

## Non-natural nucleosides based on 1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4(6*H*)-ones

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Dedicated to Prof. Henk van der Plas on the occasion of his 80<sup>th</sup> birthday

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### Abstract

Two regioselective methods for the synthesis of nucleosides in the series of 3-phenyl- and 3-ethoxycarbonyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-ones were developed. The first route involves a Vorbrüggen glycosylation reaction. The second one is based on condensation of 1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-one sodium salts with protected 1-bromo-sugar derivatives.

**Keywords:** 1,2,4-Triazolo[5,1-*c*][1,2,4]triazin-4-ones, glycosylation, NMR spectra,  $\beta$ -configuration, X-ray

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### Introduction

The synthesis of analogs of natural nucleosides based on modification of purines and pyrimidines is one of the most useful tools for development of antiviral compounds. In most cases, the structural transformations of nucleobases can be achieved by introduction or removal of different substituents. This methodology was successfully used for drug design of active antiviral agents: Brivudine [(*E*)-5-(2-bromovinyl)-2'-deoxyuridine], Idoxuridine (2'-deoxy-5-iodouridine), Famciclovir (2-[2-(2-amino-9*H*-purin-9-yl)ethyl]-1,3-propanediol diacetate).<sup>1-3</sup>

Another strategy for synthesis of antiviral compounds is based on isosteres of natural nucleobases or heterocycles containing fragments of purines or pyrimidines.

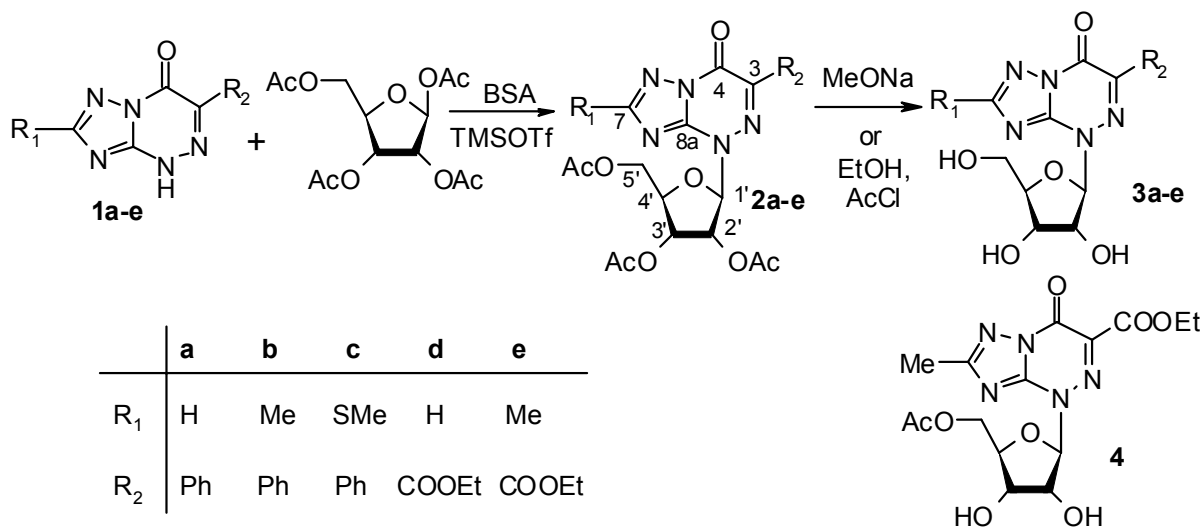
This way have been applied for the synthesis of Marbavir (1-( $\beta$ -L-ribofuranosyl)-2-isopropylamino-5,6-dichlorobenzimidazole), Ribavirin (1- $\beta$ -D-ribofuranosyl-1,2,4-triazole-3-carboxamide) and of its analogs.<sup>1,4-7</sup>

Herein, we report the synthesis of abnormal nucleosides in the series of 1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-ones, considered as fused analogues of aza-isocytosines<sup>8</sup> and exhibiting antiviral activity.<sup>9,10</sup>

## Results and Discussion

The Vorbrüggen reaction is one of the widely used routes for the synthesis of nucleosides.<sup>11</sup> This method of glycosylation involves interaction of protected sugar derivatives with appropriately silylated NH-heterocycles in the presence of a Lewis acid.

We found that the conditions of the Vorbrüggen one-step method<sup>12</sup> were useful for glycosylation of 1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-ones. Treatment on the NH-heterocycles **1a-e** with *N*,*O*-bis-(trimethylsilyl)acetamide (BSA) and trimethylsilyl triflate (TMSOTf) followed by addition of 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose at room temperature gave compounds **2a-e** (Scheme 1). Although there are three possible positions for *N*-glycosylation (N1, N6 or N8), only products of *N*-1 glycosylation were observed. The sugar fragments in **2a-e** had exclusively the  $\beta$ -configuration.

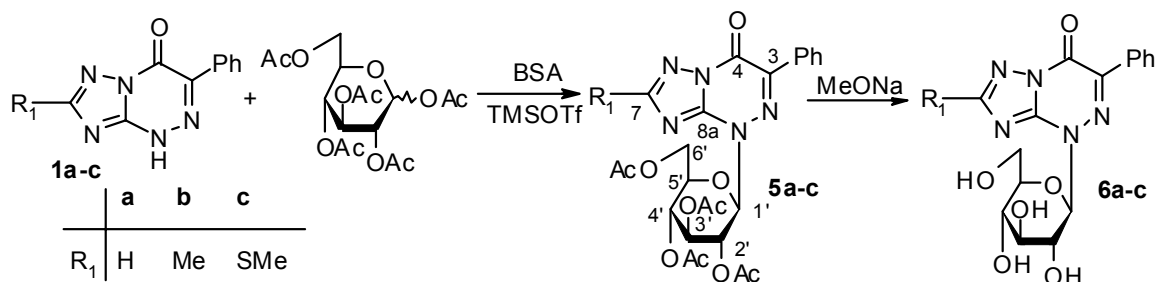


**Scheme 1**

Removing the protecting acetyls of the compounds **2a-c** in sodium methoxide solution gave nucleosides **3a-c**. Meanwhile the deacetylation of **2d,e** was carried out in acidic medium by mixture ethanol with acetyl chloride. Attempts to remove the acetyl-protecting groups in

compound **2d,e** by reaction with sodium ethoxide gave products of decomposition or incomplete deacetylation — for example, the monoacetyl derivative **4** was obtained from **2e**.

