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Benzannulation of 2-Alkenylindoles using Aldehydes by Sequential Triple-Relay Catalysis: A Route to Carbazoles and Carbazole Alkaloids

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Abstract: Benzannulation of 2-alkenylindoles with readily available aldehydes, under one-pot sequential triple-relay-catalysis, provides an easy access to several structurally unique carbazoles including 2- and 3-alkenylcarbazoles. This *protecting group-free* method enabled one-pot synthesis of alkaloids such as hyellazole and 6-chlorohyellazole, and the formal syntheses of seven other alkaloids. Construction of the core structure, present in murastifoline A, murrafoline E, and related alkaloids was also demonstrated. Even conjugated 3,3′-biscarbazoles can also be synthesized by *one-pot, two-fold sequential triple-relay catalysis.*

Keywords: alkaloids; annulation; carbazoles; conjugated materials; sequential catalysis

The carbazole framework is a privileged structural motif (Figure 1) present in a large number of natural products, drugs, and biologically active compounds.[1–3] In addition, numerous compounds, containing the carbzole core, show antiviral, antimalarial, and antitumor activities indicating their increasing potential in medicinal chemistry.[4] Beside this, cabazoles have broad range of importance in materials chemistry due to their wide band gap, thermal, electrical, and optical properties.[5] The carbazole-based oligomers are very important scaffolds due to their significant applications in photo-conductors,[6] electroluminescent materials,[7] charge transporting, and emitting materials in organic light-emitting diodes.[8]

A literature survey on the construction of carbazoles reveals that the synthetic strategies can be categorized into two major classes: (i) formation of the middle pyrrole ring *via* either C–N or C–C coupling of aniline derivatives,[9,10] and (ii) benzannulation of functionalized indoles.[11,12] Although the first one is comparatively well explored, it requires functionalized aniline derivatives, prepared by tedious synthetic efforts. On the other hand, benzannulation methods recently have gained particular interest due to the easy accessibility of the desired indole precursors. For instance, Itami et al. developed the formation of carbazoles from *N*-protected indoles using a Pd-Cu-Ag trimetallic system.[11b] Huang and Wang reported a tandem Cp*Rh(III) and Brønsted acid-catalyzed

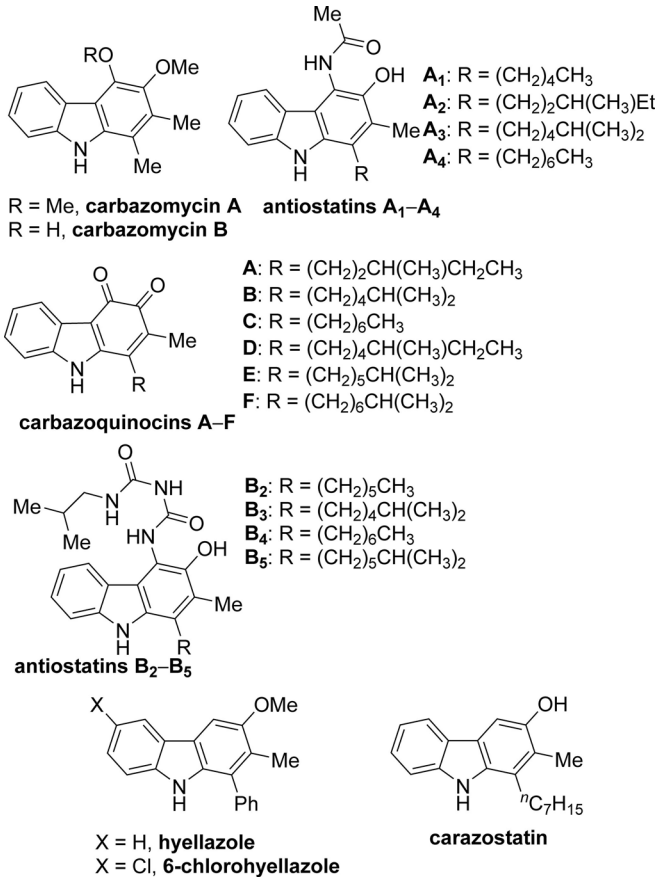


Figure 1. Some representative carbazole alkaloids.

