

Cobalt-Mediated [2+2+2] Cycloadditions of Pyrimidine Derivatives to Alkynes

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Abstract: The scope and limitations of the cobalt-mediated [2+2+2] cycloaddition of pyrimidine derivatives to alkynes has been investigated. The 5,6-double bond of these heterocyclic nuclei has been found to participate in an entirely intermolecular fashion to generate chemo- and stereoselectively novel, fused and substituted 5,6-dihydropyrimidine cobalt complexes, which upon oxidative demetallation liberate the correspond-

ing new heterocyclic ligand. On the other hand, 1-alkynyl pyrimidines have been found to be suitable partners in the cocyclization with disubstituted alkynes, such as bis(trimethylsilyl)acetylene (BTMSA) or dimethyl 2-butyne-1,4-diolate (DMAD), to allow the direct prep-

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aration of hitherto unknown dihydro-pyrido[3,2-*ij*]quinazoline cobalt complexes. Effects of the substitution on the pyrimidine nucleus, the cocyclization partner, the complex auxiliary, and the reaction conditions were examined, and in some cases competing pathways that lead to [CpCo(cyclobutadienes)], cyclopentadienone complexes, and compounds that arise from a C–H activation-type reaction were observed.

Introduction

The cobalt-mediated [2+2+2] cycloaddition is a powerful synthetic method to form carbon–carbon bonds,^[1] and provides chemo-, regio- and stereoselective pathways to various natural products and compounds of theoretical interest.^[2] Studies on heteroaromatic double bonds have shown the ability of these systems to readily participate in the cobalt-mediated cyclization with alkynes. This methodology has been used for the rapid construction of complexed dihydroindoles by the reaction of either the indole 2,3-double bond^[3] or the pyrrole 2,3-double bond.^[4] Imidazoles,^[5] furans, and thiophenes^[6] have also been found to be effective in this process. The success of such heterocyclic olefins and particularly of enamides in these transformations,^[7] led us to consider pyrimidines as cyclization partners.^[8] Because of the extremely diverse physiological activity exhibited by the

pyrimidine nucleus^[9] and its presence in a multitude of biologically important molecules, for example nucleic acids, extensive synthetic attention has been given to this core substrate.^[10] More particularly, the selective modification of nucleosides is a challenge in the quest for the development of medicinal agents effective for the treatment of cancer and viral infections, such as herpes and AIDS.^[11] Part of this effort has involved the utilization of the 5,6-double bond for synthetic elaboration by means of inter- and intramolecular electrophilic additions^[12] or cycloaddition processes, such as 6 π -electrocyclizations, [2+2] cycloadditions, [3+2] photoadditions,^[13] and [4+2] Diels–Alder reactions with appropriately functionalized pyrimidones.^[14] In this paper, we wish to report the scope and limitations of our studies which are directed towards the chemo-, regio-, and stereoselective participation of pyrimidine derivatives in cobalt-mediated [2+2+2] cycloaddition reactions as a new synthetic entry to modified nucleosides.

Results and Discussion

Preparation of the cycloaddition partners: In order to examine the feasibility of cobalt-mediated cycloadditions to the pyrimidine nucleus, we prepared various derivatives by adaptation or by the application of standard literature procedures. In general, these substrates cannot be used in their N–H form in the [2+2+2] cycloaddition because of their insolubility in common organic solvents. However, 1*N*,3*N*-

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dimethylated substrates **1a–d**,^[15] imides **1e–g**,^[16] imidates **2** and **4**,^[17] or enamines **3**^[16,18] show good solubility in most organic solvents and can be readily prepared in good yields. Similarly, permethylation (*N* and *O*)^[19] or selective *O*-acylation^[20] of nucleosides allows the preparation of soluble derivatives **1h–l** (Tables 1–4). Compounds **1–4** were employed as substrates in potential intermolecular [2+2+2] cycloaddition to α,ω -diynes.

Conversely, 1*N*-alkylation or acylation of pyrimidines **5** gives rise to suitable functionalized substrates **6** (Table 5) for the study of the cocyclization with substituted alkynes, such as BTMSA or DMAD. Since attempted direct selective alkylation at N1 of both uracil and thymine resulted in a mixture of 1,3-dialkylpyrimidinediones,^[21] we chose a two-step sequence through the readily available 3*N*-aroyl intermediates **5** ($R^1 = \text{COAr}$; Table 5).^[22]

Alkylation of pyrimidinediones **5** with NaOH in glyme, KOH in acetone or, under phase-transfer catalysis, Et_3N in ethanol or diazabicyclononene (DBN), resulted in very poor yields of **6** (< 5 %) and partial or complete hydrolysis of the amide function. However, it was found that by the use of anhydrous K_2CO_3 in a mixture of dry DMSO and dry THF in a ratio of 1:8, the alkylation of **5** either with 4-iodo-1-butyne or 5-iodo-1-pentyne proceeded cleanly to give only the desired 1-alkylpyrimidines **6a–d** in acceptable yields. Compound **6e** could be obtained selectively in 32 % yield with Et_3N in a mixture of $\text{EtOH}/\text{H}_2\text{O}$ (1:1). Direct acylation of uracil (**5**: $R^1 = R^2 = \text{H}$) with 4-pentynoyl chloride^[23] following a reported procedure afforded **6f** in 60 % yield.^[13] The cyano derivatives **6g** ($n = 1$) and **6h** ($n = 1$) have been prepared in 60 % and 66 % yields, respectively, by Michael addition of the corresponding pyrimidinediones to acrylonitrile,^[24] while **6i** ($n = 2$, $R^1 = R^2 = \text{H}$) was obtained in 37 % yield by direct alkylation of **5** ($R^1 = \text{COPh}$, $R^2 = \text{H}$) with 4-chlorobutyroni-

Abstract in French: Nous décrivons une étude détaillée sur la réactivité de diverses pyrimidines vis-à-vis de la réaction de cycloaddition [2+2+2] induite par les complexes du cobalt(I). Dans un premier temps, nous avons montré que la double liaison C5–C6 de ces hétérocycles participe de manière intermoléculaire à une cycloaddition chimio- et stéréosélective avec des α,ω -diynes pour conduire aux complexes diéniques du cobalt attendus. Ces dérivés organométalliques constituent des précurseurs de nouveaux squelettes hétérocycles de type quinoxaline par simple décomplexation oxydante. Par ailleurs, l'utilisation de 1-alcynyl pyrimidines permet de réaliser des cocyclisations avec des dérivés acétyléniques disubstitués comme le bis(triméthylsilyl)acétylène (BTMSA) ou le diméthyl 2-butyn-1,4-dioate (DMAD) conduisant à la construction du squelette dihydropyrido[3,2-ij]quinoxaline sous forme de complexe diénique du cobalt. Nous avons étudié en détail les différents paramètres de ces cycloadditions en faisant varier la substitution sur le noyau hétérocyclique, la nature du complexe de cobalt et les conditions opératoires afin d'éviter la formation parasite de complexes cyclobutadiényles, cyclopentadiénones et des sous-produits issus de réactions d'activation de liaisons C–H.

Table 1. Preparation of pyrimidines **1a–l**.

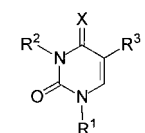
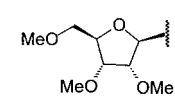
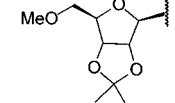
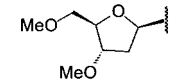
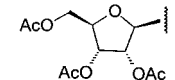
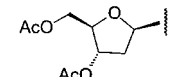
						
	R ¹	R ²	R ³	X	Yield (%)	
1a	Me	Me	H	O	89	
1b	Me	Me	Me	O	97	
1c	Me	Me	F	O	88	
1d	Me	Me	H	S	92	
1e	Me	Me	H	NMe	66	
1f	Me	Me	H	NEt	54	
1g	COPh	COPh	H	NCOPh	48	
1h		Me	H	O	99	
1i		Me	H	O	100	
1j		Me	H	O	85	
1k		H	H	O	80	
1l		H	H	O	94	

Table 2. Preparation of pyrimidines **2a,b**.

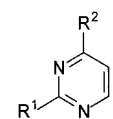
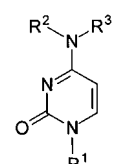
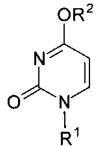
			
	R^1	R^2	Yield [%]
2a	Cl	Cl	75
2b	OMe	OMe	64

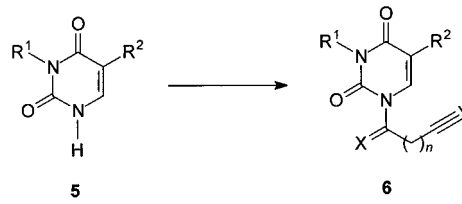
Table 3. Preparation of pyrimidines **3a–d**.

				
	R^1	R^2	R^3	Yield [%]
3a	H	H	Ac	59
3b	Pr	H	Ac	72
3c	Me	Me	H	80
3d	Me	Me	Me	98

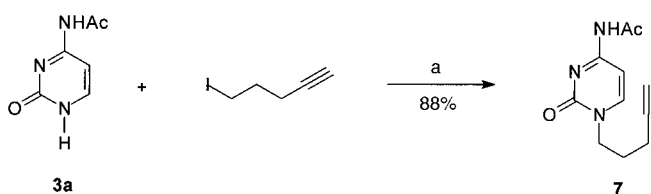
trile by the use of K_2CO_3 in THF and concomitant saponification of the benzoyl protecting group at N3. Similarly, alkylation of *N*-acetylcytosine (**3a**) gave the desired 1*N*-(1-pentyne) derivative **7** in 88 % yield (Scheme 1).

Table 4. Preparation of pyrimidines **4a–d**.


	R ¹	R ²	Yield [%]
4a	Me	Me	64
4b	Me	Et	80
4c	Me	<i>n</i> Pr	88
4d	Et	Me	88

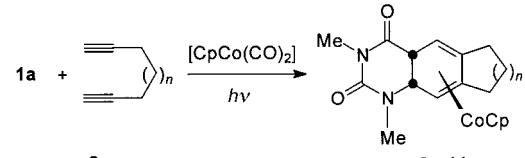
Table 5. Preparation of pyrimidines **6a–i**.


	R ¹	R ²	X	<i>n</i>	Y	Yield [%]
6a	COPh	H	H ₂	2	C–H	81
6b	COPh	H	H ₂	1	C–H	33
6c	COPh	Me	H ₂	2	C–H	76
6d	COPhNO ₂ - <i>p</i>	H	H ₂	2	C–H	35
6e	H	H	H ₂	2	C–H	32
6f	H	H	O	2	C–H	60
6g	COPh	H	H ₂	1	N	60
6h	H	H	H ₂	1	N	66
6i	H	H	H ₂	2	N	37

Scheme 1. Alkylation of acetylcytosine. Reagents and conditions: a) K₂CO₃ (1.1 equiv), DMSO, 70 °C, 8 h.

Cyclization of pyrimidines 1–4 with α,ω -diynes: We first examined the reaction of 1,3-dimethyluracil (**1a**) with α,ω -diynes **8a–c** in the presence of [CpCo(CO)₂] in refluxing, irradiated toluene (18 h). The desired complexes **9a–11a** were formed only in fair yields owing to the incomplete conversion of the starting materials. In an attempt to optimize the reaction of **1a** with 1,7-octadiyne (**8b**), the cyclization was carried out in refluxing xylene for 20 h, which resulted in the complete conversion of **1a** and a 76% isolated yield of complex **10a** (Table 6).

In contrast with the results obtained from the reaction of the pyrrole and imidazole nuclei,^[25] these results show that the heterocyclic 5,6-double bond of uracil derivative **1a** can be engaged in an intermolecular fashion to give complexes **9a–11a**, which have a *syn* configuration. Because of the lack of reference compounds, the relative stereochemistry of the ligand with respect to the CpCo fragment was assigned on the basis of the well-documented magnetic anisotropy of co-

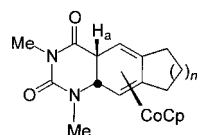
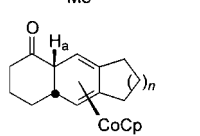
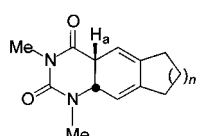
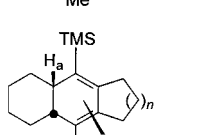
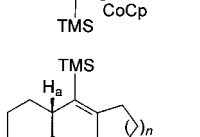
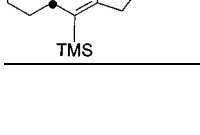
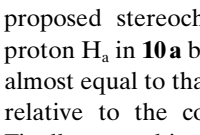
Table 6. Cycloaddition of **1a** to α,ω -diynes **8a–c**.


8a–c			9a–11a		
	<i>n</i>	<i>T</i> [°C]	Solvent	Complex	Yield [%] ^[a]
8a	1	110	toluene	9a	53 (96)
8b	2	110	toluene	10a	57 (89)
8c	3	110	toluene	11a	22 (94)
8b	2	140	xylene	10a	76

[a] Values in brackets are based on consumed **1a**.

balt.^[2,26] The observed anisotropic effect and the comparison of the chemical shifts of the methine proton H_a at the ring junction in **9a–11a** with the corresponding carbocyclic analogue **12**^[26] are consistent with the proposed stereochemistry (Table 7). In addition to the good agreement of the

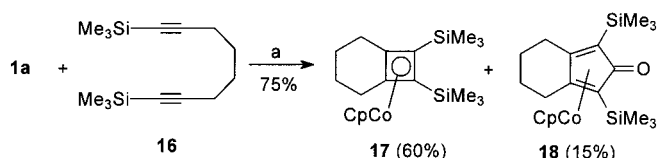
Table 7. ¹H NMR shifts (δ) for H_a and $\Delta\delta$ H_a between complexes and free ligands.

	<i>n</i>	H _a	$\Delta\delta$ H _a
 9a	1	2.71	-
 10a	2	2.67	0.13
 11a	3	2.62	-
 12	2	2.63	-
 13	2	2.54	0.13
 14	2	2.41	0.11
 15	2	2.30	0.11

proposed stereochemistry, the deshielding ($\Delta\delta$ H_a) of the proton H_a in **10a** by cobalt, relative to the free ligand **13**,^[27] is almost equal to that found for the *syn* carbocyclic complex **14** relative to the corresponding free ligand **15**^[26] (Table 7). Finally, unambiguous support for these assignments was obtained by an X-ray structural determination of **10j** (major diastereomer, vide infra).^[8]

Having shown the participation of the 5,6-double bond of uracil derivatives in the [2+2+2] cycloaddition, we then

turned our attention to the scope and limitations of this reaction. The first finding was the high sensitivity of this process to steric hindrance. Indeed, compounds **1b** and **1c**, derived from thymine and 5-fluorothymine, respectively, were not affected by prolonged irradiation in the presence of $[\text{CpCo}(\text{CO})_2]$ in refluxing toluene or xylene. Similarly, no reaction was observed with dimethyluracil **1a** and 1,8-bis(trimethylsilyl)-1,7-octadiyne (**16**),^[28] which gave rise to the formation of the known cyclobutadiene and cyclopentadienone complexes **17** and **18**^[29] (Scheme 2).



