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Diastereoselective access to *C*,*C*-glycosyl amino acids *via* iron-catalyzed, auxiliary-enabled MHAT coupling†

Mylène Lang, Damien Tardieu, Benoit Pousse, Philippe Compain* and Nicolas Kern*

Access to *C*,*C*-glycosyl amino acids as a novel class of glycomimetics is reported by means of radical generation, intermolecular addition and stereoselective reduction *via* a metal-induced hydrogen atom transfer (MHAT) sequence. The 'matched' coupling of *exo*-D-glycals with an enantiopure dehydroalanine bearing a (*R*)-configured benzyl oxazolidinone enables a singular case of two-fold diastereocontrol under iron catalysis. In the common *exo*-D-glucal series, the nature of the C-2 substituent was found to play a key role from both reactivity and stereocontrol aspects.

Glycoproteins, as ubiquitous components of mammal tissues, are involved in multiple biological processes such as cell signaling, growth regulation and immunity.[1,2] In the realm of pharmaceutical research, linking an amino acid chain to sugar(s) also stands as an established way to improve stability towards proteases and increase membrane permeability.[3] As the overwhelming majority of natural glycopeptides comprise enzymatically labile C–O or C–N linkages (with *C*-mannosyl tryptophan as the sole exception[4]), unnatural *C*-glycopeptides both furnish useful probes to facilitate the elucidation of essential processes *in vivo*, as well as stable drug or vaccine candidates.[5] This promising potential has therefore aroused intense synthetic efforts to construct C-linked sugar amino acid (SAA) building blocks.[6,7] Formal ''deletion'' of the linking O- or N-atom ideally calls for the direct coupling of a pyranosyl unit activated at C-1[8] with a functionalized two-carbon synthon bearing the (masked) AA motif. Such step-economic and convergent disconnection however adds challenges, especially regarding stereoselectivity and functional orthogonality. Notably, Ackermann and Li & Liu independently demonstrated the virtue of Pd-catalyzed C(sp^2)–H and C(sp^3)–H activation to assemble a persilylated iodoglycal and auxiliary-tagged enantiopure amino acid (Fig. 1a).[9] While excellent yields and diastereoselectivities (β to nitrogen, *i.e.* at C-1′) could be achieved, efficient introduction of key O- or N-functionality at the C-2 site in such adducts can be nontrivial. Another mild approach involves the generation of glycosyl radicals[10] and trapping with dehydroalanine-type acceptors (DHAs). Very recently, two photoinduced variants emanated from the groups of Di

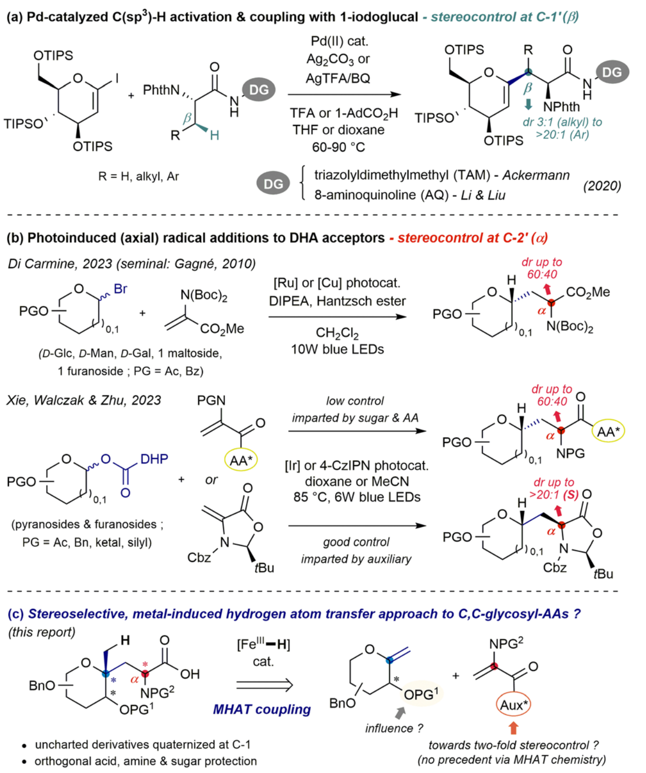

Fig. 1 Recent convergent strategies to assemble *C*-glycosyl amino acids from pyranosides and (C_2) amino acid synthons (a) and (b) and aims of this work (c).

