Cycloaddition

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Catalytic Asymmetric Synthesis of Cyclopentyl β-Amino Esters by [3+2] Cycloaddition of Enecarbamates with Electrophilic Metalloenolcarbene Intermediates

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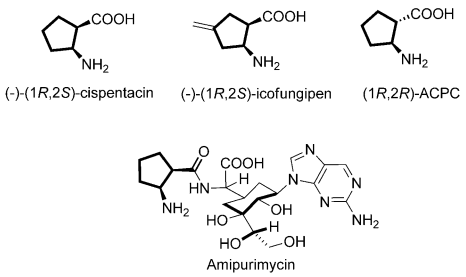
Dedicated to Professor Henri Brunner on the occasion of his 80th birthday

Abstract: *Chiral cyclopentyl β-amino esters are formed catalytically by [3+2] cycloaddition reactions of enecarbamates with electrophilic metalloenolcarbenes in high yield with up to 98% ee and excellent diastereocontrol. Use of β-silyl-substituted enoldiazoacetates with a chiral dirhodium catalyst and trans-β-arylvinylcarbamates are optimal for this transformation, which occurs with hydrogen-bond association between the vinylcarbamate and the intermediate metalloenolcarbene. Reductive conversion of the protected amino esters forms highly functionalized cyclopentyl β-amino acids and 3-aminocyclopentanones.*

Enantiomerically pure carbocyclic β-amino acids and their derivatives are key structural elements of many natural products, antibiotics, and building blocks in peptide synthesis.[1] One of the largest and most important groups of carbocyclic β-amino acids are those with cyclopentyl rings (Scheme 1).[1b,2] As examples, cispentacin and icofungipen



Scheme 1. Bioactive cyclopentyl β-amino acids and derivatives.

exhibit noteworthy antifungal and antibacterial activities,[3] *trans*-aminocyclopentanecarboxylic acid [(1*R*,2*R*)-ACPC] has been applied for constructing β-peptide antibiotics,[4] and amipurimycin is active against *Pyricularia oryzae*.[5] As a consequence of their high biological potential, significant effort has been devoted to asymmetric syntheses of cyclopentyl β-amino acids and their derivatives.[2] However, most methodologies have focused on stoichiometric asymmetric synthesis[6] or resolution,[7] and few have provided highly enantioselective access to highly functionalized substrates.[8]

Recently, metalloenolcarbenes which are generated catalytically from stable enoldiazo compounds have emerged as a synthetically useful class of carbene precursors when paired with transition-metal catalysts.[9] Metalloenolcarbene intermediates exhibit electrophilic character at both the carbene (**A**; Scheme 2) and vinylogous positions (**B**). We have demonstrated that these metalloenolcarbenes undergo [3+3] cycloaddition with a variety of 1,3-dipolar species to form diverse heterocyclic compounds in high yields and selectivities,[9a,f] and we have been searching for new applications of [3+2] cycloadditions which also occur with high stereocontrol. Coming from a long history of vinylcarbene reaction chemistry,[10] the group of Davies recently reported a highly enantioselective formal [3+2] cycloaddition of enoldiazoacetates[11] which formed cyclopentenones from sterically crowded silyl enol ethers (Scheme 2a). In our effort to form β-aminocyclopentanecarboxylates by [3+2] cycloadditions we reported the dirhodium-catalyzed annulation of silylated ketene imines and enoldiazoacetates, but without stereocontrol (Scheme 2b).[12] We envisioned that conveniently prepared nucleophilic enecarbamates,[13] despite their propensity to undergo N–H insertion with metal carbenes,[14] could also undergo [3+2] cycloaddition with electrophilic metalloenolcarbenes, and we now report the first highly diastereoselective and enantioselective [3+2] cycloaddition of *trans*-β-arylvinylcarbamates with metalloenolcarbene, thus generating enantiomerically pure cyclopentyl β-amino esters, which can be converted into functionalized cyclopentyl β-amino acids (Scheme 2c).