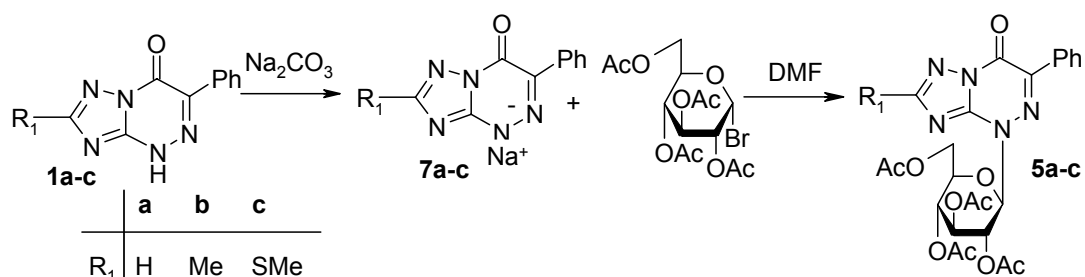
The reaction of 1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-ones **1a-c** with  $\beta$ -D-glucose pentaacetate were carried out under the same conditions (BSA and TMSOTf) to give protected nucleoside **5a-c** in 40-50% yield (Scheme 2).



**Scheme 2**

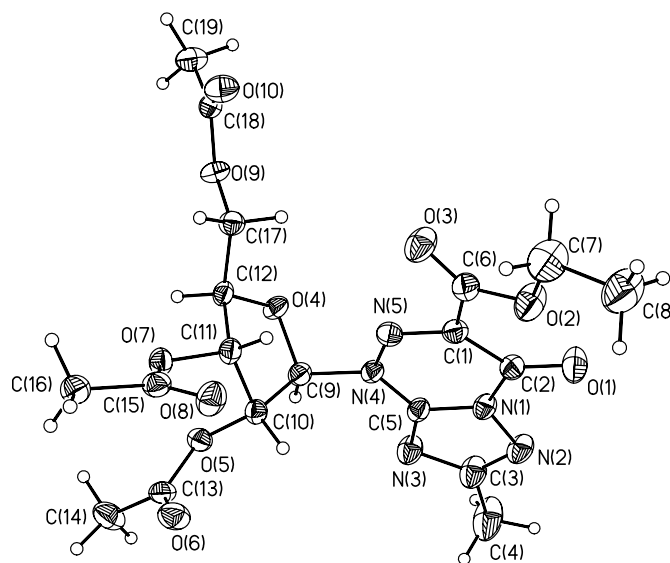
Following removal of the protection groups the nucleosides **6a-c** were produced. The best conditions for deacetylation were found to be heating of **5a-c** under reflux in MeONa/MeOH solution.

Reactions of purines and pyrimidine sodium salts with halogen derivatives of sugars provide an alternative nucleoside-forming methodology.<sup>13-16</sup> Previously reported conditions for alkylation of azolo[5,1-*c*][1,2,4]triazin-4-ones sodium salts<sup>17</sup> with halo-alkanes proved to be successful for the synthesis of nucleosides, too. Compounds **5a-c** were obtained by the reaction of tetra-acetyl- $\alpha$ -D-bromoglucose and the sodium salt of 1,2,4-triazolo[5,1-*c*][1,2,4]triazinones **7a-c**, prepared from the heterocycles **1a-c** in the presence of  $\text{Na}_2\text{CO}_3$  (Scheme 3).



**Scheme 3**

The signals in both the  $^1\text{H}$ - and  $^{13}\text{C}$ - NMR spectra of compounds **2a-e** and **5a-c** were assigned using 2D-  $^1\text{H}$ ,  $^1\text{H}$  COSY,  $^1\text{H}$ ,  $^{13}\text{C}$  gHSQC and gHMBC experiments.



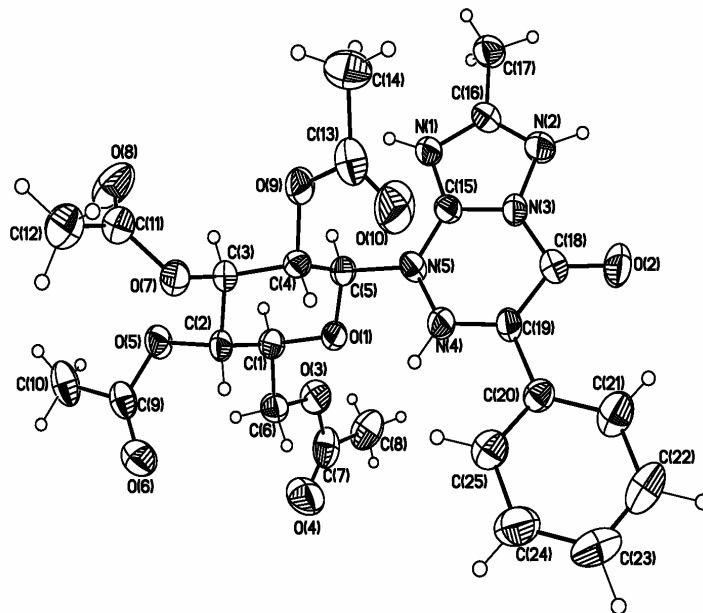
**Figure 1.** X-Ray crystal structure of compound **2e**.

The position of the tri-*O*-acetyl- $\beta$ -D-ribofuranosyl and tetra-*O*-acetyl- $\beta$ -D-glucopyranosyl fragments at the *N*-1 atom of the 1,2,4-triazine part in compounds **2a-e** and **5a-c** are evident from the observed cross-peaks between H-1' and C-8<sub>a</sub> in the HMBC spectra. NOESY spectra of **2a-e** showed the  $\beta$ -configuration of the furanoses due to the presence of correlation of peaks H-1' with H-4'. The structure of the acetylated nucleoside **2d** was confirmed by X-ray diffraction (Fig. 1). It was found that the ribofuranosyl fragment of **2d** has a 3'-*exo* twist conformation.

The derivatives of glucopyranose, **5a-c**, have a  $\beta$ -configuration, and this was also confirmed by 2D- gNOESY experiments showing cross-peaks H-1' with H-3' and H-5', and vicinal coupling constant of H-1'– H-2' ( $^3J$  9.0-9.5 Hz) in the  $^1\text{H}$  NMR.<sup>18</sup> A single-crystal X-ray diffraction analysis was carried out in order to confirm the molecular structure of **5a-c**. The molecular structure of **5c** (Fig. 2) demonstrated that the glucopyranosyl fragment is attached at the azine part, and the sugar has the  $\beta$ -configuration.

The position of the protecting group in compound **4** has been determined by the 2D- HMBC spectrum, where the signal for the carbon of the acetyl group gave cross peaks with H-5'*a* and H-5'*b*. The structures of the nucleosides **3a-e** and **6a-c** were confirmed by  $^1\text{H}$  NMR and mass spectra.

In conclusion, we have reported selective methods for synthesis of non- natural nucleosides based on 3-phenyl- and 3-ethoxycarbonyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-ones.



