Synthesis of Carbazoles by Gold(I)-Catalyzed Carbocyclization of 2-(Enynyl)indoles

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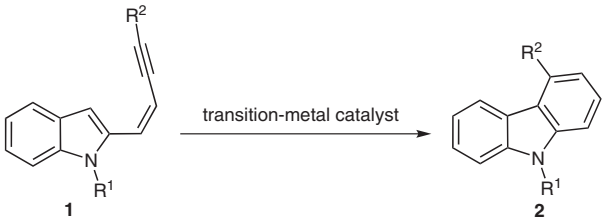
Abstract: A new synthetic protocol for carbazoles through gold(I)-catalyzed intramolecular hydroarylation of (*Z*)-2-(enynyl)indoles was achieved in good yields. The requisite (*Z*)-2-(enynyl)indoles were synthesized stereoselectively by trimethylgallium-promoted, *Z*-selective Wittig olefination of *N*-alkylindole-2-carboxaldehydes with propargyl ylides. Substrates possessing both alkyl as well as aromatic groups are well tolerated under these reaction conditions.

Key words: (*Z*)-Wittig olefination, 2-(enynyl)indoles, gold catalysis, carbocyclization, carbazoles

Carbazoles are important heterocyclic scaffolds that serve as key components in a variety of natural products and biologically active molecules.[1] Thus, it is not surprising that several synthetic approaches to these molecules have been described in the literature.[2] In contrast, recent work has focused on the development of transition-metal-catalyzed methods for the synthesis of carbazoles.[3] Of particular value are Rh(II)-catalyzed synthesis of carbazoles from biaryl azides,[3a] Pd(II)-catalyzed cyclization of 2-phenylacetanilides,[3b] Pd(II)-catalyzed cross-coupling reaction of 2-iodoanilines with silylaryl triflates,[3c] Pd(II)-catalyzed oxidative cyclization of 3-(3′-alkenyl)indoles,[3d] Pd(0)-catalyzed cross-coupling of alkynes and *N*-(3-iodophenyl)anilines,[3e] Pd(0)-catalyzed tandem Suzuki cross-coupling/S_NAr of aniline-derived boronic ester with 1,2-dihalobenzene,[3f] Pd(II)-catalyzed oxidative C–H bond amination of biaryls,[3g] and Pt(II)-catalyzed cyclization of 1-(indol-2-yl)-2,3-allenols.[3h] Typically, these protocols involve the use of palladium catalysts. While these reactions are often useful, a catalytic protocol that accomplishes the intramolecular carbocyclization of 2-(enynyl)indoles remains to be developed (Scheme 1). We felt that such transformations promise to facilitate selective construction of carbon–carbon bonds at the later stages in the synthesis of drug molecules and/or natural products. As part of our ongoing interest in the synthesis of novel heterocyclic compounds[4] under transition-metal catalysis,[4b–h] we herein report the synthesis of carbazoles via gold-catalyzed[5] intramolecular carbocylization of 2-(enynyl)indoles.

Recently, gold-catalyzed intramolecular hydroarylation of indole-tethered propargyl esters[6a] and propargyl amines[6b] have been disclosed. Both of these methods involve the use of 3-substituted indole derivatives. We were interested in the cyclization of 2-substituted indole derivatives, since the C3 of indole is more nucleophilic. Our initial investigations focused on the synthesis of the requisite 2-(enynyl)indoles by Wittig olefination of *N*-alkylindole-2-carboxaldehydes[7] **3** with propargyl ylides[8] **4**. These substrates were synthesized in good yields by standard procedures (Scheme 2). To develop the general synthesis of 2-(enynyl)indoles, Wittig reaction of model substrates **3a** and **4a** promoted by *n*-BuLi (1.5 equiv, –10 °C,THF) was performed (Scheme 3).



