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Synthesis, cytostatic and anti-HCV activity of 6-(*N*-substituted aminomethyl)-, 6-(*O*-substituted hydroxymethyl)- and 6-(*S*-substituted sulfanylmethyl)purine nucleosides

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Abstract—An efficient and facile synthesis of a large series of diverse 6-(*N*-substituted aminomethyl)-, 6-(*O*-substituted hydroxymethyl)- and 6-(*S*-substituted sulfanylmethyl)purine nucleosides (55 examples of both ribo- and 2′-deoxyribonucleosides), aimed at identifying novel homologues of natural nucleosides, was developed. The key transformation involved nucleophilic substitutions of Tol-protected 6-(mesyloxymethyl)purine nucleosides by primary or secondary amines, alcoholates or thiolates. While the 2′-deoxyribonucleosides were inactive, the ribonucleosides exerted considerable cytostatic effects and some anti-HCV activity with low selectivity.

1. Introduction

Purine nucleosides bearing diverse C-substituents (aryl, alkenyl, alkynyl or alkyl groups) in position 6 are an important class of compounds that possess a broad spectrum of biological effects: for example, cytostatic,[1] antiviral,[2] and antimicrobial[3] activity or receptor modulation.[4] Purines bearing functionalized C-substituents in position 6 could possess metabolic stability due to the C—C bond, while the presence of functional groups could allow the possibility of H-bond formation with target enzymes or receptors. However, due to a lack of practical synthetic methodologies, such compounds are still quite rare and therefore they are the subject of extensive study in our laboratory. Recently, we have reported the synthesis of 6-(hydroxymethyl)purines,[5,6] as well as of (purin-6-yl)alanines[7] and phenylalanines[8] by cross-coupling reactions[9] of 6-halopurines with protected, functionalized organometallics. 6-(Hydroxymethyl)purine ribonucleoside was found[5] to exert a significant cytostatic effect on leukaemia cell lines (IC_{50} = 10 nM). The hydroxymethyl group is a versatile intermediate for further functional group manipulation. Thus, the 6-(hydroxymethyl)purines were transformed to 6-(fluoromethyl)purines[10] via direct deoxyfluorination or via a three-step sequence consisting of mesylation, Finkelstein reaction and nucleophilic substitution by AgF. In another study the hydroxymethyl group was used in the synthesis of 6-(difluoromethyl)purines[11] via oxidation and deoxofluorination. Both 6-(fluoromethyl)-[10] and 6-(difluoromethyl)purine[11] ribonucleosides showed cytostatic effects but weaker than the parent 6-(hydroxymethyl)purine nucleoside. Continuing the study of bioactive purine derivatives bearing functionalized methyl groups in position 6, we report here on the synthesis and biological activity of 6-(*N*-substituted aminomethyl)-, 6-(*O*-substituted hydroxymethyl)- and 6-(*S*-substituted sulfanylmethyl)purines. As the mechanism of action of the parent nucleosides is yet unknown, we aimed our study at the wide diversity of substituents rather than on rational design of specific derivatives.

The C-6 aminomethyl group of purines can be considered to be a homologation of the exocyclic amino

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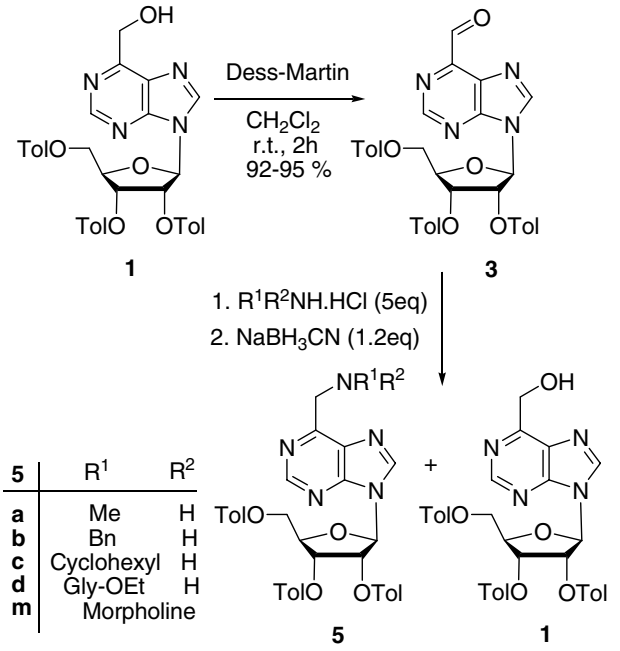
function found in the naturally occurring adenine base. This functional modification is interesting due to increased basicity of the amine and can be useful in structure–activity relationship studies. In general, (aminomethyl)purines are known[12] to be quite unstable and usually isolated as stable *N*-acyl derivatives.[12b,c] Unsubstituted (aminomethyl)purines have been prepared by catalytic hydrogenation of cyanopurines[12,13] in yields of 60–70%. Two alternative low yielding syntheses based on nucleophilic substitution of 6-(chloromethyl)purine[14] or radical substitution of purines[15] have been reported without detailed experimental procedures and spectral data. Structurally related 6-(1-aminoethyl)purines were prepared by reductive amination of 6-acetylpurines.[16] Finally, several acyclic nucleotide analogues derived from 6-(aminomethyl)purine have been shown to possess antiviral activity.[13]

Several poorly characterized 6-(alkyl- or acyloxymethyl)-[14,17] and 6-(alkyl- or acylsulfanylmethyl)purines[14,18] have been prepared from 6-(chloromethyl)purines via low yielding multistep procedures from 6-chloropurines. However, to our knowledge, no nucleoside derivatives have ever been reported and there are no data on the biological activity of any of the above-mentioned nucleobases.



Scheme 1. Synthesis of 6-(*N*-substituted aminomethyl)purines **5** by reductive amination.

2. Results and discussion

2.1. Chemistry

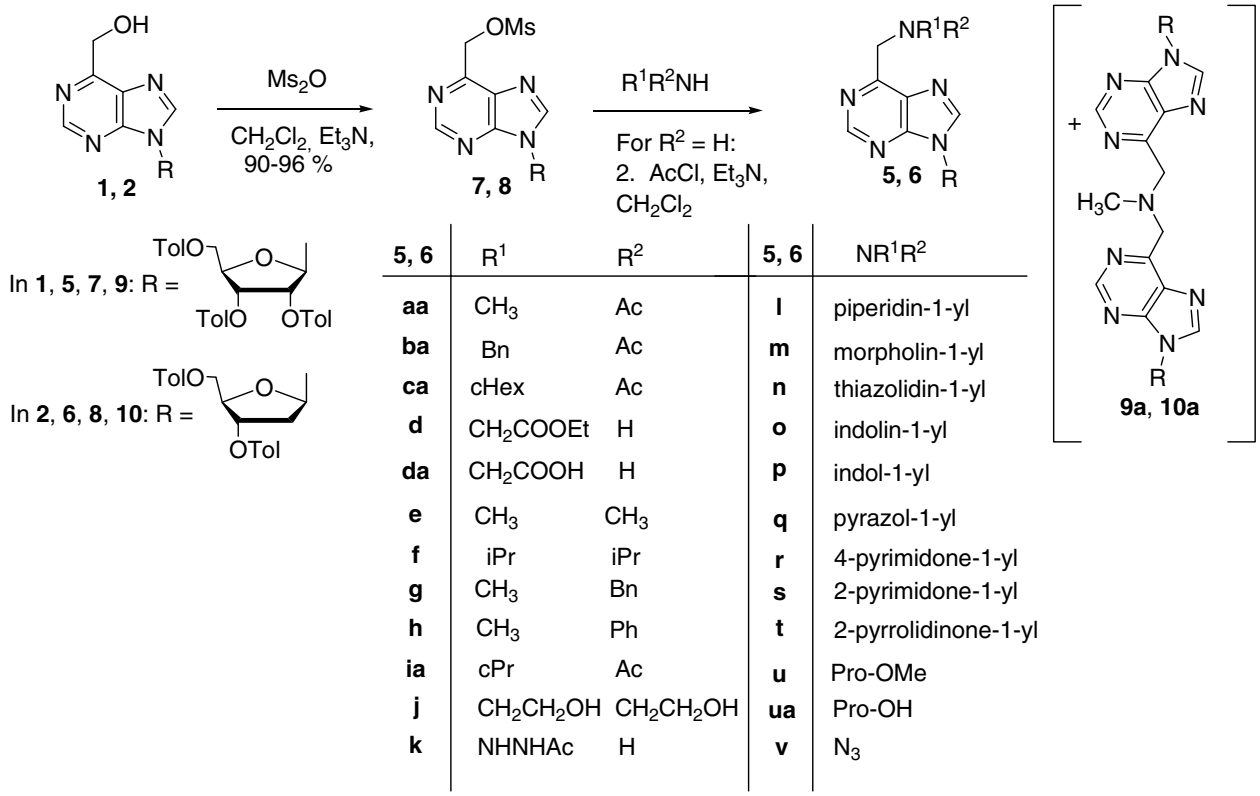
Our first attempt at the synthesis of 6-(*N*-substituted aminomethyl)purine nucleosides (both ribo- and 2′-deoxyribo series) was reductive amination[19] of protected 6-formylpurines **3** with various primary and secondary amine hydrochlorides and $NaBH_3CN$ as the reducing agent. The starting toluoyl (Tol) protected 6-formylpurine nucleosides were prepared[11] efficiently by oxidation of 6-(hydroxymethyl)purines **1** with Dess–Martin periodinane. In a typical experiment, 5 equiv of amine hydrochloride were added to the solution of 6-formylpurine **3** in methanol at room temperature, and after 30 min, 1.2 equiv of $NaBH_3CN$ reducing agent (Scheme 1). Application of this methodology afforded the corresponding protected (*N*-substituted aminomethyl)purine nucleosides **5** in moderate yields of 33–51%. Unfortunately, in all cases, the 6-(hydroxymethyl)purine **1** was formed as a by-product in yields of 17–45% (Table 1, entries 1–3), due to reduction of 6-formylpurine. On the other hand, the Tol-protecting groups of the sugar moiety were stable to the reaction conditions. In order to avoid the undesirable reduction a modified procedure consisting of stepwise addition of $NaBH_3CN$ (5× 0.25 equiv), change of solvent (ethanol instead of methanol) and increased reaction temperature (55 °C) was attempted. This modified procedure afforded the desired products **5** in improved yields (43–70%) whilst decreasing the amount of side-product **1** (0–30%) (Table 1, entries 4–8).

Despite this improvement, we were interested in the development of a practical and efficient methodology for the synthesis of (*N*-substituted aminomethyl)purine nucleosides **5** and **6**. Therefore, we tried another approach comprising nucleophilic substitution of 6-(mesyloxymethyl)purines **7** or **8** with primary or secondary amines (Scheme 2). In case of the primary amines, there is a possibility of formation of dimeric side-products, **9** or **10**, by double substitution of the amine with 2 equiv of mesylate (Scheme 2). To avoid this side-reaction, the

Table 1. Synthesis of **5** by reductive amination of 6-formylpurines **3**

Entry	Start. compd.	$R^1R^2NH{\cdot}HCl$	Conditions	Product (yield %)	By-product **1** (%)
1	**3**	$MeNH_2$	48 h, MeOH	**5a** (36)	17
2	**3**	$BnNH_2$	72 h, MeOH	**5b** (51)	20
3	**3**	$CyNH_2$	72 h, MeOH	**5c** (33)	45
4	**3**	$MeNH_2$	16 h, EtOH, SA[a]	**5a** (46)	5
5	**3**	$BnNH_2$	6 h, EtOH, 55 °C, SA[a]	**5b** (70)	0
6	**3**	$CyNH_2$	8 h, EtOH, 55 °C, SA[a]	**5c** (43)	21
7	**3**	Gly-OEt	8 h, EtOH, 55 °C, SA[a]	**5d** (50)	0
8	**3**	Morpholine	8 h, EtOH, 55 °C, SA[a]	**5m** (49)	30

[a] SA, stepwise addition of $NaBH_3CN$ (5× 0.25 equiv).



5, 6	R^1	R^2	5, 6	NR^1R^2
aa	CH_3	Ac	l	piperidin-1-yl
ba	Bn	Ac	m	morpholin-1-yl
ca	cHex	Ac	n	thiazolidin-1-yl
d	CH_2COOEt	H	o	indolin-1-yl
da	CH_2COOH	H	p	indol-1-yl
e	CH_3	CH_3	q	pyrazol-1-yl
f	iPr	iPr	r	4-pyrimidone-1-yl
g	CH_3	Bn	s	2-pyrimidone-1-yl
h	CH_3	Ph	t	2-pyrrolidinone-1-yl
ia	cPr	Ac	u	Pro-OMe
j	CH_2CH_2OH	CH_2CH_2OH	ua	Pro-OH
k	NHNHAc	H	v	N_3

Scheme 2. Synthesis of 6-(*N*-substituted aminomethyl)purines **5** and **6** by nucleophilic substitutions.

mesylates **7** or **8** were added dropwise to a solution of 10- to 20-fold excess of primary amines. As expected, the reactions with both primary and secondary amines proceeded smoothly to give the desired products **5** or **6** in excellent yields of 74–94 % based on the mesylate (Table 2, entries 1–19). Only in the reactions with methylamine, were the corresponding dimeric side-products **9** and **10** formed in low yields of 5–8% (Table 2, entries 1 and 2). While 6-(*N*,*N*-disubstituted aminomethyl)purine nucleosides were stable, the corresponding mono-substituted 6-(*N*-alkylaminomethyl)purines **5a**–**c** or **6a**–**c** were not, and after a few days turned brown to generate a complex mixture of decomposition products (presumably by air oxidation[12]). In order to isolate and characterize the 6-(*N*-monoalkylaminomethyl)purines, the secondary nitrogen was acetylated with AcCl/Et_3N to give stable acetylamide products **5aa**–**ca** or **6aa**–**ca**. Also in these nucleophilic substitutions, the Tol-ester protective groups on the sugar moiety were stable in the presence of amines and no significant deprotection was observed under the reaction conditions. This methodology provides an efficient and convenient access to the 6-(*N*-substituted aminomethyl)purine derivatives in very good yields.

Reaction of **7** with pyrrole did not proceed and the related indolyl-derivative **5p** was only formed in low yield (15%) by substitution with the sodium salt of indole (Table 2, entry 26). Therefore, an alternative approach was sought for the synthesis of **5p** based on the mild oxidation of indoline derivative **5o** with DDQ. Substitution by molecules which contain more than one nucleophilic centres such as 4- or 2-pyridone, was also studied. We observed preferential formation of *N*-substituted pyridones by reaction of their sodium salts (Scheme 3 and Table 2, entries 28–31), while reaction of pyridones in the presence of the Hünig's base furnished slightly higher amounts of *O*-substituted pyridines **13f**, **14f** and **13g**, **14g** (Scheme 3 and Table 2, entries 32–35). In contrast, substitution with 2-pyrrolidinone in the presence of the Hünig's base did not proceed. Only the reaction with sodium salt of 2-pyrrolidinone was successful to afford *N*-substituted products **5t** and **6t** in good yields (Table 2, entries 36 and 37).

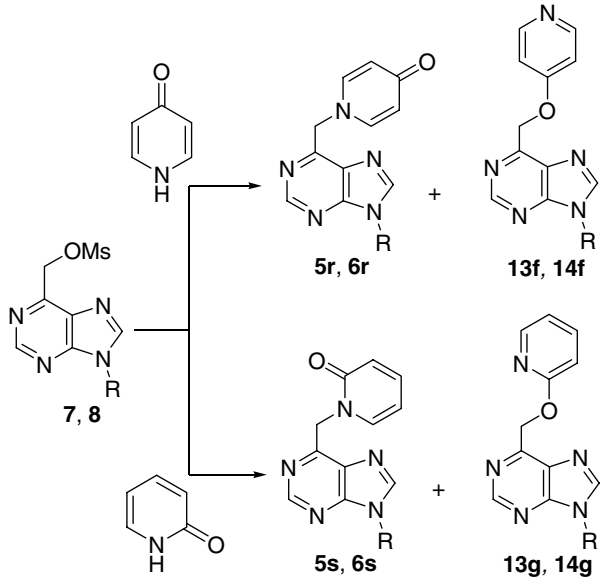
The acyl protecting groups in 6-(*N*,*N*-disubstituted aminomethyl)purine derivatives **5** and **6** were cleaved by catalytic amounts of NaOMe in methanol to yield 6-(*N*,*N*-disubstituted aminomethyl)purine nucleosides **11** or **12** in good yields (Scheme 4 and Table 3). In contrast, the toluoyl protecting groups in 6-(*N*-acetyl-*N*-alkylaminomethyl) derivatives were cleaved by aqueous ammonia in methanol at 50 °C to prevent deacetylation of the amino group.

To further employ the mesylate intermediates **7** and **8**, substitutions of the mesylate with various *O*- and *S*-nucleophiles (Scheme 5) were undertaken. Several reactions with either unfunctionalized or functionalized nucleophiles were performed, and a series of new modified purine nucleosides was prepared. Poorly nucleophilic alcohols were used as solvents in the substitution reaction with amines without observing

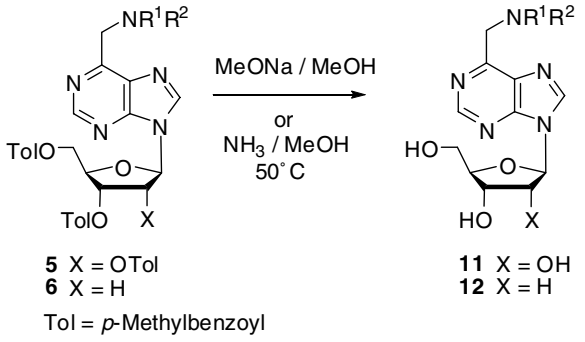
Table 2. Synthesis of **5** and **6** by nucleophilic substitutions of mesylates **7** and **8**

Entry	Start. compd.	R^1R^2NH	Conditions	Product (yield %)
1	**7**	$MeNH_2$	MeCN, 2 h, AcCl[a]	**5aa** (80) + **9a** (8)
2	**8**	$MeNH_2$	MeCN, 2 h, AcCl[a]	**6aa** (90) + **10a** (5)
3	**7**	$BnNH_2$	MeCN, 4 h, AcCl[a]	**5ba** (87)
4	**8**	$BnNH_2$	MeCN, 4 h, AcCl[a]	**6ba** (92)
5	**7**	$cHexNH_2$	MeCN, 6 h, AcCl[a]	**5ca** (82)
6	**8**	$cHexNH_2$	MeCN, 6 h, AcCl[a]	**6ca** (74)
7	**7**	Gly-OEt·HCl	MeCN, $^i Pr_2NEt$, 8 h	**5d** (82)
8	**7**	Me_2NH	MeCN, 4 h	**5e** (79)
9	**8**	Me_2NH	MeCN, 4 h	**6e** (85)
10	**7**	$^i Pr_2NH$	MeCN, 55 °C, 36 h	**5f** (78)
11	**8**	$^i Pr_2NH$	MeCN, 55 °C, 36 h	**6f** (86)
12	**7**	BnNHMe	MeCN, 8 h	**5g** (81)
13	**7**	PhNHMe	MeCN, 8 h	**5h** (62)
14	**8**	PhNHMe	MeCN, 8 h	**6h** (60)
15	**7**	$cPrNH_2$	MeCN, 6 h, AcCl[a]	**5ia** (94)
16	**8**	$cPrNH_2$	MeCN, 6 h, AcCl[a]	**6ia** (95)
17	**7**	Diethanolamine	MeCN, 8 h	**5j** (72)
18	**8**	Diethanolamine	MeCN, 8 h	**6j** (78)
19	**7**	$AcNHNH_2$	MeCN, $^i Pr_2NEt$, 24 h	**5k** (65)
20	**7**	Piperidine	MeCN, 8 h	**5l** (89)
21	**8**	Piperidine	MeCN, 8 h	**6l** (94)
22	**7**	Morpholine	MeCN, 8 h	**5m** (88)
23	**8**	Morpholine	MeCN, 8 h	**6m** (94)
24	**7**	Thiazolidine	MeCN, 8 h	**5n** (75)
25	**7**	Indoline	MeCN, 12 h,	**5o** (90)
26	**7**	Indole	MeCN, NaH, 10 h	**5p** (15)
27	**7**	Pyrazole	MeCN, 70 °C, 72 h	**5q** (73)
28	**7**	4-Pyridone	THF, NaH, 6 h	**5r** (88) + **13f** (4)
29	**8**	4-Pyridone	THF, NaH, 6 h	**6r** (85) + **14f** (4)
30	**7**	2-Pyridone	THF, NaH, 6 h	**5s** (94)
31	**8**	2-Pyridone	THF, NaH, 6 h	**6s** (95)
32	**7**	4-Pyridone	MeCN, $^i Pr_2NEt$, 50 °C, 12 h	**5r** (70) + **13f** (8)
33	**8**	4-Pyridone	MeCN, $^i Pr_2NEt$, 50 °C, 12 h	**6r** (78) + **14f** (10)
34	**7**	2-Pyridone	MeCN, $^i Pr_2NEt$, 55 °C, 48 h	**5s** (47) + **13g** (17)
35	**8**	2-Pyridone	MeCN, $^i Pr_2NEt$, 55 °C, 48 h	**6s** (38) + **14g** (22)
36	**7**	2-Pyrrolidinone	THF, NaH, 6 h	**5t** (51)
37	**8**	2-Pyrrolidinone	THF, NaH, 6 h	**6t** (72)
38	**7**	Pro-OMe·HCl	MeCN, $^i Pr_2NEt$, 50 °C, 12 h	**5u** (96)
39	**7**	NaN_3	DMF, 6 h	**5v** (95)

[a] Acetylation with $AcCl/Et_3N$ after evaporation of solvent and excess of amine.



Scheme 3. Formation of *N*- and *O*-substituted pyridones.



Scheme 4. Deprotection of toluoyl-protective groups.

any *O*-substitution. The corresponding sodium alcoholates in alcohol, however, reacted with **7** or **8** to give the desired alkoxymethylpurine nucleosides. In the case of NaOMe, simultaneous cleavage of the Tol-protecting groups occurred to directly provide free nucleosides **15a** and **16a** in moderate yields, whereas sodium phenolate gave phenyloxymethyl nucleosides **13b** and **14b** in

Table 3. Cleavage of protective groups

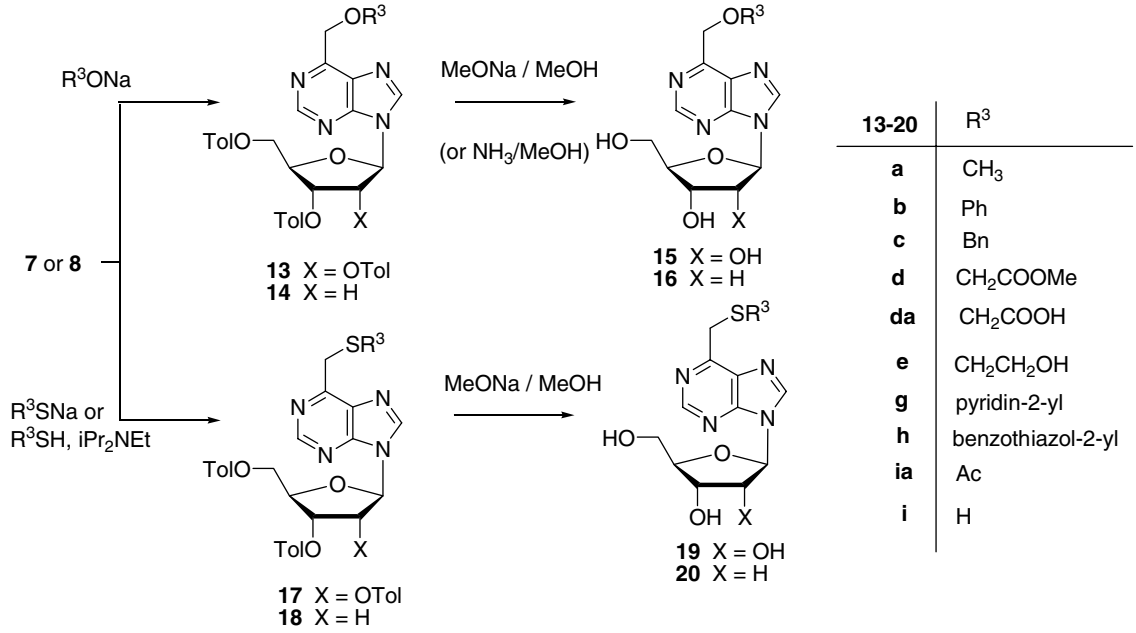
Entry	Start. compd.	Reagent	Product (yield %)
1	**5aa**	NH_3/MeOH	**11aa** (82)
2	**6aa**	NH_3/MeOH	**12aa** (92)
3	**5ba**	NH_3/MeOH	**11ba** (84)
4	**6ba**	NH_3/MeOH	**12ba** (92)
5	**5ca**	NH_3/MeOH	**11ca** (84)
6	**6ca**	NH_3/MeOH	**12ca** (86)
7	**5d**	NaOH/H_2O/THF	**11da** (65)
8	**5e**	MeONa	**11e** (71)
9	**6e**	MeONa	**12e** (88)
10	**5f**	MeONa	**11f** (65)
11	**6f**	MeONa	**12f** (60)
12	**5g**	MeONa	**11g** (84)
13	**5h**	MeONa	**11h** (89)
14	**6h**	MeONa	**12h** (80)
15	**5ia**	NH_3/MeOH	**11ia** (79)
16	**6ia**	NH_3/MeOH	**12ia** (82)
17	**5j**	MeONa	**11j** (90)
18	**6j**	MeONa	**12j** (78)
19	**5k**	NH_3/MeOH	**11k** (80)
20	**5l**	MeONa	**11l** (65)
21	**6l**	MeONa	**12l** (81)
22	**5m**	MeONa	**11m** (69)
23	**6m**	MeONa	**12m** (85)
24	**5n**	MeONa	**11n** (67)
25	**5p**	MeONa	**11p** (93)
26	**5q**	MeONa	**11q** (83)
27	**5r**	NH_3/MeOH	**11r** (70)
28	**6r**	NH_3/MeOH	**12r** (97)
29	**5s**	NH_3/MeOH	**11s** (72)
30	**6s**	NH_3/MeOH	**12s** (97)
31	**5t**	NH_3/MeOH	**11t** (61)
32	**6t**	NH_3/MeOH	**12t** (78)
33	**5u**	MeONa/NaOH/H_2O	**11ua** (78)
34	**5v**	NH_3/MeOH	**11v** (30)

excellent yields without cleavage of the protecting groups. All *S*-nucleophiles (both sodium thiolates and thiols in the presence of Hünig's base) reacted with mesylates **7** and **8** smoothly to give the desired *S*-substituted 6-(sulfanylmethyl)purine nucleosides in close to quantitative yields without cleavage of the protecting groups on the sugar (Table 4, entries 7–21).

The deprotections of the intermediates **13**, **14** and **17**, **18** were performed in analogy to the previous derivatives. Thus, 6-(*O*-substituted hydroxymethyl)- and 6-(*S*-substituted sulfanylmethyl)purine nucleosides **15**, **16** and **19**, **20** were prepared in good yields by treatment with sodium methoxide (catalytic amount) or aqueous ammonia in methanol at ambient temperature (Scheme 5) (Table 4, last column). The thioglycolate methyl esters **17d** and **18d** were hydrolysed by treatment with NaOMe followed by aq NaOH to remove all the ester groups and provide carboxylic acids **19da** and **20da**.

2.2. Biological activity

All the title 6-(*N*-substituted aminomethyl)-, 6-(*O*-substituted hydroxymethyl)- and 6-(*S*-substituted sulfanylmethyl)purine nucleosides **11**, **12**, **15**, **16**, **19**, **20** were subjected to biological activity screening. The cytostatic activity in vitro (inhibition of cell growth) was studied on the following cell cultures: (i) mouse leukaemia L1210 cells (ATCC CCL 219); (ii) human promyelocytic leukaemia HL60 cells (ATCC CCL 240); (iii) human cervix carcinoma HeLaS3 cells (ATCC CCL 2.2) and (iv) human T lymphoblastoid CCRF-CEM cell line (ATCC CCL 119). The cytostatic activities of compounds from this series were evaluated by estimating the cell count in a haematological analyzer (haemocytometer). In parallel the cell viability was determined by XTT staining.[20] Whilst the 2′-deoxyribonucleoside derivatives were all inactive, many ribonucleosides **11**, **15** or **19** exerted considerable antiproliferative effects at low micromolar concentrations (Table 5). The most susceptible cell line was human HL-60, whilst the



Scheme 5. Synthesis of **13**, **14** and **17**, **18** by nucleophilic substitutions.

Table 4. Nucleophilic substitutions of mesylates **7** and **8** with *O*- and *S*-nucleophiles and deprotection

Entry	Start. compd.	Nucleophile	Conditions	Product (yield %)	Deprotection	Product (yield %)
1	**7**	MeONa	MeOH, 12 h		Simultaneous	**15a** (30)
2	**8**	MeONa	MeOH, 12 h		Simultaneous	**16a** (44)
3	**7**	PhONa	THF, 6 h	**13b** (89)	MeONa	**15b** (86)
4	**8**	PhONa	THF, 6 h	**14b** (95)	MeONa	**16b** (90)
5				**13g**[c]	NH_3/MeOH	**15g** (80)
6				**14g**[c]	NH_3/MeOH	**16g** (89)
7	**7**	MeSNa	DME, 4 h	**17a** (96)	MeONa	**19a** (81)
8	**8**	MeSNa	DME, 4 h	**18a** (96)	MeONa	**20a** (93)
9	**7**	PhSNa	MeCN, 6 h	**17b** (76)	MeONa	**19b** (88)
10	**8**	PhSNa	MeCN, 6 h	**18b** (90)	MeONa	**20b** (91)
11	**7**	BnSH	AN, ^{i}Pr$_2$NEt, 10 h	**17c** (98)	MeONa	**19c** (89)
12	**8**	BnSH	AN, ^{i}Pr$_2$NEt, 10 h	**18c** (98)	MeONa	**20c** (92)
13	**7**	$HSCH_2CO_2Me$	AN, ^{i}Pr$_2$NEt, 10 h	**17d** (99)	MeONa/NaOH/H_2O	**19da** (75)
14	**8**	$HSCH_2CO_2Me$	AN, ^{i}Pr$_2$NEt, 10 h	**18d** (99)	MeONa/NaOH/H_2O	**20da** (83)
15	**7**	$HSCH_2CH_2OH$	AN, ^{i}Pr$_2$NEt, 10 h	**17e** (98)	MeONa	**19e** (84)
16	**8**	$HSCH_2CH_2OH$	AN, ^{i}Pr$_2$NEt, 10 h	**18e** (98)	MeONa	**20e** (93)
17	**7**	2-MPy[a]	AN, ^{i}Pr$_2$NEt, 12 h	**17g** (98)	MeONa	**19g** (78)
18	**8**	2-MPy[a]	AN, ^{i}Pr$_2$NEt, 12 h	**18g** (98)	MeONa	**20g** (57)
19	**7**	2-MBT[b]	AN, ^{i}Pr$_2$NEt, 12 h	**17h** (98)	MeONa	**19h** (86)
20	**7**	AcSK	AN, 5h	**17ia** (95)	MeONa	**19i** (57)
21	**8**	AcSK	AN, 5h	**18ia** (96)	MeONa	**20i** (86)

[a] 2-MPy, 2-mercaptopyridine.
[b] 2-MBT, 2-mercaptobenzothiazole.
[c] For synthesis of **13g** and **14g**, see Scheme 3.

CCRF-CEM and L1210 cell lines were less sensitive to most of the compounds. None of the compounds were active in HeLaS3 cell line. Within the aminomethyl series, the dialkylaminomethyl derivatives (i.e., **11e**–**11h** and **11j**–**11n**) generally exerted cytostatic effects, while acetylated monoalkylaminomethyl and heteroarylmethyl derivatives were less active. Also 6-(methoxymethyl)-, 6-(methylsulfanyl)- and 6-(benzylsulfanyl)-purine ribonucleosides **15a**, **19a** and **19c** showed considerable cytostatic activity. 6-(Sulfanylmethyl)purine ribonucleoside **19i**, the thia-analogue of the highly cytostatic[5] 6-(hydroxymethyl)purine **15i**, exerted only moderate cytostatic activity in the micromolar range. The most powerful anti-proliferative compound from the series was the azidomethyl derivative **11v** with IC_{50} values 0.4–1.9 μM. The viability data (XTT) in many cases indicate significantly lower IC_{50} values compared to the cell count IC_{50}. Taken together, this difference suggests a significant amount of apoptosis in cells upon exposure to the tested compounds. The cell cycle analysis (Tables 6 and 7) following treatment with selected compounds (**11v**, **11h**, **11j**, **15a**, **19c**, **19i**) indicated an accumulation of cells in G1 phase and depletion of S phase for compounds **11v**, **11j** and **15a**. In contrast, compounds **11h** and **19i** did not affect the S phase to a significant extent, whilst the cells treated with compound **19c** show S phase arrest. In agreement with the data on inhibition of cell proliferation all compounds with cytostatic activity induce apoptosis. None of the compounds showed any significant inhibition of adenosine deaminase[21] at 12.5 μM concentration.

The title modified nucleosides were also tested up to 100 μM for antiviral activities in HCV genotype 1b replicon[22] (Table 5). With the exception of **12ca** and **20i**, the 2′-deoxyribonucleosides were inactive, but many of the ribonucleosides displayed antiviral activity in the HCV replicon. Unfortunately, in most cases the compounds lacked selectivity. The exceptions of note were **11p**, **11v** and **19a**, which demonstrated >10-fold selectivity in the replicon huh-7 cells. Upon evaluation of these analogues in the MT-4 cell line reduced selectivity (<6-fold) was observed, consistent with the cytostatic effects measured in the other cell lines. These results suggest that the modified purine ribonucleosides interfere with critical cell growth processes and most of the activity towards HCV viral replication is non-specific.

3. Conclusions

This approach based on nucleophilic substitutions of 6-[(mesyloxy)methyl]purine nucleosides by amines, alcoholates or thiolates is a suitable methodology for the generation of diverse aminomethyl, alkyloxymethyl and alkylsulfanylmethyl derivatives of purine nucleosides as homologues of natural adenosine or inosine nucleosides. A large number of modified derivatives can be easily generated from this one common intermediate in one or two simple steps. Some of the ribonucleosides prepared exert considerable cytostatic effects.

4. Experimental

4.1. General

Starting materials. 6-Formylpurine-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine and 9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)-6-formylpurine were prepared as described in Ref. 11 6-(Methanesulfonyloxymethyl)-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)-

Table 5. Biological activities of title nucleosides **11**, **15** and **19**

Compound	Cytostatic activity IC_{50}[a] (μM)			HCV antiviral activity and cytotoxicity	
	L1210	HL60	CCRF-CEM	EC_{50}[b] (μM) HCV replicon[b]	CC_{50}[c,d] (μM) Huh7[c] (MT-4)[d]
11aa	n.a.	n.a.	n.a.	>100	>100
11ba	n.a.	n.a.	n.a.	>100	>100
11ca	n.a.	n.a.	n.a.	>100	>100
11da	n.a.	n.a.	n.a.	87	>100
11e	5.1 ± 0.4	4.0 ± 0.4	n.a.	41	>100
11f	17 ± 1.5	13 ± 0.9	n.a.	3	18
11g	4.8 ± 0.3	5.6 ± 0.3 (*2.4 ± 0.2*)	20.3 ± 1.2	9	9
11h	n.a.	4.0 ± 0.32 (*3.4 ± 0.35*)	n.a.	21	21
11ia	n.a.	n.a.	n.a.	>100	>100
11j	14.3 ± 0.85	14.7 ± 1.2 (*4.37 ± 0.33*)	6.7 ± 0.42 (*3.72 ± 0.36*)	15	10
11k	n.a.	6.6 ± 0.4 (*11.4 ± 0.2*)	18.0 ± 1.36 (*10.3 ± 1.0*)	65	>250
11l	12.16 ± 0.8	6.9 ± 0.4	n.a.	42	87
11m	n.a.	13.0 ± 0.7	n.a.	186	>250
11n	7.8 ± 0.4	5.2 ± 0.35 (*3.12 ± 0.1*)	19.6 ± 1.2	7	21
11p	n.a.	5.7 ± 0.32 (*9.1 ± 0.14*)	3.4 ± 0.21 (*1.96 ± 0.1*)	7.6	>250 (45)
11q	n.a.	n.a.	n.a.	62	>250 (48)
11r	n.a.	n.a.	n.a.	>100	>100
11s	n.a.	n.a.	n.a.	91	>100
11t	n.a.	n.a.	n.a.	14	45
11v	1.59 ± 0.09	1.88 ± 0.11 (*0.78 ± 0.02*)	0.39 ± 0.03 (*0.34 ± 0.04*)	6	>250 (32)
15a	n.a.	13.0 ± 0.9 (*1.68 ± 0.06*)	6.0 ± 0.35 (*1.14 ± 0.03*)	13	>100
15b	n.a.	n.a.	n.d.	>100	>100
15g	n.a.	12.0 ± 0.81 (*14.3 ± 0.7*)	16.6 ± 1.1 (*10.8 ± 0.65*)	>250	>250
19a	> 30	13.4 ± 1.04 (*5.0 ± 0.16*)	15.0 ± 1.1 (*3.2 ± 0.23*)	10	>100 (32)
19b	n.a.	n.a.	n.a.	>100	>100
19c	n.a.	10.7 ± 0.8 (*19.2 ± 0.58*)	9.2 ± 0.6 (*4.65 ± 0.28*)	>100	>100
19da	n.a.	n.a.	n.a.	>100	>100
19e	n.a.	n.a.	n.a.	46	>100 (>100)
19g	n.a.	n.a.	n.a.	44	>100 (>100)
19h	n.a.	n.a.	n.a.	>100	>100
19i	n.a.	3.5 ± 0.18(*1.2 ± 0.06*)	n.a.	39	54
12ca[e]	n.a.	n.a.	n.a.	20	>100 (>100)
20i[e]	n.a.	n.a.	n.a.	20	41
15i[f]	—	0.01 ± 0.0011	0.15 ± 0.0011	—	—
FUdR[g]	0.012 ± 0.003	0.012 ± 0.003	0.017 ± 0.004	—	—
2′CMeA[h]	—	—	—	0.23	>100

[a] Concentration of a compound needed to reduce population growth by 50% in vitro (in parentheses in italics values of XTT test).
[b] Antiviral activity in HCV-Con1 replicon ($N = 2$).
[c] MTT measurement of cellular toxicity in Huh-7 cells harbouring con-1 replicon ($N = 2$).
[d] Cellular toxicity in MT-4 cells ($N = 2$) in parentheses.
[e] 2′-Deoxyribonucleosides.
[f] Taken from Ref. 5a.
[g] 1-(β-D-2-Deoxy-*erythro*-pentofuranosyl)-5-fluorouracil.
[h] 2′-Methyl-adenosine.

Table 6. Cell cycle analysis of HL-60 cells: changes relative to control[a]

Compound	G1	S	G2/M
11h (3 μmol l^{-1})	1.12	0.87	1.08
11v (1 μmol l^{-1})	1.57	0.63	1.30
19c (22.5 μmol l^{-1})	1.99	0.43	0.88

[a] After 72 h treatment.

Table 7. Cell cycle analysis of HL-60 cells: changes after 72 h treatment with compound **11v**

Concentration (μmol l^{-1})	G1	S	G2/M
0	34	58	7
1	54	37	10
2.5	33	59	8
5	24	69	8

purine and 6-(methanesulfonyloxymethyl)-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine were prepared as described in Ref. 10 NMR spectra were recorded on Bruker Avance 400 MHz spectrometer (^1H at 400, ^{13}C at 100.6 MHz), a Bruker Avance (500 MHz for ^1H and 125.8 MHz for ^{13}C). Chemical shifts (in ppm, δ scale) were referenced to TMS as internal standard. The assignment of carbons was based on C,H HSQC and C,H HMBC experiments. Melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured at 25 °C on a Autopol IV (Rudolph Research Analytical) polarimeter, $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Mass spectra were measured on a ZAB-EQ (VG Analytical) spectrometer using FAB (ionization by Xe, accelerating voltage 8 kV, glycerol

matrix). Cytostatic activity tests were performed as described in Ref. 1.

4.2. General procedure for reductive aminations

An amine hydrochloride (5 mmol) was added to the solution of 6-formylpurine **3** (1 mmol) in methanol or ethanol (20 ml). After 30 min $NaBH_3CN$ was added either in one portion (90 mg, 1.2 mmol, 85% purity) or stepwise (5× 20 mg) and the mixture was stirred at ambient temperature for 24–72 h. In the case of sterically hindered amines (e.g., benzyl, cyclohexyl amine) heating of reaction mixture at 55 °C has been performed. The solvent was then evaporated, the residue was dissolved in 1 M aq NaH_2PO_4 (20 ml) and extracted with ethyl acetate (4× 25 ml). Collected organic layers were dried over $MgSO_4$, the solvent was evaporated and the oily residue was chromatographed on silica gel (hexanes/ethyl acetate, 1:1–0:1). Yields of the particular products are summarised in Table 1.

4.3. General procedure for nucleophilic substitutions of mesylates 7 and 8 with primary amines

A solution of mesylate **7** or **8** (1 mmol) in dry MeCN or THF (5 ml) was added dropwise to a solution of nucleophile (10–20 mmol) in dry MeCN or THF (10 ml). After complete consumption of starting material (monitoring by TLC) the solvent and excess of amine were evaporated in vacuo (45 °C, 130 Pa for 2 h). The residue was dissolved in CH_2Cl_2 (20 ml) and Et_3N (0.3 ml, 2.2 mmol) followed by AcCl (0.1 ml, 1.4 mmol) were added. Reaction was quenched after 8 h with 1 M aq NaH_2PO_4 (30 ml) and the mixture extracted with $CHCl_3$ (4× 30 ml). Collected organic layers were dried over $MgSO_4$, the solvent was evaporated and the oily residue was chromatographed on silica gel (hexanes/ethyl acetate, 1:1–0:1).

4.4. General procedure for nucleophilic substitutions of mesylates 7 and 8 with secondary amines

A solution of mesylate **7** or **8** (1 mmol) in dry MeCN or THF (5 ml) was added to a solution of nucleophile (1.5–4 mmol) in dry MeCN or THF (10 ml). After complete consumption of starting material (monitoring by TLC) the reaction was quenched with 1 M aq NaH_2PO_4 (40 ml) and the mixture extracted with ethyl acetate (4× 30 ml). Collected organic layers were dried over $MgSO_4$, the solvent was evaporated and the oily residue was chromatographed on silica gel (hexanes/ethyl acetate, 1:1–0:1).

4.5. General procedure for nucleophilic substitutions of mesylates 7 and 8 with *O*- or *S*-nucleophiles

A solution of mesylate **7** or **8** (1 mmol) in dry MeCN or THF (5 ml) was added to a solution of nucleophile (1.5–3 mmol) in dry MeCN or DME (10 ml). After complete consumption of starting material (monitoring by TLC) the reaction mixture was adsorbed on silica gel and chromatographed on silica (hexanes/ethyl acetate, 2/1:1/5).

