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Synthesis of Variously Substituted Allenediynes and their Cobalt (I)-Mediated [2+2+2] Cycloaddition Reactions

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Abstract: Syntheses of variously substituted allenediynes where the allene moiety is at the terminal or internal position are described. Their cobalt(I)-mediated [2+2+2] cycloaddition reactions led to the corresponding η^4-complexed tricyclic compounds ; the regioselectivity of these cyclizations depending on the substitution and the position of the allene is discussed.

Keywords : allenes ; diynes ; cyclisation ; cobalt and compounds

INTRODUCTION

Intramolecular cobalt-mediated [2+2+2] cyclizations of linear achiral enediynes containing di-, tri- and tetrasubstituted double bond have been well described.[1-5] Remarkable selectivity and high yields have been observed and have allowed a fair amount of applications in the synthesis of polycyclic natural products.[6-8]

In this connection, allenes which present cumulated C-C double bonds appear to be very promising new unsaturated partners in the cobalt-catalyzed [2+2+2] cycloadditions. Due to the versatility of their unique structure, reactions between transition metals and allene compounds have been extensively investigated[9-15] including for instance cooligomerizations,[16] intramolecular cycloisomerizations,[17,18] [4+2] and [5+1] cyclizations,[19-21] Pauson-Khand reactions,[22-24] formation of π-allyl metal complexes and electrocyclizations,[25-27] and more recently formal Alder-ene reaction.[28]

Despite allenes are good ligands in organometallic complexes, only few examples involving this moiety in [2+2+2] cycloadditions assisted by nickel (II)/(0)[29] and palladium[30] or homo Diels-Alder[31] have been reported.

Recently, we disclosed that intramolecular cyclizations of allenediynes are effected by (η^5-cyclopentadienyl)dicarbonyl cobalt [$CpCo(CO)_2$] with pronounced regio- and stereoselectivity.[32]

Indeed, depending on the double bond of the allene which is involved in the cyclization, two cobaltacyclopentadienyl intermediates **Ia** and **Ib** leading to the complexes **IIa** and **IIb** can be considered (Scheme 1).

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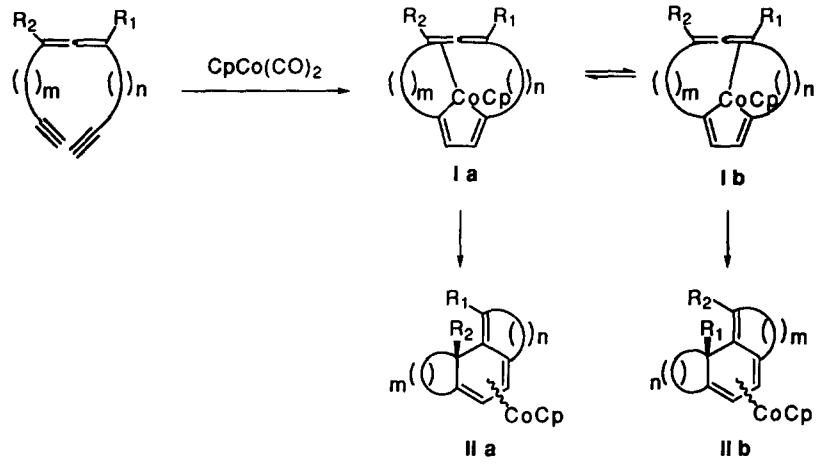


Scheme 1

In order to define the scope, the regio- and stereoselectivity of this reaction, we studied the cyclizations of differently substituted allenediynes where the allene moiety is at the terminal or internal position and where the triple bonds and the allene unit are tethered by varied carbon chains.

Herein we present the full details of the synthesis of the allene precursors which preparation has never been reported and their cobalt-mediated cyclizations.

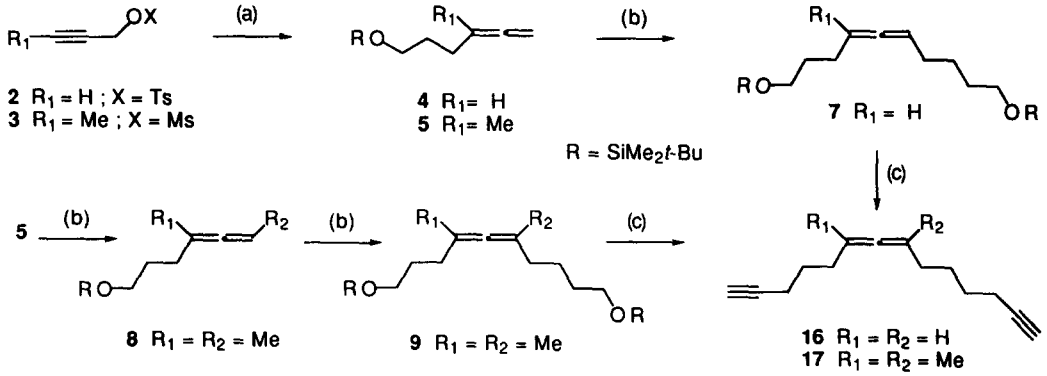
RESULTS AND DISCUSSION

Preparation of the allenediynes

The synthesis of allenic compounds has been widely investigated and highly useful methods have been developped for obtaining numerous alkylsubstituted allenes.[33-35] In all cases, we have chosen to introduce the allene unit by the copper(I) salt S_N2' displacement of propargylic leaving group (sulfonates, ethers ...) by Grignard reagent which is a general and very efficient method.[36] Thus, we prepared the allenediynes by three alternative routes : (i) synthesis by the alkylation of commercial or pre-formed allenes followed by the elaboration of the triple bonds, (ii) synthesis from pre-formed skeletons and subsequently elaboration of the allene moiety and triple bonds, (iii) synthesis from a triyne and introduction of the allene in the last step.

Synthesis of allenediynes by alkylation of pre-formed allenes. The reaction between the organocopper reagent **1** [prepared from an equivalent amount of Grignard reagent and copper(I) bromide-dimethylsulfide complex][37] and the propargylic tosylate **2** or mesylate **3** in THF provided the allene educts **4** or **5** in 70% yield (Scheme 2). These compounds were lithiated[38] in THF at -100°C using *n*-butyllithium. Reaction with 4-iodo-1-(*tert*-butyldimethylsilyloxy)butane[39] **6** or methyl iodide in the presence of HMPA (20 equiv) gave di- and trisubstituted allenes **7** and **8** in 75% and 60% yields respectively. When the reaction was run at -78°C in the

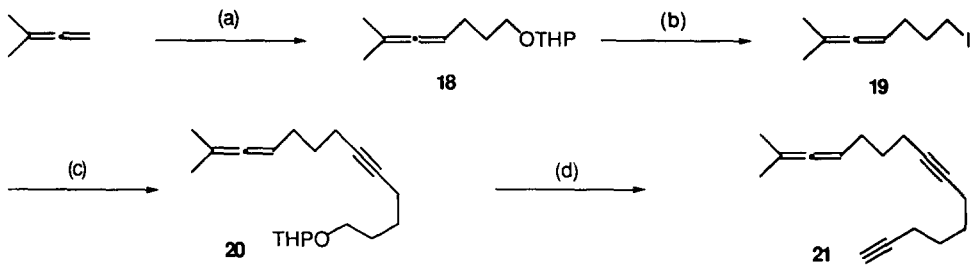
absence of HMPA, we mainly noticed the alkylation of the propargyllithium form (90%). This high selectivity is presumably due to the formation of a six-membered Li-O chelate. Deprotonation of **8** at -100°C with *n*-butyllithium, followed by alkylation with **6** in the presence of HMPA led to the tetrasubstituted allene **9** (40%). Compounds **7** and **9** were converted by using tetrabutylammonium fluoride in THF into the corresponding diols **10** and **11** which were subsequently tosylated and brominated. The reaction of the dibromides **14** and **15** with lithium acetylide-ethylenediamine complex in DMSO[40] furnished the allenediynes **16** and **17** in 30% and 42% yields.



(a) BrMg[BrCu(CH$_2$)$_3$OR] (**1**), THF, -50° C to r. t., **4** : 70% ; **5** : 70 %. (b) (i) *n*-BuLi, -100° C, THF ; (ii) HMPA (20 eq), (**6**) I(CH$_2$)$_4$OSiMe$_2$*t*-Bu , **7** : 75% or CH$_3$I, **8** : 60%, **9** : 40%. (c) (i) *n*-Bu$_4$NF, r. t., THF, **10** : 70% ; **11** : 50% ; (ii) TsCl, Et$_3$N, 4-DMAP, CH$_2$Cl$_2$, **12** and **13** : 90% ; (iii) LiBr, DMF, 70°C, **14** and **15** : 80% ; (iv) HC≡CLi.EDA, DMSO, **16**: 30% ; **17** : 42%.

Scheme 2

Similarly, the allenediyne **21** with the allene unit at the terminal position was prepared following Scheme 3.

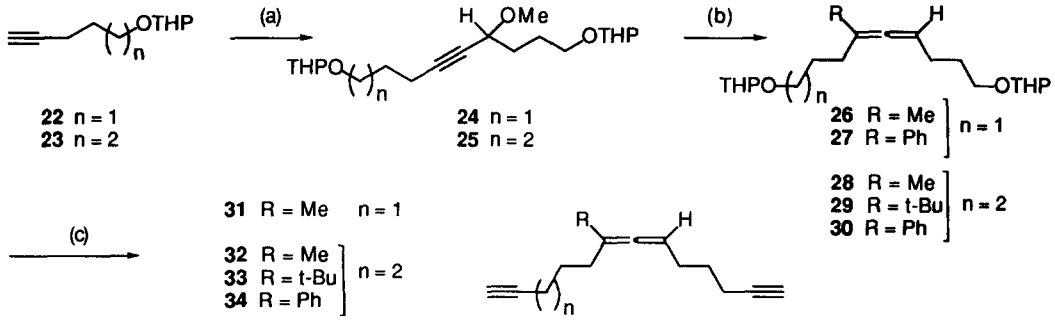


(a) *n*-BuLi, THF, -78° C, Br(CH$_2$)$_3$OTHP, 87%. (b) (i) cat. PTSA, MeOH, 91%; (ii) TsCl, 4-DMAP, Et$_3$N, CH$_2$Cl$_2$, quant. ; (iii) NaI, acetone, 90%. (c) *n*-BuLi, THF, HC≡C(CH$_2$)$_4$OTHP, 92%. (d) (i) cat. PTSA, MeOH, quant. ; [as scheme 2 (ii) quant. ; (iii) 52% ; (iv) 67%]

Scheme 3

Dimethylallene[41] was deprotonated at -78°C with *n*-butyllithium and alkylated with 3-bromo-1-(2-tetrahydropyranyloxy)propane in 87 % yield. After acid-catalyzed deprotection, successive tosylation and iodination of the resulting alcohol led to the compound **19** in 80% overall yield. The latter reacted with the lithio derivative of the tetrahydropyranyl ether of hexyn-1-ol[42] to afford the ether **20**. After acidic hydrolysis, the same sequence as the one described in Scheme 2 provided the allenediyne **21** in 35 % overall yield.

