# CHAPTER-5

## *N*-Nitrosamine directed stereoselective *O*-glycosylation reactions of 2-amino thioglycosides with NIS-TfOH under mild reaction condtions

## 5.1 Introduction

*N*-Nitroso compounds are found in a wide range of food items and cosmetics [1]. Among the different classes of *N*-Nitroso compounds, *N*-Nitrosamines received particular attention due to their carcinogenic and mutagenic properties [2]. Moreover, the compounds bearing the nitrosamine group display various biological properties including anticancer and antimicrobial activities (**Figure 5.1**) [3]. On the other hand, *N*-Nitrosamines are used as synthetic intermediates in the preparation of hydrazines, sydnones, aryl *C*-Nitroso compounds, etc [4]. Transition-metal catalyzed directing groups assisted *C*-H bond activation reactions and received great interest in modern organic synthesis [5]. In this context, the *N*-Nitrosamine functional group has emerged as a traceless directing group for the activation of ortho *C*-H bonds in aryl rings [6]. In principle, the *N*-Nitrosamine group directs the metal insertion at the *ortho*-carbon of the aryl ring that facilitates the regioselective functionalization reactions in a simple and efficient manner (**Scheme 5.1**).

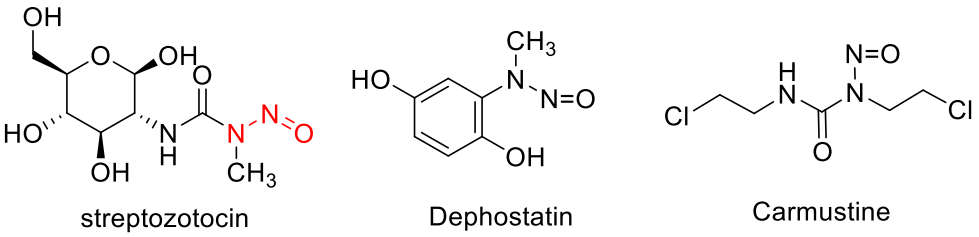
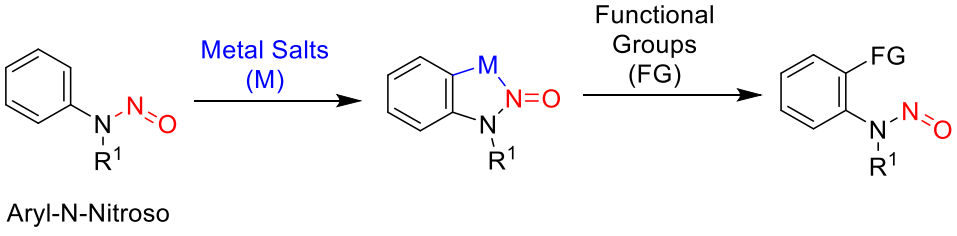
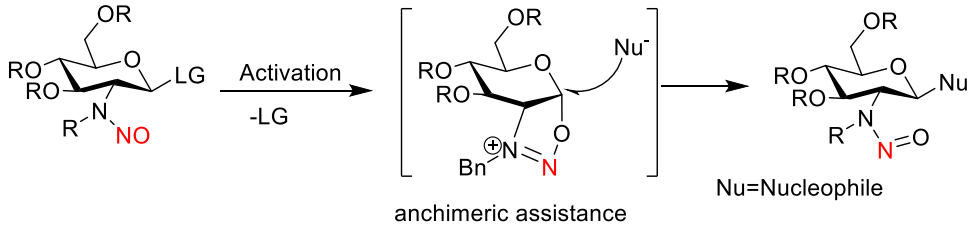



**Figure 5.1.** Biologically relevant *N*-Nitrosamines




**Scheme 5.1.** Nitrosamine-directed ortho *C*-H functionalization reactions

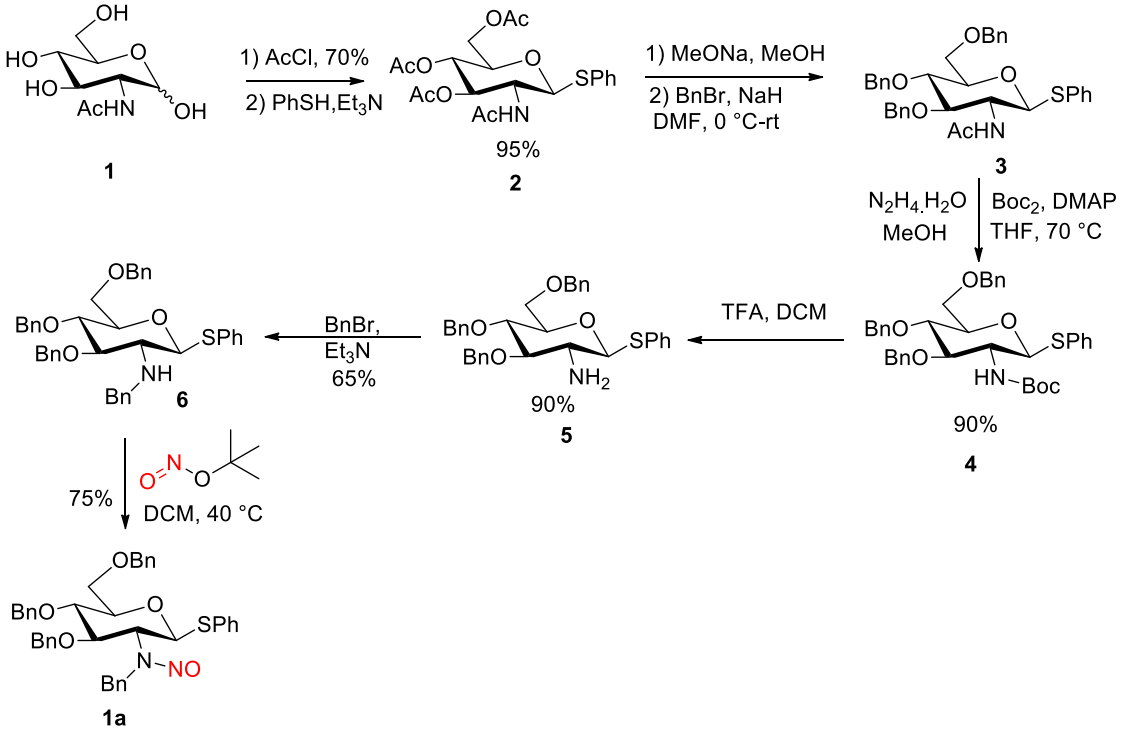
Carbohydrates are important biomolecules that play key roles in human health and diseases. Hence, the synthesis of structurally well-defined oligosaccharides is crucial for understanding the appropriate role of carbohydrates in biological systems [7]. Glycosylation reaction is the key step in the oligosaccharides assembly by which glycosides or glycoconjugates are generated with required stereochemistry at the anomeric position [8]. To achieve a high stereoselectivity in glycosylation reactions, various types of glycosyl donors and different activation strategies have been demonstrated in the literature [8, 9]. In general, the presence of a participating group in the *C*-2 position of the donor provides 1, 2-trans glycosides with excellent stereoselectivity. In particular, acyl groups (e.g. acetyl, benzoyl, etc.) were predominantly used as the directing groups for the glycosyl donors possessing hydroxyl group at the *C*-2 position [8, 9]. In the case of glycosyl donors with primary amines at the *C*-2 position, troc and phthalimide groups were used as directing groups [10]. However, participating groups for the glycosyl donors bearing secondary amines at the *C*-2 position is not well studied. In the past few years, our group research is focused on the chemistry of *N*-Nitrosamines and we have explored the synthesis and applications of *N*-Nitrosamines in various transformations [11]. In addition, our group also contributed to the synthesis of *O*-Glycosides and *C*-Glycosides, uronic acids, and photolabile protecting groups, etc [12]. With this background, here we have aimed to explore the *N*-Nitrosamine as the directing group in the glycosylation reactions to achieve 1, 2-trans glycosides **(Scheme 5.2)**.




**Scheme 5.2.** *N*-Nitrosamine as the directing group in the stereoselective glycosylation reactions.

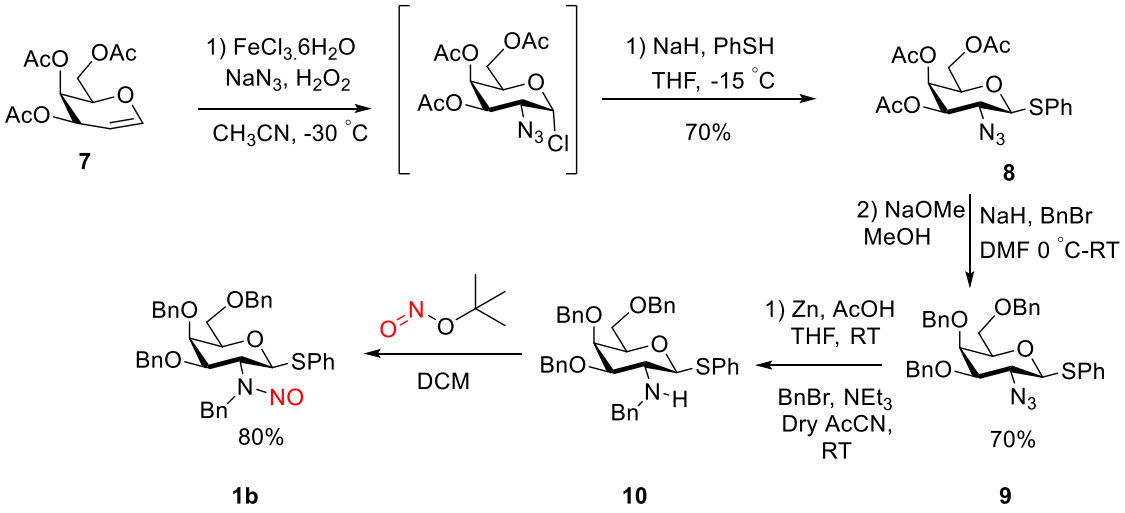
## 5.2 Results and Discussion

In the beginning, synthesis of benzyl-protected glucose and galactose *N*-Nitroso thioglycosides **1a** and **2a**, respectively was achieved as shown in **Scheme 5.3 and 5.4**. Synthesis of **1a** was achieved in 9 steps from *N*-Acetyl glucose **1**. Initially, compound **1** was converted into *O*-Acetyl β-Thioglycoside **2** *via* acetylation followed by thioglycosylation reactions. Subsequently, the compound **2** was converted into *O*-Benzyl β-Thioglycoside **3** through deacetylation followed by *O*-Benzylation reactions [13]. Further, the conversion of **3** to the free amine **5** (i.e. *N*-Deacetylation) was attempted with alkali hydroxides (NaOH and KOH) from room temperature to reflux conditions. However, these reactions gave a very low yield of the free amine **5**. Hence, alternative routes of *N*-Deacetylation reaction were investigated. Towards this end, *N*-Deacetylation was achieved in excellent yield via *N*-Boc protection followed by *N*-Deacetylation which gave *N*-Boc Thioglycoside **4** in good yield. The compound **4** was easily converted into free amine **5** using TFA in DCM at 0$^{o}$C-RT. Further, the compound **5** was *N*-Benzylated to obtain **6** which was subsequently converted into *N*-Nitroso β-Thioglucoside **1a** using tert-butyl nitrite in dichloromethane.




**Scheme 5.3.** Synthesis of benzyl-protected glucose *N*-Nitroso thioglycosides **1a**

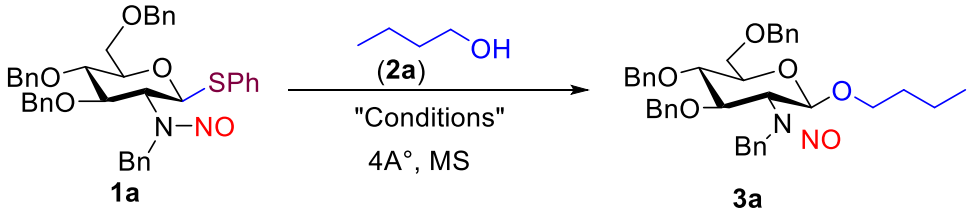
On the other hand, the compound **1b** was prepared from *O*-Acetyl D-galactal (**7**) in seven steps. Initially, the galactal **7** was converted into 2-Azido O-acetyl thioglycoside **8** via chloro-azidation followed by thioglycosylation reactions [14]. Further, *O*-Deacetylation and benzylation reactions gave the azido compound **9.** Further, the reduction of the azide group with Zn-acetic acid followed by *N*-Benzylation with benzyl bromide provided compound **10**. Further, the amino sugar **10** is converted into desired *N*-Nitroso β-Thiogalactoside **1b** using *tert*-butyl nitrite in dichloromethane. After the preparation of *N*-Nitroso donors **1a** and **1b**, the glycosylation reactions were investigated.




