Supporting Information

Chemical synthesis and antigenic activity of a phosphatidylinositol mannoside epitope from *Mycobacterium Tuberculosis*

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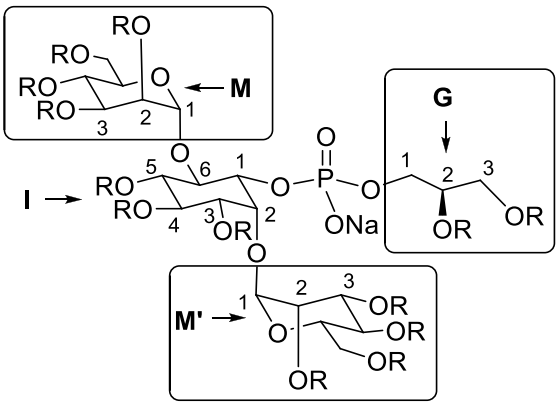
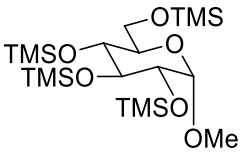
Experimental Section

For the oligosaccharides of compounds, the M/M'/I/G notation used for the ^{1}H and ^{13}C assignments on NMR spectra is as follow:





$C_{19}H_{46}O_6Si_4$

M = 482.2371

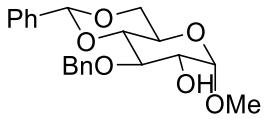
Methyl 2,3,4,6-*tetra*-*O*-trimethylsilyl-α-D-glucopyranoside **2**

Trimethylsilyl chloride (16.28 ml, 25.7 mmol) was added to a solution of methyl-α-D-glucopyranoside **1** (5.00 g, 25.7 mmol) in anhydrous pyridine (25 mL) at 0 ℃ under argon. The reaction mixture was stirred overnight, quenched with water and extracted with ethyl acetate. The organic phase was washed quickly with water, brine, dried over $MgSO_4$, filtered, and the filtrate was concentrated in vacuo to afford **2** (11.9 g, 96 % yield). [1]

Rf = 0.89 (Petroleum ether /EtOAc = 5:1)

^{1}H NMR (300MHz, $CDCl_3$): δ 0.14-0.2 (m, 4 × 9H, $Si(CH_3)_3$), 3.38 (s, 3H, OCH_3), 3.45-3.52 (m, 2H), 3.57-3.63 (m, 1H), 3.66-3.83 (m, 3H), 4.64 (d, 1H, ^{3}J = 4.5 Hz, H-1).

^{13}C NMR (100MHz, $CDCl_3$): δ 0.9 and 1.3 (C-Si), 1.4 (C-Si), 54.9 (OCH_3), 61.9 (C-6), 71.5, 72.0, 73.9, 74.9, 100.0 (C-1).



$C_{21}H_{24}O_6$

M = 372.1573

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside **4**

To an ice-cold solution of **2** (4.83 g, 0.01 mol) and benzaldehyde (3 mL, 0.03 mol) in anhydrous dichloromethane, a solution of iron(III) chloride hexahydrate (0.135 g, 0.005 mol) in acetonitrile (2 mL) was added dropwised. The reaction was stirred at 0 ℃ for 1 hour, followed by triethlysilane (1.8 mL, 0.011 mol) was added and the reaction was allowed to warm to room temperature and the progress of the reaction was monitored by TLC. After consumption of the starting material, tetrabutylammonium fluoride TBAF (4 mL of a 1M solution in THF) was added and the reaction mixture was continued stirring at room temperature for 1 hour. The solution was diluted with ethyl acetate and neutralized with a saturated $NaHCO_3$ solution. The organic phase was separated and the water phase was extracted three times with ethyl acetate. The combined organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (Petroleum ether /EtOAc = 3:1) to give the expected compound **4** (2.4g, 65% yield). [1]

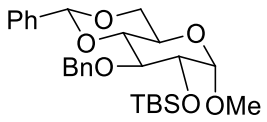
Rf = 0.26 (Petroleum ether /EtOAc = 2:1)

$[\alpha]_D^{25}$ = + 81.1 (*c* = 1.0, $CHCl_3$)

^1H NMR (400MHz, $CDCl_3$): δ 2.32 (d, 1H, ^3J = 7.5 Hz, OH), 3.48 (s, 3H, OCH_3), 3.67 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4), 3.73-3.77 (m, 1H, H-2), 3.78 (dd, 1H, ^2J = 10.0 Hz, ^3J = 10.0 Hz, H-6), 3.83 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-3), 3.84-3.89 (m, 1H, H-5), 4.32 (dd, 1H, ^2J = 10.0 Hz, ^3J = 4.0 Hz, H-6), 4.84 (d, 1H, ^3J = 4.0 Hz,

H-1), 5.6 (s, 1H, H-benzylidene).

^{13}C NMR (100MHz, $CDCl_3$): δ 55.4 (OCH_3), 62.6 (C-5), 69.0 (C-6), 72.4 (C-2), 74.8 (CH_2Ph), 78.9 (C-3), 81.9 (C-4), 99.9 (C-1), 101.3 (*C*-benzylidene).



$C_{27}H_{38}O_6Si$

M = 486.2438

Methyl

3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside **5**

Imidazole (0.626 g, 9.2 mmol) and tert-butyldimethylsilyl chloride (1.1 g, 7.3 mmol) were added to a solution of **4** (2.29 g, 6.1 mmol) in DMF (20 mL), the mixture was strirred at 45℃ overnight and the progress of reaction was monitored by TLC. After consumption of the starting material, a saturated NH_4Cl solution (20 mL) was added to the reaction mixture. The organic phase was separated and the water phase was extracted three times with ethyl acetate and washed with brine. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo to afford **5** (4.37 g, 100% yield).

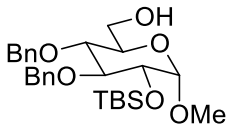
Rf = 0.41 (Petroleum ether /EtOAc = 10:1)

$[\alpha]_D^{25}$ = + 17.8 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (400MHz, $CDCl_3$): δ 0.11 and 0.12 (2s, 2 × 3H, $Si(CH_3)_2$), 0.94 (s, 9H, t-Bu), 3.46 (s, 3H, OCH_3), 3.62 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4), 3.62 (dd, 1H, ^2J = 10.0 Hz, ^3J = 10.0 Hz, H-6), 3.79 (dd, 1H, ^3J = 9.0 Hz, ^3J = 3.8 Hz, H-2), 3.84-3.92 (m, 1H, H-5), 3.90 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-3), 4.31 (dd, 1H, ^2J = 10.0 Hz , ^3J = 4.5 Hz, H-6), 4.68 (d, 1H, ^3J = 3.8 Hz, H-1), 5.57 (s, 1H, H-benzylidene).

^{13}C NMR (100MHz, $CDCl_3$): δ -4.9 and -4.4 (C-Si), 18.2 ($C(CH_3)_3$), 25.8 ($C(CH_3)_3$), 55.5 (OCH_3), 62.5 (C-5), 69.2 (C-6), 73.7 (C-2), 75.3 (CH_2Ph), 78.9 (C-3), 82.3 (C-4), 101.2 (C-1), 101.3 (C-benzylidene).

HRMS $C_{44}H_{44}O_7SK$: Calcd. $[M + K]^+$ 525.2075, Found 525.2285.



$C_{27}H_{40}O_6Si$

M = 488.2594

Methyl 3,4-di-*O*-benzyl-2-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside **6**

To a stirred solution of **5** (7.57g, 15.6 mmol) in THF solution (46.7 mL of 1M BH_3 solution in THF, 46.7 mmol), anhydrous cobalt(II) chloride $CoCl_2$ (6.01 g, 46.7 mmol) was added at 0 ℃ under argon. The blue reaction mixture was stirred at 0 ℃ for another 2 hours, then diluted with excess ethyl acetate and the dundissolved cobalt salt was removed by filtration through a Celite pad. The filtrate was treated with aqueous $NaBH_4$ (0.4 equiv.) by stirring in a two-phase condition, and the resulting black precipitate was filtered off. The organic phase was washed with a saturated $NaHCO_3$ solution, water, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel (Petroleum ether /EtOAc = 5:1) to give compound **6** (7.62g, 100% yield).

Rf = 0.30 (Petroleum ether /EtOAc = 5:1)

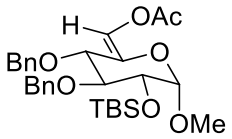
$[\alpha]_D^{25}$ = + 66.3 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (400MHz, $CDCl_3$): δ 0.12 and 0.14 (2s, 2 × 3H, $Si(CH_3)_2$), 0.95 (s, 9H, t-Bu), 3.43 (s, 3H, OCH_3), 3.55 (dd, 1H, ^3J = 10.0 Hz, ^3J = 10.0 Hz, H-4), 3.68-3.73 (m, 2H, H-6), 3.75 (d, 1H, ^3J = 3.5 Hz, H-2), 3.78-3.83 (m, 1H, H-5), 3.90 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-3), 4.66 (d, 1H, ^3J = 3.5 Hz, H-1), 4.63 and 4.97 (2d, 2H, ^2J = 11.0 Hz, Bn), 4.85 (dd, 2H, ^2J = 11.0 Hz, ^2J = 11.0 Hz, Bn).

^{13}C NMR (100MHz, $CDCl_3$): δ -4.7 and -4.4 (C-Si), 18.1 ($C(CH_3)_3$), 25.8 ($C(CH_3)_3$), 55.2 (OCH_3), 61.9(C-6), 70.8 (C-5), 74.1 (C-2), 74.9 and 75.5 (CH_2Ph), 77.5 (C-4), 82.5 (C-3), 100.3 (C-1), 127.3, 127.5, 127.8, 128.0, 128.2, 128.4, 138.2, 138.9.

Anal. Calcd for $C_{27}H_{40}O_6Si$ (488.3) : C, 66.36; H, 8.25. Found: C, 66.01; H, 8.45.

HRMS $C_{27}H_{40}O_6SiNa$: Calcd. $[M + Na]^+$ 511.2492, Found 511.2497.



$C_{29}H_{40}O_7Si$

M = 528.2543

Methyl

6-*O*-acetyl-3,4-di-*O*-benzyl-2-*O*-(*tert*-butyldimethylsilyl)-α-D-hex-5-enopyranoside **8**

Sulfur trioxide pyridine complex (2.06 g, 12.95 mmol) and N,N-Diisopropylethylamine (DIPEA) (4.43 mL) were added to a solution of **6** (1.81g 23.7 mmol) in anhydrous dicholoromethane (40 mL) at 0 ℃ under argon. After stirring for 10 minutes, DMSO (4 mL) was added. The reaction mixture was stirred at room temperature for another 2 hours, then quenched with water and the water phase was extracted with Et_2O and washed with brine. The combined organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo to afford crude aldehyde **7** (2.4g) as a yellow oil which was used directly in the next step. The yellow oil was dissolved in anhydrous acetonitrile (30 mL), to which K_2CO_3 (1.78 g, 12.4 mmol) and acetic anhydride (2 mL) were added, and the suspension was heated to refluxing for 12 hours under argon. The reaction mixture was diluted with water and extracted with Et_2O, washed with a saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (Petroleum ether /EtOAc = 5:1) to give compound **8** (1.2g, 62% yield).

Rf = 0.45 (Petroleum ether /EtOAc = 5:1)

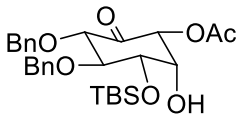
$[\alpha]_D^{25}$ = -31.3 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (300MHz, $CDCl_3$): δ 0.10 and 0.13 (2s, 2 × 3H, $Si(CH_3)_2$), 0.93(s, 9H, t-Bu),

2.19 (s, 3H, OAc),3.53 (s, 3H, OCH_3), 3.80-3.88 (m, 2H), 3.98-4.01 (m, 1H, H-4), 4.82(d, 1H, ^3J = 3.0 Hz, H-1), 7.18(d, 1H, ^3J = 3.0 Hz, H-6) .

^{13}C NMR (75MHz, $CDCl_3$): δ -4.7 and 4.4 (C-Si), 18.2 ($C(CH_3)_3$), 20.6 (CH_3CO), 25.8 ($C(CH_3)_3$), 56.3 (OCH_3), 73.3 (C-2), 74.4 and 75.5 (CH_2Ph), 77.9 (C-4), 81.8 (C-3), 101.8(C-1), 123.0(C-6), 127.4, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 135.5 (C-5), 137.7, 138.7, 167.3 (CO, acetate).

Anal. Calcd for $C_{29}H_{40}O_7Si$ (528.2) : C, 65.88; H, 7.63. Found: C, 65.74; H, 7.65.



$C_{28}H_{38}O_7Si$

M = 514.2387

1-*O*-acetyl-4,5-di-*O*-benzyl-3-*O*-(*tert*-butyldimethylsilyl)-6-oxo-*myo*-inositol **9**

To a solution of **8** (1.2 g, 2.27 mmol) in 50 mL mixture of aceton-water (4:1), mercuric acetate (5.93 g, 18.61 mmol) was added at 0℃ under argon. The reaction was stirred for 1 hour, a aqueous saturated NaCl solution (3 mL) was then added, and the mixture was stirred overnight. The reation mixture was filtered through a Celite pad to remove the yellow solid, the filtrate was extracted with ethyl acetate, washed with a saturated NaCl solution, dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (Toluene/EtOAc = 9:1) to give compound **9** (0.74 g, 64% yield).

Rf = 0.16 (Petroleum ether /EtOAc = 4:1)

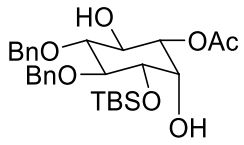
$[\alpha]_D^{25}$ = -39.6 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (400MHz, $CDCl_3$): δ 0.11 and 0.14 (2s, 2 × 3H, $Si(CH_3)_2$), 0.94 (s, 9H, t-Bu), 2.29 (s, 3H, OAc), 2.61 (s, 1H, OH), 3.91 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4), 4.09 (dd, 1H, ^3J = 9.0 Hz, ^3J = 2.5 Hz, H-3), 4.18 (dd, 1H, ^3J = 9.5 Hz, ^4J = 1.0 Hz, H-5), 4.22 (dd, 1H, ^3J = 2.5 Hz, ^3J = 2.5 Hz, H-2), 5.27 (d, 1H, ^3J = 2.5 Hz, H-1).

^{13}C NMR (100MHz, $CDCl_3$): δ -4.5 and -4.9 (C-Si), 18.0 ($C(CH_3)_3$), 20.6 (CH_3CO), 25.8 ($C(CH_3)_3$), 72.2 (C-2), 72.9 (C-3), 73.5 (CH_2Ph), 74.7(C-1), 75.9 (CH_2Ph), 82.3 (C-4), 83.5 (C-5), 127.5, 127.6, 127.9, 128.2, 128.3, 128.4, 137.3, 138.3, 169.9 (C-acetate), 197.8 (C-6).

Anal. Calcd for $C_{28}H_{38}O_7Si$ (514.2) : C, 65.34; H, 7.44. Found: C, 65.18; H, 7.36.

HRMS $C_{28}H_{38}O_7SiNa$: Calcd. $[M + Na]^+$ 537.2285, Found 537.2287.



$C_{28}H_{40}O_7Si$

M = 516.2543

1-*O*-acetyl-4,5-di-*O*-benzyl-3-*O*-(*tert*-butyldimethylsilyl)-D-*myo*-inositol **A**

To a solution of sodium triacetoxyborohydride in a mixed solvent of CH_3CN-HOAc (1:1, 8 mL) was added a solution of **9** (0.26 g 0.5 mmol) in anhydrous CH_3CN (5 mL) via syringe over 5 minutes at 0℃ under argon. The mixture was stirred for 1 hour at room temperature and the progress of the reaction was monitored by TLC. After consumption of the starting material, the mixture was quenched with water and the water phase was extracted with Et_2O, the combined organic phase was washed with a saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (Toluene/EtOAc = 4:1) to give compounds **A** (1.2 g, 93% yield) and **10** (0.05g, 7% yield)

Date for compound **A**:

Rf = 0.16 (Petroleum ether /EtOAc = 3:1)

$[\alpha]_D^{25}$ = -11.6 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (400MHz, $CDCl_3$): δ 0.10 and 0.14 (2s, 2 × 3H, $Si(CH_3)_2$), 0.93 (s, 9H, t-Bu), 2.19 (s, 3H, OAc), 3.39 (t, ^3J = 9.0 Hz, 1H, H-5), 3.74-3.81 (m, 2H, H-3 and

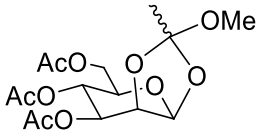
H-4), 4.06 (dd, 1H, ^{3}J = 3.0 Hz, ^{3}J = 3.0 Hz, H-2), 4.14(dd, 1H, ^{3}J = 10.0 Hz, ^{3}J = 10.0 Hz, H-6), 4.81 (dd, 1H, ^{3}J = 10.5 Hz, ^{3}J = 3.0 Hz, H-1).

^{13}C NMR (100MHz, $CDCl_3$): δ -4.8 and -4.5 (C-Si), 18.0 ($C(CH_3)_3$), 21.1 (CH_3CO), 25.8 ($C(CH_3)_3$), 70.5 (C-6), 71.1 (C-2), 72.8 (C-1), 73.5 (C-4), 75.6 and 75.7 (CH_2Ph), 81.6 (C-3), 83.1 (C-5), 127.3, 127.4, 127.8, 127.9, 128.3, 128.6, 138.4, 138.5, 170.8 (C-acetate).

MS (TOF): *m/z* = 539.3 $[M + Na]^+$.

Anal. Calcd for $C_{28}H_{40}O_7Si$ (516.2) : C, 65.09; H, 7.80. Found: C, 65.12; H, 7.81.

HRMS $C_{28}H_{40}O_7SiNa$: Calcd. $[M + Na]^+$ 539.2441, Found 539.2438.



$C_{15}H_{22}O_{10}$
M = 362.1213

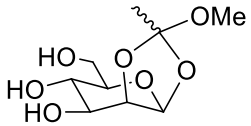
3,4,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose **11**

Acetic anhydride (54 ml, 571 mmol) was added to a solution of D-mannose (15 g, 83 mmol) in anhydrous pyridine (75 ml) at r.t. and the reaction mixture was stirred overnight. The reaction was quenched with water and extracted with dichloromethane. The organic phase was washed with aqueous HCl solution (1M) and then with saturated $NaHCO_3$, dried over $MgSO_4$, filtered and concentrated in vacuo to give a yellow oil which was used directly in the next step. The yellow oil was dissolved in anhydrous dichloromethane (80 mL), To the solution were added I_2 (25.234 g, 99.6 mmol) and triethylsilane (16 mL, 99.6 mmol). The reaction mixture was refluxed for 2 hours and cooled to r.t. To the reaction mixture were sequentially added lutidine (38 mL, 83 mmol) and methanol (20 mL, 498 mmol). The reaction was left to stir overnight at rt. The reaction mixture was quenched with a saturated $Na_2S_2O_3$ solution and extracted with dichloromethane. The organic phase was washed with saturated $NaHCO_3$, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was

chromatographed on silica gel (Petroleum ether / EtOAc = 3:1) to afford **11** as a yellow oil.

Rf = 0.23 (Petroleum ether /EtOAc = 3:1)

^{1}H NMR (400MHz, $CDCl_3$): δ 1.69 (s, 3H, CH_3), 2.01, 2.03 and 2.08 (3s, 9H, OAc), 3.23 (s, 3H, OCH_3), 3.65 (ddd, 1H, ^3J = 10.5 Hz, ^3J = 4.8 Hz, ^3J = 2.4 Hz, H-5), 4.01 (dd, 1H, ^2J = 12.0 Hz, ^3J = 2.4 Hz, H-6), 4.19 (dd, 1H, ^2J = 12.0 Hz, ^3J = 4.8 Hz, H-6), 4.56 (dd, 1H, ^3J = 4.0 Hz, ^3J = 2.4 Hz, H-2), 5.11 (dd, 1H, ^3J = 10.0 Hz, ^3J = 4.0 Hz, H-3), 5.24 (dd, 1H, ^3J = 10.5 Hz, ^3J = 10.0 Hz, H-4), 5.46 (d, 1H, ^3J = 2.4 Hz, H-1).



$C_9H_{16}O_7$

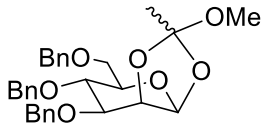
M = 236.0896

1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose **12**

A freshly preparerd sodium methoxide solution (30 mL, 0.5 M in methanol) was added to a solution of **11** (13 mg, 0.013 mmol) in methanol (100 mL) at 0 ℃. The reaction mixture was stirred at room temperature for 30 minutes and the progress of the reaction was monitored by TLC. The methanol was removed in vacuo and the residue was extracted by dichloromethane. The organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The product was chromatographed on silica gel (Petroleum ether /EtOAc = 2:1) to give compound **12**.

Rf = 0.40 (Petroleum ether /EtOAc = 2:1)

^{1}H NMR (300MHz, $CDCl_3$): δ 1.65 (s, 3H, CH_3), 3.25 (dd, 1H, ^3J = 9.3 Hz, ^3J = 2.4 Hz, H-5), 3.29 (s, 3H, OCH_3), 3.6 (t, 1H, ^3J = 9.3 Hz, H-4), 3.72 (m, 2H, H-6, H-3), 3.85 (dd, 1H, ^2J = 12.0 Hz, ^3J = 2.4 Hz, H-6), 4.48 (dd, 1H, ^3J = 3.9 Hz, ^3J = 2.4 Hz, H-2), 5.46 (d, 1H, ^3J = 2.4 Hz, H-1).



$C_{30}H_{34}O_7$

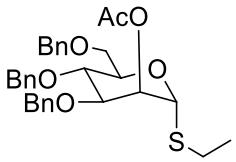
M = 506.2305

3,4,6-tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose **13**

Sodium hydride (60% dispersion in mineral oil, washed two times with petroleum ether) (23.39 g, 581 mmol) was added in portions to a solution of **12** (19.6 g, 83 mmol) in DMF (55 mL) at 0℃ under argon. The resulting suspension was stirred for 30 minutes, and benzyl bromide (44 mL, 374 mmol) in dry DMF (20 mL) was added dropwise. The mixture was stirred at room temperature overnight, quenched with methanol and extracted with ethyl acetate. The organic phase was washed with water and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel (Petroleum ether /EtOAc = 3:1) to give compound **13** in 70% yield over four steps.

Rf = 0.64 (Petroleum ether /EtOAc = 2:1)

^{1}H NMR (300MHz, $CDCl_3$): δ 1.62 (s, 3H, CH_3), 3.29 (s, 3H, OCH_3), 3.43 (ddd, 1H, ^3J = 9.5 Hz, ^3J = 4.0 Hz, ^3J = 3.0 Hz, H-5), 3.73 (m, 2H, H-6, H-3), 3.93 (t, 1H, ^3J = 9.5 Hz, H-4), 4.40 (dd, 1H, ^2J = 4.0 Hz, ^3J = 3.0 Hz, H-2), 4.94-4.52 (m, 6H, CH_2Ph), 5.37 (d, 1H, ^3J = 3.0 Hz, H-1).



