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Divergent Synthesis of Three Classes of Aryl *N*-Glycosides by Solvent Control

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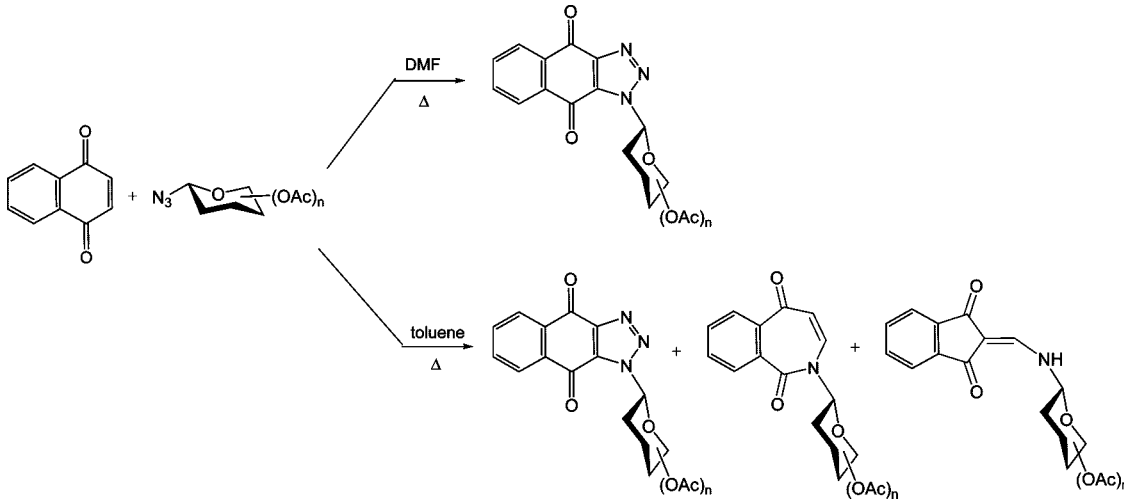

Aryl glycosides represent a group of molecules with immense biological applications and implications. While the syntheses of aryl *C*-glycosides and *O*-glycosides have been studied extensively, the preparation for aryl *N*-glycosides is relatively unexplored. By employing 1,4-naphthoquinone and glycosyl azides undergoing a [3 + 2] cycloaddition, we have developed a convenient method for constructing three different classes of aryl *N*-glycosides that include *N*-glycosylated 2-aminomethylene-1,3-indanedione, benzazepine-1,5-dione, and 9,10-anthraquinone derivatives via solvent control. It was found that conducting cycloaddition in DMF formed exclusively 9,10-anthraquinone derivatives, while less polar solvent such as toluene offered all three aryl *N*-glycosides. The synthesis of *N*-glycosylated 9,10-anthraquinone derivatives is of particular interest since no known example has been documented. The synthesis of these *N*-glycosylated heterocyclic compounds using traditional glycosylation methods could be challenging. Therefore, our diversity-oriented protocols can be viewed as an alternative and practical glycosylation approach. In addition, we have also demonstrated that alkyl azides can also undergo the same cycloaddition, further expanding the structural repertoire available for a broader interest. Initial anticancer assays have revealed that **19f** and **19k** exert mean growth percent of 17.58 and −5.95, respectively.

Introduction

Heterocyclic compounds, such as indanedione, benzazepine, and anthraquinone, have long attracted great interest due to their important biological and pharmaceutical applications, leading to the development and discovery of numerous therapeutics (Figure 1).[1,2] For example, compounds bearing 2-methylene-1,3-indanedione or 2-methylene-4-cyclopentene-1,3-dione scaffolds have been studied for their activity as fungicide,[3] antitumor agents,[4] and potential therapeutic for hypotension.[5] Benzazepine analogues have been noted to exert a wide range of pharmacological activities.[6−9] Anthraquinone, which can be viewed as part of the structural core of anthracycline, has also been the focus of synthetic effort in generating novel antibiotics or anticancer agents.[10] Finally, both naphthoquinone and an-

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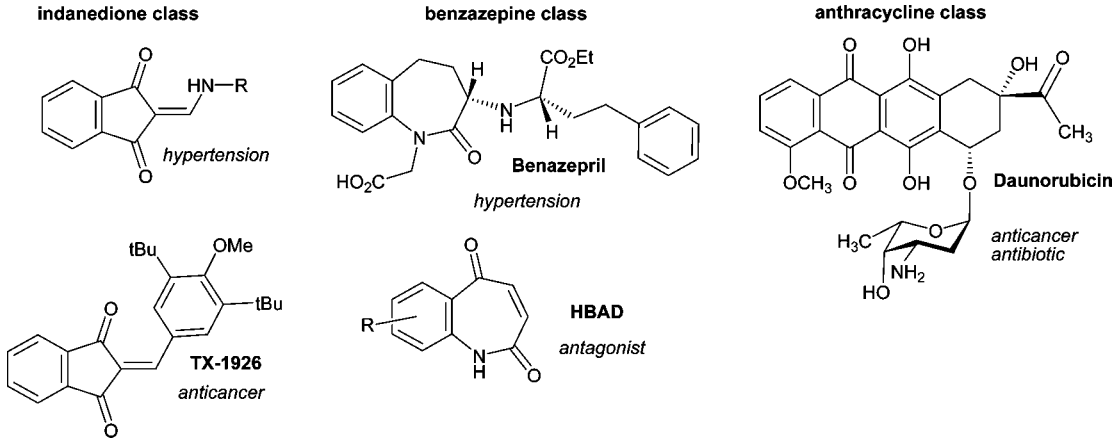

FIGURE 1. Examples of cyclic aromatic compounds.

thraquinone are known to uncouple mitochondrial oxidative phosphorylation, leading to mechanistic investigations in drug toxicity and related applications.[11] The syntheses of these three classes of cyclic aromatic compounds, in general, require multistep processes and often begin from various starting materials.[12]

Carbohydrates contain multiple stereocenters, and many of which are commercially available. These advantages make carbohydrates the ideal building blocks for diversity-oriented synthesis of molecules of interest.[13−15] To circumvent the challenges and enhance the efficiency of chemical glycosylation, our laboratory has been interested in utilizing the 1,3-dipolar cycloaddition, the "click" chemistry,[16] for facile incorporation of 1-azidosugars on structural motif of biological interest.[17,18] While various methods for the preparation of *O*- and *C*-aryl glycosides have been documented,[19,20] very little has been devoted to the synthesis of *N*-aryl glycosides.[21] The synthesis of *N*-glycosylated heterocyclic compounds is of particular interest since the amino group on any of these three classes of compounds is not considered a good nucleophile to undergo traditional glycosylation via an oxycarbenium ion intermediate. On the other hand, glycosyl amines are not stable enough to act as a nucleophile in nucleophilic substitution to make *N*-glycosyl compounds.

Azides have been known to undergo [3 + 2] cycloaddition with alkynes or alkenes.[22] The double bond between C2 and C3 of 1,4-naphthoquinone or α,β-unsaturated ketones can also be treated as an electron-deficient alkene. For example, an intramolecular cycloaddition using 2-alkylazido-1,4-benzoquinone or 1,4-naphthoquinone has been documented (Scheme 1).[23] It was reported that following the initial [3 + 2] cycloaddition carried out at 40 °C in ether, benzene, or CH_2Cl_2, triazoline **2** was observed. After prolonged heating, compound **1** was completely consumed and a mixture of azepinedione **4** (ring-expansion product) and 4-cyclopentene-1,3-dione **5** (ring-contraction product) was obtained in a 1:1 ratio. A 2-(azidoalkyl)quinone rearrangement, which may involve a diazoenedione intermediate **3** was suggested for the formation of compound **5**. Alternatively, fragmentation of triazoline **2** can lead to the formation of compound **4**. In addition, an intermolecular cycloaddition mediated by TMSOTf has recently been reported, but only azepinedione and 4-cyclopentene-1,3-dione adducts have been obtained (Scheme 2).[24] Similar mechanisms that involve the degradation of initial triazoline has been proposed

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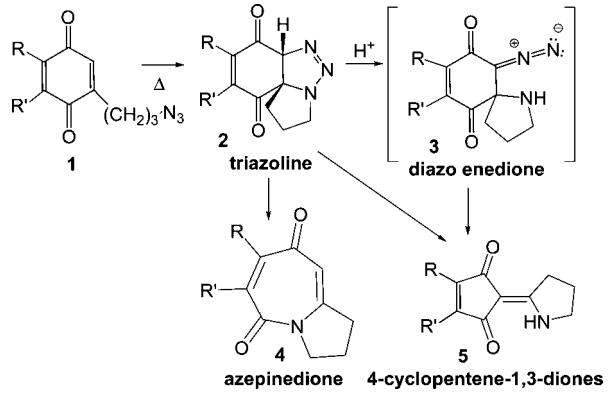
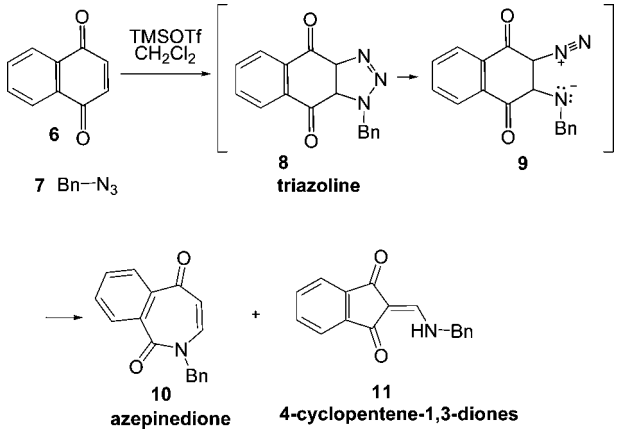
SCHEME 1



SCHEME 2



to explain the formation of **10** and **11**. Nonetheless, no triazoline adduct was isolated or reported in these investigations.

Design, Results and Discussion

In light of their biological applications, we wish to develop a method that can lead to the formation of not only azepinedione and 4-cyclopentene-1,3-dione adducts but also the cycloaddition adduct, or the oxidized form of triazoline, all of which with *carbohydrate moieties* attached. On the basis of the published studies, it appears that the lack of stability of the initial triazoline adduct leads to the formation of both ring-expansion (azepinedione) and ring-contraction (4-cyclopentene-1,3-dione) products. In fact, most of the studies focused on the photo- and thermal-mediated degradation of triazoline derivatives.[25]

We expect that, following the initial cycloaddition using naphthoquinone **6** and azido compounds **12**, it is possible to have a tautomerization that produces the *N*-glycosylated 9,10-hydroxyanthraquinone analogue **14**, which can be oxidized into the more stable 9,10-anthraquinone analogue **15** (Scheme 3). Therefore, we reason that, if the equilibrium can be shifted to favor the formation of **14**, a *N*-glycosylated cycloaddition adduct may be obtained. Although triazoline will be afforded in its oxidized form, this end product resembles both naphthoquinone and anthraquinone and could possess greater biological significance. In contrast, by employing less polar solvent, the initial triazoline may fragment into **16**, which could produce both *N*-glycosylated ring-expansion (**17**) and ring-contraction (**18**) products. Lewis acids were employed in cycloaddition of enones and azides. However, Lewis acids can facilitate the degradation of triazoline, leading to the formation of only ring-expansion and ring-contraction adducts.[24] Therefore, we intend to focus on the effect of solvents in directing the distribution of various adducts from cycloaddition.

By conducting the cycloaddition of 1,4-naphthoquinone and per-*O*-acetylated azidoglucose in DMF at 120 °C, only the oxidized cycloaddition adduct **15a** was isolated (Table 1, entry 1). Cycloaddition using dioxane, which has polarity between toluene and DMF, yielded only **15a** and **18a**. We proceeded to apply these findings on solvent effect to other glycosyl and alkyl azides. To our delight, all the cycloaddition conducted in DMF furnished *exclusively* the expected products (**15a**−**n**) with modest to excellent yields. Cycloaddition carried out using toluene as the solvent offered a mixture of **15**, **17**, and **18**. The first two components (**15** and **17**) which often have very close R_f values on TLC can be partially separated by column chromatography, leaving some fractions a mixture of **15** and **17**. The third and most polar product (**18**) can be readily separated from **15/17** as the major component.

