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Gold as Catalyst for the Hydroarylation and Domino Hydroarylation/N1−C4 Cleavage of β-Lactam-Tethered Allenyl Indoles

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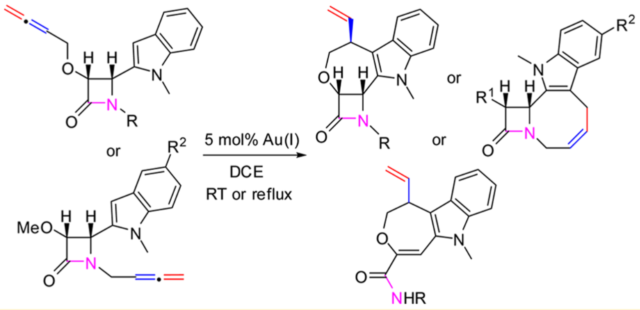
Ⓢ *Supporting Information*

ABSTRACT: Gold-catalyzed hydroarylation reaction of β-lactam-tethered allenyl indoles gives azeto-oxepino[4,5-*b*]indol-2-ones, tetrahydroazeto-azocino[3,4-*b*]indol-2-ones, and hexahydroazeto-azepino[3,4-*b*]indol-2-ones with very high levels of stereo- and regioselectivity, the 7-*exo* and 8-*endo* carbocyclization modes by attack of the indole group toward either the internal or the terminal allene carbon, respectively, being favored. Hydroarylation across the central carbon of the allene moiety has not been detected. The controlled gold-catalyzed annulations allowed the formation of fused β-lactams without harming the sensitive four-membered heterocycle. Besides, a novel gold-catalyzed domino process, namely, the allenic hydroarylation/N1−C4 β-lactam bond breakage to afford dihydro-oxepino[4,5-*b*]indole-4-carboxamides, has been discovered.



INTRODUCTION

Of the several heterocycles, β-lactams and their derivatives attracted greater attention due to their biological activities such as antibacterial, enzyme inhibitors, neuroprotectors, and antitumorals.[1] In addition to the presence of the 2-azetidinone motif in medicinally relevant substances, the β-lactam nucleus is of great importance since 2-azetidinones display relatively high reactivity due to their strained nature, making them versatile intermediates in organic synthesis.[2] Indole derivatives have also received increasing attention in view of their biological and pharmacological activities. In accordance, efforts devoted to the synthesis of both molecular frameworks remain highly desirable.

The direct formation of C−C bonds involving C−H bond cleavage is of great interest because it offers an alternative to the conventional cross-coupling strategies.[3] On the other hand, gold complexes continue to attract considerable interest in the synthetic community due to their powerful soft Lewis acidic nature.[4] In this context, the gold-catalyzed hydroarylation reaction of allenes is an important C−C bond cyclization method.[5] Recently, the gold-catalyzed carbocyclization of allenylindoles has been explored for the preparation of carbazoles, pyridoindoles, and cyclopentaindoles.[6] However, the gold-catalyzed intramolecular hydroarylation of indole-tethered allenes to afford medium-sized rings is almost uninvestigated; and just a sole example for the preparation of a seven-membered ring fused indole has been described in literature.[7] We envisioned that β-lactam-tethered allenyl indoles may be effective substrates for this purpose. Herein, we wish to report a synthesis of tetracyclic β-lactam/indole hybrids via an allenic hydroarylation approach, together with an unanticipated gold-catalyzed N1−C4 β-lactam bond breakage.

RESULTS AND DISCUSSION

Starting materials, new β-lactam-tethered allenyl indoles **5a−f** and **6a−f** were obtained from 2-azetidinone-tethered alkynyl indoles **3a−f** and **4a−f**. β-Lactams **1** and **4** (Scheme 1) were prepared as single *cis*-diastereoisomers from imines of indole-2-carboxaldehydes through Staudinger reaction with the appropriate alkoxyacetyl chloride in the presence of Et_3N.[8] Transesterification of 3-acetoxy-2-azetidinones **1a−f** with sodium methoxide in methanol gave 3-hydroxy-2-azetidinones **2a−f**, which, by treatment with propargyl bromide under basic conditions, gave 2-azetidinone-tethered alkynyl indoles **3a−f** (Scheme 1). Terminal alkynes **3** and **4** were conveniently converted into allenes **5** and **6** (Scheme 2) by treatment with paraformaldehyde in the presence of diisopropylamine and copper(I) bromide (Crabbé reaction).[9]

Initially, we started to evaluate the intramolecular hydroarylation reaction by employing β-lactam-tethered allenyl indole **5a** as model substrate. At the outset, the use of $AuCl_3$ and AuCl was tested, but both failed to catalyze the reaction in the presence or absence of any additive (Table 1, entries 1 and 2). Interestingly, when 1-benzyl-3-(buta-2,3-dienyloxy)-4-(1-methyl-1*H*-indol-2-yl)azetidin-2-one **1a** was treated with the

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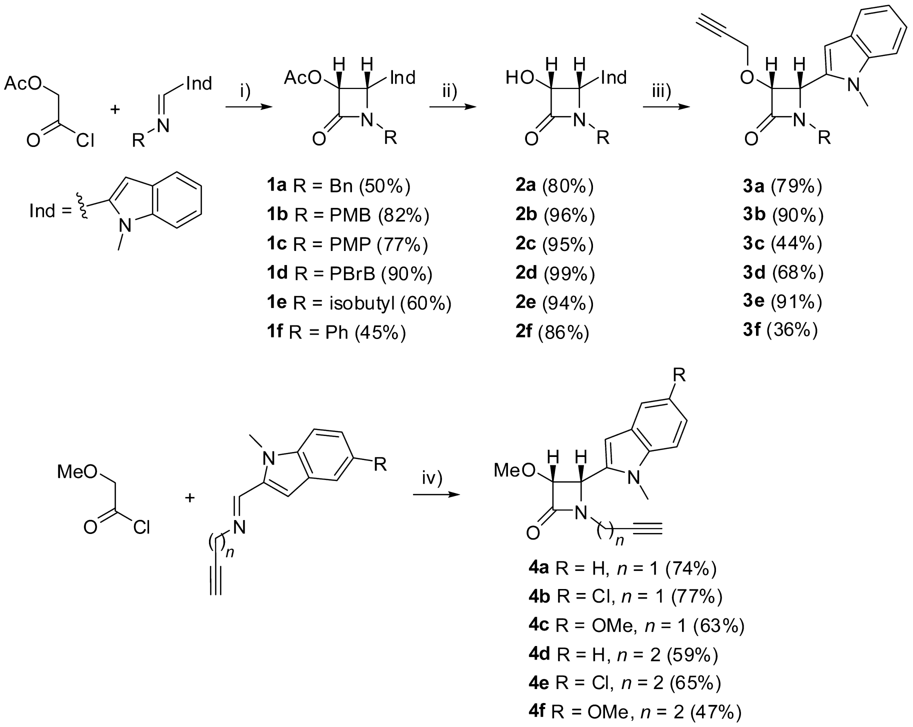
Scheme 1. Synthesis of β-Lactam-Tethered Alkynyl Indoles 3a−f and 4a−f[a]



1a R = Bn (50%)
1b R = PMB (82%)
1c R = PMP (77%)
1d R = PBrB (90%)
1e R = isobutyl (60%)
1f R = Ph (45%)

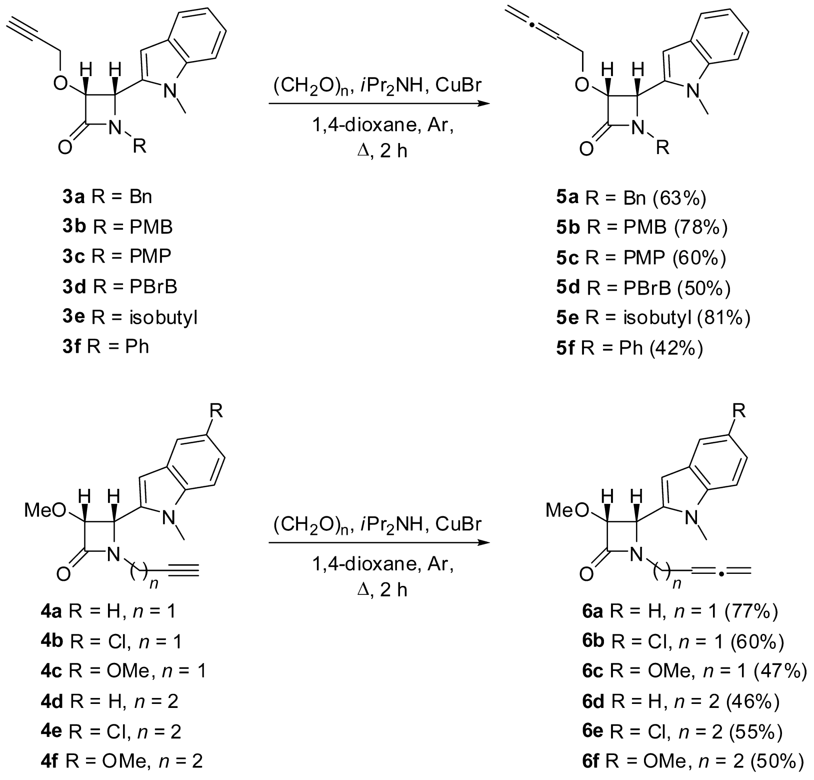
2a (80%)
2b (96%)
2c (95%)
2d (99%)
2e (94%)
2f (86%)

3a (79%)
3b (90%)
3c (44%)
3d (68%)
3e (91%)
3f (36%)

4a R = H, *n* = 1 (74%)
4b R = Cl, *n* = 1 (77%)
4c R = OMe, *n* = 1 (63%)
4d R = H, *n* = 2 (59%)
4e R = Cl, *n* = 2 (65%)
4f R = OMe, *n* = 2 (47%)

[a] Conditions: (i) Et_3N, CH_2Cl_2, rt, 14 h. (ii) Sodium methoxide, methanol, 0 °C, 30 min. (iii) Propargyl bromide, TBAI, NaOH, CH_2Cl_2, H_2O, rt, 14 h. (iv) Et_3N, toluene, 80 °C, 2 h. PMB = 4-$MeOC_6H_4CH_2$. PMP = 4-$MeOC_6H_4$. PBrB = 4-$BrC_6H_4CH_2$. TBAI = Tetrabutylammonium bromide.

Scheme 2. Preparation of β-Lactam-Tethered Allenyl Indoles 5a−f and 6a−f



3a R = Bn
3b R = PMB
3c R = PMP
3d R = PBrB
3e R = isobutyl
3f R = Ph

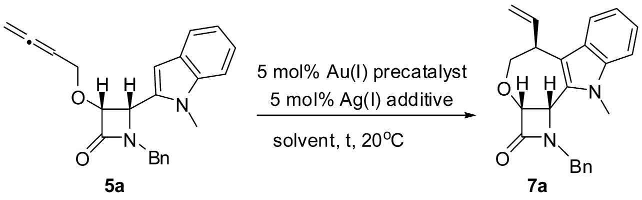
5a R = Bn (63%)
5b R = PMB (78%)
5c R = PMP (60%)
5d R = PBrB (50%)
5e R = isobutyl (81%)
5f R = Ph (42%)

4a R = H, *n* = 1
4b R = Cl, *n* = 1
4c R = OMe, *n* = 1
4d R = H, *n* = 2
4e R = Cl, *n* = 2
4f R = OMe, *n* = 2

6a R = H, *n* = 1 (77%)
6b R = Cl, *n* = 1 (60%)
6c R = OMe, *n* = 1 (47%)
6d R = H, *n* = 2 (46%)
6e R = Cl, *n* = 2 (55%)
6f R = OMe, *n* = 2 (50%)

system [AuClIPr] (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) (5 mol %)/$AgSbF_6$ (5 mol %) in 1,2-dichloroethane (DCE) at room temperature for 5 h, indolo-oxepino β-lactam **7a** was isolated in 72% yield (Table 1, entry 5). The optimal amount of catalyst was established at 5 mol % with a ratio of Au(I) salt/Ag(I) salt of 1:1. A lower loading of catalyst had the effect of lowering the conversion for a fixed reaction time (Table 1, entry 9). A screening of solvents

Table 1. Selective Hydroarylation Reaction of β-Lactam-Tethered Allenyl Indole 5a under Modified Gold-Catalyzed Conditions[a]



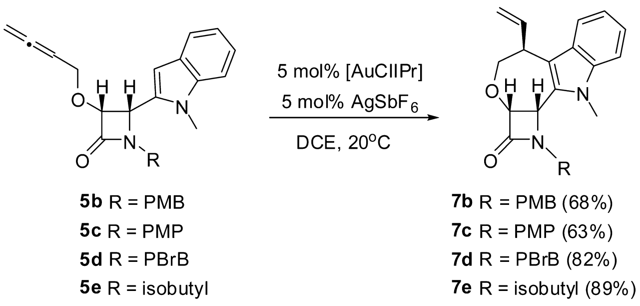
entry	Au(I) salt	Ag(I) salt	solvent/*t* (h)	yield[a]
1	$AuCl_3$		DCE/24	
2	AuCl		DCE/24	
3	$[AuClPPh_3]$	AgOTf	DCE/24	5
4	$[(Ph_3P)AuNTf_2]$		DCE/24	12[b]
5	[AuClIPr]	$AgSbF_6$	DCE/5	72
6	[AuClIPr]	AgOTf	DCE/1.5	43
7	[AuClIPr]	$AgBF_4$	DCE/3	62
8	[AuClIPr]	$AgNTf_2$	DCE/1.5	57
9	[AuClIPr][c]	$AgSbF_6$[c]	DCE/24	50
10	[AuClIPr]	$AgSbF_6$	dioxane/14	66
11	[AuClIPr]	$AgSbF_6$	toluene/18	60
12	[AuClIPr]	$AgSbF_6$[d]	DCE/5	69

[a]Yield of pure, isolated product with correct analytical and spectral data. [b]A byproduct in which the 2-azetidinone ring disappeared was also detected. [c]1 mol % was used. [d]10 mol % was used.

