Study of the Diastereoselectivity of Cobalt-Mediated [2+2+2] Cycloadditions of Substituted Linear Enediyne Esters

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Dedicated to Professor Jean Normant on the occasion of his 65th birthday

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The preparation of substituted linear enediyne esters bearing the double bond either at the terminal or at internal position and the ester substituent either at the alkyne or at the alkene terminus is presented. Their cobalt(I)-mediated [2+2+2] cyclizations produce the η^4-complexed tricyclic compounds in very good yields. The *endo*/*exo* selectivity depends on the position of the ester in the enediyne, but the cyclization can be totally diastereoselective. The asymmetric induction in the cyclization of enediynes bearing chiral esters has been studied; however, the diastereomeric excesses are low.

Introduction

Cobalt(I) complexes are quite versatile catalysts, because they allow the construction of several carbon−carbon bonds in a single chemical transformation and in highly regioselective, chemoselective, and stereoselective fashion.[1,2] Thus, in the last decades, cobalt(I)-mediated [2+2+2] cyclizations of triynes,[3−5] linear achiral enediynes,[6−10] and allenediynes[11,12] have emerged as useful synthetic tools. Various syntheses of a range of complex molecules of medicinal[13−17] and theoretical[18] interest have been presented in high yields and with remarkable selectivity.

As part of our program designed to exploit this cyclization in the synthesis of polycyclic natural products,[19] we turned our attention to the asymmetric version of this reaction, particularly to selective induction in [2+2+2] cyclizations of chiral substituted linear enediynes. As far as we are aware, no cobalt(I) cycloadditions with enediynes bearing chiral auxiliaries have been recorded in the literature, although one example of asymmetric [2+2+2] cyclization promoted, albeit with low diastereomeric excesses, by chiral cyclopentadienylcobalt complexes has been reported,[20] together with some [2+2+2] cyclizations of enediynes possessing a racemic stereogenic center in the tether between both unsaturated moieties.[21] Over the last few years, nickel(0)-mediated asymmetric [2+2+2] cyclizations have been achieved by two different strategies. One, which allows the construction of isoindoline and isoquinoline derivatives with benzylic chiral carbon centers, involved conceptually new enantiotopic group selection and hence selective formation of nickelacyclopentadiene.[22,23] The other concerns the enantioselective synthesis of molecules with helical chirality, and involved an intramolecular [2+2+2] cyclization of triynes in presence of nickel(0) complexes and chiral phosphane ligands.[24]

Our initial efforts were focused on the identification of the most appropriate substituent and its most judicious position in the polyunsaturated precursor. We were able to show that the level of diastereoselectivity of the [2+2+2] cyclization of linear enediynes could be improved over that reported in the literature by introduction of substituents such as ester, sulfoxide, or phosphane oxide groups at the terminal positions of either the triple- or the double-bond partner.[25] The ester group emerged as one of the most promising substituents for the asymmetric study in terms of stability of the complexed cycloadducts and yields of the cyclization.

Here we present the full details of the preparation and the cyclization of substituted linear enediynes esters with the double bond either at the terminal position or at the internal position in the chain. In the latter case it was observed that the reaction is totally diastereoselective. In addition, we report the results we obtained with enediynes bearing chiral esters.

Results and Discussion

Various enediynes possessing double bonds either at the terminal or at the internal position in the chain were prepared. The ester substituents were in all cases appended onto the alkyne or the alkene terminus.

Synthesis of the Substituted Enediyne Esters

The enediynes **1a** and **1b** were prepared as outlined in Scheme 1, from the already described tridec-1-ene-6,12-diyne and tetradec-1-ene-7,13-diyne.[7] Deprotonation of these precursors with *n*BuLi, followed by addition of methyl chloroformate, provided **1a** and **1b** in 83% and 73% yields, respectively. The precursors **5a** and **5b** were obtained from

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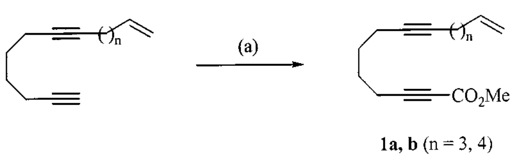
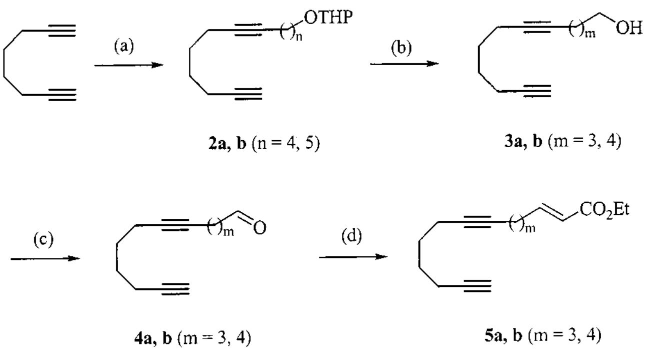
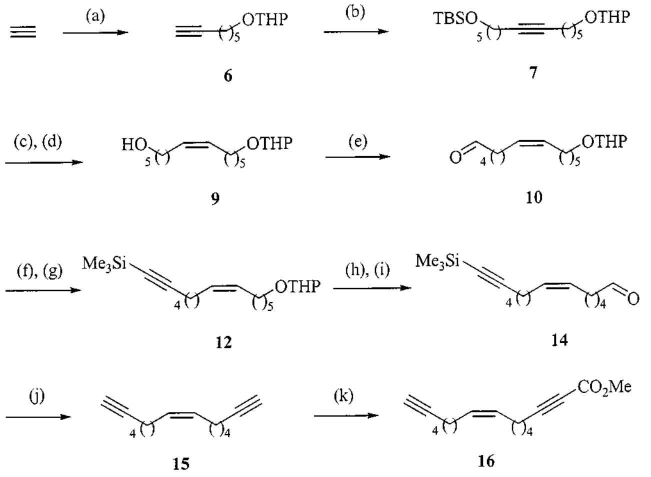


Scheme 1. Preparation of the enediynes **1a** and **1b**: (a) *n*BuLi, THF, $ClCO_2Me$, −78 °C to room temp., **1a** (*n* = 3) 83%, **1b** (*n* = 4) 73%



Scheme 2. Preparation of the enediynes **5a** and **5b**: (a) *n*BuLi, THF, HMPA, $Br(CH_2)_nOTHP$, −78 °C to room temp., **2a** (*n* = 4) 70%, **2b** (*n* = 5) 75%; (b) cat. PTSA, MeOH, **3a** (*m* = 3) 95%, **3b** (*m* = 4) quant; (c) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −78 °C to room temp., **4a** (*m* = 3) 98%, **4b** (*m* = 4) quant.; (d) $(EtO)_2P(O)CH_2CO_2Et$, LiCl, NEt_3, CH_3CN, room temp., overnight, **5a** (*m* = 3) 86%, **5b** (*m* = 4) 88%



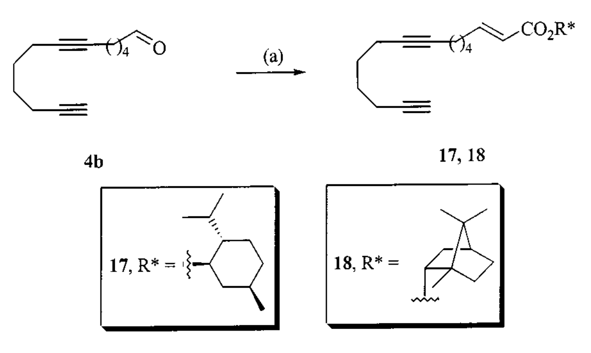
Scheme 3. Preparation of the enediyne **16**: (a) *n*BuLi, THF, DMSO, $Br(CH_2)_5OTHP$, −78 °C to room temp., quant.; (b) *n*BuLi, THF, HMPA, $Br(CH_2)_5OTBS$, −78 °C to room temp., 79%; (c) H_2 (1 atm), Lindlar Pd catalyst, quinoline, MeOH, **8**, 70%; (d) nBu_4NF, THF, 88%; (e) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −78 °C to room temp., 91%; (f) K_2CO_3, MeOH, $MeCOC(N_2)P(O)(OMe)_2$, **11**, 77%; (g) *n*BuLi, THF, $ClSiMe_3$, −78 °C to room temp., quant.; (h) cat. PTSA, MeOH, **13**, 97%; (i) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, −78 °C to room temp., 92%; (j) K_2CO_3, MeOH, $MeCOC(N_2)P(O)(OMe)_2$, 91%; (k) *n*BuLi, THF, $ClCO_2Me$, −78 °C to room temp., 37%

the dodeca-5,11-diynal **4a**[26] and the trideca-6,12-diynal **4b**, which were prepared from the commercially available 1,7-octadiyne (Scheme 2).