We were intrigued with the initial results, although complex mixture and difficulties in separating **15/17** mixtures were encountered. Interestingly, the cycloaddition of azidoxylopyranose **12g** in toluene produced a mixture of α and β anomers (**18g** and *epi*-**18g**) despite the fact that **12g** was in pure β configuration. A possible mechanism involving intramolecular tautomerization is proposed in Scheme 4. Unlike other hexoses, xylopyranose lacks the equatorial C-6, which lowers the energy barrier for the formation of a conformation-constrained imine intermediate, leading to the epimerization at C-1. The cycloaddition protocol is also applicable for the preparation of **15l** by using a diazido compound **12l**.

Deprotection of acetyl groups on cycloaddition products (**15**) and ring-contraction products (**18**) was accomplished by using K_2CO_3 in MeOH or NaOMe/MeOH (Tables 2 and 3). When NaOMe/MeOH was employed, the crude product can be readily purified using solid phase extraction (Amberlite 120(H^+)) followed with recrystallization. The concise protocol is advantageous in providing library and scale-up synthesis of compounds in this class. Unfortunately, deprotection of the acetyl groups on ring-expansion products (**17**) under various conditions failed to yield the desired products. Due to the epimerization of **18g** during the cycloaddition step, deprotection of **18g** leads to the isolation of **20g** and *epi*-**20g** (Table 3, entry 4). Deprotection of **18i** produces an adduct without a carbohydrate component (Table 3, entry 5). In general, the yields for the deprotection of acetyl groups of **18** are lower than that of **15**. It is likely that the 4-cyclopentene-1,3-dione scaffold of **18** may function as a

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(26) With the exception of **15m** and **17m**, the separation of **15/17** mixture proves to be challenging. However, for the acetylation of the mixture followed by aqueous workup, we were amazed to discover that only the **17** component was present in organic solution. Further purification of **17** by recrystallization offered the pure desired products.

(27) Among the samples, **19a**, **19d**, **19f**, **19k**, **19m**, submitted for one-dose assay, **19f** and **19k** were selected for further five-dose testing. Please refer to Supporting Information for more details.

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SCHEME 3. Proposed Role of Solvent

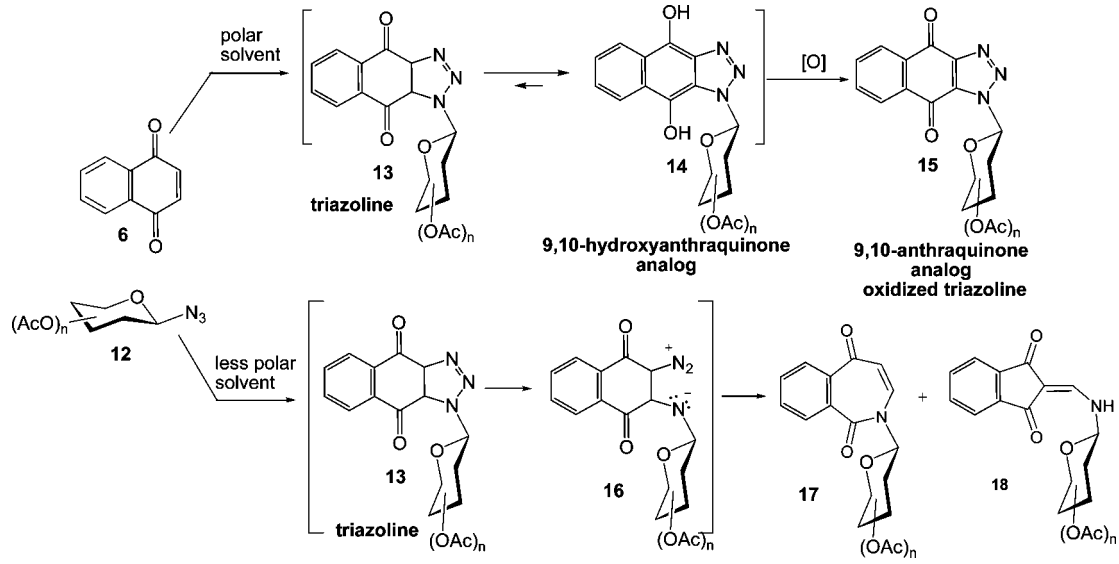


TABLE 1. Cycloaddition of Naphthoquinone and Azides[a]

entry	azido compound	solvent	yield (%)[b] 17[26]	15	18
1	per-*O*-acetylated β-D-glucopyranosyl azide (**12a**)[28]	toluene	24%	25%	33%
		dioxane		32%	19%
		DMF		67%	
2	per-*O*-acetylated β-D-galactopyranosyl azide (**12b**)[28]	toluene	17%	17%	34%
		DMF		66%	
3	per-*O*-acetylated α-D-mannopyranosyl azide (**12c**)[17]	DMF		49%	
4	per-*O*-acetylated β-lactosyl azide (**12d**)[29]	DMF		97%	
5	per-*O*-acetylated β-L-fucopyranosyl azide (**12e**)[17]	DMF		74%	
6	per-*O*-acetylated α-L-rhamnopyranosyl azide (**12f**)[17]	toluene	11%	11%	43%
		DMF		87%	
7	per-*O*-acetylated β-xylopyranosyl azide (**12g**)[17]	toluene	12%	11%	23%[c]
		DMF		85%	
8	per-*O*-acetylated 2-acetamido-2-deoxy β-D-glucopyranosyl azide (**12h**)[18]	DMF		35%	
9	per-*O*-acetylated β-cellobiosyl azide (**12i**)[28]	toluene	9%	9%	36%
		DMF		73%	
10	per-*O*-acetylated β-cellotriosyl azide (**12j**)[17]	DMF		85%	
11	per-*O*-acetylated β-D-ribofuranosyl azide (**12k**)[30]	toluene	11%	12%	20%
		DMF		79%	
12	per-*O*-acetylated 1,6-diazido-D-mannitol (**12l**)	DMF		99%	
13	per-*O*-acetylated 1-azido-D-mannitol (**12m**)	toluene	28%	34%	25%
		DMF		91%	
14	4-(*N*-*tert*-Boc-piperidinyl) azide (**12n**)	toluene	5%	64%	18%
		DMF		85%	

[a] All the cycloaddition reactions were conducted with 2/1 ratio of naphthoquinone/azide at 120 °C for 2 days. [b] With the exception of **15m** and **17m**, the yields of **15** and **17** obtained from cycloaddition in toluene were calculated from the integral ratio of ^{1}H NMR. [c] Isolated as a mixture of **18g** and *epi*-**18g**.

Michael acceptor with a loss of the carbohydrate component via an addition/elimination process. Deprotection of the Boc group on **17n** and **15n** can be fulfilled using TFA in CH_2Cl_2.

Investigation of the Reaction Conditions

Since our cycloaddition protocol was conducted using excess naphthoquinone (2 equiv) and open to air, the nature of oxidant was unclear. By comparing with the reported results,[24] it was also uncertain regarding the effect of Lewis acid, temperature, solvent, and alkyl group where the azide is attached. We employed four different azido compounds including **12a**, **12m**, **12n**, and **7**[24] (benzyl azide) for the investigation of reaction conditions. The azido group on glycosyl azide (**12a**) should be the most electron-deficient among all four azido compounds examined due to the presence of electron-withdrawing acetyl groups and the direct attachment of azide to the anomeric center. The azido group on **12m** should be more electron-rich than **12a** due to the absence of an anomeric center. However, with the presence of acetyl groups, the azido group on **12m** should be more electron-deficient than the one on alkyl azides (**12n** and **7**). As indicated in Scheme 2, cycloaddition of **6** and **7** has been reported to generate **10** and **11** but not **15o**. Therefore, it will be interesting to examine our protocol in generating **15o** (Scheme 5).

A series of cycloaddition reactions in various conditions were conducted to investigate the product distribution for **15** (9,10-anthraquinone analogue), **17** (ring-expansion), and **18** (ring-contraction) (Table 4). We noticed several interesting results.

SCHEME 4. Proposed Mechanism for Epimerization of 18g

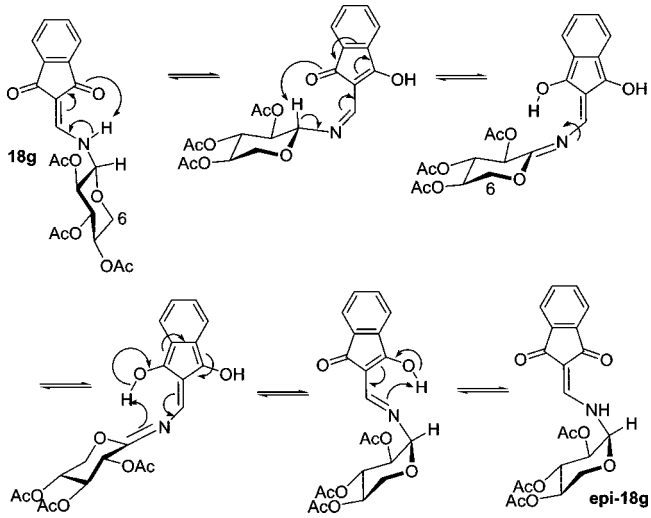
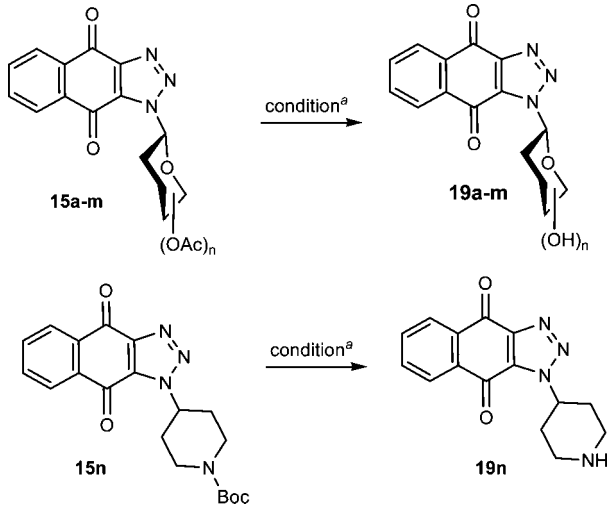


TABLE 2. Deprotection of 15

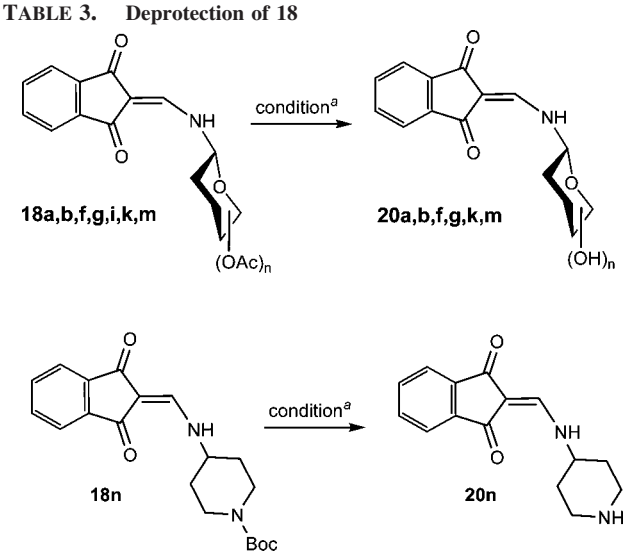


entry	reactant	condition[a]	product	yield (%)
1	**15a**	A	**19a**	99%
2	**15b**	B	**19b**	46%
3	**15c**	A	**19c**	62%
4	**15d**	A	**19d**	99%
5	**15e**	A	**19e**	41%
6	**15f**	B	**19f**	33%
7	**15g**	A	**19g**	79%
8	**15h**	A	**19h**	56%
9	**15i**	A	**19i**	99%
10	**15j**	A	**19j**	57%
11	**15k**	A	**19k**	57%
12	**15l**	A	**19l**	23%
13	**15m**	A	**19m**	97%
14	**15n**	C	**19n**	94%

[a] A: NaOMe, MeOH; B: K_2CO_3, MeOH, H_2O; C: TFA, CH_2Cl_2.