In our initial investigation, reaction of the *tert*-butyldimethylsilyl (TBS) substituted enoldiazoacetate **1a** with β-phenyl-enecarbamate **2a** in dichloromethane (DCM) was conducted at room temperature in the presence of dirhodium tetraacetate. The β-amino ester **3a** was generated in 96% yield, and after treatment with tetrabutylammonium fluoride (TBAF), **3a** gave the β-amino ester **4a** rapidly in high yield [Eq. (1)]. Neither copper [$Cu(MeCN)_4BF_4$] nor silver ($AgSbF_6$) catalysts were effective for this reaction, and enoldiazoacetamides were unreactive towards enecarbamates under these catalytic conditions.

Traditionally, the asymmetric synthesis of cyclopentyl β-amino acids have been achieved by using enzymatic or kinetic

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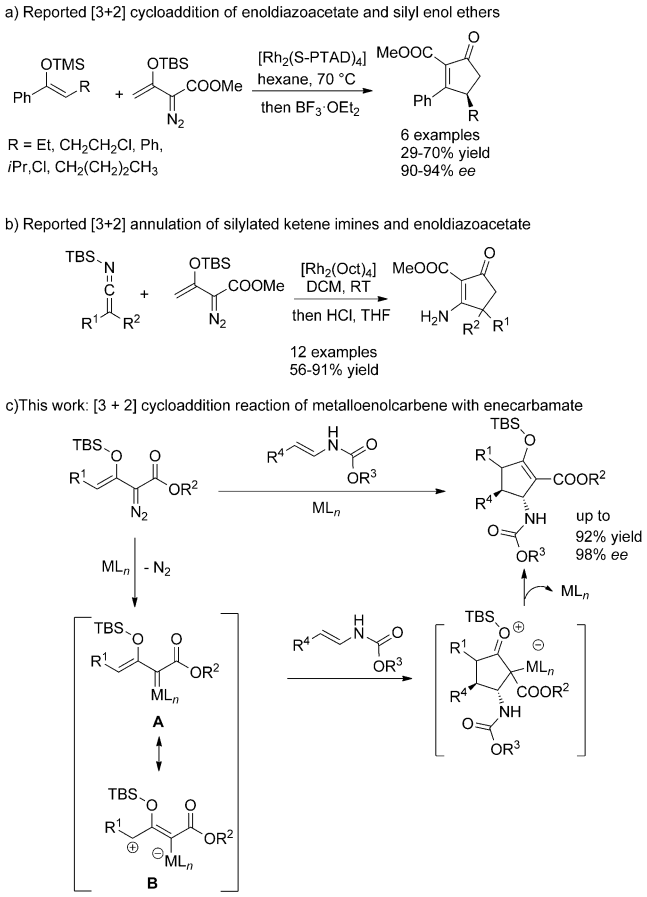
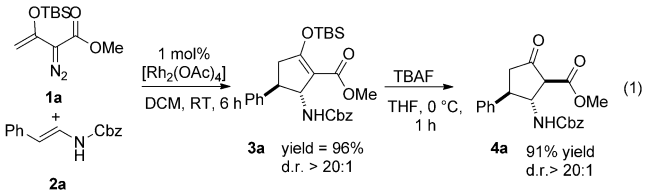
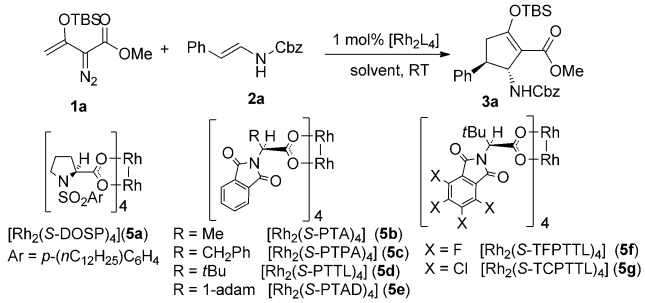


Scheme 2. a,b) Reported [3+2] cycloadditions of enoldiazoacetates. c) [3+2] cycloaddition reactions of metalloenolcarbene with *trans*-β-arylvinylcarbamates. DCM = dichloromethane, Oct = octanoate, PTAD = 1-adamantyl-(*N*-phthalimido)acetato, TBS = *tert*-butyldimethylsilyl, TMS = trimethylsilyl, THF = tetrahydrofuran.