(toluene, tetrahydrofuran, 1,4-dioxane) revealed that the reaction is best performed in DCE. Other counterions have little effect on the reaction, because changing the silver salt to AgOTf, $AgBF_4$, or $AgNTf_2$ also delivered the tetracyclic product, but in lower yields (Table 1, entries 6–8). Other Au catalysts were less effective; i.e., low conversion was obtained with $[Au(OTf)PPh_3]$ while Gagosz' catalyst $[(Ph_3P)AuNTf_2]$ leads to considerable decomposition of the starting β-lactam (Table 1, entries 3 and 4).

To ascertain the efficacy and generality of the above catalytic system, various β-lactam-tethered allenyl indoles **5b–e** were treated under the optimized conditions. The N1-substituents at the β-lactam ring were varied in terms of alkyl and aryl groups. These gold-catalyzed reactions afforded products **7b–e** in yields of 63–89% as exclusive products (Scheme 3), regioisomeric adducts not even being detected as trace products. It is obvious from the experiments that, in our functionalized systems, competitive processes are not operating, the 7-*exo* carbocyclization being favored. Besides, the new stereocenter in tetracycles **7** was created in a totally stereoselective fashion. The stereochemistry of products **7** was unambiguously determined by the NOE analysis of adduct **7d**. Tetracycles **7a–e** can be considered as hybrid scaffolds as a combination of the biologically relevant β-lactam, oxepane, and fused indole frameworks.[10] Because most of the reactions were conducted on a 50–100 mg scale, it was desirable to scale up the procedure. It is worth noting that no obvious loss of yield was observed for adduct **7a** (isolated yield: 70%) when the reaction was carried out on a 500 mg scale.

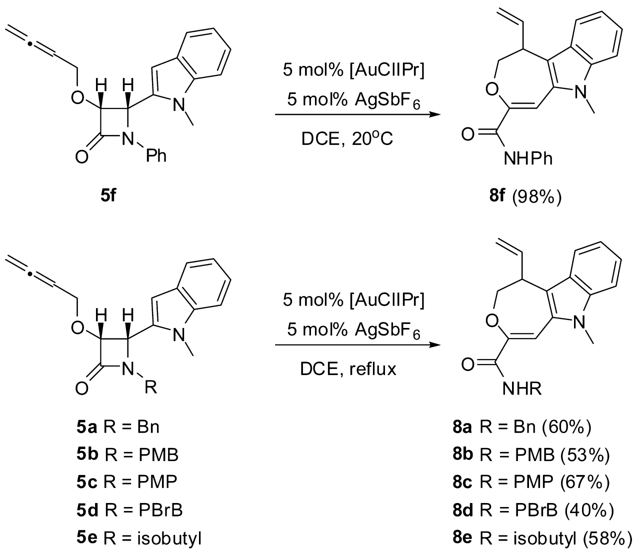
Scheme 3. Synthesis of Azeto-oxepino[4,5-*b*]indol-2-ones 7b–e through Gold-Catalyzed Intramolecular Hydroarylation Reaction of β-Lactam-Tethered Allenyl Indoles 5b–e[a]



[a]**7b**: 4.5 h; **7c**: 2.5 h; **7d**: 6.5 h; **7e**: 2 h. PMB = $4\text{-}MeOC_6H_4CH_2$. PMP = $4\text{-}MeOC_6H_4$. PBrB = $4\text{-}BrC_6H_4CH_2$.

We also performed the above reaction by using the N1-phenyl substrate **5f**. Surprisingly, the reaction does take a different course because the final product **8f**, which was obtained in almost quantitative yield, lacked the β-lactam ring (Scheme 4). The formation of dihydro-oxepino[4,5-*b*]indole-4-carboxamide **8f** may imply a selective breakage of the N1–C4 bond of the 2-azetidinone nucleus. We are aware of no report on the metal-catalyzed N1–C4 β-lactam bond cleavage.[11] Considering the significant effects of reaction temperature on the reactivity of the β-lactam ring,[2] new reaction conditions were optimized for substrates **5a–e**. Then, the effect of the reaction temperature on the reaction of β-lactam-tethered allenyl indole **5a** was investigated. When the reaction was performed at 40 °C, it proceeded rapidly and gave a separable mixture (1:1) of tetracycle **7a** and tricycle **8a**. To our delight, reasonable yields and total selectivity in favor of non-β-lactam adduct **8a** were achieved when the gold-catalyzed reaction was performed in DCE at reflux temperature (Scheme 4). Under the optimized reaction conditions, the substrate scope was subsequently investigated. Differently substituted β-lactam-tethered allenyl indoles **5b–e** were successfully employed to provide novel fused oxepino-indoles **8b–e** in reasonable yields

Scheme 4. Synthesis of 1,6-Dihydro-2*H*-oxepino[4,5-*b*]indole-4-carboxamides 8a–f through Gold-Catalyzed Hydroarylation/N1–C4 β-Lactam Cleavage of β-Lactam-Tethered Allenyl Indoles 5a–f[a]

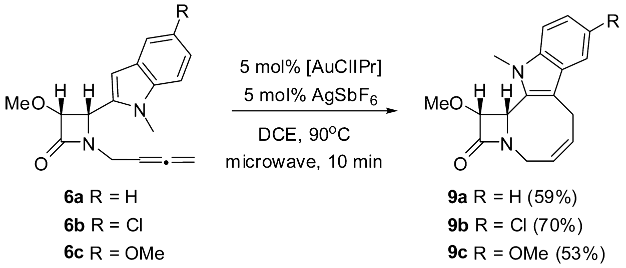


[a]**8a**: 2 h; **8b**: 2.5 h; **8c**: 2 h; **8d**: 4 h; **8e**: 1.5 h; **8f**: 1.5 h. PMB = $4\text{-}MeOC_6H_4CH_2$. PMP = $4\text{-}MeOC_6H_4$. PBrB = $4\text{-}BrC_6H_4CH_2$.

(Scheme 4). The above cascade sequence tolerated different substituents on the β-lactam nitrogen and could thus provide a good handle in building a larger α-hydroxy amide-appended indole collection. It is possible that traces of $HSbF_6$ are present in the reaction medium. A control experiment that would clarify the participation of $HSbF_6$ as the active catalyst for the β-lactam cleavage was undertaken. When indolo-oxepino β-lactam **7a** was treated with $HSbF_6 \cdot 6H_2O$ with the same catalyst ratio (5 mol %), no product **8a** was obtained, ruling out the participation of the Brønsted acid in the ring-opening process.

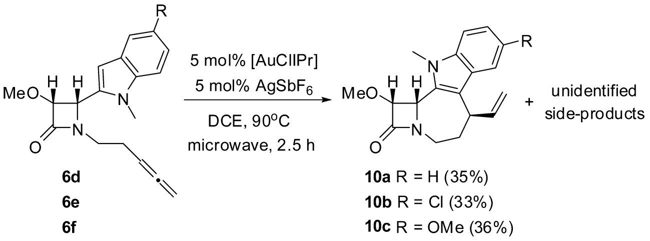
To assess the scope of this reaction, the allene moiety was moved from position C3 to N1, as in 1,4-tethered allenylindoles **6**. Attempts of the gold-catalyzed cyclization reaction of compounds **6** failed at room temperature. To our delight, when β-lactam-tethered allenyl indoles **6a−c** were tested as cyclization precursors applying microwave irradiation, after 10 min, it furnished the corresponding tetracycles **9a−c** as the sole isomers (Scheme 5). As shown in Scheme 4, various substituents with different electronic features at the indole ring showed good reactivity. Both, allenyl indoles **6** bearing electron-donating substituents (MeO) and electron-withdrawing substituents (Cl), worked well to afford the corresponding fused azocines **9**. The formation of tetrahydroazeto-azocino-[3,4-*b*]indol-2-ones **9** may be explained through an 8-*endo* carbocyclization of the indole group toward the terminal allene carbon. In this case, the gold-catalyzed annulations allowed the regioselective formation of fused β-lactams without harming the sensitive four-membered heterocycle.

Scheme 5. Synthesis of Tetrahydroazeto-azocino[3,4-*b*]indol-2-ones 9a−c through Gold-Catalyzed Intramolecular Hydroarylation Reaction of β-Lactam-Tethered Allenyl Indoles 6a−c



We also decided to undertake a study of the potential use of more diverse substrates in this novel hydroarylation mode. Thus, β-lactam-tethered allenyl indoles **6d−f** were studied by using the optimum reaction conditions obtained for homologue *N*-allenes **6a−c**. Complete conversion was observed after prolonged exposure, but unidentified side-products from isomerization or polymerization were detected in the ^1H NMR analysis of the crude reaction mixtures. We found a divergent regioselectivity compared with the transformation found with allenes **6a−c**, because tetracycles **10a−c** arising from a 7-*exo* carbocyclization were obtained as major isomers in modest yields (Scheme 6). Competing reactions lead to the exclusion of allenyl indoles **6d−f** as efficient substrates.

Scheme 6. Synthesis of Hexahydroazeto-azepino[3,4-*b*]indol-2-ones 10a−c through Gold-Catalyzed Intramolecular Hydroarylation Reaction of β-Lactam-Tethered Allenyl Indoles 6d−f



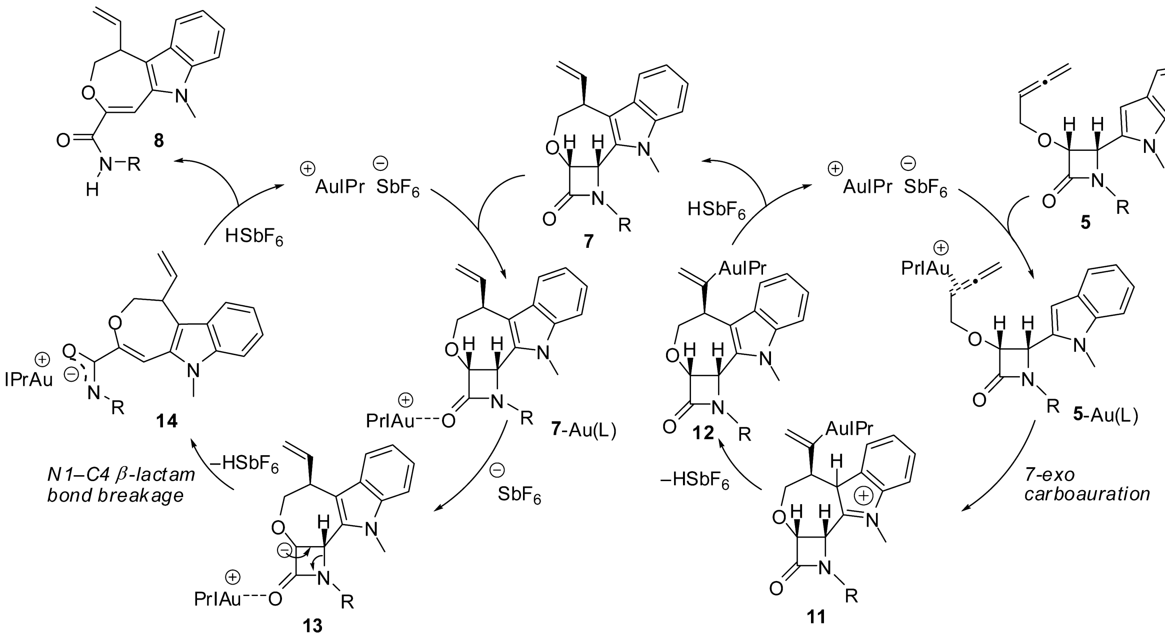
A possible pathway for the gold-catalyzed synthesis of dihydro-oxepino[4,5-*b*]indole-4-carboxamides **8** from β-lactam-tethered allenyl indoles **5** may or may not involve a tetracyclic intermediate. The obtention of tetracyclic adducts **7** at room temperature (Scheme 3) leads us to propose a mechanism, which is illustrated in Scheme 7, and occurs through azeto-oxepino[4,5-*b*]indol-2-one species **7**. In order to see if tetracycles **7** are able to rearrange to tricyclic carboxamides **8** under metal-free catalysis, reaction of **7a** was conducted in DCE at reflux temperature for 3 h in the absence of metallic salts. The reaction did not proceed. In contrast, reaction of **7a** with a catalytic amount of [$IPrAuSbF_6$] under otherwise identical conditions gave the dihydro-oxepino[4,5-*b*]indole-4-carboxamide **8a** in excellent yield. The fact that β-lactam **7a** in the presence of gold(I) was converted into carboxamide **8a** suggests the decisive role of the gold salt in promoting the rearrangement reaction. Probably, initial amide carbonyl coordination to cationic gold in tetracycles **7** is followed by proton abstraction, resulting in the stabilized carbanion **13**. Then, N1−C4 β-lactam bond cleavage should occur to generate the stabilized amide carbanion **14**. Finally, protonolysis leads to the formation of tricycles **8** with concurrent regeneration of the gold catalyst.

