Stereoselective Catalysis

DOI: 10.1002/anie.201205479

Counteranion-Directed Catalysis in the Tsuji–Trost Reaction: Stereocontrolled Access to 2,5-Disubstituted 3-Hydroxy-Tetrahydrofurans**

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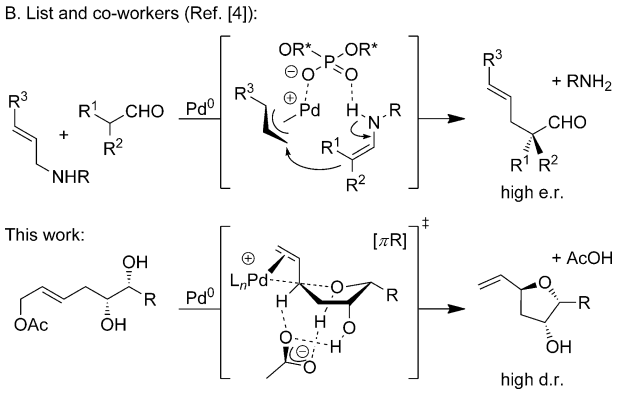
The concept of counteranion-directed catalysis (CDC) is applicable to reactions in which cationic intermediates are formed.[1] In principal, it can even be applied to transition-metal-catalyzed reactions,[2] as demonstrated for gold catalysis by Toste and co-workers,[3] and for palladium catalysis by List and co-workers.[4] The latter group showed that the positively charged π-allyl/Pd^{II} complex of the Tsuji–Trost reaction[5,6] can interact with a chiral counteranion, thus allowing an efficient direct α allylation of aldehydes by asymmetric counteranion-directed catalysis (ACDC). In the proposed mechanism, the chiral phosphate counteranion establishes hydrogen bonds with the HN moiety of the intermediate enamine as well as an ionic interaction with the charged Pd^{II} center, thus resulting in a very organized transition state (Scheme 1).



Scheme 1. Rationalized examples of CDC in the Tsuji–Trost reaction.

Herein, we disclose a highly diastereoselective synthesis of 2,5-disubstituted 3-hydroxy-tetrahydrofurans through the formation of a π-allyl/Pd^{II} intermediate, in which the carboxylate counterion plays a prominent directing role. We propose a mechanism that is based on DFT calculations and chemical experiments, and which indicates that the stereocontrol may in part be a result of the formation of an unusual noncovalent bond between the counteranion and one of the hydrogen atoms of the cationic π-allyl/Pd complex itself. The two hydroxy groups are also involved in the mechanism, and the sum of all these noncovalent interactions leads preferentially to the highly organized chiral transition state $[\pi R]^{\ddagger}$ (see Schemes 1 and 3), a prediction that accounts well for the observed diastereoselectivity.

In the course of our total synthesis of (+)-oocydin A (**1**; Figure 1),[7] we devised this convenient approach to 2,5-disubstituted 3-hydroxy-tetrahydrofuran **4** from the readily

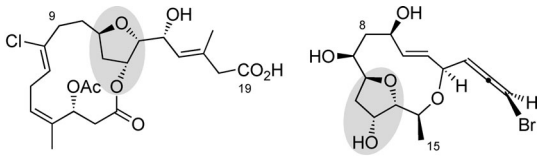


Figure 1. Examples of natural products that feature the 2,5-disubstituted 3-hydroxy-tetrahydrofuran motif.

available *syn* diol **3**, giving **4** in a surprisingly high d.r. (*trans*/*cis* = 96:4; Scheme 2). This high selectivity was unexpected, considering the work of Hara et al.,[8] who observed a poor diastereoselectivity (*trans*/*cis* = 37:63) for the cyclization of **5** to **6** (Scheme 2). This result led us to suspect a directing effect of the β-OH group in the stereoselective cyclization of **3** to **4**, and prompted us to further explore this promising reaction. The first confirmation of our hypothesis was the observation that even *anti* diol **7** cyclized diastereoselectively, leading to 2,5-disubstituted 3-hydroxy-tetrahydrofuran **8**[9] (*anti*/*syn* = 95:5, 97% yield; Scheme 2). We must emphasize that in *anti* diols as well as in *syn* diols, the newly formed vinyl function is selectively installed *trans* to the β-OH group (which does not cyclize), while the stereogenic center that bears the γ-OH group (which cyclizes) seems to have no impact on the stereoselectivity, which is counterintuitive.

