Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 5028

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COMMUNICATION

$FeCl_3$-Mediated synthesis of polysubstituted tetrahydroquinolines *via* domino Mannich/Friedel–Crafts reactions of aldehydes and amines†

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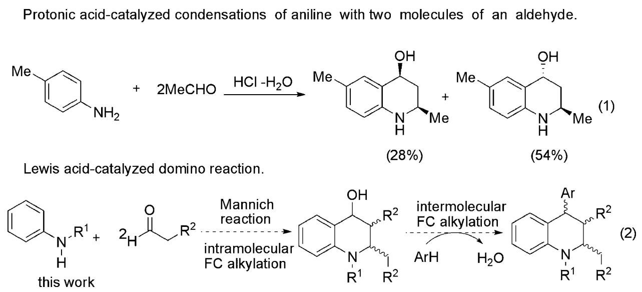
Received 25th April 2011, Accepted 17th May 2011
DOI: 10.1039/c1ob05646h

A useful method to construct highly substituted tetrahydroquinolines has been developed through an iron(III) chloride-mediated domino Mannich and intramolecular Friedel–Crafts alkylation followed by intermolecular Friedel–Crafts alkylation reactions of aliphatic aldehydes with aromatic amines.

Tetrahydroquinoline derivatives are an important class of biologically active compounds, which are widely used in organic synthesis and pharmaceutical chemistry.[1] Currently, much effort in this area is focused on constructing polysubstituted tetrahydroquinolines, for instance the aza Diels–Alder reactions,[2] hydrogenations of quinolines,[3] benzotriazole-mediated indirect electrophilic substitution,[4] electrophilic cyclization,[5] ring expansion reactions,[6] palladium-catalyzed cross-coupling reactions,[7] organocatalytic hydroarylations of enals,[8] hydroaminations of aniline alkynes,[9] and intramolecular redox reactions.[10] However, to the best of our knowledge, intermolecular Friedel–Crafts (FC) alkylation to construct polysubstituted tetrahydroquinolines has been rarely reported. Crabb *et al.* reported a protonic acid-catalyzed condensation of anilines with two molecules of an aldehyde affording a mixture of the *cis*- and *trans*- isomers of 2,6-dimethyl-4-hydroxy-1,2,3,4-tetrahydroquinoline in an approximate ratio of 1 : 2 [Scheme 1, eqn (1)].[11] In recent years, significant efforts have been focused on benzylic arylation chemistry utilising Friedel–Crafts alkylations.[12] Friedel–Crafts reactions of benzylic alcohols have been studied with traditional Lewis and Brønsted acids.[13] Beller *et al.* demonstrated that late transition metal salts such as $HAuCl_4$, $IrCl_3$, $[MesW(CO)_3]$, $RhCl_3$, H_2PdCl_4, H_2PtCl_6 and $FeCl_3$ effectively catalyze the addition of benzyl acetates and benzyl alcohol to arenes.[14] We envisioned that $FeCl_3$ is an attractive alternative to rare-earth triflates since it is non-toxic, cheap and readily available.[15] With these thoughts in mind, we decided to test a new domino reaction involving a cascade Mannich/intramolecular Friedel–Crafts alkylation/intermolecular Friedel–Crafts alkylation sequence.



Scheme 1 Proposed domino Mannich/intramoleculer FC alkylation/intermolecular FC alkylation reactions.

Domino reactions are attractive to industrial and laboratory chemists because of their potential to save solvents, reagents, time and energy.[16] Our group is persistently interested in domino reactions to synthesize various functionalized heterocyclic compounds.[17] Herein, we report our results of the cascade reactions of aliphatic aldehydes with aromatic amines in the presence of $FeCl_3$. This strategy provides a pathway in one-pot manner to the synthetically useful tetrahydroquinolines.