resolutions,[7] as well as by using chiral auxiliaries in such methods as enolate addition to imidoyl chlorides[6a] and chiral lithium amide conjugated addition.[6b] The catalytic asymmetric hydrogenation of cyclic β-(acylamino) acrylates provides an efficient approach to chiral carbocyclic β-amino esters, but only applications to unsubstituted cyclopentyl β-amino esters have been reported.[8d,e] In view of the limited availability of catalytic enantioselective methods for the synthesis of functionalized cyclopentyl β-amino esters, we sought to employ chiral dirhodium carboxylate catalysts for the reaction between **1a** and **2a**. As summarized in Table 1, exploration of $[Rh_2(S\text{-DOSP})_4]$ (**5a**) as the catalyst[15] generated **3a** in good yield and excellent diastereoselectivity.

Table 1: Optimization of reaction conditions for the enantioselective [3+2] cycloaddition of **1a** with **2a**.[a]



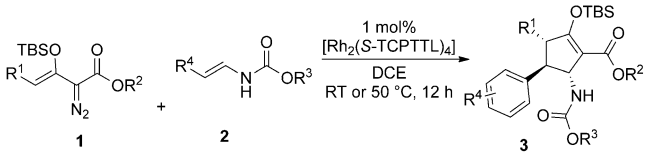
Entry	$[Rh_2L_4]$	*T* [h]	Sol.	Conv. [%][b]	Yield [%][c]	d.r.[d]	*ee* [%][e]
1	**5a**	24	DCM	100	86	>20:1	17
2	**5b**	20	DCM	100	87	>20:1	21
3	**5c**	20	DCM	100	90	>20:1	23
4	**5d**	24	DCM	94	78	>20:1	60
5	**5e**	24	DCM	93	80	>20:1	73
6	**5f**	24	DCM	100	85	>20:1	64
7	**5g**	24	DCM	100	87	>20:1	89
8	**5g**	48	hexane	48	36	>20:1	85
9	**5g**	48	toluene	85	68	>20:1	90
10	**5g**	48	Et_2O	56	44	>20:1	93
11	**5g**	24	$CHCl_3$	91	78	>20:1	87
12	**5g**	12	DCE	100	91	>20:1	91
13[f]	**5g**	12	DCE	100	83	>20:1	91

[a] Unless otherwise noted, reactions were performed at room temperature with 0.10 mmol of **2a** (1.0 equiv). An excess of **1a** (1.5 equiv) in 1.0 mL solvent was added to the reaction mixture by syringe pump over 30 minutes with continued stirring. [b] Determined by ^{1}H NMR analysis of the reaction mixtures based on the limiting reagent **2a**. [c] Yield of isolated **3a** based on the limiting reagent **2a**. [d] Determined by ^{1}H NMR analysis of the reaction mixtures. [e] Determined by chiral-phase HPLC analysis. See the Supporting Information for experimental details. [f] Reactions were performed at room temperature with 0.10 mmol of **2a** (1.0 equiv) and **1a** (1.2 equiv).

However, this reaction occurred with low enantioselectivity (entry 1). Instead, as was also realized by the group of Davies,[11] the phthalimide–amino acid ligated dirhodium catalysts[16] produced **3a** in good to excellent yields and modest to high enantioselectivities (entries 2–6). Surprisingly, $[Rh_2(S\text{-TCPTTL})_4]$ (**5g**),[16c] the chlorinated analogue of $[Rh_2(S\text{-PTTL})_4]$[16b] rather than its fluorinated analogue $[Rh_2(S\text{-TFPTTL})_4]$, proved to be the catalyst of choice, thus providing **3a** in 87% yield and 89% *ee*. Further optimization with 1 mol% $[Rh_2(S\text{-TCPTTL})_4]$ in various solvents gave the optimum 91% yield and 91% *ee* of **3a** in 1,2-dichloroethene (DCE) at room temperature (entry 12). A lower yield of **3a** was obtained when the **1a** to **2a** ratio was decreased to 1.2:1.0 (entry 13).