**Scheme 5.4.** Synthesis of benzyl-protected galactose N-Nitroso thioglycosides **2a.**

At the outset, optimization of the glycosylation conditions was performed by choosing *N*-Nitroso thioglycoside **1a** and butanol **2a** as model substrates (**Table 5.1**). The glycosylation reaction was performed in dichloromethane at 0 °C using NIS/TMSOTf, NIS/$BF_3.OEt_2$ and NIS/TfOH as activating agents. To our delight, these reactions provided the desired product **3a** in 45-71% yield with high stereoselectivity (α:β =>20:1). The stereochemistry at the anomeric position was confirmed by the 2D NMR spectrum like COSY and HSQC. The NIS/TfOH system was found to be better than other systems. Hence the activation was further performed under different temperatures. It was observed that the reaction proceeds with a better yield at -10 °C when compared with -30, 0, 10, and RT. Moreover, DCM was found to be the best solvent for the glycosylation reaction.

**Table 5.1.** Optimization of the reaction conditions.[a]



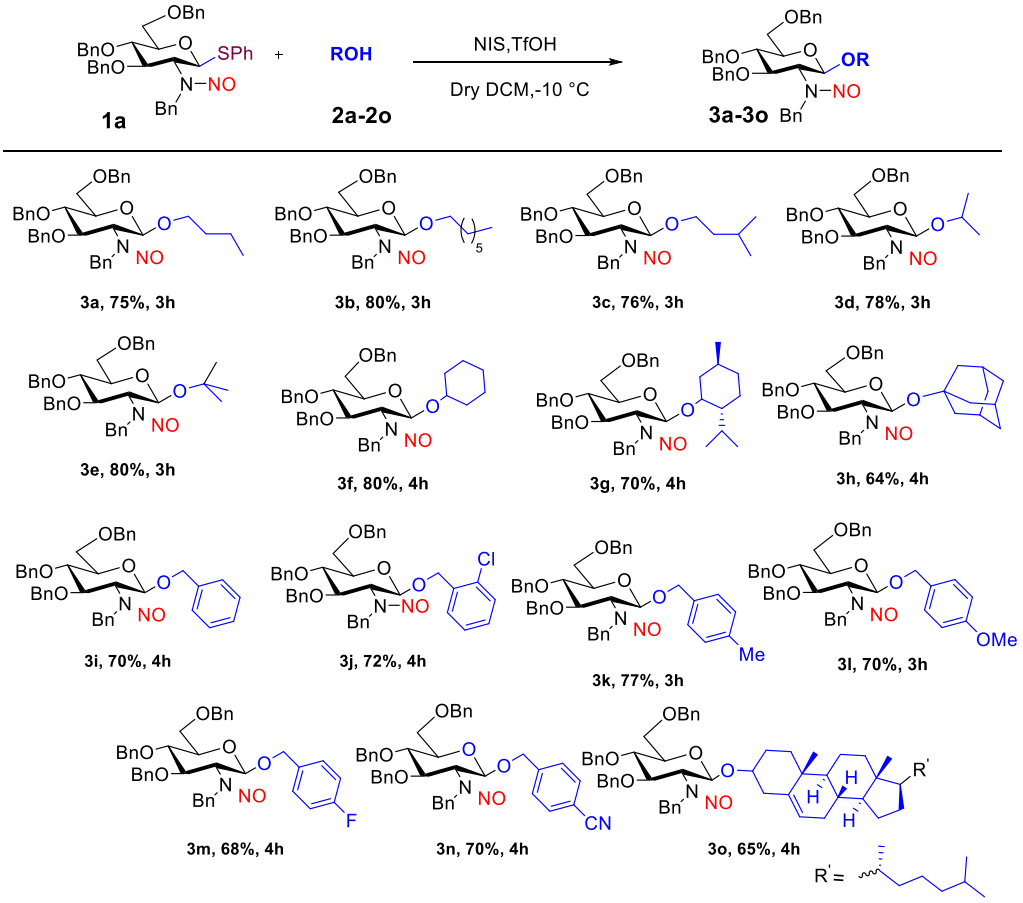

| Entry | Activation reagents (equiv.) | Solvent | Temperature (°C) | Time | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | NIS/TMSOTf (1/0.1) | DCM | 0 | 2h | 61 |
| 2 | NIS/$BF_3.OEt_2$ (1/0.1) | DCM | 0 | 6h | 45 |
| 3 | NIS/TfOH (1/0.1) | DCM | 0 | 5h | 71 |
| 4 | NIS/TfOH (1/0.1) | DCM | -30 | 4h | 74 |
| 5 | NIS/TfOH (1.2/0.1) | DCM | -10 | 3h | 75 |
| 6 | NIS/TfOH (1.2/0.1) | DCM | 10 | 6h | 69 |
| 7 | NIS/TfOH (1.2/0.1) | DCM | RT | 6h | 51 |
| 8 | NIS/TfOH (1.2/0.1) | $CH_3CN$ | -10 | 4h | 57 |
| 9 | NIS/TfOH (1.2/0.1) | $Et_2O$ | -10 | 4h | 65 |

[a]**Reaction condition:** Substrate **1a** (0.1 mmol), alcohol (3 equiv.), NIS (1.2 equiv.), TfOH (0.1 equiv.), dry DCM (3ml). [b]Isolated yield.

After establishing the optimized conditions glycosylation of different non-sugar acceptors with *N*-Nitroso thioglycoside **1a** was investigated. Glycosylation of primary alcohols such

as octanol and iso-amyl alcohol with **1a** gave the desired glycosides **3b** and **3c** in 76-80% yields. On the other hand, secondary alcohols such as isopropanol, cyclohexanol, menthol, and sterol also gave the desired glycosides in 80-81% yield with excellent stereoselectivity. Further to our delight, the tert-alcohols such as tert-butanol and adamentanol gave the desired products in 84-64% yields. Further, various functionalized benzyl alcohols were subjected to glycosylation with **1a.** These reactions gave the corresponding *O*-glycosides **3j-3k** in good to excellent yields, irrespective of the functional groups present in the benzyl alcohols.

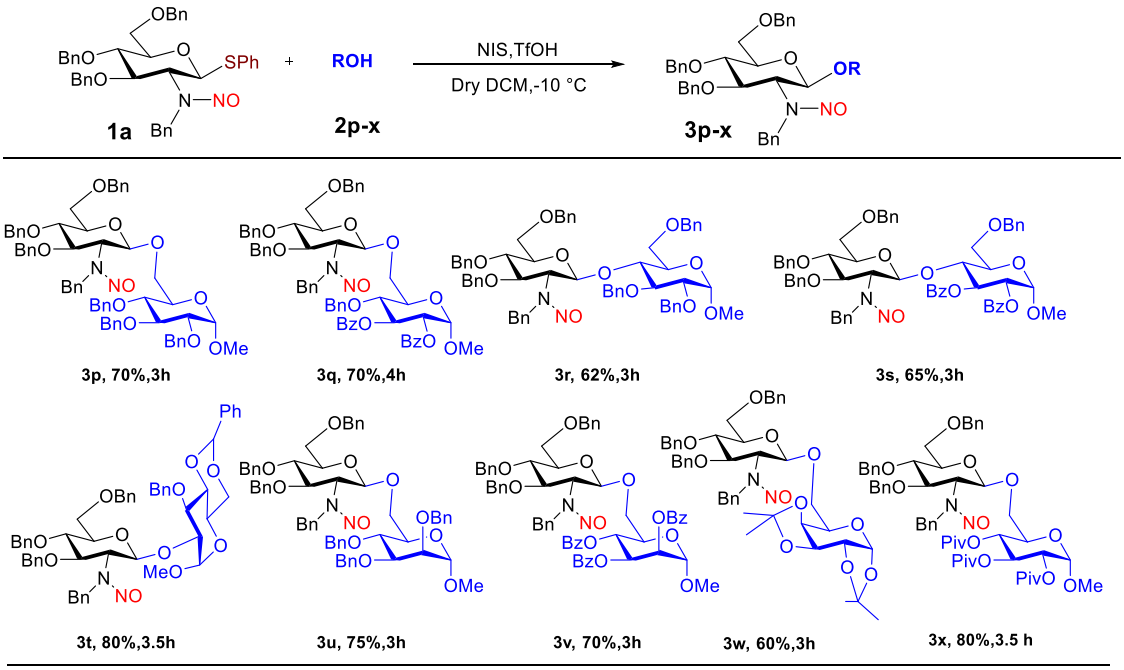
**Table 5.2:** Glycosylation of N-Nitroso Glucosamine **1a** with various alcohols




[a]**Reaction condition:** Substrate **1a** (0.1 mmol), alcohol (3 equiv.), NIS (1.2 equiv.), TfOH (0.1 equiv.), dry DCM (3ml). [b]Isolated yield.

Further, we have tried the glycosylation reaction of various sugar acceptors with N-Nitroso thioglycoside **1a.** For this investigation, different sugar acceptors with primary and secondary alcohols were prepared and subjected to the glycosylation reaction under optimized conditions. α-Methyl glucoside bearing benzyl and benzoyl protecting groups and primary alcohol gave the desired product 3p and 3q were achieved in good yields. Similarly, secondary alcohols acceptors such as α-Methyl glucoside bearing benzyl and benzoyl protecting groups 3p and 3q were achieved in good yields. Similar to glucose and mannose, galactose acceptor also participated in the glycosylation reaction and provided the desired product in excellent yield.

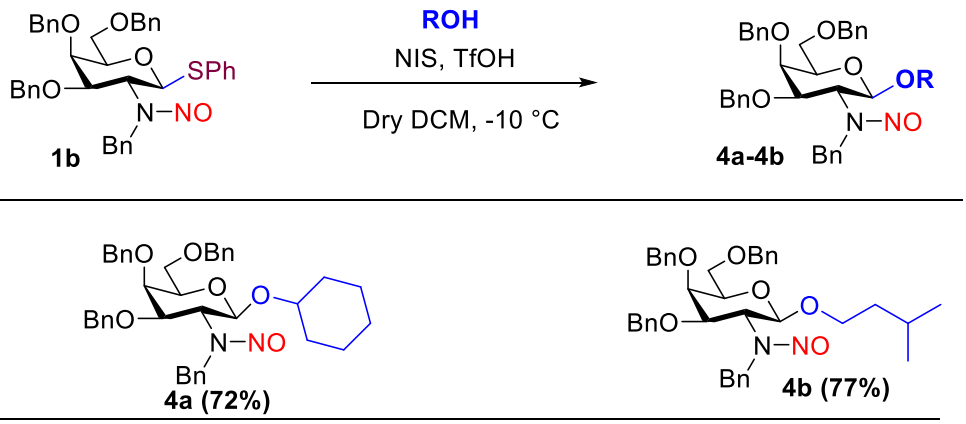
**Table 5.3:** Glycosylation of *N*-Nitroso Glucosamine **1a** with monosaccharide alcohols.




[a]**Reaction condition**: Substrate **1a** (0.1 mmol), alcohol (1.2 equiv.), NIS (1.2 equiv.), TfOH (0.1 equiv.), dry DCM (3ml). [b]Isolated yield.

Further, we have explored the glycosylation of *N*-Nitroso thioglycoside **2a** galactosamine with glycosylation reaction with primary and secondary alcohols. To our delight, these reactions gave the desired products **4a** and **4b** in good yields (72-77%).

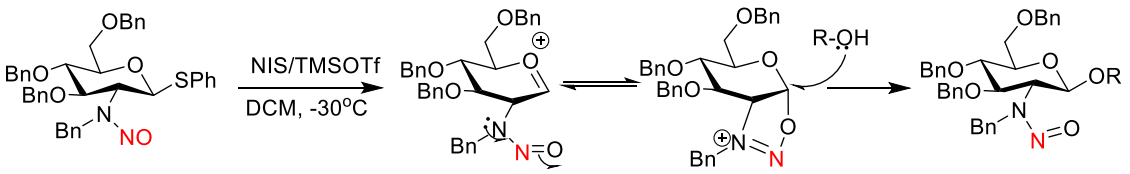
**Table 5.4:** Glycosylation of N-Nitroso Galactosamine **2a** with various alcohols.




