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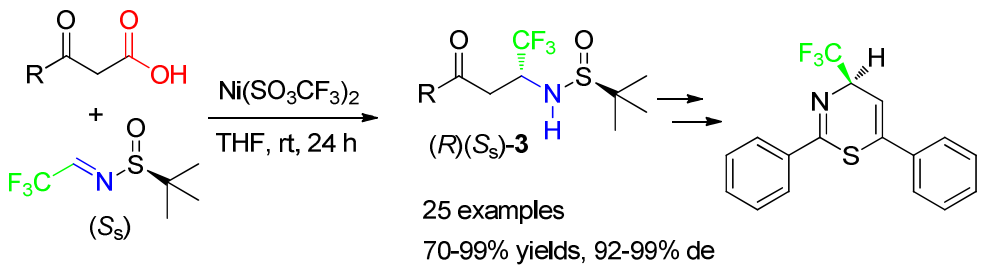

Ni-catalyzed asymmetric decarboxylative Mannich

A Ni-catalyzed asymmetric decarboxylative Mannich reaction between (S_s)-*N*-*t*-butylsulfinyl-3,3,3-trifluoro-acetaldimine and β-keto-acids was reported, affording β-trifluoromethyl-β-amino ketones with excellent yields and diastereoselectivities.

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ARTICLE TYPE

Ni-catalyzed asymmetric decarboxylative Mannich reaction for the synthesis of β-trifluoromethyl-β-amino ketones

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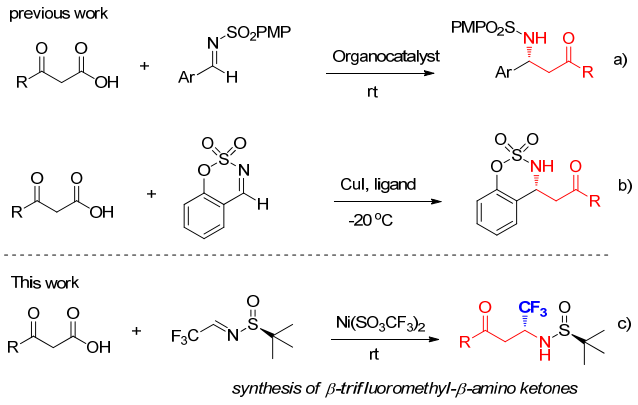
A new Ni-catalyzed asymmetric decarboxylative Mannich reaction between (S_s)-*N*-*t*-butylsulfinyl-3,3,3-trifluoro-acetaldimine and β-keto-acids was developed, which was carried out at room temperature affording β-trifluoromethyl-β-amino ketones with excellent yields and diastereoselectivities.

Fluorine-containing compounds play an increasingly important role in various chemical industries ranging from life- to material-related sciences.[1] In particular, the pharmaceutical industry critically depends on the methodological developments in fluorine chemistry for the design of more selective and potent new drugs.[2] One of these areas is the synthesis of polyfunctional fluorinated derivatives possessing keto/hydroxy/amino groups. However, preparation of such structurally complex compounds still remains a significant synthetic challenge.[3] Consistent with our continuous research on the preparation of fluorinated amines,[4-9] we have developed a method for the synthesis of β-trifluoromethyl-β-amino ketones[10] via asymmetric Mannich reaction between (S_s)-*N*-*t*-butylsulfinyl-3,3,3-trifluoro-acetaldimine **1**[11] and acetophenone derived enolates. This reaction gave moderate yields and diastereoselectivities. Especially, the reaction need strong base (LDA) and must be performed at low temperature (-78 °C). So, development of simple and efficient method for the synthesis of chiral β-trifluoromethyl-β-amino ketones becomes highly urgent.[12]

