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An improved direct synthetic approach to anhydronucleosides

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ABSTRACT

The synthesis of anhydrothioglycosyls has been improved by studying the reaction under a variety of reaction conditions including gas phase pyrolysis, heating in a solvent of high boiling point, in the presence of different bases including triethylamine, DABCO, and DBU, and in a microwave reactor.

1. Introduction

The synthesis of 2,2′- and 2,3′-anhydronucleoside has attracted considerable interest due to the possibility that these compounds can be attacked by nucleophiles at the C-2′ or C-3′ positions affording compounds with anti-AIDS activity.[1] The first reported method for the synthesis of 2,2′-anhydronucleosides involved treating 1-3′,5′-*O*-isopropylidene-2′-*O*-methanesulfonyl-β-D-xylofuranosylthymine with sodium hydroxide in ethanol at reflux to afford the corresponding 2,2′-anhydronucleoside.[2] Moreover, the action of bases ($NaHCO_3$/DMF, PhCOONa, or DB) on the appropriate 2′-*O*-phenyloxycarbonyl or 2′-*O*-methanesulfonyl derivatives of nucleosides have been used to promote anhydrization.[1d,f,g,3–5] Additionally, heating 2′-deoxy-2′-iodonucleosides in DMF with di-*n*-butyltin oxide gave the corresponding anhydronucleosides.[6] 2,2′-Anhydrothionucleosides have also been investigated and some synthetic methods have been reported.[7a,b] Moreover, a method has been reported for the synthesis of *arabino*-6-aza-2-thio-2,2′-anhydrouridine.[8]

During our study for the thermal selective synthesis of 2-glycosyl derivatives **2** from their corresponding 4-arylideneamino derivatives **1**, we accidentally discovered the gas phase thermal intramolecular substitution reaction, which led to the conversion of the 2-β-D-*N*-glucosyl, 2-β-D-*N*-galactosyl, and 2-β-D-*N*-ribosyl derivatives of 3-thioxo-2,3-dihydro-1,2,4-triazin-5(4*H*)-ones into their corresponding 3,2′-anhydro-β-D-mannosyl, 3,2′-anhydro-β-D-talosyl, and 3,2′-anhydro-β-D-arabinosyl derivatives **3** (Scheme 1).[9] The proposed mechanism for the thermal conversion of these acylated glycosyls into their anhydro derivatives is illustrated in Scheme 1. This involves the intramolecular S_N2 (5-*exo*-*tet*) attack by the sulfur on C-2′ of the glycosyl moiety followed by elimination of acetate (CH_3COO^-) and H^+, which ultimately produce acetic acid.[9]

2. Results and discussions

In the present work, we have been able to convert **4a** into the anhydro derivative **7a** thermally by static pyrolysis at 255 °C. We thought that based on the proposed mechanism the reaction could be accomplished under milder conditions in the presence of a suitable base. Hence we studied first the conversion of **4a** into the corresponding anhydro derivative **7a** by heating in xylene in the presence of DABCO, but no detectable product was found even after 24 h at reflux. However, upon heating in MW at 180–190 °C for 10 min, the starting material completely disappeared and 62–67% yield of the anhydro derivative **7a** was isolated from this reaction mixture. Changing the solvent to THF did not affect the yield of this reaction noticeably. These conditions have been optimized for this example by running the reaction at different temperature and following the product/starting material ratio by different analytical techniques including LCMS and NMR spectroscopy.

The recently established fact that the MW effect is purely thermal and not related to microwave field[10] led us to investigate this reaction in diphenyl ether (DPE) as a solvent of high boiling point. Thus, when **4a** and DABCO in DPE were heated at 190–200 °C, complete conversion took place, but the isolated yield of **7a** was

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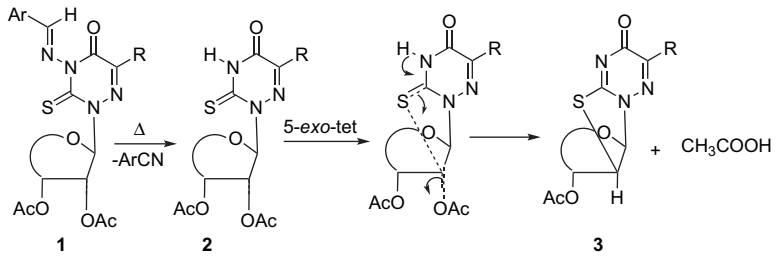


Scheme 1.

only 40% most probably due to loss of products during isolation from this solvent. An identical result was obtained by running the reaction in nitrobenzene instead of DPE with little improvement in the yield (49%, Table 1).

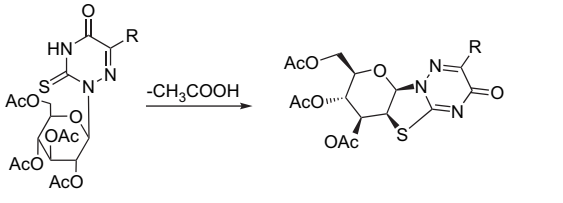
Also, conducting this reaction in ethylpyridinium tetrafluoroborate (ionic liquid, IL) in the presence of DABCO at 140 °C afforded 34% of the anhydro derivative **7a**. Compared to the reaction in xylene at the same temperature, it is clear that that IL improves the conditions required for the desired conversion of **4a** into **7a**. Table 1 summarizes the different conditions studied to convert **4a** into **7a**.

In this work, we also studied the synthesis of further examples of 2-glucosyl-1,2,4-triazines **4**–**6**. The latter were successfully converted into their corresponding anhydrothioglucosyls **7**–**9** (Scheme 2) using the conditions of entry 3 or 5 in Table 1. The yields of the anhydro derivatives **7**–**9** were in the ranges shown in Scheme 2.

Table 1
Yield and reaction conditions studied to convert **4a** into **7a**

Entry	Yield of **7a** (%)	Reaction conditions[a]
1	39	Static pyrolysis 255 °C, 20 min
2	0	DABCO/xylene, 140 °C, 24 h
3	67	DABCO/xylene, MW 190 °C, 10 min
4	62	DABCO/THF, MW 190 °C, 10 min
5	40	DABCO/DPE, oil bath 190–200 °C, 40 min
6	49	DABCO/$PhNO_2$, oil bath, 190 °C, 10 min
7	34	DABCO/IL, oil bath, 140 °C, 10 min

[a] Static pyrolysis was performed in a sealed tube as described in Section 4. All other experiments were performed by mixing **4a** (1 mmol), DABCO (2 mmol), xylene or THF (5 mL) or DPE or $PhNO_2$ or IL (0.5 mL). IL used was ethylpyridinium tetrafluoroborate.

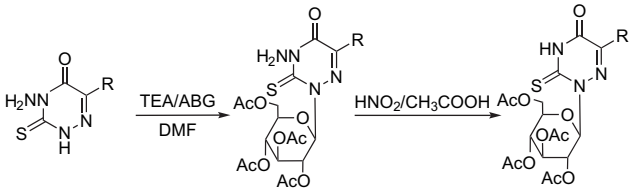


	R		
4a-c, e	CH_2Ar	**7**a-c, e	CH_2Ar 34-67%
5a, b, d	Ar	**8**a, b, d	Ar 63-88%
6a-c, e, f	CH=CHAr	**9**a-c, e, f	CH=CHAr 27-76%

Ar = a, C_6H_5, b, *p*-ClC_6H_4, c, *p*-$CH_3C_6H_4$, d, *p*-$CH_3OC_6H_4$, e, 2-thienyl, f, *p*-$O_2NC_6H_4$

Scheme 2.

The starting materials **4**–**6** used in this investigation have been prepared as outlined in Scheme 3. Thus, reacting the appropriate 4-amino-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4*H*)-ones **10**–**12** with acetobromoglucose in DMF and triethylamine afforded the corresponding 2-tetra-*O*-acetyl-β-D-glucopyranosyl derivatives **13**–**15**. The latter were readily deaminated upon treatment with nitrous acid in acetic acid to afford the corresponding 2-glucosyl derivatives **4**–**6**.