Laboratoire d'Innovation Moléculaire et Applications (LIMA), UMR 7042, Université de Strasbourg/Université de Haute-Alsace/CNRS, ECPM, 25 rue Becquerel, 67087, Strasbourg, France. E-mail: philippe.compain@unistra.fr, nicolas.kern@unistra.fr

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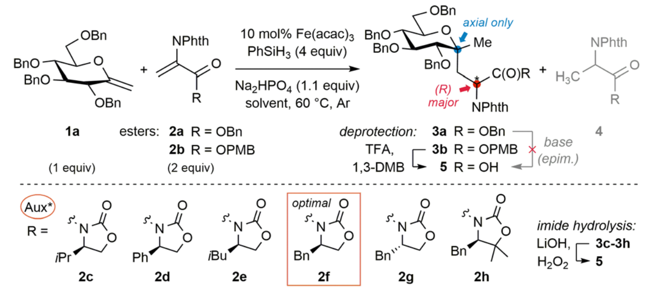
Carmine using pyranosyl bromides[11] and those from Xie, Walczak & Zhu who relied on furanosyl and pyranosyl dihydropyridyl esters (Fig. 1b).[12] Glycosyl radical additions to achiral and/or peptide-linked DHA derivatives typically proceed with axial selectivity but low control at the AA centre (α to nitrogen, *i.e.* at C-2′), emphasizing the poor level of induction imparted from the sugar and AA moieties. This trend, observed early by Kessler,[13] appears as a longstanding issue. Therefore, Xie, Walczak & Zhu employed the (*S*)-enantiomer of the Karady–Beckwith acceptor and achieved high control in most cases through *cis*-selective reduction by hydrogen atom transfer (HAT), as documented.[14]

In connection with our search for *neo*-glycoconjugates and interest in novel transformations of *exo*-glycals,[15] we questioned the viability of an MHAT (metal-induced HAT)[16,17] coupling to form *C*,*C*-glycoaminoacids, unusual adducts embedding an atypical fully substituted pseudoanomeric carbon.[18] Several intramolecular cyclization strategies were examined, all of which met with failure due to the low stability of DHA-acylated *exo*-glycals. While an intermolecular approach first appeared daunting in terms of two-fold stereocontrol (yet unreported for Fe-HAT Baran–Giese type coupling, and including an exocyclic centre), we were curious whether the inherent low stereoinduction inferred from the pyranoside (*vide supra*) could be enforced. We envisioned that such a task may be achievable through the identification of an appropriate "matched" nonracemic radical acceptor, along with careful choice of the protection patterns – especially for the C-2 hydroxyl moiety, in the vicinity of subsequently formed open-shell species (Fig. 1c).

Table 1 Optimization of the intermolecular diastereoselective catalytic MHAT coupling



Entry	Acceptor	Solvent(s)/conc. (M)	*t* (h)	Yield (%)/product	d.r.[b]
1	**2a**	EtOH (0.1)	1.5	60 (**3a**)[a]	69 : 31
2	**2a**	EtOH (0.01)	16	52 (**3a**)[a]	71 : 29
3	**2a**	EtOH (0.03)	4	77 (**3a**)[a]	73 : 27
4[c]	**2a**	EtOH (0.03)	2	40 (**3a**)[ad]	nd
5 [A]	**2b**	EtOH (0.03)	4	76 (**5**)[e]	69 : 31
6 [B]	**2b**	THF (0.03)[f]	16	66 (**5**)[e]	71 : 29
7	**2c**	EtOH (0.03)	4	50 (**5**)[e]	58 : 42
8	**2d**	EtOH (0.03)	4	Trace[d]	nd
9	**2e**	EtOH (0.03)	4	21 (**5**)[e]	70 : 30
10 [A]	**2f**	EtOH (0.03)	4	75 (**5**)[e]	88 : 12[g]
11 [B]	**2f**	THF (0.03)[f]	16	82	92 : 8[g]
12[h]	**2f**	THF (0.03)[f]	16	45	96 : 4[g]
13	**2g**	EtOH (0.03)	4	67	74 : 26
14	**2h**	EtOH (0.03)	4	31	93 : 7[g]