Scheme 2. Attempted cycloaddition of **1a** to 1,8-bis(trimethylsilyl)-1,7-octadiyne **16**. Reagents and conditions: a) $[\text{CpCo}(\text{CO})_2]$ (1.5 equiv), $h\nu$, toluene, 40 °C, 30 h.

The presence of a sulfur atom in **1d** also inhibited the reaction, probably by deactivation of the cobalt complex.^[30] A switch from the pyrimidinedione to the more aromatic pyrimidine core, as in **2a** and **2b**, also suppressed the $[2+2+2]$ cycloaddition.

However, imides **1e** and **1f** were successful in this reaction to give, after chromatography on neutral alumina, acceptable yields of the corresponding cobalt-complexed heterocycles, while the tri-*N*-benzoyl derivative **1g** failed to add to 1,7-octadiyne (**8b**) under the same conditions (Table 8).

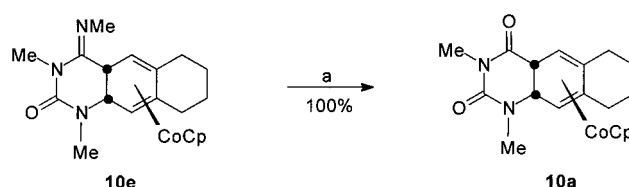
Table 8. Cyclization of **1e–g** with α,ω -diynes.

	<i>n</i>	Complex	Yield [%] ^[a]
1e	1	9e	46 (100)
1e	2	10e	79 (100)
1e	3	11e	21 (40)
1f	1	9f	40 (100)
1f	2	10f	55 (100)
1f	3	11f	22 (23)
1g	2	10g	0 (100)

[a] Values in brackets are based on consumed **1**.

The behavior of **1e** and **1f** was comparable to that of the parent pyrimidinedione **1a** and had the same regio- and stereochemical outcome. Only the 5,6-double bond of the heterocycle was involved in the cyclization, which gave only the *syn* isomer, as shown by spectral data and, furthermore, hydrolysis of **10e** gave **10a** (Scheme 3), which was identical with the sample prepared directly from **1a** (Table 6).

An extension of the method to nucleosides was of interest as a contribution to the synthesis of modified nucleosides for the development of new biologically active agents. Therefore,



Scheme 3. Hydrolysis of **10e**. Reagents and conditions: a) SiO_2 , MeOH or Al_2O_3 , H_2O , RT.

the reactivity of substrates **1h–l** towards 1,7-octadiyne (**8b**) was explored. It was gratifying that all derivatives gave the expected $[2+2+2]$ cycloadducts **10h–l** as mixtures of the four possible diastereomers in ratios that depended on the nature of the starting nucleoside (Table 9).

Table 9. Cyclization of nucleosides **1h–l** with 1,7-octadiyne (**8b**).

	L	Solvent	Complex (ratio) ^[a]	Yield [%] ^[b]
1h	CO	toluene	10h ^[c]	45 (100)
1h	CO	xylene	10h (7.5:4:1:1)	71 (94)
1i	CO	xylene	10i (2.4:1.8:1:1)	33 (54)
1j	CO	xylene	10j (45:4:1:1)	76 ^[c]
1j	C_2H_4	THF	10j (45:4:1:1)	94
1k	C_2H_4	THF	10k (1:1:1:1)	37 (59)
1l	CO	toluene	10l (1:1:1:1)	18 (23)

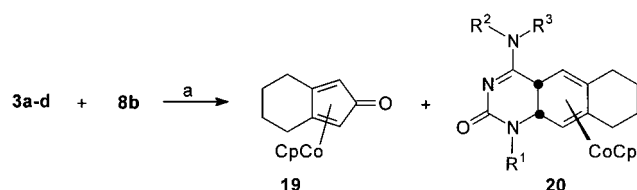
[a] Determined by ^1H NMR. [b] Values in brackets are based on consumed **1**. [c] Not determined.

This, like other related cyclizations,^[25] is strongly affected by changes in the reaction conditions. For example, the yield of **10h** was improved from 45 to 71 % by changing the solvent from toluene to boiling xylene. Even better, with $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$ ^[31] as the reagent in refluxing THF, complexes **10j** were obtained in almost quantitative yield. However, the presence of the relatively acidic N–H bond in **1k** and **1l** seems to be detrimental, since **10k** and **10l** were obtained in low yields (37 % and 18 %, respectively), even in the presence of $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$.

The observed diastereoselectivity also deserves some comments. Interestingly, we observed a very high selectivity in favor of one of the four possible isomers of **10j** (45:4:1:1) during the cycloaddition of deoxyuridine derivative **1j** with **8b** with either $[\text{CpCo}(\text{CO})_2]$ in refluxing xylene or the more efficient $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$. The corresponding uridines **1h** and **1i** gave only moderate diastereoselection, while no stereoselectivity and a very bad mass balance was observed in the case of **1k** and **1l**, regardless of the reaction conditions. Our results with regard to the diastereoselectivity observed for **1h–j** can be tentatively explained by changes in the conformation as a result of puckering in the furanose ring.^[32] It is known that pyrimidine nucleosides generally exist in the *anti* conformation; the 5,6-double bond lies more or less above the sugar ring depending on the substitution.^[33] As a

consequence, an increase in the substitution on the sugar would probably make the two faces of the olefin more accessible by the cobalt complex; this would result in a lower selectivity. The assignment of the stereochemistry was first deduced from NMR spectroscopic studies and was confirmed by X-ray diffraction analysis of **10j** (major isomer),^[8] which also supported the proposed configuration of complexes **9** and **11**.

In an effort to extend the method further, we turned our attention to the use of enamines **3**, derived from cytosine and imidates **4**. Although the enamide double bond has been found to be compatible in the [2+2+2] cycloaddition,^[7] compounds **3** gave relatively disappointing results (Scheme 4). *N*-Acetylcytosine (**3a**) failed to react with **8b** in



Scheme 4. Cycloaddition of **3** with 1,7-octadiyne **8b**. Reagents and conditions: a) $[\text{CpCo}(\text{CO})_2]$ (2 equiv), $h\nu$, toluene, reflux 20 h.

DMSO (perhaps for reasons of solubility, as **3a** is only poorly soluble in this and other solvents more typically employed in these cyclizations, such as toluene) and only led to the formation of complex **19**^[29] from the reaction of **8b** with $[\text{CpCo}(\text{CO})_2]$. In the case of **3b** and **3c**, which were soluble in toluene, once again **19** was the only organometallic complex obtained, while 9% of the desired tricyclic derivative **20d** was formed with **3d** in refluxing toluene (Scheme 4).

Changing the solvent did not help, since no reaction occurred in DME, only 6% of **20d** was obtained in THF, and in xylene extensive decomposition was observed without the generation of any isolable desired product. While it is not obvious why these cycloadditions were not successful, it is possible that, for **3a–c**, it is again the presence of an acidic N–H bond that is responsible, whereas for **3d** it may be the increased aromaticity of the system.

The results of the [2+2+2] cycloaddition of imidates **4** (Table 10) were more gratifying. Thus, **4a** provided a moderate yield (37%) of **21** with 1,7-octadiyne (**8b**, $n=2$) together with 9% of the corresponding pyrimidinedione **25** produced by the hydrolysis of the imidate function during workup. Indeed, **21** was converted quantitatively to **25** by treatment with wet silica gel. Similarly, heterocycles **4b** and **4c** gave the expected diene complexes **22** and **23**, when treated with **8b** ($n=2$), in 15% and 20% yield, respectively, accompanied by 7% of **25**. Finally, in the case of **4d**, the hydrolyzed complex **26** was the only orga-

Table 10. Cycloaddition of imidates **4** to α,ω -diynes **8a–c**.

	n	Complex	Yield [%] ^[a]
4a	2	21 + 25	37 + 9 (89)
4b	2	22 + 25	15 + 7 (73)
4c	2	23 + 25	20 + 7 (93)
4d	2	26	9 (56)
4a	1	[b]	–
4a	3	[b]	–

[a] Values in brackets are based on consumed **4**. [b] No reaction.

nometallic species isolated from the reaction mixture in 9% yield. In sharp contrast to these results, 1,6-heptadiyne (**8a**, $n=1$) and 1,8-nonadiyne (**8c**, $n=3$) failed to add to **4a** under the same experimental conditions.

Cocyclization of pyrimidines **6** with disubstituted acetylenes:

In another extension of the scope of the cyclization, the potential construction of tricyclic systems was explored by appending one of the alkyne units to the pyrimidine nucleus, as in **6** and **7**. BTMSA^[34] was chosen as the cocyclization partner owing to its very low autocyclization rate in the presence of $[\text{CpCoL}_2]$ ^[35] (Table 11). In a preliminary experiment, 1*N*-1-pentynyl derivative **6a** was photolyzed in a refluxing mixture of THF/BTMSA in the ratio 1:2 for solubility reasons. After all the starting material had been consumed, removal of the solvent and flash chromatography

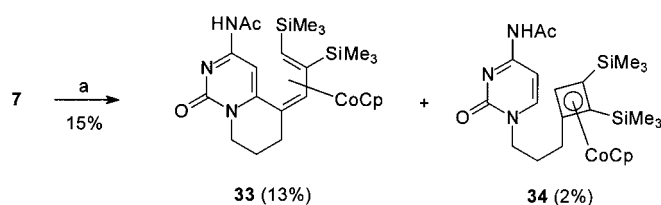
Table 11. Cocyclization of **6a–i** with disubstituted acetylenes.

	R	T [°C] ^[a]	Complex	<i>anti/syn</i> ^[b]	Yield [%] ^[c]
6a	TMS	110	27	[d]	5
6a	TMS	rt	27	5	23
6a	TMS	rt ^[e]	27 + 31	5	18 + 21
6a	COOMe	rt	28	<i>anti</i>	61
6b	COOMe	rt	[f]	–	–
6c	TMS	rt	32	–	18
6d	TMS	rt	[g]	–	–
6e	TMS	rt	29	10	35
6e	COOMe	rt	30	<i>anti</i>	73
6f	TMS	rt	[f]	–	–
6f	TMS	65	[g]	–	–
6g	TMS	85	[f]	–	–
6h	TMS	40	[f]	–	–
6i	COOMe	65	[f]	–	–

[a] Unless otherwise noted, $[\text{CpCo}(\text{CO})_2]$ was used as the reagent. [b] The designation *syn* and *anti* indicates the position of the Co atom relative to the tertiary hydrogen atoms of the ring junction. [c] Isolated. [d] Not determined. [e] $\text{L} = \text{C}_2\text{H}_4$. [f] No reaction. [g] Decomposition.

allowed the isolation of the CpCo-complex **27** as a mixture of two diastereomers in only 5 % yield (Table 11). In an effort to improve this outcome, the effects of the temperature, the cocyclization partner, the cobalt auxiliary, and the structure of the starting pyrimidines were examined.

Thus, at room temperature, the reaction of **6a** provided **27** in 23 %. Surprisingly, under these conditions addition of [CpCo(C₂H₄)₂]^[31] resulted not only in **27** but also in a new addition product, the butadiene complex **31**, derived by formal C–H activation.^[36] A similar result was obtained with cytosine derivative **7**, which gave a 23 % yield of a mixture of the two cobalt complexes **33** and **34** after photolysis for 20 h at room temperature in the presence of BTMSA and [CpCo(CO)₂] (Scheme 5).



Scheme 5. Cycloaddition of **7** with BTMSA. Reagents and conditions: a) [CpCo(CO)₂] (2 equiv), BTMSA (6 equiv), *hν*, THF, RT, 20 h.

Previous studies^[3,5] have shown that DMAD was also a very good partner in [2+2+2] cycloadditions and therefore its potential in the present system was investigated. Photolysis of **6a** and DMAD in the presence of [CpCo(CO)₂] at room temperature led to a 61 % yield of complex **28** as only one diastereomer (Table 11). Unfortunately, under the same conditions **6b**, which has a shorter tether length (*n* = 1), failed to react. In the case of the thymine derivative **6c**, the cyclobutadiene complex **32** was the only organometallic species isolated from the reaction mixture in 18 % yield. This result shows, once again, the high sensitivity of the reaction to steric hindrance (*vide supra*). Compound **6d** proved to be very unstable under the reaction conditions; it completely degraded. In light of the failure of **3a–c** and **10k,l** to undergo cycloadditions, it is of interest that the N3-unprotected pyrimidine **6e** did react with BTMSA (35 %) and DMAD (73 %) to assemble the tricyclic complexes **29** and **30**, respectively. It was thought that further activation of the heteroarene on switching from a *N*-alkynyl to a *N*-alkynoyl substituent, as in **6f**, would improve the yield of the cycloaddition. Unfortunately, **6f** remained unchanged, even after 15 h at 65 °C, and decomposed on prolonged heating. Finally, unlike related successful [2+2+2] cycloadditions of alkynenitriles^[37] to form annelated pyridines, the substrates **6g–i** are stable under the reaction conditions and none of the desired complexes were obtained.

The assignment of the stereochemistry of **27–30** was made by comparison with related systems,^[3,5] and utilized the effects of the magnetic anisotropy of cobalt in ¹H NMR spectroscopy.^[2,26] In the major isomer, the protons H_a and H_b in **27** appeared at δ = 1.65 and 2.21, respectively, as two doublets with a coupling constant of 8 Hz, whereas in the minor isomer, H_a and H_b resonated at δ = 2.55 and 3.77 as two doublets with a coupling constant of 10.5 Hz (Table 12). The deshielding

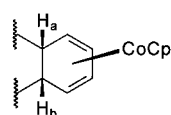
Table 12. Chemical shifts (δ) and coupling constants [Hz] in **27–30**.

27-30

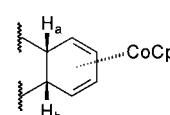
	R ¹	R	Major isomer (<i>anti</i>)			Minor isomer (<i>syn</i>)		
			H _a	H _b	<i>J</i> (H _a ,H _b)	H _a	H _b	<i>J</i> (H _a ,H _b)
27	COPh	TMS	1.65	2.21	8.1	2.55	3.77	10.5
28	COPh	COOMe	2.78	3.12	8.1	—	—	—
29	H	TMS	1.44	2.01	8.0	2.37	3.69	10.3
30	H	COOMe	2.70	2.94	8.0	—	—	—

caused by the cobalt in the *exo* position strongly suggests that the major isomer of the reaction has the *anti* configuration. The same conclusions can be drawn with respect to the chemical shifts and the coupling constants of H_a and H_b in **29**. For compounds **28** and **30**, the above comparison of the chemical shift could not be made since they were obtained as only one isomer; however, it is interesting to note that the coupling constants for H_a and H_b were the same as in complexes **27** and **29** (Table 12).