We conducted many trials to approach our goal by treating a threefold excess of *N*-methylaniline **1a** (1.2 mmol) with phenylacetaldehyde **2a** (0.4 mmol) in the presence of 0.3 equivalents of iron catalyst and 50 mg of 4 Å molecular sieves (MS) in CH_3NO_2 (3 mL) under argon. Gratifyingly, the desired product **3a** was formed in 33% and 38% yield by using of $FeCl_3$ and $FeBr_2$ respectively, after 8 h at 60 °C (Table 1, entries 1 and 4). No reaction was observed in anisole when $FeBr_2$ was used as catalyst, whereas $FeCl_3$ gave a 78% yield (entries 5 and 6). Using anisole as solvent, the yield was improved greatly. The reaction performed in other solvents afforded inferior yields (entries 7–10). Lewis acid such as $Sc(OTf)_3$ and $InCl_3$ showed comparable catalytic activity to give **3a** in 61% and 71% yield, respectively (entries 13 and 14). Brønsted acids were also examined, and only $HSbF_6{\cdot}6H_2O$ worked and gave 62% yield (entry 16), whereas TFA and TsOH did not catalyze this reaction. 10 mol% and 20 mol% of $FeCl_3$ gave lower yields (entries 19 and 20). When the reaction was conducted at ambient temperature, it proceeded with a lower reaction yield (entry 21, 45%). Surprisingly, a higher reaction temperature did not increase the yield (entry 22, 51%). As the reaction proceeds with loss of two equivalents of

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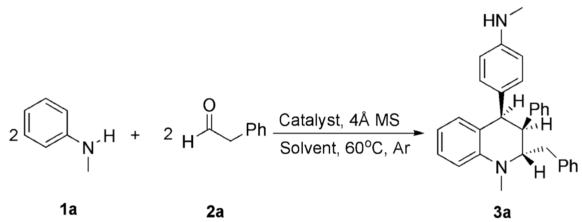
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra for compounds **3a–3k**, **4a–4f**. CCDC reference number 807037. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob05646h

Table 1 Optimization of reaction conditions[a]



Entry	Catalyst	Loading (mol%)	Solvent	Yield (%)[b]
1	$FeCl_3$	30	CH_3NO_2	33
2	$Fe(NO_3)_3$	30	CH_3NO_2	NR
3	$Fe(acac)_3$	30	CH_3NO_2	NR
4	$FeBr_2$	30	CH_3NO_2	38
5	$FeBr_2$	30	Anisole	NR
6	$FeCl_3$	30	Anisole	78
7	$FeCl_3$	30	CH_3CN	48
8	$FeCl_3$	30	DCE	39
9	$FeCl_3$	30	Toluene	38
10	$FeCl_3$	30	Chlorobenzene	22
11	$AlCl_3$	30	Anisole	NR
12	$Cu(OTf)_2$	30	Anisole	32
13	$Sc(OTf)_3$	30	Anisole	61
14	$InCl_3$	30	Anisole	71
15	$BF3{\cdot}Et_2O$	30	Anisole	47
16	$HSbF_6{\cdot}6H_2O$	30	Anisole	62
17	TFA	30	Anisole	NR
18	TsOH	30	Anisole	NR
19	$FeCl_3$	10	Anisole	15
20	$FeCl_3$	20	Anisole	31
21[c]	$FeCl_3$	30	Anisole	45
22[d]	$FeCl_3$	30	Anisole	51

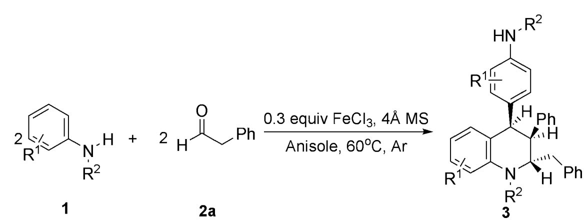
[a] Conditions: 1.2 mmol **1a**, 0.4 mmol **2a** and 50 mg of 4 Å MS with 0.3 equivalents of catalyst in solvent (3.0 mL) at 60 °C under Ar after 8 h. [b] Isolated yield. [c] Performed at room temperature after 24 h. [d] Performed at 80 °C.

water, the addition of 4 Å MS was essential. After the systematic screening, the use of 0.3 equivalents of $FeCl_3$ with 4 Å MS in dry anisole at 60 °C under argon was considered to be the optimum and selected as the standard conditions.

