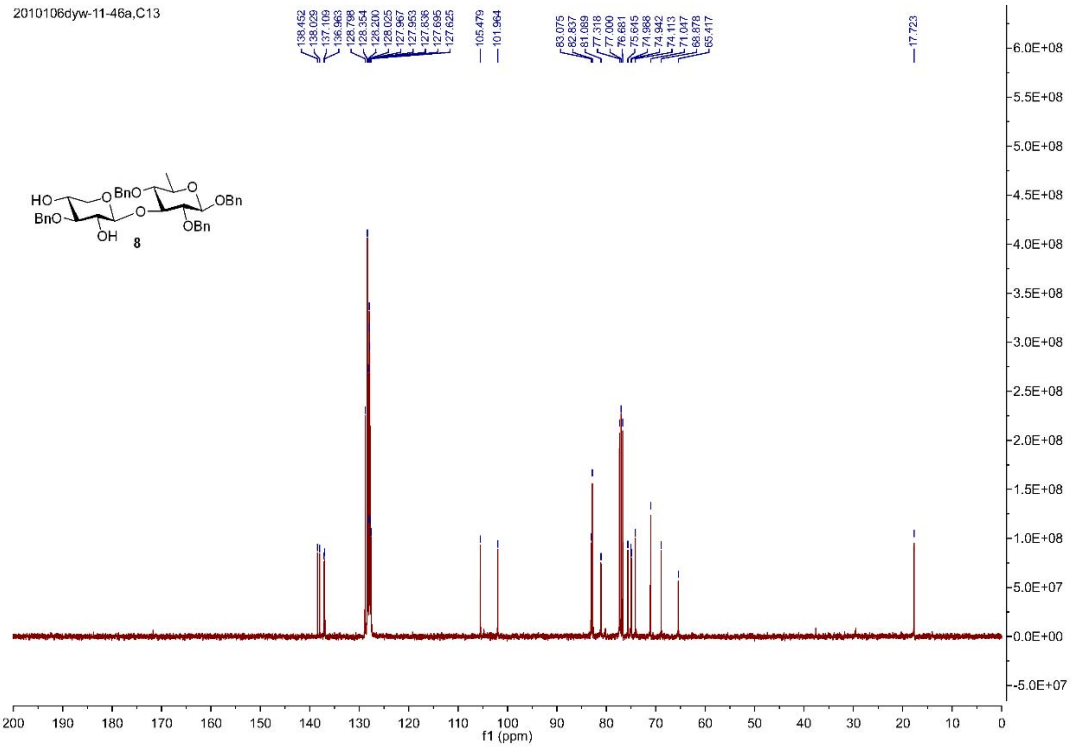
^{1}H NMR of compound **7** (400 Hz, $CDCl_3$)



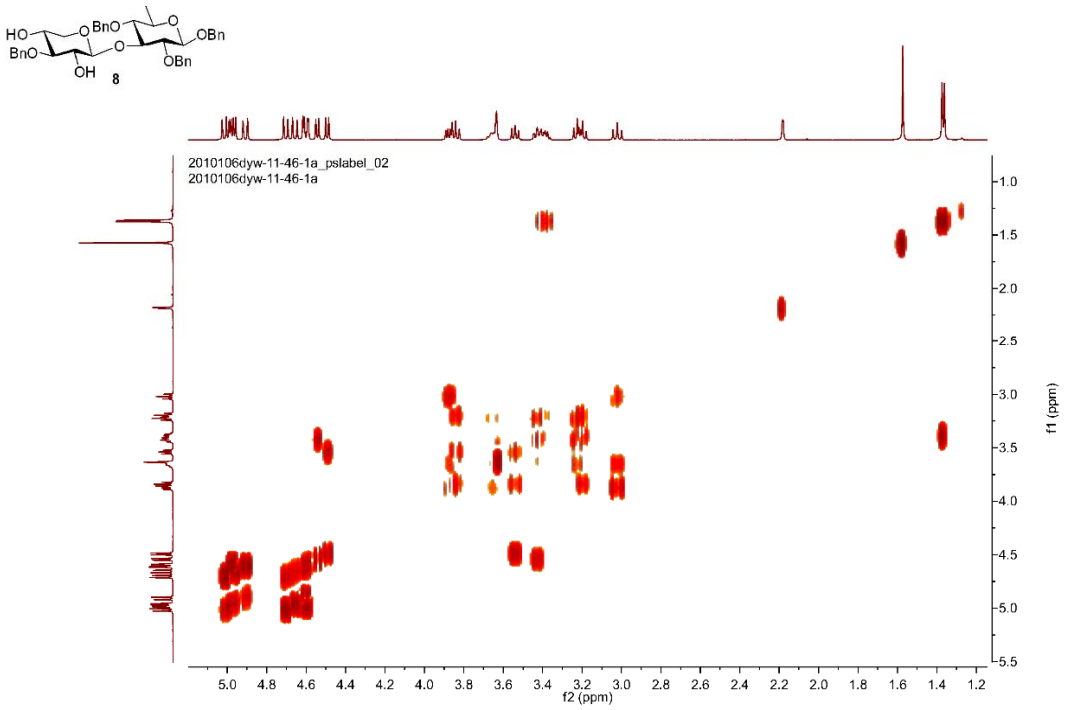
^{13}C NMR of compound **7** (126 Hz, $CDCl_3$)



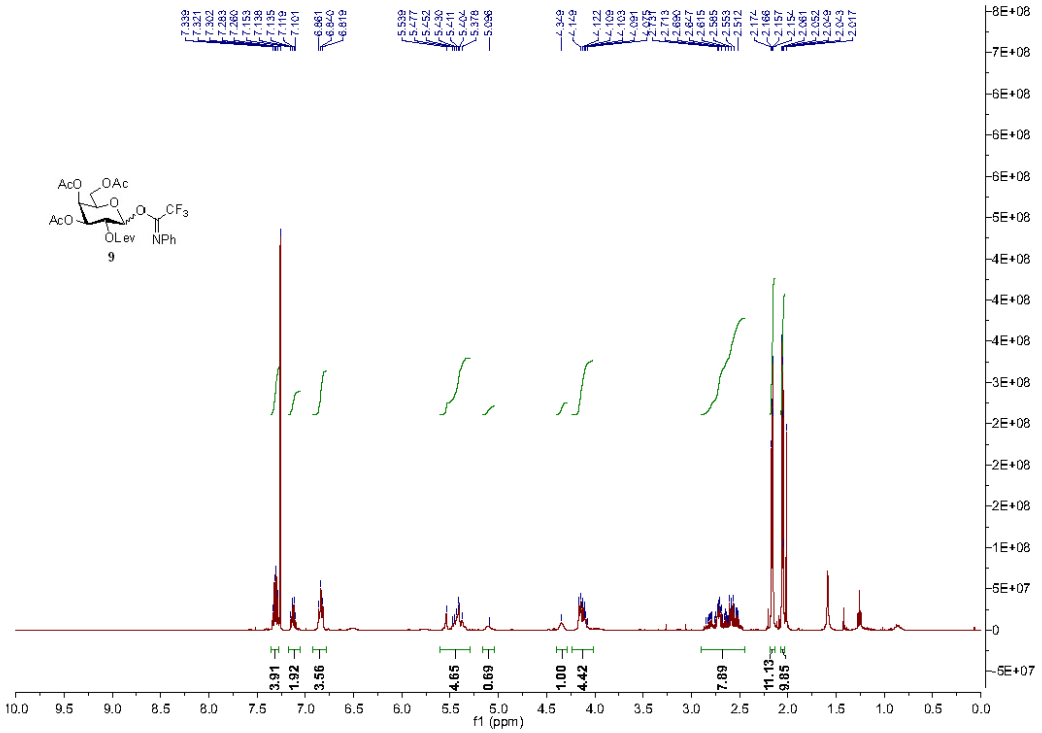
^{1}H NMR of compound **8** (500 Hz, $CDCl_3$)



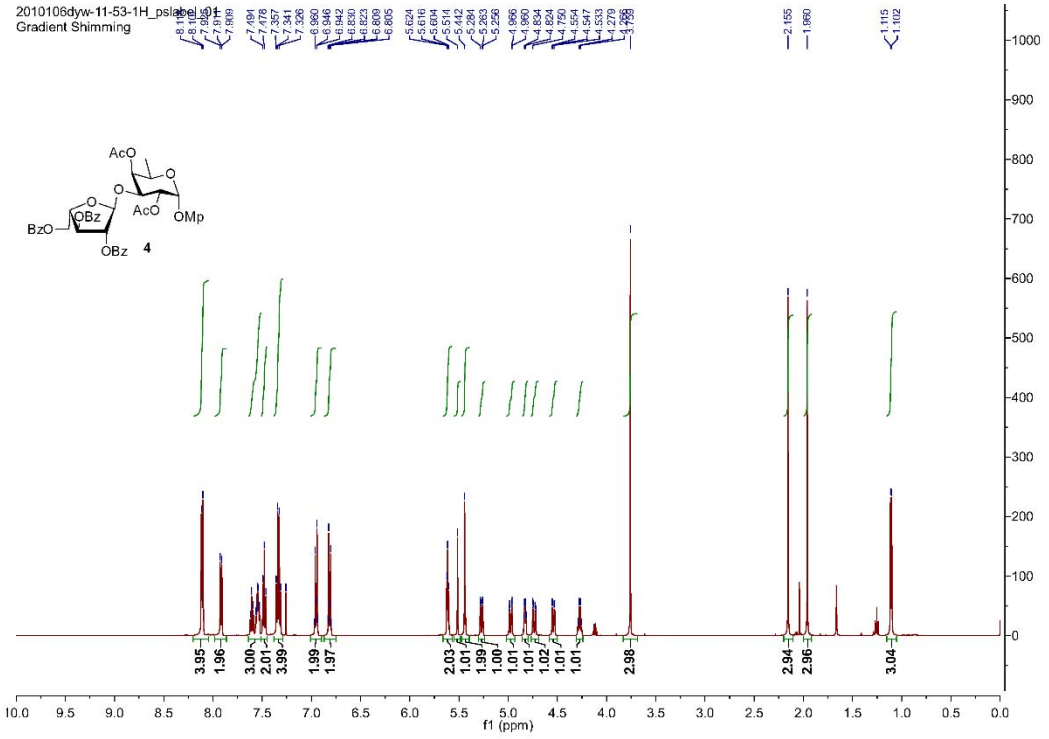
^{13}C NMR of compound **8** (126 Hz, $CDCl_3$)



