CHAPTER-2

Synthesis of Glycouronamides by the Transamidation Approach at Room Temperature

2.1 Introduction

Amide functional group is found in a wide variety of compounds including biomolecules, natural products, pharmaceutics, materials, etc [1]. In this context, glycosides and glycoconjugates possessing amide groups are important scaffolds in both chemistry and biology [2]. In particular, natural and synthetic glucuronamide derivatives are well explored as antibiotics, anticancer agents, anti-oxidants, cholinesterase (ChE) inhibitors, etc [3]. For instance, the flavonoid glucuronamide **1** (i.e. scutellarein-7-*O*-β-glucuronamide) is isolated from the medicinal plant Scoparia dulcis L and is used in folk medicine to treat different diseases [2i].

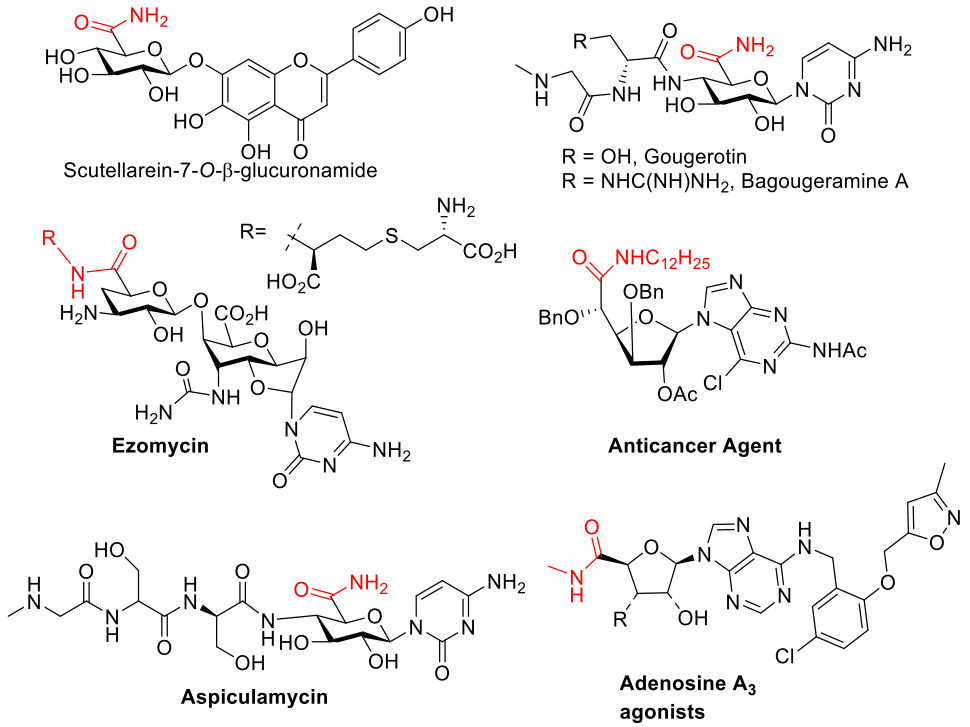
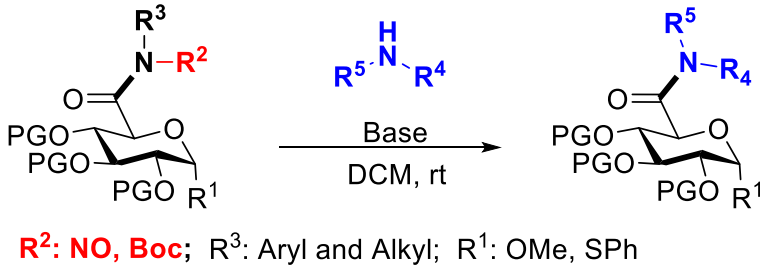


Figure 2.1 Some bioactive amide compounds

On the other hand, gougerotin, bagougeramines, aspiculamycin, bagougeramines A and B, and aspiculamycin are the natural nucleoside antibiotics with uronamide functional groups [3a]. Ezomycin is another group of uronamide compounds with anti-bacterial and anti-fungal activities [3g]. Besides these natural products, several other synthetic uronamides have also been investigated for their biological activities **(Figure 2.1)** [3a-c, 3e, 3f, 3h].

The current method of preparation of uronamides involves the conversion of uronic acids into acid chlorides, mixed anhydrides, or reactive esters followed by amidation under different reaction conditions [3a, 4]. Alternatively, direct coupling of uronic acids with amines in the presence of amide coupling agent such as *N*,*N*′-dicyclohexylcarbodiimide (DCC) was also established [5]. However, the applicability of some of these methods is limited due to different side reactions including racemization, hydrolysis, etc [3h]. Transamidation is one of the important approaches for the synthesis of amides which eliminates the use of amide coupling agents [6]. The recent developments in the transamidation chemistry allow the preparation of the amides under milder reaction conditions [7]. In the last few years, our group has been focusing on amide activation and transamidation reactions [8]. Towards this end, we demonstrated the transamidation of secondary amides via *N*-nitroso and *N*-Cbz amide intermediates [8b, 8d], synthesis of aryl and alkyl α-ketoamides *via* transamidation reactions [8c,8f], transformation of *N*-Boc-amides into aryl ketones [8a], and controlled reduction of *N*-Boc and *N*-Ts amides into aldehydes [8e]. On the other hand, our group also focused on the synthetic carbohydrate chemistry [9] and have explored the synthesis and applications of uronic acids [9h], uronic esters [9f] and photolabile groups protected uronic acid building blocks [9g], etc. In continuation of these

works, here we have demonstrated the synthesis of different functionalized uronamides via transamidation reactions under mild reaction conditions (**Scheme 2.1**).

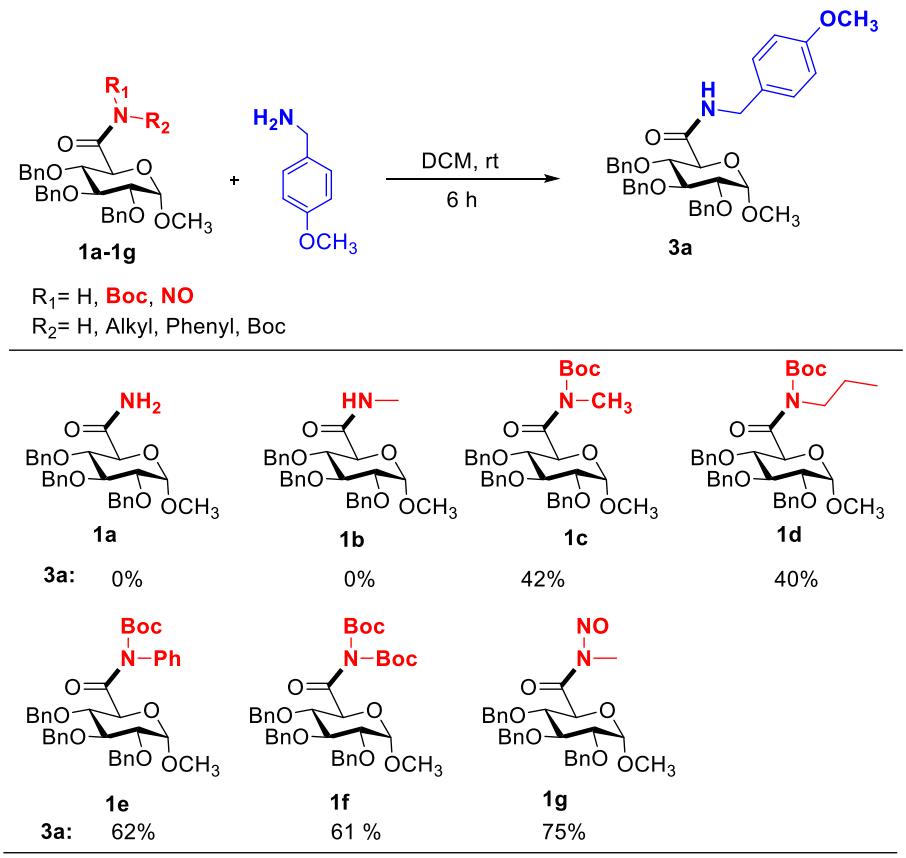


Scheme 2.1. Synthesis of functionalized uronamides via transamidation.

2.2. Results and discussion

At the outset, various *N*-functionalized *O*-protected glucuronamides **1a-1g** were subjected to the transamidation with 4-methoxybenzylamine in dichloromethane at room temperature under the base and catalyst-free conditions (**Scheme 2.2**). The primary and secondary glucuronamides **1a** and **1b** failed to provide any product while tertiary *N*-Boc and *N*-nitroso glucuronamides **1c-1g** gave the desired transamidation product **3a** in 40-75% yields within the period of 6 hours. In particular, transamidation of *N*-nitroso glucuronamide **1g** gave **3a** in 75% yield.

Scheme 2.2. Transamidation of various *N*-functionalized *O*-protected glucuronamides with 4-methoxybenzylamine.

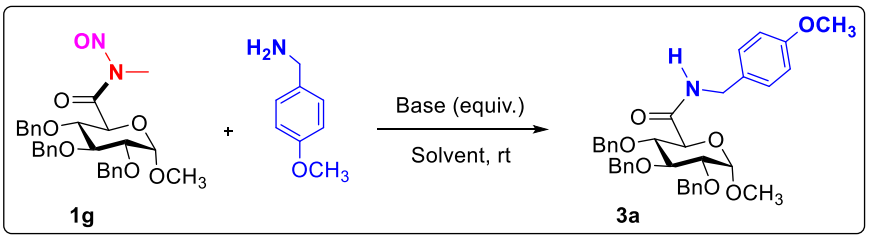


[a]Reaction conditions: Amide (**1a-1g**, 0.2 mmol, 1.0 equiv.) and 4-methoxybenzylamine (53 µL, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) at room temperature. [b]Isolated yields presented.

Further, the amide **1g** was subjected to the transamidation with 4-methoxybenzylamine in different solvents including acetonitrile, THF, 1,4-dioxane and dichloromethane (**Table 2.1, entries 1-4**). Among others, dichloromethane was found to be a better solvent and provided the product **3a** in 75% yield within 2 hours (**Table 2.1, entry 4**). Further, the transamidation was carried out in the presence of different bases including triethylamine, DBU, DABCO and K_2CO_3 (**Table 2.1, entries 5-8**). Among them, triethylamine gave the desired product **3a** in

96% yield at room temperature within 20 minutes (**Table 2.1, entry 5**). Nevertheless, the bases DBU and DABCO also gave the product **3a** in comparable yields to that of triethyl amine**.**

Table 2.1. Transamidation of *N*-Nitroso glucuronamide **1g** with 4-methoxybenzylamine in different solvents and bases.



