Direct Asymmetric Vinylogous and Bisvinylogous Mannich-Type Reaction Catalyzed by a Copper(I) Complex

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S *Supporting Information*

ABSTRACT: A direct catalytic asymmetric vinylogous Mannich-type reaction has been disclosed in good yield, excellent regio-, diastereo- and enantioselectivity. The key to control the regioselectivity is the combination of a bulky *N*-acylpyrazole and a bulky bisphosphine ligand. The catalytic system was extended to a bisvinylogous Mannich-type reaction by changing the ligand. The synthetic utility of the vinylogous products was demonstrated by several transformations.

Optically active δ-amino-α,β-unsaturated carbonyl compounds serve as structural motifs in biologically active compounds and also as synthetic intermediates.[1] One of the easiest methods to access these compounds is the catalytic asymmetric vinylogous Mannich reaction between imines and dienolate species.[2] The cyclic dienolates usually lead to the formation of γ-adducts exclusively whenever the dienolsilanes or metal dienolates are utilized.[3,4] Among linear dienolate species, dienolsilanes are the most frequently employed nucleophiles,[5] possibly due to their natural tendency to favor γ-addition.[6] Although metal dienolates would be more practical from a synthetic perspective, the α-addition product is the typical mode of reactivity in the Mannich reaction giving an aza-Morita-Baylis-Hillman-type product after isomerization of the double bond.[7]

Although the vinylogous Mukaiyama reaction has established its position in organic synthesis,[2,6c,8] it still suffers from limitations. First, the unstable dienolsilanes usually need to be prepared at a separate step. This leads to undesirable waste (silica gel, solvent, stoichiometric chlorosilanes, etc.), which conflicts with the principle of atomic economy in green chemistry.[9] Control of the geometry of dienolsilanes is another concern, and usually the inseparable mixture of 1-(*E*)- and 1-(*Z*)-dienolsilanes was obtained in standard preparation.[10] Therefore, it is desirable to develop a direct catalytic asymmetric vinylogous Mannich reaction with high regioselectivity.[2]

In 2010, Maruoka group disclosed alkenylation of aldimines with vinylogous aza-enamines.[11] Control of the geometry of the conjugated double bond in the product was proven to be difficult. Furthermore, the vinylogous aza-enamines with a C3-substituent were not applicable due to generation of a mixture of regioisomers. In 2013, Chi group reported a NHC-catalyzed asymmetric Mannich reaction of α,β-unsaturated esters and activated aldimines.[12] Although the direct vinylogous Mannich reaction was explored, the direct bisvinylogous Mannich reaction remains unknown, possibly due to challenges encountered. First,

there are three possible regio-isomers, including α-adduct, γ-adduct and ε-adduct in theory. Second, the enantioselectivity is difficult to control because the ε-position is far from the carbonyl functional group. To the best of our knowledge, there was only one example on the catalytic asymmetric bisvinylogous aldol reaction, which employed trienolsilanes as nucleophiles.[6b] Control of regioselectivity proved to be challenging with a regioselectivity less than $5/1(\varepsilon/\alpha)$ in many cases. Moreover, the enantioselectivity was not satisfactory generally, which allowed room for further improvement. We were planning to develop both vinylogous and bisvinylogous direct catalytic asymmetric Mannich-type reaction with both high regioselectivity and enantioselectivity.

It was envisioned that increasing steric hindrance of metal dienolates or trienolates would be of value to control regioselectivity. As illustrated in Scheme 1, by introducing a

Scheme 1. Generation of Copper(I)-Dienolates and Its Possible Reaction Pathways with *N*-Boc Imine 2a
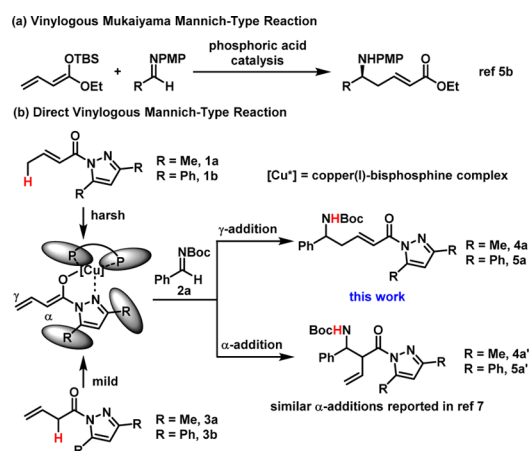
bulky pyrazole, together with employing a bulky copper(I) complex, γ-addition would be favored. The approach of electrophiles to the α-position of the dienolate was shielded by employing this strategy. An *N*-acylpyrazole functional group was also helpful to stabilize the corresponding copper(I) enolate, which might aid in control of diastereoselectivity and enantioselectivity. Moreover, *N*-acylpyrazole was reported to be a versatile functional group, which can be transformed to ester,

amide, carboxylic acid and alcohol functionalities.[13] Because direct vinylogous Michael reactions with α,β-unsaturated compounds have been reported with success,[14,15] the reaction between α,β-unsaturated N-acylpyrazole **1** and N-Boc imine **2a** was studied in the presence of copper(I) complex and common organic base.

