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

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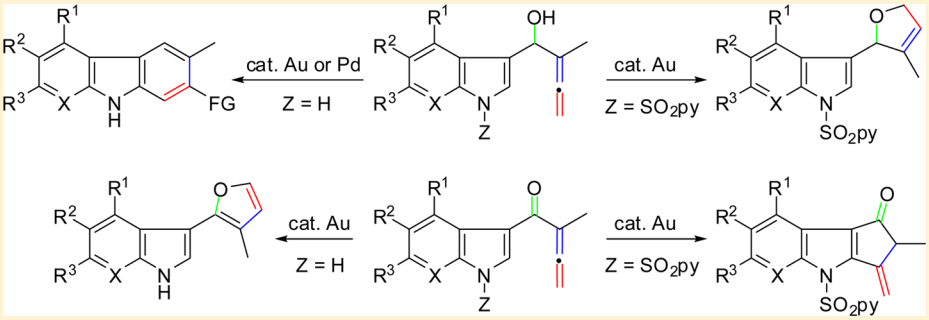
Supporting Information



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*-SO_2py-protected allenones. These cyclization reactions have been developed experimentally, and their mechanisms have additionally been investigated by a computational study.

INTRODUCTION

Allenes 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 allenes 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 allenes,[7] we wish to report here a method using gold- or palladium-based salts that enables catalytic benzannulation[8] 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*-SO_2py-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-SO_2Ar-, and 1-SO_2py-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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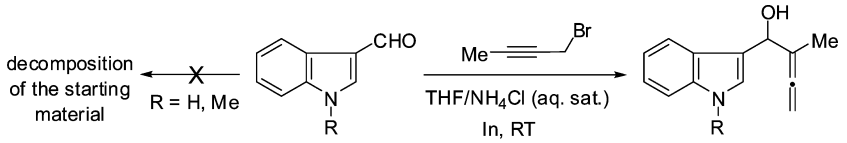
Scheme 1. Regiocontrolled Preparation of Indole-C3-Tethered α-Hydroxyallenes 2c−e[a]

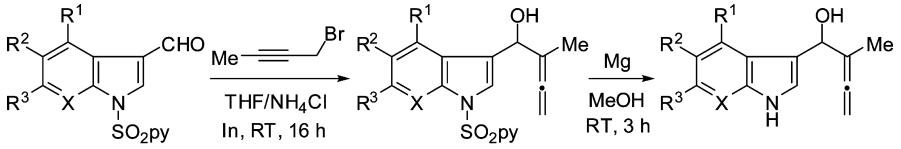


1a R = H
1b R = Me
1c R = Boc
1d R = SO_2Ar
1e R = SO_2py

2c R = Boc (77%)
2d R = SO_2Ar (51%)
2e R = SO_2py (93%)

[a]Boc = *tert*-butoxycarbonyl. Ar = (2,4,6-triisopropyl)phenyl. SO_2py = (2-pyridyl)sulfonyl.

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



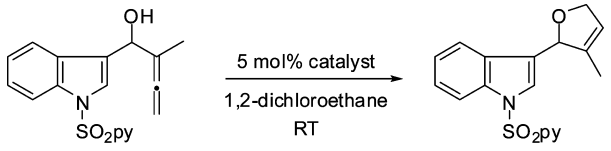
1e $R^1 = R^2 = R^3$ = H, X = CH	**2e** (93%)	**3e** (86%)
1f $R^1 = R^3$ = H, R^2 = Me, X = CH	**2f** (85%)	**3f** (67%)
1g $R^1 = R^3$ = H, R^2 = 4-Tolyl, X = CH	**2g** (76%)	**3g** (75%)
1h R^1 = Me, R^2 = OMe, R^3 = H, X = CH	**2h** (80%)	
1i $R^1 = R^2$ = H, R^3 = *i*-Pr, X = CH	**2i** (99%)	**3i** (73%)
1j $R^1 = R^2 = R^3$ = H, X = C-Me	**2j** (90%)	**3j** (99%)
1k $R^1 = R^2 = R^3$ = H, X = N	**2k** (78%)	**3k** (98%)

[a]SO_2py = (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*-SO_2Ar 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*-SO_2py-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 N1-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 [$(Ph_3P)AuNTf_2$] 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]



