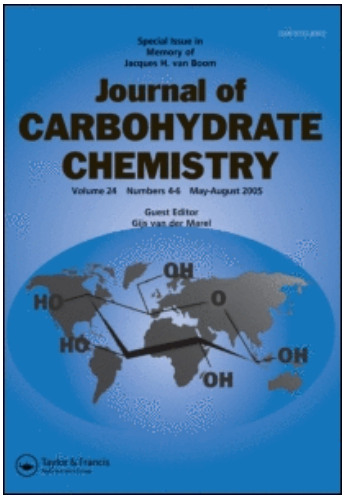

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Fuentes, José , Angulo, Manuel , Molina, José L. and Pradera, M. Angeles(1997) 'Reactions of Per-*O*-Acetylglucosyl Isothiocyanate with Enamines. A Route for the Synthesis of Pyrimidine Nucleosides', Journal of Carbohydrate Chemistry, 16: 9, 1457 — 1477
To link to this Article: DOI: 10.1080/07328309708005761
URL: http://dx.doi.org/10.1080/07328309708005761

J. CARBOHYDRATE CHEMISTRY, 16(9), 1457-1477 (1997)

REACTIONS OF PER-*O*-ACETYLGLUCOSYL ISOTHIOCYANATE WITH ENAMINES. A ROUTE FOR THE SYNTHESIS OF PYRIMIDINE NUCLEOSIDES

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Received March 24, 1997 - Final Form September 11, 1997

ABSTRACT

The reaction of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate with enamines in basic medium to form the glucosylthioamides **9-16**, the glucosylthiourea **17**, and the nucleoside analogue **18** is reported. The *N*-halogenophenyl-(**1-3**, **5-7**) and the *N*-(3,4-dimethoxybenzyl)-(**4**, **8**) enaminoesters or enaminones were prepared as precursors for **9-18**. The treatment of several of the prepared glucosylthioamides with thiophosgene yields dithioxopyrimidine nucleosides (**19-22**) with the sugar ring on position 3 of the heterocycle. Glucosylamides are isolated as byproducts. The enamino moieties of the prepared glucosylthioamides and glycosylamides have the *EEE* configuration and the thioamide or amide bond the *Z*, *anti* geometry.

INTRODUCTION

Nucleophilic addition on isothiocyanates is a very useful method for the syntheses of heterocycles and thioureas.[1] Many reactions of sugar isothiocyanates with *N*-, *O*-, and *S*-nucleophiles[2] have been described and several types of nucleoside, sugar

thiourea, macrocycle, and glycosylaminoheterocycles have been prepared in this way.[2-6] Carbon bases can provide adducts suitable for heterocyclic preparation; nevertheless, data on these reactions, using both alkyl (aryl) and sugar isothiocyanates until recently[1-3,7] have been very scarce.

Sugar amides are interesting compounds from a stereochemical point of view, the key structural aspect being the hindered internal rotation about the carbon-nitrogen amide bond as a consequence of its partial double bond character.[8,9] At the same time, these compounds are frequently found as constituents of glycoconjugates, playing an important role in molecular recognition phenomena.[10,11] Sugar thioamides are of interest as close analogues of the natural *N*-acylated amino sugars for structure-activity and enzymatic studies. The higher polarisability and volume of the sulphur atom and the increased rotational barriers of the thioamides when compared with their oxoanalogues may result in different conformational properties, which may explain differences in their biological activities.[12] As far as we know, there are no data on the *Z/E* isomerism due to hindered rotation about the C-N bond in *N*-thioacylated amino sugars where the *N*-thioacyl group has a double bond conjugated with the thiocarbonyl group. Data on glycosylamides with chains longer than two carbon atoms are also limited.[13]

Sugar thioamides have been obtained starting from the corresponding amide by replacement of the oxygen atom by sulphur with phosphorous pentasulphide.[2] *O*-Protected sugar thioacetamides can be prepared by reaction of the corresponding aminosugar with dithioacetic acid in the presence of *N,N'*-dicyclohexylcarbodiimide[2] and the thioformamido derivatives by reduction of sugar isothiocyanates with tributyltin hydride.[2,14] The limited data on reactions between sugar isothiocyanates and enamines refer only to *N*-unsubstituted enamines. In this reaction mixtures of glycosylthioamides and glycosylaminoisothiazoles are formed.

The objective of this research was to study the reaction of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate as an example of an easily available sugar isothiocyanate, with *N*-aryl and *N*-benzyl aminocrotonates and enaminones as examples of ambident (C and N) nucleophiles. Thus we have prepared two series of aminocrotonates and enaminones and report on their reactions with the above-mentioned glucosyl isothiocyanate. Glucopyranosyl thioamides or resolvable mixtures of glucopyranosyl thioamides and glucopyranosyl thioureas have been obtained depending on the nature of the *N*-substituent. At the same time, a new route for the preparation of pyrimidine nucleosides has been explored, as reaction of some glucopyranosyl thioamides with thiophosgene gives *O*-protected dithioxopyrimidine nucleoside analogues with the sugar ring on N-3.

Table 1

Relevant spectroscopic data (ν cm^{-1}, δ ppm) for compounds **1-8**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
νNH^a	3271	3258	3261	3291	3196	3236	3294	3275
$\nu C{=}O^a$	1645	1655	1667	1649	1618	1616	1591	1605
$\nu C{=}C^a$	1611	1622	1627	1604	1583	1572	1556	1518
δNH^b	10.29	10.33	10.36	8.82	12.43	12.43	12.37	11.10
$\delta C{=}O^b$	170.2	170.2	170.1	170.2	196.4	196.5	197.0	195.2

a. For KBr disc. b. In $CDCl_3$.

RESULTS AND DISCUSSION

The *N*-halogenoaryl and *N*-dimethoxybenzylaminocrotonates **1-4** and aminopentenones **5-8** were prepared from the corresponding amines and ethyl acetoacetate or acetylacetone respectively.

The structures were supported by IR and NMR spectroscopic data (see Table 1 and Experimental).

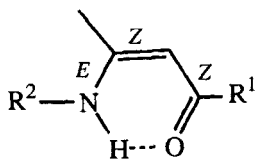
Although it has been reported[15] that the β-ketoenamines (β-enaminones[16]) and related enamino carbonyl compounds are pull-push systems which can exist in a conformational equilibrium between eight forms, IR and NMR data from compounds **1-8** indicate that the *Z Z E* chelated conformation (see formulas **1-8**) is the only one present in the solid state and in chloroform solutions. The NH (3294-3236 cm^{-1}) and C=O (1667-1645 cm^{-1} for esters **1-4** and 1618-1591 cm^{-1} for ketones **5-8**) stretching frequencies, the δNH (12.43-8.82 ppm) and δC=O (≈ 170.2 ppm for **1-4** and 197.0-195.2 ppm for **5-8**) values were indicative[4,15-17] of a chelated structure. The δNH values for **3** and **7** as representative compounds do not change on dilution, and the temperature coefficients for the NH chemical shifts measured between -40 °C and +40 °C for the same compounds were -3.38 10^{-3} and -3.06 10^{-3} ppm K^{-1} respectively, demonstrating intramolecular hydrogen bonds[18,19] and consequently the *Z Z E* as a unique conformation.

The principal *m/z* peaks in the mass spectra of compounds **1-8** are included in Table 2. Spectra were obtained using electron impact ionisation. The composition of discussed ions was confirmed by accurate mass measurements at high resolving power and metastable spectra (daughter ions) were obtained (resolution 1500) to confirm

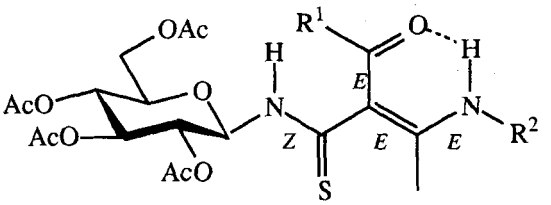
Table 2 Values and relative abundance (% of the base peak) of important *m/z* peaks in EIMS of compounds **1-8**.

Comp.	$M^{+\cdot}$	Primary fragmentation [$M^{+\cdot}$-R$^{\bullet}$]						Route A [$M^{+\cdot}$-EtOH-R$^{\bullet}$]		
		R$^{\bullet}$						R$^{\bullet}$		
		Me$^{\bullet}$	EtO$^{\bullet}$	EtOH	EtO-CO$^{\bullet}$	$C_4H_7O_2^{\bullet}$	$C_6H_{10}N_2O_2^{\cdot}$	Me$^{\bullet}$	CO	$C_2HO^{\bullet}$
1	283(100)	-	238(30)	237(80)	210(25)	196(95)	155(22)	222(25)	209(15)	196(95)
	285(100)		240(30)	239(80)	212(25)	198(95)	157(22)	224(25)	211(15)	198(95)
2	239(70)	224(6)	194(40)	193(65)	166(20)	152(100)	111(25)	178(23)	165(10)	152(100)
	241(22)	226(2)	196(13)	195(22)	168(7)	154(35)	113(8)	180(7)	167(3)	154(35)
3	273(50)	258(3)	228(30)	227(60)	200(10)	186(100)	145(12)	212(20)	199(7)	186(100)
								Route A [$M^{+\cdot}$-CH_2CO-R$^{\bullet}$]		
		Me$^{\bullet}$	CH_2CO	$CH_3CO^{\bullet}$	X$^{\bullet}$	$C_5H_8NO^{\bullet}$		Me$^{\bullet}$	X$^{\bullet}$	HX
5	253(95)	238(100)	211(15)	210(17)	174(1)	155(15)		196(20)	132(10)	131(65)
	255(95)	240(100)	213(15)	212(17)		157(15)		198(20)		
6	209(61)	194(100)	167(9)	166(18)	174(1)	111(12)		152(13)	132(2)	131(11)
	211(20)	196(33)	169(3)	168(5)		113(4)		154(5)		
7	243(45)	228(100)	201(8)	200(10)	208(50)	145(9)		186(28)	166(11)	165(15)
								-		
		Et$\cdot$ Me$\cdot$	HO$^{\bullet}$	EtOCO$^{\bullet}$ $CH_3CO^{\bullet}$	$C_6H_8O_2^{\cdot}$ $C_5H_7O^{\bullet}$	$C_6H_9O_2$ $C_5H_8O^{\bullet}$	$C_6H_{10}NO_2^{\bullet}$ $C_5H_8NO^{\bullet}$	-	-	-	-
4	279(24)	250(13)	-	206(6)	166(3)	165(4)	151(100)	-	-	-	-
8	249(35)	234(2)	232(4)	206(7)	166(3)	165(3)	151(100)	-	-	-	-

