Cobalt-Mediated [2+2+2] Cycloaddition of Alkynes to the Enamine Double Bond: A Formal Total Synthesis of γ-Lycorane

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In the presence of $CpCo(CO)_2$, bis(trimethylsilyl)acetylene reacts with the alkyne and alkene functions of 1-(6-ethynyl-1,3-benzodioxol-5-ylcarbonyl)azacyclopent-2-ene (**5c**) to create CpCo–cyclohexadiene complexes embodying the polycyclic framework of γ-lycorane. A novel regioselective fluoride-mediated removal of the 2-trimethylsilyl group from these 1,2-bis(trimethylsilyl)-substituted complexes under mild conditions allowed their successful conversion into 1,12b-didehydro-7-oxo-γ-lycorane (10 steps from 6-bromo-1,3-benzodioxole-5-carboxylic acid in 9.4% overall yield). Unusual problems associated with the application of palladium catalysts in the construction of 2-functionalized alkynylarenes related to **5c** were circumvented. In addition, $CpCo(CO)_2$ catalyzes the isomerization of the double bond of 1-acylazacyclopent-3-enes to the 2-position, but apparently is ineffective in the isomerization of *N*-(cyclopropylmethylidene)amines to azacyclopent-2-enes.

Introduction

Lycorine **1** is the most abundant alkaloid of the Amaryllidaceae family.[2] It is a plant growth inhibitor[3] and disrupts the formation of peptide bonds during protein synthesis.[4] Its skeleton, the galanthan ring system, is represented by various degradation products, the simplest being the four isomeric lycoranes **2**.[2] To our knowledge, the lycoranes have no documented pharmacological activity. Nevertheless, they have all been made by total synthesis, primarily to demonstrate the utility of new synthetic strategies. The Diels–Alder reaction, first in its intermolecular[5] and, more recently, in its intramolecular variations,[6–9] has played a prominent role as a method of constructing the C-ring of **1** and **2**. A conceptually unique approach is based on the cobalt-mediated [2+2+2] cycloaddition[10] of the double bond of an enamine and two alkynes.[11,12] A simple retrosynthetic analysis (Scheme 1) indicates how this reaction could function as the key step in the synthesis of the galanthan nucleus, as exemplified by γ-lycorane **2c**.[13,14] Thus, heterocyclic enynes **5** could couple with **4** in the presence of CpCo to give **3** by simultaneous formation of rings B and C.[10] Substituents X and Y would be chosen to stabilize the enamine,[15,16] but could be removed after cycloaddition. Oxidative demetalation,[10] protodesilylation,[17] and reduction should lead to **2c**. This paper describes the realization of Scheme 1, made possible in part by overcoming the unusual problems associated with application of palladium catalysts in the construction of 1,2-bifunctional arenes such as **5–7**, and by the discovery of a remarkably facile fluoride-induced protodesilylation of CpCo–diene complexes **3**. Also described are attempts at CpCo-mediated isomerizations leading to **5b** (from **6b**) and to **5c**.

1 lycorine

2a α-H_a, α-H_b, α-lycorane
b β-H_a, α-H_b, β-lycorane
c β-H_a, β-H_b, γ-lycorane
d α-H_a, β-H_b, δ-lycorane

3

4

5a X = H_2, Y = SPh
b X = H_2, Y = CO_2Et
c X = O, Y = H

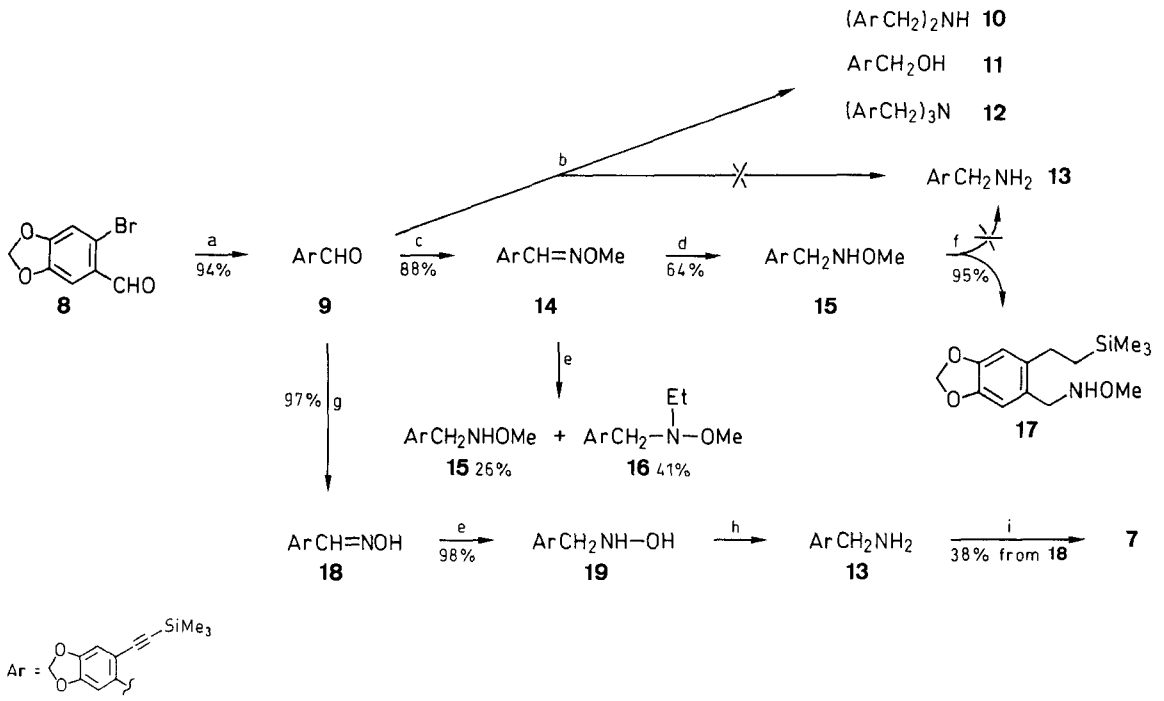
6a Y = SPh
b Y = CO_2Et

7

Scheme 1

Initial Synthetic Strategy: Preparation of Amine 7

Cycloaddition precursors **5a** and **5b** were thought to be available from acid-catalyzed rearrangement[16] of the corresponding imines **6**, in turn derived from amine **7**. The amine function of **7** was to be produced by reductive amination[18] of an aldehyde moiety with ammonia, whereas the ethynyl group was to be introduced by palladium-catalyzed coupling[19] of bromide **8**[20] (Scheme 2) with trimethylsilylacetylene (TMSA), giving **9**.[21] Reductive amination of **9** with ammonium acetate (10 equiv) and $NaBH_3CN$ according to the conditions of Borch et al.[22] gave a mixture of secondary amine **10** (37%), alcohol **11** (14%), and tertiary amine **12** (4.5%). Apparently, even in the presence of a 10-fold excess of available ammonia, the desired primary amine **13** condensed with **9**, leading to **10** as the major product, and probable source of **12**, by further coupling with **9**. When the reaction was conducted at a slightly lower pH (10 equivalents of NH_4Br instead of NH_4OAc), ^1H NMR spectral analysis of the crude product showed **10**, **11**, and **12** to be present



(a) TMSA, $PdCl_2(PhCN)_2$, PPh_3, Et_3N, reflux, 2.5 h. (b) NH_4OAc or NH_4Br, $NaBH_3CN$, MeOH, 25 °C, 33 h. (c) $MeONH_2 \cdot HCl$, pyridine/EtOH, reflux, 18 h. (d) $NaBH_3CN$, MeOH, HCl, 25 °C, 7 d. (e) $NaBH_3CN$, $MeCO_2H$, 15–40 min. (f) H_2 (1 atm), Pd–C, MeOH, 25 °C. (g) $NH_2OH \cdot HCl$, pyridine/EtOH, reflux, 8 h. (h) $TiCl_3$, NH_4OAc, THF/H_2O, 25 °C, 3 min. (i) KOH, H_2O, 25 °C, 45–120 min.

Scheme 2

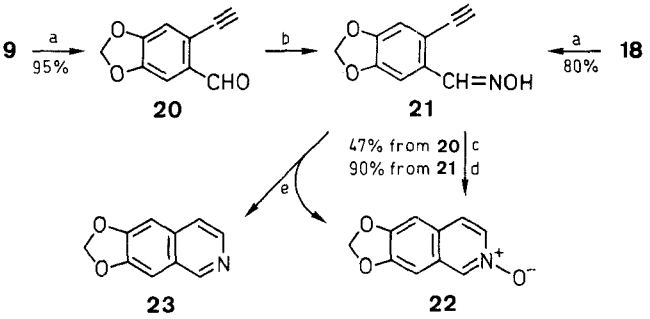
in a ratio of 3:24:1, the reduction of the carbonyl group now predominating. Pure **11** was obtained from **9** (90%) by $NaBH_4$ reduction under nearly neutral conditions.

It became clear that an indirect method of reductive amination would have to be applied. Reduction of **14** (prepared from **9**)[23] to **15** in methanol, with addition of HCl to maintain a pH of 3 to 4[22] required excess reducing agent over the course of one week. Use of acetic acid as solvent and proton source led to complete consumption of **14** within 0.5 hours, but in addition to **15**, ethylated product **16** was formed.[24] Hydrogenation[25] of **15** over Pd–C or Lindlar catalyst surprisingly gave **17**, the trimethylsilyl group failing to protect the triple bond during catalytic hydrogenation.[26]

These frustrating results led us to consider N–O cleavage of hydroxylamine **19** by buffered titanium(III).[27] The oxime **18** (from **9**)[23] was cleanly reduced to the unstable hydroxylamine **19**. In the presence of ca. 1.5 equiv of titanium(III) chloride and ammonium acetate buffer, N–O cleavage of **19** to give **13** was rapid, and workup with aqueous potassium hydroxide[19] afforded the protodesilylated amine **7** as an unstable pinkish to red solid in only moderate overall yield.

Discovery of a New Isoquinoline *N*-Oxide Synthesis

While exploring a modified approach to **7**, a sample of **9** was protodesilylated to **20** (Scheme 3). Attempted formation of the corresponding oxime **21** under the conditions that had worked so well for the conversion of **9** to **18** gave the water-soluble **22** · $0.5H_2SO_4$ as the only product isolated from a dark mixture (26% yield in a single



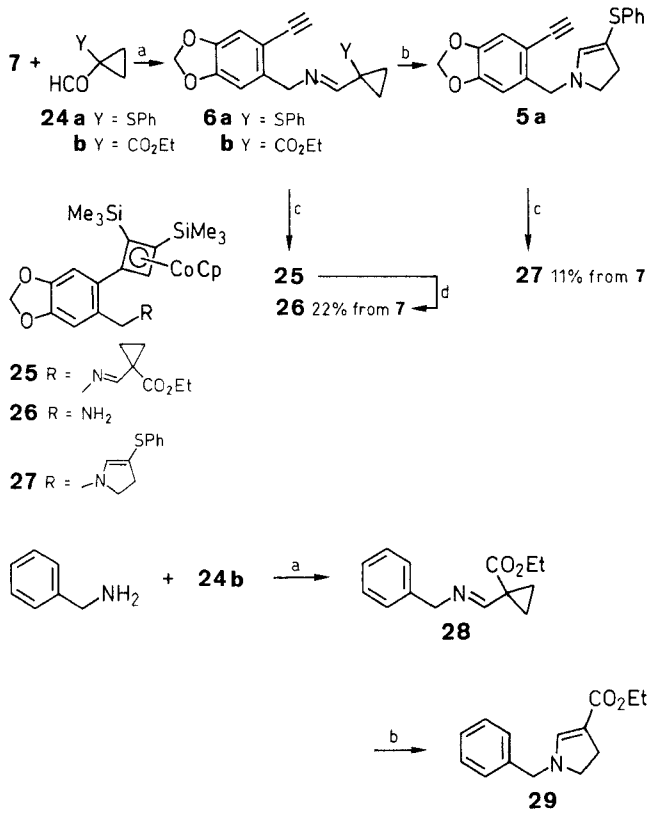
(a) KOH, MeOH/H_2O, 25 °C, 0.5–3.8 h. (b) $NH_2OH \cdot HCl$, pyridine/EtOH, 25 °C, 1.5 d. (c) pyridine/EtOH, reflux, 4 h. (d) 2-propanol, reflux, 8 h. (e) 1,2-dimethoxyethane, reflux, 5 d.

Scheme 3

unoptimized experiment). A similar base-catalyzed cyclization of 2-alkynylbenzaldehyde tosylhydrazones is known.[28] A better procedure using the same reagents involved generation of **21** at 25 °C followed by isomerization to **22** · $0.5H_2O$ at higher temperatures. For the patient, oxime **21** (from protodesilylation of **18**) is cleanly converted to **22** on storage at room temperature for one year. In refluxing 1,2-dimethoxyethane (bp 82–83 °C),[29] cyclization of **21** required 5 days and ^1H NMR spectroscopic analysis of the crude product showed a mixture of **22** and **23**[30] in a ratio of 2.5:1. In refluxing 2-propanol (bp 82.5 °C),[29] smooth transformation of **21** occurred within 8 hours, giving **22** · $0.5H_2O$. The scope of this reaction was not investigated further, but it may offer a general route to isoquinoline *N*-oxides, known precursors to isoquinolines or isoquinolones.[31]

Attempted Cycloaddition of Enamine 5a and Isomerization of Imines 6b and 29

With **7** in hand, we sought **5a** and **5b**, in which the enamine function was expected to be stabilized by an SPh or CO_2Et substituent, respectively.[16] Condensation of **7** with either **24a**[32] or **24b**[33] produced crude **6a** or **6b**. Similarly, phenylmethanamine and **24b** afforded **28**. Isomerization of **6a** to **5a**, and of **28** to **29**, was accomplished in the presence of ammonium chloride.[16] We attempted a CpCo-catalyzed version of this process, which would be reminiscent of transition-metal mediated isomerizations of vinylcyclopropanes to cyclopentenes.[34,35] When exposed to typical [2+2+2] cycloaddition conditions [0.5 equiv of $CpCo(CO)_2$, 125 °C, irradiation with a Sylvania ELH slide projector lamp],[10] the model imine **28** was left unchanged. Increasing the temperature to 155–158 °C for one day led to decomposition. Enamine **29** was undetectable in the complex mixture (^{1}H NMR). When crude imine **6b** was cocyclized with **4** in refluxing **4** (bp 133 °C),[36] a black mixture was obtained in which imine cyclobutadiene complex **25** was the only product (^{1}H NMR); hydrolysis of the crude imine afforded the corresponding amine complex **26** in low overall yield. Moreover, cocyclization of crude **5a** with **4** led to **27** as the only isolable product in low yield. We do not know if derivatives of **3** were formed in these mixtures and then decomposed. However, it is clear that at 125–133 °C the desired isomerizations (e.g., **28** to **29**) are slow compared to the coupling of alkynes by $CpCo(CO)_2$ (e.g., **6b** to **25**).

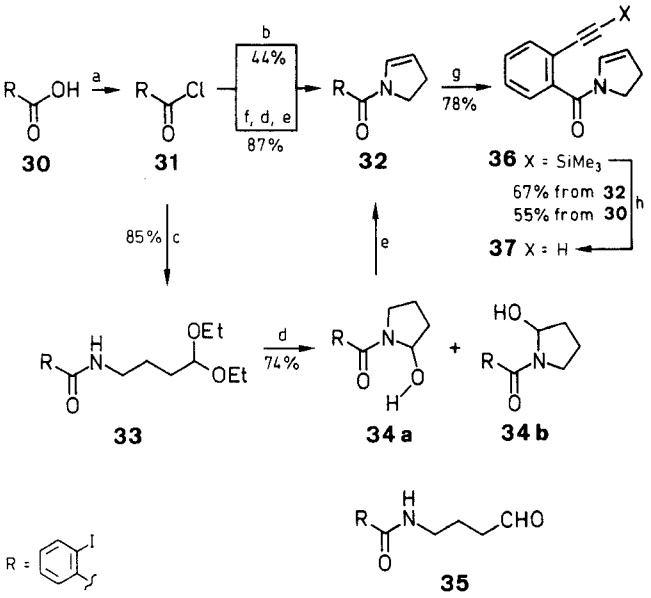


(a) Na_2SO_4, solvent 25 °C, 1.5–2 d. (b) NH_4Cl, 1,3-dimethyl- or 1,3,5-trimethylbenzene, reflux. (c) **4**, $CpCo(CO)_2$, reflux, hν. (d) H^+, H_2O, 25 °C, 8 h.

Scheme 4

A Revised Stategy: Development of Enamide Precursor Synthesis and [2+2+2] Cycloaddition Using a Model System

The difficulties encountered in the synthesis of **7** and its derivatives and the undesired formation of CpCo-cyclobutadiene complexes in the cocyclization experiments just described led to consideration of enamide[37] **5c** (Scheme 1) as a cyclization precursor, in which it was thought that the double bond would be less hindered than that of **5a** or **5b**, hence more readily incorporated into organometallic intermediate(s). Early difficulties (vide infra) in the preparation of **5c** prompted exploration of a model system without the aryl oxygen substituents (Scheme 5). The reported oxidation of azacyclopentane[38] gave the trimer, not the monomer of azacyclopent-1-ene.[39,40] Without prior monomerization,[39] the trimer could be acylated with **31**[41] to give **32** in 44 % yield after optimization of the reaction conditions. Large amounts of uncharacterized polar materials were formed in these reactions.

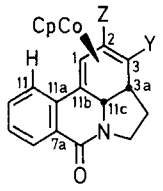


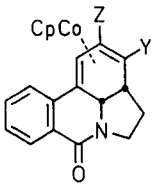
(a) $SOCl_2$, reflux. (b) azacyclopent-1-ene trimer, i-Pr_2NEt, CCl_4, 25 °C, 16 h. (c) $H_2N(CH_2)_3CH(OEt)_2$, i-Pr_2NEt, Et_2O, 0–25 °C, 0.5 h. (d) HCl, THF/H_2O, 25 °C, 5–30 min. (e) PhMe, reflux, 24 h. (f) same as (c), but in THF. (g) TMSA, $PdCl_2(PPh_3)_2$, CuI, Et_3N, 25 °C, 2–4 h. (h) KOH, $MeOH/H_2O$, 25 °C, 0.5 h.

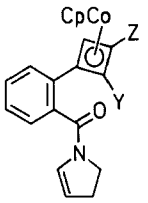
Scheme 5

An alternative route to **32** was suggested by a report[42] that catalytic hydroformylation of *N*-acetylprop-2-enamine provides a mixture of aldehydes, the terminal one (**35**, R = Me) cyclizing and dehydrating upon vacuum distillation to furnish **32** (R = Me). Thus, commercially available 4-aminobutanal diethyl acetal was acylated by **31** to **33**; acidic hydrolysis afforded **34**, containing traces of **35**, after chromatography. The orientation of the hydroxy group in the major rotamer **34a** may be assigned by comparison of the methine resonance (δ = 5.75) with that of the minor rotamer (δ = 4.90).[43] Attempted dehydration of **34** by Kugelrohr distillation (250 °C, 0.03 mmHg) led only to decomposition, but in refluxing methyl- or 1,3-dimethylbenzene smooth conversion took place to give **32** (82 % overall from acid **30**).

Table 1. Cocyclizations of **37** with Alkynes **4**, **44**, and **45**







Y = Z = $SiMe_3$ **38a** **38b** **39**

40 = diene ligand of **38a, b**

Y = Z = CO_2Me **41a** **41b**

Y = $SiMe_3$, Z = OMe **42**

Y = OMe, Z = $SiMe_3$ **43**

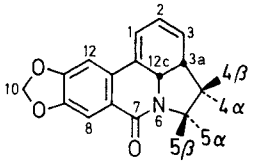
Z—≡—Y

Y = Z = CO_2Me **44**

Y = $SiMe_3$, Z = OMe **45**

Alkyne	Reaction Conditions	Products, Ratios, Yields
4	**4**/diglyme (65 : 35), hν, reflux, 148 °C	**38a** and **b** (2.2 : 1.0, total 46%), **39** (26%)
4	**4**/1,2-dimethoxyethane (5 : 3), hν, reflux, 105–106 °C	**38a** and **b** (2.2 : 1.0, total 56%), **39** (13%)
4	**4**/1,2-dimethoxyethane (1 : 1), hν, 25 °C	**38a** and **b** (4.0 : 1.0, total 73%), **39** (3.7%)
44	**44** (2.19 equiv), 1,3-dimethylbenzene, hν, reflux	**41a** and **41b** (1.5 : 1.0, total 60%)
45	**45** (4.2 equiv), methylbenzene, hν, reflux	**42** and **43** (1 : 1, total 52%)

Table 2. ^1H NMR Data for Model Galanthan Derivatives in $CDCl_3$



Hydrogens	Chemical shifts, δ ppm (J, Hz)						
	38a	**38b**	**40**	**41a**	**41b**	**42**	**43**
CpCo	β	α	–	β	α	β	β
	4.79	4.45		4.86	4.55	4.77	4.86
H1	5.11	5.76	6.42	5.72	6.33	5.08	4.96
H2[a]	$SiMe_3$	$SiMe_3$	$SiMe_3$	CO_2Me	CO_2Me	OMe	$SiMe_3$
	[0.22]	[0.25]	[0.28]	[3.71]	[3.68]	3.91	0.31
H3[a]	$SiMe_3$	$SiMe_3$	$SiMe_3$	CO_2Me	CO_2CH_3	$SiMe_3$	OCH_3
	[0.38]	[0.42]	[0.28]	[3.88]	[3.86]	0.15	3.51
H3a	2.69	1.58–1.72[b]	3.25	–[b]	–[b]	2.72	3.2–3.4[b]
	(6.6, 10.4, 11)		(6, 12.2, 12.2)			(7.5, 10.5, 10.5)	
Hα	0.76	2.04–2.24[b]	1.50	–[b]	–[b]	0.9–1.05[b]	1.08
	(7.3, 11, 11.9, 11.9)		(7.2, 12, 12, 12.2)				(8, 11, 11, 11)
Hβ	1.71	2.04–2.24[b]	2.22	–[b]	–[b]	1.75–1.85[b]	1.92
	(5.5, 6.6, 11.9)		(5.6, 6, 12)				(6, 7, 11)
H5α	4.00	≈ 4.3[b]	3.95	4.06	4.37	4.04	4.13
	(7.3, 11.8)		(7.2, 11.2)	(7.5, 11.7)	(7, 12)	(8, 11)	(7.8, 11.7)
H5β	3.20	2.86	3.06	–[b]	–[b]	3.20	3.2–3.4[b]
	(5.5, 11.8, 11.9)		(5.0, 11.6, 12)			(5.5, 11.5, 11.5)	
H8	7.93	8.03	8.04	7.97	8.08	7.93	7.93
	(1.5, 7.5)			(1.8, 7.3)	(1, 7.5)	(8.2)	(7.0)
H11	6.87	–[b]	–[b]	6.98	–[b]	6.92	6.96
	(1.5, 7.5)			(1.7, 7.3)		(7.2)	(7.2)
H11c	4.30	2.42	4.50	4.46	2.76	4.13	4.34
	(10.4)	(7.8)	(12.2)	(10.9)	(10)	(10.5)	(9)

[a] Shift refers to protons on the indicated substituent; brackets signify uncertain assignment.
[b] Resonance complicated or obscured partially or totally by other peaks in the spectrum.

Ethynylation of **32** with TMSA at ambient temperatures gave **36**, which was protodesilylated to afford **37** (5 steps, 55% overall from **30**). As seen previously for **32** (R = Me),[44] enamides **32, 36,** and **37** at ambient temperatures showed distinct NMR signals from two rotameric forms, present in ratios of 3–4 to 1.

The ready availability of **37** in gram quantities paved the way for exploration of enamide cycloadditions. Our proposed synthesis of γ-lycorane **2c** (Scheme 1) required substituents on a cocyclization partner which could be later replaced by hydrogens; because alkenylsilanes may be readily protodesilylated by acids,[17] **4** was the first alkyne to audition for the role. The poor solubility of **37** in pure **4** necessitated the addition of a more polar cosolvent; glyme or diglyme were chosen, depending on the desired reflux temperature of the reaction mixture. At all temperatures examined (Table 1) it was found that burgundy crystalline **38a** and **38b** predominated over yellow oily **39**; moreover, major isomer **38a** could be freed of **38b** by fractional crystallization.

The assignments of structures **38a** and **b** rely mainly on ^{1}H NMR spectroscopic data (including a series of decoupling experiments) which are summarized along with data for other galanthan model compounds in Table 2. In particular, the previously documented effect of the magnetic anisotropy of Co[10] allowed the position of the CpCo fragment on the ligand to be determined: the chemical shifts of H-11c were δ = 4.30 and 2.42 for **38a** and **b**, respectively. Moreover, irradiation of the Cp hydrogens of **38a** led to an NOE enhancement of the doublet for H-11 on the arene. The mixture of the diastereomers **38** on oxidative demetalation provided a single diene, **40**, in high yield.

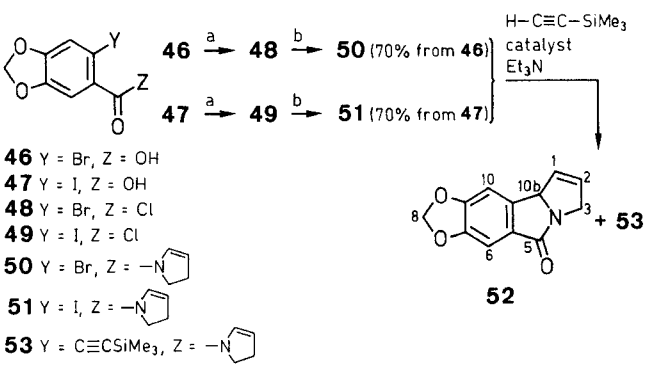
The use of dimethyl butynedioate **44** as a cocyclization partner for **37** suppressed CpCo-cyclobutadiene complex formation, leading to **41a** and **b** as a chromatographically inseparable mixture (1.5:1) in 60% yield (Table 1).

Because more complex Amaryllidaceae alkaloids, such as lycorine **1**, contain oxygen substituents on the C ring, it was of interest to see if such substituents could be introduced by the reaction of **37** with an alkoxyalkyne such as **45**.[45] Should **45** couple in a regioselective manner with **37** and $CpCo(CO)_2$,[11,46] the diene ligand presented in **42** would be produced. Subsequent demetalation and hydrolysis were envisaged to lead to an enone.[11,12] Cocyclization of **37** with **45** in refluxing methylbenzene gave a 1:1 mixture of chromatographically separable, crystalline complexes **42** and **43** (52% combined yield). Cyclobutadiene complexes other than those derived from two molecules of **45**[45] were not isolated. Several spectral features strongly implicated the structures shown. First, the proton chemical shifts of H-11c (δ = 4.13, 4.34) and the enhancements of H-11 in difference NOE spectra (irradiation of Cp–H) indicated that in each complex, CpCo was located on the same side of the diene ligand as H-11, that is, *endo* to H-11c. Second, between the two complexes the proton signals that showed the greatest differences in chemical shift were the singlets for Cp, Me_3Si, MeO, and H-1. These differences suggested that the two complexes differed in the position of Me_3Si and MeO on the ligand. Confirmation of this suspicion came from examination of the ^{13}C NMR spectra. In the spectrum of **43**, three quaternary carbon resonances (assigned with the help of DEPT)[47] were seen at δ = 145.72, 135.46, and 131.69. In comparison with spectra of complexes **38** and **42** and with tabulated data for simple benzene derivatives[48] two of the three signals were assigned to the quaternary aryl carbons C-7a and C-11a. By process of elimination, one of the three signals must be that of a carbon of the complexed diene. Since the terminal and internal diene carbons of CpCo-cyclohexadiene itself appear at δ = 53.2 and 77.6, respectively,[49] and since Pearson reports an α-substituent effect of ca. + 54 ppm for MeO substitution in $Fe(CO)_3$–diene complexes,[50] complex **42** must have MeO on the internal carbon C-2. Similarly, the ^{13}C NMR spectrum of **43** showed three quaternary carbons at δ = 144.86, 130.11, and 109.33, the latter resonance being assigned to the MeO-substituted terminal carbon, C3. The structure of **42** has been confirmed by X-ray diffraction.[51]

The successful cocyclizations presented in Table 1 encouraged us to continue our efforts to synthesize **5c**.

Synthesis of γ-Lycorane Precursor 5c

Direct acylation of the trimer of azacyclopent-1-ene with **48**[52] afforded **50** in only 11% yield. However, the four-step procedure developed for model enamide **37** gave **50** in 70% overall yield from acid **46**[52] (Scheme 6).



Substrate	Catalyst(s)	Reaction Conditions	52	53
50	$PdCl_2(PPh_3)_2$ or $Pd(Ph_3)_4$	reflux, 1–2 d	50–61%	not detectable
50	$PdCl_2[P(o\text{-tol})_3]_2$, $P(o\text{-tol})_3$	reflux, 5.5 h	35%	8–12%
51	$PdCl_2(PPh_3)_2$, CuI	25°C, 4.5 h	1.5 to 1	
51	$PdCl_2[P(o\text{-tol})_3]_2$, $P(o\text{-tol})_3$	reflux, 2 d	1.5 to 1	

(a) $SOCl_2$, reflux, 1–2 h; (b) 1. $H_2N(CH_2)_3CH(OEt)_2$, *i*-Pr_2NEt, THF, 0–25°C, 15–30 min; 2. HCl, THF/H_2O, 25°C, 0.5–2 h; 3. 1,3-dimethylbenzeme, reflux, 2–5 h.

