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Diastereoselective approach to 11-aryl steroid skeletons through a cobalt(I)-mediated [2+2+2] cyclization of allenediynes

Marc Petit, Corinne Aubert* and Max Malacria*

Université Pierre et Marie Curie-Paris 6, Laboratoire de Chimie Organique (UMR CNRS 7611), Institut de Chimie Moléculaire (FR 2769), Case 229, 4 place Jussieu, F-75252 Paris cedex 05, France

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Abstract—The cobalt(I)-mediated [2+2+2] cycloaddition reactions of allenediynes of yne-allene-yne type bearing an aryl group on the allene are described. The cyclizations are totally chemo- and regioselective and show low diastereoselectivities. η^4-Complexed tricyclic (6,6,6) compounds were obtained in good yields as mixtures of *endo*/*exo* diastereomers. The cyclization is also compatible with an oxyfunctionality at C3. By designing an allenediyne having a preexisting D ring, we succeeded in building skeletons of 11-aryl steroids in one step and in a totally diastereoselective manner and with simultaneous introduction of an angular methyl group at C10 and an aryl substituent at C11.

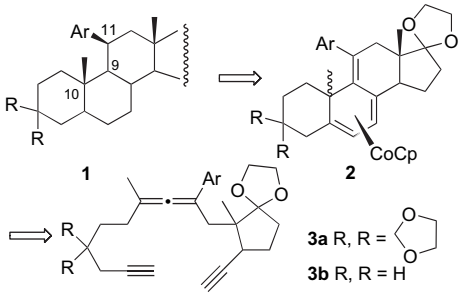
1. Introduction

In the last two decades, the synthesis, biological evaluation, and clinical applications of a new class of antiprogestational steroids, which present an 11β-aryl unit have been studied.[1,2] Due to their relevant pharmacological properties, a large number of synthetic efforts aimed at producing new compounds has been reported.[3] However the synthesis of such steroids is still in need of the development of new synthetic methods.

In the context of our interests in metal-catalyzed or radical cyclizations cascades directed toward the construction of basic skeletons of natural products,[4] we have explored the feasibility of building 11-aryl steroid frameworks by using an intramolecular cobalt(I)-mediated [2+2+2] cycloaddition reaction of allenediynes.

Transition metal-catalyzed cyclizations have already been used in the synthesis of the steroid nucleus.[5,6] As for an example, the cobalt(I) synthesis of racemic oestrone is probably the most spectacular illustration of the potency of such an approach.[7] In addition, intramolecular cyclizations of enediynes that allow the simultaneous formation of either the BCD or ABCD ring systems have been proposed.[8] Although 11-trimethylsilyl-substituted steroid frameworks have been described,[9] only one example of a low yielding access to 11-α-heterosubstituted steroid skeleton has been reported.

Our strategy depicted in Scheme 1 would allow in one step the creation of the ABC ring system and most interestingly, the simultaneous introduction of the substituents at both C11 and C10. Indeed, tetracyclic complex **2** could be reached from the intramolecular [2+2+2] cyclization of allenediyne **3** incorporating a preexisting D ring. Subsequent transformations of **2** might lead to 11β-aryl steroids **1**.



Scheme 1.

In this paper, after having presented the cyclizations of allenediynes of yne-allene-yne type, we will document and discuss the above approach that was achieved in our laboratory.[10]

2. Results and discussion

2.1. Cobalt(I)-mediated cyclizations of allenediynes of yne-allene-yne type

Allenes, which present cumulated C–C bonds are highly appealing candidates for the transition metal-catalyzed

* Corresponding authors. Tel.: +33 14427 3586; fax: +33 14427 7360; e-mail: max.malacria@upmc.fr

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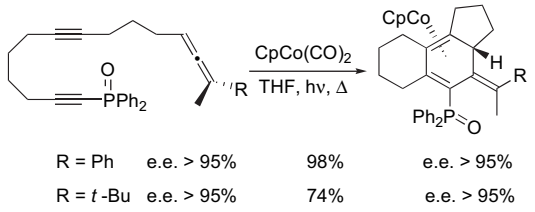
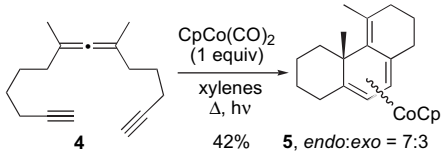
reactions. Over the last years, their reactivity in presence of various catalysts in a large variety of cyclizations and subsequently, their synthetic applications have been extensively investigated.[11,12] Although allenes are good ligands in organometallic complexes, only few examples involving this unsaturated component in [2+2+2] cycloaddition reactions have been reported.[13] Previously, it was discovered in our group that allenes are relevant partners for intramolecular [2+2+2] cocyclizations to alkynes.[14] For instance, upon treatment with $CpCo(CO)_2$, allenediynes of yne-yne-allene type furnished the corresponding cycloadducts in high yields and in a complete chemo-, regio-, and diastereoselective manner.[15] Moreover, with optically active allenes, the process can be performed with a total transfer of chirality (Scheme 2).



Scheme 2.

However, under the same conditions the allenediyne **4** with tetrasubstituted internal allene led chemo- and regioselectively to the corresponding η^4-complexed tricyclic compound **5** as a 7:3 diastereomeric mixture in moderate yield (Scheme 3).

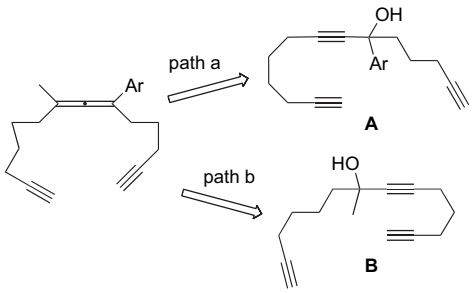


Scheme 3.

Before starting the synthesis of **2**, we initially decided to investigate the behavior of different allenediynes of yne-allene-yne type bearing an aryl group on the allene and to evaluate the influence of such substituent on the course of the cyclization.

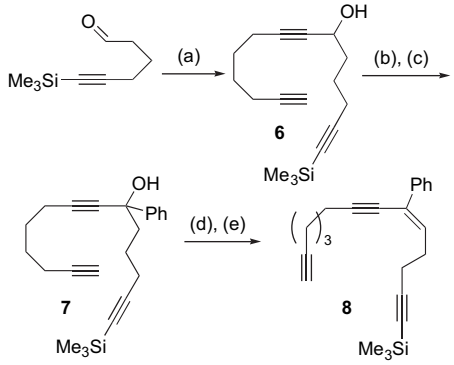
2.1.1. Preparation of the allenediynes. The preparation of allenic compounds has been widely investigated and highly useful methods have been developed for obtaining numerous substituted allenes.[16] In this study, we chose to introduce the allene unit via a copper(I) salt S_N2' displacement of propargylic sulfonate group.[17] Therefore, the allenediynes were prepared following the general sequence: (1) preparation of the requisite triyne and (2) introduction of the allene in the last step. However, it was possible to envision for this last step the addition of either methylcopper or arylcopper reagent onto the mesylates derived from the alcohol of type **A** or **B**, respectively (path a or b) (Scheme 4).

Thus, considering path a the addition of monolithiated octa-1,7 diyne to 6-trimethylsilyl-5-hexynal[18] furnished the corresponding alcohol **6**, which is readily transformed to the



Scheme 4.

tertiary alcohol **7** (Ar=Ph) (Scheme 5). However, its conversion into the corresponding mesylate failed and the enediyne **8** was obtained in 76%. Several attempts to carry out the S_N2' reaction with the corresponding methylether, even in presence of Lewis acid, were unsuccessful, the ether remaining unchanged.



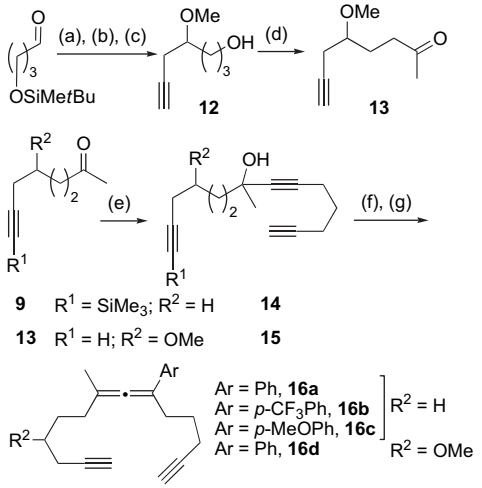
Scheme 5. (a) *n*-BuLi, octa-1,7-diyne, THF, −78 °C, 76%; (b) PCC, Al_2O_3, CH_2Cl_2, rt, 75%; (c) PhLi, THF, −78 °C, 86%; (d) *n*-BuLi, THF, −78 °C, MsCl; and (e) K_2CO_3, MeOH, rt, 76% from **7**.

In contrast, the allenediynes **16a–d** were obtained from the mesylates derived from alcohols **14** and **15** of type **B**, prepared from 8-(trimethylsilyl)-oct-7-yn-2-one[†] **9** or 5-methoxy-oct-7-yn-2-one **13**, which is readily prepared from 4-(*tert*-butyldimethylsilyloxy)-butyraldehyde[19] as described in Scheme 6.

Addition of the lithio derivative of hepta-1,6-diyne with the ketone **9** furnished the corresponding alcohol **14** in 70%. Then, the sequence—mesylation, S_N2' with arylcopper reagent, deprotection of the triple bond—led to the allenediynes **16a–c**. Starting from the ketone **13**, the whole sequence, which was carried out without purifying the intermediates led to **16d** in 36% overall yield.

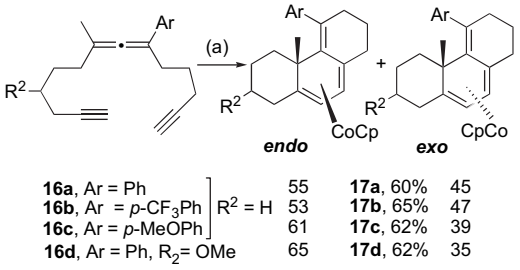
2.1.2. Cobalt(I)-mediated cyclizations of the allenediynes 16a–d. Exposure of **16a–d** to a stoichiometric amount of $CpCo(CO)_2$ in refluxing xylenes under irradiation (300 W visible lamp, 50% of its power) led to the complexed tricyclic compounds **17a–d** in 60–65% yield as a nearly 1:1

[†] 8-(Trimethylsilyl)-oct-7-yn-2-one was prepared by using the same reactions as for the parent compound 7-(trimethylsilyl)-hept-6-yn-2-one, see Ref. 18.



