# Supplementary Information

## Light-driven highly efficient glycosylation reactions

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## 1. General Information

NMR spectra were recorded with a 400 MHz spectrometer for $^{1}H$ NMR, 100 MHz for $^{13}C$ NMR. Chemical shifts δ are given in ppm relative to the residual proton signals of the deuterated solvent $CDCl_3$ for $^{1}H$ and $^{13}C$ NMR. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m). High resolution mass spectra were recorded on a 3000 mass spectrometer. For column chromatography silica gel (200-300 mesh) was used as the stationary phase. Reagents were purchased from commercial sources without further purification. Solvents were purified commonly prior to use. Experiments under UV irradiation were carried out using a medium pressure lamp purchased from Julabo Technology (Beijing) Co., Ltd. (Item No. 7825-35). Stabilized supply apparatus for the medium pressure lamp were purchased from Julabo Technology (Beijing) Co., Ltd. (Item No. 7830-61). Quartz socket tube for the medium pressure lamps were purchased from Julabo Technology (Beijing) Co., Ltd. (Item No. 7854). Constant temperature circulator which was connected to the Quartz socket tubes were purchased from Julabo Technology (Beijing) Co., Ltd. (Item No. FL601). Experiments upon visible-light irradiation were carried out using household blue LED lamps (28 W in total), purchased from JETE LED Co., Ltd.

## 2. Optimization Studies

**Table S1. Optimization of the reaction conditions**[a]

| Entry | **5a / 6a** | Activator (equiv.) | T ($^{o}$C) | Solvent | UV (min) | Additive (equiv.) | Yield (%)[b] |
|---|---|---|---|---|---|---|---|
| 1 | 1.2/1.0 | **1** (1.8) | 40 | $CH_2Cl_2$ | - | - | 0 |
| 2 | 1.2/1.0 | **2** (1.8) | 40 | $CH_2Cl_2$ | - | - | 0 |
| 3 | 1.2/1.0 | **3** (1.8) | 40 | $CH_2Cl_2$ | - | - | 0 |
| 4 | 1.2/1.0 | **4** (1.8) | 40 | $CH_2Cl_2$ | - | - | 0 |
| 5 | 1.2/1.0 | **1** (1.8) | 40 | $CH_2Cl_2$ | - | CuI (1.0 eq) | 0 |
| 6 | 1.2/1.0 | **1** (1.8) | 40 | $CH_2Cl_2$ | - | $Cu(OTf)_2$ (1.0 eq) | 0 |
| 7 | 1.2/1.0 | **1** (1.8) | 40 | $CH_2Cl_2$ | - | $(CuOTf)_2{\cdot}C_6H_6$ (1.0 eq) | 0 |
| 8 | 1.2/1.0 | **2** (1.8) | 40 | $CH_2Cl_2$ | - | CuI (1.0 eq) | 0 |
| 9 | 1.2/1.0 | **2** (1.8) | 40 | $CH_2Cl_2$ | - | $Cu(OTf)_2$ (1.0 eq) | 0 |
| 10 | 1.2/1.0 | **2** (1.8) | 40 | $CH_2Cl_2$ | - | $(CuOTf)_2{\cdot}C_6H_6$ (1.0 eq) | 0 |
| 11 | 1.2/1.0 | **3** (1.8) | 40 | $CH_2Cl_2$ | - | CuI (1.0 eq) | 0 |
| 12 | 1.2/1.0 | **3** (1.8) | 40 | $CH_2Cl_2$ | - | $Cu(OTf)_2$ (1.0 eq) | 0 |
| 13 | 1.2/1.0 | **3** (1.8) | 40 | $CH_2Cl_2$ | - | $(CuOTf)_2{\cdot}C_6H_6$ (1.0 eq) | 0 |
| 14 | 1.2/1.0 | **4** (1.8) | 40 | $CH_2Cl_2$ | - | CuI (1.0 eq) | 0 |
| 15 | 1.2/1.0 | **4** (1.8) | 40 | $CH_2Cl_2$ | - | $Cu(OTf)_2$ (1.0 eq) | 0 |
| 16 | 1.2/1.0 | **4** (1.8) | RT | $CH_2Cl_2$ | - | $(CuOTf)_2{\cdot}C_6H_6$ (1.0 eq) | 0 |
| 17 | 1.2/1.0 | **3** (1.8) | RT | $CH_2Cl_2$ | 30 | - | trace |
| 18 | 1.2/1.0 | **4** (1.8) | RT | $CH_2Cl_2$ | 30 | - | trace |
| 19 | 1.2/1.0 | **1** (1.8) | RT | DMF | 30 | - | trace |
| 20 | 1.2/1.0 | **1** (1.8) | RT | 1,4-dioxane | 30 | - | trace |
| 21 | 1.2/1.0 | **1** (1.8) | RT | ether | 30 | - | trace |
| 22 | 1.2/1.0 | **1** (1.8) | RT | THF | 30 | - | trace |
| 23 | 1.2/1.0 | **1** (1.8) | RT | DMSO | 30 | - | trace |
| 24 | 1.2/1.0 | **1** (1.8) | RT | DMA | 30 | - | trace |
| 25 | 1.2/1.0 | **1** (1.8) | RT | tolune | 30 | - | 4 |
| 26 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 30 | - | 9 |
| 27 | 1.2/1.0 | **3** (1.8) | RT | MeCN | 30 | - | trace |
| 28 | 1.2/1.0 | **4** (1.8) | RT | MeCN | 30 | - | trace |
| 29 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 60 | TTBP (1.0) | 29[c] |
| 30 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 60 | DIPEA(1.0) | 27[c] |
| 31 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 60 | (1S)-(-)-β-Pinene (1.0) | 21 |
| 32 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 60 | Benzil dimethyl ketal (0.3) | 14 |
| 33 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 60 | Benzophenone (0.3) | 9 |
| 34 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 60 | AgOTf (1.0) | 19 |
| 35 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 60 | CuI(1.0)/TTBP(2.0) | trace |
| 36 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 60 | $(CuOTf)_2{\cdot}C_6H_6$ (1.0) | 21[c] |
| 37 | 1.2/1.0 | **1** (1.8) | RT | MeCN | 60 | CuI (1.0) | 34[c] |
| 38[d] | 1.3/1.0 | **1** (1.5) | -72 | $CH_2Cl_2$ | 60 | - | 75[c] |
| 39[d] | 1.3/1.0 | **1** (2.5) | -72 | $CH_2Cl_2$ | 60 | - | 88[c] |
| 40[d] | 1.3/1.0 | **1** (2.6) | -72 | $CH_2Cl_2$ | 60 | $Cu(OTf)_2$ (1.5) | 90[c] |
| 41[d] | 1.3/1.0 | **1** (1.3) | -72 | $CH_2Cl_2$ | 60 | $Cu(OTf)_2$ (1.5) | 86[c] |
| 42[d] | 1.3/1.0 | **3** (1.5) | -72 | $CH_2Cl_2$ | 60 | $Cu(OTf)_2$ (1.5) | Trace |
| 43[d] | 1.3/1.0 | **4** (1.5) | -72 | $CH_2Cl_2$ | 60 | $Cu(OTf)_2$ (1.5) | Trace |
| 44[d] | 1.3/1.0 | **1** (1.5) | -72 | $CH_2Cl_2$ | 60 | Tetrabutylammonium triflate (1.5) | 70[c] |

[a]General conditions: **5a**, **1-4**, **6a** (0.02 mmol, 1.0 equiv.), 4 Å MS (200 mg), $CH_2Cl_2$ (2.0 mL) in quartz flask under the radiation of UV. [b]Yield determined by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Isolated yield. [d]Acceptor was added after donor was pre-activated.

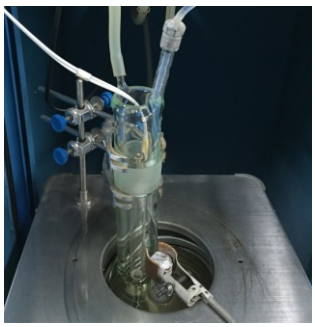
**Table S2. Optimization of the reaction conditions under the radiation of visible light.**[a]

| Entry | **5b / 6a** | Activator (equiv.) | T (°C) | Solvent | Vis. (h) | Photocat. (equiv.) | Additive (equiv.) | Yield (%)[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.3/1.0 | **1** (1.5) | 25 | $CH_2Cl_2$ | 4 | $Ru(bpy)_3(PF_6)_2$ (0.05) | $Cu(OTf)_2$ (1.5) | 77 |
| 2 | 1.3/1.0 | **1** (1.5) | 25 | $CH_2Cl_2$ | 12 | $Ru(bpy)_3(PF_6)_2$ (0.05) | $Cu(OTf)_2$ (1.5) | 80 |
| 3 | 1.3/1.0 | **1** (2.6) | 25 | $CH_2Cl_2$ | 12 | $Ru(bpy)_3(PF_6)_2$ (0.05) | $Cu(OTf)_2$ (1.5) | 95 |
| 4 | 1.3/1.0 | **1** (2.6) | 25 | $CH_2Cl_2$ | 12 | $Ru(bpy)_3(PF_6)_2$ (0.05) | - | 58 |
| 5 | 1.3/1.0 | **1** (2.6) | 25 | $CH_2Cl_2$ | 12 | $Ru(bpy)_3Cl_2$ (0.05) | - | 21 |
| 6 | 1.3/1.0 | **1** (2.6) | 25 | $CH_2Cl_2$ | 12 | $Ru(bpy)_3Cl_2$ (0.05) | $Cu(OTf)_2$ (1.5) | 67 |
| 7 | 1.3/1.0 | **1** (2.6) | 25 | $CH_2Cl_2$ | 12 | *fac*-Ir(ppy)$_3$ (0.05) | $Cu(OTf)_2$ (1.5) | trace |
| 8 | 1.3/1.0 | **1** (2.6) | 25 | $CH_2Cl_2$ | 12 | $Ru(bpy)_3Cl_2$ (0.05) | - | 32 |
| 9 | 1.3/1.0 | **1** (2.6) | 25 | $CH_2Cl_2$ | 12 | $Ru(bpy)_3Cl_2$ (0.05) | TTBP | 40 |
| 10 | 1.3/1.0 | **1** (2.6) | 25 | $CH_2Cl_2$ | 4 | $Ru(bpy)_3(PF_6)_2$ (0.05) | $Cu(OTf)_2$ (1.5) | 94 |
| 11 | 1.2/1.0 | **1** (2.4) | 25 | $CH_2Cl_2$ | 4 | $Ru(bpy)_3(PF_6)_2$ (0.05) | $Cu(OTf)_2$ (1.5) | 86 |
| 12 | 1.1/1.0 | **1** (2.2) | 25 | $CH_2Cl_2$ | 4 | $Ru(bpy)_3(PF_6)_2$ (0.05) | $Cu(OTf)_2$ (1.5) | 85 |
| 13 | 1.3/1.0 | **1** (2.0) | 25 | $CH_2Cl_2$ | 4 | $Ru(bpy)_3(PF_6)_2$ (0.05) | $Cu(OTf)_2$ (1.5) | 85 |
| 14[c] | 1.3/1.0 | **1** (2.6) | -70 | $CH_2Cl_2$ | 4 | $Ru(bpy)_3(PF_6)_2$ (0.05) | $Cu(OTf)_2$ (1.5) | trace |
| 15 | 1.3/1.0 | **1** (2.6) | 25 | $CH_2Cl_2$ | 12 | - | $Cu(OTf)_2$ (1.5) | trace |
| 16[d] | 1.3/1.0 | **1** (2.6) | 40 | $CH_2Cl_2$ | - | $Ru(bpy)_3(PF_6)_2$ (0.05) | $Cu(OTf)_2$ (1.5) | 0 |
| 17 | 1.3/1.0 | $CBr_4$ (2.6) | 25 | $CH_2Cl_2$ | 12 | $Ru(bpy)_3(PF_6)_2$ (0.05) | - | trace |
| 18 | 1.3/1.0 | $CBrCl_3$ (2.6) | 25 | $CH_2Cl_2$ | 12 | $Ru(bpy)_3(PF_6)_2$ (0.05) | - | trace |

[a]General conditions: **5b**, activator, **6a** (0.02 mmol, 1.0 equiv.), 4 Å MS (200 mg), photocatalyst, $CH_2Cl_2$ (2.0 mL) in quartz flask. [b]Yield determined by $^1$H NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [c]Acceptor was added after donor was pre-activated. [d]The system was reacted in dark for 24 h.

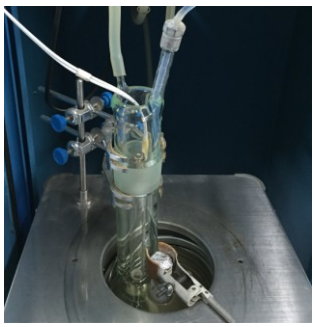
## 3. General Procedures

### 3.1 Glycosylation reactions under UV irradiation



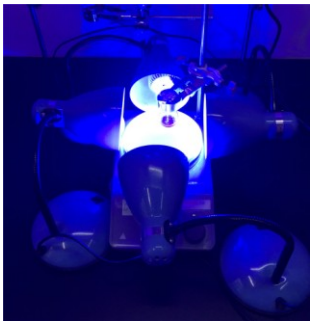
An oven-dried quartz flask equipped with a magnetic stir bar, was charged with donor (0.024 mmol), acceptor (0.02 mmol), **1** (0.03 mmol), $Cu(OTf)_2$ (0.03 mmol), activated 4Å molecular sieves (200 mg), and $CH_2Cl_2$ (2 mL). The reaction mixture was stirred for 15 min and then cooled to -72 °C under argon atmosphere. The reaction vessel was exposed to UV irradiation at -72 °C for 1 h. After disappearance of the acceptor detected by TLC, the reaction mixture was quenched by triethylamine (0.1 mL). The precipitate was filtered off, and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired products.

### 3.2 Pre-activation based glycosylation reactions under UV irradiation



An oven-dried quartz flask equipped with a magnetic stir bar, was charged with donor (0.024 mmol), **1** (0.03 mmol), $Cu(OTf)_2$ (0.03 mmol), activated 4Å molecular sieves (200 mg), and $CH_2Cl_2$ (2.0 ml). The reaction mixture was stirred for 15 min and then cooled to -72 $^oC$ under argon atmosphere. The reaction vessel was exposed to UV irradiation at -72 $^oC$ for 1 h. After disappearance of the donor detected by TLC, the removal of UV irradiation was followed by the addition of a solution of the acceptor (0.02 mmol) in dichloromethane (0.5 mL in total) via syringe. The reaction mixture was stirred and slowly warmed to room temperature, and then quenched by $Et_3N$ (0.1 mL). The precipitate was filtered off, and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired products.

### 3.3 Glycosylation reactions under visible-light irradiation



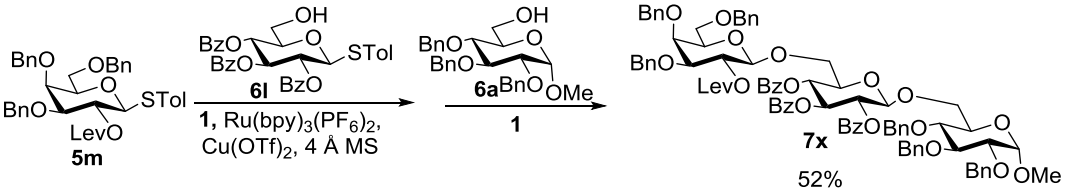
An oven-dried quartz flask equipped with a magnetic stir bar, was charged with donor (0.026 mmol), acceptor (0.02 mmol), **1** (0.052 mmol), $Cu(OTf)_2$ (0.03 mmol), $[Ru(bpy)_3](PF_6)_2$ (0.001 mmol), activated 4Å molecular sieves (200 mg), and $CH_2Cl_2$ (2 mL). The reaction mixture was exposed to visible light irradiation (four blue LED lamps, 28 W in total) at room temperature. After disappearance of the acceptor detected by TLC, the reaction mixture was quenched by triethylamine (0.1 mL). The precipitate was filtered off, and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to give the desired products.