	R		R		R
10a-c, e	CH_2Ar	**13**a-c, e	CH_2Ar	**4**a-c, e	CH_2Ar
11a, b, d	Ar	**14**a, b, d	Ar	**5**a, b, d	Ar
12a-c, e, f	CH=CHAr	**15**a-c, e, f	CH=CHAr	**6**a-c, e, f	CH=CHAr

Ar = a, C_6H_5, b, *p*-ClC_6H_4, c, *p*-$CH_3C_6H_4$, d, *p*-$CH_3OC_6H_4$, e, 2-thienyl, f, *p*-$O_2NC_6H_4$

Scheme 3.

3. Conclusion

The present study explored the optimization of the reaction conditions leading to efficient conversions of glycosyl derivatives into their valuable anhydroglycosyl derivatives. The results obtained thus far are promising, and encourage us to continue further applications to convert other glycosyl derivatives into their anhydroglycosyl derivatives, which will be a valuable starting material for the synthesis of new potential biologically active glycosyl derivatives.

4. Experimental

4.1. General

All melting points are uncorrected. IR spectra were recorded in KBr disks on a Perkin Elmer System 2000 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400, 400 MHz super-conducting NMR spectrometer. Mass spectra were measured on VG Auto-spec-Q (high resolution, high performance, tri-sector GC/MS/MS) and with LCMS using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Microanalyses were performed on LECO CH NS-932 Elemental Analyzer. The starting compounds **10**–**12** were prepared as reported and the new derivatives were prepared as described in this section.

4.2. Synthesis of anhydrothioglycosyls 7–9: general procedures

(A) A mixture of the appropriate derivatives **4**–**6** (1 mmol) and DABCO (2 mmol) in xylene or THF (2 mL) was heated in the microwave reaction tube for 10 min at 190 °C. The content of the tube was washed with petroleum ether and filtered. The precipitate was collected, purified by boiling with ethanol and charcoal, and recrystallized from ethanol.

(B) A mixture of the appropriate derivatives **4**–**6** (1 mmol), DABCO (2 mmol), and DPE (0.5 mL) was heated at 190–200 °C (oil bath) for 40 min. The contents of tube were washed with petroleum ether and the precipitate was collected, purified by

boiling with ethanol and charcoal, and recrystallized from ethanol.

(C) A mixture of **4a** (1 mmol), DABCO (2 mmol), and ethylpyridinium tetrafluoroborate (0.1 g) was heated at 140 °C (oil bath) for 10 min. The contents of tube were washed with water and filtered. After drying, the product was dissolved in $CDCl_3$ and the yield was determined by ^1H NMR spectroscopy.

(D) Compound **4a** (1 mmol) was introduced in the reaction tube (1.5×12 cm Pyrex), cooled in liquid nitrogen, sealed under vacuum (0.06 mbar), and placed in the pyrolyzer heated at 255 °C (static pyrolyzer) for 20 min. The contents of the tube were then dissolved in $CDCl_3$ and the yield was determined by ^1H NMR spectroscopy.

(E) A mixture of the appropriate derivatives **4**–**6** (1 mmol), DABCO (2 mmol), and $PhNO_2$ (0.3 mL) was heated at 190 °C (oil bath) for 40 min. The contents of tube were washed with petroleum ether and the precipitate was collected, purified by boiling with ethanol and charcoal, and recrystallized from ethanol.

4.2.1. 3,2-Anhydro-6-benzyl-2(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***7a***

Colorless needles, yield 67% (A), 40% (B), 34% (C), 39% (D), 49% (E), mp 212–213 °C. LCMS: *m*/*z*=490 (M+1); MS: *m*/*z*=489 (M^+, 100%). IR: 3030, 2937, 1758, 1732, 1665, 1515, 1369, 1238, 1106, 1059. ^1H NMR ($CDCl_3$): *δ* 2.09, 2.12, 2.13 (3s, 9H, $3CH_3CO$), 3.81 (m, 1H), 3.88 (d, 1H, *J* 14.3), 4.10 (d, 1H, *J* 14.3), 4.14 (dd, 1H, *J* 12.5, 2.0), 4.38 (dd, 1H, *J* 12.5, 4.7), 4.67 (dd, 1H, *J* 5.7, 3.4), 5.40 (t, 1H, *J* 9.6), 5.50 (dd, 1H, *J* 9.5, 5.8), 5.71 (d, 1H, *J* 3.6), 7.28 (t, 2H, *J* 8.0), 7.32 (t, 1H, *J* 7.6), 7.37 (d, 2H, *J* 8.0). ^{13}C NMR ($CDCl_3$): *δ* 20.5, 20.6, 20.7, 36.7, 46.9, 61.4, 65.0, 69.4, 72.6, 88.9, 127.0, 128.5, 129.5, 153.1, 153.4, 160.2, 168.0, 169.2, 169.7, 170.6. Anal. Calcd for $C_{22}H_{23}N_3O_8S$ (489.5): C 53.98; H 4.74; N 8.58; S 6.55. Found: C 54.18; H 4.68; N 8.71; S 6.25.

4.2.2. 3,2-Anhydro-6-p-chlorobenzyl-2(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***7b***

Colorless plates, yield 58% (A), 63% (B), mp 249–250 °C. LCMS: *m*/*z*=524 (M+1). MS: *m*/*z*=523 (M^+, 100%). IR: 2919, 2851, 1760, 1731, 1665, 1518, 1234. ^1H NMR ($CDCl_3$): *δ* 2.09, 2.12, 2.13 (3s, 9H, $3CH_3CO$), 3.83 (m, 1H), 3.84 (d, 1H, *J* 14.5), 4.05 (d, 1H, *J* 14.6), 4.16 (dd, 1H, *J* 12.5, 2.0), 4.38 (dd, 1H, *J* 12.6, 4.6), 4.68 (dd, 1H, *J* 5.6, 3.7), 5.39 (t, 1H, *J* 9.7), 5.50 (dd, 1H, *J* 9.5, 5.8), 5.72 (d, 1H, *J* 3.5), 7.29 (s, 4H). ^{13}C NMR ($CDCl_3$): *δ* 20.5, 20.6, 20.7, 36.1, 46.9, 61.3, 65.0, 69.4, 72.6, 88.9, 128.7, 130.9, 132.9, 133.8, 152.7, 160.1, 168.2, 169.2, 169.6, 170.6. Anal. Calcd for $C_{22}H_{22}ClN_3O_8S$ (523.9): C 50.43; H 4.23; N 8.02; S 6.12. Found: C 50.29; H 4.22; N 8.20; S 6.17.

4.2.3. 3,2-Anhydro-6-p-methylbenzyl-2(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***7c***

Colorless needles, yield 67% (A), 55% (B), mp 218–219 °C. LCMS: *m*/*z*=504 (M+1); MS: *m*/*z*=503.7 (M^+, 100%). IR: 3029, 2949, 1761, 1732, 1664, 1516, 1234, 1061. ^1H NMR ($CDCl_3$): *δ* 2.09, 2.12, 2.13 (3s, 9H, $3CH_3CO$), 2.34 (s, 3H, CH_3), 3.82 (m, 2H), 4.07 (d, 1H, *J* 14.4), 4.16 (dd, 1H, *J* 12.4, 2.4), 4.37 (dd, 1H, *J* 12.4, 4.8), 4.66 (dd, 1H, *J* 5.6, 4.0), 5.40 (t, 1H, *J* 9.6), 5.50 (dd, 1H, *J* 9.6, 6.0), 5.71 (d, 1H, *J* 3.6), 7.13 (d, 2H, *J* 8.0), 7.26 (d, 2H, *J* 8.0). ^{13}C NMR ($CDCl_3$): *δ* 21.1, 21.2, 21.3, 21.7, 36.9, 47.5, 62.0, 65.6, 70.0, 73.2, 89.5, 129.9, 130.0, 132.9, 137.3, 153.9, 160.8, 168.6, 169.8, 170.3, 171.2. Anal. Calcd for $C_{23}H_{25}N_3O_8S$ (503.5): C 54.86; H 5.00; N 8.35; S 6.37. Found: C 54.80; H 4.98; N 8.45; S 6.38.

