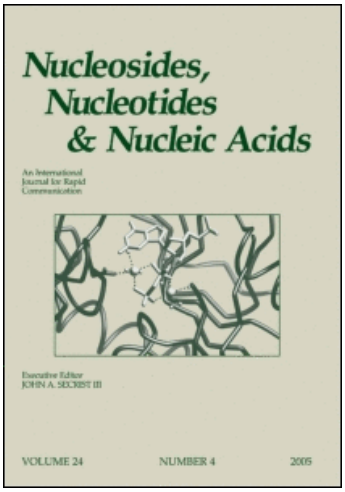

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Synthesis of Some *N*-Galactosides of 3-Aryl-5-benzyl (or Substituted Benzyl)-1,2,4-triazin-6(1*H*)-/ones or Thiones of Expected Biological Activity

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Synthesis of Some *N*-Galactosides of 3-Aryl-5-benzyl (or Substituted Benzyl)-1,2,4-triazin-6(1*H*)-/ones or Thiones of Expected Biological Activity

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ABSTRACT

The 1-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-3-aryl-5-benzyl (or substituted benzyl)-1,2,4-triazin-6(1*H*)-/ones or thiones were prepared via galactosidation of 3-aryl-5-benzyl (or substituted benzyl)-1,2,4-triazin-6(1*H*)-/ones or thiones with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide. The structure of the new galactosyl derivatives was based on both spectroscopic and chemical evidences.

Key Words: Synthesis; 1,2,4-Triazines; *N*-Galactosides.

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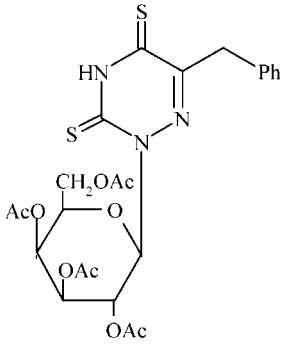
INTRODUCTION

The reported biological activity of *N*-glycosides of 1,2,4-triazines (cytotoxics, antivirals, enzyme inhibitors, immunosuppressives, antipsoriatics, bacteriostatics, antitumors, as well as floor and wall disinfectants)[1–8] together with the fact that 2-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-benzyl-1,2,4-triazine-3,5-(2*H*,4*H*)-dithione (**1**)[9] has shown anticancer activity against both MCF7 (Breast) and SF-268 (CNS) cell lines through a primary human anticancer screening (in vitro), prompted us to study the synthesis of 1-galactosyl derivatives of some 1,2,4-triazin-6(1*H*)-/ones and or thiones of expected interesting biolgical activity.



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RESULTS AND DISCUSSION

Recently, an efficient procedure was described for the selective synthesis of *N*-glycosyl derivatives of 3-thioxo-1,2,4-triazin-5(4*H*)-ones. This involves the reaction of the appropriate 1,2,4-triazine derivative with the appropriate protected glycosyl halide in basic medium (acetone/KOH or DMF/TEA or CH_3CN/TEA).[9–15] Previously, Eid et al.[12] reported that *N*-1 glucosidation takes place upon treatment of 3-phenyl-5-benzyl (or substituted benzyl)-1,2,4-triazine-6(1*H*)-thiones with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide in aqueous acetone containing one equivalent of potassium hydroxide to give the corresponding 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-3-phenyl-5-benzyl (or substituted benzyl)-1,2,4-triazine-6(1*H*)-thiones.

We report here the results of our study for the reaction of 3-phenyl-5-benzyl (or substituted benzyl)-1,2,4-triazin-6(1*H*)-/ones **4a–f** or thiones **2a–d** with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**3**) (Sch. 1). Thus, galactosidation of each of **4a–f** or **2a–d** with compound **3** in *N*,*N*-dimethylformamide containing triethylamine gave the corresponding 1-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-benzyl (or substituted benzyl)-1,2,4-triazin-6(1*H*)-/ones **6a–f** or thiones

