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C-Glycosylcrotylboronates for the Synthesis of Glycomimetics

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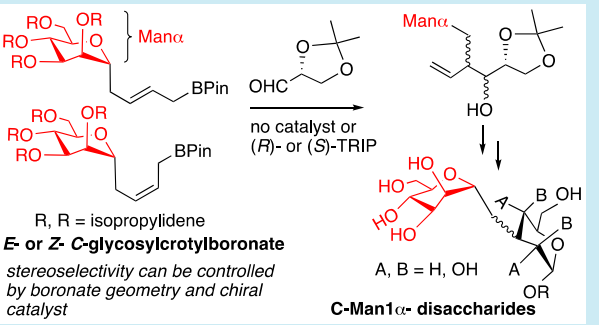
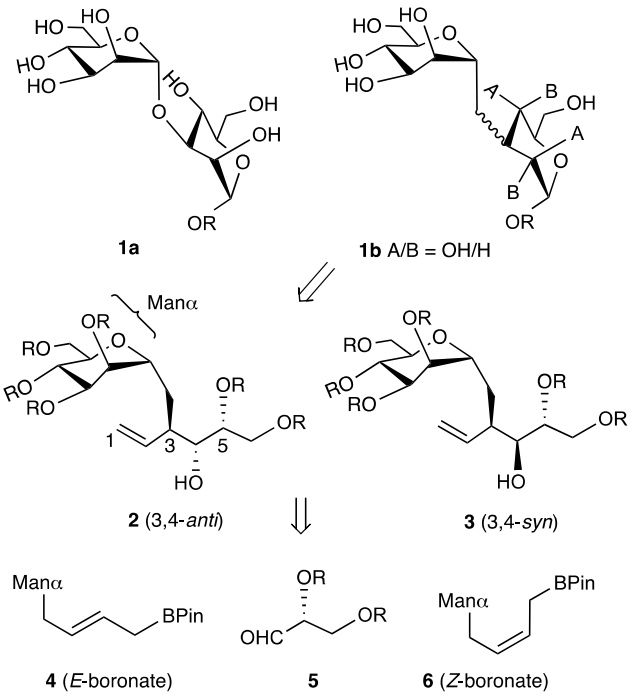
ABSTRACT: The stereoselective synthesis of *E*- and *Z*- isomers of a *C-mannosyl* crotylpinacolboronate *via* Ni-promoted reactions on an allylic acetate and a diene precursor, respectively, is described. The *E*- and *Z*-isomers reacted with 1,2-*O*-isopropylidene glyceraldehyde in the presence or absence of (*R*)- and (*S*)- TRIP catalysts, to give predominantly 3,4-*anti* and 3,4-*syn* crotylation products, respectively, with moderate to high facial selectivity. These products were transformed to biologically relevant *C-manno*-disaccharides.



Carbohydrates are involved in a variety of fundamental biological pathways and disease states.[1−3] There is a growing demand for tailored glycomimetics for deciphering these mechanisms and for use as clinical agents.[4−9] Such structures require challenging laboratory synthesis because of their intrinsic complexity. In this context, we have been developing a synthetic methodology that centers on the reaction of glycosyl crotylating agents and aldehydes.[10,11] The modularity of this approach and the versatility of the crotylation products make this a potentially broad-based method for glycomimetics. Because this strategy does not focus on construction of the glycoside (or pseudoglycoside linkage) as in more conventional glycomimetic synthesis, it opens up new glycomimetic space. We have previously illustrated this methodology with glycosylstannanes. However, these reagents have stereoselectivity limitations, and their toxicity is an additional concern.[12−15] Crotylboronate variants may mitigate these issues.[16] Herein we report the preparation of an isomeric pair of *E*- and *Z*- *C-mannosyl*-glycosylcrotylboronates and their use in the synthesis of stereochemically complex glycomimetics (Scheme 1).[9,17,18]

