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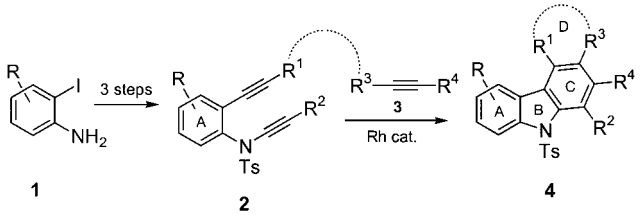
A Highly Efficient and Flexible Synthesis of Substituted Carbazoles by Rhodium-Catalyzed Inter- and Intramolecular Alkyne Cyclotrimerizations**

Bernhard Witulski* and Carole Alayrac

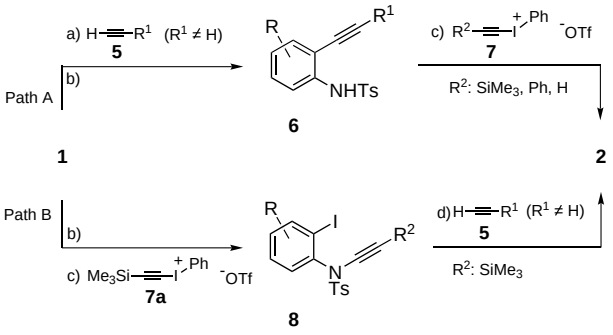
Syntheses of substituted carbazoles have attracted considerable attention because carbazole alkaloids are a growing class of natural products that exhibit a variety of biological activities.[1,2] Moreover, annelated carbazoles structurally related to the natural indolocarbazole staurosporine have gained significance because of their protein kinase C (PKC) and topoisomerase inhibitory activity.[3]

Although several syntheses of substituted carbazoles as well as chemical modifications of the carbazole nucleus are established,[1,4] the major challenge in carbazole chemistry arises from the question of how to functionalize regioselectively up to eight aromatic ring positions. We have designed a strategy for the assembly of the carbazole nucleus by an A→ABC or A→ABCD ring-formation approach that is based on the reliability of the Sonogashira reaction,[5] our previously reported synthesis of functionalized ynamides,[6] and the efficiency of transition-metal-catalyzed alkyne cyclotrimerizations (Scheme 1).[7]



Scheme 1. A→ABC or A→ABCD ring-formation approach to substituted carbazoles by rhodium-catalyzed alkyne cyclotrimerization.

The diynes **2** were prepared in three steps starting from readily available 2-iodoanilines **1**. Sonogashira reactions between **1** and terminal alkynes **5** followed by N-tosylation of the aniline functionality gave alkynes **6**, which thereafter underwent N-ethynylation with alkynyliodonium salts **7** to give the diynes **2** in good overall yields (Scheme 2, path A).



Scheme 2. a) **5** (1.3 equiv), 5 mol% $[PdCl_2(PPh_3)_2]$, 10 mol% CuI, NEt_3, DMF, room temperature, 60–98%; b) TsCl, pyridine, THF, 70–92%; c) potassium hexamethyldisilazane (KHMDS), toluene, 0°C, then addition of **7** (1.4 equiv), room temperature, 52–93% for **6**→**2**, 87–98% for **8**; d) **5** (1.4 equiv), 5 mol% $[PdCl_2(PPh_3)_2]$, 10 mol% CuI, 10 mol% PPh_3, NEt_3, DMF, 80°C, 54–68%.

Alternatively, N-ethynylation reactions with **7a** were carried out with tosylated **1** to give the ynamides **8**, which were then converted to **2** through Sonogashira reactions (Scheme 2, path B). While the conversion of **1** to **6** proceeded readily at room temperature, cross-coupling reactions with **8** to give **2** required heating to 80°C, probably because of an increase of steric hindrance. Notably, the use of trimethylsilylacetylene in the Sonogashira reaction, or the use of **7a** for the N-ethynylation reaction following either path A or B in Scheme 2 allowed further manipulations of the diynes **2** through protective group strategies.

Crossed alkyne cyclotrimerizations between diynes **2** and monoalkynes **3** promoted by Wilkinson's catalyst[6b,8] proceeded under very mild conditions (3–5 mol% $[RhCl(PPh_3)_3]$, 5–6 equivalents of **3**, toluene as solvent) to give the carbazoles **4** in high yields (Scheme 1, Table 1). Notably, the additional triple bond in **2e** did not interfere with the formation of carbazole **4e** (80% yield, Table 1, entry 5). The outstanding efficiency of the carbazole formation by crossed alkyne cyclotrimerizations is presumably a consequence of conformational restrictions present in the diynes **2**. A conformation in which both alkyne moieties are close to each other appears likely and therefore favors the overall catalytic process.