The first step of the tandem sequence should involve the formation of complex **5**-Au(L) through coordination of the gold salt to the internal allenic double bond. Species **5**-Au(L) undergoes a chemo- and regioselective intramolecular 7-*exo*-trig carbocyclization reaction to produce the auravinyl tetracycle **11**. This nucleophilic attack from the C3-indole site occurs as a result of the stability of the intermediate iminium type cation **11**. Aromatization by loss of proton generates neutral species **12**, which, followed by protonolysis of the carbon−gold bond, liberates azeto-oxepino[4,5-*b*]indol-2-one species **7**, releasing the gold catalyst into the first catalytic cycle (Scheme 7, right catalytic cycle). Next, tetracycle **7** enters the second catalytic cycle, which is also gold-catalyzed, generating ammonium species **7**-Au(L) by formation of a N−Au bond in an electrophilic fashion. Subsequent proton (H3 at the 2-azetidinone nucleus) abstraction, with concurrent N1−C4 β-lactam bond breakage in species **13**, would form the neutral amidogold(I) species **14**. Deauration linked to proton transfer liberates carboxamides **8** with concomitant regeneration of the gold catalyst, closing the second catalytic cycle (Scheme 7, left catalytic cycle).

■ CONCLUSION

In conclusion, the present study provides the first insight into the manner in which β-lactam-tethered allenyl indoles undergo carbocyclization under gold catalysis, to afford fused tetracyclic indole-β-lactams having a central seven- or eight-membered ring. In addition, a novel domino process, the gold-catalyzed allenic hydroarylation/N1−C4 β-lactam bond breakage, was discovered.

Scheme 7. Rationalization for the Gold-Catalyzed Hydroarylation/N1−C4 β-Lactam Cleavage of β-Lactam-Tethered Allenyl Indoles 5



■ EXPERIMENTAL SECTION

General Methods. NMR spectra were recorded at 25 °C on a 300 MHz instrument: ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz). 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). All reported compounds are racemic. All commercially available compounds were used without further purification.

Staudinger Reaction. General Procedure for the Preparation of Acetoxy β-Lactam-Tethered Indoles 1a−f. To a solution of the corresponding imine (10.4 mmol) in dichloromethane (35 mL) and triethylamine (4.2 mL, 30 mmol) was slowly added acetoxyacetyl chloride (13 mmol) dissolved in dichloromethane (35 mL) at 0 °C under an argon atmosphere, and stirring was continued for 14 h at room temperature. Then, 15 mL of NaHCO$_3$ (aq. sat.) was added before being partitioned between dichloromethane and water. The aqueous phase was extracted with dichloromethane (3 × 50 mL), and the combined organic extracts were washed with brine, dried (MgSO$_4$), and concentrated under reduced pressure. Chromatography of the residue using an ethyl acetate/hexanes mixture gave analytically pure compounds **1**.

*Acetoxy β-Lactam **1a**.* From 1.0 g (4.05 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1a** (711 mg, 50%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.82 (d, 1H, J = 7.8 Hz), 7.28 (m, 3H), 7.21 (m, 2H), 7.10 (m, 3H), 6.54 (s, 1H), 5.73 (d, 1H, J = 4.4 Hz), 4.91 (d, 1H, J = 14.7 Hz), 4.90 (d, 1H, J = 4.4 Hz), 3.99 (d, 1H, J = 14.8 Hz), 3.48 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 169.6, 164.1, 138.1, 134.3, 131.0, 129.0 (2C), 128.6 (2C), 128.2, 127.2, 122.0, 120.7, 119.8, 109.2, 102.9, 77.5, 53.8, 44.2, 29.6, 20.0; IR (CHCl$_3$, cm^{-1}): ν 2929, 1744, 1216, 734, 699; HRMS (ES): calcd for $C_{21}H_{20}N_2O_3$ $[M]^+$: 348.1474; found: 348.1486.

*Acetoxy β-Lactam **1b**.* From 746 mg (2.68 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1b** (825 mg, 82%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.63 (d, 1H, J = 7.9 Hz), 7.28 (m, 2H), 7.14 (t, 1H, J = 7.3 Hz), 7.07 (d, 2H, J = 8.6 Hz), 6.84 (d, 2H, J = 8.6 Hz), 6.58 (s, 1H), 5.76 (d, 1H, J = 4.4 Hz), 4.93 (d, 1H, J = 4.4 Hz), 4.89 (d, 1H, J = 14.7 Hz), 3.89 (d, 1H, J = 14.7 Hz), 3.80 (s, 3H), 3.54 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 169.6, 164.0, 159.5, 138.0, 131.1, 129.9 (2C), 127.2, 126.2, 122.0, 120.7, 119.8, 114.3 (2C), 109.2, 102.9, 77.4, 55.3, 53.6, 43.6, 29.7, 20.0; IR (CHCl$_3$, cm^{-1}): ν 2923, 1753, 1220, 731; HRMS (ES): calcd for $C_{22}H_{22}N_2O_4$ $[M]^+$: 378.1580; found: 378.1574.

*Acetoxy β-Lactam **1c**.* From 917 mg (3.47 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1c** (965 mg, 77%) as a colorless solid; mp 150−151 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.55 (d, 1H, J = 7.9 Hz), 7.33 (m, 1H), 7.32 (d, 2H, J = 9.1 Hz), 7.25 (t, 1H, J = 7.5 Hz), 7.11 (t, 1H, J = 7.4 Hz), 6.81 (d, 2H, J = 9.1 Hz), 6.52 (s, 1H), 6.01 (d, 1H, J = 4.7 Hz), 5.58 (d, 1H, J = 4.7 Hz), 3.78 (s, 3H), 3.76 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 169.6, 160.9, 156.7, 138.2, 130.5, 130.0, 127.1, 122.1, 120.8, 119.8, 118.9 (2C), 114.4 (2C), 109.1, 103.8, 76.5, 55.4 (2C), 30.1, 20.0; IR (CHCl$_3$, cm^{-1}): ν 2923, 1745, 1225, 733; HRMS (ES): calcd for $C_{21}H_{20}N_2O_4$ $[M]^+$: 364.1423; found: 364.1418.

*Acetoxy β-Lactam **1d**.* From 1.25 g (3.81 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **1d** (1.46 g, 90%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.63 (d, 1H, J = 7.8 Hz), 7.46 (d, 2H, J = 8.4 Hz), 7.32 (d, 1H, J = 7.8 Hz), 7.26 (td, 1H, J = 8.2, 1.2 Hz), 7.15 (td, 1H, J = 7.3, 1.3 Hz), 7.05 (d, 2H, J = 8.4 Hz), 6.56 (s, 1H), 5.79 (d, 1H, J = 4.4 Hz), 4.97 (d, 1H, J = 4.4 Hz), 4.88 (d, 1H, J = 14.9 Hz), 4.02 (d, 1H, J = 14.9 Hz), 3.56 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 169.6, 164.1, 138.0, 133.3, 132.1, 130.7, 130.8, 127.1, 122.3, 122.1, 120.7, 119.9, 109.3, 102.9, 77.5, 54.0, 29.7, 20.0; IR (CHCl$_3$, cm^{-1}): ν 2929, 1741, 1226, 730; HRMS (ES): calcd for $C_{21}H_{19}BrN_2O_3$ $[M]^+$: 426.0579; found: 426.0560.

*Acetoxy β-Lactam **1e**.* From 846 mg (3.95 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1e** (740 mg, 60%) as a colorless solid; mp 112−113 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.64 (d, 1H, J = 7.9 Hz), 7.35 (d, 1H, J = 7.9 Hz), 7.27 (td, 1H, J = 7.4, 1.2 Hz), 7.15 (td, 1H, J = 7.4, 1.1 Hz), 6.55 (s, 1H), 5.87 (d, 1H, J = 4.4 Hz), 5.23 (d, 1H, J = 4.4 Hz), 3.73 (s, 3H), 3.43 (dd, 1H, J = 14.0, 8.5 Hz), 2.92 (dd, 1H, J = 14.0, 5.9 Hz), 1.93 (m, 1H), 1.93 (s, 3H), 0.98 (d, 3H, J = 6.7 Hz), 0.95 (d, 3H, J = 6.7 Hz); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 169.7, 164.7, 138.0, 131.1, 127.0, 122.0, 120.7, 119.8, 109.2, 102.8, 77.4, 55.4, 47.8, 29.8, 27.1, 20.3, 20.2, 20.0; IR ($CHCl_3$, cm^{-1}): ν 2923, 1742, 1211, 704; HRMS (ES): calcd for $C_{18}H_{22}N_2O_3$ $[M]^+$: 314.1630; found: 314.1641.

*Acetoxy β-Lactam **1f**.* From 1.3 g (5.7 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **1f** (592 mg, 45%) as a colorless solid; mp 138−139 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.55 (d, 1H, J = 7.9 Hz), 7.37 (m, 3H), 7.27 (m, 3H), 7.13 (m, 2H), 6.54 (s, 1H), 6.03 (d, 1H, J = 4.8 Hz), 5.63 (d, 1H, J = 4.8 Hz), 3.79 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 169.6, 161.5, 138.2, 136.5, 130.3, 129.2 (2C), 127.1, 124.9, 122.1, 120.8, 119.8, 117.5 (2C), 109.2, 103.7, 76.4, 55.3, 30.1, 20.0; IR ($CHCl_3$, cm^{-1}): ν 2923, 1744, 1215, 730, 699; HRMS (ES): calcd for $C_{20}H_{18}N_2O_3$ $[M]^+$: 334.1317; found: 334.1325.

Transesterification of Acetate Derivatives 1. General Procedure for the Preparation of Hydroxy-β-Lactams 2. Sodium methoxide (102 mg, 1.89 mmol) was added in portions at 0 °C to a solution of the appropriate acetate derivative **1** (1.89 mmol) in methanol (18 mL). The reaction was stirred at 0 °C until disappearance of the starting material (TLC), and then water was added (3 mL). The methanol was removed under reduced pressure, the aqueous residue was extracted with ethyl acetate, and the organic layer was dried ($MgSO_4$). The solvent was removed under reduced pressure, to give analytically pure hydroxy-β-lactams **2**.

*Hydroxy β-Lactam **2a**.* From 685 mg (2.0 mmol) of the acetoxy β-lactam **1a**, compound **2a** (479 mg, 80%) was obtained as a colorless solid; mp 129−130 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.64 (d, 1H, J = 7.8 Hz), 7.33 (m, 5H), 7.18 (m, 3H), 6.55 (s, 1H), 5.07 (br s, 1H), 5.00 (d, 1H, J = 14.8 Hz), 4.92 (d, 1H, J = 4.8 Hz), 4.12 (d, 1H, J = 14.8 Hz), 3.62 (s, 3H), 2.47 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 168.0, 134.7 (2C), 132.9, 129.0 (2C), 128.6 (2C), 128.1, 127.2, 122.4, 120.7, 120.2, 109.2, 101.7, 78.5, 55.5, 44.2, 30.0; IR ($CHCl_3$, cm^{-1}): ν 3102, 2925, 1670, 1612, 750, 701; HRMS (ES): calcd for $C_{19}H_{18}N_2O_2$ $[M]^+$: 306.1368; found: 306.1364.

