

Carbocyclization versus Oxycyclization on the Metal-Catalyzed Reactions of Oxyallenyl C3-Linked Indoles

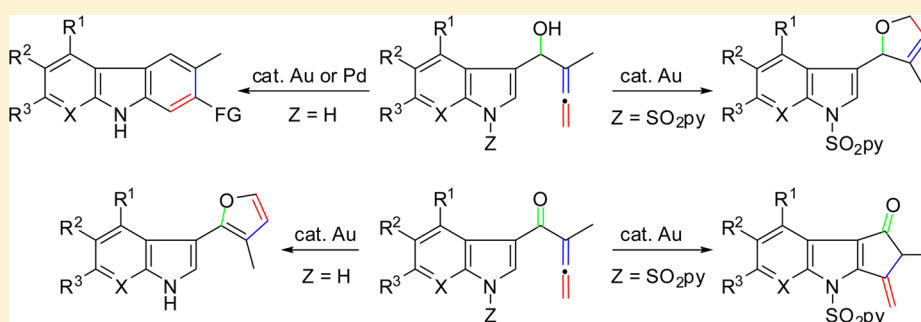
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S Supporting Information



ABSTRACT: The preparation of previously unknown (indol-3-yl)- α -allenols and -allenones was accomplished from indole-3-carbaldehydes, through indium-mediated Barbier allenylation reaction taking advantage of the *N*-(2-pyridyl)sulfonyl group. Metal-catalyzed cyclizations of oxyallenyl C3-linked indoles proceeded in two ways depending on the presence or absence of the *N*-(2-pyridyl)sulfonyl group. For allenols, gold-catalyzed oxycyclization occurred in the presence of the protecting group; in the absence of the protecting group, palladium- and gold-catalyzed benzannulations operated. On the contrary, under gold catalysis furyl-indoles were obtained as exclusive products from *NH*-allenones, while *5-endo* carbocyclization adducts were the major components starting from *N*-SO₂py-protected allenones. These cyclization reactions have been developed experimentally, and their mechanisms have additionally been investigated by a computational study.

INTRODUCTION

Allenenes have metamorphosed from a laboratory curiosity to a versatile and uniquely reactive functional group,¹ allowing chemists to prepare a variety of compounds of chemical and biological interest.² Arguably, the indole scaffold is one of the most common heterocyclic nuclei in natural and synthetic products of biological significance.³ Consequently, methods for the synthesis of new indole derivatives are highly appreciated. Because of the fact that the C3-position of an indole is the most reactive site for electrophilic functionalization, annulation of 2-allenyl derivatives to the C3 indole position has been explored in recent years.⁴ However, carbocyclization of indole-tethered allenenes to the C2 indole position is considerably less studied,⁵ with the metal-catalyzed C3–C2 cyclization being missed at the outset of this study.⁶

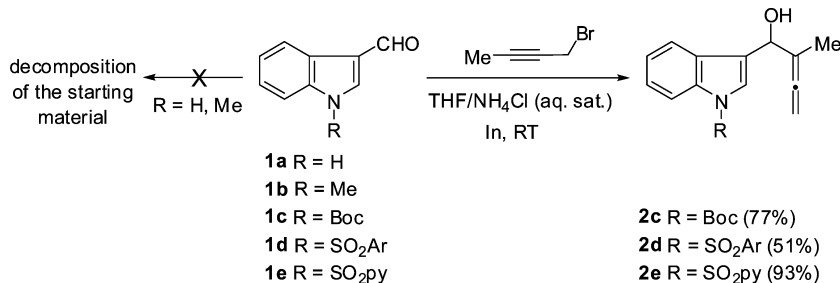
Following up on our combined interest in the area of heterocycles and allenenes,⁷ we wish to report here a method using gold- or palladium-based salts that enables catalytic benzannulation⁸ at the C2 position of allenyl C3-linked indoles to afford substituted carbazoles.⁹ Besides, a divergent reactivity (oxycyclization versus carbocyclization) has also been encountered for *N*-SO₂py-protected allenols and allenones. These

cyclization reactions have been developed experimentally, and their mechanisms have additionally been investigated by a computational study.

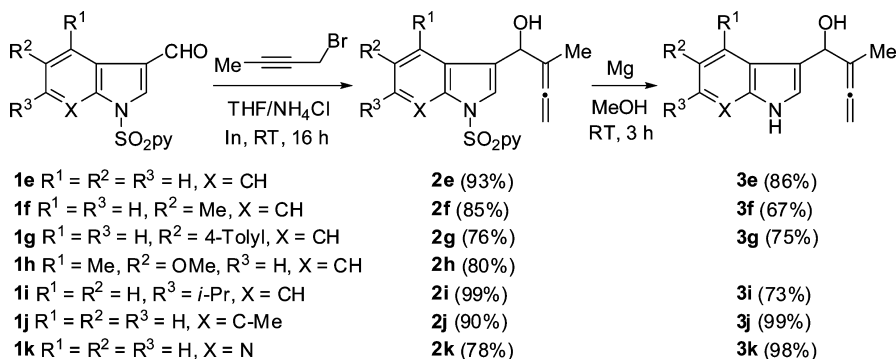
RESULTS AND DISCUSSION

The preparation of key starting materials, for example, *NH*-C3-(α -hydroxyallenyl) indoles, required for our study was an initial challenge. Starting allenyl C3-linked indoles were planned to be prepared from indole-3-carbaldehydes. Disappointingly, the widely utilized Sakurai-, Grignard-, and Barbier-type allenylations of carbonyls failed in *NH*- and *N*-alkyl-indole-3-carbaldehydes. Fortunately, it was found that the indium-mediated Barbier carbonyl-allenylation reaction in aqueous media could be achieved for indole-3-carbaldehydes possessing electron-withdrawing substituents directly attached to the nitrogen atom. The 1-Boc-, 1-SO₂Ar-, and 1-SO₂py-substituted indoles **1c–e** were more effective than 1-H-, or 1-alkyl-substituted substrates **1a** and **1b**, and the yields of C3-allenyl indoles **2c–e** were good (Scheme 1).

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Scheme 1. Regiocontrolled Preparation of Indole-C3-Tethered α -Hydroxyallenes 2c–e^a

^aBoc = *tert*-butoxycarbonyl. Ar = (2,4,6-triisopropyl)phenyl. SO₂py = (2-pyridyl)sulfonyl.

Scheme 2. Preparation of *NH*-Indole-C3-Tethered α -Hydroxyallenes 3^a

^aSO₂py = (2-pyridyl)sulfonyl.

Next, we focused on finding a cleavage procedure for the above *N*-protecting groups that could be compatible with the sensitive allenol moiety. This task was not trivial for *N*-Boc derivative **2c** and *N*-SO₂Ar derivative **2d**, because the allene functionality was not able to survive under conventional protective group removal conditions.¹⁰ Although methods for *N*-S bond cleavage of pyridyl-2-sulfonamides are known, and recent examples pertaining to indole derivatives have been reported,¹¹ no methodology exists for the removal in synthetically useful allene derivatives. Nicely, after considerable experimentation it was found that the desulfonylation of *N*-SO₂py-indoles efficiently occurred using inexpensive magnesium in methanol. Of note, the allene functionality at C3 remained intact despite its inherent reactivity. Removal of the (2-pyridyl)sulfonamide from *N*1-protected indoles **2** utilizing Mg-promoted conditions provided the corresponding *NH*-indoles **3**. Differently substituted indoles **2** at the benzene ring were well tolerated, and the yields of C3-allenyl indoles **3** were good (Scheme 2).

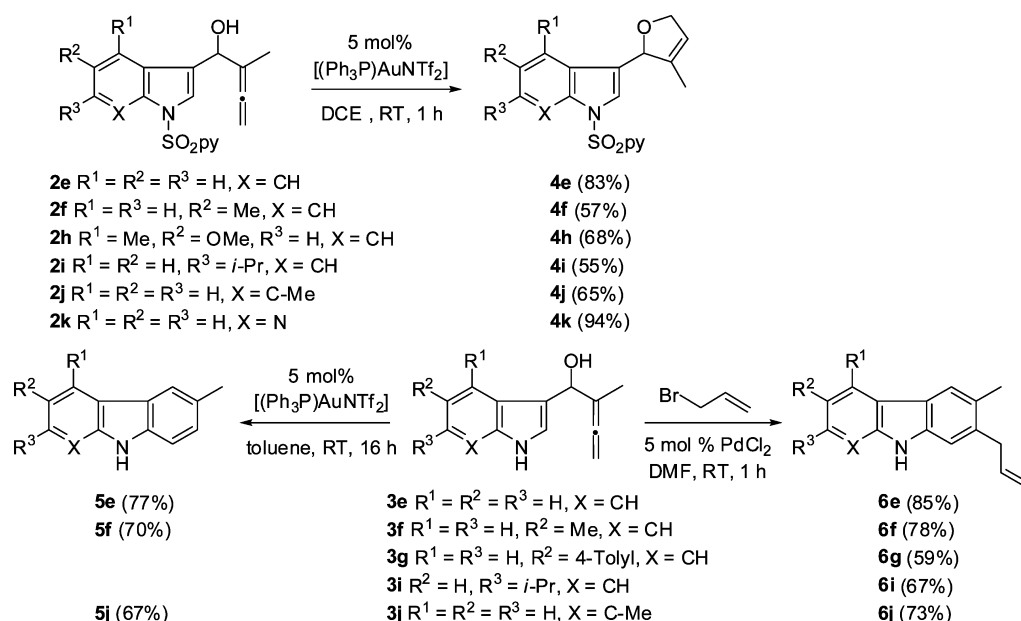
Indole-C3-tethered α -hydroxyallenes **2** and **3** have diverse reactive sites, at which two different transformations (*C*-cyclization versus *O*-cyclization) can take place. Our investigation began with allenol **2e** as model substrate. The reaction of **2e** in the presence of 5 mol % of HOTf gave rise to a very complicated mixture (Table 1, entry 1). We next investigated gold-based catalysts. Optimization of the gold salt revealed that Gagosz catalyst was the best election (Table 1, entry 6). The use of other gold(I) or gold(III) catalysts gave inferior results (Table 1, entries 2–5). Under the optimized conditions, treatment of (indol-3-yl)- α -allenol **2e** with a catalytic amount of [(Ph₃P)AuNTf₂] gave dihydrofuran-attached indole **4e** in 83% yield (Scheme 3). 1,2-Dichloroethane was the solvent of choice in terms of short reaction times and yield. Similar oxy-

Table 1. Selective Oxycyclization Reaction of Allenylindole **2e** under Modified Acid-Catalyzed Conditions^a

entry	catalyst	time (h)	yield (%)
1	HOTf	2	^b
2	AuCl ₃	2	59
3	AuCl	1.5	67
4	[AuClPPh ₃]/AgOTf	1	73
5	[AuClPPh ₃]/AgBF ₄	1	75
6	[(Ph ₃ P)AuNTf ₂]	1	83

^aYield of pure, isolated product with correct analytical and spectral data. ^bA very complicated mixture was observed.

cyclization results were encountered for C3-allenyl *N*-SO₂py-indoles **2f** and **2h–k**, to afford dihydrofuran-yl-indoles **4f–k**. These results clearly show that the gold-catalyzed cycloetherification is preferred over carbocyclization for *N*-SO₂py-protected substrates. We then investigated the reactions of substrates without having an *N*-protecting group, *NH*-indole-C3-tethered α -hydroxyallenes **3**, to determine whether they gave oxycyclization or carbocyclization. Our initial studies concentrated on the gold-catalyzed cyclization reaction of allenyl C3-linked indole **3e**. On the basis of reaction time and yield, [(Ph₃P)AuNTf₂] proved to be the most efficient catalyst, providing the desired *N*-unprotected carbazole **5e** in 77% yield after 16 h at room temperature in toluene or DCE. Substrates **3f** and **3j** with additional aromatic substituents showed no loss

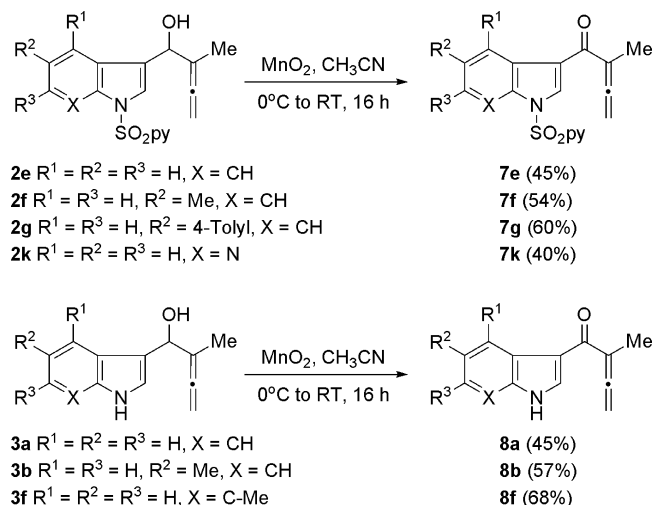
Scheme 3. Metal-Catalyzed Synthesis of (2,5-Dihydrofuran-2-yl)-indoles **4**, 3-Methyl-9H-carbazoles **5**, and 2-Allyl-3-methyl-9H-carbazoles **6**^a

^aSO₂py = (2-pyridyl)sulfonyl. NTf₂ = bis(trifluoromethanesulfonyl)imide. DCE = 1,2-dichloroethane.

of selectivity during the formation of carbazoles **5f** and **5j** (Scheme 3). In addition, carbocyclization–functionalization reactions of the allene subunit can be realized when allyl bromide is added in the palladium-catalyzed transformation of substrate **3e** to generate 2,3-disubstituted-9H-carbazole derivative **6e**. To evaluate the general applicability of this benzannulation–functionalization protocol, a series of allenyl C3-linked indole derivatives were converted under the same reaction conditions. All of the reactions delivered the substituted NH-carbazoles **6f**, **6g**, **6i**, and **6j** in good yields within acceptable reaction times (Scheme 3). Notably, despite that metal-based catalysts are well-known for their ability to promote the cycloetherification of α -allenols,¹² no traces of dihydrofurans were detected. In our case the 6-*endo* carbocyclization reaction (carbazole formation) is favored over the 5-*endo* oxycyclization (dihydrofuran formation).

