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Stereoselective Palladium-Catalyzed Alkenylation and Alkynylation of Thioglycosides

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Abstract: An efficient and unprecedented palladium-catalyzed S-glycosylation reaction of a range of alkenyl and alkynyl halides by using thiosugars as nucleophile partners has been established. With palladium diacetate in combination with Xantphos as the catalytic system, a variety of β-alkenylthioglycosides as well as β-alkynylthioglycosides can be prepared in good to excellent yields. The efficiency of this general protocol was well-demonstrated by the formal synthesis of a leaf-closure β-glucosidase inhibitor.

Keywords: β-alkenylthioglycosides; β-alkynylthioglycosides; palladium catalysis; thioglycosides

Introduction

Replacement of the anomeric oxygen in oligosaccharides and other glycoconjugates with a sulfur atom leads to the thioglycoside family, an important class of synthetic carbohydrates.[1] Alkenylthioglycosides are a subfamiliy of thioglycoconjugates, whose derivatives show promising biological activities, including leaf-closure and irreversible glycosidase inhibitors,[2] as well as precursors in melanin research biopolymers[3] (Figure 1).

Furthermore, alkenylthioglycosides can be valuable precursors[4] to alkylthioglycosides, themselves of significant biological importance.[5,6] Over the past decade, alkenylthioglycosides have received very little attention, and therefore their accessibility, an equally if not more important issue than applications, remains a challenging problem. To the best of our knowledge, only one example has been reported for the synthesis of alkenylthioglycoside *via* reaction of an electrophilic acetohaloglycoside precursor with a thioenol ether under basic conditions.[2a] Alternative routes consist of the use of selenium-containing thioglycosides as an

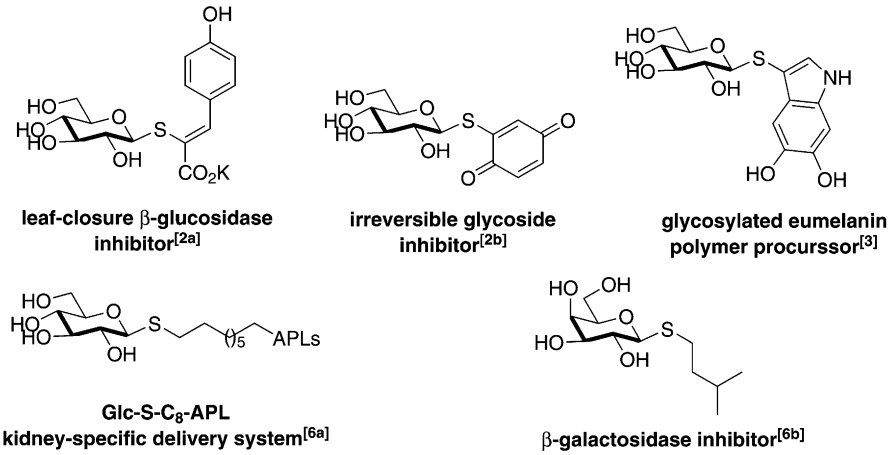


Figure 1. Chemical structures of some bioactive alkenyl or alkyl thioglycoside derivatives.

in situ generating free radical glycosidation reagent,[3] or by nucleophilic addition of the acetylated 1-thioglucose to α,β-unsaturated carbonyl compounds followed by oxidation.[2b] All these multi-step procedures however, are often moderate to low yielding, and the variety of substrates is cruelly limited. The restricted scope of existing protocols has prohibited a greater synthetic utility of alkenylthioglycosides. Therefore, the search for new selective and simple procedures presents an interesting challenge.

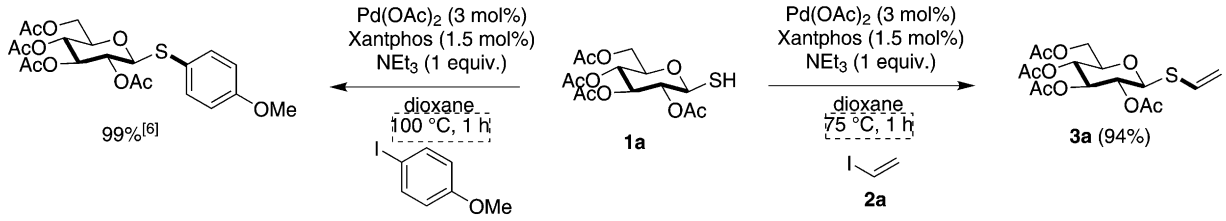
During our studies on metal-catalyzed C-heteroatom bond forming reactions,[7] we have disclosed a highly efficient and selective method for the thioglycosylation of functionalized (hetero)aryl halides by using thioglycosides as nucleophile partners in the presence of $Pd(OAc)_2$/Xantphos as the catalyst system.[8] Herein, this versatile catalyst has been extended to C–S[9] coupling of thioglycosides with alkenyl and alkynyl halides where selectivities, broad tolerance to functional groups as well as practical application were demonstrated.

Results and Discussion

Given our success with the synthesis of (hetero)arylthioglycosides, we first applied our optimal Pd-catalyzed C–S coupling conditions [$Pd(OAc)_2$ (3 mol%), Xantphos (1.5 mol%), NEt_3 (1 equiv.) in dioxane at 100 °C][10] to the coupling of β-thioglucopyranose **1a** with vinyl iodide **2a** (Scheme 1). We were delighted to find that these conditions were efficient and gave the corresponding vinylthioglycoside **3a** in an excellent 94% yield without any anomerization. Remarkably, decreasing the temperature until 75 °C was sufficient to achieve complete conversion, providing **3a** in a similar yield (94%).

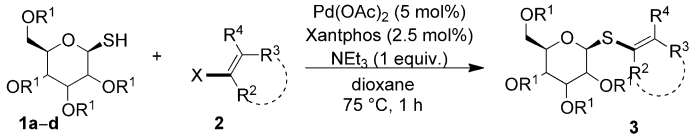
Prompted by these results, we subsequently investigated the synthesis of alkenylthioglycosides **3** (Table 1) by coupling various thioglycosides **1a–g** (Figure 2) with a variety of (*E*)- and (*Z*)-functionalized alkenyl halides **2a–p** (Table 1). Compounds **3** that feature alkenyl substituents at the sulfur atom of the sugar moiety have not previously been reported, perhaps due to the difficulty in their preparation by standard procedures.[2a]

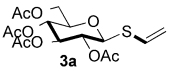
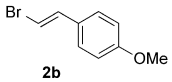
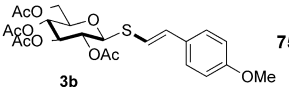
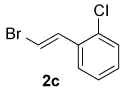
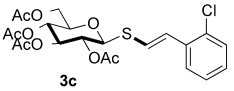
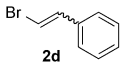
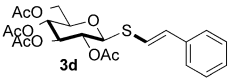
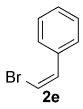
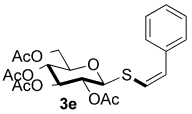
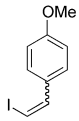
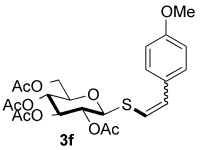
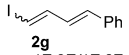
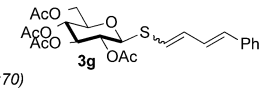
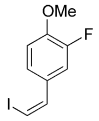
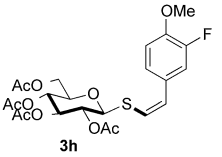
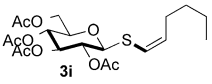
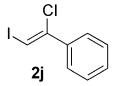
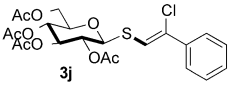
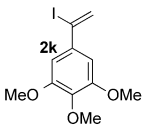
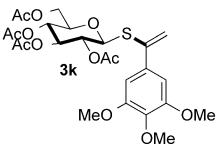
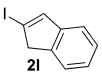
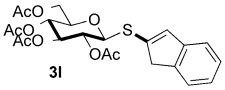
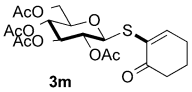
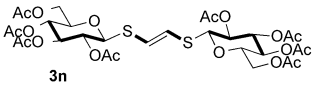
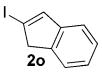
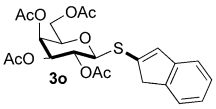
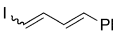
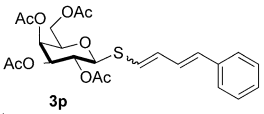
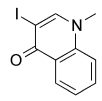
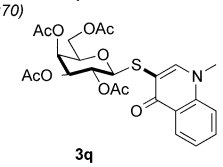
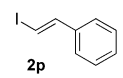
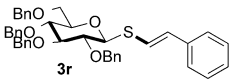
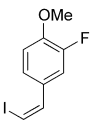
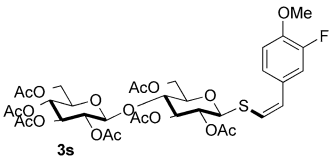
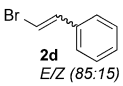
As summarized in Table 1, (*E*)-styryl bromides including **2b** and **2c** gave the corresponding alkenylthioglycoside derivatives **3b** and **3c** in good yields (entries 2 and 3). Carrying out the reaction with a diastereomeric mixture of β-bromostyrene (*E*/*Z* 85:15), the coupling proceeded stereoselectively, providing the desired product **3d** as a single *E*-isomer. This result suggested that either Z-isomer does not react or isomerizes into *E*-isomer. To verify this hypothesis, the coupling of **1a** with *Z*-bromostyrene **2e** was further tested. Under the optimized conditions, no reaction occurred and compound **3e** has never been detected, suggesting that with bromostyrene partners, the geometry of the double bond plays a critical role in the outcome of this coupling reaction. The couplings with alkenyl iodides were further examined. Carrying out the reaction with a diastereomeric mixture of β-iodostyrene **2f** (*E*/*Z* 25:75) or **2g** (1*E*,3*E*/1*E*,3*Z* 30:70), the coupling proceeded stereoselectively, providing in an excellent yields the desired products **3f** and **3g** in the same stereomeric *E*/*Z* ratio (entries 6 and 7). These results suggested that, contrary to β-bromostyrenes, both *E*- and *Z*-iodostyrene isomers displayed similar reactivity. More interestingly, pure *Z*-iodostyrene such as **2h** is also a suitable coupling partner with thioglycoside **1a** furnishing efficiently and stereoselectively β-thioglycosidated *Z*-alkene **3h** without any thermal isomerization, clearly demonstrating the mild nature of this cross-coupling reaction (entry 8). Noteworthy, *Z*-alkene reactants with long alkyl chains displayed excellent reactivity, as iodide **2i** gave β-thioglycosyl alkene **3i** in 80% yield (entry 9). These molecules are still of interest and may be used as scaffolds to build compounds such as Glc-S-C_8-APL (Figure 1). Perhaps the most striking feature of the reaction is its chemoselectivity. Halogen substituents (entry 10) were tolerated on the styryl double bond with the reaction occurring efficiently (82% yield) and selectively on the C–I bond. This chlorinated compound **3j** of particular interest, as it contains reactive handles and, as such, could be used as a foundation for the synthesis of more complex molecules.[11] Besides β-styryl halides, α-styryl halides such as α-iodostyrene **2k** also worked well, affording the corresponding alkenylthioglycoside **3k** in a good yield (entry 11). Cyclic alkenyl halides such as **2l** and **2m** gave the corresponding thioglycosylated **3l** and **3m** in 95% and 68% yields, respectively