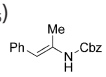
Using the optimized reaction conditions obtained with **1a** and **2a** (Table 1, entry 12), the substrate scope with respect to the enoldiazoacetates **1** and β-aryl-enecarbamates **2** was examined and these results are reported in Table 2. As indicated, different enoldiazoacetate esters underwent the [3+2] cycloaddition reaction with high diastereo- and enantiocontrol, but the highest *ee* value was obtained with the benzyl ester **1b** (entries 1 to 4). The enhanced enantioselec-

Table 2: Substrate scope for enantioselective [3+2] cycloaddition of enoldiazoacetates (**1**) with β-aryl-enecarbamates (**2**).[a]



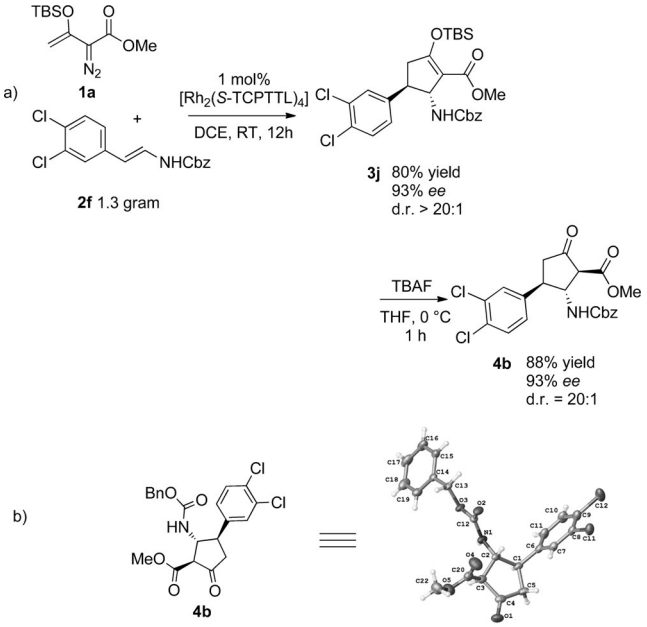
1a: R^1 = H, R^2 = Me
1b: R^1 = H, R^2 = Bn
1c: R^1 = H, R^2 = *t*Bu
1d: R^1 = Me, R^2 = Me
1e: R^1 = Ph, R^2 = Me

d.r.[c] > 20:1

Entry	1	2 (R^3, R^4)	3	Yield [%][b]	*ee* [%][d]
1	**1a**	**2a** (Bn, C_6H_5)	**3a**	91	91
2	**1b**	**2a**	**3b**	90	97
3[e,f]	**1c**	**2a**	**3c**	70	90
4[e,f]	**1d**	**2a**	**3d**	78	93
5	**1e**	**2a**	–	0	–
6	**1b**	**2b** (Bn, 4-$CH_3C_6H_4$)	**3e**	82	95
7	**1b**	**2c** (Bn, 3,4-$(MeO)_2C_6H_3$)	**3f**	85	95
8	**1b**	**2d** (Bn, 3,4-[1,3]dioxole-C_6H_3)	**3g**	86	96
9	**1a**	**2e** (Bn, 4-ClC_6H_4)	**3h**	92	92
10	**1b**	**2e**	**3i**	90	98
11	**1a**	**2f** (Bn, 3,4-$Cl_2C_6H_3$)	**3j**	85	93
12[f]	**1a**	**2g** (Bn, 4-$NO_2C_6H_4$)	**3k**	84	95
13	**1a**	**2h** (Et, C_6H_5)	**3l**	90	93
14[e,f]	**1a**	**2i** = 	**3m**	62	94
15	**1a**	**2j** (Bn, (*E*)-$CH_3CH{=}CH$)	**3n**	83	72

[a] Reactions were performed at room temperature with 0.20 mmol of **2** (1.0 equiv). A 50% molar excess of **1** (1.5 equiv) in 2.0 mL solvent was added to the reaction mixture via syringe pump over 30 minutes with continued stirring. [b] Yield of isolated **3** based on the limiting reagent **2**. [c] Determined by 1H NMR analysis of the reaction mixtures [d] Determined by chiral-phase HPLC analysis. See the Supporting Information for experimental details. [e] Reactions were performed at 50°C. [f] Reactions were performed for 24 hours.