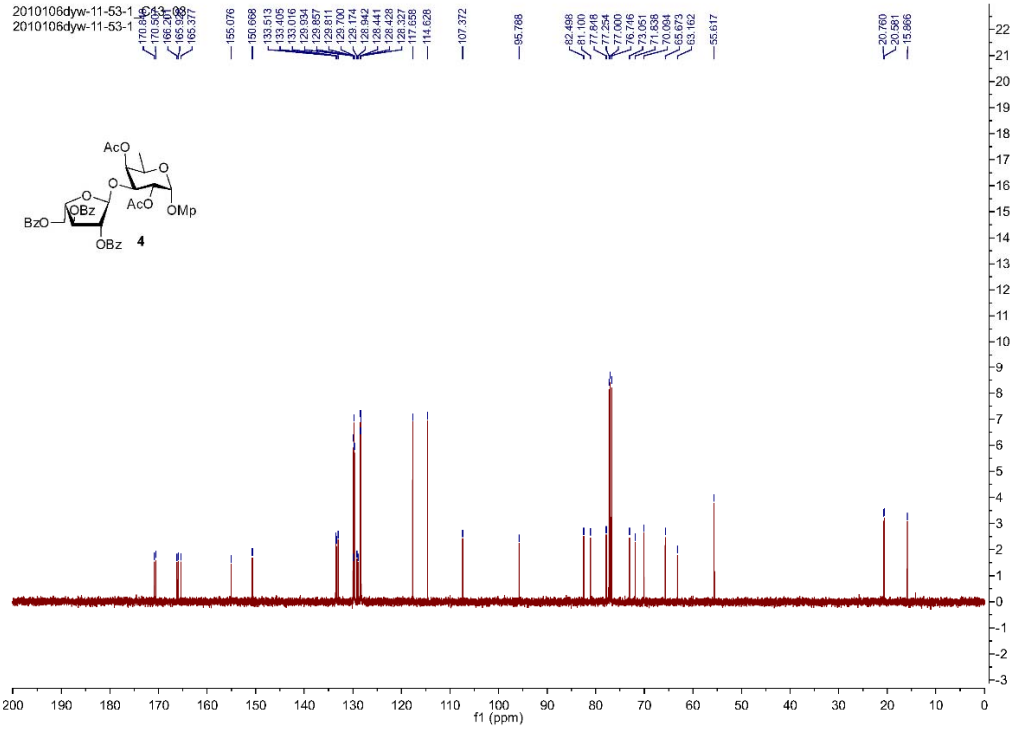
COSY of compound **8**



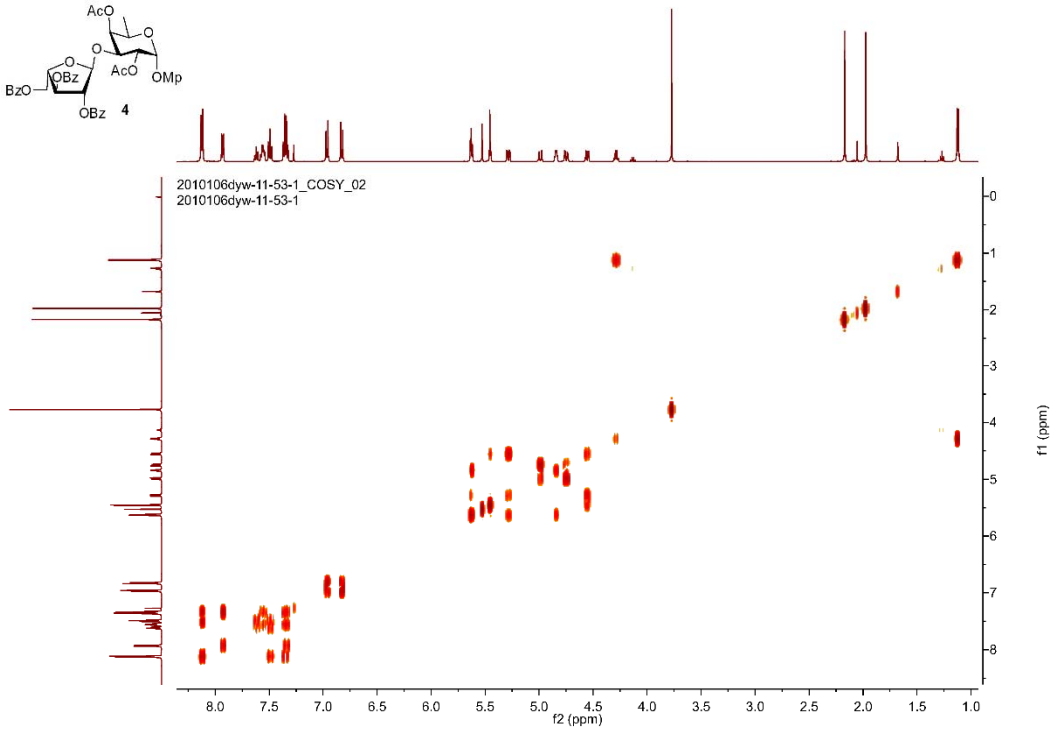
^{1}H NMR of compound **9** (400 Hz, $CDCl_3$)



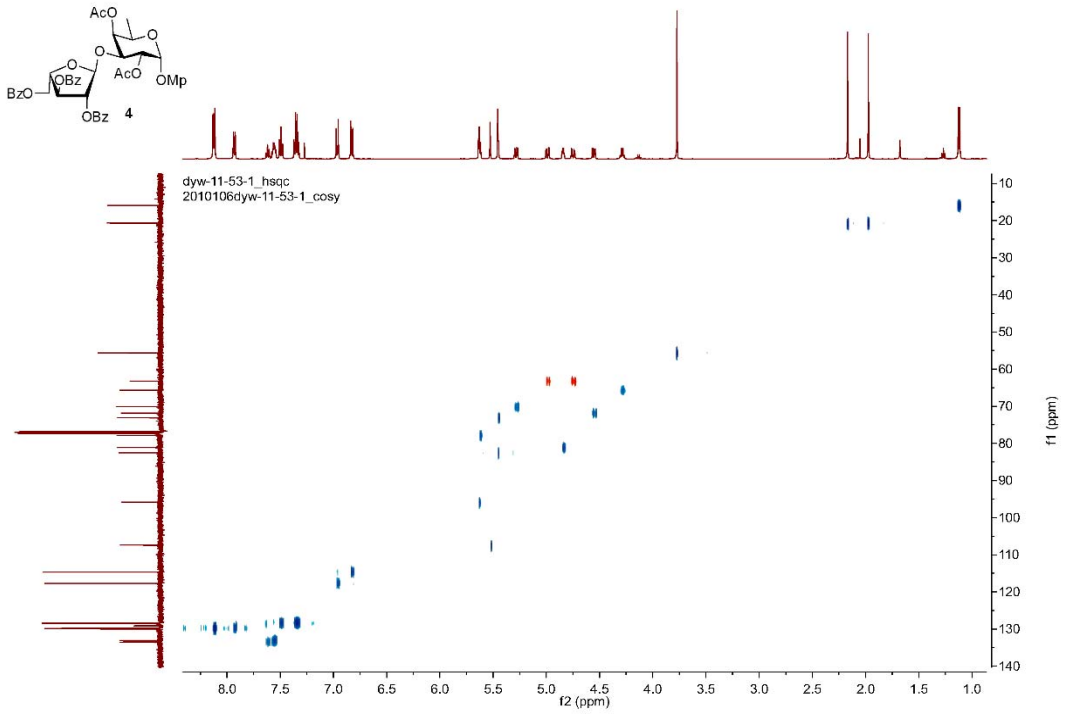
^{1}H NMR of compound **4** (500 Hz, $CDCl_3$)



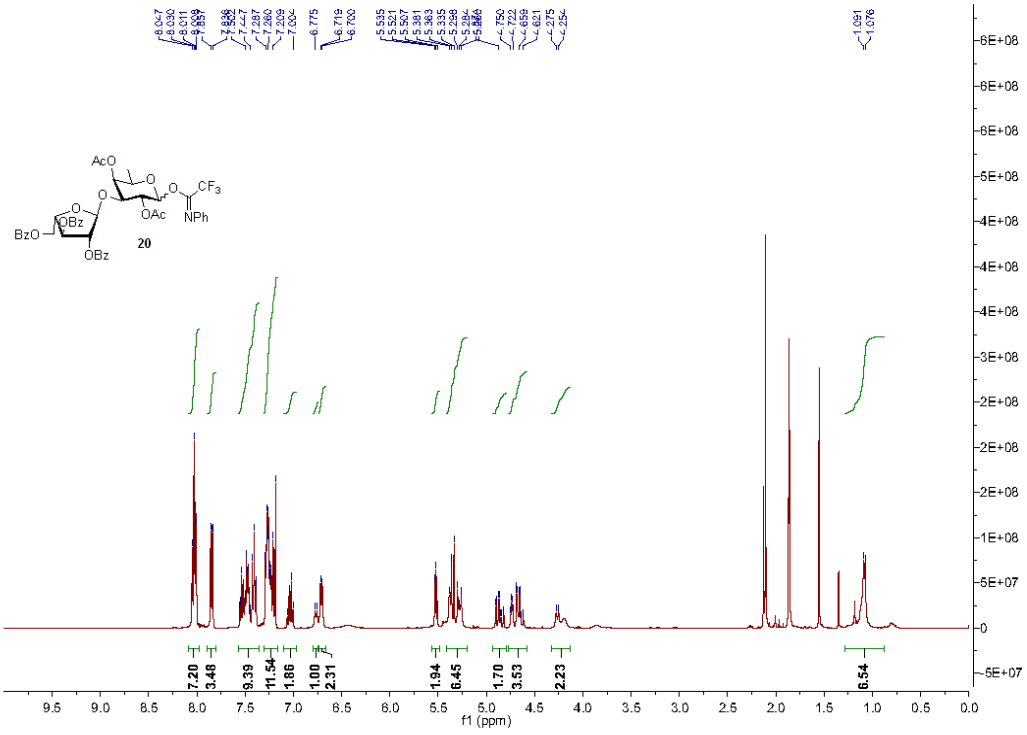
^{13}C NMR of compound **4** (126 Hz, $CDCl_3$)