[a]**Reaction condition: 1b** (0.1 mmol), alcohol (3 equiv.), NIS (1.2 equiv.), TfOH (0.1 equiv.), dry DCM (3ml).[b]Isolated yield.

### 5.3 Proposed mechanism of the reaction

A proposed mechanism of the reactions was shown in **Scheme 5.1**. Activation of thioglycoside with NIS/TfOH provides the oxonium ion intermediate **A**. Simultaneously, the *N*-Nitrosamine undergoes delocalization and provides anchimeric assistance to form the intermediate **B** and allows the acceptor to attack from the top phase and provides β-selective glycosides.

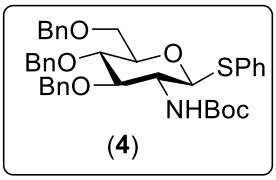


## 5.4 Conclusions:

The *N*-Nitrosamine-directed stereoselective *O*-glycosylation reactions of 2-amino thioglycosides with various acceptors were demonstrated under mild reaction conditions. The reaction was activated by using NIS/TfOH system in dichloromethane at –10 °C. Various sugar and non-sugar acceptors were successfully glycosylated with different donors including 2-amino 1-thioglucoside and 2-amino 1-thiogalactoside under optimized conditions. These reactions provided the desired β-glycosides in good to excellent yields in a short span of time.

## 5.5 Experimental Section

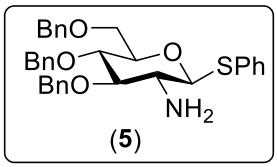
### 5.5.1 Synthesis of thio 3,4,6-tri-*O*-benzyl-2-(*tert*-butyloxycarbonylamino)-2-deoxy-β-D-glucopyranoside (4)




(**4**)

The solution of thio 2-(*N*-acetyl)-3,4,6-tri-*O*-benzyl-2-(*tert*-butyloxycarbonylamino)-2-deoxy-β-D-glucopyranoside (700 mg, 1.0 mmol) and hydrazine hydrate(1.0 mL 20 eq.) in MeOH was stirred at room temperature for 1h. After the completion of the reaction, methanol was evaporated by a rotatory evaporator, and the residue was redissolved in dichloromethane. The organic layer was washed with a saturated solution of $NaHCO_3$ respectively, dried with anhydrous sodium sulfate, and concentrated to afford the crude product which was further purified by silica gel chromatography to obtain the product.

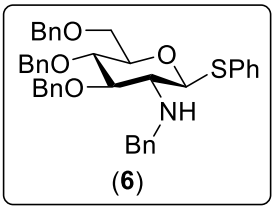
### 5.5.2 Synthesis of thio 2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (5)




(**5**)

To the solution of thio 3,4,6-tri-*O*-benzyl-2-(*tert*-butyloxycarbonylamino)-2-deoxy-β-D-glucopyranoside (700 mg, 1.0 mmol) in dichloromethane, trifluoroacetic acid (1.0 mL, 12.0 eq.) was added and the resulting reaction mixture was stirred at room temperature for 30 minutes. After the completion of the reaction, the reaction mixture was evaporated by a rotatory evaporator and redissolved in dichloromethane. The organic layer was washed with 10% $NaHCO_3$ and water and concentrated on the obtained crude product which was further purified by silica gel column chromatography to obtain a pure product.

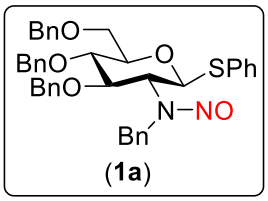
### 5.5.3 Synthesis of thio-2-*N*-benzyl amino-3, 4, 6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (6)




(**6**)

To the solution of thio 2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (550 mg,1.0 mmol) in dry AcCN, benzyl bromide ( 186.0mml, 1.5eq. ) was added then dropwise added triethylamine (196.0mml, 1.5eq.) and the resulting reaction mixture was stirred at room temperature overnight. After the completion of the reaction, the solvent was evaporated and redissolved in DCM the organic layer washed with aq. $NaHCO_3$ and water and brine solution and dried ($Na_2SO_4$) concentrated on the obtained crude product which was further purified by column chromatography to obtain a pure product.

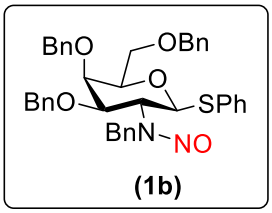
### 5.5.4 Synthesis of thio-2-*N*-benzyl-*N*-Nitroso-3, 4, 6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (1a)




(1a)

To the solution of thio 2-*N*-benzyl amine-3, 4, 6-tri-O-benzyl-2-deoxy-β-D-glucopyranoside (650mg, 1.0 mmol) in dry DCM, TBN (367.0 mml, 3.0eq.) was added and stirred at 40°C for 2h. After completion of the reaction, the solvent evaporates and redissolves in DCM and washed with water and brine solution, and dried with ($Na_2SO_4$) concentrated and further purified using silica gel chromatography and obtaining the desired product.

### 5.5.5 Synthesis of thio-2-*N*-benzyl-*N*-Nitroso-3, 4, 6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranoside (1b)




(1b)

To the solution of thio 2-*N*-benzyl amine-3, 4, 6-tri-O-benzyl-2-deoxy-β-D-galactopyranoside (650.0 mg, 1.0 mmol) in dry DCM, TBN (367.0 mml, 3eq.) was added and stirred at RT for 5h. After completion of the reaction, the solvent evaporates and redissolves in DCM and washed with water and brine solution, and dried with ($Na_2SO_4$)

concentrated and further purified using silica gel chromatography and obtaining the desired product.

### 5.5.6 General Procedure for Glycosylation

Donor (1 equiv.) and acceptor (3 equiv. for non-sugar and 1.2 equiv. for carbohydrate alcohol) were stirred in freshly dried DCM with 4 A° MS in (4-5 ml) at -10 °C. Take donor and NIS (1.2 equiv.) and keep staring for 5 min. and then add acceptor, finally add activator TfOH (0.1 equiv.) and keep for stare. The reaction completely confirms by TLC. After the complete reaction is quenched by triethylamine with a few drops, for diluting the reaction add DCM (10-15 ml) and washed with water and $NaHCO_3$ with brine solution, dry over $Na_2SO_4$, filter, and concentrated. The residue was purified by column chromatography (hexane/ ethyl acetate) using silica gel.

## 5.6. Analytical date:-

### 5.6.1 Tert-butyl ((2S,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(phenylthio)tetrahydro-2H-pyran-3-yl)carbamate (4)

Yield: 90% (591.2 mg) as a white foam. **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.55–7.52 (m, 2H), 7.30 (dt, *J* = 15.9, 6.4 Hz, 14H), 7.23 – 7.20 (m, 4H), 4.97 (d, *J* = 9.7 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 2H), 4.71 (d, *J* = 10.9 Hz, 2H), 4.59 (dd, *J* = 11.5, 5.2 Hz, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 3.93 (t, *J* = 8.4 Hz, 1H), 3.78 (dd, *J* = 10.8, 1.4 Hz, 1H), 3.72 (dd, *J* = 10.9, 4.4 Hz, 1H), 3.59 (dd, *J* = 16.7, 8.2 Hz, 2H), 3.35 (d, *J* = 8.8 Hz, 1H), 1.47 (s, 9H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ = 155.0, 138.3, 138.1, 133.2, 132.4, 128.8, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.5, 86.1, 82.7, 79.8, 79.2, 78.4, 75.2,

74.7, 73.4, 69.1, 56.3, 28.4, 27.8, 27.6, 14.17. HRMS: Calc. for $C_{38}H_{43}NO_6S$ $[M+Na]^+$: 664.2709, Obser. 664.2749.

### 5.6.2 (2S,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(phenylthio)tetrahydro-2H-pyran-3-amine (5)

Yield: 90% (531.73 mg) as a pale yellow viscous. **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.61–7.41 (m, 2H), 7.30 – 7.24 (m, 5H), 7.24 – 7.17 (m, 8H), 7.17 – 7.13 (m, 5H), 4.87 (d, *J* = 11.2 Hz, 1H), 4.70 (d, *J* = 10.9 Hz, 1H), 4.65 (dd, *J* = 11.2, 2.0 Hz, 1H), 4.60 – 4.52 (m, 2H), 4.51 – 4.42 (m, 2H), 3.76 – 3.66 (m, 2H), 3.58 (td, *J* = 9.6, 1.9 Hz, 1H), 3.52 – 3.40 (m, 2H), 2.79 (td, *J* = 9.7, 2.0 Hz, 1H), 2.69 – 2.56 (m, 2H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ = 138.4, 138.2, 138.0, 133.0, 131.9, 129.0, 128.7, 128.5, 128.4, 128.1, 128.0, 128.0, 128.0, 127.9, 127.7, 127.7, 88.1, 86.0, 79.5, 78.4, 75.6, 74.9, 73.5, 69.0, 55.4. HRMS: Calc. for $C_{33}H_{36}NO_4S$ $[M+H]^+$: 542.2365, Obser. 542.2370.

### 5.6.3 (2S,3R,4R,5S,6R)-N-benzyl-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(phenylthio)tetrahydro-2H-pyran-3-amine (6)

Yield: 65% (416.0 mg) as viscous. **$^1$H NMR** (500 MHz, $CDCl_3$) δ = 7.50–7.47 (m, 2H), 7.28 – 7.21 (m, 9H), 7.16 (m, *J* = 14.7, 11.7, 4.8 Hz, 14H), 4.86 (d, *J* = 11.1 Hz, 1H), 4.76 (dd, *J* = 23.0, 10.9 Hz, 2H), 4.53 (d, *J* = 10.8 Hz, 3H), 4.47 (d, *J* = 11.9 Hz, 1H), 3.83 (s, 2H), 3.69 (dd, *J* = 19.3, 7.5 Hz, 2H), 3.65 – 3.42 (m, 4H), 2.72 (t, *J* = 9.3 Hz, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ = 140.4, 138.4, 138.3, 138.1, 133.5, 132.1, 128.9, 128.6, 128.59, 128.5, 128.4, 128.4, 128.0, 128.0, 127.9, 127.9, 127.8, 127.6, 127.63, 127.1, 88.4, 86.1, 79.4, 78.7, 75.5, 75.0, 73.5, 69.2, 62.3, 53.5. HRMS: Calc. for $C_{40}H_{42}NO_4S$ $[M+H]^+$: 632.2865, Obser. 632.2870.

### 5.6.4 *N*-benzyl-N-((2S,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(phenylthio)tetrahydro-2H-pyran-3-yl)nitrous amide (1a)

Yield: 75% (475.88 mg) as a pale yellow solid. Melting point 123.0 °C **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.27 – 7.19 (m, 10H), 7.18 – 7.06 (m, 11H), 6.97 (dd, *J* = 6.6, 2.9 Hz, 2H), 4.99 (d, *J* = 10.3 Hz, 1H), 4.80 (d, *J* = 14.5 Hz, 1H), 4.69 (d, *J* = 10.8 Hz, 1H), 4.65 (s, 1H), 4.62 (d, *J* = 3.4 Hz, 1H), 4.53 (dd, *J* = 11.4, 5.6 Hz, 2H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.21 (dd, *J* = 18.3, 10.2 Hz, 2H), 3.99 (t, *J* = 10.0 Hz, 1H), 3.73 – 3.66 (m, 3H), 3.53 (m, *J* = 9.9, 4.0, 2.2 Hz, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 138.04, 137.84, 137.65, 133.78, 133.57, 131.92, 128.97, 128.85, 128.55, 128.45, 128.40, 128.21, 128.01, 127.94, 127.92, 127.86, 127.77, 127.59, 87.46, 79.78, 78.67, 77.35, 77.09, 76.84, 75.62, 75.15, 73.56, 71.71, 68.29, 66.70, 48.82. HRMS: Calc. for $C_{40}H_{40}N_2O_5S$ $[M+H]^+$: 661.2736, Obser. 661.2738.