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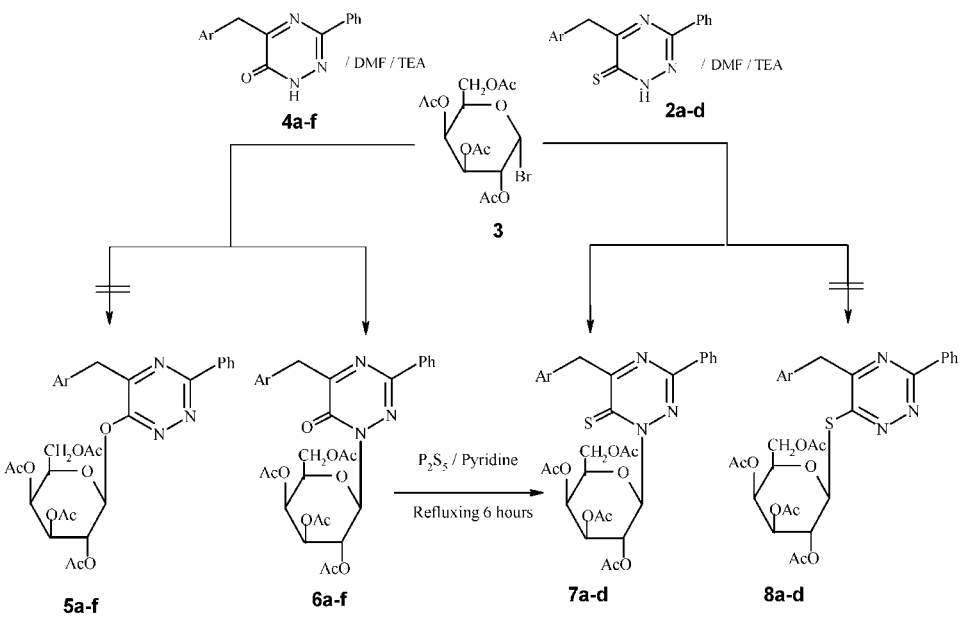

2, 4-8	Ar
a	C_6H_5
b	4-MeC_6H_4
c	4-$MeOC_6H_4$
d	4-ClC_6H_4
e	3,4-$(Me)_2C_6H_3$
f	4- $NMe_2C_6H_4$

Scheme 1.

7a–d, respectively. The structures assigned for compounds **6a–f**, **7a–d** were deduced from the following facts:

(1) The β-configuration of compounds **6a–f**, **7a–d** is supported by their ^{1}H NMR spectra which revealed the anomeric proton at δ 6.68–6.02 with a coupling constant of 8.2–10.6 Hz consistent with similar reported data.[9–15]
(2) The IR spectra of compounds **6a–f** showed the amide carbonyl function at 1705–1666 cm^{-1}, which excludes the formation of the isomeric 3-*O*-galactosyl derivatives **5a–f**.
(3) Thiation of compounds **6a–d** gave the 6(1*H*)-thiones **7a–d**.

The biological screening of the new compounds obtained in this work is still under investigation.

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EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer. ^{1}H NMR spectra were recorded at 200 MHz with a Varian GEMINI 200 spectrometer. Mass spectra (EI, 70eV) were recorded on a GCMS-QP 1000 EX spectrometer. Elemental analyses were carried out at the Microanalytical Centre, Cairo University. The starting 3-phenyl-5-benzyl (or substituted benzyl)-1,2,4-triazin-6(1*H*)-ones **4a–d** were prepared as described by Nalepa et al.[16,17] on the other hand, the new 3-phenyl-5-(3,4-dimethylbenzyl)-1,2,4-triazin-6(1*H*)-one (**4e**) and 3-phenyl-5-(4-*N*,*N*-dimethylaminobenzyl)-1,2,4-triazin-6(1*H*)-ones (**4f**) are now synthesized using the same procedure. The starting 3-phenyl-5-benzyl (or substituted benzyl)-1,2,4-triazine-6(1*H*)-thiones **2a–d**[12] and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide[18] were prepared as reported.