*Hydroxy β-Lactam **2b**.* From 800 mg (2.11 mmol) of the acetoxy β-lactam **1b**, compound **2b** (685 mg, 96%) was obtained as a colorless solid; mp 139−140 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.63 (d, 1H, J = 7.8 Hz), 7.29 (m, 2H), 7.17 (m, 1H), 7.12 (d, 2H, J = 8.3 Hz), 6.85 (d, 2H, J = 8.2 Hz), 6.55 (s, 1H), 5.05 (d, 1H, J = 4.2 Hz), 4.92 (m, 1H), 4.88 (m, 1H), 4.06 (d, 1H, J = 14.7 Hz), 3.80 (s, 1H), 3.62 (s, 3H), 2.78 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 168.1, 159.4, 138.5, 133.0, 129.9 (2C), 127.2, 126.7, 122.0, 120.7, 120.0, 114.3 (2C), 109.1, 101.7, 78.3, 55.3 (2C), 43.6, 30.0; IR ($CHCl_3$, cm^{-1}): ν 3100, 2924, 1650, 1610, 730; HRMS (ES): calcd for $C_{20}H_{20}N_2O_3$ $[M]^+$: 336.1474; found: 336.1460.

*Hydroxy β-Lactam **2c**.* From 940 mg (2.57 mmol) of the acetoxy β-lactam **1c**, compound **2c** (790 mg, 95%) was obtained as a colorless solid; mp 138−139 °C; ^1H NMR (300 MHz, DMSO, 25 °C) δ: 7.43 (d, 1H, J = 8.2 Hz), 7.35 (d, 2H, J = 9.0 Hz), 7.12 (t, 1H, J = 7.3 Hz), 6.98 (t, 1H, J = 7.0 Hz), 6.92 (d, 2H, J = 8.9 Hz), 6.13 (s, 1H), 5.68 (d, 1H, J = 4.9 Hz), 5.30 (m, 1H), 3.75 (s, 1H), 3.71 (s, 3H); ^{13}C NMR (75 MHz, DMSO, 25 °C) δ: 165.9, 155.7, 137.7, 134.7, 130.7, 126.9, 120.9, 119.8, 119.0, 118.4 (2C), 114.4 (2C), 109.3, 100.9, 77.1, 56.4, 55.2, 30.0; IR ($CHCl_3$, cm^{-1}): ν 3101, 2924, 1667, 1615, 743; HRMS (ES): calcd for $C_{19}H_{18}N_2O_3$ $[M]^+$: 322.1317; found: 322.1326.

*Hydroxy β-Lactam **2d**.* From 1.32 g (3.09 mmol) of the acetoxy β-lactam **1d**, compound **2d** (1.19 g, 99%) was obtained as a colorless solid; mp 133−134 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.63 (d, 1H, J = 7.8 Hz), 7.46 (d, 2H, J = 8.4 Hz), 7.33 (d, 1H, J = 7.9 Hz), 7.27 (td, 1H, J = 7.6, 1.2 Hz), 7.16 (td, 1H, J = 7.3, 1.3 Hz), 7.08 (d, 2H, J = 8.4 Hz), 6.52 (s, 1H), 5.06 (br s, 1H), 4.90 (d, 1H, J = 14.7 Hz), 4.89 (d, 1H, J = 5.0 Hz), 4.08 (d, 1H, J = 14.9 Hz), 3.62 (s, 3H), 3.00 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.3, 138.5, 133.6, 132.6, 132.1 (2C), 130.2 (2C), 127.1, 122.3, 122.2, 120.7, 120.1, 109.2, 101.7, 78.4, 55.6, 43.6, 30.0; IR ($CHCl_3$, cm^{-1}): ν 3100, 2930, 1669, 1617, 723; HRMS (ES): calcd for $C_{19}H_{17}BrN_2O_2$ $[M]^+$: 384.0473; found: 384.0487.

*Hydroxy β-Lactam **2e**.* From 678 mg (2.16 mmol) of the acetoxy β-lactam **1e**, compound **2e** (588 mg, 94%) was obtained as a colorless solid; mp 125−126 °C; ^1H NMR (300 MHz, DMSO, 25 °C) δ: 7.50 (d, 1H, J = 7.7 Hz), 7.42 (d, 1H, J = 8.1 Hz), 7.12 (td, 1H, J = 7.6, 1.2 Hz), 7.01 (td, 1H, J = 7.4, 0.9 Hz), 6.34 (s, 1H), 6.09 (m, 1H), 5.15 (m, 1H), 3.68 (s, 3H), 3.27 (dd, 1H, J = 13.8, 8.6 Hz), 2.90 (dd, 1H, J = 13.8, 5.7 Hz), 1.86 (m, 1H), 0.88 (d, 3H, J = 6.7 Hz), 0.87 (d, 3H, J = 6.7 Hz); ^{13}C NMR (75 MHz, DMSO, 25 °C) δ: 168.9, 137.7, 135.8, 127.1, 120.8, 119.8, 118.9, 109.3, 100.3, 77.8, 56.7, 47.3, 29.8, 26.7, 20.2, 20.1; IR ($CHCl_3$, cm^{-1}): ν 3099, 2925, 1672, 1610, 690; HRMS (ES): calcd for $C_{16}H_{20}N_2O_2$ $[M]^+$: 272.1525; found: 272.1528.

*Hydroxy β-Lactam **2f**.* From 595 mg (1.78 mmol) of the acetoxy β-lactam **1f**, compound **2f** (446 mg, 86%) was obtained as a colorless solid; mp 132−133 °C; ^1H NMR (300 MHz, DMSO, 25 °C) δ: 7.42 (m, 3H), 7.34 (m, 3H), 7.11 (m, 2H), 6.98 (t, 1H, J = 7.5 Hz), 6.43 (d, 1H, J = 7.6 Hz), 6.13 (s, 1H), 5.73 (d, 1H, J = 5.1 Hz), 5.33 (dd, 1H, J = 7.6, 5.1 Hz), 3.77 (s, 3H); ^{13}C NMR (75 MHz, DMSO, 25 °C) δ: 166.7, 137.8, 137.3, 134.6, 129.2 (2C), 127.0, 123.9, 120.9, 119.9, 119.0, 117.2 (2C), 109.3, 100.8, 77.1, 56.3, 30.0; IR ($CHCl_3$, cm^{-1}): ν 3102, 2923, 1670, 1613, 752, 698; HRMS (ES): calcd for $C_{18}H_{16}N_2O_2$ $[M]^+$: 292.1212; found: 292.1221.

Base-Promoted Reaction between Propargyl Bromide and Hydroxy-β-Lactams 2. General Procedure for the Synthesis of Propargylic Ethers 3a−f. Tetrabutyl ammonium iodide (31.9 mg, 0.086 mmol), 50% aqueous sodium hydroxide (100 mL), and propargyl bromide (13.82 mmol) were sequentially added at room temperature to a solution of the appropriate hydroxy-β-lactam **3** (8.64 mmol) in dichloromethane (100 mL). The reaction was stirred for 20 h, and then water was added (50 mL), before being partitioned between dichloromethane and water. The aqueous phase was extracted with dichloromethane (3 × 50 mL), and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures as eluent gave analytically pure compounds **3**.

*Alkynyl β-Lactam **3a**.* From 470 mg (1.55 mmol) of hydroxy-β-lactam **2a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **3a** (421 mg, 79%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.63 (d, 1H, J = 7.9 Hz), 7.31 (m, 4H), 7.26 (m, 1H), 7.17 (m, 3H), 6.59 (s, 1H), 5.19 (d, 1H, J = 4.5 Hz), 4.95 (d, 1H, J = 14.6 Hz), 4.88 (d, 1H, J = 4.7 Hz), 4.25 (dd, 1H, J = 16.1, 2.5 Hz), 4.05 (d, 1H, J = 15.0 Hz), 4.00 (dd, 1H, J = 16.1, 2.3 Hz), 3.62 (s, 3H), 2.40 (t, 1H, J = 2.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.3, 138.4, 134.6, 132.3, 128.9 (2C), 128.6 (2C), 128.0, 127.4, 122.0, 120.7, 119.8, 109.1, 103.2, 82.4, 78.2, 75.9, 57.8, 54.4, 44.3, 30.3; IR ($CHCl_3$, cm^{-1}): ν 2926, 1753, 1615, 1395, 752, 701; HRMS (ES): calcd for $C_{22}H_{20}N_2O_2$ $[M]^+$: 344.1525; found: 344.1515.

*Alkynyl β-Lactam **3b**.* From 403 mg (1.20 mmol) of hydroxy-β-lactam **2b**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **3b** (403 mg, 90%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.63 (d, 1H, J = 7.9 Hz), 7.28 (m, 2H), 7.14 (t, 1H, J = 7.9 Hz), 7.09 (d, 2H, J = 8.6 Hz), 6.83 (d, 2H, J = 8.6 Hz), 6.58 (s, 1H), 5.17 (d, 1H, J = 4.7 Hz), 4.87 (m, 1H), 4.85 (m, 1H), 4.24 (dd, 1H, J = 16.1, 2.3 Hz), 4.00 (d, 1H, J = 14.8 Hz), 3.98 (d, 1H, J = 16.1 Hz), 3.80 (s, 3H), 3.62 (s, 3H), 2.39 (t, 1H, J = 2.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.2, 159.4, 138.3, 132.4, 130.0 (2C), 127.4, 126.6, 121.9, 120.7, 119.7, 114.2 (2C), 109.1, 103.2, 82.3, 78.2, 75.8, 57.7, 55.3, 54.2, 43.7, 30.3; IR ($CHCl_3$, cm^{-1}): ν 2924, 1760, 1624, 1245, 734; HRMS (ES): calcd for $C_{23}H_{22}N_2O_3$ $[M]^+$: 374.1630; found: 374.1641.

*Alkynyl β-Lactam **3c**.* From 745 mg (2.31 mmol) of hydroxy-β-lactam **2c**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **3c** (367 mg, 44%) as a colorless solid; mp 154−155 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.57 (d, 1H, J = 7.9 Hz), 7.36 (d, 2H, J = 9.0 Hz), 7.34 (m, 1H), 7.25 (t, 1H, J = 7.5 Hz), 7.12 (t, 1H, J = 7.4 Hz), 6.81 (d, 2H, J = 9.1 Hz), 6.56 (s, 1H), 5.51 (d, 1H, J = 5.0 Hz), 5.35 (d, 1H, J = 5.0 Hz), 4.31 (dd, 1H, J = 16.1, 2.4 Hz), 4.08 (dd, 1H, J = 16.1, 2.4 Hz), 3.79 (s, 3H), 3.76 (s, 3H), 2.47 (t, 1H, J = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 163.3, 156.5, 138.6, 131.8, 130.6, 127.2, 122.0, 120.7, 119.7, 118.7 (2C), 114.4 (2C), 109.1, 103.9, 81.4, 78.1, 76.1, 57.9, 56.1, 55.5, 30.7; IR ($CHCl_3$, cm^{-1}): ν 2920, 1757, 1614, 1360, 746; HRMS (ES): calcd for $C_{22}H_{20}N_2O_3$ $[M]^+$: 360.1474; found: 360.1458.

Alkynyl β-Lactam 3d. From 1.3 g (3.37 mmol) of hydroxy-β-lactam **2d**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **3d** (970 mg, 68%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.63 (d, 1H, *J* = 7.8 Hz), 7.45 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 1H, *J* = 7.8 Hz), 7.26 (td, 1H, *J* = 7.0, 1.2 Hz), 7.15 (td, 1H, *J* = 7.3, 1.2 Hz), 7.06 (d, 2H, *J* = 8.4 Hz), 6.56 (s, 1H), 5.20 (d, 1H, *J* = 4.7 Hz), 4.87 (d, 1H, *J* = 14.8 Hz), 4.87 (d, 1H, *J* = 4.7 Hz), 4.25 (dd, 1H, *J* = 16.1, 2.4 Hz), 4.02 (d, 1H, *J* = 14.9 Hz), 4.00 (dd, 1H, *J* = 16.1, 2.4 Hz), 3.64 (s, 3H), 2.41 (t, 1H, *J* = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.3, 138.3, 133.6 (2C), 132.0 (2C), 130.3 (2C), 127.2, 122.1, 122.0, 120.7, 119.8, 109.1, 103.2, 82.4, 78.0, 76.0, 57.8, 54.5, 43.6, 30.3; IR ($CHCl_3$, cm^{-1}): ν 2920, 1753, 1640, 1390, 735; HRMS (ES): calcd for $C_{22}H_{19}BrN_2O_2$ $[M]^+$: 422.0630; found: 422.0641.