Synthesis of allenediynes from pre-formed skeletons. The tetrahydropyranyl ethers **22** and **23**[42] were lithiated at -78°C with *n*-butyllithium and condensed on the 4-(2-tetrahydropyranyloxy)-butan-1-al[43] to deliver the corresponding alcohols which were readily converted into the methylethers **24** and **25** in 72 % and 76 % overall yields respectively. Addition of Grignard reagents catalyzed by copper(I) complex in ether[44,45] led to the corresponding allenes **26-30**. The same sequence of reactions as described in Scheme 3 achieved the preparation of the trisubstituted allenediynes **31-34** in moderate to good yields (23-72%). The low yield (6%) for **34** is the result of the isomerization of the allene unit into the conjugated diene in the last step.

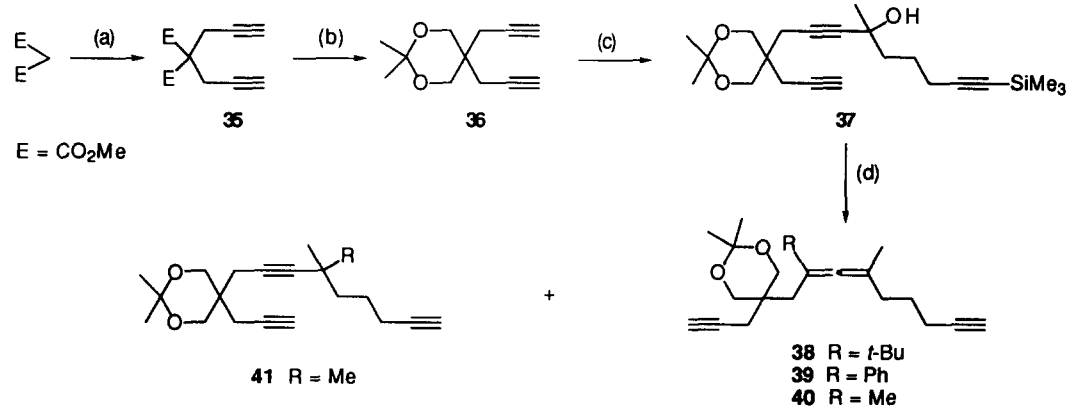


(a) (i) *n*-BuLi, THF, -78°C, $HC(O)(CH_2)_3OTHP$; (ii) NaH, THF, 0°C, MeI, **24** : 72% ; **25** : 76%. (b) $CuBr.Me_2S$, -50°C, RMgBr, Et_2O, **26** : 69% ; **27** : 84% ; **28** : 57% ; **29** : 38% ; **30** : 86%. (c) (i) cat. PTSA, MeOH ; (ii) MsCl, Et_3N, CH_2Cl_2, (iii) and (iv) as scheme 2, **31** : 23% ; **32** : 69% ; **33** : 43% ; **34** : 6%.

Scheme 4

Since the yield-limiting step of these approaches was the transformation of the protected alcohols into the corresponding terminal alkynes, an alternative route has been investigated.

Synthesis of the allenediynes from triynes. The allenediynes **38-40** were readily prepared following Scheme 5.

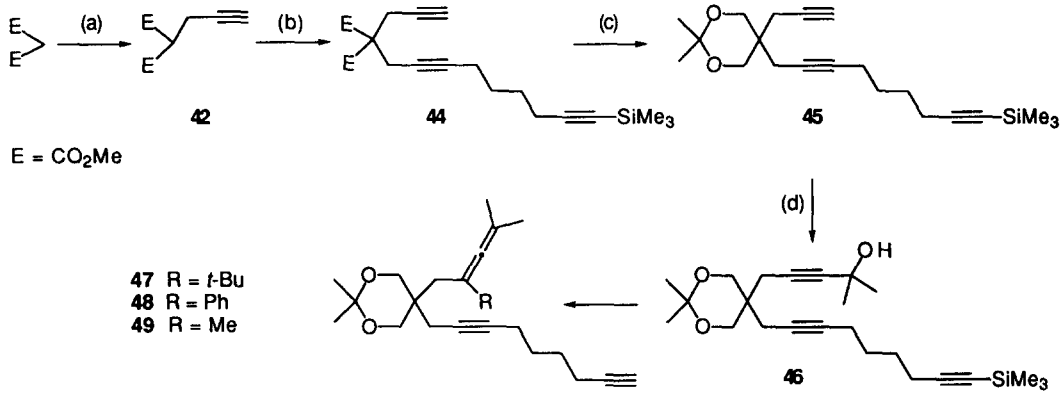


(a) NaH, $BrCH_2C{\equiv}CH$ (2 eq), THF, Δ, quant.. (b) (i) $LiAlH_4$, Et_2O, r.t., 1h ; (ii) cat. PTSA, acetone, 42%. (c) (i) -78°C *n*-BuLi, THF, ; (ii) $CH_3C(O)(CH_2)_3C{\equiv}C\text{-}SiMe_3$, THF, -78°C, 54%. (d) (i) *n*-BuLi, -78°C, THF, MsCl ; (ii) RMgX, THF, $Me_2S.CuBr$, LiBr, -50°C ; (iii) KF, DMSO, **38** : 48% ; **39** : 97% ; **40+41** : 83%.

Scheme 5

Double alkylation of the sodium derivative of dimethylmalonate with propargyl bromide quantitatively provided the compound **35**. Reduction of the ester functions followed by acid-catalyzed protection with acetone furnished the acetonide **36**. Condensation of its lithium acetylide on the 7-trimethylsilylhept-6-yn-2-one[46] led to the alcohol **37** in 89 % yield. Heterocuprate mediated reaction from the corresponding mesylate afforded, in good yields (65-97%), the allenediynes which were subsequently desilylated with potassium fluoride in DMSO[47] to yield the allenediynes **38-40** (73% to quantitative). When R = Me, the allenic and propargylic derivatives **40** and **41**, were obtained as an inseparable mixture.

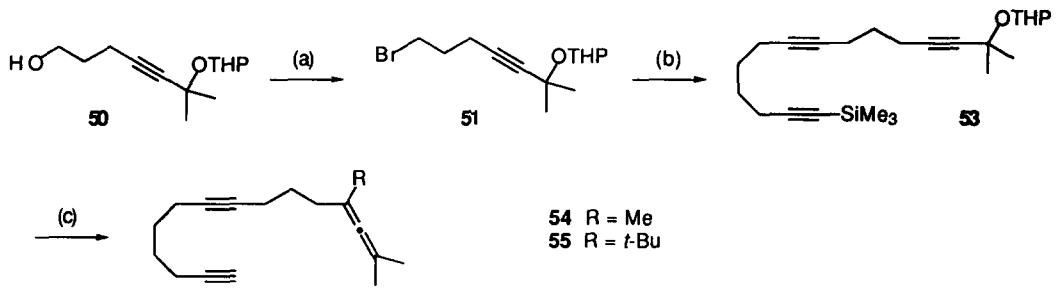
The tetrasubstituted allenediynes having the allene moiety at the terminal position were similarly prepared as described in Schemes 6 and 7. Double alkylation of the dimethylmalonate successively with propargyl bromide and 1-methanesulfonyloxy-9-trimethylsilylnon-2,8-diyne **43** [generated by alkylation of the protected propargylic alcohol with 6-bromo-1-trimethylsilylhexa-1-yne followed by hydrolysis of the ether and mesylation] gave the compound **44**. After its transformation into the acetonide **45**, its lithio derivative was added to acetone to furnish the tertiary alcohol **46**. Addition of the organocuprate on the corresponding mesylate led to the allenediynes in 60-87 % yield. Finally, the preparation of the required precursors **47-49** was achieved through the desilylation of the triple bonds.



(a) NaH, $BrCH_2C{\equiv}CH$, THF, Δ, 60%. (b) NaH, $MsOCH_2C{\equiv}C(CH_2)_4C{\equiv}CSiMe_3$ (**43**), 73%. (c) (i) $LiAlH_4$, Et_2O, r.t.,1h ; (ii) cat. PTSA, acetone, 73%. (d) *n*-BuLi, THF, -78°C, C_3H_6O, 92% (e) (i) *n*-BuLi, -78°C, THF, MsCl ; (ii) RMgX, $Me_2S.CuBr$, LiBr, THF, -50°C ; (iii) KF, DMSO, **47** : 48% ; **48** : 58% ; **49** : 72%.

Scheme 6

Successive alkylation of the lithio derivative of the 1,7-octadiyne with the bromide **51** (quantitatively prepared from the alcohol **50**[48] *via* its mesylate) and TMSCl led to the triyne **53** in 68 % overall yield (Scheme 7). After hydrolysis of the ether and mesylation of the tertiary alcohol, the heterocuprate mediated reaction furnished the corresponding allenediynes which were desilylated to afford **54** and **55** (50-62%).



(a) (i) MsCl, 4-DMAP, Et_3N, CH_2Cl_2 ; (ii) LiBr, DMF, quant. (b) (i) $HC{\equiv}C(CH_2)_4C{\equiv}CH$, *n*-BuLi, HMPA, THF, -78°C, **52** : 68% (ii) *n*-BuLi, THF, -78°C, Me_3SiCl, 81%. (c) (i) cat. PTSA, MeOH, quant. ; (ii) *n*-BuLi, THF, -78°C, MsCl ; (iii) MeMgBr or *t*-BuLi, LiCl, CuCN, THF, -78°C ; (iv) KF, DMSO, **54** : 61% ; **55** : 50%.

Scheme 7

Cobalt-mediated cyclizations of the allenediynes

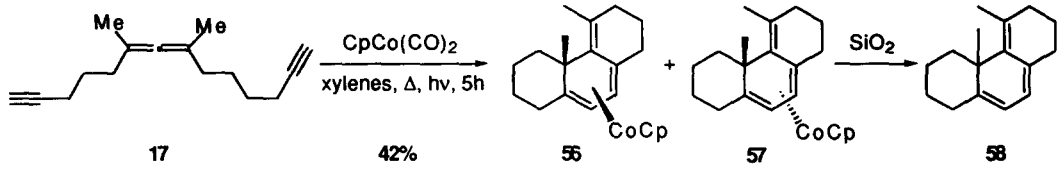
Having in hand variously substituted allenediynes, we studied their behavior in presence of cobalt (I) complexes. The cyclizations were conducted according to the usual protocol *i.e.* addition of $CpCo(CO)_2$ to a refluxing xylenes solution of allenediyne under irradiation. As previously mentionned, the two cobaltacyclopentadienes intermediates **Ia** and **Ib** (Scheme 1) can be considered. For $R_1 = R_2 = H$, a 1,3-migration of hydrogen can be expected to afford aromatic stable structures and the regeneration of the cobaltacyclopentadienyl moiety, suggesting that the process may to be catalytic.

