# Efficient Synthesis of Tetrahydroquinolines from the Reaction of Aldehyde, Aniline, and Alkene under the *In Situ* Redox of SnCl<sub>2</sub> and FeCl<sub>3</sub>

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A highly efficient three-component Povarov reaction for the synthesis of tetrahydroquinoline derivatives was reported. The reaction of aldehyde, aniline, and alkene was carried out in the presence of Sn(IV), which was generated *in situ* from the redox reaction of SnCl<sub>2</sub> and FeCl<sub>3</sub>, to afford tetrahydroquinoline derivatives in good to excellent yields. This discovery showed a sharp difference from the direct use of unstable SnCl<sub>4</sub>. Both aliphatic and aromatic aldehydes could be applied for the synthesis of the heterocycle in the reaction. The structure of the product 6-chloro-4-methyl-4-neopentyl-2-propyltetrahydroquinoline and 6-bromo-4-methyl-4-neopentyl-2-pro pyltetrahydroquinoline was confirmed by X-ray diffraction analysis.

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#### **INTRODUCTION**

Tetrahydroquinoline derivatives are very important building blocks in many natural products that exhibit biological activities in various fields [1–4], such as analgesic activity, antitumor, antiparasitic, and antioxidation. A number of synthetic methods have been developed for these valuable compounds [5–11]. Among them, the most attractive strategy for the tetrahydroquinoline skeleton is the threecomponent Povarov reaction of aldehydes, anilines, and alkenes (eq. 1) [12–16]. However, the direct use of aliphatic aldehydes containing  $\alpha$ -protons has met limitations because the condensation intermediates *N*-arylaldimines are unstable to form isomers, which lead to the formation of by-products (quinolines and secondary amine) [17–19].



For the reason above, only a few works have been reported using aliphatic aldehydes as coupling substrates in Povarov reaction to prepare tetrahydroquinolines. Jørgensen described an organocatalytic cascade reaction that comprises an intramolecular Povarov reaction of styrene-type substrates [20]. *N*-alkylaldimines, which were derived from aniline and aliphatic aldehydes *in situ*, were employed to afford tetrahydroquinolines that are catalyzed by chiral phosphoric acid [21] or by corrosive and air-sensitive  $BF_3 \cdot OEt_2$ [22]. The aza-Diels–Alder reaction of aliphatic *N*-ary laldimines with cyclopentadiene could afford ring-fused tetrahydroquinoline derivatives promoted by an N,N'-dioxide-Sc(OTf)<sub>3</sub> complex [23] or catalyzed by Dy(OTf)<sub>3</sub>, along with the observation of by-products [17,24].

On the other hand, BiCl<sub>3</sub>, cerium ammonium nitrate (CAN), Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O, and SnCl<sub>4</sub> were developed [25,26] as catalysts for the synthesis of tetrahydroquinoline, although the substrates were limited in the reactions. Therefore, developing simple and efficient synthetic methods for directly utilizing aliphatic aldehydes as partner in Povarov reaction, which give varieties of functionalized tetrahydroquinolines, is still interesting and necessary. Herein, we report a three-component Povarov reaction tolerating both aliphatic and aromatic aldehyde, aniline, and olefin, which is mediated by Sn(IV) that is generated from an *in situ* redox reaction of SnCl<sub>2</sub> and FeCl<sub>3</sub> to afford tetrahydroquinoline derivatives.

#### **RESULTS AND DISCUSSION**

Recently, we reported a formation of quinoline derivatives from one-pot reaction of aniline and aldehyde in the presence of an oxidant [27]. During the course of our study on the quinoline's formation, we found that anhydrous tin tetrachloride successfully promoted three-component Povarov

reaction of aniline, n-butyraldehyde, and diisobutylene to produce 4-methyl-4-neopentyl-2-propyltetrahydroquinoline 1 (Table 1). High yield was obtained when 1.2 equiv of SnCl<sub>4</sub> was used (entries 4 and 9). Less than 1 equiv of SnCl<sub>4</sub> led to a low yield of tetrahydroquinoline (entries 1 and 6) and to mainly observed by-product 3-ethyl-2-propylquinoline 2. Higher temperature is preferred for the reaction to obtain an excellent yield (entries 8–10). However, SnCl<sub>4</sub> is quite air-sensitive, which limited the experimental operation. This prompted us to develop a new method to replace this rigorous promoting reagent. SnCl2 is generously available and much stable in the air. It is well known that SnCl<sub>2</sub> is easily oxidized to Sn(IV) by KMnO<sub>4</sub>, iron(III) [28], chromium (IV), copper(II), and so on. Meanwhile, iron(III) chloride is inexpensive, easily available, and nontoxic enough to be a best oxidant [29]. The applications of FeCl<sub>3</sub> in various fields are attracting much attention in chemistry, such as Pechmann condensation [30], Friedel-Crafts reaction [31], and annulation reactions [19]. Thus, we tried to use a SnCl<sub>2</sub>/FeCl<sub>3</sub> system in Povarov reaction with a redox reaction between SnCl<sub>2</sub> and FeCl<sub>3</sub>, where Sn(IV) was generated in situ to promote the reaction of aniline, n-butyraldehyde, and diisobutylene to afford 4-methyl-4-neopentyl-2-propyltetrahydroquinoline 1.

