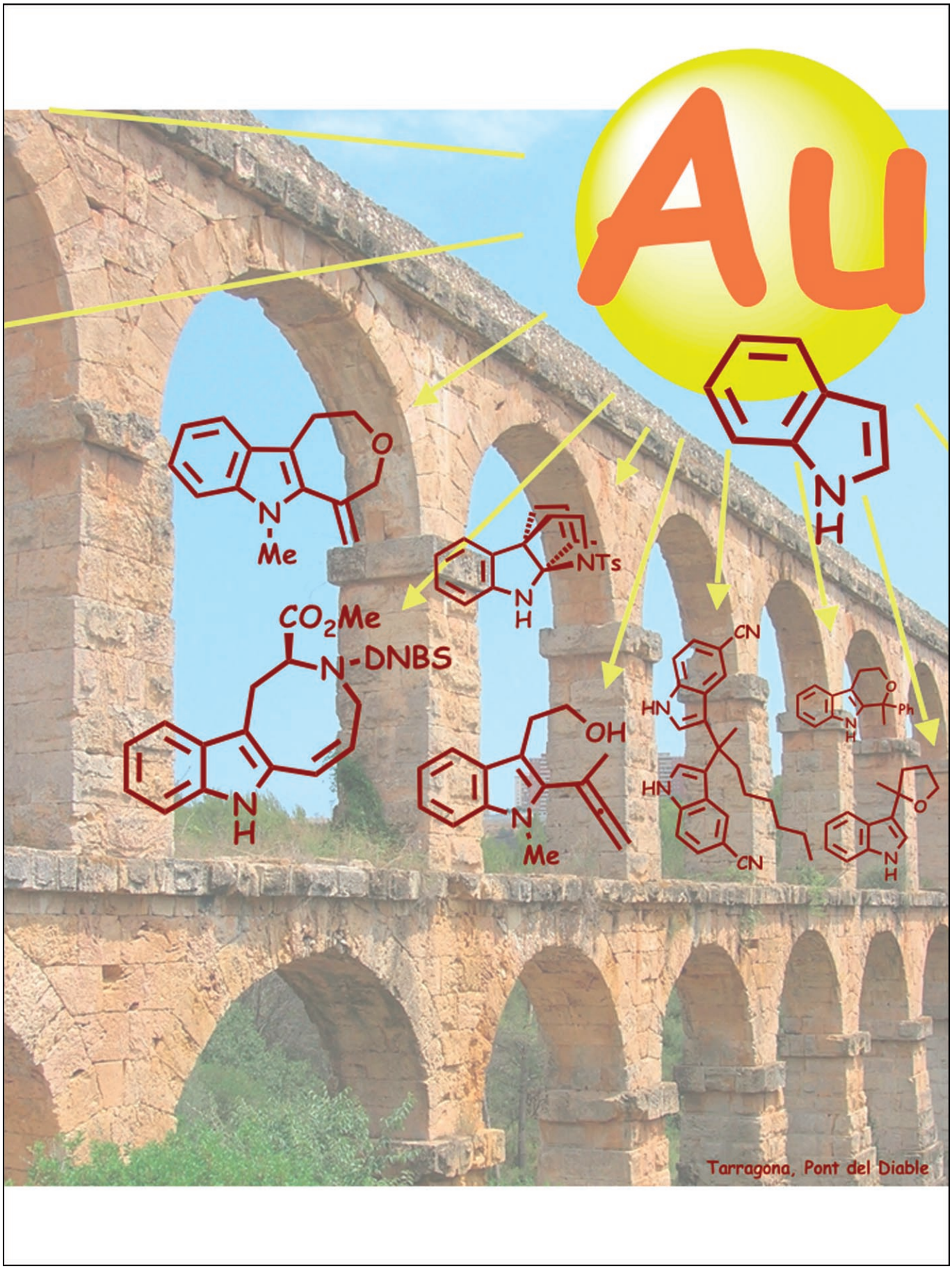
FULL PAPER

DOI: 10.1002/chem.200601324



Intra- and Intermolecular Reactions of Indoles with Alkynes Catalyzed by Gold

Catalina Ferrer, Catelijne H. M. Amijs, and Antonio M. Echavarren*[a]

Abstract: Indoles react intramolecularly with alkynes in the presence of gold catalysts to give from six- to eight-membered-ring annulated compounds. The cationic Au^I complex [Au(P{C_6H_4-(*o*-Ph)}(tBu)$_2$)(NCMe)]SbF_6 is the best catalyst for the formation of six- and seven-membered rings by 6-*endo-dig*, 6-*exo-dig*, and 7-*exo-dig* cyclizations. Indoloazocines are selectively obtained with $AuCl_3$ as catalyst in a rare 8-*endo-dig* process. In this process allenes or tetracyclic annulated derivatives are also formed as a result of an initial fragmentation reaction. The intermolecular reaction of indoles with alkynes proceeds to form 3-alkenylated intermediates that react with a second equivalent of indole to give bisindolyl derivatives. Indoles that are substituted at the 3-position react intermolecularly with alkynes to give 2-alkenylated intermediates that can be trapped intramolecularly with the appropriate nucleophiles.

Keywords: alkynes · allenes · cyclization · gold · homogeneous catalysis · indoles

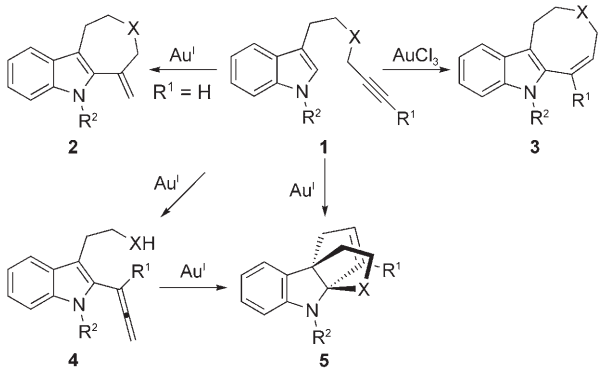
Introduction

The hydroarylation of alkynes (or alkenylation of arenes) catalyzed by electrophilic transition-metal complexes is a valuable method for the synthesis of alkenyl arenes and heteroarenes.[1,2] Reetz[3] and He[4] found independently that gold complexes are particularly active catalysts for the intermolecular hydroarylation of alkynes.[5] The intramolecular version was developed by the group Murai and Chatani by using Ru^{II}, Pt^{II},[6] or $GaCl_3$[7] as catalysts. Fürstner reported a similar reaction for the synthesis of phenanthrenes that is catalyzed by $PtCl_2$ or other metal halides.[8] Sames developed an intramolecular hydroarylation catalyzed by $PtCl_4$ that proceeds under mild conditions.[9] Cycloisomerization of ω-aryl-1-alkynes has also been performed by Nishizawa with Hg^{II} as catalyst.[10,11]

We have reported the cyclization of aryl alkynes with Pt^{II} or Au^I catalysts.[12,13] For the 5-*exo-dig* pathway, the two atoms tethering the arene and the alkyne are not enough to allow for the formation of a low-energy Wheland intermediate.

Our computational work[12] indicates that two pathways can compete in these processes: a Friedel–Crafts alkenylation and a reaction proceeding through metal cyclopropyl carbenes, which show very similar activation energies. A third mechanism was found by Fürstner in the cyclization of haloalkynyl biphenyls to form phenanthrenes with AuCl as catalyst; in this reaction the halide suffers a 1,2-shift, which indicates that in these cases the reaction proceeds via a gold vinylidene species.[8,14,15]

We found that substrates **1** cyclize readily with a cationic gold(I) complex to give azepino[4,5-*b*]indole derivatives **2**,[16,17] whereas the use of $AuCl_3$[18] leads to indoloazocines **3** by a 8-*endo-dig* process, a cyclization that has not been observed in other hydroarylations of alkynes (Scheme 1).[19] In certain cases, by performing the reactions with Au^I catalysts



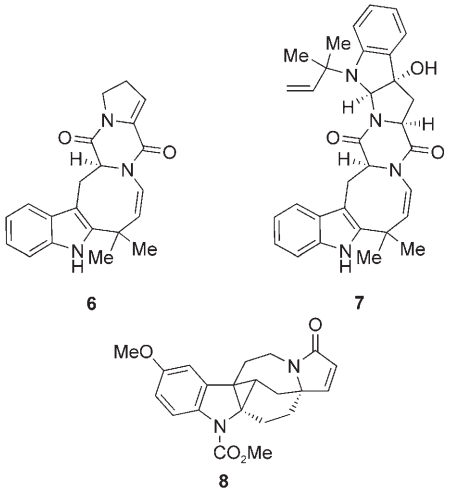
Scheme 1.

[a] C. Ferrer, Dr. C. H. M. Amijs, Prof. Dr. A. M. Echavarren
Institute of Chemical Research of Catalonia (ICIQ)
Av. Països Catalans 16, 43007 Tarragona (Spain)
Fax: (+34) 977-920-225
E-mail: aechavarren@iciq.es

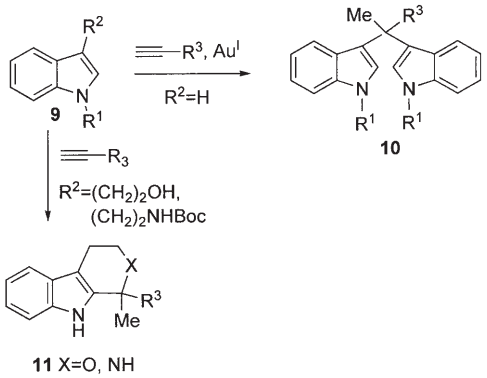
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

for longer reaction times, allenes **4** could also be formed.[20] These allenes can react further with Au^I to form tetracyclic compounds **5**. The remarkable domino transformation of **1** into **5** could be done in one step by using Au^I as catalyst.

Formation of the indoloazocine nucleus **3** is of considerable interest as this ring system is present in some indole alkaloids such as deoxyisoaustamide (**6**),[21,22] okaramine N (**7**),[23] and the lundurines (i.e. lundurine A, **8**).[24,25,26]



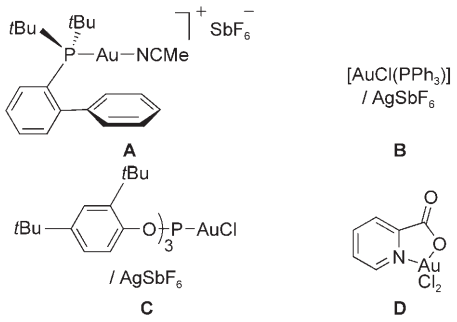
We have also found that simple indoles **9** react with terminal alkynes to form 2:1 adducts **10** in the presence of Au^I catalysts (Scheme 2).[27] Furthermore, in the case of tryptophol and tryptamine derivatives, this reaction leads to compounds **11**, in a reaction that is reminiscent of the Pictet–Spengler process.[28]



Scheme 2.

Results and Discussion

Cyclization of indoles with alkynes: We tested new Au^I complexes bearing bulky phosphanes[29,30] in the reaction of indoles with alkynes. In general, for the formation of seven-membered rings **2** (Scheme 1) the best catalyst is cationic gold(I) complex **A**,[30,31] which allows us to perform the reactions in the absence of Ag^I salts. This complex is an air-stable white solid, which is readily prepared from the corresponding gold chloride complex. In addition to catalyst **A**, we routinely screened in most cases the performance of Au^I catalysts **B**, **C**,[32] Au^{III} catalyst **D**,[33] as well as AuCl and $AuCl_3$.

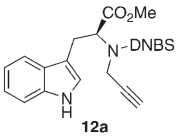
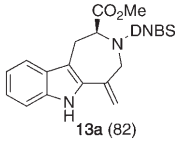
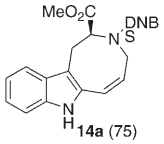
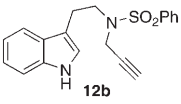
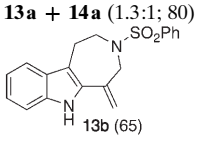
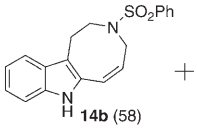
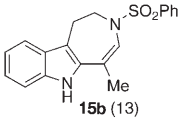
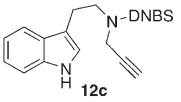
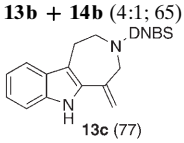
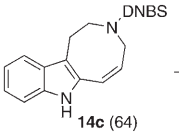
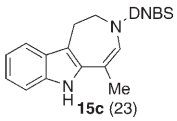
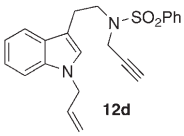
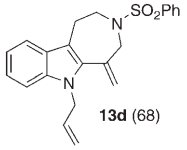
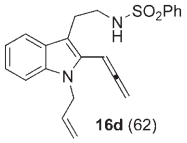
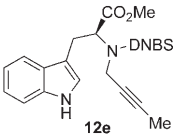
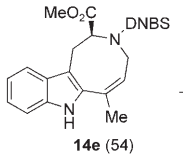
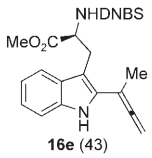
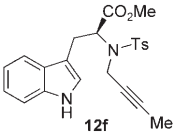
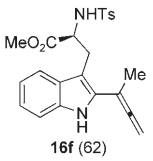
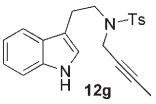
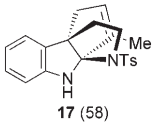


Among the solvents screened ($MeNO_2$, acetone, DMF, CH_2Cl_2, toluene), the best results were usually obtained in CH_2Cl_2, although toluene could also be used. Thus, tryptophane derivative **12a** reacted cleanly with complex **A** as catalyst at room temperature for 30 min to give azepino[4,5-*b*]indole **13a** (Table 1, entry 1).[34] In contrast, reaction of **12a** with $AuCl_3$ cleanly gave indoloazocine **14a** (Table 1, entry 2). Reaction with AuCl also provided **14a**, although in this case significant amounts of depropargylated starting material were also obtained (Table 1, entry 3). Reaction of **12a** with catalyst **B** was less selective and a 1.3:1 mixture of **13a** and **14a** was obtained (Table 1, entry 4). Similar results were obtained from **12b** and **12c** (Table 1, entries 5–9), although in these cases reaction with $AuCl_3$ gave indoloazocines **14b** and **14c** along with seven-membered ring derivatives **15b** and **15c**, respectively (Table 1, entries 6 and 9). Reactions with AuCl only led to low conversions. As expected, treatment of **13b** with 5 mol% $AuCl_3$ (CH_2Cl_2, room temperature, 16 h) led quantitatively to **15b**. *N*-Allylindole **12d** provided seven-membered ring derivative **13d** with catalyst **A** (Table 1, entry 10). Protic acids do not promote the cyclization of these substrates. Thus, treatment of **12b** with *p*-toluenesulfonic acid (10 mol%) in CH_2Cl_2 at room temperature for 16 h led only to unchanged starting material.

Surprisingly, when indole **12d** was treated with $AuCl_3$ (2 mol%) in CH_2Cl_2 at room temperature for 16 h, allene **16d** was obtained as a result of an overall intramolecular allenylation at C-2 of the indole by the *N*-propargyl chain (Table 1, entry 11). Tryptophane derivative **12e** provided indoloazocine **14e** (54%) and allene **16e** (43%) after being heated in toluene at 90°C with catalyst **A**. Allene **16f** was also obtained in 62% yield in the reaction of **12f** (Table 1, entry 13). On the other hand, **12g** gave tetracyclic derivative **17** (58%) (Table 1, entry 14). The structure of **17** was confirmed by X-ray crystallography.[35] Importantly from the mechanistic point of view (see below), tryptamine derivative **12h**, with a methyl group at the 2-position, underwent cyclization with catalyst **A** to form cleanly spiro 2-methyleneindolenenine **18** (Table 1, entry 15).

Propargylic tryptophol derivatives also led to cyclized compounds with gold(I) catalysts (Table 2).[34] Thus **19a** re-

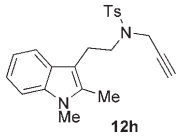
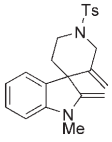
Table 1. Cyclization of tryptophane and tryptamine derivatives with alkynes catalyzed by gold.[a]

	Indole	Catalyst	*t* [h]	Product(s) (ratio; yield [%])
1	 **12a**	**A**	0.5	 **13a** (82)
2	**12a**	$AuCl_3$	0.5	 **14a** (75)
3	**12a**	AuCl	1	**14a** (70)
4	**12a**	**B**	0.5	**13a** + **14a** (1.3:1; 80)
5	 **12b**	**A**	16	 **13b** (65)
6	**12b**	$AuCl_3$	24	 **14b** (58) +  **15b** (13)
7	**12b**	**B**	16	**13b** + **14b** (4:1; 65)
8	 **12c**	**A**	16	 **13c** (77)
9	**12c**	$AuCl_3$	16	 **14c** (64) +  **15c** (23)
10	 **12d**	**A**	0.5	 **13d** (68)
11	**12d**	$AuCl_3$	16	 **16d** (62)
12[b]	 **12e**	**A**	1	 **14e** (54) +  **16e** (43)
13	 **12f**	**A**	16	 **16f** (62)
14[b]	 **12g**	**A**	48	 **17** (58)

acted with catalyst **A** at room temperature to give a mixture of oxepino[4,5-*b*]indole **20a** and allene **21a** (Table 2, entry 1). Oxepino[4,5-*b*]indole **20b** was the exclusive product in the cyclization of **19b** with catalyst **A**, whereas AuCl or catalyst **D** led to mixtures of **20b** and allene **21b** (Table 2, entries 2–4). Similar results were obtained in the reactions of **19c** and **19d** with catalyst **A** (Table 2, entries 5 and 6). Reaction of substrate **19e** with a disubstituted alkyne proceeded more sluggishly to furnish allene **21e** and tetracycle **22e** (Table 2, entry 7). Tetracyclic derivative **22e** was the only isolated product when the reaction was carried out in toluene at 90 °C (Table 2, entry 8). Cyclization of **19f** and **19g** with catalyst **A** proceeded similarly to give mixtures of diastereomers **22f**/**22f′** and **22g**/**22g′**, respectively (Table 2, entries 9 and 10). Only traces of eight-membered ring compounds were detected in the crude reaction mixtures when $AuCl_3$ or AuCl were used as catalysts in transformations of tryptophol derivatives **19a–g**.