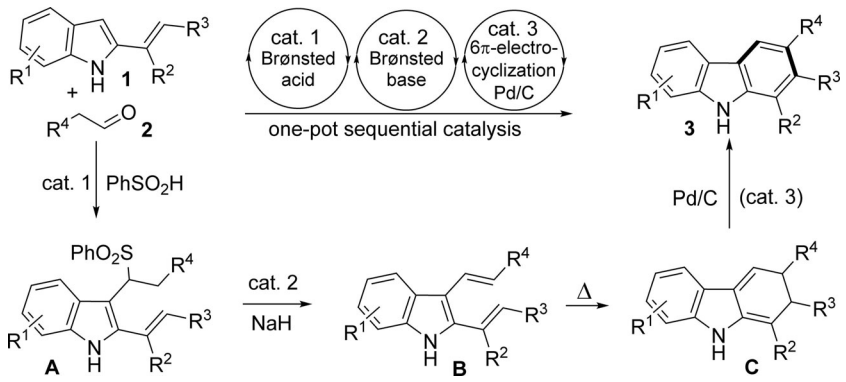
benzannulation of indoles for the synthesis of substituted carbazoles.[11c] Reddy et al. also demonstrated a [4+2] benzannulation method to obtain carbazoles from *N*-protected 2-alkenylindoles.[11g]

Despite their own advantages, most of these strategies are based on *N*-protected indoles. Apart from this, the synthesis of carbazoles by the reported synthetic strategies faces serious limitations such as functional group intolerance, limited substrate scope, complicated starting materials, regioselectivity of C–C or C–N bond formation reactions, and use of expensive catalysts. With the expectation that the benzannulation strategy will provide ample opportunity to complement the above-mentioned limitations, we have undertaken the challenge to develop a general, step- and atom-economic method to synthesize several functionalized carbazoles and carbazole alkaloids by protecting group-free, one-pot sequential triple-relay catalysis.[13,14] Our recently developed indole C-3 alkenylation method enabled us to achieve this benzannulation reaction using simple aldehydes.[14] To the best of our knowledge, simple aldehydes have not been used directly as annulating agents to construct the carbazole ring. We anticipated that this strategy may provide a direct approach to install various alkyl, alkenyl, aryl, heteroaryl, and alkoxy functional groups at the C-3 position of carbazole, which is still a major challenge when using the existing methods. Beside this, it may open a new route to synthesize various structurally unique bis-carbazoles and carbazole alkaloids in a step-economic way.

To achieve the goal, four completely different reactions need to be executed one after another without isolating a single intermediate (Scheme 1). The four reactions include: (i) a first Brønsted acid-catalyzed generation of sulfonylindole **A** using $PhSO_2H$;[14] (ii) next, a Brønsted base-catalyzed *in situ* generation of 2,3-dialkenylated indole **B**;[14] (iii) then, a 6π-electrocyclization reaction to obtain dihydrocarbazole **C**; and (iv) finally the dehydrogenation of **C** to furnish the desired carbazole **3**.

