Approach to Artificial Nucleosides from Glycoside Isothiocyanates: Synthesis of Original *N*-Glycosylated Heterostructures by Cyclocondensation Reactions

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Abstract: Unusual purine nucleoside analogues were synthesized, using the well-tried methodology in heterocyclic chemistry. This result expands the scope of accessible *N*-glycosylated heterocyclic structures. Pyrimidine, and bicyclic pyrimido[1,2-*a*]pyrimidine nucleoside analogues were prepared from common glycoside isothiocyanate precursors. Key cyclization steps were all based on a cyclocondensation reaction involving an activated heterodienic chain. Finally, thirteen pyrimido[1,2-*a*]pyrimidine nucleoside analogues **13a-m** were synthesized with a 30% yield on average, over 8 or 9 steps from one of the isothiocyanates **4a-c**. These elaborated targets were fully characterized.

Introduction

Nucleoside analogues have been widely used as antiviral and antitumor agents. Modified nucleobases have provided interesting progress in pharmaceutical applications.^[1–3] For example, 5-azacytidine and 6-azacytidine exhibit strong activity by means of their triazine skeletons (Figure 1).^[4–7] Modulation of the sugar part has also found many applications in the pharmaceutical field. Acyclovir (Zovirax®) for instance marked the beginning of a new era for antiviral drugs.^[8,9] In this molecule, an acyclic chain acts as a ribofuranose mimic (Figure 1).

Figure 1. Bioactive Nucleoside Analogues.

In this context, we published the synthesis of *N*-glycosyl 1,3,5-triazines as potential 5-azacytidine analogues.^[10] Specifically, synthesis of glycoside **1** with the acyclic sugar part of acyclovir

was carried out successfully (Figure 2). Furthermore, we have also published the synthesis of different non-natural *N*-glycosyl pyrimidines. Furanosides, pyranosides, as well as disaccharides were isolated.^[11–13] Perbenzoylated ribofuranoside **2** and peracetylated glucopyranoside **3** represent this class of targeted and isolated pyrimidines (Figure 2).

Figure 2. Modified nucleosides.

To complete the study of modified nucleosides, we considered preparing a kind of purine nucleobase analogue. Thus, while taking advantage of our knowledge in the synthesis of heterocycles,^[14–17] we broadened the range of *N*-glycosyl heterocyclic structures to sophisticated bicyclic scaffolds: pyrimido[1,2-*a*]pyrimidine-2,6-diones (Figure 3).

Figure 3. New bicyclic nucleobase analogues.

Results and Discussion

Our study was limited to three glycosyl or related groups (Figure 4). The stable β -linked ribofuranosyl and glucopyranosyl isothiocyanates **4a** (RibOBz) and **4b** (GluOAc) were easily prepared from the corresponding inexpensive perbenzoylated or peracetylated glycosides.^[11,18,19] The OAc-protected acyclic carbohydrate isothiocyanate **4c** (AcyOAc) was isolated from 1,3-dioxolane as already described.^[20]

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Figure 4. Glycosyl isothiocyanates.

Construction of the bicyclic skeleton of pyrimido[1.2-a]pyrimidines was based on two similar cyclocondensation reactions involving a 1,3-diazabutadiene, activated by a dimethylamino group on position 4 giving rise to an internal push-pull effect.^[21] The first diazabutadiene chain (**8a-c**) was synthesized in 4 steps from the isothiocyanate function (Scheme 1). Isothiocyanates **4a-c** reacted in ammonia saturated solution of toluene to give thioureas **5a-c**. It's worth noting that at this stage the reaction in a commercial 7M solution of ammonia in methanol, as used in non-glycosylated series, led to the deprotection of hydroxyl groups on the sugar moiety.^[22] Condensation of thioureas **5a-c** with *N,N*-dimethylformamide dimethyl acetal (DMF-DMA) afforded thiazadienes **6a-c**. Sulfur was then alkylated with methyl iodide to give 2-methylsulfanyl diazadienium iodides **7a-c**; and the neutralization step with triethylamine afforded diazadienes **8a-c**. All chemical yields are reported in Table 1. Cyclocondensation reactions between diazadienes **8a-c** and acetyl chlorides R^1CH_2COCl in the presence of triethylamine took place as expected (Scheme 1). This tandem [4+2] cycloaddition/loss of dimethylamine first led to limited yields when starting from diazadienium iodides, as carried out in non-glycosylated series, instead of neutral diazadienes. But in the end, good to excellent yields were reported (Table 2). Methylmalonyl chloride ($R^1 = CO_2Me$), phenylacetyl chloride ($R^1 = Ph$) and acetyl chloride ($R^1 = H$) were used. Finally, nine pyrimidine nucleoside analogues **9a-i** were prepared from the 3 isothiocyanates **4a-c**.

Scheme 1. First cyclization into pyrimidines.

Table 1. Functionalization of an isothiocyanate into a diazadienic chain (**4a-c** → **8a-c**).

Entry	Sugar	Cpd	Yd	Cpd	Yd	Cpd	Yd	Cpd	Yd
1	<i>RibOBz</i>	5a	100	6a	84	7a	85	8a	97
2	<i>GluOAc</i>	5b	100	6b	99	7b	100	8b	98
3	<i>AcyOAc</i>	5c	88	6c	99	7c	100	8c	93

Table 2. First cyclocondensation reaction from the diazadienic chain and an acyl chloride (R^1) (**8a-c** → **9a-i**).

Entry	Sugar	R^1	Compound	Yield %
1	<i>RibOBz</i>	CO_2Me	9a	71
2	<i>GluOAc</i>	CO_2Me	9b	79
3	<i>AcyOAc</i>	CO_2Me	9c	92
4	<i>RibOBz</i>	Ph	9d	97
5	<i>GluOAc</i>	Ph	9e	80
6	<i>AcyOAc</i>	Ph	9f	76
7	<i>RibOBz</i>	H	9g	97
8	<i>GluOAc</i>	H	9h	94
9	<i>AcyOAc</i>	H	9i	84

The next step for introduction of a second diazadienic chain onto the pyrimidine structure consisted in substitution of the SMe group for an amino group (Scheme 2). This could be directly and quantitatively performed with R^1 being an electron withdrawing group (CO_2Me) and the use of NH_3 gas in toluene, affording compounds **10a-c**. However, in the other cases, activation of the methylsulfanyl group into sulfone was necessary. We previously reported on the nucleophilic displacement of methylsulfanyl groups on heterocycles.^[23] The oxidation step into sulfone was carried out with a freshly distilled solution of dimethyldioxirane (DMDO) in acetone, a powerful anhydrous oxidant.^[24,25] With $R^1 =$ phenyl, isolation of the sulfones **11d-f** was achieved quantitatively, and subsequent nucleophilic substitution by ammonia provided compounds **10d-f**. Unfortunately, all attempts to isolate sulfones from compounds **9g-i** ($R^1 = H$) failed. Oxidation reaction step of the methylsulfanyl group was proven to occur by 1H NMR analysis (through methyl chemical displacement shift), but the latter resulting sulfones gradually made way for the product of hydrolysis (uracil derivative) in the NMR tube. In fact, hydrolysis took place as soon as we tried to isolate the sulfones. Immediate attempts to substitute *in situ* the methylsulfanyl group with ammonia were not fruitful. It is supposed that the aromatic character of the phenyl group stabilizes the sulfones (**11d-f**)

through an enrichment of the electronic density of the heterocycle, while the hydrogen atom does not.

Scheme 2. Direct and indirect displacement of the S-methyl group.

Guanidine like intermediates **10a-f** were then reacted with DMF-DMA to give cyclization precursors (Scheme 3). Only compound **10f** (Sugar = AcyOAc; R^1 = Ph) did not produce the expected condensation product. All chemical yields are reported in Table 3. Cyclocondensation reactions between dimethylamino-diazabutadienes **12a-e** and acetyl chlorides R^2CH_2COCl in the presence of triethylamine took place successfully (Scheme 3). As observed in non-glycosylated series, the lowest reactivity of substrates **12a-c** with R^1 = CO_2Me required the use of 6 equivalents of acyl chloride and triethylamine. Yields ranged from 75 to 99% (Table 4). Methylmalonyl chloride (R^2 = CO_2Me), acetyl chloride (R^2 = H) and methoxyacetyl chloride (R^2 = OMe) were used. Surprisingly, methylmalonyl chloride did not react at all with substrates **12d** (Sugar = RibOBz; R^1 = Ph) and **12e** (Sugar = GluOAc; R^1 = Ph) which were recovered quantitatively. In the end, thirteen pyrimido[1.2-a]pyrimidine nucleoside analogues **13a-m** were synthesized with a 30% yield on average, over 8 or 9 steps from one of the isothiocyanates **4a-c**. These elaborated targets were fully characterized.

Scheme 3. Second cyclization into pyridopyrimidines.

Table 3. Introduction of a second diazadienic chain (**9a-f** → **12a-e**).

Entry	Sugar	R^1	Cpd	Yield	Cpd	Yield
1	RibOBz	CO_2Me	10a	100	12a	96
2	GluOAc	CO_2Me	10b	100	12b	98
3	AcyOAc	CO_2Me	10c	67	12c	100
4	RibOBz	Ph	10d	100	12d	96
5	GluOAc	Ph	10e	100	12e	91
6	AcyOAc	Ph	10f	62	-	-

Table 4. Second cyclocondensation reaction from the diazadienic chain and an acyl chloride (R^2) (**12a-e** → **13a-m**).

Entry	Sugar	R^1	R^2	Compound	Yield %
1	RibOBz	CO_2Me	CO_2Me	13a	92
2	GluOAc	CO_2Me	CO_2Me	13b	80
3	AcyOAc	CO_2Me	CO_2Me	13c	87
4	RibOBz	CO_2Me	H	13d	87
5	GluOAc	CO_2Me	H	13e	86
6	AcyOAc	CO_2Me	H	13f	97
7	RibOBz	CO_2Me	OMe	13g	75
8	GluOAc	CO_2Me	OMe	13h	76
9	AcyOAc	CO_2Me	OMe	13i	85
10	RibOBz	Ph	H	13j	99

11	<i>GluOAc</i>	Ph	H	13k	97
12	<i>RibOBz</i>	Ph	OMe	13l	85
13	<i>GluOAc</i>	Ph	OMe	13m	83

Conclusions

Given the large range of accessible *N*-glycosylated heterocycles, exploration of biological properties of these artificial nucleosides is of interest. Indeed these types of *N*-nucleosides may be attractive in view of antiviral or antitumor activities. Pharmacomodulation could easily be envisioned by variation of the sugar part and/or variation of the aglycone part through further modulation of the heterocycle substituents. Deprotection of the sugar moieties should be considered for biological test purposes.

Experimental Section

General: NMR spectra were recorded at room temperature with a Bruker Avance 300 Ultra Shield or eBruker Avance III 400 spectrometer. Chemical shifts are reported in parts per million (ppm); coupling constants are reported in Hertz (Hz). Infrared (IR) spectra were recorded with a Bruker Vector 22 FTIR using KBr films or KBr pellets. Low-resolution mass spectra (MS) were recorded with a Thermo electron DSQ spectrometer. High-resolution mass spectra (HRMS) were recorded with a Bruker Autoflex III SmartBeam spectrometer (MALDI). Melting points were determined in open capillary tubes and are uncorrected. All reagents were purchased from Acros Organics or Aldrich and were used without further purification. Column chromatography was conducted on silica gel Kieselgel Si60 (40–63 μ m) from Merck. Compounds **4a–c** were synthesized according to literature procedures.^[11,20]

Typical procedure for compounds **5a–c**:

Gaseous ammonia was passed for 30 min through a solution of compounds **4a–c** in toluene, and the medium was stirred at room temperature for 6 h. The corresponding thioureas **5a–b** were obtained as pure material after removal of the solvent under reduced pressure. For **5c**, the residue was purified by chromatography on silica gel (ethyl acetate/dichloromethane 7:3).

***N*-(2',3',5'-Tri-*O*-benzoyl- β -D-ribofuranosyl)thiourea (**5a**):** m.p. 164–166°C. ¹H NMR (300 MHz, CDCl₃): δ = 4.61 (dd, *J* = 13.1 and 5.3 Hz, 1 H, 5'-H_a), 4.68–4.72 (m, 2 H, 4'-H and 5'-H_b), 5.68 (t, *J* = 5.3 Hz, 1 H, 2'-H), 5.79 (t, *J* = 5.3 Hz, 1 H, 3'-H), 6.50 (broad s, 1 H, 1'-H), 7.34–7.59 (m, 9 H, H_{ar}), 7.92–8.04 (m, 6 H, H_{ar}) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 64.1 (5'), 71.6 (3'), 74.6 (2'), 79.4 (4'), 87.3 (1'), 128.7–130.0 and 133.5–134.0 (C_{ar}), 165.7, 166.1 and 166.5 [3 C(O)Ph], 184.9 (C=S) ppm. IR (KBr): ν = 3425 (s), 3219 (m), 3064 (w), 1724 (s), 1622 (m), 1602 (m), 1583 (m), 1489 (w), 1451 (m), 1316 (m), 1272 (s) cm⁻¹. MS (Cl⁺, NH₃): *m/z* (%) = 521 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₂₇H₂₄N₂NaO₇S [M + Na]⁺ = 543.1196; found 543.1200.

***N*-(2',3',4',6'-Tetra-*O*-acetyl- β -D-glucopyranosyl)thiourea (**5b**):** m.p. 160–161°C. ¹H NMR (300 MHz, CDCl₃): δ = 2.02 and 2.03 [2 s, 6 H, 2 C(O)CH₃], 2.08 [s, 6 H, 2 C(O)CH₃], 3.85 (ddd, *J* = 9.7, 4.9 and 1.9 Hz, 1 H, 5'-H), 4.14 (dd, *J* = 12.4 and 1.9 Hz, 1 H, 6'-H_a), 4.30 (dd, *J* = 12.4 and 4.9 Hz, 1 H, 6'-H_b), 4.97 (t, *J* = 9.7 Hz, 1 H, 2'-H), 5.05 (t, *J* = 9.7 Hz, 1 H, 4'-H), 5.35 (t, *J* = 9.7 Hz, 1 H, 3'-H), 5.48 (t, *J* = 9.7 Hz, 1 H, 1'-H), 5.94 (broad s, 2 H, NH₂), 6.64 (broad d, *J* = 7.5 Hz, 1 H, NH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 20.6 and 20.8 [4 C(O)CH₃], 61.9 (6'), 68.4 (4'), 70.6 (2'), 72.7 (3'), 73.8 (5'), 83.3 (1'), 169.7, 169.9, 170.9 and 171.4 [4 C(O)CH₃], 185.1 (C=S) ppm. IR (KBr): ν = 3446 (s), 3365 (s), 3318 (s), 1748 (s), 1613 (w), 1230 (m) cm⁻¹. MS (Cl⁺, NH₃): *m/z* (%) = 407 [M + H]⁺. HRMS (ESI⁺): *m/z* calcd. for C₁₅H₂₂N₂NaO₉S [M + Na]⁺ = 429.0944; found 429.0949.

