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Copper-catalyzed one-pot synthesis of glycosylated iminocoumarins and 3-triazolyl-2-iminocoumarins†

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A general strategy was developed for the synthesis of glycosyl iminocoumarins (**5a–x**) in a one-pot, copper-catalyzed multicomponent reaction involving a domino reaction of sulfonyl azides, sugar alkynes, and salicylaldehydes *via* ketenimine intermediate formation. Similarly, glycosyl 3-triazolyl-2-iminocoumarin derivatives (**6a–o**) have also been synthesized in a one-pot, three component condensation *via* tandem "CuAAC-aldol-cyclization-dehydration" sequence. In this event, a copper-catalyzed cycloaddition reaction between 2-azidoacetonitrile and sugar alkynes furnished a triazole derivative *in situ* and activated the neighboring methylene group, inducing an aldol–cyclization–dehydration sequence in the presence of a salicylaldehyde. The yields were very good in all reactions.

Introduction

The transformation of simple substrates into a library of complex molecules with structural diversity constitutes a great challenge in organic synthesis. The use of one-pot multicomponent reactions (MCRs) is attractive in terms of atom- and step-economy, operational simplicity, and environmental friendliness for generating highly functionalized molecules with complexity and diversity.[1,2] Coumarins and iminocoumarins are privileged structural frameworks exhibiting widespread biological, medicinal, and material applications including anticancer,[3a] antitumor,[3b] antifungal,[3c] antimicrobial properties,[3d] and anti-HIV activities.[3e] Whereas iminocoumarins have been shown to be inhibitors of protein tyrosine kinase p56lck,[4a] dynamins I and II GTPase,[4b] in cancer research.[4c] Many coumarin triazoles (Fig. 1) have been widely used as drugs and in biochemistry due to their high emission yield, excellent photostability.[5] Furthermore, iminocoumarins are widely used as dyes[6a] and fluorescent sensors for the estimation of metal ions in micromolar concentrations.[6b]

During the regular practice of screening novel heterocycles as drug candidates against various diseases, it was observed that several active molecules become toxic or incapable of delivering the exact function due to lack of specificity or insolubility. In general, oligosaccharides and glycoconjugates exert important effects on many complex biological events[7] including the cellular recognition, inflammation, immune response, tumor metastasis, and bacterial and viral infections, *etc.*[8]

There is a number of naturally occurring coumarins glycosides[9] [*e.g.* dauroside A, diosfeboside A, gumoside A, eleutheroside B *etc.*[10] Fig. 2], the only coumarin C-glycoside that has been found in nature is dauroside D,[11] also known as

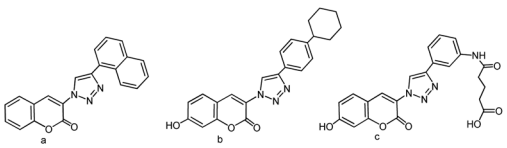

Fig. 1 Coumarin scaffolds with substituted triazoles (a–c).

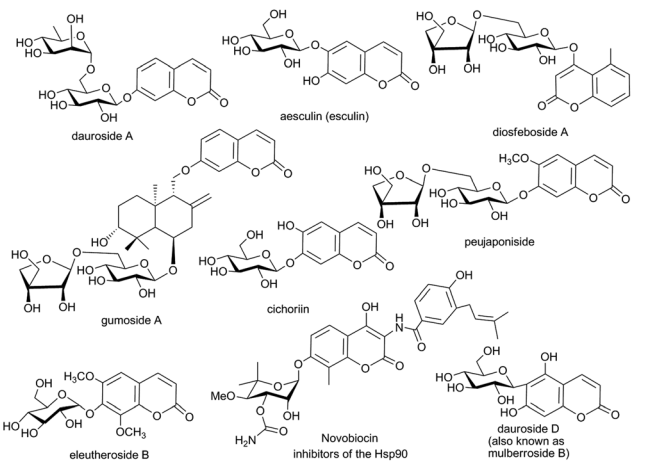

Fig. 2 Example of some biologically active natural products containing "coumarin glycoside" scaffolds.

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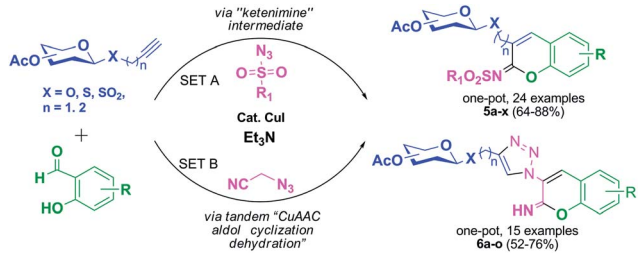
† Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR spectra are provided. See DOI: 10.1039/c3ra46844e



Scheme 1 One-pot synthesis of glycosylated iminocoumarin and 3-triazolyl-2-iminocoumarin derivatives.

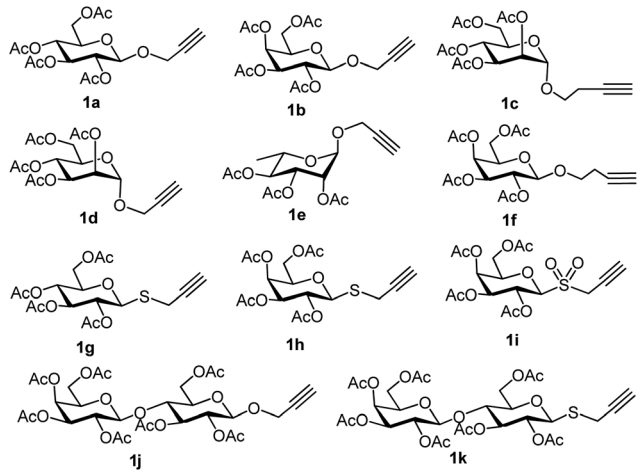


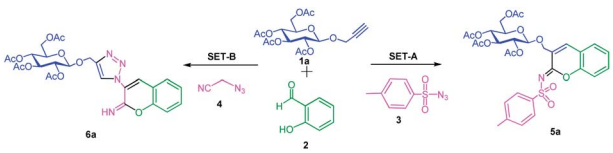
Fig. 3 Selected sugar-derived alkynes for the multicomponent reaction.

mulberroside B,[11c] which exhibits spasmolytic and hypotensive activities.[12] In accord with the intriguing biological profile of coumarins, coumarin glycoside class of scaffold compounds exhibit a broad spectrum of biological activities[13] such as anti-coagulant, anticancer, antibacterial, antifungal activity and they are also useful as fluorescent probes for studies on ultrafast DNA dynamics[14a] as well as inhibitors of the Hsp90.[14b]

In view of the biological and other applications of coumarin and iminocoumarin derivatives, a number reaction conditions have been developed for the synthesis[15,16] of coumarin glycosides. However, most of these methods have several shortcomings, such as a lack of generality or a lack of tolerance to sensitive functional groups. As a consequence, the development of simple methods for the synthesis of iminocoumarin derivatives is thus attractive and challenging. Therefore it was envisaged that linking of an iminocoumarin scaffold to a carbohydrate unit might lead to a new class of glycoconjugates that might have interesting biological profiles. Hence, a facile, one-pot synthesis of iminocoumarin glycosides and 3-triazolyl-2-iminocoumarin – glycosides using sugar alkynes, salicylaldehyde – and sulfonyl azides or 2-azidoacetonitrile is reported herein.

The copper-catalyzed Huisgen[17] cycloaddition reaction or so called "click chemistry" has already earned a great deal of medicinal interest[18] for the preparation of functionalized molecules. Exploiting this phenomenon, several methods have been developed to create functionally diverse classes of compounds using the MCR approach.[19] Similarly, reaction of propargyl glycoside with salicylaldehyde and sulfonyl azide in the presence of CuI and triethylamine, resulted in the formation of the glycosyl iminocoumarin *via* ketenimine intermediate

Table 1 Optimization of reaction conditions for the synthesis of glycosylated iminocoumarins



Entry[a]	Base	Solvent	Catalyst	Time (h) SET-A/B	Yield[b] (%) for **5a**/**6a**
1	TEA	CH_2Cl_2	CuI	10/24	40/29
2	TEA	THF	CuI	3/6	88/76
3	TEA	CH_3CN	CuI	5/10	44/20
4	K_2CO_3	THF	CuI	24/24	—/—
5	Pyridine	THF	CuI	6/24	20/—
6	TEA	THF	CuCl	6/24	40/—
7	DIPEA	THF	CuI	5/24	33/—
8	TEA	EtOH	CuI	10/12	42/55
9	TEA	MeOH	CuI	7/12	25/30
10	TEA	1,4-Dioxane	CuI	7/18	37/33
11	TEA	Toluene	CuI	8/24	31/-
12	DMAP	THF	CuI	24/24	—/—
13	TEA	THF	CuBr	24/24	Trace/—

[a] The reaction was carried out with propargyl glucoside (**1a**, 1.0 mmol), TsN_3 (**3**, 1.0 mmol)/2-azidoacetonitrile (**4**, 1.0 mmol), and salicylaldehyde (**2**, 1.0 mmol) in the presence of CuI (0.1 mmol) and base (2.0 mmol) in the appropriate solvent (5 mL) at r.t. [b] Isolated yields refer to propargyl glucoside (**1a**).

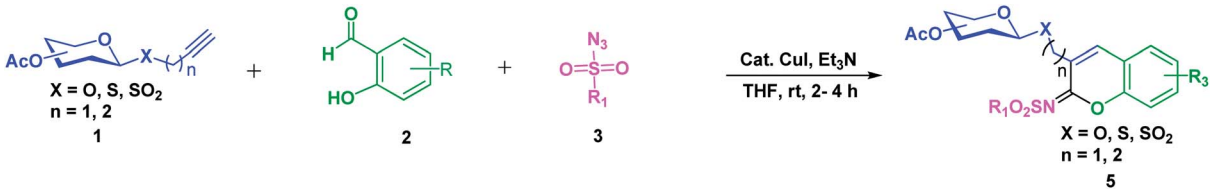
(Scheme 1, SET-A). Moreover, one-pot synthesis of glycosyl 3-triazolyl-2-iminocoumarin has also been achieved directly from the condensation of 2-azidoacetonitrile, propargyl glycoside, and salicylaldehyde in a tandem "CuAAC-aldol-cyclization-dehydration" sequence (Scheme 1, SET-B).

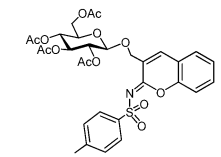
Results and discussion

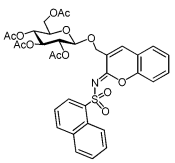
To test this hypothesis, several sugar-derived alkynes (**1a–k**) (Fig. 3) was prepared by the literature procedures.[20] Having prepared these glycosyl alkynes, initially the copper-catalyzed multicomponent reaction has been examined using propargyl glucoside (**1a**, 1.0 mmol) with tosyl azide (**3**, 1.0 mmol) and salicylaldehyde (**2**, 1.0 mmol) in the presence of copper(I) iodide (0.1 mmol) and triethylamine (2.0 mmol) in dichloromethane at room temperature (Table 1, entry 1). The reaction was sluggish and was incomplete even after 10 hours, giving the required product **5a** in only 40% yield.

