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Stereoselective and Regiodivergent Allylic Suzuki–Miyaura Cross-Coupling of 2-Ethoxydihydropyranyl Boronates: Synthesis and Confirmation of Absolute Stereochemistry of Diospongin B

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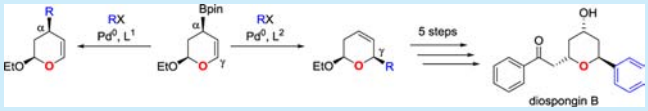
Supporting Information

ABSTRACT: Oxygen-containing heterocycles such as pyrans are a common substructure present in a variety of natural products and pharmaceutical drugs. Highly functionalized 4- and 6-aryl/heteroaryl dihydropyran derivatives are assembled by a highly stereoselective, ligand-controlled regiodivergent sp^3–sp^2 Suzuki–Miyaura cross-coupling of a 2-ethoxy dihydropyranyl boronate derived from a catalytic enantioselective inverse-electron-demand oxa[4 + 2] cycloaddition. The scope and selectivity of this method were assessed along with an application to a concise total synthesis of the diarylheptanoid natural product diospongin B.



A large number of naturally occurring compounds contain polysubstituted pyran units (Figure 1). These substances

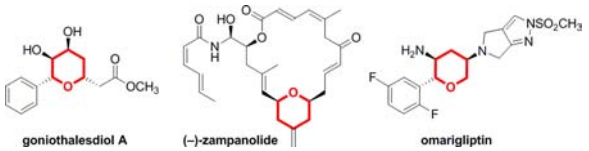
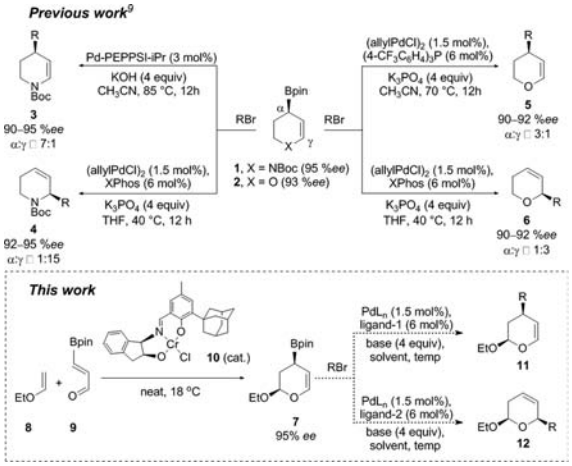


Figure 1. Natural products and pharmaceutical drugs containing a polysubstituted pyran unit.

tend to display a wide range of biological properties, including antibiotic and anticancer activity.[1] The presence of carbon-containing fragments at positions 2-, 4-, and 6-, often in various combinations, is quite frequent. Members of these classes include goniothalesdiol A,[2] as well as several macrolides such as (−)-zampanolide.[3,4] Pyran-containing molecules also have potential value in medicinal chemistry, as shown in the recent synthesis of a potent dipeptidyl peptidase-4 (DPP-4) inhibitor omarigliptin (MK-3102) developed in the Merck research laboratories.[5] The ubiquity of this "privileged" substructure both in nature and pharmacopeia warrants further development of alternate methods of synthesis.

Although various methods to introduce heteroatoms on a dihydropyran framework exist, few methods can selectively install carbon-based fragments especially through catalytic C–C coupling. Advances in catalyst-controlled regioselective Suzuki–Miyaura cross coupling of simple allylic boronates were recently reported by Organ[6] and Yang and Buchwald,[7] as well as stereoretentive coupling of optically enriched allylboronates by Aggarwal and Crudden.[8] These studies inspired us to investigate the feasibility of stereoselective and regiodivergent cross-couplings of more complex heterocyclic allylboronates. In this regard, we recently reported that chiral enantiomerically enriched heterocyclic allylic boronates **1** and **2** can be coupled with high stereochemical retention with a wide variety of aryl and alkenyl halides to afford, independently, both regioisomeric 2- and 4-substituted dehydropiperidines **3** and **4** and dihydropyrans **5** and **6** in >95:5 enantiomeric ratio (Scheme 1).[9] These highly valuable compounds are obtained in high selectivity by way of a catalyst-controlled regiodivergent mechanism. Because 2,6-disubstituted pyrans constitute a common motif in nature, we were motivated to expand the scope of this cross-coupling method to include dihydropyranyl boronate substrates of higher complexity. In particular, the use of 2-alkoxylated substrates would provide a convenient