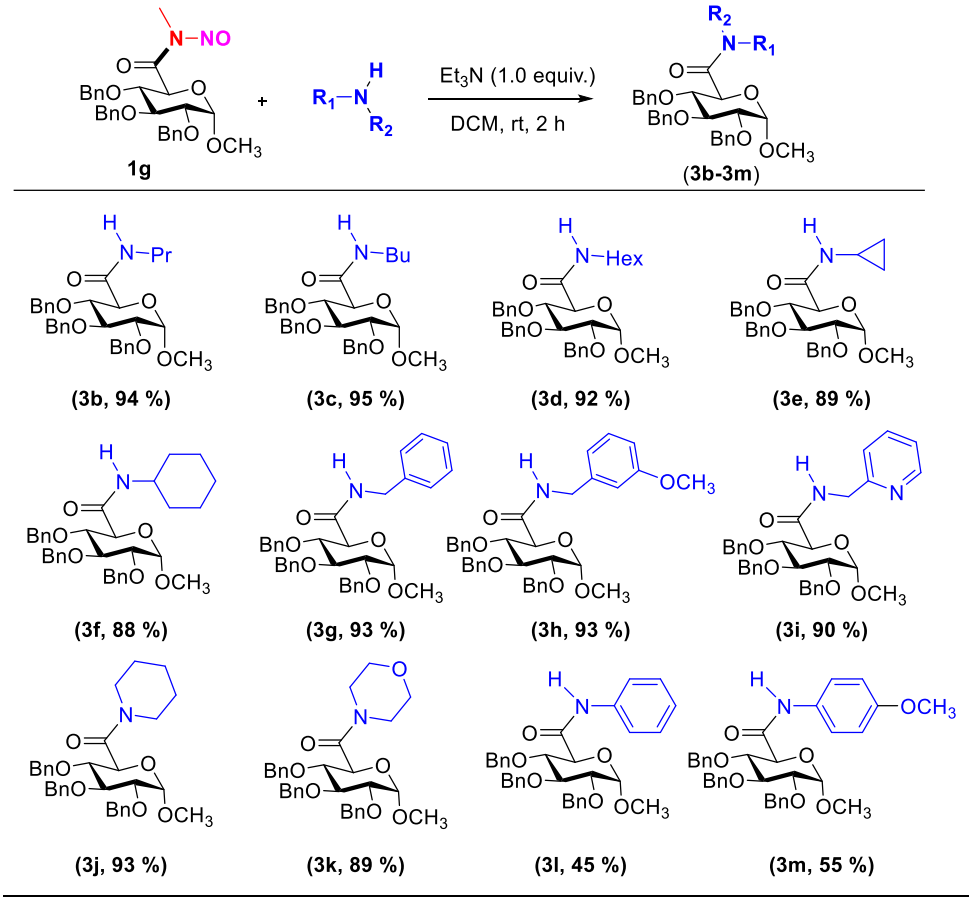
S.No.	Solvent	Base (1 equiv.)	Time (min.)	Yield[b](%)
1	AcCN	-	120	61
2	THF	-	120	59
3	1,4-dioxane	-	120	70
4	DCM	-	120	75
5	DCM	Et_3N	20	96
6	DCM	DBU	20	95
7	DCM	DABCO	20	95
8	DCM	K_2CO_3	20	91

[a]**Reaction conditions:** Amide (**1g**, 105 mg, 0.2 mmol, 1.0 equiv.) and 4-methoxybenzylamine (53 µL, 0.4 mmol, 2.0 equiv.) in DCM (2 mL) at room temperature. [b]Isolated yields.

2.3. Substrate Scope:

After establishing the optimized reaction conditions, the scope of different amines in the transamidation was investigated with *N*-nitroso amide **1g** (**Scheme 2.3**).

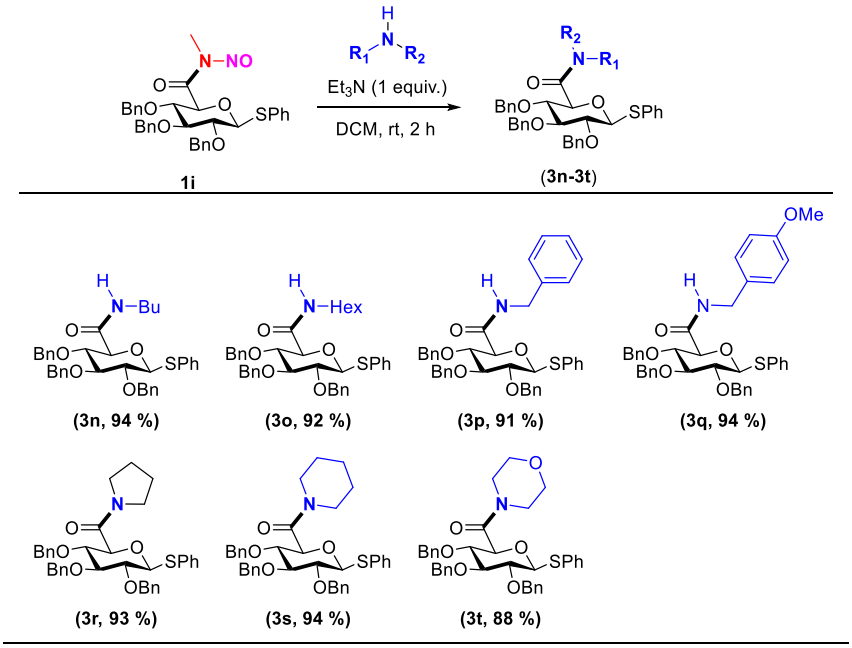
Scheme 2.3. Transamidation of *N*-methyl-*N*-nitrosoamides using various amines.



[a]Reaction conditions: Amide (**1a**, 105 mg**,** 0.2 mmol, 1.0 equiv.), amines (0.4 mmol, 2.0 equiv.), Et_3N (28 µL, 1.0 equiv.), DCM (2 mL) at room temperature. [b]Isolated yields are presented.

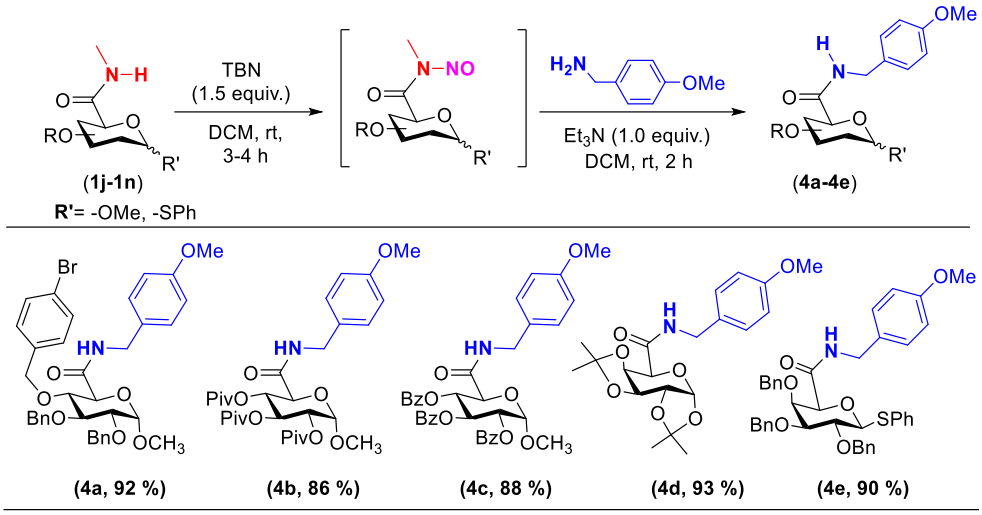
Primary amines bearing acyclic and cyclic alkyl groups participated in the transamidation reactions and gave the desired amides **3a-3f** in 88-95% yields within 2 hours duration. Similarly, transamidation of **1g** with benzyl amines and 2-picolylamine gave the desired products **3g-3i** in 90-93% yields. On the other hand, transamidation of *N*-nitroso amide **1g** with secondary amines afforded the desired products **3j-3k** in 89-93% yields. Interestingly, arylamines such as aniline and 4-methoxyaniline also underwent transamidation reactions smoothly and gave *N*-aryl uronamides **3l** and **3m** in 45% and 55% yields, respectively.

Scheme 2.4. Transamidation of *N*-methyl-*N*-nitroso thioglycoside with various amines.



[a]Reaction conditions: Amide (**1a**, 120 mg, 0.2 mmol), amines (0.4 mmol, 2.0 equiv.), Et_3N (28 µL, 1.0 equiv.), DCM (2 mL) at room temperature. [b]Isolated yields.

Scheme 2.5. Transamidation of various *N*-methyl-*N*-nitrosoamides with 4-methoxybenzylamine.

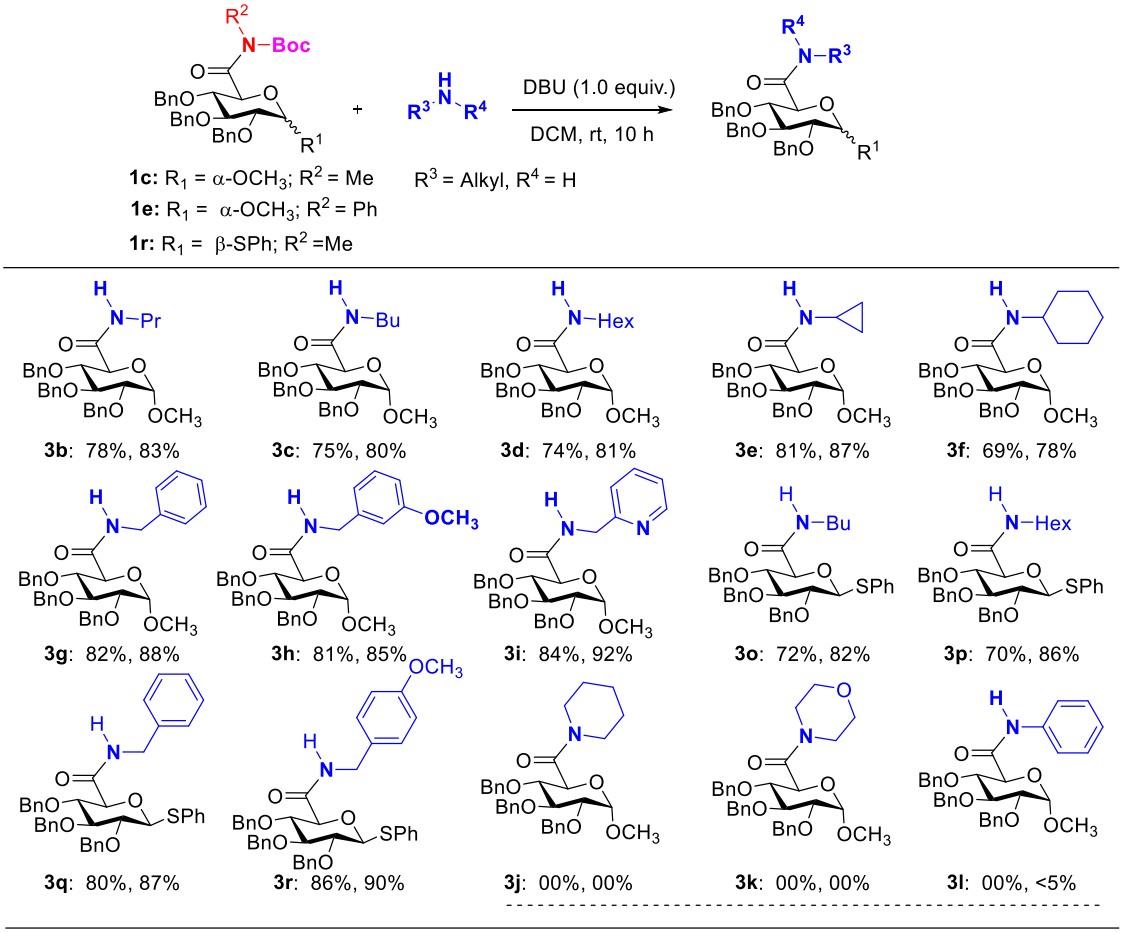


[a]Reaction conditions: Amide (**1j-1n**, 0.2 mmol, 1.0 equiv.), amines (0.4 mmol, 2.0 equiv.), Et_3N (1.0 equiv.), DCM (2 mL) at room temperature. [b]Isolated yields.

The *N*-Boc amides are relatively stable when compared with other activated amides and have often been used in transamidation reactions. Hence, we further explored the transamidation of *N*-methyl and *N*-phenyl *N*-Boc uronamides **1c, 1e** and **1r** with different amines in the presence of a base (Scheme 2.6). Triethylamine was found to be less effective and gave desired transamidation products in low yields even after overnight stirring. There was only a little improvement was observed in terms of yields with the increasing amount of triethylamine from 1.0 to 3.0 equivalents. However, DBU (1.0 equiv.) proved to be a better base than triethylamine and transamidation products were obtained in good yields within 10 hours.