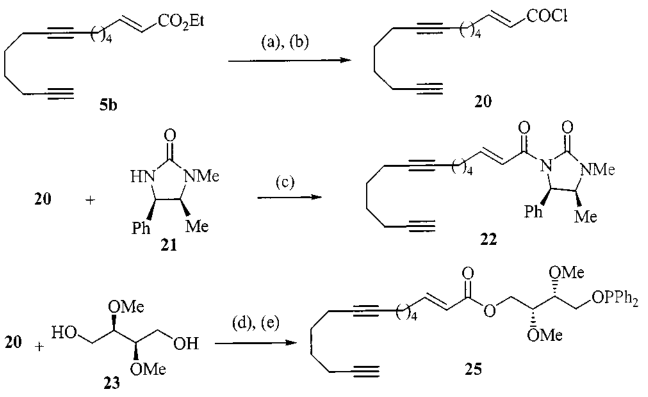
Monoalkylation of the lithio derivative of the 1,7-octadiyne with 2-(4-bromobutoxy)tetrahydropyran and with 2-(5-bromopentoxy)tetrahydropyran[27] provided the ethers **2a** and **2b**, accompanied by the corresponding dialkylated compound (12−15%). Compounds **2a** and **2b** were then successively deprotected (acid catalysis)[28] to give **3a** and **3b** and oxidized[29] to afford the aldehydes **4a** and **4b**. These were submitted to the mild alkenylation procedure of Masamune et al.[30] to provide the (*E*)-α,β-unsaturated esters **5a** and **5b** in 86% and 88% yields, respectively. The enediyne **16**, with the double bond in the internal position, was prepared from acetylene in an eleven-step sequence, as outlined in Scheme 3.

Monoalkylation[31] of acetylene with 2-(5-bromopentoxy)-tetrahydropyran quantitatively provided the ether **6**, which was then deprotonated and alkylated with (5-bromopentoxy)-*tert*-butyldimethylsilane[32] to give **7** in 79% yield. A palladium-catalyzed hydrogenation of the triple bond (**8**, 70%), followed by a selective hydrolysis of the silylated ether with *n*-tetrabutylammonium fluoride, produced the alcohol **9** (88%). This was then oxidized to afford the aldehyde **10** (91%), transformation of which to the terminal alkyne **11** in 77% yield was achieved by using the Ohira/Bestmann procedure.[33,34] Sequential silylation of the triple bond (**12**, quantitative), acid-catalyzed deprotection of the tetrahydropyranyl ether (**13**, 97%), and oxidation of the resulting alcohol (92%) afforded the enynal **14**. The direct conversion of this into the corresponding terminal alkyne was achieved by using the same method as above. Those reaction conditions, however, caused the removal of the trimethylsilyl group and produced the enediyne **15**[6] in 91% yield. The problem of the deprotection of the triple bond could be circumvented by using the Corey−Fuchs procedure.[35] Finally, **15** was alkylated with methyl chloroformate to give the enediyne precursor **16** in 37% yield.

The enediynes **17**, **18**, **22**, and **25**, bearing chiral esters at their vinylic positions, were synthesized from either the diynal **4b** or the enediyne **5b**, described above. The alkenylation of **4b** with the corresponding chiral phosphonoacetate[36] [produced by transesterification of the triethyl phosphonoacetate with (−)-menthol and (−)-borneol] gave **17** and **18** in 87% and 79% yields, respectively (Scheme 4).



Scheme 4. Preparation of the chiral ester-substituted enediynes **17** and **18**: (a) LiCl, NEt_3, $(EtO)_2P(O)CH_2CO_2R^*$, CH_3CN, **17** 87%, **18** 79%



Scheme 5. Preparation of the enediynes **22** and **24**: (a) NaOH, THF, reflux, **19** 98%; (b) $(COCl)_2$, toluene, room temp., quant.; (c) *n*BuLi, THF, −78 °C to room temp., 60%; (d) NaH, THF, 0 °C to room temp., **24** 43%; (e) NEt_3, $ClPPh_2$, toluene, 0 °C to room temp., 41%

The precursors **22** and **25** were prepared from the ester-substituted enediyne **5b**, which was first converted into the corresponding acid chloride **20** in 98% yield (Scheme 5). This was then condensed either with the lithiated anion of the imidoxazolidinone **21**[37] to provide the enediyne **22** in 60% yield, or with the sodium salt of chiral 2,3-dimethoxybutane-1,4-diol **23**[38] [generated from (+)-diisopropyl L-tartrate by (i) methylation of the diol and (ii) reduction of the diester with $LiAlH_4$] to furnish the enediyne **24** in 43% yield. Finally, the condensation of **24** and chlorodiphenylphosphane under basic conditions allowed the formation of the desired enediyne **25** in 41% yield.

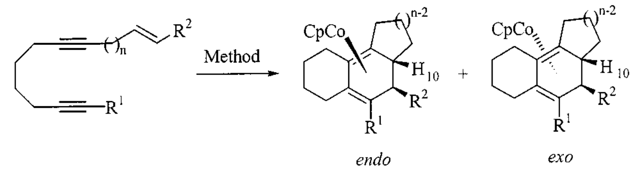
Cyclizations of the Substituted Enediyne Esters

The cyclizations of the thus prepared enediynes were conducted using two methods. In *Method A*, the cyclization was carried out with a stoichiometric amount of $CpCo(CO)_2$ in refluxing toluene under irradiation. In *Method B*, the cyclization was also carried out with a stoichiometric amount of $CpCo(CO)_2$, but in refluxing decane and without irradiation.

The cyclizations of enediynes **1a**, **1b**, **5a**, and **5b** afforded red-brown complexes as mixtures of inseparable *endo*/*exo* diastereomers of **26a**/**26b** and **30a**/**30b** in very good yields. It is interesting to note that the isolated complexes are quite stable, particularly in the cases of **26a** and **26b**, since they could be purified on silica gel with non-degassed solvents (Table 1).

We noticed that for the enediyne possessing an acetylenic ester both methods could be used to produce the cycloadducts in the same *endo*/*exo* ratio. Method A was preferred, however, for its better yields, shorter reaction time, and lesser degree of formation of degradation products. When the ester group was at the vinylic position in the enediynes, Method A gave the cycloadducts in poor yields, accompanied by intractable materials. Accordingly, although the reaction time was longer (12 h instead of 1 h for Method A), Method B was chosen without the *endo*/*exo* ratio being affected.

