

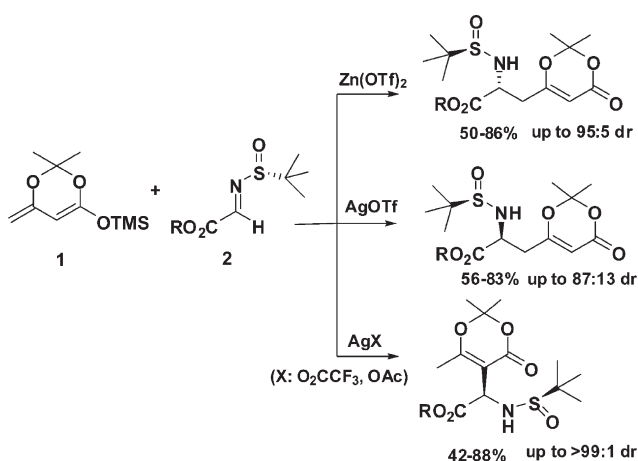
Tunable and Highly Regio- and Diastereoselective
Vinyllogous Mannich-Type Reaction of
Dioxinone-Derived Silyl Dienolate

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A tunable and highly regio- and diastereoselective vinyllogous Mannich-type reaction of dioxinone-derived silyl dienolate (**1**) with chiral *N*-*tert*-butanesulfinyl imino ester (**2**) was developed. By appropriate choice of Lewis acid catalyst, two diastereomers of the γ -product were obtained, respectively, with dr up to 95:5. The procedure for the Ag(I)-catalyzed vinyllogous Mannich-type reaction also provided facile access to the α -regioisomer with excellent diastereoselectivities (up to >99:1 dr) by changing the counterion of the Ag(I) salt.

Due to the high value of optically active α -amino acids in pharmaceutical technology, great efforts have been devoted

to the synthesis of chiral α -amino acids. Among the efficient synthetic methods,¹ the addition of nucleophiles to α -imino esters has emerged as one of the most promising and intensely investigated methods. Moreover, several investigations on the asymmetric additions of different enolate equivalents to α -imino esters (Mannich-type reactions) have also been reported.² Brassard diene and its dioxinone-derived equivalent, which were widely used in the vinyllogous aldol reactions,³ have participated in vinyllogous Mannich-type reaction to afford multisubstituted amino acid esters.⁴ The vinyllogous Mannich reaction of acetoacetate-derived dienolates could take place potentially at two different positions to give γ - and α -regioisomers (Scheme 1). Previously, exclusive γ -selectivity has always been observed in the Lewis acid-catalyzed reactions of dioxinone-derived silyl dienolate and Brassard diene.^{2b,4} However, it has been shown that both the γ -products of vinyllogous Mannich reaction, δ -amino- β -keto esters,⁵ and α -product, bearing the structural unit of β' -keto- β -amino acid, were important intermediates to the compounds possessing potential pharmaceutical and agrochemical activities.⁶ To our knowledge, there has been no reported example of α -selective Lewis acid-catalyzed vinyllogous Mannich-type reaction. Consequently, α -adducts of vinyllogous Mannich-type reaction could be achieved only by the corresponding coupling reaction of Grignard reagent.⁷ Furthermore, to achieve asymmetric α -selective Mannich-type reaction of dioxinone-derived dienolate is still a challenge. Herein, we wish to disclose the first examples of Lewis acid-catalyzed highly α -regio- and diastereoselective Mannich reactions of *N*-*tert*-butanesulfinyl imino esters with dioxinone-derived silyl dienolate and relative γ -regioselective reactions.