At the beginning,  $SnCl_2$  and  $FeCl_3$  (mole ratio was 1:2) were mixed at room temperature in ethanol. After 5 min,

 Table 1

 Formation of tetrahydroquinoline 1 in the presence of SnCl<sub>4</sub>.<sup>a</sup>



Entry	SnCl <sub>4</sub> (equiv) <sup>b</sup>	Conditions	Yield (%) <sup>c</sup>
1	0.5	25°C, 24 h	0
2	1.0	25°C, 5 h	83
3	1.1	25°C, 6 h	86
4	1.2	25°C, 5 h	93
5	1.3	25°C, 7 h	84
6	0.5	40°C, 24 h	12
7	1.0	40°C, 5 h	85
8	1.1	40°C, 5 h	90
9	1.2	40°C, 3 h	100
10	1.3	40°C, 5 h	97

<sup>a</sup>The ratio of aniline : *n*-butyraldehyde : diisobutylene is 1:1:1, and CH<sub>2</sub>Cl<sub>2</sub> was used as solvent.

<sup>b</sup>The equivalent of SnCl<sub>4</sub> is based on aniline.

<sup>c</sup>GC yield.

the color of the solution became aqua, which indicated the formation of Fe(II). Then, *n*-butyraldehyde, aniline, and diisobutylene were added sequentially. It was noticed that the color of the solution immediately turned to deep red when aniline was added. This phenomenon was similar to the reaction of the same substrates by using SnCl<sub>4</sub> alone as the promoting reagent, which suggested the formation of Sn(IV) in the SnCl<sub>2</sub>/FeCl<sub>3</sub> system. The reaction mixture was stirred at room temperature, and the tetrahydroquinoline was obtained as a mixture of cis and trans isomers in GC overall yield of 13%, accompanied with some 3-ethyl-2-propylquinoline as a by-product. Although the yield of tetrahydroquinoline was low, the result was attractive enough to trigger our interest to study continuously.

In order to improve the yield, we optimized the reaction conditions. The results are summarized in Table 2. Solvents such as dichloromethane and chloroform afforded tetrahydroquinoline in lower yields (entries 1-4). It was found that when 1 equiv of SnCl<sub>2</sub> and 2 equiv of FeCl<sub>3</sub> were stirred for 4 h at 40°C in 1,2-dichloroethane, the reaction of aniline, *n*-butyraldehyde, and diisobutylene proceeded smoothly to produce tetrahydroquinoline 1 in 61% GC combined yield (entry 5). The yield of tetrahydroquinoline was increased to 93% when the preoxidation time was shortened to 2 h and the Povarov reaction time was prolonged to 6 h, respectively (entries 5-7). Likely, the reason for this phenomenon is that some backward redox reaction occurred to decrease the formation of SnCl<sub>4</sub> slightly when the preoxidation time was prolonged. Without preoxidation, the reaction was not good (entry 9). 1 equiv of SnCl<sub>2</sub> is sufficient, and the excess amount of SnCl<sub>2</sub> was not beneficial to the reaction (entries 10 and 11). It should be noted that 0.5 equiv of  $\text{SnCl}_2$  was not efficient for the reaction to proceed (entry 12) similarly with the case of  $SnCl_4$  alone (Table 1, entries 1 and 6).

Generally, a higher temperature is favorable for most redox reactions. Thus, we tried to shorten the preoxidation time by raising the temperature. However, the yield of product was lower at 50°C (entry 13). Actually, the yield was much higher when the reaction was carried out at 30°C (entry 14). We speculated that a lower temperature is helpful for a redox reaction of the  $SnCl_2/FeCl_3$  system. In order to confirm this supposition, the reaction of  $SnCl_2$ and FeCl<sub>3</sub> was carried out at 0°C for 1 h, and then *n*-butyraldehyde, aniline, and diisobutylene were added at room temperature. As expected, the yield of the products was remarkably increased (entry 15). This clearly indicated that the redox reaction of  $SnCl_2/FeCl_3$  is exothermic. The yields of the final product were increased by lowering the preoxidation reaction temperature.