### 3.4 Glycosylation reactions under sunlight

An oven-dried quartz flask equipped with a magnetic stir bar, was charged with **5b** (0.026 mmol), **6a** (0.02 mmol), **1** (0.052 mmol), $Cu(OTf)_2$ (0.03 mmol), $[Ru(bpy)_3](PF_6)_2$ (0.001 mmol), activated

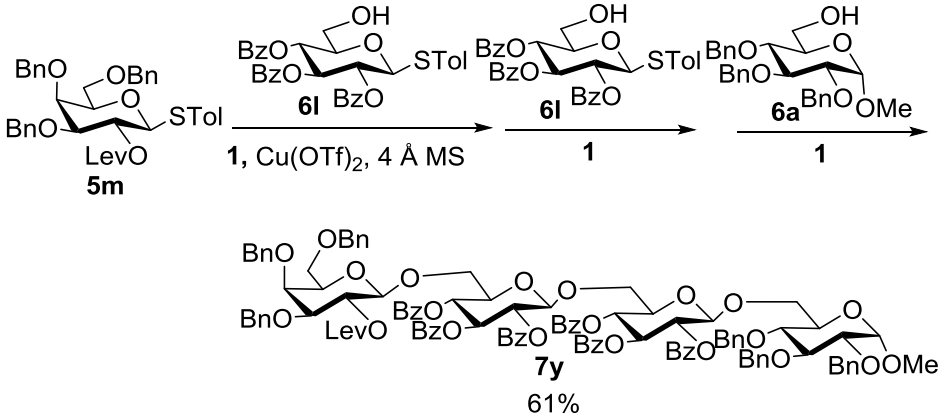
4Å molecular sieves (200 mg), and $CH_2Cl_2$ (2 mL). The reaction mixture was exposed to sunlight at room temperature. After disappearance of the acceptor detected by TLC, the reaction mixture was quenched by triethylamine (0.1 mL). The precipitate was filtered off, and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 4/1, v/v) to give the desired product **7b** (12.5 mg, 60%).

**3.5 Reactivity-based one-pot synthesis of trisaccharide 7x under visible-light irradiation**




An oven-dried quartz flask equipped with a magnetic stir bar, was charged with **5m** (0.026 mmol, 17.0 mg), **6l** (0.02 mmol, 12.0 mg), **1** (0.028 mmol, 11.3 mg), $Cu(OTf)_2$ (0.03 mmol, 10.8 mg), $[Ru(bpy)_3](PF_6)_2$ (0.001 mmol, 0.9 mg), and activated 4Å molecular sieves (400 mg). The vessel was evacuated and backfilled with argon (the cycle was performed three times) and $CH_2Cl_2$ (2 mL) was added via syringe. The reaction mixture was stirred for 10 min and then exposed to visible-light irradiation. After disappearance of the acceptor **6l** detected by TLC, the system was sirred for 10 minutes in dark, then a solution of **1** (0.03 mmol, 12.1 mg), and **6a** (0.014 mmol, 6.5 mg) in $CH_2Cl_2$ (1.0 mL) was added to the reaction mixture via syringe. A continuous exposure of the resulting mixture to illumination was maintained until the complete consumption of **6a**. The reaction mixture was quenched by triethylamine (0.1 mL). The precipitate was filtered off, and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 3/1, v/v) to give the desired product **7x** (10.7 mg, 52%, calculated based on the amount of **6a**).

**3.6 Preactivation-based one-pot synthesis of tetrasaccharide 7y under UV irradiation**




An oven-dried quartz flask equipped with a magnetic stir bar, was charged with **5m** (0.024 mmol, 15.7 mg), **1** (0.026 mmol, 10.5 mg), $Cu(OTf)_2$ (0.026 mmol, 9.4 mg), and activated 4Å molecular sieves (500 mg). The vessel was evacuated and backfilled with argon (the cycle was performed three times) and $CH_2Cl_2$ (2 mL) was added via syringe. The reaction mixture was stirred for 30 min and then cooled to -72 $^oC$ under argon atmosphere. The reaction vessel was exposed to UV irradiation at -72 $^oC$ for 1 h. UV irradiation was turned off and a solution of **6l** (0.02 mmol, 12.0 mg) in $CH_2Cl_2$ (0.5 mL) was added to the reaction mixture via syringe. The reaction mixture was stirred and slowly warmed to room temperature, and then cooled back to -72 $^oC$. After the addition of a solution of **1** (0.026 mmol, 10.5 mg) in $CH_2Cl_2$ (1 mL) to the resulting mixture, the reaction vessel was exposed to UV irradiation for 1 h again. UV irradiation was turned off and a solution of **6l** (0.016 mmol, 9.6 mg) in $CH_2Cl_2$ (0.5 mL) was added to the reaction mixture via syringe. The reaction mixture was stirred and slowly warmed to room temperature, and then cooled back to -72 $^oC$. After the addition of a solution of **1** (0.026 mmol, 10.5 mg) in $CH_2Cl_2$ (1 mL) to the resulting mixture, the reaction vessel was exposed to UV irradiation for 1 h again. UV irradiation was turned off and a solution of **6a** (0.012 mmol, 5.7 mg) in $CH_2Cl_2$ (0.5 mL) was added to the reaction mixture via syringe. The reaction mixture was stirred and slowly warmed to room temperature. The reaction mixture was quenched by triethylamine (0.1 mL) after completion of the reaction. The precipitate was filtered off, and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 2/1, v/v) to give the desired product **7y** (14.2 mg, 61%, calculated based on the amount of **6a**).

## 4. Light-Dark Interval Reactions

The addition of a solution of **5c** (0.02 mmol, 9.1 mg), **1** (0.04 mmol, 16.1 mg), $[Ru(bpy)_3](PF_6)_2$ (0.001mmol, 0.9 mg), and $Cu(OTf)_2$ (0.022 mmol, 7.9 mg) in $CD_2Cl_2$ (0.5 mL) to NMR tube was followed by the interval irradiation of blue light and dark. The system was determined by $^1H$ NMR analysis every 10 minutes. The $^1H$ NMR spectra were shown below ($CH_2Cl_2$ in $CD_2Cl_2$ was performed as internal standard).

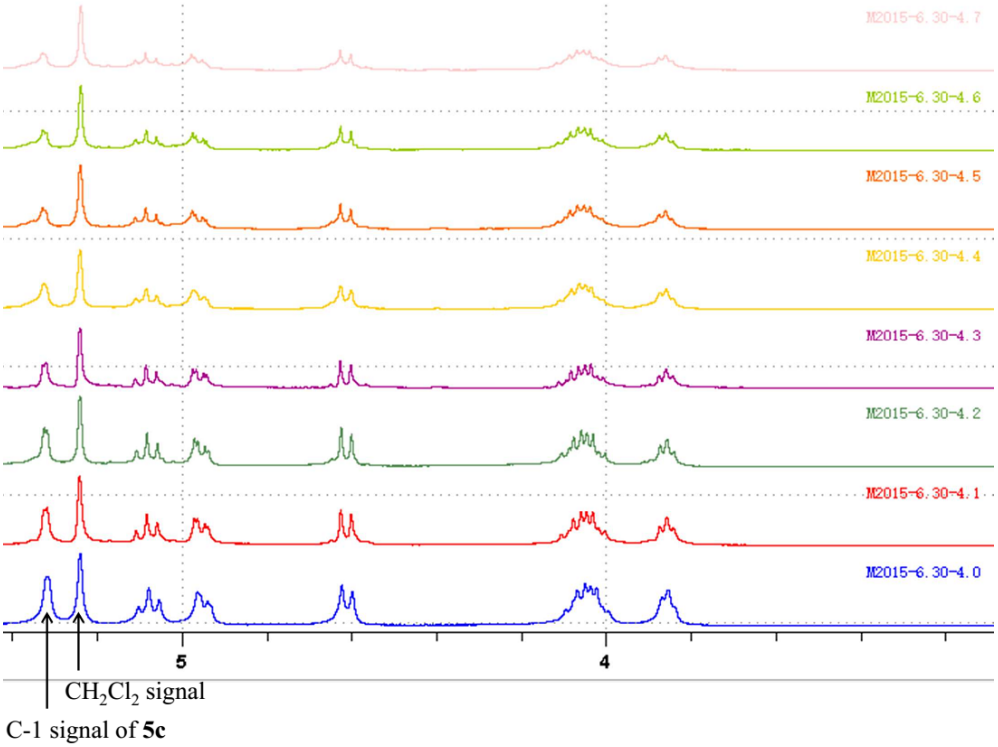
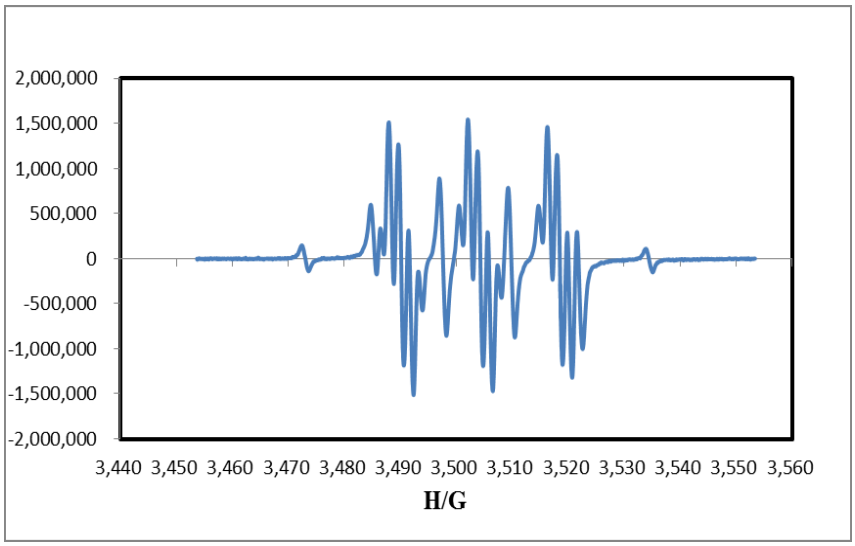



**Figure S1. $^1H$ NMR spectra of Light-Dark Interval Reactions**

## 5. EPR Experiments

(A)




(B)

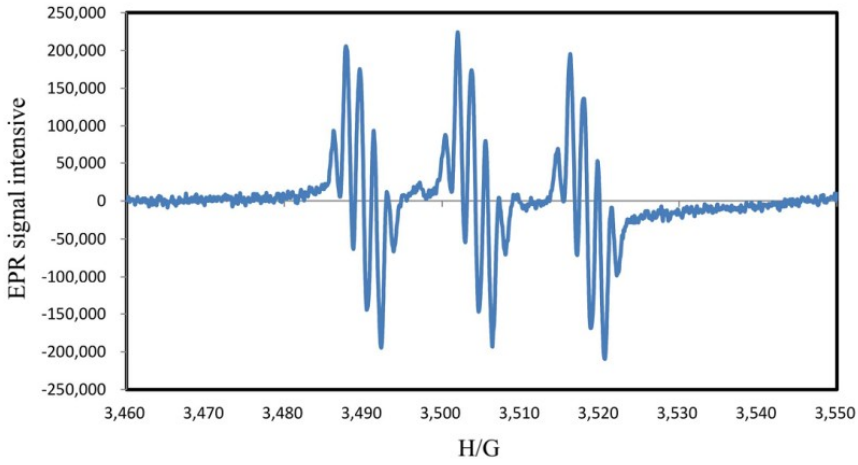



**Figure S2. EPR experiments for trapping $CF_3$ radical.** A) Under the irradiation of UV. B) Under the irradiation of visible light. A solution of **5a**, PBN, activator **1** in $CH_2Cl_2$ (1 M) was added in quartz capillary tube followed by the irradiation of UV or visible light *in situ*, the system was determined by EPR analysis at room temperature.

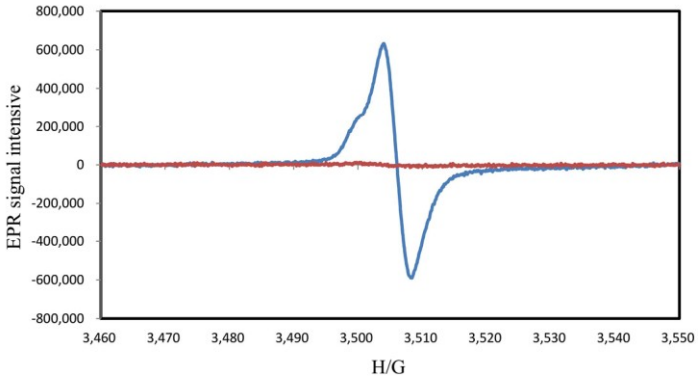



**Figure S3. Observation of dibenzothiophene radical cation by EPR experiments at room temperature.** The

blue line: a solution of activator **1** in $CH_2Cl_2$ (1 M) was added into quartz capillary tube followed by the irradiation of UV in situ, the system was determined by EPR analysis at room temperature. The red line: a solution of donor **5a**, activator **1** in $CH_2Cl_2$ (1 M) was added into quartz capillary tube followed by the irradiation of UV *in situ*, the system was determined by EPR analysis at room temperature.

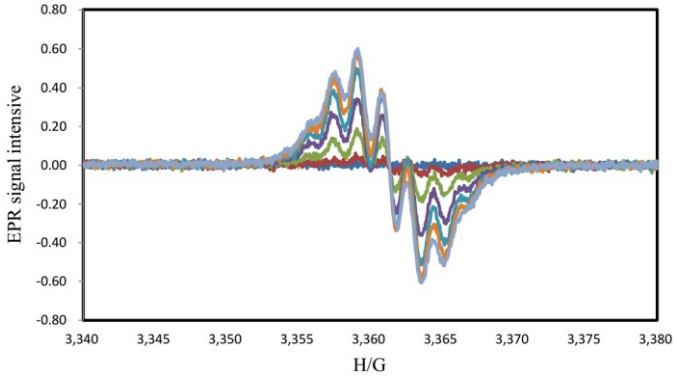



**Figure S4. Observation of dibenzothiophene radical cation by EPR experiments every 43 seconds at 200 K.** A solution of activator **1** in $CH_2Cl_2$ (1 M) was added into quartz capillary tube followed by the irradiation of UV in situ, the system was determined by EPR analysis every 43 seconds at 200 K, 7 lines in total.

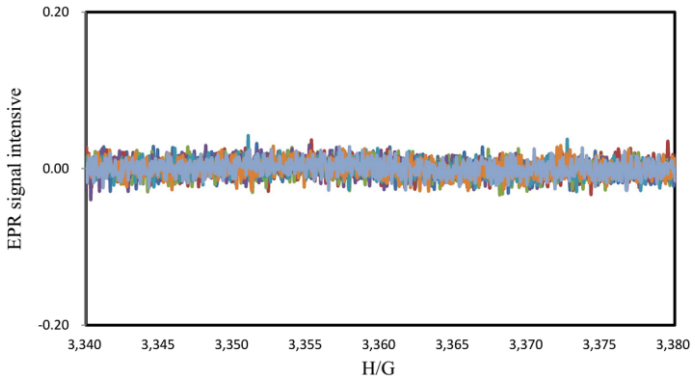
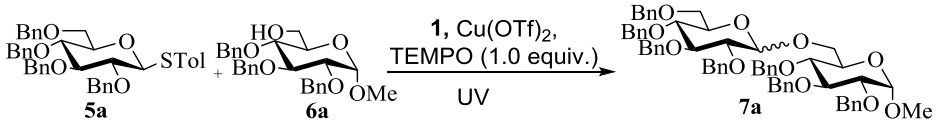
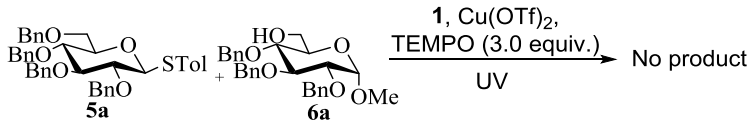



**Figure S5. EPR experiments in the presence of thioglycoside donor at 200 K.** A solution of donor **5a**, activator **1** in $CH_2Cl_2$ (1 M) was added into quartz capillary tube followed by the irradiation of UV in situ, the system was determined by EPR analysis every 43 seconds at 200 K, 7 lines in total.