Scheme 6

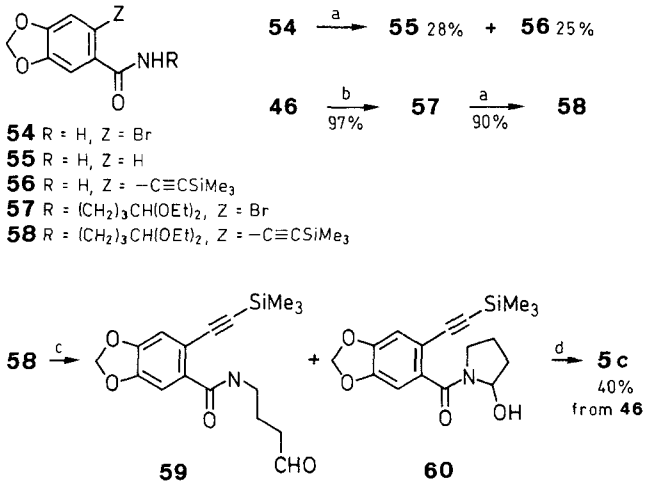
Attempted ethynylation of bromide **50** gave a single isolable product, **52**, with none of the desired product **53** detectable by TLC analysis (eventually an authentic

sample was available, vide infra). The molecular ion of $m/z = 215$ in the mass spectrum of **52** indicated that it was derived from **50** by loss of HBr. The presence of a stereogenic center in **52** was suggested by the closely-spaced doublets for diastereotopic OCH_2O protons (δ = 6.006 and 6.012, J = 1.2 Hz). This and the two resonances at δ = 5.91 (dddd, J = 1.4, 2.1, 2.5, 6.0 Hz) and 5.30 (narrow m) were consistent with the alkene function positioned as in **52**, or between C-2 and C-3. The latter possibility was rejected based on the relatively normal chemical shifts of the two alkene carbons (δ = 131.23, 127.80). Product **52** is the result of an intramolecular Heck reaction.[53]

It was thought that a more congested ligand environment about palladium might favor the approach of the linear alkyne to the metal and disfavor the approach of the enamide double bond with its attendant hydrogens, with aryl–alkyne coupling, rather than aryl–olefin coupling as a result. When **50** was treated with $PdCl_2[P(o\text{-tol})_3]_2$ under conditions similar to those used above, **53** was formed, but **52** was still the major product. In this case further modification of the ligands might have been fruitful, but Heck's group noted that phosphines more hindered than $P(o\text{-tol})_3$ were no better, and usually worse in their system.[53,54]

Ethynylation of **51** (available from **8** by way of **47**)[55,56] with TMSA and $PdCl_2(PPh_3)_2$ was complete after 4.5 hours at room temperature, but only in the presence of copper(II) iodide,[19] affording **53** and **52** (1 to 1.5). The catalyst $PdCl_2[P(o\text{-tol})_3]_2$ was inferior in this transformation.

In these palladium-catalyzed reactions, it is curious that OCH_2O-substituted iodide **51** is more reluctant to couple with TMSA than unsubstituted analog **32**. Perhaps the OCH_2O substituents in the expected insertion product $ArPdI(PPh_3)_2$ exert an electronic influence, hindering attack of acetylide on palladium.[19] The inferior leaving group ability of bromide compared to that of iodide, discouraging acetylide attack on palladium, could explain the exclusive formation of **52** from **50**.



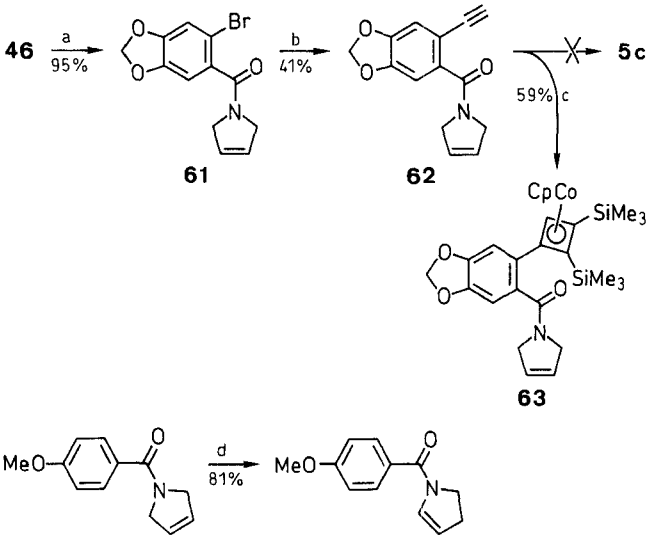
(a) TMSA, $PdCl_2(PPh_3)_2$, Et_3N or azacyclohexane, reflux. (b) 1. $SOCl_2$, reflux; 2. $H_2N(CH_2)_3CH(OEt)_2$, i-Pr_2NEt, Et_2O. (c) HCl, THF/H_2O, 25°C, 2–2.5 h. (d) 1. 1,3-dimethylbenzene, reflux, 24 h; 2. NaOH, $MeOH/H_2O$, 25°C, 45 min.

Scheme 7

Regardless, we resolved to build the offending enamide moiety after ethynylation. In exploration of an alternative route to **7**, we had observed that attempted ethynylation of primary amide **54**[57] with TMSA (2.3 equiv) gave reduction product **55**[58] and **57** in nearly equal amounts (Scheme 7). Our suspicion that in a similar ethynylation of secondary amide **57**, the interaction of palladium intermediates with the NH moiety[59] might be hindered sufficiently by the *N*-alkyl substituent so as to suppress reduction was rewarded by the clean coupling of **57** (97% from **46**) with TMSA, to produce **58**. The acetal function of **58** was hydrolyzed to produce a chromatographically separable mixture of oily aldehyde **59** (15%) and crystalline **60** (56%), the former slowly cyclizing to the latter on standing. Amide **57** was ethynylated, hydrolyzed, dehydrated, and desilylated without substantial purification of intermediates to give **5c** (five steps from the known acid **46**, 40% overall).

Attempted Generation of 5c in situ by CpCo-catalyzed Alkene Isomerization

An alternative route to **5c** would involve isomerization of its deconjugated double-bond isomer **62** (Scheme 8) by $CpCo(CO)_2$.



(a) 1. $SOCl_2$, reflux; 2. azacyclopent-3-ene, K_2CO_3, PhMe, H_2O, 0–25°C, 1 h. (b) 1. TMSA, $PdCl_2(PPh_3)_2$, Et_3N, reflux, 6.5 h; 2. KOH, $MeOH/H_2O$, 25°C, 0.5 h. (c) 4, $CpCo(CO)_2$, diglyme, reflux, hv. (d) $CpCo(CO)_2$, 1,3-dimethylbenzene, reflux.

Scheme 8

Double-bond migrations in the presence of $CpCo(CO)_2$[60] and cobalt hydride complexes[61] have been reported. Stille and Becker[44] used a number of transition metals (but not Co) in catalytic conversions of *N*-acylazacyclopent-3-enes to their conjugated, thermodynamically more stable[62] isomers. To test the feasibility of $CpCo(CO)_2$-catalyzed isomerization, we first made model amide **64** from azacyclopent-3-ene[63] and commercial 4-methoxybenzoyl

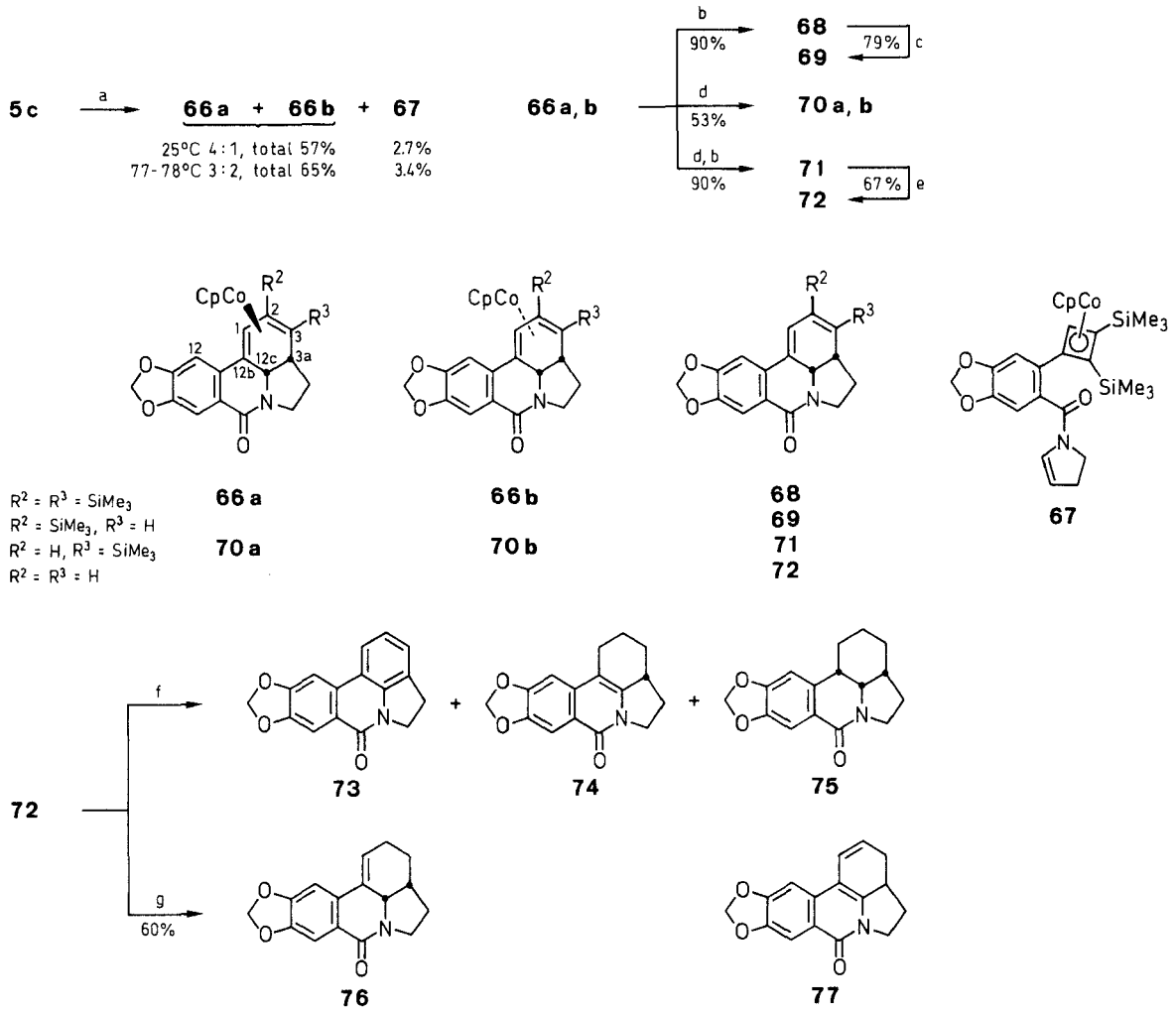
chloride. Isomerization of **64** to **65** took place in the presence of $CpCo(CO)_2$ (0.2 equiv) in refluxing 1,3-dimethylbenzene over the course of 2 days. Irradiation of the mixture with a slide projector lamp decreased the reaction time to 9 hours. Cocyclization of **62** (from **46**) with BTMSA and $CpCo(CO)_2$ (1.0 equiv) with diglyme as cosolvent gave a single product by TLC and ^1H NMR analysis of the mixture; yellow, crystalline **63** was isolated in 59% yield. It appears that coupling of the alkyne moiety of **62** and BTMSA, leading to **63**, is faster than isomerization of **62** to **5c**.

Formal Synthesis of γ-Lycorane. Regioselective Desilylation of CpCo-Diene Complexes

The obtention of **5c** in gram quantities allowed us to embark on a synthesis of γ-lycorane **2c** following Scheme 1. Under the optimal conditions developed for the cocyclization of **37** with **4** (25°C), **5c** afforded after 44 hours **66a** and **b** (57% total) and **67** (2.7%) (Scheme 9), improved yields of **66a** and **b** (65%) being obtained by conducting the cyclization under reflux in **4**–THF (1:1). The spectral characteristics of the products (Table 3) were similar to those observed for the cyclization products derived from **37**, permitting easy identification.

Oxidative demetalation of the mixture **66a,b** gave a single diene, **68**. Attempts to remove the silyl substituents by treatment with acid were only partly successful. Thus, the action of CF_3CO_2H (2.0 equiv) in degassed $CDCl_3$ in a sealed NMR tube (25°C, 4 days) resulted in selective monodesilylation to **69**. At least one minor product (ca. 10%) was detected in the mixture. More forcing treatment led to mixtures of products, probably (vide infra) arising by double bond isomerization. To circumvent these complications, attention was turned to finding methods of protodesilylation of **66**.

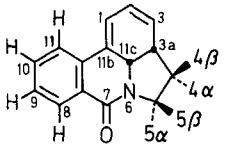
To our surprise,[64] mild treatment of **66a** and **b** with tetrabutylammonium fluoride in THF for 2–4 hours at 25°C gave selectively **70a** and **b** (total 53%), which were separable by chromatography. That only the internal Me_3Si group had been removed in each complex was apparent from ^1H NMR data, in particular, the diagnostic proton chemical shifts for H-2, close to those for H-1 (δ = 5.12–5.72), and the mutual couplings (J = 4.3–4.4 Hz) between them. NOE difference spectra of **70a** confirmed these assignments. Attempts to completely protodesilylate **66** under more forcing conditions (excess CsF, DMSO, 25–80°C, 4 days) led to desilylated, aromatized, and demetalated **73**[65] (24%) as the major product



(a) **4**, $CpCo(CO)_2$, THF, 25°C or reflux, hν. (b) $Fe(NO_3)_3 \cdot 9H_2O$, THF/H_2O, 0°C, 5 min. (c) CF_3CO_2H, deoxygenated $CDCl_3$, 25°C, 4 d. (d) Bu_4NF, THF, 25°C, 2–4 h. (e) same as (c) but at 55°C, 5–8 d. (f) H_2 (1 atm), PtO_2, EtOAc, 25°C, 3 d. (g) H_2 (1 atm), $ClRh(PPh_3)_3$, PhMe, 25°C, 4.5 h.

Scheme 9

Table 3. ^{1}H NMR Data for γ-Lycorane Precursors in $CDCl_3$



Hydrogens	Chemical shifts, δ (J, Hz)[a]							
	66a	**66b**	**68**	**69**	**70a**	**70b**	**71**	**72**
CpCo	β	α	–	–	β	α	–	–
	4.79	4.49	–	–	4.77	4.47		
H1	5.03	5.59	6.30	6.22	5.32	[5.72]	6.09	6.18
	(0.8)	(0.9)	(1.7)	(2.2)	(4.4)	(4.3)	(2.1, 5.7)	(2.2, 5.7)
H2[b]	$SiMe_3$	$SiMe_3$	$SiMe_3$	$SiMe_3$	5.41	[5.12]	6.26	[6.03][c]
	[0.21]	[0.24]	[0.27]	0.15	(4.4)	(4.3)	(5.7)	
H3[b]	$SiMe_3$	$SiMe_3$	$SiMe_3$	6.18	$SiMe_3$	$SiMe_3$	$SiMe_3$	[5.97]
	[0.38]	[0.41]	[0.27]	(0.6, 4.8)	0.10	0.12	0.14	(0.8, 5.6, 8.9)
H3a	2.66	–[c]	3.23	3.1–3.3[c]	2.67	–[c]	3.20	3.1–3.3[c]
	(6.7, 10.3, 11)		(6, 12.3, 12.4)		(6.8, 10.4, 11)		(0.8, 6.5, 12.4, 12.9)	
H4α	0.74	–[c]	1.49	1.65	0.89	–[c]	1.50	1.70
	(7.4, 11, 12, 12)		(7.2, 12, 12, 12.3)	(7.4, 12.2, 12.2, 12.2)	(7.6, 11, 12, 12)		(7.4, 12, 12, 12.4)	(7.4, 12, 12, 12.3)
H4β	1.68	–[c]	2.19	2.31	1.75	–[c]	2.21	2.32
	(5.4, 6.7, 12)		(5.2, 6, 12)	(5.4, 7.0, 12)	(5.5, 6.8, 12)		(5.2, 6.5, 12)	(5.4, 6.9, 12.3)
H5α	3.95	≈ 4.25[c]	3.90	3.99	3.98	4.30	3.95	3.97
	(7.4, 11.5)		(7.2, 11.5)	(7.4, 11.6)	(7.6, 11.7)	(7.6, 11.9)	(7.4, 11.5)	(7.4, 11.8)
H5β	3.17	–[c]	3.05	3.1–3.3[c]	3.19	–[c]	3.08	3.1–3.3[c]
	(5.4, 11.5, 12)		(5.2, 11.5, 12)		(5.5, 11.7, 12)		(5.2, 11.5, 12)	
H8	7.40	7.50	7.49	7.45	7.39	7.48	7.48	7.43
H10	5.96, 5.98	5.95, 6.00	5.99, 6.01	6.03, 6.04	5.96, 5.98	5.95, 5.99	5.97, 5.99	6.03, 6.04
H12	6.32	6.65	6.86	6.95	6.33	6.67	6.86	6.92
H12c	4.27	2.36	4.46	4.68	4.25	2.38	4.56	4.73
	(10.3)	(7.7)	(1.7, 12.4)	(13.5)[d]	(10.4)	(7.6)	(12.9)	(13)

[a] Brackets indicate uncertain assignment.
[b] Chemical shift values refer to the protons of the indicated substituent.
[c] Resonance complicated or obscured partially or totally by other peaks in the spectrum.
[d] Broadened slightly by unresolved coupling.

from a black mixture. The free diene **71** was most conveniently obtained in a one-pot sequence directly from **66** (Bu_4NF, Fe^{III}). The regiospecificity of this fluoride-induced protodesilylation may reflect the relatively greater electron density at the terminal positions of the diene in the complexes, the consequence of CpCo-back-bonding. It was subsequently shown[66] for other CpCo-diene complexes that Me_3Si groups at terminal positions may also be removed by fluoride, but only at elevated temperatures.

Protodesilylation of **71** to **72** by CF_3CO_2H required temperatures higher than those in the reaction of **68**, the latter presumably profiting from steric activation and intermediate carbocation stabilization by the additional Me_3Si group.[67] Although diene **72** showed a greater tendency to aromatize than its more-substituted analogs described above, it could be isolated from the reaction mixture in 67% yield, contaminated with ca. 10% of **73**. Well before all of **71** had been consumed, a new product, tentatively identified as isoquinolone **77**, could be detected by ^{1}H NMR spectroscopy of the reaction mixture.

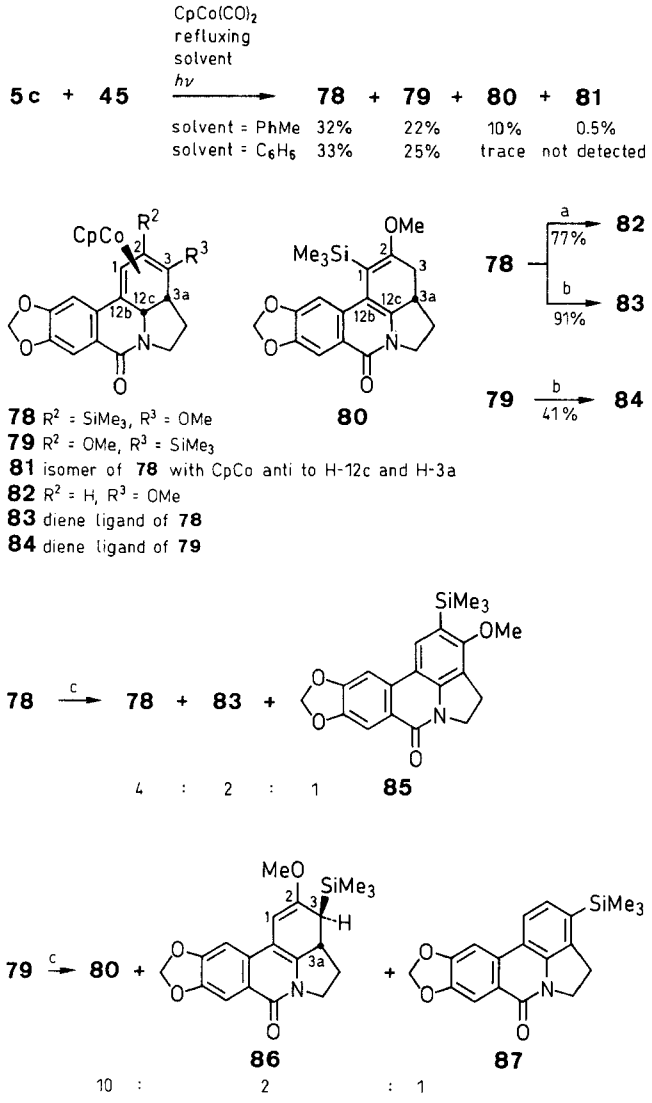
Heterogeneous catalytic hydrogenation of **72** was performed under conditions[68] which were chosen to minimize the apparently facile double bond migration. Monitoring the progress of the reduction by ^{1}H NMR spectroscopy indicated the initial generation of four products, **73**, **74**, **75**, and **76** in a ratio of 2:1:1:1, the latter eventually disappearing to afford **73**, **74**, and **75** in a ratio of 1:2:1. Chromatography allowed separation of the known[13] monohydrogenation product **74**, identified by comparison of its ^{1}H NMR, mass, and IR spectra with those published. Alkene isomerization over PtO_2 leading to an isoquinolone has been seen.[69] Products **73** and **75** were inseparable, but aromatized **73**[65] was readily identified by its ^{1}H NMR spectrum and a strong M^+ peak at 265. The presence of **75** (7-oxo-γ-lycorane) in the mixture was strongly inferred by the observation of an intense mass spectral signal for $M^+ = 271$ and by comparison of its ^{1}H NMR spectrum with those of the other three possible 7-oxolycoranes.[7] Disproportionation of dihydroaromatics to aromatics and saturated products during attempted hydrogenations is well known,[25] and presumably proceeds through the same sort of π-allyl hydride intermediate that could lead to **74**.

Homogeneous hydrogenation[70] of **72** afforded **76**, which was made by Hwang and Magnus (5 steps from 1,3-ben-

zodioxole-5-acetonitrile, 11.7% overall)[8] in a formal synthesis of γ-lycorane **2c**. Our approach, because it is less directional, is somewhat inferior in overall yield (9.4%) and more circuitous (10 steps from acid **46**). Its significance lies in its novelty and generality.

Cocyclizations of 5c with 45: Generation of C-Ring Oxygenated Galanthans

Although the lack of regioselectivity in the cocyclization of **37** with **45** to give equal amounts of **42** and **43** had to be viewed as a discouraging precedent, the potential of **5c** as a precursor to galanthans bearing oxygen substituents in the C-ring was tested. Thus, **5c** and **45** in the presence of $CpCo(CO)_2$ in refluxing methylbenzene furnished three major products derived from **5c** in a ratio of 3:2:1



(a) Bu_4NF, THF, 25°C, 0.5–2 h. (b) $CuCl_2 \cdot 2H_2O$, Et_3N, THF/H_2O, 0°C, 5 min. (c) 1,3-dimethylbenzene, reflux, 16–18 h.

Scheme 10

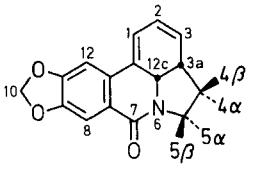
(^1H NMR integration), in addition to a minor one (Scheme 10). Table 4 summarizes the ^1H NMR spectral data for these and most of the other complexes and ligands described in this section. Chromatography of the mixture allowed complete separation of the predominant component, **78** (32%), whose spectral data are very similar to those of **43**, including a ^{13}C NMR quaternary carbon resonance at $\delta = 109.26$, assigned to C-3. Further confirmation of the regiochemistry of C-ring substitution was obtained by Bu_4NF-mediated protodesilylation to **82** (77%), whose ^1H NMR spectrum showed the expected resonances for H-1 and H-2 at $\delta = 4.80$ and 4.98, mutually split by $J = 4.8$ Hz.

Chromatography of the cyclization mixture also furnished a minor complex (0.5%), tentatively identified as **81**, isomeric with **78** with respect to the CpCo unit, by its ^1H NMR and mass spectra. Difference NOE spectra established the position of the Me_3Si group relative to the diene hydrogen, and the relatively shielded position ($\delta = 2.65$) of the doublet for H-12c indicated that CpCo was located *anti* to this proton.[10]

Only partial chromatographic separation of the two other major products, complex **79** (22%) and the organic compound **80** (10%), was achieved. Fractional crystallization gave pure **79**, whose spectral characteristics were very similar to those of **42**, including a ^{13}C NMR quaternary carbon signal at $\delta = 134.86$ which could be assigned to the methoxy-bearing C-2.

The constitution of **80** poses a more difficult challenge, as it requires postulating the occurrence of a complex set of rearrangements leading to it. Support for its formulation as **80** is circumstantial but compelling. Thus, while **80** exhibits the same M^+ peak in mass spectroscopy, NMR data indicate that it is clearly isomeric to the free ligands **83** (from **78**) and **84** (from **79**). The ^1H NMR spectrum of **80** was similar in several respects to those of dienes **83, 84**, and related complexes, summarized in Table 4. Singlets assigned to Me_3Si, MeO, and the two aryl hydrogens were visible. However, a proton resonance was not seen between $\delta = 4.2$ and 6.6, suggesting a structure featuring fully substituted alkene moieties. That a double bond had not migrated into the five-membered ring was suggested by comparing five of the seven multiplets observed between $\delta = 1.18$ and 4.16 with those of the five-spin system NCH_2CH_2CH in **83** and **84**; with the exception of the signal at $\delta = 3.27$, the multiplicities of signals at $\delta = 1.18$, 1.86, 3.27, 3.45, and 4.16 were identical, and the couplings similar. The exceptional signal at $\delta = 3.27$, ascribed to H-3a, appeared as a dddd; two of these couplings ($J = 5.8$, 8.7 Hz) were to the sixth and seventh multiplets at $\delta = 2.88$ and 2.98, assignable to two geminal protons ($J_{gem} = 19.2$ Hz), placing the two geminal protons at C-3. Thus, the two double bonds must be between C-12b and C-12c, part of an isoquinolone ring, and between C-1 and C-2. The resulting vinylisoquinolone skeleton would resemble the isoquinolone derivative **74**, which displayed similar spectral characteristics for the NCH_2CH_2CH spin system. Like **74, 80** exhibited downfield shifts for the aryl hydrogens compared to **83** and **84**, and the OCH_2O protons were isochronous. Thus, the second alkene function of **80** was situated between C-1 and C-2, with the $SiMe_3$ and MeO groups on the alkene carbons. A ^{13}C NMR quaternary carbon resonance ($\delta = 101.65$) at high field for an alkene carbon substantiated the proposal that the MeO group resided on the alkene.

Table 4. ^1H NMR Data for Methoxy-Substituted Galanthan Derivatives in $CDCl_3$



Hydrogens	Chemical shifts, δ (J, Hz)[a]							
	78	**79**	**80**[b]	**81**	**82**	**83**	**84**	**86**
CpCo	β 4.82	β 4.77	–	α 4.45	β 4.77	–	–	–
H1[c]	4.60	5.02	$SiMe_3$ 0.24	5.03	4.80 (4.8)	6.07 (2.0)	6.12 (2.2)	5.59 (2.5)
H2[c]	$SiMe_3$ 0.21	OMe 3.91	OMe 3.18	$SiMe_3$ 0.35	4.98 (1, 4.8)	$SiMe_3$ 0.15	OMe 3.61	OMe 3.68
H3[c]	OMe 3.48	$SiMe_3$ 0.14	2.98 (5.8, 19.2) 2.88 (8.7, 19.2)	OMe 3.40	OMe 3.35	OMe 3.70	$SiMe_3$ 0.16	$SiMe_3$ 0.15
H3a	3.22–3.4[d]	2.71 (7.0, 10.5, 11)	3.27 (5.8, 6.4, 8.7, 12.1)	–[d]	3.19 (1, 7.3, 12.3, 12.4)	3.34 (7, 12.5, 13)	3.18 (6.5, 12.5, 12.5)	3.42 (7.2, 11.3, 16.0)
H4α	1.03 (8, 11, 11, 12)	0.94 (7.7, 11, 11.7, 12.2)	1.18 (8.3, 11.7, 12, 12)	–[d]	1.12 (7.8, 11, 11, 11.8)	1.72 (7.5, 12, 12.1, 12.5)	1.51 (7.2, 12, 12, 12.1)	1.87 (9.0, 11.3, 11.5, 12.5)
H4β	1.88 (6.0, 6.6, 12)	1.79 (5.6, 7.0, 12)	1.86 (5.7, 6.4, 12)	–[d]	1.98 (5.7, 7.3, 12)	2.31 (5.1, 7.0, 12.1)	2.15 (5.2, 6.5, 12)	2.58 (6.3, 7.2, 12.5)
H5α	4.05 (7.9, 11.6)	3.99 (7.7, 11.7)	4.16 (8.3, 12.1)	–[d]	4.05 (7.8, 11.8)	4.05 (7.5, 11.4)	3.93 (7.2, 11.4)	4.42 (9.0, 12.4)
H5β	3.22–3.4[d]	3.18 (5.5, 11.7, 11.7)	3.45 (5.7, 11.7, 12)	–[d]	3.27 (5.7, 11.8, 11.8)	3.14 (5.1, 11.4, 12)	3.05 (5.2, 11.8, 11.8)	3.88 (6.3, 11.5, 12.4)
H8	7.36	7.41	8.32	7.47	7.37	7.46	7.50	7.79
H10	5.95, 5.95	5.96, 5.98	5.34, 5.34	5.95, 5.98	5.96, 5.96	5.97, 5.98	6.01, 6.02	6.04, 6.04
H12	6.40	6.38	6.62	6.64	6.40	6.85	6.89	6.97
H12c	4.29 (11.0)	4.12 (10.5)	–	2.65 (7.2)	4.42 (11.0)	4.71 (13)[e]	4.54 (2.0, 12.6)	–

[a] Brackets indicate uncertain assignment.
[b] Solvent = C_6D_6.
[c] Chemical shift values refer to the protons of the indicated substituent.
[d] Resonance complicated or obscured partially or totally by other peaks in the spectrum.
[e] Broadened slightly by unresolved coupling.