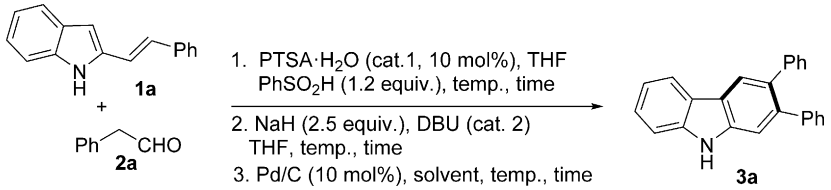
To optimize the reaction conditions, (*E*)-2-styryl-1*H*-indole **1a** and commercially available phenylacetaldehyde **2a** were chosen as model substrates. Tetrahydrofuran (THF) was found to be the suitable solvent for the C-3 alkenylation of indole. Reaction of **1a** with **2a** by using 5 mol% $PTSA{\cdot}H_2O$, 5 mol% DBU, and 5 mol% Pd/C in THF-xylene solvent system furnished **3a** in 44% yield (Table 1, entry 1). Increasing the Pd/C catalyst loading to 10 mol% and temperature for the step 3, improved the yields significantly (entries 2–4). Executing the first step at 60 °C while maintaining room temperature for the second step provided better results (entries 5 and 6). In the absence of NaH, the yield decreased considerably (entry 7). Changing the solvent for the step 3 to decalin, accelerated the reaction rate (entry 8). Other high boiling solvents, such as mesitylene and 1,2-dicholorobenzene were not suitable (entries 9 and 10). The highest yield was obtained by conducting the last step at 180 °C (84%, entry 11). While the absence of $PTSA{\cdot}H_2O$ led to a complex reaction mixture, omission of DBU only gave carbazole **3a** in 35% yield, proving their necessity for the reaction (entries 12 and 13). Finally, omitting the Pd/C catalyst, and conducting whole sequence under air provided product **3a** in 38% yield (entry 14). We also investigated the compatibility of other oxidants for the final aromatization step. Here, after conducting the 6π-electrocyclization reaction at 160 °C for 24 h in decalin (for all oxidant screenings), the reaction mixture was treated with 0.25 equiv. of iodine in dimethyl sulfoxide (1.0 mL, 24 h, at 100 °C) to furnish **3a** in 42% yield. Furthermore, one-pot treatment of the electrocyclized product with either *tert*-butyl hydroperoxide or benzoquinone as oxidants (2 equiv., 24 h) at room temperature failed to provide **3a**. However, the same reaction with 2.0 equiv. of Dess–Martin periodinane (24 h, at room temperature) provided **3a** in 49% yield.

With the optimized conditions in hand, the scope of this method was studied with various aldehydes having different functional groups. 4-Chlorophenyl- and 1-naphthylacetaldehydes successfully took part in the reaction and carbazoles **3b** and **3c** were isolated in good yields (70–79%, Scheme 2). Heteroarylacetaldehydes were also found to be suitable reaction partners



Scheme 1. Strategy for the synthesis of carbazole.

Table 1. Optimization of the reaction conditions.[a]



