Regio- and Diastereoselective Vinylogous Mannich Addition of 3-Alkenyl-2-oxindoles to α -Fluoroalkyl Aldimines

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Abstract An efficient asymmetric vinylogous Mannich (AVM) addition reaction of 3-alkenyl-2-oxindoles to α -fluoroalkyl aldimines has been developed. This reaction provided various optical active α -alkylidene- δ -amino- δ -fluoroalkyl oxindoles in excellent yields, complete γ -site regioselectivity, and excellent diastereoselectivities.

Key words fluoroalkylated compounds, oxindole, asymmetric, Mannich addition

The δ -amino- α,β -unsaturated carbonyl compounds represent an important class of units in modern organic and medicinal chemistry.¹ They are useful building blocks for the synthesis of various pharmaceuticals and biologically active natural products.² It is well known that fluorine-containing compounds are considered as the extraordinarily promising drug candidates because the introduction of fluorine atom or fluorine-containing groups into organic compounds often significantly improves the chemical, physical, and biological properties of the parent compound.^{3,4} Especially, the fluoroalkyl-substituted molecules, such as trifluoromethylated and difluoromethylated compounds, have attracted increasing attention.⁵ Thus, the incorporation of fluoroalkyl into δ -amino- α,β -unsaturated carbonyl compounds will provide novel fluorinated moieties, which might be applied in various research fields. Among them, δ -amino- δ -fluoroalkyl- α,β -unsaturated carbonyl compounds are particularly interesting, because the neighboring electron-withdrawing fluoroalkyl groups would change the basicity of imine groups, thus affecting their bioactivities. Normally, these compounds were prepared by vinylogous Mannich reactions.⁶ In 1992, Tsukamoto and Kitazume reported the Lewis acid promoted reaction of fluorinated *N,O*-acetal with trimethylsilyloxyfuran

(Scheme 1, a).⁷ The Lewis acid catalyzed vinylogous Mannich addition of trimethylsilyloxyfuran to fluorinated aldimines was disclosed by Crousse and co-workers in 2004 (Scheme 1, a).⁸ Shi's group realized the first enantioselective vinylogous Mannich reaction of fluorinated aldimines bearing a chiral auxiliary [(*S*)-1-phenylethyl group] and siloxyfurans under the catalytic environment of silver acetate and axially chiral phosphine-oxazoline ligand (Scheme 1, b).⁹ Very recently, we developed a tunable and highly regio- and diastereoselective addition reaction of acyclic silyl dienolates to α -fluoroalkyl sulfinylimines, in which the Lewis acid TMSOTf was a critical parameter in the control of γ -site regioselectivity (Scheme 1, c).¹⁰ All the previous works need silylated substrates as the nucleophiles. From the point of atom and step economy, it is worthy to investigate the addition reactions directly using α,β -unsaturated carbonyl compounds as the nucleophiles. In light of the important pharmaceutical implications of the privileged structural motif oxindole,¹¹ herein we report a regio- and diastereoselective vinylogous Mannich addition of 3-alkenyl-2-oxindoles to α -fluoroalkyl aldimines to afford various chiral α -alkylidene- δ -amino- δ -fluoroalkyl oxindoles (Scheme 1, d).

Initially, the reaction conditions were optimized using (*S*₅)-*N*-*tert*-butanesulfinyl-3,3,3-trifluoroacetaldimine (**1a**)¹² and *N*-Boc-protected 3-alkylidene-2-oxindole **2a**¹³ as the model substrates (Table 1). Treatment of the substrates with TMSOTf and Et₃N gave only a silylated intermediate of **2a**.^{13d} The desired product **3a** was not obtained (Table 1, entry 1). In view of the better nucleophilic properties of the metallic enolate intermediate in comparison to silyl enolate, LDA was chosen as the base. To our delight, the addition reaction happened in the presence of LDA, and **3a** was obtained in moderate yield, with virtually complete γ -site selectivity (>99:1 γ/α) and good diastereoselectivity (94:6 dr, Z/E = 8:1; Table 1, entry 2). Considering the fact that the addition of Lewis acid might improve the yield and diastereoselec-

