Allene-Based Gold-Catalyzed Stereodivergent Synthesis of Azapolycyclic Derivatives of Unusual Structure

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Abstract: The present study provides insights into the manner in which the configuration of β -aminoallene precursors affects their gold-catalyzed cyclization reactions. The reactivity can be switched by using indolizidinone-tethered β -aminoallenes bearing the *syn*- or the *anti*-disposition of both protons at the α - and β -allenic stereocenters. Fused heterocycles (seven examples, 60–75% yields) are obtained from

the *syn*-precursors, while a dimerization–aminoketalization–spirocyclization sequence to afford benzo[*b*]pyrrolo[3,2,1-*ij*][1,7]naphthyridin-1-ones (four examples, 34–48% yields) can be achieved starting from their *anti*-isomers.

Keywords: allenes; gold; heterocyclic compounds; selectivity; synthetic methods

Introduction

Gold complexes continue to attract considerable interest within organic synthesis due to their soft Lewis acidic nature, which allows for selective activation of π -systems.^[1]

Demands for the efficient generation of diverse drug-like small molecules continue to stimulate the development of versatile synthetic strategies. The biological properties of a typical organic compound directly depend on its molecular scaffold.^[2] Specifically, heterocyclic scaffolds with higher average saturation factor (higher proportion of sp^3 carbons) are more likely to progress through the stages of drug development than sp²-heterocycles.^[3] Besides, the configuration of an organic molecule is a key feature accounting for its biological activity.^[4] Consequently, a judicious entry to all stereoisomers of a molecule is highly desirable for stereochemistry-activity studies. Although only as the minor isomer, we have recently described the synthesis of a new spiranic azapolycyclic scaffold bearing several sterocenters through the controllable gold-catalyzed cyclization reaction of indolizidinone-tethered β-aminoallenes.^[5] Taking into account that efficient synthetic protocols for different stereoisomers of a new class of molecular scaffold open the door for further biological studies, we decided to explore the stereodivergent preparation of polyazaheterocycles (Scheme 1).

Results and Discussion

Starting materials, new indolizidinone-tethered aminoallenes 3, were obtained from cis- β -lactams 1 after several steps. (2S,3R)-4-Oxoazetidine-2-carbaldehydes **1a-d** were prepared in enantiopure form as single trans-diastereoisomers from cis-4-oxoazetidine-2-carbaldehydes through base-promoted chemoselective C-2 epimerization (Scheme 2).^[6] β-Lactam-tethered aminoallenes 2 were obtained as mixtures of chromatographically separable syn/anti isomers, taking advantage of the diphenyl hydrogen phosphate-catalyzed iminoallenylation reaction of trans-carbaldehydes with 2-[4-(trimethylsilyl)but-2-ynyl]aniline 1 (Scheme 2). β-Lactam-tethered aminoallenes syn-2ad and anti-2a-d were converted into pyrroloquinolinone-tethered β-aminoallenes syn-3a-d and anti-3a-d by treatment with sodium methoxide in methanol (Scheme 3),^[7] through a chemoselective rearrangement reaction. Partial epimerization was observed for minor isomers syn-2b-d. Fortunately, flash chromatography allowed the smooth separation of com-



Scheme 1. Stereodivergent reactivity of 4-oxoazetidine-2-carbaldehydes.



Scheme 2. Preparation of β -lactam-tethered aminoallenes *syn*-**2a**-**d** and *anti*-**2a**-**d**. *Reagents and conditions:* i) 200 mol% Na₂CO₃, acetonitrile/water (1:1), room temperature, 14 h; ii) 2 mol% (PhO)₂P(O)OH, acetonitrile, room temperature, 16–24 h. PMP = 4-MeOC₆H₄.

pounds *syn-***3b–d** from the epimeric *syn-epi-***3b–d** sub-strates.

Taking into account the sole report available in the literature on different reaction outcomes of gold-catalyzed stereoisomers,^[5] applying gold catalysis to diastereomeric indolizidinone-tethered β -aminoallenes *syn-3a-d*, *syn-epi-3b-d*, and *anti-3a-d* represents an attractive challenge in terms of stereochemically controlled reactivity. Since the catalyst may have a profound influence on the reactivity, several metallic complexes were evaluated (Table 1). Our investigation began with β -aminoallene *syn-***3a** as substrate. The reaction of *syn-***3a** in the presence of palladiumor platinum-based salts gave rise to poor conversion. Happily, improvements were observed using goldbased catalytic systems. Under the optimized conditions, treatment of β -aminoallene *syn-***3a** with 5 mol% [IPrAuCl] [IPr=1,3-bis(2,6-diisopropylphen-



Scheme 3. Preparation of indolizidinone-tethered β -aminoallenes *syn-3a–d*, *syn-epi-3b–d*, and *anti-3a–d*. *Reagents and conditions:* i) NaOMe, MeOH, room temperature, 14–40 h. PMP=4-MeOC₆H₄.

Table 1. Selective hydroamination reaction of β -aminoa	llene
syn-3a under modified metal-catalyzed conditions	

PMPHN		5 mol% catalyst 5 mol% additive DCE, r.t., <i>t</i>	► PMF	
Entry	Catalyst	Additive	<i>t</i> [h]	Yield [%] ^[a]
1	PtCl ₂	_	48	16
2 3	$PdCl_2$ AuCl_3	_	14 28	2 18
4	AuCl	-	18	21
5	$[AuClPPh_3]$	$AgSbF_6$	16 16	36 24
7	$[AuCIPPII_3]$ $[(Ph_3P)AuNTf_2]$	Ag011] –	10	34 42
8	[AuClIPr]	AgSbF ₆	14	75
9	[AuClIPr]	AgOTf	14	70
10	[AuCIIPr]	AgBF ₄ AgSbF $^{[b]}$	14	72 60
12	[AuClIPr] ^[c]	$AgSbF_6^{[c]}$	48 14	74

^[a] Yield of pure, isolated product with correct analytical and spectral data.

^[b] 1 mol% was used.

^[c] 10 mol% were used.

yl)imidazol-2-ylidene] in the presence of $AgSbF_6$ (5 mol%) gave benzo[b]pyrrolonaphthyridin-1-one **4a** in 75% yield (Table 1, entry 8). A screening of solvents (dichloromethane, tetrahydrofuran, 1,4-dioxane, toluene) revealed that the reaction is best performed in DCE (1,2-dichloroethane).