A gram-scale enantioselective [3+2] cycloaddition gave the same enantioselectivity and yield as did the small-scale reaction (Table 2, entry 11). Notably, **3j** produced the β-amino ester **4a,** after treatment of with TBAF, without loss of enantiocontrol (93% *ee*), thus suggesting the potential of this process for large-scale production of enantiopure functionalized cyclopentyl β-amino esters (Scheme 3a). The absolute

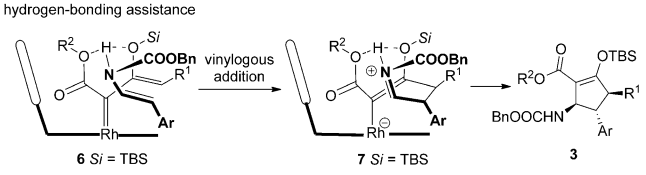


Scheme 3. a) Gram-scale enantioselective [3+2] cycloaddition of **1a** with **2f** and subsequent transformation into **4b**. b) ORTEP view of (1*S*,2*R*,3*R*)-methyl 2-(((benzyloxy)carbonyl)amino)-3-(3,4-dichlorophenyl)-5-oxocyclopentanecarboxylate (**4b**). Thermal ellipsoids shown at 50% probability.[17]

tivity from **1b** was further confirmed by the reactions of the chloro-substituted enecarbamate **2e** (92% *ee* with **1a** in entry 9, 98% *ee* with **1b** in entry 10). Reactions of the *tert*-butyl ester **1c** and γ-methylenoldiazoacetate **1d** required a higher reaction temperature (50°C) to obtain good yields with high diastereo- and enantiocontrol (entries 3 and 4), but no reaction occurred with the γ-phenylenoldiazoacetate **1e** (entry 5), thus suggesting the steric congestion in the cycloaddition process. Electronically disparate substituents on the aryl ring of **2** are well-tolerated (entries 6–12), and product yields and enantioselectivities were independent of the carbamate ester substituent (R^3)on **2**. The enecarbamate **2i**, having a methyl group instead of a hydrogen atom attached at the α-position, also underwent [3+2] cycloaddition with complete diastereocontrol and high enantioselectivity (entry 14). The alkenyl-substituted enecarbamate **2j** reacted with **1a** smoothly to form the corresponding [3+2] cycloaddition product **3n** with a lower 72% *ee* (entry 15). In addition to β-aryl-enecarbamates, the reactions of β-alkyl-enecarbamates with enoldiazoacetates were also examined, thus generating the desired [3+2] cycloaddition product in high yields and diastereoselectivities, albeit with low enantioselectivities (see the Supporting Information).

configuration of **4b** was unambiguously determined to be 1*S*,2*R*,3*R* through single-crystal X-ray analysis (Scheme 3b).[17] The compounds **3** were thus assigned as 4*R*,5*R*.

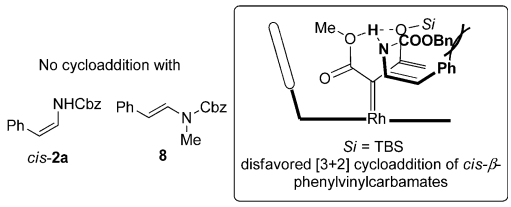
The mechanism that we propose for this [3+2] cycloaddition reaction focuses on an unprecedented hydrogen-bond association between the reactant metalloenolcarbene and the β-aryl-enecarbamates **2**, and explains the observed geometrical constraints from both enoldiazoacetates and β-aryl-enecarbamates (Scheme 4). The rhodium enolcarbene is formed at the axial position of the dirhodium catalyst with the bulky TBS group pointing away from the phthalimido blocking groups. To avoid steric interactions at the congested left-hand side of **6**, the carbonyl group may be pointing towards



Scheme 4. Proposed mechanism for the [3+2] cycloaddition of an enoldiazoacetate with a *trans*-enecarbamate.

