JOC Article

New Approach to Indole Alkaloids Based on the Intramolecular Pauson−Khand Reaction†,[1]

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The synthesis of indoles bearing alkenyl and alkynyl moieties in different positions of the nucleus is described. These compounds are used as substrates for the intermolecular Pauson−Khand reaction leading to tetracyclic cyclopentenones with formation of additional five- to seven-membered rings. Products are related to alkaloids such as mitosenes, clausines, ergotamines, or apogeissochizines.

Introduction

The Pauson−Khand reaction has become an important tool in the synthesis of natural products containing cyclopentenones.[3] In the past years, extensive studies have widened the scope of this reaction to many substrates. Skeletons derived from 1-hepten-6-yne and 1-octen-7-yne are well-known substrates, and several aromatic enynes have also given good results.[4] This improve in scope is due, in part, to gains in reactivity both in the catalytic[5] and the stoichiometric version with the introduction of new promoters and reaction conditions.[6] Among the promoters of this reaction, amine *N*-oxides and cyclohexylamine are the most popular. We have introduced zeolites as efficient promoters for the stoichiometric and catalytic versions of the Pauson−Khand reaction.[7] Also new metal catalysts, such as $Co_4(CO)_{12}$[8] and different complexes including metals such as ruthenium,[9] titanium,[10] iridium,[11] and rhodium,[12] have been used with success. Following our project devoted to the use of aromatic substrates in the intramolecular Pauson−Khand reaction we have introduced 1,2-enynoindoles as new starting materials.[1] We report herein the complete study with different substitution patterns in the indole nucleus that lead to polycyclic indoles whose structures are related to several alkaloid families.

Indole alkaloids occur widely in nature and have different and important biological activities.[13] Their structures usually include carbo- and heterocycles fused

† Dedicated to the memory of Dr. Juan C. del Amo, a victim of the terrorist attack in Madrid, 11 March, 2004.

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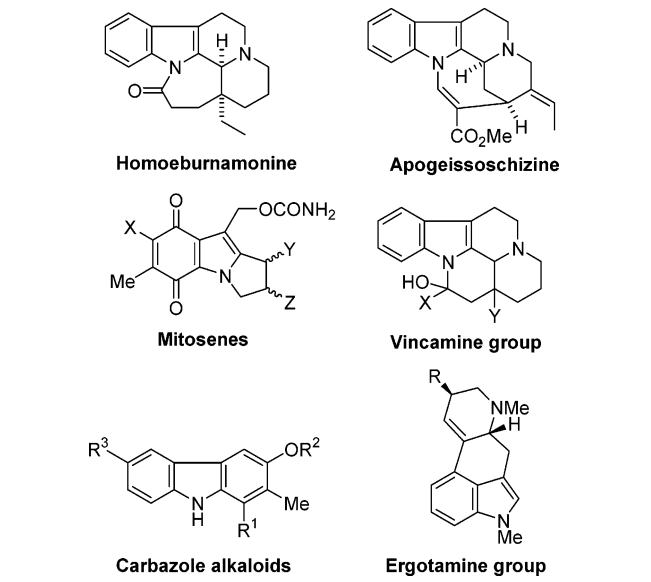

FIGURE 1. Some biologically active indole alkaloids.

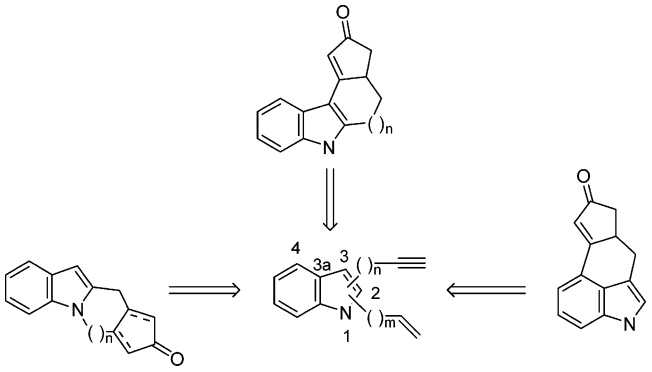

FIGURE 2. Approaches to polycylic indole skeletons using the PKR.

with the indole at the 1,2; 2,3; and 3,3a,4 positions. In Figure 1 we show examples of these three groups of compounds. Among these natural products there are alkaloids active on the central nervous system such as ergotamine or vinkamine and antitumorals such as mitomycin. All of them have received considerable attention from the synthetic point of view.[14]

Nevertheless, the Pauson−Khand reaction has not been used previously in indole chemistry, although it may allow the construction of tetracyclic structures in few steps. Figure 2 shows the approaches we describe herein that involve the synthesis of tetracyclic compounds fused by positions 1,2; 2,3; and 3,3a,4 of the indole nucleus.