4.2.4. 3,2-Anhydro-6-(2-thienylmethyl)-2-(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***7e***

Colorless plates, yield 34% (A), mp 170–172 °C. LCMS: *m*/*z*=496 (M+1). IR: 3105, 2958, 1750, 1663, 1639, 1511, 1229, 1057. ^1H NMR ($CDCl_3$): *δ* 2.09, 2.12, 2.14 (3s, 9H, $3CH_3CO$), 3.84 (m, 1H), 4.10 (d, 1H, *J* 15.4), 4.16 (dd, 1H, *J* 12.3, 2.4), 4.32 (d, 1H, *J* 15.5), 4.37 (dd, 1H, *J* 12.4, 4.6), 4.69 (dd, 1H, *J* 5.5, 3.6), 5.39 (t, 1H, *J* 9.7), 5.51 (dd, 1H, *J* 9.4, 5.7), 5.73 (d, 1H, *J* 3.7), 6.97 (dd, 1H, *J* 4.8, 3.5), 7.02 (d, 1H, *J* 3.5), 7.21 (d, 1H, *J* 4.8). Anal. Calcd for $C_{20}H_{21}N_3O_8S_2$ (495.5): C 48.48; H 4.27; N 8.48; S 12.94. Found: C 48.39; H 4.20; N 8.29; S 12.94.

4.2.5. 3,2-Anhydro-6-phenyl-2(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***8a***

Colorless needles, yield 63% (A), 87% (B), mp 235–237 °C. LCMS: *m*/*z*=476 (M+1). IR: 3059, 2958, 1751, 1659, 1553, 1507, 1488, 1416, 1371, 1240, 1111, 1064. ^1H NMR ($CDCl_3$): *δ* 2.10, 2.11, 2.16 (3s, 9H, $3CH_3CO$), 3.87 (ddd, 1H, *J* 9.8, 4.5, 2.2), 4.16 (dd, 1H, *J* 12.6, 2.2), 4.39 (dd, 1H, *J* 12.6, 4.5), 4.79 (dd, 1H, *J* 5.8, 3.7), 5.44 (t, 1H, *J* 9.7), 5.56 (dd, 1H, *J* 9.5, 5.8), 5.85 (d, 1H, *J* 3.7), 7.48 (m, 3H), 8.10 (m, 2H). ^{13}C NMR ($CDCl_3$): *δ* 20.5, 20.6, 20.7, 47.0, 61.4, 64.9, 69.4, 72.8, 89.1, 128.3, 129.0, 131.0, 131.4, 148.6, 159.7, 167.0, 169.3, 169.7, 170.6. Anal. Calcd for $C_{21}H_{21}N_3O_8S$ (475.5): C 53.05; H 4.45; N 8.84; S 6.74. Found: C 52.88; H 4.50; N 8.89; S 6.94.

4.2.6. 3,2-Anhydro-6-p-chlorophenyl-2(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***8b***

Colorless needles, yield 75% (A), 65% (B), mp 237–238 °C. LCMS: *m*/*z*=510 (M+1), 511 (M+2). IR: 2975, 2959, 2930, 2908, 1755, 1657, 1549, 1503, 1486, 1418, 1372, 1220, 1112, 1094, 1064. ^1H NMR ($CDCl_3$): *δ* 2.10, 2.11, 2.16 (3s, 9H, $3CH_3CO$), 3.88 (ddd, 1H, *J* 10.6, 4.8, 2.0), 4.16 (dd, 1H, *J* 12.4, 1.6), 4.39 (dd, 1H, *J* 12.6, 4.4), 4.79 (dd, 1H, *J* 5.4, 3.9), 5.44 (t, 1H, *J* 9.7), 5.56 (dd, 1H, *J* 9.5, 5.8), 5.85 (d, 1H, *J* 3.6), 7.43 (d, 2H, *J* 8.5), 8.11 (d, 2H, *J* 8.5). ^{13}C NMR ($CDCl_3$): *δ* 20.5, 20.6, 20.7, 47.0, 61.3, 64.9, 69.4, 72.8, 89.1, 128.6, 129.8, 130.3, 137.3, 147.4, 159.5, 167.0, 169.3, 169.7, 170.6. Anal. Calcd for $C_{21}H_{20}ClN_3O_8S$ (509.9): C 49.46; H 3.95; N 8.24; S 6.29. Found: C 49.38; H 3.95; N 8.40; S 6.23.

4.2.7. 3,2-Anhydro-6-p-methoxyphenyl-2(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***8d***

Colorless needles, yield 68% (A), 88% (B), mp 218–219 °C. MS: *m*/*z*=505 (M^+, 15%). IR: 3077, 2974, 2940, 2840, 1756, 1725, 1671, 1607, 1547, 1499, 1369, 1249, 1232, 1107, 1084, 1065, 1047. ^1H NMR ($CDCl_3$): *δ* 2.09, 2.11, 2.15 (3s, 9H, $3CH_3CO$), 3.85 (m, 1H), 3.88 (s, 3H, OCH_3), 4.16 (dd, 1H, *J* 2.0, 12.6), 4.39 (dd, 1H, *J* 12.5, 4.5), 4.77 (dd, 1H, *J* 5.6, 3.8), 5.44 (t, 1H, *J* 9.6), 5.55 (dd, 1H, *J* 9.5, 5.8), 5.82 (d, 1H, *J* 3.6), 6.97 (d, 2H, *J* 8.8), 8.16 (d, 2H, *J* 8.8). ^{13}C NMR ($CDCl_3$): *δ* 20.5, 20.6, 20.7, 47.0, 55.4, 61.4, 65.0, 69.5, 72.7, 89.2, 113.7, 123.8, 130.8, 147.9, 159.9, 161.9, 166.4, 169.2, 169.7, 170.6. Anal. Calcd for $C_{22}H_{23}N_3O_9S$ (505.5): C 52.27; H 4.59; N 8.31; S 6.34. Found: C 52.29; H 4.56; N 8.41; S 6.27.

4.2.8. 3,2-Anhydro-6-styryl-2-(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***9a***

Gray plates, yield 68% (A), 27% (E), mp 214–215 °C. MS: *m*/*z*=501 (M^+, 35%). IR: 3063, 2919, 1753, 1235, 1222. ^1H NMR ($CDCl_3$): *δ* 2.10, 2.12, 2.15 (3s, 9H, $3CH_3CO$), 3.88 (ddd, 1H, *J* 9.6, 4.2, 2.2), 4.18 (dd, 1H, *J* 12.6, 2.1), 4.40 (dd, 1H, *J* 12.6, 4.4), 4.77 (dd, 1H, *J* 5.6, 3.7), 5.44 (t, 1H, *J* 9.6), 5.55 (dd, 1H, *J* 9.6, 5.6), 5.80 (d, 1H, *J* 4.0), 7.17 (d, 1H, *J* 16.4), 7.39 (m, 3H), 7.59 (d, 2H, *J* 6.4), 8.10 (d, 1H, *J* 16.4). ^{13}C NMR ($CDCl_3$): *δ* 20.5, 20.6, 20.7, 47.0, 61.4, 65.0, 69.5, 72.8, 89.3, 119.0, 127.8, 128.8, 129.6, 135.9, 139.8, 147.2, 160.0, 166.6, 169.3, 169.7, 170.6. Anal. Calcd for $C_{23}H_{23}N_3O_8S$ (501.5): C 55.08; H 4.62; N 8.38; S 6.39. Found: C 55.09; H 4.56; N 8.41; S 6.27. HRMS=501.1201 ($C_{23}H_{23}O_8N_3S$ requires 501.1200).

4.2.9. 3,2-Anhydro-p-chlorostyryl-2-(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***9b***

Colorless needles, yield 52% (A), 66% (B), mp 243–245 °C. MS: *m*/*z*=535 (M^+, 40%). IR: 3063, 2922, 1750, 1643, 1233, 1222, 1109, 1078. ^1H NMR ($CDCl_3$): *δ* 2.10, 2.12, 2.16 (3s, 9H, $3CH_3CO$), 3.87 (ddd, 1H, *J* 9.5, 4.0, 2.5), 4.19 (dd, 1H, *J* 12.5, 2.0), 4.40 (dd, 1H, *J* 12.6, 4.4), 4.76 (dd, 1H, *J* 5.6, 3.7), 5.44 (t, 1H, *J* 9.7), 5.55 (dd, 1H, *J* 9.5, 5.9), 5.79

(d, 1H, *J* 3.6), 7.12 (d, 1H, *J* 16.3), 7.38 (d, 2H, *J* 8.4), 7.52 (d, 2H, *J* 8.4), 8.07 (d, 1H, *J* 16.3). ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.7, 46.9, 61.3, 64.9, 69.4, 72.8, 89.2, 119.6, 128.8, 129.1, 134.4, 135.4, 138.3, 146.9, 159.9, 166.7, 169.2, 169.7, 170.6. Anal. Calcd for $C_{23}H_{22}N_3O_8SCl$ (536.0): C 51.54; H 4.14; N 7.84; S 5.98. Found: C 51.35; H 4.30; N 7.73; S 5.86.

