Chemoenzymatic Synthesis of Novel 3′- and 5′-Carbazoyl Nucleoside Derivatives. Regioselective Preparation of 3′- and 5′-Alkylidencarbazoyl Nucleosides

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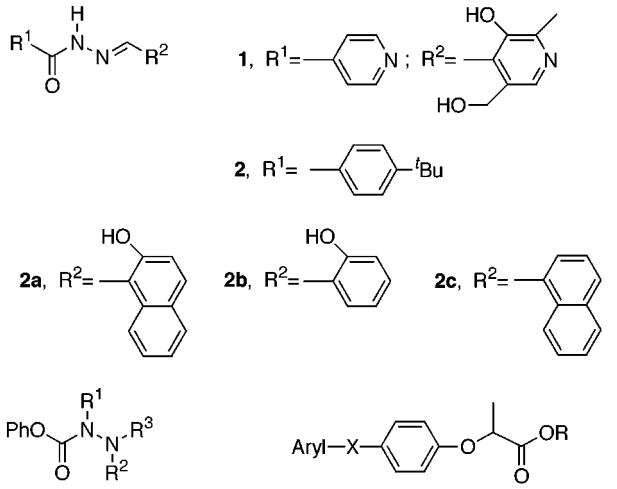
A chemoenzymatic procedure is described for the synthesis of 3′- and 5′-carbazoyl nucleoside derivatives **12a**,**b**, **13a**,**b**, **14b**,**c**, and **30b**, and these are prepared for the first time. This process involves the regioselective enzymatic alkoxycarbonylation of nucleosides and the subsequent transformation with hydrazine into novel carbazoyl nucleoside derivatives. Taking into account previously reported data (relative to nucleoside, hydrazone, carbazate, and aryloxyphenoxypropionate derivatives), 3′-alkylidencarbazoyl 2′-deoxynucleosides **15a**,**b**−**18a**,**b**, 5′-alkylidencarbazoyl 2′-deoxynucleosides **19a**,**b**−**22a**,**b**, 5′-alkylidencarbazoyl ribonucleosides of uridine **23c**−**26c**, and 5′-alkylidencarbazoyl-2′,3′-isopropylideneadenosine **31b**−**34b** emerge as interesting targets since they combine structural features found in both therapeutic nucleoside derivatives and fungicide/herbicide nucleoside analogues.

Introduction

In recent years, modified nucleoside analogues have gained importance with the discovery of several new biological and biochemical properties. The development of synthetic methods that allow access to novel classes of nucleosides is decidedly valuable. It has been reported that nucleoside analogues, some hydrazones and carbazates, as well as aryloxyphenoxypropionates show several important activities. Thus, nucleoside derivatives have been used as antitumor and antiviral agents, including their activity against the human immunodeficiency virus (HIV).[1] Similarly, *N*-acylhydrazones have been studied as potential therapeutic agents in a number of pharmaceutical contexts. For example, compound **1** (Chart 1) has been shown to be potent chelator for Fe^{3+},[2] while related compounds exhibit antimalarial properties[3] as well as antibiotic and antifungal activities.[4] Recent studies have revealed that certain *N*-acylhydrazones, such as **2** among many others, are specific inhibitors of both the RNA-dependent DNA polymerase and the RNase H activities of HIV-1 reverse transcriptase.[5] Moreover, aryl carbazates **3** exhibit fungicidal,[6] antihypertensive,[7] and anthelmintic[8] activities. On the other hand, aryloxyphenoxypropionates **4** are a widely used class of postemergent herbicides, which are highly active on grass (gramineae), but not broad-leaved (dicotyledonous) plants.[9] Many agrochemical companies have worked on the discovery and commercialization of several compounds which vary only in the type of aryl and alkyl groups of the propionate ester.[10] The agrupation of the ether oxygen atom between the aromatic rings is crucial to show activity. Thus, a drastic or total loss of herbicidal activity occurs when this atom is replaced by any of several atoms or groups[9] (as derivatives **5**, Chart 1).

Chart 1



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Exploration of the structure−activity relationships of those compounds that have structural characteristics in their molecules similar to those described previously led us to design alkylidencarbazoyl nucleosides that are promising precursors for both novel types of therapeutic nucleoside derivatives and fungicide/herbicide nucleoside analogues.

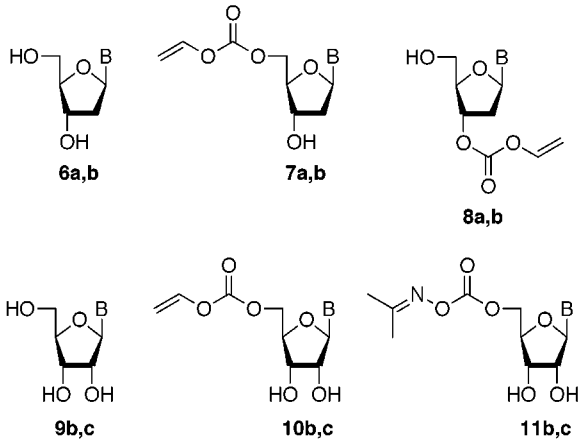
Results and Discussion

Since it is not possible to chemically introduce the carbamate group to nucleosides in a regioselective way easily, we developed a new enzymatic methodology to do this.[11] The procedure avoids time-consuming protection and deprotection steps because of the occurrence of various hydroxyl groups in the sugar skeleton of the nucleoside, steps that chemical procedures require.

Thus, we take advantage of the ability of enzymes in discerning one of several reactive positions to obtain the corresponding 5′- and 3′-carbamates of nucleosides in a direct and regioselective manner. We used the two-step procedure due to the fact that certain carbamates have been shown to be good inhibitors of many serine hydrolases.[12] This method involves the regioselective synthesis of an alkoxycarbonylated nucleoside and further reaction with an amine derivative. Among the latter, ammonia, amines, amino alcohols, diamines, and amino acids were used. Hydrazine can be considered as an amine derivative and as such might react in a way similar to that described previously.[11a,13] Following this procedure, carbazoyl derivatives could be obtained.

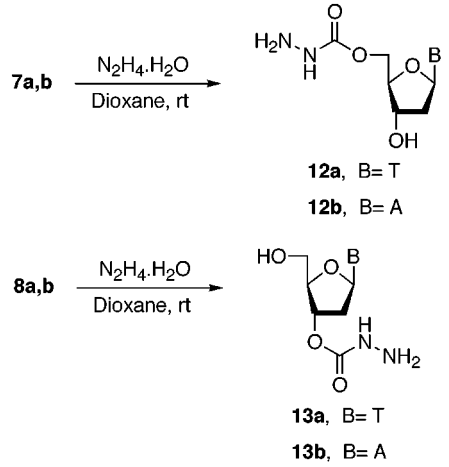
Taking into account the potential power of *Pseudomonas cepacia* lipase (PSL) and *Candida antarctica* lipase (CAL), as well as of other enzymes in nucleoside[11,13−14] and steroid[15] chemistry, we have applied these catalysts to obtain carbonates of 2′-deoxyribonucleosides **6a**,**b** or ribonucleosides **9b**,**c** (Chart 2) in a regioselective manner. Thus, to prepare carbonates **7a**,**b** and **8a**,**b**, we have used acetone *O*-[(vinyloxy)carbonyl]oxime (VCO) as alkoxycarbonylating reagent, at 30 °C in tetrahydrofuran (THF). When PSL was used 2′-deoxyribonucleoside carbonates **8a**,**b** were obtained as unique products of the enzymatic reaction. The yield ranged from moderate for adenosine (probably because of solubility problems) to good for thymidine, with only 3′-carbonate derivatives observed. If CAL was the catalyst different regioselectivity appeared depending upon the nucleoside used. Thus, in the case of thymidine, the major regioisomer **7a** (4:1, 5′-/3′-alkoxycarbonylation) was obtained. Better regioselectivity was observed when adenosine was used (9:1, **7b** vs **8b**). Vinyl or acetone carbonyloxime ribonucleoside derivatives were obtained in similar form starting from unprotected ribonucleosides **9b**,**c** (Chart 2). Thus, 5′-vinyloxycarbonylated and 5′-acetonoximecarbonylated ribonucleosides **10b**,**c** and **11b**,**c** were prepared

Chart 2



a, B= T (Thymin-1-yl); **b**, B= A (Adenin-9-yl); **c**, B= U (Uracil-1-yl)

Scheme 1



when CAL was used as catalyst in THF with VCO at 60 °C. The yield for the case of adenosine ribonucleoside is poor (20%) but was excellent (98%) for uracil ribonucleoside with regard to the total conversion of the starting material. Vinyl carbonates **10b**,**c** as well as oxime carbonates **11b**,**c** could be used as intermediates in the next step when they react with aqueous hydrazine indistinctly.

The synthetic utility of carbonate derivatives **7a**,**b**, **8a**,**b**, **10b**,**c**, and **11b**,**c** was disclosed in the preparation for the first time of carbazoyl nucleoside derivatives **12a**,**b**, **13a**,**b**, and **14b**,**c**. Thus, when 5′-carbonate nucleoside derivatives **7a**,**b** were used in the presence of hydrazine (80% in water) at room temperature, 5′-carbazoyl 2′-deoxyribonucleoside derivatives **12a**,**b** were obtained (Scheme 1). Similarly, 3′-carbazoyl 2′-deoxyribonucleoside derivatives **13a**,**b** were obtained by means of reaction of hydrazine with 3′-carbonate derivatives **8a**,**b**, giving rise to them quantitatively, in both cases.

We extended the aforementioned methodology to synthesize 5′-carbazoyl ribonucleosides such as **14b**,**c**, which were obtained in quantitative yield starting from vinyl carbonates **10b**,**c** or acetonoxime carbonates **11b**,**c** (Scheme 2). These carbazoyl derivatives of 2′-deoxyribonucleosides and ribonucleosides could be used as valuable intermediates in the preparation of alkylidencarbazate nucleoside derivatives.