First, with all attempts employing degassed solvents, sodium ascorbate, or stoichiometric naphthoquinone to avoid the oxidation of the initial triazoline product, the formation of **15** from the oxidation of the initial triazoline adduct was observed in all the cases. When stoichiometric naphthoquinone was employed, the decreased yield of **15** was noted. The results confirm that the reactant, naphthoquinone, also functions as the oxidant to oxidize the initial triazoline adducts. Second, the presence of Lewis acid (TMSOTf) is less effective in facilitating the

TABLE 3. Deprotection of 18



entry	reactant	condition[a]	product	yield (%)
1	**18a**	A	**20a**	64%
2	**18b**	A	**20b**	53%
3	**18f**	A	**20f**	39%
4	**18g**/*epi*-**18g**	A	**20g**/*epi*-**20g**	α: 35%, β: 53%
5	**18i**	A		decomposed
6	**18k**	A	**20k**	46%
7	**18m**	A	**20m**	40%
8	**18n**	B	**20n**	99%

[a] A: K_2CO_3, MeOH, H_2O; B: TFA, CH_2Cl_2.

cycloaddition than heating (temperature effect) when the electron-deficient azide **12a** was used (Table 4, entries 1 and 2). Apparently, the electron-withdrawing nature of anomeric carbon dramatically reduces the reactivity of glycosyl azides. The results support that the cycloaddition step is thermodynamically controlled and could be the rate-limiting step. Third, excellent selectivity for **15** in DMF was obtained regardless of the electronic environment of azides. For example, under the condition reported by Aube and co-workers (TMSOTf, CH_2Cl_2, rt),[24] cycloaddition between **6** and **7** provided only **10** and **11**. In contrast, using our protocol, only **15o** was produced (Table 4, entry 11). This result supports our previous speculation that DMF may favor a fast tautomerization of the initial triazoline adduct **13** followed by a fast redox reaction with excess naphthoquinone. When less polar solvents (toluene and CH_2Cl_2) were used, the triazoline adduct cannot be tautomerized completely, which leads to the fragmentation of **13** and the formation of **17** and **18** under thermodynamic conditions or with the presence of Lewis acid. Interestingly, the use of Lewis acid (TMSOTf) was ineffective in facilitating the cycloaddition when DMF (entry 13) was employed. Fourth, the electronic effect of azides also plays a role in directing the product formation: the yield for **15** increases as the electronic environment of azides changes from electron-deficient to electron-rich. For example, when the cycloaddition was conducted in degassed toluene under nitrogen, the yields for **15** varied from 24% (**15a**), 34% (**15m**), 43% (**15n**) to 61% (**15o**). Electron-rich alkyl azides increase the rate of oxidation of **14** and produce more **15** while electron-deficient azides, such as **12a**, will lower the rate of oxidation, allowing for the formation of more fragmentation products (**17** and **18**).

The elucidation of the role of naphthoquinone suggests a possible mode of anticancer activity via the uncoupling of

SCHEME 5

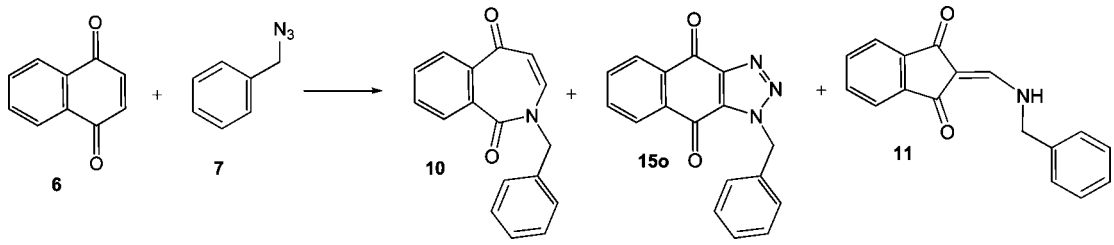


TABLE 4. Investigation of the Effect of TMSOTf and the Potential Oxidant[a]

entry	reactants (ratio)	solvent, temp, time	additives (equiv)	compounds (yield %)
1	**6/12a** (1/1)	degassed toluene, rt, 1 day then 60 °C, 1 day	TMSOTf (2)	no reaction; recovered **12a**
2	**6/12a** (1/1)	CH_2Cl_2, rt, 1 day then reflux, 1 day	TMSOTf (2)	no reaction; recovered **12a**
3	**6/12a** (1/1)	degassed DMF, 120 °C, 2 days		**15a** (38%); recovered **12a** (43%) and **6** (31%)
4	**6/12a** (2/1)	degassed DMF, 120 °C, 2 days		**15a** (61%)
5	**6/12m** (2/1)	degassed toluene, 120 °C, 2 days		**15m** (34%), **17m** (28%), **18m** (25%)
6	**6/12m** (1/1)	degassed toluene, 120 °C, 2 days	Na ascorbate (1)	**15m** (32%), **17m** (25%), **18m** (15%)
7	**6/12m** (1/1)	degassed toluene, 120 °C, 2 days		**15m** (34%), **17m** (23%), **18m** (18%)
8	**6/12n** (2/1)	degassed toluene, 120 °C, 2 days		**15n** (43%), **17n** (13%), **18n** (16%)
9	**6/12n** (2/1)	degassed DMF, 120 °C, 2 days		**15n** (85%)
10	**6/7** (2/1)	degassed toluene, 120 °C, 2 days		**15o** (61%), **10** (2%),[b] **11** (2%)[b]
11	**6/7** (2/1)	degassed DMF, 120 °C, 2 days		**15o** (82%)
12	**6/7** (1/1.5)	CH_2Cl_2, 0 °C to rt, 10 h	TMSOTf (2)	**10** (20%), **11** (40%)
13	**6/7** (2/1)	degassed DMF, 0 °C to rt, 1−2 days	TMSOTf (2)	no reaction
14	**6/7** (2/1)	degassed DMF, 120 °C, 2 days	TMSOTf (2)	**15o** (39%); recovered **6** (13%)

[a] All the reactions were conducted under N_2. [b] Estimated yields from ^{1}H NMR.

mitochondrial oxidative phosphorylation. The rate of oxidation of **14** can be tuned by the electronic effect on the employed azides, suggesting a feasible optimization of redox potential of compound **19** for disrupting the redox processes involving coenzyme Q. From the preliminary screening via the DPT/NCI program, **19f** and **19k** have shown significant anticancer activity (mean growth percent of 17.58 and −5.95, respectively) and are subjected for further investigation.[27]

Conclusion

By varying solvent, three classes of *N*-glycosylated heterocyclic compounds with immense applications can be synthesized. The cycloaddition between naphthoquinone and glycosyl and alkyl azides conducted in DMF offers excellent selectivity for the formation of biologically interesting *N*-glycosylated 9,10-anthraquinone analogues. We have also proved that alkyl azide can undergo the same cycloaddition with naphthoquinone, further expanding the structural repertoire available for a broader interest. Ongoing effort has also been directed to the attempts using 1,4-quinone and 1,4,9,10-anthratetraone as the reactants. Attempts on optimizing the yield of **17** and the condition for its sequential deprotection and purification will be performed. More biological testing will also be conducted shortly.

Experimental Section

2,3,4,5-Tetra-*O*-acetyl-1,6-diazido-1,6-dideoxy-D-mannitol (12l). A solution of D-mannitol (5.00 g, 0.027 mol), TsCl (7.82 g, 0.041 mol), and catalytic amount of DMAP in anhydrous pyridine (40 mL) was stirred at 0 °C overnight, allowing the reaction temperature to warm up to room temperature. The reaction mixture was cooled to 0 °C again, and Ac_2O (31 mL, 0.32 mol) was added slowly. After being stirred for 1 day, the reaction mixture was poured into a mixture of water/EtOAc and then stirred for several hours. The aqueous layer was separated from the organic layer and extracted with EtOAc. The combined organic layers were washed with 1 N HCl (×3), water (×2), saturated $NaHCO_{3(aq)}$ and brine, and dried over anhydrous Na_2SO_4. After removal of solvents, the crude product was re-dissolved in DMF and NaN_3 (2.67 g, 0.041 mol) was added. After being stirred at 80 °C for 1 day, the reaction was cooled and charcoal was added. After filtration through Celite and removal of solvents, crystal was formed. The crystal was collected and washed with a mixture of ether/hexane (1/1) and ether. The crystal was determined to be hexa-*O*-acetyl-D-mannitol (2.2 g, 5.07 mmol, 19%). The filtrate was concentrated and purified with a gradient column chromatography yielding **12l** (3.01 g, 7.52 mmol, 28%), **12m** (2.21 g, 5.30 mmol, 20%), and trace amount of hexa-*O*-acetyl-D-mannitol: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.37 (d, J = 8.0 Hz, 2H), 5.0 (m, 2H), 3.43 (dd, J = 13.6, 3.4 Hz, 2H), 3.23 (dd, J = 13.6, 5.7 Hz, 2H), 2.121 (s, 6H), 2.120 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 169.9, 68.7, 68.3, 50.8, 20.9, 20.8; ESI/APCI calcd for $C_{14}H_{20}N_6O_8Na^+$ ([M + Na]$^+$) *m/e* 423.1235; ESI/APCI calcd for $C_{14}H_{21}N_4O_8^+$ ([M − N_2 + H]$^+$) *m/e* 373.1354; measured *m/e* 373.1360.

2,3,4,5,6-Penta-*O*-acetyl-1-azido-1-deoxy-D-mannitol (12m). Please refer to the procedure for the preparation of **12l**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.36 (d, J = 8.8 Hz, 2H), 5.0 (m, 2H), 4.13 (dd, J = 12.5, 2.6 Hz, 1H), 4.00 (dd, J = 12.5, 5.2 Hz, 1H), 3.41 (dd, J = 13.5, 3.3 Hz, 1H), 3.20 (dd, J = 13.5, 5.6 Hz, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.6, 170.0, 169.9, 169.82, 169.79, 68.7, 68.3, 68.0, 67.5, 61.9, 50.8, 21.0, 20.9, 20.8, 20.7 (2 carbons); ESI/APCI calcd for $C_{16}H_{23}N_3O_{10}Na^+$ ([M + Na]$^+$) *m/e* 440.1276; Compound degraded during the mass spec analysis.

4-Azido-*N*-*tert*-butoxycarbonylpiperidine (12n). To a solution of 4-hydroxypiperidine (1.0 g, 4.94 mmol) in CH_2Cl_2 (10 mL) and Et_3N (1.5 mL, 6.92 mmol) was added Boc_2O (2.4 g, 5.93 mmol). After being stirred for 2 h, the reaction was diluted with EtOAc and washed with saturated $NaHCO_3$, water, and brine, and then dried over Na_2SO_4. After removal of solvents, the crude product was dissolved in anhydrous CH_2Cl_2 (50 mL) and Et_3N (1.0 mL, 7.50 mmol). The reaction mixture was cooled to 0 °C, and MsCl (0.69 mL, 8.94 mmol) was added slowly. After being stirred for 2 h, the reaction mixture was concentrated and diluted with EtOAc. The solution was filtered through Celite, and the residue was washed

with more EtOAc. The filtrate was concentrated and re-dissolved in DMF (50 mL). After the addition of NaN_3 (1.17 g, 18.0 mmol), the reaction mixture was stirred at 100 °C for 24 h. The reaction mixture was concentrated and diluted with EtOAc. The solution was filtered through Celite, and the residue was washed with more EtOAc. After the removal of solvent and purification with gradient column chromatography (hexane/EtOAc from 100/0 to 1/1), the desired product was obtained as an oil (0.90 g, 3.99 mmol, 41% for three steps): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.7 (m, 2H), 3.48 (tt, J = 13.1, 4.8 Hz, 1H), 3.01 (dt, J = 13.1, 3.4 Hz, 2H), 1.8 (m, 2H), 1.5 (m, 2H), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 79.9 (2 carbons), 57.7, 41.6, 30.7 (2 carbons), 28.5 (3 carbons); ESI/APCI calcd for $C_{10}H_{19}N_4O_2^+$ ([M + H]$^+$) *m/e* 227.1503; measured *m/e* 227.1503.