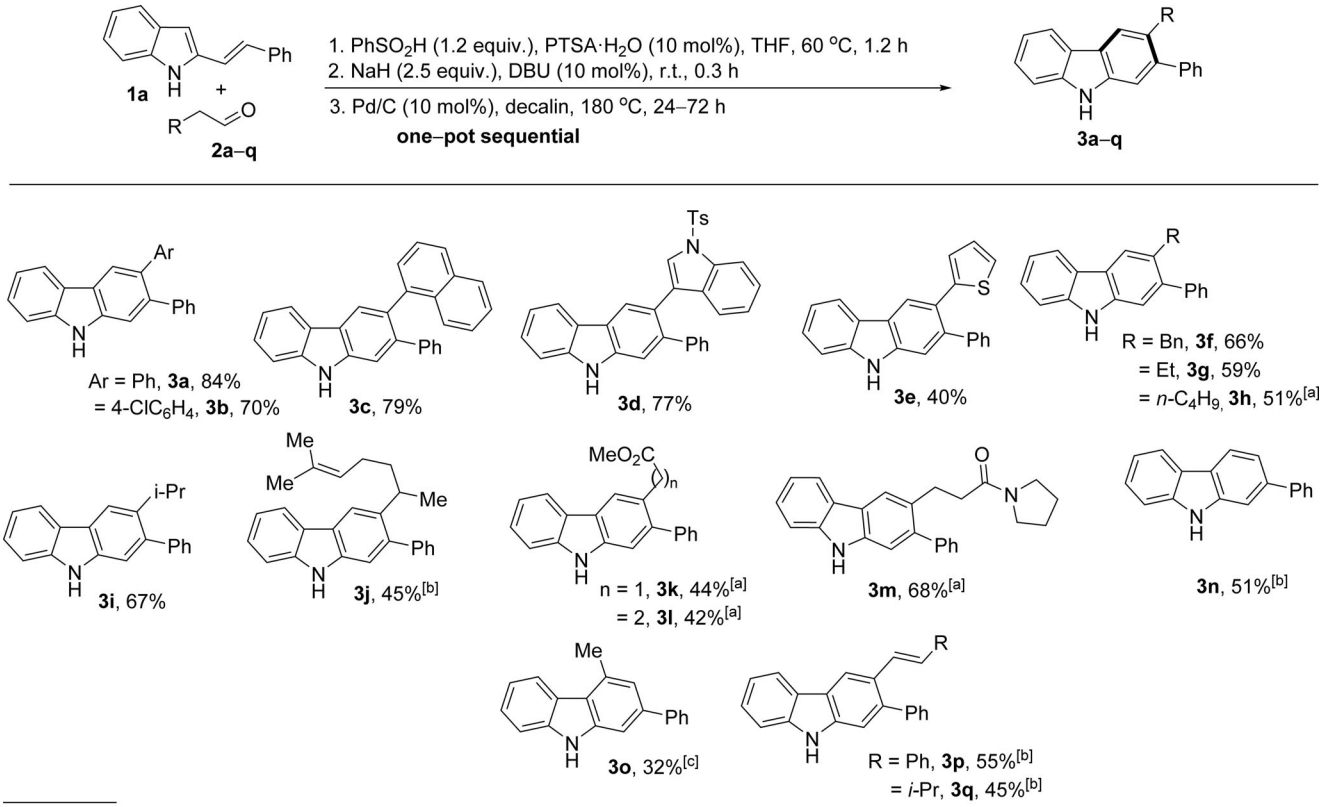
Entry	DBU [mol%]	Solvent (step 3)	Tempertaure [°C] (steps 1/2/3)	Time [h] (steps 1/2/3)	Yield[b] [%]
1[c,d]	5	xylene	r.t./r.t./140	3/0.5/72	44
2[d]	5	xylene	r.t./r.t./140	3/0.5/72	54
3[d]	5	xylene	r.t./r.t./160	3/0.5/60	72
4	10	xylene	r.t./r.t./160	2.5/0.3/60	76
5	10	xylene	60/60/160	1.2/0.3/60	69
6	10	xylene	60/r.t./160	1.2/0.3/60	78
7[e]	30	xylene	60/–/160	1.2/48	51
8	10	decalin	60/r.t./160	1.2/0.3/48	78
9	10	mesityline	60/r.t./160	1.2/0.3/60	<2
10	10	*o*-DCB	60/r.t./160	1.2/0.3/60	<2
11	**10**	**decalin**	**60/r.t./180**	**1.2/0.3/44**	**84**
12[f]	10	decalin	60/–/–	–	–
13	–	decalin	60/r.t./180	1.2/3/48	35
14[g]	10	decalin	60/r.t./180	1.2/0.3/44	38

[a] Reactions were carried out in a sealed pressure tube using 1.5 equiv. of **2a**, 1.2 equiv. of $PhSO_2H$, 2.5 equiv. of NaH.
[b] Isolated yields.
[c] 5.0 mol% of Pd/C were used.
[d] 5.0 mol% of PTSA·H_2O were used.
[e] Without NaH, and omitting step 2.
[f] Without PTSA·H_2O, step 1 was complex.
[g] Without Pd/C, in the presence of air.

(**3d** and **3e**, 40–77% yields). To synthesize comparatively less explored 3-alkylated carbazoles, various aliphatic aldehydes were subjected to the standard conditions. Aliphatic aldehydes having normal as well as branched chains were suitable substrates (**3f–j**, 45–67%). Aldehydes bearing ester and amide functional groups also furnished the desired carbazoles **3k–m** in 42–68% yields. Benzannulation using acetaldehyde was also accomplished to provide 2-phenylcarbazole **3n** in 51% yield. This opens up a route to synthesize several 2-arylcarbazoles which are difficult to synthesize by traditional cross-coupling reactions due to the difficulties associated with the synthesis of 2-halocarbazole electrophiles.[15] Acetone was also a suitable substrate for this annulation reaction albeit furnishing a lower yield of the carbazole **3o**. Alkenylated carbazoles are important building blocks for the synthesis of OLED materials, and the installation of an alkenyl unit on carbazole required significant efforts.[16] Pleasingly, 3-alkenylated carbazoles **3p** and **3q** were directly synthesized in 45–55% yields using appropriate alkenylacetaldehydes. Gratifyingly, readily synthesized 2-indolyl-1,3-dienes **1b** 'and **1c** were compatible under the reaction conditions to provide the challenging 2-alkenylated carbazoles **3r** and **3s** in 50% and 46% yields (Scheme 3).

