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Synthesis of Chiral Trifluoromethyl-Substituted Hydrazines via Pd-Catalyzed Asymmetric Hydrogenation and Reductive Amination

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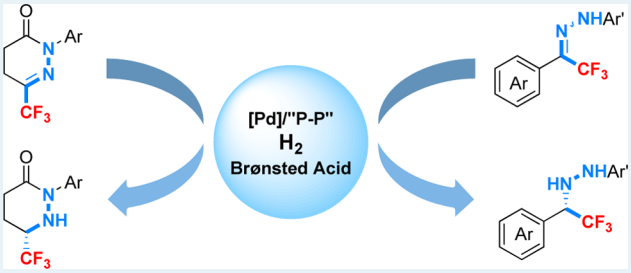
Supporting Information

ABSTRACT: An efficient approach toward the synthesis of cyclic and linear chiral trifluoromethyl substituted hydrazines was developed by Pd-catalyzed asymmetric hydrogenation of both *N*-acyl and *N*-aryl hydrazones in excellent yields and up to 97% ee. A successful reductive amination between trifluoromethyl substituted ketones and hydrazines was also achieved.



KEYWORDS: *palladium, asymmetric hydrogenation, reductive amination, trifluoromethylated hydrazines, Brønsted acid*

Chiral hydrazines, acyl hydrazines, aryl hydrazines, and other derivatives are widely used and of great importance in the biological, agricultural, and dyestuff industries. In addition, they also serve as important synthetic intermediates for heterocyclic compounds.[1] Particularly, many compounds bearing a hydrazine moiety have been found to have potential pharmacological activities, and some of them are clinically used as active pharmaceutical ingredients (APIs) of pharmaceutical drugs. For example, azacastanospermine is a potent competitive inhibitor of almond β-glucosidase and rice α-glucosidase,[2] DB07461 is a thrombin inhibitor at the experimental stage,[3] LY288513 has emerged as a promising preclinical candidate due to its cholecystokinin (CCK) inhibition.[4] Atazanavir shows inhibitive activity against HIV protease and has been applied as a therapeutic agent against AIDS,[5] etc. (Figure 1).

Over recent decades, introduction of fluorine into molecules has been receiving increasing consideration because the isosteric replacement of hydrogen enhanced the lipophilicity, metabolic stability, and bioavailability of the parent compounds.[6] Moreover, the incorporation of fluorine into a biologically active molecule causes minimal steric alterations, whereas remarkable physicochemical properties changes, thus, continue to draw many the attention of pharmaceutical chemists to this field.[7] In this context, α-trifluoromethylated hydrazines have become the subject of special interest because α-substituted trifluoromethylamino compounds are especially important and have been developed as several well-known drugs.[8]

Transition-metal-catalyzed asymmetric hydrogenation of unsaturated compounds has been widely used for the production of chiral scaffolds and building blocks.[9] Considering the ready availability and easy preparation of fluorinated hydrazones, asymmetric hydrogenation of these compounds

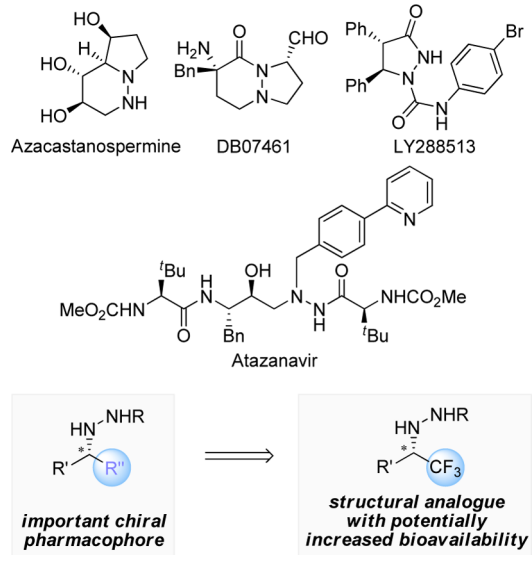


Figure 1. Examples of biologically active hydrazine-based compounds.

would provide an atom-economical and straightforward route to optically pure hydrazines (Scheme 1). Despite much progress having been achieved in asymmetric hydrogenation of C=N double bond, the hydrogenation of hydrazones still remains a great challenge. Only a few homogeneous metal catalysts have been applied to the asymmetric hydrogenation of such compounds, and the substrate scope has been limited to