4.6. 6-[(*N*-Methylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5a)

Prepared by reductive amination in 46% of yield. Yellowish foam which after 1 day turns brown to form complex mixture of decomposition products. Exact mass (FAB HR MS) found: 650.2628; calcd for $C_{36}H_{36}N_5O_7$: 650.2615. FAB MS *m*/*z* (%): 650 (MH^+, 2); 487 (8); 163 (3); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.37 and 2.42 (2× s, 9H, CH_3-Tol); 2.55 (s, 3H, CH_3N); 4.34 (s, 2H, CH_2N); 4.67 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'} = 4.2$, H-5′b); 4.82 (td, 1H, $J_{4',3'} = 4.7$, $J_{4',5'} = 4.2$, 3.2, H-4′); 4.89 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'} = 3.2$, H-5′a); 6.21 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.7$, H-3′); 6.38 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.4$, H-2′); 6.48 (d, 1H, $J_{1',2'} = 5.4$, H-1′); 7.16, 7.22 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.91 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.21 (s, 1H, H-8); 8.83 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.70 and 21.73 (CH_3-Tol); 35.99 (CH_3N); 51.94 (CH_2N); 63.42 (CH_2-5′); 71.41 (CH-3′); 73.72 (CH-2′); 81.04 (CH-4′); 86.92 (CH-1′); 125.65, 126.04 and 126.59 (C-*i*-Tol); 129.23, 129.27 and 129.34 (CH-*m*-Tol); 129.79, 129.88 and 129.89 (CH-*o*-Tol); 132.81 (C-5); 142.93 (CH-8); 144.24, 144.58 and 144.71 (C-*p*-Tol); 150.77 (C-4); 152.72 (CH-2); 159.07 (C-6); 165.17, 165.38 and 166.19 (CO). IR (CCl_4): ν = 3346, 2795, 1732, 1612, 1594, 1498, 1409, 1333, 1266, 1179, 1092, 644 cm^{-1}.

4.7. 6-[(*N*-Acetyl-*N*-methylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5aa)

Prepared by nucleophilic substitution of mesylate **7** (500 mg, 0.7 mmol) with $MeNH_2$/THF (7 ml, c = 2 mol l^{-1}) in MeCN (10 ml) and subsequent acetylation. Yield: 80% as white foam. Exact mass (FAB HR MS) found: 692.2731; calcd for $C_{38}H_{38}N_5O_8$: 692.2720. FAB MS *m*/*z* (%): 692 (MH^+, 2); 649 (0.5); 487 (32); 119 (100). A mixture of *cis*/*trans* amides ~1:0.7. ^{1}H NMR (400 MHz, $CDCl_3$): 2.21 and 2.25 (2× s, 2× 3H, CH_3CO); 2.38 and 2.42 (2× s, 18H, CH_3-Tol); 3.03 and 3.14 (2× s, 2× 3H, CH_3-N); 4.67 and 4.68 (2× dd, 2× 1H, J_{gem} = 12.1, $J_{5'b,4'} = 4.0$, H-5′b); 4.82 (m, 2H, H-4′); 4.88 and 4.90 (2× dd, 2× 1H, J_{gem} = 12.1, $J_{5'a,4'} = 3.0$, H-5′a); 4.96 and 5.10 (2× s, 2× 2H, CH_2N); 6.20 and 6.21 (2× dd, 2× 1H, $J_{3',2'} = 5.7$, $J_{3',4'} = 5.0$, H-3′); 6.37 and 6.39 (2× t, 2× 1H, $J_{2',3'} = 5.7$, $J_{2',1'} = 5.2$, H-2′); 6.47 and 6.48 (2× d, 2× 1H, $J_{1',2'} = 5.2$, H-1′); 7.16, 7.21, 7.23 and 7.26 (4× m, 6× 2H, H-*m*-Tol); 7.81, 7.90, 7.91 and 8.00 (5× m, 6× 2H, H-*o*-Tol); 8.18 and 8.22 (2× s, 2× 1H, H-8); 8.81 and 8.82 (2× s, 2× 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 20.99, 21.62 and 21.70 (**C**H_3CO and CH_3-Tol); 37.31 (CH_3N), 49.03 and 51.74 (CH_2N); 63.36 and 63.52 (CH_2-5′); 71.31 and 71.43 (CH-3′); 73.61 and 73.64 (CH-2′); 81.01 (CH-4′); 86.71 and 87.08 (CH-1′); 125.58, 125.64, 125.98, 126.02 and 126.59 (C-*i*-Tol); 129.21, 129.25, 129.27 and 129.33 (CH-*m*-Tol); 129.79 and 129.86 (CH-*o*-Tol); 132.70 (C-5); 142.91 and 143.42 (CH-8); 144.21, 144.49, 144.55, 144.66 and 144.78 (C-*p*-Tol); 150.53 (C-4); 152.70 and 152.86 (CH-2); 158.81 and 159.54 (C-6); 165.37 and 166.25 (CO-Tol); 173.69 (*C*OCH_3). IR (CCl_4): ν = 3038, 1732,

1658, 1612, 1595, 1498, 1408, 1334, 1267, 1179, 1092, 645 cm^{-1}.

4.8. Bis{*N*,*N*-[9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purin-6-yl]methyl}methylamine 9a

Prepared as by-product in nucleophilic substitution of mesylate **7** with $MeNH_2$/THF (see **5aa**). Yield: 8% as white foam. Exact mass (FAB HR MS) found: 1290.4519; calcd for $C_{71}H_{65}N_9O_{14}Na$: 1290.4549. FAB MS *m*/*z* (%): 1290 ($M+Na^+$, 3); 487 (44); 119 (100). ^1H NMR (400 MHz, $CDCl_3$): 2.36, 2.39 and 2.41 (3× s, 18H, CH_3-Tol); 2.52 (s, 3H, CH_3N); 4.32 and 4.37 (2× d, 4H, J_{gem} = 14.1, CH_2N); 4.66 (dd, 2H, J_{gem} = 12.3, $J_{5'b,4'}$ = 4.3, H-5′b); 4.81 (td, 2H, $J_{4',3'}$ = 4.9, $J_{4',5'}$ = 4.3, 3.2, H-4′); 4.88 (dd, 2H, J_{gem} = 12.3, $J_{5'a,4'}$ = 3.2, H-5′a); 6.25 (t, 2H, $J_{3',2'}$ = 5.7, $J_{3',4'}$ = 4.9, H-3′); 6.38 (t, 2H, $J_{2',3'}$ = 5.7, $J_{2',1'}$ = 5.2, H-2′); 6.48 (d, 2H, $J_{1',2'}$ = 5.2, H-1′); 7.14, 7.21 and 7.23 (3× m, 3× 4H, H-*m*-Tol); 7.81, 7.90 and 7.97 (3× m, 3× 4H, H-*o*-Tol); 8.14 (s, 2H, H-8); 8.87 (s, 2H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 (CH_3-Tol); 42.91 (CH_3N); 57.17 (CH_2N); 63.45 (CH_2-5′); 71.36 (CH-3′); 73.73 (CH-2′); 80.88 (CH-4′); 86.84 (CH-1′); 125.68, 126.05 and 126.58 (C-*i*-Tol); 129.19, 129.23 and 129.29 (CH-*m*-Tol); 129.78 and 129.87 (CH-*o*-Tol); 133.85 (C-5); 142.92 (CH-8); 144.16, 144.50 and 144.60 (C-*p*-Tol); 150.91 (C-4); 152.68 (CH-2); 158.61 (C-6); 165.18, 165.37 and 166.22 (CO).

4.9. 6-[(*N*-Acetyl-*N*-methylamino)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6aa)

Prepared by nucleophilic substitution of mesylate **8** (410 mg, 0.7 mmol) with $MeNH_2$/THF (7 ml, c = 2 mol l^{-1}) in MeCN (10 ml) and subsequent acetylation. Yield: 90% as white foam. Exact mass (FAB HR MS) found: 558.2336; calcd for $C_{30}H_{32}N_5O_6$: 558.2353. FAB MS *m*/*z* (%): 558 (MH^+, 5); 353 (2); 119 (100). A mixture of *cis*/*trans* amides ~1:0.7. ^1H NMR (400 MHz, $CDCl_3$): 2.22 and 2.26 (2× s, 6H, CH_3CO); 2.42 and 2.45 (2× s, 12H, CH_3-Tol); 2.85 (m, 2H, H-2′b); 3.03 and 3.14 (2× s, 6H, CH_3-N); 3.20 (m, 2H, H-2′a); 4.65–4.70 (m, 4H, H-5′b and H-4′); 4.77 (m, 2H, H-5′a); 4.96 and 5.10 (2× s, 4H, CH_2N); 5.83 (m, 2H, H-3′); 6.59 (m, 2H, H-1′); 7.24 and 7.29 (2× m, 8H, H-*m*-Tol); 7.91, 7.92 and 7.98 (3× m, 8H, H-*o*-Tol); 8.20 and 8.25 (2× s, 2H, H-8); 8.85 and 8.87 (2× s, 2H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.65, 21.69 and 21.74 (**C**H_3CO and CH_3-Tol); 34.47 and 37.44 (CH_3N), 37.71 and 37.75 (CH_2-2′); 49.12 and 51.69 (CH_2-pur); 63.90 and 63.99 (CH_2-5′); 74.96 and 75.07 (CH-3′); 83.08 and 83.15 (CH-4′); 84.81 and 84.99 (CH-1′); 126.32, 126.36, 126.63 and 126.66 (C-*i*-Tol); 129.28 (CH-*m*-Tol); 129.65 and 129.81 (CH-*o*-Tol); 132.68 (C-5); 142.50 and 143.03 (CH-8); 144.18, 144.22, 144.55 and 144.61 (C-*p*-Tol); 150.76 and 150.98 (C-4); 152.45 and 152.62 (CH-2); 156.43 and 157.70 (C-6); 165.92 and 166.16 (CO); 171.61 (*C*OCH_3). IR (CCl_4): ν = 3038, 1727, 1660, 1613, 1594, 1401, 1332, 1267, 1178, 1100, 646 cm^{-1}.

4.10. Bis{*N*,*N*-[9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purin-6-yl]methyl}methylamine (10a)

Prepared as by-product in nucleophilic substitution of mesylate **8** with $MeNH_2$/THF (see **6aa**). Yield: 5% as white foam. Exact mass (FAB HR MS) found: 1000.3974; calcd for $C_{55}H_{54}N_9O_{10}Na$: 1000.3994. FAB MS *m*/*z* (%): 1000 ($M+H^+$, 2); 119 (100). ^1H NMR (400 MHz, $CDCl_3$): 2.39 and 2.45 (2× s, 2× 6H, CH_3-Tol); 2.47 (s, 3H, CH_3N); 2.84 (ddd, 2H, J_{gem} = 14.2, $J_{2'b,1'}$ = 5.7, $J_{2'b,3'}$ = 2.0, H-2′b); 3.21 (ddd, 2H, J_{gem} = 14.2, $J_{2'a,1'}$ = 8.4, $J_{2'a,3'}$ = 6.4, H-2′a); 4.38 and 4.42 (2× d, 4H, J_{gem} = 14.2, CH_2N); 4.65–4.69 (m, 4H, H-5′b and H-4′); 4.75–4.80 (m, 2H, H-5′a); 5.84 (dt, 2H, $J_{3',2'}$ = 6.4, 2.0, $J_{3',4'}$ = 2.0, H-3′); 6.59 (dd, 2H, $J_{1'2'}$ = 8.4, 5.7, H-1′); 7.21 and 7.29 (2× m, 2× 4H, H-*m*-Tol); 7.91 and 7.98 (2× m, 2× 4H, H-*o*-Tol); 8.18 (s, 2H, H-8); 8.90 (s, 2H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.58 and 21.65 (CH_3-Tol); 37.57 (CH_2-2′); 42.49 (CH_3N); 57.47 (CH_2N); 63.89 (CH_2-5′); 75.02 (CH-3′); 82.96 (CH-4′); 84.74 (CH-1′); 126.32 and 126.58 (C-*i*-Tol); 129.17 and 129.19 (CH-*m*-Tol); 129.55 and 129.72 (CH-*o*-Tol); 133.78 (C-5); 142.44 (CH-8); 144.02 and 144.42 (C-*p*-Tol); 150.68 (C-4); 152.37 (CH-2); 158.37 (C-6); 165.83 and 166.05 (CO).

4.11. 6-[(*N*-Benzylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5b)

Benzylamine hydrochloride (720 mg, 5 mmol) was added to a solution of 6-formylpurine **3** (635 mg, 1 mmol) in ethanol (20 ml) and stirred at 55 °C. After 30 minutes $NaBH_3CN$ (20 mg, 0.27 mmol, 85% purity) was added. Stepwise addition of $NaBH_3CN$ (20 mg) was repeated four times every next hour. After 6 h the solvent was evaporated, the residue was dissolved in 1 M aq NaH_2PO_4 (30 ml) and extracted with ethyl acetate (4× 30 ml). Chromatography on silica gel (hexanes/AcOEt, 1:1–0:1) afforded 510 mg (70%) of **5b** as yellowish foam which after 1 day turns brown to form complex mixture of decomposition products. Exact mass (FAB HR MS) found: 726.2937; calcd for $C_{42}H_{40}N_5O_7$: 726.2928. FAB MS *m*/*z* (%): 726 (MH^+, 0.5); 487 (4); 119 (100). ^1H NMR (500 MHz, $CDCl_3$): 2.37, 2.41 and 2.42 (3× s, 3× 3H, CH_3-Tol); 3.88 (s, 2H, CH_2-Ph); 4.34 (s, 2H, CH_2-pur); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'}$ = 4.2, H-5′b); 4.82 (td, 1H, $J_{4',3'}$ = 4.7, $J_{4',5'}$ = 4.2, 3.2, H-4′); 4.89 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.2, H-5′a); 6.22 (dd, 1H, $J_{3',2'}$ = 5.8, $J_{3',4'}$ = 4.7, H-3′); 6.38 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.4, H-2′); 6.47 (d, 1H, $J_{1',2'}$ = 5.4, H-1′); 7.16 (m, 2H, H-*m*-Tol); 7.19–7.31 (m, 7H, 2× H-*m*-Tol + H-*m*,*p*-Ph); 7.34 (m, 2H, H-*o*-Ph); 7.81, 7.91 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.18 (s, 1H, H-8); 8.83 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.69 and 21.73 (CH_3-Tol); 49.33 (CH_2-pur); 53.64 (CH_2-Ph); 63.44 (CH_2-5′); 71.42 (CH-3′); 73.73 (CH-2′); 81.02 (CH-4′); 86.88 (CH-1′); 125.67, 126.05 and 126.60 (C-*i*-Tol); 126.98 (CH-*p*-Ph); 128.31 and 128.34 (CH-*o*,*m*-Ph); 129.23, 129.26 and 129.33 (CH-*m*-Tol); 129.79, 129.88 and 129.89 (CH-*o*-Tol); 132.75 (C-5); 139.87 (C-*i*-Ph); 142.68 (CH-8); 144.22, 144.57 and 144.69 (C-*p*-Tol);

150.67 (C-4); 152.72 (CH-2); 160.34 (C-6); 165.17, 165.38 and 166.20 (CO).

4.12. 6-[(*N*-Acetyl-*N*-benzylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5ba)

Prepared by nucleophilic substitution of mesylate **7** with $BnNH_2$ (15 equiv) and subsequent acetylation. Yield: 87% as white foam. Exact mass (FAB HR MS) found: 768.3041; calcd for $C_{44}H_{42}N_5O_8$: 768.3033. FAB MS *m*/*z* (%): 790 ($M+Na^+$, 10); 768 (MH^+, 1); 487 (10); 119 (100); 91 (26). A mixture of *cis*/*trans* amides ~1:1. ^1H NMR (500 MHz, $CDCl_3$): 2.26 and 2.31 (2× s, 2× 3H, CH_3CO); 2.377, 2.382, 2.413, 2.417 and 2.424 (5× s, 18H, CH_3-Tol); 4.66 and 4.67 (2× dd, 2× 1H, J_{gem} = 12.3, $J_{5'b,4'} = 4.4$, H-5′b); 4.72 and 4.73 (2× s, 2× 2H, CH_2Ph); 4.81 and 4.83 (2× td, 2× 1H, $J_{4',3'} = 4.5$, $J_{4',5'} = 4.4$, 3.2, H-4′); 4.88 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'} = 3.2$, H-5′a); 4.87 (s, 2H, CH_2N); 4.90 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'} = 3.2$, H-5′a); 5.05 and 5.09 (2× d, 2H, J_{gem} = 16.9, CH_2N); 6.19 and 6.21 (2× dd, 2× 1H, $J_{3',2'} = 5.7$, $J_{3',4'} = 4.5$, H-3′); 6.36 (t, 1H, $J_{2',3'} = 5.7$, $J_{2',1'} = 5.6$, H-2′); 6.37 (t, 1H, $J_{2',3'} = 5.7$, $J_{2',1'} = 5.3$, H-2′); 6.45 (d, 1H, $J_{1',2'} = 5.3$, H-1′); 6.47 (d, 1H, $J_{1',2'} = 5.6$, H-1′); 7.15–7.30 (m, 18H, H-*o*,*p*-Ph and H-*m*-Tol); 7.31–7.36 (m, 4H, H-*m*-Ph); 7.82, 7.90, 7.91 and 8.00 (4× m, 12H, H-*o*-Tol); 8.16 and 8.20 (2× s, 2× 1H, H-8); 8.80 and 8.81 (2× s, 2× 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 21.51, 21.70, 21.72 and 22.05 (CH_3CO and CH_3-Tol); 46.82 and 48.49 (CH_2N); 49.08 and 53.11 (CH_2Ph); 63.36 and 63.52 (CH_2-5′); 71.27 and 71.40 (CH-3′); 73.59 and 73.63 (CH-2′); 80.94 and 80.98 (CH-4′); 86.65 and 87.01 (CH-1′); 125.56, 125.61, 125.93, 125.98, 126.53 and 126.56 (C-*i*-Tol); 126.57 (CH-*o*-Ph); 127.25 and 127.61 (CH-*p*-Ph); 128.30 (CH-*o*-Ph); 128.46 and 128.84 (CH-*m*-Ph); 129.20, 129.24, 129.25, 129.26 and 129.32 (CH-*m*-Tol); 129.77, 129.84 and 129.87 (CH-*o*-Tol); 132.61 and 132.67 (C-5); 136.51 and 137.22 (C-*i*-Ph); 142.82 and 143.26 (CH-8); 144.21, 144.29, 144.55, 144.62, 144.66 and 144.79 (C-*p*-Tol); 150.89 and 150.94 (C-4); 152.65 and 152.75 (CH-2); 156.77 and 157.85 (C-6); 165.14, 165.18, 165.37, 166.18 and 166.20 (CO-Tol); 171.73 and 171.83 ($COCH_3$).

4.13. 6-[(*N*-Acetyl-*N*-benzylamino)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6ba)

Prepared by nucleophilic substitution of mesylate **8** with $BnNH_2$ (15 equiv) and subsequent acetylation. Yield: 92% as white foam. Exact mass (FAB HR MS) found: 634.2657; calcd for $C_{36}H_{36}N_5O_6$: 634.2666. FAB MS *m*/*z* (%): 634 (MH^+, 22); 353 (3); 282 (94); 119 (100); 91 (73). A mixture of *cis*/*trans* amides ~1:1. ^1H NMR (400 MHz, $CDCl_3$): 2.27 and 2.33 (2× s, 6H, CH_3CO); 2.40 and 2.45 (2× s, 12H, CH_3-Tol); 2.85 (m, 2H, H-2′b); 3.18 (m, 2H, H-2′a); 4.65–4.70 (m, 4H, H-5′b and H-4′); 4.74 and 4.76 (2× s, 4H, CH_2Ph); 4.77 (m, 2H, H-5′a); 4.88 and 5.07 (2 ×s, 4H, CH_2N); 5.83 (m, 2H, H-3′); 6.58 (m, 2H, H-1′); 7.22–7.30 (m, 14H, H-*o*,*p*-Ph and H-*m*-Tol); 7.32–7.36 (m, 4H, H-*m*-Ph); 7.92 and 7.98 (2× m, 8H, H-*o*-Tol); 8.18 and 8.22 (2× s, 2H, H-8); 8.85 and 8.86 (2× s, 2H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.54, 21.69 and 21.75 (CH_3CO and CH_3-Tol); 37.73 and 37.78 (CH_2-2′); 46.98 and 48.46 (CH_2-pur); 49.06 and 53.28 (CH_2Ph); 63.90 and 64.01 (CH_2-5′); 74.94 and 75.08 (CH-3′); 83.07 and 83.12 (CH-4′); 84.80 and 84.95 (CH-1′); 126.33, 126.36, 126,63 and 126.66 (C-*i*-Tol); 126.58 (CH-*o*-Ph); 127.24 and 127.63 (CH-*p*-Ph); 128.33 (CH-*o*-Ph); 128.48 and 128.87 (CH-*m*-Ph); 129.29 (CH-*m*-Tol); 129.65 and 129.81 (CH-*o*-Tol); 132.63 and 132.75 (C-5); 136.62 and 137.33 (C-*i*-Ph); 142.39 and 142.86 (CH-8); 144.19, 144.24, 144.55 and 144.61 (C-*p*-Tol); 150.70 and 150.84 (C-4); 152.43 and 152.54 (CH-2); 156.70 and 157.78 (C-6); 165.92 and 166.13 (CO); 171.64 and 171.82 ($COCH_3$). IR (CCl_4): ν = 3034, 1726, 1658, 1613, 1594, 1407, 1331, 1267, 1178, 1100, 646 cm^{-1}.

4.14. 6-[(*N*-Cyclohexylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5c)

Cyclohexylamine hydrochloride (680 mg, 5 mmol) was added to a solution of 6-formylpurine **3** (635 mg, 1 mmol) in ethanol (20 ml) and stirred at 55 °C. Stepwise addition of $NaBH_3CN$ was accomplished analogously as before (see **5b**). Chromatography on silica gel (hexanes/AcOEt, 1:1–0:1) afforded 310 mg (43%) of **5c** and 130 mg (21%) of alcohol **1**. Product was unstable and after few days turns brown and decomposition products were formed. Exact mass (FAB HR MS) found: 718.3252; calcd for $C_{41}H_{44}N_5O_7$: 718.3241. FAB MS *m*/*z* (%): 718 (MH^+, 7); 487 (6); 119 (100). ^1H NMR (500 MHz, $CDCl_3$): 1.12–1.30, 1.59, 1.73 and 1.97 (4× m, 10H, CH_2-cyclohex); 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 2.50 (m, 1H, CH-cyclohex); 4.34 and 4.38 (2× d, 2H, J_{gem} = 15.5, CH_2N); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'} = 4.2$, H-5′b); 4.81 (td, 1H, $J_{4',3'} = 4.7$, $J_{4',5'} = 4.2$, 3.2, H-4′); 4.89 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'} = 3.2$, H-5′a); 6.21 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.7$, H-3′); 6.37 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.4$, H-2′); 6.48 (d, 1H, $J_{1',2'} = 5.4$, H-1′); 7.16, 7.22 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.90 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.18 (s, 1H, H-8); 8.82 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.69 and 21.72 (CH_3-Tol); 24.90, 26.10 and 33.30 (CH_2-cyclohex); 47.47 (CH_2N); 56.47 (CH-cyclohex); 63.45 (CH_2-5′); 71.42 (CH-3′); 73.74 (CH-2′); 81.01 (CH-4′); 86.87 (CH-1′); 125.67, 126.05 and 126.61 (C-*i*-Tol); 129.22, 129.26 and 129.33 (CH-*m*-Tol); 129.79, 129.88 and 129.89 (CH-*o*-Tol); 132.69 (C-5); 142.63 (CH-8); 144.21, 144.56 and 144.68 (C-*p*-Tol); 150.62 (C-4); 152.73 (CH-2); 160.66 (C-6); 165.16, 165.38 and 166.20 (CO). IR (CCl_4): ν = 3328, 2929, 2855, 1732, 1613, 1595, 1497, 1409, 1333, 1266, 1179, 1092, 645 cm^{-1}.

4.15. 6-[(*N*-Acetyl-*N*-cyclohexylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5ca)

A solution of mesylate **7** (575 mg, 0.8 mmol) in MeCN (5 ml) was dropwise added to a solution of cyclohexylamine (0.9 ml, 8 mmol) in MeCN (10 ml). After completion of the reaction (monitoring by TLC) the solvent and excess of amine were evaporated in vacuo (45 °C, 130 Pa for 3 h). The residue was dissolved in CH_2Cl_2

(20 ml) and Et_3N (0.34 ml, 2.4 mmol) followed by AcCl (0.12 ml, 1.6 mmol) were added. Reaction was quenched after 8 h with 1 M aq NaH_2PO_4 (30 ml) and extracted with $CHCl_3$ (4× 30 ml). Crude oily product was chromatographed on silica gel (hexanes/AcOEt, 1/1:1/5) to gave 500 mg (82%) of **5ca** as white foam. Exact mass (FAB HR MS) found:760.3366; calcd for $C_{43}H_{46}N_5O_8$: 760.3346. FAB MS *m*/*z* (%): 782 ($M+Na^+$, 10); 760 (MH^+, 2); 487 (16); 273 (3); 119 (100). ^1H NMR (500 MHz, $CDCl_3$): 0.8–1.43, 1.53–1.96 (2× m, 2× 10H, CH_2-cyclohex); 2.14 and 2.27 (2× s, 2× 3H, CH_3CO); 2.37, 2.38, 2.41 and 2.42 (4× s, 18H, CH_3-Tol); 3.69–3.80 (m, 2× 1H, CH-cyclohex); 4.67 (dd, 1H, J_{gem} = 12.1, $J_{5'b,4'} = 4.2$, H-5′b); 4.68 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'} = 4.2$, H-5′b); 4.80 (td, 1H, $J_{4',3'} = 4.4$, $J_{4',5'} = 4.2$, 3.1, H-4′); 4.83 (ddd, 1H, $J_{4',3'} = 5.0$, $J_{4',5'} = 4.2$, 3.1, H-4′); 4.87 (dd, 1H, J_{gem} = 12.1, $J_{5'a,4'} = 3.1$, H-5′a); 4.90 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'} = 3.1$, H-5′a); 4.97 and 5.04 (2× s, 2× 2H, CH_2N); 6.19 (dd, 1H, $J_{3',2'} = 5.7$, $J_{3',4'} = 4.4$, H-3′); 6.23 (dd, 1H, $J_{3',2'} = 5.7$, $J_{3',4'} = 5.0$, H-3′); 6.35 (t, 1H, $J_{2',3'} = 5.7$, $J_{2',1'} = 5.6$, H-2′); 6.37 (t, 1H, $J_{2',3'} = 5.7$, $J_{2',1'} = 5.1$, H-2′); 6.46 (d, 1H, $J_{1',2'} = 5.6$, H-1′); 6.49 (d, 1H, $J_{1',2'} = 5.1$, H-1′); 7.16, 7.17, 7.20, 7.22, 7.26 and 7.27 (6× m, 6× 2H, H-*m*-Tol); 7.81, 7.82, 7.89, 7.91, 8.00 and 8.01 (6× m, 6× 2H, H-*o*-Tol); 8.16 and 8.21 (2× s, 2× 1H, H-8); 8.79 and 8.80 (2× s, 2× 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.71, 21.81 and 22.77 (CH_3CO and CH_3-Tol); 24.86, 25.25, 25.51, 25.69, 25.87, 30.61, 31.65 and 33.23 (CH_2-cyclohex); 42.65 and 44.84 (CH_2N); 58.27 (CH-cyclohex); 63.34 and 63.63 (CH_2-5′); 71.24 and 71.46 (CH-3′); 73.64 and 73.74 (CH-2′); 80.90 and 81.01 (CH-4′); 86.51 and 87.12 (CH-1′); 25.58, 125.65, 125.94, 126.02 and 126.58 (C-*i*-Tol); 129.20, 129.23, 129.26, 129.27, 129.32 and 129.35 (CH-*m*-Tol); 129.80, 129.86 and 129.89 (CH-*o*-Tol); 131.88 and 132.05 (C-5); 142.33 and 143.05 (CH-8); 144.20, 144.30, 144.53, 144.63 and 144.81 (C-*p*-Tol); 150.70 (C-4); 152.59 and 152.77 (CH-2); 158.49 and 159.44 (C-6); 165.23, 165.38 and 166.23 (CO-Tol); 170.90 and 171.68 ($COCH_3$). IR (CCl_4): ν = 2933, 2857, 1732, 1653, 1613, 1592, 1499, 1409, 1334, 1266, 1179, 1092, 645 cm^{-1}.

4.16. 6-[(*N*-Acetyl-*N*-cyclohexylamino)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6ca)

Prepared by nucleophilic substitution of mesylate **8** with $CyNH_2$ (15 equiv) and subsequent acetylation. Yield: 92% as white foam. Exact mass (FAB HR MS) found: 626.2969; calcd for $C_{35}H_{40}N_5O_6$: 626.2979. FAB MS *m*/*z* (%): 626 (MH^+, 2); 274 (78); 119 (100). A mixture of *cis*/*trans* amides ~7:5. ^1H NMR (500 MHz, $CDCl_3$): 0.80–1.43, 1.53–1.93 (2× m, 20H, CH_2-cyclohex); 2.14 and 2.27 (2× s, 2× 3H, CH_3CO); 2.41, 2.42, 2.44 and 2.45 (4× s, 18H, CH_3-Tol); 2.82 (ddd, J_{gem} = 14.1, $J_{2'b,1'} = 5.7$, $J_{2'b,3'} = 1.9$, H-2′b); 2.85 (ddd, J_{gem} = 14.2, $J_{2'b,1'} = 5.8$, $J_{2'b,3'} = 2.3$, H-2′b); 3.14 (ddd, J_{gem} = 14.1, $J_{2'a,1'} = 8.6$, $J_{2'a,3'} = 6.3$, H-2′a); 3.14 (ddd, J_{gem} = 14.2, $J_{2'a,1'} = 8.3$, $J_{2'a,3'} = 6.4$, H-2′a); 3.74 (tt, 1H, J_{vic} = 11.3, 3.5, CH-cyclohex); 4.58 (tt, 1H, J_{vic} = 12.1, 3.5, CH-cyclohex); 4.62–4.71 (m, 4H, H-4′ and H-5′b); 4.74–4.80 (m, 2H, H-5′a); 4.95 and 4.98 (2× d, 2H, J_{gem} = 111.6, CH_2N); 5.03(s, 2H, CH_2N); 5.82 (dt, 1H, $J_{3',2'} = 6.3$, 1.9, $J_{3',4'} = 2.0$, H-3′); 5.84 (dt, 1H, $J_{3',2'} = 6.4$, 2.3, $J_{3',4'} = 1.9$, H-3′); 6.59 (dd, 1H, $J_{1',2'} = 8.6$, 5.7, H-1′); 6.60 (dd, 1H, $J_{1',2'} = 8.3$, 5.8, H-1′); 7.24, 7.28 and 7.29 (3× m, 8H, H-*m*-Tol); 7.93 and 7.98 (2× m, 8H, H-*o*-Tol); 8.18 and 8.24 (2× s, 2× 1H, H-8); 8.82 and 8.85 (2× s, 2× 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 21.70, 21.74, 21.80 and 22.77 (CH_3CO and CH_3-Tol); 25.26, 25.50, 25.70, 25.87, 30.61, 31.64 and 31.68 (CH_2-cyclohex); 37.70 and 37.78 (CH_2-2′); 42.65 and 44.85 (CH_2N); 53.20 and 58.27 (CH-cyclohex); 63.90 and 64.05 (CH_2-5′); 74.93 and 75.11 (CH-3′); 83.03 and 83.08 (CH-4′); 84.70 and 84.88 (CH-1′); 126.30, 126.36, 126.63 and 126.66 (C-*i*-Tol); 129.28 and 129.31 (CH-*m*-Tol); 129.66 and 129.81 (CH-*o*-Tol); 131.90 and 132.06 (C-5); 141.95 and 142.63 (CH-8); 144.19, 144.24, 144.53 and 144.62 (C-*p*-Tol); 150.48 and 150.60 (C-4); 152.35 and 152.54 (CH-2); 158.37 and 159.29 (C-6); 165.94, 166.15 and 166.20 (CO-Tol); 170.90 and 171.65 ($COCH_3$). IR (CCl_4): ν = 2936, 2859, 1721, 1631, 1612, 1593, 1407, 1334, 1269, 1179, 1102, 646 cm^{-1}.

4.17. 6-[*N*-(Ethoxycarbonylmethyl)aminomethyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5d)

A solution of mesylate **7** (575 mg, 0.8 mmol) in MeCN (10 ml) was added to a solution of glycine ethyl ester hydrochloride (1.70 g, 12 mmol), $^iPr_2NEt$ (0.7 ml, 4 mmol) in MeCN (20 ml). After aqueous work-up and chromatography on silica gel (hexanes/AcOEt/MeOH, 10:20:0.3–10:30:1) 475 mg (82%) of **5d** was isolated as yellowish foam. Exact mass (FAB HR MS) found: 722.2822; calcd for $C_{39}H_{40}N_5O_9$: 722.2826. FAB MS *m*/*z* (%): 722 (MH^+, 1); 487 (6); 119 (100). ^1H NMR (500 MHz, $CDCl_3$): 1.26 (t, 3H, J_{vic} = 7.1, CH_3CH_2O); 2.38, and 2.43 (2× s, 9H, CH_3-Tol); 3.53 (s, 2H, NCH_2CO); 4.18 (q, 2H, J_{vic} = 7.1, CH_3CH_2O); 4.38 (s, 2H, pur-CH_2N); 4.66 (dd, 1H, J_{gem} = 12.4, $J_{5'b,4'} = 4.1$, H-5′b); 4.83 (td, 1H, $J_{4',3'} = 4.6$, $J_{4',5'} = 4.1$, 3.1, H-4′); 4.91 (dd, 1H, J_{gem} = 12.4, $J_{5'a,4'} = 3.1$, H-5′a); 6.23 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.6$, H-3′); 6.39 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.5$, H-2′); 6.49 (d, 1H, $J_{1',2'} = 5.5$, H-1′); 7.17, 7.23 and 7.27 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.91 and 8.01 (3× m, 3× 2H, H-*o*-Tol); 8.20 (s, 1H, H-8); 8.83 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 14.19 (CH_3CH_2O); 21.74 and 21.78 (CH_3-Tol); 49.74 (pur-CH_2N); 50.43 ($NCH2CO$); 60.81 (CH_3CH_2O); 63.38 (CH_2-5′); 71.28 (CH-3′); 73.54 (CH-2′); 80.91 (CH-4′); 86.68 (CH-1′); 125.44, 125.83 and 126.40 (C-*i*-Tol); 129.21, 129.26 and 129.34 (CH-*m*-Tol); 129.73 and 129.82 (CH-*o*-Tol); 132.58 (C-5); 142.84 (CH-8); 144.28, 144.62 and 144.72 (C-*p*-Tol); 150.61 (C-4); 152.71 (CH-2); 159.42 (C-6); 165.15, 165.38 and 166.20 (CO-Tol); 172.00 (CO-Et). IR (CCl_4): ν = 3345, 1734, 1612, 1597, 1498, 1409, 1334, 1266, 1194, 1180, 1092, 644 cm^{-1}.

4.18. 6-[(*N*,*N*-Dimethylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5e)

A solution of mesylate **7** (550 mg, 0.77 mmol) in MeCN (10 ml) was added to a solution of Me_2NH/THF

(1.54 ml, $c = 2$ mol/l, 3.08 mmol) in MeCN (10 ml). After aqueous work-up and chromatography on silica gel (hexanes/AcOEt/MeOH, 10:20:0.3–10:30:1) 405 mg (79%) of **5e** was isolated as white foam. Exact mass (FAB HR MS) found: 664.2764; calcd for $C_{37}H_{38}N_5O_7$: 664.2771. FAB MS *m/z* (%): 664 (MH^+, 7); 487 (16); 178 (5); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.38 (s, 3H, CH_3-Tol); 2.40 (s, 6H, CH_3N); 2.42 (s, 6H, CH_3-Tol); 4.04 (s, 2H, CH_2N); 4.67 (dd, 1H, $J_{gem} = 12.2$, $J_{5'b,4'} = 4.1$, H-5′b); 4.82 (td, 1H, $J_{4',3'} = 4.7$, $J_{4',5'} = 4.1$, 3.1, H-4′); 4.90 (dd, 1H, $J_{gem} = 12.2$, $J_{5'a,4'} = 3.1$, H-5′a); 6.23 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.7$, H-3′); 6.40 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.4$, H-2′); 6.48 (d, 1H, $J_{1',2'} = 5.4$, H-1′); 7.16, 7.22 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.91 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.21 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 and 21.73 (CH_3-Tol); 45.87 (CH_3N); 59.84 (CH_2N); 63.39 (CH_2-5′); 71.36 (CH-3′); 73.64 (CH-2′); 80.99 (CH-4′); 86.84 (CH-1′); 125.64, 126.02 and 126.58 (C-*i*-Tol); 129.22, 129.25 and 129.33 (CH-*m*-Tol); 129.78 and 129.87 (CH-*o*-Tol); 133.62 (C-5); 143.02 (CH-8); 144.22, 144.57 and 144.69 (C-*p*-Tol); 150.96 (C-4); 152.81 (CH-2); 158.76 (C-6); 165.17, 165.38 and 166.20 (CO). IR (CCl_4): $\nu = 3039$, 1732, 1612, 1594, 1498, 1409, 1332, 1266, 1179, 1092, 644 cm^{-1}.

4.19. 6-[(*N*,*N*-Dimethylamino)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6e)

Prepared from mesylate **8** by procedure described above (see **5e**). Yield: 85% of white crystals (mp 119–120 °C). Exact mass (FAB HR MS) found: 530.2382; calcd for $C_{29}H_{32}N_5O_5$: 530.2403. FAB MS *m/z* (%): 530 (MH^+, 18); 353 (2); 178 (64); 134 (19); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.41 and 2.45 (2× s, 2× 3H, CH_3-Tol); 2.47 (s, 6H, $(CH_3)_2N$); 2.85 (ddd, 1H, $J_{gem} = 14.3$, $J_{2'b,1'} = 5.7$, $J_{2'b,3'} = 2.1$, H-2′b); 3.21 (ddd, 1H, $J_{gem} = 14.3$, $J_{2'a,1'} = 8.5$, $J_{2'a,3'} = 6.4$, H-2′a); 4.12 (s, 2H, CH_2N); 4.64–4.70 (m, 2H, H-5′b and H-4′); 4.78 (dd, 1H, $J_{gem} = 13.3$, $J_{5'a,4'} = 5.2$, H-5′a); 5.84 (dt, 1H, $J_{3',2'} = 6.4$, 2.1, $J_{3',4'} = 2.0$, H-3′); 6.61 (dd, 1H, $J_{1'2'} = 8.5$, 5.7, H-1′); 7.23 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.91 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.24 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.68 and 21.74 (CH_3-Tol); 37.74 (CH_2-2′); 45.48 ($(CH_3)_2N$ and CH_2N); 63.91 (CH_2-5′); 75.03 (CH-3′); 83.12 (CH-4′); 84.85 (CH-1′); 126.34 and 126.63 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.64 and 129.81 (CH-*o*-Tol); 133.76 (C-5); 142.85 (CH-8); 144.21 and 144.59 (C-*p*-Tol); 150.90 (C-4); 152.54 (CH-2); 157.25 (C-6); 165.94 and 166.14 (CO). IR ($CHCl_3$): $\nu = 2827$, 2779, 1721, 1612, 1597, 1495, 1407, 1332, 1269, 1179, 1102, 646 cm^{-1}.

4.20. 6-[(*N*,*N*-Diisopropylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5f)

^{i}Pr$_2$NH (0.5 ml, 3.5 mmol) was added to a solution of mesylate **7** (575 mg, 0.8 mmol) in MeCN (10 ml) and stirred at 55 °C for 36 h. After aqueous work-up and chromatography on silica gel (hexanes/AcOEt, 1:1–1:4) 450 mg (78%) of **5f** was isolated as white foam. Exact mass (FAB HR MS) found: 720.3422; calcd for $C_{41}H_{46}N_5O_7$: 720.3397. FAB MS *m/z* (%): 720 (MH^+, 21); 487 (8); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 1.08 (d, 12H, $J_{vic} = 6.5$, $(CH_3)_2CH$); 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 3.21 (h, 2H, $J_{vic} = 6.5$, $CH(CH_3)_2$); 4.17 and 4.21 (2× d, 2H, $J_{gem} = 16.0$, CH_2N); 4.67 (dd, 1H, $J_{gem} = 12.2$, $J_{5'b,4'} = 4.1$, H-5′b); 4.82 (td, 1H, $J_{4',3'} = 4.7$, $J_{4',5'} = 4.1$, 3.1, H-4′); 4.89 (dd, 1H, $J_{gem} = 12.2$, $J_{5'a,4'} = 3.1$, H-5′a); 6.24 (dd, 1H, $J_{3',2'} = 5.7$, $J_{3',4'} = 4.7$, H-3′); 6.39 (t, 1H, $J_{2',3'} = 5.7$, $J_{2',1'} = 5.4$, H-2′); 6.47 (d, 1H, $J_{1',2'} = 5.4$, H-1′); 7.16, 7.21 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.82, 7.90 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.17 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 20.66 and 20.71 ($(CH_3)_2CH$); 21.70 and 21.73 (CH_3-Tol); 46.34 (CH_2N); 49.88 ($CH(CH_3)_2$); 63.46 (CH_2-5′); 71.34 (CH-3′); 73.69 (CH-2′); 80.90 (CH-4′); 86.83 (CH-1′); 125.70, 126.05 and 126.61 (C-*i*-Tol); 129.22, 129.24 and 129.33 (CH-*m*-Tol); 129.80 and 129.88 (CH-*o*-Tol); 132.89 (C-5); 142.29 (CH-8); 144.18, 144.53 and 144.66 (C-*p*-Tol); 150.50 (C-4); 153.03 (CH-2); 163.34 (C-6); 165.18, 165.38 and 166.23 (CO). IR (CCl_4): $\nu = 2965$, 1732, 1613, 1592, 1497, 1409, 1380, 1332, 1266, 1179, 1092, 644 cm^{-1}.

4.21. 6-[(*N*,*N*-Diisopropylamino)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6f)

Prepared from mesylate **8** by procedure described above (see **5f**). Yield: 86% of white foam. Exact mass (FAB HR MS) found: 586.3036; calcd for $C_{33}H_{40}N_5O_5$: 586.3029. FAB MS *m/z* (%): 586 (MH^+, 26); 353 (2); 234 (26); 190 (25); 148 (15); 134 (25); 119 (100); 100 (16). ^{1}H NMR (400 MHz, $CDCl_3$): 1.09 (d, 12H, $J_{vic} = 6.6$, $(CH_3)_2CH$); 2.41 and 2.45 (2× s, 9H, CH_3-Tol); 2.84 (ddd, 1H, $J_{gem} = 14.2$, $J_{2'b,1'} = 5.8$, $J_{2'b,3'} = 2.1$, H-2′b); 3.21 (ddd, 1H, $J_{gem} = 14.2$, $J_{2'a,1'} = 8.5$, $J_{2'a,3'} = 6.3$, H-2′a); 3.23 (h, 2H, $J_{vic} = 6.6$, $CH(CH_3)_2$); 4.17 and 4.22 (2× d, 2H, $J_{gem} = 15.9$, CH_2N); 4.63–4.70 (m, 2H, H-5′b and H-4′); 4.77 (dd, 1H, $J_{gem} = 11.5$, $J_{5'a,4'} = 3.5$, H-5′a); 5.84 (dt, 1H, $J_{3',2'} = 6.4$, 2.1, $J_{3',4'} = 2.2$, H-3′); 6.60 (dd, 1H, $J_{1'2'} = 8.5$, 5.8, H-1′); 7.23 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.92 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.20 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 20.64 and 20.70 ($(CH_3)_2CH$); 21.68 and 21.73 (CH_3-Tol); 37.70 (CH_2-2′); 46.26 (CH_2N); 49.93 ($CH(CH_3)_2$); 63.98 (CH_2-5′); 75.07 (CH-3′); 83.01 (CH-4′); 84.76 (CH-1′); 126.39 and 126.68 (C-*i*-Tol); 129.28 (CH-*m*-Tol); 129.66 and 129.81 (CH-*o*-Tol); 132.89 (C-5); 141.89 (CH-8); 144.14 and 144.54 (C-*p*-Tol); 150.36 (C-4); 152.78 (CH-2); 163.09 (C-6); 165.94 and 166.17 (CO). IR (CCl_4): $\nu = 2965$, 1727, 1613, 1592, 1495, 1407, 1383, 1330, 1267, 1179, 1101, 646 cm^{-1}.