In order to gain some insight into the mechanism of this reaction, DFT calculations were carried out, starting with the *syn* diol series (Scheme 3).[10,11] The nucleophilic attack of the γ-OH group at the π-allyl moiety was modeled (outer-sphere mechanism).[12] The calculations showed that cyclization transition states could not be found if the acetate counteranion was not taken into account. No convergence could be reached in the C–O bond formation with the cationic "base-

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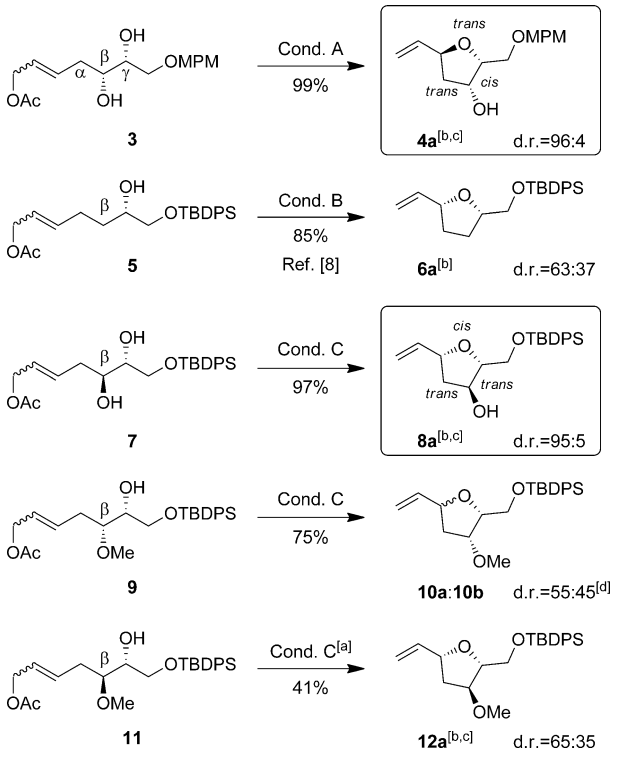
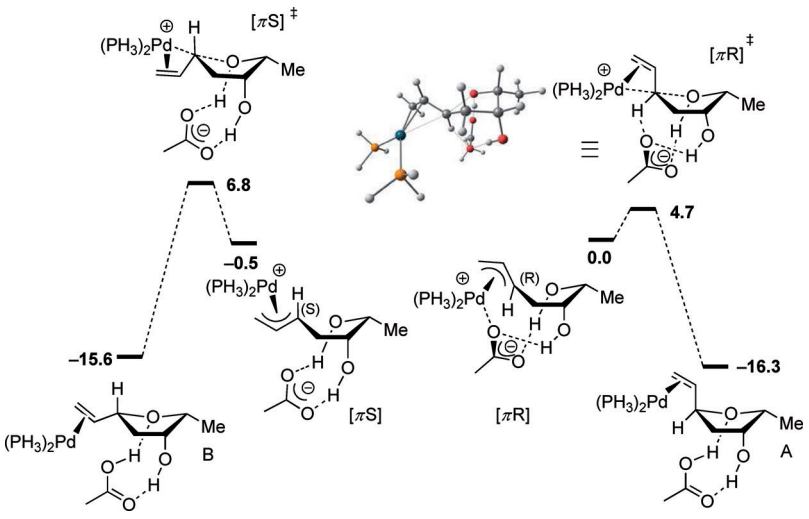
[**] The ICSN and the CNRS are acknowledged for their financial support. Dr. Géraldine Masson (ICSN), Dr. Sylvain Aubry (ICSN), and Dr. Yves Janin (Institut Pasteur, Paris) are warmly acknowledged for valuable scientific discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201205479.



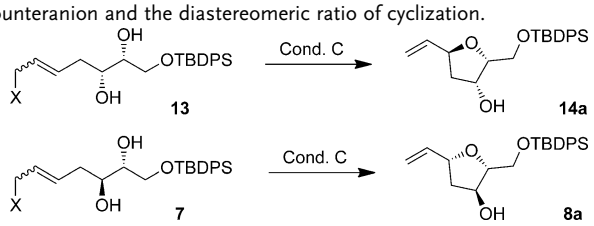
Scheme 2. Synthesis of tetrahydrofurans and directing effect of β-OH group. Reaction conditions: A) $[Pd_2(dba)_3]$, $P(4\text{-}MeOC_6H_4)_3$, THF, 40°C; B) $[Pd(dba)_2]$, PPh_3, THF, RT; C) $[Pd_2(dba)_3]$, $P(4\text{-}MeOPh)_3$, pyridine (0.5 equiv), toluene, RT. [a] Reaction performed at 50°C. [b] Major product. [c] Relative configuration established by NOESY experiments. [d] The relative configurations of **10a** and **10b** remain undetermined. MPM = methoxyphenylmethylidene, TBDPS = *tert*-butyldiphenylsilyl.

