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Mannich Reaction

Direct Access to Chiral β-Fluoroamines with Quaternary Stereogenic Center through Cooperative Cation-Binding Catalysis

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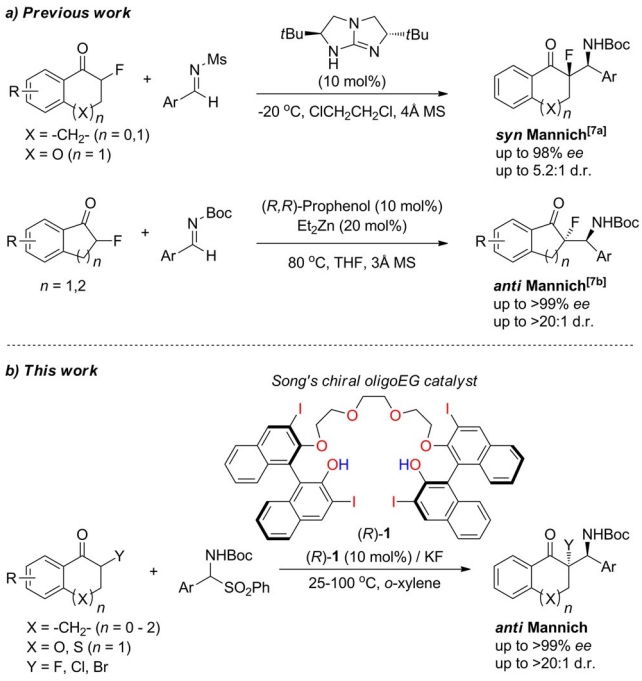
Abstract: A direct route to chiral β-fluoroamines with tetrasubstituted C–F centers through the organocatalytic Mannich reaction of α-fluoro cyclic ketones and α-amidosulfones by using a chiral oligoethylene glycol as a cation-binding catalyst and KF as a base is reported. For most substrates, nearly perfect enantioselectivities were achieved even at very high temperatures (>80 °C). The salient features of this process include a) a transition-metal-free and operationally simple procedure, b) direct use of α-amidosulfones as bench-stable precursors of sensitive imines, c) direct enolization of racemic α-fluoro cyclic ketones, and d) excellent stereoselectivity up to 99% enantiomeric excess and >20:1 diastereoselectivity (*anti*/*syn*). Thus, this protocol is easily scalable and provides a new approach for the synthesis of biologically relevant products with tetrasubstituted C–F centers. Furthermore, this protocol was also successfully extended to generate C–Cl and C–Br quaternary stereogenic centers.

Fluorine-incorporating molecules have received a great deal of interest in life sciences.[1] Owing to the higher electronegativity and oxidation potential of the fluorine atom, it can improve the pharmacological properties of a bioactive molecule by altering its lipophilicity, metabolic stability, and bioavailability compared to the non-fluorinated parent compound.[1] A nearly 20% increase in the number of fluorinated drugs has occurred in the market during the last decade.[2] Consequently, fluorinated analogues of bioactive molecules are now important tools in pharmaceutical research. Among them, molecules containing β-fluoroamine moieties are of great importance in medicinal chemistry owing to their privileged structural motif.[3] It is well known that the presence of fluorine at the β-position lowers the pK_a of neighboring amines, thus enhancing binding interactions and improving metabolic stability. This leads to increased penetration through the central nervous system (CNS) of a biological system.[4] As a consequence, the discovery of a new method for the synthesis of chiral β-fluoroamine derivatives is one of the rapidly growing research areas for synthetic chemists.[5] In particular, chiral β-fluoroamine compounds with quaternary stereogenic C–F centers[6] are expected to have very interesting pharmaceutical properties. In view of this challenging task, very recently, Tan,[7a] Trost,[7b] and their co-workers utilized catalytic asymmetric Mannich reactions with α-fluoro cycloketones and aromatic aldimines to construct β-fluoroamines with quaternary C–F stereocenters (Scheme 1 a).[8] Tan and co-workers successfully utilized chiral guanidine as an organocatalyst to afford chiral β-fluoroamine derivatives with the *syn* diastereomer as the major product.[7a] Complementary to this work, quite recently, Trost et al. utilized the dinuclear Zn/Prophenol catalyst for direct Mannich reaction to furnish highly enantioenriched β-fluoroamines with *anti* diastereoselectivity.[7b]

We recently developed[9] chiral oligoethylene glycol (EG) catalysts **1** as cooperative cation-binding catalysts[10] and success-



Scheme 1. Enantioselective synthesis of β-fluoroamines with a quaternary stereogenic C– center. *ee* = enantiomeric excess, d.r. = diastereomeric ratio.