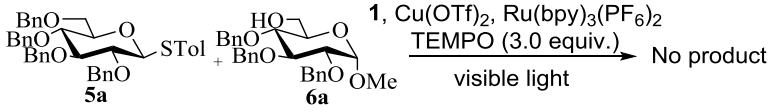
## 6. TEMPO-Trapping Experiments




According to the general procedure as described in general procedure 3.1 and an additional TEMPO (1.0 equiv.) was added. The desired product **7a** was obtained in 30% yield.

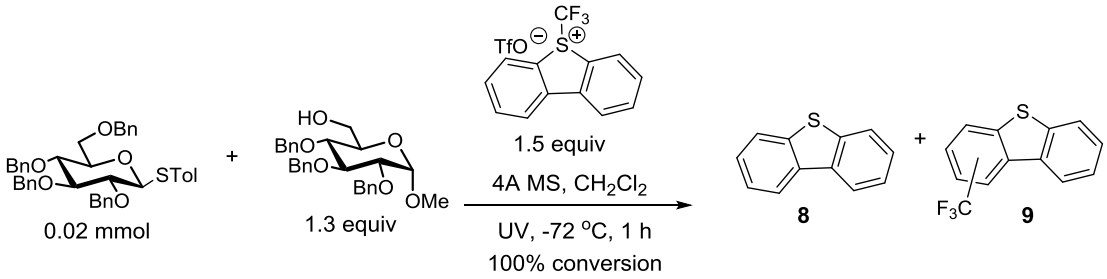



According to the general procedure as described in general procedure 3.1 and an additional TEMPO (3.0 equiv.) was added. No desired product **7a** was detected.




According to the general procedure as described in general procedure 3.3 and an additional TEMPO (3.0 equiv.) was added. No desired product **7a** was detected.

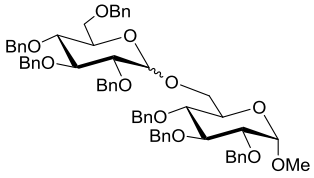
**Scheme S1. Experiments for the insight into the role of $Cu(OTf)_2$.**




## 7. Characterization of Compounds

**Methyl**

**2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (7a)**



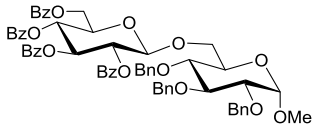
This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35-7.15 (m, 53H), 5.00-4.94 (m, 3.7H), 4.93-4.89 (m, 2H), 4.84 -4.68 (m, 9.6H), 4.67-4.63 (m, 2.6H), 4.62-4.56 (m, 3.2H), 4.55-4.49 (m, 4.9H), 4.47-4.39 (m,

1.7H), 4.35 (d, *J* = 7.8 Hz, 1H), 4.18 (dd, *J* = 10.8, 1.8 Hz, 1H), 4.02-3.93 (m, 2.2H), 3.87-3.40 (m, 20.7H), 3.35 (s, 1.6H), 3.32 (s, 3H). The $^1$H NMR data are in accordance with those reported previously.[1]

**Methyl**

**2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside**

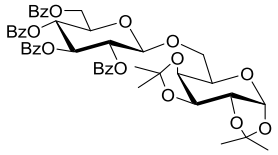
**(7b)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02-7.95 (m, 2H), 7.92-7.86 (m, 4H), 7.84-7.79 (m, 2H), 7.54-7.44 (m, 2H), 7.42-7.19 (m, 23H), 7.09-7.02 (m, 2H), 5.88 (t, *J* = 9.6 Hz, 1H), 5.67 (t, *J* = 9.7 Hz, 1H), 5.59 (dd, *J* = 9.4, 7.9 Hz, 1H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.82 (d, *J* = 7.8 Hz, 1H), 4.72 (d, *J* = 12.3 Hz, 1H), 4.68 (d, *J* = 11.3 Hz, 1H), 4.64-4.56 (m, 2H), 4.56-4.48 (m, 3H), 4.30 (d, *J* = 11.2 Hz, 1H), 4.14 (d, *J* = 9.1 Hz, 1H), 4.12-4.06 (m, 1H), 3.88 (t, *J* = 9.2 Hz, 1H), 3.79-3.68 (m, 2H), 3.42 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.40-3.34 (m, 1H), 3.20 (s, 3H). The $^1$H NMR data are in accordance with those reported previously.[1]

**6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactop**

**yranose (7c)**

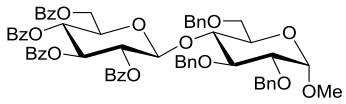



This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.05-7.80 (m, 8H), 7.58-7.26 (m, 12H), 5.90 (t, *J* = 9.5 Hz, 1H), 5.67 (t, *J* = 9.6 Hz, 1H), 5.57-5.50 (m, 1H), 5.42 (d, *J* = 5.0 Hz, 1H), 5.04 (d, *J* = 7.8 Hz, 1H), 4.64 (dd, *J* = 12.1, 3.0 Hz, 1H), 4.49 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.43 (dd, *J* = 7.9, 2.2 Hz, 1H), 4.22-3.82 (m, 6H), 1.37 (s, 3H), 1.24 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H). The $^1$H NMR data are in accordance with those reported previously.[2]

**Methyl**

**2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside**

**(7d)**

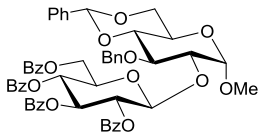



This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.88-7.87 (m, 4H), 7.79-7.77 (m, 2H), 7.57-7.12 (m, 27H), 5.62 (t, *J* = 9.5 Hz, 1H), 5.54 (t, *J* = 9.6 Hz, 1H), 5.46 (dd, *J* = 9.5, 8.0 Hz, 1H), 5.07 (d, *J* = 11.2 Hz, 1H), 4.85-4.69 (m, 4H), 4.64-4.51 (m, 2H), 4.40 (dd, *J* = 12.1, 3.2 Hz, 1H), 4.34 (d, *J* = 12.1 Hz, 1H), 4.26 (dd, *J* = 12.0, 4.9 Hz, 1H), 3.96 (t, *J* = 9.2 Hz, 1H), 3.88 (t, *J* = 9.2 Hz, 1H), 3.77-3.64 (m, 2H), 3.55-3.38 (m, 3H), 3.27 (s, 3H). The $^1$H NMR data are in accordance with those reported previously.[1]

**Methyl**

**3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucop**

**yranoside (7e)**

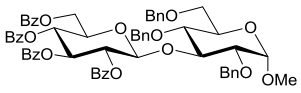



This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.07-7.77 (m, 8H), 7.61-6.96 (m, 22H), 5.91 (t, *J* = 9.6 Hz, 1H), 5.74-5.65 (m, 2H), 5.49 (s, 1H), 5.19 (d, *J* = 7.8 Hz, 1H), 4.96 (d, *J* = 3.6 Hz, 1H), 4.74 (dd, *J* = 12.2, 3.0 Hz, 1H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.45 (dd, *J* = 12.2, 5.4 Hz, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 4.26 (dd, *J* = 10.1, 4.7 Hz, 1H), 4.17-4.11 (m, 1H), 3.92 (t, *J* = 9.3 Hz, 1H), 3.84-3.75 (m, 2H), 3.68 (t, *J* = 10.2 Hz, 1H), 3.52 (t, *J* = 9.3 Hz, 1H), 3.37 (s, 3H). The $^1$H NMR data are in accordance with those reported previously.[3]

**Methyl**

**2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside**

**(7f)**

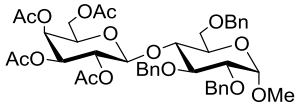



This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:3, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03-7.81 (m, 8H), 7.59-7.04 (m, 27H), 5.93 (t, *J* = 9.6 Hz, 1H), 5.70 (t, *J* = 9.6 Hz, 1H), 5.63 (t, *J* = 8.2 Hz, 1H), 5.50 (d, *J* = 7.8 Hz, 1H), 5.11 (d, *J* = 10.7 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.56-4.25 (m, 8H), 4.20-4.05 (m, 2H), 3.70-3.48 (m, 4H), 3.23 (s, 3H). The $^1$H NMR data are in accordance with those reported previously.[4]

**Methyl**

**2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside**

**(7g)**

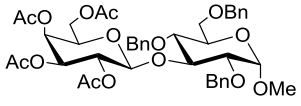



This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43-7.21 (m, 15H), 5.24 (d, *J* = 2.9 Hz, 1H), 5.08 (dd, *J* = 10.4, 8.0 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.85-4.71 (m, 4H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.59 (d, *J* = 3.7 Hz, 1H), 4.48 (d, *J* = 8.0 Hz, 1H), 4.41 (d, *J* = 12.1 Hz, 1H), 3.99-3.82 (m, 4H), 3.74 (dd, *J* = 10.6, 2.8 Hz, 1H), 3.67-3.57 (m, 2H), 3.55-3.46 (m, 2H), 3.37 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H). The $^1$H NMR data are in accordance with those reported previously.[5]

**Methyl**

**2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside**

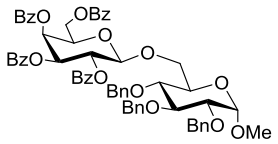
**(7h)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43-7.22 (m, 15H), 5.37 (d, *J* = 2.6 Hz, 1H), 5.27 (dd, *J* = 10.1, 8.2 Hz, 1H), 5.07-4.97 (m, 2H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.55-4.49 (m, 3H), 4.40-4.28 (m, 2H), 4.19 (dd, *J* = 11.0, 8.0 Hz, 1H), 3.97 (dd, *J* = 11.1, 6.0 Hz,

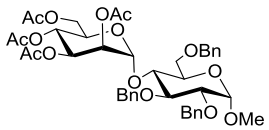
1H), 3.85 (t, *J* = 6.8 Hz, 1H), 3.76-3.49 (m, 6H), 3.30 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.00 (s, 6H). The $^1$H NMR data are in accordance with those reported previously.[5]

**Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-α-D-glucopyranoside (7i)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11-7.18 (m, 35H), 5.96 (d, *J* = 2.9 Hz, 1H), 5.84 (dd, *J* = 10.4, 8.0 Hz, 1H), 5.59 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.78-4.63 (m, 4H), 4.61-4.563 (m, 2H), 4.49 (d, *J* = 3.4 Hz, 1H), 4.44-4.33 (m, 2H), 4.28-4.16 (m, 2H), 3.89 (t, *J* = 9.3 Hz, 1H), 3.80-3.70 (m, 2H), 3.47-3.29 (m, 2H), 3.20 (s, 3H). The $^1$H NMR data are in accordance with those reported previously.[6]

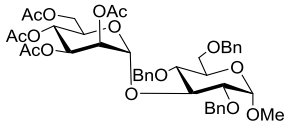
**Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-glucopyranoside (7j)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38-7.20 (m, 15H), 5.36 (s, 1H), 5.28-5.24 (m, 2H), 5.20 (t, *J* = 9.6 Hz, 1H), 5.04 (d, *J* = 11.2 Hz, 1H), 4.71-4.68 (m, 2H), 4.63-4.53 (m, 4H), 4.13 (dd, *J* = 12.2, 4.6 Hz, 1H), 3.99-3.86 (m, 3H), 3.81-3.68 (m, 4H), 3.52 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.40 (s, 3H), 2.02, 2.01, 1.95 and 1.93 (4s, 12H). The $^1$H NMR data are in accordance with those reported previously.[5]

**Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-glucopyranoside**

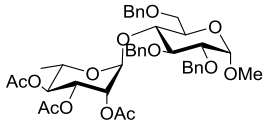
**(7k)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47-7.12 (m, 15H), 5.32-4.97 (m, 5H), 4.76 (d, *J* = 11.4 Hz, 1H), 4.61-4.19 (m, 7H), 4.00 (d, *J* = 12.2 Hz, 1H), 3.83-3.40 (m, 6H), 3.30, 2.11, 2.02, 2.02 and 1.96 (5s, 15H). The $^1$H NMR data are in accordance with those reported previously.[5]

**Methyl**

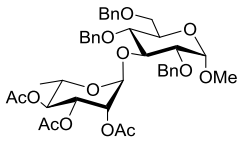
**2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside (7l)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:6, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44-7.14 (m, 15H), 5.25 (dd, *J* = 10.2, 3.4 Hz, 1H), 5.16 (dd, *J* = 3.3, 1.7 Hz, 1H), 5.11 (d, *J* = 11.0 Hz, 1H), 5.01-4.96 (m, 2H), 4.77-4.69 (m, 2H), 4.63-4.58 (m, 2H), 4.57-4.47 (m, 2H), 4.07-4.03 (m, 1H), 3.90-3.84 (m, 2H), 3.75-3.72 (m, 2H), 3.67-3.65 (m, 1H), 3.59 (dd, *J* = 9.3, 3.5 Hz, 1H), 3.37 (s, 3H), 2.06 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 0.78 (d, *J* = 6.2 Hz, 3H). The $^1$H NMR data are in accordance with those reported previously.[5]

**Methyl**

**2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside (7m)**

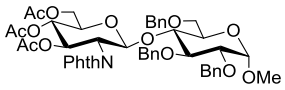



This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38-7.18 (m, 15H), 5.41-5.35 (m, 2H), 5.31 (dd, *J* = 10.1, 2.8 Hz, 1H), 4.98 (t, *J* = 10.0 Hz, 1H), 4.80-4.46 (d, *J* = 11.2 Hz, 6H), 4.56 (d, *J* = 2.8 Hz, 1H), 4.14 (t, *J* = 9.4 Hz, 1H), 4.08-3.99 (m, 1H), 3.80-3.72 (m, 2H), 3.69-3.53 (m, 3H), 3.31(s, 3H), 2.08 (s, 3H), 1.99 (s, 3H), 1.92 (s, 3H), 0.88 (d, *J* = 6.2 Hz, 3H). The $^1$H NMR data are in accordance with

those reported previously.[5]

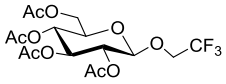
**Methyl**

**2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-glucopyranoside (7n)**



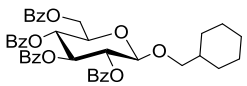

This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:3, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86-7.19 (m, 19H), 5.69 (dd, *J* = 10.6, 9.2 Hz, 1H), 5.63 (d, *J* = 8.4 Hz, 1H), 5.10 (t, *J* = 9.6 Hz, 1H), 4.99 (d, *J* = 11.8 Hz, 1H), 4.91 (d, *J* = 11.8 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.50 (d, *J* = 3.6 Hz, 1H), 4.36-4.32 (m, 2H), 4.25 (dd, *J* = 10.7, 8.4 Hz, 1H), 4.07 (dd, *J* = 12.4, 3.8 Hz, 1H), 3.97 (t, *J* = 9.3 Hz, 1H), 3.87 (t, *J* = 9.1 Hz, 1H), 3.82 (dd, *J* = 12.4, 2.1 Hz, 1H), 3.59-3.52 (m, 1H), 3.48-3.40 (m, 3H), 3.39-3.33 (m, 1H), 3.26, 1.98, 1.97 and 1.81 (4s, 12H). The $^1$H NMR data are in accordance with those reported previously.[1]

**Trifluoroethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (7o)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 5.23 (t, *J* = 9.5 Hz, 1H), 5.11 (t, *J* = 9.6 Hz, 1H), 5.04 (dd, *J* = 9.6, 7.8 Hz, 1H), 4.66 (d, *J* = 7.8 Hz, 1H), 4.27 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.20-4.07 (m, 2H), 4.01-3.92 (m, 1H), 3.74-3.69 (m, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). The $^1$H NMR data are in accordance with those reported previously.[7]

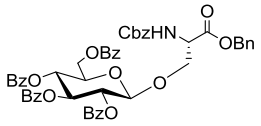
**Cyclohexylmethyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (7p)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.05-8.00 (m, 2H), 7.98-7.94 (m, 2H), 7.92-7.88 (m, 2H),

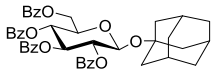
7.87-7.82 (m, 2H), 7.56-7.26 (m, 12H), 5.90 (t, *J* = 9.6 Hz, 1H), 5.68 (t, *J* = 9.7 Hz, 1H), 5.52 (dd, *J* = 9.7, 7.9 Hz, 1H), 4.81 (d, *J* = 7.8 Hz, 1H), 4.63 (dd, *J* = 12.1, 3.3 Hz, 1H), 4.51 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.19-4.10 (m, 1H), 3.73 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.32 (dd, *J* = 9.6, 6.7 Hz, 1H), 1.65-1.48 (m, 6H), 1.10-0.97 (m, *J* = 21.2, 13.8 Hz, 3H), 0.87-0.73 (m, 2H). The $^1$H NMR data are in accordance with those reported previously.[8]

**Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-L-serinate (7q)**



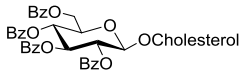

This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.04-7.81 (m, 8H), 7.57-7.21 (m, 22H), 5.87 (t, *J* = 9.6 Hz, 1H), 5.63 (t, *J* = 9.7 Hz, 1H), 5.54 (d, *J* = 7.7 Hz, 1H), 5.44 (dd, *J* = 9.4, 7.9 Hz, 1H), 5.16-5.07 (m, 2H), 5.02 (d, J = 12.2 Hz, 1H), 4.94 (d, *J* = 12.2 Hz, 1H), 4.78 (d, *J* = 7.8 Hz, 1H), 4.60 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.54-4.33 (m, 3H), 4.06-3.98 (m, 1H), 3.91 (dd, *J* = 10.3, 3.0 Hz, 1H). The $^1$H NMR data are in accordance with those reported previously.[9]

**Adamantyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (7r)**



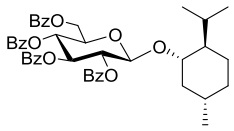

This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02-7.82 (m, 8H), 7.56-7.25 (m, 12H), 5.92 (t, *J* = 9.6 Hz, 1H), 5.55 (t, *J* = 9.7 Hz, 1H), 5.49 (dd, *J* = 9.6, 8.0 Hz, 1H), 5.12 (d, *J* = 8.0 Hz, 1H), 4.58 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.48 (dd, *J* = 11.9, 7.1 Hz, 1H), 4.20-4.15 (m, 1H), 2.04-2.00 (m, 3H), 1.84-1.80 (m, 3H), 1.67-1.63 (m, 3H), 1.57-1.44 (m, 6H). The $^1$H NMR data are in accordance with those reported previously.[8]

**Cholesteryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (7s)**



This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:6, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2H), 7.98-7.93 (m, 2H), 7.91-7.89 (m, 2H), 7.84-7.82 (m, 2H), 7.61-7.23 (m, 12H), 5.89 (t, *J* = 9.6 Hz, 1H), 5.63 (t, *J* = 9.7 Hz, 1H), 5.50 (dd, *J* = 9.7, 8.0 Hz, 1H), 5.22 (d, *J* = 4.9 Hz, 1H), 4.94 (d, *J* = 7.9 Hz, 1H), 4.60 (dd, *J* = 11.9, 3.2 Hz, 1H), 4.52 (dd, *J* = 12.0, 5.9 Hz, 1H), 4.18-4.09 (m, 1H), 3.55-3.49 (m, 1H), 2.25-0.59 (m, 43H). The $^1$H NMR data are in accordance with those reported previously.[8]

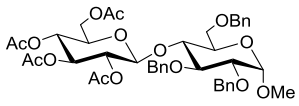
**(1S,2R,5S)-(+)-1-Mentyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (7t)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.04-8.00 (m, 2H), 7.97-7.93 (m, 2H), 7.94-7.90 (m, 2H), 7.8-7.81 (m, 2H), 7.56-7.28 (m, 12H), 5.91 (t, *J* = 9.7 Hz, 1H), 5.61-5.52 (m, 2H), 4.88 (d, *J* = 7.9 Hz, 1H), 4.63 (dd, *J* = 12.0, 3.1 Hz, 1H), 4.50 (dd, *J* = 12.0, 6.8 Hz, 1H), 4.18 (ddd, *J* = 10.0, 6.8, 3.1 Hz, 1H), 3.32 (td, *J* = 10.6, 4.3 Hz, 1H), 2.23-2.20 (m, 1H), 1.93-1.81 (m, 1H), 1.64-1.45 (m, 3H), 1.18-1.12 (m, 2H), 0.94-0.80 (m, 2H), 0.77 (d, *J* = 6.4 Hz, 3H), 0.46 (d, *J* = 7.0 Hz, 3H), 0.39 (d, *J* = 6.9 Hz, 3H). The $^1$H NMR data are in accordance with those reported previously.[8]

**Methyl**

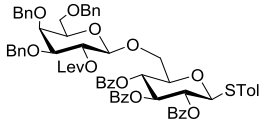
**2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside (7v)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:3, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.44-7.21 (m, 15H), 5.05-4.93 (m, 3H), 4.89 (t, *J* = 8.6 Hz, 1H), 4.74 (dd, *J* = 12.0, 8.7 Hz, 3H), 4.59 (d, *J* = 8.2 Hz, 1H), 4.58 (d, *J* = 3.9 Hz, 1H), 4.50 (d, *J* = 7.9 Hz, 1H), 4.43 (d, *J* = 12.1 Hz, 1H), 4.14 (dd, *J* = 12.6, 3.9 Hz, 1H), 3.92-3.80 (m, 3H), 3.77 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.65-3.57 (m, 2H), 3.47 (dd, *J* = 9.2, 3.7 Hz, 1H), 3.37 (s, 3H), 3.33-3.27 (m, 1H), 2.00, 1.98, 1.95 and 1.94 (4s, 12H). The $^1$H NMR data are in accordance with those reported previously.[1]

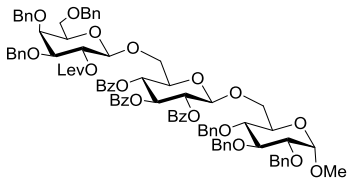
***p*-Methylphenyl**

**2,3,4-tri-*O*-benzoyl-6-*O*-(2-*O*-levulinyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (7w)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:4, v/v). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.95-7.75 (m, 6H), 7.54-7.13 (m, 28H), 5.82 (t, *J* = 9.5 Hz, 1H), 5.43-5.36 (m, 2H), 5.30 (t, *J* = 9.8 Hz, 1H), 4.98 (d, *J* = 10.0 Hz, 1H), 4.93 (d, *J* = 11.7 Hz, 1H), 4.67 (d, *J* = 12.2 Hz, 1H), 4.58 (dd, *J* = 11.7, 2.7 Hz, 2H), 4.46 (d, *J* = 8.0 Hz, 1H), 4.35 (d, *J* = 11.8 Hz, 1H), 4.30 (d, *J* = 11.8 Hz, 1H), 4.10 (dd, *J* = 8.1, 2.0 Hz, 1H), 4.00 (dd, *J* = 11.3, 1.7 Hz, 1H), 3.92 (d, *J* = 2.6 Hz, 1H), 3.70 (dd, *J* = 11.3, 7.7 Hz, 1H), 3.55-3.46 (m, 4H), 2.69-2.54 (m, 4H), 2.33 (s, 3H), 2.10 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.93, 172.00, 166.01, 165.67, 165.36, 138.74, 138.62, 138.28, 138.11, 133.73, 133.55, 133.44, 133.33, 130.25, 130.20, 130.14, 130.03, 129.66, 129.23, 129.09, 128.76, 128.70, 128.68, 128.61, 128.55, 128.51, 128.19, 128.13, 128.08, 127.95, 127.88, 101.88, 86.31, 80.60, 78.32, 74.75, 73.97, 73.82, 72.90, 72.58, 71.89, 70.76, 69.77, 68.72, 68.57, 38.23, 30.17, 28.36, 21.53; HRMS: calcd for $C_{66}H_{64}NaO_{15}S$ [M+$Na^+$], 1151.3858, found 1151.3828.

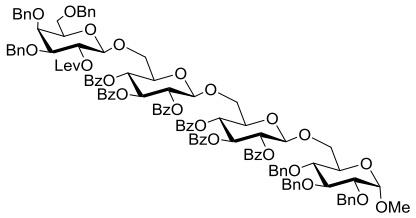
**Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(2-*O*-levulinyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranosyl]-α-D-glucopyranoside (7x)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:3, v/v). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.80-6.92 (m, 45H), 5.76 (t, *J* = 9.6 Hz, 1H), 5.45 (dd, *J* = 9.6, 7.9 Hz, 1H), 5.29-5.23 (m, 2H), 4.81-4.78 (m, 3H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.59 (d, *J* = 11.0 Hz, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.47-4.12 (m, 9H), 3.99-3.31 (m, 13H), 3.13 (s, 3H), 2.70-2.33 (m, 4H), 2.06 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.65, 171.82,

166.12, 165.71, 165.29, 139.19, 138.71, 138.58, 138.52, 138.23, 138.11, 133.72, 133.49, 133.38, 130.15, 130.06, 129.55, 129.21, 129.16, 128.78, 128.73, 128.71, 128.63, 128.59, 128.57, 128.53, 128.51, 128.49, 128.23, 128.18, 128.08, 127.87, 127.74, 127.71, 101.71 (C-1), 101.13 (C-1'), 98.39 (C-1''), 82.12, 80.62, 80.07, 75.82, 74.91, 74.76, 74.68, 73.83, 73.79, 73.75, 73.44, 72.76, 72.32, 72.22, 71.99, 69.99, 69.87, 68.55, 68.29, 67.95, 55.40, 38.20, 30.22, 28.36, 1.36; HRMS: calcd for $C_{87}H_{92}NO_{21}$ [M+$NH_4^+$], 1486.6156, found 1486.6105.

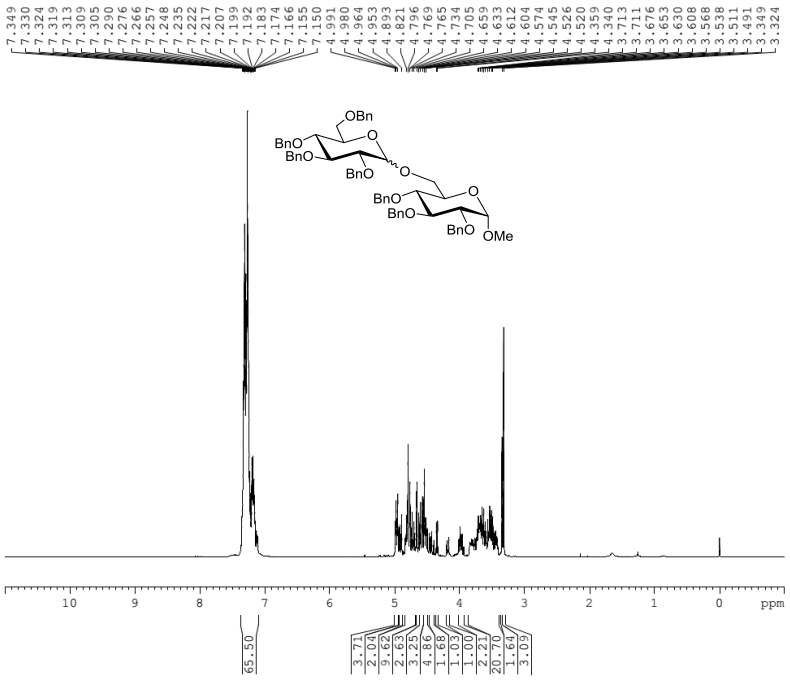
**Methyl 2,3,4-tri-*O*-benzyl-6-*O*-{2,3,4-tri-*O*-benzoyl-6-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(2-*O*-levulinyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-α-D-glucopyranoside (7y)**




This compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:2, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88-7.66 (m, 12H), 7.44-6.88 (m, 48H), 5.74-5.64 (m, 2H), 5.35 (dd, *J* = 9.6, 8.0 Hz, 1H), 5.29-5.23 (m, 3H), 5.09 (t, *J* = 9.9 Hz, 1H), 4.96 (d, *J* = 7.8 Hz, 1H), 4.83 (d, *J* = 11.5 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.66-4.25 (m, 12H), 4.10 (d, *J* = 11.3 Hz, 1H), 4.01-3.93 (m, 2H), 3.87-3.74 (m, 6H), 3.66-3.58 (m, 2H), 3.51-3.38 (m, 4H), 3.32-3.22 (m, 3H), 3.23 (s, 3H), 2.78-2.48 (m, 4H), 2.09 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 206.89, 172.18, 166.04, 165.98, 165.71, 165.64, 165.40, 165.22, 139.27, 138.93, 138.78, 138.73, 138.55, 138.32, 133.83, 133.69, 133.59, 133.48, 130.30, 130.09, 130.04, 129.80, 129.53, 129.29, 129.21, 128.83, 128.79, 128.75, 128.71, 128.69, 128.67, 128.58, 128.55, 128.53, 128.47, 128.45, 128.23, 128.18, 128.14, 128.07, 127.94, 127.90, 127.85, 127.77, 127.73, 127.65, 101.60 (C-1), 101.29 (C-1'), 101.11 (C-1''), 98.42 (C-1'''), 82.19, 81.01, 80.17, 75.72, 75.09, 74.78, 74.70, 74.56, 73.79, 73.73, 73.27, 73.05, 72.89, 72.56, 72.36, 72.11, 70.49, 69.77, 68.87, 68.63, 68.03, 67.25, 55.64, 38.17, 30.28, 28.55; HRMS: calcd for $C_{114}H_{110}NaO_{29}$ [M+$Na^+$], 1965.7025, found 1965.7032.

## 8. Copies of NMR Spectra

### $^1$H NMR of 7a




BRUKER

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EXPNO                   1
PROCNO                  1
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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                      8
DS                      2
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                 31.12
DW               60.800 usec
DE                6.50 usec
TE                297.0 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1                14.00 usec
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WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
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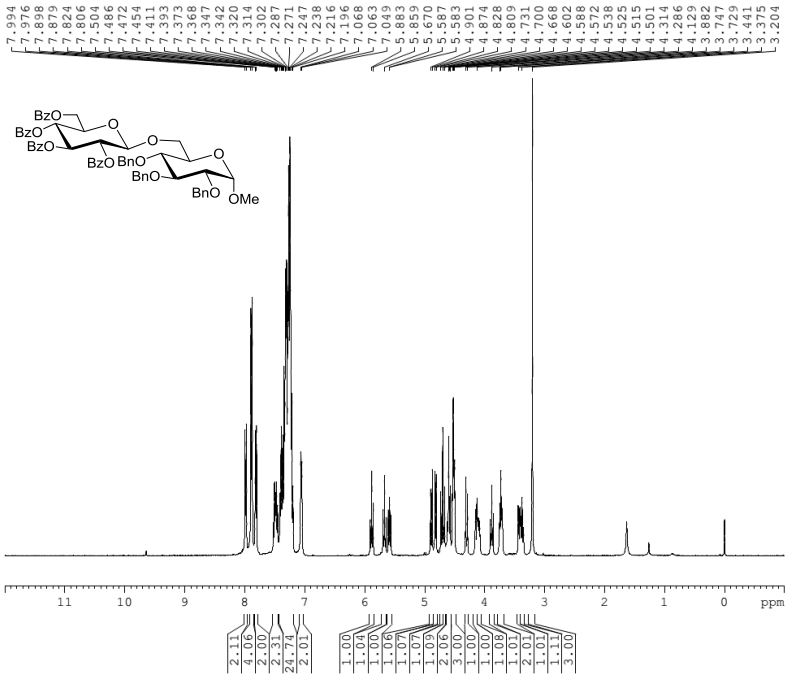
### $^1$H NMR of 7b