### 5.6.5 Synthesis of thio-2-*N*-benzyl-*N*-Nitroso-3, 4, 6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranoside (1b)

Yield: 65% (468.8 mg) as a pale yellow liquid. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.26 – 7.19 (m, 12H), 7.13 – 6.98 (m, 11H), 4.99 (d, *J* = 10.1 Hz, 1H), 4.71 (d, *J* = 11.1 Hz, 1H), 4.47 – 4.30 (m, 7H), 4.18 – 4.09 (m, 2H), 3.98 (s, 1H), 3.68 – 3.57 (m, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 138.34, 137.72, 137.04, 133.12, 131.53, 129.87, 128.95, 128.43, 128.36, 128.29, 128.18, 127.93, 127.92, 127.86, 127.80, 127.76, 127.59, 127.48, 88.134, 77.52, 74.58, 73.60, 72.46, 72.14, 68.44, 61.73. HRMS: Calc. for $C_{40}H_{40}N_2O_5S$ $[M+H]^+$: 661.2736, Obser. 661.2728.

### 5.6.6 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-butoxytetrahydro-2H-pyran-3-yl)nitrous amide (3a)

Yield: 75% (70.91mg) as a white foam. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 10H), 7.28 – 7.15 (m, 8H), 7.09 – 7.02 (m, 2H), 5.16 (d, *J* = 14.5 Hz, 1H), 4.82 – 4.74 (m, 3H), 4.67 (d, *J* = 12.2 Hz, 1H), 4.60 – 4.56 (m, 2H), 4.51 (d, *J* = 14.5 Hz, 1H), 4.45 – 4.39 (m, 2H), 3.95 – 3.86 (m, 2H), 3.76 (dd, *J* = 18.5, 6.1 Hz, 3H), 3.61 (dt, *J* = 9.8, 3.0 Hz, 1H), 3.34 (dt, *J* = 9.2, 6.8 Hz, 1H), 1.52 – 1.45 (m, 2H), 1.28 (dd, *J* = 15.0, 7.6 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 137.89, 137.71, 137.65, 133.75, 129.07, 128.45, 128.43, 128.37, 128.27, 127.84, 127.80, 127.77, 127.69, 127.65, 102.78, 82.17, 79.17, 75.41, 74.97, 74.95, 73.52, 69.85, 68.41, 67.59, 51.00, 31.41, 19.04, 13.77. HRMS: Calc. for $C_{38}H_{44}N_2O_6$ $[M+H]^+$: 625.3278, Obser. 625.3281.

### 5.6.7 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(heptyloxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3b)

Yield: 80% (80.73mg) as a white foam. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.36 – 7.25 (m, 11H), 7.21 – 7.12 (m, 7H), 7.05 – 7.01 (m, 2H), 5.15 (d, *J* = 14.5 Hz, 1H), 4.79 – 4.71 (m, 3H), 4.64 (d, *J* = 12.2 Hz, 1H), 4.57 – 4.53 (m, 2H), 4.47 (d, *J* = 14.5 Hz, 1H), 4.42 – 4.36 (m, 2H), 3.92 – 3.82 (m, 2H), 3.76 – 3.70 (m, 3H), 3.58 (dt, *J* = 9.9, 3.1 Hz, 1H), 3.31 (dt, *J* = 9.3, 6.8 Hz, 1H), 1.50 – 1.44 (m, 2H), 1.26 (m, *J* = 25.9, 15.6, 8.1 Hz, 8H), 0.88 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 137.89, 137.71, 137.65, 133.76, 129.04, 128.45, 128.42, 128.37, 128.27, 127.84, 127.80, 127.77, 127.69, 127.65, 127.64, 102.80, 82.12, 79.17, 75.40, 74.97, 74.94, 73.53, 70.19, 68.42, 67.57, 50.97, 31.71, 29.37, 28.97, 25.82, 22.57, 14.07. HRMS: Calc. for $C_{41}H_{50}N_2O_6$ $[M+H]^+$: 667.3747, Obser. 667.3747.

### 5.6.8 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(isopentyloxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3c)

Yield: 76% (73.47mg) as a white foam. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.37–7.25 (m, 11H), 7.21 – 7.13 (m, 7H), 7.06 – 7.01 (m, 2H), 5.12 (d, *J* = 14.5 Hz, 1H), 4.79 – 4.71 (m, 3H), 4.64 (d, *J* = 12.2 Hz, 1H), 4.58 – 4.53 (m, 2H), 4.48 (d, *J* = 14.5 Hz, 1H), 4.42 – 4.36 (m, 2H), 3.89 (dt, *J* = 9.2, 5.0 Hz, 2H), 3.77 – 3.70 (m, 3H), 3.58 (dt, *J* = 9.9, 3.0 Hz, 1H), 3.33 (dt, *J* = 9.3, 7.0 Hz, 1H), 1.55 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.36 (dt, *J* = 7.8, 3.9 Hz, 2H), 0.85 (dd, *J* = 7.9, 6.7 Hz, 6H). **$^{13}$C NMR** (125MHz, $CDCl_3$) $\delta$ = 137.8, 137.7, 137.6, 133.7, 129.0, 128.4, 128.4, 128.3, 128.2, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 102.7, 82.1, 79.1, 76.7, 75.3, 74.9, 74.9, 73.5, 68.4, 68.4, 67.5, 50.9, 38.0, 24.7, 22.5, 22.3. HRMS: Calc. for $C_{39}H_{46}N_2O_6$ $[M+H]^+$: 639.3434, Obser. 639.3453.

### 5.6.9 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-isopropoxytetrahydro-2H-pyran-3-yl)nitrous amide (3d)

Yield: 78% (72.09 mg) as brown viscous. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.35 – 7.31 (m, 4H), 7.30 – 7.25 (m, 6H), 7.24 (s, 1H), 7.21 – 7.13 (m, 7H), 7.04 – 7.00 (m, 2H), 5.04 (d, *J* = 14.4 Hz, 1H), 4.83 (d, *J* = 8.2 Hz, 1H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.73 (d, *J* = 10.8 Hz, 1H), 4.64 – 4.54 (m, 4H), 4.39 (dt, *J* = 10.5, 4.2 Hz, 2H), 3.91 – 3.83 (m, 2H), 3.76 – 3.68 (m, 3H), 3.61 – 3.56 (m, 1H), 1.18 (d, *J* = 6.2 Hz, 3H), 0.97 (d, *J* = 6.1 Hz, 3H). **$^{13}$C NMR** (125MHz, $CDCl_3$) $\delta$ = 137.9, 137.7, 137.6, 133.7, 129.2, 128.4, 128.4, 128.3, 128.2, 127.8, 127.8, 127.7, 127.6, 101.3, 82.5, 79.1, 75.4, 74.9, 73.4, 72.4, 68.5, 67.8, 51.5, 23.3, 21.6. HRMS: Calc. for $C_{37}H_{42}N_2O_6$ $[M+H]^+$: 611.3121, Obser. 611.3114.

### 5.6.10 *N*-benzyl-*N*-((2S,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(tert-butoxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3e)

Yield: 80% (75.64 mg) as viscous yellow;**$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.36 – 7.29 (m, 8H), 7.28 – 7.17 (m, 10H), 7.04 (dd, *J* = 6.6, 2.9 Hz, 2H), 5.09 (d, *J* = 14.2 Hz, 1H), 4.98 (d, *J* = 8.2 Hz, 1H), 4.77 (dd, *J* = 31.5, 10.8 Hz, 2H), 4.65 – 4.55 (m, 4H), 4.47 – 4.39 (m, 2H), 3.89 (dd, *J* = 10.5, 8.2 Hz, 1H), 3.77 – 3.67 (m, 3H), 3.64 – 3.60 (m, 1H), 1.16 (s, 9H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 138.0, 137.8, 137.6, 133.6, 129.4, 128.5, 128.4, 128.3, 128.2, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 97.6, 82.9, 79.2, 75.5, 74.8, 74.7, 73.4, 68.7, 68.0, 51.8, 28.4. HRMS: Calc. for $C_{38}H_{44}N_2O_6$ $[M+H]^+$: 625.3278, Obser. 625.3276.

### 5.6.11 *N*-Benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(cyclohexyloxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3f)

Yield: 80% (78.79 mg) as a white foam. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 9H), 7.28 – 7.16 (m, 9H), 7.07 – 7.02 (m, 2H), 5.15 (d, *J* = 14.4 Hz, 1H), 4.90 (d, *J* = 8.2 Hz, 1H), 4.78 (dd, *J* = 25.3, 10.8 Hz, 2H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.61 – 4.55 (m, 3H), 4.42 (dt, *J* = 10.5, 4.3 Hz, 2H), 3.90 (dd, *J* = 10.6, 8.3 Hz, 1H), 3.80 – 3.70 (m, 3H), 3.64 – 3.58 (m, 2H), 1.96 – 1.89 (m, 1H), 1.73 – 1.67 (m, 2H), 1.54 – 1.48 (m, 1H), 1.42 – 1.11 (m, 6H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 137.9, 137.7, 137.6, 133.7, 129.2, 128.4, 128.4, 128.3, 128.2, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 101.1, 82.5, 79.2, 77.7, 76.7, 75.4, 74.9, 73.4, 68.5, 67.7, 33.3, 31.4, 25.4, 23.8, 23.6. HRMS: Calc. for $C_{40}H_{46}N_2O_6$ $[M+H]^+$: 651.3434, Obser. 651.3433.

**5.6.12 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3g)**

Yield: 70% (74.88 mg) as a yellow foam. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.35 – 7.26 (m, 10H), 7.25 – 7.14 (m, 8H), 7.04 (dd, *J* = 6.5, 2.9 Hz, 2H), 4.97 (d, *J* = 14.4 Hz, 1H), 4.84 (d, *J* = 8.2 Hz, 1H), 4.76 (dd, *J* = 19.1, 10.9 Hz, 2H), 4.64 – 4.54 (m, 4H), 4.43 – 4.37 (m, 2H), 3.83 – 3.69 (m, 4H), 3.57 – 3.53 (m, 1H), 3.42 (td, *J* = 10.6, 4.2 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.74 (d, *J* = 12.1 Hz, 1H), 1.59 (dd, *J* = 9.1, 6.8 Hz, 2H), 1.27 (d, *J* = 14.9 Hz, 2H), 1.08 – 0.91 (m, 3H), 0.86 (dd, *J* = 14.4, 6.8 Hz, 6H), 0.78 (d, *J* = 6.9 Hz, 3H), 0.57 – 0.50 (m, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 138.0, 137.8, 137.8, 133.7, 129.3, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 127.6, 127.6, 127.5, 99.7, 82.6, 79.2, 77.4, 76.7, 75.3, 74.9, 74.9, 73.7, 68.7, 67.7, 51.5, 47.7, 39.8, 34.2, 31.2, 25.1, 23.0, 22.1, 20.9, 15.8. HRMS: Calc. for $C_{44}H_{54}N_2O_6$ $[M+H]^+$: 707.4060, Obser. 707.4064.

**5.6.13 *N*-((2S,3R,4R,5S,6R)-2-(((3R,5R,7R)-adamantan-1-yl)oxy)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-3-yl)-N-benzylnitrous amide (3h)**

Yield: 64% (68.07 mg) as viscous yellow. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.29 (m, *J* = 12.4, 9.7, 6.2 Hz, 9H), 7.25 – 7.15 (m, 9H), 7.08 – 6.96 (m, 2H), 5.09 (dd, *J* = 24.2, 11.2 Hz, 2H), 4.78 (d, *J* = 10.9 Hz, 1H), 4.71 (d, *J* = 10.8 Hz, 1H), 4.64 – 4.52 (m, 4H), 4.45 – 4.34 (m, 2H), 3.90 – 3.83 (m, 1H), 3.76 – 3.59 (m, 4H), 2.11 – 2.04 (m, 3H), 1.71 (d, *J* = 11.4 Hz, 3H), 1.61 – 1.51 (m, 9H).**$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 138.08, 137.79, 137.67, 133.70, 129.44, 128.50, 128.40, 128.30, 128.24, 127.80, 127.78, 127.76, 127.70, 127.65, 127.62, 127.56, 96.07, 82.89, 79.35, 77.25, 77.00, 76.75, 76.00, 75.50, 74.88,

74.72, 73.38, 68.92, 68.04, 51.94, 42.21, 36.02, 30.51. HRMS: Calc. for $C_{44}H_{50}N_2O_6$ $[M+H]^+$: 703.3747, Obser. 703.3745.