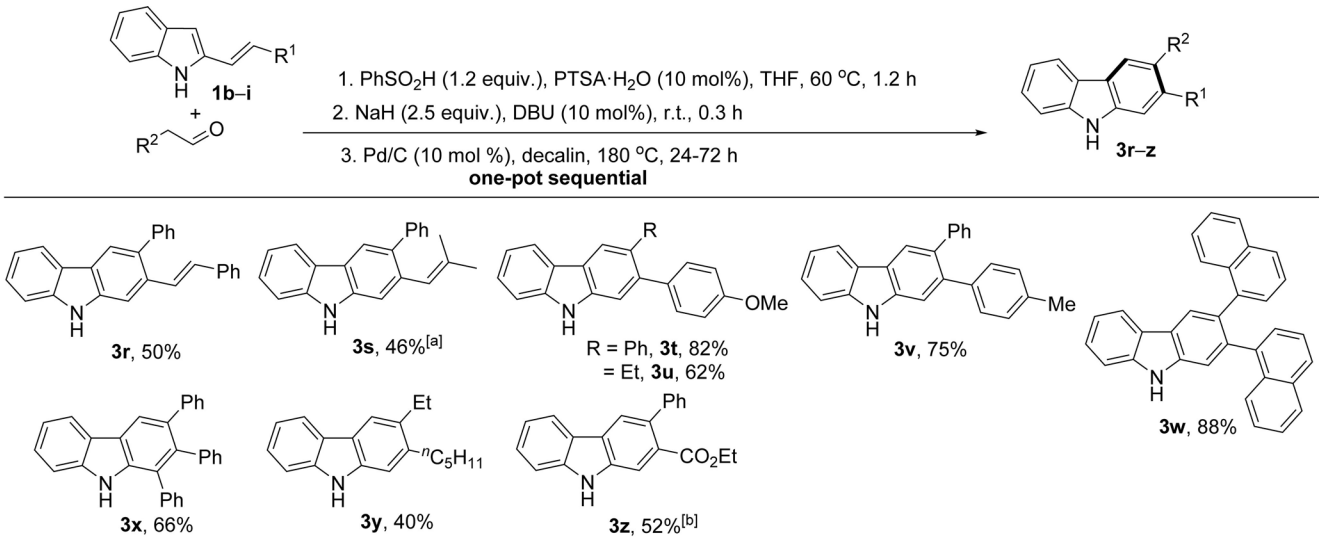
The scope of this method was further explored by varying the 2-alkenylindole partner. Several 2-arylated carbazoles **3t–v** were prepared by using the corresponding **1d** and **1e** (62–82%, Scheme 3). Although installation of two sterically hindered aryl substituents at the vicinal position of an aromatic ring is rarely reported in the literature, 2,3-dinaphthylcarbazole **3w** was readily synthesized in 88% yield. Installation of three phenyl substituents at the 1,2, and 3 positions of carbazole **3x** was also accomplished in 66% yield. Furthermore, 2,3-dialkylated carbazole **3y** was obtained in moderate yield (40%). An electron-deficient 2-alkenylindole was also found to be a suitable substrate (**3z**, 52%).

3-Hydroxy- and 3-methoxycarbazoles are a common structural motif present in many biologically active carbazole natural products (Figure 1).[1,3] Installation of a hydroxy functionality at the C-3 position of carbazole will eventually lead to many carbazole alkaloids or their advanced intermediates directly from the respective 2-alkenylindoles **1**. The success of our strategy depends on the generation of highly electron-rich enol ether intermediate **B** (Scheme 1, R^4 = OR). To confirm the sustainability of the alkoxy group present in **C** under the reaction conditions, first aldehyde **2r** was reacted with **1a**. Pleasingly, carbazole



[a] 15 mol% Pd/C used.
[b] Step 1 at room temperature, and 1.5 equiv. $PhSO_2H$.
[c] CH_2Cl_2 was used in place of THF.