BRUKER

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PROCNO                  1
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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                      8
DS                      2
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG                 72.2
DW               60.800 usec
DE                6.50 usec
TE                304.4 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                14.00 usec
SI                 65536
SF          400.1300197 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
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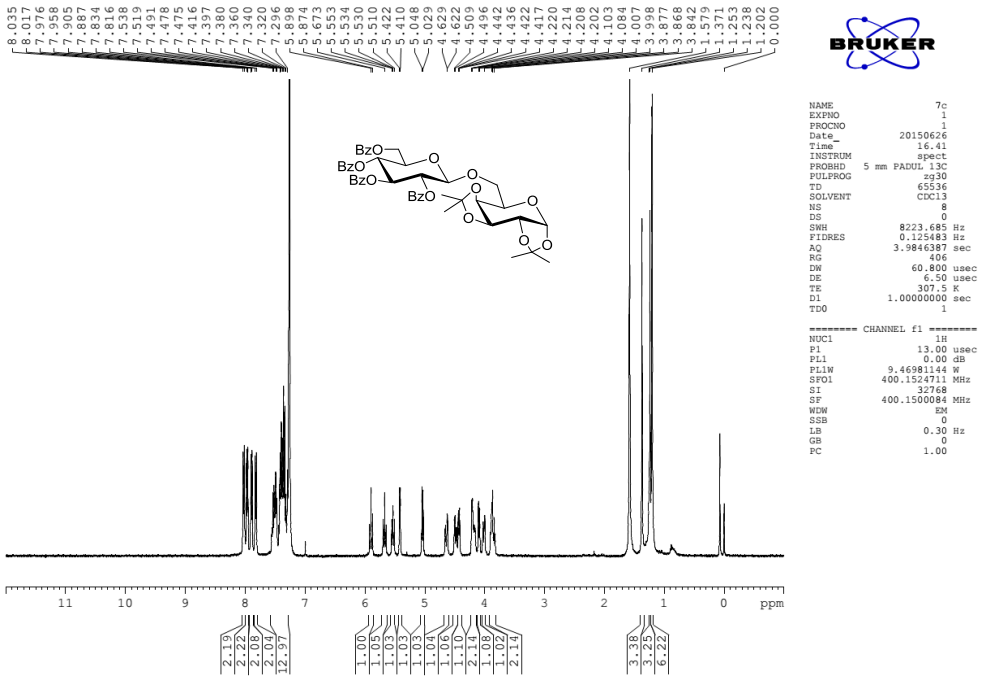
## $^1$H NMR of 7c




BRUKER

| | |
|---|---|
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| PROCNO | 1 |
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| Time_ | 16.41 |
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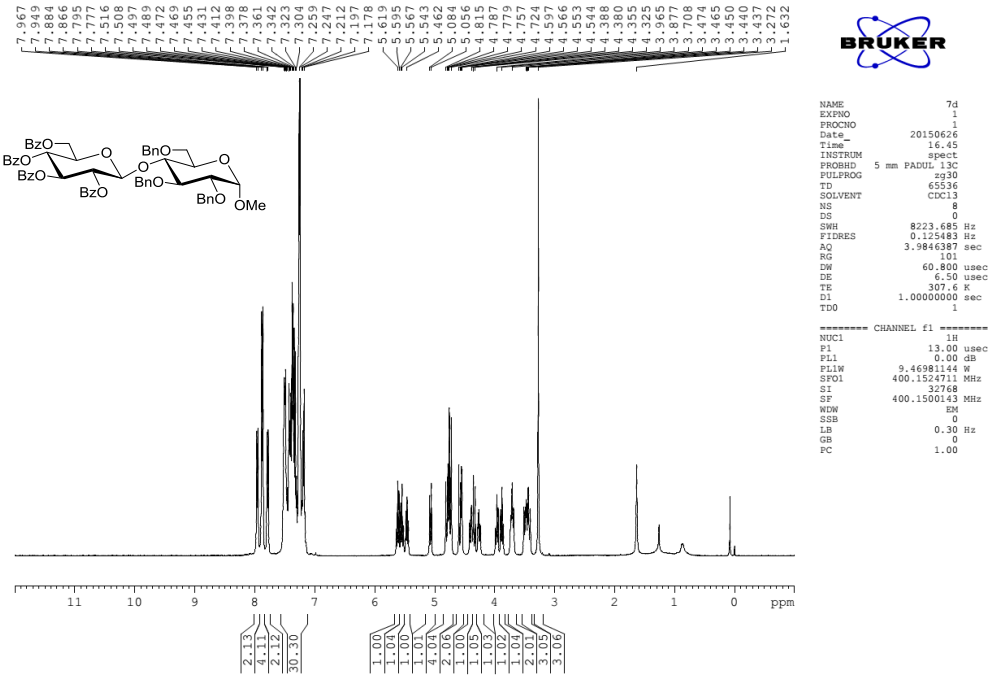
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 8 |
| DS | 0 |
| SWH | 8223.685 Hz |
| FIDRES | 0.125483 Hz |
| AQ | 3.9846387 sec |
| RG | 406 |
| DW | 60.800 usec |
| DE | 6.50 usec |
| TE | 307.5 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| NUC1 | 1H |
| P1 | 13.00 usec |
| PL1 | 0.00 dB |
| PL1W | 9.46981144 W |
| SFO1 | 400.1524711 MHz |
| SI | 32768 |
| SF | 400.1500084 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

## $^1$H NMR of 7d




BRUKER

| | |
|---|---|
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| PROCNO | 1 |
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| Time_ | 16.45 |
| INSTRUM | spect |
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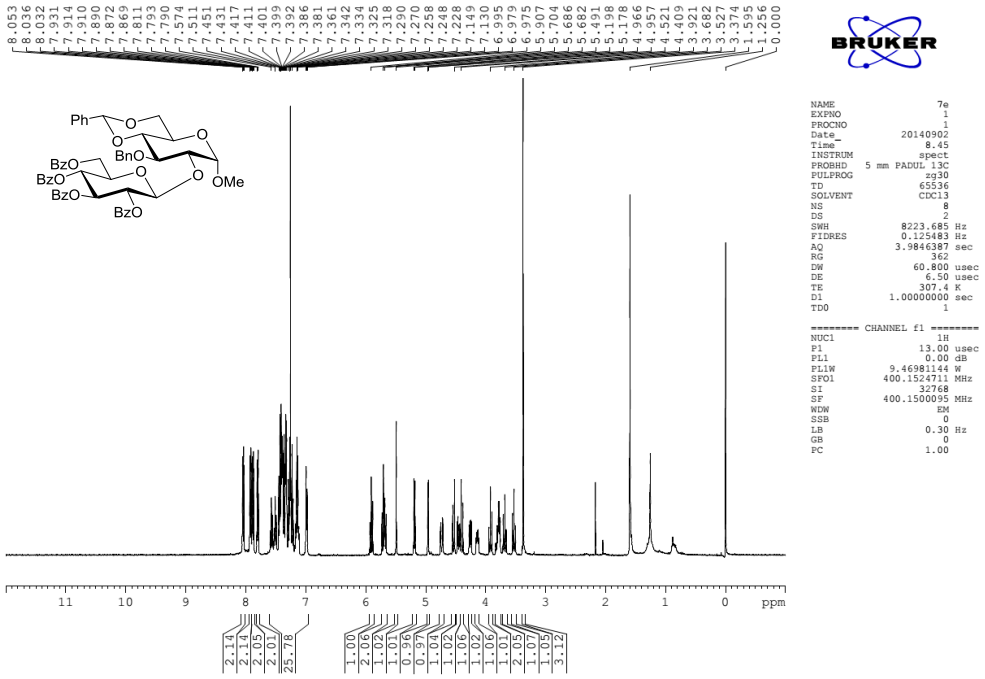
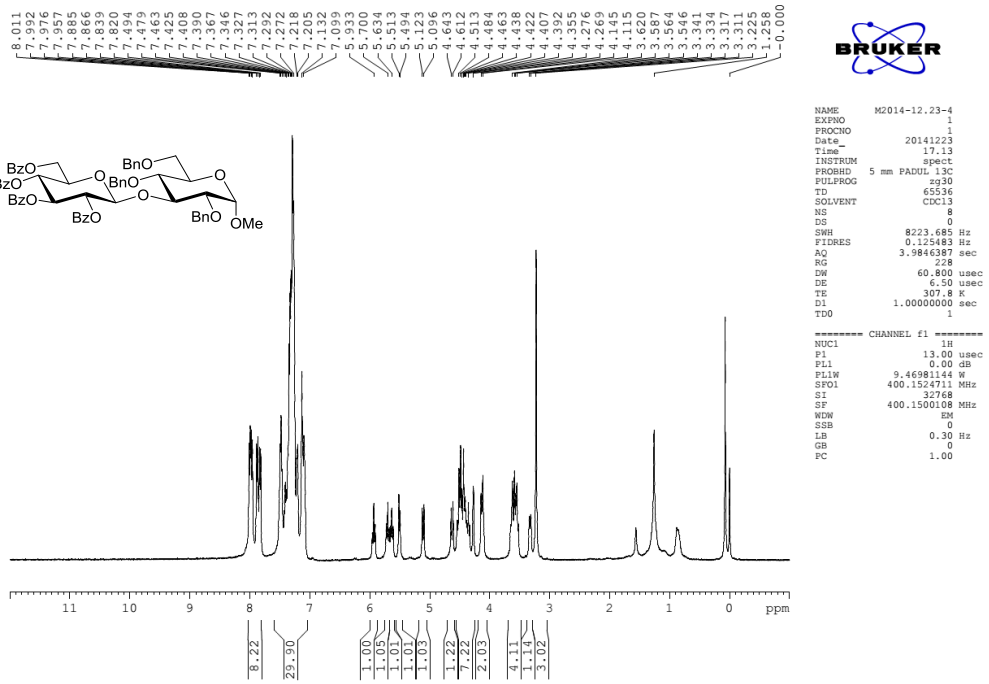
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 8 |
| DS | 0 |
| SWH | 8223.685 Hz |
| FIDRES | 0.125483 Hz |
| AQ | 3.9846387 sec |
| RG | 101 |
| DW | 60.800 usec |
| DE | 6.50 usec |
| TE | 307.6 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| NUC1 | 1H |
| P1 | 13.00 usec |
| PL1 | 0.00 dB |
| PL1W | 9.46981144 W |
| SFO1 | 400.1524711 MHz |
| SI | 32768 |
| SF | 400.1500143 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