3-Phenyl-5-(3,4-dimethylbenzyl)-1,2,4-triazin-6(1*H*)-one (4e). A suspension of 4-(3,4-dimethylbenzylidene)-2-phenyl-oxazol-5(4*H*)-one (12.3 g, 44.4 mmol) and hydrazine hydrate 99% (16 mL) in cold methanol (100 mL) was shaken till a clear solution was obtained. After the reaction mixture started to become turbid, it was allowed to stand at room temperature overnight. The formed colorless precipitate of the corresponding hydrazide was collected by filtration, dried, (11.0 g, mp. 195–6°C), then heated at reflux in sodium hydroxide solution (4.4 g NaOH dissolved in 110 mL water) for 5 min. The reaction mixture was cooled, acidified with concentrated hydrochloric acid, and diluted with an ice-water mixture. After collection of the formed colorless product by filtration, it was recrystallized from methanol to give colorless crystals of **4e** (90%); mp. 180°C; IR (KBr) 3125 (NH), 1659 (C = O amide) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.8 (brs, 1H, NH, exchangeable), 8.09–6.96 (m, 8H, ArH's), 4.26 (s, 2H, 3,4-$(CH_3)_2$-C_6H_3-C$\underline{H}_2$), 2.42, 2.29 (2s, 6H, 3,4(C$\underline{H}_3$)$_2$-C_6H_3-CH_2).

Anal. Calcd. for $C_{18}H_{17}N_3O$: C, 74.2; H, 5.88; N, 14.42. Found: C, 74.2; H, 5.9; N, 14.3.

3-Phenyl-5-(4-*N*,*N*-dimethylaminobenzyl)-1,2,4-triazin-6(1*H*)-one (4f). A suspension of 4-(4-*N*,*N*-dimethylaminobenzylidene)-2-phenyl-oxazol-5(4*H*)-one (19.5 g, 66.8 mmol) and hydrazine hydrate 99% (17 mL) in cold methanol (100 mL) was shaken till a clear solution was obtained. After the reaction mixture started to become turbid, it was allowed to stand at room temperature overnight. The formed pale yellow precipitate of the corresponding hydrazide was collected by filtration, dried (16.5 g, mp. 188°C), then it was heated at reflux in aqueous sodium hydroxide solution (6.7 g NaOH dissolved in 167.5 mL water) for 5 min. The reaction mixture was cooled, acidified with concentrated hydrochloric acid, and diluted with an ice-water mixture. After collection of the formed precipitate by filtration, it was recrystallized from methanol to give orange-yellow crystals of **4f** (74%); mp. 320° C; IR (KBr) 3421 (NH), 1655 (C=O amide) cm^{-1}; ^{1}HNMR (DMSO-d_6) δ 13.42 (s, 1H, NH, exchangeable), 8.04–6.64 (m, 9 H, ArH's), 4.0 (s, 2 H, 4-N$(CH_3)_2$-C_6H_4-C$\underline{H}_2$), 2.82 (s, 6H, 4-N(C$\underline{H}_3$)$_2$-C_6H_4-CH_2).

Anal. Calcd. for $C_{18}H_{18}N_4O$: C, 70.57; H, 5.92; N, 18.29. Found: C, 70.6; H, 5.8; N, 18.4.

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1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-benzyl (or substituted benzyl)-1,2,4-triazin-6(1*H*)-ones 6a–f. General procedure: To a solution of each of **4a–f** (10 mmol) in *N*,*N*-dimethylformamide (5 mL) and triethylamine (2 mL, 14 mmol) was added 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**3**) (4.1 g, 10 mmol). The reaction mixture was shaken for 20 min and kept overnight at room temperature. The mixture was cooled, acidified with acetic acid (1 mL), and diluted with water. The precipitate was then collected by filtration, washed with water, and dried at room temperature. Compounds **6a–f** were extracted with ethyl acetate and purified by preparative TLC (silica gel 60 GF_{254}) using ethyl acetate as an eluent. After extraction with chloroform on a soxhlet extractor, the chloroform extracts of these products were then concentrated and diluted with petroleum ether (bp. 40–60°C). The crude **6a–f** were collected by filtration, dried at room temperature, then recrystallized from diethyl ether/petroleum ether (bp. 40–60°C) to give pale yellow crystals of **6a–e** and orange-yellow crystals of **6f**.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-benzyl-1,2,4-triazin-6(1*H*)-one (6a). Using the general procedure, **4a** gave **6a** (45%); $R_f = 0.74$; mp. 70°C; IR (KBr) 1751 (C=O acetate), 1674 (C=O amide) cm^{-1}; MS m/z 594 (M^+); ^1H NMR ($CDCl_3$) δ 8.15–7.14 (m, 10H, ArH's), 6.15 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 8.2$ Hz, H-1′), 5.84 (t, 1H, $J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.2$ Hz, H-2′), 5.44 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.2$ Hz, H-4′), 5.1 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.4$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.2$ Hz, H-3′), 4.4–4.08 (m, 3H, H-5′, H-6′, H-6″), 4.27 (s, 2H, $C\underline{H}_2Ph$), 2.17–1.96 (4s, 12H, CH_3CO).