With these optimized protocols in hand, we conducted the syntheses of derivatives **4b–d** using starting materials *syn-***3b–d** (Scheme 4). With reaction times ranging from 12 to 48 h, benzo[*b*]pyrrolonaphthyridin-1-ones could be afforded in reasonable yields (66– 74%). To access more sterochemically diverse compounds, β -aminoallenes *syn-epi-***3b–d** were converted into their corresponding benzo[*b*]pyrrolonaphthyridin-1-ones *epi-***4** under the above gold-conditions (Scheme 4). Under these circumstances, specific sixmembered ring formation seems to be the exclusive tendency; with no influence of the opposite configura-



Scheme 4. Synthesis of benzo[*b*]pyrrolonaphthyridin-1-ones **4** and *epi*-**4** through gold-catalyzed intramolecular hydroamination reaction of β -aminoallenes *syn*-**3** and *syn-epi*-**3**.

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tion of the center α to the amino group and γ to the allene moiety in compounds *syn-3* and *syn-epi-3*.

It became necessary to examine whether anti-3 isomers would also serve as precursors for 6-endo-dig aminocyclizations. At this point, it was interesting to observe that β -aminoallene *anti*-3a reacted under the above gold-catalyzed conditions without formation of benzo[b]pyrrolonaphthyridin-1-one products. Noteworthy, this simple protocol allows unusual tunable selectivity. Indeed, when β -aminoallene anti-3a was treated with the catalytic system [AuClIPr]/AgSbF₆ in DCE at room temperature, spiro[benzo[e]furo-[2',3':4,5]pyrrolo[4,3,2-*hi*]indolizine-2,4'-benzo[*e*]pyrrolo[4,3,2-hi]indolizine]-1',6(2'H,4a¹H)-dione **5a** was isolated in 48% yield, along with the uncyclizated ketone **6a** (22% yield). The use of $AgSbF_6$ was tested, but it failed to catalyze the reaction in the absence of the gold salt [AuClIPr], which proved that the silver activator itself is unreactive. Next, we decided to study how the use of preformed carbene-Au(Sb_6) catalyst affected the reactivity. In the event, no appreciable differences between formed in situ and preformed complexes were found. After these control experiments it was demonstrated that the silver salt alone does not catalyze the dimerization reaction. The optimal amount of catalyst was established at 5 mol% with a ratio Au(I) salt/Ag(I) salt of 1:1. Other counter-ions provided the same reactivity but have some effect,^[8] because changing the silver salt delivered the dimeric product 5a but in lower yields (AgOTf: 30% vield, AgBF₄: 40% vield, and AgNTf₂: 36% vield). On the basis of the chemical structures of compounds 5a and 6a, it may be presumed that moisture was involved in this gold-catalyzed sequence. The scope of the spirodimerization reaction of various indolizidinone-tethered β -aminoallenes anti-3 was investigated and the results are shown in Scheme 5. The reaction occurred to give a mixture of dimeric spiro amino ketals 5 and ketones 6 with the dimeric product 5 being the major one,^[9,10] with the exception of β -aminoallene anti-3c which was free of ketone formation. Interestingly, these results indicate that the regioselectivity in the reaction was affected by the relative configuration of the precursors. It may be inferred that targeting the synthesis of dimeric spiro amino ketals **5**, the *anti*-disposition of both protons at the α and β -allenic stereocenters is required. Our divergent approach hinges on the spatial disposition of both the stereocenter α to the allene functionality and the β amino group. The structure of dimeric compounds **5** was identified by comparison with spectroscopic data from their isomers, previously reported by us.^[5] On the basis of coupling constant information between the protons in the ¹H NMR spectra of ketones **6**, the stereochemical assignment was found to be unambiguous (see Figure S1 in the Supporting Information).

The pathway depicted in Scheme 6 is proposed for the formation of fused tetracyclic products 4 and *epi*-4. Complexes *syn*-3-Au(L) and *syn-epi*-3-Au(L) were initially formed through coordination of the Au(I) salt to the distal allenic double bond. Next, regioselective 6-*endo* aminoauration forms intermediate ammonium cation type 7. Loss of proton affords neutral species 8, which followed by protonolysis of the carbon-gold bond generated diazatetracycles 4 and *epi*-4 with concurrent regeneration of the gold catalyst (Scheme 6).

It is worth noting that the reaction of β -aminoallenes *anti-3* affords adducts **5** from an allenic aminocyclization–dimerization sequence instead of that from the usually preferred conventional cycloisomerization. In order to see if ketones **6** are able to rearrange to dimeric adducts **5**, reaction of **6a** was conducted under gold catalysis. The reaction did not proceed. In the event, unaltered **6a** was recovered, and adduct **5a** was not formed. Taking into account the above experiment, the possible pathway may not involve a ketone intermediate. This experimental result, combined with our previous observations for isomeric adducts,^[5] led us to propose the following mechanism for the formation of the dimeric products (Scheme 7). Initially, [IPrAuSbF₆] coordinates to the distal allenic



Scheme 5. Synthesis of dimeric spiro amino ketals **5** and ketones **6** through gold-catalyzed reactions of β -aminoallenes *anti-3*. *Reagents and conditions:* i) 5 mol% IPrAuCl, 5 mol% AgSbF₆, DCE, room temperature, 14–46 h.



Scheme 6. Mechanistic explanation for the gold-catalyzed aminocyclization reaction of indolizidinone-tethered β -aminoallenes *syn-3* and *syn-epi-3* into benzo[*b*]pyrrolo[3,2,1-*ij*] [1,7]naphthyridin-1-ones 4 and *epi-4*.

double bond of allenes *anti*-**3** to produce *anti*-**3**-Au(L). The regioselective 5-*exo* aminocyclization reaction of the thus generated gold complex gives intermediates **9**. As experimental results reveals, dimerization *via* 5-*exo* aminocyclization falters in indolizidinone-tethered β -aminoallenes *syn*-**3**. Probably, the 5-*exo* aminoauration in *syn*-**3** is restricted by the *trans*

fusion of the hypothetical intermediate of type **9** {(1-oxohexahydrobenzo[*e*]pyrrolo[4,3,2-*hi*]indolizin-3-

ium-4-yl)methyl}gold. The loss of proton in ammonium 9 furnishes neutral species 10. Protonolysis of the carbon-gold bond of adducts 10 yields tetracyclic intermediates 11 and releases the metal catalyst into the first catalytic cycle (Scheme 7, right catalytic cycle). Species 11 may evolve to O,N-acetal 12 *via* gold-catalyzed nucleophilic addition of water.^[11] Subsequent oxidative coupling between endocyclic enamine 11 and O,N-acetal 12 with the concerted elimination of H₂, would generate spirocycles 5, therefore closing the sequence. Although merely speculative at this time, the oxidative addition of 12 to 11 under release of hydrogen should proceed with the help of molecular oxygen from air.

