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C-Glycosylation

# Synthesis of *C*-Oligosaccharides through Versatile C($sp^3$)–H Glycosylation of Glycosides

*Jun Wu, Adelina Kopp, and Lutz Ackermann**

***Abstract:*** *C-oligosaccharides are pharmacologically relevant because they are more hydrolysis-resistant than O-oligosaccharides. Despite indisputable advances, C-oligosaccharides continue to be underdeveloped, likely due to a lack of efficient and selective strategies for the assembly of the interglycosidic C–C linkages. In contrast, we, herein, report a versatile and robust strategy for the synthesis of structurally complex C-oligosaccharides via catalyzed C($sp^3$)–H activations. Thus, a wealth of complex interglycosidic (2→1)- and (1→1)-C-oligosaccharides becomes readily available by palladium-catalyzed C($sp^3$)–H glycoside glycosylation. The isolation of key palladacycle intermediates and experiments with isotopically-labeled compounds identified a trans-stereoselectivity for the C($sp^3$)–H glycosylation. The glycoside C($sp^3$)–H activation manifold was likewise exploited for the diversification of furanoses, pyranoses and disaccharides.*

Oligosaccharides are found in various biology-relevant transformations[1] and constitute the key motif of numerous therapeutics.[2] The assembly of *O*-oligosaccharides by enzymatic biosynthesis with glycosyltransferases,[3] or solid-phase synthesis[4] and through the design of glycosyl donors for one-pot glycosylation relay[5] are well documented. Of particular interest are *C*-oligosaccharides as nonhydrolyzing antimetabolites due to their significantly improved stability towards chemical hydrolysis and enzymatic degradation. *C*-oligosaccharides with a glycosidic C–C linkage are embedded in numerous naturally occurring biomolecules. As illustrated in Scheme 1a, dodecodiulose, (an analogue of trehalose),[6] or structurally complex natural products, such as anthelmintic hikizimycin[7] and neurotoxic Maitotoxin[8] embody interglycosidic C–C bonds. Thus, glycosidic C–C bond-forming strategies are of significant value for enriching the diversity of viable oligosaccharides.[9] Traditional approaches largely employed iterative chain elongation or convergent block condensations,[10] yet continue to be limited by tedious protection/deprotection processes. Although advanced protocols were developed for radical-mediated C–C bond formations[11] or radical dimerization,[12] both showed limited diastereoselectivity and substrate scope. Other methods, such as ring closing metathesis (RCM),[13] hetero-Diels–Alder cycloaddition (HDA),[14] Stille-type cross-coupling[15] or Ramberg–Bäcklund rearrangement reactions (RBR),[16] required specifically designed glycosyl.(Scheme 1b).

Glycorandomization and glycodiversification[17] provided a feasible, rapid method for the attachment and post-translational modification of carbohydrates. Considerable efforts by cross-couplings,[18] and photo-[19] or electrochemical glycosylations[20] were devoted to the selective anomeric late-stage transformation. In recent years, transition-metal catalyzed C–H activation[21] was identified as an efficient alternative for the selective glycosylation of arenes and amino acids for the construction of glycomimetic pharmacophores.[22] Site-selective functionalization of carbohydrates[23] can generate targeted scaffolds through exceptional resource-economy, and general strategies for maximizing selectivity in carbohydrate chemistry continue to be in high demand.[24] However, despite of indisputable advances, strategies for the targeted synthesis of stable *C*-oligosaccharides have proven elusive. In contrast, we have now accomplished the unprecedented regio- and stereoselective glycoside C($sp^3$)–H glycosylation, setting the stage for the controllable late-stage diversification of carbohydrates. In addition, glycorandomization and glycodiversification by C($sp^3$)–H glycosylation enabled the construction of a diversified library of conformationally-rigid *C*-oligosaccharides (Scheme 1c).