Scheme 1.

Table 1. Palladium-catalyzed coupling of β-thioglycosides **1a–g** with alkenyl halides **2**.[a]



Entry	RX	Product	Yield [%][b]
1	 **2a**	 **3a**	**94**
2	 **2b**	 **3b**	**75**
3	 **2c**	 **3c**	**65**
4	 **2d** *E/Z (85:15)*	 **3d**	**73**
5	 **2e**	 **3e**	**0**
6	 **2f** *E/Z (25:75)*	 **3f**	**97** *E/Z (25:75)*
7	 **2g** *1E,3E/1E,3Z (30:70)*	 **3g**	**84** *1E,3E/1E,3Z (30:70)*
8	 **2h**	 **3h**	**90**
9	 **2i**	 **3i**	**80**
10	 **2j**	 **3j**	**82**
11	 **2k**	 **3k**	**76**
12	 **2l**	 **3l**	**95**
13	 **2m**	 **3m**	**68**
14	 **2n**	 **3n**	**65**
15	 **2o**	 **3o**	**95**
16	 **2g** *1E,3E/1E,3Z (30:70)*	 **3p**	**89** *1E,3E/1E,3Z (30:70)*
17	 **2o**	 **3q**	**76**
18	 **2p**	 **3r**	**73**
19	 **2h**	 **3s**	**70**
20	 **2d** *E/Z (85:15)*	**3t**	**68**
21	**2k**	**3u**	**65**
22	**2k**	**3v**	**60**

[a] Reactions of **1a** (0.375 mmol) with vinyl halides (0.25 mmol) were performed in a sealed Schlenk tube at 75 °C for 1 h in dioxane (1.5 mL) in the presence of $Pd(OAc)_2$ (5 mol%), Xantphos (2.5 mol%), and Et_3N (0.25 mmol).

[b] Yield of isolated product.

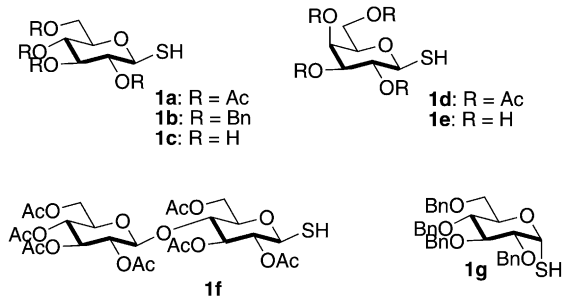


Figure 2. Thioglycosides **1a–g** used in this study.

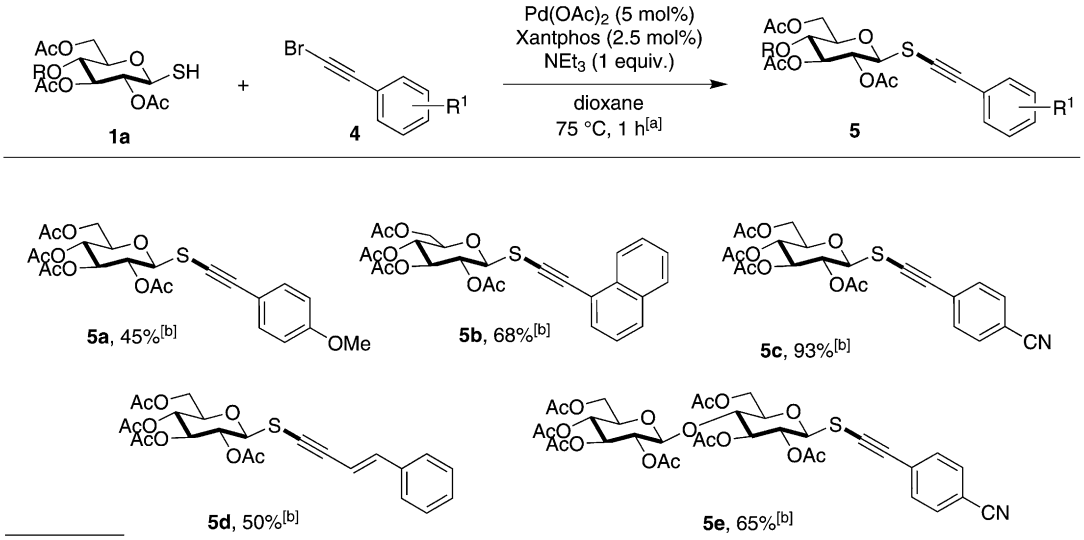
(entries 12 and 13). Performing the C–S glycosidic bond forming reaction with (*E*)-1,2-diiodoethene **2n** (ratio **1a**:**2n** = 2:1) provides the bis-β-thioglycoside **3n** in 65% yield (entry 14).

In a further set of experiments, we investigated the scope and generality of the method for a range of mono- and dithiosaccharides **1b–f** (Figure 2). As depicted in Table 1 (entries 15–22), coupling reactions proceeded cleanly in high yields without any significant side reaction such as anomerization of the resulting alkenylthioglycosides. The reaction seems to be general with respect to the sugar configuration as per-*O*-acetylated 1-thio-β-D-galactose **1d** gave the corresponding products **3o–q** in good to excellent yields (76–95%, entries 15–17). Importantly, there is no significant impact of protecting groups on the reactivity of the thiosugar derivatives since benzyl-protected carbohydrate **1b** reacts similarly to *O*-acetylated derivative **1a** furnishing the coupling product **3r** in a good 73% yield (entry 18). It is noteworthy that the reaction is not effective with perbenzylated α-D-thioglucopyranose **1g**. The coupling procedure is not limited only to monothiosaccharides but also works successfully with peracetylated β-D-disaccharide **1f** derived from D-cellobiose octaacetate. The exclusive 1,2-*trans* β-thioglycosides **3s** and **3t** were obtained in 70% and 68% yields, respectively, and the stereochemistry of the 1-4′ glycosidic bond remained intact (entries 19 and 20). More interestingly, coupling of unprotected β-D-thioglucose **1c** and β-D-thiogalactose **1e** with α-iodostyrene **2k** under this procedure furnished exclusively β-anomers **3u** and **3v** in good yields without any side product resulting from *O*-arylation under Pd catalysis.[12] A literature search did not uncover any metal-catalyzed coupling of free thioglycoside nucleophiles with C(sp^2) alkenyl halides.

In addition to the alkenyl halides evaluated above, substituted alkynyl bromides **4** were examined as aglycone coupling partners in the thioglycosylation procedure.