Substrate **23**, with a tether of only three atoms, reacted satisfactorily with catalyst **A** by a 6-*exo-dig* pathway to give **24** (Table 3, entry 1), whereas catalyst **B** gave **24** in lower yield along with dimer **25** (Table 3, entry 2).[34] The configuration of **25** at the exocyclic double bond of **25** was determined by a NOESY experiment. Decomposition of **23** was observed with $AuCl_3$. Reaction of **26** with an unprotected propargyl alcohol moiety proceeded uneventfully with Au^I catalyst **A** to give **27** (Table 3, entry 3). In contrast, reaction of **26** with catalyst $AuCl_3$ furnished ketone **28**, as a result of isomerization of the exocyclic double bond (Table 3, entry 4).

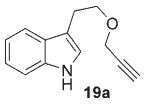
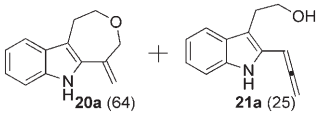
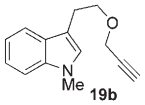
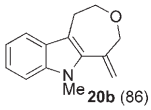
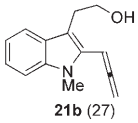
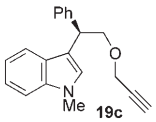
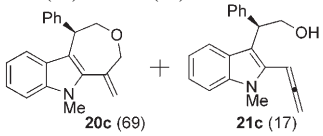
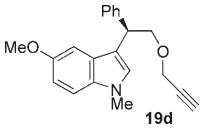
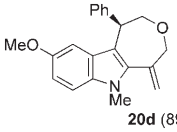
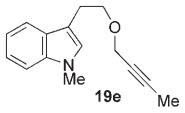
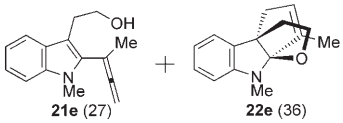
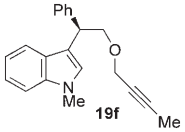
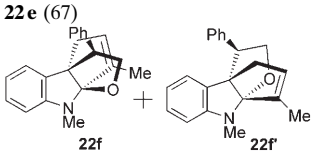
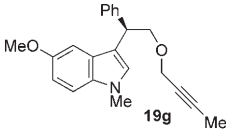
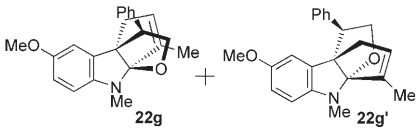
Table 1. (Continued)

	Indole	Catalyst	*t* [h]	Product(s) (ratio; yield [%])
15[b]	 **12h**	**A**	16	 **18** (80)

[a] Reactions in CH_2Cl_2 at room temperature with 5 mol% catalyst. [b] Reaction in toluene at 90°C. DNBS: 2,4-dinitrobenzenesulfonyl.

Derivative **29**, a substrate with a tether of only two atoms, reacted by a 6-*endo-dig* pathway with Au^I catalysts **A** or **B** to give **30** (Table 3, entries 5 and 6). In this case, no cyclization was observed with $AuCl_3$.

Table 2. Cyclization of tryptophol derivatives with alkynes catalyzed by gold.[a]

	Indole	Catalyst	*t* [h]	Product(s) (ratio; yield [%])
1	 **19a**	**A**	16	 **20a** (64) + **21a** (25)
2	 **19b**	**A**	1	 **20b** (86)
3	**19b**	AuCl	36	**20b** (14) +  **21b** (27)
4[b]	**19b**	**D**	16	**20b** (22) + **21b** (38)
5	 **19c**	**A**	0.5	 **20c** (69) + **21c** (17)
6	 **19d**	**A**	1	 **20d** (89)
7	 **19e**	**A**	24	 **21e** (27) + **22e** (36)
8[b]	**19e**	**A**	1.5	**22e** (67)
9[b]	 **19f**	**A**	1.5	 **22f** + **22f'**
10[b]	 **19g**	A	1.5	 **22g** + **22g'**

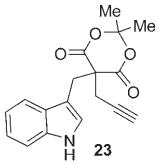
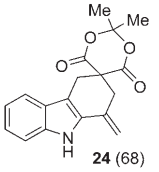
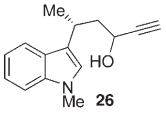
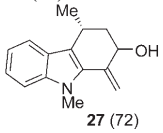
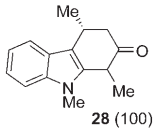
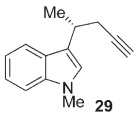
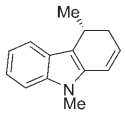
[a] Reactions in CH_2Cl_2 at room temperature with 5 mol% catalyst. [b] Reaction in toluene at 90°C.

Amide **31** afforded 5-methylene-4,5-dihydrooxazole **32** in 77% yield with catalyst **A** (Scheme 3). Catalyst **B** and $AuCl_3$ led also to **32**, although in lower yield (56–57%, 16 h, room temperature). This type of reactivity has been described by Hashmi[36] using $AuCl_3$ as catalyst, although it was reported that the 5-methylene-4,5-dihydrooxazoles suffered isomerization to the oxazoles under the reaction conditions. In our case, **32** proved to be remarkably stable and did not isomerize to the corresponding oxazole with Au^I or Au^{III} catalysts.

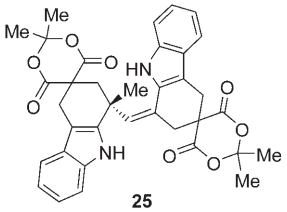
Intermolecular reaction of indoles with alkynes: The reaction of simple indoles with terminal alkynes proceeded satisfactorily in the presence of Au^I catalysts to give bisindoles **34** in a general way (Table 4). The best results were again obtained with catalyst **A**, although more electrophilic catalyst **C** could also be used. For this intermolecular process, toluene proved to be the solvent of choice in most cases. The reaction of indoles **33a**,**b** with aryl alkynes gave bisindoles **34a–g** (Table 4, entries 1–7). A single regioisomer was obtained in all cases, regardless on the nature of the substituents on the aryl. This regiochemistry is in contrast to that found by He in the reaction of **33b** with ethyl acrylate using $AuCl_3$ as catalyst.[27] The reaction shows that substituents on the indole or the aryl are well tolerated. Unlike $GaCl_3$, which was only active with phenylacetylene,[37] cationic gold(I) complexes catalyze the reaction of indoles with alkyl-substituted alkynes (Table 4, entries 8–14).

In contrast to the clean formation of **34e** in the reaction between indole (**33a**) and 3,5-bis(trifluoromethyl)phenylacetylene carried out in CH_2Cl_2 (Table 4, entry 5), when the re-

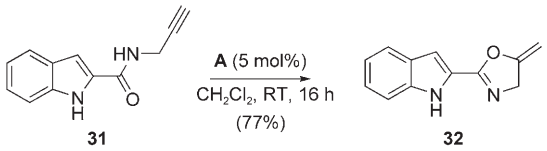
Table 3. Cyclization of indoles with alkynes tethered by 2–3 carbon chains catalyzed by gold.[a]

	Indole	Catalyst	*t* [h]	Product(s) (ratio; yield [%])
1	 **23**	**A**	0.2	 **24** (68)
2	**23**	**B**	0.5	**24** (54)[b]
3	 **26**	**A**	0.2	 **27** (72)
4	**26**	$AuCl_3$	0.2	 **28** (100)
5	 **29**	**A**	1	 **30** (92)
6	**29**	**B**	16	**30** (63)

[a] Reactions in CH_2Cl_2 at room temperature with 5 mol% catalyst. [b] Dimer **25** was obtained in 25% yield.



25



31 **32**

Scheme 3.

action was performed in toluene a mixture of [2+2] adducts **35**/**35′** was obtained (Scheme 4). Related dimers have been obtained in the acid-catalyzed reaction of indoles with ketones.[38]

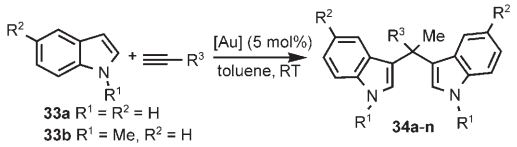
Interestingly, reaction of indole (**33a**) with prop-1-ynylbenzene led to **36** by reaction at the carbon β to the phenyl (Scheme 5), which is in contrast to that observed with aryl-substituted terminal alkynes (Table 4). The reaction can also be extended to pyrroles. Thus, 2-ethylpyrrole (**37**) reacted with phenylacetylene to give a 2+1 adduct **38** in very good yield.

When the C-3 position was substituted, the alkenylation occurred at C-2. Thus, skatole (**33e**) reacted with phenylacetylene to give a mixture of **39a**/**39a′** as a result of the dimerization of the initially formed **40**,[39] which could not be isolated under these reaction conditions. Similarly, **41a**/**41a′** were obtained in the reaction of **33e** with hex-5-ynenitrile (Scheme 6).

When the reaction of **33a** was carried out with pent-4-yn-1-ol and catalyst **A**, tetrahydrofuran **42** was obtained in 71% yield (Scheme 7). Similarly, hex-5-yn-1-ol furnished **43** (86%).

Reaction of tryptophol (**44**) with phenylacetylene occurred at the free C-2 position, followed by trapping the resulting alkene by the alcohol to give tetrahydro-pyrano[4,5-*b*]indole **45** (67%; Scheme 8). Compounds with this type of ring system have attracted attention as pharmaceuticals.[40] The alkenyl derivative **47** could be obtained in 69% yield in the reaction of protected tryptamine **46**. In this case, the cyclization to give **48** did not occur under the reaction conditions, but could be carried out by treatment of **47** with trifluoroacetic acid. The reaction of **49** proceeded intramolecularly to give **50** (55%) and **51** (31%).

Table 4. Intermolecular reaction of indoles with alkynes catalyzed by gold.[a]

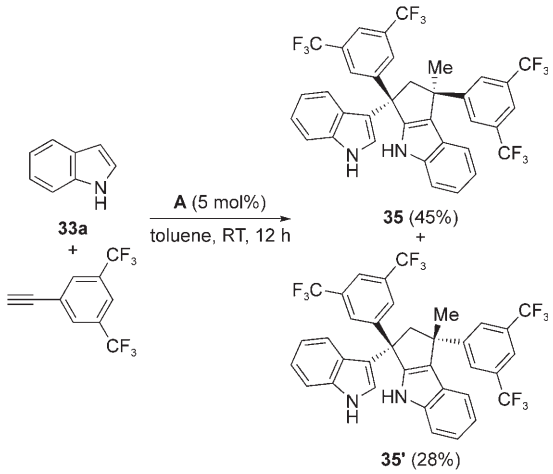


33a $R^1 = R^2 = H$
33b $R^1 = Me$, $R^2 = H$
33c $R^1 = H$, $R^2 = CN$
33d $R^1 = H$, $R^2 = Br$

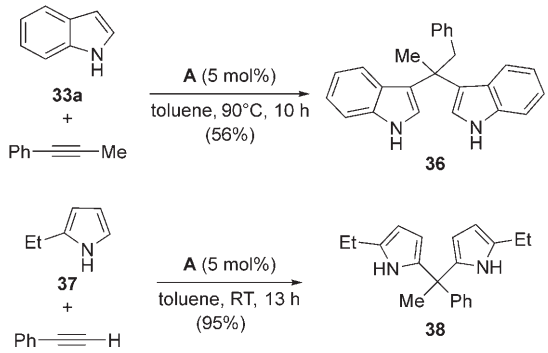
34a-n

	Indole	R^3	Catalyst	*t* [h]	Product	Yield [%]
1	**33a**	Ph	**A**	6	**34a**	99
2	**33b**	Ph	**A**	20	**34b**	89
3	**33a**	*p*-$MeOC_6H_4$	**A**	24	**34c**	71
4	**33a**	*p*-$O_2NC_6H_4$	**A**	6	**34d**	82
5[b]	**33a**	3,5-$(F_3C)_2C_6H_3$	**A**	6	**34e**	98
6	**33a**	3,5-$F_2C_6H_3$	**A**	6	**34f**	99
7	**33a**	1-pyrenyl	**C**	72	**34g**	53
8	**33a**	*n*-C_7H_{15}	**A**	6	**34h**	82
9	**33b**	*n*-C_7H_{15}	**A**	8	**34i**	84
10	**33a**	$ClCH_2(CH_2)_3$-	**A**	6	**34j**	73
11	**33a**	$NCCH_2(CH_2)_3$-	**A**	8	**34k**	83
12[b]	**33c**	*n*-C_7H_{15}	**A**	72	**34l**	67
13	**33d**	$NCCH_2(CH_2)_3$-	**A**	8	**34m**	76
14[b]	**33a**	cyclopropyl	**C**	15	**34n**	89

[a] Reactions in toluene at room temperature with 5 mol% catalyst. [b] Reaction in CH_2Cl_2 at room temperature.

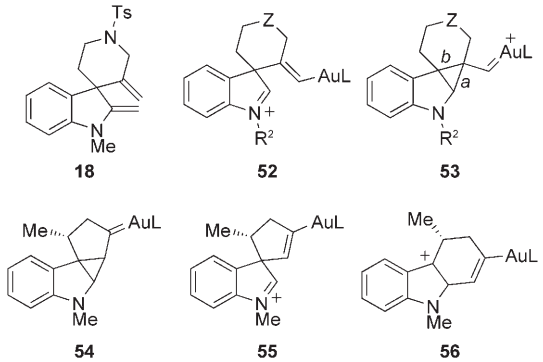


Scheme 4.

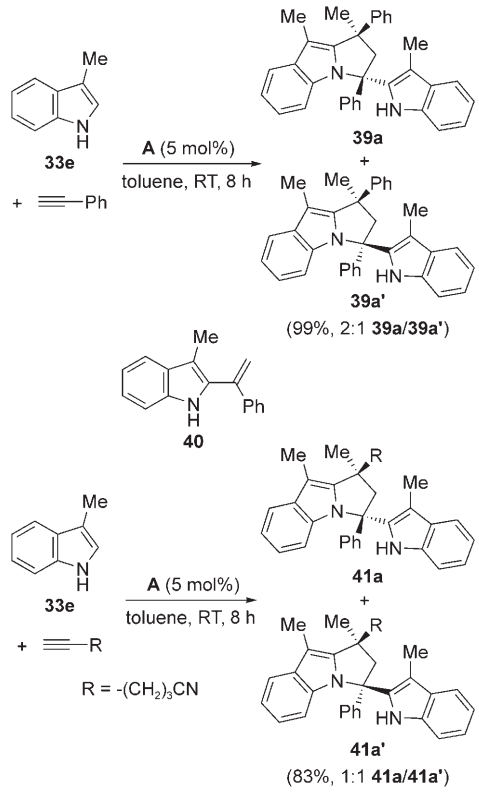


Scheme 5.

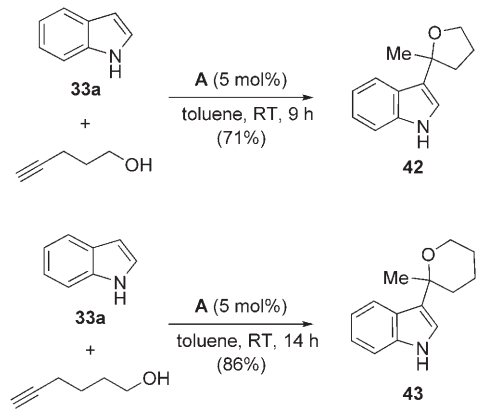
Mechanistic discussion: The isolation of spiro derivative **18** (Table 1, entry 15) suggests that cyclizations of C-3 substituted indoles catalyzed by gold(I) can take place by first forming a C–C bond at C-3 followed by a 1,2-migration to give the final indoles.[41] Thus, the 7-*exo-dig* cyclizations shown in Tables 1 and 2 presumably proceed via spiro derivatives of type **52**. Intermediates **52** could be formed directly by a



Friedel–Crafts-type reaction or indirectly, by opening of cyclopropyl carbenes **53** at C–C bond *a*.[12] However, opening of **53** at C–C bond *b* cannot be excluded. Similar intermediates are probably involved in the 6-*exo-dig* cyclizations



Scheme 6.