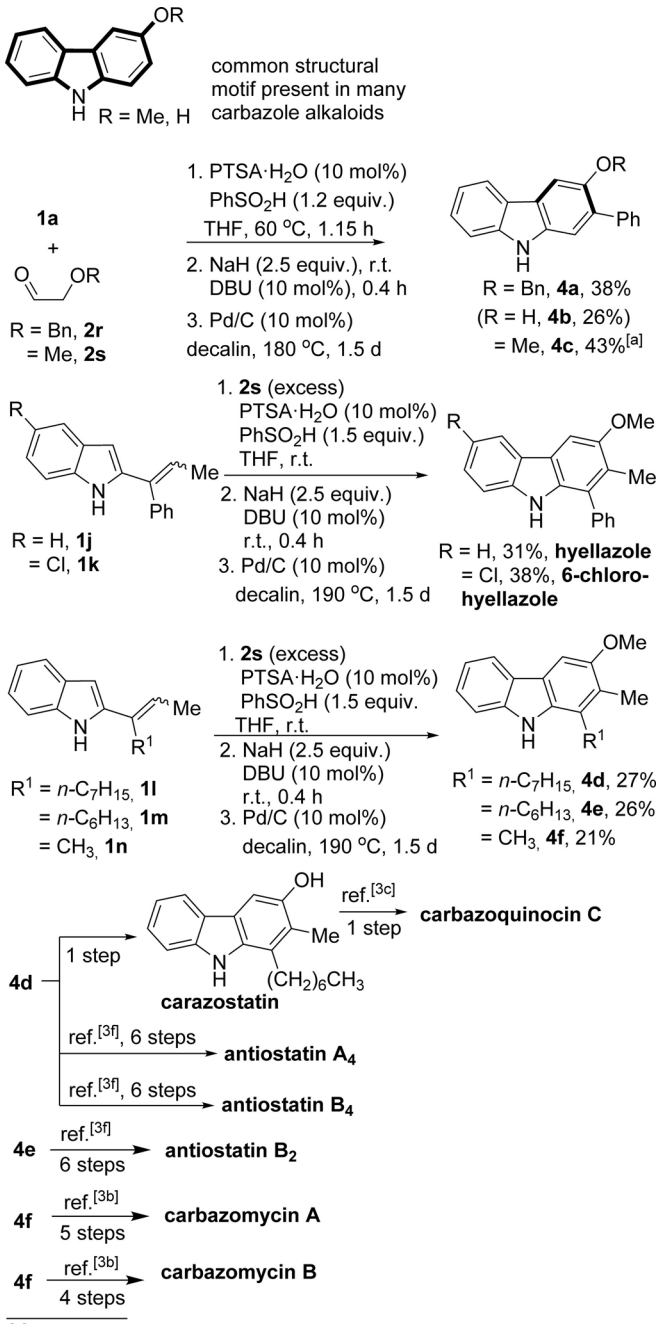
Scheme 2. Scope of aldehydes. *Reaction conditions:* **1a** (1.0 equiv.), aldehyde **2** (1.5 equiv.), $PhSO_2H$ (1.2 equiv.), PTSA·H_2O (10 mol%), THF, 60 °C; NaH (2.5 equiv.), DBU (10 mol%), THF, room temperature; Pd/C (10 mol%), decalin, 180 °C; isolated yields.



[a] Step 1 at room temperature, and 1.5 equiv $PhSO_2H$.
[b] 30 mol% PTSA·H_2O was used, and step 3 at 160 °C in xylene.

Scheme 3. Scope of 2-alkenylindoles. *Reaction conditions:* 2-alkenylindole **1** (1.0 equiv.), aldehyde **2** (1.5 equiv.), $PhSO_2H$ (1.2 equiv.), PTSA·H_2O (10 mol%), THF, 60 °C; NaH (2.5 equiv.), DBU (10 mol%), THF, room temperature; Pd/C (10 mol%), decalin, 180 °C; isolated yields.

