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One-Pot Synthesis of Diarylamines from Two Aromatic Amines via Oxidative Dearomatization–Imino Exchange–Reductive Aromatization

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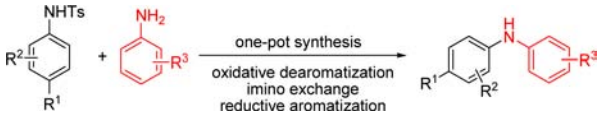
ABSTRACT



A one-pot synthetic strategy for diarylamines using only aromatic amines as starting materials has been developed. This method involved a $PhI(OAc)_2$-induced oxidative dearomatization of *N*-sulfonyl protected para-substituted anilines, a $Bi(OTf)_3$-catalyzed imino exchange reaction between *N*-sulfonyl cyclohexadienimines and aromatic amines, and a CF_3COOH/Zn mediated reductive aromatization of the resulting *N*-aryl cyclohexadienimines.

Diarylamines constitute a valuable class of compounds in biological, pharmaceutical, and material sciences.[1] They not only are found in a variety of natural products, agrochemicals, and HIV-1 protease inhibitors but also are widely used as corrosion inhibitors, antioxidants and stabilizers for rubber, and additives for the production of dyes. The classical approach to prepare diarylamines[2] is the transition-metal catalyzed N-arylation of aromatic amines, such as the Ullmann reaction[3−5] and the Buchwald–Hartwig amination.[6,7] Recently, Larock and co-workers reported a transition-metal-free N-arylation procedure with arynes as a reactive intermediate.[8] The Deng group developed a palladium-catalyzed diarylamine formation from nitroarenes and cyclohexanones using the dehydrogenation and borrowing hydrogen methodology.[9] The Nakamura group described an iron-catalyzed amination reaction of

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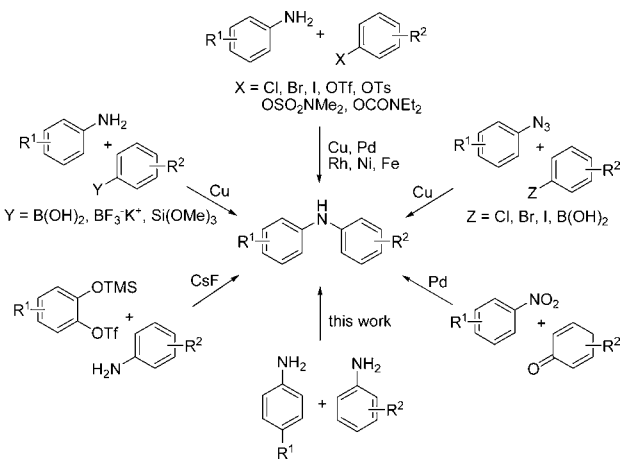
aryl bromides with *in situ* generated magnesium amides to provide diaryl- and triarylamines without the use of expensive and/or toxic metals.[10] Because of the importance of diarylamines, aside from the reliability of the existing protocols,[11,12] the search and development of an alternative method to construct such a desirable framework by using only aromatic amines as starting materials is still highly desirable (Scheme 1).

