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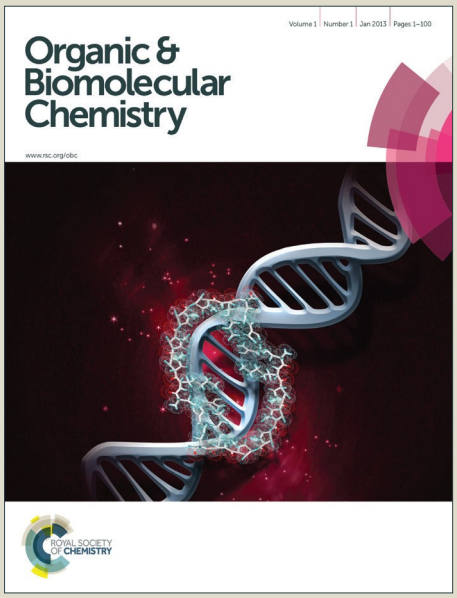

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Cooperative $FeCl_3$/DDQ System for the Regioselective Synthesis of 3-Arylindoles from β-Monosubstituted 2-Alkenylanilines

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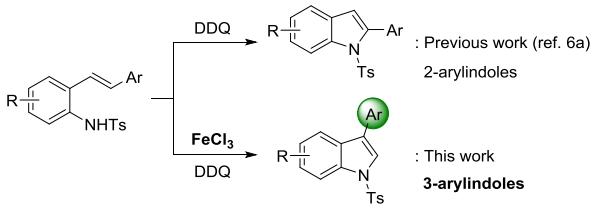
A highly regioselective synthesis of 3-arylindoles by using the cooperative $FeCl_3$/DDQ system has been developed. This new protocol represents an attractive route for the synthesis of 3-arylindoles from readily accessible non-indole precursors, β-aryl-substituted 2-styrylanilines, using inexpensive catalyst and oxidant. Noteworthy is the unique synergetic and synergistic effect of $FeCl_3$ and DDQ on the 1,2-aryl migratory process.

Indoles are one of the most significant heterocycles found in a wide range of natural products, pharmaceuticals, and other functional molecules.[1] Among them, 3-arylindoles are known to possess various biological properties[2] and also have been utilized for the synthesis of numerous natural products and pharmacologically important compounds.[3] Consequently, a diverse range of synthetic methods for the formation of 3-arylindoles from non-indole[4] or indole[5] precursors have been developed.

Recently, our group reported an operationally simple and robust C-H amidation of 2-alkenylanilines by the use of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) for the straightforward access to a diverse array of indoles in excellent yields (Scheme 1, top).[6a] In addition, the related Ag(I)-mediated[6b] and Pd(II)-catalyzed[6c] indole forming reactions from 2-alkenylanilines have been also developed, in both which an uncommon 1,2-migratory process of β-monosubstituted 2-alkenylanilines with solvent- and/or oxidant-dependence was demonstrated to be operative. However, the low regioselectivities limited their synthetic utility, giving the mixture of inseparable 3- and 2-substituted indole products (3-:2- = ≤ 4.5:1). During the course of these studies, we systematically examined various combination of Lewis acids and oxidants, and a very intriguing effect of Lewis acid, especially $FeCl_3$, on the 1,2-aryl migration was observed in the DDQ-mediated C-H amidation (Scheme 1, bottom).



Scheme 1 2- or 3-Arylindole synthesis from 2-alkenylanilines

In recent years, iron salts have attracted considerable attention as effective catalysts due to their low cost, abundance, non-toxicity, and environmentally benign properties.[7] Several examples have been reported on the oxidative coupling reactions catalyzed by $FeCl_3$ as a Lewis acid in the presence of DDQ as an oxidant.[7-8] However, to the best of our knowledge, Fe-catalyzed oxidative C-N bond forming process involving 1,2-aryl migration has not been developed.