fragmentation pathways. All compounds **1-8** presented intense molecular ions, which in the case of **1** was the base peak. The spectra of the halogenated enaminoesters **1-3** had two main groups of signals: the primary fragmentations and the route A coming from $M^{+\cdot}$- EtOH. In the three cases the most important fragmentation was cleavage of the double bond of the enamino group with loss of the ester moiety. The loss of EtO$^{\cdot}$ and the rearrangement of H with simultaneous loss of C_2H_4 and CO_2 described[10] for related enamines were also observed (see Experimental). The spectra of enaminones **5-7** also have two main groups of signals but route A starts from $M^{+\cdot}$-CH_2CO. In the case of the benzyl derivatives **4** and **8** the base peak was the dimethoxytropylium ion (*m/z* 151) and only the primary fragmentations were clearly observed. The ester **4** showed a McLafferty peak[20] at *m/z* 207.



1-8



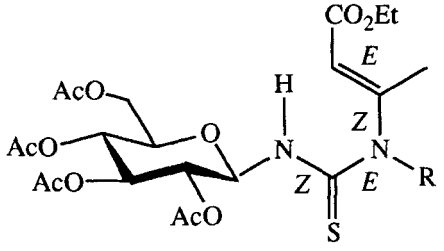
9-16

	R^1	R^2
1	OEt	*p*-BrC_6H_4
2	OEt	*p*-ClC_6H_4
3	OEt	2,4-$Cl_2C_6H_3$
4	OEt	3,4$(MeO)_2C_6H_3CH_2$
5	Me	*p*-BrC_6H_4
6	Me	*p*-ClC_6H_4
7	Me	2,4-$Cl_2C_6H_3$
8	Me	3,4$(MeO)_2C_6H_3CH_2$

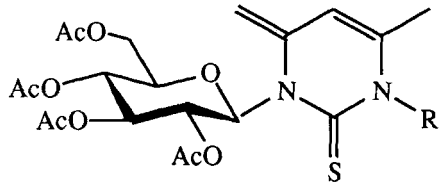
	R^1	R^2
9	OEt	*p*-BrC_6H_4
10	OEt	*p*-ClC_6H_4
11	OEt	2,4-$Cl_2C_6H_3$
12	Me	*p*-BrC_6H_4
13	Me	*p*-ClC_6H_4
14	Me	2,4-$Cl_2C_6H_3$
15	OEt	3,4$(MeO)_2C_6H_3CH_2$
16	Me	3,4$(MeO)_2C_6H_3CH_2$

Reaction of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate[21] with the enamines **1-8** gave the *N*-glucosylthioamides **9-16** in variable yield. In the case of the *N*-halogenophenyl enamines (**1-3, 5-7**) the thioamides coming from the attack of the α-carbon of the carbonyl group were the only isolated products. This coincides with reported data[7] for the reaction of a related enamine with phenyl isothiocyanate but in our

case the configuration of the C=C double bond did not change (see below), whereas in the described case it changed. The yield in the case of the 2,4-dichlorophenyl derivatives was considerably higher than in the case of monohalogeno derivatives, possibly due to the increase of the nucleophilicity of the α-carbon by the +R effect of the halogen atoms. In all cases decompositions of the isothiocyanate and the enamine in the basic medium competed with the reaction between them. Thioureas, coming from the reaction of the isothiocyanate with the corresponding amine, were detected. In spite of this, under our conditions, we achieved yields of up to 76%. In the cases of the *N*-dimethoxybenzylenamines **4** and **8** the nucleophilicity of the nitrogen atom is enhanced by the +I effect of the benzyl group, and compounds proceeding from the attack of the nitrogen atom (**17** and **18**) were the major products of the reaction together, with the thioamides **15** and **16** as minor products. The enamino ester **4** gave the thiourea **17**, and the enaminone **8**, where the enolisation of the carbonyl group is possible, produced the pyrimidine derivative **18** formed by cyclodehydration of the corresponding non-isolated thiourea.



17 R= 3,4(MeO)$_2$C$_6$H$_3$CH$_2$



18 R= 3,4(MeO)$_2$C$_6$H$_3$CH$_2$

The structures of compounds **9-18** were based on analytical and spectroscopic data (Table 3 and experimental). Although a dynamic equilibrium with contributions of three conformers around the NH-CO bond has been assumed[22] for *N*-acylribosylamines, the ^{1}H and ^{13}C NMR spectra of **9-16** showed only one signal set at 223 K, demonstrating that neither configurational stereoisomers nor conformational equilibrium exists in chloroform solutions of these compounds. The $J_{1',NH}$ values were in the range 9.5-9.2 Hz indicating antiperiplanar protons. At the same time there is a close resemblance between the chemical shifts of NHCS, H-1', and C-1' and those described[8] for *Z* glycosyl-thioformamides and thioacetamides supporting identical geometries. Both facts are in accordance with the *Z* configuration in the antiperiplanar disposition of the C-1'-NH-CS group indicated in the formulas. Additionally the δN*H*CS values (9.30-7.94 ppm) similar to those for thioformamides and thioacetamides indicate that this NH is not intramolecularly bonded; the N'*H*-C-3 resonated at ≈ 11.1 ppm for **9-11**, ≈ 13.2 ppm for

Table 3

NMR selected data (δ, ppm; *J*, Hz) for compounds **9-18** in chloroform[a]

	d_{NH}[b]	$d_{N'H}$[c]	$d_{H\text{-}1'}$	$J_{1',NH}$	$J_{1',2'}$	$d_{C\text{-}1'}$	$d_{C=S}$
9	9.30bs	11.20s	5.88t	9.4	9.4	81.2	192.3
10	9.25bs	11.10s	5.88t	9.4	9.4	81.2	193.0
11	9.00bs	11.00s	5.89t	9.4	9.4	81.2	192.5
12	7.99d	13.20s	5.88t	9.5	9.5	81.6	192.2
13	7.98d	13.23s	5.88t	9.5	9.5	81.6	192.1
14	8.01d	13.14s	5.89t	9.5	9.5	81.6	192.8
15	9.55d	12.01s	5.89dd	9.2	9.5	81.6	192.9
16	7.94d	12.03t	5.85t	9.4	9.4	81.6	190.7
17	6.55d	-	5.74dd	8.2	9.5	81.6	181.6
18[d]	-	-	7.21d	-	9.5	83.6	182.6

a. For frequencies, see experimental. b. On C-1 and C-1'. c. On C-3. d. Data for the major conformer.

12-14 and ≈ 12.0 ppm for **15** and **16** demonstrating that this proton is intramolecularly (δNH does not change on dilution) bonded to the carbonyl group. This fact and the IR frequencies, similar to those discussed above for **1-8**, support the configuration for the enamino moiety without stereochemical change during the reaction. That is, a possible stereoisomer *Z* (CO-C) *Z* (C=C) *E* (C-N) with a strong C1' -NH···CO bond and a weak N' H···CS bond is precluded. The chemical shifts for the resonances of the carbons of the enamino moiety of **9-16** were similar to the corresponding resonances of **1-8** (see Experimental) except in the case of C-2 (HC= for **1-8**) which was deshielded by the thioamido group. The mass spectra of **9-16** had the above-described peaks for the enamino moiety and the signals corresponding to the tetra-*O*-acetyl-β-D-glucopyranosyl radical (*m/z* 331 and loss of AcOH, AcO, and ketene[23]).

The NMR spectra of the major compound **17** showed δ values for the resonances of NH, H-1', C-1', and CS (Table 3) in good agreement with reported data (≈ 7.0, ≈ 5.8, ≈ 83.2, ≈ 183.3 ppm, respectively) for related glycosyl thioureas.[24,25] The structure of the thiourea was additionally supported by the presence of signals for the HC= group of the enamino moiety at δ 5.53 (1 H coupled with the CH_3 group) and at 123.1 ppm (carbon coupled to the proton at 5.53 ppm), and by the absence of a signal for the second NH group. Compound **17** can exist in various configurations by rotation of the C-N bonds (*ZZ*, *ZE*, *EZ*, and *EE*). The thioureyleneoligosaccharides,[23] other sugar thioureas,[2] and monosaccharide thioacetamides[8] in chloroform solutions at room temperature exist in the *ZZ* configuration. It has been observed that in the case of several conformational isomers a very useful parameter for the identification of this rotamer is the chemical shift

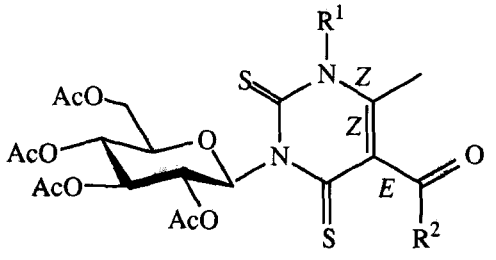
of the sugar proton directly joined to the carbon carrying the substituent. The chemical shift for the resonance of H-1' (5.74 ppm) in **17** coincides with reported data for the resonance of the same proton in *ZZ* thioureylenedisaccharides and *Z* monosaccharide thioacetamides. At the same time, the high value of the coupling constant $J_{1',NH}$ (8.2 Hz) agrees with an antiperiplanar disposition between these protons. These facts support the *Z-anti* assignment (see formula) for the C1-NH-CS group. Regarding the stereochemistry of the enamino moiety, a ROESY experiment showed NOE between HC= and NH, supporting the *E*(CS-NR), *Z*(N-C=), *E*(C=C) configuration indicated in the formula. This means that during the process the starting enamine **4** changes its configuration, which is compatible with reported data[15b,c] on the configuration and conformation of enamines.