Interestingly, the observation of the important difference in the coupling constants between *anti* and *syn* complexes seems to be quite general and even proved to be consistent over a set of 17 diene complexes prepared in this work. It also correlates well with previous studies.^[4] In short, the *syn*-diene-cobalt complex has *J*(H_a,H_b) = 10–11 Hz, while in the *anti* isomer has *J*(H_a,H_b) = 7–8 Hz (Figure 1).



Syn: *J*_{H_a-H_b} = 10–11 Hz

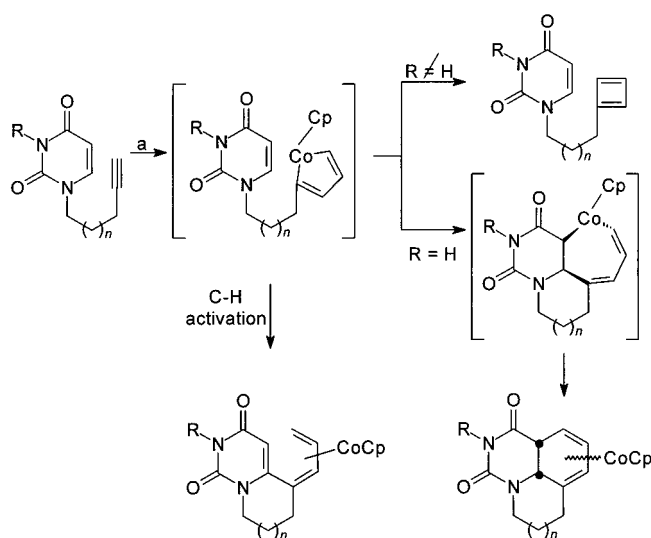


Anti: *J*_{H_a-H_b} = 7–8 Hz

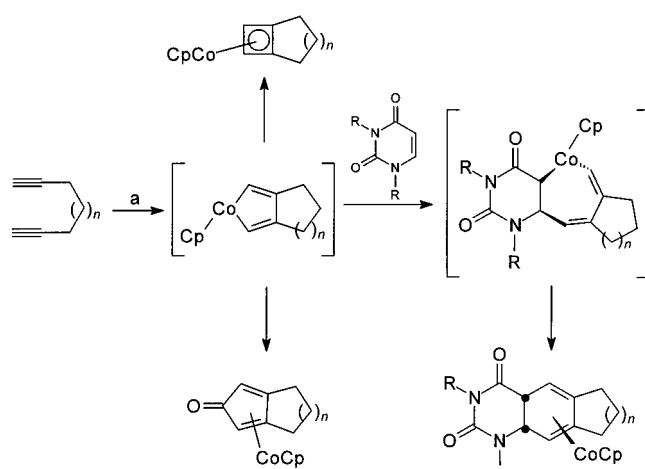
Figure 1. Coupling constants of methine protons in *syn* and *anti* diene-cobalt complexes.

Mechanistic discussion: Theoretical and experimental mechanistic investigations^[38] have led to a proposed mechanism of the [2+2+2] cycloaddition that involves cobaltacyclopentadiene or -cycloheptadiene intermediates, which are also consistent with the byproducts, such as cyclobutadiene and cyclopentadienone complexes, encountered in this study. In accordance with these findings, one can formulate Schemes 6 and 7 for the two topological variants of the cycloaddition of pyrimidines.^[39]

A further competing pathway was observed with the formation of diene complexes **31** and **33**, which result from formal C–H activation.^[36] The exact mechanism of this process is not known; however, one can envisage direct electrophilic aromatic substitution by the cobaltacyclopentadiene, oxidative addition to the C–H bond to give a (rare^[40]) Co^V species, or a β-hydride/reductive elimination sequence from the cobaltacycloheptadiene intermediate.



Scheme 6. Proposed mechanism for intramolecular cycloadditions.



Scheme 7. Proposed mechanism for intermolecular cycloadditions.

Experimental Section

General methods: Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. DME, THF, and Et₂O were freshly distilled from sodium benzophenone; toluene and xylene were distilled from potassium and sodium, respectively, and DMSO was stored over 4 Å molecular sieves. Unless otherwise specified, all reactions that involved air- or moisture-sensitive materials were carried out under an atmosphere of dry nitrogen or argon with glassware that was oven-dried overnight at 130 °C. In these experiments, reagents were usually added from Hamilton gastight syringes mounted on a syringe pump. Column chromatography was performed on flash silica gel (Merck Reagents silica gel 60, 230–400 mesh ASTM). Thin-layer chromatography (TLC) was carried out on a 250 μ coating with fluorescent indicator. Melting points were observed in open Pyrex capillary tubes with a Thomas–Hoover Unimelt apparatus and are uncorrected. Infrared spectra were obtained either on neat compounds (NaCl plates), in solution (solvent, NaCl cells), or with KBr pellets. 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 Micro-analytical Laboratory, UCB.

Preparation of 1,3-dimethylpyrimidinediones (1a–c):^[14] **General procedure:** The pyrimidinedione (10 mmol) was suspended in an aqueous NaOH solution (13%, 8 mL) and cooled to 0 °C. Dimethyl sulfate (2.5 mL) was added slowly, the reaction mixture was left for 30 min at room temperature

and then brought to reflux for 30 min. After cooling, the mixture was extracted with CHCl₃ (3 × 20 mL) and washed with saturated aqueous NaHCO₃ solution. The extract was dried over Na₂SO₄ and filtered, and the solvent removed under reduced pressure to give the crude methylated pyrimidines.

1,3-Dimethyluracil (1a): White crystals (EtOH); yield: 89%; m.p. 120–122 °C; ¹H NMR (300 MHz, CDCl₃): δ = 3.32 (s, 3H), 3.38 (s, 3H), 5.72 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H); C₆H₈N₂O₂ (140.14): calcd C 51.39, H 5.71, N 19.98; found C 51.21, H 5.63, N 19.95.

1,3-Dimethylthymine (1b): White crystals (EtOH); yield: 97%; m.p. 154–155 °C; ¹H NMR (300 MHz, CDCl₃): δ = 1.92 (s, 3H), 3.35 (s, 3H), 3.36 (s, 3H), 6.97 (m, 1H); C₇H₁₀N₂O₂ (154.17): calcd C 54.54, H 6.49, N 18.18; found C 54.39, H 6.54, N 18.22.

1,3-Dimethyl-5-fluorouracil (1c): White crystals (EtOH); yield: 88%; m.p. 128–130 °C; ¹H NMR (300 MHz, CDCl₃): δ = 3.29 (s, 3H), 3.33 (s, 3H), 7.25 (d, *J* = 5.1 Hz, 1H).

Preparation of 1,3-dimethyl-4-thiouracil (1d):^[14] 1,3-Dimethyluracil (1a) (0.840 g, 6.0 mmol) and phosphorus pentasulfide (1.05 g, 4.72 mmol) were refluxed in dry pyridine (18 mL) for 3 d. After evaporation of the pyridine under vacuum, water (50 mL) was added, and the mixture was extracted with CHCl₃ (4 × 20 mL). The organic layer was washed with water (2 × 20 mL) and dried over Na₂SO₄. Filtration and evaporation of the solvent gave an orange solid, which was chromatographed (silica gel, pentane/acetone 1:1) to give a yellow solid. Yield: 92%; m.p. 183 °C; IR (CDCl₃): $\tilde{\nu}$ = 1725, 1660, 1360, 1140 cm^{−1}; ¹H NMR (300 MHz, CDCl₃): δ = 6.90 (d, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 3.76 (s, 3H), 3.42 (s, 3H); MS (70 eV): *m/z* (%): 156 (100) [*M*⁺], 123 (24), 100 (26), 86 (7), 82 (8), 77 (9), 72 (18).

Preparation of imides (1e–g): These compounds were obtained with a reported procedure.^[15]

1,3,4-trimethyliminouracil (1e): White crystals (Et₂O); yield: 66%; m.p. 79 °C; ¹H NMR (300 MHz, CDCl₃): δ = 6.74 (d, *J* = 8.3 Hz, 1H), 5.75 (d, *J* = 8.3 Hz, 1H), 3.25 (s, 3H), 3.23 (s, 3H), 2.01 (s, 3H).

1,3-Dimethyl-*N*⁴-ethyliminouracil (1f): Pale yellow solid; yield: 54%; m.p. 88–89 °C; IR (CDCl₃): $\tilde{\nu}$ = 2970, 1670, 1610, 1460, 1400 cm^{−1}; ¹H NMR (300 MHz, CDCl₃): δ = 5.96 (d, *J* = 8.1 Hz, 1H), 3.60 (m, 9H), 1.31 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75.8 MHz, CDCl₃): δ = 151.71, 150.59, 137.33, 92.83, 42.71, 35.91, 28.31, 16.34; MS (70 eV): *m/z* (%): 167 (57) [*M*⁺], 166 (22), 111 (9), 109 (21), 96 (33), 95 (52), 83 (8), 82 (10), 81 (22); C₈H₁₃N₃O (167.21): calcd C 57.46, H 7.84, N 25.13; found C 56.80, H 7.72, N 24.65.

1,3-Dibenzoyl-*N*⁴-benzyliminouracil (1g): White crystals (EtOH); yield: 48%; m.p. 140–142 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.73 (d, *J* = 6.1 Hz, 1H), 8.08 (d, overlapping, *J* = 6.1 Hz, 2H), 7.77 (m, 4H), 7.43 (m, 10H); MS (70 eV): *m/z* (%): 423 (60) [*M*⁺], 395 (61), 394 (100), 366 (34), 318 (59), 291 (55), 105 (98).

Preparation of nucleosides (1h–j): These compounds were obtained with a reported procedure.^[18]

Tetramethyluridine (1h): White crystals from flash chromatography (hexanes/Et₂O 1:1); yield: 99%; m.p. 102 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.90 (d, *J* = 8 Hz, 1H), 5.91 (m, 1H), 5.72 (d, *J* = 8 Hz, 1H), 4.16 (m, 1H), 3.84 (m, 2H), 3.78 (dd, *J* = 11.2, 2.1 Hz, 1H), 3.59 (s, 3H), 3.55 (dd, *J* = 11.2, 2.2 Hz, 1H), 3.41 (s, 3H), 3.40 (s, 3H), 3.29 (s, 3H).

2',3'-*O*-Isopropylidene dimethyluridine (1i): Prepared by the methylation of 2',3'-*O*-isopropylidene uridine^[41] following a reported procedure.^[18] Yield: 100%; colorless thick oil; IR (CDCl₃): $\tilde{\nu}$ = 3000, 1710, 1670, 1470, 1080 cm^{−1}; ¹H NMR (300 MHz, CDCl₃): δ = 7.44 (d, *J* = 8.1 Hz, 1H), 5.80 (d, *J* = 1.4 Hz, 1H), 5.72 (d, *J* = 8.1 Hz, 1H), 4.75 (m, 2H), 4.40 (m, 1H), 3.56 (m, 2H), 3.42 (s, 3H), 3.26 (s, 3H), 1.55 (s, 3H), 1.32 (s, 3H); ¹³C NMR (75.8 MHz, CDCl₃): δ = 162.47, 150.57, 138.87, 137.98, 113.51, 100.51, 93.61, 85.26, 80.89, 72.35, 58.88, 27.08, 25.14, 24.72; MS (70 eV): *m/z* (%): 312 (4) [*M*⁺], 297 (17), 237 (45), 209 (13), 187 (76), 151 (20), 129 (100), 128 (18), 127 (19), 101 (42), 100 (41), 97 (20), 92 (16), 87 (21), 85 (24), 85 (27), 84 (23), 83 (41), 71 (52).

Trimethyldeoxyuridine (1j): Colorless oil; yield: 85%; ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.71 (d, *J* = 8.1 Hz, 1H), 6.23 (dd, *J* = 7.8, 5.9 Hz, 1H), 5.71 (d, *J* = 8.1 Hz, 1H), 4.12 (q, *J* = 2.7 Hz, 1H), 3.96 (dt, *J* = 5.7, 2.4 Hz, 1H), 3.63 (dd, *J* = 10.6, 3.0 Hz, 1H), 3.51 (dd, *J* = 10.6, 3.0 Hz, 1H), 3.38 (s, 3H), 3.32 (s, 3H), 3.25 (s, 3H), 2.41 (ddd, *J* = 13.7, 5.9, 2.4 Hz, 1H), 2.05 (ddd, *J* = 13.7, 7.8, 5.9 Hz, 1H).

Preparation of acetylnucleosides (1k) and (1l): These compounds were prepared according to a reported procedure.^[19]

2',3',5'-Tri-*O*-acetyluridine (1k): White crystals (EtOH); yield: 80%; m.p. 130 °C; ¹H NMR (300 MHz, C₆D₆): δ = 7.16 (m, 2H), 6.13 (d, J = 5 Hz, 1H), 5.61 (d, J = 8.1 Hz, 1H), 5.54 (overlapping dd, J = 5.5 Hz, 5.3, 1H), 5.44 (overlapping dd, J = 5.5 Hz, 5.3, 1H), 4.22 (m, 2H), 4.10 (m, 1H), 1.752 (s, 3H), 1.749 (s, 3H), 1.70 (s, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 183.01, 169.93, 169.59, 169.44, 163.41, 150.87, 139.42, 103.39, 88.11, 80.09, 73.34, 70.54, 63.21, 20.08, 20.05.

3',5'-Di-*O*-acetyldeoxyuridine (1l): White solid; yield: 94%; m.p. 108–109 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.47 (d, J = 10.5 Hz, 1H), 6.28 (dd, J = 10.5, 7.4 Hz, 1H), 5.74 (d, J = 10.5 Hz, 1H), 5.22 (m, J = 7.0 Hz, 1H), 4.26 (m, 3H), 2.50 (ddd, J = 7.4, 6.1, 2.0 Hz, 1H), 2.20 (m, 1H), 2.08 (s, 3H), 2.06 (s, 3H).

Preparation of pyrimidines (2): 2,6-Dichloropyrimidine (**2a**) was prepared according to a reported procedure and used for the preparation of 2,6-dichloropyrimidine (**2b**).^[16]

2,6-Dichloropyrimidine (2a): Pale yellow solid; yield: 75%; m.p. 55 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.53 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H).

2,6-Dimethoxypyrimidine (2b): Pale yellow oil; yield: 64%; ¹H NMR (300 MHz, CDCl₃): δ = 8.19 (d, J = 7.8 Hz, 1H), 6.38 (d, J = 7.8 Hz, 1H), 3.99 (s, 3H), 3.95 (s, 3H).