To prepare 5′-alkylidencarbazate nucleoside derivatives **15a**,**b**−**18a**,**b**, we began with carbazoyl nucleosides

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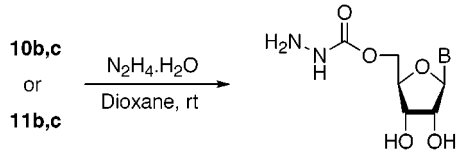
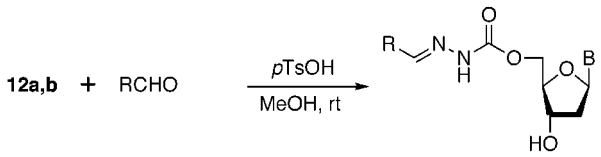
Scheme 2



14b, B= A

14c, B= U

Scheme 3



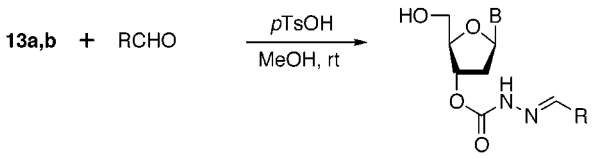
Compound	B	R	t(h)	Yield (%)
15a	T	Ph	1	80
15b	A	Ph	1.5	97
16a	T	*p*PhOPh	2	91
16b	A	*p*PhOPh	4	97
17a	T	2-Furyl	5	80
17b	A	2-Furyl	5	70
18a	T	^{n}Pr	5	60
18b	A	^{n}Pr	5	81

12a,**b** reacting with different aldehydes. The reaction took place in methanol at room temperature, catalyzed with *p*-toluenesulfonic acid (Scheme 3). It is noteworthy that in ^{1}H NMR spectra corresponding to alkylidencarbazoyl nucleoside derivatives with thymine base (**15a**−**18a**) dynamic problems appeared that showed very broad signals. These spectra gave better resolution when the temperature was raised to 45−60 °C. The reaction time ranges from 1 to 5 h and the yields from good to excellent. As shown in Scheme 3, carbazoyl nucleoside derivatives react better with aromatic than with aliphatic aldehydes. All reactions were stopped when TLC showed no starting material or the process did not evolve. Longer reaction times provoked decomposition of alkylidencarbazoyl derivatives **17a** and **17b** because they are very sensitive to acidic medium and temperature. Moreover, furfural polymerizes simultaneously in these conditions.

To obtain 3′-alkylidencarbazate nucleoside derivatives **19a**,**b**−**22a**,**b**, compounds **13a**,**b** react with various aldehydes (Scheme 4). In general, the reactivity was slightly lower than with the 5′-derivatives, and this is reflected in the reaction time. The difference was only considerable when butyraldehyde was used. Thus, the reactivity decreased in the preparation of **22b**, although the yield was excellent. At the beginning, the preparation of alkylidencarbazoyl nucleosides (**15a**,**b**−**22a**,**b**) was carried out by dissolving carbazoyl nucleosides in methanol (0.01 M) and then adding *p*-toluenesulfonic acid. By changing the addition order it is possible to use less solvent (up to 0.05 M) and employ shorter reaction times.

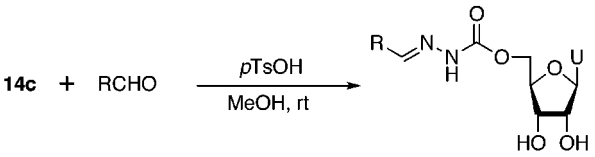
The same procedure was followed with carbazoyl derivatives of ribonucleosides **14c** to obtain alkylidencarbazoyl ribonucleosides of uridine **23c**−**26c** (Scheme 5). In these cases, the yields were very high for aromatic and heteroaromatic aldehydes and good when butyraldehyde was used.

Scheme 4



Compound	B	R	t(h)	Yield (%)
19a	T	Ph	2	90
19b	A	Ph	2	66
20a	T	*p*PhOPh	2	71
20b	A	*p*PhOPh	3	72
21a	T	2-Furyl	5	85
21b	A	2-Furyl	6	91
22a	T	^{n}Pr	6	62
22b	A	^{n}Pr	12	96

Scheme 5



Compound	R	t(h)	Yield (%)
23c	Ph	6	85
24c	*p*PhOPh	2	82
25c	2-Furyl	1	97
26c	^{n}Pr	8	60

The structural determination of these new compounds was carried out through different spectroscopic techniques. Thus, in the case of compound **19b**, and to determine the connectivity among proton and carbon atoms in the molecule, several two-dimensional experiments of nuclear magnetic resonance were done.[16] In this case, we needed to confirm the value of chemical shifts of hydroxyl group at 5′, the imine hydrogen, and both of the diasterotopic protons placed at 2′ position. Moreover, we should clarify the chemical shifts of carbon atoms at 1′, 4′, and iminic carbon as well as the presence of a carbonylic carbon (C3′−O−*C*O−N=), which apparently was missing in the ^{13}C NMR spectrum.

Most of the questions were answered with an ^{1}H−^{13}C heteronuclear correlation experiment 2D HMQC. Regarding the apparent absence of the carbonyl signal, we performed an ^{1}H−^{13}C heteronuclear correlation experiment 2D HMBC, detecting indirectly the most sensible nucleus. From its analysis, it was possible to confirm the previous assignations, and what is more, a cross-peak appears between proton H-3′ (5.54 ppm), as well as a carbon at 152.56 ppm, which corresponds to correlation H3′−O−CO via $^{3}J_{CH}$. Thus, we conclude that the carbon of carbonyl group appears overlapped with the signal of C-2 of the base moiety, which is presented at 152.56 ppm (confirmed by DEPT experiments). With the help of a COSY experiment, it was possible to determine that the broad singlet at 5.65 ppm belongs to hydroxyl group in

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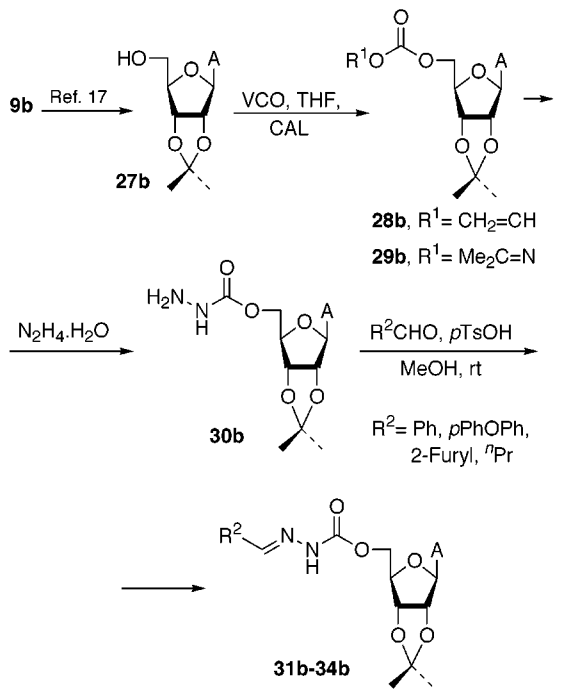
Scheme 6



the 5′ position because a cross-peak with the multiplet at 3.78 ppm corresponding to protons 5′ is observed. On the other hand, the signal at 5.54 ppm (H-3′) shows only a cross-peak with one of the 2′ hydrogens at 3.18 ppm. This means that the signal corresponds to the protons situated in relative position trans respect to H-3′; that is, the signal at 3.18 ppm belongs to H-2′α, and the signal at 2.70 ppm corresponds to H-2′β. Additionally, the relative spatial proximity between hydrogens in the "imine" moiety and the NH next to it was confirmed for derivatives **15a**,**b**−**22a**,**b**, **23c**−**26c**, and **31b**−**34b** by NOESY experiments (as is shown in all the structures).

As we mentioned previously, this general procedure has presented a limitation when adenosine ribonucleosides **23b**−**26b** were synthesized, namely the accessibility of carbonates **10b** and **11b** in sufficient amount. To increase the yield of adenosine ribonucleoside derivatives, we tried to protect the 2′,3′-diol moiety with the aim of avoiding solubility problems. Thus, solubility was increased when 2′,3′-protected ribonucleoside **27b** (Scheme 6) was used, and the enzymatic process began to improve. The chemical process did not occur in these reaction conditions. A new route was used (Scheme 6) that started with the preparation of compound **27b** from **9b** through a known procedure[17] or by buying **27b**, which is commercially accessible. Through an enzymatic reaction of VCO in THF with CAL as biocatalyst, carbonate **28b** as well as acetonoxime nucleoside **29b** were obtained in excellent yield (95%) in a ratio of 7:3. Then, the hydrazinolysis reaction of this mixture gave place to hydrazino derivative **30b** quantitatively. Similarly, the reactions of representative aldehydes, such as benzaldehyde (1 h, 90% yield), *p*-phenoxybenzaldehyde (2 h, 78%), furfural (3 h, 80%), or butyraldehyde (3 h, 75%) in methanol with acidic media yield alkylidencarbazoyl derivatives **31b**−**34b**.

The structural assignment of the compounds described in this paper is based on the analysis of their ^{1}H and ^{13}C NMR spectra and DEPT experiments. The correct assignments were confirmed by ^{1}H−^{13}C heteronuclear correlation experiments.

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Summary

A chemoenzymatic procedure has been shown involving the regioselective enzymatic alkoxycarbonylation of hydroxyl groups in nucleosides and the subsequent transformation with hydrazine giving rise, for the first time, to regioselective formation of 3′- and 5′-carbazoyl nucleoside derivatives **12a**,**b**, **13a**,**b**, **14b**,**c**, and **30b**. Direct application of these carbazoyl derivatives provided the convenient formation of 3′-alkylidencarbazoyl 2′-deoxynucleosides **15a**,**b**−**18a**,**b**, 5′-alkylidencarbazoyl 2′-deoxynucleosides **19a**,**b**−**22a**,**b**, 5′-alkylidencarbazoyl ribonucleosides of uridine **23c**−**26c**, and 5′-alkylidencarbazoyl-2′,3′-isopropylideneadenosine **31b**−**34b**, promising precursors for both novel types of therapeutic nucleoside derivatives and fungicide/herbicide nucleoside analogues. The biological activity of the above-mentioned compounds will be reported elsewhere.