4.2.10. 3,2-Anhydro-6-p-methylstyryl-2-(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***9c***

Gray plates, yield 76% (A), 27% (E), mp 263–264 °C. LCMS: *m*/*z*=516 (M+1). IR: 3075, 2927, 1759, 1737, 1675, 1538, 1506, 1409, 1238, 1211, 1109, 1094, 1055. ^{1}H NMR ($CDCl_3$): δ 2.09, 2.12, 2.15 (3s, 9H, $3CH_3CO$), 2.39 (s, 3H, CH_3), 3.87 (ddd, 1H, *J* 9.8, 4.3, 2.3), 4.18 (dd, 1H, *J* 12.6, 2.1), 4.39 (dd, 1H, *J* 12.6, 4.4), 4.67 (dd, 1H, *J* 5.7, 3.8), 5.43 (t, 1H, *J* 9.7), 5.55 (dd, 1H, *J* 9.6, 5.8), 5.80 (d, 1H, *J* 3.7), 7.12 (d, 1H, *J* 16.4), 7.21 (d, 2H, *J* 8.0), 7.49 (d, 2H, *J* 8.0), 8.06 (d, 1H, *J* 16.4). ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.7, 21.4, 46.9, 61.3, 65.0, 69.4, 72.7, 89.2, 117.8, 127.7, 129.6, 133.1, 139.6, 140.0, 147.3, 160.0, 166.5, 169.2, 169.7, 170.6. Anal. Calcd for $C_{24}H_{25}N_3O_8S$ (515.6): C 55.92; H 4.89; N 8.15; S 6.22. Found: C 55.89; H 4.94; N 8.22; S 6.20.

4.2.11. 3,2-Anhydro-6-[2-(2-thienyl)vinyl]-2-(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***9e***

Yellow plates, yield 55% (A), 60% (B), mp 274–276 °C. MS: *m*/*z*=507 (M^+, 15%). IR: 2977, 2937, 1754, 1670, 1619, 1543, 1504, 1368, 1236, 1218, 1107, 1058. ^{1}H NMR ($CDCl_3$): δ 2.09, 2.12, 2.15 (3s, 9H, $3CH_3CO$), 3.87 (ddd, 1H, *J* 9.8, 4.3, 2.2), 4.18 (dd, 1H, *J* 12.6, 2.2), 4.39 (dd, 1H, *J* 12.6, 4.4), 4.76 (dd, 1H, *J* 5.7, 3.7), 5.43 (t, 1H, *J* 9.7), 5.55 (dd, 1H, *J* 9.6, 5.8), 5.78 (d, 1H, *J* 3.8), 6.91 (d, 1H, *J* 16.0), 7.07 (dd, 1H, *J* 5.0, 3.6), 7.26 (d, 1H, *J* 3.6), 7.37 (d, 1H, *J* 5.0), 8.34 (d, 1H, *J* 16.0). ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.7, 46.9, 61.4, 65.0, 69.4, 72.8, 89.3, 118.5, 127.7, 128.1, 129.9, 133.1, 141.7, 147.0, 159.9, 166.3, 169.2, 169.7, 170.6. Anal. Calcd for $C_{21}H_{21}N_3O_8S_2$ (507.5): C 49.70; H 4.17; N 8.28; S 12.63. Found: C 49.90; H 4.22; N 8.27; S 12.60.

4.2.12. 3,2-Anhydro-6-p-nitrostyryl-2-(3,4,6-tri-O-acetyl-β-D-mannopyranosyl)-3-mercapto-1,2,4-triazin-5(2H)-one ***9f***

Yellow plates, yield 57% (A), 46% (B), mp 229–230 °C. LCMS: *m*/*z*=547 (M+1). IR: 2967, 2938, 1751, 1680, 1628, 1546, 1505, 1342, 1236, 1219, 1109, 1057. ^{1}H NMR ($CDCl_3$): δ 2.07, 2.08, 2.12 (3s, 9H, $3CH_3CO$), 3.89 (m, 1H), 4.19 (dd, 1H, *J* 12.6, 1.7), 4.33 (dd, 1H, *J* 9.6, 4.1), 4.79 (dd, 1H, *J* 5.4, 3.9), 5.44 (t, 1H, *J* 9.7), 5.56 (dd, 1H, *J* 9.5, 5.8), 5.83 (d, 1H, *J* 3.6), 7.24 (d, 1H, *J* 16.4), 7.73 (d, 2H, *J* 8.6), 8.20 (d, 1H, *J* 16.4), 8.26 (d, 2H, *J* 8.6). ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.7, 47.0, 61.6, 64.9, 69.4, 72.9, 89.2, 118.1, 124.2, 128.1, 128.3, 135.4, 137.1, 142.2, 147.9, 159.7, 166.9, 169.6, 170.5. Anal. Calcd for $C_{23}H_{22}N_4O_{10}S$ (546.5): C 50.55; H 4.06; N 10.25; S 5.87. Found: C 50.50; H 4.02; N 10.16; S 5.80.

4.3. 4-Amino-6-substituted-2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4*H*)-ones 13–15: general procedure

A mixture of **10**–**12** (10 mmol) and 2,3,4,6-*O*-tetraacetyl-α-D-glucopyranosyl bromide (4.2 g, 11 mmol) in DMF (5 ml) and triethylamine (1.0 mL) was stirred at room temperature overnight. After dilution with water (20 mL), the precipitate was collected, washed with water several times, and recrystallized from ethanol into crystals of compounds **13**–**15**.

4.3.1. 4-Amino-6-benzyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***13a***

Yellow needles, yield 77%, mp 140 °C (lit.[11a] mp 143 °C). ^{1}H NMR ($CDCl_3$): δ 1.90, 2.07, 2.09, 2.10 (4s, 12H, $4CH_3CO$), 3.96 (m, 2H), 4.05 (d, 1H, *J* 13.6), 4.18 (d, 1H, *J* 12.4), 4.28 (dd, 1H, *J* 12.6, 5.0), 5.25 (t, 1H, *J* 9.8), 5.40 (t, 1H, *J* 9.4), 5.88 (t, 1H, *J* 9.3), 6.31 (s, 2H, NH_2), 6.70 (d, 1H, *J* 9.4), 7.29 (m, 5H).

4.3.2. 4-Amino-6-p-chlorobenzyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***13b***

Colorless plates, yield 75%, mp 125 °C. LCMS: *m*/*z*=599 (M+1). ^{1}H NMR ($CDCl_3$): δ 1.91, 2.07, 2.09, 2.10 (4s, 12H, $4CH_3CO$), 3.90 (d, 1H, *J* 13.2), 3.96 (m, 1H), 4.05 (d, 1H, *J* 13.6), 4.18 (d, 1H, *J* 12.4), 4.29 (dd, 1H, *J* 12.6, 5.0), 5.25 (t, 1H, *J* 9.8), 5.41 (t, 1H, *J* 9.4), 5.87 (t, 1H, *J* 9.4), 6.32 (s, 2H, NH_2), 6.71 (d, 1H, *J* 9.4), 7.13 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 20.6 (2C), 20.7, 20.8, 36.9, 61.6, 67.7, 68.6, 73.9, 74.6, 87.2, 128.8, 130.9, 133.3, 133.5, 145.5, 146.8, 169.0, 169.5, 169.9, 170.2, 170.6. Anal. Calcd for $C_{24}H_{27}ClN_4O_{10}S$ (599.0): C 48.12; H 4.54; N 9.35; S 5.35. Found: C 48.05; H 4.42; N 9.27; S 5.20.