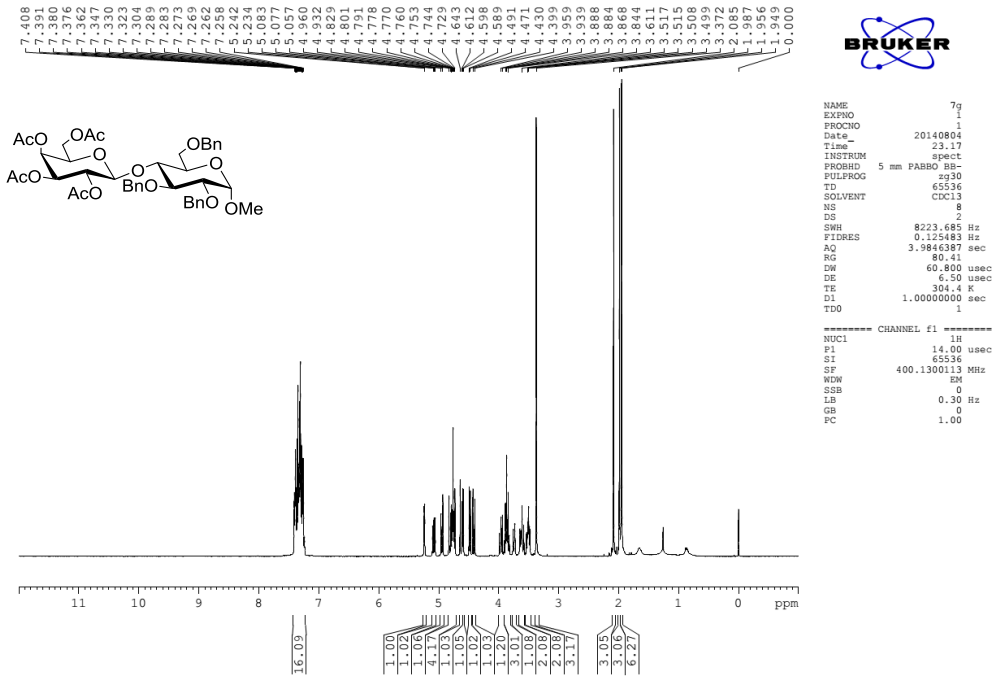
## $^1$H NMR of 7e



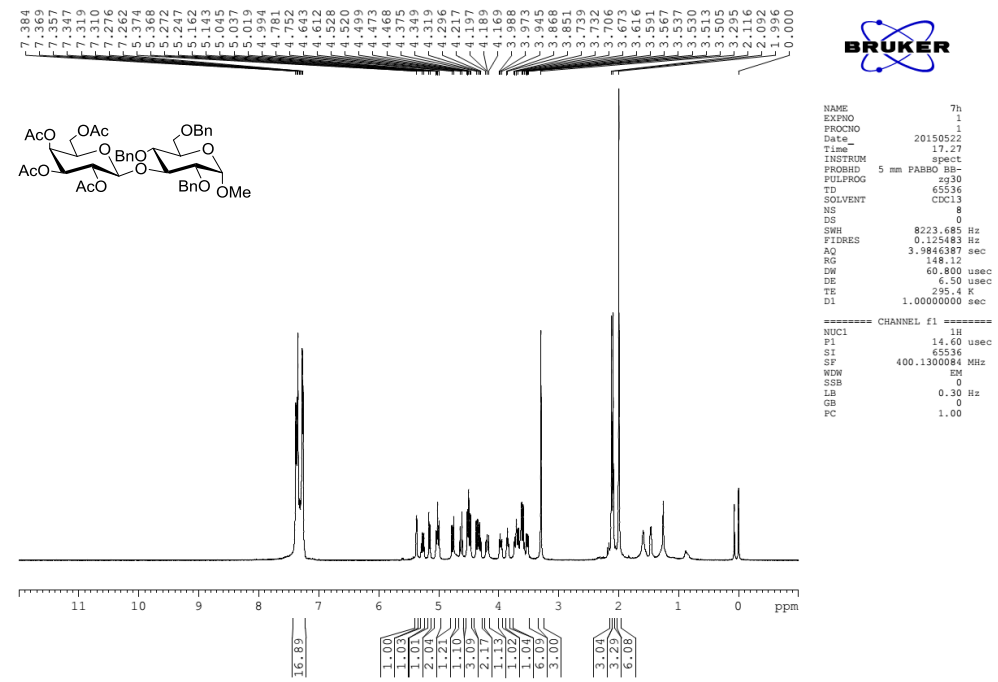

## $^1$H NMR of 7f



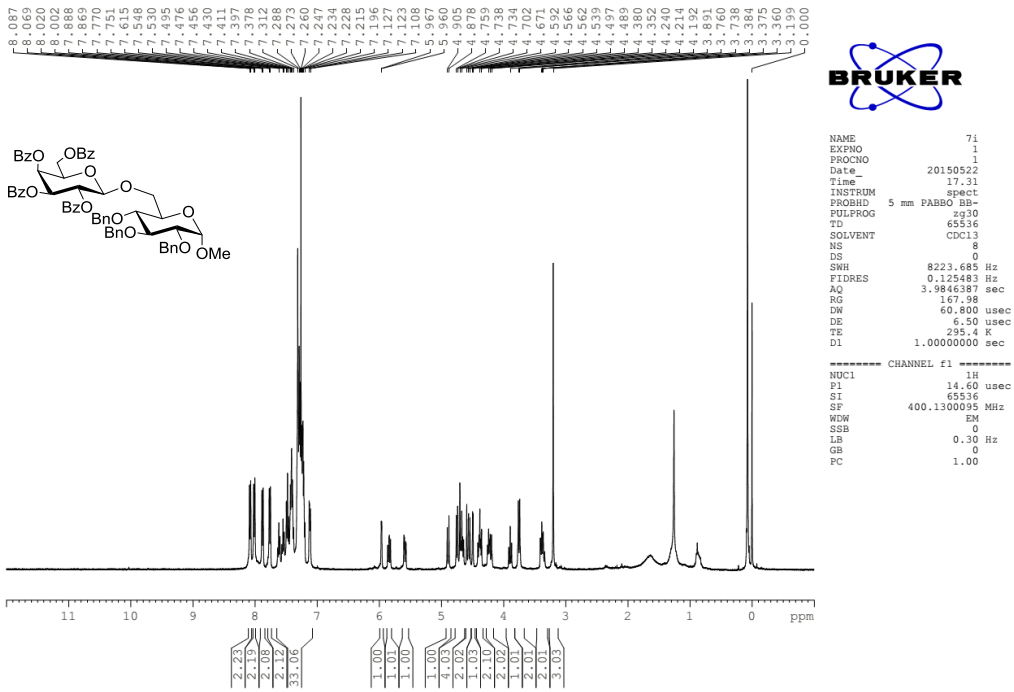
## $^1$H NMR of 7g



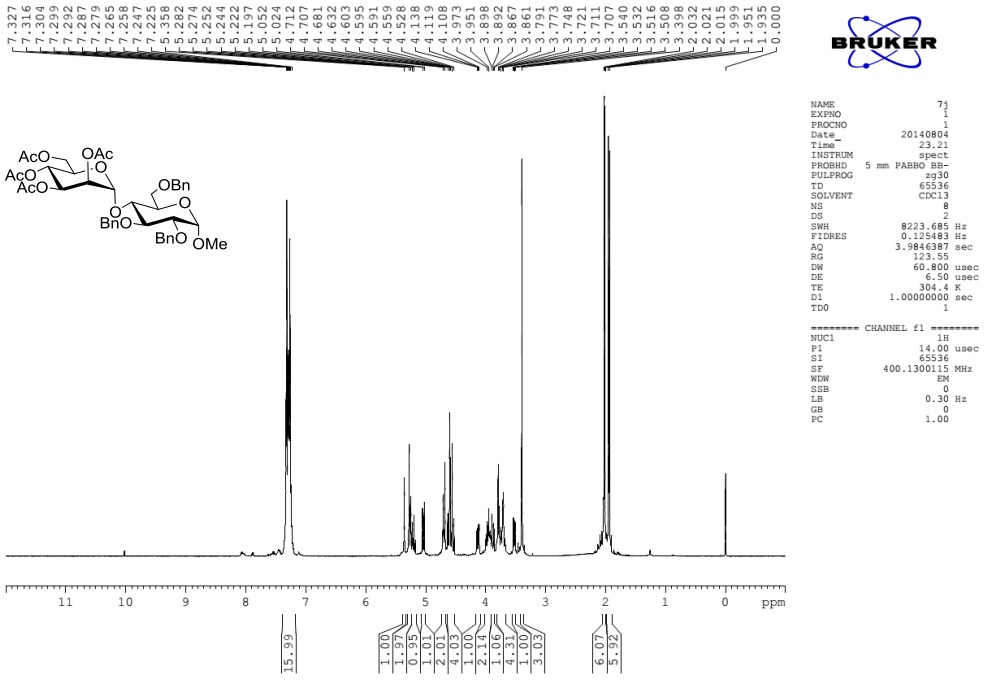

## $^1$H NMR of 7h



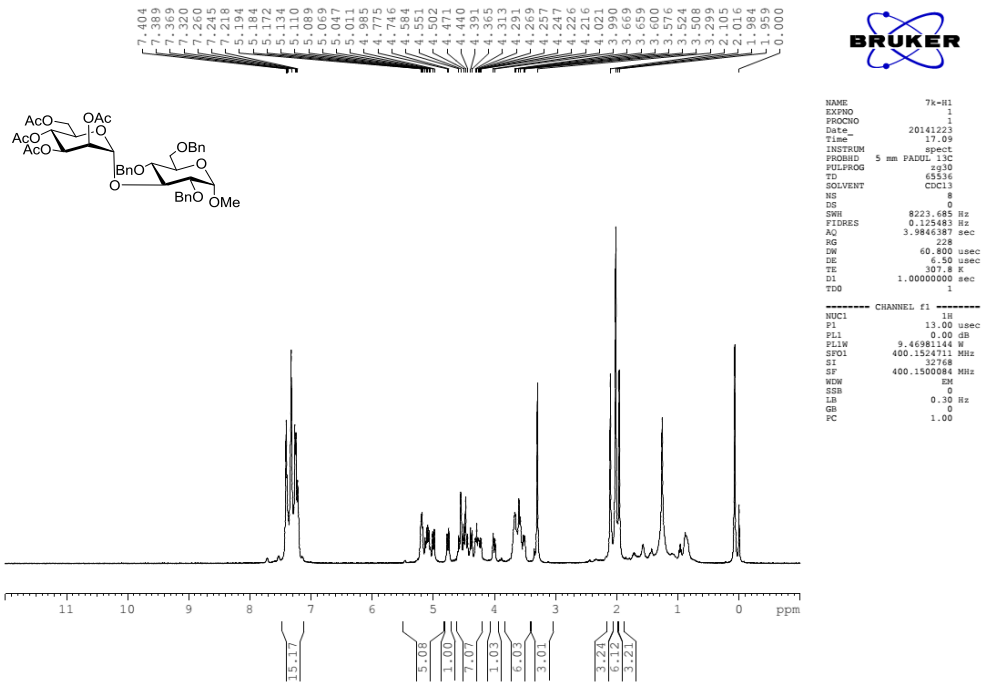
## $^1$H NMR of 7i



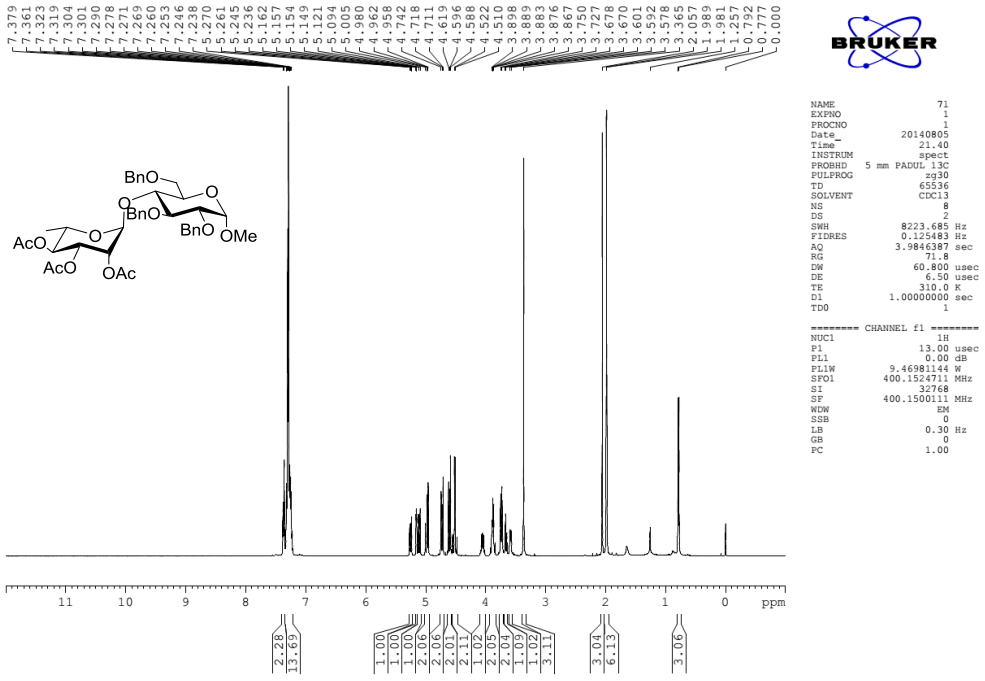

## $^1$H NMR of 7j



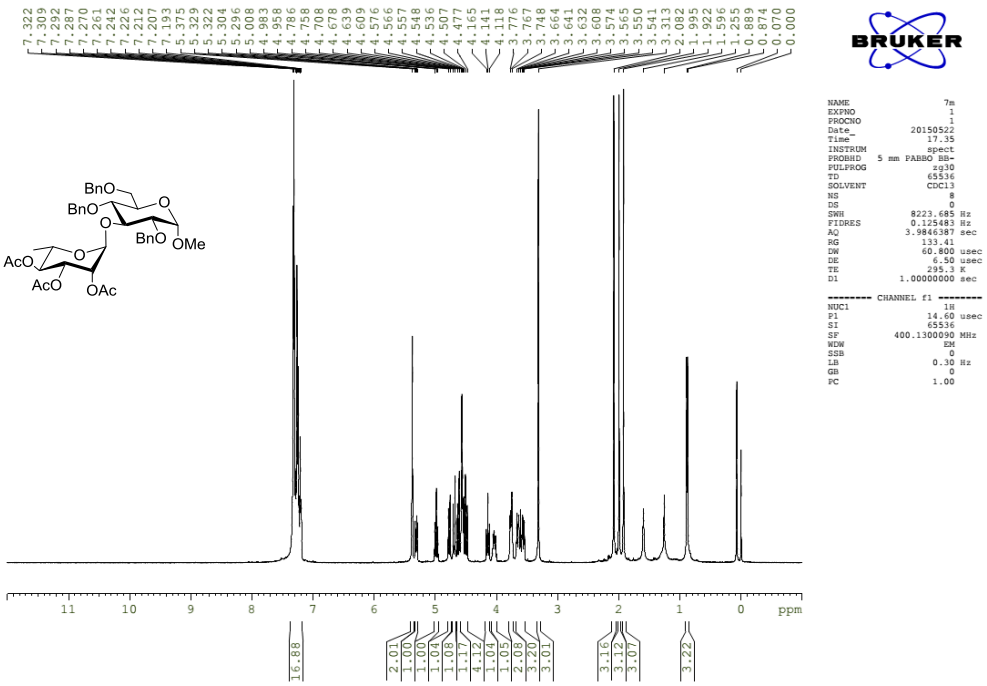
## $^1$H NMR of 7k



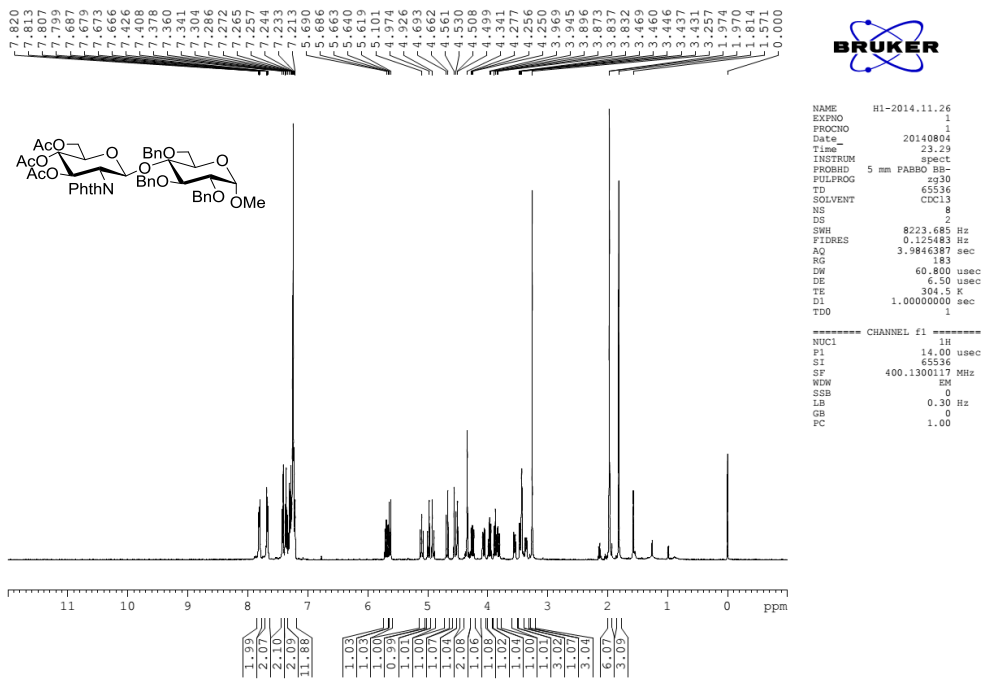

## $^1$H NMR of 7l



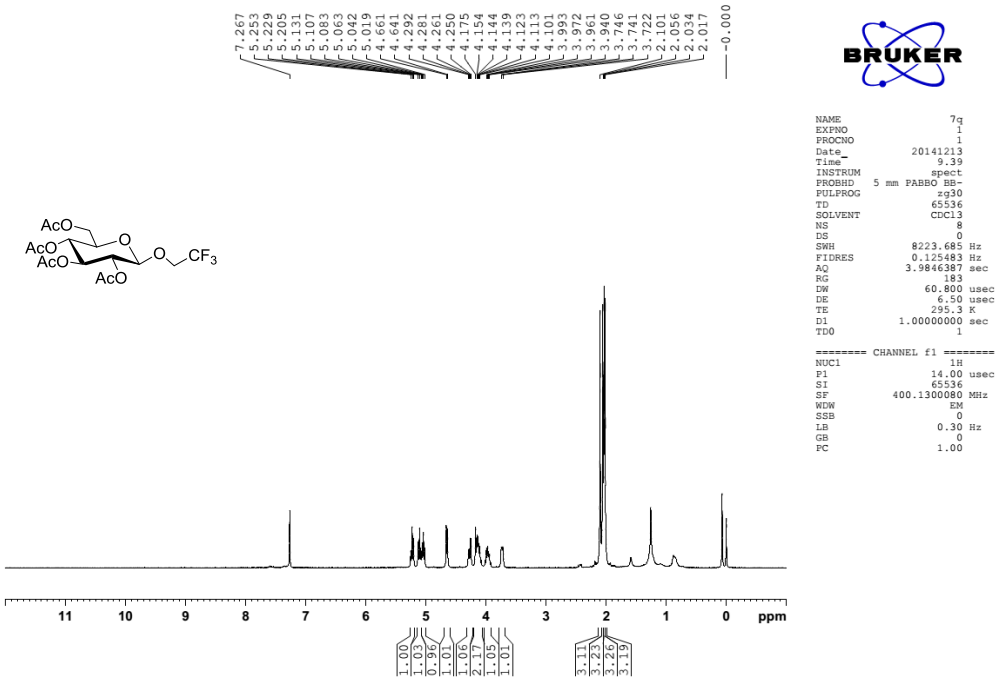
## $^1$H NMR of 7m



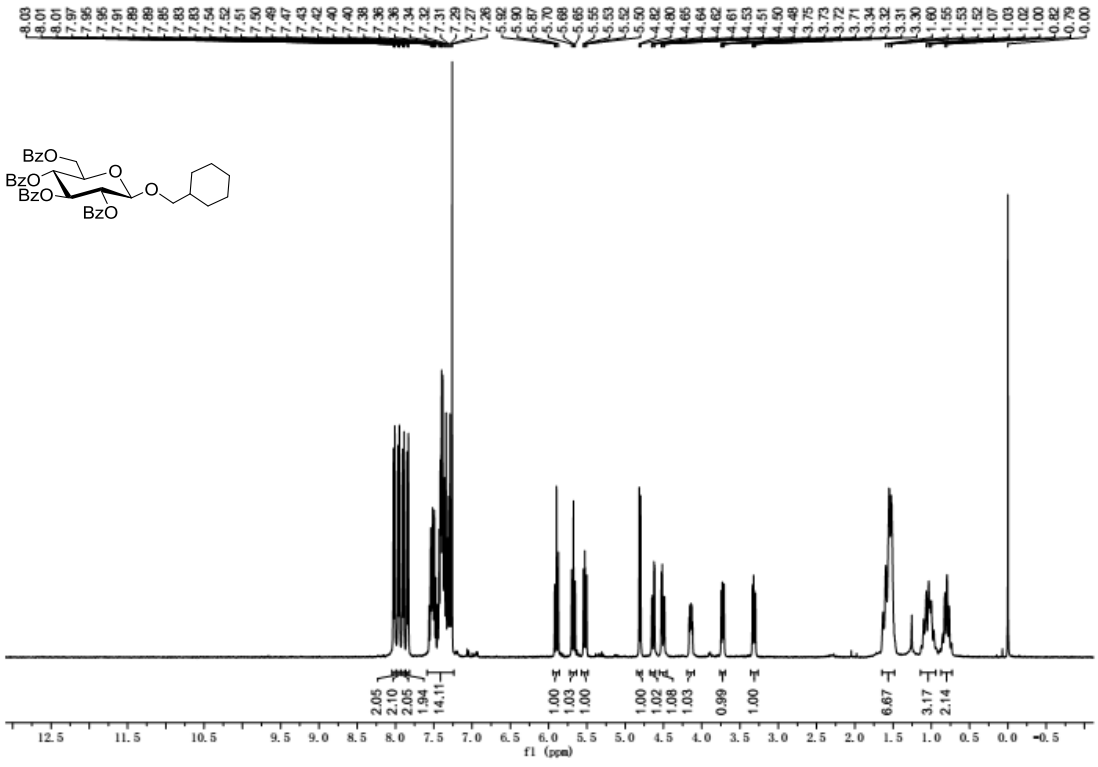

## $^1$H NMR of 7n



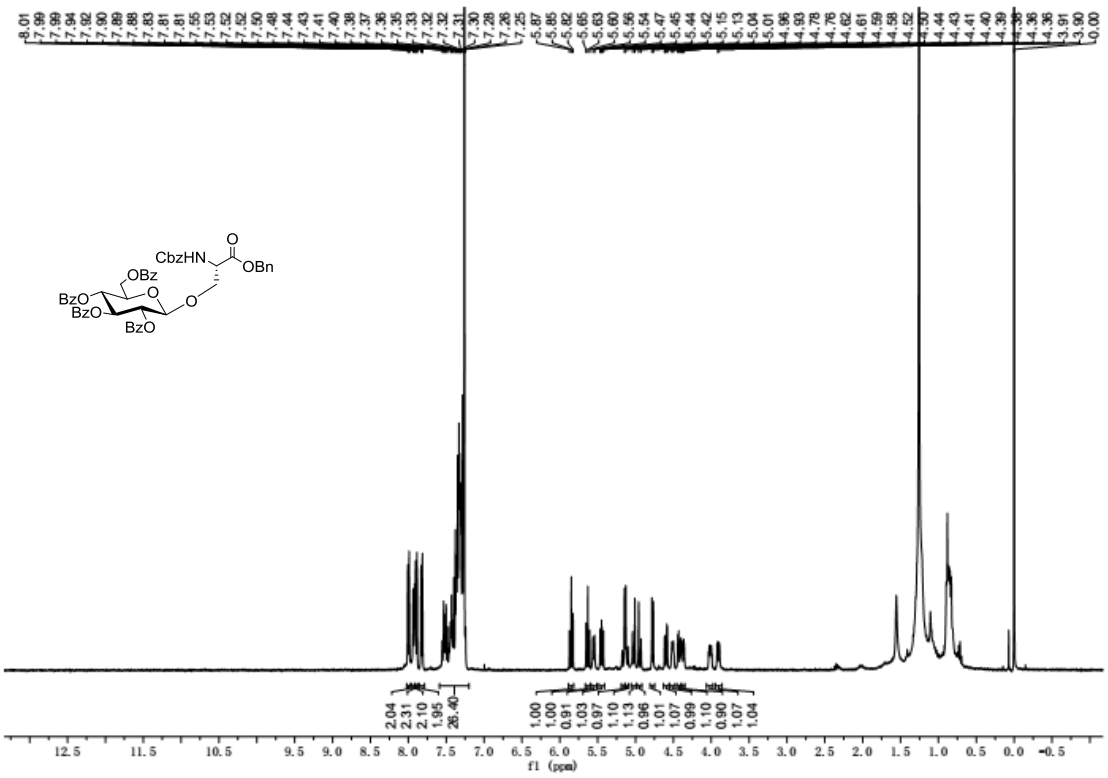
## $^1$H NMR of 7o



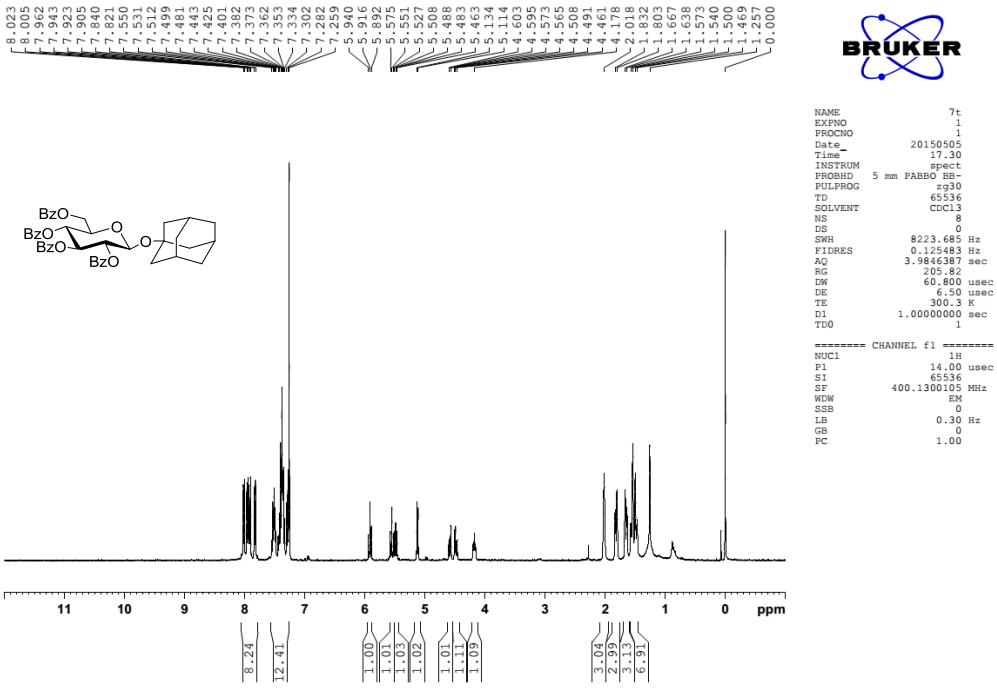

## $^1$H NMR of 7p



## $^1$H NMR of 7q



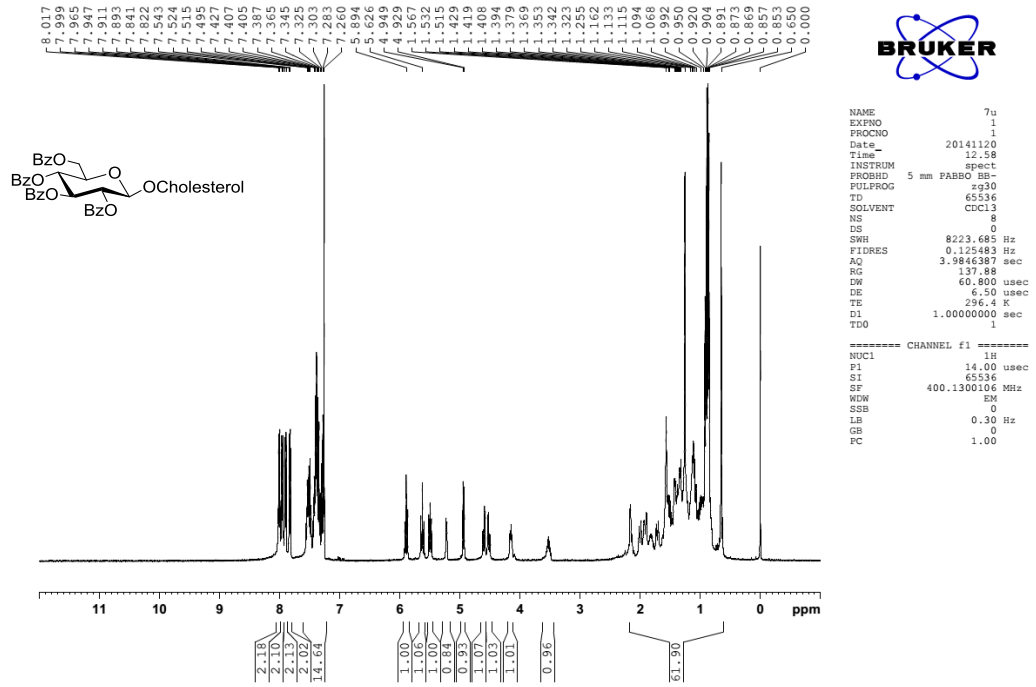