In addition to C3-(α -hydroxyallenyl) indoles, substrates with an α -ketone functionality at the allene position were also investigated. The synthesis of the indole-C3-tethered allenones was not an easy task because of the sensitivity of indolic compounds under oxidative conditions. Thus, the reaction with the reported reagent for the conversion of α -allenols into α -allenones,¹³ i.e., Dess–Martin periodinane, resulted in a complicated mixture. Fortunately, treatment of (α -hydroxyallenyl) C3-linked indoles **2** or **3** with activated manganese(IV) oxide resulted in the formation of the corresponding α -allenones **7** and **8** (Scheme 4). These species are highly sensitive and polymerize easily.

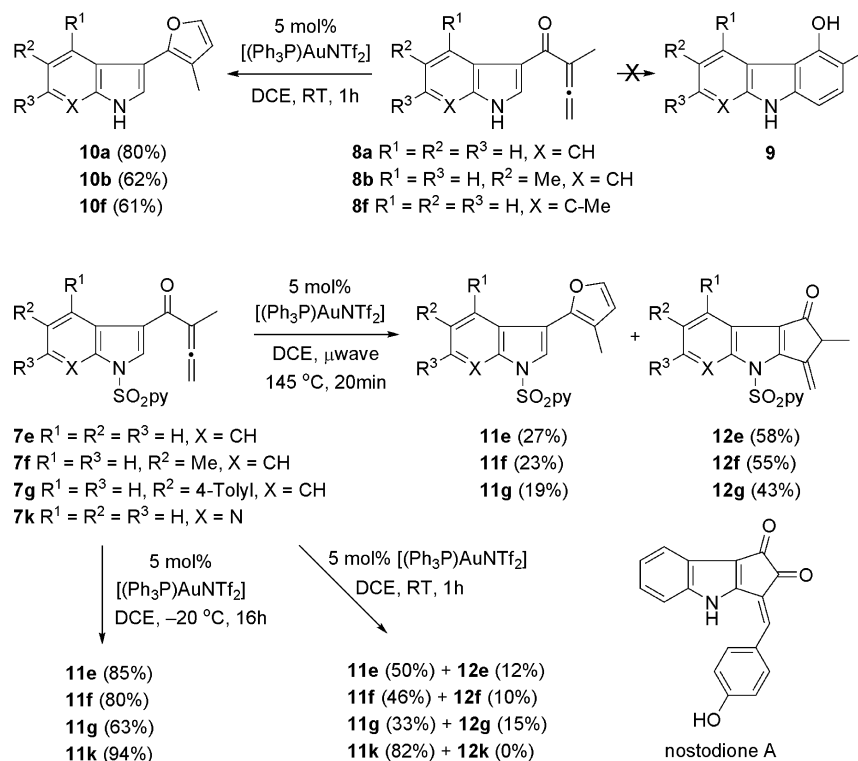
Taking cues from the reaction of NH-indole-C3-tethered α -hydroxyallenes **3**, we expected that the reaction of NH-indole-C3-tethered α -allenones **8** in the presence of a gold(I) catalyst would initially produce a carbazolone **9**. However, NH-indoles **8** displayed different reactivity, and furyl-indoles **10** were obtained as exclusive products in reasonable yields (Scheme 5).^{14,15} The high reactivity toward oxycyclization of the allenone system in **8** in comparison with allenols **3** probably resulted from the presence of the carbonyl group. As indole

Scheme 4. Preparation of Indole-C3-Tethered α -Allenones **7** and **8**^a

^aSO₂py = (2-pyridyl)sulfonyl.

ring in allenones **8** is directly conjugated to a carbonyl moiety, it is more electron-deficient than indole ring in allenols **3**. Hence, the cyclization takes place first at the oxygenated moiety to form furyl-indoles **10**. Besides, the fixed geometry of the incorporated C=O bond in allenones **8**, which led to a lower degree of conformational freedom compared with the indoles **3** with allenol side chains helps furan formation.

As for substrates **7** bearing an N-SO₂py-protective group, the reactions proceeded smoothly under the established conditions. Interestingly, under gold catalysis α -allenones **7** delivered fused tricycles **12** in addition to furyl-indoles **11** that were easily separable by flash column chromatography (Scheme 5).¹⁶ In comparison with α -allenone C3-linked NH-indoles **8**, the oxycyclization reaction of N-SO₂py allenones **7** may be partially hindered by the deactivating effect imparted by the (2-

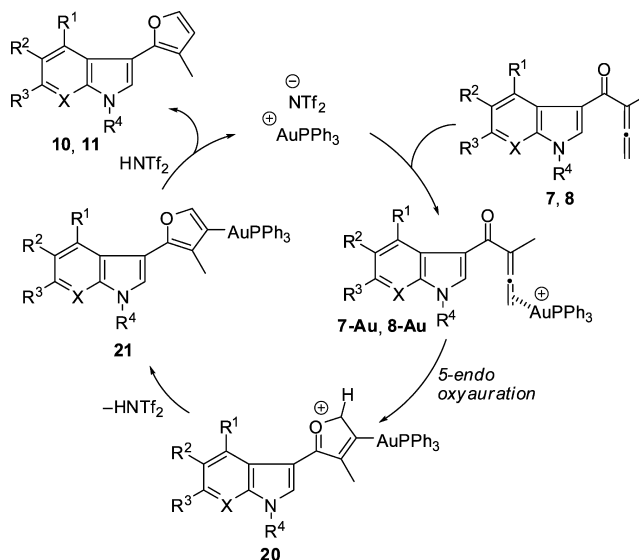
Scheme 5. Gold-Catalyzed Synthesis of (Furan-2-yl)-indoles **10** and **11**, and 2,3-Dihydrocyclopenta[*b*]indolones **12**^a

^aNTf₂ = bis(trifluoromethanesulfonyl)imide. SO₂py = (2-pyridyl)sulfonyl. DCE = 1,2-dichloroethane.

pyridyl)sulfonyl group. The formation of adducts **12** can be explained invoking a gold-catalyzed *5-endo-dig* carbocyclization toward the central allene carbon (see below). Besides, an appealing temperature effect next emerged from the observation that performing the reaction under otherwise identical conditions but at $-20\text{ }^{\circ}\text{C}$ resulted in the exclusive formation of furyl-indoles **11** in good yields (Scheme 5). Interestingly, when *N*-SO₂py allenone **7e** was treated with [(Ph₃P)AuNTf₂] in 1,2-dichloroethane at $145\text{ }^{\circ}\text{C}$ under microwave irradiation for 20 min,¹⁷ furyl-indole **11e** and cyclopentaindolone **12e** were isolated in 27 and 58% yields, respectively (Scheme 5). Similarly, the gold-catalyzed reactions of allenones **7f** and **7g** at $145\text{ }^{\circ}\text{C}$ under microwave irradiation furnished mixtures of furyl-indoles **11f** and **11g** and fused tricycles **12f** and **12g** (Scheme 5). Cyclopentaindolones **12** (major component) are easily separable by column chromatography from furyl-indoles **11** (minor component). The observed chemoselectivity dependence on the reaction temperature is apparently the result of kinetic and thermodynamic control in the cyclization process. In the reaction at low temperature, it is expected that the oxycyclization occurs, which would be more favorable than carbocyclization, leading to **11** as the kinetic product.

It is believed that the formation of compounds **4–6** proceeds through expected cyclization mechanisms,^{18–20} following known reactivity of allenes.^{1,2}

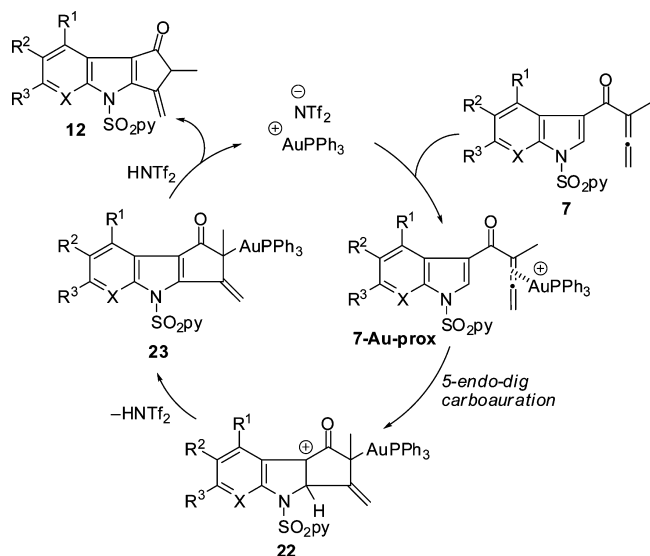
Scheme 6 describes a putative mechanism for generating furyl-indoles **10** and **11** from the cycloisomerization of indole-C3-tethered α -allenones **7** and **8**. Initially, [(Ph₃P)AuNTf₂] coordinates to the distal allenic double bond of allenones **7** and **8** to produce **7-Au** and **8-Au**. The chemo- and regioselective *5-endo* oxycyclization reaction of the thus generated gold complexes gives intermediates **20**. The loss of proton in oxonium **20** furnishes neutral species **21**. Protonolysis of the

Scheme 6. Mechanistic Explanation for the Gold-Catalyzed Synthesis of Furyl-indoles **10** and **11**

carbon–gold bond of furan **21** yields adducts **10** and **11** and eventually reforms the Au(I) catalytic species (Scheme 6).

A tentative proposal for the gold-catalyzed carbocyclization of α -allenones **7** to fused tricycles **12** is presented in Scheme 7. It is assumed that the mechanism starts with the coordination of the gold salt to the proximal allenic double bond of allenes **7** to give the corresponding complex **7-Au-prox**. Then the *5-endo-dig* carbocyclization toward the central allene carbon takes place with formation of carbocation **22**. This is followed by loss of HNTf₂ to produce neutral species **23**. The required fused

Scheme 7. Mechanistic Explanation for the Gold-Catalyzed Synthesis of Fused Tricycles 12



cyclopentenones **12** are generated from **23** by subsequent Au(I) /proton exchange and dehydration. These consecutive

steps deliberate tricycles **12**, thereby facilitating the regeneration of the gold catalyst.

Density functional theory (DFT) calculations have been carried out to gain more insight into the reaction mechanisms involving the formation of furyl-indoles **11** and tricycles **12** from α -allenones **7**. The corresponding computed reaction profiles of the reaction of allenone **7e** with the model $[(\text{Me}_3\text{P})\text{AuNTf}_2]$ as catalyst are depicted in Figure 1, which shows the corresponding free energies (at 298 K) in DCE solution (PCM-M06/def2-SVP//B3LYP/def2-SVP level).²¹

As proposed in Scheme 6, our calculations suggest that the formation of furyl-derivates **11** starts with the exergonic coordination of the AuPMe_3^+ catalyst to the distal double bond of the allenic moiety of **7e** to form **7e-Au** ($\Delta G_{298} = -10.8$ kcal/mol). Then, the *5-endo* oxyauration reaction occurs to produce the cationic intermediate **20-Au** through the transition state **TS1**. This saddle point is associated with the nucleophilic addition of the carbonyl group to the electrophilic gold-complexed distal carbon atom of the allene moiety. This process proceeds with a low activation barrier ($\Delta G_{a,298} = 8.9$ kcal/mol) in a highly exergonic transformation ($\Delta G_{R,298} = -15.0$ kcal/mol), which reflects the easiness of the reaction. **20-Au** complex is then transformed into the final furyl-indole **11e** by subsequent proton loss and protonolysis of the C–Au bond as previously reported by us.²²

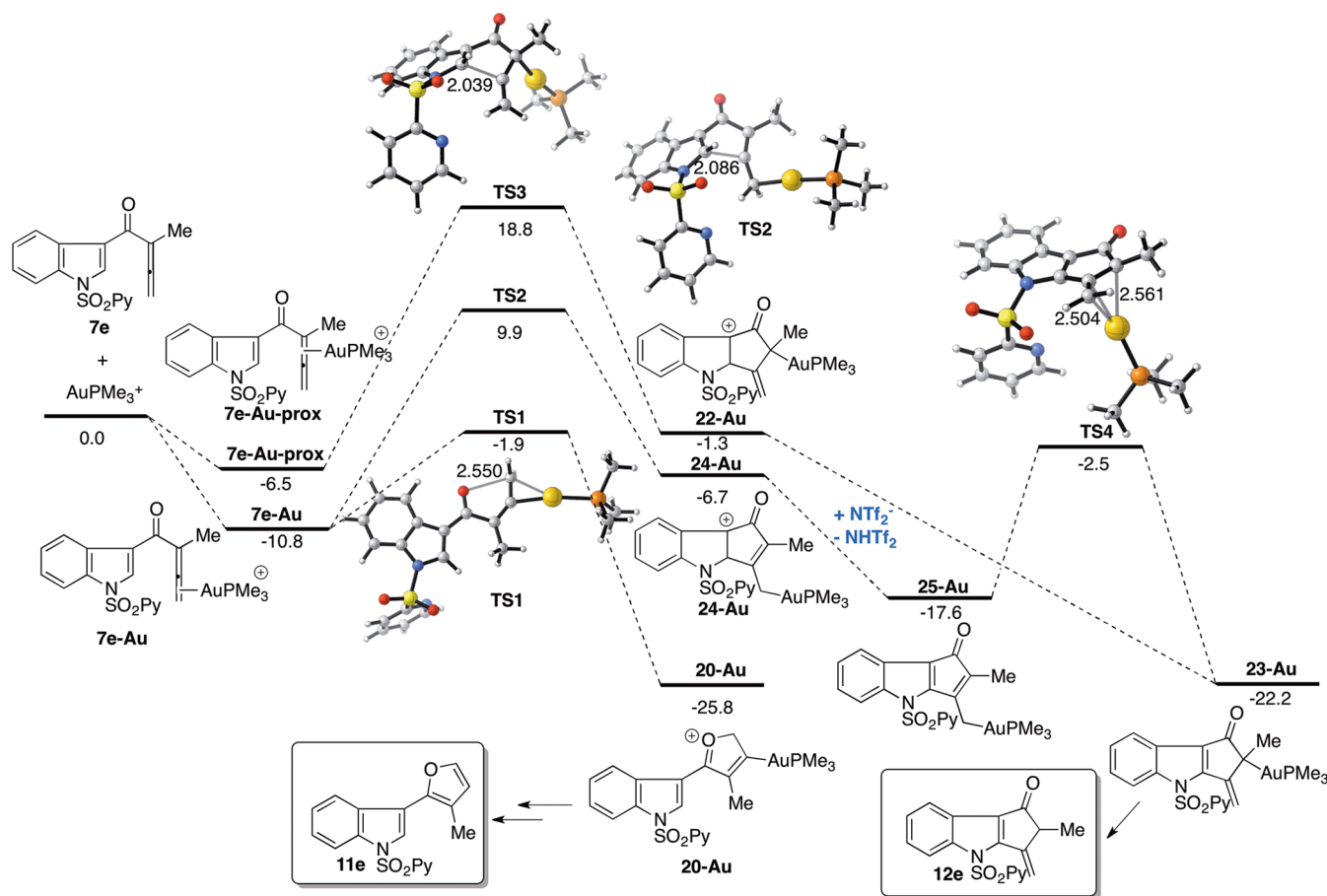


Figure 1. Computed reaction profiles for the reaction of α -allenone **7e** and $[(\text{PMe}_3)\text{AuNTf}_2]$ catalyst to produce compounds **11e** and **12e**. Relative free energies (ΔG , at 298 K) are given in kcal/mol and bond distances in the transition states in angstroms. Atoms are represented as spheres: C, gray; H, white; N, blue; O, red; P, orange, S, yellow; Au, dark yellow. All data have been computed at the PCM(DCE)-M06/def2-SVP//B3LYP/def2-SVP level.