Unfortunately, the above reaction afforded only trace product with **1** being intact. The high pK_a value of the γ-protons was postulated to lead to the inertness of **1** under the weak basic conditions. It was reported that β,γ-unsaturated carbonyl compounds were more easily transformed to the corresponding metal dienolate relative to α,β-unsaturated carbonyl compounds because of the lower pK_a value of its α-protons.[7a,16] Thus, β,γ-unsaturated N-acylpyrazole **3** was employed as the model substrate, which was prepared by coupling the commercially available but-3-enoic acid and pyrazoles in reasonable yield.

The reaction between **3a** and **2a** was studied as a model system (Table 1). In the presence of 5 mol% copper(I)-(R)-BINAP

Table 1. Optimization of the Reaction Conditions with 3a/3b and N-Boc Imine 2a[a]

entry	R	ligand	T	base	total yield[b]	4a(5a)/4a′(5a′)	ee of 4a(5a) (%)[c]
1	Me	(R)-BINAP	rt	DIPEA	99	0.6/1	16
2	Me	(R)-TOL-BINAP	rt	DIPEA	99	0.8/1	21
3	Me	(R)-SEGPHOS	rt	DIPEA	95	0.8/1	24
4	Me	(R)-DIFLUORPHOS	rt	DIPEA	88	0.6/1	20
5	Me	(R,R)-QUINOXP*	rt	DIPEA	61	0.6/1	<5
6	Me	(R,R)-Ph-BPE	rt	DIPEA	82	0.3/1	21
7	Me	(R)-QUINAP	rt	DIPEA	24	0.5/1	-10
8	Me	(R,R_p)-TANIAPHOS	rt	DIPEA	89	10/1	-39
9	Me	(R)-DTBM-SEGPHOS	rt	DIPEA	88	>20/1	86
10	Ph	(R)-DTBM-SEGPHOS	rt	DIPEA	99	>20/1	96
11	Ph	(R)-DTBM-SEGPHOS	-40	DIPEA	98	>20/1	98
12[d]	Ph	(R)-DTBM-SEGPHOS	-60	DIPEA	43	>20/1	99
13	Ph	(R)-DTBM-SEGPHOS	-40	TEA	99	>20/1	98
14[e]	Ph	(R)-DTBM-SEGPHOS	-40	TEA	99	>20/1	98

[a]**3**, 0.1 mmol; **2a**, 0.15 mmol. [b]Determined by ^{1}H NMR analysis of reaction crude mixture using CH_3NO_2 as internal standard. [c]Determined by chiral-stationary-phase HPLC analysis. [d]24 h. [e]1 mol% Cu(CH$_3$CN)$_4$PF$_6$, 1 mol% TEA and 2 equiv. **2a** employed; concentration of **3b** was 0.2 M. DIPEA = diisopropyl ethyl amine. TEA = triethyl amine.
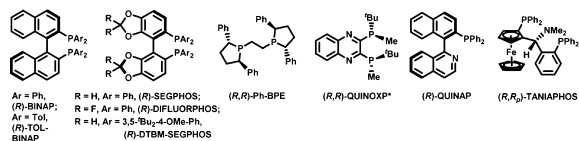
complex and 5 mol% DIPEA, the vinylogous Mannich-type reaction afforded a mixture of α-adduct and γ-adduct with a ratio of 1:0.6, favoring the α-addition as observed in literature.[7] Moreover, enantioselectivity was poor. Using (R)-TOL-BINAP instead of (R)-BINAP, the regioselectivity was slightly improved, as well as enantioselectivity. (R)-SEGPHOS, (R)-DIFLUOR-PHOS, (R,R)-QUINOXP*, (R,R)-Ph-BPE and (R)-QUINAP were not suitable ligands for this reaction, as no notably superior results were observed. Ferrocene-embedded (R,R_p)-TANIA-PHOS was beneficial to give 89% yield and 10/1 regioselectivity, favoring the γ-addition. However, the enantioselectivity was still

poor. Finally, as we envisioned, the bulky (R)-DTBM-SEGPHOS was identified as the best ligand in terms of regioselectivity and enantioselectivity. The vinylogous product was obtained in 88% yield and 86% ee, with the regioselectivity up to >20/1. Increasing the steric hindrance of the acylpyrazole (using **3b** instead of **3a**) further increased the yield and enantioselectivity with maintained high regioselectivity. Lowering the temperature from rt to −40 °C led to 98% ee. Further lowering the temperature gave extenuated reactivity. Et$_3$N was determined to be the choice due to its cheaper price.