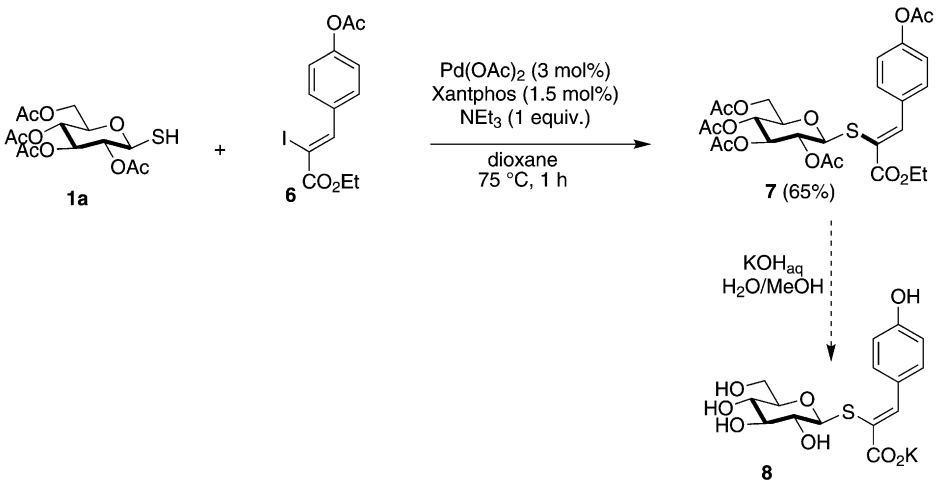
Alkynylated thioglycoside products **5a–e** were obtained diastereoselectively in good to excellent yields (Scheme 2) regardless the nature of the substituent group on the aromatic ring of the alkynyl bromide.

Finally, the synthetic potential of this protocol was well-illustrated by the formal synthesis of a leaf-closure β- glucosidase inhibitor.[2a] The key step was the coupling of 2-iodoacrylate **6** with peracetylated β-D-thioglucopyranose **1a** under optimized conditions to give acetylated thioglycoside **7** in a good 65% yield with exclusive β-selectivity (Scheme 3). Compound **7** can be converted to the leaf-closure β-glucosidase inhibitor **8** by a known procedure.[2a]



[a] Reactions of **1a** (0.375 mmol) with alkynyl halides **4** (0.25 mmol) were performed in a sealed Schlenk tube at 75 °C for 1 h in dioxane (1.5 mL) in the presence of $Pd(OAc)_2$ (5 mol%), Xantphos (2.5 mol%), and Et_3N (0.25 mmol).
[b] Yield of isolated product.

Scheme 2. Palladium-catalyzed coupling of peracetylated β-thioglucosides **1a–e** with alkynyl halides.



Scheme 3. Formal synthesis of leaf-movement inhibitor (**8**).

Conclusions

In summary, we have developed the first method to prepare alkenylated and alkynylated thioglycoside derivatives *via* Pd-catalyzed glycosylation of functionalized alkenyl and alkynyl halides. To the best of our knowledge the C(sp^2)–S and C(sp)–S glycosidic bonds were formed, for the first time, directly by using thioglycosides as a nucleophile partner in the presence of $Pd(OAc)_2$/Xantphos as the catalyst system. The reaction is highly diastereoselective, functional-group tolerant, step-economical, and proceeds stereoselectively in good to excellent yields with a variety of *Z*- and *E*-haloalkenes. We believe that this methodology will find broad applications in organic synthetic chemistry as well as in the combinatorial and pharmaceutical sciences.

Experimental Section

General Experimental Methods

The compounds were all identified by usual physical methods, i.e., ^{1}H NMR, ^{13}C NMR (J-MOD), IR, MS (ESI). ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ or DMSO-d_6 with a Bruker Avance-300. ^{1}H chemical shifts are reported in ppm from an internal standard TMS or of residual chloroform (7.27 ppm). The following abreviation are used: m (multiplet), s (singlet), bs (broad singlet), d (doublet), t (triplet) dd (doublet of doublet), td (triplet of doublet), q (quadruplet), qui (quintuplet), sex (sextuplet). ^{13}C chemical shifts are reported in ppm from the central peak of deuteriochloroform (77.14 ppm). IR spectra were measured on a Bruker Vector 22 spectrophotometer. MS were recorded on a Micromass spectrometer. Analytical TLC was performed on Merck precoated silica gel 60F plates. Merck silica gel 60 (0.015–0.040 mm) was used for column chromatography. Melting points were recorded on a Büchi B-450 apparatus and are uncorrected.

Palladium-Catalyzed Coupling of β-Thioglucose 1a with Alkenyl and Alkynyl Halides (2 and 4)

Typical procedure: A flame-dried resealable Schlenk tube was charged with $Pd(OAc)_2$ (3 mol%), Xantphos (1.5 mol%), thiosugar **1** (0.375 mmol), alkenyl or alkynyl halide **2** or **4** (0.25 mmol), and Et_3N (0.25 mmol). The Schlenk tube was capped with a rubber septum, evacuated and backfilled with argon; then, dioxane (1.5 mL) was added through the septum. The septum was replaced with a teflon screwcap. The Schlenk tube was sealed, and the mixture was stirred at 75 °C for 1 h. The resulting suspension was cooled to room temperature and filtered through celite eluting with ethyl acetate. The filtrate was concentrated and purification of the residue by silica gel column chromatography gave the desired products **3** or **5**.

Analytical Data for Alkenylthioglycosides 3

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-(vinylthio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3a): yield: 97 mg (94%); R_f = 0.25 (cyclohexane:AcOEt, 7:3); white-yellow solid; mp 95–97 °C; $[\alpha]_D^{24}$: −14.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.38 (dd, *J* = 16.8, 9.8 Hz, 1H), 5.40 (d, *J* = 5.2 Hz, 1H), 5.35 (d, *J* = 1.7 Hz, 1H), 5.20 (t, *J* = 9.3 Hz, 1H), 5.04 (td, *J* = 9.6, 3.3 Hz, 2H), 4.59 (d, *J* = 10.0 Hz, 1H), 4.21 (dd, *J* = 12.4, 5.0 Hz, 1H), 4.09 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.72 (ddd, *J* = 10.0, 4.9, 2.3 Hz, 1H), 2.03 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.59 (C=O), 170.13 (C=O), 169.37 (C=O), 169.20 (C=O), 127.36 (CH), 117.93 (CH_2), 83.26 (CH), 76.10 (CH), 73.86 (CH), 69.86 (CH), 68.22 (CH), 62.10 (CH_2), 20.74 (CH_3), 20.66 (CH_3), 20.60 ($2CH_3$); IR (neat): ν = 3452, 3394, 3148, 2170, 2144, 1756, 1738, 1590, 1433, 1366, 1247, 1206, 1092, 1030 cm^{-1}; HR-MS (ESI): *m/z* = 413.0874, calculated for $C_{16}H_{22}NaO_9S$: 413.0882.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-[(E)-4-methoxystyrylthio]tetrahydro-2H-pyran-3,4,5-triyl triacetate (3b): yield: 95 mg (75%); R_f = 0.57 (cyclohexane:AcOEt, 5:5); white-yellow solid; mp 141–143 °C; $[\alpha]_D^{24}$: −26.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 9.3 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 15.4 Hz, 1H), 6.57 (d, *J* = 15.4 Hz, 1H), 5.24 (dd, *J* = 10.3, 8.2 Hz, 1H), 5.10 (td,