Conclusions

In conclusion, the present study provides insights into the manner in which the configuration of β -aminoallene precursors affects their gold-catalyzed cyclization reactions. The reactivity can be switched by using indolizidinone-tethered β -aminoallenes bearing the *syn*or *anti*-disposition of both protons at the α - and β -allenic stereocenters. Fused heterocycles are obtained from the *syn*-precursors, while a dimerization–aminoketalization–spirocyclization sequence can be achieved starting from their *anti*-isomers.



Scheme 7. Rationalization for the gold-catalyzed heterocyclization-spirodimerization reaction of indolizidinone-tethered β -aminoallenes *anti*-3.

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Experimental Section

General Methods

¹H NMR and ¹³C NMR spectra were recorded on a Bruker DPX-300, Bruker DPX-300 BACS-60 or Bruker AV 500 spectrometers in CDCl₃, except otherwise stated. Chemical shifts are given in ppm relative to TMS (¹H, 0.0 ppm) or CDCl₃ (¹³C, 77.0 ppm). Low and high resolution mass spectra were performed on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electrospray modes (ES) unless otherwise stated. Specific rotation $[\alpha]_D$ is given in $10^{-1} \text{ deg cm}^2 \text{g}^{-1}$ at 20 °C, and the concentration (c) is expressed in grams per 100 mL. All commercially available compounds were used without further purification. Flash chromatography was performed by using silica gel 60 (230-400 mesh) or neutral alumina. Products were identified by TLC (Kieselgel 60F-254). UV light ($\lambda = 254$ nm) and a solution of phosphomolybdic acid in EtOH (1 g of phosphomolybdic acid hydrate, 100 mL EtOH) was used to develop the plates.

General Procedure for the Gold-Catalyzed Reaction of Indolizidinone-Tethered β-Aminoallenes *syn*-3a–d and *syn-epi*-3b–d

Preparation of benzo[*b*]**pyrrolonaphthyridin-1-ones 4a–d and** *epi-4***b–d:** AgSbF₆ (0.01 mmol, 5 mol%) was added to a well stirred solution of IPrAuCl (0.01 mmol, 5 mol%) in 1,2-dichloroethane (3 mL), at room temperature, in the dark. The resulting mixture was stirred for 5 min and, then, the appropriate β -aminoallene *syn-3* or *syn-epi-3* (0.20 mmol) was added. The mixture was stirred at the same temperature until the total disappearances of starting material (TLC). The solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography eluting with *n*-hexane/ethyl acetate mixtures to give analytically pure tetracyclic compounds **4**.^[12]

Tetracycle (+)-4a: From 40 mg (0.11 mmol) of β-aminoallene (-)-syn-3a, and after chromatography of the residue using *n*-hexane/ethyl acetate (7:3) as eluent gave compound (+)-4a as a pale green oil; yield: 30 mg (75%); $[\alpha]_{D}$: +30.3 (c 0.3, CHCl₃). ¹H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 8.62$ (d, 1H, J=8.3 Hz, ArH), 7.30-7.15 (m, 4H, ArH), 7.06 (td, J=8.5, 1.1 Hz, 1H, ArH), 6.90 (AA'XX', 2H, ArH), 5.64 (m, 1H, =CH), 4.81-4.66 (m, 1H, H-5), 4.11-4.01 (m, 1H, NCHH), 4.02 (d, J=3.9 Hz, 1H, H-3), 3.85-3.69 (m, 1H, CHH), 3.81 (s, 3H, OCH₃), 3.67-3.47 (m, 2H, NCHH, CHH), 3.39 (s, 3 H, OCH₃), 3.21 (dd, J=8.3, 3.9 Hz, 1 H, H-4); ¹³C NMR (75 MHz, CDCl₃, 25 °C): $\delta = 169.6$ (C=O), 156.3 (Ar), 135.0 (Ar), 129.2 (Ar), 128.9 (Ar), 127.1 (Ar), 123.8 (Ar), 123.6 (Ar), 123.2 (2Ar), 119.5 (=CH), 118.6 (Ar), 114.5 (2Ar), 80.9 (C-3), 64.1 (C-4), 58.5 (OCH₃), 57.3 (NCH₂), 55.9 (C-5), 55.4 (OCH₃), 30.4 (CH₂); IR (CHCl₃): $v = 1702 \text{ cm}^{-1}$; HR-MS (ES): m/z = 363.1702, calcd. for $C_{22}H_{23}N_2O_3[M+H]^+: 363.1703.$

Tetracycle (+)-4b: From 100 mg (0.23 mmol) of β-aminoallene (+)-*syn*-3b, and after chromatography of the residue using *n*-hexane/ethyl acetate (75:25) as eluent gave compound (+)-4b as a pale green oil; yield: 71 mg (71%); $[\alpha]_D$: +97.8 (*c* 0.3, CHCl₃). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ =8.66 (d, 1H, *J*=8.2 Hz, ArH), 7.32–7.02 (m, 8H, ArH), 6.99–6.91 (m, 2H, ArH), 6.85 (*AA*′XX′, 2H, ArH), 5.64 (br s, 1H, =CH), 4.81 (br s, 1H, H-5), 4.71 (d, *J* = 12.2 Hz, 1H, OCHH), 4.58 (d, *J* = 12.2 Hz, 1H, OCHH), 4.20 (d, *J* = 4.1 Hz, H-3), 4.03 (dd, *J* = 16.9, 2.6 Hz, 1H, NCHH), 3.83 (s, 3H, OCH₃), 3.83–3.73 (m, 1H, CHH), 3.60–3.48 (m, 2H, NCHH, CHH), 3.22 (dd, *J* = 8.3, 4.1 Hz, 1H, H-4); ¹³C NMR (75 MHz, CDCl₃, 25°C): δ=169.8 (C=O), 156.5 (Ar), 145.6 (Ar), 137.0 (Ar), 135.1 (Ar), 129.2 (Ar), 128.1 (2Ar), 128.0 (2Ar), 127.5 (Ar), 127.1 (Ar), 124.5 (Ar), 123.7 (2Ar), 123.6 (Ar), 119.6 (=CH), 118.5 (2Ar), 114.5 (2Ar), 77.42 (C-3), 71.5 (OCH₂), 63.8 (C-4), 57.8 (NCH₂), 56.1 (C-5), 55.4 (OCH₃), 30.4 (CH₂); IR (CHCl₃): v=1698 cm⁻¹; HR-MS (ES): m/z = 439.2024, calcd. for C₂₈H₂₇N₂O₃ [*M*+*H*]⁺: 439.2016.

