oxazolidin-2-ones with high enantiomeric excesses has already proved to be useful in generating a number of biologically significant targets such as mannostatin A,[15a] allosamizoline,[15a] and swainsonine.[15b]

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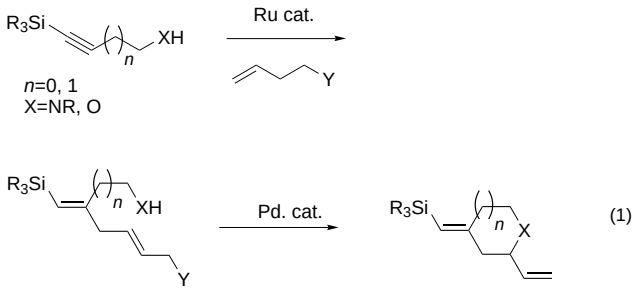
An Efficient One-Pot Enantio- and Diastereoselective Synthesis of Heterocycles**

Barry M. Trost* and Michelle R. Machacek

Heterocycles comprise the core of many complex natural products. The most common method for their formation is based on intramolecular ring closure. However, in most intramolecular closure strategies it is necessary to synthesize and then isolate the open-chain precursor. On an industrial scale the environmental and economic costs of the isolation step are considerable. In contrast, a more efficient strategy utilizes a domino alkylation–cyclization[1] to form the ring without isolation of the acyclic intermediate. For the development of ideal syntheses, processes are sought that generate multiple bonds in one pot.[2]

We aimed to design a one-pot heterocyclization process that was both efficient and permitted control of the stereochemistry of our products. We therefore focused on the Pd-catalyzed asymmetric allylic alkylation (AAA)[3,4] for the critical stereochemical determining step. This was combined with the Ru-catalyzed ene–yne coupling[5] to create the proper juxtaposition of functionality for the second step. Recently we have shown that in the presence of $[CpRu(CH_3CN)_3PF_6]$,[6] silyl-substituted alkynes form 1,4-dienes with complete regio- and stereoselectivity.[7] If the ene partner is a homoallylic group, the resulting 1,4-diene will contain a *newly formed allylic* group as illustrated in Equation (1). This intermediate



(1)

may then *without isolation* be subjected to Pd-catalyzed asymmetric allylic alkylation. An additional feature of this strategy is that the resulting vinylsilanes offer a pathway for further structural elaboration[8] and permit differentiation of the two resulting double bonds.

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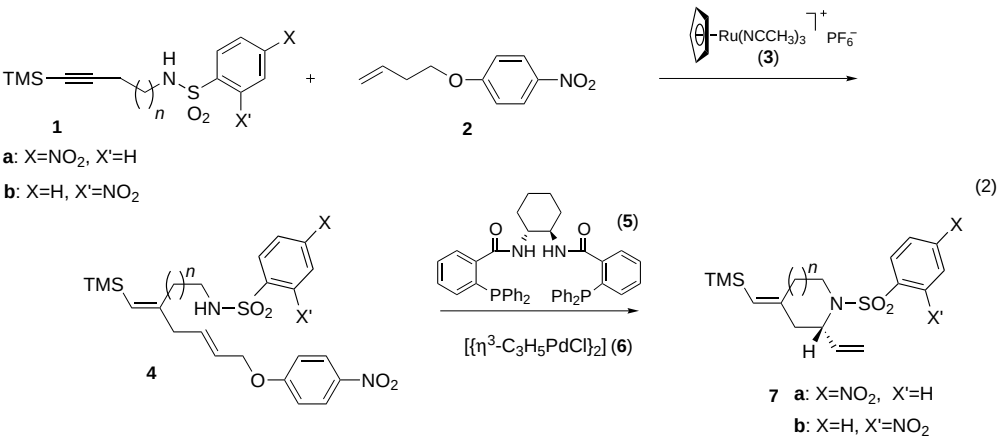
Incorporating asymmetric transition-metal catalysis into a tandem process is a formidable goal.[9] The key issue is the compatibility of the two catalyst systems. The reagents or catalysts may interfere with each other by distorting the chiral pocket that is crucial for enantioselectivity, or by acting as nondissociating ligands that shut down the catalytic cycle. For our dual catalytic reaction, we required a substituent Y that was compatible with both asymmetric allylic alkylation and the ene–yne coupling. We previously demonstrated that allylic esters serve as excellent substrates for Ru-catalyzed allylic alkylations.[10] However, to obtain high asymmetric induction, the group Y must allow the ene–yne coupling to proceed to completion *without* appreciable ionization of the resulting allylic group. This group Y must then still participate effectively in the Pd-catalyzed allylic alkylation.