Herein we disclose a highly regioselective synthesis of 3-arylindoles from β-aryl monosubstituted 2-alkenylanilines in the presence of $FeCl_3$ and DDQ as a catalyst and oxidant, respectively. In particular, the peculiar effect of $FeCl_3$ in the presence of DDQ on the 1,2-aryl migratory process is highly noteworthy. This protocol could be complementary to other methods (e.g., intramolecular cyclization of α-substituted 2-vinylanilines[6a-b] or enamines,[4c, 4g] intermolecular coupling between anilines and terminal alkynes[4a, 4d-f] or cinnamic acids[4h]) for the synthesis of 3-arylindoles using non-indole precursors, albeit with somewhat limited substrate scope.

We began our investigations on a variety of Lewis acids using **1a** and DDQ as the test substrate and oxidant, respectively (Table 1, for complete data, see ESI). Gratifyingly, it was found that $FeCl_3$ promoted 1,2-phenyl migration significantly to afford **2a** along with **3a** in a good combined, isolated yield (71%, **2a**:**3a** = 7:1) (entry 1). In contrast, other Fe(II) and Fe(III) salts gave comparable good yields of indole products but very low or no degree of migration (entries 2-4). With the exception of $InCl_3$, other Lewis acids examined afforded **3a** as a major or single

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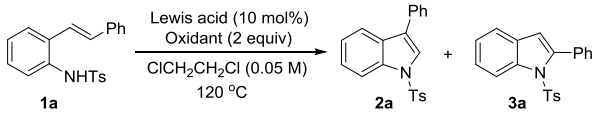
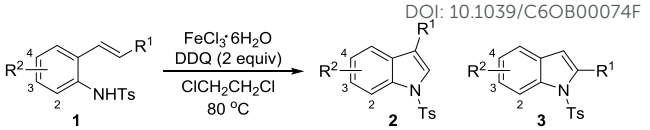
Table 1 Optimization studies: Selected data



Entry	Lewis Acid	Oxidant	Time (h)	Yield (%)[a]	**2a**:**3a**[b]
1	$FeCl_3$	DDQ	6	91 (71)	7:1
2	$FeBr_3$	DDQ	5	90	1:7
3	$Fe_2(SO_4)_3{\cdot}xH_2O$	DDQ	7	100	0:1
4	$FeCl_2$	DDQ	8	100	1:7
5	$InCl_3$	DDQ	24	100	2:1
6	$Sc(OTf)_3$	DDQ	24	81	1:2
7	$CuCl_2$	DDQ	24	100	1:24
8	$FeCl_3$	BQ	24	10	2:1
9	$FeCl_3$	$Cu(OAc)_2$	24	52	1:12
10	$FeCl_3$	*t*BuOO*t*Bu	24	40	1:1.4
11[c]	$FeCl_3$	DDQ	4	(72)	8:1
12[c]	$FeCl_3{\cdot}6H_2O$	DDQ	4	(75)	8:1
13[c-d]	-	DDQ	24	(30)	0:1
14[c-e]	$FeCl_3{\cdot}6H_2O$	-	24	(7)	10:1

[a] Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard. Value in parentheses indicates an isolated yield. [b] Determined by ^{1}H NMR. [c] At 80 °C. [d] **1a** was recovered in 43-46% yield. [e] *N*-Ts-2-Phenylindoline (**4a**) was obtained in 40% yield.