Experimental Section[18]

General Methods. *C. antarctica* lipase, CAL SP 435L, was a gift from Novo Nordisk Co., and *P. cepacia* lipase, PSL, was obtained from Amano Pharmaceutical Co. All other reagents were purchased from Aldrich, Sigma, Merck, or Fluka. Solvents were distilled over an adequate desiccant under nitrogen. Nitrobenzyl alcohol (NBA) was used as matrix when FAB $^+$ MS experiments were recorded. Compounds **7a**,**b**, **8a**,**b**, **10b**, and **11b**,**c** were previously described by us.[11,14b] Following a similar procedure, carbonate **10c** was synthesized.

5′-*O*-(Vinyloxy)carbonyluridine (10c): ^{1}H NMR (DMSO-d_6) δ 4.07 (dd, 1H, H$_{3'}$, $^3J_{HH}$ 10.5 Hz, $^3J_{HH}$ 5.1 Hz), 4.13 (m, 1H, H$_{4'}$), 4.20 (dd, 1H, H$_{2'}$, $^3J_{HH}$ 10.9 Hz, $^3J_{HH}$ 5.4 Hz), 4.44 (dd, 1H, H$_{5'\beta}$, $^3J_{HH}$ 12.2 Hz, $^3J_{HH}$ 3.4 Hz), 4.52 (dd, 1H, H$_{5'\alpha}$, $^3J_{HH}$ 11.5 Hz, $^3J_{HH}$ 6.1 Hz), 4.80 (dd, 1H, H$_{4''-cis}$, $^3J_{HH}$ 6.1 Hz, $^2J_{HH}$ 2.0 Hz), 5.06 (dd, 1H, H$_{4''-trans}$, $^3J_{HH}$ 13.6 Hz, $^2J_{HH}$ 2.0 Hz), 5.41 (d, 1H, OH$_{3'}$, $^3J_{HH}$ 5.4 Hz), 5.57 (d, 1H, OH$_{2'}$, $^3J_{HH}$ 5.4 Hz), 5.74 (dd, 1H, H$_5$, $^3J_{HH}$ 8.1 Hz, $^4J_{HH}$ 2.0 Hz), 5.86 (d, 1H, H$_{1'}$, $^3J_{HH}$ 4.8 Hz), 7.14 (dd, 1H, H$_{3''}$, $^3J_{HH}$ 14.2 Hz, $^3J_{HH}$ 6.1 Hz), 7.71 (d, 1H, H$_6$, $^3J_{HH}$ 8.1 Hz), 11.44 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 68.00 (C$_{5'}$), 69.72 (C$_{3'}$), 72.45 (C$_{2'}$), 80.75 (C$_{4'}$), 88.72 (C$_{1'}$), 98.67 (C$_{4''}$), 102.11 (C$_5$), 140.89 (C$_6$), 142.82 (C$_{3''}$), 150.66 (C$_2$), 151.93 (C=O), 163.08 (C$_4$).

General Procedure for the Synthesis of Carbazoyl Nucleosides 12a,b, 13a,b, and 14b,c. To (vinyloxy)carbonylnucleosides **7a**,**b**, **8a**,**b** or **10b**,**c** [or (acetonoxime)carbonylnucleosides **11b**,**c**] (1 mmol) in 6 mL of dry dioxane was added 2 mmol of N_2H_4·H_2O (80%) under nitrogen atmosphere. The mixture reacted at room temperature until the disappearance of the starting nucleoside (TLC monitoring). The reaction times were short in all cases: 4 h for **12a**, 1 h for **12b**, 30 min for **13a**, 2 h for **13b**, 30 min for **14b**, and 2 h for **14c**. Finally, the solvent, acetaldehyde, and excess of hydrazine were evaporated under reduced pressure. The carbazoyl derivatives **12a**,**b**, **13a**,**b**, and **14b**,**c** were synthesized in quantitative yield and did not need further purification steps (in the case of acetonoxime, a filtration with silica gel was needed).

5′-*O*-Carbazoylthimidine (12a): ^{1}H NMR (DMSO-d_6) δ 1.91 (s, 3H, H$_7$), 2.16 (ddd, 1H, H$_{2'\alpha}$, $^2J_{HH}$ 13.2 Hz, $^3J_{HH}$ 6.0 Hz, $^3J_{HH}$ 2.6 Hz), 2.34 (m, 1H, H$_{2'\beta}$), 4.02 (br s, 1H, H$_{4'}$), 4.24 (m, 5H, H$_{3'}$ + 2H$_{5'}$ + NHNH_2), 5.52 (d, 1H, OH$_{3'}$, $^3J_{HH}$ 4.3 Hz),

(18) (a) For a general spectroscopic and experimental description, see the Supporting Information. (b) In general, classical nucleoside numbering is followed. The moiety that belongs to the aldehyde part on the alkylidencarbazoyl nucleoside derivatives is considered to be a substituent and is referred as second prime (″) and third prime (‴) when necessary.

6.32 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 7.7 Hz, $^3J_{HH}$ 6.4 Hz), 7.55 (s, 1H, H_6), 8.48 (s, 1H, N*H*NH$_2$), 11.42 (br s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 12.24 (C_7), 38.60 ($C_{2'}$), 64.36 ($C_{5'}$), 70.69 ($C_{3'}$), 83.72 ($C_{1'}$), 84.25 ($C_{4'}$), 109.81 (C_5), 135.97 (C_6), 150.53 (C_2), 158.10 (C=O), 163.76 (C_4).

5′-*O*-Carbazoyl-2′-deoxyadenosine (12b): ^{1}H NMR (DMSO-d_6) δ 2.41 (ddd, 1H, $H_{2'}$, $^2J_{HH}$ 13.4 Hz, $^3J_{HH}$ 6.3 Hz, $^3J_{HH}$ 3.3 Hz), 2.94 (m, 1H, $H_{2'}$), 4.25 (m, 5H, $H_{4'}$ + 2$H_{5'}$ + NHNH_2), 4.53 (m, 1H, $H_{3'}$), 5.59 (d, 1H, $H_{3'}$, $^3J_{HH}$ 3.9 Hz), 6.48 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 7.6 Hz, $^3J_{HH}$ 6.2 Hz), 7.43 (s, 2H, NH$_2$), 8.27 (s, 1H, H_2), 8.44 (m, 2H, H_8 + N*H*NH$_2$); ^{13}C NMR (DMSO-d_6) δ 38.69 ($C_{2'}$), 64.54 ($C_{5'}$), 70.98 ($C_{3'}$), 83.13 ($C_{1'}$), 84.74 ($C_{4'}$), 119.06 (C_5), 139.36 (C_8), 149.25 (C_4), 152.67 (C_2), 156.06 (C_6), 158.13 (C=O).

3′-*O*-Carbazoylthimidine (13a): ^{1}H NMR (DMSO-d_6) δ 1.91 (s, 3H, H_7), 2.35 (m, 2H, $H_{2'}$), 3.75 (m, 2H, $H_{5'}$), 4.05 (br s, 1H, $H_{4'}$), 4.23 (br s, 2H, NHNH_2), 5.25 (m, 1H, $H_{3'}$), 5.34 (t, 1H, $OH_{5'}$, $^3J_{HH}$ 5.3 Hz), 6.29 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 8.2 Hz, $^3J_{HH}$ 5.6 Hz), 7.86 (s, 1H, H_6), 8.49 (br s, 1H, N*H*NH$_2$), 11.47 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 12.34 (C_7), 36.87 ($C_{2'}$), 61.42 ($C_{5'}$), 75.00 ($C_{3'}$), 83.67 ($C_{1'}$), 84.90 ($C_{4'}$), 109.75 (C_5), 135.81 (C_6), 150.52 (C_2), 157.53 (C=O), 163.73 (C_4).

3′-*O*-Carbazoyl-2′-deoxyadenosine (13b): ^{1}H NMR (DMSO-d_6) δ 2.53 (m overlapped with DMSO, 1H, $H_{2'}$), 3.04 (m, 1H, $H_{2'}$), 3.75 (m, 2H, $H_{5'}$), 4.17 (br s, 1H, $H_{4'}$), 4.25 (s, 2H, NHNH_2), 5.40 (d, 1H, $H_{3'}$, $^3J_{HH}$ 4.6 Hz), 5.60 (t, 1H, $OH_{5'}$, $^3J_{HH}$ 5.9 Hz), 6.44 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 7.7 Hz, $^3J_{HH}$ 6.4 Hz), 7.51 (s, 2H, NH$_2$), 8.26 (s, 1H, H_2), 8.49 (s, 1H, H_8), 8.52 (br s, 1H, N*H*NH$_2$); ^{13}C NMR (DMSO-d_6) δ 37.16 ($C_{2'}$), 61.91 ($C_{5'}$), 75.45 ($C_{3'}$), 84.13 ($C_{1'}$), 85.72 ($C_{4'}$), 119.29 (C_5), 139.62 (C_8),149.00 (C_4), 152.59 (C_2), 156.23 (C_6), 157.67 (C=O).

5′-*O*-Carbazoyladenosine (14b): ^{1}H NMR (DMSO-d_6) δ 4.31 (m, 6H, $H_{4'}$ + $H_{3'}$ + 2$H_{5'}$ + NHNH_2), 4.78 (br s, 1H, $H_{2'}$), 5.52, 5.66 (2br s, 2H, $OH_{2'}$, $OH_{3'}$), 6.03 (d, 1H, $H_{1'}$, $^3J_{HH}$ 5.9 Hz), 7.44 (s, 2H, NH$_2$), 8.27 (s, 1H, H_2), 8.48 (br s, 2H, H_8 + N*H*NH$_2$); ^{13}C NMR (DMSO-d_6) δ 64.54 ($C_{5'}$), 70.70 ($C_{3'}$), 73.13 ($C_{2'}$), 82.54 ($C_{4'}$), 87.00 ($C_{1'}$), 119.10 (C_5), 139.68 (C_8),149.75 (C_4), 152.93 (C_2), 156.17 (C_6), 158.30 (C=O).