Scheme 6. (a) $HC{\equiv}CCH_2MgBr$, THF, −30 °C, **10**: 85%; (b) NaH, THF, rt, MeI, **11**: quantitative; (c) *n*-Bu_4NF, THF, 0 °C–rt, **12**: 86%; (d) 1. $(COCl)_2$, DMSO, NEt_3, −78 °C to rt, CH_2Cl_2; 2. MeMgBr, THF; 3. $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −78 °C to rt, **13**: 75% from **12**; (e) *n*-BuLi, hepta-1,6-diyne, THF, −78 °C, **14**: 70%; (f) 1. *n*-BuLi, THF, −78 °C, MsCl; 2. ArMgBr/$Me_2S{\cdot}CuBr$/LiBr (1.5 equiv), THF, −50 °C, **16d**: 36% from **13**; and (g) K_2CO_3, MeOH, rt, **16b**: 72%; **16c**: 51%; **16d**: 33%.

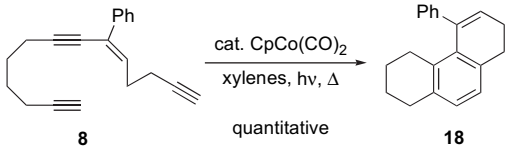
mixture of *endo*/*exo* diastereomers (Scheme 7). The *endo*/*exo* stereochemical assigments and ratios were determined by ^1H NMR on the basis of the chemical shift and integration of Cp-, dienic protons, and the angular CH_3, which is deshielded when located *syn* to cobalt and shielded when located *anti* (δCH_3 *endo*=1.80 ppm; δCH_3 *exo*=1.20 ppm).[14b,20]



Scheme 7. $CpCo(CO)_2$ (1 equiv), xylenes, hν, Δ.

Several features in these cyclizations are noteworthy: (i) they are totally regioselective and lead only to the (6,6,6) tricyclic cycloadducts; (ii) the yields are higher compared to the cyclization of allenediyne **4** due to an increase in the stability of the isolated complexes since they could be purified with non-degassed solvents on silica gel; (iii) the *endo*/*exo* diastereoselectivity is independent of the substitution on the allene; and (iv) the cyclization is compatible with an oxygenated functionality at C3.

Having in hands the diyne-ene-yne **8**, we checked its behavior in presence of a catalytic amount of $CpCo(CO)_2$ under the same conditions as above. The cycloadduct **18** was obtained in quantitative yield showing that the cyclotrimerization of the three alkynes is favored over the [2+2+2] cycloaddition of the enediyne moiety (Scheme 8).

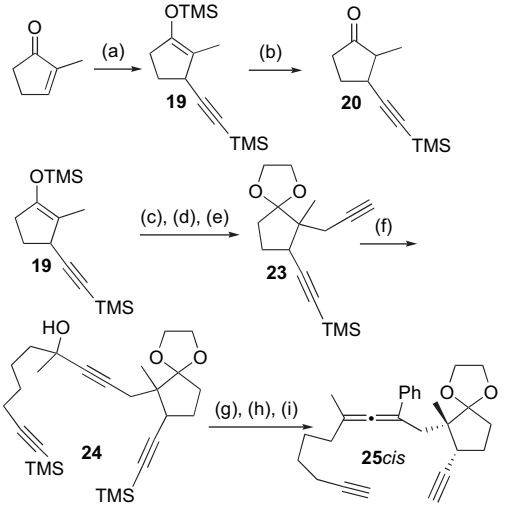


Scheme 8.

2.2. Diastereoselective approach to 11-aryl steroid skeletons

Since an aryl group was compatible with the conditions of the cyclization, we undertook the preparation of **3b** (R=H and Ar=Ph) starting from the commercially available 2-methyl-2-cyclopenten-1-one. Conjugate addition of (trimethylsilyl)ethynyl copper(I) reagent in the presence of iodotrimethylsilane provided the corresponding silyl enol ether **19** in 95% yield.[21] Subsequent acid hydrolysis furnished the ketone **20** in 85% yield.

Different methods at effecting the alkylation of **19** were quite unsuccessful; the use of MeLi or $NaNH_2$ in THF/HMPA resulted in decomposition of the starting material whereas the use of NaH led to a complex mixture of the ketone **20** and mono- and trialkylated adducts albeit in low yields (10–12%). The expected alkylated adduct was obtained from **19** with a slightly modified Nicholas reaction[22] (Scheme 9).



Scheme 9. (a) *n*-BuLi, $Me_3SiC{\equiv}CH$, TMSI, CuI, THF, −78 to −30 °C, **19**: 95%; (b) 1 M HCl, **20**: 85%; (c) $MeOCH_2{-}C{\equiv}CH{\cdot}Co_2(CO)_6$, $Et_2O{\cdot}BF_3$, CH_2Cl_2, rt, **21**: 95%; (d) CAN, acetone, rt, **22**: 78%; (e) 5 mol % PTSA, ethylene glycol (2 equiv), benzene (0.01 M), **23***cis*/*trans*: 95%; (f) *n*-BuLi, −78 °C, THF, $CH_3C(O)(CH_2)_4C{\equiv}CSiMe_3$, **24***cis*: 60%; **24***trans*: 50%; (g) *n*-BuLi; MsCl, THF, −78 °C; (h) $Me_2S{\cdot}CuBr$, PhMgCl, LiBr, THF, −50 °C, 10%; and (i) K_2CO_3, MeOH, rt, **25***cis*: quantitative.

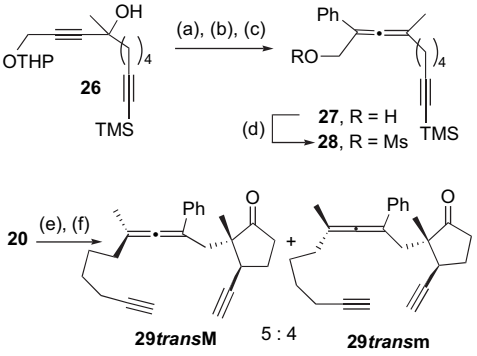
Indeed the following sequence—addition of **19** at rt to a solution of (propargyl)dicobalt hexacarbonyl cation, demetalation,[23] and acetalization[‡] of the corresponding adducts—furnished a 2:1 mixture of the ketals **23***cis*/*trans*. The cis

[‡] The acetalization proceeded in excellent yield only if the following conditions are respected: 10^{-2} M in benzene, 5 mol % PTSA, and 2 equiv of ethylene glycol.

relationship between the ethynyl and the propargyl groups for the major diastereomer was assigned by NOE NMR experiments. Alkylation of the lithium acetylide of **23***cis*/*trans* with 8-trimethylsilyl-oct-7-yn-2-one provided the corresponding alcohols **24***cis*/*trans* in 66% and 50% yields, respectively. Almost all attempts in generating the allenes through the sequence—mesylation of the alcohols followed by a S_N2' with copper(I)reagents—were unsuccessful. Only the addition of phenylcopper(I) reagent on **24***cis* furnished the corresponding allene in 10% yield whereas under the same conditions **24***trans* (or the mesylate) was recovered. Subsequent quantitative deprotection of the triple bonds afforded the allenediyne **25***cis*.

Since the allene formation occurred only for the cis adduct in poor yield, we decided to study another synthetic path to the allene **25**. As alkylation of the ketone **20** with propargyl bromide furnished the corresponding adduct in 60% yield, we checked the feasibility of such an alkylation with the mesylate **28** derived from the alcohol **27**.

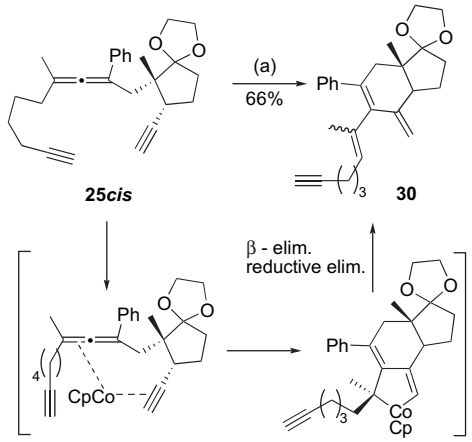
The starting material of this sequence was the alcohol **26**, which was generated from the addition of the lithium derivative of the tetrahydropyranyl propargyl ether with 8-trimethylsilyl-oct-7-yn-2-one (Scheme 10). Smooth formation of the allene and acid hydrolysis of the ether provided the alcohol **27** in 94% overall yield. The addition of the corresponding mesylate **28** to the potassium enolate of **20** afforded, after desilylation of the triple bonds, the allenediyne **29***trans* as a 5:4 mixture of two diastereomers in 50% yield over the three steps (mesylation, alkylation, and desilylation).



Scheme 10. (a) *n*-BuLi, MsCl, THF, −78 °C; (b) $Me_2S{\cdot}CuBr$, PhMgBr, LiBr, −50 °C; (c) cat. PTSA, MeOH, rt, 94% from **26**; (d) Et_3N, cat. 4-DMAP, MsCl, −40 °C, CH_2Cl_2; (e) KHMDS, −15 °C, THF; −50 °C, **28**, THF; and (f) K_2CO_3, MeOH, 50%.

The assigned stereochemistry of the major **29***trans*M, which was obtained pure after flash chromatography and crystallization, was unambiguously established by X-ray analysis.[§] In addition, NMR experiments also showed the trans relationship between the ethynyl group on the five-membered ring and the chain incorporating the allene for the minor **29***trans*m diastereomer. However, we were unable to separate it from the major diastereomer and we got a 41:59 mixture of **29***trans*(M/m).