2e **4e**

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	[$(Ph_3P)AuNTf_2$]	1	83

[a]Yield of pure, isolated product with correct analytical and spectral data. [b]A very complicated mixture was observed.

cyclization results were encountered for C3-allenyl *N*-SO_2py-indoles **2f** and **2h−k**, to afford dihydrofuranyl-indoles **4f−k**. These results clearly show that the gold-catalyzed cycloetherification is preferred over carbocyclization for *N*-SO_2py-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, [$(Ph_3P)AuNTf_2$] 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 substitutents showed no loss

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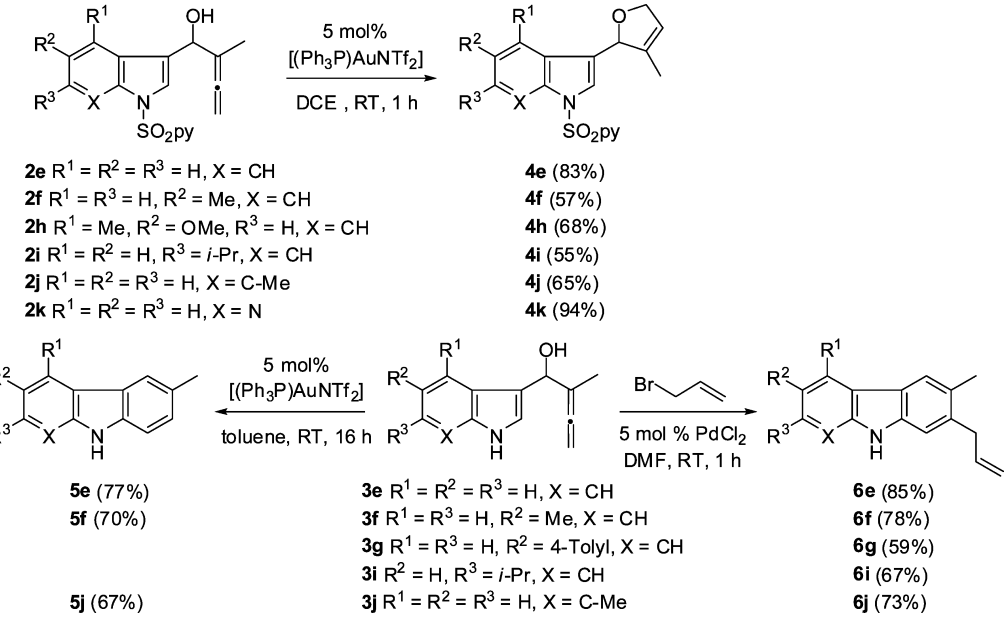
Scheme 3. Metal-Catalyzed Synthesis of (2,5-Dihydrofuran-2-yl)-indoles 4, 3-Methyl-9*H*-carbazoles 5, and 2-Allyl-3-methyl-9*H*-carbazoles 6[a]



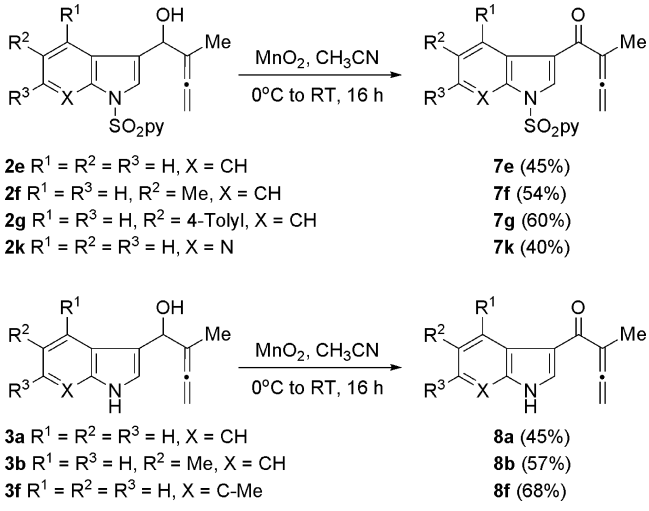
[a]SO_2py = (2-pyridyl)sulfonyl. NTf_2 = bis(trifluoromethanesulfonyl)imide. DCE = 1,2-dichloroethane.