Tetracycle (+)-4c: From 41 mg (0.10 mmol) of β-aminoallene (+)-syn-3c, and after chromatography of the residue using *n*-hexane/ethyl acetate (8:2) as eluent gave compound (+)-4c as a pale green oil; yield: 27 mg (66%); $[\alpha]_D$: +193.1 $(c \ 0.5, \text{CHCl}_3)$. ¹H NMR (300 MHz, C₆D₆, 25 °C): $\delta = 9.15$ (d, 1H, J=8.2 Hz, ArH), 7.30 (m, 2H, ArH), 7.13-7.07 (m, 1H, ArH), 7.06-7.00 (m, 2H, ArH), 6.96 (AA'XX', 2H, ArH), 6.92-6.82 (m, 2H, ArH), 6.75 (t, J=7.3 Hz, 1H, ArH), 6.68 (AA'XX', 2H, ArH), 5.07 (br s, 1H, =CH), 4.83-4.73 (m, 1H, H-5), 4.80 (d, J = 4.1 Hz, 1H, H-3), 3.70–3.62 (m, 1H, NCHH), 3.32-3.16 (m, 2H, NCHH, CHH), 3.22 (s, 3H, OCH₃), 3.02 (d, J=19.8 Hz, 1H, CHH), 2.70 (dd, J=8.2, 4.1 Hz, 1 H, H-4); ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ=169.0 (C=O), 159.1 (Ar), 157.2 (Ar), 143.2 (Ar), 135.9 (Ar), 129.6 (2 Ar), 129.2 (Ar), 129.0 (Ar), 128.6 (Ar), 127.5 (Ar), 124.8 (2 Ar), 123.8 (Ar), 123.7 (Ar), 122.4 (Ar), 119.8 (=CH), 119.2 (Ar), 117.5 (2Ar), 114.7 (2Ar), 79.5 (C-3), 64.6 (C-4), 57.2 (NCH₂), 55.7 (C-5), 54.9 (OCH₃), 30.8 (CH₂); IR (CHCl₃): v = 1704 cm⁻¹; HR-MS (ES): m/z = 425.1867, calcd. for $C_{27}H_{25}N_2O_3 [M+H]^+: 425.1860$.

Tetracycle (+)-4d: From 80 mg (0.17 mmol) of β -aminoallene (-)-syn-3d, and after chromatography of the residue using *n*-hexane/ethyl acetate (8:2) as eluent gave compound (+)-4d as a pale yellow oil; yield: 59 mg (74%); $[\alpha]_D$: +183.0 (*c* 0.4, CHCl₃). ¹H NMR (300 MHz, CDCl₃, 25°C): $\delta = 8.60$ (d, 1 H, J = 8.3 Hz, ArH), 7.22 (t, J = 6.9 Hz, 2 H, ArH) 7.14-7.08 (m, 5H, ArH), 6.92 (AA'XX', 2H, ArH), 6.81 (AA'XX', 2H, ArH), 5.72 (t, J=2.5 Hz, 1H, =CH), 4.94-4.86 (m, 1H, H-5), 4.75 (d, J = 4.1 Hz, 1H, H3), 4.00(dd, J=17.3, 2.1 Hz, 1 H, NCHH), 3.84 (d, J=20.1 Hz, 1 H, CHH), 3.76 (s, 3H, OCH₃), 3.72–3.54 (m, 2H, NCHH CH*H*), 3.35 (dd, J = 8.2, 4.1 Hz, 1 H, H-4); ¹³C NMR (75 MHz, CDCl₃, 25°C): δ=168.4 (C=O), 156.8 (Ar), 156.6 (Ar), 142.3 (Ar), 134.8 (Ar), 129.2 (Ar), 129.1 (2Ar), 128.7 (Ar), 127.2 (Ar), 127.0 (Ar), 124.4 (2 Ar), 124.1 (Ar), 123.7 (Ar), 120.0 (=CH), 118.7 (Ar), 118.3 (2Ar), 114.7 (2Ar), 79.2 (C-3), 64.5 (C-4), 57.4 (NCH₂), 55.7 (C-5), 55.4 (OCH₃), 30.5 (CH₂); IR (CHCl₃): $v = 1702 \text{ cm}^{-1}$; HR-MS (ES): m/z =459.1459, calcd. for $C_{27}H_{24}CIN_2O_3 [M+H]^+: 459.1470$.

Tetracycle (+)*-epi*-**4b**: From 25 mg (0.05 mmol) of β-aminoallene (-)-*syn-epi*-**3b**, and after chromatography of the residue using *n*-hexane/ethyl acetate (7:3) as eluent gave compound (+)-*epi*-**4b** as a pale yellow oil; yield: 15 mg (60%); $[\alpha]_{\rm D}$: +96.7 (*c* 0.1, CHCl₃). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ =8.57 (dd, *J*=8.3, 1.0 Hz, 1H, ArH), 7.30–7.10 (m, 7H, ArH), 7.04–6.98 (m, 3H, ArH), 6.76 (*AA'XX'*, 2H, ArH), 5.70 (br s, 1H, –C*H*=), 4.98 (d, *J*=11.0 Hz, 1H, OCH₂), 4.55 (d, *J*=11.0 Hz, 1H, OCH₂), 4.25 (d, *J*=

11.0 Hz, 1H, H-3), 3.94–3.65 (m, 4H, CHH, H-4, H-5), 3.75 (s, 3H, OCH₃), 3.54–3.40 (m, 2H, CHH); ¹³C NMR (75 MHz, CDCl₃, 25 °C): $\delta = 171.0$ (*C*=O), 156.8 (Ar), 141.3 (Ar), 137.3 (Ar), 134.9 (*C*=), 129.2 (Ar), 128.6 (Ar), 128.3 (Ar), 128.2 (Ar), 127.8 (Ar), 127.1 (Ar), 125.7 (Ar), 123.6 (Ar), 123.2 (Ar), 120.6 (*-C*H=), 118.4 (Ar), 114.2 (Ar), 79.4 (C-3), 72.6 (OCH₂), 67.0 (C-4), 55.4 (OCH₃), 55.0 (CH₂), 50.8 (C-5), 30.4 (CH₂); IR (CHCl₃): $\nu = 1710$ cm⁻¹; HR-MS (ES): m/z = 439.2025, calcd. for C₂₈H₂₇N₂O₃ [*M*+*H*]⁺: 439.2016.

