Organic LETTERS

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# Iron-Mediated Carboarylation/Cyclization of Propargylanilines with Acetals: A Concise Route to Indeno[2,1-*c*]quinolines

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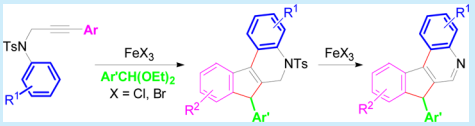
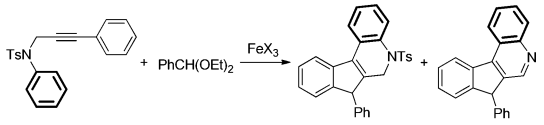
Supporting Information

**ABSTRACT:** $FeCl_3$- and $FeBr_3$-mediated tandem carboarylation/cyclization of propargylanilines with diethyl benzaldehyde acetals furnished the tetracyclic core of indeno[2,1-*c*]quinolines. 5-Tosyl-6,7-dihydro-5*H*-indeno[2,1-*c*]-quinoline and 7*H*-indeno[2,1-*c*]quinoline derivatives were obtained in good to excellent yields, respectively, by tuning the $FeX_3$ loadings and/or reaction temperatures.




Construction of functionalized carbo- and heteropolycyclic architectures with minimum operations from relatively simple building blocks has been a challenging task in organic synthesis.[1] Tetracyclic indenoquinoline fused with quinoline[2] and indene[3] frameworks is a common structural unit in a number of biologically active natural products and pharmaceuticals such as DNA topoisomerase inhibitor TAS-103[4] and its analogues **I**[5] and **II**,[6,7] etc., for anticancer treatment. Time-consuming multistep procedures have usually been applied to access an indeno[2,1-*c*]quinoline core consisting of tetracycles A–D, involving Diels–Alder[5] and Friedel–Crafts[6] reactions, cyclization,[8] and addition to carbonyl compounds.[9] Alkynes were documented to undergo versatile cycloaddition, carbocyclization, and/or cycloisomerization[10,11] to form quinolines,[12] indeno[1,2-*b*]quinolines,[13] and indeno[1,2-*c*]quinolines,[14] while indeno[2,1-*c*]quinolines have not yet been prepared by such methods.

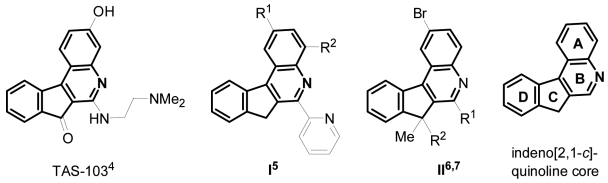
**Table 1. Screening of Reaction Conditions**[a]




1a 2a 3a 4a

| | | | yield[b] (%) | |
|---|---|---|---|---|
| entry | [Fe] (equiv) | temp (°C) | **3a** | **4a** |
| 1 | $FeCl_3$ (0.2) | 80 | 73 | 9 |
| 2[c] | $FeBr_3$ (0.2) | 80 | 75 | 14 |
| **3** | **$FeCl_3$ (0.3)** | **80** | **75** | **18** |
| 4 | $FeBr_3$ (0.3) | 80 | 71 | 19 |
| 5 | $FeCl_3$ (1.0) | 80 | 56 | 37 |
| 6 | $FeBr_3$ (1.0) | 80 | 56 | 31 |
| 7[d] | **$FeCl_3$ (1.0)** | **25** | **72** | **18** |
| 8[d] | $FeBr_3$ (1.0) | 25 | 72 | 21 |
| 9 | $FeBr_3$ (2.0) | 80 | | 54 |
| 10 | $FeBr_3$ (2.5) | 80 | | 67 |
| **11** | **$FeBr_3$ (3.0)** | **80** | | **82** |
| **12** | **$FeCl_3$ (3.0)** | **80** | | **73** |
| 13 | $FeCl_3 \cdot 6H_2O$ (3.0) | 80 | | 43 |
| 14 | $FeBr_3$ (3.0) | 100 | | 69 |
| 15 | $FeBr_3$ (3.0) | 60 | | 69 |
| 16 | $FeBr_3$ (3.0) | 25 | 34 | 31 |
| 17 | $FeCl_3$ (3.0) | 25 | | 47 |

[a]Conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), DCE (3 mL), $N_2$, 5 h. [b]Isolated yield. [c]95% conversion for **1a**. [d]**2a** (0.45 mmol), $CH_2Cl_2$ (3 mL), 18 h. DCE = 1,2-dichloroethane.