**Figure 2.** X-Ray crystal structure of compound **5b**.

## Experimental Section

**General Procedures.** IR spectra were recorded in KBr on a Perkin Elmer Spectrum One B FT-IR instrument. The  $^1\text{H}$ - and  $^{13}\text{C}$ - NMR spectra were measured on Bruker WM-250, Bruker DRX-400, and Bruker DRX-500 instruments. The  $^{13}\text{C}$ - and  $^1\text{H}$ - 2D NMR spectra were recorded on the Bruker DRX-500 spectrometer in  $\text{DMSO}-d_6$ . The mass spectra were obtained using a quadrupole Shimadzu LCMS-2010 system with a Supelco LC-18 column ( $4.6 \times 250$  mm), where a temperature of  $60^\circ\text{C}$  was maintained. The mobile phase was acetonitrile (100 %). Positive chemical APCI ionization in the selective ion-monitoring (SIM) mode was used. The capillary voltage was set at 1.5 kV and cone voltage at 15.0 V. Microanalyses were performed on a Perkin Elmer PE 2400 series II CHNS/O analyzer. TLC was carried out on Silufol UV-254 plates using ethyl acetate as the eluent; spots were visualized by exposure to UV radiation. Column chromatography was performed on Merck Kieselgel-60. 1-Bromo-2,3,5-tri-*O*-acetyl- $\alpha$ -D-glucose, 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose,  $\beta$ -D-glucose penta-acetate, *N,O*-bis-(trimethylsilyl)acetamide and trimethylsilyl triflate were purchased from Aldrich. RT denotes room temperature.

**1,2,4-Triazolo[5,1-*c*][1,2,4]triazin-4(6*H*)-ones (1a-e)** was prepared according to the procedure described earlier.<sup>19,20</sup>

**1-(2',3',5'-Tri-*O*-acetyl- $\beta$ -D-ribofuranosyl)-1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-ones (2a-e).**

*N,O*-Bis-(trimethylsilyl)acetamide (0.328 mL, 1.34 mmol), trimethylsilyl triflate (TMSOTf) (0.32 mL, 1.8 mmol) and 1,2,3,5-tetra-*O*-acetyl- $\beta$ -D-ribofuranose (0.28 g, 0.90 mmol) were added to a solution of compound (1a-e) (0.94 mmol) in 5 ml acetonitrile. The reaction mixture was left at RT for 2.5 h, diluted with 10 ml acetonitrile with a few drops of water and neutralized with NaHCO<sub>3</sub>. The resulting suspension was filtered. The filtrate was concentrated *in vacuo*. The product was isolated by column chromatography using ethyl acetate: hexane (4:1) as the eluent.

**Compound 2a.** Yield 0.20 g (45 %); mp 73 °C; [ $\alpha$ ]<sup>20</sup><sub>D</sub> -56.5° (*c* 1.0, EtOAc); MS (APCI, *m/z* (rel. %)) 472 (100%) [M+H]<sup>+</sup>; IR: CO 1721, 1745; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  1.78 (s, 3H, Me of 5'-Ac), 2.09 (s, 3H, Me of 3'-Ac), 2.11 (s, 3H, Me of 2'-Ac), 4.16 (d,d, 1H, H-5'*b*, *J*=5.0 Hz, *J*=12.5 Hz) 4.37 (d,d, 1H, H-5'*a*, *J*=3.2 Hz, *J*=12.3 Hz), 4.46 (m, H-4'), 5.67 (t, 1H, H-3', *J*=5.5 Hz), 5.91 (d,m, 1H, H-2', *J*=5.3 Hz), 6.49 (d, 1H, H-1', *J*=3.0 Hz), 7.54 (m, 3H, *m*, *p*-Ph), 8.06 (m, 2H, *o*-Ph), 8.43 (s, 1H, H-7); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  19.93 (Me of 5'-Ac), 20.08 (Me of 2'-Ac + Me of 3'-Ac), 62.30 (C-5'), 69.73 (C-3'), 72.41 (C-2'), 79.06 (C-4'), 91.38 (C-1'), 128.13 (C-*m*), 128.55 (C-*o*), 129.98 (C-*p*), 131.70 (C-*i*), 140.58 (C-3), 148.65 (C-4), 150.61 (C-8*a*), 152.86 (C-7), 169.03 (CO of 2'-Ac), 169.27 (CO, of 3'-Ac), 169.72 (CO of 5'-Ac). Calc. for C<sub>21</sub>H<sub>21</sub>N<sub>5</sub>O<sub>8</sub>: C, 53.50; H, 4.49; N, 14.86. Found: C, 54.02; H, 4.51; N, 14.20%.

**Compound 2b.** Yield 0.22 g (48 %); mp 173 °C; [ $\alpha$ ]<sup>20</sup><sub>D</sub> -53.4° (*c* 1, EtOAc); MS (APCI, *m/z* (rel. %)) 486 (100%) [M+H]<sup>+</sup>; IR: CO 1770, 1721; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  1.78 (s, 3H, (Me of 5'-Ac), 2.10 (s, 3H, (Me of 3'-Ac), 2.12 (s, 3H, (Me of 2'-Ac), 2.45 (s, 3H, Me), 4.16 (d,d, 1H, H-5'*b*, *J*=5.0 Hz, *J*=12.5 Hz) 4.36 (d,d, 1H, H-5'*a*, *J*=3.0 Hz, *J*=12.3 Hz), 4.46 (m, H-4'), 5.66 (t, 1H, H-3', *J*=5.5 Hz), 5.91 (d,m, 1H, H-2', *J*=5.3 Hz), 6.45 (d, 1H, H-1', *J*=2.5 Hz), 7.52 (m, 3H, *m*-H-, *p*-Ph), 8.06 (m, 2H, *o*-Ph); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  14.02 (Me), 19.93 (Me of 5'-Ac), 20.09 (Me of 2'-Ac + Me of 3'-Ac), 62.31(C-5'), 69.78(C-3'), 72.34(C-2'), 79.06 (C-4'), 91.15 (C-1'), 128.12 (C*m*), 128.53 (C*o*), 129.96 (C*p*), 131.78 (C*i*), 140.58 (C-3), 148.16 (C-4), 150.83 (C-8*a*), 162.51 (C-7), 169.06 (CO of 2'-Ac), 169.30 (CO of 3'-Ac), 169.73 (CO of 5'-Ac). Calc. for C<sub>22</sub>H<sub>23</sub>N<sub>5</sub>O<sub>8</sub>: C, 54.43; H, 4.78; N, 14.43. Found: C, 54.06; H, 4.80; N, 14.22%.