***N*-[(2'-*O*-Acetoxyethoxy)methyl]thiourea (**5c**):** m.p. 72–73°C. ¹H NMR (300 MHz, CDCl₃): δ = 2.09 [s, 3 H, C(O)CH₃], 3.75 [broad s, 2 H, C(O)OCH₂CH₂O], 4.20–4.25 [m, 2 H, C(O)OCH₂CH₂O], 4.67 (s, 2 H, OCH₂N), 6.64 (broad s, 2 H, NH₂), 7.79 (broad s, 1 H, NH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 20.9 [C(O)CH₃], 63.0 [C(O)OCH₂CH₂O], 65.9 [C(O)OCH₂CH₂O], 74.4 (OCH₂N), 171.1 [C(O)CH₃], 184.6 (C=S) ppm. IR (KBr): ν = 3385 (s), 3231 (s), 3191 (s), 2880 (w), 1743 (s), 1631 (s), 1248 (s) cm⁻¹. MS (EI, 70 eV): *m/z* (%) = 192 (5) [M]⁺, 132 (21), 105 (23), 60 (22), 43 (100). HRMS (ESI⁺): *m/z* calcd. for C₆H₁₂N₂NaO₃S [M + Na]⁺ = 215.0466; found 215.0468.

Typical procedure for compounds **6a–c**:

N,N-dimethylformamide dimethylacetal (1.2 eq) was added to a suspension of substituted thioureas **5a–c** (1.0 eq) in dichloromethane. The mixture was stirred at room temperature for 1 h for **6c**, 2 h for **6a** and **6b**. Then, the organic mixture was concentrated under vacuum. And the residue was purified by chromatography on silica gel (for **6a**: ethyl acetate/petroleum ether 30:70; for **6b**: ethyl acetate/petroleum ether 60:40; for **6c**: ethyl acetate/dichloromethane 70:30).

1-[(2',3',5'-Tri-*O*-benzoyl- β -D-ribofuranosyl)amino]-4-dimethylamino-1,3-thiazabuta-1,3-diene (6a**):** m.p. 99–101°C. ¹H NMR (300 MHz, CDCl₃) Major isomer (68%): δ = 2.98 and 3.12 [2 s, 6 H, N(CH₃)₂], 4.57–4.74 (m, 3 H, 4'-H and 5'-H), 5.77 (t, *J* = 5.6 Hz, 1 H, 2'-H), 5.82–5.87 (m, 1 H, 3'-H), 6.70 (dd, *J* = 8.8 and 5.6 Hz, 1 H, 1'-H), 7.33–7.59 (m, 15 H, H_{ar}), 8.82 (s, 1 H, 4-H) ppm; Minor Isomer (32%, selected data): δ = 3.05 and 3.16 [2 s, 6 H, N(CH₃)₂], 6.24 (dd, *J* = 7.3 and 3.0 Hz, 1 H, 1'-H), 7.85–8.12 (m, 15 H, H_{ar}) ppm. ¹³C NMR (75 MHz, CDCl₃) Major isomer: δ = 35.9 and 41.6 [N(CH₃)₂], 64.4 (5'), 71.8 (3'), 74.4 (2'), 79.2 (4'), 86.7 (1'), 128.5–130.0 and 133.3–133.6 (C_{ar}), 162.9 (4), 165.1–166.3 [3 C(O)Ph], 195.8 (2) ppm; Minor Isomer (selected data): δ = 36.2 and 41.8 [N(CH₃)₂], 64.1 (5'), 71.4 (3'), 75.0 (2'), 78.8 (4'), 85.9 (1'), 163.6 (4), 193.7 (2) ppm. IR (KBr): ν = 3429 (m), 3062 (f), 2928 (f), 1727 (F), 1625 (F), 1601 (m), 1583 (f), 1491 (m), 1451 (m), 1423 (f), 1336 (m), 1271 (F), 1025 (m) cm⁻¹. MS (Cl⁺, NH₃): *m/z* (%) = 576 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₃₀H₂₉N₃NaO₇S [M + Na]⁺ = 598.1618; found 598.1614.

2-[(2',3',4',6'-Tetra-*O*-acetyl- β -D-glucopyranosyl)amino]-4-dimethylamino-1,3-thiazabuta-1,3-diene (6b**):** m.p. 89–90°C. ¹H NMR (300 MHz, CDCl₃) Major isomer (77%): δ = 2.01–2.05 [m, 12 H, 4 C(O)CH₃], 3.03 and 3.14 [2 s, 6 H, N(CH₃)₂], 3.89 (ddd, *J* = 9.7, 4.3 and 2.1 Hz, 1 H, 5'-H), 4.12 (dd, *J* = 12.4 and 2.1 Hz, 1 H, 6'-H_a), 4.33 (dd, *J* = 12.4 and 4.3 Hz, 1 H, 6'-H_b), 5.08 (t, *J* = 9.7 Hz, 1 H, 2'-H), 5.08 (t, *J* = 9.7 Hz, 1 H, 4'-H), 5.38 (t, *J* = 9.7 Hz, 1 H, 3'-H), 5.93 (t, *J* = 9.7 Hz, 1 H, 1'-H), 7.06 (d, *J* = 9.7 Hz, 1 H, NH), 8.78 (s, 1 H, 4-H) ppm; Minor Isomer (23%, selected data): δ = 3.10 and 3.19 [2 s, 6 H, N(CH₃)₂], 5.60 (t, *J* = 9.6 Hz, 1 H, 1'-H), 7.14 (d, *J* = 9.6 Hz, 1 H, NH) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: δ = 20.7 [4 C(O)CH₃], 36.0 and 41.7 [N(CH₃)₂], 61.8

(6'), 68.5 (4'), 70.7 (2'), 73.2 (3'), 73.6 (5'), 82.6 (1'), 163.1 (4), 169.7. 170.0. 170.8 and 171.0 [4 C(O)CH₃], 196.7 (2) ppm; Minor Isomer (selected data): δ = 60.3 (6'), 70.5 (2'), 80.1 (1'), 163.7 (4), 195.5 (2) ppm. IR (KBr): ν = 3354 (m), 2940 (f), 1750 (F), 1629 (F), 1507 (m), 1224 (m) cm⁻¹. MS (Cl⁺, NH₃): m/z (%) = 462 [M + H]⁺. HRMS (ESI⁺): m/z calcd. for C₁₈H₂₈N₃O₃S [M + H]⁺ = 462.1546; found 462.1548.

2-[(2'-O-Acetoxyethoxy)methylamino]-4-dimethylamino-1,3-thiazabuta-1,3-diene (6c):

m.p. 67-68°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (60%): δ = 2.04 [s, 3 H, C(O)CH₃], 3.03 and 3.14 [2 s, 6 H, N(CH₃)₂], 3.80-3.83 [m, 2 H, C(O)OCH₂CH₂O], 4.14-4.19 [m, 2 H, C(O)OCH₂CH₂O], 5.25 (d, J = 6.6 Hz, 2 H, OCH₂N), 7.26 (broad t, J = 6.6 Hz, 1 H, NH), 8.84 (s, 1 H, 4-H) ppm. Minor Isomer (40%, selected data): δ = 3.08 and 3.17 [2 s, 6 H, N(CH₃)₂], 3.67-3.70 [m, 2 H, C(O)OCH₂CH₂O], 4.95 (d, J = 6.6 Hz, 2 H, OCH₂N), 7.45 (broad t, J = 6.6 Hz, 1 H, NH), 8.82 (s, 1 H, 4-H) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: δ = 21.0 [C(O)CH₃], 35.8 and 41.5 [N(CH₃)₂], 63.6 [C(O)OCH₂CH₂O], 66.7 [C(O)OCH₂CH₂O], 75.0 (OCH₂N), 163.1 (4), 171.0 [C(O)CH₃], 196.0 (2) ppm. Minor Isomer (selected data): δ = 36.1. 41.6 [N(CH₃)₂], 63.4 (OCH₂^b), 66.2 (OCH₂^a), 72.2 (NCH₂O), 163.8 (C^d) ppm. IR (KBr): ν = 3220 (m), 3012 (f), 1736 (F), 1623 (F), 1524 (m), 1491 (f) cm⁻¹. MS (EI, 70 eV): m/z (%) = 248 (3), 247 (20) [M]⁺, 160 (26), 115 (100), 98 (18), 87 (15) ppm. HRMS (EI, 70 eV): m/z calcd. for C₉H₁₇N₃O₃S [M]⁺ = 247.0991; found 247.0994.

Typical procedure for compounds 7a-c:

Methyl iodide (2 eq) was added to a suspension of thiazadiene **6a-c** (1.0 eq) in THF. The mixture was stirred at room temperature for 3 h for **7c**, 6 h for **7a** and **7b**. The solvent was removed and the residue was crystallized from ether.

1-(2',3',5'-Tri-O-benzoyl- β -D-ribofuranosyl)-4-dimethylamino-2-methylsulfanyl-1,3-diazabuta-1,3-dienium iodide (7a):

m.p. 116-118°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (85%): δ = 2.55 (s, 3 H, SCH₃), 3.16 and 3.42 [2 s, 6 H, N(CH₃)₂], 4.68 (dd, J = 11.1 and 5.4 Hz, 1 H, 4'-H), 4.82 (d, J = 5.4 Hz, 2 H, 5'-H), 5.83 (broad s, 1 H, 1'-H), 6.17 (t, J = 5.4 Hz, 1 H, 3'-H), 6.33 (dd, J = 5.4 and 3.9 Hz, 1 H, 2'-H), 7.30-7.42 and 7.47-7.54 (2 m, 9 H, H_{ar}), 7.86-7.95 and 8.07-8.10 (2 m, 6 H, H_{ar}), 8.87 (s, 1 H, 4-H), 10.46 (broad s, 1 H, NH) ppm; Minor Isomer (15%, selected data): δ = 3.10 and 3.42 [2 s, 6 H, N(CH₃)₂], 4.54 (dd, J = 11.1. 5.4 Hz, 1 H, 4'-H), 5.57 (broad s, 1 H, 1'-H), 8.28 (s, 1 H, 4-H) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: δ = 15.3 (SCH₃), 36.9 and 43.6 [N(CH₃)₂], 64.1 (5'), 71.8 (3'), 74.3 (2'), 80.4 (4'), 87.9 (1'), 128.5-128.8. 128.9. 129.8-130.0 and 133.1-133.6 (C_{ar}), 157.9 (4), 165.0-166.3 [3 C(O)Ph], 178.1 (2) ppm. IR (KBr): ν = 3434 (m), 3062 (f), 2929 (f), 1727 (F), 1647 (F), 1601 (m), 1583 (f), 1529 (m), 1452 (m), 1404 (f), 1315 (m), 1271 (F) cm⁻¹. MS (Cl⁺, NH₃): m/z (%) = 590 [M - I]⁺. HRMS (MALDI): m/z = calcd. for C₃₁H₃₂N₃O₇S [M - I]⁺ = 590.1961; found 590.1967.

1-(2',3',4',6'-Tetra-O-acetyl- β -D-glucopyranosyl)-4-dimethylamino-2-methylsulfanyl-1,3-diazabuta-1,3-dienium iodide (7b):

m.p. 175-178°C. ¹H NMR (300 MHz, CDCl₃): δ = 2.00. 2.02. 2.07 and 2.13 [4 s, 12 H, 4 C(O)CH₃], 2.57 (s, 3 H, SCH₃), 3.21 and 3.45 [2s, 6 H, N(CH₃)₂], 3.81 (d-e, J = 9.3 Hz, 1 H, 5'-H), 4.13 (d, J = 12.0 Hz, 1 H, 6'-H_a), 4.22 (dd, J = 12.3 and 4.5 Hz, 1 H, 6'-H_b), 5.10 (t, J = 9.3 Hz, 1 H, 4'-H); 5.17 (broad s, 1 H, 3'-H), 5.36 (t, J = 9.3 Hz, 1 H, 2'-H); 5.48 (broad s, 1 H, 1'-H), 8.78 (s, 1 H, 4-H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 15.4 (SCH₃), 20.7, 20.9 and 21.5 [4 C(O)CH₃], 37.1 and 41.6 [N(CH₃)₂], 61.8 (6'), 67.9 (4'), 69.8 (2'), 72.5 (3'), 74.2 (5'), 81.8 (1'), 157.4 (4), 169.5, 170.0 and 170.6 [4 C(O)CH₃], 177.0 (2) ppm. IR (KBr): ν = 3443 (F), 2938 (f), 1749 (F), 1650 (m), 1522 (m), 1231 (F) cm⁻¹. MS (Cl⁺, NH₃): m/z (%) = 476 [M - I]⁺.