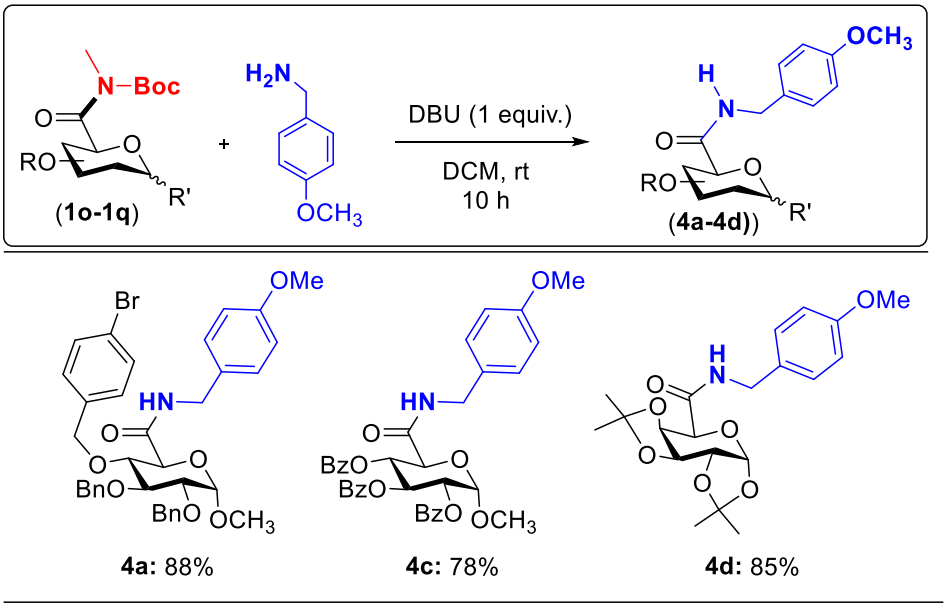
Transamidation of *N*-Boc amides **1c, 1e** and **1r** with cyclic and acyclic primary amines, benzyl amines and 2-picolylamine gave the desired products **3b-3i** and **3o-3r** in 69-92% yields. In particular, *N*-phenyl *N*-Boc amide **1e** was found to be more reactive than *N*-methyl *N*-Boc amide **1c** in terms of yield. However, transamidation of *N*-phenyl-*N*-Boc amide **1c** with secondary amines (**3j and 3k**) failed to give the desired product while Boc-deprotection was observed quantitatively. On the other hand, *N*-methyl-*N*-Boc amides didn't undergo transamidation reaction with secondary amines (**3j** and **3k**) even after overnight stirring. In the latter case, deprotection of *N*-Boc was observed only in a trace amount. Moreover, the reaction of aniline with amides **1c** and **1e** also failed to provide the desired product. Overall, it clearly indicated that *N*-nitroso uronamides proved to be better substrates for the transamidation reactions when compared with *N*-Boc uronamides.

Scheme 2.6. Transamidation of *N*-Methyl-*N*-Boc and *N*-Phenyl-*N*-Boc substrates using various primary amines.



[a]Reaction conditions: Amide (**1c**, **1e** and **1r**, 119 mg, 132 mg and 134 mg, 0.2 mmol, 1.0 equiv.), amines (0.4 mmol, 2.0 equiv.), DBU (30 µL, 1.0 equiv.), DCM (2 mL) at room temperature. [b]Isolated yields are presented.

Scheme 2.7. Transamidation of various *N*-Methyl-*N*-Boc protected uronamides using 4-methoxy benzylamine.



[a]Reaction conditions: Amides (**1o-1q**, 0.2 mmol), amines (0.4 mmol, 2.0 equiv.), DBU (30 µL, 1.0 equiv.), DCM (2 mL) at room temperature. [b]Isolated yields are presented.

After exploring the scope of amines, transamidation of different *N*-Boc uronamides were investigated. The amides **1o-1r** were subjected to the transamidation reaction with 4-methoxybenzylamine in the presence of DBU at room temperature (Scheme 2.7). To our delight, benzyl, benzoyl and isopropylidene protected glucose and galactose *N*-Boc uronamides underwent transamidation smoothly and gave corresponding uronamides **4a, 4c** and **4d** in 78-88% yields.

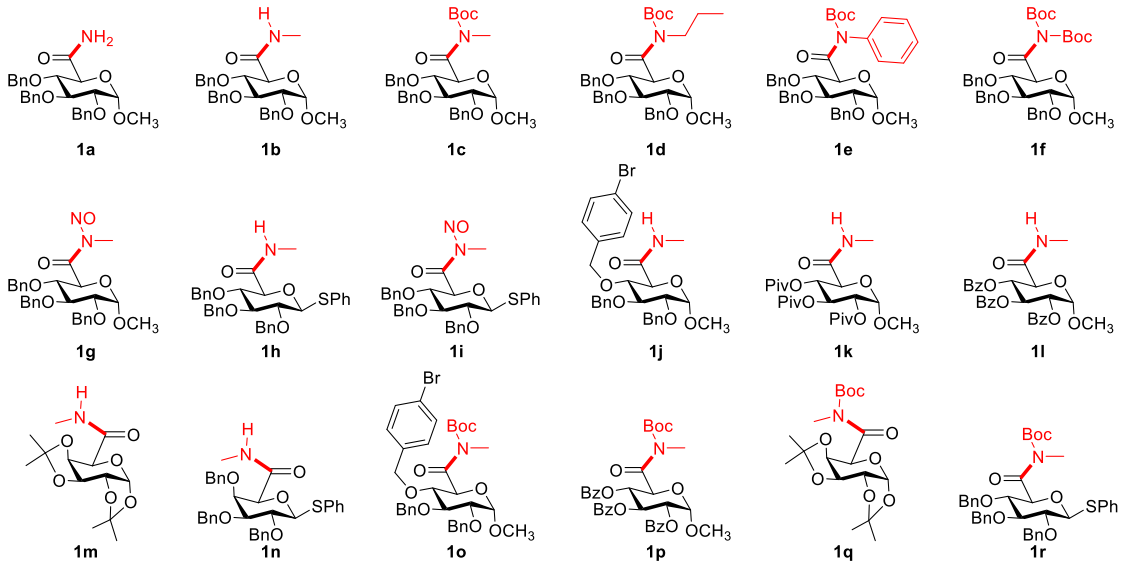
2.4. Conclusions

In conclusion, a mild and efficient method for the synthesis of various uronamides via transamidation reaction was demonstrated. *N*-Nitroso uronamides underwent transamidation with various primary and secondary amines (alkyl amines, benzyl amines and anilines) in presence of triethylamine at room temperature. On the other hand, transamidation of *N*-Boc uronamides was successfully achieved with primary amines in the presence of DBU. In general, *N*-nitroso uronamides were found to be more reactive than *N*-Boc uronamides in terms of reaction time and yields. The developed protocol is highly efficient and does not require any catalyst or high-temperature conditions.

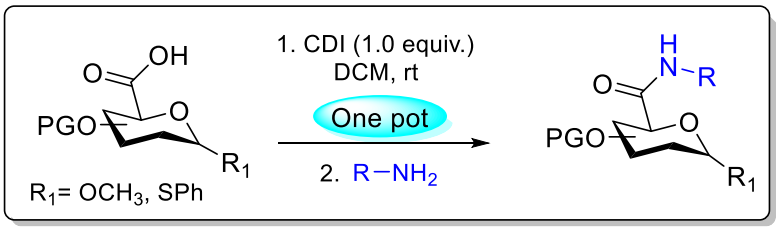
2.5. Experimental Section:

To a stirred solution of *N*-nitroso amide (0.2 mmol, 1.0 equiv.) in dichloromethane (5 mL) were added triethylamine (1.0 equiv.) and amine (2.0 equiv.) sequentially under a nitrogen atmosphere. The resulting mixture was stirred at room temperature and monitored by TLC. After completion, the reaction mixture was diluted with dichloromethane (5 mL), and washed with HCl (1.0 N, 10 mL) and brine (2 x 10 mL). The resulting organic layer was concentrated in vacuo and purified by flash chromatography (SiO_2: 100-200 mesh) using EtOAc/hexane as eluant to give analytically pure products.

2.5.1. Starting materials used for transamidation:



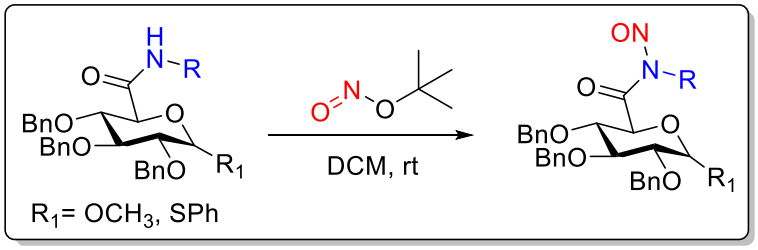
2.5.2. General procedure for preparation of sugar amides from uronic acids[1a, b]



Uronic acid (0.2 mmol, 1.0 equiv.) and 1,1'-carbonyl diimidazole (CDI) (1.0 equiv.) (10 mL) were stirred in DCM until CO_2 evolution was stopped (~ 20 min). Further, an aqueous solution of amine (7.0 equiv. in case of methylamine, 40% w/w solution and 1.5 equiv. in case of benzylamine and aniline) was added. After completion, the reaction mixture was quenched by 1N HCl (20 mL), and extracted by EA (2 x 20 mL). The organic phase was washed with brine (2 x 20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in

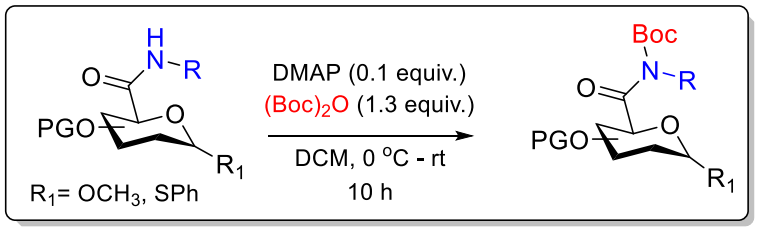
vacuo. The residue was purified by silica gel flash column chromatography (SiO_2: 100-200 mesh) to afford the desired products (**1b**, **1h**, **1j**, **1k**, **1l**, **1m** and **1n**).

2.5.3. General procedure for preparation of *N*-NO sugar amides[2a, b]



Amide (0.2 mmol, 1.0 equiv.) was stirred in dichloromethane (5 mL) approximately for 2 min at room temperature to which *tert*-butyl nitrite (1.5 equiv.) was added using syringe and allowed to stir at room temperature. The progress of the reaction was monitored by TLC. After completion, dichloromethane was evaporated and subjected for silica gel (100-200 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the corresponding *N-nitroso* amide products (**1g** and **1i**).

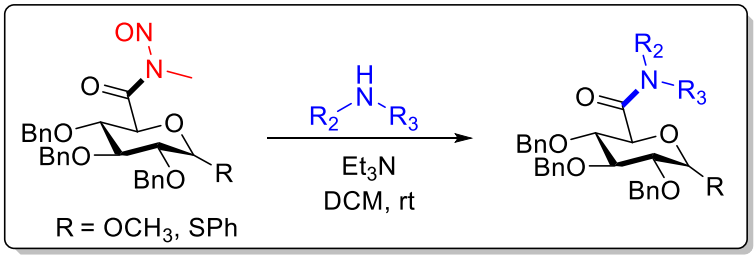
2.5.4. General procedure for preparation of *N*-Boc sugar amides[3].



An oven-dried round-bottomed flask (100 mL) was charged with secondary amide (0.2 mmol, 1.0 equiv.) and DMAP (0.1 equiv.) in dichloromethane (10 mL). Di-*tert*-butyl dicarbonate (Boc_2O) (2.0 equiv.) was added in one portion and the reaction mixture was allowed to stir until TLC showed full conversion. After completion, the reaction mixture was quenched with saturated solution of $NaHCO_3$ (10 mL) followed by extraction with EtOAc (3 × 20 mL). The organic layer was washed with H_2O (1 x 20 mL), brine (1 x 20 mL), dried and concentrated. The crude product was purified by column chromatography (SiO_2: ethyl acetate/hexane, 100-200 mesh) to obtain the corresponding *N*-Boc amides (**1c**, **1d**, **1e**, **1f**, **1o**, **1p**, **1q** and **1r**).