TABLE 1. Synthesis of 1,2-Fused Tetracyclic Indole Derivatives

conditions	promoter	$Co_2(CO)_8$ (equiv)	temp (°C)	CO (atm)
A	Me_3NO/4 Å mol sieves	1.1	0	
B	4 Å mol sieves	1.1	110	
C		1.1	110	
D	Me_3NO	1.1	0	
E		0.1	65	1

Results and Discussion

In this work, the key step reaction in the synthesis of polycyclic indoles consisted of an intramlecular Pauson−Khand reaction, which was carried out in various experimental conditions that are summarized in Table 1. The stoichiometric conditions A and B, developed in our group,[7] use molecular sieves as promoters. Conditions C and D are used in some cases for comparison purposes with A and B, respectively. Finally we tried with some substrates catalytic conditions E. All reactions were carried out in toluene.

1,2-Fused Systems. Our first aim was the synthesis of tetracyclic indoles fused by the 1,2 bond of the indole, which are summarized in Table 2. This involved the obtention of the appropriate enyno indoles. First, two (6,5,5,5) compounds were obtained, starting from 1-allyl-2-ethynylindole, **1**, and 1-propargyl-2-vinylindole, **2**.[15] The Pauson−Khand reaction was carried out in conditions A and B (Table 1). Compound **1** gave the tetracyclic compound **12**, which is structurally related with the mitosenes, in good yield. Nevertheless, **2** led to only 15% of an isomerized compound **13** under conditions A, while total decomposition of the starting material was observed with conditions B. In this case, a Nicholas-type reaction is probably competing, leading to depropargylation and decomposition of the resulting 1-unsubstituted indole.[16]

The synthesis of (6,5,6,5) derivatives was then accomplished. Thus, from 1-propargyl- or 1-allylindole-2-carbaldehyde, reaction with vinylmagnesium bromide and lithium trimethylacetylide respectively gave compounds **3** and **4**, with good yields. These substrates gave in both cases moderate yields of Pauson−Khand products under the two different conditions used. Thus, product **14** was obtained as a 1:1 mixture of diastereomers in 25−30% yield. On the other hand, compound **4** led to 20−23% yield of **15** in which the alcohol is oxidized in the reaction. In addition, a desilylation process occurred to some extent, which upon shift of the emerging double bond yielded 20−22% of the diastereomeric diketones **16** as a 1:1 mixture. We had previously observed a similar desilylation process in other aromatic substrates, and also the shift of the double bond (Table 2).[4a]

To avoid the abovementioned side reactions, compounds **3** and **4** were converted into their TBDMS derivatives **5** and **6**, which were obtained in 76% and 80%

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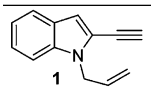
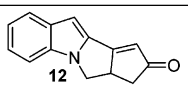
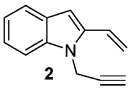
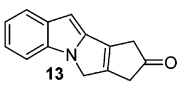
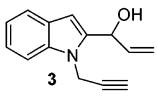
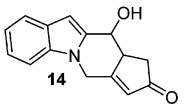
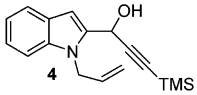
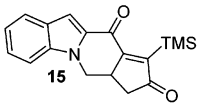
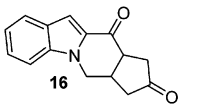
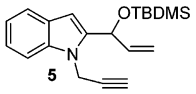
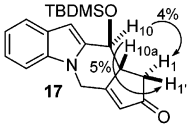
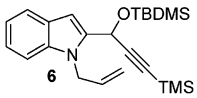
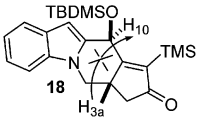
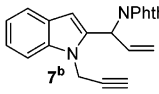
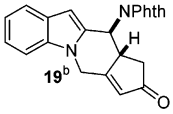
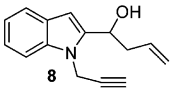
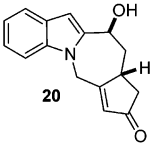
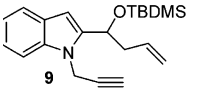
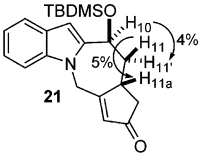
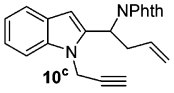
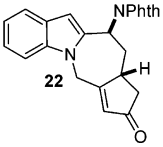
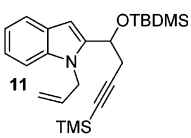
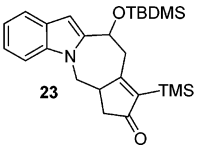
TABLE 2. Synthesis of 1,2-Fused Tetracyclic Indole Derivatives