With the optimized conditions in hand, we first explored the scope of amines for this reaction, as summarized in Table 2. The reaction proceed well with substituents on the *meta* positions of *N*-methylanilines. Aromatic amines with electron-donating groups on the benzene rings gave higher yields than those with electron-withdrawing groups except the 3-methoxy group (entries 2–7). This shows that steric effects had a strong influence on the reaction. With a 3,5-dimethyl group on the aniline, however, no desired product was obtained (entry 8). The methodology also tolerated well the R^2 position being occupied by a phenyl group, affording the desired product **3h** in 58% yield (entry 9). To investigate the steric effects, we found that 3-methyldiphenylamine **1i** reacted with **2a** to produce the major product **3i** in 47% yield, showing little steric hindrance (entry 10). Interestingly, the use of a highly hindered secondary amine **1j** was also allowed, which gave an approximate 1 : 1 mixture of two isomers of 5,6,7-trisubstituted julolidine **3j** (entry 11).[18] Furthermore, *N*-methyl-1-naphthylamine gave the by-product 5-methyl-1-naphthylamine in 50% yield, but the desired product **3k** was obtained in 10% yield (entry 12). Finally, it is worthwhile to note that *N*-methylanilines with *ortho* and *para* substituents didn't work at all. According to the ^1H NMR and X-ray diffraction analysis of **3e** (Fig. 1), the 2,3-*trans*-2,4-*trans* isomers were proved to be the major products; in most cases, the minor isomers exhibited the 2,3-*trans*-2,4-*cis* configuration.

To expand further the scope of the reaction, we also investigated other aldehydes. Aldehydes unbranched at the α-position react similarly producing 1,2,3,4-tetrahydroquinoline derivatives. Table 3 demonstrates the generality and scope of the reaction

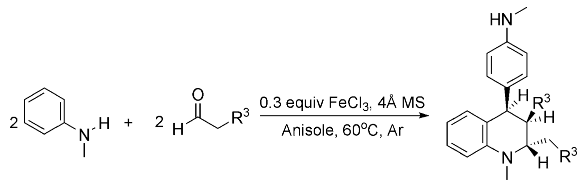
Table 2 $FeCl_3$-Mediated synthesis of tetrahydroquinolines with aromatic amines[a]



Entry	1: R^1	1: R^2	Time (h)	Yield (%)[b]	Ratio of isomers[c]
1	H	Me	8	78 (**3a**)	88 : 12
2	3-Me	Me	10	72 (**3b**)	72 : 28
3	3-OMe	Me	12	42 (**3c**)	75 : 25
4	3-F	Me	10	69 (**3d**)	90 : 10
5	3-Cl	Me	10	65 (**3e**)	86 : 14
6	3-Br	Me	14	56 (**3f**)	89 : 11
7	3-CO_2Me	Me	12	47 (**3g**)	87 : 13
8	3,5-Dimethyl	Me	10	NR	—
9	H	Ph	10	58 (**3h**)	86 : 14
10	H	3-Me-Ph	10	47 (**3i**)	79 : 21
11	1,2,3,4-Tetra-hydroquinoline		12	38 (**3j**)	51 : 49
12	*N*-Methyl-1-naphthylamine		12	10 (**3k**)	67 : 33

[a] Reactions were conducted with **1** (1.2 mmol), **2a** (0.4 mmol) and 50 mg of 4 Å MS with 0.3 equivalents of $FeCl_3$ in anisole (3 mL) at 60 °C under Ar. [b] Isolated yield. [c] The ratio of (2,3-*trans*-2,4-*trans*) isomer to (2,3-*trans*-2,4-*cis*) isomer was determined by ^1H NMR analysis.

Table 3 $FeCl_3$-Mediated synthesis of tetrahydroquinolines with aliphatic aldehydes[a]