2.5.5. General procedures for transamidation.

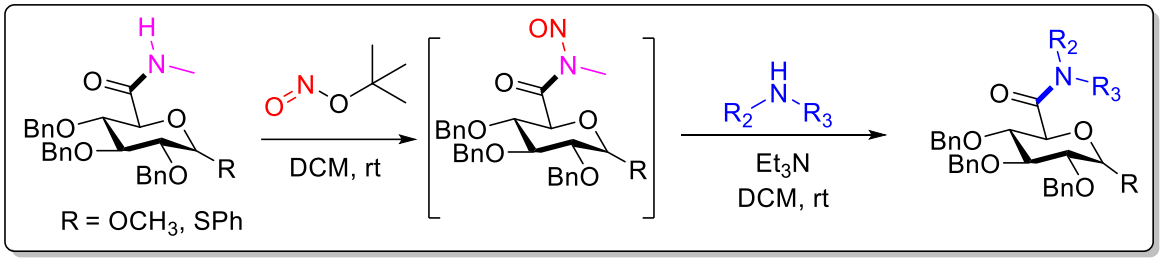
a. Procedure for transamidation with *N*-nitroso-*N*-methyl uronamides



To a stirred solution of N-nitroso amide substrate (0.2 mmol, 1.0 equiv.) in dichloromethane (5 ml) were added triethylamine (1.0 equiv.) and amine (2.0 equiv.) sequentially under a nitrogen atmosphere. The reaction mixture was stirred at room temperature and monitored by TLC. After completion, the reaction mixture was diluted with dichloromethane (5 mL) and washed with HCl (1.0 N, 10 mL) and brine (2 x 10 mL). The resulting organic layer was

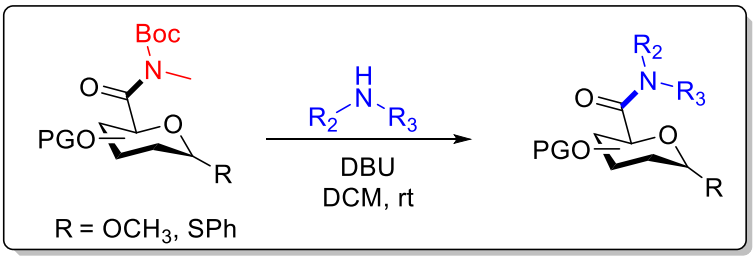
concentrated in vacuo and was purified by flash chromatography (SiO_2: 100-200 mesh) using EtOAc/hexane as eluant to give analytically pure products.

b. Procedure for transamidation with in situ generation of *N*-nitroso-*N*-methyl amides from *N*-methyl uronamides.



To a stirred solution of amide (0.2 mmol, 1.0 equiv.) in dichloromethane (5 mL) was added tert-butyl nitrite (1.5 equiv.) and allowed to stir for 2-3 h at room temperature. The external amine (2.0 equiv.) and triethyl amine (1.0 equiv.) were added to the reaction mixture and allowed to stir at room temperature and monitored by TLC. After completion, dichloromethane was evaporated and subjected to silica gel (100-200 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the corresponding transamidation products.

C. Procedure for transamidation with *N*-Boc-*N*-methyl uronamides.



To a stirred solution of N-Boc amide (0.2 mmol, 1.0 equiv.) in dichloromethane (5 ml) were added triethylamine (1.0 equiv.) and amine (2.0 equiv.) sequentially under a nitrogen atmosphere. The reaction mixture was stirred at room temperature and monitored by TLC. After completion, the reaction mixture was diluted with dichloromethane (5 mL) and washed with HCl (1.0 N, 10 mL) and brine (2 x 10 mL). The resulting organic layer was concentrated in vacuo and was purified by flash chromatography (SiO_2: 100-200 mesh) using EtOAc/hexane as eluant to give analytically pure products.

2.6. Analytical data for starting materials:

2.6.1. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxamide (1a)

Yield: 73% (38.4 mg) white solid; mp. 162-163 °C; $[\alpha]_D^{25}$= -1.7 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28–7.17 (m, 15H), 6.03 (s, 1H), 5.81 (s, 1H), 4.88 (d, *J* = 10.9 Hz, 1H), 4.76 – 4.71 (m, 3H), 4.60 – 4.54 (m, 3H), 4.01 (d, *J* = 10.0 Hz, 1H), 3.92 (t, *J* = 9.3 Hz, 1H), 3.53 – 3.49 (m, 1H), 3.47 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.4, 138.4, 137.8, 137.6, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 127.8, 127.8, 127.6, 98.3, 81.5, 80.1, 79.1, 75.8, 75.3, 73.5, 69.9, 55.7. HRMS-ESI (m/z): calcd for $C_{28}H_{31}NO_6$, $[M + H]^+$: 478.2230, found 478.2233.

2.6.2. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-*N*-methyltetrahydro-2H-pyran-2-carboxamide (1b)

Yield: 73% (38.4 mg) pale yellow viscous liquid; $[\alpha]_D^{25}$= 1.9 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 15H), 5.97 (d, *J* = 4.6 Hz, 1H), 4.88 (d, *J* = 10.9 Hz, 1H), 4.78 – 4.69 (m, 3H), 4.58 – 4.52 (m, 3H), 3.96 – 3.89 (m, 2H), 3.52 – 3.46 (m, 2H), 3.30 (s,

3H), 2.72 (d, *J* = 4.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.4, 138.5, 137.9, 137.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 98.4, 81.5, 80.2, 79.1, 75.9, 75.2, 73.5, 70.5, 55.7, 26.0. HRMS-ESI (m/z): calcd for $C_{29}H_{33}NO_6$, $[M + H]^+$: 492.2386, found 492.2392.

2.6.3. *tert*-butyl methyl((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carbonyl) carbamate (1c)

Yield: 73% (38.4 mg) as viscous liquid; $[\alpha]_D^{25}$= -0.4 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.10 (m, 15H), 5.46 (d, *J* = 9.8 Hz, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.76 – 4.71 (m, 3H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.52 (d, *J* = 3.5 Hz, 1H), 4.45 (d, *J* = 10.9 Hz, 1H), 3.94 (t, *J* = 9.4 Hz, 1H), 3.78 (t, *J* = 9.4 Hz, 1H), 3.51 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.40 (s, 3H), 3.04 (s, 3H), 1.39 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.6, 152.3, 138.6, 138.2, 138.0, 128.4, 128.3, 128.1, 127.9, 127.9, 127.7, 127.5, 127.5, 99.2, 83.5, 81.5, 80.5, 79.5, 75.7, 75.1, 73.5, 69.0, 56.2, 32.2, 27.8. HRMS-ESI (m/z): calcd for $C_{34}H_{41}NO_8$, $[M + H]^+$: 592.2910, found 592.2902.

2.6.4. *tert*-butyl propyl((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carbonyl)carbamate (1d)

Yield: 73% (38.4 mg) as transparent viscous liquid; $[\alpha]_D^{25}$= -0.1 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 15H), 5.44 (d, *J* = 9.7 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.82 – 4.79 (m, 3H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.60 (d, *J* = 3.5 Hz, 1H), 4.55 (d, *J* = 10.8 Hz, 1H), 4.01 (t, *J* = 9.4 Hz, 1H), 3.90 (t, *J* = 9.4 Hz, 1H), 3.59 (m, 3H), 3.49 (s, 3H),

1.56 – 1.51 (m, 2H), 1.47 (s, 9H), 0.86 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.3, 152.4, 138.6, 138.3, 138.0, 128.4, 128.3, 128.1, 128.1, 127.8, 127.7, 127.5, 127.4, 99.2, 83.2, 81.5, 80.3, 79.5, 75.6, 75.0, 73.5, 69.3, 56.3, 46.9, 27.8, 21.8, 11.2. HRMS-ESI (m/z): calcd for $C_{36}H_{45}NO_8$, $[M + H]^+$: 620.3223, found 620.3217.

2.6.5. *tert*-butyl phenyl((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carbonyl)carbamate (1e)

Yield: 73% (38.4 mg) as pale-yellow viscous liquid; $[\alpha]_D^{25}$= 0.1 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 18H), 6.94 – 6.92 (m, 2H), 5.17 (s, 1H), 5.04 – 5.02 (m, 1H), 4.90 – 4.86 (m, 1H), 4.80 – 4.69 (m, 3H), 4.58 – 4.50 (m, 3H), 3.92 – 3.89 (m, 1H), 3.50 – 3.47 (m, 1H), 3.30 (s, 3H), 1.25 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.7, 151.8, 138.6, 138.5, 138.4, 138.0, 128.9, 128.4, 128.3, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.7, 127.5, 127.5, 99.3, 83.4, 81.4, 80.1, 79.5, 75.6, 75.1, 73.5, 69.5, 56.3, 27.6. HRMS-ESI (m/z): calcd for $C_{39}H_{43}NO_8$, $[M + H]^+$: 654.3067, found 654.3078.

2.6.6. *Bis-tert*-butyl ((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carbonyl)dicarbamate (1f)

Yield: 73% (38.4 mg) as transparent viscous liquid; $[\alpha]_D^{25}$= 0.5 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 15H), 5.20 (d, *J* = 9.8 Hz, 1H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.79 – 4.71 (m, 3H), 4.63 (d, *J* = 10.3 Hz, 1H), 4.59 – 4.55 (m, 2H), 3.96 (t, *J* = 9.3 Hz, 1H), 3.78 (t, *J* = 9.4 Hz, 1H), 3.50 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.41 (s, 3H), 1.42 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 149.1, 138.6, 138.1, 138.0, 128.4, 128.3, 128.1, 128.1,

128.1, 127.9, 127.8, 127.5, 127.5, 99.0, 85.0, 81.5, 80.1, 79.3, 75.7, 75.2, 73.5, 68.9, 56.2, 27.5. HRMS-ESI (m/z): calcd for $C_{38}H_{47}NO_{10}$, $[M + H]^+$: 700.3092, found 700.3089.

2.6.7. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-*N*-methyl-*N*-nitrosotetrahydro-2H-pyran-2-carboxamide (1g)

Yield: 73% (38.4 mg) as transparent viscous liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.15 (m, 13H), 7.06 – 7.05 (m, 2H), 5.40 (d, *J* = 9.3 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.78 – 4.73 (m, 2H), 4.61 – 4.57 (m, 2H), 4.51 (d, *J* = 3.5 Hz, 1H), 4.05 – 4.03 (m, 2H), 3.56 – 3.53 (m, 1H), 3.29 (s, 3H), 2.96 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.9, 138.4, 138.0, 137.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.6, 99.2, 81.5, 79.4, 78.7, 75.8, 75.2, 73.6, 67.9, 56.1, 25.7. HRMS-ESI (m/z): calcd for $C_{29}H_{32}N_2O_7$, $[M + H]^+$: 521.2288, found 521.2278.

2.6.8. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-methyl-6-(phenylthio)tetrahydro-2H-pyran-2-carboxamide (1h)

Yield: 73% (38.4 mg) as white solid; mp. 182-183 °C $[\alpha]_D^{25}$= -6.8 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.28 – 7.18 (m, 18H), 6.22 (s, 1H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.73 – 4.70 (m, 2H), 4.67 – 4.64 (m, 3H), 4.59 (d, *J* = 10.6 Hz, 1H), 3.86 – 3.84 (m, 1H), 3.66 – 3.64 (m, 2H), 3.45 – 3.41 (m, 1H), 2.71 (d, *J* = 4.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.8, 138.0, 137.7, 137.5, 133.1, 131.8, 129.0, 128.4, 128.3, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.7, 127.7, 86.9, 84.3, 80.2, 79.1, 78.5, 75.1, 75.0, 74.4, 25.9. HRMS-ESI (m/z): calcd for $C_{34}H_{35}NO_5S$, $[M + H]^+$: 570.2314, found 570.2314.

2.6.8. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-methyl-*N*-nitroso-6-(phenylthio)tetrahydro-2H-pyran-2-carboxamide (1i) (Isomeric mixture)

Yield: 73% (38.4 mg) as a pale-yellow sticky solid; $[\alpha]_D^{25}$= -2.2 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.06 (m, 20H), 5.10 (d, *J* = 9.7 Hz, 1H), 4.87 – 4.66 (m, 6H), 4.16 (t, *J* = 9.5 Hz, 1H), 3.79 – 3.76 (m, 1H), 3.66 (s, 1H), 3.53 (t, *J* = 9.3 Hz, 1H), 2.98 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.1, 138.1, 137.9, 137.8, 133.3, 132.2, 131.2, 129.0, 128.5, 128.4, 128.3, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 88.7, 86.2, 80.5, 78.4, 75.9, 75.6, 75.4, 75.3, 25.8. HRMS-ESI (m/z): calcd for $C_{34}H_{34}N_2O_6S$, $[M + H]^+$: 599.2216, found 599.2206.