[a] Estimated yield by ^{1}H NMR (isolated material contaminated with **4a**). [b] Determined by ^{1}H NMR analysis of partly purified **3a** or pure **5**. [c] 20 mol% [Fe]. [d] Formation of unseparable side products. [e] Isolated yield after acidic hydrolysis to **5**. [f] 16 equiv. EtOH as additive. [g] Confirmed by HPLC. [h] At 25 °C. [A] & [B]: optimal conditions.

To begin to answer this question, *O*-benzyl-*N*-phthaloyl DHA-based acceptor **2a** was selected (Table 1). Screening of coupling conditions (catalytic Fe(acac)$_3$, phenylsilane and Na$_2$HPO$_4$ buffer in EtOH) applied to a mixture of perbenzylated *exo*-glycal **1a** (1 equiv.) and **2a** (2 equiv.) first suggested that productive radical generation from *exo*-glucals calls for specific dilute conditions and moderate catalyst loading (entries 1–4). Along with targeted adduct **3a**, alanine imidoester **4a** was identified as the main side product. Competitive reduction of *C*-radicophiles has been scarcely mentioned in the Fe-HAT literature,[19] and may be favored here considering the captodative character of the product radical,[20] partly overriding the usual cross-coupling chemoselectivity attributed to polar effects. This may also explain the use of excess electron-rich alkenes in related protocols,[19,21] inconvenient with valuable *exo*-glycals. However, formal hydrogenation of **1a** and telomerization[13] were fully avoided.[22] Since chromatographical separation of **3a** and **4a** proved tedious, base-mediated hydrolysis of the benzyl ester resulted in the epimerization of the neoformed AA stereocentre. Substitution of **2a** for PMB ester **2b** (entry 5, conditions [A]) allowed quantitative and epimerization-free acid-mediated dealkylation with TFA in conjunction with 1,3-dimethoxybenzene (DMB), yielding free acid **5**.[23] Akin to **2a**, acceptor **2b** appeared almost insoluble at 25 °C and sparingly at 60 °C; therefore inclusion of cosolvents was evaluated. Use of minimal EtOH in THF (16 equiv. to reach full conversion; entry 6, conditions [B]) resulted in close efficiency at the cost of reaction rate, which may be rationalized from the involvement of the alcohol in the rate-determining iron hydride generation step.[15] Overall, all experiments involving achiral acceptor **2b** furnished products **3** (or **5**) in moderate d.r. (close to 7 : 3). We thus moved forward by evaluating DHA-tagged chiral oxazolidinones **2c–2h**.[21,24] Unlike esters, imide coupling adducts could be carefully hydrolyzed to **5** without epimerization using minimal LiOH and H$_2$O$_2$, enabling comparison of the stereochemical course with reactions of **2b**. First, (*R*)-configured isopropyl derivative **2c** underwent addition with lower diastereoselectivity (entry 7). Phenyl analog **2d** only led to traces of the coupling adduct, while *iso*butyryl analog **2e** reacted poorly with the glycosyl radical without impacting stereoinduction (entries 8 and 9). Gratifyingly, a 'matched' case was disclosed with benzyl surrogate **2f** (*i.e.* Evans' auxiliary,[25] entry 10), which reacted efficiently and induced good diastereocontrol (88 : 12) under conditions [A]. As the stereodetermining redox termination step involves the protic solvent,[26] system [B] with minimal EtOH was evaluated and induced a slight enhancement (entry 11). Since acceptor **2f** displayed better solubility in THF, decreasing the reaction temperature to 25 °C allowed even higher control but with lower efficiency (entry 12). Consecutively, the (*S*)-enantiomer **2g** was probed to be 'mismatched' (entry 13). The *gem*-dimethyl surrogate of the optimal auxiliary[27] acted as a potent inductor, but the apparent