Table 2 Substrate scope



Entry	R^1	R^2	Fe(III)[a]	Time	Yield[b] (**2**:**3**)[c]
1	Ph	H (**1a**)	10	4 h	75% (89:11)
2[d]	4-MeOC_6H_4	H (**1b**)	5	30 min	32% (100:0)
3	4-MeC_6H_4	H (**1c**)	10	30 min	57% (100:0)
4	3-MeC_6H_4	H (**1d**)	15	6 h	74% (89:11)
5	2-MeC_6H_4	H (**1e**)	10	10 min	97% (89:11)
6[d]	1-Naphthyl	H (**1f**)	15	10 min	59% (100:0)
7[e]	4-$NO_2C_6H_4$	H (**1g**)	10	24 h	84% (0:100)
8[e]	3-$CF_3C_6H_4$	H (**1h**)	10	24 h	92% (0:100)
9	4-MeC_6H_4	4-Me (**1i**)	10	30 min	48% (100:0)
10	2-MeC_6H_4	4-MeO (**1j**)	15	10 min	79% (96:4)
11	2-MeC_6H_4	4-Me (**1k**)	10	30 min	80% (91:9)
12	2-MeC_6H_4	4-Cl (**1l**)	20	1 h	91% (92:8)
13	2-MeC_6H_4	4-NO_2 (**1m**)	25	2 h	100% (89:11)
14	2-MeC_6H_4	3-Me (**1n**)	10	30 min	67% (100:0)
15	2-MeC_6H_4	3-Cl (**1o**)	20	20 min	96% (91:9)
16	2-MeC_6H_4	3-NO_2 (**1p**)	15	8 h	98% (90:10)
17	2-MeC_6H_4	2-MeO (**1q**)	10	2 h	67% (100:0)

[a] Amount (mol%) of the used $FeCl_3{\cdot}6H_2O$. [b] Isolated yield. [c] Ratios of inseparable isomers were determined by ^{1}H NMR. [d] Using $FeCl_3$. [e] At 120 °C.

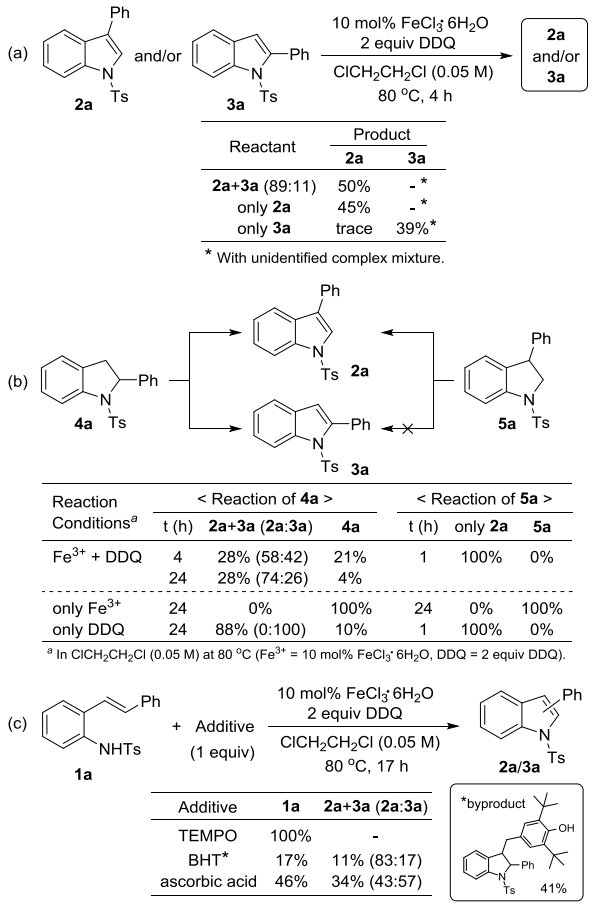
product (entries 5-7). Other oxidants and solvents were examined (entries 8-10 and see ESI): DDQ and $ClCH_2CH_2Cl$ were identified as the most effective oxidant and solvent, forming **2a** with high efficiency. Further optimization of reaction conditions (entries 11-12) showed that lower reaction temperature was beneficial for higher ratio of **2a** to **3a**, while the use of $FeCl_3{\cdot}6H_2O$ instead of $FeCl_3$ led to both comparable chemical yield and ratio.

