Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A novel cobalt (0) alkyne complex assisted "capture and release" strategy for oligosaccharide rapid assembly

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Contents

1. General methods.

All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Dichloromethane was distilled over calcium hydride. Analytical TLC was performed on silica gel 60 F254 precoated on glass plates, with detection under UV (254 nm) and/or by staining with 5% concentrated sulfuric acid in EtOH. Column chromatography was performed employing silica gel (200–300 mesh).^{1}HNMR and ^{13}C NMR spectra were recorded on Advance spectrometers. Chemical shifts (in ppm) were referenced with tetramethylsilane (δ = 0 ppm) for ^{1}H NMR and CDCl3 (δ = 77.00 ppm) for ^{13}C NMR in deuterated chloroform. Mass spectra were measured using an autoflex MALDI-TOF with α-cyano-4-hydroxycinnamic acid (CHCA) as the matrix. High resolution mass spectrometry was performed on an FT-ICR mass spectrometer.

General procedures of glycosylations

The acceptor, donor and 4 Å molecular sieves (0.25 g per 1.0 mmol acceptor) were dissolved in dry DCM (1.0 mL per 30mg of donor) under an N_2 atmosphere at 0 °C. A catalytic amount of TMSOTf was then added slowly to the solution. The reaction mixture was stirred at ambient temperature for 30 min until TLC showed that the entire acceptor was converted to product. After the glycosylation was complete, the solution was neutralized with triethylamine and the molecular sieves were filtered through Celite.

General procedure of 2-O-Ac deprotection

The substrate was dissolved in MeOH (5 mL per 0.15 mmol) and a catalytic amount of MeONa was added. The pH value was adjusted to 9-10 and the mixture was stirred for 30min at ambient temperature until TLC showed that the reaction was complete. Cation exchange resin was added to neutralize the reaction mixture to pH=7. After filtration and concentration in vacuo, the mixture was dissolved in dry toluene and concentrated in vacuo three times to remove residual water.

General procedure of cobalt-alkyne complexation

To a solution of substrate in dry DCM was added $Co_2(CO)_8$ under an Ar atmosphere at room temperature. The mixture was stirred for 15min until TLC showed that the reaction was complete. After 20 min of constant oxygen agitation, the remainder $Co_2(CO)_8$ was oxidated and the solution was filtrated through celite and concentrated in vacuo to give crude product of cobalt-alkyne complex.

General procedure of loading step

A solution of cobalt-alkyne complex in anhydrous 1,4-dioxane (5ml per 200mg resin) was concussed with ultrasonic under constant Argon agitation for 20min. Polystyrenediphenylphosphine (1.6 mmol/g) was suspended in solution at ambient temperature under an Ar atmosphere for 20min until the resin was completely swelled. The mixture was heated to 85^{o}C and vibrated in a shaking water bath for 1h until the liquid phase became colorless. The loaded resin was filtered out and dried in vacuum to give loaded resin as dark purple beads.

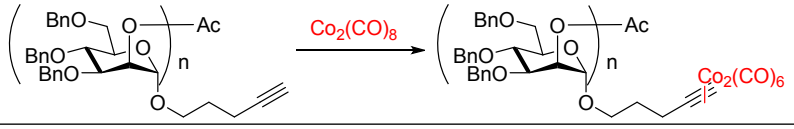
General procedure of releasing step

The loaded resin was suspended in DMF (5ml per 300mg resin) for 20min at room temperature until the resin was completely swelled. CAN was added and the reaction mixture was heated to

85°C and vibrated in a shaking water bath for 15min until the resin became golden yellow and TLC showed the release of product. After filtration and concentration in vacuo, the remainder was diluted in DCM and washed with 1mol/L HCl and brine then dried over Na_2SO_4. The remainder was then concentrated in vacuo and filtrated through a piece of alkaline aluminum oxide to obtain target product.

2. Supplementary experiments.

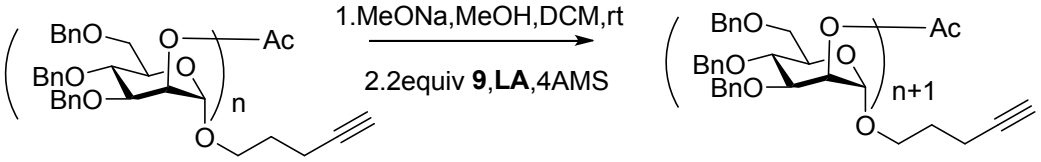
Scheme S1 Optimization of complexation in solution phase



entry	n	solvent	$Co_2(CO)_8$/equiv.	T/℃	t/min	yield[a]
1	**1**	**DCM**	**1.1**	**r.t.**		**88%**
2	4	DCM	1.1	r.t.		58%
3	4	DCM	1.5	r.t.	15	76%
4	**4**	**DCM**	**2**	**r.t.**		**90%**
5	4	MeCN	1.1	r.t.		26%
6	4	MeCN	1.1	75		25%

a:isolated yield r.t.=room temperature

Scheme S2 Optimization of deacetylation-glycosylation

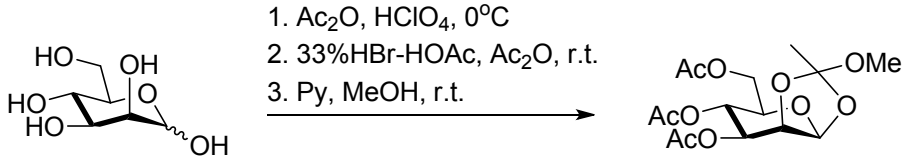


entry	n	LA	Equiv.	T/℃	yield[a]	Notes
1	3	TMSOTf	0.1	0℃→r.t.	19%	A
2	3	TMSOTf	0.1	0℃→r.t.	90%	B
3	3	TMSOTf	0.1	0℃→r.t.	80%	C
4	3	TMSOTf	0.3	0℃→r.t.	80%	C
5	**3**	**TMSOTf**	**0.1**	**0℃→r.t.**	**88%**	**D**
6	1	$Sc(OTf)_3$	0.1	0℃→r.t.	97%	B
7	1	$Sc(OTf)_3$	0.3	0℃→r.t.	100%	B
8	1	$Sc(OTf)_3$	0.1	0℃	77%	B
9	2	$Sc(OTf)_3$	0.1	0℃→r.t.	36%	C
10	2	$Sc(OTf)_3$	0.1	0℃→r.t.	63%	D
11	3	$Sc(OTf)_3$	0.1	0℃→r.t.	-	C
12	1	$In(OTf)_3$	0.1	0℃→r.t.	100%	B
13	2	$BF_3{\cdot}Et_2O$	2	0℃→r.t.	63%	C

Notes: post-treatment after acrtylation A): no post-treatment after acetylation. B): column chromatography. C): water-scavenging by toluene. D): suction filtration through diatomaceous earth, then water-scavenging by toluene.

a:isolated yield r.t.=room temperature

3. Experimental procedures.



S-1

1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-acetyl-β-D-mannopyranose (S-1)

To a stirred acetic anhydride (80ml) at 0°C was added perchloric acid (0.8ml) drop wise and the solution became light yellow. α-D-Mannose (20g) as dry powder was added in portions during 1h. The reaction was complete after 2h and the solution was poured into 0.3L ice-water in a 1L beaker. The mixture was stirred vigorously for 10min and then 300mL CH_2Cl_2 was added. The organic layer was separated, washed by saturated $NaHCO_3$ solution three times and brine and then dried over Na_2SO_4. The filtrate was evaporated and 44.6g light yellow syrup was obtained to give 1,2,3,4,6-Penta-O-acetyl-a-D-mannopyranose (44.6g, 114.9 mmol).

To a s oln. of 6 or 7 (2.43 g, 6.23 mmol) i n d ry CH

To a s oln. of 6 or 7 (2.43 g, 6.23 mmol) i n d ry CH

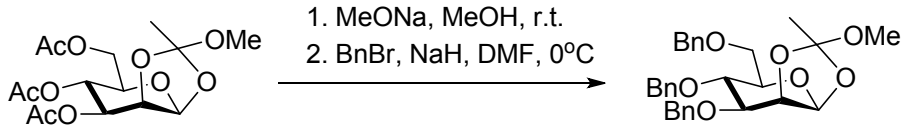
The crude product was mixed with Ac_2O (16mL, 157 mmol) and the mixture was cooled to 0 C. HBr (33% in acetic acid, 160 mL) was added to the solution, which was stirred at room temperature for 4 h. The mixture was then diluted with 200ml DCM. The organic phase was washed with brine and saturated $NaHCO_3$ three times and then dried over Na_2SO_4. After

filtration and concentration, the crude mixture was dried under high vacuum and the crude product (37.1g) was obtained as light yellow oil. [1]

2,3,4,6-Tetra-O-acetyl-a-D-mannopyranosyl bromide (37.1g, 90.1mmol) was dissolved in 120ml dry pyridine and 40ml dry MeOH and the mixture was stirred at room temperature for 12h. The reaction mixture was evaporated in vacuo, diluted with DCM and washed with brine. After dried over Na_2SO_4, the residual was filtrated and was purified on silica gel with petroleum ether/ethyl acetate 3:1 to give the product 1,2-O-(1-Methoxyethylidene)-3,4,6 -tris-O-acetyl-β-D-mannopyranose **S-1** (18.2g, 50.2mmol) in 45% yield for 3 steps as white solid.

^{1}HNMR(400MHz,$CDCCl_3$), δ 5.50(s,1H,H-1), 5.30(t,1H,H-4), 5.15(dd,1H,H-3), 4.62(s,1H,H-2), 4.24(dd,1H,H-6), 4.15(d,1H,H-6), 3.69(dt,1H,H-5), 3.28(s,3H,OCH_3), 2.13(s,3H,Ac), 2.08(s,3H,Ac), 2.06(s,3H,Ac), 1.75(s,3H,C-CH_3)

^{13}CNMR(400MHz, $CDCCl_3$), δ 170.6, 170.3, 169.4, 124.5, 97.4, 76.5, 71.3, 70.6, 65.4, 62.3, 49.9, 24.4, 20.7, 20.7, 20.6

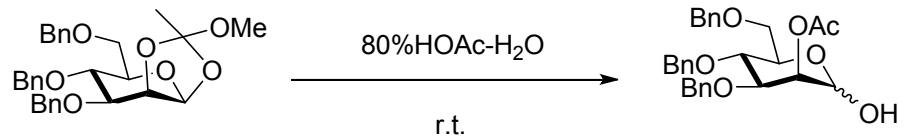


S-1 **S-2**

1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-benzyl-β-D-mannopyranose (S-2)

To a solution of 1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-acetyl-β-D-mannopyranose **S-1** (4g, 11.0mmol) in MeOH (50ml) at room temperature was added catalytic amount of MeONa. The pH value was adjusted to 9-10 and the mixture was stirred for 30min. A small amount of cation exchange resin was added to neutralize the reaction mixture to pH=8. After filtration and concentration in vacuo, the mixture was dried under vaccum to give 1,2-O- (1-Methoxyethylidene)-β-D-mannopyranose.

To a solution of the crude product (2.6g, 11.0mmol) in DMF (100ml) at 0°C was added NaH (60%, 2.0g, 49.7mmol) in portions, the mixture was stirred in ice bath for 1h. BnBr (4.9ml, 41.4mmol) was added drop wise and the reaction mixture was stirred at 0°C for 2h. The mixture was quenched with MeOH, concentrated in vacuo and washed with 1mol/L HCl, saturated $NaHCO_3$ and brine. After dried over Na_2SO_4, the mixture was purified on silica gel (petroleum ether/ethyl acetate 4:1) to give 1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-benzyl-β-D-mannopyranose **S-2** (3.82g, 6.7mmol, 61% for 2 steps) as white solid. [2]



S-2 **S-3**

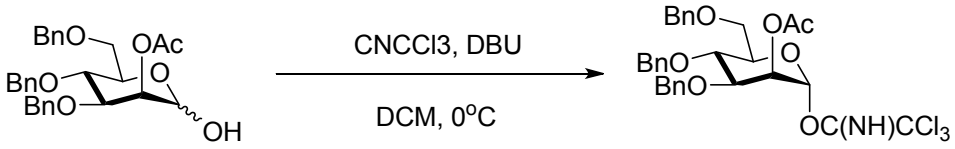
2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranose (S-3)

A solution of 1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-benzyl-β-D-mannopyranose **S-2** (3.82 g, 6.75 mmol) in acetic acid (54 ml) and water (13.5 ml) was stirred at r.t. for 4h whereupon TLC analysis (petroleum ether/ethyl acetate 2:1) indicated the complete consumption of the starting material and formation of the products. The mixture was diluted with DCM (70ml) and the organic phase was washed with saturated NaHCO3 three times and brine. After dried over

Na_2SO_4, the mixture was purified on silica gel (petroleum ether/ethyl acetate 3:1) to give 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranose **S-3** (2.38g, 4.83mmol, 62%) as colorless syrup.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.34-7.14(17H,Ar), 5.39(s,1H,H-2), 5.24(s,1H,H-1) 4.86(d,1H,$ArCH_2$), 4.71(d,1H,$ArCH_2$), 4.63(d,1H,$ArCH_2$), 4.55-4.45(m,3H,$ArCH_2$), 4.05(m,2H), δ 3.80-3.70(m,3H), δ 2.15(s,3H,Ac)

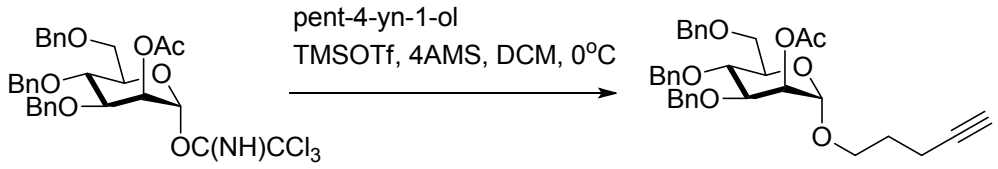
^{13}CNMR(400MHz, $CDCCl_3$), δ 170.5, 138.3, 137.9, 137.9, 128.4, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 92.6, 77.6, 75.2, 74.5, 73.5, 71.8, 71.3, 69.2, 68.9, 21.2



S-3 **9**

2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate (9)

To a solution of 2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranose **S-3** (695mg, 1.41mmol) in dry CH_2Cl_2 (10 mL) at 0°C was added $CNCCl_3$ (0.42mL, 4.22mmol) and a catalytic amount of DBU (21µl, 0.14mmol). After 2 h the reaction mixture was concentrated in vacuo and purified by flash chromatography (petroleum ether/ethyl acetate 1:0→4:1) to obtain 2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate **9** (872mg, 1.36mmol, 97%) as a colorless syrup.



9 **3**

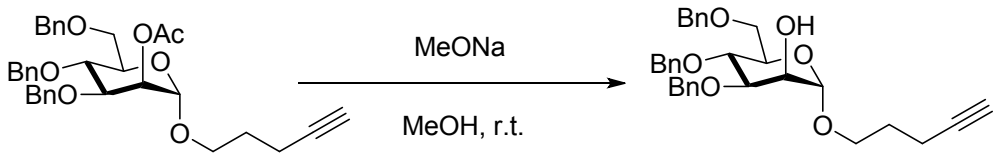
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranoside (3)

2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate **9** (262mg, 0.41mmol), pent-4-yn-1-ol (41µl, 0.447mmol) and 4 Å molecular sieves (200mg) were dissolved in dry DCM (5ml) under an N_2 atmosphere at 0 °C. The mixture was stirred for 10min. To the solution was added TMSOTf (7µl, 0.04mmol) and the reaction mixture was stirred at room temperature for 30min until TLC showed (petroleum ether/ethyl acetate 6:1x2) that the entire donor was converted to product. The solution was neutralized with triethylamine and the molecular sieves were filtered through Celite. The mixture was purified by chromatography (petroleum ether/ethyl acetate 12:1) to give product 4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranoside **3** (222mg, 0.39mmol, 98%) as pale yellow syrup.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.36-7.23(m,13H,Ar), 7.18-7.15(m,2H,Ar), 5.36(d,1H,H-1), 4.85(d,1H,$ArCH_2$), 4.83(s,1H,H-2), 4.70(d,1H,$ArCH_2$), 4.68(d,1H,$ArCH_2$), 4.56-4.63(m,3H, $ArCH_2$), 3.97(dd,1H,H-3), 3.88(t,1H,H-4), 3.81-3.74(m,3H), 3.71-3.69(d,1H,H-5), 3.51(dt,1H,O-CH2-C), 2.26(dt,2H,C-CH_2-C-CH), 2.14(s,3H,Ac), 1.92(t,1H,C-C-H), 1.78(m,2H, C-CH_2-C)

^{13}CNMR(400MHz, $CDCCl_3$), δ 170.4, 138.3, 138.1, 137.8, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.5, 97.7, 83.3, 78.1, 75.1, 74.2, 73.3, 71.7, 71.3, 68.8, 68.7,68.5, 66,0, 28.1, 21.0, 15.2

HRMS(ESI-FT-ICR): m/z calcd 558.2618, M^+, found 581.2515 $[M + Na]^+$, 597.2255$[M + K]^+$.



3 **S-4**

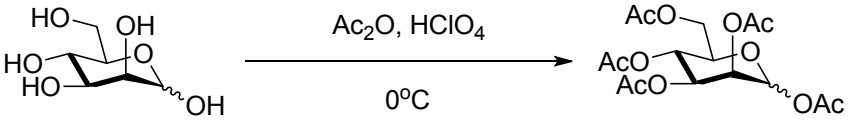
4-pentyn-1-yl 3,4,6-tri-O-benzyl-D-mannopyranoside (S-4)

To a solution of 4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranoside **3** (184mg, 0.33mmol) in MeOH (5ml) at room temperature was added catalytic amount of MeONa. The pH value was adjusted to 9-10 and the mixture was stirred for 30min. Cation exchange resin was added to neutralize the reaction mixture to pH=7. After filtration and concentration in vacuo, the mixture was purified by chromatography (petroleum ether/ethyl acetate 3:1) to give product 4-pentyn-1-yl 3,4,6-tri-O-benzyl-D-mannopyranoside **S-4** (150g, 0.29mmol, 88%) as pale yellow syrup.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.37-7.26(m,13H,Ar), 7.18-7.16(m,2H,Ar), 4.90(d,1H,H-1), 4.82(d,1H,$ArCH_2$), 4.72-4.63(m,3H,$ArCH_2$), 4.54-4.48(m,2H,$ArCH_2$), 4.02(d,1H), 3.86-3.73(m,5H), 3.69(d,1H), 3.51(dt,1H,O-CH2-C), 2.51(s,1H,OH), 2.25(dt,2H,C-*CH_2*-C-CH), 1.91(t,1H,C-C-H), 1.76(m,2H, C-CH_2-C)

^{13}CNMR(400MHz, $CDCCl_3$), δ 138.2, 138.2, 137.8, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 99.2, 83.4, 80.1, 75.1, 74.2, 73.4, 71.9, 71.0, 68.8, 68.7, 68.3, 65.8, 28.2, 20.9, 15.2

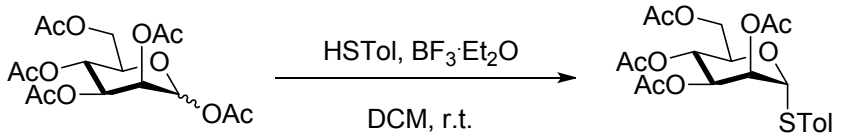
HRMS(ESI-FT-ICR): m/z calcd 516.2512, M^+, found 539.2410 $[M + Na]^+$, 555.2149$[M + K]^+$.