## $^1$H NMR of 7r



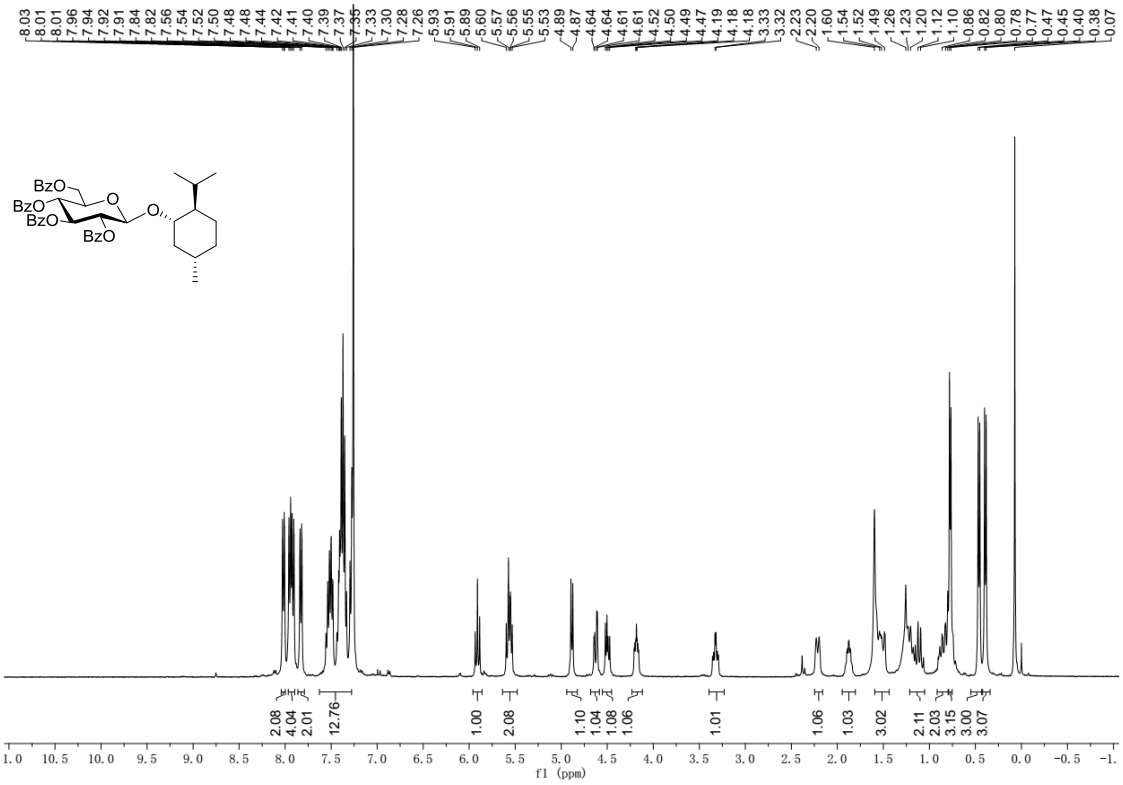

```
NAME                 7t
EXPNO                 1
PROCNO                1
Date_          20150505
Time              17.30
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG               205.82
DW               60.800 usec
DE                6.50 usec
TE               300.3 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.00 usec
SI                65536
SF          400.1300105 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

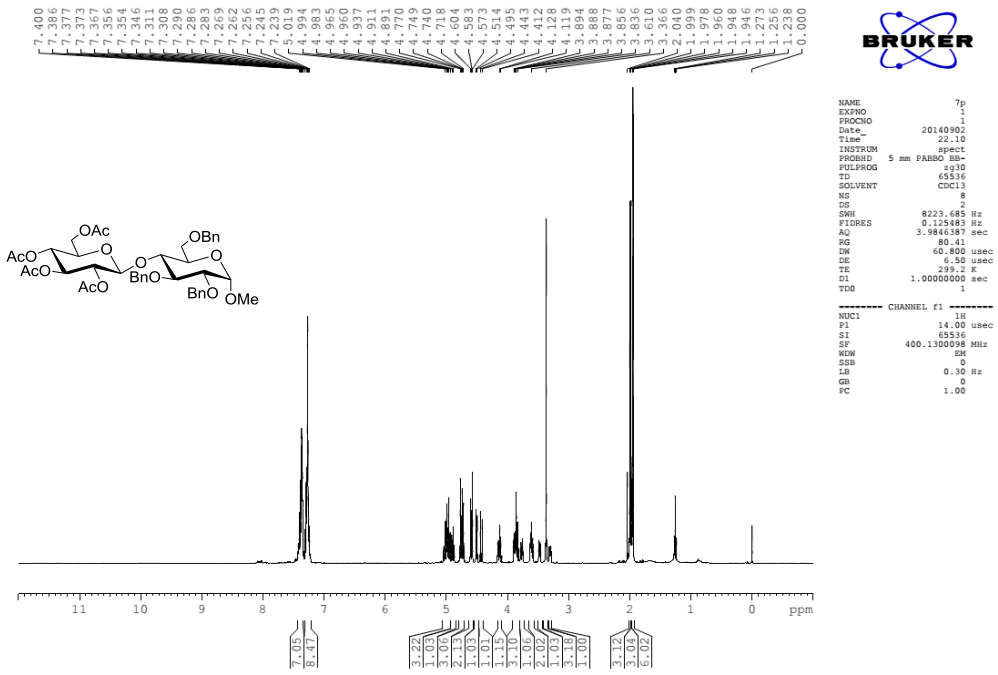
## $^1$H NMR of 7s



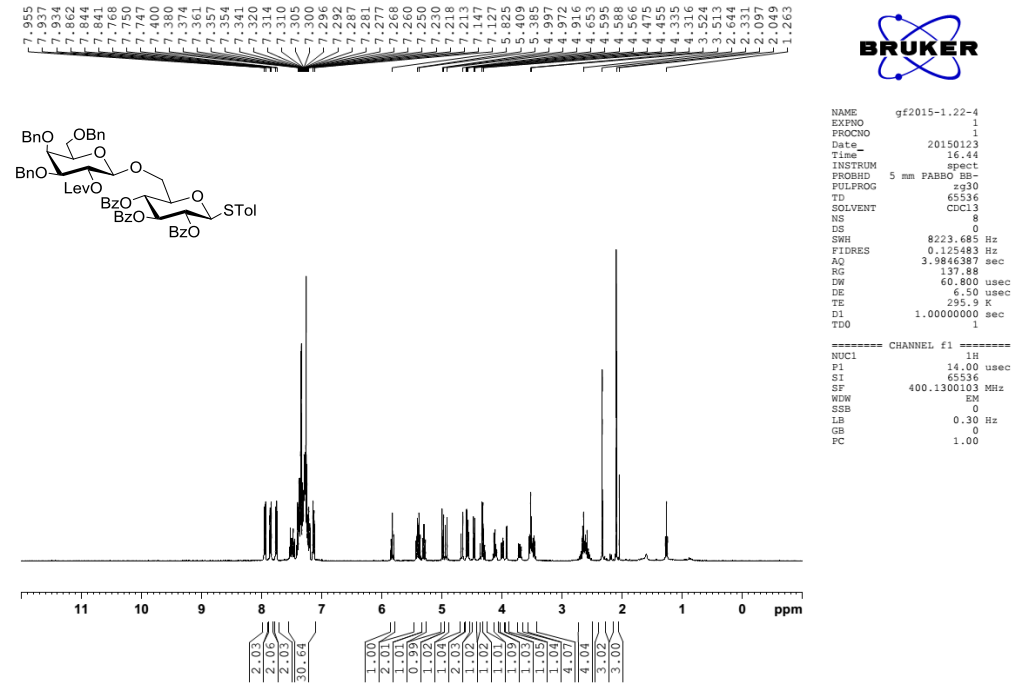

## $^1$H NMR of 7t



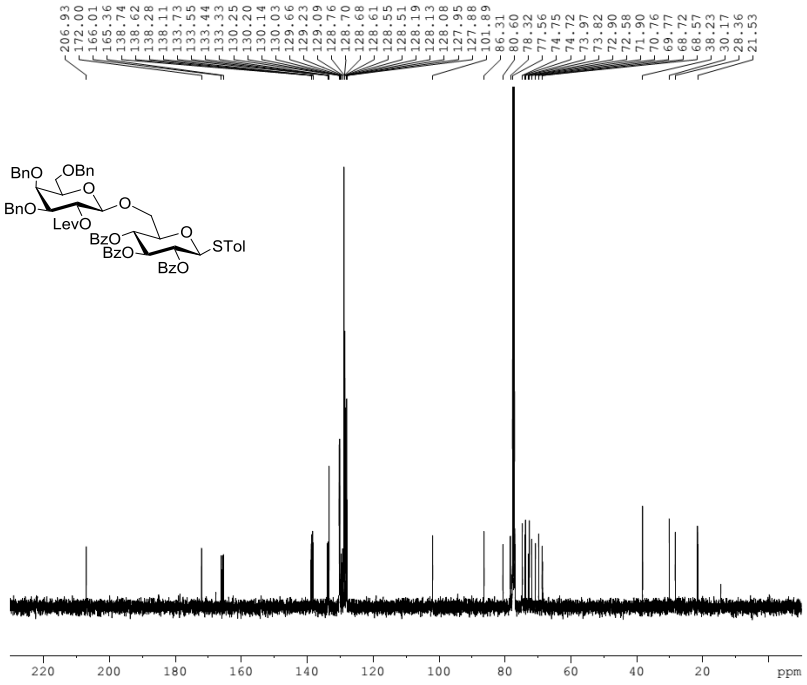
## $^1$H NMR of 7v




## $^1$H NMR of 7w



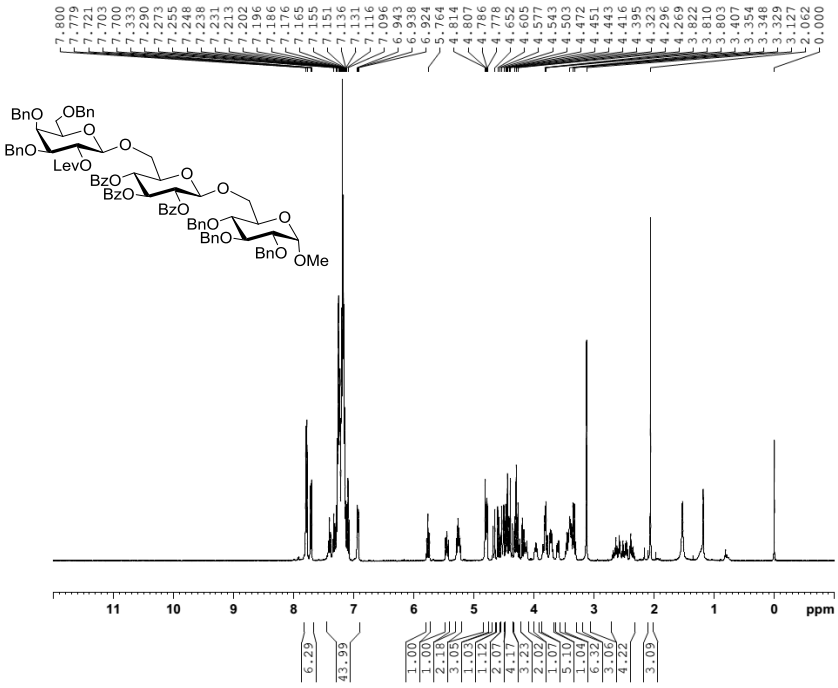
## $^{13}$C NMR of 7w