However, the position of the two alkene substituents could not be determined with certainty by experiment; in an NOE difference spectrum definite enhancements of either aryl proton resonance were not seen when either singlet for $SiMe_3$ or MeO were irradiated, and in CD_2Cl_2 at $-65°C$, the $SiMe_3$ group was conformationally mobile on the NMR time scale (300 MHz).[72] Eventually, the position of the silyl substituent at C-1 was suggested by mechanistic considerations, vide infra.

To determine the origin of **80** and possibly offer insight into the position of the $SiMe_3$ or MeO groups on the alkene, two experiments were performed. First, when pure **78** was heated in refluxing 1,3-dimethylbenzene under argon for 14 hours, it decomposed partially to give a clean mixture of unchanged **78**, the corresponding unrearranged ligand **83**, and tentatively identified dehydrogenation product **85** in a ratio of 4:2:1; **80** was not detected. However, under the same conditions pure **79** was converted into a mixture of **80, 86,** and **87** in a ratio of 10:2:1, thus implicating **79** as the source of **80** in the cocyclization reaction.

The structure of minor component **87** was indicated by the similarity of its ^1H NMR spectrum to that of **73**,[65] by the observation of M^+ at $m/z = 337$, and by its appearance in overoxidized samples of diene **71**.

The ^1H NMR data of the second minor component **86** were similar in several respects to those of **80**. Singlets assigned to Me_3Si, MeO, and the two aryl hydrogens were visible. The signals for two geminal protons in **80** were replaced by doublet ($J = 2.5$ Hz) at $\delta = 5.59$, attributed to an alkene proton, and a resonance at $\delta = 2.05$ (dd) was coupled to H-3a ($J = 16.0$ Hz) and the alkene proton ($J = 2.5$ Hz). The upfield shift of the resonance at $\delta = 2.05$ compared with that of NC*H* in **83** and **84** suggested that the diene system had migrated so as to place the aliphatic hydrogen α to $SiMe_3$, at C-3, trans to H-3a (large *J*), and subject to allylic four-bond coupling with the alkene proton (small *J*). In the infrared spectrum, the existence of isoquinolone and enol ether moieties[71] in **86** was indicated by absorptions at $\nu = 1670$, 1618, and 1596 cm^{-1}. The ^{13}C NMR and DEPT spectra of **86** showed a high-field vinylic *C*H signal at $\delta = 89.77$, consistent with the presence of R*C*H=CR(OMe).

From these experiments it is clear that at elevated temperatures **79** rearranges to give isoquinolones, perhaps by 1,5-hydrogen shifts.[60] What is responsible for the different thermal stabilities of **78** and **79** is not clear.[73] The position of the silyl substituent in **80** at C-1 is suggested by postulation of a 1,3-silyl shift[74] in intermediate(s) wherein one double bond would be between C-1 and C-2.

Conclusion

In the construction of 1,2-functionalized arene **5c**, the course of palladium-catalyzed coupling of bromoarenes and TMSA was markedly altered by the nature of the substituent ortho to the bromine, as evidenced by the formation of **52** from **50** or **51**, and by the successful ethynylation of secondary amide **57** in the face of extensive reduction of primary amide **54**.

We have shown how $CpCo(CO)_2$ enables the rapid formation of polyheterocycles, as exemplified by the transformation of tricyclic **5c** and alkyne **4** to pentacyclic complexes **66a,b** (65%). Trimethylsilyl groups at internal carbons of a CpCo-complexed diene are activated toward protodesilylation by fluoride compared to their counterparts at the terminal carbons, complementing the opposite regioselectivity of acid-mediated protodesilylation of uncomplexed dienes. Thus, sequential treatment of **66a,b** with tetrabutylammonium fluoride, iron(III), and CF_3CO_2H led to **72** (60% for the three steps), homogeneous hydrogenation of which led to **76** (60%), a known precursor of γ-lycorane **2c**. In sum, the [2+2+2] cycloaddition of two alkynes and an alkene function of an enamine can lead to six-membered rings more highly functionalized than those provided by analogous Diels–Alder protocols.

Unless otherwise noted, all starting materials and solvents were obtained from commercial suppliers and used without further purification. THF, 1,2-dimethoxyethane, and Et_2O were freshly distilled from sodium benzophenone ketyl. Diglyme was distilled at 60 mmHg from sodium. 1,4-Dioxane was distilled from $LiAlH_4$. Dry methyl-, 1,3-dimethyl-, and 1,3,5-trimethylbenzene were prepared by washing the commercially supplied material with cold conc. H_2SO_4 (3–5 times), H_2O, aqueous K_2CO_3, drying over $MgSO_4$, and then distilling from CaH_2 onto molecular sieves. *N,N*-Dimethylformamide (DMF) and DMSO were stored over 4 Å molecular sieves. Petroleum ether refers to the fraction with bp 35–60 °C. Unless otherwise specified, all reactions were carried out under an atmosphere of dry nitrogen or argon, water-sensitive experiments being performed in glassware that had been oven-dried (temperature > 100 °C) overnight. Glassware for cyclization experiments was rinsed with 1,1,1,3,3,3-hexamethyldisilazane before storage in a drying oven. In these experiments, reagents were usually added from Hamilton gastight syringes mounted on a Sage Instruments Model 341 A syringe pump. "Dried and concentrated" as applied to aqueous workups refers to treatment with $MgSO_4$, filtration, and concentration by rotary evaporation followed by storage under oil-pump vacuum, unless otherwise specified.

^1H, ^{13}C NMR, and DEPT spectra were recorded on UCB 200 MHz, UCB 250 MHz, or BVX 300 MHz instruments consisting of Cryomagnet System magnets, Nicolet 293 or 293 A¢ pulse programmers, and Nicolet Model 1180, 1180E, or 1280 data collection systems, or on a Bruker AM-500 MHz instrument. ^1H NMR data are reported for solutions in $CDCl_3$, observed at 300 MHz (unless otherwise specified) as follows: chemical shifts in parts per million (ppm) downfield from tetramethylsilane and references to residual solvent peaks (multiplicity, coupling constants *J* in Hertz, integration). The peaks are characterized by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), app (apparent). For ^1H NMR spectra the resonances due to residual $CHCl_3$ in $CDCl_3$, CHD_5 in C_6D_6, CHD_2COCD_3 in CD_3COCD_3, and $CHDCl_2$ in CD_2Cl_2 were measured at δ = 7.24, 7.15, 2.04, and 5.32, respectively. For ^{13}C NMR spectra, the central peak of the $CDCl_3$ triplet was assigned a chemical shift of δ = 77.0, that of C_6D_6 a value of 128.0, and the quintet of CD_2Cl_2 a value of 53.8 downfield of tetramethylsilane. Unless otherwise specified, ^{13}C NMR and, where noted, DEPT spectral data are reported as follows: chemical shifts in ppm downfield of tetramethylsilane, references to residual solvent peaks (number of protons on carbon), C, CH, CH_2, and CH_3 signify quaternary, methine, methylene, and methyl carbons, respectively.

Infrared spectra were obtained on a Perkin-Elmer model 681 spectrophotometer and were referenced to polystyrene (ν = 1601 cm^{-1}). The samples under scrutiny were either neat (NaCl plates), in solution (solvent, NaCl cells), or pressed into a KBr pellet. Low and high resolution mass spectra were provided by the Mass Spectral Service at the University of California, Berkeley. Elemental analyses were determined by the Microanalytical Laboratory, UCB. Melting points were observed in open Pyrex capillary tubes with a Thomas-Hoover Unimelt apparatus and are uncorrected.

Column chromatography was performed on flash silica (E. Merck Reagents silica gel 60, 230–400 mesh ASTM). Radial chromatography was carried out using a Harrison Research Chromatotron under an N_2 atmosphere. Deoxygenated solvents were used for column chromatography of cobalt complexes. Thin layer chromatography (TLC) was carried out on Analtech Uniplate silica gel plates with a 0.25 mm coating and fluorescent indicator.

6-Trimethylsilylethynyl-1,3-benzodioxole-5-carbaldehyde (9):[21]

6-Bromo-1,3-dioxole-5-carbaldehyde **8**[20] (100 mg, 0.436 mmol), $PdCl_2(PhCN)_2$ (3.30 mg, 0.0086 mmol), PPh_3 (4.57 mg, 0.0174 mmol), and freshly distilled Et_3N (15 mL) were placed in a three-neck round-bottom flask equipped with a reflux condenser and an N_2 inlet. After the solution was deoxygenated by three freeze-pump-thaw cycles, TMSA (69.3 mg, 0.707 mmol) was added via syringe and the mixture heated under reflux. Within 15 min, a color change to light green and a white precipitate were observed. After the reaction was complete (2.5 h), the solution was cooled to room temperature, the solids were filtered off, and the filtrate was concentrated to give a brown-red oil. Filtration through Al_2O_3 (neutral, activity III) with petroleum ether, then Et_2O as eluents, followed by crystallization, gave **9** (101.0 mg, 94%) as colorless needles, mp 105–106 °C.

MS: *m/z* (relative intensity) = 246 (M^+, 2), 245 (1), 232 (3), 231 (15), 172 (7), 149 (3), 131 (1), 115 (3), 75 (10), 55 (5), 44 (100).

IR ($CHCl_3$, NaCl): ν = 2960, 2900, 2850, 2780, 2570, 2520, 2150 (C≡C), 1678 (C=O), 1605, 1501, 1430, 1407, 1353, 1255 cm^{-1}.

^1H NMR (250 MHz): δ = 10.35 (s, 1 H, CHO), 7.30 (s, 1 H), 6.93 (s, 1 H), 6.05 (s, 2 H, OCH_2O), 0.24 (s, 9 H, $SiMe_3$).

^{13}C NMR (50 MHz): δ = 189.6 (C=O), 151.9, 148.5, 132.3, 123.0, 111.9, 105.4, 102.2, 100.6, 99.7, −0.48.

Anal: Calc. for $C_{13}H_{14}O_3Si$: C, 63.32; H, 5.69. Found: C, 62.90; H, 5.70.

Bis(6-trimethylsilylethynyl-1,3-benzodioxol-5-ylmethyl)amine (10), 6-Trimethylsilylethynyl-1,3-benzodioxole-5-methanol (11), and Tris(6-trimethylsilylethynyl-1,3-benzodioxol-5-ylmethyl)amine (12):

$NaBH_3CN$ (50.0 mg, 0.80 mmol) was added in one portion to a stirred solution of NH_4OAc (771 mg, 10.0 mmol) and **9** (246.1 mg, 1.00 mmol) in MeOH (25 mL). After 33 h, the green mixture was poured into CH_2Cl_2 (25 mL) and H_2O (75 mL) in a separatory funnel and basified with conc. aq NH_4OH (15 mL). The aq phase was extracted with CH_2Cl_2 (2 × 15 mL). The combined olive-green organic phases were washed with H_2O (50 mL), dried (Na_2SO_4), and concentrated. ^1H NMR spectral analysis of the greenish oily crude product (234.6 mg) showed **10**, **11**, and **12** in a ratio of 5:2:1. Flash chromatography over SiO_2 (2.3 × 20 cm) using Et_2O–petroleum ether (1:7 to 1:1) containing 1% v/v Et_3N afforded **10** (87.4 mg, 37%) as colorless crystals, mp 106–108.5 °C.

MS: *m/z* (relative intensity) = 477 (M^+, 9.0), 405 (11), 404 (33), 246 (20), 232 (14), 231 (33), 230 (13), 216 (14), 201 (11), 189 (11), 173 (11), 159 (11), 75 (13), 74 (14), 73 (100).

IR (KBr): ν = 3300 (NH), 2960, 2895, 2146 (C≡C), 1502, 1480, 1248, 1168, 1038, 930, 868, 840, 760 cm^{-1}.

^1H NMR: δ = 6.88 (s, 2 H), 6.86 (s, 2 H), 5.91 (s, 4 H), 3.84 (s, 4 H), 2.1 (br s, 1 H), 0.20 (s, 18 H).

^{13}C NMR and DEPT δ = 148.18 (C), 145.98 (C), 138.17 (C), 115.00 (C), 111.79 (CH), 108.84 (CH), 103.24 (C), 101.23 (CH_2), 97.09 (C), 51.24 (CH_2), 0.02 (CH_3).

Anal: Calc. for $C_{26}H_{31}NO_4Si_2$: C, 65.37; H, 6.54; N, 2.93. Found: C, 65.16; H, 6.46; N, 2.99.

Further elution afforded **12** (10.8 mg, 4.5%), essentially pure by ^1H NMR and TLC analysis, as a colorless film.

CIMS (CH_4): *m/z* (relative intensity) = 708 ($M^+ + 1$, 92), 707 (58, M^+), 693 (39), 692 (73), 490 (42), 476 (100), 461 (29), 408 (29), 232 (28), 231 (85).

IR ($CDCl_3$, NaCl): ν = 2960, 2895, 2145 (C≡C), 1504, 1482, 1252, 1042, 870, 848 cm^{-1}.

^1H NMR: δ = 6.96 (s, 3 H), 6.82 (s, 3 H), 5.92 (s, 6 H), 3.68 (s, 6 H), 0.23 (s, 27 H).

Finally, alcohol **11** (35.5 mg, 14%) was obtained as a colorless oil, pure by ^1H NMR and TLC analysis.

Reduction of 9 to 11:

To a stirred solution of $NaBH_4$ (88.0 mg, 2.32 mmol), absolute EtOH (25 mL), and a trace of Bromthymol Blue was added HOAc in EtOH (≈ 0.7 M) until a green color appeared. Aldehyde **9** (410.5 mg, 1.67 mmol) was added in one portion and the mixture's green color was maintained by the dropwise addition of ethanolic HCl (≈ 1 M). After 5 min, the mixture remained yellow-green without the addition of more acid. TLC (SiO_2, Et_2O–petroleum ether, 1 : 3) showed that the reaction was complete. The mixture was diluted with 5% aq KH_2PO_4 (100 mL) and extracted with Et_2O (3 × 25 mL). The combined extracts were washed with brine (25 mL), dried, and concentrated. The yellow oily crude product (413.0 mg) was purified by radial chromatography on a 2 mm SiO_2 plate, using Et_2O–petroleum ether as eluent, to afford **11** (373.0 mg, 90%) as a cloudy oil which slowly solidified, mp 56–59 °C.

MS: *m/z* (relative intensity) = 248 (M^+, 100), 233 (33), 218 (10), 175 (28), 173 (27), 115 (17), 109 (27), 85 (17), 75 (50), 73 (59).

IR (NaCl): ν = 3400 (br, OH), 2950, 2885, 2138 (C≡C), 1610, 1500, 1478, 1248, 1197, 1171, 1058, 1037, 931, 862, 839, 757 cm^{-1}.

^1H NMR: δ = 6.87 (s, 2 H), 5.95 (s, 2 H), 4.70 (s, 2 H), 2.2 (br s, 1 H, 0.23 (s, 9 H).

Anal: Calc. for $C_{13}H_{16}O_3Si$: C, 62.87; H, 6.49. Found: C, 62.66; H, 6.54.

6-Trimethylsilylethynyl-1,3-benzodioxole-5-carbaldehyde *O*-Methyloxime (14):

A solution of **9** (762 mg, 3.09 mmol) and $MeONH_2 \cdot HCl$ (270 mg, 3.23 mmol) in pyridine (15 mL) and absolute EtOH (15 mL) was stirred and heated under reflux for 18 h. The mixture was allowed to cool before it was concentrated by rotary evaporation. The residue was diluted with H_2O (20 mL) and extracted with Et_2O (3 × 5 mL). Consolidated Et_2O extracts were washed with brine (10 mL) dried (Na_2SO_4), and concentrated, leaving colorless oily **14** (762 mg, 88%), which solidified overnight under 0.01 mmHg, mp 51–53 °C.

MS: *m/z* (relative intensity) = 275 (M^+, 0.9), 246 (6.4), 245 (40), 244 (93), 231 (15), 230 (100), 228 (12), 187 (9.0), 186 (5.7).

^1H NMR: δ = 8.45 (s, 1 H, CH=N), 7.30 (s, 1 H), 6.84 (s, 1 H), 5.96 (s, 2 H), 4.61 (s, 3 H, CH_3O), 0.23 (s, 9 H).

Anal: Calc. for $C_{14}H_{17}NO_3Si$: C, 61.06; H, 6.22; N, 5.09. Found: C, 60.80; H, 6.42; N, 5.24.

***N*-Methoxy-6-trimethylsilylethynyl-1,3-benzodioxole-5-methanamine (15):**

To oxime ether **14** (236.0 mg, 0.857 mmol) in MeOH (5 mL) was added a trace of Methyl Orange and $NaBH_3CN$ (143.9 mg, 2.29 mmol). During a period of 7 d, the mixture was treated with additional $NaBH_3CN$ (total 180 mg, 2.86 mmol) in portions and a slightly red color was maintained by adding HCl–EtOH. The mixture was concentrated to dryness in the presence of SiO_2 (1 g), and the solid residue was applied as a slurry in Et_2O–petroleum ether (1 : 9) to a column of SiO_2 (20 g) in the same solvent. Elution with Et_2O–petroleum ether (1 : 3, containing 0.5% Et_3N) afforded **15** (153.5 mg, 64%) as a slightly pink oil.

MS: *m/z* (relative intensity) = 277 (M^+, 2.9), 247 (20), 246 (38), 232 (52), 231 (100), 216 (31), 201 (13), 173 (10), 73 (7.3).

IR (NaCl): ν = 3270 (br, NH), 2961, 2941, 2900, 2812, 2152 (C≡C), 1617, 1504, 1485, 1369, 1252 (C–Si), 1188, 1163, 1043, 938, 863, 846, 763 cm^{-1}.

^1H NMR: δ = 6.87 (s, 1 H), 6.82 (s, 1 H), 5.93 (s, 2 H), 4.10 (s, 2 H), 3.54 (s, 3 H), 0.23 (s, 9 H).

^{13}C NMR: δ = 148.47, 146.94, 135.64, 115.95, 112.31, 110.42, 103.23, 101.80, 97.86, 61.78, 54.68, 0.41.

Anal: Calc. for $C_{14}H_{19}NO_3Si$: C, 60.61; H, 6.91; N, 5.05. Found: C, 59.72; H, 6.47; N, 4.93.

***N*-Ethyl-*N*-methoxy-6-trimethylsilylethynyl-1,3-benzodioxole-5-methanamine (16) and 15:**

Oxime ether **14** (121.4 mg, 0.441 mmol) in HOAc (1.0 mL) was treated with $NaBH_4$ (85.6 mg, 2.26 mmol) in two portions. The mixture became foamy immediately, but after about 2 min the suds disappeared. Desired product **15** was not detectable by TLC analysis of an aliquot. A 130 mg portion (2.07 mmol) of $NaBH_3CN$ was added. TLC analysis after 0.5 h indicated that some **14** was still present, hence additional $NaBH_3CN$ (40 mg, 0.64 mmol) was added. After 10 min the thick syrupy mixture was poured into 5% aq $NaHCO_3$ (20 mL) and extracted with Et_2O (3 × 10 mL). The combined Et_2O extracts were washed with brine, dried (Na_2SO_4), and concentrated. Radial chromatography of the residue (113.0 mg) on a 1 mm SiO_2 plate using EtOAc–petroleum ether (1 : 15) afforded three fractions. The first was **16** (54.7 mg, 41%) as a clear, colorless oil.

CIMS (CH_4): *m/z* (relative intensity) = 306 (M^+, 26), 209 (37), 277 (11), 276 (45), 275 (69), 274 (38), 231 (55), 88 [100, $Et(MeO)NCH_2^+$].

IR (NaCl): ν = 2962, 2943, 2898, 2154 (C≡C), 1504, 1485, 1378, 1253 (C–Si), 1237, 1180, 1166, 1044, 941, 868, 847, 763 cm^{-1}.

^1H NMR: δ = 6.92 (s, 1 H), 6.87 (s, 1 H), 5.93 (s, 2 H), 3.93 (s, 2 H, $ArCH_2N$), 3.44 (s, 3 H, CH_3O), 2.70 (q, J = 7.1 Hz, 2 H, NCH_2Me), 1.10 (t, J = 7.1 Hz, 3 H, NCH_2CH_3).

^{13}C NMR: δ = 147.89, 146.22, 134.80, 116.38, 111.59, 110.32, 103.54, 102.37, 96.67, 61.13, 59.67, 51.98, 12.37, 0.03.

Anal: Calc. for $C_{16}H_{23}NO_3Si$: C, 62.91; H, 7.59; N, 4.59. Found: C, 62.44; H, 7.42; N, 4.54.

The second product was **15** (31.3 mg, 26%).

The third fraction, eluted with EtOAc–petroleum ether (1 : 1), contained 8.2 mg of an unidentified white solid.

^1H NMR: δ = 7.15 (br s, 1 H), 6.93 (s, 1 H), 6.78 (s, 1 H), 6.02 (s, 2 H), 4.47 (dd, J = 3.3, 14.0 Hz, 1 H), 4.22 (dd, J = 9.2, 14.0 Hz, 1 H), 3.68 (s, 3 H), 0.27 (s, 9 H).

***N*-Methoxy-6-(2-trimethylsilylethyl)-1,3-benzodioxole-5-methanamine (17):**

Alkyne **15** (108 mg, 0.389 mmol) in MeOH (10 mL) was stirred over 10% Pd–C (9.6 mg) under H_2 (1 atm). After 1.5 h, TLC analysis indicated that the reaction was complete. The mixture was filtered through a pad of Celite and the filtrate concentrated. The cloudy residual oil was taken up in a small portion of Et_2O and filtered through a cotton plug in a pipet. The filtrate was concentrated to leave **17** (104.1 mg, 95%) as a pinkish oil.

MS: *m/z* (relative intensity) = 281 (M^+, 1.0), 235 (19), 234 (43), 161 (17), 73 (100).

IR (NaCl): ν = 3240 (br, NH), 2954, 2896, 2811, 1623, 1505, 1488, 1375, 1262, 1250, 1164, 1044, 941, 859, 839 cm^{-1}.

^{1}H NMR: δ = 6.76 (s, 1 H), 6.68 (s, 1 H), 5.87 (s, 2 H), 3.96 (s, 2 H), 3.52 (s, 3 H), 2.55–2.62 (m, 2 H), 0.74–0.81 (m, 2 H), 0.33 (s, 9 H).

^{13}C NMR: δ = 146.94, 145.26, 138.19, 126.59, 110.02, 108.82, 100.70, 61.68, 52.97, 26.54, 19.28, −1.80.

Anal: Calc. for $C_{14}H_{23}NO_3Si$: C, 59.75; H, 8.24; N, 4.98. Found: C, 59.91; H, 8.15; N, 4.95.

6-Trimethylsilylethynyl-1,3-benzodioxole-5-carbaldehyde Oxime (18):

A mixture of **9** (270.0 mg, 1.10 mmol), $NH_2OH \cdot 0.5\,H_2SO_4$ (182.0 mg, 1.11 mmol), pyridine (5 mL), and absolute EtOH (5 mL) was stirred under reflux. After 1 h, additional EtOH (5 mL) was added to dissolve the residual solids. After a total of 8 h, the cooled mixture was concentrated, diluted with H_2O (10 mL), and extracted with EtOAc (3 × 10 mL). The combined EtOAc extracts were washed with brine, dried (Na_2SO_4), and concentrated. Under vacuum (0.05 mmHg) overnight, the oily residue solidified to leave **18** (299.8 mg, 104%), mp 128–136.5 °C, contaminated with pyridine. The crude product was taken up in EtOAc, filtered through a plug of glass wool in a pipet, and the filtrate concentrated as before to give **18** (277.0 mg, 97%) as white fibrous crystals, mp 142.5–144 °C.

MS: *m/z* = (relative intensity) 261 (M^+, 22), 247 (19), 246 (100), 244 (16), 228 (24), 188 (22), 187 (19), 186 (19), 172 (19), 75 (80), 73 (29).

IR (KBr): ν = 3300 (br, OH), 3015, 2960, 2915, 2155 (C≡C), 1612 (C=N), 1498, 1480, 1431, 1366, 1255, 1170, 1067, 1047, 971, 946, 934, 887, 850 cm^{-1}.

^{1}H NMR: δ = 8.54 (s, 1 H, CH=N), 7.77 (br s, 1 H, OH), 7.25 (s, 1 H), 6.87 (s, 1 H), 5.98 (s, 2 H), 0.24 (s, 9 H).

^{13}C NMR and DEPT: δ = 148.86 (CH=N), 148.80 (C), 148.52 (C), 128.71 (C), 117.58 (C), 111.70 (CH), 104.52 (CH), 101.77 (CH_2), 101.56 (C), 99.19 (C), −0.12 (Me).

Anal: Calc. for $C_{13}H_{15}NO_3Si$: C, 59.74; H, 5.79; N, 5.36. Found: C, 59.65; H, 5.87; N, 5.29.

***N*-Hydroxy-6-trimethylsilylethynyl-1,3-benzodioxole-5-methanamine (19):**

To a stirred solution of **18** (102.8 mg, 0.394 mmol) in HOAc (1 mL) was added $NaBH_3CN$ (86 mg, 1.37 mmol) in one portion. After 15 min, the syrupy mixture was transferred to a separatory funnel with the aid of Et_2O (10 mL) in several portions. The resulting cloudy solution was washed with 10% aq K_2CO_3 (2 × 10 mL) and the combined washes were back-extracted with Et_2O (2 × 10 mL). Consolidated Et_2O phases were washed with H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), and concentrated. After 0.5 h under a 0.5 mmHg vacuum, **19** (101.2 mg, 98%), homogeneous by TLC and ^{1}H NMR spectral analysis, remained as a pale pink foam.

MS: *m/z* (relative intensity) = 263 (M^+, 14), 262 (20), 246 (28), 232 (21), 231 (M^+ − NHOH, 100), 216 (22), 191 (29), 178 (75), 174 (35), 173 (20), 161 (40), 159 (24), 147 (28), 75 (84), 73 (34).

^{1}H NMR: δ = 6.87 (s, 1 H), 6.80 (s, 1 H), 6.55 (br s, 2 H), 5.92 (s, 2 H), 4.06 (s, 2 H), 0.22 (s, 9 H).

^{13}C NMR: δ = 148.04, 146.70, 134.44, 115.76, 111.85, 110.41, 102.71, 101.41, 97.65, 56.56, −0.08.

6-Ethynyl-1,3-benzodioxole-5-methanamine (7):

A solution of freshly prepared **19** (derived from 1.22 mmol of oxime **18**) in deoxygenated THF (5 mL) was added rapidly to a freshly prepared, stirred, and deoxygenated mixture of 1.3 M aq $TiCl_3$ (2.7 mL, 3.5 mmol, 2.4 equiv) and 3.9 M aq NH_4OAc (4.2 mL, 16 mmol). After 3 min, the thick green mixture was poured slowly into rapidly stirred 15% aq KOH (80 mL) under positive nitrogen pressure. Progress of the protodesilylation of **13** to **7** could be monitored by TLC (SiO_2, CH_2Cl_2–MeOH–conc NH_4OH, 90:8:2). After the desilylation was complete (45–120 min), the mixture was filtered through a pad of Celite and the gray and blue filter cake was rinsed with several portions of Et_2O (150 mL total). The combined ethereal filtrates were used in several portions to extract the aq filtrate. The combined pink organic phases were dried (Na_2SO_4), and concentrated, leaving a red oily residue (188.9 mg), which was purified by flash chromatography over SiO_2 (3.5 × 15 cm), employing CH_2Cl_2–MeOH–conc NH_4OH (95:4:1) as eluent. After rotary evaporation of the product-containing eluates and storage of the residue under an oil-pump vacuum, **7** (81.9 mg, 38% from **18**) remained as pink crystals, mp 52–58 °C.

IR (KBr): δ = 3400 (br, NH), 3375 (CC–H), 3290, 3145, 2960, 2910, 2095 (C≡C), 1500, 1487, 1254, 1228, 1038, 943, 920, 868, 852, 838 cm^{-1}.

^{1}H NMR: δ = 6.86 (s, 1 H), 6.77 (s, 1 H), 5.91 (s, 2 H), 3.83 (s, 2 H), 3.19 (s, 1 H).

^{13}C NMR and DEPT: δ = 148.42 (C), 145.94 (C), 141.41 (C), 113.26 (C), 112.23 (CH), 108.05 (CH), 101.30 (CH_2), 81.60 (C) and 80.01 (CH) (*C*≡*C*H), 45.04 (CH_2N).

Anal: Calc. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 67.53; H, 5.15; N, 8.15.

6-Ethynyl-1,3-benzodioxole-5-carbaldehyde (20):

To aldehyde **9** (248.4 mg, 1.01 mmol) in MeOH (20 mL) was added 10% aq KOH (0.2 mL). After 35 min, the cloudy mixture was diluted with H_2O (30 mL) and extracted with EtOAc (4 × 10 mL). The combined EtOAc phases were washed with 5% aq KH_2PO_4 (10 mL), dried, and concentrated, leaving **20** (167.7 mg, 95%) as a tan solid, mp 143–145 °C. An analytical sample, recrystallized from EtOH, exhibited mp 146–149 °C.

Ir (KBr): ν = 3285 (CC–H), 3100, 3058, 2920, 2858, 2108 (C≡C), 1680 (C=O), 1610, 1602, 1497, 1490, 1431, 1409, 1360, 1279, 1057, 1036, 932, 897, 864, 668 cm^{-1}.

^{1}H NMR: δ = 10.35 (s, 1 H, CHO), 7.32 (s, 1 H), 6.97 (s, 1 H), 6.06 (s, 2 H), 3.35 (s, 1 H).

Anal: Calc. for $C_{10}H_6O_3$: C, 68.97, H, 3.47. Found: C, 68.78; H, 3.36.

6-Ethynyl-1,3-benzodioxole-5-carbaldehyde Oxime (21):

A portion (0.1 mL) of 5% aq KOH was added to a stirred solution of **18** (523.4 mg, 2.00 mmol) in THF–MeOH (5 mL, 4:1). After 3.8 h, TLC analysis (SiO_2, Et_2O–petroleum ether, 1:1) of the deep purple solution indicated that the protodesilylation was complete. The mixture was poured into H_2O (30 mL) and extracted with Et_2O (4 × 15 mL). The combined extracts were washed with saturated aq NH_4Cl (25 mL), H_2O (25 mL), dried, and concentrated. Oxime **21** (302.6 mg, 80%) remained as pink crystals, mp 139–140 °C decomp. (preheated from 130 °C, temperature increase ≈ 10 °C min^{-1}). An analytical sample from Et_2O exhibited the same mp.