In our initial work using an ester for Y, the desired ene–yne coupling was always accompanied by varying amounts of Ru-catalyzed ionization. While phenol has been reported as a leaving group in simple Pd-catalyzed allylic alkylations,[11] our early efforts revealed that such reactions were not general and failed with many routine nucleophiles. We therefore examined a *p*-nitrophenyl ether to enhance the reactivity for the Pd-catalyzed step without disturbing the Ru-catalyzed step. Indeed, reaction of **1a** ($n=1$) with 1-butenyl-4-*p*-nitrophenyl ether (**2**) in the presence of a catalytic amount of ruthenium complex **3**[6] in acetone at room temperature gave the desired adduct **4** in 91 % yield as a single regio- and geometric isomer within 2 h [Eq. (2)]. Further treatment with the Pd complex



(2)

generated by mixing the precatalyst (2 mol % **6** with 6 mol % ligand **5**) in acetone in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave the piperidine **7a** ($n=1$)[12] in 72 % yield and 74 % *ee*. The choice of the *p*-nitrobenzenesulfonamide as the nucleophile derived from the compatibility of this functionality with the Ru-catalyzed ene–yne addition and its ease of removal.[13] Optimization studies of the AAA reaction revealed that solvent had the biggest impact on enantioselectivity. The best results were obtained by using chloroform (99 % yield, 90 % *ee*) or dichloromethane (100 % yield, 89 % *ee*). Because the Ru-catalyzed reaction is best run in acetone, mixed solvents were also examined. A 75:25 (v:v) mixture of dichloromethane and acetone gave 84 % *ee* which increased to 88 % *ee* by using a 90:10 (v:v) mixture. A one-pot protocol then evolved by allowing **1a** ($n=1$) and **2** in a 1:1.7 ratio to react in the presence of **3** (2 mol %) at room temperature in acetone. Addition of DBU (1 equiv) along with the precatalyst in dichloromethane and stirring for 1 h, followed by evaporation and flash chromatography, resulted in an 83 % yield of **7a** ($n=1$) with 88 % *ee* (see Table 1, entry 3). The use of the *o*-nitrobenzesulfonamide (**2b**, $n=1$) gave a somewhat higher enantiomeric excess. Under conditions where the *p*-nitro analogue **2a** ($n=1$) gave 84 % *ee*, the *o*-nitro substrate resulted in 88 % *ee*. Therefore, it is apparent that the ruthenium catalyst affects neither the chiral pocket nor the turnover of the palladium catalyst. Furthermore, the yield for the overall process is much higher than when each step is individually isolated.

The absolute configuration of this product was assigned based upon our mnemonic wherein the initial ionization constitutes the enantiodiscriminating event.[14] Support for this assignment derives from the effect of chloride salts on the enantiomeric excess. Addition of tetra-*n*-butylammonium chloride to increase the rate of π-σ-π equilibration of intermediates[15] decreases the enantiomeric excess dramatically. Entries 1–4, Table 1, summarize the results for forming the pyrrolidine and piperidine systems.

The formation of the corresponding oxygen heterocycles was examined as shown in Equation (3). To abate product volatility, a dimethylphenylsilyl(DMPS)-substituted alkyne was employed. The presence of a free alcohol on alkyne **8** led to a rate retardation that was overcome by using excess alkene partner and higher Ru catalyst loadings (10 mol %). Again, the ene–yne adduct **9** that formed as a single isomer in 75 % yield showed no propensity to cyclize. Simple alkyl alcohols are not known to participate well in enantioselective Pd π-allyl alkylations.[16,17] However, in an intramolecular sense we found that AAA reactions with simple alkyl alcohols were very successful. The alcohol nucleophiles showed a similar solvent effect wherein dichoromethane was strongly preferred. Consequently, these reactions were performed by evaporating the acetone from the first stage followed by adding a solution of Pd catalyst and base in dichloromethane. For oxygen nucleophiles, $[Pd_2(dba)_3]\cdot CHCl_3$ and triethylamine were the preferred Pd^0 source and base, respectively. Addition of tetra-*n*-butylammonium chloride had no significant effect on the enantiomeric excess. This observation is consistent with the nucleophilic addition step being the enantiodiscriminating event leading to the assigments depicted in Table 1. Entries 5 and 6, Table 1, summarize the results.