The NMR spectra of compound **18** (Table 3 and Experimental) showed strong differences when they were compared with those of **16** and **17**. Both spectra (^1H and ^{13}C) had two signal sets with different intensities (≈ 2:1 ratio), which collapsed to only one at 373 K indicating a conformational equilibrium between two conformers at room temperature. H-1' resonated at 7.21 ppm as a doublet by coupling with H-2', and no signals for the NH and CO (ketone) groups were observed, ^1H and ^{13}C resonances appearing for the $C=CH_2$ group. Additionally the FAB mass spectrum indicated a molecular weight 18 units lower than that corresponding to a thiourea similar to **17**. These data support the nucleoside 2-thioxopyrimidine structure (see formula), which is formed by cyclodehydration of the non-isolated thiourea. It is noteworthy that the chemical shift for the resonance of H-1' in **18** is similar to reported data[25,26] on related nucleosides with a thiourea group. Taking into account that the main differences between the two conformers affect the resonances of C-1', C-2', H-1', H-2', C=S, and $C=CH_2$, we think that the conformers are produced by rotation around the C1'-N bond.

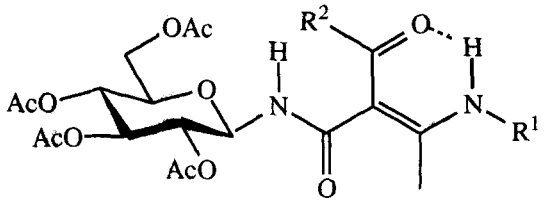
The $^3J_{H,H}$ values for the sugar rings of **9-18** showed that the $^4C_1$ conformation predominated in chloroform and Me_2SO solutions.

Treatment of the thioamides **10**, **11**, **13**, and **14** with thiophosgene in the presence of calcium carbonate gave the pyrimidine nucleoside analogues **19-22**, together with the corresponding glycosylamide originated by the hydrolysis of the CS group in the basic medium.[2] The formation of the pyrimidine ring involves isomerisation of the enamino moiety of the starting material (**10**, **11**, **13**, and **14**), which is in agreement with reported data on the stereochemical equilibrium of enaminoesters and enaminones.[15] Both the ^1H and ^{13}C NMR spectra of the nucleosides **20** and **22** showed that these compounds exist as two stereoisomers even at high temperature (50 °C in chloroform and 100 °C in Me_2SO). Considering that the spectra of the *p*-chlorophenyl derivatives **19** and **21** had only one set of signals, we propose that the stereoisomers of **20** and **22** are atropoisomers

originated by non-rotation of the (Ar)C1-N1 bond due to the ortho effect of the chlorine atom on C-2 of the phenyl ring.



19-22



23-26

	R^1	R^2
19, 23	4-ClC_6H_4	OEt
20, 24	2,4-$Cl_2C_6H_3$	OEt
21, 25	4-ClC_6H_5	Me
22, 26	2,4-$Cl_2C_6H_3$	Me

Compounds **19-22** had no signal for N*H*, and H-1' was coupled only with H-2'. The chemical shifts for H-1' and C-1' (Table 3) were similar to those described for related *N*-tetra-*O*-acetyl-β-D-glucopyranosyl derivatives.[27,28] One possible structure of glucosyliminothiazine was ruled out based on NMR spectra; for example the chemical shifts for the resonances of C-1' and C=N should be ≈ 94 and 162 ppm respectively,[29] but that is not in agreement with the experimental data of **19-22**. The byproducts **23-26** had no C=S signals, and the resonances for H-1' and C-1' appeared slightly shielded when they were compared with the same data for the parent compounds **10, 11, 13**, and **14** (Table 3), in accord with bibliographic data for glycosylthioamide-glycosylamide pairs.[8] The chemical shift for the resonances of the NH groups supported, as in the parent compounds, the hydrogen bond and the configuration indicated in the formula.

The *J* values for the sugar ring of **19-26** also supported the $^4C_1$ conformation for these compounds.

The formation of compounds **23-26** can be potentially used in the synthesis of glycosylamides.

EXPERIMENTAL

General. Optical rotations were measured for solutions in CH_2Cl_2. IR spectra were recorded as KBr discs or thin films. ^1H NMR spectra (300 and 500 MHz) were obtained for solutions in $CDCl_3$ or DMSO-d_6. Assignments were confirmed by homonuclear 2D COSY correlated experiments. The temperature coefficients for some signals were measured between 233 and 313 K. ^{13}C NMR spectra were recorded at 75.4 and 125.7 MHz. Heteronuclear 2D correlated spectra were obtained in order to assist in carbon resonance assignments. EIMS spectra (70 eV) were measured with a Kratos MS-80RFA spectrometer with an ionising current of 100 μA, an accelerating voltage of 4 kV, a resolution of 1000 or 10000 (10% valley definition), and a scan rate of 3 sec/decade. Metastable peaks in the free region were obtained at a 10 sec/decade scan rate. FAB-mass spectra were recorded with the same resolution; ions were produced by a beam of xenon atoms (6-7 KeV) using a matrix consisting of thioglycerol or 3-nitrobenzyl alcohol and NaI as salt. TLC was performed on Silica Gel HF_{254}, with detection by UV light or charring with H_2SO_4. Silica Gel 60 (Merck, 230-400 mesh) was used for preparative chromatography.

General procedure for the preparation of 1-8. To a solution of the corresponding amine (15.69 mmol) in ethyl acetoacetate (2 mL, 15.69 mmol) for **1-4** or acetylacetone for **5-8** (1.61 mL, 15.69 mmol) over molecular sieves under argon and at rt, iodine (15 mg) was added. After a time *t*, an amorphous solid (**1-3, 5-7**) or syrup (**4** and **8**) was obtained. In the cases of **1-3, 5-7** the solid was filtered off, washed with EtOH:H_2O (1:1) and characterized as indicated. For compounds **4** and **8** the solvents and reactants were eliminated under diminished pressure. The reaction was monitored by TLC (3:1 ether-hexane), giving the expected compound in each case.

Ethyl 3-(4-Bromoanilino)crotonate (1). From *p*-bromoaniline: t = 20 min; amorphous solid; yield 46%, IR ν_{max}: Table 1 and 3067, 2978, 2928, 1481, 1263, 1167, and 1061 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 1 and δ 7.44-6.94 (m, 4 H, Ar), 4.72 (s, 1 H, =CH), 4.15 (q, 2 H, CH_2CH_3), 1.99 (s, 3 H, =C-CH_3), 1.28 (t, 3 H, $^3J_{H,H}$ = 7.1 Hz, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 1 and δ 158.0 (=*C*-CH_3)117.7-138.3 (6 C, Ar), 86.8 (=CH), 58.7 (CH_2CH_3), 20.0 (=C-CH_3), 14.3 (CH_2CH_3); EIMS

Table 2 and *m/z* 213 (10) and 211 (10). HREIMS Calcd for $C_{12}H_{14}BrNO_2$: 285.0189, 283.0208. Found: 285.0189, 283.0196.

Ethyl 3-(4-Chloroanilino)crotonate[30] **(2)**. From *p*-chloroaniline: t = 20 min; amorphous solid; yield 39%, IR ν_{max}: Table 1 and 3098, 2982, 2934, 1622, 1491, 1271, 1165, and 1059 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 1 and δ 7.00-7.30 (m, 4 H, Ar), 4.72 (s, 1 H, =CH), 4.15 (q, 2 H, CH_2CH_3), 1.98 (s, 3 H, =C-CH_3), and 1.29 (t, 3 H, $^3J_{H,H}$ = 7.1 Hz, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 1 and δ 158.3 (=*C*-CH_3), 125.4-137.8 (6 C, Ar), 86.7 (=CH), 58.8 (CH_2CH_3), 20.1 (=C-CH_3), and 14.4 (CH_2CH_3); EIMS Table 2 and *m/z* 169 (4), 167 (10). HREIMS Calcd for $C_{12}H_{14}ClNO_2$: 241.0684, 239.0713. Found: 241.0695, 239.0716.

Ethyl 3-(2,4-Dichloroanilino)crotonate (3). From 2,4-dichloroaniline: t = 72 h; amorphous solid; yield 21%, IR ν_{max}: Table 1 and 3071, 2980, 1627, 1464, 1275, 1165, and 1057 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 1 and δ 7.10-7.45 (m, 3 H, Ar), 4.81 (s, 1 H, =CH), 4.18 (q, 2 H, CH_2CH_3), 1.97 (s, 3 H, =C-CH_3), and 1.29 (t, 3 H, $^3J_{H,H}$ = 7.1 Hz, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 1 and δ 157.3 (=*C*-CH_3), 135.5-126.4 (6 C, Ar), 88.4 (=CH), 59.0 (CH_2CH_3), 20.1 (=C-CH_3), and 14.4 (CH_2CH_3); EIMS Table 2 and *m/z* 201 (10). HREIMS Calcd for $C_{12}H_{13}Cl_2NO_2$: 275.0294, 273.0323. Found: 275.0297, 273.0335.