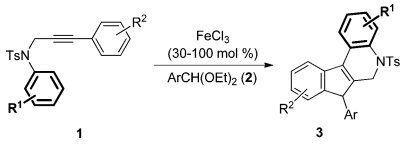



Recently, iron salts have been paid much attention as promising alternatives to traditional transition-metal catalysts[15] and also employed for the synthesis of polycyclic compounds.[16] $Fe(OTf)_3$ catalyzed the intramolecular hydroarylation of alkynes with electron-deficient arenes, building 1,2-dihydroquinolines and phenanthrenes.[12c] $FeCl_3$ mediated the intramolecular isomerization/cyclodehydration of substituted 2-[(indoline-3-ylidene)(methyl)]benzaldehydes to form benzo[*b*]carbazoles,[16b] which were used for the synthesis of indeno-fused heterocycles.[16c] We recently reported $FeX_3$-promoted Prins-type cyclization of alkynyl acetals[17] and intermolecular cyclization of diynes with acetals to give tricyclic compounds.[18] Herein, we report $FeX_3$-mediated carboarylation/cyclization/detosylation of propargylanilines with benzaldehyde acetals for the synthesis of indeno[2,1-*c*]quinolines.

**Received:** October 16, 2014

 © XXXX American Chemical Society  dx.doi.org/10.1021/ol503039j | *Org. Lett.* XXXX, XXX, XXX–XXX

**Table 2. $FeCl_3$-Catalyzed Synthesis of 5-Tosyl-6,7-dihydro-5*H*-indeno[2,1-*c*]quinolines (3)[a]**




| entry | 1 / Ar (2) | yield[b] | entry | 1 / Ar (2) | yield[b] |
|---|---|---|---|---|---|
| 1 | **1a**, X = H / Ph (**2a**) | **3a**, 75% | 11 | **1k** / Ph (**2a**) | **3k**, 89% |
| 2 | **1b**, X = Me / Ph (**2a**) | **3b**, 73% | 12 | **1l** / Ph (**2a**) | **3l**, 9% + **5a**, 53%<br>**3l**, 42%[d] + **5a**, 31%[d] |
| 3 | **1c**, X = OEt / Ph (**2a**) | **3c**, 71% | 13 | **1m** / Ph (**2a**) | **3m**, 35% + **5b**, 46% |
| 4 | **1d** / Ph (**2a**) | **3d**, 82% (90%)[c] | 14 | **1a** / 4-$MeC_6H_4$ (**2b**) | **3n** (R = 4-Me), 69%[d] |
| 5 | **1e**, X = Cl / Ph (**2a**) | **3e**, 82%[d] | 15 | **1a** / 3-$MeC_6H_4$ (**2c**) | **3o** (R = 3-Me), 71%[d] |
| 6 | **1f**, X = F / Ph (**2a**) | **3f**, 77%[d] | 16 | **1a** / 4-$ClC_6H_4$ (**2d**) | **3p** (R = 4-Cl), 73%[d] |
| 7 | **1g** / Ph (**2a**) | **3g**, 78%[d] | 17 | **1a** / 4-$BrC_6H_4$ (**2e**) | **3q** (R = 4-Br), 79%[d] |
| 8 | **1h** / Ph (**2a**) | **3h**, 75%[d] | 18 | **1a** / 3-$BrC_6H_4$ (**2f**) | **3r** (R = 3-Br), 58% |
| 9 | **1i** / Ph (**2a**) | **3i**, 77% | 19 | **1a** / 4-$FC_6H_4$ (**2g**) | **3s** (R = 4-F), 69% |
| 10 | **1j** / Ph (**2a**) | **3j**, 64% | 20 | **1a** / 2-$FC_6H_4$ (**2h**) | **3t** (R = 2-F), 80% |
| | | | 21 | **1a** / 4-$NO_2C_6H_4$ (**2i**) | **3u** (R = 4-$NO_2$), 63%[d] |
| | | | 22 | **1a** / 3-$CF_3C_6H_4$ (**2j**) | **3v** (R = 3-$CF_3$), 64%[d] |
| | | | 23 | **1a** / 2-naphthyl (**2k**) | **3w**, 63% |

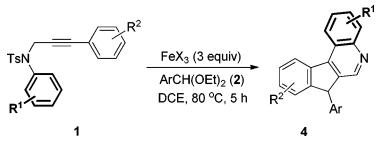
[a]Conditions: **1** (0.3 mmol), **2** (0.6 mmol), $FeCl_3$ (0.09 mmol), DCE (3 mL), 80 °C, $N_2$, 5 h. [b]Isolated yield. [c]0.09 mmol $FeBr_3$ was used as the catalyst. [d]Conditions: **1** (0.3 mmol), **2** (0.45 mmol), $FeCl_3$ (0.3 mmol), $CH_2Cl_2$ (3 mL), 25 °C, $N_2$, 18 h.