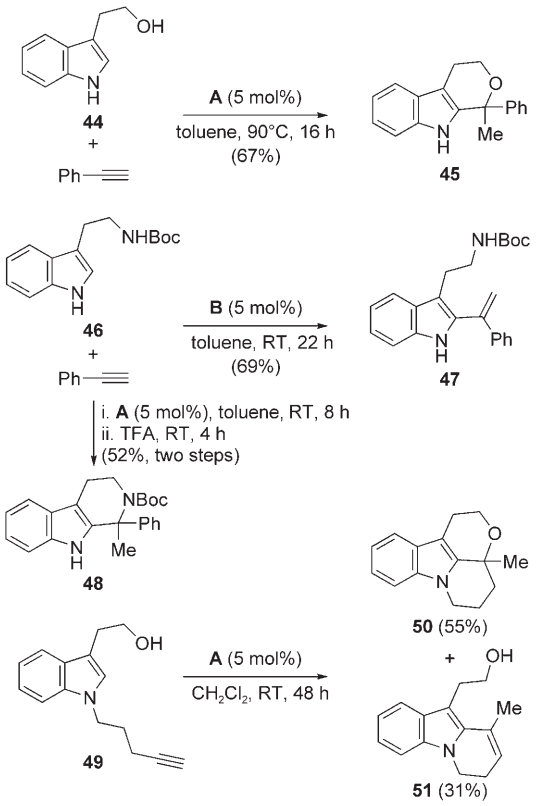


Scheme 7.

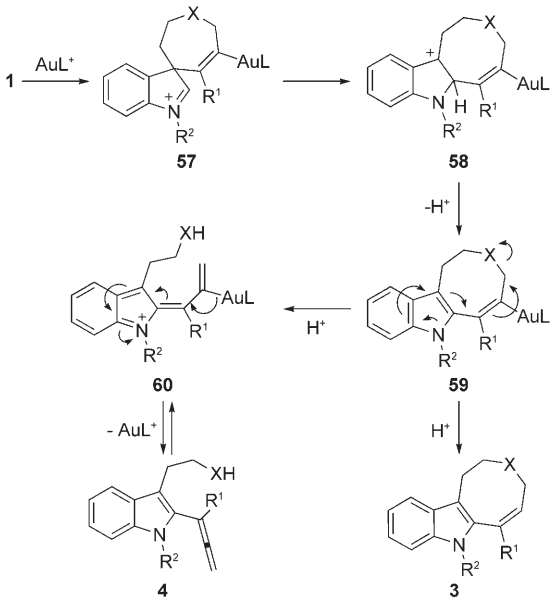
shown in Table 3. On the other hand, the 6-*endo-dig* cyclization of indole **29** (Table 3, entry 5) probably proceeds through intermediate **54**,[12] which could then open to form **55** or **56**.

Eight-membered ring compounds may also arise by a 1,2-shift of the initially formed seven-membered ring iminium cation **57** to form **58** (Scheme 9). Proton loss from **58** would give **59**, from which eight-membered ring compounds **3** would be formed. An alternative elimination from **59** would yield allenes **4** via cationic intermediate **60**.

Fragmentation does not occur once the final indoloazocines **3** have been formed. Thus, treatment of **14e** with com-



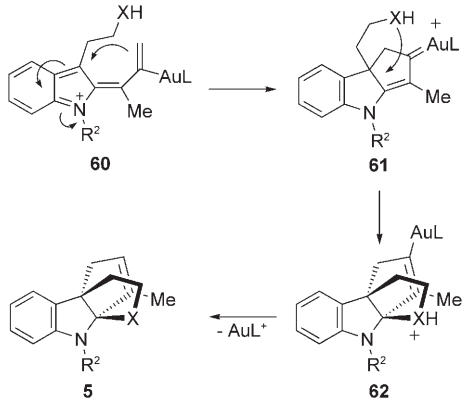
Scheme 8.



Scheme 9.

plex **A** (5 mol%) in CH_2Cl_2 at room temperature for 16 h or in toluene at 90°C for 5 h led only to unchanged starting material. Importantly, the fact that substrate **12e**, with a methyl at C-2 of the alkyne, gives an indoloazocine of type **3** excludes the involvement of gold vinylidenes in these cyclizations.[8,15]

Formation of tetracyclic compounds of type **5** (Scheme 1) such as **17** and **22e–g** (Tables 1 and 2) can be explained by a cyclization of intermediates **60** as shown in Scheme 10 to give conjugated gold carbene **61**, the Michael-type cyclization of which would lead to **62**. A protodemetalation then leads to compounds **5**.



Scheme 10.

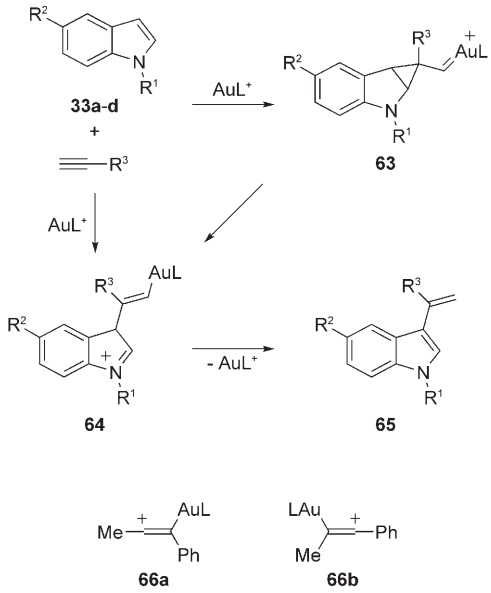
Indeed, tetracycles **5** can be formed from allenes **4**. This was confirmed by a separate reaction in which isolated allene **21e** was converted to tetracycle **22e** with 5 mol% catalyst **A**. The reaction of **19e** (Table 2, entry 8) was monitored by ^1H NMR spectroscopy in CD_2Cl_2 (3 mol%, catalyst **A**) from −40 to 0°C. At −23°C a low conversion to the allene **21e** was observed, which increased to about 50% upon raising the temperature to 0°C. The NMR tube was then left overnight at room temperature and the spectra showed that a complete conversion from the allene **21e** to the tetracycle **22e** had occurred. No other compounds were observed in this experiment. Cyclizations of indoles with allenes catalyzed by Au^I have been recently described by Widenhoefer for the formation of six- and seven-membered ring compounds, which proceeded using catalyst **A** with OTf as the counterion.[42] In these reactions, the C–C bond is formed between C-3 of the indole and C-3 of the allene, although in one case, formation of a C–C bond at C-2 of the allene was also observed. A very different cyclization of indoles with allenes formed in situ was found by Zhang to give four-membered ring compounds.[43]

The different regiochemical outcome observed in reactions catalyzed by Au^I complex **A** and $AuCl_3$ (Table 1, entries 1/2, 5/6, and 8/9) is intriguing and suggests that different mechanisms are involved in these reactions. It is worth noting that in these cases the most electrophilic Au^{III} catalyst leads to indoloazocines **3**, which according to PM3 and ab intio (B3LYP/6–31G(d)) calculations, are about 2–5 kcal mol^{-1} less stable than their seven-membered ring isomers **2**.

We have previously observed a different stereochemical outcome depending on the oxidation state of the palladium catalyst in the cyclization of allylstannanes with alkynes.[44] In the present case, however, the different regioselectivity

observed in the intramolecular reactions appears to depend more on the presence or absence of phosphine ligands as similar results are often obtained using with AuCl and $AuCl_3$ as catalyst.

In the intermolecular reactions, intermediates **63** or **64** may be formed (Scheme 11). In this context, it may be important to note that the intermolecular reaction of a furan with phenylacetylene in the presence of a Au^I catalyst[45] follows the same mechanism of the intermolecular process,[18a,b,d–f,33b,46,47] namely, cyclopropyl metal carbenes similar to **63** are the primary intermediates in that process. The initially formed 2-alkenylindoles **65**, or the 3-alkenyl regioisomers often react with a nucleophile. Although these secondary processes may be promoted by gold, it is also possible that those reactions are simple Brønsted acid catalyzed reactions, as protons are released in the catalytic cycles (see, for example, **58** to **59** in Scheme 9).[48] With terminal alkynes, the regioselectivity in the first C–C bond formation can be explained by the exclusive formation of the more substituted η^1-alkenyl–gold(I) cation. In the formation of **36** (Scheme 5) by reaction of indole (**33a**) with prop-1-ynylbenzene, both cations **66a** and **66b** may be in equilibrium, in which **66a** might be the more electrophilic species. Alternatively, the attack of indole (**33a**) might take place preferentially at the carbon bearing the methyl substituent in a η^3-alkyne–gold(I) complex.



Scheme 11.

Conclusion

In summary, we have found a facile annulation of six- to eight-membered rings on indoles by cyclization with alkynes catalyzed by gold. Cationic Au^I complex **A** is the best catalyst for the formation of six- and seven-membered rings by 6-*endo*-dig, 6-*exo*-dig, and 7-*exo-dig* cyclizations. Indoloazocines are obtained with $AuCl_3$ as catalyst in a rare 8-*endo-dig* process. Allenes of type **4** (Scheme 1) are formed by a fragmentation reaction.[49] This fragmentation may also give rise to annulated compounds **5** by a domino process catalyzed by gold. The intermolecular reaction of indoles with alkynes is also a general transformation that gives rise to products that arise from intermediate 2- or 3-alkenylindoles which often react with a second molecule of indole, alkenyl indole, or other nucleophile.

Experimental Section

General procedures and the synthesis of starting indoles is described in the Supporting Information. The following known compounds, showed spectroscopic data consistent with those described: **34a**,[50] **34b**,[50] **34c**,[51] **34d**,[52] **34n**,[53] and **47**.[54]

General procedure for the cyclization of the indole derivatives (Tables 1–3): A mixture of indole derivative (50 mg) and gold catalyst (0.05 equiv) in CH_2Cl_2 (2 mL) were stirred at room temperature for the time indicated. The mixture was filtered trough silica gel and the solvent evaporated. The residue was subjected to chromatography to give the desired product.

(*S*)-Methyl 1,2,3,4,5,6-hexahydro-5-methylene-3-(2,4-dinitrobenzenesulfonyl)azepino[4,5-*b*]indole-2-carboxylate (13a): Table 1, entry 1; orange solid; m.p. 204–206 °C; $[\alpha]_D^{23} = -110.9$ ($c = 1.0$ in DMSO); ^{1}H NMR (400 MHz, [D$_8$]DMSO, 23 °C): $\delta = 10.75$ (s, 1H), 8.59 (d, $J =$ 1.6 Hz, 1H), 7.95–7.89 (m, 2H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.13 (d, $J =$ 8.0 Hz, 1H), 7.06 (td, $J = 8.0$, 1.2 Hz, 1H), 6.99 (td, $J = 8.0$, 1.2 Hz, 1H), 5.38 (s, 1H), 5.19 (s, 1H), 4.96 (dd, $J = 11.6$, 6.4 Hz, 1H), 4.68 (d, $J =$ 17.2 Hz, 1H), 4.54 (d, $J = 17.2$ Hz, 1H), 3.70 (s, 3H), 3.55 (dd, $J = 15.6$, 6.4 Hz, 1H), 3.33 (dd, $J = 15.2$, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, [D$_8$]DMSO, DEPT, 23 °C): $\delta = 170.78$, 149.09, 146.73, 136.01, 135.90, 135.74, 132.69, 131.15 (CH), 127.12, 125.37 (CH), 122.36 (CH), 118.89 (CH), 118.68 (CH), 118.17 (CH), 110.95 (CH_2), 110.55 (CH), 108.97, 60.42 (CH), 52.38 (CH_3), 48.45 (CH_2), 24.17 (CH_2); HRMS-ESI *m*/*z* calcd for $C_{21}H_{18}N_4O_8SNa$: 509.0743; found: 509.0738 [M^++Na]; elemental analysis calcd (%) for $C_{21}H_{18}N_4O_8S \cdot 1/2\ H_2O$: C 50.91, H 3.87, N 11.31, S 6.47; found: C 51.33, H 3.88, N 11.30, S 6.39.

(*S*)-Methyl 2,3,4,7-Tetrahydro-3-(2,4-dinitrobenzenesulfonyl)-1*H*-azocino-[4,5-*b*]indole-2-carboxylate (14a): Table 1, entry 2; dark red solid; m.p. 261–263 °C; $[\alpha]_D^{23} = 30.51$ ($c = 0.5$ in DMSO); ^{1}H NMR (500 MHz, [D$_6$]DMSO, 150 °C): $\delta = 10.35$ (br s, 1H), 8.31 (d, $J = 2.2$ Hz, 1H), 8.12 (dd, $J = 8.7$, 2.2 Hz, 1H), 7.76 (d, $J = 8.7$ Hz, 1H), 7.49 (d, $J = 7.2$ Hz, 1H), 7.15 (d, $J = 7.1$ Hz, 1H), 7.05–6.99 (m, 2H), 6.45 (dd, $J = 11.9$, 1.3 Hz, 1H), 5.76 (ddd, $J = 11.9$, 5.6, 3.8 Hz, 1H), 4.82 (t, $J = 7.5$ Hz, 1H), 4.65 (dd, $J = 19.4$, 5.7 Hz, 1H), 4.25 (ddd, $J = 19.4$, 3.5, 2.7 Hz, 1H), 3.70 (s, 3H), 3.29 ppm (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 150 °C, DEPT): $\delta = 170.5$*, 149.5*, 148.0*, 137.0*, 133.5*, 132.0*, 131.86 (CH), 127.5*, 127.04 (CH), 126.35 (CH), 122.21 (CH), 121.16 (CH), 119.50 (CH), 119.29 (CH), 118.17 (CH), 111.31 (CH), 108.0*, 59.47 (CH), 52.55 (CH_3), 45.41 (CH_2), 26.26 ppm (CH_2) (* = determined in the HMBC experiment); HRMS-ESI: *m*/*z* calcd for $C_{21}H_{18}N_4O_8S$: 486.0845; found: 486.0826 [M^+]; elemental analysis calcd (%) for $C_{21}H_{18}N_4O_8S$: C 51.85, H 3.73, N 11.52, S 6.59; found: C 51.71, H 3.92, N 11.24, S 6.26.

1,2,3,4,5,6-Hexahydro-5-methylene-3-benzenesulfonylazepino[4,5-*b*]-indole (13b): Table 1, entry 5; white solid; m.p. 140–142 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 23 °C): $\delta = 10.39$ (s, 1H), 7.89 (d, $J = 7.3$ Hz, 2H), 7.59–7.44 (m, 3H), 7.45 (d, $J = 7.9$ Hz, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.09 (t, $J = 7.2$ Hz, 1H), 6.69 (t, $J = 7.4$ Hz, 1H), 5.49 (s, 1H), 5.20 (s, 1H), 4.31 (s, 2H), 3.56 (t, $J = 5.9$ Hz, 2H), 3.04 ppm (t, $J = 6.0$ Hz, 2H); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 23 °C, DEPT): $\delta = 139.23$, 137.41, 136.03, 133.16, 132.54 (CH), 129.10 (CH, 2C), 127.81, 126.71 (CH, 2C), 122.33 (CH), 118.60 (CH), 118.31 (CH), 111.93, 111.39 (CH_2), 110.76 (CH), 51.54

(CH_2), 48.61 (CH_2), 22.99 ppm (CH_2); HRMS-EI: *m/z* calcd for $C_{19}H_{18}N_2O_2S$: 338.1089; found: 338.1085 [M^+]; elemental analysis calcd (%) for $C_{19}H_{18}N_2O_2S$: C 67.43, H 5.36, N 8.28, S 9.47; found: C 67.00, H 5.38, N 8.34, S 9.52.

3-(Phenylsulfonyl)-2,3,4,7-tetrahydro-1*H*-azocino[5,4-*b*]indole (14b): Table 1, entry 6; white solid; m.p. 178–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.64 (d, *J* = 7.5 Hz, 2H), 7.61 (brs, 1H), 7.46–7.42 (m, 2H), 7.35–7.31 (m, 2H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 11.2 Hz, 1H), 5.84 (dt, *J* = 11.1, 6.6 Hz, 1H), 3.99 (d, *J* = 6.6 Hz, 2H), 3.58 (t, *J* = 5.3 Hz, 2H), 2.98 ppm (t, *J* = 5.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 140.04, 136.04, 132.06 (CH), 131.44, 128.75 (CH, 2C), 127.95, 127.31 (CH), 126.86 (CH, 2C), 123.02 (CH), 122.70 (CH), 119.72 (CH), 118.16 (CH), 112.26, 110.70 (CH), 46.21 (CH_2), 45.93 (CH_2), 24.29 ppm (CH_2); HRMS-ESI: *m/z* calcd for $C_{19}H_{19}N_2O_2S$: 339.1176; found: 339.1152 [M^++H]; elemental analysis calcd (%) for $C_{19}H_{18}N_2O_2S{\cdot}H_2O$: C 64.02, H 5.66, N 7.86, S 9.00; found: C 63.72, H 5.38, N 7.58, S 9.61.