Table 1. Cyclizations of the enediynes **1a**, **1b**, **5a**, and **5b**

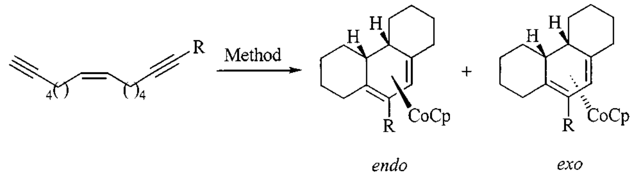


Enediyne	n	R^1	R^2	Method	Yield(%)	*endo* / *exo*	Complex
1a	3	CO_2Me	H	A	78	46 / 54	**26a**
27a	3	$SiMe_3$	H	A	85	46 / 54	**28a**
27a[7]	3	$SiMe_3$	H	B	85	0 / 100	**28a**
1b	4	CO_2Me	H	A	94	40 / 60	**26b**
27b[7]	4	$SiMe_3$	H	B	92	50 / 50	**28b**
5a	3	H	CO_2Et	B	62	78 / 22	**30a**
29a[7]	3	H	H	B	66	50 / 50	**31a**
5b	4	H	CO_2Et	B	71	86 / 14	**30b**
29b[7]	4	H	H	B	76	33 / 66	**31b**

The *endo*/*exo* ratio of the diastereomers was determined by ^1H NMR, on the basis of the integration of the cyclopentadienyl hydrogen atoms. The *endo*/*exo* stereochemical assignments of **26a**, **26b**, **30a**, and **30b** relied on spectral interpretations analogous to those of the parent compounds **28a**, **28b**, **31a**, and **31b**.[7,39] These are based on the characteristic chemical shifts of the angular hydrogen atom 10-H, which is more shielded in the *exo* diastereomer than in the *endo* one. Similarly, the ^{13}C resonance at the *endo*-methyne carbon atom C-10 occurs 8−9 ppm downfield from the analogous *exo*-methyne carbon atom.

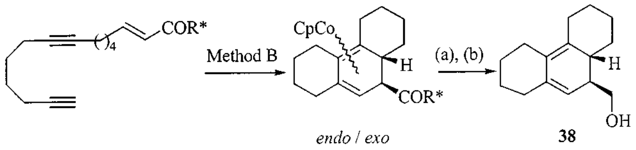
The comparison of our results to Vollhardt's findings[7,39] deserves some comment. The substitution of the trimethylsilyl group at the acetylenic position by an ester did not really affect the diastereoselectivity of the cyclization; slight modification was only observed for the production of the [2+2+2] cycloadducts. Indeed, the cyclization of **1a** resulted in a 46:54 mixture of *endo*/*exo* diastereomers, similarly to the cyclization of **27a** (R^1 = $SiMe_3$) that we carried out according to Method A, even if the latter was totally diastereoselective under thermal conditions (Method B). In addition, the proportion of the *exo* cycloadduct **26b** was slightly increased (40:60) in comparison with the cyclization of **27b**, which is not diastereoselective. In contrast, the diastereoselectivity of the cyclization (relative to the parent compounds **29a** and **29b**) was noticeably affected in favor of the *endo* complexes when the enediynes featured a vinylic ester (**5a**, **5b**). Thus, the cycloadducts **30a** and **30b** were obtained as 78:22 and 86:14 mixtures of *endo*/*exo* diastereomers, in 62% and 71% yields, respectively (Table 1).

Table 2. Cyclization of the enediyne **16**



enediyne	R	Method	Yield(%)	*endo* / *exo*	Complex
16	CO_2Me	A	65	100 / 0	**32**
33[6]	H	B	63	0 / 100	**34**

Table 3. Cyclizations of the enediynes **17**, **18**, and **22**



(a) $CuCl_2.2H_2O$, CH_3CN, r. t., 90%. (b) $LiAlH_4$, Et_2O, quant.

enediyne	Yield(%)	*endo* / *exo*	Complex	e. e. (%)[c]
17	81	86 / 14	**35**	0
18	74	86 / 14	**36**	10
22	44	Unknown	**37**	12

[c] e. e. measured on **38**

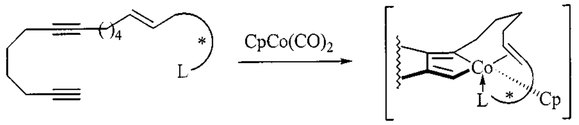
The cyclization of the enediyne **16**, with an internal (*Z*)-disubstituted double bond and an acetylenic ester, was also carried out according to Method A. This permitted the formation of the cycloadduct **32** uniquely as an *endo* diastereomer, in 65% yield (Table 2). This total diastereoselectivity was the complete opposite of that reported for the cyclization of the enediyne **33**, which did not feature any substituent at the alkyne termini.[6] The *endo* stereochemical assignment was established by ^1H NMR experiments; the chemical shifts of the angular hydrogen atoms at $\delta = 2.1$ are consistent with a *cis* relationship between the angular hydrogen atoms and the cobalt moiety.

Having determined the level of diastereoselectivity of the cyclization of linear enediynes bearing esters at their chain termini, we wanted to know whether this cyclization could be performed with any degree of asymmetric induction. Thus, we examined the behavior of enediynes **17**, **18**, **22**, and **25**, with chiral esters at the vinylic positions. Chiral esters have successfully been used as chiral auxiliaries in several reactions, particularly in asymmetric [4+2] cycloadditions.[40–43]

The cyclizations were carried out according to Method B as described above. The cycloadducts were obtained in moderate to good yields (Table 3), with *endo*/*exo* selectivities quite similar (86:14) to those found previously, except in the case of the enediyne **22**, for which we were unable to determine this ratio.

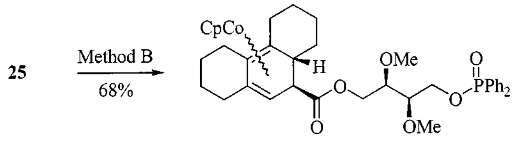
It was in all cases impossible to determine the diastereomeric excesses for each pair of cycloadducts, because the cyclopentadienyl protons of the two *endo* and the two *exo* complexes completely overlap in the ^1H NMR. In order to clarify the structures and to measure the enantiomeric excesses (*ee*), we therefore transformed the complexes **35**–**37** into the alcohol **38** by sequential (i) oxidation of the complexes with the mild agent $CuCl_2{\cdot}2H_2O$ in acetonitrile to liberate the ligand,[7] and (ii) reduction of the ester to the alcohol **38** with $LiAlH_4$. The enantiomeric excess of the cyclization was then measured from the ^{31}P NMR spectrum, using the Alexakis–Mangeney method.[44] The *ee* values were very low, which can probably be explained by the overlong distance between the chiral entity and the metal center in the transition state.

It has been reported in the literature[45] that a substrate containing a chiral auxiliary with a donor atom able to coordinate a transition metal ion tends to produce faster rates and better selectivities in various different types of reactions than a substrate without such a donor atom. Applying this finding, we examined the behavior of the enediyne **25**, bearing a vinylic chiral ester link (derived from tartaric acid), the terminus of which is a phosphorus atom. We anticipated that this would coordinate the cobalt center in the transition state (Scheme 6), and thus selectively mask one of the two faces of approach to the double bond.



Scheme 6

The enediyne **25** was subjected to the Method B cyclization conditions and, after 12 h, a mixture of the (diene)cobalt complexes **39** was isolated in 68% yield (Scheme 7). Surprisingly, although the cyclization had been performed under argon and with degassed solvents, the phosphorus atom in the cycloadducts was in an oxidized state; this oxidation presumably occurred during the purification.



39 *endo* / *exo* = 80 / 20
d. e. : 0% (for *endo* and *exo*)

Scheme 7

The *endo*/*exo* selectivity of 80:20, determined from the vinylic ester, was close to those observed for the cyclizations of the enediynes **5a**, **5b**, **17**, and **18** (ca. 86:14). However, the diastereomeric excesses in each pair of *endo* and *exo* diastereomers were close to zero (determined by ^{1}H NMR by integration of Cp). The lack of selectivity was rather unexpected, but may be explained by the length of the chiral link. The latter is probably too long (seven atoms between the double bond and the phosphorus atom) and unable to adopt the correct conformation for chelating the cobalt ion in the transition state. A shorter chiral link (five or six atoms) would probably be more appropriate, with a more compact transition state and a possible chiral link chair conformation.

Conclusion

In summary, having prepared various substituted linear enediyne esters, we showed that their cyclizations produced the corresponding cycloadducts in very good yields. In most cases, especially when the ester substituent was positioned at the alkyne, the resulting complexes were air-stable and could easily be purified and handled. Depending on the position of the ester group on the enediyne, we observed some difference in the level of the diastereoselectivity relative to the results reported in the literature. Interestingly, the *endo* selectivity increased when the double bond was substituted by an ester group rather than a hydrogen atom, whereas the presence of such a group at the alkyne terminus did not affect the selectivity of the cyclization relative to a silyl group. However, we found that the cyclization was totally diastereoselective in favor of the *endo* complexes when the double bond of the enediyne was internal and an acetylenic ester was present. Surprisingly, this selectivity is totally opposite to that observed for the cyclization of an enediyne without a substituent. Finally, we examined the behavior of enediynes possessing vinylic chiral esters; the results were quite disappointing, giving very low enantiomeric excesses. These studies are still under investigation by us, particularly the use of chiral phosphane oxides as enediyne substituents.