1-[(2'-O-Acetoxyethoxy)methyl]-4-dimethylamino-2-methylsulfanyl-1,3-diazabuta-1,3-dienium iodide (7c):

m.p. 148-150°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (78%): δ = 2.01 [s, 3 H, C(O)CH₃], 2.47 (s, 3 H, SCH₃), 3.19 and 3.41 [2 s, 6 H, N(CH₃)₂], 3.82 [dd, J = 4.7 and 4.4 Hz, 2 H, C(O)OCH₂CH₂O], 4.16 [dd, J = 4.7 and 4.4 Hz, 2 H, C(O)OCH₂CH₂O], 4.82 (s, 2 H, OCH₂N), 8.97 (s, 1 H, 4-H), 10.30 (broad s, 1 H, NH) ppm; Minor Isomer (22%): δ = 2.01 [s, 3 H, C(O)CH₃], 2.97 (s, 3 H, SCH₃), 3.19 and 3.41 [2 s, 6 H, N(CH₃)₂], 3.90 [m, 2 H, C(O)OCH₂CH₂O], 4.16 [dd, J = 4.7 and 4.4 Hz, 2 H, C(O)OCH₂CH₂O], 5.11 (s, 2 H, OCH₂N); 8.36 (s, 1 H, 4-H), 10.30 (broad s, 1 H, NH) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: δ = 14.7 (SCH₃), 20.9 [C(O)CH₃], 36.6 and 43.2 [N(CH₃)₂], 63.0 [C(O)OCH₂CH₂O], 67.2 [C(O)OCH₂CH₂O], 73.4 (OCH₂N), 157.5 (4), 170.8 [C(O)CH₃], 179.9 (2) ppm; Minor Isomer: δ = 17.6 (SCH₃), 20.9 [C(O)CH₃], 37.1 and 43.2 [N(CH₃)₂], 63.0 [C(O)OCH₂CH₂O], 67.8 [C(O)OCH₂CH₂O], 72.4 (OCH₂N), 159.2 (4), 170.8 [C(O)CH₃], 177.0 (2) ppm. IR (KBr): ν = 3205 (m), 2943 (f), 1736 (F), 1650 (F), 1540 (F), 1049 (F) cm⁻¹. MS (Cl⁺, NH₃): m/z (%) = 262 (100) [M - I]⁺, 261 (25), 242 (30), 158 (45), 134 (20). HRMS (MALDI): m/z calcd. for C₁₀H₂₀N₃O₃S [M - I]⁺ = 262.1225; found 262.1223.

Typical procedure for compounds 8a-c:

To a suspension of compound **7** (1.0 eq) in dichloromethane was added trimethylamine (2.0 eq). The mixture was stirred at room temperature for 2 h. After evaporation and extraction with a minimum of dichloromethane, the organic layer was washed with water, dried over magnesium sulfate and concentrated under reduced pressure. The residue was crystallized from ether to give **8**.

1-(2',3',5'-Tri-O-benzoyl- β -D-ribofuranosyl)-4-dimethylamino-2-methylsulfanyl-1,3-diazabuta-1,3-diene (8a):

m.p. 85-87°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (75%): δ = 2.40 (s, 3 H, SCH₃), 2.85 and 2.96 [2 s, 6 H, N(CH₃)₂], 4.69-4.80 (m, 3 H, 4'-H and 5'-H), 5.65 (t, J = 4.8 Hz, 1 H, 2'-H), 5.92-5.94 (m, 1 H, 3'-H), 6.16 (s, 1 H, 1'-H), 7.29-7.57 (m, 9 H, H_{ar}), 7.77 (s, 1 H, 4-H), 7.86-7.89. 8.02-8.06 (m, 6 H, H_{ar}) ppm; Minor Isomer (25%, selected data): δ = 2.46 (s, 3 H, SCH₃), 2.81 and 3.01 [2 s, 6 H, N(CH₃)₂] ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: δ = 14.6 (SCH₃), 34.3 and 40.5 [N(CH₃)₂], 66.2 (5'), 74.0 (3'), 77.1 (2'), 78.0 (4'), 93.2 (1'), 128.2-128.4. 129.2. 129.7 and 133.2 (C_{ar}), 154.4 (4), 163.7 (2), 165.0-168.8 [3 C(O)Ph] ppm; Minor Isomer (selected data): δ = 14.9 (SCH₃), 34.7 and 40.2 [N(CH₃)₂], 65.6 (5'), 73.2 (3'), 78.6 (4'), 92.8 (1'), 129.7 and 132.9 (C_{ar}), 154.2 (4), 161.9 (2) ppm. IR (KBr): ν = 2957 (f), 1722 (F), 1701 (F), 1646 (m), 1583 (m), 1316 (f) cm⁻¹. MS (Cl⁺, NH₃): m/z (%) = 590 [M + H]⁺. MS (EI, 70 eV): m/z (%) = 589 (4) [M]⁺, 530 (5), 445 (100), 346 (64), 250 (11). HRMS (MALDI): m/z calcd. for C₃₁H₃₂N₃O₇S [M + H]⁺ = 590.1955; found 590.1957.

1-(2',3',4',6'-Tetra-O-acetyl- β -D-glucopyranosyl)-4-dimethylamino-2-methylsulfanyl-1,3-diazabuta-1,3-diene (8b):

m.p. 109-110°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (53%): δ = 1.90. 2.01. 2.02 and 2.06 [4 s, 12 H, 4 C(O)CH₃], 2.45 (s, 3 H, SCH₃), 2.98 [s, 6 H, N(CH₃)₂], 3.77-3.85 (m, 1 H, 5'-H), 4.12 (dd, J = 12.2 and 2.0 Hz, 1 H, 6'-H_a), 4.25 (dd, J = 12.2 and 6.3 Hz, 1 H, 6'-H_b), 4.98 (d, J = 8.4 Hz, 1 H, 1'-H); 5.05-5.20 (m, 2 H, 2'-H and 4'-H), 5.27-5.31 (m, 1 H, 3'-H); 7.77 (s, 1 H, 4-H) ppm; Minor Isomer (47%, selected data): δ = 2.35 (s, 3 H, SCH₃), 3.05 [s, 6 H, N(CH₃)₂], 5.45 (d, J = 8.4 Hz, 1 H, 1'-H); 8.09 (broad s, 1 H, 4-H) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: δ = 14.7 (SCH₃), 20.7 and 20.9 [4 C(O)CH₃], 34.6 and 40.6 [N(CH₃)₂], 62.6 (6'-H), 73.2 (4'-H), 73.5, 73.7 and 73.8 (2', 3' and 5'), 86.4 (1'), 154.6 (4), 167.5 (2), 169.3-170.9 [4 C(O)CH₃] ppm; Minor Isomer (selected data): δ = 15.1 (SCH₃), 34.7 and 40.9 [N(CH₃)₂], 73.1 (4'), 88.5 (1') ppm. IR (KBr): ν = 2963 (m), 1751 (F), 1730

(F), 1635 (m), 1588 (F) cm^{-1} . MS (Cl^+ , NH_3): m/z (%) = 476 [$\text{M} + \text{H}$] $^+$. HRMS (ESI^+): m/z calcd. for $\text{C}_{19}\text{H}_{30}\text{N}_3\text{O}_5\text{S}$ [$\text{M} + \text{H}$] $^+$ = 476.1703; found 476.1705.

1-[(2'-O-Acetoxyethoxy)methyl]-4-dimethylamino-2-methylsulfanyl-1,3-diazabuta-1,3-diene (8c): colorless oil. ^1H NMR (300 MHz, CDCl_3) Major Isomer (56%): δ = 2.03 [s, 3 H, $\text{C}(\text{O})\text{CH}_3$], 2.34 (s, 3 H, SCH_3), 2.90 and 2.98 [2 s, 6 H, $\text{N}(\text{CH}_3)_2$], 3.73-3.80 [m, 2 H, $\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{O}$], 4.20-4.25 [m, 2 H, $\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{O}$], 4.97 (s, 2 H, OCH_2N), 7.71 (s, 1 H, 4-H) ppm; Minor Isomer (44%): δ = 2.03 [s, 3 H, $\text{C}(\text{O})\text{CH}_3$], 2.41 (s, 3 H, SCH_3), 2.97 and 3.03 [2 s, 6 H, $\text{N}(\text{CH}_3)_2$], 3.73-3.80 [m, 2 H, $\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{O}$], 4.20-4.25 [m, 2 H, $\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{O}$], 4.77 (s, 2 H, NCH_2O), 8.11 (s, 1 H, 4-H) ppm. ^{13}C NMR (75 MHz, CDCl_3) Major Isomer: δ = 14.4 (SCH_3), 21.0 [$\text{C}(\text{O})\text{CH}_3$], 34.3 and 40.5 [$\text{N}(\text{CH}_3)_2$], 64.0 [$\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{O}$], 65.8 [$\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{O}$], 82.8 (OCH_2N), 154.1 (4), 159.4 (2), 171.2 [$\text{C}(\text{O})\text{CH}_3$] ppm; Minor Isomer: δ = 14.6 (SCH_3), 21.0 [$\text{C}(\text{O})\text{CH}_3$], 34.6 and 40.7 [$\text{N}(\text{CH}_3)_2$], 63.8 [$\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{O}$], 66.2 [$\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{O}$], 81.8 (OCH_2N), 154.2 (4), 163.6 (2), 171.2 [$\text{C}(\text{O})\text{CH}_3$] ppm. IR (KBr): ν = 2968 (m), 1737 (F), 1635 (F), 1590 (F), 1249 (F), 1116 (F) cm^{-1} . MS (EI, 70 eV): m/z (%) = 262 (8) [$\text{M} + \text{H}$] $^+$, 214 (38), 158 (13), 98 (77), 87 (100), 61 (26), 43 (27). MS (Cl^+ , NH_3): m/z (%) = 262 [$\text{M} + \text{H}$] $^+$. HRMS (Cl^+ , NH_3): calcd. for $\text{C}_{10}\text{H}_{20}\text{N}_3\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ = 262.1225; found 262.1223.

Typical procedure for compounds 9a-i:

Triethylamine (3.0 eq) was added to a solution of glycosyldiazadiene **8a-c** (1.0 eq) in dichloromethane. Acyl chloride (3.0 eq) was added dropwise to the reaction medium at 0 $^{\circ}\text{C}$, and the reaction mixture was stirred at room temperature over a period of 2-6 h (2 h for **9e**; 3 h for **9a,d,h,i**; 6 h for **9b,c,f,g**). The solvent was then removed and the residue was dissolved in dichloromethane, washed with water, brine, dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (ethyl acetate/petroleum ether: (7:3) for **9c**; ethyl acetate/petroleum ether: (5:5) for **9b**; ethyl acetate/petroleum ether: (4:6) for **9g,h**; ethyl acetate/petroleum ether: (3:7) for **9a,f,g**; ethyl acetate/petroleum ether: (2:8) for **9d,e**

3-(2',3',5'-Tri-O-benzoyl- β -D-ribofuranosyl)-5-methoxycarbonyl-2-methylsulfanylpurimidin-4(3H)-one (9a): m.p. 92-95 $^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 2.59 (s, 3 H, SCH_3), 3.90 (s, 3 H, CO_2CH_3), 4.66-4.78 (m, 2 H, 5'-H), 4.83 (dd, J = 10.8 and 3.0 Hz, 1 H, 4'-H), 6.22-6.26 (m, 3 H, 1'-H, 2'-H and 3'-H), 7.28-7.40 (m, 6 H, H_{ar}), 7.49-7.55 (m, 3 H, H_{ar}), 7.87-8.10 (m, 6 H, H_{ar}), 8.53 (s, 1 H, 6-H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 15.9 (SCH_3), 52.4 (CO_2CH_3), 63.9 (5'), 71.4 (3'), 73.9 (2'), 80.5 (4'), 92.5 (1'), 112.8 (5), 128.5, 128.9, 129.9, 130.0, 133.2-133.7 (C_{ar}), 157.5 (6), 164.3-168.2 [2, 4 and 3 $\text{C}(\text{O})\text{Ph}$] ppm. IR (KBr): ν = 3065 (f), 3034 (f), 2951 (f), 1725 (F), 1602 (f), 1574 (f), 1491 (F), 1452 (m), 1380 (f), 1368 (f), 1271 (F) cm^{-1} . MS (Cl^+ , NH_3): m/z (%) = 662 [$\text{M} + \text{NH}_4$] $^+$, 645 [$\text{M} + \text{H}$] $^+$. HRMS (MALDI): m/z calcd. for $\text{C}_{33}\text{H}_{28}\text{N}_2\text{NaO}_{10}\text{S}$ [$\text{M} + \text{Na}$] $^+$ = 667.1357; found 667.1342.

3-(2',3',4',6'-Tetra-O-acetyl- β -D-glucopyranosyl)-5-methoxycarbonyl-2-methylsulfanylpurimidin-4(3H)-one (9b): m.p. 210-211 $^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 1.88, 1.99, 2.03 and 2.04 (4 s, 12 H, CH_3CO), 2.61 (s, 3 H, SCH_3), 3.83 (s, 3 H, CO_2CH_3), 3.91 (broad d, J = 9.5 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 4.20 (d, J = 3.6 Hz, 2 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 5.21 (t, J = 9.5 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 5.36 (t, J = 9.5 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 6.18 (t, J = 9.5 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 6.59 (d, J = 9.5 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 8.41 (s, 1 H, H^{F}) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 16.2 (SCH_3), 20.3-20.8 (4 CH_3CO), 52.3 (CO_2CH_3), 61.6 ($\text{C}^{\text{F}}_{\text{Glu}}$), 67.2 and 67.6 ($\text{C}^{\text{F}}_{\text{Glu}}$ and $\text{C}^{\text{F}}_{\text{Glu}}$), 73.0 ($\text{C}^{\text{F}}_{\text{Glu}}$), 75.4 ($\text{C}^{\text{F}}_{\text{Glu}}$), 79.7 ($\text{C}^{\text{F}}_{\text{Glu}}$), 111.1 (C^{F}), 157.0

(C^{F}), 158.1 and 164.3 (C^{F} and C^{F}), 168.6-170.4 (4 CH_3CO and CO_2CH_3) ppm. IR (KBr): ν = 3015 (f), 2962 (f), 1762 (F), 1748 (F), 1681 (m), 1575 (m), 1480 (F), 1435 (m), 1376 (m), 1330 (f), 1196 (F) cm^{-1} . MS (Cl^+ , NH_3): m/z (%) = 548 [$\text{M} + \text{NH}_4$] $^+$, 531 [$\text{M} + \text{H}$] $^+$. HRMS (ESI^+): m/z calcd. for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{NaO}_{12}\text{S}$ [$\text{M} + \text{Na}$] $^+$ = 553.1104; found 553.1105.