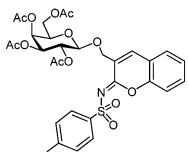
In order to optimize the reaction condition, several conditions have been screened with various solvent systems, bases

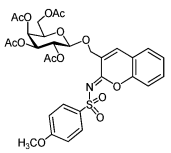
Table 2 Copper-catalyzed synthesis of glycosylated iminocoumarin

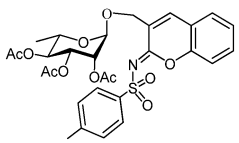


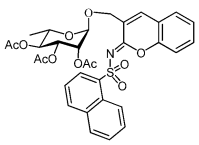

5a (88%)


5b (69%)


5c (87%)


5d (77%)


5e (88%)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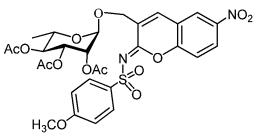
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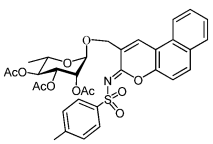
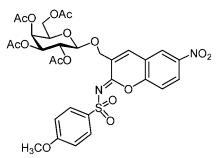

5h (72%)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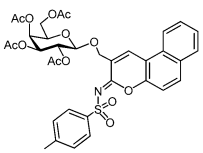
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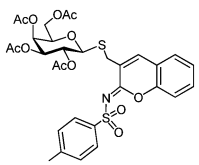
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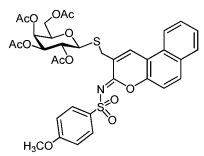
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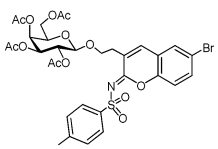
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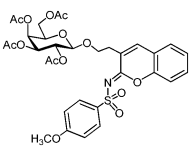
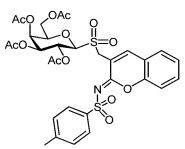
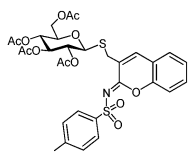

5n (79%)


5o (69%)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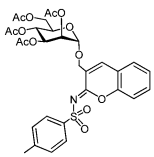
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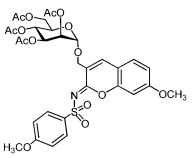
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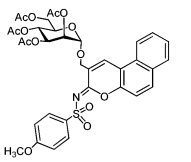
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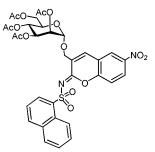
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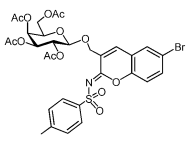
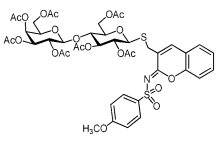

5u (67%)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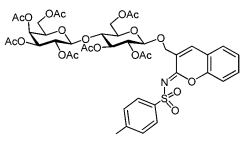
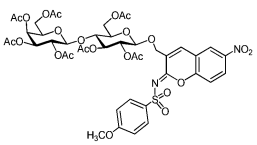

5w (79%)


5x (73%)

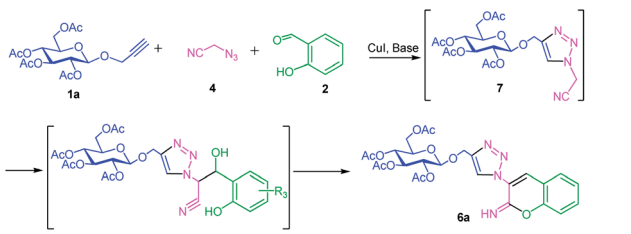
and copper salts (Table 1). When the reaction was performed in tetrahydrofuran (entry 2) for 3 hours, it went nearly to completion, giving the desired glycosyl iminocoumarin **5a** in 88% yield. As shown in Table 1, the desired product could be obtained in 42–44% yield using CH_3CN or EtOH as a solvent (Table 1, entry 3 and 8). Whereas 1,4-dioxane (entry 10) or toluene (entry 11) gave the desired product **5a** in 33% and 31% yield respectively. After the reaction solvent was changed from EtOH to MeOH a significant reduction in isolated product yield 42% and 25% respectively were observed (Table 1, entries 8 and 9).

Although the reason for getting better yields using THF as solvent is not clear, one possibility could be the solvation of copper salts by the THF through the ring oxygen atoms of THF, which improved the accessibility of the copper salts in the reactions. When triethylamine was replaced with pyridine (entry 5) in tetrahydrofuran, the yield of compound **5a** was poor (20%). Furthermore, no reaction was observed in the presence of potassium carbonate (entry 4) or 4-(*N*,*N*-dimethylamino) pyridine (entry 12). However, the required glycosyl iminocoumarin (**5a**) was obtained in a moderate yield (33%) when the reaction was performed in the presence of *N*,*N*-diisopropylethylamine (entry 7). Extensive screening of reaction parameters such as varying base, and solvent led to an optimal reaction condition triethylamine as the base and tetrahydrofuran as the solvent to produce 88% yield of compound **5a**. Next, different copper salts were tested using THF as solvent. When CuCl was used as the catalyst, the yield of the desired product was moderate (40%). However, CuBr failed to catalyze the reaction. Application of CuI as the catalyst resulted in the formation of the desired product in satisfactory yield. Considering the economic aspect and availability, CuI was the best choice for the reactions using other substrates. The reaction optimization experiments are illustrated in Table 1. The reaction condition has been generalized by using a variety of propargyl glycosides, azide and salicylaldehydes to generate a diverse range of products. Once the reaction condition was optimized for the synthesis of **5a**, it was decided to prove the generality of the reaction condition to construct glucosyl iminocoumarin derivatives with different sugar alkynes, salicylaldehyde, and sulfonyl azides. Further 4-methylbenzenesulfonyl azide, naphthalene sulfonyl azide and 4-methoxybenzenesulfonyl azide were also used in the reactions with different sugar alkynes. A series of four different substituted 2-hydroxy benzaldehyde were also investigated. In all the cases, the multicomponent reaction occurred smoothly to give the corresponding glucosyl iminocoumarin derivatives in 64–88% yields. Reactions with propargyl glycosides of deoxy sugars afforded the target compound in 2 h, whereas normal pyranosides are converted completely within 3 h. For *S*-propynyl, and sulfonyl glycosides derivatives, the reactions were completed in approximately 4 h. The time difference for complete reaction can be attributed to the respective reactivity difference among various sugars. Results of these reactions are summarized in Table 2.

Next, it was decided to study the one-pot synthesis of glucosyl 3-triazolyl-2-iminocoumarin (**6a**) directly from the condensation of 2-azidoacetonitrile **4**, propargyl glucoside **1a**, and salicylaldehyde **2** under the optimized conditions (Table 1, entry 2) *via* a tandem "CuAAC–aldol–cyclization–dehydration" sequence (Scheme 2) as "click-and activate nucleophiles" approach toward MCRs. The reaction was complete after 6 hours, giving the required product **6a** in 76% yield (Table 1, entry 2). A number of reaction conditions have been tested for the optimisation of this reaction as shown in Table 1. The desired product could be obtained in 20–55% yield using CH_3CN, CH_2Cl_2, CH_3OH, 1,4-dioxane or EtOH as a solvent (Table 1, entry 1, 3, and 8–10). Furthermore, no reaction was observed in the presence of other bases such as pyridine, K_2CO_3, DMAP and DIPEA.

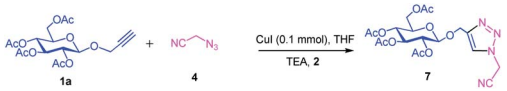
Interestingly, the influence of the third component, salicylaldehyde in the formation of triazole on the CuAAC step has also been observed here (Table 3). The rate of triazole formation was very slow when 1.0 equiv. of propargyl glucoside (**1a**) was added to 2-azidoacetonitrile (**4**) in the presence of CuI (0.1 mol) and (2 equiv.) of triethylamine (7% and 8% isolated yield at 4 h, entries 1 and 4, respectively) and the reaction rate was greatly accelerated by the addition of salicylaldehyde **2** in the presence of triethylamine (entry 2).

A possible explanation for the improved yield of the reaction may be due to the property of salicylaldehyde to act as bidentate ligand in forming a wide variety of Cu complexes with different coordination numbers and geometries.[21] In earlier studies, it was shown that some ligands such as tris-(benzyltriazolylmethyl) amine, tris-(benzimidazole) and tris-(benzothiazole) ligands significantly accelerate the CuAAC reaction *via* activation or stabilization of the catalytic Cu(I) species.[22] So it could be assumed that the deprotonated salicylaldehyde **2** can play a similar

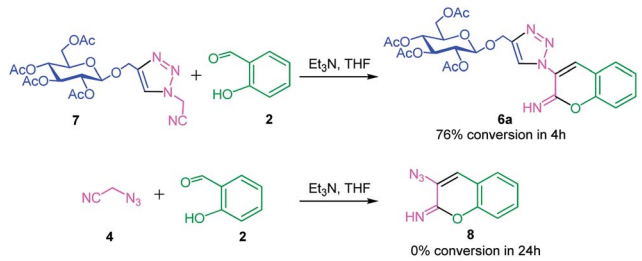


Scheme 2 One-pot synthesis of glucosyl 3-triazolyl-2-iminocoumarins in a tandem "CuAAC-aldol-cyclization-dehydration" sequence.

Table 3 Chelating role on CuAAC reaction



Entry	TEA	 2	Isolated yield of (7) 2 h	4 h
1	0	0	5%	7%
2	1.0 equiv.	0.1 equiv.	55%	82%
3	1.0 equiv.	0	22%	48%
4	0	0.1 equiv.	6%	8%



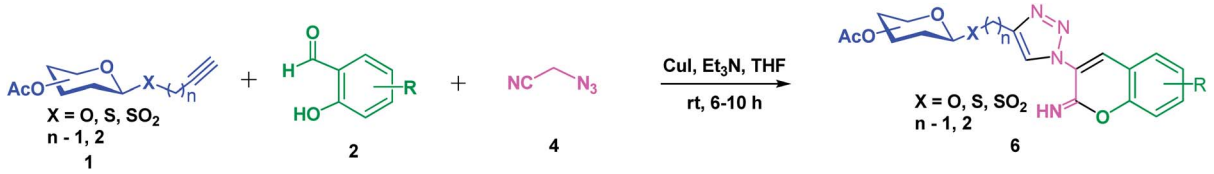
Scheme 3 Control experiments on 2-iminocoumarin formation.