4.3.3. 4-Amino-6-p-methylbenzyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***13c***

Colorless needles, yield 65%, mp 168–169 °C. MS: *m*/*z*=578 (M^+, 16%). IR: 3431, 3305, 2998, 1748, 1708, 1547, 1429, 1368, 1285, 1242, 1099, 1063, 906. ^{1}H NMR ($CDCl_3$): δ 1.92, 2.08, 2.09, 2.11 (4s, 12H, $4CH_3CO$), 2.33 (s, 3H, CH_3), 3.90 (d, 1H, *J* 13.5), 3.96 (ddd, 1H, *J* 9.8, 4.6, 1.8), 4.04 (d, 1H, *J* 13.5), 4.18 (d, 1H, *J* 12.2), 4.28 (dd, 1H, *J* 12.6, 5.0), 5.26 (t, 1H, *J* 9.8), 5.41 (t, 1H, *J* 9.4), 5.90 (t, 1H, *J* 9.4), 6.30 (s, 2H, NH_2), 6.71 (d, 1H, *J* 9.4), 7.13 (d, 2H, *J* 7.8), 7.27 (d, 2H, *J* 8.2). ^{13}C NMR ($CDCl_3$): δ 20.6 (2C), 20.7, 20.8, 21.1, 36.6, 61.6, 67.7, 68.6, 73.9, 74.6, 87.2, 129.3, 129.4, 131.8, 137.0, 146.2, 146.8, 169.0, 169.4, 169.9, 170.3, 170.6. Anal. Calcd for $C_{25}H_{30}N_4O_{10}S$ (578.6): C 51.90; H 5.23; N 9.68; S 5.54. Found: C 51.75; H 5.22; N 9.57; S 5.39.

4.3.4. 4-Amino-6-(2-thienylmethyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***13e***

Gray plates, yield 79%, mp 142–143 °C. MS: *m*/*z*=570 (M^+, 16%). IR: 3110, 2939, 1755, 1692, 1437, 1381, 1291, 1237, 1089, 1040. ^{1}H NMR ($CDCl_3$): δ 1.91, 2.06, 2.08, 2.10 (4s, 12H, $4CH_3CO$), 3.96 (ddd, 1H, *J* 9.7, 5.4, 2.9), 4.17 (m, 2H), 4.27 (m, 2H), 5.24 (t, 1H, *J* 9.8), 5.40 (t, 1H, *J* 9.5), 5.83 (t, 1H, *J* 9.4), 6.35 (s, 2H, NH_2), 6.69 (d, 1H, *J* 9.4), 6.96 (dd, 1H, *J* 4.8, 3.5), 7.04 (d, 1H, *J* 3.5), 7.21 (d, 1H, *J* 4.8). ^{13}C NMR ($CDCl_3$): δ 20.5 (2C), 20.6, 20.7, 31.0, 61.5, 67.7, 68.6, 73.8, 74.5, 87.2, 125.3, 127.1, 127.4, 136.1, 144.7, 146.6, 168.9, 169.4, 169.9, 170.2, 170.5. HRMS=570.1085 ($C_{22}H_{26}O_{10}N_4S_2$ requires 570.1084).

4.3.5. 4-Amino-6-phenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***14a***

Yellow plates, yield 54%, mp 168–169 °C (lit.[11a] mp 174 °C). ^{1}H NMR ($CDCl_3$): δ 1.97, 2.08, 2.09 (s, 3H, s, 6H, s, 3H, $4CH_3CO$), 4.00 (m, 1H), 4.18 (dd, 1H, *J* 12.5, 2.0), 4.28 (dd, 1H, *J* 12.5, 5.0), 5.24 (t, 1H, *J* 9.8), 5.45 (t, 1H, *J* 9.5), 5.97 (t, 1H, *J* 9.4), 6.51 (s, 2H, NH_2), 6.86 (d, 1H, *J* 9.4), 7.52 (m, 3H), 8.14 (m, 2H).

4.3.6. 4-Amino-6-p-chlorophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***14b***

Colorless plates, yield 78%, mp 171–172 °C. MS: *m*/*z*=584 (M^+, 15%). IR: 3335, 3228, 2958, 1753, 1741, 1693, 1435, 1368, 1231, 1061, 1034. ^{1}H NMR ($CDCl_3$): δ 1.97, 2.08, 2.09 (s, 3H, s, 6H, s, 3H, $4CH_3CO$), 4.00 (m, 1H), 4.18 (d, 1H, *J* 12.3), 4.29 (dd, 1H, *J* 12.4, 5.0), 5.25 (t, 1H, *J* 9.8), 5.46 (t, 1H, *J* 9.4), 5.96 (t, 1H, *J* 9.4), 6.51 (s, 2H, NH_2), 6.85 (d, 1H, *J* 9.3), 7.49 (d, 2H, *J* 8.4), 8.15 (d, 2H, *J* 8.4). ^{13}C NMR ($CDCl_3$): δ 20.06 (2C), 20.064, 20.7, 61.6, 67.7, 68.6, 73.8, 74.7, 87.4, 128.9, 129.1, 130.1, 137.6, 140.7, 146.5, 169.1 (2C), 169.5, 170.1, 170.6. HRMS=584.0975 ($C_{23}H_{25}ClN_4O_{10}S$ requires 584.0974).

4.3.7. 4-Amino-6-p-methoxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***14d***

Yellow plates, yield 80%, mp 133–134 °C. MS: *m*/*z*=580 (M^+, 45%). IR: 3322, 3222, 2939, 1752, 1691, 1606, 1515, 1437, 1239, 1183, 1062, 1034. ^{1}H NMR ($CDCl_3$): δ 1.97, 2.07, 2.08, 2.09 (4s, 12H, $4CH_3CO$), 3.90 (s, 3H, CH_3), 4.00 (ddd, 1H, *J* 10.0, 5.0, 2.2), 4.18 (dd, 1H, *J* 12.6, 2.2), 4.29 (dd, 1H, *J* 12.6, 5.0), 5.25 (t, 1H, *J* 9.8), 5.45 (t, 1H,

J 9.4), 5.99 (t, 1H, *J* 9.4), 6.50 (s, 2H, NH_2), 6.84 (d, 1H, *J* 9.4), 7.03 (d, 2H, *J* 8.9), 8.19 (d, 2H, *J* 8.9). ^{13}C NMR ($CDCl_3$): δ 20.56 ($2CH_3$), 20.6, 20.7, 55.4, 61.6, 67.7, 68.6, 73.9, 74.6, 87.4, 114.0, 123.1, 130.5, 141.5, 146.7, 162.0, 169.1 (2C), 169.4, 170.2, 170.6. Anal. Calcd for $C_{24}H_{28}N_4O_{11}S$ (580.6): C 49.65; H 4.86; N 9.65; S 5.52. Found: C 49.56; H 5.02; N 9.56; S 5.46.

4.3.8. 4-Amino-6-styryl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **15a**

Yellow plates, yield 80%, mp 183–185 °C (lit.[11c] mp 180 °C). ^1H NMR ($CDCl_3$): δ 1.96, 2.08, 2.09 (s, 3H, s, 3H, s, 6H, $4CH_3CO$), 4.01 (m, 1H), 4.19 (d, 1H, *J* 12.4), 4.31 (dd, 1H, *J* 12.6, 5.0), 5.28 (t, 1H, *J* 9.8), 5.44 (t, 1H, *J* 9.4), 5.98 (t, 1H, *J* 9.4), 6.44 (s, 2H, NH_2), 6.72 (d, 1H, *J* 9.4), 7.16 (d, 1H, *J* 16.4), 7.41 (m, 3H), 7.65 (d, 2H, *J* 7.0), 7.98 (d, 1H, *J* 16.4).

4.3.9. 4-Amino-6-p-chlorostyryl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **15b**

Yellow plates, yield 60%, mp 238–239 °C (lit.[11c,d] mp 240–242 °C). ^1H NMR ($CDCl_3$): δ 1.97, 2.08, 2.10 (s, 3H, s, 3H, s, 6H, $4CH_3CO$), 3.40 (m, 1H), 4.19 (d, 1H, *J* 12.8), 4.31 (dd, 1H, *J* 12.8, 5.2), 5.27 (t, 1H, *J* 9.8), 5.44 (t, 1H, *J* 9.4), 5.97 (t, 1H, *J* 9.4), 6.42 (s, 2H, NH_2), 6.72 (d, 1H, *J* 9.2), 7.12 (d, 1H, *J* 16.6), 7.39 (d, 2H, *J* 8.0), 7.58 (d, 2H, *J* 8.0), 7.93 (d, 1H, *J* 16.6).