Scheme 1 Synthesis of δ -amino- α,β -unsaturated carbonyl compounds by vinylogous Mannich reactions

tivity because of its coordination with sulfinylimine substrate,¹⁴ different Lewis acids were then investigated. Among the three typical Lewis acids, $\text{Ti}(\text{O}i\text{-Pr})_4$, AlMe_3 , and $\text{BF}_3 \cdot \text{OEt}_2$, $\text{Ti}(\text{O}i\text{-Pr})_4$ showed the highest efficiency and sharply increased the yield of **3a** from 60% to 98% (Table 1, entries 3–5). When the base was changed from LDA to KHMDS, **3a** was obtained in similar yield with much higher *Z/E* ratio (Table 1, entry 6). Finally, different solvents including toluene, Et_2O , and hexane were screened (Table 1, entries 7–9). However, no better result was obtained.

With the optimized conditions in hand, the substrate scope of direct asymmetric vinylogous Mannich (AVM) reaction was surveyed.^{15,16} The results are summarized in Scheme 2. Firstly, 3-alkylidene-2-oxindoles **2a–d** bearing diverse nitrogen protecting groups, Boc, Moc, Bn, and Me, reacted smoothly with **1a** under identical conditions, affording the corresponding products **3a–d** in moderate to good yields and excellent stereoselectivities. Additionally, the reaction conditions displayed good compatibility with the substituent pattern on the phenyl ring of the 2-oxindole. The substrates **2e–g**, bearing electron-donating and electron-withdrawing groups, can be efficiently transformed to the corresponding products in excellent yields and stereoselectivities. Subsequently, the patterns of R³ in 3-alkylidene-2-oxindole **2h–j** having aromatic groups were

tested as the substrates. The reactions proceeded well affording products **3h–j** in good yields and diastereoselectivities, although the *Z/E* ratios were comparably low. It was noteworthy that this protocol could be applied to difluoromethylated sulfinylimine **1b**. The corresponding difluoromethylated products **3k–n** were conveniently obtained under the optimal reaction conditions. The 3-(propan-2-ylidene)benzofuran-2(3*H*)-one **2o**¹⁷ was also a suitable substrate for this reaction to furnish the product **3o** in modest yield and good stereoselectivity.

The absolute configuration of these α -alkylidene- δ -amino- δ -fluoroalkyl oxindoles **3** was confirmed by X-ray crystallographic analysis of compounds **3d** (Figure 1).¹⁸ Normally, a nonchelated transition-state model was involved in the addition reaction of nucleophiles to fluorinated sulfinylimines.¹² The stereochemical outcome observed in the present study could also be explained by the nonchelated transition-state model, in which the sulfinyl oxygen coordinates to Ti(Oi-Pr)₄ and sterically shields the *Re* face of the imine. Thus, the *Si* attack from metallic enolate intermediates would produce adducts **3** with (C₅,S₅)-configurations. The high *Z/E* ratios in compound **3** might be caused by the cyclic structure of nucleophilic enolate intermediates.¹⁹ The accurate reaction mechanism still needs further investigation.

Scheme 2 Vinylogous Mannich addition of 3-alkenyl-2-oxindoles to α -fluoroalkyl aldimines

Table 1 Optimization of Reaction Conditions^a

Entry	Base	Lewis acid	Solvent	Temp (°C)	Yield (%) ^b	Z/E ^b	dr ^b
1 ^c	Et ₃ N	TMSOTf	CH ₂ Cl ₂	0 to r.t.	0	–	–
2	LDA	–	THF	–78	60	8:1	94:6
3	LDA	Ti(O <i>i</i> -Pr) ₄	THF	–78	98	6:1	94:6
4	LDA	AlMe ₃	THF	–78	58	12:1	92:8
5	LDA	BF ₃ ·OEt ₂	THF	–78	70	7:1	95:5
6	KHMDS	Ti(O <i>i</i> -Pr) ₄	THF	–78	97	16:1	93:7
7	KHMDS	Ti(O <i>i</i> -Pr) ₄	toluene	–78	87	12:1	93:7
8	KHMDS	Ti(O <i>i</i> -Pr) ₄	Et ₂ O	–78	41	2:1	94:6
9	KHMDS	Ti(O <i>i</i> -Pr) ₄	hexane	–78	18	–	–

^a Reactions were carried out using **1a** (0.33 mmol), **2a** (0.36 mmol, 1.2 equiv), base (0.36 mmol, 1.2 equiv), and Lewis acid (0.33 mmol, 1.1 equiv) in dry solvent (2.5 mL) for 12 h.