Anal. Calcd. for $C_{30}H_{31}N_3O_{10}$: C, 60.70; H, 5.26; N, 7.08. Found: C, 60.7; H, 5.1; N, 7.2.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-(4-methylbenzyl)-1,2,4-triazin-6(1*H*)-one (6b). Using the general procedure, **4b** gave **6b** (40%); $R_f = 0.75$; mp. 80°C; IR (KBr) 1751 (C=O acetate), 1682 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.45–6.9 (m, 9H, ArH's), 6.22 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 8.2$ Hz, H-1′), 5.82 (t, 1H, $J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.0$ Hz, H-2′), 5.45 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.2$ Hz, H-4′), 5.14 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.4$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.1$ Hz, H-3′), .4.3–3.9 (m, 3H, H-5′, H-6′, H-6′), 4.18 (s, 2H, 4-$CH_3C_6H_4C\underline{H}_2$), 2.32 (s, 3H, CH_3), 2.21–1.99 (4s, 12H, CH_3CO).

Anal. Calcd. for $C_{31}H_{33}N_3O_{10}$.: C, 61.28; H, 5.47. Found: C, 61.4; H, 5.6.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-(4-methoxybenzyl)-1,2,4-triazin-6(1*H*)-one (6c). Using the general procedure, **4c** gave **6c** (47%); $R_f = 0.70$; mp. 108°C; IR (KBr) 1751 (C=O acetate), 1674 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.3–6.87 (m, 9H, ArH's), 6.68 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 8.2$ Hz, H-1′), 5.92 (t, 1H, $J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.1$ Hz, H-2′), 5.48 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.4$ Hz, H-4′), 5.14 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.5$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.0$ Hz, H-3′), 4.2-3.9 (m, 3H, H-5′, H-6′, H-6′), 3.89 (s, 2H, 4-$CH_3OC_6H_4C\underline{H}_2$), 3.78 (s, 3H, OCH_3), 2.15-2.0 (4s, 12H, CH_3CO).

Anal. Calcd. for $C_{31}H_{33}N_3O_{11}$: C, 59.71; H, 5.33. Found: C, 59.5; H, 5.3.

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1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-(4-chlorobenzyl)-1,2,4-triazin-6(1*H*)-one (6d). Using the general procedure, **4d** gave **6d** (48%); $R_f = 0.73$; mp. 100°C; IR (KBr) 1751 (C=O acetate), 1666 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.22–7.15 (m, 9H, ArH's), 6.02 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 8.2$ Hz, H-1′), 5.8 (t, 1H,m$J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.0$ Hz, H-2′), 5.48 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.2$ Hz, H-4′), 5.17 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.4$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.2$ Hz, H-3′), 4.24–3.96 (m, 3H, H-5′, H-6′, H-6″), 4.24 (s, 2H, 4-$ClC_6H_4C\underline{H}_2$), 2.2–1.98 (4s, 12H, CH_3CO).