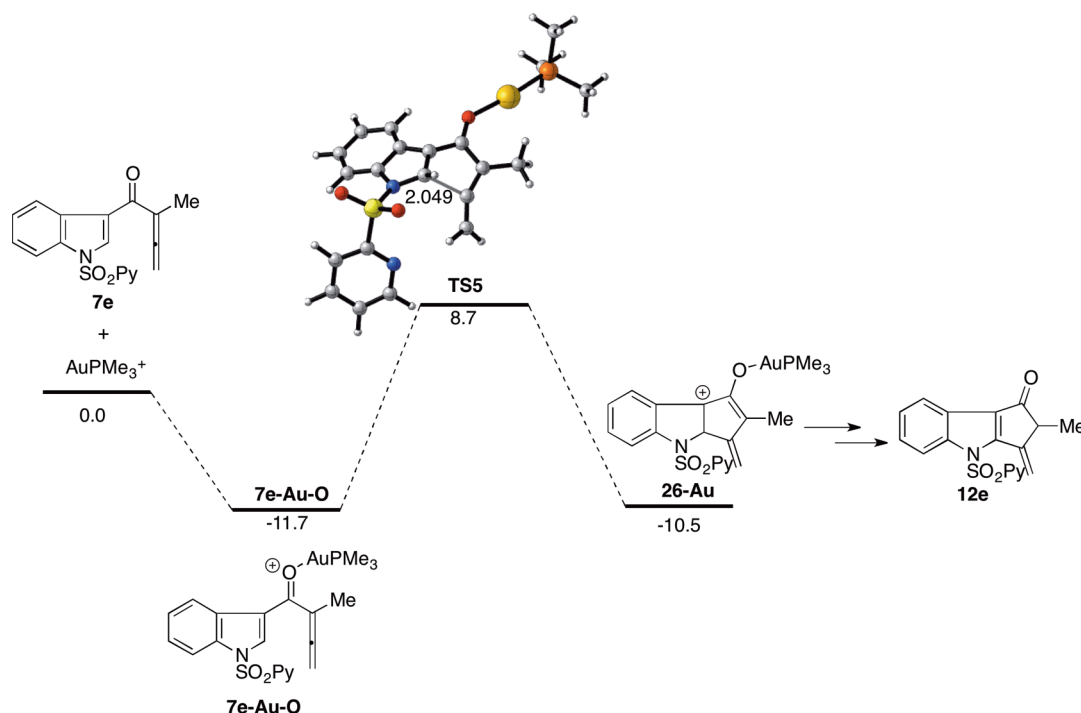


Figure 2. Computed Nazarov-type cyclization of α -allenone **7e** and $[(\text{PMe}_3)\text{AuNTf}_2]$ catalyst to produce **12e**. See caption of Figure 1 for additional details.

Scheme 7 suggests that the formation of tricyclic species **12** involves the initial proximal coordination of the gold(I)-catalyst to the allene moiety. However, our calculations indicate that this coordination mode, which leads to complex **7e-Au-prox**, is less exergonic ($\Delta G_{298} = -6.5$ kcal/mol) than the distal coordination (Figure 1). Despite that, we were able to locate on the potential energy surface a transition state (TS3), which connects **7e-Au-prox** with the cationic tricyclic intermediate **22-Au**. The computed high activation barrier ($\Delta G_{a,298} = 25.3$ kcal/mol) and endergonicity ($\Delta G_{R,298} = 5.2$ kcal/mol) make this 5-*endo-dig* carbocyclization reaction not feasible at -20°C or at room temperature. Nevertheless, tricyclic compounds **12** are formed, although as a minor component, when the reaction is conducted at room temperature (see above). This experimental finding necessarily means that a more feasible reaction pathway leading to these species should exist. Indeed, a new saddle point TS2, associated with the formation of the C–C bond from the distal complex **7e-Au**, was located. This process leads to the tricyclic cationic species **24-Au** with a lower activation barrier ($\Delta G_{a,298} = 20.7$ kcal/mol) in a less endergonic transformation ($\Delta G_{R,298} = 4.1$ kcal/mol). NTf_2^- -mediated proton loss transforms **24-Au** into the neutral species **25-Au**, which is subsequently converted in complex **23-Au** through the transition state TS4. This saddle point is associated with the 1,3-migration of the gold(I)-fragment through the π -allyl moiety of **25-Au**. The gold(I)-migration is also feasible at room temperature in view of the computed activation barrier ($\Delta G_{a,298} = 15.1$ kcal/mol) and exergonicity ($\Delta G_{R,298} = -4.6$ kcal/mol). Please note that **23-Au** can be also formed in the proximal reaction pathway by proton-loss from intermediate **22-Au**, which connects both reaction pathways. Again, protonolysis of the C–Au bond in **23-Au** will produce the final tricyclic compounds **12**.

From the data in Figure 1, it becomes obvious that the oxyacyclization process via TS1 is the preferred reaction

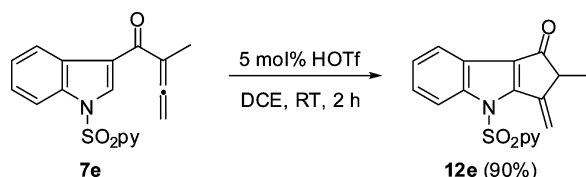
pathway from both kinetic and thermodynamic points of view. For this reason, furyl-indoles **11** are exclusively formed when the reaction is conducted at -20°C . Similarly, compounds **11** are the major reaction products when the reaction is conducted at room temperature (see Scheme 5). However, within these conditions the available thermal energy seems to be enough to overcome, at least in part, the barriers associated with TS2 and TS4 that lead to tricyclic compounds **12** as minor reaction products. Both barriers and also that involving TS3 (in the proximal reaction pathway) are easily overcome at 140°C (and microwave irradiation conditions). As a consequence, a significant amount of compounds **12** is produced together with the most favored furyl-indoles **11**.

Given that from the computational data in Figure 1 furyl-indole **11** is both the product of kinetic and thermodynamic control, we subjected the kinetic product **11** to reaction conditions to discard that the purported thermodynamic product **12** is formed. Indeed, the treatment of **11e** under microwave irradiation at 145°C in the presence of the gold salt did not result in formation of tricycle **12e**.

Alternatively, the observed indolones **12** may be formed following a Nazarov-type cyclization mechanism.²³ As shown in Figure 2, coordination of the gold(I)-catalyst to the oxygen atom of the carbonyl group of **7e** instead of the allenyl moiety leads to the exergonic formation of complex **7e-Au-O** ($\Delta G_{298} = -11.7$ kcal/mol). This species evolves to the stabilized allylic carbocation **26-Au** via TS5, a transition state associated with the C–C bond formation in a Nazarov-type cyclization reaction. This process proceeds with an activation barrier of $\Delta G_{a,298} = 20.4$ kcal/mol, which indicates that it is competitive over the processes described above involving TS2 or TS3. Complex **26-Au** will be finally converted into the final indolone **12e** after 1,3-proton migration and decooordination of the catalyst.

In addition, since at high temperature the gold catalyst may decompose to give acid, it can be suggested that the in situ generated protons may also catalyze the Nazarov-type cyclization reaction of allenones **7**. To check this hypothesis, **7e** was reacted with 5 mol % of HOTf as the catalyst (under otherwise identical conditions) and tricyclic product **12e** was formed in 90% yield (Scheme 8).²⁴ Therefore, it can be

Scheme 8. Controlled Preparation of 2,3-Dihydrocyclopenta[*b*]indolone **12e through Proton-Catalyzed Carbocyclization of Allenone **7e**^a**



^aSO₂py = (2-pyridyl)sulfonyl. DCE = 1,2-dichloroethane.

concluded that the formation of these tricycles **12** may be the result of this proton-mediated Nazarov reaction or, alternatively, of the above commented gold(I)-catalyzed process via **TSS**.

CONCLUSION

In conclusion, the chemo- and regiocontrolled cyclization of oxyallenyl C3-linked indoles into different heterocycles has been realized by using various catalysts, such as Pd(II)- and Au(I)-based salts. The scope of these protocols has been investigated and clearly demonstrates their utility for the selective preparation of furyl-indoles, carbazoles, and cyclopentaindolones from structurally related substrates. These cyclization reactions have been developed experimentally, and their mechanisms have additionally been investigated by a computational study. At present time, the application of this methodology into the selective preparation of other types of indole-based compounds is ongoing in our group.

EXPERIMENTAL SECTION

General Methods. ¹H NMR and ¹³C NMR spectra were recorded on 700, 500, 300, or 200 MHz spectrometers. NMR spectra were recorded in CDCl₃ solutions, except when otherwise stated. Chemical shifts are given in ppm relative to TMS (¹H, 0.0 ppm), or CDCl₃ (¹³C, 76.9 ppm). Low and high resolution mass spectra were taken on a QTOF LC–MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. Specific rotation [α]_D is given in 10^{−1} deg cm² g^{−1} at 20 °C, and the concentration (*c*) is expressed in g per 100 mL. All commercially available compounds were used without further purification.

Computational Details. All the calculations reported in this paper were obtained with the Gaussian 09 suite of programs.²⁵ Geometry optimizations were performed using the B3LYP²⁶ hybrid functional in combination with the double- ζ quality plus polarization def2-SVP²⁷ basis set for all atoms. Reactants and products were characterized by frequency calculations²⁸ and have positive definite Hessian matrices. Transition structures (TS) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the intrinsic reaction coordinate (IRC) method.²⁹ Single point energy calculations were computed using the dispersion-corrected meta-hybrid M06 functional, which has been recommended for transition-metal-containing species³⁰ in combination with the polarizable continuum model³¹ (PCM, using

DCE as solvent) on the B3LYP/def2-SVP optimized geometries. This level is denoted PCM(DCE)-M06/def2-SVP//B3LYP/def2-SVP.

Preparation of **1c and **1d**.** *N*-Boc derivative **1c** and *N*-SO₂Ar derivative **1d** were prepared according to previously reported procedures.^{32,33}

General Procedure for the Synthesis of 1-SO₂py-Substituted Indoles **1e–k.** Over a solution of the corresponding *NH*-indole in anhydrous THF (13 mL/mmol) at 0 °C, NaH (1.5 equiv) was added in portions. After 1.5 h of stirring, 2-pyridinsulfonyl chloride was slowly added, and the mixture was warmed to room temperature and left stirring overnight. After completion (TLC), the reaction was quenched with water and extracted with AcOEt. The organic phases were combined, washed with brine, and dried on MgSO₄. The solvent was evaporated under reduced pressure, and the mixture was purified on column chromatography, yielding analytically pure compounds. Spectroscopic and analytical data for pure forms of **1e–k** follow.

1-SO₂py-Substituted Indole **1e.** Starting from the corresponding aldehyde (200 mg, 1.38 mmol), after purification on column chromatography (hexanes/ethyl acetate, 3:1), 340 mg (86%) of the *N*-protected compound were obtained as a colorless solid: mp 189–191 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 7.41 (2H, m), 7.56 (1H, ddd, *J* = 7.6, 4.7, 0.9 Hz), 8.00 (2H, m), 8.29 (2H, m), 8.38 (1H, s), 8.65 (1H, m), 10.17 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 185.5, 154.6, 150.8, 138.4, 137.8, 135.5, 128.2, 126.3, 126.2, 125.1, 122.7, 122.6, 122.4, 113.4; IR (CHCl₃) ν = 1677, 1383, 1162, 1121 cm^{−1}; HRMS (ES) calcd for C₁₄H₁₁N₂O₃S [M + H]⁺ 287.0490, found 287.0485.

1-SO₂py-Substituted Indole **1f.** Starting from the corresponding aldehyde (250 mg, 1.57 mmol), after purification on column chromatography (hexanes/ethyl acetate, 3:1), 423 mg (90%) of the *N*-protected compound were obtained as a colorless solid: mp 194–195 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 2.46 (3H, s), 7.21 (1H, m), 7.54 (1H, m), 7.85 (1H, d, *J* = 8.5 Hz), 7.99 (1H, td, *J* = 7.7, 1.6 Hz), 8.10 (1H, s), 8.26 (1H, d, *J* = 7.9 Hz), 8.34 (1H, s), 8.65 (1H, m), 10.14 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 185.8, 154.6, 150.9, 144.9, 138.4, 138.2, 135.3, 128.2, 127.6, 126.6, 127.7, 122.5, 122.3, 113.1, 21.4; IR (CHCl₃) ν = 1679, 1390, 1177, 1122 cm^{−1}; HRMS (ES) calcd for C₁₅H₁₃N₂O₃S [M + H]⁺ 301.0647, found 301.0631.

