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Lewis Acid-Promoted Synthesis of Unsymmetrical and Highly Functionalized Carbazoles and Dibenzofurans from Biaryl Triazenes: Application for the Total Synthesis of Clausine C, Clausine R, and Clauraila A

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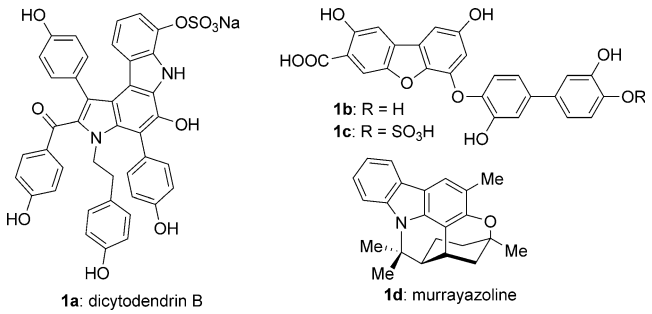
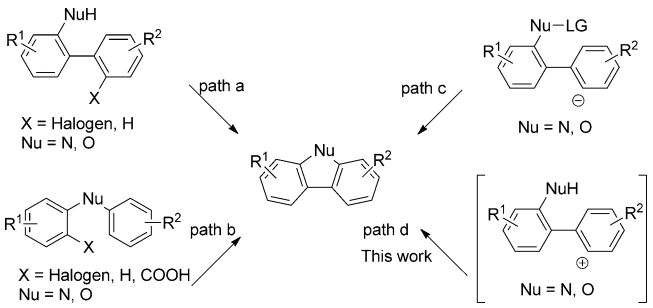
Carbazole and dibenzofuran motifs are commonly seen in bioactive natural products, such as dicytodendrin B (**1a**, Scheme 1),[1] vanillic acid derivatives (**1b** and **1c**, Scheme 1)[2] and murrayazoline (**1d**, Scheme 1).[3] They have received significant attention as synthetic targets due to their intriguing structural features and promising biological activities. A large number of classical and nonclassical methods have been developed for the synthesis of carbazole and dibenzofuran frameworks.[4] Since transition-metal-catalyzed intermolecular formation of C–N/C–O bond through nitrogen/oxygen nucleophilic displacement of aryl halides can promote various annulation reactions and provide efficient synthetic transformation for the synthesis of heterocyclic molecules, it was extensively investigated for the formation of dibenzofuran and carbazole units.[5] Recently, combined C–H bond activation/C–N or C–O formation route to carbazole and dibenzofuran has been scrutinized by the groups of Buchwald,[6] Gaunt,[7] Shi,[8] Chang,[9] and Liu[10] by using Pd or copper as catalyst (path a, Scheme 2). In addition, C–H-bond activation and intramolecular direct arylation provide efficient methods for the synthesis of carbazole and dibenzofuran.[11] Recent elegant examples include double C–H bond activation by Knolker,[12] amination/intramolecular direct arylation reaction by Ackermann and co-workers[13] and tandem decarboxylation/C–H activation reaction by Glorius and co-workers[14] (path b, Scheme 2). Furthermore, the approach to carbazole based on organometallic reagents, such as Grignard reagents has also been reported (path c, Scheme 2).[15]



Scheme 1. Natural products with dibenzofuran and carbazole motifs.



Scheme 2. Approaches to dibenzofuran and carbazole motifs. LG = leaving group.

Although considerable efforts have been directed to the synthesis of carbazole and dibenzofuran skeletons, and many useful synthetic procedures have been developed, the synthesis of highly substituted carbazole and dibenzofuran remains difficult. In view of the particularly interesting pharmacological properties[16] and wide applications in materials science,[17] new practical synthetic methods for the construction of carbarzole and dibenzofuran units are highly desired. The nucleophilic aromatic substitution of phenyl cation[18] is a straightforward, efficient, and green way to construct the carbazole and dibenzofuran cores. However, the research in this area is still rare because the phenyl cation is unstable, which limits its application in organic synthesis. Herein, based on the generation of highly activated phenyl cation intermediates, we describe a $BF_3{\cdot}OEt_2$-promoted intramolecular amination and oxylation strategy for the direct formation of dibenzofurans and carbazoles from biaryl triazenes[19] under Lewis acid conditions (path d, Scheme 2).