5-Methyl-3-(phenylsulfonyl)-1,2,3,6-tetrahydroazepino[4,5-*b*]indole (15b): Table 1, entry 6; white solid; m.p. 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.92 (brs, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.56–7.46 (m, 3H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.76 (s, 1H), 3.78 (t, *J* = 4.8 Hz, 2H), 2.97 (t, *J* = 4.9 Hz, 2H), 2.20 ppm (d, *J* = 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 139.58, 134.88, 132.92 (CH), 131.83, 129.28 (CH, 2C), 128.53, 126.28 (CH, 2C), 124.06 (CH), 122.42 (CH), 119.76 (CH), 118.13 (CH), 113.35, 111.193, 110.61 (CH), 45.89 (CH_2), 26.62 (CH_2), 18.89 ppm (CH_3); HRMS-ESI: *m/z* calcd for $C_{19}H_{19}N_2O_2S$: 339.1176; found: 339.1175 [M^++H]; elemental analysis calcd (%) for $C_{19}H_{18}N_2O_2S$: C 67.43, H 5.36, N 8.28, S 9.47; found: C 67.30, H 5.67, N 8.08, S 9.11.

3-(2,4-Dinitrobenzenesulfonyl)-5-methylene-1,2,3,4,5,6-hexahydroazepino[4,5-*b*]indole (13c): Table 1, entry 8; orange solid; m.p. 190–192 °C; ^{1}H NMR (400 MHz, [D_6]acetone, 23 °C): δ = 10.10 (brs, 1H), 8.53 (d, J = 2.2 Hz, 1H), 8.36 (dd, *J* = 8.7, 2.2 Hz, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 5.51 (s, 1H), 5.30 (s, 1H), 4.58 (s, 2H), 3.94 (t, *J* = 6.3 Hz, 2H), 3.26 ppm (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, [D_6]acetone, 23 °C, DEPT): δ = 150.58, 142.66, 138.51, 138.41, 137.48, 133.89, 132.59 (CH), 129.13, 126.90 (CH), 123.71 (CH), 120.09 (CH), 120.06 (CH), 119.35 (CH), 113.07, 111.99 (CH), 111.60 (CH_2), 52.69 (CH_2), 50.02 (CH_2), 23.90 ppm (CH_2); HRMS-ESI: *m/z* calcd for 429.0869; found: 429.0877 [M^++H]; elemental analysis calcd (%) for $C_{19}H_{16}N_4O_6S$: C 53.27, H 3.76, N 13.08, S 7.48; found: C 53.01, H 3.98, N 12.64, S 7.26.

3-(2,4-Dinitrobenzenesulfonyl)-2,3,4,7-tetrahydro-1*H*-azocino[5,4-*b*]-indole (14c): Table 1, entry 9; orange solid; m.p. 213–215 °C; ^{1}H NMR (400 MHz, [D_6]DMSO, 23 °C): δ = 10.71 (brs, 1H), 8.57 (d, *J* = 2.2 Hz, 1H), 8.15 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 6.8 Hz, 1H), 6.94 (t, *J* = 6.9 Hz, 1H), 6.43 (d, *J* = 12.0 Hz, 1H), 5.73 (dt, *J* = 12.0, 4.8 Hz, 1H), 4.27 (d, *J* = 4.8 Hz, 2H), 3.66 (t, *J* = 5.4 Hz, 2H), 3.01 ppm (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, [D_6]DMSO, DEPT): δ = 149.01, 146.82, 136.04, 135.70, 132.24, 130.67(CH), 127.10, 126.40 (CH), 126.13 (CH), 121.44 (CH), 121.02 (CH), 118.95 (CH), 118.59 (CH), 117.90 (CH), 110.61 (CH), 109.20, 47.95 (CH_2), 46.85 (CH_2), 22.80 ppm (CH_2); HRMS-CI: *m/z* calcd for $C_{19}H_{17}N_4O_6S$: 429.0869; found: 429.0854 [M^++H]; elemental analysis calcd (%) for $C_{19}H_{16}N_4O_6S{\cdot}3/2H_2O$: C 50.11, H 4.20, N 12.30, S 7.04; found: C 50.43, H 3.79, N 12.01, S 6.74.

3-(2,4-Dinitrobenzenesulfonyl)-5-methyl-1,2,3,6-tetrahydroazepino[4,5-*b*]-indole (15c): Table 1, entry 9; orange solid; ^{1}H NMR (400 MHz, [D_6]acetone, 23 °C): δ = 10.06 (brs, 1H), 8.81 (d, *J* = 1.8 Hz, 1H), 8.64 (dd, *J* = 8.7, 1.6 Hz, 1H), 8.44 (d, *J* = 8.7 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.12 (t, *J* = 7.1 Hz, 1H), 7.02 (t, *J* = 7.1 Hz, 1H), 6.70 (s, 1H), 3.96 (t, *J* = 4.9 Hz, 2H), 3.17 (t, *J* = 5.0 Hz, 2H), 2.30 ppm (d, *J* = 1.1 Hz, 3H); HRMS-ESI: *m/z* calcd for $C_{19}H_{17}N_4O_6S$: 429.0869; found: 429.0895 [M^++H].

6-Allyl-5-methylene-3-phenylsulfonyl-1,2,3,4,5,6-hexahydroazepino[4,5-*b*]indole (13d): Table 1, entry 10; white solid; m.p. 168–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.79 (d, *J* = 7.4 Hz, 2H), 7.50–7.39 (m, 4H), 7.22–7.09 (m, 3H), 5.94 (ddt, *J* = 17.1, 10.4, 4.2 Hz, 1H), 5.56 (s, 1H), 5.29 (s, 1H), 5.16 (d, *J* = 10.5 Hz, 1H), 4.89 (d, *J* = 17.0 Hz, 1H), 4.66–4.65, (m, 2H), 4.19 (s, 2H), 3.70 (t, *J* = 5.4 Hz, 2H), 3.03 ppm (t, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 139.98, 137.69, 135.91, 135.70, 133.89 (CH), 132.31 (CH), 128.92 (CH, 2C), 127.32, 127.03 (CH, 2C), 122.60 (CH), 119.77 (CH), 119.16 (CH_2), 118.46 (CH), 116.38 (CH_2), 112.68, 110.27 (CH), 55.00 (CH_2), 47.55 (CH_2), 46.42 (CH_2), 25.38 ppm (CH_2); HRMS-ESI: *m/z* calcd for $C_{22}H_{23}N_2O_2S$: 379.1480; found: 379.1464 [M^++H]; elemental analysis calcd (%) for $C_{22}H_{22}N_2O_2S{\cdot}1.5\,H_2O$: C 65.16, H 6.21, N 6.91, S 7.91; found: C 62.25, H 5.68, N 6.57, S 7.62.

***N*-{2-[1-Allyl-2-(propa-1,2-dienyl)-1*H*-indol-3-yl]ethyl}benzenesulfonamide (16d)**: Table 1, entry 11; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.75 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.44–7.37 (m, 3H), 7.26–7.15 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.26 (t, *J* = 7.1 Hz, 1H), 5.91 (ddt, *J* = 16.0, 9.7, 4.8 Hz, 1H), 5.16 (d, *J* = 7.1 Hz, 2H), 5.12 (d, *J* = 10.4 Hz, 1H), 4.87 (d, *J* = 17.2 Hz, 1H), 4.79 (d, *J* = 3.1 Hz, 2H), 4.43 (t, *J* = 5.5 Hz, 1H), 3.25 (q, *J* = 6.5 Hz, 2H), 3.02 ppm (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 211.01, 139.95, 137.11, 133.33 (CH), 132.43 (CH), 128.95 (CH, 2C), 128.37, 127.55, 126.94 (CH, 2C), 122.25 (CH), 119.76 (CH), 118.10 (CH), 116.37 (CH_2), 109.78, 109.35 (CH), 83.09 (CH), 78.54 (CH_2), 45.82 (CH_2), 43.41 (CH_2), 24.86 ppm (CH_2); HRMS-ESI *m/z* calcd for $C_{22}H_{22}N_2O_2S$: 379.1480; found: 379.1479 [M^+].

(*S*)-Methyl 3-(2,4-dinitrobenzenesulfonyl)-6-methyl-2,3,4,7-tetrahydro-1*H*-azocino[5,4-*b*]indole-2-carboxylate (14e): Table 1, entry 12; red solid; m.p. 128–130 °C; $[\alpha]_D^{23} = -116.4$ (*c* = 0.7 in acetone); ^{1}H NMR (500 MHz, [D_6]DMSO, 150 °C): δ = 10.50 (brs, 1H), 8.48 (d, *J* = 1.8 Hz, 1H), 8.33 (dd, *J* = 8.7, 1.9 Hz, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.06 (td, *J* = 7.9, 0.9 Hz, 1H), 7.01 (td, *J* = 7.9, 0.6 Hz, 1H), 5.77 (t, *J* = 6.2 Hz, 1H), 4.83 (dd, *J* = 8.2, 3.4 Hz, 1H), 4.43 (dd, *J* = 17.3, 6.0 Hz, 1H), 3.78 (dd, *J* = 17.0, 6.2 Hz, 1H), 3.59 (dd, *J* = 14.8, 8.3 Hz, 1H), 3.56 (s, 3H), 2.96 (dd, *J* = 14.8, 2.6 Hz, 1H), 2.12 ppm (s, 3H); ^{13}C NMR (125 MHz, [D_6]DMSO, 150 °C, DEPT): δ = 170.33, 149.0*, 137.68, 137.10, 136.76, 136.5*, 132.34 (CH), 131.0*, 127.83, 126.74 (CH), 123.95 (CH), 122.20 (CH), 119.77 (CH), 119.45 (CH), 118.66 (CH), 111.56 (CH), 108.00, 56.65 (CH), 52.26 (CH_3), 45.01 (CH_2), 27.43 (CH_2), 22.53 ppm (CH_3) (* = determined in the HMBC experiment); HRMS-ESI: *m/z* calcd for $C_{22}H_{20}N_4O_8SNa$: 523.0900; found: 523.0892 [M^++Na].

(*S*)-Methyl 3-[2-(buta-2,3-dien-2-yl)-1*H*-indol-3-yl]-2-(2,4-dinitrophenylsulfonamido)propanoate (16e): Table 1, entry 12; brown solid; m.p. 177–179 °C; $[\alpha]_D^{23} = 102.5$ (*c* = 0.8 in acetone); ^{1}H NMR (500 MHz, [D_6]acetone, 23 °C): δ = 10.81 (brs, 1H), 8.05 (d, *J* = 2.2 Hz, 1H), 8.03–8.02 (m, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 6.76–6.68 (m, 3H), 5.11 (dq, *J* = 12.0, 3.1 Hz, 1H), 5.06 (dq, *J* = 12.0, 3.2 Hz, 1H), 4.55 (dd, *J* = 14.8, 11.3 Hz, 1H), 2.08 ppm (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (125 MHz, [D_6]acetone, 23 °C): δ = 210.34, 172.02, 139.45, 136.23, 134.44, 130.47, 129.88, 128.50, 127.35, 125.94, 122.26, 120.24, 119.98, 119.44, 111.38, 111.24, 105.65, 78.00, 52.82, 27.92, 18.48 ppm (one carbon is missing); HRMS-ESI *m/z* calcd for $C_{22}H_{20}N_4O_8SNa$: 523.0900; found: 523.0895 [M^++Na].

(*S*)-Methyl 3-[2-(buta-2,3-dien-2-yl)-1*H*-indol-3-yl]-2-(4-methylphenylsulfonamido)propanoate (16f): Table 1, entry 14; white solid; m.p. 144–146 °C; $[\alpha]_D^{23} = 0.5$ (*c* = 0.6 in acetone); ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.84 (brs, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.1 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 5.13 (q, *J* = 3.1 Hz, 2H), 5.09 (d, *J* = 9.3 Hz, 1H), 4.17 (dt, *J* = 9.2, 7.1 Hz, 1H), 3.40 (s, 3H), 3.28 (d, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 2.13 ppm (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, DEPT): δ = 209.28, 172.21, 143.11, 136.43, 135.12, 130.63, 129.17 (CH, 2C), 129.05, 126.92 (CH, 2C), 122.27 (CH), 119.87 (CH), 118.06 (CH),110.40 (CH), 106.90, 93.30, 77.89 (CH_2), 56.13 (CH), 52.34 (CH_3), 28.53 (CH_2), 21.48 (CH_3), 17.83 ppm (CH_3); HRMS-ESI: *m/z* calcd for $C_{23}H_{24}N_2O_4NaS$: 447.1354; found: 447.1342 [M^++Na].

Tetracycle 17: Table 1, entry 14; white solid; m.p. 199–201 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.75 (d, *J* = 8.1 Hz , 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.06 (td, *J* = 7.7, 1.2 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.71 (td, *J* = 7.4, 0.8 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 5.44–5.42 (m, 2H), 3.35 (ddd,

J=10.5, 8.6, 5.8 Hz, 1H), 3.22 (ddd, J=10.5, 6.9, 4.5 Hz, 1H), 2.64–2.54 (m, 2H), 2.34 (s, 3H), 2.08 (ddd, J=12.4, 5.8, 4.5 Hz, 1H), 2.00–1.99 (m, 3H), 1.86 ppm (ddd, J=12.4, 8.6, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=148.30, 142.94, 139.74, 137.15, 133.57, 129.35 (CH, 2C), 128.49 (CH), 128.20 (CH), 127.70 (CH, 2C), 123.13 (CH), 119.09 (CH), 109.38 (CH), 103.19, 66.12, 48.61 (CH_2), 43.83 (CH_2), 37.91 (CH_2), 21.41 (CH_3), 13.38 ppm (CH_3); HRMS-CI: m/z calcd for $C_{21}H_{23}N_2O_2S$: 367.1480; found: 367.1489 [M^++H]; elemental analysis calcd (%) for $C_{21}H_{22}N_2O_2S$: C 68.82, H 6.05, N 7.64, S 8.75; found: C 68.67, H 6.10, N 7.91, S 8.68.

1-Methyl-2,3′-dimethylene-1′-tosylspiro[indoline-3,4′-piperidine] (18): Table 1, entry 15; white solid; m.p. 133–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.75 (d, J=8.1 Hz, 2H), 7.38 (d, J=8.1 Hz, 2H), 7.12 (td, J=7.6, 1.1 Hz, 2H), 6.86 (d, J=7.5 Hz, 1H), 6.61 (td, J=7.4, 1.0 Hz, 1H), 6.54 (d, J=7.9 Hz, 1H), 5.04 (s, 1H), 4.73 (s, 1H), 4.08 (d, J=13.9 Hz, 1H), 3.79 (d, J=13.7 Hz, 1H), 3.93 (d, J=2.3 Hz, 1H), 3.68 (d, J=2.3 Hz, 1H), 3.60–3.54 (m, 1H), 3.43 (ddd, J=12.8, 7.8, 5.1 Hz, 1H), 2.99 (s, 3H), 2.48 (s, 3H), 1.91–1.82 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=158.06, 146.30, 143.69, 143.02, 133.81, 133.45, 129.77 (CH, 2C), 128.22 (CH), 127.88 (CH, 2C), 123.65 (CH), 118.07 (CH), 115.38 (CH_2), 105.60 (CH), 78.03 (CH_2), 51.47, 49.85 (CH_2), 41.96 (CH_2), 37.78 (CH_2), 28.76 (CH_3), 21.59 ppm (CH_3); HRMS-EI: m/z calcd for $C_{22}H_{24}N_2O_2S$: 380.1559; found: 380.1567 [M^+]; elemental analysis calcd (%) for $C_{22}H_{24}N_2O_2S\cdot 1/3\,H_2O$: C 68.36, H 6.43, N 7.25, S 8.30; found: C 68.84, H 6.30, N 7.41, S 8.17.

5-Methylene-2,4,5,6-tetrahydro-1*H*-oxepino[4,5-*b*]indole (20a): Table 2, entry 1; white solid; m.p. 69–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.95 (br s, 1H), 7.50 (d, J=8.1 Hz, 1H), 7.31 (d, J=8.1 Hz, 1H), 7.20 (td, J=6.9, 1.1 Hz, 1H), 7.10 (td, J=6.8, 1.0 Hz, 1H), 5.28 (s, 1H), 5.18 (s, 1H), 4.48 (s, 2H), 4.12 (t, J=5.4 Hz, 2H), 3.10 ppm (t, J=5.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=141.08, 135.93, 133.30, 128.94, 123.13 (CH), 119.63 (CH), 118.85 (CH), 114.07, 110.90 (CH), 110.62 (CH_2), 75.95 (CH_2), 72.49 (CH_2), 27.50 ppm (CH_2); HRMS-ESI: m/z calcd for $C_{13}H_{14}NO$: 200.1075; found: 200.1077 [M^++H].

2-[2-(Propa-1,2-dienyl)-1*H*-indol-3-yl]ethanol (21a): Table 2, entry 1; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=8.02 (br s, 1H), 7.55 (d, J=7.7 Hz, 1H), 7.31 (d, J=7.7 Hz, 1H), 7.19 (t, J=7.6 Hz, 1H), 7.10 (t, J=7.4 Hz, 1H), 6.46 (t, J=6.7 Hz, 1H), 5.34 (d, J=6.9 Hz, 2H), 3.89–3.86 (m, 2H), 3.05 ppm (t, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=209.59, 136.25, 129.07, 128.05, 122.68 (CH), 119.60 (CH), 118.46 (CH), 110.52, 110.42 (CH), 84.66 (CH), 80.62 (CH_2), 62.89 (CH_2), 27.53 ppm (CH_2); HRMS-ESI: m/z calcd for $C_{13}H_{13}NONa$: 222.0895; found: 222.0897 [M^++Na].