Tetracycle (+)-epi-4c: From 20 mg (0.048 mmol) of β-aminoallene (-)-syn-epi-3c, and after chromatography of the residue using n-hexane/ethyl acetate (7:3) as eluent gave compound (+)-epi-4c as a pale yellow oil; yield: 13 mg (65%); $[\alpha]_{D}$: +71.7 (*c* 0.1, CHCl₃). ¹H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 9.08$ (d, J = 8.3 Hz, 1H, ArH), 7.13–7.07 (m, 4H, ArH), 6.97-6.83 (m, 6H, ArH), 6.62 (AA'XX', 2H, ArH), 5.03 (br s, 1H, -CH=), 4.77 (d, J=11.0 Hz, 1H, H-3), 3.65-3.14 (m, 4H, CHH, CHH, H-5), 3.33 (dd, J=11.0, 9.0 Hz, 1 H, H-4), 3.26 (s, 3 H, OCH₃), 2.96 (d, J = 20.1 Hz, 1H, CH*H*); ¹³C NMR (75 MHz, C₆D₆, 25 °C): $\delta = 168.9$ (*C*= O), 159.4 (Ar), 157.4 (Ar), 135.8 (C=), 134.3 (Ar), 134.1 (Ar), 129.4 (Ar), 129.3 (Ar), 129.1 (Ar), 127.6 (Ar), 125.8 (Ar), 123.6 (Ar), 123.2 (Ar), 122.2 (Ar), 118.9 (-CH=), 117.3 (Ar), 114.6 (Ar), 80.4 (C-3), 67.2 (C-4), 55.0 (OCH₃), 54.5 (CH₂), 49.8 (C-5), 30.4 (CH₂); IR (CHCl₃): v =1712 cm⁻¹; HR-MS (ES): m/z = 425.1873, calcd. for $C_{27}H_{25}N_2O_3[M+H]^+: 425.1860.$

Tetracycle (-)-epi-4d: From 25 mg (0.054 mmol) of β aminoallene (-)-syn-epi-3d, and after chromatography of the residue using *n*-hexane/ethyl acetate (8:2) as eluent gave compound (-)-epi-4d as a pale yellow oil; yield: 15 mg (61%); $[\alpha]_{D}$: -198.2 (c 0.1, CHCl₃). ¹H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 9.06$ (d, J = 8.1 Hz, 1H, ArH), 7.14–7.08 (m, 1H, ArH), 7.03 (AA'XX', 2H, ArH), 6.92-6.86 (m, 2H, ArH), 6.88 (AA'XX', 2H, ArH), 6.81 (AA'XX', 2H, ArH), 6.62 (AA'XX', 2H, ArH), 5.04 (t, J=2.4 Hz, 1H, -CH=), 4.56 (d, J=11.0 Hz, 1H, H-3), 3.59-3.40 (m, 3H, H-5, CHH), 3.29-3.20 (m, 2H, H-4, CHH), 3.27 (s, 3H, OCH₃), 2.97 (d, J = 20.2 Hz, 1H, CHH); ¹³C NMR (75 MHz, C₆D₆, 25°C): δ=168.6 (C=O), 157.8 (Ar), 157.5 (Ar), 141.4 (Ar), 135.7 (C=), 129.4 (Ar), 129.3 (Ar), 127.2 (Ar), 126.0 (Ar), 123.8 (Ar), 123.2 (Ar), 120.7 (CH=), 118.8 (Ar), 118.7 (2 Ar), 114.6 (Ar), 80.9 (C-3), 67.1 (C-4), 55.0 (OCH₃), 54.5 (CH₂), 50.4 (C-5), 30.3 (CH₂); IR (CHCl₃): $v = 1709 \text{ cm}^{-1}$; HR-MS (ES): m/z = 459.1468, calcd. for $C_{27}H_{24}CIN_2O_3$ [M+ *H*]+: 459.1470.

General Procedure for the Gold-Catalyzed Reaction of Indolizidinone-Tethered β-Aminoallenes *anti-3b-d*

Preparation of spiro[benzo[*e*]furo[2',3':4,5]pyrrolo[4,3,2*hi*]indolizine-2,4'-benzo[*e*]pyrrolo[4,3,2-*hi*]indolizine]-

1',6(2'H,4a¹H)-diones 5a–d and ketones 6a,b and 6d: AgSbF₆ (0.01 mmol, 5% mol) was added to a well stirred solution of IPrAuCl (0.01 mmol, 5% mol) in 1,2-dichloroethane (3 mL), at room temperature, in the dark. The resulting mixture was stirred for 5 min and, then, the appropriate β -aminoallene *anti*-3 (0.20 mmol) was added. The mixture was stirred at the same temperature until the total disappearances of starting material (TLC). The solvent was removed under reduced pressure and the residue was purified by flash neutral alumina column chromatography eluting with n-hexane/ethyl acetate mixtures to give analytically pure dimeric spiro amino ketals **5** and ketones **6**.

Preparation of dimeric spiro amino ketal (+)-5a and ketone (–)-6a: From 100 mg (0.28 mmol) of β -aminoallene (+)-*anti*-**3a**, and after chromatography of the residue using hexanes/ethyl acetate (55:45 \rightarrow 15:85) as eluent, the less polar compound (–)-**6a** (yield: 24 mg, 22%) and the more polar compound (+)-**5a** (yield: 50 mg, 48%) were obtained.