In order to prove that Sn(IV) worked as the active species to promote the reaction of aniline, *n*-butyraldehyde, and diisobutylene,  $SnCl_2$ ,  $FeCl_3$ , and  $FeCl_2$  were examined under the same condition, but no tetrahydroquinoline

Table 2 Formation of tetrahydroquinoline 1 under in situ redox of SnCl<sub>2</sub>/FeCl<sub>3</sub>.



Entry	Solvent	SnCl <sub>2</sub> (equiv) <sup>a</sup>	Preoxidation conditions (°C/h)	Povarov reaction conditions (°C/h)	Yield (%) <sup>b</sup>
1	CHCl <sub>3</sub>	1.0	40/4	40/3	14
2	$CH_2Cl_2$	1.0	40/4	40/3	59
3	$CH_2Cl_2$	1.2	40/3	40/3	15
4	$CH_2Cl_2$	1.2	40/2	40/3	19
5	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.0	40/4	40/3	61
6	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.0	40/3	40/5	78
7	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.0	40/2	40/6	93
8	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.0	40/1	40/2	75
9	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.0	40/0	40/2	33
10 <sup>c</sup>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.2	40/2	40/6	60
11 <sup>c</sup>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.1	40/2	40/6	84
12	CH <sub>2</sub> ClCH <sub>2</sub> Cl	0.5	30/2	30/24	Trace
13	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.0	50/2	50/3	81
14	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.0	30/2	30/1	97
15	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1.0	0/1	30/5	98 (78)

<sup>a</sup>The equivalent of SnCl<sub>2</sub> is based on aniline.

<sup>b</sup>GC overall yield.

<sup>c</sup>A little polymer of diisobutylene was detected and analyzed by GC-MS.

Table 3

Formation of tetrahydroquinolines from various aldehydes, anilines, and diisobutylene.



Entry	R <sub>1</sub>	R <sub>2</sub>	Povarov reaction time (h)	cis/trans <sup>a</sup>	Yield (%) <sup>b</sup>
1	Н	$C_3H_7$	5	1.18:1 (1)	98 (78)
2 <sup>c</sup>	Н	CH <sub>3</sub>	6	1.41:1 (3)	73 (40)
3	Н	C7H15	7	1.29:1 (4)	86 (63)
4 <sup>d</sup>	Н	ph	24	_	Trace
5 <sup>e</sup>	Н	Ph	23	1.22:1 (5)	76 (57)
6	4-CH <sub>3</sub>	$C_3H_7$	2	1.02:1 (6)	92 (75)
7	4-OCH <sub>3</sub>	$C_3H_7$	5	1.08:1 (7)	83 (74)
8	4-NO <sub>2</sub>	$C_3H_7$	9	1.02:1 (8)	85 (71)
9	4-Cl	$C_3H_7$	2	1:1.01 (9)	98 (68)
10	4-Br	$C_3H_7$	1	1.03:1 (10)	99 (79)
11	2-CH <sub>3</sub>	$C_3H_7$	5	1:1.07 (11)	100 (80)
12	2-Cl	$C_3H_7$	5	1.19:1 (12)	84 (82)
13	3-CH <sub>3</sub>	$C_3H_7$	7	1.16:1 (13)	(52)
14	3-Cl	C <sub>3</sub> H <sub>7</sub>	21	2:7:1:4 (14)	(63)

<sup>a</sup>Analyzed by GC.

<sup>b</sup>GC overall yield, isolated yields are in parentheses.

<sup>°</sup>2h of preoxidation. <sup>d</sup>74% GC yield of *N*-benzylideneaniline **15** was obtained.

<sup>e</sup>Benzaldehyde and aniline were taken place for 5 h, and then diisobutylene was added.

products were obtained; only 9%, 7%, and 7% of 3-ethyl-2propylquinoline were isolated, respectively. Combining with the color change phenomenon in the reaction solution, we believed that Sn(IV) was formed from the SnCl<sub>2</sub>/FeCl<sub>3</sub> system *in situ* to promote an aza-Diels–Alder reaction effectively toward the formation of tetrahydroquinoline derivatives. Zhang [32] reported that polymerization of methyl methacrylate was catalyzed by a SnCl<sub>2</sub>/FeCl<sub>3</sub> system, and it seemed that redox of SnCl<sub>2</sub> and FeCl<sub>3</sub> occurred. In addition, Lewis acids such as InCl<sub>3</sub>, TiCl<sub>4</sub>, FeCl<sub>3</sub>, [bmim]BF<sub>4</sub>, I<sub>2</sub>, ZrOCl<sub>2</sub>·8H<sub>2</sub>O, and CuCl were also examined as promoting agents in our reaction, but only 3-ethyl-2-propylquinoline was afforded instead of tetrahydroquinoline derivatives.