Scheme 1 Synthetic plan for carbazole

The desired enynl product was obtained in 92% yield as a mixture of *E*- and *Z*-isomers in a 45:55 ratio. The isomers were separated by column chromatography and characterized by their spectroscopic data. In the ^{1}H NMR spectrum of compound **1a′**, the olefinic protons can be readily assigned by the appearance of two distinct doublets at δ = 6.23 and 6.96 ppm, with coupling constants *J* = 15.3 and 16.0 Hz, respectively. Similarly, in isomer **1a**, the olefinic protons resonated as two distinct doublets at δ = 5.77 and 6.70 ppm, both with coupling constants of *J* = 11.4 Hz. Since the coupling constant values for isomer **1a′** were greater than for **1a**, we assigned **1a′** as the *E*- and **1a** as *Z*-isomer, respectively. Because the alkyne function is in proximity to the nucleophilic C3-carbon of indole in the *Z*-isomer **1a**, we believed that it might favor the intramolecular cyclization. For this reason, we focused only on the catalytic cyclization of *Z*-isomer **1a** leading to the product **2a** by employing nitromethane as solvent at 60 °C. The results, given in Table 1, revealed that 5 mol% $AuCl_3$, $PtBr_2$, and $AgSbF_6$, respectively, did not led to product formation (entries 1, 6 and 7). However, the combination of a gold catalyst with a silver co-catalyst[9] resulted in the formation of the expected product (entries 2–5 and 8). Fruitful results, in terms of product yield, were obtained when 5 mol% $AuCl(Ph_3P)$ in combination with 5 mol% $AgSbF_6$ was used as the catalytic system (entry

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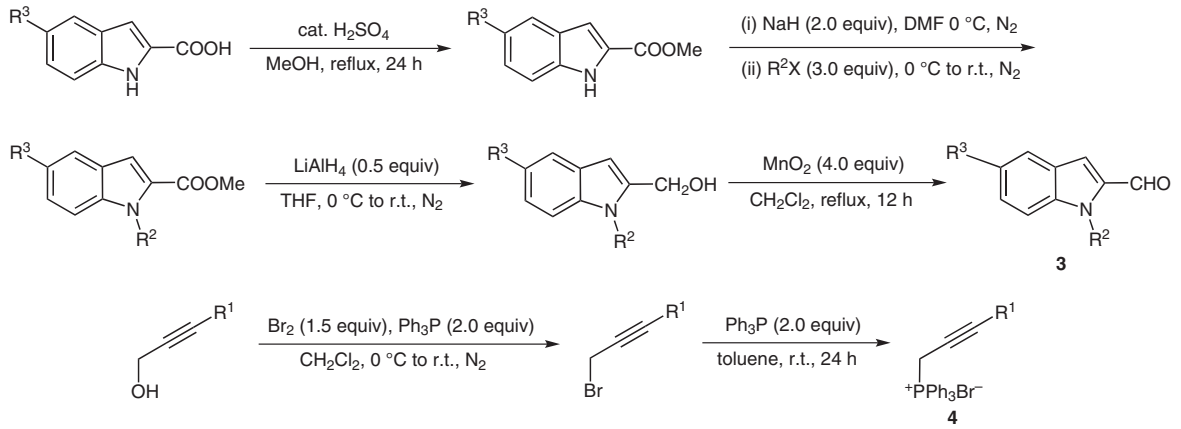
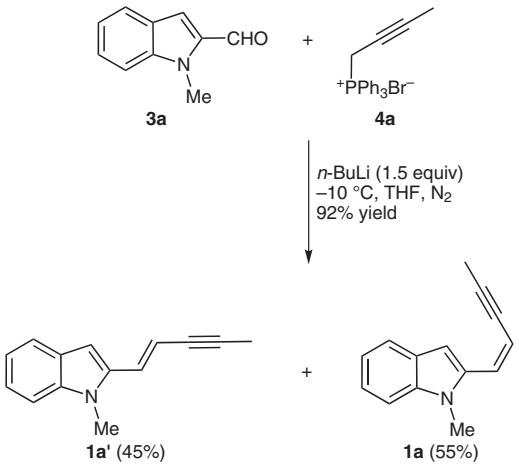


