

## RESEARCH ARTICLE

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# Enantioselective synthesis of trifluoromethyl substituted piperidines with multiple stereogenic centers *via* hydrogenation of pyridinium hydrochlorides†

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An enantioselective iridium-catalyzed hydrogenation of trifluoromethyl substituted pyridinium hydrochlorides is described. Introduction of a trifluoromethyl group increases the reactivity due to the electron-withdrawing effect. Three stereogenic centers could be generated in one operation. This methodology provides a convenient route to chiral poly-substituted piperidines with up to 90% ee.

Chiral piperidines are valuable and prevalent substructures in biologically active natural products, synthetic bioactive compounds and medicines.<sup>1</sup> In particular, the introduction of novel substituents on these framed syntheses of multiple stereocenter piperidines has been the focus of many chemists.<sup>2</sup> Among them, selective introduction of trifluoromethyl groups can greatly modify the biological properties of the target molecules which are broadly present in several important drugs, such as JAK inhibitors (Fig. 1).<sup>3</sup> Although organofluorine chemists have made tireless efforts, stereoselective synthesis of trifluoromethyl piperidines with multiple stereogenic centers is still an area which has been rarely explored to date.<sup>4</sup>

Piperidines with multiple stereogenic centers are of great significance; together with our ongoing efforts in the development of asymmetric hydrogenation of *N*-heteroaromatics, we envision that asymmetric hydrogenation of such poly-substituted trifluoromethyl pyridines would provide straightforward

access to these compounds. However, due to the stabilizing aromaticity<sup>5</sup> and strong coordination ability of pyridines and the corresponding products, which might poison catalysts, in the past 15 years only a few homogeneous Rh and Ir catalysts<sup>6</sup> and organocatalysts<sup>7</sup> have been applied to synthesize chiral piperidines through asymmetric hydrogenation of special pyridines bearing strong electron-withdrawing groups or pyridinium salts (eqn (1) and (2)). Notably, very recently, Mashima and co-workers reported an iridium-catalyzed asymmetric hydrogenation of pyridinium salts,<sup>6i</sup> giving the chiral piperidines with two or three stereogenic centers in 28–82% ee and moderate yields (eqn (3)). Herein, we report an efficient asymmetric hydrogenation of poly-substituted pyridinium salts with excellent enantio- and diastereoselectivity (eqn (4)). Notably, introduction of the trifluoromethyl group increases the reactiv-

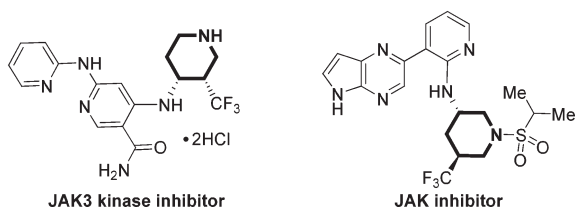
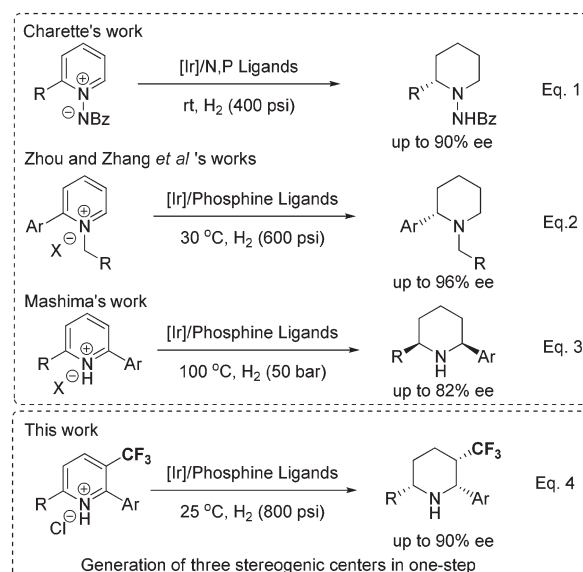


Fig. 1 Selected biologically active molecules containing the trifluoromethylpiperidine motif.