General Procedure for Cycloaddition. The glycosyl azide (0.20 g, 1 equiv) and naphthoquinone (2 equiv) were dissolved in toluene or dioxane and were heated at 120 °C for 2 days. After completion of the reaction monitored by TLC (eluted with hexane/EtOAc = 1/1), the reaction was cooled and the solvents were removed. The crude products were purified by gradient column chromatography (eluted with hexane/EtOAc from 100/0 to 55/45). Component **17** is usually the first one being eluted out followed by component **15**. In most of the cases, the majority part of **17** was mixed with **15**. However, the pure fractions of **17** and **15** can provide spectroscopic references for the evaluation of the ratio of **15** and **17** in the collected mixture using ^{1}H NMR. The most polar component **18** can be eluted the last and easily separated from the previous two components. When DMF was used as the solvent, only compound **15** was obtained.

2-(*N*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl))-2*H*-2-benzazepine-1,5-dione (17a): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (dd, J = 7.4, 1.9 Hz, 1H), 8.16 (dd, J = 7.0, 2.0 Hz, 1H), 7.8 (m, 2H), 6.94 (d, J = 11.2 Hz, 1H), 6.34 (d, J = 9.2 Hz, 1H), 6.06 (d, J = 11.1 Hz, 1H), 5.44 (t, J = 9.5 Hz, 1H), 5.26 (t, J = 9.5 Hz, 1H), 5.18 (t, J = 9.7 Hz, 1H), 4.30 (dd, J = 12.6, 4.9 Hz, 1H), 4.2 (m, 1H), 4.0 (m, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.5, 170.7, 170.1, 169.6, 169.5, 168.1, 137.4, 134.0, 133.6, 133.2, 131.6, 130.9, 129.9, 113.9, 82.5, 75.2, 73.2, 70.1, 68.1, 61.9, 21.0, 20.8 (2 carbons), 20.5; ESI/APCI calcd for $C_{24}H_{25}NO_{11}Na^+$ ([M + Na]$^+$) *m/e* 526.1320; measured *m/e* 526.1322.

1-(*N*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15a): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.33 (dd, J = 6.7, 1.9 Hz, 1H), 8.27 (dd, J = 7.1, 1.9 Hz, 1H), 7.8 (m, 2H), 6.35 (d, J = 9.5 Hz, 1H), 6.15 (t, J = 9.2 Hz, 1H), 5.50 (t, J = 9.4 Hz, 1H), 5.47 (t, J = 9.6 Hz, 1H), 4.3 (m, 2H), 4.1 (m, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.8, 174.3, 170.7, 170.3, 169.5, 169.1, 147.0, 135.6, 134.8, 134.7, 133.1, 133.0, 128.1, 127.9, 86.1, 75.4, 73.0, 69.3, 67.7, 61.6, 20.9, 20.8 (2 carbons), 20.4; ESI/APCI calcd for $C_{24}H_{23}N_3O_{11}Na^+$ ([M + Na]$^+$) *m/e* 552.1225; measured *m/e* 552.1228.

2-(*N*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl))aminomethylene-1,3-indanedione (18a): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.22 (dd, J = 13.2, 8.8 Hz, 1H), 7.8 (m, 2H), 7.70 (d, J = 13.2 Hz, 1H), 7.6 (m, 2H), 5.29 (t, J = 9.6 Hz, 1H), 5.14 (t, J = 9.2 Hz, 1H), 5.10 (t, J = 9.6 Hz, 1H), 4.6 (m, 1H), 4.23 (dd, J = 4.6, 1.2 Hz, 1H), 4.1 (m, 1H), 3.8 (m, 1H), 2.1 (m, 3H), 2.03 (s, 3H), 2.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 193.2, 189.9, 170.8, 170.2, 170.0, 169.5, 149.3, 140.4, 140.2, 134.2, 134.1, 122.6, 122.3, 107.4, 87.4, 74.4, 72.5, 70.8, 68.0, 61.8, 20.9, 20.8 (2 carbons), 20.7; ESI/APCI calcd for $C_{24}H_{26}NO_{11}^+$ ([M + H]$^+$) *m/e* 504.1500; measured *m/e* 504.1506.

2-(*N*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl))-2*H*-2-benzazepine-1,5-dione (17b): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (dd, J = 7.6, 1.4 Hz, 1H), 8.17 (dd, J = 7.2, 1.9 Hz, 1H), 7.8 (m, 2H), 7.01 (d, J = 11.1 Hz, 1H), 6.31 (d, J = 9.2 Hz, 1H), 6.08 (d, J = 11.1 Hz, 1H), 5.53 (d, J = 3.1 Hz, 1H), 5.39 (t, J = 9.7 Hz, 1H), 5.25 (dd, J = 10.1, 3.2 Hz, 1H), 4.2 (m, 3H), 2.23 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.5, 170.5, 170.1, 169.9, 169.7, 168.1, 137.4, 133.9, 133.6, 133.1, 131.9, 130.9, 129.9, 113.8, 82.9, 73.9, 71.3, 67.8, 67.2, 61.4, 20.8 (2 carbons), 20.7, 20.5; ESI/APCI calcd for $C_{24}H_{25}NO_{11}Na^+$ ([M + Na]$^+$) *m/e* 526.1320; measured *m/e* 526.1342.

1-(*N*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15b): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (dd, J = 6.9, 1.9 Hz, 1H), 8.28 (dd, J = 7.2, 2.0 Hz, 1H), 7.87 (td, J = 6.4, 1.5 Hz, 1H), 7.84 (td, J = 6.7, 1.6 Hz, 1H), 6.4 (m, 2H), 5.59 (d, J = 3.2 Hz, 1H), 5.3 (m, 1H), 4.34 (t, J = 7.0 Hz, 1H), 4.23 (dd, J = 10.0, 6.9 Hz, 1H), 4.15 (dd, J = 10.2, 6.9 Hz, 1H), 2.32 (s, 3H), 2.04 (s, 6H), 1.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.9, 174.4, 170.6 (2 carbons), 170.2, 169.0, 146.0, 135.5, 134.7, 134.6, 133.1, 133.0, 128.0, 127.8, 86.5, 74.4, 71.5, 67.0, 66.9, 61.5, 20.9, 20.8 (2 carbons), 20.5; ESI/APCI calcd for $C_{24}H_{23}N_3O_{11}Na^+$ ([M + Na]$^+$) *m/e* 552.1225; measured *m/e* 552.1230.

2-(*N*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl))aminomethylene-1,3-indanedione (18b): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.34 (dd, J = 13.1, 8.6 Hz, 1H), 7.8 (m, 2H), 7.71 (d, J = 13.4 Hz, 1H), 7.6 (m, 2H), 5.45 (d, J = 3.4 Hz, 1H), 5.33 (t, J = 10.3 Hz, 1H), 5.13 (dd, J = 10.3, 3.4 Hz, 1H), 4.59 (t, J = 8.6 Hz, 1H), 4.1 (m, 3H), 2.20 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 193.1, 189.9, 170.5, 170.2, 170.1, 170.0, 149.3, 140.3, 140.1, 134.0, 133.9, 122.4, 122.2, 107.1, 87.5, 73.0, 70.6, 68.2, 67.0, 61.5, 20.7 (2 carbons), 20.6 (2 carbons); ESI/APCI calcd for $C_{24}H_{26}NO_{11}^+$ ([M + H]$^+$) *m/e* 504.1500; measured *m/e* 504.1501.

1-(*N*-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15c): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.31 (dd, J = 7.4, 1.4 Hz, 1H), 8.20 (dd, J = 7.4, 1.2 Hz, 1H), 7.9 (m, 2H), 6.63 (s, 1H), 5.96 (d, J = 3.0 Hz, 1H), 5.49 (t, J = 10.0 Hz, 1H), 5.39 (dd, J = 10.0, 3.1 Hz, 1H), 4.3 (m, 2H), 4.2 (m, 1H), 2.18 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.6, 175.3, 170.8, 170.3, 170.1, 169.8, 145.1, 135.8, 134.7, 133.8, 133.3, 132.8, 128.2, 127.6, 83.9, 76.3, 71.2, 67.6, 65.7, 62.3, 21.0, 20.9 (2 carbons), 20.8; ESI/APCI calcd for $C_{24}H_{23}N_3O_{11}Na^+$ ([M + Na]$^+$) *m/e* 552.1225; measured *m/e* 552.1227.

1-(*N*-(4-*O*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-*β*-D-glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15d): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (dd, J = 7.0, 1.5 Hz, 1H), 8.24 (dd, J = 8.0, 1.6 Hz, 1H), 7.89 (td, J = 7.2, 1.4 Hz, 1H), 7.86 (td, J = 7.4, 1.6 Hz, 1H), 6.31 (d, J = 9.4 Hz, 1H), 6.06 (t, J = 9.6 Hz, 1H), 5.48 (t, J = 9.3 Hz, 1H), 5.40 (d, J = 3.3 Hz, 1H), 5.17 (dd, J = 10.4, 7.9 Hz, 1H), 5.01 (dd, J = 10.4, 3.4 Hz, 1H), 4.62 (t, J = 7.8 Hz, 2H), 4.1 (m, 4H), 4.0 (m, 2H), 2.18 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H), 1.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7, 174.4, 170.6, 170.3 (2 carbons), 170.2, 169.9, 169.3 (2 carbons), 146.1, 135.6, 134.7, 134.6, 133.0, 132.9, 128.0, 127.7, 101.2, 85.8, 77.7, 77.4, 77.0, 76.2, 75.4, 72.8, 71.1, 71.0, 69.5, 69.3, 66.9, 61.5, 61.1, 20.9, 20.8, 20.7, 20.4; ESI/APCI calcd for $C_{36}H_{39}N_3O_{19}Na^+$ ([M + Na]$^+$) *m/e* 840.2070; measured *m/e* 840.2088.

1-(*N*-(2,3,4-Tri-*O*-acetyl-α-D-fucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15e): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (dd, J = 6.8, 1.8 Hz, 1H), 8.26 (dd, J = 7.2, 1.4 Hz, 1H), 7.86 (td, J = 7.4, 1.6 Hz, 1H), 7.83 (td, J = 7.2, 2.0 Hz, 1H), 6.37 (d, J = 9.4 Hz, 1H), 6.31 (t, J = 9.6 Hz, 1H), 5.42 (d, J = 3.2 Hz, 1H), 5.31 (dd, J = 9.7, 3.4 Hz, 1H), 4.24 (dd, J = 12.6, 6.2 Hz, 1H), 2.33 (s, 3H), 2.03 (s, 3H), 1.82 (s, 3H), 1.27 (d, J = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.9, 174.5, 171.0, 170.3, 169.1, 145.9, 135.5, 134.6 (2 carbons), 133.1, 133.0, 128.0, 127.9, 86.4, 73.2, 72.0, 70.0, 67.1, 21.0, 20.8, 20.5, 16.2; ESI/APCI calcd for $C_{22}H_{21}N_3O_9Na^+$ ([M + Na]$^+$) *m/e* 494.1170; measured *m/e* 494.1180.