$C_{31}H_{36}O_6S$

M = 536.2233

Ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside **14**

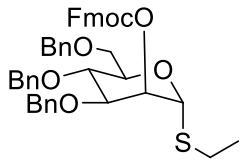
To a stirred suspension of **13** (5 g, 10 mmol) and 4 Å molecurar sieves (0.5 g) in

anhydrous acetonitrile (20 mL), ethanethiol (4 mL, 54 mmol) was added via syringe, mercury(II) bromide (0.73 g, 2 mmol) was then added. The reaction mixture was stirred at room temperature overnight and quenched with water, filtered through Celite. The Celite pad was washed with ethyl acetate, the organic phase was separated and the water phase was extracted three times with ethyl acetate. The combined organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The product was chromatographed on silica gel (Petroleum ether /EtOAc = 7:2) to give pure α-anomer **14** (3.23 g, 60% yield).[2]

Rf = 0.84 (Petroleum ether /EtOAc = 2:1)

$[\alpha]_D^{25}$ = +81 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (250MHz, $CDCl_3$): δ 1.36 (t, 3H, ^3J = 7.5 Hz, SCH_2CH_3), 2.25 (s, 3H, OAc), 2.61 (m, 2H, SCH_2CH_3), 3.66 and 3.83 (ddd, 2H, ^2J = 11.0 Hz, ^3J = 4.0 Hz, ^3J = 2.0 Hz, H-6), 3.89 (dd, 1H, ^3J = 9.0 Hz , ^3J = 3.5 Hz, H-3), 3.93 (dd, 1H, ^3J = 9.5 Hz , ^3J = 9.0 Hz, H-4), 4.50 (m, 1H, H-5), 4.86-4.43 (6H, m, CH_2Ph), 5.32 (d, 1H, ^3J = 1.5 Hz, H-1), 5.43 (dd, 1H, ^3J = 3.5 Hz, ^3J = 1.5 Hz, H-2).



$C_{44}H_{44}O_7S$

M = 716.2808

Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-1-thio-α-D-mannopyranoside **B1**

A freshly preparerd sodium methoxide solution (30 mL, 0.5 M in methanol) was added to a solution of **14** (13.90 g, 0.026 mol) in methanol (100 mL) at 0 ℃. The reaction mixture was stirred at room temperature for 30 minutes and the progress of the reaction was monitored by TLC. The methanol was removed in vacuo and the

residue was extracted by dichloromethane. The organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo to give a yellow oil. Without purification, pyridine (4 mL) was added to a solution of the crude in anhydrous dichloromethane (60 mL), followed 9-Fluorenylmethyl chloroformate (Fomc-Cl) (10.06 g, 0.039 mol) was added. The reaction mixture was stirred at room temperature overnight and monitored by TLC. The reaction mixture was quenched with water and extracted with dichloromethane. The organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel (Petroleum ether / dichloromethane = 1:2) to afford **B1** (13.87 g, 75% yield over two steps).

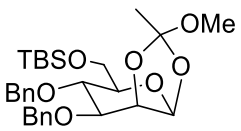
Rf = 0.42 (Petroleum ether /EtOAc = 4:1)

$[\alpha]_D^{25}$ = + 37.7 (*c* = 1.0, CH_2Cl_2)

^{1}H NMR (400MHz, $CDCl_3$): δ 1.33 (t, 3H, ^3J = 7.5 Hz, SCH_2CH_3), 2.65 (m, 2H, SCH_2CH_3), 3.76 (dd, 1H, ^3J = 11.0 Hz, ^3J = 1.5 Hz, H-6), 3.89 (dd, 1H, ^3J = 11.0 Hz, ^3J = 4.5 Hz, H-6), 4.04 (dd, 1H, ^3J = 9.5 Hz, ^3J = 9.5 Hz, H-4), 4.20-4.26 (m, 1H, H-5), 4.30 (t, 1H, ^3J = 7.5 Hz, H-Fmoc), 5.32 (dd, 1H, ^3J = 1.5 Hz, ^3J = 1.5 Hz, H-2), 5.48 (d, 1H, ^3J = 1.5 Hz, H-1).

^{13}C NMR (100MHz, $CDCl_3$): δ 14.9 (SCH_2CH_3), 25.5 (SCH_2CH_3), 46.6 (*C*H-Fmoc), 68.9 (C-6), 70.3 (CH_2-Fmoc), 71.9 (CH_2Ph), 72.0 (C-5), 74.6 (C-4), 74.6 (C-2), 75.3 (CH_2Ph), 78.6 (C-3), 82.1 (C-1), 154.9 (*C*O-Fmoc).

HRMS $C_{44}H_{44}O_7SNa$: Calcd. $[M + Na]^+$ 739.2706, Found 739.2709.



$C_{29}H_{42}O_7Si$

M = 530.2700

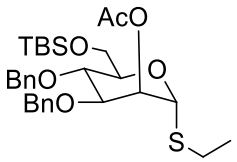
3,4-di-*O*-benzyl-6-*O*-(tert-butyldimethylsilyl)-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose **15**

tert-butyldimethylsilyl chloride (TBDMSCl) (1.81 g, 0.012mol) was added to a solution of **12** (2.48 g, 0.01mol) and imidazole (2.14g, 0.03 mol) in anhydrous DMF (25 mL) at 0℃ under argon. The reaction mixture was stirred overnight, quenched with water and extracted with ethyl acetate. The organic phase was washed quickly with water, brine, dried over MgSO4 and concentrated in vacuo. The residue in DMF was added sodium hydride (60% dispersion in mineral oil, washed two times with petroleum ether) (1.47 g, 36.84 mmol) in portions at 0℃ under argon. The resulting suspension was stirred for 30 minutes, and benzyl bromide (2.5 mL, 21.2 mmol) in dry DMF (2 mL) was added dropwise. The mixture was stirred at room temperature overnight, quenched with methanol and extracted with ethyl acetate. The organic phase was washed with water and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (Petroleum ether /EtOAc = 4:1) to give compound **15** (2.54 g, 46% yield).

Rf = 0.55 (Petroleum ether /EtOAc = 3:1)

^{1}H NMR (400MHz, $CDCl_3$): δ 0.10 (s, 6H, $Si(CH_3)_2$), 0.93 (s, 9H, t-Bu), 1.76(s, 3H, CH_3), 3.25 (ddd, 1H, ^3J = 9.0 Hz, ^3J = 3.5 Hz, ^3J = 2.0 Hz, H-5), 3.33 (s, 3H, OCH_3), 3.74 (dd, 1H, ^3J = 9.0 Hz, ^3J = 4.0 Hz, H-3), 3.84 (dd, 1H, ^2J = 11.0 Hz, ^3J = 2.0 Hz, H-6), 3.96 (dd, 1H, ^2J = 11.0 Hz, ^3J = 3.5 Hz, H-6), 4.02 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4), 4.38 (dd, 1H, ^3J = 4.0 Hz, ^3J = 2.5 Hz, H-2), 5.33 (d, 1H, ^3J = 2.5 Hz, H-1).

HRMS $C_{29}H_{42}O_7SiNa$: Calcd. $[M + Na]^+$ 553.2598, Found 553.2610.



$C_{30}H_{44}O_6SSi$

M = 560.2628

Ethyl 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-

α-D-mannopyranoside **16**

To a stirred suspension of **15** (2.47 g, 4.65mmol) and 4 Å molecurar sieves (0.5 g) in anhydrous acetonitrile (20 mL), ethanethiol (1.86 mL, 25.11 mmol) was added via syringe, mercury(II) bromide (0.20 g, 0.56 mmol) was then added. The reaction mixture was stirred at room temperature overnight and quenched with water, filtered through Celite. The Celite pad was washed with ethyl acetate, the organic phase was separated and the water phase was extracted three times with ethyl acetate. The combined organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The product was chromatographed on silica gel (Petroleum ether /EtOAc = 9:1) to give compound **16** (1.88g, 72% yield).

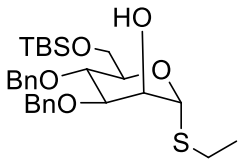
Rf = 0.66 (Petroleum ether /EtOAc = 5:1)

$[\alpha]_D^{25}$ = +78.2 (*c* = 1.2, $CHCl_3$)

^{1}H NMR (400MHz, $CDCl_3$): δ 0.10 and 0.12 (2s, 2 × 3H, $Si(CH_3)_2$), 0.95 (s, 9H, t-Bu), 1.30 (t, 3H, ^3J = 7.5 Hz, SCH_2CH_3), 2.17 (s, 3H, OAc), 2.55-2.73 (m, 2H, SCH_2CH_3), 3.85 (dd, 1H, ^3J = 11.5 Hz , ^3J = 1.5 Hz, H-3), 3.91-4.04 (m, 3H, H-6, H-5, H-4), 5.29 (d, 1H, ^3J = 1.0 Hz, H-1), 5.43 (d, 1H, ^3J = 2.0 Hz, H-2).

^{13}C NMR (100MHz, $CDCl_3$): δ -5.3 and -5.1 (C-Si), 14.9 (SCH_2CH_3), 18.3 ($C(CH_3)_3$), 21.1(CH_3CO), 25.3 (SCH_2CH_3), 25.9 ($C(CH_3)_3$), 62.3 (C-6), 70.8, 71.9 (CH_2Ph), 73.1, 75.2 (CH_2Ph), 78.5, 82.1, 170.4 (*C*-acetate).

HRMS $C_{30}H_{44}O_6SSiNa$: Calcd. $[M + Na]^+$ 583.2526, Found 583.2526.



$C_{28}H_{42}O_5SSi$

M = 518.2522

Ethyl 3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-α-D-mannopyranoside **21**

A freshly prepared sodium methoxide solution (3 mL, 0.5 M in methanol) was added to a solution of **20** (1.78 g, 3.17 mmol) in methanol (20 mL). The reaction mixture was stirred at room temperature for 30 minutes and monitored by TLC. The methanol was removed in vacuo and the residue was extracted by dichloromethane, washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel (Petroleum ether /EtOAc = 9:1) to give compound **21** (1.63g, 99% yield).

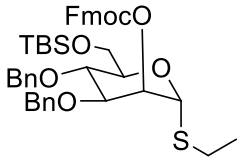
Rf = 0.45(Petroleum ether /EtOAc = 5:1)

$[\alpha]_D^{25}$ = +126.6 (*c* = 1.8, $CHCl_3$)

^{1}H NMR (400MHz, $CDCl_3$): δ 0.10 and 0.12 (2s, 2 × 3H, $Si(CH_3)_2$), 0.95 (s, 9H, *t*-Bu), 1.32 (t, 3H, ^3J = 7.5 Hz, SCH_2CH_3), 2.54-2.75 (m, 3H, OH, SCH_2CH_3), 3.84 (dd, 1H, ^3J = 9.5 Hz, ^3J = 9.5 Hz, H-4), 3.87-3.94 (m, 3H, 2 × H-6, H-3), 4.06 (ddd, 1H, ^3J = 9.5Hz, ^3J = 3.5Hz, ^3J = 3.5Hz, H-5), 4.11 (br s, 1H, H-2), 5.39 (s, 1H, H-1).

^{13}C NMR (100MHz, $CDCl_3$): δ -5.3 and -5.2 (C-Si), 14.7 (SCH_2CH_3), 18.3 ($C(CH_3)_3$), 24.6 (SCH_2CH_3), 25.9 ($C(CH_3)_3$), 62.6 (C-6), 69.9, 72.2 (CH_2Ph), 72.9, 74.6, 75.1 (CH_2Ph), 80.5, 82.9, 170.4 (C-acetate).

HRMS $C_{28}H_{42}O_5SSiNa$: Calcd. $[M + Na]^+$ 541.2420, Found 541.2425.



$C_{43}H_{52}O_7SSi$

M = 740.3203

Ethyl

3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-1-thio-α-D-mannopyranoside **B2**

A freshly prepared sodium methoxide solution (3 mL, 0.5 M in methanol) was added to a solution of 20 (1.78 g, 3.17 mmol) in methanol (20 mL). The reaction mixture

was stirred at room temperature for 30 minutes and monitored by TLC. The methanol was removed in vacuo and the residue was extracted by dichloromethane, washed with water, dried over MgSO4, filtered, and concentrated in vacuo. The residue was dissolved in anhydrous dichloromethane (30 mL), Pyridine (1 mL) was added, and followed 9-Fluorenylmethyl chloroformate (Fmoc-Cl) (1.21g, 4.68 mmol) was added to this solution. The reaction mixture was stirred at room temperature overnight and monitored by TLC. The reaction mixture was quenched with water and extracted with dichloromethane. The organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel (Petroleum ether /EtOAc = 8:1) to afford **B2** (1.94g, 86% yield).

Rf = 0.66 (Petroleum ether /EtOAc = 5:1)

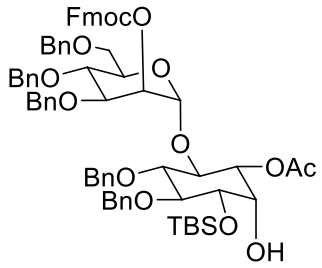
$[\alpha]_D^{25}$ = +44.1 (*c* = 1.2, $CHCl_3$)

^{1}H NMR (400MHz, $CDCl_3$): δ 0.10 and 0.14 (2s, 2 × 3H, $Si(CH_3)_2$), 0.95 (s, 9H, t-Bu), 1.31 (t, 3H, ^3J = 7.5 Hz, SCH_2CH_3), 2.65 (m, 2H, SCH_2CH_3), 3.87 (dd, 1H, ^3J = 11.0 Hz, ^3J = 1.5 Hz, H-6), 3.93-4.08 (m, 4H, H-3, H-4, H-6, H-5), 4.27 (t, 1H, ^3J = 7.5 Hz, H-Fmoc), 5.30 (dd, 1H, ^3J = 1.5 Hz, ^3J = 1.5 Hz, H-2), 5.40 (d, 1H, ^3J = 1.5 Hz, H-1).

^{13}C NMR (100MHz, $CDCl_3$): δ -5.3 and -5.1 (C-Si), 14.9 (SCH_2CH_3), 18.3 ($C(CH_3)_3$), 25.3 (SCH_2CH_3), 25.9 ($C(CH_3)_3$), 46.7 (CH-Fmoc), 62.4 (C-6), 70.1 (CH_2-Fmoc), 71.9 (CH_2Ph), 73.3 (C-5), 74.5 (C-4), 74.6 (C-2), 75.3 (CH_2Ph), 78.6 (C-3), 81.8 (C-1), 154.9 (CO-Fmoc).

MS (TOF): *m/z* = 763.3 $[M + Na]^+$.

HRMS $C_{43}H_{52}O_7SSiNa$: Calcd. $[M + Na]^+$ 763.3101, Found 763.3099.



$C_{70}H_{78}O_{14}Si$

M = 1170.5161

1-*O*-acetyl-4,5-di-*O*-benzyl-3-*O*-(*tert*-butyldimethylsilyl)-6-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl]-D-*myo*-inositol **20**

Compounds **A** (0.12 g, 0.232 mmol) and **B1** (0.183 g, 0.255 mmol) were coevaporated from dry dichloromethane and dried under high vacuum for 30 minutes and then flushed with argon. Anhydrous dichloromethane (3 mL) was added followed by 3 Å molecular sieves, NIS (0.063 g, 0.278 mmol) was added and the reaction was cooled to -20 ℃, TMSOTf (23.2 μL, 0.0232 mmol) was added dropwise. After stirring at -20 ℃ for 2 hours, the mixture was allowed to warm to room temperature, the reaction was quenched with phosphate buffer (PH=7), and the mixture was filtered through a small column of Celite. The Celite was washed with dichloromethane, a saturated $Na_2S_2O_3$ solution was added to the filtrate and it turned to colorless. The organic phase was separated and the water phase was extracted three times with dichloromethane, then the combined organic phase washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Petroleum ether /EtOAc = 5:1) to give compound **20** (0.174 g, 64% yield).

Date for compound **20**:

Rf = 0.40 (Petroleum ether /EtOAc = 3:1)

$[\alpha]_D^{25}$ = + 0.9 (*c* = 1.0, $CHCl_3$)

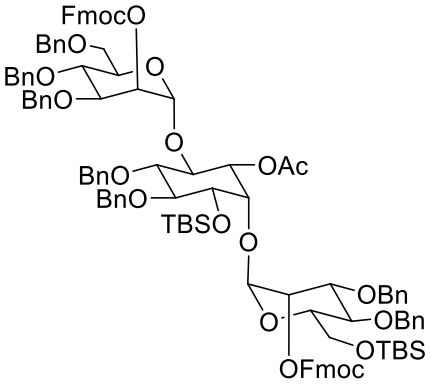
^{1}H NMR (4 00MHz, $CDCl_3$): δ 0.10 and 0.14 (2s, 2 × 3H, $Si(CH_3)_2$), 0.94 (s, 9H, *t*-Bu), 2.16 (s, 3H, OAc), 3.32 (dd, 1H, ^2J = 12.5 Hz, ^3J = 1.0 Hz, H-6M), 3.37 (dd, 1H, ^2J = 12.5 Hz, ^3J = 2.5 Hz, H-6M), 3.41 (dd, 1H, ^3J = 9.5 Hz, ^3J = 9.5 Hz, H-5I), 3.77 (dd, 1H, ^3J = 9.0 Hz, ^3J = 2.5 Hz, H-3I), 3.85 (dd, 1H，^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4I), 3.99 (dd, 1H, ^3J = 9.0 Hz, ^3J = 3.0 Hz, H-3M), 4.00-4.05 (m, 1H, H-5M), 4.06 (dd, 1H,

^3J = 2.0 Hz, ^3J = 2.0 Hz, H-2I), 4.09 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4M), 3.90 (dd, 1H, ^3J = 10.0 Hz, ^3J = 10.0 Hz, H-6I), 4.88 (dd, 1H, ^3J = 11.0 Hz, ^3J = 2.5 Hz, H-1I), 5.15 (dd, 1H, ^3J = 2.0 Hz, ^3J = 2.0 Hz, H-2M), 5.41 (d, 1H, ^3J = 1.5 Hz, H-1M).

^{13}C NMR (100MHz, $CDCl_3$): δ -4.7 and -4.6 (C-Si), 17.9 ($C(CH_3)_3$), 21.1 (CH_3CO), 25.8 ($C(CH_3)_3$), 46.5 (CH-Fmoc), 68.2 (C-6M), 70.3 (CH-Fmoc), 71.0 (C-5M), 71.6 (C-2I), 71.7 (CH_2Ph), 73.0 (C-3I), 73.3 (CH_2Ph, C-2M), 74.2 (C-4M, C-1I), 74.4 (C-6I), 75.0 (CH_2Ph), 75.6 (CH_2Ph), 75.7 (CH_2Ph), 77.7 (C-3M), 81.0 (C-5I), 82.3 (C-4I), 97.9 (C-1M), 154.8 (CO-Fmoc), 171.7(C-acetate).

MS (TOF): *m/z* = 1193.6 $[M + Na]^+$.

HRMS $C_{70}H_{78}O_{14}SiNa$: Calcd. $[M + Na]^+$ 1193.5059, Found 1193.5063.



$C_{111}H_{124}O_{21}Si_2$

M = 1848.8174

1-*O*-acetyl-2-*O*-[3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl]-4,5-di-*O*-benzyl-6-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenylmethyloxycarbonyl)-α-D-mannopyranosyl]-3-*O*-(*tert*-butyldimethylsilyl)-D-*myo*-inositol **21**

Compounds **20** (100 mg, 0.085 mmol) and **B2** (81.6 mg, 0.112 mmol) were

coevaporated from dry dichloromethane and dried under high vacuum for 30 minutes and then flushed with argon. Anhydrous dichloromethane (2 mL) was added followed by 3 Å molecular sievess, NIS (29 mg, 0.129 mmol) was added and the solution was cooled to -20 ℃, TMSOTf (8.6 μL, 0.0086 mmol) was added dropwise. After stirring at -20 ℃ for 2 hours, the mixture was allowed to warm to room temperature, the reaction was quenched with phosphate buffer (pH=7), and the mixture was filtered through a small column of Celite. The Celite was washed with dichloromethane, a saturated $Na_2S_2O_3$ solution was added to the filtrate and it turned to colorless. The organic phase was separated and the water phase was extracted three times with dichloromethane, then the combined organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Petroleum ether /EtOAc = 8:1) to give compound **21** (70 mg, 82% yield).

Date for compound **21**:

Rf = 0.58 (Petroleum ether /EtOAc = 5:1)

$[\alpha]_D^{25}$ = + 8.0 (*c* = 1.0, $CHCl_3$)

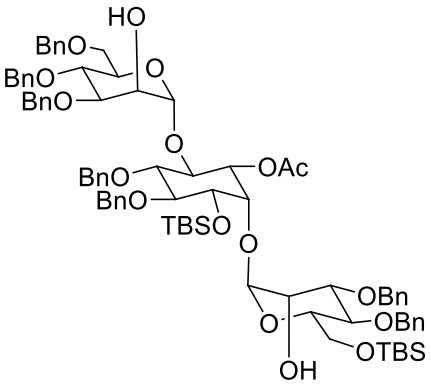
^{1}H NMR (400MHz, $CDCl_3$): δ 0.05, 0.10, 0.12, 0.15 (4s, 4 × 3H, $SiCH_3$), 0.91 and 0.98 (2s, 2 × 9H, *t*-Bu), 2.06 (s, 3H, OAc), 3.20-3.34 (m, 2H, H-6M), 3.71 (dd, 1H, ^3J = 10.0 Hz, ^3J = 2.0 Hz, H-3I), 3.79 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4I), 3.84-3.89 (m, 1H, H-6M'), 3.89-3.94 (m, 1H, H-5M), 3.97 (dd, 1H, ^3J = 9.5Hz, ^3J = 3.0 Hz, H-3M), 4.06-4.13 (m, 5H, H-6M', H-5M', H-3M', H-4M, H-2I), 4.18 (dd, 1H, ^3J = 10.0 Hz, ^3J = 10.0 Hz, H-6I), 4.25 (dd, 1H, ^3J = 7.5 Hz, ^3J = 7.5 Hz, H-4M'), 4.89 (dd, 1H, ^3J = 6.0 Hz, ^3J = 2.0 Hz, H-1I), 5.08 (d, 1H, ^3J = 1.5 Hz, H-1M'), 5.13 (dd, 1H, ^3J = 6.0 Hz, ^3J = 2.0 Hz, H-2M), 5.30 (dd, 1H, ^3J = 2.5 Hz, ^3J = 2.5 Hz, H-2M'), 5.41 (d, 1H, ^3J = 1.5 Hz, H-1M).

^{13}CNMR (100MHz, $CDCl_3$): δ -5.4, -4.9, -4.5, -4.4 (C-Si), 18.3 ($C(CH_3)_3$), 20.8 (CH_3CO), 25.9 ($C(CH_3)_3$), 26.2 ($C(CH_3)_3$), 46.6 and 46.7 (CH-Fmoc), 61.7 (C-6M'), 68.1 (C-6M), 69.9 and 70.2 (CH_2-Fmoc), 71.7 (CH_2Ph), 71.8 (CH_2Ph), 72.2 (C-3I), 72.7(C-2M'), 72.9 (C-2M), 73.3 (C-5M), 73.3 (CH_2Ph), 73.5 (C-4M'), 74.0 (C-4M), 74.9 (C-1I), 75.0 (CH_2Ph), 75.5 (CH_2Ph), 75.7 (C-6I), 75.9 (CH_2Ph), 77.2 (C-5M'),

77.8 (C-3M), 78.9 (C-3M', C-2I), 81.4 (C-5I), 81.6 (C-4I), 98.1(C-1M), 99.3 (C-1M'), 154.8 (CO-Fmoc), 171.8(C-acetate).

MS (TOF): *m/z* = 1849.9 $[M + H]^+$.

HRMS $C_{111}H_{124}O_{21}Si_2Na$: Calcd. $[M + Na]^+$ 1871.8071, Found 1871.8060.



$C_{81}H_{104}O_{17}Si_2$

M = 1404.6812

1-*O*-acetyl-2-*O*-[3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranosyl]-4,5-di-*O*-benzyl-6-*O*-[3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl]-3-*O*-(*tert*-butyldimethylsilyl)-D-*myo*-inositol **22**

Triethylamine (150 μL) was added to a solution of **21** in anhydrous THF (1.5 mL) and the reaction mixture was stirred at room temperature for 4 hours, then the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (Petroleum ether /EtOAc = 3:1) to give **22 (**43 mg, 72% yield).