^b Ratios and yields were determined by ¹⁹F NMR spectroscopy of the crude reaction mixture using benzotrifluoride as an internal standard.

^c Base (0.33 mmol, 1.1 equiv) and Lewis acid (0.36 mmol, 1.2 equiv).

Figure 1 X-ray crystal structure of **3d** and proposed transition-state model

It should be mentioned that the *N*-*tert*-butylsulfinyl group can serve not only as an efficient chiral auxiliary, but also as an amine protecting group.²⁰ It could be readily

cleaved under mild acidic conditions. After deprotection, the trifluoromethylated free amines **4** can be easily obtained in high yield (Scheme 3).

Scheme 3 Conversion of **3d** into the free primary amine **4**

In summary, we have demonstrated a practical and efficient approach to synthesize α -alkylidene- δ -amino- δ -fluoroalkyl oxindoles via a regio- and stereoselective vinylogous Mannich-type reaction of fluorinated *N*-*tert*-butanesulfinyl aldimines with 3-alkenyl-2-oxindoles. This protocol displayed broad substrate scope, good functional-group compatibility, and satisfactory stereocontrol. Further applications of this method for the preparation of new fluorinated bioactive molecules are in progress.

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Supporting Information

Supporting information for this article is available online at <http://dx.doi.org/10.1055/s-0034-1379600>.

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- (15) **General Procedure for the Synthesis of α -Alkylidene- δ -amino- δ -fluoroalkyl Oxindoles**
A solution of KHMDS (0.36 mL, 1 M solution in THF) was slowly added to a dried Schlenk flask containing 3-alkenyl-2-oxindoles **2** (0.36 mmol) in THF (2.0 mL) at -78°C under N_2 atmosphere. After stirring at -78°C for 1 h, the mixture of **1** (0.3 mmol) and $\text{Ti}(\text{O}i\text{-Pr})_4$ (0.33 mmol) in THF (1.0 mL) was added dropwise, and the mixture was stirred for 12 h at -78°C . Then sat. aq. NH_4Cl solution and H_2O was added at -78°C . The mixture was brought to r.t. After 5 min, the mixture was filtered through Celite, and the filtrate was extracted with EtOAc. The combined organic solution was dried over MgSO_4 . After the removal of volatile solvents under vacuum, the crude product was purified by silica gel column chromatography to give the required product.
- (16) **Analytical Data for Compound 3a**
Mp $60\text{--}61^\circ\text{C}$. $[\alpha]_{\text{D}}^{17.0} +187.7$ (c 0.41, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ = 7.88 (d, J = 8.2 Hz, 1 H), 7.60 (d, J = 7.8 Hz, 1 H), 7.35 (t, J = 7.9 Hz, 1 H), 7.20 (t, J = 7.7 Hz, 1 H), 4.35 (dd, J = 24.4, 11.2 Hz, 2 H), 4.19–3.96 (m, 1 H), 2.62 (dd, J = 12.7, 3.8 Hz, 1 H), 2.43 (s, 3 H), 1.67 (s, 9 H), 1.06 (s, 9 H). ^{19}F NMR (377 MHz, CDCl_3): δ = -74.87 (d, J = 6.5 Hz, 3 F). ^{13}C NMR (101 MHz, CDCl_3): δ = 166.5, 152.0, 149.1, 138.3, 128.9, 125.6, 125.2 (q, J = 284.8 Hz), 124.1, 123.9, 123.2, 114.6, 84.6, 57.2, 56.4 (q, J = 30.2 Hz), 35.3, 28.1, 24.2, 22.2. IR (KBr): ν_{max} = 3261, 3060, 2975, 1731, 1613, 1462, 1535, 1300, 1258, 1157, 1090, 841, 748 cm^{-1} . MS (EI): m/z = 497.2 $[\text{M} + \text{Na}]^+$. ESI-HRMS: m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{29}\text{F}_3\text{N}_2\text{O}_4\text{SNa}$: 497.1692; found: 497.1712.
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