Substrate	Product	Yield (%) A[a]	B[a]	C[a]	D[a]
 **1**	 **12**	45	70	-	-
 **2**	 **13**	15	0	-	-
 **3**	 **14**	12+13	15+15	-	-
 **4**	 **15**	20	23	-	-
	 **16**	10+10	11+11	-	-
 **5**	 **17**	65	65	10	25
 **6**	 **18**	55	75	-	-
 **7**[b]	 **19**[b]	75	70	-	-
 **8**	 **20**	20	10	0	-
 **9**	 **21**	65	75	40	-
 **10**[c]	 **22**	10	30	0	-
 **11**	 **23**	15	40	10	-

[a] For conditions see Table 1. A: TMANO, 4 Å mol sieves, rt. B: 4 Å mol sieves, reflux. C: reflux. D: TMANO, rt. [b] Phth = phthalimide.

yield, respectively. These compounds gave readily the polycyclic structures **17** and **18**. In addition, we converted compound **3** into the phthalimido derivative **7** by means of a Mitsunobu reaction, and this derivative gave the adduct **19**. Yields were good in these three cases, yielding slightly better results in conditions B, with only molecular sieves as promoters. Compound **5** was also reacted using conditions C and D (see Table 1), both without the zeolites, giving only 10% and 25% yield, respectively, in these conditions, showing the positive effect of molecular sieves in these reactions. Only the diastereomer depicted in Table 2 was detected by NMR in the three cases. The relative configuration was assigned by means of NOE experiments.

At this point we thought of trying the obtention of (6,5,7,5) tetracyclic systems using this methodology. Thus compounds **8**−**11** were obtained by reaction of the appropriate indole-2-carbaldehyde with allylmagnesium bromide or trimethylsilylpropargyllithium, followed by protection (compound **9**) or Mitsunobu reaction (compound **10**). These compounds were submitted to Pauson−Khand reactions in the same three different abovementioned conditions (A−C). Compound **8** reacted with very low yield to give **20**, which could be isolated and characterized. On the other hand compound **9** gave with good yield the desired cycloheptaindole, **21**. This result was the first case described of the formation of a seven-membered ring via intramolecular Pauson−Khand reaction with good yield. The phthalimido derivative **10** gave worse results. Compound **9** appears to have several structural features that favor the cyclization process. Not only the planarity of the indole nucleus but also the buttressing effect of the OTBDMS group are probably responsible for this result. Compounds **8** and **10**, with groups different from the OTBDMS present in **9**, do react although with moderate conversions whereas compound **11**, reacts slightly better. Comparing the three reaction conditions used, the positive effect of the molecular sieves is clear and conditions B are the best ones. Compounds **20**−**23** were obtained as a single diastereomer. The stereochemistry of **20**, **21**, and **22** was assigned with NOE experiments as the one depicted in Table 1. We show the main NOE increments observed for compounds **17**, **18**, and **21** in the table.

The difficulty in achieving medium-sized rings via Pauson−Khand reactions seems to be related to the low population of the reactive conformation. Some oxabicyclic compounds have been described,[16] and recently two groups have described an efficient Pauson−Khand reaction in allenes, catalyzed by rhodium, that gives bicyclo-[5.3.0]decadienones with good yields.[17] The planarity of the aromatic rings may have a decisive influence on the reactivity of enynes connected through them.