No significant evolution of allenediyne **16** was noticed when a catalytic amount of $CpCo(CO)_2$ was used in boiling xylenes under irradiation. However, when the reaction was carried out with one equivalent of $CpCo(CO)_2$, **16** was consumed after 30 min showing the high reactivity of the allene moiety in presence of the cobalt mediator. Neither the cobalt complexes nor the decomplexated structures were isolated, but only untractable materials were formed.

Similarly, the trisubstituted allenediynes **31-34** exhibited the same behavior. We anticipated that the degradation could be due either to the sensitivity of the complexed diene to uncontrolled rearrangement or to a competitive process close to the oligomerization. Such a process has already been reported to be competitive to the [2+2+2] cyclization in rhodium-catalyzed trimerization of alkynes, which leads to hexadienynes instead of the benzenic compounds.[49]

Gratifyingly, exposure of the tetrasubstituted allenediyne **17** to a stoichiometric amount of $CpCo(CO)_2$ in boiling xylenes under irradiation for 5 hours furnished red-brown complexes in 42% isolated yield. A 7:3 mixture of two diastereomers **56** and **57** was obtained. The ^1H- and ^{13}C-NMR spectra were consistent with two [6.6.6] tricyclic structures meaning that the selectivity was in favor of the thermodynamically most stable products (Scheme 8). Particularly, their assigments were based on the characteristic chemical shifts of the dienic, cyclopentadienyl and methyl hydrogens. The major isomer **56** exhibited two doublets at 5.11 and 4.27 ppm (J = 3.8 Hz) and three singlets at 4.60, 1.72 indicating a *cis* relationship between the angular methyl and the cobalt moiety[2] and 1.62 for the vinylic methyl. Free ligand **58** was formed from a mixture of **56** and **57** on filtration

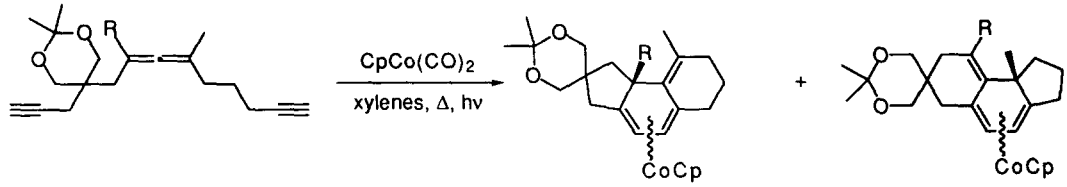
through silica gel in 20% yield. This low yield could be explained by the high oxygene sensitivity of the triene **58**, which has already been observed in the case of dienes resulting of intramolecular enediynes cyclizations.[3]



17 **42%** **56** **57** **58**

Scheme 8

Under the standard conditions of cyclization, **38** furnished the complexed tricyclic compound **59** as a single diastereomer (Scheme 9). The same pattern of resonances as for **56** between 4.10 and 4.88 ppm established unambiguously the complexed dienic structure. The chemical shift of the methyl at 1.65 ppm indicated its vinylic position meaning that the *t*-Bu group is angular. According to the literature,[1] the deshielded resonance for *t*-Bu at 1.15 ppm was more in agreement with an *endo* than an *exo* relationship with the metal.



38 R = *t*-Bu	**54 %** (3h)	100 (*endo*) ; **59**	0
39 R = Ph		unexploitable mixture	
40 R = Me	**70%** (2h)	50 (*endo*/*exo*) ; **60**	50 (*endo*/*exo*) ; **61**

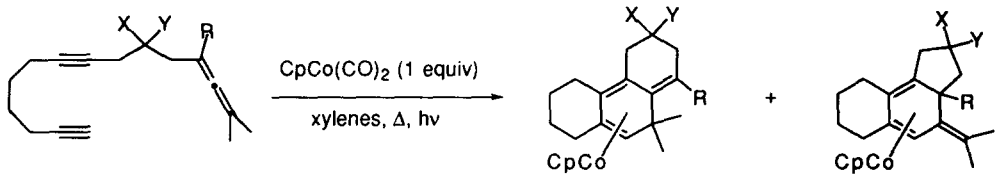
Scheme 9

On the contrary, the cyclizations of **39** and **40** were not regioselective. We got an unexploitable mixture from **39** which could not be identified. However, the ^{1}H-NMR spectrum of the crude mixture indicated the resonances for dienic protons meaning that the cyclization had occured without selectivity. The cyclization of **40** in presence of the inseparable triyne **41** provided the aromatic compound resulting from the trimerization of **41** and two complexes **60** and **61** in 70% yield. We were unable to separate these complexes to determine the relationship between the metal and the angular methyl. The lack of selectivity in these last cases was quite puzzling. Why would the presence of phenyl or methyl relatively to the *tert*-butyl group have such a profound influence on the course of the cyclization? To check further on this question, we were curious to establish the stereochemical fate of the cyclization of the terminal allenediynes **21**, **47-49** and **54-55**.

Thus, the tri-and tetrasubstituted allenediynes **21** and **47-49** cyclized successfully under the conditions described for **17** to provide either the tricyclic [6.6.5] or [6.6.6] compounds **62**, **63**, **64**, and **65** as only one diastereomer in high isolated yields (70-87%) (Scheme 10).

The results showed that the substitution of the allene function is a determining factor on the regiochemical outcome of the cyclization. However, for an identical substitution of the allene, the reaction is significantly influenced by the presence or not of the acetonide on the tether.

If the admitted mechanism for the [2+2+2] cyclization of enediynes,[5] is still pertinent in this cycloaddition, we could first envision the formation of the cobaltacyclopentadiene. Then, to accomplish the cyclization, the metallacycle has to be brought into the proximity of the allenic function. The contrasted regioselectivity can be understood in terms of the site preference of the allenyl group in coordination plus additionnal transannular steric interactions and/or conformationnal equilibrium. Such considerations could justify the different reactivities between **47**, **49** and **54**, **55**. The presence of the acetonide on the tether probably increases the number of non-bonding interactions in the intermediates of the reaction and furthermore produces a totally selective reaction.



21 X, Y = H ; R = H	72 %	0	100 (**62**)
54 X, Y = H ; R = Me		unexploitable mixture	
55 X, Y = H ; R = *t*-Bu		unexploitable mixture	
47 X, Y =  ; R = *t*-Bu	80 %	0	100 (**63**)
48 X, Y = " ; R = Ph	87 %	100 (**64**)	0
49 X, Y = " ; R = Me	70 %	100 (**65**)	0

Scheme 10

Electronic factors could be involved too, especially in the case of **48**. Indeed, the participation of the cumulated double bond maintained the conjugation of the system during the process of the cyclization and allowed the formation of the tricyclic [6.6.6] compound.

CONCLUSION

In summary, we have described different syntheses of variously substituted allenediynes where the allene moiety is at the terminal or internal position. We have shown that allenes are quite good partners for the [2+2+2] cycloaddition reaction. However, the reaction markedly depends on the position and the substitution of the allene ; in the major cases, the cobalt(I) cyclization led to the corresponding η^4-complexed tricyclic compound regio- and diastereoselectively. At this point of our study, although it seems difficult to rationalize the factors governing these selectivities and to predict the behavior of the allenediynes in presence of cobalt(I) complexes, their cyclizations are interesting for synthetic purposes. Indeed, free ligands may be regarded as constituting the BCD or ABC (with an angular methyl) moieties of steroids. This could be useful considering an approach in asymmetric version from an optically pure allene.

EXPERIMENTAL SECTION

^{1}H-NMR and ^{13}C-NMR spectra were taken on 200 MHz Bruker AC 200, 400 MHz JEOL 65X 400 and Bruker ARX 400 spectrometers. Chemical shifts are reported in ppm referenced to the residual proton resonances of the solvants. Infrared (IR) spectra were recorded by using a Perkin Elmer 1420 spectrometer. Mass spectra (MS) were obtained on GC-MS Hewlett-Packard HP 5971 apparatus. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F 254. Silica gel Merck Geduran SI (40-63 μm) was used for column chromatography using Still method.[50] PE and EE mean petroleum ether and diethyl ether.

Preparation of the allenediynes.

Synthesis of the allenediynes 16 and 17. (a) General procedure for the preparation of the allenes 4 and 5: To a cooled (-50°C) THF (50 mL) solution of copper (I) bromide-dimethylsulfide complex (8.4 g, 40 mmol) and lithium bromide (5g, 40 mmol) was added a solution of Grignard reagent derived from 3-bromo-1-*tert*-butyldimethylsilyloxy propane (40 mmol) in THF (100 mL). After being stirred at -30°C for 1h, a solution of 1-*para*-toluenesulfonyloxy-prop-3-yne **2** (8.4 g, 40 mmol) or 1-methanesulfonyloxy-but-2-yne[51] **3** (5.9 g, 40 mmol) in THF (50 mL). After the reaction mixture was stirred at room temperature for 30 min, it was hydrolyzed with a solution of NH_4Cl/NH_4OH (2/1) and extracted with ether (100 mL). The organic layer was washed with a saturated solution of brine (2x50 mL), dried over $MgSO_4$, filtered and concentrated. Purification of the residue by flash chromatography (PE/EE = 80/20) afforded the allene **4** or **5**. **1-(*tert*-Butyldimethylsilyloxy)-hexa-4,5-diene (4)** (5.43 g, 64 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.10 (m ,1 H), 4.64 (m, 2H), 3.63 (t, J = 6.4 Hz, 2H), 2.10 (m, 2H), 1.63 (quint, J = 6.4 Hz, 2H), 0.88 (s, 9H), 0.04 (s, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 208.5, 89.5, 74.9, 62.4, 31.2, 25.9 (3C), 24.7, 18.4, -5.1 (2C) ; IR (neat) 1950, 1250, 850 cm^{-1}. **4-Methyl-1-(*tert*-butyldimethylsilyloxy)-hexa-4,5-diene (5)** (6.32 g, 70 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.59-4.53 (m, 2H), 3.61 (t, J = 6.5 Hz, 2H), 1.98-1.91 (m, 2H), 1.88-1.85 (m, 5H), 0.88 (s, 9H), 0.03 (s, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 206.1, 98.2, 74.1, 62.7, 30.6, 29.7, 25.9 (3C), 18.8, 18.3, -5.3 (2C) ; IR (neat) 1950, 1250, 850 cm^{-1}.