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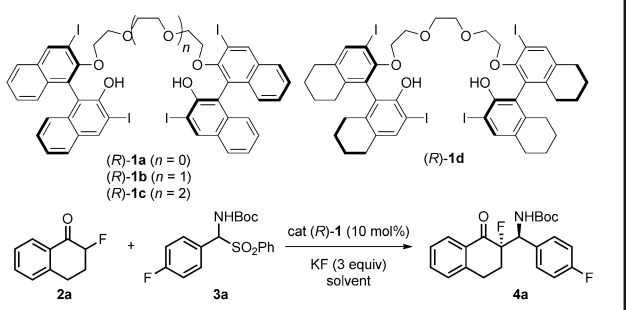
fully applied them to a desilylative kinetic resolution of silyl-protected secondary alcohols,[9e] an asymmetric Strecker synthesis of α-amino acids,[9d] and a kinetic resolution of β-sulfonyl ketones through enantioselective β-elimination.[9f] In continuation of our research on exploring other challenging catalytic asymmetric reactions using **1** (in Scheme 1b), we wished to develop direct catalytic enantioselective Mannich reactions, allowing direct use of α-fluoro cyclic ketones as donors together with α-amidosulfones[11] instead of sensitive corresponding imines, as well as directly affording β-amino α-fluoro cyclic ketones with tetrasubstituted C–F centers. We believed that our cation-binding catalyst system was ideally suited for this reaction in which potassium fluoride, upon activation by the chiral cation-binding catalyst, would enable the generation of the corresponding imine substrate in situ from α-amidosulfones as well as the enolate substrate in situ from ketones. Subsequently, the catalyst would bring both activated reaction partners together in proximity, resulting in a product with high asymmetric induction.

Here, we report a transition-metal-free straightforward route to highly enantio- and diastereoenriched β-fluoroamine derivatives with quaternary C–F centers through a direct organocatalytic Mannich reaction with α-fluoroketones and α-amidosulfones by using a cation-binding catalyst (Scheme 1b). Excellent enantio- and diastereoselectivity was obtained with a variety of fluoro cyclic ketones and α-amidosulfones even at very high temperatures (>80 °C). This protocol was also successfully extended to generate C–Cl and C–Br quaternary stereogenic centers.

Our initial investigation of the asymmetric Mannich reaction of α-amidosulfone **3a** with α-fluorotetralone **2a** as a model substrate is summarized in Table 1. The effect of the catalyst structure [(*R*)-**1a**–**d**] on the reaction outcome was first investigated with a catalyst loading of 10 mol% in toluene at room temperature. As we expected based on our knowledge of the catalytic performance of chiral oligoEGs **1a**–**1d**,[9] catalyst **1b** was found to be the best in terms of the enantioselectivity of the major diastereomer (99% *ee*, Table 1, entry 2). In further experiments, different solvents were examined (entry 2 and entries 5–8). Toluene and xylenes proved to be the optimal choice. In nonpolar solvents such as toluene and *o*-xylene, 54% of starting material **2** (Table 1, entries 2 and 8) was converted into product with 99% *ee* after 48 h, whereas in polar aprotic solvents (Table 1, entries 5–7), <30% conversion was attained even after running the reaction for more than 48 h. Although we observed the formation of the desired Mannich product with perfect enantiopurity (>99% *ee*), the reaction proceeded too slowly (Table 1, entries 2 and 8). To improve the conversion, we next attempted different conditions by changing the reaction temperature and concentration. Upon further optimization, we were pleased to observe that an increase in the reaction rate was paralleled by an increase in temperature and concentration without diminishing the enantioselectivity or the diastereoselectivity (Table 1, entries 9–11). Finally, at 80 °C and very high concentrations (1 M), the reaction proceeded with full conversion (84% isolated yield) within 24 h (entry 11), with excellent enantioselectivity (95% *ee*) and diastereoselectivity (1:7 for *anti*).[12] Further increase in the temperature to 100 °C resulted only in a concomitant decrease in enantioselectivity to 94% *ee*, indicating a relatively high stability for the transition state (entry 12).