The cobalt(I)-mediated cyclizations were carried out in the presence of a stoichiometric amount of $CpCo(CO)_2$ in boiling xylenes under irradiation and depending on the stereochemical relationship (cis or trans) between the ethynyl group and the chain incorporationg the allene, we disclosed two different trends. Indeed, the allenediyne **25***cis* afforded the bicyclic yne-trienic compound **30** as a mixture of diastereomers in 66% yield. This cycloadduct could result from a formal Alder ene type reaction between the ethynyl group and the double bond of the allene bearing the methyl group (Scheme 11).



Scheme 11. (a) $CpCo(CO)_2$ (1 equiv), xylenes, hν, Δ.

Such an Alder ene reaction, which had already been observed by our group[24] occurs competitively with the [2+2+2] cyclization when the latter is disfavored for geometrical reasons. In the present case, molecular models show that both of the unsaturations can be easily brought closer together, thus allowing a straightforward complexation of cobalt. After oxidative coupling, β-elimination followed by reductive elimination furnished compound **30**.

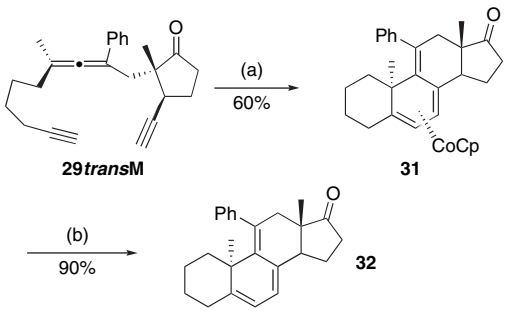
In contrast, the allenediyne **29***trans*M in presence of a stoichiometric amount of the cobalt(I) mediator gave the expected fused tetracyclic complex **31** in 60% yield as a single diastereomer (Scheme 12). On the basis of ^{1}H NMR spectrum, the cis relationship between CpCo and the A/B angular methyl was established (δ=1.75 ppm). The structure of **31** was secured by a single crystal X-ray analysis,[¶] which showed an *endo* stereochemistry between CpCo and the vicinal methyl group and a trans relationship between the two angular methyl groups. The free ligand **32** could be readily obtained in 90% yield upon the treatment of the complex **31** with silica gel. Therefore, the cyclization and decomplexation sequence could also be carried out without purifying the complex to allow the formation of 11-aryl steroid skeleton in 48% overall yield.

Although the minor allenediyne **29***trans*m was not obtained pure, it appears interesting to check if it could exhibit the same reactivity as the major diastereomer. Thus, a mixture of **29***trans*(M/m) (41:59)[‖] was exposed to the usual

[§] Crystal structure of **29***trans* has been deposited at the Cambridge Crystallographic Data Centre with the following deposition number: CCDC 245955; see Ref. 10 supporting information.

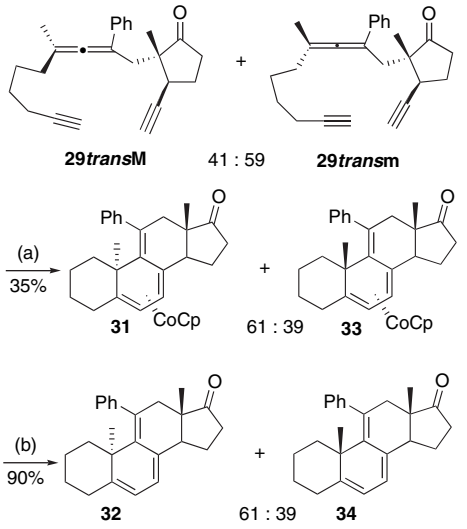
[¶] Crystal structure of **31** has been deposited at the Cambridge Crystallographic Data Centre with the following deposition number: CCDC 245954; see Ref. 10.

[‖] The ratio **29***trans*(M/m) (41:59) was determined by GC and **31:33** (61:39) by ^{1}H NMR on the basis of the integration of Cp-protons.



Scheme 12. (a) $CpCo(CO)_2$ (1 equiv), xylenes, hν, Δ and (b) SiO_2, CH_2Cl_2, rt.

conditions of cyclization and this led to (61:39) mixture of complexes **31** and **33** in 35% yield, which reveals to be the *exo* complex (Scheme 13).

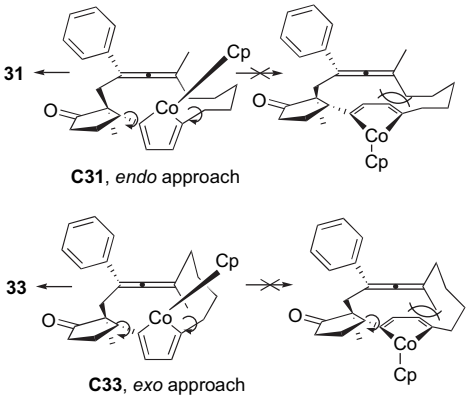


Scheme 13. (a) $CpCo(CO)_2$ (1 equiv), xylenes, hν, Δ and (b) SiO_2, CH_2Cl_2, rt.

The results were unexpected: the yield is inferior to the cyclization of **29***trans*M and the ratio of the cycloadducts is different from the starting material one meaning that **33** could be less stable than **31** or/and the cyclization of **29**m is more difficult than the cyclization of **29**M leading to degradation. Indeed, besides **31** and **33**, intractable materials were formed. In addition, a third compound was isolated, which may potentially result from an unanticipated side reaction of **29***trans*m, but we were unable to unambiguously identify its structure. Based upon similarities of spectral data, it seems to exhibit the steroid framework, which has been modified by several double bond migrations.

Finally, the mixture of **31** and **33** underwent efficient decomplexation with silica gel to furnish the free ligands **32** and **34** in 90%, the ratio 61:39 remaining unchanged.

The total diastereoselectivity observed for the cyclization of both diastereomers **29***trans* could be explained by the most probable mechanism of the [2+2+2], which may involve a cobaltacyclopentadiene.[15] The latter could react with the double bond of the allene bearing the methyl group via an intramolecular [4+2] cycloaddition process, which will deliver the fused tetracyclic complex (Scheme 14). Due to the presence of the five-membered ring, the intermediate cobaltacyclopentadienes **C31** and **C33** are quite rigid. For **C31**, the most favored approach of the polyunsaturated partners in which the non-bonded interactions are minimized is the *endo* approach relatively to the chain, which would lead to the *endo* complex **31**. On the contrary for **C33**, the *exo* approach relatively to the chain would be the favored one.



Scheme 14.

Thus, the diastereoselectivity of the cyclization for such allenediynes appears to be controlled by the stereochemistry of the allene.

3. Conclusion

In summary, we reported that the cobalt(I)-mediated [2+2+2] cyclizations of allenediynes of yne-allene-yne type bearing an aryl group on the allene are totally chemo- and regioselective and show low diastereoselectivities. η^4-Complexed tricyclic (6,6,6) compounds were obtained in good yields as mixtures of *endo*/*exo* diastereomers, which are independent of the substitution of the allene. The cyclization is also compatible with an oxyfunctionality at C3.

Having disclosed that aryl substituted allenes are relevant partners for these cyclizations, we carefully designed an allenediyne having a preexisting D ring. We observed that, depending on the stereochemical relationship (cis or trans) between the ethynyl group on the five-membered ring and the chain incorporating the allene, two different trends occurred in the cobalt(I)-mediated cyclizations. If *trans*-11-aryl steroids have been built in one step and in a totally diastereoselective manner, with simultaneous introduction of an angular methyl group at C10 and an aryl substituent at C11 in 48% overall yield. In contrast, if cis then the allenediyne **25***cis* furnished a bicyclic yne-trienic compound in 66% yield resulting from a formal Alder ene reaction between the ethynyl group and the double bond of the allene bearing the methyl group.

Interestingly we also observed that the diyne-ene-yne **8** furnished in a quantitative yield the corresponding cycloadduct bearing an aryl substituent at C11. This result could open a new synthetic pathway to the steroid nucleus by designing a judiciously functionalized unsaturated precursor.

4. Experimental

4.1. General

Reactions were carried out under argon in flame-dried glassware, with magnetic stirring and degassed anhydrous solvents. All commercially available reagents were used without further purification unless otherwise noted. All solvents were reagent grade and distilled under positive pressure of dry nitrogen before use. THF was distilled from sodium/benzophenone. Xylenes and benzene were distilled from CaH_2. Solid reagents were dried in vacuo (0.5–0.1 mmHg). Thin layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel. Merck Geduran SI 60 Å silica gel (35–70 μm) was used for column chromatography. PE and EE refer to petroleum ether and Et_2O.

Chemical shifts are reported in parts per million referenced to the residual proton resonances of the solvents (δ=7.26 for $CDCl_3$; δ=7.16 for C_6D_6). Coupling constants (J) are given in hertz (Hz). The terms m, s, d, t, q, and quint refer to multiplet, singlet, doublet, triplet, quartet, and quintet; br means that the signal is broad. Coupling constants are expressed in hertz. We use (I), (II), (III), and (IV) to characterize primary, secondary, tertiary, and quaternary carbons.

Elemental analyses were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie—low resolution mass spectra (MS) and high resolution mass spectra (HRMS) were measured by Service de spectrométrie de masse de l'ICSN-CNRS, Gif-sur-Yvette. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer (ATR diamond spectrometer). Absorbance frequencies are given at maximum of intensity in cm^{-1}.

4.1.1. 6-Phenyl-1-(trimethylsilyl)-tetradeca-1,7,13-triyn-6-ol (7). To a solution of alcohol **6** (1.85 g, 6.74 mmol) in CH_2Cl_2 (65 mL) were successively added neutral alumina (10 g) and pyridinium chlorochromate (PCC, 2 g, 9.44 mmol, 1.4 equiv). The mixture was stirred until completion of the reaction by TLC and then, was filtered on Celite pad. The filtered solution was successively washed with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (PE/EE=90/10) and furnished the ketone (1.37 g, 75%). IR (neat) 3060, 2970, 2850, 2200, 1630, 1440, 1240 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.42 (t, J=7.1 Hz, 2H), 2.37 (t, J=7.1 Hz, 2H), 2.18 (m, 2H), 2.10 (t, J=7.1 Hz, 2H), 1.85 (t, J=2.5 Hz, 1H), 1.69–1.57 (m, 4H), 1.40 (qt, J=7.1, 7.1 Hz, 2H), −0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1 (IV), 106.6 (IV), 92.6 (IV), 84.7 (IV), 82.5 (IV), 81.0 (IV), 69.3 (III), 44.7 (II), 27.6 (II), 26.3 (II), 22.9 (II), 19.4 (II), 17.7 (II), 17.4 (II), 0.0 (3C, I). HRMS calcd for $C_{17}H_{24}OSi$ (272.46) (MH^+) 273.160. Found 273.167.