(b) General procedure for the preparation of the tri- and tetrasubstituted allenes 7, 8 and 9 : At -100°C, *n*-BuLi (1.5 M in hexanes, 2 mmol) was added to a solution of allene **4** (0.424 g, 2 mmol) or **5** (0.452 g, 2 mmol) in THF (10 mL). After being stirred at -100°C for 1h, HMPA (2 mL, 40 mmol) was added followed by a dropwise addition of a solution of 4-iodo-1-(*tert*-butyldimethylsilyloxy)-butane **6** (0.628 g, 2 mmol) in THF (20 mL) or methyl iodide (1.99 g, 14 mmol). After the mixture was warmed to room temperature, it was diluted with ether (50 mL), washed with saturated solution of NH_4Cl (2x50 mL) and brine (2x50 mL), dried over $MgSO_4$ and concentrated. The crude residue was purified by flash chromatography (PE/EE = 95/5) to afford the trisubstituted allenes **7** and **8**. The same reaction from **8** with alkyl iodide **6** led to the allene **9**. **1,10-di-(*tert*-Butyldimethylsilyloxy)-deca-4,5-diene (7)** (0.6 g, 75 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.11-5.05 (m, 2H), 3.62 (t, J = 6.1 Hz, 2H), 3.58 (t, J = 6.1 Hz, 2H), 2.04-1.90 (m, 4H), 1.67-1.25 (m, 6H), 0.88 (s, 18H), 0.03 (s, 12H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.8, 91.2, 90.6, 63.0, 62.5, 32.9, 32.3, 28.7, 25.9 (6C), 25.5, 25.2, 18.3 (2C), -5.0 (4C) ; IR (neat) 1950, 1250, 850 cm^{-1}. **1-*tert*-Butyldimethylsilyloxy-4-methyl-hepta-4,5-diene (8)** (0.29 g, 60 %).^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.92 (m ,1 H), 3.57 (t, J = 6.6 Hz, 2H), 1.90-1.88 (m, 2H), 1.61 (d, J = 2.7 Hz, 3H), 1.58 (quint, J = 6.6 Hz, 2H), 1.57 (d, J = 7.2 Hz, 3H), 0.84 (s, 9H), 0.05 (s, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.8, 98.3, 85.0, 62.8, 30.7, 30.1, 25.9

(3C), 19.5, 18.3, 14.9, -5.2 (2C) ; IR (neat) 1960 850 cm^{-1}. **1,10-di-(*tert*-Butyldimethylsilyloxy)-4,6-dimethyldeca-4,5-diene (9)** (0.34 g, 40 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.61 (t, *J* = 6.6 Hz, 2H), 3.59 (t, *J* = 6.6 Hz, 2H), 1.94-1.88 (m, 4H), 1.63 (s, 3H), 1.62 (s, 3H), 1.60-1.59 (m, 2H), 1.55-1.45 (m, 2H), 1.40-1.30 (m, 2H), 0.88 (s, 18H), 0.04 (s, 12H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.2, 98.5, 98.1, 63.3, 63.0, 34.2, 32.5, 31.0, 30.6, 25.9 (6C), 24.2, 19.7, 19.4, 18.4 (2C), -5.3 (4C) ; IR (neat) 1950 850 cm^{-1}.

(c) General procedure for the preparation of the allenediynes 16 and 17 : (i) Deprotection of the alcohol To a solution of allenediether **7** or **9** (4 mmol) in THF (10 mL) was added a 1 M solution of *n*-Bu_4NF in THF (8 mL, 2 eq). After being stirred at room temperature for 2h, the mixture was partitioned between ether (3x20 mL) and brine (3x20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification of the residue by flash chromatography (ether) gave the diols **10** or **11**. **Deca-4,5-diene-1,10-diol (10)** (0.48 g, 70 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.12-5.07 (m, 2H), 3.69-3.62 (m, 4H), 2.01-1.98 (m, 4H), 1.73-1.59 (m, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.0, 91.2, 90.5, 62.7, 62.2, 32.2, 32.1, 28.7, 28.5, 25.1 ; IR (neat) 3340, 1950 cm^{-1}. **4,6-Dimethyldeca-4,5-diene-1,10-diol (11)** (0.4 g, 50 %). ^{1}H-NMR (400 MHz, $CDCl_3$) 3.58 (t, *J* = 6.4 Hz, 2H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.64 (m, 4H), 1.60 (s, 3H), 1.59 (s, 3H), 1.70-1.28 (m, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.4, 96.5, 95.9, 62.6, 62.4, 34.1, 32.1, 30.7, 30.6, 23.7, 19.4, 19.3 ; IR (neat) 3340, 1950 cm^{-1}. (ii) Tosylation To a solution of diol **10** (0.511 g, 3 mmol) or **11** (0.594 g, 3 mmol) in CH_2Cl_2 (10 mL) in presence of NEt_3 (2 mL, 8 mmol) and 4-DMAP (18 mg, 0.15 mmol) was added a solution of tosyl chloride (1.3 g, 6.6 mmol) in CH_2Cl_2 (10 mL). After stirring for 2h at room temperature, the reaction mixture was hydrolyzed with saturated solution of NH_4Cl (20 mL) and extracted. The organic layer was washed with brine (2x30 mL), dried ($MgSO_4$) and concentrated. The crude product was used in the next step without purification. **1,10-Di-(*para*-toluenesulfonyloxy)-deca-4,5-diene (12)** (1.29 g, 90 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 4H), 7.30 (d, *J* = 8.0 Hz, 4H), 4.90-4.93 (m, 2H), 4.01-3.95 (m, 2H), 2.40 (s, 6H), 1.98-1.83 (m, 4H), 1.76-1.58 (m, 4H), 1.39-1.34 (m, 4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.9, 144.8 (2C), 132.9 (2C), 129.7 (4C), 127.7 (4C), 91.0, 89.6, 70.3, 69.9, 28.1, 27.9 (2C), 24.6, 24.3, 21.5 (2C) ; IR (neat) 1950 cm^{-1}. **4,6-Dimethyl-1,10-(*para*-toluenesulfonyloxy)-deca-4,5-diene (13)** (1.37 g, 90 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 4H), 7.43 (d, *J* = 8.2 Hz, 4H), 4.10 (t, *J* = 6.0 Hz, 2H), 4.08 (t, *J* = 6.0 Hz, 2H), 2.50 (s, 6H), 1.97 (ddd, *J* = 4.4, 3.3, 2.8 Hz, 2H), 1.88 (ddd, *J* = 4.4, 3.3, 2.8 Hz, 2H), 1.80-1.68 (m, 4H), 1.64 (s, 3H), 1.62 (s, 3H), 1.44 (m, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 197.9, 144.6 (2C), 133.0 (2C), 129.7 (4C), 127.7 (4C), 98.8, 97.4, 70.5, 70.3, 33.4, 29.7, 28.3, 26.9, 23.2, 21.6 (2C), 19.5, 19.2 ; IR (neat) 2950, 1950 cm^{-1}. (iii) Bromation : A solution of ditosylate **12** (0.956 g, 2 mmol) or **13** (1.01 g, 2 mmol) and lithium bromide (0.7 g, 8 mmol) in DMF (20 mL) was heated at 50°C for 2h. Then, the reaction mixture was partitioned between ether (3x50 mL) and water (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. The crude residue was purified by flash chromatography (PE/EE = 80/20) to give the dibromide **14** or **15**. **1,10-Dibromo-deca-4,5-diene (14)** (0.474 g, 80 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.05-4.98 (m, 2H), 3.36 (t, *J* = 6.6 Hz, 2H), 3.32 (t, *J* = 6.6 Hz, 2H), 2.09-1.71 (m, 8H), 1.54-1.43 (m, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.0, 90.8, 89.4, 33.4, 32.9, 32.0, 31.8, 27.8, 27.4, 27.1 ; IR (neat) 1950 cm^{-1}. **4,6-Dimethyl-1,10-dibromo-deca-4,5-diene (15)** (0.52 g, 80 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.48 (t, *J* = 7.2 Hz, 2H), 3.47 (t, *J* = 7.2 Hz, 2H), 2.13-2.09 (m, 2H), 2.02-1.90 (m, 6H), 1.71 (s, 3H), 1.70 (s, 3H), 1.58 (quint, *J* = 7.2 Hz, 2H) ; ^{13}C-NMR (100

MHz, $CDCl_3$) δ 198.3, 98.5, 97.1, 33.8, 33.5, 33.3, 32.6, 32.2, 30.8, 26.1, 19.5, 19.3 ; IR (neat) 1950 cm^{-1}. (iv) Alkylation : To a suspension of lithium acetylide-ethylenediamine complex (0.46 g, 5 mmol) in DMSO (5 mL) was added dropwise a solution of dibromide **14** (0.459 g, 1.5 mmol) or **15** (0.49 g, 1.5 mmol) in DMSO (5 mL). After being stirred at room temperature for 2h, the mixture was hydrolyzed with water (50 mL) and extracted with pentane (3x50 mL). The organic layer was washed with brine (50 mL), dried ($MgSO_4$) and concentrated. Purification of the crude residue by flash chromatography (pentane) led to the allenediyne **16** or **17**. **Tetradeca-6,7-diene-1,13-diyne (16)** (84 mg, 30 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.06 (m, 2H), 2.16 (td, *J* = 7.2, 2.7 Hz, 2H), 2.12 (td, *J* = 7.2, 2.7 Hz, 2H), 2.03 (m, 2H), 1.93 (m, 2H), 1.87 (t, *J* = 2.7 Hz, 2H), 1.57 (quint, *J* = 7.2 Hz, 2H) 1.69 (m, 4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.0, 90.9, 90.1, 84.5, 84.3, 68.4, 68.2, 28.4, 28.3, 28.1, 27.8, 18.2, 17.8, 15.3 ; IR (neat) 3300, 2100, 1960 cm^{-1}. Anal. Calcd. for $C_{14}H_{18}$: C, 90.26 ; H, 9.74. Found: C, 89.91 ; H, 9.63. **6,8-Dimethyl-tetradeca-6,7-diene-1,13-diyne (17)** (0.135 g, 42 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.26-2.21 (m, 4H), 2.07-2.03 (m, 2H), 1.99-1.94 (m, 4H), 1.69 (s, 3H), 1.68 (s, 3H), 1.70-1.60 (m, 2H), 1.59-1.54 (m, 4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.2, 98.3, 97.5, 84.6 (2C), 68.0 (2C), 33.7, 33.3, 27.9, 26.6, 26.5, 19.5, 19.4, 18.4, 18.0 ; IR (neat) 3300, 2100, 1960 cm^{-1}. Anal. Calcd. for $C_{16}H_{22}$: C, 89.65 ; H, 10.35. Found : C, 89.31 ; H, 9.95.