2-(*N*-(2,3,4-Tri-*O*-acetyl-α-D-rhamnopyranosyl))-2*H*-2-benzazepine-1,5-dione (17f): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.4 (m, 1H),

8.19 (dd, J = 6.7, 2.2 Hz, 1H), 7.7 (m, 2H), 7.2 (m, 1H), 6.09 (s, 1H), 5.93 (dd, J = 11.5, 0.7 Hz, 1H), 5.71 (d, J = 3.4 Hz, 1H), 5.29 (dd, J = 12.9, 3.4 Hz, 1H), 5.14 (t, J = 9.7 Hz, 1H), 3.8 (m, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 1.99 (s, 3H), 1.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.4, 170.1, 169.9 (2 carbons), 167.3, 137.2, 133.9, 133.7, 133.2, 132.8, 130.8, 129.8, 111.4, 82.7, 74.3, 70.6, 70.4, 69.0, 21.0 (2 carbons), 20.8, 17.8; ESI/APCI calcd for $C_{22}H_{24}NO_9^+$ ([M + H]$^+$) *m/e* 446.1451; measured *m/e* 446.1446.

1-(*N*-(2,3,4-Tri-*O*-acetyl-α-D-rhamnopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15f): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (dd, J = 7.5, 1.5 Hz, 1H), 8.25 (dd, J = 7.4, 1.4 Hz, 1H), 7.88 (td, J = 7.3, 1.5 Hz, 1H), 7.85 (td, J = 7.3, 1.4 Hz, 1H), 6.68 (d, J = 0.8 Hz, 1H), 5.89 (t, J = 0.9 Hz, 1H), 5.4 (m, 2H), 4.0 (m, 1H), 2.21 (s, 3H), 2.13 (s, 3H), 2.05 (s, 3H), 1.42 (d, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7, 175.0, 170.5, 170.2, 169.9, 145.0, 135.8, 134.7, 133.1, 133.3, 132.8, 128.2, 127.8, 84.0, 74.9, 71.1, 70.2, 68.1, 21.0 (2 carbons), 20.8, 17.7; ESI/APCI calcd for $C_{22}H_{21}N_3O_9Na^+$ ([M + Na]$^+$) *m/e* 494.1170; measured *m/e* 494.1177.

2-(*N*-(2,3,4-Tri-*O*-acetyl-α-D-rhamnopyranosyl))aminomethylene-1,3-indanedione (18f): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.41 (dd, J = 13.2, 8.8 Hz, 1H), 7.82 (d, J = 13.0 Hz, 1H), 7.7−7.8 (m, 2H), 7.5−7.6 (m, 2H), 5.50 (t, J = 1.4 Hz, 1H), 5.1 (m, 2H), 5.00 (d, J = 8.9 Hz, 1H), 3.7 (m, 1H), 2.30 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H), 1.24 (d, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.5, 189.9, 170.5, 170.4, 170.0, 149.5, 140.3, 140.1, 134.0, 133.9, 122.5, 121.9, 106.7, 84.2, 72.8, 71.1, 69.8, 69.5, 21.0, 20.9, 20.8, 17.7; ESI/APCI calcd for $C_{22}H_{24}NO_9^+$ ([M + H]$^+$) *m/e* 446.1451; measured *m/e* 446.1439.

2-(*N*-(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl))-2*H*-2-benzazepine-1,5-dione (17g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (dd, J = 2.4, 1.6 Hz, 1H), 8.15 (dd, J = 6.9, 1.9 Hz, 1H), 7.8 (m, 2H), 6.93 (d, J = 11.2 Hz, 1H), 6.24 (d, J = 9.4 Hz, 1H), 6.03 (d, J = 11.1 Hz, 1H), 5.44 (t, J = 9.5 Hz, 1H), 5.19 (t, J = 9.4 Hz, 1H), 5.10 (dt, J = 4.7, 0.7 Hz, 1H), 4.27 (dd, J = 11.4, 5.7 Hz, 1H), 3.58 (t, J = 10.9 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 1.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.6, 170.1 (2 carbons), 170.0, 168.1, 137.4, 133.9, 133.6, 133.1, 131.7, 130.9, 129.8, 113.7, 83.2, 72.7, 70.3, 68.9, 65.7, 20.8 (2 carbons), 20.5; ESI/APCI calcd for $C_{21}H_{22}NO_9^+$ ([M + H]$^+$) *m/e* 432.1289; measured *m/e* 432.1294.

1-(*N*-(2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (dd, J = 7.7, 1.9 Hz, 1H), 8.25 (dd, J = 7.1, 1.8 Hz, 1H), 7.8 (m, 2H), 6.29 (d, J = 9.2 Hz, 1H), 6.09 (t, J = 9.3 Hz, 1H), 5.47 (t, J = 9.4 Hz, 1H), 5.3 (m, 1H), 4.35 (dd, J = 11.6, 5.6 Hz, 1H), 3.67 (t, J = 10.2 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 1.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.8, 174.5, 170.3, 169.9, 169.2, 146.1, 135.6, 134.7, 134.6, 133.1, 133.0, 128.0, 127.9, 86.7, 72.6, 69.5, 68.6, 65.9, 20.9 (2 carbons), 20.4; ESI/APCI calcd for $C_{21}H_{19}N_3O_9Na^+$ ([M + Na]$^+$) *m/e* 480.1014; measured *m/e* 480.1007.

2-(*N*-(2,3,4-Tri-*O*-acetyl-D-xylopyranosyl))aminomethylene-1,3-indanedione (18g): (α/β = 1/1) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.5 (m, 1H), 9.4 (m, 1H), 7.67 (d, J = 13.2 Hz, 2H), 7.6−7.8 (m, 8H), 5.3 (m, 2H), 5.14 (dd, J = 5.7, 2.0 Hz, 1H), 5.0 (m, 3H), 4.8 (m, 1H), 4.61 (t, J = 5.6 Hz, 1H), 4.2 (m, 1H), 3.9 (m, 1H), 3.8 (m, 1H), 3.5 (m, 1H), 2.20 (s, 3H), 2.09 (s, 6H), 2.05 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.7, 193.2, 189.9, 189.8, 170.0, 170.0, 169.9 (2 carbons), 169.8, 169.0, 149.6, 149.5, 140.4 (2 carbons), 140.2, 140.1, 134.2, 134.1 (2 carbons), 134.0, 122.6, 122.5, 122.2, 122.0, 107.3, 107.2, 87.2, 82.4, 71.1, 70.3, 68.3, 68.2, 67.7, 66.9, 64.1, 63.2, 21.0, 20.9 (3 carbons), 20.7 (2 carbons); ESI/APCI calcd for $C_{21}H_{22}NO_9^+$ ([M + H]$^+$) *m/e* 432.1289; measured *m/e* 432.1303.

1-(*N*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15h): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, J = 5.8 Hz, 1H), 8.35 (d, J = 5.7 Hz, 1H), 7.9 (m, 2H), 6.59 (d, J = 9.7 Hz, 1H), 5.83 (t, J = 9.4 Hz, 1H), 5.76 (d, J = 7.6 Hz, 1H), 5.27 (t, J = 9.6 Hz, 1H), 4.60 (d, J = 9.8, 7.8 Hz, 1H), 4.32 (dd, J = 12.6, 4.9 Hz, 1H), 4.1 (m, 2H), 2.09 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 1.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.2 (2 carbons), 170.8 (2 carbons), 170.7, 169.6, 146.0, 135.1 (3 carbons), 134.2, 128.2 (3 carbons), 89.6, 75.2, 71.4, 68.2, 61.9, 54.9, 23.3, 20.9, 20.8 (2 carbons); ESI/APCI calcd for $C_{24}H_{24}N_4O_{10}Na^+$ ([M + Na]$^+$) *m/e* 551.1385; measured *m/e* 551.1395.

2-(*N*-(4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl))-2*H*-2-benzazepine-1,5-dione (17i): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (dd, J = 7.4, 1.8 Hz, 1H), 8.15 (dd, J = 7.9, 2.0 Hz, 1H), 7.8 (m, 2H), 6.87 (d, J = 11.1 Hz, 1H), 6.28 (d, J = 9.3 Hz, 1H), 6.01 (d, J = 11.1 Hz, 1H), 5.41 (t, J = 8.9 Hz, 1H), 5.1 (m, 3H), 4.96 (t, J = 8.0 Hz, 1H), 4.56 (d, J = 7.9 Hz, 1H), 4.53 (dd, J = 12.2, 7.9 Hz, 1H), 4.39 (dd, J = 12.5, 4.3 Hz, 1H), 4.16 (dd, J = 12.1, 4.3 Hz, 1H), 4.08 (dd, J = 12.4, 7.9 Hz, 1H), 3.9 (m, 2H), 3.7 (m, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H),1.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.6, 170.7 (2 carbons), 170.4, 169.7, 169.6, 169.5, 169.2, 168.0, 137.3, 134.0, 133.7, 133.2, 131.5, 130.9, 129.8, 113.7, 100.9, 82.5, 76.2, 76.0, 73.1, 72.7, 72.3, 71.8, 70.2, 67.9, 61.9, 61.8, 21.1, 20.9, 20.8 (3 carbons), 20.7, 20.5; ESI/APCI calcd for $C_{36}H_{41}NO_{19}Na^+$ ([M + Na]$^+$) *m/e* 814.2165; measured *m/e* 814.2165.

1-(*N*-(4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15i): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30 (dd, J = 7.8, 1.5 Hz, 1H), 8.19 (dd, J = 7.3, 1.3 Hz, 1H), 7.84 (td, J =7.4, 1.4 Hz, 1H), 7.81 (td, J = 7.4, 1.6 Hz, 1H), 6.27 (d, J = 9.5 Hz, 1H), 6.02 (t, J = 9.6 Hz, 1H), 5.42 (t, J = 9.4 Hz, 1H), 5.16 (t, J = 9.3 Hz, 1H), 5.07 (t, J = 9.7 Hz, 1H), 4.95 (t, J = 8.0 Hz, 1H), 4.6 (m, 2H), 4.40 (dd, J = 12.5, 4.5 Hz, 1H), 4.0 (m, 4H), 3.7 (m, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.8, 174.5, 170.7, 170.4, 170.3, 169.9, 169.5, 169.3 (2 carbons), 146.2, 135.6, 134.7, 134.6, 133.1, 133.0, 128.1, 127.7, 101.1, 86.0, 76.3, 75.7, 73.1, 72.6, 72.3, 71.8, 69.4, 68.0, 61.8, 61.3, 20.9, 20.8, 20.7 (3 carbons), 20.6, 20.4; ESI/APCI calcd for $C_{36}H_{39}N_3O_{19}Na^+$ ([M + Na]$^+$) *m/e* 840.2070; measured *m/e* 840.2083.

2-(*N*-(4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl))aminomethylene-1,3-indanedione (18i): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.25 (dd, J = 13.0, 8.2 Hz, 1H), 7.8 (m, 2H), 7.68 (d, J = 13.1 Hz, 1H), 7.7 (m, 2H), 5.31 (t, J = 8.9 Hz, 1H), 5.17 (t, J = 9.1 Hz, 1H), 5.13 (t, J = 9.6 Hz, 1H), 5.09 (t, J = 9.9 Hz, 1H), 4.94 (t, J = 8.0 Hz, 1H), 4.60 (t, J = 8.7 Hz, 1H), 4.5 (m, 2H), 4.39 (dd, J = 12.6, 4.5 Hz, 1H), 4.1 (m, 2H), 3.81 (t, J = 9.0 Hz, 1H), 3.7 (m, 2H), 2.15 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.3, 189.9, 170.7, 170.4 (2 carbons), 170.1, 169.8, 169.5, 169.3, 149.3, 140.4, 140.2, 134.2, 134.1, 122.6, 122.3, 107.3, 101.1, 87.1, 76.1, 75.2, 73.1, 72.3, 72.0, 71.8, 71.0, 67.9, 61.8, 61.7, 21.1, 20.9, 20.8 (3 carbons), 20.7 (2 carbons); ESI/APCI calcd for $C_{36}H_{41}NO_{19}Na^+$ ([M + Na]$^+$) *m/e* 814.2165; measured *m/e* 814.2158.