S-5

1,2,3,4,6-Penta-O-acetyl-a-D-mannopyranose (S-5)

To a stirred acetic anhydride (40ml) at 0°C was added perchloric acid (0.4ml) drop wise and the solution became light yellow. α-D-Mannose (10g) as dry powder was added in portions during 1h. The reaction was complete after 2h and the solution was poured into 0.3L ice-water in a 1L beaker. The mixture was stirred vigorously for 10min and then 300mL CH_2Cl_2 was added. The organic layer was separated, washed by saturated $NaHCO_3$ solution three times and brine and then dried over Na_2SO_4. The filtrate was purified by chromatography (petroleum ether/ethyl acetate 2:1) and light yellow syrup was obtained to give 1,2,3,4,6-Penta-O-acetyl-a-D-mannopyranose **S-5** (20.3g, 52.0 mmol, 94%).

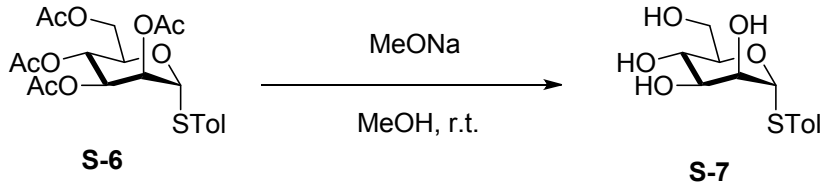


S-5 **S-6**

β-D-Mannopyranoside, 4-methylphenyl 1-thio-, 2,3,4,6-tetraacetate (S-6)

To a solution of 1,2,3,4,6-Penta-O-acetyl-a-D-mannopyranose **S-5** (20.3g, 52.1mmol) and HSTol (7.1g, 57.3mmol) in dry DCM (100ml) at room temperature was added BF3•Et2O (19.7ml, 156.3mmol). The reaction mixture was stirred for 30min until TLC showed (petroleum

ether/ethyl acetate 3:1) the total conversion of reactant. The mixture washed with saturated NaHCO3 three times and brine. After dried over Na_2SO_4, the mixture was purified on silica gel (petroleum ether/ethyl acetate 3:1) to give β-D-Glucopyranoside, 4-methylphenyl 1-thio-, 2,3,4, 6-tetraacetate **S-6** (21.3g, 46.9mmol, 90%) as pale yellow syrup after concentration. [3]



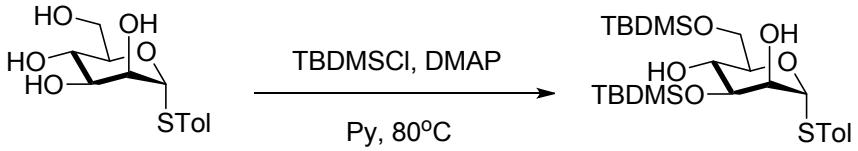
S-6 **S-7**

α-D-Mannopyranoside, 4-methylphenyl 1-thio (S-7)

To a solution ofβ-D-Glucopyranoside, 4-methylphenyl 1-thio-, 2,3,4,6-tetraacetate **S-6** (21.3g, 46.9mmol) in MeOH (60ml) at room temperature was added catalytic amount of MeONa. The pH value was adjusted to 9-10 and the mixture was stirred for 30min. Cation exchange resin was added to neutralize the reaction mixture to pH=7. After filtration, the mixture was concentrated in vacuo to give product α-D-Mannopyranoside, 4-methylphenyl 1-thio **S-7** (13.4g, 46.9mmol, 100%) as white solid.

^{1}HNMR(400MHz,MeOD), δ 7.38(d,2H, Ar), 7.11(d,2H, Ar), 5.34(d,1H, H-1)， 4.06-4.02(m,2H), 3.82-3.68(m,4H), 2.28(s,3H,Ac)

^{13}CNMR(400MHz,MeOD), δ 138.6, 133.2, 131.8, 130.5, 90.5, 75.3, 73.5, 72.9, 68.4, 62.3, 48.8, 20.9



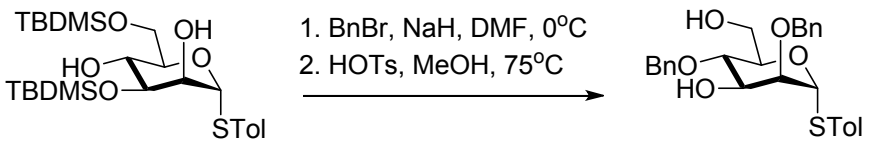
S-7 **S-8**

α-D-Mannopyranoside, 4-methylphenyl 3,6-bis-*O*-[(1,1-dimethylethyl)dimethylsilyl]-1-thio (S-8)

To a solution of α-D-Mannopyranoside, 4-methylphenyl 1-thio **S-7** (3.0g, 10.48mmol) in dry pyridine (60ml) was added TBDMSCl (6.32g, 41.94mmol) and catalytic amount of DMAP. The reaction mixture was stirred at 80°C for 10h. The mixture was concentrated in vacuo, diluted with DCM and then washed with 1mol/L HCl, saturated $NaHCO_3$ and brine. After dried over Na_2SO_4, the mixture was purified on silica gel (petroleum ether/ethyl acetate 10:1) to give α-D-Mannopyranoside, 4-methylphenyl 3,6-bis-*O*-[(1,1-dimethylethyl)dimethylsilyl]-1-thio **S-8** (3.53g, 6.86mmol, 67%) as colorless syrup.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.43(d,2H, Ar), 7.18(d,2H, Ar), 5.57(d,1H, H-1)，4.19(dt,1H,H-5), 4.10(d,1H,H-2), 3.96-3.89(m,3H,H-4,H-6), 3.86(dd,1H,H-3), 2.95(s,1H,OH), 2.85(s,1H,OH), 2.39(s,3H,PhMe), 1.00(s,9H,tBu), 0.97(s,9H,tBu), 0.25(s,3H,Me), 0.24(s,3H,Me), 0.15(s,6H,Me)

^{13}CNMR(400MHz, $CDCCl_3$), δ 137.5, 131.9, 130.1, 129.7, 87.3, 73.3, 72.5, 71.5, 70.7, 64.8, 25.8, 25.7, 21.0, 18.3, 18.0, -4.4, -4.8, -5.5



S-8 **S-9**

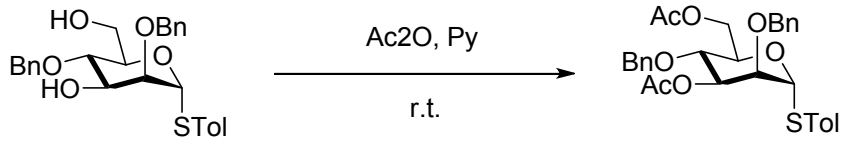
β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-*O*-(benzyl)-1-thio (S-9)

To a solution of theα-D-Mannopyranoside, 4-methylphenyl 3,6-bis-*O*-[(1,1-dimethylethyl) dimethylsilyl]-1-thio **S-8** (3.53g, 6.86mmol) in DMF (100ml) at 0°C was added BnBr (3.3ml, 27.46mmol) drop wise, the mixture was stirred in ice bath for 1h. NaH (60%, 659mg, 16.47mmol) was added in portions, and the reaction mixture was stirred at 0°C for 2h. The mixture was quenched with MeOH, concentrated in vacuo and washed with 1mol/L HCl, saturated $NaHCO_3$ and brine. After dried over Na_2SO_4, the mixture was concentrated in vacuo and dried under vaccum to give crude product β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-*O*-(benzyl)- 3,6-bis-*O*-[(1,1-dimethylethyl)dimethylsilyl]-1-thio.

To the solution of crude product (5.31g) in MeOH (50ml) was added catalytic amount of TsOH. The reaction mixture was stirred and refluxed at 75°C for 4h. The mixture was concentrated in vacuo and purified on silica gel (petroleum ether/ethyl acetate 3:1) to give β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-*O*-(benzyl)-1-thio **S-9** (1.43g, 3.06mmol, 45% for 2 steps) as pale yellow syrup.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.37-7.28(m,12H,Ar), 7.11(d,2 H,Ar), 5.49(s,1H,H-1), 4.91(d,1H,$ArCH_2$), 4.70(d,1H,$ArCH_2$), 4.66(d,1H,$ArCH_2$), 4.54(d,1H,$ArCH_2$), 4.13(d,1H,H-5), 4.00(d,1H,H-6), 3.99(s,1H,H-2), 3.83(dd,1H,H-6), 3.81(d,1H,H-3), 3.75(t,1H,H-4), 2.32(s,3H,Ac)

^{13}CNMR(400MHz, $CDCCl_3$), δ 138.1, 138.0, 137.2, 132.5, 129.9, 129.7, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 85.4, 79.6, 76.4, 74.9, 72.4, 72.3, 72.0, 62.0, 21.0



S-9 **S-10**

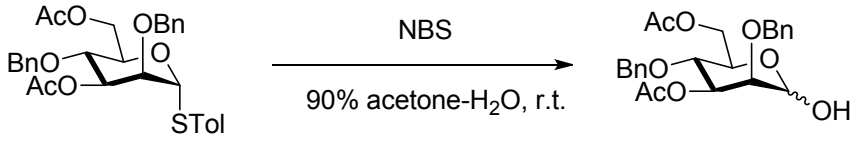
β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-*O*-(benzyl)-3,6-bis-O-acetyl-1-thio (S-10)

To the solution ofβ-D-Mannopyranoside, 4-methylphenyl 2,4-bis-*O*-(benzyl)-1-thio **S-9** (1.25g, 2.68mmol) in pyridine (30ml) at ambient temperature was added acetic anhydride (30ml). The mixture was stirred for 2h until TLC monitored (petroleum ether/ethyl acetate 4:1) the completion of the reaction. The mixture was concentrated in vacuo, washed with 1mol/L HCl, saturated $NaHCO_3$ and brine then dried over Na_2SO_4. The residual was purified by chromatography (petroleum ether/ethyl acetate 6:1) to obtain β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-*O*-(benzyl)-3,6-bis-O-acetyl-1-thio **S-10** (1.24g, 2.25mmol, 84%) as colorless syrup.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.37-7.30(m,12H,Ar), 7.11(d,2H,Ar), 5.47(d,1H,H-1), 5.20(dd,1H,H-3), 4.72(d,1H,$ArCH_2$), 4.68(d,1H,$ArCH_2$), 4.59(d,1H,$ArCH_2$), 4.49(d,1H,$ArCH_2$), 4.39(m,1H,H-5), 4.32(d,2H,H-6), 4.11(dd,1H,H-2), 3.97(t,1H,H-4), 2.32(s,3H,ArMe), 2.04(s,3H,Ac), 1.99(s,3H,Ac)

^{13}CNMR(400MHz, $CDCCl_3$), δ 170.6, 169.9, 137.8, 137.7, 137.5, 132.3, 129.8, 129.7, 128.4, 128.3, 127.8, 127.8, 127.7, 127.7, 85.4, 76.8, 74.7, 73.7, 73.5, 72.1, 70.5, 63.3, 21.0, 20.9, 20.7

HRMS(ESI-FT-ICR): m/z calcd 550.2025, M^+, found 573.1923 $[M + Na]^+$, 589.1662$[M + K]^+$.



S-10 **S-11**

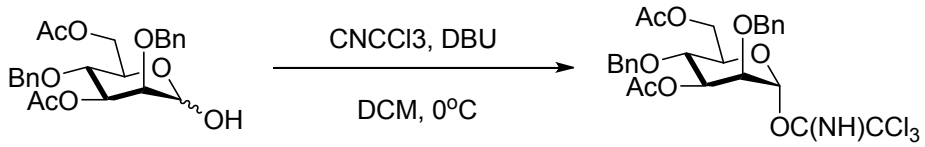
3,6-bis-O-Acetyl-2,4-tri-O-benzyl-D-mannopyranose (S-11)

To a solution of β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-*O*-(benzyl)-3,6-bis-O-acetyl-1-thio **S-10** (1,24g, 2.25mmol) in 90% acetone-H_2O (30ml) was added NBS (1.6g, 9.01mmol) under dark condition. The reaction mixture was stirred at room temperature for 10h. The mixture was evaporated in vacuo and diluted with DCM (100ml). After washed with saturated $Na_2S_2O_3$, 1mol/L HCl, saturated $NaHCO_3$ and brine, the remainder was dried over Na_2SO_4 and purified on silica gel (petroleum ether/ethyl acetate 2:1) to give 3,6-bis-O-Acetyl-2,4-tri-O-benzyl-D-mannopyranose **S-11** (812mg, 1.82mmol, 81%) as colorless syrup.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.36-7.27(m,10H,Ar), 5.31(dd,1H,H-3), 5.21(d,1H,H-1,α/β), 4.70(d,1H,$ArCH_2$), 4.63(d,1H,$ArCH_2$), 4.59(d,1H,$ArCH_2$), 4.55(d,1H,$ArCH_2$), 4.36(dd,1H,H-6), 4.23(dd,1H,H-6), 4.09(m,1H,H-5), 3.94(t,1H,H-4), 3.88(dd,1H,H-2), 2.04(s,3H,Ac), 1.97(s,3H,Ac)

^{13}CNMR(400MHz, $CDCCl_3$), δ 170.9, 170.1, 137.8, 137.7, 128.3, 128.3, 127.7, 127.7, 127.6, 127.6, 93.6, 92.2, 76.1, 74.6, 73.4, 73.3, 72.8, 69.7, 63.3, 20.9, 20.7

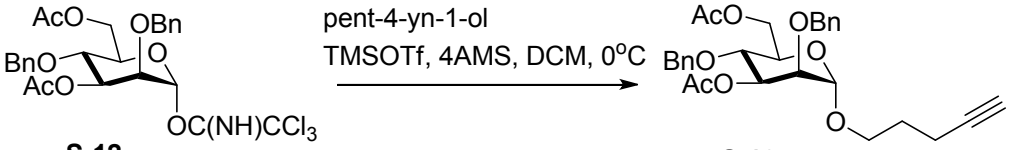
HRMS(ESI-FT-ICR): m/z calcd 444.1784, M^+, found 467.1682 $[M + Na]^+$, 483.1421$[M + K]^+$.



S-11 **S-12**

3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranosyl trichloroacetimidate (S-12)

To a solution of 3,6-bis-O-Acetyl-2,4-tri-O-benzyl-D-mannopyranose **S-11** (812mg, 1.83mmol) in dry CH_2Cl_2 (10 mL) at 0°C was added $CNCCl_3$ (0.55mL, 5.48mmol) and a catalytic amount of DBU (27μl, 0.18mmol). After 2 h the reaction mixture was concentrated in vacuo and purified by flash chromatography (petroleum ether/ethyl acetate 1:0→4:1) to obtain 2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate **S-12** (1.035g, 1.76mmol, 96%) as a colorless syrup.



S-12 **S-13**

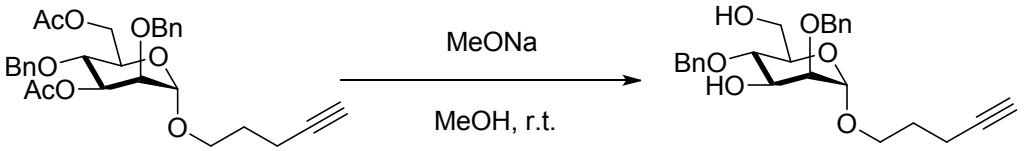
4-pentyn-1-yl 3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranoside (S-13)

2-O-acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl trichloroacetimidate **S-12** (1.035g, 1.76mmol), pent-4-yn-1-ol (187μl, 2.01mmol) and 4 Å molecular sieves (400mg) were dissolved in dry DCM (10ml) under an N_2 atmosphere at 0 °C. The mixture was stirred for 10min. To the solution was added TMSOTf (33μl, 0.18mmol) and the reaction mixture was stirred at room temperature for 30min until TLC showed (petroleum ether/ethyl acetate 3:1) that the entire donor was converted to product. The solution was neutralized with triethylamine and the molecular sieves were filtered through Celite. The mixture was purified by chromatography (petroleum ether/ethyl acetate 10:1) to give product 4-pentyn-1-yl 3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranoside **S-13** (898mg, 1.76mmol, 100%) as colorless syrup.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.35-7.25(m,10H,Ar), 5.23(dd,1H,H-3), 4.83(d,1H,H-1), 4.69(d,1H, $ArCH_2$), 4.66(d,1H, $ArCH_2$), 4.57(d,1H, $ArCH_2$), 4.57(d,1H, $ArCH_2$), 4.34(dd,1H,H-6), 4.29(dd,1H,H-6), 3.93(t,1H,H-4), 3.89(dt,1H,H-5), 3.86(dd,1H,H-2), 3.80(dt,1H,O-CH2-C), 3.50(dt,1H,O-CH2-C), 2.27(dt,2H,C-CH_2-C-CH), 2.07(s,3H,Ac), 1.98(s,3H,Ac), 1.93(t,1H,C-C-H), 1.78(m,2H, C-CH_2-C)

^{13}CNMR(400MHz, $CDCCl_3$), δ 170.8, 170.1, 137.8, 137.8, 128.4, 128.4, 127.9, 127.8, 127.8, 127.7, 97.8, 83.4, 75.9, 74.7, 73.8, 73.3, 72.9, 69.7, 68.8, 66.1, 63.3, 28.1, 21.0, 20.9, 15.2

HRMS(ESI-FT-ICR): m/z calcd 510.2254, M^+, found 533.2151 $[M + Na]^+$, 549.1891$[M + K]^+$.



S-13 **11**

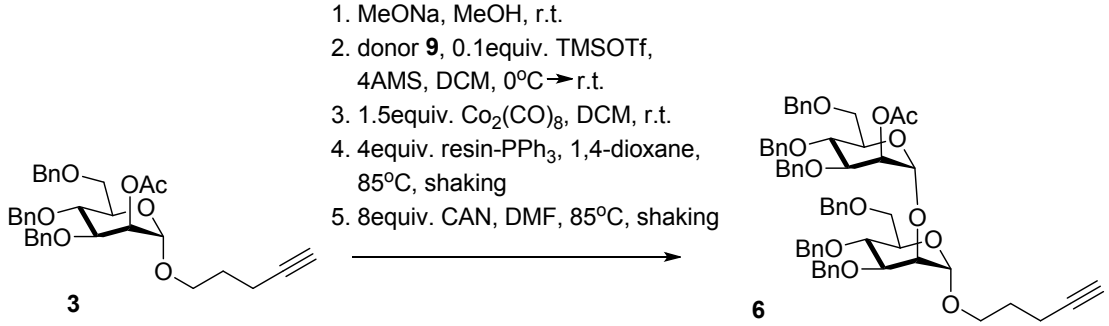
4-pentyn-1-yl 2,4-bis-O-benzyl-D-mannopyranoside (11)

To a solution of 4-pentyn-1-yl 3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranoside **S-13** (898mg, 1.76mmol) in MeOH (30ml) at room temperature was added catalytic amount of MeONa. The pH value was adjusted to 9-10 and the mixture was stirred for 30min. Cation exchange resin was added to neutralize the reaction mixture to pH=7. After filtration and concentration in vacuo, the mixture was purified by chromatography (petroleum ether/ethyl acetate 3:1) to give product 4-pentyn-1-yl 2,4-bis-O-benzyl-D-mannopyranoside **11** (605mg, 1.41mmol, 81%) as colorless syrup.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.40-7.27(m,10H,Ar), 4.90(d,1H,$ArCH_2$), 4.85(s,1H,H-1), 4.74-4.59(m,3H,$ArCH_2$), 3.99(dt,1H,H-3), 3.85(dd,1H,H-6), 3.80(dd,1H,H-6), 3.80(dt,1H,O-CH_2-C), 3.73(dd,1H,H-2), 3.68(t,1H,H-4) 3.62(dt,1H,H-5), 3.46(dt,1H,O-CH_2-C), 2.32(d,1H,OH), 2.25(dt,2H,C-*CH_2*-C-CH), 1.95(t,1H,C-C-H), 1.94(d,1H,OH), 1.75(m,2H, C-CH_2-C)

^{13}CNMR(400MHz, $CDCCl_3$), δ 138.33, 137.7, 128.6, 128.5, 128.1, 128.0, 127.8, 127.8, 97.2, 83.4, 78.4, 76.4, 74.9, 73.1, 71.7, 71.3, 68.8, 65.7, 62.2, 28.1, 15.1

HRMS(ESI-FT-ICR): m/z calcd 426.2042, M^+, found 449.1940 $[M + Na]^+$, 465.1679$[M + K]^+$.