3-[(2'-O-Acetoxyethoxy)methyl]-5-methoxycarbonyl-2-methylsulfanylpurimidin-4(3H)-one (9c): m.p. 88-90 $^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 2.01 (s, 3 H, CH_3CO), 2.60 (s, 3 H, SCH_3), 3.83 (dd, J = 5.5 and 3.9 Hz, 2 H, OCH_2^{a}), 3.86 (s, 3 H, CO_2CH_3), 4.16 (dd, J = 5.5 and 3.9 Hz, 2 H, OCH_2^{b}), 5.60 (s, 2 H, NCH_2O), 8.52 (s, 1 H, H^{F}) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 15.2 (SCH_3), 20.9 (CH_3CO), 52.4 (CO_2CH_3), 63.1 (OCH_2^{b}), 68.5 (OCH_2^{a}), 73.5 (NCH_2O), 111.6 (C^{F}), 158.0 (C^{F}), 159.0 (C^{F}), 164.6 (CO_2CH_3), 169.8 (C^{F}), 170.9 (CH_3CO) ppm. IR (KBr): ν = 3023 (f), 2848 (f), 1730 (F), 1706 (F), 1695 (F), 1569 (m), 1241 (F) cm^{-1} . MS (ESI^+): m/z (%) 352 [$\text{M} + \text{K}$] $^+$, 339 [$\text{M} + \text{Na}$] $^+$. HRMS (ESI^+): m/z calcd. for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{NaO}_6\text{S}$ [$\text{M} + \text{Na}$] $^+$ = 339.0627; found 339.0626.

3-(2',3',5'-Tri-O-benzoyl- β -D-ribofuranosyl)-2-methylsulfanyl-5-phenylpyrimidin-4(3H)-one (9d): m.p. 152-154 $^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 2.59 (s, 3 H, SCH_3), 4.68 (dd, J = 11.6 and 5.1 Hz, 1 H, 5'-H_a), 4.73-4.79 (m, 1 H, 4'-H), 4.85 (dd, J = 11.6 and 3.2 Hz, 1 H, 5'-H_b), 6.31-6.36 (m, 3 H, 1'-H, 2'-H and 3'-H), 7.27-7.65 (m, 14 H, H_{ar}), 7.93 (s, 1 H, 6-H), 7.94-7.97 and 8.08-8.11 (m, 6 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 15.7 (SCH_3), 63.5 (5'), 71.2 (3'), 74.3 (2'), 80.3 (4'), 92.6 (1'), 123.6 (5), 128.4-128.7, 129.1, 129.9, 130.1 and 133.1-133.7 (C_{ar}), 149.5 (6), 160.7 and 161.2 (2 and 4), 165.2, 165.6 and 166.5 [3 $\text{C}(\text{O})\text{Ph}$] ppm. IR (KBr): ν = 3065 (f), 3032 (f), 2927 (f), 1723 (F), 1684 (m), 1601 (f), 1584 (f), 1506 (F), 1450 (f), 1369 (f), 1315 (m), 1269 (F) cm^{-1} . MS (EI, 70 eV): m/z (%) = 662 (1) [M] $^+$, 445 (49), 201 (36), 105 (100), 77 (25). MS (Cl^+ , NH_3): m/z (%) = 680 [$\text{M} + \text{NH}_4$] $^+$, 663 [$\text{M} + \text{H}$] $^+$. HRMS (MALDI): m/z calcd. for $\text{C}_{37}\text{H}_{30}\text{N}_2\text{NaO}_8\text{S}$ [$\text{M} + \text{Na}$] $^+$ = 685.1615; found 685.1606.

3-(2',3',4',6'-Tetra-O-acetyl- β -D-glucopyranosyl)-2-methylsulfanyl-5-phenylpyrimidin-4(3H)-one (9e): m.p. 159-160 $^{\circ}\text{C}$. ^1H -RMN (300 MHz, CDCl_3): δ = 1.88, 2.03, 2.07 and 2.09 (4s, 12 H, CH_3CO), 2.63 (s, 3 H, SCH_3), 3.95 (broad d, J = 9.6 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 4.23 (s, 2 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 5.29 (t, J = 9.6 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 5.41 (t, J = 9.6 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 6.31 (t, J = 9.6 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 6.68 (d, J = 9.6 Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 7.34-7.42 (m, 3 H, H_{ar}), 7.55-7.57 (m, 2 H, H_{ar}), 7.88 (s, 1 H, H^{F}) ppm. ^{13}C RMN (75 MHz, CDCl_3): δ = 16.0 (SCH_3), 20.2-20.8 (4 CH_3CO), 61.5 ($\text{C}^{\text{F}}_{\text{Glu}}$), 67.6 ($\text{C}^{\text{F}}_{\text{Glu}}$ and $\text{C}^{\text{F}}_{\text{Glu}}$), 73.0 ($\text{C}^{\text{F}}_{\text{Glu}}$), 75.2 ($\text{C}^{\text{F}}_{\text{Glu}}$), 79.9 ($\text{C}^{\text{F}}_{\text{Glu}}$), 121.6 ($\text{C}^{\text{F}}_{\text{Glu}}$), 128.2-128.4 (5 CH_{ar}), 133.2 (C_{ar}), 149.4 (C^{F}), 160.9 and 161.5 (C^{F} and C^{F}), 169.5-170.4 (4 CH_3CO) ppm. IR (KBr): ν = 3066 (f), 2938 (f), 1756 (F), 1741 (F), 1672 (m), 1500 (F), 1235 (F) cm^{-1} . MS (EI, 70 eV): m/z (%) = 549 (14), 548 (36) [M] $^+$, 331 (59), 218 (41), 169 (100), 127 (28), 109 (37). HRMS (EI, 70 eV): m/z calcd. for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_{10}\text{S}$ [M] $^+$ = 548.1465; found 548.1466.

3-[(2'-O-Acetoxyethoxy)methyl]-2-methylsulfanyl-5-phenylpyrimidin-4(3H)-one (9f): m.p. 54 $^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 2.06 (s, 3 H, CH_3CO), 2.60 (s, 3 H, SCH_3), 3.89 (dd, J = 6.5 and 4.8 Hz, 2 H, OCH_2^{a}), 4.29 (dd, J = 6.5 and 4.8 Hz, 2 H, OCH_2^{b}), 5.67 (s, 2 H, NCH_2O), 7.35-7.44 (m, 3 H, H_{ar}), 7.63-7.65 (m, 2 H, H_{ar}), 7.97 (s, 1 H, H^{F}) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 14.7 (SCH_3), 20.7 (CH_3CO), 63.0 (OCH_2^{b}), 68.0 (OCH_2^{a}), 73.3 (NCH_2O), 122.1 (C^{F}), 128.2-128.4 (CH_{ar}), 133.1 (C_{ar}), 149.8 (C^{F}), 161.5 and 162.6 (C^{F} and C^{F}), 170.8 (CH_3CO) ppm. IR (KBr): ν = 3087 (f), 2931 (f), 1764 (F), 1736 (F), 1663 (F), 1581 (f), 1501 (F), 1231 (F) cm^{-1} .

MS (EI, 70 eV): m/z (%) = 334 (48) $[M]^+$, 219 (42), 218 (34), 116 (18), 91 (20), 87 (100), 43 (58) cm^{-1} . MS (CI^+ , NH_3): m/z (%) = 352 $[M + \text{NH}_4]^+$, 335 $[M + \text{H}]^+$. HRMS (CI^+ , NH_3): m/z (%) = calculée pour $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_4\text{S}$ $[M + \text{H}]^+ = 335.1066$; found 335.1066.

3-(2',3',5'-Tri-O-benzoyl- β -D-ribofuranosyl)-2-

methylsulfanylpurimidin-4(3H)-one (9g): m.p. 78-81°C. ^1H NMR (300 MHz, CDCl_3) Major Isomer (76 %): $\delta = 2.53$ (s, 3 H, SCH_3), 4.69 (dd, $J = 11.3$ and 5.6 Hz, 1 H, 5'-H_a), 4.75-4.80 (m, 1 H, 4'-H), 4.85 (dd, $J = 11.3$ and 3.5 Hz, 1 H, 5'-H_b), 6.21 (d, $J = 6.3$ Hz, 1 H, 5-H), 6.26-6.32 (m, 3 H, 1'-H, 2'-H and 3'-H), 7.29-7.41 (m, 6 H, H_{ar}), 7.50-7.55 (m, 3 H, H_{ar}), 7.74 (d, $J = 6.3$ Hz, 1 H, 6-H), 7.91-7.98 and 8.08-8.11 (m, 6 H, H_{ar}) ppm; Minor Isomer (24 %, selected data): $\delta = 4.61$ (dd, $J = 11.3$ and 5.6 Hz, 1 H, 5'-H_a), 5.29 (dd, $J = 11.3$ and 3.5 Hz, 1 H, 5'-H_b), 6.12 (d, $J = 6.3$ Hz, 1 H, 5-H), 7.68 (d, $J = 6.3$ Hz, 1 H, 6-H) ppm. ^{13}C NMR (75 MHz, CDCl_3) Major Isomer: 15.6 (SCH_3), 63.9 (5'), 71.4 (3'), 73.9 (2'), 80.2 (4'), 91.8 (1'), 111.7 (5), 128.3-128.5, 128.9, 129.8 and 133.1-133.6 (C_{ar}), 151.9 (6), 161.3 (2), 162.7 (4), 165.1-166.3 [3 C(O)Ph] ppm; Minor Isomer (selected data): $\delta = 63.3$ (5'), 71.0 (3'), 78.8 (4'), 87.5 (1'), 110.1 (5), 151.4 (6), 161.9 (2) ppm. IR (KBr): $\nu = 3064$ (F), 2931 (F), 1726 (F), 1690 (F), 1601 (F), 1583 (f), 1495 (F), 1363 (f), 1315 (m), 1268 (F) cm^{-1} . MS (CI^+ , NH_3): m/z (%) = 604 $[M + \text{NH}_4]^+$, 587 $[M + \text{H}]^+$. HRMS (MALDI): m/z calcd. for $\text{C}_{31}\text{H}_{26}\text{N}_2\text{NaO}_8\text{S}$ $[M + \text{Na}]^+ = 609.1302$; found 609.1306.

3-(2',3',4',6'-Tetra-O-acetyl- β -D-glucopyranosyl)-2-

methylsulfanylpurimidin-4(3H)-one (9h): m.p. 151-152°C. ^1H NMR (300 MHz, CDCl_3): $\delta = 1.88$, 1.99, 2.03 and 2.05 (4 s, 12 H, CH_3CO), 2.55 (s, 3 H, SCH_3), 3.90 (broad d, $J = 9.5$ Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 4.21 (d, $J = 3.4$ Hz, 2 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 5.23 (t, $J = 9.5$ Hz, 1 H, $\text{H}^{\text{A}}_{\text{Glu}}$), 5.37 (t, $J = 9.5$ Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 6.10 (d, $J = 6.4$ Hz, 1 H, H^{F}), 6.23 (t, $J = 9.5$ Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 6.54 (d, $J = 9.5$ Hz, 1 H, $\text{H}^{\text{I}}_{\text{Glu}}$), 7.65 (d, $J = 6.4$ Hz, 1 H, H^{F}) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 16.0$ (SCH_3), 20.2-20.8 (4 CH_3CO), 61.5 ($\text{C}^{\text{C}}_{\text{Glu}}$), 67.6 ($\text{C}^{\text{C}}_{\text{Glu}}$ and $\text{C}^{\text{A}}_{\text{Glu}}$), 73.0 ($\text{C}^{\text{G}}_{\text{Glu}}$), 75.2 ($\text{C}^{\text{B}}_{\text{Glu}}$), 79.4 ($\text{C}^{\text{I}}_{\text{Glu}}$), 109.8 (C^{D}), 151.9 (C^{E}), 161.6 and 163.2 (C^{C} and C^{A}), 169.5-170.5 (4 CH_3CO) ppm. IR (KBr): $\nu = 2984$ (f), 2972 (f), 2929 (f), 1758 (F), 1744 (F), 1686 (f), 1580 (f), 1489 (F), 1373 (m), 1233 (F), 1219 (F) cm^{-1} . MS (EI, 70 eV): m/z (%) = 472 (8) $[M]^+$, 412 (16), 353 (22), 331 (47), 253 (25), 237 (33), 169 (99), 143 (42), 109 (63), 43 (100). HRMS (CI^+ , NH_3): m/z (%) = calcd. for $\text{C}_{19}\text{H}_{25}\text{N}_2\text{O}_{10}\text{S}$ $[M + \text{H}]^+ = 473.1230$; found 473.1232.

3-[(2'-O-Acetoxyethoxy)methyl]-2-methylsulfanylpurimidin-4(3H)-

one (9i): m.p. 49-50°C. ^1H NMR (300 MHz, CDCl_3): $\delta = 2.02$ (s, 3 H, CH_3CO), 2.53 (s, 3 H, SCH_3), 3.77-3.80 (m, 2 H, OCH_2^{a}), 4.14-4.17 (m, 2 H, OCH_2^{b}), 5.55 (s, 2 H, NCH_2O), 6.16 (d, $J = 6.5$ Hz, 1 H, H^{F}), 7.71 (d, $J = 6.5$ Hz, 1 H, H^{F}) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 15.0$ (SCH_3), 20.9 (CH_3CO), 63.1 (OCH_2^{b}), 68.0 (OCH_2^{a}), 77.1 (NCH_2O), 110.5 (C^{D}), 152.3 (C^{E}), 162.3 and 164.3 (C^{C} and C^{A}), 170.9 (COCH_3) ppm. IR (KBr): $\nu = 3093$ (f), 2950 (f), 1734 (F), 1730 (F), 1680 (F), 1665 (F), 1239 (F) cm^{-1} . MS (EI, 70 eV): m/z (%) = 258 (7) $[M]^+$, 198 (8), 171 (18), 155 (16), 143 (44), 87 (100), 61 (22), 43 (47) cm^{-1} . MS (ESI^+): m/z (%) 297 $[M + \text{K}]^+$, 281 $[M + \text{Na}]^+$, 259 $[M + \text{H}]^+$. HRMS (ESI^+): m/z calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{NaO}_4\text{S}$ $[M + \text{Na}]^+ = 281.0572$; found 281.0571.

Typical procedure for compounds 10a-f:

Gaseous ammonia was passed for 1 h through a solution of compounds **9a-c** (for **10a-c**) or **11d-f** (for **10d-f**) in toluene, and the medium was stirred

at room temperature for 48 h (6 days for **10c**). The corresponding 2-aminopyrimidine **10a,c,d,f** were obtained as pure material after removal of the solvent under reduced pressure. For glucopyranosyl, the residue was purified by chromatography on silica gel (ethyl acetate/dichloromethane (4:6) for **10b**; ethyl acetate/petroleum ether: (4:6) for **10e**).