5′-*O*-Carbazoyluridine (14c): ^{1}H NMR (DMSO-d_6) δ 4.13 (m, 7H, $H_{2'}$ + $H_{3'}$ + $H_{4'}$ + 2$H_{5'}$ + NHNH_2), 5.55 (br s, 2H, $OH_{2'}$ + $OH_{3'}$), 5.80 (d, 1H, H_5, $^3J_{HH}$ 7.9 Hz), 5.91 (d, 1H, $H_{1'}$, $^3J_{HH}$ 5.6 Hz), 7.73 (d, 1H, H_6, $^3J_{HH}$ 7.2 Hz), 8.49 (s, 1H, N*H*NH$_2$); ^{13}C NMR (DMSO-d_6) δ 63.97 ($C_{5'}$), 70.02 ($C_{3'}$), 72.66 ($C_{2'}$), 81.99 ($C_{4'}$), 87.82 ($C_{1'}$), 102.29 (C_5), 140.82 (C_6), 150.90 (C_2), 158.08 (C=O), 163.25 (C_4).

General Procedure for the Synthesis of Alkylidencarbazoyl Nucleosides 15a,b−22a,b and 23c−26c. To carbazoyl nucleosides **12a**,**b**, **13a**,**b**, or **14c** (0.10 mmol) in 2 mL of dry methanol was added first *p*-toluenesulfonic acid (0.04 mmol) and then the corresponding aldehyde (0.11 mmol) under nitrogen atmosphere. The mixture reacted at room temperature until disappearance of starting nucleoside or when the process did not evolve (TLC monitoring), which is reported in the tables of Schemes 3−5. The solvent was evaporated at reduced pressure and products were purified by flash chromatography column with 10%, 5%, or 0% MeOH/EtOAc. Yields are collected in the tables of Schemes 3−5.

5′-[3″-(Phenylidene)carbazoyl]thimidine (15a): ^{1}H NMR (45 °C, DMSO-d_6) δ 1.75 (br s, 3H, H_7), 2.24 (ddd, 2H, $H_{2'\alpha}$, $^2J_{HH}$ 13.2 Hz, $^3J_{HH}$ 6.0 Hz, $^3J_{HH}$ 2.4 Hz), 2.42 (br s, 2H, $H_{2'\beta}$), 4.13 (s, 1H, $H_{4'}$), 4.34 (m, 1H, $H_{5'\beta}$), 4.42 (s, 1H, $H_{3'}$), 4.48 (m, 2H, $H_{5'\alpha}$ + $OH_{3'}$), 6.35 (t, 1H, $H_{1'}$, $^3J_{HH}$ 6.9 Hz), 7.49 (m, 3H, 2H_m + H_p), 7.58 (s, 1H, H_6), 7.69 (s, 2H, H_o), 8.16 (s, 1H, N=CH), 11.21 (s, 1H, =NNH), and 11.28 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 12.05 (C_7), 38.76 ($C_{2'}$), 65.09 (br s, $C_{5'}$), 70.98 (br s, $C_{3'}$), 83.99 ($C_{1'}$), 84.16 ($C_{4'}$), 109.74 (C_5), 126.62 (2C_o), 129.76 (2C_m), 129.77 (C_p), 134.22 (C_{ipso}), 135.81 (C_6), 144.31 (br s, C=N), 150.53 (C_2), 153.31 (C=O), 163.64 (C_4).

5′-[3″-(Phenylidene)carbazoyl]-2′-deoxyadenosine (15b): ^{1}H NMR (DMSO-d_6) δ 2.48 (br s, 1H, $H_{2'\alpha}$), 3.00 (m, 1H, $H_{2'\beta}$), 4.24 (m, 1H, $H_{4'}$), 4.44 (m, 2H, $H_{5'}$), 4.60 (br s, 1H, $H_{3'}$), 5.66 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 4.0 Hz), 6.51 (m, 1H, $H_{1'}$), 7.41 (s, 2H, NH$_2$), 7.48 (s, 3H, 2H_m + H_p), 7.70 (s, 2H, 2H_o), 8.13 (s, 1H, N=CH), 8.27 (s, 1H, H_2), 8.46 (s, 1H, H_8), 11.38 (br s, 1H, =NNH); ^{13}C NMR (DMSO-d_6) δ 38.77 ($C_{2'}$), 65.02 (br s, $C_{5'}$), 71.04 (br s, $C_{3'}$), 83.32 ($C_{1'}$), 84.62 ($C_{4'}$), 119.08 (C_5), 126.72 (C_o), 128.83 (C_m), 129.71 (C_p), 134.29 (C_{ipso}), 139.36 (br s, C_8), 144.39 (br s, C=N), 149.27 (C_4), 152.74 (C_2), 153.34 (C=O), 156.09 (C_6).

5′-[3″-(*p*-Phenoxyphenylidene)carbazoyl]thimidine (16a): ^{1}H NMR (45 °C, DMSO-d_6) δ 1.75 (br s, 3H, H_7), 2.23 (m, 1H, $H_{2'\alpha}$), 2.42 (br s, 1H, $H_{2'\beta}$), 4.13 (s, 1H, $H_{4'}$), 4.34 (m, 1H, $H_{5'\beta}$), 4.41 (s, 1H, $H_{3'}$), 4.46 (m, 1H, $H_{5'\alpha}$), 5.44 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 4.1 Hz), 6.34 (t, 1H, $H_{1'}$, $^3J_{HH}$ 6.9 Hz), 7.10 (d, 2H, 2H_m, $^3J_{HH}$ 8.2 Hz), 7.15 (d, 2H, 2$H_{o'}$,$^3J_{HH}$ 8.2 Hz), 7.28 (t, 1H, $H_{p'}$, $^3J_{HH}$ 7.2 Hz), 7.52 (apparent t, 2H, $H_{m'}$,$^3J_{HH}$ 8.2 Hz, $^3J_{HH}$ 7.6 Hz), 7.57 (s, 1H, H_6), 7.70 (d, 2H, H_o,$^3J_{HH}$ 7.6 Hz), 8.14 (s, 1H, N=CH), 11.14 (s, 1H, =NNH), 11.27 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 11.83 (C_7), 38.84 ($C_{2'}$), 65.05 (br s, $C_{5'}$), 71.02 (br s, $C_{3'}$), 84.10 ($C_{1'}$), 84.23 ($C_{4'}$), 109.62 (C_5), 118.29 (C_m), 119.14 ($C_{o'}$), 123.94 ($C_{p'}$), 128.40 (C_o), 129.38 (C_{ipso}), 130.10 ($C_{m'}$), 135.67 (C_6), 143.65 (br s, C=N), 150.43 (C_2), 153.30 (C=O), 155.95 ($C_{ipso'}$), 158.13 (C_p), 163.53 (C_4).

5′-[3″-(*p*-Phenoxyphenylidene)carbazoyl]-2′-deoxyadenosine (16b): ^{1}H NMR (DMSO-d_6) δ 2.46 (br s, 1H, $H_{2'\alpha}$), 2.98 (ddd, 1H, $H_{2'\beta}$, $^2J_{HH}$ 13.5 Hz, $^3J_{HH}$ 6.7 Hz, $^3J_{HH}$ 6.7 Hz), 4.19 (br s, 1H, $H_{4'}$), 4.34 (br s, 1H, $H_{5'}$), 4.48 (dd, 1H, $H_{5'}$, $^3J_{HH}$ 11.3 Hz, $^3J_{HH}$ 3.1 Hz), 4.58 (br s, 1H, $H_{3'}$), 5.62 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 4.1 Hz), 6.50 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 6.9 Hz, $^3J_{HH}$ 6.2 Hz), 7.10 (d, 2H, H_m, $^3J_{HH}$ 7.5 Hz), 7.16 (d, 2H, $H_{o'}$, $^3J_{HH}$ 7.5 Hz), 7.28 (t, 1H, $H_{p'}$, $^3J_{HH}$ 7.2 Hz), 7.34 (s, 2H, NH$_2$), 7.52 (dd, 2H, $H_{m'}$, $^3J_{HH}$ 8.2 Hz, $^3J_{HH}$ 7.6 Hz), 7.72 (d, 2H, H_o, $^3J_{HH}$ 7.6 Hz), 8.10 (s, 1H, N=CH), 8.25 (s, 1H, H_2), 8.44 (s, 1H, H_8), 11.30 (br s, 1H, =NNH); ^{13}C NMR (DMSO-d_6) δ 38.57 ($C_{2'}$), 64.86 ($C_{5'}$), 70.95 ($C_{3'}$), 83.19 ($C_{1'}$), 84.48 ($C_{4'}$), 118.16 (C_m), 118.98 (C_5), 119.12 ($C_{o'}$), 123.88 ($C_{p'}$), 128.36 (C_o), 129.26 (C_{ipso}), 130.00 ($C_{m'}$), 139.02 (C_8), 143.54 (br s, C=N), 149.11 (C_4), 152.48 (C_2), 153.13 (C=O), 155.78 (C_6), 155.91 ($C_{ipso'}$), 157.00 (C_p).