Rf = 0.25 (Petroleum ether /EtOAc = 2:1)

$[\alpha]_D^{25}$ = + 41.9 (*c* = 1.0, $CHCl_3$)

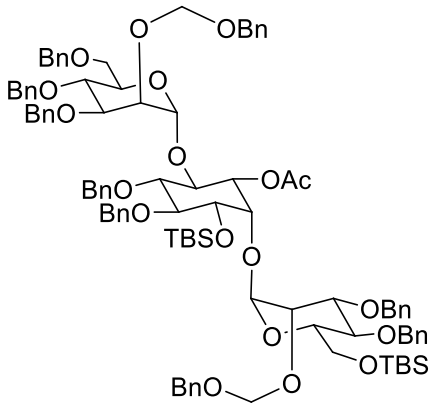
^{1}H NMR (4 00MHz, $CDCl_3$): δ 0.05, 0.09, 0.10 (3s, 12H, $SiCH_3$), 0.89 and 0.93 (2s, 2 × 9H, *t*-Bu), 2.15 (s, 3H, OAc), 3.19 (dd, 1H, ^2J = 11.0 Hz, ^3J = 1.0 Hz, H-6M), 3.26 (dd, 1H, ^2J = 11.0 Hz, ^3J = 2.5 Hz, H-6M), 3.40 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-5I), 3.69 (dd, 1H, ^3J = 10.0 Hz, ^3J = 2.0 Hz, H-3I), 3.78 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4I), 3.79-3.85 (m, 1H, H-6M'), 3.86-3.96 (m, 6H, H-5M', H-4M', H-3M,

H-5M, H-2M, H-3M'), 4.00 (dd, 1H, ^{3}J = 11.5 Hz, ^{3}J = 2.5 Hz, H-6M'), 4.02-4.09 (m, 2H, H-4M, H-2I), 4.10-4.19 (m, 2H, H-2M', H-6I), 4.86-4.91 (m, 1H, H-1I), 5.06 (d, 1H, ^{3}J = 1.0 Hz, H-1M'), 5.24 (d, 1H, ^{3}J = 1.0 Hz, H-1M).

^{13}C NMR (100MHz, $CDCl_3$): δ -5.3, -5.0, -4.5, -4.4 (C-Si), 18.3 ($C(CH_3)_3$), 21.1 (CH_3CO), 25.9 ($C(CH_3)_3$), 26.2 ($C(CH_3)_3$), 61.9 (C-6M'), 68.1 (C-6M), 68.6, 68.7, 71.2, 72.0 (CH_2Ph), 72.2, 72.6, 73.2 (CH_2Ph), 73.5, 73.9, 74.9 (CH_2Ph), 75.1 (CH_2Ph), 75.3 (CH_2Ph), 75.5, 75.6, 75.8 (CH_2Ph), 77.4, 79.1, 79.9, 81.6, 99.9 (C-1M), 100.4 (C-1M'), 170.2 (C-acetate).

MS (TOF): *m/z* = 1427.7 $[M + Na]^+$.

HRMS $C_{81}H_{104}O_{17}Si_2Na$: Calcd. $[M + Na]^+$ 1427.6710, Found 1427.6735.



$C_{97}H_{120}O_{19}Si_2$

M = 1644.7962

1-*O*-acetyl-2-*O*-[2-*O*-benzyloxymethyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl) -α-D-mannopyranosyl]-4,5-di-*O*-benzyl-6-*O*-[2-*O*-benzyloxymethyl-3,4,6-tri-*O*-benz yl-α-D-mannopyranosyl]-3-*O*-(*tert*-butyldimethylsilyl)-D-*myo*-inositol **23**

Benzyl chloromethyl ether (BOMCl) (20.8 µL, 0.15 mmol) was added to a mixture of N,N-Diisopropylethylamine (DIPEA) (31.2 µL, 0.18 mmol), tetrabutylammonium iodide (2.2 mg, 0.006 mmol) and **22** (42 mg, 0.03 mmol) in anhydrous THF (100 µL) at 0 ℃. The reaction mixture was stirred at room temperature for 24 hours, then the solvents were removed in vacuo. The residue was purified by silica gel column

chromatography (Petroleum ether /EtOAc = 5:1) to give **23** (27 mg, 55% yield).

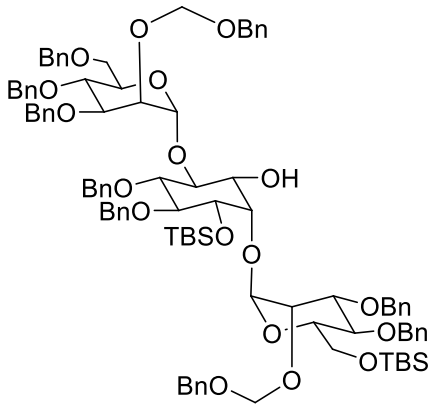
Rf = 0.50 (Petroleum ether /EtOAc = 5:1)

$[\alpha]_D^{25}$ = + 46.6 (c = 0.89, $CHCl_3$)

^{1}H NMR (4 00MHz, $CDCl_3$): δ 0.04, 0.07, 0.08, 0.10 (4s, 4 × 3H, $SiCH_3$), 0.92 and 0.93 (2s, 2 × 9H, *t*-Bu), 1.85 (s, 3H, OAc), 3.20 (dd, 1H, ^2J = 10.8 Hz, ^3J = 1.0 Hz, H-6M), 3.30 (dd, 1H, ^2J = 10.8 Hz, ^3J = 2.5 Hz, H-6M), 3.37 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-5I), 3.68 (dd, 1H, ^3J = 9.5 Hz, ^3J = 2.0 Hz, H-3I), 3.76 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4I), 3.83-4.08 (m, 9H, H-6M', H-5M', H-3M', H-3M, H-4M, H-5M, H-2M, H-2M', H-2I), 4.16 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-6I), 4.27 (dd, 1H, ^3J = 9.5 Hz, ^3J = 9.5 Hz, H-4M'), 4.78-4.82 (m, 1H, H-1I), 5.25 (d, 1H, ^3J = 1.5 Hz, H-1M'), 5.35 (d, 1H, ^3J = 1.9 Hz, H-1M).

^{13}C NMR (100MHz, $CDCl_3$): δ -5.4, -5.1, -4.6, -4.4 (C-Si), 18.3 ($C(CH_3)_3$), 18.5 ($C(CH_3)_3$), 20.4 (CH_3CO), 25.9 ($C(CH_3)_3$), 26.3 ($C(CH_3)_3$), 61.9 (C-6M'), 65.4, 68.4 (C-6M), 69.2, 69.4, 71.9, 72.1, 72.3, 73.0, 73.1, 73.9 (C-4M'), 74.3, 74.5, 74.8, 75.2, 75.3, 75.4, 75.8, 76.9, 78.3, 78.6, 79.1, 81.5, 81.6, 94.1 and 95.7 (OCH_2O), 98.8 (C-1M), 100.3 (C-1M'), 170.6 (*C*-acetate).

HRMS $C_{97}H_{120}O_{19}Si_2Na$: Calcd. $[M + Na]^+$ 1667.7860, Found 1667.7849.



$C_{95}H_{118}O_{18}Si_2$

M = 1602.7857

2-*O*-[2-*O*-benzyloxymethyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mann

opyranosyl]-4,5-di-*O*-benzyl-6-*O*-[2-*O*-benzyloxymethyl-3,4,6-tri-*O*-benzyl-α-D-man nopyranosyl]-3-*O*-(*tert*-butyldimethylsilyl)-D-*myo*-inositol **24**

A freshly preparerd sodium methoxide solution (1 mL, 0.5 M in methanol) was added to a solution of **23** (26 mg, 0.016 mmol) in methanol (2 mL) at 0 ℃ and the reaction mixture was stirred at room temperature for 30 minutes and monitored by TLC. The methanol was removed in vacuo and the residue was extracted by dichloromethane. The organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel (Petroleum ether /EtOAc = 9:1) to give compound **24** (25 mg, 99% yield).

Rf = 0.52 (Petroleum ether /EtOAc = 5:1)

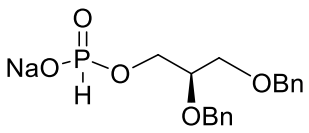
$[\alpha]_D^{25}$ = + 0.42 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (400MHz, $CDCl_3$): δ 0.03, 0.08, 0.10, 0.11 (4s, 4 × 3H, $SiCH_3$), 0.91 and 0.94 (2s, 2 × 9H, *t*-Bu), 3.30-3.58 (m, 4H), 3.59-3.75 (m, 3H), 3.78-3.92 (m, 4H), 3.92-4.10 (m, 5H), 4.11-4.29 (m, 3H), 5.34 (s, 1H, H-1M'), 5.41 (s, 1H, H-1M).

^{13}C NMR (75 MHz, $CDCl_3$): δ -5.3, -5.0, -4.6, -4.5 (C-Si), 18.3($C(CH_3)_3$), 25.9 ($C(CH_3)_3$), 26.1 ($C(CH_3)_3$), 62.2 (C-6M'), 69.3 (C-6M), 69.6, 70.9, 71.8, 71.9, 72.0, 73.0, 73.3, 74.1, 74.8, 74.9, 75.2, 78.6, 79.3, 80.1, 81.5, 94.7 and 94.9 (OCH_2O), 95.6 (C-1M), 100.5 (C-1M').

MS (TOF): *m/z* = 1625.9 $[M + Na]^+$.

HRMS $C_{95}H_{118}O_{18}Si_2Na$: Calcd. $[M + Na]^+$ 1625.7754, Found 1625.7722.



$C_{17}H_{20}NaO_5P$

M = 358.0946

Sodium (*2R*)-2,3-di-*O*-benzyl-glyceryl 1-hydrogenphosphonate building block **C**

To a solution of imidazole (1.83g, 26.9 mmol) in anhydrous toluene (30 mL) was added triethylamine (2.1 ml, 15.3 mmol) and phosphorus trichloride (0.8 ml, 9 mmol) at 0 ℃ and the reaction mixture was stirred for 15 minutes. Then a solution of (s)-(-)-2,3-dibenzyloxy-1-propanol **17** (0.10 g, 0.15 mmol) in anhydrous toluene (1 mL) was added dropwise at 0 ℃ over 30 minutes, the reaction mixture was stirred for another 3 hours, quenched with an aqueous Py-H_2O (4:1, 25 mL) solution and extracted with dichloromethane. The organic phase was washed with 6M HCl solution, 10M NaOH aq solution. The organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel (dichloromethane/methanol = 3:1) to give compound **C** (0.4 g, yield 77%). [3]

Rf = 0.1 (dichloromethane/methanol = 10:1)

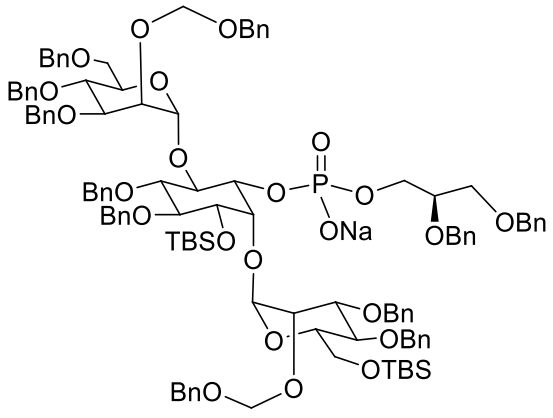
$[\alpha]_D^{25}$ = + 3.2 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$/CD_3OD:3/1): δ 3.59 (dd, 1H, $^2J_{3,3}$ = 10.5 Hz, $^3J_{3,2}$ = 5.5 Hz, H-3G), 3.66 (dd, 1H, $^2J_{3,3}$ = 10.5 Hz, $^3J_{3,2}$ = 4.0 Hz, H-3G), 3.76-3.85 (m, 1H, H-2G), 3.99 (ddd, 1H, $^2J_{1,1}$ = 11 Hz, $^3J_{P,H}$ = 7.5 Hz, $^3J_{1,2}$ = 5.0 Hz, H-1 G), 6.70 (d, 1H, $^1J_{P,H}$ = 618 Hz, H-P).

^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD:3/1): δ 63.3 (d, $^2J_{P\text{-}C}$ = 4.5 Hz, C-1G), 69.3 (C-3G), 72.2 and 73.4 (CH_2Ph), 77.2 (d, $^3J_{P\text{-}C}$ = 7.2 Hz, C-2G).

^{31}P NMR (121 MHz, $CDCl_3$/CD_3OD:3/1): δ = -5.62

HRMS $C_{17}H_{20}NaO_5P$: Calcd. $[M - Na]^-$ 335.1048, Found 335.1045.



$C_{112}H_{136}NaO_{23}PSi_2$

M = 1958.8646

Sodium [(*2R*)-2,3-di-*O*-benzyl-glycerol]
2-*O*-[2-*O*-benzyloxymethyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranosyl]-4,5-di-*O*-benzyl-6-*O*-[2-*O*-benzyloxymethyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl]-3-*O*-(*tert*-butyldimethylsilyl)-D-*myo*-inositol 1-phosphate **25**

Compounds **24** (20 mg , 0.012 mmol) and building block **C** (12.8 mg, 0.036 mmol) were coevaporated from dry dichloromethane and dried under high vacuum for 30 minutes and then flushed with argon. Anhydrous pyridine (1 mL) was added followed by 4 Å molecular sieves, pivaloyl chloride (15 µL, 0.12 mmol) was added and the solution was stirred at room temperature for another 2 hours. A solution of iodine (15 mg, 0.06 mmol) in 98% pyridine (1 mL) was added dropwise, and the reaction mixture was stirred for 1 hour. The mixture was filtered through a small column of Celite. The Celite was washed with dichloromethane, a saturated $Na_2S_2O_3$ solution was added to the filtrate and it turned to colorless. The organic phase was separated and the water phase was extracted three times with dichloromethane, then the combined organic phase was washed with water, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (dichloromethane/methanol = 15:1) to give compound **25** (20 mg, yield 85%).

Rf = 0.42 (dichloromethane/methanol = 15:1)

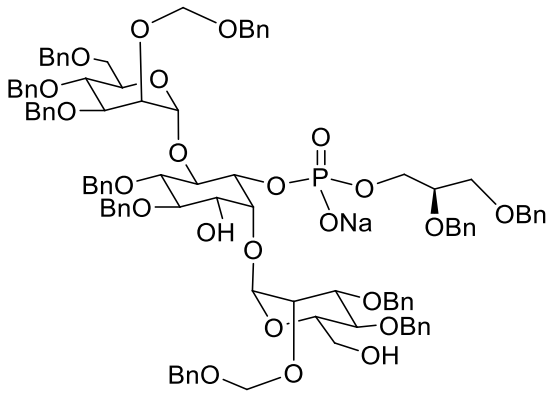
$[\alpha]_D^{25}$ = + 15.2 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD:3/1): δ -0.01, 0.00, 0.02, 0.06 (4s, 4 × 3H, $SiCH_3$), 0.86 and 0.87 (2s, 2 × 9H, *t*-Bu), 3.15-3.31 (m, 3H, H-6M, H-6M', H-5I), 3.42-3.62 (m, 4H, H-3G, H-3I, H-3M), 3.68-3.78 (m, 3H, H-4M, H-2G, H-4I), 3.80-4.15 (m, 10H, H-6M', H-5M', H-4M', H-5M, H-3M', H-2I, H-1I, H-1G), 4.15-4.20 (m, 1H, H-6I), 4.28-4.34 (m, 2H , H-2M, H-2M'), 5.39 (s, 1H, H-1M'), 5.58 (s, 1H, H-1M).

^{13}C NMR (75 MHz, $CDCl_3/CD_3OD$:3/1): δ -5.6, -5.3, -4.8, -4.7 (C-Si), 18.1 ($C(CH_3)_3$), 18.2 ($C(CH_3)_3$), 25.8 ($C(CH_3)_3$), 26.0 ($C(CH_3)_3$), 61.9 (C-6M'), 65.8 (C-1G), 68.6 (C-6M), 69.7 (C-3G, C-3I), 71.5 (C-5M), 72.3 (C-3M, C-3M'), 72.9 (C-4M', C-4M), 73.3 (C-5M'), 74.5 (C-6I, C-1I), 77.1 (C-2G), 78.9 (C-1G), 79.2 (C-2I), 81.4 (C-5I), 81.9 (C-4I), 93.2 and 93.9 (OCH_2O), 98.4 (C-1M), 100.7 (C-1M').

^{31}P NMR (162MHz, $CDCl_3/CD_3OD$:3/1): δ = -0.38

HRMS $C_{112}H_{136}O_{23}PSi_2$: Calcd. $[M - Na]^-$ 1935.8749, Found 1935.8761.



$C_{100}H_{108}NaO_{23}P$

M = 1730.6917

Sodium [(2R)-2,3-di-*O*-benzyl-glycerol]
2-*O*-(2-*O*-benzyloxymethyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl)-4,5-di-*O*-benzyl-6-*O*-(2-*O*-benzyloxymethyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-D-*myo*-inositol 1-phosphate **26**

TBAF (20 µL, 20 mmol) was added to a solution of **25** (7.8 mg, 4 mmol) in anhydrous THF (0.2 mL) and the mixture was sirred at 40℃ for 24 hours, then the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (dichloromethane/methanol = 10:1) to give **26** (5.8 mg, 85% yield).

Rf = 0.12 (dichloromethane/methanol = 15:1)

$[\alpha]_D^{25}$ = + 14.2 (*c* = 1.0, $CHCl_3$)

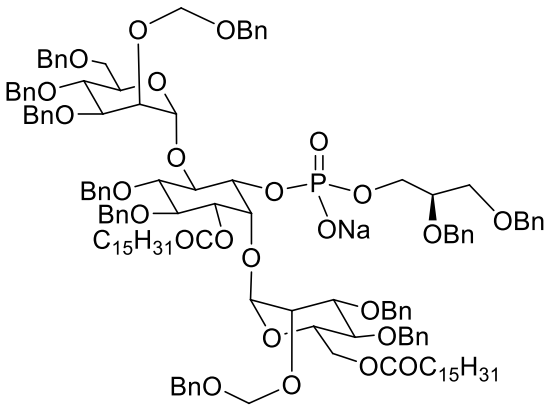
^{1}H NMR (400MHz, $CDCl_3/CD_3OD$:3/1): δ 3.25-3.33 (m, 3H, H-6M, H-5I), 3.47-3.60 (m, 3H, H-3I, H-3G), 3.60-3.70 (m, 2H, H-4I, H-5M), 3.74 (dd, 1H, ^3J = 9.5 Hz, ^3J = 9.5 Hz, H-4M), 3.77-3.85 (m, 1H, H-2G), 3.89-3.96 (m, 2H, H-3M, H-3M'), 3.99-4.30 (m, 8H, H-4M', H-5M', H-6M', H-6I, H-1G, H-2M'), 4.33-4.38 (m, 1H, H-2M), 4.46-4.51 (m, 1H, H-1I), 4.52-4.55 (m, 1H, H-2I), 5.49 (s, 1H, H-1M'), 5.61 (s, 1H, H-1M).

^{13}C NMR (100 MHz, $CDCl_3/CD_3OD$:3/1): δ 62.0 (C-2G), 65.4 (C-6M'), 69.2 (C-6M), 70.3 (C-5M), 70.9 (C-3G, C-3I), 72.9 (C-5M'), 73.0 (C-4M'), 73.1 (C-6I, C-2M', C-2M, C-1I), 75.0 (C-4M), 75.9 (C-2I), 78.0 (C-3M), 78.9 (C-1G), 79.1 (C-3M'), 81.5 (C-5I), 81.9 (C-4I), 93.7 and 94.0 (OCH_2O), 98.5 (C-1M and C-1M').

^{31}P NMR (161MHz, $CDCl_3/CD_3OD$:3/1): δ = -1.48

MS (TOF): *m/z* = 1707.9 $[M - Na]^-$.

HRMS $C_{100}H_{108}O_{23}P$: Calcd. $[M - Na]^-$ 1707.7019, Found 1707.7015.



$C_{132}H_{168}NaO_{25}P$

M = 2207.1510

Sodium [(2R)-2,3-di-*O*-benzyl-glycerol]

2-*O*-(2-*O*-benzyloxymethyl-3,4-di-*O*-benzyl-6-*O*-palmitoyl-α-D-mannopyranosyl)-4,

5-di-*O*-benzyl-6-*O*-(2-*O*-benzyloxymethyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-

3-*O*-palmitoyl-D-*myo*-inositol

1-phosphate **27**

To a solution of **26** (5 mg, 0.00257 mmol) in toluene (0.5 mL), palmitic acid (1.3 mg, 5.14 mmol), 4-Dimethylaminopyridine (DMAP) (0.63 mg, 5.14 mmol) and N,N'-Dicyclohexylcarbodiimide (DCC) (1.06 mg, 5.14 mmol) were added at room temperature. The reaction mixture was stirred at 100 ℃ for 12 hours and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (dichloromethane/methanol = 15:1) to give **27** (5 mg, 89% yield).

Rf = 0.40 (dichloromethane/methanol = 15:1)

$[\alpha]_D^{25}$ = + 8.9 (*c* = 1.0, $CHCl_3$)

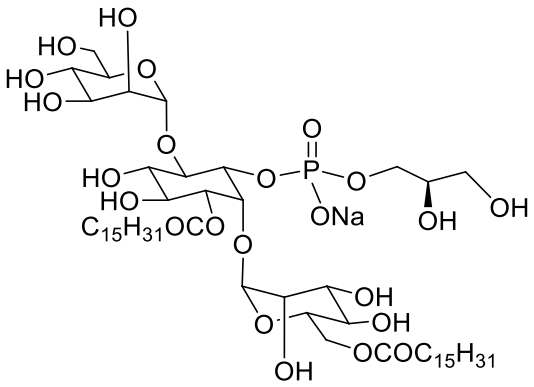
^{1}H NMR (400MHz, $CDCl_3$/CD_3OD:3/1): δ 0.85 (t, 6 H, ^3J = 6.4 Hz, CH_3), 1,24 (brs, 52H, CH_2), 1.91-2.12 (m, 2H, I-COO-CH_2), 2.12-2.18 (m, 2H, M-COO-CH_2), 3.28-3.41 (m, 3H, H-6M, H-5I), 3.49-3.56 (m, 1H, H-3G), 3.59-3.65 (m, 1H, H-3G), 3.78 (t, 1H, ^3J = 10.0 Hz, ^3J = 10.0 Hz, H-4I), 3.81-3.87 (m, 1H, H-2G), 3.92-4.17 (m, 9 H, H-3M, H-3M', H-4M, H-4M', H-5M, H-5M', H-6M', H-6I), 4.27-4.32 (m, 1H, H-1I), 4.33-4.36 (m, 1H, H-2M'), 4.46-4.49 (m, 2H, H-2M, H-2I), 5.48 (s, 1H, H-1M'), 5.73 (s, 1H, H-1M).

^{13}C NMR (100MHz, $CDCl_3$/CD_3OD:3/1): δ 13.8 (CH_3), 29.6 (CH_2), 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 34.0 (CH_2), 34.1 (CH_2), 68.5 (C-6M, C-6M'), 70.8 (C-3G), 71.2 (C-2G), 71.3 (C-3I), 71.5 (C-4M, C-4M'), 72.9 (C-5M, C-5M'), 73.0 (C-1I, C-2M', C-2M, C-6I), 77.1 (C-2I), 78.0 (C-3M, C-3M'), 79.0 (C-1G), 79.8 (C-4I), 81.5 (C-5I), 94.0 and 94.1 (OCH_2O), 98.8 (C-1M), 100.0 (C-1M'), 172.8 (COO), 174.1 (COO).

^{31}P NMR (161MHz, $CDCl_3$/CD_3OD:3/1): δ= -0.74

MS (TOF): *m/z* = 2184.2 $[M - Na]^-$.

HRMS $C_{132}H_{168}O_{25}P$: Calcd. $[M- Na]^-$ 2184.1611, Found 2184.1639.



$C_{53}H_{98}NaO_{23}P$

M = 1156.6134

Sodium [(2R)-glycerol]

2-*O*-(6-*O*-palmitoyl-α-D-mannopyranosyl)-6-*O*-(α-D-mannopyranosyl)-3-*O*-palmitoyl-D-*myo*-inositol 1-phosphate **Ac_2PIM_2**

20% $Pd(OH)_2/C$ (0.5 mg) was added to a solution of **27** (1 mg, 0.9 mmol) in mixed solvent methanol and ethyl acetate (1:1, 0.5 mL) under 1 atm H_2. The reaction mixture was stirred at room temperature for 24 hours and the solvents were removed in vacuo. The residue was purified by silica gel column chromatography (EtOAc/MeOH/H_2O = 8:3:0.5) to give **Ac_2PIM_2** (0.4 mg, 80% yield).