Ethyl 3-(3,4-Dimethoxybenzylamino)crotonate (4). From 4,5-dimethoxybenzylamine: t = 30 min; syrup; yield 43%, IR ν_{max}: Table 1 and, 3056, 2966, 2943, 1604, 1510, 1452, 1269, 1167, and 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 1 and δ 6.82-6.70 (m, 3 H, Ar), 4.46 (s, 1 H, =CH), 4.29 (d, 2 H, $J_{H,NH}$ = 6.1 Hz, CH_2 of Bn), 4.03 (q, 2 H, CH_2CH_3), 3.81, 3.80, (each s, each 3 H, 2 OCH_3), 1.86 (s, 3 H, =C-CH_3), and 1.19 (t, 3 H, $^3J_{H,H}$ 7.1 Hz, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 1 and δ 161.5 (=*C*-CH_3), 119.3 (=C-CH_3), 131.0-109.9 (6 C, Ar), 83.0 (=CH), 55.8 (2C, 2 OCH_3), 58.3 (CH_2CH_3), 46.5 (CH_2 of Bn), and 4.5 (CH_2CH_3); EIMS Table 2 and *m/z* 207 (3). HREIMS Calcd for $C_{15}H_{21}NO_4$: 279.1470. Found: 279.1465.

4-(4-Bromoanilino)-3-penten-2-one (5). From *p*-bromoaniline: t = 15 h; amorphous solid; yield 38%, IR ν_{max}: Table 1 and 3059, 2982, 2926, 1618, 1583, 1495, 1275, and 1184 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 1 and δ 7.46-6.96 (m, 4 H, Ar), 5.20 (s, 1 H, =CH), 2.10 (s, 3 H, $COCH_3$), and 1.98 (s, 3 H, =C-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 1 and δ , 159.3 (=*C*-CH_3), 118.5-137.7 (6 C, Ar), 98.0 (=CH), 29.0 ($COCH_3$), and 19.6 (=C-CH_3); EIMS Table 2.

Anal. Calcd for $C_{11}H_{12}BrNO$ (254.14): C, 51.99; H, 4.76; N, 5.51. Found: C, 51.98; H, 4.60; N, 5.79.

4-(4-Chloroanilino)-3-penten-2-one (6). From *p*-chloroaniline: t = 15 h; amorphous solid; yield 49%, IR ν_{max}: Table 1 and 3038, 2978, 2926, 1616, 1572, 1495,

1277, and 1184 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): Table 1 and δ , 7.32-7.02 (m, 4 H, Ar), 5.21 (s, 1 H, =CH), 2.10 (s, 3 H, $COCH_3$), and 1.98 (s, 3 H, =C-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 1 and δ, 159.6 (=*C*-CH_3), 137.2-125.8 (6 C, Ar), 98.0 (=CH), 29.1 ($COCH_3$), 19.7 (=C-CH_3); EIMS Table 2. HREIMS Calcd for $C_{11}H_{12}ClNO$: 209.0607. Found: 209.0607.

4-(2,4-Dichloroanilino)-3-penten-2-one (7). From 2,4-dichloroaniline: *t* = 17 h; amorphous solid; yield 43%, IR ν_{max}: Table 1 and 3045, 2970, 2868, 1556, 1460, 1271, 1176, and 1051 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 1 and δ 7.47-7.13 (m, 3 H, Ar), 5.28 (s, 1 H, =CH), 2.13 (s, 3 H, $COCH_3$), and 1.94 (s, 3 H, =C-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 1 and δ 159.0 (=*C*-CH_3), 135.1-127.1 (6 C, Ar), 98.8 (=CH), ,29.2 ($COCH_3$), and 19.6 (=C-CH_3); EIMS Table 2. HREIMS Calcd for $C_{11}H_{11}Cl_2NO$: 243.0218. Found: 243.0227.

4-(3,4-Dimethoxybenzylamino)-3-penten-2-one (8). From 4,5-dimethoxybenzylamine: *t* = 25 h; syrup; yield 58%, IR ν_{max}: Table 1 and 3046, 2961, 2841, 1518, 1454, 1244, 1152, and 1024 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 1 and δ 6.83-6.76 (m, 3 H, Ar), 5.03 (s, 1 H, =CH), 4.39 (s, 2 H, $J_{H,NH}$ = 6.3 Hz, CH_2), 3.87, 3.86 (each s, each 3 H, 2 OCH_3), 2.02 (s, 3 H, $COCH_3$), and 1.92 (s, 3 H, =C-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 1 and δ 162.8 (=*C*-CH_3), 149.9-109.1 (6 C, Ar), 95.7 (=CH)18.7 (=C-CH_3), 55.8, 55.7 (each 1 C, 2 OCH_3), 46.4 (CH_2 of Bn), and 28.7 ($COCH_3$); EIMS Table 2. HREIMS Calcd for $C_{14}H_{19}NO_3$: 249.1365. Found: 249.1369.

Anal. Calcd for $C_{14}H_{19}NO_3$ (249.31): C, 67.45; H, 7.68; N, 5.62. Found: C, 67.54; H, 7.59; N, 5.62.

General procedure for the preparation of 9-18. A solution of 2, 3, 4, 6-tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate (0.39 mmol) in DMF (0.4 mL) was added during *t* hours to a stirred solution of the corresponding enamine (**1-8**) (0.26 mmol) and KOH (0.1 mmol) in DMF (0.5 mL) over molecular sieves and under an argon atmosphere. The reaction was monitored by TLC (3:1 ether-hexane) and then poured into ice-water, extracted with ether, washed with water, dried over $MgSO_4$, filtered and concentrated to dryness. The remaining residue was purified as indicated in each case.

3-(4-Bromoanilino)-2-ethoxycarbonyl-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-butenethioamide (9). From **1**: *t* = 20 min ; column chromatography (1:1 ether-hexane) of the residue gave an amorphous solid (23%); $[\alpha]_D^{18}$ -8.2° (*c* 1.7); IR ν_{max}: 3185, 2994, 2898, 1753, 1649, 1595, 1370, 1254, and 1045 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 3 and δ 7.51-7.01 (m, 4 H, Ar), 5.37 (t, 1 H, H-3'), 5.15 (t, 1 H, $J_{2',3'}$ = 9.4 Hz, H-2'), 5.11 (t, 1 H, $J_{3',4'}$ = 9.4 Hz, $J_{4',5'}$ = 9.5 Hz, H-4'), 4.31 (dd, 1 H, $J_{5',6'a}$ = 4.6 Hz, $J_{6'a,6'b}$ = 12.4 Hz, H-6'a), 4.23 (q, 2 H, $^3J_{H,H}$ = 7.1 Hz, CH_2CH_3), 4.12 (dd, 1 H, $J_{5',6'b}$ = 2.1 Hz, H-6'b), 3.88 (ddd, 1 H, H-5'), 2.09 (s, 3 H, =C-CH_3), 2.08, 2.04

(each s, each 3 H, 2 Ac), 2.03 (s, 6 H, 2 Ac), and 1.30 (t, 3 H, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.6 (2 C, COOEt and $COCH_3$), 170.2, 169.9, 169.5 (3 $COCH_3$), 157.6 (=C-CH_3), 136.6-127.4 (6 C, Ar), 117.1 (=C-CO), 73.5 (C-5'), 73.0 (C-3'), 70.4 (C-2'), 68.3 (C-4'), 61.6 (C-6'), 60.7 (CH_2CH_3), 20.6 (=C-CH_3), 20.5 (4 C, 4 $COCH_3$), and 14.0 (CH_2CH_3), FABMS *m/z* 697, 695 $[M+Na]^+$.

Anal. Calcd for $C_{27}H_{33}BrN_2O_{11}S$ (673.56): C, 48.15; H, 4.94; N, 4.16; S, 4.76. Found: C, 48.36; H, 4.76; N, 4.15; S, 4.93.

3-(4-Chloroanilino)-2-ethoxycarbonyl-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-butenethioamide (10). From **2**: t = 11 h; column chromatography (1:1 ether-hexane) of the residue gave an amorphous solid (24%); $[\alpha]_D^{28}$ -20.0° (*c* 0.5); IR ν_{max}: 3297, 2969, 1753, 1651, 1601, 1370, 1252, and 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.36-7.07 (m, 4 H, Ar), 5.37 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.4$ Hz, H-3'), 5.15 (t, 1 H, H-2'), 5.11 (t, 1 H, $J_{4',5'} = 9.5$ Hz, H-4'), 4.31 (dd, 1 H, $J_{5',6'a} = 5.0$ Hz, $J_{6'a,6'b} = 12.5$ Hz, H-6'a), 4.23 (q, 2 H, $^3J_{H,H} = 7.1$ Hz, CH_2CH_3), 4.11 (dd, 1 H, $J_{5',6'b} = 2.0$ Hz, H-6'b), 3.88 (ddd, 1 H, H-5'), 2.10 (s, 3 H, =C-CH_3), 2.07, 2.04 (each s, each 3 H, 2 Ac), 2.03 (s, 6 H, 2 Ac), and 1.29 (t, 3 H, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.6 (2 C, COOEt and $COCH_3$), 170.2, 169.9, 169.5 (3 $COCH_3$), 156.7 (=C-CH_3), 136.1-127.1 (6 C, Ar), 116.7 (=C-CO), 73.5 (C-5'), 73.1 (C-3'), 70.4 (C-2'), 68.4 (C-4'), 61.7 (C-6'), 60.7 (CH_2CH_3), 20.6 (=C-CH_3), 20.5 (4 C, 4 $COCH_3$), 14.1 (CH_2CH_3); FABMS *m/z* 651 $[M+Na]^+$.