To a cooled (−78 °C) solution of the previously prepared ketone (1.37 g, 5.1 mmol) in Et_2O (20 mL) was added a solution of phenyllithium (1.8 M in THF, 6.72 mmol, 1.2 equiv). The mixture was stirred until completion of the reaction by TLC and diluted with Et_2O, washed with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by flash chromatography (PE/EE=85/15) led to the alcohol **7** (1.33 g, 86%). IR (neat) 3450, 3060, 2970, 2850, 2200, 1630, 1440, 1240 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.28 (m, 5H), 2.43 (t, J=6.4 Hz, 2H), 2.27 (m, 2H), 2.19 (m, 2H), 1.99 (t, J=2.8 Hz, 1H), 2.10–1.90 (m, 2H), 1.75 (m, 6H), 0.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 (IV), 127.9 (2C, III), 127.5 (III), 126.4 (2C, III), 107.0 (IV), 88.5 (IV), 84.3 (IV), 83.8 (IV), 79.8 (IV), 79.0 (IV), 68.5 (III), 44.0 (II), 27.5 (II), 27.4 (II), 23.9 (II), 19.6 (II), 18.2 (II), 17.8 (II), 0.0 (3C, I).

4.1.2. 1-Trimethylsilyl-6-phenyl-tetradec-5-ene-1,7,13-triyne (8). Step 1. To a cooled (−78 °C) solution of **7** (1.07 g, 3.1 mmol), in THF (20 mL) was added a solution of *n*-BuLi (2.2 M in hexane, 3.1 mmol). After being stirred for 10 min at −78 °C, mesyl chloride (0.24 mL, 3.1 mmol) was added. The mixture was stirred for additional 30 min and neutralized with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude residue was used without further purification in the next step.

Step 2. At rt, to a solution of the previously prepared compound in MeOH (5 mL) was added K_2CO_3 (3.43 g, 24.8 mmol, 8 equiv). The mixture was stirred until TLC indicated the completion of the reaction. Then, the reaction mixture was diluted with Et_2O, washed successively with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by flash chromatography (PE/EE=95/5) gave **8** (0.605 g, 76%). IR (neat) 3060, 2970, 2850, 1640, 1440, 850 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7 (m, 2H), 7.34 (m, 2H), 7.27 (m, 1H), 6.42 (t, J=7.4 Hz, 1H), 2.70 (m, 2H), 2.50 (m, 2H), 2.42 (m, 2H), 2.29 (m, 2H), 2.01 (t, J=3.5 Hz, 1H), 1.99 (t, J=3.5 Hz, 1H), 1.77 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (IV), 137.2 (IV), 132.2 (IV), 128.6 (2C, III), 128.3 (III), 127.1 (2C, III), 85.2 (IV), 85.0 (IV), 84.7 (IV), 84.2 (IV), 68.3 (III), 67.9 (III), 32.0 (II), 29.9 (II), 29.5 (II), 24.9 (II), 23.5 (II), 22.5 (II).

4.1.3. 7-(*tert*-Butyldimethylsilyloxy)-hept-1-yn-4-ol (10). At −30 °C, to a solution of 4-(*tert*-butyldimethylsilyloxy)-butyraldehyde (15.46 g, 76.4 mmol) in Et_2O (80 mL) was slowly added a solution of propargylic magnesiumbromide (80 mmol, 1.05 equiv). The resulting solution was warmed up to rt and stirred for 2 h. Then, the mixture was diluted with Et_2O, washed successively with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by flash chromatography (PE/EE=80/20) led to **10** (15.8 g, 85%). IR (neat) 3450, 2950, 2200, 1450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 3.77–3.62 (m, 2H), 3.23 (br s, 1H), 2.39 (dd, J=3.2, 2.8 Hz, 2H), 2.03 (t, J=2.43 Hz, 1H), 1.80–1.78 (m, 2H), 1.69–1.65 (m, 2H), 0.89 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.3 (IV), 70.4 (III), 69.8 (III), 63.4 (II), 33.6 (II), 29.1 (II), 27.2 (II), 25.9 (3C, I), 18.3 (IV), −5.3 (2C, I).

4.1.4. 1-(*tert*-Butyldimethylsilyloxy)-4-methoxy-hept-6-yne (11). At 0 °C, to a suspension of sodium hydride (60% in mineral oil, 1 g, 24 mmol, 1.2 equiv) in THF (60 mL) was added a solution of alcohol **10** (4.85 g, 20 mmol) in

THF (60 mL). After 30 min at rt, iodomethane (6.2 mL, 14.2 g, 100 mmol, 5 equiv) was added. After being stirred for 2 h, the resulting mixture was diluted with Et_2O, washed successively with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography (PE/EE=95/5) to furnish the ether **11** (5.12 g, quantitative). IR (neat) 2950, 2200, 1450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 3.74 (m, 1H), 3.64–3.61 (m, 2H), 3.37 (s, 3H), 2.42–2.38 (m, 2H), 1.98 (t, J=2.48 Hz, 1H), 1.68–1.55 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.0 (IV), 79.0 (I), 69.9 (III), 63.1 (II), 57.0 (III), 29.8 (II), 28.5 (II) 26.0 (3C, I), 23.2 (II), 18.4 (IV), −5.2 (2C, I).

4.1.5. 4-Methoxy-hept-6-yn-1-ol (12). At 0 °C, to a solution of **11** (5.12 g, 20 mmol) in THF (100 mL) was added dropwise a 1 M solution in THF of TBAF (20 mL, 20 mmol). The reaction was stirred at rt until TLC indicated the completion of the reaction. Then, it was diluted with Et_2O, washed successively with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by flash chromatography (PE/AcOEt=60/40) led to **12** (2.44 g, 86%). IR (neat) 3450, 2970, 2200, 1450, 870 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 3.74 (m, 1H), 3.63–3.60 (m, 2H), 3.35 (s, 3H), 2.42–2.38 (m, 2H), 1.98 (t, J=2.48 Hz, 1H), 1.68–1.55 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.1 (IV), 79.5 (I), 70.5 (IV), 63.0 (II), 57.0 (III), 30.4 (II), 28.8 (II), 23.3 (II).

4.1.6. 5-Methoxy-oct-7-yn-2-one (13). Step 1. To a cooled solution (−78 °C) of oxalyl chloride (4 mL, 46 mmol, 1.3 equiv) in CH_2Cl_2 (130 mL) was added dropwise a solution of DMSO (6.5 mL, 91 mmol, 2.6 equiv) in CH_2Cl_2 (70 mL). After 5 min, a solution of **12** (5 g, 35 mmol) in CH_2Cl_2 (50 mL) was added dropwise and after being stirred for an additional 15 min, triethylamine (24 mL, 175 mmol, 5 equiv) was added. The mixture was allowed to warm to rt, diluted with Et_2O, washed successively with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude residue was used without further purification in the next step.

Step 2. At 0 °C, to a solution of the preceding aldehyde in Et_2O (40 mL) was added a solution of methylmagnesium bromide (3 M in Et_2O, 12.8 mL, 1.1 equiv). The mixture was warmed up to rt, stirred until TLC indicated the completion of the reaction. Then, it was diluted with Et_2O, washed successively with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude residue was used without further purification in the next step.

Step 3. The previously prepared alcohol was oxidized following the same procedure as described for step 1. Purification by flash chromatography (PE/EE=90/10) gave the ketone **13** (4.07 g, 75% from **12**). IR (neat) 3300, 2970, 2200, 1650, 1450, 870 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 3.74 (m, 1H), 3.37 (s, 3H), 2.42–2.38 (m, 4H), 2.10 (s, 3H), 1.98 (t, J=2.48 Hz, 1H), 1.80–1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2 (IV), 81.1 (IV), 79.5 (I), 70.5 (III), 57.0 (III), 47.3 (I), 31.4 (II), 28.7 (II), 23.3 (II).

4.1.7. 7-Methyl-1-(trimethylsilyl)-tetradeca-1,8,13-triyn-7-ol (14). At −78 °C n-BuLi (2.1 M in hexane, 29.1 mL, 61.1 mmol, 1.2 equiv) was added dropwise to a solution of hepta-1,6-diyne (10 g, 102 mmol, 2 equiv) in THF (300 mL). After being stirred at −78 °C for 30 min, a solution of 8-(trimethylsilyl)-oct-7-yn-2-one **9** (10 g, 50.9 mmol, 1 equiv) in THF (50 mL) was added. The reaction mixture was warmed up at rt, stirred for 2 h and was diluted with Et_2O, washed successively with a saturated solution of NH_4Cl, brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification by flash chromatography (PE/EE=90/10) furnished **14** (10.28 g, 70%). IR (neat) 3400, 3300, 2240, 2180, 1240, 840 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 2.34–2.25 (m, 4H), 2.23 (m, 2H), 1.96 (t, J=2.6 Hz, 1H), 1.70 (qt, J=7.04 Hz, 2H), 1.68–1.54 (m, 6H), 1.44 (s, 3H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.4, (IV), 84.8 (IV), 84.6 (IV), 82.5 (2C, IV), 68.9 (III), 68.2 (IV), 57.0 (III), 43.4 (II), 30.1 (I), 28.8 (II), 27.6 (II), 24.1 (II), 19.9 (II), 17.7 (II), 17.6 (II), 0.2 (3C, I). Anal. Calcd for $C_{26}H_{32}O_2Si$ (288.50): C, 74.94; H, 9.78. Found: C, 75.08; H, 9.66.