free" system.[10] On the other hand, when the acetate was H-bonded to the cyclizing OH group, transition states could be located on the potential-energy surface.[13–14] While the interaction with the cyclizing OH group is a prerequisite,



Scheme 3. DFT calculations of the two pathways leading to the major (**A**) and the minor (**B**) product (Gibbs free energy, kcal mol^{-1}).

Table 1: Correlation between the pK_a value of the conjugated acid of the counteranion and the diastereomeric ratio of cyclization.



Entry	Leaving group	Relative configuration	d.r.	pK_a of HX in H_2O
1	*tert*-$BuCO_2^-$	*syn* (**13a**)	96:4 (**14a/b**)	5.01
		anti (**7a**)	95:5 (**8a/b**)	
2	$MeCO_2^-$	*syn* (**13**)	92:8 (**14a/b**)	4.76
		anti (**7**)	94:6 (**8a/b**)	
3	*p*-$MeOPhCO_2^-$	*syn* (**13b**)	90:10 (**14a/b**)	4.47
		anti (**7b**)	90:10 (**8a/b**)	
4	$PhCO_2^-$	*syn* (**13c**)	88:12 (**14a/b**)	4.20
		anti (**7c**)	86:14 (**8a/b**)	

the one with the β-OH function is beneficial in terms of energy.[10] The more stable starting diastereomers [πS] and [πR] both exhibit two O···HO interactions, [πR] also shows a weak O···Pd interaction.[15] Instead of this ion pairing, $[\pi R]^{\ddagger}$ shows quite a strong hydrogen bond with the π-allyl system. This interaction is not geometrically feasible in $[\pi S]^{\ddagger}$, which lies higher in free energy than $[\pi R]^{\ddagger}$ ($\Delta\Delta G^{\ddagger} = 2.1$ kcal mol^{-1}). Thus, the diastereomer derived from complex **A** is predicted to prevail, which is indead observed experimentally. With this model, which is based on noncovalent interactions, experimental results can also be predicted for the *anti* diol series.[10]

A set of chemical experiments was performed with substrates **7** and **13**, which feature different counteranions, the conjugated acids of which have different pK_a values (Table 1). A clear correlation could be observed between the d.r. and the pK_a value, independent of the relative configuration of the starting diol. Counteranions that corresponded to weaker acids gave better diastereomeric ratios (Table 1, entries 1 and 2), which is logical because they have a greater tendency to form H-bonds than counteranions that correspond to stronger acids (Table 1, entries 3 and 4).

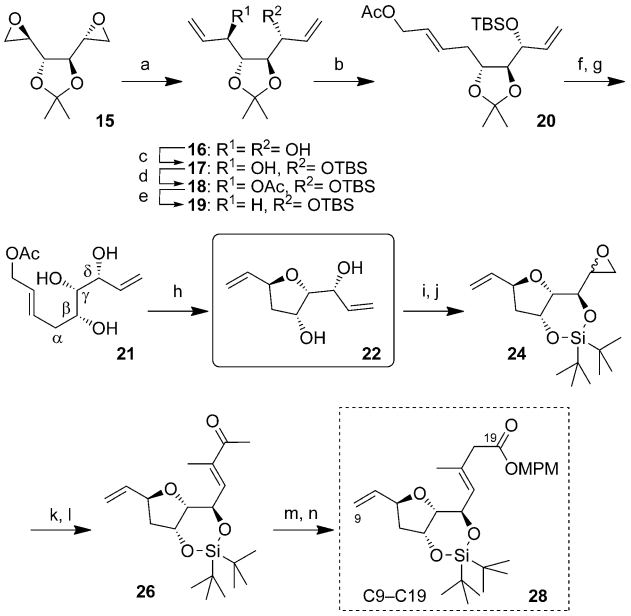
We also prepared β-OH-protected substrates **9** and **11** (Scheme 2), which are able to form only one H-bond with the counteranion. As expected, both substrates cyclized with a slower rate, gave incomplete conversions even at higher temperatures, and resulted in a highly reduced diastereoselectivity, comparable to substrate **5**, which has no β-OH group. Calculations that were made on simplified analogues of **9** and **11** confirmed this observation.[10]