Rf = 0.15 (EtOAc/MeOH/H_2O = 8:3:0.5)

^{1}H NMR (700MHz, CD_3OD): δ 0.85 (t, 6H, ^3J = 7.0 Hz, CH_3), 1,32 (brs, 48H, CH_2), 1.60-1.72 (m, 4H), 2.36-2.39 (m, 2H, M-CH_2), 2.39-2.49 (m, 2H, I-CH_2), 3.32-3.35 (m, 1H, H-6I), 3.59 (dd, 1H, ^2J = 11.5 Hz, ^3J = 5.5 Hz, H-3G), 3.59 (dd, 1H, ^2J = 11.5 Hz, ^3J = 5.0 Hz, H-3G), 3.70 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4M'), 3.72 (dd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, H-4M), 3.74 (dd, 1H, ^2J = 11.5 Hz, ^3J = 5.0 Hz, H-6M), 3.76 (dd, 1H, ^3J = 9.5 Hz, ^3J = 3.5 Hz, H-3M), 3.76 (dd, 1H, ^3J = 10.5 Hz, ^3J = 9.5 Hz, H-4I), 3.80 (dd, 1H, ^3J = 9.5 Hz, ^3J = 3.5 Hz, H-3M'), 3.80-3.84 (m, 1H, H-2G), 3.85 (dd, 1H, ^2J = 11.5 Hz, ^3J = 2.5 Hz, H-6M), 3.88 (dd, 1H, ^3J = 9.5 Hz, ^3J = 9.5 Hz, H-5I), 3.96-4.02 (m, 2H, H-1G), 4.03 (dd, 1H, ^3J = 3.5 Hz, ^3J = 1.5 Hz, H-2M),

4.04-4.07 (m, 2H, H-5M, H-5M'), 4.15 (dd, 1H, ^3J = 3.5 Hz, ^3J = 1.5 Hz, H-2M'), 4.26 (ddd, 1H, ^3J = 9.0 Hz, ^3J = 9.0 Hz, ^3J = 2.0 Hz, H-1I), 4.29 (dd, 1H, ^2J = 11.5 Hz, ^3J = 5.5 Hz, H-6M'), 4.33 (dd, 1H, ^2J = 11.5 Hz, ^3J = 2.5 Hz, H-6M'), 4.48 (dd, 1H, ^3J = 2.5 Hz, ^3J = 2.5 Hz, H-2I), 4.81 (dd, 1H, ^3J = 10.5 Hz, ^3J = 2.5 Hz, H-3I), 5.12 (d, 1H, ^3J = 1.5 Hz, H-1M'), 5.29 (d, 1H, ^3J = 1.5 Hz, H-1M).

^{13}C NMR (100MHz, CD_3OD): δ 12.2 (CH_3), 24.0 (CH_2), 28.5 (CH_2), 33.0 (CH_2-M), 33.1 (CH_2-I), 61.0 (C-6M), 61.7 (C-3G), 63.0 (C-6M'), 65.7 (C-1G), 66.6 (C-4M, C-4M'), 69.7 (C-2M'), 69.8 (C-2M), 70.4 (C-3M), 70.6 (C-3M', C-4I), 70.9 (C-2G), 71.2 (C-3I), 72.1 (C-5M), 72.6 (C-5M'), 73.0 (C-6I), 74.8 (C-2I), 76.6 (C-1I), 78.0 (C-5I), 100.8 (C-1M), 101.5 (C-1M'). 173.2 (COO), 174.2 (COO).

^{31}P NMR (121MHz, CD_3OD): δ = 0.40

MS (TOF): *m/z* = 1133.5 $[M - Na]^-$.

HRMS $C_{53}H_{98}O_{23}P$: Calcd. $[M- Na]^-$ 1133.6237, Found 1133.6238.

Evaluation of antigenic activity

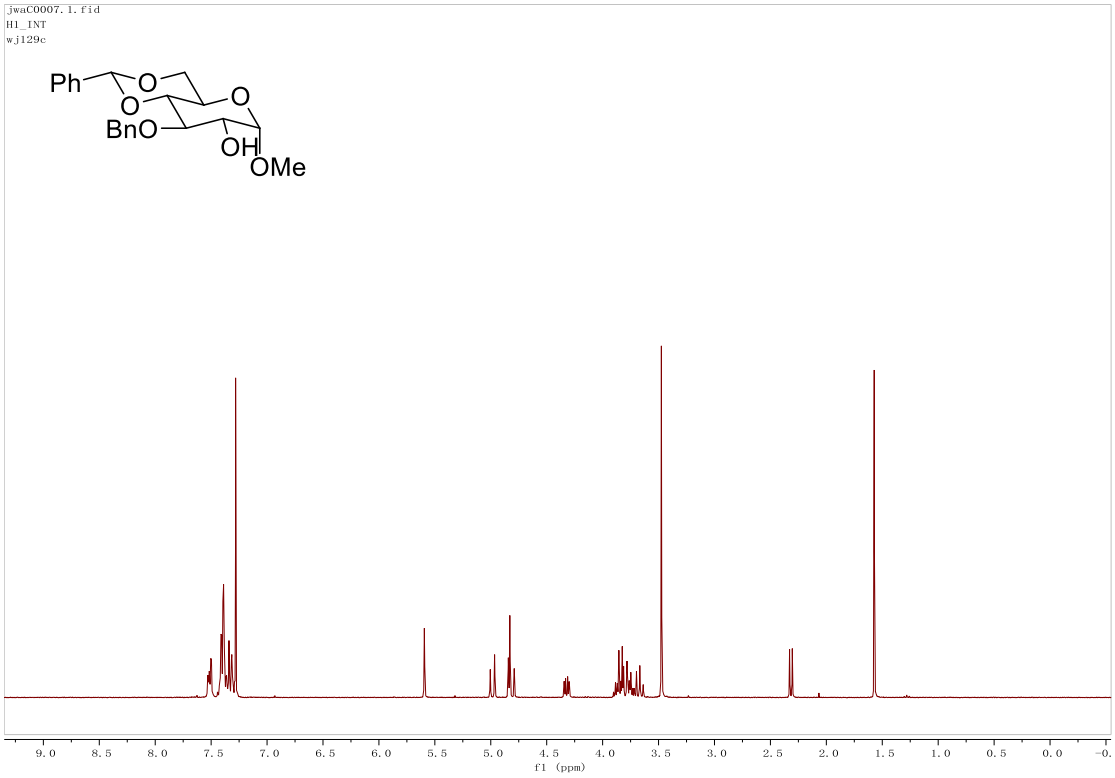
APCs (THP-1-CD1b cells) were pulsed for 4 h with different acyl forms of Ac_nPIMs (PIM_2, PIM_6, natural Ac_4PIM_2, natural Ac_3PIM_2, natural Ac_2PIM_2, synthetic Ac_2PIM_2, **Figure 3B**). After washing, APCs were plated (THP-1-CD1b, 5×10^4/well) and co-cultured overnight with T cells (5×10^4/well). Culture supernatants were then harvested, and cytokine release was measured by standard ELISA using antibodies specific for interferon-γ (IFN-γ).

[1] Bourdreux, Y.; Lemetais, A.; Urban, D.; Beau, J.-M., Iron(iii) chloride-tandem catalysis for a one-pot regioselective protection of glycopyranosides. *Chemical Communications* **2011,** *47* (7), 2146-2148.

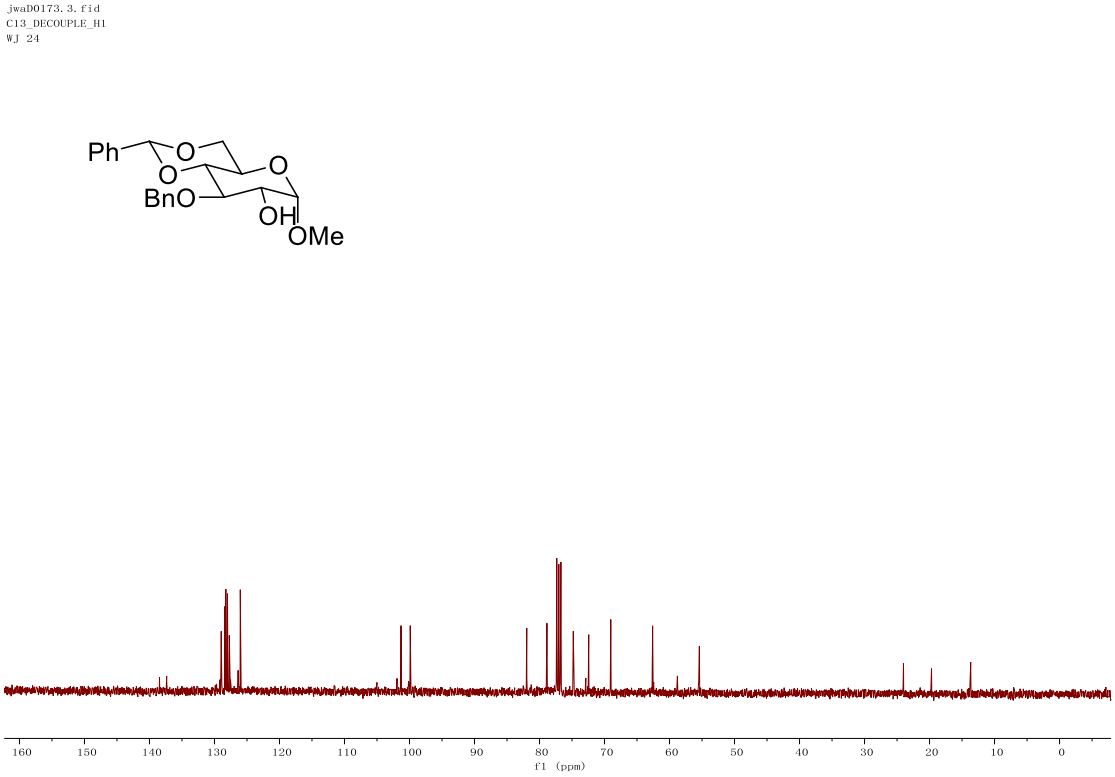
[2] Düffels, A.; Green, L. G.; Ley, S. V.; Miller, A. D., Synthesis of High-Mannose Type Neoglycolipids: Active Targeting of Liposomes to Macrophages in Gene Therapy. *Chemistry – A European Journal* **2000,** *6* (8), 1416-1430.

[3] Liu, X.; Stocker, B. L.; Seeberger, P. H., Total Synthesis of Phosphatidylinositol Mannosides of Mycobacterium tuberculosis. *Journal of the American Chemical Society* **2006,** *128* (11), 3638-3648.

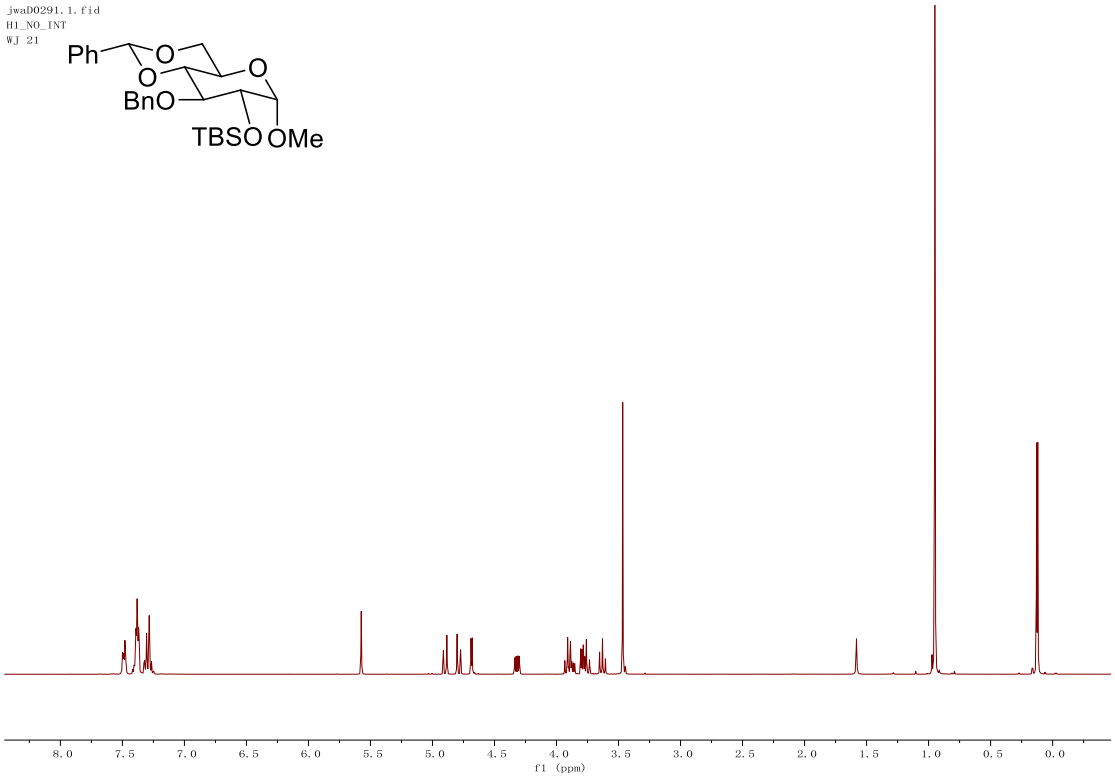
^{1}H NMR of Compound **4** (400MHz, $CDCl_3$)



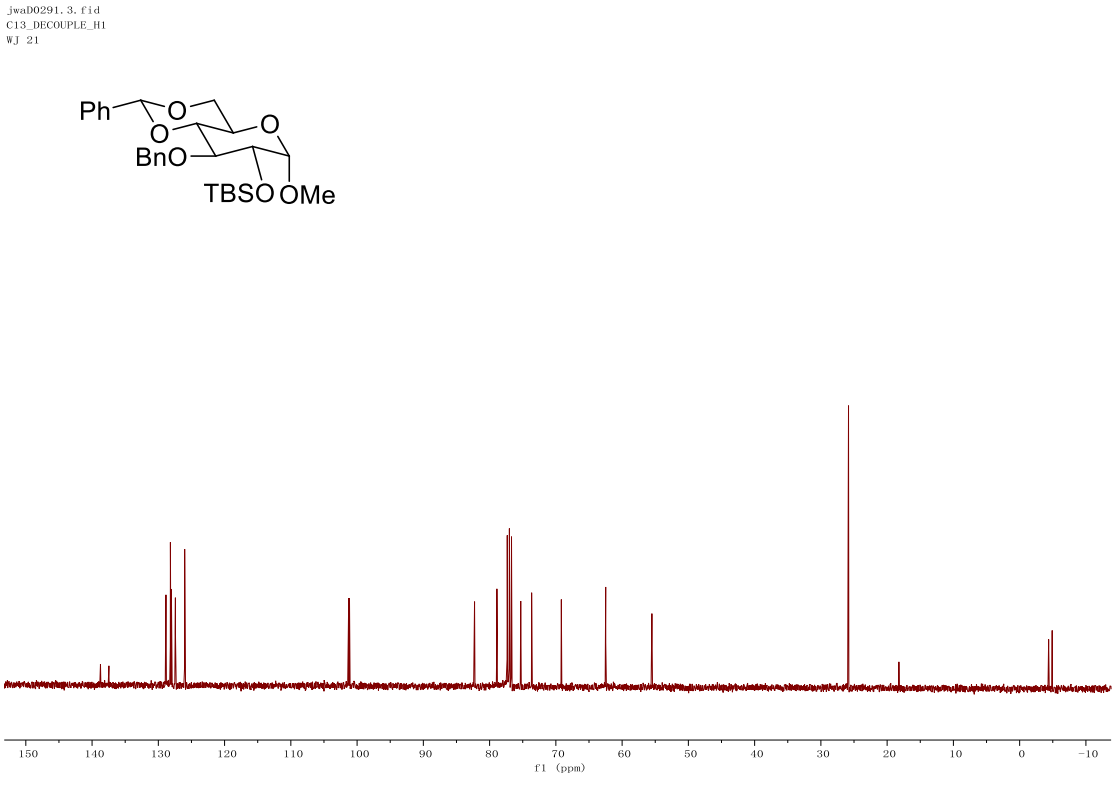
^{13}C NMR of Compound **4** (100MHz, $CDCl_3$)



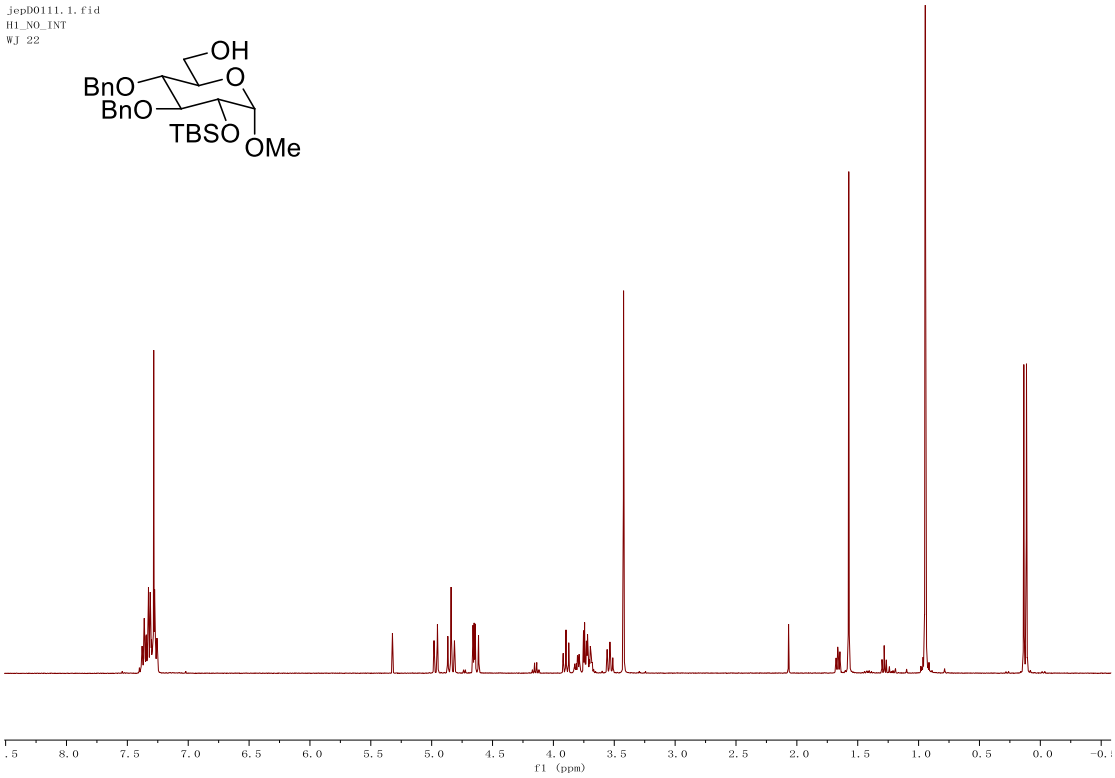
^{1}H NMR of Compound **5** (400MHz, $CDCl_3$)



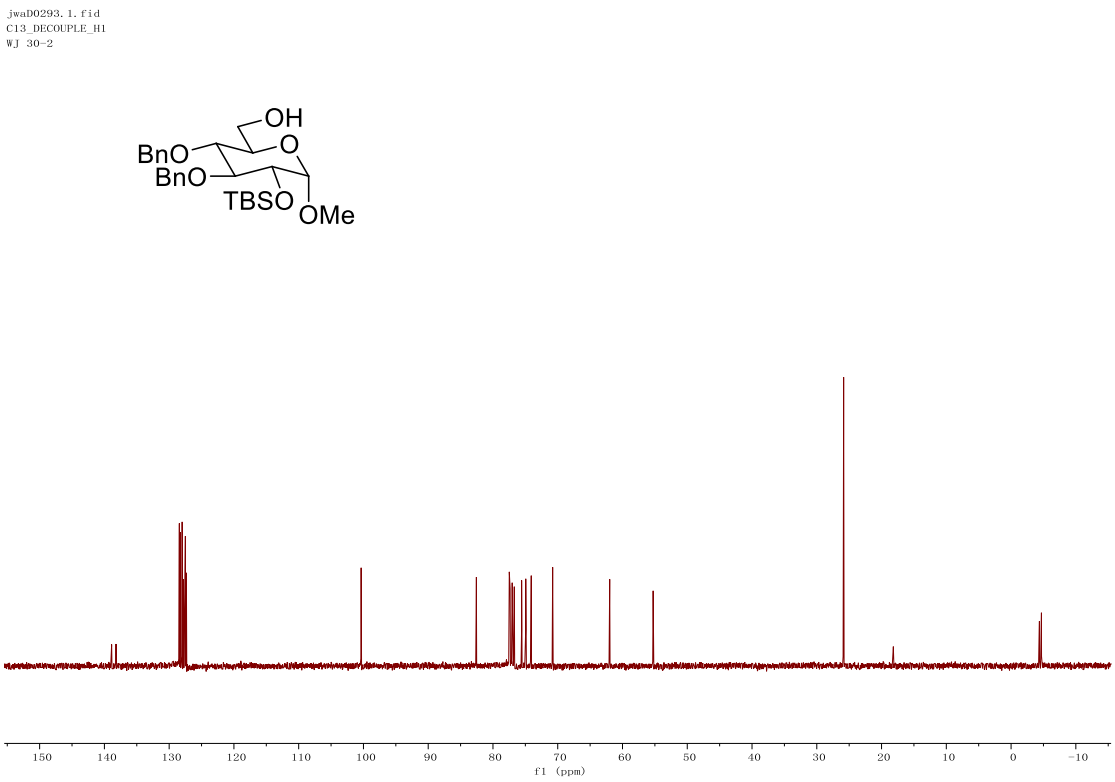
^{13}C NMR of Compound **5** (100MHz, $CDCl_3$)



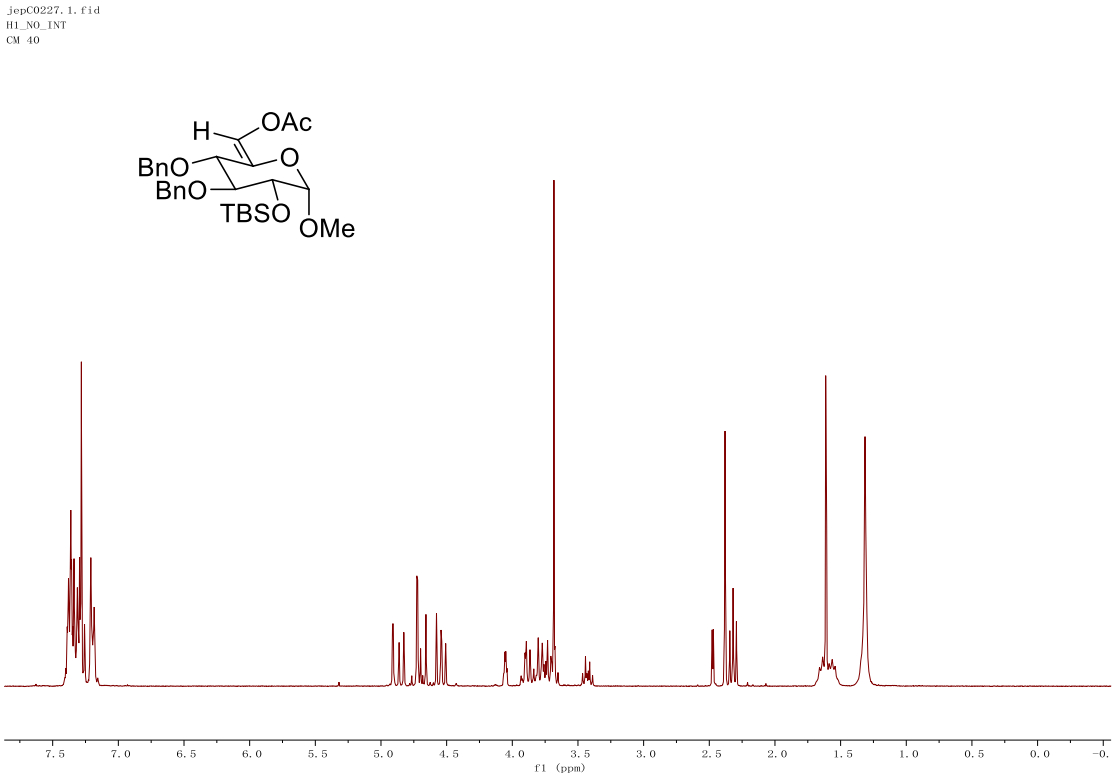
^{1}H NMR of Compound **6** (400MHz, $CDCl_3$)