J=9.6, 5.8 Hz, 2H), 4.60 (d, J=9.9 Hz, 1H), 4.25 (dd, J=12.4, 4.8 Hz, 1H), 4.16 (dd, J=12.4, 2.3 Hz, 1H), 3.80 (s, 3H), 3.76 (ddd, J=10.0, 4.9, 2.4 Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=170.75 (C=O), 170.29 (C=O), 169.49 (C=O), 169.35 (C=O), 159.76 (CH), 135.93 (C), 129.23 (2CH), 127.73 (CH), 115.11 (2CH), 114.24 (CH), 83.92 (CH), 76.22 (CH), 74.03 (CH), 70.03 (CH), 68.34 (CH), 62.21 (CH_2), 55.43 (CH_3), 20.81 (2CH_3), 20.68 (2CH_3); IR (neat): ν= 3459, 2245, 2015, 1755, 1739, 1606, 1511, 1467, 1366, 1251, 1209, 1175, 1129, 1090 cm^{-1}; HR-MS (ESI): m/z=519.1282, calculated for $C_{23}H_{28}NaO_{10}S$: 519.1295.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(E)-2-chlorostyryl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (3c): yield: 81 mg (65%); R_f=0.68 (cyclohexane:AcOEt, 5:5); white-yellow solid; mp 64–66 °C; $[\alpha]_D^{24}$: −176.0 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.47 (dd, J=7.5, 1.9 Hz, 1H), 7.33 (dd, J=7.6, 1.6 Hz, 1H), 7.25–7.12 (m, 2H), 7.08 (d, J=15.6 Hz, 1H), 6.78 (d, J=15.6 Hz, 1H), 5.26 (t, J=9.3 Hz, 1H), 5.13 (td, J=9.6, 7.3 Hz, 2H), 4.72 (d, J=9.9 Hz, 1H), 4.27 (dd, J=12.4, 4.9 Hz, 1H), 4.16 (dd, J=12.4, 2.2 Hz, 1H), 3.80 (ddd, J=10.0, 4.8, 2.3 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=170.71 (C=O), 170.22 (C=O), 169.45 (C=O), 169.31 (C=O), 134.49 (C), 132.65 (C), 129.91 (CH), 128.99 (CH), 128.89 (CH), 127.05 (CH), 126.68 (CH), 122.03 (CH), 83.60 (CH), 76.32 (CH), 73.92 (CH), 69.92 (CH), 68.24 (CH), 62.13 (CH_2), 20.78 (CH_3), 20.74 (CH_3), 20.66 (2CH_3); IR (neat): ν=3474, 2203, 1755, 1739, 1593, 1365, 1208, 1091, 1032, 955 cm^{-1}; HR-MS (ESI): m/z= 523.0784, calculated for $C_{22}H_{25}ClNaO_9S$: 523.0800.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-[(E)-styrylthio]-tetrahydro-2H-pyran-3,4,5-triyl triacetate (3d): yield: 85 mg (73%); R_f=0.29 (cyclohexane:AcOEt, 7:3); white-yellow solid; mp 113–115 °C; $[\alpha]_D^{24}$: −160.0 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.39–7.18 (m, 5H), 6.75 (s, 2H), 5.25 (t, J=9.3 Hz, 1H), 5.11 (m, 2H), 4.65 (d, J=9.9 Hz, 1H), 4.26 (dd, J=12.4, 4.9 Hz, 1H), 4.16 (dd, J=12.4, 2.3 Hz, 1H), 3.78 (ddd, J=10.0, 4.9, 2.4 Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=170.70 (C=O), 170.24 (C=O), 169.46 (C=O), 169.31 (C=O), 136.35 (C), 134.93 (CH), 128.79 (CH), 128.40 (2CH), 128.09 (CH), 126.33 (2CH), 118.33 (CH), 83.75 (CH), 76.26 (CH), 73.96 (CH), 70.05 (CH), 68.31 (CH), 62.20 (CH_2), 20.79 (2CH_3), 20.69 (2CH_3); IR (neat): ν=3438, 3386, 3356, 3301, 3252, 2526, 2253, 2159, 2025, 1946, 1756, 1217, 1037 cm^{-1}; HR-MS (ESI): m/z= 489.1182, calculated for $C_{22}H_{26}NaO_9S$: 489.1190.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-[(4-methoxystyryl)thio]tetrahydro-2H-pyran-3,4,5-triyl triacetate (3f): yield: 125 mg (97%); R_f=0.57 (cyclohexane:AcOEt, 5:5); white-yellow oil; $[\alpha]_D^{24}$: +40.0 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, Z isomer): δ=7.33 (d, J=8.6 Hz, 2H), 6.85 (d, J=8.6 Hz, 2H), 6.56 (d, J=10.7 Hz, 1H), 6.21 (d, J=10.7 Hz, 1H), 5.33–5.01 (m, 3H), 4.63 (d, J=10.0 Hz, 1H), 4.27 (dd, J=12.4, 4.8 Hz, 1H), 4.13 (dd, J=12.4, 1.8 Hz, 1H), 3.79 (s, 3H), 3.77–3.72 (m, 1H), 2.07 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=170.72 (C=O), 170.25 (C=O), 169.43 (C=O), 169.26 (C=O), 158.86 (C), 130.26 (2CH), 129.04 (C), 128.95 (CH), 117.78 (CH), 113.81 (2CH), 84.78 (CH), 76.34 (CH), 73.97 (CH), 70.11 (CH), 68.21 (CH), 62.11 (CH_2), 55.35 (CH_3), 20.81 (CH_3), 20.66 (CH_3); ^{1}H NMR (300 MHz, $CDCl_3$, E isomer): δ=7.28 (d, J=9.3 Hz, 2H), 6.84 (d, J=8.7 Hz, 2H), 6.74 (d, J=15.4 Hz, 1H), 6.57 (d, J=15.4 Hz, 1H), 5.24 (dd, J=10.3, 8.2 Hz, 1H), 5.10 (td, J=9.6, 5.8 Hz, 2H), 4.60 (d, J=9.9 Hz, 1H), 4.25 (dd, J=12.4, 4.8 Hz, 1H), 4.16 (dd, J=12.4, 2.3 Hz, 1H), 3.80 (s, 3H), 3.76 (ddd, J=10.0, 4.9, 2.4 Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=170.75 (C=O), 170.29 (C=O), 169.49 (C=O), 169.35 (C=O), 159.76 (CH), 135.93 (C), 129.23 (2CH), 127.73 (CH), 115.11 (2CH), 114.24 (CH), 83.92 (CH), 76.22 (CH), 74.03 (CH), 70.03 (CH), 68.34 (CH), 62.21 (CH_2), 55.43 (CH_3), 20.81 (2CH_3), 20.68 (2CH_3); HR-MS (ESI): m/z=519.1284, calculated for $C_{23}H_{28}NaO_{10}S$: 519.1295.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(3E)-4-phenylbuta-1,3-dien-1-yl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (3g): yield: 103 mg (89%); R_f=0.54 (cyclohexane:AcOEt, 5:5); white-yellow solid; mp 86–88 °C; $[\alpha]_D^{24}$: −10.0 (c 1.0, $CHCl_3$); mixture *1E,3E/1E,3Z* (30:70); ^{1}H NMR (300 MHz, $CDCl_3$, *Z isomer*): δ=7.40 (m, 2H), 7.30 (m, 2H), 7.22 (m, 1H), 7.00 (dd, J=10.8, 15.5 Hz, 1H), 6.58 (d, J=15.5 Hz, 1H), 6.47 (dd, J=9.4, 10.8 Hz, 1H), 6.16 (d, J=9.4 Hz, 1H), 5.23 (m, 1H), 5.12 (m, 1H), 5.11 (m, 1H), 4.63 (m, 1H), 4.26 (dd, J=12.4, 4.8 Hz, 1H), 4.13 (dd, J=12.4, 2.2 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, *Z isomer*): δ=170.71 (C=O), 170.25 (C=O), 169.44 (C=O), 169.27 (C=O), 137.01 (C), 134.55 (CH), 131.99 (CH), 128.07 (CH), 126.73 (2CH), 124.03 (CH), 123.74 (2CH), 120.08 (CH), 83.79 (CH), 76.30 (CH), 73.95 (CH), 70.20 (CH), 63.21 (CH), 62.10 (CH_2), 20.80 (CH_3), 20.74 (CH_3), 20.66 (2CH_3); ^{1}H NMR (300 MHz, $CDCl_3$, *E isomer*): δ=7.40 (m, 2H), 7.30 (m, 2H), 7.22 (m, 1H), 6.58 (d, J=15.5 Hz, 1H), 6.53 (m, 1H), 6.36 (m, 1H), 5.23 (m, 1H), 5.12 (m, 1H), 5.11 (m, 1H), 4.63 (m, 1H), 4.26 (dd, J=12.4, 4.8 Hz, 1H), 4.13 (dd, J=12.4, 2.2 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, *E isomer*): δ=170.71 (C=O), 170.25 (C=O), 169.44 (C=O), 169.27 (C=O), 137.01 (C), 134.55 (CH), 131.99 (CH), 128.07 (CH), 126.73 (2CH), 124.03 (CH), 123.74 (2CH), 121.48 (CH), 83.79 (CH), 76.30 (CH), 73.95 (CH), 70.20 (CH), 63.21 (CH), 62.10 (CH_2), 20.80 (CH_3), 20.74 (CH_3), 20.66 (2CH_3); IR (neat): ν=3309, 3134, 2358, 2135, 1755, 1740, 1711, 1365, 1247, 1211, 1091, 1033 cm^{-1}; HR-MS (ESI): m/z=515.1333, calculated for $C_{24}H_{28}NaO_9S$: 515.1346.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-[(3-fluoro-4-methoxystyryl)thio]tetrahydro-2H-pyran-3,4,5-triyl triacetate (3h): yield: 115 mg (90%); R_f=0.55 (cyclohexane:AcOEt, 5:5); white-yellow solid; mp 143–145 °C; $[\alpha]_D^{24}$: +26.0 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.17 (dd, J=12.7, 2.1 Hz, 1H), 7.09 (d, J=8.5 Hz, 1H), 6.90 (t, J=8.6 Hz, 1H), 6.48 (d, J=10.8 Hz, 1H), 6.27 (d, J=10.8 Hz, 1H), 5.34–5.02 (m, 3H), 4.63 (d, J=9.8 Hz, 1H), 4.26 (dd, J=12.5, 4.7 Hz, 1H), 4.18–4.07 (m, 1H), 3.86 (s, 3H), 3.76 (ddd, J=9.8, 4.6, 2.2 Hz, 1H), 2.06 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=170.66 (C=O), 170.18 (C=O), 169.39 (C=O), 169.19 (C=O), 151.97 (C, d, J=245.4 Hz), 146.87 (C, d, J=10.8 Hz), 129.59 (C, d, J=6.7 Hz), 127.92 (CH), 125.12 (CH, d, J=2.9 Hz), 119.29 (CH), 116.33 (CH, d, J=19.1 Hz), 113.12 (CH), 84.21 (CH), 76.37 (CH), 73.89 (CH), 70.05 (CH), 68.14 (CH), 62.05 (CH_2), 56.30 (CH), 20.77 (CH_3), 20.61 (3CH_3); ^{19}F NMR