Palladium catalysis offers an opportunity for diastereo- as well as enantiocontrol in reactions. Table 2 summarizes the extent to which the chiral ligands overcame the intrinsic diastereoselectivity of the substrates. Enantiomerically pure

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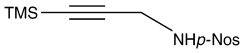
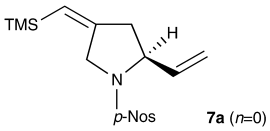
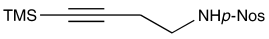
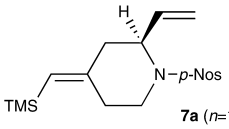
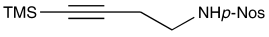
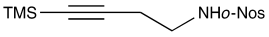
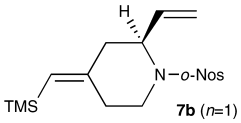
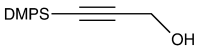
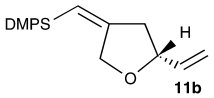
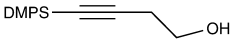
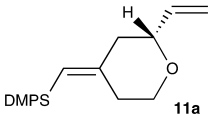
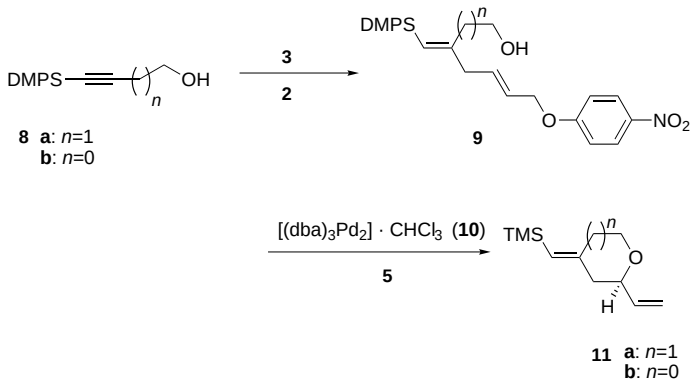
Table 1. Examples of enantioselective formation of heterocycles.

Entry	Alkyne	Product	Conditions[a]	Yield	*ee* [%][b]
1		 **7a** (*n*=0)	A	90	91
2		 **7a** (*n*=1)	A	90	84
3		**7a** ($n=1$)	B	83	88
4		 **7b** (*n*=1)	A	90	88
5		 **11b**	C	84	76
6		 **11a**	C	80	94

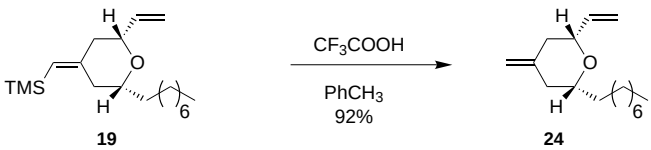
[a] Conditions: A: a) 5 mol% **3**, CH_3COCH_3, RT, 3–4 h; b) 2 mol% **6**, 6 mol% **5**, DBU, RT, CH_2Cl_2:CH_3COCH_3 (75:25) 1 h. B: a) 2 mol% **3**, CH_3COCH_3, RT, 3–4 h; b) 2 mol% **6**, 6 mol% **5**, DBU, CH_2Cl_2:CH_3COCH_3 (90:10). C: a) 10 mol% **3**, CH_3COCH_3, RT, 3–4 h; b) 2 mol% **6**, 6 mol% **5**, $(C_2H_5)_3N$, 0 °C, CH_2Cl_2. [b] Enantiomeric excess (*ee*) determined by HPLC.