4-pentyn-1yl 2-O-acetyl-3,4,6-tri-O-benzyl-R-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (6)

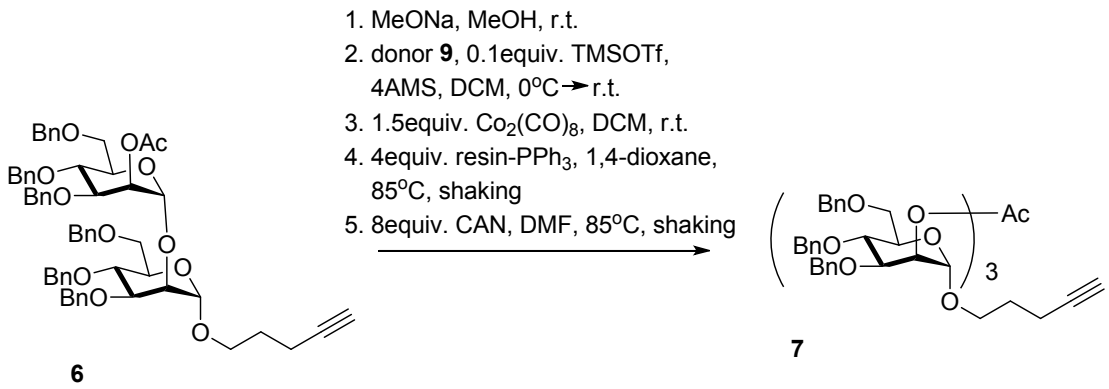
144mg of compound **6** (0.145mmol, 81%) was obtained as a colorless syrup by the capture-release separation from the glycosylation between donor **9** (228mg, 0.358mmol) and acceptor **3** (100mg, 0.179mmol) after 2-O-Ac deprotection, glycosylation, cobalt-alkyne complexation, loading step and releasing step.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.35-7.14(m, 30H,Ar), 5.54(d,1H,H-1), 5.07(d,1H,H-1), 4.87-4.83(m,3H), 4.68-4.64(m,5H), 4.56(d,1H,$ArCH_2$), 4.51(d,1H,$ArCH_2$), 4.46(d,1H,$ArCH_2$), 4.40(d,1H,$ArCH_2$), 3.99-3.94(m,3H), 3.88(dd,1H), 3.84(t,2H), 3.79-3.68(m,7H), 3.35(dt,1H,O-CH2-C), 2.19(dt,2H,C-*CH_2*-C-CH), 2.12(s,3H,Ac), 1.89(t,1H,C-C-H), 1.70(m,2H, C-CH_2-C)

^{13}CNMR(400MHz, $CDCCl_3$), δ 170.1, 138.4, 138.4, 138.3, 138.3, 138.1, 137.9, 128.3, 128.3, 128.2, 128.1, 128.0, 127.7 127.7 127.6 127.6 127.5 127.5 127.4 127.3, 99.5, 98.6, 83.5, 79.6, 78.1, 77.2, 75.1, 75.0, 74.8, 74.5, 74.3, 73.3, 73.2, 72.0, 71.8, 71.8, 71.7, 69.2, 69.0, 68.7, 65.8, 28.2, 21.1,

15.2

HRMS(ESI-FT-ICR): m/z calcd 990.4554, M^+, found 1013.4452 $[M + Na]^+$, 1029.4191$[M + K]^+$.



6 **7**

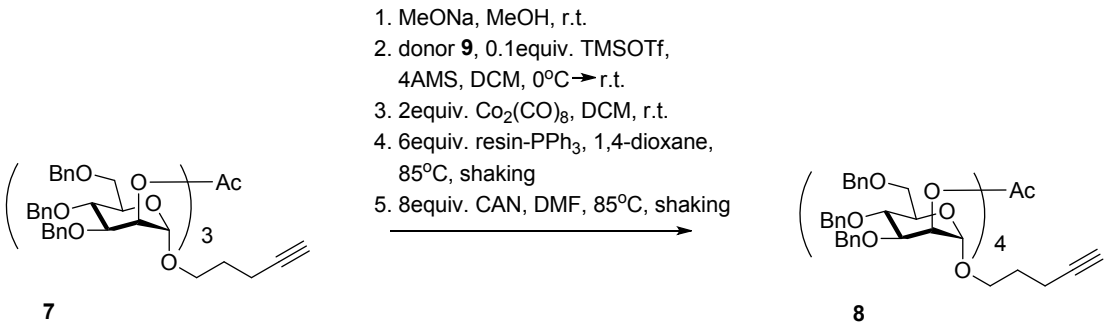
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (7)

145mg of compound **7** (0.102mmol, 70%) was obtained as a colorless syrup by the capture-release separation from the glycosylation between donor **9** (185mg, 0.290mmol) and acceptor **6** (144mg, 0.145mmol) after 2-O-Ac deprotection, glycosylation, cobalt-alkyne complexation, loading step and releasing step.

^{1}HNMR(400MHz,$CDCl_3$), δ 7.34-7.13(m,45H,Ar), 5.54(s,1H,H-1), 5.18(s,1H,H-1), 5.05(s,1H,H-1), 4.91(s,1H), 4.85-4.79(m,3H), 4.69-4.65(m,3H), 4.61(s,1H), 4.58(s,1H), 4.56(d,3H), 4.53(s,2H), 4.49(dd,2H), 4.45-4.41(m,2H), 4.31(dd,1H), 4.10(s,1H), 3.99(t,1H), 3.95(s,1H), 3.93(d,1H), 3.90(d,3H), 3.84(dd,1H), 3.80-3.76(m,3H), 3.72(m,3H), 3.70-3.65(m,3H), 3.53(d,1H), 3.31(dt,1H,O-CH2-C), 2.15(dt,2H,C-*CH_2*-C-CH), 2.12(s,3H,Ac), 1.87(t,1H,C-C-H), 1.69(m,2H, C-CH_2-C)

^{13}CNMR(400MHz, $CDCl_3$), δ 170.0, 138.5, 138.5, 138.3, 138.3, 138.2, 138.1, 137.9, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.4, 127.3, 100.5, 99.3, 98.6, 83.5, 79.4, 79.2, 78.0, 77.2, 75.0, 75.0, 74.9, 74.7, 74.7, 74.1, 73.2, 73.2, 73.2, 72.1, 72.0, 71.8, 71.8, 69.5, 69.2, 68.7, 68.6, 65.8, 28.2, 21.1, 15.2

HRMS(ESI-FT-ICR): m/z calcd 1422.6491, M^+, found 1445.6389 $[M + Na]^+$, 1461.6128$[M + K]^+$.



7 **8**

4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-,4,6-tri-O-benzyl-α-D-man nopyranoside (8)

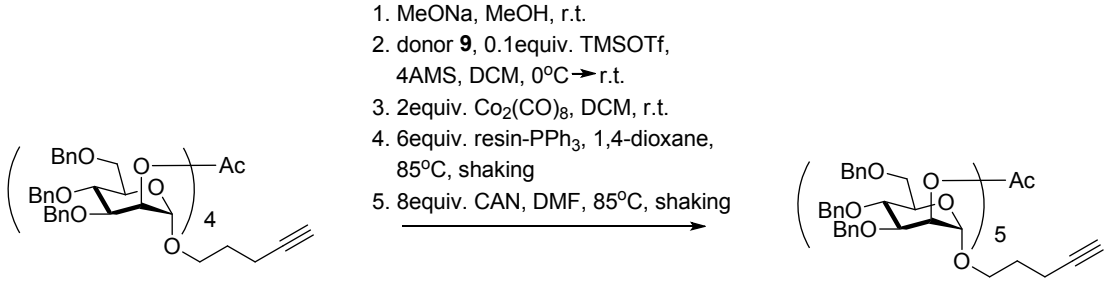
148mg of compound **8** (0.080mmol, 78%) was obtained as a colorless syrup by the capture-release separation from the glycosylation between donor **9** (130mg, 0.204mmol) and acceptor **7** (145mg, 0.102mmol) after 2-O-Ac deprotection, glycosylation, cobalt-alkyne complexation,

loading step and releasing step.

^{1}HNMR(400MHz,$CDCl_3$), δ 7.35-7.03(m,60H,Ar), 5.55(s,1H,H-1), 5.21(s,1H,H-1), 5.18(s,1H,H-1), 5.04(s,1H,H-1), 4.93(s,1H), 4.86-4.79(m,4H), 4.76(d,2H), 4.68-4.65(m,2H), 4.64(d,2H), 4.59(d,2H), 4.56(s,2H), 4.55(s,2H), 4.52(d,2H), 4.50(d,1H), 4.45(d,1H), 4.43(d,2H), 4.38(d,2H), 4.32(d,2H), 4.16(d,1H), 4.09(s,2H), 3.99(m,1H), 3.94(s,2H), 3.92(s,1H), 3.89(d,2H), 3.85(d,1H), 3.80(d,1H), 3.74(m,4H), 3.72(s,1H), 3.69(d,2H), 3.65(d,2H), 3.60(d,2H), 3.46(d,1H), 3.29(dt,1H,O-CH2-C), 2.15(dt,2H,C-CH_2-C-CH), 2.12(s,3H,Ac), 1.87(t,1H,C-C-H), 1.67(m,2H, C-CH_2-C)

^{13}CNMR(400MHz, $CDCl_3$), δ 170.0, 138.6, 138.5, 138.4, 138.4, 138.3, 138.2, 138.1, 138.0, 128.8, 128.3, 128.2, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 101.1, 100.7, 99.3, 98.7, 83.6, 79.4, 79.3, 79.2, 79.2, 78.2, 77.2, 75.7, 75.4, 75.1, 75.0, 74.9, 74.8, 74.6, 74.2, 73.3, 73.2, 73.1, 72.3, 72.2, 72.1, 71.9, 71.8, 71.7, 69.6, 69.4, 69.3, 68.6, 65.8, 28.3, 21.1, 15.2

HRMS(ESI-FT-ICR): m/z calcd 1855.8461, M^+, found 1878.8359 $[M + Na]^+$, 1894.8098 $[M + K]^+$.



8 **10**

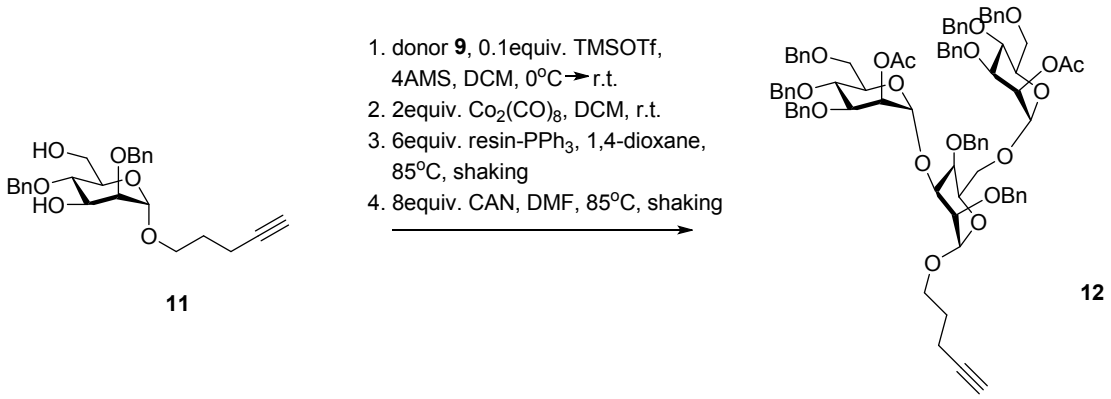
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-Obenzyl-α-D-mannopyranoside (10)

183mg of compound **10** (0.060mmol, 75%) was obtained as a pale yellow syrup by the capture-release separation from the glycosylation between donor **9** (102mg, 0.160mmol) and acceptor **8** (148mg, 0.080mmol) after 2-O-Ac deprotection, glycosylation, cobalt-alkyne complexation, loading step and releasing step.

^{1}HNMR(400MHz,$CDCl_3$), δ 7.36-6.96(m,75H,Ar), 5.56(s,1H,H-1), 5.25(s,2H,H-1), 5.16(s,1H,H-1), 5.05(s,1H,H-1), 4.96(s,1H), 4.88(d,1H), 4.83(d,2H), 4.76(t,2H), 4.68(d,1H), 4.65(s,1H), 4.62(s,2H), 4.59(s,3H), 4.55(s,4H), 4.51(s,3H), 4.49(s,1H), 4.46(s,1H), 4.43(s,2H), 4.40(s,2H), 4.38(s,2H), 4.35(s,1H), 4.22(d,1H), 4.17(s,1H), 4.14(s,1H), 4.11(s,2H), 4.08(s,1H), 4.00(s,1H), 3.96(s,5H), 3.89(s,3H), 3.84(s,1H), 3.82(s,2H), 3.79(d,1H), 3.73(s,5H), 3.69(s,2H), 3.64(s,2H), 3.61(s,2H), 3.53(d,1H), 3.45(d,1H), 3.29(dt,1H,O-CH2-C), 2.15(dt,2H,C-CH_2-C-CH), 2.12(s,3H,Ac), 1.86(t,1H,C-C-H), 1.79(m,2H, C-CH_2-C)

^{13}CNMR(400MHz, $CDCl_3$), δ 170.0, 138.6, 138.4, 138.4, 138.3, 138.3, 138.1, 138.0, 132.5, 129.8, 128.8, 128.7, 128.6, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 101.3, 100.7, 99.3, 98.6, 83.6, 79.6, 79.5, 79.2, 79.1, 79.0, 78.1, 77.2, 76.1, 75.8, 75.5, 75.1, 75.0, 74.9, 74.8, 74.7, 74.7, 74.2, 73.2, 73.2, 72.3, 72.2, 72.0, 71.8, 71.8, 71.7, 71.6, 69.6, 69.6, 69.3, 68.6, 65.8, 28.3, 21.1, 15.2

HRMS(ESI-FT-ICR): m/z calcd 2288.0398, M^+, found 2311.0296 $[M + Na]^+$.



11 **12**

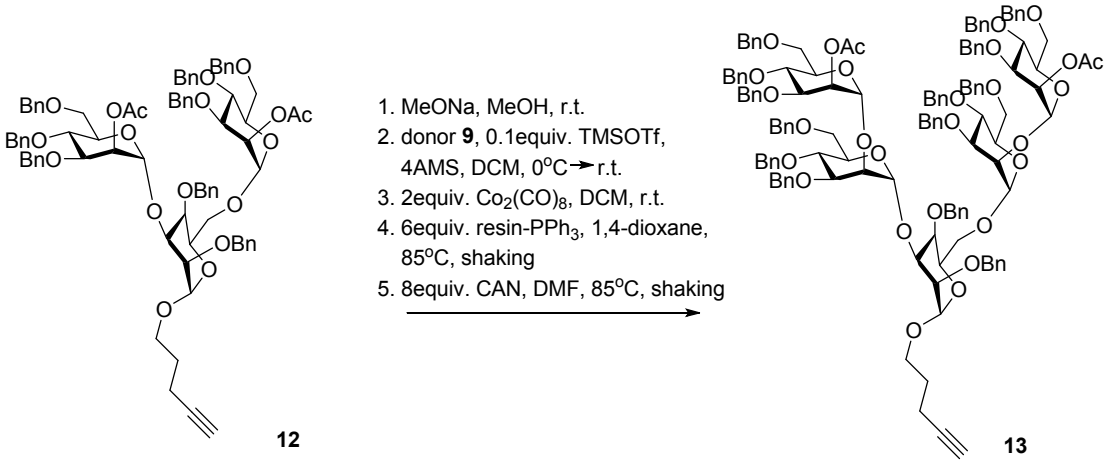
4-pentyn-1-yl 2,4-bis-O-benzyl-3,6-di-O-(2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl)-α-D-mannopyranoside (12)

123mg of compound **12** (0.094mmol, 80%) was obtained as a pale yellow syrup by the capture-release separation from the glycosylation between donor **11** (499mg, 0.710mmol) and acceptor **8** (50mg, 0.117mmol) after glycosylation, cobalt-alkyne complexation, loading step and releasing step.

^{1}HNMR(400MHz,$CDCCl_3$), δ 7.32-7.10(m,40H,Ar), 5.50(s,1H,H-1), 5.48(s,1H,H-1), 5.19(s,1H,H-1), 4.96(s,1H), 4.88(d,1H,$ArCH_2$), 4.85(d,1H,$ArCH_2$), 4.77(s,1H), 4.74(d,1H,$ArCH_2$), 4.66(d,1H), 4.64(d,2H), 4.61(d,3H), 4.48(d,2H), 4.45(d,3H), 4.42(d,2H), 4.13-4.10(dd,1H), 4.04-4.01(dd,1H), 3.96-3.93(dd,2H), 3.91-3.81(m,6H), 3.76-3.70(m,3H), 3.68-3.67(m,2H), 3.64(d,2H), 3.58(d,1H), 3.38(dt,1H,O-CH2-C), 2.19(dt,2H,C-CH_2-C-CH), 2.15(s,3H,Ac), 2.09(s,3H,Ac), 1.94(t,1H,C-C-H), 1.67(m,2H, C-CH_2-C)

^{13}CNMR(400MHz, $CDCCl_3$), δ 170.2, 170.1, 138.5, 138.4, 138.1, 138.0, 128.3, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 99.7, 98.0, 96.9, 83.5, 78.0, 77.5, 77.5, 77.2, 75.0, 75.0, 74.8, 74.7, 74.2, 74.0, 73.3, 73.3, 72.1, 72.0, 71.7, 71.3, 71.2, 71.1, 68.9, 68.8, 68.7, 68.5, 68.3, 66.4, 65.8, 28.0, 21.1, 21.0, 15.1

HRMS(ESI-FT-ICR): m/z calcd 1374.6127, M^+, found 1397.6025 $[M + Na]^+$.



12 **13**

4-pentyn-1-yl 2,4-bis-O-benzyl-3,6-di-O-[2-O-(2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl)-3,4,6-tri-O-benzyl-D-mannopyranosyl]-α-D-mannopyranoside (13)

147mg of compound **13** (0.067mmol, 70%) was obtained as a pale yellow syrup by the capture-release separation from the glycosylation between donor **9** (359mg, 0.564mmol) and acceptor **12** (123mg, 0.094mmol) after 2-O-Ac deprotection, glycosylation, cobalt-alkyne complexation,

loading step and releasing step.