Several aldehydes were examined, and the results are listed in Table 3. The three-component "one-pot" reactions proceeded smoothly to afford the corresponding products when aliphatic aldehydes were used as partners, such as acetaldehyde, n-butyraldehyde, and caprylic aldehyde (Table 3, entries 1–3). When the reaction of benzaldehyde was carried out, only a trace of tetrahydroquinoline was produced along with 74% GC yield of N-benzylideneaniline 15 and some polymer of diisobutylene (Table 3, entry 4). It seems that the reaction of benzaldehyde and aniline was far more sluggish. Moreover, probably, the intermediate N-benzylideneaniline is stable [33], and the polymerization of diisobutylene competed with the cycloaddition of N-benzylideneaniline and diisobutylene, leading to a decrease in the yield of tetrahydroquinoline. Therefore, the reaction of benzaldehyde and aniline was carried out firstly for 5 h after the preoxidation of SnCl<sub>2</sub>/FeCl<sub>3</sub>, in which lots of N-benzylideneaniline were formed, and then diisobutylene was added. As can be seen in Table 3 (entry 5), the corresponding product was obtained in an overall GC yield of 76%, and the isolated yield was 57%.

The reactions with various anilines were also studied (Table 3, entries 6–14). It was found that aniline with an electron-withdrawing group or electron-donating groups could work well to afford the corresponding products in high yields. Unfortunately, the process displayed poor stereoselectivity, thereby leading to nearly equimolecular mixtures of diastereomers.

The structures of compounds were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and HRMS. The products were obtained as a mixture of cis and trans isomers, which were not separable by column chromatography. 6-Chloro-4-methyl-4-neopentyl-2-propyltetrahydroquinoline (**9**-*trans*) and 6-bromo-4-methyl-4-neopentyl-2-propyl tetrahydroquinoline (**10**-*trans*) were isolated by recrystallization, respectively. Structures of **9**-*trans* and **10**-*trans* were confirmed by X-ray analysis, as shown in Figure 1. It clearly demonstrates that structures of compound **9**-*trans* and **10**-*trans* were in trans configuration.

The reactions of m-substituted anilines should give four isomers, as shown in Scheme 1. In fact, the reaction of



Figure 1. X-ray molecular structure of 9 and 10 with the atom numbering.

Scheme 1. Possibility of isomers with the reaction of *m*-substituted aniline.



*n*-butyraldehyde, *m*-chloroaniline, and diisobutylene produced four isomers with a ratio of 2:7:1:4 in an overall isolated yield of 63% (Table 3, entry 14). However, when the reaction of *n*-butyraldehyde, *m*-toluidine, and diisobutylene was carried out, only two isomers were observed with a ratio of 1.16:1 in an overall isolated yield

 Table 4

 Reaction with various alkenes.



Entry	Alkenes <sup>a</sup>	Povarov reaction time (h)	Tetrahydroquinolines cis/trans <sup>b</sup>	Yield (%) <sup>c</sup>
1 2	$\begin{array}{c} H_2C=CH(CH_2)_3CH_3\\ \\ \hline \\ CH=CH_2\\ \hline \\ \hline \\ \end{array}$	23 4	2.36:1 (16) — (17)	52 (45) 100 (74)
3		5	— ( <b>18</b> )	58 (37)
4	(3 equiv)	5	— ( <b>19</b> )	85

<sup>a</sup>Unless noted otherwise, the alkenes were used as 1 equiv (based on aniline). <sup>b</sup>Analyzed by GC. <sup>c</sup>GC overall yield, isolated yields are in parentheses.

of 52% (Table 3, entry 13). Unfortunately, these isomers could not be separated as pure compounds by column chromatography, which is similar to the cases in literature [13,34].