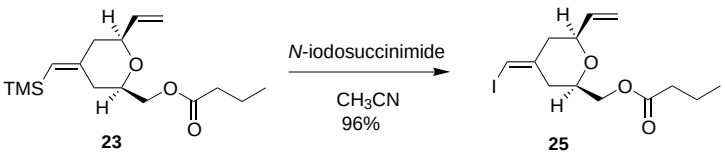
(3)

substrates of known absolute configuration were employed in all cases. As expected, a matched and mismatched pair[15] was formed. In piperidine formation, the *cis* isomer predominates 2:1 with the achiral 1,3-bis(diphenylphosphanyl)propane (dppp) ligand. Under matched conditions, the *cis* isomer is formed nearly exclusively (Table 2, entry 2), while when the mismatched ligand system is used, the *trans* isomer is favored 2:1 (Table 2, entry 1). In the case of oxygen heterocyles, the level of control exercised by the ligands increased. For the furan system (Table 2, entries 3 and 4), the *cis*:*trans* ratio switched from 10:1 in the matched case to 1:3.5 in the mismatched. These selectivities compare to a 4:1 *cis*:*trans* ratio with the achiral ligand dppp. Dramatically, in pyran formation (Table 2, entries 5–8) the selectivity was complete—the *cis* isomer was formed exclusively in the matched cases (Table 2, entries 5 and 8) and the *trans* isomer was formed exclusively in the mismatched cases (Table 2,entries 6 and 7). Cyclization methods for forming *cis* 2,6-disubstituted tetrahydropyrans are prevalent. However, very few methods offer direct access to the thermodynamically unfavorable *trans*-pyran in isomerically pure form.[18] For this class of substrates, the ability of the chiral ligands to control relative stereochemistry[19] is indeed impressive and indicates the potential of this catalytic system.

In addition to providing access to a very important class of compounds, this methodology also introduces several functional groups into the heterocycle that readily allow further elaboration. For example, the resulting vinylsilane moiety offers access to a variety of stereochemically defined trisubstitued alkenes by *ipso*-substitution reactions. We were also able to smoothly convert the vinylsilane to a vinyl iodide [Eq. (4b)], allowing access to many cross-coupling reactions. The resulting vinyl-



(4a)



(4b)

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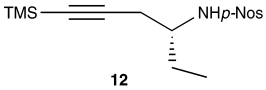
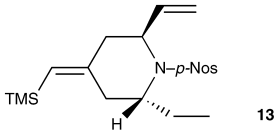
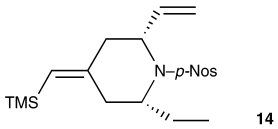
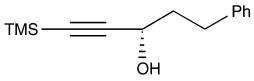
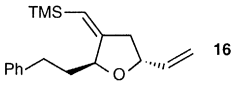
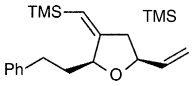
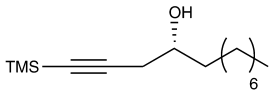
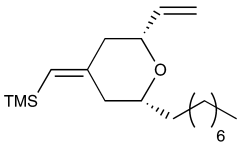
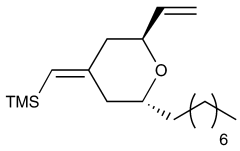
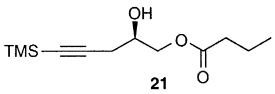
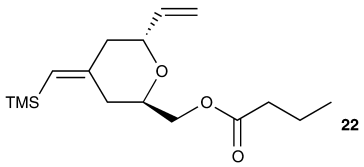
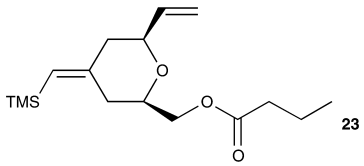
Table 2. Examples of diastereoselective formation of heterocycles.

Entry	Alkyne	Ligand	Major Product	Conditions[a]	Yield	d.r.[b]
1	 **12**	**5**	 **13**	A	73	2:1
2	**12**	*ent*-**5**	 **14**	A	68	99:1
3	 **15**	**5**	 **16**	C	87	3.5:1
4	**15**	*ent*-**5**	 **17**	C	80	10:1
5	 **18**	**5**	 **19**	C	80	> 97:3
6	**18**	*ent*-**5**	 **20**	C	80	> 97:3
7	 **21**	**5**	 **22**	C	60	> 97:3
8	**21**	*ent*-**5**	 **23**	C	58	> 97:3

[a] See footnote [a] of Table 1 for conditions. [b] Ratios determined by ^{1}H NMR spectroscopy.

silane also acts to differentiate the two resulting double bonds and can ultimately be converted to the parent methylene by protodesilation without altering the regiochemistry by isomerization of the double bond [Eq. (4a)].

