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Small libraries of fused quinazolinone-sugars. Access to quinazolinedione nucleosides

Jolanta Girniene,[a,b] Guillaume Apremont,[a] Arnaud Tatibouët,[a,*] Algirdas Sackus[b] and Patrick Rollin[a]

[a]*Institut de Chimie Organique et Analytique, UMR CNRS 6005, Université d'Orléans, BP 6759, F-45067 Orléans, France*
[b]*Department of Organic Chemistry, , Kaunas University of Technology, LT-3028 Kaunas, Lithuania*

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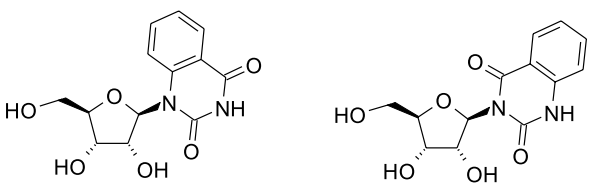
Abstract—Unprotected carbohydrates can readily be converted into base-modified nucleosides and deoxynucleosides through a short sequence involving the condensation of anthranilic acid derivatives with a suitably protected sugar-derived 2-alkylthio-1,3-oxazoline.

1. Introduction

Over the past thirty years, natural as well as synthetic nucleosides and nucleotides have been the cornerstone of antiviral therapies against hepatitis virus (HBV), herpes virus (VZV) and human immunodeficiency virus (HIV).[1] Many of those compounds exhibit antiproliferative, antibiotic and antifungal activities and some have been used as probes for DNA damages,[2] as well as in the anti-sense approach and DNA-probe technology with fluorescence properties.[3] Investigations were also undertaken on the physico-chemical parts of DNA base-to-base interactions (hydrogen bonding and stacking).[4,5] It is also well admitted that introducing diversity either into the carbohydrate or into the heterocyclic moiety of nucleosides—from natural modified nucleosides, methylated bases in the bacteria world or in RNA duplex[6] as well as new antibiotic analogues like oxanosine[7] or modified purines or pyrimidines[8] but also pyrazoles, imidazoles, phthalimides, pteridines and lumazines[9]-leads to promising molecules with a therapeutical potential. In a search for novel structural features, we have turned our attention to the quinazolinedione moiety.

To construct such bases, two general methods for nucleoside preparation could be applied from the literature, one using the glycosylation method,[10] which may lead to anomeric selectivity problems, and the other based on a multistep process to assemble entirely the base onto the carbohydrate template.[11] Our study was based on an old reaction between carbohydrates and thiocyanic acid giving 1,3-oxazolidine-2-thione (OZT) fused with a carbohydrate furan ring. OZT was the basic structure to develop a convergent preparation of fused quinazolinone-sugars and quinazolinedione nucleosides. Earlier approaches performed to obtain quinazolinedione nucleosides involve condensation of an activated ribo- or 2-deoxyribo-donor with quinazoline derivatives.[12] We herein develop a new flexible approach to what can be called *iso*-quinazolinedione nucleosides (Scheme 1).

Our convergent approach to synthesize benzopyrimidine-modified nucleosides involves a sugar derived OZT and anthranilic acid. Condensation reactions of anthranilic acid derivatives have already been explored.[13] Within the frame of a research program centered on the preparation and reactivity of chiral natural OZT, such reactions were explored.[14,15] Application of the process of anthranilic acid condensation with per-benzylated OZT led to new homochiral quinazolinone derivatives. Extension of the cyclocondensation process to sugar-derived OZT constitutes a promising extension of this reaction to new base-modified nucleosides and nucleotides.[16]



Scheme 1. Quinazolinedione nucleoside and its *iso* derivative.

Keywords: 1,3-Oxazolidine-2-thione; Nucleoside; Quinazolinone; Quinazolinedione; Anthranilic acid.
* Corresponding author. Tel.: +3323-849-4854; fax: +3323-841-7281; e-mail address: arnaud.tatibouet@univ-orleans.fr

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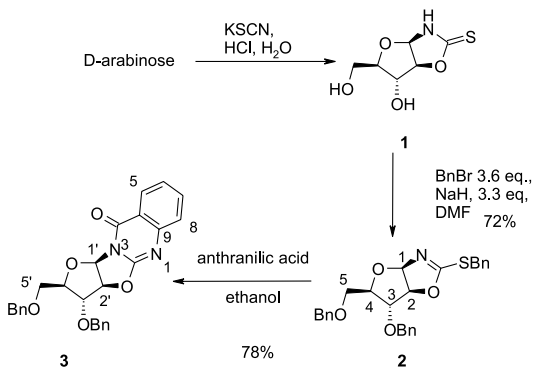


Scheme 2. The cyclocondensation process to quinazolinone via a benzylthiooxazoline intermediate in the D-arabino series.

2. Results and discussion

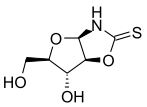
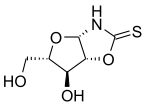
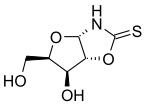
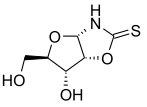
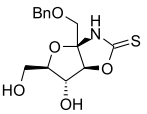
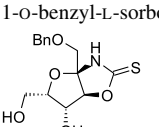
2.1. Quinazolinones preparation

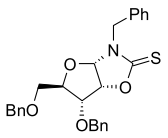
Our approach is illustrated in Scheme 2 with D-arabinose. Scheme 2: the cyclocondensation process to quinazolinone via a benzylthiooxazoline intermediate in the D-arabino series.

The preparation of the D-arabino derived OZT **1** is straightforward.[17] Standard conditions were applied to various series of sugars: D- and L-arabinose, D-xylose, D-ribose (aldopentose series) as well as D-fructose and L-sorbose (hexoketose series). On pentoses and partially protected hexoketoses (1-*O*-benzyl-D-fructose and 1-*O*-benzyl-L-sorbose), the OZT were prepared in one step using potassium thiocyanate under acidic conditions. This reaction allowed us to produce diverse OZT in which the configuration of the sugar ring was unambigously defined. A furano-conformation and an anomeric configuration controlled by the location of the hydroxyl group on C-2 was observed. In addition, in D-fructo- and L-sorbo-derivatives, known to usually give mixtures of furanose or pyranose OZT, the benzyl protection on the first primary position determined the formation of only one isomer out of the seven that could be expected from an unprotected ketohexoses.

Prior to cyclocondensation, the OZT **1** has to be activated through *S*-alkylation. This sequence furnishes the per-*O*- and -*S*-benzylated compound **2** in reasonable yields for a two-step sequence (Table 1). Alkylation of the other OZT (**4**–**8**) afforded the 2-benzylthiooxazolines (**9**–**13**) with yields ranging from 38 to 73%. For most of the compounds *N*-alkylation was not observed except with the D-ribo OZT **6**, for which 24% of *N*-benzylation was obtained (Scheme 3).

Table 1. Application of the procedure previously described for miscellaneous aldoses and ketoses

OZT		Alkylthiooxazoline (two step yields)	Quinazolinone EtOH, m.s. 3 Å (*t*BuOH, CSA, m.s 3 Å)
1	D-arabino 	**2** 38%	**3** 78% (92%)
4	L-arabino 	**9** 41%	**14** 79%
5	D-xylo 	**10** 50%	**15** 75%
6	D-ribo 	**11** 42%	**16** 65%
7	1-O-benzyl-D-fructo 	**12** 64%	**17** 14% (50%)
8	1-O-benzyl-L-sorbo 	**13** 38%	**18** 16% (70%)



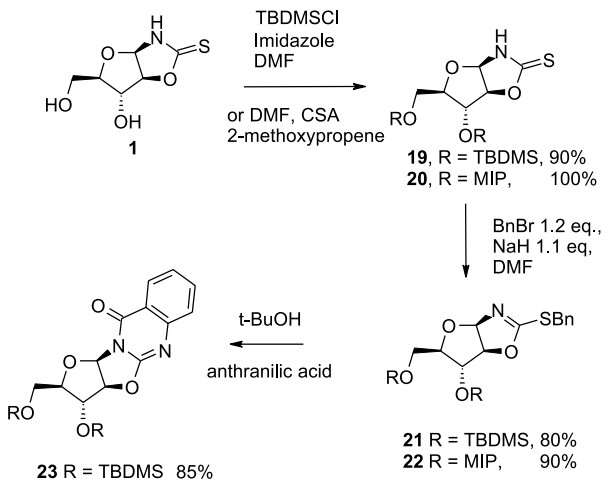
11a

Scheme 3. *N*-benzyl derivative isolated from D-ribo OZT.

Condensation of 2-benzylthio-1,3-oxazoline **2** with anthranilic acid in dry ethanol offers an efficient access to the D-arabino derived quinazolinone **3** in good yield. Application of the process to other alkylthiooxazolines (**9**–**11**) generated the quinazolinones (**14**–**16**) in similar yields. In the case of D-fructo **12** and L-sorbo **13** derivatives however, yields were poor and non-reproducible. Those results might be explained by a steric hindrance of the benzyloxymethyl group attached to the anomeric carbon. Moreover, a competing nucleophilic attack of ethanol providing the corresponding 2-ethoxy-1,3-oxazoline analogues was observed.

Improvement of the conditions was investigated using various solvents such as DMF or *tert*-butanol. In aprotic media (DMF), no condensation was detected whereas in *tert*-butanol only a slow reaction occurred. Activation was performed through addition of two equivalents of camphorsulfonic acid. In such conditions, cyclocondensations occurred in reasonable yield for D-fructo **17** and L-sorbo **18** derivatives (57 and 70%, respectively). When applied to the D-arabino derivative **2**, the above conditions resulted in much improved yields (92%).

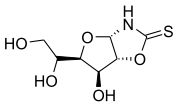
Discrimination of hydroxyls versus the OZT moiety allowed a more flexible approach to cyclocondensations. Selective protection of hydroxyls was performed either with TBDMS group or with mixed acetals, thus allowing selective activation of the OZT as benzylthiooxazoline intermediates (Scheme 4). Mixed acetal (methoxyisopropylidene, MIP) did not appear stable enough for an efficient cyclocondensation. In contrast, silyl derivatives gave the cycloadducts in 70% yield albeit together with some O-deprotection. Skipping the acidic catalysis resulted in an increased yield of 85%.



Scheme 4. The alternative approach to quinazolinone.

Table 2. Application on silylated OZT of cyclocondensation

OZT	Silylated alkylthiooxazoline	Quinazolinone *t*BuOH
D-Arabino **1**	**21** 72%	**23** 85%
L-Arabino **4**	**24** 75%	**27** 83%
D-Xylo **5**	**25** 79%	**28** 95%
D-Gluco	**26** 48%	**29** 59%



This sequence of reaction has been successfully applied to other carbohydrate series—namely L-arabino, D-xylo and D-gluco (Table 2). The silylation–thioalkylation sequence led to the formation of alkylthiooxazoline derivatives in much better yields than through direct per-alkylation. Even with a more complex structure, such as for the D-gluco derivative **26**, the process is still competitive.

Applying the cyclocondensation conditions with anthranilic acid on the *O*-silylated benzylthiooxazolines **21**, **24**, **25** gave similar yields as with the perbenzylated derivatives. With the more complex D-gluco-alkylthiooxazoline **26**, a somewhat lower yield was observed, maybe for hindrance reason.

2.2. The limits of cyclocondensation

A panel of 1,2-aminoaromatic acids was condensed with the D-arabino per-benzylated alkylthiooxazoline **2** as a model. Using the first procedure developed, results (Table 3) showed that the presence of a withdrawing group hampered to some extent the reaction. Replacing in anthranilic acid of the benzene ring by pyridine (2-aminonicotinic acid) expectedly did not allow the transformation into the desired compound.

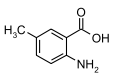
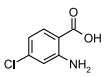
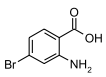
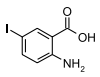
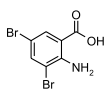
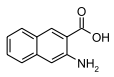
Applying the conditions developed for hindered compounds led to dramatic improvement of the yields most significantly with withdrawing groups (chloro-, bromo- and iodoanthranilic acid). However, those conditions remained inefficient in condensing aminonicotinic acid and dibromoanthranilic acid.