Preparation of enamines (3): These compounds were prepared according to a reported procedure.^[16,17]

Acetylcytosine (3a): White solid; yield: 59%; m.p. > 310 °C; ¹H NMR (300 MHz, [D₆]DMSO): δ = 7.80 (d, J = 10.8 Hz, 1H), 7.10 (d, J = 10.8 Hz, 1H), 2.10 (s, 3H); C₆H₇N₃O₂ (153.14): calcd C 47.06, H 4.61, N 27.44; found C 47.14, H 4.64, N 27.79.

1-Propylacetylcytosine (3b): White solid; yield: 72%; m.p. 162 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.70 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 3.81 (t, J = 6.9 Hz, 2H), 2.35 (s, 3H), 1.75 (m, 2H), 0.98 (t, J = 7.1 Hz, 3H).

1,N⁴-Dimethylcytosine (3c): White solid; yield: 80%; m.p. 179 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.00 (d, J = 8.4 Hz, 1H), 5.60 (m, 2H), 3.35 (s, 3H), 2.80 (s, 3H).

1,N⁴,N⁴-Trimethylcytosine (3d): White solid; yield: 98%; m.p. 175 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.60 (d, J = 7.5 Hz, 1H), 5.70 (d, J = 7.5 Hz, 1H), 3.48 (s, 3H), 3.20 (m, 6H).

Preparation of imidates (4): These compounds were prepared by alkylation of the corresponding 2,6-dialkylpyrimidines.^[16]

1-Methyl-4-methoxypyrimidine-2-one (4a): Pale yellow solid; yield: 64%; m.p. 145 °C; ¹H NMR (300 MHz, [D₆]DMSO): δ = 7.98 (d, J = 6.6 Hz, 1H), 5.98 (d, J = 6.6 Hz, 1H), 3.73 (s, 3H), 3.56 (s, 3H).

1-Methyl-4-ethoxypyrimidine-2-one (4b): Pale yellow solid; yield: 80%; m.p. 136 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.50 (d, J = 8.3 Hz, 1H), 5.51 (d, J = 8.3 Hz, 1H), 4.00 (q, J = 6.7 Hz, 2H), 3.10 (s, 3H), 0.98 (t, J = 6.7 Hz, 3H).

1-Methyl-4-propoxypyrimidine-2-one (4c): Pale yellow solid; yield: 88%; m.p. 108–110 °C; IR (CDCl₃): $\tilde{\nu}$ = 2975, 1670, 1640, 1310 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 7.38 (d, J = 7.1 Hz, 1H), 5.82 (d, J = 7.2 Hz, 1H), 4.29 (t, J = 6.8 Hz, 2H), 3.48 (s, 3H), 1.72 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ¹³C NMR (75.8 MHz, CDCl₃): δ = 171.08, 158.60, 147.38, 95.00, 67.98, 37.35, 21.31, 9.78; MS (70 eV): m/z (%): 168 (23) [M^+], 139 (22), 138 (31), 127 (70), 126 (100), 110 (56), 109 (15), 84 (88), 83 (96), 82 (35), 82 (29); for C₈H₁₂N₂O₂: C 57.13, H 7.19, N 16.65; found C 56.56, H 6.79, N 16.61.

1-Ethyl-4-methoxypyrimidine-2-one (4d): Pale yellow solid; yield: 88%; m.p. 90 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.48 (d, J = 7.2 Hz, 1H), 5.88 (d, J = 7.2 Hz, 1H), 3.93 (s, 3H), 3.89 (q, J = 7.3 Hz, 2H), 1.33 (t, J = 7.3 Hz, 3H).

Preparation of pyrimidines (6): 1-(1-Pentynyl)-3-benzoyluracil (6a). Anhydrous K₂CO₃ (0.889 g, 4.58 mmol) and 5-iodo-1-pentyne^[42] (0.893 g, 4.58 mmol) was added to a solution of 3-benzoyluracil (**5**: R¹ = C₆H₅, R² = H)^[23] (0.90 g, 4.16 mmol) in dry DMSO (5 mL) and dry THF (40 mL). The mixture was stirred under nitrogen at room temperature for 22 h, filtered through a short pad of Celite, and then rinsed with CHCl₃ (50 mL). The solvent was evaporated under reduced pressure. Water (50 mL) was added, and the mixture then extracted with CHCl₃ (3 × 60 mL). The combined

organic extracts were washed successively with 5 % aqueous HCl (10 mL) and brine (20 mL), and then dried over Na₂SO₄. Filtration and evaporation of the solvent gave a pale yellow oil. Purification by flash chromatography (SiO₂, MeOH/CHCl₃ 1:99) gave pure **6a** as white crystals. Yield: 0.95 g (81 %); m.p. 101 °C; IR (C₆D₆): $\tilde{\nu}$ = 3300, (3100–2950, weak), 1755, 1715, 1675, 1635, 1600, 1435, 1250 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 7.92 (dd, J = 7.8, 0.7 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 5.80 (d, J = 8.0 Hz, 1H), 3.91 (t, J = 6.8 Hz, 2H), 2.30 (td, J = 6.8, 2.6 Hz, 2H), 2.07 (t, J = 5.0 Hz, 1H), 1.94 (q, J = 6.8 Hz, 2H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 169.73, 162.46, 149.95, 144.36, 134.74, 132.43, 130.38, 129.21, 101.53, 82.64, 70.27, 47.79, 27.14, 15.49; MS (70 eV): m/z (%): 282 (1) [M^+], 254 (3), 212 (3), 177 (13), 105 (100), 77 (81); C₁₆H₁₄N₂O₃ (282.30): calcd C 68.08, H 4.96, N 9.93; found C 68.07, H 4.98, N 9.95.

1-(1-Butynyl)-3-benzoyluracil (6b): This compound was prepared as above from 4-iodo-1-butyne.^[42] Flash chromatography (silica gel, MeOH/CHCl₃ (1:99) gave white crystals. Yield: 33%; m.p. 142–145 °C; IR (CHCl₃): $\tilde{\nu}$ = 3305, 2930, 1755, 1710, 1670, 1600, 1390, 1180 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 7.74 (m, 5H), 7.38 (d, J = 7.9 Hz, 1H), 5.79 (d, J = 7.9 Hz, 1H), 3.90 (t, J = 2.6 Hz, 2H), 2.11 (t, J = 2.6 Hz, 1H); ¹³C NMR (75.8 MHz, CDCl₃): δ = 168.61, 162.40, 149.42, 144.97, 135.11, 131.16, 130.31, 129.09, 101.42, 79.66, 71.98, 47.80, 18.53; MS (70 eV): m/z (%): 268 (3) [M^+], 240 (26), 188 (8), 106 (25), 105 (100), 82 (23), 78 (15), 77 (94), 76 (9), 70 (8).

1-(1-Pentynyl)-3-benzoylthymine (6c): This compound was prepared as above from 3-benzoylthymine (**5c**).^[22] Flash chromatography (silica gel, MeOH/CHCl₃ 0.5:99.5) gave **6c** as a colorless oil. Yield: 76%; IR (C₆D₆): $\tilde{\nu}$ = 3300, 3100, 3070, 3040, 1755, 1710, 1670, 1250, 1040 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 8.05 (d, J = 7.5 Hz, 2H), 7.74 (t, J = 6.6 Hz, 1H), 7.63 (t, J = 5.6 Hz, 2H), 7.28 (s, 1H), 4.00 (t, J = 6.2 Hz, 2H), 2.44 (m, 2H), 2.16 (m, 1H), 2.09 (m, 2H), 2.09 (s, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 170.02, 163.37, 149.99, 140.96, 134.93, 132.33, 130.47, 129.30, 109.86, 82.93, 70.35, 47.73, 27.50, 15.67, 12.32; MS (70 eV): m/z (%): 297 (6) [M^+], 296 (28), 268 (13), 251 (1), 191 (24), 149 (24), 121 (29), 105 (100), 96 (21), 77 (94), 51 (50).

1-(1-Pentynyl)-3-(*p*-nitrobenzoyl)uracil (6d): This compound was prepared as above from 3-*p*-nitrobenzoylthymine (**5d**).^[22] Flash chromatography (silica gel, MeOH/CHCl₃ 1:99) gave **6d** as a colorless oil. Yield: 35%; IR (CDCl₃): $\tilde{\nu}$ = 3310, (3120–2950, weak), 2260, 1765, 1715, 1675, 1610, 1535, 1350, 1250 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 8.31 (d, J = 9.0 Hz, 2H), 8.08 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 8.1 Hz, 1H), 5.81 (d, J = 8.1 Hz, 1H), 3.92 (t, J = 7.0 Hz, 2H), 2.30 (td, J = 7.0, 2.6 Hz, 2H), 2.07 (t, J = 2.6 Hz, 1H), 1.94 (q, J = 7.0 Hz, 2H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 168.87, 162.44, 151.13, 149.84, 145.05, 136.52, 131.21, 124.28, 101.47, 82.69, 70.50, 48.05, 27.17, 15.54; MS (70 eV): m/z (%): 327 (3) [M^+], 275 (8), 257 (7), 177 (37), 150 (100), 104 (85), 76 (61); C₁₆H₁₃N₃O₅ (327.30): calcd C 58.72, H 4.00, N 12.84; found C 57.35, H 4.09, N 11.98.

1-(1-Pentynyl)uracil (6e): Et₃N (8 mL) and 5-iodo-1-pentyne^[42] (1.46 g, 7.5 mmol) was added to a solution of 3-benzoyluracil (**5a**)^[22] (1.08 g, 5 mmol) in a mixture of EtOH and H₂O (1:1, 20 mL). The mixture was heated at 50 °C for 21 h. Most of the solvent was evaporated under reduced pressure, and CHCl₃ (60 mL) was added to the residue, which was then filtered through a short pad of Celite. The filtrate was washed with H₂O (3 × 20 mL), and the organic layer dried over Na₂SO₄. Evaporation of the solvent gave a yellow oil which was purified by flash chromatography (SiO₂, CHCl₃/MeOH 98:2). Yield: 0.28 g (32 %); white crystals; m.p. 128–130 °C; IR (CHCl₃): $\tilde{\nu}$ = 3400, 3320, 3010, 1700, 1460, 1230 cm⁻¹; ¹H NMR (300 MHz, [D₆]acetone): δ = 7.55 (d, J = 8.0 Hz, 1H), 5.54 (dd, J = 8.0, 1.7 Hz, 1H), 3.84 (t, J = 7.0 Hz, 2H), 2.41 (t, J = 2.5 Hz, 1H), 2.27 (td, J = 7.0, 2.5 Hz, 2H), 1.89 (q, J = 7.0 Hz, 2H); ¹³C NMR (75.8 MHz, [D₆]acetone): δ = 164.38, 151.75, 146.10, 101.82, 83.54, 70.72, 48.11, 28.29, 15.91; MS (70 eV): m/z (%): 178 (6) [M^+], 150 (15), 133 (31), 113 (72), 107 (90), 82 (100); C₉H₁₀N₂O₂ (178.19): calcd C 60.66, H 5.66; N 15.79; found C 60.443, H 5.70, N 15.61.

1-(4-Pentynoyl)uracil (6f): 4-Pentynoyl chloride^[23] (1.4 g, 12 mmol) was added in one portion to a magnetically stirred suspension of powdered uracil (1.12 g, 10 mmol) in CH₃CN (10 mL) and pyridine (2 mL) at room temperature. The resulting brown mixture remained heterogeneous throughout. After 3.5 h, the suspension was filtered and washed with CH₃CN and hexanes. Recrystallization from THF gave pure **6f**. Yield: 1.15 g (60 %); white crystals; m.p. 187 °C (decomp); IR (KBr): $\tilde{\nu}$ = 3450,

3290, 3040, 2845, 1730, 1635, 1405, 1265, 1160 cm⁻¹; ¹H NMR (300 MHz, [D₆]acetone): δ = 8.22 (d, J = 8.5 Hz, 1H), 5.83 (dd, J = 8.5, 2.0 Hz, 1H), 3.38 (t, J = 7.0 Hz, 2H), 2.56 (td, J = 7.0, 2.6 Hz, 2H), 2.39 (t, J = 2.6 Hz, 1H); ¹³C NMR (300 MHz, [D₆]DMSO): δ = 171.44, 162.92, 149.47, 137.56, 104.47, 83.24, 71.60, 37.89, 13.53; MS (70 eV): m/z (%): 192 (4) [M^+], 164 (5), 113 (54), 81 (81), 69 (64), 53 (100); C₉H₈N₂O₃ (192.17): calcd C 56.22, H 4.16, N 14.57; found C 56.00, H 4.26, N 14.79.

1-Cyanoethyl-3-benzoyluracil (6g): 3-Benzoyluracil (**5a**)^[22] (0.432 g, 2 mmol) was suspended in H₂O (5 mL) and EtOH (95%, 5 mL). Et₃N (2 mL) was added, and the solid dissolved. Acrylonitrile (2.5 mL) was added, and the mixture was allowed to stand at room temperature for 21 h. After this time, a white precipitate formed. The mixture was then cooled to 0 °C and filtered. The white precipitate was washed with cold water and dried in vacuo for 24 h to give **6g**. Yield: 0.356 g (60%); white solid; m.p. 168–170 °C; IR (KBr): $\tilde{\nu}$ = 3100, 2250, 1740, 1700, 1660, 1600, 1435, 1260, 1230 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 7.94 (d, J = 7.4 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.54 (m, 2H), 7.39 (d, J = 8.0 Hz, 1H), 5.84 (d, J = 8.0 Hz, 1H), 4.01 (t, J = 6.3 Hz, 2H), 2.84 (t, J = 6.3 Hz, 2H); ¹³C NMR (75.8 MHz, [D₆]DMSO): δ = 169.43, 162.23, 149.39, 146.31, 135.59, 131.02, 130.33, 129.49, 118.28, 101.07, 43.79, 16.94; MS (70 eV): m/z (%): 269 (2) [M^+], 242 (0.5), 241 (30), 105 (100), 77 (89), 53 (43), 51 (50); C₁₄H₁₁N₃O₃ (269.26): calcd C 62.45, H 4.12, N 15.60; found C 62.26, H 4.12, N 15.41.

1-Cyanoethyluracil (6h): This compound was prepared by Michael addition of uracil to acrylonitrile following the reported procedure.^[24] Yield: 66%; white crystals; m.p. 230 °C; IR (DMSO): $\tilde{\nu}$ = 3010, 2800, 1700, 1635, 1460, 1240 cm⁻¹; ¹H NMR (300 MHz, [D₆]DMSO): δ = 7.67 (d, J = 7.9 Hz, 1H), 5.60 (d, J = 7.9 Hz, 1H), 3.93 (t, J = 6.5 Hz, 2H), 2.89 (t, J = 6.5 Hz, 2H); ¹³C NMR (75.8 MHz, [D₆]DMSO): δ = 163.61, 150.69, 145.28, 118.33, 101.27, 43.27, 16.87; MS (70 eV): m/z (%): 165 (29) [M^+], 125 (36), 82 (100), 53 (39); C₇H₇N₃O₂ (165.15): calcd C 50.90, H 4.20, N 25.40; found C 50.67, H 4.02, N 25.18.