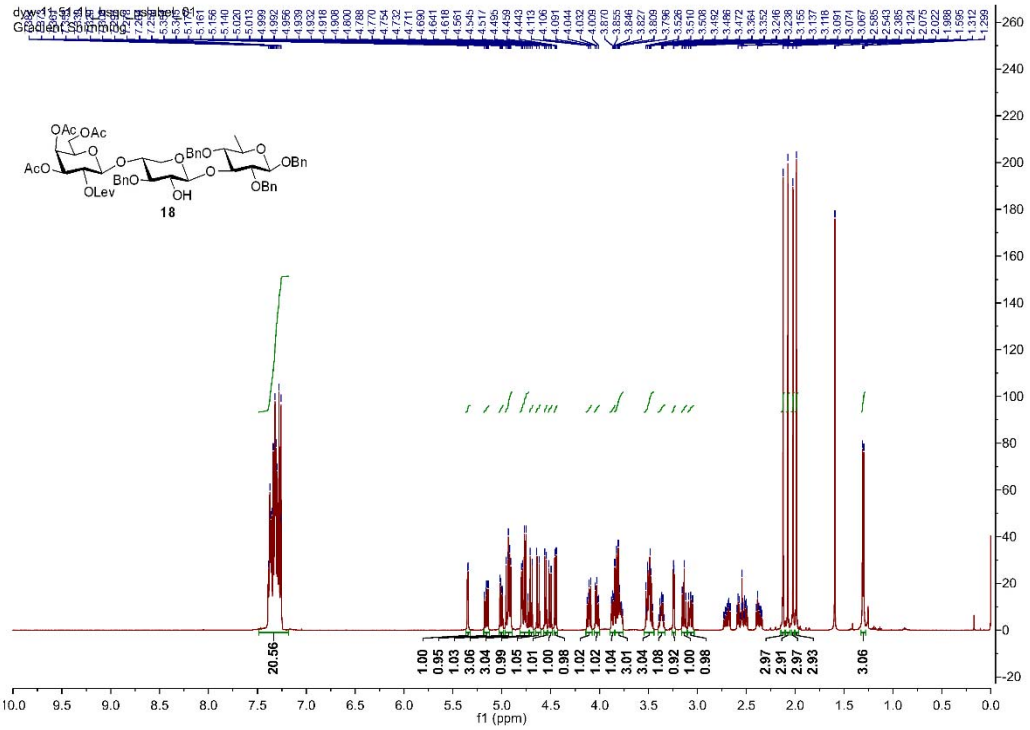
COSY of compound **4**



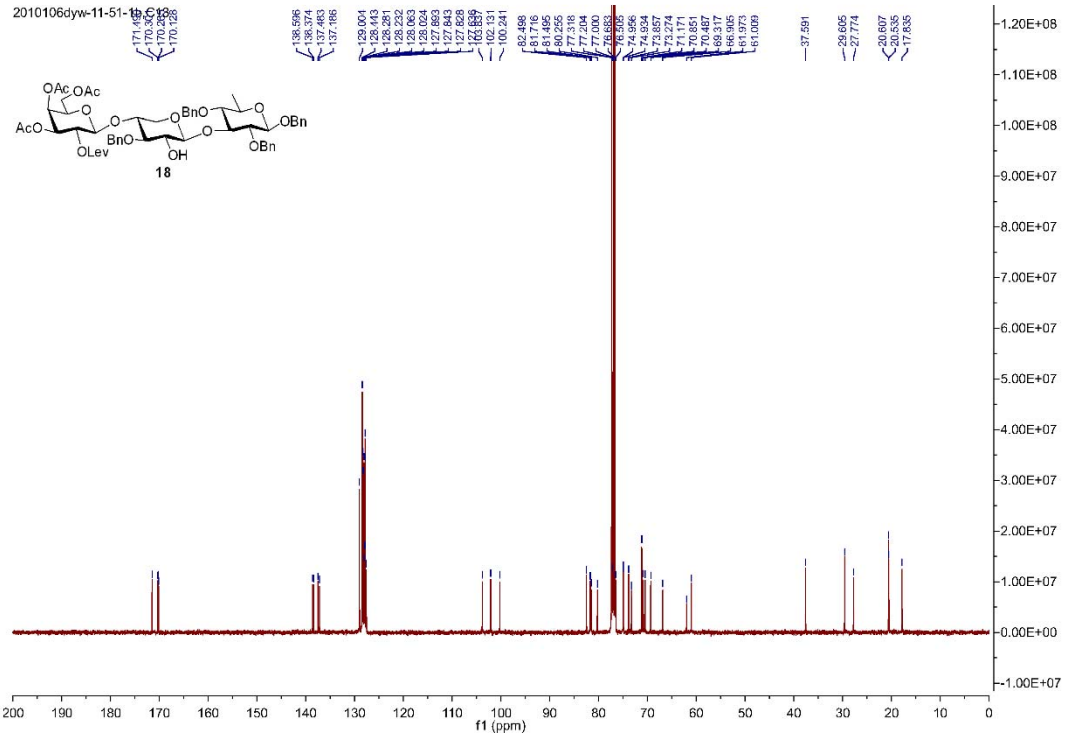
HSQC of compound **4**



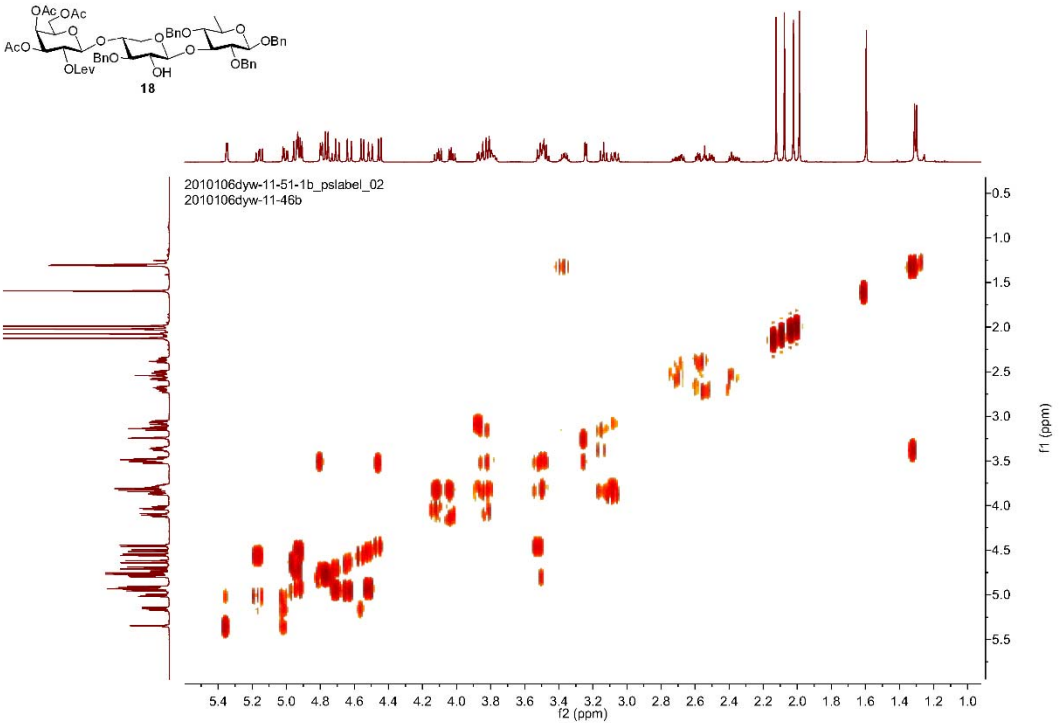
^{1}H NMR of compound **20** (400 Hz, $CDCl_3$)



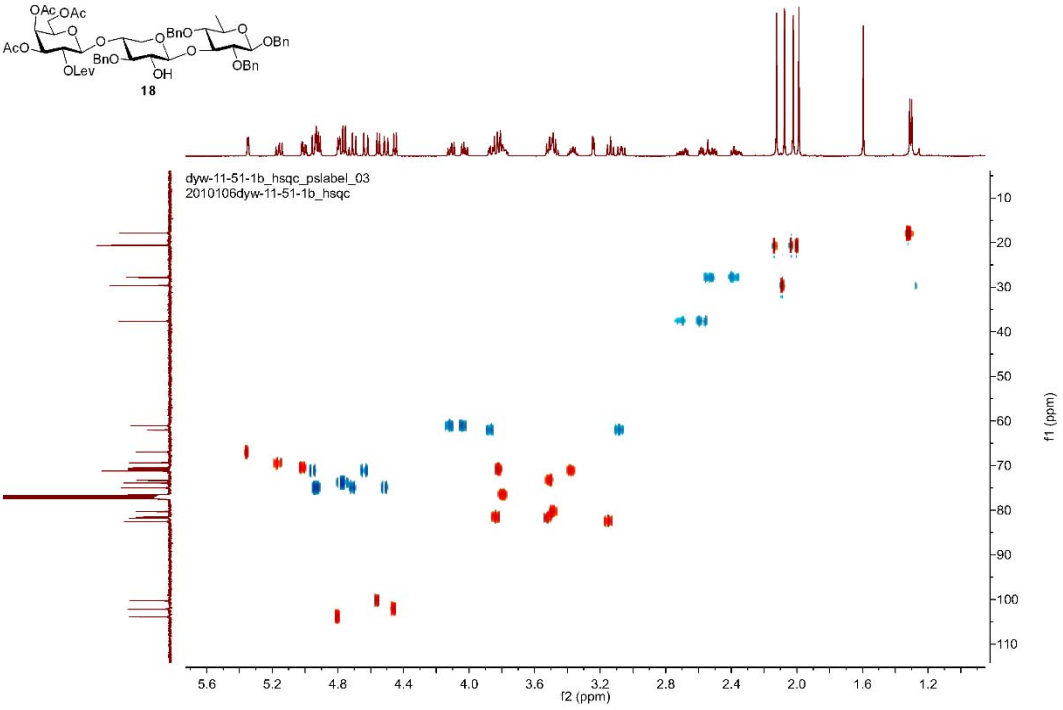
^{1}H NMR of compound **18** (500 Hz, $CDCl_3$)



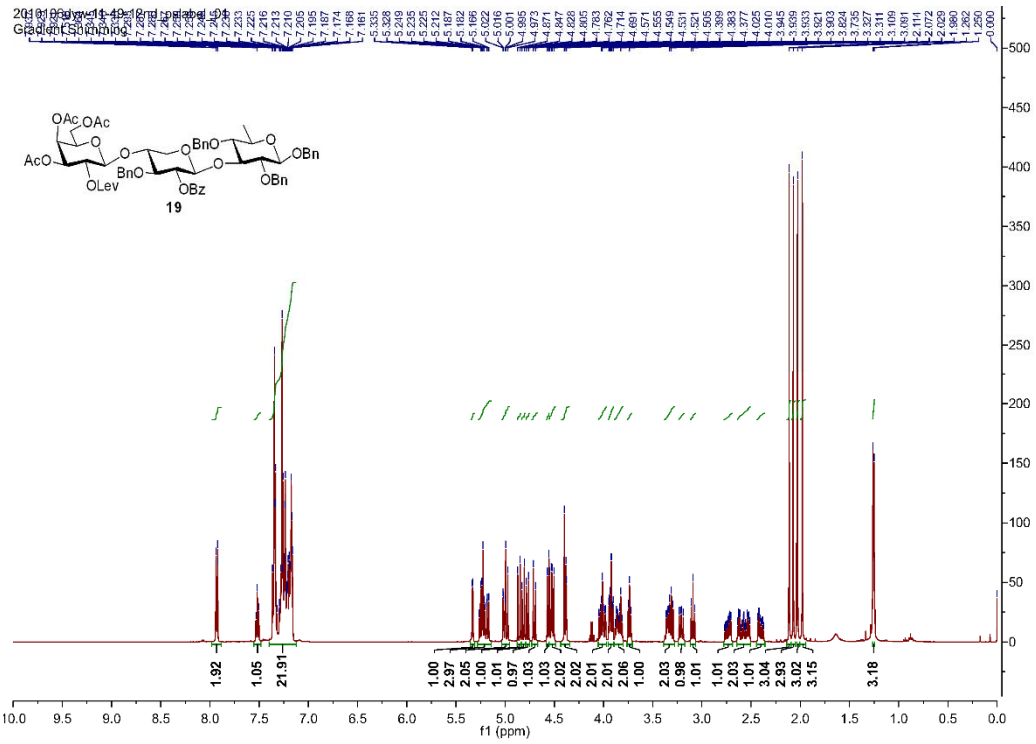
^{13}C NMR of compound **18** (126 Hz, $CDCl_3$)



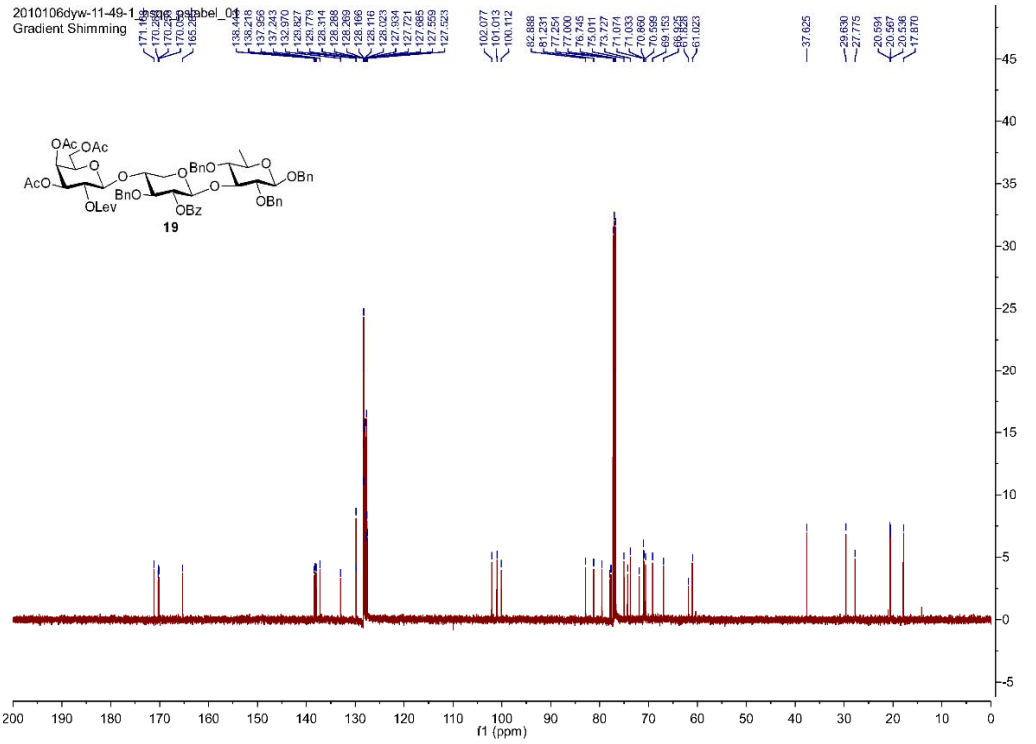
COSY of compound **18**



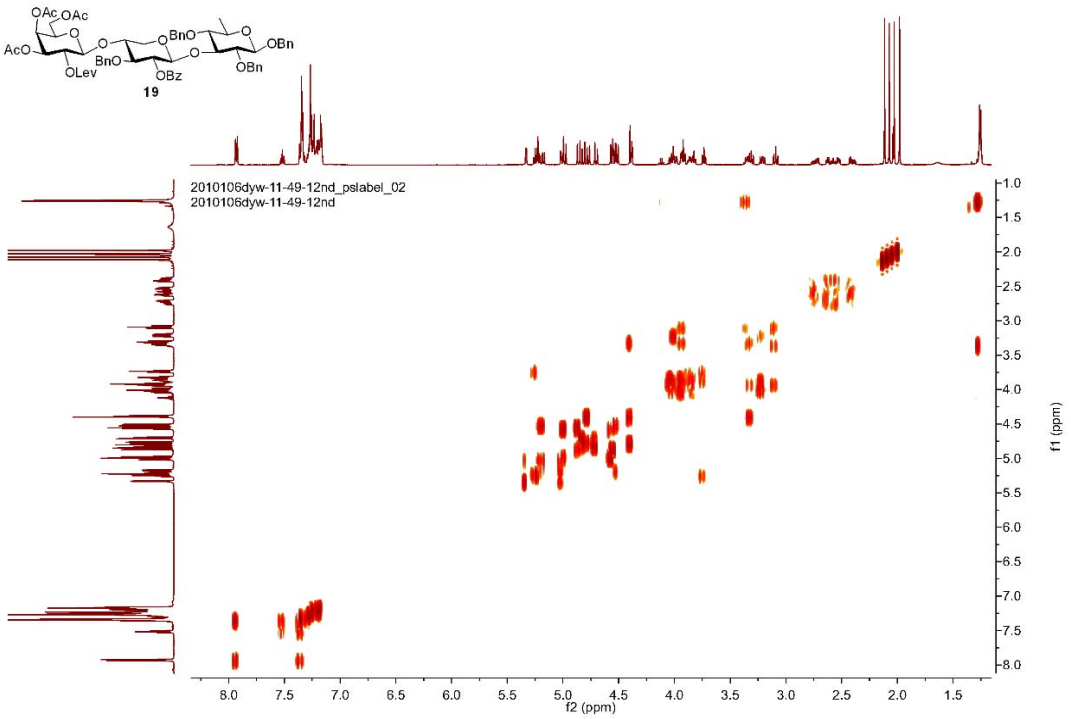
HSQC of compound **18**



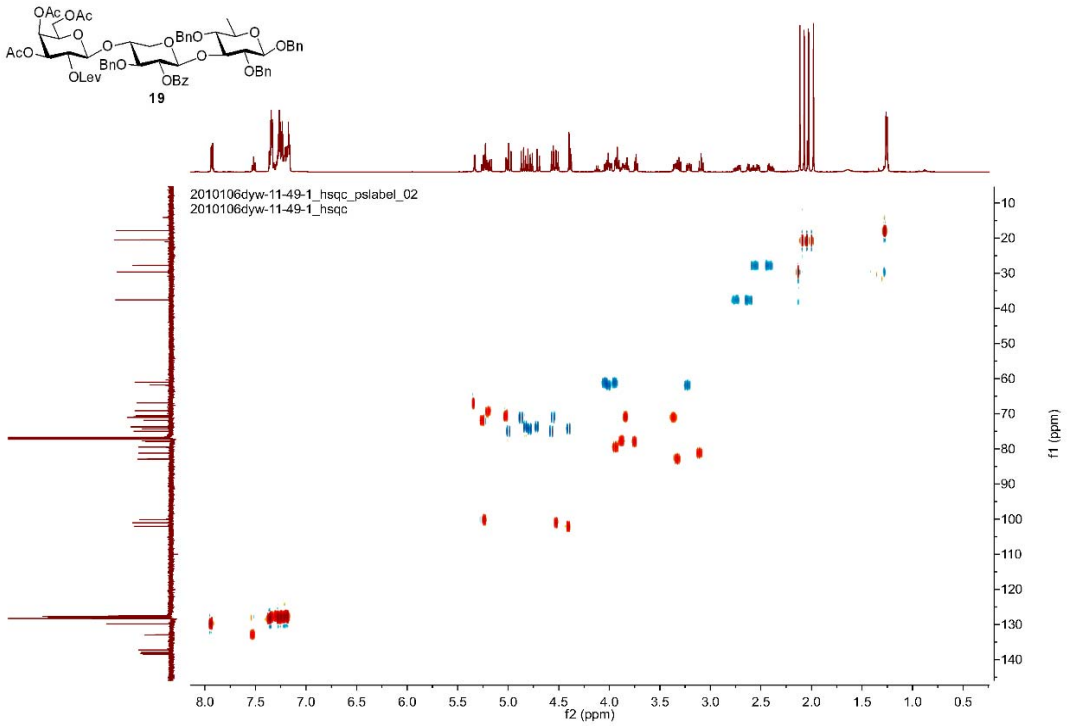
^{1}H NMR of compound **19** (500 Hz, $CDCl_3$)