Experimental Section

General Remarks: Reactions were carried out under argon, with magnetic stirring and degassed solvents when necessary. Ether and THF were distilled from sodium/benzophenone under nitrogen before use. CH_2Cl_2, CH_3CN, benzene, and toluene were dried and distilled from CaH_2. HMPA was distilled under reduced pressure after drying with CaH_2. − Thin layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel. Merck Geduran SI 60 A silica gel (35−70 μm) was used for column chromatography according to Still's method.[46] PE and EE refer to petroleum ether and Et_2O. − The melting points reported were measured with a Reichert hot stage apparatus and are uncorrected. − IR spectra were recorded with a Perkin−Elmer 1420 spectrometer. − ^{1}H NMR and ^{13}C NMR spectra were recorded with 200-MHz AC 200 and 400 MHz ARX 400 Bruker spectrometers. Chemical shifts are given in ppm, 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, quint refer to multiplet, singlet, doublet, triplet, quadruplet, quintuplet; br means that the signal is broad. For ^{13}C NMR, coupling constants correspond to the C−P coupling. − Elemental analysis were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie (Paris VI). − Compounds **4a**, **15**, **21**, **23**, **26a**, **26b**, **27a**, **27b**, **29a**, **29b**, **30a**, **30b**, **32**, **33** have already been described in the literature (see text for references).

Enediynes 1a, 1b. − General Procedure: A solution of *n*-butyllithium in hexane (2.2 M, 5 mL, 11 mmol, 1.1 equiv.) was added dropwise to a cooled (−78 °C) solution of tridec-1-ene-6,12-diyne (1.742 g, 10 mmol, 1 equiv.) or tetradec-1-ene-7,13-diyne[7] (1.883 g, 10 mmol, 1 equiv.) in THF (15 mL). After the mixture had been stirred for 30 min at −78 °C, neat methyl chloroformate (1.04 g, 11 mmol, 1.1 equiv.) was added in one portion and the reaction mixture was allowed to warm to room temperature over 1 h. The reaction mixture was diluted with Et_2O, washed with a saturated solution of NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash chromatography.

Methyl Tetradec-13-ene-2,8-diynoate (1a): R_f = 0.52 (PE/EE = 8:2). − Yield 1.93 g (83%). − IR (neat): ṽ = 3080, 2940, 2860, 2240, 1715, 1435, 1330, 1255, 1080, 995, 915, 820, 750 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49−1.78 (m, 6 H), 2.09−2.22 (m, 6 H), 2.37 (t, *J* = 6.9 Hz, 2 H), 3.76 (s, 3 H), 4.96 (tdd, *J* = 10.2, 1.6, 1.0 Hz), 5.03 (tdd, *J* = 17.0, 3.4, 1.6 Hz), 5.80 (tdd, *J* = 17.0, 10.2, 6.5 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1 (3 C), 26.4, 27.9, 28.1, 32.7, 52.4, 72.9, 79.3, 80.4, 89.3, 114.9, 137.9, 154.1. − $C_{15}H_{20}O_2$ (232.3): calcd. C 77.55, H 8.68; found C 77.46, H 8.69.

Methyl Pentadec-14-ene-2,8-diynoate (1b): R_f = 0.48 (PE/EE = 9:1). − Yield 1.806 g (73%). − IR (neat): ṽ = 3060, 2920, 2850, 2310, 2230, 1710, 1635, 1450, 1430, 1325, 1250, 1070, 990, 910, 810, 750 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65−1.74 (m, 4 H), 1.76−1.94 (m, 4 H), 2.00−2.05 (m, 2 H), 2.09−2.17 (m, 4 H), 2.33 (t, *J* = 7.1 Hz, 2 H), 3.72 (s, 3 H), 4.91 (tdd, *J* = 10.3, 1.8, 1.0 Hz), 4.97 (tdd, *J* = 17.1, 2.0, 1.8 Hz), 5.77 (tdd, *J* = 17.1, 10.3, 6.7 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2 (2 C), 18.5, 26.5, 27.9, 28.0, 28.4, 33.2, 52.5, 73.0, 79.2, 80.6, 89.3, 114.4, 138.6, 154.1. − $C_{16}H_{22}O_2$ (246.3): calcd. C 78.01 H 9.00; found C 78. 22, H 8.86.

Diynes 2a and 2b. − General Procedure: A solution of *n*-butyllithium in hexane (2.5 M, 10 mL, 25 mmol) was added dropwise to a cooled (−78 °C) solution of 1,7-octadiyne (32.5 mmol, 1.3 equiv.) in THF (40 mL) and the mixture was stirred for 1 h. HMPA (17.4 mL, 100 mmol, 4 equiv.) was then added dropwise, followed after 15 min by a solution of the appropriate bromide (25 mmol, 1 equiv.) in THF (25 mL). The reaction mixture was allowed to warm to room temperature, stirred for 2 h, and then diluted with Et_2O. The organic layer was washed with a saturated solution of NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash chromatography.

2-(Dodeca-5,11-diynyloxy)tetrahydropyran (2a): R_f = 0.67 (PE/EE = 5:5). − Yield 4.59 g (70%). − IR (neat): ṽ = 3290, 2110, 1450, 1430, 1350, 1200, 1130, 1120, 1070, 1030, 900, 870, 810 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.56 (m, 14 H), 1.87 (t, *J* = 2.4 Hz, 1 H), 2.11 (m, 6 H), 3.45 (m, 2 H), 3.82 (m, 2 H), 4.55 (t, *J* = 3.4 Hz, 1 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17, 18.2, 18.6, 19.6, 25.5, 25.9, 27.5, 28.0, 28.9, 30.7, 62.2, 68.4, 68.6, 79.7, 80.2, 84.2, 98.7.

2-(Trideca-6,12-diynyloxy)tetrahydropyran (2b): R_f = 0.46 (PE/EE = 9:1). − Yield 5.18 g (75%). − IR (neat): ṽ = 3300, 2940, 2860, 2240, 2110, 1450, 1440, 1350, 1260, 1200, 1130, 1115, 1070, 1030, 970, 900, 860, 810, 630 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.59 (m, 16 H), 1.92 (t, J = 2.7 Hz, 1 H), 2.14 (m, 6 H), 3.41 (m, 2 H), 3.78 (m, 2 H), 4.55 (t, J = 3.1 Hz, 1 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.0, 18.3, 18.7, 19.7, 25.5 (2 C), 27.6, 28.1, 29.0, 29.3, 30.8, 62.3, 67.5, 68.4, 79.7, 80.5, 84.3, 98.8. − $C_{18}H_{28}O_2$ (276.4): calcd. C 78.21, H 10.21; found C 78.16, H 10.27.

Diynols 3a and 3b. − General Procedure: PTSA (71 mg, 0.37 mmol, 0.02 equiv.) was added to a solution of the ether **2a** or **2b** (18.7 mmol, 1 equiv.) in MeOH (19 mL) at room temperature. The reaction was monitored by TLC. After completion, the resulting solution was diluted with Et_2O, washed with a saturated solution of NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by chromatography.

Dodeca-5,11-diyn-1-ol (3a): R_f = 0.33 (PE/EE = 5:5). − Yield 3.17 g (95%). − IR (neat): $\tilde{\nu}$ = 3300, 3280, 2110, 1430, 1320, 1240, 1050, 630 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.40−1.62 (m, 8 H), 1.91 (t, J = 2.6 Hz, 1 H), 2.10−2.20 (m, 6 H), 3.59 (t, J = 6.1 Hz, 2 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.0, 18.2, 18.5, 25.3, 27.5, 28.0, 31.8, 62.4, 68.5, 78.0, 80.2, 84.3.