### 5.6.14 *N*-benzyl-N-((2R,3R,4R,5S,6R)-2,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-3-yl)nitrous amide (3i)

Yield: 70% (69.78 mg) as a pale yellow foam. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.37 – 7.26 (m, 13H), 7.23 – 6.99 (m, 12H), 5.08 (d, *J* = 14.5 Hz, 1H), 4.86 (dd, *J* = 9.9, 5.7 Hz, 2H), 4.77 (d, *J* = 10.8 Hz, 1H), 4.72 (d, *J* = 10.9 Hz, 1H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 2H), 4.48 (dd, *J* = 16.4, 13.1 Hz, 2H), 4.41 – 4.34 (m, 2H), 3.97 (dd, *J* = 10.5, 8.3 Hz, 1H), 3.76 (dd, *J* = 14.2, 6.0 Hz, 3H), 3.62 – 3.57 (m, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 137.8, 137.7, 137.6, 136.5, 133.6, 129.0, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 126.9, 101.7, 82.2, 79.1, 75.4, 75.0, 74.9, 73.5, 71.3, 68.3, 67.4, 65.3, 50.9. HRMS: Calc. for $C_{44}H_{50}N_2O_6$ $[M+H]^+$: 703.3747, Obser. 703.3745. . HRMS: Calc. for $C_{41}H_{42}N_2O_6$ $[M+H]^+$ : 659.3121, Obser. 659.3119.

### 5.6.15 *N*-Benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-((2-chlorobenzyl)oxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3j)

Yield: 72% (75.53 mg) as brown syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.34 (m, *J* = 14.3, 9.8, 5.0 Hz, 10H), 7.27–7.10 (m, 12H), 7.09–7.04 (m, 2H), 5.09 (d, *J* = 14.5 Hz, 1H), 4.93 (dd, *J* = 15.3, 10.4 Hz, 2H), 4.83–4.74 (m, 2H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.62–4.51 (m, 4H), 4.45 – 4.37 (m, 2H), 4.04 (dd, *J* = 10.3, 8.4 Hz, 1H), 3.85–3.74 (m, 3H), 3.64 (dt, *J* = 9.8, 2.8 Hz, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 137.85, 137.72, 137.60, 134.48, 133.71, 133.08, 129.44, 129.25, 129.12, 129.06, 128.46, 128.44, 128.40, 128.30,

127.86, 127.80, 127.79, 127.73, 127.71, 127.67, 126.77, 101.91, 82.20, 79.05, 75.41, 75.11, 74.95, 73.58, 68.43, 68.27, 67.37, 50.77. HRMS: Calc. for $C_{41}H_{41}ClN_2O_6$ $[M+H]^+$: 693.2731, Obser. 693.2734.

### 5.6.16 *N*-benzyl-N-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-((4-methylbenzyl)oxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3k)

Yield: 77% (78.40 mg) as a pale yellow foam. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.37 – 7.26 (m, 10H), 7.23 – 6.99 (m, 15H), 5.13 (d, *J* = 14.5 Hz, 1H), 4.84 – 4.64 (m, 5H), 4.56 (dd, *J* = 11.5, 3.3 Hz, 2H), 4.47 – 4.42 (m, 2H), 4.38 (dt, *J* = 9.0, 4.2 Hz, 2H), 3.95 (dd, *J* = 10.5, 8.3 Hz, 1H), 3.79 – 3.72 (m, 3H), 3.58 (dt, *J* = 9.9, 3.0 Hz, 1H), 2.34 (d, *J* = 5.5 Hz, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 137.9, 137.7, 137.7, 137.6, 133.6, 133.4, 129.0, 129.0, 128.4, 128.4, 128.4, 128.2, 128.0, 127.8, 127.7, 127.7, 127.6, 127.6, 101.6, 82.1, 79.1, 75.4, 75.0, 74.9, 73.5, 71.1, 68.3, 67.5, 51.0, 21.1. HRMS: Calc. for $C_{42}H_{44}N_2O_6$ $[M+H]^+$: 673.3278, Obser. 673.3283.

### 5.6.17 *N*-benzyl-N-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-((4-methoxybenzyl)oxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3l)

Yield: 70% (72.97 mg) as brown syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.37 – 7.26 (m, 9H), 7.24 (d, *J* = 3.5 Hz, 2H), 7.17 – 7.07 (m, 9H), 7.04 – 7.00 (m, 2H), 6.85 – 6.81 (m, 2H), 5.10 (d, *J* = 14.5 Hz, 1H), 4.83 – 4.76 (m, 3H), 4.71 (d, *J* = 10.9 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.56 (dd, *J* = 11.5, 4.0 Hz, 2H), 4.47 – 4.35 (m, 4H), 3.94 (dd, *J* = 10.5, 8.3 Hz, 1H), 3.80 (d, *J* = 4.0 Hz, 3H), 3.78 (t, *J* = 4.2 Hz, 2H), 3.74 (t, *J* = 6.7 Hz, 1H), 3.58 (dd, *J* = 8.0, 5.1 Hz, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 159.3, 137.8, 137.7, 137.6, 133.6, 129.6, 129.0, 128.6, 128.4, 128.4, 128.4, 128.2, 127.8, 127.7, 127.7, 127.6,

127.6, 113.7, 101.5, 82.1, 79.1, 75.4, 75.0, 74.9, 73.5, 71.0, 68.4, 67.5, 55.2, 51.0. . HRMS: Calc. for $C_{42}H_{44}N_2O_7$ $[M+H]^+$: 689.3227, Obser. 689.3263.

### 5.6.18 *N*-benzyl-N-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-((4-fluorobenzyl)oxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3m)

Yield: 68% (69.64 mg) as a white foam. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.38 – 7.23 (m, 13H), 7.22 – 7.11 (m, 5H), 7.09 – 6.93 (m, 6H), 4.98 (d, *J* = 14.5 Hz, 1H), 4.85 (d, *J* = 8.3 Hz, 1H), 4.82 – 4.71 (m, 3H), 4.64 (d, *J* = 12.2 Hz, 1H), 4.59 – 4.52 (m, 3H), 4.42 – 4.31 (m, 3H), 3.96 (dd, *J* = 10.4, 8.4 Hz, 1H), 3.76 (dd, *J* = 10.7, 6.4 Hz, 3H), 3.59 (dt, *J* = 9.9, 3.0 Hz, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 163.3, 161.4, 137.8, 137.6, 137.5, 133.5, 132.4, 132.3, 129.7, 129.6, 129.0, 128.4, 128.4, 128.3, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 115.3, 115.1, 101.6, 82.4, 79.0, 75.4, 75.0, 74.9, 73.5, 70.5, 68.3, 67.4, 50.9. HRMS: Calc. for $C_{41}H_{41}FN_2O_6$ $[M+H]^+$: 677.3027, Obser. 677.3026.

### 5.6.19 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-((4-cyanobenzyl)oxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3n)

Yield: 70% (72.43 mg) as pale yellow syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.55 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.26 (m, 11H), 7.22 – 7.05 (m, 11H), 4.90 – 4.53 (m, 9H), 4.36 (m, *J* = 19.4, 10.7, 6.4 Hz, 3H), 4.02 (dd, *J* = 10.5, 8.3 Hz, 1H), 3.88 – 3.73 (m, 3H), 3.59 (dt, *J* = 9.9, 3.0 Hz, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 142.2, 137.6, 137.5, 137.4, 133.6, 132.1, 129.1, 128.4, 128.4, 128.4, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 118.7, 111.4, 101.7, 82.7, 78.9, 75.5, 75.1, 75.0, 73.5, 70.1, 68.2, 67.4, 50.8. HRMS: Calc. for $C_{42}H_{41}N_3O_6$ $[M+H]^+$: 684.3074, Obser. 684.3071.

**5.6.20 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3o)**

Yield: 65% (92.20 mg) as a light yellow foam. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 10H), 7.27 – 7.16 (m, 8H), 7.06 (dd, *J* = 6.3, 3.0 Hz, 2H), 5.30 (d, *J* = 4.9 Hz, 1H), 4.97 (d, *J* = 14.4 Hz, 1H), 4.89 (d, *J* = 8.2 Hz, 1H), 4.81 – 4.55 (m, 6H), 4.44 – 4.37 (m, 2H), 3.89 (dd, *J* = 10.4, 8.3 Hz, 1H), 3.79 – 3.70 (m, 3H), 3.62 – 3.56 (m, 1H), 3.50 – 3.43 (m, 1H), 2.04 – 1.81 (m, 7H), 1.55 – 1.27 (m, 13H), 1.10 – 0.87 (m, 20H), 0.69 (s, 3H).**$^{13}$C NMR** (125 MHz, $CDCl_3$) *δ* = 139.9, 139.7, 137.9, 137.7, 137.6, 133.7, 129.3, 128.4, 128.4, 128.3, 128.3, 127.8, 127.7, 127.6, 127.6, 122.2, 56.7, 56.1, 51.5, 50.0, 42.2, 39.7, 39.4, 38.3, 37.1, 36.5, 36.1, 35.7, 31.8, 31.7, 29.4, 28.2, 28.0, 24.2, 23.7, 22.8, 22.5, 21.0, 19.3, 18.6, 11.8. HRMS: Calc. for $C_{61}H_{80}N_2O_6$ $[M+H]^+$: 937.6095, Obser. 937.6087.

**5.6.21 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(((2R,3R,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3p)**

Yield: 70% (107.54 mg) as a pale yellow syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) *δ* = 7.29 – 7.19 (m, 23H), 7.17 – 7.16 (m, 3H), 7.10 – 7.02 (m, 7H), 6.92 (dd, *J* = 6.6, 2.9 Hz, 2H), 5.08 (d, *J* = 14.3 Hz, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.74 – 4.60 (m, 7H), 4.56 (d, *J* = 17.9 Hz, 1H), 4.50 (dd, *J* = 8.2, 4.7 Hz, 2H), 4.47 (d, *J* = 3.0 Hz, 1H), 4.44 (d, *J* = 1.6 Hz, 1H), 4.28 (dt, *J* = 8.8, 4.2 Hz, 2H), 4.21 (d, *J* = 11.0 Hz, 1H), 4.00 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.89 – 3.84 (m, 2H), 3.67 – 3.60 (m, 4H), 3.49 (ddd, *J* = 15.8, 8.8, 4.1 Hz, 2H), 3.36 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.26 (s, 3H), 3.13 – 3.09 (m, 1H)**. $^{13}$C NMR** (125 MHz, $CDCl_3$)

δ 138.7, 138.1, 138.0, 137.9, 137.7, 137.5, 133.6, 129.1, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 102.9, 98.0, 82.5, 81.8, 79.4, 79.1, 77.7, 75.7, 75.4, 75.2, 74.9, 74.8, 73.5, 73.2, 69.6, 68.5, 68.4, 67.3, 55.3, 51.2. HRMS: Calc. for $C_{62}H_{66}N_2O_{11}$ $[M+Na]^+$: 1037.4564, Obser. 1037.4569.

**5.6.22 (2S,3R,5R,6R)-6-((((2R,3R,4R,5S,6R)-3-(benzyl(nitroso)amino)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)methyl)-5-(benzyloxy)-2-methoxytetrahydro-2H-pyran-3,4-diyl dibenzoate (3q)**

Yield: 70% (110.50 mg) as yellow syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 8.00 (d, *J* = 8.2 Hz, 3H), 7.54 – 7.51 (m, 2H), 7.42 – 7.29 (m, 20H), 7.24 – 7.15 (m, 8H), 7.11 (dd, *J* = 6.6, 2.8 Hz, 2H), 6.02 (t, *J* = 9.3 Hz, 1H), 5.13 – 5.09 (m, 2H), 4.97 (dd, *J* = 21.5, 11.2 Hz, 2H), 4.85 – 4.78 (m, 3H), 4.70 – 4.61 (m, 3H), 4.46 (d, *J* = 10.9 Hz, 2H), 4.40 – 4.31 (m, 2H), 4.15 (dd, *J* = 11.2, 1.8 Hz, 1H), 4.06 (dd, *J* = 10.5, 8.3 Hz, 1H), 3.96 – 3.92 (m, 1H), 3.83 (d, *J* = 3.2 Hz, 2H), 3.79 (d, *J* = 9.2 Hz, 1H), 3.72 (dd, *J* = 11.2, 4.1 Hz, 1H), 3.66 – 3.62 (m, 1H), 3.56 (t, *J* = 9.6 Hz, 1H), 3.38 (s, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 166.0, 165.6, 137.9, 137.7, 137.5, 137.5, 133.7, 133.2, 133.0, 129.9, 129.7, 129.5, 129.3, 129.1, 128.6, 128.4, 128.3, 128.3, 128.3, 128.2, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 102.8, 96.9, 83.2, 79.1, 76.1, 75.5, 75.3, 74.9, 74.6, 73.5, 72.6, 72.1, 69.6, 68.5, 68.1, 67.5. HRMS: Calc. for $C_{62}H_{62}N_2O_{13}$ $[M+Na]^+$: 1065.4150, Obser. 1065.4155.