(188 MHz, $CDCl_3$): $\delta = -133.31$ (s); IR (neat): $\nu = 3375$, 2139, 2006, 1754, 1740, 1513, 1285, 1209, 1120, 1032 cm^{-1}; HR-MS (ESI): $m/z = 537.1191$, calculated for $C_{23}H_{27}FNaO_{10}S$: 537.1201.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(Z)-hex-1-en-1-yl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (3i): yield: 100 mg (80%); $R_f = 0.53$ (cyclohexane:AcOEt, 6:4); white-yellow solid; mp 85–87 °C; $[\alpha]_D^{24}$: +13.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.03$ (d, $J = 9.3$ Hz, 1H), 5.75 (dt, $J = 9.2$, 7.2 Hz, 1H), 5.19 (t, $J = 9.3$ Hz, 1H), 5.06 (td, $J = 9.6$, 5.4 Hz, 2H), 4.52 (d, $J = 9.9$ Hz, 1H), 4.23 (dd, $J = 12.4$, 4.8 Hz, 1H), 4.10 (dd, $J = 12.4$, 2.3 Hz, 1H), 3.71 (ddd, $J = 10.0$, 4.7, 2.4 Hz, 1H), 2.05 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.40–1.14 (m, 6H), 0.85 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.68$ (C=O), 170.23 (C=O), 169.42 (C=O), 169.21 (C=O), 134.79 (CH), 118.11 (CH), 83.54 (CH), 76.16 (CH), 74.01 (CH), 70.17 (CH), 68.27 (CH), 62.15 (CH_2), 30.95 (CH_2), 28.95 (CH_2), 22.30 (CH_2), 20.77 (CH_3), 20.69 (CH_3), 20.64 ($2CH_3$), 13.94 (CH_3); IR (neat): $\nu = 3449$, 2961, 2362, 2167, 1756, 1740, 1366, 1210, 1093 cm^{-1}; HR-MS (ESI): $m/z = 469.1505$, calculated for $C_{20}H_{30}NaO_9S$: 469.1503.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(Z)-2-chloro-2-phenylvinyl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (3j): yield: 101 mg (82%); $R_f = 0.43$ (cyclohexane:AcOEt, 6:4); white-yellow solid; mp 148–150 °C; $[\alpha]_D^{24}$: −61.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz,): $\delta = 7.58$–7.46 (m, 2H), 7.40–7.23 (m, 3H), 6.79 (s, 1H), 5.19 (dq, $J = 27.6$, 9.2 Hz, 3H), 4.72 (d, $J = 9.8$ Hz, 1H), 4.25 (dd, $J = 12.4$, 4.9 Hz, 1H), 4.14 (dd, $J = 12.4$, 2.1 Hz, 1H), 3.79 (ddd, $J = 10.0$, 4.6, 2.2 Hz, 1H), 2.05 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.60$ (C=O), 170.15 (C=O), 169.41 (C=O), 169.20 (C=O), 136.85 (C), 131.50 (C), 128.74 (CH), 128.53 (2CH), 125.96 (2CH), 118.13 (CH), 82.52 (CH), 76.47 (CH), 73.78 (CH), 70.15 (CH), 68.16 (CH), 62.07 (CH_2), 20.74 (CH_3), 20.62 ($3CH_3$); IR (neat): $\nu = 3375$, 3192, 2362, 2145, 2029, 1970, 1757, 1740, 1711, 1364, 1206, 1090, 1060 cm < $^{M->1}$; HR-MS (ESI): $m/z = 523.0798$, calculated for $C_{22}H_{25}ClNaO_9S$: 523.0800.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[1-(3,4,5-trimethoxyphenyl)vinyl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (3k): yield: 105 mg (76%); $R_f = 0.47$ (cyclohexane:AcOEt, 5:5); white-yellow solid; mp 44–46 °C; $[\alpha]_D^{24}$: −71.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.74$ (s, 2H), 5.54 (s, 1H), 5.49 (s, 1H), 5.22–4.97 (m, 4H), 4.61 (d, $J = 9.8$ Hz, 1H), 4.17 (dd, $J = 12.4$, 5.0 Hz, 1H), 4.04 (dd, $J = 12.3$, 2.2 Hz, 1H), 3.85 (s, 6H), 3.84 (s, 3H), 3.60–3.50 (m, 1H), 2.04 (s, 6H), 1.97 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.58$ (C=O), 170.20 (C=O), 169.39 (C=O), 169.22 (C=O), 153.06 (2C), 142.25 (C), 138.78 (C), 134.26 (C), 116.45 (CH_2), 104.95 (2CH), 84.32 (CH), 75.92 (CH), 73.97 (CH), 70.11 (CH), 68.25 (CH), 62.12 (CH_2), 60.96 (CH_3), 56.23 ($2CH_3$), 20.72 ($2CH_3$), 20.64 (CH_3), 20.61 (CH_3); IR (neat): $\nu = 3411$, 3181, 3090, 2944, 2511, 2182, 2029, 1987, 1756, 1578, 1504, 1412, 1366, 1323, 1214 cm^{-1}; HR-MS (ESI): $m/z = 579.1497$, calculated for $C_{25}H_{32}NaO_{12}S$: 579.1507.

(2S,3R,4S,5R,6R)-2-[(1H-inden-2-yl)thio]-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3l): yield: 113 mg (95%); $R_f = 0.46$ (cyclohexane:AcOEt, 6:4); white-yellow solid; mp 139–141 °C; $[\alpha]_D^{24}$: −31.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.36$ (d, $J = 7.3$ Hz, 1H), 7.32–7.27 (m, 1H), 7.22 (d, $J = 7.4$ Hz, 1H), 7.14 (td, $J = 7.3$, 1.5 Hz, 1H), 6.89 (d, $J = 0.6$ Hz, 1H), 5.25 (t, $J = 9.3$ Hz, 1H), 5.07 (ddd, $J = 16.2$, 9.4, 6.8 Hz, 2H), 4.77 (d, $J = 10.0$ Hz, 1H), 4.27–4.13 (m, 2H), 3.77 (ddd, $J = 10.0$, 5.0, 2.7 Hz, 1H), 3.65–3.45 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.53$ (C=O), 170.17 (C=O), 169.41 (C=O), 169.30 (C=O), 144.16 (C), 143.44 (C), 136.90 (C), 133.64 (CH), 126.72 (CH), 124.91 (CH), 123.32 (CH), 120.48 (CH), 84.17 (CH), 76.01 (CH), 73.88 (CH), 70.01 (CH), 68.29 (CH), 62.26 (CH_2), 43.74 (CH_2), 20.74 ($2CH_3$), 20.61 ($2CH_3$); IR (neat): $\nu = 3378$, 3307, 3065, 2559, 2364, 2164, 2093, 2007, 1755, 1513, 1366, 1213, 1121, 1060, 1033 cm^{-1}; HR-MS (ESI): $m/z = 501.1175$, calculated for $C_{23}H_{26}NaO_9S$: 501.1190.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-[(6-oxocyclohex-1-en-1-yl)thio]tetrahydro-2H-pyran-3,4,5-triyl triacetate (3m): yield: 78 mg (68%); $R_f = 0.45$ (cyclohexane:AcOEt, 5:5); white-yellow oil; $[\alpha]_D^{24}$: −40.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.23$ (t, $J = 4.3$ Hz, 1H), 5.23 (t, $J = 9.3$ Hz, 1H), 5.06 (td, $J = 9.6$, 3.3 Hz, 2H), 4.78 (d, $J = 10.0$ Hz, 1H), 4.20 (dd, $J = 12.3$, 5.0 Hz, 1H), 4.12 (dd, $J = 12.3$, 2.4 Hz, 1H), 3.70 (ddd, $J = 10.1$, 5.1, 2.5 Hz, 1H), 2.52 (dt, $J = 16.7$, 5.7 Hz, 3H), 2.09 (m, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.24$ (C=O), 170.60 (C=O), 170.24 (C=O), 169.56 (C=O), 151.08 (CH), 132.71 (C), 82.63 (CH), 76.03 (CH), 74.09 (CH), 69.64 (CH), 68.44 (CH), 62.32 (CH_2), 38.67 (CH_2), 27.75 (CH_2), 22.60 (CH_2), 20.83 ($2CH_3$), 20.72 ($2CH_3$); IR (neat): $\nu = 3451$, 3068, 2262, 2123, 2050, 1979, 1752, 1368, 1215 cm^{-1}; HR-MS (ESI): $m/z = 481.1164$, calculated for $C_{20}H_{26}NaO_{10}S$: 481.1139.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(E)-2-{[(2R,3S,4R,5S,6S)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl]thio}vinyl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (3n): yield: 122 mg (65%); $R_f = 0.40$ (cyclohexane:AcOEt, 5:5); white-yellow solid; mp 82–84 °C; $[\alpha]_D^{24}$: +30.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.46$ (s, 2H), 5.16 (tt, $J = 11.7$, 9.2 Hz, 6H), 4.53 (d, $J = 9.6$ Hz, 2H), 4.27 (dd, $J = 12.5$, 4.7 Hz, 2H), 4.17 (dd, $J = 12.4$, 2.2 Hz, 2H), 3.76 (ddd, $J = 9.4$, 4.4, 2.2 Hz, 2H), 2.08 (s, 6H), 2.04 (s, 6H), 2.01 (s, 6H), 1.98 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.75$ (2C=O), 170.27 (2C=O), 169.42 (2C=O), 169.18 (2C=O), 124.71 (2CH), 83.56 (2CH), 76.33 (2CH), 73.98 (2CH), 69.86 (2CH), 68.14 (2CH), 62.04 ($2CH_2$), 20.88 ($2CH_3$), 20.78 ($2CH_3$), 20.68 ($4CH_3$); IR (neat): $\nu = 3426$, 3184, 3112, 2356, 2335, 2149, 2012, 1755, 1738, 1711, 1431, 1365, 1248, 1204, 1092 cm^{-1}; HR-MS (ESI): $m/z = 775.1556$, calculated for $C_{30}H_{40}NaO_{18}S_2$: 775.1548.