4.22. 6-[(*N*-Benzyl-*N*-methylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5g)

N-Benzylmethylamine (0.36 ml, 2.8 mmol) was added to a solution of mesylate **7** (500 mg, 0.7 mmol) in MeCN (20 ml). After aqueous work-up and chromatography

on silica gel (hexanes/AcOEt, 2:1–1:2) 420 mg (81%) of **5g** was isolated as white foam. Exact mass (FAB HR MS) found: 740.3072; calcd for $C_{43}H_{42}N_5O_7$: 740.3084. FAB MS *m*/*z* (%): 740 (MH^+, 3); 487 (7); 119 (100); 91 (22). ^{1}H NMR (400 MHz, $CDCl_3$): 2.34 (s, 3H, CH_3N); 2.38, 2.41 and 2.42 (3× s, 3× 3H, CH_3-Tol); 3.71 (s, 2H, CH_2Ph); 4.13 (s, 2H, CH_2pur); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'} = 4.1$, H-5′b); 4.81 (td, 1H, $J_{4',3'} = 4.7$, $J_{4',5'} = 4.1$, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'} = 3.1$, H-5′a); 6.23 (dd, 1H, $J_{3',2'} = 5.7$, $J_{3',4'} = 4.7$, H-3′); 6.39 (t, 1H, $J_{2',3'} = 5.7$, $J_{2',1'} = 5.4$, H-2′); 6.47 (d, 1H, $J_{1',2'} = 5.4$, H-1′); 7.16 (m, 2H, H-*m*-Tol); 7.20 (m, 1H, H-*p*-Ph); 7.22 and 7.23 (2× m, 2× 2H, H-*m*-Tol); 7.27 (m, 2H, H-*m*-Ph); 7.37 (m, 2H, H-*o*-Ph); 7.82, 7.90 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.20 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 and 21.73 (CH_3-Tol); 42.80 (CH_3N); 57.70 (CH_2pur); 62.33 (CH_2Ph); 63.41 (CH_2-5′); 71.36 (CH-3′); 73.67 (CH-2′); 80.97 (CH-4′); 86.85 (CH-1′); 125.65, 126.02 and 126.58 (C-*i*-Tol); 126.88 (CH-*p*-Ph); 127.02 (CH-*m*-Ph); 129.22, 129.25, 129.27 and 129.33 (CH-*m*-Tol); 129.79 and 129.87 (CH-*o*-Tol); 132.72 (C-5); 138.25 (C-*i*-Ph); 142.84 (CH-8); 144.21, 144.56 and 144.68 (C-*p*-Tol); 150.86 (C-4); 152.78 (CH-2); 159.26 (C-6); 165.17, 165.38 and 166.21 (CO). IR (CCl_4): ν = 2790, 1732, 1612, 1593, 1496, 1454, 1409, 1331, 1266, 1179, 1092, 644 cm^{-1}.

4.23. 6-[(*N*-Methyl-*N*-phenylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5h)

N-Methylaniline (0.35 ml, 3.2 mmol) was added to a solution of mesylate **7** (575 mg, 0.8 mmol) in MeCN (20 ml) under Ar atmosphere. After aqueous work-up and chromatography on silica gel (hexanes/AcOEt, 2:1–1:2) 360 mg (62%) of **5h** was isolated as white foam. Exact mass (FAB HR MS) found: 726.2953; calcd for $C_{42}H_{40}N_5O_7$: 726.2928. FAB MS *m*/*z* (%): 726 (MH^+, 1); 487 (8); 134 (6); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.37 and 2.41 (2× s, 9H, CH_3-Tol); 3.23 (s, 3H, CH_3N); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'} = 4.2$, H-5′b); 4.81 (td, 1H, $J_{4',3'} = 4.6$, $J_{4',5'} = 4.2$, 3.1, H-4′); 4.87 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'} = 3.1$, H-5′a); 4.98 (s, 2H, CH_2N); 6.21 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.6$, H-3′); 6.38 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.5$, H-2′); 6.47 (d, 1H, $J_{1',2'} = 5.5$, H-1′); 6.68 (m, 1H, H-*p*-Ph); 6.88 (m, 2H, H-*o*-Ph); 7.16 (m, 2H, H-*m*-Tol); 7.18 (m, 2H, H-*m*-Ph); 7.23 and 7.24 (2× m, 2× 2H, H-*m*-Tol); 7.81, 7.90 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.21 (s, 1H, H-8); 8.82 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.71 and 21.73 (CH_3-Tol); 39.87 (CH_3N); 54.19 (CH_2N); 63.47 (CH_2-5′); 71.36 (CH-3′); 73.66 (CH-2′); 80.98 (CH-4′); 86.81 (CH-1′); 112.64 (CH-*o*-Ph); 116.85 (CH-*p*-Ph); 125.64, 126.01 and 126.58 (C-*i*-Tol); 129.05 (CH-*m*-Ph); 129.22, 129.25 and 129.33 (CH-*m*-Tol); 129.79, 129.87 and 129.89 (CH-*o*-Tol); 132.98 (C-5); 142.82 (CH-8); 144.21, 144.57 and 144.68 (C-*p*-Tol); 149.36 (C-*i*-Ph); 150.96 (C-4); 152.82 (CH-2); 159.64 (C-6); 165.17, 165.38 and 166.22 (CO). IR (CCl_4): ν = 2822, 1732, 1612, 1593, 1507, 1408, 1333, 1266, 1179, 1092, 644 cm^{-1}.

4.24. 6-[(*N*-Methyl-*N*-phenylamino)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6 h)

Prepared from mesylate **8** by procedure described above (see **5h**). Yield: 60% of white foam. Exact mass (FAB HR MS) found: 592.2551; calcd for $C_{34}H_{34}N_5O_5$: 592.2560. FAB MS *m*/*z* (%): 592 (MH^+, 27); 353 (3); 240 (55); 134 (60); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.41 and 2.44 (2× s, 2× 3H, CH_3-Tol); 2.84 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'} = 5.8$, $J_{2'b,3'} = 2.6$, H-2′b); 3.19 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'} = 8.4$, $J_{2'a,3'} = 6.2$, H-2′a); 3.25 (s, 3H, CH_3N); 4.63–4.70 (m, 2H, H-5′b and H-4′); 4.76 (m, 1H, H-5′a); 4.98 (s, 2H, CH_2N); 5.83 (dt, 1H, $J_{3',2'} = 6.2$, 2.6, $J_{3',4'} = 2.1$, H-3′); 6.59 (dd, 1H, $J_{1'2'} = 8.4$, 5.8, H-1′); 6.68 (m, 1H, H-*p*-Ph); 6.89 (m, 2H, H-*o*-Ph); 7.18 (m, 2H, H-*m*-Ph); 7.22 and 7.28 (2× m, 2× 2H, H-*m*-Tol); 7.91 and 7.97 (2× m, 2× 2H, H-*o*-Tol); 8.24 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 and 21.74 (CH_3-Tol); 37.73 (CH_2-2′); 39.95 (CH_3N); 54.14 (CH_2N); 63.97 (CH_2-5′); 75.05 (CH-3′); 83.08 (CH-4′); 84.88 (CH-1′); 112.62 (CH-*o*-Ph); 116.82 (CH-*p*-Ph); 126.37 and 126.66 (C-*i*-Tol); 129.05 (CH-*m*-Ph); 129.28 and 129.30 (CH-*m*-Tol); 129.66 and 129.82 (CH-*o*-Tol); 133.01 (C-5); 142.44 (CH-8); 144.17 and 144.56 (C-*p*-Tol); 149.32 (C-*i*-Ph); 150.80 (C-4); 152.56 (CH-2); 159.48 (C-6); 165.94 and 166.17 (CO). IR (CCl_4): ν = 2822, 1727, 1613, 1592, 1507, 1406, 1331, 1267, 1178, 1100, 645 cm^{-1}.

4.25. 6-[(*N*-Acetyl-*N*-cyclopropylamino)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5i)

A solution of mesylate **7** (500 mg, 0.7 mmol) in MeCN (10 ml) was dropwise added to a solution of cyclopropylamine (0.5 ml, 7.2 mmol) in MeCN (10 ml). After completion of the reaction (monitoring by TLC) the solvent and excess of amine were evaporated in vacuo (45 °C, 130 Pa for 2 h). The residue was dissolved in CH_2Cl_2 (20 ml) and Et_3N (0.3 ml, 2.2 mmol) followed by AcCl (0.1 ml, 1.4 mmol) were added. Reaction was quenched after 8 h with 1 M aq NaH_2PO_4 (30 ml) and extracted with $CHCl_3$ (4× 30 ml). Crude oily product was chromatographed on silica gel (hexanes/AcOEt, 1:1–1:5) to give 472 mg (94%) of **5i** as white foam. Exact mass (FAB HR MS) found: 718.2884; calcd for $C_{40}H_{40}N_5O_8$: 718.2877. FAB MS *m*/*z* (%): 718 (MH^+, 0.5); 487 (2); 133 (92); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 0.80–0.90 (m, 4H, CH_2-cycloprop); 2.34 (s, 3H, CH_3CO); 2.38, 2.416 and 2.422 (3× s, 3× 3H, CH_3-Tol); 2.95 (tt, 1H, J_{vic} = 6.9, 3.6, CH-cycloprop); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'} = 4.3$, H-5′b); 4.81 (td, 1H, $J_{4',3'} = 4.5$, $J_{4',5'} = 4.3$, 3.2, H-4′); 4.88 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'} = 3.2$, H-5′a); 5.09 (s, 2H, CH_2N); 6.19 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.5$, H-3′); 6.36 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.5$, H-2′); 6.48 (d, 1H, $J_{1',2'} = 5.5$, H-1′); 7.16, 7.21 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.89 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.17 (s, 1H, H-8); 8.79 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 9.37 and 9.41 (CH_2-cycloprop); 21.70 and 21.73 (CH_3-Tol); 22.55 (CH_3CO); 31.55 (CH-cycloprop); 48.49 (CH_2N); 63.55 (CH_2-5′); 71.42 (CH-3′); 73.63 (CH-2′); 80.99 (CH-4′); 86.62 (CH-1′); 125.63,

126.00 and 126.58 (C-*i*-Tol); 129.21, 129.24 and 129.34 (CH-*m*-Tol); 129.79, 129.86 and 129.89 (CH-*o*-Tol); 132.38 (C-5); 142.63 (CH-8); 144.21, 144.55 and 144.66 (C-*p*-Tol); 150.85 (C-4); 152.61 (CH-2); 158.57 (C-6); 165.15, 165.38 and 166.22 (CO-Tol); 174.47 (*C*OCH$_3$). IR (CCl_4): ν = 3010, 1732, 1669, 1613, 1594, 1497, 1409, 1334, 1266, 1179, 1092, 645 cm^{-1}.

4.26. 6-[(*N*-Acetyl-*N*-cyclopropylamino)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6i)

Prepared from mesylate **8** by procedure described above (see **5i**). Yield: 95% of white foam. Exact mass (FAB HR MS) found: 584.2529; calcd for $C_{32}H_{34}N_5O_6$: 584.2509. FAB MS *m*/*z* (%): 584 (MH$^+$, 25); 353 (3); 232 (83); 190 (17); 133 (20); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 0.73–0.93 (m, 4H, CH_2-cycloprop); 2.35 (s, 3H, CH_3CO); 2.41 and 2.45 (2× s, 2× 3H, CH_3-Tol); 2.83 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'} = 5.8$, $J_{2'b,3'} = 2.1$, H-2′b); 2.98 (tt, 1H, J_{vic} = 6.9, 4.1, CH-cycloprop); 3.15 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'} = 8.5$, $J_{2'a,3'} = 6.4$, H-2′a); 4.63–4.70 (m, 2H, H-5′b and H-4′); 4.76 (m, 1H, H-5′a); 5.09 (s, 2H, CH_2N); 5.82 (dt, 1H, $J_{3',2'} = 6.4$, 2.1, $J_{3',4'} = 1.9$, H-3′); 6.59 (dd, 1H, $J_{1',2'} = 8.5$, 5.8, H-1′); 7.24 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.91 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.19 (s, 1H, H-8); 8.82 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 9.39 and 9.41 (CH_2-cycloprop); 21.68 and 21.74 (CH_3-Tol); 22.54 (*C*H$_3$CO); 31.68 (CH-cycloprop); 37.78 (CH_2-2′); 48.61 (CH_2N); 64.02 (CH_2-5′); 75.09 (CH-3′); 83.06 (CH-4′); 84.77 (CH-1′); 126.37 and 126.67 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.66 and 129.82 (CH-*o*-Tol); 133.36 (C-5); 142.23 (CH-8); 144.19 and 144.55 (C-*p*-Tol); 150.64 (C-4); 152.37 (CH-2); 158.46 (C-6); 165.94 and 166.19 (CO-Tol); 174.47 (*C*OCH$_3$). IR (CCl_4): ν = 3010, 1726, 1668, 1613, 1594, 1390, 1333, 1267, 1178, 1101, 646 cm^{-1}.

4.27. 6-{[*N*,*N*-Bis(2-hydroxyethyl)amino]methyl}-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5j)

Diethanolamine (0.22 ml, 2.3 mmol) was added to a solution of mesylate **7** (400 mg, 0.56 mmol) in MeCN (10 ml). After aqueous work-up and chromatography on silica gel (AcOEt/MeOH, 10:0.1–10:2) 290 mg (72%) of **5j** was isolated as white foam. Exact mass (FAB HR MS) found: 724.2947; calcd for $C_{39}H_{42}N_5O_9$: 724.2983. FAB MS *m*/*z* (%): 724 (MH$^+$, 2); 487 (4); 237 (3); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 2.83 (m, 4H, CH_2N); 3.63 (m, 4H, CH_2O); 4.23 and 4.25 (2× d, 2H, J_{gem} = 16.1, CH_2pur); 4.68 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'} = 4.5$, H-5′b); 4.82 (td, 1H, $J_{4',3'} = 4.9$, $J_{4',5'} = 4.5$, 3.3, H-4′); 4.88 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'} = 3.3$, H-5′a); 6.20 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.9$, H-3′); 6.38 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.3$, H-2′); 6.45 (d, 1H, $J_{1',2'} = 5.3$, H-1′); 7.16, 7.21 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.90 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.27 (s, 1H, H-8); 8.78 (s, 1H, H-2). ^{13}C NMR (125.80 MHz, $CDCl_3$): 21.71 and 21.73 (CH_3-Tol); 57.39 (CH_2N); 57.60 (CH_2pur); 59.43 (CH_2O); 63.42 (CH_2-5′); 71.29 (CH-3′); 73.62 (CH-2′); 81.04 (CH-4′); 87.28 (CH-1′); 125.59, 125.97 and 126.59 (C-*i*-Tol); 129.23, 129.25 and 129.31 (CH-*m*-Tol); 129.80, 129.86 and 129.90 (CH-*o*-Tol); 132.70 (C-5); 143.42 (CH-8); 144.21, 144.57 and 144.71 (C-*p*-Tol); 150.98 (C-4); 152.53 (CH-2); 161.04 (C-6); 165.16, 165.35 and 166.21 (CO). IR (CCl_4): ν = 3382, 1727, 1612, 1593, 1499, 1409, 1335, 1267, 1093, 646 cm^{-1}.

4.28. 6-{[*N*,*N*-Bis(2-hydroxyethyl)amino]methyl}-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6j)

Prepared from mesylate **8** by procedure described above (see **5j**). Yield: 78% of white foam. Exact mass (FAB HR MS) found: 590.2598; calcd for $C_{31}H_{36}N_5O_7$: 590.2615. FAB MS *m*/*z* (%): 590 (MH$^+$, 12); 238 (44); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.41 and 2.45 (2× s, 2× 3H, CH_3-Tol); 2.83 (m, 4H, CH_2N); 2.85 (ddd, 1H, J_{gem} = 14.4, $J_{2'b,1'} = 5.8$, $J_{2'b,3'} = 2.0$, H-2′b); 3.21 (ddd, 1H, J_{gem} = 14.4, $J_{2'a,1'} = 8.2$, $J_{2'a,3'} = 6.5$, H-2′a); 3.63 (m, 4H, CH_2O); 4.19 and 4.25 (2× d, 2H, J_{gem} = 16.0, CH_2-pur); 4.64–4.70 (m, 2H, H-5′b and H-4′); 4.76 (m, 1H, H-5′a); 5.83 (dt, 1H, $J_{3',2'} = 6.5$, 2.0, $J_{3',4'} = 2.0$, H-3′); 6.61 (dd, 1H, $J_{1'2'} = 8.2$, 5.8, H-1′); 7.24 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.91 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.28 (s, 1H, H-8); 8.82 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 and 21.75 (CH_3-Tol); 37.63 (CH_2-2′); 57.39 (CH_2N); 57.75 (CH_2-pur); 59.41 (CH_2O); 63.88 (CH_2-5′); 74.96 (CH-3′); 83.21 (CH-4′); 85.13 (CH-1′); 126.33 and 126.63 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.66 and 129.82 (CH-*o*-Tol); 132.68 (C-5); 142.94 (CH-8); 144.17 and 144.56 (C-*p*-Tol); 150.84 (C-4); 152.29 (CH-2); 160.89 (C-6); 165.90 and 166.15 (CO). IR (CCl_4): ν = 3382, 1721, 1612, 1593, 1407, 1334, 1269, 1179, 1102, 647 cm^{-1}.

4.29. 6-[(2-Acetylhydrazinyl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5k)

Acetylhydrazide (416 mg, 5.6 mmol) was added to a solution of mesylate **7** (200 mg, 0.28 mmol) and ^{i}Pr$_2$NEt (0.1 ml, 0.57 mmol) in MeCN (10 ml). After aqueous work-up and chromatography on silica gel (AcOEt/MeOH, 1:0–10:1) 125 mg (65%) of **5k** was isolated as white foam. Exact mass (FAB HR MS) found: 693.2686; calcd for $C_{37}H_{37}N_6O_8$: 693.2673. FAB MS *m*/*z* (%): 693 (MH$^+$, 2); 487 (14); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 1.94 (s, 3H, CH_3CO); 2.38, 2.417 and 2.422 (3× s, 3× 3H, CH_3-Tol); 4.53 (s, 2H, CH_2N); 4.67 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'} = 4.2$, H-5′b); 4.83 (td, 1H, $J_{4',3'} = 4.7$, $J_{4',5'} = 4.2$, 3.2, H-4′); 4.90 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'} = 3.2$, H-5′a); 5.37 (bs, 1H, NH); 6.21 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.7$, H-3′); 6.38 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.4$, H-2′); 6.48 (d, 1H, $J_{1',2'} = 5.4$, H-1′); 7.16, 7.22 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.80, 7.91 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.24 (s, 1H, H-8); 8.26 (bs, 1H, NH-CO); 8.82 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 21.29 (*C*H$_3$CO); 21.71 and 21.74 (CH_3-Tol); 53.91 (CH_2N); 63.38 (CH_2-5′); 71.35 (CH-3′); 73.69 (CH-2′); 81.03 (CH-4′); 86.96 (CH-1′); 125.55, 125.95 and 126.54 (C-*i*-Tol); 129.24, 129.28 and 129.33 (CH-*m*-Tol); 129.77 and 129.87

(CH-*o*-Tol); 132.25 (C-5); 143.10 (CH-8); 144.29, 144.63 and 144.77 (C-*p*-Tol); 151.04 (C-4); 152.55 (CH-2); 159.33 (C-6); 165.19, 165.39 and 166.18 (CO-Tol); 168.98 (CON).

4.30. 6-[(Piperidin-1-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5l)

Piperidine (0.32 ml, 3.2 mmol) was added to a solution of mesylate **7** (575 mg, 0.8 mmol) in MeCN (10 ml). After aqueous work-up and chromatography on silica gel (hexanes/AcOEt, 1:1–0:1) 500 mg (89%) of **5l** was isolated as white foam. Exact mass (FAB HR MS) found: 704.3105; calcd for $C_{40}H_{42}N_5O_7$: 704.3084. FAB MS *m*/*z* (%): 704 (MH^+, 8); 487 (7); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 1.42 (bm, 2H, CH_2-pip); 1.61 (p, 4H, J_{vic} = 5.9, CH_2-pip); 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 2.55 (bm, 4H, CH_2N-pip); 4.05 (s, 2H, CH_2N); 4.66 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'} = 4.1$, H-5′b); 4.82 (td, 1H, $J_{4',3'} = 4.7$, $J_{4',5'} = 4.1$, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'} = 3.1$, H-5′a); 6.24 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.7$, H-3′); 6.40 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.4$, H-2′); 6.48 (d, 1H, $J_{1',2'} = 5.4$, H-1′); 7.16, 7.22 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.82, 7.90 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.20 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.70 and 21.73 (CH_3-Tol); 24.05 and 25.72 (CH_2-pip); 54.97 (CH_2N-pip); 59.27 (CH_2N); 63.40 (CH_2-5′); 71.34 (CH-3′); 73.66 (CH-2′); 80.95 (CH-4′); 86.85 (CH-1′); 125.65, 126.01 and 126.58 (C-*i*-Tol); 129.22, 129.25 and 129.33 (CH-*m*-Tol); 129.79, 129.87 and 129.88 (CH-*o*-Tol); 133.93 (C-5); 142.91 (CH-8); 144.21, 144.56 and 144.69 (C-*p*-Tol); 150.84 (C-4); 152.84 (CH-2); 157.85 (C-6); 165.18, 165.38 and 166.21 (CO). IR (CCl_4): ν = 2937, 1732, 1613, 1594, 1498, 1409, 1331, 1266, 1179, 1092, 644 cm^{-1}.

4.31. 6-[(Piperidin-1-yl)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6l)

Prepared from mesylate **8** by procedure described above (see **5l**). Yield: 94% of white foam. Exact mass (FAB HR MS) found: 570.2723; calcd for $C_{32}H_{36}N_5O_5$: 570.2716. FAB MS *m*/*z* (%): 570 (MH^+, 30); 353 (2); 218 (100); 134 (24); 119 (91). ^{1}H NMR (400 MHz, $CDCl_3$): 1.43 (bm, 2H, CH_2-pip); 1.62 (p, 4H, J_{vic} = 5.6, CH_2-pip); 2.41 and 2.45 (2× s, 2× 3H, CH_3-Tol); 2.56 (bm, 4H, CH_2N-pip); 2.85 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'} = 5.7$, $J_{2'b,3'} = 2.1$, H-2′b); 3.21 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'} = 8.4$, $J_{2'a,3'} = 6.4$, H-2′a); 4.05 (s, 2H, CH_2N); 4.63–4.70 (m, 2H, H-5′b and H-4′); 4.78 (m, 1H, H-5′a); 5.84 (dt, 1H, $J_{3',2'} = 6.4$, 2.1, $J_{3',4'} = 2.1$, H-3′); 6.60 (dd, 1H, $J_{1'2'} = 8.4$, 5.7, H-1′); 7.23 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.92 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.22 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 and 21.74 (CH_3-Tol); 24.05 and 25.72 (CH_2-pip); 37.73 (CH_2-2′); 55.00 (CH_2N-pip); 59.28 (CH_2N); 63.95 (CH_2-5′); 75.06 (CH-3′); 83.07 (CH-4′); 84.81 (CH-1′); 126.36 and 126.65 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.65 and 129.81 (CH-*o*-Tol); 133.93 (C-5); 142.49 (CH-8); 144.18 and 144.57 (C-*p*-Tol); 150.68 (C-4); 152.60 (CH-2); 158.59 (C-6); 165.94 and 166.16 (CO). IR (CCl_4): ν = 2937, 1726, 1613, 1594, 1496, 1408, 1329, 1267, 1178, 1101, 646 cm^{-1}.

4.32. 6-[(Morpholin-4-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5m)

Morpholine (0.2 ml, 2.24 mmol) was added to a solution of mesylate **7** (400 mg, 0.56 mmol) in MeCN (10 ml). After aqueous work-up and chromatography on silica gel (hexanes/AcOEt, 1:1–0:1) 347 mg (88%) of **5m** was isolated as white foam. Exact mass (FAB HR MS) found: 706.2850; calcd for $C_{39}H_{40}N_5O_8$: 706.2877. FAB MS *m*/*z* (%): 706 (MH^+, 3); 487 (7); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.38, and 2.42 (2× s, 9H, CH_3-Tol); 2.62 (bt, 4H, J_{vic} = 4.5, CH_2N-morph); 3.75 (t, 4H, J_{vic} = 4.5, CH_2O-morph); 4.08 (s, 2H, CH_2N); 4.66 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'} = 4.2$, H-5′b); 4.82 (td, 1H, $J_{4',3'} = 4.7$, $J_{4',5'} = 4.2$, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'} = 3.1$, H-5′a); 6.23 (dd, 1H, $J_{3',2'} = 5.7$, $J_{3',4'} = 4.7$, H-3′); 6.40 (t, 1H, $J_{2',3'} = 5.7$, $J_{2',1'} = 5.4$, H-2′); 6.47 (d, 1H, $J_{1',2'} = 5.4$, H-1′); 7.16, 7.22 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.91 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.21 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.71 and 21.74 (CH_3-Tol); 54.02 (CH_2N-morph); 58.95 (CH_2N); 63.39 (CH_2-5′); 66.77 (CH_2O-morph); 71.33 (CH-3′); 73.63 (CH-2′); 80.97 (CH-4′); 86.93 (CH-1′); 125.61, 125.99 and 126.57 (C-*i*-Tol); 129.24, 129.26 and 129.33 (CH-*m*-Tol); 129.79 and 129.87 (CH-*o*-Tol); 133.89 (C-5); 143.15 (CH-8); 144.23, 144.59 and 144.74 (C-*p*-Tol); 150.96 (C-4); 152.84 (CH-2); 157.89 (C-6); 165.19, 165.38 and 166.19 (CO). IR (CCl_4): ν = 2961, 1732, 1613, 1595, 1498, 1410, 1333, 1266, 1179, 1119, 1092, 644 cm^{-1}.

4.33. 6-[(Morpholin-4-yl)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6m)

Prepared from mesylate **8** by procedure described above (see **5m**). Yield: 94% of white foam. Exact mass (FAB HR MS) found: 572.2518; calcd for $C_{31}H_{34}N_5O_6$: 572.2509. FAB MS *m*/*z* (%): 572 (MH^+, 9); 353 (4); 220 (53); 134 (28); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.42 and 2.46 (2× s, 2× 3H, CH_3-Tol); 2.63 (bt, 4H, J_{vic} = 4.7, CH_2N-morph); 2.86 (ddd, 1H, J_{gem} = 14.1, $J_{2'b,1'} = 5.7$, $J_{2'b,3'} = 2.0$, H-2′b); 3.22 (ddd, 1H, J_{gem} = 14.1, $J_{2'a,1'} = 8.6$, $J_{2'a,3'} = 6.4$, H-2′a); 3.76 (t, 4H, J_{vic} = 4.7, CH_2O-morph); 4.09 (s, 2H, CH_2N); 4.65–4.70 (m, 2H, H-5′b and H-4′); 4.80 (dd, 1H, J_{gem} = 13.3, $J_{5'b,4'} = 5.0$, H-5′a); 5.85 (dt, 1H, $J_{3',2'} = 6.4$, 2.0, $J_{3',4'} = 2.0$, H-3′); 6.62 (dd, 1H, $J_{1'2'} = 8.6$, 5.7, H-1′); 7.24 and 7.30 (2× m, 2× 2H, H-*m*-Tol); 7.93 and 7.99 (2× m, 2× 2H, H-*o*-Tol); 8.24 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.73 and 21.78 (CH_3-Tol); 37.63 (CH_2-2′); 53.97 (CH_2N-morph); 58.88 (CH_2N); 63.91 (CH_2-5′); 66.72 (CH_2O-morph); 75.00 (CH-3′); 83.03 (CH-4′); 84.76 (CH-1′); 126.17 and 126.49 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.60 and 129.78 (CH-*o*-Tol); 133.79 (C-5); 142.74 (CH-8); 144.24 and 144.62 (C-*p*-Tol); 150.70 (C-4); 152.59 (CH-2); 157.61 (C-6); 165.94 and 166.15 (CO). IR (CCl_4): ν = 2819, 1721, 1612, 1598, 1497, 1408, 1333, 1269, 1179, 1103, 646 cm^{-1}.

4.34. 6-[(Thiazolidin-3-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5n)

Thiazolidine (0.28 ml, 3.6 mmol) was added to a solution of mesylate **7** (645 mg, 0.9 mmol) in MeCN (10 ml). After aqueous work-up and chromatography on silica gel (hexanes/AcOEt, 1:1–1:5) 480 mg (75%) of **5n** was isolated as white foam. Exact mass (FAB HR MS) found: 708.2508; calcd for $C_{38}H_{38}N_5O_7S$: 708.2492. FAB MS *m*/*z* (%): 708 (MH^+, 2); 487 (11); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 3.04 (t, 2H, J_{vic} = 6.4, H-5-thiazolidine); 3.21 (t, 2H, J_{vic} = 6.4, H-4-thiazolidine); 4.12 (s, 2H, H-2-thiazolidine); 4.23 (s, 2H, CH_2N); 4.66 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'}$ = 4.1, H-5′b); 4.82 (td, 1H, $J_{4',3'}$ = 4.6, $J_{4',5'}$ = 4.1, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'}$ = 3.1, H-5′a); 6.22 (dd, 1H, $J_{3',2'}$ = 5.8, $J_{3',4'}$ = 4.6, H-3′); 6.40 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.5, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.5, H-1′); 7.16, 7.22 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.91 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.22 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.70 and 21.73 (CH_3-Tol); 29.63 (CH_2-5-thia); 53.48 (CH_2-2-thia); 58.38 (CH_2-4-thia); 61.28 (CH_2N); 63.40 (CH_2-5′); 71.38 (CH-3′); 73.63 (CH-2′); 81.04 (CH-4′); 86.88 (CH-1′); 125.62, 126.01 and 126.57 (C-*i*-Tol); 129.23, 129.27 and 129.34 (CH-*m*-Tol); 129.79 and 129.87 (CH-*o*-Tol); 133.46 (C-5); 143.25 (CH-8); 144.24, 144.59 and 144.72 (C-*p*-Tol); 151.07 (C-4); 152.91 (CH-2); 158.37 (C-6); 165.17, 165.38 and 166.19 (CO). IR (CCl_4): ν = 2949, 2875, 1732, 1612, 1597, 1498, 1409, 1334, 1266, 1179, 1092, 644 cm^{-1}.

4.35. 6-[(Indolin-1-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5o)

Indoline (0.15 ml, 1.26 mmol) was added to a solution of mesylate **7** (300 mg, 0.42 mmol) in MeCN (15 ml). After aqueous work-up and chromatography on silica gel (hexanes/AcOEt, 1:1–1:5) 278 mg (90%) of **5o** was isolated as white foam. Exact mass (FAB HR MS) found: 738.2951; calcd for $C_{43}H_{40}N_5O_7$: 738.2928. FAB MS *m*/*z* (%): 738 (MH^+, 1); 487 (6); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.38, 2.41 and 2.42 (3× s, 3× 3H, CH_3-Tol); 3.00 (t, 2H, J_{vic} = 8.4, H-3-indoline); 3.59 (t, 2H, J_{vic} = 8.4, H-2-indoline); 4.67 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'}$ = 4.2, H-5′b); 4.67 (s, 2H, CH_2N); 4.82 (td, 1H, $J_{4',3'}$ = 4.6, $J_{4',5'}$ = 4.2, 3.1, H-4′); 4.89 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'}$ = 3.1, H-5′a); 6.22 (dd, 1H, $J_{3',2'}$ = 5.8, $J_{3',4'}$ = 4.6, H-3′); 6.40 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.4, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.4, H-1′); 6.65 (td, 1H, $J_{5,4}$ = $J_{5,6}$ = 7.4, $J_{5,7}$ = 1.0, H-5-indoline); 6.71 (bd, 1H, $J_{7,6}$ = 7.8, H-7-indoline); 7.01–7.08 (m, 2H, H-4,6-indoline); 7.16, 7.22 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.90 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.23 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.71 and 21.74 (CH_3-Tol); 28.67 (CH_2-3-indoline); 50.61 (CH_2N); 54.46 (CH_2-2-indoline); 63.43 (CH_2-5′); 71.36 (CH-3′); 73.65 (CH-2′); 80.99 (CH-4′); 86.87 (CH-1′); 107.47 (CH-7-indoline); 117.98 (CH-5-indoline); 124.35 (CH-6-indoline); 125.63, 126.00 and 126.57 (C-*i*-Tol); 127.25 (CH-4-indoline); 129.22, 129.26 and 129.33 (CH-*m*-Tol); 129.79 (C-3a-indoline and CH-*o*-Tol); 129.87 and 129.88 (CH-*o*-Tol); 132.20 (C-5); 143.02 (CH-8); 144.23, 144.58 and 144.70 (C-*p*-Tol); 151.03 (C-4); 151.94 (C-7a-indoline); 152.84 (CH-2); 158.54 (C-6); 165.18, 165.38 and 166.22 (CO).

4.36. 6-[(Indol-1-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5p)

4.36.1. Method A. Indole (88 mg, 0.75 mmol) was added to a suspension of NaH (28 mg, 0.7 mmol, 60% purity) in MeCN (10 ml). After 30 min. solution of mesylate **7** (430 mg, 0.6 mmol) in MeCN (10 ml) was added. After aqueous work-up and chromatography on silica gel (hexanes/AcOEt, 1:1–1:5) 66 mg (15%) of **5p** was isolated as white foam.

4.36.2. Method B. Oxidation of indoline derivative **5o** with DDQ. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (100 mg, 0.44 mmol) was added to a solution of **5o** (245 mg, 0.33 mmol) in toluene (20 ml) and stirred for 3 h at ambient temperature. Unfortunately, monitoring of reaction mixture by TLC is impossible due to the same R_f of starting compound and product. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 1:1–1:5) to give 182 mg (74%) of product **5p** as white foam.

Exact mass (FAB HR MS) found: 736.2750; calcd for $C_{43}H_{38}N_5O_7$: 736.2771. FAB MS *m*/*z* (%): 736 (MH^+, 4); 487 (14); 119 (50). ^{1}H NMR (400 MHz, $CDCl_3$): 2.36 and 2.41 (2× s, 9H, CH_3-Tol); 4.65 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'}$ = 4.1, H-5′b); 4.80 (td, 1H, $J_{4',3'}$ = 4.5, $J_{4',5'}$ = 4.1, 3.1, H-4′); 4.86 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.1, H-5′a); 5.76 (s, 2H, CH_2N); 6.18 (dd, 1H, $J_{3',2'}$ = 5.8, $J_{3',4'}$ = 4.5, H-3′); 6.35 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.5, H-2′); 6.46 (d, 1H, $J_{1',2'}$ = 5.5, H-1′); 6.54 (dd, 1H, $J_{3,2}$ = 3.2, $J_{3,7}$ = 0.9, H-3-indole); 7.05 (ddd, 1H, $J_{5,4}$ = 7.9, $J_{5,6}$ = 7.0, $J_{5,7}$ = 1.1, H-5-indole); 7.16 (m, 2H, H-*m*-Tol); 7.15 (ddd, 1H, $J_{6,7}$ = 7.9, $J_{6,5}$ = 7.0, $J_{6,4}$ = 1.3, H-6-indole); 7.21 and 7.23 (2× m, 2× 2H, H-*m*-Tol); 7.43 (d, 1H, $J_{2,3}$ = 3.2, H-2-indole); 7.56 (dq, 1H, $J_{7,6}$ = 7.9, $J_{7,5}$ = 1.1, $J_{7,3}$ = 0.9, $J_{7,4}$ = 0.6, H-7-indole); 7.58 (dt, 1H, $J_{4,5}$ = 7.9, $J_{4,6}$ = 1.3, $J_{4,7}$ = 0.6, H-4-indole); 7.79, 7.89 and 7.97 (3× m, 3× 2H, H-*o*-Tol); 8.25 (s, 1H, H-8); 8.78 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 and 21.73 (CH_3-Tol); 47.11 (CH_2N); 63.43 (CH_2-5′); 71.37 (CH-3′); 73.67 (CH-2′); 81.08 (CH-4′); 86.85 (CH-1′); 101.94 (CH-3-indole); 109.88 (CH-7-indole); 119.57 (CH-5-indole); 120.85 (CH-4-indole); 121.71 (CH-6-indole); 125.60, 125.99 and 126.55 (C-*i*-Tol); 128.59 (C-3a-indole); 128.94 (CH-2-indole); 129.21, 129.25 and 129.33 (CH-*m*-Tol); 129.77, 129.86 and 129.88 (CH-*o*-Tol); 132.74 (C-5); 136.30 (C-7a-indole); 143.49 (CH-8); 144.22, 144.58 and 144.69 (C-*p*-Tol); 151.35 (C-4); 152.94 (CH-2); 155.98 (C-6); 165.15, 165.36 and 166.18 (CO). IR (CCl_4): ν = 3040, 1732, 1612, 1598, 1498, 1463, 1409, 1334, 1266, 1179, 1091, 643 cm^{-1}.

4.37. 6-[(Pyrazol-1-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5q)

Pyrazole (145 mg, 2.13 mmol) was added to a solution of mesylate **7** (300 mg, 0.42 mmol) in MeCN (15 ml) and stirred for 3 days at 75 °C. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 1:1–1:5) to give 210 mg (73%) of **5q** as white foam. Exact mass (FAB HR MS) found: 687.2535; calcd for $C_{38}H_{35}N_6O_7$: 687.2567. FAB MS *m*/*z* (%): 687 (MH^+, 1); 119 (75). ^{1}H NMR (400 MHz, $CDCl_3$): 2.37 and 2.42 (2× s, 9H, CH_3-Tol); 4.66 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'}$ = 4.1, H-5′b); 4.81 (td, 1H, $J_{4',3'}$ = 4.5, $J_{4',5'}$ = 4.1, 3.1, H-4′); 4.88 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.1, H-5′a); 5.82 (s, 2H, CH_2N); 6.19 (dd, 1H, $J_{3',2'}$ = 5.7, $J_{3',4'}$ = 4.5, H-3′); 6.30 (t, 1H, $J_{4,3}$ = 1.8, $J_{4,5}$ = 2.1, H-4-pyrazole); 6.37 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.6, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.6, H-1′); 7.15, 7.22 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.54 (dd, 1H, $J_{3,4}$ = 1.8, $J_{3,5}$ = 0.4, H-3-pyrazole); 7.66 (dd, 1H, $J_{5,4}$ = 2.1, $J_{5,3}$ = 0.4, H-5-pyrazole); 7.80, 7.90 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.25 (s, 1H, H-8); 8.83 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.71 (CH_3-Tol); 52.45 (CH_2N); 63.44 (CH_2-5′); 71.40 (CH-3′); 73.61 (CH-2′); 81.11 (CH-4′); 86.82 (CH-1′); 106.13 (CH-4-pyrazole); 125.57, 125.97 and 126.53 (C-*i*-Tol); 129.21, 129.26 and 129.34 (CH-*m*-Tol); 129.77, 129.85 and 129.87 (CH-*o*-Tol); 130.45 (CH-5-pyrazole); 132.72 (C-5); 140.07 (CH-3-pyrazole); 143.74 (CH-8); 144.24, 144.59 and 144.70 (C-*p*-Tol); 151.42 (C-4); 152.97 (CH-2); 155.17 (C-6); 165.13, 165.36 and 166.17 (CO). IR (CCl_4): *v* = 3039, 1732, 1612, 1598, 1498, 1409, 1334, 1266, 1179, 1090, 643 cm^{-1}.

4.38. 6-[(4-Oxopyridin-1(4*H*)-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5r) and 6-[(Pyridin-4-yloxy)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (13f)

4.38.1. Method A. Dry THF (10 ml) was added to a mixture of 4-pyridone (43 mg, 0.45 mmol) and NaH (15 mg, 0.36 mmol, 60% purity) under Ar atmosphere and stirred for 45 min. Then a solution of mesylate **7** (215 mg, 0.3 mmol) in THF (5 ml) was added to preformed solution of sodium salt of 4-pyridone. After aqueous work-up (extraction with AcOEt) and chromatography on silica gel (hexanes/AcOEt/MeOH, 10:20:0.3–10:60:4) two compounds were isolated. Less polar was *O*-substituted pyridine derivative **13f**, 8 mg (4%) and more polar was *N*-substituted pyridone **5r**, 188 mg (88%).

4.38.2. Method B. ^{i}Pr$_2$NEt (0.42 ml, 2.4 mmol) was added to a solution of mesylate **7** (575 mg, 0.8 mmol) and 4-pyridone (305 mg, 3.2 mmol) in MeCN (15 ml) and stirred at 50 °C for 12 h. After aqueous work-up (extraction with AcOEt) and chromatography two compounds were isolated: 46 mg (8%) of **13f**, and 400 mg (70%) of **5r**.

For **5r**: White foam. Exact mass (FAB HR MS) found: 714.2577; calcd for $C_{40}H_{36}N_5O_8$: 714.2564. FAB MS *m*/*z* (%): 714 (MH^+, 29); 487 (4); 228 (29); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.38 and 2.43 (2× s, 9H, CH_3-Tol); 4.67 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'}$ = 4.3, H-5′b); 4.84 (td, 1H, $J_{4',3'}$ = 4.7, $J_{4',5'}$ = 4.3, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'}$ = 3.1, H-5′a); 5.35 (s, 2H, CH_2N); 6.18 (dd, 1H, $J_{3',2'}$ = 5.9, $J_{3',4'}$ = 4.7, H-3′); 6.36 (t, 1H, $J_{2',3'}$ = 5.9, $J_{2',1'}$ = 5.3, H-2′); 6.41 (m, 2H, H-3,5-py); 6.47 (d, 1H, $J_{1',2'}$ = 5.3, H-1′); 7.16, 7.23 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.60 (m, 2H, H-2,6-py); 7.79, 7.91 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.29 (s, 1H, H-8); 8.81 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.70, 21.72 and 21.73 (CH_3-Tol); 56.47 (CH_2N); 63.33 (CH_2-5′); 71.30 (CH-3′); 73.69 (CH-2′); 81.13 (CH-4′); 87.23 (CH-1′); 118.82 (CH-3,5-py); 125.47, 125.90 and 126.52 (C-*i*-Tol); 129.27, 129.30 and 129.33 (CH-*m*-Tol); 129.77 and 129.86 (CH-*o*-Tol); 132.63 (C-5); 140.68 (CH-2,6-py); 144.34 (C-*p*-Tol); 144.42 (CH-8); 144.70 and 144.88 (C-*p*-Tol); 151.65 (C-4); 152.97 (CH-2); 153.15 (C-6); 165.22, 165.38 and 166.15 (CO); 178.93 (C-4-py). IR (CCl_4): *v* = 1727, 1640, 1612, 1577, 1499, 1406, 1335, 1267, 1093, 643 cm^{-1}.