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-9*H*-carbazole derivative **6e**. To evaluate the general applicability of this benzannulation−functionalization protocol, a series of allenyl C3-linked indole derivates 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]



[a]SO_2py = (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*-SO_2py-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*-SO_2py allenones **7** may be partially hindered by the deactivating effect imparted by the (2-

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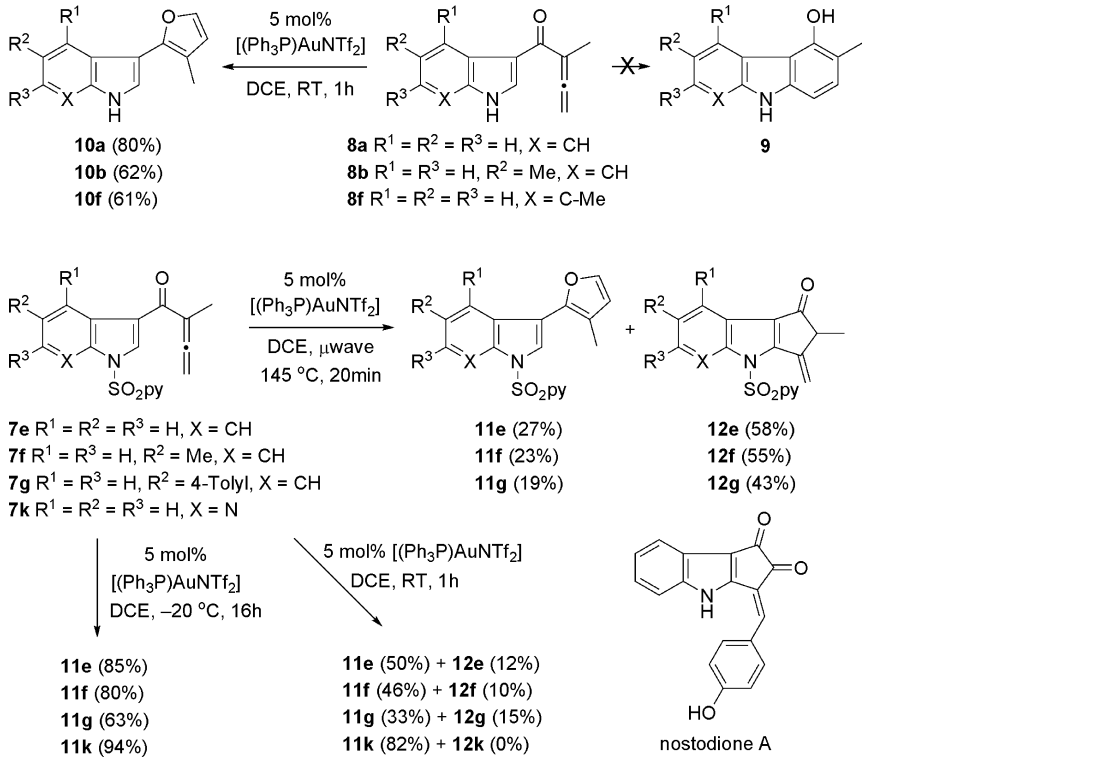
Scheme 5. Gold-Catalyzed Synthesis of (Furan-2-yl)-indoles 10 and 11, and 2,3-Dihydrocyclopenta[*b*]indolones 12[a]



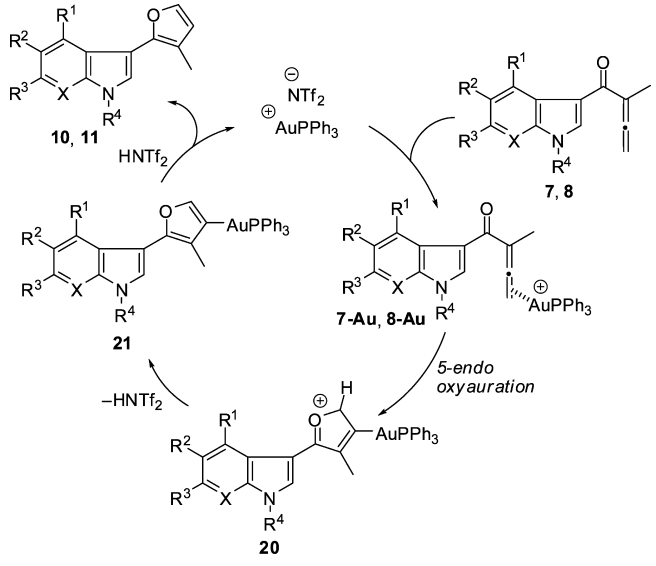
[a]NTf_2 = bis(trifluoromethanesulfonyl)imide. SO_2py = (2-pyridyl)sulfonyl. DCE = 1,2-dichloroethane.