Alkynyl β-Lactam 3e. From 530 mg (1.95 mmol) of hydroxy-β-lactam **2e**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **3e** (552 mg, 91%) as a colorless solid; mp 98−99 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.61 (d, 1H, *J* = 7.8 Hz), 7.35 (d, 1H, *J* = 8.2 Hz), 7.26 (td, 1H, *J* = 7.4, 1.2 Hz), 7.17 (td, 1H, *J* = 7.4, 1.1 Hz), 6.55 (s, 1H), 5.26 (d, 1H, *J* = 4.6 Hz), 5.11 (d, 1H, *J* = 4.6 Hz), 4.25 (dd, 1H, *J* = 16.1, 2.4 Hz), 4.00 (dd, 1H, *J* = 16.1, 2.4 Hz), 3.77 (s, 3H), 3.42 (dd, 1H, *J* = 13.9, 8.5 Hz), 2.87 (dd, 1H, *J* = 13.9, 5.8 Hz), 2.42 (t, 1H, *J* = 2.4 Hz), 1.90 (m, 1H), 0.94 (d, 3H, *J* = 6.5 Hz), 0.92 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 167.0, 138.4, 132.5, 127.2, 122.0, 120.7, 119.8, 109.1, 103.3, 82.1, 78.2, 75.8, 57.7, 56.0, 47.8, 30.5, 27.1, 20.3, 20.2; IR ($CHCl_3$, cm^{-1}): ν 2930, 1763, 1640, 1390, 690; HRMS (ES): calcd for $C_{19}H_{22}N_2O_2$ $[M]^+$: 310.1681; found: 310.1681.

Alkynyl β-Lactam 3f. From 424 mg (1.45 mmol) of hydroxy-β-lactam **2f**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **3f** (172 mg, 36%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.58 (d, 1H, *J* = 7.9 Hz), 7.43 (d, 2H, *J* = 7.6 Hz), 7.30 (m, 4H), 7.11 (t, 2H, *J* = 7.3 Hz), 6.57 (s, 1H), 5.55 (d, 1H, *J* = 5.1 Hz), 5.37 (d, 1H, *J* = 5.1 Hz), 4.32 (dd, 1H, *J* = 16.1, 2.3 Hz), 4.08 (dd, 1H, *J* = 16.1, 2.4 Hz), 3.76 (s, 3H), 2.48 (t, 1H, *J* = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 163.9, 138.5, 137.0, 131.6, 129.2 (2C), 127.2, 124.7, 122.0, 120.7, 119.7, 117.4 (2C), 109.1, 103.8, 81.3, 78.0, 76.2, 57.9, 56.0, 30.7; IR ($CHCl_3$, cm^{-1}): ν 2934, 1750, 1614, 1425, 750, 703; HRMS (ES): calcd for $C_{21}H_{18}N_2O_2$ $[M]^+$: 330.1368; found: 330.1363.

Staudinger Reaction. General Procedure for the Preparation of Alkynyl β-Lactam-Tethered Indoles 4a−f. To a solution of the corresponding imine (10.4 mmol) in dichloromethane (35 mL) and triethylamine (4.2 mL, 30 mmol) was slowly added methoxyacetyl chloride (13 mmol) dissolved in dichloromethane (35 mL) at room temperature under an argon atmosphere. Stirring was continued for 2 h at 80 °C. The reaction was allowed to warm to room temperature, and then, 15 mL of $NaHCO_3$ (aq. sat.) was added before being partitioned between dichloromethane and water. The aqueous phase was extracted with dichloromethane (3 × 50 mL), and the combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue using an ethyl acetate/hexanes mixture gave analytically pure compounds **4**.

Alkynyl β-Lactam 4a. From 632 mg (3.22 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **4a** (641 mg, 74%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.62 (dd, 1H, *J* = 7.8, 0.9 Hz), 7.36 (dd, 1H, *J* = 8.3, 0.8 Hz), 7.26 (td, 1H, *J* = 8.3, 1.2 Hz), 7.14 (td, 1H, *J* = 7.4, 1.1 Hz), 6.58 (s, 1H), 5.19 (d, 1H, *J* = 4.7 Hz), 4.87 (d, 1H, *J* = 4.7 Hz), 4.47 (dd, 1H, *J* = 17.7, 2.6 Hz), 3.82 (dd, 1H, *J* = 17.6, 2.5 Hz), 3.82 (s, 3H), 3.31 (s, 3H), 2.25 (t, 1H, *J* = 2.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.1, 138.4, 132.3, 127.3, 122.0, 120.7, 119.8, 109.1, 103.0, 86.1, 75.9, 73.0, 58.5, 54.9, 30.4, 29.7; IR ($CHCl_3$, cm^{-1}): ν 2920, 1750, 1618, 1246, 1243; HRMS (ES): calcd for $C_{16}H_{16}N_2O_2$ $[M]^+$: 268.1212; found: 268.1224.

Alkynyl β-Lactam 4b. From 678 mg (2.94 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **4b** (689 mg, 77%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.56 (d, 1H, *J* = 1.5 Hz), 7.26 (d, 1H, *J* = 8.9 Hz), 7.19 (dd, 1H, *J* = 8.8, 2.0 Hz), 6.51 (s, 1H), 5.15 (d, 1H, *J* = 4.8 Hz), 4.87 (d, 1H, *J* = 4.7 Hz), 4.45 (dd, 1H, *J* = 17.7, 2.5 Hz), 3.82 (dd, 1H, *J* = 17.7, 2.5 Hz), 3.77 (s, 3H), 3.31 (s, 3H), 2.25 (t, 1H, *J* = 2.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.0, 136.7, 133.9, 128.2, 125.5, 122.3, 120.0, 110.1, 102.5, 86.1, 75.8, 73.2, 58.6, 54.8, 30.6, 29.8; IR ($CHCl_3$, cm^{-1}): ν 2926, 1751, 1620, 1256, 1237; HRMS (ES): calcd for $C_{16}H_{15}ClN_2O_2$ $[M]^+$: 302.0822; found: 302.0825.

Alkynyl β-Lactam 4c. From 324 mg (1.43 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **4c** (271 mg, 71%) as a colorless solid; mp 160−161 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.24 (d, 1H, *J* = 8.9 Hz), 7.07 (d, 1H, *J* = 2.5 Hz), 6.91 (dd, 1H, *J* = 8.9, 2.5 Hz), 6.49 (s, 1H), 5.15 (d, 1H, *J* = 4.6 Hz), 4.86 (d, 1H, *J* = 4.6 Hz), 4.45 (dd, 1H, *J* = 17.7, 2.5 Hz), 3.86 (s, 3H), 3.80 (dd, 1H, *J* = 17.7, 2.5 Hz), 3.76 (s, 3H), 3.30 (s, 3H), 2.25 (t, 1H, *J* = 2.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.1, 154.3, 133.7, 132.7, 127.6, 112.4, 109.8, 102.5, 102.3, 86.1, 75.9, 73.0, 58.5, 55.9, 54.8, 30.5, 29.7; IR ($CHCl_3$, cm^{-1}): ν 2932, 1756, 1635, 1260, 1248; HRMS (ES): calcd for $C_{17}H_{18}N_2O_3$ $[M]^+$: 298.1317; found: 298.1317.

Alkynyl β-Lactam 4d. From 884 mg (4.17 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **4d** (696 mg, 59%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.81 (d, 1H, *J* = 7.8 Hz), 7.35 (d, 1H, *J* = 8.2 Hz), 7.25 (td, 1H, *J* = 7.6, 1.2 Hz), 7.13 (td, 1H, *J* = 7.4, 1.1 Hz), 6.56 (s, 1H), 5.24 (d, 1H, *J* = 4.6 Hz), 4.89 (d, 1H, *J* = 4.6 Hz), 3.80 (m, 1H), 3.78 (s, 3H), 3.29 (s, 3H), 3.23 (m, 1H), 2.47 (m, 2H), 2.01 (t, 1H, *J* = 2.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 167.0, 138.4, 132.7, 127.3, 122.0, 120.7, 119.8, 109.1, 103.1, 86.0, 80.7, 70.5, 58.5, 56.1, 38.8, 30.5, 17.8; IR ($CHCl_3$, cm^{-1}): ν 2920, 1747, 1630, 1259, 1230; HRMS (ES): calcd for $C_{17}H_{18}N_2O_2$ $[M]^+$: 282.1368; found: 282.1376.

Alkynyl β-Lactam 4e. From 700 mg (2.86 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **4e** (589 mg, 65%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.54 (d, 1H, *J* = 1.9 Hz), 7.24 (d, 1H, *J* = 8.8 Hz), 7.17 (dd, 1H, *J* = 8.8, 2.0 Hz), 6.48 (s, 1H), 5.21 (d, 1H, *J* = 4.6 Hz), 4.87 (d, 1H, *J* = 4.6 Hz), 3.77 (m, 1H), 3.75 (s, 3H), 3.28 (s, 3H), 3.22 (m, 1H), 2.48 (m, 2H), 2.01 (t, 1H, *J* = 2.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.8, 136.7, 134.3, 128.1, 125.4, 122.1, 119.9, 110.1, 102.4, 85.9, 80.6, 70.5, 58.5, 55.9, 38.9, 30.6, 17.8; IR ($CHCl_3$, cm^{-1}): ν 2932, 1754, 1610, 1390, 1215; HRMS (ES): calcd for $C_{17}H_{17}ClN_2O_2$ $[M]^+$: 316.0979; found: 316.0969.

Alkynyl β-Lactam 4f. From 406 mg (1.69 mmol) of the appropriate imine, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **4f** (247 mg, 47%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.23 (d, 1H, *J* = 8.9 Hz), 7.06 (d, 1H, *J* = 2.4 Hz), 6.91 (dd, 1H, *J* = 8.9, 2.5 Hz), 6.47 (s, 1H), 5.19 (d, 1H, *J* = 4.6 Hz), 4.87 (d, 1H, *J* = 4.6 Hz), 3.85 (s, 3H), 3.79 (m, 1H), 3.74 (s, 3H), 3.28 (s, 3H), 3.25 (m, 1H), 2.48 (m, 2H), 2.01 (t, 1H, *J* = 2.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 167.0, 154.2, 133.8, 133.1, 127.5, 122.4, 109.8, 102.6, 102.2, 86.0, 80.7, 70.5, 58.5, 56.0, 55.8, 38.8, 30.9, 17.8; IR ($CHCl_3$, cm^{-1}): ν 2926, 1758, 1623, 1298, 1234; HRMS (ES): calcd for $C_{18}H_{20}N_2O_3$ $[M]^+$: 312.1474; found: 312.1470.

Cu-Catalyzed Reaction of β-Lactam-Tethered Alkynyl Indoles 3 and 4. General Procedure for the Preparation of β-Lactam-Tethered Allenyl Indoles 5a−f and 6a−f. A well stirred solution of $(CH_2O)_n$ (0.5 mmol), CuI (0.1 mmol), the appropriate alkyne **3** or **4** (0.2 mmol), and *N*,*N*-diisopropylethylamine (Hüning's base) (0.36 mmol) in dioxane (1 mL) was refluxed under an argon atmosphere. When the reaction was complete, as monitored by TLC, it was cooled to rt. Water (5 mL) was added before being extracted with ethyl acetate (3 × 15 mL). The organic phase was washed with water (2 × 5 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure compounds **5** or **6**. Spectroscopic and analytical data for previously allenes **5** or **6** follow.

*Allenyl β-Lactam **5a**.* From 406 mg (1.20 mmol) of alkynyl-β-lactam **3a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **5a** (266 mg, 63%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.62 (d, 1H, J = 7.8 Hz), 7.28 (m, 5H), 7.15 (m, 3H), 6.59 (s, 1H), 4.98 (d, 1H, J = 4.5 Hz), 4.92 (d, 1H, J = 14.9 Hz), 4.91 (m, 1H), 4.83 (d, 1H, J = 4.4 Hz), 4.64 (m, 2H), 4.01 (d, 1H, J = 14.7 Hz), 3.96 (t, 1H, J = 2.3 Hz), 3.94 (t, 1H, J = 2.3 Hz), 3.62 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 209.6, 166.7, 138.4, 134.7, 132.4, 128.9 (2C), 128.7 (2C), 128.0, 127.4, 121.9, 120.7, 119.7, 109.1, 103.6, 86.7, 83.5, 75.8, 68.7, 55.0, 44.2, 30.4; IR (CHCl$_3$, cm^{-1}): ν 2953, 1756, 1616, 1397, 751, 701; HRMS (ES): calcd for $C_{23}H_{22}N_2O_2$ $[M]^+$: 358.1681; found: 358.1693.