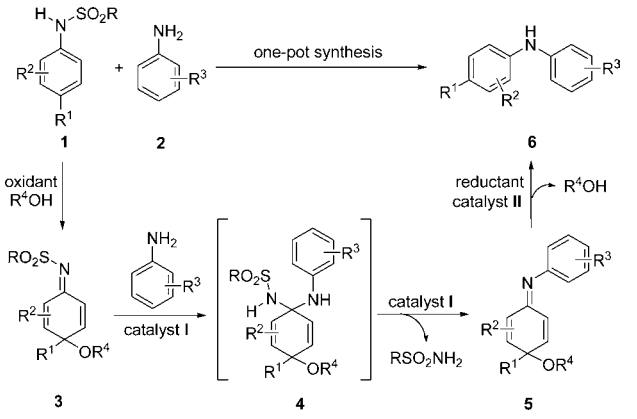
As a result of the inherent functionalities stored within the aromatic systems, dearomatization[13] of aromatic amines provided a powerful tool to build complex nitrogen-containing molecules.[14] The oxidative dearomatization of para-substituted anilines forms cyclohexadienimines. The Kerr,[15] Quideau,[16] and Canesi[17] groups have developed 1,4-additions of cyclohexadienimines to convert these motifs into useful molecules. In contrast, the 1,2-addition of cyclohexadienimines has received much less scrutiny. Our planned one-pot synthetic strategy for diarylamines from two aromatic amines involved an oxidative dearomatization of *N*-sulfonyl protected para-substituted anilines, an imino exchange between the *in situ* generated *N*-sulfonyl cyclohexadienimines and aromatic amines, and a reductive aromatization of the resulting *N*-aryl cyclohexadienimines (Scheme 2).

Scheme 1. Strategies for the Preparation of Diarylamines



First, we investigated the imino exchange reaction between 4-methoxybenzenamine and cyclohexadienimine **3a**, which was prepared from the oxidative dearomatization of

Scheme 2. One-Pot Synthesis of Diarylamines from Two Aromatic Amines



N-Ts protected *p*-toluidine in methanol with $PhI(OAc)_2$ as the oxidant (Table 1). No reaction was observed in the absence of a catalyst. To promote the 1,2-addition and the subsequent elimination of $TsNH_2$, various Lewis acids were examined. Except for $Au(PPh_3)Cl$, a range of metal salts exhibited catalytic activities in the imino exchange reaction. $Bi(OTf)_3$ was the best catalyst for the formation of *N*-aryl cyclohexadienimine **5aa**. More importantly, $Bi(OTf)_3$ could efficiently promote the imino exchange reaction in methanol (Table 1, entry 14), which made it possible to combine the oxidative dearomatization and the imino exchange reaction into a one-pot procedure.

We next investigated the reductive aromatization of *N*-aryl cyclohexadienimine **5aa** in methanol. When $NaBH_4$ was used as the reductant together with 1 equiv of $BF_3 \cdot Et_2O$, the reaction was very complex (Table 2, entry 1). Interestingly, when $BF_3 \cdot Et_2O$ was used alone, the reaction gave rise to the desired diarylamine **6aa** in a 34% yield (Table 2, entry 2). Analysis of the reaction mixture indicated the formation of benzoquinone. It was supposed that benzoquinone was formed from the oxidation of 4-methoxybenzenamine, which was generated from the hydrolysis of *N*-aryl cyclohexadienimine. Indeed, the addition of 1 equiv of 4-methoxybenzenamine in the $BF_3 \cdot Et_2O$-catalyzed reaction led to an improvement in the product yield (Table 2, entry 3).

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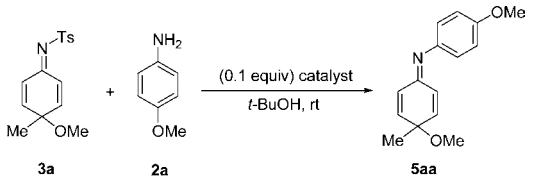
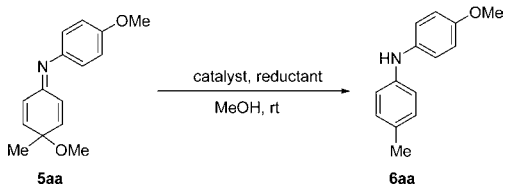
Table 1. Evaluation of Catalyst for Imino Exchange Reaction[a]



entry	catalyst	**5aa** (%)[b]	entry	catalyst	**5aa** (%)[b]
1	–	0	8	$In(OTf)_3$	44
2	$Au(PPh_3)Cl$	<5	9	$Fe(OTf)_2$	68
3	CuBr	75	10	$Yb(OTf)_3$	73
4	AgOTf	90	11	$Sc(OTf)_3$	93
5	$Cu(OTf)_2$	92	12	$Dy(OTf)_3$	67
6	$Zn(OTf)_2$	72	13	$Bi(OTf)_3$	96
7	$Ni(OTf)_2$	91	14[c]	$Bi(OTf)_3$	95

[a] General reaction conditions: reactions performed on 0.2 mmol scale using 1.1 equiv of **2a**, 10 mol % catalyst in *t*-BuOH (2 mL) at 25 °C, unless noted. [b] Reported yields are of the isolated product based on compound **3a**. [c] MeOH was used as solvent.