**5.6.23 *N*-benzyl-*N*-((2S,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(((2R,3R,5R,6S)-4,5-bis(benzyloxy)-2-((benzyloxy)methyl)-6-methoxytetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3r)**

Yield: 62% (95.25 mg) as yellow syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.32 – 7.18 (m, 20H), 7.17 – 7.04 (m, 15H), 5.39 (d, *J* = 8.1 Hz, 1H), 5.04 (d, *J* = 14.3 Hz, 1H), 4.79 – 4.71 (m, 3H), 4.65 – 4.50 (m, 5H), 4.45 – 4.34 (m, 5H), 4.26 – 4.18 (m, 2H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.78 (dt, *J* = 18.7, 9.0 Hz, 2H), 3.70 (s, 1H), 3.67 – 3.46 (m, 5H), 3.34 – 3.20 (m, 2H), 3.12 (s, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 138.6, 138.2, 138.1, 138.0, 137.8, 137.8, 134.1, 129.3, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.5, 127.3, 127.3, 101.5, 97.4, 82.9, 81.3, 79.5, 76.0, 75.5, 74.9, 74.7, 73.8, 73.5, 73.3, 69.4, 68.6, 68.4, 54.9, 51.3. HRMS: Calc. for $C_{62}H_{66}N_2O_{11}$ $[M+H]^+$: 1015.4745, Obser. 1015.4748.

### 5.6.24 (2S,3R,5R,6R)-5-(((2S,3R,4R,5S,6R)-3-(benzyl(nitroso)amino)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)-6-((benzyloxy)methyl)-2-methoxytetrahydro-2H-pyran-3,4-diyl dibenzoate (3s)

Yield: 65% (102.61 mg) as yellow syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.90 (m, *J* = 19.8, 8.1, 1.0 Hz, 3H), 7.45 – 7.37 (m, 2H), 7.32 – 7.12 (m, 28H), 6.99 – 6.97 (m, 1H), 6.95 – 6.93 (m, 1H), 5.69 (dd, *J* = 29.5, 19.7 Hz, 1H), 5.10 – 4.98 (m, 2H), 4.76 – 4.47 (m, 6H), 4.41 – 4.26 (m, 3H), 4.25 – 4.08 (m, 4H), 3.63 (dd, *J* = 10.6, 8.2 Hz, 1H), 3.45 – 3.39 (m, 1H), 3.39 – 3.20 (m, 7H), 3.20 – 3.07 (m, 2H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 165.9, 165.8, 138.0, 137.7, 137.7, 137.6, 133.5, 133.1, 132.6, 130.3, 129.8, 129.8, 129.7, 129.2, 128.4, 128.4, 128.3, 128.2, 128.1, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 101.1, 96.9, 82.6, 79.4, 75.4, 74.8, 74.6, 73.1, 72.8, 72.7, 72.0, 70.7, 69.4, 68.7, 68.4, 67.6, 55.3, 52.2. HRMS: Calc. for $C_{62}H_{62}N_2O_{13}$ $[M+H]^+$: 1043.4330, Obser. 1043.4333.

**5.6.25 *N*-benzyl-*N*-((2S,3R,4R,5S,6R)-4,5-bis(benzyloxy)-2-(((4aR,6S,7R,8aR)-8-(benzyloxy)-6-methoxy-2-phenylhexahydropyrano[3,2-d][1,3]dioxin-7-yl)oxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-3-yl)nitrous amide (3t)**

Yield: 80% (162.0 mg) as yellow syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.38 – 7.33 (m, 2H), 7.29 – 7.21 (m, 7H), 7.21 – 7.11 (m, 12H), 7.11 – 6.97 (m, 7H), 6.96 – 6.85 (m, 2H), 5.44 (s, 1H), 5.25 (d, *J* = 14.6 Hz, 1H), 5.01 (d, *J* = 8.2 Hz, 1H), 4.79 (d, *J* = 3.6 Hz, 1H), 4.62 (dd, *J* = 19.5, 10.8 Hz, 3H), 4.51 – 4.39 (m, 3H), 4.32 (m, *J* = 16.7, 15.4, 9.2 Hz, 4H), 4.21 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.90 – 3.71 (m, 4H), 3.68 – 3.55 (m, 4H), 3.47 (m, *J* = 14.2, 11.7, 5.5 Hz, 2H), 3.33 (s, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 138.3, 137.9, 137.9, 137.8, 137.3, 133.9, 129.4, 129.0, 128.5, 128.4, 128.3, 128.3, 127.9, 127.9, 127.9, 127.9, 127.7, 127.6, 126.1, 103.6, 101.5, 100.3, 83.0, 81.7, 79.2, 77.8, 77.6, 75.4, 75.0, 74.9, 74.8, 73.5, 69.2, 68.5, 67.4, 62.2, 55.4, 51.1. HRMS: Calc. for $C_{55}H_{58}N_2O_{11}$ $[M+Na]^+$: 945.3938, Obser. 945.3948.

**5.6.26 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(((2R,3R,4S,5S,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3u)**

Yield: 75% (115.22 mg) as yellow syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.32 (d, *J* = 7.4 Hz, 8H), 7.29 – 7.20 (m, 18H), 7.14 – 7.05 (m, 7H), 6.97 – 6.92 (m, 2H), 5.57 (d, *J* = 14.6 Hz, 1H), 4.89 (d, *J* = 11.1 Hz, 1H), 4.76 – 4.66 (m, 6H), 4.64 – 4.57 (m, 4H), 4.54 – 4.50 (m, 2H), 4.45 (d, *J* = 1.7 Hz, 1H), 4.38 (t, *J* = 10.0 Hz, 2H), 4.18 (dd, *J* = 25.0, 12.4 Hz, 2H), 3.93 – 3.85 (m, 2H), 3.74 (dd, *J* = 11.9, 6.3 Hz, 4H), 3.69 – 3.48 (m, 4H), 3.27 – 3.24 (m, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 138.5, 138.4, 138.2, 138.2, 138.0, 137.8, 133.8, 129.1, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.8,

127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 103.6, 99.1, 81.3, 80.1, 79.2, 75.4, 75.1, 75.0, 74.9, 74.9, 74.6, 73.5, 72.9, 72.1, 71.3, 68.7, 68.5, 67.3, 54.9, 50.9. HRMS: Calc. for $C_{62}H_{66}N_2O_{11}$ $[M+H]^+$: 1015.4745, Obser. 1015.4751.

**5.6.27 (2R,3R,4S,5S,6S)-2-((((2R,3R,4R,5S,6R)-3-(benzyl(nitroso)amino)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)methyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate (3v)**

Yield: 70% (111.98 mg) as yellow syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.99 – 7.72 (m, 6H), 7.47 – 7.23 (m, 8H), 7.21 – 7.01 (m, 19H), 6.88 (dd, *J* = 6.6, 2.6 Hz, 2H), 5.80 (dd, *J* = 10.1, 3.4 Hz, 1H), 5.69 – 5.43 (m, 3H), 4.89 (d, *J* = 1.3 Hz, 1H), 4.72 – 4.54 (m, 3H), 4.46 (dd, *J* = 19.0, 11.5 Hz, 2H), 4.40 – 4.32 (m, 2H), 4.28 (d, *J* = 10.8 Hz, 1H), 4.22 – 4.11 (m, 2H), 4.01 (dd, *J* = 11.0, 1.9 Hz, 1H), 3.87 (dd, *J* = 10.5, 8.3 Hz, 1H), 3.62 (td, *J* = 8.8, 4.3 Hz, 4H), 3.49 – 3.44 (m, 1H), 3.39 (s, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 165.7, 165.6, 165.5, 137.95, 137.8, 134.0, 133.5, 133.2, 129.9, 129.9, 129.8, 129.4, 129.1, 129.0, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 127.9, 127.9, 127.8, 127.8, 127.8, 127.6, 103.3, 98.6, 81.2, 79.1, 77.4, 75.4, 75.1, 75.0, 73.6, 70.7, 70.0, 69.9, 68.9, 68.3, 67.6, 67.4, 55.7, 50.7. HRMS: Calc. for $C_{62}H_{60}N_2O_{14}$ $[M+H]^+$: 1057.4123, Obser. 1057.4112.

**5.6.28 *N*-benzyl-*N*-((2R,3R,4R,5S,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-((2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)tetrahydro-2H-pyran-3-yl)nitrous amide (3w)**

Yield: 60% (73.63 mg) as brown syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.28 – 7.19 (m, 9H), 7.17 (s, 2H), 7.14 – 7.02 (m, 7H), 6.98 (dd, *J* = 6.6, 2.8 Hz, 2H), 5.54 – 5.34 (m,

2H), 4.68 (dd, *J* = 9.7, 4.1 Hz, 3H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.51 – 4.41 (m, 4H), 4.37 (d, *J* = 10.8 Hz, 1H), 4.30 (d, *J* = 14.9 Hz, 1H), 4.22 (dd, *J* = 5.1, 2.4 Hz, 1H), 4.07 – 3.96 (m, 2H), 3.85 (dd, *J* = 4.8, 1.9 Hz, 1H), 3.78 (dd, *J* = 10.6, 8.3 Hz, 1H), 3.70 – 3.58 (m, 3H), 3.50 (m, *J* = 10.5, 6.1, 3.1 Hz, 2H), 1.46 (s, 3H), 1.35 (d, *J* = 3.6 Hz, 3H), 1.25 (t, *J* = 8.2 Hz, 6H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 138.0, 137.9, 137.9, 134.4, 129.3, 128.5, 128.5, 128.3, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 109.5, 108.6, 103.9, 96.4, 81.4, 79.2, 75.5, 75.0, 75.0, 73.7, 71.3, 70.9, 70.4, 69.8, 68.4, 67.2, 66.9, 50.6, 26.2, 26.0, 25.0, 24.5. HRMS: Calc. for $C_{46}H_{54}N_2O_{11}$ $[M+H]^+$: 811.3806, Obser. 811.3814.

### 5.6.29 (2R,3R,5R,6S)-2-((((2R,3R,4R,5S,6R)-3-(benzyl(nitroso)amino)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)methyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (3x)

Yield: 80% (120.72 mg) as yellow syrup. **$^{1}$H NMR** (500 MHz, $CDCl_3$) $\delta$ = 7.30–7.01 (m, 18H), 6.93 (dd, *J* = 6.5, 3.0 Hz, 2H), 5.48 (dd, *J* = 19.4, 9.9 Hz, 1H), 5.24 (t, *J* = 12.4 Hz, 1H), 4.87 – 4.79 (m, 2H), 4.74 – 4.59 (m, 4H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.49 – 4.41 (m, 2H), 4.30 (dt, *J* = 25.0, 13.6 Hz, 3H), 3.90 (m, *J* = 19.0, 9.5, 7.0 Hz, 2H), 3.76 – 3.59 (m, 4H), 3.51 – 3.40 (m, 2H), 3.25 (d, *J* = 10.1 Hz, 3H), 1.22 – 1.16 (m, 2H), 1.13 – 1.09 (m, 6H), 1.07 (s, 8H), 1.06 – 1.01 (m, 11H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) $\delta$ = 177.7, 177.0, 176.8, 137.9, 137.8, 137.8, 133.9, 129.1, 128.6, 128.5, 128.3, 127.9, 127.8, 127.8, 127.8, 127.7, 103.1, 96.6, 81.7, 79.1, 75.4, 75.1, 75.0, 73.7, 71.2, 69.6, 68.7, 68.6, 68.5, 68.4, 67.3, 55.8, 50.6, 38.8, 38.8, 27.2, 27.1, 27.0. HRMS: Calc. for $C_{56}H_{72}N_2O_{14}$ $[M+H]^+$: 997.5062, Obser. 997.5070.