Scheme 1. Suzuki–Miyaura Cross-Coupling of Heterocyclic Allylic Boronates



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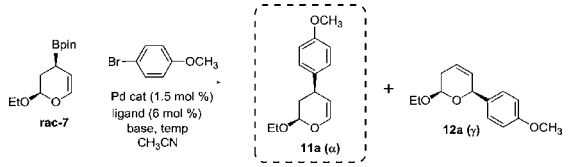
functional group to further transform the resulting cross-coupling products. To this end, we planned to evaluate the suitability of 2-ethoxy dihydropyranyl boronate **7** produced by the enantioselective oxa[4 + 2] cycloaddition[10] catalyzed by Jacobsen's chiral chromium complex **10** (Scheme 1).[11]

Initially, it was uncertain whether our previously optimized cross-coupling conditions for allylboronate **2** would be suitable for substrate **7**.[9] Nonetheless, previous reaction conditions were used as a starting point toward the identification of an optimized regioselective synthesis of α- and γ-products **11a** and **12a** (Table 1).[12] The standard conditions previously used with **2** for the

Table 1. Optimization of the α Regioisomer 11a[a]



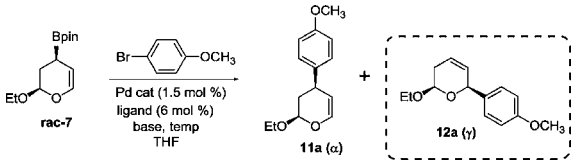
entry	Pd source	ligands	base	temp (°C)	yield (%)[c]	α:γ[d]
1	$(AllylPdCl)_2$	$(p\text{-}CF_3C_6H_5)_3P$	K_3PO_4	70	64	84:16
2	$(AllylPdCl)_2$	$(p\text{-}CF_3C_6H_5)_3P$	KOH	70	26	83:17
3	$(AllylPdCl)_2$	$(p\text{-}FC_6H_5)_3P$	K_3PO_4	70	54	85:15
4	$(AllylPdCl)_2$	PPh_3	K_3PO_4	70	43	83:17
5	Pd-PEPPSI-IPR	–	K_3PO_4	70	49	50:50
6	Pd-PEPPSI-IPent	–	K_3PO_4	70	16	74:26
7[b]	$(AllylPdCl)_2$	Xantphos	K_3PO_4	70	16	55:45
8[b]	$(AllylPdCl)_2$	dppf	K_3PO_4	70	50	55:45
9[b]	$(AllylPdCl)_2$	$Ph_2P(CH_2)_3$	K_3PO_4	70	32	57:43
10[b]	$(AllylPdCl)_2$	$Ph_2P(CH_2)_4$	K_3PO_4	70	21	76:24
11	**$(AllylPdCl)_2$**	**$(p\text{-}CF_3C_6H_5)_3P$**	**K_3PO_4**	**85**	**73**	**83:17**

[a]Reaction scale: *rac*-**7** (0.30 mmol, 1.2 equiv), 4-bromoanisole (0.25 mmol, 1.0 equiv), Pd catalyst (3.75 mmol, 1.5 mol %), ligand (15 mmol, 6 mol %), base (1.25 mmol, 4 equiv) unless indicated otherwise. [b]3.1 mol % of ligand used. [c]Isolated yield of the major regioisomer **11a**. [d]Regioisomer ratio (α:γ) was measured from the ^{1}H NMR spectra of crude products. Ligands: Xantphos = 4,5-bis-(diphenylphosphino)-9,9-dimethylxanthene; dppf = 1,1′-bis-(diphenylphosphino)ferrocene.

synthesis of α-isomers, $[(allyl)PdCl]_2$ with potassium phosphate as a base in acetonitrile, proved to be efficient toward the synthesis of **11a**.[9] Under these conditions, **11a** was obtained selectively (84:16) in moderate yield (entry 1). These conditions could not be improved using an alternate base (KOH) that was optimal toward the piperidine allylboronate **1** (entry 2).[9] Previous work on **2** showed that α-selectivity was favored with the use of weaker σ-donating ligands. With **7**, however, the yield and selectivity could not be improved when tris(4-fluorophenyl)phosphine was used (entry 3). Organ's Pd-PEPPSI-i-Pr and Pd-PEPPSI-i-Pent catalysts (entries 5 and 6), previously known to offer high α-selectivity,[6,9] as well as bidentate phosphine ligands (entries 7−10), showed no improvement of regioselectivity or yield. Upon increasing the reaction temperature to 85 °C using the same conditions as entry 1, the regioselectivity for **11a** improved to a ratio of 83:17 with an acceptable yield of 73% (entry 11).