1-Cyanopropyluracil (6i): 4-Chlorobutyronitrile (0.11 mL, 1.2 mmol) and K₂CO₃ (0.152 g, 1.1 mmol) were successively added to a solution of 3-benzoyluracil (**5a**)^[22] (0.261 g, 1 mmol) in a mixture dry THF and dry DMSO (10:1, 10 mL). The solution was heated at 60 °C for 12 h. Cooling, filtration, and evaporation of the solvents in vacuo gave a crude solid, which was purified by flash chromatography (silica gel, CHCl₃/CH₃OH 4:1). Yield: 37%; white crystals; m.p. 157 °C; IR (CHCl₃): $\tilde{\nu}$ = 3400, 2975, 2260, 1700, 1630, 1240, 1053, 1010 cm⁻¹; ¹H NMR (300 MHz, [D₆]DMSO): δ = 8.21 (d, J = 7.8 Hz, 1H), 6.15 (d, J = 7.8 Hz, 1H), 4.33 (t, J = 6.9 Hz, 2H), 3.10 (m, 4H); ¹³C NMR (75.8 MHz, CDCl₃): δ = 164.95, 150.73, 147.29, 125.95, 101.61, 47.20, 31.67, 27.06; MS (70 eV): m/z (%): 179 (26) [M^+], 139 (18), 126 (31), 125 (20), 113 (29), 112 (47), 108 (16), 96 (26), 83 (12), 82 (100), 70 (15).

1-(1-Pentynyl)-N⁴-acetylcytosine (7): This compound was prepared from acetylcytosine (**3a**) and 5-iodo-1-pentynyl^[42] with the procedure described for **6a** (vide supra). Flash chromatography (silica gel, CHCl₃/CH₃OH 85:15) gave **7** as a white solid. Yield: 88%; m.p. 171 °C; IR (CDCl₃): $\tilde{\nu}$ = 3400, 1725, 1665, 1490, 1230 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 7.84 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 4.03 (t, J = 6.8 Hz, 2H), 2.32 (s, 3H), 2.25 (m, 2H), 2.02 (m, 3H); ¹³C NMR (75.8 MHz, CDCl₃): δ = 171.48, 163.02, 155.51, 148.96, 96.73, 82.14, 69.92, 49.62, 26.54, 24.56, 15.22; MS (70 eV): m/z (%): 219 (78) [M^+], 204 (88), 176 (18), 167 (95), 161 (17), 148 (9), 138 (100), 125 (64), 111 (66), 95 (41), 81 (94), 67 (88), 54 (36); C₁₁H₁₃N₃O₂ (219.24): calcd C 60.01, H 5.78, N 18.77; found C 60.18, H 5.78, N 18.62.

General Procedure for [CpCoL₂] Cyclizations: The pyrimidine (1 mmol) was dissolved in the appropriate solvent (10 mL) in a round bottom flask (50 mL) equipped with a coil condenser. This mixture was then degassed under nitrogen by three freeze-pump-thaw cycles on a vacuum line and then brought to the required temperature. The diyne (1.5 to 2 mmol) was dissolved in the same solvent (7 mL) and degassed as before, then [CpCo(CO)₂] (1.5 to 2 mmol) was added by means of a syringe. The resulting solution was loaded into a gastight syringe (10 mL) and added to the pyrimidine by means of a syringe pump over a period of 18–22 h. During the addition, the flask was irradiated with a slide projector lamp (sylvania ELH 300 W) at a distance of 5 cm from the center of the flask with an applied potential of 65 V. Note that for reactions carried out at room temperature, it was necessary to blow air across the surface of the flask. The mixture was then cooled at room temperature and the black solution was

filtered through a short pad of Celite and rinsed with the reaction solvent until the filtrate was clear. The solvent was then removed in vacuo and the residue subjected to flash chromatography (silica gel or neutral alumina). Note that when the reactions were carried out with [CpCo(C₂H₅)₂]^[31] THF was used as solvent and nitrogen replaced by argon. Simultaneous addition of the cocyclizing alkyne in THF (5 mL) and [CpCo(C₂H₅)₂] in THF (5 mL) was performed with two syringe pumps. No irradiation was used under these conditions.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,8a,9- η)-1,3-dimethyl-1,2,3,4,4a-endo, 9a-endo-hexahydro-2,4-dioxo-cyclopenta[g]quinazoline]cobalt (9a**):** From **1a** (0.145 g, 1.035 mmol), [CpCo(CO)₂] (0.373 g, 2.07 mmol), and **8a** (0.191 g, 2.07 mmol) in toluene (10 mL), with irradiation under reflux for 19 h. Flash chromatography (SiO₂, hexanes/Et₂O 20:80) gave orange crystals. Yield: 0.194 g (53%); m.p. 152–154 °C; IR (C₆D₆): $\tilde{\nu}$ = 3100, 2960, 1700, 1665, 1665, 1420, 1295, 755 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.25 (s, 5H), 3.47 (d, J = 4.9 Hz, 1H), 3.19 (s, 3H), 3.14 (dd, J = 10.7, 3.4 Hz, 1H), 2.99 (d, J = 3.4 Hz, 1H), 2.74 (s, 3H), 2.71 (dd, J = 10.7, 4.9 Hz, 1H), 2.27 (m, 1H), 2.02 (m, 3H), 1.85 (m, 1H), 1.74 (m, 1H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 171.08, 151.20, 100.15, 99.51, 80.56, 56.15, 45.55, 43.97, 42.29, 33.28, 31.84, 31.77, 27.75, 24.06; MS (70 eV): m/z (%): 356 (0.13) [M^+], 355 (0.12), 354 (0.73), 232 (6), 231 (9), 204 (8), 175 (73), 145 (100), 117 (83), 115 (88), 91 (48), 77 (17), 65 (20); C₁₈H₂₁CoN₂O₂ (356.31): calcd C 60.68, H 5.94, N 7.86; found C 60.42, H 5.96, N 7.77.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,8a,9- η)-1,3-dimethyl-1,2,3,4,4a-endo, 9a-endo-hexahydro-2-oxo-4-methylimino-cyclopenta[g]quinazoline]cobalt (9e**):** From **1e** (0.128 g, 0.83 mmol), **8a** (173 μ L, 1.33 mmol), and [CpCo(CO)₂] (186 μ L, 1.33 mmol) in toluene (16 mL), with irradiation under reflux for 18 h. Flash chromatography on neutral alumina (pentane/AcOEt 1:9) gave an orange oil. Yield: 0.141 g (46%). Cooling in pentane gave orange crystals; m.p. 93–95 °C; IR (CH₂Cl₂): $\tilde{\nu}$ = 2940, 1660, 1630, 1480, 1150 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.35 (s, 5H), 3.35 (s, 3H), 3.18 (s, 3H), 3.10 (m, 1H), 3.07 (m, 2H), 3.02 (m, 1H), 2.78 (s, 3H), 2.20 (m, 1H), 1.97 (m, 3H), 1.80 (m, 1H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 158.20, 154.08, 100.01, 99.56, 80.53, 57.18, 45.29, 42.14, 39.40, 36.52, 33.33, 31.98, 31.87, 30.64, 24.22; MS (70 eV): m/z (%): 369 (52) [M^+], 354 (20), 312 (26), 289 (47), 288 (23), 287 (35), 244 (29), 243 (21), 242 (71), 239 (21), 215 (92), 188 (21), 187 (100), 158 (92), 144 (27), 124 (68), 121 (41), 117 (20), 115 (45), 71 (20); HRMS: calcd for C₁₉H₂₄CoN₃O 369.125; found 369.125.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,8a,9- η)-1,3-dimethyl-1,2,3,4,4a-endo, 9a-endo-hexahydro-2-oxo-4-ethylimino-cyclopenta[g]quinazoline]cobalt (9f**):** From **1f** (0.167 g, 1 mmol), **8a** (209 μ L, 1.8 mmol), and [CpCo(CO)₂] (240 μ L, 1.9 mmol) in toluene (16 mL), with irradiation under reflux for 20 h. Flash chromatography (neutral alumina, pentane/AcOEt 1:99) gave orange crystals. Yield: 0.150 g (40%); m.p. 127–129 °C; IR (CH₂Cl₂): $\tilde{\nu}$ = 2950, 1680, 1640, 1490 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.30 (s, 5H), 3.39 (m, 2H), 3.38 (s, 3H), 3.18 (m, 2H), 3.09 (m, 1H), 3.01 (m, 1H), 2.76 (s, 3H), 2.20 (m, 2H), 1.90 (m, 4H), 1.34 (t, J = 7.2 Hz, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 156.37, 154.25, 100.05, 99.40, 80.40, 57.35, 45.22, 43.72, 42.69, 39.86, 33.26, 31.94, 31.84, 31.60, 24.19, 17.67; MS (70 eV): m/z (%): 383 (46) [M^+], 326 (30), 273 (36), 258 (36), 256 (34), 242 (40), 239 (42), 175 (27), 174 (36), 158 (25), 124 (100), 121 (33), 115 (34); HRMS: calcd for C₂₀H₂₆CoN₃O 383.141; found 383.141.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1,3-dimethyl-1,2,3,4,4a-endo, 6,7,8,9,10a-endo-decahydro-2,4-dioxo-benzol[g]quinazoline]cobalt (10a**):** From **1a** (0.40 g, 2.85 mmol), [CpCo(CO)₂] (1.03 g, 5.71 mmol), and **8b** (0.606 g, 5.71 mmol) in xylene (20 mL), with irradiation under reflux for 20 h. Flash chromatography (SiO₂, hexanes/AcOEt 65:35) gave orange crystals. Yield: 0.804 g (76%); m.p. 130–131 °C; IR (neat): $\tilde{\nu}$ = 3100, 2940, 1700, 1660, 1485, 1300, 1005, 815 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.32 (s, 5H), 3.24 (s, 3H), 3.23 (d overlapping, 1H), 3.13 (dd, J = 11.0, 3.3 Hz, 1H), 2.80 (s, 3H), 2.78 (d overlapping, 1H), 2.67 (dd, J = 11.0, 4.9 Hz, 1H), 2.34 (m, 1H), 1.99 (m, 2H), 1.72 (m, 3H), 1.43 (m, 2H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 170.63, 151.17, 93.73, 93.17, 81.16, 56.53, 48.69, 46.69, 41.67, 33.44, 28.90, 28.83, 27.68, 23.49, 23.35; MS (70 eV): m/z (%): 370 (27) [M^+], 369 (22), 368 (100), 302 (30), 187 (26), 172 (12), 124 (76), 91 (20), 57 (20); C₁₉H₂₃CoN₂O₂ (370.34): calcd C 61.62, H 6.26, N 7.56; found C 60.96, H 6.17, N 7.66.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1,3-dimethyl-1,2,3,4,4a-endo, 6,7,8,9,10a-endo-decahydro-2-oxo-4-methylimino-benzol[g]quinazoline]cobalt (10e**):** From **1e** (0.153 g, 1 mmol), **8b** (240 μ L, 1.8 mmol), and

[CpCo(CO)₂] (224 µL, 1.8 mmol) in toluene (16 mL), with irradiation under reflux for 20 h. Flash chromatography (neutral alumina, pentane/acetone (7:3) gave a thick orange oil. Yield: 0.383 g (79 %); IR (CH₂Cl₂): $\tilde{\nu}$ = 2930, 1660, 1630, 1475, 805 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.35 (s, 5H), 3.41 (s, 3H), 3.18 (s, 3H), 3.10 (m, 2H), 2.84 (m, 1H), 2.79 (s, 3H), 2.62 (m, 1H), 2.10 (m, 1H), 1.67 (m, 7H); ¹³C NMR (75.8 MHz, CDCl₃): δ = 159.00, 154.33, 93.83, 93.49, 81.18, 57.48, 48.15, 44.72, 39.28, 36.77, 33.51, 30.38, 29.55, 29.08, 23.61, 23.60; MS (70 eV): m/z (%): 383 (100) [M^+], 381 (29), 326 (38), 303 (58), 301 (36), 272 (52), 258 (47), 256 (86), 229 (60), 187 (35), 172 (35), 128 (34), 124 (47), 97 (32), 85 (29), 83 (30), 71 (46); HRMS: calcd for C₂₀H₂₆CoN₃O 383.141; found: 383.140. When the flash chromatography was performed on neutral Al₂O₃ deactivated with 3 % H₂O or SiO₂ and eluted with a mixture of MeOH/CHCl₃, **10e** was completely transformed to the cobalt complex **10a**.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1,3-dimethyl-1,2,3,4,4a-endo,6,7,8,9,10a-endo-decahydro-2-oxo-4-ethylimino-benzol[quinazoline]-cobalt (**10f**): From **1f** (0.117 g, 0.7 mmol), **8b** (157 µL, 1.26 mmol), and [CpCo(CO)₂] (168 µL, 1.33 mmol) in toluene (12 mL), with irradiation under reflux for 22 h. Flash chromatography (neutral alumina, pentane/AcOEt (1:9) gave orange crystals. Yield: 0.153 g (55 %); m.p. 92–94 °C; IR (CH₂Cl₂): $\tilde{\nu}$ = 2980, 2940, 1670, 1640, 1490, 1470, 820 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.34 (s, 5H), 3.41 (s, 3H), 3.37 (m, 2H), 3.12 (m, 2H), 2.83 (d, J = 2.7 Hz, 1H), 2.77 (s, 3H), 2.72 (d, J = 3.3 Hz, 1H), 2.12 (m, 2H), 1.82 (m, 2H), 1.69 (m, 2H), 1.82 (m, 2H), 1.69 (m, 2H), 1.50 (m, 2H), 1.34 (t, J = 7.2 Hz, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 156.34, 154.47, 93.71, 92.70, 80.96, 57.83, 48.34, 45.51, 43.81, 39.37, 33.51, 30.52, 29.11, 28.83, 23.63, 23.54, 17.72; MS (70 eV): m/z (%): 397 (51) [M^+], 340 (37), 287 (36), 272 (32), 270 (33), 256 (46), 229 (63), 188 (28), 187 (66), 172 (22), 128 (54), 124 (100); HRMS: calcd for C₂₁H₂₈CoN₃O 397.156; found 397.156.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1-(1'- β -ribofuranose-2',3',5'-trimethoxy)-3-methyl-1,2,3,4,4a-endo,6,7,8,9,10a-endo-decahydro-2,4-dioxo-benzol[quinazoline]-cobalt (**10h**) (major isomer): From **1h** (0.20 g, 0.666 mmol), [CpCo(CO)₂] (0.18 g, 0.999 mmol), and **8b** (0.106 g, 0.999 mmol) in xylene (10 mL), with irradiation under reflux for 18 h. Another addition of [CpCo(CO)₂] (0.18 g, 0.999 mmol) and **8b** (0.106 g, 0.999 mmol) in xylene (3 mL), and irradiation at reflux for additional 20 h. Flash chromatography (SiO₂, hexanes/AcOEt 3:2) gave an orange oil. Yield: 0.249 g (71 %). This oil was a mixture of four diastereomers in the ratio 7.5:4:1:1. Compound **10h** was obtained as a 5:1 mixture by preparative TLC (hexanes/AcOEt, 45:55). Orange crystals; m.p. 75–77 °C; IR (C₆D₆): $\tilde{\nu}$ = 3090, 3085, 3040, 2930, 1700, 1670, 1480, 1125, 1090, 680 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂): δ = 5.48 (d, J = 4.6 Hz, 1H), 4.71 (s, 5H), 4.01 (m, 2H), 3.92 (dd, overlapping, J = 5.2 Hz, 1H), 3.82 (dd, overlapping, J = 5.4 Hz, 1H), 3.68 (dd, J = 10.6, 3.1 Hz, 1H), 3.54 (dd, J = 10.6, 4.5 Hz, 1H), 3.46 (s, 3H), 3.44 (s, 3H), 3.42 (s, 3H), 3.26 (d, J = 2.5 Hz, 1H), 3.06 (overlapping d, 1H), 2.89 (s, 3H), 2.75 (dd, J = 10.4, 5.7 Hz, 1H), 2.28 (m, 3H), 2.01 (m, 3H), 1.71 (m, 2H); ¹³C NMR (125.8 MHz, C₆D₆): δ = 171.54, 151.77, 94.74, 92.20, 91.36, 81.09, 80.30, 79.17, 72.62, 58.89, 58.11, 57.74, 53.92, 52.60, 44.78, 39.78, 29.04, 28.84, 27.39, 23.61, 23.46; MS (70 eV): m/z (%): 530 (42) [M^+], 464 (12), 356 (37), 256 (21), 187 (13), 175 (23), 159 (23), 143 (55), 124 (33), 115 (34), 101 (51), 71 (37), 45 (100); C₂₆H₃₃CoN₂O₆ (530.51): calcd C 58.84, H 6.60, N 5.28; found C 57.94, H 6.50, N 5.10.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1-(2',3'-isopropylidene-5'-methyluridine)-3-methyl-1,2,3,4,4a-endo,6,7,8,9,10a-endo-decahydro-2,4-dioxo-benzol[quinazoline]-cobalt (**10i**): From **1i** (0.312 g, 1 mmol), **8b** (270 µL, 2 mmol), and [CpCo(CO)₂] (224 µL, 1.8 mmol) in xylene (18 mL), with irradiation under reflux for 19 h. Flash chromatography (SiO₂, pentane/Et₂O 9:1) allowed the separation of the four diastereomers **10ia** (0.067 g), **10ib** (0.050 g), **10ic** (0.031 g), **10id** (0.027 g) with a total yield of 33 %.