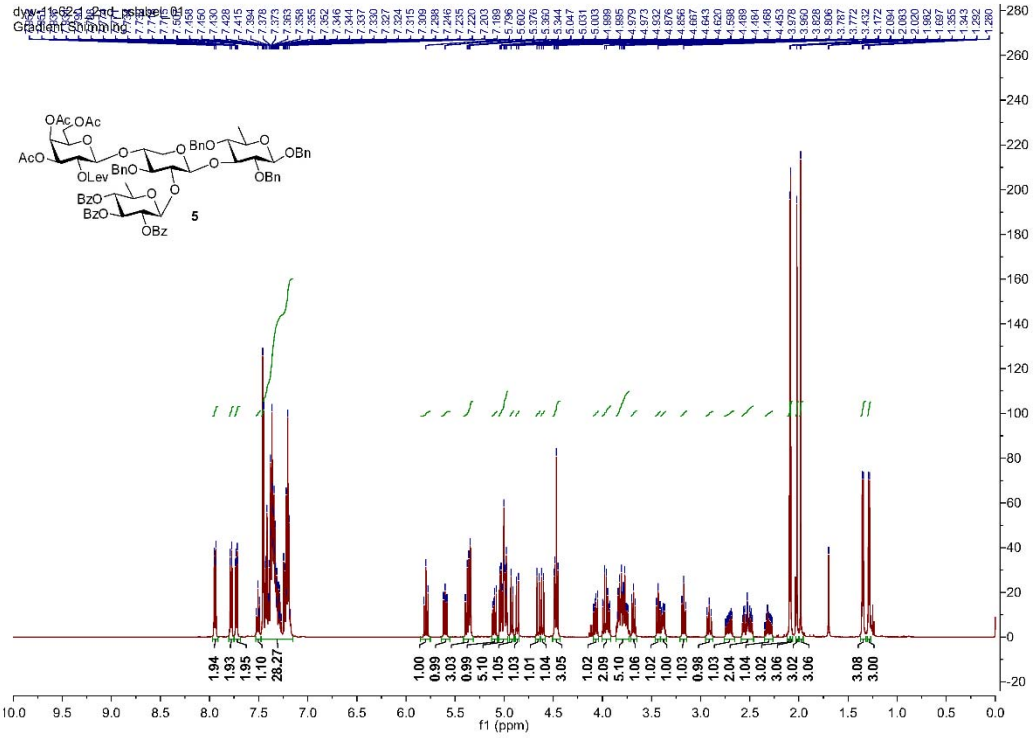
^{13}C NMR of compound **19** (126 Hz, $CDCl_3$)



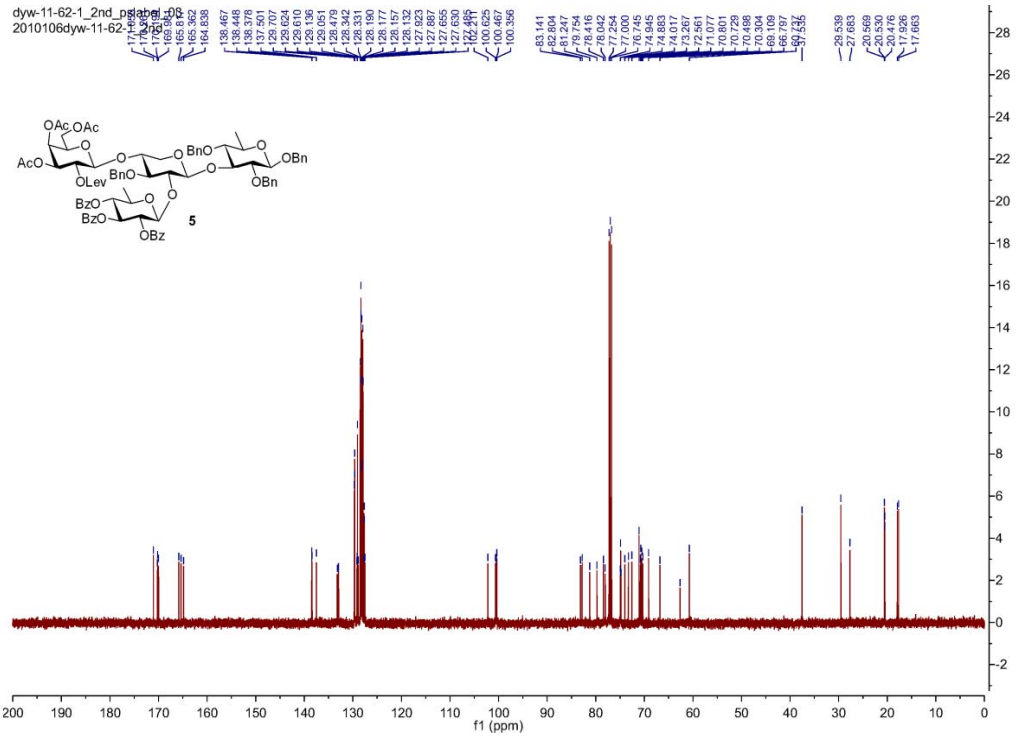
COSY of compound **19**



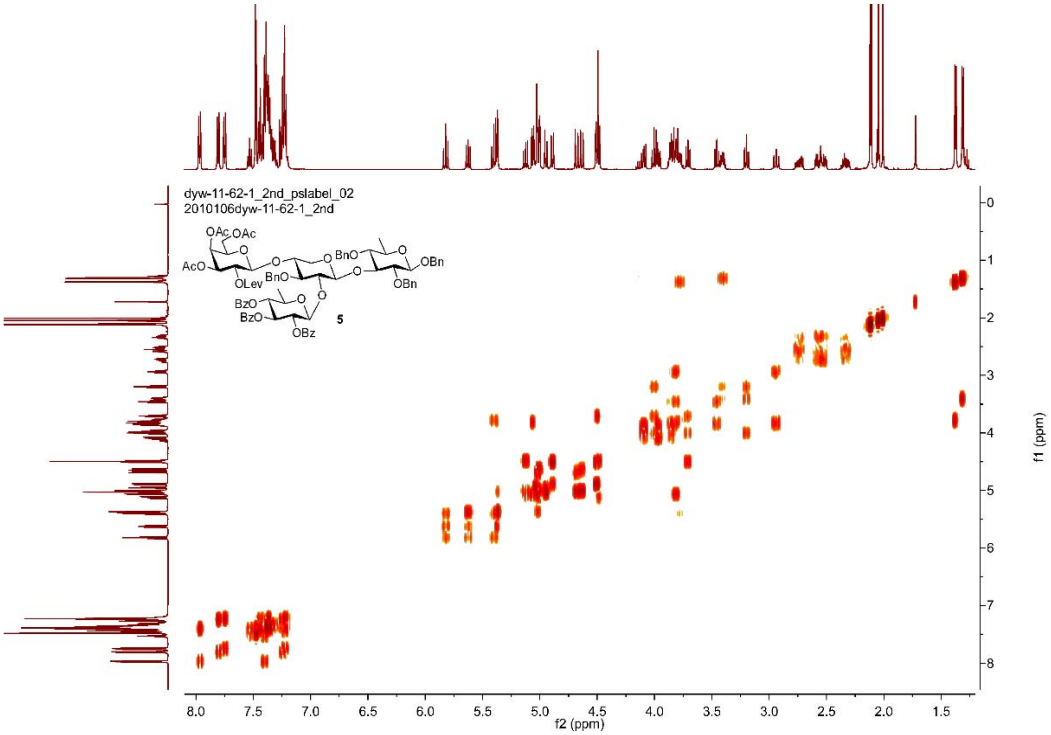
HSQC of compound **19**



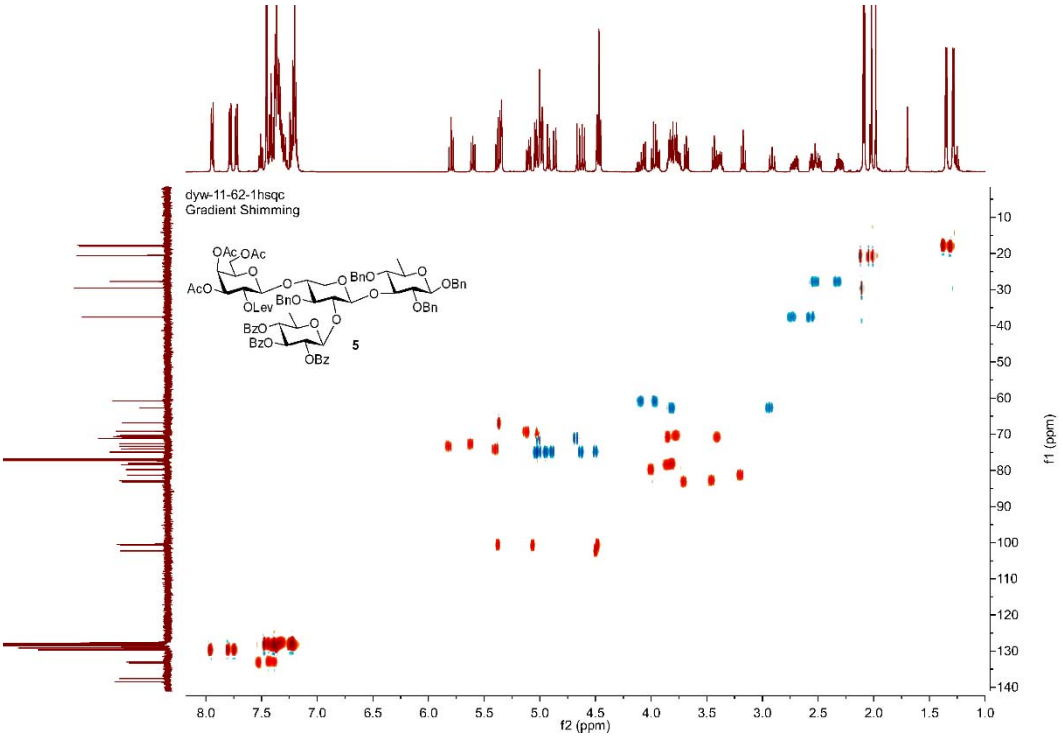
^{1}H NMR of compound **5** (500 Hz, $CDCl_3$)



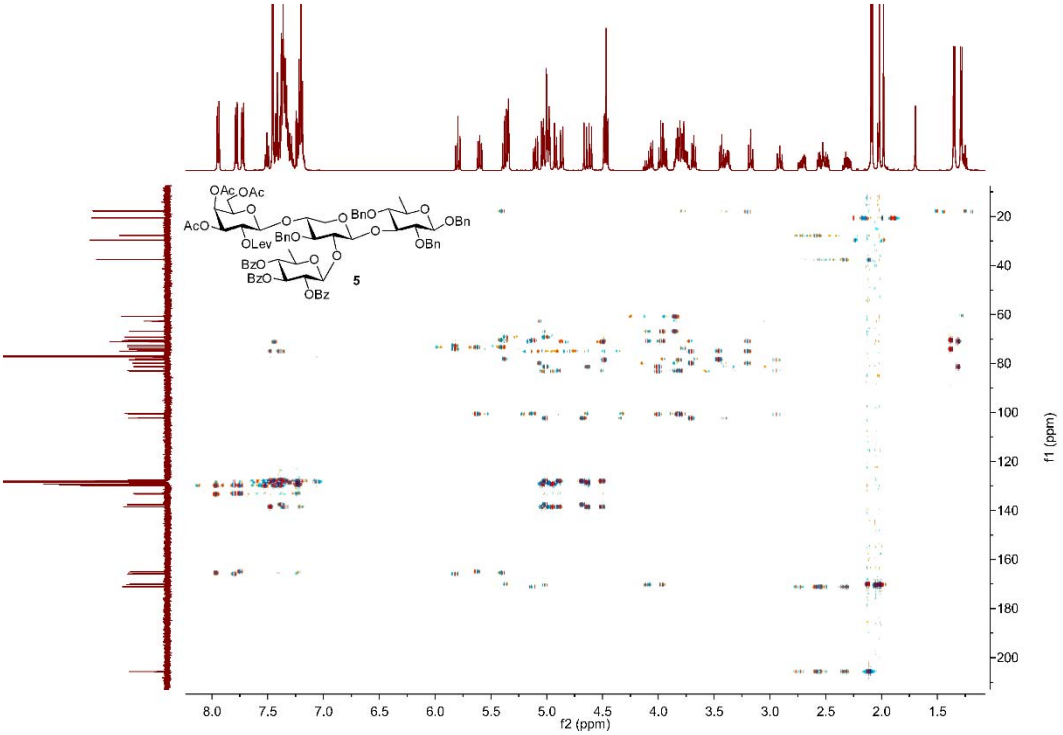
^{13}C NMR of compound **5** (126 Hz, $CDCl_3$)