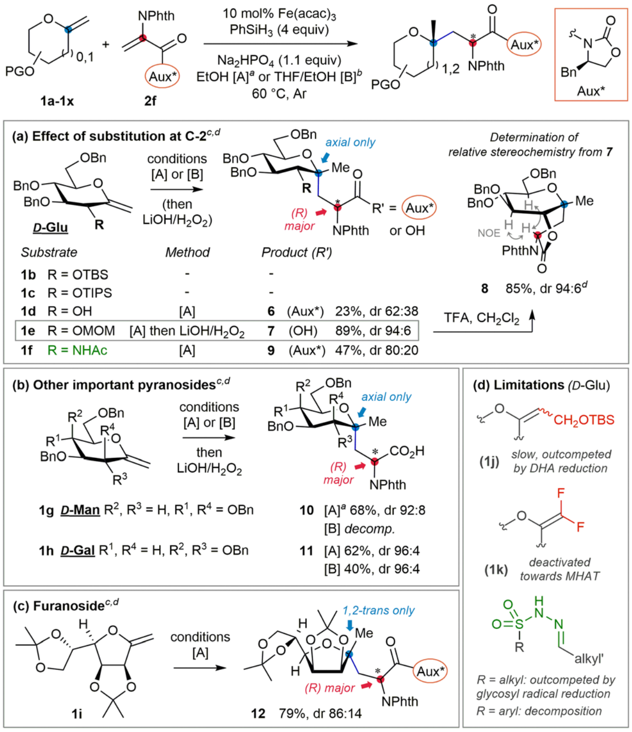


Fig. 2 (a) Identification of the optimal *exo*-glucal protection pattern and derivatization. (b) Application to mannosyl and galactosyl surrogates. (c) Application to furanoside. (d) Main limitations observed through this study. [a] Reaction time: 3–4 h. [b] Reaction time: 12–16 h (full conv obs). [c] Isolated yields. [d] dr determined by ^{1}H NMR analysis of isolated products due to overlaps.