We also carried out experiments to proof the existence of the unusual H-bonding interaction involving the π-allyl/Pd species, as suggested by DFT calculations. Expecting an isotopic effect, we synthesized **3D**, an analogue of **3** in which the hydrogen atom that

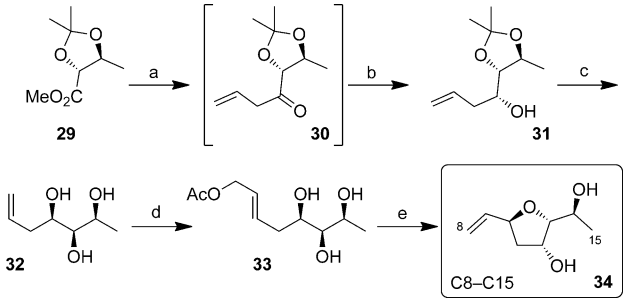
supposedly forms the H-bond, was replaced by a deuterium atom.[16] Allyl acetate **3D** cyclized to **4D** with a d.r. of 91:9 (experiment repeated twice), instead of the d.r. of 96:4 that was observed for **4** under the same experimental conditions. It is known that C–D···O bonding is slightly weaker than C–H···O bonding in comparison,[17] hence this small decrease of the observed d.r. is likely due to an isotopic effect, which confirms the existence of an H-bonding interaction involving the π-allyl/Pd moiety.

This synthetic method is particularly valuable with regard to its efficiency and the abundance of the tetrahydrofuran motif in natural products.[18] Many of these have very intriguing structures and/or interesting biological properties, hence the existence of a great number of strategies and methods that are aimed at their synthesis.[19] The very encouraging results mentioned above led us to subject complex allylacetates to this reaction in order to evaluate the scope of this transformation with regard to the synthesis of fragments of natural products. Thus, we synthesized **28**, the C9–C19 fragment of (+)-oocydin A (**1**). In the key step, triol **21** was subjected to our Pd catalysis conditions and cyclized into tetrahydrofuran **22** in 80% yield and with a good d.r. of 90:10 (Scheme 4). Because **21** is a triol, tetrahydropyran derivatives could have been obtained through a concurrent pathway involving the δ-OH group. This reaction fortunately did not occur, thus showing that the title reaction is both stereo- and chemoselective. The small decrease in diastereoselectivity observed here is likely due to the supplementary δ-OH function, which could disturb the formation of $[\pi R]^+$ by forming a detrimental H-bond. Triol **21** was readily synthesized from known bis(epoxide) **15**.[20] The reaction of **15** with a sulfur ylide[21] led to the corresponding bis(allylic alcohol) **16**, and a selective monoprotection gave allylic alcohol **17**. The latter was transformed into allyl acetate **18**, which was regioselectively reduced to diene **19**.[22] Allyl acetate **20** was obtained through a selective[23] cross-metathesis reaction,[24] which involved exclusively the less-hindered alkene function of diene **19**. Compound **20** was deprotected,[25] furnishing key triol **21**, which was then transformed to tetrahydrofuran **22**. We pursued our synthesis from **22** by using a $VO(acac)_2$-directed epoxidation,[26] which gave **23**. Mild reaction conditions[27] provided the cyclic silanyle ether **24**. The racemic Co^{III}–salen complex reported by Jacobsen[28] catalyzed the mild hydrolysis of fragile epoxide **24** into diol **25** in good yield. $NaIO_4$-promoted oxidative cleavage of **25** furnished an aldehyde that was immediately transformed into (*E*)-α,β-unsaturated ketone **26**,[29–30] and subsequently into diazo ketone **27**.[31] Compound **28**, the C9–C19 fragment of (+)-oocydin A (**1**), was cleanly obtained through the Ag^I-catalyzed Wolff rearrangement of diazo ketone **27**.[32] It is noteworthy that in terms of number of steps, selectivity, and mildness of conditions, the method we developed for the synthesis of 2,5-disubstituted 3-hydroxy-tetrahydrofurans favorably compares with the conventional method, namely the Roush and Micalizio method.[33] The latter was used by Hoye and Wang in their remarkably elegant total synthesis of (+)-oocydin A (**1**).[34]