Scheme 2 Synthesis of *N*-alkylindole-2-carboxaldehydes **3** and propargyl ylides **4**



Scheme 3 *n*-BuLi-promoted Wittig olefination of **3a**

3).[10] The ^{1}H NMR spectrum of product **2a** in $CDCl_3$, exhibited a sharp singlet at δ = 2.97 ppm that indicated the presence of methyl protons attached to an aryl ring. In the ^{13}C NMR spectrum, a peak at δ = 20.9 ppm confirmed the presence of a methyl group attached directly to an aryl ring. Having optimized the reaction conditions, we applied the same conditions for the sequential isomerization/carbocyclization of a mixture of *Z*- and *E*-isomers (**1a** and **1a′**). We found that only the *Z*-isomer underwent the reaction, and the unreacted *E*-isomer was recovered quantitatively (Scheme 4).

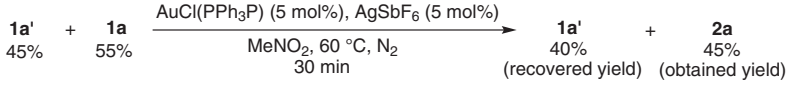
In order to circumvent this limitation, we envisaged the stereoselective synthesis of (*Z*)-2-(enynl)indoles. Recently, Nishimura et al. reported the *Z*-selective Wittig reaction of aromatic aldehydes with propargyl ylides using trimethylgallium (TMG) as base.[11] By applying the same reaction conditions on model substrates **3a** and **4a**, to our delight, we obtained the products in excellent overall yield with the *Z*-isomer being formed in 79% and *E*-isomer being formed in 14%. Application of the TMG-promoted Wittig reaction conditions to all the tested substrates yielded (*Z*)-2-(enynyl)indoles as the major isomer in good chemical yields.[12] With a satisfactory procedure for the stereoselective synthesis of (*Z*)-2-(enynyl)indoles in hand, we next turned our attention to the cyclization of various (*Z*)-2-(enynyl)indoles under our previously optimized gold-catalyzed cyclization conditions (Table 1, entry 3).[13]

Table 1 Screening of Carbophilic Lewis Acids for the Carbocyclization of (*Z*)-(Enynyl)indole **1a**[a]

Entry	Catalyst	Yield (%)[b]
1	5 mol% $AuCl_3$	–
2	5 mol% $AuCl_3$, 5 mol% $AgSbF_6$	20
3	5 mol% $AuCl(PPh_3)$, 5 mol% $AgSbF_6$	81
4	5 mol% $AuCl(PPh_3)$, 5 mol% $AgBF_4$	60
5	5 mol% $AuCl(PPh_3)$, 5 mol% AgOTf	35
6	5 mol% $PtBr_2$	–
7	5 mol% $AgSbF_6$	–
8	5 mol% $AuCl(Me_3P)$, 5 mol% $AgSbF_6$	55

[a] All reactions were carried out in nitromethane at 60 °C under N_2.
[b] Isolated yield.

Starting materials with a wide range of alkyl substituents on the indole nitrogen as well as on the alkyne functionality all gave good yields of product (Table 2, entries 1–19). The reaction time and product yield for all substrates were found to be similar, irrespective of the nature of the substituents. However, alkynes possessing aryl groups resulted in only moderate yield of products even after a long



Scheme 4 Carbocyclization of a mixture of *E*- and *Z*-isomers (**1a′** and **1a**)

reaction time (entry 20). We also expect that, using this protocol, substrates such as bromoindoles could lead to the formation of bromocarbazoles, which could subsequently be cross-coupled.[14]