**Compound 2c.** Yield 0.24 g (50 %); mp 121 °C; [ $\alpha$ ]<sup>20</sup><sub>D</sub> -38.3° (*c* 1, EtOAc); MS (APCI, *m/z* (rel. %)) 518 (100%) [M+H]<sup>+</sup>, 519 (32.7%) [M+1+H]<sup>+</sup>, 520 (6.7%) [M+2+H]<sup>+</sup>; IR: CO 1711 1747; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  1.78 (s, 3H, Me of 5'-Ac), 2.10 (s, 3H, Me of 3'-Ac), 2.12 (s, 3H, Me of 2'-Ac), 2.67 (s, 3H, SMe), 4.15 (d,d, 1H, H-5'*b*), *J*=5.0 Hz, *J*=12.5 Hz) 4.36 (d,d, 1H, H-5'*a*), *J*=3.5 Hz, *J*=12.5 Hz), 4.46 (m, H-4'), 5.67 (t, 1H, H-3', *J*=5.5 Hz), 5.89 (d,m, 1H, H-2' *J*=5.0 Hz), 6.40 (d, 1H, H-1', *J*=2.5 Hz), 7.52 (m, 3H, *m*-, *p*-Ph), 8.05 (m, 2H, *o*-Ph); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  13.40 (SMe), 19.93 (Me of 5'-Ac), 20.08 (Me of 2'-Ac + Me of 3'-Ac), 62.28(C-5'), 69.70 (C-3'), 72.33 (C-2'), 79.04 (C-4'), 91.35 (C-1'), 128.13 (C-*m*), 128.52 (C-*o*), 130.05 (C-*p*), 131.66 (C-*i*), 140.98 (C-3), 147.34 (C-4), 151.11 (C-8*a*), 165.33 (C-7), 169.02 (CO of 2'-Ac), 169.27 (CO of 3'-Ac), 169.50 (CO of 5'-Ac). Calc. for C<sub>22</sub>H<sub>23</sub>N<sub>5</sub>O<sub>8</sub>S: C, 51.06; H, 4.48; N, 13.53. Found: C, 51.22; H, 4.48; N, 13.63%.

**Compound 2d.** Yield 0.20 g, (46 %); mp 127 °C; [ $\alpha$ ]<sup>20</sup><sub>D</sub> -75.9° (*c* 1, EtOAc); MS (APCI, *m/z* (rel. %)) 468 (100%) [M+H]<sup>+</sup>; IR: CO 1759, 1744; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.41 (t, 3H, Me of OEt),

2.03 (s, 3H, Me of 5'-Ac), 2.11 (s, 6H, Me of 3'-Ac + Me of 2'-Ac), 4.26 (d,d, 2H, H-5b',  $J=6.0$  Hz,  $J=12.0$  Hz), 4.39 (d,d, 2H, H-5a',  $J=3.5$  Hz,  $J=12.2$  Hz), 4.36-4.48 (m, 3H, (CH<sub>2</sub> of OEt + H-4')), 5.63 (t, 1H, H-3',  $J=5.5$  Hz), 5.83 (m, 1H, H-2'), 6.54 (d, 1H, H-1',  $J=3.0$  Hz), 8.17 (s, 1H H-7). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.99 (Me of OEt); 20.34 (Me of 5'-Ac), 20.39 (Me of 2'-Ac), 20.54 (Me of 3'-Ac), 63.02 (OCH<sub>2</sub> + C-5'), 70.60 (C-3'), 73.07 (C-2'), 80.92 (C-4'), 93.26 (C-1'), 133.19 (C-3), 145.61 (C-4), 150.27 (C-8a), 153.36 (C-7), 159.52 (CO), 169.56 (CO of 2'-Ac + CO of 3'-Ac), 170.35 (CO of 5'-Ac). Calc. for C<sub>18</sub>H<sub>21</sub>N<sub>5</sub>O<sub>10</sub>: C, 46.26; H, 4.53; N, 14.98. Found: C, 46.13; H, 4.54; N, 14.78%.

**Compound 2e.** Yield 0.19 g, (42 %); mp 153 °C;  $[\alpha]^{20}_D$  -60.3° (*c* 1, EtOAc); MS (APCI, *m/z* (rel. %)) 482 (100%) [M+H]<sup>+</sup>; IR: CO 1751, 1758; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.20 (t, 3H, Me of OEt), 2.04 (s, 3H, Me of 5'-Ac), 2.12 (s, 6H, Me of 3'-Ac + 2'-Ac), 2.55 (s, 3H, Me), 4.26 (d,d, 2H, H-5b',  $J=6.0$  Hz,  $J=12.3$  Hz), 4.39 (d,d, 2H, H-5a',  $J=3.5$  Hz,  $J=12.3$  Hz), 4.41-4.49 (m, 3H, CH<sub>2</sub> of OEt + H-4'), 5.65 (t, 1H, H-3',  $J=5.0$  Hz), 5.87 (m, 1H, H-2'), 6.52 (d, 1H, H-1',  $J=3.0$  Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  13.99 (Me of OEt), 14.61 (Me), 20.36 (Me of 5'-Ac), 20.40 (Me of 2'-Ac), 20.54 (Me of 3'-Ac), 62.98 (OCH<sub>2</sub> + C-5'), 70.62 (C-3'), 72.93 (C-2'), 81.43 (C-4'), 92.93 (C-1'), 133.20 (C-3), 145.37 (C-4), 150.39 (C-8a), 159.65 (CO), 164.37 (C-7), 169.37 (CO of 2'-Ac + CO of 3'-Ac), 170.34 (CO of 5'-Ac). Calc. for C<sub>19</sub>H<sub>23</sub>N<sub>5</sub>O<sub>10</sub>: C, 47.40; H, 4.82; N, 14.55. Found: C, 47.06; H, 4.92; N, 14.31%.

**1-( $\beta$ -D-Ribofuranosyl)-3-phenyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-ones (3a-c).** Compound (2a-c) (0.4 mmol) was added to a sodium methoxide solution, which was prepared from sodium (0.03 g, 1.30 mmol) and methanol (4 ml). The reaction mixture was refluxed for 0.5 h, cooled, neutralized acetic acid and concentrated *in vacuo*. The product was isolated by column chromatography using ethyl acetate as the eluent.