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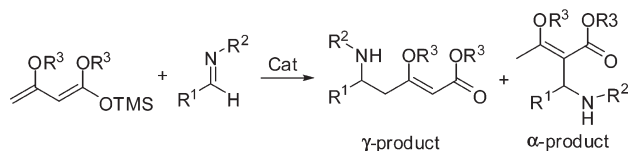
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SCHEME 1. Vinylogous Mannich-Type Reaction of Acetoacetate-Derived Dienolates


The chiral sulfinyl group was widely used as an efficient and powerful auxiliary group for asymmetric induction.⁸ Initially, the reaction of chiral (*S_R*)-*N*-*tert*-butanesulfinylimino acetate (*S_R*)-**2a** with dioxinone-derived silyl dienolate **1** (Scheme 2) was carried out in the presence of AgOTf catalyst (10 mol %) to give the product γ -**3a** (γ -**3aa** + γ -**3ab**) in 83% yield. The ¹H NMR of the product mixture showed that the reaction had both high regioselectivity (γ -**3a**/ α -**4a** = 30:1) and good diastereoselectivity [dr (**3aa**/**3ab**) = 85:15] (Table 1, entry 1).

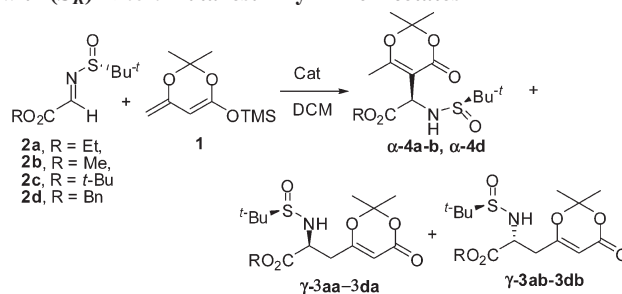
By using AgClO₄ as a catalyst, good γ -regio- and diastereoselectivity of γ -**3a** were also obtained (entry 2). With Cu(OTf)₂, CuOTf, and Zn(OTf)₂ as catalyst, the reactions of **2a** with **1** in DCM at -78 °C also provided excellent γ -regioselectivities (γ -**3a**/ α -**4a** up to > 50:1) and high diastereoselectivities (dr up to 8:92) (entries 3–5). However, it was noteworthy that the main product was γ -**3ab**. Although the absolute values were similar, the observed diastereomeric ratio was opposite to the cases of AgOTf and AgClO₄, which was confirmed by ¹H NMR and HPLC analyses of the crude products.

Interestingly, it was found that the counterion of Ag(I) salt influenced the regioselectivity of the reaction strongly. If the counterions of the catalyst were changed from ⁻OTf to ⁻OAc, the reaction of **2a** with **1** in DCM at -78 °C afforded high α -selectivity (α -**4a**/ γ -**3a** = 48:1) in high yield of α -**4a** with an excellent diastereoselectivity (96:4 dr) (entry 6). Under the same conditions, AgNO₃ and AgOCOCF₃ also provided excellent α -selectivity (α / γ up to > 50:1) in good yield of α -**4a** and excellent diastereoselectivities (up to 98:2 dr) (entries 7 and 8).

To further demonstrate that the regio- and diastereoselectivity of the vinylogous Mannich-type reactions can be regulated by Lewis acid catalysts, several chiral imino esters (**2a–d**) were tested (Scheme 2). The results were summarized in Table 2. For Zn(OTf)₂-catalyzed reactions of **1** with **2**, excellent γ -selectivity was achieved (α / γ < 1:50) and γ -**3ab–3db** were obtained in moderate to good yields, but the diastereoselectivities increased slightly with bulky group of the imino ester (**2c**, R = *tert*-butyl) (entries 4–7). On the other hand, despite the slight decrease of both the reactivities and regioselectivities, AgOTf-catalyzed reactions maintained the γ -selectivity and provided a reversal of the stereoselectivity and high diastereoselectivities (entries 1–3). For less reactive imines such as *N*-*tert*-butanesulfinylbenzaldimine (**2e**), the reaction of **2e** with **1** could not proceed at -78 °C.

The AgOCOCF₃- or AgOAc-catalyzed reactions selectively occurred at the α -position (Table 2, entries 8–12).