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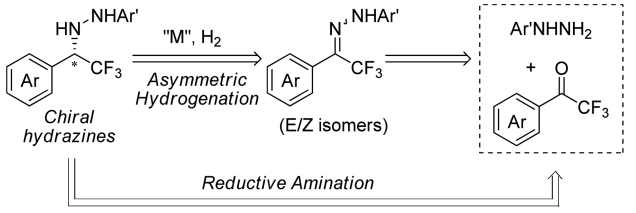
Scheme 1. Challenges in the Synthesis of Trifluoromethylated Hydrazines via Hydrogenation



Challenges:

(a) the E/Z isomers of hydrazones make stereoselective reduction difficult;

(b) the instability and strong coordination ability of both substrates and products hinder the hydrogenation.

N-acyl hydrazones.[10] The major obstacles to advancement in this research area are as follows: (a) the *E*/*Z* isomers of certain substrates make stereoselective reduction difficult;[11] (b) the instability and strong coordination ability of both substrates and products hinder hydrogenation. Consequently, seeking new, efficient metal catalysts with broad substrate scope would be very desirable in organic synthesis and drug research.

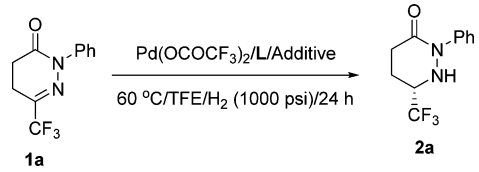
Recently, our group successfully developed a Pd-catalyzed asymmetric hydrogenation of fluorinated aromatic pyrazol-5-ols via capture of the active tautomers,[12] which heightened our interest in hydrogenation of the fluorinated hydrazones. Herein, we report our initial findings on the asymmetric hydrogenation of both *N*-acyl and *N*-aryl α-trifluoromethylated hydrazones.

Initially, the readily available 2-phenyl-6-(trifluoromethyl)-4,5-dihydropyridazin-3(2*H*)-one **1a**, which can be synthesized by condensation of γ-ketoacids with simple hydrazines according to the reported procedure,[13] was selected as the model substrate for investigation. To our delight, the hydrogenation of **1a** furnished the desirable hydrazine **2a** with 95% ee and 56% conversion by employing Pd-$(OCOCF_3)_2$/(*S*)-MeO−BiPhep as the catalyst, which has been used advantageously as a homogeneous catalyst in the hydrogenation[14] (Table 1, entry 1). The low reactivity may be ascribed to the strong coordination effects and the relatively electron-enriched nature of hydrazones that impeded the hydrogenation. Subsequently, the effect of other acids, including benzoic acid, L-CSA, D-CSA, and TsOH·H_2O, were investigated. To our disappointment, no acid gave a better result than TFA, which was used in the initial screening of reaction conditions.

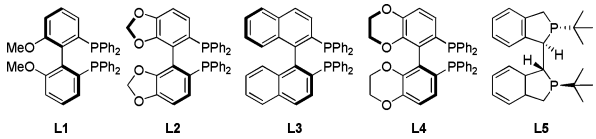
Further examinations focused on screening of ligands. From the evaluation of the various commercially available chiral bisphosphine ligands, the best enantioselectivity and conversion were obtained with (*S*)-SegPhos **L2** (entry 6). The elevating of reaction temperature could increase the activity (entry 10). When the catalyst dosage was increased to 5 mol % and the reaction time was prolonged to 48 h, the full conversion was obtained without loss of enantioselectivity (entry 11). Therefore, the optimal reaction conditions were established as $Pd(OCOCF_3)_2$/**L2**/80 °C/TFA.