Anal. Calcd. for $C_{30}H_{30}N_3O_{10}Cl$: C, 57.37; H, 4.81. Found: C, 57.4; H, 4.7.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-(3,4-dimethylbenzyl)-1,2,4-triazin-6(1*H*)-one (6e). Using the general procedure, **4e** gave **6e** (63%); $R_f = 0.71$; mp. 84°C; IR (KBr) 1751 (C=O acetate), 1682 (C=O amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.34–6.9 (m, 8H, ArH's), 6.21 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 9$ Hz, H-1′), 6.1 (t, 1H, $J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.2$ Hz, H-2′), 5.5 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.2$ Hz, H-4′), 5.2 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.4$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.0$ Hz, H-3′), 4.24–4.00 (m, 5H, H-5′, H-6′, H-6″, 4-$(CH_3)_2C_6H_3C\underline{H}_2$), 2.72, 2.39 (2s, 6H, 3,4-$(C\underline{H}_3)_2C_6H_3CH_2$), 2.39–1.96 (4s, 12H, CH_3CO).

Anal. Calcd. for $C_{32}H_{35}N_3O_{10}$: C, 61.83; H, 5.67; N, 6.76. Found: C, 62.0; H, 5.7; N, 6.8.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-(4-*N*,*N*-dimethylamino-benzyl)-1,2,4-triazin-6(1*H*)-one (6f). Using the general procedure, **4f** gave **6f** (58%); $R_f = 0.71$; mp. 78°C; IR (KBr) 1751 (C=O acetate), 1705 (C=O amide) cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.06–6.69 (m, 9H, ArH's), 6.58 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 9$ Hz, H-1′), 5.9 (t, 1H, $J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.6$ Hz, H-2′), 5.61 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.1$ Hz, H-4′), 5.3 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.4$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.1$ Hz, H-3′), 4.2–3.9 (m, 5H, H-5′, H-6′, H-6″), 4-$(CH_3)_2NC_6H_4C\underline{H}_2$), 3.08 (s, 6H, 4-$(C\underline{H}_3)_2NC_6H_4CH_2$), 2.14–1.92 (4s, 12H, CH_3CO).

Anal. Calcd. for $C_{32}H_{36}N_4O_{10}$: C, 60.37; H, 5.70; N, 8.80. Found: C, 60.4; H, 5.6; N, 8.7.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-benzyl (or substituted benzyl)-1,2,4-triazine-6(1*H*)-thiones 7a–d. General Procedure (A): 2a–d (10 mmol) in *N*,*N*-dimethylformamide (5 mL) and triethylamine (2 mL, 14 mmol) was added 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**3**) (4.1 g, 10 mmol). The reaction mixture was shaken for 20 min and kept overnight at room temperature. The mixture was cooled, acidified with acetic acid (1 mL), and diluted with water. The precipitate was collected by filtration, washed several times with water, dried at ambient temperature, extracted with ethyl acetate, and purified by preparative TLC (silica gel 60 GF_{254}) using ethyl acetate as an eluent. The products were then extracted with chloroform on a soxhlet extractor, and the chloroform extracts of these products were then concentrated and diluted with petroleum ether (bp. 40–60°C). After collection of the crude products by filtration, they were recystallized from diethyl ether/petroleum ether (bp. 40–60°C) to give yellow crystals of **7a–d**.

General Procedure (B): To a solution of each of **6a–d** (10 mmol) in dry pyridine (5 mL) was added phosphorous pentasulfide (0.45 g, 2 mmol). The reaction mixture

was heated at reflux for 6 h. After cooling, the products were extracted from the oily materials with ethanol (10 mL). The supernatant solutions were decanted, acidified with acetic acid (0.5 mL), concentrated, and diluted with water. The precipitates were collected by filtration, dried at room temperature, dissolved in diethyl ether and treated with charcoal (0.5 g), filtered, and the filtrates evaporated at room temperature. The resulting solids were recystallized from diethyl ether/petroleum ether (bp. 40–60°C) to give yellow crystals of **7a–d**.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-benzyl-1,2,4-triazine-6(1*H*)-thione (7a). Using the general procedure (A/or B), **2a**/or **6a** gave **7a** (62%/or 50%); mp. 140°C; IR (KBr) 1751 (C=O acetate) cm^{-1}; MS m/z 610 (M^+); ^1H NMR ($CDCl_3$) δ 8.52–6.95 (m, 10H, ArH's), 6.2 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 9$ Hz, H-1′), 5.95 (t, 1H, $J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.6$ Hz, H-2′), 5.5 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.4$ Hz, H-4′), 5.25 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.4$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.1$ Hz, H-3′), 4.25–3.9 (m, 3H, H-5′, H-6′, H-6″), 3.85 (s, 2H, $C\underline{H}_2Ph$), 2.23–1.97 (4s, 12H, CH_3CO).