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SCHEME 2. Vinylogous Mannich-Type Reaction of Dienolate 1 with (*S_R*)-*N*-*tert*-Butanesulfinylimino Acetates 2

TABLE 1. The Vinylogous Mannich Reaction of 2a with 1^a

entry	catalyst	time (h)	yield (%)	α - 4a / γ - 3a ^b	Dr of γ - 3a ^b	dr of 4a (%) ^c
1	AgOTf	48	83	1:30	85:15	
2	AgClO ₄	24	61 ^d	1:10	83:17	
3	CuOTf	12	85	1:34	21:79	
4	Cu(OTf) ₂	24	73	< 1:50	24:74	
5	Zn(OTf) ₂	48	86	1:54	8:92	
6	AgOAc	24	83	48:1		98:2
7	AgNO ₃	24	84	49:1		94:6
8	AgOCOCF ₃	24	87	> 50:1		98:2

^aCatalyst loading 10 mol %, reaction temperature -78 °C in DCM.

^bDetermined by ¹H NMR of the product mixture (dr = *S_R*:*C_S*:*S_R*:*C_R*).

^cDetermined by chiral HPLC analysis. ^d¹H NMR yield.

Both the reactivity and diastereoselectivity of the α -regioselective reactions were much higher (dr up to > 99:1) than that of the triflates-catalyzed γ -selective reactions. In the case of **2d**, the reaction took a relatively longer time to complete, with a low yield and regioselectivity (entry 11). Interestingly, when methanol (2 equiv) was added into the AgOTf-catalyzed reaction system, the γ -selectivity switched to α -selectivity with a high diastereoselectivity (97:3 dr) (entry 13).⁹ However, the reaction of **1** with **2c** catalyzed by AgOAc was sluggish to give a complicated mixture. When (*S_S*)-**2a** was employed in the reaction with **1** in the presence of AgOCOCF₃, α -**4a** was obtained as the main product (α / γ = 20:1) with high diastereoselectivity (97:3 dr) (entry 9); however, the configuration of the newly formed chiral carbon center was opposite to that obtained from the reaction of (*S_R*)-**2a** (entry 8) based on the analysis of HPLC.

The vinylogous Mannich product could be transformed into piperidinediones. According to the reference procedure,¹⁰ γ -**3db** (R = Bn), which was produced from the Zn(OTf)₂-catalyzed reaction of **1** with **2d**, was converted into optically active (-)-**6d** through the removal of chiral sulfinyl group (**5db**, 98% ee after crystallization) and subsequent cyclization (Scheme 3). The product (-)-**6d** was an efficient precursor of chiral natural amino acid, 4-hydroxyproline.¹¹

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TABLE 2. The (Vinylogous) Mannich Reactions of **2** with **1^a**

entry	2	catalyst	time (h)	product	yield	$\alpha : \gamma^b$ (4 : 3)	dr of 3 ^c	dr of 4 ^c	
1		AgOTf	48		γ-3aa	83	1:30	87:13	-
2		AgOTf	48		γ-3ba	56	1:25	82:18	-
3		AgOTf	60		γ-3ca	40	1:3.0	85:15	-
4	2a	Zn(OTf) ₂	48		γ-3ab	86	<1:50	8:92	-
5	2b	Zn(OTf) ₂	48		γ-3bb	57	<1:50	8:92	-
6	2c	Zn(OTf) ₂ ^f	60		γ-3cb	50	<1:50	5:95	-
7		Zn(OTf) ₂	48		γ-3db	70	<1:50	6:94	-
8	2a	AgOOCOCF ₃	24		α-4a	87	<50:1	-	98:2
9	2a^d	AgOOCOCF ₃	24		α-4a	82	15:1	-	97:3
10	2b	AgOOCOCF ₃	24		α-4b	89	30:1	-	99:1 ^e
11	2d	AgOAc	40		α-4d	42	4.6:1	-	96.5:3.5
12	2b	AgOAc	24	α-4b	56	6.4:1	-	>99:1 ^e	
13	2a	AgOTf / MeOH ^g	24	α-4a	96 ^h	7.4:1	-	97:3	

^aCatalyst loading 10 mol %, reaction temperature $-78\text{ }^\circ\text{C}$. ^bDetermined by ¹HNMR of the product mixture. ^cDetermined by HPLC analysis of the crude products (**3**: dr=*S_R*,*C_S*:*S_R*,*C_R*). ^d(*S_S*)-**2a** was used. ^eDetermined by HPLC analysis of its derivative **8b**. ^f20% Zn(OTf)₂ was used. ^g2 equiv of MeOH was added. ^h¹HNMR yield.