Decarboxylative Mannich reaction of β-keto acids, which could form in situ the enolates under mild condition[13] and easily construct β-amino ketones structures in cascade mode,[14] has attracted broad attentions in synthetic chemistry community. Recently, Lu group reported an organocatalytic decarboxylative Mannich reaction of β-keto acids for the synthesis of chiral β-amino ketones at room temperature with moderate enantioselectivities (Scheme 1a).[15] Very recently, Ma group developed a Cu-catalyzed decarboxylative Mannich reaction of β-keto acids at -20 °C with excellent enantioselectivities (Scheme 1b).[16] However, the asymmetric decarboxylative Mannich reaction of β-keto acids for the synthesis of chiral trifluoromethylated β-amino ketones has never been reported. Herein, we would like to report a Ni-catalyzed asymmetric decarboxylative Mannich reaction of trifluoro-acetaldimine at room temperature for the synthesis of chiral β-trifluoromethyl-β-amino ketones with excellent chemical yields and high diastereoselectivities (Scheme 1c)



Scheme 1 Asymmetric decarboxylative Mannich reaction of β-keto acid.

Initially, we chose β-keto acid **2a** and imine **1** as model substrates for the reaction condition optimization, and the results were shown in Table 1. We were pleased to find that the reaction could proceed smoothly with CF_3COOLi as catalyst in THF at room temperature, affording the desired product **3a** with 65% yield and 96:4 diastereoselectivity after 12 h (entry 1). $Pd(OAc)_2$ also worked for this reaction with excellent diastereoselectivity (98:2 dr), but the yield decreased dramatically (35%, entry 2). To further improve the reaction efficiency, several metal triflate salts were examined (entries 3-11). Among the divalent metals, such as Mg (entry 3), Ni (entry 4), Zn (entry 5), Ni-triflate catalyzed reaction gave the best result (96% yield, 98:2 dr, entry 4). Interestingly, a series of trivalent metals also could catalyze the addition reaction with almost complete stereocontrol, however the target product (*R*)(S_s)-**3a** was isolated in only moderate yields (24%-67%, entries 6-11). Then, several other Ni(II) salt were tried, such as $Ni(acac)_2$ (entry 12), $Ni(OAc)_2·4H_2O$ (entry 13), $NiNO_3·6H_2O$ (entry 14) and $NiCl_2·6H_2O$ (entry 15). However, no improvement was found at all. Solvent also showed great effect on this reaction. The use of 1,4-dioxane (entry 20), diethyl ether (entry 21), chloroform (entry 22) afforded the product (*R*)(S_s)-**3a** with good diastereoselectivity but in rather lower chemical yields (51%-72%). Finally, we conducted additional experiments to optimize the loading amount of the catalyst (entries 23-24). These experiments showed that decreasing the amount of $Ni(OTf)_2$ catalyst to 10 mol% also could provide the desired product **3a** with 92% chemical yield and 99:1 dr when the reaction was prolonged to 24 h.

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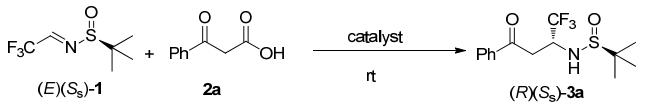
Table 1. Optimization of decarboxylative Mannich addition reaction conditions.[a]



(*E*)(*S*$_s$)-**1** **2a** (*R*)(*S*$_s$)-**3a**

Entry	Catalyst (mol %)	Solvent	Time (h)	Yield (%)[b]	Dr[c]
1	CF_3COOLi (30)	THF	12	65	96:4
2	$Pd(OAc)_2$ (30)	THF	12	35	98:2
3	$Mg(SO_3CF_3)_2$ (30)	THF	12	75	99:1
4	$Ni(SO_3CF_3)_2$ (30)	THF	12	96	98:2
5	$Zn(SO_3CF_3)_2$ (30)	THF	12	53	99:1
6	$Fe(SO_3CF_3)_3$ (30)	THF	12	31	99:1
7	$In(SO_3CF_3)_3$ (30)	THF	12	24	96:4
8	$Sc(SO_3CF_3)_3$ (30)	THF	12	40	>99:1
9	$La(SO_3CF_3)_3$ (30)	THF	12	35	96:4
10	$Sm(SO_3CF_3)_3$ (30)	THF	12	60	>99:1
11	$Yb(SO_3CF_3)_3$ (30)	THF	12	67	>99:1
12	$Ni(acac)_2$ (30)	THF	12	82	82:18
13	$Ni(OAc)_2{\cdot}4H_2O$ (30)	THF	12	76	80:20
14	$NiNO_3{\cdot}6H_2O$ (30)	THF	12	97	97:3
15	$NiCl_2{\cdot}6H_2O$ (30)	THF	12	85	93:7
20	$Ni(SO_3CF_3)_2$ (30)	1,4-dioxane	12	51	>99:1
21	$Ni(SO_3CF_3)_2$ (30)	ether	12	72	95:5
22	$Ni(SO_3CF_3)_2$ (30)	$CHCl_3$	12	28	97:3
23	$Ni(SO_3CF_3)_2$ (20)	THF	24	94	>99:1
24	$Ni(SO_3CF_3)_2$ (10)	THF	24	92	>99:1