Initially, the reaction of propargylaniline (**1a**) with diethyl benzaldehyde acetal (**2a**) was performed to screen the reaction conditions (Table 1). With 20 mol % $FeCl_3$ as the catalyst at 80 °C, the reaction proceeded to form 5-tosyl-6,7-dihydro-5*H*-indeno[2,1-*c*]quinoline (**3a**, 73%) and 7*H*-indeno[2,1-*c*]-quinoline (**4a**, 9%), achieving 100% conversion for **1a** (Table 1, entry 1). Increasing the $FeX_3$ loading rendered **1a** to be completely converted (Table 1, entries 1−4), but use of 1 equiv of $FeX_3$ deteriorated the selectivity to yield **3a** (56%) and **4a** (<40%). Longer reaction time enhanced the yield of **4a** to 42−47%. To our delight, the reaction afforded **3a** in 72% yield at ambient temperature (Table 1, entries 7 and 8). At 80 °C, $FeBr_3$ (3 equiv) acted more efficiently than $FeCl_3$ and $FeCl_3 \cdot 6H_2O$ to generate **4a** (82%) (Table 1, entries 9−13). Varying temperatures at 100 or 60 °C by using $FeBr_3$ as the promoter lowered the yield of **4a** (69%), and ambient temperature led to indiscriminative formation of **3a** (34%) and **4a** (31%) (Table 1, entries 14−17). Thus, the optimal conditions for the preparation of **3a** and **4a** (Table 1, entries 3 and 11) were achieved. It is noted that other Lewis acids such as $SnCl_4$ could also promoted the reaction: under the conditions employed for entry 7 of Table 1, the reaction using 1 equiv of $SnCl_4$ afforded **3a** in 54% yield.

Under the optimized conditions, the substrate scope for the synthesis of **3** was explored (Table 2). Propargylanilines **1a−g** reacted with **2** to afford **3a−g** in 71−90% yields, exhibiting no obvious substituent effect from the NAr moieties (Table 2, entries 1−7). *o*- or *m*-methyl on the aryl group of a propargyl moiety favored the formation of **3h** (75%) and **3i** (77%), while a *p*-methyl lowered the yield of **3j** (64%) (Table 2, entries 8−10). A *p*-methyl on the aryl group of the NAr functional group facilitated the generation of **3k** (Table 2, entry 11). 1,2-Dihydroquinolines **5a** (53%) and **5b** (46%) were isolated from the reactions of **1l** and **1m**, respectively (Table 2, entries 12 and 13). Substituted acetals **2b−k** reacted to give diverse target products **3n−w** (58−80%) (Table 2, entries 14−23). It should be noted that arylpropargylaniline of type **1** bearing a *p*-OMe substituent only reacted to give a product of type **3** in 33% yield. The acetals derived from heterocyclic aromatic aldehydes such as 2-furaldehyde and 2-thiophenaldehyde could not undergo the desired reactions. The acetals of the alkyl aldehydes are not very stable under the stated conditions[17,18] and were not applied in the reactions.