*Synthesis of the allenediyne **21**.* (a) To a THF (20 mL) solution of dimethylallene[43] (1.36 g, 20 mmol) was added *n*-BuLi (1.5 M in hexanes, 16 mL, 22 mmol) at -78°C. After being stirred at -78°C for 2h, a solution of 3-bromo-1-(2-tetrahydropyranyloxy)propane (4.2 g, 18 mmol) in THF (20 mL) was added. The resulting mixture was warmed to room temperature for 3h, diluted with ether (100 mL) and washed with saturated solution of NH_4Cl (100 mL). The organic layer was separated, washed with brine (2x80 mL), dried ($MgSO_4$) and concentrated. Purification of the residue by flash chromatography (PE/EE = 80/20) furnished **1-(2-Tetrahydropyranyl- oxy)-6-methyl-hepta-4,5-diene (18)** (3.37 g, 87 %). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.97-4.95 (m, 1H), 4.58-4.57 (m, 1H), 3.88-3.74 (m, 2H), 3.50-3.26 (m, 2H), 2.05-2.00 (m, 2H), 1.66-1.53 (m, 8H), 1.67 (s, 3H), 1.66 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.6, 98.6, 95.0, 88.2, 66.7, 62.1, 30.7, 29.0, 25.6, 25.4, 20.3 (2C), 19.5 ; IR (neat) 2940, 1960 cm^{-1}. (b) *(i)* To a solution of **18** (2.33 g, 11 mmol) in MeOH (20 mL) was added PTSA monohydrate (150 mg, 0.8 mmol). After being stirred for 2h at room temperature, the reaction mixture was partitioned between ether (3x50 mL) and saturated solution of $NaHCO_3$ (50 mL). The organic layers were washed with saturated solution of brine, dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (PE/EE = 80/20) to yield the corresponding alcohol (1.26 g, 91%) ; *(ii)* The alcohol was tosylated as described for **12** and **13** ; *(iii)* A solution of the tosylate (2.68 g, 9.6 mmol) in acetone (100 mL) was refluxed for 1h in presence of sodium iodide (3 g, 20 mmol). After cooling the mixture, it was hydrolyzed with water (100 mL) and extracted with ether (3x50 mL). The organic layer was dried, concentrated and purified by flash chromatography (PE/EE = 80/20) to afford **1-Iodo-6-methylhepta-4,5-diene 19** (2 g, 90%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.88-4.84 (m, 1H), 3.18 (t, *J* = 7.2 Hz, 2H), 1.94 (t, *J* = 7.2 Hz, 2H), 1.87 (quint, *J* = 7.2 Hz, 2H), 1.66 (s, 3H), 1.64 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.9, 95.7, 86.8, 32.7, 29.8, 20.7 (2C), 6.3 ; IR (neat) 1960 cm^{-1}. (c) At -78°C, to a solution of 1-(2-tetrahydropyranyloxy)-hex-5-yne (1.46 g, 8 mmol) in THF (20 mL) was added *n*-BuLi (1.50 M in hexanes, 5.6 mL, 8 mmol). The mixture was allowed to warm to room temperature and was stirred for 90 min. After cooling at -78°C, HMPA (7 mL, 40 mmol) and successively iodide **19** (0.944 g, 4 mmol) were added. Then, the reaction mixture was warmed to room temperature and diluted with ether (50 mL). The organic layer was washed successively with saturated solution of NH_4Cl (100 mL), brine (100 mL), dried over $MgSO_4$ and concentrated. The crude residue was purified by flash chromatography (PE/EE = 80/20) to afford **12-Methyl-1-**

(2-tetrahydropyranyloxy)-trideca-10,11-dien-5-yne 20 (1.07 g, 92%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.93-4.85 (m, 1H), 4.58 (t, *J* = 7.2 Hz, 1H), 3.89-3.66 (m, 2H), 3.52-3.32 (m, 2H), 2.18-2.11 (m, 4H), 2.04-1.94 (m, 2H), 1.97-1.53 (m, 12H), 1.65 (s, 3H), 1.63 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.9, 98.7, 94.9, 87.9, 80.2, 79.9, 67.0, 62.2, 30.8, 28.9, 28.6, 28.3, 25.9, 25.5, 20.6 (2C), 19.3, 18.6, 18.1 ; IR (neat) 2220, 1960 cm^{-1}. (d) The compound **20** was submitted to the same sequence of reactions as described for **16** and **17** and furnished **14-Methyl-pentadeca-12,13-dien-1,7-diyne 21** (35% overall from **20**). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.94-4.82 (m, 1H), 2.28-2.10 (m, 6H), 2.04-1.94 (m, 2H), 1.91 (t, *J* = 2.6 Hz, 1H), 1.65 (s, 3H), 1.63 (s, 3H), 1.62-1.50 (m, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.9, 94.6, 87.9, 84.1, 80.3, 79.6, 68.3, 28.6, 28.3, 28.0, 27.5, 20.6 (2C), 18.3, 18.1, 17.9 ; IR (neat) 3300, 2100, 1960 cm^{-1}.

Synthesis of allenediynes 31-34. (a) *(i)*To a solution of 1-(2-tetrahydropyranyloxy)-pent-4-yne[44] **22** (6.34 g, 38 mmol) or 1-(2-tetrahydropyranyloxy)-hex-5-yne[44] **23** (6.86 g, 38 mmol) in THF (40 mL) was added at -78°C *n*-BuLi (1.6 M in hexanes, 24 mL, 38 mmol). After being stirred at -78°C for 10 min, a solution of 4-(2-tetrahydropyranyloxy)-butan-1-al[45] (7.25 g, 42 mmol) in THF (40 mL) was added. After warming up to room temperature (30 min), the reaction mixture was diluted with ether (100 mL). The organic layer was washed with brine (2x100 mL), dried over $MgSO_4$ and concentrated. Purification by flash chromatography (petroleum ether/ether = 80/20) furnished the corresponding alcohols (83%) ; *(ii)* A solution of the alcohol (30 mmol) in THF (20 mL) was added at room temperature to a suspension of sodium hydride (30 mmol) in THF (50 mL). After stirring for 1h, methyl iodide (3.72 mL, 60 mmol) was added. Then, after 10 min the reaction mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted with ether (100 mL). The organic layer was washed with brine, dried and concentrated. Filtration (PE/EE = 50/50) on silica furnished **24** and **25** (92%). **4-Methoxy-1,9-di-(2-tetrahydropyranyloxy)-nona-5-yne (24)** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.50 (brs, 2H), 3.90 (m, 1H), 3.88-3.68 (m, 4H), 3.51-3.35 (m, 4H), 3.34 (s, 3H), 2.31 (td, *J* = 6.9, 1.8 Hz, 2H), 1.83-1.60 (m, 10H), 1.58-1.45 (m, 8H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 98.6, 98.5, 85.7, 78.9, 71.1, 67.0, 65.8, 62.0 (2C), 56.1 (2C), 32.7, 32.6, 30.6, 30.5, 29.2, 25.5, 25.4, 19.2 (2C) ; IR (neat) 2150 cm^{-1}. **1,10-Di-(2-tetrahydropyranyloxy)-dec-5-yn-4-ol (25)** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.60 (m, 2H), 3.97 (m, 1H), 3.79-3.42 (m, 8H), 3.40 (s, 3H), 2.29 (t, *J* = 6.6 Hz, 2H), 1.84-1.56 (m, 20H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 98.7, 98.6, 86.1, 78.8, 71.2, 66.9, 66.8, 66.2, 62.1, 56.1, 32.7, 32.6, 30.6, 28.8, 25.5 (2C), 25.4 (2C), 19.6, 19.5, 18.5 ; IR (neat) 2150 cm^{-1}.

(b) General procedure for the preparation of the allenes 26-30 To a cooled (-50°C) solution of **24** (2.90 g, 8 mmol) in Et_2O (40 mL) were added Me_2S.CuBr (0.115 g, 0.6 mmol) and successively the Grignard reagent (16 mmol, 2 equiv) and HMPA (4 mL). After the mixture was allowed to room temperature and completion of the reaction by TLC, it was hydrolyzed with a saturated solution of NH_4OH/NH_4Cl (2/1). The organic layer was washed with this solution (3 times) and brine (2x100 mL), dried ($MgSO_4$) and concentrated. Purification of the crude residue by flash chromatography afforded the allenes **26-30**. **4-Methyl-1,9-di-(2-tetrahydropyranyloxy)-nona-4,5-diene (26)** (1.86 g, 69%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.07-4.97 (m, 1H), 4.68 (br s, 2H), 3.88-3.60 (m, 4H), 3.51-3.03 (m, 4H), 2.23-1.89 (m, 4H), 1.79-1.50 (m, 19H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.0, 99.3, 98.7 (2C), 90.1, 67.3, 67.1, 66.9, 62.2, 30.7 (2C), 30.5, 29.2, 27.8, 27.7, 25.8, 25.4 (2C), 19.6, 19.4 ; IR (neat) 2980, 1960 cm^{-1}. MS (*m/z*) 338, 170, 125, 85. Anal. Calcd. for $C_{20}H_{34}O_4$: C, 70.69 ; H, 10.12. Found: C, 70.83 ; H, 10.09. **4-Phenyl-1,9-di-(2-**

tetrahydropyranyloxy)-nona-4,5-diene (27) (2.69 g, 89%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.12 (m, 5H), 5.50 (m, 1H), 4.60-4.51 (m, 2H), 3.90-3.72 (m, 4H), 3.53-3.40 (m, 4H), 2.56-2.30 (m, 2H), 2.17 (t, J = 6.6 Hz, 2H), 1.90-1.51 (m, 16H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.7, 137.2, 128.3 (2C), 126.5, 125.9 (2C), 115.4, 105.8, 98.9, 94.5, 67.2, 67.1, 62.3 (2C), 30.8 (2C), 29.4, 28.3, 26.6, 25.9, 25.6, 19.7, 15.9, 15.4 ; IR (neat) 1960, 1600 cm^{-1}. **6-Methyl-1,10-di-(2-tetrahydropyranyloxy)-deca-4,5-diene (28)** (1.60 g, 57%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.04-4.93 (m, 1H), 4.56-4.54 (m, 2H), 3.87-3.68 (m, 4H), 3.50-3.30 (m, 4H), 2.03-2.00 (m, 2H), 1.95-1.82 (m, 2H), 1.80-1.71 (m, 2H), 1.64 (d, J = 2.7 Hz, 3H), 1.69-1.44 (m, 16H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.2, 99.5, 98.8, 98.6, 89.6, 67.4, 66.9, 62.2 (2C), 33.8, 30.7 (2C), 29.3 (2C), 25.9, 25.5 (2C), 24.2, 19.6, 19.5, 19.3 ; IR (neat) 1960 cm^{-1}. **6-*tert*-Butyl-1,10-di-(2-tetrahydropyranyloxy)-deca-4,5-diene (29)** (1.20 g, 38%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.32-5.18 (m, 1H), 4.63-4.60 (m, 2H), 3.93-3.88 (m, 4H), 3.84-3.75 (m, 4H), 2.10-2.05 (m, 2H), 2.00-1.97 (m, 2H), 1.88-1.78 (m, 2H), 1.75-1.50 (m, 16H), 1.06 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.5, 113.8, 98.8, 98.6, 92.7, 67.6, 67.2, 62.3, 62.2, 30.7 (2C), 29.6, 29.5 (3C) 29.4 (2C), 26.7, 26.2, 25.5 (2C), 24.9, 19.6 (2C) ; IR (neat) 2940, 1960 cm^{-1}. **6-Phenyl-1,10-di-(2-tetrahydropyranyloxy)-deca-4,5-diene (30)** (2.28 g, 69%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.2 Hz, 2H), 7.30 (d, J = 7.2 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 5.55-5.51 (m, 1H), 4.58-4.55 (m, 2H), 3.88-3.74 (m, 4H), 3.50-3.39 (m, 4H), 2.44-2.31 (m, 2H), 2.25- 2.17 (m, 2H), 1.83-1.21 (m, 18H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.4, 137.1, 128.3, 126.5 (2C), 125.8 (2C), 105.8, 98.9, 98.8, 94.1, 67.4, 66.9, 62.3, 62.2, 30.7 (2C), 29.7, 29.4, 29.3, 25.8 (2C), 25.5, 24.7, 19.6 (2C) ; IR (neat) 2940, 1950, 1590 cm^{-1}.