Table 2. Evaluation of Conditions for Reductive Aromatization



entry	catalyst (equiv)	reductant (equiv)	**6aa** (%)[a]
1	$BF_3 \cdot Et_2O$ (1)	$NaBH_4$ (1)	0
2	$BF_3 \cdot Et_2O$ (1)	–	34
3	$BF_3 \cdot Et_2O$ (1)	4-$MeOC_6H_4NH_2$ (1)	60
4	$BF_3 \cdot Et_2O$ (1)	4-$MeOC_6H_4NH_2$ (2)	53
5	$BF_3 \cdot Et_2O$ (2)	4-$MeOC_6H_4NH_2$ (1)	56
6	$BF_3 \cdot Et_2O$ (1)	4-HOC_6H_4OH (1)	52
7	CF_3COOH (1)	4-$MeOC_6H_4NH_2$ (1)	65
8	CF_3COOH (1)	PPh_3 (1)	27
9	CF_3COOH (1)	PBu_3 (1)	31
10	CF_3COOH (1)	H_2 (1 atmo)	36
11	CF_3COOH (1)	Sn (1)	<5
12	CF_3COOH (1)	Mg (1)	36
13	CF_3COOH (1)	Zn (1)	83
14	CF_3COOH (2)	Zn (2)	94

[a] Reported yields are of the isolated product based on compound **5aa**.

Increasing the amount of 4-methoxybenzenamine or $BF_3 \cdot Et_2O$ did not improve the yield (Table 2, entries 4 and 5). Screening of a variety of Lewis acids or Brønsted acids revealed that 2,2,2-trifluoroacetic acid could also promote the reductive aromatization in methanol (Table 2, entry 7). Moreover, we were pleased to find that the yield of the desired product was improved to 83% by using a combination of 2,2,2-trifluoroacetic acid and zinc dust (Table 2, entry 13). When the amounts of 2,2,2-trifluoroacetic acid and Zn dust were increased to 2 equiv, the reductive aromatization reaction afforded diarylamine **6aa** in a 94% yield.

Isopropanol and tertiary butanol could also be used as the medium for the imino exchange reaction and the reductive aromatization reaction. However, the oxidative dearomatization of *N*-Ts protected *p*-toluidine in isopropanol or tertiary butanol did not form the corresponding cyclohexadienimines due to the poor nucleophilicity of these alcohols. When isopropanol or tertiary butanol was used together with 2 equiv of methanol, the reactions gave rise to cyclohexadienimine **3a** in low yields (< 10%).

With the optimized reaction conditions established, the one-pot synthesis of diarylamines was investigated, and representative results were shown in Table 3. For various 4-substituted anilines, the reactions proceeded smoothly leading to the corresponding diarylamines in moderate to good yields. A steric hindrance effect was observed in the imino exchange reaction when 2,4-dimethylbenzenamine **1h** was used as the substrate (Table 3, entry 8). When *N*-Ts protected 4-methoxybenzenamine **1i** was used, the oxidative dearomatization proceeded smoothly, but the imino exchange reaction was very complex (Table 3, entry 9). A variety of aromatic amines could be used as reaction partners for this one-pot synthesis. When sterically hindered amines **2e**–**g** were used as nucleophiles, the desired diarylamines were still obtained with good yields (Table 3, entries 13–15). The reaction system displayed good tolerance toward a range of functional groups. When unprotected aminophenol **2h** or **2i** was employed, the reaction afforded the corresponding *N*-arylated aminophenol[18] **6ah** or **6ai** in a 91 or 83% yield, respectively (Table 3, entries 16 and 17). In addition, the one-pot reaction between 2-iodobenzenamine and *p*-toluidine