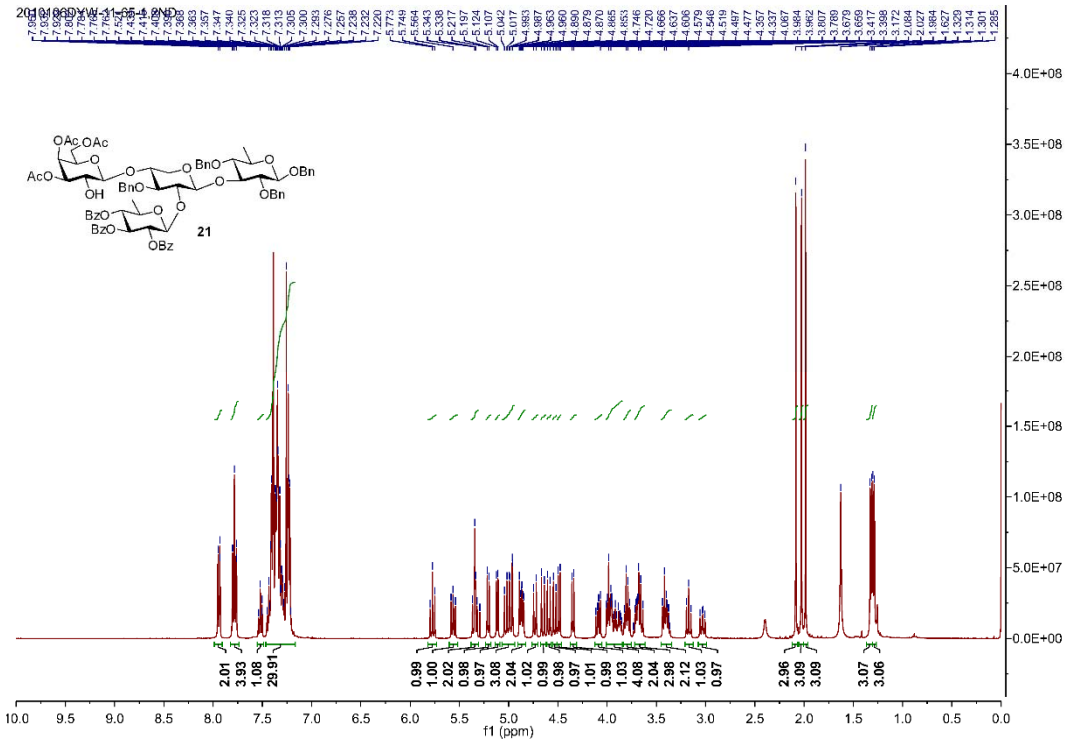
COSY of compound **5**



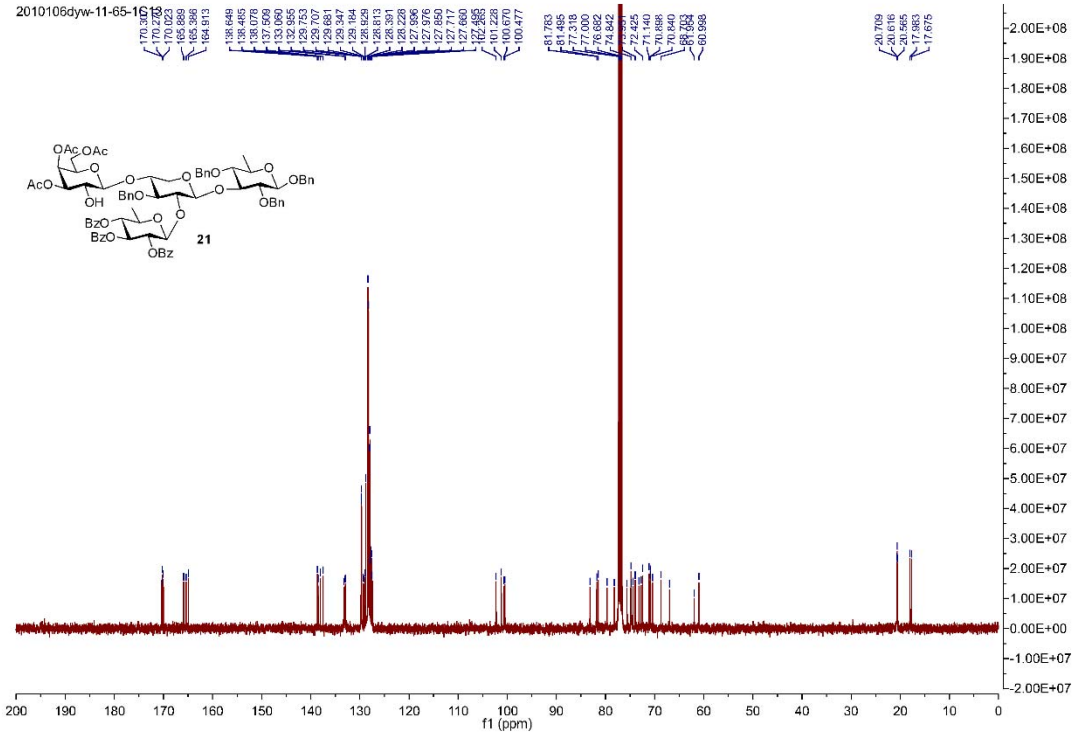
HSQC of compound **5**



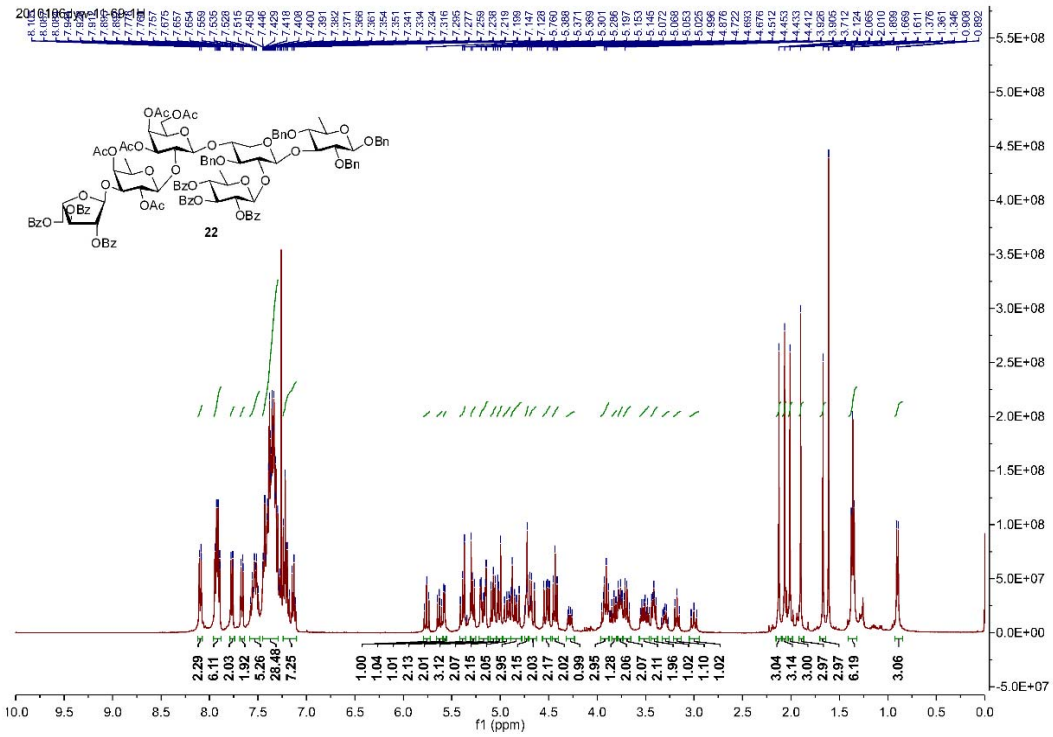
HMBC of compound **5**



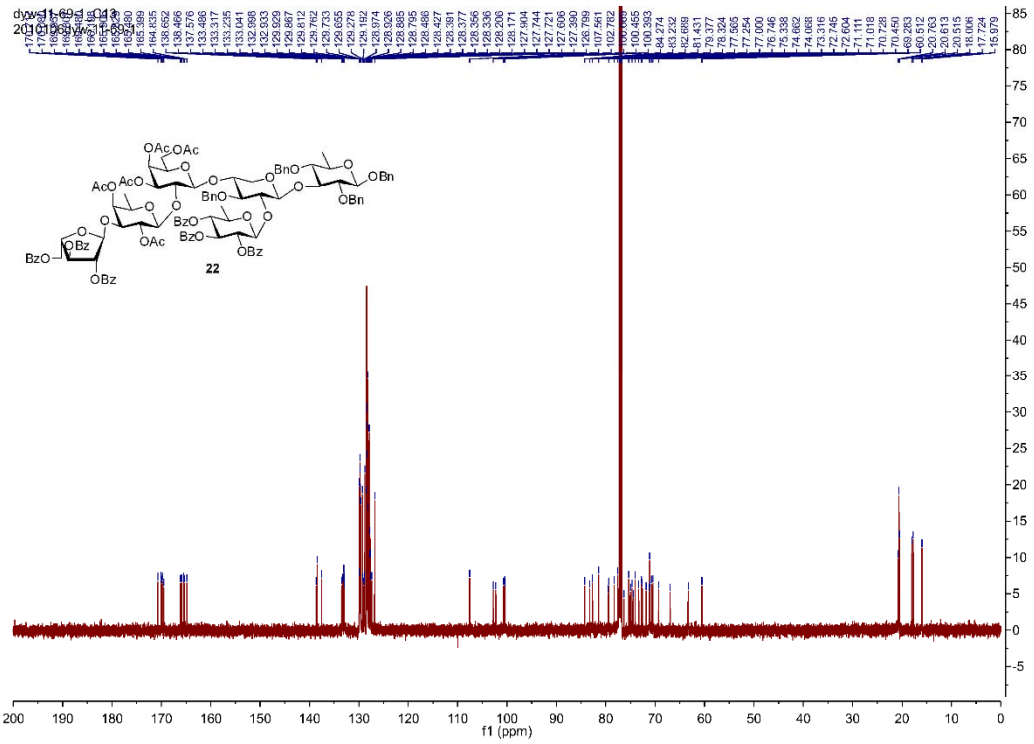
^{1}H NMR of compound **21** (400 Hz, $CDCl_3$)



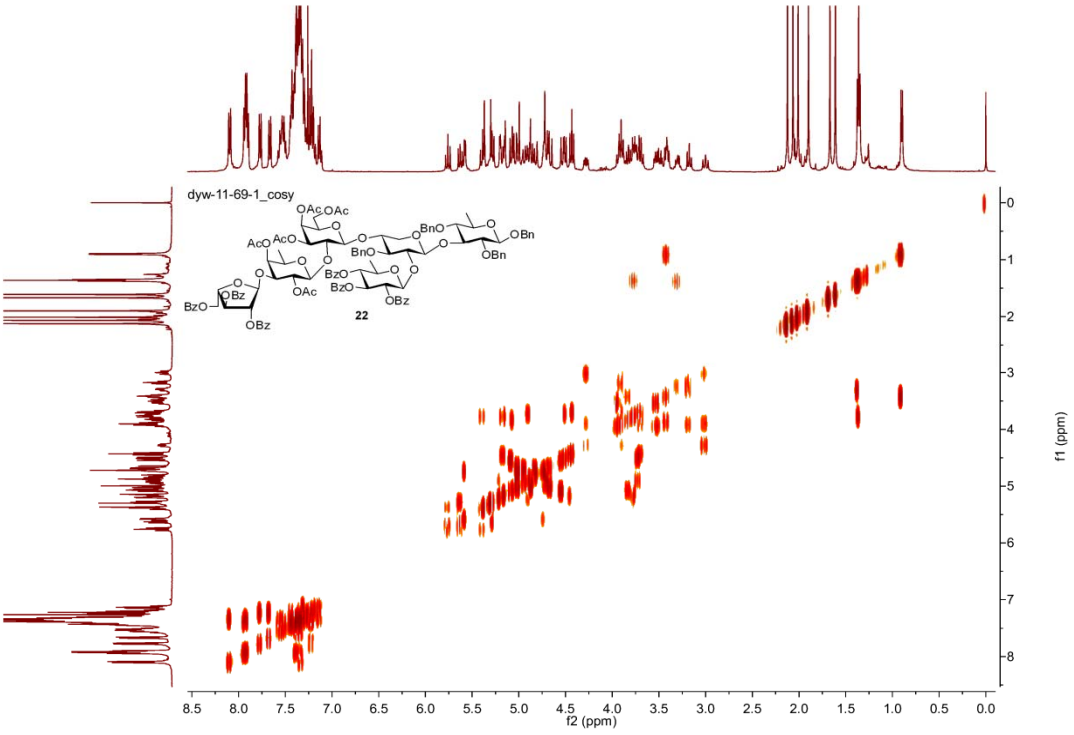
^{13}C NMR of compound **21** (101 Hz, $CDCl_3$)