For **13f**: white foam. Exact mass (FAB HR MS) found: 714.2581; calcd for $C_{40}H_{36}N_5O_8$: 714.2564. FAB MS *m*/*z* (%): 714 (MH^+, 16); 487 (6); 228 (4); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.38, 2.41 and 2.42 (3× s, 3× 3H, CH_3-Tol); 4.67 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'}$ = 4.2, H-5′b); 4.83 (td, 1H, $J_{4',3'}$ = 4.7, $J_{4',5'}$ = 4.2, 3.1, H-4′); 4.91 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'}$ = 3.1, H-5′a); 5.63 (s, 2H, CH_2O); 6.22 (dd, 1H, $J_{3',2'}$ = 5.9, $J_{3',4'}$ = 4.7, H-3′); 6.39 (t, 1H, $J_{2',3'}$ = 5.9, $J_{2',1'}$ = 5.3, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.3, H-1′); 6.97 (m, 2H, H-3,5-py); 7.16, 7.23 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.91 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.27 (s, 1H, H-8); 8.42 (m, 2H, H-2,6-py); 8.89 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.71 and 21.74 (CH_3-Tol); 63.33 (CH_2-5′); 65.96 (CH_2O); 71.33 (CH-3′); 73.73 (CH-2′); 81.08 (CH-4′); 87.09 (CH-1′); 110.62 (CH-3,5-py); 125.56, 125.96 and 126.55 (C-*i*-Tol); 129.26, 129.29 and 129.34 (CH-*m*-Tol); 129.78 and 129.88 (CH-*o*-Tol); 132.70 (C-5); 143.87 (CH-8); 144.29, 144.65 and 144.80 (C-*p*-Tol); 151.10 (CH-2,6-py); 151.45 (C-4); 152.91 (CH-2); 154.88 (C-6); 164.50 (C-4-py); 165.20, 165.38 and 166.17 (CO). IR (CCl_4): *v* = 1727, 1612, 1594, 1500, 1410, 1335, 1267, 1093, 643 cm^{-1}.

4.39. 6-[(4-Oxopyridin-1(4*H*)-yl)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6r) and 6-[(Pyridin-4-yloxy)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (14f)

Prepared from mesylate **8** by procedures described above (see **5r** and **13f**).

4.39.1. Method A. Compound **6r** (85%) as white crystals (mp 219–220 °C) and 4% of **14f** as white foam.

4.39.2. Method B. Compound **6r** (78%) and 10% of **14f**.

For **6r**: Exact mass (FAB HR MS) found: 580.2209; calcd for $C_{32}H_{30}N_5O_6$: 580.2196. FAB MS *m*/*z* (%):

580 (MH^+, 35); 228 (94); 133 (11); 119 (100); 96 (15). ^1H NMR (500 MHz, $CDCl_3$): 2.42 and 2.45 (2× s, 9H, CH_3-Tol); 2.87 (ddd, 1H, $J_{gem} = 14.2$, $J_{2'b,1'} = 5.9$, $J_{2'b,3'} = 2.2$, H-2′b); 3.21 (ddd, 1H, $J_{gem} = 14.2$, $J_{2'a,1'} = 8.2$, $J_{2'a,3'} = 6.4$, H-2′a); 4.65–4.69 (m, 2H, H-5′b and H-4′); 4.78 (dd, 1H, $J_{gem} = 13.3$, $J_{5'a,4'} = 5.2$, H-5′a); 5.33 (s, 2H, CH_2N); 5.84 (dt, 1H, $J_{3',2'} = 6.4$, 2.2, $J_{3',4'} = 2.3$, H-3′); 6.36 (m, 2H, H-3,5-py); 6.59 (dd, 1H, $J_{1'2'} = 8.2$, 5.9, H-1′); 7.22 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.59 (m, 2H, H-2,6-py); 7.90 and 7.97 (2× m, 2× 2H, H-*o*-Tol); 8.31 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.70 and 21.74 (CH_3-Tol); 37.75 (CH_2-2′); 56.44 (CH_2N); 63.84 (CH_2-5′); 74.88 (CH-3′); 83.28 (CH-4′); 85.20 (CH-1′); 118.90 (CH-3,5-py); 126.24 and 126.56 (C-*i*-Tol); 129.27 and 129.31 (CH-*m*-Tol); 129.62 and 129.80 (CH-*o*-Tol); 132.67 (C-5); 140.49 (CH-2,6-py); 144.03 (CH-8); 144.29 and 144.66 (C-*p*-Tol); 151.47 (C-4); 152.72 (CH-2); 153.08 (C-6); 165.91 and 166.10 (CO); 178.86 (C-4-py). IR ($CHCl_3$): ν = 1721, 1640, 1612, 1602, 1578, 1497, 1406, 1333, 1269, 1179, 1102, 644 cm^{-1}.

For **14f**: Exact mass (FAB HR MS) found: 580.2206; calcd for $C_{32}H_{30}N_5O_6$: 580.2196. FAB MS *m/z* (%): 580 (MH^+, 30); 353 (2); 228 (29); 134 (13); 119 (100); 96 (18). ^1H NMR (500 MHz, $CDCl_3$): 2.41 and 2.45 (2× s, 9H, CH_3-Tol); 2.87 (ddd, 1H, $J_{gem} = 14.2$, $J_{2'b,1'} = 5.9$, $J_{2'b,3'} = 2.3$, H-2′b); 3.21 (ddd, 1H, $J_{gem} = 14.2$, $J_{2'a,1'} = 8.3$, $J_{2'a,3'} = 6.4$, H-2′a); 4.65–4.70 (m, 2H, H-5′b and H-4′); 4.79 (dd, 1H, $J_{gem} = 13.2$, $J_{5'a,4'} = 5.1$, H-5′a); 5.61 and 5.64 (2 ×d, 2H, $J_{gem} = 13.3$, CH_2O); 5.84 (dt, 1H, $J_{3',2'} = 6.4$, 2.3, $J_{3',4'} = 2.2$, H-3′); 6.61 (dd, 1H, $J_{1'2'} = 8.3$, 5.9, H-1′); 6.98 (m, 2H, H-3,5-py); 7.22 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.90 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.30 (s, 1H, H-8); 8.42 (m, 2H, H-2,6-py); 8.94 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.69 and 21.75 (CH_3-Tol); 37.80 (CH_2-2′); 63.87 (CH_2-5′); 65.98 (CH_2O); 74.97 (CH-3′); 83.22 (CH-4′); 85.03 (CH-1′); 110.60 (CH-3,5-py); 126.29 and 126.58 (C-*i*-Tol); 129.28 and 129.31 (CH-*m*-Tol); 129.63 and 129.81 (CH-*o*-Tol); 132.71 (C-5); 143.48 (CH-8); 144.25 and 144.63 (C-*p*-Tol); 151.14 (CH-2,6-py); 151.27 (C-4); 152.66 (CH-2); 154.71 (C-6); 164.45 (C-4-py); 165.93 and 166.12 (CO). IR ($CHCl_3$): ν = 1721, 1612, 1594, 1574, 1500, 1408, 1333, 1269, 1179, 1102, 645 cm^{-1}.

4.40. 6-[(2-Oxopyridin-1(2*H*)-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5s) and 6-[(Pyridin-2-yloxy)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (13g)

4.40.1. Method A. Analogously as in synthesis of the 4-pyridone derivatives **5r** and **13f**. Only *N*-substituted pyridone **5s** was isolated in the yield of 94% as white foam.

4.40.2. Method B. Analogously as in synthesis of the 4-pyridone derivatives **5r** and **13f**. But slightly higher temperature was used (55 °C) and prolongation of reaction time was necessary (48 h). Yields: 47% of *N*-substituted pyridone **5s** as white foam and 17% of *O*-substituted pyridine derivative **13g** as white foam.

For **5s**: Exact mass (FAB HR MS) found: 714.2571; calcd for $C_{40}H_{36}N_5O_8$: 714.2564. FAB MS *m/z* (%): 736 ($M+Na^+$, 18); 487 (8); 228 (4); 119 (100). ^1H NMR (500 MHz, $CDCl_3$): 2.38, 2.415 and 2.419 (3× s, 3× 3H, CH_3-Tol); 4.67 (dd, 1H, $J_{gem} = 12.2$, $J_{5'b,4'} = 4.2$, H-5′b); 4.81 (td, 1H, $J_{4',3'} = 4.4$, $J_{4',5'} = 4.2$, 3.2, H-4′); 4.87 (dd, 1H, $J_{gem} = 12.2$, $J_{5'a,4'} = 3.2$, H-5′a); 5.61 and 5.65 (2× d, 2H, $J_{gem} = 15.8$, CH_2N); 6.18 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.4$, H-3′); 6.21 (td, 1H, $J_{5,6} = 6.8$, $J_{5,4} = 6.6$, $J_{5,3} = 1.4$, H-5-py); 6.37 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.7$, H-2′); 6.49 (d, 1H, $J_{1',2'} = 5.7$, H-1′); 6.60 (ddd, 1H, $J_{3,4} = 9.1$, $J_{3,5} = 1.4$, $J_{3,6} = 0.7$, H-3-py); 7.15, 7.21 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.36 (ddd, 1H, $J_{4,3} = 9.1$, $J_{4,5} = 6.6$, $J_{4,6} = 2.1$, H-4-py); 7.47 (ddd, 1H, $J_{6,5} = 6.8$, $J_{6,4} = 2.1$, $J_{6,3} = 0.7$, H-6-py); 7.81, 7.90 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.23 (s, 1H, H-8); 8.79 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.70 and 21.73 (CH_3-Tol); 49.54 (CH_2N); 63.53 (CH_2-5′); 71.4 (CH-3′); 73.59 (CH-2′); 81.11 (CH-4′); 86.70 (CH-1′); 105.97 (CH-5-py); 121.15 (CH-3-py); 125.59, 125.99 and 126.55 (C-*i*-Tol); 129.20, 129.25 and 129.35 (CH-*m*-Tol); 129.78, 129.86 and 129.89 (CH-*o*-Tol); 132.64 (C-5); 138.58 (CH-6-py); 139.87 (CH-4-py); 143.37 (CH-8); 144.23, 144.57 and 144.67 (C-*p*-Tol); 151.13 (C-4); 152.82 (CH-2); 155.55 (C-6); 162.59 (C-2-py); 165.14, 165.37 and 166.20 (CO). IR (CCl_4): ν = 1731, 1668, 1612, 1596, 1541, 1498, 1410, 1336, 1267, 1179, 1093, 644 cm^{-1}.

For **13g**: Exact mass (FAB HR MS) found: 714.2545; calcd for $C_{40}H_{36}N_5O_8$: 714.2564. FAB MS *m/z* (%): 736 ($M+Na^+$, 4); 714 (MH^+, 1); 487 (9); 228 (2); 119 (100). ^1H NMR (500 MHz, $CDCl_3$): 2.38, 2.41 and 2.42 (3× s, 3× 3H, CH_3-Tol); 4.67 (dd, 1H, $J_{gem} = 12.3$, $J_{5'b,4'} = 4.1$, H-5′b); 4.82 (td, 1H, $J_{4',3'} = 4.6$, $J_{4',5'} = 4.1$, 3.1, H-4′); 4.89 (dd, 1H, $J_{gem} = 12.3$, $J_{5'a,4'} = 3.1$, H-5′a); 5.89 and 5.92 (2× d, 2H, $J_{gem} = 14.9$, CH_2O); 6.22 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.6$, H-3′); 6.39 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.4$, H-2′); 6.49 (d, 1H, $J_{1',2'} = 5.4$, H-1′); 6.86 (ddd, 1H, $J_{5,4} = 7.1$, $J_{5,6} = 5.1$, $J_{5,3} = 1.0$, H-5-py); 6.93 (dt, 1H, $J_{3,4} = 8.4$, $J_{3,5} = 1.0$, $J_{3,6} = 0.9$, H-3-py); 7.16, 7.22 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.59 (ddd, 1H, $J_{4,3} = 8.4$, $J_{4,5} = 7.1$, $J_{4,6} = 2.0$, H-4-py); 7.82, 7.90 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.09 (ddd, 1H, $J_{6,5} = 5.1$, $J_{6,4} = 2.0$, $J_{6,3} = 0.9$, H-6-py); 8.23 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.70 and 21.74 (CH_3-Tol); 63.39 (CH_2-5′); 63.70 (CH_2O); 71.36 (CH-3′); 73.69 (CH-2′); 81.01 (CH-4′); 86.84 (CH-1′); 111.31 (CH-3-py); 117.21 (CH-5-py); 125.63, 126.00 and 126.55 (C-*i*-Tol); 129.22, 129.26 and 129.34 (CH-*m*-Tol); 129.77, 129.87 and 129.88 (CH-*o*-Tol); 132.50 (C-5); 138.65 (CH-4-py); 143.19 (CH-8); 144.23, 144.57 and 144.69 (C-*p*-Tol); 146.73 (CH-6-py); 151.12 (C-4); 152.81 (CH-2); 157.41 (C-6); 162.97 (C-2-py); 165.17, 165.38 and 166.21 (CO). IR (CCl_4): ν = 1732, 1612, 1598, 1572, 1498, 1474, 1433, 1334, 1266, 1179, 1092, 644 cm^{-1}.

4.41. 6-[(2-Oxopyridin-1(2*H*)-yl)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6s) and 6-[(Pyridin-2-yloxy)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (14g)

Prepared from mesylate **8** by procedures described above (see **5s** and **13g**).

4.41.1. Method A. Only *N*-substituted pyridone **6s** was isolated in the yield of 95% as white crystals (mp 164–165 °C).

4.41.2. Method B. Compound **6s** (38%) and 22% of **14g** as white foam.

For **6s**: Exact mass (FAB HR MS) found: 580.2203; calcd for $C_{32}H_{30}N_5O_6$: 580.2196. FAB MS *m/z* (%): 602 ($M+Na^+$, 44); 580 (MH^+, 8); 353 (4); 228 (84); 134 (11); 119 (100); 96 (8). ^{1}H NMR (500 MHz, $CDCl_3$): 2.41 and 2.44 (2× s, 9H, CH_3-Tol); 2.83 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'} = 5.8$, $J_{2'b,3'} = 2.1$, H-2′b); 3.17 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'} = 8.5$, $J_{2'a,3'} = 6.3$, H-2′a); 4.63–4.70 (m, 2H, H-5′b and H-4′); 4.76 (m, 1H, H-5′a); 5.60 and 5.66 (2× d, 2H, J_{gem} = 15.8, CH_2N); 5.82 (dt, 1H, $J_{3',2'} = 6.3$, 2.1, $J_{3',4'} = 2.0$, H-3′); 6.23 (td, 1H, $J_{5,4} = J_{5,6} = 6.7$, $J_{5,3} = 1.4$, H-5-py); 6.59 (dd, 1H, $J_{1',2'} = 8.5$, 5.8, H-1′); 6.60 (ddd, 1H, $J_{3,4} = 9.2$, $J_{3,5} = 1.4$, $J_{3,6} = 0.7$, H-3-py); 7.23 and 7.28 (2× m, 2× 2H, H-*m*-Tol); 7.38 (ddd, 1H, $J_{4,3} = 9.2$, $J_{4,5} = 6.7$, $J_{4,6} = 2.0$, H-4-py); 7.49 (ddd, 1H, $J_{6,5} = 6.7$, $J_{6,4} = 2.0$, $J_{6,3} = 0.7$, H-6-py); 7.92 and 7.97 (2× m, 2× 2H, H-*o*-Tol); 8.25 (s, 1H, H-8); 8.83 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.69 and 21.74 (CH_3-Tol); 37.74 (CH_2-2′); 49.74 (CH_2N); 63.98 (CH_2-5′); 75.07 (CH-3′); 83.14 (CH-4′); 84.91 (CH-1′); 105.97 (CH-5-py); 121.14 (CH-3-py); 126.33 and 126.62 (C-*i*-Tol); 129.29 and 129.30 (CH-*m*-Tol); 129.65 and 129.81 (CH-*o*-Tol); 132.64 (C-5); 138.67 (CH-6-py); 139.93 (CH-4-py); 143.01 (CH-8); 144.21 and 144.57 (C-*p*-Tol); 150.91 (C-4); 152.56 (CH-2); 155.39 (C-6); 162.61 (C-2-py); 165.93 and 166.17 (CO). IR ($CHCl_3$): ν = 1721, 1659, 1612, 1594, 1543, 1496, 1408, 1336, 1269, 1179, 1102, 645 cm^{-1}.

For **14g**: Exact mass (FAB HR MS) found: 580.2209; calcd for $C_{32}H_{30}N_5O_6$: 580.2196. FAB MS *m/z* (%): 602 ($M+Na^+$, 10); 580 (MH^+, 1); 228 (19); 119 (38); 95 (20). ^{1}H NMR (400 MHz, $CDCl_3$): 2.40 and 2.45 (2× s, 9 H, CH_3-Tol); 2.85 (ddd, 1H, J_{gem} = 14.1, $J_{2'b,1'} = 5.8$, $J_{2'b,3'} = 2.2$, H-2′b); 3.20 (ddd, 1H, J_{gem} = 14.1, $J_{2'a,1'} = 8.4$, $J_{2'a,3'} = 6.4$, H-2′a); 4.64–4.70 (m, 2H, H-5′b and H-4′); 4.78 (m, 1H, H-5′a); 5.84 (dt, 1H, $J_{3',2'} = 6.4$, 2.2, $J_{3',4'} = 2.0$, H-3′); 5.89 and 5.93 (2 × d, 2H, J_{gem} = 15.3, CH_2O); 6.61 (dd, 1H, $J_{1',2'} = 8.4$, 5.8, H-1′); 6.87 (ddd, 1H, $J_{5,4} = 7.1$, $J_{5,6} = 5.1$, $J_{5,3} = 1.0$, H-5-py); 6.94 (dt, 1H, $J_{3,4} = 8.4$, $J_{3,5} = 1.0$, $J_{3,6} = 0.9$, H-3-py); 7.22 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.60 (ddd, 1H, $J_{4,3} = 8.4$, $J_{4,5} = 7.1$, $J_{4,6} = 2.0$, H-4-py); 7.90 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.09 (ddd, 1H, $J_{6,5} = 5.1$, $J_{6,4} = 2.0$, $J_{6,3} = 0.9$, H-6-py); 8.25 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.68 and 21.74 (CH_3-Tol); 37.80 (CH_2-2′); 63.72 (CH_2O); 63.93 (CH_2-5′); 75.06 (CH-3′); 83.12 (CH-4′); 84.88 (CH-1′); 111.32 (CH-3-py); 117.22 (CH-5-py); 126.36 and 126.63 (C-*i*-Tol); 129.28 and 129.29 (CH-*m*-Tol); 129.64 and 129.82 (CH-*o*-Tol); 132.51 (C-5); 138.67 (CH-4-py); 142.78 (CH-8); 144.19 and 144.57 (C-*p*-Tol); 146.71 (CH-6-py); 150.95 (C-4); 152.56 (CH-2); 157.25 (C-6); 163.01 (C-2-py); 165.94 and 166.15 (CO). IR ($CHCl_3$): ν = 1721, 1612, 1599, 1573, 1496, 1474, 1434, 1408, 1334, 1269, 1179, 1102, 645 cm^{-1}.

4.42. 6-[(2-Oxopyrrolidin-1-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5t)

2-Pyrrolidinone (90 μl, 1.2 mmol) was added to a suspension of NaH (39 mg, 0.96 mmol, 60% purity) in dry THF (10 ml) under Ar atmosphere and stirred for 45 min. Then a solution of mesylate **7** (575 mg, 0.8 mmol) in THF (5 ml) was added to the preformed solution of sodium salt of 2-pyrrolidinone. Reaction was quenched with 1 M aq NaH_2PO_4 (40 ml) and the mixture extracted with AcOEt (4× 30 ml). Collected organic layers were dried with $MgSO_4$, the solvent was evaporated and the residue chromatographed on silica gel (hexanes/AcOEt, 1:1–1:5) to give 285 mg (51%) of **5t** as white foam. Exact mass (FAB HR MS) found: 704.2735; calcd for $C_{39}H_{38}N_5O_8$: 704.2720. FAB MS *m/z* (%): 726 ($M+Na^+$, 7); 487 (6); 134 (7); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.08 (m, 2H, H-4-pyrr); 2.38, 2.42 and 2.43 (3× s, 3× 3H, CH_3-Tol); 2.50 (t, 2H, J_{vic} = 8.1, H-3-pyrr); 3.47 (t, 2H, J_{vic} = 7.1, H-5-pyrr); 4.67 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'} = 4.3$, H-5′b); 4.82 (td, 1H, $J_{4',3'} = 4.6$, $J_{4',5'} = 4.3$, 3.2, H-4′); 4.89 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'} = 3.2$, H-5′a); 4.99 (s, 2H, CH_2N); 6.20 (dd, 1H, $J_{3',2'} = 5.8$, $J_{3',4'} = 4.6$, H-3′); 6.38 (t, 1H, $J_{2',3'} = 5.8$, $J_{2',1'} = 5.5$, H-2′); 6.47 (d, 1H, $J_{1',2'} = 5.5$, H-1′); 7.16, 7.22 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.90 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.21 (s, 1H, H-8); 8.81 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 17.91 (CH_2-4-pyrr); 21.69 and 21.72 (CH_3-Tol); 30.52 (CH_2-3-pyrr); 44.08 (CH_2N); 47.71 (CH_2-5-pyrr); 63.43 (CH_2-5′); 71.35 (CH-3′); 73.58 (CH-2′); 80.98 (CH-4′); 86.81 (CH-1′); 125.58, 125.96 and 126.54 (C-*i*-Tol); 129.21, 129.24 and 129.32 (CH-*m*-Tol); 129.77, 129.84 and 129.86 (CH-*o*-Tol); 132.75 (C-5); 143.22 (CH-8); 144.24, 144.58 and 144.70 (C-*p*-Tol); 151.05 (C-4); 152.70 (CH-2); 156.76 (C-6); 165.15, 165.37 and 166.19 (CO); 175.88 (C-2-pyrr). IR (CCl_4): ν = 1700, 1612, 1595, 1493, 1334, 1267, 1179, 1093, 645 cm^{-1}.

4.43. 6-[(2-Oxopyrrolidin-1-yl)methyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (6t)

Prepared from mesylate **8** by procedure described above (see **5t**). Yield: 72% of **6t** as white foam. Exact mass (FAB HR MS) found: 570.2354; calcd for $C_{31}H_{32}N_5O_6$: 570.2353. FAB MS *m/z* (%): 592 ($M+Na^+$, 33); 570 (MH^+, 8); 353 (3); 218 (80); 134 (10); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.09 (m, 2H, H-4-pyrr); 2.42 and 2.45 (2× s, 2× 3H, CH_3-Tol); 2.51 (t, 2H, J_{vic} = 7.8, H-3-pyrr); 2.84 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'} = 5.8$, $J_{2'b,3'} = 2.1$, H-2′b); 3.18 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'} = 8.4$, $J_{2'a,3'} = 6.4$, H-

2′a); 3.50 (t, 2H, J_{vic} = 6.9, H-5-pyrr); 4.63–4.69 (m, 2H, H-5′b and H-4′); 4.77 (m, 1H, H-5′a); 5.00 (s, 2H, CH_2N); 5.83 (dt, 1H, $J_{3',2'}$ = 6.4, 2.1, $J_{3',4'}$ = 2.1, H-3′); 6.59 (dd, 1H, $J_{1'2'}$ = 8.4, 5.8, H-1′); 7.23 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.91 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.22 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 19.97 (CH_2-4-pyrr); 21.68 and 21.73 (CH_3-Tol); 30.55 (CH_2-3-pyrr); 37.72 (CH_2-2′); 44.11 (CH_2N); 47.82 (CH_2-5-pyrr); 63.95 (CH_2-5′); 75.03 (CH-3′); 83.10 (CH-4′); 84.85 (CH-1′); 126.34 and 126.63 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.64 and 129.81 (CH-*o*-Tol); 132.75 (C-5); 142.78 (CH-8); 144.22 and 144.57 (C-*p*-Tol); 150.87 (C-4); 152.47 (CH-2); 156.67 (C-6); 165.94 and 166.16 (CO); 175.91 (C-2-pyrr). IR (CCl_4): ν = 1699, 1613, 1595, 1493, 1439, 1423, 1408, 1332, 1268, 1178, 1101, 646 cm^{-1}.

4.44. 6-[(2-Methoxycarbonylpyrrolidin-1-yl)methyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5u)

Mixture of mesylate **7** (205 mg, 0.29 mmol), L-proline methyl ester hydrochloride (93 mg, 0.56 mmol) and ^{i}Pr$_2$-NEt (0.1 ml, 0.56 mmol) in MeCN (15 ml) was stirred at 50 °C for 12 h. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 1:1–0:1) to give 205 mg (96%) of product **5u** as oil. Exact mass (FAB HR MS) found: 748.3003; calcd for $C_{41}H_{42}N_5O_9$: 748.2983. FAB MS *m*/*z* (%): 770 (M+Na$^+$, 100); 748 (MH$^+$, 8); 487 (7); 119 (85). ^{1}H NMR (400 MHz, $CDCl_3$): 1.76–1.83 (m, 1H, H-4b-Pro); 1.88–2.03 (m, 2H, H-3b-Pro and H-4a-Pro); 2.12–2.17 (m, 1H, H-3a-Pro); 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 2.68 (m, 1H, H-5b-Pro); 3.22 (m, 1H, H-5a-Pro); 3.58 (m, 1H, H-2-Pro); 3.65 (s, 3H, CH_3O); 4.29 and 4.46 (2× d, 2H, J_{gem} = 14.0, CH_2-pur); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'}$ = 4.1, H-5′b); 4.81 (td, 1H, $J_{4',3'}$ = 4.7, $J_{4',5'}$ = 4.1, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.1, H-5′a); 6.22 (dd, 1H, $J_{3',2'}$ = 5.7, $J_{3',4'}$ = 4.7, H-3′); 6.39 (t, 1H, $J_{2',3'}$ = 5.7, $J_{2',1'}$ = 5.5, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.5, H-1′); 7.16, 7.22 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.90 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.19 (s, 1H, H-8); 8.84 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 and 21.72 (CH_3-Tol); 23.16 (CH_2-4-Pro); 29.31 (CH_2-3-Pro); 53.58 (CH_2-pur and CH_2-5-Pro); 59.12 (CH_3O); 63.44 (CH_2-5′); 64.87 (CH-2-Pro); 71.38 (CH-3′); 73.60 (CH-2′); 80.97 (CH-4′); 86.81 (CH-1′); 125.62, 126.00 and 126.58 (C-*i*-Tol); 129.20, 129.24 and 129.32 (CH-*m*-Tol); 129.78, 129.85 (CH-*o*-Tol); 133.44 (C-5); 142.98 (CH-8); 144.19, 144.55 and 144.67 (C-*p*-Tol); 150.91 (C-4); 152.71 (CH-2); 156.01 (C-6); 165.13, 165.36 and 166.18 (CO-Tol); 170.62 (*C*OOMe). IR (CCl_4): ν = 1733, 1612, 1594, 1435, 1409, 1333, 1266, 1179, 1092, 645 cm^{-1}.

4.45. 6-(Azidomethyl)-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (5v)

Sodium azide (50 mg, 0.77 mmol) was added to a solution of mesylate **7** (360 mg, 0.5 mmol) in DMF (10 ml) and stirred at ambient temperature for 6 h. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 1:1–1:4) to give 314 mg (95%) of product **5v** as oil. Exact mass (FAB HR MS) found: 662.2383; calcd for $C_{35}H_{32}N_7O_7$: 662.2363. FAB MS *m*/*z* (%): 662 (MH$^+$, 0.5); 487 (3); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'\ b,4'}$ = 4.1, H-5′b); 4.83 (m, 1H, H-4′); 4.84 (s, 2H, CH_2N_3); 4.91 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.1, H-5′a); 6.21 (dd, 1H, $J_{3',2'}$ = 5.7, $J_{3',4'}$ = 4.7, H-3′); 6.39 (t, 1H, $J_{2',3'}$ = 5.7, $J_{2',1'}$ = 5.4, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.4, H-1′); 7.16, 7.23 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.91 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.25 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.71 and 21.75 (CH_3-Tol); 50.55 (CH_2N); 63.33 (CH_2-5′); 71.35 (CH-3′); 73.70 (CH-2′); 81.09 (CH-4′); 87.00 (CH-1′); 125.56, 125.97 and 126.52 (C-*i*-Tol); 129.23, 129.27 and 129.34 (CH-*m*-Tol); 129.75 and 129.87 (CH-*o*-Tol); 132.54 (C-5); 143.61 (CH-8); 144.28, 144.62 and 144.75 (C-*p*-Tol); 151.26 (C-4); 152.82 (CH-2); 155.50 (C-6); 165.16, 165.37 and 166.16 (CO). IR (CCl_4): ν = 2102, 1732, 1612, 1599, 1498, 1409, 1334, 1266, 1179, 1091, 643 cm^{-1}.

4.46. 6-(Phenyloxymethyl)-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (13b)

Phenol (85 mg, 0.9 mmol) was added to a suspension of NaH (30 mg, 0.75 mmol, 60% purity) in dry THF (10 ml) under Ar atmosphere and stirred for 30 min. Then a solution of mesylate **7** (430 mg, 0.6 mmol) in THF (5 ml) was added to the preformed solution of sodium phenoxide. Reaction was quenched with 1 M aq NaH_2PO_4 (40 ml) and the mixture extracted with $CHCl_3$ (4× 40 ml). Collected organic layers were dried with $MgSO_4$, the solvent was evaporated and the residue chromatographed on silica gel (hexanes/AcOEt, 2:1–1:2) to give 380 mg (89%) of **13b** as oil. Exact mass (FAB HR MS) found: 713.2583; calcd for $C_{41}H_{37}N_4O_8$: 713.2611. FAB MS *m*/*z* (%): 713 (MH$^+$, 3); 487 (8); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.38, 2.41 and 2.42 (3× s, 9H, CH_3-Tol); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'}$ = 4.1, H-5′b); 4.82 (td, 1H, $J_{4',3'}$ = 4.7, $J_{4',5'}$ = 4.1, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.1, H-5′a); 5.59 (s, 2H, CH_2O); 6.22 (dd, 1H, $J_{3',2'}$ = 5.7, $J_{3',4'}$ = 4.7, H-3′); 6.39 (t, 1H, $J_{2',3'}$ = 5.7, $J_{2',1'}$ = 5.4, H-2′); 6.49 (d, 1H, $J_{1',2'}$ = 5.4, H-1′); 6.95 (m, 1H, H-*p*-Ph); 7.06 (m, 1H, H-*o*-Ph); 7.16 (m, 2H, H-*m*-Tol); 7.22 and 7.25 (m, 2H, H-*m*-Tol); 7.27 (m, 1H, H-*m*-Ph); 7.81, 7.91 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.25 (s, 1H, H-8); 8.90 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.71 and 21.74 (CH_3-Tol); 63.36 (CH_2-5′); 66.37 (CH_2N); 71.37 (CH-3′); 73.72 (CH-2′); 81.08 (CH-4′); 86.94 (CH-1′); 114.95 (CH-*o*-Ph); 121.32 (CH-*p*-Ph); 125.61, 126.00 and 126.55 (C-*i*-Tol); 129.23, 129.27 and 129.34 (CH-*m*-Tol); 129.45 (H-*m*-Ph); 129.77, 129.87 and 129.88 (CH-*o*-Tol); 132.65 (C-5); 143.50 (CH-8); 144.25, 144.59 and 144.72 (C-*p*-Tol); 151.31 (C-4); 152.93 (CH-2); 156.43 (C-6); 158.44 (C-*i*-Ph); 165.17, 165.37 and 166.18 (CO). IR (CCl_4): ν = 1732, 1612, 1600, 1589, 1495, 1409, 1334, 1266, 1179, 1092, 643 cm^{-1}.

4.47. 6-(Phenyloxymethyl)-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (14b)

Prepared analogously as **13b**. Yield: 95% as oil. Exact mass (FAB HR MS) found: 579.2245; calcd for $C_{33}H_{31}N_4O_6$: 579.2244. FAB MS *m*/*z* (%): 579 (MH^+, 12); 227 (60); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.40 and 2.45 (2× s, 6H, CH_3-Tol); 2.86 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'}$ = 5.8, $J_{2'b,3'}$ = 2.0, H-2′b); 3.20 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'}$ = 8.2, $J_{2'a,3'}$ = 6.4, H-2′a); 4.65–4.69 (m, 2H, H-5′b and H-4′); 4.79 (dd, 1H, J_{gem} = 13.3, $J_{5'a,4'}$ = 5.1, H-5′a); 5.59 (s, 2H, CH_2O); 5.84 (dt, 1H, $J_{3',2'}$ = 6.4, 2.0, $J_{3',4'}$ = 2.2, H-3′); 6.61 (dd, 1H, $J_{1'2'}$ = 8.2, 5.8, H-1′); 6.96 (m, 1H, H-*p*-Ph); 7.08 (m, 1H, H-*o*-Ph); 7.22 (m, 2H, H-*m*-Tol); 7.27 (m, 1H, H-*m*-Ph); 7.29 (m, 2H, H-*m*-Tol); 7.90 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.28 (s, 1H, H-8); 8.95 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.69 and 21.75 (CH_3-Tol); 37.83 (CH_2-2′); 63.90 (CH_2-5′); 66.39 (CH_2O); 75.04 (CH-3′); 83.19 (CH-4′); 84.97 (CH-1′); 114.94 (CH-*o*-Ph); 121.32 (CH-*p*-Ph); 126.35 and 126.62 (C-*i*-Tol); 129.29 and 129.30 (CH-*m*-Tol); 129.45 (H-*m*-Ph); 129.63 and 129.82 (CH-*o*-Tol); 132.69 (C-5); 143.11 (CH-8); 144.21 and 144.59 (C-*p*-Tol); 151.14 (C-4); 152.68 (CH-2); 156.25 (C-6); 158.44 (C-*i*-Ph); 165.93 and 166.13 (CO). IR (CCl_4): *ν* = 1727, 1613, 1600, 1588, 1495, 1408, 1331, 1267, 1178, 1100, 645 cm^{-1}.

4.48. 6-(Methylsulfanylmethyl)-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (17a)

MeSNa (36 mg, 0.46 mmol, 90% purity) was added to a solution of mesylate **7** (300 mg, 0.42 mmol) in dry 1,2-dimethoxyethane (15 ml) and stirred for 2 h. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 1:1–1:4) to give 270 mg (96%) of **17a** as oil. Exact mass (FAB HR MS) found: 667.2233; calcd for $C_{36}H_{35}N_4O_7S$: 667.2226. FAB MS *m*/*z* (%): 667 (MH^+, 6); 487 (12); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.15 (s, 3H, CH_3S); 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 4.12 (s, 2H, CH_2S); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'}$ = 4.1, H-5′b); 4.82 (td, 1H, $J_{4',3'}$ = 4.5, $J_{4',5'}$ = 4.1, 3.0, H-4′); 4.90 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.0, H-5′a); 6.23 (t, 1H, $J_{3',2'}$ = 5.5, $J_{3',4'}$ = 4.5, H-3′); 6.40 (t, 1H, $J_{2',3'}$ = 5.5, $J_{2',1'}$ = 5.5, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.5, H-1′); 7.16, 7.22 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.90 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.21 (s, 1H, H-8); 8.81 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 15.91 (CH_3S); 21.73 (CH_3-Tol); 34.50 (CH_2S); 63.41 (CH_2-5′); 71.37 (CH-3′); 73.69 (CH-2′); 81.02 (CH-4′); 86.95 (CH-1′); 125.62, 126.00 and 126.56 (C-*i*-Tol); 129.23, 129.36 and 129.44 (CH-*m*-Tol); 129.81, 129.91 and 129.94 (CH-*o*-Tol); 132.80 (C-5); 142.91 (CH-8); 144.23, 144.58 and 144.70 (C-*p*-Tol); 151.01 (C-4); 152.60 (CH-2); 159.27 (C-6); 165.17, 165.38 and 166.19 (CO). IR (CCl_4): *ν* = 1733, 1612, 1594, 1497, 1408, 1333, 1266, 1179, 1092, 644 cm^{-1}.

4.49. 6-(Methylsulfanylmethyl)-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (18a)

Prepared analogously as **17a**. Yield: 96% as oil. Exact mass (FAB HR MS) found: 533.1870; calcd for $C_{28}H_{29}N_4O_5S$: 533.1859. FAB MS *m*/*z* (%): 533 (MH^+, 11); 181 (62); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.17 (s, 3H, CH_3S); 2.41 and 2.45 (2× s, 6H, CH_3-Tol); 2.85 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'}$ = 5.8, $J_{2'b,3'}$ = 2.1, H-2′b); 3.20 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'}$ = 8.4, $J_{2'a,3'}$ = 6.4, H-2′a); 4.13 (s, 2H, CH_2S); 4.66–4.69 (m, 2H, H-5′b and H-4′); 4.78 (dd, 1H, J_{gem} = 13.3, $J_{5'a,4'}$ = 5.3, H-5′a); 5.84 (dt, 1H, $J_{3',2'}$ = 6.4, 2.1, $J_{3',4'}$ = 2.1, H-3′); 6.60 (dd, 1H, $J_{1'2'}$ = 8.4, 5.8, H-1′); 7.23 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.91 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.230 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 15.96 (CH_3S); 21.69 and 21.75 (CH_3-Tol); 34.52 (CH_2S); 37.79 (CH_2-2′); 63.94 (CH_2-5′); 75.05 (CH-3′); 83.12 (CH-4′); 84.89 (CH-1′); 126.34 and 126.62 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.63 and 129.81 (CH-*o*-Tol); 132.78 (C-5); 142.56 (CH-8); 144.19 and 144.57 (C-*p*-Tol); 150.83 (C-4); 152.50 (CH-2); 159.13 (C-6); 165.93 and 166.14 (CO). IR (CCl_4): *ν* = 1727, 1613, 1594, 1494, 1438, 1407, 1331, 1267, 1178, 1100, 645 cm^{-1}.

4.50. 6-(Phenylsulfanylmethyl)-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (17b)

PhSNa (150 mg, 1.02 mmol, 90% purity) was added to a solution of mesylate **7** (500 mg, 0.70 mmol) in dry MeCN (15 ml) and stirred for 4 h. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 2:1–1:2) to give 390 mg (76%) of **17 b** as oil. Exact mass (FAB HR MS) found: 729.2392; calcd for $C_{41}H_{37}N_4O_7S$: 729.2383. FAB MS *m*/*z* (%): 729 (MH^+, 3); 487 (18); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 4.58 and 4.61 (2× d, 2H, J_{gem} = 13.5, CH_2S); 4.66 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'}$ = 4.2, H-5′b); 4.81 (ddd, 1H, $J_{4',3'}$ = 4.7, $J_{4',5'}$ = 4.2, 3.1, H-4′); 4.89 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'}$ = 3.1, H-5′a); 6.21 (dd, 1H, $J_{3',2'}$ = 5.8, $J_{3',4'}$ = 4.7, H-3′); 6.36 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.5, H-2′); 6.46 (d, 1H, $J_{1',2'}$ = 5.5, H-1′); 7.13 (m, 1H, H-*p*-Ph); 7.16 (m, 2H, H-*m*-Tol); 7.20 (m, 2H, H-*m*-Ph); 7.22 and 7.25 (2× m, 2× 2H, H-*m*-Tol); 7.39 (m, 2H, H-*o*-Ph); 7.81, 7.90 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.18 (s, 1H, H-8); 8.80 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 21.71 and 21.74 (CH_3-Tol); 35.40 (CH_2S); 63.39 (CH_2-5′); 71.35 (CH-3′); 73.67 (CH-2′); 81.02 (CH-4′); 86.85 (CH-1′); 125.60, 125.98 and 126.54 (C-*i*-Tol); 126.65 (CH-*p*-Ph); 128.83 (CH-*m*-Ph); 129.23, 129.26 and 129.35 (CH-*m*-Tol); 129.77, 129.86 and 129.88 (CH-*o*-Tol); 130.13 (CH-*o*-Ph); 132.94 (C-5); 135.09 (C-*i*-Ph); 143.02 (CH-8); 144.25, 144.59 and 144.71 (C-*p*-Tol); 150.96 (C-4); 152.76 (CH-2); 158.16 (C-6); 165.15, 165.38 and 166.19 (CO). IR (CCl_4): *ν* = 3064, 1732, 1612, 1595, 1497, 1409, 1333, 1266, 1179, 1092, 644 cm^{-1}.

4.51. 6-(Phenylsulfanylmethyl)-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (18b)

Prepared analogously as **17b**. Yield: 90% as oil. Exact mass (FAB HR MS) found: 595.2004; calcd for $C_{33}H_{31}N_4O_5S$: 595.2015. FAB MS *m*/*z* (%): 595 (MH^+, 13); 243 (64); 119 (95). ^{1}H NMR (400 MHz, $CDCl_3$): 2.41 and 2.45 (2× s, 6H, CH_3-Tol); 2.84 (ddd, 1H,

J_{gem} = 14.2, $J_{2'b,1'}$ = 5.8, $J_{2'b,3'}$ = 2.0, H-2′b); 3.18 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'}$ = 8.3, $J_{2'a,3'}$ = 6.4, H-2′a); 4.59 and 4.63 (2× d, 2H, J_{gem} = 13.6, CH_2S); 4.65–4.69 (m, 2H, H-5′b and H-4′); 4.77 (dd, 1H, J_{gem} = 13.4, $J_{5'a,4'}$ = 5.4, H-5′a); 5.83 (dt, 1H, $J_{3',2'}$ = 6.3, 2.1, $J_{3',4'}$ = 2.1, H-3′); 6.58 (dd, 1H, $J_{1'2'}$ = 8.3, 5.8, H-1′); 7.15 (m, 1H, H-*p*-Ph); 7.22 (m, 2H, H-*m*-Ph); 7.22 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.42 (m, 2H, H-*o*-Ph); 7.90 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.21 (s, 1H, H-8); 8.84 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.70 and 21.75 (CH_3-Tol); 35.32 (CH_2S); 37.78 (CH_2-2′); 63.92 (CH_2-5′); 75.04 (CH-3′); 83.13 (CH-4′); 84.91 (CH-1′); 126.33 and 126.61 (C-*i*-Tol); 126.57 (CH-*p*-Ph); 128.84 (CH-*m*-Ph); 129.29 (CH-*m*-Tol); 129.63 and 129.81 (CH-*o*-Tol); 129.92 (CH-*o*-Ph); 132.92 (C-5); 135.30 (C-*i*-Ph); 142.63 (CH-8); 144.21 and 144.58 (C-*p*-Tol); 150.79 (C-4); 152.51 (CH-2); 158.01 (C-6); 165.93 and 166.14 (CO). IR (CCl_4): ν = 3064, 1727, 1613, 1594, 1585, 1494, 1440, 1407, 1331, 1267, 1178, 1100, 645 cm^{-1}.