*Allenyl β-Lactam **5b**.* From 434 mg (1.16 mmol) of alkynyl-β-lactam **3b**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **5b** (353 mg, 78%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.62 (d, 1H, J = 7.7 Hz), 7.32 (d, 1H, J = 8.0 Hz), 7.25 (td, 1H, J = 8.1, 1.2 Hz), 7.14 (td, 1H, J = 7.9, 1,2 Hz), 7.08 (d, 2H, J = 8.6 Hz), 6.82 (d, 2H, J = 8.6 Hz), 6.58 (s, 1H), 4.96 (d, 1H, J = 4.5 Hz), 4.92 (t, 1H, J = 6.9 Hz), 4.85 (d, 1H, J = 14.5 Hz), 4.80 (d, 1H, J = 4.5 Hz), 4.63 (m, 2H), 3.96 (d, 1H, J = 14.9 Hz), 3.94 (m, 2H), 3.79 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 209.6, 166.5, 159.3, 138.4, 132.6, 130.0 (2C), 127.4, 126.7, 121.9, 120.7, 119.7, 114.2 (2C), 109.1, 103.6, 86.7, 83.5, 75.7, 68.7, 55.3, 54.8, 43.7, 30.4; IR (CHCl$_3$, cm^{-1}): ν 2950, 1752, 1615, 1398, 734; HRMS (ES): calcd for $C_{24}H_{24}N_2O_3$ $[M]^+$: 388.1787; found: 388.1784.

*Allenyl β-Lactam **5c**.* From 262 mg (0.73 mmol) of alkynyl-β-lactam **3c**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **5c** (165 mg, 60%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.49 (d, 1H, J = 7.9 Hz), 7.27 (d, 2H, J = 9.0 Hz), 7.25 (d, 1H, J = 8.2 Hz), 7.16 (td, 1H, J = 8.3, 1,2 Hz), 7.03 (td, 1H, J = 7.9, 1.0 Hz), 6.71 (d, 2H, J = 9.1 Hz), 6.49 (s, 1H), 5.38 (d, 1H, J = 4.8 Hz), 5.06 (d, 1H, J = 4.8 Hz), 4.90 (q, 1H, J = 6.9 Hz), 4.57 (m, 2H), 3.94 (dd, 2H, J = 6.8, 1.2 Hz), 3.70 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 209.7, 163.7, 156.5, 138.7, 132.0, 130.7, 127.3, 122.0, 120.7, 119.7, 118.7, 114.4 (2C), 109.1, 104.2, 86.7, 82.7, 75.8, 68.8, 56.8, 55.4, 30.9; IR (CHCl$_3$, cm^{-1}): ν 2945, 1759, 1618, 1387, 735; HRMS (ES): calcd for $C_{23}H_{22}N_2O_3$ $[M]^+$: 374.1630; found: 374.1616.

*Allenyl β-Lactam **5d**.* From 489 mg (1.55 mmol) of alkynyl-β-lactam **3d**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **5d** (339 mg, 50%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.63 (d, 1H, J = 7.7 Hz), 7.44 (d, 2H, J = 8.3 Hz), 7.33 (d, 1H, J = 8.2 Hz), 7.26 (td, 1H, J = 6.9, 1.2 Hz), 7.14 (t, 1H, J = 7.9 Hz), 7.05 (d, 2H, J = 8.5 Hz), 6.57 (s, 1H), 4.99 (d, 1H, J = 4.5 Hz), 4.92 (qu, 1H, J = 7.0 Hz), 4.85 (d, 1H, J = 12.7 Hz), 4.82 (d, 1H, J = 4.4 Hz), 4.65 (m, 2H), 3.99 (d, 1H, J = 12.2 Hz), 3.96 (m, 2H), 3.64 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 209.6, 166.6, 138.4, 133.7, 132.1, 132.0 (2C), 130.3 (2C), 127.3, 122.1, 122.0, 120.7, 119.8, 109.1, 103.6, 86.6, 83.5, 75.8, 68.8, 55.0, 43.6, 30.5; IR (CHCl$_3$, cm^{-1}): ν 2952, 1758, 1620, 1297, 754; HRMS (ES): calcd for $C_{23}H_{21}BrN_2O_2$ $[M]^+$: 436.0786; found: 436.0799.

*Allenyl β-Lactam **5e**.* From 524 mg (1.69 mmol) of alkynyl-β-lactam **3e**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **5e** (443 mg, 81%) as a colorless solid; mp 98−99 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.61 (d, 1H, J = 7.7 Hz), 7.35 (d, 1H, J = 8.2 Hz), 7.25 (td, 1H, J = 7.4, 1.2 Hz), 7.13 (td, 1H, J = 7.3, 1.2 Hz), 6.56 (s, 1H), 5.07 (m, 1H), 5.05 (m, 1H), 4.94 (q, 1H, J = 6.7 Hz), 4.65 (m, 2H), 3.96 (m, 2H), 3.78 (s, 3H), 3.89 (dd, 1H, J = 13.9, 8.5 Hz), 2.83 (dd, 1H, J = 13.9, 5.9 Hz), 1.89 (m, 1H), 0.93 (d, 3H, J = 6.6 Hz), 0.91 (d, 3H, J = 6.6 Hz); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 209.5, 167.3, 138.4, 132.6, 127.3, 121.9, 120.6, 119.7, 109.1, 103.7, 86.7, 83.3, 75.7, 68.7, 56.6, 47.8, 30.6, 27.1, 20. 4, 20.3; IR (CHCl$_3$, cm^{-1}): ν 2953, 1759, 1614, 1395, 741; HRMS (ES): calcd for $C_{20}H_{24}N_2O_2$ $[M]^+$: 324.1838; found: 324.1845.

*Allenyl β-Lactam **5f**.* From 68 mg (0.21 mmol) of alkynyl-β-lactam **3f**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **5f** (30 mg, 42%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.59 (d, 1H, J = 7.8 Hz), 7.43 (d, 2H, J = 8.5 Hz), 7.28 (m, 4H), 7.14 (d, 1H, J = 7.9 Hz), 7.10 (t, 1H, J = 7.4 Hz), 6.60 (s, 1H), 5.52 (d, 1H, J = 4.9 Hz), 5.17 (d, 1H, J = 5.0 Hz), 5.00 (q, 1H, J = 6.9 Hz), 4.67 (m, 2H), 4.04 (dt, 2H, J = 7.2, 2.2 Hz), 3.80 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 209.7, 164.3, 138.7, 137.1, 131.9, 129.2 (2C), 127.2, 124.6, 122.0, 120.7), 119.7, 117.3 (2C), 109.1, 104.1, 86.6, 82.6, 75.8, 68.9, 56.6, 30.9; IR (CHCl$_3$, cm^{-1}): ν 2955, 1755, 1619, 1395, 752, 700; HRMS (ES): calcd for $C_{22}H_{20}N_2O_2$ $[M]^+$: 344.1525; found: 344.1519.

*Allenyl β-Lactam **6a**.* From 292 mg (1.1 mmol) of alkynyl-β-lactam **4a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **6a** (236 mg, 77%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.61 (d, 1H, J = 7.9 Hz), 7.35 (d, 1H, J = 8.0 Hz), 7.25 (td, 1H, J = 8.2, 1.0 Hz), 7.13 (td, 1H, J = 7.5, 0.9 Hz), 6.57 (s, 1H), 5.12 (d, 1H, J = 4.5 Hz), 5.11 (m, 1H), 4.85 (d, 1H, J = 4.7 Hz), 4.80 (m, 2H), 4.27 (m, 1H), 3.78 (s, 3H), 3.60 (m, 1H), 3.30 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 209.2, 166.7, 138.4, 132.8, 127.3, 121.9, 120.7, 119.7, 109.0, 103.1, 85.9, 85.1, 77.4, 58.5, 55.3, 38.6, 30.4; IR (CHCl$_3$, cm^{-1}): ν 2954, 1760, 1616, 1390, 1240; HRMS (ES): calcd for $C_{17}H_{18}N_2O_2$ $[M]^+$: 282.1368; found: 282.1379.

*Allenyl β-Lactam **6b**.* From 320 mg (1.06 mmol) of alkynyl-β-lactam **4b**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **6b** (201 mg, 60%) as a colorless solid; mp 105−106 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.56 (d, 1H, J = 1.9 Hz), 7.25 (d, 1H, J = 8.8 Hz), 7.18 (dd, 1H, J = 8.7, 1.9 Hz), 6.50 (s, 1H), 5.10 (m, 1H), 5.09 (d, 1H, J = 5.0 Hz), 4.85 (d, 1H, J = 4.7 Hz), 4.80 (m, 2H), 4.26 (m, 1H), 3.75 (s, 3H), 3.60 (m, 1H), 3.30 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 209.2, 166.6, 136.7, 134.3, 128.2, 125.4, 122.1, 120.0, 110.1, 102.5, 85.8, 85.0, 77.9, 58.5, 55.1, 38.7, 30.7; IR (CHCl$_3$, cm^{-1}): ν 2950, 1753, 1624, 1379, 1251; HRMS (ES): calcd for $C_{17}H_{17}ClN_2O_2$ $[M]^+$: 316.0979; found: 316.0977.

*Allenyl β-Lactam **6c**.* From 170 mg (0.57 mmol) of alkynyl-β-lactam **4c**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **6c** (84 mg, 47%) as a colorless solid; mp 111−112 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.23 (d, 1H, J = 8.9 Hz), 7.06 (d, 1H, J = 2.4 Hz), 6.91 (dd, 1H, J = 8.9, 2.5 Hz), 6.48 (s, 1H), 5.10 (m, 1H), 5.09 (d, 1H, J = 4.6 Hz), 4.84 (d, 1H, J = 4.6 Hz), 4.80 (m, 2H), 4.26 (m, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.59 (m, 1H), 3.29 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 209.2, 166.7, 154.3, 133.8, 133.1, 127.6, 112.3, 109.8, 102.7, 102.3, 85.9, 85.1, 77.4, 58.5, 55.9, 55.2, 38.5, 30.6; IR (CHCl$_3$, cm^{-1}): ν 2950, 1755, 1623, 1387, 1236; HRMS (ES): calcd for $C_{18}H_{20}N_2O_3$ $[M]^+$: 312.1474; found: 312.1474.

*Allenyl β-Lactam **6d**.* From 215 mg (0.76 mmol) of alkynyl-β-lactam **4d**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **6d** (104 mg, 46%) as a colorless oil; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.51 (d, 1H, J = 7.8 Hz), 7.25 (d, 1H, J = 8.2 Hz), 7.15 (td, 1H, J = 7.6, 1.2 Hz), 7.03 (td, 1H, J = 7.4, 1.1 Hz), 6.46 (s, 1H), 4.98 (d, 1H, J = 4.5 Hz), 4.97 (m, 1H), 4.70 (d, 1H, J = 4.7 Hz), 4.62 (m, 2H), 3.67 (s, 3H), 3.62 (m, 1H), 3.17 (s, 3H), 3.06 (m, 1H), 2.15 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 208.7, 166.8, 138.3, 132.8, 127.2, 121.8, 120.5, 119.6, 109.0, 103.0, 86.5, 85.7, 75.7, 58.3, 55.6, 39.5, 30.4, 26.1; IR (CHCl$_3$, cm^{-1}): ν 2960, 1757, 1616, 1387, 1234; HRMS (ES): calcd for $C_{18}H_{20}N_2O_2$ $[M]^+$: 296.1525; found: 296.1525.

*Allenyl β-Lactam **6e**.* From 166 mg (0.52 mmol) of alkynyl-β-lactam **4e**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **6e** (95 mg, 55%) as a colorless solid; mp 98−99 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.56 (d, 1H, J = 1.9 Hz), 7.25 (d, 1H, J = 8.8 Hz), 7.18 (td, 1H, J = 8.7, 2.0 Hz), 6.49 (s, 1H), 5.05 (q, 1H, J = 6.7 Hz), 5.04 (d, 1H, J = 4.5 Hz), 4.81 (d, 1H, J = 4.6 Hz), 4.72 (m, 2H), 3.75 (s, 3H), 3.69 (m, 1H), 3.29 (s, 3H), 3.16 (m, 1H), 2.25 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C) δ: 208.8, 166.9, 136.8, 134.4, 128.2, 125.5, 122.2, 120.0, 110.1, 102.6, 86.5, 85.8, 75.9, 58.5, 55.6, 39.7, 30.7, 26.2; IR (CHCl$_3$, cm^{-1}): ν 2950, 1756, 1624, 1385, 1238; HRMS (ES): calcd for $C_{18}H_{19}ClN_2O_2$ $[M]^+$: 330.1135; found: 330.1135.