It is interesting to comment on the diastereoselective outcome of these reactions. When having bulky groups such as TBDMS or Phth in the starting materials, a single diastereomer compound is always obtained, in which this group is at the same side as the hydrogen at the fusion. A rationalization of this stereochemistry is

(17) (a) Gao, D.; Brummond, K. M. *Org. Lett.* **2003**, *5*, 3491−3494. (b) Mukai, C.; Nomura, I.; Yamanishi, K.; Hanaoka, M. *Org. Lett.*, **2002**, *4*, 1755−1758. (b) Brummond, K. M.; Chen, H.; Fisher, K. D.; Kerekes, A. D.; Rickards, B.; Sill, P. C.; Geib, S. J. *Org. Lett.* **2002**, *4*, 1931−1934.

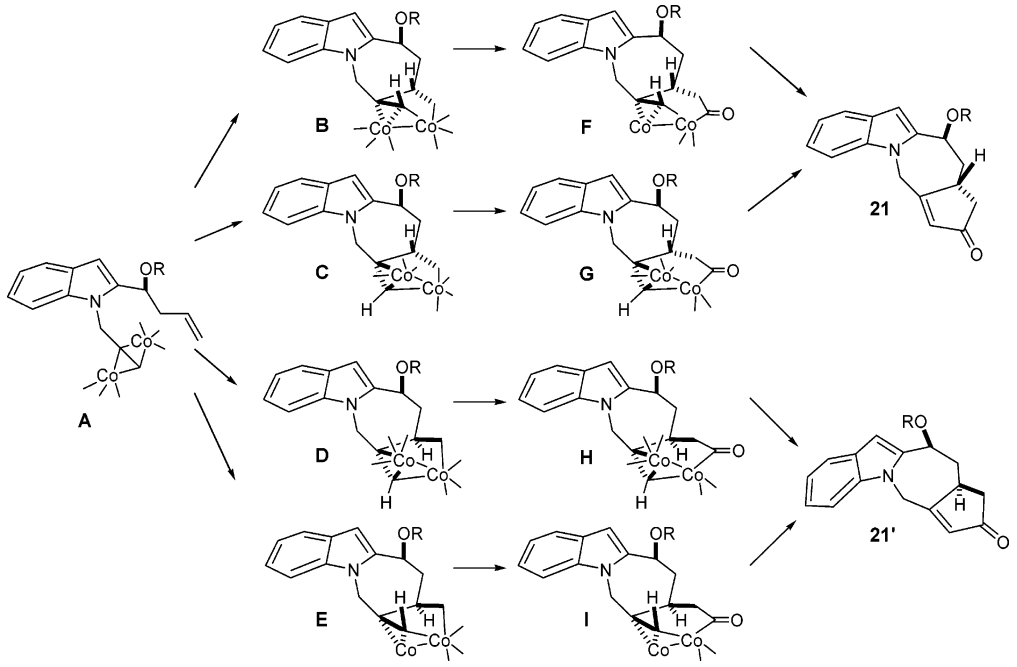
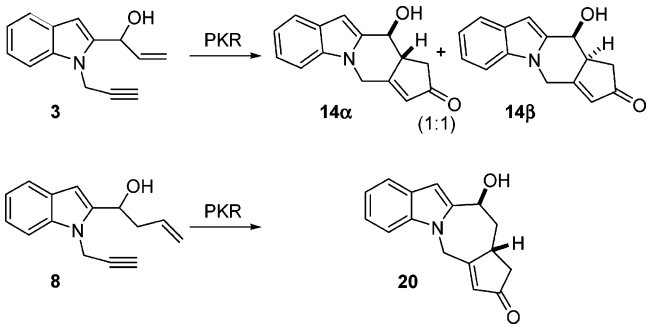


FIGURE 3. Possible intermediates in the formation of **21**.

SCHEME 1



depicted in Figure 3. Pericàs has shown the relative stabilities of the four possible intermediate complexes obtained upon insertion of the carbon double bond in the cobalt complex.[18] Taking as a model the formation of compound **21**, the complex **A** can give, upon insertion of the olefine fragment, intermediates **B**−**E**. Insertion of CO would give complexes **F**−**I.** Then **F** and **G** and **H** and **I** would lead respectively to isomers **21** and **21′** (not observed). Complex **B**, which minimizes the interaction of the substituent OR with the metalacycle, would be the most stable, giving the observed product **21**. This diastereoselection may have its origin in the bulky protecting group used, as it does not happen with the parent alcohols. Other effects as the coordination of lone pairs of the oxygen with the metal cannot be discarded.