Compound 10ia: orange crystals; m.p. 44–46 °C; IR (CH₂Cl₂): $\tilde{\nu}$ = 2920, 1700, 1660, 1460 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 5.58 (d, J = 1.6 Hz, 1H), 5.21 (dd, J = 6.4, 1.6 Hz, 1H), 5.05 (dd, J = 6.5, 4.4 Hz, 1H), 4.54 (m, 1H), 4.24 (s, 5H), 3.70 (m, 2H), 3.14 (s, 3H), 3.11 (m, 1H), 3.08 (s, 3H), 3.02 (d, J = 3.1 Hz, 1H), 2.56 (dd, J = 10.8, 5.2 Hz, 1H), 2.33 (m, 1H), 2.32 (m, 1H), 2.12 (m, 1H), 1.70 (m, 6H), 1.56 (s, 3H), 1.27 (s, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 170.70, 151.32, 113.54, 95.38, 93.86, 92.89, 86.13, 85.87, 82.88, 81.54, 73.85, 58.81, 55.89, 50.78, 45.76, 40.98, 28.97, 28.74, 27.62, 27.50, 25.54, 23.55, 23.40; MS (70 eV): m/z (%): 542 (70) [M^+], 356 (25), 256 (30), 187 (69), 172 (42), 159 (34), 129 (100), 128 (19), 124 (37), 101 (33), 71 (9); HRMS: calcd for C₂₇H₃₅CoN₂O₆ 542.183; found 542.183.

Compound 10ib: orange crystals; m.p. 59–63 °C; ¹H NMR (300 MHz, C₆D₆): δ = 5.10 (br d, J = 8.9 Hz, 3H), 4.58 (m, 1H), 4.46 (s, 5H), 3.80 (m, 2H), 3.37 (m, 2H), 3.32 (s, 3H), 3.18 (s, 3H), 3.15 (m, 1H), 2.16 (m, 3H), 2.02 (m, 1H), 1.91 (m, 1H), 1.75 (m, 2H), 1.50 (m, 2H), 1.49 (s, 3H), 1.23 (s, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 169.31, 113.19, 98.06, 93.38, 91.01, 87.50, 85.35, 83.39, 81.11, 74.45, 58.83, 56.39, 52.73, 51.57, 45.27, 28.68, 28.67, 27.48, 27.26, 25.37, 23.62, 23.54; MS (70 eV): m/z (%): 542 (72) [M^+], 187 (76), 172 (48), 159 (38), 129 (100), 124 (36), 101 (37), 71 (8).

Compound 10ic: orange crystals; m.p. 47–50 °C; ¹H NMR (300 MHz, C₆D₆): δ = 5.45 (d, J = 2.0 Hz, 1H), 5.31 (dd, J = 6.5, 2.0 Hz, 1H), 5.06 (dd, J = 6.6, 4.4 Hz, 1H), 4.50 (m, 1H), 4.36 (s, 5H), 3.68 (m, 2H), 3.38 (m, 1H), 3.36 (s, 3H), 3.13 (m, 1H), 3.12 (s, 3H), 2.83 (m, 1H), 2.22 (dd, J = 7.4, 1.2 Hz, 1H), 2.10 (m, 2H), 1.80 (m, 3H), 1.55 (s, 3H), 1.50 (m, 3H), 1.14 (s, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 168.99, 152.08, 113.70, 96.54, 96.13, 93.46, 90.82, 85.63, 85.30, 82.76, 81.12, 73.81, 58.85, 54.01, 52.14, 51.37, 45.19, 28.55, 27.79, 27.35, 27.31, 25.41, 23.50; MS (70 eV): m/z (%): 542 (62) [M^+], 231 (59), 187 (68), 172 (46), 159 (68), 129 (100), 124 (38), 101 (33), 71 (13).

Compound 10id: orange crystals; m.p. 52–55 °C; ¹H NMR (300 MHz, C₆D₆): δ = 5.23 (d, J = 1.1 Hz, 1H), 5.16 (dd, J = 6.4, 1.3 Hz, 1H), 5.08 (dd, J = 6.3, 4.0 Hz, 1H), 4.61 (dd, J = 6.5, 1.9 Hz, 1H), 4.28 (s, 5H), 3.74 (dd, J = 5.6, 2.0 Hz, 1H), 3.43 (dd, J = 10.7, 3.0 Hz, 1H), 3.22 (d, J = 3.1 Hz, 1H), 3.17 (s, 3H), 3.10 (dd, J = 5.2, 2.3 Hz, 1H), 3.06 (s, 3H), 2.59 (dd, J = 10.8, 5.2 Hz, 1H), 2.15 (m, 2H), 1.90 (m, 1H), 1.70 (m, 2H), 1.57 (s, 3H), 1.50 (m, 3H), 1.25 (s, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 171.18, 151.01, 113.25, 97.45, 94.35, 92.54, 87.23, 85.23, 83.39, 81.14, 74.33, 58.81, 58.27, 51.35, 45.93, 41.07, 29.11, 28.51, 27.55, 27.32, 25.37, 23.59, 23.43; MS (70 eV): m/z (%): 542 (54) [M^+], 356 (22), 256 (30), 187 (64), 172 (37), 159 (32), 129 (100), 124 (37), 101 (34), 71 (7).

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1-(1'- β -2'-deoxyribofuranose-3',5'-dimethoxy)-3-methyl-1,2,3,4,4a-endo,6,7,8,9,10a-endo-decahydro-2,4-dioxobenzol[quinazoline]-cobalt (**10j**) (major isomer): From **1j** (0.20 g, 0.74 mmol), [CpCo(C₂H₄)₂] (0.266 g, 1.48 mmol), and **8b** (0.157 g, 1.48 mmol) in THF (14 mL) at reflux without irradiation for 2 h. Flash chromatography (SiO₂, hexanes/AcOEt 1:1) gave an orange oil (yield: 0.349 g, 94 %) of a mixture of four diastereomers in the ratio 45:4:1:1. **10j** was obtained after a second flash chromatography (SiO₂, hexanes/AcOEt 55:45) as yellow crystals; m.p. 156–158 °C; IR (C₆D₆): $\tilde{\nu}$ = 2980, 2930, 2820, 1705, 1670, 1460, 1200, 1100, 1060 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂): δ = 5.89 (dd, J = 8.3, 6.1 Hz, 1H), 4.71 (s, 5H), 3.98 (m, 2H), 3.92 (dt, J = 6.1, 3.2 Hz, 1H), 3.59 (overlapping dd, 2H), 3.46 (s, 3H), 3.33 (s, 3H), 3.29 (d, J = 2.8 Hz, 1H), 3.03 (d, J = 5.7 Hz, 1H), 2.88 (s, 3H), 2.69 (dd, J = 10.0, 5.7 Hz, 1H), 2.33 (m, 1H), 2.28 (m, 1H), 2.24 (m, 1H), 2.03 (m, 5H), 1.76 (m, 1H), 1.67 (m, 1H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 171.78, 151.71, 95.01, 92.18, 87.02, 82.26, 81.68, 81.07, 73.59, 58.94, 56.50, 53.54, 52.49, 44.55, 39.80, 35.20, 29.17, 27.63, 28.81, 23.67, 23.51; MS (70 eV): m/z (%): 500 (15) [M^+], 356 (15), 354 (20), 256 (9), 159 (33), 145 (14), 124 (25), 113 (35), 87 (20), 59 (5), 45 (100); C₂₅H₃₃CoN₂O₅ (500.48): calcd C 59.99, H 6.65, N 5.60; found C 59.78, H 6.67, N 5.65. For details of the X-ray crystallographic data of **10j**, see ref. [8].

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1-(1'- β -ribofuranose-2',3',5'-triacetate)-3-methyl-1,2,3,4,4a-endo,6,7,8,9,10a-endo-decahydro-2,4-dioxo-benzol[quinazoline]-cobalt (**10k**): From **1k** (0.20 g, 0.595 mmol), [CpCo(C₂H₄)₂] (0.161 g, 0.893 mmol), and **8b** (0.126 g, 1.19 mmol) in THF (10 mL) at reflux without irradiation for 16 h. Addition of [CpCo(C₂H₄)₂] and diyne was carried out at reflux within 1 h and the was refluxed for a further 15 h. Flash chromatography (SiO₂, hexanes/EtOAc, 45:55) gave an inseparable mixture of four diastereomers in a ratio of 1:1:1:1 as an orange oil. Yield: 0.133 g (37 %); IR (C₆D₆): $\tilde{\nu}$ = 3100, 3040, 2940, 1760, 1720, 1680, 1370, 1225 cm⁻¹; ¹H and ¹³C NMR spectra were too complicated to be described; however, they clearly showed the presence of four diastereomers, for example: four Cp signals at δ = 4.76, 4.75, 4.74 and 4.72 with equal integration values; MS (70 eV): m/z (%): 600 (2) [M^+], 354 (16), 259 (10), 189 (26), 139 (29), 124 (17), 105 (17), 97 (21), 66 (13), 43 (100); C₂₈H₃₃CoN₂O₉ (600.51): calcd C 56.00, H 5.50, N 4.67; found C 55.74, H 5.52, N 4.52.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1-(1'- β -2'-deoxyribofuranose-3',5'-diacetate)-1,2,3,4,4a-endo,6,7,8,9,10a-endo-deca-2,4-dioxo-benzol[quinazoline]-cobalt (**10l**): From **1l** (0.312 g, 1 mmol), **8b** (270 µL, 2 mmol), and [CpCo(CO)₂] (224 µL, 1.8 mmol) in toluene (21 mL), with irradiation under reflux for 20 h. Flash chromatography (SiO₂, hexane/AcOEt 1:9)