6-Methyl-5-methylene-2,4,5,6-tetrahydro-1*H*-oxepino[4,5-*b*]indole (20b): Table 2, entry 2; yellow solid; m.p. 67 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.52 (d, J=7.9 Hz, 1H), 7.30 (d, J=7.9 Hz, 1H), 7.25 (dt, J=8.0, 1.1 Hz, 1H), 7.13 (dt, J=7.9, 1.1 Hz, 1H), 5.62 (d, J=0.7 Hz, 1H), 5.23 (d, J=1.2 Hz, 1H), 4.36 (s, 2H), 4.06–4.04 (m, 2H), 3.75 (s, 3H), 3.08–3.05 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=139.6 (C), 138.5 (C), 127.4 (C), 122.5 (CH), 119.7 (CH), 119.1 (CH_2), 118.7 (CH), 113.6 (C), 109.9 (CH), 76.9 (CH_2), 71.5 (CH_2), 31.7 (CH_3), 27.8 ppm (CH_2); HRMS-ESI: m/z calcd for $C_{14}H_{16}NO$: 214.1232; found: 214.1227 [M^++H]; elemental analysis calcd (%) for $(C_{14}H_{15}NO)_5\cdot H_2O$: C 77.53, H 7.16, N 6.46; found: C 78.01, H 7.14, N 6.60.

2-[2-(Buta-2,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl]ethanol (21b): Table 2, entry 3; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.59 (d, J=8.0 Hz, 1H), 7.29 (d, J=8.2 Hz, 1H), 7.22 (dt, J=7.0, 1.0 Hz, 1H), 7.11 (dt, J=7.0, 1.0 Hz, 1H), 4.85 (q, J=3.3 Hz, 2H), 3.87 (t, J=6.5 Hz, 2H), 3.70 (s, 3H), 3.05 (t, J=6.6 Hz, 2H), 2.06 (t, J=3.2 Hz, 3H), 1.47 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=209.6 (C), 137.4 (C), 135.5 (C), 128.0 (C), 121.9 (CH), 119.4 (CH), 118.9 (CH), 109.4 (CH), 108.2 (C), 91.3 (C), 74.4 (CH_2), 63.3 (CH_2), 30.6 (CH_3). 28.6 (CH_2), 20.5 ppm (CH_3); HRMS-EI: m/z calcd for $C_{15}H_{17}NO$: 227.1310; found: 227.1310 [M^+].

(*R*)-6-Methyl-5-methylene-1-phenyl-2,4,5,6-tetrahydro-1*H*-oxepino[4,5-*b*]-indole (20c): Table 2, entry 5; yellow oil; $[\alpha]_D^{23}$=43.8 (c=1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.29 (d, J=8.2 Hz , 1H), 7.24–7.14 (m, 7H), 6.98 (t, J=7.3 Hz, 1H), 5.69 (s, 1H), 5.36 (s, 1H), 4.58 (d, J=12.2 Hz, 1H), 4.51–4.48 (m, 1H), 4.47 (d, J=12.1 Hz, 1H), 4.22 (dd, J=12.0, 5.9 Hz, 1H), 4.15 (dd, J=12.1, 3.7 Hz, 1H), 3.78 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=142.55, 138.79, 138.47, 136.12, 128.38 (CH, 2C), 128.28 (CH, 2C), 127.19, 126.35 (CH), 122.41 (CH), 119.53 (CH), 119.52 (CH_2), 119.33 (CH), 115.24, 109.61 (CH), 76.92 (CH_2), 74.95 (CH_2), 45.62 (CH), 31.41 ppm (CH_3); HRMS-EI: m/z calcd for $C_{20}H_{19}NO$: 289.1467; found: 289.1475 [M^+].

(*S*)-2-[1-Methyl-2-(propa-1,2-dienyl)-1*H*-indol-3-yl]-2-phenylethanol (21c): Table 2, entry 5; yellow oil; $[\alpha]_D^{23}$=7.3 (c=0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.46 (d, J=8.2 Hz, 1H), 7.36–7.34 (m, 2H), 7.30–7.27 (m, 3H), 7.21–7.17 (m, 2H), 7.01 (td, J=7.0, 1.0 Hz, 1H), 6.44 (t, J=7.0 Hz, 1H), 5.16 (d, J=7.1 Hz, 2H), 4.68 (t, J=7.6 Hz, 1H), 4.37–4.35 (m, 2H), 3.80 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=211.20, 141.54, 138.08, 130.16, 128.42 (CH, 2C), 127.99 (CH, 2C), 126.60, 126.31 (CH), 121.91 (CH), 119.90 (CH), 119.51 (CH), 112.32, 109.23 (CH), 83.54 (CH), 78.42 (CH_2), 65.23 (CH_2), 45.10 (CH), 30.94 ppm (CH_3); HRMS-EI: m/z calcd for $C_{20}H_{19}NO$: 298.1467; found: 298.1467 [M^+].

(*R*)-9-Methoxy-6-methyl-5-methylene-1-phenyl-2,4,5,6-tetrahydro-1*H*-oxepino[4,5-*b*]indole (20d): Table 2, entry 6; yellow solid; $[\alpha]_D^{23}$=125.8 (c=0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.24–7.23 (m, 4H), 7.19 (d, J=9.0 Hz, 1H), 7.19–7.13 (m, 1H), 6.85 (dd, J=8.9, 2.5 Hz, 1H), 6.63 (d, J=2.4 Hz, 1H), 5.67 (s, 1H), 5.34 (s, 1H), 4.56 (AB, J=12.5 Hz, 1H), 4.46 (AB, J=12.5 Hz, 1H), 4.43 (dd, J=5.7, 3.8 Hz, 1H), 4.23 (AB of doublet, J=12.1, 5.8 Hz, 1H), 4.16 (AB of doublet, J=12.1, 3.8 Hz, 1H), 3.75 (s, 3H), 3.69 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=154.2 (C), 142.6 (C), 139.0 (C), 134.1 (C), 128.6 (CH), 128.5 (CH), 127.7 (C), 126.5 (CH), 119.6 (CH_2), 115.0 (C), 112.6 (CH), 110.5 (CH), 101.5 (CH), 100.5 (C), 77.1 (CH_2), 75.2 (CH_2), 56.0 (CH_3), 45.8 (CH), 31.7 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{21}H_{21}NO_2Na$: 342.1470; found: 342.1469 [M^++Na]; elemental analysis calcd (%) for $(C_{21}H_{21}NO_2)_4\cdot 3H_2O$: C 75.76, H 6.81, N 4.21; found: C 75.71, H 6.53, N 5.12.

2-[2-(Buta-2,3-dien-2-yl)-1-methyl-1*H*-indol-3-yl]ethanol (21e): Table 2, entry 7; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.59 (d, J=8.0 Hz, 1H), 7.29 (d, J=8.2 Hz, 1H), 7.22 (dt, J=7.0, 1.0 Hz, 1H), 7.11 (dt, J=7.0, 1.0 Hz, 1H), 4.85 (q, J=3.3 Hz, 2H), 3.87 (t, J=6.5 Hz, 2H), 3.70 (s, 3H), 3.05 (t, J=6.6 Hz, 2H), 2.06 (t, J=3.2 Hz, 3H), 1.47 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=209.6 (C), 137.4 (C), 135.5 (C), 128.0 (C), 121.9 (CH), 119.4 (CH), 118.9 (CH), 109.4 (CH), 108.2 (C), 91.3 (C), 74.4 (CH_2), 63.3 (CH_2), 30.6 (CH_3). 28.6 (CH_2), 20.5 ppm (CH_3); HRMS-EI: m/z calcd for $C_{15}H_{17}NO$: 227.1310; found: 227.1310 [M^+].

Tetracycle 22e: Table 2, entry 7; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.09 (dt, J=7.7, 1.3 Hz, 1H), 7.06 (dd, J=7.3, 1.1 Hz, 1H), 6.66 (dt, J=7.4, 0.9 Hz, 1H), 6.34 (d, J=7.9 Hz, 1H), 5.38 (q, J=1.6 Hz, 1H), 4.02 (ddd, J=8.8, 6.8, 2.0 Hz, 1H), 3.57 (ddd, J=10.7, 8.8, 5.0 Hz, 1H), 2.97 (s, 3H), 2.65 (AB of quintet, J=17.0, 2.3 Hz, 1H), 2.60 (AB of quintet, J=17.0, 2.3 Hz, 1H), 2.34 (ddd, J=11.9, 5.0, 2.2 Hz, 1H), 2.11 (ddd, J=11.9, 10.8, 6.8 Hz, 1H), 1.93 ppm (q, J=2.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=152.1 (C), 139.0 (C), 133.7 (C), 128.4 (CH), 127.8 (CH), 123.5 (CH), 118.2 (C), 117.6 (CH), 105.5 (CH), 68.7 (CH_2), 62.4 (C), 44.3 (CH_2), 43.6 (CH_2), 30.1 (CH_3), 13.5 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{15}H_{17}NONa$: 250.1208; found: 250.1216 [M^++Na]; elemental analysis calcd (%) for $C_{15}H_{17}NO$: C 79.26, H 7.54, N 6.16; found: C 79.31, H 7.54, N 6.52.

Tetracycles 22f/22f′: Table 2, entry 9; 3:1 isomer mixture of **22f/22f′** as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.37–7.23 (m, 5H; minor), 7.28–7.25 (m, 3H; major), 7.15 (td, J=7.6, 1.3 Hz, 1H; minor), 7.11 (dd, J=7.3, 1.1 Hz, 1H; minor), 7.04 (td, J=7.6, 1.2 Hz, 1H; major), 6.99–6.97 (m, 2H; major), 6.71 (td, J=7.4, 0.9 Hz, 1H; minor), 6.42 (d, J=7.8 Hz, 1H; minor), 6.36 (d, J=7.9 Hz, 1H; major), 6.32 (td, J=7.4, 0.9 Hz, 1H; major), 5.83 (dd, J=7.4, 0.9 Hz, 1H; major), 5.48–5.46 (m, 1H; major), 5.27–5.25 (m, 1H; minor), 4.20 (dd, J=8.6, 6.2 Hz, 1H; major), 4.12 (dd, J=9.1, 4.6 Hz, 1H; minor), 4.05 (dd, J=9.0, 5.8 Hz, 1H; minor), 3.90 (dd, J=11.6, 8.6 Hz, 1H; major), 3.54 (dd, J=11.8, 6.1 Hz, 1H), 3.07 (s, 3H; minor), 3.04 (s, 3H; major), 2.92 (dq, J=16.9, 2.2 Hz, 1H; major), 2.50 (dq, J=16.9, 2.2 Hz, 1H; major), 2.27 (dq, J=

17.6, 2.1 Hz, 1H; minor), 2.18 (dq, J=17.6, 2.4 Hz, 1H; minor), 1.99 (dt, J=3.8, 2.1 Hz, 3H; major), 1.97 ppm (dt, J=7.4, 0.9 Hz, 3H; minor); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=152.34 (major), 151.14 (minor), 140.75 (minor), 139.42 (major), 138.05 (minor), 136.35 (major), 135.14 (minor), 129.22 (CH, minor), 128.93 (CH, 2C, major), 128.90, 128.53 (CH, 2C, minor), 128.33 (CH, 2C, minor), 128.29 (CH, minor), 128.19 (CH, major), 127.89 (CH, 2C, major), 127.62 (CH, major), 127.17 (CH, major), 126.85 (CH, minor), 126.31 (CH, major), 123.40 (CH, minor), 118.50, 117.44 (CH, minor), 116.40 (CH, major), 105.54 (CH, minor), 104.62 (CH, major), 73.00 (CH_2, minor), 71.57 (CH_2, major), 66.14 (minor), 65.77 (major), 58.55 (CH, major), 57.72 (CH, minor), 44.75 (CH_2, major), 39.20 (CH_2, minor), 29.95 (CH_3, minor), 29.72 (CH_3, major), 13.31 (CH_3, minor), 13.22 ppm (CH_3, major); HRMS-ESI: m/z calcd for $C_{21}H_{21}NONa$: 326.1521; found: 326.1521 [M^++Na].

Tetracycles 22g/22g′: Table 2, entry 10; 2.5:1 mixture of **22g/22g′** as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.35–7.28 (m, 4H), 7.25–7.23 (m, 3H), 7.19–7.16 (m, 1H), 7.00–6.98 (m, 2H), 6.75 (d, J=2.6 Hz, 1H; minor), 6.71 (dd, J=8.4, 2.6 Hz, 1H; minor), 6.62 (dd, J=8.5, 2.6 Hz, 1H; major), 6.33 (d, J=8.4 Hz, 1H; minor), 6.27 (d, J=8.5 Hz, 1H; major), 5.44 (s, 1H), 5.43 (s, 1H), 5.23 (q, J=1.6 Hz, 1H; minor), 4.19 (dd, J=8.6, 6.2 Hz, 1H; major), 4.09 (AB of doublet, J=9.1, 4.7 Hz, 1H; minor), 4.03 (AB of doublet, J=9.1, 5.8 Hz, 1H; minor), 3.90 (dd, J=11.7, 8.7 Hz, 1H; major), 3.77 (s, 3H; minor), 3.52 (dd, J=11.7, 6.2 Hz, 1H; major), 3.50–3.48 (m, 1H), 3.39 (s, 3H; major), 3.01 (s, 3H; minor), 2.98 (s, 3H; major), 2.89 (d of quintet, J=16.9, 2.1 Hz, 1H; major), 2.48 (dquint, J=16.9, 2.4 Hz, 1H; major), 2.23 (AB of quintet, J=17.4, 2.3 Hz, 1H; minor), 2.17 (AB of quintet, J=17.4, 2.3 Hz, 1H; minor), 1.96 (q, J=1.8 Hz, 3H; major), 1.94 ppm (q, J=1.7 Hz, 3H; minor); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=153.0 (C, minor), 151.9 (C, major), 147.2 (C, major), 140.8 (C, minor), 139.9 (C, major), 138.5 (C, minor), 136.6 (C, minor), 136.5 (C. major), 130.0 (C, major), 129.1 (CH, major), 129.0 (CH, minor), 128.8 (CH, minor), 128.5 (CH, minor), 128.2 (CH, major), 127.4 (CH, major), 127.3 (CH, major), 127.1 (CH, minor), 119.1 (C, minor), 114.6 (CH, major), 113.1 (CH, major), 112.8 (CH, minor), 111.4 (CH, minor), 106.2 (CH, minor), 105.6 (CH, major), 73.3 (CH_2, minor), 71.8 (CH_2, major), 66.5 (C, minor), 66.2 (C, major), 58.3 (CH, major), 57.8 (CH, minor), 56.4 (CH_3, minor), 56.2 (CH_3, major), 44.5 (CH_2, major), 39.1 (CH_2, minor), 30.9 (CH_3, minor), 30.6 (CH_3, major), 13.3 (CH_3, minor), 13.2 ppm (CH_3, major); HRMS-ESI: m/z calcd for $C_{22}H_{23}NO_2Na$: 356.1626; found: 356.1624 [M^++Na]; elemental analysis calcd (%) for $(C_{22}H_{23}NO_2)_2{\cdot}H_2O$: C 77.16, H 7.06, N 4.09; found: C 77.25, H 6.74, N 4.46.

1,2,3,4-Tetrahydro-1-methylenecarbazol-3-spiro-5′-(1,3-dioxane-4,6-dione) (24): Table 3, entry 1; white solid; m.p. 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=8.12 (brs, 1H), 7.42 (d, J=7.9 Hz, 1H), 7.31 (d, J=8.2 Hz, 1H), 7.19 (td, J=7.1, 1.1 Hz, 1H), 7.08 (td, J=7.6, 0.9 Hz, 1H), 5.29 (s, 1H), 5.01 (s, 1H), 3.49 (s, 2H), 3.15 (s, 2H), 1.82 (s, 3H), 1.79 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=168.66, 136.88, 131.64, 131.46, 126.86, 123.52 (CH), 119.90 (CH), 118.52 (CH), 111.10 (CH), 108.82, 107.03 (CH_2), 105.09, 49.85, 39.06 (CH_2), 29.99 (CH_2), 29.28 (CH_3), 28.09 ppm (CH_3); HRMS-CI m/z calcd for $C_{18}H_{18}NO_4$: 312.1236; found: 312.1227 [M^++H].

Dimer 25: Table 3, entry 2; brown solid; m.p. 285–287 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=9.42 (s, 1H), 8.12 (s, 1H), 7.42 (d, J=7.8 Hz, 1H), 7.22 (d, J=8.0 Hz, 1H), 6.93 (td, J=6.5, 1.4 Hz, 1H), 6.88 (t, J=7.0 Hz, 1H), 6.81–6.76 (m, 2H), 6.74 (d, J=7.4 Hz, 1H), 6.56 (d, J=8.1 Hz, 1H), 5.56 (s, 1H), 3.73 (d, J=16.2 Hz, 1H), 3.65 (d, J=16.0 Hz, 1H), 3.61 (d, J=16.3 Hz, 1H), 3.49 (d, J=15.7 Hz, 1H), 3.13 (d, J=13.0 Hz, 1H), 2.64 (d, J=14.1 Hz, 1H), 2.51 (d, J=14.4 Hz, 1H), 2.32 (d, J=13.2 Hz, 1H), 1.99 (s, 3H), 1.94 (s, 3H), 1.86 (s, 3H), 1.85 (s, 3H), 1.52 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=171.00, 170.41, 169.88, 136.85, 136.68, 134.20, 133.90, 132.25, 125.37, 124.82, 122.10 (CH), 121.78 (CH), 119.41 (CH), 118.89 (CH), 118.62 (CH), 117.35 (CH), 117.20 (CH), 111.35 (CH), 110.95 (CH), 106.16, 105.87, 102.40, 52.97, 49.44, 46.67 (CH_2), 41.89 (CH_2), 35.51, 32.44 (CH_2), 29.98 (CH_3), 29.96 (CH_3), 29.52 (CH_3), 28.63 (CH_3), 28.56 (CH_3), 28.19 ppm (CH_2); HRMS-CI: m/z calcd for $C_{36}H_{35}N_2O_8$: 623.2393; found: 623.2393 [M^++H]; the configuration at the exocylic double bond was determined by a NOESY experiment.