Anal. Calcd for $C_{27}H_{33}ClN_2O_{11}S$ (629.10): C, 51.55; H, 5.29; N, 4.45; S, 5.10. Found: C, 51.60; H, 5.26; N, 4.28; S, 5.27.

3-(2,4-Dichloroanilino)-2-ethoxycarbonyl-*N* -(2,3,4,6-tetra-*O* -acetyl-β-D-glucopyranosyl)-2-butenethioamide (11). From **3**: t = 7.5 h; column chromatography (1:1 ether-hexane) of the residue gave a solid (48 %); $[\alpha]_D^{22}$ +0.0° (*c* 0.4); IR ν_{max}: 3181, 2990, 1750, 1653, 1603, 1370, 1250, and 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 3 and δ 7.49-7.12 (m, 3 H, Ar), 5.38 (t, 1 H, $J_{2',3'} = 9.5$ Hz, $J_{3',4'} = 9.5$ Hz, H-3'), 5.13 (t, 1 H, H-2'), 5.11 (t, 1 H, $J_{4',5'} = 9.5$ Hz, H-4'), 4.32 (dd, 1 H, $J_{5',6'a} = 4.6$ Hz, $J_{6'a,6'b} = 12.4$ Hz, H-6'a), 4.25 (q, 2 H, $^3J_{H,H} = 7.1$ Hz, CH_2CH_3), 4.11 (dd, 1 H, $J_{5',6'b} = 2.2$ Hz, H-6'b), 3.88 (ddd, 1 H, H-5'), 2.07 (s, 3 H, =C-CH_3), 2.04 (s, 3 H, Ac), 2.03 (s, 6 H, 2 Ac), 2.02 (s, 3 H, Ac), and 1.29 (t, 3 H, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.5 (2 C, COOEt and $COCH_3$), 170.3, 169.8, 169.4 (3 $COCH_3$), 157.3 (=C-CH_3), 130.0-127.6 (6 C, Ar), 116.5 (=C-CO), 73.5 (C-5'), 72.9 (C-3'), 70.4 (C-2'), 68.3 (C-4'), 61.6 (C-6'), 60.7 (CH_2CH_3), 20.6 (=C-CH_3), 20.5 (4 C, 4 $COCH_3$), and 14.0 (CH_2CH_3); FABMS *m/z* 685 $[M+Na]^+$.

Anal. Calcd for $C_{27}H_{32}Cl_2N_2O_{11}S$ (663.55): C, 48.87; H, 4.86; N, 4.22; S, 4.83. Found: C, 48.95; H, 4.83; N, 4.19; S, 4.89.

2-Acetyl-3-(4-bromoanilino)-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-butenethioamide (12). From **4**: t = 3 h; column chromatography (6:1 ether-hexane) of the residue gave an amorphous solid (43%); $[\alpha]_D^{19}$ +30.7° (c 1.0); IR ν_{max}: 3162, 2998, 2930, 1755, 1603, 1368, 1219, and 1034 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 3 and δ 7.50-6.97 (m, 4 H, Ar), 5.41 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.5$ Hz, H-3'), 5.09 (t, 2 H, $J_{4',5'} = 9.5$ Hz, H-2', 4'), 4.37 (dd, 1 H, $J_{5',6'a} = 5.1$ Hz, $J_{6'a,6'b} = 12.4$ Hz, H-6'a), 4.06 (dd, 1 H, $J_{5',6'b} = 2.2$ Hz, H-6'b), 3.89 (ddd, 1 H, H-5'), 2.15 (s, 3 H, $COCH_3$ ketone), 2.05, 2.04 (each s, each 6 H, 4 $COCH_3$ ester), and 1.96 (s, 3 H, =C-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 205.7 ($COCH_3$ ketone), 171.0, 170.4, 169.8, 169.5 (4 $COCH_3$ ester), 158.3 (=C-CH_3), 136.7-120.0 (6 C, Ar), 116.5 (=I-CO), 74.0 (C-5'), 72.6 (C-3'), 70.5 (C-2'), 68.3 (C-4'), 61.4 (C-6'), 27.2 ($COCH_3$ ketone), 20.6 ($COCH_3$ ester), 20.5 (3 C, 3 $COCH_3$ ester), and 16.9 (=C-CH_3); FABMS m/z 665, 667 $[M+Na]^+$.

Anal. Calcd for $C_{26}H_{31}BrN_2O_{10}S$ (643.53): C, 48.53; H, 4.86; N, 4.35; S, 4.98. Found: C, 48.57; H, 4.55; N, 4.48; S, 5.28..

2-Acetyl-3-(4-chloroanilino)-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-butenethioamide (13). From **5**: t = 2 h; column chromatography (1:1 ether-hexane) of the residue gave an amorphous solid (52%); $[\alpha]_D^{28}$ +26.5° (c 1.0); IR ν_{max}: 3289, 2957, 2868, 1750, 1601, 1370, 1223, and 1042 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 3 and δ 7.34-7.04 (m, 4 H, Ar), 5.41 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.5$ Hz, H-3'), 5.09 (t, 2 H, $J_{4',5'} = 9.5$ Hz, H-2', 4'), 4.37 (dd, 1 H, $J_{5',6'a} = 5.0$ Hz, $J_{6'a,6'b} = 12.4$ Hz, H-6'a), 4.06 (dd, 1 H, $J_{5',6'b} = 2.2$ Hz, H-6'b), 3.89 (ddd, 1 H, H-5'), 2.16 (s, 3 H, $COCH_3$ ketone), 2.05-2.04 (m, 12 H, 4 $COCH_3$ ester), and 1.96 (s, 3 H, =C-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 3 and δ 205.7 ($COCH_3$ ketone), 170.9, 170.3, 169.7, 169.4 (4 $COCH_3$ ester), 158.4 (=C-CH_3), 136.2-126.8 (6 C, Ar), 116.4 (=C-CO), 74.0 (C-5'), 72.5 (C-3'), 70.4 (C-2'), 68.2 (C-4'), 61.4 (C-6'), 27.1 ($COCH_3$ ketone), 20.5 (4 C, 4 $COCH_3$ ester), and 16.8 (=C-CH_3); FABMS m/z 621 $[M+Na]^+$.

Anal. Calcd for $C_{26}H_{31}ClN_2O_{10}S$ (599.07): C, 52.13; H, 5.21; N, 4.68; S, 5.35. Found: C, 51.94; H, 5.55; N, 4.31; S, 5.17.

2-Acetyl-3-(2,4-dichloroanilino)-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-butenethioamide (14). From **7**: t = 10 h: column chromatography (3:1 ether-hexane) of the residue gave an amorphous solid (76%); $[\alpha]_D^{28}$ +28.0° (c 1.0); IR ν_{max}: 3314, 2924, 2857, 1748, 1604, 1370, 1250, 1036 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 3 and δ 7.48-7.12 (m, 3 H, Ar), 5.41 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.5$ Hz, H-3'), 5.10 (t, 2 H, $J_{4',5'} = 9.5$ Hz, H-2', 4'), 4.37 (dd, 1 H, $J_{5',6'a} = 5.0$ Hz, $J_{6'a,6'b} = 12.4$ Hz, H-6'a), 4.07 (dd, 1 H, $J_{5',6'b} = 2.1$ Hz, H-6'b), 3.89 (ddd, 1 H, H-5'), 2.18 (s, 3 H, $COCH_3$ ketone), 2.06, 2.05 (each s, each 6 H, 4 $COCH_3$ ester), and 1.92 (s, 3 H, =C-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 3 and δ 205.3 (CO ketone), 170.8, 170.3, 169.7, 169.4 (4

CO ester), 158.1 (=*C*-CH_3), 134.1-127.5 (6 C, Ar), 117.0 (=*C*-CO), 74.0 (C-5'), 72.5 (C-3'), 70.4 (C-2'), 68.2 (C-4'), 61.4 (C-6'), 27.1 (CO*C*H_3 ketone), 20.5 (4 C, 4 CO*C*H_3 ester), and 16.8 (=C-*C*H_3); FABMS *m/z* 655 $[M+Na]^+$.

Anal. Calcd for $C_{26}H_{30}Cl_2N_2O_{10}S$ (633.52): C, 49.30; H, 4.77; N, 4.42; S, 5.06. Found: C, 49.06; H, 4.93; N, 4.37; S, 5.10..

3-(3,4-Dimethoxybenzylamino)-2-ethoxycarbonyl-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-butenethioamide (15) and *N*-(3,4-Dimethoxybenzyl)-*N*-(2-ethoxycarbonyl-1-methylvinyl)-*N'*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)thiourea (17). From **7**; *t* = 12 h; column chromatography (1:1, 12:1 ether-hexane) of the residue yielded **15** (7%) and **17** (17%) as amorphous solids.