MS: *m/z* (relative intensity) = 189 (M^+, 100), 188 (17), 172 (M^+ − OH, 76), 142 (21), 114 (47), 89 (22), 87 (44), 86 (26), 77 (25), 74 (22), 62 (22).

IR (KBr): 3500 (br, OH), 3300 (CC–H), 3060, 2995, 2915, 2100 (C≡C), 1611, 1496, 1487, 1358, 1264, 1160, 1045, 955, 941, 931, 879 cm^{-1}.

^{1}H NMR (acetone-d_6): δ = 10.44 (s, 1 H), 8.49 (s, 1 H), 7.25 (s, 1 H), 6.92 (s, 1 H), 6.07 (s, 2 H), 2.89 (s, 1 H, CC–H).

^{13}C NMR and DEPT (acetone-d_6): δ = 149.74 (C), 149.54 (C), 147.20 (CH=N), 130.85 (C), 116.35 (C), 112.20 (CH), 104.58 (CH), 103.02 (OCH_2O), 83.41 (C≡*C*H), 81.08 (*C*≡C).

Anal: Calc. for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.41. Found: C, 63.45; H, 3.62; N, 7.37.

1,3-Dioxolo[4,5-*g*]isoquinoline-6-oxide (22):

A solution of oxime **21** (53.3 mg, 0.282 mmol) in 2-propanol (8 mL) was stirred and heated under reflux. After 8 h, TLC analysis showed that **21** had been cleanly converted into **22**. The dark mixture was concentrated to dryness and the residue in CH_2Cl_2 was passed through SiO_2 (3 cm) in a pipet, eluting with MeOH–CH_2Cl_2 (gradient 1:19 to 1:4) until all of the product had been recovered. Concentration of the combined eluates and storage of the beige flaky residue over P_4O_{10} left **22** · 0.5 H_2O (52.6 mg, 90%), mp 221–224 °C.

MS: *m/z*: (relative intensity) = 189 (M^+, 100), 173 (M^+ − O, 15), 172 (15), 162 (19), 161 (25).

IR (KBr): ν = 3105, 3040, 2920, 1633, 1622, 1493, 1470, 1459, 1427, 1340, 1328, 1245 (N–O), 1179, 1143, 1093, 1027, 932, 890, 871, 812, 734 cm^{-1}.

^1H NMR: δ = 8.53 (d, J = 1.4 Hz, 1 H), 8.00 (dd, J = 1.7, 7.0 Hz, 1 H), 7.43 (d, J = 7.0 Hz, 1 H), 7.02 (s, 1 H), 6.94 (s, 1 H), 6.09 (s, 2 H).

Anal: Calc. for $C_{10}H_7NO_3 \cdot 0.5H_2O$: C, 60.61; H, 4.07; N, 7.07. Found: C, 60.88; H, 3.94; N, 7.02.

The original discovery of the cyclization reaction proceeded as follows: A mixture of **20** (538 mg, 3.09 mmol), $NH_2OH \cdot 0.5\,H_2SO_4$ (511 mg, 3.12 mmol), pyridine (25 mL), and absolute EtOH (25 mL) was heated under reflux for 0.5 d. The cooled, black mixture was concentrated and the residue partitioned between H_2O (25 mL) and EtOAc (25 mL). The golden aq phase was extracted with EtOAc (2 × 25 mL). Further workup of the EtOAc phases gave small amounts of the impure oxime derived from **8**. The aq phase was concentrated to dryness, and the pale yellow flaky solid residue (1.47 g) was recrystallized from hot H_2O (5 mL) and the crystals so obtained were dried in vacuo over P_4O_{10} overnight to give **22** · $0.5\,H_2SO_4$ (193.0 mg, 26%), mp 278 °C (dec).

IR (KBr): ν = 3450 (br), 3055, 3030, 2915, 2850, 2450 (br, $^+$NO–H), 1615, 1490, 1460, 1420, 1322, 1258, 1118, 1028, 938, 860 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 9.08 (s, 1 H, H-5), 8.26 (dd, J = 1.8, 7.1 Hz, 1 H), 7.93 (d, J = 7.1 Hz, 1 H), 7.50 (s, 1 H), 7.45 (s, 1 H), 6.27 (s, 2 H), 3.85 (br s).

Anal. Calc. for $C_{10}H_8NO_5S_{0.5}$: C, 50.42; H, 3.38; N, 5.88; S, 6.73. Found: C, 50.60; H, 3.16; N, 5.79; S, 6.55.

Ethyl 1-[*N*-(6-Ethynyl-1,3-benzodioxole-5-ylmethyl)iminomethyl]-cyclopropane-1-carboxylate (6b):

Amine **7** (52.0 mg, 0.296 mmol) in $CDCl_3$ (0.5 mL) was added to a stirred mixture of ethyl 1-formylcyclopropanecarboxylate **24b**[33] (42.2 mg, 0.297 mmol) and Na_2SO_4 (14.5 mg, 0.102 mmol) in CH_2Cl_2 (2 mL). After 40 h, ^1H NMR spectroscopic analysis of an aliquot indicated that reaction was complete. The red mixture was filtered through a cotton plug in a pipet, the filtrate concentrated, and the residue stored under a vacuum (0.1 mmHg) for 4 h, leaving **6b** (84.8 mg, 96%) as a deep red viscous oil.

^1H NMR: δ = 8.56 (s, 1 H, CH=N), 6.87 (s, 1 H), 6.71 (s, 1 H), 5.92 (s, 2 H), 4.63 (s, 2 H, CH_2N), 4.17 (q, J = 7.1 Hz, 2 H, OCH_2), 3.18 (s, 1 H, C≡CH), 1.51 (m, 4 H, cyclopropane CH_2), 1.25 (t, J = 7.1 Hz, 3 H, OCH_2CH_3).

^{13}C NMR and DEPT: δ = 172.76 (CO_2Et), 163.99 (CH=N), 148.42 (C), 145.96 (C), 137.21 (C), 113.48 (C), 111.93 (CH), 108.37 (CH), 101.31 (OCH_2O), 81.69 (C≡CH), 80.35 (C≡CH), 61.58 (CH_2), 60.87 (CH_2), 27.23 (C of cyclopropane), 20.65 (CH_2 of cyclopropane), 14.18 (CH_3CH_2O).

Ethyl 1-[*N*-(Phenylmethyl)iminomethyl]cyclopropane-1-carboxylate (28):

Phenylmethanamine (927.8 mg, 8.65 mmol), **24b**[33] (1.240 g, 8.75 mmol), and Na_2SO_4 (206.7 mg, 1.45 mmol) were stirred in Et_2O (10 mL) for 23 h. Capillary GC showed that some starting materials were still present, hence another portion of Na_2SO_4 (130 mg, 0.915 mmol) was added and the mixture stirred for another 12 h. After filtration and removal of solvent, the residue was subjected to Kugelrohr distillation to give **28** (1.909 g, 95%) as a colorless oil, bp 170 °C (10 mmHg).

MS: m/z (relative intensity) = 231 (M^+, 24), 230 (11), 203 (18), 202 (77), 186 (64), 184 (26), 158 (59), 156 (43), 104 (26), 92 (29), 91 (100).

IR (NaCl): ν = 3075, 3055, 3020, 2975, 2890, 2825, 1725 (EtOC=O), 1657 (C=N), 1452, 1366, 1308, 1168, 1145, 1027, 745, 697 cm^{-1}.

^1H NMR (C_6D_6): δ = 8.59 (t, J = 1.2 Hz, 1 H, CH=N), 7.0–7.25 (m, 5 H), 4.36 (d, J = 1.2 Hz, 2 H, CH_2N=CH), 4.01 (q, J = 7.1 Hz, 2 H, OCH_2), 1.43–1.56 (m, 4 H, cyclopropyl H), 0.88 (t, J = 7.1 Hz, 3 H, OCH_2CH_3).

Anal: Calc. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.53; H, 7.42; N, 5.94.

Ethyl 1-(Phenylmethyl)azacyclopent-2-ene-3-carboxylate (29):

A stirred mixture of **28** (448.3 mg, 1.938 mmol) and NH_4Cl (41.3 mg, 0.772 mmol, 0.40 equiv) in dry 1,3-dimethylbenzene (8 mL) was heated under reflux for 45 h. Examination of an aliquot by ^1H NMR spectroscopy revealed a ≈ 5% conversion of **28** into **29**. Solvent was removed from the cooled mixture by vacuum transfer, dry 1,3,5-trimethylbenzene (8 mL) was added to the residue, and the resulting mixture was stirred under reflux for 14 h. Solvent was removed as above, the residue taken up in Et_2O, filtered, the filter cake rinsed with Et_2O, and the combined filtrates concentrated. The residue was subjected to Kugelrohr distillation to afford **29** as a pale yellow oil, bp 150 °C (0.02 mmHg).

MS: m/z (relative intensity) = 231 (M^+, 74), 229 (17), 186 (32), 184 (13), 160 (13), 91 (100).

IR (NaCl): ν = 3060, 3025, 2975, 2930, 2860, 1673 (C=O), 1594 (C=C), 1455, 1441, 1372, 1341, 1260, 1201, 1160 (br), 1078, 1028, 752, 700 cm^{-1}.

^1H NMR: δ = 7.2–7.4 (m, 5 H), 7.13 (t, J = 1.0 Hz, 1 H, NCH=C), 4.18 (s, 2 H, $ArCH_2N$), 4.11 (q, J = 7.1 Hz, 2 H, OCH_2), 3.33 (t, J = 10 Hz, 2 H, NCH_2CH_2), 2.75 (dt, J = 1.0, 10 Hz, 2 H, CH_2CH_2), 1.23 (t, J = 7.1 Hz, 3 H, OCH_2CH_3).

Anal: Calc. for $C_{14}H_{17}NO_2$: C, 72.20; H, 7.41; N, 6.06. Found: C, 72.89; H, 7.19; N, 9.98.

(Ethyl 1-[*N*-(6-[(1,2,3,4-η^4)-2,3-Bis(trimethylsilyl)-1,3-cyclobutadien-1-yl]-1,3-benzodioxol-5-ylmethyl)iminomethyl]cyclopropane-1-carboxylate)(η^5-2,4-cyclopentadien-1-yl)cobalt (25) and (6-[(1,2,3,4-η^4)-2,3-Bis(trimethylsilyl)-1,3-cyclobutadien-1-yl]-1,3-benzodioxole-5-methanamine)(η^5-2,4-cyclopentadien-1-yl)cobalt (26):

Alkyne **4** (2 mL) was added to crude **6b** (84.8 mg, 0.284 mmol) in 1,2-dimethoxyethane (2 mL). The small amount of flocculent precipitate that formed was removed by filtration through a small cotton plug in a pipet, rinsing the filter cake with **4**–1,2-dimethoxyethane (2 mL, 1:1). The combined plum-colored filtrates were deoxygenated by three cycles of freeze-pump-thaw, $CpCo(CO)_2$ (120 µL, 0.93 mmol, 3.3 equiv) was added, the resulting mixture was transferred to a 10 mL gastight syringe, and added to deoxygenated, boiling **4** (10 mL) in a flask irradiated by a Sylvania ELH lamp, powered at 40 V, over the course of 12 h. After an additional 12 h the black mixture was allowed to cool, all volatile materials were removed by vacuum transfer, the black residue was taken up in CH_2Cl_2, filtered under N_2 through a pad of Filter Aid, and the filter cake was rinsed with CH_2Cl_2 (≈ 20 mL) until the filtrate was colorless. The combined black filtrates were concentrated, leaving a black oily residue (0.281 g), containing **4** and **25**.

^1H NMR: δ = 8.47 (s, CH=N), 6.87 and 6.57 (two s, total 2 H, aryl H), 5.92 (s, OCH_2O), 4.87 (br s, $ArCH_2N$), 4.70 (s, Cp), 4.46 (s, cyclobutadiene H), 4.0–4.3 (br m, OCH_2), 1.2–1.4 (br m, CH_2CH_2 and OCH_2CH_3), 0.12 and 0.16 (two s, $SiMe_3$).

To crude **25** in THF (10 mL) was added oxalic acid monohydrate (370 mg), in THF–H_2O (6 mL, 5:1). After 8 h, the black mixture was concentrated and the residue was triturated with Et_2O (5 mL). The mixture was filtered and the black and yellow filter cake was washed with Et_2O. The dried precipitate (202 mg) and dilute aq NaOH were extracted with Et_2O (1 × 20 mL, 2 × 10 mL) and EtOAc (3 × 10 mL). The combined organic phases were washed with dilute aq NaOH, H_2O, brine, dried, and concentrated, leaving essentially pure (TLC) **26** (37.8 mg), further purified by radial chromatography (30.7 mg, 22% overall from amine **7**) to give a deep yellow viscous oil.

MS: m/z (relative intensity) = 469 (M^+, 100), 397 (21), 396 (23, $M^+ - SiMe_3$), 395 (26), 371 (7.4, $M^+ - TMSA$), 369 (8.9), 357 (51), 330 (20), 299 (39, $M^+ - BTMSA$), 298 (42), 294 [39, $CoCp(BTMSA)^+$], 275 (39), 256 (30), 124 (20), 73 (38).

IR (NaCl): ν = 3300 (br, NH), 2958, 2895, 1504, 1489, 1454, 1403, 1385, 1245 (C–Si), 1042, 937, 839, 811 cm^{-1}.

^1H NMR: δ = 6.88 (s, 1 H), 6.67 (s, 1 H), 5.90 (s, 2 H), 4.87 (s, 5 H, Cp), 3.8–4.0 (m, 2 H, $ArCH_2NH_2$), 0.12 (s, 9 H), 0.11 (s, 9 H).

Anal: Calc. for $C_{23}H_{32}CoNO_2Si_2$: C, 58.82; H, 6.87; N, 2.98. Found: C, 58.64; H, 6.71; N, 2.86.

N-{[1-(Thiophenyl)cycloprop-1-yl]methylidene}-6-ethynyl-1,3-benzodioxole-5-methanamine (6a), 1-(6-Ethynyl-1,3-benzodioxol-5-ylmethyl)-3-(thiophenyl)azacyclopent-2-ene (5a), and {1-{6-[(1,2,3,4-η^4)-2,3-Bis(trimethylsilyl)-1,3-cyclobutadien-1-yl]-1,3-benzodioxole-5-ylmethyl}-3-(thiophenyl)azacyclopent-2-ene}-(η^5-2,4-cyclopentadien-1-yl)cobalt (27):

A mixture of **7** (81.9 mg, 0.467 mmol), 1-(thiophenyl)cyclopropanecarbaldehyde[32] (79.7 mg, 0.447 mmol) and Na_2SO_4 (14.8 mg, 0.014 mmol) in 1,3-dimethylbenzene (3 mL) was stirred for 1.5 d, after which ^{1}H NMR spectral analysis of an aliquot revealed that the formation of **6a** was complete.

^{1}H NMR (C_6D_6): δ = 7.85 (s, 1 H, CH=N), 7.36 (dd, 0.9, 7.7 Hz, 2 H), 7.04 (t, J = 7.5 Hz, 2 H), 6.91 (t, J = 7.5 Hz, 1 H), 6.90 (s, 1 H), 6.79 (s, 1 H), 5.14 (s, 2 H, OCH_2O), 4.56 (d, J = 0.8 Hz, 2 H, $ArCH_2N$), 2.76 (s, 1 H, C≡CH), 1.47–1.51 (AA' m of AA'BB', 2 H, cyclopropane H), 1.03–1.07 (BB' m of AA'BB', 2 H, cyclopropane H). The mixture was filtered through a frit into a 25 mL round-bottom flask and the filter cake was rinsed with a little 1,3-dimethylbenzene. NH_4Cl (14.9 mg, 0.278 mmol) was added to the combined filtrates, the fritted funnel was replaced by a condenser, and the stirred mixture was heated under reflux for 3.5 h. Inspection of an aliquot showed that the conversion of **6a** to **5a** was complete.

^{1}H NMR (C_6D_6): δ = 7.39 (d, J = 7.5 Hz, 2 H), 6.8–7.1 (m, partially obscured by residual 1,3-dimethylbenzene), 6.74 (s, 1 H), 6.26 (s, 1 H), 5.16 (s, 2 H, OCH_2O), 3.86 (s, 2 H, $ArCH_2N$), 2.86 (t, J = 9 Hz, 2 H, NCH_2CH_2), 2.78 (s, 1 H, C≡CH), 2.42 (t, J = 9 Hz, 2 H, NCH_2CH_2).

The cooled dark red-brown supernatant was withdrawn into a 10 mL syringe. Meanwhile, a deoxygenated solution of $CpCo(CO)_2$ (170 mg, 0.95 mmol) and **4** (3 mL) was placed in another syringe and a sample of **4** (7 mL) was deoxygenated under reflux. The boiling **4** was irradiated (ELH lamp, 30 V) as the solutions of **5a** and $CpCo(CO)_2$ were added over the course of 5.5 h. After the addition was complete, the black mixture was allowed to cool before it was concentrated by vacuum transfer. The residual brown–black oil (160 mg) was radially chromatographed on a 2 mm SiO_2 plate, employing Et_2O–petroleum ether (1:6), EtOAc–petroleum ether (1:1), and EtOAc as eluents. Complex **27** (33.3 mg, 11 % from **7** and 4.3 % from **18**) was obtained as a bright yellow viscous oil.

MS: m/z (relative intensity) = 629.1636 (M^+, 0.3, calc. for $C_{33}H_{40}CoNO_2SSi_2$, 629.1650), 453.1127 (1.7, calc. for $M^+ - PhSC_4H_5N$, 453.1137).

^{1}H NMR (200 MHz): δ = 7.1–7.35 (m, 5 H, SC_6H_5), 6.96 (s, 1 H), 6.77 (s, 1 H), 6.36 (t, J = 1.3 Hz, 1 H, NCH=C), 5.96 (s, 2 H, OCH_2O), 4.91 (s, 5 H, Cp), 4.48 (s, 1 H, cyclobutadiene H), 4.04 (d, J = 13.5 Hz, 1 H, NC*H*HAr), 3.91 (d, J = 13.5 Hz, 1 H, NCH*H*Ar), 3.1–3.35 (m, 2 H, NCH_2CH_2), 2.57 (dt, J = 1.3, 9 Hz, 2 H, NCH_2CH_2), 0.41 and 0.40 (two s, total 18 H).

1-(2-Iodobenzoyl)azacyclopent-2-ene (32) Directly from 31:

To a stirred solution of 2-iodobenzoyl chloride **31**[41] (299.7 mg, 1.12 mmol) and i-Pr_2NEt (150.6 mg, 1.16 mmol) in CCl_4 (3 mL) was added azacyclopent-1-ene trimer (88 mg, 0.42 mmol, 1.13 equiv). The mixture immediately warmed slightly and became cloudy. Within minutes an orange-red oil separated. After 16 h, EtOAc (30 mL) and H_2O (30 mL) were added and the mixture was stirred vigorously. Tan solids remained undissolved after several min. The aq phase was extracted with EtOAc (10 mL), the combined organic phases were washed with dilute aq HOAc, dilute aq K_2CO_3, brine, dried, and concentrated. Flash chromatography of the pale orange oily crude product (296 mg), using EtOAc–CH_2Cl_2 (1:9) as eluent, afforded **32** (146.9 mg, 44 %) as a pale yellow oil.

MS: m/z (relative intensity) = 299 (M^+, 27), 232 (6.4), 231 (100, C_7H_4IO), 203 (20, C_6H_4I), 147 (14), 107 (8.5), 105 (9.2), 77 (12), 76 (27), 75 (24).

IR (NaCl): ν = 3095, 3055, 2955, 2920, 2890, 2860, 1639 (C=O), 1606 (C=C), 1585, 1465, 1420, 1378, 1215, 1040, 1015, 994, 828, 766, 737 cm^{-1}.

^{1}H NMR of major rotamer: δ = 7.81 (d, J = 8 Hz, 1 H), 7.38 (t, J = 7.5 Hz, 1 H), 7.25 (dd, J = 1.6, 7.5 Hz, 1 H), 7.07 (dd, J = 1.3, 7.6 Hz, 1 H), 5.94 (td, J = 2.2, 4.5 Hz, 1 H, NC*H*=CH), 5.20 (td, J = 2.3, 4.5 Hz, 1 H, NCH=C*H*), 4.02 (t, J = 8.7 Hz, 2 H, NCH_2), 2.64–2.76 (m, 2 H). Partial ^{1}H NMR of minor rotamer: 5.39 (td, J = 2.3, 4.5 Hz, 1 H, NC*H*=CH), 3.52 (t, J = 8.7 Hz, 2 H, NCH_2).

Anal: Calc. for $C_{11}H_{10}INO$: C, 44.17; H, 3.37; N, 4.68. Found: C, 43.95; H, 3.45; N, 4.70.

***N*-(4,4-Diethoxybutyl)-2-iodobenzamide (33)**

Over the course of 5 min, **31** (1.338 g, 5.01 mmol) in Et_2O (8 mL) was added to a stirred, ice-cold solution of 4,4-diethoxybutanamine (Aldrich, 0.84 g, 5.21 mmol) and i-Pr_2NEt (0.650 g, 5.03 mmol) in Et_2O (20 mL). A white precipitate began to form during the addition. Once addition was complete, the cooling bath was removed. After 0.5 h the thick pasty mixture was washed with H_2O (20 mL, all solids dissolved) and the aq phase extracted with Et_2O (2 × 10 mL). The consolidated organic phases were washed with dilute aq HCl, 10 % aq K_2CO_3, and brine. After drying ($MgSO_4$), filtration, and concentration of the filtrate, **33** (1.670 g, 85 %) remained as a colorless, viscous oil.

MS: m/z (relative intensity) = 316 (0.7), 301 (28, $M^+ - 2EtO$), 300 (12), 232 (7.4), 232 (100, C_7H_4IO), 203 (30, C_6H_4I), 174 (26), 105 (53), 104 (11), 77 (44), 76 (73), 75 (14).

IR (NaCl): ν = 3450 (br, NH), 3040, 2965, 2920, 1642 (C=O), 1582, 1463, 1407, 1096, 1070, 1013, 767, 748 cm^{-1}.

^{1}H NMR: δ = 7.75–7.80 (m, 1 H), 7.18–7.4 (m, 2 H), 7.04 (two t, J = 7.4 Hz), 1 H), 5.72 [narrow m, 0.4 H, C*H*$(OEt)_2$ of minor rotamer], 4.58 [narrow m, 0.6 H, C*H*$(OEt)_2$ of major rotamer], 3.9 (br s, 0.4 H, NH of minor rotamer), 3.4–3.8 (m, 4 H, OCH_2), 3.28 (br s, 0.6 H, NH of major rotamer), 2.97–3.05 (m, 1.2 H, NCH_2 of major rotamer), 2.75–2.81 (m, 0.8 H, NCH_2 of minor rotamer), 1.75–2.2 (m, 4 H, CH_2CH_2), 1.16–1.22 (m, 3.6 H, OCH_2CH_3 of major rotamer), 0.88–0.95 (m, 2.4 H, OCH_2CH_3 of minor rotamer).

1-(2-Iodobenzoyl)azacyclopentan-2-ol (34) and *N*-4-(Oxobutyl)-2-iodobenzamide (35)

Aqueous HCl (4 %, 5 mL) was added to **33** (1.175 mg, 3.00 mmol) in THF (5 mL). After 5 min, the mixture was extracted with Et_2O (3 × 20 mL), the extracts were washed with 10 % aq K_2CO_3 (10 mL), brine, dried, and concentrated. The oily residue was flash chromatographed, using EtOAc–CH_2Cl_2 (gradient 1:4 to 1:2), to give a mixture (30:10:1 by ^{1}H NMR) of **34a**, **34b**, and **35** (708 mg, 74 %) as a viscous pale yellow oil.

MS: m/z (relative intensity) = 317 (M^+, 6.8), 260 (5.4), 231 (94, C_7H_4IO), 203 (36, C_6H_4I), 106 (10), 105 (100), 104 (15), 77 (49), 76 (91).

IR (NaCl): ν = 3370 (br, OH), 3042, 2965, 2875, 1728 (relatively weak, CH=O of **35**), 1610–1630 (br, NC=O), 1582, 1465, 1420 (br), 1240, 1180, 1152, 1104, 1040, 1032, 954, 811, 767, 750 cm^{-1}.

^{1}H NMR: δ = 9.70 (br s, 0.03 H, CHO of **35**), 7.74 (d, J = 8.0 Hz, 1 H), 7.32 (t, J = 7 Hz, 1 H), 7.01 (d of app t, J = 1.4, 7.5 Hz, 1 H), 5.75 (narrow m, 0.75 H, H-2 of **34a**), 4.90 (narrow m, 0.25 H, H-2 of **34b**), 4.44 (br s, 0.75 H, disappears after addition of D_2O, OH of **34a**), 3.6–3.8 (m, 0.75 H), 3.4–3.6 (m, 0.25 H), 2.9–3.4 (m, 1 H), 2.50 (br s, 0.25 H, disappears after addition of D_2O, OH of **34b**), 1.6–2.2 (m, 4 H).

Anal: Calc. for $C_{11}H_{12}INO_2$: C, 41.66; H, 3.82; N, 4.42. Found: C, 41.83; H, 4.00; N, 4.41.

Three-Step Conversion of 31 to 32 without Substantial Purification of Intermediates 33 and 34:

A solution of 4,4-diethoxybutanamine (0.925 g, 5.74 mmol, 1.11 equiv) and i-Pr_2NEt (0.675 g, 5.22 mmol, 1.01 equiv) in THF (20 mL) was stirred and the flask chilled in ice as a solution of **31** (1.380 g, 5.18 mmol) in THF (10 mL) was added dropwise over 10

min. Once addition was complete, the cooling bath was removed. Conc aq HCl (3 mL) in H_2O (30 mL) was added to the cloudy mixture after 15 min. One-half hour later, the mixture was diluted with H_2O (100 mL), extracted with Et_2O (4 × 50 mL), the combined organic phases were washed with 2% aq K_2CO_3 (50 mL), brine, dried, and concentrated, leaving 1.67 g of a viscous oil, mostly **34**, but containing traces of **35**, by TLC analysis. The oil was dissolved in methylbenzene (100 mL) and heated under reflux for 23 h. The cooled solution was concentrated, affording chromatographically homogeneous SiO_2, EtOAc–CH_2Cl_2, 1:4, $R_f = 0.65$) **32** as an amber viscous oil (1.348 g, 87%).

1-[2-(Trimethylsilylethynyl)benzoyl]azacyclopent-2-ene (36):

Et_3N (50 mL) was distilled from CaH_2 into a flask containing **32** (0.512 g, 1.71 mmol). The resulting solution was deoxygenated under reflux for 0.5 h, cooled, and treated with TMSA (0.5 mL, 3.6 mmol, 2.1 equiv), $PdCl_2(PPh_3)_2$ (7.1 mg, 0.010 mmol, 0.005 equiv), and CuI (2.2 mg, 0.012 mmol, 0.006 equiv). After 1.75 h, TLC analysis indicated that little **36** had formed. Thus, more $PdCl_2(PPh_3)_2$ (11.1 mg, 0.009 equiv) and TMSA (0.25 mL, 1.0 equiv) were added. After 2.5 h, conversion of **32** into **36** was complete. The residue left from vacuum transfer was taken up in H_2O (15 mL), extracted with Et_2O (3 × 10 mL), the extracts were washed with dil aq KH_2PO_4, brine, dried, and concentrated. The residual dark brown oil (0.470 g) was flash chromatographed over SiO_2 (2.5 × 20 cm), employing EtOAc–CH_2Cl_2 (1:19) as eluant to give **36** in analytically pure (208.8 mg) and slightly impure (150.9 mg) fractions (total, 78%), both pale yellow oils.

MS: *m/z* (relative intensity) = 269 (M^+, 13), 268 (5.0), 254 (3.3), 203 (5.1), 202 (17), 201 (100, $M^+ - C_4H_6N$), 145 (11), 143 (13), 93 (11).

IR (NaCl): ν = 3062, 2958, 2897, 2862, 2162 (C≡C), 1642 (C=O), 1616 (C=C), 1562, 1483, 1450, 1417, 1371, 1251 (C–Si), 1219, 1001, 868, 847, 761 cm^{-1}.

^1H NMR: δ = 7.39–7.43 (m, 1 H), 7.21–7.39 (m, 3 H), 7.05 (td, J = 2, 4 Hz, 0.2 H, NC*H*=CH of minor rotamer), 6.03 (td, J = 2.1, 4.2 Hz, 0.8 H, NC*H*=CH of major rotamer), 5.31 (td, J = 2, 4 Hz, 0.2 H, NCH=C*H* of minor rotamer), 5.11 (td, J = 2.5, 4.2 Hz, 0.8 H, NCH=C*H* of major rotamer), 3.96 (t, J = 8.8 Hz, 1.6 H, CH_2N of major rotamer), 3.63 (t, J = 8.6 Hz, 0.4 H, CH_2N of minor rotamer), 2.65 (dt, J = 2.1, 8.8 Hz, and other unassignable peaks, total 2 H, NCH_2CH_2 for both rotamers), 0.13 (s, 9 H).

^{13}C NMR of major rotamer: δ = 165.30 (C=O), 139.20, 132.03, 130.36, 129.08, 128.72, 127.23, 120.22, 111.34, 101.73, 98.50, 44.79, 28.39, −0.41.

Anal: Calc. for $C_{16}H_{19}NOSi$: C, 71.33; H, 7.11; N, 5.20. Found: C, 71.05; H, 7.12; N, 5.06.