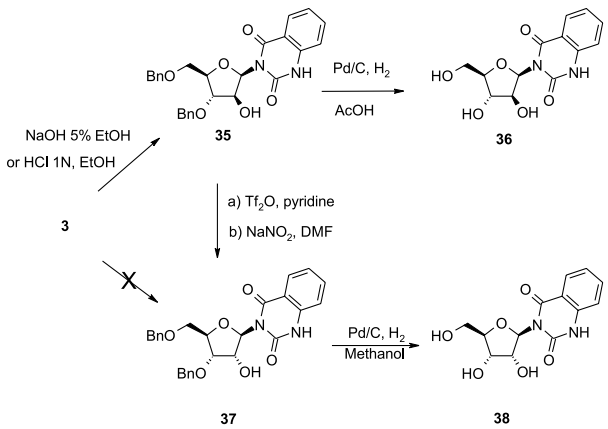
2.3. Nucleosides synthesis

Having in hand an efficient and short three steps protocol to generate new base modified 2,2′-anhydronucleosides, we have explored the ability of the newly formed heterocycles to generate the corresponding nucleosides and deoxynucleosides. To validate our approach to base-modified nucleosides, we have investigated the ring-cleavage of quinazolinones on the D-arabino model (Scheme 5). Inspired by the well-documented 2,2′-anhydronucleoside chemistry, we have reacted the D-arabino derivative **3** under basic and acidic conditions. In both cases hydrolysis of the anhydro ring was effected with good yields—67 and 73%, respectively—and complete configuration retention at the 2′-hydroxylated position.

All our attempts to induce a direct inversion aimed at producing the D-ribo-configuration failed. Thus, we obtained a D-arabino compound **35** which incorporates a

Table 3. Extension to diverse amino-aromatic acids

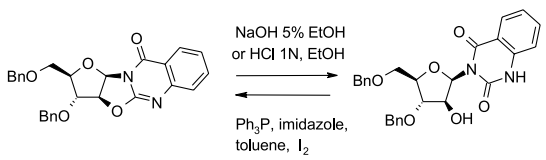
Amino acids								
EtOH, ms 4 Å	75% **3**	78% **30**	38% **31**	40% **32**	—	—	—	0%
*t*BuOH, ms 4 Å	92%	89%	86%	94%	78% **33**	0%	65% **34**	0%



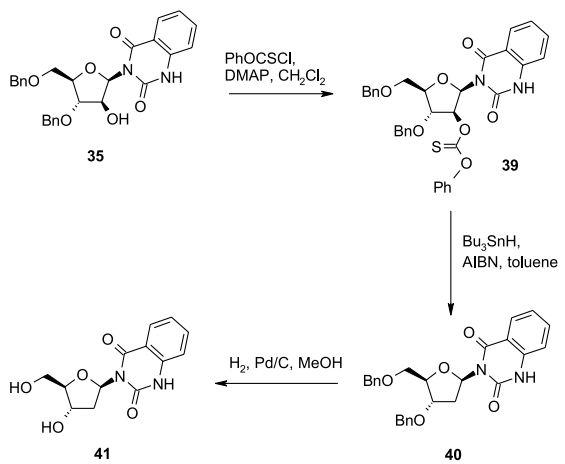
Scheme 5. Routes to base-modified nucleosides in the D-arabino series.

quinazolinedione system as the base. Further hydrogenolysis of benzyl groups (H_2 and Pd/C) afforded the D-arabino-nucleoside analogue **36** with 74% yield.

To obtain the natural carbohydrate analogue, inversion of configuration was required: among the diverse methods applied, the most efficient in our hands was the two steps process involving triflic anhydride activation of the alcohol followed by inversion with sodium nitrite. An interesting aspect of our investigations was the clean intramolecular cyclisation to the anhydro derivative, observed under standard Garegg conditions (Scheme 6).



Scheme 6. 2,2′-Anhydro formation under Garegg conditions.



Scheme 7. Deoxynucleoside formation.

Finally, the deoxynucleoside analogue was prepared through a Barton–McCombie process (Scheme 7).

The thionocarbonate **39** was prepared (85%) under basic conditions, then deoxygenated with tributylstannane to the deoxynucloside **40** in 62% yield. The fully deprotected structure **41** was obtained (62% yield) through Pd-catalysed hydrogenolysis.

3. Conclusion

In summary, a concise (5–8 steps) and practical synthesis of base-modified nucleosides has been disclosed starting from native carbohydrates through OZT derivatives. This procedure constitutes an original application of cyclo-condensations involving anthranilic acid and analogues. The reaction has been extended with success to different sugar series (pentoses and hexoses) and also to diverse heterocyclic systems (halogenoanthranilic acid and amino-naphtalenic acid), leading to a small library of base-modified anhydronucleosides.

4. Experimental

4.1. General methods

Melting points were determined on a Köfler hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX250 at 250 MHz and 62.89 MHz, respectively. The chemical shifts (δ) are reported in ppm downfield from TMS as the internal standard. Coupling constants (J) are reported in Hz. Specific rotations were measured at 20 °C using a Perkin–Elmer polarimeter 141. HR-ESI-TOF-mass spectra were recorded on a Micromass LC TOF spectrometer. Evaporation was conducted in vacuo with a Büchi rotary evaporator. Analytical TLC was carried out on precoated silica gel 60F-254 plates (E. Merck) and spots were detected by UV light (254 nm) and by heat treatment with a 10/85/5 mixture of sulfuric acid, ethanol and water. Flash column chromatography was performed on Kieselgel 60 (230–400 mesh) silica gel (E. Merck).

4.2. Chemical procedure

4.2.1. General protocol for the per-benzylation of sugar-OZT. The sugar OZT (1 equiv.) was dissolved in DMF and cooled in an ice-bath. NaH (4 equiv.) was added portionwise then benzyl bromide (4 equiv.). The reaction was brought to room temperature and stirred until completion (few hours). Ice-cold water was poured in and the mixture was extracted with AcOEt (3×50 mL). Organic phases were collected and

washed thoroughly with water, then brine and dried over $MgSO_4$. Per-benzylated compounds were purified by column chromatography using petroleum ether–ethyl acetate eluents.

4.2.2. 2-Benzylthio-4,5-dihydro-(3′,5′-di-*O*-benzyl-1′,2′-dideoxy-β-D-arabinofuranoso) [1,2-*d*]-oxazole 2. Eluent: petroleum ether–ethyl acetate 80/20, yellow oil (1.83 g, 76%); $[\alpha]_D$=−71 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.20 (dd, 1H, $J_{5a,4}$=7.0 Hz, $J_{5a,5b}$=10.2 Hz, *H-5a*); 3.40 (dd, 1H, $J_{5b,4}$=5.3 Hz, *H-5b*); 4.00–4.11 (m, 1H, *H-3*); 4.15–4.28 (m, 3H, *H-4*, SCH_2-Ph); 4.36 (d, 1H, *J*=12.1 Hz, CH_2-Ph); 4.43 (d, 1H, CH_2-Ph); 4.49 (d, 1H, *J*=12.1 Hz, CH_2-Ph); 4.55 (d, 1H, CH_2-Ph); 4.85 (dd, 1H, $J_{2,1}$=6.0 Hz, $J_{2,3}$= 1.0 Hz, *H-2*); 6.01 (d, 1H, *H-1*), 7.10–7.30 (m, 15H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ 36.1 (S-*C*H_2-Ph); 69.4 (*C*-5); 76.1 (*C*H_2-Ph); 73.1 (*C*H_2-Ph); 81.9 (*C-4*); 85.4 (*C-3*); 88.1 (*C-2*); 100.7 (*C-1*); 126.4; 126.7; 127.0; 127.5; 127.7; 127.8; 128.2; 128.3; 128.4; 128.9 (*C*H_{Ar}); 137.5; 137.8; 138.8 (*Cq*); 169.2 (*C*-S); IR (NaCl): 1608 cm^{-1} (C═N); MS IS *m*/*z* =462.0 [M+H$^+$]; HRMS: calcd for $C_{21}H_{23}NO_4$ (353.1627), found (353.1632).

4.2.3. 2-Benzylthio-4,5-dihydro-(3′,5′-di-*O*-benzyl-1′,2′-dideoxy-β-L-arabinofuranoso) [1,2-*d*]-oxazole 9. Eluent: petroleum ether–ethyl acetate 80/20, yellow oil (0.99 g, 48%); $[\alpha]_D$=+72 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.23 (dd, 1H, $J_{5a,4}$=7.1 Hz, $J_{5a,5b}$=10.2 Hz, *H-5a*); 3.41 (dd, 1H, $J_{5b,4}$=5.5 Hz, *H-5b*); 4.05 (d, 1H, $J_{3,4}$=2.2 Hz, *H-3*); 4.16–4.28 (m, 3H, *H-4*, SCH_2-Ph); 4.39 (d, 1H, *J*=12.3 Hz, CH_2-Ph); 4.45 (d, 1H, CH_2-Ph); 4.52 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.57 (d, 1H, CH_2-Ph); 4.88 (dd, 1H, $J_{2,1}$=6.0 Hz, $J_{2,3}$=0.9 Hz, *H-2*); 6.03 (d, 1H, *H-1*), 7.15–7.38 (m, 15H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ 36.2 (S*C*H_2-Ph); 69.5 (*C-5*); 71.8; 73.2 (*C*H_2-Ph); 81.7 (*C-4*); 83.9 (*C-3*); 88.3 (*C-2*); 100.8 (*C-1*); 127.6; 127.7; 127.8; 127.9; 128.0; 128.1; 128.3; 128.4; 128.5; 128,6; 129.0 (*C*H_{Ar}); 136.3; 137.0; 137.9 (*Cq*); 169.4 (*C-S*); IR (NaCl): 1608 cm^{-1} (C═N); MS IS *m*/*z*=462.5 [M+H$^+$]; HRMS: calcd for $C_{27}H_{27}NO_4S$ (461.1660), found (461.1669).

4.2.4. 2-Benzylthio-4,5-dihydro-(3′,5′-di-*O*-benzyl-1′,2′-dideoxy-β-D-xylofuranoso) [1,2-*d*]-oxazole 10. Eluent: petroleum ether–ethyl acetate 80/20, yellow oil (1.52 g, 50%); $[\alpha]_D$=+37 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.82–3.88 (m, 2H, *H-5*); 3.92–3.97 (m, 1H, *H-4*); 4.06 (d, 1H, $J_{3,4}$=3.2 Hz, *H-3*); 4.31 (d, 1H, *J*=13.2 Hz, SCH_2-Ph); 4.37 (d, 1H, *J*=13.2 Hz, SCH_2-Ph); 4.56 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.58 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.65 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.72 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.89 (d, 1H, $J_{2,1}$=5.5 Hz, *H-2*); 6.19 (d, 1H, *H-1*), 7.28–7.44 (m, 15H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ 36.5 (S*C*H_2-Ph); 67.0 (*C-5*); 72.2; 73.5 (*C*H_2-Ph); 77.5 (*C-4*); 81.0 (*C-3*); 85.5 (*C-2*); 99.9 (*C-1*); 127.7; 127.8; 128.0; 128.3; 128.4; 128.5; 128.6; 129.0 (*C*H_{Ar}); 136.2; 137.2; 138.2 (*Cq*); 165.5 (*C*-S); IR (NaCl): 1606 cm^{-1} (C═N); MS IS *m*/*z*=462.5 [M+H$^+$]; HRMS: calcd for $C_{27}H_{27}NO_4S$ (461.1660), found (461.1665).

4.2.5. 2-Benzylthio-4,5-dihydro-(3′,5′-di-*O*-benzyl-1,2-dideoxy-β-D-ribofuranoso) [1,2-*d*]-oxazole 11. Eluent: petroleum ether–ethyl acetate 80/20, white solid (3.5 g; 73%); $[\alpha]_D$=+34 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.62 (dd, 1H, $J_{5a,4}$=3.6 Hz, $J_{5a,5b}$=10.9 Hz, *H-5a*); 3.66–3.76(m, 1H, *H-4*); 3.80 (dd, 1H, $J_{5b,4}$=1.9 Hz, *H-5b*); 4.01 (dd, 1H, $J_{3,2}$=5.1 Hz, $J_{3,4}$=8.9 Hz, *H-3*); 4.27 (d, 1H, *J*=13.2 Hz, SCH_2-Ph); 4.34 (d, 1H, SCH_2-Ph); 4.51 (d, 1H, *J*=12.0 Hz, CH_2-Ph); 4.52 (d, 1H, *J*=11.5 Hz, CH_2-Ph); 4.82 (dd, 1H, $J_{2,3}$=$J_{2,1}$=5.3 Hz, *H-2*); 6.03 (d, 1H, *H-1*), 7.22–7.42 (m, 15H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ 37.0 (S*C*H_2-Ph); 67.7 (*C-5*); 72.8 (*C*H_2-Ph); 73.9 (*C*H_2-Ph); 77.0 (*C-4*); 78.0 (*C-3*); 80.9 (*C-2*); 100.1 (*C-1*); 128.1; 128.1; 128.4; 128.5; 128.8; 128.9; 129.0; 129.5 (*C*H_{Ar}); 136.6; 137.7; 138.4 (*Cq*); 171.5 (*C*-S); IR (NaCl): 1605 cm^{-1} (C═N); MS IS *m*/*z*=462.0 [M+H$^+$]; 484.0 [M+Na$^+$]; HRMS: calcd for $C_{27}H_{27}NO_4S$ (461.1660), found (461.1662).

