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EDGE ARTICLE

A concise, efficient synthesis of sugar-based benzothiazoles through chemoselective intramolecular C–S coupling†

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Sugar-based benzothiazoles are a new class of molecules promising for many biological applications. Here, we have synthesized a wide range of sugar-based benzothiazoles from readily accessible glycosyl thioureas by chemoselective, palladium-catalyzed C–S coupling reactions. Corroborated by theoretical calculations, a mechanistic investigation indicates that the coordination to the palladium by a pivaloyl carbonyl group and the presence of intramolecular hydrogen bonding play important roles in the efficiency and chemoselectivity of reaction. These fluorescent glycoconjugates can be observed to readily enter mammalian tumor cells and exhibit potential *in vitro* antitumor activity.

Introduction

Benzothiazoles are an important class of heterocycles which have been identified in a broad range of biologically important molecules.[1,2] Representatives of this class of compounds exhibit promising activity against diabetes,[3] Alzheimer's diseases,[4] and different cancers.[5] Similarly, organic compounds containing glycoconjugates have also generated significant attention for their essential roles in many physiological processes and for their potential applications as tumor markers, receptors and antibodies.[6] We herein report the synthesis of a series of compounds that contain a combination of benzothiazole and glycosyl moieties with potentially synergistic therapeutic properties.

Recent advances in carbon–heteroatom bond formation[7] have enabled several methods for the preparation of benzothiazoles and their analogues. One representative method for the preparation of benzothiazoles involves metal-catalyzed cyclization of *ortho*-halo substituted aromatic compounds.[7g] Alternatively, benzothiazoles can be prepared through either a C–H functionalization/intramolecular C–S bond-formation process or decarboxylative cross-coupling of 2-nitrobenzoic acid with benzyl thiol.[7k,7n] Despite the promise of these methods, there are significant limitations typically associated with the need of *ortho*-halo-substituted precursors and multi-step procedures under stringent reaction conditions.[7m,7t] In particular, the synthesis of sugar-based benzothiazoles is a substantially daunting task because of the added functionality and stereochemical complexity of carbohydrates.

Continuing our longstanding interest in developing novel C–S bond-forming reactions for the efficient construction of heterocyclic frameworks,[7n,8] we envisioned a new, concise route to sugar-based benzothiazoles as shown in Fig. 1. In this approach, sugar-substituted *N*-arylthiourea substrates (**4a–o**) were subjected to a palladium(II)-catalyzed C–H activation followed by an intramolecular cyclization process to afford the corresponding benzothiazoles (**5a–o**). To the best of our knowledge, the reaction described herein is the first example of a tandem C–S coupling reaction involving sugar moieties from easily accessible substrates under relatively mild reaction conditions.

Results and discussion

Preparation of glycosyl benzothiazoles *via* thiourea precursors

Glycosyl thiourea precursors **4a–o** could be readily prepared in three steps from commercially available starting materials. Bromination of pivaloylated sugar substrate (**1**) by using 33% hydrobromic acid in acetic acid gave β-glycosyl bromide (**2**).[6g] A subsequent step involving a phase-transfer reaction in the presence of potassium thiocyanate and tetrabutylammonium bromide afforded *N*-glycoside (**3**). Treatment of the *N*-glycoside **3** with substituted phenylamines in acetonitrile at room

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† Electronic supplementary information (ESI) available: Synthetic, analytical, crystallographic, computational and biological assay details. See DOI: 10.1039/c2sc20248d