Deoxy sugars are essential components of numerous bioactive natural products, drugs and glycoconjugates. Changing the composition and length of the attached oligosaccharides can profoundly alter their bioactivities. Thus, the efficient synthesis and controllable glycosylation of deoxy sugars are of major importance.[25] Hence, we initiated our studies with 2-deoxy-β-glycoside **1a** and glycosyl donor 1-iodo-glucal **2a** as model substrates for the challenging C($sp^3$)–H glycosylation. In this context, we wondered whether the initial C–H activation of deoxy sugar with palladium(II) acetate would give a cyclopalladaglycoside complex. This palladacycle would serve as the key *C*-glycosyl acceptor for the saccharide assembly by the subsequent reaction with 1-iodo-glucal donor **2a** (Scheme 1c). After considerable optimization of all reaction

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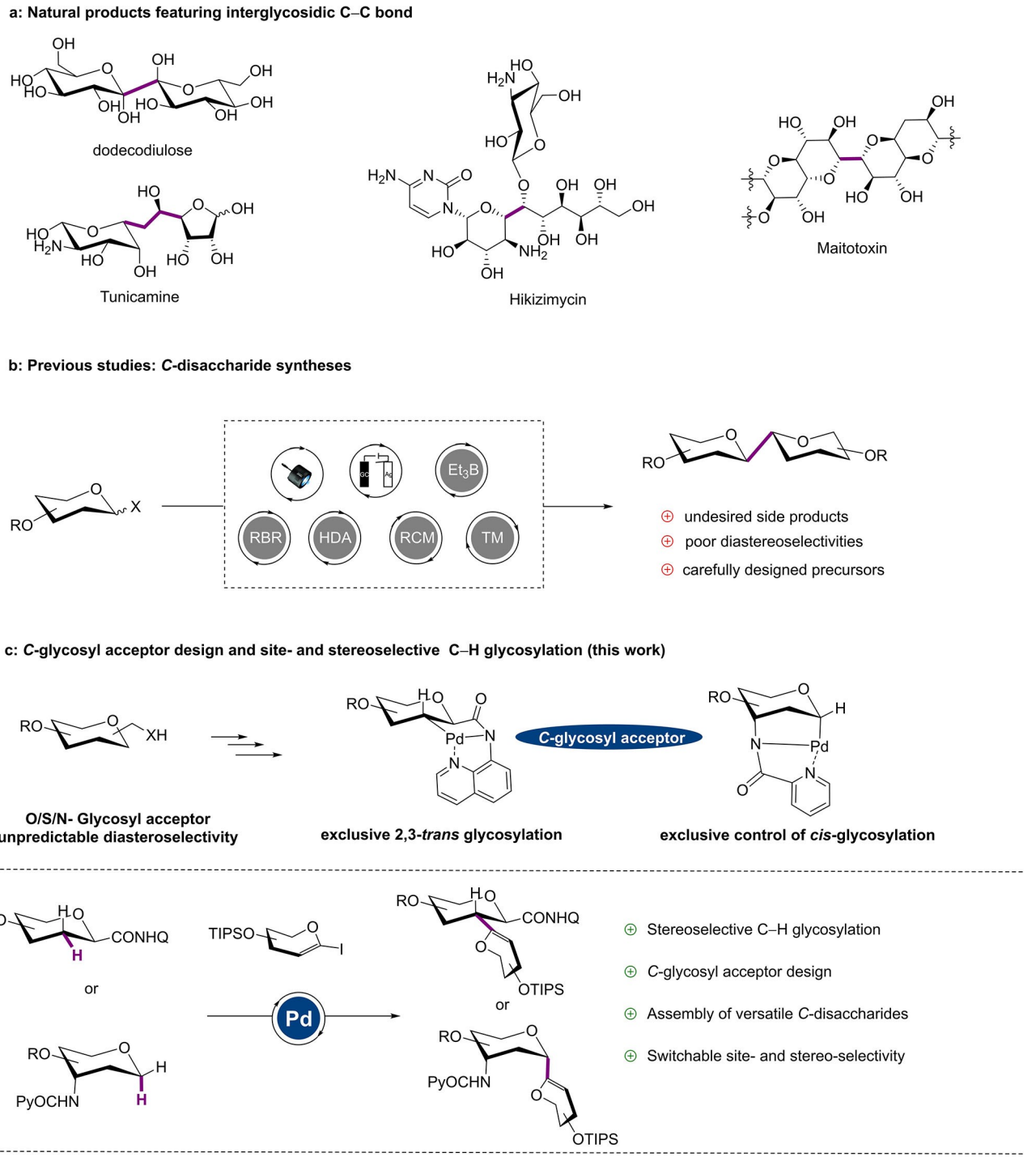
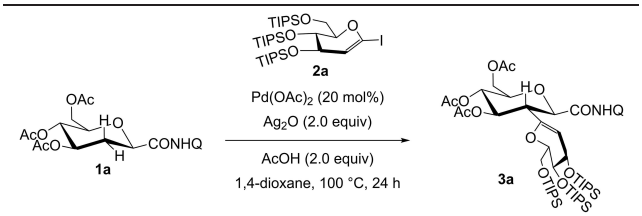