Mimetics of the Man1α-3Man **1a** were selected as a test bed because of their biological relevance. This disaccharide is a subunit of complex glycoproteins on the surface of a number of viral pathogens and is believed to be integral to the early stages of virus attachment and entry into host cells.[19−21] Accordingly, analogues of **1a** are of interest as probes of these mechanisms and as therapeutics.[22−27] Glycoside isosteres, in which the anomeric or ring oxygen, respectively, is replaced with "CH_2", commonly referred to as *C*-glycosides and carbasugars, are particularly relevant because of their stability to enzymatic and chemical hydrolysis and nuanced conformational characteristics compared to their *O*-acetal parents.[28−34]

Scheme 1. Crotylation Way to *C-manno*-Disaccharides



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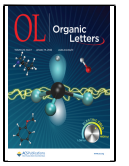

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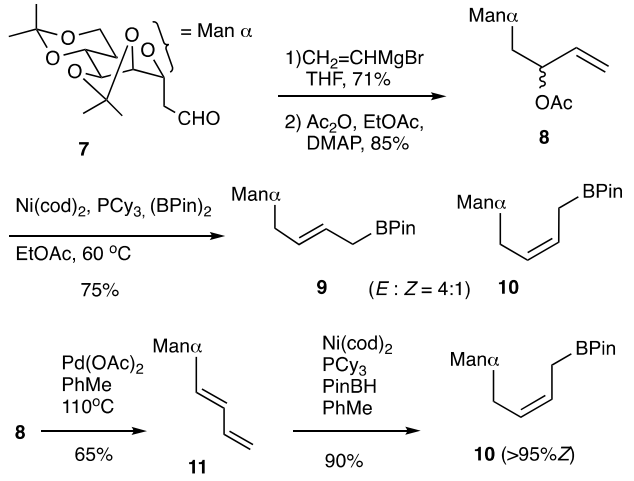
Against this backdrop, we envisaged a synthesis of *C*-*manno*-disaccharides **1b** with varying stereochemistry that is based on elaboration of crotylation products from the reaction of the *E*- or *Z*-glycosylboronate, **4** or **6**, and aldehyde **5**.[35] Following stereoselectivity trends for simpler crotylboronates, these *E* and *Z* boronates were expected to favor 3,4- *anti* and *syn* products, respectively.[14−16] One or other of the individual *anti* or *syn* diastereomers may be favored by the inherent chirality of the substrates and/or by the presence of a chiral catalyst. In contrast, as revealed in our earlier studies, *E* and *Z* crotylstannanes both favor 3,4-*syn* products but often with significant amounts of *anti* diastereomers.

The synthesis of *E* and *Z* boronates started from a central allylic acetate **8**, which was readily obtained from the reaction of vinylmagnesium bromide with the known *C*-mannose aldehyde **7** (available in three steps from methyl-α-D-*manno*-pyranoside) and acetylation of the resulting alcohol (Scheme 2).[36] The $Ni(cod)_2$ promoted reaction of **8** with bis-

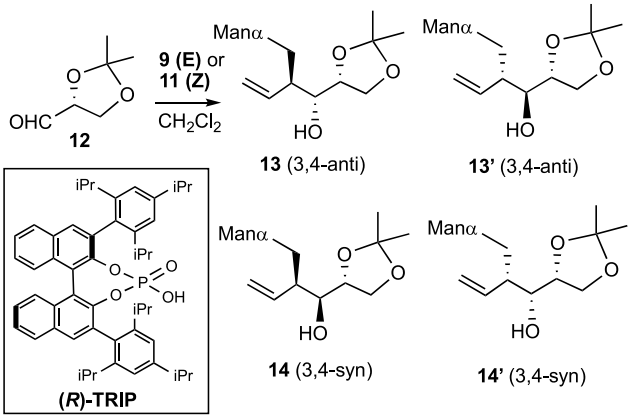
Scheme 2. Synthesis of *E*- and *Z*- *C*-Glycosyl Crotylboronates