We also used our methodology in the synthesis of compound **34** (Scheme 5), the C8–C15 fragment of (−)-obtusallene III (**2**; Figure 1).[35] The cyclization of triol **33** was again chemo- and diastereoselective, and tetrahydrofuran **34** was obtained in good yield and d.r. Homoallylic alcohol **31** was synthesized from commercially available ester **29** through the one-pot transformation of its ester function into the



Scheme 4. Second generation synthesis of the C9–C19 fragment of (+)-oocydin A (**1**). Reaction conditions: a) *n*BuLi, Me_3SI, THF, 45 °C, 76%; b) second generation Grubbs' catalyst, (*Z*)-but-2-ene-1,4-diyl diacetate (neat), 45 °C, 74%; c) NaH, TBSCl, DME, 0 °C; d) Ac_2O, 4-DMAP, pyridine, RT, 98% (over 2 steps); e) $[Pd_2(dba)_3]$, nBu_3P, HCO_2H, Et_3N, THF, 60 °C, 97%; f) TBAF, THF, RT, 98%; g) $CeCl_3 \cdot (H_2O)_7$, oxalic acid, MeCN, reflux, 90%; h) cond. C in Scheme 2, 40 °C, 80% (d.r. = 90:10); i) $VO(acac)_2$, *t*BuO_2H, PhMe, 90 °C, 75%; j) $(tBu)_2Si(OTf)_2$, 2,6-lutidine, TTBP, CH_2Cl_2, 0 °C, 80%; k) *rac*-Co^{III}–salen, H_2O, THF, RT, 80%; l) $NaIO_4$, silica gel, CH_2Cl_2, RT, then $PO(OEt)_2CHMeCOMe$, NaH, THF, 0 °C, 83%; m) $CF_3COOCH_2CF_3$, *n*BuLi, HMDS, THF, −78 °C, then Et_3N, H_2O, MsN_3, MeCN, 35 °C, 50% (over 2 steps); n) $PhCO_2Ag$, Et_3N, MPMOH, THF, RT, 60%. acac = acetylacetonate, DMAP = dimethylaminopyridine, DME = 1,2-dimethoxyethane, HMDS = hexamethyldisilazane, TBAF = tetrabutylammonium fluoride, TBS = *tert*-butyldimetylsilyl, TTBP = 2,4,6-tri-*tert*-butylpyrimidine.



Scheme 5. Synthesis of the C8–C15 fragment of (−)-obtusallene III (**2**). Reaction conditions: a) MeNH(OMe)·HCl, LiHMDS, THF, −20 °C → 0 °C, then $H_2C{=}CHCH_2MgCl$; b) K-Selectride, THF, Et_2O, −78 °C, 61% (over 3 steps); c) 2 M HCl, H_2O, vacuum, 85%; d) allyl acetate, second generation Grubbs' catalyst, CH_2Cl_2, 82%; e) cond. A in Scheme 2, 35 °C, 78%, d.r. = 90:10.

desired ketone via a Weinreb amide.[36] The resulting β,γ-unsaturated ketone **30** was diastereoselectively reduced to alcohol **31** using K-Selectride. The *iso*-propylidene protective group of **31** was removed, leading to triol **32**, which gave the key intermediate **33** as a mixture of *E*/*Z* isomers through cross-metathesis with allyl acetate.[24]

To conclude, a new example of counteranion-directed catalysis of the Tsuji–Trost reaction has been described. The method constitutes a novel diastereoselective approach toward 2,5-disubstituted 3-hydroxy-tetrahydrofurans. The selectivity was rationalized by DFT calculations, which showed the prominent role of the counteranion establishing noncovalent interactions. This mechanistic proposal is strongly supported by a series of chemical experiments. Classically used in more efficient and elegant strategies of synthesis, substrate-directed chemical reactions[37–38] allow step and atom economy and provide a pathway toward the ideal total synthesis.[39] We have demonstrated the relevance of our approach for the total synthesis of natural products through our syntheses of fragments of (+)-oocydin A (**1**) and (−)-obtusallene III (**2**). Many other natural products can be targeted with our method, as it allows facile access to four out of the eight possible stereoisomers of 2,5-disubstituted 3-hydroxy-tetrahydrofuran analogues.

Received: July 11, 2012
Published online: September 20, 2012

Keywords: counteranion-directed catalysis · hydrogen bonds · natural products · palladium · tetrahydrofuran

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