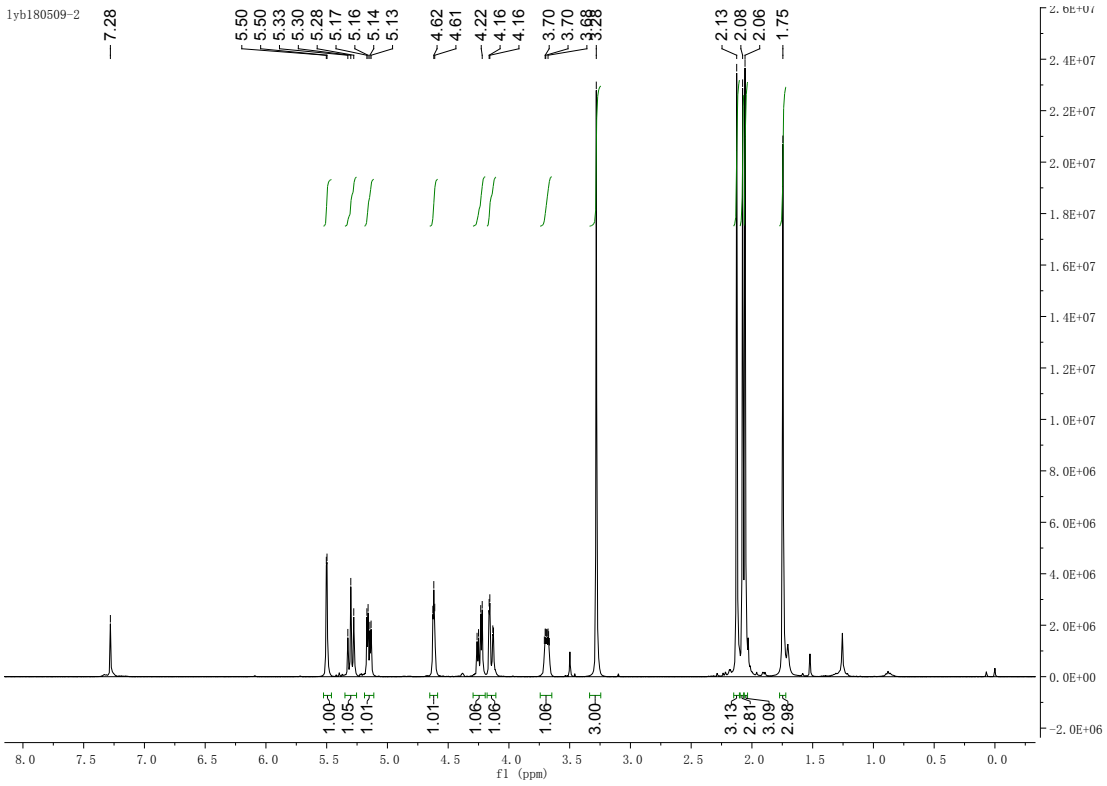
^{1}HNMR(400MHz,$CDCl_3$), δ 7.31-7.13(m,70H,Ar), 5.52(s,2H,H-1), 5.18(s,1H,H-1), 5.07(s,1H,H-1), 5.05(s,1H,H-1), 4.93(s,1H), 4.87(d,2H), 4.81(s,1H), 4.77(d,1H), 4.70(d,2H), 4.65(s,1H), 4.62(s,1H), 4.60(s,2H), 4.57(d,3H), 4.54(s,2H), 4.51(s,1H), 4.47(s,1H), 4.45(s,1H), 4.41(m,2H), 4.38(s,2H), 4.35(s,1H), 4.28(d,1H), 4.09(s,1H), 4.05(d,2H), 3.98(d,2H), 3.93(d,2H), 3.89(s,1H), 3.86(s,1H), 3.84(d,2H), 3.81(s,1H), 3.79(s,1H), 3.64(m,7H), 3.60(s,1H), 3.50-3.46(m,2H), 3.36(d,2H), 2.15(dt,2H,C-CH_2-C-CH), 2.10(s,6H,Ac, 1.90(t,1H,C-C-H), 1.64(m,2H, C-CH_2-C)

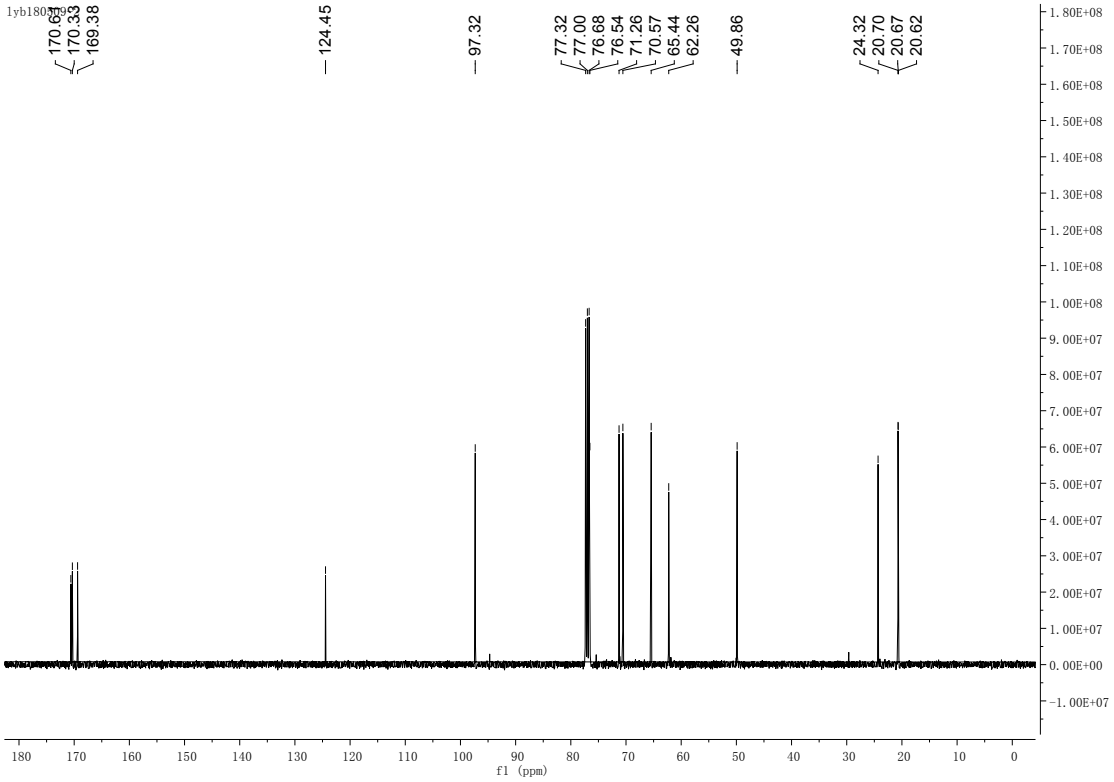
^{13}CNMR(400MHz, $CDCl_3$), δ 170.0, 170.0, 138.5, 138.4, 138.4, 138.3, 138.2, 138.2, 138.1, 138.0, 128.4, 128.3, 128.2, 128.1, 128.1, 128.1, 127.9, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 127.3, 127.2, 126.9, 101.0, 99.5, 99.2, 99.1, 96.9, 83.5, 79.6, 79.1, 78.1, 78.0, 77.8, 75.0, 74.9, 74.7, 74.7, 74.5, 74.4, 74.2, 74.0, 73.3, 73.2, 73.1, 72.6, 71.9, 71.9, 71.8, 71.3, 71.2, 69.5, 68.9, 68.9, 68.8, 68.6, 68.2, 66.5, 65.9, 28.1, 26.8, 21.1, 15.2

HRMS(ESI-FT-ICR): m/z calcd 2240.0034, M^+, found 2262.9932 $[M + Na]^+$.

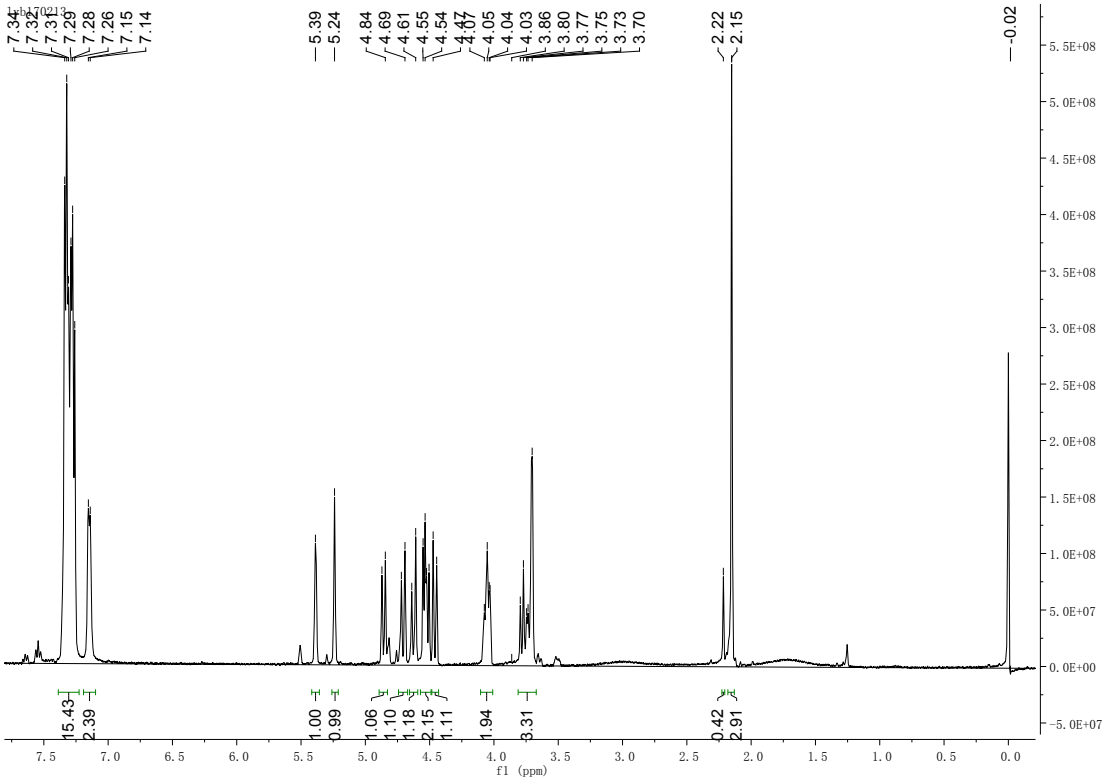
4. NMR Chart.

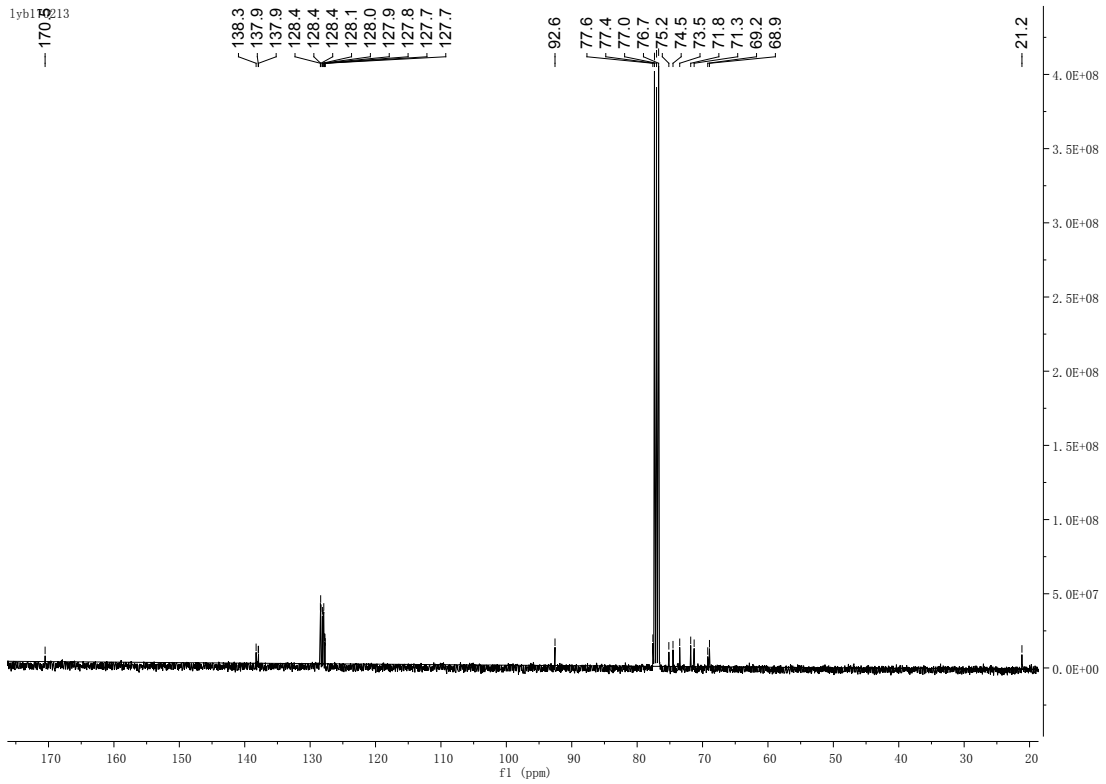
1,2-O-(1-Methoxyethylidene)-3,4,6-tris-O-acetyl-β-D-mannopyranose (S-1)



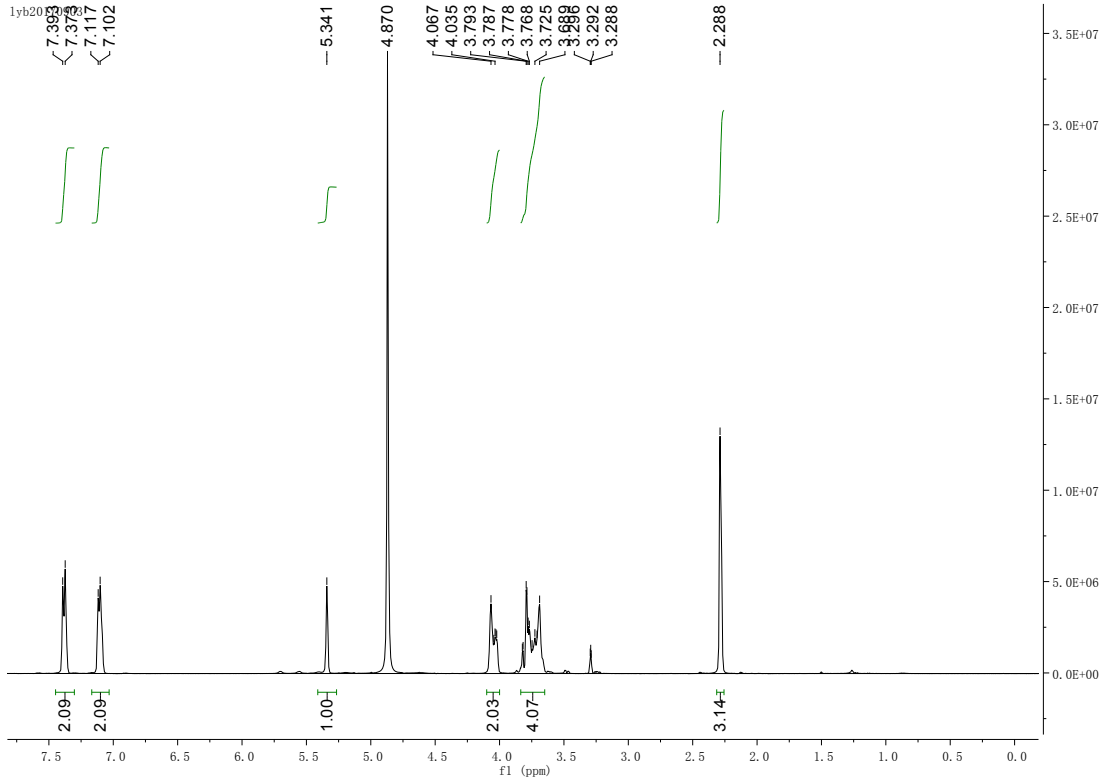


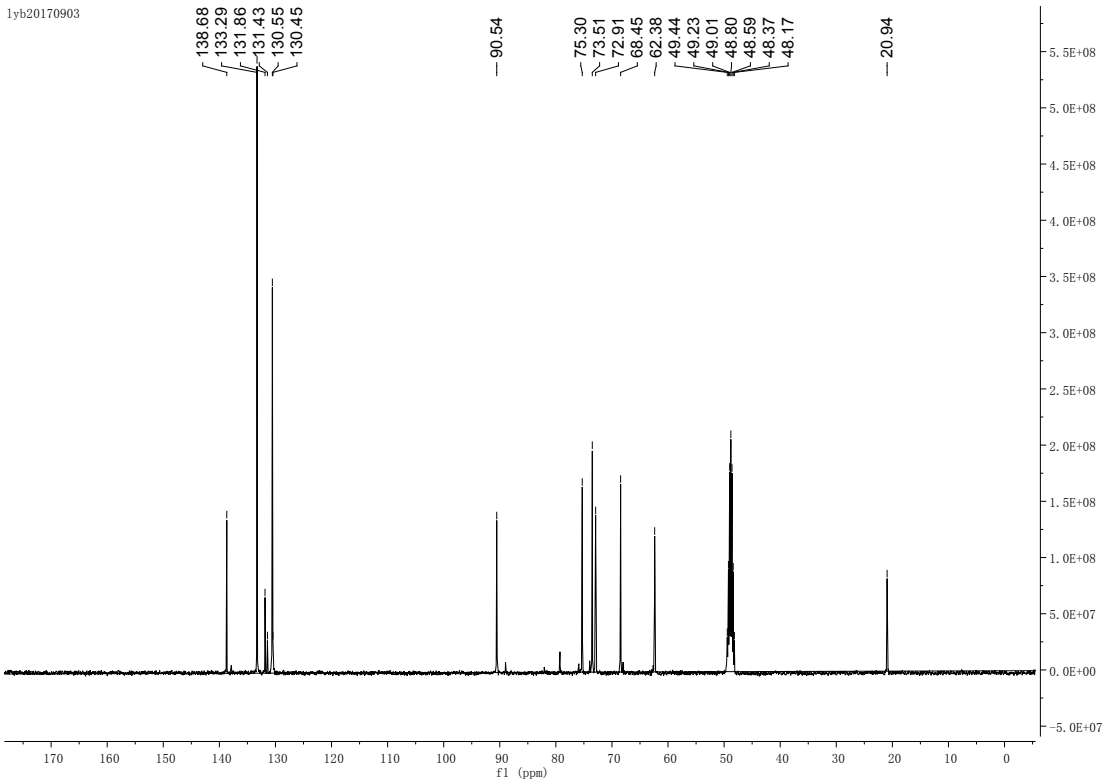
2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranose (S-3)