Trideca-6,12-diyn-1-ol (3b): R_f = 0.18 (PE/EE = 7:3). − Yield 3.59 g (quantitative). − IR (neat): $\tilde{\nu}$ = 3600, 3420, 3300, 2940, 2860, 2110, 1450, 1420, 1320, 1040, 920, 630 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57−1.68 (m, 10 H), 2.04 (t, J = 2.5 Hz, 1 H), 2.28 (m, 6 H), 3.70 (t, J = 5.6 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2, 18.4, 18.9, 25.2, 27.7, 28.2, 29.0, 32.4, 62.9, 74.1, 80.0, 84.5. − $C_{13}H_{20}O$ (192.3): calcd. C 81.20, H 10.48; found C 81.04, H 10.56.

Diynals 4a and 4b. − General Procedure: A solution of DMSO (4.47 mL, 63 mmol, 2.3 equiv.) in CH_2Cl_2 (60 mL) was added dropwise to a cooled (−78 °C) solution of oxalyl chloride (3.1 mL, 35.5 mmol, 1.3 equiv.) in CH_2Cl_2 (60 mL). After 5 min, a solution of **3a** or **3b** (27.35 mmol, 1 equiv.) in CH_2Cl_2 (70 mL) was added dropwise. After 30 min at −78 °C, NEt_3 (19 mL, 136.8 mmol, 5 equiv.) was added quickly. The mixture was allowed to warm to room temperature (1 h), diluted with Et_2O, washed with a saturated solution of NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography.

Trideca-6,12-diynal (4b): R_f = 0.42 (PE/EE = 7:3). − Yield 5.2 g (quantitative). − IR (neat): $\tilde{\nu}$ = 3300, 2940, 2860, 2840, 2110, 1720, 1450, 1430, 1405, 1390, 1330, 1260, 635 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48−1.70 (m, 8 H), 1.92 (t, J = 2.5 Hz, 1 H), 2.14 (m, 6 H), 2.42 (td, 2 H, J = 7.1, 1.5 Hz), 9.73 (t, J = 1.5 Hz, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.3, 18.6, 18.9, 21.6, 27.9, 28.3, 28.8, 43.7, 68.8, 73.5, 80.1, 84.6, 202.8. − $C_{13}H_{18}O$ (190.3): calcd. C 82.06, H 9.53; found C 81.98, H 9.23.

Enediynes 5a and 5b. − General Procedure: A solution of triethyl phosphonoacetate (9.42 mmol, 1 equiv.) in CH_3CN (10 mL) was added at room temperature to a solution of LiCl (0.439 g, 10.4 mmol, 1.1 equiv.) in CH_3CN (10 mL). After 15 min, NEt_3 (1.44 mL, 10.36 mmol, 1.1 equiv.) was added and the reaction mixture was stirred for 15 min. A solution of **4a** or **4b** (9.42 mmol, 1 equiv.) in CH_3CN (10 mL) was then added and the reaction mixture was stirred overnight. The resulting mixture was diluted with Et_2O, washed with a saturated solution of NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. Purification by flash chromatography afforded **5a** and **5b**.

Ethyl Tetradec-2-ene-7,13-diynoate (5a): R_f = 0.54 (PE/EE = 8:2). − Yield 1.99 g (86%). − IR (neat): $\tilde{\nu}$ = 3300, 2980, 2940, 2860, 2120, 1720, 1655, 1455, 1445, 1435, 1370, 1320, 1270, 1190, 1150, 1100, 1040, 980, 865, 635 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.1 Hz, 3 H), 1.56−1.65 (m, 6 H), 1.95 (t, J = 2.7 Hz, 1 H), 2.15−2.22 (m, 6 H), 2.30 (q, J = 7.0 Hz, 2 H), 4.17 (q, J = 7.1 Hz, 2 H), 5.83 (d, J = 15.7 Hz, 1 H), 6.94 (dt, J = 15.7, 6.9 Hz, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 17.8, 18.1 (2 C), 27.2, 27.4, 27.8, 31.0, 60.0, 68.3, 79.4, 80.3, 84.1, 121.7, 148.2, 166.5. − $C_{16}H_{22}O_2$ (246.3): calcd. C 78.01, H 9.00; found C 78.02, H 9.03.

Ethyl Pentadec-2-ene-8,14-diynoate (5b): R_f = 0.61 (PE/EE = 9:1). − Yield 2.16 g (88%). − IR (neat): $\tilde{\nu}$ = 3300, 2980, 2940, 2860, 2110, 1705, 1650, 1460, 1440, 1430, 1390, 1365, 1310, 1270, 1190, 1145, 1090, 1040, 970, 845, 635 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, J = 7.1 Hz, 3 H), 1.46−1.65 (m, 8 H), 1.95 (t, J = 2.6 Hz, 1 H), 2.13−2.24 (m, 8 H), 4.17 (q, J = 7.1 Hz, 2 H), 5.81 (dt, J = 15.8, 1.6 Hz, 1 H), 6.95 (dt, J = 15.8, 7.1 Hz, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 17.9, 18.2, 18.4, 27.0, 27.4, 27.9, 28.3, 31.6, 60.1, 68.3, 79.9 (2 C), 84.2, 121.4, 148.8, 166.6. − $C_{17}H_{24}O_2$ (260.4): calcd. C 78.42, H 9.29; found C 78.45, H 9.32.

2-(Hept-6-ynyloxy)tetrahydropyran (6): At −10 °C, acetylene was condensed into THF (280 mL) for 30 min in a four-necked flask, equipped with mechanic stirrer, thermometer, and an acetylene entry port. At −78 °C, *n*-butyllithium (26.1 mL, 2.3 M solution in hexane, 1.2 equiv.) and, after 5 min, DMSO (53.3 mL, 750 mmol, 15 equiv.) were successively added dropwise. After the mixture had been stirred for 30 min, neat 2-(5-bromopentyloxy)tetrahydropyran[27] (12.56 g, 50 mmol, 1 equiv.) was added and the solution was allowed to warm to room temperature, stirred overnight, diluted with Et_2O, washed with a saturated solution of NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (PE/EE = 8:2) to give **6**. R_f = 0.6. − Yield 9.81 g (quantitative). − IR (neat): $\tilde{\nu}$ = 3300, 2930, 2850, 2100, 1450, 1430, 1360, 1345, 1315, 1245, 1195, 1130, 1110, 1070, 1025, 970, 860, 805 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42−1.84 (m, 12 H), 1.92 (t, J = 2.6 Hz, 1 H), 2.17 (td, 2 H, J = 6.5, 2.6 Hz), 3.31−3.52 (m, 2 H), 3.66−3.90 (m, 2 H), 4.55 (AB, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4, 19.7, 25.5 (2 C), 28.4, 29.3, 30.8, 62.4, 67.4, 68.3, 84.6, 98.9. − $C_{12}H_{20}O_2$ (196.3): calcd. C 73.43, H 10.27; found C 73.22, H 10.15.

***tert*-Butyldimethyl[12-(tetrahydropyran-2-yloxy)dodec-6-ynyloxy]silane (7):** *n*-Butyllithium (25.6 mL; 1.5 M solution in hexane) was added dropwise to a cooled (−78 °C) solution of **6** (36.6 mmol, 1 equiv.) in THF (37 mL) and the mixture was stirred for 1 h. Successively, HMPA (25.5 mL, 146.3 mmol, 4 equiv.) and, after 15 min, a solution of (5-bromopentyloxy)*tert*-butyldimethylsilane[32] (36.6 mmol, 1 equiv.) in THF (37 mL) were added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 2 h, then diluted in Et_2O and washed with a saturated solution of NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (PE/EE = 7:3) afforded **7**. R_f = 0.67. − Yield 11.47 g (79%). − IR (neat): $\tilde{\nu}$ = 2960−2900, 2860, 2180, 1465, 1440, 1390, 1360, 1350, 1325, 1255, 1200, 1185, 1140, 1125−1090, 1080, 1030, 980, 940, 910, 870, 835, 810, 775, 680, 660 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 6 H), 0.89 (s, 9 H), 1.38−1.86 (m, 18 H), 2.10−2.18 (m, 4 H), 3.35−3.42 (m, 1 H), 3.47−3.53 (m, 1 H), 3.61 (t, J = 6.1 Hz, 2 H), 3.71−3.77 (m, 1 H), 3.83−3.91 (m, 1 H), 4.58 (t, J = 4.1 Hz, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.3 (2 C), 18.3, 18.7 (2 C), 19.6, 25.1, 25.4 (2 C), 26.0 (3 C), 28.9 (2 C), 29.2, 30.7, 32.3, 62.2, 63.1, 67.4, 80.0 (2 C), 98.8. − $C_{23}H_{44}O_3Si$ (396.7): calcd. C 69.64, H 11.18; found C 69.89, H 11.29.