5′-[3″-(2‴-Furylidene)carbazoyl]thimidine (17a): ^{1}H NMR (50 °C, DMSO-d_6) δ 1.78 (s, 3H, H_7), 2.35 (m, 2H, $H_{2'}$), 4.11 (m, 1H, $H_{4'}$), 4.38 (m, 3H, $H_{3'}$ + $H_{5'}$), 5.39 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 3.3 Hz), 6.34 (m, 1H, $H_{1'}$), 6.66 (dd, 1H, $H_{4'''}$, $^3J_{HH}$ 3.3 Hz, $^3J_{HH}$ 1.6 Hz), 6.87 (d, 1H, $H_{3'''}$, $^3J_{HH}$ 3.3 Hz), 7.58 (s, 1H, H_6), 7.82 (s, 1H, $H_{5'''}$), 8.04 (s, 1H, N=CH), 11.10, 11.20 (br s, 2H, =NNH and NH); ^{13}C NMR (50 °C, DMSO-d_6) δ 11.97 (C_7), 38.44 ($C_{2'}$), 65.27 (br s, $C_{5'}$), 70.72 (br s, $C_{3'}$), 83.88 ($C_{1'}$), 84.04 ($C_{4'}$), 109.73 (C_5), 112.02 ($C_{4'''}$), 112.67 ($C_{3'''}$), 134.52 (br s, C=N), 135,99 (C_6), 144.77 ($C_{5'''}$), 149.30 ($C_{2'''}$), 150.56 (C_2), 153.02 (br s, C=O), 163.67 (C_4).

5′-[3″-(2‴-Furylidene)carbazoyl]-2′-deoxyadenosine (17b): ^{1}H NMR (DMSO-d_6) δ 2.45 (m, 1H, $H_{2'\alpha}$), 3.02 (m, 1H, $H_{2'\beta}$), 4.40 (m, 4H, $H_{3'}$ + $H_{4'}$ + 2$H_{5'}$), 5.65 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 3.3 Hz), 6.52 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 6.6 Hz, $^3J_{HH}$ 5.9 Hz), 6.71 (dd, 1H, $H_{4'''}$, $^3J_{HH}$ 3.3 Hz, $^3J_{HH}$ 1.6 Hz), 6.94 (d, 1H, $H_{3'''}$, $^3J_{HH}$ 3.3 Hz), 7.43 (s, 2H, NH$_2$), 7.90 (s, 1H, $H_{5'''}$), 8.02 (s, 1H, N=CH), 8.28 (s, 1H, H_2), 8.49 (br s, 1H, H_8), 11.33 (br s, 1H, =NNH); ^{13}C NMR (DMSO-d_6) δ 38.77 ($C_{2'}$), 65.19 (br s, $C_{5'}$), 71.12 (br s, $C_{3'}$), 83.38 ($C_{1'}$), 84.75 ($C_{4'}$), 112.10 ($C_{4'''}$), 112.82 ($C_{3'''}$), 119.00 (C_5), 134.51 (br s, C=N), 140.05 (C_8), 144.87 ($C_{5'''}$), 149.04 ($C_{2'''}$), 149.33 (C_4), 151.04 (C_2), 153.22 (br s, C=O), 154.76 (C_6).

5′-[3″-(Propylidene)carbazoyl]thimidine (18a): δ ^{1}H NMR (60 °C, DMSO-d_6) δ 0.99 (t, 3H, $H_{3'''}$, $^3J_{HH}$ 7.4 Hz), 1.56 (tq, 2H, $H_{2'''}$, $^3J_{HH}$ 7.4 Hz, $^3J_{HH}$ 7.0 Hz), 1.86 (s, 3H, H_7), 2.22 (m, 3H, $H_{1'''}$ + $H_{2'}$), 2.36 (m, 1H, $H_{2'}$), 4.09 (m, 1H, $H_{4'}$), 4.27 (dd, 1H, $H_{5'}$, $^2J_{HH}$ 12.1 Hz, $^3J_{HH}$ 4.7 Hz), 4.37 (m, 1H, $H_{3'}$), 4.42 (dd, 1H, $H_{5'}$, $^2J_{HH}$ 11.9 Hz, $^3J_{HH}$ 3.3 Hz), 5.31 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 4.1 Hz), 6.31 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 8.0 Hz, $^3J_{HH}$ 5.9 Hz), 7.46 (t, 1H, N=CH, $^3J_{HH}$ 5.5 Hz), 7.53 (s, 1H, H_6), 10.57, 11.15 (br s, 2H, =NNH and NH); ^{13}C NMR (DMSO-d_6) δ 12.02 (C_7), 13.48 ($C_{3'''}$), 19.32 ($C_{2'''}$), 33.60 ($C_{1'''}$), 38.62 ($C_{2'}$), 64.72 (br s, $C_{5'}$), 70.73 (br s, $C_{3'}$), 83.91 ($C_{1'}$), 84.18 ($C_{4'}$), 109.60 (C_5), 135.84 (C_6), 148.30 (br s, C=N), 150.44 (C_2), 153.15 (C=O), 163.62 (C_4).

5′-[3″-(Propylidene)carbazoyl]-2′-deoxyadenosine (18b): ^{1}H NMR (DMSO-d_6) δ 0.98 (t, 3H, $H_{3'''}$, $^3J_{HH}$ 7.4 Hz), 1.55 (tq, 2H, $H_{2'''}$, $^3J_{HH}$ 7.4 Hz, $^3J_{HH}$ 7.4 Hz), 2.24 (m, 2H, $H_{1'''}$), 2.34 (ddd, 1H, $H_{2'\alpha}$, $^2J_{HH}$ 13.3 Hz, $^3J_{HH}$ 6.1 Hz, $^3J_{HH}$ 3.1 Hz), 2.92 (m, 1H, $H_{2'\beta}$), 4.17 (m, 1H, $H_{4'}$), 4.35 (m, 2H, $H_{5'}$), 4.54 (m, 1H, $H_{3'}$), 5.50 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 3.7 Hz), 6.49 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 7.8 Hz, $^3J_{HH}$ 4.9 Hz), 7.25 (s, 2H, NH$_2$), 7.42 (t, 1H, N=CH, $^3J_{HH}$ 5.3 Hz), 8.25 (s, 1H, H_2), 8.43 (br s, 1H, H_8), 10.70 (br s, 1H, =NNH); ^{13}C NMR (DMSO-d_6) δ 13.46 ($C_{3'''}$), 19.39 ($C_{2'''}$), 33.54

($C_{1'''}$), 38.76 ($C_{2'}$), 64.66 ($C_{5'}$), 70.98 ($C_{3'}$), 83.14 ($C_{1'}$), 84.58 ($C_{4'}$), 118.98 (C_5), 139.20 (C_8), 148.10 (br s, C=N), 149.18 (C_4), 152.56 (C_2), 153.16 (C=O), 155.97 (C_6).

3′-[3″-(Phenylidene)carbazoyl]thimidine (19a): ^{1}H NMR (DMSO-d_6) δ 1.91 (s, 3H, H_7), 2.43 (m, 2H, $H_{2'}$), 3.79 (m, 2H, $H_{5'}$), 4.17 (br s, 1H, $H_{4'}$), 5.38 (m, 2H, $OH_{5'}$ + $H_{3'}$), 6.36 (t, 1H, $H_{1'}$, $^3J_{HH}$ 7.4 Hz), 7.54 (m, 3H, $2H_m$ + H_p), 7.76 (m, 2H, H_o), 7.89 (s, 1H, H_6), 8.17 (s, 1H, N=CH), 11.50 (br s, 2H, =NNH + NH); ^{13}C NMR (MeOH-d_4) δ 12.81 (C_7), 38.90 ($C_{2'}$), 63.33 ($C_{5'}$), 77.96 ($C_{3'}$), 86.36 ($C_{1'}$), 87.14 ($C_{4'}$), 112.19 (C_5), 128.57 ($2C_o$), 130.04 ($2C_m$), 131.41 (C_p), 135.87 (C_{ipso}), 138.14 (C_6), 147.57 (C=N), 152.71 (C_2), 155.89 (C=O), 166.63 (C_4).

3′-[3″-(Phenylidene)carbazoyl]-2′-deoxyadenosine (19b): ^{1}H NMR (DMSO-d_6) δ 2.70 (m overlapped with DMSO, 1H, $H_{2'\beta}$), 3.18 (m, 1H, $H_{2'\alpha}$), 3.78 (m, 2H, $H_{5'}$), 4.29 (br s, 1H, $H_{4'}$), 5.54 (d, 1H, $H_{3'}$, $^3J_{HH}$ 5.3 Hz), 5.65 (m, 1H, $OH_{5'}$), 6.51 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 10.4 Hz, $^3J_{HH}$ 6.2 Hz), 7.53 (m, 5H, NH_2 + H_m + H_p), 7.78 (m, 2H, H_o), 8.20 (br s, 1H, N=CH), 8.28 (s, 1H, H_2), 8.52 (s, 1H, H_8), 11.57 (br s, 1H, =NNH); ^{13}C NMR (DMSO-d_6) δ 36.88 ($C_{2'}$), 61.84 ($C_{5'}$), 76.03 ($C_{3'}$), 84.01 ($C_{1'}$), 85.50 ($C_{4'}$), 119.27 (C_5), 126.77 ($2C_o$), 128.86 ($2C_m$), 129.78 (C_p), 134.31 (C_{ipso}), 139.56 (C_8), 144.71 (C=N), 148.98 (C_4), 152.56 (C=O + C_2), 156.23 (C_6).