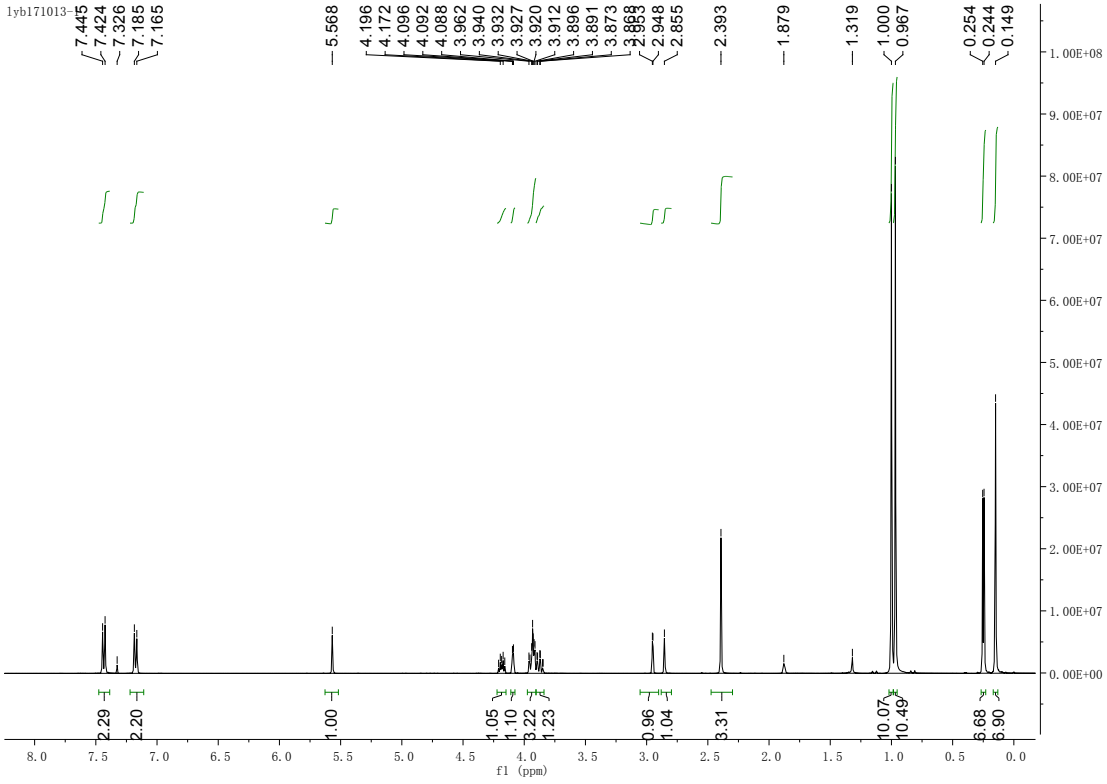


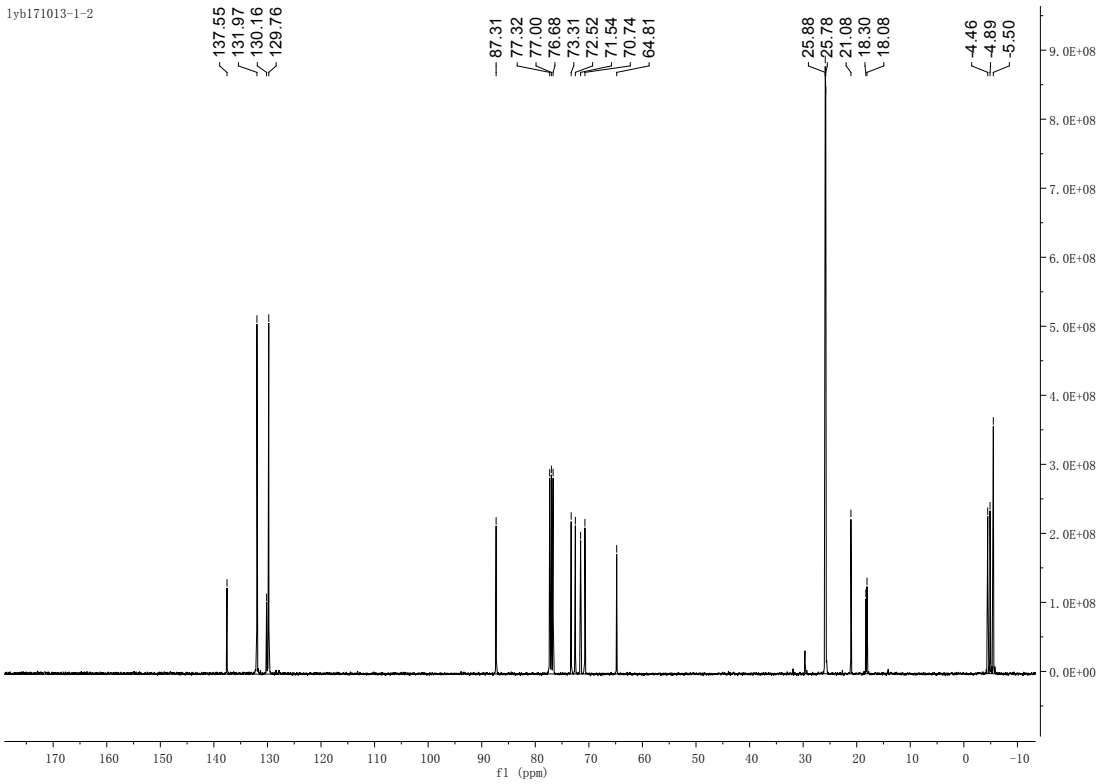
α-D-Mannopyranoside, 4-methylphenyl 1-thio (S-7)



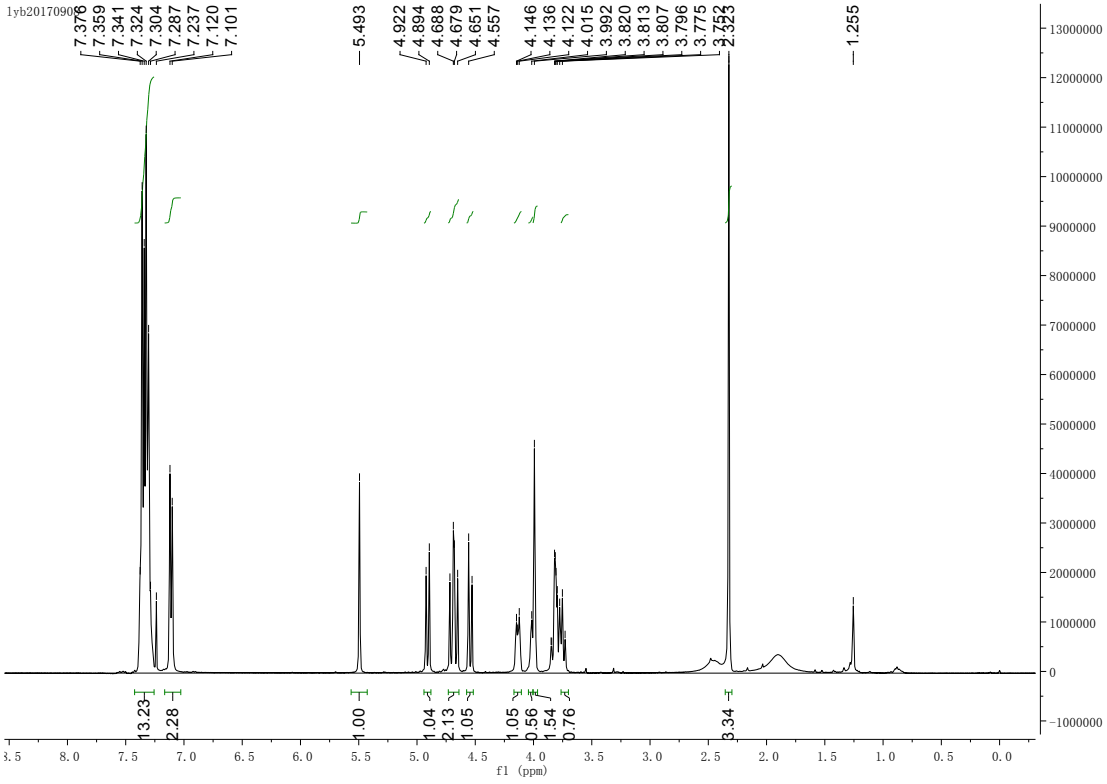


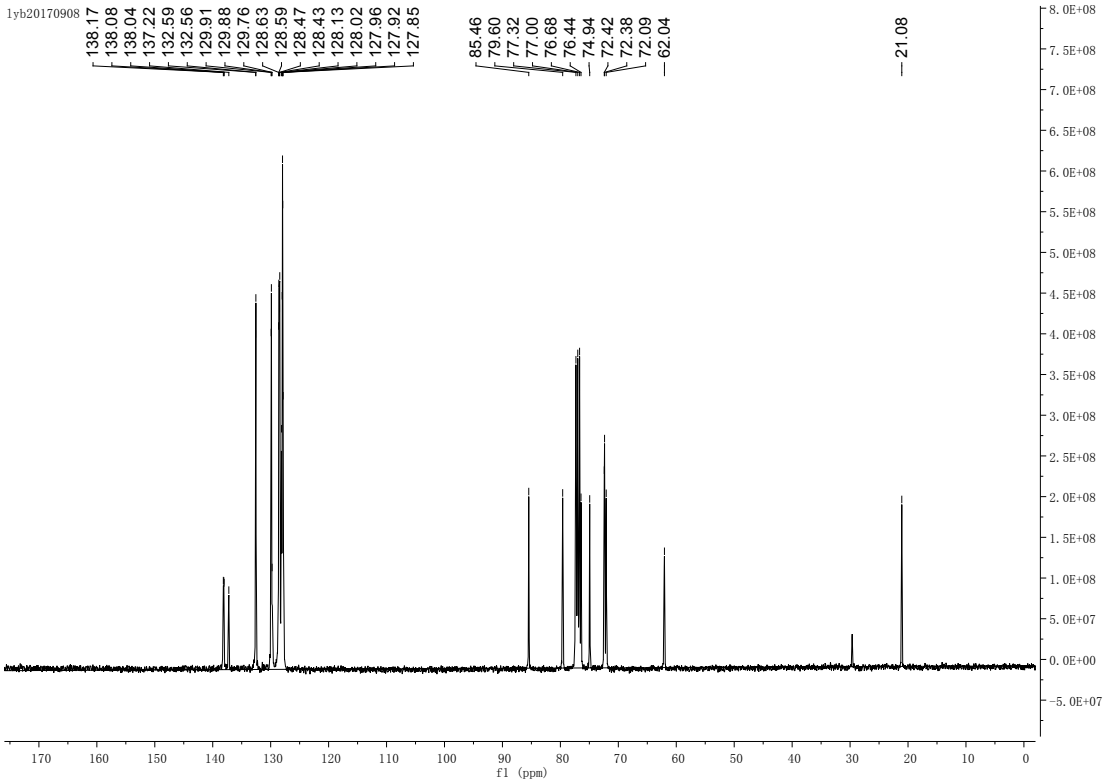
α-D-Mannopyranoside, 4-methylphenyl 3,6-bis-*O*-[(1,1-dimethylethyl)dimethylsilyl]-1-thio (S-8)



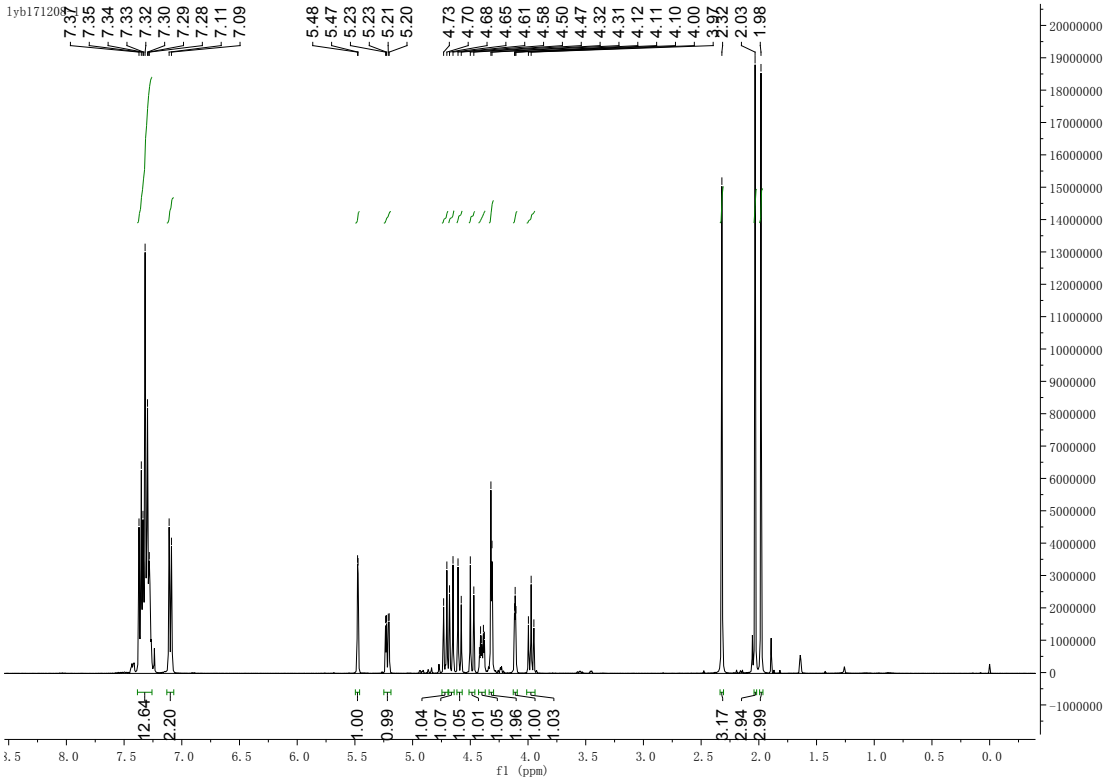


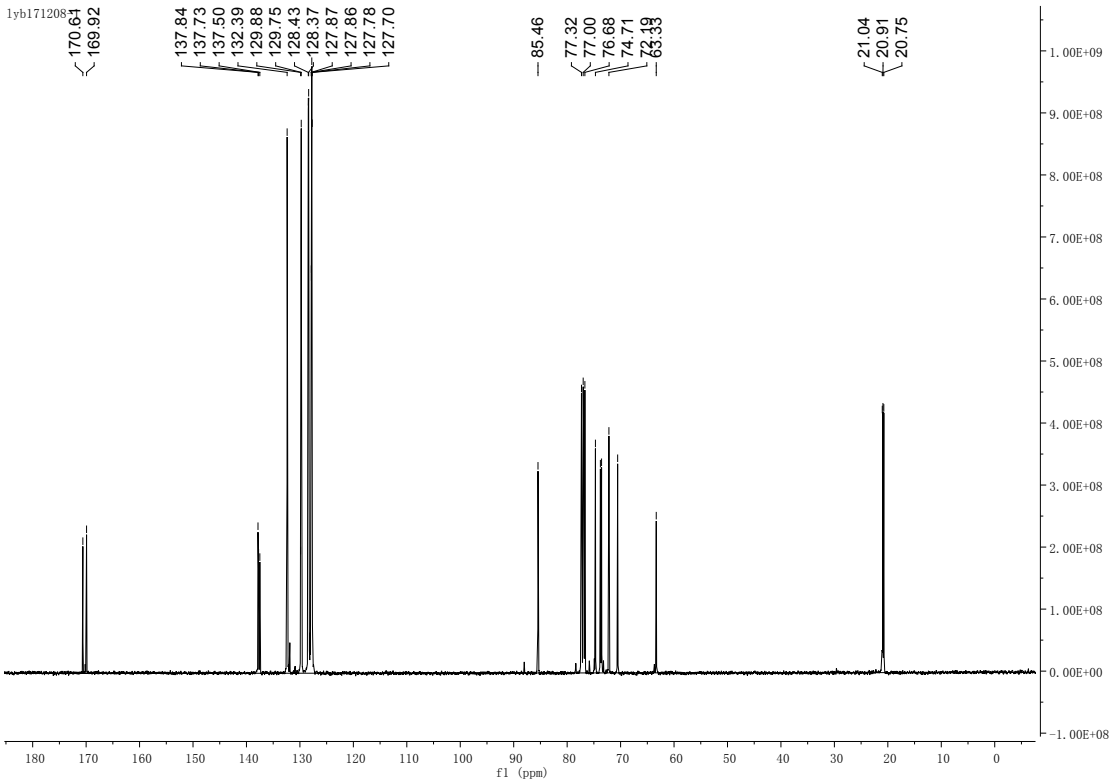
β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-*O*-(benzyl)-1-thio (S-9)



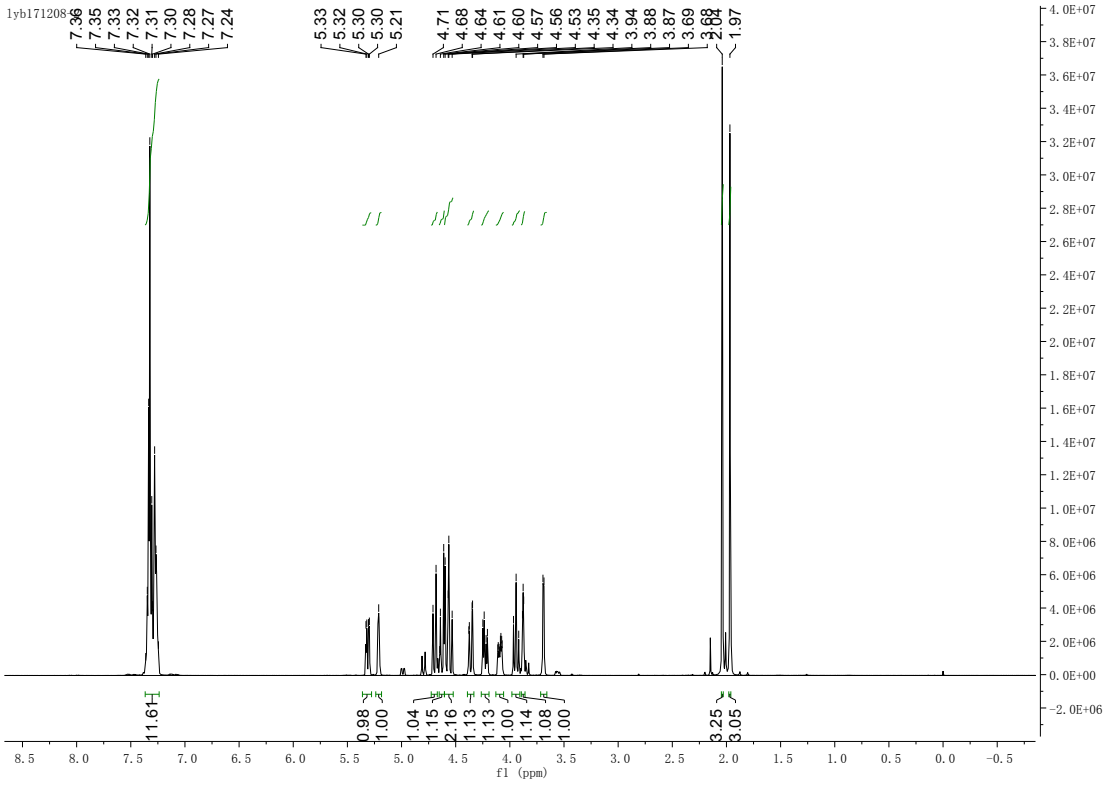


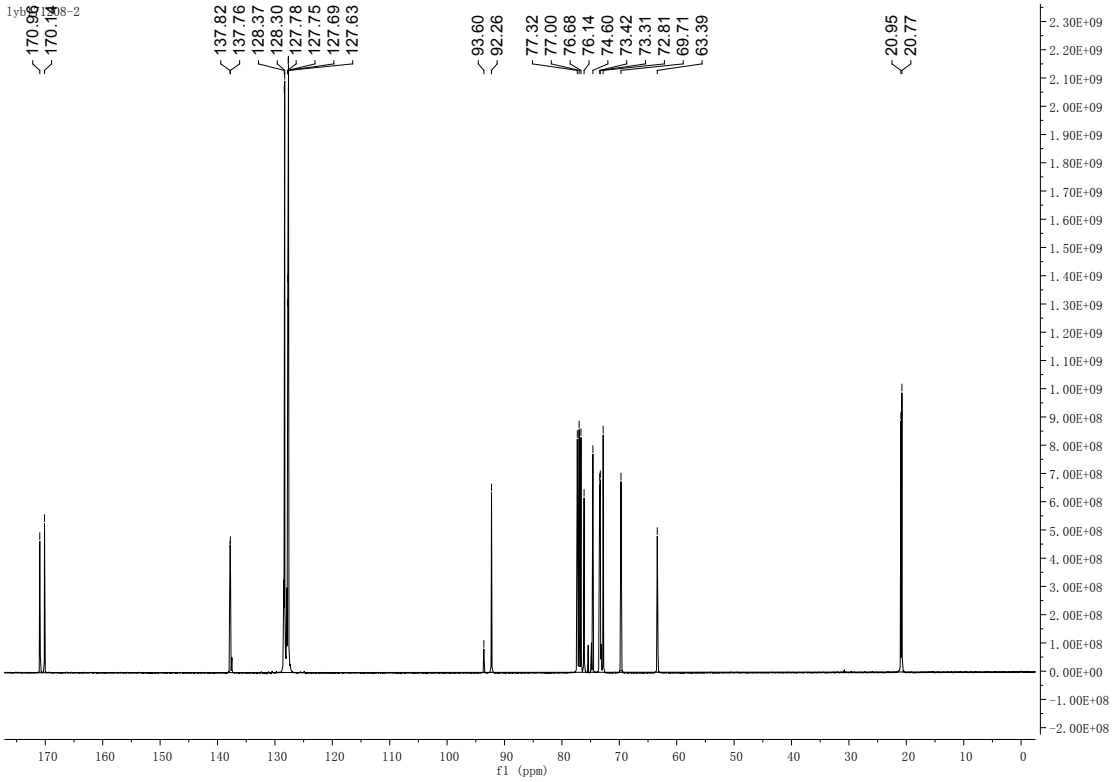
β-D-Mannopyranoside, 4-methylphenyl 2,4-bis-*O*-(benzyl)-3,6-bis-O-acetyl-1-thio (S-10)