4.3.10. 4-Amino-6-p-methylstyryl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **15c**

Yellow plates, yield 75%, mp 244–245 °C. MS: *m*/*z*=590 (M^+, 75%). IR: 3225, 3170, 2936, 1753, 1725, 1243, 1185. ^1H NMR ($CDCl_3$): δ 1.96, 2.08, 2.10 (s, 3H, s, 3H, s, 6H, $4CH_3CO$), 2.41 (s, 3H, CH_3), 3.99 (m, 1H), 4.19 (d, 1H, *J* 12.4), 4.31 (dd, 1H, *J* 12.7, 4.9), 5.28 (t, 1H, *J* 9.7), 5.44 (t, 1H, *J* 9.4), 5.97 (t, 1H, *J* 9.4), 6.43 (s, 2H, NH_2), 6.71 (d, 1H, *J* 9.3), 7.11 (d, 1H, *J* 16.3), 7.23 (d, 2H, *J* 7.8), 7.56 (d, 2H, *J* 7.8), 7.96 (d, 1H, *J* 16.3). HRMS=590.1677 ($C_{26}H_{30}O_{10}N_4S$ requires 590.1677).

4.3.11. 4-Amino-6-[2-(2-thienyl)vinyl]-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **15e**

Yellow plates, yield 70%, mp 196–198 °C. MS: *m*/*z*=582 (M^+, 100%). IR: 3297, 3207, 2943, 1753, 1435, 1367, 1277, 1238, 1062, 1040. ^1H NMR ($CDCl_3$): δ 1.96, 2.08, 2.09, 2.10 (4s, 12H, $4CH_3CO$), 3.99 (ddd, 1H, *J* 9.9, 4.8, 1.9), 4.19 (dd, 1H, *J* 12.5, 1.8), 4.31 (dd, 1H, *J* 12.6, 5.1), 5.28 (t, 1H, *J* 9.8), 5.44 (t, 1H, *J* 9.4), 5.94 (t, 1H, *J* 9.4), 6.42 (s, 2H, NH_2), 6.73 (d, 1H, *J* 9.4), 6.93 (d, 1H, *J* 16.1), 7.09 (dd, 1H, *J* 4.5, 3.5), 7.35 (d, 1H, *J* 3.5), 7.40 (d, 1H, *J* 4.5), 8.12 (d, 1H, *J* 16.1). ^{13}C NMR ($CDCl_3$): δ 20.61 (2C), 20.6, 20.8, 61.6, 67.8, 68.5, 73.9, 74.7, 87.6, 116.3, 128.0, 128.2, 130.3, 132.0, 140.9, 141.4, 146.7, 168.8, 168.9, 169.5, 170.2, 170.6. HRMS=582.1087 ($C_{23}H_{26}O_{10}N_4S_2$ requires 582.1084).

4.3.12. 4-Amino-6-p-nitrostyryl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **15f**

Yellow plates, yield 65%, mp 264–266 °C. MS: *m*/*z*=621 (M^+, 13%). IR: 2925, 1752, 1633, 1435, 1342, 1232. ^1H NMR ($CDCl_3$): δ 1.97, 2.08, 2.10 (s, 3H, s, 3H, s, 6H, $4CH_3CO$), 4.01 (m, 1H), 4.19 (dd, 1H, *J* 12.5, 1.6), 4.31 (dd, 1H, *J* 12.6, 5.2), 5.27 (t, 1H, *J* 9.8), 5.45 (t, 1H, *J* 9.5), 5.96 (t, 1H, *J* 9.4), 6.45 (s, 2H, NH_2), 6.73 (d, 1H, *J* 9.4), 7.29 (d, 1H, *J* 16.4), 7.79 (d, 2H, *J* 8.8), 8.03 (d, 1H, *J* 16.4), 8.29 (d, 2H, *J* 8.8). ^{13}C NMR ($CDCl_3$): δ 20.56 (2C), 20.6, 20.7, 61.6, 67.7, 68.5, 73.8, 74.7, 87.6, 121.4, 124.2, 128.3, 136.1, 139.9, 141.8, 146.6, 148.0, 168.9, 169.0, 169.4, 170.1, 170.5. HRMS=621.1395 ($C_{25}H_{27}O_{12}N_5S$ requires 621.1394).

4.4. 2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4*H*)-ones 4–6: general procedure

To a solution of **13**–**15** (1 mmol) in acetic acid (5 mL) was added sodium nitrite (0.2 g) with stirring over a period of 10 min. The reaction mixture was then stirred at room temperature overnight. After dilution with cold ice/water mixture (20 g), the precipitate was collected and crystallized from ethanol.

4.4.1. 6-Benzyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **4a**

Yellow plates, yield 87%, mp 158–160 °C (lit.[11a] mp 162 °C). LCMS: *m*/*z*=550 (M+1). IR: 3243, 3182, 3029, 2987, 1754, 1707, 1489, 1371, 1252, 1228, 1078, 1044. ^1H NMR ($CDCl_3$): δ 1.95, 2.07, 2.09, 2.12 (4s, 12H, $4CH_3CO$), 3.89 (d, 1H, *J* 13.6), 3.95 (m, 1H), 4.02 (d, 1H, *J* 13.6), 4.19 (d, 1H, *J* 11.2), 4.30 (dd, 1H, *J* 12.6, 4.9), 5.2 (t, 1H *J* 9.8), 5.4 (t, 1H, *J* 9.2), 5.8 (t, 1H, *J* 9.3), 6.7 (d, 1H, *J* 9.3), 7.3 (m, 5H), 9.40 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.56 (2C), 20.6, 20.7, 36.3, 61.5, 67.6, 68.6, 73.8, 74.5, 85.8, 127.3, 128.7, 129.5, 133.0, 150.1, 150.3, 169.1, 169.4, 170.2, 170.6, 174.7.

4.4.2. 6-p-Chlorobenzyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **4b**

Colorless plates, yield 85%, mp 134–136 °C. LCMS: *m*/*z*=585 (M+1). IR: 3243, 2949, 1754, 1709, 1489, 1371, 1250, 1226, 1043. ^1H NMR ($CDCl_3$): δ 1.94, 2.02, 2.06, 2.10 (4s, 12H, $4CH_3CO$), 3.84 (d, 1H, *J* 6.8), 3.92 (m, 1H), 3.94 (d, 1H, *J* 5.2), 4.18 (d, 1H, *J* 11.6), 4.29 (dd, 1H, *J* 12.6, 4.7), 5.23 (t, 1H, *J* 9.8), 5.40 (t, 1H, *J* 9.5), 5.77 (t, 1H, *J* 9.4), 6.67 (d, 1H, *J* 9.3), 7.30 (m, 4H), 10.57 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.56 (2C), 20.6, 20.7, 35.7, 61.5, 67.6, 68.7, 73.7, 74.5, 85.8, 128.8, 130.9, 132.9, 133.3, 149.9, 150.3, 169.1, 169.4, 170.2, 170.6, 174.6. Anal. Calcd for $C_{24}H_{26}ClN_3O_{10}S$ (584.0): C 49.36; H 4.49; N 7.20; S 5.49. Found: C 49.29; H 4.43; N 7.19; S 5.44.

4.4.3. 6-p-Methylbenzyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **4c**

Colorless plates, yield 75%, mp 170–172 °C. LCMS *m*/*z*=564 (M+1). IR: 3246, 2969, 1754, 1708, 1489, 1252, 1225, 1076, 1044. ^1H NMR ($CDCl_3$): δ 1.96, 207, 2.09, 2.11 (4s, 12H, $4CH_3CO$), 2.33 (s, 3H, CH_3), 3.85 (m, 3H), 4.19 (d, 1H, *J* 11.6), 4.29 (dd, 1H, *J* 12.0, 5.0), 5.25 (t, 1H, *J* 9.6), 5.40 (t, 1H, *J* 9.2), 5.80 (t, 1H, *J* 9.1), 6.65 (d, 1H, *J* 9.1), 7.13 (d, 2H, *J* 7.2), 7.26 (d, 2H, *J* 7.3), 9.75 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.56 (2C), 20.6, 20.7, 21.0, 36.0, 61.5, 67.6, 68.6, 73.8, 74.4, 85.8, 129.3, 129.4, 131.4, 137.0, 150.3, 150.5, 169.1, 169.4, 170.2, 170.6, 174.7. Anal. Calcd for $C_{25}H_{29}N_3O_{10}S$ (563.6): C 53.28; H 5.19; N 7.46; S 5.69. Found: C 53.14; H 5.18; N 7.45; S 5.68.