3′-[3″-(*p*-Phenoxyphenylidene)carbazoyl]thimidine (20a): ^{1}H NMR (DMSO-d_6) δ 1.91 (s, 3H, H_7), 2.43 (m, 2H, $H_{2'}$), 3.78 (m, 2H, $H_{5'}$), 4.17 (br s, 1H, $H_{4'}$), 5.39 (m, 2H, $OH_{5'}$ + $H_{3'}$), 6.36 (t, 1H, $H_{1'}$, $^3J_{HH}$ 7.4 Hz), 7.14 (d, 2H, H_m, $^3J_{HH}$ 11.5 Hz), 7.20 (d, 2H, $H_{o'}$, $^3J_{HH}$ 10.8 Hz), 7.31 (t, 1H, $H_{p'}$, $^3J_{HH}$ 7.4 Hz), 7.55 (dd, 2H, $H_{m'}$, $^3J_{HH}$ 8.2 Hz, $^3J_{HH}$ 7.2 Hz), 7.77 (d, 2H, H_o, $^3J_{HH}$ 8.5 Hz), 7.88 (s, 1H, H_6), 8.14 (s, 1H, N=CH), 11.50 (br s, 2H, =NNH + NH); ^{13}C NMR (DMSO-d_6) δ 12.64 (C_7), 37.13 ($C_{2'}$), 61.78 ($C_{5'}$), 76.04 ($C_{3'}$), 84.20 ($C_{1'}$), 85.17 ($C_{4'}$), 110.36 (C_5), 118.72 (C_m), 119.70 ($C_{o'}$), 124.61 ($C_{p'}$), 129.09 (C_o), 129.61 (C_{ipso}), 130.68 ($C_{m'}$), 136.36 (C_6), 144.91 (C=N), 150.98 (C_2), 153.30 (C=O), 156.19 ($C_{ipso'}$), 158.68 (C_p), 164.39 (C_4).

3′-[3″-(*p*-Phenoxyphenylidene)carbazoyl]-2′-deoxyadenosine (20b): ^{1}H NMR (DMSO-d_6) δ 2.70 (m overlapped with DMSO, 1H, $H_{2'\beta}$), 3.12 (m, 1H, $H_{2'\alpha}$), 3.78 (m, 2H, $H_{5'}$), 4.28 (br s, 1H, $H_{4'}$), 5.53 (d, 1H, $H_{3'}$, $^3J_{HH}$ 5.6 Hz), 5.65 (m, 1H, $OH_{5'}$), 6.50 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 8.4 Hz, $^3J_{HH}$ 5.7 Hz), 7.15 (d, 2H, H_m, $^3J_{HH}$ 10.5 Hz), 7.20 (d, 2H, $H_{o'}$, $^3J_{HH}$ 11.5 Hz), 7.32 (t, 1H, $H_{p'}$, $^3J_{HH}$ 7.4 Hz), 7.56 (m, 4H, $2H_{m'}$ + NH_2), 7.79 (d, 2H, H_o, $^3J_{HH}$ 8.9 Hz), 8.17 (br s, 1H, N=CH), 8.28 (s, 1H, H_2), 8.52 (s, 1H, H_8), 11.52 (br s, 1H, =NNH); ^{13}C NMR (DMSO-d_6) δ 36.90 ($C_{2'}$), 61.84 ($C_{5'}$), 76.03 ($C_{3'}$), 84.01 ($C_{1'}$), 85.50 ($C_{4'}$), 118.28 (C_5), 119.27, 119.41 (C_m, $C_{o'}$), 124.17 ($C_{p'}$), 128.61 (C_o), 129.34 (C_{ipso}), 130.26 ($C_{m'}$), 139.75 (C_8), 144.30 (C=N), 148.97 (C_4), 152.54 (C_2), 155.83 (C=O), 156.22 (C_6), 158.25 (2C, C_p, $C_{ipso'}$).

3′-[3″-(2‴-Furylidene)carbazoyl]thimidine (21a): ^{1}H NMR (DMSO-d_6) δ 1.89 (s, 3H, H_7), 2.41 (m, 2H, $H_{2'}$), 3.76 (m, 2H, $H_{5'}$), 4.14 (s, 1H, $H_{4'}$), 5.30 (m, 1H, $OH_{5'}$), 5.38 (d, 1H, $H_{3'}$, $^3J_{HH}$ 4.8 Hz), 6.32 (m, 1H, $H_{1'}$), 6.69 (dd, 1H, $H_{4'''}$, $^3J_{HH}$ 3.4 Hz, $^3J_{HH}$ 1.4 Hz), 6.92 (d, 1H, $H_{3'''}$, $^3J_{HH}$ 3.4 Hz), 7.84 (s, 1H, H_6), 7.88 (s, 1H, $H_{5'''}$), 8.03 (s, 1H, N=CH), 11.41 (br s, 2H, =NNH + NH); ^{13}C NMR (DMSO-d_6) δ 12.21 (C_7), 36.67 ($C_{2'}$), 61.36 ($C_{5'}$), 75.53 ($C_{3'}$), 83.62 ($C_{1'}$), 84.68 ($C_{4'}$), 109.69 (C_5), 111.95 ($C_{4'''}$), 112.63 ($C_{3'''}$), 134.50 (C=N), 135,70 (C_6), 144.71 ($C_{5'''}$), 149.26 ($C_{2'''}$), 150.45 (C_2), 152.44 (C=O), 163.63 (C_4).

3′-[3″-(2‴-Furylidene)carbazoyl]-2′-deoxyadenosine (21b): ^{1}H NMR (DMSO-d_6) δ 2.70 (overlapped with DMSO, $H_{2'}$), 3.13 (m, 1H, $H_{2'}$), 3.78 (m, 2H, $H_{5'}$), 4.28 (s, 1H, $H_{4'}$), 5.54 (d, 1H, $H_{3'}$, $^3J_{HH}$ 4.9 Hz), 5.64 (br s, 1H, $OH_{5'}$), 6.51 (dd, 1H, $H_{1'}$, $^3J_{HH}$ 8.4 Hz, $^3J_{HH}$ 5.7 Hz), 6.73 (dd, 1H, $H_{4'''}$, $^3J_{HH}$ 3.3 Hz, $^3J_{HH}$ 1.6 Hz), 6.97 (d, 1H, $H_{3'''}$, $^3J_{HH}$ 3.6 Hz), 7.51 (s, 2H, NH_2), 7.93 (s, 1H, $H_{5'''}$), 8.08 (s, 1H, N=CH), 8.28 (s, 1H, H_2), 8.52 (s, 1H, H_8), 11.48 (br s, 1H, =NNH); ^{13}C NMR (DMSO-d_6) δ 36.87 ($C_{2'}$), 61.81 ($C_{5'}$), 76.01 ($C_{3'}$), 83.98 ($C_{1'}$), 85.43 ($C_{4'}$), 112.05 ($C_{4'''}$), 112.80 ($C_{3'''}$), 119.24 (C_5), 134.68 (C=N), 139.52 (C_8), 144.81 ($C_{5'''}$), 148.94 ($C_{2'''}$), 149.29 (C_4), 152.51 (C=O + C_2), 156.19 (C_6).

3′-[3″-(Propylidene)carbazoyl]thimidine (22a): ^{1}H NMR (DMSO-d_6) δ 0.98 (t, 3H, $H_{3'''}$, $^3J_{HH}$ 7.5 Hz), 1.55 (tq, 2H, $H_{2'''}$, $^3J_{HH}$ 7.5 Hz, $^3J_{HH}$ 6.9 Hz), 1.88 (s, 3H, H_7), 2.24 (dt, 2H, $H_{1'''}$, $^3J_{HH}$ 7.5 Hz, $^3J_{HH}$ 5.5 Hz), 2.37 (m, 2H, $H_{2'}$), 3.74 (m, 2H, $H_{5'}$), 4.09 (br s, 1H, $H_{4'}$), 5.30 (m, 2H, $H_{3'}$ + $OH_{5'}$), 6.29 (m, 1H, $H_{1'}$), 7.42 (br s, 1H, N=CH), 7.83 (s, 1H, H_6), 10.97 (br s, 1H, =NNH), 11.42 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 12.34 (C_7), 13.61 ($C_{3'''}$), 19.50 ($C_{2'''}$), 33.68 ($C_{1'''}$), 36.74 ($C_{2'}$), 61.40 ($C_{5'}$), 75.18 ($C_{3'}$), 83.60 ($C_{1'}$), 84.77 ($C_{4'}$), 109.77 (C_5), 135.78 (C_6), 148.67 (C=N), 150.52 (C_2), 152.56 (C=O), 163.72 (C_4).

3′-[3″-(Propylidene)carbazoyl]-2′-deoxyadenosine (22b): ^{1}H NMR (DMSO-d_6) δ 0.99 (t, 3H, $H_{3'''}$, $^3J_{HH}$ 7.5 Hz), 1.55 (tq, 2H, $H_{2'''}$, $^3J_{HH}$ 7.5 Hz, $^3J_{HH}$ 6.9 Hz), 2.25 (m, 2H, $H_{1'''}$), 2.60 (overlapped with DMSO, $H_{2'}$), 3.04 (m, 1H, $H_{2'}$), 3.74 (m, 2H, $H_{5'}$), 4.20 (s, 1H, $H_{4'}$), 5.44 (m, 1H, $H_{3'}$), 5.59 (br s, 1H, $OH_{5'}$), 6.44 (m, 1H, $H_{1'}$), 7.45 (br s, 1H, N=CH), 7.51 (s, 2H, NH_2), 8.24 (s, 1H, H_2), 8.48 (s, 1H, H_8), 11.05 (br s, 1H, =NNH); ^{13}C NMR (DMSO-d_6) δ 13.66 ($C_{3'''}$), 19.56 ($C_{2'''}$), 33.72 ($C_{1'''}$), 36.92 ($C_{2'}$), 61.83 ($C_{5'}$), 75.63 ($C_{3'}$), 83.98 ($C_{1'}$), 85.51 ($C_{4'}$), 119.24 (C_5), 139.58 (C_8), 148.96 (C=N + C_4), 152.43 (C=O + C_2), 156.12 (C_6).