***Scheme 1.*** *C*-oligosaccharides synthesis via C($sp^3$)–H glycosylation of glycosides. a) Natural products featuring interglycosidic *C*-linkages. b) Methodologies for *C*-disaccharide synthesis. c) *C*-glycosyl acceptor design and C–H glycosylation of glycosides.

parameters (Table 1 and see more details in the Supporting Information Table 1), we observed that the C($sp^3$)–H activation of glycoside **1a** in 1,4-dioxane delivered the equatorial C($sp^3$)–H glycosylated product **3a** in 73 % yield with $Ag_2O$ and AcOH as additives (entry 1). A slightly reduced catalytic efficiency was observed in the absence of AcOH, when other silver salts were probed (entries 2–4). Control experiments verified the essential roles of the catalyst and of the silver salt (entries 5–8).

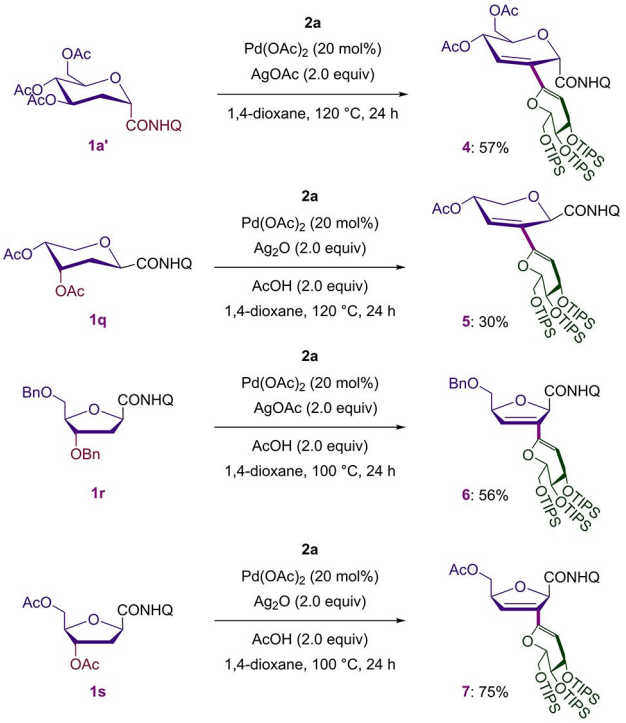
Then, we examined the influence of the absolute configuration at the anomeric center (Scheme 2). When anomeric α-glucoside was subjected to the optimized conditions, the β-desacetoxyl elimination product **4** was selectively formed. In this case, a *cis*-C–H activation favored a C($sp^3$)–H activation along with a β-acetoxyl- elimination.[24c]

***Table 1:*** Optimization of reaction conditions.[a]




| Entry | Deviation from the standard conditions | Yield [%][b] |
|---|---|---|
| 1 | None | 73 |
| 2 | $Ag_2O$ instead of $Ag_2O$/HOAc | 59 |
| 3 | AgOAc instead of $Ag_2O$/HOAc | 53 |
| 4 | $Ag_2CO_3$ instead of $Ag_2O$/HOAc | 51 |
| 5 | $Pd(OAc)_2$ (5 mol%) | 29 |
| 6 | $Ag_2O$ (0.5 equiv) | 45 |
| 7 | no $Pd(OAc)_2$ | – |
| 8 | no $Ag_2O$ | – |

[a] **1a** (0.10 mmol), **2a** (0.15 mmol). $Pd(OAc)_2$ (20 mol%), $Ag_2O$ (0.20 mmol), AcOH (0.20 mmol), 1,4-dioxane (1.0 mL), 100 °C, 24 h. [b] Isolated yield.