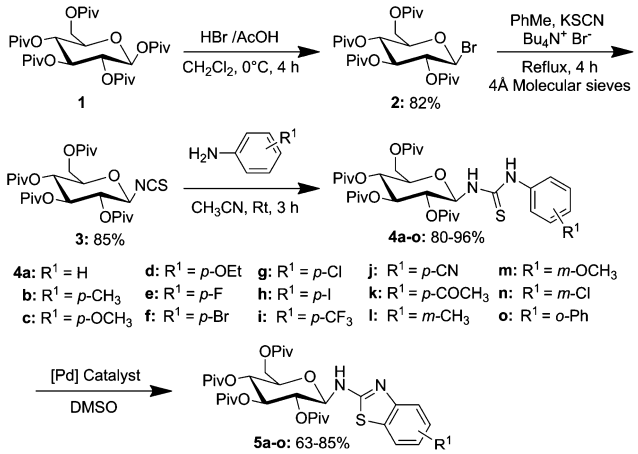


Fig. 1 Synthetic strategy to access sugar-based benzothiazoles. Bromination of pivaloylated sugar substrate (**1**) gives gycosyl bromide (**2**). A phase-transfer reaction in the presence of potassium thiocyanate and tetrabutylammonium bromide as well as molecular sieves (4 Å) in toluene leads to *N*-glycoside (**3**). Cross-coupling of compound **3** with substituted phenylamines at room temperature results in sugar-substituted *N*-arylthioureas (**4a–o**). Palladium-catalyzed intramolecular cyclization of **4a–o** enables access to glycosyl benzothiazoles (**5a–o**). Piv = *t*-butyl carbonyl.

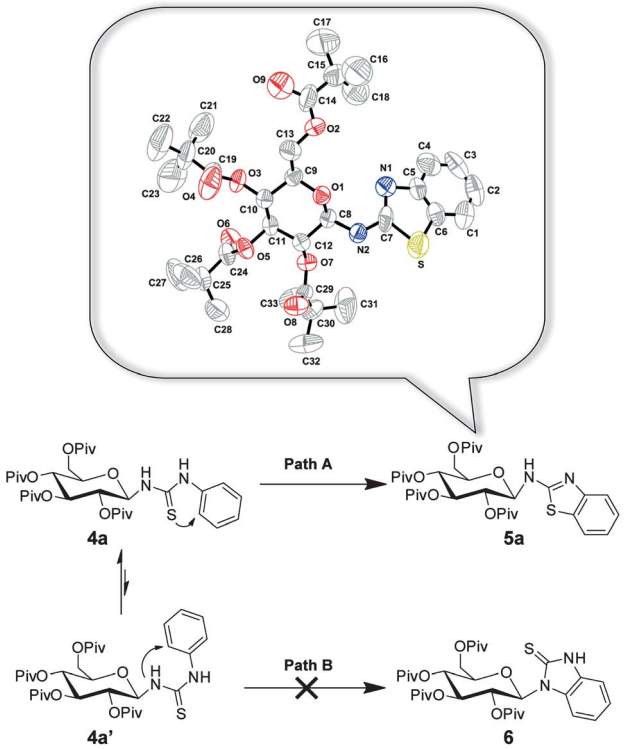
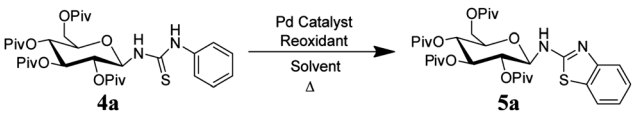


Fig. 2 Regiochemistry of palladium-catalyzed intramolecular cyclization of sugar-substituted *N*-arylthiourea. (Inset) ORTEP diagram of **5a** showing atom-labelling scheme. Hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

temperature led to the formation of sugar-substituted *N*-arylthioureas **4a–o** in high yield. Note that only the β-anomer was observed in each step.

We next examined the conversion of *N*-arylthiourea **4a** to sugar-based benzothiazole (**5a**). After careful screening of palladium and copper catalysts, solvents and reaction temperatures, we found that the reaction with 10 mol% $Pd(OAc)_2$ in dimethyl sulfoxide (DMSO) under an oxygen atmosphere[9] led to the desired product **5a** in 38% yield after 12 h at 60 °C (Table 1, entry 1). No C–S coupling product was obtained in the presence of CuI (50 mol%) or AgOAc (20 mol%) as reoxidants after 12 h at

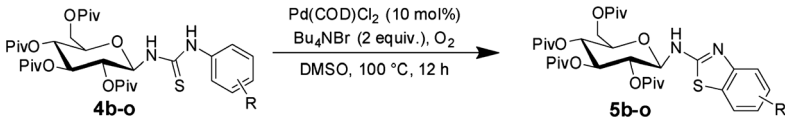
Table 1 Screening of reaction conditions for the synthesis of sugar-based benzothiazoles[a]