(2S,3R,4S,5S,6R)-2-[(1H-Inden-2-yl)thio]-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3o): yield: 113 mg (95%); $R_f = 0.46$ (cyclohexane:AcOEt, 6:4); white-yellow solid; mp 132–134 °C; $[\alpha]_D^{24}$: −30.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.36$ (d, $J = 7.3$ Hz, 1H), 7.31–7.18 (m, 2H), 7.14 (dd, $J = 10.2$, 4.3 Hz, 1H), 6.90 (s, 1H), 5.44 (d, $J = 3.1$ Hz, 1H), 5.32 (t, $J = 9.9$ Hz, 1H), 5.27 (s, 1H), 5.08 (dd, $J = 9.9$, 3.3 Hz, 1H), 4.76 (d, $J = 9.9$ Hz, 1H), 4.25–4.09 (m, 2H), 3.99 (t, $J = 6.4$ Hz, 1H), 3.70–3.41 (m, 2H), 2.10 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.35$ (C=O), 170.11 (C=O), 170.02 (C=O), 169.41 (C=O), 144.23 (C), 143.30 (C), 137.37 (C), 132.77 (CH), 126.67 (CH), 124.74 (CH), 123.24 (CH), 120.29 (CH), 84.55 (CH), 74.72 (CH),

71.95 (CH), 67.34 (CH), 67.19 (CH), 61.88 (CH_2), 43.48 (CH_2), 20.81 (CH_3), 20.68 (CH_3), 20.64 (CH_3), 20.58 (CH_3); IR (neat): $\nu = 3428, 3300, 3051, 2358, 2208, 2181, 2146, 1752, 1457, 1245, 1219, 1085, 1058\ cm^{-1}$; HR-MS (ESI): $m/z =$ 501.1190, calculated for $C_{23}H_{26}NaO_9S$: 501.1190.

(2R,3S,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(3E)-4-phenylbuta-1,3-dien-1-yl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (3p): yield: 110 mg (89%); $R_f = 0.62$ (cyclohexane:AcOEt, 5:5); white-yellow oil; $[\alpha]_D^{24}$: +22.0 (*c* 1.0, $CHCl_3$); mixture *1E,3E/1E,3Z* (30:70); ^{1}H NMR (300 MHz, $CDCl_3$, *Z isomer*): $\delta = 7.39$ (m, 2H), 7.30 (m, 2H), 7.21 (m, 1H), 6.99 (dd, $J = 11.0$, 15.6 Hz, 1H), 6.57 (d, $J = 15.6$ Hz, 1H), 6.44 (dd, $J = 9.4$, 11.0 Hz, 1H), 6.18 (d, $J = 9.4$ Hz, 1H), 5.44 (d, $J = 3.2$ Hz, 1H), 5.34 (t, $J = 9.8$ Hz, 1H), 5.07 (dd, $J =$ 10.0, 3.4 Hz, 1H), 4.62 (dd, $J = 9.4$, 3.9 Hz, 1H), 4.14 (dd, $J =$ 6.5, 3.9 Hz, 2H), 4.04–3.92 (m, 1H), 2.16 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, *Z isomer*): $\delta = 170.39$ (C=O), 170.23 (C=O), 170.06 (C=O), 169.39 (C=O), 137.02 (C), 134.25 (CH), 131.02 (CH), 128.70 (2CH), 127.98 (CH), 126.67 (2CH), 124.04 (CH), 120.78 (CH), 84.27 (CH), 74.83 (CH), 71.90 (CH), 67.51 (CH), 67.26 (CH), 61.40 (CH_2), 20.80 (CH_3), 20.71 ($2CH_3$), 20.61 (CH_3); ^{1}H NMR (300 MHz, $CDCl_3$, *E isomer*): $\delta = 7.39$ (m, 2H), 7.30 (m, 2H), 7.21 (m, 1H), 6.76 (dd, $J = 10.5$, 15.6 Hz, 1H), 6.54 (dd, $J = 10.5$, 14.9 Hz, 1H),6.49 (d, $J = 15.6$ Hz, 1H), 6.38 (d, $J = 14.9$ Hz, 1H), 5.44 (d, $J = 3.2$ Hz, 1H), 5.34 (t, $J = 9.8$ Hz, 1H), 5.07 (dd, $J = 10.0$, 3.4 Hz, 1H), 4.62 (dd, $J = 9.4$, 3.9 Hz, 1H), 4.14 (dd, $J = 6.5$, 3.9 Hz, 2H), 4.04–3.92 (m, 1H), 2.16 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, *E isomer*): $\delta = 170.39$ (C=O), 170.23 (C=O), 170.06 (C=O), 169.39 (C=O), 137.02 (C), 132.34 (CH), 131.02 (CH), 128.70 (2CH), 127.98 (CH), 127.48 (CH), 126.67 (2CH),122.24 (CH), 84.27 (CH), 74.83 (CH), 71.90 (CH), 67.51 (CH), 67.26 (CH), 61.40 (CH_2), 20.80 (CH_3), 20.71 ($2CH_3$), 20.61 (CH_3); IR (neat): $\nu = 3460$, 3298, 3149, 2929, 2369, 2328, 2192, 2032, 1751, 1370, 1219, 1086, 917 cm^{-1}; HR-MS (ESI): $m/z = 515.1332$, calculated for $C_{24}H_{28}NaO_9S$: 515.1346.

(2R,3S,4S,5R,6S)-2-(Acetoxymethyl)-6-[(1-methyl-4-oxo-1,4-dihydroquinolin-3-yl)thio]tetrahydro-2H-pyran-3,4,5-triyl triacetate (3q): yield: 99 mg (76%); $R_f = 0.22$ (cyclohexane:AcOEt, 2:8); white-yellow solid; mp 85–87 °C; $[\alpha]_D^{24}$: −111.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.45$ (d, $J = 8.0$ Hz, 1H), 7.99 (s, 1H), 7.69 (t, $J = 7.4$ Hz, 1H), 7.42 (dd, $J = 12.2$, 5.7 Hz, 2H), 5.40 (d, $J = 3.0$ Hz, 1H), 5.25 (t, $J = 9.9$ Hz, 1H), 5.05 (dd, $J = 9.9$, 3.3 Hz, 2H), 4.12 (ddd, $J = 14.3$, 9.8, 6.8 Hz, 2H), 3.97 (dd, $J = 11.2$, 6.8 Hz, 1H), 3.82 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 1.96 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 175.95$ (C=O), 170.29 (C=O), 170.03 (C=O), 149.10 (CH), 140.39 (C), 132.60 (CH), 127.45 (CH), 126.43 (C), 124.76 (CH), 115.54 (CH), 109.89 (C), 83.39 (CH), 74.43 (CH), 72.07 (CH), 67.83 (CH), 67.48 (CH), 61.24 (CH_2), 40.89 (CH_3), 21.10 (CH_3), 20.78 (CH_3), 20.67 (CH_3), 20.56 (CH_3); IR (neat): $\nu = 3324$, 3264, 3178, 2335, 1745, 1621, 1548, 1621, 1548, 1499, 1367, 1219, 1084 cm^{-1}; HR-MS (ESI): $m/z = 544.1271$, calculated for $C_{24}H_{27}NNaO_{10}S$: 544.1253.