1-(*N*-(4-*O*-(4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15j): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.33 (dd, J = 7.2, 1.7 Hz, 1H), 8.24 (dd, J = 7.9, 1.7 Hz, 1H), 7.8 (m, 2H), 6.37 (d, J = 9.3 Hz, 1H), 5.99 (t, J = 9.3 Hz, 1H), 5.55 (t, J = 9.3 Hz, 1H), 5.4 (m, 4H), 5.07 (t, J = 10.0 Hz, 1H), 4.86 (dd, J = 10.6, 4.1 Hz, 1H), 4.79 (dd, J = 10.3, 4.1 Hz, 1H), 4.65 (dd, J = 12.4, 2.4 Hz, 1H), 4.5 (m, 1H), 4.3 (m, 4H), 4.0 (m, 5H), 2.17 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 6H), 2.00 (s, 3H), 1.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.7, 174.3, 170.7 (2 carbons), 170.6, 170.5, 170.3, 170.2, 170.0, 169.8, 169.5, 169.2, 146.0, 135.5, 134.6, 134.4, 133.0, 132.9, 128.0, 127.7, 96.2, 95.6, 85.5, 75.6, 75.2, 72.9, 72.4, 71.8, 70.6, 70.2, 69.8, 69.4, 69.3, 68.6, 68.0, 62.3, 62.1, 61.4, 21.0, 20.9 (2 carbons), 20.8, 20.7, 20.6 (4 carbons),

20.3; ESI/APCI calcd for $C_{48}H_{55}N_3O_{27}Na^+$ ([M + Na]$^+$) *m/e* 1128.2915; measured *m/e* 1128.2903.

2-(*N*-(2,3,5-Tri-*O*-acetyl-*β*-D-ribofuranosyl))-2*H*-2-benzazepine-1,5-dione (17k). Compound **17k** was eluted out after compound **15k**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (dd, J = 9.3, 2.1 Hz, 1H), 8.17 (dd, J = 9.2, 2.1 Hz, 1H), 7.7−7.8 (m, 2H), 7.07 (d, J = 11.1 Hz, 1H), 6.30 (d, J = 4.4 Hz, 1H), 5.97 (d, J = 11.2 Hz, 1H), 5.38 (t, J = 5.8 Hz, 1H), 5.34 (d, J = 5.2 Hz, 1H), 4.4 (m, 3H), 2.14 (s, 3H), 2.09 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.4, 170.4, 169.8, 169.7, 168.0, 137.2, 133.9, 133.6, 133.2, 131.8, 131.3, 129.8, 113.1, 90.6, 79.8, 73.7, 70.1, 63.0, 21.0, 20.7 (2 carbons); ESI/APCI calcd for $C_{21}H_{22}NO_9^+$ ([M + H]$^+$) *m/e* 432.1295; measured *m/e* 432.1287.

1-(*N*-(2,3,5-Tri-*O*-acetyl-*β*-D-ribofuranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15k). Compound **17k** was eluted out after compound **15k**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, J = 7.4 Hz, 1H), 8.25 (d, J = 7.5 Hz, 1H), 7.9 (m, 2H), 6.97 (d, J = 2.8 Hz, 1H), 6.2 (m, 1H), 5.84 (t, J = 5.6 Hz, 1H), 4.6 (m, 1H), 4.48 (dd, J = 12.4, 3.1 Hz, 1H), 4.23 (dd, J = 12.4, 4.5 Hz, 1H), 2.17 (s, 3H), 2.16 (s, 3H), 2.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7, 175.3, 170.7, 169.7, 169.6, 145.6, 135.7, 134.7, 134.0, 133.2, 132.9, 128.1, 127.8, 89.9, 81.6, 74.2, 70.9, 62.6, 20.8, 20.7 (2 carbons); ESI/APCI calcd for $C_{21}H_{19}N_3O_9Na^+$ ([M + Na]$^+$) *m/e* 480.1014; measured *m/e* 480.1013.

2-(*N*-(2,3,5-Tri-*O*-acetyl-*β*-D-ribofuranosyl))aminomethylene-1,3-indanedione (18k): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.38 (dd, J = 13.0, 8.6 Hz, 1H), 7.75 (d, J = 13.2 Hz, 1H), 7.7−7.8 (m, 2H), 7.6 (m, 2H), 5.33 (dd, J = 5.3, 3.4 Hz, 1H), 5.24 (t, J = 5.5 Hz, 1H), 5.17 (dd, J = 8.6, 5.6 Hz, 1H), 4.31 (dd, J = 6.0, 2.9 Hz, 1H), 4.2 − 4.3 (m, 2H), 2.25 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.6, 189.9, 170.8, 169.8, 169.7, 148.9, 140.2, 140.1, 134.1, 133.9, 122.5, 122.0, 106.6, 91.4, 80.7, 74.9, 71.4, 63.4, 21.1, 20.8, 20.6; ESI/APCI calcd for $C_{21}H_{22}NO_9^+$ ([M + H]$^+$) *m/e* 432.1289; measured *m/e* 432.1289.

2,3,4,5-Tetra-*O*-acetyl-1,6-bis(1*H*-naphtho[2,3-*d*]triazole-4,9-dione)-1,6-dideoxy-D-mannitol (15l): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.31 (d, J = 7.6 Hz, 2H), 8.16 (d, J = 7.5 Hz, 2H), 7.85 (td, J = 7.4, 1.1 Hz, 2H), 7.78 (td, J = 7.5, 1.2 Hz, 2H), 5.56 (d, J = 7.8 Hz, 2H), 5.49 (t, J = 9.2 Hz, 2H), 5.09 (dd, J = 14.2, 2.1 Hz, 2H), 4.94 (dd, J = 14.2, 9.3 Hz, 2H), 2.23 (s, 6H), 1.94 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7 (2 carbons), 175.9 (2 carbons), 170.5 (2 carbons), 169.9 (2 carbons), 145.7 (2 carbons), 135.6 (2 carbons), 134.6 (2 carbons), 133.9 (2 carbons), 133.7 (2 carbons), 132.8 (2 carbons), 128.1 (2 carbons), 127.5 (2 carbons), 68.7 (2 carbons), 68.4 (2 carbons), 51.2 (2 carbons), 20.9 (2 carbons), 20.6 (2 carbons); ESI/APCI calcd for $C_{34}H_{29}N_6O_{12}^+$ ([M + H]$^+$) *m/e* 713.1838; measured *m/e* 713.1851.

2,3,4,5,6-Penta-*O*-acetyl-1-(2*H*-2-benzazepine-1,5-dione)-1-dideoxy-D-mannitol (17m). Compound **17m** eluted out after **15m**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.4 (m, 1H), 8.2 (m, 1H), 7.7−7.8 (m, 2H), 6.73 (d, J = 10.9 Hz, 1H), 5.85 (d, J = 11.0 Hz, 1H), 5.52 (dd, J = 8.9, 2.3 Hz, 1H), 5.4−5.5 (m, 2H), 5.2 (m, 1H), 4.62 (dd, J = 12.5, 2.7 Hz, 1H), 4.23 (dd, J = 12.5, 2.7 Hz, 1H), 4.10 (dd, J = 12.5, 5.2 Hz, 1H), 3.53 (dd, J = 13.9, 9.1 Hz, 1H), 2.19 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.6, 170.8, 170.6, 170.1 (2 carbons), 170.0, 167.4, 137.9, 137.2, 133.9, 133.7, 133.2, 130.9, 129.8, 112.2, 69.6, 68.3, 68.1, 67.7, 62.0, 54.6, 21.1, 21.0 (2 carbons), 20.9 (2 carbons); ESI/APCI calcd for $C_{26}H_{30}NO_{12}^+$ ([M + H]$^+$) *m/e* 548.1768; measured *m/e* 548.1765.

2,3,4,5,6-Penta-*O*-acetyl-1-(1*H*-naphtho[2,3-*d*]triazole-4,9-dione)-1-dideoxy-D-mannitol (15m): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, J = 7.2 Hz, 1H), 8.18 (d, J = 7.3 Hz, 1H), 7.8 (m, 2H), 5.5 (m, 2H), 5.3 (m, 1H), 5.1 (m, 1H), 5.00 (dd, J = 14.1, 2.1 Hz, 1H), 4.89 (dd, J = 12.5, 9.4 Hz, 1H), 4.19 (dd, J = 12.5, 2.7 Hz, 1H), 4.03 (dd, J = 12.5, 5.1 Hz, 1H), 2.26 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.7, 175.8, 170.7, 170.6, 170.0, 169.9, 169.8, 145.6, 135.6, 134.5, 133.9, 133.6, 132.8, 128.0, 127.5, 68.9, 68.1, 68.0, 67.3, 61.9, 51.4, 21.0, 20.9, 20.8, 20.7, 20.6; ESI/APCI calcd for $C_{26}H_{27}N_3O_{12}Na^+$ ([M + Na]$^+$) *m/e* 596.1487; measured *m/e* 596.1502.

2,3,4,5,6-Penta-*O*-acetyl-1-(aminomethylene-1,3-indanedione)-1-dideoxy-D-mannitol (18m): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.3 (m, 1H), 7.7 (m, 2H), 7.6 (m, 2H), 7.24 (d, J = 13.8 Hz, 1H), 5.40 (dd, J = 9.3, 2.2 Hz, 1H), 5.30 (dd, J = 9.4, 2.3 Hz, 1H), 5.1 (m, 1H), 5.0 (m, 1H), 4.16 (dd, J = 12.6, 2.7 Hz, 1H), 4.02 (dd, J = 12.6, 5.0 Hz, 1H), 3.5 (m, 1H), 3.4 (m, 1H), 2.15 (s, 3H), 2.08 (s, 3H), 2.06 (s, 6H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.5, 190.2, 171.1, 170.8, 170.2, 170.0, 169.8, 152.4, 140.1, 140.0, 133.6, 133.6, 122.2, 121.7, 105.5, 68.2, 67.9, 67.8, 67.3, 62.0, 49.7, 21.0, 21.0, 20.9, 20.8, 20.8; ESI/APCI calcd for $C_{26}H_{30}NO_{12}^+$ ([M + H]$^+$) *m/e* 548.1768; measured *m/e* 548.1757.

1-(4-(*N*-*tert*-Butoxycarbonylpiperidinyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15n): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.33 (dd, J = 7.5, 1.7 Hz, 1H), 8.22 (dd, J = 6.9, 2.1 Hz, 1H), 7.86 (td, J = 7.6, 1.7 Hz, 1H), 7.81 (td, J = 7.6, 1.7 Hz, 1H), 5.36 (tt, J = 7.2, 4.5 Hz, 1H), 4.3 (m, 2H), 2.97 (t, J = 11.7 Hz, 2H), 2.1−2.4 (m, 4H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 177.0, 175.7, 154.6, 145.6, 135.4, 134.5, 133.3, 133.0, 133.0, 127.9, 127.5, 80.3 (2 carbons), 59.2, 42.9, 31.7 (2 carbons), 28.5 (3 carbons); ESI/APCI calcd for $C_{20}H_{23}N_4O_4^+$ ([M + H]$^+$) *m/e* 383.1714; measured *m/e* 383.1726.

2-(*N*-(4-(*N*-*tert*-Butoxycarbonylpiperidinyl)))aminomethylene-1,3-indanedione (18n): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.2 (m, 1H), 7.74 (d, J = 14.4 Hz, 1H), 7.7 (m, 2H), 7.6 (m, 2H), 4.1 (m, 2H), 3.4 (m, 1H), 2.86 (t, J = 11.4 Hz, 2H), 2.0 (m, 2H), 1.6 (m, 2H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.0, 190.2, 154.7, 150.0, 140.0, 133.6, 133.5, 122.1, 121.5, 104.8, 80.4, 57.0 (2 carbons), 43.0 (2 carbons), 32.8 (2 carbons), 28.6 (3 carbons); ESI/APCI calcd for $C_{20}H_{25}N_2O_4^+$ ([M + H]$^+$) *m/e* 357.1809; measured *m/e* 357.1807.