(pinacolato) diboron delivered predominantly the *E*-crotylpinacolboronate **9** (*E*:*Z* = 4:1).[37] For the *Z*-boronate, **8** was first transformed to diene **11** following the Tsuji elimination protocol.[38] $Ni(cod)_2$ mediated 1,4-hydroboration on **11** with pinacolborane delivered *Z*-pinacolboronate **10**.[39] That the hydroboration was highly selective for 1,4-addition was confirmed by oxidation of the crude reaction product to the alcohol derivative of **10** exclusively (Supporting Information). The *E*-enriched and *Z*-crotylboronates were isolated in 75 and 90% yield after silica gel column chromatography and determined to be 80% *E* and greater than 95% *Z*, respectively, as judged by ^{1}H NMR analysis. Stereochemistry was assigned by comparison with the NMR data for simple *E* and *Z* crotylboronates and was consistent with the stereochemistry of the derived crotylation products (*vide infra*).[37,39] A CM strategy was also investigated as this allows for direct access to **9** and **10** from the *C*-allyl precursor **7**.[40−44] However, these reactions gave poor selectivity for the *E*-boronates with the *E*-selective catalysts, Grubbs I and Grubbs II, and no CM products with the *Z*-selective Grubbs catalyst (Supporting Information).

The aldehyde partner for the crotylation reactions 2,3-*O*-isopropylidene-L-glyceraldehyde **12** was selected for three reasons (Scheme 3). First the documented reactions of **12**

Scheme 3. Crotylation Reactions[a]



Reaction Conditions	Total Yield (%)	Relative Ratio 13	13'	14	14'
9, no cat.	73	53	100	23	<2
9, 9 mol% (R)-TRIP	55	100	12	20	<2
9, 9 mol% (S)-TRIP	68	19	100	26	<2
11, no cat.	74	<2	15	100	4
11, 7 mol% (R)-TRIP	66	<2	18	100	39
11, 7 mol% (S)-TRIP	58	<2	4	100	<2

[a]Reactions of the *E*- and *Z*- boronates were performed over 16 and 4 h respectively, with 1.5 eq 12 and 0.1 M **9** or **10**, in the presence or absence of catalyst. Product ratios were determined from ^{1}H NMR of the unseparated mixture of crotylation products.

with simple crotylboronates provides a benchmark for our study.[45] Second, **12** is easily obtained on large scale.[46] Third, crotylation products derived from **9**, **10**, and **12** can be transformed in a straightforward fashion to a variety of biologically relevant glycomimetics.[47] Reactions were performed in CH_2Cl_2 at room temperature with or without a chiral acid catalyst. In the absence of the catalyst, the *Z*-boronate was noticeably more reactive than the *E*, with complete consumption of boronate observed after 4 and 16 h, respectively. The *E*-enriched boronate gave a 73% yield of predominantly the 3,4-*anti* products **13**/**13′** and a minor amount of the 3,4-*syn* product **14**, with no observation of the other *syn* isomer **14′** within the limits of ^{1}H NMR detection. (**13**:**13′**:**14**:**14′**, respective ratio 53:100:23:<2). That the ratio of the *syn* isomer **14** correlated with the proportion of *Z*-isomer in the starting boronate suggests that **14** originated primarily from the *Z*- and not the *E*- isomer in the starting crotylboronate mixture. The reaction of the *Z*-boronate with **12** gave a 74% yield of predominantly the 3,4-*syn* product **14**, minor amounts of the other *syn* diastereomer **14′**, and the *anti* product **13′** (**13**:**13′**:**14**:**14′**, respective ratio <2:15:100:4).