4a was isolated in 38% yield along with 26% of its debenzylated analogue **4b** (Scheme 4). Conducting the whole sequence under air as discussed earlier (Table 1, entry 14), provided product **4a** in 17% yield, and no **4b** was detected. To avoid debenzylation and to install the required methoxy functional group, aldehyde **2s** was chosen, and product **4c** was isolated in 43% yield. To our delight, despite the presence of benzyloxy or methoxy leaving groups, no dealkoxylated product **3n** was detected. Treatment of the crude aldehyde **2s** with **1j** furnished the desired hyellazole natural product in 31% yield in one-pot.[1a,3a,c,g] In a similar fashion, synthesis of 6-chlorohyellazole was also accomplished from **1k** in 38% yield. Finally, *o*-methylcarazostatin **4d** was synthesized in one-pot from **1l**. *o*-Methylcarazostatin **4d** was previously used for synthesis of antiostatin A_4, antiostatin B_4, and carbazoquinocin C.[3c,f,k,l] Two more advanced intermediates **4e** and **4f** were also prepared in 26% and 21% yields, respectively. Synthesis of alkaloid antiostatin B_2 was reported from **4e**,[3f] and carbazomycin A and carbazomycin B from **4f**.[3b,h–j]



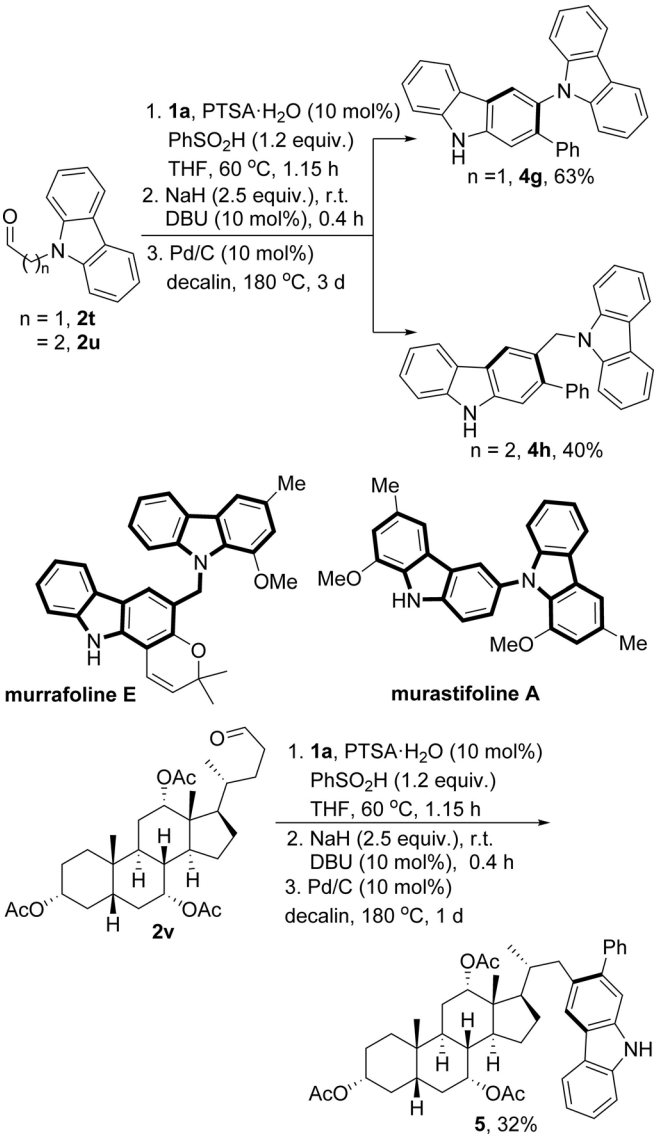
[a] Step 1 at room temperature, step 2 at 60 °C, 1.5 equiv. of $PhSO_2H$.

Scheme 4. Synthesis of carbazole alkaloids.