1-SO₂py-Substituted Indole **1g.** Starting from the corresponding aldehyde (250 mg, 1.06 mmol), after purification on column chromatography (dichloromethane/ethyl acetate, 2:1), 395 mg (99%) of the *N*-protected compound were obtained as a colorless solid: mp 201–202 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 2.42 (3H, s), 7.29 (2H, m), 7.61 (3H, m), 8.01 (2H, m), 8.29 (1H, dt, *J* = 7.9, 1.0 Hz), 8.39 (1H, s), 8.50 (1H, m), 8.66 (1H, m), 10.18 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 185.6, 154.6, 151.0, 138.7, 138.5, 138.4, 137.7, 137.3, 134.7, 129.6 (2C), 128.3, 127.3 (2C), 127.0, 125.7, 122.8, 122.6, 120.7, 113.7, 21.1; IR (CHCl₃) ν = 1678, 1384, 1163, 1120 cm^{−1}; HRMS (ES) calcd for C₂₁H₁₇N₂O₃S [M + H]⁺ 377.0960, found 377.0943.

1-SO₂py-Substituted Indole **1h.** Starting from the corresponding aldehyde (350 mg, 1.846 mmol), after purification on column chromatography (hexanes/ethyl acetate, 1:1), 500 mg (82%) of the *N*-protected compound were obtained as a pale yellow solid: mp 166–168 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 2.69 (3H, s), 3.88 (3H, s), 6.99 (1H, d, *J* = 0.1 Hz), 7.54 (1H, ddd, *J* = 7.7, 4.7, 0.9 Hz), 7.80 (1H, d, *J* = 9.1 Hz), 7.98 (1H, td, *J* = 7.7, 1.6 Hz), 8.23 (1H, d, *J* = 7.9 Hz), 8.39 (1H, s), 8.64 (1H, m), 10.17 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ 184.9, 155.2, 154.6, 150.9, 139.7, 138.4, 130.9, 128.2, 127.4, 124.5, 127.7, 120.9, 111.3, 110.5, 56.7, 14.4; IR (CHCl₃) ν = 1689, 1391, 1165, 1119 cm^{−1}; HRMS (ES) calcd for C₁₆H₁₅N₂O₄S [M + H]⁺ 331.0753, found 331.0747.

1-SO₂py-Substituted Indole **1i.** Starting from the corresponding aldehyde (350 mg, 1.815 mmol), after purification on column chromatography (hexanes/ethyl acetate, 1:1), 683 mg (97%) of the *N*-protected compound were obtained as a colorless solid: mp 190–191 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 1.16 (6H, d, *J* = 6.8 Hz), 2.92 (1H, sept, *J* = 6.8 Hz), 7.15 (1H, d, *J* = 8.3 Hz), 7.42 (1H, dd, *J* = 7.8, 4.7 Hz), 7.72 (1H, s), 7.87 (1H, td, *J* = 7.7, 1.4 Hz), 8.06 (1H, d, *J* = 8.2 Hz), 8.13 (1H, d, *J* = 7.9 Hz), 8.21 (1H, s), 8.52 (1H,

m), 10.00 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 185.7, 154.5, 150.9, 147.9, 138.5, 137.6, 135.9, 128.3, 124.4, 124.2, 127.7, 122.4, 122.3, 111.1, 34.6, 24.3 (2C); IR (CHCl_3) ν = 1672, 1399, 1192, 1122 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 329.0960, found 329.0954.

1-SO₂py-Substituted Indole 1j. Starting from the corresponding aldehyde (200 mg, 1.26 mmol), after purification on column chromatography (hexanes/ethyl acetate, 2:1), 290 mg (77%) of the *N*-protected compound were obtained as a colorless solid: mp 194–195 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 2.54 (3H, s), 7.14 (1H, d, J = 7.29 Hz), 7.29 (1H, m), 7.58 (1H, ddd, J = 7.7, 4.7, 1.2 Hz), 8.04 (1H, td, J = 7.9, 1.8 Hz), 8.20 (1H, dt, J = 7.9, 0.9 Hz), 8.26 (1H, m), 8.55 (1H, s), 8.64 (1H, m), 10.18 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 185.7, 156.2, 150.7, 141.2, 138.6, 135.7, 129.8, 128.3, 128.1, 125.4, 124.1, 122.3, 121.6, 120.5, 21.7; IR (CHCl_3) ν = 1680, 1394, 1187, 1127 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 301.0647, found 301.0641.

1-SO₂py-Substituted Indole 1k. Starting from the corresponding aldehyde (250 mg, 1.712 mmol), after purification on column chromatography (hexanes/ethyl acetate, 2:1), 428 mg (87%) of the *N*-protected compound were obtained as a pale yellow solid: mp 194–195 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 7.22 (1H, dd, J = 7.9, 4.8 Hz), 7.47 (1H, ddd, J = 7.8, 4.7, 1.1 Hz), 7.95 (1H, td, J = 7.7, 1.6 Hz), 8.31 (1H, dd, J = 4.8, 1.6 Hz), 8.43 (1H, s), 8.48 (1H, m), 8.52 (1H, m), 10.02 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 185.4, 154.5, 150.6, 147.7, 146.7, 138.4, 137.4, 131.6, 128.4, 124.7, 120.8, 119.8, 119.1; IR (CHCl_3) ν = 1686; 1396; 1190; 1137 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 288.0443, found 288.0437.

Indium-Promoted Reaction between 1-Bromo-2-butyne and Indole-3-carbaldehydes 1. General Procedure for the Synthesis of α -Allenic Alcohols 2. 1-Bromo-2-butyne (3.0 mmol) was added to a well stirred suspension of the appropriate aldehyde **1** (1.0 mmol) and indium powder (6.0 mmol) in THF/ NH_4Cl (aq. sat.) (1:5, 5 mL) at 0 °C. The reaction was stirred at rt for 16 h. After disappearance of the starting material (TLC), the mixture was extracted with ethyl acetate (3 \times 5 mL). The organic extract was washed with brine, dried (MgSO_4) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of **2** follow.

α -Allenic Alcohol 2c. Starting from aldehyde **1c** (120 mg, 0.49 mmol), 108 mg (77%) of the allenol were obtained as a pale yellow oil, after purification on column chromatography (hexanes/ethyl acetate, 5:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.58 (12H, s), 4.84 (2H, m), 5.32 (1H, s), 7.13 (1H, m), 7.23 (1H, td, J = 7.6, 1.3 Hz), 7.52 (2H, m), 8.05 (1H, d, J = 7.9 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 205.2, 149.8, 136.0, 128.6, 124.5, 123.6, 122.6, 121.4, 120.1, 115.3, 101.5, 83.8, 77.7, 69.2, 28.2 (3C), 14.4; IR (CHCl_3) ν = 3508–3350, 1540, 1019 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$ 300.1600, found 300.1594.

α -Allenic Alcohol 2d. Starting from aldehyde **1d** (190 mg, 0.46 mmol), 120 mg (51%) of the allenol were obtained as a pale yellow oil, after purification on column chromatography (hexanes/ethyl acetate, 8:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.02 (12H, d, J = 6.7 Hz, 4Me), 1.17 (6H, d, J = 7.0 Hz), 1.65 (3H, t, J = 3.1 Hz), 2.83 (1H, sept, J = 6.9 Hz), 4.11 (2H, sept, J = 6.7 Hz), 4.84 (2H, m), 5.32 (1H, s), 7.11 (4H, m), 7.33 (1H, m), 7.45 (1H, s), 7.54 (1H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 205.6, 155.0, 151.8, 136.1, 131.9, 131.9, 128.5, 124.7, 124.7 (2C), 123.6, 122.9, 121.8, 120.9, 113.1, 101.7, 77.6, 69.5, 34.6, 28.9 (2C), 24.9 (4C), 23.9 (2C), 14.8; IR (CHCl_3) ν = 3501–3344, 1542, 1022 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{28}\text{H}_{36}\text{NO}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 466.2416, found 466.2410.

α -Allenic Alcohol 2e. Starting from aldehyde **1e** (60 mg, 0.209 mmol), 66 mg (93%) of the allenol were obtained as a pale yellow oil, after purification on column chromatography (hexanes/ethyl acetate, 2:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.65 (3H, t, J = 3.1 Hz), 4.95 (2H, m), 5.41 (1H, s), 7.28 (2H, m); 7.47 (1H, ddd, J = 7.7, 4.7, 1.0 Hz), 7.63 (1H, d, J = 7.4 Hz), 7.71 (1H, s), 7.91 (1H, td, J = 7.4, 1.8 Hz), 8.03 (1H, d, J = 8.8 Hz), 8.13 (1H, d, J = 8.1 Hz), 8.61 (1H,

m); ^{13}C NMR (75 MHz, CDCl_3) δ 205.2, 155.4, 150.4, 138.1, 135.9, 129.0, 127.5, 125.1, 124.8, 123.4, 123.1, 122.3, 120.7, 113.9, 101.3, 77.9, 69.1, 14.3; IR (CHCl_3) ν = 3509–3352, 1542, 1038 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 341.0960, found 341.0954.

α -Allenic Alcohol 2f. Starting from aldehyde **1f** (500 mg, 1.660 mmol), 501 mg (85%) of the allenol were obtained as a pale yellow oil, after purification on column chromatography (hexanes/ethyl acetate, 3:2): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.63 (3H, t, J = 3.0 Hz), 2.41 (3H, s), 4.94 (2H, m), 5.36 (1H, s), 7.13 (1H, d, J = 8.5 Hz), 7.38 (1H, s), 7.44 (1H, ddd, J = 7.7, 4.7, 1.1 Hz), 7.64 (1H, m), 7.86 (2H, m), 8.08 (1H, d, J = 7.8 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 205.5, 155.7, 150.8, 138.5, 134.4, 133.5, 129.7, 127.9, 126.6, 125.6, 123.3, 122.7, 120.9, 114.0, 101.6, 78.8, 69.3, 21.9, 14.8; IR (CHCl_3) ν = 3512–3353, 1540, 1038 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 355.1116, found 355.1111.

α -Allenic Alcohol 2g. Starting from aldehyde **1g** (320 mg, 0.851 mmol), 280 mg (76%) of the allenol were obtained as a pale yellow oil, after purification on column chromatography (hexanes/ethyl acetate, 2:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.67 (3H, t, J = 3.2 Hz), 2.43 (3H, s), 4.96 (2H, m), 5.45 (1H, s), 7.29 (2H, m), 7.52 (4H, m), 7.73 (1H, s), 7.81 (1H, d, J = 1.3 Hz), 7.93 (1H, td, J = 7.4, 1.6 Hz), 8.07 (1H, dd, J = 8.6, 0.4 Hz), 8.17 (1H, d, J = 7.9 Hz), 8.63 (1H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 205.1, 155.3, 150.5, 138.4, 138.3, 138.2, 136.9, 136.8, 135.1, 129.6 (2C), 127.7, 127.2 (2C), 125.5, 124.3, 123.2, 118.9, 114.1, 101.3, 78.0, 69.1, 21.1, 14.3; IR (CHCl_3) ν = 3512–3342, 1544, 1032 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 431.1429, found 431.1424.

α -Allenic Alcohol 2h. Starting from aldehyde **1h** (500 mg, 1.515 mmol), 470 mg (80%) of the allenol were obtained as a pale yellow oil, after purification on column chromatography (hexanes/ethyl acetate, 2:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.64 (3H, t, J = 3.1 Hz), 2.39 (3H, s), 3.74 (3H, s), 4.73 (2H, m), 5.42 (1H, s), 6.80 (1H, d, J = 9.1 Hz), 7.33 (1H, ddd, J = 7.6, 4.7, 1.0 Hz), 7.59 (1H, s), 7.70 (1H, d, J = 9.1 Hz), 7.77 (1H, td, J = 7.7, 1.7 Hz), 7.97 (1H, d, J = 8.0 Hz), 8.47 (1H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 205.8, 155.2, 154.2, 150.4, 138.1, 130.9, 129.7, 127.5, 127.0, 124.4, 122.3, 119.2, 111.5, 109.7, 101.9, 78.1, 60.7, 56.8, 15.5, 12.0; IR (CHCl_3) ν = 3512–3342, 1544, 1023 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4\text{SNa}$ [$\text{M} + \text{Na}$] $^+$ 407.1041, found 407.1036.

α -Allenic Alcohol 2i. Starting from aldehyde **1i** (633 mg, 1.930 mmol), 787 mg (99%) of the allenol were obtained as a pale yellow oil, after purification on column chromatography (hexanes/ethyl acetate, 2:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.20 (6H, d, J = 6.9 Hz), 1.53 (3H, t, J = 3.03 Hz), 2.93 (1H, sept, J = 6.8 Hz), 4.85 (2H, m), 5.27 (1H, s), 7.03 (1H, dd, J = 8.3, 1.5 Hz), 7.36 (1H, ddd, J = 7.6, 4.7, 1.0), 7.43 (1H, d, J = 8.2 Hz), 7.54 (1H, d, J = 0.9 Hz), 7.81 (2H, m), 8.02 (1H, d, J = 8.0 Hz), 8.51 (1H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 205.0, 155.3, 150.4, 146.3, 138.0, 136.1, 127.6, 127.1, 124.6, 123.00, 122.4, 122.3, 120.3, 111.6, 101.3, 77.9, 69.0, 34.5, 24.4 (2C), 14.3; IR (CHCl_3) ν = 3512–3351, 1533, 1039 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 383.1429, found 383.1424.

α -Allenic Alcohol 2j. Starting from aldehyde **1j** (160 mg, 0.533 mmol), 170 mg (90%) of the allenol were obtained as a brown oil, after purification on column chromatography (hexanes/ethyl acetate, 5:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.68 (3H, t, J = 3.1 Hz), 2.61 (3H, s), 4.97 (2H, m), 5.43 (1H, s), 7.07 (1H, d, J = 7.3 Hz), 7.17 (1H, t, J = 7.4 Hz), 7.50 (2H, m), 7.84 (1H, s), 7.93 (1H, td, J = 7.6, 1.7 Hz), 8.02 (1H, d, J = 7.9 Hz), 8.62 (1H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 205.3, 150.3, 138.2, 135.8, 131.0, 128.5, 127.9, 127.4, 125.0, 123.85, 122.4, 122.0, 118.3, 115.3, 101.2, 77.8, 69.0, 22.0, 14.4; IR (CHCl_3) ν = 3508–3343, 1544, 1029 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 355.1116, found 355.1111.