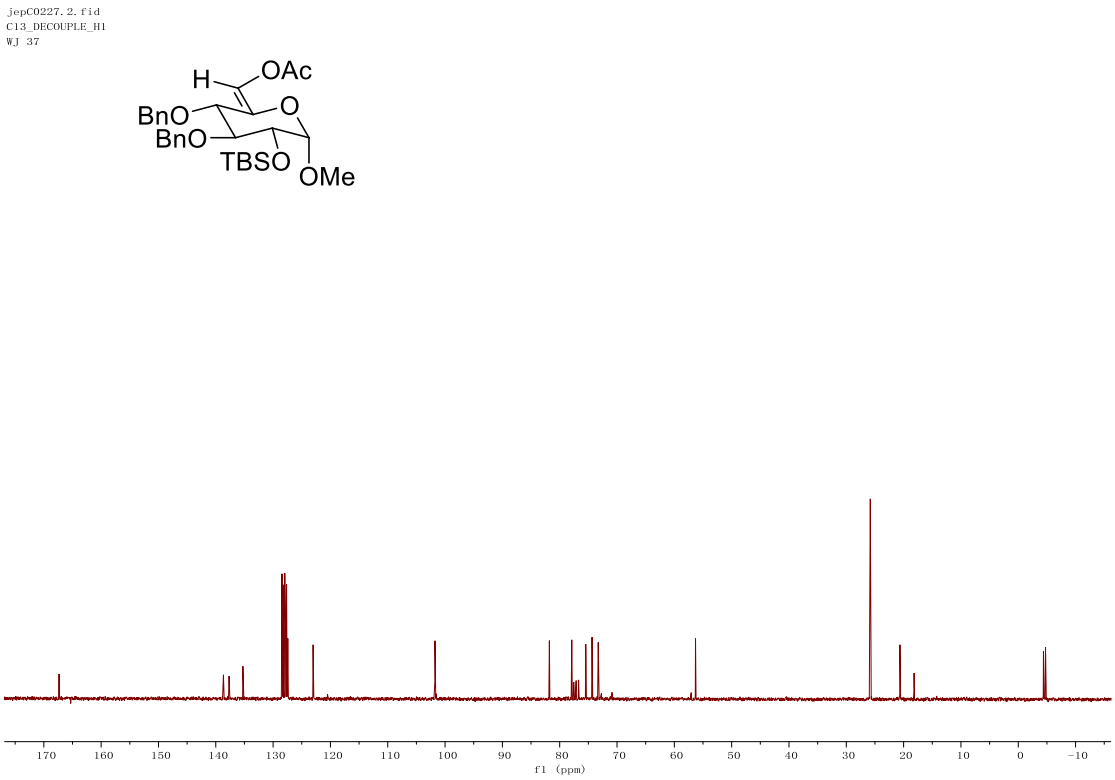
^{13}C NMR of Compound **6** (100MHz, $CDCl_3$)



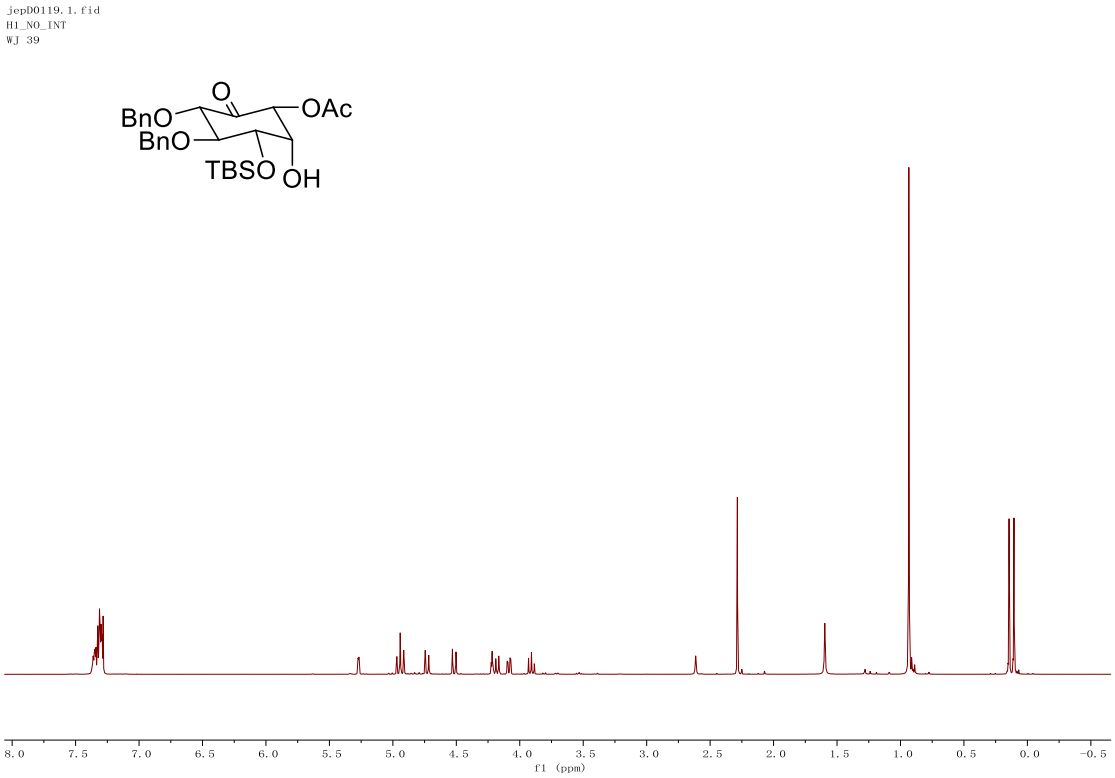
^{1}H NMR of Compound **8** (400MHz, $CDCl_3$)



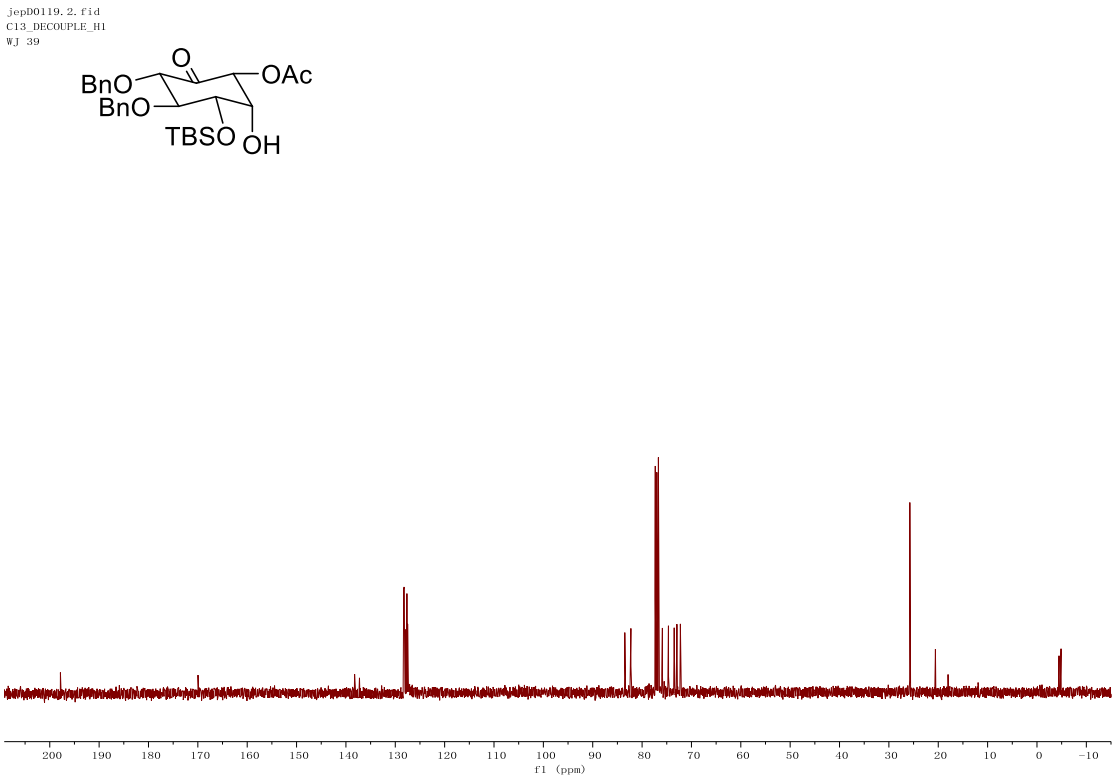
^{13}C NMR of Compound **8** (100MHz, $CDCl_3$)



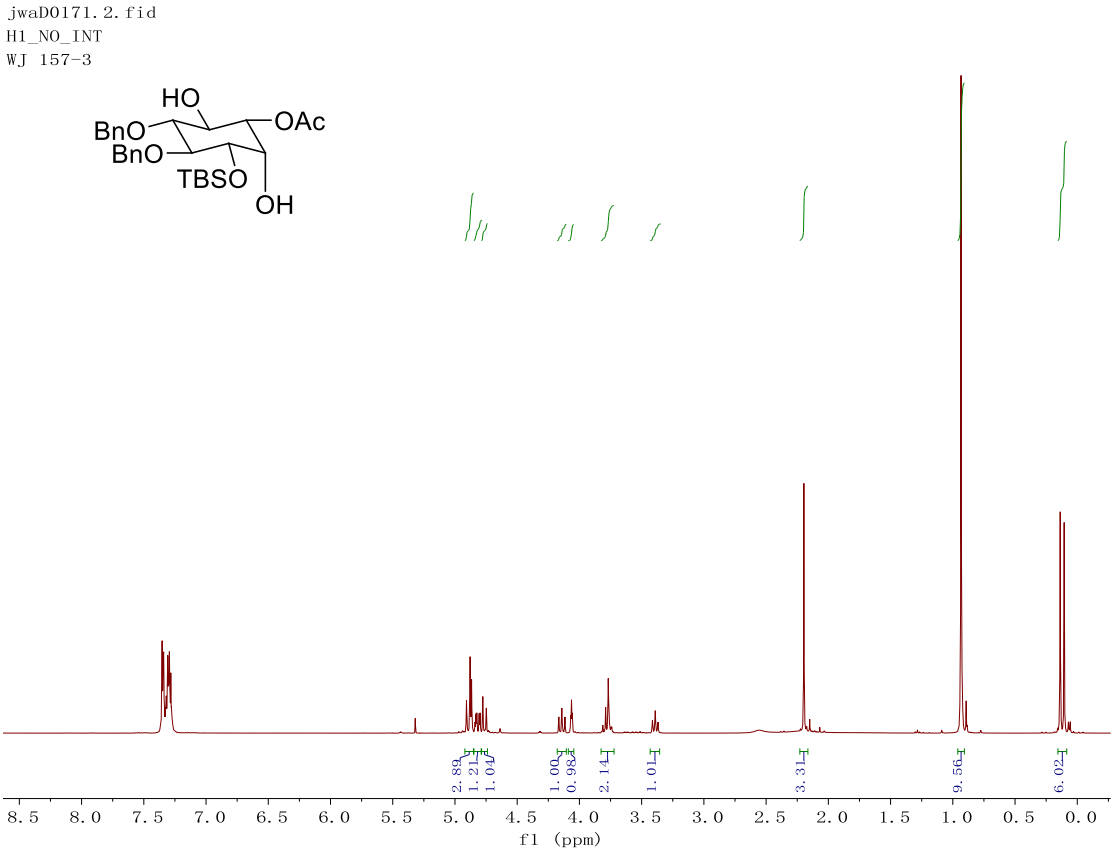
^{1}H NMR of Compound **9** (400MHz, $CDCl_3$)



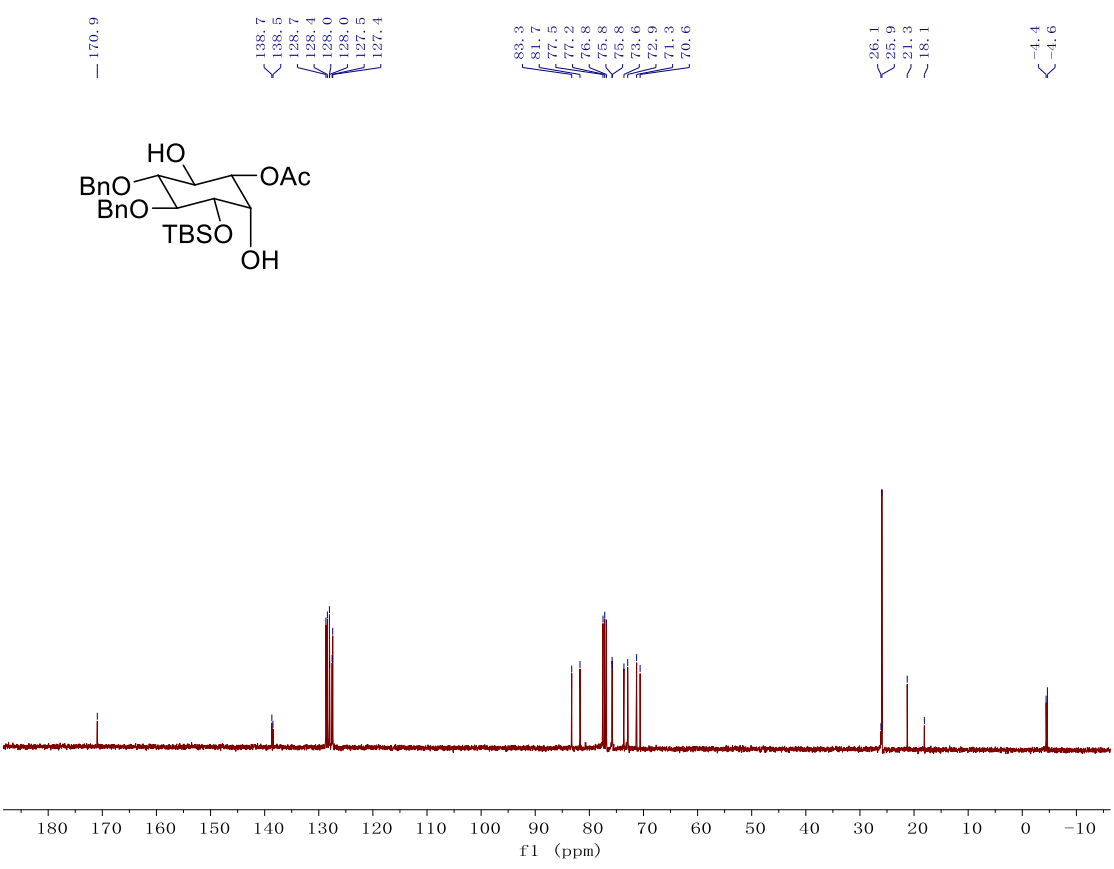
^{13}C NMR of Compound **9** (100MHz, $CDCl_3$)



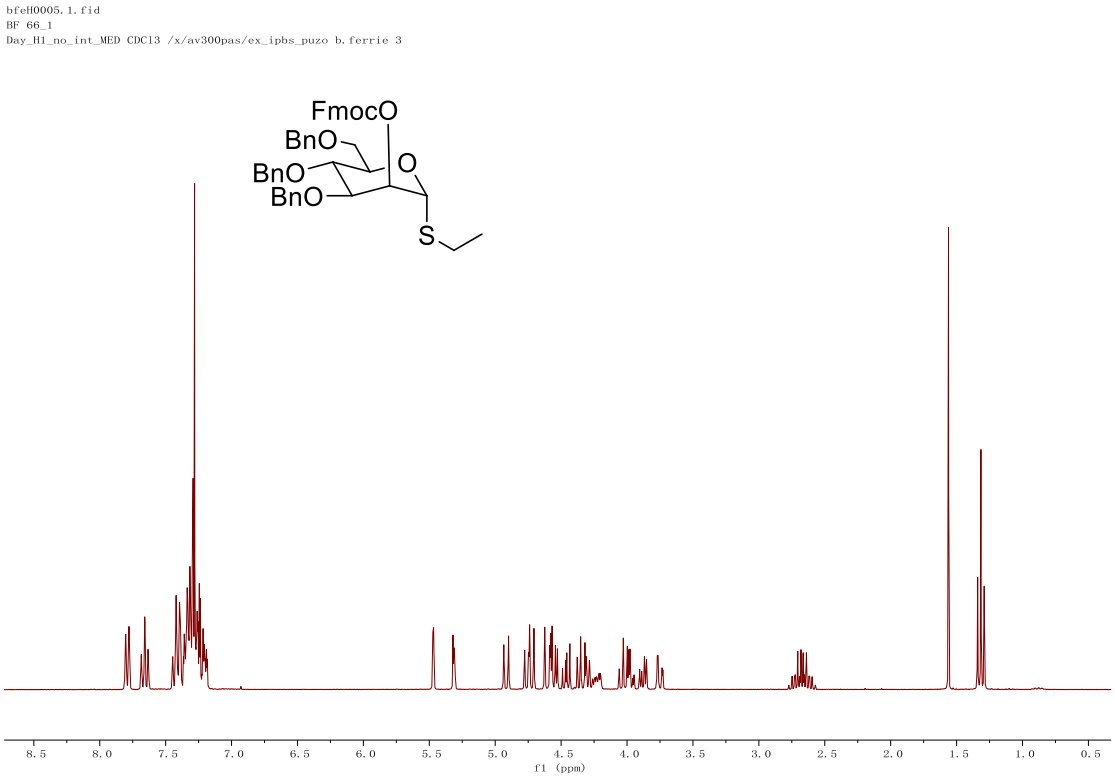
^{1}H NMR of building block **A** (400MHz, $CDCl_3$)



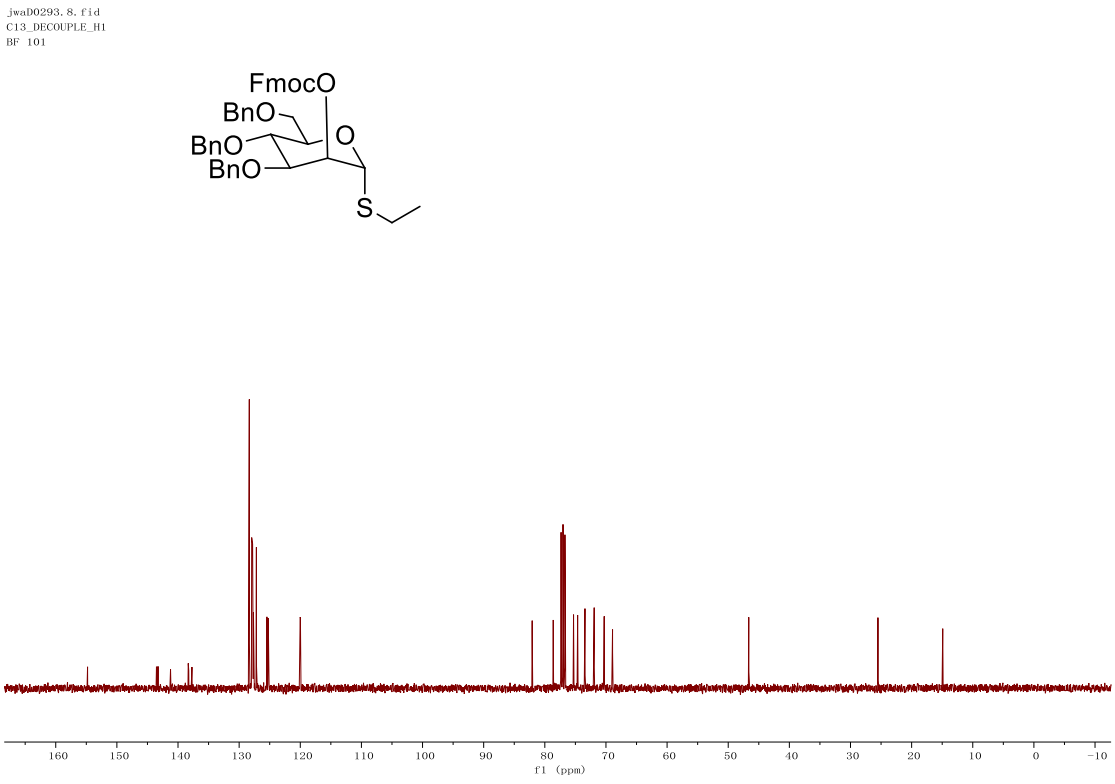
^{13}C NMR of building block **A** (100MHz, $CDCl_3$)



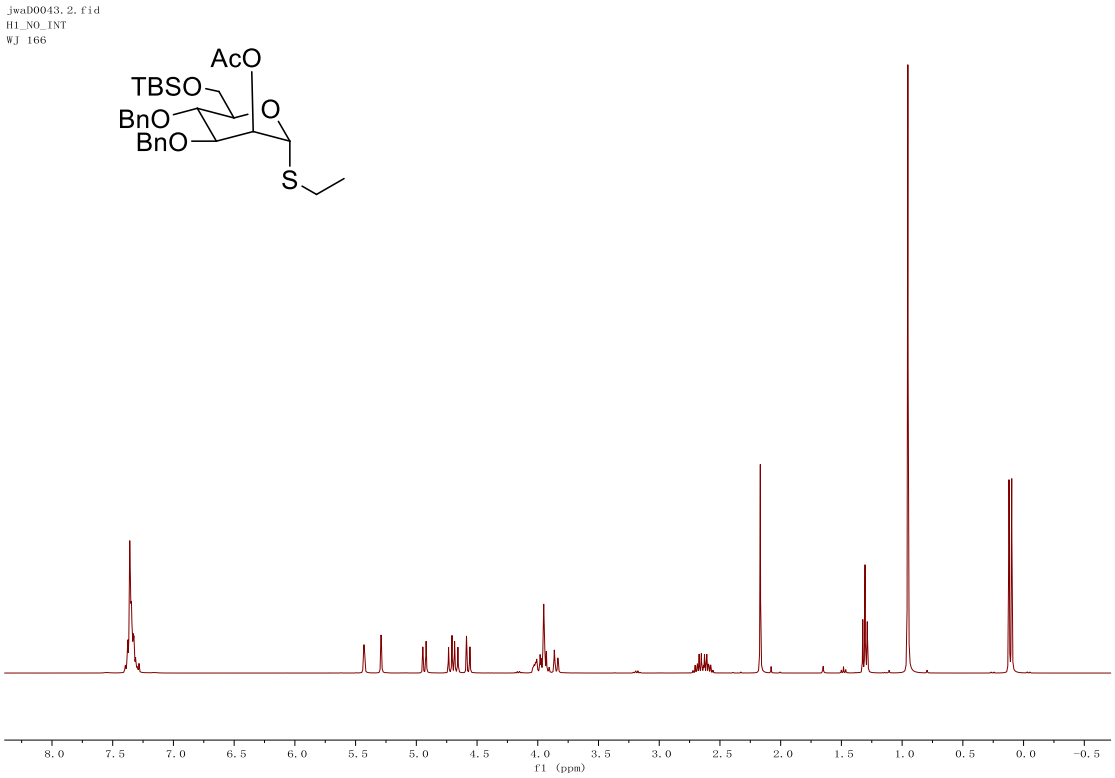
^{1}H NMR of building block **B1** (400MHz, $CDCl_3$)