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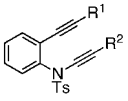
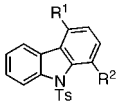
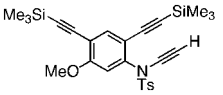
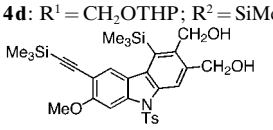
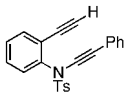
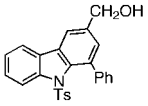
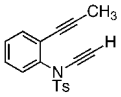
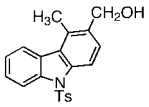
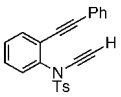
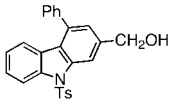
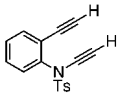
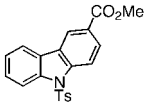
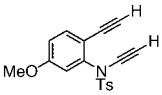
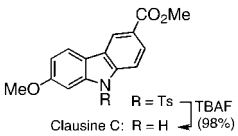
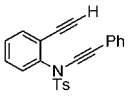
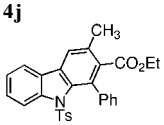
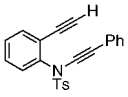
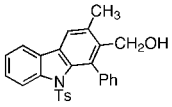
Table 1. Functionalized carbazoles **4** through rhodium-catalyzed crossed alkyne cyclotrimerizations (3–5 mol% $[RhCl(PPh_3)_3]$, 5–6 equivalents of monoalkyne **3**, toluene, room temperature, 1–12 h).

Entry	Diyne **2**	Monoalkyne **3**	Carbazole **4**	Isomer ratio	Yield [%]
					
1	**2a**: $R^1 = H$; $R^2 = H$	**3a**	**4a**: $R^1 = H$; $R^2 = H$		90
2	**2b**: $R^1 = CH_2OTHP$;[a] $R^2 = H$	**3a**	**4b**: $R^1 = CH_2OTHP$; $R^2 = H$		95
3	**2c**: $R^1 = H$; $R^2 = Ph$	**3a**	**4c**: $R^1 = H$; $R^2 = Ph$		98
4[b]	**2d:** $R^1 = CH_2OTHP$; $R^2 = SiMe_3$ 	**3a** 	**4d**: $R^1 = CH_2OTHP$; $R^2 = SiMe_3$ 		90
5[c]	**2e** 	**3b** 	**4e** 		80
6	**2c** 	**3c**	**4f** 	(5:1)	95
7	**2f** 	**3c**	**4g** 	toluene: (3.5:1) ethanol: (1.4:1)	89 71
8	**2g** 	**3c** 	**4h** 	toluene: (1.5:1) ethanol: (5.8:1)	97 68
9	**2a** 	**3d**	**4i** 	(4:1)	72
10	**2h** 	**3d** 	**4j** 	(3.8:1)	78
11	**2c** 	**3e** 	**4k** 	(6:1)	91
12	**2c**	**3f**	**4l**	(1:1)	98

[a] THP = tetrahydropyran. [b] $T = 80\,^{\circ}C$, 17 h. [c] $T = 40\,^{\circ}C$, 19 h.

Cyclotrimerizations of diynes **2** with the terminal monoalkyne **3c** afforded one major regioisomer of **4** (Table 1, entries 6–8).[9] In agreement with previously reported crossed alkyne cyclotrimerizations utilizing Wilkinson's catalyst,[8e,g] regioselectivities observed in the carbazole series were based on a complex interplay between steric factors and on solvent effects. In the case of **4g**, for which the *ortho* isomer was favored, the regioselectivity was best in toluene (Table 1, entry 7), whereas in the case of **4h**, for which the *meta* isomer was favored, the selectivity could be significantly improved by using ethanol as solvent (Table 1, entry 8). Furthermore, regioselectivity was influenced by electronic parameters. Although electron-deficient monoalkynes are poor cyclotrimerization partners, the reaction of propiolic ester **3d** with the diynes **2a** and **2h** afforded the carbazoles **4i** (72% yield, ratio of isomers 4:1) and **4j** (78% yield, ratio of isomers 3.8:1), respectively, as major isomers. Using the electron-deficient disubstituted monoalkyne **3e** a high selectivity was achieved in the preparation of carbazole **4k** (Table 1, entry 11). The latter result was again driven by electronic effects