The *anti* vs *syn* bias for the *E* and *Z* boronates follows the trend for simpler crotylboronates, which has been explained by a Zimmerman Traxler closed transition state model.[13−16] There was no significant facial selectivity for the reaction of the *E*-boronate (*i.e.*, **13′**:**13**; 53:100), whereas, **14** was essentially the only *syn* diastereomer in the reaction for the Z-boronate (i.e **14**:**14′**; 100:4). These results are in line with the reactions of aldehyde **12** and simple *E*- and *Z*- crotyl pinacol boronates, wherein the former showed essentially no facial selectivity, as is the case for *E*-glycosylboronate **9**, and the latter showed the

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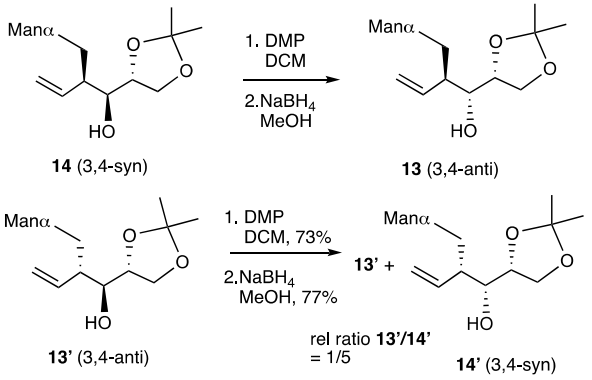
same facial bias that was observed for *Z*-glycosylboronate **10**.[42] Thus, facial selectivity for both the simple and the more substituted glycosyl crotylboronates appear to be controlled by the chirality in the aldehyde (*i.e.*, Felkin selectivity).

The crotylations were next performed in the presence of (*R*)- and (*S*)- TRIP to evaluate whether facial selectivity can be influenced by a chiral promoter. In agreement with the reported stereoselectivity trends for these catalysts, the reaction of *E*-boronate **9** with (*R*)-TRIP and (*S*)-TRIP, favored **13** and **13′**, respectively (*i.e.*, **13**/**13′** = 100/12 vs 19/100).[48−50] In contrast, the facial bias for the *Z*-boronate **10**, in the presence of both the (*R*) and (*S*) catalyst, was the same, albeit much higher for the latter. These data may represent matched/mismatched diastereoselectivity, wherein the influence of the (*S*) catalyst is matched to directing effects from the substrates, and the opposite bias of the (*R*) catalyst is mismatched and dominated by substrate factors.[45] Taken together these observations suggest that these TRIP catalysts may be more effective when the intrinsic selectivity of the substrates is low and illustrate the challenges in applying stereochemical trends for relatively simple, achiral substrates to highly substituted, chiral variants, particularly polyhydroxylated frameworks with multiple, potentially ligating sites.[51,52]

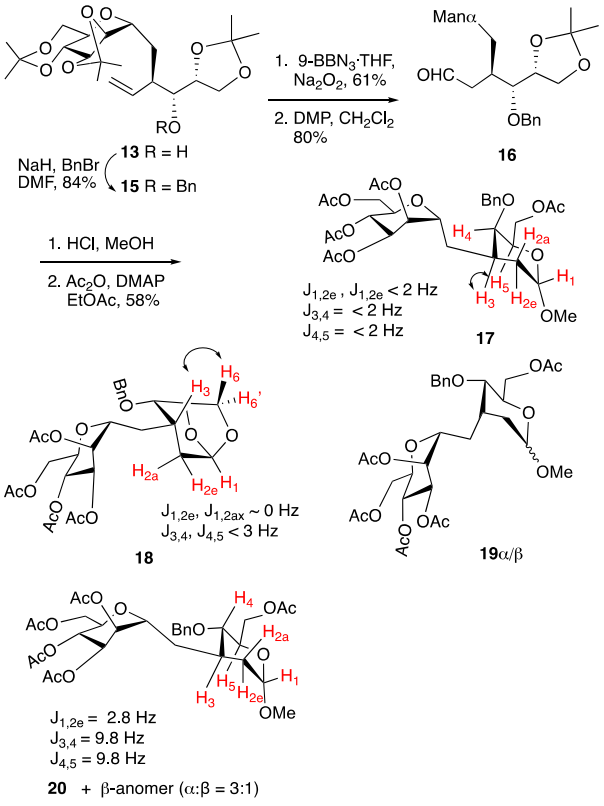
The stereochemistry of the crotylation products was deduced from NMR analysis of disaccharide derivatives of **13**, **13′**, and **14** (*vide infra*). These assignments were self-consistent with oxidation−reduction reaction sequences on individual diastereomers (Scheme 4). Thus, **14** led to **13** exclusively, and **13′** produced a 1:5 mixture of **13′** and a diastereomeric product that was different from **13′** and **14** and assigned as **14′**.