Compound **15** had $[\alpha]_D^{21}$ -9.0° (*c* 0.32); IR ν_{max}: 3300, 2963, 2863, 1750, 1647, 1593, 1371, 1227, and 1036 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 3 and δ 6.85 (m, 3 H, Ar), 5.35 (t, 1 H, $J_{2',3'}$=$J_{3',4'}$= 9.4 Hz, H-3'), 5.16 (t, 1 H, H-2'), 5.11 (dd, 1 H, $J_{4',5'}$= 10.0 Hz, H-4'), 4.49 (m, 2 H, CH_2 of Bn), 4.30 (dd, 1 H, $J_{5',6'a}$= 4.4 Hz, $J_{6'a,6'b}$= 12.4 Hz, H-6'a), 4.20 (q, 2 H, $^3J_{H,H}$= 7.1 Hz, C*H*$_2$CH$_3$), 4.11 (dd, 1 H, $J_{5',6'b}$= 2.2 Hz, H-6'b), 3.88 (s, 6 H, 2 OCH_3), 3.88-3.82 (m, 1 H, H-5'), 2.18 (s, 3 H, =C-CH_3), 2.07, 2.03, 2.02, 2.01 (each, s, each 3 H, 4 Ac), and 1.27 (t, 3 H, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 3 and δ 170.6–169.0 (5 C, *C*OOEt, 4 *C*OCH_3), 164.7 (=*C*-CH_3), 149.2-110.3 (6 C, Ar), 101.1 (=*C*-CO), 73.2 (C-5'), 70.3 (C-3'), 68.3 (2 C, C-2', 4'), 61.7 (C-6'), 60.4 (*C*H_2CH$_3$), 55.9, 55.8 (2 OCH_3), 47.6 (CH_2 of Bn), 20.5 (4 C, 4 CO*C*H_3), 19.8 (=C-*C*H_3), and 14.0 (CH_2CH_3); FABMS *m/z* 691 $[M+Na]^+$. HRFABMS Calcd for $C_{30}H_{40}N_2O_{13}SCs$: 801.1316. Found: 801.1305.

Compound **17** had $[\alpha]_D^{19}$ -13.2° (*c* 0.5); IR ν_{max}: 3366, 2957, 2863, 1746, 1647, 1518, 1371, 1227, and 1036 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 3 and δ 7.07-6.75 (m, 3 H, Ar), 5.53 (m, 1 H, =CH), 5.36 (t, 1 H, $J_{2',3'}$= $J_{3',4'}$= 9.5 Hz, H-3'), 5.25, 5.10 (each d, each 1 H, $^2J_{H,H}$= 14.9 Hz, CH_2 of Bn), 5.07 (t, 1 H, $J_{4',5'}$= 9.5 Hz, H-4'), 4.96 (t, 1 H, H-2'), 4.34 (dd, 1 H, $J_{5',6'a}$= 4.5 Hz, $J_{6a,6b}$= 12.3 Hz, H-6'a), 4.19 (q, 2 H, $^3J_{H,H}$= 7.1 Hz, C*H*$_2$CH$_3$), 4.10 (dd, 1 H, $J_{5',6'b}$= 2.1 Hz, H-6'b), 3.87, 3.86 (each s, each 3 H, 2 OCH_3), 3.86-3.84 (m, 1 H, H-5'), 2.17 (d, 3 H, $^4J_{H,H}$< 1.0 Hz, =C-CH_3), 2.10, 2.03 (each, s, each 3 H, 2 Ac), 2.00 (s, 6 H, 2 Ac), and 1.28 (t, 3 H, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 3 and δ 171.1, 170.6, 169.8, 169.5 (4 *C*OCH_3), 164.7 (COOEt), 152.8 (=*C*-CH_3), 148.9-110.8 (6 C, Ar), 123.1 (=CH), 73.3 (C-5'), 72.6 (C-3'), 70.5 (C-2'), 68.3 (C-4'), 61.5 (C-6'), 60.6 (*C*H_2CH$_3$), 55.9, 55.8 (2 OCH_3), 55.2 (CH_2 of Bn), 20.6, 20.5. (2 CO*C*H_3), 20.4 (2 C, 2 CO*C*H_3), 19.3 (=C-*C*H_3), and 14.5 (CH_2CH_3); FABMS *m/z* 691 $[M+Na]^+$. HRFABMS Calcd for $C_{30}H_{40}N_2O_{13}SNa$: 691.2159. Found 691.2158.

2-Acetyl-3-(3,4-dimethoxybenzylamino)-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-butenethioamide (16) and 1-(3,4-Dimethoxybenzyl)-6-methyl-4-methylene-3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-thioxotetrahydropyrimidine (18). From **8**; *t* = 5 h; column chromatography (1:1, 12:1 ether-hexane) of the residue yielded **16** (16%) and **18** (37%) as amorphous solids.

Compound **16** had $[\alpha]_D^{21}$ -11.0° (*c* 0.65); IR ν_{max}: 3291, 2947 2841, 1753, 1599, 1370, 1229, and 1038 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): Table 3 and δ 6.85-6.76 (m, 3 H, Ar), 5.39 (t, 1 H, $J_{2',3'}$= $J_{3',4'}$= 9.4 Hz, H-3'), 5.08 (t, 1 H, $J_{4',5'}$= 9.4 Hz, H-4'), 5.07 (t, 1 H, H-2'), 4.39 (m, 2 H, CH_2 of Bn), 4.37 (dd, 1 H, $J_{5',6'a}$= 5.1 Hz, $J_{6'a,6'b}$= 12.4 Hz, H-6'a), 4.06 (dd, 1 H, $J_{5',6'b}$= 2.1 Hz, H-6'b), 3.90-3.87 (m, 1 H, H-5'), 3.88, 3.87 (each s, each 3 H, 2 OCH_3), 2.07 (s, 3 H, $COCH_3$ ketone), 2.05, 2.04, 2.03, 2.02 (each s, each 3 H, 4 $COCH_3$ ester), and 1.99 (s, 3 H, =C-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): Table 3 and δ 206.5 (CO ketone), 170.7, 170.2, 169.6, 169.3 (4 CO ester), 161.1 (=*C*-CH_3), 149.3-110.2 (6 C, Ar), 115.3 (=*C*-CO), 73.8 (C-5'), 72.6 (C-3'), 70.4 (C-2'), 68.3 (C-4'), 61.4 (C-6'), 55.8 (2 C, 2 OCH_3), 46.8 (CH_2 of Bn), 26.9 ($COCH_3$ ketone), 20.4 ($COCH_3$ ester), 20.3 (3 C, 3 $COCH_3$ ester), and 15.9 (=C-CH_3); FABMS *m/z* 661 $[M+Na]^+$. HRFABMS Calcd for $C_{29}H_{36}N_2O_{12}SCs$: 769.1013. Found: 769.1043.

Compound **18** had $[\alpha]_D^{24}$ ≈-0.0° (*c* 1.2); IR ν_{max}: 3352, 2961, 1750, 1649, 1537, 1371, 1227, 1038 cm^{-1}; ^1H NMR[31] (500 MHz, $CDCl_3$): Table 3 and δ 7.36 (d, 1 H, $J_{1',2'}$= 9.8 Hz, H-1'**B**), 6.84-6.75 (m, 6 H, Ar**A**, **B**), 5.98 (t, 1 H, $J_{2',3'}$= 9.5 Hz, H-2'**A**), 5.80-5.76 (m, 2 H, CH*H* of Bn**A**, **B**), 5.65 (s, 1 H, =CH**A**), 5.60 (s, 1 H, =CH**B**), 5.49 (t, 1 H, $J_{2',3'}$= 9.8 Hz, H-2'**B**), 5.37 (t, 1 H, $J_{3',4'}$= 9.5 Hz, H-3'**A**), 5.34 (t, 1 H, $J_{3,4}$= 9.8 Hz, H-3'**B**), 5.32-5.26 (m, 2 H, C*H*H of Bn**A**, **B**), 5.20 (t, 1 H, $J_{4',5'}$= 9.5 Hz, H-4'**A**), 5.17 (t, 1 H, $J_{4',5'}$= 9.8 Hz, H-4'**B**), 4.80 (bs, 2 H, =C*H*H**A**, **B**), 4.34-4.30 (m, 2 H, H-6'a**A**, **B**), 4.30 (dd, 1 H, $J_{5',6'b}$= 3.9 Hz, $J_{6'a,6'b}$= 12.5 Hz, H-6'b**B**), 4.22 (dd, 1 H, $J_{5',6'b}$= 2.1 Hz, $J_{6'a,6'b}$= 12.5 Hz, H-6'b**A**), 3.99 (bs, 2 H, =CH*H***A**, **B**), 3.86, 3.85 (each s, each 3 H, 2 OCH_3**A**), 3.87, 3.84 (each s, each 3 H, 2 OCH_3**B**), 3.92 (ddd, 1 H, $J_{5',6'a}$= 3.5 Hz, H-5'**A**), 3.90-3.85 (m, 1 H, H-5'**B**), 2.18 (s, 3 H, =C-CH_3**A**), 2.10, 2.07, 2.03, 1.99 (each s, each 3 H, 4 Ac**B**), 2.09, 2.06, 2.02, 1.97 (each s, each 3 H, 4 Ac**A**), and 1.92 (s, 3 H, =C-CH_3**B**); ^{13}C NMR[31] (125.7 MHz, $CDCl_3$): Table 3 and δ 181.4 (CS**B**), 170.3, 169.9, 169.2 168.8 (4 CO**A**), 170.2, 169.6, 169.5, 169.3 (4 CO**B**), 149.2 (=C**A**), 149.1 (=C**B**), 148.2 (=C**A**), 148.0 (=C**B**), 138.6-109.5 (12 C, Ar**A**, **B**), 111.2-109.5 (2 C, =CH**A**, **B**), 94.0 (=CH_2**A**), 88.9 (C-1'**B**), 88.8 (=CH_2**B**), 74.3 (C-5'**B**), 74.2 (C-5'**A**), 73.9 (C-3'**A**), 73.6 (C-3'**B**), 70.0 (C-2'**B**), 67.7 (C-4'**B**), 67.6 (C-4'**A**), 65.6 (C-2'**A**), 61.3 (2 C, C-6'**A**, **B**), 55.8-55.7 (5 C, CH_2 of Bn**A**, 4 OCH_3**A**, **B**), 53.6 (CH_2 of Bn**B**), 20.5-20.3 (8 C, 8 $COCH_3$**A**, **B**), 19.6 (=C-CH_3B), and 19.3 (=C-CH_3A). FABMS *m/z* 643 $[M+Na]^+$. HRFABMS Calcd for $C_{29}H_{36}N_2O_{11}SNa$ 643.1938. Found: 643.1900.