As the dienophile component, alkenes play an important role in [4+2]-cycloaddition. Reactions of highly activated alkenes are usually beneficial to achieve the goal in high yields. In the report of Kouznetsov [35], the dienophile component is usually limited to electron-rich alkenes, such as enamines, enamides, and enol ethers, and cyclic conjugated dienes. In our reactions, many kinds of alkenes were examined, such as styrene, cyclopentadiene, and hexene. The results are listed in Table 4. It was found that reactions of hexene and styrene proceeded well to give the corresponding products in good to excellent yields (Table 4, entries 1 and 2). The reactions of styrene and cyclopentadiene gave one single diastereomer respectively in high yield. It should be noted that the reaction of ethyl vinyl ether afforded by-product 3-ethyl-2-propylquinoline 2. The reaction of cyclohexene did not produce tetrahydroquinolines under the certain condition.

The mechanism of the Povarov reaction has long been a topic of controversy. Several recent theoretical studies indicated that the Povarov reactions proceed through either a concerted [36] mechanism or a stepwise mechanism [21b,24,31,37] via a cationic intermediate according to the nature of the dienophile used. In our case, the results wherein using the benzaldehyde (Table 3, entries 4 and 5), occurring under our experimental conditions, first

afforded *N*-benzylideneaniline led us to speculate that a stepwise mechanism could account for the formation of tetrahydroquinoline from aniline, aldehyde, and alkene mediated by *in situ* redox of  $SnCl_2$  and  $FeCl_3$ . Thus, the reaction would be viewed as a nucleophilic-type attack of alkene to the *N*-arylimine with a concomitant cyclization with formation of zwitterionic intermediates [38].

### CONCLUSION

In conclusion, a highly efficient Povarov reaction of aniline, aldehyde, and alkene promoted by Sn(IV), which was generated *in situ* from redox reaction of SnCl<sub>2</sub> and FeCl<sub>3</sub>. was developed. The product tetrahydroquinoline derivatives were obtained in high yields. It was found that aniline with electron-withdrawing groups or electron-donating groups could be used in the reaction to give the corresponding products in excellent yield. The reactions of aliphatic aldehydes and aromatic aldehydes were also efficient, which significantly expanded the scope of substrates accessible through the Povarov reaction. The SnCl<sub>2</sub> and FeCl<sub>3</sub> used in the reaction are more environment-friendly and easily available than anhydrous SnCl<sub>4</sub> or other strong corrosive Lewis acids. To the best of our knowledge, this is the first example to report a SnCl<sub>2</sub>/FeCl<sub>3</sub> system used in a three-component Povarov reaction to synthesize tetrahydroquinolines, which aroused great interest in the synthesis of heterocyclic compounds. Further detailed investigations into the reaction mechanism and the role of Sn(IV) are in progress.

## EXPERIMENTAL

Unless noted otherwise, all starting materials were obtained from commercial supplies and used without further purification. The reaction was monitored by GC analysis. Mass spectra were determined on an Apex IV FT-ICR mass spectrometer (Bruker Company, Madison, WI). <sup>1</sup>H-NMR spectra were recorded at JEOL JNM-ECA 600 in CDCl<sub>3</sub> using TMS as internal standard. <sup>13</sup>C-NMR spectra were recorded at 150 MHz using CDCl<sub>3</sub> as an internal standard. Column chromatography was performed on silica gel (300–400 mesh); gradients of petroleum ether and Et<sub>2</sub>O were used as eluent.

General procedure: synthesis of 4-methyl-4-neopentyl-2-p**ropyltetrahydroquinoline** (1). SnCl<sub>2</sub> (0.3694 g, 1.9483 mmol) was added to a dried Schlenk tube with a Teflon-coated magnetic stir bar under N<sub>2</sub> atmosphere, and then CH<sub>2</sub>ClCH<sub>2</sub>Cl (12.7 mL) was added as a solvent. FeCl<sub>3</sub> (0.6320 g, 2.0×1.9483 mmol) was added with stirring. This reaction was stirred at 0°C for 1 h. The color of this solution turned to aqua. Then, n-butyraldehyde (0.176 mL, 1.9483 mmol), aniline (0.178 mL, 1.9483 mmol), and diisobutylene (0.304 mL, 1.9483 mmol) were added sequentially to the solution at room temperature. The color turned to white from deep red during this process. Dodecane was added as an internal standard. The reaction was stirred at room temperature and monitored by GC analysis until the reaction was finished, and then it was quenched with 3M ammonia aqueous solution and extracted with  $Et_2O$  (30 mL × 3). The combined organic layers were washed with H<sub>2</sub>O and brine in sequential order, then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The residue was purified by silica gel chromatography using (Et<sub>2</sub>O: petroleum ether = 1:20) as eluent to give the product as a mixture of cis and trans isomers of 4-methyl-4-neopentyl-2-propyl tetrahydroquinoline 1.

The other compounds were prepared similarly.

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