2.6.9. (2S,3S,4S,5R,6S)-4,5-bis(benzyloxy)-3-((4-bromobenzyl)oxy)-6-methoxy-*N*-methyltetrahydro-2H-pyran-2-carboxamide (1j)

Yield: 73% (38.4 mg) as white solid; mp. 183-184 °C $[\alpha]_D^{25}$= -4.9 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.20 (m, 10H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.05 (s, 1H), 4.87 (d, *J* = 10.9 Hz, 1H), 4.73 – 4.69 (m, 2H), 4.59 – 4.50 (m, 4H), 3.95 (d, *J* = 9.9 Hz, 1H), 3.88 (t, *J* = 9.3 Hz, 1H), 3.47 – 3.43 (m, 2H), 3.29 (s, 3H), 2.71 (d, *J* = 4.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.4, 138.4, 137.8, 136.8, 131.3, 129.8, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 121.6, 98.3, 81.3, 80.1, 79.0, 75.8, 74.2, 73.4, 70.4, 55.7, 25.9. HRMS-ESI (m/z): calcd for $C_{29}H_{32}BrNO_5$, $[M + H]^+$: 554.1542, found 554.1536.

2.6.10. (2S,3R,4S,5S,6S)-2-methoxy-6-(methylcarbamoyl)tetrahydro-2H-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (1k)

Yield: 73% (38.4 mg) as a pale yellow sticky solid; $[\alpha]_D^{25}$= -10.9 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.39 (d, *J* = 4.2 Hz, 1H), 5.60 (t, *J* = 9.8 Hz, 1H), 5.12 (t, *J* = 9.8 Hz, 1H), 5.02 (d, *J* = 3.7 Hz, 1H), 4.77 (dd, *J* = 10.1, 3.7 Hz, 1H), 4.20 (d, *J* = 10.2 Hz, 1H), 3.40 (s, 3H), 2.80 (d, *J* = 4.9 Hz, 3H), 1.19 (s, 9H), 1.17 (s, 9H), 1.12 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.7, 176.7, 176.6, 167.7, 96.7, 70.9, 69.4, 68.8, 68.4, 56.0, 38.7, 38.6, 38.6, 27.1, 26.9, 25.7. HRMS-ESI (m/z): calcd for $C_{23}H_{39}NO_9$, $[M + H]^+$: 474.2703, found 474.2711.

2.6.11. (2S,3R,4S,5S,6S)-2-methoxy-6-(methylcarbamoyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (1l)

Yield: 73% (38.4 mg) as pale yellow viscous liquid; $[\alpha]_D^{25}$= 7.7 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 4H), 7.80 – 7.78 (m, 2H), 7.44 – 7.18 (m, 9H), 6.52 (d, *J* = 4.6 Hz, 1H), 6.10 (t, *J* = 9.9 Hz, 1H), 5.56 (t, *J* = 9.9 Hz, 1H), 5.23 (d, *J* = 3.5 Hz, 1H), 5.16 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.42 (d, *J* = 10.2 Hz, 1H), 3.39 (s, 3H), 2.74 – 2.73 (m, 3H). **^{13}C NM**R (125 MHz, $CDCl_3$) δ 167.7, 165.8, 165.5, 165.3, 133.4, 133.1, 133.0, 129.8, 129.8, 129.5, 129.1, 128.9, 128.6, 128.4, 128.3, 128.2, 97.05, 71.7, 70.2, 69.7, 68.3, 56.0, 25.8. HRMS-ESI (m/z): calcd for $C_{29}H_{27}NO_9$, $[M + H]^+$: 534.1764, found 534.1751.

2.6.12. (3aR,5S,5aR,8aS,8bR)-*N*-2,2,7,7-pentamethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carboxamide (1m)

Yield: 73% (38.4 mg) as white sticky solid; $[\alpha]_D^{25}$= -17.7 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.51 (d, *J* = 4.0 Hz, 1H), 5.52 – 5.51 (m, 1H), 4.64 – 4.57 (m, 2H), 4.29 –

4.23 (m, 2H), 2.80 (d, *J* = 4.7 Hz, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.27 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.7, 109.2, 109.0, 96.1, 71.2, 70.7, 70.2, 68.5, 25.8, 25.7, 25.4, 24.6, 23.9. HRMS-ESI (m/z): calcd for $C_{13}H_{21}NO_6$, $[M + H]^+$: 288.1447, found 288.1438.

2.6.13. (2S,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-methyl-6-(phenylthio)tetrahydro-2H-pyran-2-carboxamide (1n)

Yield: 73% (38.4 mg) as white sticky solid; $[\alpha]_D^{25}$= 1.8 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.29 – 7.18 (m, 15H), 7.14 – 7.12 (m, 3H), 6.58 (d, *J* = 4.9 Hz, 1H), 4.77 (d, *J* = 11.1 Hz, 2H), 4.69 – 4.50 (m, 5H), 4.37 (d, *J* = 2.0 Hz, 1H), 3.86 – 3.81 (m, 2H), 3.56 (dd, *J* = 9.2, 2.8 Hz, 1H), 2.73 (d, *J* = 5.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.6, 138.5, 138.0, 137.8, 133.6, 131.2, 129.0, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.3, 87.4, 83.0, 78.1, 76.6, 75.6, 74.9, 74.8, 72.2, 25.8. HRMS-ESI (m/z): calcd for $C_{34}H_{35}NO_5S$, $[M + H]^+$: 570.2314, found 570.2321.

2.6.14. *tert*-butyl methyl((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-(phenylthio)tetrahydro-2H-pyran-2-carbonyl)carbamate (1o)

Yield: 73% (38.4 mg) as yellowish syrup; $[\alpha]_D^{25}$= -1.6 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.27 – 7.13 (m, 18H), 5.02 (d, *J* = 9.6 Hz, 1H), 4.83 – 4.74 (m, 5H), 4.67 – 4.61 (m, 2H), 3.99 (t, *J* = 9.4 Hz, 1H), 3.70 (t, *J* = 9.0 Hz, 1H), 3.46 (t, *J* = 9.3 Hz, 1H), 3.08 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.1, 152.2, 138.3, 138.2, 138.0, 133.9, 131.2, 128.8, 128.4, 128.3, 128.3, 128.0, 127.9, 127.7, 127.6, 127.1,

88.1, 86.3, 83.5, 80.7, 79.3, 76.7, 75.7, 75.3, 75.2, 31.9, 27.9. HRMS-ESI (m/z): calcd for $C_{39}H_{43}NO_7S$, $[M + H]^+$: 670.2838, found 670.2842.

2.6.15. *tert*-butyl ((2S,3S,4S,5R,6S)-4,5-bis(benzyloxy)-3-((4-bromobenzyl)oxy)-6-methoxy tetrahydro-2H-pyran-2-carbonyl)(methyl)carbamate (1p)

Yield: 73% (38.4 mg) as pale yellow viscous liquid; $[\alpha]_D^{25}$= -3.6 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 12H), 6.96 (d, *J* = 8.3 Hz, 2H), 5.43 (d, *J* = 9.7 Hz, 1H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.73 – 4.64 (m, 3H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.52 (d, *J* = 3.5 Hz, 1H), 4.40 (d, *J* = 11.3 Hz, 1H), 3.92 (t, *J* = 9.4 Hz, 1H), 3.77 (t, *J* = 9.4 Hz, 1H), 3.49 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.40 (s, 3H), 3.03 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.4, 152.3, 138.6, 137.9, 137.3, 131.2, 129.2, 128.4, 128.3, 128.1, 127.9, 127.7, 127.5, 121.2, 99.2, 83.5, 81.4, 80.4, 79.5, 75.6, 74.2, 73.4, 69.1, 56.3, 32.2, 27.8. HRMS-ESI (m/z): calcd for $C_{34}H_{40}BrNO_7$, $[M + Na]^+$: 676.1886, found 676.1898

2.6.16. (2S,3S,4S,5R,6S)-2-((tert-butoxycarbonyl)(methyl)carbamoyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate (1q)

Yield: 73% (38.4 mg) as pale-yellow viscous liquid; $[\alpha]_D^{25}$= 3.8 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 6H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.19 (m, 7H), 6.15 – 6.10 (m, 1H), 5.95 (d, *J* = 9.9 Hz, 1H), 5.79 (t, *J* = 9.7 Hz, 1H), 5.23 – 5.22 (m, 2H), 3.49 (s, 3H), 3.02 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 165.8, 165.7, 164.8, 152.5, 133.3, 133.1, 133.0, 129.9, 129.8, 129.7, 129.6, 129.2, 129.2, 129.0, 128.3, 128.2,

97.9, 83.5, 71.8, 70.9, 70.1, 68.4, 56.8, 32.5, 27.8. HRMS-ESI (m/z): calcd for $C_{34}H_{35}NO_{11}$, $[M + Na]^+$: 656.2108, found 656.2097.

2.6.17 *tert*-butyl methyl((3aR,5S,5aR,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo) [4,5-b:4',5'-d]pyran-5-carbonyl)carbamate (1r)

Yield: 73% (38.4 mg) as white sticky solid; $[\alpha]_D^{25}$= -8.8 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.64 (d, *J* = 5.1 Hz, 1H), 5.54 (s, 1H), 4.70 – 4.69 (m, 1H), 4.61 – 4.59 (m, 1H), 4.34 – 4.33 (m, 1H), 3.09 (d, *J* = 0.8 Hz, 3H), 1.49 (s, 3H), 1.45 (s, 9H), 1.42 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.6, 152.8, 110.1, 109.0, 96.8, 83.2, 71.5, 71.4, 70.2, 70.0, 31.7, 27.8, 25.8, 25.6, 25.0, 24.9. HRMS-ESI (m/z): calcd for $C_{18}H_{29}NO_8$, $[M + H]^+$: 388.1971, found 388.1968.

2.7. Analytical data for transamidation products:

2.7.1. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-*N*-(4-methoxybenzyl)tetrahydro 2H-pyran-2-carboxamide (3a)

Yield: 96% (116 mg) as white solid; mp. 161-162 °C; $[\alpha]_D^{25}$= -1.1 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 11H), 7.24 – 7.21 (m, 4H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.32 (t, *J* = 5.1 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.83 – 4.74 (m, 3H), 4.64 – 4.57 (m, 3H), 4.41 – 4.37 (m, 1H), 4.33 – 4.29 (m, 1H), 4.06 (d, *J* = 9.9 Hz, 1H), 3.98 (t, *J* = 9.3 Hz, 1H), 3.75 (s, 3H), 3.61 – 3.57 (m, 1H), 3.53 (dd, *J* = 9.7, 3.5 Hz, 1H),

3.37 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.5, 159.0, 138.4, 137.8, 137.8, 129.7, 129.2, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.6, 127.5, 114.0, 98.3, 81.4, 80.1, 79.1, 75.8, 75.0, 73.4, 70.6, 55.7, 55.1, 42.8. HRMS-ESI (m/z): calcd for $C_{36}H_{39}NO_7$, $[M + H]^+$: 598.2805, found 598.2785.

2.7.2. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-*N*-propyltetrahydro-2H-pyran-2-carboxamide (3b)

Yield: 94% (99 mg) as white solid; mp. 163-164 °C; $[\alpha]_D^{25}$= -1.6 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 15H), 6.01 (s, 1H), 4.87 (d, *J* = 10.9 Hz, 1H), 4.77 – 4.68 (m, 3H), 4.58 – 4.53 (m, 3H), 3.96 – 3.89 (m, 2H), 3.52 – 3.50 (m, 1H), 3.49 – 3.46 (m, 1H), 3.30 (s, 3H), 3.21 – 3.16 (m, 1H),3.10 – 3.03 (m, 1H), 1.40 – 1.36 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.7, 138.5, 137.9, 137.8, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 127.5, 98.4, 81.4, 80.3, 79.1, 75.8, 75.1, 73.4, 70.6, 55.6, 40.9, 22.5, 11.2. HRMS-ESI (m/z): calcd for $C_{31}H_{37}NO_6$, $[M + H]^+$: 520.2699, found 520.2686.

2.7.3. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-butyl-6-methoxytetrahydro-2H-pyran-2-carboxamide (3c)

Yield: 95% (102 mg) as white sticky solid; $[\alpha]_D^{25}$= -1.2 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 14H), 7.25 (s, 1H), 6.03 (t, *J* = 5.4 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.84 – 4.76 (m, 3H), 4.66 – 4.61 (m, 3H), 4.03 – 3.97 (m, 2H), 3.60 – 3.53 (m, 2H), 3.38 (s, 3H), 3.32 – 3.26 (m, 1H), 3.20 – 3.16 (m, 1H), 1.43 – 1.38 (m, 2H), 1.31 – 1.26 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.7, 138.5, 137.9, 137.9, 128.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.7, 127.6, 98.4, 81.4, 80.3, 79.1, 75.8, 75.1, 73.5,

70.7, 55.7, 39.0, 31.3, 19.9, 13.6. HRMS-ESI (m/z): calcd for $C_{32}H_{39}NO_6$, $[M + H]^+$: 534.2856, found 534.2848.