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 °C resulted in the exclusive formation of furyl-indoles **11** in good yields (Scheme 5). Interestingly, when *N*-SO_2py allenone **7e** was treated with $[(Ph_3P)AuNTf_2]$ in 1,2-dichloroethane at 145 °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 °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, $[(Ph_3P)AuNTf_2]$ 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 carbon−gold bond of furan **21** yields adducts **10** and **11** and eventually reforms the Au(I) catalytic species (Scheme 6).

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



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 $HNTf_2$ to produce neutral species **23**. The required fused

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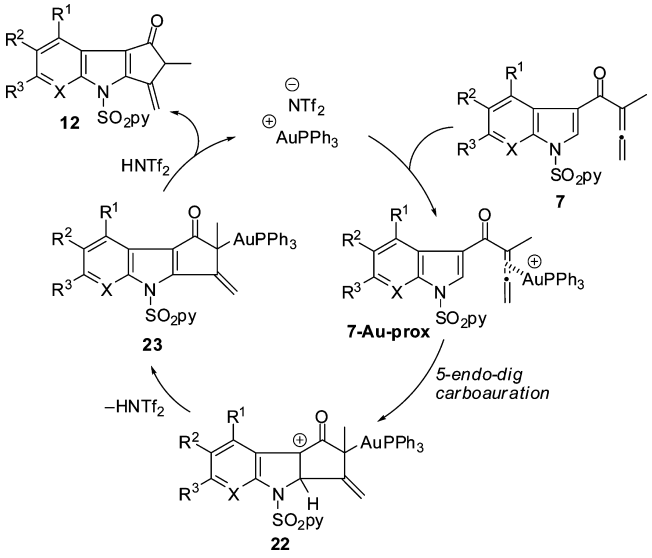
Scheme 7. Mechanistic Explanation for the Gold-Catalyzed Synthesis of Fused Tricycles 12



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 $[(Me_3P)AuNTf_2]$ 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]