Entry[a]	[Pd] Source (mol%)	Reoxidant (mol%)	Solvent	*T*/°C	Yield (%)[b]
1	$Pd(OAc)_2$ (10)	O_2	DMSO	60	38[c]
2	$Pd(OAc)_2$ (20)	O_2	DMSO	60	63[c]
3	$Pd(OAc)_2$ (10)	$Cu(OAc)_2$ (20)	DMSO	60	48[c]
4	$Pd(OAc)_2$ (10)	$PhI(OAc)_2$ (100)	PhMe	60	40
5	$Pd(OAc)_2$ (10)	PPh_3 (20)	PhMe	60	35
6	$Pd(PPh_3)_4$ (10)	MnO_2 (10)	CH_3CN	60	36
7	$Pd(OAc)_2$ (10)	CuI(50)	DMSO	100	0[c]
8	$Pd(OAc)_2$ (10)	AgOAc (20)	DMSO	100	0
9	$Pd(OAc)_2$ (10)	$Cu(OTf)_2$ (20)	DMSO	100	53
10	$PdCl_2$ (10)	O_2	DMSO	100	75
11	$Pd(COD)Cl_2$ (10)	O_2	DMSO	100	85[c]
12	$Pd(COD)Cl_2$ (10)	Air	DMSO	100	80[c]
13	$Pd(COD)Cl_2$ (5)	O_2	DMSO	100	60[c]
14	$Pd(COD)Cl_2$ (10)	O_2	PhMe	100	72[c]
15	$Pd(COD)Cl_2$ (10)	O_2	DMF	100	76[c]
16	$Pd(COD)Cl_2$ (10)	O_2	CH_3CN	100	67[c]

[a] All the reactions were carried out in presence of glycosyl thiourea **4a** (0.14 mmol), a solvent (3 mL), and a palladium catalyst. [b] Conversion determined by ^1H NMR spectroscopy. [c] Yield obtained through use of Bu_4NBr (2 equivalents) as an additive.

Table 2 Effect of the aryl substitutions on sugar-based benzothiazole formation[a]