5′-[3″-(Phenylidene)carbazoyl]uridine (23c): ^{1}H NMR (DMSO-d_6) δ 4.11 (br s, 1H, $H_{3'}$), 4.17 (br s, 1H, $H_{4'}$), 4.28 (br s, 1H, $H_{2'}$), 4.39 (br s, 1H, $H_{5'\beta}$), 4.45 (m, 1H, $H_{5'\alpha}$), 5.41 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 4.9 Hz), 5.55 (d, 1H, $OH_{2'}$, $^3J_{HH}$ 4.9 Hz), 5.75 (br s, 1H, H_5), 5.93 (br s, 1H, $H_{1'}$), 7.50 (s, 3H, $2H_m$ + H_p), 7.74 (m, 3H, $2H_o$ + H_6), 8.15 (s, 1H, N=CH), 11.32 (br s, 1H, =NNH), 11.43 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 64.64 (br s, $C_{5'}$), 70.14 (br s, $C_{3'}$), 72.56 (br s, $C_{2'}$), 81.81 ($C_{4'}$), 87.90 (br s, $C_{1'}$), 102.16 (C_5), 126.81 (C_o), 128.83 (C_m), 129.81 (C_p), 134.17 (C_{ipso}), 140.79 (br s, C_6), 144.45 (br s, C=N), 150.82 (C_2), 153.25 (C=O), 163.01 (C_4).

5′-[3″-(*p*-Phenoxyphenylidene)carbazoyl]uridine (24c): ^{1}H NMR (DMSO-d_6) δ 4.13 (br s, 1H, $H_{3'}$), 4.18 (br s, 1H, $H_{4'}$), 4.30 (br s, 1H, $H_{2'}$), 4.37 (dd, 1H, $H_{5'\beta}$, $^2J_{HH}$ 12.0 Hz, $^3J_{HH}$ 4.5 Hz), 4.45 (dd, 1H, $H_{5'\alpha}$, $^2J_{HH}$ 11.7 Hz, $^3J_{HH}$ 2.8 Hz), 5.33 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 4.8 Hz), 5.48 (d, 1H, $OH_{2'}$, $^3J_{HH}$ 5.5 Hz), 5.60 (br s, 1H, H_5), 5.94 (d, 1H, $H_{1'}$, $^3J_{HH}$ 5.5 Hz), 7.11 (d, 2H, H_m, $^3J_{HH}$ 8.9 Hz), 7.16 (d, 2H, $H_{o'}$, $^3J_{HH}$ 8.2 Hz), 7.28 (t, 1H, $H_{p'}$, $^3J_{HH}$ 7.5 Hz), 7.52 (dd, 2H, $H_{m'}$, $^3J_{HH}$ 8.9 Hz, $^3J_{HH}$ 7.6 Hz), 7.74 (d, 2H, H_o, $^3J_{HH}$ 8.2 Hz), 7.78 (m, 1H, H_6), 8.15 (s, 1H, N=CH), 11.17 (br s, 1H, =NNH), 11.35 (br s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 64.60 (br s, $C_{5'}$), 70.16 (br s, $C_{3'}$), 72.65 (br s, $C_{2'}$), 81.80 ($C_{4'}$), 88.00 (br s, $C_{1'}$), 102.15 (C_5), 118.31 (C_m), 119.32 ($C_{o'}$), 124.11 ($C_{p'}$), 128.68 (C_o), 129.26 (C_{ipso}), 130.23 ($C_{m'}$), 140.72 (br s, C_6), 143.86 (br s, C=N), 150.81 (C_2), 153.30 (C=O), 155.89 ($C_{ipso'}$), 158.23 (C_p), 163.01 (C_4).

5′-[3″-(2‴-Furylidene)carbazoyl]uridine (25c): ^{1}H NMR (DMSO-d_6) δ 4.11 (s, 1H, $H_{3'}$), 4.17 (s, 1H, $H_{4'}$), 4.30 (s, 1H, $H_{2'}$), 4.42 (s, 2H, $H_{5'}$), 5.57 (m, 2H, $OH_{2'}$ + $OH_{3'}$), 5.76 (br s, 1H, H_5), 5.95 (d, 1H, $H_{1'}$, $^3J_{HH}$ 3.3 Hz), 6.72 (dd, 1H, $H_{4'''}$, $^3J_{HH}$ 3.3 Hz, $^3J_{HH}$ 2.0 Hz), 6.95 (d, 1H, $H_{3'''}$, $^3J_{HH}$ 3.3 Hz), 7.82 (br s, 1H, N=CH), 7.90 (s, 1H, $H_{5'''}$), 8.05 (s, 1H, H_6), 11.38 (br s, 1H, =NNH), 11.52 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 64.59 ($C_{5'}$), 70.10 ($C_{3'}$), 72.50 ($C_{2'}$), 81.68 ($C_{4'}$), 87.95 (br s, $C_{1'}$), 102.02 (C_5), 111.98 ($C_{4'''}$), 112.59 ($C_{3'''}$), 134.37 (br s, C_6), 140.75 (C=N), 144.64 ($C_{5'''}$), 149.24 ($C_{2'''}$), 150.72 (C_2), 153.07 (br s, C=O), 162.91 (C_4).

5′-[3″-(Propylidene)carbazoyl]uridine (26c): ^{1}H NMR (DMSO-d_6) δ 0.99 (t, 3H, $H_{3'''}$, $^3J_{HH}$ 7.3 Hz), 1.57 (tq, 2H, $H_{2'''}$, $^3J_{HH}$ 7.4 Hz, $^3J_{HH}$ 7.2 Hz), 2.24 (dt, 2H, $H_{1'''}$, $^3J_{HH}$ 6.7 Hz, $^3J_{HH}$ 6.6 Hz), 4.05 (d, 1H, $H_{3'}$, $^3J_{HH}$ 4.2 Hz), 4.13 (s, 1H, $H_{4'}$), 4.23 (d, 1H, $H_{2'}$, $^3J_{HH}$ 4.9 Hz), 4.34 (s, 2H, $H_{5'}$), 5.33 (d, 1H, $OH_{3'}$, $^3J_{HH}$ 4.2 Hz), 5.46 (d, 1H, $OH_{2'}$, $^3J_{HH}$ 5.6 Hz), 5.67 (s, 1H, H_5), 5.91 (s, 1H, $H_{1'}$), 7.43 (s, 1H, N=CH), 7.78 (br s, 1H, H_6), 10.76 (br s, 1H, =NNH), 11.39 (s, 1H, NH); ^{13}C NMR (DMSO-d_6) δ 13.48 ($C_{3'''}$), 19.43 ($C_{2'''}$), 33.60 ($C_{1'''}$), 64.24 (br s, $C_{5'}$), 70.12 (br s, $C_{3'}$), 72.53 ($C_{2'}$), 81.75 (br s, $C_{4'}$), 87.81 ($C_{1'}$), 101.96 (C_5), 140.77 (C_6), 148.33 (br s, C=N), 150.71 (C_2), 153.10 (C=O), 162.89 (C_4).

Enzymatic Alkoxycarbonylation of 2′,3′-Isopropylidenadenosine 27b with Acetone *O*-[(Vinyloxy)carbonyl]-oxime and CAL. Synthesis of 5′-Alkoxycarbonyl-2′,3′-isopropylidenadenosines 28b and 29b. This procedure is similar to that described for the enzymatic alkoxycarbonylation of nucleosides **6a**,**b** and **9b**,**c**, except that here an inert atmosphere is necessary, the ratio of CAL is 1 g/mmol, and the ratio of carbonate is 10:1. The purification was carried out with EtOAc by means of flash chromatography, obtaining **28b** (66.5%) and **29b** (28.5%).

5′-*O*-(Vinyloxy)carbonyl-2′,3′-isopropylidenadenosine (28b): ^{1}H NMR ($CDCl_3$) δ 1.39, 1.62 (2s, 6H, 2Me), 4.37 (m, 1H, $H_{5'}$), 4.50 (m, 2H, $H_{4'} + H_{5'}$), 4.57 (dd, 1H, $H_{4''-cis}$, $^3J_{HH}$ 6.1 Hz, $^2J_{HH}$ 1.9 Hz), 4.93 (dd, 1H, $H_{4''-trans}$, $^3J_{HH}$ 13.8 Hz, $^2J_{HH}$ 2.1 Hz), 5.12 (dd, 1H, $H_{3'}$, $^3J_{HH}$ 6.3 Hz, $^3J_{HH}$ 3.1 Hz), 5.46 (dd, 1H, $H_{2'}$, $^3J_{HH}$ 6.3 Hz, $^3J_{HH}$ 2.1 Hz), 5.94 (s, 2H, NH_2), 6.13 (d, 1H, $H_{1'}$, $^3J_{HH}$ 1.9 Hz), 7.00 (dd, 1H, $H_{3''}$, $^3J_{HH}$ 14.1 Hz, $^3J_{HH}$ 6.1 Hz), 7.90 (s, 1H, H_8), 8.34 (s,1H, H_2); ^{13}C NMR ($CDCl_3$) δ 25.26, 27.05 (2Me), 67.58 ($C_{5'}$), 81.40 ($C_{3'}$), 84.11 ($C_{2'}$), 84.45 ($C_{4'}$), 90.76 ($C_{1'}$), 98.25 ($C_{4''}$), 114.61 (Me_2C), 120.11 (C_5), 139.61 (C_8), 142.32 ($C_{3''}$),149.15 (C_4), 152.20 (C=O), 153.14 (C_2), 155.52 (C_6).

5′-*O*-(Acetoxime)carbonyl-2′,3′-isopropylidenadenosine (29b): ^{1}H NMR (MeOH-d_4) δ 1.59 (s, 3H, β-Me), 1.80 (s, 3H, α-Me), 2.15 (d, 6H, N=CMe_2, $^4J_{HH}$ 1.3 Hz), 4.69 (m, 3H, $H_{4'} + H_{5'}$), 5.33 (dd, 1H, $H_{3'}$, $^3J_{HH}$ 6.2 Hz, $^3J_{HH}$ 2.7 Hz), 5.69 (dd, 1H, $H_{2'}$, $^3J_{HH}$ 6.2 Hz, $^3J_{HH}$ 2.4 Hz), 6.43 (d, 1H, $H_{1'}$, $^3J_{HH}$ 2.2 Hz), 8.40 (s, 1H, H_2), 8.46 (s, 1H, H_8); ^{13}C NMR (MeOH-d_4) δ 16.97, 21.68 (Me_2C=N), 25.78 (β-Me), 27.70 (α-Me), 69.21 ($C_{5'}$), 83.17 ($C_{3'}$), 85.86 ($C_{2'}$), 86.23 ($C_{4'}$), 92.37 ($C_{1'}$), 115.70 (Me_2C), 120.76 (C_5), 147.77 (C_8), 150.47 (C_4), 154.10 (C_2), 155.34 (C=O), 157.46 (C_6), 166.37 (Me_2C=N).