With the optimized reaction conditions, the substrate scope was studied (Table 2). In regard to aromatic imines, both

Table 2. Substrate Scope of the Direct Catalytic Asymmetric Vinylogous Mannich-Type Reaction of 3b and N-Boc Imines 2[a]
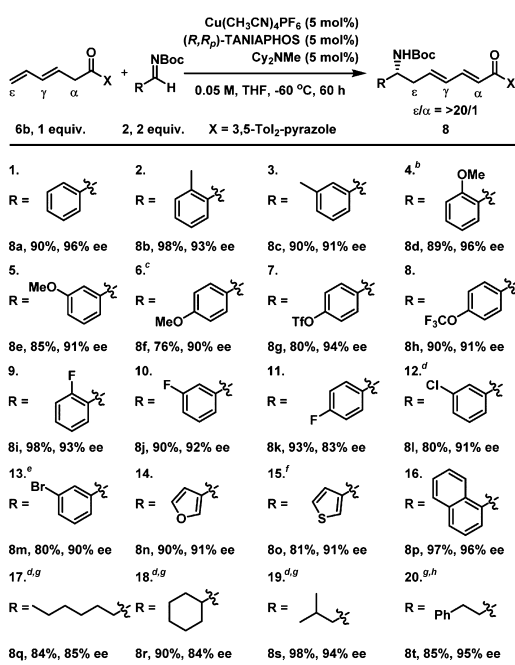

[a]**3b**, 0.2 mmol; **2**, 0.4 mmol. Isolated yield reported. Regioselectivity determined by ^{1}H NMR analysis of reaction crude mixture. Enantioselectivity determined by chiral-stationary-phase HPLC analysis. [b]1.01 g **2a** used. [c]−60 °C, 24 h. [d]0 °C. [e]4 equiv. N-Boc imine employed.

electron-donating and withdrawing substituents were well tolerated (entry 1−11). This reaction was not sensitive to the position of a substituent on the phenyl ring of the aromatic imine. However, sterically congested *ortho*-substituted aromatic imine required lower temperature and longer reaction time to obtain the good yield and enantioselectivity. The reaction conditions were also applicable to heteroaromatic imines, giving the products (**5l**, **5m** and **5n**) in excellent yield, regioselectivity and enantioselectivity. Moreover, 2-naphthyl imine and 1-naphthyl imine reacted with **3b** to afford the products (**5o** and **5p**) in excellent yield, regioselectivity and enantioselectivity. Remarkably, aliphatic imines containing acidic α-protons and thus sensitive to basic conditions were also competent substrates in this reaction (entry 17−20). Several vinylogous products (**5c**, **5d**, **5f**, **5g** and **5p**) were obtained in >99% ee, which significantly facilitate its application in organic synthesis without enantiomeric enrichment in the subsequent transformation. A gram scale reaction of **3b** and

2a in the presence of 1 mol% copper(I) catalyst and 1 mol% Et₃N afforded the constant results (entry 1), which highlights the robustness of this methodology. The absolute configuration of **5a** was determined to be *S* by transformation of **5a** to a known compound in several steps (see SI). The configurations of other vinylogous products were assigned by analogy.

In the following bisvinylogous reaction, (*R*,*R*ₚ)-TANIAPHOS performed as the best ligand in terms of yield, regioselectivity and enantioselectivity (see Table S1, SI). Further optimization of reaction conditions identified Cy₂NMe as the choice base, −60 °C as the choice reaction temperature and **6b** as the choice substrate. The bisvinylogous reaction was more challenging as 5 mol% copper(I) complex and Cy₂NMe were required for the study of substrate scope (Table 3). Aromatic imines with both

Table 3. Substrate Scope of the Direct Catalytic Asymmetric Bisvinylogous Mannich-Type Reaction of 6b and N-Boc Imines 2[a]


[a] **6b**, 0.2 mmol; **2**, 0.4 mmol. Isolated yield reported. Regioselectivity determined by ¹H NMR analysis of reaction crude mixture. Enantioselectivity determined by chiral-stationary-phase HPLC analysis. *[b]* 72 h. *[c]* ε/α = 9/1. *[d]* −70 °C, 100 h. *[e]* ε/α = 12/1 *[f]* ε/α = 18/1. *[g]* 4 equiv. *N*-Boc imine employed. *[h]* 100 h.