**Compound 3a.** Yield 0.082 g, (57%); mp 216 °C;  $[\alpha]^{20}_D$  -55.1° (*c* 0.3, MeCN); MS (APCI, *m/z* (rel. %)) 346 (100%) [M+H]<sup>+</sup>; IR: CO 1717; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  3.26-3.53 (m, 1H, H-5'b), 3.61-3.66 (m, 1H, H-5'a), 3.97 (q, 1H, H-4',  $J = 5.5$  Hz), 4.36 (q, 1H, H-3',  $J=6.0$  Hz), 4.65 (m, 1H, OH), 4.67 (m, 1H, H-2'), 5.21 (d, 1H, OH,  $J=6.0$  Hz), 5.55 (d, 1H, OH,  $J=4.8$  Hz), 6.25 (d, 1H, H-1',  $J=2.8$  Hz), 7.53 (m, 3H, *m*-, *p*-Ph), 8.00 (m, 2H, *o*-Ph), 8.46 (s, 1H, H-7). Calc. for C<sub>15</sub>H<sub>15</sub>N<sub>5</sub>O<sub>5</sub>·H<sub>2</sub>O: C, 49.59; H, 4.72; N, 19.28. Found: C, 49.31; H, 4.73; N, 19.62%.

**Compound 3b.** Yield 0.101 g, (65%); mp 210 °C;  $[\alpha]^{20}_D$  -52.9° (*c* 0.2, EtOAc); MS (APCI, *m/z* (rel. %)) 360 (100%) [M+H]<sup>+</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  2.48 (s, 3H, Me), 3.48-3.55 (m, 1H, H-5'b), 3.60-3.66 (m, 1H, H-5'a), 3.95 (q, 1H, H-4',  $J=4.5$  Hz), 4.36 (q, 1H, H-3',  $J=5.5$  Hz), 4.53 (m, 1H, OH), 4.66 (m, 1H, H-2'), 5.20 (d, 1H, OH,  $J=6.2$  Hz), 5.55 (d, 1H, OH,  $J=4.2$  Hz), 6.19 (d, 1H, H-1',  $J=2.8$  Hz), 7.53 (m, 3H, *m*-, *p*-Ph), 8.01 (m, 2H, *o*-Ph); Calc. for C<sub>16</sub>H<sub>17</sub>N<sub>5</sub>O<sub>5</sub>·H<sub>2</sub>O: C, 50.93; H, 5.08; N, 18.56. Found: C, 51.30; H, 4.77; N, 18.64%.

**Compound 3c.** Yield 0.099 g (61%); mp 167 °C  $[\alpha]^{20}_D$  -61.4° (*c* 0.5, MeCN); MS (APCI, *m/z* (rel. %)) 392 (100%) [M+H]<sup>+</sup>, 393 (19.5%) [M+1+H]<sup>+</sup>, 394 (9.0%) [M+2+H]<sup>+</sup>. IR: CO, 1727cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  2.66 (s, 3H, SMe), 3.47-3.52 (m, 1H, H-5'b), 3.61-3.65 (m, 1H, H-5'a), 3.96 (q, 1H, H-4',  $J=4.5$  Hz), 4.34 (q, 1H, H-3',  $J=5.0$  Hz), 4.50-4.56 (m, 2H, OH + H-2'), 4.99 (d, 1H, OH,  $J=6.0$  Hz), 5.30 (d, 1H, OH,  $J=5.0$  Hz), 6.19 (d, 1H, H-1',  $J=3.5$  Hz), 7.48 (m, 3H,

*m*-, *p*-Ph), 8.03 (m, 2H, *o*-Ph); Calc. for C<sub>16</sub>H<sub>17</sub>N<sub>5</sub>O<sub>5</sub>S·H<sub>2</sub>O: C, 46.94; H, 4.68; N, 17.11. Found: C, 46.50; H, 4.49; N, 17.19%.

**1-(β-D-Ribofuranosyl)-3-ethoxycarbonyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-ones (3d,e).**

Compound **2d** or **2e** (0.4 mmol) was added to a solution of HCl prepared from anhydrous ethanol (10 mL) and acetyl chloride (2 mL). The resulting solution was kept at r.t. for 48 h, then neutralized with AcONa and evaporated *in vacuo*. The product was isolated by column chromatography using ethyl acetate: hexane (3:1) as the eluent.

**Compound 3d.** Yield 0.02 g, (15%); mp 183 °C, [α]<sup>20</sup><sub>D</sub> -64.2° (*c* 0.3, MeCN); MS (APCI, *m/z* (rel. %)) 342 (100%) [M+H]<sup>+</sup>; IR: CO 1742, 1710; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 1.40 (t, 3H, Me of OEt), 3.50-3.55 (m, 1H, H-5'*b*), 3.57-3.64 (m, 1H, H-5'*a*), 4.02 (q, 1H, H-4', *J*=4.2 Hz), 4.22 (q, 1H, H-3', *J*=4.2 Hz), 4.37-4.50 (m, 4H, OCH<sub>2</sub> of OEt + H-2' + OH), 4.93 (d, 1H, OH, *J*=6.0 Hz), 5.28 (d, 1H, OH, *J*=5.0 Hz), 6.19 (d, 1H, H-1', *J*=3.5 Hz), 8.17(s, 1H, H-7). Calc. for C<sub>12</sub>H<sub>15</sub>N<sub>5</sub>O<sub>7</sub>: C, 42.23; H, 4.43; N, 20.52. Found: C, 42.17; H, 5.00; N, 19.98%.

**Compound 3e.** Yield 0.017 g, (12%); mp 108 °C; [α]<sup>20</sup><sub>D</sub> -42.9° (*c* 0.3, MeCN); MS (APCI, *m/z* (rel. %)) 356 (100%) [M+H]<sup>+</sup>; IR: CO 1741, 1707; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 1.40 (t, 3H, Me of OEt), 2.49 (s, 3H, Me), 3.51-3.55 (m, 1H, H-5'*b*), 3.60-3.64 (m, 1H, H-5'*a*), 4.02 (q, 1H, H-4', *J*=3.7 Hz), 4.25-4.32 (m, 1H, H-3'), 4.37-4.50 (m, 4H, OCH<sub>2</sub> of OEt + H-2' + OH), 4.93 (d, 1H, OH, *J*=5.0 Hz), 5.27 (d, 1H, OH, *J*=3.7 Hz), 6.14 (d, 1H, H-1', *J*=3.3 Hz). Calc. for C<sub>13</sub>H<sub>17</sub>N<sub>5</sub>O<sub>7</sub>: C, 43.95; H, 4.82; N, 19.71. Found: C, 43.80; H, 5.01; N, 19.98%.

**1-(5'-O-Acetyl-β-D-ribofuranosyl)-3-ethoxycarbonyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazin-4-**

**one (4).** Compound (**2e**) (0.19 g, 0.4 mmol) was added to a sodium methoxide solution, which was prepared from sodium (0.005 g, 0.022 mmol) and anhydrous ethanol (15 mL). The reaction mixture was kept at r.t. for 0.25 h, cooled, neutralized with acetic acid and concentrated *in vacuo*.