The previous reaction conditions used toward the efficient synthesis of the γ-isomer **6** were applied to the synthesis of **12a** (Table 2).[9] Strong σ-donating alkylphosphine ligands such as XPhos favored the formation of the γ-product **12a** with very high regioselectivity (entry 1). Although every dialkylarylphosphine ligand that was tested gave similarly high regioselectivity,

Table 2. Optimization of the γ Regioisomer 12a[a]



entry	Pd source	ligands	base	temp (°C)	yield (%)[b]	α:γ[c]
1	$(AllylPdCl)_2$	XPhos	K_3PO_4	40	82	7:93
2	$(AllylPdCl)_2$	CyJohnPhos	K_3PO_4	40	61	6:94
3	$(AllylPdCl)_2$	RuPhos	K_3PO_4	40	75	5:95
4	**$(AllylPdCl)_2$**	**SPhos**	**K_3PO_4**	**40**	**86**	**5:95**

[a]Reaction scale: *rac*-**7** (0.30 mmol, 1.2 equiv), 4-bromoanisole (0.25 mmol, 1.0 equiv), Pd catalyst (3.75 mmol, 1.5 mol %), ligand (15 mmol, 6 mol %), base (1.25 mmol, 4 equiv). [b]Isolated yield of the major regioisomer **12a**. [c]Regioisomer ratio (α:γ) was measured from the ^{1}H NMR spectra of crude products. Ligands: XPhos = 2-(dicyclohexylphosphino)-2′,4′,6′-triisopropylbiphenyl; CyJohnPhos = 2-(dicyclohexylphosphino)biphenyl; RuPhos = 2-(dicyclohexylphosphino)-2′,6′-diisopropoxybiphenyl; SPhos = 2-(dicyclohexylphosphino)-2′,6′-dimethoxybiphenyl.

SPhos was the optimal one, affording **12a** in 86% yield and 95:5 regioselectivity (entry 4). With the optimized conditions for regiodivergent synthesis of both α- and γ-regioisomers in hand, the scope of aryl bromides was explored next.

As described previously by our group and others, the synthesis of substrate **7** involves the enantioselective hetero[4 + 2] cycloaddition between ethyl vinyl ether **8** and boronoacrolein **9** catalyzed by Jacobsen's tridentate chromium complex **10**.[10] This transformation was applied in a number of three-component stereoselective oxa[4 + 2] cycloaddition/allylboration reactions toward the synthesis of numerous bioactive molecules.[10a,13] To begin the evaluation of the reaction scope, we prepared cycloadduct **7** in a good yield with high enantioselectivity (77%, 95% ee) using carefully distilled **9**, 4 A molecular sieves as the drying agent, and a 3 mol % loading of **10** (Scheme 2).[14]

A range of sp^2-hybridized organobromide substrates were tested to demonstrate the general efficiency of this method. The α-coupling products **11a−e** were isolated in good yields with high regioselectivity. The regioselectivity was lower for the coupling product **11a** of electron-rich *p*-methoxyphenyl bromide (83:17 α:γ) relative to the product **11b** of the electron-poor *p*-(trifluoromethyl)phenyl bromide (93:7 α:γ). The *N*-Boc-5-bromoindole substrate, which was not investigated in our previous work,[9] afforded **11d** in high regioselectivity (90:10 α:γ). Alkenyl bromides appear to be suitable with this method. The reaction between **7** and β-bromostyrene afforded **11e** in high yield and high regioselectivity (81%, 91:9 α:γ). The conditions used toward the synthesis of γ-products resulted in a slightly improved yield over the α-isomers. Thus, product **12a** of *p*-methoxyphenyl bromide was obtained in a slightly higher yield (86%) and regioselectivity (5:95 γ:α) over the product **12b** of the electron-deficient (trifluoromethyl)phenyl bromide (80%, 8:92 α:γ). The conditions favoring γ-selectivity with the *N*-Boc-5-bromoindole gave **12d** in a very high yield (97%) and high regioselectivity (3:97 α:γ). Surprisingly, the reaction between **7** and β-bromostyrene gave **12e** in a yield (80%) and regioselectivity (2:98 α:γ) higher than our previous example between **2** and β-bromostyrene (70%, 25:75 α:γ).[9] With all examples, there did not appear to be any indication of the