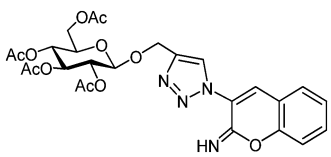
chelating role to promote the reaction, though to a lesser extent. The "click-and-activate" concept was demonstrated in the following control experiments (Scheme 3). Treatment of glucosyl triazole (**7**) with 1.0 equiv. of **2** and 2.0 equiv. of triethylamine in THF led to the formation of 3-triazolyl-2-iminocoumarin (**6a**) in 76% yield in 4 h, whereas 2-azidoacetonitrile (**4**) failed to afford any amount of 3-azido-2-iminocoumarin (**8**) under the same conditions.

Since the reaction condition requires same base and solvent in both steps, it was decided to run the entire three-component condensation in one pot synthesis as follows Table 4.

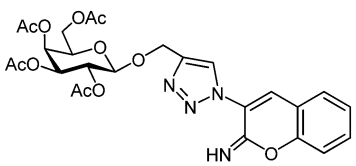
It is worth noting that two rings and four bonds of three different types (*e.g.* one C–C, one C–O, and two C–N bonds) were formed in one pot three component condensation and all four new bonds are formed with 2-azidoacetonitrile (**4**). This three-component reaction provides rapid access to a diverse range of glycosylated 3-triazolyl-2-iminocoumarins by condensing a variety of salicylaldehydes (**2**) and sugar derived alkynes (**1a–k**) with **4** as shown in Table 4. Both electron-donating and electron-withdrawing groups are tolerated at various positions on the salicylaldehyde component.

Table 4 Copper-catalyzed one-pot synthesis of glycosylated 3-triazolyl-2-iminocoumarins

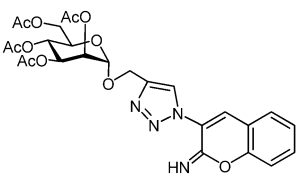




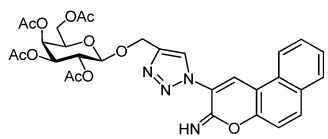
6a (76%)



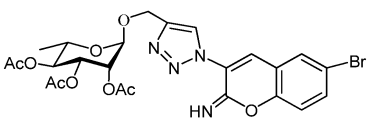
6b (75%)



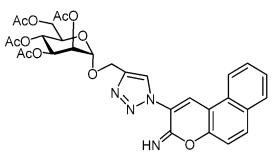
6c (76%)



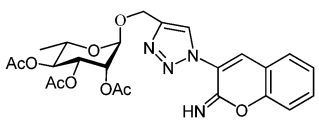
6d (62%)



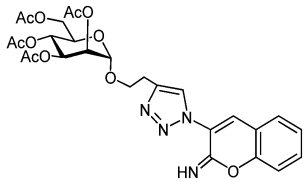
6e (63%)



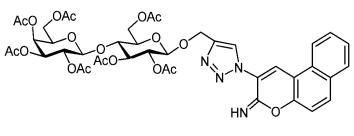
6f (55%)



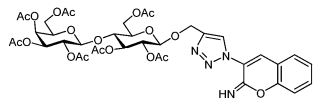
6g (74%)



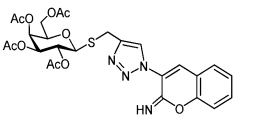
6h (73%)



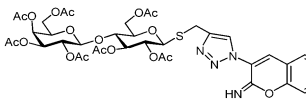
6i (52%)



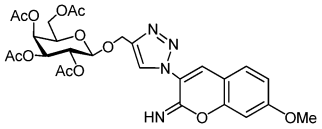
6j (72%)



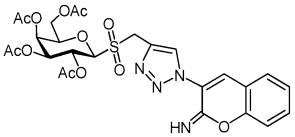
6k (65%)



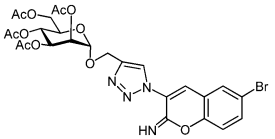
6l (62%)



6m (66%)



6n (56%)



6o (56%)

Conclusions

In summary, synthesis of a variety of glycosyl iminocoumarins and glycosyl 3-triazolyl-2-iminocoumarin derivatives in which the carbohydrate unit is attached to the C-3 carbon of the iminocoumarin skeletons as well as triazole linked iminocoumarins have been achieved in good yield through copper catalysed multicomponent reaction and "click-and-activate nucleophiles" protocol. The resulting glycosyl iminocoumarins can serve as intermediates for the synthesis of the corresponding coumarin glycosides. The present strategy therefore provides a path to the synthesis of a series triazole linked glycosyl iminocoumarins and simple glycosyl iminocoumarins that might have interesting biological profiles.

Experimental

General methods

All reactions were monitored by thin layer chromatography over silica gel-coated TLC plates. The spots on TLC were visualized by warming ceric sulfate [2% $Ce(SO_4)_2$ in 5% H_2SO_4 in EtOH]-sprayed plates on a hot plate. Silica gel 230–400 mesh was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded on Bruker DPX-400 MHz spectrometer. Chemical shifts δ are given in ppm relative to the residual signals of tetramethylsilane in $CDCl_3$ for ^1H and ^{13}C NMR. Coupling constants are given in Hertz. ESI-MS were recorded on a JEOL spectrometer. Elementary analysis was carried out on Carlo ERBA analyzer. IR spectra were recorded on Shimadzu Spectrophotometers. Optical rotations were determined on Autopol III polarimeter. Commercially available grades of organic solvents of adequate purity are used in all reactions.

Typical experimental protocol for the synthesis of 2-propynyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (1a)

To a solution of penta-*O*-acetyl-β-D-glucopyranose (10 g, 25.6 mmol) in anhydrous CH_2Cl_2 (200 mL) was added freshly distilled propargyl alcohol (1.8 mL, 30.7 mmol) and $BF_3 \cdot OEt_2$ (4.8 mL, 38.4 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 6 h. After completion of the reaction, the reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed with saturated aqueous $NaHCO_3$, and water, dried (Na_2SO_4) and concentrated which was crystallised (CH_2Cl_2–hexane) to obtain the compound **1a** (9.10 g, 92%) as a white solid. mp 112–113 °C; $[\alpha]_D^{25}$ −40 (*c* 1.0, $CHCl_3$); IR (KBr): 3060, 2128, 1744, 1633, 1566, 1081, 758, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.26 (t, $J = 9.4$ Hz, 1H), 5.12 (t, $J = 9.5$ Hz, 1H), 5.04 (t, $J = 9.1$ Hz, 1H), 4.80 (d, $J = 8.0$ Hz, 1H), 4.39 (br s, 2H), 4.31–4.27 (m, 1H), 4.18–4.15 (m, 1H), 3.77–3.73 (m, 1H), 4.29 (t, $J = 2.8$ Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.2, 169.4 (2C), 98.1, 78.1, 75.5, 72.8, 71.9, 70.9, 68.3, 61.8, 55.9, 20.7, 20.6, 20.5 (2C); ESI-MS: *m*/*z* 409.1 $[M + Na]^+$. Anal. calcd for $C_{17}H_{22}O_{10}$ (386.12): C, 52.85; H, 5.74. Found: C, 52.74; H, 5.83%.

General procedure for the preparation of compound (5a–x)

To a solution of carbohydrate-derived alkyne (1.0 mmol), TsN_3 (1.0 mmol), CuI (0.1 mmol), and salicylaldehyde (1.0 mmol) in THF (5 mL) was dropwise added Et_3N (2.0 mmol) at room temperature and the mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated and the residue was diluted with CH_2Cl_2 (20 mL) and washed successively with H_2O (10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane–EtOAc; 1 : 1) to give the corresponding glycosyl iminocoumarin derivative.

Data for 5a. White solid; yield 88% (580 mg); mp 110–3112 °C; $[\alpha]_D^{25}$ +110 (*c* 1.0, $CHCl_3$); IR (KBr): 3019, 2400, 1754, 1564, 1403, 1320, 1043, 927, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, $J = 8.3$ Hz, 2H), 7.68 (s, 1H), 7.49–7.44 (m, 2H), 7.33 (d, $J = 8.1$ Hz, 1H), 7.29–7.25 (m, 3H), 5.14 (t, $J = 9.5$ Hz, 1H), 5.06–4.99 (m, 2H), 4.69 (dd, $J = 1.4$, 15.4 Hz, 1H), 4.57 (d, $J = 8.0$ Hz, 1H), 4.46 (dd, $J = 1.4$, 15.4 Hz, 1H), 4.20 (dd, $J = 4.8$, 12.4 Hz, 1H), 4.03 (dd, $J = 2.3$, 12.4 Hz, 1H), 3.64–3.59 (m, 1H), 2.34 (s, 3H), 1.97 (s, 6H), 1.96 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.1, 169.5, 169.4, 156.0, 151.9, 143.5, 138.7, 137.6, 131.9, 129.3 (2C), 128.3, 127.6 (2C), 126.1, 125.9, 119.2, 116.4, 100.9, 72.6, 72.0, 71.3, 68.2, 66.3, 61.7, 21.6, 20.7, 20.6, 20.5 (2C); ESI-MS: *m*/*z* 660.0 $[M + H]^+$. Anal. calcd for $C_{31}H_{33}NO_{13}S$ (659.16): C, 56.44; H, 5.04. Found: C, 56.27; H, 5.25%.

Data for 5b. White solid; yield 69% (480 mg); mp 115–116 °C; $[\alpha]_D^{25}$ +109 (*c* 1.0, $CHCl_3$); IR (KBr): 3023, 2403, 1750, 1633, 1564, 1380, 1219, 1046, 759, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, $J = 8.6$ Hz, 1H), 8.48 (d, $J = 7.4$ Hz, 1H), 7.99 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.66 (s, 1H), 7.58–7.54 (m, 2H), 7.50–7.39 (m, 3H), 7.27–7.17 (m, 2H), 5.07–4.97 (m, 3H), 4.67 (d, $J = 15.4$, 1H), 4.49 (d, $J = 7.4$ Hz, 1H), 4.43 (d, $J = 15.3$ Hz, 1H), 4.12 (dd, $J = 4.6$, 12.6 Hz, 1H), 3.97 (dd, $J = 1.6$, 12.4 Hz, 1H), 3.50–3.47 (m, 1H), 1.96 (s, 3H), 1.94 (s, 3H), 1.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.1, 169.5, 169.4, 156.4, 151.9, 137.9, 137.4, 134.2, 134.1, 131.9, 128.7 (2C), 128.6, 128.3, 127.9, 126.7, 126.0, 125.9, 125.7, 124.2, 119.1, 116.3, 100.9, 72.6, 71.9, 71.2, 68.2, 66.3, 61.7, 20.8, 20.7, 20.6 (2C); ESI-MS: *m*/*z* 696.0 $[M + H]^+$. Anal. calcd for $C_{34}H_{33}NO_{13}S$ (695.16): C, 58.70; H, 4.78. Found: C, 58.58; H, 4.90%.