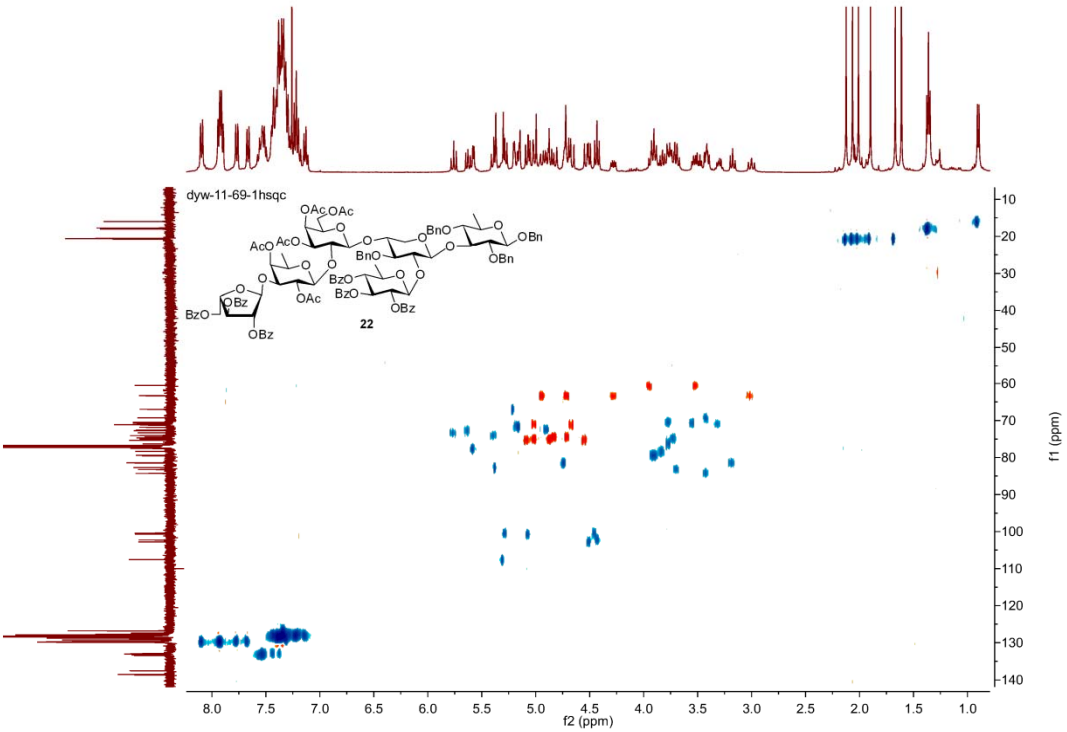
^{1}H NMR of compound **22** (400 Hz, $CDCl_3$)



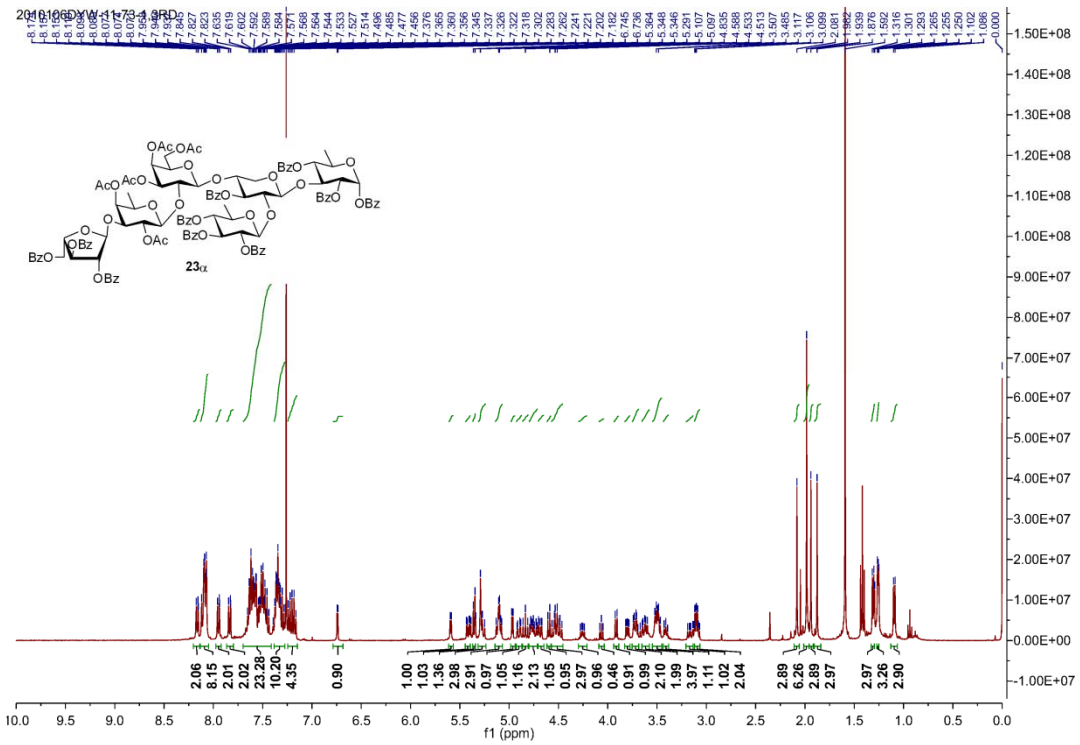
^{13}C NMR of compound **22** (126 Hz, $CDCl_3$)



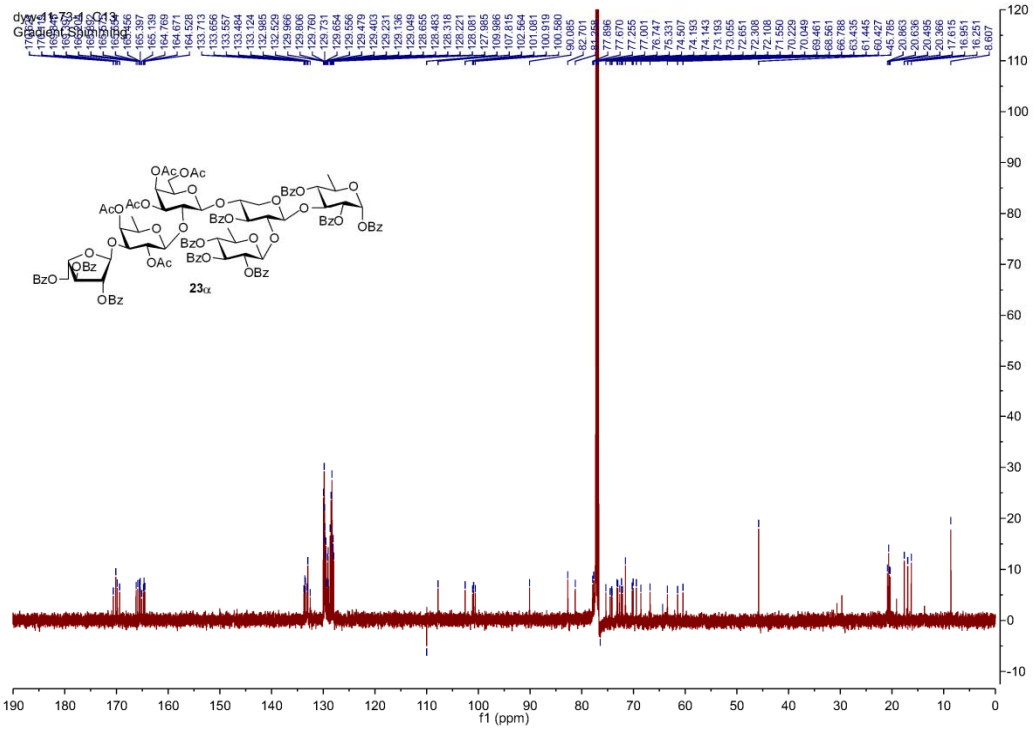
COSY of compound **22**



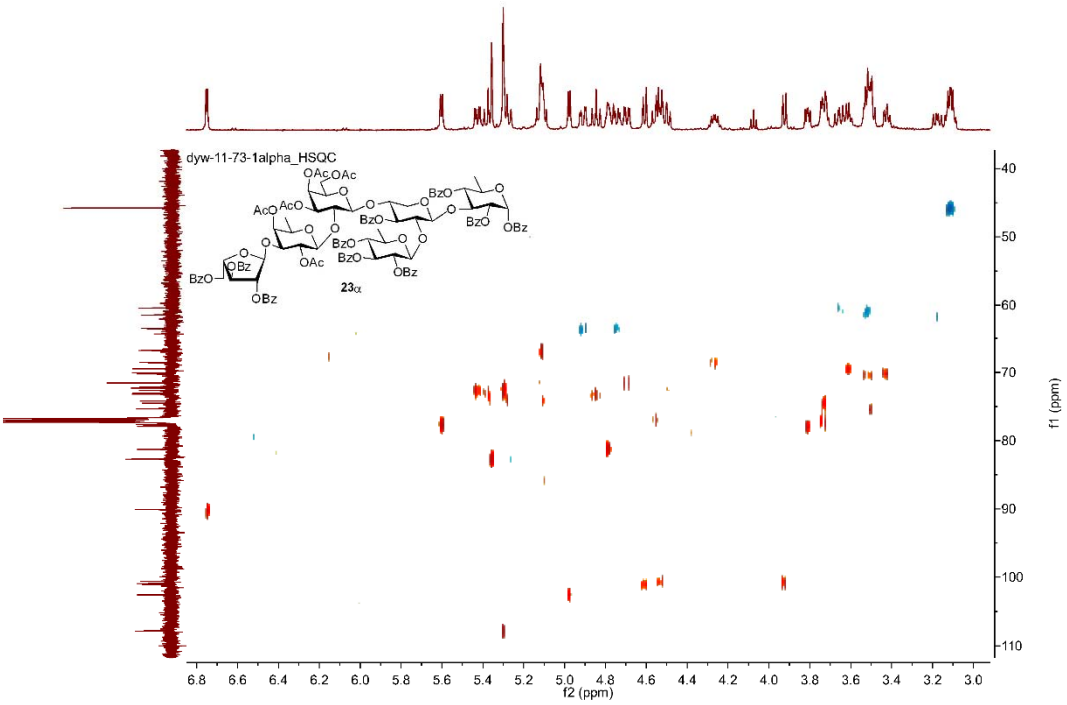
HSQC of compound **22**



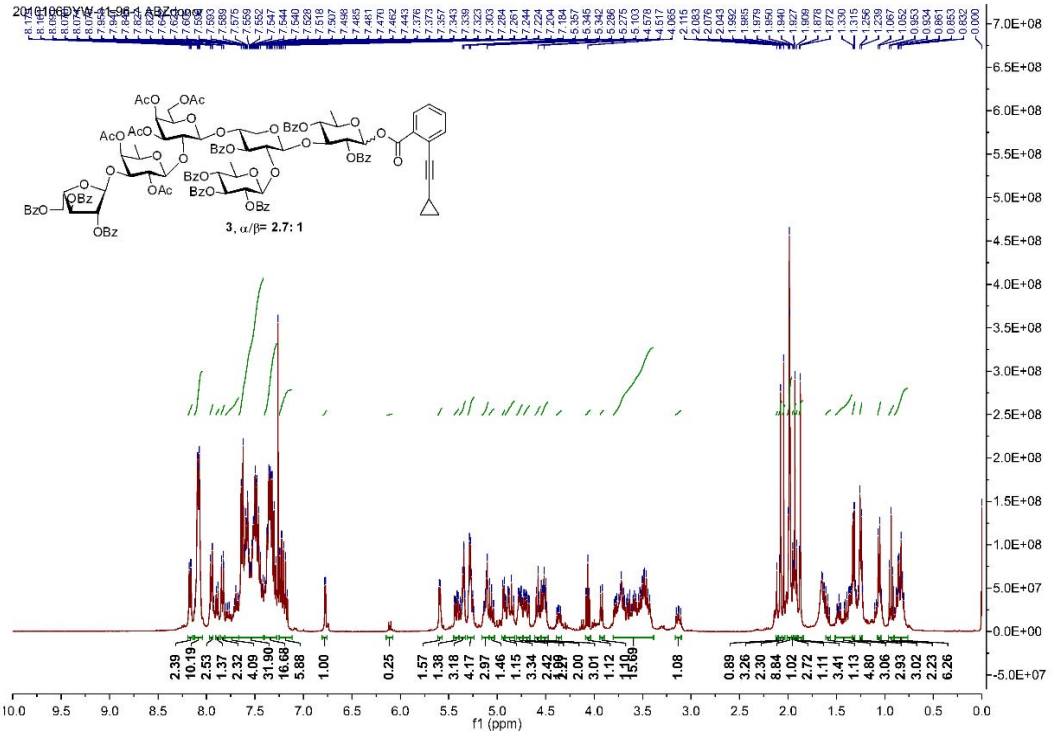
^{1}H NMR of compound **23α** (400 Hz, $CDCl_3$)