Control experiment employing only DDQ gave **3a** as a sole product with a low conversion as our previous report[6a] (entry 13), whereas the use of only $FeCl_3{\cdot}6H_2O$ resulted in a very small amount of indole products (7%, **2a**:**3a** = 10:1) along with the corresponding indoline product (**4a**) in 40% yield (entry 14). These findings indicate that there is a remarkable synergetic and synergistic effect of $FeCl_3$ and DDQ which are both essential and can obviously increase the reactivity and selectivity for this 1,2-migratory transformation. Compared to several examples on more general 1,2-aryl migration in indole forming reactions from β,β-disubstituted 2-alkenylanilines,[9] the related process of β-*monosubstituted* 2-alkenylaniline derivatives has been very rarely observed in very few examples even with only low selectivities (3-arylindole:2-arylindole = 1:9.1 ~ 4.5:1),[10] making this finding of great interest and significance. To the best of our knowledge, this represents the very first example of highly selective 1,2-aryl migration using the cooperative $FeCl_3$/DDQ system for the regioselective synthesis of 3-arylindoles from β-aryl-substituted 2-styrylanilines.

With the optimized reaction conditions in hand, we first explored the substituent effect (R^1) at the alkene moiety. Both electron-rich and -neutral aryl groups irrespective of the position of their substituents could migrate to give the corresponding 3-arylindole **2** with high selectivities and little steric dependence (Table 2, entries 1-6). In contrast, electron-withdrawing aryl substituents such as NO_2 resulted in no rearrangement (entries 7-8), alluding to the involvement of a cationic rearrangement.[6, 9-10]

Next, we investigated the effects of substituents (R^2) residing on the aromatic moiety of *N*-Ts-anilines (entries 9-17). Both electron-donating and –withdrawing substituents were well tolerated regardless of their position, showing an electronic dependence. Electron-donating substituents appeared to facilitate 1,2-aryl migration considerably rather than their electron-withdrawing counterparts, leading to generally faster completion of the reactions and higher selectivities for **2** over **3**. It should be noted that most reactions completed after rather short reaction time and were quite sensitive to the amount of Fe(III) catalyst. In general, when the used amount of $FeCl_3$ increased, the ratios of **2** to **3** increased while the combined yields decreased (Figure S1 in ESI). Unfortunately, efforts to expand the scope of this protocol into a selective migration in the related reaction of β,β-diaryl-2-alkenylanilines as well as application to benzofuran synthesis were unsuccessful.

To gain mechanistic insight into this reaction, a series of control experiments were performed. When **2a** alone or the mixture of **2a** and **3a** were subjected to the standard reaction conditions, only **2a** was recovered in 45-50% yields without any **3a** (Scheme 2a). On the other hand, trace amount of **2a** was observed in the reaction of **3a** under the same conditions. All these reactions produced some unidentified complex mixture along with significant decomposition of indole compounds, **2a** and **3a** both. In the light of our observation (Table 1, entry 14) and previous reports[11] on $FeCl_3$-catalyzed inter- or intramolecular hydroamination between *N*-Ts-amines and olefins, the reaction of a putative intermediate, indoline **4a**, either (1) under our standard reaction conditions, (2) employing only $FeCl_3{\cdot}6H_2O$ as



Reactant	Product 2a	Product 3a
2a+**3a** (89:11)	50%	- *
only **2a**	45%	- *
only **3a**	trace	39%*

* With unidentified complex mixture.

Reaction Conditions[a]	< Reaction of **4a** > t (h)	**2a**+**3a** (**2a**:**3a**)	**4a**	< Reaction of **5a** > t (h)	only **2a**	**5a**
Fe^{3+} + DDQ	4	28% (58:42)	21%	1	100%	0%
	24	28% (74:26)	4%			
only Fe^{3+}	24	0%	100%	24	0%	100%
only DDQ	24	88% (0:100)	10%	1	100%	0%

[a] In $ClCH_2CH_2Cl$ (0.05 M) at 80 °C (Fe^{3+} = 10 mol% $FeCl_3 \cdot 6H_2O$, DDQ = 2 equiv DDQ).