Dimeric spiro amino ketal (+)-5a: Pale yellow oil; $[\alpha]_{D}$: +31.0 (c 0.1, CHCl₃). ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 8.12$ (d, 1H, J = 8.2 Hz, ArH), 7.29 (m, 1H, ArH), 7.24– 7.11 (m, 4H, ArH), 7.06–6.85 (m, 9H, ArH), 6.70 (d, J=8.7, 1H, ArH), 4.77 (m, 2H, H4, H4'), 4.26 (d, J=4.7 Hz, 1H, H-3) 4.19 (t, J=6.4, 1H, H-5'), 4.10 (d, J=4.6 Hz, 1H, H-3'), 4.01 (d, J=8.0 Hz, 1 H, H-5"), 3.90 (s, 3 H, OCH₃), 3.89 (s, 3 H, OCH₃), 3.51 (s, 3 H, OCH₃), 3.03 (d, *J*=15.2 Hz, 1 H, C_{Ar}-CHH) 2.97 (s, 3H, OCH₃), 2.87 (d, J=18.3 Hz, 1H, CHH), 2.45 (q, J=6.3 Hz, 1H, CHH), 1.98-1.73 (m, 3H, C-5"-CHH, CAr-CHH, H-5"), 1.11 (m, 1H, C-5"-CHH), 1.06 (s, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃, 25 °C): $\delta = 170.2$ (C=O), 169.6 (C=O), 157.9 (Ar), 152.4 (Ar), 139.7 (Ar), 136.4 (Ar), 135.9 (Ar), 133.6 (Ar), 133.4 (Ar), 128.4 (Ar), 128.1 (Ar), 127.11 (Ar), 127.0 (Ar), 126.4 (Ar), 125.5 (Ar), 124.5 (Ar), 123.5 (Ar), 120.65 (Ar), 117.04 (4Ar), 114.5 (Ar), 113.15 (Ar), 107.12 (O-Cspir-N) 86.5 (O-Cspir), 83.0 (C-3), 80.5 (C-3'), 75.3 (C-Me), 60.6 (C-5"), 60.3 (OCH₃), 60.0 (OCH₃), 59.0 (C-5'), 58.2 (C-4'), 56.6 (C-4), 55.7 (OCH₃), 55.5 (OCH₃) 53.2 (C-5), 36.5 (CH₂), 34.9 (C_{Ar}-CH₂), 29.5 (C-5"-CH₂), 25.0 (CH₃); IR (CHCl₃): v =1710 cm⁻¹; HR-MS (ES): m/z = 741.3307, calcd. for $C_{44}H_{45}N_4O_7 [M+H]^+: 741.3283.$

Ketone (-)-6a: Colorless oil; $[\alpha]_D$: -7.2 (*c* 0.1, CHCl₃). ¹H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 8.80$ (d, 1 H, J =7.9 Hz, ArH), 7.29–7.24 (m, 1H, ArH), 7.15 (d, J=7.0 Hz, 1H, ArH), 7.06 (t, *J*=7.2 Hz, 1H, ArH), 6.76 (AA'*XX*', 2H, ArH), 6.58 (AA'XX', 2H, ArH), 4.44 (ddd, J=8.8, 6.3, 4.6 Hz, 1 H, H-4), 4.22 (d, J = 6.4 Hz, 1 H, H-3), 4.20 (dd, J =10.5, 4.5 Hz, 1 H, H-5), 3.74 (s, 3 H, OCH₃), 3.63 (d, J =8.7 Hz, 1H, NH), 3.36 (s, 3H, OCH₃), 3.28 (ddd, J=12.7, 10.7, 4.6 Hz, 1 H, H-6), 3.12 (dd, J=16.0, 4.6 Hz, CHH), 2.84 (dd, J=15.7, 13.0 Hz, 1H, CHH), 2.08 (s, 3H, CH₃CO);¹³C NMR (125 MHz, CDCl₃, 25 °C): $\delta = 209.6$ (C=O), 169.3 (C=O), 153.0 (Ar), 141.4 (Ar), 135.5 (Ar), 128.8 (Ar), 127.7 (Ar), 124.0 (Ar), 123.9 (Ar), 119.2 (Ar), 115.5 (2Ar), 114.9 (2Ar), 79.3 (C-3), 59.7 (C-4), 58.9 (OCH₃), 55.7 (OCH₃), 52.8 (C-5), 44.9 (C-6), 31.2 (CH₂), 29.7 (CH₃); IR (CHCl₃): $v = 1704 \text{ cm}^{-1}$; HR-MS (ES): m/z = 381.1810, calcd. for $C_{22}H_{25}N_2O_4 [M+H]^+: 381.1809.$

Preparation of dimeric spiro amino ketal (+)-5b and ketone (–)-6b: From 125 mg (0.28 mmol) of β -aminoallene (+)-*anti*-**3b**, and after chromatography of the residue using hexanes/ethyl acetate (7:3 \rightarrow 1:1) as eluent, the less polar compound (–)-**6b** (yield: 13 mg, 10%) and the more polar compound (+)-**5b** (yield: 41 mg, 34%) were obtained.

Dimeric spiro amino ketal (+)-5b: Pale yellow oil; $[\alpha]_{D}$: +4.8 (*c* 0.1, CHCl₃). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 8.12 (d, 1H, *J*=8.2 Hz, Ar), 7.30–7.21 (m, 7H, ArH), 7.20– 7.10 (m, 8H, ArH), 7.03 (t, *J*=7.4 Hz, 1H, ArH), 6.91 (s, 4H, Ar), 6.86–6.82 (m, 4H, ArH), 6.71 (d, *J*=7.4 Hz, 1H, ArH), 4.95 (d, *J*=12.6 Hz, 1H, OCHH'), 4.78–4.74 (m, 3H, H-4', H-4, OCHH'), 4.65 (d, *J*=12.3 Hz, 1H, OCHH), 4.40