dx.doi.org/10.1021/ol503039j | *Org. Lett.* XXXX, XXX, XXX−XXX

**Table 3. $FeX_3$-Mediated Synthesis of 7*H*-Indeno[2,1-*c*]quinolines (4)[a]**

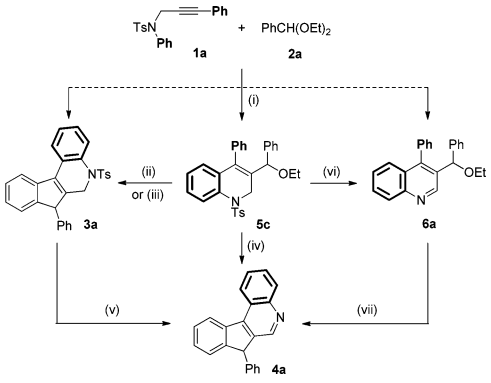



1 4

| entry | 1 / Ar (2) | yield[b] | entry | 1 / Ar (2) | yield[b] |
|---|---|---|---|---|---|
| 1 | **1a**, X = H / Ph (**2a**)[c] | **4a**, 82% | 12 | **1h** / Ph (**2a**)[d] | **4l**, 75% |
| 2 | **1b**, X = Me / Ph (**2a**)[d] | **4b**, 74% | 13 | **1j**, X = Me / Ph (**2a**)[c] | **4m**, 84% |
| 3 | **1c**, X = OEt / Ph (**2a**)[d] | **4c**, 71% | 14 | **1r**, X = OMe/Ph (**2a**)[c] | **4n**, 81% |
| 4 | **1n** / Ph (**2a**)[c] | **4d**, 88% | 15 | **1i**, X = H / Ph (**2a**)[c] | **4o**, 96% |
| 5 | **1d** / Ph (**2a**)[c] | **4e**, 69% | 16 | **1k**, X = Me / Ph (**2a**)[c] | **4p**, 98% |
| 6 | **1e**, X = Cl / Ph (**2a**)[d] | **4f**, 70% | 17 | **1l**, X = H / Ph (**2a**)[d] | **4q**, 61% |
| 7 | **1f**, X = F / Ph (**2a**)[d] | **4g**, 67% | 18 | **1m**, X = Me / Ph (**2a**)[c] | **4r**, 67% |
| 8 | **1o**, X = Ac / Ph (**2a**)[c] | **4h**, 51% | 19 | **1a** / 4-$MeC_6H_4$ (**2b**)[d] | **4s**, 74% |
| 9 | **1p**, X = Cl / Ph (**2a**)[d] | **4i**, 88% | 20 | **1a** / 4-$MeOC_6H_4$ (**2l**)[d] | **4t**, 53% |
| 10 | **1q**, X = F / Ph (**2a**)[c] | **4j**, 70% | 21 | **1a** / 4-$ClC_6H_4$ (**2d**)[d] | **4u**, 60% |
| 11 | **1g** / Ph (**2a**)[d] | **4k**, 61% | 22 | **1a**/2-$FC_6H_4$ (**2h**)[d] | **4v**, 71% |
| | | | 23 | **1a**/2-naphthyl (**2k**)[d] | **4w**, 64% |

[a]Conditions: **1** (0.3 mmol), **2** (0.6 mmol), $FeX_3$ (0.9 mmol), DCE (3 mL), 80 °C, $N_2$, 5 h. [b]Isolated yield. [c]Using $FeBr_3$. [d]Using $FeCl_3$.

**Scheme 1. Control Experiments[a]**




[a]Conditions: DCE as the solvent, $N_2$, 80 °C, 5 h; (i) 10 mol % $FeCl_3$ or $FeBr_3$, 27−28%; (ii) 30 mol % $FeCl_3$ or $FeBr_3$, 82−83%; (iii) 1 equiv $FeCl_3$ or $FeBr_3$, $CH_2Cl_2$, 25 °C, 18 h; (iv) 3 equiv $FeCl_3$ or $FeBr_3$, 64−65%; (v) 3 equiv $FeCl_3$ or $FeBr_3$, 58−72%; (vi) 10 equiv NaOMe, THF, reflux, 24 h, 33%; (vii) 3 equiv $FeCl_3$ or $FeBr_3$, 74−77%. THF = tetrahydrofuran.

Next, the protocol generality for the preparation of **4** was investigated under the optimal conditions (Table 3). Both $FeBr_3$ and $FeCl_3$ could promote the desired reactions. Substituents such as Me, OEt, Cl, F, and Ac were tolerated on the aryl groups of the NAr moieties (Table 3, entries 1−11). Unsubstituted **1a** and 2-Me- and 2-Cl-substituted substrates **1n** and **1p** efficiently underwent the reactions with **2a**, giving **4a** (82%), **4d** (88%), and **4i** (88%), respectively (Table 3, entries 1, 4, and 9). The 4- and 3-electron-withdrawing substituents rendered low yields for **4g** (67%), **4h** (51%), and **4k** (61%). A methyl or methoxy on the aryl group of a propargyl moiety of **1** did not exhibit obvious effect on the yields of **4l**−**n** (75−84%), whereas 3,5-dimethyls remarkably improved the formation of **4o** (96%) and **4p** (98%) (Table 3, entries 12−16). An electron-withdrawing substituent such as chloro on the aryl functional unit of a propargyl moiety of **1** deteriorated the reaction efficiency to give **4q** (61%) and **4r** (67%). Compound **1a** also reacted with other acetals to form the target products **4s**−**w** in 53−74% yields (Table 3, entries 19−23).