2-Amino-3-(2',3',5'-tri-O-benzoyl- β -D-ribofuranosyl)-5-

methoxycarbonylpurimidin-4(3H)-one (10a): m.p. 133-135°C. ^1H NMR (300 MHz, CDCl_3): $\delta = 3.80$ (s, 3 H, CO_2CH_3), 4.69-4.72 (m, 1 H, 4'-H), 4.78 (dd, $J = 12.3$ and 2.4 Hz, 1 H, 5'-H_a), 4.87 (dd, $J = 12.3$ and 3.6 Hz, 1 H, 5'-H_b), 5.95 (dd, $J = 6.9$ and 4.2 Hz, 1 H, 3'-H), 6.11 (t, $J = 6.9$ Hz, 1 H, 2'-H), 6.20 (d, $J = 6.9$ Hz, 1 H, 1'-H), 6.81 (broad d, 2 H, NH_2), 7.31-7.47 and 7.49-7.58 (2 m, 9 H, H_{ar}), 7.92-7.96 and 8.05-8.07 (m, 6 H, H_{ar}), 8.23 (s, 1 H, 6-H) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 51.8$ (CO_2CH_3), 63.5 (5'), 70.1 (2'), 70.4 (3'), 81.2 (4'), 84.0 (1'), 105.5 (5), 128.3, 128.6-130.1 and 133.9 (C_{ar}), 157.9 and 158.5 (2 and 4), 161.7 (6), 164.7-166.1 [3 C(O)Ph and CO_2CH_3] ppm. IR (KBr): $\nu = 3431$ (F), 3215 (m), 2951 (f), 1728 (F), 1635 (m), 1601 (m), 1574 (m), 1490 (m), 1451 (f), 1384 (f), 1315 (m), 1269 (F) cm^{-1} . MS (CI^+ , NH_3): m/z (%) = 614 $[M + \text{H}]^+$. HRMS (MALDI): m/z calcd. for $\text{C}_{32}\text{H}_{27}\text{N}_3\text{NaO}_{10}$ $[M + \text{Na}]^+ = 636.1589$; found 636.1591.

3-(2',3',4',6'-Tetra-O-acetyl- β -D-glucopyranosyl)-2-amino-5-

methoxycarbonylpurimidin-4(3H)-one (10b): m.p. 125-127°C. ^1H NMR (300 MHz, CDCl_3): $\delta = 1.91$, 2.00, 2.05 and 2.08 (4 s, 12 H, CH_3CO), 3.81 (s, 3 H, CO_2CH_3), 4.02-4.06 (m, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 4.07-4.10 (m, 1 H, $\text{H}^{\text{A}}_{\text{Glu}}$), 4.37 (dd, $J = 12.9$ and 4.8 Hz, 1 H, $\text{H}^{\text{B}}_{\text{Glu}}$), 5.19 (t, $J = 9.6$ Hz, 1 H, $\text{H}^{\text{A}}_{\text{Glu}}$), 5.42 (t, $J = 9.6$ Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 5.72 (t, $J = 9.6$ Hz, 1 H, $\text{H}^{\text{F}}_{\text{Glu}}$), 6.66 (d, $J = 9.6$ Hz, 1 H, $\text{H}^{\text{I}}_{\text{Glu}}$), 6.70 (broad s, 2 H, NH_2), 8.43 (s, 1 H, H^{F}) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 20.3$, 20.6 and 20.8 (4 CH_3CO), 51.9 (CO_2CH_3), 61.6 ($\text{C}^{\text{C}}_{\text{Glu}}$), 66.7 ($\text{C}^{\text{C}}_{\text{Glu}}$), 67.7 ($\text{C}^{\text{A}}_{\text{Glu}}$), 72.7 ($\text{C}^{\text{G}}_{\text{Glu}}$), 75.8 ($\text{C}^{\text{B}}_{\text{Glu}}$), 79.4 ($\text{C}^{\text{I}}_{\text{Glu}}$), 105.1 (C^{D}), 157.8 and 158.2 (C^{C} and C^{A}), 162.3 (C^{E}), 164.8 (CO_2CH_3), 169.6, 169.7, 169.9 and 170.5 (4 CH_3CO) ppm. IR (KBr): $\nu = 3439$ (F), 3219 (m), 2954 (f), 2851 (f), 1754 (F), 1704 (m), 1621 (m), 1574 (m), 1520 (m), 1489 (m), 1436 (f), 1369 (m), 1223 (F) cm^{-1} . MS (CI^+ , NH_3): m/z (%) = 500 $[M + \text{H}]^+$. HRMS (MALDI): m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_3\text{NaO}_{12}$ $[M + \text{Na}]^+ = 522.1330$; found 522.1333.

3-[(2'-O-Acetoxyethoxy)methyl]-2-amino-5-

methoxycarbonylpurimidin-4(3H)-one (10c): m.p. 143-145°C. ^1H NMR (300 MHz, CDCl_3): $\delta = 2.04$ (s, 3 H, CH_3CO), 3.80-3.90 (m, 2 H, OCH_2^{a}), 3.84 (s, 3 H, CO_2CH_3), 4.20 (dd, $J = 4.5$ and 4.2 Hz, 2 H, OCH_2^{b}), 5.57 (s, 2 H, NCH_2O), 6.89 (broad s, 2 H, NH_2), 8.50 (s, 1 H, H^{F}) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 20.9$ (CH_3CO), 52.0 (CO_2CH_3), 62.7 (OCH_2^{b}), 67.9 (OCH_2^{a}), 77.2 (NCH_2O), 105.6 (C^{D}), 158.9 (C^{E}), 159.2 (C^{A}), 162.3 (C^{C}), 165.2 (CO_2CH_3), 170.9 (CH_3CO) ppm. IR (KBr): $\nu = 3411$ (m), 3211 (m), 2988 (f), 2953 (f), 2908 (f), 1733 (F), 1707 (F), 1690 (m), 1669 (m), 1532 (m), 1499 (f), 1463 (f), 1379 (f), 1361 (f), 1293 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 285 (8) $[M]^+$, 226 (8), 183 (17), 170 (34), 138 (77), 87 (89), 57 (25), 43 (100). HRMS (MALDI): m/z calcd. for $\text{C}_{11}\text{H}_{15}\text{N}_3\text{NaO}_6$ $[M + \text{Na}]^+ = 308.0853$; found 308.0866.

2-Amino-3-(2',3',5'-tri-O-benzoyl- β -D-ribofuranosyl)-5-

phenylpyrimidin-4(3H)-one (10d): m.p. 190°C (degradation). ^1H NMR (300 MHz, CDCl_3): $\delta = 4.68$ -4.72 (m, 1 H, 4'-H), 4.84-4.86 (m, 2 H, 5'-H), 5.82 (broad s, 2 H, NH_2), 6.00 (dd, $J = 6.6$ and 4.8 Hz, 1 H, 3'-H), 6.17 (t, $J = 6.6$ Hz, 1 H, 2'-H), 7.18 (d, $J = 6.6$ Hz, 1 H, 1'-H), 7.29-7.37 and 7.48-7.61 (m, 14 H, H_{ar}), 7.70 (s, 1 H, 6-H), 7.93-7.96 and 8.07-8.10 (m, 6 H,

H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.7 (5'), 70.3 (3'), 70.8 (2'), 81.1 (4'), 84.8 (1'), 117.7 (5), 127.4, 128.3-129.0, 130.7-130.1, 133.9 and 134.3 (C_{ar}), 152.3 (6), 154.6 (2), 161.2 (4), 165.4, 165.7 and 166.2 [3 C(O)Ph] ppm. IR (KBr): ν = 3427 (m), 3162 (m), 2956 (f), 1727 (F), 1680 (m), 1601 (m), 1526 (F), 1451 (m), 1316 (F), 1268 (m) cm^{-1} . MS (Cl^+ , NH_3): m/z (%) = 632 [$M + H$] $^+$. HRMS (MALDI): m/z calcd. for $C_{36}H_{29}N_3NaO_8$ [$M + Na$] $^+$ = 654.1847; found 654.1865.

3-(2',3',4',6'-Tetra-O-acetyl- β -D-glucopyranosyl)-2-amino-5-phenylpyrimidin-4(3H)-one (10e): m.p. 207-210°C. 1H NMR (300 MHz, $CDCl_3$): δ = 1.90, 2.02, 2.06 and 2.10 (4s, 12 H, CH_3CO), 4.04 (ddd, J = 9.6, 4.2 and 2.1 Hz, 1 H, H^{6}_{Glu}), 4.14 (dd, J = 12.6 and 2.1 Hz, 1 H, H^{6a}_{Glu}), 4.39 (dd, J = 12.6 and 4.2 Hz, 1 H, H^{6b}_{Glu}), 5.22 (t, J = 9.6 Hz, 1 H, H^4_{Glu}), 5.44 (t, J = 9.6 Hz, 1 H, H^5_{Glu}), 5.87 (t, J = 9.6 Hz, 1 H, H^2_{Glu}), 5.98 (broad s, 2 H, NH_2), 6.72 (d, J = 9.6 Hz, 1 H, H^1_{Glu}), 7.29-7.40 and 7.51-7.54 (m, 5 H, H_{ar}), 7.76 (s, 1 H, H^6) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3, 20.7 and 20.8 (4 CH_3CO), 61.6 (C^5_{Glu}), 67.0 and 67.6 (C^2_{Glu} and C^4_{Glu}), 72.8 (C^3_{Glu}), 75.5 (C^5_{Glu}), 79.9 (C^1_{Glu}), 116.5 (C^5), 127.5 (CH_{ar}), 128.0 and 128.5 (CH_{ar}), 134.2 (C_{ar}), 153.2 (C^6), 154.4 (C^2), 160.7 (C^4), 169.6, 169.8 and 170.5 (4 CH_3CO) ppm. IR (KBr): ν = 3436 (m), 3343 (m), 3022 (f), 2964 (f), 1745 (F), 1673 (m), 1614 (m), 1572 (F), 1472 (f), 1326 (m), 1292 (F) cm^{-1} . MS (Cl^+ , NH_3): m/z (%) = 518 [$M + H$] $^+$. HRMS (MALDI): m/z calcd. for $C_{24}H_{27}N_3NaO_{10}$ [$M + Na$] $^+$ = 540.1589; found 540.1586.

3-[(2'-O-Acetoxyethoxy)methyl]-2-amino-5-phenylpyrimidin-4(3H)-one (10f): m.p. 125-128°C. 1H NMR (300 MHz, $CDCl_3$): δ = 2.06 (s, 3 H, CH_3CO), 3.87 (dd, J = 6.3 and 4.8 Hz, 2 H, OCH_2), 4.23 (dd, J = 6.3 and 4.8 Hz, 2 H, OCH_2), 5.63 (s, 2 H, NCH_2O), 5.94 (broad s, 2 H, NH_2), 7.29-7.41 (m, 3 H, H_{ar}), 7.56-7.59 (m, 2 H, H_{ar}), 7.80 (s, 1 H, H^6) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9 (CH_3CO), 62.9 (OCH_2^b), 67.7 (OCH_2^a), 72.4 (NCH_2O), 117.1 (C^5), 127.4-128.5 (CH_{ar}), 134.3 (C_{ar}), 152.6 (C^6), 155.8 and 161.6 (C^2 and C^4), 171.0 (CH_3CO) ppm. IR (KBr): ν = 3429 (F), 3064 (f), 2952 (f), 1740 (m), 1678 (F), 1637 (F), 1589 (m), 1484 (m), 1374 (f), 1291 (f) cm^{-1} . MS (Cl^+ , NH_3): m/z (%) = 304 [$M + H$] $^+$. MS (EI, 70 eV): m/z (%) = 303 (5) [M] $^+$, 187 (7), 117 (16), 116 (26), 87 (33), 43 (100). HRMS (MALDI): m/z calcd. for $C_{15}H_{17}N_3NaO_4$ [$M + Na$] $^+$ = 326.1111; found 326.1123.

Typical procedure for compounds 11d-f:

DMDO in acetone (0.075 mol.L $^{-1}$, 2.5 eq) was added at 0°C to methylsulfide **9d-f** (1.0 eq). The reaction mixture was stirred for 30 minutes while letting the temperature go back up to room temperature. The mixture was evaporated under reduced pressure to afford **11d-f** in a pure form as a white solid (instable compounds).

3-(2',3',5'-Tri-O-benzoyl- β -D-ribofuranosyl)-2-methylsulfonyl-5-phenylpyrimidin-4(3H)-one (11d): 1H NMR (300 MHz, $CDCl_3$): δ = 3.45 (s, 3 H, SO_2CH_3), 4.66-4.71 (m, 1 H, 4'-H), 4.66-4.71 (m, 2 H, 5'-H), 6.32 (dd, J = 7.8 and 7.2 Hz, 1 H, 3'-H), 6.44 (dd, J = 7.2 and 2.4 Hz, 1 H, 2'-H), 6.86 (d, J = 2.4 Hz, 1 H, 1'-H), 7.23-7.66 (m, 14 H, H_{ar}), 7.89-7.95 (m, 5 H, H_{ar} and 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.5 (SO_2CH_3), 63.3 (5'), 70.8 (3'), 73.4 (2'), 80.6 (4'), 91.5 (1'), 128.4-128.9 (C_{ar}), 129.1 (5), 129.7-130.1, 131.5-131.7 and 133.1-133.5 (C_{ar}), 146.6 (6), 154.1 (2), 159.3 (4), 165.2, 165.5 and 166.3 [3 C(O)Ph] ppm. MS (Cl^+ , NH_3): m/z (%) = 712 [$M + NH_4$] $^+$, 695 [$M + H$] $^+$.