[a] Reaction conditions: **2a** (0.16 mmol), imine **1** (0.1 mmol), catalyst, solvent (2 mL), at room temperature. [b] Isolated yields. [c] Determined by ^{19}F NMR analysis.

With the optimized reaction conditions in hand, we next proceeded to study the substrate scope of this decarboxylative Mannich addition reaction (Scheme 2). The reaction showed a wide range of β-keto acids scope, and proceeded smoothly to give the corresponding β-trifluoromethyl-β-amino ketones **3a-y** in excellent yields (70%-99%) and high diastereoselectivities (94:6->99:1). For the substrates with *para*-substituted phenyl group **2b-2j**, either electronic properties or steric bulk of the substituent had almost no noticeable effect on the diastereoselectivity of the reactions. For example, product **3g**, bearing bulky *iso*-propyl group was also isolated as diastereomerically pure compound in quantitative chemical yield. The reactions with the substrates containing *meta*-substituted phenyl ring, also could proceed smoothly resulting in a bit lower chemical yields (**3k-3m**). To have more structurally interesting derivatives, a di-substituted starting β-keto acid **2o** was examined in the reaction, and >99:1 diastereoselectivity was obtained along with 98% chemical yield (**3o**). Naphthyl containing keto-acids **2x**,**y** cleanly reacted with imine **1** affording the target products **3x**,**y** in excellent yields and diastereoselectivity, and the reaction of 2-naphthyl substituted keto-acids **2y** gave a little bit better yield and diastereoselectivity (98% yield, >99:1 dr). The reaction could also well tolerate the heterocyclic and ester substituted groups as disclosed by the addition reaction of β-keto acid **2w** and **2p**, giving the corresponding products **3w**,**p** with excellent results. Finally we examined a series of aliphatic group containing β-keto acids **2q-t**. It was noticed that these substrates with alkyl groups also worked very well in the decarboxylative Mannich reactions, yielding the products **3q-t** as diastereomerically pure compounds with excellent yields. However, for the substrate with *para*-NO_2 substituted phenyl group **2z**, almost no desired product was found even the reaction time was increased to 48 h.