α -Allenic Alcohol 2k. Starting from aldehyde **1k** (428 mg, 1.491 mmol), 400 mg (78%) of the allenol were obtained as a pale yellow oil, after purification on column chromatography (hexanes/ethyl acetate, 1:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.69 (3H, t, J = 3.2 Hz), 4.96 (2H, m), 5.40 (1H, s), 7.17 (1H, dd, J = 7.9, 4.8 Hz), 7.50 (1H, ddd, J = 7.6, 4.7, 1.6 Hz), 7.9 (1H, s), 7.97 (2H, m), 8.35 (1H, dd, J = 4.8, 1.6 Hz), 8.49 (1H, d, J = 7.9 Hz), 8.61 (1H, m); ^{13}C NMR (75

MHz, CDCl_3) δ 204.9, 155.4, 150.2, 148.0, 145.1, 138.1, 129.5, 127.7, 125.0, 124.1, 121.5, 120.0, 119.0, 101.3, 78.2, 69.1, 14.5; IR (CHCl_3) ν = 3508–3337, 1542, 1039 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$ 342.0912, found 342.0907.

Magnesium-Promoted Desulfonylation of Allenic *N*-SO₂py-Indoles 2. General Procedure for the Synthesis of Allenic *NH*-Indoles 3. Over a solution of the corresponding allenol 2 (1 mmol) in MeOH (8 mL) at 0 °C, Mg powder was added in one portion (10 equiv). The mixture was stirred and left to warm up to room temperature. After completion (TLC, usually 2–3 h), NH_4Cl (aq. sat.) (8 mL) and Et_2O (8 mL) were added. The mixture was stirred for 1 h and then extracted with AcOEt. The organic extract was washed with brine, dried (MgSO_4) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of 3 follow.

α -Allenic Alcohol 3e. Starting from *N*-SO₂py-protected allenol 2e (60 mg, 0.176 mmol), 30 mg (86%) of the *NH* adduct were obtained as a pale yellow oil, and used in the next step without further purification: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.66 (3H, t, J = 3.2 Hz), 4.97 (2H, m), 5.46 (1H, s), 7.20 (3H, m), 7.38 (1H, dd, J = 8.0, 1.0 Hz), 7.72 (1H, d, J = 7.3 Hz), 8.16 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 204.8, 136.7, 125.8, 122.7, 122.3, 119.8, 119.8, 117.0, 111.3, 102.5, 77.7, 69.1, 15.0; IR (CHCl_3) ν = 3524–3300, 3418, 1567 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{13}\text{H}_{14}\text{NO}$ $[\text{M} + \text{H}]^+$ 200.1075, found 200.1070.

α -Allenic Alcohol 3f. Starting from *N*-SO₂py-protected allenol 2f (500 mg, 1.412 mmol), 200 mg (67%) of the *NH* adduct were obtained as a pale yellow oil, and used in the next step without further purification: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.57 (3H, t, J = 3.1 Hz), 2.37 (3H, s), 4.89 (2H, m), 5.32 (1H, s), 6.96 (1H, d, J = 9.2 Hz), 7.07 (1H, d, J = 2.3, 1.0 Hz), 7.16 (2H, m), 7.41 (1H, s), 7.95 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 204.8, 135.0, 129.0, 126.1, 124.0, 127.8, 119.5, 116.6, 110.9, 102.5, 77.8, 69.0, 21.6, 15.0; IR (CHCl_3) ν = 3524–3291, 3418, 1567 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{14}\text{H}_{16}\text{NO}$ $[\text{M} + \text{H}]^+$ 214.1232, found 214.1226.

α -Allenic Alcohol 3g. Starting from *N*-SO₂py-protected allenol 2g (280 mg, 0.653 mmol), 140 mg (75%) of the *NH* adduct were obtained as a pale yellow oil, after purification on column chromatography (hexanes/ethyl acetate, 2:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.71 (3H, t, J = 3.1 Hz), 2.44 (3H, s), 5.07 (2H, m), 5.51 (1H, s), 7.29 (4H, m), 7.52 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 204.8, 150.5, 139.7, 138.2, 136.1, 133.3, 129.4 (2C), 127.3 (2C), 123.21, 122.2, 118.2, 117.4, 111.4, 102.5, 77.8, 69.1, 21.1, 15.0; IR (CHCl_3) ν = 3535–3301, 3422, 1566 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{20}\text{H}_{20}\text{NO}$ $[\text{M} + \text{H}]^+$ 290.1545, found 290.1539.

α -Allenic Alcohol 3i. Starting from *N*-SO₂py-protected allenol 2i (350 mg, 0.916 mmol), 160 mg (73%) of the *NH* adduct were obtained as a pale yellow oil, and used in the next step without further purification: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.22 (6H, d, J = 7.0 Hz), 1.56 (3H, t, J = 3.0 Hz), 2.93 (1H, sept, J = 7.0 Hz), 4.87 (2H, m), 5.33 (1H, s), 6.96 (1H, dd, J = 8.4, 1.5 Hz), 7.06 (1H, d, J = 2.3), 7.13 (1H, m), 7.55 (1H, d, J = 8.3 Hz), 7.96 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 205.2, 144.0, 137.5, 124.3, 122.5, 119.9, 119.6, 117.4, 108.8, 78.0, 69.6, 34.7, 24.9 (2C), 15.4; IR (CHCl_3) ν = 3510–3349, 1533, 1039 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{16}\text{H}_{20}\text{NO}$ $[\text{M} + \text{H}]^+$ 242.1545, found 242.1539.

α -Allenic Alcohol 3j. Starting from *N*-SO₂py-protected allenol 2j (160 mg, 0.452 mmol), 100 mg (99%) of the *NH* adduct were obtained as a pale yellow oil, and used in the next step without further purification: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.57 (3H, t, J = 3.0 Hz), 2.41 (3H, s), 4.87 (2H, m), 5.36 (1H, s), 6.98 (2H, m), 7.14 (1H, d, J = 2.5 Hz), 7.47 (1H, m), 7.96 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 205.2, 136.7, 125.7, 123.3, 122.6, 120.8, 120.4, 118.0, 117.9, 102.8, 78.1, 69.6, 17.0, 15.3; IR (CHCl_3) ν = 3530–3299, 3422, 1567 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{14}\text{H}_{16}\text{NO}$ $[\text{M} + \text{H}]^+$ 214.1232, found 214.1226.

α -Allenic Alcohol 3k. Starting from *N*-SO₂py-protected allenol 2k (100 mg, 0.293 mmol), 57 mg (98%) of the *NH* adduct were obtained as a pale yellow oil, and used in the next step without further

purification: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.68 (3H, t, J = 3.2 Hz), 4.98 (2H, m), 5.45 (1H, s), 7.12 (1H, dd, J = 7.9, 4.8 Hz), 7.38 (1H, s), 8.07 (1H, dd, J = 8.0, 1.5 Hz), 8.33 (1H, m), 10.67 (1H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 204.7, 149.2, 142.9, 128.7, 123.2, 118.6, 115.8, 115.5, 102.4, 77.8, 69.2, 14.9; IR (CHCl_3) ν = 3508–3337, 1560, 1039 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$ 201.1028, found 201.1022.

Manganese-Promoted Oxidation of Allenol-Tehered Indoles 2 and 3. General Procedure for the Synthesis of Indole-C3-Tethered α -Allenones 7 and 8. Over a solution of the corresponding allenol (1 mmol) in anhydrous MeCN (11 mL) at 0 °C, previously activated MnO_2 was added in one portion (10 equiv). The mixture was warmed up to room temperature and stirred overnight. After completion (TLC), the crude was filtered through a pad of Celite, and the solvent was evaporated under reduced pressure. The resulting mixture was immediately used in the next step, as it showed quick decomposition on solution in most of the cases.

α -Allenone 7e. Starting from allenol 2e (235 mg, 0.680 mmol), 180 mg (45%) of the allenone were obtained as a dark gum, after purification on column chromatography (deactivated silica gel, hexanes/ethyl acetate, 2:1): ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.95 (3H, t, J = 2.9 Hz), 5.16 (2H, q, J = 2.9 Hz), 7.24 (2H, m), 7.41 (1H, m), 7.85 (2H, m), 8.11 (2H, m), 8.32 (1H, s), 8.51 (1H, m); ^{13}C NMR (75 MHz, acetone- d_6) δ 216.9, 188.1, 155.4, 151.8, 140.1, 135.7, 134.6, 129.7, 129.4, 126.4, 125.5, 123.8, 123.4, 120.3, 114.2, 103.4, 79.7, 14.8; IR (CHCl_3) ν = 1933, 1635, 1381, 1186 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$ 339.0803, found 339.0798.

α -Allenone 7f. Starting from allenol 2f (235 mg, 0.680 mmol), 216 mg (54%) of the allenone were obtained as a brown oil, and used immediately in the next step, as it showed quick decomposition on solution: ^1H NMR (300 MHz, acetone- d_6 , 25 °C) δ 1.94 (3H, t, J = 2.9 Hz), 2.35 (3H, s), 5.16 (2H, q, J = 3.1 Hz), 7.05 (1H, dd, J = 8.5, 1.0 Hz), 7.40 (1H, ddd, J = 7.8, 4.7, 1.0 Hz), 7.73 (1H, d, J = 8.4 Hz), 7.84 (1H, td, J = 7.7, 1.8 Hz), 7.92 (1H, m), 8.08 (1H, d, J = 7.9 Hz), 8.3 (3H, m), 8.51 (1H, m); IR (CHCl_3) ν = 1942, 1658, 1381, 1188 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$ 353.0960, found 353.0954.

α -Allenone 7g. Starting from allenol 2g (200 mg, 0.466 mmol), 120 mg (60%) of the allenone were obtained as a brown oil, after purification on column chromatography (deactivated silica gel, hexanes/ethyl acetate, 2:1): ^1H NMR (300 MHz, acetone- d_6 , 25 °C) δ 1.82 (3H, t, J = 2.9 Hz), 2.19 (3H, s), 5.26 (2H, q, J = 2.9 Hz), 7.10 (2H, m), 7.39 (2H, m), 7.47 (1H, dd, J = 8.5, 1.9 Hz), 7.54 (1H, ddd, J = 7.7, 4.5, 1.0 Hz), 7.88 (1H, dd, J = 8.8, 0.5 Hz), 8.03 (1H, td, J = 7.8, 1.6 Hz), 8.21 (2H, m), 8.36 (1H, s), 8.50 (1H, m); ^{13}C NMR (75 MHz, acetone- d_6) δ 216.9, 188.1, 155.4, 151.9, 140.1, 138.9, 137.8, 135.2, 130.5 (2C), 129.7, 129.2, 127.9 (2C), 125.9, 125.6, 123.8, 121.3, 120.5, 116.2, 114.6, 103.4, 79.8, 21.1, 14.9; IR (CHCl_3) ν = 1939, 1632, 1364, 1188 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$ 429.1273, found 429.1267.

α -Allenone 7k. Starting from allenol 2k (215 mg, 0.630 mmol), 86 mg (40%) of the allenone were obtained as an orange oil, after purification on column chromatography (deactivated silica gel, hexanes/ethyl acetate, 2:1): ^1H NMR (300 MHz, acetone- d_6 , 25 °C) δ 1.85 (3H, t, J = 2.9 Hz), 5.34 (2H, q, J = 2.9 Hz), 7.23 (1H, dd, J = 7.9, 4.7 Hz), 7.58 (1H, ddd, J = 7.7, 4.7, 1.0 Hz), 8.09 (1H, td, J = 7.7, 1.6 Hz), 8.14 (1H, dd, J = 4.7, 1.6 Hz), 8.34 (1H, m), 8.37 (1H, m), 8.45 (1H, m), 8.53 (1H, s); ^{13}C NMR (75 MHz, acetone- d_6) δ 216.8, 187.5, 155.6, 151.5, 147.9, 146.6, 139.7, 134.2, 132.2, 129.7, 125.3, 121.9, 121.4, 117.8, 103.0, 80.0, 14.9; IR (CHCl_3) ν = 1957, 1633, 1379, 1188 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$ 340.0756, found 340.0750.

α -Allenone 8a. Starting from allenol 3e (255 mg, 1.280 mmol), 108 mg (45%) of the allenone were obtained as an orange oil, after purification on column chromatography (deactivated silica gel, hexanes/ethyl acetate, 3:1): ^1H NMR (300 MHz, acetone- d_6 , 25 °C) δ 1.81 (3H, t, J = 3.1 Hz), 5.04 (2H, q, J = 3.1 Hz), 7.08 (2H, m), 7.35 (1H, m), 8.15 (2H, m); ^{13}C NMR (75 MHz, acetone- d_6) δ 213.7, 186.2, 133.0, 132.8, 126.2, 122.4, 122.1, 121.4, 121.2, 111.2, 101.3,

76.7, 14.0; IR (CHCl₃) ν = 1935, 1641, 1381, 1186 cm⁻¹; HRMS (ES) calcd for C₁₃H₁₂NO [M + H]⁺ 198.0919, found 198.0913.

α -Allenone 8b. Starting from allenol 3f (277 mg, 1.300 mmol), 158 mg (57%) of the allenone were obtained as a brown oil, and used immediately in the next step, as it showed quick decomposition on solution.

α -Allenone 8c. Starting from allenol 3j (125 mg, 0.587 mmol), 85 mg (68%) of the allenone were obtained as a brown oil, and used immediately in the next step, as it showed quick decomposition on solution.

General Procedure for the Au-Catalyzed Oxycyclization of C3-Allenyl N-SO₂py-Indoles 2. Preparation of (2,5-Dihydrofuran-2-yl)-indoles 4. [(Ph₃P)AuNTf₂] (0.005 mmol) was added to a stirred solution of the corresponding allene 2 (0.1 mmol) in 1,2-dichloroethane (1.3 mL) under argon. The resulting mixture was stirred at room temperature until disappearance of the starting material (TLC). After filtration through a pad of Celite, the mixture was extracted with ethyl acetate (3 \times 5 mL), and the combined extracts were washed twice with brine. The organic layer was dried (MgSO₄) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure adducts 4.

Dihydrofuran 4e. From 56 mg (0.164 mmol) of allene 2e, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound 4e (46 mg, 83%) as a pale yellow oil: ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 8.50 (1H, m), 8.02 (1H, d, *J* = 7.9 Hz), 7.92 (1H, d, *J* = 8.2 Hz), 7.78 (1H, td, *J* = 7.7, 1.7 Hz), 7.57 (1H, s), 7.45 (1H, d, *J* = 7.6 Hz), 7.36 (1H, ddd, *J* = 7.7, 4.7, 1.0 Hz), 7.18 (2H, m), 5.66 (2H, m), 4.70 (2H, m), 1.52 (3H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 155.3, 150.5, 138.1, 137.1, 136.0, 129.1, 127.6, 125.8, 124.8, 123.5, 122.3, 121.8, 121.6, 120.2, 113.9, 83.5, 75.2, 15.5; IR (CHCl₃, cm⁻¹) ν 2850, 1377, 1188, 599; HRMS (ES) calcd for C₁₈H₁₇N₂O₃S [M + H]⁺ 341.0960, found 341.0954.