Data for 5c. White solid; yield 87% (573 mg); mp 95–97 °C; $[\alpha]_D^{25}$ +89 (*c* 1.0, $CHCl_3$); IR (KBr): 3022, 2403, 1748, 1633, 1566, 1454, 1219, 1153, 1081, 759, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.71 (s, 1H), 7.49–7.44 (m, 2H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.29–7.24 (m, 3H), 5.34 (d, $J = 3.4$ Hz, 1H), 5.24 (dd, $J = 8.0$,10.3 Hz, 1H), 4.97 (dd, $J = 3.5$,10.4 Hz, 1H), 4.70 (dd, $J = 1.3$, 15.6 Hz, 1H), 4.56 (d, $J = 8.0$ Hz, 1H), 4.45 (dd, $J = 1.4$, 15.4 Hz, 1H), 4.07 (d, $J = 6.7$ Hz, 2H), 3.86 (t, $J = 6.6$ Hz, 1H), 2.33 (s, 3H), 2.08 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 169.9, 169.6, 155.9, 151.9, 143.5, 138.7, 137.6, 131.9, 129.3 (2C), 128.3, 127.6 (2C), 126.1, 125.9, 119.2, 116.4, 101.4, 70.9, 70.7, 68.9, 67.0, 66.2, 61.2, 21.5, 20.8, 20.6 (2C), 20.5; ESI-MS: *m*/*z* 660.0 $[M + H]^+$. Anal. calcd for $C_{31}H_{33}NO_{13}S$ (659.16): C, 56.44; H, 5.04. Found: C, 56.28; H, 5.22%.

Data for 5d. Solid; yield 77% (520 mg); mp 105–107 °C; $[\alpha]_D^{25}$ +98 (*c* 1.0, $CHCl_3$); IR (KBr): 3021, 2268, 1633, 1566, 1454, 1219, 1081, 758, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.9 Hz, 2H), 7.69 (s, 1H), 7.49–7.44 (m, 2H), 7.35–7.25 (m, 2H), 6.92 (d, J = 8.9 Hz, 2H), 5.34 (d, J = 3.3 Hz, 1H), 5.24 (dd, J = 7.9, 10.5 Hz, 1H), 4.98 (dd, J = 3.5, 10.5 Hz, 1H), 4.72 (dd, J = 1.4, 15.3 Hz, 1H), 4.57 (d, J = 7.9 Hz, 1H), 4.45 (dd, J = 1.3, 15.3 Hz, 1H), 4.07 (d, J = 6.2 Hz, 1H), 3.88–3.85 (m, 1H), 3.77 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 169.9, 169.7, 162.9, 155.8, 151.9, 137.4, 133.8, 131.9, 129.8 (2C), 128.3, 126.1, 125.9, 119.2, 116.3, 113.9 (2C), 101.4, 70.9, 70.7, 68.9, 67.0, 66.3, 61.2, 55.6, 20.8, 20.6 (2C), 20.5; ESI-MS: m/z 676.0 $[M + H]^+$. Anal. calcd for $C_{31}H_{33}NO_{14}S$ (675.16): C, 55.11; H, 4.92. Found: C, 55.01; H, 5.03%.

Data for 5e. Solid; yield 88% (529 mg); mp 85–87 °C; $[\alpha]_D^{25}$ +77 (*c* 1.0, $CHCl_3$); IR (KBr): 3021, 2402, 1632, 1568, 1485, 1405, 1218, 1083, 927, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.2 Hz, 2H), 7.72 (s, 1H), 7.49–7.46 (m, 2H), 7.33–7.23 (m, 4H), 5.29–5.26 (m, 2H), 5.03 (t, J = 9.5 Hz, 1H), 4.79 (br s, 1H), 4.59 (d, J = 15.2 Hz, 1H), 4.31 (d, J = 15.3 Hz, 1H), 3.91–3.84 (m, 1H), 2.32 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H), 1.16 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 170.1, 169.9, 156.1, 152.0, 143.5, 138.6, 137.5, 132.0, 129.3 (2C), 128.4, 127.6 (2C),125.9, 125.8, 119.0, 116.3, 97.4, 70.8, 69.6, 69.1, 66.9, 63.9, 21.5, 20.9, 20.8, 20.7, 17.4; ESI-MS: m/z 602.0 $[M + H]^+$. Anal. calcd for $C_{29}H_{31}NO_{11}S$ (601.16): C, 57.90; H, 5.19. Found: C, 57.76; H, 5.31%.

Data for 5f. Light yellow syrup; yield 69% (440 mg); $[\alpha]_D^{25}$ +57 (*c* 1.0, $CHCl_3$); IR (neat): 3020, 1744,1634, 1553, 1515, 1466, 1218, 1048, 770, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, J = 8.6 Hz, 1H), 8.47 (d, J = 7.4 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.66 (s, 1H), 7.55–7.50 (m, 2H), 7.46–7.36 (m, 3H), 7.21–7.17 (m, 1H), 7.12 (d, J = 8.2 Hz, 1H), 5.28–5.24 (m, 2H), 5.02 (t, J = 9.6 Hz, 1H), 4.75 (br s, 1H), 4.56 (dd, J = 1.3, 15.2 Hz, 1H), 4.28 (dd, J = 1.3, 15.2 Hz, 1H), 3.84–3.77 (m, 1H), 2.06 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H), 1.11 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 170.1, 169.9, 156.4, 151.9, 137.8, 137.4, 134.1, 134.0, 132.0, 128.7, 128.6, 128.5, 128.3, 127.9, 126.7, 125.9, 125.7, 125.6, 124.1, 118.9, 116.2, 97.3, 70.8, 69.5, 69.1, 66.9, 63.8, 20.9, 20.8, 20.7, 17.3; ESI-MS: m/z 638.0 $[M + H]^+$. Anal. calcd for $C_{32}H_{31}NO_{11}S$ (637.16): C, 60.27; H, 4.90. Found: C, 60.16; H, 5.05%.

Data for 5g. Solid; yield 70% (463 mg); mp 90–92 °C; $[\alpha]_D^{25}$ +67 (*c* 1.0, $CHCl_3$); IR (KBr): 3017, 2363, 1659, 1610, 1512, 1436, 1246, 1091, 759, 601 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (dd, J = 2.8, 9.0 Hz, 1H), 7.92 (d, J = 9.1 Hz, 2H), 7.81 (s, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 9.1 Hz, 1H), 6.84 (d, J = 9.1 Hz, 2H), 5.29–5.26 (m, 2H), 5.03 (t, J = 9.6 Hz, 1H), 4.80 (br s, 1H), 4.56 (d, J = 15.4 Hz, 1H), 4.31 (d, J = 15.5 Hz, 1H), 3.87–3.82 (m, 1H), 3.79 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H), 1.16 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2 (2C), 169.9, 163.3, 154.8, 154.1, 144.8, 135.6, 132.5, 129.7, 128.7, 128.4, 126.5, 124.0, 119.3, 117.7, 114.1 (2C), 97.5, 70.7, 69.5, 69.1, 67.1, 63.8, 55.7, 20.8, 20.7 (2C), 17.4; ESI-MS: m/z 685.1 $[M + Na]^+$. Anal. calcd for $C_{29}H_{30}N_2O_{14}S$ (662.14): C, 52.57; H, 4.56. Found: C, 52.43; H, 4.66%.

Data for 5h. Yellow oil; yield 72% (469 mg); $[\alpha]_D^{25}$ +69 (*c* 1.0, $CHCl_3$); IR (neat): 3018, 2363, 1748, 1636, 1553, 1466, 1405, 1218, 1085, 770, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.23 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 9.1 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.67–7.63 (m, 1H), 7.54–7.49 (m, 1H), 7.40 (d, J = 9.1 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 5.39–5.36 (m, 2H), 5.07 (t, J = 9.7 Hz, 1H), 4.86 (br s, 1H), 4.68 (dd, J = 1.3, 15.3 Hz, 1H), 4.39 (dd, J = 1.2, 15.3 Hz, 1H), 3.95–3.88 (m, 1H), 2.33 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.18 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 169.9, 156.1, 151.7, 143.4, 138.9, 133.4, 133.3, 130.7, 129.3 (2C), 128.9, 128.8, 128.6, 127.6 (2C), 126.8, 125.1, 121.8, 115.8, 113.8, 97.3, 70.9, 69.8, 69.1, 67.2, 64.1, 21.6, 20.9, 20.8 (2C), 17.4; ESI-MS: m/z 651.9 $[M + H]^+$. Anal. calcd for $C_{33}H_{33}NO_{11}S$ (651.17): C, 60.82; H, 5.10. Found: C, 60.71; H, 5.22%.

Data for 5i. White solid; yield 73% (526 mg); mp 120–122 °C; $[\alpha]_D^{25}$ −78 (*c* 1.0, $CHCl_3$); IR (KBr): 3020, 2328, 1629, 1564, 1216, 1159, 1086, 1020, 909, 759, 677 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.38–8.31 (m, 2H), 7.94 (d, J = 9.0 Hz, 2H), 7.76 (s, 1H), 7.51 (d, J = 9.0 Hz, 1H), 6.95 (d, J = 9.0 Hz, 2H), 5.35 (d, J = 3.4 Hz, 1H), 5.24 (dd, J = 8.0, 10.4 Hz, 1H), 4.99 (dd, J = 3.4, 10.5 Hz, 1H), 4.70 (dd, J = 1.4, 15.3 Hz, 1H), 4.56 (d, J = 8.0 Hz, 1H), 4.42 (dd, J = 1.3, 15.5 Hz, 1H), 4.07 (t, J = 6.3 Hz, 2H), 3.87 (t, J = 6.8 Hz, 1H), 3.80 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 170.3, 169.7, 163.3, 154.8, 153.9, 144.9, 135.5, 132.7, 129.7 (2C), 128.9, 126.4, 123.9, 119.5, 117.7, 114.1 (2C), 101.2, 70.9, 70.6, 68.8, 66.9, 65.7, 61.1, 55.7, 20.8, 20.7 (2C), 20.6; ESI-MS: m/z 721.0 $[M + H]^+$. Anal. calcd for $C_{31}H_{32}N_2O_{16}S$ (720.14): C, 51.67; H, 4.48. Found: C, 51.58; H, 4.63%.

Data for 5j. White foam; yield 72% (510 mg); $[\alpha]_D^{25}$ −44 (*c* 1.0, $CHCl_3$); IR (neat): 3020, 2326, 1633, 1560, 1457, 1383, 1318, 1255, 1214, 1160, 1086, 1070, 1002, 905, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.34 (d, J = 8.4 Hz, 1H), 7.97–7.93 (m, 3H), 7.85 (d, J = 8.4 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.26 (d, J = 7.8 Hz, 2H), 5.38–5.31 (m, 2H), 5.03 (dd, J = 3.3, 10.5 Hz, 1H), 4.87 (d, J = 15.5 Hz, 1H), 4.61 (d, J = 8.1 Hz, 1H), 4.49 (d, J = 15.4 Hz, 1H), 4.11–4.09 (m, 2H), 3.89 (t, J = 6.5 Hz, 1H), 2.34 (s, 3H), 2.11 (s, 3H), 1.96 (s, 6H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 170.0 (2C), 155.9, 151.6, 143.4, 138.9, 133.6, 133.3, 130.8, 129.3 (2C), 128.9, 128.8, 128.7, 127.6 (2C), 126.8, 125.5, 121.9, 115.9, 114.2, 101.6, 71.0, 70.5, 69.2, 67, 3, 67.0, 66.6, 61.3, 21.6, 20.9, 20.7 (2C), 20.5; ESI-MS: m/z 710.0 $[M + H]^+$. Anal. calcd for $C_{35}H_{35}NO_{13}S$ (709.18): C, 59.23; H, 4.97. Found: C, 59.11; H, 5.15%.