4.2.6. 1-*N*-Benzyl-3,5-di-*O*-benzyl-1-*N*,2-*O*-thiocarbonyl-β-D-ribofuranosylamine 11a. Eluent: petroleum ether–ethyl acetate 80/20, oil (1.18 g; 24%); $[\alpha]_D$=+128 (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.56 (dd, 1H, $J_{5a,4}$=3.8 Hz, $J_{5a,5b}$=11.3 Hz, *H*-5a); 3.75 (dd, 1H, $J_{5b,4}$=1.9 Hz, *H-5b*); 3.85 (ddd, 1H, $J_{4,3}$=9.1 Hz, *H-4*); 4.99 (dd, 1H, $J_{3,2}$=5.3 Hz, *H-3*); 4.42 (d, 1H, *J*=14.8 Hz, NCH_2-Ph); 4.44 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.51 (d, 1H, *J*=11.6 Hz, CH_2-Ph); 4.53 (d, 1H, CH_2-Ph); 4.75 (d, 1H, CH_2-Ph); 4.85 (dd, 1H, $J_{2,1}$=5.3 Hz, *H-2*); 5.31 (d, 1H, NCH_2-Ph); 5.50 (d, 1H, *H-1*), 7.22–7.41 (m, 15H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ 48.0 (N*C*H_2-Ph); 66.1 (*C-5*); 71.7 (*C*H_2-Ph); 72.6 (*C*H_2-Ph); 76.1; 76.6; 77.4 (*C-4*, *C-3*, *C-2*); 89.2 (*C-1*); 126.8; 126.9; 127.0; 127.3; 127.4; 127.5; 127.6; 127.7; 127.9 (*C*H_{Ar}); 133.7; 136.0; 136.7 (*Cq*); 187.6 (*C*═S); MS IS *m*/*z*=462,0 [M+H$^+$]; 484,0 [M+Na$^+$]; HRMS: calcd $C_{27}H_{27}NO_4S$ (461.1660), found (461.1665).

4.2.7. 2-Benzylthio-4,5-dihydro-(1′,4′,6′-tri-*O*-benzyl-2′,3′-dideoxy-β-D-fructofuranoso) [2,3-*d*]-oxazole 12. Eluent: petroleum ether–ethyl acetate 80/20, oil (0.75 g; 64%); $[\alpha]_D$=−37 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.36 (dd, 1H, $J_{6a,6b}$=10.3 Hz, $J_{6a,5}$=6.1 Hz, *H*-6a); 3.47 (dd, 1H, $J_{6b,5}$=5.3 Hz, *H-6b*); 3.70 (d, 1H, $J_{1a,1b}$=10.6 Hz, *H-1a*); 3.78 (d, 1H, *H-1b*); 4.06 (dd, 1H, $J_{4,3}$=1.9 Hz, $J_{4,5}$=4.4 Hz, *H-4*); 4.20–4.34 (m, 3H, SCH_2-Ph, *H-5*); 4.45–4.65 (m, 6H, CH_2-Ph); 4.96 (d, 1H, *H-3*); 7.19–7.38 (m, 20H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ 36.3 (S*C*H_2); 69.6 (*C-6*); 71.8; 73.4; 73.6 (*C*H_2-Ph); 72.1 (*C-1*); 82.1 (*C-5*); 84.6 (*C-4*); 89.0 (*C-3*); 110.0 (*C-2*); 127.6; 127.7; 127.8; 127.9; 128.4; 128.5; 128.6; 129.1; 136.5 (*C*H_{Ar}); 137.2; 138.0; 138.1 (*C*q_{Ar}); 168.6 (*C*-S); IR (NaCl): 1596 cm^{-1} (C═N); MS IS *m*/*z*=582.5 [M+H$^+$]; HRMS: calcd for $C_{35}H_{35}NO_5S$ (581.2235), found (581.2244).

4.2.8. 2-Benzylthio-4,5-dihydro-(1′,4′,6′-tri-*O*-benzyl-2′,3′-dideoxy-*a*-L-sorbofuranoso) [2,3-*d*]-oxazole 13. Eluent: petroleum ether–ethyl acetate 80/20, oil (0.17 g; 42%); $[\alpha]_D$=−32 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.73–3.88 (m, 2H, *H-6*, *H-1*); 3.92–4.00 (m, 2H, *H-5*, *H-4*); 4.23 (d, 1H, *J*=13.2 Hz, SCH_2-Ph); 4.31 (d, 1H, SCH_2-Ph); 4.44 (d, 1H, *J*=11.9 Hz; CH_2-Ph); 4.46 (d, 1H, CH_2-Ph); 4.52–4.65 (m, 4H, CH_2-Ph); 4.83 (s, 1H, *H-3*); 7.12–7.40 (m, 20H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ 36.5 (S*C*H_2); 67.0 (*C-6*); 71.5 (*C-1*); 71.8; 73.5; 73.7 (*C*H_2-Ph); 78.6; 81.2 (*C-4*, *C-5*); 85.7 (*C-3*); 109.4 (*C-2*); 127.6; 127.7; 127.8; 127.9; 128.3; 128.4; 128.5; 128.6; 129.1 (*C*H_{Ar}); 136.3; 137.4; 138.0; 138.2 (*C*q_{Ar}); 188.8 (*C*═S); IR (NaCl): 1600 cm^{-1} (C═N); MS IS *m*/*z*=582.5 [M+H$^+$];; HRMS: calcd for $C_{35}H_{35}NO_5S$ (581.2235), found (581.2231).

4.2.9. 2-Benzylthio-4,5-dihydro-(3′,5′-bis-*O*-(1-methoxy-1-methylethyl)-1′,2′-dideoxy-β-D-arabinofuranoso) [1,2-*d*]-oxazole 22. The sugar OZT **1** (0.1 g, 0.52 mmol) was dissolved in DMF under Ar and cooled in an ice-bath. 2-Methoxypropene (5 equiv.) then CSA (0.1 equiv.) were added. The reaction was run at room temperature for 16 h. At completion, the solution was basified with Et_3N, diluted with water, then extracted with AcOEt. The organic phases obtained were collected and washed thoroughly with water then brine. After evaporation, the residue was dissolved in DMF and after cooling in an ice bath, NaH (2 equiv.) was added portionwise then benzyl bromide (2 equiv.). The reaction was brought to room temperature and stirred until completion of the reaction (2 h). Ice-cold water was poured in then the mixture was extracted with AcOEt (3×50 mL). Organic phases were collected and washed thoroughly with water, then brine. Purification was effected by column chromatography with eluents of petroleum ether–ethyl acetate, yielding **22**; eluent: petroleum ether–ethyl acetate 95/5, oil (0.22 g; 94%); $[\alpha]_D=-115$ (*c* 0.1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.29; 1.31; 1.37; 1.41 (4 s, 12H, $(CH_3)_2C$); 3.18; 3.22 (2 s, 6H, CH_3O); 3.22–3.32 (m, 1H, *H-5a*); 3;39 (dd, 1H, $J_{5b,4}=8.2$ Hz, $J_{5b,5a}=9.7$ Hz, *H-5b*); 4.15 (ddd, 1H, $J_{4,5a}=6.0$ Hz, *H-4*); 4.28 (s, 2H, SCH_2-Ph); 4.42 (d, 1H, $J_{3,4}=2.2$ Hz, *H-3*); 4.87 (d, 1H, $J_{2,1}=6.0$ Hz, *H-2*); 6.08 (d, 1H, *H-1*); 7.25–7.45 (m, 5H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ 24.3; 24.4; 24.8; 25.3 ($(CH_3)_2C$); 36.4 (SCH_2-Ph); 48.7; 49.1 (CH_3O); 60.8 (*C-5*); 75.8 (*C-3*); 84.2 (*C-4*); 90.1 (*C-2*); 100.9 (*C-1*); 101.1; 101.7 (*Cq*); 127.7; 128.7; 129.1 (CH_{Ar}); 136.7 (*Cq*); 169.1 (*C*-S); IR (NaCl): 1603 cm^{-1} (C=N); MS IS *m*/*z*=426.0 $[M+H^+]$; 448.0 $[M+Na^+]$; HRMS: calcd for $C_{21}H_{31}NO_6S$ (425.1872), found (425.1876).

4.2.10. General protocol for the silylation/benzylation of sugar-OZTs. The sugar-OZT (1 equiv.) was dissolved in DMF (0.2 M) under Ar and cooled in an ice-bath. Imidazole, then TBDMSCl (1.2 equiv./OH group) were added. The reaction was kept at room temperature until completion, then extracted with AcOEt and water. The organic phases were collected and washed with water (4–5 times) and brine, then dried over $MgSO_4$. After evaporation, the silylated OZT was purified by column chromatography with petroleum ether-AcOEt solvent mixtures. The purified OZT was dissolved in DMF, cooled in an ice-bath, NaH (1.2 equiv.) was added portionwise then benzyl bromide (1.2 equiv.). The reaction was brought to room temperature and stirred until completion of the reaction (few hours). Ice-cold water was poured in then the mixture was extracted with AcOEt (3×50 mL). Organic phases were collected and washed thoroughly with water, then brine and dried over $MgSO_4$. The benzylated compounds were purified by column chromatography with eluents of petroleum ether–ethyl acetate.

4.2.11. 2-Benzylthio-4,5-dihydro-(3′,5′-di-*O*-*tert*butyldimethylsilyl-1′,2′-dideoxy-β-D-arabinofuranoso) [1,2-*d*]-oxazole 21. Eluent: petroleum ether–ethyl acetate 90/10, oil (0.23 g; 95%); $[\alpha]_D=-51$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.05; 0.12; 0.13; 0.15 (4s, 12H, CH_3Si); 0.90; 0.93 (2s, 18H, $(CH_3)C$); 3.33 (dd, 1H, $J_{5a,5b}=10.6$ Hz, *H-5a*); 3.61 (dd, 1H, *H-5b*); 3.97 (ddd, 1H, $J_{4,3}=2.8$ Hz, $J_{4,5a}=4.7$ Hz, $J_{4,5b}=8.5$ Hz, *H-4*); 4.29 (d, 1H, *J*=13.2 Hz, SCH_2-Ph); 4.33 (d, 1H, SCH_2-Ph); 4.42 (sl, 1H, *H-3*); 4.77 (dd, 1H, $J_{2,1}=6.0$ Hz, $J_{2,3}=1.1$ Hz, *H-2*); 6.07 (d, 1H, *H-1*); 7.23–7.42 (m, 5H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ −5.3; −4.8 (CH_3Si); 18.1; 18.4 ($(CH_3)_3C$); 25.8; 26.0 ($(CH_3)_3C$); 36.4 (SCH_2-Ph); 62.3 (*C-5*); 76.6 (*C-3*); 86.4 (*C-4*); 91.0 (*C-2*); 100.6 (*C-1*); 127.7; 128.7; 129.1 (CH_{Ar}); 136.5 (*Cq*); 169.6 (*C*-S); IR (NaCl): 1609 cm^{-1} (C=N); MS IS *m*/*z*=510.0 $[M+H^+]$; HRMS: calcd for $C_{25}H_{43}NO_4SSi_2$ (509.2451), found (509.2458).