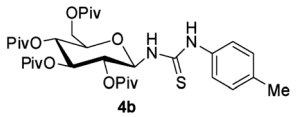
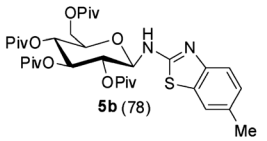
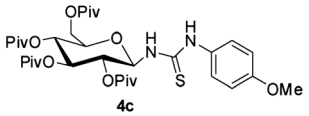
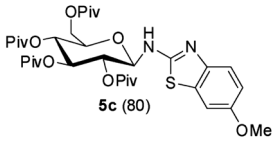
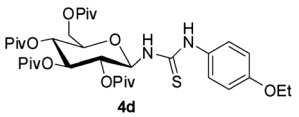
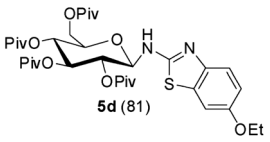
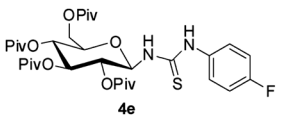
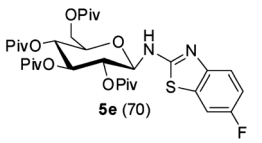
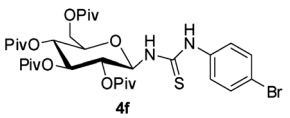
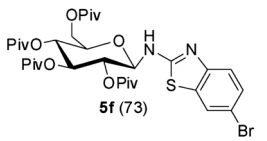
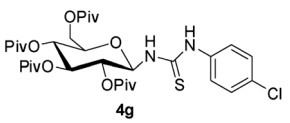
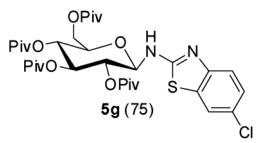
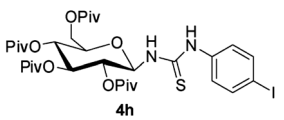
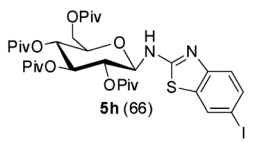
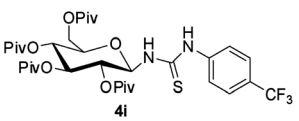
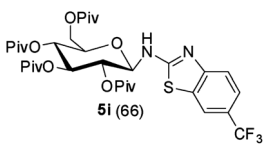
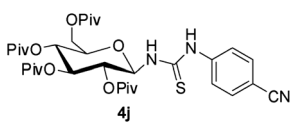
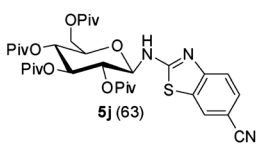
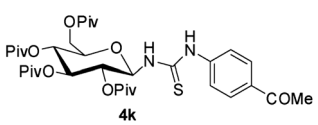
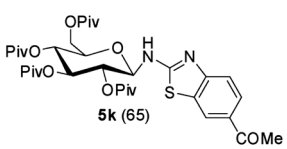
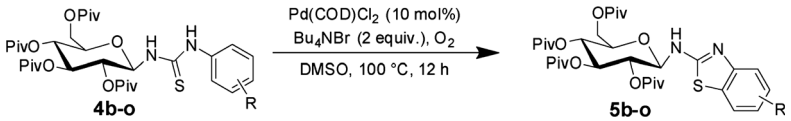
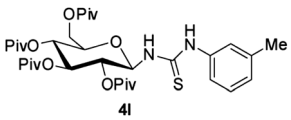
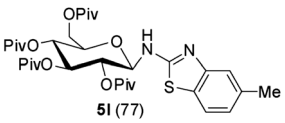
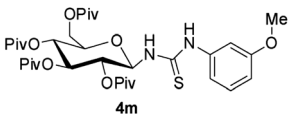
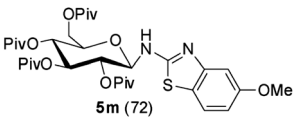
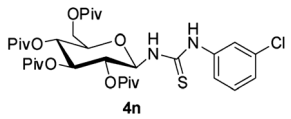
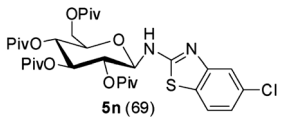
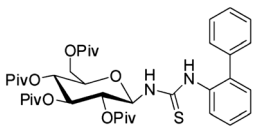
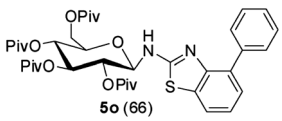
Entry	Substrate **4**	Product **5** (Yield%)[b]
1	 **4b**	 **5b** (78)
2	 **4c**	 **5c** (80)
3	 **4d**	 **5d** (81)
4	 **4e**	 **5e** (70)
5	 **4f**	 **5f** (73)
6	 **4g**	 **5g** (75)
7	 **4h**	 **5h** (66)
8	 **4i**	 **5i** (66)
9	 **4j**	 **5j** (63)
10	 **4k**	 **5k** (65)

Table 2 (*Contd.*)



Entry	Substrate **4**	Product **5** (Yield%)[b]
11	 **4l**	 **5l** (77)
12	 **4m**	 **5m** (72)
13	 **4n**	 **5n** (69)
14	 **4o**	 **5o** (66)

[a] All the reactions were carried out with glycosyl thiourea **4b–o** (0.14 mmol each) in DMSO (3 mL) in the presence of Pd catalyst and Bu_4NBr additive. [b] Yields of isolated products are the average of at least two experiments.

100 °C (Table 1, entries 7 and 8). Notably, the combination of $Pd(OAc)_2$ (10 mol%) and $Cu(OAc)_2$ (20 mol%) gave an improved yield of **5a** of 48% (Table 1, entry 3). The alternative combination of $Pd(OAc)_2$ (10 mol%) and one equivalent of $PhI(OAc)_2$ under an oxygen atmosphere led to the formation of **5a** in 40% yield (Table 1, entry 4). The utilization of MnO_2 (10 mol%) as the reoxidant, previously employed by Batey *et al.*,[10] did not give an improved yield (Table 1, entry 6). However, the use of $Cu(OTf)_2$ in this capacity resulted in the desired product **5a** in 53% yield (Table 1, entry 9). Alternative palladium catalysts such as $PdCl_2$ and $Pd(COD)Cl_2$ were more effective at 100 °C under an oxygen atmosphere, providing **5a** in 75% and 85% yield, respectively (Table 1, entries 10 and 11). Further variation in solvents did not lead to improvement in reaction yield (Table 1, entries 14–16).

The chemospecific formation of a C–S bond rather than the alternative C–N bond, as confirmed by single-crystal X-ray crystallography (Table S1, ESI†) of the as-synthesized benzothiazole **5a**, is striking considering that an intramolecular amination to give glycosyl benzimidazole (**6**) is quite feasible (Fig. 2).