Data for 5k. Light yellow syrup; yield 72% (486 mg); $[\alpha]_D^{25}$ +54 (*c* 1.0, $CHCl_3$); IR (neat): 3020, 2403,1634, 1549, 1515, 1465, 1218, 1152, 1042, 759, 678 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.6 Hz, 2H), 7.68 (s, 1H), 7.50–7.36 (m, 3H), 7.29–7.24 (m, 3H), 5.31 (d, J = 3.1 Hz, 1H), 5.12 (t, J = 9.9 Hz, 1H), 4.90 (dd, J = 3.3, 9.9 Hz, 1H), 4.64 (d, J = 10.0 Hz, 1H), 3.97–3.95 (m, 2H), 3.78–3.66 (m, 3H), 2.36 (s, 3H), 2.07 (s, 3H), 1.98 (s, 3H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 169.9, 169.7, 157.6, 152.1, 143.5, 139.5, 138.9, 132.1, 129.4 (2C), 127.9, 127.5 (2C), 125.9, 119.2, 116.5 (2C), 84.5, 74.3, 71.7, 67.4, 67.2, 61.3,

29.9, 21.5, 20.8, 20.7, 20.6, 20.5; ESI-MS: *m*/*z* 676.0 $[M + H]^+$. Anal. calcd for $C_{31}H_{33}NO_{12}S_2$ (675.14): C, 55.10; H, 4.92. Found: C, 54.97; H, 5.03%.

Data for 5l. Yellow oil; yield 66% (489 mg); $[\alpha]_D^{25}$ +34 (*c* 1.0, $CHCl_3$); IR (neat): 3019, 2400, 1664, 1553, 1405, 1215, 1086, 756, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.5 Hz, 2H), 7.96–7.85 (m, 2H), 7.66–7.52 (m, 2H), 7.49 (d, J = 8.6 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 5.31 (d, J = 3.1 Hz, 1H), 5.15 (t, J = 9.7 Hz, 1H), 4.93 (dd, J = 3.2, 10.0 Hz, 1H), 4.72 (d, J = 10.0 Hz, 1H), 3.95 (dd, J = 3.5, 6.6 Hz, 1H), 3.82–3.77 (m, 3H), 3.80 (s, 3H), 3.71 (t, J = 6.6 Hz, 1H), 2.07 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 169.9, 169.8, 157.5, 151.8, 144.9, 139.2, 135.5, 133.7, 133.4, 131.3, 130.8, 129.6 (2C), 129.2, 128.6, 126.8, 121.5, 116.1, 115.1, 113.9 (2C), 84.8, 74.3, 71.7, 67.5, 67.2, 61.3, 55.6, 30.3, 20.8, 20.7, 20.6, 20.5; ESI-MS: *m*/*z* 742.0 $[M + H]^+$. Anal. calcd for $C_{35}H_{35}NO_{13}S_2$ (741.15): C, 56.67; H, 4.76. Found: C, 56.53; H, 4.88%.

Data for 5m. Light brown oil; yield 82% (616 mg); $[\alpha]_D^{25}$ −115 (*c* 1.0, $CHCl_3$); IR (neat): 3020, 2403,1664, 1612, 1599, 1533, 1460, 1218, 1134, 1072, 909, 680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 2.3 Hz, 1H), 7.62–7.58 (m, 1H), 7.51 (s, 1H), 7.34–7.28 (m, 3H), 5.37 (d, J = 3.2 Hz, 1H), 5.13 (dd, J = 8.0, 10.6 Hz, 1H), 4.97 (dd, J = 3.4, 10.5 Hz, 1H), 4.42 (d, J = 8.0 Hz, 1H), 4.15–4.05 (m, 3H), 3.86 (t, J = 6.6 Hz,1H), 3.77–3.72 (m, 1H), 2.90–2.76 (m, 2H), 2.42 (s, 3H), 2.13 (s, 3H), 2.05 (s, 3H), 1.96 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.1, 170.0, 169.3, 157.4, 150.9, 143.5, 139.4, 138.9, 134.2, 130.3, 129.4 (2C), 127.9, 127.3 (2C), 121.2, 118.3, 117.9, 101.0, 70.7 (2C), 68.8, 66.9, 66.6, 61.2, 31.2, 21.5, 20.7, 20.6, 20.5, 20.4; ESI-MS: *m*/*z* 752.1 $[M + H]^+$. Anal. calcd for $C_{32}H_{34}BrNO_{13}S$ (751.09): C, 51.07; H, 4.55. Found: C, 50.91; H, 4.69%.

Data for 5n. White foam; yield 79% (544 mg); $[\alpha]_D^{25}$ −27 (*c* 1.0, $CHCl_3$); IR (neat): 3020, 2230, 1636, 1569, 1458, 1375, 1303, 1216, 1158, 1086, 837, 677 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 9.0 Hz, 2H), 7.59 (s, 1H), 7.52 (d, J = 7.6 Hz, 2H), 7.40–7.31 (m, 2H), 7.01 (d, J = 9.0 Hz, 2H), 5.37 (d, J = 3.1 Hz, 1H), 5.14 (dd, J = 8.0, 10.6 Hz, 1H), 4.99 (dd, J = 3.4, 10.4 Hz, 1H), 4.46 (d, J = 8.0 Hz, 1H), 4.13–4.10 (m, 3H), 3.90 (t, J = 6.6 Hz, 1H), 3.85 (s, 3H), 3.83–3.76 (m, 1H), 2.93–2.77 (m, 2H), 2.12 (s, 3H), 2.05 (s, 3H), 1.95 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.1, 169.9, 169.3, 162.9, 157.9, 152.1, 140.7, 133.6, 131.5, 12.6 (2C), 128.0, 126.5, 125.6, 119.6, 116.1, 113.8 (2C), 101.0, 70.7, 70.6, 68.8, 67.0, 66.8, 61.6, 55.6, 31.2, 20.6, 20.5, 20.4, 20.3; ESI-MS: *m*/*z* 690.0 $[M + H]^+$. Anal. calcd for $C_{32}H_{35}NO_{14}S$ (689.17): C, 55.73; H, 5.12. Found: C, 55.59; H, 5.25%.

Data for 5o. Yellow syrup; yield 69% (488 mg); $[\alpha]_D^{25}$ +37 (*c* 1.0, $CHCl_3$); IR (neat): 3010, 2330, 1736, 1669, 1530, 1458, 1365, 1213, 1158, 1036, 877, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.3 Hz, 2H), 7.92 (s, 1H), 7.60–7.54 (m, 2H), 7.37–7.33 (m, 4H), 5.74 (t, J = 9.8 Hz, 1H), 5.44 (d, J = 3.3 Hz, 1H), 5.14 (dd, J = 3.4, 10.0 Hz, 1H), 4.92 (d, J = 10.0 Hz, 1H), 4.85 (d, J = 14.6 Hz, 1H), 4.16–4.09 (m, 4H), 2.41 (s, 3H), 2.13 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 169.8, 169.1, 157.3, 152.5, 145.1, 144.1, 138.2, 133.2, 129.6 (2C), 128.9, 127.7 (2C), 126.3, 118.9, 117.9, 116.4, 88.9, 75.1, 71.4, 66.8, 63.2, 60.9, 51.9, 21.5, 20.7 (2C), 20.6, 20.5; ESI-MS: *m*/*z* 707.9 $[M + H]^+$. Anal. calcd for $C_{31}H_{33}NO_{14}S_2$ (707.13): C, 52.61; H, 4.70. Found: C, 52.54; H, 4.79%.

Data for 5p. Yellow oil; yield 65% (439 mg); $[\alpha]_D^{25}$ +22 (*c* 1.0, $CHCl_3$); IR (neat): 3021, 2229, 1628, 1574, 1455, 1375, 1321, 1259, 1089, 1019, 911, 838, 759, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.4 Hz, 2H), 7.68 (s, 1H), 7.51–7.36 (m, 3H), 7.29 (d, J = 8.3 Hz, 3H), 5.06–4.88 (m, 3H), 4.65 (d, J = 10.0 Hz, 1H), 4.11 (dd, J = 4.7, 12.4 Hz, 1H), 3.95 (dd, J = 1.4, 12.5 Hz, 1H), 3.70 (dd, J = 14.5 Hz, 2H), 3.50–3.46 (m, 1H), 2.36 (s, 3H), 1.95 (s, 6H), 1.93 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.1, 169.5, 169.4, 157.6, 152.1, 143.5, 139.6, 138.9, 132.1, 129.4 (2C), 127.9, 127.6, 127.5 (2C), 125.9, 119.3, 116.5, 84.1, 75.6, 73.7, 70.2, 68.1, 61.9, 29.8, 21.6, 20.7, 20.6, 20.5 (2C); ESI-MS: *m*/*z* 676.0 $[M + H]^+$. Anal. calcd for $C_{31}H_{33}NO_{12}S_2$ (675.14): C, 55.10; H, 4.92. Found: C, 54.98; H, 5.03%.

Data for 5q. White foam; yield 85% (560 mg); $[\alpha]_D^{25}$ −33 (*c* 1.0, $CHCl_3$); IR (neat): 3010, 2368, 1635, 1561, 1375, 1216, 1158, 1086, 1051, 968, 677 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.2 Hz, 2H), 7.72 (s, 1H), 7.51–7.47 (m, 2H), 7.35–7.23 (m, 4H), 5.34–5.22 (m, 3H), 4.87 (br s, 1H), 4.61 (d, J = 15.1 Hz, 1H), 4.29 (d, J = 15.3 Hz, 1H), 4.26–4.21 (m, 1H), 4.06–4.01 (m, 2H), 2.33 (s, 3H), 2.09 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.1, 170.0, 169.7, 156.1, 152.1, 143.5, 138.7, 137.9, 132.1, 129.5 (2C), 128.4, 127.6 (2C), 125.9, 125.5, 18.9, 116.4, 97.5, 69.3, 69.1, 69.0, 65.9, 64.2, 62.3, 21.5, 20.8, 20.7, 20.6 (2C); ESI-MS: *m*/*z* 659.9 $[M + H]^+$. Anal. calcd for $C_{31}H_{33}NO_{13}S$ (659.16): C, 56.44; H, 5.04. Found: C, 56.27; H, 5.25%.