With the optimal conditions in hand, exploration of substrate scope was carried out. The results are summarized in Table 2. Gratifyingly, a variety of 2-aryl substituted substrates were smoothly converted to the corresponding hydrazines with excellent enantioselectivities (92−97% ee). The electronic properties of the substituents on the phenyl ring had little effect on the activities and enantioselectivities (entry 4 vs entries 5−9). The position of the fluoro group slightly affected

Table 1. Condition Optimization[a]

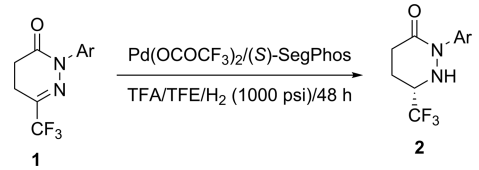


entry	L	additive	yield (%)[b]	ee (%)[c]
1	**L1**	TFA	56	95
2	**L1**	PhCOOH		
3	**L1**	L-CSA	13	97
4	**L1**	D-CSA	39	96
5	**L1**	TsOH·H_2O	25	96
6	**L2**	TFA	75	96
7	**L3**	TFA	49	92
8	**L4**	TFA	63	96
9	**L5**	TFA	37	83
10[d]	**L2**	TFA	81	95
11[e]	**L2**	TFA	> 95	95



[a]Reaction conditions: $Pd(OCOCF_3)_2$ (2 mol %), **L** (2.1 mol %), **1a** (0.2 mmol), additive (0.2 mmol), H_2 (1000 psi), TFE (2 mL), 60 °C, 24 h. [b]Determined by ^{1}H NMR. [c]Determined by HPLC. [d]80 °C. [e]$Pd(OCOCF_3)_2$ (5 mol %), **L** (5.5 mol %), 80 °C, 48 h.

Table 2. Pd-Catalyzed Asymmetric Hydrogenation of Hydrazones 1[a]



entry	1	Ar	yield (%)[b]	ee (%)[c]
1	**1a**	C_6H_5	94	95 (+)
2	**1b**	3-MeC_6H_4	91	95 (+)
3	**1c**	4-MeC_6H_4	95	95 (+)
4	**1d**	4-$MeOC_6H_4$	93	95 (+)
5	**1e**	3-ClC_6H_4	95	95 (+)
6	**1f**	4-ClC_6H_4	93	97 (*S*)
7	**1g**	2-FC_6H_4	82	92 (+)
8	**1h**	3-FC_6H_4	90	95 (+)
9	**1i**	4-FC_6H_4	92	96 (+)
10	**1j**	3,4-$Me_2C_6H_3$	86	95 (−)
11	**1k**	3,5-$Me_2C_6H_3$	97	96 (+)

[a]Reaction conditions: $Pd(OCOCF_3)_2$ (5 mol %), (*S*)-SegPhos (5.5 mol %), **1** (0.2 mmol), H_2 (1000 psi), TFA (0.2 mmol), TFE (2 mL), 80 °C, 48 h. [b]Isolated yield. [c]Determined by HPLC.

the reaction reactivity; the sterically hindered o-fluorinated substrate gave the hydrazine **2g** with 82% of yield and 92% ee (entry 7). It was noted that the best result of up to 97% ee was provided when 4-chlorophenyl was introduced (entry 6).

To further estimate the application possibility, a range of acyclic arylated hydrazones (**3a**−**3j**) were also investigated (Table 3). This kind of hydrazones and the corresponding hydrazine products has no electron-withdrawing group on the nitrogen atom and is to be slowly oxidized in air, thus making

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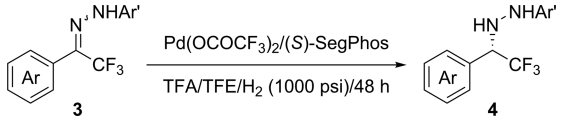
Table 3. Pd-Catalyzed Asymmetric Hydrogenation of Hydrazones 3[a]



3 4

entry	Ar	Ar′	yield (%)[b]	ee (%)[c]
1	C_6H_5	C_6H_5	94 (**4a**)	92 (*S*)
2	C_6H_5	4-MeC_6H_4	89 (**4b**)	93 (−)
3	C_6H_5	3-MeC_6H_4	87 (**4c**)	93 (+)
4	C_6H_5	4-FC_6H_4	93 (**4d**)	93 (+)
5	4-MeC_6H_4	C_6H_5	91 (**4e**)	92 (+)
6	3-MeC_6H_4	C_6H_5	94 (**4f**)	92 (+)
7	4-FC_6H_4	C_6H_5	91 (**4g**)	91 (+)
8	3,4-Me$_2$C$_6$H$_3$	C_6H_5	93 (**4h**)	91 (+)
9	3,5-Me$_2$C$_6$H$_3$	C_6H_5	92 (**4i**)	93 (+)
10	*β*-naphthyl	C_6H_5	92 (**4j**)	93 (+)

[a]Reaction conditions: Pd(OCOCF$_3$)$_2$ (5 mol %), (*S*)-SegPhos (5.5 mol %), **3** (0.2 mmol), H_2 (1000 psi), TFA (0.2 mmol), TFE (2 mL), 80 °C, 48 h. [b]Isolated yield. [c]Determined by HPLC.