(2*S*,4*R*)-2,3,4,9-Tetrahydro-4,9-dimethyl-1-methylene-1*H*-carbazol-2-ol and (2*R*,4*R*)-2,3,4,9-tetrahydro-4,9-dimethyl-1-methylene-1*H*-carbazol-2-ol (27): Table 3, entry 3; white solid; m.p. 118–120 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ=7.66 (d, J=7.9 Hz, 1H; minor), 7.61 (d, J=8.0 Hz, 1H; major), 7.30 (d, J=8.3 Hz, 1H), 7.22 (t, J=8.6 Hz, 1H), 7.08 (t, J=7.5 Hz, 1H; major), 7.07 (t, J=7.6 Hz, 1H; minor), 5.47 (s, 1H; minor), 5.42 (s, 1H; major), 5.36 (s, 1H; major), 5.34 (s, 1H; minor), 4.60 (br d, J=7.4 Hz, 1H; major), 4.44 (br d, J=10.0 Hz, 1H; minor), 3.82 (s, 3H; major), 3.81 (s, 3H; minor), 3.43–3.35 (m, 1H; major), 3.35–3.31 (m, 1H; minor), 2.35 (ddd, J=12.6, 6.2, 3.9 Hz, 1H; minor), 2.18 (ddd, J=12.8, 8.8, 6.6, 1H; major), 1.90 (ddd, J=13.1, 5.3, 3.6, 1H; major), 1.77 (br s, 1H), 1.65 (ddd, J=12.0, 10.7, 5.4, 1H; minor), 1.49 (d, J=6.8 Hz, 3H; minor), 1.44 ppm (d, J=6.5 Hz, 3H; major); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, DEPT): δ=141.35 (minor), 140.89 (major), 139.88 (minor), 139.81, (major), 132.52 (minor), 131.79 (major), 125.73 (minor), 125.67 (major), 122.64 (CH, major), 122.51 (CH, minor), 120.25 (CH, minor), 119.87 (CH, major), 119.26 (CH, major), 119.21 (CH, minor), 118.08 (major), 117.78 (minor), 109.46 (CH, minor), 109.39 (CH, major), 107.09 (CH_2, major), 105.80 (CH_2, minor), 71.43 (CH_2, minor), 70.39 (CH, major), 42.95 (CH_2, minor), 41.34 (CH_2, major), 31.92 (CH_2, major), 31.74 (CH, minor), 27.52 (CH_3, minor), 25.33 (CH_3, major), 22.16 (CH_3, minor), 21.66 ppm (CH_3, major); HRMS-ESI m/z calcd for $C_{15}H_{18}NO$ 228.1388; found: 228.1384 [M^++H].

(4*R*,1*S*)-3,4-Dihydro-1,4,9-trimethyl-1*H*-carbazol-2(9*H*)-one and (4*R*,1*R*)-3,4-dihydro-1,4,9-trimethyl-1*H*-carbazol-2(9*H*)-one (28): Table 3, entry 4; white solid; m.p. 109–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.85 (d, J=8.1 Hz, 1H; major), 7.56 (d, J=9.0 Hz, 1H; minor), 7.29 (d, J=8.1 Hz, 1H), 7.21 (t, J=8.0 Hz, 1H), 7.12 (td, J=7.9, 1.0 Hz, 1H), 3.66 (s, 3H; major), 3.63 (s, 3H; minor), 3.62–3.56 (m, 2H; major), 3.50–3.45 (m, 2H; minor), 3.10 (dd, J=13.3, 6.8 Hz, 1H; minor), 2.80 (dd, J=14.0, 6.3 Hz, 1H; major), 2.64 (dd, J=14.0, 4.6 Hz, 1H; major), 2.37 (dd, J=13.3, 3.1 Hz, 1H; minor), 1.52 (d, J=7.2 Hz, 3H; major), 1.50 (d, J=7.0, 3H; minor), 1.38 (d, J=6.9, 3H; major), 1.31 ppm (d, J=6.9, 3H; minor); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=211.51 (minor), 211.24 (major), 138.28 (minor), 138.10, (major), 136.29 (major), 135.56 (minor), 125.54 (major), 125.46 (minor), 121.52 (CH), 119.37 (CH), 118.61 (CH), 113.82 (major), 113.61 (minor), 109.11 (CH, minor), 109.09 (CH, major), 46.64 (CH_2, major), 44.16 (CH_2, minor), 42.65 (CH_3, minor), 41.61 (CH_3, major), 29.81 (CH_2, major), 29.63 (CH, minor), 28.07 (CH_2, minor), 27.54 (CH_2, major), 23.18 (CH_3, major), 22.66 (CH_3, minor), 19.80 (CH_3, major), 18.52 ppm (CH_3, major); HRMS-ESI: m/z calcd for $C_{15}H_{18}NO$: 228.1388; found: 228.1381 [M^++H].

(*R*)-4,9-Dihydro-4,9-dimethyl-3*H*-carbazole (30): Table 3, entry 5; white solid; m.p. 75–77 °C; $[\alpha]_D^{23}=-9.6$ (c=0.9 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ=7.65 (dt, J=8.0, 0.8 Hz, 1H), 7.24 (d, J=8.4 Hz, 1H), 7.13 (td, J=6.8 1.2 Hz, 1H), 7.06 (td, J=8.0, 0.8 Hz, 1H), 6.52 (ddd, J=10.0, 2.4, 1.6 Hz, 1H), 5.95 (ddd, J=10.0, 5.2, 4.0 Hz, 1H), 3.67 (s, 3H), 3.30–3.21 (m, 1H), 2.63 (ddd, J=17.2, 4.0, 2.8 Hz, 1H), 2.25 (ddd, J=17.2, 5.2, 1.6 Hz, 1H), 1.27 ppm (d, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ=137.24, 133.81, 126.94 (CH), 125.87, 120.81 (CH), 119.18 (CH), 118.54 (CH), 116.39 (CH), 113.78, 109.03 (CH), 32.91 (CH_2), 29.04 (CH_3), 26.48 (CH), 20.17 ppm (CH_3); HRMS-CI m/z calcd for $C_{13}H_{13}N$: 198.1283; found: 198.1287 [M^++H].

2-(4,5-Dihydro-5-methyleneoxazol-2-yl)1*H*-indole (32): Scheme 3; white solid; m.p. 175–177 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ=9.64 (br s, 1H), 7.70 (d, J=8.0 Hz, 1H), 7.40 (d, J=8.3 Hz, 1H), 7.31 (t, J=7.9 Hz, 1H), 7.16 (t, J=7.4 Hz, 1H), 7.15 (s, 1H), 4.88 (q, J=2.9 Hz, 1H), 4.69 (t, J=2.6 Hz, 2H), 4.43 ppm (q, J=2.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, DEPT): δ=159.02, 158.26, 137.35, 127.63, 124.90 (CH), 124.20, 122.16 (CH), 120.68 (CH), 111.59 (CH), 107.26 (CH), 84.40 (CH_2), 57.11 ppm (CH_2); HRMS-CI: m/z calcd for $C_{12}H_{11}N_2O$: 199.0871; found: 199.0872 [M^++H].

General procedure for the gold-catalyzed intermolecular reactions of indoles with alkynes (Table 4 and Schemes 4–8): The alkyne (0.51–0.85 mol) was added to a mixture of indole derivative (0.84 mol) and gold catalyst (0.05 mol) in toluene (4 mL). The reaction mixtures were

stirred at room temperature (unless stated otherwise) for the stated time. The mixtures were filtered trough silica gel with CH_2Cl_2 and the solvents evaporated. The residue was subjected to chromatography to give the desired product.

3,3′-{1-[3,5-bis(trifluoromethyl)phenyl]ethane-1,1-diyl}bis(1*H*-indole) (34e): Table 4, entry 5; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.98 (brs, 2H), 7.88 (brs, 2H), 7.73 (brs, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.17 (dt, J = 7.0, 1.0 Hz, 2H), 6.96 (dt, J = 1.1, 7.2 Hz, 2H), 6.65 (d, J = 2.6 Hz, 2H), 2.40 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 23 °C, DEPT): δ = 151.0 (C), 137.4 (C), 131.1 (q, J(C,F) = 33.1 Hz, C), 128.5 (d, J(C,F) = 3.1 Hz, CH), 126.0 (C), 123.6 (CH), 123.1 (C), 122.6 (C), 122.2 (CH), 121.6 (CH), 120.2 (m, CH), 119.6 (CH), 111.6 (CH), 44.1 (C), 28.9 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{26}H_{18}N_2F_6Na$: 495.1272; found: 495.1268 [M^++Na].

3,3′-[1-(3,5-Difluorophenyl)ethane-1,1-diyl]bis(1*H*-indole) (34f): Table 4, entry 6; yellow solid; m.p. 171 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.88 (brs, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.17 (dt, J = 7.1, 1.1 Hz, 2H), 6.99 (dt, J = 7.1, 1.0 Hz, 2H), 6.94 (dd, J(H,F) = 9.4 Hz, J(H,H) = 2.2 Hz, 2H), 6.66 (tt, J(H,F) = 8.7, J(H,H) = 2.3 Hz, 1H), 6.63 ppm (d, J = 2.6 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 162.9 (dd, J(C,F) = 246.8, 13.0 Hz, C), 152.8 (t, J-(C,F) = 7.8 Hz, C), 137.3 (C), 126.2 (C), 123.6 (C), 123.5 (CH), 122.0 (CH), 121.9 (CH), 119.4 (CH), 111.5 (CH), 111.3 (q, J(C,F) = 6.6 Hz, CH), 101.5 (t, J(C,F) = 25.6 Hz, CH), 44.1 (C), 28.7 ppm (CH_3); HRMS-ESI m/z calcd for $C_{24}H_{18}N_2F_2Na$: 395.1336; found: 395.1353 [M^++Na]; elemental analysis calcd (%) for $(C_{24}H_{18}F_2N_2)_3 \cdot H_2O$: C 76.17, H 4.97, N 7.40; found: C 76.00, H 4.97, N 7.63.

3,3′-(1-(Pyren-1-yl)ethane-1,1-diyl)bis(1*H*-indole) (34g): Table 4, entry 7; beige solid; m.p. 210 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 8.53 (d, J = 9.5 Hz, 1H), 8.28 (d, J = 8.2 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.11 (dd, J = 7.5, 1.1 Hz, 1H), 8.03 (q, J = 8.9 Hz, 2H), 8.00 (d, J = 7.5 Hz, 1H), 7.93–7.89 (m, 3H), 7.66 (d, J = 9.5 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 9.1 Hz, 2H), 7.11 (dt, J = 7.1, 1.0 Hz, 2H), 6.88 (dt, J = 7.2, 1.0 Hz, 2H), 6.76 (d, J = 2.4 Hz, 2H), 2.77 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 142.0 (C), 137.3 (C), 131.6 (C), 130.6 (C), 130.5(C), 129.9 (C), 127.7 (CH), 127.3 (CH), 127.1 (CH), 126.8 (CH), 126.7 (C), 126.2 (C), 125.8 (CH), 125.3 (CH), 125.2 (C), 125.1 (C), 124.9 (CH), 124.8 (CH), 124.7 (CH), 124.0 (CH), 122.2 (CH), 121.8 (CH), 119.3 (CH), 111.4 (CH). 45.4 (C), 30.6 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{34}H_{24}N_2Na$: 483.1837; found: 483.1839 [M^++Na]; elemental analysis calcd (%) for $(C_{34}H_{24}N_2)_3 \cdot 4H_2O$: C 84.27, H 5.55, N 5.78; found: C 84.23, H 5.69, N 5.54.

3,3′-(Decane-2,2-diyl)bis(1*H*-indole) (34h): Table 4, entry 8; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.91 (brs, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 2.4 Hz, 2H), 7.05 (dt, J = 7.2, 1.1 Hz, 2H), 6.84 (dt, J = 7.0, 0.9 Hz, 2H), 2.38–2.33 (m, 2H), 1.84 (s, 3H), 1.24–1.13 (m, 8H), 0.81 ppm (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C): δ = 137.2 (C), 126.7 (C), 124.7 (C), 121.5 (CH), 121.4 (CH), 121.3 (CH), 118.7 (CH), 111.1 (CH), 40.7 (CH_2), 38.6 (C), 32.1 (CH_2), 30.2 (CH_2), 27.1 (CH_3), 24.7 (CH_2), 22.9 (CH_2), 14.3 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{24}H_{28}N_2Na$: 367.2150; found: 367.2162 [M^++Na]; elemental analysis calcd (%) for $(C_{24}H_{28}N_2)_2 \cdot H_2O$: C 81.54, H 8.27, N 7.92; found: C 81.32, H 8.15, N 7.55.

3,3′-(Decane-2,2-diyl)bis(1-methyl-1*H*-indole) (34i): Table 4, entry 9; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.44 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.15 (dt, J = 7.1, 0.8 Hz, 2H), 6.93 (s, 2H), 6.90 (dt, J = 7.1, 0.8 Hz, 2H), 3.78 (s, 6H), 2.42–2.38 (m, 2H), 1.88 (s, 3H), 1.33–1.17 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 137.8 (C), 127.1 (C), 126.3 (CH), 123.3 (C), 121.7 (CH), 120.9 (CH), 118.1 (CH), 109.1 (CH), 41.1 (CH_2), 38.6 (C), 32.8 (CH_3), 32.0 (CH_2), 30.3 (CH_2), 27.5 (CH_3), 24.8 (CH_2), 22.9 (CH_2), 14.3 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{26}H_{32}N_2Na$: 395.2463; found: 395.2458.0 [M^++Na]; elemental analysis calcd (%) for $(C_{26}H_{32}N_2)_3 \cdot H_2O$: C 82.49, H 8.70, N 7.40; found: C 82.42, H 8.27, N 7.55.

3,3′-(5-Chloropentane-2,2-diyl)bis(1*H*-indole) (34j): Table 4, entry 10; white solid; m.p. 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.96 (s, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 2.4 Hz, 2H), 7.07 (dt, J = 7.1, 1.2 Hz, 2H), 6.85 (dt, J = 7.1, 1.1 Hz, 2H), 3.45 (t, J = 6.7 Hz, 2H), 2.52–2.48 (m, 2H), 1.86 (s, 3H), 1.70–1.63 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 137.2 (C), 126.4 (C), 123.9 (C), 121.7 (CH), 121.4 (CH), 121.3 (CH), 118.9 (CH), 111.2 (CH), 46.2 (CH_2), 38.3 (C), 38.1 (CH_2), 28.5 (CH_2), 27.3 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{21}H_{21}ClN_2Na$: 359.1291; found: 359.1300 [M^++Na]; elemental analysis calcd (%) for $C_{21}H_{21}ClN_2$: C 74.88, H 6.28, N 8.32; found: C 74.17, H 6.28, N 8.31.

5,5-Di(1*H*-indol-3-yl)hexanenitrile (34k): Table 4, entry 11; white solid; m.p. 185–187 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.97 (brs, 2H), 7.34–7.31 (m, 4H), 7.08 (dt, J = 7.0, 1.1, 2H), 7.07 (d, J = 2.5, 2H), 6.86 (dt, J = 7.1, 1.1 Hz, 2H), 2.52–2.48 (m, 2H), 2.20 (t, J = 7.2 Hz, 2H), 1.86 (s, 3H), 1.57–1.50 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 137.2 (C), 126.3 (C), 123.5 (C), 121.8 (CH), 121.4 (CH), 121.2 (CH), 120.2 (C), 119.1 (C), 111.3 (CH), 39.8 (CH_2), 38.4 (C), 27.3 (CH_3), 21.3 (CH_2), 17.8 ppm (CH_2); HRMS-ESI: m/z calcd for $C_{22}H_{21}N_3Na$: 350.1633; found: 350.1630 [M^++Na]; elemental analysis calcd (%) for $C_{22}H_{21}N_3$: C 80.70, H 6.46, N 12.83; found: C 80.23, H 6.53, N 12.66.

3,3′-(Octane-2,2-diyl)bis(1*H*-indole-5-carbonitrile) (34l): Table 4, entry 12; white solid; m.p. 206 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 8.47 (brs, 2H) 7.43 (s, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 2.4 Hz, 2H), 7.27 (dd, J = 8.6, 1.4 Hz, 2H), 2.28–2.24 (m, 2H), 1.77 (s, 3H), 1.26–1.08 (m, 8H), 0.81 ppm (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 138.9 (C), 126.4 (CH), 126.1 (C), 125.0 (C), 124.8 (CH), 122.9 (CH), 121.2 (C), 112.4 (CH), 102.0 (C), 40.6 (CH_2), 38.0 (C), 32.0 (CH_2), 30.0 (CH_2), 27.2 (CH_3), 24.4 (CH_2), 22.8 (CH_2), 14.2 ppm (CH_3); HRMS-ESI m/z calcd for $C_{26}H_{26}N_4Na$: 417.2055; found: 417.2075 [M^++Na]; elemental analysis calcd (%) for $C_{26}H_{26}N_4$: C 79.16, H 6.64, N 14.20; found: C 78.70, H 6.70, N 13.75.