Table 1. Optimization of reaction conditions.[a]

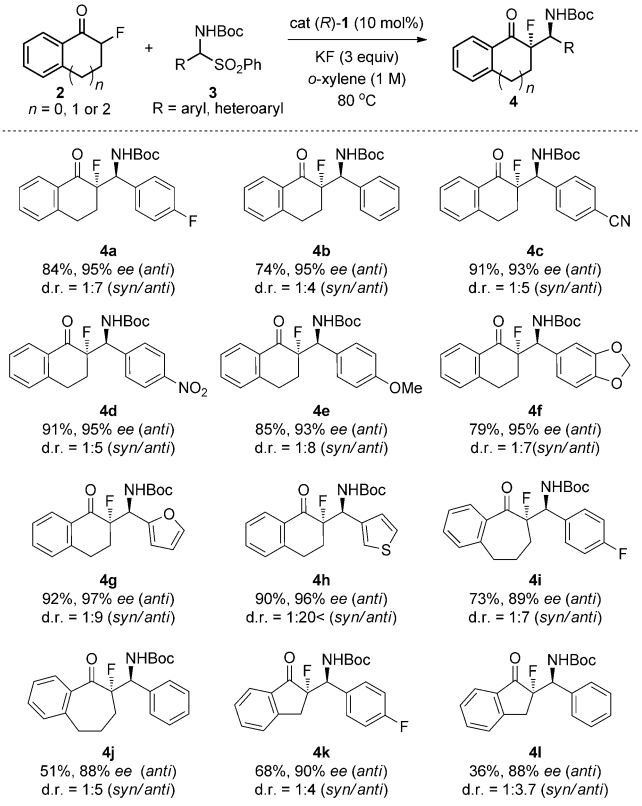


Entry	Catalyst	Solvent	**2** [M]	*t* [h]	*T* [°C]	Conv.[b] [%]	*ee*[c] [%]	d.r.[d]
1	(*R*)-**1a**	toluene	0.1	66	RT	30	85	1:7
2	(*R*)-**1b**	toluene	0.1	48	RT	21	>99	n.d.[e]
3	(*R*)-**1c**	toluene	0.1	48	RT	12	0	n.d.
4	(*R*)-**1d**	toluene	0.1	48	RT	9	96	n.d.
5	(*R*)-**1b**	THF	0.1	48	RT	10	89	n.d.
6	(*R*)-**1b**	dioxane	0.1	48	RT	14	99	n.d.
7	(*R*)-**1b**	CH_2Cl_2	0.1	48	RT	20	99	n.d.
8	(*R*)-**1b**	*o*-xylene	0.1	48	RT	54	99	n.d.
9	(*R*)-**1b**	*o*-xylene	0.1	50	70	74	99	1:5
10	(*R*)-**1b**	*o*-xylene	0.25	50	70	96	>99	1:10
11	(*R*)-**1b**	*o*-xylene	1.0	24	80	98	95	1:7
12	(*R*)-**1b**	*o*-xylene	1.0	20	100	100	94	1:5

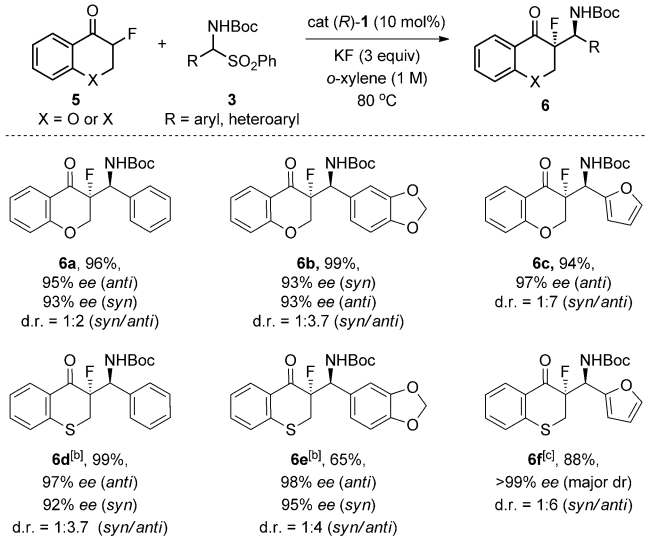
[a] Unless otherwise indicated, reactions were performed with **2a** (0.1 mmol), **3a** (0.15 mmol), KF (3 equiv), and catalyst (*R*)-**1** (10 mol%). [b] Conversion was determined by ^{1}H NMR integration. [c] The *ee* was determined by HPLC analysis using a chiral stationary phase. [d] The relative and absolute configuration of the major diasteromer was unambiguously assigned as *anti* and [$(S)_{C-F}$, $(S)_{C-NHBoc}$], respectively, by comparison of the coupling constant and the retention time of HPLC with the literature data.[7b] [e] n.d. = not determined.