Data for 5r. White solid; yield 81% (571 mg); mp 96–98 °C; $[\alpha]_D^{25}$ −43 (*c* 1.0, $CHCl_3$); IR (KBr): 3022, 2363, 1747, 1633, 1554, 1376, 1218, 1051, 758, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.9 Hz, 2H), 7.65 (s, 1H), 7.39 (d, J = 9.2 Hz, 1H), 6.91 (d, J = 9.1 Hz, 2H), 6.86–6.83 (m, 2H), 5.32–5.21 (m, 3H), 4.86 (br s, 1H), 4.57 (d, J = 14.5 Hz, 1H), 4.27–4.20 (m, 2H), 4.06–3.99 (m, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 2.09 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.1, 170.0, 169.7, 163.1, 162.9, 156.4, 153.9, 138.3, 133.7, 129.5 (2C), 129.3, 121.8, 114.3, 113.8 (2C), 112.7, 100.5, 97.5, 69.4, 69.1, 68.9, 65.9, 64.3, 62.2, 56.1, 55.6, 20.8, 20.7 (3C); ESI-MS: *m*/*z* 706.0 $[M + H]^+$. Anal. calcd for $C_{32}H_{35}NO_{15}S$ (705.17): C, 54.46; H, 5.00. Found: C, 54.34; H, 5.15%.

Data for 5s. Solid; yield 75% (544 mg); mp 99–101 °C; $[\alpha]_D^{25}$ +66 (*c* 1.0, $CHCl_3$); IR (KBr): 3024, 2363,1664, 1622, 1599, 1460, 1218, 1134, 1072, 872, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.22 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 9.1 Hz, 1H), 7.83 (d, J = 8.3 Hz, 1H), 7.68–7.64 (m, 1H), 7.54–7.51 (m, 1H), 7.42 (d, J = 9.0 Hz, 1H), 6.93 (d, J = 9.0 Hz, 2H), 5.41 (dd, J = 3.4, 10.0 Hz, 1H), 5.35 (dd, J = 1.6, 3.5 Hz, 1H), 5.28 (t, J = 9.8 Hz, 1H), 4.94 (br s, 1H), 4.69 (d, J = 15.1 Hz, 1H), 4.38 (d, J = 15.1 Hz, 1H), 4.26 (dd, J = 8.2, 8.5 Hz, 1H), 4.12–4.04 (m, 2H), 3.77 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.2, 170.0, 169.7, 162.9, 155.9, 151.8, 133.7, 133.5, 133.4, 130.7, 129.7 (2C), 129.1, 128.8, 128.6, 126.8, 124.8, 121.7, 115.9, 113.9 (2C), 113.7, 97.4, 69.5, 69.2, 69.1, 65.9, 64.4, 62.3, 55.6, 20.9, 20.8, 20.7 (2C); ESI-

MS: *m*/*z* 725.9 $[M + H]^+$. Anal. calcd for $C_{35}H_{35}NO_{14}S$ (725.17): C, 57.93; H, 4.86. Found: C, 57.82; H, 4.99%.

Data for 5t. Yellow oil; yield 72% (533 mg); $[\alpha]_D^{25}$ +57 (*c* 1.0, $CHCl_3$); IR (neat): 3016, 2854, 2104, 1561, 1455, 1216, 1160, 1089, 853, 760, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, $J = 9.0$ Hz, 1H), 8.43–8.38 (m, 2H), 8.29–8.25 (m, 1H), 8.00 (d, $J = 8.2$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.77 (s, 1H), 7.58–7.47 (m, 3H), 7.35 (d, $J = 9.1$ Hz, 1H), 5.31–5.26 (m, 2H), 5.22 (t, $J = 9.4$ Hz, 1H), 4.82 (br s, 1H), 4.53 (d, $J = 15.3$ Hz, 1H), 4.26 (d, $J = 15.4$ Hz, 1H), 4.15 (dd, $J = 4.3$, 5.4 Hz, 1H), 3.95–3.88 (m, 2H), 2.08 (s, 3H), 1.96 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.1 (2C), 169.6, 154.7, 154.6, 144.9, 136.7, 135.9, 134.5, 134.2, 128.9, 128.6, 128.5, 128.2, 128.1, 126.9, 126.5, 125.2, 124.1, 123.9, 119.2, 117.6, 97.5, 69.1 (2C), 68.9, 65.8, 6.8, 62.1, 20.8, 20.7 (2C), 20.6; ESI-MS: *m*/*z* 741.0 $[M + H]^+$. Anal. calcd for $C_{34}H_{32}N_2O_{15}S$ (740.15): C, 55.13; H, 4.35. Found: C, 55.01; H, 4.46%.

Data for 5u. Yellow oil; yield 67% (494 mg); $[\alpha]_D^{25}$ +77 (*c* 1.0, $CHCl_3$); IR (KBr): 3009, 2303, 1643, 1506, 1414, 1209, 1081, 998, 759, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.78 (s, 1H), 7.71 (br s, 1H), 7.47–7.46 (m, 1H), 7.27–7.24 (m, 3H), 5.35 (d, $J = 3.3$ Hz, 1H), 5.25 (dd, $J = 8.0$, 10.4 Hz, 1H), 4.99 (dd, $J = 3.3$,10.2 Hz, 1H), 4.74 (dd, $J = 1.3$, 15.4 Hz, 1H), 4.57 (d, $J = 8.0$ Hz, 1H), 4.47 (dd, $J = 1.5$, 15.1 Hz, 1H), 4.09–4.06 (m, 2H), 3.87 (t, $J = 6.6$ Hz, 1H), 2.34 (s, 3H), 2.09 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.93(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.1, 169.9, 169.3, 157.4, 150.8, 143.4, 138.8 (2C), 134.1, 130.2, 130.1 (2C), 127.7, 127.8 (2C), 121.1, 118.2, 119.9, 100.9, 70.6 (2C), 68.8, 66.9, 66.5, 61.1, 21.5, 20.6 (2C), 20.4 (2C); ESI-MS: *m*/*z* 738.2 $[M + H]^+$. Anal. calcd for $C_{31}H_{32}BrNO_{13}S$ (737.07): C, 50.41; H, 4.37. Found: C, 50.32; H, 4.44%.

Data for 5v. Brown oil; yield 64% (627 mg); $[\alpha]_D^{25}$ +28 (*c* 1.0, $CHCl_3$); IR (neat): 3022, 2603, 1749, 1654, 1599, 1498, 1381, 1219, 1157, 1044, 758, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, $J = 8.7$ Hz, 2H), 7.68 (s, 1H), 7.51–7.37 (m, 3H), 7.29–7.25 (m, 1H), 6.96 (d, $J = 8.5$ Hz, 2H), 5.27 (d, $J = 3.2$ Hz, 1H), 5.08–4.99 (m, 2H), 4.97–4.86 (m, 2H), 4.53 (d, $J = 10.0$ Hz, 1H), 4.43 (d, $J = 8.0$ Hz, 1H), 4.34 (11.7 Hz, 1H), 4.03–3.99 (m, 2H), 3.84–3.77 (m, 3H), 3.80 (s, 3H), 3.68–3.64 (m, 1H), 3.58–3.55 (m, 1H), 3.48–3.44 (m, 1H), 2.07 (s, 3H), 1.98 (s, 6H), 1.96 (s, 6H), 1.89 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.1 (2C), 170.0, 169.7, 169.6, 169.2, 162.9, 157.5, 152.0, 139.5, 133.5, 131.9, 129.5 (2C), 128.1, 127.9, 125.8, 119.3, 116.5, 113.9 (2C), 100.9, 83.6, 76.6, 75.9, 73.5, 71.0, 70.6, 70.1, 69.0, 66.7, 62.2, 60.7, 55.6, 29.1, 20.8, 20.7, 20.6 (4C), 20.5; ESI-MS: *m*/*z* 980.0 $[M + H]^+$. Anal. calcd for $C_{43}H_{49}NO_{21}S_2$ (979.22): C, 52.70; H, 5.04. Found: C, 52.58; H, 5.13%.

Data for 5w. White solid; yield 79% (748 mg); mp 121–123 °C; $[\alpha]_D^{25}$ −88 (*c* 1.0, $CHCl_3$); IR (KBr): 3023, 2373,1749, 1634, 1566, 1376, 1253, 1221, 1056, 904, 758, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, $J = 8.1$ Hz, 2H), 7.66 (s, 1H), 7.50–7.43 (m, 2H), 7.36–7.25 (m, 4H), 5.28 (d, $J = 2.7$ Hz, 1H), 5.13 (t, $J = 9.3$ Hz, 1H), 5.04 (dd, $J = 8.1$, 10.4 Hz, 1H), 4.97–4.87 (m, 2H), 4.64 (dd, $J = 1.7$, 15.2 Hz, 1H), 4.53 (d, $J = 8.1$ Hz, 1H), 4.56–4.37 (m, 3H), 4.09–3.99 (m, 3H), 3.83–3.72 (m, 2H), 3.54–3.52 (m, 1H), 2.35 (s, 3H), 2.09 (s, 3H), 1.99 (br s, 15H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.3, 170.1, 170.0, 169.8, 169.7, 169.1, 156.0, 151.9, 143.5, 138.7, 137.5, 131.9, 129.3 (2C), 128.3, 126.2, 127.6 (2C), 125.9, 119.1, 116.4, 101.1, 100.7, 76.1, 72.9, 72.6, 71.6, 70.9, 70.7, 69.1, 66.6, 66.2, 61.9, 60.8, 21.6, 20.8 (2C), 20.6 (4C), 20.5; ESI-MS: *m*/*z* 970.2 $[M + Na]^+$. Anal. calcd for $C_{43}H_{49}NO_{21}S$ (947.25): C, 54.48; H, 5.21. Found: C, 54.37; H, 5.32%.

Data for 5x. White solid; yield 73% (766 mg); mp 123–125 °C; $[\alpha]_D^{25}$ −51 (*c* 1.0, $CHCl_3$); IR (KBr): 3021, 2463,1654, 1639, 1566, 1515, 1460, 1218, 1072, 755, 678 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, $J = 2.6$ Hz, 1H), 8.35–8.31 (m, 1H), 7.94 (d, $J = 9.1$ Hz, 2H), 7.72 (s, 1H), 7.51 (d, $J = 9.2$ Hz, 1H), 6.96 (d, $J = 9.0$ Hz, 2H), 5.29 (d, $J = 2.6$ Hz, 1H), 5.15 (t, $J = 9.4$ Hz, 1H), 5.04 (dd, $J = 8.0$, 10.5 Hz, 1H), 4.97–4.88 (m, 2H), 4.61 (dd, J = 1.7, 15.1 Hz, 1H), 4.53 (d, $J = 8.0$ Hz, 1H), 4.44–4.39 (m, 3H), 4.10–3.99 (m, 3H), 3.84–3.74 (m, 2H), 3.81 (s, 3H), 3.55–3.51 (m, 1H), 2.09 (s, 3H), 2.00 (s, 9H), 1.99 (s, 3H), 1.98 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 170.1, 170.0, 169.8, 169.7, 169.1, 163.3, 154.8, 153.9, 144.9, 135.6, 132.7, 129.7 (2C), 129.2, 126.4, 123.9, 119.5, 117.7, 114.1 (2C), 101.0, 100.8, 75.9, 72.9, 72.4, 71.5, 70.9, 70.7, 69.1, 66.6, 65.9, 61.5, 60.8, 55.7, 20.8 (2C), 20.6 (4C), 20.5; ESI-MS: *m*/*z* 1031.1 $[M + Na]^+$. Anal. calcd for $C_{43}H_{48}N_2O_{24}S$ (1008.23): C, 51.19; H, 4.80. Found: C, 51.05; H, 4.92%.