If we compare the stereochemical result of the reaction of **3** with that of **8**, we can see that the hydroxy group present in these two substrates may act as directing group as in the directed PKR (Scheme 1).[19] Thus, in the case of **8** the distance for the interaction of the hydroxy would be adequate to give a more rigid intermediate that would enhance the diastereoselectivity. In **3** this distance is too short to allow simultaneous coordination of the olefin and the hydroxyl group.[20]

2,3-Fused Systems. Our next aim was the synthesis of appropriately 2,3-disubstituted indoles for the synthesis of tetracyclic systems fused onto face b of the indole. The obtention of 6,5,6,5 systems was accomplished from 2-allyl or 2-(3-butenyl)-3-ethynylindoles. Starting from indole-2-carbaldehyde and following literature methods, a 3-iodo derivative, **25**, was obtained that was submitted to Sonogashira coupling to give **26**.[21] The reaction of **26** with a suitable Grignard reagent gave **27** and **28**, which were *O*-silylated to yield **29** and **30** and methylated to give, finally, **31** and **32**. (Scheme 2)

These substrates were submitted to the PKR in the same above conditions (conditions A and B) with the results summarized in Table 3.

The alcohols **27** and **28** again gave bad results, and extensive decomposition was observed in both reaction conditions. On the other hand, compounds **29**−**32** gave the corresponding Pauson−Khand adducts, conditions B being the ones that gave better results. The formation of six-membered rings was in these cases more favorable, reaching excellent results in the formation of **36**. Compounds **33**, **34**, and **35** were obtained with low to moderate yields. This is somewhat an unexpected result as five-membered rings are normally formed better than six-membered ones. The presence of the aromatic nucleus may explain the result. Also low reactivity of all of these substrates (except **32**) at room temperature makes necessary the use of refluxing toluene, and thus may involve partial decomposition of starting materials. More surprising is the stereochemical outcome of these reactions.

(18) Castro, J.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron* **1995**, *51*, 6541.

(19) Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199 and references therein.

(20) We have observed similar results with other aromatic substrates; see: Blanco-Urgoiti, B.; Casarrubios, L.; Domínguez, G.; Pérez-Castells, J. *Tetrahedron Lett.* **2001**, *42*, 3315−3317.

(21) Choshi, T.; Sada, T.; Fujimoto, H.; Nagayama, C.; Sugino, E.; Hibino, S. *J. Org. Chem.* **1997**, *62*, 2535.

SCHEME 2

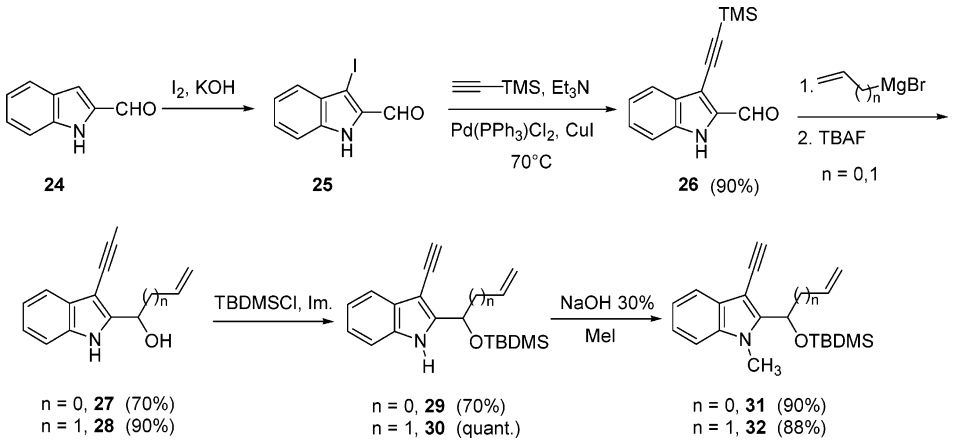
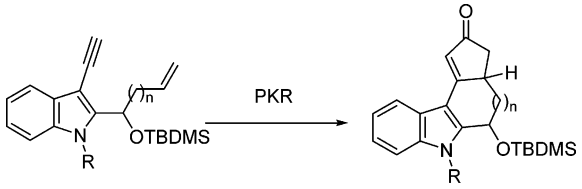