2.7.4. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-hexanoyl-6-methoxytetrahydro-2H-pyran-2-carboxamide (3d)

Yield: 92% (104 mg) as white solid; mp. 118-120 °C; $[\alpha]_D^{25}$= -1.2 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 15H), 6.04 (t, *J* = 5.0 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.84 – 4.76 (m, 3H), 4.66 – 4.61 (m, 3H), 4.03 – 3.97 (m, 2H), 3.60 – 3.53 (m, 2H), 3.38 (s, 3H), 3.30 – 3.25 (m, 1H),3.20 – 3.14 (m, 1H), 1.43 – 1.39 (m, 2H), 1.26 – 1.24 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.7, 138.5, 137.9, 137.8, 128.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.7, 127.6, 98.4, 81.4, 80.3, 79.1, 75.8, 75.1, 73.5, 70.6, 55.6, 39.3, 31.3, 29.2, 26.5, 22.4, 13.9. HRMS-ESI (m/z): calcd for $C_{34}H_{41}NO_7$, $[M + H]^+$: 576.2961, found 576.2949.

2.7.5. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-cyclopropyl-6-methoxytetrahydro-2H-pyran-2-carboxamide (3e)

Yield: 89% (93 mg) as white sticky solid; $[\alpha]_D^{25}$= -1.3 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 15H), 6.08 (s, 1H), 4.87 (d, *J* = 10.9 Hz, 1H), 4.77 – 4.68 (m, 3H), 4.57 (d, *J* = 11.2 Hz, 2H), 4.53 (d, *J* = 3.5 Hz, 1H), 3.93 – 3.88 (m, 2H), 3.50 – 3.44 (m, 2H), 3.30 (s, 3H), 2.68 – 2.64 (m, 1H), 0.69 – 0.67 (m, 2H), 0.35 – 0.34 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.2, 138.5, 137.9, 137.8, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 127.8, 127.8, 127.6, 98.4, 81.4, 80.2, 79.1, 75.8, 75.2, 73.5, 70.5, 55.7, 22.4, 6.5, 6.3. HRMS-ESI (m/z): calcd for $C_{31}H_{35}NO_6$, $[M + H]^+$: 518.2543, found 518.2533.

2.7.6. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-cyclohexyl-6-methoxytetrahydro-2H-pyran-2-carboxamide (3f)

Yield: 88% (99 mg) as white sticky solid; $[\alpha]_D^{25}$= -3.4 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 15H), 5.93 (d, *J* = 7.9 Hz, 1H), 4.93 (d, *J* = 10.9 Hz, 1H), 4.83 – 4.74 (m, 3H), 4.67 – 4.61 (m, 3H), 4.01 – 3.96 (m, 2H), 3.79 – 3.75 (m, 1H), 3.60 – 3.53 (m, 2H), 3.39 (s, 3H), 1.91 – 1.82 (m, 2H), 1.68 – 1.64 (m, 3H), 1.15 – 0.99 (m, 4H), 0.89 – 0.83 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.9, 138.6, 138.0, 138.0, 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 127.7, 127.6, 98.4, 81.4, 80.5, 79.2, 75.9, 75.2, 73.5, 70.8, 55.7, 48.0, 33.0, 32.8, 25.4, 24.7 (2C). HRMS-ESI (m/z): calcd for $C_{34}H_{41}NO_6$, $[M + H]^+$: 560.3012, found 560.3000.

2.7.7. (2S,3S,4S,5R,6S)-*N*-benzyl-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxamide (3g)

Yield: 93% (106 mg) as white sticky solid; $[\alpha]_D^{25}$= -1.4 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 20H), 6.39 (t, *J* = 5.6 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.83 – 4.74 (m, 3H), 4.65 – 4.58 (m, 3H), 4.49 – 4.45 (m, 1H), 4.39 – 4.34 (m, 1H), 4.09 (d, *J* = 9.9 Hz, 1H), 3.99 (t, *J* = 9.3 Hz, 1H), 3.60 (dd, *J* = 9.8, 9.0 Hz, 1H), 3.54 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.37 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.8, 138.5, 137.9, 137.8, 137.7, 128.7, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.6, 98.5, 81.5, 80.2, 79.2, 75.9, 75.2, 73.5, 70.7, 55.8, 43.4. HRMS-ESI (m/z): calcd for $C_{35}H_{37}NO_6$, $[M + H]^+$: 568.2699, found 568.2689.

2.7.8. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-*N*-(3-methoxybenzyl)tetrahydro-2H-pyran-2-carboxamide (3h)

Yield: 93% (112 mg) as white sticky solid; $[\alpha]_D^{25}$= -1.2 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 12H), 7.25 – 7.17 (m, 5H), 6.80 – 6.77 (m, 2H), 6.38 (t, *J* = 5.4 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.83 – 4.73 (m, 3H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.61 – 4.59 (m, 2H), 4.47 – 4.43 (m, 1H), 4.35 – 4,31 (m, 1H), 4.12 – 4.07 (m, 1H), 3.99 (t, *J* = 9.3 Hz, 1H), 3.74 (s, 3H), 3.61 – 3.57 (m, 1H), 3.54 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.38 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.7, 159.8, 139.2, 138.5, 137.9, 137.7, 129.7, 128.4, 128.3, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 120.1, 113.5, 113.0, 98.4, 81.4, 80.2, 79.1, 75.8, 75.1, 73.5, 70.6, 55.7, 55.1, 43.3. HRMS-ESI (m/z): calcd for $C_{36}H_{39}NO_7$, $[M + H]^+$: 598.2805, found 598.2801.

2.7.9. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-*N*-(quinolin-3-ylmethyl)tetrahydro-2H-pyran-2-carboxamide (3i)

Yield: 90% (103 mg) as white solid; mp. 157-158 °C; $[\alpha]_D^{25}$= -1.5 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 4.8 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.28 – 7.26 (m, 5H), 7.25 – 7.07 (m, 13H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.76 – 4.72 (m, 2H), 4.65 (d, *J* = 10.5 Hz, 1H), 4.59 – 4.56 (m, 2H), 4.53 – 4.48 (m, 3H), 4.08 (d, *J* = 9.9 Hz, 1H), 3.93 (t, *J* = 9.3 Hz, 1H), 3.60 – 3.56 (m, 1H), 3.51 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.9, 155.7, 148.9, 138.5, 137.9, 137.8, 136.7, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 127.8, 127.5, 122.3, 122.0, 98.4, 81.4, 80.1, 79.1, 75.8, 75.0, 73.5, 70.8, 55.7, 44.2. HRMS-ESI (m/z): calcd for $C_{34}H_{36}N_2O_6$, $[M + H]^+$: 569.2652, found 569.2641.

2.7.10. piperidin-1-yl((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methanone (3j)

Yield: 93% (102 mg) as viscous liquid; $[\alpha]_D^{25}$= -4.9 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.15 (m, 15H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.78 – 4.73 (m, 3H), 4.61 (d, *J* = 10.6 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 3.5 Hz, 1H), 4.46 – 4.44 (m, 1H), 3.94 – 3.92 (m, 2H), 3.69 – 3.65 (m, 1H), 3.54 – 3.51 (m, 1H), 3.48 – 3.43 (m, 1H), 3.40 – 3.37 (m, 1H), 3.35 (s, 3H), 3.30 – 3.26 (m, 1H), 1.56 – 1.42 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.6, 138.6, 138.4, 137.9, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.8, 127.5, 127.5, 99.4, 81.4, 79.5, 79.2, 75.7, 75.2, 73.6, 66.2, 56.2, 46.8, 43.4, 26.5, 25.4, 24.4. HRMS-ESI (m/z): calcd for $C_{33}H_{39}NO_6$, $[M + H]^+$: 546.2856, found 546.2845.

2.7.11. morpholino((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methanone (3k)

Yield: 89% (98 mg) as white sticky solid; $[\alpha]_D^{25}$= -3.5 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 15H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.88 (d, *J* = 3.1 Hz, 1H), 4.86 – 4.83 (m, 2H), 4.68 (d, *J* = 7.4 Hz, 1H), 4.66 (d, *J* = 8.8 Hz, 1H), 4.60 (d, *J* = 3.5 Hz, 1H), 4.50 (d, *J* = 9.0 Hz, 1H), 4.02 – 3.99 (m, 2H), 3.70 – 3.57 (m, 7H), 3.53 – 3.51 (m, 2H), 3.43 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.1, 138.5, 138.2, 137.8, 128.4, 128.3, 128.3, 128.1, 128.0, 127.8, 127.8, 127.7, 127.6, 99.4, 81.4, 79.5, 79.2, 75.7, 75.3, 73.7, 66.5, 66.5, 66.1, 56.4, 46.0, 42.5. HRMS-ESI (m/z): calcd for $C_{32}H_{37}NO_7$, $[M + H]^+$: 548.2648, found 548.2651.

2.7.12. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-N-phenyltetrahydro-2H-pyran-2-carboxamide (3l)

Yield: 45% (50 mg) as white sticky solid; $[\alpha]_D^{25}$= 1.4 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.37 – 7.34 (m, 2H), 7.29 – 7.16 (m, 17H), 7.02 (t, *J* = 7.4 Hz, 1H),

4.90 (d, *J* = 10.9 Hz, 1H), 4.80 – 4.72 (m, 3H), 4.60 – 4.55 (m, 3H), 4.12 (d, *J* = 10.0 Hz, 1H), 3.97 (t, *J* = 9.3 Hz, 1H), 3.58 – 3.50 (m, 2H), 3.33 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 138.3, 137.8, 137.4, 137.1, 128.9, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.8, 127.6, 124.3, 119.6, 98.4, 81.4, 80.1, 79.0, 75.8, 75.4, 73.5, 70.7, 55.8. HRMS-ESI (m/z): calcd for $C_{34}H_{35}NO_6$, $[M + H]^+$: 554.2543, found 554.2534.

2.7.13. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxy-*N*-(4-methoxyphenyl)tetrahydro-2H-pyran-2-carboxamide (3m)

Yield: 55% (65 mg) as white solid; mp. 159-160 °C; $[\alpha]_D^{25}$= -0.9 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.30 – 7.22 (m, 12H), 7.18 – 7.16 (m, 5H), 6.76 (d, *J* = 9.0 Hz, 2H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.80 – 4.72 (m, 3H), 4.61 – 4.56 (m, 3H), 4.10 (d, *J* = 10.0 Hz, 1H), 3.97 (t, *J* = 9.3 Hz, 1H), 3.71 (s, 3H), 3.59 – 3.55 (m, 1H), 3.52 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.35 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.5, 156.4, 138.5, 137.9, 137.6, 130.4, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 121.4, 114.1, 98.5, 81.5, 80.3, 79.2, 75.9, 75.4, 73.5, 70.8, 55.8, 55.4. HRMS-ESI (m/z): calcd for $C_{35}H_{37}NO_7$, $[M + H]^+$: 584.2648, found 584.2648.

2.7.14. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-butyl-6-(phenylthio)tetrahydro-2H-pyran-2-carboxamide (3n)

Yield: 94% (115 mg) as white sticky solid; $[\alpha]_D^{25}$= -16.2 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.30 – 7.28 (m, 3H), 7.25 – 7.16 (m, 15H), 6.18 (t, *J* = 5.3 Hz, 1H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.72 – 4.64 (m, 5H), 4.57 (d, *J* = 10.5 Hz, 1H), 3.83 – 3.82 (m, 1H), 3.65 – 3.63 (m, 2H), 3.45 – 3.42 (m, 1H), 3.19 – 3.14 (m, 2H), 1.38 – 1.35 (m, 2H), 1.26 – 1.21 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.1,

138.0, 137.7, 137.6, 132.8, 132.4, 129.0, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.7, 86.7, 84.4, 80.2, 79.4, 78.6, 75.2, 75.0, 74.5, 38.8, 31.3, 19.9, 13.6. HRMS-ESI (m/z): calcd for $C_{37}H_{41}NO_5S$, $[M + H]^+$: 612.2784, found 612.2778.