Initially, we treated amino-triazene **2** with $BF_3{\cdot}OEt_2$ in DMF, leading to the formation of the desired carbazole **4a** in 50% yield (Scheme 3). Interestingly, when we treated ditriazene **3a** ($R^1 = R^2 = Bn$) with $BF_3{\cdot}OEt_2$ in EtOH, the yield of the formation of carbazole **4a** increased to 80%. Subsequently, we tested different substituents on the tri-

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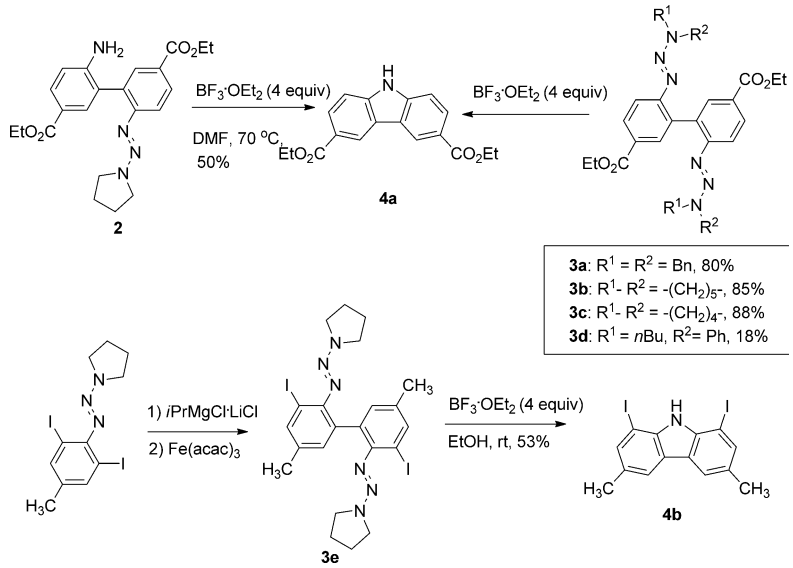
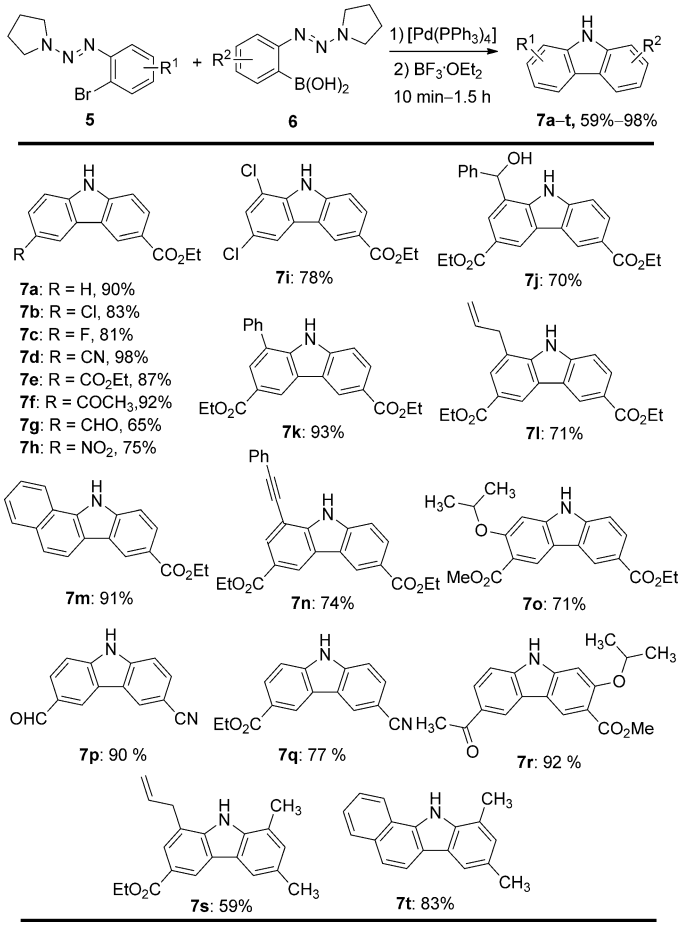


Scheme 3. Synthesis of functionalized carbozoles from diphenyltriazenes.