(c) General procedure for the preparation of the allenediynes 31-34 Successive hydrolysis of the ethers, mesylation of the corresponding alcohols, bromation and alkylation with lithium acetylide-ethylenediamine complex were carried out according to the procedures fully described for **16** and **17** and furnished the allenediynes **31-34**. **6-Methyl-trideca-6,7-diene-1,12-diyne (31)** (23% from **26**). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.10-5.05 (m, 1H), 2.30-2.24 (m, 4H), 2.14-2.06 (m, 4H), 2.00 (t, J = 2.7 Hz, 2H), 1.72 (d, J = 2.7 Hz, 3H), 1.70-1.62 (m, 4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.6, 99.2, 89.9, 84.7 (2C), 68.6 (2C), 33.2, 28.6, 28.3, 26.7, 19.7, 18.3, 18.1 ; IR (neat) 3300, 2940, 2100, 1960 cm^{-1}. Anal. Calcd. for $C_{14}H_{18}$: C, 90.26 ; H, 9.70. Found ; C, 89.97 ; H, 9.80. MS (*m/z*) 185, 143, 129, 105, 91. **8-Methyl-tetradeca-6,7-diene-1,13-diyne (32)** (69% from **28**). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.08-5.03 (m, 1H), 2.27 (td, J = 7.1, 2.7 Hz, 4H), 2.25-2.22 (m, 2H), 2.11 (t, J = 7.1 Hz, 2H), 2.00 (t, J = 2.7 Hz, 2H), 1.71 (d, J = 2.7 Hz, 3H), 1.68 (quint, J = 7.1 Hz, 2H), 1.65-1.58 (m, 4H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.4, 99.3, 89.3, 84.6, 84.5, 68.3, 68.2, 33.4, 28.3, 27.8 (2C), 26.5, 19.2, 18.2, 17.8 ; IR (neat) 3300, 2940, 2100, 1960 cm^{-1}. Anal. Calcd. for $C_{15}H_{20}$: C, 89.94 ; H, 10.06. Found : C, 89.54 ; H, 9.90. **8-*tert*-Butyl-tetradeca-6,7-diene-1,13-diyne (33)** (43% from **29**). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.25 (m, 1H), 2.25 (td, J = 7.1, 2.7 Hz, 1H), 2.22-2.20 (m, 2H), 2.11-2.08 (m, 2H), 1.98 (t, J = 2.7 Hz, 2H), 1.65 (quint, J = 7.1 Hz, 2H), 1.64-1.55 (m, 4H), 1.03 (s, 9H) ; IR (neat) 3300, 2940, 2100, 1960 cm^{-1}. **8-Phenyl-tetradeca-6,7-diene-1,13-diyne (34)** (6% from **30**). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.7 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.17 (t, J = 7.7 Hz, 1H), 5.55-5.51 (m, 1H), 2.50-2.45 (m, 4H), 2.30-2.10 (m, 4H), 1.97 (t, J = 2.7 Hz, 2H), 1.83-1.75 (m, 6H) ; IR (neat) 3300, 2100, 1960, 1600 cm^{-1}.

Synthesis of the allenediynes 38-49 . (a) General procedure for the preparation of the compounds 35, 42 and 44 To a suspension of sodium hydride (50% in oil, 9.2 g, 200 mmol) in THF (200 mL) was added a

solution of dimethylmalonate (20 g, 125 mmol) in THF (150 mL). After being stirred at room temperature for 1h, propargyl bromide (80% in toluene, 20 mL, 300 mmol) was added. The mixture was refluxed for 3h and after cooling, it was quenched by a saturated solution of NH_4Cl and extracted with ether (300 mL). The organic layer was washed with brine, dried and concentrated. Purification by flash chromatography (petroleum ether/ether = 70/30) led **36**. The same reaction with 1 equiv of NaH and 1 equiv of propargyl bromide led after being stirred overnight at room temperature **42**. Compound **44** was obtained by the same procedure from **42** by using 1-methanesulfonyloxy-9-trimethylsilylnon-2,8-diyne **44**. **Methyl methyl-2,2-di(prop-2-ynyl) propane-dioate (35)** (26 g, quant.) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 6H), 2.95 (d, *J* = 2.6 Hz, 4H), 2.02 (t, *J* = 2.6 Hz, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.0 (2C), 78.3 (2C), 71.9 (2C), 56.5, 53.1 (2C), 22.7 (2C) ; IR (neat) 3300, 2100, 1730 cm^{-1}. **Methyl methyl-(2-propynyl) propane-dioate (42)** (12.7 g, 60%) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 6H), 3.61 (t, *J* = 7.2 Hz, 1H), 2.78 (td, *J* = 7.8, 2.7 Hz, 2H), 2.22 (t, *J* = 2.7 Hz, 1H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.2 (2C), 79.7, 70.5, 52.8 (2C), 52.5, 18.4 ; IR (neat) 3290, 2960, 2120, 1740 cm^{-1}. MS (*m/z*) 171, 139, 111. **Methyl methyl-(9-trimethylsilyl-nona-2,8-diyne) - (2-propynyl)-propane-dioate (44)** (73%) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 6H), 2.94 (m, 4H), 2.29-2.13 (m, 4H), 2.00 (t, *J* = 2.4 Hz, 1H), 1.55-1.41 (m, 4H), 0.12 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 169.4 (2C), 107.1, 84.6, 83.5, 78.7, 74.2, 71.6, 56,7, 53.1 (2C), 27.8, 27.5, 23.1, 22.7, 19.4, 18.2, 0.2 (3C) ; IR (neat) 2980, 2960, 2160, 2120, 1740, 1450, 1250, 850 cm^{-1}.

(b) General procedure for the obtention of the acetonides 36 and 45 (i) A solution of diester **35** (4.2 g, 20 mmol) or **44** (7.2 g, 20 mmol) in ether (20 mL) was added to a suspension of $LiAlH_4$ (1.5 g, 40 mmol) in ether (20 mL) at 0°C. After being stirred for 1h, the reaction mixture was diluted with CH_2Cl_2, the excess of hydride was hydrolyzed with saturated solution of Na_2SO_4 and the resulting solution was dried over $MgSO_4$, filtered and concentrated. The crude residues were used without purification in the next step. (ii) A solution of the crude diol in acetone (20 mL) in presence of PTSA (0.38 g, 2 mmol) was refluxed for 3h. The mixture was quenched with saturated solution of $NaHCO_3$ and extracted with ether. The organic layer was washed with brine, dried and concentrated. Purification by flash chromatography (PE/EE = 80/20) afforded the acetonide **36** or **45**. **2,2-Dimethyl-5,5-di-(prop-2-ynyl)-[1,3] dioxane (36)** (1.6 g, 42%) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 4H), 2.45 (d, *J* = 2.7 Hz, 4H), 2.03 (t, *J* = 2.7 Hz, 2H), 1.39 (s, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 98.2, 79.7 (2C), 71.4 (2C), 65.8 (2C), 34.8, 23.7 (2C), 22.6 (2C) ; IR (neat) 3300, 2100 cm^{-1}. **2-Prop-2-ynyl-2-(9-trimethylsilyl-nona-2,8-diynyl)-[1,3] dioxane (45)** (4.9 g, 72%) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 4H), 2.35 (d, *J* = 2.3 Hz, 2H), 2.28 (s, 2H), 1.99 (t, *J* = 2.3 Hz, 1H), 2.17-2.13 (m, 4H), 1.54-1.52 (m, 4H), 1.35 (s, 6H), 0.07 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 106.8, 98.1, 84.7, 82.9, 80.2, 75.4, 71.2, 65.9 (2C), 35.2, 28.7, 27.7, 24.3, 23.2 (2C), 22.8, 19.4, 18.3, 0.2 (3C) ; IR (neat) 3280, 2960, 2130, 1240 cm^{-1}.

(c) General procedure for the preparation of the compounds 37 and 46. To a cooled (-78°C) THF (10 mL) solution of **36** (1.92 g, 10 mmol) or **45** (3.44 g, 10 mmol) was added dropwise *n*-BuLi (2.2 M in hexanes, 4.95 mL, 11 mmol). After being stirred for 10 min, a solution of 7-trimethylhept-6-yn-2-one[46] (1.82 g, 10 mmol) or acetone (0.58 g, 10 mmol) in THF (10 mL) was added. The reaction mixture was warmed up to room temperature (30 min) and was hydrolyzed with saturated solution of NH_4Cl (2x20 mL) and extracted with ether (40 mL). The organic layer was washed with brine (40 mL), dried and concentrated. Purification by flash chromatography (PE/EE = 50/50) furnished the compound **37** or **46** respectively. **1-(2,2-Dimethyl-5-prop-2-ynyl-[1,3]dioxan-5-ynyl)-4-methyl-9-tri-methylsilyl-nona-2,8-diyn-4-ol (37)** (2.01, 54%) ^{1}H-

NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 4H), 2.39 (s, 3H), 2.38 (d, J = 2.7 Hz, 2H), 2.26-2.24 (m, 2H), 2.02 (t, J = 2.7 Hz, 1H), 1.74-1.67 (m, 4H), 1.44 (s, 3H), 1.39 (s, 6H), 0.12 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 107.0, 98.3, 87.1, 84.9, 79.9, 79.1, 71.5, 67.9, 65.9 (2C), 42.9, 35.3, 30.3, 24.2, 24.1, 23.5, 22.9 (2C), 19.9, 0.2 (3C) ; IR (neat) 3450, 3300, 2980, 2220, 2180, 2120, 1250, 840 cm^{-1}. **5-[2,2-dimethyl-5-(9-Trimethylsilyl-nona-2,8-diynyl)-[1,3]dioxan-5-yl]-2-methyl-pentan-3-yne-2-ol (46)** (3.37 g, 84%) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 4H), 2.40 (s, 2H), 2.30 (s, 2H), 2.23-2.20 (m, 4H), 1.64-1.59 (m, 4H), 1.50 (s, 6H), 1.41 (s, 6H), 0.14 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 106.9, 97.9, 93.1, 92.1, 88.0, 82.8, 78.1, 75.5, 65.9 (2C), 35.3, 31.6 (2C), 27.9, 27.6, 23.9, 23.4, 23.2, 22.9, 19.3, 18.2, 0.5 (3C) ; IR (neat) 3300, 2960, 2130, 1240, 840 cm^{-1}. Anal. Calcd. for $C_{24}H_{38}O_3Si$: C, 71.59 ; H, 9.51. Found : C, 71.48 ; H, 9.48.