gave an inseparable mixture of four diastereomers in a ratio of 1:1:1:1 as red crystals. Yield: 0.091 g (18 %); m.p. 60–62 °C; IR (CH₂Cl₂): $\tilde{\nu}$ = 2940, 1740, 1705, 1665, 1370, 1240, 810 cm⁻¹; ¹H and ¹³C NMR spectra were too complicated to be described; however they showed the presence of four diastereomers; MS (70 eV): m/z (%): 542 (2) [M^+], 281 (16), 160 (13), 159 (100), 129 (21), 113 (52), 106 (18), 105 (20), 91 (37), 81 (80), 79 (13); C₂₆H₃₁CoN₂O₇ (542.47): calcd C 57.57, H 5.76, N 5.16; found C 57.34, H 5.76, N 4.99.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,10a,11- η)-1,3-dimethyl-1,2,3,4,4a-endo, 11a-endo-hexahydro-2,4-dioxo-cyclohepta[g]quinazoline]cobalt (11a): From **1a** (0.14 g, 0.999 mmol), [CpCo(CO)₂] (0.36 g, 2 mmol), and **8c** (0.24 g, 2 mmol) in toluene (10 mL), with irradiation under reflux for 20 h. Flash chromatography (SiO₂, hexanes/Et₂O 25:75) gave yellow-orange crystals. Yield: 0.85 g (22 %); m.p. 129–132 °C; IR (C₆D₆): $\tilde{\nu}$ = 3090, 3000, 2930, 2850, 1700, 1665, 1470, 1420, 1360, 1295, 1110, 1000, 755 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.37 (s, 5H), 3.23 (s, 3H), 3.14 (d, J = 4.7 Hz, 1H), 3.03 (dd, J = 10.9, 3.0 Hz, 1H), 2.73 (s, 3H), 2.71 (d overlapping J = 3.0 Hz, 1H), 2.62 (dd, J = 10.9, 4.7 Hz, 1H), 2.28 (m, 1H), 2.16 (m, 1H), 2.01 (m, 1H), 1.76 (m, 1H), 1.45 (m, 6H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 171.29, 151.34, 97.24, 95.87, 80.67, 56.77, 52.93, 51.79, 42.17, 35.20, 35.08, 33.52, 32.49, 29.60, 29.04, 27.75; MS (70 eV): m/z (%): 384 (28) [M^+], 383 (23), 382 (100), 380 (13), 317 (2), 316 (11), 314 (12), 258 (2), 253 (7), 200 (7), 186 (10), 124 (29); C₂₀H₂₅CoN₂O₂ (384.36): calcd C 62.49, H 6.56, N 7.29; found C 61.95, H 6.68, N 6.86.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,10a,11- η)-1,3-dimethyl-1,2,3,4,4a-endo, 11a-endo-hexahydro-2-oxo-4-methylimino-cyclohepta[g]quinazoline]cobalt (11e): From **1e** (0.153 g, 1 mmol), **8c** (271 μ L, 1.8 mmol), and [CpCo(CO)₂] (224 μ L, 1.8 mmol) in toluene (16 mL), with irradiation under reflux for 20 h. Flash chromatography (neutral alumina, pentane/AcOEt 1:99) gave orange crystals. Yield: 0.084 g (21 %); m.p. 158–161 °C; IR (CH₂Cl₂): $\tilde{\nu}$ = 2940, 2870, 1665, 1635, 1480, 1460, 1435, 1150, 813 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.45 (s, 5H), 3.42 (s, 3H), 3.18 (s, 3H), 3.08 (m, 2H), 2.82 (m, 1H), 2.77 (s, 3H), 2.75 (m, 1H), 2.30 (m, 2H), 1.87 (m, 2H), 1.50 (m, 6H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 158.71, 153.93, 97.05, 95.80, 80.73, 57.39, 52.75, 49.60, 38.75, 36.52, 35.60, 35.24, 33.58, 32.67, 31.06, 29.73, 29.20; MS (70 eV): m/z (%): 397 (40) [M^+], 340 (29), 317 (34), 272 (25), 270 (40), 340 (29), 317 (34), 272 (25), 270 (40), 243 (47), 200 (25), 186 (33), 141 (34), 135 (35), 124 (100), 91 (21); HRMS: calcd for C₂₁H₂₈CoN₃O 397.156; found 397.157.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,10a,11- η)-1,3-dimethyl-1,2,3,4,4a-endo, 11a-endo-hexahydro-2-oxo-4-ethylimino-cyclohepta[g]quinazoline]cobalt (11f): From **1f** (0.167 g, 1 mmol), **8c** (271 μ L, 1.8 mmol), and [CpCo(CO)₂] (240 μ L, 1.9 mmol) in toluene (16 mL), with irradiation under reflux for 22 h. Flash chromatography (neutral alumina, pentane/AcOEt 1:9) gave orange crystals. Yield: 0.062 g (22 %); m.p. 117–119 °C; IR (CH₂Cl₂): $\tilde{\nu}$ = 2960, 2930, 1680, 1650, 1440, 813 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.42 (s, 5H), 3.40 (s, 3H), 3.38 (m, 2H), 3.08 (m, 2H), 2.82 (d, J = 2.7 Hz, 1H), 2.76 (s, 3H), 2.71 (d, J = 3.5 Hz, 1H), 2.28 (m, 2H), 1.88 (m, 2H), 1.59 (m, 6H), 1.36 (t, J = 7.2 Hz, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 156.56, 154.35, 97.12, 95.59, 80.50, 57.67, 52.66, 50.20, 43.83, 39.13, 35.47, 35.24, 33.44, 32.66, 30.69, 29.20, 28.66, 17.71; MS (70 eV): m/z (%): 411 (56) [M^+], 354 (51), 303 (25), 301 (46), 286 (49), 285 (23), 284 (59), 270 (58), 243 (98), 230 (33), 229 (100), 200 (35), 186 (83), 172 (69), 141 (36), 135 (72), 124 (89), 84 (83); HRMS: calcd for C₂₂H₃₀CoN₃O 411.172; found 411.172.

(5,5a,9a,10- η)-1,3-dimethyl-1,2,3,4,4a-endo,6,7,8,9,10a-endo-decahydro-2,4-dioxo-benzo[g]quinazoline (13): An ice-cold solution of CuCl₂ (0.368 g, 2.16 mmol) and Et₃N (0.066 g, 0.648 mmol) in H₂O (15 mL) was added slowly to a cold (0 °C) solution of complex **10a** (0.20 g, 0.54 mmol) in THF (30 mL). The reaction was monitored by TLC and after 2 min all the starting material had disappeared. The mixture was concentrated by rotary evaporation, the residue ($\approx$ 10 mL) extracted with CHCl₃ (3 $\times$ 30 mL), successively washed with water (2 $\times$ 30 mL) and saturated aqueous NaCl (20 mL), and then dried over MgSO₄. Filtration and evaporation of the solvent gave a pale yellow oil. Preparative TLC (hexanes/AcOEt, 2:3) gave **13**. Yield: 0.12 g (91 %); white crystals; m.p. 112–114 °C; IR (C₆D₆): $\tilde{\nu}$ = 2940, 2860, 1715, 1675, 1480, 1415, 1280, 1100 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 5.83 (brd, J = 1.7 Hz, 1H), 5.50 (d, J = 6.0 Hz, 1H), 3.33 (m, 1H), 3.24 (s, 3H), 2.69 (s, 3H), 2.54 (dd, J = 7.6, 6.6 Hz, 1H), 2.17 (m, 1H), 1.91 (m, 3H), 1.33 (m, 2H), 1.16 (m, 2H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 24.36 (2 CH₂), 170.03, 153.17, 138.33, 136.22, 118.38, 117.70, 52.87, 39.67, 33.47, 30.98, 30.83, 27.72, 24.36 (2CH₂); MS (70 eV): m/z (%): 246 (100)

[M^+], 245 (95), 244 (17), 229 (9), 218 (28), 217 (40), 188 (20), 159 (28), 132 (34), 104 (76), 91 (69); C₁₄H₁₈N₂O₂ (246.31): calcd C 68.21, H 7.31, N 11.37; found C 67.94, H 7.39, N 10.80.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1-methyl-1,2,4a-endo,6,7,8,9,10a-endo-octahydro-2-oxo-4-N,N'-dimethylamino-benzo[g]quinazoline]cobalt (20d): From **3d** (0.153 g, 1 mmol), **8b** (260 μ L, 2 mmol), and [CpCo(CO)₂] (248 μ L, 2 mmol) in toluene (27 mL), with irradiation under reflux for 20 h. Flash chromatography (SiO₂, CHCl₃/CH₃OH, 7:3) gave a brown oil of **20d**. Yield: 0.028 g (9 %); MS (70 eV): m/z (%): 383 (100) [M^+], 381 (41), 317 (33), 316 (22), 315 (81), 300 (21), 259 (136), 258 (48), 256 (25), 230 (22), 229 (79), 217 (32), 201 (29), 189 (76), 187 (29), 172 (25), 158 (46), 157 (58), 156 (19), 142 (20), 130 (25), 129 (83), 128 (29), 124 (64), 116 (39).

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1-methyl-1,2,4a-endo,6,7,8,9,10a-endo-octahydro-2-oxo-4-methoxy-benzo[g]quinazoline]cobalt (21): From **4a** (0.140 g, 1 mmol), **8b** (200 μ L, 1.5 mmol), and [CpCo(CO)₂] (186 μ L, 1.5 mmol) in toluene (16 mL), with irradiation under reflux for 17 h. Flash chromatography (SiO₂, pentane/acetone, 1:4) gave **21** (0.358 mmol) and **25** (0.097 mmol, vide infra). The total yield of the reaction was 46 %. **21**: orange crystals; m.p. 128–130 °C; IR (CHCl₃): $\tilde{\nu}$ = 2980, 1630, 1435, 1250, 1075, 1015 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.28 (s, 5H), 3.54 (s, 3H), 3.25 (dd, J = 12.6, 3.2 Hz, 1H), 2.91 (s, 3H), 2.87 (m, 2H), 2.38 (dd, J = 11.3, 4.8 Hz, 1H), 2.12 (m, 1H), 1.93 (m, 2H), 1.66 (m, 3H), 1.45 (m, 2H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 173.61, 155.12, 93.95, 92.76, 81.07, 58.65, 53.70, 50.03, 45.34, 36.78, 33.12, 28.91, 28.68, 23.39, 23.28; MS (70 eV): m/z (%): 370 (100) [M^+], 367 (55), 363 (20), 304 (63), 301 (55), 288 (18), 245 (15), 187 (18), 124 (27); C₁₉H₂₃CoN₂O₂ (370.34): calcd C 61.62, H 6.26, N 7.56; found C 61.83, H 6.08, N 7.49.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1-methyl-1,2,4a-endo,6,7,8,9,10a-endo-octahydro-2-oxo-4-ethoxy-benzo[g]quinazoline]cobalt (22): From **4b** (0.140 g, 1 mmol), **8b** (200 μ L, 1.5 mmol), and [CpCo(CO)₂] (186 μ L, 1.5 mmol) in toluene (16 mL), with irradiation under reflux for 17 h. Flash chromatography (SiO₂, pentane/acetone, 1:4) gave **22** (0.037 g) and **25** (0.013 g). The total yield of the reaction was 22 %. Compound **22**: Orange crystals; m.p. 111–113 °C; IR (C₆D₆): $\tilde{\nu}$ = 2990, 2940, 1690, 1660, 1630, 1610, 1430, 1380, 1240, 1020 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.30 (s, 5H), 4.27 (m, 1H), 4.07 (m, 1H), 3.26 (dd, J = 11.0, 2.7 Hz, 1H), 2.92 (m, 4H), 2.88 (d, J = 2.7 Hz, 1H), 2.40 (dd, J = 11.0, 4.8 Hz, 1H), 2.20 (m, 1H), 1.97 (m, 2H), 1.70 (m, 3H), 1.48 (m, 2H), 1.05 (t, J = 7.1 Hz, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 173.18, 155.16, 94.02, 92.58, 81.70, 62.36, 58.63, 50.83, 45.44, 36.69, 33.17, 29.04, 28.72, 23.76, 23.63, 14.35; MS (70 eV): m/z (%): 384 (57) [M^+], 354 (29), 288 (100), 230 (23), 189 (44), 187 (36), 186 (32), 160 (21), 159 (24), 158 (23), 131 (23), 129 (26), 128 (25), 116 (21), 115 (21), 91 (44), 77 (12); HRMS: calcd for C₂₀H₂₅CoN₂O₂ 384.125; found 384.125.

(η^5 -2,4-Cyclopentadien-1-yl)[(5,5a,9a,10- η)-1-methyl-1,2,4a-endo,6,7,8,9,10a-endo-octahydro-2-oxo-4-propoxy-benzo[g]quinazoline]cobalt (23): From **4c** (0.168 g, 1 mmol), **8b** (240 μ L, 1.8 mmol), and [CpCo(CO)₂] (224 μ L, 1.8 mmol) in toluene (16 mL), with irradiation under reflux for 18 h. Flash chromatography (SiO₂, hexanes/acetone, 1.5:4.5) gave **23** (0.093 g) and **25** (0.014 g). The total yield of the reaction was 27 %. **23**: Orange crystals; m.p. 76–77 °C; IR (CH₂Cl₂): $\tilde{\nu}$ = 2900, 1630, 1620, 1320, 1280 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.30 (s, 5H), 4.20 (m, 1H), 4.02 (m, 1H), 3.26 (dd, J = 11.2, 3.3 Hz, 1H), 2.95 (d, J = 4.8 Hz, 1H), 2.92 (s, 3H), 2.88 (d, J = 3.2 Hz, 1H), 2.42 (dd, J = 11.2, 4.7 Hz, 1H), 2.22 (m, 1H), 1.97 (m, 2H), 1.68 (m, 3H), 1.50 (m, 4H), 0.79 (t, J = 7.4 Hz, 3H); ¹³C NMR (75.8 MHz, C₆D₆): δ = 173.34, 155.16, 94.00, 92.62, 81.11, 68.08, 58.59, 50.09, 45.63, 36.83, 33.17, 29.02, 28.71, 23.43, 23.32, 22.31, 10.65; MS (70 eV): m/z (%): 398 (65) [M^+], 354 (39), 288 (74), 272 (59), 243 (24), 231 (44), 230 (100), 229 (36), 202 (33), 189 (77), 187 (22), 187 (21), 186 (40), 160 (32), 159 (53), 131 (27), 129 (31), 128 (23), 124 (70), 116 (22), 91 (37); HRMS: calcd for C₂₁H₂₇CoN₂O₂ 398.140; found 398.139.

(η^5 -2,4-Cyclopentadien-1-yl)-[(5,5a,9a,10- η)-1-methyl-1,2,3,4,4a-endo, 6,7,8,9,10a-endo-decahydro-2,4-dioxo-benzo[g]quinazoline]cobalt (25): From hydrolysis of the corresponding imidates. For example, **22** (10 mg, 0.026 mmol) was added to a suspension of flash SiO₂ (3 g) in acetone (4 mL), which contained H₂O (1 mL) and was then left to stand at room temperature for 20 h. After filtration through a short pad of Celite and drying over Na₂SO₄, evaporation of the solvent gave **25** with a very high purity (90 %). Orange crystals; m.p. 197 °C (decomp); IR (CH₂Cl₂): $\tilde{\nu}$ = 2368, 2312, 1692, 780 cm⁻¹; ¹H NMR (300 MHz, C₆D₆): δ = 4.28 (s, 5H), 3.13 (d, J = 4.5 Hz, 1H), 3.08 (dd, J = 9.4, 2.8 Hz, 1H), 2.72 (d, J = 2.8 Hz,

1H), 2.70 (s, 3H), 2.50 (dd, $J = 11.0$, 4.5 Hz, 1H), 2.46 (m, 1H), 2.30 (m, 1H), 1.95 (m, 2H), 1.70 (m, 3H), 1.42 (m, 2H); ^{13}C NMR (75.8 MHz, C_6D_6): $\delta = 171.55$, 150.50, 94.25, 93.79, 81.42, 58.54, 48.12, 45.20, 41.47, 32.62, 29.12, 29.02, 23.52, 23.40; MS (70 eV): m/z (%): 356 (26) [M^+], 355 (19), 353 (100), 350 (12), 288 (13), 187 (15), 159 (9), 128 (12), 124 (54); HRMS: calcd for $\text{C}_{18}\text{H}_{21}\text{CoN}_2\text{O}_2$ 356.093; found 356.093.

(η^5 -2,4-Cyclopentadien-1-yl)-[(5,5a,9a,10- η)-1-ethyl-1,2,3,4,4a-endo, 6,7,8,9,10a-endo-decahydro-2,4-dioxo-benz[g]quinazoline]cobalt (26): From **4d** (0.154 g, 1 mmol), **8b** (240 μL , 1.8 mmol), and $[\text{CpCo}(\text{CO})_2]$ (224 μL , 1.8 mmol) in toluene (16 mL), with irradiation under reflux for 19 h. Flash chromatography (SiO_2 , hexanes/acetone, 1:9) gave an orange oil. Yield: 0.028 g (9%); ^1H NMR (300 MHz, C_6D_6): $\delta = 4.27$ (s, 5H), 3.45 (m, 1H), 3.34 (dd, $J = 10.8$, 3.1 Hz, 1H), 3.11 (d, $J = 5.0$ Hz, 1H), 3.05 (m, 1H), 2.73 (d, $J = 3.0$ Hz, 1H), 2.40 (m, 2H), 1.95 (m, 2H), 1.68 (m, 3H), 1.45 (m, 2H), 1.04 (t, $J = 7.0$ Hz, 3H).