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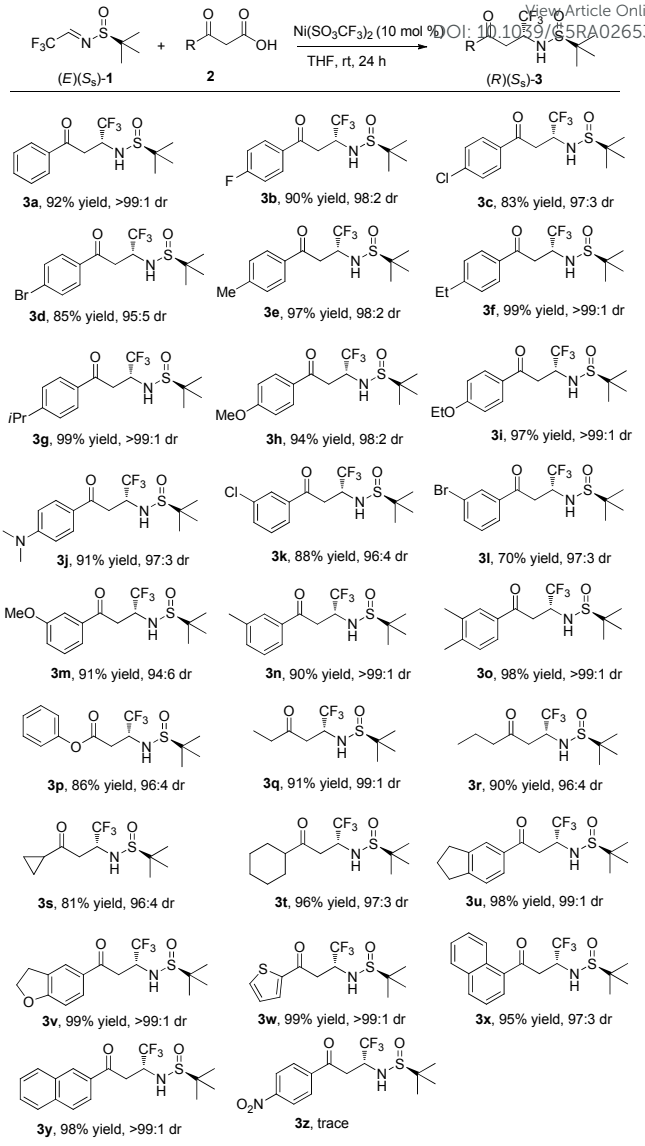

Scheme 2 Substrate scope of the asymmetric decarboxylative Mannich addition reactions. [a] Reaction conditions: **2** (0.16 mmol), imine **1** (0.1 mmol), $Ni(OTf)_2$ (10 mol %), in THF at room temperature for 24 h. [b] Isolated yields. [c] Determined on crude reaction mixtures by ^{19}F NMR analysis.

The next study was to determine the absolute configuration of the major products **3**. Throughout the study, we noticed that the major products **3a-y** have a different ^{19}F-NMR data as compared with the previously reported (*S*)(*S*$_s$)-β-trifluoromethyl-β-amino ketones obtained from the asymmetric Mannich reaction.[10] So, we synthesized the diastereomer (*S*)(*S*$_s$)-**3** using the reported method[10] and conducted its deprotection to free amine (*S*)-**4** (Scheme 3a). Diastereomeric compound (*R*)(*S*$_s$)-**3**, obtained in this work, was also deprotected to produce free amino-ketone (*R*)-**4** (Scheme 3c). Finally, the racemic-**4** was prepared with the same method for (*R*)-**4** (Scheme 3b). Then, we conducted their detailed analysis by using chiral HPLC (see SI), which clearly showed that the compound obtained in the current decarboxylative Mannich system and that from previous Mannich

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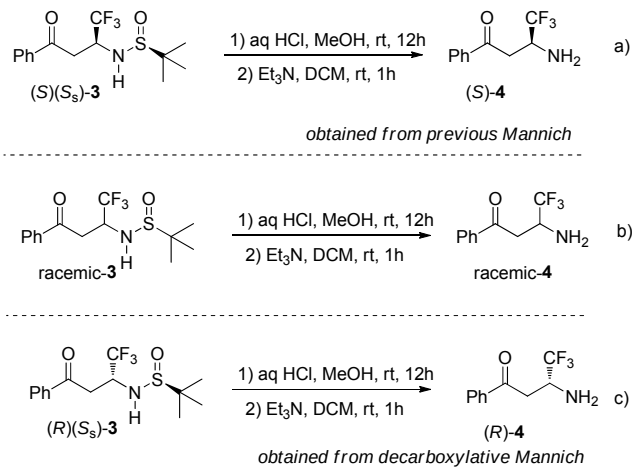
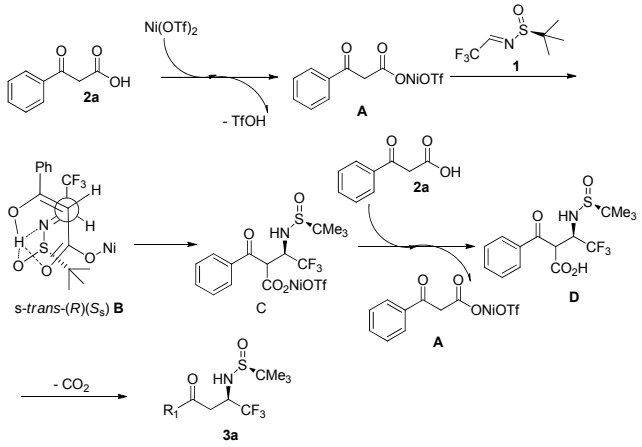
reaction[10] are enantiomers (see SI), and have opposite absolute configuration. So, the absolute configuration of compound **4** obtained in the current system is assigned as (*R*), and the absolute configuration of major products **3a-y**, were assigned as (*R*)(*S*$_s$) accordingly.