(d) General procedure for the formation of the allenediynes 38-49 (i) To a solution of the alcohol **37** (3.81 g, 10.2 mmol) or **47** (4.1 g, 10.2 mmol) in THF (10 mL) was added *n*-BuLi (2.5 M in hexanes, 4.5 mL, 10.2 mmol) at -78°C and followed after 5 min by mesyl chloride (0.5 mL, 11.6 mmol). *(ii)* After being stirred for 5 min at -78°C, the resulting solution was transferred into a solution of copper(I) reagent prepared as previously described and the reaction was carried out as above (1a) to furnished the corresponding allenes.(iii) To a solution of potassium fluoride (2.9 g, 50 mmol) in DMSO (50 mL) was added a solution of the silylated allenediynes (10 mmol) in DMSO (10 mL) and some drops of water. After being stirred for 2h at room temperature, the reaction mixture was filtered and the resulting solution was diluted in ether (100 mL) and washed with brine (3x80 mL), dried and concentrated. Purification of the residue by flash chromatography (petroleum ether/ether = 90/10) furnished the allenediynes **38-49**. **5-(2-*tert*-Butyl-4-methylnona-2,3-dien-8-ynyl)-2,2-dimethyl-5-prop-2-ynyl-[1,3] dioxane (38)** (1.67 g, 48%).^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 2H), 3.71 (d, J = 4.3 Hz, 2H), 2.57 (d, J = 2.7 Hz, 2H), 2.20 (td, J = 6.9, 2.3 Hz, 2H), 2.06-2.01 (m, 4H), 1.94 (t, J = 2.3 Hz, 2H), 1.65 (s, 3H), 1.46 (quint, J = 7.3 Hz, 2H), 1.40 (s, 3H), 1.37 (s, 3H), 1.00 (s, 9H) ; IR (neat) 3300, 2100 cm^{-1}. **2,2-Dimethyl-5-(4-methyl-2-phenyl-nona-1,2-dien-8-ynyl)-5-(prop-2-ynyl)-1-[1,3]-dioxane (39)** (3.58 g, 97%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.14 (m, 5H), 3.70 (s, 2H), 3.65 (m, 2H), 2.56 (m, 2H), 2.50 (d, J = 2.5 Hz, 2H), 2.27-2.14 (m, 4H), 2.03 (t, J = 2.5 Hz, 1H), 1.94 (t, J = 2.5 Hz, 1H), 1.82 (s, 3H), 1.69 (quint, J = 7.2 Hz, 2H), 1.40 (s, 3H), 1.38 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.5, 138.7, 128.4 (2C), 126.6 (2C), 126.3, 100.8, 100.2, 98.1, 84.2, 81.2, 71.3, 68.7, 66.8, 66.7, 36.5, 33.4 (2C), 26.5 (2C), 22.8, 21.4, 18.9, 18.2 ; IR (neat) 3300, 2960, 2160, 2120, 1940, 1600, 1240, 850 cm^{-1}. **2,2-Dimethyl-5-(2,4-dimethyl-nona-2,3-dien-8-ynyl)-5-prop-2-ynyl-[1,3] dioxane (40)** (83% as an inseparable mixture with **41**). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 4H), 2.50 (d, J = 2.5 Hz, 2H), 2.16 (td, J = 7.0, 2.5 Hz, 2H), 2.06-1.85 (m, 6H), 1.66 (s, 6H), 1.65-1.56 (m, 2H), 1.38 (s, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.3, 98.1, 97.2, 93.4, 84.4, 81.3, 70.8, 68.4, 66.9, 66.8, 36.9, 36.2, 33.3, 29.5, 26.8, 26.4, 22.2 (2C), 20.9, 19.3 ; IR (neat) 3300, 2930, 2100 cm^{-1}. **2,2-Dimethyl-5-[4,4-dimethyl-nona-2,8-diynyl)-5-prop-2-ynyl-[1,3] dioxane (41)** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 2H), 3.72 (s, 2H), 2.40 (d, J = 2.7 Hz, 2H), 2.28 (s, 2H), 2.17 (td, J = 7.1, 2.7 Hz, 2H), 1.98 (t, J = 2.7 Hz, 2H), 1.66-1.61 (m, 4H), 1.60 (s, 6H), 1.36 (s, 6H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 98.1, 91.0, 81.3, 80.3, 75.2, 71.2 (2C), 65.9 (2C), 42.5, 35.3, 24.7, 23.1, 22.9, 22.6, 22.2 (2C), 20.9, 19.3, 18.8 ; IR (neat) 3300, 2100 cm^{-1}. **5-(2-*tert*-Butyl-4-methyl-penta-2,3-dienyl)-2,2-dimethyl-5-nona-2,8-diynyl-[1,3] dioxane (47)** (1.81 g, 48%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 2H), 3.74 (s, 2H), 2.56 (t, J = 2.3 Hz, 2H), 2.24-2.18 (m, 4H), 2.03 (s, 2H), 1.96 (t, J = 2.3 Hz, 1H), 1.67 (s, 6H), 1.65-1.59 (m, 4H), 1.59 (s, 3H), 1.42 (s, 3H), 1.03 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.4, 123.2, 105.4, 98.0, 96.2, 84.6, 81.6, 76.8, 68.5,

67.3, 35.9, 34.9, 30.1, 29.9, 29.5, 28.1 (2C), 27.7, 26.5, 21.8, 21.5 (2C), 20.8, 18.4, 18.1 ; IR (neat) 3300, 2100, 1960 cm^{-1}. **2,2-Dimethyl-5-(4-methyl-2-phenyl-penta-2,3-dienyl)-5-nona-2,8-diynyl-[1,3] dioxane (48)** (2.3 g, 58%) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.9 Hz, 2H), 7.13-7.10 (m, 2H), 7.02 (t, *J* = 7.9 Hz, 1H), 3.55 (m, 4H), 2.54 (s, 2H), 2.48 (t, *J* = 2.6 Hz, 2H), 2.29-223 (m, 4H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.83 (s, 6H), 1.66-1.60 (m, 4H), 1.42 (s, 3H), 1.41 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.1, 139.4, 128.6 (2C), 125.9 (2C), 125.8, 99.1, 98.3, 97.8, 84.5, 82.6, 77.2, 68.7, 66.5 (2C), 36.9, 33.7, 32.4, 28.4, 27.9, 26.6, 23.4, 21.9, 20.8, 18.8, 18.4 ; IR (neat) 3300, 2940, 2240, 2100, 1960, 1600 cm^{-1}. **5-(2,4-Dimethyl-penta-2,3-dienyl)-2,2-dimethyl-5-nona-2,8-diynyl-[1,3] dioxane (49)** (72% as an inseparable mixture with **50**). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.65 (br s, 4H), 2.42 (t, *J* = 2.1 Hz, 2H), 2.24-2.14 (m, 4H), 1.90 (s, 2H), 1.89 (t, *J* = 2.1 Hz, 1H), 1.64-1.55 (m, 4H), 1.60 (s, 3H), 1.59 (s, 6H), 1.36 (s, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.6, 97.9, 93.5, 91.8, 84.2, 81.9, 77.9, 68.5, 66.9 (2C), 37.1, 31.3, 28.1, 27.5, 26.9, 22.5, 22.1, 21.1, 20.8 (2C), 18.3, 17.9 ; IR (neat) 2940, 2100, 1960 cm^{-1}.

Preparation of the allenediynes 53 and 54. (a) **2-methyl-7-bromo-2-(2-tetrahydropyranyloxy)hept-3-yne (51)** The bromide **51** was prepared following the procedure described for **14** and **15**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.00 (t, *J* = 5.0 Hz, 1H), 3.93 (m, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 3.50 (m, 2H), 2.40 (t, *J* = 6.5 Hz, 2H), 2.02 (quint, *J* = 6.5 Hz, 2H), 1.90-1.60 (m, 2H), 1.56-1.50 (m, 4H), 1.50 (s, 3H), 1.45 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 96.2, 84.0, 82.1, 71.3, 63.6, 32.4, 32.1, 31.5, 30.9, 30.2, 25.5, 20.8, 17.4 ; IR ($CDCl_3$) 2230, 1240, 1150, 1120, 1070, 1030, 980 cm^{-1}. *(b)* (i) **14-Methyl-14-(2-tetrahydropyranyloxy) pentadeca-1,7,12-triyne (52)** To a THF (10 mL) solution of 1,7-octadiyne (1.6 g, 15 mmol) was added dropwise *n*-BuLi (2.4 M in hexanes, 4.1 mL, 10 mmol) at -78°C. After being stirred for 30 min at -78°C, HMPA (7 mL, 40 mmol) and a solution of **51** (1.43 g, 5 mmol) in THF (5 mL) were successively added. After warming up to room temperature, the reaction mixture was diluted with ether (60 mL) and washed with with saturated solution of NH_4Cl(50 mL) and brine (2x50mL). The organic layers were dried ($MgSO_4$) and concentrated. The crude residue was purified by flash chromatography (PE/EE = 90/10) to afford the triyne **52** (1.06 g, 68%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.99 (t, *J* = 5.4 Hz, 1H), 3.90 (dt *J* = 11.6, 6.4 Hz, 1H), 3.44 (dt, *J* =11.6, 6.4 Hz, 1H), 2.26 (t, *J* = 7.0 Hz, 2H), 2.20-2.01 (m, 6H), 1.92 (t, *J* = 2.6 Hz, 1H), 1.80-1.70 (m, 1H), 1.64 (quint, *J* = 7.0 Hz, 2H), 1.60-1.55 (m, 5H), 1.55-1.50 (m, 4H), 1.45 (s, 3H), 1.41 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 96.1, 84.1, 83,5, 83.1, 80.2, 79.5, 71.3, 68.5, 63.4, 32.1, 31.0, 30.2, 30.0, 28.3. 28.0, 27.6, 25.5, 20.7, 18.3, 18.0, 17.9, 17.8 ; IR ($CDCl_3$) 3300, 2225, 2105, 1250, 1120, 1170, 1030, 980 cm^{-1}. (ii) **14-Methyl-14-(2-tetrahydropyranyloxy)-1-(trimethylsilyl)penta-deca-1,7,12-triyne (53)** At -78°C, *n*-BuLi (2.4 M in hexanes, 1.7 mL, 4 mmol) was added dropwise to a solution of **52** (1.06 g, 3.4 mmol) in THF (10 mL). After being stirred at -78°C for 30 min, TMSCl (0.9 mL, 7 mmol) was added. After warming up to r.t. , the reaction mixture was partitionned between ether (50 mL) and a saturated solution of NH_4Cl (50 mL). The organic layer was washed with brine (2x50 mL), dried and concentrated. Purification of the crude residue by flash chromatography (PE/EE = 90/10) furnished **53** (1.07 g, 81%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.97 (t, *J*= 5.8 Hz, 1H), 4.00-3.70 (m, 1H), 3.50-3.30 (m, 1H), 2.24 (t, *J* = 6.8 Hz, 2H), 2.20-2.00 (m, 6H), 1.64 (quint, *J* = 6.7 Hz, 2H), 1.55-1.40 (m, 10H), 1.43 (s, 3H), 1.39 (s, 3H), 0.06 (s, 9H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) δ 107.0, 96.0, 84.4, 83.4, 83.0, 80.2, 79.2, 71.2, 63.4, 31.9, 30.9, 30.0, 28.2, 28.0, 27.6, 25.3, 20.6, 19.3, 18.2, 17.8 (2C), 0.0 (3C) ; IR ($CDCl_3$) 2220, 1180, 1250, 1120, 1070, 1030, 840 cm^{-1}.