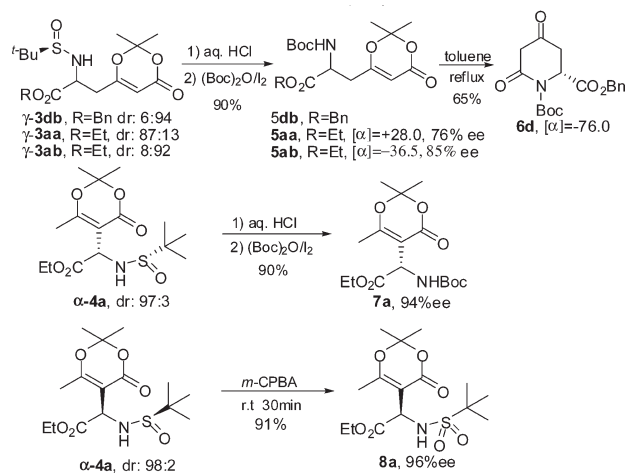
By comparing the optical rotation of **6d** ($[\alpha]_{\text{D}}^{20} -76.0$) with the literature value of the (*S*)-isomer¹² ($[\alpha]_{\text{D}}^{20} +76.1$), the configuration of **6d** was deduced as (*R*), which meant the configuration of the newly formed chiral center of the γ -product was (*R*). Meanwhile, γ -**3aa** (R = Et, dr = 87:13) and γ -**3ab** (R = Et, dr = 8:92) were employed in the reactions

for removal of the chiral sulfinyl group under the same conditions to give optically active **5aa** and **5ab**, respectively. In terms of the signs of optical rotation, the chiral center of (+)-**5aa** ($[\alpha] +28$) and (–)-**5ab** ($[\alpha] -36.5$) should have opposite configurations.

On the basis of the above results, the configuration of γ -**3aa** from the AgOTf-catalyzed reaction can be deduced to be (*S_R*,*C_S*), while the configuration of γ -**3ab** from the Zn(OTf)₂-catalyzed ones should be (*S_R*,*C_R*).

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SCHEME 3. Derivation of the Vinylogous Mannich Products



The product α -**4a** was readily converted into **7a** under the same conditions and to **8a** through the *m*-CPBA oxidation in excellent yields without the racemization (Scheme 3). The absolute configuration of the chiral carbon center in **8a** was deduced as (*R*) according to X-ray structural analysis of a single crystal (see the Supporting Information). Consequently, the absolute configuration of α -**4a** was determined as (*S_R*, *C_R*).

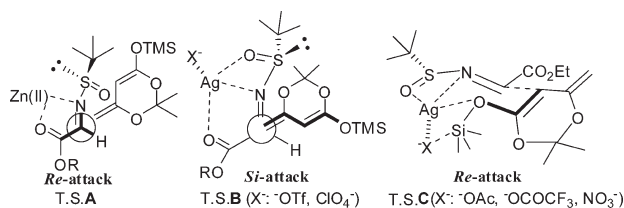


FIGURE 1. Proposed transition states for the vinylogous Mannich-type reaction of silyl dienolate **1** with imino ester **2**.

In terms of the triflate salt-catalyzed reaction, the γ -selectivity is a rational outcome through the normal pathway of chiral sulfinylimines catalyzed by Lewis acid.^{4,8} For the Zn(OTf)₂-catalyzed vinylogous Mannich reaction, the transition state should adopt the T.S.A mode (Figure 1) in which Zn²⁺ could coordinate to the carbonyl oxygen and the imine nitrogen,^{8c} and *Re*-attack leads to the *R*-configuration of the newly formed chiral carbon center. In contrast, it could be proposed that Ag⁺ (AgOTf or AgClO₄) coordinates to the sulfinyl oxygen atom, the carbonyl oxygen atom, and the sulfinyl nitrogen atom (T.S.B),^{8c,8d} affording the isomer due to *Si*-attack.