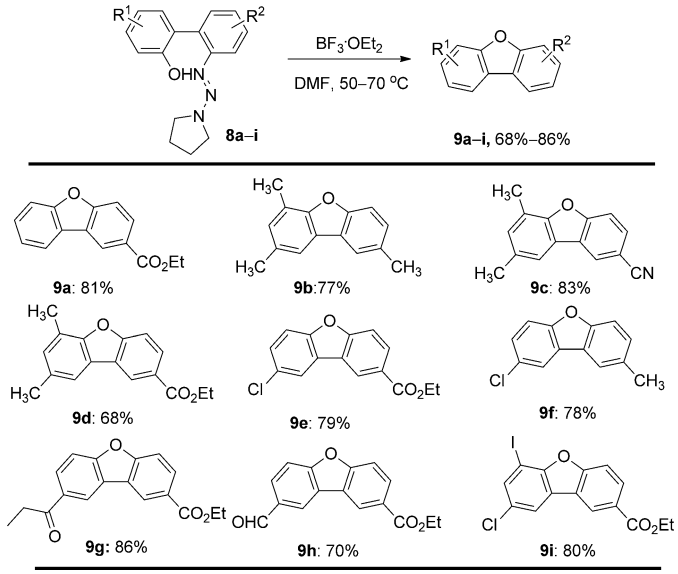
azene motif and found that when $R^1=R^2=$-$(CH_2)_4$- (**3c**), the yield of the formation of carbazole **4a** increased to 88%. Whereas using aromatic amine as the protecting group (**3d**, $R^1=n$Bu, $R^2=$Ph), the yield of the formation of carbazole **4a** decreased to 18%. We then extended the reaction to diiodo substrate **3e**, which was obtained from the homocoupling of monoiodo triazene Grignard reagent in the presence of $Fe(acac)_3$,[15] (acac = acetylacetonate) and the diiodocarbazole **4b** was formed in 53% yield.

Following the success of the formation of carbazoles **4a** and **4b**, the scope of this transformation was studied using various functionalized biaryl triazenes. The results of the tandem cross-coupling/nucleophilic aromatic substitution approach to functionalized carbazoles are summarized in Scheme 4. Thus, heating (2-bromo-phenyl)-pyrrolidin-1-yl-diazene (**5a**) with 3-borono-4-(1-pyrrolidinylazo)-benzoic acid ethyl ester (**6a**) in the presence of $Pd(PPh_3)_4$ gave biaryl triazene in excellent yield, which was subsequently treated with BF_3·OEt_2, to give the desired 9*H*-carbazole-3-carboxylic acid ethyl ester (**7a**) in 90% yield. The bromotriazenes bearing either electron-withdrawing groups or electron-donating groups can all be converted to their corresponding carbazoles (**7b–h**, **7p–r**, Scheme 4) after coupling with boronic triazenes and being treated with BF_3·OEt_2 in 65–98% yields. Sterically hindered substrates can also be converted to their corresponding carbazoles (**7i–l**, **7n** and **7s**) in 59–93% yields. The boronic triazenes with different substituted groups, such as CN, O*i*Pr, and dimethyl groups, can also be converted to their corresponding carbazoles in 59–92% yields (**7p–t**). In particular, when it came to dimethyl phenyl triazene boronic acid, carbazoles **7s** and **7t** were formed directly without further treatment with BF_3·OEt_2. Functional groups, such as carbonyl group of ketone (**7f** and **7r**) and aldehyde (**7g** and **7p**), hydroxyl (**7j**), alkynyl (**7n**), alkenyl (**7l** and **7s**), and nitro groups (**7h**), can be tolerated in this Lewis acid-promoted process.