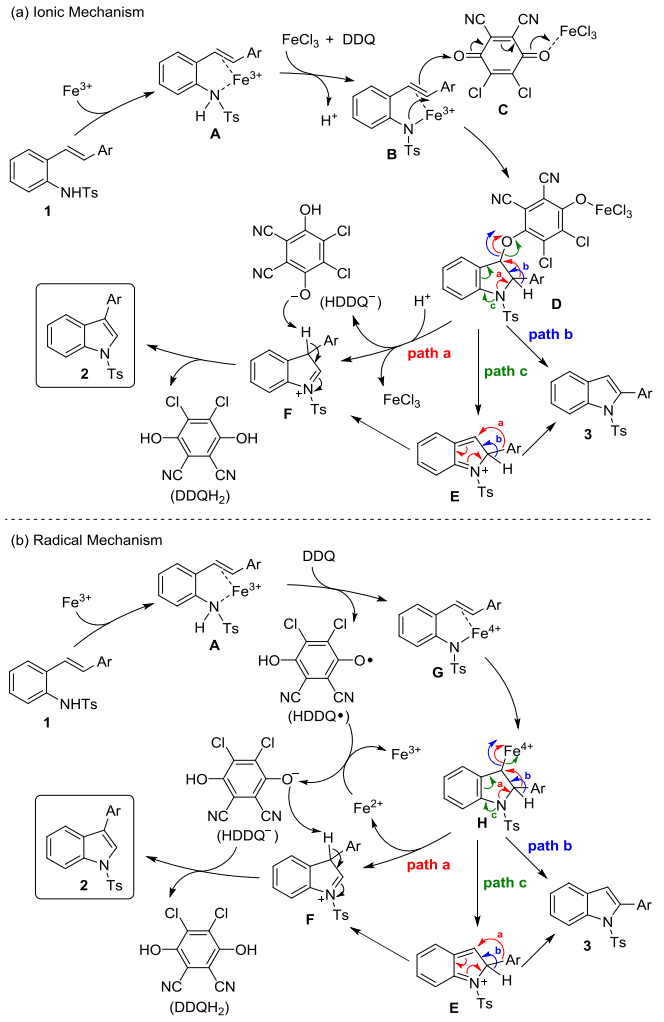
Additive	**1a**	**2a**+**3a** (**2a**:**3a**)
TEMPO	100%	-
BHT*	17%	11% (83:17)
ascorbic acid	46%	34% (43:57)

Scheme 2

a sole catalyst, or (3) using only DDQ was performed (Scheme 2b). No reaction occurred in the presence of only $FeCl_3 \cdot 6H_2O$, while DDQ promoted the oxidation reaction of **4a** to afford only **3a**. In sharp contrast, very intriguingly, the mixture of **2a** and **3a** was obtained in the reaction of **4a** under the standard reaction conditions, albeit in a low yield and selectivity. After longer reaction time, almost two times increase of the selectivity was observed without increasing the chemical yield. On the other hand, the reaction of the other regioisomeric indoline **5a** under the standard reaction conditions led to the formation of only **2a** quantitatively in only 1 h, so did that using only DDQ.

To further investigate if the generation of indoline intermediates (i.e., **4** or **5**) and the transformation of **3** into **2** were involved during the reaction, the reaction of **1a** (and **1p**) was monitored by TLC and ^{1}H NMR analyses by withdrawing aliquots at regular intervals (Figure S2 in ESI). However, neither **4a** nor **5a** (and the corresponding indolines derived from **1p**) was observed. In contrast, products **2** and **3** were forming continuously, while the ratio of **2** to **3** remained almost constant during the reaction. Interestingly, in comparison with the outcomes in Scheme 2a, conspicuous decomposition of **2a** and **3a** was not observed during the reaction progress. These findings suggest that initially generated both 2- substituted indoles (e.g., **3a**) and indolines (e.g., **4a**) are the unlikely intermediates in the rearrangement.