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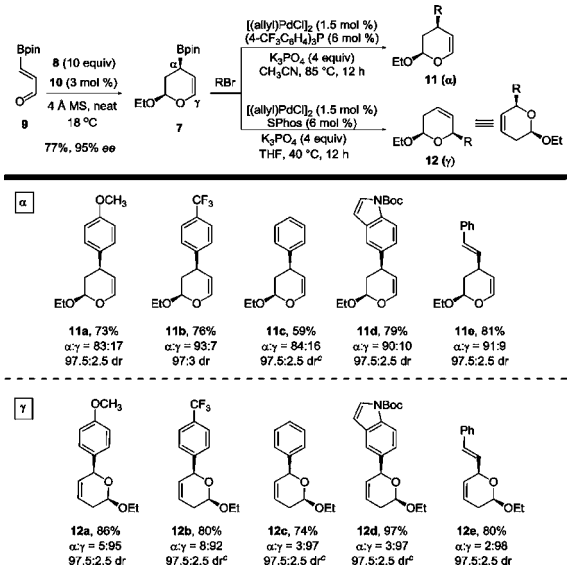
Scheme 2. Scope of sp²-Hybridized Organobromides[a,b]

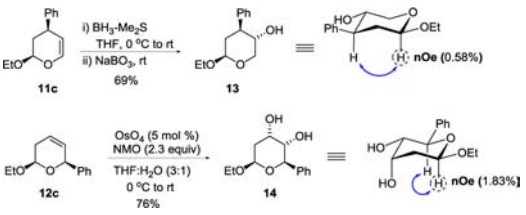


[a]Reaction scale: **7** (0.30 mmol, 1.2 equiv), RBr (0.25 mmol, 1.0 equiv), Pd catalyst (3.75 mmol, 1.5 mol %), ligand (15 mmol, 6 mol %), base (1.25 mmol, 4 equiv). [b]Regioisomer ratio (α:γ) was measured from the ^{1}H NMR spectra of crude products. [c]Diastereomeric ratio was determined by chiral HPLC analysis of modified products (see the Supporting Information).

formation of *trans* diastereomers as well as any erosion of enantiomeric purity as revealed by chiral HPLC analysis. Therefore, on the basis of a limited set of aryl halides, these results confirm that allylic boronate **7** displays a reaction scope comparable to that of **2**.

In our previous investigation of the regiodivergent asymmetric Suzuki–Miyaura coupling of the dihydropyran allylboronate **2**, we were unable to confirm unambiguously that the reaction proceeds with overall retention of stereochemistry.[9] Our tentative assignment relied on a correlation with a natural product synthesized from the piperidine allylboronate **1**. Here, we sought to obtain stronger evidence in support of a stereoretentive cross-coupling mechanism with dihydropyranyl allylboronates. To this end, we planned to prepare crystalline derivatives suitable for X-ray diffraction. Selective hydroboration of **11c** followed by oxidation of the favored isomer gave **13** with a 3-hydroxy group *trans* to the phenyl and ethoxy substituents (Scheme 3). Likewise, the *trans*-diol **14** was synthesized as a

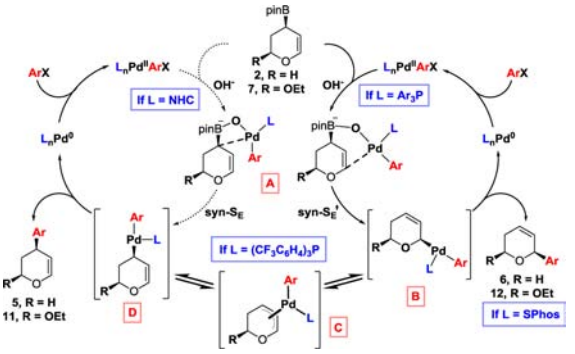
Scheme 3. Modification of Cross-Coupling Products



single diastereomer from **12c** via an Upjohn dihydroxylation.[15] The relevant spatial correlations obtained by NOE enhancement confirmed a 2,4-*cis* substitution for **13** and a 2,6-*cis* stereochemistry for **14**. This assessment was further supported by the X-ray crystallographic data of **13** and **14** (see the Supporting Information).