Next we extended the work to construct dibenzofuran units. Initially, we treated phenol triazene **8a**, which can be prepared by using the Suzuki–Miyaura cross-coupling reaction, with BF_3·OEt_2 (4.0 equiv) in EtOH at room temperature and the desired product dibenzofuran-2-carboxylic acid ethyl ester (**9a**, Scheme 5) was obtained in 30% yield. However, when DMF was used as the solvent, the yield increased to 81%. Upon exploring the scope of the intramolecular oxylation, a number of phenol–triazene substrates (**8b–8i**) were examined



Scheme 4. Scope of synthesis functionalized carbazoles by a tandem cross-coupling/nucleophilic aromatic substitution approach. All reactions were carried out with bromotriazene (0.5 mmol), boronic triazene (0.8 mmol), Cs_2CO_3 (1.25 mmol) and $[Pd(PPh_3)_4]$ (0. 025 mmol) in dioxane (4 mL) at 100 °C for 12 h. Then, the crude cross-coupling product reacts with BF_3·OEt_2 (2.0 mmol) in EtOH (4 mL) at room temperature for 10 min to 1.5 h. Yields shown are of the isolated product after flash column chromatography. Carbazoles **7s** and **7t** were formed directly without further treatment with BF_3·OEt_2.

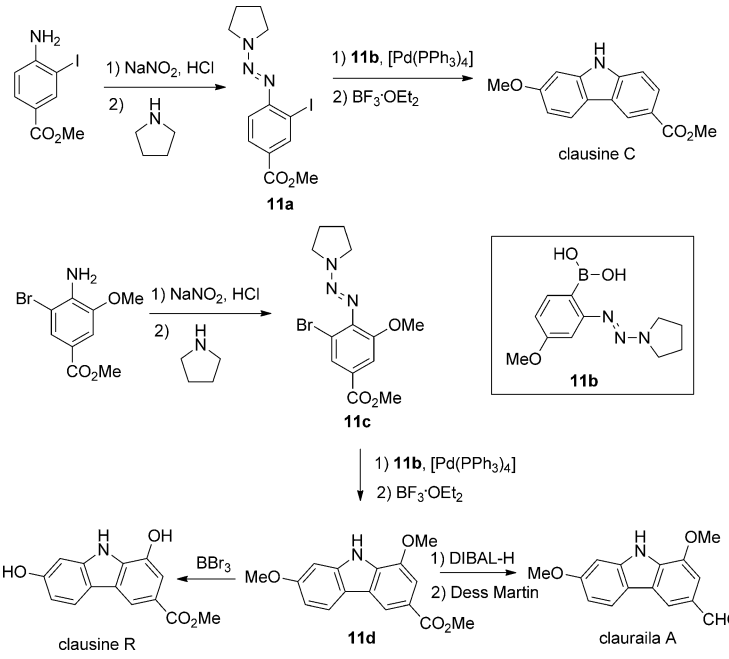


Scheme 5. Scope of synthesis functionalized dibenzofurans from phenol–triazene substrates. All reactions were carried out with phenol–triazene (0.5 mmol), BF_3·OEt_2 (2.0 mmol) in DMF (20 mL) at 50 or 70 °C for 3–7.5 h. Yields shown are of the isolated product after flash column chromatography.

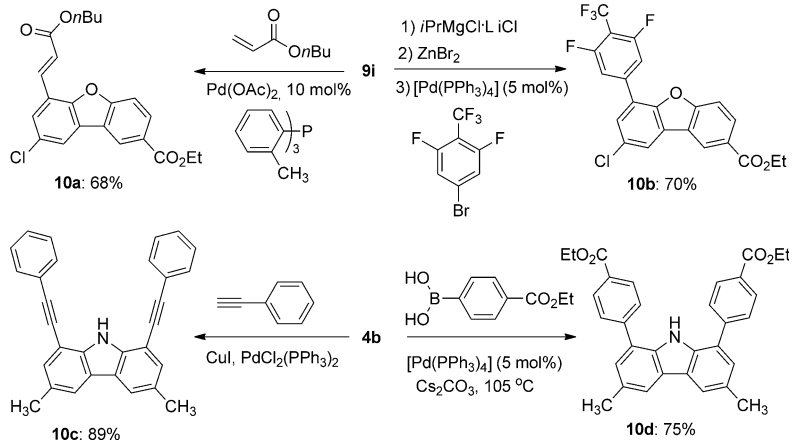
and the results were summarized in Scheme 5. The electron properties at both the phenol moiety and the triazene moiety do not significantly influence the outcome of the reaction. The substrates bearing either electron-donating (**8b**, **8c**, and **8d**) or electron-withdrawing groups on the phenols (**8e–i**) all give their corresponding cyclization products in good to excellent yields (68–86%). Functional groups, such as carbonyl of ketone (**9g**) and aldehyde (**9h**), ester (**9d–e** and **9g**), cyano (**9c**), and iodo (**9i**) can be tolerated in this Lewis acid-promoted reaction.