**5.6.30 *N*-benzyl-N-((2R,3R,4R,5R,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(cyclohexyloxy)tetrahydro-2H-pyran-3-yl)nitrous amide (4a)**

Yield: 72% (70.25 mg) as a yellow foam. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 10H), 7.18 – 7.07 (m, 8H), 7.00 (dd, *J* = 6.5, 3.1 Hz, 2H), 5.18 (d, *J* = 14.5 Hz, 1H), 4.79 (d, *J* = 7.8 Hz, 1H), 4.71 (d, *J* = 11.3 Hz, 1H), 4.49 – 4.37 (m, 5H), 4.33 – 4.14 (m, 3H), 3.96 (d, *J* = 1.1 Hz, 1H), 3.66 – 3.44 (m, 4H), 1.60 – 1.51 (m, 3H), 1.38 (d, *J* = 5.2 Hz, 1H), 1.30 – 1.21 (m, 2H), 1.16 – 1.00 (m, 4H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 138.3, 137.8, 137.3, 133.8, 129.2, 128.4, 128.3, 128.2, 128.1, 127.8, 127.8, 127.7, 127.6, 127.6, 127.4, 101.5, 80.8, 77.5, 74.6, 73.6, 73.5, 72.3, 68.6, 64.3, 51.7, 33.3, 31.3, 25.4, 23.8, 23.6. HRMS: Calc. for $C_{40}H_{46}N_2O_6$ $[M+H]^+$: 651.3434, Obser. 651.3428.

**5.6.31 *N*-benzyl-N-((2R,3R,4R,5R,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(isopentyloxy)tetrahydro-2H-pyran-3-yl)nitrous amide (4b)**

Yield: 77% (74.2 mg) as yellow syrup. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 10H), 7.13 – 7.00 (m, 10H), 5.17 (d, *J* = 14.6 Hz, 1H), 4.68 (dd, *J* = 28.9, 9.6 Hz, 2H), 4.42 (m, *J* = 20.4, 14.7, 5.7 Hz, 5H), 4.27 – 4.16 (m, 3H), 3.97 (d, *J* = 1.5 Hz, 1H), 3.80 – 3.76 (m, 1H), 3.59 (m, *J* = 15.8, 8.3, 4.6 Hz, 3H), 3.25 (dd, *J* = 16.4, 7.2 Hz, 1H), 1.46 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.31 – 1.24 (m, 2H), 0.75 (dd, *J* = 8.4, 6.7 Hz, 6H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 138.2, 137.7, 137.2, 133.8, 129.0, 128.4, 128.3, 128.2, 128.2, 128.1, 127.8, 127.8, 127.7, 127.6, 127.5, 127.4, 103.2, 80.5, 74.6, 73.6, 73.5, 72.2, 68.4, 64.1, 51.3, 38.0, 24.7, 22.6, 22.3. HRMS: Calc. for $C_{39}H_{46}N_2O_6$ $[M+H]^+$: 639.3434, Obser. 639.3430.