5,5-Bis(5-bromo-1*H*-indol-3-yl)hexanenitrile (34m): Table 4, entry 13; white solid; m.p. 203 °C; ^{1}H NMR (400 MHz, [D$_6$]acetone, 23 °C): δ = 10.32 (brs, 2H), 7.48 (d, J = 2.6 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 1.9 Hz, 2H), 7.05 (dd, J = 8.6, 2.0 Hz, 2H), 2.51–2.47 (m, 2H), 2.42 (t, J = 7.2 Hz, 2H), 1.83 (s, 3H), 1.55–1.48 ppm (m, 2H); ^{13}C NMR (100 MHz, [D$_6$]acetone, 23 °C, DEPT): δ = 137.1 (C), 128.9 (C), 124.5 (CH), 124.0 (CH), 123.4 (CH), 123.2 (C), 120.7 (C), 114.0 (CH), 111.9 (C), 40.3 (CH_2), 38.3 (C), 27.4 (CH_3), 22.0 (CH_2), 17.5 ppm (CH_2); HRMS-ESI: m/z calcd for $C_{22}H_{19}Br_2N_3Na$: 505.9843; found: 505.9859 [M^++Na]; elemental analysis calcd (%) for $C_{22}H_{19}Br_2N_3$: C 54.46, H 3.95, N 8.66; found: C 54.14, H 3.92, N 8.79.

1,3-Bis[3,5-bis(trifluoromethyl)phenyl]-3-(1*H*-indol-3-yl)-1-methyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (35/35′): Scheme 4; first isomer: yellow solid; m.p. 106–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 8.02 (brs, 1H), 7.96 (brs, 1H), 7.82 (brs, 3H), 7.75 (brs, 2H), 7.64 (brs, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.32 (d J = 8.2 Hz, 1H), 7.27–7.23 (m, 1H), 7.16 (t, J = 7.7 Hz, 2H), 7.01–6.95 (m, 2H), 6.57 (d, J = 2.7 Hz, 1H), 3.72 (AB, J = 13.4 Hz, 1H), 3.33 (AB, J = 13.4 Hz, 1H), 1.86 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 151.8 (C), 149.6 (C), 145.3 (C), 141.6 (C), 137.3 (C), 132.3 (AB, J = 33.1 Hz, C), 131.9 (AB, J = 16.1 Hz, C), 131.8 (AB, J = 33.1 Hz, C), 131.6 (AB, J = 16.1 Hz, C), 127.8 (d, J = 2.8 Hz, CH), 126.7 (d, J = 2.2 Hz, CH), 125.3 (C), 124.9 (d, J = 9.9 Hz, C), 124.4 (C), 123.5 (C), 123.1 (CH), 122.9 (CH), 122.6 (CH), 122.1 (d, J = 9.9 Hz, C), 121.1 (m, CH), 121.0 (CH), 120.5 (CH), 120.1 (m, CH), 119.6 (CH), 119.3 (C), 119.1 (CH), 112.8 (CH), 112.0 (CH), 64.7 (CH_2), 52.0 (C), 47.7 (C), 29.3 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{36}H_{23}N_2F_{12}$: 711.1670; found: 711.1698 [M^++H]; elemental analysis calcd (%) for $(C_{36}H_{22}F_{12}N_2)_2 \cdot H_2O$: C 60.00, H 3.22, N 3.89; found: C 60.14, H 3.39, N 3.83; second isomer: (28%), yellow solid; m.p. 107–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 8.14 (brs, 1H), 8.07 (s, 1H), 7.65 (s, 2H), 7.58–7.55 (m, 3H), 7.50 (s, 2H), 7.42 (t, J = 8.3 Hz, 2H), 7.29–7.20 (m, 3H), 7.03–6.96 (m, 2H), 6.54 (d, J = 2.7 Hz, 1H), 3.76 (AB, J = 13.4 Hz, 1H), 3.49 (AB, J = 13.4 Hz, 1H), 1.92 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 151.6 (C), 147.9 (C), 145.5 (C), 141.4 (C), 137.4 (C), 132.5–131.1 (m, C, 2C), 127.4 (brs, CH), 126.5 (brs, CH), 125.5 (C), 124.8 (d, J = 11.6 Hz, C), 124.1 (C), 123.7 (C), 123.1 (CH), 123.0 (CH), 122.6 (CH), 122.2 (d, J = 11.6 Hz, C), 121.2 (CH), 120.7 (m, CH), 120.6 (CH), 120.2 (m, CH), 119.8 (C), 119.7 (CH), 119.0 (CH), 112.9 (CH), 112.0 (CH), 63.7 (CH_2), 51.8 (C), 47.8 (C), 30.2 ppm (CH_3); HRMS-ESI m/z calcd for $C_{36}H_{23}N_2F_{12}$: 711.1670; found:

711.1694 [M^++H]; elemental analysis calcd (%) for $C_{36}H_{22}F_{12}N_2$: C 60.85, H 3.12, N 3.94; found: C 60.74, H 3.52, N 4.13.

3,3′-(1-Phenylpropane-2,2-diyl)bis(1*H*-indole) (36): Scheme 5: white solid; m.p. 197 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.94 (brs, 2H), 7.36 (d, J = 8.2 Hz), 7.34 (d, J = 8.2 Hz, 2H), 7.11–7.01 (m, 5H), 7.00 (d, J = 2.6 Hz, 2H), 6.85 (dt, J = 7.1, 0.9 Hz, 2H), 6.60 (d, J = 7.1 Hz, 2H), 3.69 (s, 2H), 1.68 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 138.8 (C), 137.2 (C), 130.9 (CH), 127.2 (CH), 126.7 (C), 125.9 (CH), 123.8 (C), 121.6 (CH), 121.5 (CH), 121.3 (CH), 119.0 (CH), 111.2 (CH), 45.9 (CH_2), 39.4 (C), 26.7 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{25}H_{22}N_2Na$: 373.1681; found: 373.1691 [M^++Na]; elemental analysis calcd (%) for $C_{25}H_{22}N_2$·0.5: C 83.53, H 6.45, N 7.79; found: C 82.90, H 6.18, N 7.75.

5,5′-(1-Phenylethane-1,1-diyl)bis(2-ethyl-1*H*-pyrrole) (38): Scheme 5; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.52 (brs, 2H), 7.30–7.19 (m, 3H), 7.16–7.14 (m, 2H), 5.83 (t, J = 3.1 Hz, 2H), 5.80 (t, J = 3.0 Hz, 2H), 2.54 (q, J = 7.7 Hz, 4H), 2.00 (s, 3H), 1.19 ppm (t, J = 7.6 Hz, 6H);. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 147.8 (C), 136.2 (C), 133.7 (C), 128.2 (CH), 127.6 (CH), 126.7 (CH), 106.4 (CH), 104.0 (CH), 44.9 (C), 28.9 (CH_3), 21.0 (CH_2), 13.6 ppm (CH_3); HRMS-ESI m/z calcd for $C_{20}H_{24}N_2Na$: 315.1837; found: 315.1851 [M^++Na]; elemental analysis calcd (%) for $(C_{20}H_{24}N_2)_7$·H_2O: C 81.43, H 8.30, N 9.50; found: C 81.68, H 7.97, N 9.20.

1,9-Dimethyl-3-(3-methyl-1*H*-indol-2-yl)-1,3-diphenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (39a/39a′): Scheme 6; 2.1:1 isomer mixture as a white solid; m.p. 231–237 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.64 (d, J = 7.9 Hz, 1H; major), 7.61 (d, J = 8.2 Hz, 1H; minor), 7.54 (brs, 1H; minor), 7.43 (brs, 1H; major), 7.41–7.34 (m, 7H), 7.29–7.00 (m, 10H), 6.96 (t, J = 7.8 Hz, 2H), 6.90 (dt, J = 7.1, 1.2 Hz, 2H), 6.44 (d, J = 9.1 Hz, 1H; minor), 6.42 (d, J = 8.6 Hz, 1H; major), 3.85 (AB, J = 13.1 Hz, 1H; major) 3.67 (AB, J = 12.7 Hz, 1H; minor), 3.58 (AB, J = 12.7 Hz, 1H; minor), 3.39 (AB, J = 13.1 Hz, 1H; major), 2.25 (s, 3H; major), 2.15 (s, 3H; minor), 2.10 (s, 3H; minor), 1.96 (s, 3H; major), 1.75 (s, 3H; major), 1.60 ppm (s, 3H; minor); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 146.8 (C), 146.4 (C), 145.9 (C), 145.7 (C), 141.9 (C), 141.1 (C), 134.9 (C), 134.3 (C) 134.2 (C), 134.0 (C), 133.7 (C), 133.3 (C), 132.1 (C), 131.8 (C), 130.2 (C), 130.0 (C), 129.0 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 127.7 (CH), 127.5 (CH), 126.6 (CH), 126.5 (CH), 126.2 (CH), 125.9 (CH), 122.0 (CH), 121.8 (CH), 121.5 (CH), 119.6 (CH), 119.5 (CH), 119.3 (CH), 119.2 (CH), 119.1 (CH), 119.0 (CH), 118.6 (CH), 118.3 (CH), 111.2 (CH), 110.8 (CH), 110.6 (CH), 110.4 (CH), 108.6 (C), 108.2 (C), 102.8 (C), 102.2 (C), 68.0 (C), 65.4 (CH_2), 64.6 (CH_2), 53.6 (C), 45.4 (C), 46.2 (C), 27.5 (CH_3), 26.1 (CH_3), 10.4 (CH_3), 10.1 (CH_3), 8.8 (CH_3), 8.5 ppm (CH_3); HRMS-ESI: m/z calcd for $C_{34}H_{30}N_2Na$: 489.2307; found: 489.2328 [M^++Na]; elemental analysis calcd (%) for $(C_{34}H_{30}N_2)_3$·H_2O: C 86.40, H 6.54, N 5.93; found: C 86.61, H 6.67, N 6.03.

4,4′-(1,9-Dimethyl-3-(3-methyl-1*H*-indol-2-yl)-2,3-dihydro-1*H*-pyrrolo-[1,2-*a*]indole-1,3-diyl)dibutanenitrile (41a/41a′): Scheme 6; **41a′**: yellow solid; m.p. 96 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.69 (brs, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.56–7.54 (m, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.21–7.14 (m, 2H), 7.12–7.11 (m, 3H), 2.97 (AB, J = 13.5 Hz, 1H) 2.81 (AB, J = 13.5 Hz, 1H), 2.72 (ddd, J = 14.3, 12.5, 4.2 Hz, 1H), 2.49 (ddd, J = 14.5, 12.3, 4.2 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 2.26–2.20 (m, 2H), 2.02 (t, J = 7.0 Hz, 2H), 1.66–1.61 (m, 3H), 1.60 (s, 3H), 1.50–1.39 (m, 2H), 1.08–1.02 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 146.3 (C), 138.2 (C), 134.5 (C), 133.8 (C), 131.5 (C), 130.5 (C), 122.1 (CH), 122.0 (CH), 120.0 (CH), 119.7 (CH), 119.4 (CH), 119.4 (C), 119.2 (C), 118.4 (CH), 111.1 (CH), 110.2 (CH), 105.1 (C), 102.2 (C), 64.5 (C), 55.5 (CH_2), 41.2 (CH_2), 41.1 (C), 38.2 (CH_2), 26.2 (CH_3), 21.7 (CH_2), 20.0 (CH_2), 17.6 (CH_2), 17.2 (CH_2), 10.2 (CH_3), 8.6 ppm (CH_3); HRMS-ESI m/z calcd for $C_{30}H_{32}N_4Na$: 471.2525; found: 471.2513 [M^++Na]; elemental analysis calcd (%) for $C_{30}H_{32}N_4$·0.75H_2O: C 76.24, H 7.39, N 11.85; found: C 76.33, H 7.01, N 11.67; **41a′**: (40%), yellow solid; m.p. 105–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.61 (d, J = 7.5 Hz, 1H), 7.54–7.51 (m, 1H), 7.37 (brs, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.21–7.13 (m, 2H), 7.10–7.06 (m, 3H), 2.92 (AB, J = 12.9 Hz, 1H), 2.81–2.74 (m, 1H), 2.75 (AB, J = 12.9, 1H), 2.65–2.57 (m, 1H), 2.45 (t, J = 6.9 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 2.34–2.32 (m, 2H), 2.07–2.03 (m, 2H), 1.83–1.58 (m, 2H), 1.37–1.31 (m, 2H), 1.11 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 146.3 (C), 138.2 (C), 134.3 (C), 133.8 (C), 131.4 (C), 130.4 (C), 122.0 (CH), 121.9 (CH), 120.0 (CH), 119.6 (CH), 119.5 (C), 119.3 (CH), 119.2 (C), 118.3 (CH), 111.1 (CH), 109.9 (CH), 105.1 (C), 101.3 (C), 64.6 (C), 52.7 (CH_2), 41.1 (C), 39.1 (CH_2), 37.7 (CH_2), 27.4 (CH_3), 21.6 (CH_2), 20.1 (CH_2), 17.9 (CH_2), 17.3 (CH_2), 10.1 (CH_3), 8.3 ppm (CH_3); HRMS-ESI m/z calcd for $C_{30}H_{32}N_4Na$: 471.2525; found: 471.2513 [M^++Na]; elemental analysis calcd (%) for $C_{30}H_{32}N_4$·H_2O: C 77.22, H 7.34, N 12.01; found: C 77.24, H 7.21, N 11.44.

3-(2-Methyltetrahydrofuran-2-yl)-1*H*-indole (42): Scheme 7; white solid; m.p. 88 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 8.01 (brs, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 7.10 (d, J = 2.1 Hz, 1H), 4.06–3.95 (m, 2H), 2.44–2.38 (m, 1H), 2.09–2.02 (m, 2H), 1.99–1.91 ppm (m, 1H), 1.70 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 137.2 (C), 125.3 (C), 123.3 (C), 122.0 (CH), 120.6 (CH), 120.5 (CH), 119.5 (CH), 111.4 (CH), 82.0 (C), 67.5 (CH_2), 38.6 (CH_2), 28.7 (CH_3), 26.3 ppm (CH_2); HRMS-EI m/z calcd for $C_{13}H_{15}NO$: 201.1154; found: 201.1163 [M^+]; elemental analysis calcd (%) for $C_{13}H_{15}NO$: C 77.58, H 7.51, N 6.96; found: C 77.55, H 7.35, N 7.13.

3-(2-Methyltetrahydro-2*H*-pyran-2-yl)-1*H*-indole (43): Scheme 7; white solid; m.p. 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 8.05 (brs, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.20 (dt, J = 7.1, 1.2 Hz, 1H), 7.11 (dt, J = 7.0, 1.1 Hz, 1H), 7.01 (d, J = 2.5 Hz, 1H), 3.76–3.71 (m, 1H), 3.46 (dt, J = 11.3, 2.8 Hz, 1H), 2.27–2.21 (m, 1H), 1.81–1.60 (m, 4H), 1.57 (s, 3H), 1.44–1.39 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 137.0 (C), 1.26.1 (C), 122.1 (CH), 121.8 (CH), 121.7 (CH), 120.3 (C), 119.7 (CH), 111.2 (CH), 74.4 (C), 63.0 (CH_2), 35.7 (CH_2), 31.3 (CH_3), 26.0 (CH_2), 20.4 ppm (CH_2); HRMS-ESI: m/z calcd for $C_{14}H_{17}NO$: 215.1310; found: 215.1311 [M^+]; elemental analysis calcd (%) for $C_{14}H_{17}NO$: C 78.10, H 7.96, N 6.51; found: C 77.60, H 7.72, N 6.69.

1-Methyl-1-phenyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indole (45): Scheme 8; yellow solid; m.p. 152 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.78 (brs, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.38–7.35 (m, 3H), 7.34–7.28 (m, 3H), 7.21 (dt, J = 7.1, 1.2 Hz, 1H), 7.15 (dt, J = 6.9, 1.0 Hz, 1H), 4.03 (ddd, J = 11.7, 5.7, 3.0 Hz, 1H), 3.73 (ddd, J = 11.6, 9.5, 4.3 Hz, 1H), 3.01 (ddd, J = 15.3, 9.6, 5.7 Hz, 1H), 2.74 (ddd, J = 15.4, 4.2, 3.1 Hz, 1H), 1.90 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 144.6 (C), 136.8 (C), 136.1 (C), 128.4 (CH), 128.0 (CH), 127.2 (C), 126.9 (CH), 122.2 (CH), 119.9 (CH), 118.7 (CH), 111.1 (CH), 108.5 (C), 76.2 (C), 60.9 (CH_2), 28.2 (CH_3), 22.5 ppm (CH_2); HRMS-ESI: m/z calcd for $C_{18}H_{17}NO$: 263.1310; found: 263.1310 [M^+]; elemental analysis calcd (%) for $C_{18}H_{17}NO$: C 82.10, H 6.51, N 5.32; found: C 81.71, H 6.42, N 5.41.