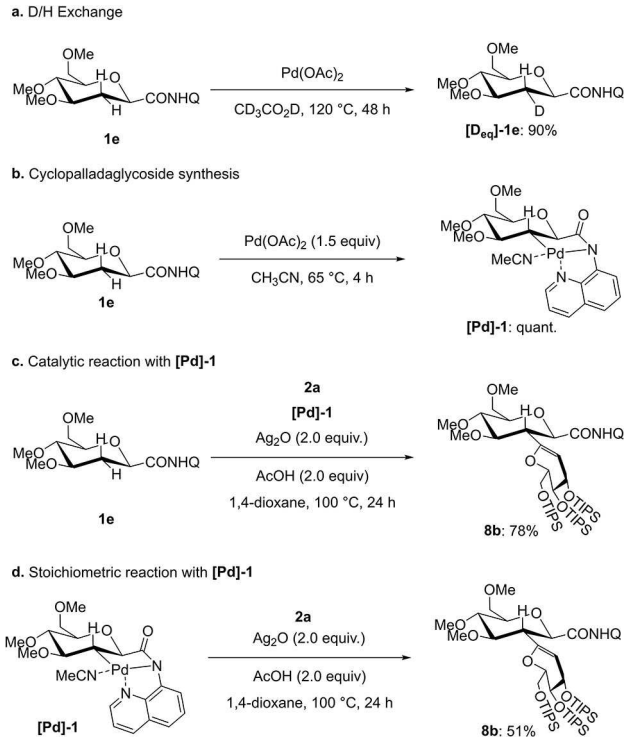



***Scheme 2.*** β-Elimination of various glycosides.

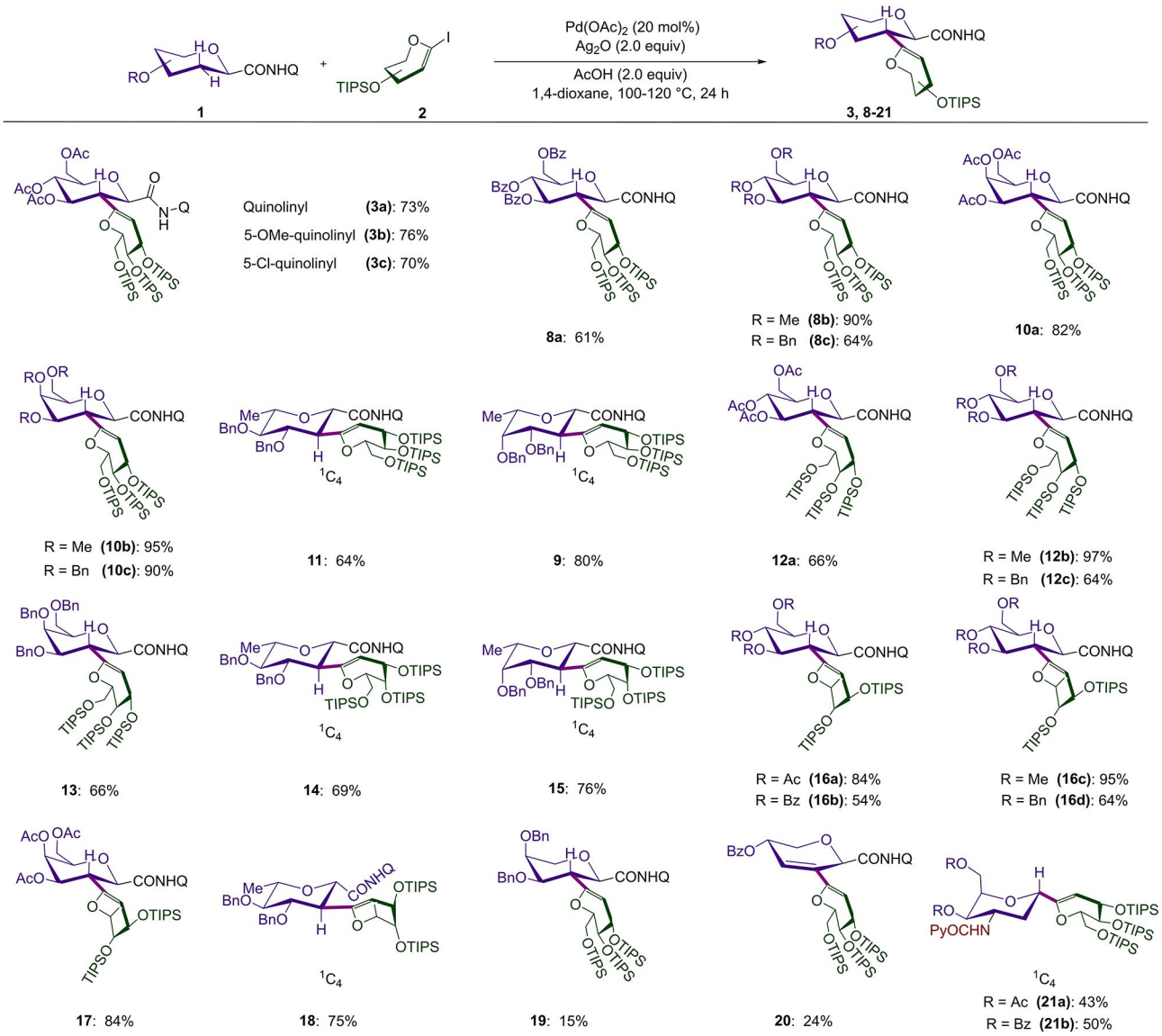
2-Deoxy-xyloside **1q** with an axial acetoxyl group at the *C3* position gave a suppressed catalytic efficiency due to the steric effect exerted by the *C3*-axial substituent. Furanosides derived from 2-deoxy ribose with different leaving groups gave the β-eliminated products **6** and **7** with excellent selectivities.

To gain insights into the C($sp^3$)–H palladation, we therefore conducted transformations with isotopically labelled $CD_3CO_2D$ as the solvent. The H/D exchange experiment showed that the equatorial hydrogen was selectively deuterated to give compound [$\mathbf{D_{eq}}$]-**1e** (Scheme 3a). This finding was indicative of a t*rans*-C($sp^3$)–H palladation. Furthermore, cyclopalladaglycoside complexes **[Pd]-1** and **[Pd]-2** were independently prepared, which provided evidence for a *trans*- C–H activation (Scheme 3b). Catalytic (Scheme 3c) or stochiometric (Scheme 3d) amounts of the cyclopalladaglycoside complexes were identified as viable (see S73, S74 in the Supporting Information). Intermolecular competition experiments provided strong support for a facile C–H metalation with a minor kinetic isotopic effect (KIE) of $k_H/k_D \approx 1.1$ (see S68 in the Supporting Information).