3-(2',3',4',6'-Tetra-O-acetyl- β -D-glucopyranosyl)-2-methylsulfonyl-5-phenylpyrimidin-4(3H)-one (11e): 1H NMR (300 MHz, $CDCl_3$): δ = 1.96, 2.02, 2.04 and 2.06 (4s, 12 H, CH_3CO), 3.44 (s, 3 H, SO_2CH_3), 3.89-3.94 (m, 1 H, H^{6}_{Glu}), 4.24 and 4.25 (2 s, 2 H, H^{6}_{Glu}), 5.30 (t, J = 9.6, 1 H, H^4_{Glu}), 5.41 (t, J = 9.6 Hz, 1 H, H^5_{Glu}), 6.16 (broad s, 1 H, H^1_{Glu}), 6.36 (t, J = 9.6 Hz, 1 H, H^2_{Glu}), 7.43-7.46 and 7.60-7.63 (m, 5 H, H_{ar}), 7.85 (s, 1 H, H^6) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 20.7 and 20.9 (4 CH_3CO), 41.9 (SO_2CH_3), 61.8 (C^5_{Glu}), 67.7 (C^2_{Glu} and C^4_{Glu}), 72.2 (C^3_{Glu}), 75.0 (C^5_{Glu}), 84.9 (C^1_{Glu}), 128.7-129.6 (CH_{ar} and C_{ar}), 131.7 (C^5), 145.6 (C^6), 154.0 (C^2), 159.5 (C^4), 169.5, 170.1 and 170.8 (4 CH_3CO) ppm. MS (Cl^+ , NH_3): m/z (%) = 598 [$M + NH_4$] $^+$, 581 [$M + H$] $^+$.

3-[(2'-O-Acetoxyethoxy)methyl]-2-methylsulfonyl-5-phenylpyrimidin-4(3H)-one (11f): 1H NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 3 H, CH_3CO), 3.44 (s, 3 H, SO_2CH_3), 3.98 (dd, J = 6.3 and 4.8 Hz, 2 H, OCH_2), 4.24 (dd, J = 6.3 and 4.8 Hz, 2 H, OCH_2), 5.97 (s, 2 H, NCH_2O), 7.45-7.47 (m, 3 H, H_{ar}), 7.64-7.67 (m, 2 H, H_{ar}), 8.00 (s, 1 H, H^6) ppm. MS (Cl^+ , NH_3): m/z (%) = 384 [$M + NH_4$] $^+$, 367 [$M + H$] $^+$.

Typical procedure for compounds 12a-e:

N,N-dimethylformamide dimethylacetal (1.2 eq) was added to a solution of aminopyrimidinone **10a-e** (1.0 eq) in dichloromethane. The mixture was stirred at reflux for 3 h to 6 h (3 h for **12b-e**, 6 h for **12a**). The solvent was removed and the residue purified by chromatography on silica gel (ethyl acetate for **12b** and **12e**; ethyl acetate/petroleum ether: (7:3) for **12d**; ethyl acetate/petroleum ether: (6:4) for **12a**; ethyl acetate/ethanol: (9:1) for **12c**).

3-(2',3',5'-Tri-O-benzoyl- β -D-ribofuranosyl)-2-[(*N,N*-dimethylaminomethyle)amino]-5-methoxycarbonylpyrimidin-4(3H)-one (12a): m.p. 133-135°C. 1H NMR (300 MHz, $CDCl_3$): δ = 3.06 and 3.18 [2 s, 6 H, $N(CH_3)_2$], 3.87 (s, 3 H, CO_2CH_3), 4.69-4.80 (m, 3 H, 4'-H and 5'-H), 6.25-6.35 (m, 2 H, 2'-H and 3'-H), 7.13 (s, 1 H, 1'-H), 7.27-7.37 (m, 6 H, H_{ar}), 7.47-7.52 (m, 3 H, H_{ar}), 7.87-7.93 and 8.02-8.04 (m, 6 H, H_{ar}), 8.52 (s, 1 H, 6-H), 8.71 (s, 1 H, $N=CH$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.0 and 42.0 [$N(CH_3)_2$], 51.9 (CO_2CH_3), 64.6 (5'), 71.9 (2'), 74.4 (3'), 79.4 (4'), 89.2 (1'), 109.0 (5), 128.4, 129.2, 129.5, 129.8-129.9 and 133.1-133.4 (C_{ar}), 159.6 (2), 159.8 ($N=CH$), 160.7 (6), 161.6 (4), 165.1-166.5 [3 C(O)Ph and CO_2CH_3] ppm. IR (KBr): ν = 3062 (f), 2948 (f), 1727 (F), 1699 (m), 1634 (m), 1567 (f), 1480 (F), 1386 (m), 1279 (F) cm^{-1} . MS (Cl^+ , NH_3): m/z (%) = 669 [$M + H$] $^+$. HRMS (MALDI): m/z calcd. for $C_{35}H_{32}N_4NaO_{10}$ [$M + Na$] $^+$ = 691.2011; found 691.1994.

3-(2',3',4',6'-Tetra-O-acetyl- β -D-glucopyranosyl)-2-[(*N,N*-dimethylaminomethyle)amino]-5-methoxycarbonylpyrimidin-4(3H)-one (12b): m.p. 89-91°C. 1H NMR (300 MHz, $CDCl_3$): δ = 1.88, 1.98, 2.01 and 2.03 (4 s, 12 H, CH_3CO), 3.26 and 3.31 (2 s, 6 H, $N(CH_3)_2$), 3.84 (s, 3 H, CO_2CH_3), 3.86-3.90 (m, 1 H, H^{6}_{Glu}), 4.06 (dd, J = 10.5 and 1.8 Hz, 1 H, H^{6a}_{Glu}), 4.26 (dd, J = 12.4 and 5.0 Hz, 1 H, H^{6b}_{Glu}), 5.12 (t, J = 9.6 Hz, 1 H, H^4_{Glu}), 5.29 (t, J = 9.6 Hz, 1 H, H^5_{Glu}), 6.50 (t, J = 9.6 Hz, 1 H, H^2_{Glu}), 6.56 (d, J = 9.6 Hz, 1 H, H^1_{Glu}), 8.47 (s, 1 H, H^6), 8.72 (s, 1 H, $N=CH$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7 (4 CH_3CO), 36.3 and 42.0 ($N(CH_3)_2$), 51.9 (CO_2CH_3), 62.3 (C^5_{Glu}), 68.2 (C^4_{Glu}), 68.9 (C^2_{Glu}), 74.3 (C^3_{Glu}), 74.8 (C^5_{Glu}), 78.8 (C^1_{Glu}), 107.5 (C^5), 159.3 ($N=CH$), 160.1 (C^2), 161.1 (C^6), 161.6 (C^4), 165.5 (CO_2CH_3), 169.8, 169.9 and 170.0 (4 CH_3CO) ppm. IR (KBr): ν = 2953 (f), 2854 (f), 1753 (F), 1701 (m), 1636 (m), 1481 (F), 1379 (m), 1229 (F), 1036 (m) cm^{-1} . MS (Cl^+ , NH_3): m/z (%) = 555 [$M + H$] $^+$. HRMS (MALDI): m/z calcd. for $C_{23}H_{30}N_4NaO_{12}$ [$M + Na$] $^+$ = 577.1752; found 577.1739.

3-[(2'-O-Acetoxyethoxy)methyl]-2-[(N,N-dimethylaminomethylen)amino]-5-methoxycarbonylpyrimidin-4(3H)-one (12c): m.p. 104–106°C. ¹H NMR (300 MHz, CDCl₃): δ = 2.02 (s, 3 H, CH₃CO), 3.18 and 3.23 (2 s, 6 H, N(CH₃)₂), 3.84 (s, 3 H, CO₂CH₃), 3.89 (dd, *J* = 4.9 and 4.6 Hz, 2 H, OCH₂^a), 4.16 (dd, *J* = 4.9 and 4.6 Hz, 2 H, OCH₂^b), 5.74 (s, 2 H, NCH₂O), 8.51 (s, 1 H, H⁶), 8.73 (s, 1 H, N=CH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 21.0 (CH₃CO), 35.8 and 41.8 (N(CH₃)₂), 51.9 (CO₂CH₃), 63.6 (OCH₂^b), 68.5 (OCH₂^a), 71.7 (NCH₂O), 108.3 (C⁵), 159.6 (N=CH), 160.6 (C²), 160.9 (C⁶), 162.1 (C⁴), 165.7 (CO₂CH₃), 171.0 (CH₃CO) ppm. IR (KBr): ν = 3021 (f), 2982 (f), 2942 (f), 1728 (F), 1694 (F), 1675 (m), 1622 (m), 1570 (m), 1488 (F), 1440 (m), 1381 (m), 1278 (m), 1261 (f) cm⁻¹. MS (EI, 70 eV): *m/z* (%) = 340 (5) [M]⁺, 237 (9), 225 (37), 193 (53), 150 (11), 98 (26), 87 (23), 43 (100). HRMS (MALDI): *m/z* calcd. for C₁₄H₂₀N₄NaO₆ [M + Na]⁺ = 363.1275; found 363.1277.

3-(2',3',5'-Tri-O-benzoyl-β-D-ribofuranosyl)-2-[(N,N-dimethylaminomethylen)amino]-5-phenylpyrimidin-4(3H)-one (12d): m.p. 114–116°C. Two Isomers in ratio 90/10. ¹H NMR (300 MHz, CDCl₃): δ = 3.03 and 3.13 [2 s, 6 H, N(CH₃)₂], 4.73–4.84 (m, 3 H, 4'-H and 5'-H), 6.41 (broad s, 2 H, 2'-H and 3'-H), 7.27–7.52 (m, 14 H, 1'-H and H_{ar}), 7.65–7.68 (m, 2 H, H_{ar}), 7.85 (s, 1 H, 6-H), 7.92–7.95 and 8.07–8.10 (m, 5 H, H_{ar}), 8.58 (s, 1 H, N=CH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 35.5 and 41.7 [N(CH₃)₂], 64.2 (5'), 71.7 (3'), 74.8 (2'), 79.7 (4'), 90.3 (1'), 120.6 (5), 127.3, 128.3–128.4, 129.2, 129.7–130.0, 132.0–133.0 and 134.5 (C_{ar}), 151.4 (6), 158.1 (N=CH and 2), 161.7 (4), 165.1, 165.4 and 166.5 [3 C(O)Ph] ppm. IR (KBr): ν = 3066 (f), 2983 (f), 1732 (F), 1718 (F), 1630 (F), 1583 (f), 1485 (F), 1450 (m), 1377 (F), 1315 (m), 1276 (F) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 687 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₃₉H₃₄N₄NaO₈ [M + Na]⁺ = 709.2269; found 709.2261.

3-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranosyl)-2-[(N,N-dimethylaminomethylen)amino]-5-phenylpyrimidin-4(3H)-one (12e): m.p. 138–140°C. Two Isomers in ratio 85/15. ¹H NMR (300 MHz, CDCl₃): δ = 1.89, 2.00, 2.03 and 2.05 (4s, 12 H, CH₃CO), 3.22 and 3.28 (2 s, 6 H, N(CH₃)₂), 3.92 (ddd, *J* = 9.6, 4.5 and 1.8 Hz, 1 H, H⁶_{Glu}), 4.11 (dd, *J* = 12.6 and 1.8 Hz, 1 H, H^{6a}_{Glu}), 4.32 (dd, *J* = 12.6 and 4.5 Hz, 1 H, H^{6b}_{Glu}), 5.18 (t, *J* = 9.6 Hz, 1 H, H⁴_{Glu}), 5.33 (t, *J* = 9.6 Hz, 1 H, H³_{Glu}), 5.57 (t, *J* = 9.6 Hz, 1 H, H²_{Glu}), 6.64 (d, *J* = 9.6 Hz, 1 H, H¹_{Glu}), 7.28–7.40 and 7.58–7.61 (m, 5 H, H_{ar}), 7.82 (s, 1 H, H⁶), 8.68 (s, 1 H, N=CH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 20.6 and 20.8 (4 CH₃CO), 35.9 and 41.5 (N(CH₃)₂), 62.2 (C⁶_{Glu}), 68.0 (C²_{Glu}), 69.3 (C⁴_{Glu}), 74.2 (C³_{Glu}), 74.6 (C⁵_{Glu}), 79.3 (C¹_{Glu}), 118.7 (C⁵), 127.4 (CH_{ar}), 128.2 and 128.3 (CH_{ar}), 134.6 (C_{ar}), 152.0 (C⁶), 157.6 (N=CH), 158.1 (C²), 162.3 (C⁴), 169.8–170.6 (4 CH₃CO) ppm. IR (KBr): ν = 3024 (f), 2951 (f), 1760 (F), 1751 (F), 1629 (F), 1582 (f), 1493 (F), 1458 (m), 1367 (m), 1297 (f) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 573 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₂₇H₃₂N₄NaO₁₀ [M + Na]⁺ = 595.2011; found 595.2027.

Typical procedure for compounds 13a-i:

Acyl chloride (3.0 eq) was added to a solution of **12a-c** (1.0 eq) in dichloromethane. Triethylamine (3.0 eq) was added dropwise to the reaction medium at 0 °C, and the reaction mixture was stirred at room temperature for 2 h. Then, acyl chloride (3.0 eq) and triethylamine (3.0 eq) were added once again at 0 °C, and the reaction mixture was stirred at room temperature for 1 h to 6 h (1 h for **13a-f,h,i** and 6 h for **13g**). The solvent was then removed and the residue was dissolved in

dichloromethane, washed with water, brine, dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (ethyl acetate/petroleum ether: (4:6) for **13a**, **13e** and **13h**; ethyl acetate/petroleum ether: (6:4) for **13b**; ethyl acetate/petroleum ether: (7:3) for **13c**; ethyl acetate/petroleum ether: (3:7) for **13d**, **13g** and **13i**; ethyl acetate/petroleum ether: (5:5) for **13f**).