Scheme 4. Stereochemical Correlation of Crotylation Products



The crotylation products were next transformed to *C*-2-deoxydisaccharides *via* a five-step sequence of reactions (Scheme 5). Thus, the 3,4-*anti* diastereomer **13** was converted to benzyl ether **15**. Hydroboration-oxidation on **15**, oxidation of the derived primary alcohol to aldehyde **16**, exposure of **16** to methanolic HCl, and acetylation of the resulting product provided **17**. A similar sequence of reactions on the other 3,4-*anti* diastereomer **13′** led to a mixture of the anhydro sugar **18** and methyl glycosides **19α/β** (Supporting Information). As for **13**, performing this reaction sequence on **14** provided the methyl pyranoside framework but as a mixture of *α*-glycoside **20** and its *β*-anomer. We speculate that the formation of the 1,6-anhydrosugar from **13′** (and not **13** and **14**) may result from stabilization of the $^{1}C_{4}$ conformation of the newly formed

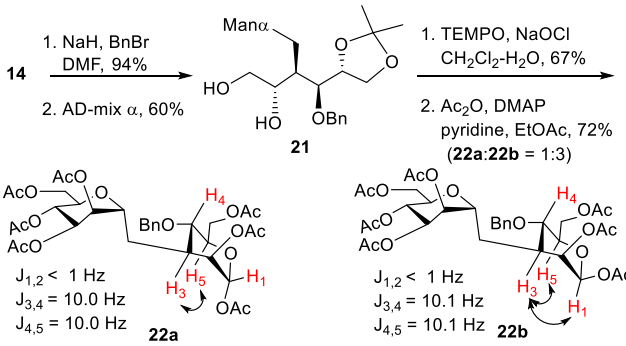
Scheme 5. Transformation of Crotylation Products to 2-Deoxy *C*-Disaccharides



sugar ring because of stereochemical effects.[53] The stereochemistry in the newly formed sugar ring in **17**, **18**, and **20** was based on the absolute configuration in the aldehyde precursor **12**, vicinal $J_{H,H}$ coupling constants, and/or H3/H5 NOEs.

For the fully oxygenated *C*-Man1*α*-3Man disaccharide, dihydroxylation of the benzyl ether derivative of **14** using AD-mix *α* provided a mixture of the diol **21** and its diastereomer in a 4:1 respective ratio (Scheme 6). Selective

Scheme 6. Synthesis of C-Man*α*1-3Man disaccharides



oxidation of **21** using TEMPO and NaOCl afforded the derived aldehyde, which existed as a mixture of cyclic acetal dimers. Treatment of this mixture with methanolic HCl and acetylation of the product afforded the anomeric acetates **22a** and **22b**. The stereochemistry in these products was assigned as described for the deoxydisaccharides (*vide supra*).

In summary, the stereoselective preparation of these *E* and Z glycosyl crotylboronates and their application to the synthesis of challenging *C*-disaccharide frameworks bodes well for wider

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applications in complex glycomimetic synthesis. BINOL derived phosphoric catalysts show promise for controlling stereoselectivity in the pivotal aldehyde crotylation reactions of these chiral, polyoxygenated "reagents", but their broader scope remains to be evaluated.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c03845.

Experimental procedures, physical data, and copies of NMR spectra for **8**−**11**, **13**−**22**, and selected other new compounds (PDF)

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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