4.4.4. 6-(2-Thienylmethyl)-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **4e**

Brown plates, yield 78%, mp 122–124 °C. MS: *m*/*z*=555 (M^+, 5%). IR: 3109, 2939, 1754, 1719, 1477, 1370, 1238, 1038. ^1H NMR ($CDCl_3$): δ 1.95, 2.08, 2.11, 2.12 (4s, 12H, $4CH_3CO$), 3.94 (ddd, 1H, 9.4, 4.4, 2.0), 4.11 (d, 1H, *J* 15.2), 4.17 (m, 2H), 4.28 (dd, 1H, *J* 12.4, 4.4), 5.23 (t, 1H, *J* 9.6), 5.40 (t, 1H, *J* 9.5), 5.74 (t, 1H, *J* 9.4), 6.65 (d, 1H, *J* 9.2), 6.96 (dd, 1H, *J* 4.8, 3.5), 7.02 (d, 1H, *J* 3.5), 7.21 (d, 1H, *J* 4.8), 10.55 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.57 (2C), 20.6, 20.7, 30.3, 61.5, 67.6, 68.7, 73.6, 74.4, 85.7, 125.4, 127.1, 127.5, 127.6, 135.8, 148.8, 150.5, 169.1, 170.2, 170.7, 174.8. HRMS=555.0973 ($C_{22}H_{25}O_{10}N_3S_2$ requires 555.0975).

4.4.5. 6-Phenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one **5a**

Pale yellow plates, yield 90%, mp 157–158 °C (lit.[11a] mp 160 °C). IR: 3240, 3063, 2940, 1753, 1716, 1478, 1428, 1371, 1285, 1230, 1111, 1037. ^1H NMR ($CDCl_3$): δ 2.02, 2.08, 2.085, 2.09 (4s, 12H, $4CH_3CO$), 4.00 (ddd, 1H, *J* 10.0, 4.8, 2.0), 4.19 (dd, 1H, *J* 12.4, 2.0), 4.30 (dd, 1H, *J* 12.4, 4.8), 5.24 (t, 1H, *J* 9.8), 5.45 (t, 1H, *J* 9.5), 5.89 (t, 1H, *J* 9.4), 6.79 (d, 1H, *J* 9.3), 7.51 (m, 3H), 8.11 (m, 2H), 9.74 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.058 (2C), 20.6, 20.7, 61.5, 67.7, 68.7, 73.7, 74.6, 86.0, 128.6, 128.8, 130.1, 131.5, 145.9, 150.2, 169.2, 169.5, 170.1, 170.6, 174.2. HRMS=535.1257 ($C_{23}H_{25}N_3O_{10}S$ requires 535.1255).

4.4.6. 6-p-Chlorophenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***5b***

Yellow plates, yield 80%, mp 216–217 °C. MS: *m*/*z*=569 (M^+, 12%). IR: 3220, 3163, 2946, 1752, 1720, 1595, 1579, 1483, 1424, 1400, 1369, 1289, 1259, 1230, 1190, 1092, 1063, 1040. ^{1}H NMR ($CDCl_3$): δ 2.01, 2.08, 2.085, 2.09 (4s, 12H, $4CH_3CO$), 4.00 (ddd, 1H, *J* 10.4, 5.2, 2.4), 4.20 (dd, 1H, *J* 12.0, 2.0), 4.31 (d, 1H, *J* 11.9), 5.25 (t, 1H, *J* 9.8), 5.45 (t, 1H, *J* 9.4), 5.87 (t, 1H, *J* 9.4), 6.77 (d, 1H, *J* 9.6), 7.47 (m, 2H), 8.12 (m, 2H), 9.82 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.6 (2C), 20.63, 20.7, 61.5, 67.7, 68.7, 73.6, 74.7, 86.0, 128.6, 128.9, 130.1, 137.9, 144.7, 150.2, 169.2, 169.5, 170.1, 170.6, 174.1. HRMS=569.0867 ($C_{23}H_{24}ClO_{10}N_3S$ requires 569.0865).

4.4.7. 6-p-Methoxyphenyl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***5d***

Pale yellow crystals, yield 75%, mp 217–218 °C. MS: *m*/*z*=565 (M^+, 50%). IR: 3217, 3166, 2947, 2908, 1751, 1714, 1606, 1284, 1256, 1228, 1215, 1188, 1062, 1035.^{1}H NMR ($CDCl_3$): δ 2.00, 2.08, 2.09 (s, 3H, s, 3H, s, 6H, $4CH_3CO$), 3.89 (s, 3H, OCH_3), 3.99 (m, 1H), 4.19 (dd, 1H, *J* 12.6, 1.7), 4.31 (dd, 1H, *J* 12.6, 4.6), 5.25 (t, 1H, *J* 9.8), 5.44 (t, 1H, *J* 9.4), 5.90 (t, 1H, *J* 9.4), 6.76 (d, 1H, *J* 9.3), 7.00 (d, 2H, *J* 9.0), 8.15 (d, 2H, *J* 9.0), 9.82 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.56 (2C), 20.6, 20.7, 55.4, 61.5, 67.7, 68.6, 73.7, 74.6, 86.0, 114.0, 122.7, 130.6, 145.3, 150.5, 162.2, 169.2, 169.5, 170.1, 170.6, 174.0. Anal. Calcd for $C_{24}H_{27}N_3O_{11}S$ (565.6): C 50.97; H 4.81; N 7.43; S 5.67. Found: C 50.80; H 4.67; N 7.70; S 5.62.

4.4.8. 6-Styryl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***6a***

Plate yellow crystals, yield 85%, mp 212–213 °C (lit.[11b] mp 215 °C). IR: 3061, 2920, 2850, 1753, 1714, 1382, 1371, 1231, 1060, 1041. ^{1}H NMR ($CDCl_3$): δ 1.99, 2.08, 2.09, 2.11 (4s, 12H, $4CH_3CO$), 3.98 (m, 1H), 4.18 (d, 1H, *J* 12.1), 4.33 (dd, 1H, *J* 12.4, 4.5), 5.27 (t, 1H, *J* 9.8), 5.43 (t, 1H, *J* 9.5), 5.88 (t, 1H, *J* 9.4), 6.64 (d, 1H, *J* 9.3), 7.10 (d, 1H, *J* 16.4), 7.41 (m, 3H), 7.64 (d, 2H, *J* 6.7), 7.99 (d, 1H, *J* 16.4), 9.40 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5 (2C), 20.7, 61.5, 67.4, 68.9, 72.7, 75.0, 89.7, 118.7, 127.9, 128.8, 129.7, 135.8, 140.4, 149.1, 150.9, 161.2, 168.7, 169.3, 170.1, 170.5.

4.4.9. 6-p-Chlorostyryl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***6b***

Yellow plates, yield 40%, mp 256–258 °C (lit.[11c,d] mp 260 °C). LCMS: *m*/*z*=596 (M+1). IR: 3055, 2922, 1750, 1629, 1233. ^{1}H NMR ($CDCl_3$): δ 1.99, 2.08, 2.09, 2.11 (4s, 12H, $4CH_3CO$), 3.98 (ddd, 1H, *J* 10.0, 4.9, 2.0), 4.19 (dd, 1H, *J* 12.6, 2.0), 4.33 (dd, 1H, *J* 12.6, 5.1), 5.26 (t, 1H, *J* 9.8), 5.43 (t, 1H, *J* 9.5), 5.87 (t, 1H, *J* 9.4), 6.67 (d, 1H, *J* 9.3), 7.06 (d, 1H, *J* 16.4), 7.39 (d, 2H, *J* 8.4), 7.56 (d, 2H, *J* 8.4), 7.93 (d, 1H, *J* 16.4), 9.75 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 21.2, 21.23, 21.3, 21.4, 62.2, 68.5, 69.3, 74.7, 75.0, 86.9, 119.4, 129.4, 129.6, 129.7, 135.2, 135.6, 137.3, 144.8, 155.5, 169.7, 170.1, 170.8, 171.3. Anal. Calcd for $C_{25}H_{26}ClN_3O_{10}S$ (596.0): C 50.38; H 4.40; N 7.05; S 5.38. Found: C 50.59; H 4.15; N 7.04; S 5.51.