2.7.15. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-hexanoyl-6-(phenylthio)tetrahydro-2H-pyran-2-carboxamide (3o)

Yield: 92% (118 mg) as white solid; mp. 148-149 °C; $[\alpha]_D^{25}$= -3.4 [c 0.1, $CHCl_3$], **^{1}H NMR (**500 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.31 – 7.27 (m, 4H), 7.25 – 7.17 (m, 14H), 6.20 (d, *J* = 5.3 Hz, 1H), 4.78 (d, *J* = 10.5 Hz, 1H), 4.73 – 4.70 (m, 2H), 4.68 – 4.64 (m, 3H), 4.58 (d, *J* = 10.5 Hz, 1H), 3.84 – 3.82 (m, 1H), 3.67 – 3.64 (m, 2H), 3.46 – 3.42 (m, 1H), 3.19 – 3.14 (m, 2H), 1.21 (d, *J* = 7.9 Hz, 8H), 0.81 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.1, 138.0, 137.7, 137.6, 132.9, 132.3, 129.0, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.7, 86.7, 84.4, 80.2, 79.5, 78.6, 75.2, 75.0, 74.5, 39.1, 31.4, 29.3, 26.5, 22.5, 13.9. HRMS-ESI (m/z): calcd for $C_{39}H_{43}NO_6S$, $[M + H]^+$: 654.2889, found 654.2898.

2.7.16. (2S,3S,4S,5R,6S)-*N*-benzyl-3,4,5-tris(benzyloxy)-6-(phenylthio)tetrahydro-2H-pyran-2-carboxamide (3p)

Yield: 91% (118 mg) as white solid; mp. 168-169 °C; $[\alpha]_D^{25}$= -5.5 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.30 – 7.17 (m, 20H), 7.16 – 7.14 (m, 3H), 6.50 (t, *J* = 5.7 Hz, 1H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.70 – 4.61 (m, 5H), 4.56 (d, *J* = 10.6 Hz, 1H), 4.39 – 4.30 (m, 2H), 3.88 (d, *J* = 7.8 Hz, 1H), 3.69 – 3.63 (m, 2H), 3.43 – 3.40 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.1, 138.0, 137.7, 137.7, 137.6, 132.7, 132.5, 129.0, 128.6, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.5, 86.6, 84.4, 80.2,

79.3, 78.6, 75.2, 75.0, 74.5, 43.1. HRMS-ESI (m/z): calcd for $C_{40}H_{39}NO_5S$, $[M + H]^+$: 646.2627, found 646.2618.

2.7.17. (2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-(4-methoxybenzyl)-6-(phenylthio)tetrahydro -2H-pyran-2-carboxamide (3q)

Yield: 94% (127 mg) as transparent viscous liquid $[\alpha]_D^{25}$= -4.1 [c 0.1, $CHCl_3$] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.29 – 7.17 (m, 18H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.76 – 6.73 (m, 2H), 6.43 (t, *J* = 5.6 Hz, 1H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.71 – 4.55 (m, 6H), 4.32 – 4.24 (m, 2H), 3.87 – 3.85 (m, 1H), 3.70 (s, 3H), 3.67 – 3.63 (m, 2H), 3.43 – 3.39 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.0, 159.0, 138.0, 137.7, 137.6, 132.6, 132.6, 129.8, 129.1, 129.0, 128.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 114.0, 86.7, 84.5, 80.2, 79.4, 78.6, 75.2, 75.0, 74.5, 55.2, 42.6. HRMS-ESI (m/z): calcd for $C_{41}H_{41}NO_6S$, $[M + H]^+$: 676.2733, found 676.2729.

2.7.18. pyrrolidin-1-yl((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-(phenylthio)tetrahydro-2H-pyran-2-yl)methanone (3r)

Yield: 93% (114 mg) as white solid; mp. 148-149 °C; $[\alpha]_D^{25}$= -1.1 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 2H), 7.32 – 7.13 (m, 18H), 4.84 – 4.64 (m, 6H), 4.60 (d, *J* = 9.7 Hz, 1H), 4.01 (t, *J* = 9.3 Hz, 1H), 3.80 (d, *J* = 9.5 Hz, 1H), 3.66 (t, *J* = 9.0 Hz, 1H), 3.49 – 3.33 (m, 3H), 3.23 – 3.19 (m, 2H), 1.72 – 1.64 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.3, 138.5, 138.5, 138.0, 133.4, 132.9, 129.0, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.8, 127.7, 88.6, 86.4, 80.5, 79.1, 77.3, 75.9, 75.6, 75.2, 46.2, 46.0, 26.0, 24.2. HRMS-ESI (m/z): calcd for $C_{37}H_{39}NO_5S$, $[M + H]^+$: 610.2627, found 610.2618.

2.7.19. piperidin-1-yl((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-(phenylthio)tetrahydro-2H-pyran-2-yl)methanone (3s)

Yield: 94% (118 mg) as white solid; mp. 123-124 °C; $[\alpha]_D^{25}$= -5.7 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 7.32 – 7.30 (m, 2H), 7.27 – 7.14 (m, 16H), 4.84 – 4.80 (m, 3H), 4.79 (d, *J* = 10.3 Hz, 1H), 4.72 (d, *J* = 10.5 Hz, 1H), 4.67 (d, *J* = 10.3 Hz, 1H), 4.63 (d, *J* = 9.7 Hz, 1H), 4.06 (t, *J* = 9.3 Hz, 1H), 3.94 (d, *J* = 9.4 Hz, 1H), 3.67 (t, *J* = 9.0 Hz, 1H), 3.58 – 3.55 (m, 1H), 3.48 – 3.44 (m, 1H), 3.41 – 3.36 (m, 1H), 3.15 – 3.05 (m, 2H), 1.49 – 1.46 (m, 4H), 1.30 – 1.26 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.8, 138.5, 138.3, 137.9, 133.0, 132.7, 128.9, 128.4, 128.3, 128.2, 128.2, 128.0, 127.8, 127.8, 127.7, 127.6, 127.5, 88.5, 86.4, 80.3, 78.7, 75.8, 75.4, 75.3, 75.0, 46.5, 43.3, 26.3, 25.4, 24.4. HRMS-ESI (m/z): calcd for $C_{38}H_{41}NO_5S$, $[M + H]^+$: 624.2784, found 624.2771.

2.7.20. morpholino((2S,3S,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-(phenylthio)tetrahydro-2H-pyran-2-yl)methanone (3t)

Yield: 88% (110 mg) as white sticky solid; $[\alpha]_D^{25}$= -1.9 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 7.32 – 7.24 (m, 8H), 7.23 – 7.14 (m, 10H), 4.84 – 4.79 (m, 4H), 4.75 (d, *J* = 10.5 Hz, 1H), 4.69 – 4.64 (m, 2H), 4.05 (t, *J* = 9.2 Hz, 1H), 3.85 (d, *J* = 9.4 Hz, 1H), 3.70 – 3.66 (m, 2H), 3.58 – 3.52 (m, 2H), 3.48 – 3.44 (m, 1H), 3.38 – 3.33 (m, 1H), 3.28 – 3.20 (m, 2H), 3.09 – 3.00 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.1, 138.3, 138.2, 137.7, 132.9, 132.7, 129.1, 128.4, 128.4, 128.2, 128.2, 128.1, 127.9, 127.9, 127.7, 127.6, 88.7, 86.3, 80.3, 78.3, 75.8, 75.5, 75.2, 75.0, 66.5, 45.7, 42.4. HRMS-ESI (m/z): calcd for $C_{37}H_{39}NO_6S$, $[M + H]^+$: 626.2576, found 626.2580.

2.7.21. (2S,3S,4S,5R,6S)-4,5-bis(benzyloxy)-3-((4-bromobenzyl)oxy)-6-methoxy-*N*-(4-methoxybenzyl) tetrahydro-2H-pyran-2-carboxamide (4a)

Yield: 92% (115 mg) as light brown solid; mp. 170-172 ℃; $[\alpha]_D^{25}$= -1.9 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 3H), 7.25 – 7.17 (m, 9H), 7.04 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.25 (t, *J* = 5.5 Hz, 1H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.72 – 4.67 (m, 2H), 4.59 – 4.54 (m, 2H), 4.51 (d, *J* = 3.5 Hz, 1H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.27 (d, *J* = 5.5 Hz, 2H), 3.98 (d, *J* = 9.9 Hz, 1H), 3.89 (t, *J* = 9.3 Hz, 1H), 3.69 (s, 3H), 3.48 – 3.43 (m, 2H), 3.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.5, 159.0, 138.4, 137.8, 136.8, 131.3, 129.6, 129.6, 129.2, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6, 121.5, 114.0, 98.3, 81.3, 80.1, 79.0, 77.2, 75.8, 74.1, 73.4, 70.5, 55.7, 55.2, 42.8. HRMS-ESI (m/z): calcd for $C_{36}H_{38}BrNO_6$, $[M + H]^+$: 660.1961, found 660.1968.

2.7.22. (2S,3R,4S,5S,6S)-2-methoxy-6-((4-methoxybenzyl)carbamoyl)tetrahydro-2H-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) (4b)

Yield: 86% (108 mg) as a light brown sticky solid; $[\alpha]_D^{25}$= 14.7 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.51 (t, *J* = 5.5 Hz, 1H), 5.54 (t, *J* = 9.8 Hz, 1H), 5.08 (t, *J* = 9.8 Hz, 1H), 4.91 (d, *J* = 3.7 Hz, 1H), 4.68 (dd, *J* = 10.1, 3.7 Hz, 1H), 4.39 – 4.34 (m, 1H), 4.22 – 4.19 (m, 1H), 4.17 (d, *J* = 10.3 Hz, 1H), 3.73 (s, 3H), 3.32 (s, 3H), 1.13 (s, 9H), 1.09 (s, 9H), 1.05 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.7, 176.8, 176.6, 166.9, 159.0, 129.7, 129.2, 114.0, 96.6, 77.2, 70.8, 69.3, 68.7, 68.4, 56.1,

55.2, 42.5, 38.6, 38.6, 38.6, 27.1, 27.1, 26.8. HRMS-ESI (m/z): calcd for $C_{30}H_{45}NO_{10}$, $[M + H]^+$: 580.3122, found 580.3132.

2.7.23. (2S,3R,4S,5S,6S)-2-methoxy-6-((4-methoxybenzyl)carbamoyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate (4c)

Yield: 88% (111 mg) as a light brown sticky solid; $[\alpha]_D^{25}$= 15.5 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 4H), 7.81 – 7.79 (m, 2H), 7.46 – 7.41 (m, 2H), 7.38 – 7.35 (m, 1H), 7.33 – 7.29 (m, 4H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.65 (t, *J* = 5.6 Hz, 1H), 6.11 (t, *J* = 9.9 Hz, 1H), 5.59 (t, *J* = 9.9 Hz, 1H), 5.20 (d, *J* = 3.5 Hz, 1H), 5.14 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.46 (d, *J* = 10.2 Hz, 1H), 4.40 – 4.37 (m, 1H), 4.27 – 4.23 (m, 1H), 3.74 (s, 3H), 3.39 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.9, 165.8, 165.6, 165.4, 159.1, 133.5, 133.1, 133.1, 129.9, 129.9, 129.6, 129.3, 129.2, 129.0, 128.7, 128.5, 128.4, 128.3, 128.2, 114.1, 97.1, 71.7, 70.2, 69.7, 68.5, 56.1, 55.2, 42.6. HRMS-ESI (m/z): calcd for $C_{36}H_{33}NO_{10}$, $[M + H]^+$: 640.2183, found 640.2172.

2.7.24. (3aR,5S,5aR,8aS,8bR)-*N*-(4-methoxybenzyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-carboxamide (4d)

Yield: 93% (73 mg) as a light brown sticky solid; $[\alpha]_D^{25}$= -10.3 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.7 Hz, 2H), 6.78 – 6.77 (m, 3H), 5.48 (d, *J* = 4.9 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.0 Hz, 1H), 4.62 – 4.58(m, 2H), 4.29 – 4.28 (m, 2H), 4.18 – 4.14 (m, 1H), 3.72 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.2, 158.8, 129.9, 128.9, 113.8, 109.3, 109.2, 96.1, 70.6, 70.3, 68.7, 55.2, 42.2, 25.9, 25.8, 24.7, 24.1. HRMS-ESI (m/z): calcd for $C_{20}H_{27}NO_7$, $[M + H]^+$: 394.1866, found 394.1864.