(c) Procedure for the preparation of the allenediynes 54 and 55 : Successive hydrolysis of the ethers, mesylation of the corresponding alcohols, heterocuprate additions and desilylation of the triple bond were carried out according the procedures fully described for **38-49**.

12,14-Dimethyl-1-(trimethylsilyl)pentadeca-12,13-dien-1,7-diyne (54) ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.30-2.00 (m, 6H), 2.00-1.90 (m, 3H), 1.61 (s, 6H), 1.60-1.40 (m, 6H), 1.59 (s, 3H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) 198.8, 94.1 91.1, 84.2, 80.6, 79.6, 68.4, 33.5, 28.2, 28.0, 27.5, 27.1, 20.9 (2C), 19.5, 18.3, 18.0 ; IR (neat) 3300, 2120, 1960, 1440, 1080 cm^{-1}. **14-Methyl-12-(1,1-dimethylethyl)-pentadeca-12,13-dien-1,7-diyne (55)** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.30-2.19 (m, 6H), 2.00 (t, *J* = 7.0 Hz, 2H), 1.94 (t, *J* = 2.1 Hz, 1H), 1.66 (s, 6H), 1.59-1.38 (m, 6H), 1.02 (s, 9H) ; ^{13}C-NMR (50 MHz, $CDCl_3$) 197.3, 110.2, 96.6, 84.2, 80.7, 79.4, 68.3, 34.0, 29.4 (3C), 28.0, 27.7, 27.5, 26.3, 20.9 (2C), 18.3, 18.2, 17.9 ; IR (neat) 3300, 2100, 1950 cm^{-1}.

Cobalt(I)-mediated cyclizations of allenediynes.

General procedure for the [2+2+2] cycloaddition reactions. The reaction was carried out under argon in a flame-dried flask, prealably washed with hexamethyldisilazane, and all the solutions were degassed by three freeze-pump-thaw cycles. To a solution of allenediyne (1 mmol) in refluxing xylenes (10 mL) was added $CpCo(CO)_2$ (180 mg, 125 μL, 1 mmol). Light from a projector lamp (ELW, 300W, 80% of its power) was directed at the reaction mixture during the reaction. The reaction was monitored by TLC and after the completion, the solvent was removed by vaccum transfer. The residue was purified by flash chromatography on silica or alumina under argon.

η^4-(8a,9,10,10a)-4a-*endo*-5-dimethyl-1,2,3,4,4a,6,7,8-octahydrophenantrene-η^5 cyclopentadienylcobalt (56) ^{1}H-NMR (400 MHz, C_6D_6) δ 5.11 (d, *J* = 3.8 Hz, 1H), 4.60 (s, 5H), 4.27 (d, *J* = 3.8 Hz, 1H), 2.22-2.16 (m, 2H), 2.10-1.45 (m, 8H), 1.72 (s, 3H), 1.62 (s, 3H), 1.28-1.16 (m, 2H), 1.11-1.01 (m, 2H) ; ^{13}C-NMR (100 MHz, C_6D_6) 141.6, 123.5, 81.2 (5C), 79.0, 76.2, 73.9, 70.7, 56.6, 37.5, 36.5, 35.3, 31.8, 28.2, 26.0, 25.1, 24.2, 21.5.

η^4-(8a,9,10,10a)-4a-*exo*-5-dimethyl-1,2,3,4,4a,6,7,8-octahydrophenantrene-η^5 cyclopentadienylcobalt (57) ^{1}H-NMR (400 MHz, C_6D_6) δ 4.79 (d, *J* = 3.8 Hz,1H), 4.56 (s, 5H), 4.54 (d, *J*=3.8 Hz, 1H), 2.22-2.16 (m, 2H), 2.10-1.45 (m, 8H), 1.61 (s, 3H), 1.14 (s, 3H), 1.28-1.16 (m, 2H), 1.11-1.01 (m, 2H) ; ^{13}C-NMR (100 MHz, C_6D_6) δ 142.4, 121.7, 80.8 (5C), 77.6, 77.4, 75.6, 75.5, 47.1, 39.8, 37.8, 35.5, 34.9, 31.7, 26.0, 24.6, 22.9, 21.9.

4a-5-dimethyl-1,2,3,4,4a,6,7,8-octahydro-phenantrene (58) ^{1}H-NMR (400 MHz, C_6D_6) δ 5.29 (br s, 2H), 2.09-1.90 (m, 2H), 1.89-1.60 (m, 2H), 1.59-1.45 (m, 2H) 1.37 (s, 3H), 1.30-1.17 (m, 8H), 0.79 (s, 3H) ; ^{13}C-NMR (100 MHz, C_6D_6) δ 151.2, 141.5, 138.9, 137.8, 122.5, 114.8, 48.2, 41.0, 37.5, 35.1, 28.9, 28.1, 26.2, 26.1, 24.5, 22.5.

Compound (59) (0.25 g, 54 %) ; ^{1}H-NMR(400 MHz, C_6D_6) δ 4.88 (d, *J* =3.0 Hz, 1H), 4.56 (s, 5H), 4.09 (d, *J* =3.0 Hz, 1H), 3.74-3.42 (m, 4H), 2.28-2.24 (m, 2H), 1.79-1.70 (m, 4H), 1.65 (s, 3H), 1.50 (s, 3H), 1.42 (s, 3H), 1.34-1.19 (m, 4H), 1.15 (s, 9H) ; ^{13}C-NMR (100 MHz, C_6D_6) δ 139.2, 132.3, 98.0, 81.3 (5C), 77.6, 74.6, 69.6, 67.6, 66.6 (2C), 54.2, 42.9, 37.7, 37.4, 37.2, 33.1, 31.9 (3C), 31.7, 29.8, 25.6, 22.7, 21.5.

Compounds (60) and (61) (0.29 g, 70% as an inseparable mixture of **60** and **61**) ; ^{1}H-NMR (400 MHz, C_6D_6) δ 4.90 (d, *J* = 2.6 Hz, 1H), 4.53 (s, 5H), 4.51 (s, 5H), 4.49 (d, *J* = 2.6 Hz, 1H), 4.44 (d, *J* = 2.6 Hz, 1H), 4.17 (d,*J* = 2.6 Hz, 1H), 3.59 (s, 4H), 3.54 (s, 4H), 2.13 (s, 2H), 2.06 (s, 2H), 2.01, (s, 2H), 1.92 (s, 2H), 1.81 (s, 2H), 1.75 (m, 2H) 2.68-2.62 (m, 4H), 1.55 (s, 6H), 1.54 (s, 6H), 1.50 (s, 3H), 1.49 (s, 3H),1.66-1.47 (m, 4H), 1.43 (s, 3H) 1.38 (s, 3H).

Compound (62) (0.24 g, 72%) ; ^{1}H-NMR (400 MHz, C_6D_6) δ 4.51 (s, 5H), 3.48 (s ,1H), 2.51-1.50 (m, 15H), 1.74 (s, 3H), 1.59 (s, 3H), 1.50-1.40 (m, 1H) ; ^{13}C NMR (100 MHz C_6D_6) δ 138.9, 116.2, 88.7, 88.3, 81.1 (5C), 72.0, 49.6, 45.4, 34.2, 31.8, 29.6, 26.7, 23.7, 23.5 (2C), 22.8, 19.9.

Compound (63) (0.39 g, 80%) ; ^{1}H-NMR (400 MHz, C_6D_6) δ 4.69 (s, 5H), 4.47 (d, *J* = 11.2 Hz, 1H), 3.92 (d, *J* = 11.2 Hz, 1H), 3.66 (m, 2H), 2.60 (ddd, *J* = 16.4, 10.3, 6.0 Hz, 1H), 2.47 (s, 1H), 2.40-2.32 (m, 2H), 2;19-2.00 (m, 4H), 1.87-1.81 (m, 1H), 1.69 (s, 3H), 1.62 (s, 3H), 1.59-1.50 (m, 4H) overlapped with 1.55 (s, 3H), 1.33 (s, 9H), 1.27 (s, 3H) ; ^{13}C-NMR (100 MHz, C_6D_6) δ 144.7, 130.8, 98.9, 92.0, 88.0, 82.1 (5C), 71.6, 67.0, 66.9, 66.1, 63.2, 40.7, 40.6, 39.6, 39.2, 33.0 (3C), 32.9, 32.8, 31.0, 28.1, 27.0, 25.3, 23.9, 22.8.

Compound (64) (0.45 g, 87%) ; ^{1}H-NMR (400 MHz, C_6D_6) δ 7.29-7.03 (m, 5H), 4.66 (s, 5H), 4.05 (d, *J* = 11.3 Hz, 1H), 3.72 (d, *J* = 11.2 Hz, 1H), 3.65 (m, 2H), 2.80-2.77 (m, 2H), 2.44-2.35 (m, 1H) overlapped with 2.40 (s, 1H), 2.16-2.05 (m, 2H), 2.14 (m, 2H), 2.08-2.00 (m, 1H), 1.91-1.73 (m, 2H), 1.70 (m, 2H), 1.66 (s, 3H), 1.46 (s, 3H), 1.33 (s, 3H), 0.92 (s, 3H) ; ^{13}C-NMR (100 MHz, C_6D_6) δ 146.1, 144.3, 129.6, 128.2 (2C), 125.8 (2C), 124.1, 98.0, 91.9, 89.1, 81.5 (5C), 68.4, 67.8, 63.2, 59.5, 44.1, 43.2, 36.9, 32.3, 32.1, 31.8, 30.4, 27.8, 27.1, 24.5, 23.2, 20.3.

Compound (65) (0.32 g, 70%) ; ^{1}H-NMR (400 MHz, C_6D_6) δ 4.51 (s, 5H), 3.85 (d, *J* = 11.2 Hz, 1H), 3.57 (d, *J* = 11.2 Hz, 1H), 3.55-3.38 (m, 2H), 2.65-2.55 (m, 2H), 2.37 (s, 1H), 2.30-2.19 (m, 1H), 2.09-1.95 (m, 1H), 2.07-1.75 (m, 2H), 1.95-1.87 (m, 1H), 1.72-1.52 (m, 3H), 1.51 (s, 6H), 1.40-1.19 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 0.97 (s, 3H) ; ^{13}C-NMR (100 MHz, C_6D_6) δ 141.2, 116.0, 96.7, 89.9, 87.4, 80.4 (5C), 67.2, 66.7, 62.0, 58.9, 39.0 (2C), 35.6, 31.0, 29.2, 29.1, 28.3, 26.1, 25.8, 23.1, 22.0, 21.0, 19.5.

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