With the optimal catalytic conditions in hand, we then evaluated the generality of our protocol with α-amidosulfones as the electrophilic partner. As shown in Scheme 2, a variety of aromatic and heteroaromatic Boc-α-amidosulfones (Boc = *tert*-butyloxycarbonyl) were successfully reacted with racemic α-fluoro cyclic ketones **2** in the presence of KF (3 equiv) and catalyst (*R*)-**1b** (10 mol%) in *o*-xylene (1 M). Regardless of the electronic and steric nature of the substituents on the aromatic ring, all α-amidosulfones **3** as imine precursors tested in this study were smoothly converted to the corresponding Mannich products **4a**–**4j** in excellent yields and with almost perfect *ee* values. Heteroaromatic substrates such as 3-furyl (**4g**) and 3-thienyl (**4h**) also afforded excellent yields and stereoselectivities (Scheme 2).

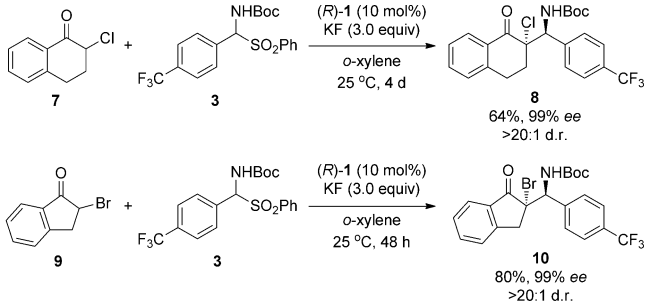
We then investigated other types of α-fluoro cyclic ketones with five- to seven-membered carbocyclic rings for this reaction. As shown in Scheme 2, fluorobenzosuberones **2** (*n* = 2) and fluoroindanones (*n* = 0) also proved to be excellent Mannich donors, furnishing the Mannich product **4i**–**4l** in high-to-excellent enantioselectivity (88–95% *ee*).[13]



Scheme 2. Substrate scope for the Mannich reaction of **2** to α-amidosulfone **3**. Reactions were performed with **2** (0.3 mmol), **3** (0.45 mmol), and (*R*)-**1 b** (10 mol%) in *o*-xylene (1 M) at 80 °C for 24 h (in the case of **4 a**–**d**) or 36 h (in the case of **4 e**). The yield was determined after chromatographic purification, and the *ee* was determined by HPLC analysis using a chiral stationary phase. The d.r. was determined by ^{1}H NMR spectroscopy.



Scheme 3. Substrate scope for the Mannich reaction of **5** to α-amidosulfone **3**. [a] Reactions were performed with **5** (0.3 mmol), **3** (0.45 mmol), and (*R*)-**1 b** (10 mol%) in *o*-xylene (1 M) at 80 °C for 28 h; [b] reactions were performed with **5** (0.2 mmol), **3** (0.3 mmol), and (*R*)-**1 b** (10 mol%) in *o*-xylene (1 M) at 70 °C for 36 h; [c] reactions were performed with **5** (0.3 mmol), **3** (0.45 mmol), and (*R*)-**1 b** (10 mol%) in *o*-xylene (1 M) at 70 °C for 28 h.



Scheme 4. Mannich reaction of **7** or **8** to α-amidosulfone **3**. Reactions were performed with **7** or **8** (0.5 mmol), **3** (1.5 equiv), and (*R*)-**1** (10 mol%) in *o*-xylene (5.0 mL) at 25 °C.

The substrate scope was also successfully extended to chromanones and thiochromanones, which are present in many biologically active natural compounds.[14] α-Fluorochromanones and α-fluorothiochromanones were smoothly converted to the corresponding Mannich products **6 a**–**6 f** with excellent enantioselectivity (up to 99% *ee* for the major diastereomer) and reasonable diastereomeric ratio (up to 7:1 d.r. for *anti*) (Scheme 3).

We were further interested in expanding our optimized catalytic conditions to the Mannich reaction of other halogenated cyclic ketones such as **7** and **9** to generate C–Cl and C–Br quaternary stereogenic centers[15] in the corresponding products, respectively. The preliminary results of this significant transformation are as shown in Scheme 4. To our delight, ketones **7** and **9** furnished the Mannich products **8** and **10**, respectively, in quantitative yield with almost perfect enantio- and diastereoselectivity at room temperature (Scheme 4).