## 5.7. Spectra few compounds.

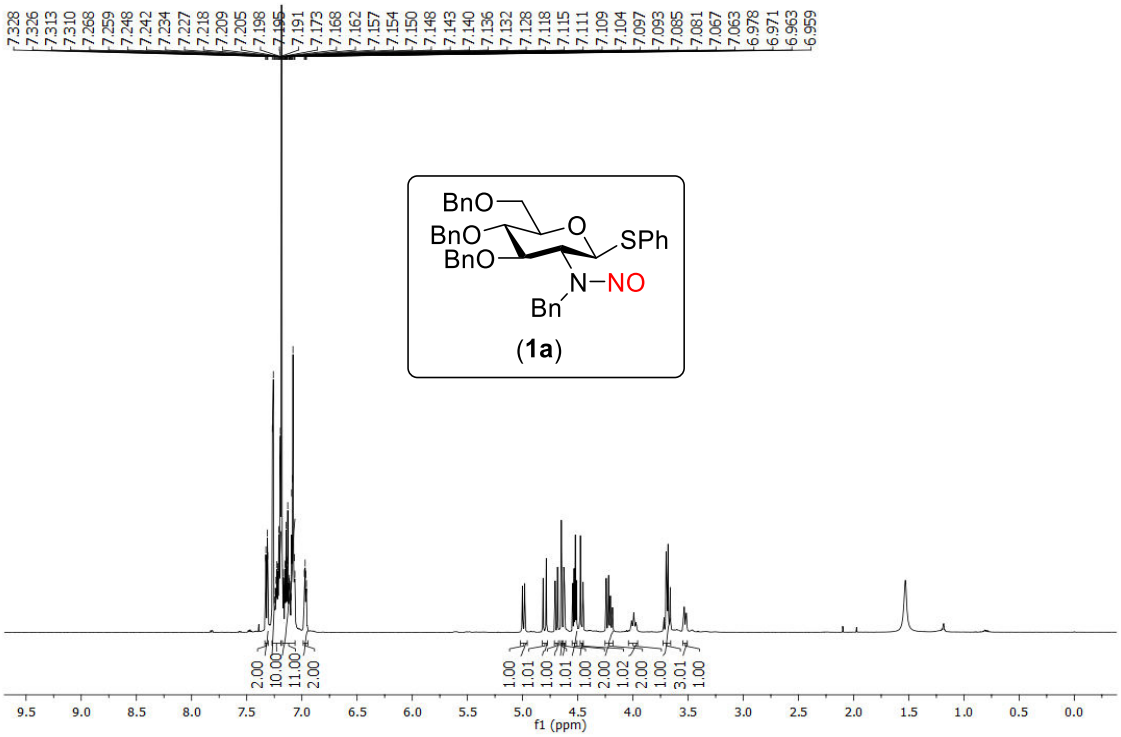



**Figure 5.2 $^{1}$H NMR Spectra of product 1a in $CDCl_3$**

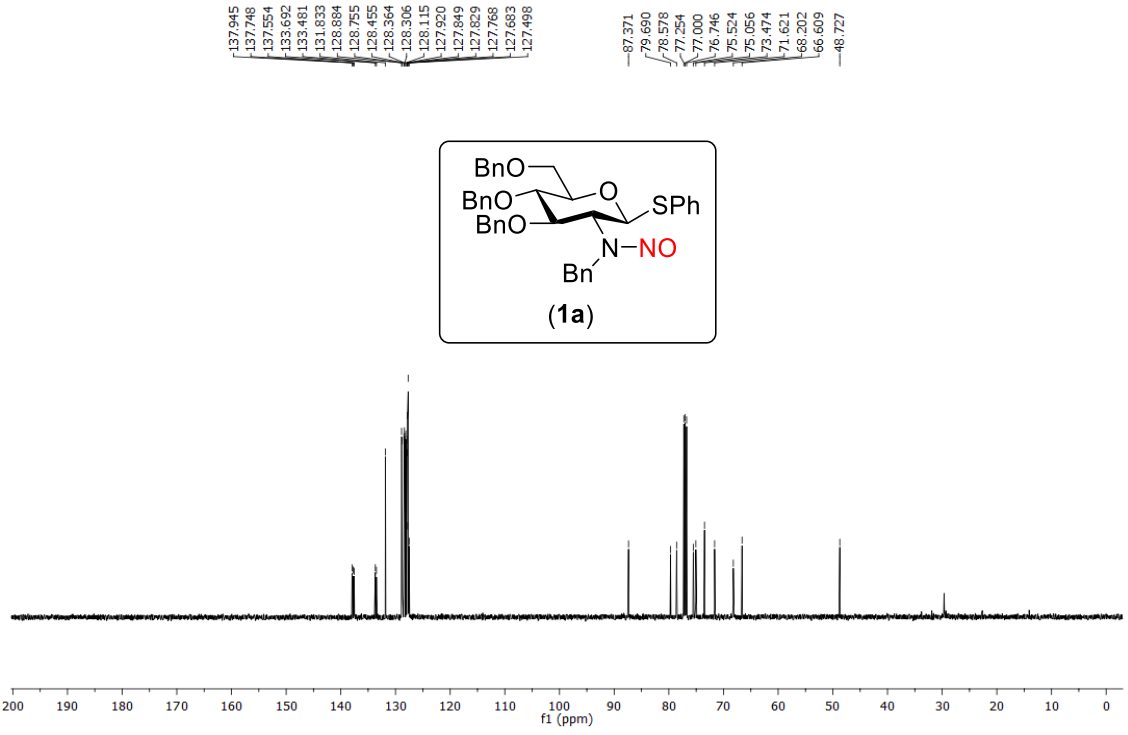



**Figure 5.3 $^{13}$C NMR Spectra of product 1a in $CDCl_3$**

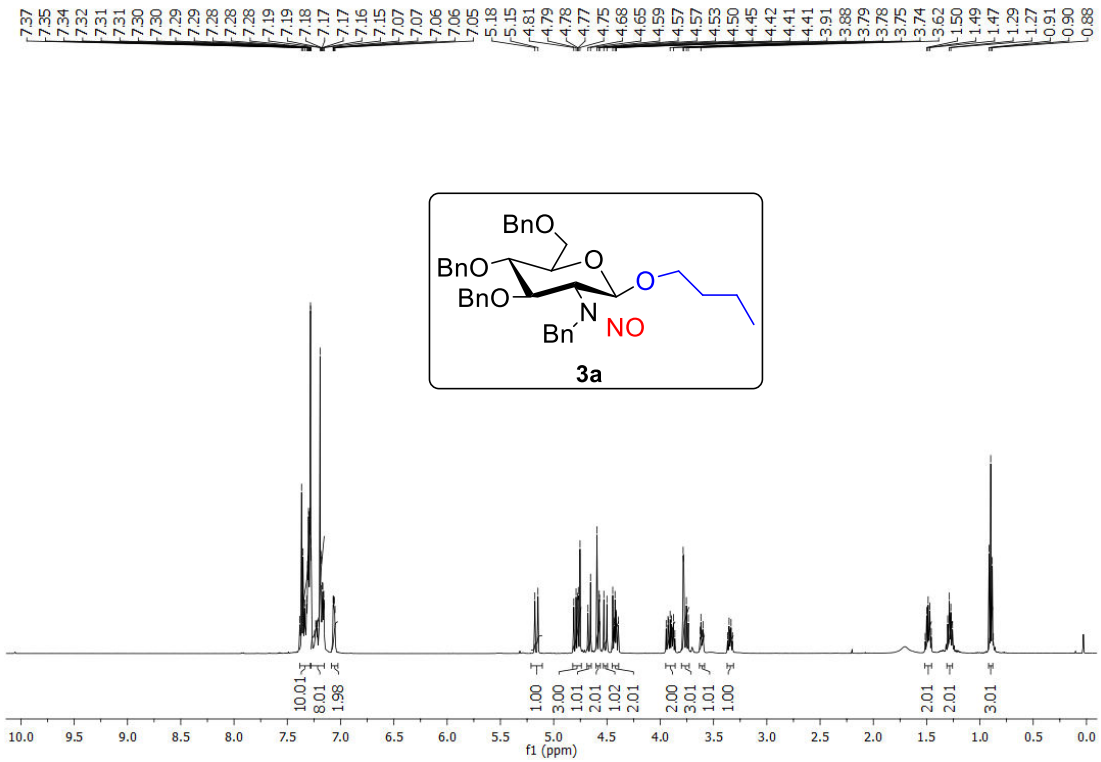



**Figure 5.4 $^{1}$H NMR Spectra of product 3a in $CDCl_3$**

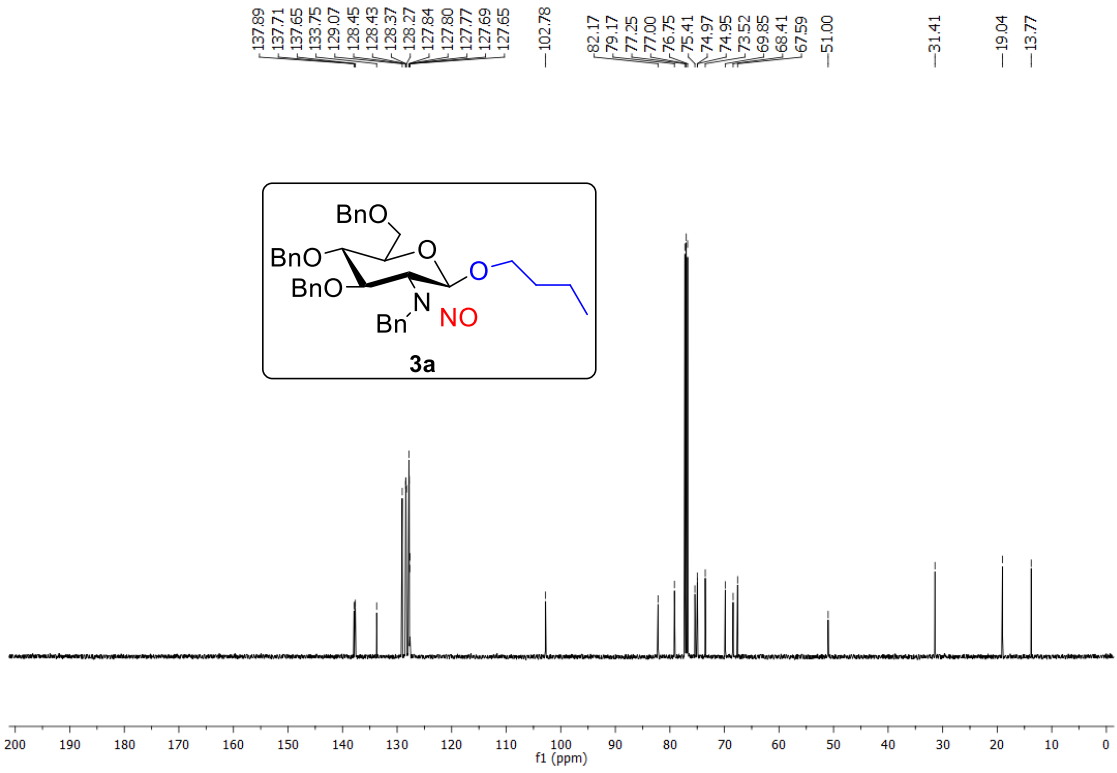



**Figure 5.5 $^{13}$C NMR Spectra of product 3a in $CDCl_3$**

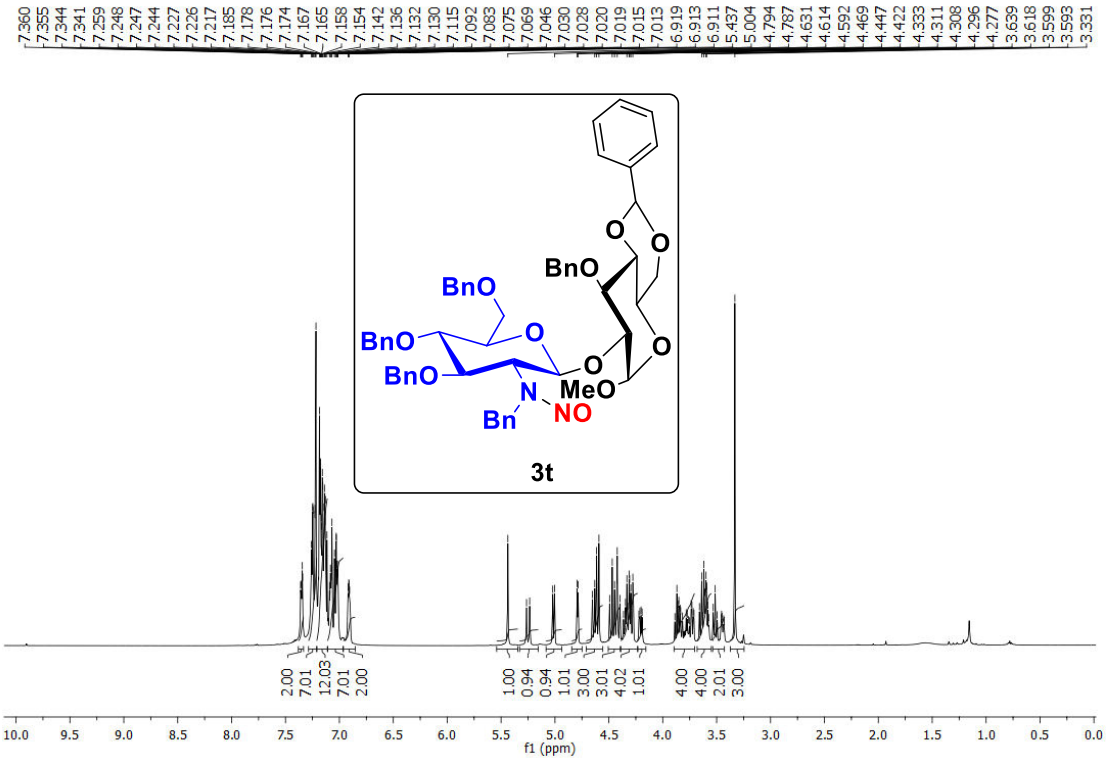



**Figure 5.6 $^{1}$H NMR Spectra of product 3t in $CDCl_3$**

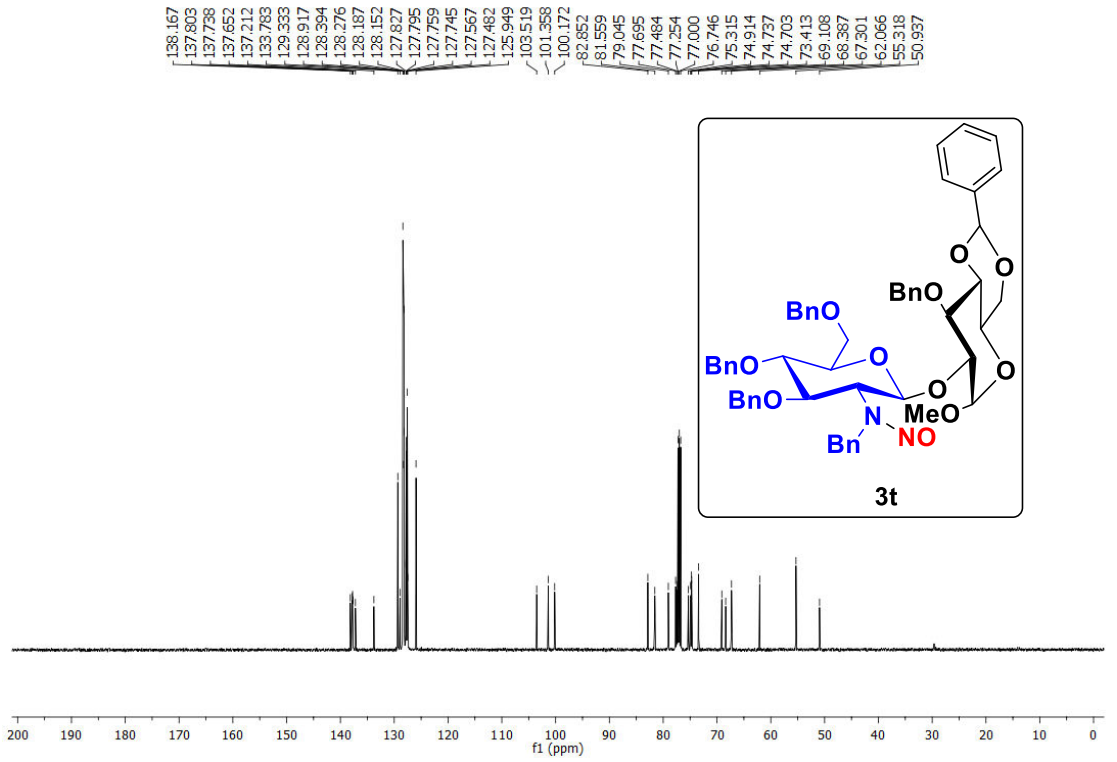



**Figure 5.7 $^{13}$C NMR Spectra of product 3t in $CDCl_3$**

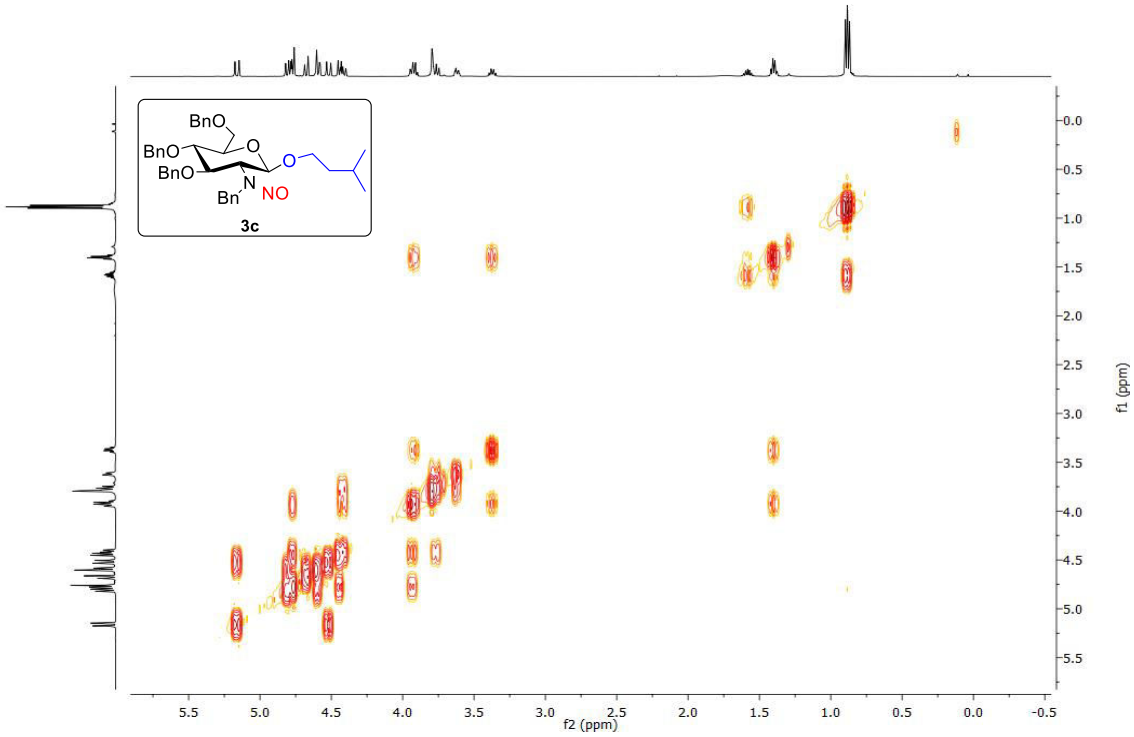



**Figure 5.8 COSY NMR Spectra of product 3c in $CDCl_3$**

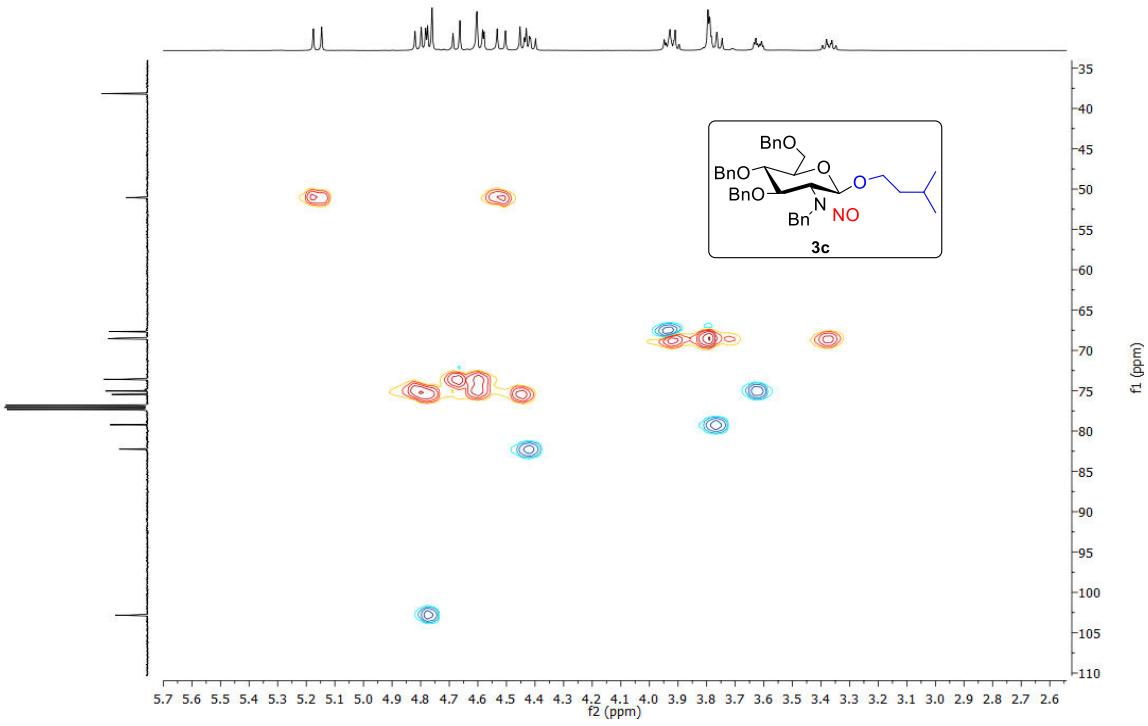



**Figure 5.9 HSQC NMR Spectra of product 3c in $CDCl_3$**

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