Allenyl β-Lactam **6f**. From 500 mg (1.6 mmol) of alkynyl-β-lactam **4f**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **6f** (261 mg, 50%) as a colorless oil; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 7.23 (d, 1H, J = 8.9 Hz), 7.06 (d, 1H, J = 2.3 Hz), 6.90 (dd, 1H, J = 8.9, 2.5 Hz), 6.48 (s, 1H), 5.05 (m, 1H), 5.03 (d, 1H, J = 4.4 Hz), 4.79 (d, 1H, J = 4.5 Hz), 4.72 (m, 2H), 3.90 (s, 3H), 3.73 (s, 3H), 3.68 (m, 1H), 3.20 (s, 3H), 3.15 (m, 1H), 2.24 (m, 2H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 208.8, 166.9, 154.2, 133.8, 133.2, 127.5, 122.3, 109.8, 102.7, 102.2, 86.5, 85.8, 75.8, 58.4, 55.8, 55.6, 39.6, 30.6, 26.2; IR ($\mathrm{CHCl_3}$, cm^{-1}): ν 2950, 1760, 1615, 1394, 1243; HRMS (ES): calcd for $\mathrm{C_{19}H_{22}N_2O_3}$ $[M]^+$: 326.1630; found: 326.1630.

General Procedure for the Gold-Catalyzed Hydroarylation Reaction of β-Lactam-Tethered Allenyl Indoles 5. Preparation of Azeto-oxepino[4,5-*b*]indol-2-ones 7. The appropriate allene **5** (1.0 mmol) was added to a stirred solution of [AuClIPr] (0.05 mmol) and $\mathrm{AgSbF_6}$ (0.05 mmol) in 1,2-dichloroethane (13.0 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 ($\mathrm{MgSO_4}$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate or dichloromethane/ethyl acetate mixtures gave analytically pure tetracyclic compounds **7**.

Tetracycle **7a**. From 85 mg (0.24 mmol) of allene **5a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **7a** (61 mg, 72%) as a colorless solid; mp 142−143 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 8.02 (d, 1H, J = 8.0 Hz), 7.28 (m, 4H), 7.21 (m, 3H), 7.08 (td, 1H, J = 7.3, 1.4 Hz), 5.73 (m, 1H), 5.49 (d, 1H, J = 5.0 Hz), 5.32 (d, 1H, J = 16.6 Hz), 5.23 (dd, 1H, J = 10.0, 1.3 Hz), 5.01 (d, 1H, J = 5.0 Hz), 4.90 (d, 1H, J = 15.8 Hz), 4.19 (m, 2H), 4.14 (d, 1H, J = 15.8 Hz), 3.98 (m, 1H), 3.35 (s, 3H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 167.7, 137.9, 137.4, 135.2, 129.3, 128.9 (2C), 128.0, 127.7, 127.6 (2C), 122.8, 121.1, 119.3, 117.6, 115.1, 109.2, 87.5, 70.5, 54.7, 44.6, 43.9, 29.8; IR ($\mathrm{CHCl_3}$, cm^{-1}): ν 2933, 1751, 1132, 927, 743, 700; HRMS (ES): calcd for $\mathrm{C_{23}H_{22}N_2O_2}$ $[M]^+$: 358.1681; found: 358.1694.

Tetracycle **7b**. From 33 mg (0.085 mmol) of allene **5b**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **7b** (23 mg, 68%) as a colorless oil; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 7.67 (d, 1H, J = 8.0 Hz), 7.21 (m, 2H), 7.09 (m, 3H), 6.82 (d, 2H, J = 8.6 Hz), 5.73 (m, 1H), 5.46 (d, 1H, J = 5.0 Hz), 5.32 (d, 1H, J = 17.0 Hz), 5.23 (d, 1H, J = 10.1 Hz), 4.99 (d, 1H, J = 5.0 Hz), 4.84 (d, 1H, J = 15.6 Hz), 4.18 (m, 2H), 4.07 (d, 1H, J = 15.6 Hz), 3.97 (m, 1H), 3.77 (s, 3H), 3.37 (s, 3H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 167.6, 159.3, 137.8, 137.4, 128.9 (2C), 127.8, 127.5, 127.1, 122.7, 121.0, 119.3, 117.5, 115.0, 114.3 (2C), 109.1, 87.4, 70.4, 55.3, 54.5, 44.0, 43.9, 29.8; IR ($\mathrm{CHCl_3}$, cm^{-1}): ν 2935, 1750, 1134, 929, 735; HRMS (ES): calcd for $\mathrm{C_{24}H_{24}N_2O_3}$ $[M]^+$: 388.1787; found: 388.1764.

Tetracycle **7c**. From 59 mg (0.16 mmol) of allene **5c**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **7c** (27 mg, 63%) as a colorless solid; mp 109−110 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 7.70 (d, 1H, J = 7.9 Hz), 7.34 (m, 2H), 7.19 (d, 2H, J = 9.1 Hz), 7.14 (m, 1H), 6.82 (d, 2H, J = 9.1 Hz), 5.75 (m, 1H), 5.51 (d, 1H, J = 5.1 Hz), 5.41 (d, 1H, J = 5.1 Hz), 5.27 (d, 1H, J = 17.1 Hz), 5.17 (dd, 1H, J = 10.1, 1.3 Hz), 4.27 (m, 1H), 4.23 (m, 1H), 4.06 (m, 1H), 3.77 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 165.0, 157.8, 138.0, 137.2, 129.6, 127.9, 127.6, 123.0, 122.1 (2C), 121.0, 119.6, 117.5, 115.5, 114.6 (2C), 109.5, 87.0, 69.9, 57.0, 55.4, 43.6, 30.6; IR ($\mathrm{CHCl_3}$, cm^{-1}): ν 2933, 1755, 1129, 929, 738; HRMS (ES): calcd for $\mathrm{C_{23}H_{22}N_2O_3}$ $[M]^+$: 374.1630; found: 374.1637.

Tetracycle **7d**. From 131 mg (0.30 mmol) of allene **5d**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **7d** (107 mg, 82%) as a colorless solid; mp 155−156 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 7.57 (d, 1H, J = 8.0 Hz), 7.33 (d, 2H, J = 8.5 Hz), 7.17 (m, 1H), 7.14 (t, 1H, J = 7.6 Hz), 6.99 (m, 1H), 6.98 (d, 2H, J = 8.2 Hz), 5.63 (m, 1H), 5.39 (d, 1H, J = 5.0 Hz), 5.21 (d, 1H, J = 16.9 Hz), 5.15 (dd, 1H, J = 10.2, 1.5 Hz), 4.91 (d, 1H, J = 5.1 Hz), 4.68 (d, 1H, J = 15.9 Hz), 4.10 (m, 1H), 4.07 (m, 1H), 4.05 (d, 1H, J = 15.8 Hz), 3.85 (m, 1H), 3.31 (s, 3H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 167.7, 137.8, 137.1, 134.3, 132.0 (2C), 129.2 (2C), 127.4, 127.3, 122.9, 121.9, 121.0, 119.4, 117.7, 115.1, 109.1, 87.5, 70.5, 57.0, 54.8), 44.0, 43.9, 29.9; IR ($\mathrm{CHCl_3}$, cm^{-1}): ν 2935, 1753, 1129, 924, 732; HRMS (ES): calcd for $\mathrm{C_{23}H_{21}BrN_2O_2}$ $[M]^+$: 436.0786; found: 436.0804.

Tetracycle **7e**. From 53 mg (0.16 mmol) of allene **5e**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **7e** (47 mg, 89%) as a colorless solid; mp 143−144 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 7.69 (d, 1H, J = 8.1 Hz), 7.29 (m, 2H), 7.10 (td, 1H, J = 7.1, 1.9 Hz), 5.73 (m, 1H), 5.43 (d, 1H, J = 5.0 Hz), 5.33 (d, 1H, J = 16.5 Hz), 5.22 (d, 1H, J = 10.1 Hz), 5.05 (d, 1H, J = 5.1 Hz), 4.19 (m, 1H), 4.16 (m, 1H), 3.96 (m, 1H), 3.78 (s, 3H), 3.26 (dd, 1H, J = 14.1, 8.2 Hz), 3.04 (dd, 1H, J = 14.1, 6.4 Hz), 1.70 (m, 1H), 0.87 (d, 3H, J = 2.3 Hz), 0.84 (d, 3H, J = 2.2 Hz); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 167.6, 137.8, 137.2, 128.5, 127.5, 122.8, 121.2, 119.3, 117.7, 114.9, 109.2, 87.2, 70.4, 56.0, 49.7, 44.0, 30.1, 27.8, 20.3, 20.2; IR ($\mathrm{CHCl_3}$, cm^{-1}): ν 2935, 1752, 1130, 925, 732; HRMS (ES): calcd for $\mathrm{C_{20}H_{24}N_2O_2}$ $[M]^+$: 324.1838; found: 324.1832.

General Procedure for the Gold-Catalyzed Hydroarylation/N1−C4 β-Lactam Cleavage of β-Lactam-Tethered Allenyl Indoles 5. Preparation of 1,6-Dihydro-2*H*-oxepino[4,5-*b*]-indole-4-carboxamides 8. The appropriate allene **5** (1.0 mmol) was added to a stirred solution of [AuClIPr] (0.05 mmol) and $\mathrm{AgSbF_6}$ (0.05 mmol) in 1,2-dichloroethane (13.0 mL) under argon. The resulting mixture was stirred at room temperature (**5f**) or at 84 °C (**5a−e**), 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 ($\mathrm{MgSO_4}$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure tricyclic compounds **8**.

Tricycle **8a**. From 85 mg (0.24 mmol) of allene **5a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **8a** (51 mg, 60%) as a colorless oil; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 7.52 (d, 1H, J = 7.9 Hz), 7.36 (m, 4H), 7.33 (m, 3H), 7.23 (s, 1H), 7.15 (br s, 1H), 7.10 (t, 1H, J = 7.9 Hz), 6.02 (m, 1H), 5.15 (d, 1H, J = 10.1 Hz), 5.06 (d, 1H, J = 17.0 Hz), 4.67 (dd, 1H, J = 11.1, 3.3 Hz), 4.57 (m, 2H), 4.19 (m, 1H), 4.04 (dd, 1H, J = 11.1, 1.3 Hz), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 162.9, 148.0, 138.1, 137.7, 130.7, 128.7 (2C), 128.1, 127.6 (2C), 127.0, 122.9, 119.7, 118.6, 117.0, 116.8, 109.4, 101.0, 72.9, 43.8, 43.2, 29.6; IR ($\mathrm{CHCl_3}$, cm^{-1}): ν 3401, 2925, 1682, 1522, 1361, 755, 700; HRMS (ES): calcd for $\mathrm{C_{23}H_{22}N_2O_2}$ $[M]^+$: 358.1681; found: 358.1680.

Tricycle **8b**. From 40 mg (0.10 mmol) of allene **5b**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **8b** (21 mg, 53%) as a colorless oil; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 7.55 (d, 1H, J = 7.9 Hz), 7.33 (d, 2H, J = 8.6 Hz), 7.32 (m, 1H), 7.29 (m, 1H), 7.28 (m, 1H), 7.13 (td, 1H, J = 7.4, 1.3 Hz), 7.14 (br s, 1H), 6.93 (d, 2H, J = 8.6 Hz), 6.04 (m, 1H), 5.18 (d, 1H, J = 10.1 Hz), 5.09 (d, 1H, J = 17.0 Hz), 4.69 (dd, 1H, J = 11.1, 3.4 Hz), 4.54 (m, 2H), 4.21 (m, 1H), 4.05 (dd, 1H, J = 11.1, 1.3 Hz), 3.85 (s, 6H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 162.7, 159.1, 148.1, 137.7, 137.5, 130.6, 130.2, 129.4 (2C), 126.9, 122.8, 119.6, 118.5, 116.8, 116.7, 114.0 (2C), 109.4, 100.9, 72.8, 55.3, 43.2, 43.1, 29.5; IR ($\mathrm{CHCl_3}$, cm^{-1}): ν 3400, 2928, 1685, 1528, 1403, 735; HRMS (ES): calcd for $\mathrm{C_{24}H_{24}N_2O_3}$ $[M]^+$: 388.1787; found: 388.1798.

Tricycle **8c**. From 71 mg (0.19 mmol) of allene **5c**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **8c** (48 mg, 67%) as a colorless solid; mp 148−149 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C) δ: 8.51 (s, 1H), 7.56 (d, 2H, J = 9.1 Hz), 7.50 (dt, 1H, J = 7.9, 0.9 Hz), 7.26 (m, 2H), 7.22 (m, 1H), 7.07 (td, 1H, J = 7.3, 1.3 Hz), 6.87 (d, 2H, J = 9.1 Hz), 6.03 (m, 1H), 5.16 (dt, 1H, J = 10.0, 1.3 Hz), 5.05 (dt, 1H, J = 17.0, 1.4 Hz), 4.75 (dd, 1H, J = 11.1, 3.3 Hz), 4.19 (m, 1H), 4.07 (dd, 1H, J = 11.1, 1.4 Hz), 3.78 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 160.4, 156.4, 148.0, 137.7, 137.6, 130.8, 130.6, 126.9, 123.0, 121.4 (2C), 119.7, 118.7, 117.1, 117.0, 114.2 (2C), 109.5, 101.4, 73.0, 55.4, 43.1, 29.5; IR ($CHCl_3$, cm^{-1}): ν 3398, 2920, 1678, 1530, 1354, 736; HRMS (ES): calcd for $C_{23}H_{22}N_2O_3$ $[M]^+$: 374.1630; found: 374.1630.