1-Benzyl-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (15o): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30 (dd, J = 7.5, 1.8 Hz, 1H), 8.20 (dd, J = 7.4, 1.6 Hz, 1H), 7.81 (td, J = 7.3, 1.6 Hz, 1H), 7.78 (td, J = 7.1, 1.5 Hz, 1H), 7.5 (m, 2H), 7.3 (m, 3H), 5.99 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.0, 175.6, 145.9, 135.4 (2 carbons), 134.5 (2 carbons), 134.1, 133.6, 133.3, 133.0, 129.3 (2 carbons), 128.9, 128.1, 127.6, 54.0; ESI/APCI calcd for $C_{17}H_{12}N_3O_2^+$ ([M + H]$^+$) *m/e* 290.0930; measured *m/e* 290.0931.

General Procedure for the Deprotection of Acetyl Groups Using NaOMe/MeOH. To a solution of starting material (0.10 g, **15**) in anhydrous MeOH (10 mL), a catalytic amount of NaOMe (ca. 1 M in MeOH) was added. The solution was stirred at room temperature for 1 h. After complete consumption of the starting material, the reaction mixture was loaded to a column packed with Amberlite 120 (H^+) resin, which was balanced with MeOH. The column was eluted with more MeOH, and the eluent was collected. After the removal of the solvent, the product was purified by recrystallization from a mixture of MeOH/EtOAc/hexane.

General Procedure for the Deprotection of Acetyl Groups Using K_2CO_3/MeOH/H_2O. To a solution of starting material (0.10 g, **18**) in MeOH (10 mL) and few drops of water, a catalytic amount of K_2CO_3 was added and the solution was stirred at room temperature for 1 h. After complete consumption of the starting material, the reaction was quenched with Amberlite 120 (H^+) resin and filtered through Celite. After removal of the solvent, the crude product was purified by gradient column chromatography (eluted with CH_2Cl_2/MeOH from 100/0 to 4/1). The collected product was further purified by recrystallization from a mixture of MeOH/EtOAc/hexane.

1-(*N*-(*β*-D-Glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19a). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 99%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.2 (m, 2H), 8.0 (m, 2H), 6.15 (d, J = 9.2 Hz, 1H), 5.5 (m, 1H), 5.34 (d, J = 5.2 Hz, 1H), 5.22 (d, J = 5.6 Hz, 1H), 4.6 (m, 1H), 4.1 (m, 1H), 3.7 (m, 1H), 3.5 (m, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.5, 175.4, 145.6, 136.0,

135.4, 135.1, 133.6, 133.4, 127.7, 127.6, 88.2, 81.4, 77.6, 72.2, 70.2, 61.4; ESI/APCI calcd for $C_{16}H_{15}N_3O_7Na^+$ ([M + Na]$^+$) *m/e* 384.0802; measured *m/e* 384.0801.

1-(*N*-(β-D-Galactopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19b). Please refer to the general procedure for the deprotection of acetyl groups using K_2CO_3/MeOH/H_2O (yield 46%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.2 (m, 2H), 8.0 (m, 2H), 6.13 (d, *J* = 9.1 Hz, 1H), 5.37 (d, *J* = 5.4 Hz, 1H), 5.1 (m, 1H), 4.8 (m, 1H), 4.69 (t, *J* = 5.4 Hz, 1H), 4.4 (m, 1H), 3.8 (m, 1H), 3.79 (t, *J* = 5.7 Hz, 1H), 3.5 (m, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.5, 175.5, 145.5, 135.9, 135.3, 135.1, 133.6, 133.5, 127.7 (2 carbons), 88.4, 79.7, 74.3, 69.5, 68.9, 61.0; ESI/APCI calcd for $C_{16}H_{15}N_3O_7Na^+$ ([M + Na]$^+$) *m/e* 384.0802; measured *m/e* 384.0801.

1-(*N*-(α-D-Mannopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19c). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 62%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.2 (m, 2H), 7.9 (m, 2H), 6.38 (s, 1H), 5.05 (s, 2H), 4.89 (s, 1H), 4.65 (s, 1H), 4.09 (s, 1H), 3.82 (d, *J* = 11.7 Hz, 1H), 3.5 (m, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.7, 175.5, 145.0, 135.9, 135.3, 134.1, 133.6, 133.4, 127.7 (2 carbons), 87.8, 82.1, 74.0, 70.6, 67.0, 61.8; ESI/APCI calcd for $C_{16}H_{15}N_3O_7Na^+$ ([M + Na]$^+$) *m/e* 384.0802; measured *m/e* 384.0806.

1-(*N*-(4-*O*-(β-D-Galactopyranosyl)-β-D-glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19d): Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 99%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.2 (m, 2H), 7.9 (m, 2H), 6.22 (d, *J* = 9.3 Hz, 1H), 5.72 (s, 1H), 5.14 (d, *J* = 4.0 Hz, 1H), 4.99 (s, 1H), 4.83 (s, 1H), 4.68 (s, 1H), 4.65 (s, 1H), 4.56 (s, 1H), 4.31 (d, *J* = 7.2 Hz, 1H), 4.2 (m, 1H), 3.8 (m, 1H), 3.6 (m, 7H), 3.3 (m, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.5, 175.3, 145.7, 136.0, 135.4, 135.2, 133.6, 133.4, 127.7, 127.6, 104.5, 87.8, 80.4, 79.1, 76.3, 75.7, 73.9, 71.9, 71.2, 68.9, 61.1, 60.7; ESI/APCI calcd for $C_{22}H_{25}N_3O_{12}Na^+$ ([M + Na]$^+$) *m/e* 546.1330; measured *m/e* 546.1331.

1-(*N*-(α-D-Fucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19e). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 41%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.18 (dd, *J* = 7.5, 1.8 Hz, 1H), 8.15 (dd, *J* = 6.8, 1.5 Hz, 1H), 7.9 (m, 2H), 6.11 (d, *J* = 9.1 Hz, 1H), 5.34 (d, *J* = 5.4 Hz, 1H), 5.08 (s, 1H), 4.83 (s, 1H), 4.4 (m, 1H), 3.98 (dd, *J* = 12.6, 6.2 Hz, 1H), 3.63 (s, 2H), 1.19 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.6, 175.5, 145.5, 135.9, 135.3, 135.0, 133.6, 133.5, 127.6 (2 carbons), 88.3, 74.7, 74.5, 71.7, 69.1, 17.2; ESI/APCI calcd for $C_{16}H_{15}N_3O_6Na^+$ ([M + Na]$^+$) *m/e* 368.0853; measured *m/e* 368.0853.

1-(*N*-(α-D-Rhamnopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19f): Please refer to the general procedure for the deprotection of acetyl groups using K_2CO_3/MeOH/H_2O (yield 33%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.1 − 8.2 (m, 2H), 8.0 (m, 2H), 6.36 (s, 1H), 5.08 (d, *J* = 5.6 Hz, 1H), 5.02 (d, *J* = 5.9 Hz, 1H), 4.89 (d, *J* = 5.8 Hz, 1H), 4.1 (m, 1H), 3.6 (m, 2H), 3.4 (m, 1H), 3.33 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.7, 175.5, 145.0, 135.9, 135.3, 134.0, 133.5, 133.4, 127.6 (2 carbons), 87.9, 76.6, 73.3, 71.8, 70.7, 18.5; ESI/APCI calcd for $C_{16}H_{15}N_3O_6Na^+$ ([M + Na]$^+$) *m/e* 368.0853; measured *m/e* 368.0855.

1-(*N*-(β-D-Xylopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19g). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 79%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.2 (m, 2H), 8.0 (m, 2H), 6.08 (d, *J* = 9.2 Hz, 1H), 5.54 (d, *J* = 5.4 Hz, 1H), 5.38 (d, *J* = 5.2 Hz, 1H), 5.26 (d, *J* = 5.1 Hz, 1H), 4.11 (dt, *J* = 12.2, 9.0 Hz, 1H), 3.96 (dd, *J* = 11.1, 5.2 Hz, 1H), 3.57 (m, 1H), 3.41(m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.6, 175.3, 145.7, 135.9, 135.3, 135.1, 133.6, 133.4, 127.7, 127.6, 88.9, 77.6, 72.1, 69.7, 69.4; ESI/APCI calcd for $C_{15}H_{13}N_3O_6Na^+$ ([M + Na]$^+$) *m/e* 354.0697; measured *m/e* 354.0699.

1-(*N*-(2-Acetamido-β-D-glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19h). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 56%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.21 (d, *J* = 5.7 Hz, 1H), 8.20 (d, *J* = 5.6 Hz, 1H), 7.9 (m, 3H), 6.02 (d, *J* = 9.6 Hz, 1H), 5.31 (d, *J* = 5.4 Hz, 2H), 4.7 (m, 1H), 4.1 (m, 1H), 3.7 (m, 1H), 3.5 (m, 4H), 1.58 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.7, 170.0 (2 carbons), 145.8, 135.5 (3 carbons), 134.6, 127.8 (3 carbons), 91.5, 81.1, 74.2, 70.6, 61.4, 56.1, 23.3; ESI/APCI calcd for $C_{18}H_{18}N_4O_7Na^+$ ([M + Na]$^+$) *m/e* 425.1068; measured *m/e* 425.1068.

1-(*N*-(4-*O*-(β-D-Glucopyranosyl)-β-D-glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19i). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 99%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.2 (m, 2H), 8.0 (m, 2H), 6.22 (d, *J* = 9.2 Hz, 1H), 5.71 (s, 1H), 5.30 (s, 1H), 5.03 (s, 2H), 4.98 (s, 1H), 4.68 (s, 2H), 4.37 (d, *J* = 7.8 Hz, 1H), 4.21 (s, 1H), 3.6 (m, 7H), 3.3 (m, 2H), 3.20 (t, *J* = 8.6 Hz, 1H), 3.08 (t, *J* = 9.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.5, 175.3, 145.7, 135.9, 135.4, 135.2, 133.6, 133.4, 127.7, 127.6, 103.8, 87.8, 80.1, 79.1, 77.5, 77.1, 75.8, 74.0, 71.9, 70.8, 61.8, 60.7; ESI/APCI calcd for $C_{22}H_{25}N_3O_{12}Na^+$ ([M + Na]$^+$) *m/e* 546.1330; measured *m/e* 546.1326.

1-(*N*-(4-*O*-(4-*O*-(β-D-Glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19j). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 57%): ^{1}H NMR(DMSO-d_6, 400 MHz) δ 8.2 (m, 2H), 8.0 (m, 2H), 6.20 (d, *J* = 8.9 Hz, 1H), 5.15 (d, *J* = 3.6 Hz, 1H), 5.01 (d, *J* = 3.6 Hz, 1H), 4.2 (m, 1H), 3.5 (m, 27H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.5, 175.3, 145.7, 136.0, 135.3, 135.2, 133.6, 133.4, 127.8, 127.6, 101.5 (2 carbons), 101.3, 80.2, 79.7, 79.3, 77.1, 74.2, 74.0, 73.8, 73.2, 72.7, 72.5, 71.7, 70.6, 61.5, 61.0, 49.3; ESI/APCI calcd for $C_{28}H_{35}N_3O_{17}Na^+$ ([M + Na]$^+$) *m/e* 708.1859; measured *m/e* 708.1851.

1-(*N*-(β-D-Ribofuranosyl))-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19k). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 57%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.2 (m, 2H), 8.0 (m, 2H), 6.60 (d, *J* = 3.0 Hz, 1H), 5.73 (s, 1H), 5.34 (s, 1H), 4.7 (m, 1H), 4.35 (t, *J* = 5.2 Hz, 1H), 4.05 (dd, *J* = 13.8, 5.6 Hz, 1H), 3.62 (dd, *J* = 11.9, 3.9 Hz, 1H), 3.48 (dd, *J* = 11.9, 5.7 Hz, 1H), 3.33 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.6, 175.6, 145.5, 135.8, 135.3, 135.2, 133.7, 133.5, 127.6 (2 carbons), 92.3, 86.7, 74.9, 71.2, 62.2; ESI/APCI calcd for $C_{15}H_{13}N_3O_6Na^+$ ([M + Na]$^+$) *m/e* 354.0697; measured *m/e* 354.0703.