the catalyst face[18] to avoid steric interactions between the ester alkyl group and the pendant phthaloyl ligands. The enecarbamate approaches the chiral rhodium carbene from the front face (**6**). Intermolecular hydrogen bonding occurs between the enecarbamate and enolcarbene and ensures vinylogous addition to form the intermediate **7**. The *trans*-aryl group of the carbonate extends beyond the ligands' carboxylate oxygen atoms and into the chiral pocket of $[Rh_2(S\text{-TCPTTL})_4]$. The intramolecular iminium ion addition to the catalyst-activated vinyl ether functional group occurs with release of the catalyst and generates the [3+2] cycloaddition product **3**.[19] In addition, the tetrachlorophthaloyl units in the chiral pocket of $[Rh_2(S\text{-TCPTTL})_4]$ permit π-stacking interactions with the aryl substituent group on the substrate, thus fixing it in a conformation to achieve high stereocontrol.[20]

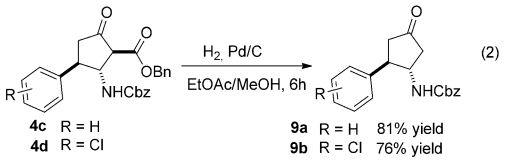
This mechanistic proposal is consistent with the absolute configuration obtained for the [3+2] cycloaddition product and for the significantly higher enantioselectivities obtained with aryl enecarbamates rather than with their alkyl or vinyl analogues. Also, when $R^1 = Me$ there are no severe steric constraints on enantiocontrol, although higher reaction temperatures were required. However, as anticipated from this model, no reaction occurred when $R^1 = Ph$. This model predicts that neither *cis*-**2a** nor *N*-methyl-*trans*-enecarbamate **8** will undergo cycloaddition with the metalloenolcarbene because of the steric interference and/or the absence of hydrogen bonding, and this is in fact what was observed (Scheme 5).

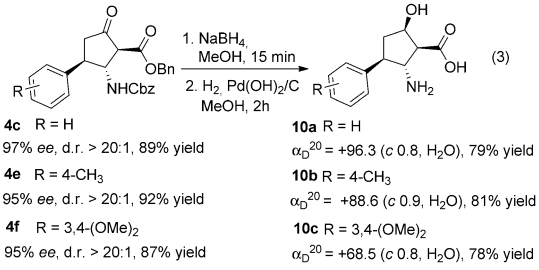


Scheme 5. Reaction results of *cis*-**2a** and **7**. Disfavored transition state of [3+2] cycloaddition of *cis*-β-phenylvinylcarbamate.

Efforts devoted to exploring the synthetic versatility of these novel amino esters demonstrated the ease of access to functionalized cyclopentylamines and to enantioenriched functionalized cyclopentyl β-amino acids. Treatment of the β-amino esters **4** under classic hydrogenation conditions gave the decarboxylation products **9** in good yield [Eq. (2)]. To prevent decarboxylation, **4** was first reduced with complete stereocontrol to the corresponding alcohol using sodium borohydride, then subjected to catalytic hydrogenation in a one-pot reaction. As outlined in Equation (3), a series of aryl/hydroxyl-substituted cyclopentyl-β-amino acids **10** were successfully obtained from [3+2] cycloaddition products in this convenient one-pot reduction and deprotection sequence without loss of optical purity.

In summary, we have developed the first diastereoselective and highly enantioselective [3+2] cycloaddition process of enoldiazoacetates with vinylcarbamates, and it provides access to functionalized chiral cyclopentyl β-amino esters. Also, a convenient one-pot deprotection, reduction, and





hydrogenolysis from chiral cyclopentyl β-amino esters furnishes enantioenriched 5-hydroxy-3-aryl-β-amino acids in good yields, as well as direct access to 3-aminocyclopentanones by deprotection and hydrogenolysis/decarboxylation. The convenience of this methodology, absence of N–H insertion, high selectivities, and potential synthetic versatility of the cycloaddition products suggest broad applicability in the synthesis of chiral cyclopentyl β-amino acids and functionalized cyclopentyl structures.

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Keywords: amino acids · cycloaddition · diazo compounds · enantioselectivity · rhodium

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