*Tricycle **8d**.* From 72 mg (0.17 mmol) of allene **5d**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **8d** (29 mg, 40%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.55 (d, 1H, J = 8.0 Hz), 7.52 (d, 2H, J = 8.5 Hz), 7.34 (t, 1H, J = 8.2 Hz), 7.31 (m, 1H), 7.29 (m, 1H), 7.28 (d, 2H, J = 8.5 Hz), 7.21 (m, 1H), 7.14 (t, 1H, J = 7.3 Hz), 6.04 (m, 1H), 5.20 (dt, 1H, J = 10.1, 1.3 Hz), 5.10 (dt, 1H, J = 17.0, 1.5 Hz), 4.72 (dd, 1H, J = 11.1, 3.4 Hz), 4.60 (dd, 1H, J = 14.9, 6.1 Hz), 4.52 (dd, 1H, J = 14.9, 6.0 Hz), 4.23 (m, 1H), 4.07 (dd, 1H, J = 11.1, 1.3 Hz), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 163.0, 147.7, 137.6, 137.6, 137.2, 131.8 (2C), 130.5, 129.7 (2C), 126.9, 122.9, 121.4, 119.7, 118.6, 117.0, 116.9, 109.4, 101.1, 72.8, 43.1, 43.1, 29.6; IR ($CHCl_3$, cm^{-1}): ν 3390, 2928, 1682, 1526, 1359, 747; HRMS (ES): calcd for $C_{23}H_{21}BrN_2O_2$ $[M]^+$: 436.0786; found: 436.0774.

*Tricycle **8e**.* From 46 mg (0.14 mmol) of allene **5e**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **8e** (26 mg, 58%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.52 (d, 1H, J = 7.9 Hz), 7.31 (d, 1H, J = 8.2 Hz), 7.24 (td, 1H, J = 7.6, 1.1 Hz), 7.20 (s, 1H), 7.10 (td, 1H, J = 7.4, 1.3 Hz), 6.92 (t, 1H, J = 5.5 Hz), 6.03 (m, 1H), 5.17 (dt, 1H, J = 10.1, 1.3 Hz), 5.08 (dt, 1H, J = 17.1, 1.4 Hz), 4.71 (dd, 1H, J = 11.1, 3.4 Hz), 4.20 (m, 1H), 4.06 (dd, 1H, J = 11.1, 1.4 Hz), 3.81 (s, 3H), 3.23 (m, 2H), 1.88 (m, 1H), 0.99 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 162.9, 148.3, 137.7, 137.5, 130.7, 126.9, 122.7, 119.6, 118.5, 116.8, 116.6, 109.4, 100.6, 72.8, 47.0, 43.1, 29.5, 28.6, 20.2 (2C); IR ($CHCl_3$, cm^{-1}): ν 3398 (NH), 2930, 1685, 1524, 1369; HRMS (ES): calcd for $C_{20}H_{24}N_2O_2$ $[M]^+$: 324.1838; found: 324.1843.

*Tricycle **8f**.* From 30 mg (0.09 mmol) of allene **5f**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound **8f** (29 mg, 98%) as a colorless solid; mp 181−182 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.57 (s, 1H), 7.63 (d, 2H, J = 7.6 Hz), 7.48 (d, 1H, J = 7.9 Hz), 7.28 (m, 4H), 7.21 (s, 1H), 7.07 (m, 2H), 6.02 (m, 1H), 5.15 (dt, 1H, J = 10.0, 1.4 Hz), 5.04 (dt, 1H, J = 17.0, 1.4 Hz), 4.76 (dd, 1H, J = 11.1, 3.3 Hz), 4.19 (m, 1H), 4.07 (dd, 1H, J = 11.1, 1.5 Hz), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 160.6, 147.8, 137.7, 137.6, 130.6, 129.0 (2C), 126.9, 124.4, 123.1, 119.8 (2C), 119.7, 118.7, 117.3, 117.0, 109.5, 101.7, 73.0, 55.4, 43.1, 29.6; IR ($CHCl_3$, cm^{-1}): ν 3397, 2930, 1684, 1523, 1353, 754, 701; HRMS (ES): calcd for $C_{22}H_{20}N_2O_2$ $[M]^+$: 344.1525; found: 344.1518.

General Procedure for the Gold-Catalyzed Hydroarylation of β-Lactam-Tethered Allenyl Indoles 6. Preparation of Tetrahydroazeto-azocino[3,4-*b*]indol-2-ones 9 and Hexahydroazeto-azepino[3,4-*b*]indol-2-ones 10. The appropriate allene **6** (1.0 mmol) was added to a stirred solution of [AuClIPr] (0.05 mmol) and $AgSbF_6$ (0.05 mmol) in 1,2-dichloroethane (13.0 mL) under argon. The resulting mixture was stirred at 90 °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 hexanes/ethyl acetate mixtures gave analytically pure tetracyclic compounds **9** and **10**.

*Tetracycle **9a**.* From 58 mg (0.21 mmol) of allene **6a**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **9a** (34 mg, 59%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.60 (d, 1H, J = 7.8 Hz), 7.28 (d, 1H, J = 7.3 Hz), 7.22 (td, 1H, J = 8.1, 1.2 Hz), 7.13 (td, 1H, J = 7.3, 1.4 Hz), 6.08 (m, 1H), 5.34 (m, 1H), 5.07 (d, 1H, J = 4.2 Hz), 4.92 (d, 1H, J = 4.4 Hz), 4.77 (d, 1H, J = 18.5 Hz), 3.98 (dd, 1H, J = 14.7, 7.4 Hz), 3.70 (s, 3H), 3.61 (d, 1H, J = 18.5 Hz), 3.35 (m, 1H), 3.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 167.4, 136.9, 131.6, 129.5, 127.1, 123.1, 121.8, 119.3, 115.3, 115.3, 108.8, 87.8, 58.3 (2C), 42.6, 29.9, 20.6; IR ($CHCl_3$, cm^{-1}): ν 2935, 1750, 1132, 929; HRMS (ES): calcd for $C_{17}H_{18}N_2O_2$ $[M]^+$: 282.1368; found: 282.1372.

*Tetracycle **9b**.* From 85 mg (0.27 mmol) of allene **6b**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **9b** (59 mg, 70%) as a colorless solid; mp 158−159 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.54 (dd, 1H, J = 1.7, 0.7 Hz), 7.16 (d, 1H, J = 0.6 Hz), 7.15 (d, 1H, J = 1.7 Hz), 6.03 (m, 1H), 5.35 (m, 1H), 5.04 (d, 1H, J = 4.5 Hz), 4.91 (d, 1H, J = 4.4 Hz), 4.76 (d, 1H, J = 18.4 Hz), 3.95 (dd, 1H, J = 14.8, 7.2 Hz), 3.67 (s, 3H), 3.61 (d, 1H, J = 18.3 Hz), 3.34 (s, 3H), 3.23 (dd, 1H, J = 14.8, 9.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 167.2, 135.2, 131.3, 131.1, 128.0, 125.1, 123.3, 122.0, 117.5, 114.9, 109.8, 85.7, 58.4, 58.1, 42.6, 30.1, 20.6; IR ($CHCl_3$, cm^{-1}): ν 2939, 1753, 1138, 933; HRMS (ES): calcd for $C_{17}H_{17}ClN_2O_2$ $[M]^+$: 316.0979; found: 316.0990.

*Tetracycle **9c**.* From 49 mg (0.16 mmol) of allene **6c**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound **9c** (26 mg, 53%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.16 (d, 1H, J = 8.9 Hz), 7.02 (d, 1H, J = 2.3 Hz), 6.87 (dd, 1H, J = 8.8, 2.4 Hz), 6.09 (m, 1H), 5.34 (m, 1H), 5.05 (br s, 1H), 4.91 (br s, 1H), 4.75 (d, 1H, J = 18.5 Hz), 3.95 (dd, 1H, J = 14.9, 7.3 Hz), 3.88 (s, 3H), 3.67 (s, 3H), 3.61 (m, 1H), 3.32 (s, 3H), 3.27 (dd, 1H, J = 14.7, 9.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 167.4, 154.1, 132.2, 131.4, 130.0, 127.2, 123.2, 114.8, 112.1, 109.6, 99.8, 85.7, 58.4 (2C), 56.0), 42.6, 30.1, 20.7; IR ($CHCl_3$, cm^{-1}): ν 2939, 1752, 1127, 945; HRMS (ES): calcd for $C_{18}H_{20}N_2O_3$ $[M]^+$: 312.1474; found: 312.1481.

*Tetracycle **10a**.* From 35 mg (0.12 mmol) of allene **6d**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **10a** (12 mg, 35%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.48 (d, 1H, J = 7.9 Hz), 7.29 (m, 1H), 7.22 (td, 1H, J = 8.2, 1.2 Hz), 7.11 (td, 1H, J = 7.3, 1.1 Hz), 6.09 (m, 1H), 5.17 (dt, 1H, J = 10.1, 2.7 Hz), 5.15 (m, 1H), 5.05 (dt, 1H, J = 17.0, 1.6 Hz), 4.96 (dd, 1H, J = 4.5, 1.6 Hz), 4.15 (m, 1H), 4.06 (m, 1H), 3.67 (s, 3H), 3.38 (s, 3H), 3.28 (m, 1H), 2.24 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.4, 159.7, 138.4, 131.9, 127.3, 121.7, 119.2, 118.0, 116.8, 115.3, 115.5, 108.8, 85.9, 57.9, 56.1, 37.9, 36.9, 30.5, 29.7; IR ($CHCl_3$, cm^{-1}): ν 2940, 1748, 1129, 930; HRMS (ES): calcd for $C_{18}H_{20}N_2O_2$ $[M]^+$: 296.1525; found: 296.1531.

*Tetracycle **10b**.* From 39 mg (0.12 mmol) of allene **6e**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **10b** (13 mg, 33%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.42 (dd, 1H, J = 1.8, 0.6 Hz), 7.18 (d, 1H, J = 0.6 Hz), 7.17 (d, 1H, J = 1.9 Hz), 6.06 (m, 1H), 5.18 (dt, 1H, J = 10.1, 1.6 Hz), 5.12 (d, 1H, J = 4.5 Hz), 5.03 (dt, 1H, J = 17.0, 1.6 Hz), 4.94 (dd, 1H, J = 4.5, 1.6 Hz), 4.10 (m, 1H), 3.97 (m, 1H), 3.64 (s, 3H), 3.39 (s, 3H), 3.25 (m, 1H), 2.22 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.3, 138.1, 135.4, 133.4, 128.3, 125.1, 121.9, 117.6, 117.1, 115.2, 109.8, 85.9, 58.0, 56.0, 37.9, 36.9, 31.7, 30.7; IR ($CHCl_3$, cm^{-1}): ν 2947, 1751, 1133, 928; HRMS (ES): calcd for $C_{18}H_{19}ClN_2O_2$ $[M]^+$: 330.1135; found: 330.1135.

*Tetracycle **10c**.* From 102 mg (0.31 mmol) of allene **6f**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **10c** (37 mg, 36%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.19 (d, 1H, J = 8.6 Hz), 6.90 (m, 1H), 6.88 (dd, 1H, J = 8.6, 2.5 Hz), 6.08 (m, 1H), 5.17 (dt, 1H, J = 10.1, 1.5 Hz), 5.12 (d, 1H, J = 4.4 Hz), 5.06 (dt, 1H, J = 17.0, 1.7 Hz), 4.95 (dd, 1H, J = 4.5, 1.5 Hz), 4.12 (m, 1H), 3.99 (m, 1H), 3.85 (s, 3H), 3.63 (s, 3H), 3.36 (s, 3H), 3.27 (m, 1H), 2.24 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 166.4, 154.1, 138.3, 132.5, 132.4, 127.6, 116.8 117.1, 114.9, 111.7, 109.5, 100.2, 85.9, 57.8, 56.1, 56.0, 37.9, 37.0, 31.8, 30.7; IR ($CHCl_3$, cm^{-1}): ν 2947, 1751, 1139, 926; HRMS (ES): calcd for $C_{19}H_{22}N_2O_3$ $[M]^+$: 326.1630; found: 326.1632.

■ ASSOCIATED CONTENT

Supporting Information

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

The authors declare no competing financial interest.

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