(2R,3R,4S,5R,6S)-3,4,5-Tris(benzyloxy)-2-[(benzyloxy)-methyl]-6-{[(E)-styryl]thio}tetrahydro-2H-pyran (3r): yield: 120 mg (73%); $R_f = 0.62$ (cyclohexane:AcOEt, 8:2); white-yellow solid; mp 86–88 °C; $[\alpha]_D^{24}$: +80.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, acetone): $\delta = 7.45$–7.21 (m, 25H), 7.14 (d, $J = 15.8$ Hz, 1H), 6.77 (d, $J = 15.8$ Hz, 1H), 4.99–4.77 (m, 6H), 4.69 (d, $J = 11.2$ Hz, 1H), 4.59 (m, 2H), 3.87–3.56 (m, 6H); ^{13}C NMR (75 MHz, acetone): $\delta = 139.91$ (C), 139.67 (C), 139.62 (C), 139.46 (C), 137.92 (C), 130.93 (CH), 129.49 (CH), 129.09 (13CH), 129.02 (CH), 128.84 (CH), 128.68 (CH), 128.48 (2CH), 128.38 (2CH), 128.23 (2CH), 128.04 (CH), 126.71 (CH), 122.61 (CH), 87.32 (CH), 85.33 (CH), 82.21 (CH), 80.14 (CH), 78.87 (CH), 76.04 (CH_2), 75.63 (CH_2), 75.43 (CH_2), 73.83 (CH_2), 70.00 (CH_2); IR (neat): $\nu =$ 3339, 3068, 2366, 2148, 1998, 1947, 1600, 1496, 1361, 1210, 1157, 1090 cm^{-1}; HR-MS (ESI): $m/z = 681.2627$, calculated for $C_{42}H_{42}NaO_5S$: 681.2645.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(2R,3R,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6-{[(Z)-3-fluoro-4-methoxystyryl]thio}tetrahydro-2H-pyran-3-yl]oxy}tetrahydro-2H-pyran-3,4,5-triyl triacetate (3s): yield: 140 mg (70%); $R_f = 0.32$ (cyclohexane:AcOEt, 5:5); white-yellow solid; mp 210–212 °C; $[\alpha]_D^{24}$: −10.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.19$ (dd, $J = 12.7$, 2.1 Hz, 1H), 7.09 (m, 1H), 6.91 (t, $J = 8.7$ Hz, 1H), 6.48 (d, $J = 10.7$ Hz, 1H), 6.24 (d, $J = 10.8$ Hz, 1H), 5.26–5.01 (m, 4H), 4.96–4.87 (m, 1H), 4.61 (d, $J = 9.8$ Hz, 1H), 4.49 (dd, $J = 10.5$, 4.7 Hz, 2H), 4.37 (dd, $J = 12.5$, 4.3 Hz, 1H), 4.11 (dd, $J = 12.1$, 5.1 Hz, 1H), 4.04 (dd, $J = 12.4$, 2.1 Hz, 1H), 3.88 (s, 3H), 3.80 (d, $J = 9.1$ Hz, 1H), 3.72–3.58 (m, 2H), 2.12 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.60$ (C=O), 170.40 (C=O), 170.32 (C=O), 169.86 (C=O), 169.54 (C=O), 169.43 (C=O), 169.19 (C=O), 151.99 (d, $J = 243.7$ Hz, C), 147.04 (d, $J = 30.0$ Hz, C), 129.64 (d, $J =$ 3.7 Hz, C), 127.84 (CH), 125.16 (d, $J = 2.9$ Hz, CH), 119.56 (CH), 116.40 (d, $J = 19.3$ Hz, CH), 113.16 (CH), 100.96 (CH), 84.29 (CH), 77.30 (CH), 76.33 (CH), 73.62 (CH), 73.06 (CH), 72.17 (CH), 71.75 (CH), 70.41 (CH), 67.92 (CH), 62.19 (CH_2), 61.69 (CH_2), 56.38 (CH_3), 20.96 (CH_3), 20.78 (CH_3), 20.65 ($5CH_3$); ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -133.26$; IR (neat): $\nu = 2359$, 1739, 1619, 1433, 1323, 1261, 1210, 1119, 1020, 963 cm^{-1}; HR-MS (ESI): $m/z =$ 825.2056, calculated for $C_{35}H_{43}FNaO_{18}S$: 825.2046.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(2R,3R,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6-{[(E)-styryl]thio}tetrahydro-2H-pyran-3-yl]oxy}tetrahydro-2H-pyran-3,4,5-triyl triacetate (3t): yield: 128 mg (68%); $R_f =$ 0.38 (cyclohexane:AcOEt, 5:5); white-yellow solid; mp 208–210 °C; $[\alpha]_D^{24}$: −20.0 (*c* 1.0, $CDCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.36$–7.11 (m, 6H), 6.67 (d, $J = 1.9$ Hz, 1H), 5.24–4.91 (m, 4H), 4.90–4.80 (m, 1H), 4.55 (d, $J = 9.9$ Hz, 1H), 4.45 (dd, $J = 9.0$, 4.5 Hz, 2H), 4.31 (dd, $J = 12.5$, 4.2 Hz, 1H), 4.05 (dd, $J = 12.1$, 5.1 Hz, 1H), 3.97 (dd, $J = 12.4$, 2.0 Hz, 1H), 3.72 (t, $J = 9.4$ Hz, 1H), 3.66–3.54 (m, 2H), 2.01 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 170.55 (C=O), 170.36 (C=O), 170.29 (C=O), 169.82 (C=O), 169.57 (C=O), 169.38 (C=O), 169.15 (C=O), 136.39 (C), 134.98 (CH), 128.77 (2CH), 128.06 (CH), 126.29 (2CH), 118.40 (CH), 100.93 (CH), 83.50 (CH), 77.12 (CH), 76.42 (CH), 73.56 (CH), 73.03 (CH), 72.12 (CH), 71.71 (CH), 70.28 (CH), 67.86 (CH), 62.18 (CH_2), 61.62 (CH_2), 20.87 (CH_3), 20.77 (CH_3), 20.73 (CH_3), 20.61 ($4CH_3$); IR (neat): $\nu = 3462$, 3369, 3224, 3010, 2588, 2319, 2215, 2143, 1755, 1741, 1367, 1230, 1213, 1036 cm^{-1}; HR-MS (ESI): $m/z =$ 777.2036, calculated for $C_{34}H_{42}NaO_{17}S$: 777.2035.

(2R,3S,4S,5R,6S)-2-(Hydroxymethyl)-6-{[1-(3,4,5-trimethoxyphenyl)vinyl]thio}tetrahydro-2H-pyran-3,4,5-triol (3u): yield: 66 mg (65%); R_f = 0.33 (DCM:MeOH, 85:15); white-yellow solid; mp 86–88 °C; $[\alpha]_D^{24}$: −70.0 (*c* 1.0, MeOH); ^{1}H NMR (300 MHz, MeOD): δ = 6.91 (s, 2H), 5.55 (s, 1H), 5.53 (s, 1H), 4.49 (d, *J* = 9.2 Hz, 1H), 3.86 (s, 6H), 3.83 (d, *J* = 2.4 Hz, 1H), 3.79 (d, *J* = 2.3 Hz, 1H), 3.77 (s, 3H), 3.67–3.58 (m, 2H), 3.33 (s, 1H), 3.20–3.07 (m, 1H); ^{13}C NMR (75 MHz, MeOD): δ = 154.25 (C), 144.62 (C), 139.15 (C), 136.74 (C), 115.21 (CH_2), 106.20 (2CH), 87.67 (CH), 81.97 (CH), 79.75 (CH), 74.06 (CH), 71.29 (CH), 62.74 (CH_2), 61.14 (CH_3), 56.69 (2CH_3); IR (neat): ν = 3438, 3386, 3356, 3301, 3252, 2526, 2253, 2159, 2025, 1946, 1756, 1217, 1037 cm^{-1}; HR-MS (ESI): *m/z* = 411.1076, calculated for $C_{17}H_{24}NaO_8S$: 411.1084.

(2R,3R,4S,5R,6S)-2-(Hydroxymethyl)-6-{[1-(3,4,5-trimethoxyphenyl)vinyl]thio}tetrahydro-2H-pyran-3,4,5-triol (3v): yield: 59 mg (60%); R_f = 0.33 (DCM:MeOH, 85:15); white-yellow solid; mp 90–92 °C; $[\alpha]_D^{24}$: −107.0 (*c* 1.0, MeOH); ^{1}H NMR (300 MHz, MeOD): δ = 6.92 (s, 2H), 5.54 (s, 2H), 4.46 (d, *J* = 9.8 Hz, 1H), 3.87 (m, 1H), 3.86 (s, 6H), 3.77 (s, 3H), 3.71–3.59 (m, 4H), 3.48–3.38 (m, 2H); ^{13}C NMR (75 MHz, MeOD): δ = 154.24 (C), 144.84 (C), 143.65 (C), 136.78 (C), 115.02 (CH_2), 106.13 (CH), 88.23 (CH), 80.54 (CH), 76.34 (CH), 71.16 (CH), 70.33 (CH), 62.46 (CH_2), 61.13 (CH_3), 56.65 (2CH_3); IR (neat): ν = 3476, 3342, 3315, 2431, 2357, 2192, 2106, 1991, 1576, 1323 cm^{-1}; HR-MS (ESI): *m/z* = 411.1076, calculated for $C_{17}H_{24}NaO_8S$: 411.1084.