The iododibenzofuran and iodocarbazole can be converted to their corresponding cross-coupling products using transition-metal-catalyzed reactions.[20] Thus, the Heck reaction took place when we heated iodo-dibenzofuran **9i** with butyl acrylate in the presence of $Pd(OAc)_2$ and tri-*o*-tolylphosphine and provided the coupling product **10a** in 68% yield (Scheme 6). After Mg/I exchange with *i*PrMgCl·LiCl and transmetalation with $ZnBr_2$, the iodo-dibenzofuran **9i** underwent a Negishi cross-coupling reaction with 5-bromo-1,3-difluoro-2-(trifluoromethyl)benzene and provided the F-substituted compound **10b** in 70% yield. The Sonogashira and Suzuki coupling reactions with the diiodo-carbazole **4b** gave the corresponding coupling products **10c** and **10d** in 89 and 75% yields, respectively.

The Lewis acid-promoted approach is a powerful method for the construction of functionalized carbazoles in total synthesis of carbazole alkaloids. Scheme 7 outlines the total synthesis of clausine C,[21] clausine R,[22] and clauraila A[23] using the BF_3·OEt_2-promoted annulation process as a key step. The Suzuki-Miyaura cross-coupling between iodo-triazene **11a** and triazene–boronic acid **11b** can furnish the formation of biaryl ditriazene. After removing the catalyst



Scheme 7. Total synthesis of clausine C, clausine R, and clauraila A.



Scheme 6. Coupling reactions of iodo-substituted dibenzofuran and carbazole.

by flash column chromatography, extended treatment of the biaryl ditriazene with BF_3·OEt_2 led to the corresponding product clausine C in 71% yield. Carbazole **11d** can be prepared in a same procedure. Demethylation of **11d** with BBr_3 afforded carbazole clausine R in 68% yield. Also in this case, clauraila A was formed in 72% yield after treating **11d** with DIBAL-H and Dess–Martin reagents (Scheme 7).

In summary, we have developed a Lewis acid-promoted nucleophilic aromatic substitution approach to the regioselective synthesis of highly substituted carbazoles and dibenzofurans in good to excellent yields. These reactions are carried out in mild conditions with good tolerance to a variety of functional groups. Furthermore, this new protocol was successfully applied to the synthesis of natural carbazole alkaloids, such as clausine C, clausine R and clauraila A. Further investigations of the reaction mechanism and synthetic applications are underway.

Experimental Section

In a 50 mL Schlenk tube, aryltriazene **5a** (0.5 mmol, 1.0 equiv), phenylboronic acid **6a** (0.8 mmol, 1.6 equiv), $Pd(PPh_3)_4$ (0.025 mmol, 0.05 equiv), and Cs_2CO_3 (1.25 mmol, 2.5 equiv) were dissolved in dioxane (4.0 mL). The tube was filled with N_2 and immediately sealed with a Teflon lined cap. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. After the reaction mixture was cooled to room temperature, water was added. The resulting mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The obtained mixture was dissolved in EtOH (4.0 mL) and cooled to 0 °C. Next, $BF_3{\cdot}OEt_2$ (0.26 mL, 4.0 equiv) was added dropwise. After the mixture was stirred for 10 min at 0 °C, it was warmed to room temperature and stirred for another 10 min to 1.5 h. Then H_2O was added and the reaction mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure. The pure carbazole **7a** was obtained in 90% yield after purification by silica gel chromatography.

Acknowledgements

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Keywords: alkaloids · carbazole · dibenzofuran · nucleophilic substitution · regioselectivity · triazene

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