Synthesis of 5′-Carbazoyl-2′,3′-isopropylidenadenosine (30b). The general procedure, similar to that described for the synthesis of carbazoyl nucleosides **12a**,**b**, **13a**,**b**, and **14b**,**c**, was followed: ^{1}H NMR (MeOH-d_4) δ 1.57 (s, 3H, β-Me), 1.79 (s, 3H, α-Me), 4.39 (dd, 1H, $H_{5'}$, $^2J_{HH}$ 11.6 Hz, $^3J_{HH}$ 5.9 Hz), 4.52 (dd, 1H, $H_{5'}$, $^2J_{HH}$ 11.2 Hz, $^3J_{HH}$ 4.6 Hz), 5.25 (m, 1H, $H_{3'}$), 5.64 (m, 1H, $H_{2'}$), 6.39 (d, 1H, $H_{1'}$, $^3J_{HH}$ 2.6 Hz), 8.41 (m, 2H, $H_2 + H_8$); ^{13}C NMR (MeOH-d_4) δ 25.79 (β-Me), 27.70 (α-Me), 66.10 ($C_{5'}$), 83.24 ($C_{3'}$), 85.63 ($C_{2'}$), 86.28 ($C_{4'}$), 92.01 ($C_{1'}$), 115.75 (Me_2C), 120.74 (C_5), 141.62 (C_8), 150.48 (C_4), 154.29 (C_2), 157.57 (C_6), 160.25 (C=O).

Synthesis of 5′-[3″-(Alkylidene)carbazoyl]-2′,3′-isopropylidenadenosines 31b−34b. The general procedure, similar to that described for the synthesis of alkylidenecarbazoyl nucleosides **15a**,**b**−**22a**,**b** and **23c**−**26c**, was followed.

5′-[3″-(Phenylidene)carbazoyl]-2′,3′-isopropylidenadenosine (31b): ^{1}H NMR (MeOH-d_4) δ 1.58 (s, 3H, β-Me), 1.80 (s, 3H, α-Me), 4.52 (m, 1H, $H_{5'}$), 4.68 (m, 2H, $H_{4'} + H_{5'}$), 5.33 (dd, 1H, $H_{3'}$, $^3J_{HH}$ 6.2 Hz, $^3J_{HH}$ 2.8 Hz), 5.70 (dd, 1H, $H_{2'}$, $^3J_{HH}$ 6.2 Hz, $^3J_{HH}$ 2.1 Hz), 6.41 (s, 1H, $H_{1'}$), 7.54 (s, 3H, $2H_m + H_p$), 7.86 (br s, 2H, H_o), 8.10 (br s, 1H, N=CH), 8.42 (br s, 1H, H_2), and 8.44 (br s,1H, H_8); ^{13}C NMR (MeOH-d_4) δ 25.82 (β-Me), 27.75 (α-Me), 66.24 ($C_{5'}$), 83.34 (br s, $C_{3'}$), 85.64 (br s, $C_{2'}$), 86.35 (br s, $C_{4'}$), 92.18 (br s, $C_{1'}$), 115.87 (Me_2C), 120.82 (C_5), 128.53 (C_o), 129.99 (C_m), 131.33 (C_p), 135.87 (C_{ipso}), 141.79 (C_8), 147.37 (C=N), 150.55 (C_4), 154.30 (C_2), 156.05 (C_6), 157.63 (C=O).

5′-[3″-(*p*-Phenoxyphenylidene)carbazoyl]-2′,3′-isopropylidenadenosine (32b): ^{1}H NMR (DMSO-d_6) δ 1.44 (s, 3H, β-Me), 1.66 (s, 3H, α-Me), 4.31 (br s, 1H, $H_{5'}$), 4.45 (dd, 1H, $H_{5'}$, $^2J_{HH}$ 11.8 Hz, $^3J_{HH}$ 4.2 Hz), 4.52 (br s, 1H, $H_{4'}$), 5.19 (dd, 1H, $H_{3'}$, $^3J_{HH}$ 5.9 Hz, $^3J_{HH}$ 2.4 Hz), 5.57 (br s, 1H, $H_{2'}$), 6.31 (d, 1H, $H_{1'}$, $^3J_{HH}$ 2.1 Hz), 7.10 (d, 2H, H_m, $^3J_{HH}$ 8.3 Hz), 7.16 (d, 2H, $H_{o'}$, $^3J_{HH}$ 8.3 Hz), 7.29 (t, 1H, $H_{p'}$, $^3J_{HH}$ 7.3 Hz), 7.41 (br s, 2H, NH_2), 7.52 (dd, 2H, $H_{m'}$, $^3J_{HH}$ 8.3 Hz, $^3J_{HH}$ 7.6 Hz), 7.71 (d, 2H, H_o, $^3J_{HH}$ 7.6 Hz), 8.09 (br s, 1H, N=CH), 8.27 (s, 1H, H_2), 8.42 (s, 1H, H_8), 11.25 (br s, 1H, =NNH); ^{13}C NMR (DMSO-d_6) δ 25.21 (β-Me), 27.04 (α-Me), 64.32 (br s, $C_{5'}$), 81.31 ($C_{3'}$), 83.26 (br s, $C_{2'}$), 83.65 ($C_{4'}$), 89.17 ($C_{1'}$), 113.44 (Me_2C), 118.23 (C_m), 119.36 ($C_5 + C_{o'}$), 124.11 ($C_{p'}$), 128.54 (C_o), 129.28 (C_{ipso}), 130.22 ($C_{m'}$), 139.62 (br s, C_8), 143.86 (br s, C=N), 148.84 (C_4), 152.83 (C=O + C_2), 155.82 ($C_{ipso'}$), 156.13 (C_6), 158.18 (C_p).

5′-[3″-(2‴-Furylidene)carbazoyl]-2′,3′-isopropylidenadenosine (33b): ^{1}H NMR (50 °C, MeOH-d_4) δ 1.59 (s, 3H, β-Me), 1.81 (s, 3H, α-Me), 4.56 (m, 2H, $H_{5'}$), 4.62 (m overlapped with H_2O signal, 1H, $H_{4'}$), 5.30 (dd, 1H, $H_{3'}$, $^3J_{HH}$ 5.7 Hz, $^3J_{HH}$ 2.6 Hz), 5.72 (dd, 1H, $H_{2'}$, $^3J_{HH}$ 6.4 Hz, $^3J_{HH}$ 2.9 Hz), 6.42 (d, 1H, $H_{1'}$, $^3J_{HH}$ 2.6 Hz), 6.68 (dd, 1H, $H_{4'''}$, $^3J_{HH}$ 3.3 Hz, $^3J_{HH}$ 1.5 Hz), 6.93 (d, 1H, $H_{3'''}$, $^3J_{HH}$ 3.1 Hz), 7.71 (s, 1H, $H_{5'''}$), 8.00 (s, 1H, N=CH), 8.40 (s, 1H, H_2), 8.47 (br s, 1H, H_8); ^{13}C NMR (MeOH-d_4) δ 25.84 (β-Me), 27.77 (α-Me), 66.24 (br s, $C_{5'}$), 83.36 (br s, $C_{3'}$), 85.69 (br s, $C_{2'}$), 86.31 (br s, $C_{4'}$), 92.20 (br s, $C_{1'}$), 113.16 ($C_{4'''}$), 113.74 (br s, $C_{3'''}$), 115.75 (br s, Me_2C), 120.71 (br s, C_5), 137.13 (br s, C=N), 141.77 (br s, C_8), 146.08 ($C_{5'''}$), 150.62 ($C_{2'''}$), 151.21 (C_4), 154.26 (C_2), 155.74 (C_6), 157.55 (C=O).

5′-[3″-(Propylidene)carbazoyl]-2′,3′-isopropylidenadenosine (34b): ^{1}H NMR (MeOH-d_4) δ 1.13 (t, 3H, $H_{3'''}$, $^3J_{HH}$ 7.3 Hz), 1.58 (s, 3H, β-Me), 1.70 (m, 2H, $H_{2'''}$), 1.80 (s, 3H, α-Me), 2.37 (m, 2H, $H_{1'''}$), 4.47 (m, 1H, $H_{5'}$), 4.60 (dd, 1H, $H_{5'}$, $^2J_{HH}$ 11.6 Hz, $^3J_{HH}$ 4.2 Hz), 4.66 (m, 1H, $H_{4'}$), 5.29 (m, 1H, $H_{3'}$), 5.68 (m, 1H, $H_{2'}$), 6.41 (d, 1H, $H_{1'}$, $^3J_{HH}$ 2.2 Hz), 7.44 (t, 1H, N=CH, $^3J_{HH}$ 5.1 Hz), 8.42 (m, 2H, $H_2 + H_8$); ^{13}C NMR (MeOH-d_4) δ 14.30 ($C_{3'''}$), 21.23 ($C_{2'''}$), 25.81 (β-Me), 27.75 (α-Me), 35.40 ($C_{1'''}$), 66.00 ($C_{5'}$), 83.36 ($C_{3'}$), 85.65 ($C_{2'}$), 86.28 ($C_{4'}$), 92.12 (br s, $C_{1'}$), 115.74 (Me_2C), 120.75 (C_5), 141.73 (C_8), 150.52 (C_4), 151.38 (C=N), 154.28 (C_2), 155.79 (C=O), 157.58 (C_6).

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Supporting Information Available: Complete ^{1}H and ^{13}C NMR spectral data in addition to mp, optical rotations, IR, microanalysis, and MS (and/or HRMS) data (35 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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