Scope of chemoselective intramolecular C–S cross-coupling of glycosyl thioureas 4b–o

In a further set of experiments, we investigated the scope and generality of the method for a range of sugar-substituted *N*-arylthioureas in the presence of $Pd(COD)Cl_2$ as catalyst (10 mol%) and tetrabutylammonium bromide (2 equivalents) under an oxygen atmosphere. Substrates (**4b–k**) containing either an electron donating (Table 2, entries 1–3) or withdrawing group (Table 2, entries 4–7) at the 4-position showed similar reactivity to the parent **4a**, although yields were slightly lower for strongly electron withdrawing groups (Table 2, entries 8–10). Substrates **4l–n** with the substituent at the 3-position reacted regiospecifically at the sterically less-hindered 6-position. In all cases, no regio- or stereoisomers were observed during the reaction (Table 2, entries 11–13). In addition, we found that the *ortho*-substitution of the thiourea with a bulky phenyl group at the 2-position had no significant effect on the reaction yield (Table 2, entry 14).

Interestingly, palladium-catalyzed coupling reactions involving non-carbohydrate thiourea derivatives (**7–10**) did not proceed to give the benzothiazole products under standard reaction conditions (Fig. 3). More surprisingly, a non-pivaloylated glycosyl thiourea substrate (**11**) failed to undergo the C–S coupling. By comparison, the reaction of a different pivaloylated glycosyl thiourea (**12**) proceeded to afford the coupling product in high yield (80%). Taken together with our data obtained from previous metal-catalyzed asymmetric reactions involving pivaloylated sugars,[11] these results suggest that the pivaloyl carbonyl group might play a significant role in mediating the intramolecular C–S coupling reactions.[12]

Mechanistic studies of C–S cross-couplings

A plausible mechanism for the Pd(II)-catalyzed C–S coupling is proposed in Fig. 4 on the basis of our experimental observations

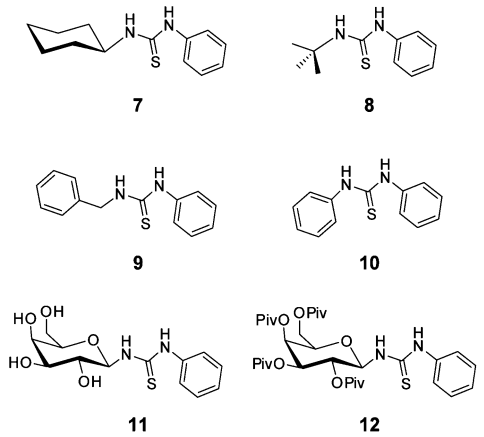


Fig. 3 Reactivity screening of various thiourea derivatives.

and density functional theory calculations. We suggest that the Pd metal coordinates to both the S atom of the thiourea and O atom of one of the neighboring pivaloyl carbonyl groups, resulting in the formation of a Pd(II) arene complex **A**. Transient intermediate **A** subsequently undergoes cyclopalladation to afford intermediate **C** *via* stabilized cation **B**. Intramolecular hydrogen bonding between the 2-*O*-pivaloyl carbonyl group and the amide N–H group of the thiourea moiety assists in stabilizing these conformations. Cyclopalladated intermediate **C** then undergoes reductive elimination and the resulting Pd(0) species is reoxidized to regenerate the Pd(II) catalyst by molecular oxygen or another oxidant to complete the catalytic cycle.[13] The pivaloyl carbonyl groups serve as a ligand donor to the Pd center and as a hydrogen bond acceptor of the thiourea's N–H group to create a coordination environment where the reactive functionalities are brought into proximity for the coupling reaction to occur. The selectivity of the C–S bond formation over the C–N bond is likely a result of this lower energy reaction pathway *via* intermediates