1-(2',3',5'-Tri-O-benzoyl-β-D-ribofuranosyl)-3,7-dimethoxycarbonyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13a): m.p. 143–145°C. ¹H NMR (300 MHz, CDCl₃): δ = 3.89 and 3.94 (2 s, 6 H, 2 CO₂CH₃), 4.64 (dd, *J* = 11.3 and 5.5 Hz, 1 H, 5'-H_a), 4.75–4.84 (m, 2 H, 4'-H and 5'-H_b), 6.17–6.22 (m, 2 H, 2'-H and 3'-H), 7.07 (broad s, 1 H, 1'-H), 7.28–7.39 and 7.47–7.58 (m, 9 H, H_{ar}), 7.82–8.05 (m, 6 H, H_{ar}), 8.67 (s, 1 H, 8-H), 9.39 (s, 1 H, 4-H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 52.4 and 53.1 (2 CO₂CH₃), 63.4 (5'), 70.9 (3'), 73.5 (2'), 79.5 (4'), 88.8 (1'), 108.7 (7), 113.3 (3), 128.3, 128.7, 128.8, 129.5, 129.8 and 133.1–133.6 (C_{ar}), 138.8 (8), 153.2 and 155.6 (2 and 6), 160.2 (4), 161.2 and 163.1 (CO₂CH₃ and 9a), 165.2–166.2 [3 C(O)Ph] ppm. IR (KBr): ν = 3064 (f), 2955 (f), 1763 (F), 1730 (F), 1602 (f), 1517 (F), 1452 (m), 1375 (f), 1316 (m) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 724 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₃₇H₂₉N₃NaO₁₃ [M + Na]⁺ = 746.1593; found 746.1593.

1-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranosyl)-3,7-dimethoxycarbonyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13b): m.p. 197–199°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (70%): δ = 1.90, 2.03 and 2.05 (4 s, 12 H, CH₃CO), 3.87–3.92 (m, 1 H, H⁶_{Glu}), 3.92 and 3.94 (2 s, 6 H, 2 CO₂CH₃), 4.18–4.21 (m, 2 H, 2 H⁶_{Glu}), 5.22 (t, *J* = 9.6 Hz, 1 H, H⁶_{Glu}), 5.38 (t, *J* = 9.6 Hz, 1 H, H⁶_{Glu}), 6.34 (d, *J* = 9.3 Hz, 1 H, H¹_{Glu}), 6.43 (t, *J* = 9.3 Hz, 1 H, H²_{Glu}), 8.81 (s, 1 H, H⁶), 9.38 (s, 1 H, H⁴) ppm; Minor Isomer (30%, selected data): δ = 6.15 (t, *J* = 9.3 Hz, 1 H, H²_{Glu}), 6.72 (d, *J* = 9.3 Hz, 1 H, H¹_{Glu}), 8.69 (s, 1 H, H⁶), 9.34 (s, 1 H, H⁴) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: 20.6–20.8 (4 CH₃CO), 52.6 and 53.3 (2 CO₂CH₃), 61.9 (C⁶_{Glu}), 67.7 (C⁴_{Glu}), 68.7 (C²_{Glu}), 73.4 (C³_{Glu}), 75.1 (C⁵_{Glu}), 80.6 (C¹_{Glu}), 109.3 and 112.1 (C³ and C⁷), 139.5 (C⁴), 149.7, 153.4 and 155.8 (C², C⁶ and C^{9a}), 160.5 (C⁶), 161.3 and 163.3 (2 CO₂CH₃), 169.3–170.4 (4 CH₃CO) ppm; Minor Isomer (selected data): δ = 60.5 (C⁶_{Glu}), 73.2 (C³_{Glu}), 82.5 (C¹_{Glu}), 138.4 (C⁴) ppm. IR (KBr): ν = 2955 (f), 2924 (f), 2853 (f), 1759 (F), 1582 (f), 1516 (F), 1371 (m), 1229 (F), 1036 (m) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 627 [M + NH₄]⁺, 610 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₂₅H₂₇N₃NaO₁₅ [M + Na]⁺ = 632.1334; found 632.1334.

3-[(2'-O-Acetoxyethoxy)methyl]-3,7-dimethoxycarbonyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13c): m.p. 156–157°C. ¹H NMR (300 MHz, CDCl₃): δ = 1.98 (s, 3 H, CH₃CO), 3.85 (s, 3 H, CO₂CH₃), 3.86–3.90 (m, 2 H, OCH₂^a), 3.91 (s, 3 H, CO₂CH₃), 4.14 (dd, *J* = 4.8 and 4.5 Hz, 2 H, OCH₂^b), 5.81 (s, 2 H, NCH₂O), 8.71 (s, 1 H, H⁶), 9.34 (s, 1 H, H⁴) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 20.8 (CH₃CO), 52.4 and 53.2 (2 CO₂CH₃), 63.1 (OCH₂^b), 69.3 (OCH₂^a), 72.7 (NCH₂O), 108.3 (C⁷), 113.3 (C³), 138.8 (C⁴), 151.0, 153.4 and 156.0 (C², C⁶ and C^{9a}), 161.2 (C⁶) and 163.3 (2 CO₂CH₃), 170.8 (CH₃CO) ppm. IR (KBr): ν = 3059 (f), 2957 (f), 1760 (F), 1735 (F), 1646 (f), 1515 (F), 1457 (m), 1360 (f), 1285 (m) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 413 [M + NH₄]⁺, 396 [M + H]⁺ cm⁻¹. MS (EI, 70 eV): *m/z* (%) = 396 (9), 395 (5) [M]⁺, 336 (19), 308 (33), 292 (64), 248 (58), 87 (100), 43 (67). HRMS (MALDI): *m/z* calcd. for C₁₆H₁₇N₃NaO₉ [M + Na]⁺ = 418.0857; found 418.0857.

1-(2',3',5'-Tri-O-benzoyl-β-D-ribofuranosyl)-3-methoxycarbonyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13d): m.p. 136-138°C. ¹H NMR (300 MHz, CDCl₃): δ = 3.94 (s, 3 H, CO₂CH₃), 4.64 (dd, *J* = 11.4 and 5.4 Hz, 1 H, 5'-H_a), 4.73-4.85 (m, 2 H, 4'-H and 5'-H_b), 6.20-6.30 (m, 2 H, 2'-H and 3'-H), 6.25 (d, *J* = 6.8 Hz, 1 H, 7-H), 7.09 (broad s, 1 H, 1'-H), 7.28-7.40 (m, 6 H, H_{ar}), 7.48-7.57 (m, 3 H, H_{ar}), 7.85 (d, *J* = 6.8 Hz, 1 H, 8-H), 7.86-8.06 (m, 6 H, H_{ar}), 9.34 (s, 1 H, 4-H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 53.0 (CO₂CH₃), 63.7 (5'), 71.2 (3'), 73.6 (2'), 79.5 (4'), 88.5 (1'), 107.1 (7), 112.6 (3), 128.4, 128.9, 129.6, 129.8, 133.2 and 133.6 (C_{ar}), 138.9 (8), 154.1 (4), 155.5 and 156.6 (2 and 6), 161.5 (9a), 165.2-166.3 [3 C(O)Ph and CO₂CH₃] ppm. IR (KBr): ν = 3070 (f), 2955 (f), 1761 (m), 1726 (F), 1601 (f), 1526 (m), 1451 (f), 1363 (f), 1316 (f) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 666 [M + H]⁺, 665 [M]⁺. HRMS (MALDI): *m/z* calcd. for C₃₅H₂₇N₃NaO₁₁ [M + Na]⁺ = 688.1538; found 688.1540.

1-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranosyl)-3-methoxycarbonyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13e): m.p. 171-173°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (69%): δ = 1.88, 2.00, 2.03 and 2.05 (4 s, 12 H, CH₃CO), 3.85-3.90 (m, 1 H, H⁶_{Glu}), 3.92 (s, 3 H, OCH₃), 4.16-4.20 (m, 2 H, 2 H⁶_{Glu}), 5.22 (t, *J* = 9.3 Hz, 1 H, H⁴_{Glu}), 5.35 (t, *J* = 9.3 Hz, 1 H, H³_{Glu}), 6.27 (d, *J* = 6.9 Hz, 1 H, H⁷), 6.34 (d, *J* = 9.2 Hz, 1 H, H¹_{Glu}), 6.49 (t, *J* = 9.2 Hz, 1 H, H²_{Glu}), 7.94 (d, *J* = 6.9 Hz, 1 H, H⁸), 9.29 (s, 1 H, H⁴) ppm; Minor Isomer (31%, selected data): δ = 3.93 (s, 3 H, OCH₃), 6.66 (d, *J* = 9.2 Hz, 1 H, H¹_{Glu}), 7.84 (d, *J* = 6.9 Hz, 1 H, H⁸), 9.26 (s, 1 H, H⁴) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: 20.6, 20.7 and 20.8 (4 CH₃CO), 53.1 (CO₂CH₃), 62.0 (C⁶_{Glu}), 68.0 (C⁴_{Glu}), 68.4 (C²_{Glu}), 73.7 (C³_{Glu}), 75.0 (C⁵_{Glu}), 80.4 (C¹_{Glu}), 107.6 (C⁷), 111.4 (C³), 139.5 (C⁴), 149.2 (C^{9a}), 154.9 (C⁸), 156.3 and 156.6 (C² and C⁶), 161.6 (CO₂CH₃), 169.3-170.0 (4 CH₃CO) ppm; Minor Isomer (selected data): δ = 73.4 (C³_{Glu}), 74.9 (C⁵_{Glu}), 82.2 (C¹_{Glu}), 107.1 (C⁷), 113.5 (C³), 138.5 (C⁴), 154.0 (C^{9a}), 154.3 (C⁸), 161.8 (CO₂CH₃) ppm. IR (KBr): ν = 3084 (f), 2957 (f), 2854 (f), 1753 (F), 1646 (m), 1522 (F), 1369 (m), 1234 (F), 1036 (m) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 569 [M + NH₄]⁺, 552 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₂₃H₂₅N₃NaO₁₃ [M + Na]⁺ = 574.1280; found 574.1264.

3-[(2'-O-Acetoxyethoxy)methyl]-3-methoxycarbonyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13f): m.p. 162-164°C. ¹H NMR (300 MHz, CDCl₃): δ = 2.04 (s, 3 H, CH₃CO), 3.92-3.95 (m, 5 H, OCH₂^a and CO₂CH₃), 4.21 (dd, *J* = 4.8 and 4.5 Hz, 2 H, OCH₂^b), 5.82 (s, 2 H, NCH₂O), 6.26 (d, *J* = 6.6 Hz, 1 H, H⁷), 7.95 (d, *J* = 6.6 Hz, 1 H, H⁸), 9.37 (s, 1 H, H⁴) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 21.0 (CH₃CO), 53.2 (CO₂CH₃), 63.4 (OCH₂^b), 69.3 (OCH₂^a), 72.5 (NCH₂O), 106.9 (C⁷), 112.6 (C³), 139.0 (C⁴), 148.6 (C^{9a}), 155.2 (C⁸), 156.6 and 158.6 (C² and C⁶), 161.8 (CO₂CH₃), 171.0 (CH₃CO) ppm. IR (KBr): ν = 3065 (f), 2956 (f), 1731 (F), 1641 (f), 1522 (m), 1483 (m), 1380 (f), 1318 (f), 1289 (m) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 355 [M + NH₄]⁺, 338 [M + H]⁺. MS (EI, 70 eV): *m/z* (%) = 338 (19) [M + H]⁺, 278 (27), 249 (35), 234 (71), 222 (48), 190 (58), 87 (100), 43 (73). HRMS (MALDI): *m/z* calcd. for C₁₄H₁₅N₃NaO₇ [M + Na]⁺ = 360.0802; found 360.0809.

1-(2',3',5'-Tri-O-benzoyl-β-D-ribofuranosyl)-7-methoxy-3-methoxycarbonyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13g): m.p. 151-153°C. ¹H NMR (300 MHz, CDCl₃): δ = 3.82 (s, 3 H, OCH₃), 3.94 (s, 3 H, CO₂CH₃), 4.64 (dd, *J* = 11.4 and 5.1 Hz, 1 H, 5'-H_a), 4.71-4.81 (m, 2 H, 4'-H and 5'-H_b), 6.13-6.33 (m, 2 H, 2'-H and 3'-H), 7.00 (broad s, 1 H, 1'-H), 7.31-7.41 (m, 7 H, H_{ar} and 8-H), 7.49-7.57 (m, 3 H, H_{ar}), 7.86-8.05 (m, 6 H, H_{ar}), 9.32 (s, 1 H, 4-H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 53.1 (CO₂CH₃), 57.2 (OCH₃), 63.7 (5'), 71.1 (3'), 73.5 (2'), 79.3 (4'), 88.4 (1'), 112.4 (3), 128.5-129.8 (C_{ar}), 133.3 (8), 133.7 (C_{ar}), 138.7 (4), 140.9 (7),

153.5 and 155.5 (2 and 6), 161.2 (9a), 165.4-166.3 [3 C(O)Ph and CO₂CH₃] ppm. IR (KBr): ν = 3069 (f), 2954 (f), 1758 (m), 1725 (F), 1600 (m), 1560 (m), 1492 (f), 1451 (m), 1364 (f), 1316 (m) cm⁻¹. MS (ESI⁺), *m/z*: 718 [M + Na]⁺, 696 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₃₆H₂₉N₃NaO₁₂ [M + Na]⁺ = 718.1643; found 718.1659.

1-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranosyl)-7-methoxy-3-methoxycarbonyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13h): m.p. 191-194°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (74%): δ = 1.88, 2.00, 2.04 and 2.05 (4 s, 12 H, CH₃CO), 3.86-3.90 (m, 1 H, H⁶_{Glu}), 3.89 (s, 3 H, OCH₃), 3.91 (s, 3 H, CO₂CH₃), 4.15-4.19 (m, 2 H, 2 H⁶_{Glu}), 5.20 (t, *J* = 9.2 Hz, 1 H, H⁴_{Glu}), 5.35 (t, *J* = 9.2 Hz, 1 H, H³_{Glu}), 6.32 (d, *J* = 9.2 Hz, 1 H, H¹_{Glu}), 6.50 (t, *J* = 9.2 Hz, 1 H, H²_{Glu}), 7.54 (s, 1 H, H⁸), 9.26 (s, 1 H, H⁴) ppm; Minor Isomer (26%, selected data): δ = 6.20 (t, *J* = 9.2 Hz, 1 H, H²_{Glu}), 6.58 (d, *J* = 9.3 Hz, 1 H, H¹_{Glu}), 7.43 (s, 1 H, H⁸), 9.22 (s, 1 H, H⁴) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: 20.6, 20.7, 20.9 and 21.1 (4 CH₃CO), 53.1 (CO₂CH₃), 57.2 (OCH₃), 62.2 (C⁶_{Glu}), 68.1 (C⁴_{Glu}), 68.3 (C²_{Glu}), 73.8 (C³_{Glu}), 74.9 (C⁵_{Glu}), 80.2 (C¹_{Glu}), 111.3 (C³), 130.3 (C⁸), 139.3 (C⁴), 141.2 (C⁷), 153.6, 156.3 and 161.7 (C², C⁶ and C^{9a}), 169.7-170.3 (4 CH₃CO and CO₂CH₃) ppm; Minor Isomer (selected data): δ = 53.5 (CO₂CH₃), 57.3 (OCH₃), 62.0 (C⁶_{Glu}), 68.7 (C⁴_{Glu}), 69.4 (C²_{Glu}), 73.6 (C³_{Glu}), 74.8 (C⁵_{Glu}), 82.0 (C¹_{Glu}), 113.4 (C³), 138.3 (C⁴), 140.8 (C⁷), 153.5, 154.9 and 161.8 (C², C⁶ and C^{9a}) ppm. IR (KBr): ν = 3050 (f), 2957 (f), 2852 (f), 1749 (F), 1729 (F), 1598 (m), 1415 (f), 1366 (f), 1267 (F), 1036 (m) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 599 [M + NH₄]⁺, 582 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₂₄H₂₇N₃NaO₁₄ [M + Na]⁺ = 604.1385; found 604.1371.