2.7.25. (2S,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-*N*-(4-methoxybenzyl)-6-(phenylthio)tetrahydro -2H-pyran-2-carboxamide (4e)

Yield: 90% (113 mg) as brown sticky solid; $[\alpha]_D^{25}$= 0.9 [c 0.1, $CHCl_3$], **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.31 – 7.17 (m, 15H), 7.14 – 7.12 (m, 1H), 7.07 – 7.04 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.80 (t, *J* = 5.8 Hz, 1H), 6.65 – 6.62 (m, 2H), 4.80 (d, *J* = 11.1 Hz, 1H), 4.71 – 4.51 (m, 6H), 4.39 – 4.35 (m, 2H), 4.25 – 4.20 (m, 1H), 3.89 – 3.83 (m, 2H), 3.68 (s, 3H), 3.58 (dd, *J* = 9.2, 2.8 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.7, 158.8, 138.5, 138.0, 137.8, 132.8, 132.1, 129.5, 128.9, 128.8, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 127.6, 127.5, 127.3, 113.9, 86.9, 83.1, 78.0, 76.6, 75.6, 74.7, 74.7, 72.3, 55.2, 42.4. HRMS-ESI (m/z): calcd for $C_{42}H_{43}NO_6S$, $[M + H]^+$: 690.2889, found 690.2875.

2.8 Spectral data for few products

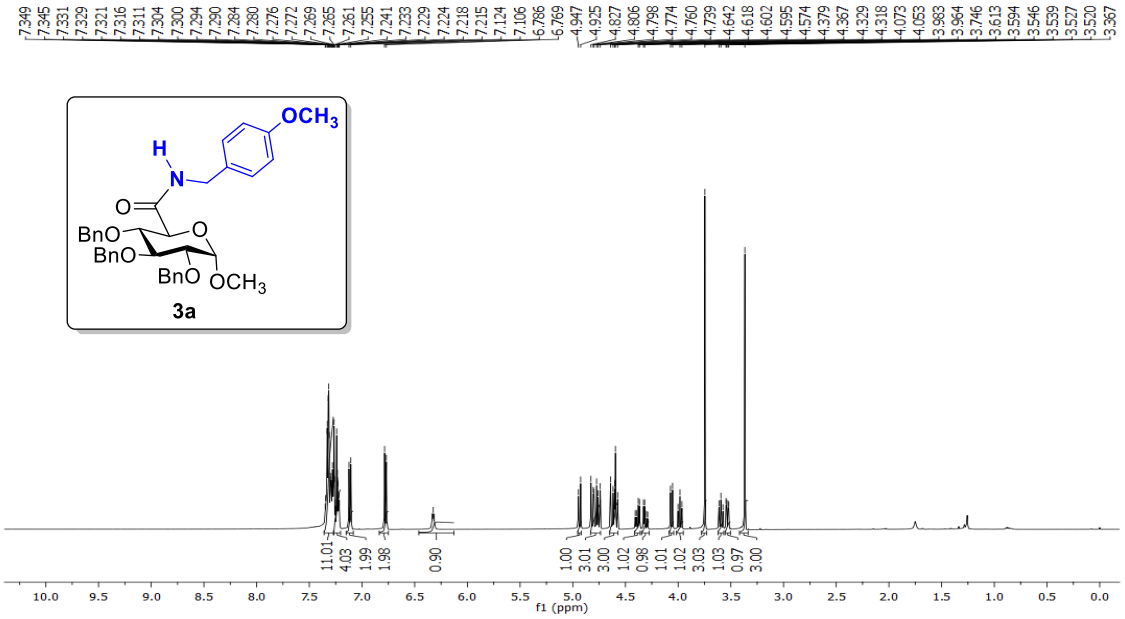


Figure 2.2 ^{1}H NMR Spectra for 3a in $CDCl_3$

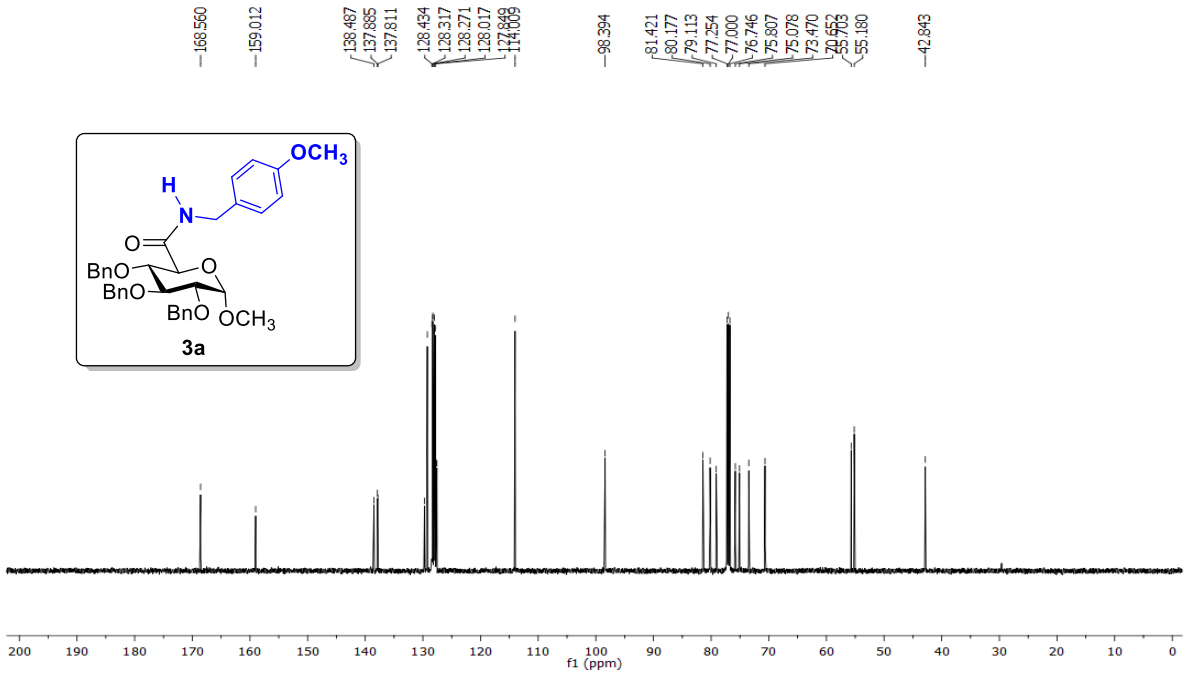


Figure 2.3 ^{13}C NMR Spectra for 3a in $CDCl_3$

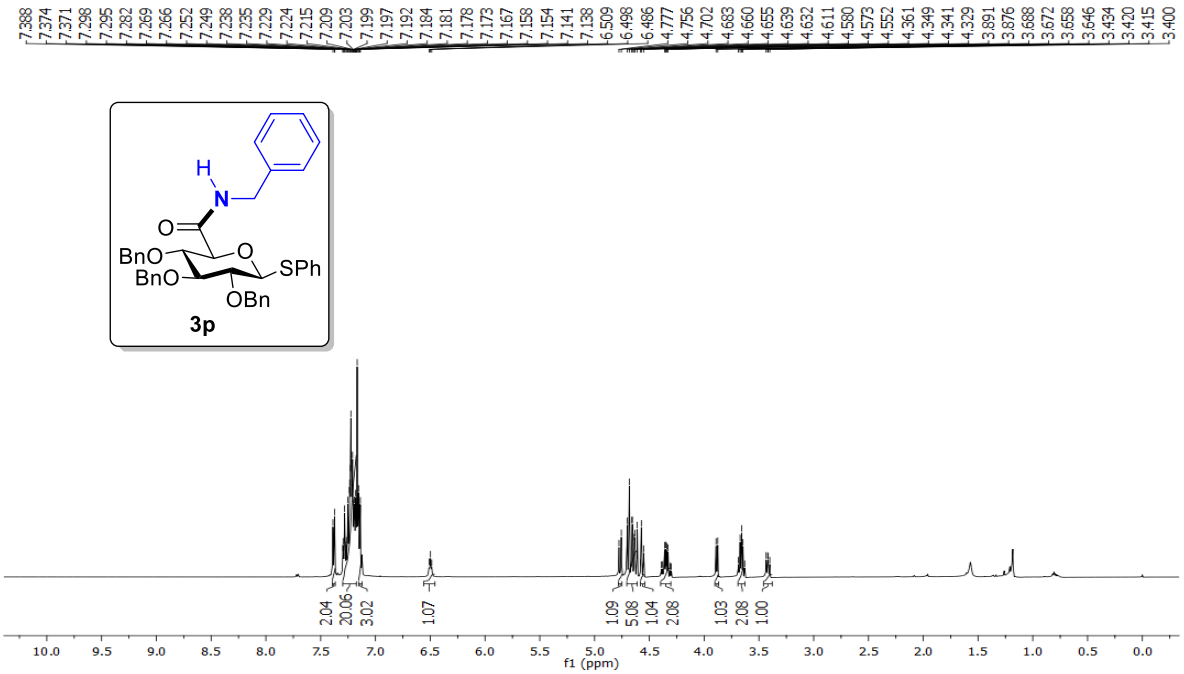


Figure 2.4 ^{1}H NMR Spectra for 3p in $CDCl_3$

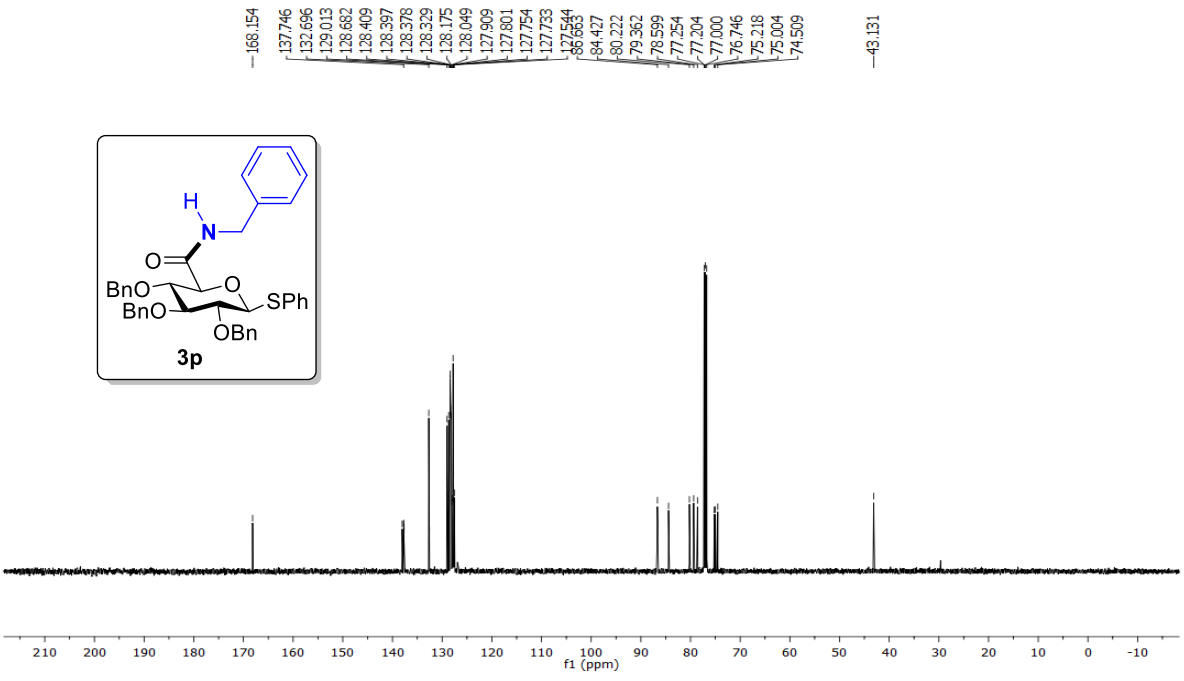


Figure 2.5 ^{13}C NMR Spectra for 3p in $CDCl_3$

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