lower stability of parent acceptor **2h** only enabled moderate yields (entry 14). The observation that all auxiliaries and conditions afforded the same major diastereoisomer of **5** stands in line with previous reports involving pyranosides, where the degree but not the direction of stereoselectivity could be influenced.[13,14] Furthermore, closer examination of related work[12] reveals that stereoinduction in the termination step is usually lower for pyranosides bearing equatorial O- or N-functionality at C-2. In contrast to mannosides or 2-deoxy derivatives for example, their orientation may partly impede the population of a favorable conformer for stereoselective termination (*vide infra*). A series of *exo*-D-glucals diversely protected at C-2 were thus examined (Fig. 2a).‡ With relatively bulky silyl groups (**1b** & **1c**) negligible conversions were observed while DHA reduction predominated. The solvolytically unstable free-hydroxyl derivative **1d** only led to the corresponding adduct **6** in low yield and d.r. Pleasingly, stable and less hindered methoxymethyl (MOM) derivative **1e** led to the highest yield and stereoselectivity (94 : 6) observed. Orthogonal removal of the auxiliary in **7** and acid-mediated lactonization to **8** were straightforward and allowed unambiguous assignment of the (*R*)-configuration of the AA by ^{1}H NOESY analysis. In view of the importance of 2-amino-*C*-glycosides,[28] coupling of the seldom (2-acetamido)*exo*-glycal[29] **1f** could be achieved in moderate yield and stereoselectivity, granting with adduct **9** a first entry to 2-amido-*C*,*C*-glycosidic motifs. Considering these results, we speculate that (1) steric impediment of the olefin in **1** is detrimental to radical generation; (2) alongside competitive processes efficiency is also correlated to the chemical stability of the often sensitive *exo*-glycal; and (3) high stereoselectivities are obtained when the C-2 position of the sugar is relatively unhindered. As mentioned above, if the optimized acceptor and conditions enable enforcement of two-fold stereocontrol in the D-gluco series, extension to related important pyranosides should be feasible. This was probed with *exo*-D-mannal **1g** and *exo*-D-galactal **1h**, whose corresponding coupling adducts **10** and **11** were successfully isolated after direct hydrolysis (Fig. 2b). As notable, selective MOM protection at C-2 was not mandatory here to achieve high control. The (very) decent chemical yields obtained from these fragile, electron-rich terminal *exo*-glycals again testify of the relative mildness of the Fe-HAT conditions. Although optimized for pyranosides, the protocol also allowed the efficient conversion of furanoside **1i** into adduct **12** with significant control at the AA centre (Fig. 2c). The main limitations concern trisubstituted[15] and electronically deactivated difluoroolefins,[30] which do not undergo MHAT at a sufficient rate with respect to DHA derivatives (Fig. 2d). On the other hand, sulfonylhydrazone acceptors used for reductive alkylation[31] either seem to: (1) lack sufficient reactivity towards tertiary glycosyl radicals (alkylsulfonyl derivatives), whose reduction thus leads to formal alkene hydrogenation, or (2) undergo nonselective fragmentation (arylsulfonyl derivatives).

Based on our results and taking account of Poli & Holland's studies,[26] a tentative model for the stereocontrolled formation of the AA centre may be envisioned from two perspectives (Fig. 3). Following generation of an iron(III) enolate *via* inner-sphere electron transfer from Fe(II)(acac)$_2$ species (a), a non-chelated model – expectable considering a moderately Lewis acidic and coordinatively saturated Fe(III) complex – may explain the preference for *si*-face 'concerted' protonation from a metal-bound EtOH molecule leading to the (*R*)-configuration while accounting for the effect of substituents at C-2, in close vicinity of the aryl moiety presented by the auxiliary. Additional shielding of the *re*-face is imposed by the angular methyl group, while the flat phthalimide can partly rotate to minimize steric interactions with the former methyl and the auxiliary, also restricting the rotation of the pseudoanomeric C–C bond. Similar considerations may apply to a proton-coupled electron transfer process (b), in which a conjugated π-type radical in its

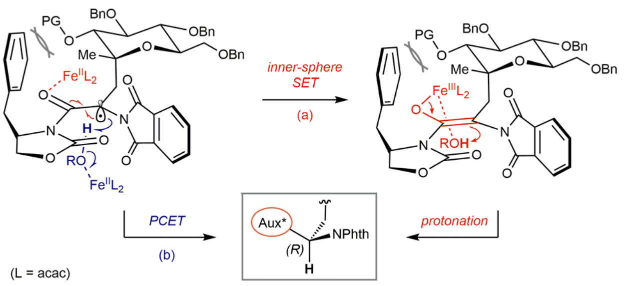


Fig. 3 Proposed models for stereoselective termination *via* SET/protonation (a) or proton-coupled electron transfer (b) in the D-gluco series.

ground state would adopt a similar planar geometry, poised to undergo stereoselective PCET from alcohol-bound Fe(II) species.

In conclusion, a novel entry to rare *C*,*C*-glycosyl amino acids was established. Guided by a systematic study of substituents and auxiliary effects, high two-fold stereocontrol was achieved in the direct assembly of *exo*-glycals with dehydroalanine acceptors, representing a first case using the MHAT intermolecular coupling pathway. Further development of new catalytic stereocontrolled reactions of *exo*-glycals is underway and will be reported in due course.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Due to the varying polarities of adducts, from this stage the auxiliary was cleaved only if required for an easier purification.

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