TABLE 3. Synthesis of 2,3-Fused Tetracyclic Indole Derivatives



substrate	R	*n*	method	product	yield (%)
29	H	0	B	**33** (1:1)	15
30	H	1	A	**34** (1:1)	20/22
			B		30/35
31	Me	0	B	**35**	40
32	Me	1	A	**36**	65
			B		85
			E		45

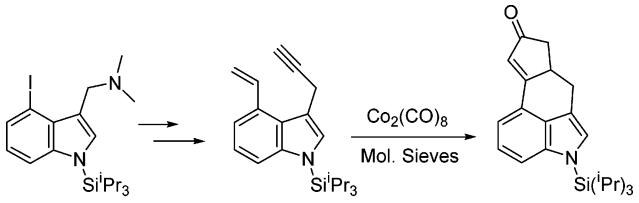
When indoles bearing a methyl in the nitrogen are used, total diastereoselectivity is observed, which almost disappears with nonmethylated substrates **29** and **30**. With the best compound of this group, **32**, we tried a catalytic reaction (method E, Table 1). However, we only obtained a 45% yield of **36** which is far from the result reached with the stoichiometric conditions.

3,3a,4-Fused Systems. We planned finally the synthesis of a compound that could serve as precursor for the synthesis of ergot alkaloids. By means of a directed lithiation we had described the synthesis of a 4-iodogramine derivative, which upon Stille coupling and displacement of the corresponding ammonium salt with a Grignard reagent gave compound **37**.[22] This compound was submitted to the PKR under the usual conditions. We also used in this case the catalytic protocol E. The results showed the formation of **38** with good yield using method B and moderate yield using catalytic conditions E. Compound **38** may be an interesting intermediate in the synthesis of ergot alkaloids (Scheme 3).

Conclusion

We describe here the synthesis of several polycyclic indoles using the PKR. The reaction works well in the construction of five-, six-, and seven-membered rings, tolerating silyl ethers and phthalimido groups in the substrate, while giving poor yields with unprotected hydroxyls. These compounds are interesting intermediates in the synthesis of natural alkaloids. Most of these reactions give only one diastereomer. However, these substrates give poor results when trying to switch to catalytic conditions. In view of the gain in molecular complexity this methodology can be interesting in the design of the synthesis of alkaloid derivatives. Thus, we are currently working on transforming the cyclopentenone ring in **38** in order to effect a synthesis of ergotamine derivatives. Compound **36** is also being used as starting material for the synthesis of carbazole derivatives.

SCHEME 3



Experimental Section

General Procedures for Pauson−Khand Reactions. Method A. The enyne (2.00 mmol) was dissolved in dry toluene (40 mL) at room temperature under argon, in a flask containing eight times the mass of the enyne of powdered 4 Å molecular sieves. To this solution was added 2.40 mmol of $Co_2(CO)_8$, and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The reaction was then cooled to −10 °C with an ice/salt bath, and a suspension of Me_3NO (18.00 mmol) in toluene at 0 °C was added dropwise. After 18 h of stirring, the mixture was filtered, the solvent was evaporated under vacuum, and the crude was purified and/or separated by flash chromatography (hexane/EtOAc mixtures).

Method B. The enyne (2.00 mmol) was dissolved in dry toluene (40 mL) at room temperature under argon, in a flask containing eight times the mass of the enyne of powdered 4 Å molecular sieves. To this solution was added 2.40 mmol of $Co_2(CO)_8$, and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The reaction was refluxed for 18 h. After filtration and solvent elimination the crude was

(22) Pérez-Serrano, L.; Casarrubios, L.; Domínguez, G.; Pérez-Castells, J. *Tetrahedron* **2002**, *58*, 5407−5415.

purified and/or separated by flash chromatography (hexane/EtOAc mixtures).

Method C. The enyne (2.00 mmol) was dissolved in dry toluene (40 mL) at room temperature under argon. To this solution was added 2.40 mmol of $Co_2(CO)_8$, and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The reaction was refluxed for 18 h. After filtration and solvent elimination the crude was purified and/or separated by flash chromatography (hexane/EtOAc mixtures).