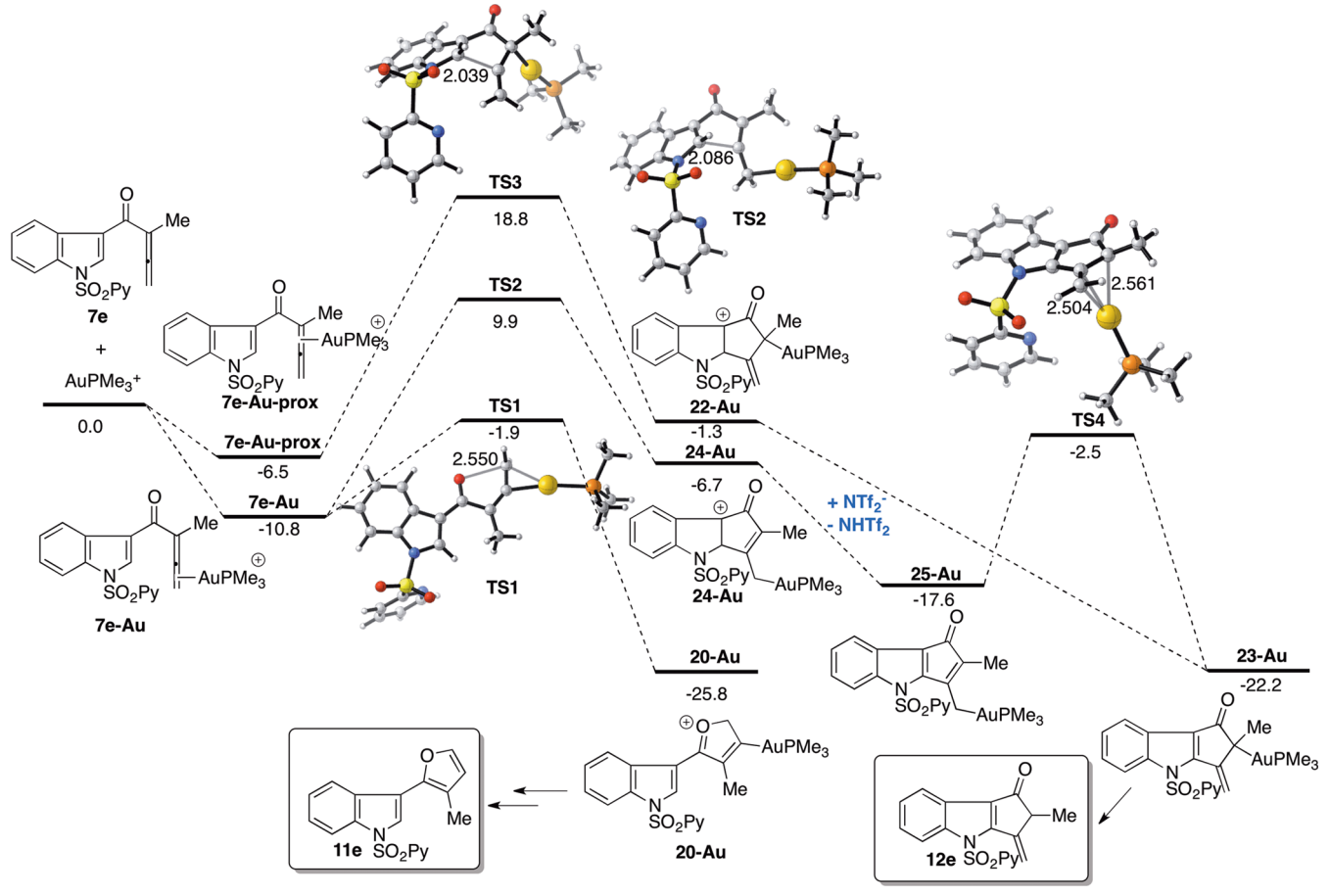


Figure 1. Computed reaction profiles for the reaction of α-allenone **7e** and $[(PMe_3)AuNTf_2]$ catalyst to produce compounds **11e** and **12e**. Relative free energies (ΔG, at 298 K) are given in kcal/mol and bond distances in the transition states in angstroms. Atoms are represented as spheres: 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.

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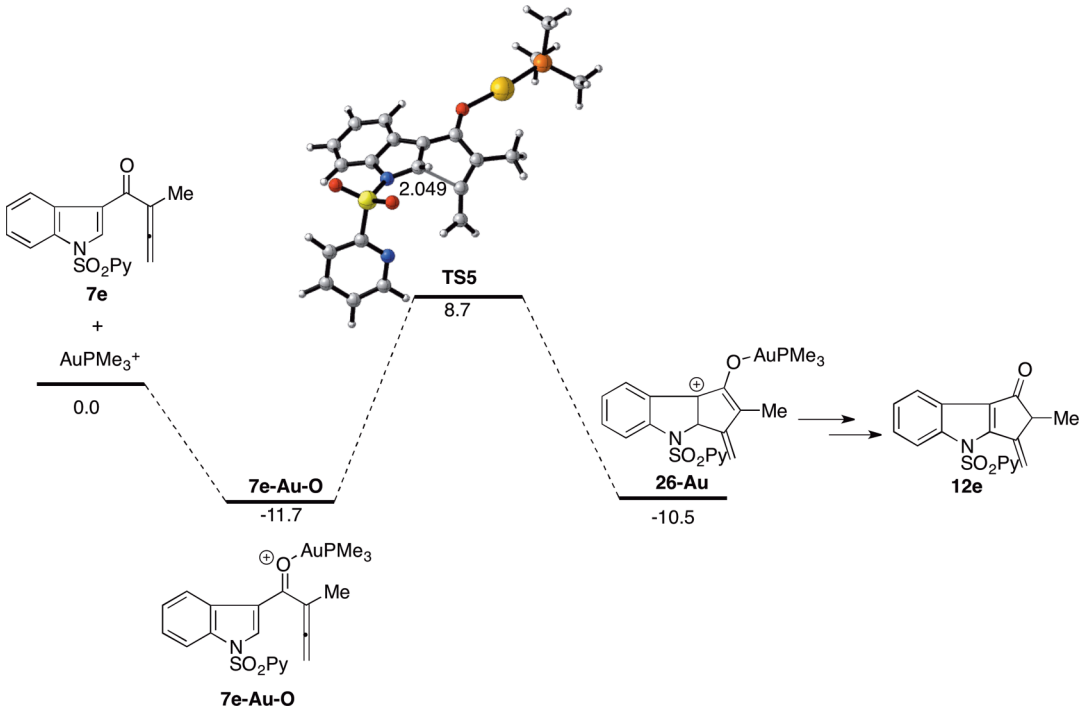