4.52. 6-(Benzylsulfanylmethyl)-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (17c)

Benzyl mercaptan (50 μl, 0.42 mmol) was added to a solution of mesylate **7** (200 mg, 0.28 mmol) and $^{i}Pr_2EtN$ (50 μl, 0.29 mmol) in dry MeCN (10 ml) and stirred for 8 h. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 2:1–1:2) to give 203 mg (98%) of **17c** as oil. Exact mass (FAB HR MS) found: 743.2565; calcd for $C_{42}H_{39}N_4O_7S$: 743.2539. FAB MS *m*/*z* (%): 743 (MH^+, 3); 487 (6); 257 (3); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.38, 2.41 and 2.42 (3× s, 3× 3H, CH_3-Tol); 3.81 (s, 2H, CH_2Ph); 4.08 (s, 2H, CH_2-pur); 4.67 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'}$ = 4.2, H-5′b); 4.83 (td, 1H, $J_{4',3'}$ = 4.7, $J_{4',5'}$ = 4.2, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'}$ = 3.1, H-5′a); 6.22 (dd, 1H, $J_{3',2'}$ = 5.8, $J_{3',4'}$ = 4.7, H-3′); 6.38 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.4, H-2′); 6.47 (d, 1H, $J_{1',2'}$ = 5.4, H-1′); 7.17 (m, 2H, H-*m*-Tol); 7.18 (m, 1H, H-*p*-Ph); 7.22 (m, 2H, H-*m*-Tol); 7.24 (m, 2H, H-*m*-Ph); 7.25 (m, 2H, H-*m*-Tol); 7.36 (m, 2H, H-*o*-Ph); 7.83, 7.91 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.20 (s, 1H, H-8); 8.81 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 21.70 and 21.73 (CH_3-Tol); 31.92 (CH_2-pur); 36.43 (CH_2-Ph); 63.42 (CH_2-5′); 71.36 (CH-3′); 73.69 (CH-2′); 80.99 (CH-4′); 86.85 (CH-1′); 125.62, 125.99 and 126.55 (C-*i*-Tol); 126.97 (CH-*p*-Ph); 128.30 (CH-*m*-Ph); 129.11 (CH-*o*-Ph); 129.22, 129.25 and 129.33 (CH-*m*-Tol); 129.77, 129.86 and 129.88 (CH-*o*-Tol); 132.69 (C-5); 137.83 (C-*i*-Ph); 142.82 (CH-8); 144.24, 144.57 and 144.70 (C-*p*-Tol); 150.93 (C-4); 152.68 (CH-2); 159.47 (C-6); 165.16, 165.37 and 166.19 (CO). IR (CCl_4): ν = 3034, 1733, 1612, 1593, 1495, 1454, 1409, 1333, 1266, 1179, 1092, 643 cm^{-1}.

4.53. 6-(Benzylsulfanylmethyl)-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (18c)

Prepared analogously as **17c**. Yield: 98% as oil. Exact mass (FAB HR MS) found: 609.2148; calcd for $C_{34}H_{33}N_4O_5S$: 609.2172. FAB MS *m*/*z* (%): 609 (MH^+, 1); 257 (12); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.40 and 2.45 (2× s, 6H, CH_3-Tol); 2.85 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'}$ = 5.8, $J_{2'b,3'}$ = 2.1, H-2′b); 3.18 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'}$ = 8.3, $J_{2'a,3'}$ = 6.4, H-2′a); 3.83 (s, 2H, CH_2Ph); 4.08 (s, 2H, CH_2-pur); 4.66–4.70 (m, 2H, H-5′b and H-4′); 4.79 (dd, 1H, J_{gem} = 13.6, $J_{5'a,4'}$ = 5.5, H-5′a); 5.84 (dt, 1H, $J_{3',2'}$ = 6.4, 2.1, $J_{3',4'}$ = 2.1, H-3′); 6.59 (dd, 1H, $J_{1'2'}$ = 8.3, 5.8, H-1′); 7.20 (m, 1H, H-*p*-Ph); 7.22 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.25 (m, 2H, H-*m*-Ph); 7.38 (m, 2H, H-*o*-Ph); 7.91 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.22 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.68 and 21.75 (CH_3-Tol); 31.92 (CH_2-pur); 36.47 (CH_2-Ph); 37.83 (CH_2-2′); 63.95 (CH_2-5′); 75.06 (CH-3′); 83.12 (CH-4′); 84.88 (CH-1′); 126.37 and 126.64 (C-*i*-Tol); 126.99 (CH-*p*-Ph); 128.33 (CH-*m*-Ph); 129.13 (CH-*o*-Ph); 129.30 (CH-*m*-Tol); 129.64 and 129.82 (CH-*o*-Tol); 132.70 (C-5); 137.88 (C-*i*-Ph); 142.40 (CH-8); 144.20 and 144.57 (C-*p*-Tol); 150.77 (C-4); 152.46 (CH-2); 159.37 (C-6); 165.93 and 166.15 (CO). IR (CCl_4): ν = 3033, 1727, 1613, 1593, 1495, 1454, 1407, 1331, 1267, 1178, 1101, 645 cm^{-1}.

4.54. 6-[(Methoxycarbonylmethyl)sulfanylmethyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (17d)

Methyl thioglycolate (0.19 ml, 2.13 mmol) was added to a solution of mesylate **7** (500 mg, 0.70 mmol) and $^{i}Pr_2EtN$ (0.19 ml, 1.09 mmol) in dry MeCN (15 ml) and stirred for 8 h. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 2:1–1:2) to give 502 mg (99%) of **17d** as oil. Exact mass (FAB HR MS) found: 725.2266; calcd for $C_{38}H_{37}N_4O_9S$: 725.2281. FAB MS *m*/*z* (%): 725 (MH^+, 4); 487 (10); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 3.42 (s, 2H, SCH_2CO); 3.69 (s, 3H, CH_3O); 4.29 (s, 2H, CH_2-pur); 4.67 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'}$ = 4.2, H-5′b); 4.82 (td, 1H, $J_{4',3'}$ = 4.6, $J_{4',5'}$ = 4.2, 3.2, H-4′); 4.90 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'}$ = 3.2, H-5′a); 6.21 (dd, 1H, $J_{3',2'}$ = 5.8, $J_{3',4'}$ = 4.6, H-3′); 6.39 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.5, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.5, H-1′); 7.17, 7.22 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.91 and 8.00 (3× m, 3× 2H, H-*o*-Tol); 8.21 (s, 1H, H-8); 8.80 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 21.71 and 21.74 (CH_3-Tol); 32.65 (CH_2-pur); 33.43 (SCH_2CO); 52.43 (CH_3O); 63.43 (CH_2-5′); 71.37 (CH-3′); 73.63 (CH-2′); 81.04 (CH-4′); 86.88 (CH-1′); 125.60, 125.998 and 126.55 (C-*i*-Tol); 129.23, 129.26 and 129.34 (CH-*m*-Tol); 129.78, 129.86 and 129.88 (CH-*o*-Tol); 132.73 (C-5); 143.11 (CH-8); 144.25, 144.59 and 144.72 (C-*p*-Tol); 151.06 (C-4); 152.73 (CH-2); 158.59 (C-6); 165.16, 165.38 and 166.19 (CO-Tol); 170.51 (COOMe). IR (CCl_4): ν = 3038, 1733, 1612, 1595, 1497, 1454, 1409, 1333, 1266, 1179, 1092, 644 cm^{-1}.

4.55. 6-[(Methoxycarbonylmethyl)sulfanylmethyl]-9-(2-deoxy-3,5-di- *O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (18d)

Prepared analogously as **17d**. Yield: 99% as oil. Exact mass (FAB HR MS) found: 591.1926; calcd for

$C_{30}H_{31}N_4O_7S$: 591.1913. FAB MS *m/z* (%): 591 (MH^+, 8); 239 (40); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.41 and 2.45 (2× s, 6H, CH_3-Tol); 2.85 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'}$ = 5.8, $J_{2'b,3'}$ = 2.1, H-2′b); 3.20 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'}$ = 8.4, $J_{2'a,3'}$ = 6.4, H-2′a); 3.44 (s, 2H, SCH_2CO); 3.72 (s, 3H, CH_3O); 4.30 (s, 2H, CH_2-pur); 4.65–4.69 (m, 2H, H-5′b and H-4′); 4.78 (dd, 1H, J_{gem} = 13.3, $J_{5'a,4'}$ = 5.3, H-5′a); 5.84 (dt, 1H, $J_{3',2'}$ = 6.2, 2.0, $J_{3',4'}$ = 2.0, H-3′); 6.59 (dd, 1H, $J_{1'2'}$ = 8.3, 5.8, H-1′); 7.22 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.90 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.23 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.68 and 21.74 (CH_3-Tol); 32.67 (CH_2-pur); 33.51 (SCH_2CO); 37.78 (CH_2-2′); 52.44 (CH_3O); 63.94 (CH_2-5′); 75.05 (CH-3′); 83.14 (CH-4′); 84.94 (CH-1′); 126.35 and 126.63 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.63 and 129.81 (CH-*o*-Tol); 132.72 (C-5); 142.69 (CH-8); 144.20 and 144.57 (C-*p*-Tol); 150.89 (C-4); 152.49 (CH-2); 158.46 (C-6); 165.92 and 166.13 (CO-Tol); 170.49 (COOMe). IR (CCl_4): ν = 3037, 1728, 1613, 1595, 1494, 1436, 1407, 1332, 1267, 1178, 1101, 645 cm^{-1}.

4.56. 6-[(2-Hydroxyethyl)sulfanylmethyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (17e)

2-Mercaptoethanol (0.15 ml, 2.14 mmol) was added to a solution of mesylate **7** (500 mg, 0.70 mmol) and ^{i}Pr$_2$EtN (0.19 ml, 1.09 mmol) in dry MeCN (15 ml) and stirred for 8 h. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 1:1–0:1) to give 478 mg (98%) of **17e** as oil. Exact mass (FAB HR MS) found: 697.2308; calcd for $C_{37}H_{37}N_4O_8S$: 697.2332. FAB MS *m/z* (%): 697 (MH^+, 4); 487 (12); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 2.81 (m, 2H, CH_2S); 3.90 (m, 2H, CH_2O); 4.28 (s, 2H, CH_2-pur); 4.67 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'}$ = 4.1, H-5′b); 4.83 (td, 1H, $J_{4',3'}$ = 4.6, $J_{4',5'}$ = 4.1, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.1, H-5′a); 6.20 (dd, 1H, $J_{3',2'}$ = 5.7, $J_{3',4'}$ = 4.6, H-3′); 6.37 (t, 1H, $J_{2',3'}$ = 5.7, $J_{2',1'}$ = 5.4, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.4, H-1′); 7.16, 7.23 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.91 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.23 (s, 1H, H-8); 8.81 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.71 and 21.74 (CH_3-Tol); 31.99 (CH_2S); 35.98 (CH_2O); 62.11 (CH_2-pur); 63.39 (CH_2-5′); 71.37 (CH-3′); 73.72 (CH-2′); 81.10 (CH-4′); 86.98 (CH-1′); 125.58, 125.98 and 126.54 (C-*i*-Tol); 129.24, 129.27 and 129.35 (CH-*m*-Tol); 129.77, 129.87 and 129.88 (CH-*o*-Tol); 132.57 (C-5); 143.20 (CH-8); 144.28, 144.61 and 144.75 (C-*p*-Tol); 151.03 (C-4); 152.75 (CH-2); 159.57 (C-6); 165.19, 165.37 and 166.18 (CO). IR ($CHCl_3$): ν = 3300, 1727, 1612, 1596, 1498, 1409, 1335, 1267, 1180, 1093, 644 cm^{-1}.

4.57. 6-[(2-Hydroxyethyl)sulfanylmethyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (18e)

Prepared analogously as **17e**. Yield: 98% as oil. Exact mass (FAB HR MS) found: 563.1993; calcd for $C_{29}H_{31}N_4O_6S$: 563.1964. FAB MS *m/z* (%): 563 (MH^+, 14); 211 (65); 119 (100). ^{1}H NMR (500 MHz, $CDCl_3$): 2.41 and 2.45 (2× s, 6H, CH_3-Tol); 2.82 (m, 2H, CH_2S); 2.87 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'}$ = 5.8, $J_{2'b,3'}$ = 2.0, H-2′b); 3.18 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'}$ = 8.1, $J_{2'a,3'}$ = 6.5, H-2′a); 3.91 (m, 2H, CH_2O); 4.29 (s, 2H, CH_2-pur); 4.65–4.69 (m, 2H, H-5′b and H-4′); 4.78 (dd, 1H, J_{gem} = 13.2, $J_{5'a,4'}$ = 5.1, H-5′a); 5.83 (dt, 1H, $J_{3',2'}$ = 6.5, 2.0, $J_{3',4'}$ = 2.2, H-3′); 6.59 (dd, 1H, $J_{1'2'}$ = 8.1, 5.8, H-1′); 7.22 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.90 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.25 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.68 and 21.74 (CH_3-Tol); 32.03 (CH_2S); 36.08 (CH_2O); 37.84 (CH_2-2′); 62.19 (CH_2-pur); 63.90 (CH_2-5′); 75.01 (CH-3′); 83.23 (CH-4′); 85.09 (CH-1′); 126.31 and 126.58 (C-*i*-Tol); 129.21 and 129.39 (CH-*m*-Tol); 129.66 and 126.79 (CH-*o*-Tol); 132.53 (C-5); 142.85 (CH-8); 144.24 and 144.60 (C-*p*-Tol); 150.82 (C-4); 152.63 (CH-2); 159.47 (C-6); 165.93 and 166.13 (CO). IR ($CHCl_3$): ν = 3293, 1721, 1612, 1597, 1496, 1407, 1333, 1269, 1179, 1102, 646 cm^{-1}.

4.58. 6-[(Pyridin-2-yl)sulfanylmethyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (17g)

2-Mercaptopyridine (310 mg, 2.79 mmol) was added to a solution of mesylate **7** (500 mg, 0.70 mmol) and ^{i}Pr$_2$EtN (0.37 ml, 2.1 mmol) in dry MeCN (15 ml) and stirred for 8 h. Reaction mixture was adsorbed on silica gel and chromatographed ($CHCl_3$/MeOH, 99:1–98:2) to give 500 mg (98%) of **17g** as oil. Exact mass (FAB HR MS) found: 730.2326; calcd for $C_{40}H_{36}N_5O_7S$: 730.2335. FAB MS *m/z* (%): 730 (MH^+, 8); 487 (17); 119 (100). ^{1}H NMR (400 MHz, $CDCl_3$): 2.38 and 2.42 (2× s, 9H, CH_3-Tol); 4.66 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'}$ = 4.1, H-5′b); 4.81 (td, 1H, $J_{4',3'}$ = 4.6, $J_{4',5'}$ = 4.1, 3.1, H-4′); 4.89 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.1, H-5′a); 4.95 and 4.99 (2× d, 2H, J_{gem} = 14.3, CH_2S); 6.21 (dd, 1H, $J_{3',2'}$ = 5.8, $J_{3',4'}$ = 4.6, H-3′); 6.39 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.5, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.5, H-1′); 6.96 (ddd, 1H, $J_{5,4}$ = 7.4, $J_{5,6}$ = 4.9, $J_{5,3}$ = 1.1, H-5-py); 7.16, 7.21 and 7.25 (3× m, 3× 2H, H-*m*-Tol); 7.27 (dt, 1H, $J_{3,4}$ = 8.1, $J_{3,5}$ = 1.1, $J_{3,6}$ = 1.0, H-3-py); 7.46 (ddd, 1H, $J_{4,3}$ = 8.1, $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.9, H-4-py); 7.81, 7.90 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.22 (s, 1H, H-8); 8.40 (ddd, 1H, $J_{6,5}$ = 4.9, $J_{6,4}$ = 1.9, $J_{6,3}$ = 1.0, H-6-py); 8.81 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.70 and 21.73 (CH_3-Tol); 31.15 (CH_2S); 63.41 (CH_2-5′); 71.38 (CH-3′); 73.67 (CH-2′); 81.02 (CH-4′); 86.84 (CH-1′); 119.68 (CH-5-py); 121.97 (CH-3-py); 125.63, 126.01 and 126.55 (C-*i*-Tol); 129.21, 129.25 and 129.34 (CH-*m*-Tol); 129.77, 129.86 and 129.88 (CH-*o*-Tol); 133.11 (C-5); 135.99 (CH-4-py); 142.95 (CH-8); 144.22, 144.56 and 144.68 (C-*p*-Tol); 149.45 (CH-6-py); 150.84 (C-4); 152.86 (CH-2); 157.54 (C-2-py); 158.49 (C-6); 165.15, 165.37 and 166.20 (CO). IR (CCl_4): ν = 1732, 1612, 1593, 1580, 1496, 1453, 1415, 1334, 1266, 1179, 1092, 644 cm^{-1}.

4.59. 6-[(Pyridin-2-yl)sulfanylmethyl]-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (18 g)

Prepared analogously as **17g**. Yield: 98% as oil. Exact mass (FAB HR MS) found: 596.1989; calcd for

$C_{32}H_{30}N_5O_5S$: 596.1968. FAB MS *m/z* (%): 596 (MH^+, 5); 244 (50); 119 (100). ^1H NMR (400 MHz, $CDCl_3$): 2.41 and 2.45 (2× s, 6H, CH_3-Tol); 2.85 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'}$ = 5.8, $J_{2'b,3'}$ = 2.0, H-2′b); 3.19 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'}$ = 8.4, $J_{2'a,3'}$ = 6.4, H-2′a); 4.65–4.69 (m, 2H, H-5′b and H-4′); 4.77 (dd, 1H, J_{gem} = 13.4, $J_{5'a,4'}$ = 5.4, H-5′a); 4.95 and 5.00 (2× d, 2H, J_{gem} = 14.2, CH_2S); 5.83 (dt, 1H, $J_{3',2'}$ = 6.4, 2.0, $J_{3',4'}$ = 2.0, H-3′); 6.59 (dd, 1H, $J_{1'2'}$ = 8.4, 5.8, H-1′); 6.97 (ddd, 1H, $J_{5,4}$ = 7.3, $J_{5,6}$ = 4.9, $J_{5,3}$ = 1.0, H-5-py); 7.22 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.27 (ddd, 1H, $J_{3,4}$ = 8.1, $J_{3,5}$ = 1.0, $J_{3,6}$ = 1.0, H-3-py); 7.47 (ddd, 1H, $J_{4,3}$ = 8.1, $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.9, H-4-py); 7.90 and 7.97 (2× m, 2× 2H, H-*o*-Tol); 8.25 (s, 1H, H-8); 8.42 (ddd, 1H, $J_{6,5}$ = 4.9, $J_{6,4}$ = 1.9, $J_{6,3}$ = 1.0, H-6-py);8.86 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 and 21.74 (CH_3-Tol); 31.15 (CH_2S); 37.79 (CH_2-2′); 63.94 (CH_2-5′); 75.07 (CH-3′); 83.13 (CH-4′); 84.91 (CH-1′); 119.67 (CH-5-py); 121.07 (CH-3-py); 126.36 and 126.63 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.63 and 129.81 (CH-*o*-Tol); 133.10 (C-5); 135.99 (CH-4-py); 142.55 (CH-8); 144.18 and 144.55 (C-*p*-Tol); 149.44 (CH-6-py); 150.67 (C-4); 152.61 (CH-2); 157.77 (C-2-py); 158.33 (C-6); 165.93 and 166.14 (CO). IR (CCl_4): *v* = 3049, 1727, 1613, 1593, 1579, 1562, 1494, 1453, 1447, 1418, 1332, 1267, 1178, 1101, 645 cm^{-1}.

4.60. 6-[(Benzothiazol-2-yl)sulfanylmethyl]-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (17h)

2-Mercaptobenzothiazole (350 mg, 2.09 mmol) was added to a solution of mesylate **7** (500 mg, 0.70 mmol) and $^iPr_2EtN$ (0.19 ml, 1.09 mmol) in dry MeCN (15 ml) and stirred for 8 h. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 2:1–1:2) to give 540 mg (98%) of **17h** as foam. Exact mass (FAB HR MS) found: 786.2096; calcd for $C_{42}H_{36}N_5O_7S_2$: 786.2056. FAB MS *m/z* (%): 786 (MH^+, 1); 487 (10); 119 (100). ^1H NMR (500 MHz, $CDCl_3$): 2.37, 2.41 and 2.42 (3× s, 3× 3H, CH_3-Tol); 4.66 (dd, 1H, J_{gem} = 12.3, $J_{5'b,4'}$ = 4.1, H-5′b); 4.82 (td, 1H, $J_{4',3'}$ = 4.7, $J_{4',5'}$ = 4.1, 3.1, H-4′); 4.90 (dd, 1H, J_{gem} = 12.3, $J_{5'a,4'}$ = 3.1, H-5′a); 5.12 and 5.16 (2× d, 2H, J_{gem} = 14.3, CH_2S); 6.21 (dd, 1H, $J_{3',2'}$ = 5.8, $J_{3',4'}$ = 4.7, H-3′); 6.39 (t, 1H, $J_{2',3'}$ = 5.8, $J_{2',1'}$ = 5.4, H-2′); 6.48 (d, 1H, $J_{1',2'}$ = 5.4, H-1′); 7.16, 7.22 and 7.24 (3× m, 3× 2H, H-*m*-Tol); 7.28 (ddd, 1H, $J_{6,7}$ = 8.0, $J_{6,5}$ = 7.3, $J_{6,4}$ = 1.2, H-6-benzothiazole); 7.38 (ddd, 1H, $J_{5,4}$ = 8.2, $J_{5,6}$ = 7.3, $J_{5,7}$ = 1.3, H-5-benzothiazole); 7.73 (ddd, 1H, $J_{7,6}$ = 8.0, $J_{7,5}$ = 1.3, $J_{7,4}$ = 0.6, H-7-benzothiazole); 7.81 (m, 2H, H-*o*-Tol); 7.85 (ddd, 1H, $J_{4,5}$ = 8.2, $J_{4,6}$ = 1.2, $J_{4,7}$ = 0.6, H-4-benzothiazole); 7.91 and 7.98 (2× m, 2× 2H, H-*o*-Tol); 8.25 (s, 1H, H-8); 8.83 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, $CDCl_3$): 21.70 and 21.74 (CH_3-Tol); 34.35 (CH_2S); 63.35 (CH_2-5′); 71.35 (CH-3′); 73.69 (CH-2′); 81.07 (CH-4′); 86.95 (CH-1′); 120.95 (CH-7-benzothiazole); 121.78 (CH-4-benzothiazole); 124.30 (CH-6-benzothiazole); 125.59, 125.98 and 126.52 (CH-5-benzothiazole and C-*i*-Tol); 129.23, 129.26 and 129.34 (CH-*m*-Tol); 129.75, 129.86 and 129.88 (CH-*o*-Tol); 133.04 (C-5); 135.55 (C-7a-benzothiazole); 143.32 (CH-8); 144.27, 144.60 and 144.72 (C-*p*-Tol); 151.00 (C-4); 152.82 (CH-2); 153.08 (C-3a-benzothiazole); 156.37 (C-6); 165.17, 165.37 and 166.19 (C-2-benzothiazole and CO). IR (CCl_4): *v* = 1732, 1612, 1595, 1496, 1463, 1457, 1429, 1409, 1334, 1266, 1179, 1092, 643 cm^{-1}.

4.61. 6-(Acetylsulfanylmethyl)-9-(2,3,5-tri-*O*-toluoyl-β-D-ribofuranosyl)purine (17ia)

Potassium thioacetate (96 mg, 0.84 mmol) was added to a solution of mesylate **7** (410 mg, 0.57 mmol) in dry MeCN (15 ml) and stirred for 6 h. Reaction mixture was adsorbed on silica gel and chromatographed (hexanes/AcOEt, 2:1–1:2) to give 375 mg (95%) of **17ia** as foam. Exact mass (FAB HR MS) found: 695.2200; calcd for $C_{37}H_{35}N_4O_8S$: 695.2176. FAB MS *m/z* (%): 695 (MH^+, 4); 487 (9); 119 (100). ^1H NMR (400 MHz, $CDCl_3$): 2.377 (s, 3H, CH_3-Tol); 2.382 (s, 3H, CH_3CO); 2.42 (s, 6H, CH_3-Tol); 4.65 (s, 2H, CH_2S); 4.66 (dd, 1H, J_{gem} = 12.2, $J_{5'b,4'}$ = 4.1, H-5′b); 4.81 (ddd, 1H, $J_{4',3'}$ = 4.7, $J_{4',5'}$ = 4.1, 3.1, H-4′); 4.89 (dd, 1H, J_{gem} = 12.2, $J_{5'a,4'}$ = 3.1, H-5′a); 6.21 (dd, 1H, $J_{3',2'}$ = 5.7, $J_{3',4'}$ = 4.7, H-3′); 6.39 (t, 1H, $J_{2',3'}$ = 5.7, $J_{2',1'}$ = 5.5, H-2′); 6.47 (d, 1H, $J_{1',2'}$ = 5.5, H-1′); 7.16, 7.22 and 7.26 (3× m, 3× 2H, H-*m*-Tol); 7.81, 7.90 and 7.99 (3× m, 3× 2H, H-*o*-Tol); 8.23 (s, 1H, H-8); 8.81 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.70 and 21.73 (CH_3-Tol); 30.15 (**C**H_3CO); 30.22 (CH_2S); 63.41 (CH_2-5′); 71.38 (CH-3′); 73.62 (CH-2′); 81.06 (CH-4′); 86.88 (CH-1′); 125.62, 126.01 and 126.56 (C-*i*-Tol); 129.26, 129.26 and 129.34 (CH-*m*-Tol); 129.78, 129.86 and 129.88 (CH-*o*-Tol); 133.02 (C-5); 143.23 (CH-8); 144.23, 144.58 and 144.70 (C-*p*-Tol); 150.93 (C-4); 152.84 (CH-2); 157.31 (C-6); 165.15, 165.37 and 166.19 (CO-Tol); 193.89 (S-CO). IR (CCl_4): *v* = 1732, 1702, 1612, 1594, 1497, 1454, 1409, 1334, 1266, 1179, 1093, 643, 623 cm^{-1}.

4.62. 6-(Acetylsulfanylmethyl)-9-(2-deoxy-3,5-di-*O*-toluoyl-β-D-*erythro*-pentofuranosyl)purine (18ia)

Prepared analogously as **17ia**. Yield: 96% as foam. Exact mass (FAB HR MS) found: 561.1784; calcd for $C_{29}H_{29}N_4O_6S$: 561.1808. FAB MS *m/z* (%): 561 (MH^+, 6); 209 (27); 167 (14); 119 (100). ^1H NMR (500 MHz, $CDCl_3$): 2.39 (s, 3H, CH_3CO); 2.41 and 2.45 (2× s, 2× 3H, CH_3-Tol); 2.85 (ddd, 1H, J_{gem} = 14.2, $J_{2'b,1'}$ = 5.8, $J_{2'b,3'}$ = 2.1, H-2′b); 3.20 (ddd, 1H, J_{gem} = 14.2, $J_{2'a,1'}$ = 8.4, $J_{2'a,3'}$ = 6.4, H-2′a); 4.64–4.69 (m, 2H, H-5′b and H-4′); 4.66 (s, 2H, CH_2S); 4.77 (m, 1H, H-5′a); 5.83 (dt, 1H, $J_{3',2'}$ = 6.4, 2.1, $J_{3',4'}$ = 2.1, H-3′); 6.58 (dd, 1H, $J_{1'2'}$ = 8.4, 5.8, H-1′); 7.23 and 7.29 (2× m, 2× 2H, H-*m*-Tol); 7.90 and 7.97 (2× m, 2× 2H, H-*o*-Tol); 8.25 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.69 and 21.74 (CH_3-Tol); 30.16 (**C**H_3CO); 30.22 (CH_2S); 37.75 (CH_2-2′); 63.92 (CH_2-5′); 75.05 (CH-3′); 83.15 (CH-4′); 84.95 (CH-1′); 126.35 and 126.62 (C-*i*-Tol); 129.29 (CH-*m*-Tol); 129.63 and 129.81 (CH-*o*-Tol); 133.03 (C-5); 142.85 (CH-8); 144.20 and 144.57 (C-*p*-Tol); 150.73 (C-4); 152.59 (CH-2); 157.13 (C-6); 165.93 and 166.14 (CO); 193.89 (S-CO). IR (CCl_4): *v* = 1727, 1703, 1613, 1594, 1494, 1454, 1407, 1332, 1266, 1178, 1100, 645, 623 cm^{-1}.

4.63. General procedure for cleavage of toluoyl protective groups

4.63.1. Method A. A 1-M methanolic MeONa (100 μl, 0.1 mmol) was added to a solution of protected purine nucleosides **5**, **6**, **13**, **14**, **17**, **18** (0.5 mmol) in methanol (30 ml) and the mixture was stirred at ambient temperature. After complete deprotection the product was adsorbed on silica gel and chromatographed (ethyl acetate/methanol, 1:0–7:3).

4.63.2. Method B. An aqueous ammonia (1 ml) was added to a solution of protected purine nucleoside **5** or **6** (0.5 mmol) in methanol (30 ml) and the mixture was stirred at 50 °C in sealed flask. After complete deprotection the reaction mixture was adsorbed on silica gel and chromatographed (ethyl acetate/methanol, 1:0–7:3).

4.64. 6-[(*N*-Acetyl-*N*-methyl)aminomethyl]-9-(β-D-ribofuranosyl)purine (11aa)

Prepared from **5aa** (360 mg) by deprotection method B to give 145 mg (82%) of **11aa** as white foam. $[\alpha]_D^{20} - 43.1$ ($c = 3.16$, H_2O). Exact mass (FAB HR MS) found: 338.1453; calcd for $C_{14}H_{20}N_5O_5$: 338.1464. FAB MS *m*/*z* (%): 338 (MH^+, 18); 206 (100); 164 (10); 134 (12). A mixture of *cis*/*trans* amides ~1:1. ^{1}H NMR (400 MHz, DMSO-d_6): 2.08 and 2.10 (2× s, 6H, CH_3CO); 2.87 and 3.15 (2× s, 6H, CH_3-N); 3.57 (m, 2H, H-5′b); 3.69 (m, 2H, H-5′a); 3.98 (m, 2H, H-4′); 4.19 (m, 2H, H-3′); 4.64 (m, 2H, H-2′); 4.96 and 5.02 (2× s, 4H, CH_2-pur); 5.10 (m, 2H, OH-5′); 5.24 and 5.25 (2× d, 2H, $J_{OH,3'} = 5.0$, OH-3′); 5.54 (d, 2H, $J_{OH,2'} = 5.9$, OH-2′); 6.03 and 6.05(2× d, 2H, $J_{1',2'} = 6.0$, H-1′); 8.79, 8.85 and 8.92 (3× s, 4H, H-8 and H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 21.64 and 21.75 (*C*H_3CO); 34.00 and 37.50 (**C**H_3-N); 48.78 and 51.26 (CH_2-pur); 61.42 and 61.47 (CH_2-5′); 70.48 and 70.53 (CH-3′); 73.83 and 73.85 (CH-2′); 85.92 (CH-4′); 87.77 and 87.84 (CH-1′); 131.89 and 132.13 (C-5); 144.68 and 145.13 (CH-8); 150.83 and 151.08 (C-4); 151.89 and 152.16 (CH-2); 156.55 and 157.74 (C-6); 170.61 and 170.68 (CO). IR (KBr): $\nu = 3421$, 1628, 1598, 1496, 1404, 1334, 1210, 1126, 1085, 1055, 645 cm^{-1}.

4.65. 6-[(*N*-Acetyl-*N*-methyl)aminomethyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12aa)

Prepared from **6aa** (360 mg) by deprotection method B to give 190 mg (92%) of **12aa** as lyophilized solid. $[\alpha]_D^{20} - 17.0$ ($c = 2.93$, H_2O). Exact mass (FAB HR MS) found: 322.1525; calcd for $C_{14}H_{20}N_5O_4$: 322.1515. FAB MS *m*/*z* (%): 322 (MH^+, 27); 206 (100); 164 (12); 134 (16). A mixture of *cis*/*trans* amides ~1:1. ^{1}H NMR (400 MHz, DMSO-d_6): 2.07 and 2.10 (2× s, 6H, CH_3CO); 2.35 (m, 2H, H-2′b); 2.79 (m, 2H, H-2′a); 2.86 and 3.14 (2× s, 6H, CH_3-N); 3.52 (m, 2H, H-5′b); 3.62 (m, 2H, H-5′a); 3.89 (m, 2H, H-4′); 4.45 (m, 2H, H-3′); 4.95 and 5.00 (2× s, 4H, CH_2-pur); 4.98 (m, 2H, OH-5′); 5.36 (m, 2H, OH-3′); 6.48 (m, 2H, H-1′); 8.75 and 8.81 (2× s, 2H, H-8); 8.84 and 8.91 (2× s, 2H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 21.64 and 21.75 (*C*H_3CO); 33.99 and 37.47 (*C*H_3-N); 39.39(CH_2-2′); 48.73 and 51.25 (CH_2-pur); 61.71 and 61.74 (CH_2-5′); 70.80 and 70.83 (CH-3′); 83.87 and 83.96 (CH-1′); 88.17 and 88.20 (CH-4′); 131.90 and 132.14 (C-5); 144.60 and 145.06 (CH-8); 150.54 and 150.79 (C-4); 151.81 and 152.07 (CH-2); 156.41 and 157.61 (C-6); 170.59 and 170.67 (CO). IR (KBr): $\nu = 3409$, 1631, 1596, 1495, 1401, 1333, 1211, 1094, 1057, 646 cm^{-1}.

4.66. 6-[(*N*-Acetyl-*N*-benzyl)aminomethyl]-9-(β-D-ribofuranosyl)purine (11ba)

Prepared from **5ba** (430 mg) by deprotection method B to give 195 mg (84%) of **11ba** as white foam. $[\alpha]_D^{20} - 28.8$ ($c = 2.59$, MeOH). Anal. calcd for $C_{20}H_{23}N_5O_5 \cdot H_2O$: C, 55.68; H, 5.84; N, 16.23; found: C, 55.46; H, 5.66; N, 15.85. Exact mass (FAB HR MS) found: 414.1766; calcd for $C_{20}H_{24}N_5O_5$: 414.1777. FAB MS *m*/*z* (%): 414 (MH^+, 42); 282 (100); 240 (11); 191 (15); 149 (21); 134 (36); 91 (85). A mixture of *cis*/*trans* amides ~1:0.6. ^{1}H NMR (400 MHz, DMSO-d_6): 2.12 and 2.24 (2× s, 6H, CH_3CO); 3.54–3.61 (m, 2H, H-5′b); 3.66–3.73 (m, 2H, H-5′a); 3.96–4.00 (m, 2H, H-4′); 4.17–4.21 (m, 2H, H-3′); 4.55 and 4.78 (2× s, 4H, CH_2Ph); 4.61–4.66 (m, 2H, H-2′); 4.91 and 4.94 (2× s, 4H, CH_2-pur); 5.09–5.13 (m, 2H, OH-5′); 5.24 (d, 1H, $J_{OH,3'} = 5.0$, OH-3′); 5.26 (d, 1H, $J_{OH,3'} = 5.0$, OH-3′); 5.54 (d, 1H, $J_{OH,2'} = 6.0$, OH-2′); 5.55 (d, 1H, $J_{OH,2'} = 6.0$, OH-2′); 6.03 (d, 1H, $J_{1',2'} = 5.7$, H-1′); 6.04 (d, 1H, $J_{1',2'} = 5.6$, H-1′); 7.21–7.24, 7.26–7.31 and 7.36–7.39 (3× m, 10H, H-*o*,*m*,*p*-Ph); 8.79 and 8.84 (2× s, 2H, H-8); 8.86 and 8.92 (2× s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 21.52 and 21.95 (*C*H_3CO); 46.89 and 48.43 (CH_2-pur); 48.52 and 52.89 (CH_2Ph); 61.39 and 61.47 (CH_2-5′); 70.43 and 70.53 (CH-3′); 73.83 and 73.89 (CH-2′); 85.86 and 85.89 (CH-4′); 87.77 and 87.85 (CH-1′); 126.99 (CH-*o*-Ph); 127.15 and 127.46 (CH-*p*-Ph); 127.87 (CH-*o*-Ph); 128.44 and 128.86 (CH-*m*-Ph); 131.95 and 134.26 (C-5); 137.75 and 137.85 (C-*i*-Ph); 144.66 and 145.10 (CH-8); 150.82 and 151.04 (C-4); 151.88 and 152.14 (CH-2); 156.37 and 157.57 (C-6); 170.77 and 170.96 (*C*OCH_3). IR (KBr): $\nu = 3379$, 1656, 1631, 1596, 1496, 1418, 1333, 1209, 1086, 1056, 646 cm^{-1}.

4.67. 6-[(*N*-Acetyl-*N*-benzyl)aminomethyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12ba)

Prepared from **6ba** (330 mg) by deprotection method B to give 190 mg (92%) of **12ba** as white foam. $[\alpha]_D^{20} - 9.1$ ($c = 2.37$, MeOH). Anal. calcd for $C_{20}H_{23}N_5O_4 \cdot H_2O$: C, 57.82; H, 6.07; N, 16.86; found: C, 57.89; H, 5.69; N, 16.45. Exact mass (FAB HR MS) found: 398.1832; calcd for $C_{20}H_{24}N_5O_4$: 398.1828. FAB MS *m*/*z* (%): 398 (MH^+, 18); 282 (100); 240 (9); 191 (8); 148 (9); 134 (21); 91 (50). A mixture of *cis*/*trans* amides ~1 : 0.6. ^{1}H NMR (400 MHz, DMSO-d_6): 2.11 and 2.24 (2× s, 6H, CH_3CO); 2.32–2.38 (m, 2H, H-2′b); 2.74–2.82 (m, 2H, H-2′a); 3.50–3.56 (m, 2H, H-5′b); 3.60–3.66 (m, 2H, H-5′a); 3.88–3.91 (m, 2H, H-4′); 4.43–4.47 (m, 2H, H-3′); 4.55 and 4.77 (2× s, 4H, CH_2Ph); 4.91 and 4.93 (2× s, 4H, CH_2-pur); 4.98–5.01 (m, 2H, OH-5′);

5.36 (m, 2H, OH-3′); 6.47 (m, 2H, H-1′); 7.20–7.23, 7.25–7.30 and 7.35–7.39 (3× m, 10H, H-*o,m,p*-Ph); 8.75 and 8.80 (2× s, 2H, H-8); 8.85 and 8.90 (2× s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 21.51 and 21.95 (CH_3CO); 39.44 (CH_2-2′); 46.83 and 48.43 (CH_2-pur); 48.53 and 52.86 (CH_2Ph); 61.71 and 61.75 (CH_2-5′); 70.79 and 70.84 (CH-3′); 83.88 and 83.96 (CH-1′); 88.17 and 88.19 (CH-4′); 126.97 (CH-*o*-Ph); 127.12 and 127.44 (CH-*p*-Ph); 127.85 (CH-*o*-Ph); 128.41 and 128.84 (CH-*m*-Ph); 131.96 and 132.27 (C-5); 137.73 and 137.84 (C-*i*-Ph); 144.57 and 145.04 (CH-8); 150.52 and 150.73 (C-4); 151.80 and 152.03 (CH-2); 156.24 and 157.42 (C-6); 170.74 and 170.95 (COCH$_3$). IR (KBr): ν = 3413, 1653, 1635, 1596, 1496, 1419, 1333, 1210, 1095, 1057, 645 cm^{-1}.

4.68. 6-[(*N*-Acetyl-*N*-cyclohexyl)aminomethyl]-9-(β-D-ribofuranosyl)purine (11ca)

Prepared from **5ca** (300 mg) by deprotection method B to give 135 mg (84%) of **11ca** as white crystals (mp 75–77 °C, crystallization from EtOH/heptane). $[\alpha]_D^{20}$ − 31.7 (c = 2.48, H_2O). Anal. calcd for $C_{19}H_{27}N_5O_5{\cdot}H_2O$: C, 53.89; H, 6.90; N, 16.54; found: C, 53.87; H, 7.06; N, 16.09. Exact mass (FAB HR MS) found: 406.2084; calcd for $C_{19}H_{28}N_5O_5$: 406.2090. FAB MS m/z (%): 406 (MH^+, 9); 274 (100); 232 (21); 148 (28); 134 (37). A mixture of *cis*/*trans* amides ~1:1. ^{1}H NMR (500 MHz, DMSO-d_6): 1.15–1.73 and 1.82–1.88 (2× m, 20H, CH_2-cyclohex); 2.06 and 2.12 (2× s, 2× 3H, CH_3); 3.56 and 3.57 (2× ddd, 2× 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 5.7, $J_{5'b,4'}$ = 4.1, H-5′b); 3.68 and 3.69 (2× ddd, 2× 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.7, $J_{5'a,4'}$ = 4.1, H-5′a); 3.77 (m, 1H, CH-cyclohex); 3.97 and 3.98 (2× q, 2× 1H, $J_{4',5'}$ = 4.1, $J_{4',3'}$ = 3.8, H-4′); 4.18 and 4.19 (2× q, 2× 1H, $J_{3',2'}$ = 4.9, $J_{3',OH}$ = 4.0, $J_{3',4'}$ = 3.8, H-3′); 4.32 (m, 1H, CH-cyclohex); 4.65 and 4.66 (2× q, 2× 1H, $J_{2',OH}$ = 6.0, $J_{2',1'}$ = 5.8, $J_{2',3'}$ = 4.7, H-2′); 4.87 and 5.00 (2× s, 2× 2H, CH_2N); 5.10 and 5.11 (2× t, 2× 1H, $J_{OH,5'}$ = 5.7, OH-5′); 5.25 and 5.28 (2× d, 2× 1H, $J_{OH,3'}$ = 4.0, OH-3′); 5.56 (d, 2H, $J_{OH,2'}$ = 6.0, OH-2′); 6.02 and 6.04 (2× d, 2× 1H, $J_{1',2'}$ = 5.8, H-1′); 8.75 (s, 1H, H-8); 8.79 (s, 1H, H-2); 8.84 (s, 1H, H-8); 8.90 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, DMSO-d_6): 21.78 and 22.78 (CH_3); 24.99, 25.20, 25.51, 25.61, 30.20 and 31.24 (CH_2-cyclohex); 42.45 and 44.62 (CH_2N); 52.87 and 57.36 (CH-cyclohex); 61.47 and 61.53 (CH_2-5′); 70.52 and 70.60 (CH-3′); 73.75 and 73.79 (CH-2′); 85.93 and 85.97 (CH-4′); 87.72 and 87.78 (CH-1′); 131.49 and 131.54 (C-5); 144.23 and 144.97 (CH-8); 150.58 and 150.86 (C-4); 151.65 and 152.04 (CH-2); 158.22 and 159.22 (C-6); 169.61 and 170.65 (CO). IR (KBr): ν = 3409, 2931, 2857, 1623, 1596, 1497, 1416, 1334, 1211, 1124, 1084, 1055, 647 cm^{-1}.