The product was isolated by column chromatography using ethyl acetate: hexane (7:1) as the eluent. Yield: 0.087 g, (55%); mp 92 °C; [α]<sup>20</sup><sub>D</sub> -31.3° (*c* 0.5, MeCN); MS (APCI, *m/z* (rel. %)) 398 (100%) [M+H]<sup>+</sup>; IR: CO 1744, 1732, 1706; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.41 (t, 3H, Me of OEt), 2.05 (s, 3H, Me of OAc), 2.53 (s, 3H, Me), 3.35 (br. s, 1H, OH), 4.03 (br. s, 1H, OH), 4.27 (d,d, 2H, H-5'*b*', *J*=6.5 Hz, *J*=11.7 Hz), 4.27 (d,d, 2H, H-5'*a*', *J*=3.5 Hz, *J*=11.0 Hz), 4.40-4.46 (m, 3H, CH<sub>2</sub> of OEt + H-4'), 4.55 (t, 1H, H-3', *J*=5.0 Hz), 4.78 (d, 1H, H-2', *J*=4.0 Hz), 6.47 (d, 1H, H-1', *J*=2.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.04 (CH<sub>3</sub> of OEt), 14.53 (Me), 20.65 (Me of Ac), 63.01 (CH<sub>2</sub> of OEt), 63.95 (C-5'), 71.31 (C-3'), 73.72 (C-2'), 82.84 (C-4'), 95.22 (C-1'), 132.55 (C-3), 145.67 (C-4), 150.90 (C-8*a*), 160.20 (CO), 164.61 (C-7), 171.10 (CO of Ac). Calc. for C<sub>15</sub>H<sub>19</sub>N<sub>5</sub>O<sub>8</sub>: C, 45.34; H, 4.82; N, 17.63. Found: C, 45.55; H, 5.03; N, 17.26%.

**1-(2',3',4',5'-Tetra-O-acetyl-β-D-glucopyranosyl)-3-phenyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazin-**

**4-ones (5a-c).** **Method A.** *N,O*-bis-(Trimethylsilyl)acetamide (0.328 ml, 1.34 mmol), trimethylsilyl triflate (TMSOTf) (0.32 ml, 1.8 mmol) and β-D-glucose penta-acetate (0.39 g, 1.00 mmol) were added to a solution of compound (**1a-c**) (0.94 mmol) in 7 mL acetonitrile. The reaction mixture was left at r.t. for 2.5 h, diluted with 10 mL acetonitrile with a few drops water, and neutralized (NaHCO<sub>3</sub>). The resulting suspension was filtered, the filtrate concentrated *in*



*vacuo*, and the product isolated by column chromatography using ethyl acetate: hexane (3:1) as the eluent.

**Method B.** Compound (**1a-c**) (0.94 mmol) was suspended in a 17% sodium carbonate solution (3 mL). The precipitate was filtered off and dried. The resulting solid was dissolved in DMF (5 mL), acetobromo- $\alpha$ -D-glucose (0.390 g, 0.95 mmol) was added, and the mixture was heated on a water bath for 3 h. Then the reaction mixture was concentrated *in vacuo*. The product was isolated by column chromatography using ethyl acetate: hexane (3:1) as eluent.

**Compound 5a.** Yield of (A) 0.23 g, (45%); of B 0.15g, (30%); mp 184 °C;  $[\alpha]^{20}_D$  -37.4° (*c* 0.3, MeCN); MS (APCI, *m/z* (rel. %)) 544 (100%)  $[M+H]^+$ ; IR: CO 1749, 1724;  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  1.97 (s, 3H, Me of 2'-Ac), 2.00 (s, 3H, Me of 6'-Ac), 2.01 (s, 3H, Me of 3'-Ac), 2.03 (s, 3H, Me of 4'-Ac), 4.04 (d,d, 1H, H-6'*b*, *J*=2 Hz, *J*=12 Hz), 4.19 (d,d, 1H, H-6'*a*, *J*=5.0 Hz, *J*=12.5 Hz), 4.47 (m, 1H, H-5'), 5.08 (t, 1H, H-4', *J*=10.0 Hz), 5.69 (t, 1H, H-3', *J*=9.5 Hz), 5.89 (t, 1H, H-2', *J*=9.5 Hz), 6.50 (d., 1H, H-1', *J*=9.0 Hz), 7.53 (m, 3H, *m-p*-Ph), 8.01 (m, 2H, *o*-Ph), 8.45 (s, 1H, H-7).  $^{13}C$  NMR (DMSO- $d_6$ ):  $\delta$  20.08 (Me of Ac), 20.15 (Me of Ac + Me of Ac), 20.25 (Me of Ac), 61.43 (C-6'), 67.44 (C-2' + C-4'), 72.60 (C-3'), 72.94 (C-5'), 85.00 (C-1'), 128.00 (C*m*), 128.80 (C*o*), 129.90 (C*p*), 131.69 (C*i*), 141.50 (C-3), 148.50 (C-4), 151.10 (C-8*a*), 152.85 (C-7), 168.64 (CO of 2'-Ac), 169.06 (CO of 4'-Ac), 169.34 (CO of 3'-Ac), 169.91 (CO of 6'-Ac). Calc. for C<sub>24</sub>H<sub>25</sub>N<sub>5</sub>O<sub>10</sub>·H<sub>2</sub>O: C, 52.84; H, 4.99; N, 12.84. Found: C, 52.41; H, 4.62; N, 11.99%.

**Compound 5b.** Yield of (A) 0.25 g, (48%); of (B) 0.17 g, (33%). mp 243 °C;  $[\alpha]^{20}_D$  -35.5° (*c* 0.3, MeCN); MS (APCI, *m/z* (rel. %)) 558 (100%)  $[M+H]^+$ ; IR: CO 1746, 1735;  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  1.85 (s, 3H, Me of 2'-Ac), 1.95 (s, 3H, Me of 6'-Ac), 1.97 (s, 3H, Me of 3'-Ac), 2.02 (s, 3H, Me of 4'-Ac), 2.47 (s, 3H, Me), 4.02 (*d,x m*, 1H, H-6'*b*, *J*=12.0 Hz), 4.20 (d,d, 1H, H-6'*a*, *J*=4.5 Hz, *J*=12.7 Hz), 4.48 (m, 1H, H-5'), 5.07 (t, 1H, H-4', *J*=9.5 Hz), 5.68 (t, 1H, H-3', *J*=10.0 Hz), 5.87 (t, 1H, H-2', *J*=9.5 Hz), 6.53 (d, 1H, H-1', *J*=9.0 Hz), 7.52 (m, 3H, *m-p*-Ph), 7.99 (m, 2H, *o*-Ph).  $^{13}C$  NMR (DMSO- $d_6$ ):  $\delta$  14.18 (Me), 20.21 (Me of Ac), 20.30 (Me of Ac + Me of Ac), 20.39 (Me of Ac), 61.39 (C-6'), 67.39 (C-2' + C-4'), 72.61 (C-3'), 72.90 (C-5'), 84.72 (C-1'), 128.10 (C*m*), 128.89 (C*o*), 139.98 (C*p*), 131.88 (C-*i*), 140.78 (C-3), 148.24 (C-4), 151.28 (C-8*a*), 162.51 (C-7), 168.79 (CO of 2'-Ac), 169.19 (CO of 4'-Ac), 169.45 (CO of 3'-Ac), 169.88 (CO of 6'-Ac). Calc. for C<sub>25</sub>H<sub>27</sub>N<sub>5</sub>O<sub>10</sub>: C, 53.86; H, 4.88; N, 12.56. Found: C, 53.81; H, 4.50; N, 12.43%.