1,6-Bis(1*H*-naphtho[2,3-*d*]triazole-4,9-dione)-1,6-dideoxy-D-mannitol (19l). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 23%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.21 (dd, *J* = 7.5, 2.3 Hz, 2H), 8.17 (dd, *J* = 7.3, 2.4 Hz, 2H), 7.9 (m, 4H), 5.07 (dd, *J* = 7.7, 3.3 Hz, 2H), 5.07 (d, *J* = 6.3 Hz, 2H), 4.87 (dd, *J* = 13.4, 9.4 Hz, 2H), 4.79 (d, *J* = 8.2 Hz, 2H), 4.1 (m, 2H), 3.72 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.7 (2 carbons), 175.7 (2 carbons), 145.5 (2 carbons), 135.8 (2 carbons), 135.5 (2 carbons), 135.3 (2 carbons), 133.7 (4 carbons), 127.7 (4 carbons), 71.9 (2 carbons), 69.9 (2 carbons), 55.0 (2 carbons); ESI/APCI calcd for $C_{26}H_{20}N_6O_8Na^+$ ([M + Na]$^+$) *m/e* 567.1235; measured *m/e* 567.1236.

1-(1*H*-Naphtho[2,3-*d*]triazole-4,9-dione)-1-dideoxy-D-mannitol (19m). Please refer to the general procedure for the deprotection of acetyl groups using NaOMe/MeOH (yield 97%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.1 (m, 2H), 7.9 (m, 2H), 5.05 (dd, *J* = 13.4, 3.1 Hz, 1H), 4.97 (d, *J* = 6.4 Hz, 1H), 4.83 (dd, *J* = 13.4, 9.5 Hz, 1H), 4.63 (d, *J* = 7.3 Hz, 1H), 4.50 (d, *J* = 4.9 Hz, 1H), 4.40 (s, 1H), 4.27 (d, *J* = 7.7 Hz, 1H), 4.1 (m, 1H), 3.71 (t, *J* = 7.6 Hz, 1H), 3.6 (m, 1H), 3.57 (t, *J* = 8.1 Hz, 1H), 3.5 (m, 1H), 3.4 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.6, 175.6, 145.4, 135.8, 135.4, 135.3, 133.6 (2 carbons), 127.6, 127.5, 72.0, 71.8,

70.1, 70.0, 64.4, 55.0; ESI/APCI calcd for $C_{16}H_{18}N_3O_7^+$ ([M + H]$^+$) *m/e* 364.1139; measured *m/e* 364.1141.

1-(4-Piperidinyl)-1*H*-naphtho[2,3-*d*]triazole-4,9-dione (19n). A solution of **15n** (0.13 g, 0.34 mmol) in CH_2Cl_2 (4 mL) and TFA (1 mL) was stirred at 0 °C for 30 min. After completion of the reaction, the reaction mixture was concentrated and purified with column chromatography (eluted with CH_2Cl_2/MeOH from 100/0 to 4/1). The desired product was obtained as a solid (0.090 g, 0.32 mmol, 94%): ^{1}H NMR (D_2O, 300 MHz) δ 7.82 (dd, J = 5.5, 1.1 Hz, 1H), 7.75 (dd, J = 5.5, 1.0 Hz, 1H), 7.64 (td, J = 4.5, 0.7 Hz, 1H), 7.60 (td, J = 4.0, 0.7 Hz, 1H), 5.39 (tt, J = 14.8, 8.3 Hz, 1H), 3.62 (dt, J = 13.7, 3.4 Hz, 2H), 3.3 (m, 2H), 2.4 (m, 4H); ^{13}C NMR (D_2O, 100 MHz) δ 178.2, 175.5, 144.8, 135.9, 135.5, 133.7, 132.5, 132.1, 127.7, 127.4, 55.8, 42.8 (2 carbons), 27.9 (2 carbons); ESI/APCI calcd for $C_{15}H_{15}N_4O_2^+$ ([M + H]$^+$) *m/e* 283.1190; measured *m/e* 283.1189.

2-(*N*-(*β*-D-Glucopyranosyl))aminomethylene-1,3-indanedione (20a). Please refer to the general procedure for the deprotection of acetyl groups using K_2CO_3/MeOH/H_2O (yield 64%): ^{1}H NMR (CD_3OD, 400 MHz) δ 8.00 (s, 1H), 7.74 (m, 4H), 4.61 (d, J = 8.4 Hz, 1H), 3.90 (dd, J = 12.0, 1.9 Hz, 1H), 3.72 (dd, J = 12.0, 5.3 Hz, 1H), 3.4 (m, 4H); ^{13}C NMR (CD_3OD, 100 MHz) δ 193.1, 191.0, 151.2, 139.8, 139.7, 133.8, 133.7, 121.7, 121.3, 101.8, 88.8, 79.3, 77.1, 73.3, 69.8, 61.3; ESI/APCI calcd for $C_{16}H_{18}NO_7^+$ ([M + H]$^+$) *m/e* 336.1078; measured *m/e* 336.1088.

2-(*N*-(*β*-D-Galactopyranosyl))aminomethylene-1,3-indanedione (20b). Please refer to the general procedure for the deprotection of acetyl groups using K_2CO_3/MeOH/H_2O (yield 53%): ^{1}H NMR (CD_3OD, 400 MHz) δ 8.01 (s, 1H), 7.68 (m, 4H), 4.56 (d, J = 8.6 Hz, 1H), 3.93 (d, J = 2.8 Hz, 1H), 3.7−3.8 (m, 4H), 3.59 (dd, J = 9.5, 3.1 Hz, 1H); ^{13}C NMR (CD_3OD, 100 MHz) δ 193.2, 191.0, 151.2, 139.8, 139.7, 133.8, 133.7, 121.6, 121.3, 104.8, 89.4, 78.0, 74.0, 70.8, 69.3, 61.4; ESI/APCI calcd for $C_{16}H_{18}NO_7^+$ ([M + H]$^+$) *m/e* 336.1078; measured *m/e* 336.1085.

2-(*N*-(α-D-Rhamnopyranosyl))aminomethylene-1,3-indanedione (20f). Please refer to the general procedure for the deprotection of acetyl groups using K_2CO_3/MeOH/H_2O (yield 39%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.6 (m, 1H), 8.03 (d, J = 6.0 Hz, 1H), 7.7 (m, 4H), 5.36 (d, J = 5.3 Hz, 1H), 4.94 (s, 1H), 4.93 (d, J = 5.3 Hz, 1H), 4.86 (d, J = 4.3 Hz, 1H), 3.8 (m, 1H), 3.2 (m, 3H), 1.18 (d, J = 6.0 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 193.3, 189.5, 151.8, 139.9, 134.5 (2 carbons), 122.2, 121.8 (2 carbons), 104.7, 85.6, 74.6, 73.9, 71.8, 70.6, 18.5; ESI/APCI calcd for $C_{16}H_{18}NO_6^+$ ([M + H]$^+$) *m/e* 320.1129; measured *m/e* 320.1136.

2-(*N*-(α-D-Xylopyranosyl))aminomethylene-1,3-indanedione (*epi*-20g). Please refer to the general procedure for the deprotection of acetyl groups using K_2CO_3/MeOH/H_2O (yield 35%): ^{1}H NMR (CD_3OD, 300 MHz) δ 8.10 (s, 1H), 7.7 (m, 4H), 5.09 (d, J = 2.4 Hz, 1H), 3.95 (dd, J = 12.0, 2.8 Hz, 1H), 3.81 (t, J = 5.5 Hz, 1H), 3.6−3.7 (m, 2H), 3.5 (m, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 193.4, 190.7, 151.1 (2 carbons), 139.7, 139.6, 133.7, 133.7, 121.6, 121.2, 83.9, 70.3, 70.0, 68.5, 65.6; ESI/APCI calcd for $C_{15}H_{16}NO_6^+$ ([M + H]$^+$) *m/e* 306.0972; measured *m/e* 306.0977.

2-(*N*-(*β*-D-Xylopyranosyl))aminomethylene-1,3-indanedione (20g). Please refer to the general procedure for the deprotection of acetyl groups using K_2CO_3/MeOH/H_2O (yield 53%): ^{1}H NMR (CD_3OD, 300 MHz) δ 7.90 (s, 1H), 7.6−7.7 (m, 4H), 4.52 (d, J = 8.2 Hz, 1H), 3.95 (dd, J = 11.3, 5.2 Hz, 1H), 3.5 (m, 1H), 3.2−3.4 (m, 3H); ^{13}C NMR (CD_3OD, 75 MHz) δ 192.9, 190.9, 150.9, 139.6 (2 carbons), 133.7, 133.6, 121.5, 121.2, 104.8, 89.3, 76.6, 72.9, 69.4, 67.6; ESI/APCI calcd for $C_{15}H_{16}NO_6^+$ ([M + H]$^+$) *m/e* 306.0972; measured *m/e* 306.0976.

2-(*N*-(*β*-D-Ribofuranosyl))aminomethylene-1,3-indanedione (20k). Please refer to the general procedure for the deprotection of acetyl groups using K_2CO_3/MeOH/H_2O (yield 46%): ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.62 (dd, J = 13.5, 6.7 Hz, 1H), 8.00 (d, J = 14.2 Hz, 1H), 7.6−7.7 (m, 4H), 5.31 (d, J = 6.2 Hz, 1H), 5.1 (m, 3H), 4.06 (dd, J = 10.5, 5.1 Hz, 1H), 4.0 (m, 1H), 3.85 (d, J = 2.9 Hz, 1H), 3.5−3.6 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 192.2, 189.7, 150.9, 140.0, 139.9, 134.4 (2 carbons), 122.1, 121.7, 104.4, 94.2, 86.2, 75.9, 71.4, 61.9; ESI/APCI calcd for $C_{15}H_{16}NO_6^+$ ([M + H]$^+$) *m/e* 306.0972; measured *m/e* 306.0976.

1-(Aminomethylene-1,3-indanedione)-1-dideoxy-D-mannitol (20m). Please refer to the general procedure for the deprotection of acetyl groups using K_2CO_3/MeOH/H_2O (yield 40%): ^{1}H NMR(DMSO-d_6, 300 MHz) δ 9.55 (s, 1H), 7.80 (s, 1H), 7.6 (m, 4H), 4.0−5.0 (m, 5H), 3.4−3.7 (m, 8H); ^{13}C (DMSO-d_6, 100 MHz) δ 190.2, 189.0, 154.4, 139.8 (2 carbons), 133.9 (2 carbons), 122.0 (2 carbons), 103.5, 71.8, 70.8, 70.0, 69.6, 64.6, 54.2; ESI/APCI calcd for $C_{16}H_{20}NO_7^+$ ([M + H]$^+$) *m/e* 338.1234; measured *m/e* 338.1246.

2-(*N*-(4-Piperidinyl))aminomethylene-1,3-indanedione (20n). Compound **20n** was prepared similarly as the preparation of **19n** (yield 99%): ^{1}H NMR (D_2O, 300 MHz) δ 7.4 (m, 2H), 7.31 (s, 1H), 7.16 (td, J = 4.5, 1.7 Hz, 1H), 7.06 (td, J = 4.1, 1.4 Hz, 1H), 3.65 (tt, J = 11.3, 3.8 Hz, 1H), 3.5 (m, 1H), 3.4 (m, 1H), 3.01 (td, J = 13.0, 2.7 Hz, 2H), 2.1 (m, 2H), 1.88 (dd, J = 14.0, 4.1 Hz, 1H), 1.77 (dd, J = 13.0, 4.1 Hz, 1H); ^{13}C NMR (D_2O, 100 MHz) δ 193.5, 192.4, 151.0, 138.2 (2 carbons), 134.2, 134.0, 121.6, 121.2, 103.3, 54.6, 42.8 (2 carbons), 28.7 (2 carbons); ESI/APCI calcd for $C_{15}H_{17}N_2O_2^+$ ([M + H]$^+$) *m/e* 257.1285; measured *m/e* 257.1293.

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Supporting Information Available: ^{1}H, ^{13}C, and related spectra of the synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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