***tert*-Butyl-2-[2-(1-phenylvinyl)-1*H*-indol-3-yl]ethylcarbamate (47)**: Scheme 8; white solid; m.p. 151 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.89 (brs, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.35 (s, 5H), 7.30 (d, J = 8.1 Hz, 1H), 7.20 (dt, J = 7.0, 1.2 Hz, 1H), 7.13 (dt, J = 7.0, 1.1 Hz, 1H), 5.71 (d, J = 1.0 Hz, 1H), 5.53 (d, J = 1.0 Hz, 1H), 4.52 (brs, 1H), 3.36 (q, J = 6.7 Hz, 2H), 2.90 (t, J = 6.7 Hz, 2H), 1.39 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 156.0 (C), 141.2 (C), 140.2 (C), 135.6 (C), 135.0 (C), 128.8 (C), 128.7 (CH), 128.6 (CH), 127.9 (CH), 122.8 (CH), 119.9 (CH), 119.4 (CH), 117.1 (CH_2), 112.3 (C), 111.0 (CH), 79.1 (C), 41.2 (CH_2), 28.6 (CH_3), 25.4 ppm (CH_2); HRMS-ESI: m/z calcd for $C_{23}H_{26}N_2O_2Na$: 385.1892; found: 385.1898 [M^++Na].

Tetracycle 50: Scheme 8; white solid; m.p. 96–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.49 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.19 (dt, J = 7.1, 1.3 Hz, 1H), 7.14 (t, J = 7.4, 1.2 Hz, 1H), 4.35 (ddd, J = 11.9, 10.7, 5.2 Hz, 1H), 4.25 (ddd, J = 11.4, 6.6, 1.8 Hz, 1H), 4.15 (ddd, J = 12.0, 7.1, 1.4 Hz, 1H), 3.54 (td, J = 11.6, 6.1 Hz, 1H), 3.02 (ddd, J = 15.5, 10.6, 7.2 Hz, 1H), 2.74 (ddd, J = 15.5, 5.1, 1.3 Hz, 1H), 2.39–2.26 (m, 1H), 2.20–2.12 (m, 1H), 2.07 (dt, J = 12.2, 3.7 Hz, 1H), 1.68 (td, J = 13.1, 4.1 Hz, 1H), 1.65 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): δ = 140.5 (C), 139.3 (C), 128.9 (C), 121.4 (CH), 120.1 (CH), 118.5 (CH), 110.4 (CH), 104.2 (C), 70.9 (C), 59.9 (CH_2), 43.1 (CH_2), 34.9(CH_2), 24.2 (CH_3), 22.4 (CH_2), 21.0 ppm (CH_2); HRMS-ESI: m/z calcd for $C_{15}H_{17}NONa$: 250.1208; found: 250.1217 [M^++Na]; elemental analysis

calcd (%) for $C_{15}H_{17}NO$: C 79.26, H 7.54, N 6.16; found: C 78.57, H 7.41, N 6.59.

2-(9-Methyl-6,7-dihydropyrido[1,2-*a*]indol-10-yl)ethanol (51): Scheme 8; white solid; m.p. 117 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): $\delta = 7.59$ (d, $J = 7.9$ Hz, 1H), 7.24–7.23 (m, 1H), 7.22 (dt, $J = 8.2$, 1.0 Hz, 1H), 7.08 (dt, $J = 6.5$, 1.5 Hz, 1H), 5.77–5.74 (m, 1H), 4.04 (t, $J = 6.9$ Hz, 2H), 3.88 (t, $J = 6.6$ Hz, 2H), 3.26 (t, $J = 6.6$ Hz, 2H), 2.57–2.52 (m, 2H), 2.29 (q, $J = 1.7$ Hz, 3H), 1.46 ppm (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, DEPT): $\delta = 136.3$ (C), 133.4 (C), 129.1 (C), 128.8 (C), 122.6 (CH), 122.5 (CH), 119.3 (CH), 118.9 (CH), 108.7 (CH), 108.1 (C), 63.9 (CH_2), 39.9 (CH_2), 28.5 (CH_2), 24.4 (CH_2), 21.2 ppm (CH_3); HRMS-ESI: *m/z* calcd for $C_{15}H_{17}NONa$: 250.1208; found: 250.1217 [M^++Na].

Acknowledgements

We are grateful to the MEC (projects CTQ2004-02869, NAN2004-08881-C02-02), Consolider Ingenio 2010, Grant SD2006-003), the AGAUR (project 2005 SGR 00993 and predoctoral fellowship to C.F), and the ICIQ Foundation for financial support. We also thank E. Escudero-Adán and Dr. J. Benet-Buchholz (X-ray diffraction unit, ICIQ) for the structure of **17**.

[1] C. Nevado, A. M. Echavarren, *Synthesis* **2005**, 167–182.
[2] M. Bandini, E. Emer, S. Tommasi, A. Umani-Ronchi, *Eur. J. Org. Chem.* **2006**, 3527–3544.
[3] M. Reetz, K. Sommer, *Eur. J. Org. Chem.* **2003**, 3485–3496.
[4] Z. Shi, C. He, *J. Org. Chem.* **2004**, *69*, 3669–3671.
[5] See also: A. S. K. Hashmi, M. C. Blanco, *Eur. J. Org. Chem.* **2006**, 4340–4342.
[6] N. Chatani, H. Inoue, T. Ikeda, S. Murai, *J. Org. Chem.* **2000**, *65*, 4913–4918.
[7] H. Inoue, N. Chatani, S. Murai, *J. Org. Chem.* **2002**, *67*, 1414–1417.
[8] a) A. Fürstner, V. Mamame, *J. Org. Chem.* **2002**, *67*, 6264–6267; b) A. Fürstner, V. Mamame, *Chem. Commun.* **2003**, 2112–2113; c) V. Mamane, P. Hannen, A. Fürstner, *Chem. Eur. J.* **2004**, *10*, 4556–4575.
[9] a) S. J. Pastine, S. W. Youn, D. Sames, *Org. Lett.* **2003**, *5*, 1055–1058; b) S. J. Pastine, S. W. Youn, D. Sames, *Tetrahedron* **2003**, *59*, 8859–8868.
[10] M. Nishizawa, H. Takao, V. K. Yadav, H. Imagawa, T. Sugihara, *Org. Lett.* **2003**, *5*, 4563–4565.
[11] Cyclization of silyloxyalkynes with Tf_2NH: L. Zhang, S. A. Kozmin, *J. Am. Chem. Soc.* **2004**, *126*, 10204–10205.
[12] C. Nevado, A. M. Echavarren, *Chem. Eur. J.* **2005**, *11*, 3155–3164.
[13] C. Nieto-Oberhuber, M. P. Muñoz, E. Buñuel, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 2456–2460; *Angew. Chem. Int. Ed.* **2004**, *43*, 2402–2406.
[14] I. V. Seregin, V. Gevorgyan, *J. Am. Chem. Soc.* **2006**, *128*, 12050–12051.
[15] E. Soriano, J. Marco-Contelles, *Organometallics* **2006**, *25*, 4542–4553.
[16] For recent transition-metal catalyzed annulations on indoles: a) E. M. Beccalli, G. Broggini, *Tetrahedron Lett.* **2003**, *44*, 1919–1921; b) E. M. Ferreira, B. M. Stoltz, *J. Am. Chem. Soc.* **2003**, *125*, 9578–9579; c) C. Liu, X. Han, X. Wang, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2004**, *126*, 3700–3701; d) C. Liu, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2004**, *126*, 10250–10251; e) C. Bressy, D. Alberico, M. Lautens, *J. Am. Chem. Soc.* **2005**, *127*, 13148–13149; f) B. A. Bhanu Prasad, F. K. Yoshimoto, R. Sarpong, *J. Am. Chem. Soc.* **2005**, *127*, 12468–12469; g) X. Han, A. Widenhoefer, *Org. Lett.* **2006**, *8*, 3801–3804; h) Review on palladium-catalyzed synthesis and functionalization of indoles: S. Cacchi, G. Fabrizi, *Chem. Rev.* **2005**, *105*, 2873–2920.
[17] Review on indolic natural products: M. Somei, F. Yamada, *Nat. Prod. Rep.* **2005**, *22*, 73–103.
[18] Lead references on the formation of C–C bonds by activation of alkynes with $AuCl_3$: a) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, *122*, 11553–11554; b) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *Org. Lett.* **2001**, *3*, 3769–3771; c) C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* **2003**, *9*, 2627–2635; d) A. S. K. Hashmi, L. Ding, J. W. Bats, P. Fischer, W. Frey, *Chem. Eur. J.* **2003**, *9*, 4339–4345; e) A. S. K. Hashmi, J. P. Weyrauch, M. Rudolph, E. Kurpejovic, *Angew. Chem.* **2004**, *116*, 6707–6709; *Angew. Chem. Int. Ed.* **2004**, *43*, 6545–6547; f) A. S. K. Hashmi, M. Rudolph, J. P. Weyrauch, M. Wölfle, W. Frey, Jan W. Bats, *Angew. Chem.* **2005**, *117*, 2858–2861; *Angew. Chem. Int. Ed.* **2005**, *44*, 2798–2801.
[19] For a rare cycloisomerization of 1,7-enynes with stoichiometric $Co_2(CO)_8$ to give 1,3-cyclooctadienes: H. Kagoshima, M. Hayashi, Y. Hashimoto, K. Saigo, *Organometallics* **1996**, *15*, 5439–5441.
[20] Preliminary communication on the intramolecular reaction of indoles with alkynes: C. Ferrer and A. M. Echavarren, *Angew. Chem.* **2006**, *118*, 1123–1127; *Angew. Chem. Int. Ed.* **2006**, *45*, 1105–1109.
[21] a) P. S. Steyn, *Tetrahedron Lett.* **1971**, *12*, 3331–3334; b) P. S. Steyn, *Tetrahedron* **1973**, *29*, 107–120; c) P. G. Sames, *Fortschr. Chem. Org. Naturst.* **1975**, *32*, 51–117.
[22] Synthesis of **6** and related alkaloids: P. S. Baran, E. J. Corey, *J. Am. Chem. Soc.* **2002**, *124*, 7904–7905.
[23] Synthesis of **7**: P. S. Baran, C. A. Guerrero, E. J. Corey, *J. Am. Chem. Soc.* **2003**, *125*, 5628–5629.
[24] T.-S. Kam, K.-H. Lim, K. Yoganathan, M. Hayashi, K. Komiyama, *Tetrahedron* **2004**, *60*, 10739–10745.
[25] Indoloazocines as intermediates for the synthesis of other indole alkaloids: M. E. Kuehne, S. D. Cowen, F. Xu, L. S. Borman, *J. Org. Chem.* **2001**, *66*, 5303–5316.
[26] Synthesis of indoloazocines: L. G. Voskressensky, T. N. Borisova, L. N. Kulikova, A. V. Varlamov, M. Catto, C. Altomare, A. Carotti, *Eur. J. Org. Chem.* **2004**, 3128–3135, and references therein.
[27] The reaction between *N*-methylindole and ethyl acrylate catalyzed by $AuCl_3$ gives a bisindolyl derivative in which the two indole groups are attached at C-3: Z. Li, Z. Shi, C. He, *J. Organomet. Chem.* **2005**, *690*, 5049–5054.
[28] For a Pictet–Spengler reaction catalyzed by $AuCl_3$/AgOTf: S. W. Youn, *J. Org. Chem.* **2006**, *71*, 2521–2523.
[29] C. Nieto-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179.
[30] C. Nieto-Oberhuber, S. López, M. P. Muñoz, D. J. Cárdenas, E. Buñuel, C. Nevado, A. M. Echavarren, *Angew. Chem.* **2005**, *117*, 6302–6304; *Angew. Chem. Int. Ed.* **2005**, *44*, 6146–6148.
[31] E. Herrero-Gómez, C. Nieto-Oberhuber, S. López, J. Benet-Buchholz and A. M. Echavarren, *Angew. Chem.* **2005**, *117*, 5581–5585; *Angew. Chem. Int. Ed.* **2006**, *45*, 5455–5459.
[32] S. López, E. Herrero-Gómez, P. Pérez-Galán, C. Nieto-Oberhuber, A. M. Echavarren, *Angew. Chem.* **2005**, *117*, 6175–6178; *Angew. Chem. Int. Ed.* **2006**, *45*, 6029–6032.
[33] a) A. Dar, K. Moss, S. M. Cottrill, R. V. Parish, C. A. McAuliffe, R. G. Pritchard, B. Beagley, J. Sandbank, *J. Chem. Soc. Dalton Trans.* **1992**, 1907–1913; b) A. S. K. Hashmi, J. P. Weyrauch, M. Rudolph, E. Kurpejovic, *Angew. Chem.* **2004**, *116*, 6707–6709; *Angew. Chem. Int. Ed.* **2004**, *43*, 6545–6547.
[34] See the Supporting Information for the synthesis and characterization data of starting indoles reported in Tables 1–3.
[35] See Supporting Information for the X-ray structure of **17**.
[36] a) A. S. K. Hashmi, J. P. Weyrauch, W. Frey, J. W. Bats, *Org. Lett.* **2004**, *6*, 4391–4394; b) See also: A. S. K. Hashmi, M. Rudolph, S. Schymura, J. Visus, W. Frey, *Eur. J. Org. Chem.* **2006**, 4905–4909.
[37] J. S. Yadav, B. V. S. Reddy, B. Padmavani, M. Kumar Gupta, *Tetrahedron Lett.* **2004**, *45*, 7577–7579.
[38] D. S. C. Black, D. C. Craig, N. Kumar, *Tetrahedron Lett.* **1991**, *32*, 1587–1590.
[39] S. Kano, E. Sugino, S. Shibuya, S. Hibino, *J. Org. Chem.* **1981**, *46*, 2979–2981.
[40] H. Zhang, X. Li, J. C. Lanter, Z. Sui, *Org. Lett.* **2005**, *7*, 2043–2046, and references therein

[41] Involvement of 3,3-disubstituted indolenines in 1,2-migrations to form indoles: a) A. H. Jackson, P. Smith, *Chem. Commun. (London)* **1967**, 264–266; b) A. H. Jackson, P. Smith, *Tetrahedron* **1968**, *24*, 403–413; c) A. H. Jackson, P. Smith, *Tetrahedron* **1968**, *24*, 2227–2239; d) A. Ganesan, C. H. Heathcock, *Tetrahedron Lett.* **1993**, *34*, 439–440.
[42] A. Zhang, C. Liu, R. E. Kinder, X. Han, H. Qian, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2006**, *128*, 9066–9073.
[43] L. Zhang *J. Am. Chem. Soc.* **2005**, *127*, 16804–16805.
[44] B. Martín-Matute, E. Buñuel, D. J. Cárdenas, M. Méndez, C. Nieto-Oberhuber, A. M. Echavarren, *J. Organomet. Chem.* **2003**, *687*, 410–419.
[45] A. S. K. Hashmi, M. C. Blanco, E. Kurpejovic, W. Frey, J. W. Bats, *Adv. Synth. Catal.* **2006**, *348*, 709–713.
[46] a) A. S. K. Hashmi, J. P. Weyrauch, E. Kurpejovic, T. M. Frost, B. Miehlich, W. Frey, J. W. Bats, *Chem. Eur. J.* **2006**, *12*, 5806–5814; b) A. S. K. Hashmi, P. Haufe, C. Schmid, A. Rivas Nass, W. Frey, *Chem. Eur. J.* **2006**, *12*, 5376–5382; c) A. S. K. Hashmi, R. SalathéW. Frey, *Chem. Eur. J.* **2006**, *12*, 6991–6996.
[47] a) B. Martín-Matute, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem.* **2001**, *113*, 4890–4893; *Angew. Chem. Int. Ed.* **2001**, *40*, 4754–4757; b) B. Martín-Matute, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2003**, *125*, 5757–5766.
[48] For pertinent discussions on the role of Brønsted acids in additions of nucleophiles to alkenes: a) Z. Li, J. Zhang, C. Brouer, C.-G. Yang, N. W. Reich, C. He, *Org. Lett.* 2006, 8, 4175–4178; b) D. C. Rosenfeld, S. Shekhar, A. Takemiya, M. Itsunomiya, J. F. Hartwig, *Org. Lett.* **2006**, *8*, 4179–4182.
[49] Review on synthetic applications of allenes: S.-M. Ma, *Chem. Rev.* **2005**, *105*, 2829–2872.
[50] W. Noland, M. R. Venkiteswaran, *J. Org. Chem.* **1961**, *26*, 4263–4269.
[51] M. Zolfigol, P. Salehi, M. Shiri, *Phosphorus Sulfur Silicon Relat. Elem.* **2004**, *179*, 4043–4045.
[52] Z.-H. Zhang, L. Yin, Y.-M. Wang, *Synthesis* **2005**, 1949 –1954.
[53] T. J. K. Gibbs, N. C. O. Tomkinson, *Org. Biomol. Chem.* **2005**, *3*, 4043–4045.
[54] Y. Horiguchi, M. Nakamura, A. Kida, H. Kodama, T. Saitoh, T. Sano, *Heterocycles* **2003**, *59*, 691–705.

Received: September 14, 2006
Published online: January 8, 2007