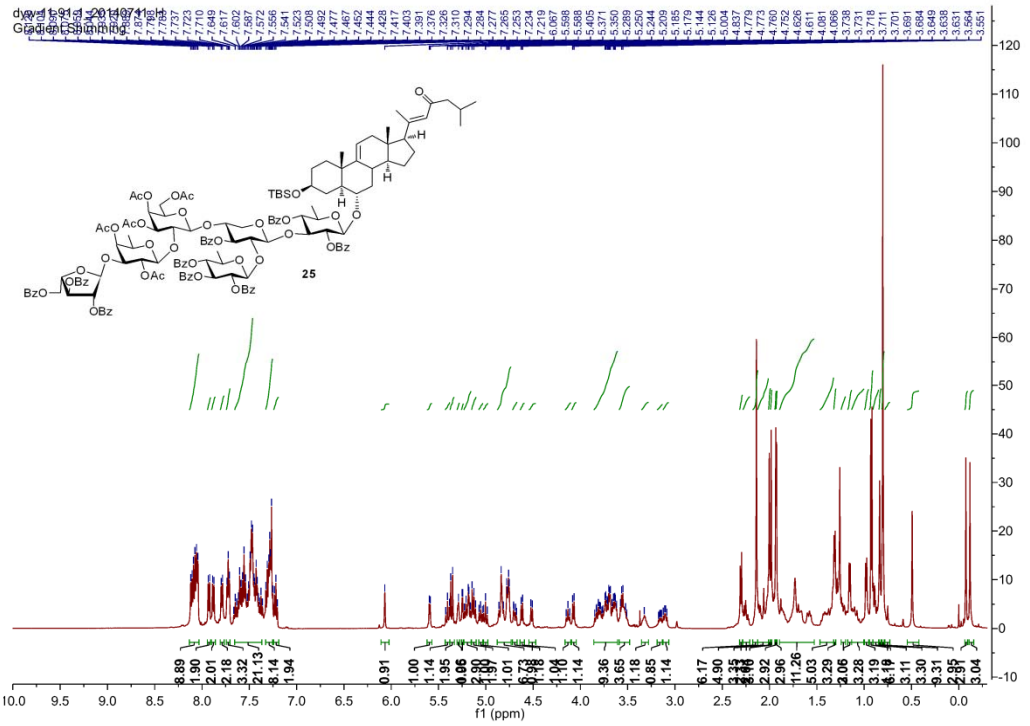
^{13}C NMR of compound **23α** (126 Hz, $CDCl_3$)



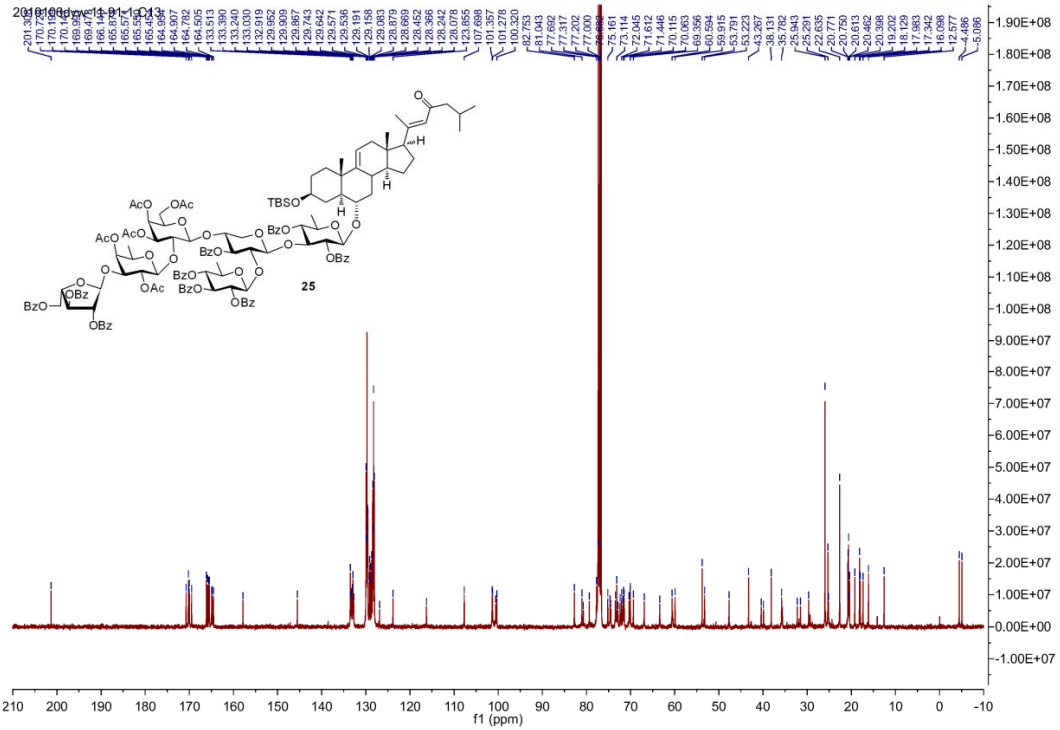
HSQC of compound **23α**



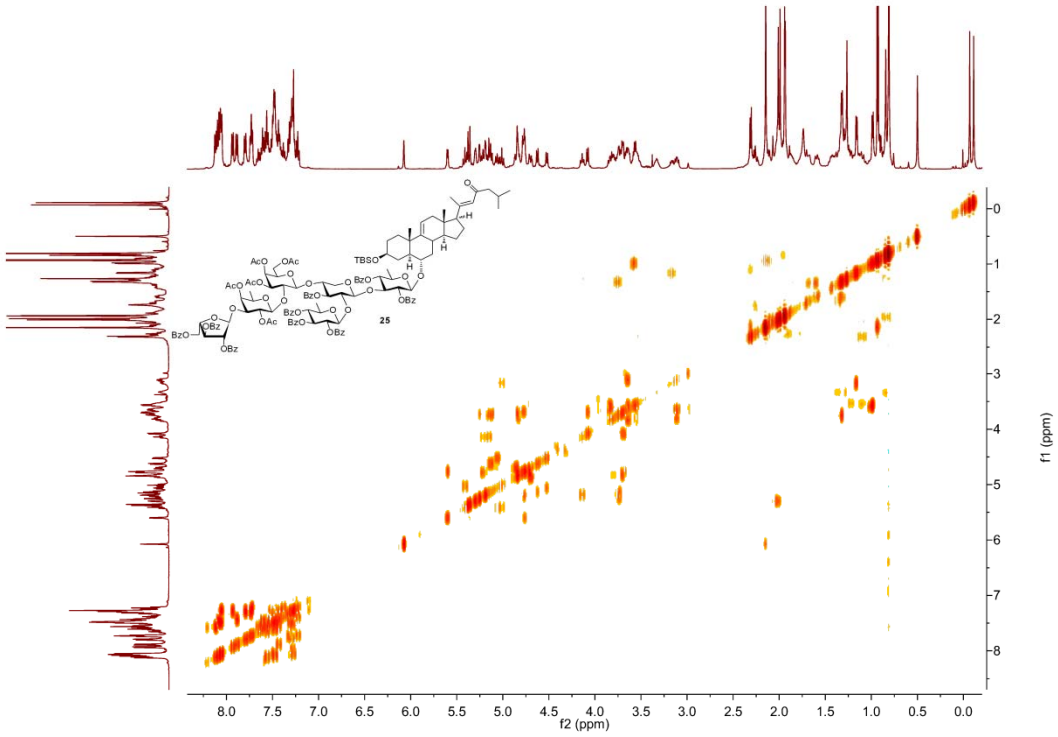
^{1}H NMR of compound **3** (400 Hz, $CDCl_3$)



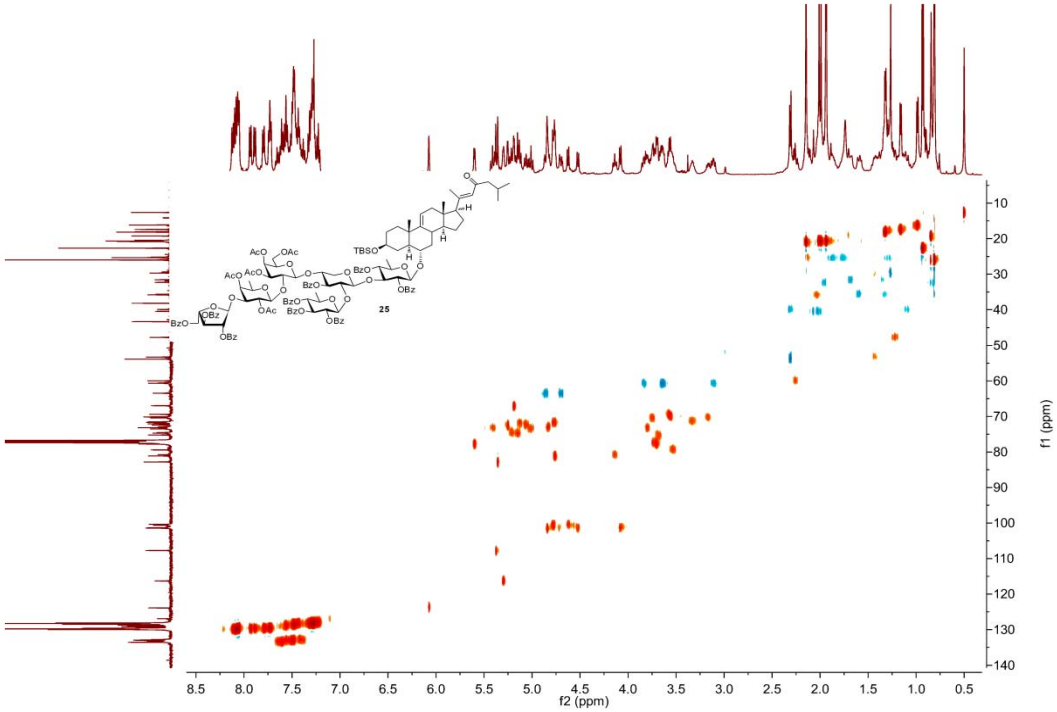
^{1}H NMR of compound **25** (500 Hz, $CDCl_3$)



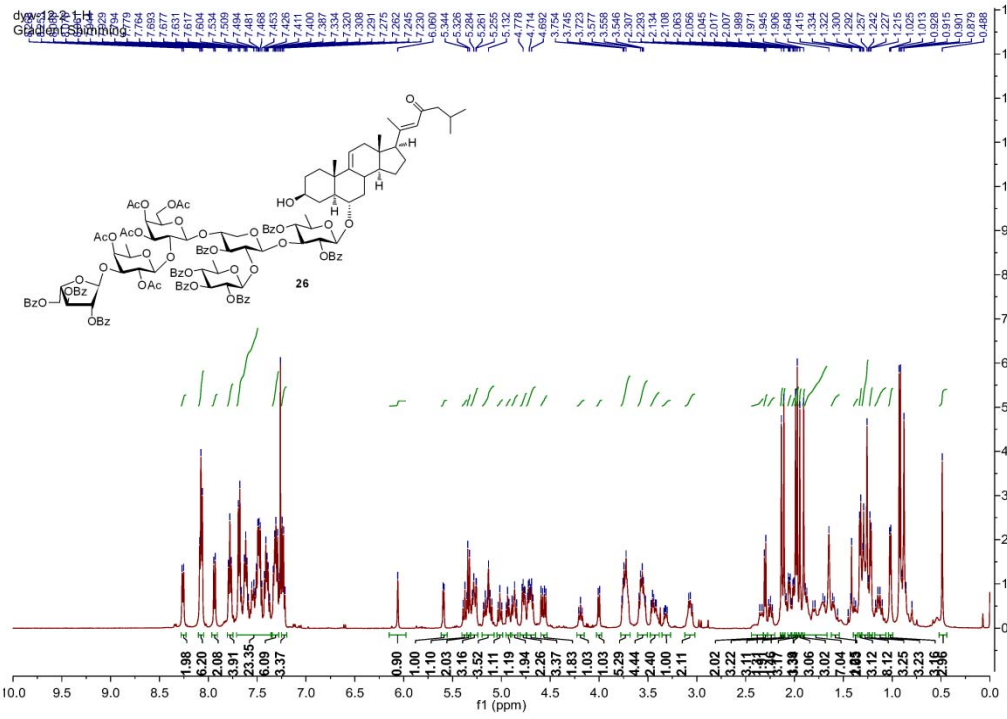
^{13}C NMR of compound **25** (126 Hz, $CDCl_3$)