4.2.12. 2-Benzylthio-4,5-dihydro-(3′,5′-di-*O*-*tert*butyldimethylsilyl-1′,2′-dideoxy-α-L-arabinofuranoso) [1,2-*d*]-oxazole 24. Eluent: petroleum ether–ethyl acetate 90/10, white foam (2.42 g; 80%); $[\alpha]_D=+51$ (*c* 1.1, CH_2Cl_2); ^1H NMR ($CDCl_3$): δ −0.07; 0.02; 0.03 (3 s, 12H, CH_3Si); 0.78; 0.80 (2 s, 18H, $(CH_3)C$); 3.21 (dd, 1H, $J_{5a,5b}=10.5$ Hz, $J_{5b,4}=8.8$ Hz, *H-5b*); 3.49 (dd, 1H, $J_{5a,4}=4.9$ Hz, *H-5b*); 3.86 (m, 1H, *H-4*); 4.21 (d, 1H, *J*=13.2 Hz, SCH_2-Ph); 4.24 (d, 1H, SCH_2-Ph); 4.30 (s, 1H, *H-3*); 4.67 (d, 1H, $J_{2,1}=5.8$ Hz, *H-2*); 5.96 (d, 1H, *H-1*); 7.16–7.29 (m, 5H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ −5.1; −4.6 (CH_3Si); 18.2; 18.5 ($(CH_3)_3C$); 25.9; 26.0; 26.1; 26.2 ($(CH_3)_3C$); 36.6 (SCH_2-Ph); 62.5 (*C-5*); 77.1 (*C-3*); 86.6 (*C-4*); 91.2 (*C-2*); 100.7 (*C-1*); 127.9; 128.9; 129.3 (CH_{Ar}); 136.9 (*Cq*); 169.8 (*C*-S); IR (NaCl): 1609 cm^{-1} (C=N); MS IS *m*/*z*=510.5 $[M+H^+]$; HRMS: calcd for $C_{25}H_{43}NO_4SSi_2$ (509.2451), found (509.2455).

4.2.13. 2-Benzylthio-4,5-dihydro-(3′,5′-di-*O*-*tert*butyldimethylsilyl-1′,2′-dideoxy-β-D-xylofuranoso) [1,2-*d*]-oxazole 25. Eluent: petroleum ether–ethyl acetate 90/10, oil (0.23 g; 95%); $[\alpha]_D=+41$ (*c* 1.1, MeOH); ^1H NMR ($CDCl_3$): δ 0.07; 0.11; 0.13 (3 s, 12H, CH_3Si); 0.91; 0.92 (2s, 18H, $(CH_3)C$); 3.55–3.77 (m, 1H, *H-4*); 3.80–3.90 (m, 2H, *H-5*); 4.25 (d, 1H, $J_{3,4}=3.0$ Hz, *H-3*); 4.32 (s, 2H, SCH_2-Ph); 4.70 (d, 1H, $J_{2,1}=5.4$ Hz, *H-2*); 6.09 (d, 1H, *H-1*); 7.20–7.35 (m, 5H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ −4.6; −4.5; −4.3; −4.1; −3.8; −3.5 (CH_3Si); 18.1; 18.3 ($(CH_3)_3C$); 25.7; 26.0 ($(CH_3)_3C$); 36.5 (SCH_2-Ph); 59.9 (*C-5*); 74.9 (*C-3*); 79.8 (*C-4*); 88.8 (*C-2*); 99.6 (*C-1*); 127.7; 128.6; 129.0 (CH_{Ar}); 136.3 (*Cq*); 169.4 (*C*-S); IR (NaCl): 1609 cm^{-1} (C=N); MS IS *m*/*z*=510.5 $[M+H^+]$; HRMS: calcd for $C_{25}H_{43}NO_4SSi_2$ (509.2451), found (509.2452).

4.2.14. 2-Benzylthio-4,5-dihydro-(3′,5′,7′-tri-*O*-*tert*butyldimethylsilyl-1′,2′-dideoxy-β-D-glucofuranoso) [1,2-*d*]-oxazole 26. Eluent: petroleum ether–ethyl acetate 90/10, oil (0.23 g; 95%); $[\alpha]_D=+60$ (*c* 1.1, MeOH); ^1H NMR ($CDCl_3$): δ 0.09; 0.10; 0.11; 0.15; 0.17 (5s, 18H, CH_3Si); 0.88–0.93 (m, 27H, $(CH_3)C$); 3.55 (dd, 1H, $J_{4,3}=2.6$ Hz, $J_{4,5}=6.6$ Hz, *H-4*); 3.69 (dd, 1H, $J_{6a,6b}=10.9$ Hz, *H-6b*); 3.90 (dd, 1H, *H-6a*); 4.04–4.13 (m, 1H, *H-5*); 4.23 (d, 1H, SCH_2-Ph); 4.31–4.28 (m, 1H, *H-3*); 4.34 (d, 1H, SCH_2-Ph); 4.69 (d, 1H, $J_{2,1}=5.4$ Hz, *H-2*); 6.01 (d, 1H, *H-1*); 7.23–7.26 (m, 5H, CH_{Ar}); ^{13}C NMR ($CDCl_3$): δ −5.2; −5.1; −4.4; −4.2; 4.1; −3.4 (CH_3Si); 18.1; 18.3; 18.4 ($(CH_3)_3C$); 25.9; 26.1 ($(CH_3)_3C$); 36.5 (SCH_2-Ph); 65.2 (*C-6*); 71.5 (*C-5*); 75.0 (*C-3*); 80.2 (*C-4*); 87.2 (*C-2*); 99.1 (*C-1*); 127.6; 128.6; 129.0 (CH_{Ar}); 136.3 (*Cq*); 169.3 (*C*-S); MS IS *m*/*z*=654.5 $[M+H^+]$; HRMS: calcd for $C_{33}H_{51}NO_5SSi_2$ (629.3026), found (629.3031).

4.2.15. Generals protocols for cyclocondensation. *Method A*: The benzylthiooxazoline (1 equiv.) was dissolved in

ethanol, then molecular sieves 3 Å and the anthranilic acid derivative (1.3 equiv.) were added. The solution was refluxed overnight, then poured into an aqueous solution of $NaHCO_3$ (5%) and extracted with CH_2Cl_2 (3×50 mL). The organic phases were collected, washed with water, brine then dried over $MgSO_4$. The crude mixture obtained after drying in vacuo was purified by column chromatography.

Method B: The benzylthiooxazoline (1 equiv.) was dissolved in *tert*-butanol then molecular sieves 3 Å, camphorsulfonic acid (CSA) (1.1 equiv.), the anthranilic acid derivative (1.3 equiv.) were added. The solution was refluxed overnight, then poured into an aqueous solution of $NaHCO_3$ (5%) and extracted with CH_2Cl_2 (3×50 mL). The organic phases were collected, washed with water, brine then dried over $MgSO_4$. The crude mixture obtained after drying in vacuo was purified by column chromatography.

4.2.16. O^2,$O^{2'}$-Anhydro-3-(3′,5′-di-*O*-benzyl-β-D-arabinofuranosyl)-2,4-quinazolinedione 3. (Method B) Eluent: petroleum ether–ethyl acetate 70/30, yellow solid (2.62 g; 89%), mp=101–103 °C; $[\alpha]_D$=167 (*c* 0.59, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.33 (dd, 1H, $J_{5'a,4'}$=3.8 Hz, $J_{5'a,5'b}$=10.4 Hz, *H-5′a*); 3.76 (dd, 1H, $J_{5'b,4'}$=4.4 Hz, *H-5′b*); 4.17 (d, 1H, *J*=12.2 Hz, CH_2-Ph); 4.24 (d, 1H, CH_2-Ph); 4.38 (d, 1H, $J_{3',4'}$=2.2 Hz, *H-3′*); 4.41–4.47 (m, 1H, *H-4′*); 4.59 (d, 1H, *J*=11.6 Hz, CH_2-Ph); 4.65 (d, 1H, CH_2-Ph); 5.23 (d, 1H, $J_{2',1'}$=6.0 Hz, *H-2′*); 6.60 (d, 1H, *H-1′*), 6.68–7.07 (m, 2H, CH_{Ar}); 7.14–7.20 (m, 3H, CH_{Ar}); 7.27–7.41 (m, 6H, *H-6′*, 5×CH_{Ar}); 7.45 (dd, 1H, $J_{8,6}$=0.6 Hz, $J_{8,7}$=8.2 Hz, *H-8*); 7.64 (ddd, 1H, $J_{7,5}$=1.3 Hz, $J_{7,6}$=7.2 Hz, *H-7*); 8.31 (dd, 1H, $J_{6,5}$=8.2 Hz, *H-5*); ^{13}C NMR ($CDCl_3$): δ 69.0 (*C-5′*); 72.4; 73.4 (*C*H_2-Ph); 83.3 (*C-3′*); 85.5 (*C-4′*); 85.9 (*C-2′*); 87.7 (*C-1′*); 118.9 (*C-9*); 124.9 (*C-6*); 126.3 (*C-8*); 127.2 (*C-5*); 127.8; 127.9; 128.1; 128.3; 128.4; 128.7 (*C*H_{Ar}); 135.1 (*C-7*); 136.5; 137.1 (*Cq*); 149.1 (*C-10*); 156.7 (*C-2*) 160.2 (*C-4*); IR (NaCl): 1693 cm^{-1} (C=N); 1646 cm^{-1} (C=O); MS IS *m/z*=457.5 [M+H$^+$]; HRMS: calcd for $C_{27}H_{24}N_2O_5$ (456.1685), found (456.1690).

4.2.17. O^2,$O^{2'}$-Anhydro-3-(3′,5′-di-*O*-benzyl-α-L-arabinofuranosyl)-2,4-quinazolinedione 14. (Method A) Eluent: petroleum ether–ethyl acetate 70/30, yellow solid (79 mg; 79%); mp=101–103 °C; $[\alpha]_D$=−169 (*c* 0.55, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.35 (dd, 1H, $J_{5'a,4'}$=3.8 Hz, $J_{5'a,5'b}$=10.7 Hz, *H-5′a*); 3.39 (dd, 1H, $J_{5'b,4'}$=4.4 Hz, *H-5′b*); 4.19 (d, 1H, *J*=12.3 Hz, CH_2-Ph); 4.25 (d, 1H, CH_2-Ph); 4.39 (d, 1H, $J_{3',4'}$=2.2 Hz, *H-3′*); 4.43–4.48 (m, 1H, *H-4′*); 4.61 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.67 (d, 1H, CH_2-Ph); 5.23 (d, 1H, $J_{2',1'}$=5.7 Hz, *H-2′*); 6.62 (d, 1H, *H-1′*), 6.99–7.07 (m, 2H, CH_{Ar}); 7.14–7.22 (m, 3H, CH_{Ar}); 7.28–7.42 (m, 6H, *H-6*, 5×CH_{Ar}); 7.47 (dd, 1H, $J_{8,6}$=0.9 Hz, *H-8*); 7.66 (ddd, 1H, $J_{7,5}$=$J_{7,6}$=7.2 Hz, $J_{7,5}$=1.6 Hz, *H-7*); 8,23 (dd, 1H, $J_{5,6}$=8.0 Hz, *H-5*); ^{13}C NMR ($CDCl_3$): δ 69.1 (*C-5′*); 72.5; 73.5 (*C*H_2-Ph); 83.6 (*C-3′*); 85.4 (*C-4′*); 86.0 (*C-2′*); 87.7 (*C-1′*); 119.0 (*C-9*); 125.0 (*C-6*); 126.4 (*C-8*); 127. (*C-5*); 127.9; 128.0; 128.2; 128.4; 128.5; 128.8 (*C*H_{Ar}); 135.2; 136.5 (*Cq*); 137.1 (*C-7*); 149.2 (*C-10*); 154.7 (*C-2*) 160.3 (*C-4*); IR (NaCl): 1693 cm^{-1} (C=N); 1646 cm^{-1} (C=O); MS IS *m/z*=457.0 [M+H$^+$]; HRMS: calcd for $C_{27}H_{24}N_2O_5$ (456.1685), found (456.1694).