```
NAME          GF2015-1.22-4-C13
EXPNO                         1
PROCNO                        1
Date_                  20150126
Time                      10.32
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         784
DS                           4
SWH                  26041.666 Hz
FIDRES               0.397364 Hz
AQ                   1.2583412 sec
RG                       161.46
DW                       19.200 usec
DE                         6.50 usec
TE                       296.7 K
D1                   1.25000000 sec
D11                  0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                         9.00 usec
SI                        32768
SF                100.6127369 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

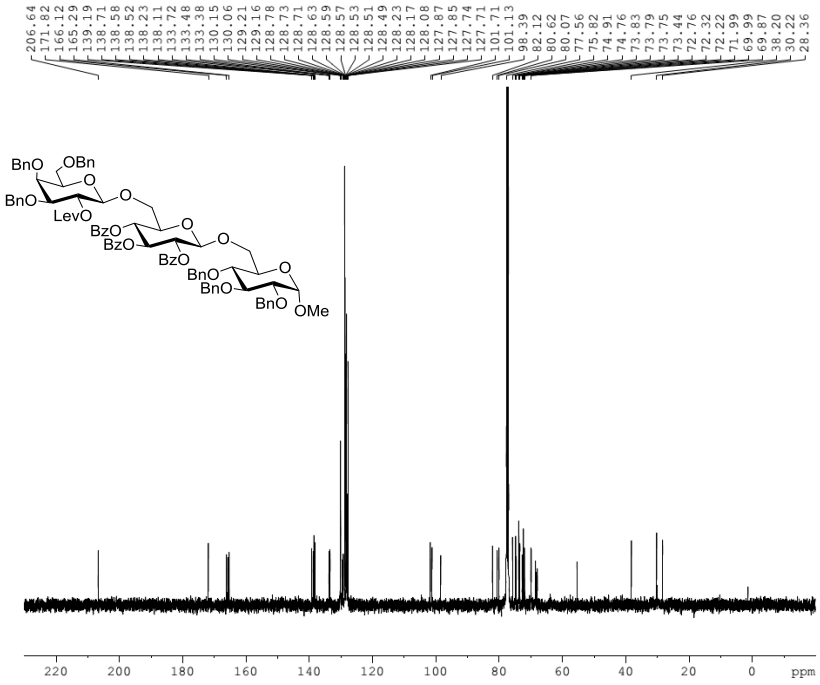
## $^{1}$H NMR of 7x




```
NAME          M2015-8.13-3
EXPNO                   11
PROCNO                   1
Date_             20150815
Time                 0.35
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                       8
DS                       0
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                  161.46
DW                  60.800 usec
DE                    6.50 usec
TE                  295.5 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.00 usec
SI                    65536
SF            400.1300401 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

## $^{13}$C NMR of 7x

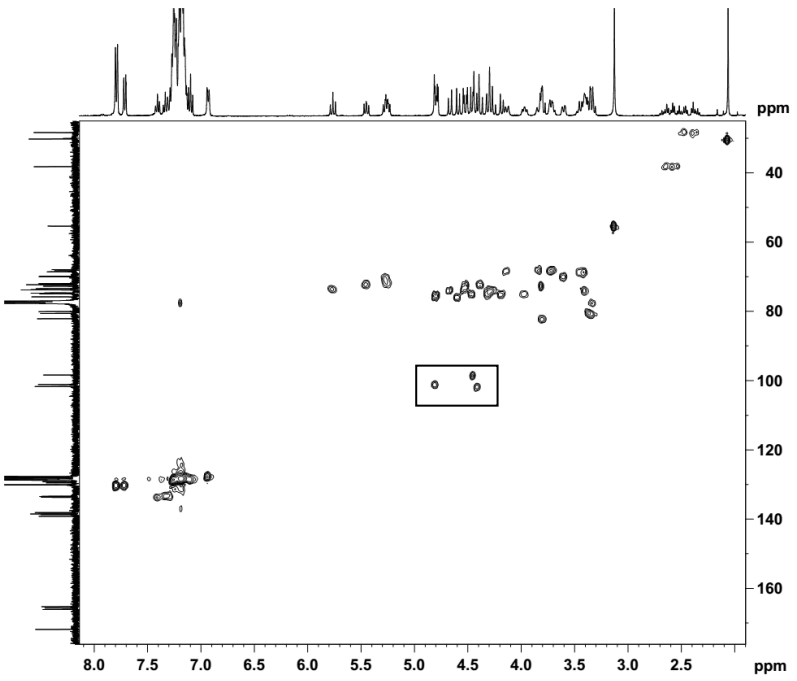



BRUKER

```
NAME            M2015-8.13-3
EXPNO                      2
PROCNO                     1
Date_               20150815
Time                   4.12
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                CDCl3
NS                      5000
DS                         4
SWH                26041.666 Hz
FIDRES             0.397364 Hz
AQ                 1.2583412 sec
RG                    205.82
DW                   19.200 usec
DE                    6.50 usec
TE                   296.4 K
D1                 1.25000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                      9.00 usec
SI                      32768
SF               100.6127362 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

## HSQC of 7x

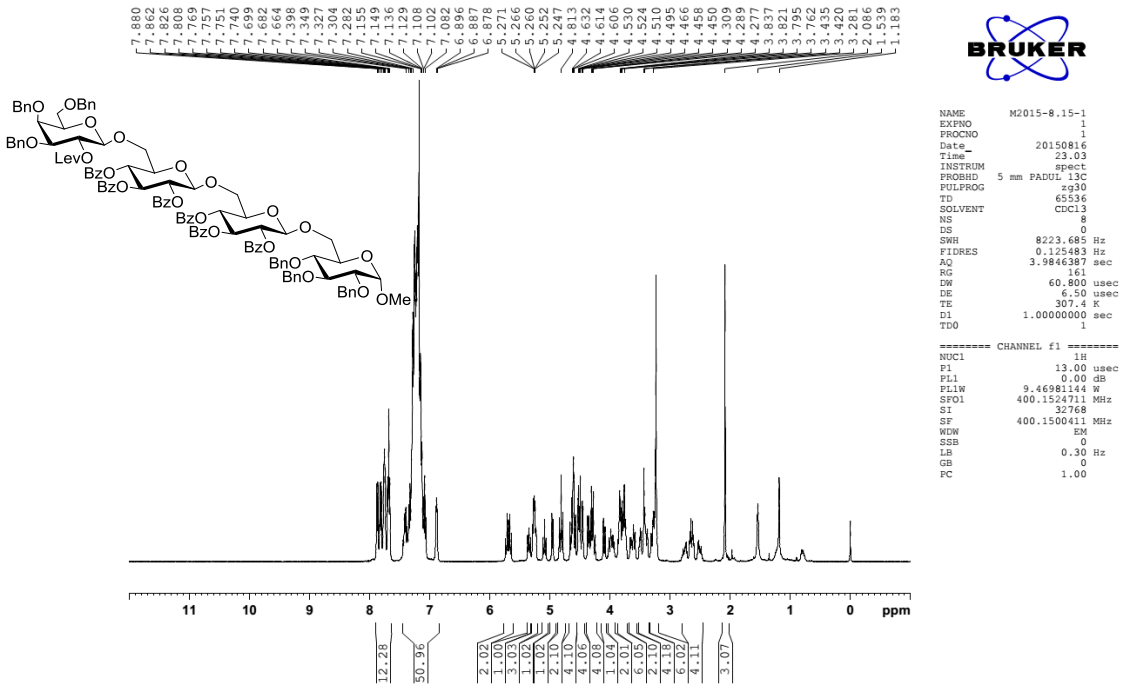



BRUKER

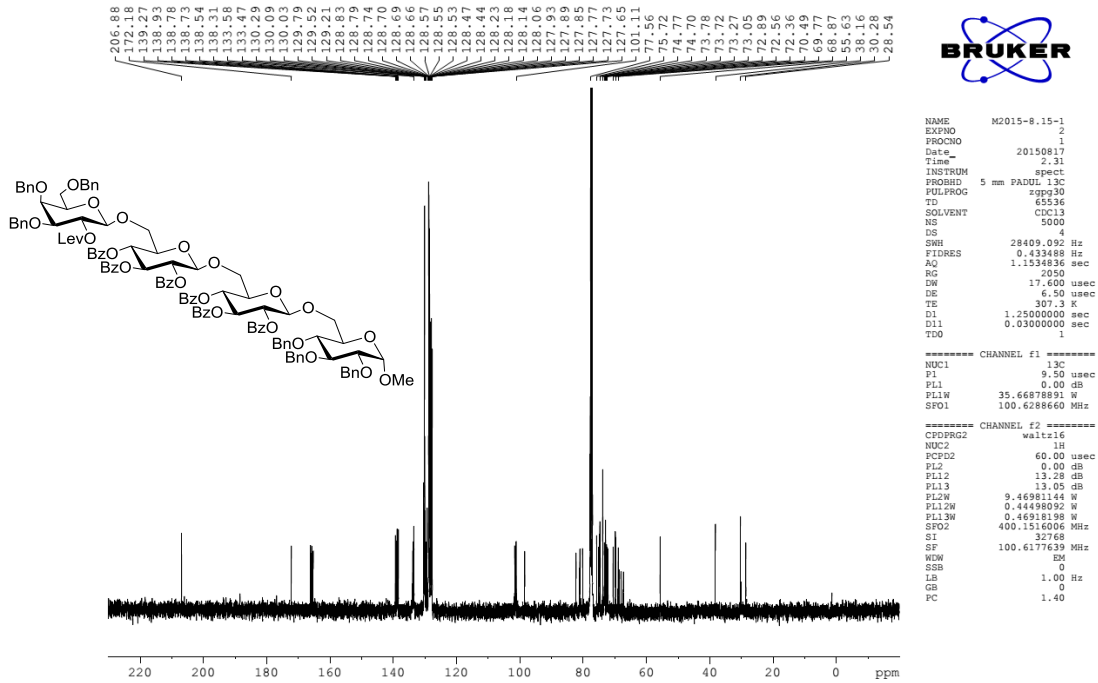
```
NAME            M2015-8.13-3
EXPNO                      5
PROCNO                     1
Date_               20150815
Time                   7.01
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              hsqcetgp
TD                      1024
SOLVENT                CDCl3
NS                         4
DS                        16
SWH                4000.000 Hz
FIDRES             3.906250 Hz
AQ                 0.1280500 sec
RG                    205.82
DW                   125.000 usec
DE                    6.50 usec
TE                   294.9 K
CNST2              145.00000000
D0                 0.00000300 sec
D1                 1.50000000 sec
D4                 0.00172414 sec
D11                0.03000000 sec
D16                0.00020000 sec
IN0                0.00002485 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                     1H
P1                     14.00 usec
P2                     28.00 usec
P28                  1000.00 usec
ND0                        2
TD                       128
SFO1               100.6218 MHz
FIDRES             157.219177 Hz
SW                 199.997 ppm
FnMODE          Echo-Antiecho
SI                      1024
SF               400.1300350 MHz
WDW                     QSINE
SSB                         2
LB                      0.00 Hz
GB                          0
PC                      1.40
SI                      1024
MC2             echo-antiecho
SF                 100.6127169 MHz
WDW                     QSINE
SSB                         2
LB                      0.00 Hz
GB                          0
```

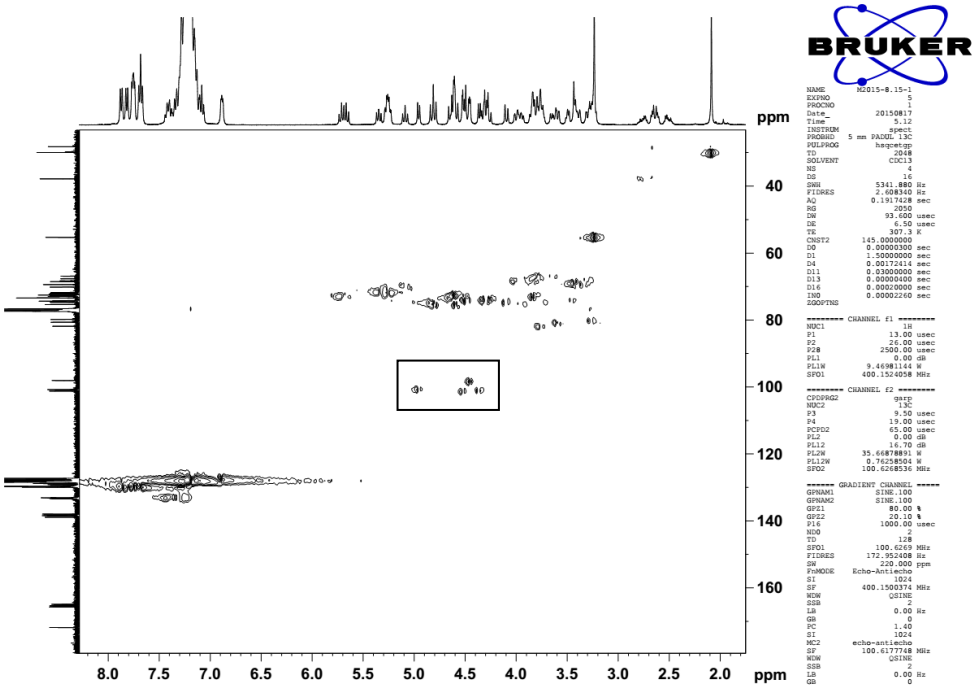
## $^{1}$H NMR of 7y




## $^{13}$C NMR of 7y



**HSQC of 7y**

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