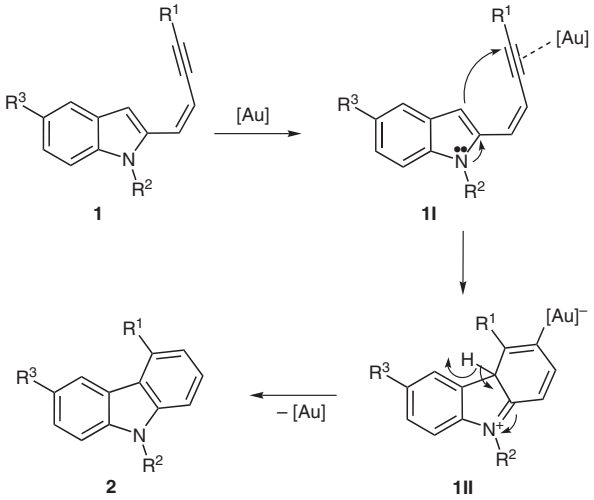
Table 2 Gold(I)-Catalyzed Carbocyclization of (*Z*)-2-(Enynyl)indole **1** to Carbazole **2**[a]

Entry	(*Z*)-2-(Enynyl) indole (**1**)	R^1	R^2	R^3	Carbazole (**2**)[b]	Time (h)	Yield (%)[c]
1	**1a**	Me	Me	H	**2a**	0.30	81
2	**1b**	Et	Me	H	**2b**	0.20	80
3	**1c**	Pr	Me	H	**2c**	0.20	79
4	**1d**	Bu	Me	H	**2d**	0.20	78
5	**1e**	pentyl	Me	H	**2e**	0.45	78
6	**1f**	Me	Et	H	**2f**	0.40	80
7	**1g**	Et	Et	H	**2g**	1.0	79
8	**1h**	Pr	Et	H	**2h**	0.50	73
9	**1i**	pentyl	Et	H	**2i**	0.45	75
10	**1j**	hexyl	Et	H	**2j**	0.45	75
11	**1k**	Me	Bu	H	**2k**	0.30	80
12	**1l**	Et	Bu	H	**2l**	0.20	77
13	**1m**	Pr	Bu	H	**2m**	0.30	78
14	**1n**	Me	Bn	H	**2n**	0.30	71
15	**1o**	Me	Me	MeO	**2o**	0.20	83
16	**1p**	Et	Me	MeO	**2p**	0.20	80
17	**1q**	Et	Et	Me	**2q**	0.20	76
18	**1r**	hexyl	Et	Me	**2r**	0.30	75
19	**1s**	Et	Bu	Me	**2s**	0.30	74
20	**1t**	*p*-tolyl	Me	Me	**2t**	1.30	50

[a] All reactions were carried out at 60 °C in nitromethane using 5 mol% $AuCl(Ph_3P)$ and 5 mol% $AgSbF_6$.
[b] All products were characterized by IR, ^1H NMR, ^{13}C NMR and mass spectroscopy.
[c] Isolated yield.

A tentative mechanism to explain the formation of carbazole **2** is given in Scheme 5.[15] The carbophilic gold catalyst activates alkyne **1** to form a -complex intermediate **1I**. Subsequent nucleophilic attack of the C3-carbon of indole leads to the 6-*endo*-dig intermediate **1II**. The latter species, upon proto-deauration, results in the formation of carbazole **2**.

In summary, an efficient gold-catalyzed protocol for the carbocyclization of (*Z*)-2-(enynl)indoles to carbazoles has been developed. This method offers advantages including moderate reaction conditions and no formation of by-products. Further exploration of these transformations



Scheme 5 Tentative mechanism

with structurally diverse carbocycles is underway and will be reported in due course.