4.2. General procedure for the preparation of allenediynes 16a–c

A THF solution of arylmagnesium chloride or bromide (2.6 mmol, 1.5 equiv) was added dropwise at −50 °C to a suspension of $Me_2S\cdot CuBr$ (0.535 g, 2.6 mmol, 1.5 equiv) and LiBr (0.224 g, 2.6 mmol, 1.5 equiv) in THF (20 mL) and the resulting mixture was stirred at −50 °C for 15 min.

At −78 °C, a 2.1 M solution of n-BuLi in hexane (0.82 mL, 1.73 mmol, 1 equiv) was added dropwise to a solution of the alcohol **14** (0.50 g, 1.73 mmol). After being stirred for 5 min, pure mesyl chloride (0.15 mL, 1.90 mmol, 1.1 equiv) was added. The resulting solution was stirred for 5 min and transferred via a cannula into a solution of the previously prepared copper(I) reagent. After stirring for 30 min at −50 °C, the temperature was allowed to warm up at rt. The reaction mixture was hydrolyzed with a saturated solution of NH_4Cl/NH_4OH (2/1) and partitioned with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give the corresponding allenediynes. The crude mixture was used in the next step without any further purification.

K_2CO_3 (1.88 g, 13.6 mmol, 8 equiv) was added to a solution of previously prepared crude compound in MeOH (10 mL) and the resulting mixture was stirred until TLC had indicated the completion of the reaction. The mixture was diluted with Et_2O, washed with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (PE/EE=9/1) led to the allenediynes **16a–c**.

4.2.1. (3-Methyl-1-pent-4-ynyl-nona-1,2-dien-8-ynyl)-benzene (16a). 0.344 g, 72%. IR (neat) 2950, 2210, 2180, 1960, 1440, 950 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.37 (m, 2H), 7.25 (m, 1H), 2.61 (t, J=7.3 Hz, 2H), 2.36 (dt, J=4.6, 2.4 Hz, 2H), 2.24 (m, 2H), 2.17 (m, 2H), 2.05 (t, J=2.44 Hz, 1H), 2.01 (t, J=2.5 Hz, 1H), 1.87 (s, 3H), 1.84 (m, 2H), 1.82 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2 (IV), 138.0 (IV), 128.4 (2C, III), 126.3

(III), 125.9 (2C, III), 103.9 (IV), 103.1 (IV), 84.5 (2C, IV), 68.6 (2C, III), 33.9 (II), 29.3 (II), 28.4 (II), 27.0 (II), 26.8 (II), 19.8 (II), 18.9 (I), 18.2 (II). HRMS calcd for $C_{21}H_{24}$ (276.42) (MH^+) 277.188. Found: 277.187.

4.2.2. 1-(3-Methyl-1-pent-4-ynyl-nona-1,2-dien-8-ynyl)-4-trifluoromethyl-benzene (16b). 0.303 g, 51%. IR (neat) 2950, 2210, 2180, 1960, 1440 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J=8.0 Hz, 2H), 7.50 (d, J=8.0 Hz, 2H), 2.56 (t, J=7.6 Hz, 2H), 2.34–2.30 (m, 2H), 2.22–2.18 (m, 2H), 2.16–2.13 (m, 2H), 2.01 (t, J=1.6 Hz, 1H), 1.96 (t, J=2.4 Hz, 1H), 1.84 (s, 3H), 1.81–1.77 (m, 2H), 1.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1 (IV), 144.2 (q, J=81 Hz, IV), 142.0 (IV), 126.3 (q, J=140 Hz, IV), 127.7 (III), 126.0 (2C, III), 125.2 (III), 103.9 (IV), 103.5 (IV), 84.2 (2C, IV), 68.7 (III), 68.4 (III), 33.7 (II), 29.1 (II), 28.2 (II), 26.9 (II), 26.7 (II), 18.8 (I), 18.3 (II), 18.1 (II).

4.2.3. 1-Methoxy-4-(3-methyl-1-pent-4-ynyl-nona-1,2-dien-8-ynyl)-benzene (16c). 0.175 g, 33%. IR (neat) 2980, 2200, 2180, 1960, 1440 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 2H), 6.89 (m, 2H), 3.82 (s, 3H), 2.52 (t, J=7.3 Hz, 2H), 2.33–2.29 (m, 2H), 2.22–2.20 (m, 2H), 2.12 (m, 2H), 2.01 (t, J=2.5 Hz, 1H), 1.97 (t, J=2.5 Hz, 1H), 1.82 (s, 3H), 1.80–1.79 (m, 2H), 1.61–1.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6 (IV), 158.3 (IV), 132.2 (IV), 127.0 (2C, III), 113.8 (2C, III), 103.6 (IV), 102.8 (IV), 84.5 (2C, IV), 68.6 (III), 68.4 (III), 55.3 (I), 33.9 (II), 29.5 (II), 28.3 (II), 27.0 (II), 26.8 (II), 19.1 (I), 18.3 (II), 18.2 (II).

4.2.4. (6-Methoxy-3-methyl-1-pent-4-ynyl-nona-1,2-dien-8-ynyl)-benzene (16d). It was obtained using the same procedure as for the preparation of **14** (the intermediate alcohol was not purified) followed by the sequence described for **16a–c**. 0.303 g, 36% overall yield. IR (neat) 2950, 2210, 2180, 1960, 1440 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 2H), 7.33 (m, 2H), 7.25 (m, 1H), 3.72 (m, 1H), 3.35 (s, 3H), 2.61 (t, J=7.4 Hz, 2H), 2.36 (dt, J=4.7, 2.5 Hz, 2H), 2.24 (m, 2H), 2.17 (m, 2H), 2.05 (t, J=2.5 Hz, 1H), 2.01 (t, J=2.5 Hz, 1H), 1.87 (s, 3H), 1.84 (m, 2H), 1.82 (m, 2H). ^{13}C NMR (100 Hz, $CDCl_3$) δ 201.2 (IV), 138.0 (IV), 128.4 (2C, III), 126.3 (III), 125.9 (2C, III), 103.9 (IV), 103.1 (IV), 84.5 (2C, IV), 78.7 (I), 68.6 (2C, III), 57.1 (III), 33.9 (II), 29.3 (II), 28.4 (II), 26.8 (II), 19.8 (II), 18.9 (I), 18.2 (II).

4.3. General procedure for the preparation of the cycloadducts 17a–d

Cyclopentadienyldicarbonylcobalt(I) (1.2 equiv) was added to a boiling solution of allenediyne **16a–d** (1 equiv) in xylenes degassed by three freeze-pump-thaw cycles and was irradiated (light from projector lamp; ELW, 300 W, 50% of its power). The reaction was monitored by TLC and after completion, the reaction mixture was concentrated in vacuo. The crude oil was purified by flash chromatography (the solvents of chromatography were not degassed) either on deactivated alumina with 3% H_2O (PE) or on silica gel neutralized with NEt_3 and dried (PE/EE 95/5) to furnish **17a–d** as an inseparable *endo*/*exo* mixture.

4.3.1. Cycloadduct (17a). 0.180 g, 60% (*endo*/*exo*=55/45).

17a *endo*: ^1H NMR (400 MHz, C_6D_6) δ 7.83 (m, 2H), 7.46 (m, 3H), 5.24 (d, J=3.9 Hz, 1H), 4.37 (s, 5H), 4.36 (d, J=3.9 Hz, 1H), 2.45–2.42 (m, 2H), 2.2–2.05 (m, 2H), 1.96–1.95 (m, 2H), 1.81 (s, 3H), 1.57–1.56 (m, 4H), 1.33–1.31 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6) δ 150.3 (IV), 142.3 (IV), 126.0 (IV), 129–125 (5C, III), 81.7 (5C, III), 76.9 (III), 73.5 (IV), 72.8 (III), 65.2 (IV), 48.2 (IV), 36.9 (II), 36.5 (II), 35.0 (II), 31.8 (II), 27.5 (I), 26.4 (II), 25.0 (II), 24.7 (II).

17a *exo*: ^1H NMR (400 MHz, C_6D_6) δ 7.32–7.23 (m, 5H), 4.91 (d, J=3.9 Hz, 1H), 4.64 (s, 5H), 4.47 (d, J=3.9 Hz, 1H), 2.35–2.22 (m, 2H), 2.2–2.05 (m, 2H), 1.88–1.83 (m, 2H), 1.57–1.56 (m, 4H), 1.55–1.45 (m, 4H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 146.3 (IV), 144.2 (IV), 126.0 (IV), 129–125 (5C, III), 80.9 (5C, III), 78.0 (III), 77.5 (IV), 76.0 (III), 65.3 (IV), 48.2 (IV), 40.9 (II), 37.7 (II), 37.4 (II), 35.6 (II), 30.8 (II), 26.1 (II), 24.3 (I), 22.7 (II). HRMS calcd for $C_{26}H_{29}Co$ (400.44) $(MH)^+$ 401.168. Found: 401.165.

4.3.2. Cycloadduct (17b). 0.268 g, 65% (*endo*/*exo*=53/47).

17b *endo*: ^1H NMR (400 MHz, C_6D_6) δ 7.48 (d, J=8.2 Hz, 2H), 7.13 (d, J=8.2 Hz, 2H), 5.2 (d, J=3.9 Hz, 1H), 4.33 (d, J=3.9 Hz, 1H), 4.26 (s, 5H), 2.35–2.25 (m, 2H), 2.2–2.05 (m, 2H), 1.91–1.85 (m, 2H), 1.67 (s, 3H), 1.57–1.56 (m, 4H), 1.49–1.45 (m, 2H), 1.33–1.31 (m, 2H). ^{13}C NMR (100 MHz, C_6D_6) δ 150.3 (2C, IV), 142.3 (2C, IV), 126.0 (IV), 129–125 (4C, III), 81.6 (5C, III), 77.0 (III), 73.5 (IV), 72.7 (III), 65.2 (IV), 48.2 (IV), 37.1 (II), 36.8 (II), 36.2 (II), 31.5 (II), 27.6 (I), 26.3 (II), 24.4 (II), 24.2 (II).