**Compound 5c.** Yield of (A) 0.28 g, (50%); of (B) 0.22g, (40%); mp 224 °C;  $[\alpha]^{20}_D$  -25.9° (*c* 0.5, MeCN); MS (APCI, *m/z* (rel. %)) 590 (100.0%)  $[M+H]^+$ , 591 (27.0%)  $[M+1+H]^+$ , 592 (12.37%)  $[M+1+H]^+$ ; IR, CO 1750, 1720;  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  1.96 (s, 3H, Me of 2'-Ac), 1.97 (s, 3H, Me of 6'-Ac), 2.01 (s, 3H, Me of 3'-Ac), 2.02 (s, 3H, Me of 4'-Ac), 2.68 (s, 3H, SMe), 4.02 (*d x m*, 1H, H-6'*b*, *J*=12 Hz), 4.16 (dd, 1H, H-6'*a*, *J*=4.5 Hz, *J*=12 Hz), 4.46 (m, 1H, H-5'), 5.07 (t, 1H, H-4', *J*=9.5 Hz), 5.67 (t, 1H, H-3', *J*=9.5 Hz), 5.85 (t, 1H, H-2', *J*=9.0 Hz), 6.50 (d., 1H, H-1', *J*=9.5 Hz), 7.52 (m, 3H, *m-p*-Ph), 7.99 (m, 2H, *o*-Ph);  $^{13}C$  NMR (DMSO- $d_6$ ):  $\delta$  13.51 (SMe), 20.21 (Me of Ac), 20.32 (Me of Ac + Me of Ac), 20.40 (Me of Ac), 61.48 (C-6'), 67.39 (C-2' + C-4'), 72.60 (C-3'), 72.96 (C-5'), 84.70 (C-1'), 128.14 (C*m*), 128.80 (C*o*), 130.12 (C*p*), 131.79 (C*i*), 141.24 (C-3), 147.45 (C-4), 151.70 (C-8*a*), 165.35 (C-7), 168.84 (CO of 2'-Ac), 169.22

(CO of 4'-Ac), 169.50 (CO of 3'-Ac), 169.91 (CO of 6'-Ac). Calc. for  $C_{25}H_{27}N_5O_{10}S$ : C, 50.93; H, 4.62; N, 11.88. Found: C, 50.81; H, 4.62; N, 11.67%.

**1-( $\beta$ -D-Glucopyranosyl)-3-phenyl-1,2,4-triazolo[5,1-c][1,2,4]triazin-4-ones (6a-c).** Compound (**5a-c**) (0.4 mmol) was added to a sodium methoxide solution, prepared from sodium (0.03 g, 1.30 mmol) and methanol (5 ml). The reaction mixture was heated at reflux for 0.5 h, cooled, neutralized with acetic acid and concentrated *in vacuo*. The product was isolated by column chromatography using ethyl acetate as the eluent.

**Compound 6a.** Yield 0.076 g, (48%); mp 211 °C;  $[\alpha]^{20}_D$  2.9° (*c* 0.3, MeCN); MS (APCI, *m/z* (rel. %)) 376 (100%)  $[M+H]^+$ . IR: CO, 1717  $cm^{-1}$ .  $^1H$  NMR (DMSO-*d*<sub>6</sub>):  $\delta$  3.25-3.34 (m, 1H, H-6'*b*), 3.34-3.57 (m, 3H, H-6'*a* + H-5' + H-4'), 3.69-3.76 (m, 1H, H-3'), 4.07 (m, 1H, H-2'), 4.39 (t, 1H, OH, *J*=5.7 Hz), 5.03 (d, 1H, OH, *J*=5.2 Hz), 5.15 (d, 1H, OH, *J*=4.7 Hz), 5.25 (d, 1H, OH, *J*=4.5 Hz), 5.70 (d, 1H, H-1', *J*=8.3 Hz), 7.50 (m, 3H, *m*-, *p*-Ph), 8.03 (m, 2H, *o*-Ph), 8.30 (s, 1H, H-7). Calc. for  $C_{16}H_{17}N_5O_6 \cdot H_2O$ : C, 48.86; H, 4.87; N, 17.80. Found: C, 48.24; H, 4.84; N, 17.28%.

**Compound 6b.** Yield 0.099 g, (64%); mp 237 °C;  $[\alpha]^{20}_D$  30.5° (*c* 0.5, DMSO); MS (APCI, *m/z* (rel. %)) 390 (100%)  $[M+H]^+$ . IR: CO 1717  $cm^{-1}$ .  $^1H$  NMR (DMSO-*d*<sub>6</sub>):  $\delta$  2.48 (s, 3H, Me), 3.23-3.36 (m, 1H, H-6'*b*), 3.40-3.54 (m, 3H, H-6'*a* + H-5' + H-4'), 3.69-3.73 (m, 1H, H-3'), 4.05 (m, 1H, H-2'), 4.27 (t, 1H, OH, *J*=5.0 Hz), 4.92 (br. s, 1H, OH), 5.02 (br. s, 1H, OH), 5.18 (br. s, 1H, OH), 5.67 (d, 1H, H-1', *J*=8.7 Hz), 7.48 (m, 3H, *m*-, *p*-Ph), 8.04 (m, 2H, *o*-Ph). Calc. for  $C_{17}H_{19}N_5O_6$ : C, 52.44; H, 4.92; N, 17.99. Found: C, 52.19; H, 4.91; N, 18.04%.