Inclusion of TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl), BHT (3,5-di-*tert*-butyl-4-hydroxytoluene), or ascorbic acid as an additive had deleterious effect, shutting down the reaction either completely or to a large extent (Scheme 2c). In the presence of BHT, the corresponding trapping product was obtained as a byproduct. These results may suggest a mechanism involving a radical intermediate during the reaction. However, it cannot be ruled out that DDQ was consumed by its direct reaction with these additives, thus leading to depletion of DDQ oxidant and ineffective reaction as well as the formation of a byproduct.



Scheme 3 Proposed mechanism

Although a clear mechanistic picture is elusive at this juncture, a plausible mechanistic proposal is presented in Scheme 3. $FeCl_3$ might play two important roles as a Lewis acid[8]: (1) increasing the oxidizing power by coordination with the carbonyl O atom of DDQ and (2) increasing the reactivity of substrate **1** by chelation to promote an intramolecular cyclization for an initial C-N bond formation. Two plausible mechanisms, i.e., either 1) ionic[8e, 8g] or 2) radical[8b] mechanism can be conceived for this oxidative cyclization reaction. In an ionic mechanism (Scheme 3a),[8e, 8g] species **B** is generated by deprotonation from species **A**, which is initially formed by a chelation of Fe(III) with sulfonamide and alkene moieties of **1**. Then sequential intramolecular C-N bond and intermolecular C-O bond forming

reactions between **B** and the activated DDQ **C** by coordination to Fe(III) takes place to afford the species **D**. Next, the intermediate **D** is most likely to undergo a 1,2-aryl migration directly (path a) or indirectly via **E** (path c) to give **F** and regenerate the catalytically active Fe(III) species along with $HDDQ^-$. Subsequent deprotonation of **F** by $HDDQ^-$ forms the desired 3-arylindole **2**. The formation of 2-arylindole **3** can be derived from re-aromatization directly from **D** (path b) or through **E** (path c) by the loss of a proton. When an aryl substituent (Ar) is not electron-rich enough, its expected much less or no participation in the process of **D** → **F** can explain the only formation of **3** (e.g., **3g** and **3h**, Table 2, entries 7-8).

Alternatively, a radical mechanism could be also conceived (Scheme 3b).[8b] Species **A** is oxidized by DDQ to afford the electrophilic Fe(IV) species **G**, which then undergoes an alkene insertion to generate **H**. Next, the intermediate **H** is most likely to undergo a 1,2-aryl migration directly (path a) or indirectly via **E** (path c) to give **F** along with Fe(II), which is reoxidized by HDDQ• to regenerate the catalytically active Fe(III) species. As mentioned above, subsequent deprotonation of **F** by $HDDQ^-$ occurs to give **2**. In this pathway, $FeCl_3$ seems to be involved in single electron transfer process as an essential catalyst for the reaction. However, 1,2-aryl migration in this oxidative cyclization reaction was also promoted to some extent (albeit less than $FeCl_3$) by other Lewis acids (e.g., $InCl_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, $ZnCl_2$, $MgCl_2$), which are incapable of catalyzing oxidative coupling processes via higher oxidation state. Therefore, although a mechanism remains elusive at this juncture, the ionic mechanism seems to work more generally in this cooperative Lewis acid ($FeCl_3$)/DDQ system.

In summary, we have developed a highly regioselective synthesis of 3-arylindoles by using the cooperative $FeCl_3$/DDQ system, involving 1,2-aryl migration. This new protocol represents an attractive route for the synthesis of 3-arylindoles from non-indole precursors, readily accessible β-aryl-substituted 2-styrylanilines, using inexpensive catalyst and oxidant, mostly after short reaction time. Noteworthy is the unprecedented, unique catalytic effect of $FeCl_3$ in the presence of DDQ on the 1,2-aryl migratory process.

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