4.2.18. O^2, $O^{2'}$-Anhydro-3-(3′,5′-di-*O*-benzyl-α-D-xylofuranosyl)-2,4-quinazolinedione 15. (Method A) Eluent: petroleum ether–ethyl acetate 50/50, yellow foam (144 mg; 75%); $[\alpha]_D$=−169 (*c* 0.55, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.77 (dd, 1H, $J_{5'a,4'}$=6.0 Hz, $J_{5'a,5'b}$=10.0 Hz, *H-5′a*); 3.84 (dd, 1H, $J_{5b,4}$=6.0 Hz, *H-5′b*); 4.21 (ddd, 1H, $J_{3',4'}$=3.5 Hz, *H-4′*); 4.32 (d, 1H, *H-3′*); 4.48 (d, 1H, *J*=12 Hz, CH_2-Ph); 4.55 (d, 1H, *J*=12 Hz, CH_2-Ph); 4.64 (d, 1H, *J*=12 Hz, CH_2-Ph); 4.73 (d, 1H, *J*=12 Hz, CH_2-Ph); 5.16 (d, 1H, $J_{2',1'}$=5.3 Hz, *H-2′*); 6.60 (d, 1H, *H-1′*); 7.23–7.38 (m, 11H, Ph-H, *H-6*); 7.46 -d, 1H, $J_{8,7}$=8.2 Hz, *H-8*); 7.64 (ddd, 1H, $J_{7,5}$=1.6 Hz, $J_{7,6}$=7.2 Hz, *H-7*); 8.17 (dd, 1H, $J_{5,6}$=7.8 Hz, *H-5*); ^{13}C NMR ($CDCl_3$): δ 66.8 (*C-5′*); 72.9 (*C*H_2-Ph); 73.7 (*C*H_2-Ph); 79.7 (*C-4′*); 80.4 (*C-3′*); 83.7 (*C-2′*); 86.5 (*C-1′*); 119.0 (*C-9*); 125.1 (*C-6*); 126.3 (*C-8*); 127.0 (*C-5*); 127.2; 127.9; 128.0; 128.3; 128.4; 128.7 (*C*H_{Ar}); 135.2 (*C-7*); 136.8; 137.7; 148.8 (*C-10*); 154.5 (*C-2*); 160.2 (*C-4*); IR (NaCl): 1659 cm^{-1} (C=N); 1701 cm^{-1} (C=O); MS IS *m/z*=457 [M+H$^+$]; HRMS: calcd for $C_{27}H_{24}N_2O_5$ (456.1685), found (456.1683).

4.2.19. O^2, $O^{2'}$-Anhydro-3-(3′,5′-di-*O*-benzyl-β-D-ribofuranosyl)-2,4-quinazolinedione 16. (Method A) Eluent: petroleum ether–ethyl acetate 70/30, yellow solid (1.66 g; 82%); mp=83–85 °C; $[\alpha]_D$=263 (*c* 0.55; $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.64 (dd, 1H, $J_{5'a,4'}$=3.2 Hz, $J_{5'a,5'b}$=11.3 Hz, *H-5′a*); 3.81 (dd, 1H, $J_{5'b,4'}$=1.9 Hz, *H-5′b*); 3.98–4.06 (m, 1H, *H-4′*); 4.24 (dd, 1H, $J_{3',2'}$=5.1 Hz, $J_{3',4'}$=8.5 Hz, *H-3′*); 4.48 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.58 (d, 1H, CH_2-Ph); 4.63 (d, 1H, *J*=11.5 Hz, CH_2-Ph); 4.79 (d, 1H, CH_2-Ph); 5.11 (dd, 1H, $J_{2',1'}$=5.3 Hz, *H-2′*); 6.55 (d, 1H, *H-1′*), 7.24–7.42 (m, 11H, *H-6*, CH_{Ar}); 7.53 (d, 1H, $J_{8,7}$=7.7 Hz, *H-8*); 7.69 (ddd, 1H, $J_{7,5}$=1.3 Hz, $J_{7,6}$=7.2 Hz, *H-7*); 8.22 (d, 1H, $J_{5,6}$=8.0 Hz, *H-5*); ^{13}C NMR ($CDCl_3$): δ 67.1 (*C-5′*); 73.0; 73.7 (*C*H_2-Ph); 76.7 (*C-3′*); 78.6 (*C-2′*); 79.1 (*C-4′*); 86.4 (*C-1′*); 119.0 (*C-9*); 125.1 (*C-6*); 126.4 (*C-8*); 127.2 (*C-5*); 127.8; 127.9; 128.2; 128.4; 128.5; 128.6 (*C*H_{Ar}); 135.3 (*C-7′*); 136.9; 137.7 (*Cq*); 149.0 (*C-10*); 155.1 (*C-2*) 160.3 (*C-4*); IR (NaCl): 1656 cm^{-1} (C=N); 1702 cm^{-1} (C=O); MS IS *m/z*=457 [M+H$^+$]; HRMS: calcd for $C_{27}H_{24}N_2O_5$ (456.1685), found (456.1691).

4.2.20. O^2, $O^{3'}$-Anhydro-3-(1′,4′,6′-tri-*O*-benzyl-β-D-fructofuranosyl)-2,4-quinazolinedione 17. (Method B with 2 equiv. of CSA) Eluent: petroleum ether–ethyl acetate 80/20, pale yellow oil (90 mg; 57%); $[\alpha]_D$=−31 (*c* 0.74; $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.30 (dd, 1H, $J_{6'a,5'}$=3.6 Hz, $J_{6'a,6'b}$=10.7 Hz, *H-6′a*); 3.37 (dd, 1H, $J_{6'b,5'}$=4.2 Hz, *H-6′b*); 3.92 (d, 1H, $J_{1'a,1'b}$=10.4 Hz, *H-1′a*); 4.13 (d, 1H, *J*=12.3 Hz, CH_2-Ph); 4.19 (d, 1H, CH_2-Ph); 4.33 (dd, 1H, $J_{4,3}$=0.9 Hz, $J_{4',5'}$=2.5 Hz, *H-4′*); 4.45–4.71 (m, 6H, 2 CH_2-Ph, *H-1′b*, *H-5′*); 5.14 (s, 1H, *H-3′*); 6.95–7.03 (m, 2H, CH_{Ar}); 7.11–7.39 (m, 14H, *H-6*, CH_{Ar}); 7.43–7.50 (m, 1H, *H-8*); 7.36 (ddd, 1H, $J_{7,5}$=1.6 Hz, $J_{7,6}$=$J_{7,8}$=7.2 Hz, *H-7*); 8.20 (dd, 1H, $J_{5,6}$=8.0 Hz, *H-5*); ^{13}C NMR ($CDCl_3$): δ 68.5 (*C-6′*); 69.1 (*C-1′*); 72.2; 73.5; 73.7 (*C*H_2-Ph); 84.1 (*C-4′*); 86.3 (*C-5′*); 87.2 (*C-3′*); 100.7 (*C-2′*); 119.4 (*C-9*); 124.7 (*C-6*); 126.2 (*C-8*); 127.1 (*C-5*); 127.8; 127.9; 128.0; 128.3; 128.4; 128.5; 128.6; 128.7 (*C*H_{Ar}); 135.0 (*C-7*); 136.6; 137.1; 137.4 (*Cq*); 149.1 (*C-10*); 155.2 (*C-2*) 160.7 (*C-4*); IR (NaCl): 1695 (C=N); 1648 (C=O); MS IS *m/z*=577.5 [M+H$^+$]; HRMS: calcd for $C_{35}H_{32}N_2O_6$ (576.2260), found (576.2267).

4.2.21. *O*2³, *O* 3′-Anhydro-3-(1′,4′,6′-tri-*O*-benzyl-α-L-sorbofuranosyl)-2,4-quinazolinedione 18. (Method B with 2 equiv. of CSA) Eluent: petroleum ether–ethyl acetate 80/20, pale yellow oil (110 mg; 70%); $[\alpha]_D=-28$ (*c* 1.04; $CHCl_3$); ^1H NMR ($CDCl_3$): δ 3.40 (dd, 1H, $J_{6'a,5'}$=5.0 Hz, $J_{6'a,6'b}$=10.0 Hz, *H-6′a*); 3.79 (dd, 1H, $J_{6'b,5'}$=5.8 Hz, *H-6′b*); 3.80 (d, 1H, $J_{1'a,1'b}$=10.0 Hz, *H-1′a*); 4.19–4.27 (m, 2H, *H-4′*, *H-5′*); 4.43 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.46 (d, 1H, *J*=12.3 Hz, CH_2-Ph); 4.47 (d, 1H, *J*=14.4 Hz, CH_2-Ph); 4.58 (d, 1H, CH_2-Ph); 4.62 (d, 1H, CH_2-Ph); 4.78 (d 1H, *H-1′b*); 5.01 (s, 1H, *H-3′*); 7.15–7.36 (m, 16H, *H-6*, CH_{Ar}); 7.49 (dd, 1H, $J_{8,6}$=0.6 Hz, $J_{8,7}$=7.9 Hz, *H-8*); 7.65 (ddd, 1H, $J_{7,5}$=1.6 Hz, *H-7*); 8.19 (dd, 1H, $J_{5,6}$=7.9 Hz, *H-5*); ^{13}C NMR ($CDCl_3$): δ 68.4 (*C-6′*); 67.7 (*C-1′*); 72.5; 73.6; 73.7 (*C*H_2-Ph); 80.4; 80.8 (*C-4′*, *C-5′*); 84.4 (*C-3′*); 99.7 (*C-2′*); 119.6 (*C-9*); 124.9 (*C-6*); 126.2 (*C-8*); 127.2 (*C-5*); 127.8; 127.9; 128.3; 128.4; 128.5; 128.7 (*C*H_{Ar}); 135.1 (*C-7*); 136.8; 137.4; 137.7 (*Cq*); 148.8 (*C-10*); 155.0 (*C-2*) 160.7 (*C-4*); IR (NaCl): 1699 (C═N); 1647 (C═O); MS IS *m*/*z*=577.5 [M+H⁺]; HRMS: calcd for $C_{35}H_{32}N_2O_6$ (576.2260), found (576.2263).

4.2.22. *O* 2′, *O* 2′-Anhydro-3-(3′,5′-di-*O*-*tert*butyldimethylsilyl-β-D-arabinofuranosyl)-2,4-quinazolinedione 23. (Method B without CSA) Eluent: petroleum ether–ethyl acetate 90/10, white solid (124 mg; 85%); mp: 111–112 °C; $[\alpha]_D=-193$ (*c* 0.45; $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.06; 0.20; 0.23 (3 s, 12H, CH_3Si); 0.80; 0.97 (2s, 18H, (CH_3)C); 3.52 (dd, 1H, $J_{5'a,4'}$=6.9 Hz, $J_{5'a,5'b}$=11 Hz, *H-5′a*); 3.67 (dd, 1H, $J_{5'b,4'}$=4.2 Hz, *H-5′b*); 4.14–4.22 (m, 1H, *H-4′*); 4.73 (dd, 1H, $J_{3',2'}$=1.3 Hz, $J_{3',4'}$=3.1 Hz, *H-3′*); 5.14 (dd, 1H, $J_{2',1'}$=5.6 Hz, *H-2′*); 6.62 (d, 1H, *H-1′*), 7.36 (ddd, 1H, $J_{6,8}$=1.2 Hz, $J_{6,5}=J_{6,7}$=7.2 Hz, *H-6*); 7.53 (dd, 1H, $J_{8,7}$= 8.2 Hz, *H-8*); 7.70 (ddd, 1H, $J_{7,5}$=1.5 Hz, *H-7*); 8.23 (dd, 1H, *H-5*); ^{13}C NMR ($CDCl_3$): δ −5.5; −5.4; −4.8; −4.7 (CH_3Si); 18.0; 18.2 ((CH_3)$_3$*C*); 25.7; 25.8 ((*C*H$_3$)$_3$C); 61.8 (*C-5′*); 75.9 (*C-3′*); 86.7 (*C-1′*); 88.4 (*C-2′*); 88.8 (*C-4′*); 118.9 (*C-9*); 125.1 (*C-6*); 126.4 (*C-8*); 127.2 (*C-5*); 135.2 (*C-7*); 149.0 (*C-10*); 154.2 (*C-2*) 160.1 (*C-4*); IR (NaCl): 1698 (C═N); 1647 (C═O); MS IS *m*/*z*=505.5 [M+H⁺]; HRMS: calcd for $C_{25}H_{40}N_2O_5Si_2$ (504.2475), found (504.2486).