17b *exo*: ^1H NMR (400 MHz, C_6D_6) δ 7.48 (d, J=8.2 Hz, 2H), 7.13 (d, J=8.2 Hz, 2H), 4.90 (d, J=3.9 Hz, 1H), 4.63 (s, 5H), 4.44 (d, J=3.9 Hz, 1H), 2.35–2.25 (m, 2H), 2.2–2.05 (m, 2H), 1.91–1.85 (m, 2H), 1.57–1.56 (m, 4H), 1.49–1.45 (m, 2H), 1.33–1.31 (m, 2H), 1.06 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 150.3 (2C, IV), 143.0 (2C, IV), 126.0 (IV), 129–125 (4C, III), 81.6 (5C, III), 78.1 (III), 76.0 (III), 73.5 (IV), 65.2 (IV), 48.2 (IV), 40.8 (II), 35.5 (II), 34.8 (II), 30.7 (II), 25.9 (II), 24.2 (I), 22.6 (II), 22.5 (II). IR (neat): 3250, 2950, 2920, 1950, 1630, 1470, 1450, 1350, 850 cm^{-1}. HRMS calcd for $C_{27}H_{28}CoF_3$ (468.44) $(MH)^+$ 469.148. Found: 469.154.

4.3.3. Cycloadduct (17c). 0.152 g, 62% (*endo*/*exo*=61/39).

17c *endo*: ^1H NMR (400 MHz, C_6D_6) δ 7.16 (m, 2H), 6.85 (m, 2H), 5.25 (d, J=3.9 Hz, 1H), 4.38 (s, 5H), 4.37 (d, J=3.9 Hz, 1H), 3.57 (s, 3H), 2.52–2.48 (m, 2H), 2.2–2.05 (m, 2H), 1.99–1.87 (m, 4H), 1.84 (s, 3H), 1.57–1.56 (m, 2H), 1.47–1.36 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6) δ 158.0 (IV), 142.5 (IV), 129.9 (IV), 128.1 (2C, III), 127.2 (IV), 112.1 (2C, III), 81.6 (5C, III), 76.9 (III), 73.3 (IV), 72.7 (III), 64.4 (IV), 54.6 (I), 48.2 (IV), 36.9 (II), 36.6 (II), 35.1 (II), 31.8 (II), 27.5 (I), 26.4 (II), 25.0 (II), 24.6 (II).

16c *exo*: ^1H NMR (400 MHz, C_6D_6) δ 7.75 (m, 2H), 7.09 (m, 2H), 4.93 (d, J=3.9 Hz, 1H), 4.65 (s, 5H), 4.48 (d, J=3.9 Hz, 1H), 3.37 (s, 3H), 2.52–2.48 (m, 2H), 2.2–2.05 (m, 2H), 1.99–1.87 (m, 4H), 1.57–1.56 (m, 2H), 1.47–1.36 (m, 4H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 157.9, 142.3,

129.9, 129.8 (2C), 127.2, 113.4 (2C), 80.9 (5C), 78.0 (III), 76.0 (III), 74.8 (IV), 65.5 (IV), 54.5 (I), 46.7 (IV), 40.9 (II), 37.9 (II), 37.4 (II), 35.6 (II), 30.9 (II), 26.2 (II), 24.2 (I), 22.8 (II). HRMS calcd for $C_{27}H_{31}CoO$ $(MH)^+$ 431.179. Found: 431.177.

4.3.4. Cycloadduct (17d). 0.077 g, 62% (*endo*/*exo*=65/35). This cyclization led to the formation of an inseparable mixture of four diastereomers *endo*/*exo* and it was impossible to fully describe the compounds particularly the ^{13}C NMR spectra were unexploitable. Only the characteristic data in ^1H NMR are given.

17d *endo* (two diastereomers): 7.60 (m, 4H), 7.46 (m, 6H), 5.62 (d, *J*=3.9 Hz, 1H), 5.35 (d, *J*=3.9 Hz, 1H), 4.33 (s, 5H), 4.31 (s, 5H), 4.65 (d, *J*=3.9 Hz, 1H), 4.41 (d, *J*=3.9 Hz, 1H), 3.38 (s, 3H), 3.36 (m, 2H), 3.35 (s, 3H), 2.45–1.3 (m, 24H), 1.54 (s, 3H), 1.45 (s, 3H).

17d *exo* (two diastereomers): 7.60 (m, 4H), 7.46 (m, 6H), 5.02 (d, *J*=3.9 Hz, 1H), 4.99 (d, *J*=3.9 Hz, 1H), 4.76 (s, 5H), 4.67 (s, 5H), 4.66 (d, *J*=3.9 Hz, 1H), 4.5 (d, *J*=3.9 Hz, 1H), 3.32 (m, 2H), 3.30 (s, 3H), 3.28 (s, 3H), 2.45–1.3 (m, 24H), 1.02 (s, 3H), 0.96 (s, 3H).

4.3.5. 5-Phenyl-1,2,3,4,7,8-hexahydro-phenanthrene (18). 0.150 g, quantitative. IR (neat) 3060, 2970, 2850, 1630, 1440, 850 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 2H), 7.28–7.25 (m, 3H), 7.09 (d, *J*=7.6 Hz, 1H), 7.00 (d, *J*=7.6 Hz, 1H), 6.28 (t, *J*=5.1 Hz, 1H), 2.79 (t, *J*=6.6 Hz, 2H), 2.71 (t, *J*=7.1 Hz, 2H), 2.29–2.24 (m, 2H), 2.01 (t, *J*=6.2 Hz, 2H), 1.66 (m, 2H), 1.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (IV), 141.2 (IV), 137.2 (IV), 136.6 (IV), 135.0 (IV), 134.8 (IV), 132.2 (III), 128.6 (2C, III), 128.3 (III), 127.1 (2C, III), 126.6 (III), 125.0 (III), 31.0 (II), 30.6 (II), 30.1 (II), 23.9 (II), 23.5 (II), 22.9 (II).

4.3.6. 2-Methyl-2-prop-2-ynyl-3-(trimethylsilylethynyl)-cyclopentanone (22). To a cooled (−78 °C) solution of (propargyl)methyl ether hexacarbonyl dicobalt complex (0.69 g, 1.92 mmol, 1.03 equiv) in CH_2Cl_2 (8 mL) was added $Et_2O{\cdot}BF_3$ (0.5 mL, 1.92 mmol, 1.03 equiv). After warming up at rt, the reaction mixture was stirred for 15 min and silyl enol ether **19**[21] (0.50 g, 1.87 mmol) was added. After being stirred at rt until completion of the reaction (TLC), the reaction mixture was diluted with Et_2O, washed with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to furnish the ketones **21**. The crude mixture was used in the next step without any further purification.

To a solution of the previously prepared ketones **21** in acetone (250 mL) was added portionwise CAN (8.2 g, 14.96 mmol, 8 equiv). After being stirred for 5 min at rt, the reaction mixture was diluted with Et_2O (1 L), washed successively with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash chromatography (PE/EE=95/5) of the residue furnished the ketones **22***cis*/*trans* (0.318 g, cis/trans=2/1, 74% over the two steps).

22*cis*: ^1H NMR (400 MHz, $CDCl_3$) δ 3.28 (dd, *J*=11.2, 6.8 Hz, 1H), 2.49–2.05 (m, 6H), 1.96 (t, *J*=2.4 Hz, 1H), 1.02 (s, 3H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.4 (IV), 104.9 (IV), 88.2 (IV), 80.4 (IV), 71.0 (III), 51.3 (IV), 36.7 (III), 36.6 (II), 25.9 (II), 25.2 (II), 18.0 (I), 0.2 (3C, I). EIMS (*m*/*z*, %) 233 (100), 217 (35).

22*trans*: ^1H NMR (400 MHz, $CDCl_3$) δ 2.87 (t, *J*=13.8 Hz, 1H), 2.44–2.00 (m, 6H), 1.97 (t, *J*=2.4 Hz, 1H), 1.14 (s, 3H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.4 (IV), 105.0 (IV), 89.2 (IV), 80.5 (IV), 70.5 (III), 51.2 (IV), 39.8 (III), 35.5 (II), 25.7 (II), 23.7 (II), 20.7 (I), 0.0 (3C, I). EIMS (*m*/*z*, %) 233 (100), 217 (35).

4.3.7. Trimethyl-(6-methyl-6-prop-2-ynyl-1,4-dioxa-spiro[4,4]non-7-ylethynyl)-silane (23). A solution of ketone **22***cis*/*trans* (0.313 g, 1.35 mmol), ethylene glycol (0.15 mL, 2.7 mmol, 2 equiv) and PTSA (0.01 g, 0.07 mmol, 0.05 equiv) in benzene (13 mL) was refluxed with a Dean–Stark apparatus for 12 h. After being cooled at rt, the reaction mixture was diluted with Et_2O, washed successively with a 2:1 saturated solution of NH_4Cl/NH_4OH and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Filtration through silica gel (PE/EE=9/1) gave the acetals **23***cis*/*trans* (0.355 g, cis/trans=2/1, 95%).

23*cis*: Mp 62–64 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 3.89 (m, 4H), 2.69 (t, *J*=17.7 Hz, 1H), 2.51–2.26 (m, 2H), 1.98–1.88 (m, 3H), 1.79–1.66 (m, 2H), 1.09 (s, 3H), 0.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.0 (IV), 107.2 (IV), 87.8 (IV), 83.2 (IV), 69.0 (III), 65.5 (II), 64.8 (II), 48.9 (IV), 40.2 (III), 33.6 (II), 26.7 (II), 23.0 (II), 19.7 (I), 0.2 (3C, I). Anal. Calcd for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75. Found: C, 69.33; H, 8.95.

23*trans*: ^1H NMR (400 MHz, $CDCl_3$) δ 4.00–3.85 (m, 4H), 2.69 (t, *J*=17.7 Hz, 1H), 2.29 (m, 2H), 1.99–1.87 (m, 3H), 1.79–1.62 (m, 2H), 1.16 (s, 3H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.0 (IV), 107.1 (IV), 87.4 (IV), 82.5 (IV), 69.5 (III), 65.1 (II), 64.6 (II), 48.4 (IV), 39.0 (III), 33.2 (II), 26.0 (II), 23.7 (II), 16.6 (I), 0.2 (3C, I). Anal. Calcd for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75. Found: C, 69.33; H, 8.95.