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[19] The assignment of relative configuration was straightforward by NMR spectroscopy. Since the absolute stereochemistry of the starting substrate is known, the absolute configuration of the newly created allylic stereogenic center is also known. These stereochemical assignments are furthermore consistent with our mnemonic and with those made in Table 1.

General Synthesis of Semiconductor Chalcogenide Nanorods by Using the Monodentate Ligand *n*-Butylamine as a Shape Controller**

Jian Yang,* Can Xue, Shu-Hong Yu,* Jing-Hui Zeng, and Yi-Tai Qian

Currently, research on fundamental properties and practical applications of nanomaterials are attracting much attention.[1] However, most studies have focused on the size effect of nanocrystals. In fact, the shape of semiconductor nanomaterials has considerable influence on physical properties and is also important in many potential applications, such as solar cells, light-emitting diodes, and scanning-microscopy probes.[2] In spite of this, since little is known about the mechanism of crystal growth of anisotropic nanocrystals, shape control of nanocrystals remains a challenge to synthetic chemists.[1c,3]

Over the past few years, remarkable progress has been made in the shape control of nanomaterials. Alivisatos et al. controlled the size and shape of CdSe nanocrystals in the presence of strong ligands.[4] This approach was extended to control the size and shape of magnetic cobalt nanocrystals.[5] Lieber et al. developed a laser-assisted catalytic growth (LCG) technique to synthesize a broad range of binary and ternary semiconductor nanowires by a vapor–liquid–solid (VLS) mechanism.[6] Highly crystalline III–V semiconductor nanowires were synthesized by a solution–liquid–solid (SLS) method introduced by Buhro et al.[7] Recently, Weller et al. grew ZnO nanorods by oriented attachment of small quasi-spherical particles by concentrating and refluxing a solution.[8] Very thin one- (1D) and two-dimensional (2D) $CdWO_4$ nanocrystals with controlled aspect ratios were conveniently fabricated at ambient temperature or by hydrothermal ripening.[9] However, to the best of our knowledge, a general route for the synthesis of various semiconductor chalcogenide nanorods under mild solution conditions has still not been realized.

We have successfully controlled the size and shape of semiconductor nanocrystals by means of solvothermal reactions.[10–12] In-depth studies on the formation processes of these nanorods provided useful guidelines for the preparation of 1D nanocrystals.[10,11] We found that the anisotropic nature of the building blocks in the crystal structure, which are infinite linear chains in the case of M_2S_3 (M = Sb, Bi), plays a crucial role in the formation of nanorods.[11,12] In other words, this 1D growth of nanocrystals is actually the outward embodiment of the internal crystal structure.

The temporal evolution of CdS nanocrystals in solvothermal reactions demonstrated that ethylenediamine (en) molecules adsorbed on the surface of CdS play a critical role in the formation of nanorods.[10] FTIR spectra of these en molecules show that they are not in chelating (*cis*) configuration but in *trans* configuration. Reetz et al. reported that a nonchelating coordination mode of α-hydroxycarboxylates on a metal surface is likely to be the morphology-determining factor in shape-selective preparation.[13] However, on the basis of IR data alone, it is difficult to judge whether the mode of coordination between Cd^{2+} on the surface and en molecules is monodentate (Scheme 1a) or bridging (Scheme 1b), although it is possible that the en molecules in both cases are in the *trans* configuration.

Because *n*-butylamine has only one anchor atom, its coordination mode with metal ions must be monodentate (Scheme 1c), and hence we employed it as solvent to clarify this point. First, CdS nanocrystals were chosen as the target to examine whether the same reaction in a monodentate ligand can produce nanorods. In the IR spectrum of the as-prepared CdS nanocrystals, the characteristic absorption peak at 1573.0 cm^{-1} can be unambiguously assigned to the NH_2 bending vibration, which is shifted to lower frequency relative to that of pure *n*-butylamine[14] (see Supporting Information). A red shift of the C–N bending vibration resulting from

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