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ity due to the electron-withdrawing effect. Three stereogenic centers could be generated in one operation.

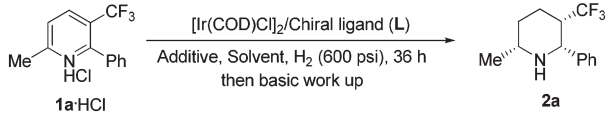
On the basis that the extraneous Brønsted acid could activate substrates and accelerate iminium/enamine isomerization to facilitate hydrogenation,<sup>8</sup> we tried asymmetric hydrogenation of pyridinium hydrochloride. To our delight, 6-methyl-2-phenyl-3-trifluoromethylpyridinium hydrochloride (**1a**-HCl) could be hydrogenated in full conversion with 67% ee and excellent diastereoselectivity (Table 1, entry 1). Subsequently, different solvents were examined (entries 2–7) and the mixture solvents of dichloromethane (DCM) and isopropanol with a ratio of 3/1 gave the best result in terms of both enantioselectivity and conversion (85% ee and >95% conversion; entry 6). Sequentially, various halogen source additives (TCCA: trichloroisocyanuric acid, DCDMH: 1,3-dichloro-5,5-dimethylhydantoin and DBDMH: 1,3-dibromo-5,5-dimethylhydantoin) were tested, and gave similar ee values between 81 and 85% (entries 8–10). Some commercially available chiral bisphosphine ligands were also evaluated (entries 11–13), and the best result was achieved with (*R*)-DifluorPhos **L3** (88% ee and >95% conversion; entry 12). Finally, 90% ee was achieved when the temperature was decreased to 25 °C, but the conversion reduced to 85%. Gratifyingly, full conversion with an identical enantioselectivity was obtained (entry 15, 90% ee) when the

hydrogen pressure was raised to 800 psi with 2.5 mol% catalyst. Thus, the optimized conditions were established as: [Ir(COD)Cl]<sub>2</sub>/(*R*)-DifluorPhos/TCCA/(DCM/*i*-PrOH)/H<sub>2</sub> (800 psi)/25 °C.

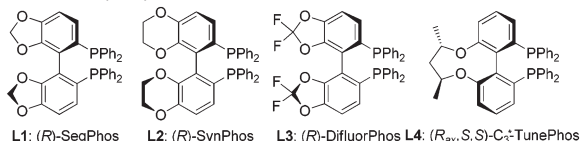
With the optimized reaction conditions in hand, exploration of the substrate scope was carried out (Table 2). As expected, various substrates performed very well under standard reaction conditions. The electronic properties and position of substituents on the aromatic ring had a marginal effect on the reactivity and enantioselectivity (entries 1–8). Subsequently, the 6-ethyl-2-phenyl-3-(trifluoromethyl)pyridinium hydrochloride (**1i**-HCl) was also tested, 87% ee and 82% yield were obtained (entry 9). The absolute configuration of hydrogenation product **2f** was assigned to be *cis*-(2*R*,3*S*,6*R*) based on single crystal X-ray diffraction analysis (Fig. 2).<sup>9</sup>

In order to further estimate the application possibility, we applied this attractive protocol to the hydrogenation of the simple 2,6-disubstituted pyridinium hydrochloride. Gratifyingly, the reaction proceeded with moderate enantioselectivity and moderate to good reactivity (Scheme 1). In contrast to the asymmetric reduction of 3-(trifluoromethyl)pyridinium hydrochloride **1**, in these cases the reactions were carried out under