Analytical Data for Alkynylthioglycosides 5a–e and Product 7

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(4-methoxyphenyl)ethynyl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (5a): yield: 56 mg (45%); (R_f = 0.31 cyclohexane:AcOEt, 7:3); white-yellow oil; $[\alpha]_D^{24}$: −43.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.29 (td, *J* = 17.0, 9.2 Hz, 2H), 5.17–5.09 (m, 1H), 4.59 (d, *J* = 9.4 Hz, 1H), 4.26 (dd, *J* = 12.5, 4.8 Hz, 1H), 4.18 (dd, *J* = 12.5, 2.5 Hz, 1H), 3.82 (s, 3H), 3.80–3.73 (m, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.78 (C=O), 170.34 (C=O), 169.46 (C=O), 169.15 (C=O), 160.39 (C), 134.22 (2CH), 114.87 (C), 114.13 (2CH), 97.29 (C), 84.71 (CH), 76.65 (CH), 74.11 (CH), 70.93 (C), 69.96 (CH), 68.08 (CH), 62.16 (CH_2), 55.47 (CH_3), 20.85 (CH_3), 20.82 (CH_3), 20.71 (2CH_3); IR (neat): ν = 3422, 3337, 3215, 3106, 2483, 2263, 2030, 1987, 1758, 1509, 1251 cm^{-1}; HR-MS (ESI): *m/z* = 517.1136, calculated for $C_{23}H_{26}NaO_{10}S$: 517.1139.

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((naphthalen-1-ylethynyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5b): yield: 87 mg (68%); R_f = 0.32 (cyclohexane:AcOEt, 7:3); white-yellow oil; $[\alpha]_D^{24}$: +47.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.85–7.73 (m, 3H), 7.51 (m, 3H), 5.33 (dt, *J* = 22.5, 9.2 Hz, 2H), 5.16 (t, *J* = 9.5 Hz, 1H), 4.66 (d, *J* = 9.4 Hz, 1H), 4.28 (dd, *J* = 12.5, 4.8 Hz, 1H), 4.20 (dd, *J* = 12.5, 2.2 Hz, 1H), 3.81 (ddd, *J* = 9.9, 4.7, 2.3 Hz, 1H), 2.12 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.79 (C=O), 170.35 (C=O), 169.47 (C=O), 169.18 (C=O), 133.17 (C), 132.96 (C), 132.32 (CH), 128.59 (CH), 128.15 (CH), 128.01 (CH), 127.89 (CH), 127.08 (CH), 126.73 (CH), 120.01 (C), 97.60 (C), 84.65 (CH), 76.66 (CH), 74.01 (CH), 73.08 (C), 69.98 (CH), 67.99 (CH), 62.08 (CH_2), 20.84 (CH_3), 20.81 (CH_3), 20.73 (CH_3), 20.70 (CH_3); IR (neat): ν = 3284, 3207, 2370, 2163, 1954, 1757, 1745, 1711, 1365, 1210, 1060 cm^{-1}; HR-MS (ESI): *m/z* = 537.1183, calculated for $C_{26}H_{26}NaO_9S$: 537.1195.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(4-cyanophenyl)ethynyl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (5c): yield: 113 mg (93%); R_f = 0.41 (cyclohexane:AcOEt, 6:4); white-yellow solid; mp 87–89 °C; $[\alpha]_D^{24}$: −71.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 5.38–5.23 (m, 2H), 5.14 (t, *J* = 9.6 Hz, 1H), 4.62 (d, *J* = 9.4 Hz, 1H), 4.26 (dd, *J* = 12.5, 4.9 Hz, 1H), 4.17 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.80 (ddd, *J* = 10.0, 4.9, 2.4 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.64 (C=O), 170.25 (C=O), 169.48 (C=O), 169.12 (C=O), 132.19 (4CH), 127.56 (C), 118.51 (C), 112.02 (C), 95.96 (C), 84.23 (CH), 78.35 (CN), 76.84 (CH), 73.94 (CH), 69.83 (CH), 67.95 (CH), 62.09 (CH_2), 20.82 (CH_3), 20.68 (3CH_3); IR (neat): ν = 3489, 3428, 2360, 2173, 1756, 1488, 1366, 1212, 1090 cm^{-1}; HR-MS (ESI): *m/z* = 512.0988, calculated for $C_{23}H_{23}NNaO_9S$: 512.0991.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(E)-4-phenylbut-3-en-1-yn-1-yl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (5d): yield: 61 mg (50%); R_f = 0.58 (cyclohexane:AcOEt, 5:5); black oil; $[\alpha]_D^{24}$: +54.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$). δ = 7.46–7.27 (m, 5H), 7.01 (d, *J* = 16.2 Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 5.33–5.20 (m, 2H), 5.15 (ddd, *J* = 9.6, 6.8, 2.8 Hz, 1H), 4.59 (dd, *J* = 7.0, 2.6 Hz, 1H), 4.27 (dd, *J* = 12.5, 4.8 Hz, 1H), 4.18 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.79 (ddd, *J* = 9.9, 4.8, 2.4 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.76 (C=O), 170.32 (C=O), 169.47 (C=O), 169.17 (C=O), 142.59 (CH), 136.11 (C), 129.02 (CH), 128.87 (2CH), 126.54 (2CH), 107.73 (CH), 96.85 (C), 84.70 (CH), 76.66 (CH), 74.78 (C), 74.01 (CH), 70.05 (CH), 68.06 (CH), 62.13 (CH_2), 20.87 (CH_3), 20.77 (CH_3), 20.70 (2CH_3); IR (neat): ν = 3479, 3443, 3327, 3300, 3222, 2867, 2372, 2316, 2135, 2021, 1967, 1756, cm^{-1}; HR-MS (ESI): *m/z* = 513.1180, calculated for $C_{24}H_{26}NaO_9S$: 513.1190.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(2R,3R,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6-{[(4-cyanophenyl)ethynyl]thio}tetrahydro-2H-pyran-3-yl]oxy}tetrahydro-2H-pyran-3,4,5-triyl triacetate (5e): yield: 126 mg (65%); R_f = 0.30 (cyclohexane:AcOEt, 6:4); white-yellow solid; mp 74–76 °C; $[\alpha]_D^{24}$: −20.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 5.27–5.17 (m, 2H), 5.15–5.01 (m, 2H), 4.95–4.82 (m, 1H), 4.64–4.54 (m, 1H), 4.50 (d, *J* = 8.1 Hz, 2H), 4.36 (dd, *J* = 12.5, 4.1 Hz, 1H), 4.10 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.02 (dd, *J* = 12.4, 2.0 Hz, 1H), 3.92–3.75 (m, 1H), 3.75–3.58 (m, 2H), 2.06 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.49 (C=O), 170.28 (C=O), 170.24 (C=O), 169.79 (C=O), 169.35 (2C=O), 169.12 (C=O), 132.14 (4CH), 127.59 (C), 118.42 (C), 111.97 (C), 100.91 (CH), 95.57 (C), 84.21 (CH), 78.74 (CN), 77.68 (CH), 76.07 (CH), 73.70 (CH), 72.94 (CH), 72.07 (CH), 71.68 (CH), 70.01 (CH), 67.87 (CH), 62.06 (CH_2), 61.64 (CH_2), 20.88 (CH_3), 20.71 (2CH_3), 20.60 (4CH_3); IR (neat): ν =

3411, 3338, 3231, 2363, 2227, 2076, 2030, 1970, 1758, 1741, 1603, 1366, 1228, 1168, 1035 cm^{-1}; HR-MS (ESI): m/z = 800.1815, calculated for $C_{35}H_{39}NNaO_{17}S$: 800.1831.

(2R,3R,4S,5R,6S)-2-(Acetoxymethyl)-6-{[(Z)-1-(4-acetoxyphenyl)-3-ethoxy-3-oxoprop-1-en-2-yl]thio}tetrahydro-2H-pyran-3,4,5-triyl triacetate (7): yield: 96 mg (65%); R_f = 0.42 (cyclohexane:AcOEt, 5: 5); white-yellow solid; mp 88–90 °C; $[\alpha]_D^{24}$: +59.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.85 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 8.6 Hz, 2H), 5.24–5.13 (m, 1H), 5.06 (t, J = 9.6 Hz, 2H), 4.90 (d, J = 9.9 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 4.19 (dd, J = 12.4, 5.0 Hz, 1H), 4.01 (dd, J = 12.3, 2.2 Hz, 1H), 3.61 (ddd, J = 7.4, 4.7, 2.2 Hz, 1H), 2.30 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.70 (C=O), 170.29 (C=O), 169.53 (C=O), 169.47 (C=O), 169.13 (C=O), 165.91 (C=O), 151.91 (C), 146.29 (CH), 132.58 (2CH), 131.77 (C), 122.77 (C), 121.61 (2CH), 84.47 (CH), 76.02 (CH), 74.07 (CH), 71.03 (CH), 68.36 (CH), 62.17 (CH_2), 62.09 (CH_2), 21.27 (CH_3), 20.68 (4CH_3), 14.46 (CH_3); IR (neat): ν = 3428, 3247, 3144, 2359, 2237, 2168, 2017, 2001, 1754, 1712, 1601, 1505, 1368, 1217, 1194, 1037 cm^{-1}; HR-MS (ESI): m/z = 619.1455, calculated for $C_{27}H_{32}NaO_{13}S$: 619.1456.

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