1-[(2-Ethynyl)benzoyl]azacyclopent-2-ene (37) from 32:

A 500 mL round-bottom flask containing a stir bar was charged with **32** (3.29 g, 11.0 mmol) and Et_3N (200 mL) distilled from CaH_2. The flask was capped with a rubber septum, and TMSA (2.74 g, 27.9 mmol, 2.54 equiv), $PdCl_2(PPh_3)_2$ (76.7 mg, 0.109 mmol, 0.01 equiv) and CuI (20.7 mg, 0.109 mmol, 0.01 equiv) were added. The pale yellow mixture turned cloudy and its color changed to brown over the next 2 h. TLC indicated that the conversion of **32** into **36** was complete. The mixture was concentrated to dryness by rotary evaporation and the residue partitioned between H_2O (200 mL) and Et_2O (3 × 100 mL). The combined pale brown extracts were washed with 10% aq NaH_2PO_4 (150 mL), brine (100 mL), dried, and concentrated. To the residual dark brown oil (3.43 g) in MeOH was added 5% aq KOH (1 mL). After 35 min, the dark brown mixture was diluted with H_2O, extracted with EtOAc (3 × 100 mL), the organic phases washed with H_2O (200 mL), dried, and concentrated to dryness. Under a gentle stream of N_2 the gummy brown residue was triturated with hot hexanes (250 mL, in three portions) to leave behind brown polar material. The combined golden supernatants contained 2.33 g of a brown oil which was flash chromatographed on SiO_2 (100 g) using EtOAc–CH_2Cl_2 (gradient 1:10 to 1:8) as eluants. After storage under 0.5 mmHg for 2 d, the amber oily product solidified to give **37** (1.46 g, 67%) as a beige solid, mp 50–53 °C.

MS: *m/z* (relative intensity) = 197 (M^+, 24), 169 (20), 130 (18), 129 (100, $M^+ - C_4H_6N$), 101 (75).

IR (NaCl) ν = 3265 (CC–H), 3210, 3045, 2940, 2900, 2875, 2842, 2090 (C≡C), 1627 (C=O), 1608 (C=C), 1559, 1480, 1443, 1418, 1364, 1209, 996, 829, 757, 708 cm^{-1}.

^1H NMR: δ = 7.49 (d, J = 7 Hz, 1 H), 7.25–7.42 (m, 3 H), 7.06 (narrow m, 0.2 H, NC*H*=CH of minor rotamer), 6.02 (narrow m, 0.8 H, NC*H*=CH of major rotamer), 5.34 (narrow m, 0.2 H, NCH=C*H* of minor rotamer), 5.13 (narrow m, 0.8 H, NCH=C*H* of major rotamer), 4.00 (t, J = 8.8 Hz, 1.6 H, NCH_2 of major rotamer), 3.60 (t, J = 8.7 Hz, 0.4 H, NCH_2 of minor rotamer), 3.17 (s, 0.2 H, C≡CH of minor rotamer), 3.14 (s, 0.8 H, C≡CH of major rotamer), 2.67 (slightly br t, J = 8.8 Hz, 2 H, NCH_2CH_2 of both rotamers).

^1H NMR (C_6D_6): δ = 7.33–7.38 (m, 1 H), 7.28 (td, J = 2.2, 4.3 Hz, 0.2 H, NC*H*=CH of minor rotamer), 7.18–7.24 (m, 1 H), 6.86–6.98 (m, 2 H), 5.90 (td, J = 2.2, 4.3 Hz, 0.8 H, NC*H*=CH of major rotamer), 4.90 (td, J = 2.5, 4.3 Hz, 0.2 H, NCH=C*H* of minor rotamer), 4.68 (td, J = 2.5, 4.3 Hz, 0.8 H, NCH=C*H* of major rotamer), 3.91 (t, J = 9.0 Hz, 1.6 H, NCH_2 of major rotamer), 3.25 (t, J = 9.0 Hz, 0.4 H, NCH_2 of minor rotamer), 2.97 and 2.92 (two s, 0.8 and 0.2 H, C≡CH), 2.08–2.2 (m, 2 H, NCH_2CH_2 of both rotamers).

^{13}C NMR and DEPT of major rotamer: δ = 165.19 (C=O), 139.41 (C), 132.93 (CH), 130.02 (CH), 129.16 (CH), 128.97 (CH), 127.04 (CH), 119.47 (C), 111.89 (CH), 81.03 (C≡*C*H), 80.57 (*C*≡CH), 44.92 (CH_2N), 28.46 (CH_2CH_2N).

Anal: Calc. for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.00; H, 5.57; N, 7.07.

Cocyclization of 37 with 4 at 148 °C to Give (η^5-2,4-Cyclopentadien-1-yl){(1,2,3,11b-η^4)-3a-*endo*,4,5,11c-*endo*-tetrahydro-2,3-bis(trimethylsilyl)-7*H*-pyrrolo[3,2,1-*de*]phenanthridin-7-one}cobalt (38a), (η^5-2,4-Cyclopentadien-1-yl){(1,2,3,11b-η^4)-3a-*exo*,4,5,11c-*exo*-tetrahydro-2,3-bis(trimethylsilyl)-7*H*-pyrrolo[3,2,1-*de*]phenanthridin-7-one}cobalt (38b) and (η^5-2,4-Cyclopentadien-1-yl){1-{2-[(1,2,3,4-η^4)-2,3-bis(trimethylsilyl)-1,3-cyclobutadien-1-yl]benzoyl}-azacyclopent-2-ene}cobalt (39):

An oven-dried, N_2-purged three-necked flask equipped with an immersion thermometer in a Teflon adaptor, a coil condenser, and a magnetic stir bar was charged with a portion (15 mL) of a solvent mixture, containing **4** (65 mL) and diglyme (35 mL). The mixture was stirred and deoxygenated under reflux (measured temperature of solution = 148 °C) for 0.5 h. The flask was irradiated with a Sylvania ELH slide projector lamp powered at 35 V. Meanwhile, a solution of **37** (197.0 mg, 1.00 mmol) in the above mixture (8 mL) was degassed by three cycles of freeze-pump-thaw, blanketed with N_2, and transferred to a syringe. In the same manner a second syringe was charged with a deoxygenated solution (5 mL) of $CpCo(CO)_2$ (250 mg, 1.39 mmol). The reactants were added to the refluxing, irradiated solvent mixture over 9.5 h. During the reaction, TLC analysis (SiO_2, EtOAc–CH_2Cl_2 1:7) of aliquots removed by syringe, pumped to dryness and redissolved in CH_2Cl_2, showed that **37** was present in only trace amounts. Volatile material was removed by vacuum transfer, and the crude mixture analyzed by ^1H NMR to reveal **38a**, **38b** and **39** in a ratio of 2.2:1.0:1.8. Flash chromatography over SiO_2 (4 × 20 cm) employing EtOAc–CH_2Cl_2 (1:10) as eluent first afforded pure **39** (97.9 mg, 20%). An impure fraction (36.7 mg) was purified by radial chromatography on a 1 mm SiO_2 plate using EtOAc–CH_2Cl_2 (1:19) to give additional **39** (28.5 mg, 5.8%, total 25.8%) as a yellow oil.

MS: *m/z* (relative intensity) = 491.1510 (M^+, 40, calc. for $C_{26}H_{34}CoNOSi_2$, 491.1511), 490 (37), 489 (100), 423 (12, $M^+ - C_4H_6N$), 418 (21), 417 (31), 416 (89), 407 (13), 366 (15), 352 (12), 351 (15), 350 (20), 334 (11), 278 (13), 276 (15), 73 (26).

IR (NaCl): ν = 3095, 3055, 2950, 2890, 2858, 1638 and 1611 (C=O and C=C), 1491, 1456, 1415, 1369, 1318, 1247, 1108, 1000, 853, 836, 810, 758 cm^{-1}.

^1H NMR: δ = 7.35–7.42 (m, 1 H), 7.04–7.26 (m, 3 H), 7.05 (td, J = 2.2, 4.4 Hz, 0.2 H, NCH of minor rotamer), 5.78 (narrow m,

0.8 H, NCH of major rotamer), 5.29 (td, $J = 2$, 4 Hz, 0.2 H, NCH=C*H* of minor rotamer), 5.00 (narrow m, 0.8 H, NCH=C*H* of major rotamer), 4.81 and 4.80 (two s, total 5 H, Cp of minor and major rotamer, respectively), 4.51 (s, 0.2 H) and 4.44 (s, 0.8 H) (cyclobutadiene H), 3.8–4.05 (m, 2 H, NCH_2), 2.55–2.68 (m, 2 H, $CH_2CH=$), 0.16 and 0.05 (two s, 1.8 H each, $SiMe_3$ of minor rotamer), 0.15 and 0.06 (two s, 7.2 H each, $SiMe_3$ of major rotamer).

After the elution of **39**, fractions containing **38a** and **38b** were obtained, combined, and concentrated, leaving a partly crystalline, dark red oil (329.7 mg), impure by TLC analysis. Recrystallization from CH_2Cl_2–hexanes using N_2 to evaporate and deoxygenate the solvent and a pipet to withdraw the mother liquor from the crystals afforded **38a** and **38b**, free from impurities, in a ratio of 2.5 to 1 (226.6 mg, 46 %).

MS: *m/z* (relative intensity) = 491 (M^+, 20), 476 (3.6), 393 (3.7), 322 (18), 321 [100, $M^+ - (Me_3Si)_2C_2$], 294 (6.7), 233 (3.8), 224 (3.9), 196 (3.3), 161 (3.0), 124 (4.9), 73 (6.2).

IR (KBr): ν = 3080, 3050, 2940, 2885, 2848, 1640 (C=O), 1596, 1460, 1430, 1412, 1296, 1257, 1241, 1129, 1009, 830, 748, 687 cm^{-1}.

Pure **38a**, mp 242–243 °C, could be obtained by further fractional crystallization of the mixture.

^1H NMR: δ = 7.93 (dd, $J = 1.5$, 7.5 Hz, 1 H), 7.37 (dt, $J = 1.5$, 7.5 Hz, 1 H), 7.30 (dt, $J = 1.1$, 7.5 Hz, 1 H), 6.87 (dd, $J = 1.1$, 7.5 Hz, 1 H), 5.11 (s, 1 H), 4.79 (s, 5 H), 4.30 (d, $J = 10.4$ Hz, 1 H, irradiation simplified the signal at 2.69 to a dd), 4.00 (dd, $J = 7.3$, 11.8 Hz, 1 H, irradiation changed the dddd at 0.76 to an apparent, q, $J = 11$ Hz, and simplified somewhat the ddd at 3.20), 3.20 (ddd, $J = 5.5$, 11.8, 11.9 Hz, 1 H), 2.69 (ddd, $J = 6.6$, 10.4, 11 Hz, 1 H), 1.71 (ddd, $J = 5.5$, 6.6, 11.9 Hz, 1 H), 0.76 (dddd, $J = 7.3$, 11, 11.9, 11.9 Hz, 1 H, irradiation changed the dd at 4.00 to a d, $J = 12$ Hz, and altered the appearance of the signals at 1.71, 2.69, 3.20), 0.38 (s, 9 H), 0.22 (s, 9 H).

^{13}C NMR and DEPT: δ = 162.57 (C=O), 144.97 (C), 131.31 (CH), 130.30 (C), 128.26 (CH), 126.11 (CH), 125.69 (CH), 88.40 (CH), 84.49 (C), 81.10 (CH, Cp), 63.50 (CH), 61.48 (C), 56.13 (C), 49.92 (CH_2), 41.86 (CH), 34.60 (CH_2), 2.34 (CH_3), 1.81 (CH_3).

Anal: Calc. for $C_{26}H_{34}CoNOSi_2$: C, 63.52; H, 6.97; N, 2.85. Found (for the mixture of **38a** and **38b**): C, 63.27; H, 6.99; N, 2.97.

Partial characterization of **38b**, admixed with **38a**.

^1H NMR: δ = 8.03 (d, $J = 7.3$ Hz, 1 H), 5.76 (s, 1 H, diene H), 4.45 (s, 5 H, Cp), 4.3 (m, overlapping with signal from **38a**, 1 H, irradiation simplified the resonances at 2.86 and 2.0–2.2, NCH_{endo}), 2.86 (ddd, $J = 7$, 12, 12 Hz, 1 H), 2.42 (d, $J = 7.8$ Hz, 1 H, NCH), 2.0–2.2 (m, 2 H, CH_2CH), 1.58–1.7 (m partially obscured by signal from **38a**, $CH_{endo}CHN$), 0.42 (s, 9 H), 0.25 (s 9 H).

^{13}C NMR and DEPT: δ = 161.33 (C=O), 84.42 (diene CH), 81.72 (CH, Cp), 3.45, 3.35 ($SiMe_3$).

Cocyclization of 37 with 4 at 105–106 °C:

By a procedure similar to that described for the reaction at 148 °C, **37** (242.2 mg, 1.23 mmol) in **4** and 1,2-dimethoxyethane (10 mL, 5:3) and $CpCo(CO)_2$ (320 mg, 1.78 mmol, 1.44 equiv) in the same solvent mixture (7 mL) were added over the course of 44 h to boiling, irradiated solvent (23 mL). After an additional 2 h, TLC analysis indicated that **37** had been consumed. ^1H NMR spectroscopic analysis of the crude product revealed the presence of **38a**, **38b**, and **39** in a ratio of 2:1:0.8. Workup as above afforded **39** (76.4 mg, 13 %) and a mixture of **38a** and **38b** (341.7 mg, 56 %).

Cocyclization of 37 with 4 at 25 °C:

In a 100 mL round-bottom flask containing a stir bar, a sample of **4** and 1,2-dimethoxyethane (24 mL, 1:1) was degassed by three freeze-pump-thaw cycles before it was blanketed with N_2 and the flask was capped with a septum. The contents of the flask were stirred and irradiated by a Sylvania ELH projector lamp powered at 60 V. A solution of $CpCo(CO)_2$ (0.30 g, 1.67 mmol) and **37** (197.3 mg, 1.00 mmol) in the same solvent mixture (6 mL), degassed by three cycles of freeze-pump-thaw, was added to the reaction flask over the course of 1.5 d. After an additional 7 h, the mixture was worked up as above. Flash chromatography of the crude product (**38a** and **38b** 4:1 by ^1H NMR) afforded **39** (18.3 mg, 3.7 %) and **38a** and **38b** (total 358.8 mg, 73 %), pure as judged by ^1H NMR and TLC.

Oxidative Demetalation of 38a and 38b to Give *cis*-3a,4,5,11c-Tetrahydro-2,3-bis(trimethylsilyl)-7*H*-pyrrolo[3,2,1-*de*]phenanthridin-7-one (40):

To an ice-cold, deoxygenated, stirred solution of **38a** and **38b** (407.8 mg, 0.829 mmol) in THF (15 mL) and MeCN (10 mL) was added a deoxygenated solution of $Fe(NO_3)_3 \cdot 9H_2O$ (1.003 g, 2.48 mmol, 3.0 equiv) in MeCN (8 mL) and H_2O (3 mL). The burgundy color of the mixture changed to orange, then to pale green. TLC analysis after 1 min indicated that the demetalation was complete. After 5 min, the olive-green mixture was diluted with ice-cold water (100 mL), and extracted with Et_2O in several portions. The combined extracts were washed with aq $NaHCO_3$, H_2O, and brine, dried, and concentrated. The crude product was crystallized from Et_2O–hexanes under N_2 at − 78 °C. The cold supernatant was removed with a pipet and the product was rinsed with pentane in the cold. After storage, **40** (265.0 mg, 87 %) remained as white flakes, mp 112–114 °C.

MS: *m/z* (relative intensity) = 367 (M^+, 28), 366 (29), 352 (8.5), 295 (15), 294 (63, $M^+ - SiMe_3$), 293 (9.3), 278 (7.9), 197 [9.6, $M^+ - (Me_3Si)_2C_2$], 73 (100).

IR (KBr): ν = 3065, 2955, 2900, 2870, 1658 (C=O), 1600, 1469, 1418, 1388, 1260, 1249, 941, 922, 870, 836, 748 cm^{-1}.

^1H NMR: δ = 8.04 (d, $J = 7.5$ Hz, 1 H), 7.32–7.48 (m, 3 H), 6.42 (s, 1 H, diene H), 4.50 (d, $J = 12.2$ Hz, 1 H, NCH, irradiation caused the signal at 3.25 to simplify to a dd, $J = 6$, 12 Hz), 3.95 (dd, $J = 7.2$, 11.2 Hz, 1 H, irradiation changed the absorption at 1.50 to an app q, $J = 12$ Hz, and changed the appearance of the signal at 3.06), 3.25 (ddd, $J = 6$, 12.2, 12.2 Hz, 1 H, irradiation caused the d at 4.50 to change to a s, and altered the appearance of the resonances at 1.50 and 2.22), 3.06 (ddd, $J = 5.0$, 11.6, 12 Hz, 1 H), 2.22 (ddd, $J = 5.0$, 6, 12 Hz, 1 H, irradiation left the resonances at 3.95 and 4.50 unchanged but altered signals at 1.50, 3.06, 3.25), 1.50 (dddd, $J = 7.2$, 12, 12, 12.2 Hz, 1 H), 0.28 (two s, 18 H).

^{13}C NMR: δ = 163.00, 151.19, 141.85, 136.81, 131.67, 129.91, 128.27, 128.13, 125.99, 123.16, 121.55, 54.59, 43.17, 41.53, 33.40, 1.95, 1.63.

Anal: Calc. for $C_{21}H_{29}NOSi_2$: C, 68.61; H, 7.95; N, 3.81. Found: C, 68.82; H, 8.02; N, 3.73.

Cocyclization of 37 with 44 to Give (η^5-2,4-Cyclopentadien-1-yl)-{dimethyl (1,2,3,3a-η^4)-3a-*endo*-4,5,11c-*endo*-tetrahydro-7-oxo-7*H*-pyrrolo[3,2,1-*de*]phenanthridine-2,3-dicarboxylate}cobalt (41a) and (η^5-2,4-Cyclopentadien-1-yl){dimethyl (1,2,3,3a-η^4)-3a-*exo*-4,5,11b-*exo*-tetrahydro-7-oxo-7*H*-pyrrolo[3,2,1-*de*]phenanthridine-2,3-dicarboxylate}cobalt (41b):

From separate syringes, deoxygenated solutions of $CpCo(CO)_2$ (141 mg, 0.783 mmol, 1.59 equiv) in 1,3-dimethylbenzene (5 mL), and **37** (97.0 mg, 0.492 mmol) mixed with **44** (Aldrich, redistilled, 53.4 mg, 1.08 mmol, 2.19 equiv) in 1,3-dimethylbenzene (5 mL) were added over the course of 16.5 h to stirred, boiling, and irradiated (ELH lamp, 30 V) 1,3-dimethylbenzene (15 mL). Volatile materials were removed from the mixture by vacuum transfer and the black-brown residue was taken up in a small portion of EtOAc before it was filtered through a 2 cm plug of neutral Al_2O_3 (activity III) in a pipet. The Al_2O_3 was washed with EtOAc ($\approx$ 5 mL) until the eluate was colorless. Combined eluates were concentrated by vacuum transfer. The dark brown residue contained **41a** and **41b** in a ratio of 1.5 to 1 (^1H NMR). Radial chromatography on a 2 mm Al_2O_3 plate using EtOAc–CH_2Cl_2 (1:8) afforded an early fraction of dark red foam containing **41a** and **41b**, essentially pure by ^1H NMR (83.4 mg, 37 %) and an analytical sample of **41a** and **41b** (72.3 mg, 32 %) as dark red crystals, mp 224–229 °C.

MS: *m/z* = 463.0837 (M^+, calc. for $C_{24}H_{22}CoNO_5$, 463.0829).

IR (KBr): ν = 3100, 3060, 3030, 2950, 2860, 1700–1730 (OC=O), 1655 (NC=O), 1435, 1250, 1096 cm^{-1}.

Partial ^1H NMR of major isomer: δ = 7.97 (dd, J = 1.8, 7.3 Hz, 1 H), 7.3–7.55 (m, 2 H), 6.98 (dd, J = 1.7, 7.3 Hz, 1 H), 5.72 (s, 1 H, diene H), 4.86 (s, 5 H, Cp), 4.46 (d, J = 10.9 Hz, 1 H, NCH), 4.06 (dd, J = 7.5, 11.7 Hz, 1 H, NC*H*H), 3.88 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3).

Partial ^1H NMR of minor isomer: δ = 8.08 (dd, J = 1, 7.5 Hz, 1 H), 7.3–7.55 (m, 3 H), 6.33 (s, 1 H, diene H), 4.55 (s, 5 H, Cp), 4.37 (dd, J = 7, 12 Hz, 1 H, NC*H*H), 3.86 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 2.76 (d, J = 10 Hz, 1 H, NCH).

Cocyclization of 37 with 45 to give (η^5-2,4-Cyclopentadien-1-yl)-{(1,2,3,11b-η^4)-3a-*endo*-4,5,11c-*endo*-tetrahydro-2-methoxy-3-(trimethylsilyl)-7*H*-pyrrolo[3,2,1-*de*]phenanthridin-7-one}cobalt (42) and (η^5-2,4-Cyclopentadien-1-yl){(1,2,3,11b-η^4)-3a-*endo*-4,5,11c-*endo*-tetrahydro-3-methoxy-2-(trimethylsilyl)-7*H*-pyrrolo[3,2,1-*de*]-phenanthridin-7-one}cobalt (43):

From separate syringes, deoxygenated solutions of $CpCo(CO)_2$ (509 mg, 2.83 mmol, 5.33 equiv) in toluene (8 mL) and **37** (104.5 mg, 0.531 mmol) mixed with **45**[45] (287.0 mg, 4.21 equiv) in toluene (8 mL) were added over the course of 11 h to stirred, irradiated, and boiling toluene (15 mL). After boiling the mixture for another 1.5 h, TLC analysis indicated the complete consumption of **37** and the presence of two major products. The cooled mixture was concentrated by vacuum transfer and the brown-red residue, containing **42** and **43** in a ratio of 1:1 (^1H NMR), was purified by chromatography over neutral Al_2O_3 (80 g of activity IV), using EtOAc–petroleum ether. The first fractions contained (η^5-2,4-cyclopentadien-1-yl)-{(1,2,3,4-η^4)-3,4-dimethoxy-1,2-bis(trimethylsilyl)-1,3-cyclobutadiene}cobalt[45] and its regioisomer (110 mg). Subsequently, **42** was eluted to give red-black crystals (46.5 mg, 19%), mp 179–183 °C.

MS: m/z = 449 (M^+, 11), 448 (6.6), 447 (18), 417 (3.6), 382 (1.6), 381 (5.3), 345 (2.8), 326 (9.3), 325 (26, M^+ – CpCo), 324 (13), 323 (2.9), 311 (10), 310 (41, M^+ – CpCo – Me), 294 (13), 293 (11), 278 (13), 252 (15), 220 (20), 189 (49), 124 (28, $CpCo^+$), 89 (24), 75 (10), 73 (100), 59 (82).

IR (KBr): ν = 2962, 2905, 2865, 1648 (C=O), 1601, 1463, 1424, 1402, 1338, 1260, 1246, 1227, 1205, 1111, 1093, 1018, 928, 871, 833, 809, 759 and 707 cm^{-1}.

^1H NMR: δ = 7.93 (d, J = 8.2 Hz, 1 H), 7.37 (t, J = 7 Hz, 1 H), 7.29 (t, J = 7 Hz, 1 H), 6.92 (d, J = 7.2 Hz, 1 H), 5.08 (s, 1 H, diene H), 4.77 (s, 5 H, Cp), 4.13 (d, J = 10.5 Hz, 1 H, $CH_{endo}N$), 4.04 (dd, J = 8, 11 Hz, 1 H), 3.91 (s, 3 H), 3.20 (ddd, J = 5.5, 11.5, 11.5 Hz, 1 H), 2.72 (ddd, J = 7.5, 10.5, 10.5 Hz, 1 H), 1.75–1.85 (m, 1 H), 0.9–1.05 (m, 1 H), 0.15 (s, 9 H).

^{13}C NMR and DEPT (CD_2Cl_2): δ = 162.00 (C=O), 145.72 (C-7a), 135.46 (C, C–OMe), 131.69 (C-11a), 131.39 (CH), 128.16 (CH), 126.33 (CH), 126.18 (CH), 80.77 (CH, Cp), 65.57 (CH), 64.00 (CH), 55.14 (CH_3O), 50.73 (C), 49.70 (NCH_2), 43.68 (*C*–$SiMe_3$), 43.40 (CH), 34.48 (NCH_2CH_2), 0.18 [CH_3, $Si(CH_3)_3$].

Anal: Calc. for $C_{24}H_{28}NO_2SiCo$: C, 64.12; H, 6.28; N, 3.12. Found: C, 63.84; H, 6.27; N, 2.97.

Continued elution provided a mixture of **42** and **43** (34.9 mg, 15%), followed by pure **43** (42.3 mg, 18%), obtained as brick-red crystals, mp 233–234 °C.

MS: m/z (relative intensity) = 449 (M^+, 20), 448 (22), 447 (73), 446 (17), 430 (10), 418 (11), 417 (41), 381 (18), 365 (5.9), 351 (7.8), 345 (4.7), 325 (3.2, M^+ – CpCo), 324 (4.1), 310 (6.0), 295 (9.8), 294 (45, M^+ – CpCo – OMe), 293 (9.5), 292 (8.9), 278 (11), 252 (4.8), 234 (3.8), 124 (8.8, $CpCo^+$), 73 (100).

IR (KBr): ν = 3035, 2950, 2935, 2855, 1652 (C=O), 1602, 1470, 1421, 1348, 1247, 1205, 1135, 1032, 840, 805, 759, 699 cm^{-1}.

^1H NMR: δ = 7.93 (d, J = 7.0 Hz, 1 H), 7.36 (t, J = 7 Hz, 1 H), 7.30 (t, J = 7 Hz, 1 H), 6.96 (d, J = 7.2 Hz, 1 H), 4.96 (s, 1 H, diene H), 4.86 (s, 5 H, Cp), 4.34 (d, J = 9 Hz, 1 H, NCH_{endo}), 4.13 (dd, J = 7.8, 11.7, 1 H, $NCH\mathit{H}_{exo}$), 3.51 (s, 3 H), 3.2–3.4 (m, 2 H), 1.92 (ddd, J = 6, 7, 11 Hz, 1 H, $CHC\mathit{H}_{endo}H_{exo}$), 1.08 (dddd, J = 8, 11, 11, 11 Hz, 1 H, $CHCH_{endo}\mathit{H}_{exo}$), 0.31 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR: δ = 162.21 (C=O), 144.86, 131.25, 130.11, 127.83, 126.03, 125.48, 109.33 (*C*–OMe), 80.19 (Cp), 67.43, 63.72, 59.06, 55.07, 49.20, 40.67, 31.82, – 0.46 (one of the upfield signals appears to be due to two isochronous carbons).

Anal: Calc. for $C_{24}H_{28}NO_2SiCo$: C, 64.12; H, 6.28; N, 3.12. Found: C, 64.09; H, 6.12; N, 3.09.

1-[(6-Bromo-1,3-benzodioxol-5-ylcarbonyl]azacyclopent-2-ene (50) from Acid 46:

A stirred mixture of **46**[52] (2.45 g, 10.0 mmol) and $SOCl_2$ (20 mL) was heated to reflux for 1 h before excess $SOCl_2$ was removed by vacuum transfer. The pale yellow residue solidified, mp 88–91 °C (lit[52] for **48**, mp 89–91 °C) after storage under 0.01 mmHg for 1 h. The acid chloride was dissolved in THF (50 mL) and a mixture of 4,4-diethoxybutanamine (1.945 g, 12.1 mmol) and i-Pr_2NEt (2.656 g, 20.5 mmol) was added dropwise over 5 min. After 10 min, the reaction was quenched with a solution of conc aq HCl (5 mL) in H_2O (50 mL) and subjected to standard workup, leaving 2.43 g of a foamy residue which was dissolved in 1,3-dimethylbenzene (125 mL). The resulting solution was heated to reflux for 5 h, volatile components were removed by vacuum transfer, and the semisolid residue which remained was purified by flash chromatography over SiO_2 (60 g) using EtOAc–CH_2Cl_2 (1:8). Concentration of the eluate gave **50** (2.062 g, 70%) as a white solid, mp 112–113 °C.

MS: m/z (relative intensity) = 297 [M^+ (^{81}Br), 23], 295 [M^+ (^{79}Br), 23], 229 [99, M^+ (^{81}Br) – C_4H_6N], 227 [100, M^+ (^{79}Br) – C_4H_6N], 201 [12, M^+ (^{81}Br) – C_4H_6NCO], 199 [12, M^+ (^{79}Br) – C_4H_6NCO], 143 (10), 93 (24), 80 (10), 79 (19).

IR (NaCl, $CHCl_3$): ν = 3008, 2898, 1633 and 1617 (C=O and C=C), 1503, 1483, 1446, 1240, 1220, 1211, 1042 cm^{-1}.

^1H NMR 7.00 (td, J = 2.2, 4.4 Hz, 0.2 H, NCH of minor rotamer), 6.96 (s, 0.2 H), 6.95 (s, 0.8 H), 6.74 (s, 0.8 H), 6.72 (s, 0.2 H), 6.00 (td, J = 2.2, 4.4 Hz, 0.8 H, NCH of major rotamer), 5.97 (s, 2 H, OCH_2O), 5.34 (td, J = 2.4, 4.3 Hz, 0.2 H, NCH=C*H* of minor rotamer), 5.17 (td, J = 2.5, 4.4 Hz, 0.8 H, NCH=C*H* of major rotamer), 3.95 (t, J = 8.8 Hz, 1.6 H, NCH_2 of major rotamer), 3.56 (t, J = 8.8 Hz, 0.4 H, NCH_2 of minor rotamer), 2.6–2.75 (m, 2 H, CH_2CH=).

^{13}C NMR of major rotamer: δ = 164.17 (C=O), 149.10 and 147.43 (C_{Ar}–O), 130.89, 129.70, 112.78, 112.53, 110.59, 108.21, 102.10, 44.76 (NCH_2), 28.59 (NCH_2CH_2).

Anal: Calc. for $C_{12}H_{10}NBrO_3$: C, 48.67; H, 3.40; N, 4.73. Found: C, 48.66; H, 3.32; N, 4.61.