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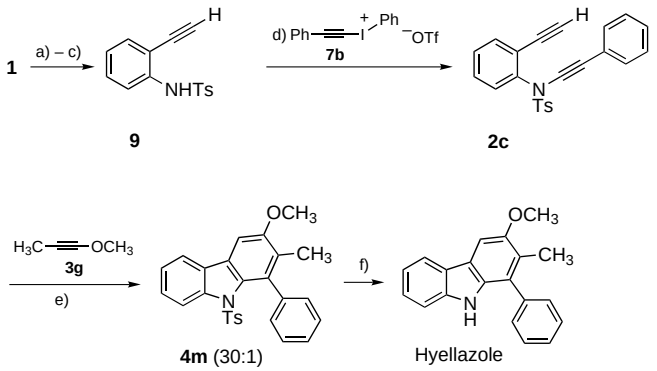
as revealed by the lack of regioselectivity observed with the electron-neutral disubstituted monoalkyne **3f** (Table 1, entry 12).

To illustrate the applicability of our method in natural product synthesis, the target-oriented syntheses of two naturally occurring carbazole alkaloids—clausine C and hyellazole—were investigated. Clausine C,[10] which was recently isolated from the stem bark of *Clausena excavata*, a wild shrub that has been claimed to be a useful folk medicine in the treatment of snake bites, was readily accessible after deprotection of carbazole **4j** (Table 1, entry 10) with tetrabutylammonium fluoride (TBAF) in refluxing THF (98% yield).[11] Clausine C was thus obtained in six steps from 2-iodo-5-methoxyaniline with an overall yield of 40%.

Further potential of our methodology was demonstrated through the straightforward synthesis of hyellazole, a marine carbazole alkaloid isolated from the blue-green algae *Hyella caespitosa*.[12] The key step of our synthesis resides in the regioselective alkyne cyclotrimerization of diyne **2c** with 1-methoxy-propyne **3g** (Scheme 3). Based on previous results with electron-deficient monoalkynes, we expected that the use of an electron-rich monoalkyne as cyclotrimerization partner would invert the regioselective outcome of the reaction as observed with **3e** (Table 1, entry 11). Indeed, carbazole **4m** was obtained with excellent chemo- and regioselectivity by utilizing the electron-rich monoalkyne **3g** and Wilkinson's catalyst (89% yield, isomer ratio = 30:1, toluene, 20°C). Isomerically pure hyellazole was thereafter obtained through deprotection of the tosyl group (Ts) with TBAF in refluxing THF followed by crystallization. With only six steps starting from commercially available 2-iodoaniline and an overall yield of 39%, this synthesis of hyellazole becomes the most efficient one in terms of conciseness and overall yield.[13]



Scheme 3. Synthesis of hyellazole: a) trimethylsilylacetylene (1.3 equiv), 5 mol% $[PdCl_2(PPh_3)_2]$, 10 mol% CuI, Et_3N, DMF room temperature, quant.; b) TsCl, pyridine, THF, 89%; c) TBAF, THF, 0°C, 90%; d) KHMDS, toluene, 0°C, then addition of **7b** (1.4 equiv), 56%; e) **3g** (10 equiv), 10 mol% $[RhCl(PPh_3)_3]$, toluene, room temperature, 89%; f) TBAF, THF, reflux, 98%.

Finally, the intramolecular version of this new carbazole synthesis offered a straightforward access to annelated carbazoles (Scheme 4). Although intramolecular alkyne cyclotrimerizations are completely regioselective due to an additional tether, the synthesis of the corresponding triynes is normally much more demanding. However, in the carbazole series this could be easily solved by using the Sonogashira reaction for the assembly of the triynes **13**, and **15a** and **15b**. They were obtained in 80, 71, and 66% overall yield, respectively, starting from **11**. Intramolecular cyclotrimerizations in the presence of 2–5 mol% Wilkinson's catalyst afforded then the annelated carbazoles **4n**, **4o**, and **4p** (77–99% yield). Notably, the intramolecular version not only allowed the use of two ynamide moieties, it also offered the possibility for a six-membered-ring annelation that cannot be achieved easily in the corresponding crossed version of this reaction.

In conclusion, we have developed a novel synthesis of substituted carbazoles based on *inter*- and *intra*molecular alkyne cyclotrimerizations. The flexibility of this approach and the diversity of the carbazole substitution pattern that can be reached now permits application of this methodology in the synthesis of natural products and drug-related targets.