General procedure for the preparation of compound (6a–o)

To a solution of 2-azidoacetonitrile (1.0 mmol), appropriate carbohydrate-derived alkyne (1.0 mmol), CuI (0.1 mmol), and salicylaldehyde (1.0 mmol) in THF (5 mL) was dropwise added Et_3N (2.0 mmol) at room temperature and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated and the residue was diluted with CH_2Cl_2 (20 mL) and washed successively with H_2O (10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4) and concentrated. The resulting crude product was purified by column chromatography (basic alumina, hexane–EtOAc; 1 : 1) to give the corresponding glycosylated 3-triazolyl-2-iminocoumarin derivatives.

Data for 6a. White solid; yield 76% (435 mg); mp 102–104 °C; $[\alpha]_D^{25}$ +87 (*c* 1.0, $CHCl_3$); IR (KBr): 3019, 2361, 1711, 1649, 1511, 1460, 1389, 1229, 1069, 750, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.95 (s, 1H), 7.41–7.36 (m, 2H), 7.17–7.08 (m, 2H), 5.13 (t, $J = 9.3$ Hz, 1H), 5.06–4.92 (m, 3H), 4.84 (d, $J = 12.8$ Hz, 1H), 4.63 (d, $J = 8.1$ Hz, 1H), 4.22 (dd, $J = 4.7$, 12.8 Hz, 1H), 4.10 (dd, $J = 2.3$, 12.5 Hz, 1H), 3.71–3.66 (m, 1H), 2.02 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.2, 169.5 (2C), 152.5, 143.4, 131.7, 128.7 (2C), 127.8, 125.3, 124.4 (2C), 118.2, 115.4, 99.5, 72.8, 71.9, 71.1, 68.3, 62.5, 61.9, 20.7, 20.6, 20.5 (2C); ESI-MS: *m*/*z* 573.1 $[M + H]^+$. Anal. calcd for $C_{26}H_{28}N_4O_{11}$ (572.17): C, 54.54; H, 4.93. Found: C, 54.41; H, 5.07%.

Data for 6b. White solid; yield 75% (429 mg); mp 120–122 °C; $[\alpha]_D^{25}$ −73 (*c* 1.0, $CHCl_3$); IR (KBr): 3021, 2461, 1711, 1659, 1515, 1460, 1389, 1219, 1072, 759, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 7.96 (s, 1H), 7.68 (s, 1H), 7.39–7.36 (m, 2H), 7.16–7.08 (m, 2H), 5.33 (d, $J = 2.3$ Hz, 1H), 5.18 (dd, $J = 8.1$, 10.5 Hz, 1H), 4.97–4.93 (m, 2H), 4.86–4.81 (m, 1H), 4.61 (d, $J = 8.1$ Hz, 1H), 4.13–4.09 (m, 2H), 3.92–3.88 (m, 1H), 2.08 (s, 3H),

1.99 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.3, 170.1, 169.6, 152.5, 143.5, 131.7, 128.7 (2C), 127.7, 125.3, 124.4 (2C), 118.3, 115.4, 100.0, 70.9, 70.8, 68.7, 67.1, 62.5, 61.4, 20.7, 20.6, 20.5 (2C); ESI-MS: *m*/*z* 573.1 $[M + H]^+$. Anal. calcd for $C_{26}H_{28}N_4O_{11}$ (572.17): C, 54.54; H, 4.93. Found: C, 54.41; H, 5.07%.

Data for 6c. Solid; yield 76% (435 mg); mp 117–119 °C; $[\alpha]_D^{25}$ +61 (*c* 1.0, $CHCl_3$); IR (neat): 3019, 2400, 1745, 1630, 1564, 1420, 1215, 1082, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 7.95 (s, 1H), 7.69 (s, 1H), 7.39–7.34 (m, 2H), 7.15–7.07 (m, 2H), 5.29–5.19 (m, 3H), 4.94 (br s, 1H), 4.82 (d, J = 12.5 Hz, 1H), 4.70 (d, J = 12.4 Hz, 1H), 4.23 (dd, 5.3, 12.3 Hz, 1H), 4.07–4.01 (m, 2H), 2.07 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 169.9, 169.8, 169.7, 152.5, 142.8, 131.6, 128.7 (2C), 127.8, 125.4, 124.3 (2C), 118.2, 115.3, 96.9, 69.4, 69.0, 68.7, 66.0, 62.3, 60.8, 20.8, 20.7, 20.6 (2C); ESI-MS: *m*/*z* 573.1 $[M + H]^+$. Anal. calcd for $C_{26}H_{28}N_4O_{11}$ (572.17): C, 54.54; H, 4.93. Found: C, 54.41; H, 5.07%.

Data for 6d. Colorless; yield 62% (386 mg); $[\alpha]_D^{25}$ −53 (*c* 1.0, $CHCl_3$); IR (neat): 3012, 2019, 1718, 1614, 1355, 1301, 1110, 1019, 911, 729, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1H), 8.71 (s, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.86–7.79 (m, 2H), 7.64–7.57 (m, 2H), 7.48–7.45 (m, 1H), 7.24 (d, J = 8.5 Hz, 1H), 5.34 (d, J = 2.9 Hz, 1H), 5.20 (dd, J = 8.0, 10.3 Hz, 1H), 5.00–4.95 (m, 2H), 4.88 (d, J = 12.4 Hz, 1H), 4.63 (d, J = 8.0 Hz, 1H), 4.18–4.09 (m, 2H), 3.91 (t, J = 6.9 Hz, 1H), 2.09 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.3, 170.2, 169.7, 151.9, 143.6, 139.2, 132.8, 130.2, 129.5, 128.9, 128.4 (2C), 125.9 (2C), 123.7, 121.6, 115.6, 112.1, 100.0, 70.9, 70.8, 68.7, 67.1, 62.5, 61.4, 20.8, 20.7 (2C), 20.6; ESI-MS: *m*/*z* 623.1 $[M + H]^+$. Anal. calcd for $C_{30}H_{30}N_4O_{11}$ (622.19): C, 57.88; H, 4.86. Found: C, 57.77; H, 4.93%.

Data for 6e. Yellow oil; yield 63% (373 mg); $[\alpha]_D^{25}$ +43 (*c* 1.0, $CHCl_3$); IR (neat): 3022, 2129, 1618, 1524, 1355, 1321, 1209, 1019, 911, 868, 729, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.99 (s, 1H), 7.86 (s, 1H), 7.60 (d, J = 2.2 Hz, 1H), 7.54 (dd, J = 2.2, 8.7 Hz, 1H), 7.06 (d, J = 8.7 Hz, 1H), 5.30 (dd, J = 3.6, 10.0 Hz, 1H), 5.26 (dd, J = 1.7, 3.5 Hz, 1H), 5.09 (t, J = 9.8 Hz, 1H), 4.92 (d, J = 1.5 Hz, 1H), 4.89 (d, J = 12.4 Hz, 1H), 4.75 (d, J = 12.4 Hz, 1H), 4.01–3.94 (m, 1H), 2.15 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.25 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 170.0, 169.9, 151.9, 151.4, 143.3, 134.2, 130.8, 126.1, 125.8, 125.4, 120.1, 117.1, 116.8, 96.9, 71.1, 69.7, 69.1, 66.7, 60.7, 20.9, 20.8, 20.7, 17.4; ESI-MS: *m*/*z* 593.1 $[M + H]^+$. Anal. calcd for $C_{24}H_{25}BrN_4O_9$ (592.08): C, 48.58; H, 4.25. Found: C, 48.47; H, 4.34%.

Data for 6f. Brown oil; yield 55% (342 mg); $[\alpha]_D^{25}$ +47 (*c* 1.0, $CHCl_3$); IR (neat): 3010, 2202,1744, 1563, 1415, 1360, 1119, 1044, 980, 758, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 4.74 (s, 1H), 8.18 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.71 (s, 1H), 7.67–7.63 (m, 1H), 7.54–7.50 (m, 1H), 7.30–7.27 (m, 1H), 5.41–5.30 (m, 3H), 5.05 (d, J = 1.6 Hz, 1H), 4.94 (d, J = 12.4 Hz, 1H), 4.81 (d, J = 12.4 Hz, 1H), 4.34 (dd, J = 5.1, 12.3 Hz, 1H), 4.18–4.13 (m, 2H), 2.17 (s, 3H), 2.15 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.0, 169.8, 169.7, 151.9, 142.9, 132.7, 130.2, 129.4, 128.9 (2C), 128.4 (2C), 125.9 (2C), 125.4, 121.5, 115.7, 111.9, 97.0, 69.5, 69.1, 68.8, 66.1, 62.4, 60.9, 20.9, 20.8, 20.7, 20.6; ESI-MS: *m*/*z* 623.1 $[M + H]^+$. Anal. calcd for $C_{30}H_{30}N_4O_{11}$ (622.19): C, 57.88; H, 4.86. Found: C, 57.77; H, 4.94%.

Data for 6g. White foam; yield 74% (380 mg); $[\alpha]_D^{25}$ −72 (*c* 1.0, $CHCl_3$); IR (neat): 3020, 2402,1744, 1663, 1515, 1360, 1219, 1044, 758, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 7.94 (s, 1H), 7.69 (s, 1H), 7.38–7.34 (m, 2H), 7.14–7.06 (m, 2H), 5.24–5.18 (m, 2H), 5.01 (t, J = 9.9 Hz, 1H), 4.84 (d, J = 1.4 Hz, 1H), 4.81 (d, J = 12.2 Hz, 1H), 4.67 (d, 12.2 Hz, 1H), 3.94–3.87 (m, 1H), 2.06 (s, 3H), 1.96 (s, 3H), 1.89 (s, 3H), 1.17 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 169.9, 169.8, 152.5, 143.1, 131.6, 128.7 (2C), 127.7, 125.3, 124.3 (2C), 118.3, 115.4, 96.9, 71.0, 69.7, 69.1, 66.6, 60.6, 20.9, 20.8, 20.7, 17.4; ESI-MS: *m*/*z* 515.1 $[M + H]^+$. Anal. calcd for $C_{24}H_{26}N_4O_9$ (514.17): C, 56.03; H, 5.09. Found: C, 55.91; H, 5.24%.