Previous investigations into the mechanism of this allylic sp³–sp² cross-coupling reaction, with **1** and **2**, concluded that, depending on the catalyst used, either a *syn*-S_E or *syn*-S_E' transmetalation occurs from an oxyborate-coordinated palladium species **A** (Scheme 4).[8b,9,16] Both phosphine-based

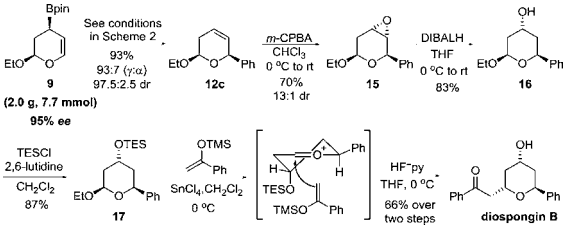
Scheme 4. Proposed Ligand-Controlled Catalytic Cycle



ligands, SPhos and $(4\text{-}CF_3C_6H_4)_3P$, are believed to promote a S_E' transmetalation to form the η^1 γ-allylpalladium species **B**.[8,9,16] When bound to a weaker σ-donating triarylphosphine, such as $(4\text{-}CF_3C_6H_4)_3P$, **B** may undergo isomerization to the higher valency π-allyl intermediate **C**, thus providing access via σ–π equilibration to the thermodynamic, heteroatom-conjugated σ-bonded Pd(II) complex **D**.[9] This pathway leads to the α-isomers **5** and **11**. On the other hand, strong σ-donor bulky ligands such as SPhos may suppress the formation of allylpalladium intermediate **C** with their well-known ability to promote a faster rate of reductive elimination.[17] By virtue of this effect, the erosion of regioselectivity is minimized, leading to the kinetically favored γ-isomers **6**/**12**. This effect may be further enhanced by the σ-inductive electron-withdrawing ethoxy group present in **7**, which should lead to a faster reductive elimination.[18]

To establish the potential of this method toward the synthesis of biologically active polysubstituted pyrans containing an aryl substituent, we planned a synthesis of diospongin B. Diospongin B is a diarylheptanoid natural product that displays potent antiosteoporotic activity (Scheme 5).[19] The synthesis began

Scheme 5. Synthesis of Diospongin B



with the selective epoxidation of **12c** using *m*-CPBA, affording **15** in a 76% yield and 13:1 *anti*-selectivity.[20] It was followed with a selective epoxide ring opening using DIBALH followed by silyl protection of the hydroxyl group using chlorotriethylsilane (TESCl), which gave **17** with a 72% yield over two steps. Then, Mukaiyama-type addition onto the in situ generated oxocarbenium species favored the formation of the desired 2,6-*trans* product. The stereoselectivity can be rationalized by the nucleophilic addition onto the favored chairlike transition state[21] and is supported by previous investigations toward the

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synthesis of diospongin B.[22a] After a final deprotection of the TES ether, the natural product was obtained in a 66% yield over two steps. Curiously, the sign of optical rotation of our synthetic diospongin B [$[\alpha]^{20}_{D}$ = +22.8 (*c* 0.70, $CHCl_3$)] was opposite to the optical rotation of the isolated natural diospongin B [$[\alpha]^{20}_{D}$ = −23.4 (*c* 0.60, $CHCl_3$)] as originally reported by Kadota and co-workers.[19] Although the configurational assignment of **7** as well as the analysis of subsequent intermediates supported our stereochemical assignment, nearly all previous syntheses of diospongin B reported were consistent with Kadota's initial report and counter to our own.[22] In the end, a recent asymmetric synthesis and detailed investigation into the absolute stereochemistry of diospongin B by Hashimoto and co-workers [$[\alpha]^{20}_{D}$ = +22.3 (*c* 0.62, $CHCl_3$)][23] as well as a corrigendum by Kadota supported our assignment.[24]

In conclusion, the ligand-controlled stereoretentive and regiodivergent Suzuki−Miyaura cross-coupling of heterocyclic allylboronates was applied toward a 2-ethoxy dihydropyranyl boronate substrate (**7**) derived from a catalytic enantioselective inverse-electron demand oxa[4 + 2] cycloaddition. This method was systematically optimized for substrate **7**, and a scope similar to that for the des(2-ethoxy) analogue **2** was demonstrated with a representative set of aryl and alkenyl bromides. Both α- and γ-cross-coupling products can be obtained independently in high optical purity and with high regio- and diastereoselectivity. Through NMR and X-ray crystallographic analyses, the coupling step was determined to proceed with retention of stereochemistry. This method was applied to a concise synthesis and confirmation of absolute stereochemistry of diospongin B.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01906.

Experimental procedures, characterization data, and spectral reproductions for all new compounds (PDF)
X-ray crystallographic data of compound **13** (CIF)
X-ray crystallographic data of compound **14** (CIF)
X-ray crystallographic data of compound **15** (CIF)

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Notes

The authors declare no competing financial interest.

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(14) The enantiomeric excess of **7** was measured on the corresponding secondary homoallylic alcohol produced from a highly diastereoselective allylboration with retention of stereochemistry (see the Supporting Information).[10]
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(24) See footnote 17 in ref 23.

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