Anti and syn-(η^5 -2,4-cyclopentadien-1-yl)-[(7a,8,9,10- η)-2-benzoyl-1,2,3,4,6,7,10a,10b-octahydro-9,10-bis-(trimethylsilyl)-5H-1,3-dioxopyrido-[3,2- i]quinazoline]cobalt complexes (27): From **6a** (0.10 g, 0.355 mmol), $[\text{CpCo}(\text{CO})_2]$ (0.115 g, 0.638 mmol), in THF (3 mL), and BTMSA (6 mL), with irradiation at room temperature for 17 h. The two diastereomers were inseparable by flash chromatography (SiO_2 , hexanes/ Et_2O 2:3) and fractional recrystallization (Et_2O /hexanes). **27**: Yield: 0.058 g (23%); *anti*/*syn* = 5, orange crystals; m.p. 103–105 °C; IR (C_6D_6): $\tilde{\nu} = 2950$, 1755, 1705, 1675, 1600, 1250, 970, 850 cm^{-1} ; ^1H NMR (400 MHz, C_6D_6): $\delta = 8.00$ (d, $J = 7.4$ Hz, 2H), 4.48 (s, 1H), 4.06 (s, 5H), 2.26 (m, 1H), 2.21 (d, $J = 8.0$ Hz, 1H), 1.65 (m, d overlapping $J = 8.0$ Hz, 2H), 1.20 (m, 4H), 0.45 (s, 9H), 0.35 (s, 9H); ^{13}C NMR (125.8 MHz, C_6D_6): $\delta = 170.33$, 169.43, 150.63, 133.83, 133.70, 130.56, 128.77, 87.58, 84.18, 81.70, 71.01, 61.50, 59.84, 45.54, 44.07, 34.74, 23.57, 4.89, 3.41; MS (70 eV): m/z (%): 576 (4) [M^+], 437 (2), 332 (7), 179 (17), 142 (62), 124 (14), 115 (32), 107 (87), 80 (100), 74 (55); $\text{C}_{29}\text{H}_{37}\text{CoN}_2\text{O}_3\text{Si}_2$ (576.73): calcd C 60.34, H 6.42, N 4.86; found C 60.02, H 6.65, N 4.87.

(η^5 -2,4-Cyclopentadien-1-yl)-[(7a,8,9,10- η)-2-benzoyl-1,2,3,4,6,7,10a,10b-octahydro-9,10-dicarboxylate-5H-1,3-dioxopyrido[3,2- i]quinazoline]-cobalt (28): From **6a** (0.10 g, 0.355 mmol), $[\text{CpCo}(\text{CO})_2]$ (0.115 g, 0.64 mmol), and DMAD (0.252 g, 1.78 mmol) in THF (10 mL), with irradiation at room temperature for 21 h. Flash chromatography (SiO_2 , hexanes/ Et_2O 1:9) gave *anti*-**28** as orange crystals which sublimed without melting at 84 °C. Yield: 0.119 g (61%); IR (CD_2Cl_2): $\tilde{\nu} = 2950$, 1750, 1725, 1700, 1675, 1600, 1450, 1255, 1200 cm^{-1} ; ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 7.97$ (m, 2H), 7.69 (t, $J = 7.3$ Hz, 1H), 7.55 (t, $J = 7.5$ Hz, 2H), 5.62 (s, 1H), 4.99 (s, 5H), 4.42 (m, 1H), 3.81 (s, 3H), 3.60 (s, 3H), 3.12 (d, $J = 8$ Hz, 1H), 2.86 (m, 1H), 2.78 (d, $J = 7.4$ Hz, 1H), 1.91 (m, 4H); ^{13}C NMR (75.8 MHz, CD_2Cl_2): $\delta = 172.11$, 170.67, 170.52, 167.59, 150.04, 135.04, 132.78, 130.46, 129.31, 83.76, 79.57, 78.30, 72.06, 60.01, 54.27, 52.86, 52.12, 46.50, 43.75, 33.98, 23.74; MS (70 eV): m/z (%): 548 (3) [M^+], 246 (3), 218 (3), 142 (83), 141 (77), 124 (61), 115 (47), 105 (81), 78 (100), 77 (86), 66 (45); $\text{C}_{27}\text{H}_{25}\text{CoN}_2\text{O}_7$ (584.44): calcd C 59.12, H 4.56, N 5.11; found C 58.85, H 4.81, N 4.82.

Anti and syn-(η^5 -2,4-cyclopentadien-1-yl)-[(7a,8,9,10- η)-1,2,3,4,6,7,10a,10b-octahydro-9,10-bis-(trimethylsilyl)-5H-1,3-dioxopyrido[3,2- i]quinazoline]-cobalt complexes (29): From **6e** (0.146 g, 0.82 mmol), $[\text{CpCo}(\text{CO})_2]$ (0.266 g, 1.476 mmol) in THF (8 mL), and BTMSA (6 mL), with irradiation at room temperature for 17 h. The two diastereomers were inseparable by flash chromatography (SiO_2 , $\text{CHCl}_3/\text{MeOH}$ 99:1) and fractional recrystallization (Et_2O /hexanes). **29**: Yield: 0.135 g (35%); *anti*/*syn* = 10; orange crystals; m.p. 168 °C (decomp); IR (C_6D_6): $\tilde{\nu} = 3380$, 3190, 2950, 1700, 1675, 1260, 1250, 855, 830 cm^{-1} ; ^1H NMR (300 MHz, C_6D_6): $\delta = 9.47$ (brs, 1H), 6.18 (s, 1H), 4.62 (s, 5H), 4.41 (m, 1H), 2.16 (m, 1H), 2.01 (d, $J = 8.0$ Hz, 1H), 1.64 (m, 1H), 1.41 (d, $J = 8.0$ Hz, 1H), 1.12 (m, 3H), 0.47 (s, 9H), 0.32 (s, 9H); ^{13}C NMR (75.8 MHz, C_6D_6): $\delta = 170.66$, 151.83, 86.89, 83.73, 81.66, 72.48, 61.54, 60.39, 44.87, 43.46, 34.85, 23.71, 4.49, 3.29; MS (70 eV): m/z (%): 474 (4), 473 (13), 472 (38) [M^+], 457 (7), 399 (26), 347 (13), 331 (44), 259 (53), 146 (13), 124 (23), 84 (99), 73 (100); $\text{C}_{22}\text{H}_{33}\text{CoN}_2\text{O}_2\text{Si}_2$ (472.62): calcd C 55.91, H 7.04, N 5.93; found C 57.76, H 6.87, N 5.93.

(η^5 -2,4-Cyclopentadien-1-yl)-[(7a,8,9,10- η)-1,2,3,4,6,7,10a,10b-octahydro-9,10-dicarboxylate-1,3-dioxopyrido[3,2- i]quinazoline]cobalt (30): From **6e** (0.147 g, 0.82 mmol), $[\text{CpCo}(\text{CO})_2]$ (0.266 g, 1.476 mmol), and DMAD (0.583 g, 4.1 mmol) in THF (10 mL), with irradiation at room temperature for 21 h. Flash chromatography (SiO_2 , $\text{CHCl}_3/\text{MeOH}$ 99.5:0.5) gave

orange-red crystals. Yield: 0.235 g (73%); m. p. 210 °C (decomp); IR (CDCl_3): $\tilde{\nu} = 3390$, 2950, 1710, 1485, 1450, 1430, 1265 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): $\delta = 7.49$ (s, 1H), 5.56 (s, 1H), 4.90 (s, 5H), 4.51 (m, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 2.94 (d, $J = 8.0$ Hz, 1H), 2.78 (m, 1H), 2.70 (d, $J = 8.0$ Hz, 1H), 1.83 (m, 4H); ^{13}C NMR (75.8 MHz, CD_2Cl_2): $\delta = 172.22$, 170.88, 168.45, 151.60, 83.51, 78.90, 78.15, 72.27, 61.19, 55.01, 52.79, 52.11, 45.92, 43.55, 34.24, 23.91; MS (70 eV): m/z (%): 444 (28) [M^+], 442 (2), 383 (2), 378 (4), 318 (42), 288 (34), 287 (100), 246 (26), 229 (17), 215 (13), 158 (11), 124 (15), 118 (3); $\text{C}_{20}\text{H}_{21}\text{CoN}_2\text{O}_6$ (444.33): calcd C 54.05, H 4.73, N 6.30; found C 53.29, H 4.71, N 5.99.

(η^5 -2,4-Cyclopentadien-1-yl)-[5-(1,2,3,4- η)-2,3-bis(trimethylsilyl)-propene-diyl]-2-benzoyl-1,2,3,5,6,7,8,9-octahydro-1,3-dioxopyrido[1,2- c]pyrimidine]-cobalt (31): From **6a** (0.28 g, 0.709 mmol), $[\text{CpCo}(\text{C}_2\text{H}_5)_2]$ (0.191 g, 1.06 mmol) in THF (5 mL), and BTMSA (5 mL) at room temperature with irradiation (lamp at about 15 cm from the flask, power on Variac set to 40) for 2 h. Flash chromatography (SiO_2 ; hexanes/ AcOEt 55:45) gave orange-red crystals. Yield: 88 mg (21%); m.p. 143 °C (decomp); IR (CD_2Cl_2): $\tilde{\nu} = 2960$, 2900, 1740, 1685, 1655, 1600, 1450, 1265, 1255, 900, 855, 840 cm^{-1} ; ^1H NMR (300 MHz, C_6D_6): $\delta = 8.05$ (m, 2H), 6.93 (m, 3H), 4.57 (s, 5H), 4.39 (m, 1H), 3.29 (s, 1H), 2.59 (m, 1H), 2.30 (m, 1H), 2.29 (s, 1H), 1.65 (m, 1H), 1.48 (m, 1H), 1.35 (m, 1H), 0.98 (s, 1H), 0.47 (s, 9H), 0.10 (s, 9H); ^{13}C NMR (75.8 MHz, C_6D_6): $\delta = 172.33$, 171.67, 150.49, 134.19, 134.04, 130.63, 128.85, 91.15, 87.69, 83.85, 80.77, 71.54, 62.31, 50.77, 31.92, 38.08, 17.31, 3.85, 1.54; MS (70 eV): m/z (%): 576 (2) [M^+], 575 (4), 574 (10), 508 (2), 469 (5), 404 (3), 329 (12), 179 (24), 142 (84), 124 (32), 115 (42), 105 (100), 77 (65); $\text{C}_{29}\text{H}_{37}\text{CoN}_2\text{O}_3\text{Si}_2$ (576.73): calcd C 60.34, H 6.42, N 4.86; found C 60.29, H 6.45, N 4.53.

(η^5 -2,4-Cyclopentadien-1-yl)-[1-(1,2,3,4- η)-2,3-bis(trimethylsilyl)-1,3-cyclobuta-dien-1-yl]-propyl-3-benzoyl-5-methylthymine]cobalt (32): From **6c** (0.20 g, 0.676 mmol), $[\text{CpCo}(\text{CO})_2]$ (0.182 g, 1.014 mmol) in THF (7 mL), and BTMSA (10 mL) at room temperature, with irradiation for 18 h. Flash chromatography (SiO_2 , hexanes/ Et_2O 3:7) gave an orange-yellow oil. Yield: 71 mg (29%); IR (CH_2Cl_2): $\tilde{\nu} = 2960$, 1755, 1705, 1660, 1600, 1440, 1250, 845, 815 cm^{-1} ; ^1H NMR (300 MHz, C_6D_6): $\delta = 7.92$ (d, $J = 7.0$ Hz, 2H), 7.01 (m, 1H), 6.93 (m, 2H), 6.01 (s, 1H), 4.73 (s, 5H), 4.15 (s, 1H), 3.27 (m, 1H), 3.12 (m, 1H), 1.71 (m, overlapping, 1H), 1.69 (s, 3H), 1.50 (m, 2H), 0.18 (s, 9H), 0.89 (m, 1H), 0.14 (s, 9H); MS (70 eV): m/z (%): 590 (9) [M^+], 486 (3), 420 (3), 294 (5), 205 (8), 179 (14), 105 (100), 77 (62); HMRS: calcd for $\text{C}_{30}\text{H}_{39}\text{CoN}_2\text{O}_3\text{Si}_2$ 590.754; found 590.685.

(η^5 -2,4-Cyclopentadien-1-yl)-[5-(1,2,3,4- η)-2,3-bis(trimethylsilyl)-propene-diyl]-1,2,3,5,6,7,8,9-hexahydro-1-oxo-3- N -acetylaminopyrido[1,2- c]pyrimidine]cobalt (33) and (η^5 -2,4-cyclopentadien-1-yl)-[1-(1,2,3,4- η)-2,3-bis(trimethylsilyl)-1,3-cyclobutadien-1-yl]-propyl- N -acetylcytosine]cobalt (34): From **7** (0.109 g, 0.5 mmol), BTMSA (3 mL, 3 mmol), and $[\text{CpCo}(\text{CO})_2]$ (124 μL , 1 mmol) in THF (19 mL), with irradiation at room temperature for 20 h. Flash chromatography (SiO_2 , pentane/ AcOEt 3:7) gave **33** (32 mg, 20%) and **34** (7 mg, 3%).

Compound 33: Red oil; ^1H NMR (300 MHz, C_6D_6): $\delta = 4.50$ (m, 1H), 4.37 (s, 5H), 3.38 (s, 1H), 2.55 (m, 1H), 2.30 (m, 1H), 2.10 (s, 3H), 2.06 (s, 1H), 1.50 (m, 4H), 0.48 (s, 3H); MS (70 eV): m/z (%): 514 (44) [M^+], 511 (29), 373 (30), 372 (28), 314 (19), 298 (20), 124 (24), 114 (23), 75 (36), 74 (24), 73 (100), 57 (23).

Compound 34: Yellow oil; ^1H NMR (300 MHz, C_6D_6): $\delta = 7.46$ (d, $J = 7.2$, 1H), 6.47 (d, $J = 7.2$ Hz, 1H), 4.70 (s, 5H), 4.20 (s, 1H), 3.38 (m, 2H), 2.26 (s, 3H), 1.65 (m, 4H), 0.15 (s, 3H), 0.10 (s, 3H); MS (70 eV): m/z (%): 514 (48) [M^+], 382 (25), 294 (18), 196 (14), 182 (15), 168 (17), 167 (18), 149 (18), 124 (24), 116 (24), 83 (20), 81 (19), 75 (64), 74 (41), 73 (100), 69 (16), 59 (28), 57 (18).

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