4.69. 6-[(*N*-Acetyl-*N*-cyclohexyl)aminomethyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12ca)

Prepared from **6ca** (260 mg) by deprotection method B to give 140 mg (86%) of **12ca** as white foam. $[\alpha]_D^{20}$ − 16.3 (c = 2.50, MeOH). Anal. calcd for $C_{19}H_{27}N_5O_4{\cdot}H_2O$: C, 56.01; H, 7.17; N, 17.19; found: C, 56.38; H, 7.51; N, 16.78. Exact mass (FAB HR MS) found: 390.2125; calcd for $C_{19}H_{28}N_5O_4$: 390.2141. FAB MS m/z (%): 390 (MH^+, 9); 274 (100); 231 (14); 192 (12); 149 (22); 134 (30). A mixture of cis/trans amides ~1:1. ^{1}H NMR (400 MHz, DMSO-d_6): 1.17–1.71 and 1.84–1.86 (2× m, 20H, CH_2-cyclohex); 2.05 and 2.11 (2× s, 6H, CH_3); 2.35 (m, 2H, H-2′b); 2.80 (m, 2H, H-2′a); 3.52 (m, 2H, H-5′b); 3.62 (m, 2H, H-5′a); 3.76 (m, 1H, CH-cyclohex); 3.89 (m, 2H, H-4′); 4.32 (m, 1H, CH-cyclohex); 4.45 (m, 2H, H-3′); 4.86 and 4.98 (2× s, 4H, CH_2N); 4.99 (m, 2H, OH-5′); 5.36 (m, 2H, OH-3′); 6.47 (m, 2H, H-1′); 8.72 (s, 1H, H-8); 8.78 (s, 1H, H-2); 8.80 (s, 1H, H-8); 8.89 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 21.76 and 22.77 (CH_3); 24.98, 25.19, 25.50, 25.60, 30.19 and 31.24 (CH_2-cyclohex); 39.34 and 39.36 (CH_2-2′); 42.40 and 44.60 (CH_2N); 52.88 and 57.35 (CH-cyclohex); 61.74 and 61.79 (CH_2-5′); 70.84 and 70.88 (CH-3′); 83.83 and 83.95 (CH-1′); 88.15 and 88.20 (CH-4′); 131.48 and 131.51 (C-5); 144.10 and 144.85 (CH-8); 150.26 and 150.54 (C-4); 151.56 and 151.91 (CH-2); 158.06 and 159.06 (C-6); 169.57 and 170.61 (CO). IR (KBr): ν = 3421, 2932, 2857, 1624, 1595, 1496, 1452, 1420, 1333, 1212, 1096, 1058, 647 cm^{-1}.

4.70. 6-[*N*-(Hydroxycarbonylmethyl)aminomethyl]-9-(β-D-ribofuranosyl)purine (11da)

An aq NaOH (3.5 ml, c = 0.5 mol/l) was added to a solution of protected nucleoside **5d** (330 mg, 0.46 mmol) in methanol (10 ml) and stirred at rt for 1 h. Next, the solvent was evaporated and the residue was purified by HPLC on C18 column with H_2O/MeOH as mobile phase to give 85 mg (55%) of **11da** as lyophilized solid. $[\alpha]_D^{20}$ − 18.5 (c = 2.19, H_2O). Anal. calcd for $C_{13}H_{17}N_5O_6{\cdot}2H_2O$ C, 41.60; H, 5.64; N, 18.66; found: C, 42.02; H, 5.42; N, 18.38. Exact mass (FAB HR MS) found: 340.1263; calcd for $C_{13}H_{18}N_5O_6$: 340.1257. FAB MS m/z (%): 340 (MH^+, 12); 208 (10); 149 (8). ^{1}H NMR (500 MHz, DMSO-d_6): 3.39 (s, 2H, NCH_2CO); 3.58 (dd, 1H, J_{gem} = 12.0, $J_{5'b,4'}$ = 4.1, H-5′b); 3.69 (dd, 1H, J_{gem} = 12.0, $J_{5'a,4'}$ = 4.1, H-5′a); 3.98 (q, 1H, $J_{4',5'}$ = 4.1, $J_{4',3'}$ = 3.6, H-4′); 4.19 (dd, 1H, $J_{3',2'}$ = 5.0, $J_{3',4'}$ = 3.6, H-3′); 4.36 (s, 2H, NCH_2pur); 4.63 (t, 1H, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 5.0, H-2′); 6.04 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 8.84 (s, 1H, H-8); 8.93 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, DMSO-d_6): 48.32 (NCH_2pur); 50.14 (NCH_2CO); 61.43 (CH_2-5′); 70.48 (CH-3′); 73.90 (CH-2′); 85.92 (CH-4′); 87.83 (CH-1′); 131.94 (C-5); 144.94 (CH-8); 150.81 (C-4); 151.91 (CH-2); 156.88 (C-6); 171.25 (CO). IR (KBr): ν = 3409, 1631, 1607, 1585, 1498, 1404, 1337, 1211, 1123, 1083, 1055, 644 cm^{-1}.

4.71. 6-[(*N*,*N*-Dimethylamino)methyl]-9-(β-D-ribofuranosyl)purine (11e)

Prepared from **5e** (380 mg) by deprotection method A to give 125 mg (71%) of **11e** as white solid (mp 175–177 °C). $[\alpha]_D^{20}$ − 35.9 (c = 1.81, H_2O). Anal. calcd for $C_{13}H_{19}N_5O_4{\cdot}H_2O$: C, 47.70; H, 6.47; N, 21.39; found: C, 48.03; H, 6.66; N, 20.95. Exact mass (FAB HR MS) found: 310.1523; calcd for $C_{13}H_{20}N_5O_4$: 310.1515. FAB MS m/z (%): 310 (MH^+, 45); 266 (7); 178 (100);

134 (38). ^{1}H NMR (400 MHz, DMSO-d_6): 2.24 (s, 6H, $(CH_3)_2N$); 3.56 (dd, 1H, J_{gem} = 12.1, $J_{5'b,4'}$ = 3.7, H-5′b); 3.67 (dd, 1H, J_{gem} = 12.1, $J_{5'a,4'}$ = 4.0, H-5′a); 3.89 (s, 2H, CH_2N); 3.98 (q, 1H, $J_{4',5'}$ = 4.0, 3.7, $J_{4',3'}$ = 3.6, H-4′); 4.20 (dd, 1H, $J_{3',2'}$ = 4.8, $J_{3',4'}$ = 3.6, H-3′); 4.64 (t, 1H, $J_{2',1'}$ = 5.8, $J_{2',3'}$ = 4.8, H-2′); 5.20 (b, 1H, OH-5′); 5.35 (b, 1H, OH-3′); 5.65 (b, 1H, OH-2′); 6.03 (d, 1H, $J_{1',2'}$ = 5.8, H-1′); 8.81 (s, 1H, H-8); 8.88 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 45.48 ($(CH_3)_2N$); 59.05 (CH_2N); 61.46 (CH_2-5′); 70.54 (CH-3′); 73.82 (CH-2′); 85.91 (CH-4′); 87.72 (CH-1′); 133.53 (C-5); 144.81 (CH-8); 151.06 (C-4); 151.77 (CH-2); 157.53 (C-6). IR (KBr): ν = 3409, 2830, 2783, 1599, 1499, 1404, 1334, 1210, 1124, 1085, 1055, 645 cm^{-1}.

4.72. 6-[(*N*,*N*-Dimethylamino)methyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12e)

Prepared from **6e** (390 mg) by deprotection method B to give 190 mg (88%) of **12e** as white foam. $[\alpha]_D^{20}$ − 19.6 (c = 2.86, H_2O). Anal. calcd for $C_{13}H_{19}N_5O_3{\cdot}1/2H_2O$: C, 51.65; H, 6.67; N, 23.16; found: C, 52.04; H, 6.69; N, 23.00. Exact mass (FAB HR MS) found: 294.1563; calcd for $C_{13}H_{20}N_5O_3$: 294.1566. FAB MS m/z (%): 294 (MH$^+$, 60); 250 (9); 178 (100); 134 (56). ^{1}H NMR (400 MHz, DMSO-d_6): 2.24 (s, 6H, $(CH_3)_2N$); 2.35 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.5, H-2′b); 2.79 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.2, $J_{2'a,3'}$ = 6.0, H-2′a); 3.52 and 3.62 (2× dt, 2H, J_{gem} = 11.7, $J_{5',OH}$ = 5.5, $J_{5',4'}$ = 4.6, H-5′); 3.88 (s, 2H, CH_2N); 3.89 (td, 1H, $J_{4',5'}$ = 4.6, $J_{4',3'}$ = 3.0, H-4′); 4.45 (ddt, 1H, $J_{3',2'}$ = 6.0, 3.5, $J_{3',OH}$ = 4.1, $J_{3',4'}$ = 3.0, H-3′); 4.99 (t, 1H, $J_{OH,5'}$ = 5.5, OH-5′); 5.36 (d, 1H, $J_{OH,3'}$ = 4.1, OH-3′); 6.47 (t, 1H, $J_{1',2'}$ = 7.2, 6.3, H-1′); 8.75 (s, 1H, H-8); 8.88 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.38 (CH_2-2′); 45.45 ($(CH_3)_2N$); 59.01(CH_2-pur); 61.75 (CH_2-5′); 70.84 (CH-3′); 83.86 (CH-1′); 88.16 (CH-4′); 133.43 (C-5); 144.65 (CH-8); 150.74 (C-4); 151.66 (CH-2); 157.39 (C-6). IR (KBr): ν = 3421, 2828, 2780, 1598, 1497, 1401, 1333, 1211, 1096, 1058, 646 cm^{-1}.

4.73. 6-[*N*,*N*-(Diisopropylamino)methyl]-9-(β-D-ribofuranosyl)purine (11f)

Prepared from **5f** (400 mg) by deprotection method A to give 132 mg (65%) of **11f** as foam. $[\alpha]_D^{20}$ − 42.2 (c = 1.67, H_2O). Exact mass (FAB HR MS) found: 366.2132; calcd for $C_{17}H_{28}N_5O_4$: 366.2141. FAB MS m/z (%): 366 (MH$^+$, 100); 276 (12); 234 (100); 190 (42); 148 (29); 134 (49). ^{1}H NMR (400 MHz, DMSO-d_6): 1.02 (d, 12H, J_{vic} = 6.6, $(CH_3)_2CH$); 3.14 (p, 2H, J_{vic} = 6.6, $CH(CH_3)_2$); 3.57 (dd, 1H, J_{gem} = 12.0, $J_{5'b,4'}$ = 4.1, H-5′b); 3.68 (dd, 1H, J_{gem} = 12.0, $J_{5'a,4'}$ = 4.1, H-5′a); 3.97 (q, 1H, $J_{4',5'}$ = 4.1, $J_{4',3'}$ = 3.4, H-4′); 4.05 (s, 2H, CH_2N); 4.18 (dd, 1H, $J_{3',2'}$ = 5.0, $J_{3',4'}$ = 3.4, H-3′); 4.66 (dd, 1H, $J_{2',1'}$ = 5.9, $J_{2',3'}$ = 5.0, H-2′); 6.02 (d, 1H, $J_{1',2'}$ = 5.9, H-1′); 8.76 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 20.89 and 20.90 ($(CH_3)_2CH$); 45.48 (CH_2N); 48.51 ($CH(CH_3)_2$); 61.54 (CH_2-5′); 70.59 (CH-3′); 73.69 (CH-2′); 85.92 (CH-4′); 87.65 (CH-1′); 132.85 (C-5); 144.37 (CH-8); 150.83 (C-4); 151.87 (CH-2); 161.73 (C-6); 172.21 (CO). IR (KBr): ν = 3354, 2962, 1597, 1499, 1405, 1335, 1212, 1119, 1086, 1055, 645 cm^{-1}.

4.74. 6-[*N*,*N*-(Diisopropylamino)methyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12f)

Prepared from **6f** (400 mg) by deprotection method A to give 145 mg (60%) of **12f** as white foam. $[\alpha]_D^{20}$ − 15.9 (c = 2.08, H_2O). Exact mass (FAB HR MS) found: 350.2185; calcd for $C_{17}H_{28}N_5O_3$: 350.2192. FAB MS m/z (%): 350 (MH$^+$, 53); 234 (47); 190 (41); 148 (23); 134 (100); 114 (97); 100 (23). ^{1}H NMR (400 MHz, DMSO-d_6): 1.02 (d, 12H, J_{vic} = 6.6, $(CH_3)_2CH$); 2.34 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.3, H-2′b); 2.79 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.3, $J_{2'a,3'}$ = 5.9, H-2′a); 3.13 (p, 2H, J_{vic} = 6.6, $CH(CH_3)_2$); 3.52 and 3.62 (2× dd, 2H, J_{gem} = 11.8, $J_{5',4'}$ = 4.6, H-5′); 3.89 (td, 1H, $J_{4',5'}$ = 4.6, $J_{4',3'}$ = 3.0, H-4′); 4.03 (s, 2H, CH_2N); 4.44 (ddd, 1H, $J_{3',2'}$ = 5.9, 3.3, $J_{3',4'}$ = 3.0, H-3′); 6.46 (t, 1H, $J_{1',2'}$ = 7.3, 6.3, H-1′); 8.72 (s, 1H, H-8); 8.84 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 20.91 ($(CH_3)_2CH$); 39.32 (CH_2-2′); 45.46 (CH_2N); 48.46 ($CH(CH_3)_2$); 61.80 (CH_2-5′); 70.90 (CH-3′); 83.80 (CH-1′); 88.14 (CH-4′); 132.85 (C-5); 144.24 (CH-8); 150.52 (C-4); 151.79 (CH-2); 161.63 (C-6). IR (KBr): ν = 3401, 2965, 1595, 1497, 1400, 1333, 1211, 1096, 1058, 647 cm^{-1}.

4.75. 6-[(*N*-Benzyl-*N*-methylamino)methyl]-9-(β-D-ribofuranosyl)purine (11g)

Prepared from **5g** (390 mg) by deprotection method A to give 170 mg (84%) of **11g** as yellowish hygroscopic solid. $[\alpha]_D^{20}$ − 36.6 (c = 2.27, MeOH). Anal. calcd for $C_{19}H_{23}N_5O_4{\cdot}H_2O$: C, 56.57; H, 6.25; N, 17.36; found: C, 56.55; H, 6.31; N, 17.05. Exact mass (FAB HR MS) found: 386.1836; calcd for $C_{19}H_{24}N_5O_4$: 386.1828. FAB MS m/z (%): 386 (MH$^+$, 4); 254 (23); 162 (16); 147 (8); 134 (34); 91 (100). ^{1}H NMR (500 MHz, DMSO-d_6): 2.17 (s, 3H, CH_3N); 3.58 (ddd, 1H, J_{gem} = 12.1, $J_{5'b,OH}$ = 6.1, $J_{5'b,4'}$ = 4.1, H-5′b); 3.67 (s, 2H, CH_2Ph); 3.69 (ddd, 1H, J_{gem} = 12.1, $J_{5'a,OH}$ = 5.0, $J_{5'a,4'}$ = 4.3, H-5′a); 3.98 (q, 1H, $J_{4',5'}$ = 4.3, 4.1 $J_{4',3'}$ = 3.1, H-4′); 4.05 (s, 2H, CH_2pur); 4.19 (q, 1H, $J_{3',OH}$ = 4.9, $J_{3',2'}$ = 4.9, $J_{3',4'}$ = 3.1, H-3′); 4.65 (q, 1H, $J_{2',OH}$ = 6.0, $J_{2',1'}$ = 5.8, $J_{2',3'}$ = 4.9, H-2′); 5.12 (t, 1H, $J_{OH,5'}$ = 6.1, 5.0, OH-5′); 5.25 (d, 1H, $J_{OH,3'}$ = 4.9, OH-3′); 5.54 (d, 1H, $J_{OH,2'}$ = 6.0, OH-2′); 6.04 (d, 1H, $J_{1',2'}$ = 5.8, H-1′); 7.23 (m, 1H, H-*p*-Ph); 7.31 (m, 2H, H-*m*-Ph); 7.37 (m, 2H, H-*o*-Ph); 8.80 (s, 1H, H-8); 8.92 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, DMSO-d_6): 42.08 (CH_3N); 57.13 (CH_2pur); 61.35 (CH_2Ph); 61.50 (CH_2-5′); 70.55 (CH-3′); 73.81 (CH-2′); 85.92 (CH-4′); 87.75 (CH-1′); 127.08 (CH-*p*-Ph); 128.29 (CH-*m*-Ph); 128.96 (CH-*o*-Ph); 133.53 (C-5); 139.04 (C-*i*-Ph); 144.81 (CH-8); 151.07 (C-4); 151.85 (CH-2); 157.85 (C-6). IR (KBr): ν = 3401, 2795, 1598, 1497, 1454, 1405, 1334, 1210, 1080, 1055, 646 cm^{-1}.

4.76. 6-[(*N*-Methyl-*N*-phenylamino)methyl]-9-(β-D-ribofuranosyl)purine (11h)

Prepared from **5h** (350 mg) by deprotection method A to give 160 mg (89%) of **11h** as white foam. $[\alpha]_D^{20}$ − 50.3

(c = 3.60, $CHCl_3$). Exact mass (FAB HR MS) found: 372.1678; calcd for $C_{18}H_{22}N_5O_4$: 372.1672. FAB MS m/z (%): 372 (MH^+, 19); 240 (23); 134 (36). ^{1}H NMR (400 MHz, DMSO-d_6): 3.22 (s, 3H, CH_3N); 3.56 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 6.0, $J_{5'b,4'}$ = 4.1, H-5′b); 3.68 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.2, $J_{5'a,4'}$ = 4.2, H-5′a); 3.97 (q, 1H, $J_{4',5'}$ = 4.2, 4.1, $J_{4',3'}$ = 3.6, H-4′); 4.18 (q, 1H, $J_{3',OH}$ = 4.9, $J_{3',2'}$ = 4.7, $J_{3',4'}$ = 3.6, H-3′); 4.65 (q, 1H, $J_{2',OH}$ = 6.0, $J_{2',1'}$ = 5.8, $J_{2',3'}$ = 4.7, H-2′); 4.99 (s, 2H, CH_2N); 5.10 (t, 1H, $J_{OH,5'}$ = 6.0, 5.2, OH-5′); 5.25 (d, 1H, $J_{OH,3'}$ = 4.9, OH-3′); 5.54 (d, 1H, $J_{OH,2'}$ = 6.0, OH-2′); 6.02 (d, 1H, $J_{1',2'}$ = 5.8, H-1′); 6.55 (m, 1H, H-*p*-Ph); 6.76 (m, 2H, H-*o*-Ph); 7.08 (m, 2H, H-*m*-Ph); 8.83 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.85 (CH_3N); 53.08 (CH_2N); 61.47 (CH_2-5′); 70.53 (CH-3′); 73.75 (CH-2′); 85.93 (CH-4′); 87.77 (CH-1′); 111.95 (CH-*o*-Ph); 115.98 (CH-*p*-Ph); 129.03 (CH-*m*-Ph); 132.44 (C-5); 144.86 (CH-8); 149.09 (C-*i*-Ph); 150.96 (C-4); 152.00 (CH-2); 158.91 (C-6). IR ($CHCl_3$): ν = 3305, 2825, 1596, 1507, 1418, 1335, 1116, 1083, 1048, 645 cm^{-1}.

4.77. 6-[(*N*-Methyl-*N*-phenylamino)methyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12h)

Prepared from **6 h** (230 mg) by deprotection method A to give 110 mg (80%) of **12h,** as white foam. $[\alpha]_D^{20}$ + 11.7 (c = 2.58, MeOH). Anal. calcd for $C_{18}H_{20}N_5O_3{\cdot}H_2O$: C, 57.90; H, 6.21; N, 18.76; found: C, 57.86; H, 5.85; N, 18.39. Exact mass (FAB HR MS) found: 378.1559; calcd for $C_{18}H_{21}N_5O_3Na$: 378.1542. FAB MS m/z (%): 378 (M+Na$^+$, 8); 240 (41); 224 (17); 160 (23); 147 (35); 134 (81); 77 (51). ^{1}H NMR (400 MHz, DMSO-d_6): 2.34 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.5, H-2′b); 2.79 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.1, $J_{2'a,3'}$ = 6.0, H-2′a); 3.21 (s, 3H, CH_3N); 3.52 and 3.62 (2× dt, 2H, J_{gem} = 11.7, $J_{5',OH}$ = 5.7, $J_{5',4'}$ = 4.6, H-5′); 3.88 (td, 1H, $J_{4',5'}$ = 4.6, $J_{4',3'}$ = 3.0, H-4′); 4.44 (ddt, 1H, $J_{3',2'}$ = 6.0, 3.5, $J_{3',OH}$ = 4.2, $J_{3',4'}$ = 3.0, H-3′); 4.98 (s, 2H, CH_2N); 4.98 (t, 1H, $J_{OH,5'}$ = 5.7, OH-5′); 5.35 (d, 1H, $J_{OH,3'}$ = 4.2, OH-3′); 6.46 (t, 1H, $J_{1',2'}$ = 7.1, 6.3, H-1′); 6.55 (m, 1H, H-*p*-Ph); 6.76 (m, 2H, H-*o*-Ph); 7.08 (m, 2H, H-*m*-Ph); 8.79 (s, 1H, H-8); 8.84 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.32 (CH_2-2′); 39.84 (CH_3-N); 53.08 (CH_2-pur); 61.74 (CH_2-5′); 70.83 (CH-3′); 83.90 (CH-1′); 88.17 (CH-4′); 111.94 (CH-*o*-Ph); 115.95 (CH-*p*-Ph); 129.01 (CH-*m*-Ph); 132.43 (C-5); 144.75 (CH-8); 149.08 (C-*i*-Ph); 150.66 (C-4); 151.90 (CH-2); 158.76 (C-6). IR (KBr): ν = 3408, 3066, 2820, 1598, 1507, 1419, 1334, 1210, 1096, 1056, 750, 645 cm^{-1}.

4.78. 6-[(*N*-Acetyl-*N*-cyclopropylamino)methyl]-9-(β-D-ribofuranosyl)purine (11i)

Prepared from **5i** (450 mg) by deprotection method B to give 180 mg (79%) of **11i** as white hygroscopic solid (mp ~50 °C). $[\alpha]_D^{20}$ − 26.8 (c = 3.53, H_2O). Anal. calcd for $C_{16}H_{21}N_5O_5{\cdot}1/2H_2O$: C, 51.61; H, 6.08; N, 18.81; found: C, 51.84; H, 6.09; N, 18.38. Exact mass (FAB HR MS) found: 364.1631; calcd for $C_{16}H_{22}N_5O_5$: 364.1621. FAB MS m/z (%): 364 (MH^+, 31); 232 (100); 190 (52); 134 (37). ^{1}H NMR (500 MHz, DMSO-d_6): 0.79 and 0.89 (2× m, 4H, CH_2-cycloprop); 2.20 (s, 3H, CH_3CO); 2.99 (tt, 1H, J_{vic} = 7.0, 3.9, CH-cycloprop); 3.57 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 5.9, $J_{5'b,4'}$ = 4.1, H-5′b); 3.68 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.3, $J_{5'a,4'}$ = 4.0, H-5′a); 3.97 (q, 1H, $J_{4',5'}$ = 4.1, 4.0, $J_{4',3'}$ = 3.5, H-4′); 4.18 (q, 1H, $J_{3',OH}$ = 4.7, $J_{3',2'}$ = 4.2, $J_{3',4'}$ = 3.7, H-3′); 4.64 (q, 1H, $J_{2',1'}$ = 5.8, $J_{2',OH}$ = 5.7, $J_{2',3'}$ = 4.2, H-2′); 4.91 (2× d, 2H, J_{gem} = 17.6, CH_2N); 5.11 (t, 1H, $J_{OH,5'}$ = 5.9, 5.3, OH-5′); 5.25 (d, 1H, $J_{OH,3'}$ = 4.7, OH-3′); 5.55 (d, 1H, $J_{OH,2'}$ = 5.7, OH-2′); 6.03 (d, 1H, $J_{1',2'}$ = 5.8, H-1′); 8.79 (s, 1H, H-8); 8.83 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, DMSO-d_6): 9.18 (CH_2-cycloprop); 22.55 (CH_3CO); 31.67 (CH-cycloprop); 48.29 (CH_2N); 61.50 (CH_2-5′); 70.56 (CH-3′); 73.82 (CH-2′); 85.93 (CH-4′); 87.77 (CH-1′); 131.73 (C-5); 144.63 (CH-8); 150.81 (C-4); 151.90 (CH-2); 158.19 (C-6); 173.12 (CO). IR (KBr): ν = 3400, 3012, 1635, 1596, 1498, 1420, 1403, 1335, 1211, 1121, 1083, 1055, 647 cm^{-1}.

4.79. 6-[(*N*-Acetyl-*N*-cyclopropylamino)methyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12i)

Prepared from **6i** (460 mg) by deprotection method B to give 225 mg (82%) of **12i** as white hygroscopic solid (mp 129–131 °C). $[\alpha]_D^{20}$ − 7.6 (c = 2.10, H_2O). Anal. calcd for $C_{16}H_{21}N_5O_4$: C, 55.32; H, 6.09; N, 20.16; found: C, 54.95; H, 6.17; N, 20.09. Exact mass (FAB HR MS) found: 370.1494; calcd for $C_{16}H_{21}N_5O_4$+Na: 370.1491. FAB MS m/z (%): 370 (M+Na$^+$, 28); 348 (MH^+, 6); 254 (17); 232 (31); 209 (12); 133 (88). ^{1}H NMR (400 MHz, DMSO-d_6): 0.78 and 0.88 (2× m, 2× 2H, CH_2-cycloprop); 2.20 (s, 3H, CH_3CO); 2.34 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.5, H-2′b); 2.79 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.3, $J_{2'a,3'}$ = 5.9, H-2′a); 2.98 (tt, 1H, J_{vic} = 7.0, 3.9, CH-cycloprop); 3.52 and 3.62 (2× dt, 2H, J_{gem} = 12.0, $J_{5',OH}$ = 5.4, $J_{5',4'}$ = 4.6, H-5′); 3.89 (td, 1H, $J_{4',5'}$ = 4.6, $J_{4',3'}$ = 3.0, H-4′); 4.45 (ddt, 1H, $J_{3',2'}$ = 5.9, 3.5, $J_{3',OH}$ = 4.1, $J_{3',4'}$ = 3.0, H-3′); 4.92 (s, 2H, CH_2N); 5.00 (t, 1H, $J_{OH,5'}$ = 5.4, OH-5′); 5.36 (d, 1H, $J_{OH,3'}$ = 4.1, OH-3′); 6.47 (dd, 1H, $J_{1',2'}$ = 7.3, 6.3, H-1′); 8.70 (s, 1H, H-8); 8.82 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 9.15 (CH_2-cycloprop); 22.53 (CH_3CO); 31.63 (CH-cycloprop); 39.36 (CH_2-2′); 48.24 (CH_2N); 61.74 (CH_2-5′); 70.83 (CH-3′); 83.86 (CH-1′); 88.17 (CH-4′); 131.72 (C-5); 144.52 (CH-8); 150.49 (C-4); 151.79 (CH-2); 158.04 (C-6); 173.06 (CO). IR (KBr): ν = 3392, 3269, 1626, 1594, 1500, 1422, 1404, 1332, 1210, 1097, 1060, 645 cm^{-1}.

4.80. 6-[*N*,*N*-Bis(2-hydroxyethyl)aminomethyl]-9-(β-D-ribofuranosyl)purine (11j)

Prepared from **5j** (260 mg) by deprotection method A to give 120 mg (90%) of **11j** as yellow hygroscopic oil. Product was purified by extraction of aqueous solution with Et_2O (removing of methyl toluate) and by chromatography on reverse phase (C-18, mobile phase—H_2O/MeOH). Exact mass (FAB HR MS) found: 370.1742; calcd for $C_{15}H_{24}N_5O_6$: 370.1727. FAB MS m/z (%): 392 (M+Na$^+$, 58); 370 (MH^+, 17); 238 (13); 134 (11); 115 (100). ^{1}H NMR (400 MHz, DMSO-d_6): 2.69 (m, 4H, CH_2N); 3.47 (m, 4H, CH_2O); 3.57 (dd, 1H, J_{gem} = 12.0, $J_{5'b,4'}$ = 4.0, H-5′b); 3.68 (ddd, 1H,

J_{gem} = 12.0, $J_{5'a,4'}$ = 4.1, H-5′a); 3.97 (q, 1H, $J_{4',5'}$ = 4.1, 4.0, $J_{4',3'}$ = 3.7, H-4′); 4.16 (s, 2H, CH_2-pur); 4.19 (dd, 1H, $J_{3',2'}$ = 4.8, $J_{3',4'}$ = 3.7, H-3′); 4.61 (dd, 1H, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 4.8, H-2′); 6.03 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 8.84 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 55.19 (CH_2-pur); 56.97 (CH_2N); 59.15 (CH_2O); 61.48 (CH_2-5′); 70.45 (CH-3′); 73.97 (CH-2′); 85.97 (CH-4′); 87.85 (CH-1′); 132.88 (C-5); 144.67 (CH-8); 150.92 (C-4); 151.78 (CH-2); 159.41 (C-6). IR (KBr): ν = 3428, 1601, 1585, 1499, 1406, 1334, 1212, 1082, 1048, 646 cm^{-1}.

4.81. 6-[*N,N*-Bis(2-hydroxyethyl)aminomethyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12j)

Prepared from **6j** (300 mg) by deprotection method A to give 140 mg (78%) of **12j** as white hygroscopic oil. Purification of product was accomplished analogously as above (see **11j**). $[\alpha]_D^{20}$ − 17.3 (*c* = 2.13, H_2O). Anal. calcd for $C_{15}H_{23}N_5O_5\cdot 1/2H_2O$: C, 49.72; H, 6.68; N, 19.33; found: C, 49.86; H, 6.62; N, 18.91. Exact mass (FAB HR MS) found: 354.1769; calcd for $C_{15}H_{24}N_5O_5$: 354.1777. FAB MS *m*/*z* (%): 354 (MH^+, 60); 238 (43); 174 (100); 134 (23). ^{1}H NMR (400 MHz, DMSO-d_6): 2.35 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.4, H-2′b); 2.69 (m, 4H, CH_2N); 2.79 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.2, $J_{2'a,3'}$ = 6.0, H-2′a); 3.46 (m, 4H, CH_2O); 3.53 and 3.62 (2× dd, 2H, J_{gem} = 11.7, $J_{5',4'}$ = 4.5, H-5′); 3.89 (td, 1H, $J_{4',5'}$ = 4.5, $J_{4',3'}$ = 3.0, H-4′); 4.15 (s, 2H, CH_2-pur); 4.45 (ddd, 1H, $J_{3',2'}$ = 6.0, 3.4, $J_{3',4'}$ = 3.0, H-3′); 6.48 (t, 1H, $J_{1',2'}$ = 7.2, 6.3, H-1′); 8.79 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.40 (CH_2-2′); 55.19 (CH_2-pur); 56.98 (CH_2N); 59.20 (CH_2O); 61.74 (CH_2-5′); 70.83 (CH-3′); 83.88 (CH-1′); 88.20 (CH-4′); 132.88 (C-5); 144.57 (CH-8); 150.61 (C-4); 151.68 (CH-2); 159.34 (C-6). IR (KBr): ν = 3392, 1597, 1585, 1497, 1402, 1334, 1212, 1093, 1057, 646 cm^{-1}.

4.82. 6-[(2-Acetylhydrazinyl)methyl]-9-(β-D- ribofuranosyl)purine (11k)

Prepared from **5k** (200 mg) by deprotection method B to give 79 mg (80%) of **11k** as white lyophilized solid. Exact mass (FAB HR MS) found: 339.1416; calcd for $C_{13}H_{19}N_6O_5$: 339.1417. FAB MS *m*/*z* (%): 339 (MH^+, 95); 207 (23); 148 (54); 134 (20). ^{1}H NMR (400 MHz, DMSO-d_6): 1.74 (s, 3H, CH_3); 3.57 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 6.0, $J_{5'b,4'}$ = 4.2, H-5′b); 3.69 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.3, $J_{5'a,4'}$ = 4.1, H-5′a); 3.98 (q, 1H, $J_{4',5'}$ = 4.2, 4.1, $J_{4',3'}$ = 3.6, H-4′); 4.19 (td, 1H, $J_{3',OH}$ = 4.9, $J_{3',2'}$ = 4.9, $J_{3',4'}$ = 3.6, H-3′); 4.30 (d, 2H, $J_{CH_2,NH}$ = 5.8, CH_2NH); 4.64 (q, 1H, $J_{2',OH}$ = 5.8, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 4.9, H-2′); 5.12 (t, 1H, $J_{OH,5'}$ = 6.0, 5.3, OH-5′); 5.26 (d, 1H, $J_{OH,3'}$ = 4.9, OH-3′); 5.54 (d, 1H, $J_{OH,2'}$ = 5.8, OH-2′); 5.60 (dt, 1H, $J_{NH,CH2}$ = 5.8, $J_{NH,NH}$ = 6.4, N**H**-CH_2); 6.04 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 8.81 (s, 1H, H-8); 8.90 (s, 1H, H-2); 9.40 (d, 1H, $J_{NH,NH}$ = 6.4, N**H**-Ac). ^{13}C NMR (100.6 MHz, DMSO-d_6): 20.84 (CH_3); 52.00 (CH_2NH); 61.46 (CH_2-5′); 70.49 (CH-3′); 73.83 (CH-2′); 85.89 (CH-4′); 87.77 (CH-1′); 132.59 (C-5); 144.79 (CH-8); 150.90 (C-4); 151.89 (CH-2); 157.44 (C-6); 168.36 (CO). IR (KBr): ν = 3392, 3292, 1654, 1600, 1585, 1498, 1405, 1335, 1211, 1122, 1085, 1055, 645 cm^{-1}.

4.83. 6-[(Piperidin-1-yl)methyl]-9-(β-D-ribofuranosyl)purine (11l)

Prepared from **5l** (600 mg) by deprotection method A to give 195 mg (65%) of **11l** as white hygroscopic solid (mp 80–82 °C). $[\alpha]_D^{20}$ − 32.5 (*c* = 1.26, H_2O). Exact mass (FAB HR MS) found: 350.1818; calcd for $C_{16}H_{24}N_5O_4$: 350.1828. FAB MS *m*/*z* (%): 350 (MH^+, 22); 218 (28); 134 (8). ^{1}H NMR (500 MHz, DMSO-d_6): 1.33 (m, 2H, CH_2-pip); 1.45 (p, 4H, J_{vic} = 5.8, CH_2-pip); 2.47 (bm, 4H, CH_2N-pip); 3.57 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 5.7, $J_{5'b,4'}$ = 4.0, H-5′b); 3.68 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.3, $J_{5'a,4'}$ = 4.2, H-5′a); 3.92 (s, 2H, CH_2N); 3.98 (q, 1H, $J_{4',5'}$ = 4.2, 4.0, $J_{4',3'}$ = 3.3, H-4′); 4.19 (q, 1H, $J_{3',2'}$ = 4.9, $J_{3',OH}$ = 4.6, $J_{3',4'}$ = 3.3, H-3′); 4.65 (q, 1H, $J_{2',OH}$ = $J_{2',1'}$ = 5.8, $J_{2',3'}$ = 4.9, H-2′); 5.13 (t, 1H, $J_{OH,5'}$ = 5.7, 5.3, OH-5′); 5.27 (d, 1H, $J_{OH,3'}$ = 4.6, OH-3′); 5.57 (d, 1H, $J_{OH,2'}$ = 5.8, OH-2′); 6.03 (d, 1H, $J_{1',2'}$ = 5.8, H-1′); 8.79 (s, 1H, H-8); 8.88 (s, 1H, H-2). ^{13}C NMR (125.8 MHz, DMSO-d_6): 23.90 and 25.74 (CH_2-pip); 54.32 (CH_2N-pip); 58.83 (CH_2N); 61.47 (CH_2-5′); 70.55 (CH-3′); 73.78 (CH-2′); 85.92 (CH-4′); 87.70 (CH-1′); 133.56 (C-5); 144.80 (CH-8); 151.02 (C-4); 151.77 (CH-2); 157.40 (C-6). IR (KBr): ν = 3402, 2936, 2856, 1598, 1499, 1407, 1334, 1210, 1102, 1056, 646 cm^{-1}.

4.84. 6-[(Piperidin-1-yl)methyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12l)

Prepared from **6l** (480 mg) by deprotection method A to give 228 mg (81%) of **12l** as white hygroscopic solid (mp ~60 °C). $[\alpha]_D^{20}$ − 16.6 (*c* = 2.47, H_2O). Anal. calcd for $C_{16}H_{23}N_5O_3\cdot H_2O$: C, 54.69; H, 7.17; N, 19.93; found: C, 54.44; H, 7.08; N, 19.45. Exact mass (FAB HR MS) found: 334.1888; calcd for $C_{16}H_{24}N_5O_3$: 334.1879. FAB MS *m*/*z* (%): 334 (MH^+, 97); 218 (100); 134 (45). ^{1}H NMR (400 MHz, DMSO-d_6): 1.32 (m, 2H, CH_2-pip); 1.45 (p, 4H, J_{vic} = 5.7, CH_2-pip); 2.34 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.5, H-2′b); 2.46 (bt, 4H, J_{vic} = 5.7, CH_2N-pip); 2.79 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.4, $J_{2'a,3'}$ = 5.9, H-2′a); 3.52 and 3.62 (2× ddd, 2H, J_{gem} = 11.8, $J_{5',4'}$ = 4.6, H-5′); 3.89 (td, 1H, $J_{4',5'}$ = 4.6, $J_{4',3'}$ = 3.0, H-4′); 3.90 (s, 2H, CH_2N); 4.45 (dt, 1H, $J_{3',2'}$ = 5.9, 3.5, $J_{3',4'}$ = 3.0, H-3′); 5.00 (bs, 1H, OH-5′); 5.38 (bs, 1H, OH-3′); 6.47 (t, 1H, $J_{1',2'}$ = 7.4, 6.3, H-1′); 8.74 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 23.92 and 25.75 (CH_2-pip); 39.37 (CH_2-2′); 54.33 (CH_2N-pip); 58.84 (CH_2N); 61.76 (CH_2-5′); 70.86 (CH-3′); 83.87 (CH-1′); 88.17 (CH-4′); 133.58 (C-5); 144.69 (CH-8); 150.72 (C-4); 151.68 (CH-2); 157.35 (C-6). IR (KBr): ν = 3413, 2935, 2855, 1598, 1497, 1403, 1332, 1210, 1100, 1057, 646 cm^{-1}.

4.85. 6-[(Morpholin-4-yl)methyl]-9-(β-D-ribofuranosyl)purine (11m)

Prepared from **5m** (340 mg) by deprotection method A to give 116 mg (69%) of **11m** as yellowish hygroscopic

solid (mp ~60 °C). $[\alpha]_D^{20}$ − 34.3 (c = 2.07, H_2O). Exact mass (FAB HR MS) found: 352.1617; calcd for $C_{15}H_{22}N_5O_5$: 352.1621. FAB MS m/z (%): 352 (MH^+, 100); 220 (98); 134 (33). ^{1}H NMR (400 MHz, DMSO-d_6): 2.52 (m, 4H, CH_2N-morph); 3.54 (m, 4H, CH_2O-morph); 3.57 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 6.0, $J_{5'b,4'}$ = 4.0, H-5′b); 3.69 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.2, $J_{5'a,4'}$ = 4.9, H-5′a); 3.96 (s, 2H, CH_2N); 3.98 (q, 1H, $J_{4',5'}$ = 4.2, 4.0, $J_{4',3'}$ = 3.5, H-4′); 4.19 (td, 1H, $J_{3',OH}$ = 5.0, $J_{3',2'}$ = 4.9, $J_{3',4'}$ = 3.5, H-3′); 4.65 (q, 1H, $J_{2',OH}$ = 6.0, $J_{2',1'}$ = 5.8, $J_{2',3'}$ = 4.9, H-2′); 5.11 (t, 1H, $J_{OH,5'}$ = 6.0, 5.2, OH-5′); 5.25 (d, 1H, $J_{OH,3'}$ = 5.0, OH-3′); 5.54 (d, 1H, $J_{OH,2'}$ = 6.0, OH-2′); 6.03 (d, 1H, $J_{1',2'}$ = 5.8, H-1′); 8.80 (s, 1H, H-8); 8.90 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 53.89 (CH_2N-morph); 58.69 (CH_2N); 61.75 (CH_2-5′); 66.63 (CH_2O-morph); 70.81 (CH-3′); 74.08 (CH-2′); 86.19 (CH-4′); 88.03 (CH-1′); 133.81 (C-5); 145.19 (CH-8); 151.38 (C-4); 152.09 (CH-2); 157.10 (C-6). IR (KBr): ν = 3360, 2825, 1599, 1499, 1455, 1407, 1335, 1210, 1114, 1057, 865, 647 cm^{-1}.

4.86. 6-[(Morpholin-4-yl)methyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12m)

Prepared from **6m** (550 mg) by deprotection method A to give 275 mg (85%) of **12m** as yellowish hygroscopic solid (mp 128–130 °C). $[\alpha]_D^{20}$ − 18.4 (c = 1.81, H_2O). Anal. calcd for $C_{15}H_{21}N_5O_4{\cdot}H_2O$: C, 50.98; H, 6.56; N, 19.82; found: C, 50.82; H, 6.28; N, 19.56. Exact mass (FAB HR MS) found: 336.1680; calcd for $C_{15}H_{22}N_5O_4$: 336.1672. FAB MS m/z (%): 336 (MH^+, 19); 220 (100); 134 (52). ^{1}H NMR (400 MHz, DMSO-d_6): 2.35 (ddd, 1H, J_{gem} = 13.4, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.5, H-2′b); 2.51 (m, 4H, CH_2N-morph); 2.79 (ddd, 1H, J_{gem} = 13.4, $J_{2'a,1'}$ = 7.3, $J_{2'a,3'}$ = 5.9, H-2′a); 3.52 (ddd, 1H, J_{gem} = 11.8, $J_{5'b,OH}$ = 5.8, $J_{5'b,4'}$ = 4.6, H-5′b); 3.54 (m, 4H, CH_2O-morph); 3.62 (ddd, 1H, J_{gem} = 11.8, $J_{5'a,OH}$ = 5.5, $J_{5'a,4'}$ = 4.6, H-5′a); 3.89 (td, 1H, $J_{4',5'}$ = 4.6, $J_{4',3'}$ = 3.0, H-4′); 3.95 (s, 2H, CH_2N); 4.45 (m, 1H, $J_{3',2'}$ = 5.9, 3.5, $J_{3',OH}$ = 4.2, $J_{3',4'}$ = 3.0, H-3′); 5.00 (t, 1H, $J_{OH,5'}$ = 5.8, 5.5, OH-5′); 5.36 (d, 1H, $J_{OH,3'}$ = 4.2, OH-3′); 6.47 (t, 1H, $J_{1',2'}$ = 7.3, 6.3, H-1′); 8.76 (s, 1H, H-8); 8.88 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.36 (CH_2-2′); 53.60 (CH_2N-morph); 58.40 (CH_2N); 61.73 (CH_2-5′); 66.34 (CH_2O-morph); 70.83 (CH-3′); 83.87 (CH-1′); 88.17 (CH-4′); 133.53 (C-5); 144.82 (CH-8); 150.79 (C-4); 151.72 (CH-2); 156.69 (C-6). IR (KBr): ν = 3402, 2819, 1599, 1498, 1455, 1403, 1334, 1210, 1112, 1056, 863, 645 cm^{-1}.