1a 2 4

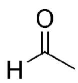
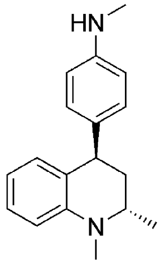
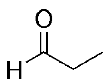
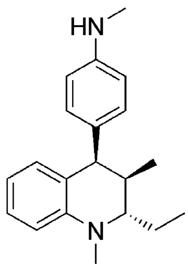
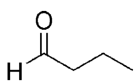
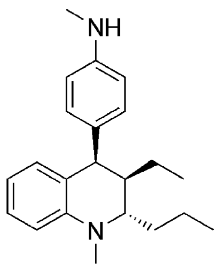
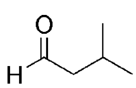
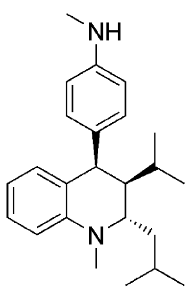
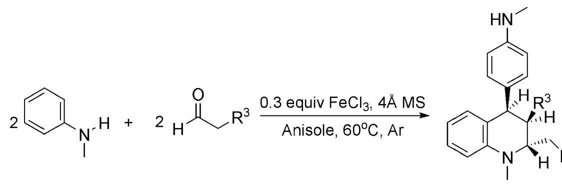
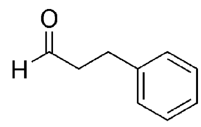
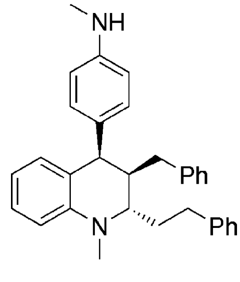
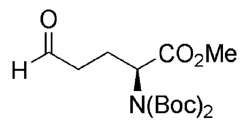
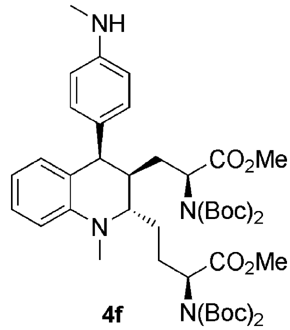
Entry	Aldehyde	Product	Yield (%)[b]	Ratio of isomers[c]
1	 **2a**	 **4a**	38	90 : 10
2	 **2b**	 **4b**	48	94 : 6
3	 **2c**	 **4c**	40	88 : 12
4	 **2d**	 **4d**	38	>99 : 1

Table 3 *(Contd.)*



1a **2** **4**

Entry	Aldehyde	Product	Yield (%)[b]	Ratio of isomers[c]
5	 **2e**	 **4e**	70	48 : 52
6	 **2f**	 **4f**	42	<1 : 99[d]

[a] Reactions were conducted with **1a** (1.2 mmol), 0.4 mmol of **2**, 50 mg of 4 Å MS and 0.3 equivalents of $FeCl_3$ in anisole (3 mL) at 60 °C under Ar after 10 h. [b] Isolated yield. [c] Determined by the ^{1}H NMR analysis. [d] dr = 3 : 1.

of *N*-methylaniline **1a** with aliphatic aldehydes **2** to form the corresponding products under optimized conditions. However, acetaldehyde was less efficient in this transformation (entry 1). The increase in the length of the aldehyde chain caused a decrease in yield of the reaction (entries 2-4). When octanal was added to the reaction system, no desired product was observed. Enolization of the aldehyde becomes difficult with the increase in chain length. In addition, reactions of 3-phenylpropanal with *N*-methylaniline can also be carried out, affording a mixture of 1 : 1 isomers, which was determined from the ^{1}H NMR spectrum, in 70% combined yield (entry 5). When enantiomerically pure methyl-(*S*)-2-*N*,*N*-di-*tert*-butoxycarbonyl-5-oxopentanoate **2f**, which can be readily synthesized in four conventional steps from L-glutamic acid,[19] was subjected to the standard reaction conditions, the product **4f** was obtained as a mixture of 3 : 1 diastereoisomers (entry 6). The enantiomeric excess of each isomer was determined to be higher than 99% by chiral HPLC analysis. It appears that **2f** did not racemize during this process. The relative configurations of the major isomers **4a**, **4b**, and **4f** were assigned by Nuclear Overhauser Effect (NOE) spectroscopy (*cf.* ESI†) and additionally confirmed by an X-ray crystal structure analysis of **3e** (Fig. 1).

The mechanism for this transformation is proposed to be as depicted in Scheme 2.[20] Iminium ion **A** is formed by the condensation of aniline **1** with aldehyde **2**, which adds to a molecule of iron(III) enolate[21] **2′** to produce aldehyde **B** by a Mannich reaction.[22] Then, aldehyde **B** undergoes an $FeCl_3$-catalyzed intramolecular Friedel–Crafts type ring closure to furnish a benzyl alcohol intermediate **C**, which in the presence of a proton loses water and releases $FeCl_3$ to produce carbocation intermediate **D**. Finally, excess *N*-protected aniline[23] as the aromatic nucleophile attacks the carbocation intermediate **D** *via* an intermolecular Friedel–Crafts reaction, which loses a proton to afford tetrahydroquinoline skeleton **3** or **4**. In this transformation, carbocation intermediate **D** is the key intermediate leading to compound **3** or **4**. If we decrease the temperature or reduce the catalyst loading, there will be some iminium ion **A** left unreacted. Thus, the S_N1 step to generate carbocation intermediate **D** is the rate determining step.