Figure 2. Computed Nazarov-type cyclization of α-allenone **7e** and $[(PMe_3)AuNTf_2]$ catalyst to produce **12e**. See caption of Figure 1 for additional details.

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 (ΔG_{298} = −6.5 kcal/mol) than the distal coordination (Figure 1). Despite that, we were able to locate on the potential energy sufarce 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 oxycyclization 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** (ΔG_{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 decoordination of the catalyst.

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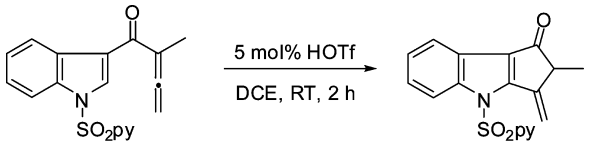
In addition, since at high temperature the gold catalyst may decompose to give acid, it can be suggested that the in situ generated protons may also catalyze the Nazarov-type cyclization reaction of allenones **7**. To check this hypothesis, **7e** was reacted with 5 mol % of HOTf as the catalyst (under otherwise identical conditions) and tricyclic product **12e** was formed in 90% yield (Scheme 8).[24] Therefore, it can be 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 **TS5**.

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



[a]SO_2py = (2-pyridyl)sulfonyl. DCE = 1,2-dichloroethane.

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. ^{1}H NMR and ^{13}C NMR spectra were recorded on 700, 500, 300, or 200 MHz spectrometers. NMR spectra were recorded in $CDCl_3$ solutions, except when otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), or $CDCl_3$ (^{13}C, 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 $[\alpha]_D$ is given in 10^{-1} deg cm^2 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 B3LYP[26] hybrid functional in combination with the double-ζ quality plus polarization def2-SVP[27] basis set for all atoms. Reactants and products were characterized by frequency calculations[28] 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 species[30] in combination with the polarizable continuum model[31] (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*-SO_2Ar derivative **1d** were prepared according to previously reported procedures.[32,33]

General Procedure for the Synthesis of 1-SO_2py-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 $MgSO_4$. 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-SO_2py-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; ^{1}H NMR (300 MHz, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 ($CHCl_3$) ν = 1677, 1383, 1162, 1121 cm^{-1}; HRMS (ES) calcd for $C_{14}H_{11}N_2O_3S$ $[M + H]^+$ 287.0490, found 287.0485.

1-SO_2py-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; ^{1}H NMR (300 MHz, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 ($CHCl_3$) ν = 1679, 1390, 1177, 1122 cm^{-1}; HRMS (ES) calcd for $C_{15}H_{13}N_2O_3S$ $[M + H]^+$ 301.0647, found 301.0631.

1-SO_2py-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; ^{1}H NMR (300 MHz, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 ($CHCl_3$) ν = 1678, 1384, 1163, 1120 cm^{-1}; HRMS (ES) calcd for $C_{21}H_{17}N_2O_3S$ $[M + H]^+$ 377.0960, found 377.0943.

1-SO_2py-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; ^{1}H NMR (300 MHz, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 ($CHCl_3$) ν = 1689, 1391, 1165, 1119 cm^{-1}; HRMS (ES) calcd for $C_{16}H_{15}N_2O_4S$ $[M + H]^+$ 331.0753, found 331.0747.