4.3.8. Methyl-1-[6-methyl-7-(trimethylsilylethynyl)-1,4-dioxa-spiro[4,4]non-6-yl]-10-trimethylsilyl-deca-2,9-diyn-4-ol (24). To a cooled (−78 °C) solution of **23** (0.50 g, 1.81 mmol) in THF (10 mL) was added dropwise *n*-BuLi (2.5 M in hexane, 0.72 mL, 1.81 mmol). After being stirred at −78 °C for 30 min, a solution of 8-(trimethylsilyl)-oct-7-yn-2-one (0.355 g, 1.81 mmol) in THF (5 mL) was added. The temperature was allowed to warm up at rt, the mixture was stirred until TLC had indicated the completion of the reaction. The reaction was diluted with Et_2O, washed with a saturated solution of NH_4Cl, brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash chromatography (PE/EE=85/15) afforded the alcohols **24***cis* and **24***trans*.

24*cis*: 0.564 g, 66%. IR(neat) 3610, 2980, 2950, 2290, 2000, 1470, 1390, 1350 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 3.90 (m, 4H), 2.70 (t, *J*=17.7 Hz, 1H), 2.45 (m, 2H), 2.30–2.24 (m, 4H), 1.81–1.69 (m, 2H), 1.60–1.59 (m, 6H), 1.44 (s, 3H), 1.08 (s, 3H), 0.13 (s, 9H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.1 (IV), 107.3 (2C, IV), 87.6

(IV), 84.4 (IV), 82.5 (2C, IV), 68.2 (IV), 65.5 (II), 64.8 (II), 49.1 (IV), 43.3 (II), 40.2 (III), 33.7 (II), 30.0 (I), 28.8 (II), 26.7 (II), 24.1 (II), 23.2 (II), 20.3 (II), 19.9 (I), 0.28 (3C, I), 0.22 (3C, I). Anal. Calcd for $C_{27}H_{44}O_3Si_2$: C, 68.59; H, 9.38. Found: C, 68.44; H, 9.57.

24*trans*: 0.43 g, 50%. IR(neat) 3610, 2980, 2950, 2290, 2000, 1470, 1390, 1350 cm^{-1}. ^1H NMR (200 MHz, C_6D_6) δ 3.77–3.50 (m, 2H), 3.46–3.35 (m, 2H), 2.90 (t, J=18.7 Hz, 1H), 2.54 (br s, 2H), 2.11 (t, J=13.7 Hz, 2H), 1.92–1.52 (m, 10H), 1.46 (s, 3H), 1.44 (s, 3H), 0.22 (s, 9H), 0.18 (s, 9H). ^{13}C NMR (50 MHz, C_6D_6) δ 119.0 (IV), 108.9 (2C, IV), 88.5 (IV), 87.1 (IV), 85.6 (IV), 82.4 (IV), 68.9 (IV), 66.0 (II), 65.6 (II), 49.9 (IV), 44.7 (II), 40.6 (III), 34.4 (II), 31.2 (I), 30.2 (II), 26.6 (II), 25.6 (II), 25.4 (II), 21.2 (II), 18.3 (I), 1.3 (6C, I). Anal. Calcd for $C_{27}H_{44}O_3Si_2$: C, 68.59; H, 9.38. Found: C, 68.44; H, 9.57.

4.3.9. 7-Ethynyl-6-methyl-6-(4-methyl-2-phenyl-deca-2,3-diene-9-ynyl)-1,4-dioxa-spiro[4,4]nonane (25*cis*). A 1.5 M THF solution of phenylmagnesium chloride (1.28 mL, 1.92 mmol, 1.5 equiv) was added dropwise at −50 °C to a suspension of $Me_2S\cdot CuBr$ (1.92 mmol, 1.5 equiv) and LiBr (0.167 g, 1.92 mmol, 1.5 equiv) in THF (20 mL) and the resulting mixture was stirred at −50 °C for 15 min.

At −78 °C, a 2.1 M solution of *n*-BuLi in hexane (0.61 mL, 1.28 mmol) was added dropwise to a solution of the alcohol **24***cis* (0.61 g, 1.28 mmol). After being stirred for 5 min, pure mesyl chloride (0.12 mL, 1.53 mmol, 1.2 equiv) was added. The resulting solution was stirred for 5 min and transferred via a cannula into a solution of the previously prepared copper(I) reagent. After stirring for 30 min at −50 °C, the temperature was allowed to warm up at rt. The reaction mixture was hydrolyzed with a saturated solution of NH_4Cl/NH_4OH (2/1) and partitioned with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude mixture was used in the next step without any further purification.

K_2CO_3 (1.42 g, 10.24 mmol, 8 equiv) was added to the previously prepared silylated allenediyne in MeOH (10 mL) and the resulting mixture was stirred until TLC had indicated the completion of the reaction. The mixture was diluted with Et_2O, washed with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash chromatography (PE/EE=9/1) to yield allenediyne **25***cis* (two diastereomers, 0.05 g, 10%). IR(neat) 3100, 2970, 2150, 2010, 1470 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.27 (m, 2H), 7.17 (m, 1H), 3.95 (t, J=8.8 Hz, 2H), 3.86 (t, J=8.8 Hz, 2H), 3.14–3.04 (m, 1H), 2.80 (m, 1H), 2.43–2.33 (m, 1H), 2.17–2.12 (m, 6H), 1.94–1.92 (m, 4H), 1.79 (s, 3H), 1.60–1.56 (m, 4H), 1.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (**25***cis*, major) 203.2 (IV), 140.2 (IV), 128.0 (2C, III), 126.3 (2C, III), 125.9 (III), 119.1 (IV), 103.2 (IV), 101.8 (IV), 87.2 (IV), 79.0 (IV), 70.3 (III), 68.2 (III), 64.8 (2C, II), 49.7 (IV), 37.8 (III), 33.9 (II), 32.9 (II), 32.4 (II), 28.3 (II), 26.8 (II), 26.6 (II), 20.7 (I), 18.7 (II), 18.3 (I). δ (**25***cis*, minor) 203.2 (IV), 140.2 (IV), 128.0 (2C, III), 126.3 (2C, III), 125.9 (III), 119.1 (IV), 103.2 (IV), 101.7 (IV), 87.2 (IV), 79.0 (IV), 70.5 (III), 68.3 (III), 64.8 (2C, II), 49.7 (IV), 38.0 (III), 33.7 (II), 32.8 (II), 32.2 (II), 28.3 (II), 26.9 (II), 26.5 (II), 20.7 (I), 18.7 (II), 18.3 (I).

4.3.10. 4-Methyl-1-(tetrahydropyran-2-yloxy)-10-trimethylsilyl-deca-2,9-diyn-4-ol (26). To a cooled (−78 °C) solution of 8-trimethylsilyl-oct-7-yn-2-one (1.19 g, 6.04 mmol, 1 equiv) in THF (10 mL) was added at −78 °C the lithium acetylide derived from tetahydropyranyl propargyl ether (0.6 M in THF, 6.04 mmol, 1 equiv). After warming up at rt, the reaction mixture was stirred until TLC indicated the completion, diluted with Et_2O, washed with a saturated solution of NH_4Cl, brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Flash chromatography (PE/EE=9/1) of the residue furnished the alcohol **26** (1.93 g, 95%). IR(neat) 3400, 2950, 2100, 1250, 930 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.78 (t, J=3.2 Hz, 1H), 4.24 (d, J=8.4 Hz, 2H), 3.82–3.76 (m, 1H), 3.52–3.47 (m, 1H), 2.20 (t, J=6.4 Hz, 2H), 1.77–1.48 (m, 12H), 1.43 (s, 3H), 0.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.4 (IV), 96.6 (III), 89.9 (IV), 84.6 (IV), 79.0 (IV), 67.9 (IV), 61.9 (II), 54.3 (II), 43.0 (II), 30.2 (II), 28.7 (II), 29.7 (I), 25.4 (II), 24.0 (II), 19.8 (II), 18.9 (II), 0.2 (3C, I). Anal. Calcd for $C_{19}H_{32}O_3Si$: C, 67.81; H, 9.58. Found: C, 68.03; H, 9.67.

4.3.11. 4-Methyl-2-phenyl-10-trimethylsilyl-deca-2,3-dien-9-yn-1-ol (27). To a cooled (−50 °C) THF (50 mL) suspension of $Me_2S\cdot CuBr$ (1.82 g, 8.85 mmol, 1.5 equiv) and LiBr (0.77 g, 8.85 mmol, 1.5 equiv) was added dropwise a solution of phenylmagnesium bromide (2.7 M in Et_2O, 8.85 mmol, 1.5 equiv). The resulting mixture was stirred for 15 min (during this period a yellow precipitate appeared).

At −78 °C, *n*-BuLi (2.4 M in hexane, 2.46 mL, 5.9 mmol, 1 equiv) was added to a solution of alcohol **26** (2 g, 5.9 mmol, 1 equiv) in THF (20 mL) and after 5 min, pure mesyl chloride (0.51 mL, 6.49 mmol, 1.1 mmol) was added. The resulting solution was stirred for 5 min and was added to the previously prepared copper(I) reagent. After being stirred at −50 °C for 30 min, the reaction mixture was allowed to warm to rt. Then, the reaction was hydrolyzed with a 2:1 saturated solution of NH_4Cl/NH_4OH, diluted with Et_2O, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was used in the next step without any further purification.