Data for 6h. Light yellow syrup; yield 73% (428 mg); $[\alpha]_D^{25}$ +69 (*c* 1.0, $CHCl_3$); IR (neat): 3010, 2302,1684, 1525, 1360, 1119, 1024, 758, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 7.91 (s, 1H), 7.73 (s, 1H), 7.39-7.32 (m, 2H), 7.14–7.06 (m, 2H), 5.28 (dd, J = 3.4, 10.0 Hz, 1H), 5.22–5.17 (m, 2H), 4.81 (br s, 1H), 4.19 (dd, J = 5.3, 12.3 Hz, 1H), 4.06-3.96 (m, 2H), 3.85–3.71 (m, 2H), 3.09–3.04 (m, 2H), 2.08 (s, 3H), 2.04 (s, 3H), 1.94 (s, 3H),1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 169.9, 169.6 (2C), 152.4, 144.4, 136.9, 133.7, 128.5 (2C), 127.3, 124.2 (2C), 119.8, 115.3, 97.6, 76.9, 69.5, 69.1, 68.6, 66.0, 62.3, 26.1, 20.8, 20.7, 20.6, 20.5; ESI-MS: *m*/*z* 587.1 $[M + H]^+$. Anal. calcd for $C_{27}H_{30}N_4O_{11}$ (586.19): C, 55.29; H, 5.16. Found: C, 55.21; H, 5.25%.

Data for 6i. Semi solid; yield 52% (473 mg); $[\alpha]_D^{25}$ +89 (*c* 1.0, $CHCl_3$); IR (neat): 3010, 2119, 1608, 1474, 1375, 1321, 1259, 1120, 1089, 911, 838, 677 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (s, 1H), 8.82 (s, 1H), 8.25 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.71–7.67 (m, 2H), 7.57–7.53 (m, 1H), 7.34 (d, J = 9.1 Hz, 1H), 5.35 (d, J = 3.1 Hz, 1H), 5.19 (t, J = 9.3 Hz, 1H), 5.11 (dd, J = 8.0, 10.5 Hz, 1H), 5.00–4.93 (m, 4H), 4.68 (d, J = 8.0 Hz, 1H), 4.56–4.49 (m, 2H), 4.17–4.08 (m, 3H), 3.90–3.82 (m, 2H), 3.70–3.66 (m, 1H), 2.15 (s, 3H), 2.14 (s, 3H), 2.06 (s, 6H), 2.04 (s, 3H).2.03 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.2, 170.1, 169.8 (2C), 169.1, 151.9, 143.6, 132.7, 130.3, 129.5, 128.9, 128.4 (2C), 125.9 (2C), 125.2, 124.3, 121.6, 115.7, 112.1, 101.0, 99.3, 76.2, 72.8 (2C), 71.5, 71.0, 70.7, 69.1, 66.7, 62.5, 62.0, 60.8, 20.9, 20.8, 20.7, 20.6 (3C), 20.5; ESI-MS: *m*/*z* 911.2 $[M + H]^+$. Anal. calcd for $C_{42}H_{46}N_4O_{19}$ (910.27): C, 55.38; H, 5.09. Found: C, 55.29; H, 5.18%.

Data for 6j. White solid; yield 72% (619 mg); mp 118–120 °C; $[\alpha]_D^{25}$ −49 (*c* 1.0, $CHCl_3$); IR (KBr): 3024, 2163,1727, 1654, 1593, 1460, 1379, 1226, 1114, 855, 773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 7.96 (s, 1H), 7.42–7.33 (m, 2H), 7.17 7.09 (m, 2H), 5.27 (d, J = 3.1 Hz, 1H), 5.11 (t, J = 9.9 Hz, 1H), 5.03 (dd, J = 8.0, 10.5 Hz, 1H), 4.93–4.78 (m, 4H), 4.58 (d, J = 8.0 Hz, 1H), 4.46–4.40 (m, 2H), 4.07–3.98 (m, 3H), 3.82–3.73 (m, 2H), 3.60–3.57 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 1.98 (s, 6H), 1.96 (s, 3H), 1.94 (s, 3H).1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.2, 170.1, 169.8, 169.7, 169.1, 152.5, 136.9, 133.7, 131.7, 128.7 (2C), 124.3 (2C), 119.8, 116.8, 115.4, 101.0, 99.2, 76.2, 72.8, 72.7, 71.5, 70.9, 70.7, 69.1, 66.6, 62.4, 62.0, 60.8, 20.9,

20.8, 20.7, 20.6 (3C), 20.5; ESI-MS: *m*/*z* 861.1 $[M + H]^+$. Anal. calcd for $C_{38}H_{44}N_4O_{19}$ (860.26): C, 53.02; H, 5.15. Found: C, 52.89; H, 5.27%.

Data for 6k. Yellow oil; yield 65% (382 mg); $[\alpha]_D^{25}$ +38 (*c* 1.0, $CHCl_3$); IR (neat): 3024, 2303,1654, 1639, 1515, 1420, 1208, 1072, 759, 673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 7.98 (s, 1H), 7.68 (s, 1H), 7.41–7.36 (m, 2H), 7.17–7.08 (m, 2H), 5.38 (d, J = 3.2 Hz, 1H), 5.22 (t, J = 9.9 Hz, 1H), 4.98 (dd, J = 3.4, 10.5 Hz, 1H), 4.54 (d, J = 10.0 Hz, 1H), 4.14–4.06 (m, 3H), 3.94–3.88 (m, 2H), 2.09 (s, 3H), 1.97 (s, 6H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.3, 170.0, 169.7, 152.5, 136.9, 131.6, 128.7 (2C), 127.7, 124.5, 124.3 (2C), 118.3, 115.4, 83.1, 74.5, 71.8, 67.3, 67.2, 61.5, 24.3, 20.8, 20.7, 20.6, 20.5; ESI-MS: *m*/*z* 589.0 $[M + H]^+$. Anal. calcd for $C_{26}H_{28}N_4O_{10}S$ (588.15): C, 53.06; H, 4.79. Found: C, 52.94; H, 4.91%.

Data for 6l. Light brown syrup; yield 62% (543 mg); $[\alpha]_D^{25}$ −57 (*c* 1.0, $CHCl_3$); IR (neat): 3019, 2400, 1749,1628, 1515, 1405, 1216, 1042, 756, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 7.99 (s, 1H), 7.65 (s, 1H), 7.43–7.37 (m, 2H), 7.18–7.09 (m, 2H), 5.28 (d, J = 3.0 Hz, 1H), 5.12 (t, J = 9.1 Hz, 1H), 5.03 (dd, J = 8.0, 10.4 Hz, 1H), 4.94–4.86 (m, 2H), 4.50 (d, J = 10.0 Hz, 1H), 4.44–4.39 (m, 2H), 4.09–3.99 (m, 4H), 3.87–3.73 (m, 3H), 3.62–3.58 (m, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 1.99 (s, 6H), 1.96 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.3, 170.2, 170.1, 169.7, 169.6, 169.1, 152.5, 136.9, 133.7, 131.6, 128.7 (2C), 127.8, 124.4 (2C), 118.3, 115.4, 101.1, 82.2, 76.6, 76.1, 73.8, 70.9, 70.7, 70.3, 69.1, 62.2, 60.9, 24.2, 20.9, 20.8, 20.7, 20.6 (3C), 20.5; ESI-MS: *m*/*z* 877.1 $[M + H]^+$. Anal. calcd for $C_{38}H_{44}N_4O_{18}S$ (876.23): C, 52.05; H, 5.06. Found: C, 51.94; H, 5.18%.

Data for 6m. Yellow oil; yield 66% (397 mg); $[\alpha]_D^{25}$ +51 (*c* 1.0, $CHCl_3$); IR (neat): 3029, 2210, 1849, 1628, 1415, 1322, 1042, 988, 756, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 7.90 (s, 1H), 7.61 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 6.75–6.65 (m, 2H), 5.36 (br s, 1H), 5.18 (dd, J = 8.1, 10.5 Hz, 1H), 5.00–4.95 (m, 2H), 4.85–4.78 (m, 1H), 4.66–4.63 (m, 1H), 4.15–4.10 (m, 2H), 3.98–3.93 (m, 1H), 3.82 (s, 3H), 2.10 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.1, 170.0, 169.6, 162.8, 154.1, 145.5, 129.6 (2C), 128.3, 125.2, 123.5, 113.0, 111.6 (2C), 100.5, 70.8 (2C), 68.7, 67.1, 62.5, 61.4, 55.8, 20.7, 20.6 (2C), 20.5; ESI-MS: *m*/*z* 603.1 $[M + H]^+$. Anal. calcd for $C_{27}H_{30}N_4O_{12}$ (602.18): C, 53.82; H, 5.02. Found: C, 53.73; H, 5.11%.

Data for 6n. Yellow oil; yield 56% (347 mg); $[\alpha]_D^{25}$ +38 (*c* 1.0, $CHCl_3$); IR (neat): 3029, 2210, 1849, 1628, 1415, 1322, 1042, 988, 756, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 7.85 (s, 1H), 7.58 (s, 1H), 7.31–7.28 (m, 2H), 7.05–6.97 (m, 2H), 5.59 (t, J = 9.5 Hz, 1H), 5.31 (br s, 1H), 4.99 (dd, J = 3.0, 9.9 Hz, 1H), 4.72 (d, J = 14.4 Hz, 1H), 4.47 (d, J = 10.0 Hz, 1H), 4.26 (d, J = 14.4 Hz, 1H), 4.05 (br s, 3H), 2.02 (s, 3H), 1.87 (s, 3H), 1.82 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 169.9, 169.1, 152.6, 136.9, 131.9, 128.8 (2C), 128.2, 127.1, 124.5 (2C), 119.8, 115.4, 86.2, 75.5, 71.3, 66.9, 63.1, 61.4, 47.6, 20.7, 20.6 (2C), 20.5; ESI-MS: *m*/*z* 621.1 $[M + H]^+$. Anal. calcd for $C_{26}H_{28}N_4O_{12}S$ (620.14): C, 50.32; H, 4.55. Found: C, 50.24; H, 4.63%.

Data for 6o. Yellow oil; yield 56% (364 mg); $[\alpha]_D^{25}$ +63 (*c* 1.0, $CHCl_3$); IR (neat): 3011, 2320, 1725, 1520, 1480, 1115, 1082, 988, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.99 (s, 1H), 7.86 (s, 1H), 7.59 (d, J = 2.5 Hz, 1H), 7.53 (dd, J = 2.3, 8.7, 1H), 7.05 (d, J = 8.6 Hz, 1H), 5.35–5.25 (m, 3H), 5.00 (d, J = 1.6 Hz, 1H), 4.89 (d, J = 12.6 Hz, 1H), 4.77 (d, J = 12.5 Hz, 1H), 4.30 (dd, 5.4, 12.5 Hz, 1H), 4.14–4.05 (m, 2H), 2.14 (s, 3H), 2.12 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 169.9, 169.8, 169.7, 151.9, 151.4, 142.9, 134.2, 130.8, 126.2, 125.7, 125.5, 120.1, 117.1, 116.7, 97.0, 69.5, 69.0, 68.8, 66.1, 62.4, 60.8, 20.8 (2C), 20.7, 20.6; ESI-MS: *m*/*z* 651.1 $[M + H]^+$. Anal. calcd for $C_{26}H_{27}BrN_4O_{11}$ (650.08): C, 47.94; H, 4.18. Found: C, 47.85; H, 4.27%.

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