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(12) **Typical procedure for the *Z*-selective Wittig olefination:** To a degassed solution of propargyl ylide **4a** (395 mg, 1.2 mmoL) in anhydrous THF (5 mL) under an N_2 atmosphere, was added Me_3Ga (1.0 M in hexane, 1.5 mL, 1.5 mmoL) and the mixture was stirred for 10 min at 0 °C. To this reaction mixture was added a solution of *N*-methylindole-2-carboxaldehyde (**3a**; 158 mg, 1.00 mmoL) in THF (5 mL) and stirring was continued for 5 h. After completion of the reaction as indicated by TLC, the reaction was quenched with ice-cold water and extracted with EtOAc (3 × 20 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by column chromatography over silica gel (100–200 mesh) to afford the pure *Z*-isomer (154 mg, 79%) and *E*-isomer (27 mg, 14%). **1-Methyl-2-[(*Z*)-pent-1-en-3-ynyl]-1*H*-indole (1a′):** Brown paste. IR (neat): 2928, 1733, 1430, 1224, 1119 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.21 (s, 3 H, CH_3), 3.71 (s, 3 H, NCH_3), 5.77 (d, *J* = 11.4 Hz, 1 H, indolyl-CH=C*H*), 6.70 (d, *J* = 11.4 Hz, 1 H, indolyl-C*H*=CH), 7.14–7.15 (m, 1 H, ArH), 7.21–7.30 (m, 2 H, ArH), 7.55 (s, 1 H, indolyl-C(3)H), 7.69 (d, *J* = 7.6 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 5.2, 29.5, 78.9, 95.5, 102.9, 108.5, 109.3, 119.9, 121.2, 122.5, 125.3, 127.8, 128.5, 136.1. MS (EI): *m*/*z* = 195 [M^+]. Anal. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71; N, 7.17. Found: C, 85.98; H, 6.76; N, 7.17. **1-Methyl-2-[(*E*)-pent-1-en-3-ynyl]-1*H*-indole(1a):** Black paste. IR (neat): 2917, 1735, 1425, 1222, 1123 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.08 (s, 3 H, CH_3), 3.78 (s, 3 H, NCH_3), 6.23 (d, *J* = 15.3 Hz, 1 H, indolyl-CH=C*H*), 6.75 (s, 1 H, indolyl-C(3)H), 6.96 (d, *J* = 16.05 Hz, 1 H, indolyl-C*H*=CH), 7.12 (t, *J* = 7.6 Hz, 1 H, ArH), 7.23 (t, *J* = 7.6 Hz, 1 H, ArH), 7.28 (d, *J* = 8.4 Hz, 1 H, ArH), 7.59 (d, *J* = 7.6 Hz, 1 H, ArH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 4.7, 29.8, 79.3, 89.5, 99.3, 109.3, 110.4, 120.1, 120.7, 122.2, 127.8, 128.5, 137.4, 138.3. MS (EI): *m*/*z* = 195 [M^+]. Anal. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71; N, 7.17. Found: C, 86.25; H, 6.65; N, 7.10

(13) **Typical procedure for the carbocyclization of (*Z*)-(2-enynyl) indoles:** To an air-dried Schlenk flask under N_2 atmosphere was added 5 mol% $AuCl(Ph_3P)$ and 5 mol% $AgSbF_6$, followed by nitromethane (1 mL) and the mixture was stirred for 15 min at room temperature. A solution of **5a** (1.0 mmoL) in nitromethane (2 mL) was added and the mixture was stirred at 60 °C. After completion of the reaction as indicated by TLC, the reaction was quenched in water and extracted with EtOAc (3 × 20 mL). The organic layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography to afford pure 4,9-dimethylcarbazole (**2a**) as a colorless solid. Mp 105–106 °C (Lit.[16] 105–105.5 °C). IR (KBr): 3055, 3025, 2952, 2928, 2855, 1625, 1599, 1560, 1467, 1420, 1132 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.97 (s, 3 H, Ar-CH_3), 3.89 (s, 3 H, NCH_3), 7.09–7.13 (m, 1 H, ArH), 7.30–7.35 (m, 2 H, ArH), 7.45–7.50 (m, 1 H, ArH), 7.55–7.59 (m, 1 H, ArH), 8.25–8.29 (m, 1 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9, 29.1, 106.2, 108.4, 119.0, 120.7, 121.5, 122.5, 123.6, 125.2, 125.6, 133.6, 141.1, 141.2. MS (EI): *m*/*z* = 195 [M^+]. Anal. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.70; N, 7.08. Found: C, 85.95; H, 6.75; 7.20

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