***tert*-Butyldimethyl[12-(tetrahydropyran-2-yloxy)dodec-6-enyloxy]silane (8):** Lindlar Pd catalyst (180 mg) and quinoline (1 mL) were added successively at room temperature to a solution of **7** (15 mmol, 1 equiv.) in methanol (20 mL). The mixture was stirred for 72 h under hydrogen (1 atm). The solution was then filtered through Celite, washed with toluene, and concentrated. The crude product was purified by flash chromatography (PE/EE = 7:3) to furnish **8**. $R_f = 0.67$. − Yield 4.18 g (70%). − IR (neat): $\tilde{\nu}$ = 3010, 2940, 2900, 2860, 1460, 1440, 1390, 1360, 1350, 1255, 1200, 1140, 1120, 1110, 1080, 1040, 1030, 910, 840, 815, 775 cm^{-1}. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.05 (s, 6 H), 0.87 (s, 9 H), 1.29−1.40 (m, 8 H), 1.43−1.63 (m, 8 H), 1.68−1.75 (m, 1 H), 1.78−1.90 (m, 1 H), 2.03 (m, 4 H), 3.38 (m, 1 H), 3.50 (m, 1 H), 3.60 (t, J = 6.8 Hz, 2 H), 3.73 (m, 1 H), 3.87 (m, 1 H), 5.35 (AB, 2 H). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = −5.3 (2 C), 18.3, 19.6, 25.4 (2 C), 25.9 (4 C), 27.1, 27.2, 29.5 (2 C), 29.6, 30.7, 32.7, 62.2, 63.2, 67.5, 98.7, 129.7, 129.8. − $C_{23}H_{46}O_3Si$ (398.7): calcd. C 69.29, H 11.63; found C 69.35, H 11.54.

12-(Tetrahydropyran-2-yloxy)dodec-6-en-1-ol (9): A THF solution of nBu$_4$NF (1 M, 11.52 mmol, 1.1 equiv.) was added at 0 °C to a solution of **8** (10.48 mmol, 1 equiv.) in THF (22 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was diluted with Et$_2$O, washed with a saturated solution of NH$_4$Cl and brine, dried with MgSO$_4$, filtered, and concentrated. Purification was by flash chromatography (PE/EE = 7:3). $R_f = 0.11$. − Yield 2.62 g (88%). − IR (neat): $\tilde{\nu}$ = 3560−3250, 3010, 2920, 2860, 1460, 1440, 1350, 1320, 1260, 1200, 1140, 1120, 1070, 1030, 970, 910, 870, 810 cm^{-1}. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.30−1.43 (m, 8 H), 1.45−1.62 (m, 8 H), 1.67−1.75 (m, 1 H), 1.78−1.85 (m, 1 H), 1.91−2.10 (m, 4 H), 3.36 (m, 1 H), 3.49 (m, 1 H), 3.61 (t, J = 6.6 Hz, 2 H), 3.71 (m, 1 H), 3.86 (m, 1 H), 4.57 (t, J = 4.2 Hz, 1 H), 5.34 (AB, 2 H). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.5, 25.3, 25.4, 25.8, 27.0 (2 C), 29.4 (2 C), 29.5, 30.6, 32.6, 62.2, 62.7, 67.5, 98.7, 129.6, 129.8. − $C_{17}H_{32}O_3$ (284.4): calcd. C 71.79, H 11.34; found C 71.66, H 11.28.

12-(Tetrahydropyran-2-yloxy)dodec-6-enal (10): The aldehyde **10** was prepared using the procedure described for **4a** and **4b**. R_f = 0.39 (PE/EE = 7:3). − Yield 2.39 g (91%). − IR (neat): $\tilde{\nu}$ = 3010, 2940, 2860, 2720, 1725, 1455, 1440, 1410, 1385, 1350, 1260, 1200, 1180, 1140, 1120, 1080, 1030, 1020, 990, 970, 905, 870, 810 cm^{-1}. − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.20−1.80 (m, 16 H), 1.90−2.05 (m, 4 H), 2.38 (td, 2 H, J = 7.2, 1.8 Hz), 3.26−3.47 (m, 2 H), 3.62−3.87 (m, 2 H), 4.51 (t, J = 3.0 Hz, 1 H), 5.30 (AB, 2 H), 9.71 (t, J = 1.8 Hz, 1 H). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 19.6, 21.6, 25.4, 25.8, 26.8, 27.1, 29.2, 29.5, 29.6, 30.7, 43.7, 62.3, 67.5, 98.5, 129.0, 130.3, 202.6. − $C_{17}H_{30}O_3$ (282.4): calcd. C 72.30, H 10.71; found C 72.14, H 10.72.

2-(Tridec-6-en-12-ynyloxy)tetrahydropyran (11): K$_2$CO$_3$ (2.34 g, 16.93 mmol, 2 equiv.) and a solution of freshly prepared dimethyl 1-diazo-2-oxopropylphosphonate (1.95 g, 10.16 mmol, 1.2 equiv.) in MeOH (50 mL) were added successively, at room temperature and under argon, to a solution of **10** (2.39 g, 8.47 mmol, 1 equiv.) in MeOH (100 mL). The reaction mixture was stirred overnight, then diluted with Et$_2$O, washed with a saturated solution of NH$_4$Cl and brine, dried with MgSO$_4$, filtered, and concentrated. The crude residue was purified by flash chromatography (PE/EE = 7:3) to furnish **11**. R_f = 0.39. − Yield 1.83 g (77%). − IR (neat): $\tilde{\nu}$ = 3310, 3010, 2940, 2860, 2120, 1455, 1440, 1380, 1365, 1350, 1320, 1260, 1200, 1180, 1140, 1120, 1080, 1030, 1020, 990, 975, 905, 870, 815, 630 cm^{-1}. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.32−1.65 (m, 14 H), 1.68−1.73 (m, 1 H), 1.75−1.85 (m, 1 H), 1.94 (t, J = 2.6 Hz, 1 H), 1.96−2.05 (m, 4 H), 2.18 (td, 2 H, J = 7.0, 2.6 Hz), 3.36 (m, 1 H), 3.48 (m, 1 H), 3.72 (m, 1 H), 3.86 (m, 1 H), 4.57 (t, J = 2.6 Hz, 1 H), 5.35 (AB, 2 H). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 18.2, 19.6, 25.4, 25.8, 26.5, 27.1, 27.9, 28.6, 29.5, 29.6, 30.6, 62.2, 67.5, 68.1, 84.4, 98.7, 129.2, 130.0. − $C_{18}H_{30}O_2$ (278.433): calcd. C 77.65, H 10.86; found C 77.62, H 10.92.