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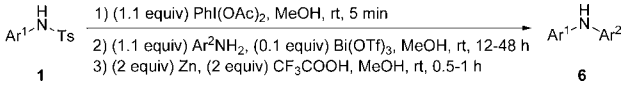
Table 3. One-Pot Synthesis of Diarylamines from Two Aromatic Amines



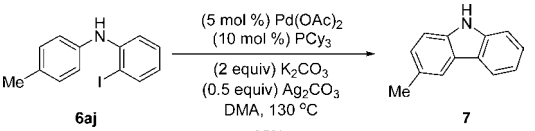
1 **6**

entry	Ar^1	Ar^2	**6** (%)[a]
1	4-MeC_6H_4	4-$MeOC_6H_4$	**6aa** (83)
2	4-$nBuC_6H_4$	4-$MeOC_6H_4$	**6ba** (75)
3	4-EtC_6H_4	4-$MeOC_6H_4$	**6ca** (88)
4	4-$iPrC_6H_4$	4-$MeOC_6H_4$	**6da** (70)
5	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**6ea** (45)
6	4-PhC_6H_4	4-$MeOC_6H_4$	**6fa** (63)
7	3,4-$(Me)_2C_6H_3$	4-$MeOC_6H_4$	**6ga** (73)
8	2,4-$(Me)_2C_6H_3$	4-$MeOC_6H_4$	**6ha** (35)
9	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**6ia** (0)
10	4-MeC_6H_4	C_6H_5	**6ab** (76)
11	4-MeC_6H_4	4-MeC_6H_4	**6ac** (80)
12	4-MeC_6H_4	4-$iPrC_6H_4$	**6ad** (80)
13	4-MeC_6H_4	2-MeC_6H_4	**6ae** (98)
14	4-MeC_6H_4	2,6-$(Me)_2C_6H_3$	**6af** (73)
15	4-MeC_6H_4	2,4,6-$(Me)_3C_6H_2$	**6ag** (80)
16	4-MeC_6H_4	4-HOC_6H_4	**6ah** (91)
17	4-MeC_6H_4	2-HOC_6H_4	**6ai** (83)
18	4-MeC_6H_4	2-IC_6H_4	**6aj** (48)
19	4-MeC_6H_4	4-FC_6H_4	**6ak** (85)
20	4-MeC_6H_4	1-naphthyl	**6al** (85)
21	4-MeC_6H_4	4-pyridyl	**6am** (0)
22	4-MeC_6H_4	1,3-$(CH_3)_2$-1*H*-pyrazol-5-yl	**6an** (0)

[a] Reported yields are of the isolated products based on compounds **1**.

generated 2-iodo-*N*-*p*-tolylbenzenamine **6aj** in a reasonable yield. Under the transition-metal catalyzed N-arylation conditions, iodo substitution in aromatic amines is unlikely to survive. The reaction of 4-amino-pyridine or 5-amino-1,3-dimethyl-1*H*-pyrazole was very complex, and product **6am** or **6an** was not isolated (Table 2, entries 21 and 22).

Scheme 3. Conversion of 2-Iodo-*N*-*p*-tolylbenzenamine **6aj**



6aj **7**

Diarylamine **6aj** could be converted to 3-methyl-9*H*-carbazole **7** via a palladium-catalyzed intramolecular direct arylation[19] (Scheme 3).

In conclusion, we have developed a new strategy for accessing diarylamines using only aromatic amines as starting materials. This one-pot synthesis involves an oxidative dearomatization, an imino exchange reaction, and a reductive aromatization. Currently, extending its scope and exploring its reaction mechanism and possible synthetic applications are being pursued, and these results will be reported in due course.

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Supporting Information Available. Experimental procedures, characterization data, copies of ^1H and ^{13}C NMR of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.