With the optimized C($sp^3$)–H glycoside glycosylation in hand, we examined its generality of the C($sp^3$)–H glycosylation (Scheme 4). First, quinolines (Q) with different substituents (**3a**–**3c**) were found to be compatible. Second, 2-deoxy-glucoside with benzoyl groups (Bz) delivered the desired glucosyl-*C*-[2→1]-glucal **8a**. Third, methyl and benzyl ethers proved feasible. When the C($sp^3$)–H glycosides glycosylation was applied to galactosides, excellent catalytic efficiencies were observed for the galactosyl-*C*-[2→1]-glucal **10a**–**10c** construction. 2,6-Deoxy-rhamnoside and 2,6-deoxy-fucose, important components of naturally occurred *C*-glycosides, could be used for the preparation of rhamnosyl-*C*-[2→1]-glucal **11** and fucosyl-*C*-[2→1]-glucal **9**. 1-Iodo-galactal **2b** was utilized for the saccharide assembly, and proved powerful for the construction of various *C*-disaccharides, such as glucosyl-*C*-[2→1]-galactal **12a**–**12c**, galactosyl-*C*-[2→1]-galactal **13**, rhamnosyl-*C*-[2→1]-galactal **14** and fucosyl-*C*-[2→1]-galactal **15** with selective *trans*-C($sp^3$)–H glycosylation. In addition to the glycals **2a** and **2b**, glycosyl donor **2c** derived from rhamnose also proved