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(d, J=4.6, Hz, 1H, H-3'), 4.30 (t, J=6.2 Hz, 2H, H-3, OCHH), 4.17 (dd, J=8.0, 1.3 Hz, 1H, H-5'), 3.97 (d, J= 4.5 Hz, H-5) 3.90 (s, 6H, 2OCH₃), 3.03 (d, J=15.2 Hz, 1H, CHH), 2.83 (d, J = 18.4 Hz, 1H, C_{Ar}-CHH), 2.45 (ddd, J =14.1, 8.0, 1.5 Hz, 1 H, H-5"), 2.01 (d, J=15.2 Hz, 1 H, CHH), 1.84–1.79 (m, 2H, C_{Ar}-CH*H*, C-5″-CHH), 1.14–1.09 (m, 4H, C-5″-CH*H*, CH₃); ¹³C NMR (125 MHz, CDCl₃, 25°C): $\delta =$ 170.5 (C=O), 170.4 (C=O), 157.8 (Ar), 152.5 (Ar), 139.8 (Ar), 137.7 (Ar), 137.6 (Ar), 136.7 (Ar), 135.8 (Ar), 133.6 (Ar), 133.4 (Ar), 128.5 (Ar), 128.1 (2 Ar), 127.8 (2 Ar), 127.7 (2 Ar), 127.5 (Ar), 127.1 (2 Ar), 127.0 (Ar), 126.9 (Ar), 126.3 (Ar), 125.4 (Ar), 124.5 (Ar), 123.4 (Ar), 120.6 (Ar), 117.4 (2 Ar), 114.5 (Ar), 113.3 (Ar), 107.2 (O-Cspir-N), 86.4 (O-Cspir), 79.2 (C-3'), 77.4 (C-3), 75.3 (C-Me), 73.0 (OCH₂), 72.8 (OCH₂'), 60.6 (C-5), 58.9 (C-4'), 58.2 (C-5'), 56.8 (C-4), 55.7 (OCH₃), 55.5 (OCH₃), 52.9 (C-5"), 36.4 (C_{Ar}-CH₂), 35.0 (CH_2) , 29.4 $(C-5''-CH_2)$, 25.0 (CH_3) ; IR $(CHCl_3)$: v =1710 cm⁻¹; HR-MS (ES): m/z = 893.3895, calcd. for $C_{56}H_{53}N_4O_7 [M+H]^+: 893.3909.$

Ketone (-)-6b; Pale yellow oil; $[\alpha]_D$: -4.7 (*c* 0.1, CHCl₃). ¹H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 8.79$ (d, J = 8.3 Hz, 1H, ArH), 7.33–7.18 (m, 6H, ArH), 7.14 (d, J=7.1 Hz, 1H, ArH), 7.05 (t, J=7.4 Hz, 1H, ArH), 6.75 (AA'XX', 2H, ArH), 6.56 (AA'XX', 2H, ArH), 4.6 (s, 2H, OCH₂), 4.34 (br s, 2H, H-3, H-4), 4.15 (dd, J=10.6, 4.1 Hz, 1H, H-5), 3.76 (s, 3H, OCH₃), 3.76–3.68 (br s, 1H, NH), 3.27 (ddd, J=13.0, 10.8, 4.3 Hz, 1 H, H-6), 3.10 (dd, J=16.0, 4.6 Hz, CHH), 2.83 (dd, J=16.0, 12.9 Hz, 1 H, CHH), 2.08 (s, 3 H, CH₃CO);¹³C NMR (125 MHz, CDCl₃, 25 °C): $\delta = 209.6$ (C=O), 169.7 (C=O), 153.0 (Ar), 141.5 (Ar), 136.6 (Ar), 135.6 (Ar), 128.8 (Ar), 128.4 (2Ar), 128.1 (2Ar), 128.0 (Ar), 127.7 (Ar), 124.0 (Ar), 123.9 (Ar), 119.1 (Ar), 115.8 (2Ar), 114.9 (2Ar), 76.3 (C-3), 72.7 (OCH₂), 59.7 (C-4), 55.7 (OCH₃), 53.2 (C-5), 45.0 (C-6), 31.3 (CH₂), 29.8 (CH₃); IR (CHCl₃): v =1699 cm⁻¹; HR-MS (ES): m/z = 457.2124, calcd. for $C_{28}H_{29}N_2O_4 [M+H]^+: 457.2122.$

Dimeric spiro amino ketal (+)-5c: From 54 mg (0.13 mmol) of β -aminoallene (+)-anti-3c, and after chromatography of the residue using *n*-hexane/ethyl acetate (55:45) as eluent gave compound (+)-5c as a colorless solid; yield: 23 mg (42%); mp 250–252 °C; $[\alpha]_{D}$: +103.4 (*c* 0.3, CHCl₃). ¹H NMR (500 MHz, C₆D₆, 25°C): $\delta = 8.65$ (d, 1 H, J =8.2 Hz, ArH), 7.65 (d, 1H, J=7.3, ArH), 7.08-7.04 (m, 5H, ArH), 7.02-6.96 (m, 4H, ArH), 6.92-6.90 (m, 3H, ArH), 6.83-6.76 (m, 8H, ArH), 6.65 (d, 2H, J=7.8 Hz, ArH), 6.50 (d, J=8.7, 2H, ArH), 4.70 (d, J=5.6, 2H, H-3, H-3'), 4.59 (t, J=6.4, 1H, H-5'), 4.38 (t, J=4.6 Hz, 1H, H-4), 4.01 (t, J=6.4, 1J=8.0, Hz, 1H, H-4', 3.68 (d, J=4.4 Hz, 1H, H-5''), 3.57 (s, 3H, OCH₃), 3.41 (s, 3H, OCH₃), 2.80 (m, 2H, CHH, C_{Ar}-CHH), 2.30 (q, J=6.3 Hz, 1 H, H-5), 1.79 (m, 3 H, C_{Ar}-CHH, C-5"-CHH, CHH), 1.05 (m, 1H, C-5"-CHH), 0.85 (s, 3H, CH₃); ¹³C NMR (125 MHz, C₆D₆, 25 °C): $\delta = 168.8$ (C=O), 168.3 (C=O), 159.7 (Ar), 159.5 (Ar), 158.3 (Ar), 153.1 (Ar), 140.0 (Ar), 136.9 (Ar), 136.6 (Ar), 134.4 (Ar), 134.3 (Ar), 129.4 (4Ar), 129.1 (4Ar), 128.8 (Ar), 127.5 (Ar), 127.4 (Ar), 126.5 (Ar), 125.5 (Ar), 124.8 (Ar), 124.1 (Ar), 122.0 (Ar), 121.6 (Ar), 121.1 (Ar), 117.9 (Ar), 116.6 (4Ar), 116.2 (4Ar), 107.4 (O-Cspir-N), 86.6 (O-Cspir), 80.3 (C-3), 77.7 (C-3'), 75.6 (C-Me), 60.9 (C-5"), 59.0 (C-5'), 58.4 (C-4'), 57.0 (C-4), 55.4 (OCH₃), 55.3 (OCH₃), 53.4 (C-5), 36.9 (C_{Ar}-CH₂), 35.1 (CH_2) , 29.7 $(C-5''-CH_2)$, 24.8 (CH_3) ; IR $(CHCl_3)$: v=

1714 cm⁻¹; HR-MS (ES): m/z = 865.3636, calcd. for $C_{54}H_{49}N_4O_7 [M+H]^+$: 865.3596.