**Compound 6c.** Yield 0.053 g, (30%); mp 258 °C;  $[\alpha]^{20}_D$  3.5° (*c* 0.1, MeCN); MS (APCI, *m/z* (rel. %)) 422 (100%)  $[M+H]^+$ , 423 (26.6%)  $[M+1+H]^+$ , 424 (10.5%)  $[M+2+H]^+$ . IR: CO 1718;  $^1H$  NMR (DMSO-*d*<sub>6</sub>):  $\delta$  2.68 (s, 3H, SMe), 3.22-3.34 (m, 1H, H-6'*b*), 3.39-3.52 (m, 3H, H-6'*a* + H-5' + H-4'), 3.69-3.73 (m, 1H, H-3'), 4.07 (m, 1H, H-2'), 4.25 (t, 1H, OH, *J*=5.2 Hz), 4.92 (d, 1H, OH, *J*=5.2 Hz), 5.02 (d, 1H, OH, *J*=5.0 Hz), 5.18 (d, 1H, OH, *J*=4.5 Hz), 5.70 (d, 1H, H-1', *J*=9.0 Hz), 7.50 (m, 3H, *m*-, *p*-Ph), 8.03 (m, 2H, *o*-Ph). Calc. for  $C_{17}H_{19}N_5O_6S \cdot H_2O$ : C, 46.46; H, 4.82; N, 15.94. Found: C, 46.70; H, 4.79; N, 15.20%.

**X-Ray data collection and structure refinement.** Data collection for compound **2e** (crystallized from 2-propanol) was carried out using a Bruker SMART 1000 CCD diffractometer using graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å). X-ray data of blocked nucleoside **5c** (crystallized from acetic acid) were collected on CAD4 Enraf-Nonius graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å). All calculations were carried out the SHELXTL program package.<sup>21</sup> A summary of the fundamental crystal and refinement data is given in Table 1. Crystallographic data for **2e** and **5b** have been deposited at Cambridge Crystallographic Date Centre. The CCDC numbers are listed in Table 1. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK: FAX: +44 (1223) 336033, e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

**Table 1.** Crystal data and structure refinement for compounds **2e** and **5c**

Crystal Data	<b>2e</b>	<b>5c</b>
Identification code	CCDC-720052	CCDC-720053
Empirical formula	C <sub>19</sub> H <sub>23</sub> N <sub>5</sub> O <sub>10</sub>	C <sub>25</sub> H <sub>27</sub> N <sub>5</sub> O <sub>10</sub>
Formula weight	481.42	557.52
Temperature (K)	120(2)	293(3)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	P 21 21 2	P 21 21 22
Unit cell dimension	a (Å) 16.3319(15) b (Å) 16.6892(15) c (Å) 8.1038(8)	a (Å) 10.715(2) b (Å) 11.172(2) c (Å) 21.733(4)
	α (°) 90.00 β (°) 90.00 γ (°) 90.00	α (°) 90.00 β (°) 90.00 γ (°) 90.00
Volume (Å <sup>3</sup> )	2208.8(4)	2601.6(8)
Z	4	4
Density (calculated) (mg/m <sup>3</sup> )	1.448	1.423
Absorption coefficient	0.119	0.112
F(000)	1008	1.002
Theta range (°)	1.74 to 27	1.87 to 26.99
Index ranges	-20 ≤ h ≤ 19 -21 ≤ k ≤ 21 -10 ≤ l ≤ 10	0 ≤ h ≤ 13 0 ≤ k ≤ 14 -3 ≤ l ≤ 27
Reflection collected	18615	3210
Independent reflection	4814 [R(int)=0.0575]	3173 [R(int)=0.0549]
Completeness to theta (°)	99.7%	99.1%
Date/ restraints/ parameters	4814 / 0 / 312	3173 / 0 / 366
Goodness-of-fit on F <sup>2</sup>	1.037	1.002
R [I>2σ(I)]	0.0342(3676 reflns.)	0.0434 (1311 reflns.)
R <sub>w</sub> F (all data)	0.0589	0.0921

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## References

1. De Clercq, E. *Clinical Microbiological Reviews* **2001**, *14*, 382.
2. De Clercq, E. *J. Pharmacology and Experimental Therapeutics* **2001**, *297*, 1.
3. Jones, P.S. *Antiviral Chemistry & Chemotherapy* **1998**, *9*, 283.
4. De Clercq, E. *Nature Rev. Drug Discov.* **2002**, *1*, 13.
5. De Clercq, E. *J. Antimicrobial Chemotherapy* **2003**, *51*, 1079.
6. Eizuru, Y. *Antiviral Chem. & Chemotherapy* **2003**, *14*, 299.
7. Almerico, A. M.; Lauria, A.; Diana, P.; Barraja, P.; Cirrincione, G.; Dattolo, G. *ARKIVOC* **2000**, (iv), 486.
8. Farras, J.; Lleo, M. der M.; Vilarrasa, J. *Tetrahedron Lett.* **1996**, 901.
9. Rusinov, V. L.; Ulomsky, E. N.; Chupakhin, O. N.; Zubairov, M.M; Kapustin, A. B.; Mitin, N. I.; Ziravetskii, M. I.; Vinograd, I. A. *Pharm. Chem. J.* **1990**, *24*, 646.
10. Chupakhin, O. N.; Rusinov, V. L.; Ulomsky, E. N.; Charushin, V. N.; Petrov, A. Yu., Kiselev, O. I. Patent RU 2294936, 2007; *Chem. Abstr.* **2007**, *146*, 316946.
11. Vorbrüggen, H. *Acc. Chem. Res.* **1995**, *28*, 509.
12. Vorbrüggen, H.; Bennua, B. *Chem. Ber.* **1981**, *114*, 1279.
13. Davoll, J.; Lowy, B. *J. Am. Chem. Soc.* **1951**, *73*, 1650
14. Baker, B. R.; Joseph, J. P.; Schaub, R. E.; Williams, J. H. *J. Org. Chem.* **1954**; *19*, 1780.
15. Gough, G.; Helen Maguire, M. *J. Med. Chem.* **1967**, *10*; 475.
16. Kazimierczuk, Z.; Cottam, H.B.; Revankar, G.R.; Robins, R. K. *J. Am. Chem. Soc.*, **1984**, *106*, 6379.
17. Ulomskii, E. N.; Rusinov, V. L.; Chupakhin, O. N.; Rusinov, G. L.; Chernyshev, A. I.; Aleksandrov, G. G. *Chem. Heterocyclic Compounds* **1987**, *23*, 1236.
18. Altona, C.; Haasnoot, C. A. G. *Org. Mag. Resonan.* **1980**, *13*, 417.
19. Ulomskii, E. N.; Deev, S. L.; Shestakova, T. S.; Rusinov, V. L.; Chupakhin O. N. *Russian Chemical Bulletin* **2002**, *51*, 1737; *Chem. Abstr.* **2003**, *138*, 368861k.
20. Ulomskii, E. N.; Deev, S. L.; Tkachev A. N.; Moiseev I. K.; Rusinov, V. L. *Zh. Org. Khim.* **1999**, *35*, 1384; *Chem. Abstr.* **2003**, *138*, 4579m.
21. Sheldrick, G.M. SHELXTL-98, Version 5.10; Bruker-AXS Inc., Madison, WI, USA, **1998**.