Attempted Coupling of 50 with TMSA with Formation of 5,10b-Dihydro-5-oxo-3*H*-[1,3]-dioxolo[4,5-*f*]pyrrolo[2,1-*a*]isoindole (52):

Et_3N (10 mL) was distilled from CaH_2 into a flask containing **50** (146.7 mg, 0.495 mmol) and the resulting mixture deoxygenated by three cycles of freeze-pump-thaw before $Pd(P(Ph)_3)_4$ (23 mg, 0.020 mmol, 0.04 equiv) was added. The starting material was the only compound detectable by TLC analysis after 1.5 h. TMSA (300 µL, 2.12 mmol, 4.3 equiv) was added, and the mixture was boiled for 2 d. The brown residue obtained after removal of volatiles was taken up in 5% aq KH_2PO_4 and extracted with EtOAc. The combined EtOAc phases were washed with brine, dried, and concentrated. Flash chromatography of the crude product (125 mg) afforded **52** (65.0 mg, 61%), mp 137–143 °C. An analytical sample (from EtOAc–cyclohexane, 45.7 mg) exhibited mp 143–146 °C.

MS: m/z (relative intensity) = 215 (64, M^+), 214 (48), 187 (100), 185 (18), 156 (14), 129 (22), 128 (28), 104 (11), 102 (23), 101 (18), 76 (22), 75 (26), 74 (20).

IR (KBr): ν = 3100, 3058, 2918, 2879, 1690 (C=O), 1612 (C=C), 1506, 1479, 1396, 1383, 1350, 1332, 1312, 1296, 1261, 1237, 1214, 1192, 1042, 1029, 1011, 931, 922, 870, 837, 821, 784, 759, 699 cm^{-1}.

^1H NMR: δ = 7.11 (s, 1 H), 6.84 (s, 1 H), 6.012 (d, J = 1.2 Hz, 1 H, OC*H*HO), 6.006 (d, J = 1.2 Hz, 1 H, OCH*H*O), 5.98–6.01 (m, 1 H), 5.91 (dddd, J = 1.4, 2.1, 2.5, 6.0 Hz, 1 H), 5.28–5.33 (m, 1 H, enhanced in difference NOE experiment when the s at 6.84 was irradiated, NCHAr), 4.50 (dddd, J = 2.1, 2.1, 3.0, 15.6 Hz, 1 H), 3.89 (dddd, J = 1.4, 2.5, 4.0, 15.6 Hz, 1 H).

^{13}C NMR and DEPT: δ = 175.27 (C=O), 151.90 (C), 148.50 (C), 143.04 (C), 131.23 (CH), 127.80 (CH), 126.41 (CH), 103.83 (CH), 102.64 (CH), 102.01 (OCH_2O), 68.99 (NCHAr), 51.48 (CH_2N).

Anal: Calc. for $C_{12}H_9NO_3$: C, 66.97; H, 4.21; N, 6.51. Found: C, 66.93; H, 4.13; N, 6.57.

In another experiment, **50** (262.9 mg, 0.888 mmol), TMSA (177.4 mg, 1.80 mmol, 2.03 equiv), and $PdCl_2(PPh_3)_2$ (12.5 mg, 0.0178 mmol, 0.02 equiv) in Et_3N (15 mL) were heated to reflux for 24 h to give **52** (94.8 mg, 50%).

Coupling of 50 with TMSA to give 52 and 1-[(6-Trimethylsilyl-ethynyl)-1,3-benzodioxol-5-ylcarbonyl]azacyclopent-2-ene (53):

A deoxygenated solution of **50** (147.8 mg, 0.499 mmol), TMSA (0.30 mL, 4.2 equiv), $PdCl_2[P(o\text{-tol})_3]_2$ (15.2 mg, 0.0193 mmol, 0.04 equiv), and $P(o\text{-tol})_3$ (23.6 mg, 0.0776 mmol, 0.155 equiv, 4 mole/mole Pd) in Et_3N (10 mL, freshly distilled from CaH_2) was stirred and heated to reflux for a period of 5.5 h, at the end of which the color of the mixture had changed from yellow to black. The cooled mixture was concentrated by rotary evaporation and the residue was partitioned between Et_2O and H_2O. Further workup gave a brown oil (193 mg) which was purified by flash chromatography over SiO_2 (1.5 × 20 cm) using EtOAc–CH_2Cl_2 (1:9). Fractions 4–6 contained **53** (12.4 mg, 8%) as a pale yellow oil.

MS: *m/z* (relative intensity) = 313 (M^+, 23), 298 (3.8), 246 (28), 245 (100, $M^+ - C_4H_6N$), 189 (13), 84 (12).

IR (NaCl, neat): ν = 3055, 2965, 2900, 2865, 2157 (C≡C), 1695, 1638 and 1617 (C=O and C=C), 1507, 1488, 1472, 1447, 1410, 1378, 1289, 1251 (Si–C), 1181, 1156, 1038, 932, 860, 844, 764 cm^{-1}.

^{1}H NMR: δ = 7.0–7.05 (m, 0.15 H, NCH of minor rotamer), 6.844 and 6.837 (two s, total 1 H), 6.81 (s, 0.85 H), 6.77 (s, 0.15 H), 5.97 (s, 2 H, OCH_2O), 5.33 (td, J = 2.5, 4.3 Hz, 0.15 H, NCH=C*H* of minor rotamer), 5.15 (td, J = 2.5, 4.4 Hz, 0.85 H, NCH=C*H* of major rotamer), 3.95 (t, J = 9 Hz, 1.7 H, NCH_2 of major rotamer), 3.73 (t, J = 9 Hz, 0.3 H, NCH_2 of minor rotamer), 2.60–2.74 (m, 2 H, NCH_2CH_2), 0.14 and 0.13 [two s, 9 H total, $Si(CH_3)_3$ of minor and major rotamers, respectively].

Fractions 9–12 contained **52** (37.4 mg, 35%).

1-(6-Iodo-1,3-benzodioxol-5-ylcarbonyl)azacyclopent-2-ene (51):

A stirred solution of acid **47**[55] (301.5 mg, 1.03 mmol) in $SOCl_2$ (5 mL) was heated to reflux for 1.75 h before volatile material was removed by vacuum transfer. After storage under an oil-pump vacuum for 6 h, the reddish solid residue (mp 100–105 °C) was dissolved in THF (5 mL) and treated with 4,4-diethoxybutanamine (210 mg, 1.30 mmol) and *i*-Pr_2NEt (134 mg, 1.04 mmol) as in the synthesis of **50**. After acidic hydrolysis, thermal dehydration, and flash chromatography, **51** (247.1 mg, 70%) was obtained as a white solid, mp 109–110 °C.

MS: *m/z* (relative intensity) = 343 (M^+, 61), 276 (30), 275 (100, $M^+ - C_4H_6N$), 274 (21), 247 (26, $M^+ - C_4H_6NCO$), 247 (26), 189 (14), 149 (13), 121 (11), 120 (43), 119 (17), 62 (27).

IR (KBr): 3100, 2915, 2855, 1640 and 1616 (C=O and C=C), 1496, 1477, 1428, 1405, 1386, 1356, 1233, 1031, 929, 815 cm^{-1}.

^{1}H NMR: δ = 7.134 and 7.129 (two s, total 1 H, from minor and major rotamers, respectively), 6.95 (td, J = 2.2, 4.3 Hz, 0.2 H, NCH of minor rotamer), 6.68 and 6.67 (two s, total 1 H, from major and minor rotamers, respectively), 5.94 (td, J = 2.2, 4.4 Hz, 0.8 H, NCH of major rotamer), 5.93 (s, 2 H, OCH_2O), 5.32 (td, J = 2.6, 4.3 Hz, 0.2 H, NCH=C*H* of minor rotamer), 5.15 (td, J = 2.6, 4.4 Hz, 0.8 H, NCH=C*H* of major rotamer), 3.91 (t, J = 8.8 Hz, 1.6 H, NCH_2 of major rotamer), 3.49 (t, J = 8.7 Hz, 0.4 H, NCH_2 of minor rotamer), 2.58–2.72 (m, 2 H, NCH_2 CH_2).

^{13}C NMR and DEPT of major rotamer: δ = 165.54 (C=O), 148.85 (C), 148.21 (C), 135.26 (C), 129.62 (CH), 118.37 (CH), 112.52 (CH), 108.01 (CH), 101.88 (OCH_2O), 81.33 (C-I), 44.69 (CH_2), 28.51 (CH_2).

^{13}C and DEPT of minor rotamer: δ = 165.18 (C=O), 148.67 (C), 148.4 (C), 135.98 (C), 128.63 (C), 118.37 (CH), 112.97 (CH), 107.16 (CH), 101.88 (OCH_2O), 80.58 (C), 46.91 (CH_2), 29.68 (CH_2).

Anal: Calc. for $C_{12}H_{10}NO_3I$: C, 42.01; H, 2.94; N, 4.08. Found: C, 42.02; H, 2.93; N, 4.02.

Attempted Ethynylation of 6-Bromo-1,3-benzodioxole-5-carboxamide (54) to give 1,3-Benzodioxole-5-carboxamide (55) and 6-(Trimethylsilylethynyl)-1,3-benzodioxole-5-carboxamide (56):

Amide **54**[57] (112.7 mg, 0.463 mmol) dissolved in azacyclohexane (10 mL, Alfa 98%) was deoxygenated before TMSA (104.6 mg, 1.07 mmol, 2.3 equiv), $PdCl_2(PPh_3)_2$ (7.5 mg, 0.011 mol, 0.023 equiv) and CuI (1.8 mg, 0.020 equiv) were added, and the mixture was heated to reflux for 1.4 h. The cooled mixture was rotary evaporated to dryness and the residue was partitioned between H_2O (10 mL) and EtOAc (2 × 10 mL). Further aqueous workup afforded a brown solid (126.8 mg), containing **55** and **56** (≈ 1:1 by ^{1}H NMR analysis). Radial chromatography (2 mm SiO_2 plate) using EtOAc–CH_2Cl_2 (1:4) eluted **56** (30.0 mg, 25%) as a pale brown solid, mp 134–139 °C. An analytical sample from another experiment exhibited mp 140.5–142 °C.

MS: *m/z* (relative intensity) = 261 (M^+, 7.2), 246 (24), 228 (27), 187 (13), 93 (88), 92 (10), 80 (56), 79 (100), 78 (11), 77 (42), 66 (33), 65 (25).

IR (KBr): ν = 3442, 3423, 3171 (br), 2960, 2146 (C≡C), 1677 (C=O), 1602, 1506, 1481, 1434, 1376, 1252, 1177, 1040, 935, 864, 762 cm^{-1}.

^{1}H NMR: δ = 7.79 (br s, 1 H, NH), 7.58 (s, 1 H), 6.89 (s, 1 H), 6.32 (br s, 1 H, NH), 6.00 (s, 2 H, OCH_2O), 0.23 [s, 9 H, $Si(CH_3)_3$].

Anal: Calc. for $C_{18}H_{15}NO_3Si$: C, 59.74; H, 5.79; N, 5.36. Found: C, 59.66; H, 5.87; N, 5.24.

Further elution with EtOAc–CH_2Cl_2 (1:1) afforded **55** (21.7 mg, 28%) as a pale brown solid, mp 160–161 °C (lit[58] mp 165–166 °C).

^{1}H NMR: δ = 7.32 (dd, J = 1.5, 8.0 Hz, 1 H, H-6), 7.29 (d, J = 1.5 Hz, 1 H, H-4), 6.81 (d, J = 8.0 Hz, 1 H, H-8), 6.01 (s, 2 H, OCH_2O), 5.9 (br s, NH_2).

***N*-(4,4-Diethoxybutyl)-6-bromo-1,3-benzodioxole-5-carboxamide (57):**

To a solution of crude **48** [mp 88–91 °C, from acid **46** (734 mg, 3.00 mmol)] in Et_2O (20 mL) was added rapidly 4,4-diethoxybutanamine (616 mg, 3.82 mmol, 1.27 equiv) and *i*-Pr_2NEt (386 mg, 2.99 mmol, 1.00 equiv). After 10 min, aqueous workup led to the isolation of **57** (1.129 g, 97%) as a pale yellow oil which solidified slowly under oil pump vacuum, mp 53.5–56 °C.

MS: *m/z* (relative intensity) = 389 (0.5), 388 (0.4), 387 (0.6), 386 (0.4), 360 (45), 358 (42), 344 (17), 343 (11), 342 (18), 271 (20), 269 (20), 229 (100), 227 (100), 190 (38), 149 (19), 103 (59), 75 (49), 70 (42).

IR (KBr): ν = 3265 (br, NH), 3060, 2961, 2918, 2875, 1638 (C=O), 1540, 1498, 1472, 1407, 1388, 1371, 1341, 1282, 1234, 1121, 1057, 1033, 929, 860 cm^{-1}.

^{1}H NMR: δ = 6.98 (s, 1 H), 6.96 (s, 1 H), 6.22 (br s, 1 H, NH), 5.98 (s, 2 H, OCH_2O), 4.48 [m, 1 H, C*H*$(OEt)_2$], 3.55–3.68 (m, 2 H), 3.36–3.54 (m, 4 H), 1.6–1.8 (m, 4 H), 1.16 (t, J = 7.0 Hz, 6 H) (many signals broadened by amide rotamerism).

^{13}C NMR and off-resonance experiment: δ = 167.02 (C=O), 149.24 (C), 147.18 (C), 131.18 (C), 112.89 (CH), 110.40 (C), 109.21 (CH), 102.49 (CH), 102.09 (OCH_2O), 61.30 (CH_2), 39.73 (CH_2), 30.99 (CH_2), 24.23 (CH_2), 15.18 (CH_3).

Anal: Calc. for $C_{16}H_{22}NO_5Br$: C, 49.62; H, 5.73; N, 3.62; Br, 20.63. Found: C, 49.54; H, 5.86; N, 3.57; Br, 20.4.

***N*-(4,4-Diethoxybutyl)-6-(trimethylsilylethynyl)-1,3-benzodioxole-5-carboxamide (58):**

To a deoxygenated, stirred solution of **57** (464.6 mg, 1.20 mmol) and TMSA (330 µL, 2.3 mmol, 1.9 equiv) was added $PdCl_2(PPh_3)_2$ (22.0 mg, 0.031 mmol, 0.026 equiv), and the mixture was heated to reflux for 2 h. The cooled cloudy brown mixture was concentrated to dryness by rotary evaporation, and the coffee-brown residue was partitioned between H_2O (50 mL) and Et_2O (3 × 25 mL). The combined brown Et_2O extracts were washed with dilute aq KH_2PO_4

(50 mL), brine (50 mL), dried, and concentrated leaving a dark brown oil (527 mg) containing one major product by TLC. Flash chromatography over SiO_2 using EtOAc–CH_2Cl_2 (1:7) as eluant gave **58** (441.2 mg, 90%) as a chromatographically homogeneous, brown, viscous oil.

MS: *m/z* (relative intensity) = 405 (M^+, 2.6), 376 (11), 360 (18), 331 (11), 330 (48), 286 (14), 274 (13), 260 (12), 247 (13), 246 (37), 245 (92), 187 (11), 173 (11), 149 (11), 103 (12), 98 (15), 94 (12), 93 (39), 80 (21), 79 (38), 77 (24), 75 (100), 73 (13), 69 (11), 66 (17), 65 (13), 57 (15), 55 (15).

IR (NaCl): ν = 3395, 3310 (br), 2970, 2920, 2890, 2135 (C≡C), 1656 (C=O), 1648, 1612, 1534, 1503, 1480, 1355, 1246, 1173, 1124, 1056, 1033, 928, 845, 772, 755 cm^{-1}.

^1H NMR: δ = 7.76 (br s, 1 H, NH), 7.55 (s, 1 H), 6.89 (s, 1 H), 6.00 (s, 2 H, OCH_2O), 4.48 [m, 1 H, C*H*$(OEt)_2$], 3.5–3.65 (m, 2 H), 3.3–3.5 (m, 4 H), 1.67 (m, 4 H), 1.17 (t, J = 7.0 Hz, 6 H), 0.25 (s, 9 H).

^{13}C NMR and DEPT: δ = 164.91 (C=O), 148.98 (C), 148.55 (C), 131.12 (C), 113.36 (C), 112.60 (CH), 109.95 (CH), 103.56 (C), 102.42 (CH), 101.93 (CH_2), 100.13 (C), 61.10 (CH_2), 39.86 (CH_2), 31.19 (CH_2), 24.77 (CH_2), 15.18 (CH_3), −0.32 (CH_3).

Anal: Calc. for $C_{21}H_{31}NO_5Si$: C, 62.19; H, 7.71; N, 3.45. Found: C, 61.78; H, 7.78; N, 3.33.

Hydrolysis of 58 to give *N*-(4-Oxobutyl)-6-(trimethylsilylethynyl)-1,3-benzodioxole-5-carboxamide (59) and 2-Hydroxy-1-[6-(trimethylsilylethynyl)-1,3-benzodioxol-5-ylcarbonyl]azacyclopentane (60):

Bromide **57** (129.6 mg, 0.335 mmol) was converted into crude **58** (155.4 mg) as above. A solution of 101.2 mg (65%) of the crude acetal in THF–H_2O–conc aq HCl 4:4:1 (≈ 5 mL) was stirred for 2.5 h. The mixture was diluted with H_2O and extracted with Et_2O. Further workup gave an amber cloudy oil (80.7 mg), which was purified by radial chromatography (2 mm SiO_2 plate, EtOAc–CH_2Cl_2 1:4 as eluant) to give **59** (10.8 mg, 15% from **57**) as an amber viscous oil.

IR (NaCl): ν = 3400 (br, N–H), 2965, 2905, 2158 (C≡C), 1730 (HC=O), 1630 cm^{-1} (NC=O).

^1H NMR: δ = 9.78 (t, J = 1.1 Hz, 1 H, CHO), 7.85 (br s, 1 H, NH), 7.55 (s, 1 H, H-4), 6.90 (s, 1 H, H-7), 6.01 (s, 2 H, OCH_2O), 3.46 (dt, J = 6, 7 Hz, 2 H, NCH_2), 2.55 (dt, J = 1.1, 7.2 Hz, 2 H, C*H*$_2$CHO), 1.93 (quintet, J = 7 Hz, 2 H, $CH_2CH_2CH_2$), 0.25 [s, 9 H, $Si(CH_3)_3$]; extraneous signals at δ = 6.87 (s), 6.76 (s), 5.99 (s), 0.18 (s), suggested contamination by ≈ 20% of an unidentified compound.

Further elution afforded **60** (40.9 mg, 56% from **57**) as a colorless solid, mp 121–124 °C.

MS: *m/z* (relative intensity): δ = 331 (M^+, 10), 313 (4.8), 303 (6.1), 302 (13), 274 (12), 261 (16), 260 (11), 258 (27), 247 (34), 246 (57), 245 (100, $M^+ - C_4H_8NO$), 231 (20), 230 (40), 187 (28), 173 (28), 115 (31), 84 (29), 75 (31), 73 (43), 69 (40).

IR (KBr): ν = 3360 (br, O–H), 3080, 3055, 2960, 2920, 2880, 2153 (C≡C), 1610 (br, with shoulder at 1640, C=O), 1495, 1457, 1406, 1360, 1336, 1261, 1189, 1180, 1147, 1109, 1035, 958, 935, 920, 893, 867, 844, 769 cm^{-1}.

^1H NMR: δ = 6.86 and 6.85 (two s, ratio of heights ≈ 1 to 2, total 1 H), 6.750 and 6.745 (two s, ratio of heights ≈ 1 to 2, total 1 H), 5.970 and 5.966 (two s, ratio of heigths ≈ 1 to 2, total 2 H), 5.73 (m, 0.7 H, NC*H*OH of major rotamer), 5.16 (br d, J ≈ 4 Hz, 0.3 H, NC*H*OH of minor rotamer), 4.24 (br s, 0.7 H, OH of major rotamer), 3.52–3.72 (m, 0.7 H), 3.28–3.48 (m, 1.7 H), 3.18 (br s, 0.3 H, OH of minor rotamer), 1.86–2.28 (m) and 1.7–1.86 (m) (total 3.6 H), 0.16 (s, 9 H).

^{13}C NMR and DEPT of major rotamer: δ = 169.50 (C=O), 148.23 (C), 147.96 (C), 134.75 (C), 113.53 (C), 111.76 (CH), 106.77 (CH), 101.81 (CH_2), 101.62 (C), 96.39 (C), 81.86 (NCHOH), 47.45 (CH_2), 32.43 (CH_2), 23.38 (CH_2), −0.22 (CH_3).

Minor rotamer: δ = 167.89 (C=O), 148.56 (C), 147.93 (C), 135.67 (C), 112.67 (C), 111.70 (CH), 107.14 (CH), 101.88 (CH_2), acetylenic carbons not seen, 83.21 (NC*H*OH), 44.86 (CH_2), 34.06 (CH_2), 21.27 (CH_2), −0.29 (CH_3).

Anal: Calc. for $C_{17}H_{21}NO_4Si$: C, 61.60; H, 6.39; N, 4.23. Found: C, 61.35; H, 6.44; N, 4.14.

1-(6-Ethynyl-1,3-benzodioxol-5-ylcarbonyl)azacyclopent-2-ene (5c):

Bromide **57** (16.24 g, 42.0 mmol) was ethynylated with TMSA (10.0 mL, 71.3 mmol, 1.70 equiv), $PdCl_2(PhCN)_2$ (81.7 mg, 0.213 mmol, 0.005 equiv) and PPh_3 (110.4 mg, 0.421 mmol, 0.010 equiv) in boiling, freshly distilled Et_3N (500 mL) for 24 h. The cooled yellow-brown mixture was concentrated by rotary evaporation and the residue was stirred with THF (200 mL) and 3 N aq HCl (160 mL). After 2 h, the mixture was diluted with H_2O (1 L) and extracted with Et_2O (3 × 200 mL). The combined extracts were washed successively with H_2O (2 × 300 mL) and saturated aq $NaHCO_3$ (300 mL) before they were dried, filtered and the filtrate concentrated. All aq washings and $MgSO_4$ were back-extracted with additional Et_2O (1 × 100 mL). A suspension of the yellow solid residue in 1,3-dimethylbenzene (400 mL) was heated under reflux for 24 h. The solvent was removed from the dark brown mixture by vacuum transfer. To a stirred solution of the residue in MeOH (100 mL) was added aq NaOH (2%, 2 mL). After 45 min, dilution with H_2O (500 mL) followed by extraction with Et_2O, EtOAc, drying, filtration and solvent removal afforded a brown semisolid residue. The crude product was triturated with boiling cyclohexane (6 × 150 mL) to leave behind 1.4 g of polar brown material. The combined supernatants were concentrated and the residue was flash chromatographed over SiO_2 (2 × 12 in, 150 g), using EtOAc–petroleum ether (1:3 to 2:1). Fractions 14–19 afforded yellowish crystals of **5c** (4.74 g, 47%), mp 125–133 °C, which were recrystallized from EtOAc–hexanes (≈ 15 mL and ≈ 10 mL) to give pure product, mp 132.5–134 °C (4.22 g, 41.6%). The mother liquor afforded a second crop, mp 122–130 °C (0.13 g, 1.3%). Another run on 3.65-mmol scale gave **5c** (41%) as pale yellow crystals, mp 130–133 °C.

MS: *m/z* (relative intensity) = 241 (M^+, 12), 213 (8.8), 174 (7.1), 173 (100, $M^+ - C_4H_6N$), 145 (11), 89 (14), 87 (14), 69 (14).

IR (KBr): ν = 3225, 3211, 3114, 3059, 3041, 2954, 2912, 2876, 2094 (C≡C), 1628 and 1613 (C=O and C=C), 1502, 1489, 1452, 1410, 1375, 1251, 1034, 935, 817 cm^{-1}.

^1H NMR: δ = 7.00 (td, J = 2.1, 4.4 Hz, 0.2 H, NCH= of minor rotamer), 6.87 (s, 0.2 H), 6.86 (s, 0.8 H), 6.76 (s, 0.8 H), 6.74 (s, 0.2 H), 6.08 (td, J = 2.1, 4.3 Hz, 0.8 H, NCH= of major rotamer), 5.96 (s, 2 H), 5.31 (td, J = 2.5, 4.4 Hz, 0.2 H, NCH=C*H* of minor rotamer), 5.14 (td, J = 2.5, 4.4 Hz, 0.8 H, NCH=C*H* of major rotamer), 3.94 (t, J = 8.8 Hz, 1.6 H), 3.64 (t, J = 8.7 Hz, 0.4 H), 3.06 (s, 0.2 H), 3.03 (s, 0.8 H), 2.65 (ddt, J = 2.1, 2.5, 8.8 Hz, 2 H).

^{13}C NMR and DEPT (M = major rotamer, m = minor rotamer): δ = 164.56 (C, M), 164.51 (C, m), 148.42 (C, m), 148.30 (C, M), 148.09 (c, M), 147.95 (C, m), 135.08 (C, m), 134.33 (C, M), 130.14 (CH, M), 129.07 (CH, m), 113.20 (C, M), 112.54 (CH, m), 112.39 (C, m), 112.39 (C, m), 112.20 (CH, m), 112.13 (CH, M), 111.83 (CH, M), 107.55 (CH, M), 106.80 (CH, m), 101.85 (CH_2, M + m), 80.48 [C, M (+ m?)], 79.64 (CH, M), 79.30 (CH, m), 46.62 (CH_2, m), 44.97 (CH_2, M), 29.81 (CH_2, m), 28.42 (CH_2, M).

Anal: Calc. for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.45; H, 4.56; N, 5.73.

1-(4-Methoxybenzoyl)azacyclopent-3-ene (64):

To a stirred solution of 4-methoxybenzoyl chloride (Aldrich, 1.708 g, 10.0 mmol) in toluene (20 mL) was added azacyclopent-3-ene hydrochloride[63] (1.15 g, 10.9 mmol), K_2CO_3 (3.00 g, 21.7 mmol) and ice-cold H_2O (20 mL). The mixture warmed to ambient temperature as the solids dissolved. After 1 h, the aq phase was separated and was extracted with EtOAc (10 mL). The combined organic phases were dried, and concentrated, leaving a thick syrup, crystallized from CCl_4–cyclohexane to give **64** (1.73 g, 85%) as beige crystals, mp 75–76.5 °C.

MS: *m/z* (relative intensity) = 203 (M^+, 65), 136 (8.9), 135 (100, $M^+ - C_4H_6N$), 92 (11), 77 (9.2).

IR (KBr): 3070, 3010, 2975, 2962, 2860, 1632 (C=O), 1608 (C=C), 1574, 1518, 1428, 1408, 1304, 1251, 1178, 1027, 844, 684 cm^{-1}.

^{1}H NMR: δ = 7.50 (AA' m, 2 H), 6.88 (BB' m, 2 H), 5.87 (m, 1 H), 5.72 (m, 1 H), 4.42 (br s, 2 H), 4.23 (br s, 2 H), 3.80 (s, 3 H).

Anal: Calc for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.44; N, 6.89. Found: C, 70.83; H, 6.45; N, 6.88.

Isomerization of 64 to 1-(4-Methoxybenzoyl)azacyclopent-2-ene (65):

Amide **64** (202.4 mg, 1.00 mmol) in 1,3-dimethylbenzene (10 mL) was stirred and deoxygenated under reflux for 25 min before $CpCo(CO)_2$ (18 mg, 0.10 mmol) was added. ^{1}H NMR spectroscopic analysis of an aliquot after 4 h under reflux showed only traces of **65**. Another portion (18 mg) of $CpCo(CO)_2$ was added. After a total of 2 d, analysis of an aliquot indicated that isomerization of **64** to **65** was complete. The dark mixture was allowed to cool to ambient temperature before solvent was removed by vacuum transfer. The residue was purified by flash chromatography over SiO_2 using EtOAc–CH_2Cl_2 (1:3) to give **65** (163.6 mg, 81%) as a greenish viscous oil.

MS: *m/z* (relative intensity) = 203 (15, M^+), 136 (8.6), 135 (100, $M^+ - C_4H_6N$), 107 (10), 92 (20), 77 (27), 64 (12).

^{1}H NMR: δ = 7.48 (AA' m, 2 H), 6.90 (BB' m, 2 H), 6.50 (narrow m, 1 H, NCH), 5.16 (narrow m, 1 H, NCH=C*H*), 3.98 (t, *J* = 8.8 Hz, 2 H, NCH_2), 3.82 (s, 3 H, OCH_3), 2.68 (ddt, *J* = 2.4, 2.4, 8.8 Hz, 2 H, CH_2CH=CH).

Anal: Calc. for $C_{12}H_{13}NO_2$: C, 70.92; 6.44; N, 6.89. Found: C, 70.54; H, 6.42; N, 6.91.

1-(6-Bromo-1,3-benzodioxol-5-ylcarbonyl)azacyclopent-3-ene (61):

Crude acid chloride **48**, mp 88.5–90°C, derived from acid **46** (972 mg, 3.97 mmol), was used to acylate azacyclopent-3-ene hydrochloride (550 mg, 5.21 mmol) as in the preparation of **64**. The crude product after removal of solvents weighed 1.121 g (95%) and consisted of analytically pure, fine crystals, mp 145.5–148°C.

MS: *m/z* (relative intensity) = 298 (5.6), 297 (41), 296 (6.0), 295 (40), 230 (10), 229 (100), 228 (10), 227 (100), 216 (25), 201 (17), 199 (18), 149 (35), 145 (12), 143 (22), 135 (14), 121 (12), 119 (10), 91 (10), 90 (15), 69 (22), 68 (22), 67 (15), 65 (18), 63 (21), 62 (36), 61 (11).

IR (NaCl, $CHCl_3$): ν = 3010, 2906, 2868, 1642 (C=O), 1619 (C=C), 1504, 1486, 1452, 1240, 1042 cm^{-1}.

^{1}H NMR: δ = 6.96 (s, 1 H), 6.72 (s, 1 H), 5.97 (s, 2 H), 5.82–5.90 (m, 1 H), 5.70–5.77 (m, 1 H), 4.37–4.40 (m, 2 H), 3.97–4.01 (m, 2 H).