3-[(2'-O-Acetoxyethoxy)methyl]-7-methoxy-3-methoxycarbonyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13i): m.p. 178-180°C. ¹H NMR (300 MHz, CDCl₃): δ = 2.05 (s, 3 H, CH₃CO), 3.88-3.95 (m, 8 H, OCH₂^a, OCH₃ and CO₂CH₃), 4.21 (dd, *J* = 4.8 and 4.5 Hz, 2 H, OCH₂^b), 5.79 (s, 2 H, NCH₂O), 7.54 (s, 1 H, H⁸), 9.34 (s, 1 H, H⁴) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 21.0 (CH₃CO), 53.1 (CO₂CH₃), 57.3 (OCH₃), 63.3 (OCH₂^b), 69.1 (OCH₂^a), 72.2 (NCH₂O), 112.4 (C³), 131.4 (C⁸), 138.7 (C⁴), 140.7 and 141.3 (C³ and C^{9a}), 153.6 and 156.4 (C² and C⁶), 161.8 (CO₂CH₃), 171.0 (CH₃CO) ppm. IR (KBr): ν = 3077 (f), 2956 (f), 1729 (F), 1635 (f), 1598 (F), 1520 (f), 1434 (m), 1383 (m), 1293 (F) cm⁻¹. MS (CI⁺, NH₃): *m/z* (%) = 385 [M + NH₄]⁺, 368 [M + H]⁺. MS (EI, 70 eV): *m/z* (%) = 367 (10) [M]⁺, 264 (17), 251 (43), 87 (100), 43 (56). HRMS (MALDI): *m/z* calcd. for C₁₅H₁₇N₃NaO₈ [M + Na]⁺ = 390.0908; found 390.0912.

Typical procedure for compounds 13j-m:

Acyl chloride (3.0 eq) was added to a solution of **12d,e** (1.0 eq) in dichloromethane. Triethylamine (3.0 eq) was added dropwise to the reaction medium at 0 °C, and the reaction mixture was stirred at room temperature for 3 h to 4 h (3 h for **13k-m** and 4 h for **13j**). The solvent was then removed and the residue was dissolved in dichloromethane, washed with water, brine, dried with magnesium sulfate and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (ethyl acetate/petroleum ether: (2:8) for **13j**; ethyl acetate/dichloromethane: (2:8) for **13k**; ethyl acetate/petroleum ether: (3:7) for **13l**; ethyl acetate/petroleum ether: (5:5) for **13m**).

1-(2',3',5'-Tri-O-benzoyl-β-D-ribofuranosyl)-3-phenyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13j): m.p. 161-163°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (91 %): δ = 4.64 (dd, *J* = 12.0 and 5.1 Hz, 1 H, 5'-H_a), 4.76-4.80 (m, 1 H, 4'-H), 4.85 (dd, *J* = 12.0 and 3.3 Hz, 1 H, 5'-

H_b), 6.25 (d, *J* = 6.6 Hz, 1 H, 7-H), 6.28–6.33 (m, 2 H, 2'-H and 3'-H), 7.22 (broad d, *J* = 7.5 Hz, 1 H, 1'-H), 7.29–7.55 (m, 14 H, H_{ar}), 7.87 (d, *J* = 6.6 Hz, 1 H, 8-H), 7.88–8.06 (m, 6 H, H_{ar}), 8.79 (s, 1 H, 4-H) ppm; Minor Isomer (9 %): δ = 4.54 (dd, *J* = 12.0 and 5.1 Hz, 1 H, 5'-H_a), 4.76–4.80 (m, 1 H, 4'-H), 4.85 (dd, *J* = 12.0 and 3.3 Hz, 1 H, 5'-H_b), 6.25 (d, *J* = 6.6 Hz, 1 H, 7-H), 6.28–6.33 (m, 2 H, 2'-H and 3'-H), 7.22 (broad d, *J* = 7.5 Hz, 1 H, 1'-H), 7.29–7.55 (m, 14 H, H_{ar}), 7.87 (d, *J* = 6.6 Hz, 1 H, 8-H), 7.88–8.06 (m, 6 H, H_{ar}), 8.63 (s, 1 H, 4-H) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: 63.4 (5'), 71.1 (3'), 73.9 (2'), 74.9 (4'), 89.0 (1'), 106.8 (7), 122.9 (3), 128.4–129.9 (C_{ar} and 4), 131.2, 133.2 and 133.6 (C_{ar}), 149.6 (9a), 153.6 (8), 157.4 and 158.8 (2 and 6), 165.4, 165.7 and 166.4 [3 C(O)Ph] ppm. IR (KBr): ν = 2979 (f), 2955 (f), 1736 (F), 1705 (F), 1601 (f), 1583 (m), 1494 (m), 1450 (f), 1383 (m), 1316 (F) cm⁻¹. MS (Cl⁺, NH₃): *m/z* (%) = 684 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₃₉H₂₉N₃NaO₉ [M + Na]⁺ = 706.1796; found 706.1787.

1-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranosyl)-3-phenyl-1H-

pyrimido[1,2-a]pyrimidine-2,6-dione (13k): m.p. 237–240°C. ¹H NMR (300 MHz, CDCl₃) Major Isomer (55 %): δ = 1.89, 2.02, 2.04 and 2.05 (4 s, 12 H, CH₃CO), 3.88–3.95 (m, 1 H, H⁶_{Glu}), 4.21–4.22 (m, 2 H, H⁶_{Glu}), 5.29 (t, *J* = 9.3 Hz, 1 H, H⁴_{Glu}), 5.38 (t, *J* = 9.3 Hz, 1 H, H³_{Glu}), 6.25 (d, *J* = 6.6 Hz, 1 H, H⁷), 6.45 (d, *J* = 9.3 Hz, 1 H, H¹_{Glu}), 6.62 (t, *J* = 9.3 Hz, 1 H, H²_{Glu}), 7.42–7.46 (m, 3 H, H_{ar}), 7.55–7.63 (m, 2 H, H_{ar}), 7.97 (d, *J* = 6.6 Hz, 1 H, H⁸), 8.74 (s, 1 H, H⁴) ppm; Minor Isomer (45 %, selected data): δ = 1.88, 2.02, 2.04 and 2.06 (4 s, 12 H, CH₃CO), 5.27 (t, *J* = 9.3 Hz, 1 H, H⁴_{Glu}), 5.39 (t, *J* = 9.3 Hz, 1 H, H³_{Glu}), 6.29 (d, *J* = 6.6 Hz, 1 H, H⁷), 6.32 (t, *J* = 9.3 Hz, 1 H, H²_{Glu}), 6.77 (d, *J* = 9.3 Hz, 1 H, H¹_{Glu}), 7.87 (d, *J* = 6.6 Hz, 1 H, H⁸), 8.67 (s, 1 H, H⁴) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: 20.6, 20.7 and 20.8 (CH₃CO), 61.9 (C⁶_{Glu}), 67.8 (C⁴_{Glu}), 68.5 (C²_{Glu}), 73.8 (C³_{Glu}), 74.9 (C⁵_{Glu}), 80.7 (C¹_{Glu}), 107.3 (C⁷), 121.4 (C³), 128.7–129.0 (CH_{ar}), 129.6 (C⁴), 131.2 (C_{ar}), 146.7 (C⁶), 153.7 (C⁸), 159.5 (C²), 169.4–170.1 (CH₃CO) ppm; Minor Isomer (selected data): δ = 68.4 (C²_{Glu}), 73.5 (C³_{Glu}), 74.8 (C⁵_{Glu}), 82.0 (C¹_{Glu}), 106.7 (C⁷), 123.8 (C³), 130.6 (C⁴), 131.1 (C_{ar}), 148.9 (C⁶), 153.4 (C⁸), 158.5 (C²) ppm. IR (KBr): ν = 3028 (f), 2951 (f), 1755 (F), 1714 (F), 1585 (f), 1514 (F), 1494 (m), 1368 (f), 1321 (f) cm⁻¹. MS (Cl⁺, NH₃): *m/z* (%) = 570 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₂₇H₂₇N₃NaO₁₁ [M + Na]⁺ = 592.1538; found 592.1543.

1-(2',3',5'-Tri-O-benzoyl-β-D-ribofuranosyl)-7-methoxy-3-phenyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13l): m.p. 131–133°C.

¹H NMR (300 MHz, CDCl₃): δ = 3.85 (s, 3 H, OCH₃), 4.66 (dd, *J* = 11.7 and 5.1 Hz, 1 H, 5'-H_a), 4.74–4.79 (m, 1 H, 4'-H), 4.83 (dd, *J* = 11.7 and 3.3 Hz, 1 H, 5'-H_b), 6.30–6.39 (m, 2 H, 2'-H and 3'-H), 7.13–7.18 (m, 1 H, 1'-H), 7.28–7.63 (m, 14 H, H_{ar}), 7.90–8.07 (m, 7 H, 8-H and H_{ar}), 8.75 (s, 1 H, 4-H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 57.2 (OCH₃), 63.4 (5'), 71.0 (3'), 73.8 (2'), 79.3 (4'), 88.5 (1'), 122.6 (3), 128.4–129.9 (C_{ar} and 4), 131.3, 133.2 and 133.6 (C_{ar}), 140.9, 148.3 and 148.5 (7, 8 and 9a), 153.9 and 158.7 (2 and 6), 165.4, 165.6 and 166.4 [3 C(O)Ph] ppm. IR (KBr): ν = 3062 (f), 2956 (f), 1726 (F), 1599 (m), 1552 (m), 1493 (m), 1451 (f), 1366 (f), 1316 (m) cm⁻¹. MS (Cl⁺, NH₃): *m/z* (%) = 714 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₄₀H₃₁N₃NaO₁₀ [M + Na]⁺ = 736.1901; found 736.1909.

1-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranosyl)-7-methoxy-3-phenyl-1H-pyrimido[1,2-a]pyrimidine-2,6-dione (13m): m.p. 103–105°C.

¹H NMR (300 MHz, CDCl₃) Major Isomer (62 %): δ = 1.90, 2.04, 2.05 and 2.07 (4 s, 12 H, CH₃CO), 3.88–3.95 (m, 4 H, H⁶_{Glu} and OCH₃), 4.17–4.24 (m, 2 H, H⁶_{Glu}), 5.28 (t, *J* = 9.3 Hz, 1 H, H⁴_{Glu}), 5.38 (t, *J* = 9.3 Hz, 1 H, H³_{Glu}), 6.43 (d, *J* = 9.3 Hz, 1 H, H¹_{Glu}), 6.64 (t, *J* = 9.3 Hz, 1 H, H²_{Glu}), 7.43–7.46 (m, 3 H, H_{ar}), 7.56–7.64 (m, 2 H, H_{ar}), 7.61 (s, 1 H, H⁴),

8.71 (s, 1 H, H⁸) ppm; Minor Isomer (38 %, selected data): δ = 1.89, 2.03, 2.05 and 2.08 (4 s, 12 H, CH₃CO), 3.88–3.95 (m, 4 H, H⁶_{Glu} and OCH₃), 4.17–4.24 (m, 2 H, H⁶_{Glu}), 5.27 (t, *J* = 9.3 Hz, 1 H, H⁴_{Glu}), 5.39 (t, *J* = 9.3 Hz, 1 H, H³_{Glu}), 6.34 (t, *J* = 9.3 Hz, 1 H, H²_{Glu}), 6.70 (d, *J* = 9.3 Hz, 1 H, H¹_{Glu}), 7.43–7.46 (m, 3 H, H_{ar}), 7.49 (s, 1 H, H⁴), 7.56–7.64 (m, 2 H, H_{ar}), 8.65 (s, 1 H, H⁸) ppm. ¹³C NMR (75 MHz, CDCl₃) Major Isomer: 20.8, 20.9 and 21.2 (CH₃CO), 57.1 (OCH₃), 62.1 (C⁶_{Glu}), 68.0 (C⁴_{Glu}), 68.4 (C²_{Glu}), 73.9 (C³_{Glu}), 74.9 (C⁵_{Glu}), 80.6 (C¹_{Glu}), 121.3 (C³), 128.8–129.1 (CH_{ar}), 129.6 (C⁴), 130.2 (C_{ar}), 139.5 (C^{9a}), 141.2 (C⁶), 154.0 (C⁸), 159.6 (C²), 169.7–170.9 (CH₃CO) ppm; Minor Isomer (selected data): δ = 68.4 (C²_{Glu}), 73.5 (C³_{Glu}), 74.8 (C⁵_{Glu}), 82.0 (C¹_{Glu}), 106.7 (C⁷), 123.8 (C³), 130.6 (C⁴), 131.1 (C_{ar}), 148.9 (C⁶), 153.4 (C⁸), 158.5 (C²) ppm. IR (KBr): ν = 2957 (f), 2927 (f), 1756 (F), 1708 (m), 1646 (f), 1552 (F), 1496 (m), 1448 (f), 1368 (f) cm⁻¹. MS (Cl⁺, NH₃): *m/z* (%) = 600 [M + H]⁺. HRMS (MALDI): *m/z* calcd. for C₂₈H₂₉N₃NaO₁₂ [M + Na]⁺ = 622.1643; found 622.1660.

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