Reactions of glucosylthioamides with thiophosgene. To a heterogeneous mixture of the corresponding thioamides **10, 11, 13,** and **14** (0.079 mmol) in chloroform (1.6 mL) and calcium carbonate (0.474 mmol) in water (1.6 mL), thiophosgene (0.237 mmol) was added. The mixture was stirred vigorously at room temperature for *t* h, and then filtered; the organic layer was separated, washed with water, dried, and concentrated to dryness. The residue was purified as indicated in each case. The following compounds were prepared in this manner.

1-(4-Chlorophenyl)-5-ethoxycarbonyl-6-methyl-3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,4-dithioxotetrahydropyrimidine (19) and 3-(4-chloroanilino)-2-ethoxycarbonyl-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-buteneamide (23). From thioamide **10**; *t* = 30 min.; preparative TLC (40:1 dichloromethane: methanol) of the residue yielded **19** (23 %) and **23** (28 %) as amorphous solids.

Compound **19** had $[\alpha]_D^{21}$ +6.7° (*c* 0.9); IR ν_{max}: 3287, 2965, 2091, 1753, 1373, 1225, 1090, and 1040 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.50-7.47 (m, 4 H, Ar), 5.29 (t, 1 H, $J_{2',3'}$= $J_{3',4'}$= 9.3 Hz, H-3'), 5.21 (dd, 1 H, H-2'), 5.07 (dd, 1 H, $J_{4',5'}$= 9.9 Hz, H-4'), 4.29-4.24 (m, 2 H, CH_2CH_3), 4.21 (dd, 1 H, $J_{5',6'a}$= 6.3 Hz, $J_{6'a,6'b}$= 12.3 Hz, H-6'a), 4.18 (dd, 1 H, $J_{5',6'b}$= 2.5 Hz, H-6'b), 3.89 (ddd, 1 H, H-5'), 2.14, 2.05, 2.03, 2.02 (each s, each 3 H, 4 Ac), 1.86 (s, 3 H, =C-CH_3), and 1.32 (t, 3 H, $^3J_{H,H}$= 7.1, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.8, 170.2, 169.4, 169.1 (4 $COCH_3$), 165.6 (COOEt), 143.6 (=C-CH_3), 138.6-129.8 (6 C, Ar), 119.0 (=C-CO), 74.0 (C-5'), 73.0 (C-3'), 71.7 (C-2'), 68.6 (C-4'), 62.3 (C-6'), 62.2 (CH_2CH_3), 21.8, 20.9 (each 1 C, 2 $COCH_3$), 20.5 (4 C, 3 $COCH_3$, =C-CH_3), and 13.9 (CH_2CH_3); FABMS *m/z* 693 $[M+Na]^+$. HRFABMS Calcd for $C_{28}H_{31}ClN_2O_{11}S_2Na$: 693.0956. Found: 693.0970.

Compound **23** had $[\alpha]_D^{22}$ +28.0° (*c* 1.0); IR ν_{max}: 3256, 2963, 1753, 1578, 1371, 1225, 1088, and 1038 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.36-7.05 (m, 4 H, Ar), 5.32 (t, 1 H, $J_{2',3'}$=$J_{3',4'}$= 9.4 Hz, H-3'), 5.13[32] (t, 1 H, $J_{4',5'}$= 9.4 Hz, H-4'), 5.12[32] (t, 1 H, H-2'), 4.27 (q, 3 H, $^3J_{H,H}$= 7.1 Hz, CH_2CH_3), 4.31 (dd, 1 H, $J_{5',6'a}$= 4.1 Hz, $J_{6'a,6'b}$= 12.4 Hz, H-6'a), 4.12 (dd, 1 H, $J_{5',6'b}$= 2.2 Hz, H-6'b), 3.84 (ddd 1 H, H-5'), 2.26 (s, 3 H, =C-CH_3), 1.32 (t, 3 H, CH_2CH_3), 2.09, 2.05, 2.04, 2.03 (each s, each 3 H, 4 Ac); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 170.8–168.4, (6 C, 4 $COCH_3$, COOEt and COamide), 160.6 (=C-CH_3), 136.5-127.2 (6 C, Ar), 116.5 (=C-CO), 73.3 (C-3', 5'), 70.1[32] (C-2'), 68.2[32] (C-4'), 61.7 (C-6'), 60.4 (CH_2CH_3), 20.7 ($COCH_3$), 20.5 (4 C, 3 $COCH_3$ and =C-CH_3), and 14.2 (CH_2CH_3); FABMS *m/z* 635 $[M+Na]^+$. HRFABMS Calcd for $C_{27}H_{33}ClN_2O_{12}Na$: 635.16200. Found: 635.16060.

1-(2,4-Dichlorophenyl)-5-ethoxycarbonyl-6-methyl-3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,4-dithioxotetrahydropyrimidine (20), and 3-(2,4-dichloroanilino)-2-ethoxycarbonyl-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-butenea-

mide (24). From thioamide **11**; t = 30 min.; preparative TLC (60:1 dichloromethane: methanol) of the residue yielded **20** (18 %) and **24** (23 %) as amorphous solids.

Compound **20** was a ≈ 1:1 mixture of conformers (**a** and **b**) which had $[\alpha]_D^{21}$ ≈0.0° (*c* 1.3); IR ν_{max}: 3283, 2961, 2049, 1751, 1375, 1223, and 1042 cm^{-1}; ^1H NMR[33] (500 MHz, $CDCl_3$): δ 7.57-7.17 (m, 6 H, Ar), 5.29 (t, 2 H, $J_{2',3'}$= 9.0 Hz, $J_{3',4'}$= 9.0 Hz, H-3'**a**, **b**), 5.23, 5.20 (each t, each 1 H, H-2'**a**, **b**), 5.07 (dd, 2 H, $J_{4',5'}$= 10.1 Hz, H-4'**a**, **b**), 4.27 (q, 4 H, $^3J_{H,H}$= 7.1 Hz, CH_2CH_3**a**, **b**), 4.30-4.11 (m, 4 H, H-6'a, b'**a**, **b**), 3.89 (m, 2 H, H-5'**a**, **b**), 2.14, 2.05 (each s, each 6 H, 4 Ac), 2.04 (s, 3 H, Ac), 2.03 (s, 6 H, 2 Ac), 2.02 (s, 3 H, Ac), 1.85, 1.84 (each s, each 3 H, =C-CH_3**a**, **b**), 1.32, and 1.31 (t, 6 H, CH_2CH_3**a**, **b**); ^{13}C NMR[33] (125.7 MHz, $CDCl_3$): δ 170.8, 170.2, 169.5, 169.2 (8 $COCH_3$**a**, **b**), 165.5, 165.4 (*C*OOEt**a**, **b**), 143.3, 143.2 (=*C*-CH_3**a**, **b**), 136.5-128.9 (12 C, Ar**a**, **b**), 119.0 (2 C, =*C*-CO**a**, **b**), 74.1 (2 C, C-5'**a**, **b**), 73.1 (2 C, C-3'**a**, **b**), 71.8, 71.7 (C-2'**a**, **b**), 68.6 (2 C, C-4'**a**, **b**), 62.4 (2 C, CH_2CH_3**a**, **b**), 62.3, 62.2 (C-6'**a**, **b**), 20.9-20.4 (10 C, 8 $COCH_3$**a**, **b**, =C-CH_3**a**, **b**), 13.9, and 13.8 (CH_2CH_3**a**, **b**); FABMS *m/z* 727 $[M+Na]^+$. HRFABMS Calcd for $C_{28}H_{30}Cl_2N_2O_{11}S_2Na$: 727.0566. Found: 727.0551.

Compound **24** had $[\alpha]_D^{21}$ -7.2° (*c* 1.2); IR ν_{max}: 3285, 2951, 1751, 1580, 1373, 1227, 1090, and 1048 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.50-7.09 (m, 3 H, Ar), 5.39 (t, 1 H, H-1'), 5.32 (t, 1 H, $J_{2',3'}$=$J_{3',4'}$= 9.4 Hz, H-3'), 5.12[32] (t, 1 H, $J_{4',5'}$= 9.4 Hz, H-4'), 5.10[32] (t, 1 H, H-2'), 4.35-4.23 (m, 3 H, H-6'a, CH_2CH_3), 4.11 (dd, 1 H, $J_{5',6'b}$= 2.2 Hz, $J_{6'a,6'b}$= 12.4 Hz, H-6'b), 3.84 (ddd, 1 H, $J_{5',6'a}$= 4.1 Hz, H-5'), 2.20 (s, 3 H, =C-CH_3), 2.09, 2.04, 2.03, 2.02 (each s, each 3 H, 4 Ac), and 1.33 (t, 3 H, $^3J_{H,H}$= 7.1 Hz, CH_2CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.5 (CO amide), 170.0–168.6, (5 C, 4 $COCH_3$ and *C*OOEt), 159.1 (=*C*-CH_3), 134.4-127.7 (6 C, Ar), 116.3 (=*C*-CO), 73.3 (2 C, C-3', 5'), 70.2[32] (C-2'), 68.2[32] (C-4'), 61.7 (C-6'), 60.5 (CH_2CH_3), 20.6 ($COCH_3$), 20.5 (3 C, 2 $COCH_3$ and =C-CH_3), 20.3 ($COCH_3$), and 14.2 (CH_2CH_3); FABMS *m/z* 669 $[M+Na]^+$. HRFABMS Calcd for $C_{27}H_{32}Cl_2N_2O_{12}Na$: 669.1230. Found: 669.1232.