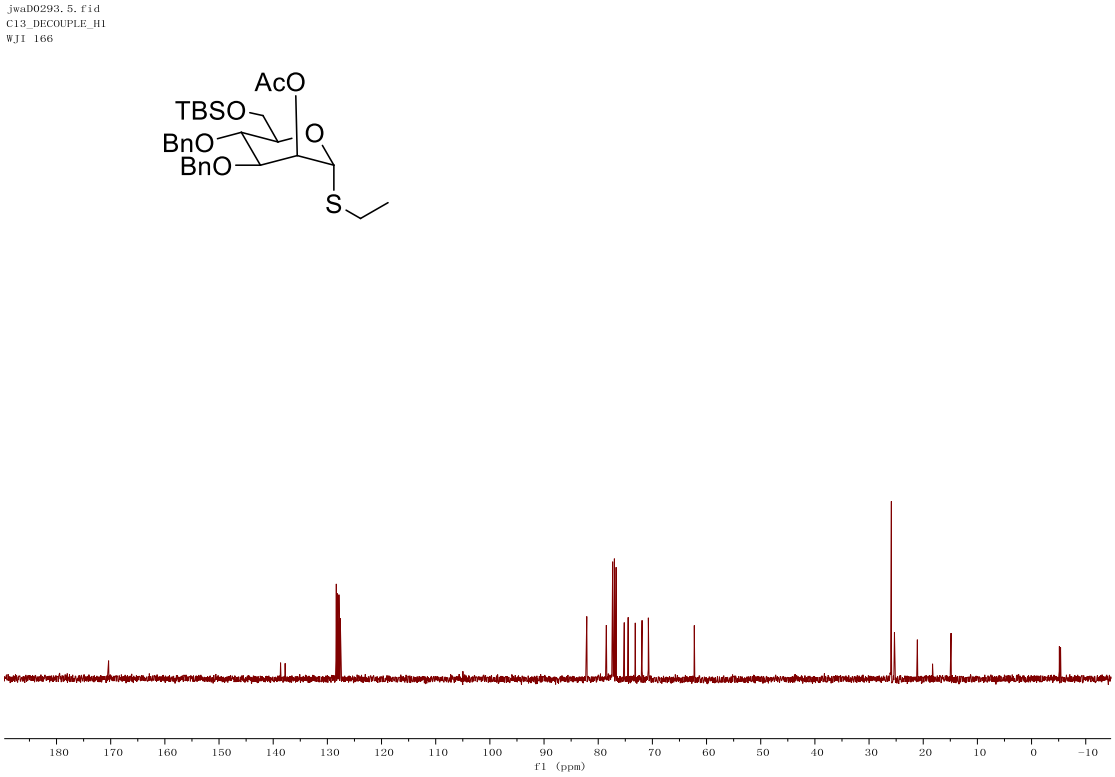
^{13}C NMR of buiding block **B1** (100MHz, $CDCl_3$)



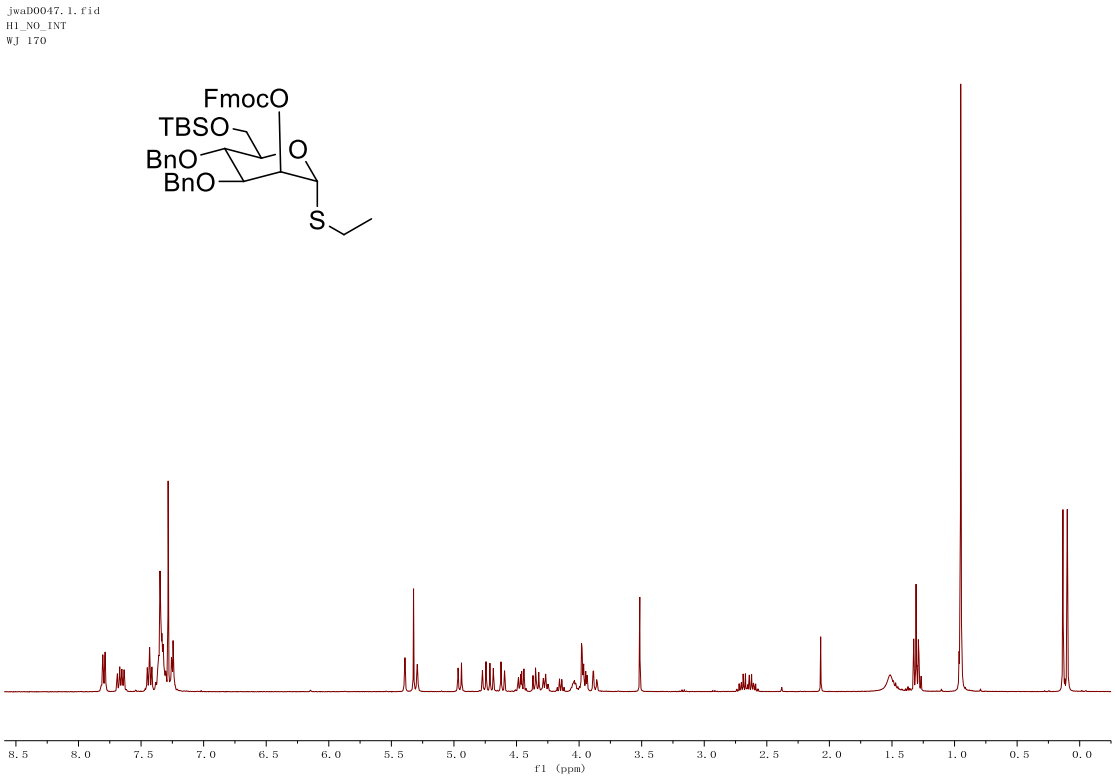
^{1}H NMR of Compound **16** (400MHz, $CDCl_3$)



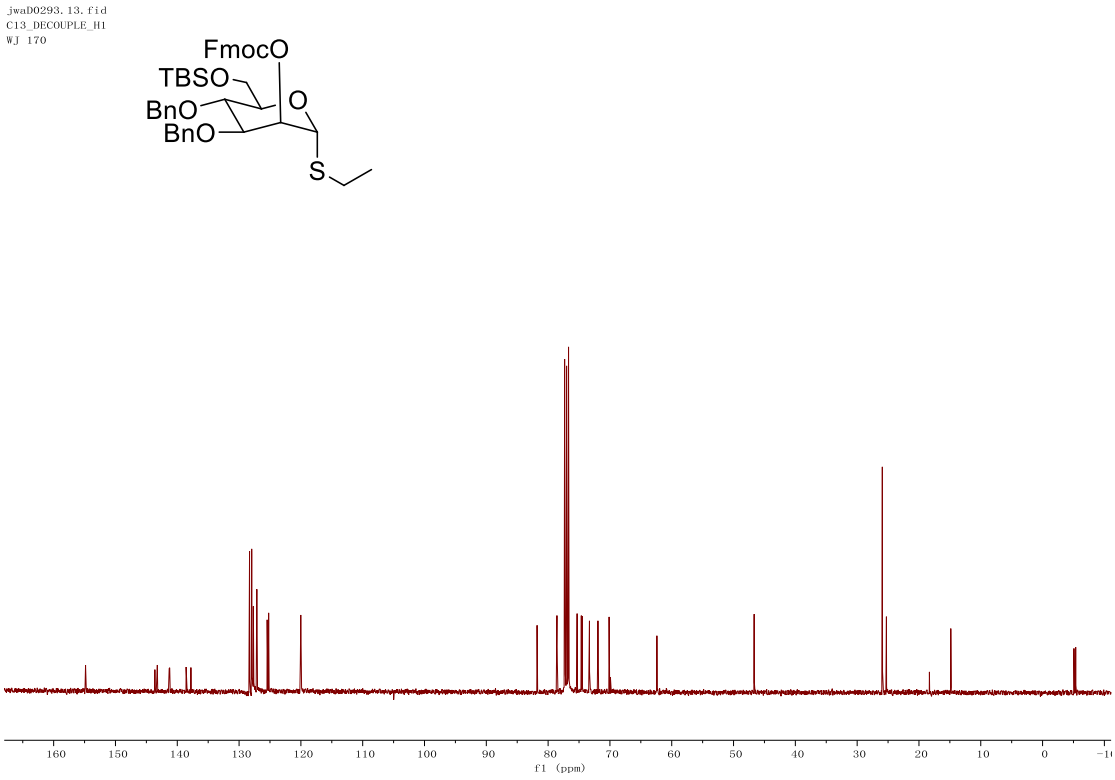
^{13}C NMR of Compound **16** (100MHz, $CDCl_3$)



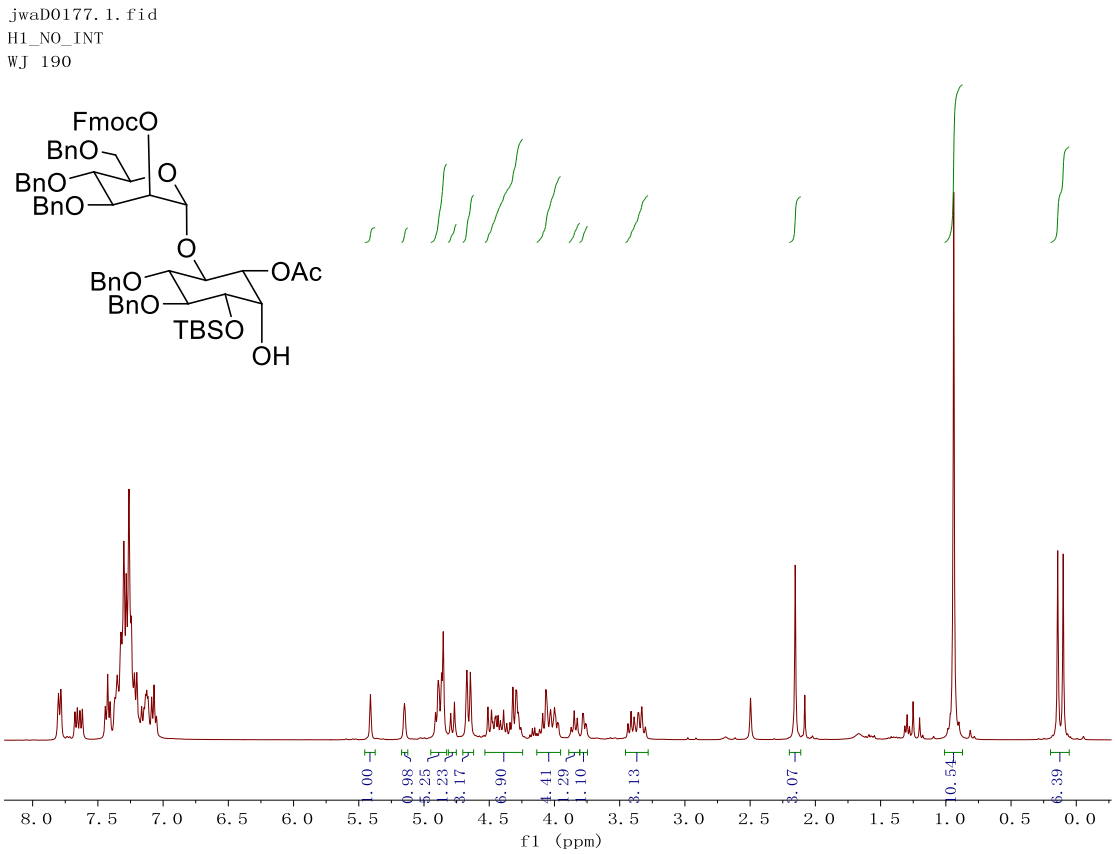
^{1}H NMR of building block **B2** (400MHz, $CDCl_3$)



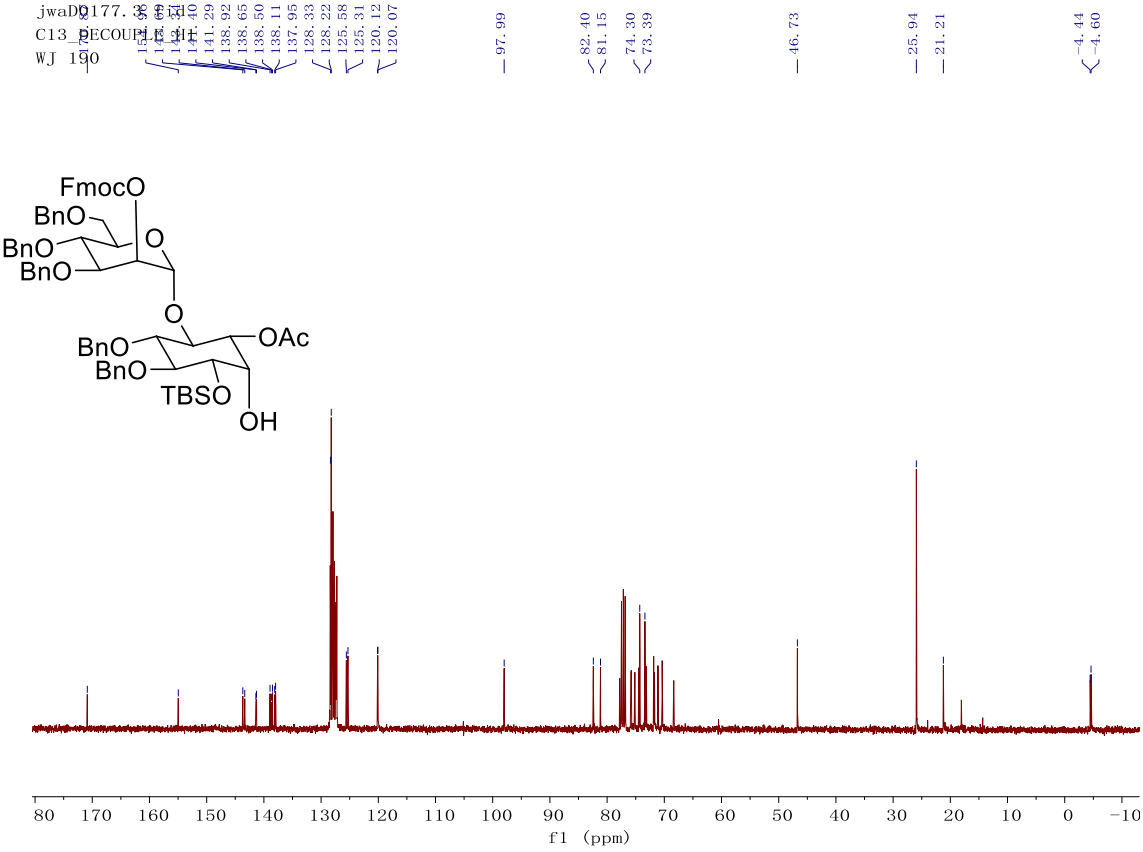
^{13}C NMR of building block **B2** (100MHz, $CDCl_3$)



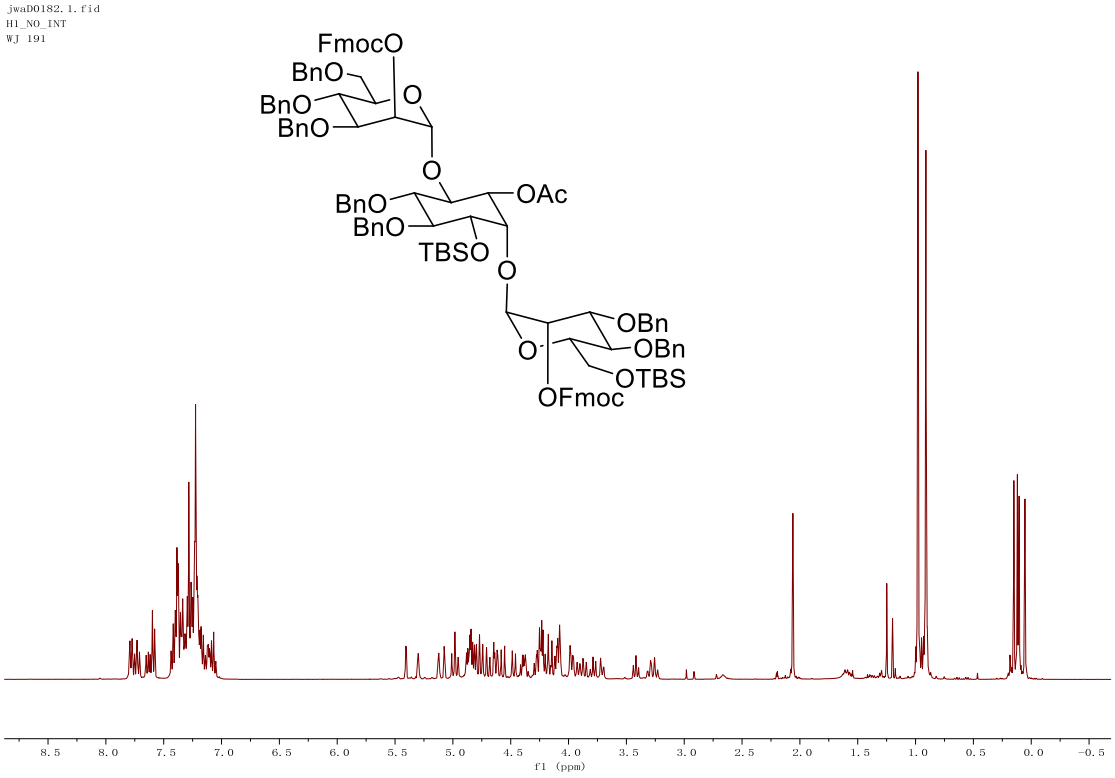
^{1}H NMR of Compound **20** (400MHz, $CDCl_3$)



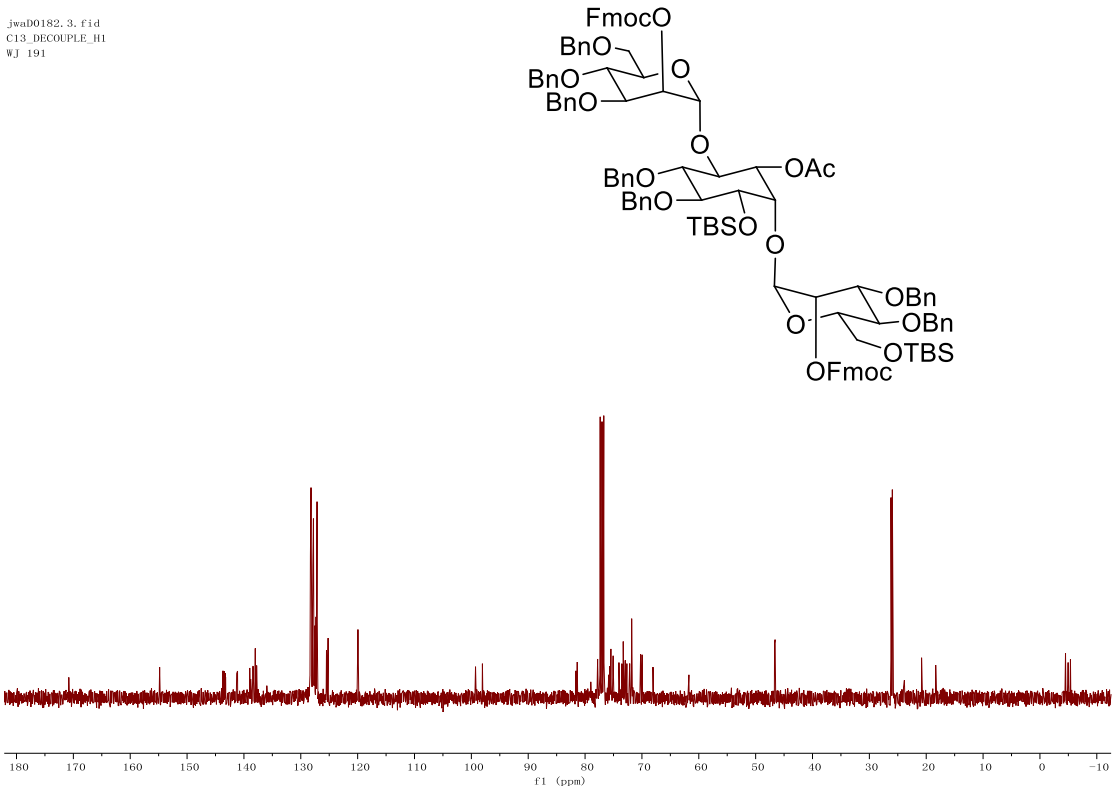
^{13}C NMR of Compound **20** (100MHz, $CDCl_3$)



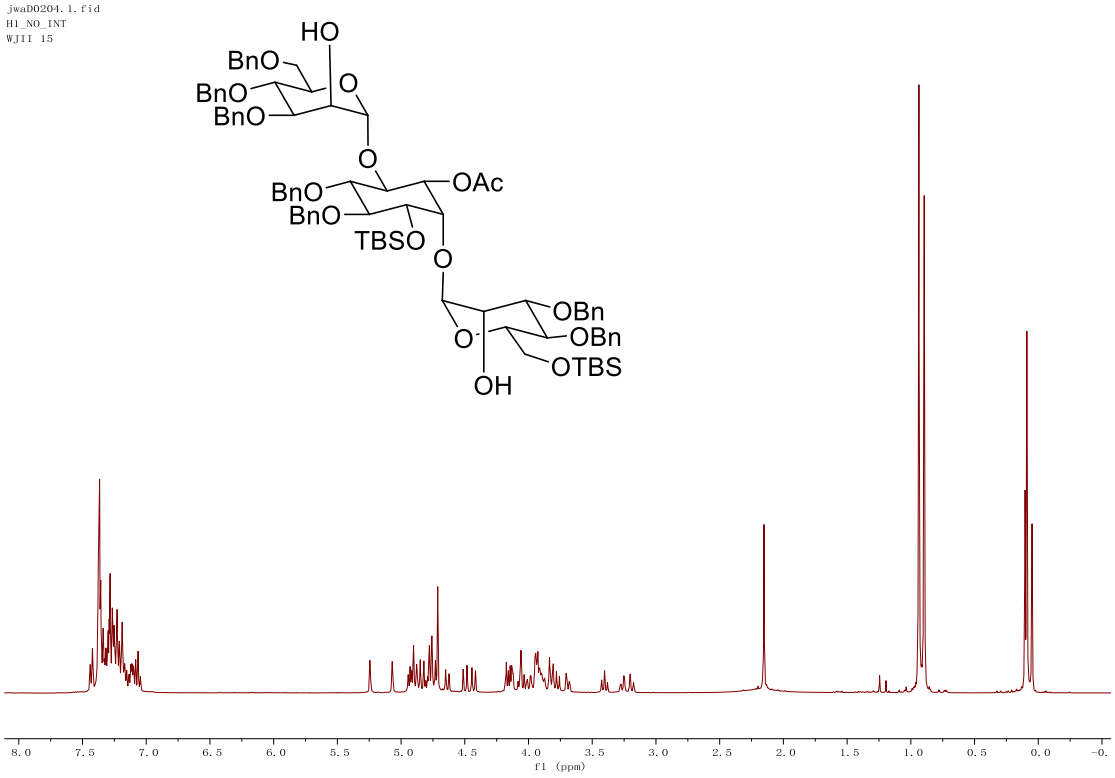
^{1}H NMR of Compound **21**(400MHz, $CDCl_3$)