4.2.23. *O* 2′, *O* 2′-Anhydro-3-(3′,5′-di-*O*-*tert*butyldimethylsilyl-β-L-arabinofuranosyl)-2,4-quinazolinedione 27. (Method B without CSA) Eluent: petroleum ether–ethyl acetate 90/10, white gum (82 mg; 85%); $[\alpha]_D=+144$ (*c* 1.0; CH_2Cl_2); ^1H NMR ($CDCl_3$): δ 0.06; 0.12; 0.32; 0.36 (4s, 12H, CH_3Si); 0.93; 1.10 (2s, 18H, (CH_3)C); 3.60–3.82 (m, 2H, *H-5′*); 4.27–4.39 (m, 1H, *H-4′*); 4.86 (d, 1H, $J_{3',4'}$=2.2 Hz, *H-3′*); 5.26 (d, 1H, $J_{2',1'}$=6.3 Hz, *H-2′*); 6.75 (d, 1H, *H-1′*), 7.47 (dd, 1H, $J_{6,5}=J_{6,7}$=7.8 Hz, *H-6*); 7.64 (d, 1H, $J_{8,7}$=8.0 Hz, *H-8*); 7.82 (dd, 1H, *H-7*); 8.34 (dd, 1H, *H-5*); ^{13}C NMR ($CDCl_3$): δ −5.5; −5.2; −4.6; −4.5 (CH_3Si); 18.2; 18.4 ((CH$_3$)$_3$*C*); 25.9 ((*C*H$_3$)$_3$C); 62.0 (*C-5′*); 76.1 (*C-3′*); 86.6 (*C-4′*); 88.6 (*C-2′*); 88.9 (*C-1′*); 123.7 (*C-9*); 126.1 (*C-6*); 127.8 (*C-8*); 129.4 (*C-5*); 130.8 (*C-7*); 137.5 (*C-10*); 143.5 (*C-2*) 160.9 (*C-4*); MS IS *m*/*z*=505.5 [M+H⁺]; HRMS: calcd for $C_{25}H_{40}N_2O_5Si_2$ (504.2475), found (504.2482).

4.2.24. *O* 2′, *O* 2′-Anhydro-3-(3′,5′-di-*O*-*tert*butyldimethylsilyl-β-D-xylofuraosyl-2,4-quinazolinedione 28. (Method B without CSA) Eluent: petroleum ether–ethyl acetate 90/10, white solid (124 mg; 99%); mp: 69–71 °C; $[\alpha]_D=+133$ (*c* 1.1; CH_2Cl_2); ^1H NMR ($CDCl_3$): δ 0.04; 0.06; 0.19; 0.22 (4s, 12H, CH_3Si); 0.88; 0.96 (2s, 18H, (CH_3)C); 3.82–3.92 (m, 1H, *H-5′*); 3.97–3.99 (m, 1H, *H-4′*); 4.55 (dd, 1H, $J_{3',2'}$=1.3 Hz, $J_{3',4'}$=3.2 Hz, *H-3′*); 5.04 (d, 1H, $J_{2',1'}$= 5.2 Hz, *H-2′*); 6.60 (d, 1H, *H-1′*), 7.30 (dd, 1H, $J_{6,5}=J_{6,7}$=8.0 Hz, *H-6*); 7.47 (d, 1H, $J_{8,7}$=8.2 Hz, *H-8*); 7.62 (dd, 1H, *H-7*); 8.23 (dd, 1H, *H-5*); ^{13}C NMR ($CDCl_3$): δ −5.5; −5.4; −4.8 (CH_3Si); 18.0; 18.2((CH$_3$)$_3$*C*); 25.7; 25.8 ((*C*H$_3$)$_3$C); 59.3 (*C-5′*); 74.0 (*C-3′*); 81.8 (*C-4′*); 86.2 (*C-2′*); 86.3 (*C-1′*); 118.9 (*C-9*); 124.9 (*C-6*); 126.2 (*C-8*); 127.0 (*C-5*); 135.0 (*C-7*); 148.8 (*C*-10); 154.2 (*C-2*); 160.1 (*C*-4); IR (NaCl): 1696 (C═N); 1651 (C═O); MS IS *m*/*z*=505.5 [M+H⁺]; HRMS: calcd for $C_{25}H_{40}N_2O_5Si_2$ (504.2475), found (504.2483).

4.2.25. *O* 2′, *O* 2′-Anhydro-3-(3′,5′,6′-tri-*O*-*tert*butyldimethylsilyl-β-D-glucofuranosyl)-2,4-quinazolinedione 29. (Method B without CSA) Eluent: petroleum ether–ethyl acetate 90/10, white solid (85 mg; 59%); mp: 71–74 °C; $[\alpha]_D=+140$ (*c* 1.0; CH_2Cl_2); ^1H NMR ($CDCl_3$): δ −0.11; −0.04; 0.06; 0.08; 0.18; 0.21 (6s, 18H, CH_3Si); 0.62; 0.84; 0.93 (3s, 27H, (CH_3)C); 3.82–3.92 (m, 2H, *H-6′*); 3.96 (dd, 1H, $J_{5',4'}$=4.2 Hz, *H-4′*); 4.06–4.09 (m, 1H, *H-5′*); 4.55 (d, 1H, $J_{3',4'}$=2.4 Hz, *H-3′*); 5.02 (d, 1H, $J_{2',1'}$=4.8 Hz, *H-2′*); 6.56 (d, 1H, *H-1′*), 7.33 (ddd, 1H, $J_{6,8}$=1.0 Hz, $J_{6,5}=J_{6,7}$=8.1 Hz, *H-6*); 7.50 (d, 1H, $J_{8,7}$=7.7 Hz, *H-8*); 7.64 (ddd, 1H, $J_{7,5}$=1.6 Hz, *H-7*); 8.20 (dd, 1H, *H-5*); ^{13}C NMR ($CDCl_3$): δ −5.8; −5.7; −4.3; −4.1; −4.0; −3.3 (CH_3Si); 18.1; 18.3 ((CH$_3$)$_3$*C*); 25.7; 25.8; 26.0 ((*C*H$_3$)$_3$C); 64.1 (*C-6′*); 70.7 (*C-5′*); 74.3 (*C-3′*); 81.7 (*C-4′*); 85.5 (*C-2′*); 86.0 (*C-1′*); 119.2 (*C-9*); 125.2 (*C-6*); 126.4 (*C-8*); 127.2 (*C-5*); 135.2 (*C-7*); 148.9 (*C-10*); 154.8 (*C-2*) 160.2 (*C-4*); IR (NaCl): 1701 (C═N); 1647 (C═O); MS IS *m*/*z*=505.5 [M+H⁺]; HRMS: calcd for $C_{32}H_{56}N_2O_6Si_3$ (648.3446), found (648.3457).

4.2.26. O², O²′-Anhydro-3-(3′,5′-di-*O*-benzyl-β-D-arabinofuranosyl)-6-methyl-2,4-quinazolinedione 30. (Method B) Eluent: petroleum ether–ethyl acetate 70/30, white solid (89 mg; 92%); mp: 125–128 °C; $[\alpha]_D=98$ (*c* 1; $CHCl_3$); ^1H NMR ($CDCl_3$): δ 2.41 (s, 3H, CH_3); 3.35 (d, 2H, $J_{5'a,5'b}$=4.4 Hz, *H-5′*); 4.18 (d, 1H, *J*=12.2 Hz, CH_2-Ph); 4.25 (d, 1H, CH_2-Ph); 4.37 (d, 1H, $J_{3',4'}$=2.2 Hz, *H-3′*); 4.40–4.47 (m, 1H, *H-4′*); 4.59 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.64 (d, 1H, CH_2-Ph); 5,21 (d, 1H, $J_{2',1'}$=6.0 Hz, *H-2′*); 6.59 (d, 1H, *H-1′*), 6.69–7.08 (m, 2H, CH_{Ar}); 7.13–7.22 (m, 3H, CH_{Ar}); 7.27–7.41 (m, 6H, *H-8*, CH_{Ar}); 7.46 (dd, 1H, $J_{7,5}$=2.0 Hz, $J_{7,8}$=8.7 Hz, *H-7*); 7.98 (s, 1H, *H-5*); ^{13}C NMR ($CDCl_3$): 21.0 (*C*H$_3$); 69.0 (*C-5′*); 72.4; 73.4 (*C*H$_2$-Ph); 83.5 (*C-3′*); 85.2 (*C-4′*); 85.8 (*C-2′*); 87.6 (*C-1′*); 118.6 (*C-9*); 126.1 (*C-8*); 126.7 (*C-5*); 126.8; 126.9; 128.0; 128.3; 128.7 (*C*H$_{Ar}$); 134.9 (*C-7*); 136.4; 136.5 (*Cq*); 137.2 (*C-6*); 146.9 (*C-10*); 154.2 (*C-2*); 160.2 (*C-4*); IR (KBr): 1686 (C═N); 1643 (C═O); MS IS *m*/*z*=471.5 [M+H⁺], 493.5 [M+Na⁺]; HRMS: calcd for $C_{28}H_{26}N_2O_5$ (470.1841), found (470.1848).

4.2.27. *O* 2′, *O* 2′-Anhydro-3-(3′,5′-di-*O*-benzyl-β-D-arabinofuranosyl)-7-chloro-2,4-quinazolinedione 31. (Method B) Eluent: petroleum ether–ethyl acetate 90/10, white solid (91 mg; 86%); mp: 96–98 °C; $[\alpha]_D=-128$ (*c* 1; $CHCl_3$); ^1H

NMR ($CDCl_3$): δ 3.33 (dd, 1H, $J_{5'a,4'}$=3.3 Hz, $J_{5'a,5'b}$=10.5 Hz, *H-5'a*); 3.40 (dd, 1H, $J_{5'b,4'}$=3.9 Hz, *H-5'b*); 4.15 (d, 1H, *J*=12.2 Hz, CH_2-Ph); 4.22 (d, 1H, CH_2-Ph); 4.37 (d, 1H, $J_{3',4'}$=1.9 Hz, *H-3'*); 4.41–4.49 (m, 1H, *H-4'*); 4.59 (d, 1H, *J*=11.6 Hz, CH_2-Ph); 4.65 (d, 1H, CH_2-Ph); 5.24 (d, 1H, $J_{2,1}$=6.0 Hz, *H-2'*); 6.59 (d, 1H, *H-1'*), 6.96–7.05 (m, 2H, *H-6*, *H-8*); 7.12–7.43 (m, 10H, CH_{Ar}); 8.10 (d, 1H, $J_{5,6}$=8.5 Hz, *H-5*); ^{13}C NMR ($CDCl_3$): δ 69.1 (*C-5*); 72.5; 73.5 (*C*H_2-Ph); 83.7 (*C-3'*); 85.7 (*C-4'*); 86.1 (*C-2'*); 87.8 (*C-1'*); 117.4 (*C-9*); 125.4 (*C-6*); 126.0 (*C-8*); 127.8; 127.9; 128.1; 128.3; 128.4; 128.8 (*C-5*, *C*H_{Ar}); 136.4; 136.9 (*Cq*); 141.2 (*C-7*); 150.2 (*C-10*); 155.5 (*C-2*) 159.6 (*C-4*); IR (KBr): 1687 (C=N); 1647 (C=O); MS IS *m/z*=491 [M+H^+], 513 [M+Na^+]; HRMS: calcd for $C_{27}H_{23}ClN_2O_5$ (490.1295), found (490.1302).

4.2.28. O^2, O$^{2'}$-Anhydro-3-(3',5'-di-*O*-benzyl-β-D-arabinofuranosyl)-6-bromo-2,4-quinazolinedione 32. (Method B) Eluent: petroleum ether–ethyl acetate 90/10, white solid (109 mg; 94%); mp: 75–77 °C; $[\alpha]_D$=−167 (*c* 1.0; $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.24 (dd, 1H, $J_{5'a,4'}$=3.4 Hz, $J_{5'a,5'b}$=10.4 Hz, *H-5'a*); 3.30 (dd, 1H, $J_{5'b,4'}$=4.2 Hz, *H-5'b*); 4.06 (d, 1H, *J*=12.6 Hz, CH_2-Ph); 4.13 (d, 1H, CH_2-Ph); 4.28 (d, 1H, $J_{3',4'}$=1.7 Hz, *H-3'*); 4.32–4.40 (m, 1H, *H-4'*); 4.50 (d, 1H, *J*=11.6 Hz, CH_2-Ph); 4.56 (d, 1H, CH_2-Ph); 5.15 (d, 1H, $J_{2',1'}$=6.0 Hz, *H-2'*); 6,50 (d, 1H, *H-1'*), 6.88–7.33 (m, 11H, *H-8*, CH_{Ar}); 7.60 (dd, 1H, $J_{7,5}$=2.3 Hz, $J_{7,8}$=8.7 Hz, *H-7*); 8.21 (d, 1H, *H-5*); ^{13}C NMR ($CDCl_3$): δ 69.0 (*C-5'*); 72.5; 73,4 (*C*H_2-Ph); 83.6 (*C-3'*); 85.7 (*C-4'*); 86.1 (*C-2'*); 87.8 (*C-1'*); 118.0 (*C-9*); 120.5 (*C-6*); 127.8; 127.9; 128.0; 128.1; 128.4; 128.5; 128.7; 128.8 (*C-8*, *C*H_{Ar}); 129.6 (*C-5*); 136.4; 136.9 (*Cq*); 138.1 (*C-7*); 148.0 (*C-10*); 155.5 (*C-2*) 159.0 (*C-4*); IR (NaCl): 1694 (C=N); 1649 (C=O); MS IS *m/z*=537 [M+H^+]; 559 [M+Na^+]; HRMS: calcd for $C_{27}H_{23}BrN_2O_5$ (534.0790), found (534.0796).