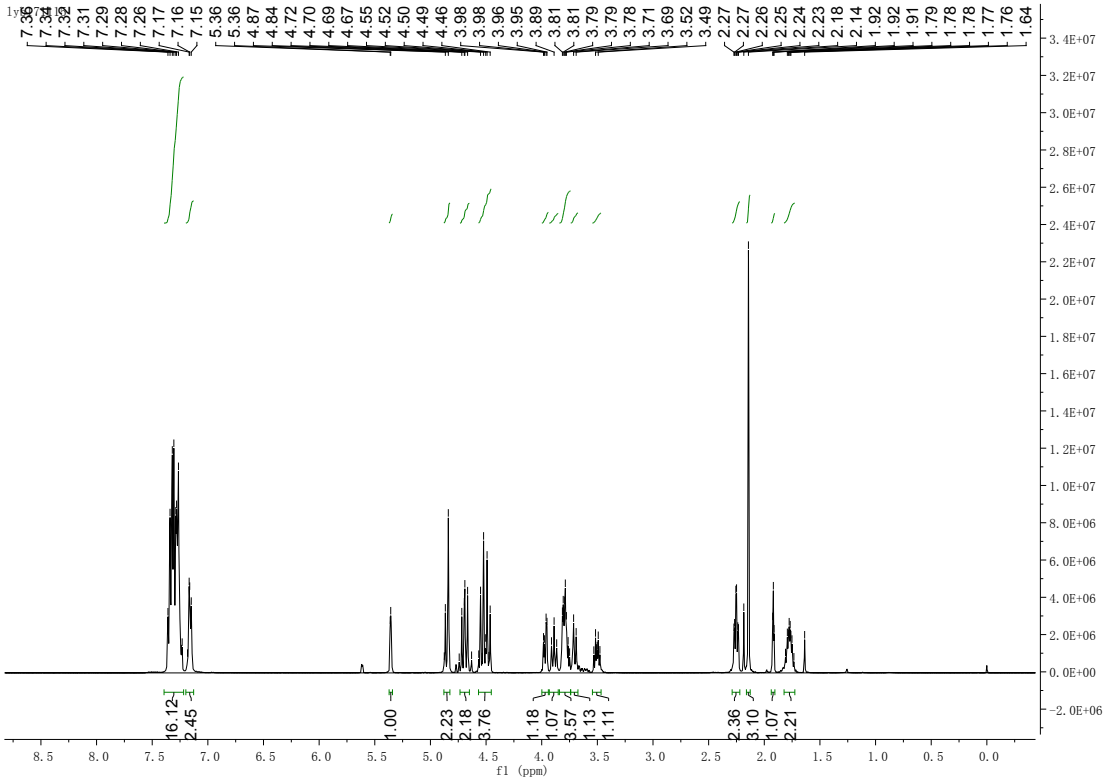


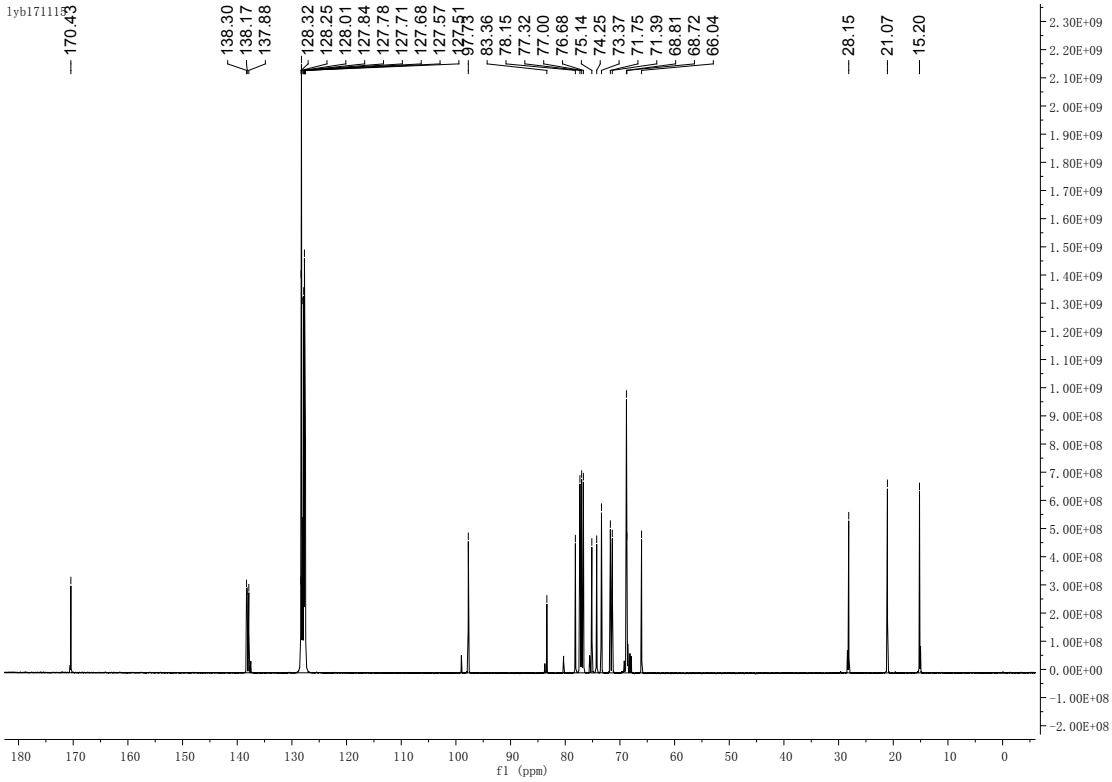
3,6-bis-O-Acetyl-2,4-tri-O-benzyl-D-mannopyranose (S-11)



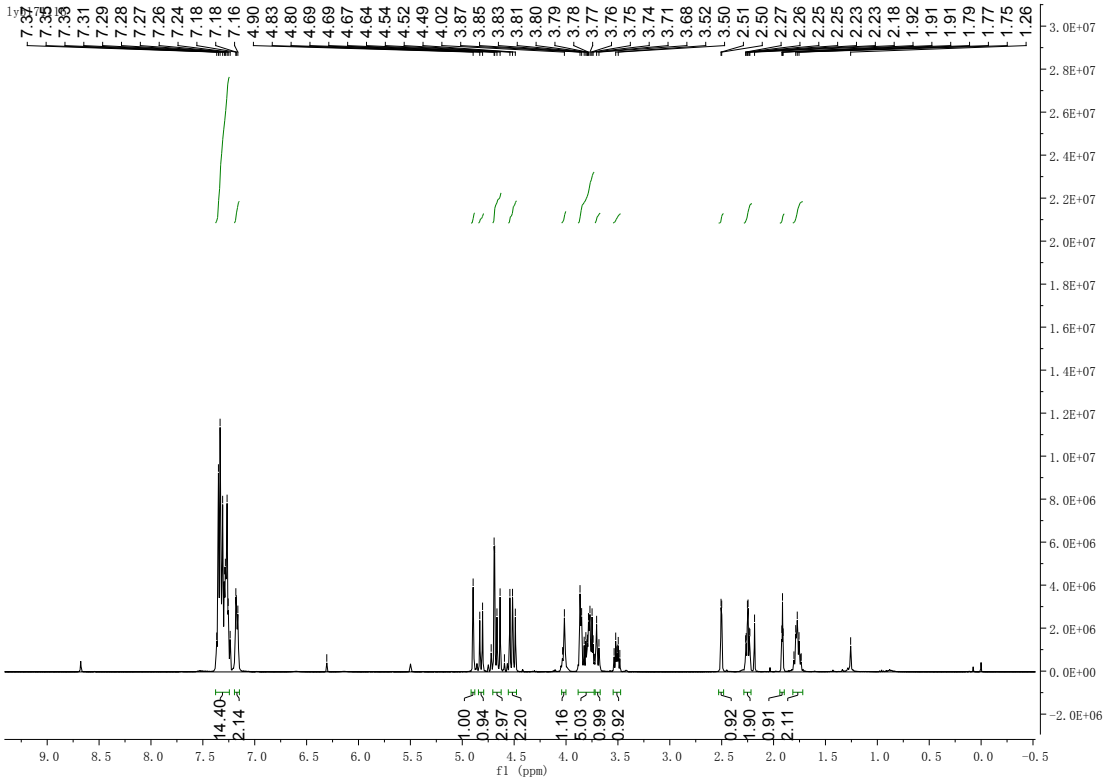


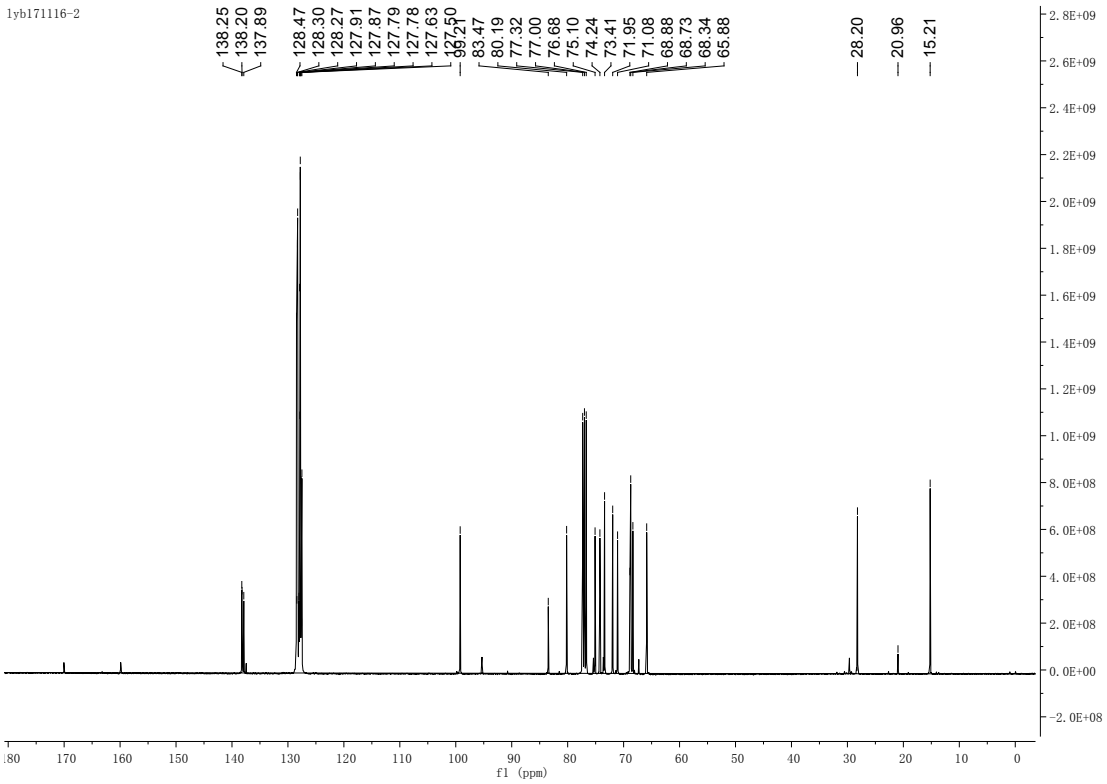
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranoside (3)



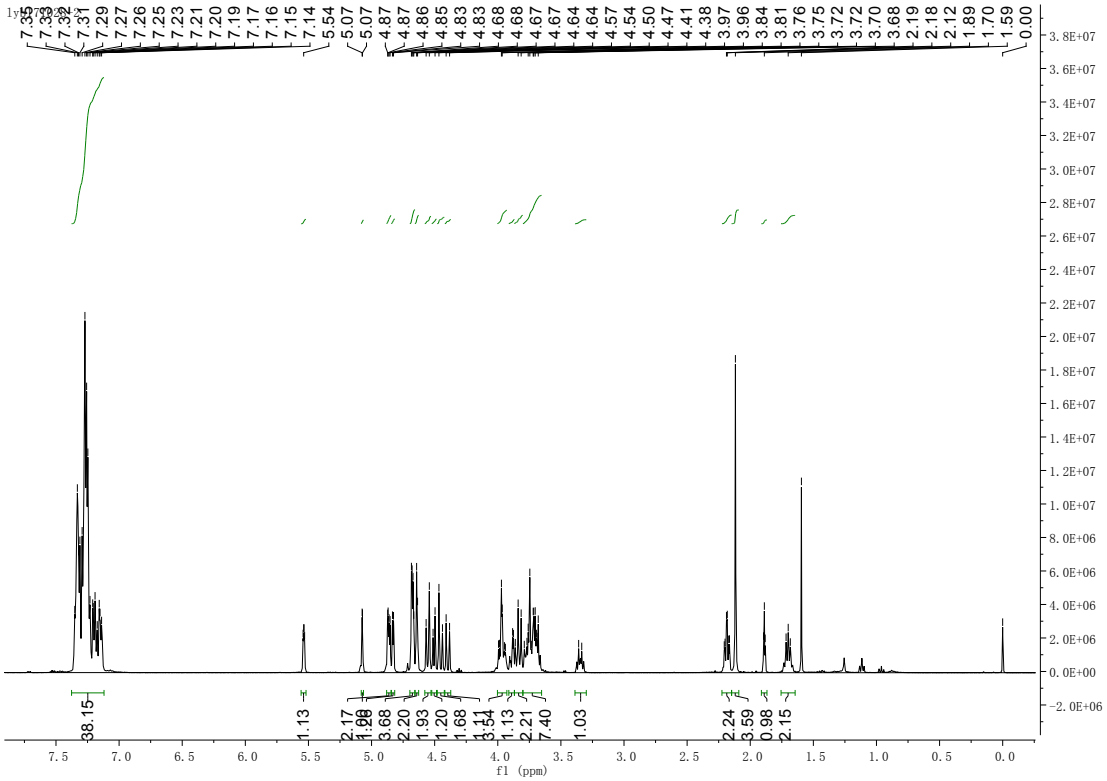


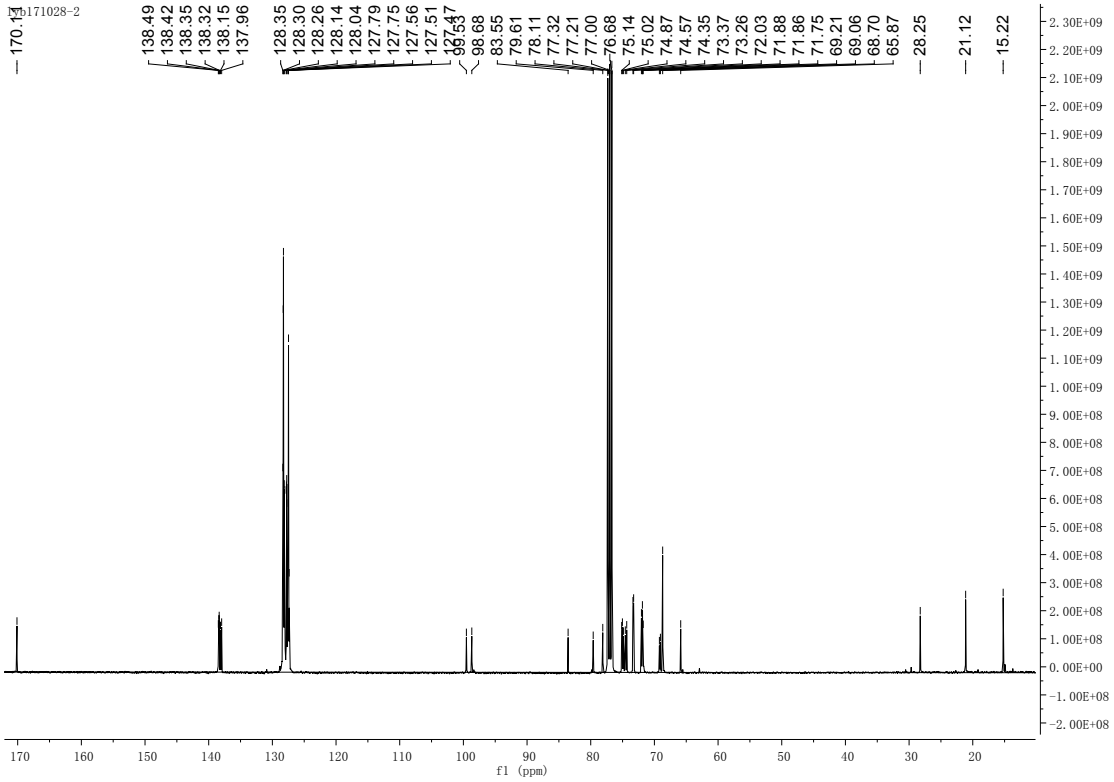
4-pentyn-1-yl 3,4,6-tri-O-benzyl-D-mannopyranoside (S-4)