Method D. The enyne (2.00 mmol) was dissolved in dry toluene (40 mL) at room temperature under argon. To this solution was added 2.40 mmol of $Co_2(CO)_8$, and the resulting mixture was stirred for 2 h until total complexation of the enyne (TLC). The reaction was then cooled to −10 °C with an ice/salt bath, and a suspension of Me_3NO (18.00 mmol) in toluene at 0 °C was added dropwise. After 18 h of stirring, the mixture was filtered, the solvent was evaporated under vacuum, and the crude was purified and/or separated by flash chromatography (hexane/EtOAc mixtures).

Method E. The enyne (2.00 mmol) was dissolved in dry toluene (40 mL) at room temperature under CO atmosphere (1 atm), in a flask containing two times the mass of the enyne of powdered 4 Å molecular sieves. To this solution was added 0.20 mmol of $Co_2(CO)_8$, and the resulting mixture was stirred for 18 h at 65 °C. After filtration through Celite, the solvent was evaporated under vacuum, and the crude product was purified by flash chromatography (hexane/EtOAc mixtures).

3a,4-Dihydro-3*H*-benzo[*e*]cyclopenta[*a*]pyrrolizin-2-one, 12. Following method A, from 0.362 g of **1** and after purification by flash chromatography (hexane/EtOAc 6:1−4:1), 0.182 g (45%) of **12** was obtained as a yellow solid, mp 148−149 °C (hexane/EtOAc). Following method B, 0.404 g (70%) of **12** was obtained: ^{1}H NMR ($CDCl_3$) 2.55 (dd, 1H, $J_1 = 17.0$ Hz $J_2 = 5.5$ Hz), 2.83 (dd, 1H, $J_1 = 17.0$ Hz $J_2 = 6.6$ Hz), 3.77 (t, 1H, $J = 9.0$ Hz), 4.02−4.16 (m, 1H), 4.64 (t, 1H, $J = 8.8$ Hz), 6.24 (d, 1H, $J = 2.2$ Hz), 6.88 (s, 1H), 7.16 (dt, 1H, $J_1 = 7.7$ Hz $J_2 = 1.1$ Hz), 7.30 (dt, 1H, $J_1 = 7.7$ Hz $J_2 = 1.1$ Hz), 7.35 (d, 1H, $J = 7.7$ Hz), 7.70 (d, 1H, $J = 8.2$ Hz); ^{13}C NMR ($CDCl_3$) 207.7, 170.0, 134.7, 134.4, 132.7, 124.1, 122.5, 120.6, 120.0, 110.2, 99.6, 48.7, 48.3, 41.0. IR (KBr) 2870, 1705, 1630, 1330. Anal. Calcd for $C_{14}H_{11}NO$: C. 80.36; H. 5.30; N. 6.69. Found: C. 80.45; H. 5.56; N. 6.57.

(11*S,12a*R**)-11-(*tert*-Butyldimethylsilyloxy)-4,11,12,-12a-tetrahydro-1*H*-cyclopenta[5,6]azepine[1,2-*a*]indole-2-one, 21.** Following method A, from 0.678 g of **9** and after purification by flash chromatography (hexane/EtOAc 10:1), 0.475 g (65%) of **21** was obtained as a pale yellow oil. Following method B, 0.540 g (75%) of **21** was obtained. Following method C, 0.300 g (40%) of **21** was obtained: ^{1}H NMR ($CDCl_3$) −0.13 (s, 3H), 0.15 (s, 3H), 0.90 (s, 9H), 1.56 (dd, 1H, $J_1 = 13.2$. Hz, $J_2 = 12.6$ Hz), 2.08 (dd, 1H, $J_1 = 19.2$ Hz, $J_2 = 2.2$ Hz), 2.55−2.63 (m, 1H), 2.77 (dd, 1H, $J_1 = 19.2$ Hz, $J_2 = 6.6$ Hz), 3.62−3.71 (m, 1H), 4.98 (d, 1H, $J = 13.5$ Hz), 5.21 (d, 1H, $J = 6.0$ Hz); 5.27 (d, 1H, $J = 13.5$ Hz), 6.10 (s, 1H), 6.36 (s, 1H), 7.10 (t, 1H, $J = 7.7$ Hz), 7.25 (t, 1H, $J = 8.2$ Hz), 7.38 (d, 1H, $J = 8.2$ Hz), 7.57 (d, 1H, $J = 7.7$ Hz); ^{13}C NMR ($CDCl_3$) 207.8, 174.6, 141.2, 136.6, 131.9, 127.1, 121.9, 120.9, 119.5, 108.5, 101.0, 66.9, 44.2, 42.8, 41.4, 38.4, 25.7, 18.0, −5.1, −5.4; IR (neat) 2920, 1710, 1460. Anal. Calcd for $C_{22}H_{29}NO_2Si$: C. 71.89; H. 7.95; N. 3.81. Found: C. 71.96; H. 7.88; N. 3.86.