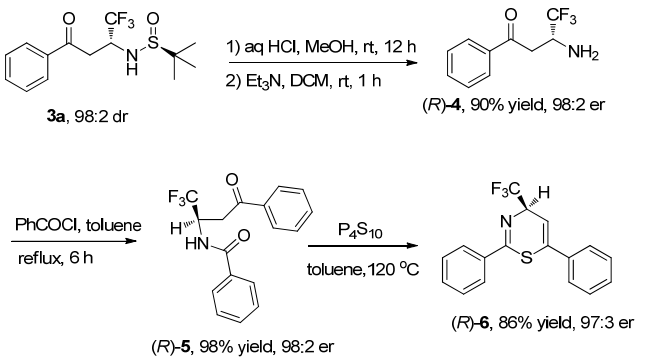
Scheme 3 Preparation of enantiomeric free amines (*S*)-**4**, (*R*)-**4** and racemic-**4** by deprotection of **3**.

According to the above results and previous reports,[13-16] a plausible mechanistic pathway for this decarboxylative Mannich reaction was proposed in Scheme 4. Initially, catalyst Ni(OTf)$_2$ reacts with β-keto acid **2a** to generate intermediate **A**. Then, intermediate **A** adds to chiral imine **1** to form intermediate **C** via the transition state **B**. In transition state **B**, the enolate hydrogen is supposed to coordinate with the oxygen of the S-O group. Therefore the enolate O-H bond can be weakened to generate the negative charge on the corresponding carbon, which accelerates the addition step. The intermediate **C** reacts with starting material **2a** affording the intermediate **D**, along with the formation of intermediate **A** for the next catalytic cycle. Fortunately, the intermediate **D** has been detected by HRMS from the reaction mixture. The final step of this reaction is decarboxylation, resulting in the final product **3a** with *R* configuration.



Scheme 4 Possible mechanism for the asymmetric decarboxylative Mannich reaction.

Finally, the cyclization derivatization of the obtained β-trifluoromethyl-β-amino ketone product **3a** was carried out (Scheme 5). (*R*)(*S*$_s$)-**3a** undergoes deprotection, aminoacylation and cyclization with phosphorus pentasulfide to give the (*R*)-2,6-diphenyl-4-(trifluoromethyl)-4*H*-1,3-thiazine[17] **6** with good chemical yields. Also, almost no racemation was found during the three-step transformations.



Scheme 5 Cyclization derivatization of **3a**.

In summary, we developed an asymmetric Ni-catalyzed decarboxylative Mannich reaction of chiral imine for the synthesis of β-trifluoromethyl-β-amino ketone for the first time. The reaction has a broad scope of keto-acid substrates and could be carried out under room temperature with excellent chemical yields and diastereoselectivities. The reaction provides a new and easy way for the preparation of chiral trifluoromethylated β-amino ketones, even for the large-scale preparation.

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† Electronic Supplementary Information (ESI) available: [Experimental procedures, full spectroscopic data for compounds **3-6** and copies of ^{1}H NMR and ^{13}C NMR spectra]. See DOI: 10.1039/b000000x/

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