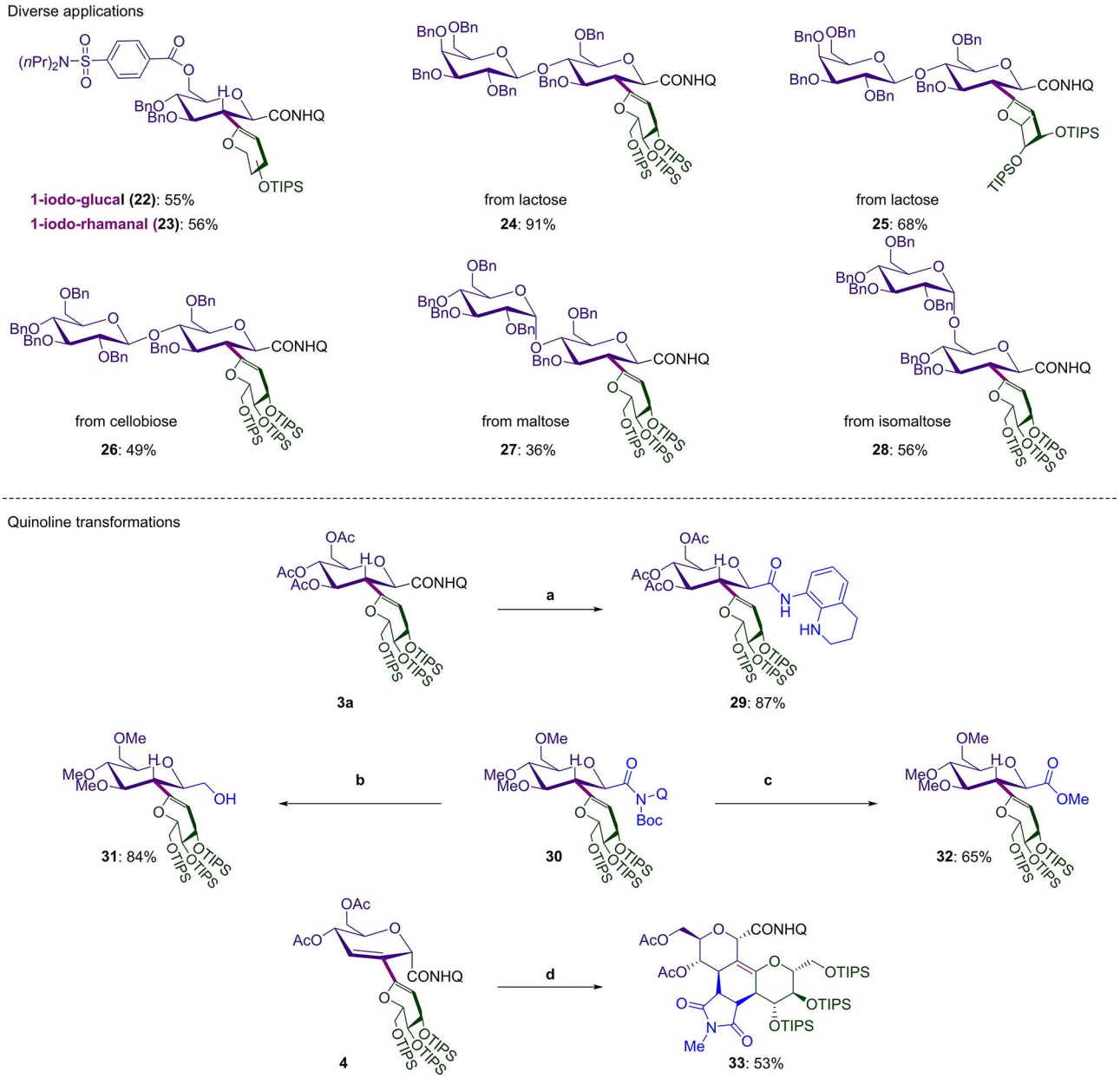

***Scheme 3.*** Key mechanistic studies.




***Scheme 4.*** Versatility and robustness of C($sp^3$)–H glycosides glycosylation.

amenable to 2-deoxy-glucosides, galacotosides, delivering disaccharides **16a**–**16d** and **17** in moderate to excellent yields. Especially, this approach provided facile access to the rhamnosyl- *C*-[2→1]-rhamnal **18** that is challenging to prepare by conventional methods. Arabinoside bearing an *C3* equatorial group was probed, and the elimination product was not formed (**19**). The catalytic efficiency of 2-deoxy-xyloside with an axial- OAc functional group at *C3* position was suppressed due to the steric effect of the *C3* axial protecting group along with β-eliminated product **20**. To demonstrate transition metal-catalyzed diversification of our saccharide assembly strategy by C($sp^3$)–H glycosylation of glycosides, designed glycosides with the removable picolinic amide (PyCONH) was employed and precisely aimed for the anomeric C($sp^3$)–H glycosylation for the construction of interglycosidic (1→1)-*C*-oligosaccharides. To our delight, we observed that glycosides bearing an axial picolinic amide at the *C3* position allowed for the formation of altrose-*C*-[1→1]-glucal **21a** and **21b** with exclusive α-selectivity.

Our saccharide assembly strategy proved likewise amenable to the challenging diversification of more structurally complex motifs (Scheme 5). Probenecid-glucoside hybrid was examined with different glycosyl donors **2a** and **2c**. Here, the glycodiversification (**22** and **23**) was characterized by exclusive β-selective C($sp^3$)–H glycosylation. Protected disaccharides, such as lactose, cellobiose, maltose and isomaltose, were also efficiently converted within a one-pot diastereoselective trisaccharides synthesis **24**–**28**. Treatment of disaccharide **3a** with a palladium catalyst and molecular hydrogen