(3a*S,5*R**)-5-(*tert*-Butyldimethylsilyloxy)-6-methyl-3,-3a,4,5-tetrahydro-6*H*-ciclopenta[*c*]carbazol-2-one, 36.** Method A: From 0.34 g of **32** and after purification by flash chromatography (hexane/EtOAc 4:1), 0.24 g (65%) of **36** was obtained as a white solid, mp >190 °C dec (hexane/AcOEt). Method B: 0.31 g (85%) of **36** was obtained. Method E: 0.18 g (45%) of **36** was obtained: ^{1}H NMR ($CDCl_3$) 0.24 (s, 6H), 0.90 (s, 9H), 1.94 (td, 1H, $J_1 = 13.7$ Hz, $J_2 = 3.3$ Hz), 2.17 (dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 4.4$ Hz), 2.41 (dt, 1H, $J_1 = 13.7$ Hz, $J_2 = 2.7$ Hz), 2.68 (dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 7.2$ Hz), 3.54−3.64 (m, 1H), 3.79 (s, 3H), 5.17 (t, 1H, $J = 2.7$ Hz), 6.33 (d, 1H, $J = 1.1$ Hz), 7.28−7.37 (m, 2H), 7.39 (d, 1H, $J = 7.1$ Hz), 7.76 (d, 1H, $J = 7.7$ Hz); ^{13}C NMR ($CDCl_3$) 207.7, 170.4, 142.6, 138.0, 124.0, 123.4, 121.9, 120.3, 119.0, 110.0, 108.6, 62.0, 40.2, 38.8, 34.4, 29.7, 25.6, 18.0, −3.8, −4.5; IR (KBr) 2920, 2820, 1690, 1670, 1600. Anal. Calcd For $C_{22}H_{29}NO_2Si$: C. 71.89; H. 7.95; N. 3.81. Found: C. 71.99; H. 8.06; N. 3.69.

4-Triisopropylsilyl-4,6,6a,7-tetrahydroindeno[6,5,4-*cd*]-indol-8-one, 38. Method A: From 0.33 g of **37** and after purification by flash chromatography (hexane/EtOAc 4:1), 0.22 g (50%) of **38** was obtained as a pale yellow oil. Method B: 0.18 g (60%) of **38** was obtained. Method E: 0.10 g (37%) of **38** was obtained: ^{1}H NMR ($CDCl_3$) 1.14 (d, 18H, $J = 7.1$ Hz), 1.64−1.77 (m, 3H), 2.30 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 3.8$ Hz), 2.65−2.76 (m, 1H), 2.88 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 6.0$ Hz), 3.31−3.41 (m, 2H), 6.53 (d, 1H, $J = 1.6$ Hz), 7.06 (s, 1H), 7.22 (t, 1H, $J = 7.7$ Hz), 7.38 (d, 1H, $J = 7.7$ Hz), 7.51 (d, 1H, $J = 8.2$ Hz); ^{13}C NMR ($CDCl_3$) 208.6, 173.5, 139.4, 131.5, 126.9, 124.0, 123.9, 122.5, 116.4, 116.1, 113.8, 42.6, 39.9, 28.0, 18.0, 12.6. IR (neat) 1700, 1620, 1450. Anal. Calcd For $C_{23}H_{31}NOSi$: C. 75.56; H. 8.55; N. 3.83. Found: C. 75.68; H. 8.69; N. 3.75.

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Supporting Information Available: Full characterization of compounds **26**, **3**, **8**, **4**, **27**, **28**, **5**, **6**, **9**, **11**, **29**, **30**, **7**, **10**, **31**, **32**, **13**, **14**, **15**, **16**, **17**, **19**, **20**, **22**, **23**, **33**, **34**, and **35**. This material is available free of charge via the Internet at http://pubs.acs.org.

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