Based on our experimental results and our previous reports regarding cation-binding catalysis, the plausible reaction mechanism is illustrated in Figure 1. In the first step, **Complex I** is formed by the complexation of KF with the catalyst, and then engages with amidosulfone to form **Complex II**. Subsequently, elimination of the sulfinate group from amidosulfone affords an imine activated through hydrogen bonding as dictated in

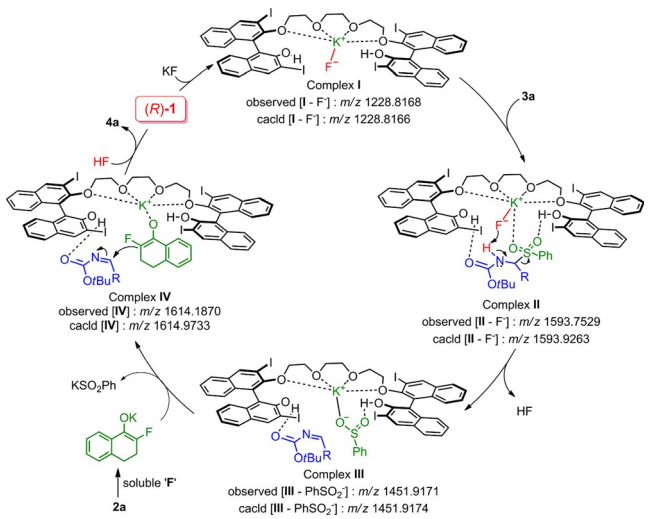


Figure 1. A proposed reaction mechanism and observation of the intermediates.

Complex III. The subsequent coordination of potassium enolate (generated in situ from cyclic ketones with KF) to the catalyst is followed by its addition to the imine to provide the enantio- and diastereoenriched adducts [up to 99% *ee* and up to >20:1 d.r. (*anti*/*syn*)]. As shown in the proposed mechanism, the cation-binding (K^+) to the catalyst is critical to induce high reactivity and enantioselectivity in the enantio-determining step through formation of the chiral cage. To support this proposed reaction mechanism, we conducted an in situ electrospray ionization mass spectroscopy (ESI-MS) analysis of the reaction mixture (see the Supporting Information). Gratifyingly, some proposed intermediates could be observed in the measurements of ESI-MS (positive ion mode). The signals at $m/z = 1228.8168$, 1593.7529, 1451.9171, and 1614.1870 correspond to [**I**–F^-], [**II**–F^-], [**III**–$PhSO_2^-$], and [**IV**], respectively.

In summary, we have developed a transition-metal-free straightforward strategy for the synthesis of highly enantio- and diastereoenriched β-fluoroamine derivatives with quaternary C–F centers through direct organocatalytic Mannich reactions with fluoroketones and α-amidosulfones by using a cation-binding catalyst and KF as a base. Excellent enantio- and diastereoselectivities were obtained with a variety of fluoro cyclic ketones and α-amidosulfones even at a very high temperature (80 °C), perhaps owing to the conformational stability of the transition state. The salient features of this process include a) a transition-metal-free and operationally simple procedure, b) direct use of α-amidosulfones as bench-stable precursors of sensitive imines, enabling the use of a broad scope of α-amidosulfones, c) direct enolization of racemic α-fluoro cyclic ketones, and d) excellent stereoselectivity with up to 99% *ee* and >20:1 d.r. (*anti*/*syn*). This protocol was also successfully extended to generate C–Cl and C–Br quaternary stereogenic centers. Thus, we believe that this protocol can provide a new approach for the synthesis of diverse biologically relevant products with quaternary stereogenic C–halogen centers. The extension of this strategy to the synthesis of quaternary carbon in acyclic systems is currently underway in our laboratory.

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Keywords: cation-binding catalysis · chiral oligoethylene glycol catalyst · Mannich reaction · quaternary stereogenic center · β-fluoroamines

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[12] Instead of α-amido sulfone **3a**, the direct use of the corresponding imine afforded comparable catalytic results. The product **4a** was obtained in 67% yield with 92% *ee* for the *anti* diastereomer (d.r. = 1:7 for *syn*/*anti*).

[13] However, acyclic α-fluoroketones such as 2-fluoro-1-phenylpropan-1-one and 2-fluoro-3-methyl-1-phenylbutan-1-one did not undergo the reaction under the same conditions.

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