1-SO_2py-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; ^{1}H NMR (300 MHz, $CDCl_3$, 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,

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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 $C_{17}H_{17}N_2O_3S$ $[M + H]^+$ 329.0960, found 329.0954.

1-SO$_2$py-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; ^{1}H 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 $C_{15}H_{13}N_2O_3S$ $[M + H]^+$ 301.0647, found 301.0641.

1-SO$_2$py-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; ^{1}H 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 $C_{13}H_{10}N_3O_3S$ $[M + H]^+$ 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 × 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): ^{1}H 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 $C_{18}H_{22}NO_3$ $[M + H]^+$ 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): ^{1}H 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 $C_{28}H_{36}NO_3S$ $[M + H]^+$ 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): ^{1}H 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 $C_{18}H_{17}N_2O_3S$ $[M + H]^+$ 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): ^{1}H 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 $C_{19}H_{18}N_2O_3S$ $[M + H]^+$ 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): ^{1}H 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 $C_{25}H_{23}N_2O_3S$ $[M + H]^+$ 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): ^{1}H 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 $C_{20}H_{20}N_2O_4SNa$ $[M + Na]^+$ 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): ^{1}H 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 $C_{21}H_{23}N_2O_3S$ $[M + H]^+$ 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): ^{1}H 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 $C_{19}H_{19}N_2O_3S$ $[M + H]^+$ 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): ^{1}H 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

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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 $C_{17}H_{16}N_3O_3S$ $[M + H]^+$ 342.0912, found 342.0907.

Magnesium-Promoted Desulfonylation of Allenic *N*-SO_2py-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*-SO_2py-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 $C_{13}H_{14}NO$ $[M + H]^+$ 200.1075, found 200.1070.

α-Allenic Alcohol ***3f***. Starting from *N*-SO_2py-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 $C_{14}H_{16}NO$ $[M + H]^+$ 214.1232, found 214.1226.

α-Allenic Alcohol ***3g***. Starting from *N*-SO_2py-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 $C_{20}H_{20}NO$ $[M + H]^+$ 290.1545, found 290.1539.

α-Allenic Alcohol ***3i***. Starting from *N*-SO_2py-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 $C_{16}H_{20}NO$ $[M + H]^+$ 242.1545, found 242.1539.

α-Allenic Alcohol ***3j***. Starting from *N*-SO_2py-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 $C_{14}H_{16}NO$ $[M + H]^+$ 214.1232, found 214.1226.

α-Allenic Alcohol ***3k***. Starting from *N*-SO_2py-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 $C_{12}H_{13}N_2O$ $[M + H]^+$ 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 $C_{18}H_{15}N_2O_3S$ $[M + H]^+$ 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 $C_{19}H_{17}N_2O_3S$ $[M + H]^+$ 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 $C_{25}H_{21}N_2O_3S$ $[M + H]^+$ 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 $C_{17}H_{14}N_3O_3S$ $[M + H]^+$ 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,

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76.7, 14.0; IR ($CHCl_3$) ν = 1935, 1641, 1381, 1186 cm^{-1}; HRMS (ES) calcd for $C_{13}H_{12}NO$ $[M + H]^+$ 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*-SO_2py-Indoles 2. Preparation of (2,5-Dihydrofuran-2-yl)-indoles 4. $[(Ph_3P)AuNTf_2]$ (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 × 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 **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, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$, 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 ($CHCl_3$, cm^{-1}) ν 2850, 1377, 1188, 599; HRMS (ES) calcd for $C_{18}H_{17}N_2O_3S$ $[M + H]^+$ 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, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$, 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 ($CHCl_3$, cm^{-1}) ν 2850, 1381, 1178, 536; HRMS (ES) calcd for $C_{19}H_{19}N_2O_3S$ $[M + H]^+$ 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, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$, 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 ($CHCl_3$, cm^{-1}) ν 2851, 1377, 1189, 568; HRMS (ES) calcd for $C_{20}H_{21}N_2O_4S$ $[M + H]^+$ 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, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$, 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 ($CHCl_3$, cm^{-1}) ν 2850, 1379, 1190, 599; HRMS (ES) calcd for $C_{21}H_{21}N_2O_3S$ $[M + H]^+$ 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, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$, 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 ($CHCl_3$, cm^{-1}) ν 2849, 1386, 1188, 590; HRMS (ES) calcd for $C_{19}H_{19}N_2O_3S$ $[M + H]^+$ 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, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$, 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 ($CHCl_3$, cm^{-1}) ν 2844, 1382, 1176, 603; HRMS (ES) calcd for $C_{17}H_{16}N_3O_3S$ $[M + H]^+$ 342.0912, found 342.0907.