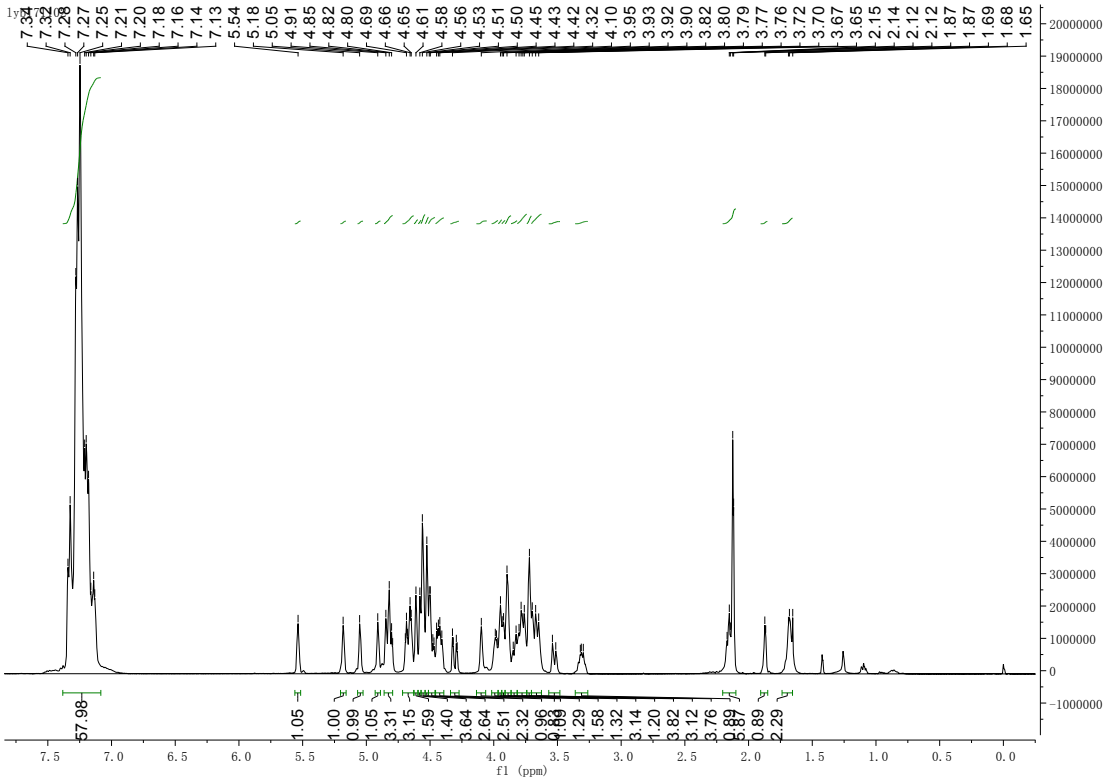


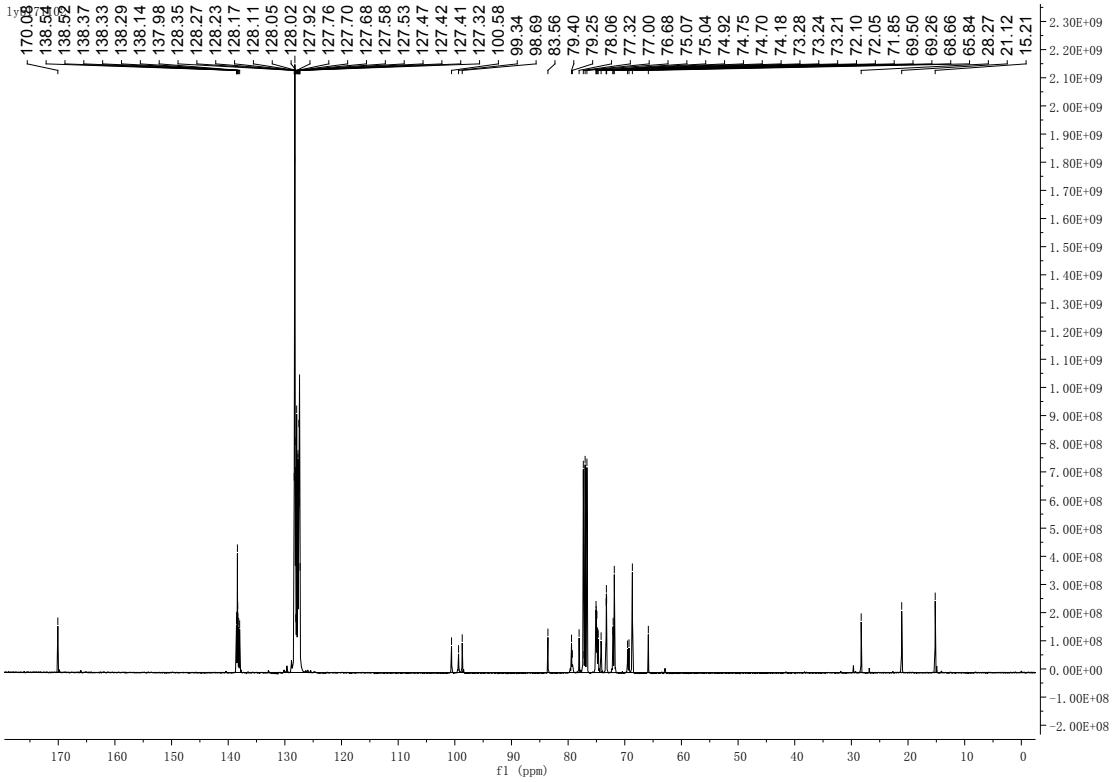
4-pentyn-1yl 2-O-acetyl-3,4,6-tri-O-benzyl-R-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (6)



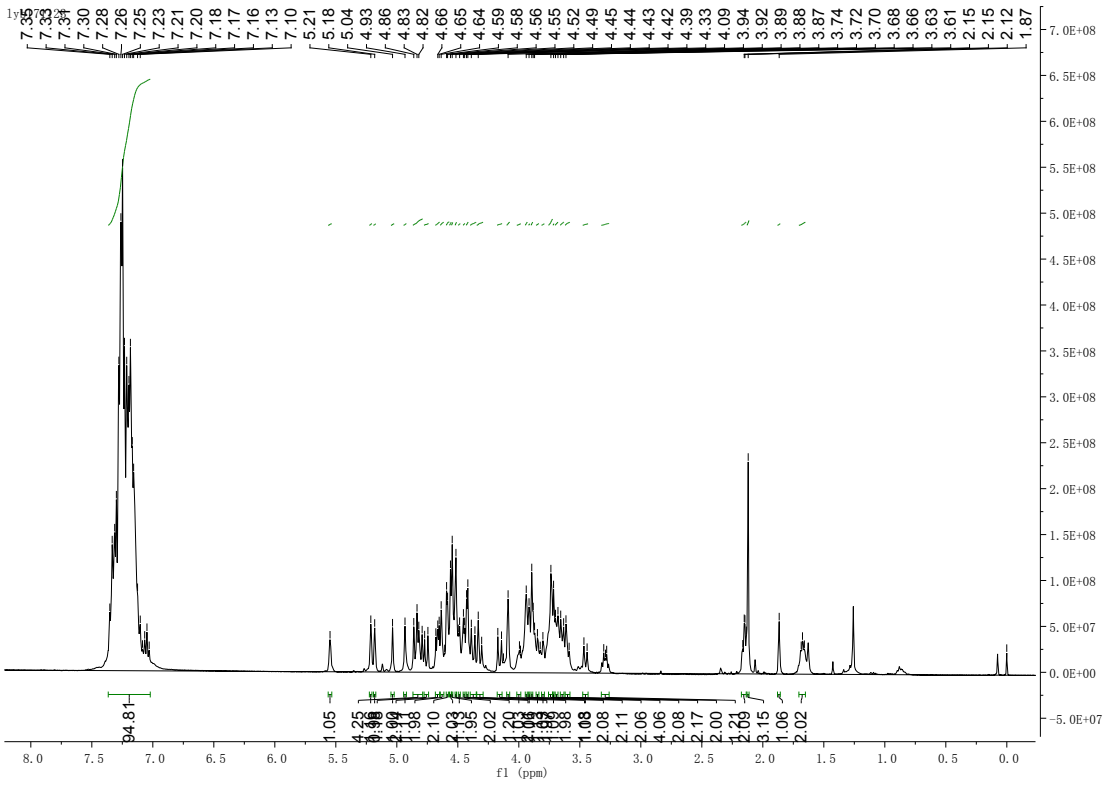


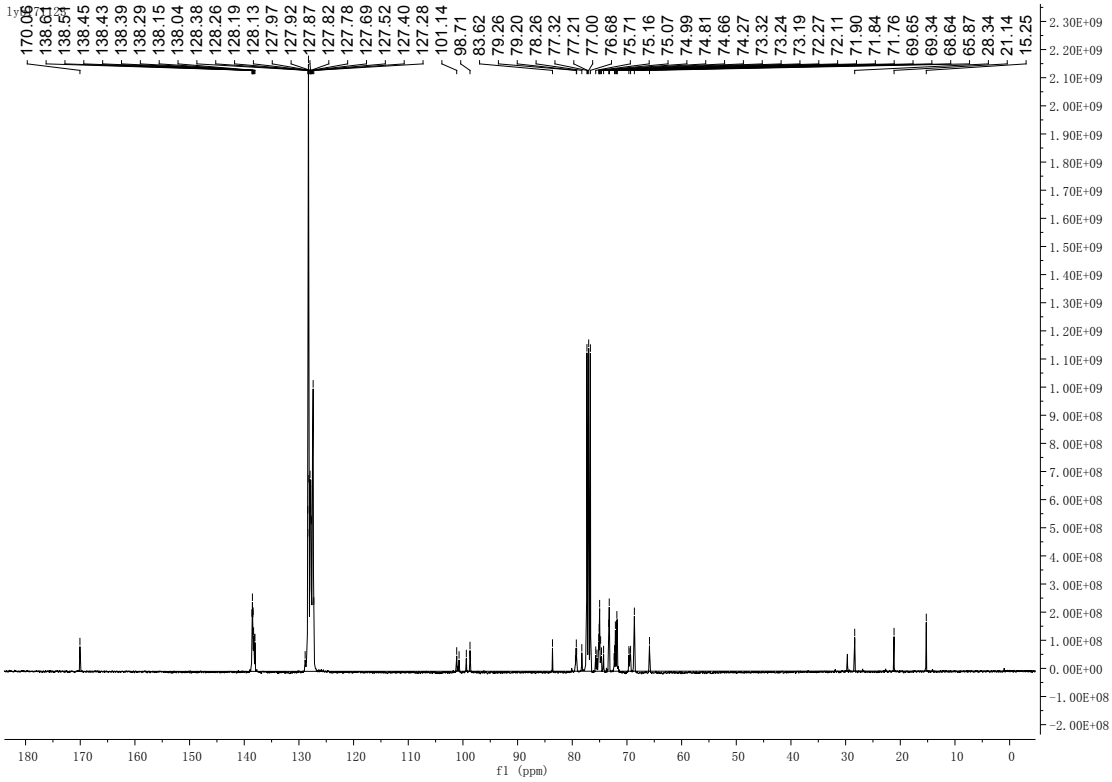
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl- α -D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl- α -D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl- α -D-mannopyranoside (7)



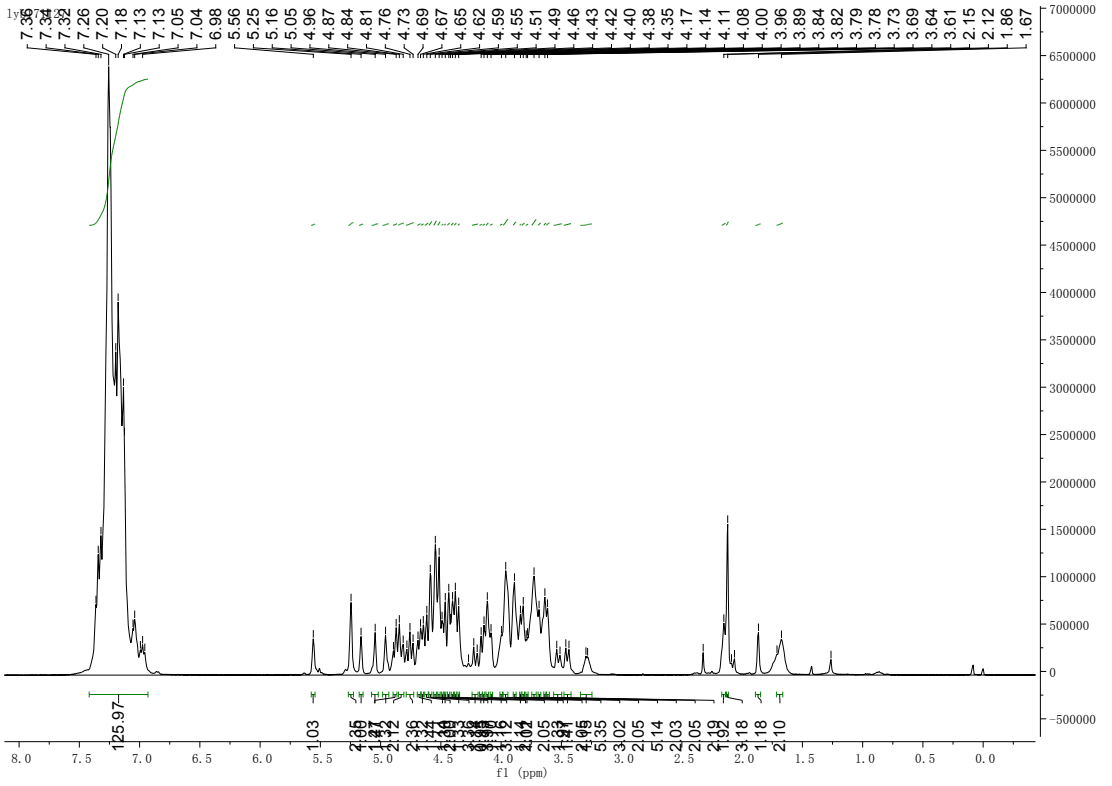


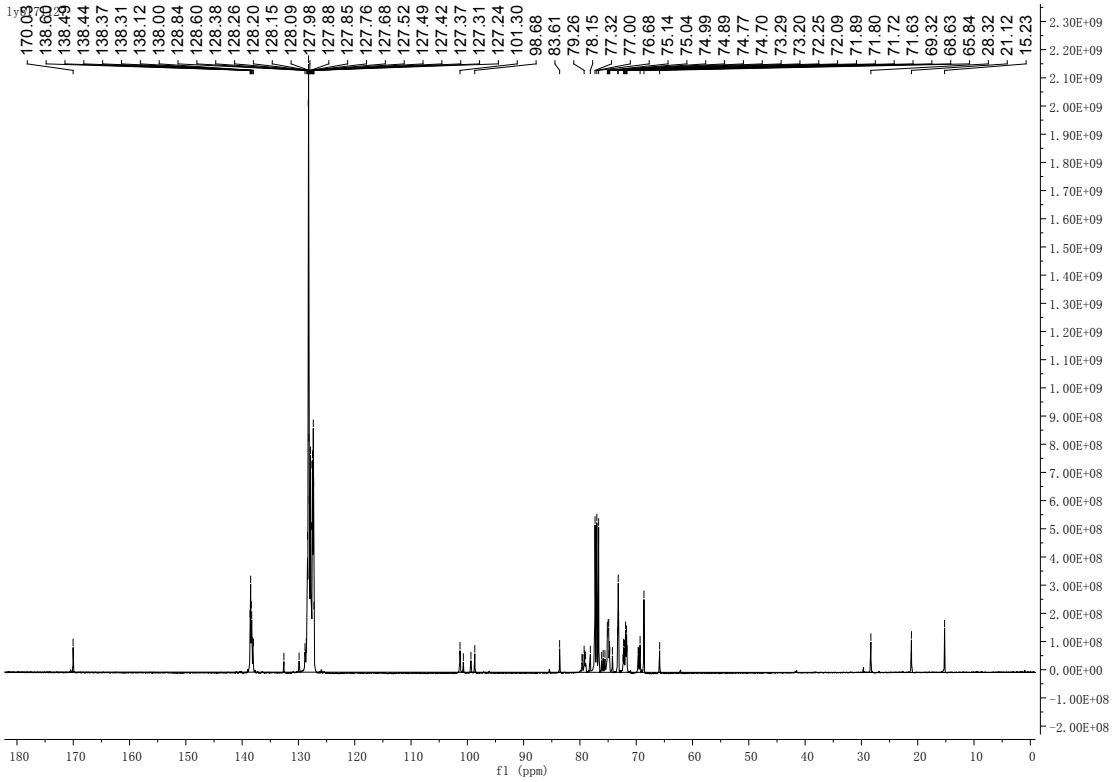
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl- α -D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl- α -D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl- α -D-mannopyranosyl-(1→2)-,4,6-tri-O-benzyl- α -D-man nopyranoside (8)



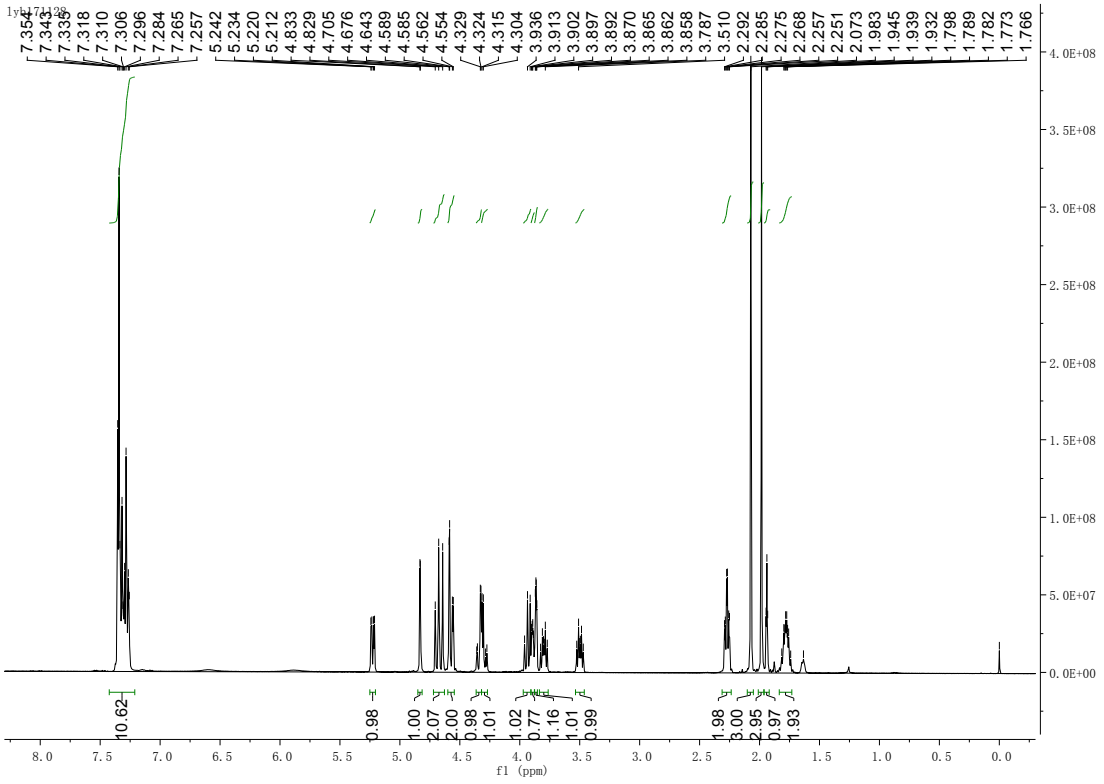


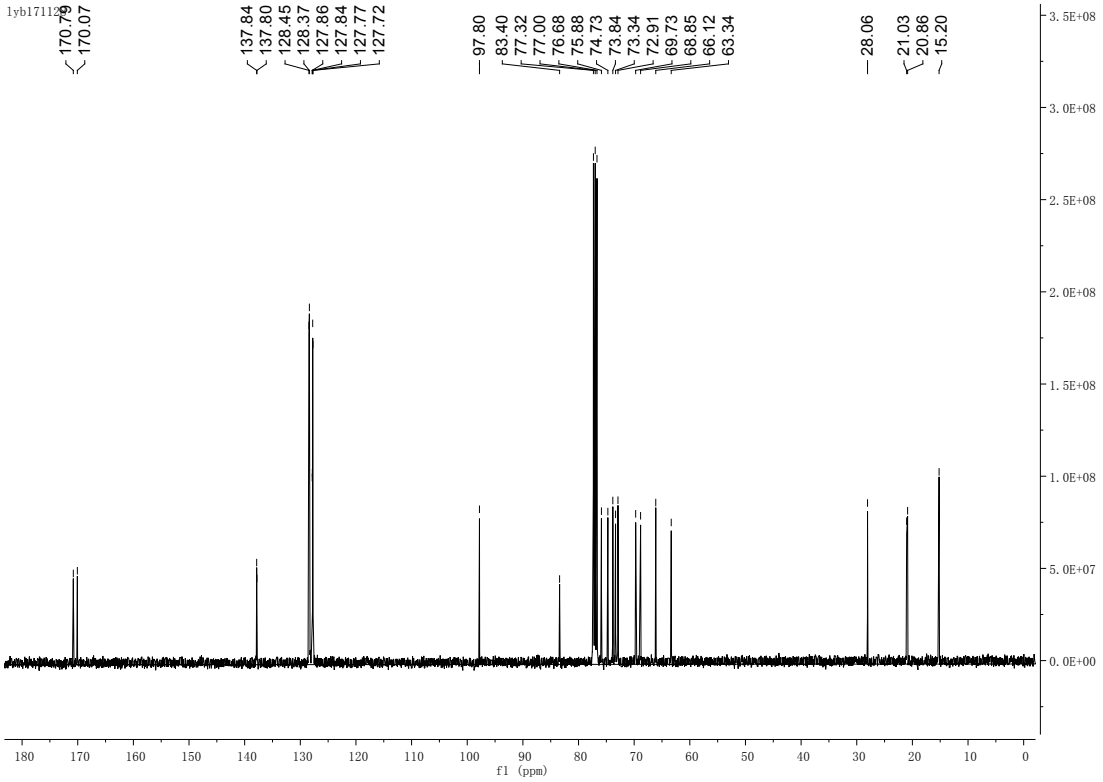
4-pentyn-1-yl 2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-Obenzyl-α-D-mannopyranoside (10)