**Table 1** The evaluation of reaction parameters<sup>a</sup>

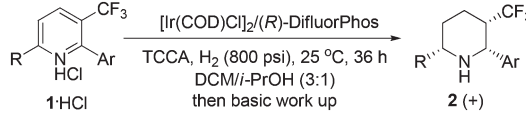


Entry	Solvent	Additive	L	Conv. <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	THF	TCCA	<b>L1</b>	>95	67
2	DCM (D)	TCCA	<b>L1</b>	91	82
3	Benzene	TCCA	<b>L1</b>	89	79
4	<i>i</i> -PrOH(P)	TCCA	<b>L1</b>	97	79
5	D/P (1 : 1)	TCCA	<b>L1</b>	>95	82
6	D/P (3 : 1)	TCCA	<b>L1</b>	>95	85
7	D/P (4 : 1)	TCCA	<b>L1</b>	>95	83
8	D/P (3 : 1)	DCDMH	<b>L1</b>	>95	83
9	D/P (3 : 1)	DBDMH	<b>L1</b>	>95	81
10	D/P (3 : 1)	NCS	<b>L1</b>	>95	82
11	D/P (3 : 1)	TCCA	<b>L2</b>	96	78
12	D/P (3 : 1)	TCCA	<b>L3</b>	>95	88
13	D/P (3 : 1)	TCCA	<b>L4</b>	>95	79
14 <sup>d</sup>	D/P (3 : 1)	TCCA	<b>L3</b>	85	90
15 <sup>e</sup>	D/P (3 : 1)	TCCA	<b>L3</b>	>95	90



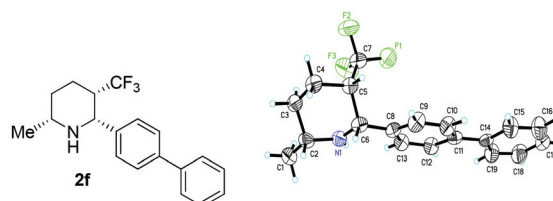
<sup>a</sup> Reaction conditions: **1a**-HCl (0.125 mmol), [Ir(COD)Cl]<sub>2</sub> (2.0 mol%), ligand (4.4 mol%), H<sub>2</sub> (600 psi), solvent (3.0 mL), additive (10 mol%), 36 h, 50 °C. <sup>b</sup> Reaction conversion and dr were determined by <sup>1</sup>H NMR spectroscopy. In all cases, dr >20 : 1. <sup>c</sup> Determined by HPLC analysis of the corresponding *N*-benzoyl derivatives. <sup>d</sup> 25 °C. <sup>e</sup> [Ir(COD)Cl]<sub>2</sub> (2.5 mol%), (*R*)-DifluorPhos (5.5 mol%), H<sub>2</sub> (800 psi), 25 °C.

**Table 2** Asymmetric hydrogenation of 3-(trifluoromethyl)pyridinium hydrochloride (**1**-HCl)<sup>a</sup>

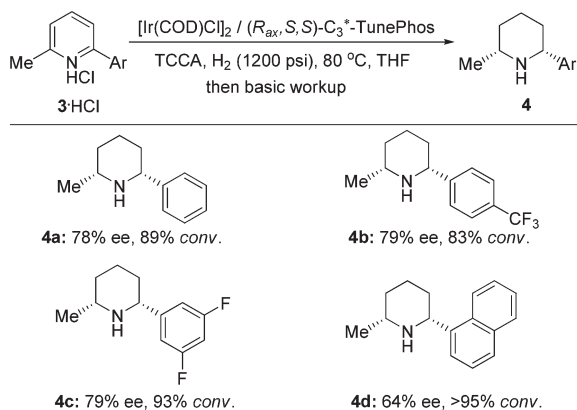


Entry	R/Ar	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	Me/C <sub>6</sub> H <sub>5</sub>	95 ( <b>2a</b> )	90
2	Me/4-MeC <sub>6</sub> H <sub>4</sub>	84 ( <b>2b</b> )	89
3	Me/3-MeC <sub>6</sub> H <sub>4</sub>	84 ( <b>2c</b> )	88
4	Me/4-MeOC <sub>6</sub> H <sub>4</sub>	94 ( <b>2b</b> )	88
5	Me/2-Naphthyl	93 ( <b>2e</b> )	89
6 <sup>d</sup>	Me/4-C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub>	90 ( <b>2f</b> )	87 (2 <i>R</i> ,3 <i>S</i> ,6 <i>R</i> )
7	Me/4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	85 ( <b>2g</b> )	86
8	Me/3,5-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	72 ( <b>2h</b> )	84
9	Et/C <sub>6</sub> H <sub>5</sub>	82 ( <b>2i</b> )	87