4.2.29. *O*^{2}, *O*$^{2'}$-Anhydro-3-(3',5'-di-*O*-benzyl-β-D-arabinofuranosyl)-6-iodo-2,4-quinazolinedione 33. (Method B) Eluent: petroleum ether–ethyl acetate 70/30, white solid (98 mg; 78%); mp: 90–93 °C; $[\alpha]_D$=−173 (*c* 0.85; $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.32 (dd, 1H, $J_{5'a,4'}$=3.5 Hz, $J_{5'a,5'b}$=10.4 Hz, *H-5'a*); 3.38 (dd, 1H, $J_{5'b,4'}$=4.1 Hz, *H-5'b*); 4.14 (d, 1H, *J*=12.2 Hz, CH_2-Ph); 4,21 (d, 1H, CH_2-Ph); 4.36 (d, 1H, $J_{3',4'}$=2.2 Hz, *H-3'*); 4.41–4.48 (m, 1H, *H-4'*); 4.58 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.64 (d, 1H, CH_2-Ph); 5.24 (d, 1H, $J_{2',1'}$=6.0 Hz, *H-2'*); 6.28 (d, 1H, *H-1'*), 6.96–7.04 (m, 2H, CH_{Ar}); 7.13–7.23 (m, 4H, *H-8*, CH_{Ar}); 7.26–7.40 (m, 5H, CH_{Ar}); 7.86 (dd, 1H, $J_{7,5}$=2.2 Hz, $J_{7,8}$=8.5 Hz, *H-7*); 8.48 (d, 1H, *H-5*); ^{13}C NMR ($CDCl_3$): δ 69.0 (*C-5'*); 72.5; 73.4 (*C*H_2-Ph); 83.6 (*C-3'*); 85.6 (*C-4'*); 86.1 (*C-2'*); 87.8 (*C-1'*); 88.3 (*C-6*); 120.8 (*C-9*); 127.8; 127.9; 128.1; 128.2; 128.3; 128.4; 128.7 (*C-8*, *C*H_{Ar}); 135.7 (*C-5*); 136.4; 136.9 (*Cq*); 143.6 (*C-7*); 148.5 (*C-10*); 155.1 (*C-2*) 158.8 (*C-4*); IR (KBr): 1691 (C=N); 1650 (C=O); MS IS *m/z*=583 [M+H^+], 605 [M+Na^+]; HRMS: calcd for $C_{27}H_{23}IN_2O_5$ (656.9623), found (656.9619).

4.2.30. *O*^{2}, *O*$^{2'}$-Anhydro-3-(3',5'-di-*O*-benzyl-β-D-arabinofuranosyl)-5,6-naphtyl-2,4-pyrimidinedione 34. (Method B) Eluent: CH_2Cl_2-MeOH 98/2, pale yellow solid (71 mg; 65%); mp: 97–100 °C; $[\alpha]_D$=−147 (*c* 0.64; $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.36 (dd, 1H, $J_{5'a,4'}$=3.6 Hz, $J_{5'a,5'b}$=10.4 Hz, *H-5'a*); 3.41 (dd, 1H, $J_{5'b,4'}$=4.4 Hz, *H-5'b*); 4.16 (d, 1H, *J*=12.3 Hz, CH_2-Ph); 4.25 (d, 1H, CH_2-Ph); 4.40 (d, 1H, $J_{3',4'}$=2.2 Hz, *H-3'*); 4.44–4.50 (m, 1H, *H-4'*); 4,62 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.68 (d, 1H, CH_2-Ph); 5.25 (d, 1H, $J_{2,1}$=5.6 Hz, *H-2'*); 6.65 (d, 1H, *H-1'*), 6.99–7.06 (m, 2H, CH_{Ar}); 7.09–7.16 (m, 3H, CH_{Ar}); 7.29–7.43 (m, 5H, CH_{Ar}); 7.48 (ddd, 1H, $J_{8,6}$=1.3 Hz, $J_{8,7}$=6.6 Hz, $J_{8,9}$=8.2 Hz, *H-8*); 7.57 (ddd, 1H, $J_{7,9}$=1.3 Hz, $J_{7,6}$=6.6 Hz, *H-7*); 7.84–7.92 (m, 2H, *H-9*, *H-10*); 8.00 (d, 1H, *H-6*); 8.83 (s, 1H, *H-5*); ^{13}C NMR ($CDCl_3$): δ 69.1 (*C-5'*); 72.5; 73.5 (*C*H_2-Ph); 83.6 (*C-3'*); 85.4 (*C-4'*); 85.9 (*C-2'*); 87.5 (*C-1'*); 118.2 (*C-11*); 123.3 (*C-10*); 125.9 (*C-8*); 127.6 (*C-9*); 127.8; 127.9; 128.2; 128.4; 128.5; 128.8 (*C*H_{Ar}); 128.9 (*C-7*); 129.1 (*C-5*); 129.5 (*C-6*); 130.4 (*C-13*); 136.5 (*C-14*); 137.1; 137.3 (*Cq*); 143.5 (*C-12*); 154.0 (*C-2*) 160.8 (*C-4*); IR (KBr): 1690 (C=N); 1650 (C=O); MS IS *m/z*=507.5 [M+H^+], 529.5 [M+Na^+]; HRMS: calcd for $C_{31}H_{26}N_2O_5$ (506.1841), found (506.1843).

4.2.31. 3-(3',5'-Di-*O*-benzyl-β-D-arabinosyl)-2,4-quinazolinedione 35. The anhydro-nucleoside **3** (0.5 g; 1.1 mmol) dissolved in EtOH (40 mL) and HCl (2 M, 10 mL) was heated at 50 °C for 4 days. Ethanol was removed in vacuo then extraction with ethyl acetate - 5% aqueous solution of $NaHCO_3$ was performed. The organic fractions were collected and washed with H_2O then dried over $MgSO_4$. After evaporation, the residue was purified on column chromatography with petroleum ether–ethyl acetate (6/4). Compound **35** was isolated as a white solid (390 mg; 76%), mp: 90–92 °C; $[\alpha]_D$=−77 (*c* 0.59; $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.53 (d, 1H, $J_{OH,2'}$=11.0 Hz, O*H-2'*); 3.74 (dd, 1H, $J_{5'a,4'}$=3.1 Hz, $J_{5'a,5'b}$=10.4 Hz, *H-5'a*); 3.88 (dd, 1H, $J_{5'b,4'}$=7.5 Hz, *H-5'b*); 4.06–4.17 (m, 1H, *H-4'*); 4.29 (d, 1H, $J_{3',2'}$=5.7 Hz, $J_{3',4'}$=7.5 Hz, *H-3'*); 4.54 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 4.60 (d, 1H, CH_2-Ph); 4.62–4.75 (m, 2H, *H-2'*, CH_2-Ph); 4.85 (d, 1H, *J*=11.9 Hz, CH_2-Ph); 6.79 (d, 1H, $J_{1',2'}$=7.9 Hz, *H-1'*), 6.95 (d, 1H, $J_{8,7}$=8.2 Hz, *H-8*); 7.08–7.39 (m, 11H, *H-6*, CH_{Ar}); 7.50 (ddd, 1H, $J_{7,5}$=1.3 Hz, $J_{7,6}$=8.5 Hz, *H-7*); 7.90 (dd, 1H, $J_{5,6}$=8.2 Hz, *H-5*); 9.75 (s, 1H, N*H*); ^{13}C NMR ($CDCl_3$): δ 70.9 (*C-5'*); 72.3; 73.3 (*C*H_2-Ph); 79.1 (*C-2'*); 79.2 (*C-4'*); 82.1 (*C-1'*); 85.9 (*C-3'*); 114.6 (*C-9*); 115.2 (*C-8*); 123.7 (*C-6*); 127.7; 127.8; 127.9; 128.0; 128.4; 128.6 (*C-5*, *C*H_{Ar}); 135.6 (*C-7*); 138.0; 138.1 (*Cq*); 138.4 (*C-10*); 152.0 (*C-2*); 163.2 (*C-4*); IR (KBr): 1661 (C=O); 1724 (C=O); MS IS *m/z*=475.5 [M+H^+], 497.5 [M+Na^+]; HRMS: calcd for $C_{27}H_{26}N_2O_6$ (474.1791), found (474.1789).

4.2.32. 3-β-D-Arabinosyl-2,4-quinazolinedione 36. The benzylated compound **35** (0.21 g; 0.44 mmol) was dissolved in acetic acid (5 mL) containing Pd/C 10% (0.2 g) and stirred overnight under hydrogen pressure at room temperature. The solution was filtered over Celite®, evaporated to give pure **36** (96 mg, 74%), mp: 178–183 °C; $[\alpha]_D$=27 (*c* 1.0; pyridine); ^{1}H NMR ($CDCl_3$): δ 3.55–3.68 (m, 3H, *H-4'*, *H-5'*); 4.18–4.28 (m, 2H, *H-2'*, *H-3'*); 6.55 (d, 1H, $J_{1',2'}$=7.5 Hz, *H-1'*); 7.08–7.22 (m, 2H, *H-6*, *H-8*); 7.59 (ddd, 1H, $J_{7,5}$=1.5 Hz, $J_{7,6}$=$J_{7,8}$=8.0 Hz, *H-7*); 7.85 (d, 1H, $J_{5,6}$=8.0 Hz, *H-5*);; ^{13}C NMR ($CDCl_3$): δ 62.1 (*C-5'*); 76.2 (*C-2'*); 76.9 (*C-3'*); 81.4 (*C-1'*); 83.1 (*C-4'*); 114.2 (*C-9*); 115.4 (*C-8*); 122.8 (*C-6*); 127.8 (*C-5*); 135.5 (*C-7*); 139.9 (*C-10*); 150.4 (*C-2*); 162.5 (*C-4*); IR (KBr): 1688 (C=O); 1744 (C=O); MS IS *m/z*=295 [M+H^+], 317 [M+Na^+];

HRMS: calcd for $C_{13}H_{14}N_2O_6$ (294.0852), found (294.0854); calcd for $C_{13}H_{14}N_2O_6$ (H 4.80, C 53.06, N 9.52), found (H 4.85, C 52.64, N 9.45).

4.2.33. 3-(3′,5′-Di-*O*-benzyl-β-D-ribosyl)-2,4-quinazolinedione 37. Compound **35** (136 mg; 0.29 mmol) was dissolved in CH_2Cl_2 (2 mL) then pyridine (162 μl; 2.01 mmol) and DMAP (4 mg; 0.03 mmol) were added. The solution was cooled to -78 °C, then triflic anhydride (218 μl, 0,86 mmol) was slowly added. The reaction was slowly brought to room temperature and stirred 1 h more. After treatment with water, the mixture was extracted twice with CH_2Cl_2. The organic phases collected were washed with aqueous solution of $NaHCO_3$ (5%), then water, and dried over $MgSO_4$. The solvent was removed. The crude residue was dissolved in DMF (1 mL), then sodium nitrite (91 mg, 1.32 mmol) was added. The solution was stirred overnight at room temperature. After hydrolysis with HCl 1 M (2.5 mL), extraction was performed with CH_2Cl_2. Collected organic phases were neutralized (5% $NaHCO_3$ aqueous solution) then washed with water and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified on silica gel to yield compound **37** (60 mg; 48%) as a white solid; mp: 61–64 °C; $[\alpha]_D=-112$ (*c* 0.5; $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.22 (d, 1H, $J_{OH,2'}$=4.1 Hz, O*H*-2′); 3.75 (d, 2H, $J_{5'a,5'b}$=5.0 Hz, *H*-5′); 4.21 (ddd, 1H, $J_{4',3'}$=7.2 Hz, *H*-4′); 4.53–4.68 (m, 5H, *H*-3′, CH_2-Ph); 4.79 (ddd, 1H, $J_{2',1'}$=2.5 Hz, $J_{2',3'}$=6.3 Hz, *H*-2′); 6,53 (d, 1H, *H*-1′), 7.02 (d, 1H, $J_{8,7}$=7.9 Hz, *H*-8); 7.13 (ddd, 1H, $J_{6,8}$=0.9 Hz, $J_{6,5}=J_{6,7}$=7.9 Hz, *H*-6); 7.22–7.37 (m, 10H, CH_{Ar}); 7.49 (ddd, 1H, $J_{7,5}$=1.3 Hz, *H*-7); 7.97 (dd, 1H, *H*-5); 10.37 (sl, 1H, N*H*); ^{13}C NMR ($CDCl_3$): δ 70.4 (*C*-5′); 71.4 (*C*-2′); 73.4; 73.5 (*C*H_2-Ph); 78.8 (*C*-3′); 80.9 (*C*-4′); 89.5 (*C*-1′); 114.8 (*C*-9); 115.3 (*C*-8); 123.5 (*C*-6); 127.7; 127.8; 128.2; 128.4; 128.8 (*C*-5, *C*H_{Ar}); 135.4 (*C*-7); 137.2; 138.1; 138.7 (*C*-10, *Cq*); 151.7 (*C*-2); 162.0 (*C*-4); IR (KBr): 1667 (C═O); 1723 (C═O); MS IS *m*/*z*=475.5 [M+H$^+$], 497.5 [M+Na$^+$]; HRMS: calcd for $C_{27}H_{26}N_2O_6$ (474.1791), found (474.1797).