In summary, we have developed a simple method for a one-pot domino Mannich/intramolecular Friedel–Crafts alkylation/intermolecular Friedel–Crafts alkylation reactions by using iron(III) chloride as catalyst, which leads to the synthesis of 1,2,3,4-tetrahydroquinoline derivatives. The advantages of this method

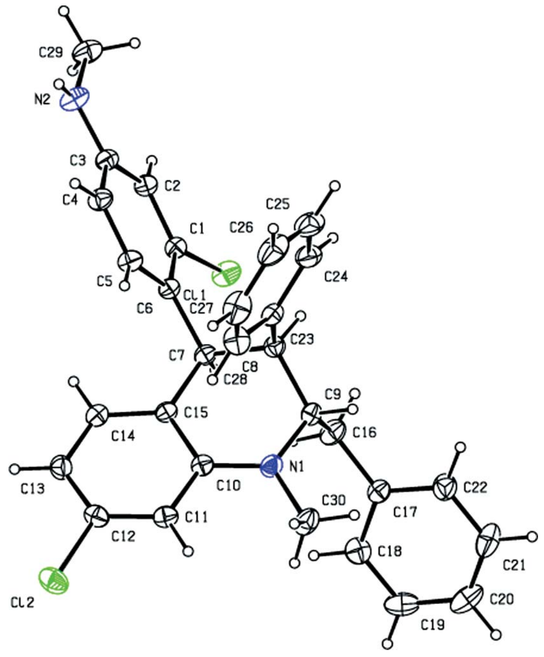
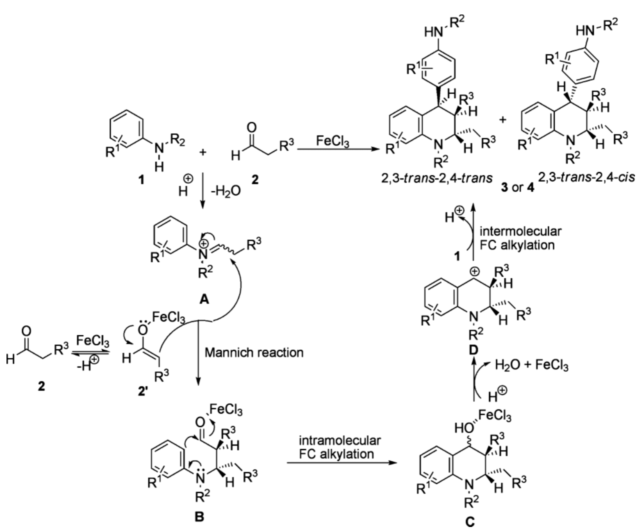


Fig. 1 X-Ray structure of compound **3e**.



Scheme 2 Plausible reaction mechanism.

include good substrate generality, mild conditions, environment-friendly catalyst and easy availability of starting materials. Further exploration of Lewis acid-catalyzed reactions to construct useful structures is the future goal of our research group.

Typical experimental procedure for $FeCl_3$-mediated synthesis of 3a–3k, 4a–4f

To a solution of **1** (1.2 mmol), **2** (0.4 mmol) and 4 Å MS 50 mg in dry anisole (3 mL) was added $FeCl_3$ (19.5 mg, 0.12 mmol). The mixture was stirred under argon at 60 °C. On completion of the reaction as shown by TLC analysis, the reaction mixture was filtered and partitioned between sat. aq. $NaHCO_3$ and ethyl acetate. The aqueous layer was further extracted with ethyl acetate (3 × 20 mL). The combined organic extracts was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography using petroleum ether/ethyl acetate as eluent on alkalescent silica gel to give the desired product.

Acknowledgements

We thank the NSF (NSF-20872052, NSF-20090443, NSF-21072080), and the Fundamental Research Funds for the Central Universities (lzujbky-2010-k09) for financial support.

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