Anal. Calcd. for $C_{30}H_{31}N_3O_9S$: C, 59.10; H, 5.12; N, 6.89. Found: C, 59.3; H, 5.2; N, 7.0.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-(4-methylbenzyl)-1,2,4-triazine-6(1*H*)-thione (7b). Using the general procedure (A/or B), **2b**/or **6b** gave **7b** (53% /or 48%); mp. 190°C; IR (KBr) 1751 (C=O acetate) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.5–6.95 (m, 9H, ArH's), 6.2 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 9$ Hz, H-1′), 6.0 (t, 1H, $J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.5$ Hz, H-2′), 5.51 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.2$ Hz, H-4′), 5.2 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.5$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.1$ Hz, H-3′), 4.2–4.0 (m, 3H, H-5′, H-6′, H-6″), 3.85 (s, 2H, 4-$CH_3C_6H_4C\underline{H}_2$), 2.28 (s, 3H, 4-$C\underline{H}_3C_6H_4CH_2$), 2.2–1.95 (4s, 12H, CH_3CO).

Anal. Calcd. for $C_{31}H_{33}N_3O_9S$: C, 59.70; H, 5.33; N, 6.74. Found: C, 59.6; H, 5.2; N, 6.6.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-(4-methoxybenzyl)-1,2,4-triazine-6(1*H*)-thione (7c). Using the general procedure (A/or B), **2c**/or **6c** gave **7c** (60% / or 52%); mp. 140°C; IR (KBr) 1751 (C=O acetate) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.5–6.99 (m, 9H, ArH's), 6.19 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 10.6$ Hz, H-1′), 5.99 (t, 1H, $J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.7$ Hz, H-2′), 5.49 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.4$ Hz, H-4′), 5.19 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.4$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.1$ Hz, H-3′), 4.20–3.92 (m, 3H, H-5′, H-6′, H-6″), 3.85 (s, 2H, 4-$CH_3OC_6H_4C\underline{H}_2$), 3.76 (s, 3H, OCH_3), 2.18–1.98 (4s, 12H, CH_3CO).

Anal. Calcd. for $C_{31}H_{33}N_3O_{10}S$: C, 58.21; H, 5.2. Found: C, 58.3; H, 5.2.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3-phenyl-5-(4-chlorobenzyl)-1,2,4-triazine-6(1*H*)-thione (7d). Using the general procedure (A/or B), **2d**/or **6d** gave **7d** (85%/or 50%); mp. 150°C; IR (KBr) 1751 (C=O acetate) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.4–7.0 (m, 9H, ArH's), 6.22 (d, 1H, $J_{H\text{-}1'\text{-}H\text{-}2'} = 9$ Hz, H-1′), 5.96 (t, 1H, $J = (J_{H\text{-}2'\text{-}H\text{-}1'} + J_{H\text{-}2'\text{-}H\text{-}3'})/2 = 9.6$ Hz, H-2′), 5.51 (d, 1H, $J_{H\text{-}4'\text{-}H\text{-}3'} = 3.4$ Hz, H-4′), 5.22 (dd, 1H, $J_{H\text{-}3'\text{-}H\text{-}4'} = 3.5$ Hz, $J_{H\text{-}3'\text{-}H\text{-}2'} = 10.2$ Hz, H-3′), 4.22–4.0 (m, 3H, H-5′, H-6′, H-6″), 3.85 (s, 2H, 4-$ClC_6H_4C\underline{H}_2$), 2.22–1.94 (4s, 12H, CH_3CO).

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Anal. Calcd. for $C_{30}H_{30}N_3O_9SCl$: C, 55.94; H, 4.69; N, 6.52. Found: C, 56.1; H, 4.7; N, 6.4.

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