^{13}C NMR: δ = 166.92, 148.78, 147.55, 132.01, 125.69, 125.11, 112.83, 109.62, 107.14, 102.03, 54.51, 52.69.

Anal: Calc. for $C_{12}H_{10}NO_3Br$: C, 48.67; H, 3.40; N, 4.73. Found: C, 48.61; H, 3.40; N, 4.75.

1-(6-Ethynyl-1,3-benzodioxol-5-ylcarbonyl)azacyclopent-3-ene (62):

A deoxygenated solution of **61** (169.2 mg, 0.582 mmol), TMSA (0.25 mL, 1.8 mmol, 3 equiv), and $PdCl_2(PPh_3)_2$ (10.5 mg, 0.026 equiv) in freshly distilled Et_3N (15 mL) was stirred under reflux for 6.5 h. The brown residue which remained after concentration of the mixture was purified by filtration through a plug of SiO_2 and by radial chromatography (2 mm SiO_2 plate, EtOAc–CH_2Cl_2 1:7 eluant) to give 161.8 mg of a golden viscous oil. To a solution of the oil in MeOH (5 mL) was added aq KOH (5%, 3 drops). After 30 min, the yellow mixture was diluted with H_2O (20 mL) and extracted with Et_2O (4 × 20 mL). The combined extracts were washed with brine (2 × 20 mL), dried, and concentrated to furnish a yellow solid (89.6 mg), recrystallized from THF–hexanes to give **62** (58.1 mg, 41%) as golden needles, mp 187–190°C.

MS: *m/z* (relative intensity) = 241 (16, M^+), 240 (32), 227 (6.2), 226 (45), 214 (12), 213 (17), 212 (7.9), 174 (17), 173 (100, $M^+ - C_4H_6N$), 146 (38), 145 (34), 115 (18), 89 (52), 88 (17), 87 (80), 86 (38), 68 (14), 67 (19), 63 (14), 62 (16).

IR (KBr): ν = 3220 (CC–H), 2955, 2922, 2880, 2862, 1641 (C=O), 1613 (C=C), 1503, 1465, 1420, 1395, 1363, 1260, 1201, 1148, 1033, 1008, 927, 870, 782, 676 cm^{-1}.

^{1}H NMR: δ = 6.89 (s, 1 H), 6.74 (s, 1 H), 5.97 (s, 2 H), 5.81–5.88 (m, 1 H), 5.68–5.73 (m, 1 H), 4.36 (br s, 2 H), 4.07 (br s, 2 H), 3.03 (s, 1 H).

^{13}C NMR: δ = 167.53, 148.48, 147.75, 135.72, 125.57 125.27, 112.25, 112.18, 106.53, 101.80, 80.65, 79.09, 54.43, 52.81.

Anal: Calc. for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60, N, 5.81. Found: C, 69.41; H, 4.75; N, 5.72.

Cocyclization of 61 with 4 to {1-{6-[(1,2,3,4-η^4)-2,3-Bis-(trimethylsilyl)-1,3-cyclobutadien-1-yl]-1,3-benzodioxole-5-carbonyl}azacyclopent-3-ene}(η^5-2,4-cyclopentadien-1-yl)cobalt (63)

From separate syringes, deoxygenated solutions of **62** (122.2 mg, 0.507 mmol) in dry diglyme (5 mL) and of $CpCo(CO)_2$ (90 mg, 0.500 mmol) in **4** (3 mL) were added to irradiated, stirred, deoxygenated **4** (5 mL) under reflux, over the course of 6 h. After an additional 1.5 h, the mixture was allowed to cool, and the volatiles were removed by vacuum transfer. TLC analysis of the orange oily residue showed one yellow spot, with only traces of other compounds. Radial chromatography (1 mm Al_2O_3 plate, EtOAc–CH_2Cl_2, 1:25) gave 232.7 mg of oily **63**, contaminated with diglyme (^{1}H NMR). Recrystallization from aq MeOH and drying of the product overnight in vacuo over P_4O_{10} gave pure **63** (160.1 mg, 59%) as yellow crystals, mp 151–152°C.

MS: *m/z* (relative intensity) = 535 (11, M^+), 437 (1.8, $M^+ - Me_3SiC_2H$), 366 (16), 365 [100, $M^+ - (Me_3Si)_2C_2$], 149 (16), 124 (13, $CoCp^+$), 97 (16), 73 (81).

IR (KBr): ν = 2960, 2900, 2860, 1643 (C=O), 1621 (C=C), 1510, 1493, 1438, 1248, 1039, 857, 840, 817 cm^{-1}.

^{1}H NMR: δ = 6.83 (s, 1 H), 6.61 (s, 1 H), 5.94 (s, 2 H, OCH_2O), 5.78–5.88 (m, 1 H), 5.60–5.67 (m, 1 H), 4.82 (s, 5 H, Cp), 4.47 (s, 1 H, cyclobutadiene H), 4.38 (br d, *J* ≈ 15 Hz, 1 H), 4.19 (br d, *J* ≈ 15 Hz, 1 H), 3.98 (br d, *J* ≈ 15 Hz, 1 H), 3.73 (br d, *J* ≈ 15 Hz, 1 H), 0.14 (s, 9 H), 0.02 (s, 9 H).

Anal: Calc. for $C_{27}H_{34}CoNO_3Si_2$: C, 60.53; H, 6.40; N, 2.62. Found: C, 60.40; H, 6.47; N, 2.68.

Optimized Cocyclization of 5c with 4 to {(1,2,3,12b-η^4)-3a-*endo*, 4,5,12c-*endo*-Tetrahydro-2,3-bis(trimethylsilyl)-7*H*-[1,3]dioxolo-[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one}(η^5-2,4-cyclopentadien-1-yl)cobalt (66a), {(1,2,3,12b-η^4)-3a-*exo*,4,5,12c-*exo*-Tetrahydro-2,3-bis(trimethylsilyl)-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one}(η^5-2,4-cyclopentadien-1-yl)cobalt (66b), {1-{6-[(1,2,3,4-η^4)-2,3-Bis(trimethylsilyl)-1,3-cyclobutadien-1-yl]-1,3-benzodioxole-5-carbonyl}azacyclopent-2-ene}(η^5-2,4-cyclopentadien-1-yl)cobalt (67):

In a 50 mL three-necked round-bottom flask equipped with stir bar, immersion thermometer, glass stopper and coil reflux condenser a mixture of dry THF (15 mL) and **4** (15 mL) was deoxygenated under reflux. A slide projector lamp powered at 60 V was trained on the flask. Meanwhile, a solution of **5c** (365.7 mg, 1.52 mmol) in **4** (2 mL) and THF (6 mL) was degassed by three cycles of freeze-pump-thaw before it was blanketed with N_2 and $CpCo(CO)_2$ (426 mg, 2.36 mmol, 1.5 equiv) was added.

The resulting solution was added to the boiling (77–78°C), irradiated **4**–THF mixture via syringe over the course of 19 h. ^{1}H NMR spectroscopic analysis of the residue remaining after vacuum transfer of the volatiles showed **66a**, **66b**, and **67** to be present in a ratio of ≈ 5.4:3.6:1. The mixture was flash chromatographed over SiO_2 (2.5 × 21 cm) using deoxygenated EtOAc–CH_2Cl_2 (1:50, 1:9, 1:4, 0.25 L each). Fractions 1–3 afforded **67** (27.3 mg, 3.4%) as a yellow semisolid. A sample from a previous run, exhibiting identical NMR spectra, had mp 142–150°C.

MS: *m/z* (relative intensity) = 535 (14, M^+), 467 (2.1, $M^+ - C_4H_6N$), 437 (2.5, $M^+ - Me_3SiC{\equiv}CH$), 366 (19), 365 [100, $M^+ - (Me_3Si)_2C_2$], 339 (3.2), 338 (4.0), 306 (3.6), 299 (3.1), 277 (3.8), 271 (5.8), 269 (4.8), 268 (4.7), 229 (4.7), 132 (7.6), 131 (15), 81 (11), 78 (11), 73 (19), 69 (23).

IR (KBr): ν = 2950, 2895, 1638 (C=O), 1615 (C=C), 1505, 1493, 1429, 1245, 1108, 1038, 840 cm^{-1}.

^{1}H NMR: δ = 7.01 (narrow m, 0.15 H, NCH of minor rotamer), 6.84 (s, 0.85 H), 6.67 (s, 0.3 H), 5.95 (s, 2 H), 5.84 (narrow m, 0.85 H,

NCH of major rotamer), 5.29 (narrow m, 0.15 H, NCH=C*H* of minor rotamer), 5.00 (narrow m, 0.85 H, NCH=C*H* of major rotamer), 4.81 and 4.82 (two s, total 5 H, Cp of major and minor rotamers, respectively), 4.47 (s, 0.15 H) and 4.40 (s, 0.85 H) (cyclobutadiene H), 3.75–4.00 (m, 1.7 H, NCH_2 of major rotamer), 3.3–3.6 (m, 0.3 H, NCH_2 of minor rotamer), 2.5–2.7 (m, 2 H, NCH_2CH_2 of both rotamers), 0.05 and 0.15 [slightly br s, total 18 H, $Si(CH_3)_3$ of both rotamers].

Anal: Calc. for $C_{27}H_{34}NO_3CoSi_2$: C, 60.53; H, 6.40; N, 2.62. Found: C, 60.61; H, 6.59; N, 2.39.

Fractions 8–15 were combined and rotary evaporated to near-dryness. Pentane was added to initiate crystallization of the residue. The supernatant was removed with a pipet and **66a** and **66b** (526.8 mg, 65 %) were obtained as burgundy flakes, mp 195–215 °C.

MS: *m/z* (relative intensity) = 535 (22, M^+), 534 (13), 533 (30), 460 (20), 411 (21, $M^+ - CpCo$), 410 (36), 409 (14), 322 (11), 97 (14), 96 (10), 84 (14), 83 (18), 73 (100).

IR (KBr): ν = 2950, 2916, 2895, 2852, 1643 (C=O), 1615, 1601, 1500, 1473, 1453, 1425, 1410, 1390, 1322, 1265, 1245, 1034, 1013, 863, 834, 806, 754 cm^{-1}.

^1H NMR of major isomer **66a**: δ = 7.40 (s, 1 H), 6.32 (s, 1 H), 5.98 (d, J = 1.3 Hz, 1 H), 5.96 (d, J = 1.3 Hz, 1 H), 5.03 (d, J = 0.8 Hz, 1 H), 4.79 (s, 5 H), 4.27 (d, J = 10.3 Hz, 1 H), 3.95 (dd, J = 7.4, 11.5 Hz, 1 H), 3.17 (ddd, J = 5.4, 11.5, 12 Hz, 1 H), 2.66 (ddd, J = 6.7, 10.3, 11 Hz, 1 H), 1.68 (ddd, J = 5.4, 6.7, 12 Hz, 1 H), 0.74 (dddd, J = 7.4, 11, 12, 12 Hz, 1 H), 0.38 (s, 9 H), 0.21 (s, 9 H).

^1H NMR of minor isomer **66b**: δ = 7.50 (s, 1 H), 6.65 (s, 1 H), 6.00 (d, J = 1.2 Hz, 1 H), 5.95 (d, J = 1.2 Hz, 1 H), 5.59 (d, J = 0.9 Hz, 1 H), 4.49 (s, 5 H), ≈ 4.25 (obscured by signal from major isomer), 2.83 (ddd, J = 5.6, 6.4, 12 Hz, 1 H), 2.36 (d, J = 7.7 Hz, 1 H), 2.0–2.25 (m, 2 H), 1.57 (m, 1 H), 0.41 (s, 9 H), 0.24 (s, 9 H).

^{13}C NMR and DEPT of major isomer **66a**: δ = 162.15 (C=O), 150.09 (C), 146.08 (C), 140.65 (C), 124.58 (C), 108.24 (CH), 105.54 (CH), 101.39 (OCH_2O), 87.61 (CH of diene), 84.22 (C–Si), 80.98 (CH, Cp), 63.44 (CHN), 61.81 (C), 55.93 (C), 49.80 (CH_2N), 41.76 (*C*HCHN), 34.62 (*C*H_2CH_2N), 2.10 (CH_3), 1.72 (CH_3).

Partial ^{13}C NMR and DEPT of minor isomer **66b**: δ = 160.92 (C=O), 150.79 (C), 145.49 (C), 139.54 (C), 108.53 (CH), 101.39 (OCH_2O), 100.73 (CH), 81.64 (CH, Cp), 80.73 (C), 59.18 (CH), 47.06 (CH), 43.43 (CH_2), 33.72 (CH_2), 3.40 (CH_3), 3.29 (CH_3).

Anal: Calc. for $C_{27}H_{34}CoNO_3Si_2$: C, 60.53; H, 6.40; N, 2.62. Found: C, 60.36; H, 6.55; N, 2.64.

Demetalation of 66a,b to give 3a-*cis*,4,5,12c-*cis*-Tetrahydro-2,3-bis(trimethylsilyl)-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (68):

A mixture of complexes **66a,b** (52.9 mg, 0.099 mmol) was demetalated with $Fe(NO_3)_3 \cdot 9H_2O$ by the same procedure used for **38** to give, after crystallization from Et_2O–hexanes, **68** (36.5 mg, 90 %) as beige crystals, mp 171–174 °C.

MS: *m/z* (relative intensity) = 411 (36, M^+), 410 (35), 396 (13), 368 (9.2), 339 (25), 338 (100), 322 (15), 241 (28), 149 (13), 147 (10), 97 (14), 95 (11), 85 (12), 83 (15), 81 (23), 73 (32).

IR (KBr): ν = 2940, 2890, 2855, 1645 (C=O), 1609, 1498, 1468, 1408, 1387, 1365, 1272, 1246, 1225, 1032, 935, 863, 834 cm^{-1}.

^1H NMR: δ = 7.49 (s, 1 H), 6.86 (s, 1 H), 6.30 (d, J = 1.7 Hz, 1 H), 6.01 (d, J = 1.2 Hz, 1 H), 5.99 (d, J = 1.2 Hz, 1 H), 4.46 (dd, J = 1.7, 12.4 Hz, 1 H), 3.90 (dd, J = 7.2, 11.5 Hz, 1 H), 3.23 (ddd, J = 6, 12.3, 12.4 Hz, 1 H), 3.05 (ddd, J = 5.2, 11.5, 12 Hz, 1 H), 2.19 (ddd, J = 5.2, 6, 12 Hz, 1 H), 1.49 (dddd, J = 7.2, 12, 12, 12.3 Hz, 1 H), 0.27 (s, 18 H).

^{13}C NMR and DEPT: δ = 162.84 (C), 150.78 (C), 148.16 (C), 141.90 (C), 132.68 (C), 126.14 (C), 124.66 (C), 121.05 (CH), 107.95 (CH), 102.85 (CH), 101.67 (OCH_2O), 54.94 (CHN), 43.18 (*C*HCHN), 41.67 (CH_2N), 33.26 (*C*H_2CH_2N), 1.95 (CH_3), 1.65 (CH_3).

Anal: Calc. for $C_{22}H_{29}NO_3Si_2$: C, 64.19; H, 7.10; N, 3.40. Found: C, 64.16; H, 7.18; N, 3.42.

Protodesilylation of 68 to 3a-*cis*,4,5,12c-*cis*-Tetrahydro-2-trimethylsilyl-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (69):

A 5 mm o.d. NMR tube with standard taper 14/20 female joint was purged with N_2 before **68** (40.5 mg, 0.0983 mmol) was added, and $CDCl_3$, filtered through a plug of Al_2O_3 (activity I), was added. CF_3CO_2H (15.5 µL, 0.201 mmol, 2.0 equiv) was added to the resulting solution, and additional filtered $CDCl_3$ was used to rinse the walls of the tube. The pale yellow solution (volume ≈ 1 mL) was degassed by three freeze-pump-thaw cycles before the tube was sealed. The progress of the reaction was monitored by ^1H NMR spectroscopy. After 4 d, **68** was not detectable and **69** was the major product. However, peaks from one or perhaps two additional products were seen (integrations relative to one proton of **69** = 1.0 H): δ = 7.75 (s, 0.2 H), 7.10 (s, 0.1 H), 7.08 (s, 0.1 H), 6.72 (dd, J = 3.3, 9.7 Hz, 0.1 H), 6.56 (d, J = 9.7 Hz, 0.1 H), 6.04 (a, 0.3 H), 5.88–5.96 (m, 0.15 H), 5.78–5.85 (m, 0.1 H), 3.2–3.4 (m, overlapping with signal from **69**), 2.63 (ddd, J = 6, 7, 13 Hz, 0.1 H), 2.51 (ddd, J = 6, 7.5, 13 Hz, 0.1 H), 1.97 ppm (dd?, J = 10, 12 Hz, 0.1 H). The solution was concentrated in a flask on a rotary evaporator, then under oil pump vacuum for 5 min, leaving a greenish-yellow oil (45.2 mg). The product was crystallized from Et_2O-petroleum ether to give **69** (26.3 mg, 79 %) as a beige powder, mp 145–152 °C. An analytical sample was prepared by dissolution in Et_2O and filtration through a cotton plug in a pipet. The filtrate was deoxygenated and chilled by bubbling N_2 through it and hexanes were added in portions over several min to initiate crystallization. The mixture was stored under N_2 at −40 °C overnight before the supernatant was carefully removed with a pipet. Storage in vacuo left **69** (20.4 mg) as beige microcrystals, mp 147–153 °C.

MS: *m/z* (relative intensity) = 339 (70, M^+), 338 (58), 322 (12), 310 (16), 296 (17), 266 (27), 264 (10), 149 (16), 137 (11), 296 (17), 266 (27), 264 (10), 149 (16), 137 (11), 97 (10), 95 (13), 83 (13), 81 (42), 73 (29), 71 (17), 69 (100).

IR (KBr): ν = 2952, 2893, 1648 (C=O), 1612, 1470, 1411, 1369, 1271, 1247, 1229, 1038, 840 cm^{-1}.

^1H NMR ($CDCl_3$, CF_3CO_2H in reaction mixture): δ = 7.45 (s, 1 H), 6.95 (s, 1 H), 6.22 (d, J = 2.2 Hz, 1 H, ArC=C*H*), 6.18 (dd, J = 0.6, 4.8 Hz, 1 H, CHC*H*=CSiMe$_3$), 6.04 (d, J = 1.1 Hz, 1 H), 6.03 (d, J = 1.1 Hz, 1 H), 4.68 (slightly br d, J = 13.5 Hz, 1 H), 3.99 (dd, J = 7.4, 11.6 Hz, 1 H), 3.1–3.3 (m, 2 H), 2.31 (ddd, J = 5.4, 7.0, 12.2 Hz, 1 H), 1.65 (dddd, J = 7.4, 12.2, 12.2, 12.2 Hz, 1 H), 0.15 (s, 9 H).

Anal: Calc. for $C_{19}H_{21}NO_3Si$: 67.22; H, 6.24; N, 4.13. Found: C, 66.92; H, 6.08; N, 4.00.

Fluoride-Induced Protodesilylation of 66a and 66b to [(1,2,3,12b-η^4)-3a-*endo*,4,5,12c-*endo*-Tetrahydro-3-trimethylsilyl-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one](η^5-2,4-cyclopentadien-1-yl)cobalt (70a) and [(1,2,3,12b-η^4)-3a-*exo*,4,5,12c-*exo*-Tetrahydro-3-trimethylsilyl-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one](η^5-2,4-cyclopentadien-1-yl)cobalt (70b):

To a stirred, deoxygenated solution of **66a** and **66b** (≈ 5:1 mixture, 53.5 mg, 0.100 mmol total) in dry THF (2 mL) was added Bu_4NF in THF (0.200 mL of 1 M, 2 equiv) via syringe. After 3.8 h, the mixture was processed directly by flash chromatography on SiO_2. First to be isolated were 3.7 mg (8 %) of impure **70b** as a red semisolid residue. From its ^1H NMR spectrum and that of a crude mixture of **70a** and **70b** from another experiment the following signals could be identified: δ = 7.48 (s, 1 H, H-8), 6.67 (s, 1 H, H-12), 5.99 (d, J = 1.2 Hz, 1 H, OC*H*HO), 5.95 (d, J = 1.2 Hz, 1 H, OCH*H*O), 5.72 (d, J = 4.3 Hz, 1 H, diene H), 5.12 (d, J = 4.3 Hz, 1 H, diene H), 4.47 (s, 5 H, Cp), 4.30 (dd, J = 7.6, 11.9 Hz, 1 H), 2.86 (ddd, J = 6.3, 11.7, 11.7 Hz, 1 H), 2.38 (d, J = 7.6 Hz, 1 H, H-12c-*endo*), 2.1–2.3 (m, 2 H?), 0.12 (s, 9 H).

Further elution gave pure **70a** (20.8 mg, 45 %) as fine brown needles, mp 201–203 °C.

MS: *m/z* (relative intensity) = 463 (M^+, 23), 462 (29), 461 (100, $M^+ - 2H$), 396 (14), 395 (61, $M^+ - C_4H_6N$), 339 (26, $M^+ - CpCo$), 338 (22), 322 (8.2), 320 (8.4), 266 (23), 73 (26).

IR (KBr): ν = 3015, 2945, 2915, 2850, 1640 (C=O), 1596, 1498, 1472, 1431, 1409, 1316, 1265, 1245, 1032, 834 cm^{-1}.

^1H NMR: δ = 7.39 (s, 1 H, H-8), 6.33 (s, 1 H, H-12), 5.98 (d, J = 1.2 Hz, 1 H), 5.96 (d, J = 1.2 Hz, 1 H), 5.41 (d, J = 4.4 Hz, 1 H; enhanced in a difference NOE experiment on irradiation of the trimethylsilyl resonance at δ = 0.10, H-2), 5.32 (d, J = 4.4 Hz, 1 H; enhanced in a difference NOE experiment when the s at 6.33, assigned to H-12, was irradiated, H-1), 4.77 (s, 5 H), 4.25 (d, J = 10.4 Hz, 1 H; irradiation caused the peak at 2.67 to simplify to a dd), 3.98 (dd, J = 7.6, 11.7 Hz, 1 H), 3.19 (ddd, J = 5.5, 11.7, 12 Hz, 1 H), 2.67 (ddd, J = 6.8, 10.4, 11 Hz, 1 H), 1.75 (ddd, J = 5.5, 6.8, 12 Hz, 1 H), 0.89 (dddd, J = 7.6, 11, 12, 12 Hz, 1 H), 0.10 (s, 9 H).

^{13}C NMR and DEPT: δ = 161.85 (C=O), 150.11 (C), 146.19 (C), 140.43 (C), 124.88 (C), 108.27 (CH), 105.33 (CH), 101.40 (CH_2), 81.54 (CH of diene), 80.46 (CH, Cp), 79.91 (CH of diene), 63.81 (CHN), 58.94 (C of diene terminus), 53.01 (C of diene terminus), 49.58 (CH_2N), 41.47 (CHCHN), 34.57 (CH_2CH_2), −0.08 (CH_3).

Anal: Calc. for $C_{24}H_{26}CoNO_3Si$: C, 62.19; H, 5.65; N, 3.02. Found: C, 61.90; H, 5.75; N, 2.91.

Complete Desilylation of 66a,b to Give 4,5-Dihydro-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (73):

To a stirred, deoxygenated mixture of CsF (1.36 mmol, 16.4 molar equiv) and DMSO (3 mL) was added **66a,b** (44.4 mg, 0.0829 mmol). TLC analysis indicated that monodesilylation to **70a,b** was complete in 6 h. The mixture was stirred and heated at 55–60 °C for 24 h without change. After 3 d at 79–80 °C, **70a,b** or any other colored compounds had disappeared and the black mixture was cooled, diluted with H_2O (20 mL), and extracted with CH_2Cl_2 (3 × 10 mL). The combined CH_2Cl_2 extracts were washed with H_2O (10 mL), dried, and concentrated, leaving 34.1 mg of a brown gum. ^1H NMR analysis showed two major products, **73** and an unidentified compound, in a ratio of 2:1. Radial chromatography (1 mm SiO_2 plate, EtOAc–petroleum ether, 2:1) afforded **73** (5.2 mg, 24%) as a beige powder, mp 227–229 °C (lit[65] 232–234 °C).

^1H NMR: δ = 7.89 (s, 1 H), 7.73 (d, J = 7.9 Hz, 1 H), 7.53 (s, 1 H), 7.27 (d, J = 7.2 Hz, 1 H), 7.17 (dd, J = 7.2, 7.9 Hz, 1 H), 6.11 (s, 2 H), 4.47 (br t, J = 8 Hz, 2 H), 3.41 (t, J = 8 Hz, 2 H). Further elution with EtOAc gave 2.9 mg of an unidentified material, mp 145–150 °C.

Sequential Desilylation and Demetalation of 66a,b to Give 3a-*cis*,4,5,12c-*cis*-Tetrahydro-3-trimethylsilyl-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (71):

Complexes **66a,b** (710.6 mg, 1.326 mmol) in THF (15 mL) were desilylated with Bu_4NF in THF (1 M, 2.0 mL, 1.5 equiv) in 2 h at ambient temperature as in the preparation of **67a,b**. The flask was chilled in ice for several min before a deoxygenated solution of $Fe(NO_3)_3 \cdot 9H_2O$ (1.342 g, 3.33 mmol, 2.5 equiv) in THF (5 mL) and H_2O (2 mL) was added. (Addition of less than 2.5 equiv of oxidant resulted in incomplete demetalation, even after 0.5 h at 0 °C. After 2 min, the mixture was poured into ice-cold water and extracted with Et_2O. Further workup gave a yellow solid residue, which was dissolved in CH_2Cl_2 and passed through a column of SiO_2 (1 × 5 cm), eluting with EtOAc–CH_2Cl_2. Solvent removal left 435.3 mg (97%) of pale yellow crystals, mp 185–200 °C. Recrystallization from EtOAc–hexanes afforded chromatographically homogeneous **71** (383 mg, 85%) as colorless crystals, mp 198–200.5 °C. An analytical sample from a previous run (yield, 90%) exhibited 197–201 °C.

MS: m/z (relative intensity) = 339 (M^+, 89), 338 (75), 324 (10), 310 (12), 296 (14), 266 (100, $M^+ - SiMe_3$), 264 (17), 236 (7.0), 208 (8.0), 180 (5.8), 73 (25).

IR (KBr): ν = 2955, 2885, 1648 (C=O), 1616, 1600, 1502, 1476, 1411, 1392, 1368, 1275, 1246, 1230, 1192, 1118, 1036, 939, 913, 838, 776, 754 cm^{-1}.

^1H NMR: δ = 7.48 (s, 1 H), 6.86 (s, 1 H), 6.26 (slightly br d, J = 5.7 Hz, 1 H; enhanced in a difference NOE experiment when s at 0.14 was irradiated, H-2), 6.09 (dd, J = 2.1, 5.7 Hz, 1 H; enhanced in a difference NOE experiment when s at 6.86, associated with H-12, was irradiated, H-1), 5.99 (d, J = 1.2 Hz, 1 H), 5.97 (d, J = 1.2 Hz, 1 H), 4.56 (slightly br d, J = 12.9 Hz, 1 H), 3.95 (dd, J = 7.4, 11.5 Hz, 1 H), 3.20 (dddd, J = 0.8, 6.5, 12.4, 12.9 Hz, 1 H), 3.08 (ddd, J = 5.2, 11.5, 12 Hz, 1 H), 2.21 (ddd, J = 5.2, 6.5, 12 Hz, 1 H), 1.50 (dddd, J = 7.4, 12, 12, 12.4 Hz, 1 H), 0.14 (s, 9 H).

^{13}C NMR and DEPT: δ = 162.08 (C=O), 150.68 (C), 148.17 (C), 140.69 (C), 131.97 (C), 129.28 (CH), 128.66 (C), 124.64 (C), 116.08 (CH), 107.85 (CH), 102.71 (CH), 101.59 (CH_2), 55.35 (CH), 41.48 (CH_2), 40.49 (CH), 32.70 (CH_2), −1.38 (CH_3).

Anal: Calc. for $C_{19}H_{21}NO_3Si$: C, 67.22; H, 6.24; N, 4.13. Found: C, 67.40; H, 6.26; N, 4.13.

Protodesilylation of 71 to 3a-*cis*,4,5,12c-*cis*-Tetrahydro-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,4,1-*de*]phenanthridin-7-one (72):

A resealable thick-walled glass tube fitted with a Teflon stopcock was charged with **71** (340.3 mg, 1.00 mmol), and $CHCl_3$ (15 mL) that had been filtered through activity grade I Al_2O_3 and CF_3CO_2H (154 µL, 2.00 mmol) were added. The mixture was immediately subjected to three cycles of freeze-pump-thaw. The sealed tube was heated in an oil bath at 55 °C. After 2.5 d, an aliquot was removed from the cooled mixture under positive N_2 pressure. ^1H NMR and TLC analyses indicated that ≈ 75% of **71** had been converted into **72** and some aromatic products. Another 77 µL (1.00 mmol) of CF_3CO_2H was added and heating continued for 3 d, causing most of **71** to disappear. Volatile material was removed by vacuum transfer and flash chromatography of the gummy residue over SiO_2 using deoxygenated EtOAc–petroleum ether provided **72** contaminated with **73** and other impurities. Crystallization from Et_2O resulted in **72** as off-white crystals (180 mg, 67%), still not completely free of **73** (ca. 10% by NMR analysis), but nevertheless used as such in the next step: mp 136–141 °C.

MS: m/z (relative intensity) = 267 (M^+, 100), 266 (73), 239 (6), 226 (7), 208 (7).

^1H NMR of the reaction mixture with CF_3CO_2H present: δ = 7.43 (s, 1 H), 6.92 (s, 1 H), 6.18 (dd, J = 2.2, 5.7 Hz, 1 H), 6.04 (d, J = 1.2 Hz) and 6.03 (d, J = 1.2 Hz) (OCH_2O) and m for one of the diene H (total 3 H), 5.97 (ddd, J = 0.8, 5.6, 8.9 Hz, 1 H), 4.73 (slightly br d, J ≈ 13 Hz, 1 H), 3.97 (dd, J = 7.4, 11.8 Hz, 1 H), 3.1–3.3 (m, 2 H), 2.32 (ddd, J = 5.4, 6.9, 12.3 Hz, 1 H), 1.70 (dddd, J = 7.4, 12, 12, 12.3 Hz, 1 H).