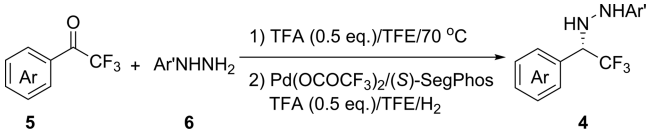
the hydrogenation difficult. To our delight, the substrates with different aryl groups could be hydrogenated smoothly, providing the corresponding N-arylated *N*′-alkyl hydrazine derivatives with high enantioselectivities and yields. The *β*-naphthyl hydrazone **3j** could also be hydrogenated with 92% yield and 93% of enantioselectivity (entry 10).

The absolute configurations of hydrogenation products **2f** and **4a** were determined by X-ray diffraction analysis by recrystallization from the mixture solvent dichloromethane/*n*-hexane.[15] The configurations of the other chiral products are assigned by analogy.

Direct metal-catalyzed asymmetric reductive amination is a more efficient and operationally simpler method for construction of chiral amines as to hydrogenation of the corresponding imines. Although much progress has been achieved in this area,[16] the development of a new catalytic system and expansion of the substrate scope are highly desired and of great significance. Therefore, the direct catalytic asymmetric reductive amination was also explored in this study. At the beginning, no desired product was observed with exposure of ketone **5a**, trifluoroacetic acid, and hydrazine **6** under the optimal conditions. What's more, the addition of 4 or 5 Å MS has no noticeable promotion effect on the reactivity. This result is probably caused by the difficulty of generation of trifluoromethyl hydrazones, and the starting ketone could be hydrogenated before the reduction amination takes place. Thus, we turned to stirring the ketone, aryl hydrazine and trifluoroacetic acid for 4 h at 70 °C in a tube under nitrogen atmosphere first, then moving the reaction mixture to a hydrogen atmosphere. As expected, the desirable hydrazine **4a** was obtained with 90% ee and 88% yield (entry 1, Table 4). Subsequently, the substrate scope was examined. The reductive amination reactions worked very well to give the desired *α*-trifluoromethyl-substituted hydrazines with slightly lower enantioselectivities and yields compared with the hydrogenation of the corresponding hydrazones.

In summary, we have developed an efficient method for synthesis of cyclic and linear chiral *α*-trifluoromethylated hydrazines through enantioselective palladium-catalyzed asymmetric hydrogenation of both *N*-aryl and *N*-acyl hydrazones in excellent yields and up to 97% of enantioselectivities. A

Table 4. Asymmetric Reductive Amination[a]



5 6 4

entry	Ar	Ar′	yield (%)[b]	ee (%)[c]
1	C_6H_5	C_6H_5	88 (**4a**)	90 (*S*)
2	C_6H_5	3-MeC_6H_4	84 (**4c**)	89 (+)
3	C_6H_5	4-FC_6H_4	86 (**4d**)	90 (+)
4	3-MeC_6H_4	C_6H_5	82 (**4f**)	92 (+)
5	3,4-Me$_2$C$_6$H$_3$	C_6H_5	87 (**4h**)	92 (+)

[a]Pd(OCOCF$_3$)$_2$ (5 mol %), (*S*)-SegPhos (5.5 mol %), ketone **5** (0.22 mmol), arylhydrazine **6** (0.2 mmol), H_2 (1000 psi), TFA (0.2 mmol), TFE (2 mL), 80 °C, 48 h. [b]Isolated yields. [c]Determined by HPLC.

successful reductive amination between trifluoromethyl-substituted ketones and hydrazines was also achieved. Further investigations on asymmetric hydrogenation of functionalized hydrazones are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01641.

Experimental materials and procedures, X-ray crystallographic analysis of products, NMR of substrates and products, and HPLC for racemic and chiral products (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(15) CCDC 1410066 and CCDC 1410075 contain the supplementary crystallographic data for this paper. These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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