4.4.10. 6-p-Methylstyryl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***6c***

Yellow plates, yield 77%, mp 243–245 °C. MS: *m*/*z*=575 (M^+, 15%). IR: 3027, 2924, 1753, 1724, 1243, 1195, 1060, 1042. ^{1}H NMR ($CDCl_3$): δ 1.99, 2.08, 2.09, 2.11 (4s, 12H, $4CH_3CO$), 2.40 (s, 3H CH_3), 3.98 (ddd, 1H, *J* 10.2, 5.1, 2.0), 4.20 (dd, 1H, *J* 12.5, 2.0), 4.33 (dd, 1H, *J* 12.6, 5.0), 5.27 (t, 1H, *J* 9.8), 5.43 (t, 1H, *J* 9.4), 5.88 (t, 1H, *J* 9.4), 6.67 (d, 1H, *J* 9.4), 7.06 (d, 1H, *J* 16.4), 7.22 (d, 2H, *J* 8.0), 7.54 (d, 2H, *J* 8.0), 7.96 (d, 1H, *J* 16.4), 9.61 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.6 (2C), 20.7, 20.8, 21.5, 61.5, 67.7, 68.5, 73.8, 74.6, 86.2, 115.8, 127.9, 129.6, 132.9, 139.8, 140.3, 145.1, 150.5, 169.0, 169.5, 170.2, 170.6, 173.6. HRMS=575.1565 ($C_{26}H_{29}N_3O_{10}S$ requires 575.1568).

4.4.11. 6-[2-(2-Thienyl)vinyl]2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***6e***

Yellow plates, yield 83%, mp 228–229 °C. MS: *m*/*z*=567 (M^+, 34%). IR: 3550, 3420, 2941, 1752, 1715, 1489, 1245, 1194, 1044. ^{1}H NMR ($CDCl_3$): δ 1.99, 2.08, 2.09, 2.12 (4s, 12H, $4CH_3CO$), 3.97 (ddd, 1H, *J* 10.1, 4.9, 2.0), 4.19 (dd, 1H, *J* 12.6, 1.8), 4.33 (dd, 1H, *J* 12.6, 5.0), 5.27 (t, 1H, *J* 9.8), 5.43 (t, 1H, *J* 9.5), 5.85 (t, 1H, *J* 9.4), 6.68 (d, 1H, *J* 9.2), 6.88 (d, 1H, *J* 16.1), 7.09 (dd, 1H, *J* 5.0, 3.5), 7.34 (d, 1H, *J* 3.5), 7.41 (d, 1H, *J* 5.0), 8.13 (d, 1H, *J* 16.1), 9.46 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.4 (3C), 20.5, 61.4, 67.6, 68.4, 73.6, 74.1, 85.5, 116.3, 127.6, 127.9, 129.9, 131.6, 141.3, 144.4, 151.3, 168.8, 169.2, 169.9, 170.4, 174.3. HRMS=567.0977 ($C_{23}H_{25}N_3O_{10}S_2$ requires 567.0976).

4.4.12. 6-p-Nitrostyryl-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***6f***

Yellow plates, yield 75%, mp 239–240 °C. MS: *m*/*z*=606 (M^+, 30%). IR: 3107, 2937, 1754, 1717, 1517, 1343, 1279, 1232, 1107, 1060, 1042. ^{1}H NMR ($CDCl_3$): δ 2.01, 2.08, 2.10, 2.11 (4s, 12H, $4CH_3CO$), 3.99 (ddd, 1H, *J* 10.1, 5.0, 2.1), 4.19 (dd, 1H, *J* 12.6, 2.0), 4.34 (dd, 1H, *J* 12.6, 5.1), 5.26 (t, 1H, *J* 9.8), 5.44 (t, 1H, *J* 9.5), 5.87 (t, 1H, *J* 9.4), 6.69 (d, 1H, *J* 9.3), 7.22 (d, 1H, *J* 16.4), 7.78 (d, 2H, *J* 8.8), 8.02 (d, 1H, *J* 16.4), 8.28 (d, 2H, *J* 8.8), 9.61 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 20.9, 21.0, 21.1, 21.6, 62.1, 68.1, 69.1, 73.3, 73.6, 85.4, 123.1, 124.7, 129.1, 135.1, 142.6, 144.6, 147.9, 152.0, 169.5, 170.0, 170.1, 170.6, 175.2. HRMS=606.1263 ($C_{25}H_{26}N_4O_{12}S$ requires 606.1262).

4.5. 4-Amino-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4*H*)-ones 10–12: general procedure

The appropriate α-ketoacid (10 mmol) was added slowly to a hot solution of thiocarbohydrazide (10 mmol) in water (15 mL). The reaction mixture was then heated under reflux for 10 min. After cooling, the precipitate was collected, washed with cold water, and recrystallized from DMF.

4.5.1. 4-Amino-6-(2-thienylmethyl)-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***10e***

Buff plates, yield 75%, mp 184–185 °C. MS: *m*/*z*=240 (M^+, 100%). IR: 3298, 3211, 3165, 3011, 3087, 2988, 1970, 1548, 1521, 1398, 1251, 1238, 770, 690. ^{1}H NMR (DMSO-d_6): δ 4.11 (s, 2H, CH_2), 6.51 (s, 2H, NH_2), 6.96 (br, 2H), 7.38 (br, 1H), 13.93 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 30.9, 125.9, 127.5, 127.7, 138.4, 146.6, 148.9, 169.3. HRMS=240.0132 ($C_8H_8N_4O_{10}S_2$ requires 240.0134).

4.5.2. 4-Amino-6-p-chlorophenyl-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***11b***

Pale yellow needles, yield 80%, mp 251–252 °C. IR: 3299, 3206, 3083, 3039, 1662, 1557, 1538, 1510, 1404, 1391, 1327, 1248, 1239, 1101, 863, 832. ^{1}H NMR (DMSO-d_6): δ 6.60 (s, 2H, NH_2), 7.54 (d, 2H, *J* 8.0), 7.99 (d, 2H, *J* 8.0), 14.24 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 128.8, 130.2, 131.3, 135.3, 141.9, 148.5, 168.2. Anal. Calcd for $C_9H_7ClN_4OS$ (254.7): C 42.44; H 2.77; N 22.00; S 12.59. Found: C 42.50; H 2.89; N 22.00; S 12.62.

4.5.3. 4-Amino-6-p-methylstyryl-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***12c***

Yellow plates, yield 90%, mp 271 °C (lit.[11e] mp 269–271 °C). ^{1}H NMR (DMSO-d_6): δ 2.33 (s, 3H, CH_3), 6.50 (s, 2H, NH_2), 7.07 (d, 1H, *J* 16.4), 7.23 (d, 2H, *J* 7.7), 7.55 (d, 2H, *J* 7.7), 7.80 (d, 1H, *J* 16.4), 14.10 (s, 1H, NH).

4.5.4. 4-Amino-6-[2-(2-thienyl)vinyl]-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***12e***

Yellow plates, yield 57%, mp 245–248 °C. MS: *m*/*z*=252 (M^+, 100%). IR: 3295, 3202, 3067, 1665, 1615, 1559, 1536, 1493, 1394, 1241, 1202, 750, 688. ^{1}H NMR (DMSO-d_6): δ 6.54 (s, 2H, NH_2), 6.80 (d, 1H, *J* 16.2), 7.13 (dd, 1H, *J* 5.0, 4.0), 7.44 (d, 1H, *J* 4.0), 7.64 (d, 1H, *J*

5.0), 8.00 (d, 1H, *J* 16.2), 14.13 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 118.9, 128.5, 129.1, 129.2, 130.4, 141.7, 141.8, 148.7, 167.8. HRMS=252.0134 ($C_9H_8N_4OS_2$ requires 252.0133).

4.5.5. 4-Amino-6-p-nitrostyryl-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-one ***12f***

Yellow plates, yield 76%, mp 270–271 °C. MS: m/z=291 (M^+, 99%). IR: 3326, 3085, 3034, 2941, 1674, 1594, 1556, 1514, 1341, 1278, 1246, 739. ^{1}H NMR (DMSO-d_6): δ 6.58 (s, 2H, NH_2), 7.34 (d, 1H, *J* 16.4), 7.90 (d, 1H, *J* 16.4), 7.96 (d, 2H, *J* 8.6), 8.23 (d, 2H, *J* 8.6), 14.25 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 129.5, 129.8, 133.8, 138.3, 146.4, 148.0, 152.6, 153.7, 173.1. Anal. Calcd for $C_{11}H_9N_5O_3S$ (291.3): C 45.36; H 3.11; N 24.04; S 11.01. Found: C 45.30; H 3.09; N 24.00; S 11.02.

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References and notes

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