^{13}C NMR and DEPT: δ = 159.73 (C=O), 152.23 (C), 148.52 (C), 133.04 (C), 128.10 (CH), 125.81 (C), 121.61 (C), 121.34 (CH), 118.11 (CH), 107.94 (CH), 103.16 (CH), 102.16 (CH_2), 56.35 (CH), 42.30 (CH_2), 37.59 (CH), 31.96 (CH_2).

Anal: Calc. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.68; N, 4.78; N, 5.17.

Hydrogenation of 72 over PtO_2 to give 73, 1,2,3,3a-*cis*,4,5,12b-*cis*,12c-*cis*-Octahydro-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (75) and 1,2,3,3a,4,5-Hexahydro-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (74):

A stirred mixture of diene **72** (14.1 mg), PtO_2 (2.5 mg), and EtOAc (2 mL) was blanketed with N_2, then with H_2, at 1 atm. After 10.5 h, TLC analysis of an aliquot showed that **72** was absent, and one spot other than that for **73** was visible. ^1H NMR spectroscopic analysis of an aliquot confirmed the consumption of the **72**, but showed four compounds, **73**, **74**, **75**, and **76**, in a ratio of 2:1:1:1. After 2 d, the mixture was filtered, the filtrate concentrated, and the residue (12.7 mg) radially chromatographed (1 mm SiO_2 plate, EtOAc–CH_2Cl_2, gradient 1:2 to 1:1). Initial fractions provided 4.5 mg of beige powder, a mixture of **73** and **75**, in a ratio of 1:1.

MS (at 15 eV to avoid extensive fragmentation of parent ion): m/z (relative intensity) = 272 (15.6), 271 (M^+ for **75**, 100), 270 (5.8), 269 (4.9), 267 (1.8), 266 (13), 265 (M^+ for **73**, 87), 264 (0.9).

^1H NMR of **75**: δ = 7.51 (s, 1 H, H-8), 6.60 (s, 1 H, H-12), 5.97 (d, J = 1.3 Hz) and 5.96 (d, J = 1.3 Hz) (total 2 H, OCH_2O), 3.84 (narrow m, 1 H), 3.75 (slightly br t, J = 11 Hz, 1 H), 3.61 (slightly br dt, J = 8, 11 Hz, 1 H), 2.77 (ddd, J = 4.8, 4.8, 12.0 Hz, 1 H), 2.26 (ddd, J = 5.7, 11, 11 Hz, 1 H), 1.85–2.0 (m, 1 H) (some resonances obscured by H_2O peak 1.5–1.8), 1.0–1.4 (m, 4 or 5 H).

Subsequent fractions contained **74**[13] (6.0 mg).

MS: *m/z* (relative intensity) = 270 (30), 269 (M^+, 100), 268 (27), 241 (30), 240 (39), 170 (8.9), 142 (9.4), 86 (27), 85 (25).

IR (KBr): ν = 3050, 3020, 2920, 2845, 1680, 1603, 1483, 1452, 1420, 1241, 1032, 685 cm^{-1}.

Homogeneous Hydrogenation of 72 to 2,3,3a-*cis*,4,5,12c-*cis*-Hexahydro-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (76):

Hydrogen gas was bubbled through a stirred, deoxygenated mixture of **72** (30.0 mg, 0.112 mmol) and $ClRh(PPh_3)_3$ (5.4 mg, 0.0058 mmol, 5%) in methylbenzene (5 mL). Within 5 min, the catalyst dissolved to form a pale yellow solution. After 4.5 h, ^1H NMR spectroscopic analysis of an aliquot showed that the conversion of **72** into **76** was complete. The residue remaining after rotary evaporation was filtered through flash SiO_2 in a pipet, using EtOAc–CH_2Cl_2 (1:4) to eluate the product; after solvent removal **76** (26.3 mg), mp 130–145 °C, remained. Recrystallization from CH_2Cl_2–heptane afforded pure **76** (18.1 mg, 60%) as colorless crystals, mp 144–147 °C (lit[8] 145–147 °C).

^1H NMR (C_6D_6): δ = 8.04 (s, 1 H, H-8), 6.76 (s, 1 H, H-12), 5.63 (ddd, J = 2.2, 2.2, 6.6 Hz, 1 H, H-1), 5.24 (d, J = 1.1 Hz) and 5.22 (d, J = 1.1 Hz) (total 2 H, OCH_2O), 3.4–3.7 (m, 3 H), 1.65–1.85 (m, 2 H), 1.4–1.6 (m, 2 H), 1.1–1.25 (m, 2 H), 0.75 (dddd, J = 4.2, 12, 12, 12 Hz, 1 H).

Cocyclization of 5c with 45 to give [(1,2,3,12b-η^4)-3a-*endo*,4,5,12c-*endo*-Tetrahydro-3-methoxy-2-trimethylsilyl-7*H*-[1,3]dioxolo[4,5-*j*]-pyrrolo[3,2,1-*de*]phenanthridin-7-one](η⁵-2,4-cyclopentadien-1-yl)-cobalt (78), [(1,2,3,12b-η^4)-3a-*endo*,4,5,12c-*endo*-Tetrahydro-2-methoxy-3-trimethylsilyl-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]-phenanthridin-7-one](η⁵-2,4-cyclopentadien-1-yl)cobalt (79), 3,3a,4,5-Tetrahydro-2-methoxy-1-trimethylsilyl-7*H*-[1,3]dioxolo-[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (80), and [(1,2,3,12b-η^4)-3a-*exo*,4,5,12c-*exo*-Tetrahydro-3-methoxy-2-trimethylsilyl-7*H*-[1,3]-dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one](η⁵-2,4-cyclopentadien-1-yl)cobalt (81):

To a solution of **5c** (723.5 mg, 3.00 mmol) and **45** (1.1512 g, 8.99 mmol, 3.0 equiv) in methylbenzene (20 mL), previously degassed by five freeze-pump-thaw cycles, was added $CpCo(CO)_2$ (1.25 g, 6.94 mmol, 2.3 equiv). The resulting solution was added over the course of 2.5 d to stirred, irradiated (ELH lamp powered at 40 V) methylbenzene (50 mL) at reflux. After an additional 8 h, the mixture was allowed to cool before volatiles were removed by vacuum transfer. ^1H NMR spectroscopic analysis of the crude product indicated the presence of **78**, **79**, and **80** in a ratio of 3:2:1. The mixture was flash chromatographed over SiO_2 (125 g, 4 × 20 cm), eluting with deoxygenated EtOAc–petroleum ether–Et_3N (gradient 50:150:1 to 25:25:1), then EtOAc–Et_3N (200:1). Fractions 2 and 3 (174.6 mg, mp 210–215 °C dec) consisted of **79** and **80** in a ratio of 5:1. Fractions 4–10 (0.25 g) contained the two products in a ratio of 1.5:1 (total yield of **79** and **80**, 22 and 10%, respectively). Fractional crystallization of fractions 2–10 from CH_2Cl_2–heptane (bubbling N_2 through the solution to evaporate CH_2Cl_2, and to chill and deoxygenate the mixture) was repeated three times to afford pure **79** (97.4 mg, 6.6%) as fine brick-red needles, mp 228–229 °C.

MS: *m/z* (relative intensity) = 491 (M^+, 100), 461 (12), 426 (12), 425 (43), 418 (11), 389 (17), 368 (13).

IR (KBr): ν = 2965, 2910, 1646 (C=O), 1473, 1461, 1456, 1428, 1411, 1270, 1228, 1037, 838, 809 cm^{-1}.

^1H NMR: δ = 7.41 (s, 1 H), 6.38 (s, 1 H), 5.98 (d, J = 1.3 Hz, 1 H), 5.96 (d, J = 1.3 Hz, 1 H), 5.02 (s, 1 H), 4.77 (s, 5 H), 4.12 (d, J = 10.5 Hz, 1 H), 3.99 (dd, J = 7.7, 11.7 Hz, 1 H), 3.91 (s, 3 H), 3.18 (ddd, J = 5.6, 11.7, 11.7 Hz, 1 H), 2.71 (ddd, J = 7.0, 10.5, 11 Hz, 1 H), 1.79 (ddd, J = 5.6, 7.0, 12 Hz, 1 H), 0.94 (dddd, J = 7.7, 11, 11.7, 12 Hz, 1 H), 0.14 (s, 9 H).

^{13}C NMR and DEPT: δ = 161.76 (C=O), 150.03 (C), 146.65 (C), 140.79 (C), 134.86 (C, C–OMe), 125.53 (C), 108.36 (CH), 105.56 (CH), 101.41 (OCH_2O), 80.35 (CH, Cp), 64.48 (CH), 63.80 (CH), 54.79 (CH_3O), 50.63 (C at diene terminus), 49.45 (CH_2N), 43.40 (C at diene terminus), 43.02 (*C*HCHN), 34.26 (*C*H_2*C*H_2N), 0.13 (CH_3).

Anal: Calc. for $C_{25}H_{28}CoNO_4Si$: C, 60.84; H, 5.72; N, 2.84. Found: C, 60.64; H, 5.76; N, 2.91.

No attempts were made to purify and characterize **80** rigorously here, as this task was accomplished more conveniently with its more efficient preparation from **79** (vide infra).

Continued chromatography of the reaction mixture led to collection of fractions 13–21, which after rotary evaporation gave complex **78** (448.8 mg, 30.3%) as copper-colored flakes, mp 230–234 °C.

MS: *m/z* (relative intensity) = 493 (M^+, 22), 492 (25), 391 (76), 474 (10), 462 (12), 461 (43), 426 (11), 425 (44), 418 (11), 395 (15), 339 (25), 338 (100, M^+ – CpCo – OMe), 337 (10), 322 (20), 278 (9.6), 124 (17), 73 (30).

IR (KBr): ν = 3085, 2955, 2890, 1644 (C=O), 1599, 1498, 1467, 1410, 1350, 1322, 1275, 1241, 1222, 1197, 1132, 1032, 932, 839, 803 cm^{-1}.

^1H NMR: δ = 7.36 (s, 1 H), 6.40 (s, 1 H), 5.95 (m, 2 H), 4.82 (s, 5 H), 4.60 (s, 1 H), 4.29 (d, J = 11.0 Hz, 1 H), 4.05 (dd, J = 7.9, 11.6 Hz, 1 H), 3.48 (s, 3 H), 3.22–3.4 (m, 2 H), 1.88 (ddd, J = 6.0, 6.6, 12 Hz, 1 H), 1.03 (dddd, J = 8, 11, 11, 12 Hz, 1 H), 0.27 (s, 9 H).

^{13}C NMR and DEPT: δ = 161.80 (C=O), 149.90 (C), 146.00 (C), 140.66 (C), 124.40 (C), 109.26 (*C*–OMe), 107.97 (CH), 105.57 (CH), 101.33 (OCH_2O), 80.15 (CH, Cp), 79.58 (CH of diene), 67.24 (C–Si), 63.81 (CHN), 59.26 (C at diene terminus), 55.07 (CH_3O), 49.16 (CH_2N), 40.67 (*C*HCHN), 31.91 (*C*H_2*C*H_2N), – 0.48 (CH_3).

Anal: Calc. for $C_{25}H_{28}CoNO_4Si$: C, 60.84; H, 5.72; N, 2.84. Found: C, 60.70; H, 5.66; N, 2.84.

From further elution, fractions 22–26 (53.1 mg) contained **78** and **81** in a ratio of 3:1 (by ^1H NMR), separable by radial chromatography on a 2 mm SiO_2 plate, employing EtOAc–CH_2Cl_2 (gradient 1:7 to 1:2) as eluant. In this way, more pure **78** (35.9 mg, 2.4%, total yield 32.7%) was obtained, in addition to its isomer **81** (6.7 mg, 0.5%), a red viscous oil. Crystallization from $CDCl_3$–petroleum ether gave 5.4 mg of a pale orange solid, mp 110–115 °C.

MS: *m/z* (relative intensity) = 493 (M^+, 58), 492 (34), 491 (100, M^+ – 2 H), 474 (8.5), 462 (12), 461 (40), 425 (52), 395 (15), 368 (30), 367 (80, M^+ – CpCo), 339 (24), 338 (88), 323 (27), 322 (92), 278 (41), 124 (29), 73 (32).

^1H NMR: δ = 7.47 (s, 1 H), 6.64 (s, 1 H), 5.98 (d, J = 1.0 Hz, 1 H), 5.95 (d, J = 1.0 Hz, 1 H), 5.03 (s, 1 H), 4.45 (s, 5 H), 4.41 (dd, J = 8.5, 12 Hz, 1 H), 3.40 (s, 3 H), 3.06 (ddd, J = 6, 12, 12 Hz, 1 H), 2.65 (d, J = 7.2 Hz, 1 H, NCH_{endo}), 2.56 (ddd, J = 3, 8, 12 Hz, 1 H), 2.1–2.3 (m, 2 H), 0.35 (s, 9 H).

Fluoride-Induced Protodesilylation of 78 to [(1,2,3,12b-η^4)-3a-*endo*, 4,5,12c-*endo*-Tetrahydro-3-methoxy-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo-[3,2,1-*de*]phenanthridin-7-one](η⁵-2,4-cyclopentadien-1-yl)cobalt (82):

To an oxygen-free, stirred solution of **78** (81.2 mg, 0.165 mmol) and Et_3N (36 µL, 0.26 mmol) in dry THF (5 mL) was added Bu_4NF in THF (1 M, 0.25 mL, 1.5 equiv). After 0.7 h, the mixture was poured onto a flash SiO_2 column (1.5 × 15 cm) packed in EtOAc–petroleum ether (1:3). The column was eluted with deoxygenated EtOAc. Colored fractions were combined and concentrated, and the residue was recrystallized from CH_2Cl_2–petroleum ether to give **82** (53.9 mg, 77%) as deep-garnet-red rods, mp 200–201 °C.

MS: *m/z* (relative intensity) = 421 (M^+, 22), 420 (12), 419 (50), 389 (12), 354 (14), 353 (77, $M^+ - C_4H_6N$), 298 (18), 297 (86, M^+ – CpCo), 296 (34), 295 (11), 282 (32, M^+ – CpCo—Me), 267 (22), 266 (100, M^+ – CpCo – OMe), 265 (13), 264 (12), 254 (24), 189 (68), 124 (19, $CpCo^+$), 59 (11).

IR (KBr): ν = 3080, 2970, 2935, 2880, 2855, 1642 (C=O), 1618, 1601, 1505, 1476, 1412, 1347, 1341, 1271, 1224, 1200, 1168, 1140, 1079, 1033, 1011, 919, 820, 799, 651 cm^{-1}.

^1H NMR: δ = 7.37 (s, 1 H, H-8), 6.40 (s, 1 H, enhanced when Cp s at 4.77 was irradiated in an NOE difference spectrum, H-12), 5.96 (m,

2H), 4.98 (dd, J = 1, 4.8 Hz, 1H, H-2), 4.80 (d, J = 4.8 Hz, 1H, signal enhanced in an NOE difference spectrum when s at 6.40 was irradiated, H-1), 4.77 (s, 5H), 4.42 (d, J = 11.0 Hz, 1H), 4.05 (dd, J = 7.8, 11.8 Hz, 1H), 3.35 (s, 3H), 3.27 (ddd, J = 5.7, 11.8, 11.8 Hz, 1H), 3.19 (dddd, J = 1, 7.3, 11.0, 11 Hz, 1H, irradiation of the dd at 4.98 eliminated the smallest coupling; irradiation of the dddd at 3.19 simplified the peaks at 4.98, 4.42, 1.98, 1.12), 1.98 (ddd, J = 5.7, 7.3, 11 Hz, 1H), 1.12 (dddd, J = 7.8, 11, 11, 11.8 Hz, 1H).

Anal: Calc. for $C_{22}H_{20}CoNO_4$: C, 62.71; H, 4.78; N, 3.33. Found: C, 62.57; H, 4.71; N, 3.30.

Oxidative Demetalation of 78 to *cis*-3a,4,5,12c-Tetrahydro-3-methoxy-2-trimethylsilyl-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (83):

To a deoxygenated, stirred, ice-cold solution of **78** (84.5 mg, 0.172 mmol) and Et_3N (48 µL, 0.344 mmol, 2.0 equiv) in 10 mL of THF was added a deoxygenated solution of $CuCl_2 \cdot 2H_2O$ (125.1 mg, 0.734 mmol, 4.3 equiv) in THF–H_2O (9:1, 5 mL). After 5 min, the green–blue cloudy mixture was poured into ice water (30 mL) and extracted with CH_2Cl_2 (4 × 10 mL). The partly emulsified mixture was filtered through a pad of Filter Aid as needed. The combined CH_2Cl_2 extracts were washed with aq $NaHCO_3$ (5%, 20 mL), H_2O (20 mL), dried, and concentrated to give **83** (57.6 mg, 91%) as a yellow solid, mp 187–190°C. An analytical sample (35.4 mg, 56%) from THF–hexanes at −50°C was obtained as pale yellow crystals, mp 193.5–196.5°C.

MS: m/z (relative intensity) = 369 (M^+, 90), 368 (36), 355 (25), 354 (100, M^+ − Me), 338 (11), 326 (15), 322 (18), 297 (14), 296 (75, M^+ − $SiMe_3$), 295 (12), 264 (15), 81 (17), 73 (28), 71 (17), 69 (42).

IR (KBr): ν = 2945, 2900, 1640 (C=O), 1561, 1498, 1469, 1408, 1368, 1276, 1245, 1219, 1199, 1166, 1094, 1037, 1006, 933, 838 cm^{-1}.

^1H NMR: δ = 7.46 (s, 1H), 6.85 (s, 1H), 6.07 (d, J = 2.0 Hz, 1H, H-1), 5.98 (d, J = 1.2 Hz, 1H), 5.97 (d, J = 1.2 Hz, 1H), 4.71 (slightly br d, J = 13 Hz, 1H, irradiation of which simplified the ddd at 3.34), 4.05 (dd, J = 7.5, 11.4 Hz, 1H), 3.70 (s, 3H), 3.34 (ddd, J = 7.0, 12.5, 13 Hz, 1H), 3.14 (ddd, J = 5.1, 11.4, 12 Hz, 1H), 2.31 (ddd, J = 5.1, 7.0, 12.1 Hz, 1H), 1.72 (dddd, J = 7.5, 12, 12.1, 12.5 Hz, 1H), 0.15 (s, 9H).

^{13}C NMR and DEPT: δ = 165.82 (C=O), 151.15 (C), 147.73 (C), 133.12 (C), 124.09 (C), 121.0 (CH of diene), 120.71 (C), 109.01 (C), 107.73 (CH), 102.83 (CH), 102.14 (OCH_2O), 58.46 (CHN), 55.91 (CH_3O), 42.56 (CH_2N), 38.21 (CHCHN), 31.85 (CH_2CH_2N), −0.68 (CH_3) (one aryl C missing).

Anal: Calc. for $C_{20}H_{23}NO_4Si$: C, 65.03; H, 6.28; N, 3.79. Found: C, 64.96; H, 6.16; N, 3.71.

Oxidative Demetalation of 79 to *cis*-3a,4,5,12c-Tetrahydro-2-methoxy-3-trimethylsilyl-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (84):

In a procedure similar to that described for **78**, **79** (45.9 mg, 0.093 mmol) was oxidized by $CuCl_2 \cdot 2H_2O$ (70.6 mg, 0.414 mmol, 4.45 equiv) in THF (10 mL) and Et_3N (22.8 mg, 0.225 mmol, 2.4 equiv) to afford, after crystallization from Et_2O–hexanes, **84** (13.9 mg, 41%) as fine white needles, mp 109–112°C.

MS: m/z (relative intensity) = 369 (M^+, 100), 368 (58), 355 (25), 354 (95, M^+ − Me), 324 (10), 296 (32), 280 (15), 265 (11), 264 (20), 85 (17), 83 (11), 81 (28), 73 (23), 71 (28), 69 (66), 68 (10).

IR (KBr): ν = 2950, 2895, 1647 (C=O), 1613, 1502, 1472, 1412, 1383, 1368, 1279, 1239, 1130, 1038, 1029, 941, 868, 840 cm^{-1}.

^1H NMR: δ = 7.50 (s, 1H), 6.89 (s, 1H), 6.12 (d, J = 2.2 Hz, 1H, H-1), 6.02 (d, J = 1.2 Hz, 1H), 6.01 (d, J = 1.2 Hz, 1H), 4.54 (dd, J = 2.0, 12.6 Hz, 1H, irradiation simplified the ddd at 3.18), 3.93 (dd, J = 7.2, 11.4 Hz, 1H), 3.61 (s, 3H, OCH_3), 3.18 (ddd, J = 6.5, 12.5, 12.6 Hz, 1H), 3.05 (ddd, J = 5.2, 11.8, 11.8 Hz, 1H), 2.15 (ddd, J = 5.2, 6.5, 12 Hz, 1H), 1.51 (dddd, J = 7.2, 12, 12, 12 Hz, 1H), 0.16 (s, 9H).

Anal: Calc. for $C_{20}H_{23}NO_4Si$: C, 65.03; H, 6.28; N, 3.79. Found: C, 64.85; H, 6.18; N, 3.78.

Thermolysis of 79 to give 80, *trans*-3,3a, 4,5-Tetrahydro-2-methoxy-3-trimethylsilyl-7*H*-[1,3]dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (86) and 4,5-Dihydro-3-trimethylsilyl-7*H*-[1,3]dioxolo-[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (87):

A $(Me_3Si)_2NH$-rinsed, oven-dried 25 mL round-bottom flask with stir bar and reflux condenser was charged with dry 1,3-dimethylbenzene (10 mL) and **79** (70.8 mg, 0.143 mmol). The stirred solution was deoxygenated with argon before it was heated at reflux for 18 h, the time necessary for **79** to disappear (TLC). The black mixture was concentrated by vacuum transfer and a portion of the residue in filtered (basic Al_2O_3) $CDCl_3$ passed through a small plug of neutral Al_2O_3 (activity III) into an NMR tube; peaks due to **80**, **86**, and **87** (ratio 10:2:1) could be identified in the ^1H NMR spectrum of the filtrate. One, perhaps two unidentified compounds were present in slightly lesser amounts than **87**. The crude mixture was radially chromatographed on a 2 mm SiO_2 plate, using deoxygenated EtOAc–CH_2Cl_2 (gradient 1:7 to 1:4) as eluant.

Fractions 3–5 contained slightly impure **86** (2.3 mg, 4.8%).

^1H NMR: δ = 7.91 (s, 1H), 7.74 (d, J = 7.9 Hz, 1H, H-1 or H-2), 7.57 (s, 1H), 7.31 (d, J = 7.9 Hz, 1H, H-2 or H-1), 6.12 (s, 2H, OCH_2O), 4.47 (t, J = 8 Hz, 2H, NCH_2), 3.45 (t, J = 8 Hz, 2H, NCH_2CH_2), 0.34 [s, 9H, $Si(CH_3)_3$].

Evaporation of fractions 6–13 left brick-red foam (12.3 mg), mostly **80** (^1H NMR), but containing ≈ 30% of an unidentified CpCo-diene complex.

Fractions 14–19 afforded **80** (23.3 mg, 44%) as a beige foam, homogeneous by ^1H NMR spectroscopic and TLC analysis. The compound crystallized after Et_2O was added to the oily residue from evaporation of a $CDCl_3$ solution, to give beige crystals, mp 180–190°C.

MS: m/z (relative intensity) = 369 (M^+, 43), 368 (17), 367 (15), 355 (16), 354 (58, M^+ − Me), 296 (28, M^+ − $SiMe_3$), 295 (10), 280 (14), 278 (11), 265 (14), 264 (19), 122 (24), 89 (15), 77 (13), 75 (14), 74 (24), 73 (100).

IR (KBr): ν = 2945, 2895, 1694, 1610 (isoquinolone), 1491, 1422, 1292, 1249, 1121, 1097, 1039, 942, 840, 831 cm^{-1}.

^1H NMR (C_6D_6): δ = 8.32 (s, 1H, H-8), 6.62 (s, 1H, H-12), 5.34 (s, 2H), 4.16 (dd, J = 8.3, 12.1 Hz, 1H, H-5α), 3.45 (ddd, J = 5.7, 11.7, 12 Hz, 1H, H-5β; irradiation caused the peaks at 4.16, 1.86, 1.18 to simplify), 3.27 (dddd, J = 5.8, 6.4, 8.7, 12.1 Hz, 1H, H-3aβ; irradiation had no effect on the peaks at 4.16 and 3.45, but changed the resonances at 1.86 and 1.18, and simplified the two dd near 2.9 to two d, each with J = 19), 3.18 (s, 3H), 2.98 (dd, J = 5.8, 19.2, 1H, H-3α), 2.88 (dd, J = 8.7, 19.2 Hz, 1H, H-3β), 1.86 (ddd, J = 5.7, 6.4, 12, 1H, H-4β; irradiation had no effect on the peaks at 4.16, 2.98 and 2.88, but changed the peak at 3.27 and simplified that at 3.45), 1.18 (dddd, J = 8.3, 11.7, 12, 12 Hz, 1H, H-4α; irradiation had no effect on the signals at 2.98 and 2.88, but reduced noticeably the complexity of the multiplets at 4.16, 3.27 and 1.86), 0.24 [s, 9H, $Si(CH_3)_3$].

^{13}C NMR and DEPT (C_6D_6): δ = 161.32 (C), 159.69 (C), 151.92 (C), 147.09 (C), 140.43 (C), 134.16 (C), 121.85 (C), 112.34 (C), 106.82 (CH, C-8 or C-12), 101.65 (SiC-1), 101.62 (OCH_2O), 99.94 (CH, C-12 or C-8), 55.27 (OCH_3), 47.17 (CH_2N), 42.64 (CH, C-3a), 31.74 (CH_2), 25.45 (CH_2), 1.07 [$Si(CH_3)_3$].

Anal: Calc. for $C_{20}H_{23}NO_4Si$: C, 65.03; H, 6.28; N, 3.79. Found: C, 65.09; H, 6.28; N, 3.85.

Fractions 22–25 delivered **86** (6.4 mg, 12%) as beige crystals, mp 187–189°C (preheated from 180°C).

MS: m/z (relative intensity) = 369 (M^+, 25), 368 (12), 367 (11), 354 (16, M^+ − Me), 296 (15, M^+ − $SiMe_3$), 295 (10), 280 (17), 278 (12), 265 (24), 264 (37), 195 (15), 123 (11), 122 (53), 89 (10), 77 (25), 75 (30), 74 (15), 73 (83).

IR (KBr): ν = 3080, 2970, 2950, 2895, 1669, 1618, 1596, 1492, 1480, 1457, 1296, 1241, 1038, 847 cm^{-1}.

^1H NMR: δ = 7.79 (s, 1H), 6.97 (s, 1H), 6.04 (s, 2H, OCH_2O), 5.59 (d, J = 2.5 Hz, 1H, H-1), 4.42 (dd, J = 9.0, 12.4 Hz, 1H), 3.88 (ddd,

J = 6.3, 11.5, 12.4 Hz, 1 H), 3.68 (s, 3 H, CH_3O), 3.42 (ddd, J = 7.2, 11.3, 16.0 Hz, 1 H), 2.58 (ddd, J = 6.3, 7.2, 12.5 Hz, 1 H), 2.05 (dd, J = 2.5, 16.0 Hz, 1 H), 1.87 (dddd, J = 9.0, 11.3, 11.5, 12.5 Hz, 1 H), 0.15 (s, 9 H).

^{1}H NMR (C_6D_6): δ = 8.45 (s, 1 H), 7.04 (s, 1 H), 5.42 (d, J = 2.5 Hz, 1 H, H-1), 5.28 (d, J = 1.2 Hz, 1 H), and 5.27 (d, J = 1.2 Hz, 1 H) (OCH_2O), 4.19 (dd, J = 9.0, 12.2 Hz, 1 H), 3.42 (ddd, J = 7, 11, 12 Hz, 1 H), 3.18 (s, 3 H, CH_3O), 2.87 (ddd, J = 7.3, 11.3, 16.1 Hz, 1 H), 1.72 (ddd, J = 7.3, 11, 12 Hz, 1 H), 1.70 (dd, J = 2.5, 16.1 Hz, 1 H), 1.05 (dddd, J = 9.0, 11, 11, 12 Hz, 1 H), 0.10 (s, 9 H).

^{13}C NMR and DEPT (C_6D_6): δ = 158.51 (C), 155.81 (C), 152.08 (C), 146.99 (C), 136.23 (C), 132.56 (C), 107.05 (CH), 104.87 (C), 101.51 (OCH_2O), 99.38 (CH), 89.77 (*C*H=COMe), 54.41 (CH_3O), 47.63 (CH_2N), 41.06 (CH), 33.85 (CH), 32.46 (*C*H_2CH), −0.46 [$Si(CH_3)_3$] (one aryl peak missing).

Thermolysis of 78.

By a procedure similar to that used for **79**, a deoxygenated solution of **78** (46.2 mg) in 1,3-dimethylbenzene (5 mL) was stirred and heated at reflux for 16 h before solvent was removed by vacuum transfer. The red and black residue was taken up in CH_2Cl_2 and passed through 1 × 2 cm of basic Al_2O_3, eluting the products with EtOAc–CH_2Cl_2 (1:4). Concentration of the combined eluates left an orange flaky solid (36.3 mg). ^{1}H NMR spectroscopic analysis indicated the presence of **78**, **83**, and **85** in a ratio of 4:2:1, and the absence of **80**.

For **84**: ^{1}H NMR: δ = 7.87 (s, 1 H), 7.77 (s, 1 H), 7.51 (s, 1 H), 6.11 (s, 2 H, OCH_2O), 4.45 (t, J = 8.2 Hz, 2 H, NCH_2), 3.99 (s, 3 H, OCH_3), 3.59 (t, J = 8 Hz, 2 H, NCH_2CH_2), 0.32 [s, 9 H, $Si(CH_3)_3$].

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