In the cases of AgOAc, AgOCOCF₃, and AgNO₃, the counterion may play an important role in the α -regioselectivity by interacting with the TMS to enhance the coordination between Ag⁺ and the oxygen of silyl dienolate (Figure 1, T.S.C),^{4d} which leads to *Re*-attack to give α -product with (*S_R*, *C_R*)-configurations. However, under the catalysis of AgOTf or AgClO₄, the larger anions, OTf⁻ and ClO₄⁻,

inhibited the approach of OTMS to Ag⁺ and resulted in the γ -selectivity (Figure 1, T.S.B. vs. T.S.C).¹³ When Zn(OAc)₂ and Cu(OAc)₂ were used in the reaction of **2a** with **1**, no product was detected during the reaction. It could be suggested that a proper Ag(I) salt catalyst¹⁴ plays an essential role for the α -selective Mannich-type reaction of **1** and **2**.

In conclusion, a highly α -regio- and diastereoselective vinylogous Mannich-type reaction of dioxinone-derived silyl dienolate catalyzed by Ag(I) salts was developed. Ag⁺ and its counterions played a crucial role in controlling the α - and γ -selectivities, and achieving high diastereoselectivities. The regioselectivity could be tuned by the appropriate choice of Lewis acid catalysts used in the reaction. The method also provided a feasible route to synthesize multisubstituted chiral amino acids.

Experimental Section

General Procedure for the Regio- and Diastereoselective Vinylogous Mannich Reaction of Silyl Dienolate **1 and α -Imino Ester **2**.** Lewis acid (0.02 mmol) and α -imino ester **2a–d** (0.2 mmol) were charged in a dried 5 mL flask under argon, followed by addition of CH₂Cl₂ (0.9 mL). The solution was cooled to -78 °C, then after 30 min silyl dienolate **1** (0.3 mmol) was added. After stirring for the indicated time, brine (10 mL) was added, followed by extraction with CH₂Cl₂. The combined organic phases were dried with Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1/1 to 1/2) to afford product **3a–d** and **4a,b,d**.

Ethyl 2-(tert-butoxycarbonylamino)-3-(2,2-dimethyl-4-oxo-4H-1,3-dioxin-6-yl)propanoate (3a): colorless oil, 86% yield; ¹H NMR (300 MHz, CDCl₃) δ 5.20 (s, 1H), 5.13–5.10 (m, 1H), 4.27–3.88 (m, 3H), 2.84 (m, 2H), 2.72 (d, *J* = 5.6 Hz, 2H), 1.66 (s, 6H), 1.32–1.18 (m, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 199.9, 167.0, 165.1, 151.3, 84.8, 62.6, 53.9, 50.5, 40.6, 27.9, 14.0; IR (film) ν_{max} 3278, 1732, 1639 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₅H₂₆N₁O₆S₁ [M]⁺ 348.1475, found 348.1485.

Ethyl 2-((*R*)-1,1-dimethylethylsulfonamido)-2-(2,2,6-trimethyl-4-oxo-4H-1,3-dioxin-5-yl)acetate (4a): white solid, 87% yield; ¹H NMR (300 MHz, CDCl₃) δ 4.78 (d, *J* = 3.1 Hz, 1H), 4.71 (br, 1H), 4.30–4.16 (m, 2H), 2.18 (s, 3H), 1.70 (s, 3H), 1.68 (s, 3H), 1.23 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 170.1, 167.3, 160.0, 105.8, 104.3, 62.4, 56.0, 52.6, 25.1, 25.0, 22.5, 17.6, 14.0; IR (film) ν 2249, 1743, 1684, 1597, 1580, 1515, 1448, 1252, 1209 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₅H₂₅N₁O₆S₁ [M]⁺ 347.1403, found 347.1400.

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Supporting Information Available: Experimental procedure characterization data of the products, chiral HPLC separations for ee determination, and X-ray structural data of **8a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(13) Ion radius: CH₃COO⁻ < CF₃COO⁻ (0.156 nm) < NO₃⁻ (0.189 nm) < ClO₄⁻ (0.240 nm) < CF₃SO₃⁻ (0.256 nm); Sunderrajan, S.; Freeman, B. D.; Hall, C. K. *Ind. Eng. Chem. Res.* **1999**, *38*, 4051–4059.

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