To probe the reaction mechanism, control experiments were conducted (Scheme 1). Compound **1a** reacted with **2a** in the presence of 10 mol % of $FeCl_3$ or $FeBr_3$ to afford 1-tosyl-1,2-dihydroquinoline **5c** (27−28%) via intermolecular carboarylation/cyclization, which further reacted under the stated conditions as shown in Tables 2 and 3 to give **3a** and **4a** in decent yields, respectively. Compound **3a** could be converted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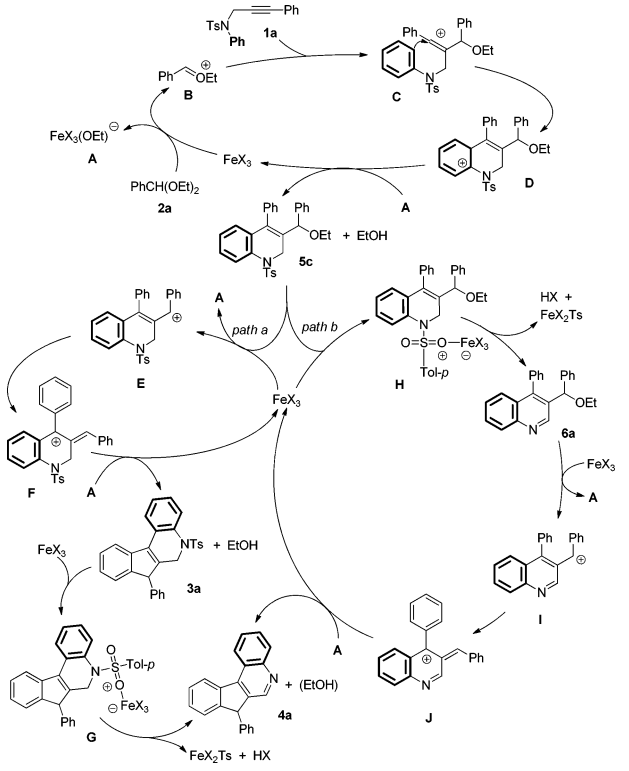
**Scheme 2. Proposed Mechanism**




to **4a** with $FeCl_3$ or $FeBr_3$ as the promoter. These results have revealed that both **5** and **3** can act as the intermediates to form **4** in the catalytic cycle. 4-Phenylquinoline (**6a**)[19] could also be utilized to access **4a**, further suggesting that species of types **5** and **6** may be generated as the reaction intermediates. It is noteworthy that **3a**, **4i**, and **5c** were structurally confirmed by X-ray crystallographic analysis (see the Supporting Information).

A plausible mechanism is proposed (Scheme 2). Acetal **2a** initially reacts with $FeX_3$ (X = Cl or Br) to form $FeX_3(OEt)^-$ anion (**A**) and oxocarbonium cation $PhCH{=}OEt^+$ (**B**).[17,18] Cation **B** interacts with propargylaniline **1a** to generate vinyl carbocation **C** stabilized by an aryl group, which undergoes intramolecular Friedel–Crafts reaction to yield **D**. Deprotonation of **D** by species **A** forms intermediate **5c** and ethanol, regenerating $FeX_3$. Following path a, species **5c** is converted to product **3a**[20] via the possible cationic species **E**[21] and **F**[18] assisted by $FeX_3$. Compound **3a** further reacts with $FeX_3$ to undergo detosylation/aromatization,[12] forming **4a**. Compound **5c** may also react with $FeX_3$ to form **6a** via species **H** by detosylation/aromatization (path b), which further undergoes carboarylation with $FeX_3$ to furnish **4a** and ethanol and regenerate the catalyst.

In summary, $FeX_3$-mediated tandem reactions of propargylanilines with aromatic aldehyde acetals form indeno[2,1-*c*]quinolines in good to excellent yields through carboarylation/cyclization under mild conditions. The present synthetic method provides a concise and nontoxic metal-mediated route to highly functionalized heteropolycyclic architectures.

## ■ ASSOCIATED CONTENT

### Supporting Information

Complete experimental procedures and characterization data for the prepared compounds; X-ray crystallographic data for **3a**, **4i**, and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21272232).

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dx.doi.org/10.1021/ol503039j | *Org. Lett.* XXXX, XXX, XXX–XXX