Dihydrofuran 4f. From 110 mg (0.320 mmol) of allene 2f, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound 4f (64 mg, 57%) as a pale yellow oil: ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 8.5 (1H, m), 7.99 (1H, d, *J* = 7.9 Hz), 7.79 (1H, d, *J* = 9.1 Hz), 7.51 (1H, s), 7.35 (1H, m), 7.20 (2H, m), 7.04 (1H, dd, *J* = 8.5, 1.5 Hz), 5.66 (2H, m), 4.69 (2H, m), 2.30 (3H, s), 1.53 (3H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 155.6, 150.8, 138.5, 137.5, 134.5, 133.5, 129.6, 127.9, 126.6, 126.3, 122.7, 121.9, 120.4, 113.9, 83.8, 77.6, 75.5, 21.8, 13.0; IR (CHCl₃, cm⁻¹) ν 2850, 1381, 1178, 536; HRMS (ES) calcd for C₁₉H₁₉N₂O₃S [M + H]⁺ 355.1116, found 355.1111.

Dihydrofuran 4h. From 140 mg (0.364 mmol) of allene 2h, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound 4h (112 mg, 68%) as a pale orange oil: ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 8.49 (1H, m), 7.97 (1H, dd, *J* = 7.9, 0.9 Hz), 7.77 (2H, m), 7.35 (2H, m), 6.83 (1H, d, *J* = 9.1 Hz), 5.91 (1H, m), 5.70 (1H, s), 4.56 (2H, m), 3.74 (3H, m), 2.45 (3H, s), 1.74 (3H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 155.2, 154.3, 150.4, 138.0, 136.9, 130.8, 130.2, 127.5, 127.2, 123.3, 122.5, 122.3, 119.4, 111.4, 109.9, 82.4, 73.9, 57.0, 13.5, 11.9; IR (CHCl₃, cm⁻¹) ν 2851, 1377, 1189, 568; HRMS (ES) calcd for C₂₀H₂₁N₂O₄S [M + H]⁺ 385.1222, found 385.1217.

Dihydrofuran 4i. From 120 mg (0.312 mmol) of allene 2i, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound 4i (40 mg, 55%) as a pale yellow oil: ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 8.52 (1H, m), 7.99 (1H, dt, *J* = 7.9, 1.0 Hz), 7.77 (2H, m), 7.51 (1H, s), 7.36 (2H, m), 7.03 (1H, dd, *J* = 8.2, 1.5 Hz), 5.64 (2H, m), 4.69 (2H, m), 2.92 (1H, sept, *J* = 7.0 Hz), 1.52 (3H, s), 1.20 (6H, d, *J* = 7.0 Hz); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 155.2, 150.5, 146.3, 138.1, 137.1, 136.3, 127.6, 127.2, 125.3, 122.5, 122.3, 121.7, 121.5, 119.9, 111.6, 83.5, 75.2, 34.5, 24.4 (2C), 12.6; IR (CHCl₃, cm⁻¹) ν 2850, 1379, 1190, 599; HRMS (ES) calcd for C₂₁H₂₁N₂O₃S [M + H]⁺ 381.1273, found 381.1267.

Dihydrofuran 4j. From 60 mg (0.169 mmol) of allene 2j, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound 4j (39 mg, 65%) as a pale yellow oil: ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 8.52 (1H, m), 7.86 (1H, m), 7.84 (1H,

td, *J* = 7.9, 1.8 Hz), 7.69 (1H, s), 7.35 (2H, m), 7.01 (2H, m), 5.67 (2H, m), 4.71 (2H, m), 2.49 (3H, s), 1.55 (3H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 156.8, 150.3, 138.2, 137.2, 135.9, 131.2, 128.8, 128.5, 124.9, 123.9, 122.0, 121.6, 121.0, 118.0, 83.5, 75.2, 22.0, 12.6; IR (CHCl₃, cm⁻¹) ν 2849, 1386, 1188, 590; HRMS (ES) calcd for C₁₉H₁₉N₂O₃S [M + H]⁺ 355.1116, found 355.1111.

Dihydrofuran 4k. From 70 mg (0.205 mmol) of allene 2k, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound 4k (68 mg, 94%) as a pale yellow oil: ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 8.58 (1H, m), 8.48 (1H, d, *J* = 7.9 Hz), 8.34 (1H, dd, *J* = 4.8, 1.4 Hz), 7.96 (1H, td, *J* = 7.7, 1.6 Hz), 7.84 (2H, m), 7.47 (1H, ddd, *J* = 7.7, 4.7, 1.0 Hz), 7.15 (1H, dd, *J* = 8.0, 4.0 Hz), 4.80 (2H, m), 5.57 (2H, m), 1.63 (3H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 155.2, 150.3, 148.1, 145.1, 138.1, 136.8, 128.9, 127.8, 125.7, 124.1, 121.8, 121.5, 119.1, 118.8, 83.6, 75.3, 12.5; IR (CHCl₃, cm⁻¹) ν 2844, 1382, 1176, 603; HRMS (ES) calcd for C₁₇H₁₆N₃O₃S [M + H]⁺ 342.0912, found 342.0907.

General Procedure for the Au-Catalyzed Benzannulation of C3-Allenyl NH-Indoles 3. Preparation of 3-Methyl-9H-carbazoles 5. [(Ph₃P)AuNTf₂] (0.005 mmol) was added to a stirred solution of the corresponding allene 3 (0.1 mmol) in toluene (1.3 mL) under argon. The resulting mixture was stirred at room temperature until disappearance of the starting material (TLC). After filtration through a pad of Celite, the mixture was extracted with ethyl acetate (3 \times 5 mL), and the combined extracts were washed twice with brine. The organic layer was dried (MgSO₄) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure adducts 5.

Carbazole 5e. From 60 mg (0.302 mmol) of allene 3e, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound 5e (41 mg, 77%) as a colorless solid: mp 208–209 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 7.96 (1H, m), 7.89 (1H, m), 7.80 (1H, s), 7.33 (2H, m), 7.26 (1H, d, *J* = 8.1 Hz), 7.15 (2H, m), 2.46 (3H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 139.8, 137.7, 128.8, 127.2, 125.7, 125.3, 120.3, 120.3, 120.0, 119.2, 110.6, 110.2, 21.5; IR (CHCl₃, cm⁻¹) ν 3426, 1456, 1176, 715; HRMS (ES) calcd for C₁₃H₁₃N [M + H]⁺ 182.0970, found 182.0964.

Carbazole 5f. From 70 mg (0.328 mmol) of allene 3f, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound 5f (44 mg, 70%) as a colorless solid: mp 214–215 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 7.76 (2H, m), 7.21 (4H, m), 2.45 (6H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 138.1 (2C), 135.8 (2C), 128.5 (2C), 127.0 (2C), 123.4 (2C), 110.2 (2C), 21.5 (2C); IR (CHCl₃, cm⁻¹) ν 3425, 1456, 1176, 720; HRMS (ES) calcd for C₁₄H₁₄N [M + H]⁺ 196.1126, found 196.1121.

Carbazole 5j. From 80 mg (0.376 mmol) of allene 3j, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent gave compound 5j (48 mg, 67%) as a colorless solid: mp 175–176 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 7.96 (1H, d, *J* = 7.7 Hz), 7.93 (1H, s), 7.81 (2H, m), 7.26 (1H, m), 7.06 (2H, m), 2.80 (3H, s), 2.51 (3H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ 136.0, 133.7, 129.2, 127.4, 126.6, 125.9, 120.8, 119.9, 119.7, 118.3, 110.7, 108.6, 21.9, 21.5; IR (CHCl₃, cm⁻¹) ν 3426, 1456, 1176, 715; HRMS (ES) calcd for C₁₄H₁₄N [M + H]⁺ 196.1126, found 196.1121.

General Procedure for the Pd(II)-Catalyzed Carbocyclization of C3-Allenyl NH-Indoles 3 in Presence of Allyl Bromide. Preparation of 2-Allyl-3-methyl-9H-carbazoles 6. Palladium(II) chloride (0.005 mmol) was added to a stirred solution of the corresponding allene 3 (0.10 mmol) and allyl bromide (0.50 mmol) in *N,N*-dimethylformamide (0.6 mL). The reaction was stirred under argon atmosphere until disappearance of the starting material (TLC). Water (0.5 mL) was added before being extracted with ethyl acetate (3 \times 4 mL). The organic phase was washed with water (2 \times 2 mL), dried (MgSO₄) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure adducts 6.

Carbazole 6e. From 60 mg (0.302 mmol) of allene 3e, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound 6e (46 mg, 85%) as a colorless solid: mp 128–129 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 7.94 (1H, d, *J* = 7.7

Hz), 7.81 (1H, s), 7.75 (1H, s), 7.31 (2H, m), 7.14 (2H, m), 5.98 (1H, m), 4.98 (2H, m), 3.46 (2H, m), 2.37 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 139.6, 138.6, 137.6, 134.9, 129.7, 125.2, 121.7, 121.2, 120.6, 120.0, 119.2, 115.4, 111.7, 110.5, 37.9, 20.3; IR (CHCl_3 , cm^{-1}) ν 3413, 1469, 1241; HRMS (ES) calcd for $\text{C}_{16}\text{H}_{16}\text{N}$ [$\text{M} + \text{H}$] $^+$ 222.1283, found 222.1277.

Carbazole 6f. From 50 mg (0.235 mmol) of allene **3f**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **6f** (42 mg, 78%) as a colorless solid: mp 132–133 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 7.71 (2H, m), 7.21 (2H, m), 7.11 (2H, m), 5.96 (1H, m), 4.98 (2H, m), 3.44 (2H, m), 2.43 (3H, s), 2.36 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 139.3, 138.2, 138.0, 135.0, 129.9, 128.9, 126.9, 124.0, 121.9, 120.8, 120.4, 115.7, 112.0, 110.5, 38.3, 21.8, 20.7; IR (CHCl_3 , cm^{-1}) ν 3411, 1473, 1241; HRMS (ES) calcd for $\text{C}_{17}\text{H}_{18}\text{N}$ [$\text{M} + \text{H}$] $^+$ 236.1439, found 236.1433.

Carbazole 6g. From 70 mg (0.244 mmol) of allene **3g**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent gave compound **6g** (44 mg, 59%) as a colorless solid: mp 113–114 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.13 (1H, s), 7.84 (1H, s), 7.79 (1H, s), 7.54 (4H, m), 7.37 (1H, m), 7.16 (2H, m), 5.99 (1H, m), 5.00 (2H, m), 3.46 (2H, m), 2.38 (3H, s), 2.34 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 139.4, 139.1, 137.6, 136.0, 135.1, 132.8, 129.9, 129.5 (2C), 127.4, 127.1 (2C), 124.7, 124.0, 121.8, 120.6, 118.4, 115.4, 111.8, 110.6, 37.9, 21.1, 20.4; IR (CHCl_3 , cm^{-1}) ν 3413, 1477, 1241; HRMS (ES) calcd for $\text{C}_{23}\text{H}_{21}\text{N}$ [$\text{M} + \text{H}$] $^+$ 311.1674, found 311.1665.

Carbazole 6i. From 72 mg (0.301 mmol) of allene **3i**, and after chromatography of the residue using hexanes/ethyl acetate (12:1) as eluent gave compound **6i** (53 mg, 67%) as a colorless solid: mp 126–127 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 7.84 (1H, s), δ 7.84 (1H, s), 7.71 (1H, m), 7.15 (1H, s), 7.10 (1H, s), 7.01 (1H, dd, J = 8.2, 1.0 Hz), 5.97 (1H, m), 4.96 (2H, m), 3.45 (2H, m), 2.98 (1H, sept, J = 7.0 Hz), 2.36 (3H, s), 1.26 (6H, d, J = 7.0 Hz); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 146.7, 140.0, 138.7, 137.7, 137.1, 134.2, 129.5, 120.3, 119.8, 118.4, 115.3, 111.6, 110.7, 108.0, 37.9, 34.6, 24.5 (2C), 20.3; IR (CHCl_3 , cm^{-1}) ν 3407, 1484, 1240; HRMS (ES) calcd for $\text{C}_{19}\text{H}_{22}\text{N}$ [$\text{M} + \text{H}$] $^+$ 264.1752, found 264.1747.

Carbazole 6j. From 80 mg (0.376 mmol) of allene **3j**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound **6j** (63 mg, 73%) as a colorless solid: mp 128–129 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 7.79 (1H, d, J = 7.7 Hz), 7.41 (1H, s), 7.07 (3H, m), 5.99 (1H, m), 4.97 (2H, m), 3.46 (2H, m), 2.47 (3H, s), 2.38 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 150.8, 137.6, 134.7, 132.6, 129.8, 128.9, 125.9, 120.7, 119.4, 117.7, 115.3, 111.8, 105.0, 102.9, 37.9, 20.3, 16.91; IR (CHCl_3 , cm^{-1}) ν 3408, 1489, 1240; HRMS (ES) calcd for $\text{C}_{17}\text{H}_{18}\text{N}$ [$\text{M} + \text{H}$] $^+$ 236.1439, found 236.1434.

General Procedure for the Au-Catalyzed Oxycyclization of C3-Allenyl *NH*-Indoles 8. Preparation of 3-(Furan-2-yl)-indoles 10. $[(\text{Ph}_3\text{P})\text{AuNTf}_2]$ (0.005 mmol) was added to a stirred light-protected solution of the corresponding allenone **8** (0.1 mmol) in 1,2-dichloroethane (1.3 mL) under argon. The resulting mixture was stirred at room temperature until disappearance of the starting material (TLC). After filtration through a pad of Celite, the mixture was extracted with ethyl acetate (3 \times 5 mL), and the combined extracts were washed twice with brine. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure adducts **10**.