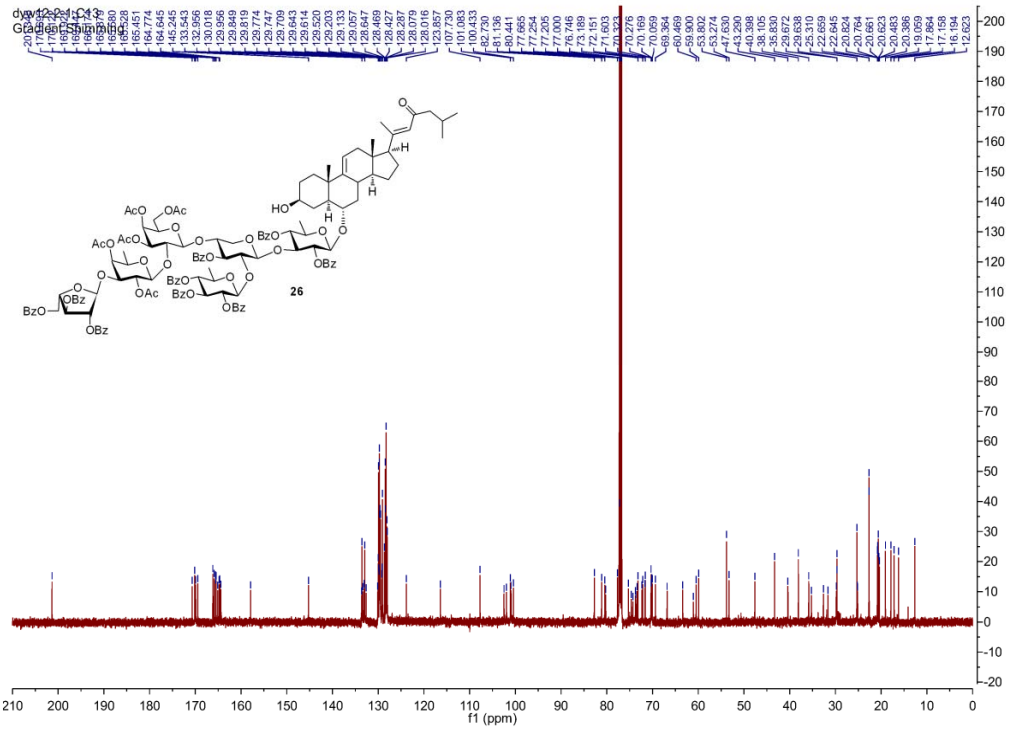
COSY of compound **25**



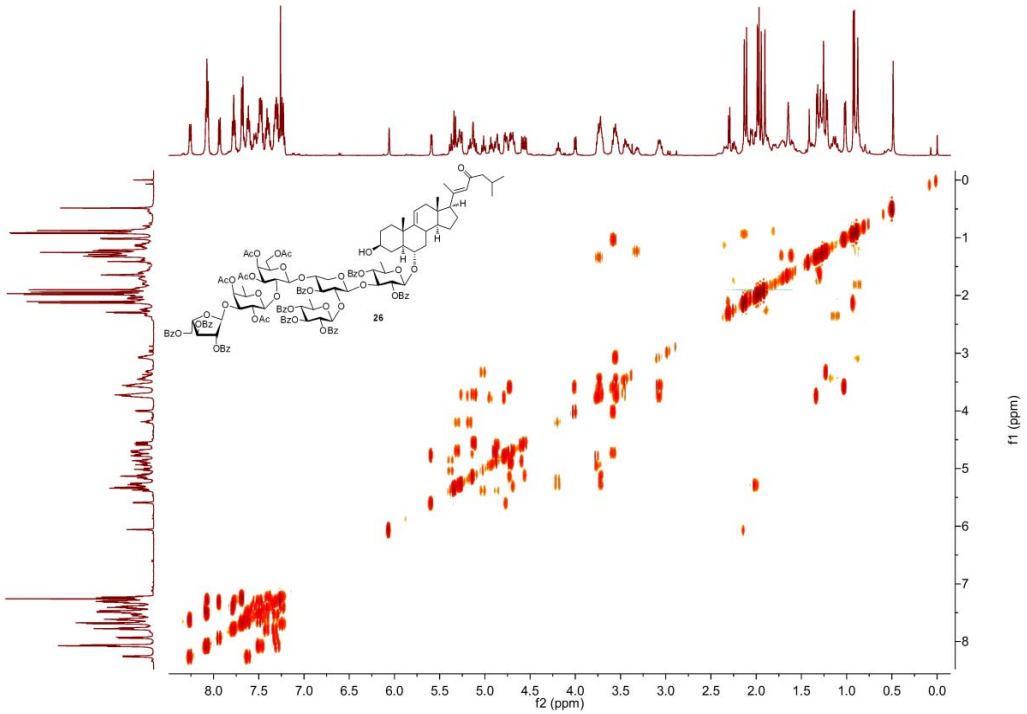
HSQC of compound **25**



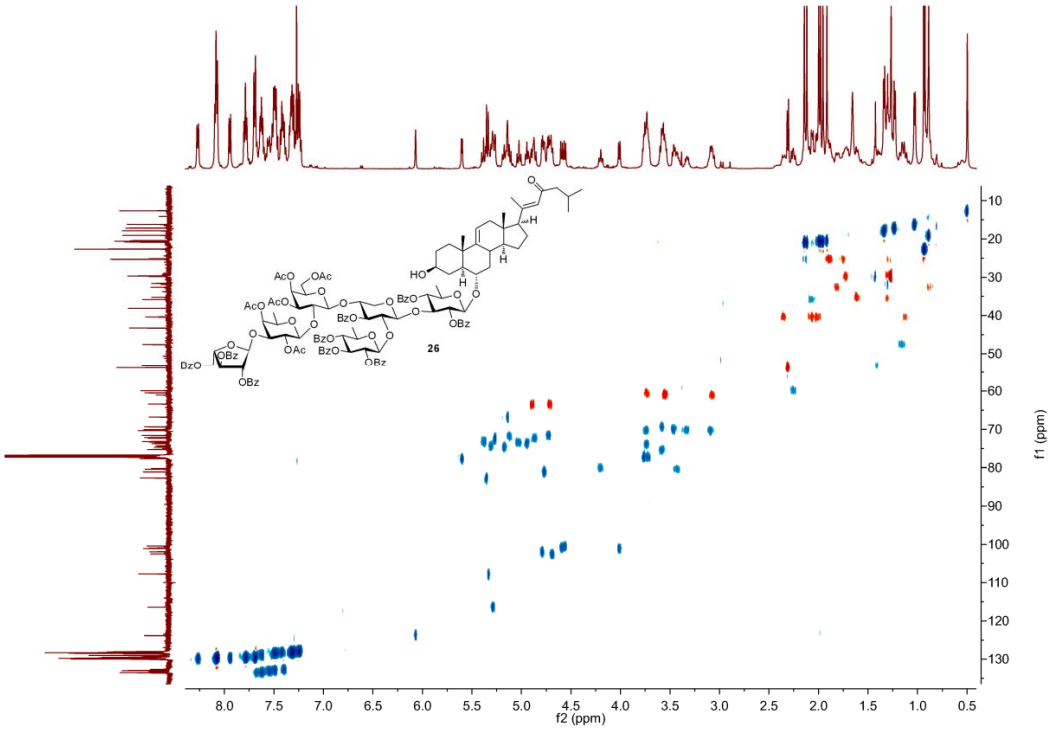
^{1}H NMR of compound **26** (500 Hz, $CDCl_3$)



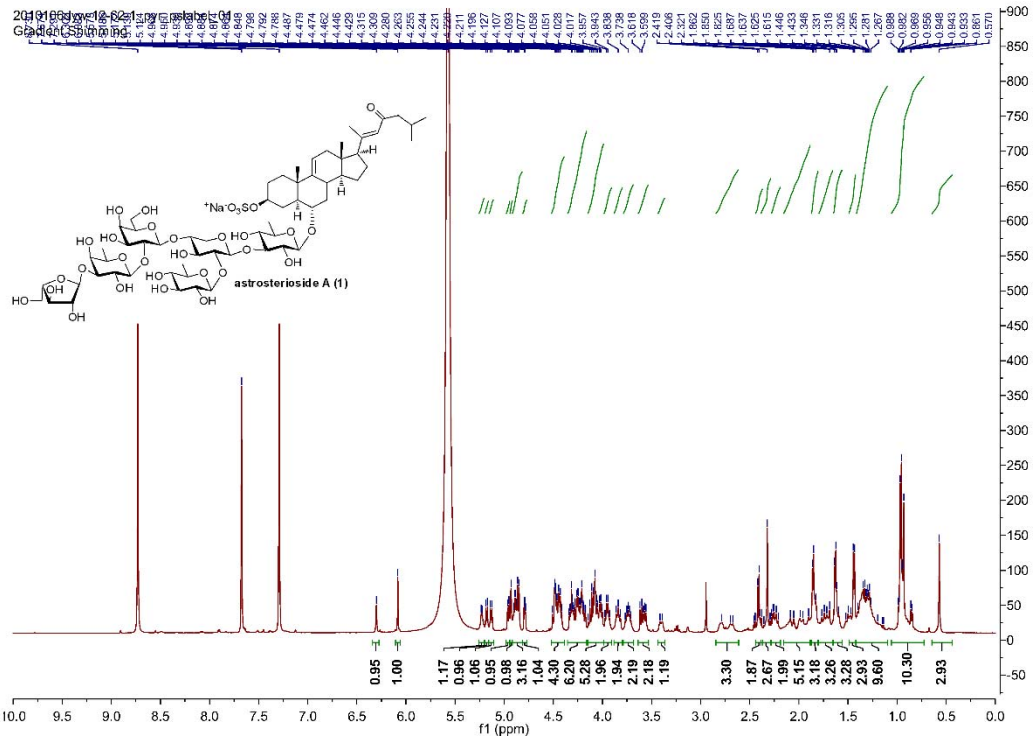
^{13}C NMR of compound **26** (126 Hz, $CDCl_3$)



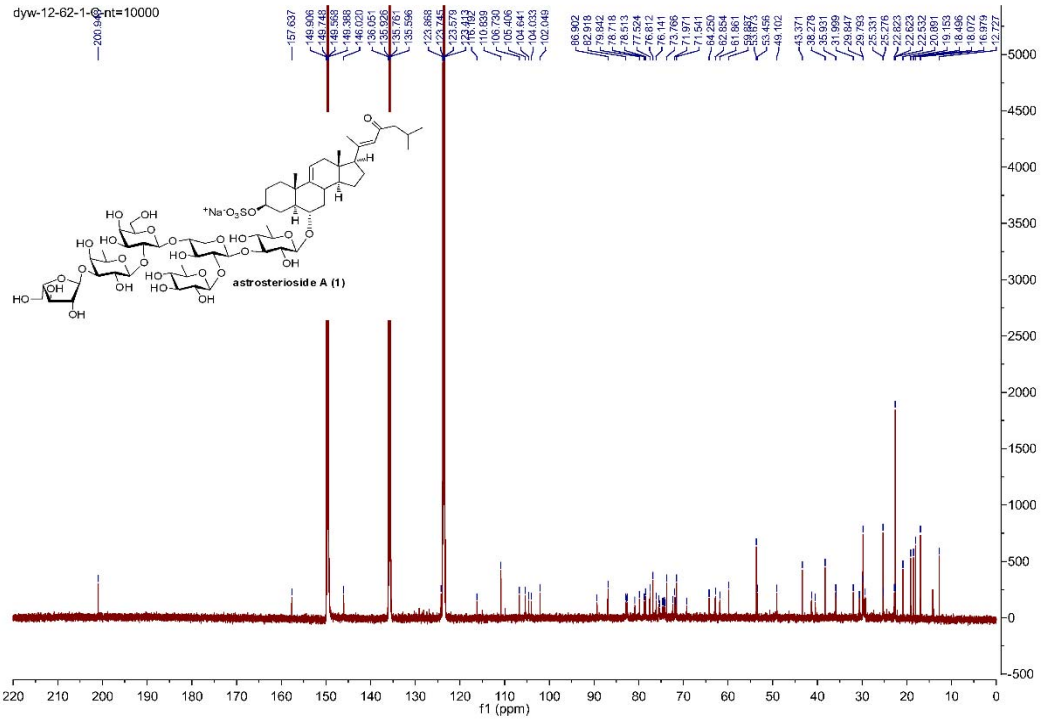
COSY of compound **26**



HSQC of compound **26**



^{1}H NMR of compound **1** (500 MHz, pyridine-d5)



^{13}C NMR of compound **1** (126 MHz, pyridine-d5)