Preparation of dimeric spiro amino ketal (+)-5d and ketone (–)-6d: From 100 mg (0.22 mmol) of β -aminoallene (+)-*anti*-3d, and after chromatography of the residue using hexanes/ethyl acetate (8:2 \rightarrow 1:1) as eluent, the less polar compound (+)-6d (yield: 20 mg, 20%) and the more polar compound (+)-5d (yield: 40 mg, 42%) were obtained.

Dimeric spiro amino ketal (+)-5d: Pale yellow oil; $[\alpha]_D$: +30.0 (c 0.1, CHCl₃). ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 8.13$ (d, 1H, J = 8.2 Hz, Ar), 7.32 (d, 1H, J = 7.6 Hz, ArH), 7.26-7.18 (m, 3H, ArH), 7.16-7.11 (m, 3H, ArH), 7.04 (t, J=7.5 Hz, 1H, ArH), 7.00 (AA'XX', 2H, ArH), 6.97-6.91 (m, 1H, ArH), 6.92-6.77 (m, 6H, ArH), 6.71-6.63 (m, 4H, ArH), 6.40 (AA'XX', 2H, ArH), 5.14 (d, J=4.7 Hz, 1H, H-3), 5.03 (d, J=6.4 Hz, 1H, H-3'), 4.91 (t, J=4.6 Hz, 1 H, H-5), 4.88 (t, J = 6.4 Hz, 1 H, H-4'), 4.28 (t, J = 6.6 Hz, 1 H, H-5'), 4.11 (d, J = 4.4 Hz, 1 H, H-5), 3.89 (s, 3 H, OCH₃), 3.84 (s, 3H, OCH₃), 3.04 (d, J=15.2 Hz, 1H, C_{Ar}-CHH), 2.84 (d, J=18.3 Hz, 1 H, CHH), 2.48 (q, J=5.6 Hz, 1 H, H-5"), 2.03 (d, J = 15.2 Hz, 1H, C_{Ar}-CHH) 1.86–1.82 (m, 2H, C-5"-CHH, CHH), 1.15 (dd, J = 13.4, 6.2 Hz, 1H, C-5"-CHH), 1.09 (s, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃, 25°C): $\delta = 168.5$ (C=O), 168.2 (C=O), 159.9 (Ar), 157.2 (Ar), 156.9 (Ar), 152.7 (Ar), 139.5 (Ar), 135.6 (Ar), 135.5 (Ar), 133.4 (Ar), 133.2 (Ar), 129.1 (2 Ar), 128.6 (2 Ar), 128.5 (Ar), 128.1 (Ar), 127.2 (Ar), 127.1 (Ar), 126.6 (Ar), 126.2 (Ar), 125.3 (Ar), 124.9 (Ar), 123.5 (Ar), 120.7 (Ar), 117.5 (Ar), 117.1 (2Ar), 116.5 (2Ar), 107.1 (O-Cspir-N), 86.6 (O-Cspir), 79.9 (C-3), 76.9 (C-3'), 75.4 (C-Me), 60.8 (C-5"), 58.4 (C-5'), 58.3 (C-4'), 56.5 (C-5), 55.7 (OCH₃), 55.6 (OCH₃), 53.0 (C-5), 36.3 (CH₂), 35.0 (C_{Ar}-CH₂), 29.5 (C5-"-CH₂), 25.0 (CH₃); IR (CHCl₃): $v = 1714 \text{ cm}^{-1}$; HR-MS (ES): m/z =933.2796, calcd. for $C_{54}H_{47}Cl_2N_4O_7 [M+H]^+$: 933.2816.

Ketone (+)-6d: Colorless oil; $[\alpha]_{D}$: +6.1 (*c* 0.1, CHCl₃). ¹H NMR (500 MHz, CDCl₃, 25 °C): $\delta = 8.84$ (d, 1 H, J =8.3 Hz, ArH), 7.19-7.07 (m, 5H, ArH), 6.82 (AA'XX', 2H, ArH), 6.66 (AA'XX', 2H, ArH), 6.51 (AA'XX', 2H, ArH), 5.05 (d, J = 6.4 Hz, 1 H, H-3), 4.60 (ddd, J = 9.5, 6.5, 4.2 Hz, 1 H, H-4), 4.30 (dd, J = 10.5, 4.6 Hz, 1 H, H-5), 3.71 (s, 3 H, OCH₃), 3.59 (d, *J*=10.5 Hz, 1 H, NH), 3.33 (ddd, *J*=12.8, 10.5, 4.5 Hz, 1 H, H-6), 3.15 (dd, J=15.9, 4.5 Hz, CHH), 2.89 $(dd, J=15.7, 12.9 Hz, 1H, CHH), 2.12 (s, 3H, CH_3CO);$ ¹³C NMR (125 MHz, CDCl₃, 25 °C): $\delta = 209.2$ (C=O), 168.3 (C=O), 156.5 (Ar), 153.2 (Ar), 141.0 (Ar), 135.4 (Ar), 129.3 (2 Ar), 129.1 (Ar), 127.8 (Ar), 127.2 (Ar), 124.3 (Ar), 124.0 (Ar), 119.0 (Ar), 117.6 (2Ar), 116.2 (2Ar), 114.7 (2Ar), 77.6 (C-3), 59.5 (C-4), 55.7 (OCH₃), 53.8 (C-5), 44.9 (C-6), 31.1 (CH₂), 29.7 (CH₃); IR (CHCl₃): $v = 1704 \text{ cm}^{-1}$; HR-MS (ES): m/z = 477.1579, calcd. for $C_{27}H_{26}ClN_2O_4$ $[M+H]^+$: 477.1576.

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actinophenanthroline B

actinophenanthroline C

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- [12] Experimental procedures as well as full spectroscopic and analytical data for compounds not included in this Experimental Section are described in the Supporting Information. It contains compound characterization data, experimental procedures, and copies of NMR spectra for all new compounds.