Furan 10a. From 60 mg (0.305 mmol) of allenone **8a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **10a** (48 mg, 80%) as a colorless solid: mp 91–92 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.14 (1H, s), 7.97 (1H, d, J = 7.7 Hz), 7.36 (1H, d, J = 1.8 Hz), 7.30 (1H, d, J = 7.4 Hz), 7.22 (1H, d, J = 2.5 Hz), 7.14 (2H, m), 6.29 (1H, d, J = 1.6 Hz), 2.12 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 146.6, 140.0, 135.8, 129.4, 125.7, 122.8, 121.5, 121.4, 120.4, 114.0, 111.1, 109.0, 11.3; IR (CHCl_3 , cm^{-1}) ν 3401, 2932, 1373, 749; HRMS (ES) calcd for $\text{C}_{13}\text{H}_{12}\text{NO}$ [$\text{M} + \text{H}$] $^+$ 198.0919, found 198.0913.

Furan 10b. From 75 mg (0.356 mmol) of allenone **8b**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **10b** (46 mg, 62%) as a colorless solid: mp 91–93 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.07 (1H, s), 7.77 (1H, s), 7.37 (1H, d, J = 1.8 Hz), 7.19 (2H, m), 6.98 (1H, dd, J = 8.3, 1.4 Hz), 6.28 (1H, d, J = 1.8 Hz), 2.40 (3H, s), 2.11 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 146.7, 139.9, 134.2, 129.8, 125.9, 124.4, 121.6, 120.9, 113.9, 113.9, 110.7, 108.5, 21.6, 11.3; IR (CHCl_3 , cm^{-1}) ν 3400, 2929, 1386, 756; HRMS (ES) calcd for $\text{C}_{14}\text{H}_{14}\text{NO}$ [$\text{M} + \text{H}$] $^+$ 212.1075, found 212.1070.

Furan 10f. From 100 mg (0.474 mmol) of allenone **8f**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **10f** (61 mg, 61%) as a pale yellow gum: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.08 (1H, s), 7.84 (1H, d, J = 7.9 Hz), 7.36 (1H, d, J = 1.8 Hz), 7.23 (1H, d, J = 2.6 Hz), 7.02 (2H, m), 6.28 (1H, d, J = 1.6 Hz), 2.42 (3H, s), 2.12 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 146.6, 140.0, 134.4, 125.2, 123.2, 121.2, 120.6, 120.2, 119.1, 114.0, 114.0, 109.5, 16.6, 11.3; IR (CHCl_3 , cm^{-1}) ν 3409, 2924, 1379, 747; HRMS (ES) calcd for $\text{C}_{14}\text{H}_{14}\text{NO}$ [$\text{M} + \text{H}$] $^+$ 212.1075, found 212.1070.

General Procedure for the Au-Catalyzed Oxycyclization of C3-Allenyl *N*-SO₂py-Indoles 7 at Low Temperature. Preparation of 3-(Furan-2-yl)-indoles 11. $[(\text{Ph}_3\text{P})\text{AuNTf}_2]$ (0.005 mmol) was added to a stirred light-protected solution of the corresponding allenone **7** (0.1 mmol) in 1,2-dichloroethane (1.3 mL) under argon at –20 °C. The resulting mixture was stirred at –20 °C until disappearance of the starting material (TLC). After filtration through a pad of Celite, the mixture was extracted with ethyl acetate (3 \times 5 mL), and the combined extracts were washed twice with brine. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure adducts **11**.

Furan 11e. From 70 mg (0.207 mmol) of allenone **7e**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **11e** (57 mg, 85%) as a pale yellow gum: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.50 (1H, m), 8.05 (1H, d, J = 7.9 Hz), 7.95 (1H, m), 7.78 (1H, td, J = 7.7, 1.8 Hz), 7.67 (1H, m), 7.37 (2H, m), 7.23 (2H, m), 6.30 (1H, d, J = 1.7 Hz), 2.18 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 155.2, 150.6, 144.3, 141.1, 138.2, 135.0, 129.0, 127.7, 125.2, 123.9, 122.9, 122.3, 122.3, 117.3, 114.3, 114.3, 113.7, 11.5; IR (CHCl_3 , cm^{-1}) ν 3143, 1446, 1375, 1185, 1128, 745; HRMS (ES) calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 339.0803, found 339.0798.

Furan 11f. From 100 mg (0.284 mmol) of allenone **7f**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **11f** (60 mg, 80%) as a colorless gum: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.51 (1H, m), 8.01 (1H, d, J = 7.9 Hz), 7.82 (2H, m), 7.64 (1H, s), 7.39 (3H, m), 7.08 (1H, dd, J = 8.5, 1.5 Hz), 6.31 (1H, d, J = 1.8 Hz), 2.35 (2H, s), 2.18 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 155.2, 150.5, 144.4, 141.1, 138.1, 134.3, 134.1, 133.6, 132.0, 127.6, 126.5, 123.1, 122.3, 122.0, 117.2, 114.3, 113.3, 21.5, 11.5; IR (CHCl_3 , cm^{-1}) ν 3141, 1475, 1429, 1375, 1186, 1128, 601; HRMS (ES) calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 353.0960, found 353.0954.

Furan 11g. From 80 mg (0.187 mmol) of allenone **7g**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **11g** (49 mg, 63%) as a colorless gum: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.52 (1H, m), 8.13 (1H, d, J = 1.8 Hz), 8.01 (2H, m), 7.81 (1H, m), 7.69 (1H, s), 7.41 (5H, m), 7.18 (2H, m), 6.32 (1H, d, J = 1.8 Hz), 2.31 (2H, s), 2.20 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 155.2, 150.6, 144.2, 141.2, 138.5, 138.3, 138.2, 137.4, 136.9, 129.5 (2C), 127.7, 127.3 (2C), 124.6, 123.4, 122.3, 120.5, 117.4, 115.2, 114.6, 114.3, 113.8, 21.1, 11.5; IR (CHCl_3 , cm^{-1}) ν 3144, 1440, 1375, 1184, 1128, 746; HRMS (ES) calcd for $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 429.1273, found 429.1267.

Furan 11k. From 80 mg (0.234 mmol) of allenone **7k**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **11k** (74 mg, 94%) as a colorless solid: mp 86–87 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.48 (1H, m), 8.41 (1H, d, J = 7.9 Hz), 8.28 (2H, m), 7.88 (1H, td, J = 7.9, 1.8 Hz), 7.84 (1H,

s), 7.41 (2H, m), 7.14 (2H, m), 6.31 (1H, d, $J = 1.7$ Hz), 2.21 (3H, s); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 155.2, 150.3, 147.2, 145.4, 144.0, 141.2, 138.1, 131.1, 127.8, 124.2, 122.1, 121.3, 119.4, 117.3, 114.5, 111.6, 11.4; IR (CHCl_3 , cm^{-1}) ν 2928, 1370, 757; HRMS (ES) calcd for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 340.0756, found 340.0750.

General Procedure for the Au-Catalyzed Carbocyclization of C3-Allenyl N-SO₂py-Indoles 7 under Microwave Heating. Preparation of 2,3-Dihydrocyclopenta[b]indolones 12. $[(\text{Ph}_3\text{P})\text{AuNTf}_2]$ (0.005 mmol) was added to a stirred light-protected solution of the corresponding allenone 7 (0.1 mmol) in 1,2-dichloroethane (1.3 mL). The resulting mixture was stirred at 145 °C under microwave irradiation until disappearance of the starting material (TLC). After filtration through a pad of Celite, the mixture was extracted with ethyl acetate (3×5 mL), and the combined extracts were washed twice with brine. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave analytically pure adducts 11 and 12.

Reaction of Allenone 7e. From 70 mg (0.207 mmol) of allenone 7e, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 19 mg (27%) of the less polar compound 11e and 38 mg (58%) of the more polar compound 12e were obtained.

Cyclopentaindolone 12e. Orange solid: mp 199–200 °C; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.47 (1H, m), 8.10 (2H, m), 7.86 (2H, m), 7.43 (1H, ddd, $J = 7.6, 4.7, 1.027$ Hz), 7.31 (2H, m), 6.51 (1H, d, $J = 1.2$ Hz), 5.39 (1H, d, $J = 1.2$ Hz), 3.35 (1H, m) 1.34 (3H, d, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 196.7, 158.9, 155.3, 150.7, 143.0, 138.3, 137.8, 128.4, 128.2, 127.0, 125.4, 122.3, 122.1, 121.7, 115.6, 114.3, 52.0, 15.4; IR (CHCl_3 , cm^{-1}) ν 2923, 1700, 1452, 1192; HRMS (ES) calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 339.0803, found 339.0798.

Reaction of Allenone 7f. From 100 mg (0.284 mmol) of allenone 7f, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 19 mg (27%) of the less polar compound 11f and 18 mg (23%) of the more polar compound 12f were obtained.

Cyclopentaindolone 12f. Orange gum: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.47 (1H, m), 7.99 (2H, m), 7.84 (H, td, $J = 7.7, 1.7$ Hz), 7.42 (2H, m), 7.12 (1H, m), 6.48 (1H, d, $J = 1.2$ Hz), 5.37 (1H, d, $J = 1.2$ Hz), 3.35 (1H, m), 2.34 (3H, s), 1.32 (3H, d, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 196.9, 158.1, 150.6, 138.2, 137.8, 134.3, 134.1, 129.4, 129.2, 128.3, 128.1, 122.3, 121.6, 118.0, 115.2, 114.0, 52.0, 21.2, 15.4; IR (CHCl_3 , cm^{-1}) ν 2931, 1703, 1447, 1188; HRMS (ES) calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 353.0960, found 353.0954.

Reaction of Allenone 7g. From 80 mg (0.187 mmol) of allenone 7g, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 14 mg (19%) of the less polar compound 11g and 34 mg (43%) of the more polar compound 12g were obtained.

Cyclopentaindolone 12g. Orange gum: ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 8.50 (1H, m), 8.15 (1H, d, $J = 8.9$ Hz), 8.04 (2H, m), 7.87 (1H, td, $J = 7.9, 1.6$ Hz), 7.55 (H, dd, $J = 8.8, 1.9$ Hz), 7.43 (4H, m), 7.16 (1H, s), 6.51 (1H, d, $J = 0.9$ Hz), 5.40 (1H, d, $J = 0.9$ Hz), 3.37 (1H, m), 2.32 (3H, s), 1.35 (3H, d, $J = 7.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 197.1, 158.8, 155.7, 151.1, 142.6, 139.1, 138.7, 138.2, 137.8, 137.7, 130.0, 128.8, 128.6, 127.6 (2C), 126.6, 123.0, 122.7, 120.0, 116.1, 114.7, 52.4, 21.5, 15.8; IR (CHCl_3 , cm^{-1}) ν 2931, 1703, 1447, 1188; HRMS (ES) calcd for $\text{C}_{25}\text{H}_{21}\text{N}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$ 429.1273, found 429.1267.

Procedure for the Proton-Catalyzed Carbocyclization of Allenone 7e. Preparation of 2,3-Dihydrocyclopenta[b]indolone 12e. HOTf (0.005 mmol) was added to a stirred light-protected solution of allenone 7e (34 mg, 0.10 mmol) in 1,2-dichloroethane (1.3 mL). The resulting mixture was stirred at room temperature for 2 h. Saturated aqueous sodium hydrogen carbonate (1 mL) was added, and the mixture was extracted with ethyl acetate (3×5 mL). The organic extract was washed twice with brine. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate (3:1) gave 29 mg (90%) of analytically pure adduct 12e.

■ ASSOCIATED CONTENT

■ Supporting Information

Schemes S1–S3, computational details and copies of the ^1H NMR and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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■ REFERENCES

- (1) (a) Yu, S.; Ma, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 3074. (b) Rivera-Fuentes, P.; Diederich, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 2818. (c) Cumulenes and Allenes. In *Science of Synthesis, Houben-Weyl Method of Molecular Transformation*; Krause, N., Ed.; George Thieme: Stuttgart, 2007; Vol. 44. (d) Ma, S. *Chem. Rev.* **2005**, *105*, 2829. (e) *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, 2004.
- (2) (a) Lechel, T.; Pfengle, F.; Reissig, H.-U.; Zimmer, R. *ChemCatChem* **2013**, DOI: 10.1002/cctc.201200875. (b) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994. (c) Alcaide, B.; Almendros, P. *Chem. Rev.* **2011**, *111*, 311. (d) Aubert, C.; Fensterbank, L.; Garcia, P.; Malacria, M.; Simonneau, A. *Chem. Rev.* **2011**, *111*, 1954. (e) Brasholz, M.; Reissig, H.-U.; Zimmer, R. *Acc. Chem. Res.* **2009**, *42*, 45. (f) Bongers, N.; Krause, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 2178. (g) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3590.
- (3) (a) Vicente, R. *Org. Biomol. Chem.* **2011**, *9*, 6469. (b) Kochanowska-Karamyan, A. J.; Hamann, M. T. *Chem. Rev.* **2010**, *110*, 4489. (c) Horton, D. A.; Bourne, G. T.; Smythe, M. L. *Chem. Rev.* **2003**, *103*, 893. (d) Faulkner, D. J. *Nat. Prod. Rep.* **2002**, *19*, 1.
- (4) (a) Alcaide, B.; Almendros, P.; Alonso, J. M.; Fernández, I. *Chem. Commun.* **2012**, *48*, 6604. (b) Kong, W.; Qiu, Y.; Zhang, X.; Fu, C.; Ma, S. *Adv. Synth. Catal.* **2012**, *354*, 2339. (c) Kong, W.; Fu, C.; Ma, S. *Chem.—Eur. J.* **2011**, *17*, 13134. (d) Alcaide, B.; Almendros, P.; Alonso, J. M.; Quirós, M. T.; Gadziński, P. *Adv. Synth. Catal.* **2011**, *353*, 1871. (e) Kong, W.; Fu, C.; Ma, S. *Chem. Commun.* **2009**, 4572. (f) Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Quian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066.
- (5) For the N1–C2 cyclization, see: (a) Zeldin, R. M.; Toste, F. D. *Chem. Sci.* **2011**, *2*, 1706. (b) Barluenga, J.; Piedrafita, M.; Ballesteros, A.; Suárez-Sobrinho, A. L.; González, J. M. *Chem.—Eur. J.* **2010**, *16*, 11827.
- (6) (a) Three examples for the metal-free dithiophosphoric acid catalyzed cyclization have been described: Shapiro, N. D.; Rauniyar, V.; Hamilton, G. L.; Wu, J.; Toste, F. D. *Nature* **2011**, *470*, 245. (b) After the initiation of our efforts, a report appeared describing the gold-catalyzed preparation of cyclopenta[b]indoles. See: Chen, B.; Fan, W.; Chai, G.; Ma, S. *Org. Lett.* **2012**, *14*, 3616.
- (7) (a) Alcaide, B.; Almendros, P.; Quirós, M. T.; López, R.; Menéndez, M. I.; Sochacka-Ćwikła, A. *J. Am. Chem. Soc.* **2013**, *135*, 898. (b) Alcaide, B.; Almendros, P.; Luna, A.; Prieto, N. *J. Org. Chem.* **2012**, *77*, 11388.
- (8) Despite that benzannulation strategies are gradually providing access to a wide range of aromatic compounds, drawbacks that include

harsh reaction conditions and poor control of chemo- and regioselectivity are usually encountered. For reviews, see: (a) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, 28, 187. (b) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, 100, 2901. For selected recent examples, see: (c) Tejedor, D.; López-Tosco, S.; González-Platas, J.; García-Tellado, F. *Chem.—Eur. J.* **2011**, 17, 9571. (d) Zhou, H.; Xing, Y.; Yao, J.; Lu, Y. *J. Org. Chem.* **2011**, 76, 4582. (e) Dohi, T.; Washimi, N.; Kamitanaka, T.; Fukushima, K.; Kita, Y. *Angew. Chem., Int. Ed.* **2011**, 50, 6142. (f) Xie, P.; Huang, Y.; Chen, R. *Chem.—Eur. J.* **2012**, 18, 7362.