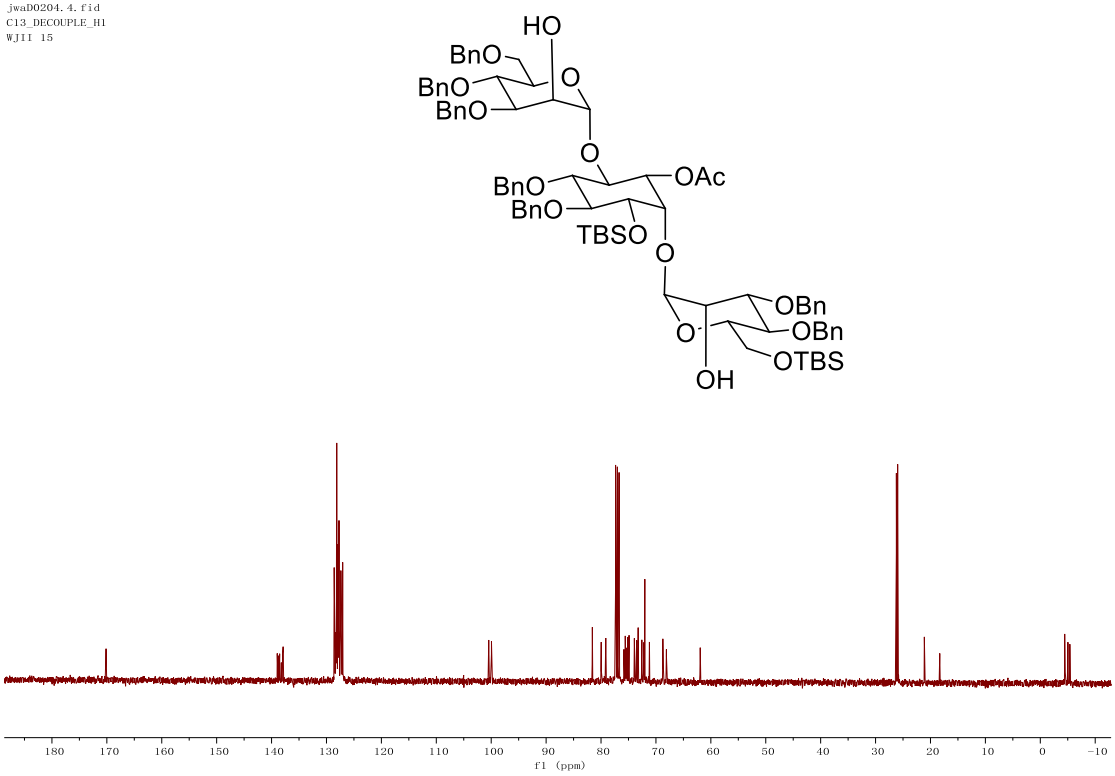
^{13}C NMR of Compound **21** (100MHz, $CDCl_3$)



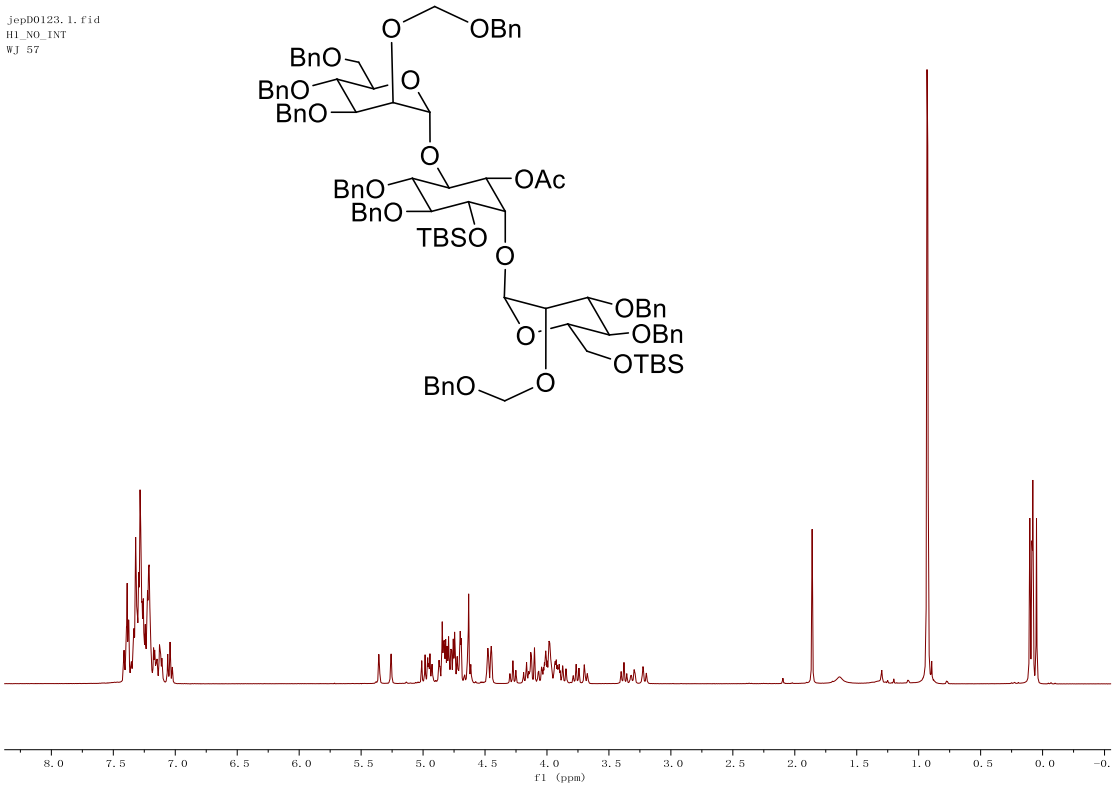
^{1}H NMR of Compound **22** (400MHz, $CDCl_3$)



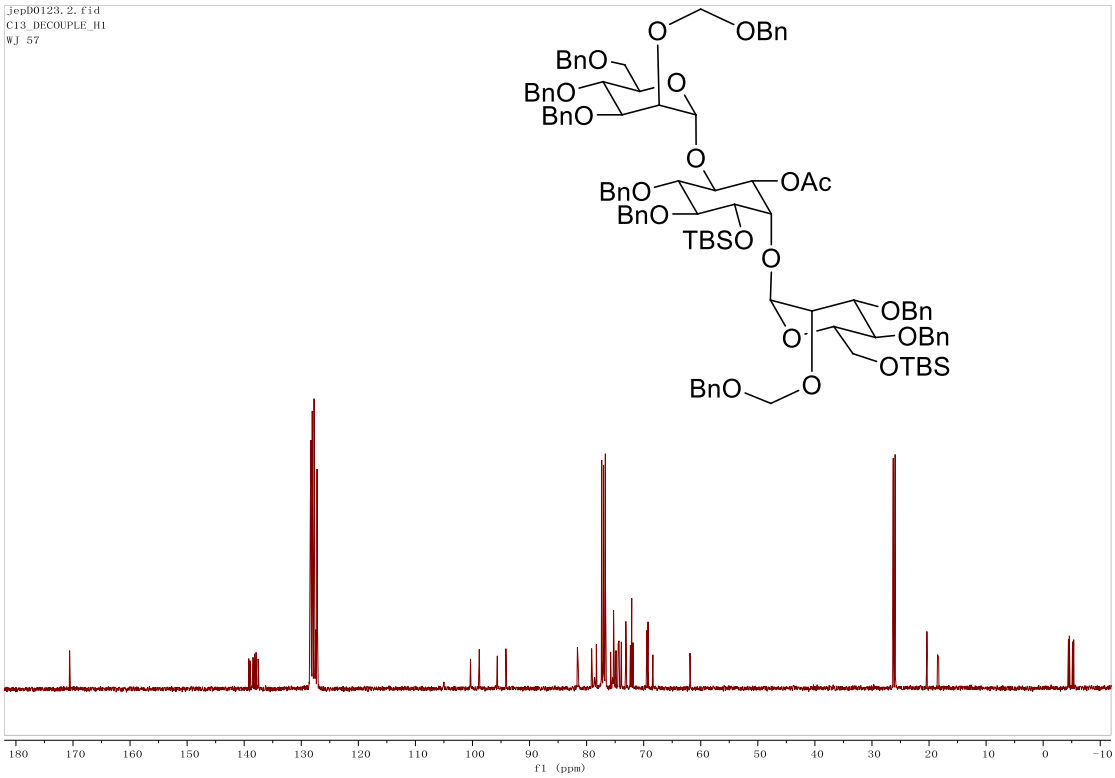
^{13}C NMR of Compound **22** (100MHz, $CDCl_3$)



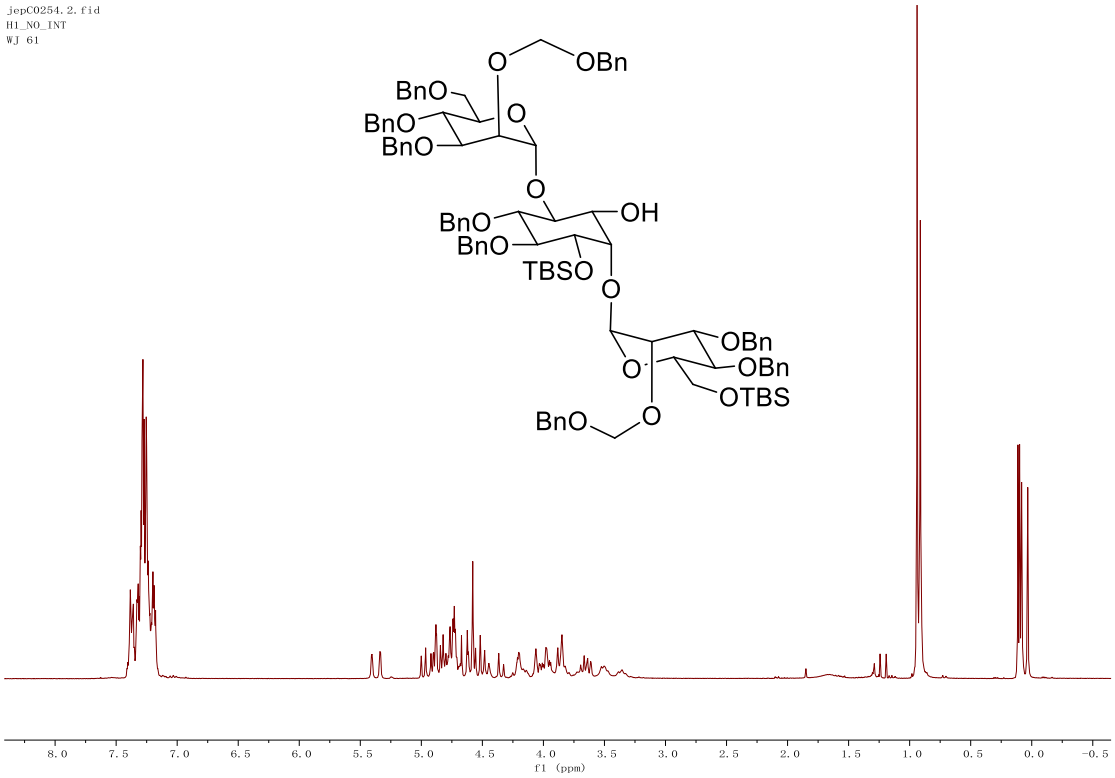
^{1}H NMR of Compound **23** (400MHz, $CDCl_3$)



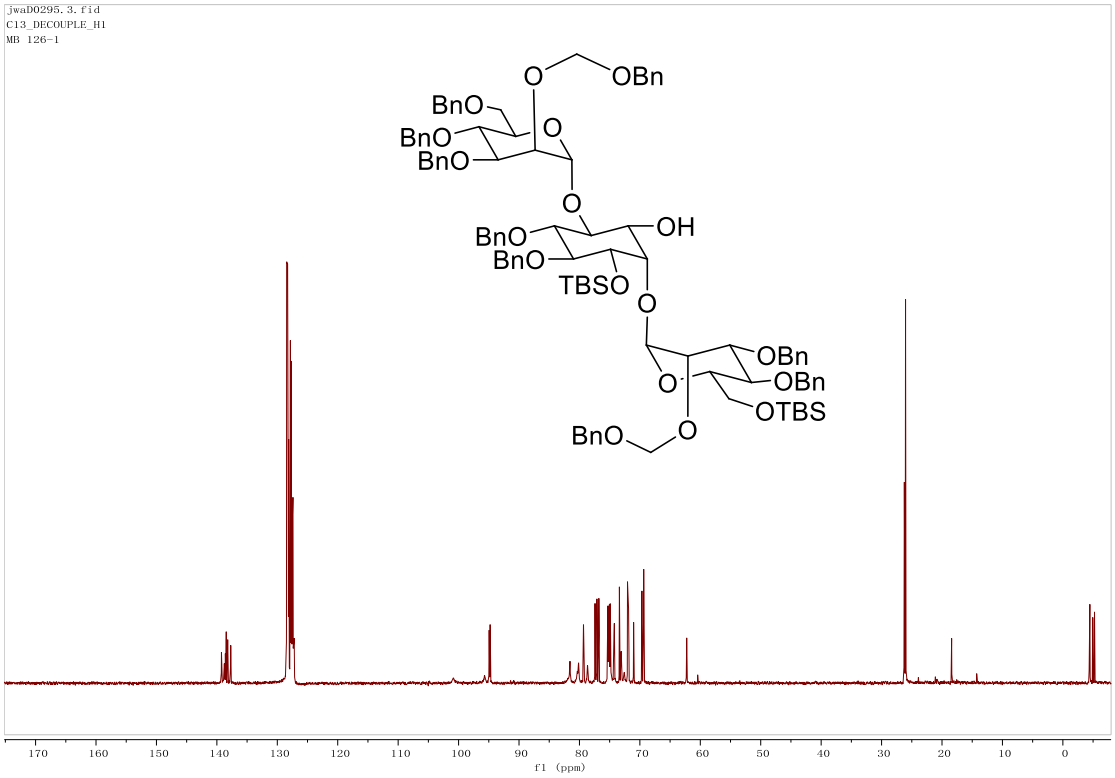
^{13}C NMR of Compound **23** (100MHz, $CDCl_3$)



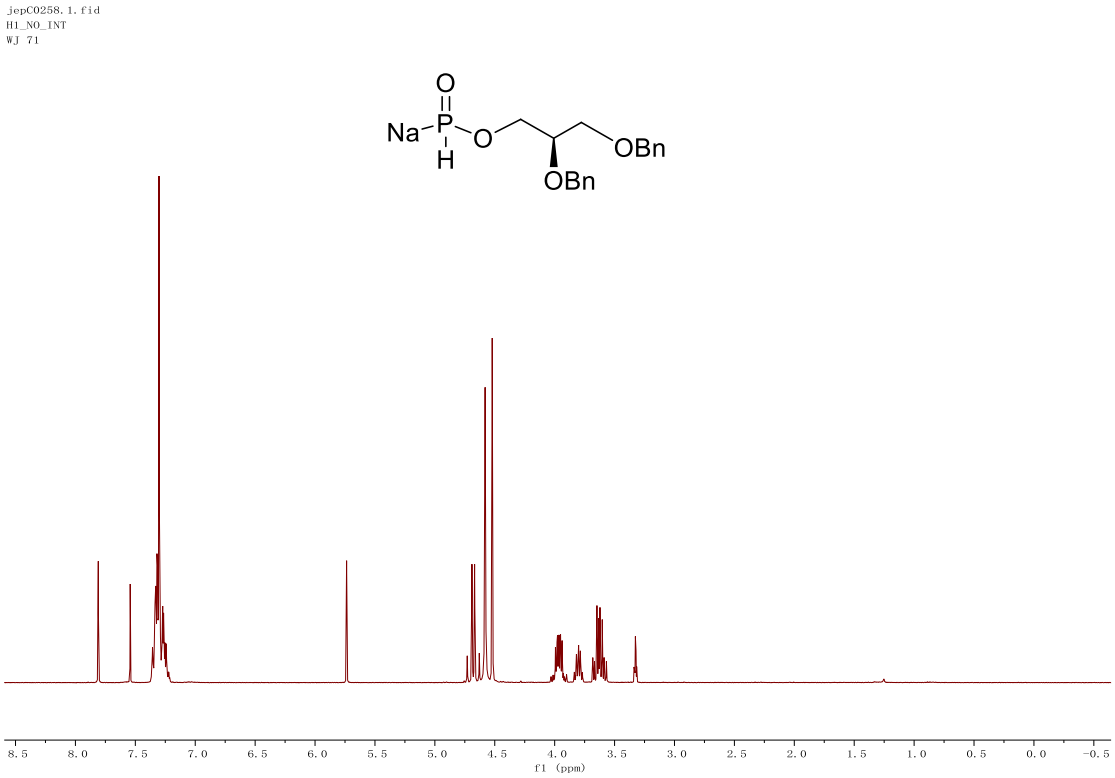
^{1}H NMR of Compound **24** (400MHz, $CDCl_3$)



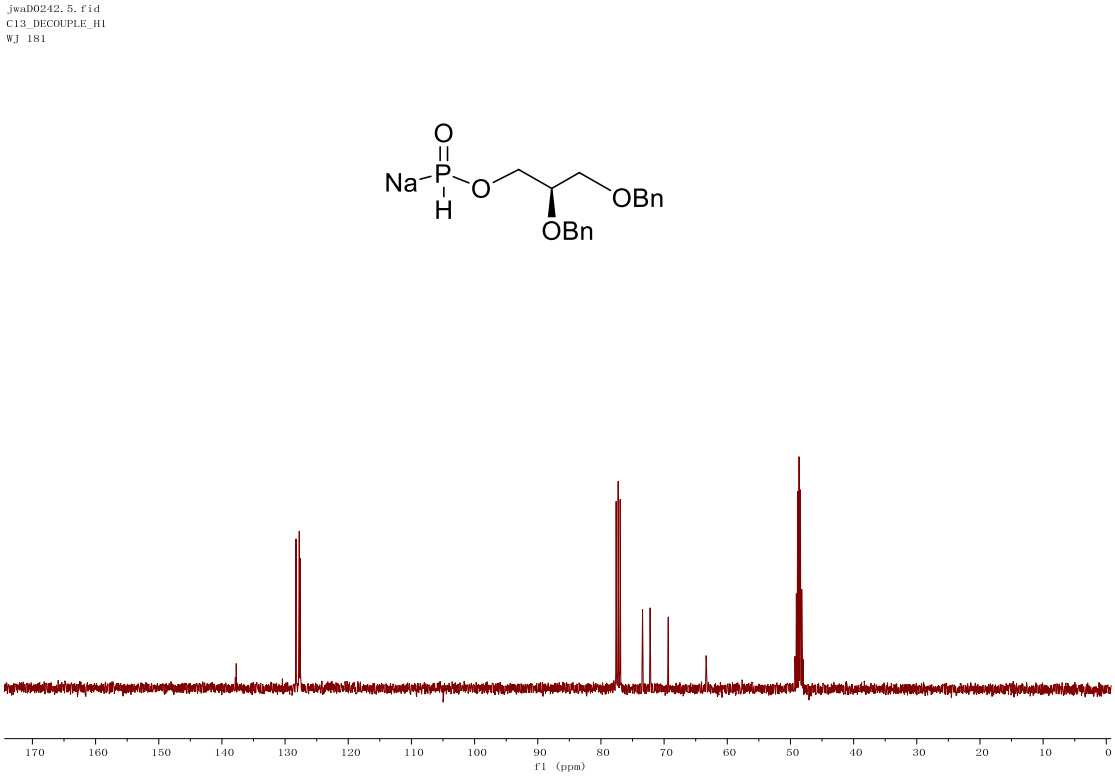
^{13}C NMR of Compound **24** (100MHz, $CDCl_3$)



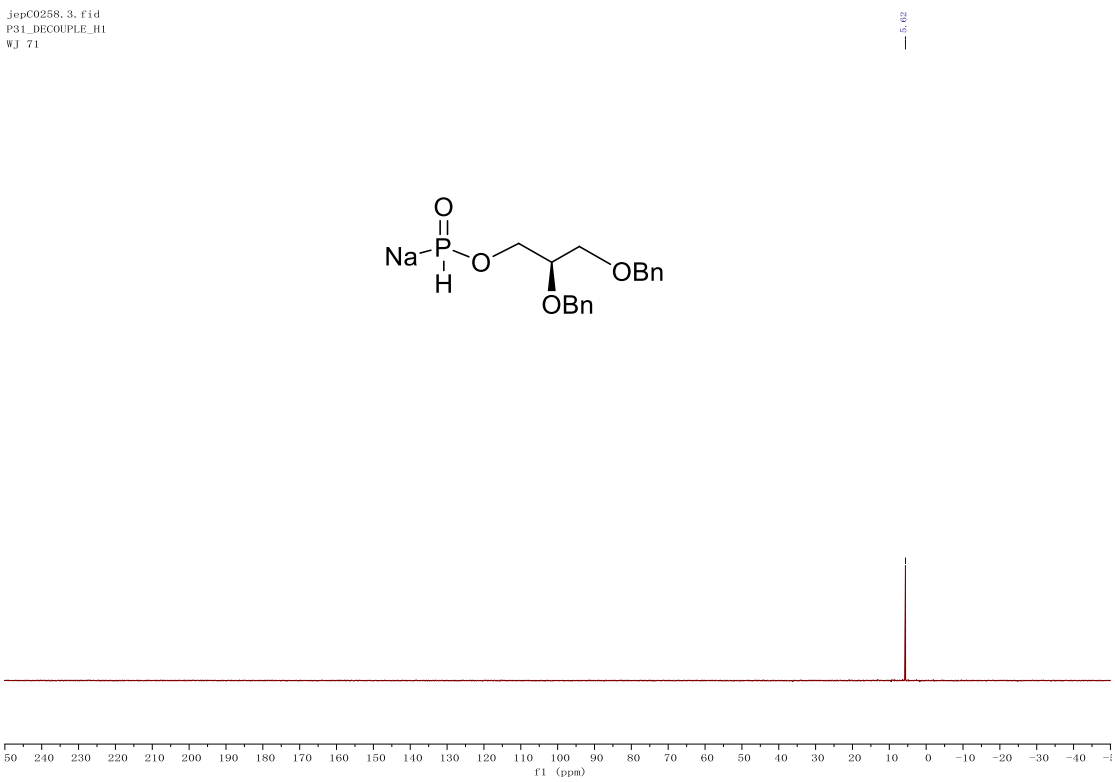
^{1}H NMR of building block **C** (300 MHz, $CDCl_3/CD_3OD$:3/1)



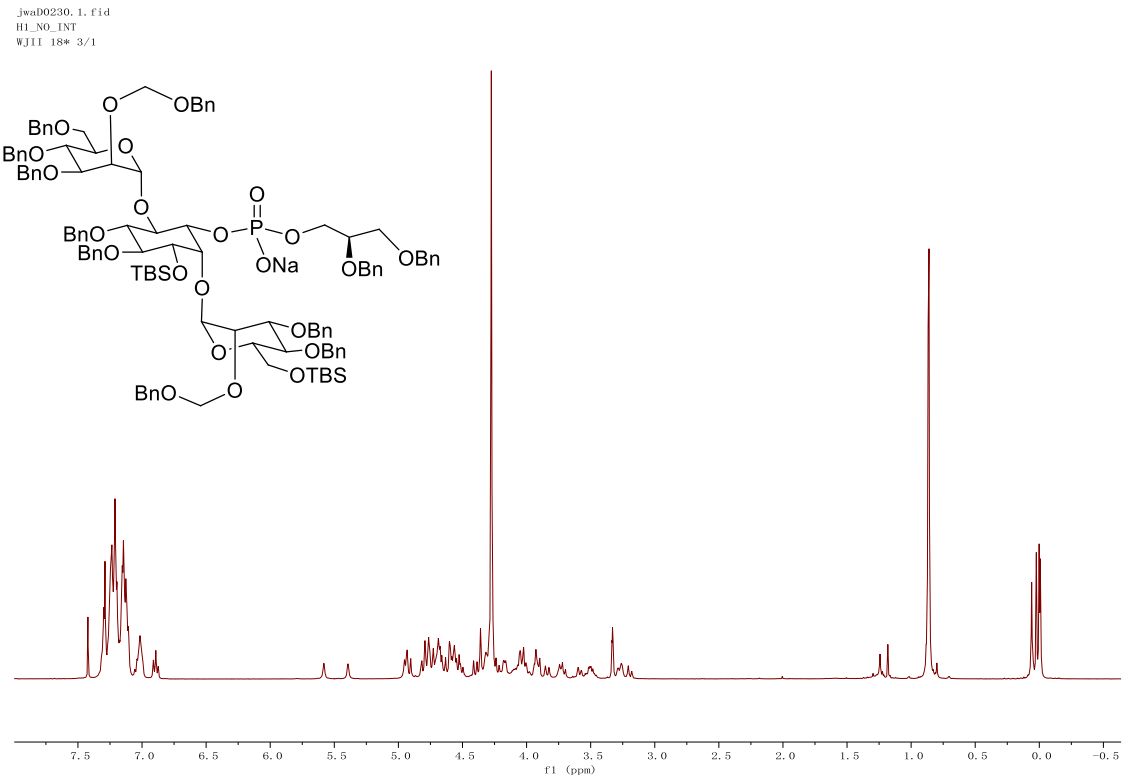
^{13}C NMR of building block **C** (100 MHz, $CDCl_3/CD_3OD$:3/1)