Trimethyl[13-(tetrahydropyran-2-yloxy)tridec-7-en-1-ynyl]silane (12): The preparation followed the procedure described for **1a** and **1b**. R_f = 0.63 (PE/EE = 7:3). − Yield 2.27 g (quantitative). − IR (neat): $\tilde{\nu}$ = 3010, 2930, 2850, 2170, 1455, 1250, 1200, 1140, 1120, 1080, 1035, 1025, 990, 970, 910, 840, 760, 700, 640 cm^{-1}. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.15 (s, 9 H), 1.32−1.64 (m, 14 H), 1.66−1.74 (m, 1 H), 1.77−1.89 (m, 1 H), 1.98−2.09 (m, 4 H), 2.23 (t, J = 6.8 Hz, 2 H), 3.39 (m, 1 H), 3.49 (m, 1 H), 3.74 (m, 1 H), 3.86 (m, 1 H), 4.58 (t, J = 2.8 Hz, 1 H), 5.36 (AB, 2 H), − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 0.1 (3 C), 19.6, 19.7, 25.5, 25.9, 26.6, 28.1, 27.1, 28.8, 29.5, 29.6, 30.7, 62.2, 67.5, 84.3, 98.8, 107.4, 129.4, 130.0. − $C_{21}H_{38}O_2Si$ (350.6): calcd. C 71.94, H 10.92; found C 71.75, H 10.88.

13-(Trimethylsilanyl)tridec-6-en-12-yn-1-ol (13): The procedure was the same as that described for **3a** and **3b**. R_f = 0.43 (PE/EE = 5:5). − Yield 1.67 g (97%). − IR (neat): $\tilde{\nu}$ = 3620, 3010, 2930, 2860, 2170, 1455, 1430, 1405, 1320, 1250, 1045, 840, 640 cm^{-1}. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.15 (s, 9 H), 1.36−1.60 (m, 10 H), 2.04 (m, 4 H), 2.23 (t, J = 6.9 Hz, 2 H), 3.65 (t, J = 6.6 Hz, 2 H), 5.38 (AB, 2 H). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 0.14 (3 C), 19.7, 25.4, 26.6, 27.1, 28.2, 28.8, 29.5, 32.6, 62.9, 84.3, 107.5, 129.6, 129.9. − $C_{16}H_{30}OSi$ (266.5): calcd. C 72.11, H 11.35; found C 72.22, H 11.29.

13-(Trimethylsilanyl)tridec-6-en-12-ynal (14): Obtained by using the procedure described for **4a** and **4b**. R_f = 0.69 (PE/EE = 5:5). − Yield 1.52 g (92%). − IR (neat): $\tilde{\nu}$ = 3010, 2940, 2860, 2730, 2170, 1720, 1455, 1430, 1405, 1320, 1250, 840, 640 cm^{-1}. − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 0.16 (s, 9 H), 1.35−1.60 (m, 6 H), 1.66 (quint, J = 7.7 Hz, 2 H), 2.06 (t, J = 6.8 Hz, 4 H), 2.24 (t, J = 7.0 Hz, 2 H), 2.44 (td, 2 H, J = 7.4, 1.6 Hz), 5.38 (AB, 2 H), 9.78 (t, J = 1.6 Hz, 1 H). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 0.2 (3 C), 19.7, 21.7, 26.7, 26.9, 28.2, 28.8, 29.1, 43.8, 84.4, 107.4, 129.3, 130.0, 202.7. − $C_{16}H_{28}OSi$ (264.5): calcd. C 72.66, H 10.67; found C 72.49, H 10.71.

Methyl Pentadec-8-ene-2,14-diynoate (16): The preparation used the procedure described for **1a** and **1b**. R_f = 0.67 (PE/EE = 7:3). − Yield 0.082 g (37%). − IR (neat): $\tilde{\nu}$ = 3310, 3010, 2940, 2860, 2120, 1710, 1460, 1440, 1330, 1260, 1080, 820, 640 cm^{-1}. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.40−1.63 (m, 8 H), 1.95 (t, J = 2.4 Hz, 1 H), 2.05 (m, 4 H), 2.19 (td, 2 H, J = 6.8, 2.4 Hz), 2.34 (t, J = 7.0 Hz, 2 H), 3.76 (s, 3 H), 5.37 (AB, 2 H). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 18.2, 18.4, 26.4, 26.6, 26.9, 27.9, 28.6, 28.7, 52.5, 68.2, 72.8, 84.4, 89.6, 129.2, 129.9, 154.1. − $C_{16}H_{22}O_2$ (246.3): calcd. C 78.01, H 9.00; found C 77.85, H 9.01.

2-Isopropyl-5-methylcyclohexyl Pentadec-2-ene-8,14-diynoate (17): The preparation followed the procedure described for **5a** and **5b**. R_f = 0.7 (PE/EE = 7:3). − Yield 0.543 g (87%). − IR (neat): $\tilde{\nu}$ = 3300, 3000, 2940, 2860, 1700, 1650, 1450, 1430, 1365, 1310, 1290, 1270, 1180, 1145, 1090, 1010, 980, 910 cm^{-1}. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.77 (dd, 3 H, J = 6.9, 3.3 Hz), 0.90 (m, 6 H), 1.02 (m, 2 H), 1.22 (m, 1 H), 1.40 (m, 1 H), 1.47−1.73 (m, 11 H), 1.88 (m, 1 H), 1.96 (t, J = 2.5 Hz, 1 H), 2.02 (m, 1 H), 2.21 (m, 8 H), 4.74 (tt, J = 10.8, 4.0 Hz), 5.82 (dt, J = 15.6, 0.8 Hz, 1 H), 6.94 (td, J = 15.6, 3.4 Hz). − ^{13}C NMR (100 MHz, CDCl$_3$): δ = 16.5, 18.1, 18.3, 18.6, 20.8, 22.1, 23.6, 26.4, 27.2, 27.6, 28.1, 28.6, 31.5, 31.8, 34.4, 41.1, 47.2, 68.5, 73.9, 80.1 (2 C), 84.5, 121.9, 148.5, 166.4. − $[\alpha]^{20}$ = −53 (*c* = 1.45, $CHCl_3$).

1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl Pentadec-2-ene-8,14-diynoate (18): The preparation followed the procedure described for **5a** and **5b**. R_f = 0.72 (PE/EE = 7:3). − Yield 1.02 g (79%). − IR (neat): ṽ = 3300, 2940, 2860, 2105, 1710, 1650, 1450, 1440, 1370, 1360, 1300, 1265, 1180, 1140, 1110, 1030, 975, 630 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82 (s, 3 H), 0.85 (s, 3 H), 0.89 (s, 3 H), 0.98 (m, 1 H), 1.23 (m, 2 H), 1.40−1.80 (m, 10 H), 1.93 (t, *J* = 2.8 Hz, 1 H), 1.97 (m, 1 H), 2.16 (m, 8 H), 2.32 (m, 1 H), 4.90 (m, 1 H), 5.82 (d, *J* = 15.6 Hz, 1 H), 6.92 (td, *J* = 15.6, 6.9 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 18.0, 18.3, 18.6, 18.9, 19.8, 27.2 (2 C), 27.6, 28.1 (2 C), 28.5, 31.7, 36.6, 44.9, 47.9, 48.9, 68.5, 79.6, 80.0 (2 C), 84.3, 121.9, 148.6, 167.1. − $[\alpha]^{20}$ = −29.8 (*c* = 1.05, $CHCl_3$).

Pentadec-2-ene-8,14-diynoic Acid (19): NaOH (32.93 mmol, 3 equiv.) in H_2O (31 mL) was added to a solution of **5b** (10.98 mmol, 1 equiv.) in THF (44 mL), and the reaction mixture was refluxed overnight. The solution was then allowed to cool to room temperature, hydrolyzed with 44 mL of a saturated solution of $NaHCO_3$, and extracted with Et_2O (76 mL). At 0 °C, the aqueous layer was acidified with a 6 N HCl solution to pH = 1, and was then extracted with CH_2Cl_2 (66 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated. Pure **19** was obtained. Yield 2.512 g (98%). − IR (neat): ṽ = 3500, 3300, 2930, 2850, 2110, 1690, 1640, 1450, 1420, 1300, 1280, 1220, 1050, 980, 900 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.47−1.69 (m, 8 H), 1.96 (t, *J* = 2.5 Hz, 1 H), 2.13−2.31 (m, 8 H), 5.84 (d, *J* = 15.6 Hz, 1 H), 7.09 (td, *J* = 15.6, 6.9 Hz), 10.8 (br. s, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1, 18.3, 18.6, 27.0, 27.6, 28.1, 28.5, 31.9, 68.5, 79.9, 80.1, 84.3, 121.0, 152.1, 172.2. − M.p. 34−36 °C. − $C_{15}H_{20}O_2$ (232.321): calcd. C 77.55, H 8.68; found C 77.42, H 8.74.