(9) The carbazole nucleus is both widely distributed in nature as well as representing a key molecular motif in materials science. For selected reviews, see: (a) Schmidt, A. W.; Reddy, K. R.; Knölker, H.-J. *Chem. Rev.* **2012**, 112, 3193. (b) Roy, J.; Jana, A. K.; Mal, D. *Tetrahedron* **2012**, 68, 6099. (c) Li, J.; Grimsdale, A. G. *Chem. Soc. Rev.* **2010**, 39, 2399. (d) Knölker, H.-J. *Chem. Lett.* **2009**, 38, 13. (e) Choi, T. A.; Czerwonka, R.; Forke, R.; Jäger, A.; Knöll, J.; Krah, M. P.; Krause, T.; Reddy, K. R.; Franzblau, S. G.; Knölker, H.-J. *Med. Chem. Res.* **2008**, 17, 374. (f) Knölker, H.-J.; Reddy, K. R. *Chemistry and Biology of Carbazole Alkaloids*. In *The Alkaloids*; Cordell, G. A., Ed.; Academic Press: Amsterdam, 2008; Vol. 65, pp 1–430. (g) Knölker, H.-J. *Top. Curr. Chem.* **2005**, 244, 115. (h) Knölker, H.-J.; Reddy, K. R. *Chem. Rev.* **2002**, 102, 4303.

(10) (a) *Protective Groups in Organic Synthesis*, 4th ed.; Wutz, P. G. M., Greene, T. W., Eds.; Wiley: Hoboken, NJ, 2006. (b) *Protecting Groups*, 3rd ed.; Kocienski, P. J., Ed.; Thieme: Stuttgart, 2003.

(11) (a) García-Rubia, A.; Urones, B.; Gómez Arrayás, R.; Carretero, J. C. *Chem.—Eur. J.* **2010**, 16, 9676. (b) García-Rubia, A.; Gómez Arrayás, R.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2009**, 48, 6511. (c) Pak, C. S.; Lim, D. S. *Synth. Commun.* **2001**, 31, 2209.

(12) (a) Hoffmann-Röder, A.; Krause, N. *Org. Lett.* **2001**, 3, 2537. (b) Ma, S.; Gao, W. *J. Org. Chem.* **2002**, 67, 6104. (c) Alcaide, B.; Almendros, P.; Martínez del Campo, T.; Fernández, I. *Chem. Commun.* **2011**, 47, 9054. (d) Hashmi, A. S. K.; Blanco, M. C.; Fischer, D.; Bats, J. W. *Eur. J. Org. Chem.* **2006**, 1387. (e) Kim, S.; Lee, P. H. *J. Org. Chem.* **2012**, 77, 215.

(13) Alcaide, B.; Almendros, P.; Martínez del Campo, T. *Eur. J. Org. Chem.* **2007**, 2844.

(14) Allenones have been reported to undergo selective cyclization or dimerization reactions to afford furans. (a) Marshall, J. A.; Robinson, E. D. *J. Org. Chem.* **1990**, 55, 3450. (b) Marshall, J. A.; Bartley, G. S. *J. Org. Chem.* **1994**, 59, 7169. (c) Marshall, J. A.; Wallace, E. M. *J. Org. Chem.* **1995**, 60, 796. (d) Hashmi, A. S. K. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1581. (e) Hashmi, A. S. K.; Schwarz, L. *Chem. Ber./Recl.* **1997**, 130, 1449. (f) Hashmi, A. S. K.; Schwarz, L.; Choi, J. H.; Frost, T. M. *Angew. Chem., Int. Ed.* **2000**, 39, 2285. (g) Hashmi, A. S. K.; Schwarz, L.; Bolte, M. *Eur. J. Org. Chem.* **2004**, 1923. (h) Zhou, C.-Y.; Chan, P. W. H.; Che, C.-M. *Org. Lett.* **2006**, 8, 325. (i) ref 13.

(15) Generally, the presence of two or more different heterocyclic moieties in a single molecule often enhances the biocidal profile remarkably. For example, it has been reported that natural and synthetic 3-heteroaryl-indoles possess potent biological activities: (a) Hanssen, K. Ø.; Schuler, B.; Williams, A. J.; Demissie, T. B.; Hansen, E.; Andersen, J. H.; Svenson, J.; Blinov, K.; Repisky, M.; Mohn, F.; Meyer, G.; Svendsen, J.-S.; Ruud, K.; Elyashberg, M.; Gross, L.; Jaspars, M.; Isaksson, J. *Angew. Chem., Int. Ed.* **2012**, 51, 12238. (b) Kumar, D.; Arun, V.; Kumar, N. M.; Acosta, G.; Noel, B.; Shah, K. *ChemMedChem* **2012**, 7, 1915. (c) Raju, R.; Gromyko, O.; Fedorenko, V.; Luzhetskyy, A.; Müller, R. *Tetrahedron Lett.* **2012**, 53, 3009. (d) Queiroz, K. C. S.; Milani, R.; Ruela-de-Sousa, R. R.; Fuhler, G. M.; Justo, G. Z.; Zambuzzi, W. F.; Duran, N.; Diks, S. H.; Spek, C. A.; Ferreira, C. V.; Peppelenbosch, M. P. *PLoS One* **2012**, 7, e45362. (e) Diana, P.; Carbone, A.; Barraja, P.; Montalbano, A.; Parrino, B.; Lopercolo, A.; Pennati, M.; Zaffaroni, N.; Cirrincione, G. *Chem-MedChem* **2011**, 6, 1300. (f) Jian, W.; Yamashita, H.; Levitt, J. M.; Lerner, S. P.; Sonpavde, G. *Mol. Cancer Ther.* **2009**, 8, 1772. (g) Fernández, R.; Martín, M. J.; Rodríguez-Acebes, R.; Reyes, F.; Francesch, A.; Cuevas, C. *Tetrahedron Lett.* **2008**, 49, 2283. (h) Pettit, G. R.; Knight, J. C.; Herald, D. L.; Davenport, R.; Pettit, R. K.; Tucker,

B. E.; Schmidt, J. M. *J. Nat. Prod.* **2002**, 65, 1793. (i) Nishida, A.; Fuwa, M.; Fujikawa, Y.; Nakahata, E.; Furuno, A.; Nakagawa, M. *Tetrahedron Lett.* **1998**, 39, 5983. (j) Sakemi, S.; Sun, H. H. *J. Org. Chem.* **1991**, 56, 4304. (k) Burres, N.; Barber, D.; Gunasekera, S.; She, L.; Clement, J. *Biochem. Pharmacol.* **1991**, 42, 745. (l) Joshi, B. S.; Taylor, W. L.; Bhate, D. S.; Karmarkar, S. S. *Tetrahedron* **1963**, 19, 1437.

(16) The cyclopenta[b]indole motif has been shown to be a privileged core and is present in several natural products such as paspalinine, paspalicine, paxilline, penitrem D, and yuehchukene, among others. (a) Tagami, K.; Liu, C.; Minami, A.; Noike, M.; Isaka, T.; Fueki, S.; Shichijo, Y.; Toshima, H.; Gomi, K.; Dai, T.; Oikawa, H. *J. Am. Chem. Soc.* **2013**, 135, 1260. (b) Enomoto, M.; Morita, A.; Kuwahara, S. *Angew. Chem., Int. Ed.* **2012**, 51, 12833. (c) Ratni, H.; Blum-Kaelin, D.; Dehmlow, H.; Hartman, P.; Jablonski, P.; Masciadri, R.; Maugeais, C.; Patiny-Adam, A.; Panday, N.; Wright, M. *Bioorg. Med. Chem. Lett.* **2009**, 19, 1654. (d) Naka, H.; Akagi, Y.; Yamada, K.; Imahori, T.; Kasahara, T.; Kondo, Y. *Eur. J. Org. Chem.* **2007**, 4635. (e) Smith, A. B., III; Kanoh, N.; Ishiyama, H.; Minakawa, N.; Rainier, J. D.; Hartz, R. A.; Cho, Y. S.; Cui, H.; Moser, W. H. *J. Am. Chem. Soc.* **2003**, 125, 8228. (f) Leung, T. W. T.; Cheng, G.; Chui, C. H.; Ho, S. K. W.; Lau, F. Y.; Tjong, J. K. J.; Poon, T. C. C.; Kong, Y. C. *Chemotherapy* **2000**, 46, 62. In particular, the 3-methylene-2,3-dihydrocyclopenta[b]indol-1(4H)-one scaffold, which appears in the natural product nostodione A, is present in fused tricycles **12**: (g) Ekebergh, A.; Börje, A.; Mårtensson, J. *Org. Lett.* **2012**, 14, 6274. (h) Soule, T.; Palmer, K.; Gao, Q. J.; Potrafka, R. M.; Stout, V.; Garcia-Pichel, F. *BMC Genomics* **2009**, 10. (i) Shim, S. H.; Chlipala, G.; Orjala, J. *J. Microbiol. Biotechnol.* **2008**, 18, 1655.

(17) For an overview on microwave effects in chemical transformations, see: (a) Kappe, O.; Pieber, B.; Dallinger, D. *Angew. Chem., Int. Ed.* **2013**, 52, 1088. For a monograph, see: (b) *Microwaves in Organic Synthesis*, 3rd ed.; de la Hoz, A., Loupy, A., Eds.; Wiley-VCH: Weinheim, 2012.

(18) A possible pathway for the gold-catalyzed achievement of (2,5-dihydrofuran-2-yl)-indoles **4** may initially involve the formation of a complex **2-Au** through coordination of the gold salt to the distal allenic double bond of allenenes **2**. Next, chemo- and regioselective 5-*endo* oxyauration forms species **13**, which after loss of a proton generates neutral species **14**. Protonolysis of the carbon–gold bond of **14** liberates adducts **4** with concurrent regeneration of the Au(I) catalytic species following a similar reaction mechanism as previously reported^{12d} (see Supporting Information, Scheme S1).

(19) Scheme S2 (Supporting Information) comprises a mechanistic rationale for the [(Ph₃P)AuNTf₂]-catalyzed conversion of *NH*-indole-C3-tethered α -hydroxyallenes **3** into carbazoles **5**. First, gold precatalyst formed complex **3-Au** through coordination of the cationic gold to the distal allenic double bond. Next, chemo- and regioselective attack from the 2-position of the indole occurs through 6-*endo* carboauration to form carbocation **15**. Loss of HNTf₂ generates neutral species **16**, which followed by protonolysis of the carbon–gold bond and dehydration afforded carbazoles **5** with concomitant regeneration of the gold catalyst. Alternatively, a mechanism through reactivity at the indole C3 could be proposed. The likely 5-*endo* cyclization leads to a spiro intermediate that undergoes 1,2-migration and subsequent aromatization to give carbazole **5**.

(20) A schematic representation of possible events that take place in the formation of allyl-carbazoles **6** from α -hydroxyallenes **3** is shown in Scheme S3 (Supporting Information). Initial Pd(II)-coordination to the 1,2-diene moiety gave an allenepalladium complex **3-Pd**, which suffers a chemo- and regioselective 6-*endo* carbopalladation reaction to give the zwitterionic species **17**. Palladadihydrocarbazole **17** reacted with allyl bromide via **18** to form intermediate **19**, which after a *trans* β -heteroatom elimination with concurrent dehydration under the reaction conditions forms carbazoles **6** with concurrent regeneration of the palladium(II) catalyst.

(21) See Computational Details in the Supporting Information.

(22) (a) Alcaide, B.; Almendros, P.; Cembellín, S.; Martínez del Campo, T.; Fernández, I. *Chem. Commun.* **2013**, 49, 1282. (b) Alcaide,

B.; Almendros, P.; Martínez del Campo, T.; Soriano, E.; Marco-Contelles, J. L. *Chem.—Eur. J.* **2009**, *15*, 1909.

(23) For a review on Nazarov cyclization, see: (a) Tius, M. A. *Eur. J. Org. Chem.* **2005**, 2193. For the Nazarov cyclization of vinyl allenyl ketones, see: (b) Hashmi, A. S. K.; Bats, J. W.; Choi, J.-H.; Schwarz, L. *Tetrahedron Lett.* **1998**, *39*, 7491.

(24) For details, please, see the Experimental Section.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision B.1; Gaussian, Inc.: Wallingford, CT, 2009.

(26) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785. (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(27) Weigend, F.; Alhrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(28) McIver, J. W.; Komornicki, A. K. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

(29) González, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(30) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

(31) (a) Miertuš, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117. (b) Pascual-Ahuir, J. L.; Silla, E.; Tuñón, I. *J. Comput. Chem.* **1994**, *15*, 1127. (c) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.

(32) Larsson, R.; Blanco, N.; Johansson, M.; Sterner, O. *Tetrahedron Lett.* **2012**, *53*, 4966.

(33) Berry, J.; Bradshaw, T.; Fictner, I.; Iduna, R.; Chew, E.; Stevens, M.; Westwell, A. D. *J. Med. Chem.* **2005**, *48*, 639.