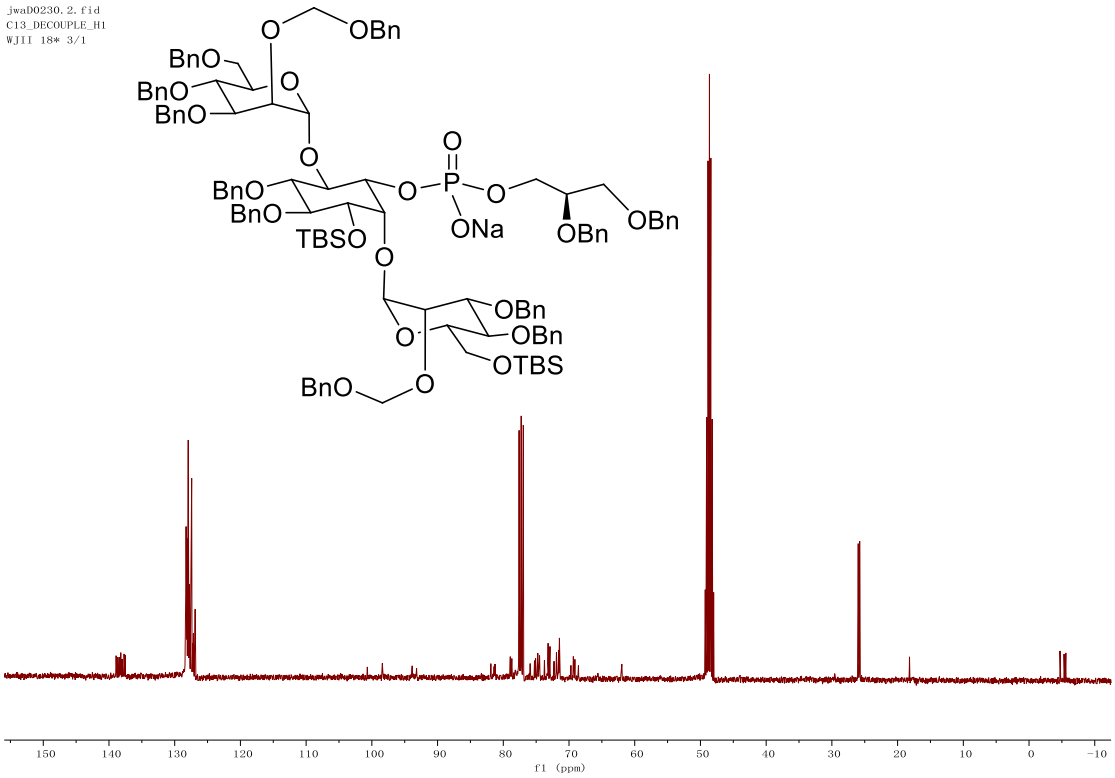
^{31}P NMR of building block **C** (121 MHz, $CDCl_3/CD_3OD$:3/1)



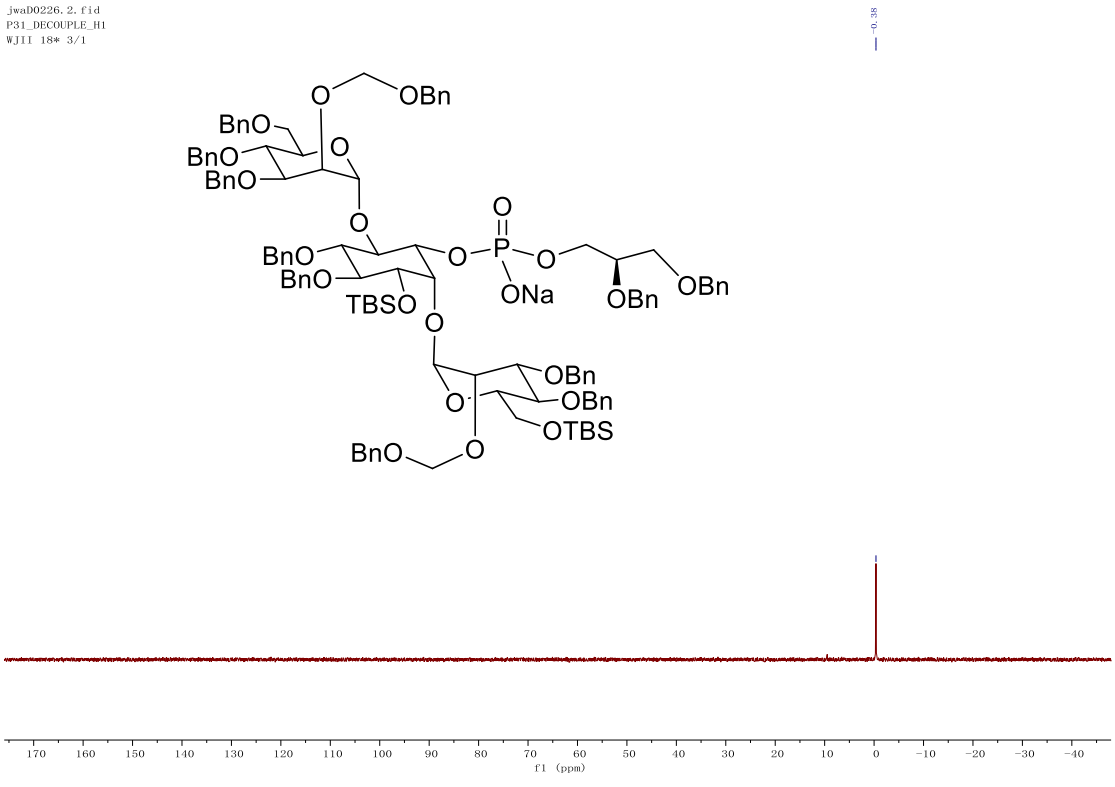
^{1}H NMR of compound **25** (400 MHz, $CDCl_3/CD_3OD$:3/1)



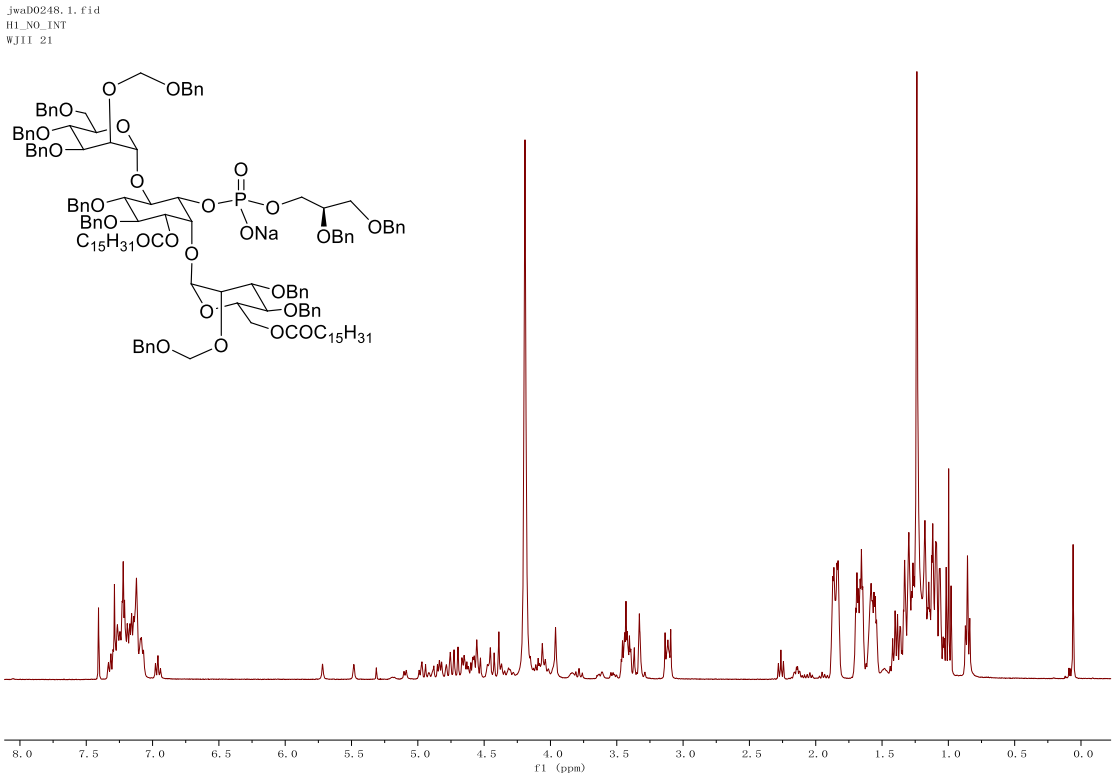
^{13}C NMR of Compound **25** (75 MHz, $CDCl_3/CD_3OD$:3/1)



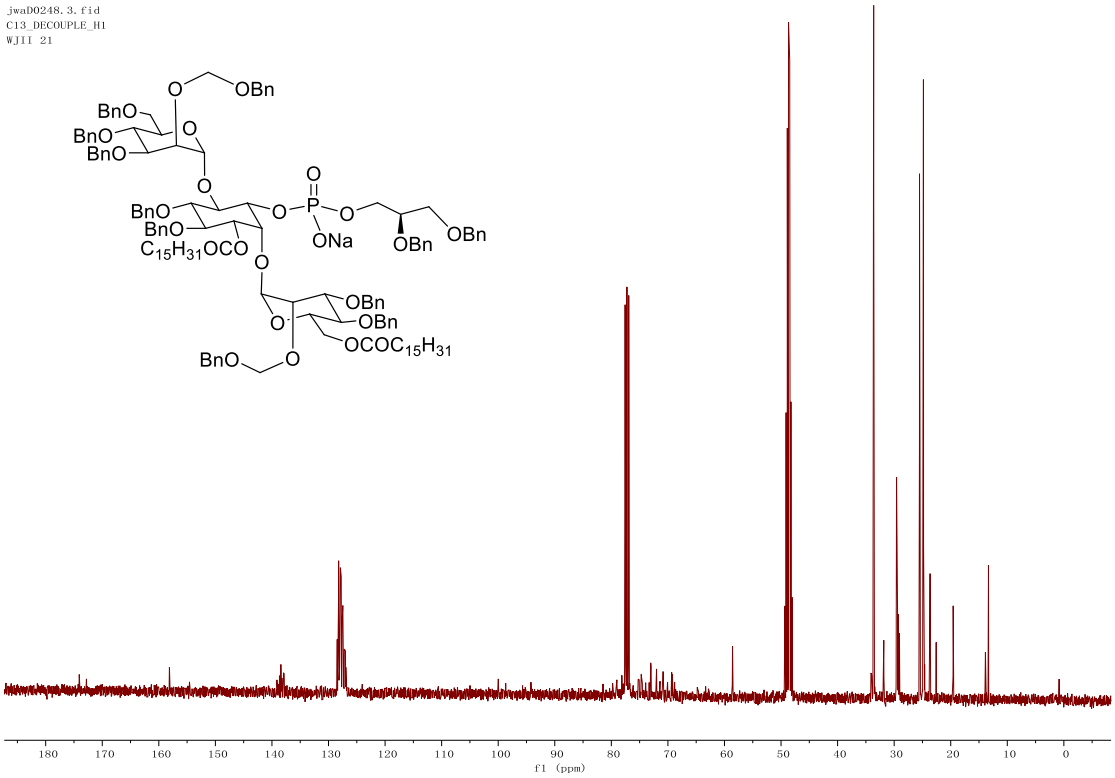
^{31}P NMR of Compound **25** (162MHz, $CDCl_3/CD_3OD$:3/1)



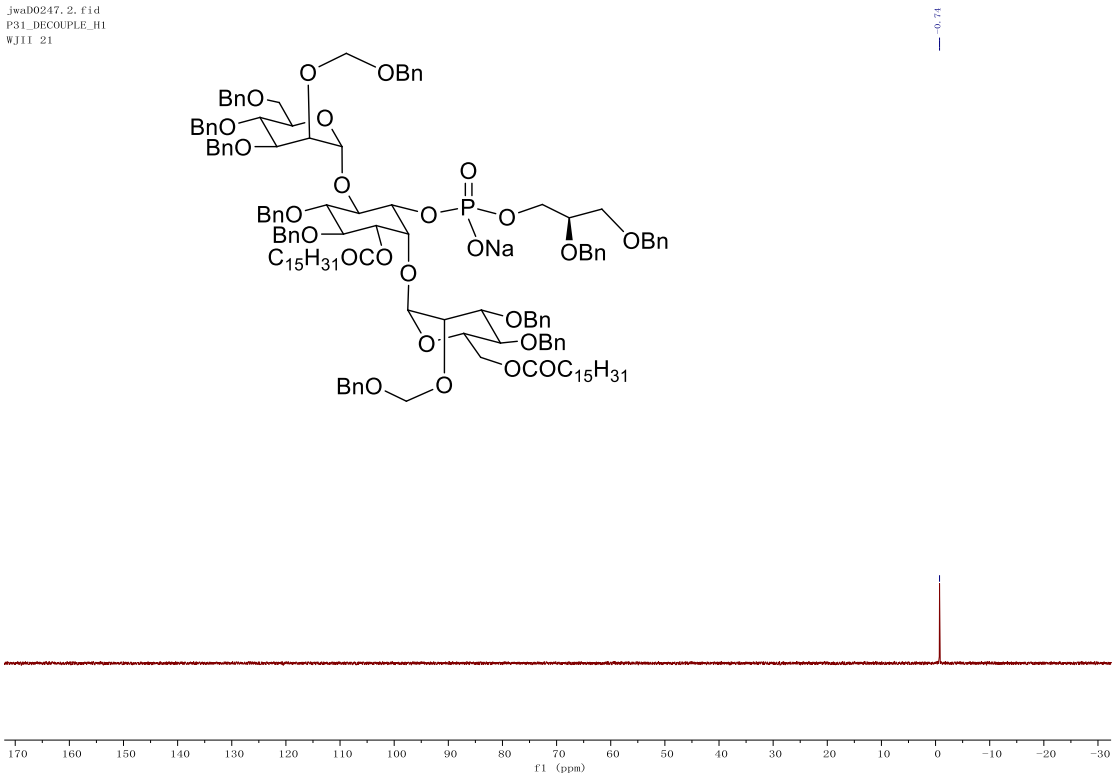
^{1}H NMR of compound **27** (400MHz, $CDCl_3/CD_3OD$:3/1)



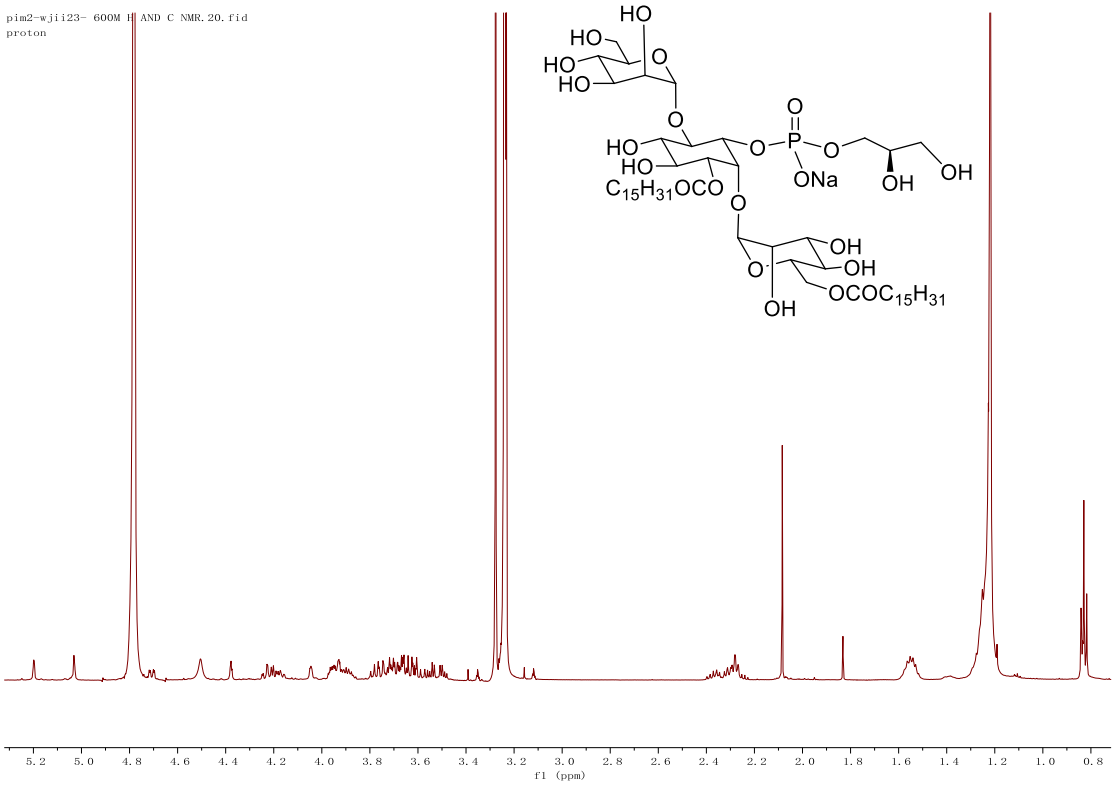
^{13}C NMR of Compound **27** (100MHz, $CDCl_3/CD_3OD$:3/1)



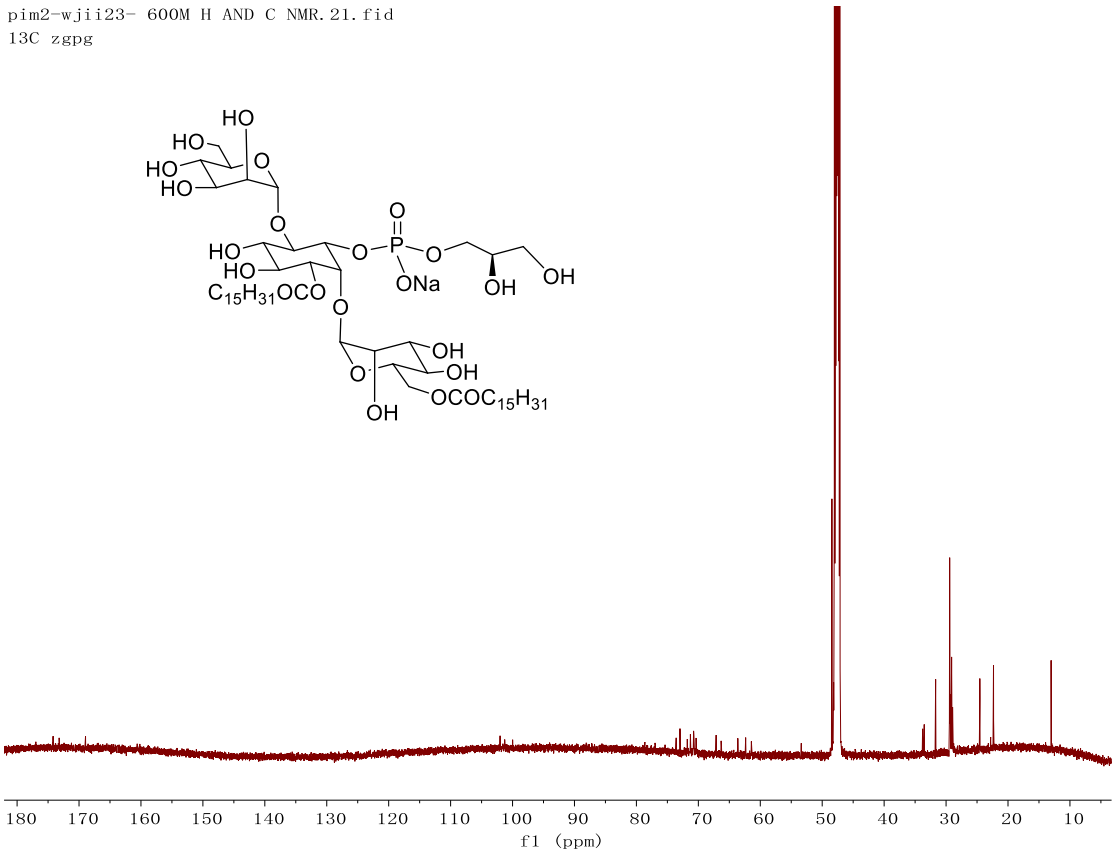
^{31}P NMR of Compound **27** (161MHz, $CDCl_3/CD_3OD$:3/1)



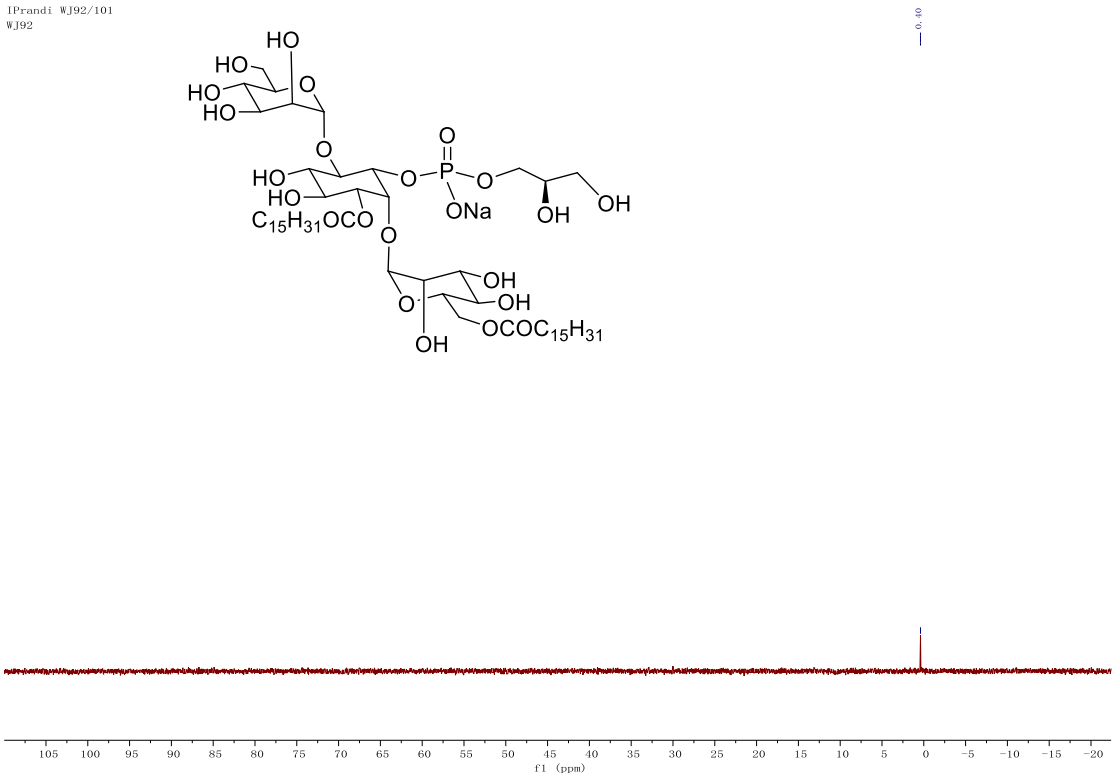
^{1}H NMR of synthetic **Ac_2PIM_2** (600MHz, CD_3OD)



^{13}C NMR of synthetic **Ac_2PIM_2** (600MHz, CD_3OD)



^{31}P NMR of synthetic **Ac_2PIM_2** (121MHz, CD_3OD)



HRMS of synthetic **Ac_2PIM_2**