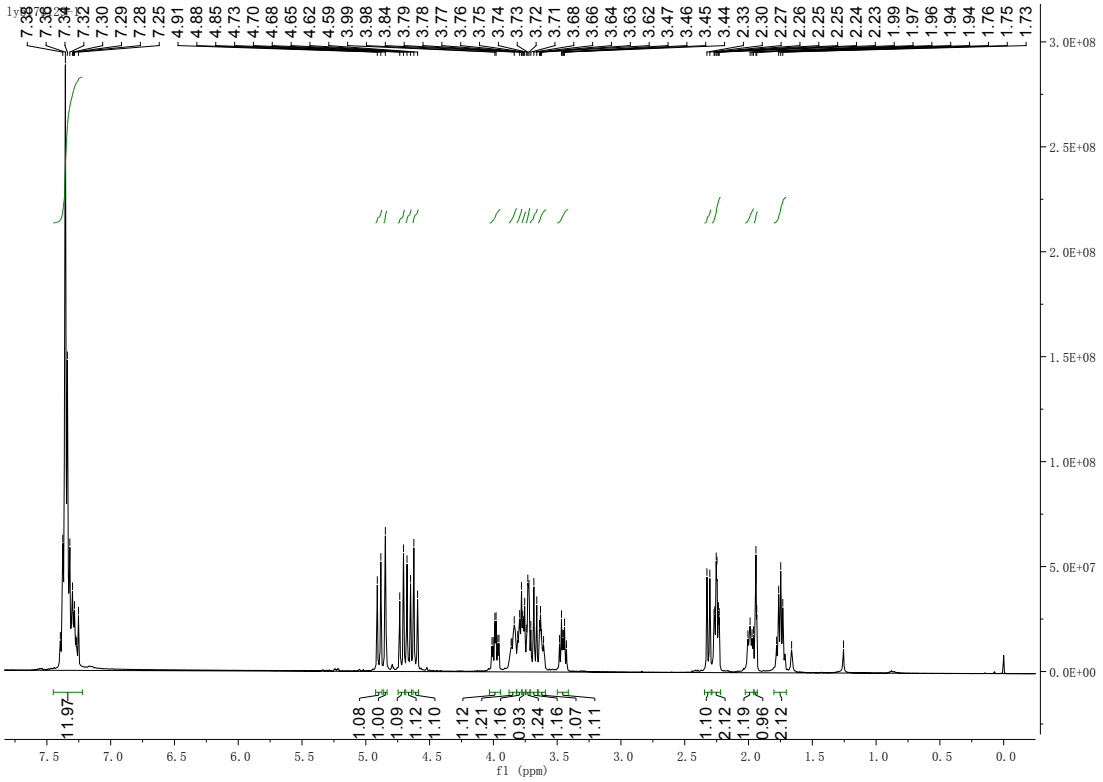


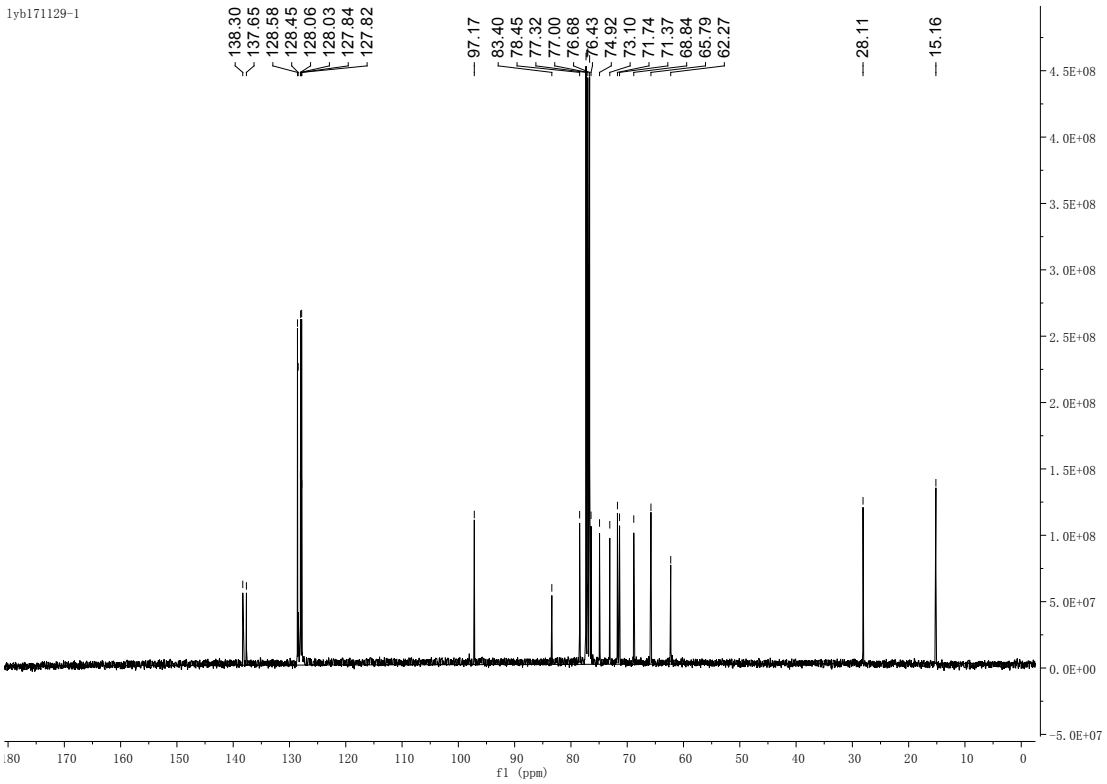
4-pentyn-1-yl 3,6-bis-O-acetyl-2,4-bis-O-benzyl-D-mannopyranoside (S-13)



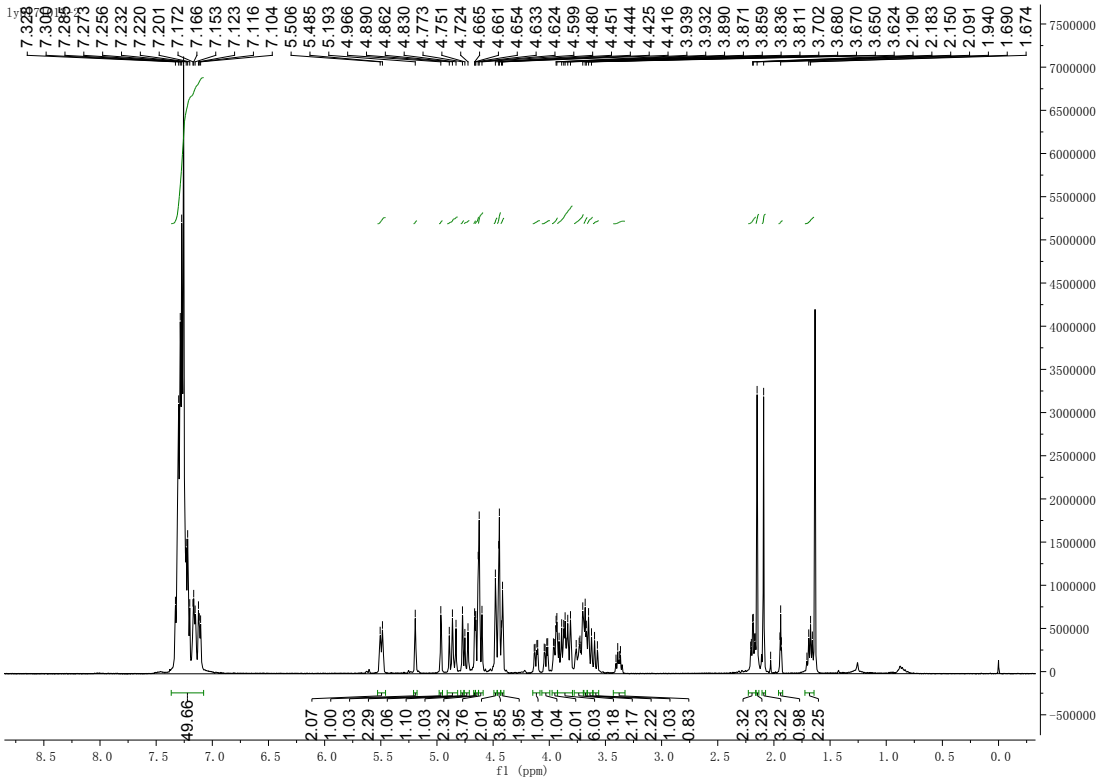


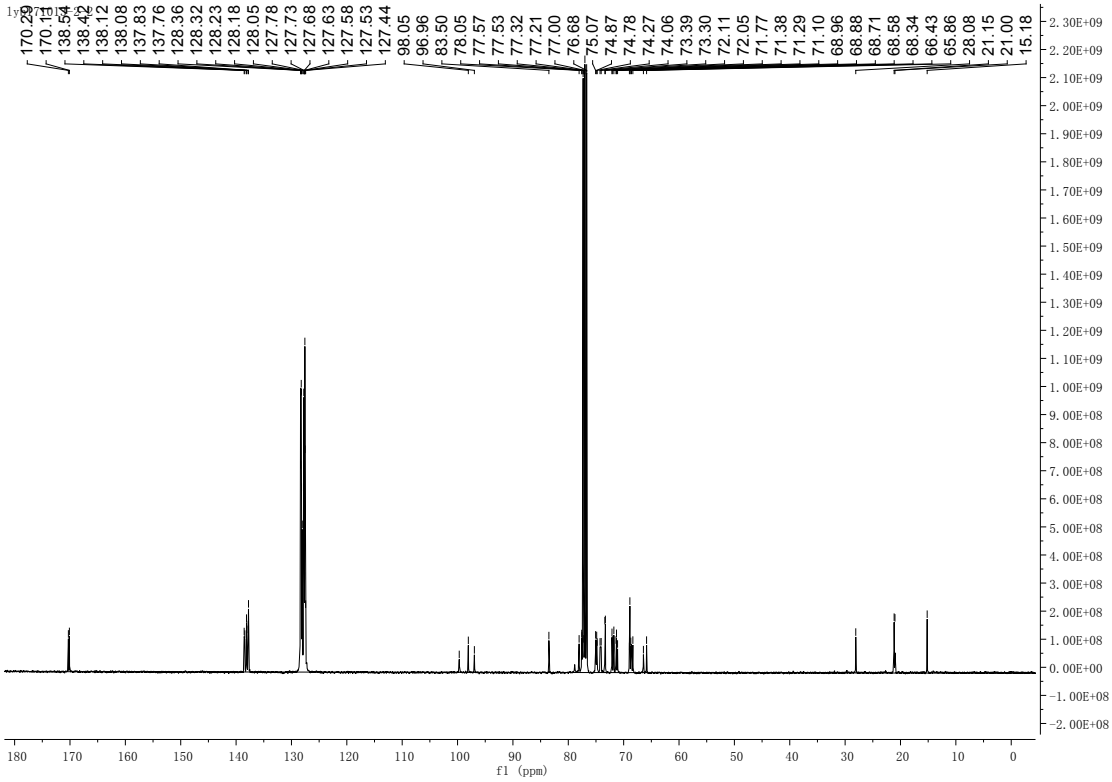
4-pentyn-1-yl 2,4-bis-O-benzyl-D-mannopyranoside (11)



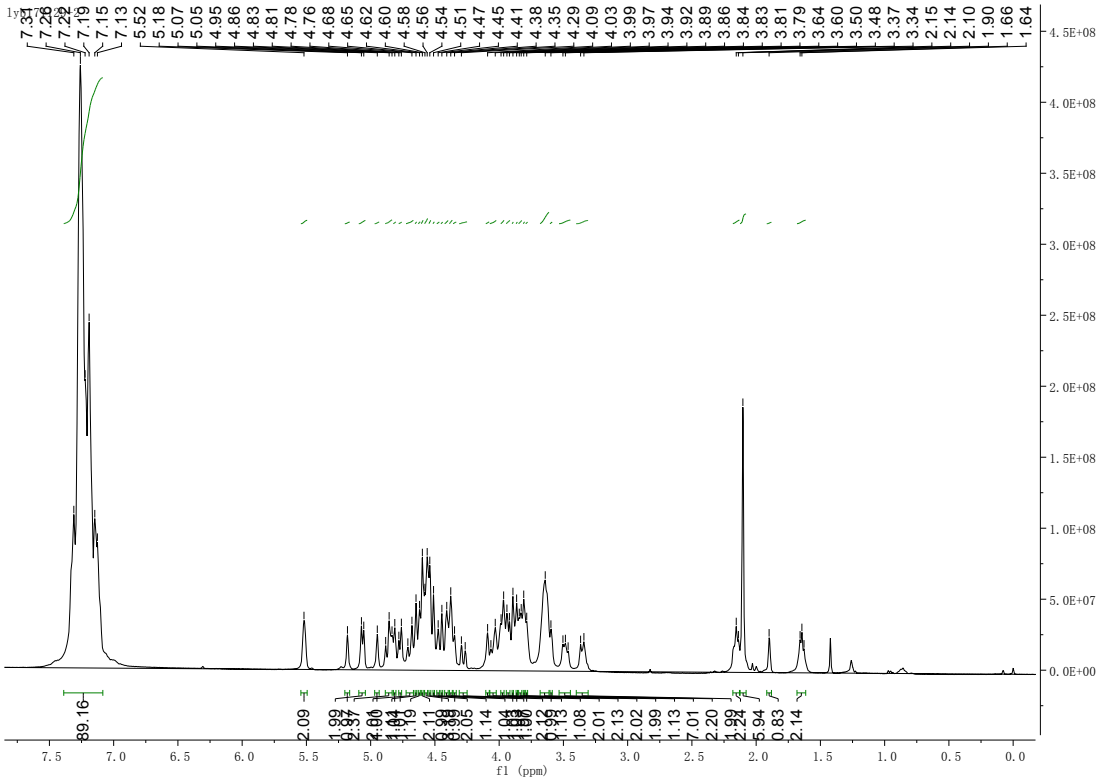


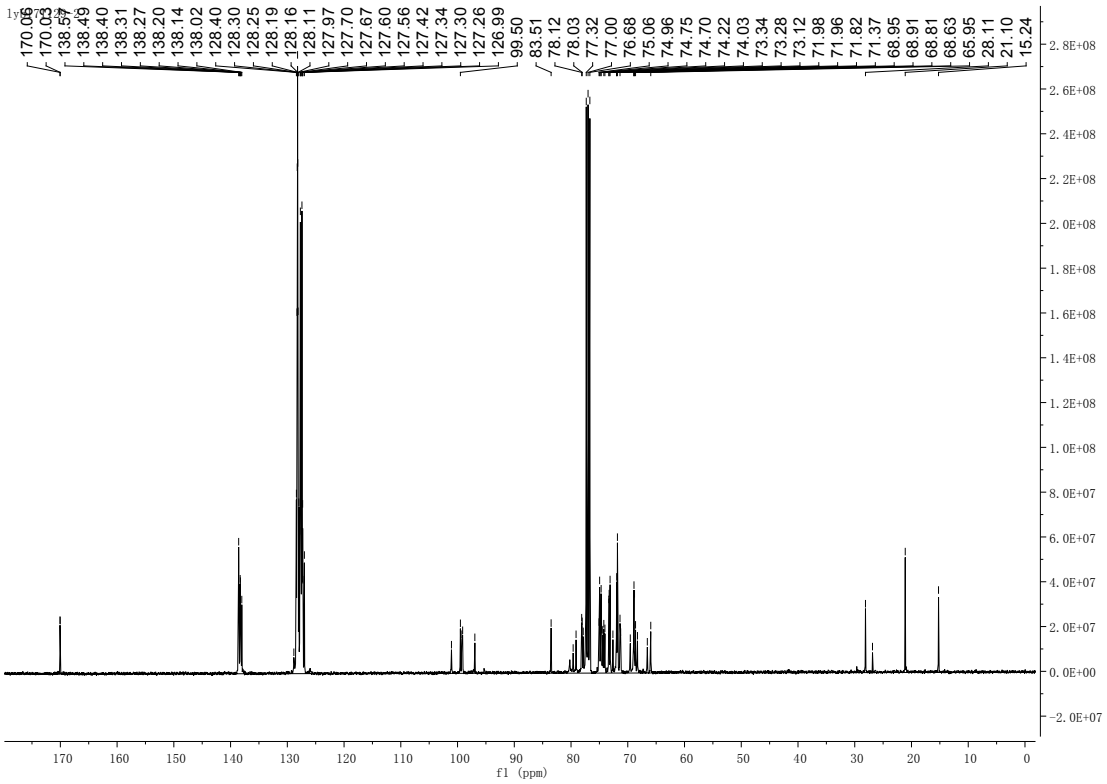
4-pentyn-1-yl 2,4-bis-O-benzyl-3,6-di-O-(2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl)- α -D-mannopyranoside (12)





4-pentyn-1-yl 2,4-bis-O-benzyl-3,6-di-O-[2-O-(2-O-Acetyl-3,4,6-tri-O-benzyl-D-mannopyranosyl)-3,4,6-tri-O-benzyl-D-mannopyranosyl]- α -D-mannopyranoside (13)





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