4.87. 6-[(Thiazolidin-3-yl)methyl]-9-(β-D-ribofuranosyl)purine (11n)

Prepared from **5n** (450 mg) by deprotection method A to give 148 mg (67%) of **11n** as lyophilized solid. $[\alpha]_D^{20}$ − 38.1 (c = 2.73, H_2O). Anal. calcd for $C_{14}H_{19}N_5O_4S{\cdot}H_2O$: C, 45.27; H, 5.70; N, 18.86; found: C, 45.12; H, 5.43; N, 18.42. Exact mass (FAB HR MS) found: 354.1234; calcd for $C_{14}H_{20}N_5O_4S$: 354.1236. FAB MS m/z (%): 354 (MH^+, 22); 222 (17); 134 (13). ^{1}H NMR (400 MHz, DMSO-d_6): 2.94 (t, 2H, J_{vic} = 6.4, H-5-thiazolidine); 3.11 (t, 2H, J_{vic} = 6.4, H-4-thiazolidine); 3.57 (dd, 1H, J_{gem} = 12.0, $J_{5'b,4'}$ = 3.8, H-5′b); 3.69 (dd, 1H, J_{gem} = 12.0, $J_{5'a,4'}$ = 4.2, H-5′a); 3.95 (s, 2H, H-2-thiazolidine); 3.98 (q, 1H, $J_{4',5'}$ = 4.2, 3.8, $J_{4',3'}$ = 3.7, H-4′); 4.17 (s, 2H, CH_2N); 4.19 (dd, 1H, $J_{3',2'}$ = 5.0, $J_{3',4'}$ = 3.7, H-3′); 4.64 (t, 1H, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 5.0, H-2′); 5.10 (bs, 1H, OH-5′); 5.25 (bs, 1H, OH-3′); 5.54 (bs, 1H, OH-2′); 6.04 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 8.82 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 29.19 (CH_2-5-thiazolidine); 52.74 (CH_2-2-thiazolidine); 58.15 (CH_2-4-thiazolidine); 61.08 (CH_2N); 61.44 (CH_2-5′); 70.48 (CH-3′); 73.83 (CH-2′); 85.89 (CH-4′); 87.81 (CH-1′); 133.12 (C-5); 144.98 (CH-8); 151.16 (C-4); 151.96 (CH-2); 157.61 (C-6). IR (KBr): ν = 3425, 1600, 1499, 1405, 1335, 1210, 1120, 1083, 1051, 645 cm^{-1}.

4.88. 6-[(Indol-1-yl)methyl]-9-(β-D-ribofuranosyl)purine (11p)

Prepared from **5p** (175 mg) by deprotection method A to give 85 mg (93%) of **11p** as yellowish foam. $[\alpha]_D^{20}$ − 32.7 (c = 1.99, MeOH). Exact mass (FAB HR MS) found: 382.1532; calcd for $C_{19}H_{20}N_5O_4$: 382.1515. FAB MS m/z (%): 382 (MH^+, 52); 250 (100); 134 (14); 117 (38). ^{1}H NMR (400 MHz, DMSO-d_6): 3.57 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 6.0, $J_{5'b,4'}$ = 4.1, H-5′b); 3.68 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.2, $J_{5'a,4'}$ = 4.2, H-5′a); 3.97 (q, 1H, $J_{4',5'}$ = 4.2, 4.1, $J_{4',3'}$ = 3.5, H-4′); 4.19 (td, 1H, $J_{3',OH}$ = 5.0, $J_{3',2'}$ = 4.8, $J_{3',4'}$ = 3.5, H-3′); 4.64 (q, 1H, $J_{2',OH}$ = 6.0, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 4.8, H-2′); 5.09 (t, 1H, $J_{OH,5'}$ = 6.0, 5.2, OH-5′); 5.24 (d, 1H, $J_{OH,3'}$ = 5.0, OH-3′); 5.53 (d, 1H, $J_{OH,2'}$ = 6.0, OH-2′); 5.86 (s, 2H, CH_2N); 6.03 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 6.46 (dd, 1H, $J_{3,2}$ = 3.2, $J_{3,7}$ = 0.8, H-3-indole); 6.98 (ddd, 1H, $J_{5,4}$ = 7.9, $J_{5,6}$ = 7.0, $J_{5,7}$ = 1.1, H-5-indole); 7.06 (ddd, 1H, $J_{6,7}$ = 8.2, $J_{6,5}$ = 7.0, $J_{6,4}$ = 1.2, H-6-indole); 7.49 (dq, 1H, $J_{7,6}$ = 8.2, $J_{7,5}$ = 1.1, $J_{7,3}$ = 0.8, $J_{7,4}$ = 0.8, H-7-indole); 7.52 (dt, 1H, $J_{4,5}$ = 7.9, $J_{4,6}$ = 1.2, $J_{4,7}$ = 0.8, H-4-indole); 7.54 (d, 1H, $J_{2,3}$ = 3,2, H-2-indole); 8.83 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 46.58 (CH_2-pur); 61.41 (CH_2-5′); 70.48 (CH-3′); 73.79 (CH-2′); 85.94 (CH-4′); 87.89 (CH-1′); 101.16 (CH-3-indole); 110.10 (CH-7-indole); 119.29 (CH-5-indole); 120.52 (CH-4-indole); 121.31 (CH-6-indole); 128.36 (C-3a-indole); 129.98 (CH-2-indole); 132.09 (C-5); 136.19 (C-7a-indole); 145.47 (CH-8); 151.30 (C-4); 152.17 (CH-2); 155.65 (C-6). IR (KBr): ν = 3422, 1600, 1498, 1463, 1400, 1335, 1208, 1120, 1082, 1053, 744, 645 cm^{-1}.

4.89. 6-[(Pyrazol-1-yl)methyl]-9-(β-D-ribofuranosyl)purine (11q)

Prepared from **5q** (205 mg) by deprotection method A to give 82 mg (83%) of **11q** as white solid (mp 76–78 °C). $[\alpha]_D^{20}$ − 40.2 (c = 2.93, MeOH). Anal. calcd for $C_{14}H_{16}N_6O_4{\cdot}H_2O$: C, 48.00; H, 5.18; N, 23.99; found: C, 48.06; H, 4.97; N, 23.56. Exact mass (FAB HR MS) found: 333.1305; calcd for $C_{14}H_{17}N_6O_4$: 333.1311. FAB MS m/z (%): 333 (MH^+, 59); 201 (44); 133 (13). ^{1}H NMR (400 MHz, DMSO-d_6): 3.57 (ddd, 1H, J_{gem} = 11.8, $J_{5'b,OH}$ = 5.8, $J_{5'b,4'}$ = 4.2, H-5′b); 3.69 (ddd, 1H, J_{gem} = 11.8, $J_{5'a,OH}$ = 5.1, $J_{5'a,4'}$ = 4.2, H-

5′a); 3.98 (q, 1H, $J_{4',5'} = 4.2$, $J_{4',3'} = 3.5$, H-4′); 4.19 (td, 1H, $J_{3',OH} = 5.0$, $J_{3',2'} = 4.8$, $J_{3',4'} = 3.5$, H-3′); 4.64 (q, 1H, $J_{2',OH} = 5.9$, $J_{2',1'} = 5.7$, $J_{2',3'} = 4.8$, H-2′); 5.10 (t, 1H, $J_{OH,5'} = 5.8$, 5.1, OH-5′); 5.25 (d, 1H, $J_{OH,3'} = 5.0$, OH-3′); 5.56 (d, 1H, $J_{OH,2'} = 5.9$, OH-2′); 5.81 (s, 2H, CH_2-pur); 6.04 (d, 1H, $J_{1',2'} = 5.7$, H-1′); 6.28 (t, 1H, $J_{4,3} = 1.8$, $J_{4,5} = 2.1$, H-4-pyrazole); 7.41 (dd, 1H, $J_{3,4} = 1.8$, $J_{3,5} = 0.4$, H-3-pyrazole); 7.92 (dd, 1H, $J_{5,4} = 2.1$, $J_{5,3} = 0.4$, H-5-pyrazole); 8.87 (s, 2H, H-8 and H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 51.87 (CH_2-N); 61.41 (CH_2-5′); 70.48 (CH-3′); 73.84 (CH-2′); 85.92 (CH-4′); 87.87 (CH-1′); 105.50 (CH-4-pyrazole); 131.63 (CH-5-pyrazole); 132.14 (C-5); 139.27 (CH-3-pyrazole); 145.40 (CH-8); 151.33 (C-4); 152.08 (CH-2); 155.07 (C-6). IR (KBr): ν = 3351, 3119, 1601, 1498, 1400, 1335, 1209, 1121, 1088, 1054, 760, 645 cm^{-1}.

4.90. 6-[(4-Oxopyridin-1(4*H*)-yl)methyl]-9-(β-D-ribofuranosyl)purine (11r)

Prepared from **5r** (500 mg) by deprotection method B to give 175 mg (70%) of **11r** as white crystals (mp 202–204 °C). $[\alpha]_D^{20}$ − 36.2 (c = 2.87, H_2O). Anal. calcd for $C_{16}H_{17}N_5O_5 \cdot 1/2H_2O$: C, 52.17; H, 4.93; N, 19.01; found: C, 51.86; H, 4.85; N, 18.58. Exact mass (FAB HR MS) found: 360.1300; calcd for $C_{16}H_{18}N_5O_5$: 360.1308. FAB MS m/z (%): 360 (MH^+, 71); 228 (100); 134 (32); 96 (87). ^{1}H NMR (400 MHz, DMSO-d_6): 3.57 (br dt, 1H, $J_{gem} = 12.0$, $J_{5'b,OH} = 4.5$, $J_{5'b,4'} = 4.1$, H-5′b); 3.69 (br dt, 1H, $J_{gem} = 12.0$, $J_{5'a,OH} = 4.5$, $J_{5'a,4'} = 4.1$, H-5′a); 3.98 (q, 1H, $J_{4',5'} = 4.1$, $J_{4',3'} = 3.6$, H-4′); 4.19 (dd, 1H, $J_{3',2'} = 5.1$, $J_{3',4'} = 3.6$, H-3′); 4.63 (t, 1H, $J_{2',1'} = 5.6$, $J_{2',3'} = 5.1$, H-2′); 5.12 (bt, 1H, $J_{OH,5'a} = 4.5$, OH-5′); 5.41 (bs, 1H, OH-3′); 5.64 (s, 2H, CH_2N); 5.69 (bs, 1H, OH-2′); 6.05 (d, 1H, $J_{1',2'} = 5.6$, H-1′); 6.09 (m, 2H, H-3,5-py); 7.73 (m, 2H, H-2,6-py); 8.90 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 55.53 (CH_2N); 61.38 (CH_2-5′); 70.42 (CH-3′); 73.94 (CH-2′); 85.93 (CH-4′); 87.93 (CH-1′); 117.50 (CH-3,5-py); 131.65 (C-5); 142.25 (CH-2,6-py); 145.50 (CH-8); 151.18 (C-4); 152.21 (CH-2); 154.78 (C-6); 177.46 (C-4-py).

IR (KBr): ν = 3401, 3221, 1646, 1606, 1554, 1491, 1403, 1340, 1202, 1124, 1082, 1064, 646 cm^{-1}.

4.91. 6-[(4-Oxopyridin-1(4*H*)-yl)methyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12r)

Prepared from **6r** (515 mg) by deprotection method B to give 297 mg (97%) of **12r** as white crystals (mp 225–227 °C). $[\alpha]_D^{20}$ − 19.8 (c = 3.07, H_2O). Anal. calcd for $C_{16}H_{17}N_5O_4 \cdot H_2O$: C, 53.18; H, 5.30; N, 19.38; found: C, 53.38; H, 4.96; N, 18.97. Exact mass (FAB HR MS) found: 344.1364; calcd for $C_{16}H_{18}N_5O_4$: 344.1359. FAB MS m/z (%): 344 (MH^+, 11); 228 (8). ^{1}H NMR (400 MHz, DMSO-d_6): 2.36 (ddd, 1H, $J_{gem} = 13.3$, $J_{2'b,1'} = 6.4$, $J_{2'b,3'} = 3.7$, H-2′b); 2.78 (ddd, 1H, $J_{gem} = 13.3$, $J_{2'a,1'} = 7.1$, $J_{2'a,3'} = 6.0$, H-2′a); 3.52 (dd, 1H, $J_{gem} = 11.8$, $J_{5'b,4'} = 4.6$, H-5′b); 3.62 (dd, 1H, $J_{gem} = 11.8$, $J_{5'a,4'} = 4.8$, H-5′a); 3.89 (td, 1H, $J_{4',5'} = 4.8$, 4.6, $J_{4',3'} = 3.1$, H-4′); 4.45 (dt, 1H, $J_{3',2'} = 6.0$, 3.7, $J_{3',4'} = 3.1$, H-3′); 5.05 (bs, 1H, OH-5′); 5.45 (bs, 1H, OH-3′); 5.63 (s, 2H, CH_2N); 6.09 (m, 2H, H-3,5-py); 6.48 (t, 1H, $J_{1',2'} = 7.1$, 6.4, H-1′); 7.72 (m, 2H, H-2,6-py); 8.86 (s, 1H, H-8); 8.90 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.21 (CH_2-2′); 55.33 (CH_2N); 61.43 (CH_2-5′); 70.50 (CH-3′); 83.84 (CH-1′); 88.03 (CH-4′); 117.29 (CH-3,5-py); 131.47 (C-5); 142.06 (CH-2,6-py); 145.26 (CH-8); 150.69 (C-4); 151.91 (CH-2); 154.44 (C-6); 177.26 (C-4-py). IR (KBr): ν = 3393, 3225, 1646, 1603, 1555, 1491, 1401, 1341, 1207, 1057, 645 cm^{-1}.

4.92. 6-[(2-Oxopyridin-1(2*H*)-yl)methyl]-9-(β-D-ribofuranosyl)purine (11s)

Prepared from **5s** (610 mg) by deprotection method B to give 220 mg (72%) of **11s** as white hygroscopic solid (mp ~90 °C). $[\alpha]_D^{20}$ − 34.4 (c = 3.14, H_2O). Anal. calcd for $C_{16}H_{17}N_5O_5 \cdot H_2O$: C, 50.93; H, 5.08; N, 18.56; found: C, 51.31; H, 4.93; N, 18.15. Exact mass (FAB HR MS) found: 360.1299; calcd for $C_{16}H_{18}N_5O_5$: 360.1308. FAB MS m/z (%): 360 (MH^+, 34); 228 (100); 134 (22); 96 (10). ^{1}H NMR (500 MHz, DMSO-d_6): 3.57 (ddd, 1H, $J_{gem} = 12.0$, $J_{5'b,OH} = 6.0$, $J_{5'b,4'} = 4.1$, H-5′b); 3.69 (ddd, 1H, $J_{gem} = 12.0$, $J_{5'a,OH} = 5.2$, $J_{5'a,4'} = 4.2$, H-5′a); 3.98 (q, 1H, $J_{4',5'} = 4.2$, 4.1, $J_{4',3'} = 3.4$, H-4′); 4.19 (td, 1H, $J_{3',OH} = 4.9$, $J_{3',2'} = 4.8$, $J_{3',4'} = 3.4$, H-3′); 4.65 (q, 1H, $J_{2',OH} = 6.0$, $J_{2',1'} = 5.8$, $J_{2',3'} = 4.8$, H-2′); 5.10 (t, 1H, $J_{OH,5'} = 6.0$, 5.2, OH-5′); 5.25 (d, 1H, $J_{OH,3'} = 4.9$, OH-3′); 5.57 (d, 1H, $J_{OH,2'} = 6.0$, OH-2′); 5.60 (s, 2H, CH_2N); 6.04 (d, 1H, $J_{1',2'} = 5.8$, H-1′); 6.29 (td, 1H, $J_{5,6} = 6.8$, $J_{5,4} = 6.6$, $J_{5,3} = 1.4$, H-5-py); 6.37 (ddd, 1H, $J_{3,4} = 8.9$, $J_{3,5} = 1.4$, $J_{3,6} = 0.6$, H-3-py); 7.48 (ddd, 1H, $J_{4,3} = 8.9$, $J_{4,5} = 6.6$, $J_{4,6} = 2.1$, H-4-py); 7.85 (ddd, 1H, $J_{6,5} = 6.8$, $J_{6,4} = 2.1$, $J_{6,3} = 0.6$, H-6-py); 8.81 (s, 1H, H-2); 8.82 (s, 1H, H-8). ^{13}C NMR (125.8 MHz, DMSO-d_6): 49.75 (CH_2N); 61.47 (CH_2-5′); 70.54 (CH-3′); 73.83 (CH-2′); 85.95 (CH-4′); 87.86 (CH-1′); 105.21 (CH-5-py); 119.66 (CH-3-py); 131.68 (C-5); 140.71 (CH-4-py); 140.95 (CH-6-py); 144.91 (CH-8); 150.80 (C-4); 151.95 (CH-2); 155.99 (C-6); 161.72 (C-2-py). IR (KBr): ν = 3401, 1657, 1596, 1578, 1542, 1497, 1414, 1336, 1211, 1121, 1084, 1055, 646 cm^{-1}.

4.93. 6-[(2-Oxopyridin-1(2*H*)-yl)methyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12s)

Prepared from **6s** (515 mg) by deprotection method B to give 297 mg (97%) of **12s** as white crystals (mp 148–150 °C). $[\alpha]_D^{20}$ − 14.5 (c = 3.32, H_2O). Anal. calcd for $C_{16}H_{17}N_5O_4$: C, 55.97; H, 4.99; N, 20.40; found: C, 55.66; H, 5.12; N, 20.01. Exact mass (FAB HR MS) found: 344.1369; calcd for $C_{16}H_{18}N_5O_4$: 344.1359. FAB MS m/z (%): 344 (MH^+, 8); 228 (82); 134 (16). ^{1}H NMR (400 MHz, DMSO-d_6): 2.35 (ddd, 1H, $J_{gem} = 13.3$, $J_{2'b,1'} = 6.4$, $J_{2'b,3'} = 3.5$, H-2′b); 2.80 (ddd, 1H, $J_{gem} = 13.3$, $J_{2'a,1'} = 7.3$, $J_{2'a,3'} = 5.9$, H-2′a); 3.52 and 3.62 (2× dt, 2H, $J_{gem} = 11.8$, $J_{5',OH} = 5.5$, $J_{5',4'} = 4.7$, H-5′); 3.89 (td, 1H, $J_{4',5'} = 4.7$, $J_{4',3'} = 3.0$, H-4′); 4.45 (ddt, 1H, $J_{3',2'} = 5.9$, 3.5, $J_{3',OH} = 4.0$, $J_{3',4'} = 3.0$, H-3′); 4.99 (t, 1H, $J_{OH,5'} = 5.5$, OH-5′); 5.37 (d, 1H, $J_{OH,3'} = 4.0$, OH-3′); 5.58 (s, 2H, CH_2N); 6.29 (td, 1H, $J_{5,6} = 6.8$, $J_{5,4} = 6.6$, $J_{5,3} = 1.4$, H-5-py);

6.37 (ddd, 1H, $J_{3,4}$ = 9.0, $J_{3,5}$ = 1.4, $J_{3,6}$ = 0.6, H-3-py); 6.48 (t, 1H, $J_{1',2'}$ = 7.3, 6.4, H-1′); 7.47 (ddd, 1H, $J_{4,3}$ = 9.0, $J_{4,5}$ = 6.6, $J_{4,6}$ = 2.1, H-4-py); 7.85 (ddd, 1H, $J_{6,5}$ = 6.8, $J_{6,4}$ = 2.1, $J_{6,3}$ = 0.6, H-6-py); 8.79 (s, 1H, H-8); 8.80 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.35 (CH_2-2′); 49.71 (CH_2N); 61.72 (CH_2-5′); 70.81 (CH-3′); 83.96 (CH-1′); 88.20 (CH-4′); 105.18 (CH-5-py); 119.65 (CH-3-py); 131.67 (C-5); 140.68 (CH-4-py); 140.94 (CH-6-py); 144.82 (CH-8); 150.50 (C-4); 151.85 (CH-2); 155.86 (C-6); 161.71 (C-2-py). IR (KBr): ν = 3444, 3282, 1660, 1601, 1579, 1538, 1491, 1417, 1339, 1216, 1103, 1063, 647 cm^{-1}.

4.94. 6-[(2-Oxopyrrolidin-1-yl)methyl]-9-(β-D-ribofuranosyl)purine (11t)

Prepared from **5t** (280 mg) by deprotection method B to give 85 mg (61%) of **1t** as foam. $[\alpha]_D^{20}$ − 32.0 (c = 2.18, H_2O). Exact mass (FAB HR MS) found: 350.1455; calcd for $C_{15}H_{20}N_5O_5$: 350.1464. FAB MS m/z (%): 350 (MH^+, 5); 218 (38); 134 (10). ^{1}H NMR (500 MHz, DMSO-d_6): 1.99 (m, 2H, H-4-pyrr); 2.30 (t, 2H, J_{vic} = 8.4, H-3-pyrr); 3.48 (t, 2H, J_{vic} = 7.2, H-5-pyrr); 3.57 (dd, 1H, J_{gem} = 12.0, $J_{5'b,4'}$ = 4.0, H-5′b); 3.69 (dd, 1H, J_{gem} = 12.0, $J_{5'a,4'}$ = 4.1, H-5′a); 3.97 (q, 1H, $J_{4',5'}$ = 4.1, 4.0, $J_{4',3'}$ = 3.6, H-4′); 4.19 (dd, 1H, $J_{3',2'}$ = 4.9, $J_{3',4'}$ = 3.6, H-3′); 4.63 (t, 1H, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 4.9, H-2′); 4.85 (2× d, 2H, J_{gem} = 17.1, CH_2N); 5.10 (bs, 1H, OH-5′); 5.30 (bs, 1H, OH-3′); 5.60 (bs, 1H, OH-2′); 6.04 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 8.82 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 17.76 (CH_2-4-pyrr); 30.22 (CH_2-3-pyrr); 43.64 (CH_2N); 47.52 (CH_2-5-pyrr); 61.44 (CH_2-5′); 70.50 (CH-3′); 73.87 (CH-2′); 85.91 (CH-4′); 87.79 (CH-1′); 132.07 (C-5); 144.96 (CH-8); 151.03 (C-4); 152.00 (CH-2); 156.54 (C-6); 174.68 (C-2-pyrr). IR ($CHCl_3$): ν = 3318, 1675, 1598, 1495, 1419, 1335, 1121, 1084, 646 cm^{-1}.

4.95. 6-[(2-Oxopyrrolidin-1-yl)methyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (12t)

Prepared from **6t** (245 mg) by deprotection method B to give 112 mg (78%) of **12t** as white foam. $[\alpha]_D^{20}$ − 24.7 (c = 2.23, H_2O). Anal. calcd for $C_{15}H_{19}N_5O_4{\cdot}H_2O$: C, 52.62; H, 5.89; N, 20.46; found: C, 52.55; H, 5.78; N, 20.09. Exact mass (FAB HR MS) found: 334.1505; calcd for $C_{15}H_{20}N_5O_4$: 334.1515. FAB MS m/z (%): 334 (MH^+, 8); 218 (100); 134 (17). ^{1}H NMR (400 MHz, DMSO-d_6): 1.99 (m, 2H, H-4-pyrr); 2.30 (t, 2H, J_{vic} = 7.8, H-3-pyrr); 2.35 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.5, H-2′b); 2.79 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.1, $J_{2'a,3'}$ = 6.0, H-2′a); 3.48 (t, 2H, J_{vic} = 7.0, H-5-pyrr); 3.52 and 3.62 (2× dt, 2H, J_{gem} = 11.7, $J_{5',OH}$ = 5.5, $J_{5',4'}$ = 4.6, H-5′); 3.89 (td, 1H, $J_{4',5'}$ = 4.6, $J_{4',3'}$ = 3.0, H-4′); 4.45 (ddt, 1H, $J_{3',2'}$ = 6.0, 3.5, $J_{3',OH}$ = 4.2, $J_{3',4'}$ = 3.0, H-3′); 4.85 (s, 2H, CH_2N); 4.99 (t, 1H, $J_{OH,5'}$ = 5.5, OH-5′); 5.36 (d, 1H, $J_{OH,3'}$ = 4.2, OH-3′); 6.47 (t, 1H, $J_{1',2'}$ = 7.1, 6.3, H-1′); 8.78 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 17.75 (CH_2-4-pyrr); 30.21 (CH_2-3-pyrr); 39.40 (CH_2-2′); 43.60 (CH_2N); 47.49 (CH_2-5-pyrr); 61.71 (CH_2-5′); 70.80 (CH-3′); 83.90 (CH-1′); 88.18 (CH-4′); 132.06 (C-5); 144.86 (CH-8); 150.71 (C-4); 151.89 (CH-2); 156.38 (C-6); 174.63 (C-2-pyrr). IR (KBr): ν = 3397, 1671, 1596, 1493, 1465, 1420, 1402, 1333, 1211, 1094, 1056, 645 cm^{-1}.

4.96. 6-[(2-Hydroxycarbonylpyrrolidin-1-yl)methyl]-9-(β-D-ribofuranosyl)purine (11u)

Prepared from **5u** (190 mg) by deprotection method A and subsequent treatment with aq NaOH (0.5 M) to give 75 mg (78%) of **11u** as white solid (mp 110–112 °C). $[\alpha]_D^{20}$ − 21.7 (c = 2.53, H_2O). Anal. calcd for $C_{16}H_{21}N_5O_6{\cdot}1/2H_2O$: C, 49.48; H, 5.71; N, 18.03; found: C, 49.16; H, 5.90; N, 17.66. Exact mass (FAB HR MS) found: 380.1580; calcd for $C_{16}H_{22}N_5O_6$: 380.1570. FAB MS m/z (%): 380 (MH^+, 100); 248 (44); 201 (49); 134 (39). ^{1}H NMR (500 MHz, DMSO-d_6): 1.63–1.78 (m, 2H, H-4-pro); 1.88 (ddt, 1H, J_{gem} = 12.7, $J_{3b,4}$ = 8.5, 3.8, $J_{3b,2}$ = 4.7, H-3b-pro); 2.10 (dq, 1H, J_{gem} = 12.7, $J_{3a,2}$ = 9.3, $J_{3b,4}$ = 8.6, H-3a-pro); 2.65 (td, 1H, J_{gem} = 9.2, $J_{5b,4}$ = 9.0, 7.1, H-5b-pro); 3.04 (ddd, 1H, J_{gem} = 9.2, $J_{5a,4}$ = 7.3, 3.2, H-5a-pro); 3.58 (dd, 1H, J_{gem} = 12.0, $J_{5'b,4'}$ = 4.0, H-5′b); 3.63 (dd, 1H, $J_{2,5}$ = 9.3, 4.7, H-2-pro); 3.69 (dd, 1H, J_{gem} = 12.0, $J_{5'a,4'}$ = 4.2, H-5′a); 3.98 (q, 1H, $J_{4',5'}$ = 4.2, 4.0, $J_{4',3'}$ = 3.6, H-4′); 4.19 (dd, 1H, $J_{3',2'}$ = 4.9, $J_{3',4'}$ = 3.6, H-3′); 4.27 and 4.51 (2× d, 2H, J_{gem} = 14.6, CH_2N); 4.64 (dd, 1H, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 4.9, H-2′); 5.10, 5.25 and 5.55 (3× bs, 3H, OH-2′,3′,5′); 6.05 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 8.85 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, DMSO-d_6): 23.80 (CH_2-4-pro); 29.47 (CH_2-3-pro); 53.32 (CH_2-5-pro); 54.23 (CH_2N); 61.43 (CH_2-5′); 65.20 (CH-2-pro); 70.49 (CH-3′); 73.87 (CH-2′); 85.93 (CH-4′); 87.79 (CH-1′); 132.63 (C-5); 144.94 (CH-8); 151.00 (C-4); 151.90 (CH-2); 157.26 (C-6); 174.62 (COOH). IR (KBr): ν = 3392, 1635, 1605, 1498, 1403, 1335, 1210, 1124, 1086, 1056, 646 cm^{-1}.

4.97. 6-(Azidomethyl)-9-(β-D-ribofuranosyl)purine (11v)

Prepared from **5v** (260 mg) by deprotection method B to give 37 mg (30%) of **11v** as white foam. Exact mass (FAB HR MS) found: 308.1119; calcd for $C_{11}H_{14}N_7O_4$: 308.1107. FAB MS m/z (%): 308 (MH^+, 17); 176 (52); 148 (36); 135 (35). ^{1}H NMR (400 MHz, DMSO-d_6): 3.58 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 5.9, $J_{5'b,4'}$ = 4.1, H-5′b); 3.70 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.2, $J_{5'a,4'}$ = 4.2, H-5′a); 3.99 (q, 1H, $J_{4',5'}$ = 4.2, 4.1, $J_{4',3'}$ = 3.5, H-4′); 4.20 (td, 1H, $J_{3',OH}$ = 5.0, $J_{3',2'}$ = 4.8, $J_{3',4'}$ = 3.5, H-3′); 4.64 (q, 1H, $J_{2',OH}$ = 5.9, $J_{2',1'}$ = 5.6, $J_{2',3'}$ = 4.8, H-2′); 4.87(s, 2H, CH_2N_3); 5.10 (t, 1H, $J_{OH,5'}$ = 5.9, 5.2, OH-5′); 5.26 (d, 1H, $J_{OH,3'}$ = 5.0, OH-3′); 5.56 (d, 1H, $J_{OH,2'}$ = 5.9, OH-2′); 6.06 (d, 1H, $J_{1',2'}$ = 5.6, H-1′); 8.88 (s, 1H, H-8); 8.98 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 49.82 (CH_2N_3); 61.38 (CH_2-5′); 70.44 (CH-3′); 73.91 (CH-2′); 85.91 (CH-4′); 87.90 (CH-1′); 131.99 (C-5); 145.45 (CH-8); 151.30 (C-4); 152.14 (CH-2); 155.14 (C-6).

4.98. 6-(Methoxymethyl)-9-(β-D-ribofuranosyl)purine (15a)

Prepared from **7** (430 mg, 0.6 mmol) by reaction with 1M MeONa/MeOH (0.9 ml, 0.9 mmol) in MeOH

(30 ml) to give 53 mg (30%) of **15a** as white solid (mp 125–126 °C). $[\alpha]_D^{20}$ − 26.1 (*c* = 1.34, MeOH). Anal. calcd for $C_{12}H_{16}N_4O_5$.: C, 48.65; H, 5.44; N, 18.91; found: C, 48.61; H, 5.29; N, 18.50. Exact mass (FAB HR MS) found: 297.1194; calcd for $C_{12}H_{17}N_4O_5$: 297.1199. FAB MS *m/z* (%): 297 (MH^+, 43); 267 (5); 253 (5); 165 (100). ^{1}H NMR (500 MHz, DMSO-d_6): 3.39 (s, 3H, CH_3O); 3.57 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 6.0, $J_{5'b,4'}$ = 4.0, H-5′b); 3.69 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.2, $J_{5'a,4'}$ = 4.1, H-5′a); 3.98 (q, 1H, $J_{4',5'}$ = 4.1, 4.0, $J_{4',3'}$ = 3.6, H-4′); 4.19 (td, 1H, $J_{3',OH}$ = 5.0, $J_{3',2'}$ = 5.0, $J_{3',4'}$ = 3.6, H-3′); 4.64 (q, 1H, $J_{2',OH}$ = 6.0, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 5.0, H-2′); 4.83 and 4.86 (2× d, 2H, J_{gem} = 13.1, CH_2O); 5.11 (t, 1H, $J_{OH,5'}$ = 6.0, 5.2, OH-5′); 5.25 (d, 1H, $J_{OH,3'}$ = 5.0, OH-3′); 5.54 (d, 1H, $J_{OH,2'}$ = 6.0, OH-2′); 6.05 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 8.83 (s, 1H, H-8); 8.92 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, DMSO-d_6): 58.71 (CH_3O); 61.43 (CH_2-5′); 70.29 (CH_2O); 70.49 (CH-3′); 73.86 (CH-2′); 85.90 (CH-4′); 87.80 (CH-1′); 132.56 (C-5); 145.15 (CH-8); 151.33 (C-4); 151.99 (CH-2); 156.63 (C-6). IR (KBr): *ν* = 3401, 3118, 1619, 1602, 1496, 1404, 1334, 1213, 1114, 1099, 1065, 642 cm^{-1}.

4.99. 6-(Methoxymethyl)-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (16a)

Prepared from **8** (200 mg, 0.34 mmol) by reaction with 1 M MeONa/MeOH (0.45 ml, 0.45 mmol) in MeOH (20 ml) to give 42 mg (44%) of **16a** as white solid (mp 156–157 °C). $[\alpha]_D^{20}$ − 14.1 (*c* = 1.61, MeOH). Anal. calcd for $C_{12}H_{16}N_4O_4$: C, 51.42; H, 5.75; N, 19.99; found: C, 51.06; H, 5.48; N, 19.51. Exact mass (FAB HR MS) found: 281.1242; calcd for $C_{12}H_{17}N_4O_4$: 281.1250. FAB MS *m/z* (%): 281 (MH^+, 46); 165 (44); 149 (5); 134 (5). ^{1}H NMR (400 MHz, DMSO-d_6): 2.35 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.5, H-2′b); 2.79 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.0, $J_{2'a,3'}$ = 6.0, H-2′a); 3.38 (s, 3H, CH_3O); 3.53 (ddd, 1H, J_{gem} = 11.7, $J_{5'b,OH}$ = 5.6, $J_{5'b,4'}$ = 4.7, H-5′b); 3.63 (dt, 1H, J_{gem} = 11.7, $J_{5'a,OH}$ = 5.0, $J_{5'a,4'}$ = 5.0, H-5′a); 3.89 (td, 1H, $J_{4',5'}$ = 5.0, 4.7, $J_{4',3'}$ = 3.0, H-4′); 4.45 (ddt, 1H, $J_{3',2'}$ = 6.0, 3.5, $J_{3',OH}$ = 4.1, $J_{3',4'}$ = 3.0, H-3′); 4.83 (s, 2H, CH_2-pur); 4.98 (t, 1H, $J_{OH,5'}$ = 5.6, 5.0, OH-5′); 5.36 (d, 1H, $J_{OH,3'}$ = 4.1, OH-3′); 6.48 (t, 1H, $J_{1',2'}$ = 7.0, 6.3, H-1′); 8.79 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.41 (CH_2-2′); 58.67 (CH_3O); 61.70 (CH_2-5′); 70.26 (CH_2-pur); 70.79 (CH-3′); 83.91 (CH-1′); 88.17 (CH-4′); 132.55 (C-5); 145.04 (CH-8); 151.01 (C-4); 151.86 (CH-2); 156.47 (C-6). IR (KBr): *ν* = 3332, 3105, 2824, 1596, 1586, 1500, 1395, 1339, 1226, 1096, 1052, 653 cm^{-1}.

4.100. 6-(Phenyloxymethyl)-9-(β-D-ribofuranosyl)purine (15b)

Prepared from **13b** (355 mg) by deprotection method A to give 153 mg (86%) of **15b** as white solid (mp 167–168 °C). $[\alpha]_D^{20}$ − 43.2 (*c* = 2.55, MeOH). Exact mass (FAB HR MS) found: 359.1343; calcd for $C_{17}H_{19}N_4O_5$: 359.1355. FAB MS *m/z* (%): 359 (MH^+, 29); 227 (100); 134 (58). ^{1}H NMR (400 MHz, DMSO-d_6): 3.58 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 5.9, $J_{5'b,4'}$ = 4.1, H-5′b); 3.70 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.2, $J_{5'a,4'}$ = 4.1, H-5′a); 3.99 (q, 1H, $J_{4',5'}$ = 4.1, $J_{4',3'}$ = 3.6, H-4′); 4.20 (td, 1H, $J_{3',OH}$ = 5.0, $J_{3',2'}$ = 5.0, $J_{3',4'}$ = 3.6, H-3′); 4.65 (q, 1H, $J_{2',OH}$ = 5.9, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 5.0, H-2′); 5.10 (t, 1H, $J_{OH,5'}$ = 5.9, 5.2, OH-5′); 5.25 (d, 1H, $J_{OH,3'}$ = 5.0, OH-3′); 5.54(s, 2H, CH_2O); 5.55 (d, 1H, $J_{OH,2'}$ = 5.9, OH-2′); 6.06 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 6.94 (m, 1H, H-*p*-Ph); 7.04 (m, 1H, H-*o*-Ph); 7.28 (m, 1H, H-*m*-Ph); 8.88 (s, 1H, H-8); 8.96 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 61.30 (CH_2-5′); 66.06 (CH_2O); 70.47 (CH-3′); 73.86 (CH-2′); 85.92 (CH-4′); 87.82 (CH-1′); 114.77 (CH-*o*-Ph); 121.13 (CH-*p*-Ph); 129.69 (H-*m*-Ph); 132.45 (C-5); 145.44 (CH-8); 151.47 (C-4); 152.09 (CH-2); 155.23 (C-6); 158.45 (C-*i*-Ph). IR (KBr): *ν* = 3361, 3284, 1603, 1584, 1498, 1438, 1399, 1339, 1253, 1211, 1089, 1077, 764, 649 cm^{-1}.

4.101. 6-(Phenyloxymethyl)-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (16b)

Prepared from **14b** (310 mg) by deprotection method A to give 165 mg (90%) of **16b** as white solid (mp 152–153 °C). $[\alpha]_D^{20}$ − 4.4 (*c* = 2.27, MeOH). Anal. calcd for $C_{17}H_{18}N_4O_4{\cdot}H_2O$: C, 56.66; H, 5.59; N, 15.55; found: C, 56.99; H, 5.25; N, 15.22. Exact mass (FAB HR MS) found: 343.1398; calcd for $C_{17}H_{19}N_4O_4$: 343.1406. FAB MS *m/z* (%): 343 (MH^+, 16); 227 (100); 134 (24). ^{1}H NMR (400 MHz, DMSO-d_6): 2.37 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.6, H-2′b); 2.81 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'}$ = 7.2, $J_{2'a,3'}$ = 6.0, H-2′a); 3.53 and 3.63 (2× dt, 2H, J_{gem} = 11.7, $J_{5',OH}$ = 5.7, $J_{5',4'}$ = 4.6, H-5′); 3.90 (td, 1H, $J_{4',5'}$ = 4.6, $J_{4',3'}$ = 3.0, H-4′); 4.46 (ddt, 1H, $J_{3',2'}$ = 6.0, 3.6, $J_{3',OH}$ = 4.2, $J_{3',4'}$ = 3.0, H-3′); 4.98 (t, 1H, $J_{OH,5'}$ = 5.7, OH-5′); 5.36 (d, 1H, $J_{OH,3'}$ = 4.2, OH-3′); 5.52 (s, 2H, CH_2O); 6.49 (t, 1H, $J_{1',2'}$ = 7.2, 6.3, H-1′); 6.94 (m, 1H, H-*p*-Ph); 7.04 (m, 1H, H-*o*-Ph); 7.28 (m, 1H, H-*m*-Ph); 8.84 (s, 1H, H-8); 8.94 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.39 (CH_2-2′); 61.69 (CH_2-5′); 66.03 (CH_2O); 70.77 (CH-3′); 83.97 (CH-1′); 88.20 (CH-4′); 114.77 (CH-*o*-Ph); 121.11 (CH-*p*-Ph); 129.69 (H-*m*-Ph); 132.47 (C-5); 145.39 (CH-8); 151.18 (C-4); 152.00 (CH-2); 155.10 (C-6); 158.46 (C-*i*-Ph). IR (KBr): *ν* = 3337, 3275, 1603, 1587, 1495, 1447, 1406, 1341, 1245, 1229, 1212, 1095, 1032, 758, 648 cm^{-1}.

4.102. 6-[(Pyridin-2-yl)oxymethyl]-9-(β-D-ribofuranosyl)purine (15g)

Prepared from **13g** (80 mg) by deprotection method B to give 32 mg (80%) of **15 g** as white lyophilized solid. $[\alpha]_D^{20}$ − 28.2 (*c* = 0.39, H_2O). Anal. calcd for $C_{16}H_{17}N_5O_5{\cdot}1/2H_2O$: C, 52.17; H, 4.93; N, 19.01; found: C, 51.82; H, 4.82; N, 18.59. Exact mass (FAB HR MS) found: 360.1296; calcd for $C_{16}H_{18}N_5O_5$: 360.1308. FAB MS *m/z* (%): 360 (MH^+, 4); 228 (8); 134 (5). ^{1}H NMR (400 MHz, DMSO-d_6): 3.57 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 5.9, $J_{5'b,4'}$ = 4.1, H-5′b); 3.69 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.0, $J_{5'a,4'}$ = 4.1, H-5′a); 3.98 (q, 1H, $J_{4',5'}$ = 4.1, $J_{4',3'}$ = 3.6, H-4′); 4.19 (td, 1H, $J_{3',OH}$ = 4.9, $J_{3',2'}$ = 4.9, $J_{3',4'}$ = 3.6, H-3′); 4.65 (q, 1H, $J_{2',OH}$ = 5.9, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 4.9, H-2′); 5.01 (t, 1H,

$J_{OH,5'} = 5.9$, 5.0, OH-5′); 5.25 (d, 1H, $J_{OH,3'} = 4.9$, OH-3′); 5.55 (d, 1H, $J_{OH,2'} = 5.9$, OH-2′); 5.81 (s, 2H, CH_2-pur); 6.04 (d, 1H, $J_{1',2'} = 5.7$, H-1′); 6.94 (dt, 1H, $J_{3,4} = 8.4$, $J_{3,5} = 0.9$, $J_{3,6} = 0.8$, H-3-py); 6.98 (ddd, 1H, $J_{5,4} = 7.1$, $J_{5,6} = 5.1$, $J_{5,3} = 0.9$, H-5-py); 7.74 (ddd, 1H, $J_{4,3} = 8.4$, $J_{4,5} = 7.1$, $J_{4,6} = 2.0$, H-4-py); 8.07 (ddd, 1H, $J_{6,5} = 5.1$, $J_{6,4} = 2.0$, $J_{6,3} = 0.8$, H-6-py); 8.82 (s, 1H, H-8); 8.88 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 61.43 (CH_2-5′); 63.34 (CH_2-pur); 70.49 (CH-3′); 73.83 (CH-2′); 85.91 (CH-4′); 87.79 (CH-1′); 111.11 (CH-3-py); 117.61 (CH-5-py); 131.86 (C-5); 139.51 (CH-4-py); 145.05 (CH-8); 146.81 (CH-6-py); 151.14 (C-4); 151.93 (CH-2); 156.31 (C-6); 162.78 (C-2-py). IR (KBr): ν = 3409, 1599, 1572, 1499, 1474, 1433, 1405, 1335, 1287, 1211, 1082, 1055, 780, 645 cm^{-1}.