General Procedure for the Au-Catalyzed Benzannulation of C3-Allenyl *NH*-Indoles 3. Preparation of 3-Methyl-9*H*-carbazoles 5. $[(Ph_3P)AuNTf_2]$ (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 × 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 **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, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$, 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 ($CHCl_3$, cm^{-1}) ν 3426, 1456, 1176, 715; HRMS (ES) calcd for $C_{13}H_{12}N$ $[M + H]^+$ 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, $CDCl_3$, 25 °C) δ 7.76 (2H, m), 7.21 (4H, m), 2.45 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$, 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 ($CHCl_3$, cm^{-1}) ν 3425, 1456, 1176, 720; HRMS (ES) calcd for $C_{14}H_{14}N$ $[M + H]^+$ 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, $CDCl_3$, 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); ^{13}C NMR (75 MHz, $CDCl_3$, 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 ($CHCl_3$, cm^{-1}) ν 3426, 1456, 1176, 715; HRMS (ES) calcd for $C_{14}H_{14}N$ $[M + H]^+$ 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-9*H*-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 × 4 mL). The organic phase was washed with water (2 × 2 mL), dried ($MgSO_4$) 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, $CDCl_3$, 25 °C) δ 7.94 (1H, d, J = 7.7

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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 $C_{16}H_{16}N$ $[M + H]^+$ 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; ^{1}H 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 $C_{17}H_{18}N$ $[M + H]^+$ 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; ^{1}H 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 $C_{23}H_{21}N$ $[M + H]^+$ 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; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.84 (1H, d, J = 8.04 Hz), 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 $C_{19}H_{22}N$ $[M + H]^+$ 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; ^{1}H 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 $C_{17}H_{18}N$ $[M + H]^+$ 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. $[(Ph_3P)AuNTf_2]$ (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 × 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; ^{1}H 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 $C_{13}H_{12}NO$ $[M + H]^+$ 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; ^{1}H 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 $C_{14}H_{14}NO$ $[M + H]^+$ 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: ^{1}H 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 $C_{14}H_{14}NO$ $[M + H]^+$ 212.1075, found 212.1070.

General Procedure for the Au-Catalyzed Oxycyclization of C3-Allenyl *N*-SO_2py-Indoles 7 at Low Temperature. Preparation of 3-(Furan-2-yl)-indoles 11. $[(Ph_3P)AuNTf_2]$ (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 × 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: ^{1}H 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 $C_{18}H_{15}N_2O_3S$ $[M + H]^+$ 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: ^{1}H 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 $C_{19}H_{17}N_2O_3S$ $[M + H]^+$ 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: ^{1}H 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 $C_{25}H_{21}N_2O_3S$ $[M + H]^+$ 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; ^{1}H 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 $C_{17}H_{14}N_3O_3S$ $[M + H]^+$ 340.0756, found 340.0750.

General Procedure for the Au-Catalyzed Carbocyclization of C3-Allenyl *N*-SO_2py-Indoles 7 under Microwave Heating. Preparation of 2,3-Dihydrocyclopenta[*b*]indolones 12. $[(Ph_3P)AuNTf_2]$ (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; ^{1}H 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 $C_{18}H_{15}N_2O_3S$ $[M + H]^+$ 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: ^{1}H 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 $C_{19}H_{17}N_2O_3S$ $[M + H]^+$ 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: ^{1}H 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 $C_{25}H_{21}N_2O_3S$ $[M + H]^+$ 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 ^{1}H 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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(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 allenes **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 [$(Ph_3P)AuNTf_2$]-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 $HNTf_2$ 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.

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