afforded product **29** bearing a newly formed piperidine hydrogen bond donor. The amide-linked quinoline was successfully cleaved under mild reaction conditions via a two-step sequence, resulting in either the primary alcohol **31** or the ester **32**. Finally, a DA-reaction set the stage for the efficient construction of polycyclic




***Scheme 5.*** Late-stage diversification and quinoline amide transformation. General conditions: a) Pd/C, $H_2$ (1.0 atm), EtOAc/MeOH, 16 h. b) $LiAlH_4$, $N_2$, 0 °C 2 h. c) $K_2CO_3$, MeOH, 12 h. d) *N*-methylmaleimide, toluene, 110 °C, 3 h.

product **33** with four newly formed stereocenters with defined configuration in a single step.

In conclusion, we have devised an enabling platform for the late-stage C($sp^3$)–H glycosylation of deoxyglycosides to establish the modular assembly of unnatural *C*-disaccharides and *C*-trisaccharides. Thus, a *C*-glycosyl acceptor was designed for a *C*-disaccharide synthesis and systematically explored for a versatile saccharide assembly. Our strategy proved to be efficient, diastereoselective, broadly applicable and operationally simple, highlighting the remarkable prospects of the thus-obtained *C*-oligosaccharide. The removable quinolinyl amide enabled a switchable syntheses of diastereoselective interglycosidic (2→1)- and (1→1)-*C*-disaccharides. This glycorandomization by palladium-catalyzed C-($sp^3$)–H glycosylation of 2-deoxy-glycosides allowed for the straightforward synthesis of a variety of complex products that are difficult to prepare by thus far existing methods. We hope that our findings on C($sp^3$)–H glycosylations for saccharide assembly will stimulate novel stereoselective modifications of complex carbohydrates.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** C(sp$^3$)–H Activation · *C*-Disaccharide Synthesis · 2-Deoxyglycosides · Palladium Catalysis

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