5 -Acetyl -1-(4-chlorophenyl)-6-methyl-3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,4-dithioxotetrahydropyrimidine (21) and 2-acetyl-3-(4-chloroanilino)-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-buteneamide (25). From thioamide **13**; t = 4 h; preparative TLC (8:1 toluene:acetone) of the residue yielded **21** (24 %) and **25** (31 %) as amorphous solids.

Compound **21** had $[\alpha]_D^{21}$ ≈0.0° (*c* 0.1); IR ν_{max}: 3368, 2957, 2861, 1753, 1593, 1371, 1256, and 1032 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.51-7.08 (m, 4 H, Ar), 5.31 (m, 1 H, H-3'), 5.22 (m, 1 H, H-2'), 5.07 (dd, 1 H, $J_{3',4'}$= 9.1 Hz, $J_{4',5'}$= 10.1 Hz, H-4'), 4.23-4.19 (m, 2 H, H-6'a, 6'b), 3.90 (ddd, 1 H, $J_{5',6'a}$= 5.9 Hz, $J_{5',6'b}$= 2.9 Hz, H-5'), 2.38 (s, 3 H, $COCH_3$ ketone), 2.15, 2.06, 2.03, 2.02 (each, s, each 3 H, 4 $COCH_3$ ester), and 1.79 (s, 3 H, =C-CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 201.1 (*C*OCH_3 ketone), 170.7,

170.1, 169.4, 169.2 (4 *C*OCH$_3$ ester), 142.9 (=*C*-CH$_3$), 138.5-128.7 (6 C, Ar), 124.8 (=*C*-CO), 86.7 (C-1'), 74.0 (C-5'), 72.9 (C-3'), 71.5 (C-2'), 68.5 (C-4'), 62.1 (C-6'), 31.2 (CO*C*H$_3$ketone), 20.5 (4 C, 4 CO*C*H$_3$ester), and 15.1 (=C-*C*H$_3$); FABMS *m/z* 663 [M+Na]$^+$. HRFABMS Calcd for $C_{27}H_{30}ClN_2O_{10}S_2$: 641.1030. Found: 641.1016.

Compound **25** had $[\alpha]_D^{21}$ +4.5° (*c* 0.66); IR ν_{max}: 3331, 2957, 2863, 1751, 1599, 1371, 1258, and 1036 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.03 (m, 4 H, Ar), 5.34 (t, 1 H, $J_{2',3'}$=$J_{3',4'}$= 9.6 Hz, H-3'), 4.98 (t, 1 H, H-2'), 5.08 (t, 1 H, $J_{4',5'}$= 9.6 Hz, H-4'), 4.34 (dd, 1 H, $J_{5',6'a}$= 4.7 Hz, $J_{6'a,6'b}$= 12.4 Hz, H-6'a), 4.07 (dd, 1 H, $J_{5',6'b}$= 2.4 Hz, H-6'b), 3.86 (ddd, 1 H, H-5'), 2.15 (s, 3 H, COCH$_3$ ketone), 2.05, 2.06 (each s, each 3 H, 2 COCH$_3$ ester), 2.03 (s, 6 H, 2 COCH$_3$ ester), and 1.96 (s, 3 H, =C-CH$_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 193.0 (*C*OCH$_3$ ketone), 170.5 (CO amide), 170.4 (2 *C*OCH$_3$ ester), 169.4, 169.8, (2 *C*OCH$_3$ ester), 160.3 (=*C*-CH$_3$), 136.0-126.9 (6 C, Ar), 108.7 (=*C*-CO), 73.5 (C-5'),72.7 (C-3'), 70.2 (C-2'), 68.2 (C-4'), 61.5 (C-6'), 27.4 (CO*C*H$_3$ ketone), 20.5 (4 C, 4 CO*C*H$_3$ ester), and 17.0 (=C-*C*H$_3$); FABMS *m/z* 605 [M+Na]$^+$. HRFABMS Calcd for $C_{26}H_{32}ClN_2O_{11}$: 583.1695. Found: 583.1684.

5- Acetyl- 1- (2,4 - dichlorophenyl)- 6 - methyl -3- (2,3,4,6 -tetra-*O* -acetyl- β-glucopyranosyl)-2,4-dithioxotetrahydropyrimidine (22), and 2-acetyl-3-(2,4-dichloroanilino)-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-buteneamide (26). From thioamide **14**; *t* = 50 min; preparative TLC (8:1 toluene:acetone) of the residue yielded **22** (21 %) and **26** (28 %) as amorphous solids.

Compound **22** was a ~1:1 mixture of conformers (**a** and **b**) which had IR ν_{max}: 2951, 2861, 1751, 1584, 1373, 1225, and 1040 cm^{-1}; ^{1}H NMR[33] (500 MHz, $CDCl_3$): δ 7.57-7.17 (m, 6 H, Ar**a**, **b**), 5.30 (t, 2 H, $J_{2',3'}$=$J_{3',4'}$= 9.3 Hz, H-3'**a**, **b**), 5.23 5.22 (each t, each 1 H, H-2'**a**, **b**), 5.07 (t, 2 H, $J_{4',5'}$= 9.3 Hz, H-4'**a**, **b**), 4.25-4.16 (m, 4 H, H-6'a, 6'b**a**, **b**), 3.90 (m, 2 H, H-5'**a**, **b**), 2.40 (s, 3 H, COCH$_3$**b** ketone), 2.38 (s, 3 H, COCH$_3$**a** ketone), 2.15-2.01 (m, 24 H, 8 COCH$_3$ **a**, **b** ester), and 1.78 (s, 6 H, =C-CH$_3$**a**, **b**); ^{13}C NMR[33] (125.7 MHz, $CDCl_3$): δ 201.0, 200.7 (*C*OCH$_3$**a**, **b** ketone), 170.7, 170.1, 169.4, 169.2 (each 2 C, 8 *C*OCH$_3$**a**, **b** ester), 142.5, 142.4 (=*C*-CH$_3$**a**, **b**), 136.4-128.8 (12 C, Ar**a**, **b**), 124.7, 124.6 (=*C*-CO**a**, **b**), 74.1 (2 C, C-5'**a**, **b**), 72.9 (2 C, C-3'**a**, **b**), 71.5 (2 C, C-2'**a**, **b**), 68.5 (2 C, C-4'**a**, **b**), 62.1 (2 C, C-6'**a**, **b**), 31.3, 31.2 (CO*C*H$_3$ ketone **a**, **b**), 20.9 (2 C, 4 CO*C*H$_3$ ester **a**, **b**), 20.5 (6 C, 6 CO*C*H$_3$ ester **a**, **b**), and 20.0 (2 C, =C-*C*H$_3$**a**, **b**); FABMS *m/z* 697 [M+Na]$^+$. HRFABMS Calcd for $C_{27}H_{28}Cl_2N_2O_{10}S_2Cs$: 806.9617. Found: 806.9616.

Compound **26** had $[\alpha]_D^{19}$≈ -0.0° (*c* 0.4); IR ν_{max}: 3368, 2957, 2861, 1753, 1593, 1371, 1256, and 1032 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49-7.11 (m, 3 H, Ar), 5.34 (t, 1 H, $J_{2',3'}$=$J_{3',4'}$= 9.7 Hz, H-3'), 5.08 (t, 1 H, $J_{4',5'}$= 9.7 Hz, H-4'), 4.99 (t, 1 H, H-2'), 4.33 (dd, 1 H, $J_{5',6'a}$= 4.6 Hz, $J_{6'a,6'b}$= 12.4 Hz, H-6'a), 4.08 (dd, 1 H, $J_{5',6'b}$= 2.2 Hz, H-

6'b), 3.86 (ddd, 1 H, H-5'), 2.17 (s, 3 H, $COCH_3$ ketone), 2.05, 2.03 (each s, each 6 H, 4 $COCH_3$ ester), and 1.91 (s, 3 H, =C-CH_3); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 193.6 ($COCH_3$ ketone), 170.4, 170.1, 169.8, 169.4 (4 $COCH_3$ ester), 169.3 (CO amide), 160.1 (=C-CH_3), 133.9-127.6 (6 C, Ar), 109.4 (=C-CO), 73.5 (C-5'), 72.7 (C-3'), 70.2 (C-2'), 68.2 (C-4'), 61.5 (C-6'), 27.4 ($COCH_3$ ketone), 20.6 ($COCH_3$ ester), 20.5 (3 C, 3 $COCH_3$ ester), and 16.9 (=C-CH_3); FABMS *m/z* 639 $[M+Na]^+$. HRFABMS Calcd for $C_{26}H_{30}Cl_2N_2O_{11}SCs$: 749.0304. Found: 749.0281.

When the reactions of **10**, **11**, **13**, **14** with thiophosgene were carried out at 0 °C, the same results were obtained.

ACKNOWLEDGMENTS

We thank the Dirección General de Investigación Científica y Técnica of Spain for financial support (grant number PB 94/1440-C02-01), the Fundación Cámara of the University of Seville for a grant to J.L. Molina, and the Ministerio de Educación y Cultura of Spain for a grant to M. Angulo.

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30. We have found in the literature a preparation of this compound [see S. Coffey, J. K. Thomson, and F. J. Wilson, *J. Chem. Soc.*, 856 (1936)] but the structure is only based in the elemental analysis of nitrogen.
31. **A** and **B** are the major and the minor diastereomers respectively.
32. Assignments may be interchanged.
33. **a** and **b** are conformers.