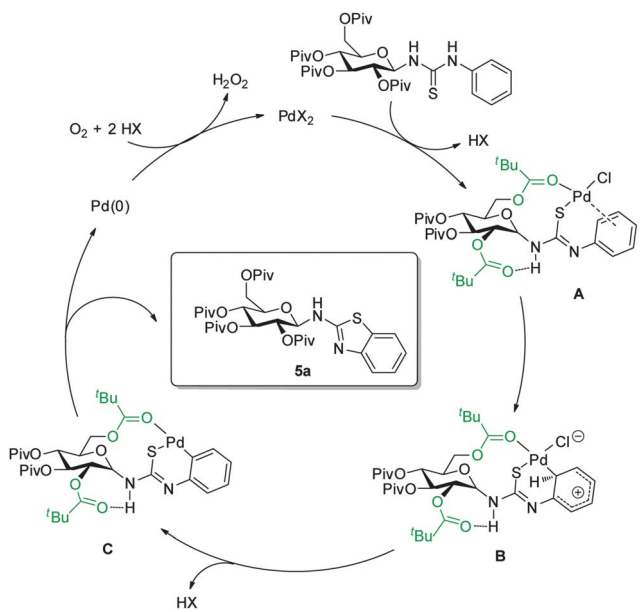


Fig. 4 Proposed catalytic cycle for the synthesis of **5a**.

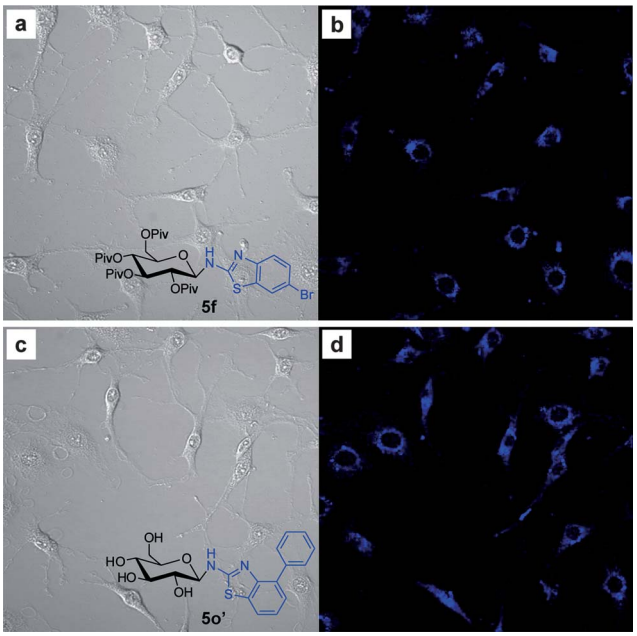


Fig. 5 Evaluation of cell staining of the cross-coupled products by fluorescence microscopy. (**a** and **c**) Representative normal light contrast images of C6 glioma cells loaded with **5f** and **5o′** (80 μM each) in Hank's Balanced Salts Solution for 1 h at 37 °C. (**b** and **d**) The corresponding fluorescence images of the cells loaded with **5f** and **5o′**, respectively.

B and **C** in the presence of intramolecular hydrogen bonds (See ESI†).

Cytotoxicity analysis and cell staining/imaging study of the cross-coupled products

We next assessed the cytostatic reactivity of our newly synthesized sugar-based benzothiazoles and their de-pivaloylated products towards a human myeloid leukemia cell line (HL-60 cells) and three cell lines derived from a gastric carcinoma (BGC-823 cells), a liver carcinoma (Bel-7402 cells), and an oral carcinoma (KB cells). This investigation revealed that sugar-based benzothiazole **5a** is a potent cytotoxic agent against these cell lines. Compounds **5a′–o′**, prepared by de-pivaloylation of the corresponding sugar-based benzothiazoles,[6a] exhibited increased cytotoxic potency (Table S2, ESI†). When used for cell staining (C6 glioma cancer cell), fluorescent benzothiazole substrates **5f** and **5o′** exhibited potent growth inhibition. The retention of fluorescence signals within these cells was not compromised even after 1 h of incubation at 37 °C (Fig. 5).

Conclusions

In conclusion, we have developed a rather general, catalytic method for the chemoselective synthesis of various substituted sugar-based benzothiazoles from readily accessible glycosyl thiourea precursors. Our mechanistic investigation suggests that the unusual intramolecular C–S coupling reaction stems from the metal–pivaloyl carbonyl coordination and may be assisted by the presence of intramolecular hydrogen bonding. We have also demonstrated antitumor activity and imaging in living mammalian cells by these fluorescent glycoconjugates. Further

studies to elucidate the reaction mechanism and explore the biological activity of this new class of sugar-based benzothiazoles are currently underway in our laboratories.

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