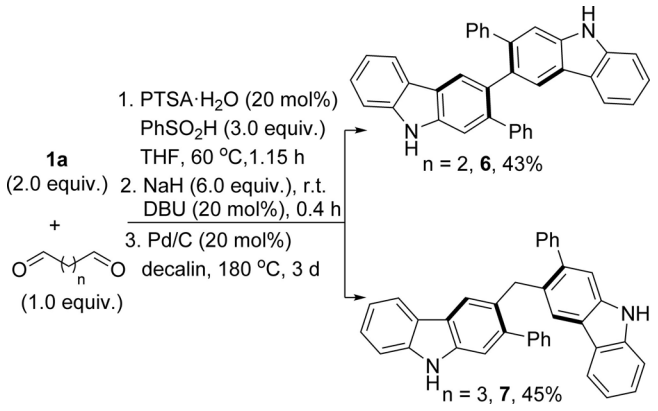
Among the four possible core structures of biscarbazoles accessible *via* C–N coupling, 3,9′- and 2,9′-biscarbazoles are of particular interest due to their well-studied pharmacological properties.[1a,c,17] Beside these, 3,9′-linked carbazole oligomers exhibit photoemission properties with high quantum yield.[8b] The present methods to prepare them by transition metal-catalyzed C–N cross-coupling reactions require a protecting group for the carbazole electrophile.[18] A protecting group-free synthesis of 3,9′-biscarbazole **4g** was realized by using aldehyde **2t** (63%, Scheme 5). The core structure present in biscarbazole **4g** is also found in many carbazole alkaloids, such as murastifoline A.[17a] In a similar way methylene-linked biscarbazole **4h** was also prepared in 40% yield using aldehyde **2u**. The core structure of **4h** is found in the biscarbazole-based natural products murrafoline E, bismurrayafoline A, and bismurrayafolinol.[17c,d] Acetate-protected cholic acid-derived aldehyde **2v** also reacted with **1a** to provide the highly functionalized carbazole **5** in 32% yield.

Considering the importance of 3,3′-biscarbazole for the preparation of conjugated poly(3,6-carbazole)s,[19] a method was developed to obtain **6** directly from **1a**. Here biscarbazole **6** was synthesized in 43% yield using succinaldehyde by the one-pot, 2-fold sequential triple-relay catalysis associated with eight distinct steps having an average yield of 90% for each (Scheme 6). Similarly, a methylene-linked biscarbazole **7** was also synthesized in 45% yield using glutaraldehyde (Scheme 6).

In summary, benzannulation of 2-alkenylindoles using readily available aldehydes was achieved to construct structurally diverse carbazoles. The usefulness of the method was demonstrated by synthesizing carbazole alkaloids or their advanced intermediates. Alkenylated carbazoles, an important class of monomers to obtain conjugated-organic materials, were also prepared in one step. A protecting group-free synthesis of 3,9′-biscarbazole was also realized by this method. This method was also further extended to furnish 3,3′-biscarbazole by one-pot, 2-fold sequential triple-relay catalysis. We believe that this method has high potential to provide a facile route to carbazole-based conjugated materials in a step- and atom-economic way.



Scheme 5. Synthesis of the C–N biscarbazole alkaloid core structure.



Scheme 6. Synthesis of biscarbazoles by one-pot, 2-fold sequential triple-relay catalysis.

Experimental Section

Representative Method for the Synthesis of 3a

THF (0.4 mL) was added to a mixture of $PhSO_2H$ (0.24 mmol) and PTSA·H_2O (0.02 mmol) in a 15-mL sealed pressure tube. To the resulting reaction mixture **1a** (0.20 mmol) and a solution of **2a** (0.30 mmol) in THF (0.6 mL) were added and the mixture heated at 60 °C with continuous stirring. Upon complete consumption of the starting material, the reaction mixture was cooled down to room temperature, NaH (0.50 mmol) and DBU (0.02 mmol) were added successively and stirring was continued at room temperature. Upon complete consumption of sulfonylindole **A**, Pd/C (0.02 mmol) was added to the reaction mixture along with 2.0 mL decalin, the sealed tube was filled with nitrogen gas and heated to 180 °C. After completion of the reaction, the crude residue was directly purified by silica gel column chromatography to obtain **3a**; yield: 84%; see the Supporting Information for details.

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