<sup>a</sup> Reaction conditions: **1**-HCl (0.125 mmol), (*R*)-DifluorPhos (5.5 mol%), [Ir(COD)Cl]<sub>2</sub> (2.5 mol%), H<sub>2</sub> (800 psi), DCM-*i*-PrOH (3 : 1, 3.0 mL), TCCA (10 mol%), 36 h, 25 °C. <sup>b</sup> Isolated yields and in all cases dr >20 : 1. <sup>c</sup> Determined by HPLC analysis of the corresponding benzamide. <sup>d</sup> The absolute configuration was determined by single crystal X-ray diffraction analysis of **2f**.



**Fig. 2** X-ray crystal structure of compound **2f**.



**Scheme 1** Asymmetric hydrogenation of 2,6-disubstituted pyridinium hydrochloride (**3-HCl**). Reaction conditions: **3-HCl** (0.125 mmol),  $(R_{ax}, S, S)\text{-C}_3^*\text{-TunePhos}$  (2.2 mol%),  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (1.0 mol%),  $\text{H}_2$  (1200 psi), THF (3.0 mL), TCCA (10 mol%), 24 h, 80 °C. Reaction conversion and dr were determined by  $^1\text{H}$  NMR spectroscopy. In all cases, dr >20 : 1.

relatively harsh conditions (1200 psi hydrogen pressure and 80 °C). The reactivity discrepancy of these two types of substrates might be ascribed to the electron-withdrawing ability of the trifluoromethyl group that activates pyridine to facilitate hydrogenation.

In conclusion, an efficient and direct approach to chiral trifluoromethyl substituted piperidines with multiple stereogenic centers has been successfully developed *via* iridium-catalyzed asymmetric hydrogenation of the corresponding pyridinium hydrochlorides with up to 90% ee. Three stereogenic centers could be generated in one operation. Introduction of the trifluoromethyl group increases the reactivity of pyridine hydrogenation due to the strong electron-withdrawing effect. Meanwhile, this attractive protocol can also be applied to the asymmetric hydrogenation of the simple 2,6-disubstituted pyridinium hydrochlorides with moderate reactivity and enantioselectivity. Further investigations on asymmetric hydrogenation of poly-substituted heteroaromatics are currently ongoing in our laboratory.

## Experimental section

### Typical procedure for asymmetric hydrogenation of **1a**

In a nitrogen-filled glove box, a mixture of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (2.1 mg, 0.0031 mmol) and  $(R)$ -DifluorPhos (4.7 mg, 0.0069 mmol) in dichloromethane-isopropanol (3 : 1, 1.0 mL) was stirred at room temperature for 15–20 min, using a syringe the mixture was transferred to a stainless steel autoclave, in which the substrate **1a-HCl** (34.0 mg, 0.20 mmol) and TCCA (2.9 mg, 0.0125 mmol) had been placed beforehand. Then, dichloromethane-isopropanol (3 : 1, 2.0 mL) was added. The hydrogenation was performed at 25 °C under 800 psi hydrogen pressure for 36 h. After carefully releasing the hydrogen, triethylamine (56  $\mu\text{L}$ , 0.40 mmol) was added and the mixture was

stirred for 30 min. The organic layer was separated and extracted with dichloromethane twice, and the combined organic extracts were dried over sodium sulfate and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography using petroleum ether-ethyl acetate to give the desired product **2a** as pale oil (29 mg, 95% yield). Enantiomeric excess was determined by HPLC for the corresponding benzamide (OJ-H, elute: hexanes-*i*-PrOH = 90/10, detector: 220 nm, flow rate: 1.0 mL  $\text{min}^{-1}$ ), 30 °C,  $t_1$  = 10.6 min (maj),  $t_2$  = 15.3 min (90% ee).

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