To a solution of the previously prepared crude mixture in MeOH (30 mL) was added PTSA (0.118 g, 0.6 mmol, 0.1 equiv). After being stirred at rt until TLC had indicated the completion of the reaction, the mixture was diluted with Et_2O, washed successively with a saturated solution of $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash chromatography (PE/EE=85/15) afforded **27** (1.73 g, 94% over the two steps). IR(neat) 3400, 2950, 2200, 1640, 1240, 930 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.21 (m, 5H), 4.53 (br s, 2H), 2.25–2.16 (m, 4H), 1.86 (s, 3H), 1.67–1.37 (m, 4H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6 (IV), 135.5 (IV), 128.6 (2C, III), 126.8 (III), 126.0 (2C, III) 115.4 (IV), 107.3 (IV), 106.1 (IV), 84.7 (IV), 61.8 (II), 33.7 (II), 28.1 (II), 26.6 (II), 19.7 (II), 19.0 (I), 0.2 (3C, I). Anal. Calcd for $C_{20}H_{28}OSi$: C, 76.86; H, 9.03. Found: C, 76.86; H, 9.21.

4.3.12. 3-Ethynyl-2-methyl-2-(4-methyl-2-phenyl-deca-2,3-dien-9-ynyl)-cyclopentanone (29*trans*). To a cooled (−50 °C) THF (50 mL) solution of KHMDS (1.10 g, 5.54 mmol) was added a solution of ketone **20**[21](1.29 g, 6.65 mmol, 1.2 equiv) in THF (50 mL). After warming up at −15 °C, the reaction mixture was stirred for 45 min. Then, after being cooled to −50 °C a solution of the mesylate (2.16 g, 5.54 mmol, 1 equiv) [generated from alcohol **27**] in THF (10 mL) was added. After stirring for 30 min at −50 °C, the temperature was allowed to warm up at rt. The reaction mixture was hydrolyzed with a saturated solution of NH_4Cl/NH_4OH (2/1) and partitioned with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude mixture was used in the next step without any further purification.

To a solution of the crude allenediyne previously prepared in MeOH (20 mL) was added K_2CO_3 (6.15 g, 44.3 mmol, 8 equiv) at rt. The reaction was stirred at rt until TLC had indicated the completion of the reaction. The mixture was diluted with Et_2O, washed successively with a saturated solution of NH_4Cl and brine, dried over MgSO4, filtered, and concentrated in vacuo. Purification by flash chromatography (PE/EE 9/1) furnished a 5:4 mixture of **29*trans*** (0.954 g, 50%).

Successive recrystallization in pentane allowed the isolation of pure major **29*trans*M** (0.300 g). IR(neat) 2970, 2900, 2100, 1675, 1640, 930 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.31–7.28 (m, 2H), 7.21–7.17 (m, 1H), 3.38 (m, 1H), 2.94 (d, J=15.6 Hz, 1H), 2.64 (d, J=15.6 Hz, 1H), 2.41–2.16 (m, 4H), 1.98–1.92 (m, 4H), 1.72 (s, 3H), 1.54 (m, 6H), 1.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.8 (IV), 203.0 (IV), 138.0 (IV), 128.3 (2C, III), 126.6 (III), 126.3 (2C, III), 103.2 (IV), 100.8 (IV), 84.2 (IV), 83.6 (IV), 68.6 (III), 68.3 (III), 51.3 (IV), 36.3 (II), 34.3 (III), 33.8 (II), 28.2 (II), 26.4 (II), 25.7 (II), 20.7 (I), 18.3 (I), 18.2 (II). HRMS calcd for $C_{25}H_{28}O$ $(MH)^+$ 345.214. Found: 345.222.

29*trans*m: ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.31–7.28 (m, 2H), 7.21–7.17 (m, 1H), 3.38 (m, 1H), 2.97 (d, J=15.5 Hz, 1H), 2.63 (d, J=15.6 Hz, 1H), 2.41–2.16 (m, 4H), 1.98–1.92 (m, 4H), 1.79 (s, 3H), 1.54 (m, 6H), 1.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.8 (IV), 202.9 (IV), 137.9 (IV), 128.2 (2C, III), 126.6 (III), 126.2 (2C, III), 103.4 (IV), 100.6 (IV), 84.2 (IV), 83.6 (IV), 71.5 (III), 68.6 (III), 51.2 (IV), 36.3 (II), 34.4 (III), 33.9 (II), 28.2 (II), 26.6 (II), 25.7 (II), 20.8 (I), 18.3 (2C, II and I), 18.2 (II).

4.3.13. Cycloadduct (30). $CpCo(CO)_2$ (20 μL, 0.16 mmol, 1.2 equiv) was added to a boiling solution of **25*cis*** (0.049 g, 0.13 mmol) in xylenes (10 mL) degassed by three freeze-pump-thaw cycles and was irradiated (light from projector lamp; ELW, 300 W, 50% of its power). The reaction was monitored by TLC and after completion, the reaction mixture was concentrated in vacuo. The crude oil was purified by flash chromatography (the solvents of chromatography were not degassed) either on deactivated alumina with 3% H_2O (PE) or on silica gel neutralized with NEt_3 and dried (PE/EE 95/5) to furnish **30** (0.033 g, 66%) as a mixture of diastereomers. IR(neat) 3300, 2950, 2100, 1640, 930 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.15 (m, 5H), 5.11–4.77 (m, 3H), 3.94–3.88 (m, 4H), 2.6–2.5 (m, 2H), 2.17–1.67 (m, 8H), 1.57 (s, 3H), 1.42–1.32 (m, 4H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1 (IV), 133.8 (IV), 128.4 (2C, III), 128.0 (IV), 127.9 (IV), 127.6 (2C, III), 127.4 (IV), 126.4 (III), 119.9 (IV), 116.0 (III), 113.7 (II), 84.7 (IV), 68.2 (III), 65.3 (II), 64.4 (II), 49.2 (III), 45.5 (IV), 37.8 (II), 36.1 (II), 34.2 (II), 29.8 (II), 28.2 (II), 27.6 (II), 26.4 (I), 17.8 (I). HRMS Calcd for $C_{27}H_{32}O_2$ (388.54) $(MH)^+$ 389.248. Found: 389.248.

4.3.14. Cycloadduct (31). The procedure is identical as the one described for (**30**). The cyclization was carried out with $CpCo(CO)_2$ (27 μL, 0.19 mmol, 1.2 equiv) and a solution of **29*trans*M** (0.054 g, 0.16 mmol) in degassed xylenes (10 mL). Purification by flash chromatography (PE/EE 9/1) gave **31** (0.045 g, 60%) as a red solid. Mp 68–70 °C. ^1H NMR (400 MHz, C_6D_6) δ 7.26–7.21 (m, 2H), 7.18–7.11 (m, 3H), 5.04 (d, J=4.2 Hz, 1H), 4.59 (s, 5H), 4.46 (d, J=4.2 Hz, 1H), 2.41 (d, J=17.4 Hz, 1H), 2.29–2.22 (m, 1H), 2.15 (d, J=17.4 Hz, 1H), 1.98–1.89 (m, 4H), 1.75 (s, 3H), 1.60–1.15 (m, 8H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 218.0 (IV), 145.9 (IV), 144.8 (IV), 129.6 (IV), 128.2 (2C, III), 127.8 (III), 125.9 (2C, III), 80.8 (5C, III), 77.6 (IV), 75.1 (III), 73.5 (III), 63.7 (IV), 50.0 (III), 48.0 (IV), 47.2 (IV), 46.1 (II), 41.0 (II), 35.8 (II), 35.7 (II), 30.8 (II), 27.7 (I), 22.5 (II), 21.3 (II), 14.7 (I). HRMS Calcd for $C_{30}H_{33}CoO$ (468.52) $(MH)^+$ 469.194. Found: 469.194.

4.3.15. Compound (32). A solution of complex **31** (0.08 g, 0.17 mmol) in CH_2Cl_2 (5 mL) was stirred in presence of silica gel at rt. The reaction was monitored by TLC and after completion, the reaction mixture was filtered and furnished **32** (0.052 g, 90%). IR (neat) 2970, 2900, 2100, 1675, 1640, 930 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.18 (m, 3H), 7.11 (m, 2H), 5.63 (m, 2H), 2.56–2.45 (m, 3H), 2.32–2.23 (m, 3H), 2.09–2.06 (m, 2H), 1.88 (m, 1H), 1.65 (m, 2H), 1.45 (m, 1H), 1.27 (s, 3H), 1.25–1.23 (m, 3H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.8 (IV), 147.4 (IV), 146.2 (IV), 140.2 (IV), 134.7(IV), 132.1 (IV), 128.3 (III), 128.2 (III), 127.4 (III), 126.0 (2C, III), 118.1 (III), 116.0 (III), 47.3 (II), 46.8 (III), 46.5 (IV), 43.0 (IV), 39.8 (II), 36.3 (II), 33.1 (II), 27.3 (II), 26.1 (I), 23.2 (II), 21.1 (II), 14.3 (I). HRMS Calcd for $C_{25}H_{28}O$ (344.49) $(MH)^+$ 345.214. Found: 345.221.

4.3.16. Cycloadduct (33). The procedure is the same as the one described for (**31**). The cyclization was carried out with a 41:59 mixture of **29*trans*(M/m)** (0.200 g, 0.59 mmol) and $CpCo(CO)_2$ (100 μL, 0.70 mmol, 1.2 equiv) in degassed xylenes (10 mL). Purification by flash chromatography (PE/EE 9/1) gave a 61:39 mixture of **31** and **33** (0.097 g, 35%). Besides 0.0264 g of unidentified compound was isolated. (**33**): ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 2H), 7.18–7.11 (m, 3H), 4.98 (d, J=4.2 Hz, 1H), 4.64 (s, 5H), 4.54 (d, J=4.2 Hz, 1H), 2.41 (d, J=17.4 Hz, 1H), 2.29–2.22 (m, 1H), 2.15 (d, J=17.4 Hz, 1H), 1.98–1.89 (m, 4H), 1.60–1.15 (m, 8H), 1.01 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.1 (IV), 146.4 (IV), 145.5 (IV), 129.6 (IV), 128.2 (2C, III), 127.8 (III), 125.9 (2C, III), 80.8 (5C, III), 77.6 (IV), 75.1 (III), 73.5 (III), 64.0 (IV), 50.5 (III), 46.9 (IV), 46.3 (IV), 45.5 (II), 39.1 (II),

35.7 (II), 33.1 (II), 30.0 (II), 25.8 (I), 25.6 (II), 21.2 (II), 14.0 (I).

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