electron-donating and electron-withdrawing substituents were suitable substrates (entry 1−13). However, in the cases of entry 6 and entry 13, the bisvinylogous Mannich-type reactions proceeded with decreased regioselectivity (ε/α = 9/1 and ε/α = 12/1), which led to the lower yield of ε-adduct. Furthermore, the enantioselectivity of bisvinylogous product **8k** was eroded slightly by introducing a *para*-F substituent on the phenyl ring. The heteroaromatic imines, as well as 1-naphthyl imine, served also as appropriate substrates. The labile aliphatic imines were well tolerated under the current basic system without significantly eroded yield, but lower temperature and longer reaction time were necessary for high enantioselectivity and high yield. The bisvinylogous products **8q**, **8r**, **8s** and **8t** were isolated in good to excellent yield and enantioselectivity, together with excellent regioselectivity. The absolute configuration of **8a** was determined to be *R* through transformation of **8a** to a reported compound in

several steps (see SI). The configurations of other bisvinylogous products were assigned tentatively.

The vinylogous reaction conditions were successfully extended to the substituted *β*,*γ*-unsaturated *N*-acylpyrazoles (Scheme 2).

Scheme 2. Direct Catalytic Asymmetric Vinylogous Mannich-Type Reactions with Substituted *β*,*γ*-Unsaturated *N*-Acylpyrazoles
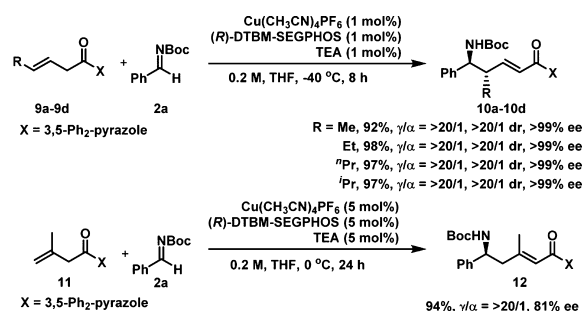
An array of aliphatic substituents, including methyl, ethyl, propyl and isopropyl, was well tolerated at the *γ*-position. It is noteworthy that products **10a−10d** were isolated in >99% ee. As for the *β*-methyl substrate **11**, higher reaction temperature, more catalyst loading and longer reaction time were required to compensate for its lower reactivity. The product **12** was obtained in excellent yield and regioselectivity, but the enantioselectivity was moderate.

The *α*,*β*-unsaturated *N*-acylpyrazole in vinylogous Mannich-type product was a versatile functional group.[17] *N*-Acylpyrazole served as a useful ester equivalent (Scheme 3).[13] For example,

Scheme 3. Transformation of Vinylogous Mannich-Type Product 5a
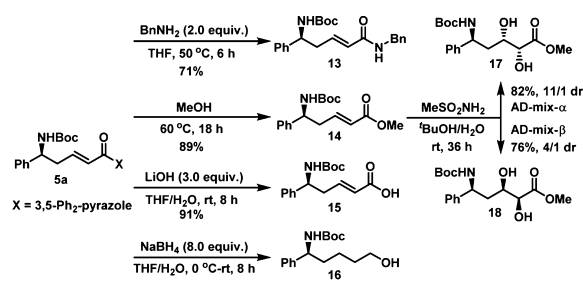
typical aminolysis proceeded to afford amide **13** in 71% yield. The alcoholysis occurred to generate the ester **14** in 89% yield. The hydrolysis of **5a** gave the free *α*,*β*-unsaturated acid **15** in 91% yield. An exhaustive reduction of **5a** gave the 1,5-amino-alcohol **16** in 81% yield. Moreover, the *α*,*β*-unsaturated double bond was a transformative functional group, which was converted to vicinal diol **17** and **18** in good yield and acceptable diastereoselectivity under the conditions of Sharpless asymmetric dihydroxylation.[18]

In summary, a highly stereo- and regioselective catalytic asymmetric vinylogous Mannich-type reaction was developed. The methodology has a broad substrate scope, mild reaction conditions, low catalyst loading and leads to products that are readily transformed. The key to control the regioselectivity was the combination of a bulky pyrazole and a bulky phosphine ligand. Moreover, by switching the chiral phosphine ligand, the vinylogous catalytic system was extended to the bisvinylogous Mannich-type reaction with excellent yield, regio- and

enantioselectivity. The expansion of the catalytic system to other vinylogous reactions and application to natural product synthesis are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b13042.

> Experimental procedures procedures, characterizations and analytic data of products, and spectra of NMR and HPLC (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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