4.2.34. 3-β-D-Ribosyl-2,4-quinazolinedione 38. The benzylated compound **37** (95 mg; 0.2 mmol) was dissolved in CH_3OH (5 mL) containing Pd/C 10% (0.1 g) and stirred overnight under hydrogen pressure at room temperature. The solution was filtered over Celite®, and purified by silica gel chromatography to give pure **38** (53 mg, 90%); mp: 220–222 °C; $[\alpha]_D=-124$ (*c* 1; DMSO); ^{1}H NMR ($CDCl_3$): δ 3.39–3.52 (m, 1H, *H*-5′*a*); 3.58–3.77 (m, 2H, *H*-4′, *H*-5′*b*); 4.17 (dd, 1H, $J_{3',2'}$=6.0 Hz, $J_{3',4'}$=6.3 Hz, *H*-3′); 4.48–4.68 (m, 2H, *H*-2′, O*H*-5′); 4.89 (d, 1H, $J_{OH,3'}$=6.6 Hz, O*H*-3′); 5.07 (d, 1H, $J_{OH,2'}$=4.7 Hz, O*H*-2′); 6.20 (d, 1H, $J_{1',2'}$=3.6 Hz, *H*-1′); 7.10–7.30 (m, 2H, *H*-6, *H*-8); 7.66 (ddd, 1H, $J_{7,5}$=1.3 Hz, $J_{7,6}$=8.5 Hz, $J_{7,8}$=8.2 Hz, *H*-7); 7.93 (d, 1*H*, $J_{5,6}$=7.5 Hz, *H*-5), 11.45 (sl, 1H, N*H*); ^{13}C NMR ($CDCl_3$): δ 62.4 (*C*-5′); 70.2 (*C*-3′); 71.1 (*C*-2′); 84.4 (*C*-4′); 88.1 (*C*-1′); 113.8 (*C*-9); 115.1 (*C*-8); 122,8 (*C*-6); 127.7 (*C*-5); 135.5 (*C*-7); 139.5 (*C*-10); 149.8 (*C*-2); 162.0 (*C*-4); IR (KBr): 1664 (C═O); 1724 (C═O); MS IS *m*/*z*=317 [M+Na$^+$]; HRMS: calcd for $C_{13}H_{14}N_2O_6$ (294.0852), found (294.0853); calcd for $C_{13}H_{14}N_2O_6$ (H 4.80, C 53.06, N 9.52), found (H 4.96, C 53.03, N 9.34).

4.2.35. 3-(3′,5′-Di-*O*-benzyl-2′-*O*-phenoxythiocarbonyl-β-D-arabinosyl)-2,4-quinazolinedione 39. Compound **35** (0.3 g; 0.63 mmol) was dissolved in CH_2Cl_2; DMAP (0.17 g, 1.38 mmol) then phenyl chlorothionoformiate (0.194 mL; 1.38 mmol) were added successively. The mixture was stirred overnight at room temperature, then NaOH (1 M) was added and extraction was performed with CH_2Cl_2. The collected organic phases were washed with HCl 1 M, water and finally dried over $MgSO_4$. After solvent removal, column chromatography purification (petroleum ether/AcOEt 6/4) afforded compound **39** (0.33 g, 85%) as a colourless gum; $[\alpha]_D=-17$ (*c* 1.0; $CDCl_3$); ^{1}H NMR ($CDCl_3$): δ 3.84 (dd, 1H, $J_{5'b,4'}$=3.1 Hz, $J_{5'b,5'a}$=10.4 Hz, *H*-5′*b*); 4.01 (dd, 1H, $J_{5'a,4'}$=7.9 Hz, *H*-5′*a*); 4.25–4.35 (m, 1H, *H*-4′); 4.53 (d, 1H, J_{gem}=11.9 Hz, CH_2-Ph); 4.62 (d, 1H, CH_2-Ph); 4.66 (d, 1H, J_{gem}=11.6 Hz, CH_2-Ph); 4.73 (d, 1H, CH_2-Ph); 4.96 (dd, 1H, $J_{3',2'}$=6.6 Hz, $J_{3',4'}$=7.9 Hz, *H*-3′); 6.10 (dd, 1H, $J_{2',1'}$=8.2 Hz, *H*-2′); 6.57–6.65 (m, 2H, CH_{Ar}); 6.90–7.40 (m, 16H, *H*-1′, *H*-6, *H*-8, CH_{Ar}); 7.51 (ddd, 1H, $J_{7,6}=J_{7,8}=J_{5,6}$=8.2 Hz, *H*-7); 8.04 (dd, 1H, $J_{5,7}$=1.3 Hz, *H*-5); 10.43 (s, 1H, N*H*); ^{13}C NMR ($CDCl_3$): δ 71.0 (*C*-5′); 73.1; 73.4 (*C*H_2-Ph); 79.6 (*C*-1′); 79.8 (*C*-4′); 82.4 (*C*-3′); 86.9 (*C*-2′); 114.6 (*C*-9); 115.2 (*C*-8); 121.3 (*C*H_{Ar}); 123.7 (*C*-6); 126.7; 127.9; 128.0; 128.1; 128.4; 128.6; 128.8; 129.6 (*C*-5′,*C*H_{Ar}); 135.6 (*C*-7); 137.7; 138.0; 138.5 (*Cq*); 151.4 (*C*-10); 153.1 (*C*-2); 161.6 (*C*-4); 193.7 (*C*═S); IR (KBr): 1225 (C═S); 1649 (C═O); 1730 (C═O); MS IS *m*/*z*=611,5 [M+H$^+$]; 633,5 [M+Na$^+$]; HRMS: calcd for $C_{34}H_{30}N_2O_7S$ (610.1774), found (610.1776).

4.2.36. 3-(3′,5′-Di-*O*-benzyl-2′-deoxy-β-D-ribofuranosyl)-2,4-quinazolinedione 40. Compound **39** (0.137 g; 0.29 mmol) dissolved in toluene (2 mL) was reacted with Bu_3SnH (80 μL; 0.3 mmol) and a catalytic amount of AIBN (0.1 equiv.) under reflux for 3 h. After toluene removal, the residue was dissolved in pentane (10 mL) then washed three times with acetonitrile (3×10 mL). The collected phases were washed twice with pentane, then evaporated and the residue was purified by column chromatography (petroleum ether/AcOEt 6/4) to yield **40** (63 mg; 62%) as a white gum; $[\alpha]_D=-29$ (*c* 0.8; $CDCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.36 (ddd, 1H, $J_{2'b,3'}$=5.3 Hz, $J_{2'b,1'}$=9.0 Hz, $J_{2'a,2'b}$=13.4 Hz, *H*-2′*b*); 2.95 (ddd, 1H, $J_{2'a,1'}$=4.3 Hz, $J_{2'a,3'}$=7.9 Hz, *H*-2′*a*); 3.79 (dd, 1H, $J_{5'b,4'}$=4.9 Hz, $J_{5'b,5'a}$=10.2 Hz, *H*-5′*b*); 3.85 (dd, 1H, $J_{5'a,4'}$=7.0 Hz, *H*-5′*a*); 4.23–4.33 (m, 1H, *H*-4′); 4.47–4.69 (m, 5H, *H*-3′, CH_2-Ph); 6.94 (dd, 1H, *H*-1′); 7.01 (d, 1H, *H*-8); 7.10–7.44 (m, 11H, *H*-6, CH_{Ar}); 7.49 (ddd, 1H, $J_{7,5}$=1.3 Hz, $J_{7,6}=J_{7,8}$=8.5 Hz, *H*-7); 7.97–8.05 (m, 1H, *H*-5); 10.42 (s, 1H, N*H*); ^{13}C NMR ($CDCl_3$): δ 35.9 (*C*-2′); 71.2 (*C*-5′); 72.2; 73.3 (*C*H_2-Ph); 80.4 (*C*-3′); 82.4 (*C*-1′); 84.0 (*C*-4′); 115.0 (*C*-8, *C*-9); 123.5 (*C*-6); 127.6; 127.8; 127.9; 128.0; 128.4; 128.5; 128.6 (*C*-5, *C*H_{Ar}); 135.3 (*C*-7); 138.2; 138.3 (*Cq*); 138.6 (*C*-10); 151.6 (*C*-2); 162.0 (*C*-4); IR (KBr): 1655 (C═O); 1728 (C═O); MS IS *m*/*z*=459 [M+H$^+$]; 481 [M+Na$^+$]; HRMS: calcd for $C_{27}H_{26}N_2O_5$ (458.1841), found (458.1839).

4.2.37. 3-(2′-Deoxy-β-D-ribofuranosyl)-2,4-quinazolinedione 41. The solution was filtered over Celite®, and purified by silica gel chromatography to give pure **38** (53 Compound **40** (0.1 g; 0.22 mmol) was dissolved in MeOH (2 mL) containing Pd/C 10% (0.1 g) and stirred overnight under hydrogen pressure at room temperature. After

filtration over Celite® and evaporation, the residue was purified on silica gel (AcOEt/MeOH 95/5) to give **41** (38 mg; 62%) as a white solid; mp: 175–178 °C; $[\alpha]_D$=0 (*c* 1.0; DMSO); ^{1}H NMR (DMSO): δ 1.99 (ddd, 1H, $J_{2'b,3'}$= 4.7 Hz, $J_{2'b,1'}$=8.2 Hz, $J_{2'b,2'a}$=13.0 Hz, *H-2'b*); 2.79 (ddd, 1H, $J_{2'a,1'}$=6.0 Hz, $J_{2'a,3'}$=7.2 Hz, *H-2'a*); 3.43–3.56 (m, 1H, *H-5b*); 3.58–3.75 (m, 2H, *H-4'*, *H-5'a*); 4.30–4.45 (m, 1H, *H-3'*); 4.52–4.67 (m, 1H, O*H-5'*); 5.10 (d, 1H, $J_{OH,3'}$=4.7 Hz, O*H-3'*); 6.66 (dd, 1H, *H-1'*); 7.10–7.30 (m, 2H, *H-6*, *H-8*); 7.64 (ddd, 1H, $J_{7,5}$=1.3 Hz, $J_{7,6}$=$J_{7,8}$=8.3 Hz, *H-7*); 7.91 (dd, 1H, $J_{5,6}$=7.9 Hz, *H-5*); 11.38 (s, 1H, N*H*); ^{13}C NMR (DMSO): δ 36.8 (*C-2'*); 62.3 (*C-5'*); 71.2 (*C-3'*); 81.4 (*C-1'*); 87.5 (*C-4'*); 114.0 (*C-9*); 115.0 (*C-8*); 122.7 (*C-6*); 127.6 (*C-5*); 135.3 (*C-7'*); 139.4 (*C-10*); 149.7 (*C-2*); 162.0 (*C-4*); IR (KBr): 1658 (C═O); 1722 (C═O); MS IS *m*/*z*=279 [M+H$^+$]; 301 [M+Na$^+$]; HRMS: calcd for $C_{13}H_{14}N_2O_5$ (278.0802), found (278.0806); calcd for $C_{13}H_{14}N_2O_5$ (H 5.07, C 56.10, N 10.07), found (H 5.12, C 55.64, N 9.97).

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