4.103. 6-[(Pyridin-2-yl)oxymethyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (16g)

Prepared from **14g** (95 mg) by deprotection method B to give 50 mg (89%) of **16g** as white lyophilized solid. $[\alpha]_D^{20} - 18.2$ (c = 1.89, H_2O). Anal. calcd for $C_{16}H_{17}N_5O_4 \cdot 1/2H_2O$: C, 54.54; H, 5.15; N, 19.88; found: C, 54.60; H, 4.89; N, 19.69. Exact mass (FAB HR MS) found: 344.1346; calcd for $C_{16}H_{18}N_5O_4$: 344.1359. FAB MS m/z (%): 344 (MH^+, 3); 228 (44); 134 (8). ^{1}H NMR (400 MHz, DMSO-d_6): 2.36 (ddd, 1H, $J_{gem} = 13.3$, $J_{2'b,1'} = 6.3$, $J_{2'b,3'} = 3.5$, H-2′b); 2.80 (ddd, 1H, $J_{gem} = 13.3$, $J_{2'a,1'} = 7.2$, $J_{2'a,3'} = 6.0$, H-2′a); 3.52 and 3.62 (2× dt, 2H, $J_{gem} = 11.6$, $J_{5',OH} = 5.5$, $J_{5',4'} = 4.7$, H-5′); 3.89 (td, 1H, $J_{4',5'} = 4.7$, $J_{4',3'} = 3.1$, H-4′); 4.45 (ddt, 1H, $J_{3',2'} = 6.0$, 3.5, $J_{3',OH} = 4.1$, $J_{3',4'} = 3.1$, H-3′); 4.98 (t, 1H, $J_{OH,5'} = 5.5$, OH-5′); 5.36 (d, 1H, $J_{OH,3'} = 4.1$, OH-3′); 5.80 (s, 2H, CH_2O-py); 6.48 (t, 1H, $J_{1',2'} = 7.2$, 6.3, H-1′); 6.93 (dt, 1H, $J_{3,4} = 8.4$, $J_{3,5} = 0.9$, $J_{3,6} = 0.9$, H-3-py); 6.98 (ddd, 1H, $J_{5,4} = 7.1$, $J_{5,6} = 5.1$, $J_{5,3} = 0.9$, H-5-py); 7.74 (ddd, 1H, $J_{4,3} = 8.4$, $J_{4,5} = 7.1$, $J_{4,6} = 2.0$, H-4-py); 8.07 (ddd, 1H, $J_{6,5} = 5.1$, $J_{6,4} = 2.0$, $J_{6,3} = 0.9$, H-6-py); 8.78 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.38 (CH_2-2′); 61.71 (CH_2-5′); 63.33 (CH_2O); 70.80 (CH-3′); 83.93 (CH-1′); 88.18 (CH-4′); 111.11 (CH-3-py); 117.60 (CH-5-py); 131.88 (C-5); 139.51 (CH-4-py); 144.99 (CH-8); 146.81 (CH-6-py); 150.85 (C-4); 151.84 (CH-2); 156.16 (C-6); 162.78 (C-2-py). IR (KBr): ν = 3369, 1598, 1571, 1498, 1474, 1433, 1401, 1335, 1287, 1210, 1094, 1056, 780, 645 cm^{-1}.

4.104. 6-(Methylsulfanylmethyl)-9-(β-D-ribofuranosyl)purine (19a)

Prepared from **17a** (400 mg) by deprotection method A to give 152 mg (81%) of **19a** as white solid (mp 142–143 °C). $[\alpha]_D^{20} - 33.9$ (c = 3.18, H_2O). Anal. calcd for $C_{12}H_{16}N_4O_4S$: C, 46.14; H, 5.16; N, 17.94; found: C, 46.10; H, 5.12; N, 17.62. Exact mass (FAB HR MS) found: 313.0959; calcd for $C_{12}H_{17}N_4O_4S$: 313.0971. FAB MS m/z (%): 313 (MH^+, 74); 181 (75); 134 (17). ^{1}H NMR (400 MHz, DMSO-d_6): 2.13 (s, 3H, CH_3S); 3.57 (ddd, 1H, $J_{gem} = 12.0$, $J_{5'b,OH} = 6.0$, $J_{5'b,4'} = 4.1$, H-5′b); 3.69 (ddd, 1H, $J_{gem} = 12.0$, $J_{5'a,OH} = 5.1$, $J_{5'a,4'} = 4.2$, H-5′a); 3.98 (q, 1H, $J_{4',5'} = 4.2$, 4.1, $J_{4',3'} = 3.4$, H-4′); 4.06 (s, 2H, CH_2S); 4.19 (td, 1H, $J_{3',OH} = 4.9$, $J_{3',2'} = 4.8$, $J_{3',4'} = 3.5$, H-3′); 4.65 (q, 1H, $J_{2',OH} = 6.0$, $J_{2',1'} = 5.8$, $J_{2',3'} = 4.8$, H-2′); 5.11 (t, 1H, $J_{OH,5'} = 6.0$, 5.1, OH-5′); 5.25 (d, 1H, $J_{OH,3'} = 4.9$, OH-3′); 5.54 (d, 1H, $J_{OH,2'} = 6.0$, OH-2′); 6.03 (d, 1H, $J_{1',2'} = 5.8$, H-1′); 8.81 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 15.74 (CH_3); 33.77 (CH_2S); 61.46 (CH_2-5′); 70.52 (CH-3′); 73.79 (CH-2′); 85.92 (CH-4′); 87.80 (CH-1′); 132.17 (C-5); 144.80 (CH-8); 151.05 (C-4); 152.01 (CH-2); 158.46 (C-6). IR (KBr): ν = 3445, 3234, 1602, 1584, 1497, 1407, 1337, 1218, 1096, 1065, 721, 640 cm^{-1}.

4.105. 6-(Methylsulfanylmethyl)-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (20a)

Prepared from **18a** (250 mg) by deprotection method A to give 130 mg (93%) of **20a** as lyophilized hygroscopic solid. $[\alpha]_D^{20} - 10.4$ (c = 1.83, MeOH). Exact mass (FAB HR MS) found: 297.1014; calcd for $C_{12}H_{17}N_4O_3S$: 297.1021. FAB MS m/z (%): 297 (MH^+, 28); 181 (100); 134 (21). ^{1}H NMR (400 MHz, DMSO-d_6): 2.12 (s, 3H, CH_3S); 2.35 (ddd, 1H, $J_{gem} = 13.2$, $J_{2'b,1'} = 6.3$, $J_{2'b,3'} = 3.5$, H-2′b); 2.80 (ddd, 1H, $J_{gem} = 13.2$, $J_{2'a,1'} = 7.0$, $J_{2'a,3'} = 5.8$, H-2′a); 3.53 and 3.62 (2× dt, 2H, $J_{gem} = 11.7$, $J_{5',OH} = 5.5$, $J_{5',4'} = 4.6$, H-5′); 3.89 (td, 1H, $J_{4',5'} = 4.6$, $J_{4',3'} = 2.9$, H-4′); 4.05 (s, 2H, CH_2S); 4.45 (ddt, 1H, $J_{3',2'} = 5.8$, 3.5, $J_{3',OH} = 4.2$, $J_{3',4'} = 3.0$, H-3′); 4.99 (t, 1H, $J_{OH,5'} = 5.5$, OH-5′); 5.36 (d, 1H, $J_{OH,3'} = 4.2$, OH-3′); 6.47 (t, 1H, $J_{1',2'} = 7.0$, 6.3, H-1′); 8.76 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 15.73 (CH_3); 33.76 (CH_2S); 39.37 (CH_2-2′); 61.73 (CH_2-5′); 70.82 (CH-3′); 83.94 (CH-1′); 88.18 (CH-4′); 132.18 (C-5); 144.71 (CH-8); 150.75 (C-4); 151.92 (CH-2); 158.33 (C-6). IR (KBr): ν = 3436, 1602, 1582, 1494, 1402, 1333, 1212, 1093, 1056, 725, 644 cm^{-1}.

4.106. 6-(Phenylsulfanylmethyl)-9-(β-D-ribofuranosyl)purine (19b)

Prepared from **17b** (360 mg) by deprotection method A to give 163 mg (88%) of **19b** as white foam. $[\alpha]_D^{20} - 37.7$ (c = 2.57, MeOH). Exact mass (FAB HR MS) found: 375.1140; calcd for $C_{17}H_{19}N_4O_4S$: 375.1127. FAB MS m/z (%): 375 (MH^+, 52); 243 (100); 134 (53). ^{1}H NMR (400 MHz, DMSO-d_6): 3.57 (ddd, 1H, $J_{gem} = 11.9$, $J_{5'b,OH} = 5.6$, $J_{5'b,4'} = 4.1$, H-5′b); 3.69 (ddd, 1H, $J_{gem} = 11.9$, $J_{5'a,OH} = 4.9$, $J_{5'a,4'} = 4.2$, H-5′a); 3.97 (q, 1H, $J_{4',5'} = 4.2$, 4.1, $J_{4',3'} = 3.4$, H-4′); 4.18 (td, 1H, $J_{3',OH} = 4.9$, $J_{3',2'} = 4.8$, $J_{3',4'} = 3.5$, H-3′); 4.63 (q, 1H, $J_{2',OH} = 6.0$, $J_{2',1'} = 5.7$, $J_{2',3'} = 4.8$, H-2′); 4.64 (s, 2H, CH_2S); 5.10 (t, 1H, $J_{OH,5'} = 5.6$, 4.9, OH-5′); 5.24 (d, 1H, $J_{OH,3'} = 4.9$, OH-3′); 5.54 (d, 1H, $J_{OH,2'} = 6.0$, OH-2′); 6.02 (d, 1H, $J_{1',2'} = 5.7$, H-1′); 7.18 (m, 1H, H-*p*-Ph); 7.28 (m, 2H, H-*m*-Ph); 7.44 (m, 2H, H-*o*-Ph); 8.83 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 33.91 (CH_2S); 61.43 (CH_2-5′); 70.48 (CH-3′); 73.79 (CH-2′); 85.91 (CH-4′); 87.84 (CH-1′); 126.24 (CH-*p*-Ph); 128.46 (CH-*o*-Ph); 129.16 (CH-*m*-Ph); 132.34 (C-5); 135.93 (C-*i*-Ph); 144.99 (CH-8); 151.05 (C-4); 152.04 (CH-2); 157.23 (C-6). IR (KBr): ν = 3420, 1598, 1584, 1497, 1439, 1405, 1335, 1210, 1084, 1053, 742, 644 cm^{-1}.

4.107. 6-(Phenylsulfanylmethyl)-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (20b)

Prepared from **18b** (355 mg) by deprotection method A to give 194 mg (91%) of **20b** as white hygroscopic foam. $[\alpha]_D^{20}$ − 12.2 (*c* = 2.21, MeOH). Anal. calcd for $C_{17}H_{18}N_4O_3S{\cdot}H_2O$: C, 54.24; H, 5.36; N, 14.88; found: C, 54.08; H, 4.98; N, 14.95. Exact mass (FAB HR MS) found: 359.1180; calcd for $C_{17}H_{19}N_4O_3S$: 359.1178. FAB MS *m*/*z* (%): 359 (MH^+, 38); 243 (100); 134 (40). ^{1}H NMR (400 MHz, DMSO-d_6): 2.34 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.5, H-2′b); 2.79 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.2, $J_{2'a,3'}$ = 6.0, H-2′a); 3.52 and 3.62 (2× dt, 2H, J_{gem} = 11.7, $J_{5',OH}$ = 5.5, $J_{5',4'}$ = 4.6, H-5′); 3.89 (td, 1H, $J_{4',5'}$ = 4.6, $J_{4',3'}$ = 3.0, H-4′); 4.44 (ddt, 1H, $J_{3',2'}$ = 6.0, 3.5, $J_{3',OH}$ = 4.2, $J_{3',4'}$ = 3.0, H-3′); 4.63 (s, 2H, CH_2N); 4.98 (t, 1H, $J_{OH,5'}$ = 5.5, OH-5′); 5.35 (d, 1H, $J_{OH,3'}$ = 4.2, OH-3′); 6.46 (t, 1H, $J_{1',2'}$ = 7.2, 6.3, H-1′); 7.17 (m, 1H, H-*p*-Ph); 7.28 (m, 2H, H-*m*-Ph); 7.43 (m, 2H, H-*o*-Ph); 8.78 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 33.89 (CH_2S); 39.36 (CH_2-2′); 61.70 (CH_2-5′); 70.79 (CH-3′); 83.97 (CH-1′); 88.18 (CH-4′); 126.22 (CH-*p*-Ph); 128.44 (CH-*o*-Ph); 129.15 (CH-*m*-Ph); 132.34 (C-5); 135.96 (C-*i*-Ph); 144.91 (CH-8); 150.76 (C-4); 151.95 (CH-2); 157.09 (C-6). IR (KBr): *ν* = 3428, 1598, 1583, 1495, 1439, 1400, 1334, 1210, 1092, 1056, 743, 644 cm^{-1}.

4.108. 6-(Benzylsulfanylmethyl)-9-(β-D-ribofuranosyl)purine (19c)

Prepared from **17c** (190 mg) by deprotection method A to give 88 mg (89%) of **19c** as white foam. $[\alpha]_D^{20}$ − 23.5 (*c* = 1.98, MeOH). Exact mass (FAB HR MS) found: 389.1270; calcd for $C_{18}H_{21}N_4O_4S$: 389.1284. FAB MS *m*/*z* (%): 389 (MH^+, 75); 257 (100); 134 (38); 91 (83). ^{1}H NMR (400 MHz, DMSO-d_6): 3.58 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 6.0, $J_{5'b,4'}$ = 4.1, H-5′b); 3.68 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.1, $J_{5'a,4'}$ = 4.1, H-5′a); 3.85 (s, 2H, CH_2-Ph); 3.99 (q, 1H, $J_{4',5'}$ = 4.1, $J_{4',3'}$ = 3.5, H-4′); 4.02 (s, 2H, CH_2-pur); 4.20 (td, 1H, $J_{3',OH}$ = 5.0, $J_{3',2'}$ = 4.8, $J_{3',4'}$ = 3.5, H-3′); 4.65 (q, 1H, $J_{2',OH}$ = 6.0, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 4.8, H-2′); 5.11 (t, 1H, $J_{OH,5'}$ = 6.0, 5.1, OH-5′); 5.25 (d, 1H, $J_{OH,3'}$ = 5.0, OH-3′); 5.55 (d, 1H, $J_{OH,2'}$ = 6.0, OH-2′); 6.04 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 7.24 (m, 1H, H-*p*-Ph); 7.32 (m, 2H, H-*m*-Ph); 7.40 (m, 2H, H-*o*-Ph); 8.83 (s, 1H, H-8); 8.88 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 31.29 (CH_2-pur); 35.62 (CH_2-Ph); 61.44 (CH_2-5′); 70.50 (CH-3′); 73.83 (CH-2′); 85.90 (CH-4′); 87.85 (CH-1′); 127.07 (CH-*p*-Ph); 128.50 (CH-*m*-Ph); 129.21 (CH-*o*-Ph); 132.13 (C-5); 138.44 (C-*i*-Ph); 144.82 (CH-8); 151.07 (C-4); 152.03 (CH-2); 158.55 (C-6). IR (KBr): *ν* = 3409, 1597, 1581, 1495, 1454, 1405, 1334, 1210, 1081, 1055, 702, 645 cm^{-1}.

4.109. 6-(Benzylsulfanylmethyl)-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (20c)

Prepared from **18c** (195 mg) by deprotection method A to give 110 mg (92%) of **20c** as white hygroscopic foam. $[\alpha]_D^{20}$ − 3.5 (*c* = 2.12, MeOH). Exact mass (FAB HR MS) found: 373.1339; calcd for $C_{18}H_{21}N_4O_3S$: 373.1334. FAB MS *m*/*z* (%): 373 (MH^+, 74); 257 (100); 166 (8); 134 (36); 91 (66). ^{1}H NMR (400 MHz, DMSO-d_6): 2.36 (ddd, 1H, J_{gem} = 13.3, $J_{2'b,1'}$ = 6.3, $J_{2'b,3'}$ = 3.5, H-2′b); 2.80 (ddd, 1H, J_{gem} = 13.3, $J_{2'a,1'}$ = 7.1, $J_{2'a,3'}$ = 6.0, H-2′a); 3.54 and 3.63 (2× dt, 2H, J_{gem} = 11.7, $J_{5',OH}$ = 5.6, $J_{5',4'}$ = 4.7, H-5′); 3.84 (s, 2H, CH_2-Ph); 3.90 (td, 1H, $J_{4',5'}$ = 4.7, $J_{4',3'}$ = 3.0, H-4′); 4.01 (s, 2H, CH_2-pur); 4.46 (ddt, 1H, $J_{3',2'}$ = 6.0, 3.5, $J_{3',OH}$ = 4.2, $J_{3',4'}$ = 3.0, H-3′); 4.99 (t, 1H, $J_{OH,5'}$ = 5.6, OH-5′); 5.36 (d, 1H, $J_{OH,3'}$ = 4.2, OH-3′); 6.47 (t, 1H, $J_{1',2'}$ = 7.1, 6.3, H-1′); 7.23 (m, 1H, H-*p*-Ph); 7.31 (m, 2H, H-*m*-Ph); 7.40 (m, 2H, H-*o*-Ph); 8.78 (s, 1H, H-8); 8.87 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 31.31 (CH_2-pur); 35.63 (CH_2-Ph); 39.40 (CH_2-2′); 61.73 (CH_2-5′); 70.82 (CH-3′); 83.96 (CH-1′); 88.18 (CH-4′); 127.04 (CH-*p*-Ph); 128.47 (CH-*m*-Ph); 129.19 (CH-*o*-Ph); 132.14 (C-5); 138.44 (C-*i*-Ph); 144.73 (CH-8); 150.76 (C-4); 151.93 (CH-2); 158.42 (C-6). IR (KBr): *ν* = 3411, 3063, 1597, 1582, 1494, 1453, 1400, 1334, 1211, 1101, 1057, 703, 645 cm^{-1}.

4.110. 6-[(Hydroxycarbonylmethyl)sulfanylmethyl]-9-(β-D-ribofuranosyl)purine (19da)

Prepared from **17d** (480 mg, 0.66 mmol) by deprotection method A and subsequent treatment with aq NaOH (0.5 M). Sodium salt of the product was converted to acidic form *via* Dowex 50 in pyridinium cycle. After evaporation of volatiles and crystallization (EtOH/AcOEt/heptane) 176 mg (75%) of **19da** was obtained as white solid (mp 180–182 °C). $[\alpha]_D^{20}$ − 13.6 (*c* = 2.01, H_2O). Exact mass (FAB HR MS) found: 357.0875; calcd for $C_{13}H_{17}N_4O_6S$: 357.0869. FAB MS *m*/*z* (%): 357 (MH^+, 8); 223 (56); 134 (16). ^{1}H NMR (400 MHz, DMSO-d_6): 3.22 (s, 2H, SCH_2CO); 3.57 (m, 1H, H-5′b); 3.67 (m, 1H, H-5′a); 3.98 (m, 1H, H-4′); 4.12 (s, 2H, CH_2-pur); 4.19 (m, 1H, H-3′); 4.64 (m, 1H, H-2′); 5.19 (m, 1H, OH-5′); 5.47 (m, 1H, OH-3′); 5.78 (m, 1H, OH-2′); 6.02 (d, 1H, $J_{1',2'}$ = 5.8, H-1′); 8.80 (s, 1H, H-8); 8.83 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 32.15 (CH_2-pur); 38.35 (SCH_2CO); 61.47 (CH_2-5′); 70.53 (CH-3′); 73.86 (CH-2′); 85.96 (CH-4′); 87.82 (CH-1′); 132.01 (C-5); 144.64 (CH-8); 150.95 (C-4); 151.96 (CH-2); 159.23 (C-6); 173.61 (COOH).

4.111. 6-[(Hydroxycarbonylmethyl)sulfanylmethyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (20da)

Prepared from **18d** (395 mg) in similar way as **19da**. Yield: 83% as white solid (mp 130–132 °C). $[\alpha]_D^{20}$ − 15.1 (*c* = 2.38, H_2O). Exact mass (FAB HR MS) found: 341.0936; calcd for $C_{13}H_{17}N_4O_5S$: 341.0920. FAB MS *m*/*z* (%): 341 (MH^+, 6); 223 (28); 134 (7). ^{1}H NMR (500 MHz, DMSO-d_6): 2.35 (ddd, 1H, J_{gem} = 13.1, $J_{2'b,1'}$ = 6.2, $J_{2'b,3'}$ = 3.7, H-2′b); 2.78 (dt, 1H, J_{gem} = 13.1, $J_{2'a,1'}$ = 7.3, $J_{2'a,3'}$ = 6.0, H-2′a); 3.19 (s, 2H, SCH_2CO); 3.53 (dd, 1H, J_{gem} = 11.9, $J_{5'b,4'}$ = 4.4, H-5′b); 3.62 (dd, 1H, J_{gem} = 11.9, $J_{5'a,4'}$ = 4.7, H-5′a); 3.88 (td, 1H, $J_{4',5'}$ = 4.7, 4.4, $J_{4',3'}$ = 2.8, H-4′); 4.09 (s, 2H, CH_2-pur); 4.45 (dt, 1H, $J_{3',2'}$ = 6.0, 3.7, $J_{3',4'}$ = 2.8, H-3′); 5.12 (bs, 1H, OH-5′); 5.50 (bs, 1H,

OH-3′); 6.45 (t, 1H, $J_{1',2'} = 7.3$, 6.2, H-1′); 8.75 (s, 1H, H-8); 8.81 (s, 1H, H-2). ^{13}C NMR (125.7 MHz, DMSO-d_6): 32.15 (CH_2-pur); 38.62 (SCH_2CO); 39.41 (CH_2-2′); 61.70 (CH_2-5′); 70.76 (CH-3′); 83.93 (CH-1′); 88.20 (CH-4′); 132.02 (C-5); 144.54 (CH-8); 150.64 (C-4); 151.89 (CH-2); 159.24 (C-6); 173.18 (COOH). IR (KBr): ν = 3401, 1595, 1497, 1399, 1335, 1213, 1095, 1057, 646 cm^{-1}.

4.112. 6-[(2-Hydroxyethyl)sulfanylmethyl]-9-(β-D-ribofuranosyl)purine (19e)

Prepared from **17e** (460 mg) by deprotection method A to give 180 mg (84%) of **19e** as white hygroscopic foam. $[\alpha]_D^{20}$ − 30.0 (c = 1.03, H_2O). Anal. calcd for $C_{13}H_{18}N_4O_5S{\cdot}1/2H_2O$: C, 44.44; H, 5.45; N, 15.94; found: C, 44.81; H, 5.51; N, 15.56. Exact mass (FAB HR MS) found: 343.1085; calcd for $C_{13}H_{19}N_4O_5S$: 343.1076. FAB MS m/z (%): 343 (MH^+, 18); 211 (19); 134 (9). ^{1}H NMR (400 MHz, DMSO-d_6): 2.68 (m, 2H, CH_2S); 3.55 (m, 2H, CH_2O); 3.58 (ddd, 1H, J_{gem} = 11.9, $J_{5'b,OH} = 6.0$, $J_{5'b,4'} = 4.0$, H-5′b); 3.69 (ddd, 1H, J_{gem} = 11.9, $J_{5'a,OH} = 5.2$, $J_{5'a,4'} = 4.0$, H-5′a); 3.98 (q, 1H, $J_{4',5'} = 4.0$, $J_{4',3'} = 3.4$, H-4′); 4.11 (s, 2H, CH_2-pur); 4.19 (td, 1H, $J_{3',OH} = 4.9$, $J_{3',2'} = 4.8$, $J_{3',4'} = 3.4$, H-3′); 4.65 (q, 1H, $J_{2',OH} = 6.0$, $J_{2',1'} = 5.8$, $J_{2',3'} = 4.8$, H-2′); 4.82 (t, 1H, $J_{OH,5'} = 5.5$, CH_2OH); 5.11 (t, 1H, $J_{OH,5'} = 6.0$, 5.2, OH-5′); 5.24 (d, 1H, $J_{OH,3'} = 4.9$, OH-3′); 5.54 (d, 1H, $J_{OH,2'} = 6.0$, OH-2′); 6.03 (d, 1H, $J_{1',2'} = 5.8$, H-1′); 8.81 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 31.84 (CH_2-S); 34.61 (CH_2O); 60.55 (CH_2-pur); 61.47 (CH_2-5′); 70.53 (CH-3′); 73.80 (CH-2′); 85.94 (CH-4′); 87.81 (CH-1′); 132.05 (C-5); 144.83 (CH-8); 151.05 (C-4); 152.04 (CH-2); 158.86 (C-6). IR (KBr): ν = 3306, 1599, 1498, 1404, 1335, 1211, 1100, 1080, 1053, 645 cm^{-1}.

4.113. 6-[(2-Hydroxyethyl)sulfanylmethyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (20e)

Prepared from **18e** (370 mg) by deprotection method A to give 200 mg (93%) of **20e** as white hygroscopic foam. $[\alpha]_D^{20}$ − 17.6 (c = 3.04, H_2O). Exact mass (FAB HR MS) found: 327.1119; calcd for $C_{13}H_{19}N_4O_4S$: 327.1127. FAB MS m/z (%): 327 (MH^+, 15); 211 (72); 134 (28). ^{1}H NMR (400 MHz, DMSO-d_6): 2.35 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'} = 6.3$, $J_{2'b,3'} = 3.5$, H-2′b); 2.68 (m, 2H, CH_2S); 2.80 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'} = 7.3$, $J_{2'a,3'} = 5.9$, H-2′a); 3.55 (m, 2H, CH_2O); 3.54 and 3.63 (2× dt, 2H, J_{gem} = 11.7, $J_{5',OH} = 5.5$, $J_{5',4'} = 4.5$, H-5′); 3.89 (td, 1H, $J_{4',5'} = 4.5$, $J_{4',3'} = 2.9$, H-4′); 4.10 (s, 2H, CH_2-pur); 4.45 (ddt, 1H, $J_{3',2'} = 5.8$, 3.5, $J_{3',OH} = 4.2$, $J_{3',4'} = 3.0$, H-3′); 4.82 (t, 1H, $J_{OH,5'} = 5.5$, CH_2OH); 4.99 (t, 1H, $J_{OH,5'} = 5.5$, OH-5′); 5.36 (d, 1H, $J_{OH,3'} = 4.2$, OH-3′); 6.47 (t, 1H, $J_{1',2'} = 7.3$, 6.3, H-1′); 8.77 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 31.82 (CH_2-S); 34.60 (CH_2O); 39.37 (CH_2-2′); 60.55 (CH_2-pur); 61.74 (CH_2-5′); 70.83 (CH-3′); 83.95 (CH-1′); 88.19 (CH-4′); 132.06 (C-5); 144.74 (CH-8); 150.76 (C-4); 151.95 (CH-2); 158.73 (C-6). IR (KBr): ν = 3271, 1598, 1495, 1403, 1335, 1212, 1095, 1057, 645 cm^{-1}.

4.114. 6-[(Pyridin-2-yl)sulfanylmethyl]-9-(β-D-ribofuranosyl)purine (19g)

Prepared from **17g** (660 mg) by deprotection method A to give 260 mg (78%) of **19g** as white solid (mp 170–172 °C). $[\alpha]_D^{20}$ − 38.0 (c = 2.66, MeOH). Anal. calcd for $C_{16}H_{17}N_5O_4S$: C, 51.19; H, 4.56; N, 18.66; found: C, 50.97; H, 4.50; N, 18.25. Exact mass (FAB HR MS) found: 376.1093; calcd for $C_{16}H_{18}N_5O_4S$: 376.1080. FAB MS m/z (%): 376 (MH^+, 15); 244 (100); 165 (13); 134 (40). ^{1}H NMR (400 MHz, DMSO-d_6): 3.57 (ddd, 1H, J_{gem} = 11.9, $J_{5'b,OH} = 5.9$, $J_{5'b,4'} = 4.1$, H-5′b); 3.69 (ddd, 1H, J_{gem} = 11.9, $J_{5'a,OH} = 5.2$, $J_{5'a,4'} = 4.1$, H-5′a); 3.98 (q, 1H, $J_{4',5'} = 4.1$, $J_{4',3'} = 3.5$, H-4′); 4.19 (td, 1H, $J_{3',OH} = 5.0$, $J_{3',2'} = 4.8$, $J_{3',4'} = 3.5$, H-3′); 4.64 (q, 1H, $J_{2',OH} = 6.0$, $J_{2',1'} = 5.7$, $J_{2',3'} = 4.8$, H-2′); 4.91 (s, 2H, CH_2S); 5.10 (t, 1H, $J_{OH,5'} = 5.9$, 5.2, OH-5′); 5.24 (d, 1H, $J_{OH,3'} = 5.0$, OH-3′); 5.54 (d, 1H, $J_{OH,2'} = 6.0$, OH-2′); 6.03 (d, 1H, $J_{1',2'} = 5.7$, H-1′); 7.13 (ddd, 1H, $J_{5,4} = 7.4$, $J_{5,6} = 4.9$, $J_{5,3} = 0.9$, H-5-py); 7.42 (dt, 1H, $J_{3,4} = 8.1$, $J_{3,5} = 0.9$, $J_{3,6} = 1.0$, H-3-py); 7.66 (ddd, 1H, $J_{4,3} = 8.1$, $J_{4,5} = 7.4$, $J_{4,6} = 1.9$, H-4-py); 8.43 (ddd, 1H, $J_{6,5} = 4.9$, $J_{6,4} = 1.9$, $J_{6,3} = 1.0$, H-6-py); 8.84 (s, 1H, H-8); 8.86 (s, 1H, H-2). ^{13}C ^{13}C NMR (100.6 MHz, DMSO-d_6): 30.62 (CH_2S); 61.43 (CH_2-5′); 70.49 (CH-3′); 73.81 (CH-2′); 85.92 (CH-4′); 87.86 (CH-1′); 120.27 (CH-5-py); 121.71 (CH-3-py); 132.41 (C-5); 136.99 (CH-4-py); 144.97 (CH-8); 149.53 (CH-6-py); 150.93 (C-4); 152.06 (CH-2); 157.07 (C-6); 157.71 (C-2-py). IR (KBr): ν = 3402, 3061, 1595, 1583, 1501, 1451, 1414, 1401, 1339, 1215, 1127, 1062, 1026, 647 cm^{-1}.

4.115. 6-[(Pyridin-2-yl)sulfanylmethyl]-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (20g)

Prepared from **18g** (410 mg) by deprotection method A to give 140 mg (57%) of **20g** as white solid (mp 105–109 °C). Anal. calcd for $C_{16}H_{17}N_5O_3S$: C, 52.16; H, 4.92; N, 19.01; found: C, 52.51; H, 4.76; N, 18.63. Exact mass (FAB HR MS) found: 360.1141; calcd for $C_{16}H_{18}N_5O_3S$: 360.1130. FAB MS m/z (%): 360 (MH^+, 62); 244 (83); 165 (6); 134 (24). ^{1}H NMR (400 MHz, DMSO-d_6): 2.35 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'} = 6.2$, $J_{2'b,3'} = 3.5$, H-2′b); 2.80 (ddd, 1H, J_{gem} = 13.2, $J_{2'\ a,1'} = 7.2$, $J_{2'a,3'} = 5.9$, H-2′a); 3.52 and 3.62 (2× bm, 2H, H-5′); 3.89 (td, 1H, $J_{4',5'} = 4.5$, $J_{4',3'} = 2.8$, H-4′); 4.45 (bm, 1H, H-3′); 4.90 (s, 2H, CH_2S); 4.98 (bm, 1H, OH-5′); 5.36 (bm, 1H, OH-3′); 6.47 (t, 1H, $J_{1',2'} = 7.2$, 6.2, H-1′); 7.13 (ddd, 1H, $J_{5,4} = 7.4$, $J_{5,6} = 4.9$, $J_{5,3} = 0.9$, H-5-py); 7.42 (dt, 1H, $J_{3,4} = 8.1$, $J_{3,5} = 0.9$, $J_{3,6} = 1.0$, H-3-py); 7.66 (ddd, 1H, $J_{4,3} = 8.1$, $J_{4,5} = 7.4$, $J_{4,6} = 1.9$, H-4-py); 8.43 (ddd, 1H, $J_{6,5} = 4.9$, $J_{6,4} = 1.9$, $J_{6,3} = 1.0$, H-6-py); 8.79 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 30.61 (CH_2S); 39.37 (CH_2-2′); 61.70 (CH_2-5′); 70.79 (CH-3′); 83.99 (CH-1′); 88.18 (CH-4′); 120.25 (CH-5-py); 121.69 (CH-3-py); 132.41 (C-5); 136.97 (CH-4-py); 144.89 (CH-8); 149.52 (CH-6-py); 150.63 (C-4); 151.97 (CH-2); 156.92 (C-6); 157.73 (C-2-py). IR (KBr): ν = 3412, 3269, 3063, 1595, 1578, 1498, 1455, 1416, 1398, 1336, 1219, 1087, 1050, 648 cm^{-1}.

4.116. 6-[(Benzothiazol-2-yl)sulfanylmethyl]-9-(β-D-ribofuranosyl)purine (19h)

Prepared from **17h** (520 mg) by deprotection method A to give 245 mg (86%) of **19h** as white solid (mp 98–99 °C). $[\alpha]_D^{20}$ − 40.6 (c = 2.40, MeOH). Anal. calcd for $C_{18}H_{17}N_5O_4S_2 \cdot 1/2H_2O$: C, 49.08; H, 4.12; N, 15.90; S, 14.56; found: C, 48.99; H, 4.48; N, 15.48; S, 14.52. Exact mass (FAB HR MS) found: 432.0817; calcd for $C_{18}H_{18}N_5O_4S_2$: 432.0800. FAB MS m/z (%): 432 (MH^+, 20); 300 (35); 134 (23). ^{1}H NMR (400 MHz, DMSO-d_6): 3.58 (ddd, 1H, J_{gem} = 11.9, $J_{5'b,OH}$ = 5.8, $J_{5'b,4'}$ = 4.1, H-5′b); 3.70 (ddd, 1H, J_{gem} = 11.9, $J_{5'a,OH}$ = 5.1, $J_{5'a,4'}$ = 4.1, H-5′a); 3.99 (q, 1H, $J_{4',5'}$ = 4.1, $J_{4',3'}$ = 3.3, H-4′); 4.20 (td, 1H, $J_{3',OH}$ = 5.0, $J_{3',2'}$ = 5.0, $J_{3',4'}$ = 3.5, H-3′); 4.65 (q, 1H, $J_{2',OH}$ = 6.0, $J_{2',1'}$ = 5.6, $J_{2',3'}$ = 5.0, H-2′); 5.10 (t, 1H, $J_{OH,5'}$ = 5.8, 5.1, OH-5′); 5.17 (s, 2H, CH_2S); 5.25 (d, 1H, $J_{OH,3'}$ = 5.0, OH-3′); 5.55 (d, 1H, $J_{OH,2'}$ = 6.0, OH-2′); 6.05 (d, 1H, $J_{1',2'}$ = 5.6, H-1′); 7.37 (ddd, 1H, $J_{6,7}$ = 8.3, $J_{6,5}$ = 7.2, $J_{6,4}$ = 1.2, H-6-benzothiazole); 7.47 (ddd, 1H, $J_{5,4}$ = 8.3, $J_{5,6}$ = 7.2, $J_{5,7}$ = 1.2, H-5-benzothiazole); 7.85 (ddd, 1H, $J_{7,6}$ = 8.3, $J_{7,5}$ = 1.2, $J_{7,4}$ = 1.0, H-7-benzothiazole); 8.02 (ddd, 1H, $J_{4,5}$ = 8.3, $J_{4,6}$ = 1.2, $J_{4,7}$ = 1.0, H-4-benzothiazole); 8.89 (s, 1H, H-8); 8.91 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 34.10 (CH_2-S); 61.41 (CH_2-5′); 70.47 (CH-3′); 73.87 (CH-2′); 85.94 (CH-4′); 87.92 (CH-1′); 121.41 (CH-7-benzothiazole); 122.05 (CH-4-benzothiazole); 124.77 (CH-6-benzothiazole); 126.61 (CH-5-benzothiazole); 132.37 (C-5); 134.98 (C-7a-benzothiazole); 145.28 (CH-8); 151.03 (C-4); 152.11 (CH-2); 152.75 (C-3a-benzothiazole); 155.24 (C-6); 166.05 (C-2-benzothiazole). IR (KBr): ν = 3563, 3361, 3265, 1594, 1498, 1456, 1425, 1390, 1337, 1219, 1122, 1095, 1054, 754, 649 cm^{-1}.

4.117. 6-(Mercaptomethyl)-9-(β-D-ribofuranosyl)purine (19i)

Prepared from **17ia** (180 mg) by deprotection method A to give 45 mg (58%) of **19i** as white solid (mp 154–156 °C). $[\alpha]_D^{20}$ − 58.4 (c = 2.0, H_2O). Exact mass (FAB HR MS) found: 299.0823; calcd for $C_{11}H_{15}N_4O_4S$: 299.0814. FAB MS m/z (%): 299 (MH^+, 10); 165 (38); 134 (36). ^{1}H NMR (400 MHz, DMSO-d_6): 3.58 (ddd, 1H, J_{gem} = 12.0, $J_{5'b,OH}$ = 6.0, $J_{5'b,4'}$ = 4.0, H-5′b); 3.70 (ddd, 1H, J_{gem} = 12.0, $J_{5'a,OH}$ = 5.2, $J_{5'a,4'}$ = 4.2, H-5′a); 3.99 (q, 1H, $J_{4',5'}$ = 4.2, 4.0, $J_{4',3'}$ = 3.5, H-4′); 4.19 (td, 1H, $J_{3',OH}$ = 4.8, $J_{3',2'}$ = 4.8, $J_{3',4'}$ = 3.5, H-3′); 4.39(s, 2H, CH_2S); 4.65 (q, 1H, $J_{2',OH}$ = 6.0, $J_{2',1'}$ = 5.7, $J_{2',3'}$ = 4.8, H-2′); 5.11 (t, 1H, $J_{OH,5'}$ = 6.0, 5.2, OH-5′); 5.25 (d, 1H, $J_{OH,3'}$ = 4.8, OH-3′); 5.55 (d, 1H, $J_{OH,2'}$ = 6.0, OH-2′); 6.04 (d, 1H, $J_{1',2'}$ = 5.7, H-1′); 8.78 (s, 1H, H-8); 8.85 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 38.93 (CH_2-S); 61.48 (CH_2-5′); 70.50 (CH-3′); 73.78 (CH-2′); 85.92 (CH-4′); 87.83 (CH-1′); 132.95 (C-5); 145.03 (CH-8); 151.07 (C-4); 152.04 (CH-2); 156.63 (C-6). IR (KBr): ν = 3401, 1596, 1497, 1405, 1335, 1212, 1120, 1083, 1055, 643 cm^{-1}.

4.118. 6-(Mercaptomethyl)-9-(2-deoxy-β-D-*erythro*-pentofuranosyl)purine (20i)

Prepared from **18ia** (380 mg) by deprotection method A to give 120 mg (63%) of **20i** as white solid (mp 91–94 °C). $[\alpha]_D^{20}$ − 41.9 (c = 1.7, H_2O). Exact mass (FAB HR MS) found: 283.0860; calcd for $C_{11}H_{15}N_4O_3S$: 283.0865. FAB MS m/z (%): 283 (MH^+, 12); 165 (49); 134 (74); 117 (28). ^{1}H NMR (400 MHz, DMSO-d_6): 2.36 (ddd, 1H, J_{gem} = 13.2, $J_{2'b,1'}$ = 6.2, $J_{2'b,3'}$ = 3.5, H-2′b); 2.80 (ddd, 1H, J_{gem} = 13.2, $J_{2'a,1'}$ = 7.4, $J_{2'a,3'}$ = 5.8, H-2′a); 3.54 and 3.63 (2× dt, 2H, J_{gem} = 11.7, $J_{5',OH}$ = 5.5, $J_{5',4'}$ = 4.5, H-5′); 3.90 (td, 1H, $J_{4',5'}$ = 4.5, $J_{4',3'}$ = 3.0, H-4′); 4.37 (s, 2H, CH_2S); 4.45 (ddt, 1H, $J_{3',2'}$ = 5.8, 3.5, $J_{3',OH}$ = 4.2, $J_{3',4'}$ = 3.0, H-3′); 5.00 (t, 1H, $J_{OH,5'}$ = 5.5, OH-5′); 5.36 (d, 1H, $J_{OH,3'}$ = 4.2, OH-3′); 6.47 (t, 1H, $J_{1',2'}$ = 7.4, 6.2, H-1′); 8.73 (s, 1H, H-8); 8.82 (s, 1H, H-2). ^{13}C NMR (100.6 MHz, DMSO-d_6): 39.03 (CH_2S); 39.39 (CH_2-2′); 61.74 (CH_2-5′); 70.82 (CH-3′); 83.96 (CH-1′); 88.18 (CH-4′); 132.90 (C-5); 144.91 (CH-8); 150.74 (C-4); 151.92 (CH-2); 156.50 (C-6). IR (KBr): ν = 3392, 1597, 1496, 1400, 1334, 1212, 1096, 1056, 645 cm^{-1}.

5. Biological assays

5.1. Cytostatic activity assays

Inhibition of the cell growth was estimated in *mouse lymphocytic leukaemia L1210 cells* (ATCC CCL 219), *CCRF-CEM T lymphoblastoid cells* (human acute lymphoblastic leukaemia, ATCC CCL 119), *human promyelocytic leukaemia HL-60 cells* (ATCC CCL 240) and *human cervix carcinoma HeLa S3 cells* (ATCC CCL 2.2). *L1210 cells*, *CCRF-CEM cells* and *HL-60* cells were cultivated in RPMI 1640 medium supplemented with calf foetal serum using 24-well tissue culture plates. The endpoint of the cell growth was 72 h following the drug addition. Cells were then counted in Celtac MEK 5208 (NIHON KOHDEN) haematological analyzer. *HeLa S3 cells* were seeded to 24-well dishes in RPMI 1640 HEPES modified with foetal calf serum. Forty-eight hours following the drug addition the cultivation was stopped and the cell growth was evaluated after methylene blue addition. The cell viability was quantified using XTT[23] standard spectrophotometric assay (Roche Molecular Biochemicals). The inhibitory potency of the compounds tested was expressed as IC_{50} values. The cell cycle analysis by flow cytometry (BD FACSAria) was performed by using ethanol-fixed cells stained with propidium iodide in buffer containing RNase A.

5.1.1. EC_{50} determination in HCV replicon cells.[24] Con-1/lucneo replicon cells were seeded in 96-well plates at a density of 8×10^3 cells per well in 100 μL of culture medium, excluding Geneticin. Compound was serially diluted in 100% DMSO and then added to the cells at a 1:200 dilution, achieving a final concentration of 0.5% DMSO and a total volume of 200 μL. Plates were incubated at 37 °C for 3 days, after which culture medium was removed and cells were lysed in lysis buffer provided

by Promega's luciferase assay system. Following the manufacturer's instruction, 100 μL of luciferase substrate was added to the lysed cells and the luciferase activity was measured in a TopCount luminometer. EC_{50} was calculated by non-linear regression. Parallel plates treated with the same drug dilutions were assayed for cytotoxicity using the Promega CellTiter-Glo cell viability assay.

5.1.2. CC_{50} determination in HCV replicon cells. Replicon cells were seeded in 96-well plates at a density of 8×10^3 cells per well in 100 μL of culture medium, excluding Geneticin. Compound was serially diluted in 100% DMSO and then added to the cells at a 1:200 dilution, achieving a final concentration of 0.5% DMSO and a total volume of 200 μL. Plates were incubated at 37 °C for 3 days after which 100 μL of CellTiter Glo reagent was added to each well and luminescence was read in a TopCount luminometer.

5.1.3. CC_{50} determination in MT4 cells. Cells were seeded in 384-well plates at 2×10^3 cells/well in 20μL of culture medium. Compounds were serially diluted in culture medium and added to each well for a final volume of 40 μL. Plates were incubated for 5 days, after which cell survival was determined by addition of 40 μL of CellTiter Glo reagent followed by luminescence readout.

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