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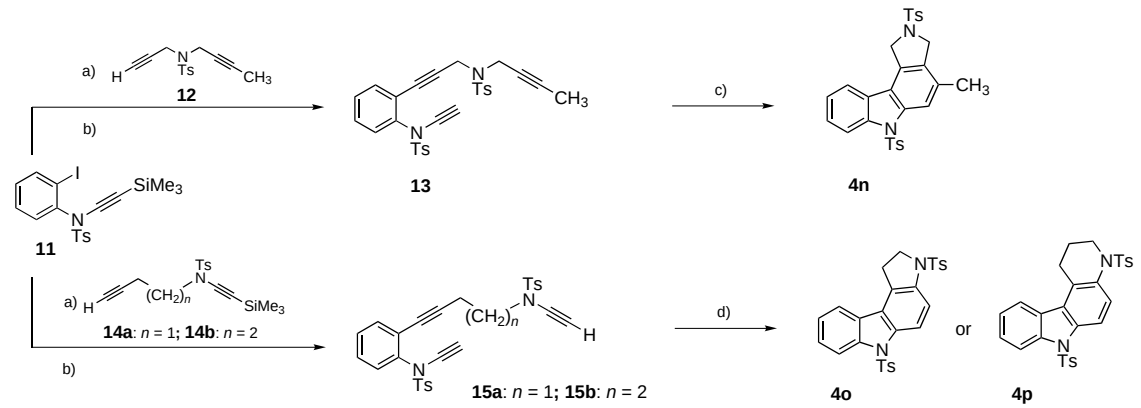

Scheme 4. Annelated carbazoles by intramolecular alkyne cyclotrimerization. a) terminal alkyne **12** or **14a** or **14b** (1.3 equiv), 5 mol% $[PdCl_2(PPh_3)_2]$, 10 mol% CuI, 10 mol% PPh_3, Et_3N, DMF, 80°C, 2 h, **13** (89%), **15a** or **15b**, (79–84%); b) TBAF, THF, 0°C, 10 min., 85–90%; c) 2 mol% $[RhCl(PPh_3)_2]$, toluene, room temperature, 12 h, 99%; d) 5 mol% $[RhCl(PPh_3)_2]$, CH_2Cl_2, 40°C, 15 h, **4o** (95%), **4p** (77%).

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Transannular Radical Cascade as an Approach to the Diastereoselective Synthesis of Linear Triquinane**

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Diastereoselective constructions of polycyclic structures such as triquinanes by 5-*exo*-radical-cyclization cascade reactions that start from a templating ring are well-known;[1] from acyclic systems only a few such reactions involve diastereoselective processes.[2] However, transannular cyclizations, which are nowadays frequently used as a key step in the synthesis of polycyclic frameworks,[3] have been poorly described as an efficient means of reaching linear triquinane systems diastereoselectively. There is only one specific example reported by Winkler in which linear triquinanes were obtained as a mixture of diastereomers, from suitably substituted cycloocta-1,5-dienes, by a unique transannular process.[4]

During the last decade, we have been interested in the development of highly chemo-, regio-, and stereoselective cascade processes which rely on radical transannular reactions.[5] The diastereoselective total synthesis of the protoilludane *epi*-illudol, which has an angularly fused 4,6,5-tricyclic framework, was achieved by a cascade of radical transannular cyclizations from a (bromomethyl)dimethylsilyl (BMDMS) ether of a cycloundeca-4,8-dien-1-yne (Scheme 1).[5b] By following the same type of cascade, we believed that switching the BMDMS-ether tether from the C-1 atom to the C-4 atom should now lead to a triquinane skeleton of type **1**. We anticipated that the disubstituted double-bond geometry would be crucial for the behavior of the transannular cascade. In fact, when the *Z*,*E* precursor **2** was submitted to radical cyclization conditions, the generated vinyl radical cyclized regioselectively in a 6-*endo* mode, leading to the 6,7-bicyclic compound **4**(Scheme 1).[5c] In contrast, we report herein the stereoselective construction of a linear triquinane through an unprecedented cascade of diastereoselective transannular cyclizations from an *E*,*E* precursor.

Access to precursor **3** was envisaged by following a similar strategy to that developed for the eleven-membered ring **2**, by using Nozaki-Hiyama-Kishi-Takai (NHKT) macrocyclization as the key step. Thus, *E*-heptenal **6** (as a common precursor),[6] was subjected to the mild Horner-Wadsworth-Emmons olefination conditions described by Masamune and Roush[7] to furnish, after tetrabutylammonium fluoride (TBAF) mediated cleavage of the resulting silylated ether, the *E*-α,β-unsaturated ester **7**. Dess-Martin oxidation[8] of the homoal-

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