1,5-Dimethyl-3-pentadec-2-ene-8,14-diynoyl-4-phenylimidazolidin-2-one (22): Oxalyl chloride (2.745 g, 21.63 mmol, 2 equiv.) was added, at room temperature and under argon, to a solution of **19** (2.51 g, 10.81 mmol, 1 equiv.) in toluene (40 mL). After being stirred for 20 h, the solution was concentrated and the crude product **20** was used in the next step without purification. − At −78 °C, a solution of *n*-butyllithium in hexane (2 M, 4.51 mL, 9.02 mmol, 1 equiv.) was added dropwise to a solution of imidoxazolidinone **21** (1.72 g, 9.02 mmol, 1 equiv.) in THF (45 mL), and the solution was stirred for 10 min. The previously prepared acid chloride **20** in THF (18 mL) was then added and the reaction mixture was allowed to warm to room temperature over 1 h, diluted with CH_2Cl_2, washed with a saturated solution of NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (PE/AcOEt = 7:3) to furnish **22**. R_f = 0.31. − Yield 2.18 g (60%). − IR (neat): ṽ = 3300, 3020, 2970, 2930, 2850, 2110, 1715, 1665, 1630, 1450, 1420, 1390, 1355, 1325, 1300, 1280, 1250, 1225, 1200, 1170, 1070, 980, 690, 630 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.6 Hz, 3 H), 1.45−1.73 (m, 8 H), 2.02 (t, *J* = 2.6 Hz, 1 H), 2.20−2.35 (m, 8 H), 2.91 (s, 3 H), 3.98 (m, 1 H), 5.43 (d, *J* = 8.5 Hz, 1 H), 7.06 (dt, *J* = 15.2, 7.1 Hz, 1 H), 7.24 (d, *J* = 8.1 Hz, 2 H), 7.33−7.42 (m, 3 H), 7.54 (dt, *J* = 15.2, 1.5 Hz, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 17.9, 18.2, 18.5, 27.3, 27.5, 27.9, 28.1, 28.5, 32.1, 53.9, 59.4, 68.3, 79.8, 80.2, 84.0, 121.8, 126.9, 128.0 (2 C), 128.5 (2 C), 136.6, 149.0, 155.9, 164.8. − $C_{26}H_{32}N_2O_2$ (404.5): calcd. C 77.19, H 7.97; found C 76.89, H 7.89. − $[\alpha]^{20}$ = −70.4 (*c* = 1.15, $CHCl_3$).

4-Hydroxy-2,3-dimethoxybutyl Pentadec-2-ene-8,14-diynoate (24): A solution of chiral 2,3-dimethoxybutane-1,4-diol **23** (1.44 g, 9.6 mmol, 1.1 equiv.) in THF (15 mL) was added dropwise, at 0 °C and under argon, to a suspension of sodium hydride (60% in oil, 0.36 g, 9 mmol, 1 equiv.) in THF (10 mL). The reaction mixture was allowed to warm to room temperature over 1 h and a solution of the previously prepared acid chloride **20** (see above, 9.02 mmol, 1 equiv.) in THF (15 mL) was then added. After stirring for 2 h, the solution was diluted with Et_2O and washed with a saturated solution of NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash chromatography (PE/AcOEt = 3:7) to yield **24**. R_f = 0.31. − Yield 1.42 g (43%). − IR (neat): ṽ = 3580, 3300, 2980, 2920, 2850, 2820, 2100, 1710, 1645, 1450, 1440, 1430, 1260, 1180, 1135, 1090, 1030, 975, 900, 630 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.48−1.68 (m, 8 H), 1.97 (t, *J* = 2.5 Hz, 1 H), 2.17−2.27 (m, 8 H), 3.45 (q, *J* = 4.6 Hz, 1 H), 3.50 (s, 3 H), 3.52 (s, 3 H), 3.66 (q, *J* = 5.6 Hz, 1 H), 3.76 (ABX, 2 H), 4.32 (ABX, 2 H), 5.86 (d, *J* = 15.8 Hz, 1 H), 7.00 (td, *J* = 15.8, 7.1 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 18.2, 18.5, 27.0, 27.5, 27.9, 28.4, 31.7, 58.7, 58.9, 61.2, 62.8, 68.4, 79.5, 79.9 (2 C), 80.4, 84.2, 120.8, 149.9, 166.4. − $C_{21}H_{32}O_5$ (364.5): calcd. C 69.20, H 8.85; found C 69.11, H 8.90. − $[\alpha]^{20}$ = 2.1 (*c* = 1.75, $CHCl_3$).

Compound 25: NEt_3 (2 mmol, 1 equiv.) was added, at room temperature and under argon, to a solution of **24** (0.73 g, 2 mmol, 1 equiv.) in toluene (5 mL), and the reaction mixture was stirred for 30 min. Neat chlorodiphenylphosphane (2 mmol, 1 equiv.) was then added. After 20 h, the solution was filtered, washed with toluene, and concentrated. The residue was purified by flash chromatography (PE/AcOEt = 3:7) to give **25**. R_f = 0.48. − Yield 0.448 g (41%). − IR (neat): ṽ = 3300, 3050, 2920, 2850, 2820, 2100, 1710, 1650, 1475, 1450, 1430, 1270, 1185, 1140, 1090, 1035, 990, 975, 900, 840, 775, 690, 635 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.48−1.65 (m, 8 H), 1.97 (t, *J* = 2.6 Hz, 1 H), 2.18−2.25 (m, 8 H), 3.42 (s, 3 H), 3.45 (s, 3 H), 3.44−3.62 (m, 2 H), −3.95−4.09 (m, 2 H), 4.25−4.35 (ABX, 2 H), 5.85 (d, *J* = 15.6 Hz, 1 H), 6.96 (td, *J* = 15.6, 6.9 Hz), 7.35−7.40 (m, 6 H), 7.51 (td, 4 H, *J* = 7.6, 2.0 Hz). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 18.2, 18.5, 27.0, 27.5, 28.0, 28.5, 31.7, 59.1 (2 C), 62.8, 68.0 (*J* = 72.6 Hz), 68.4, 78.2, 79.9 (2 C), 80.5 (*J* = 30.3 Hz), 84.2, 121.0, 128.3 (4 C, *J* = 27.8 Hz), 129.4 (2 C), 130.5 (4 C, *J* = 86.6 Hz), 141.8 (2 C, *J* = 72.8 Hz), 149.6, 166.3. − ^{31}P NMR (162 MHz, $CDCl_3$): δ = 117.1. − $C_{33}H_{41}O_5P$ (548.7): calcd. C 72.24, H 7.53; found C 72.06, H 7.73. − $[\alpha]^{20}$ = 0.92 (*c* = 1.3, $CHCl_3$).

General Procedure for the Cyclisation of Enediynes: In most cyclizations, the complexes were obtained as a inseparable mixtures of *endo*/*exo* cycloadducts (four compounds). In some cases, one pair of cycloadducts is fully described; for the other one we give only the characteristic data. In the case of complexes **37**, we were unable to describe the mixture.

Method A: Dicarbonyl(cyclopentadienyl)cobalt (0.37 mmol, 1.2 equiv.) was added to a boiling solution of the enediyne (0.31 mmol, 1 equiv.) in toluene (9 mL), previously degassed by three freeze-pump-thaw cycles. The mixture was irradiated (light from a projector lamp; ELW, 300 W, 80% power). The reaction was monitored by TLC and after completion (about 1 h) the reaction mixture was purified by flash chromatography either on deactivated alumina (4% H_2O) or on silica gel.

Method B: Dicarbonyl(cyclopentadienyl)cobalt (0.37 mmol, 1.2 equiv.) was added to a boiling solution of the enediyne (0.31 mmol, 1 equiv.) in decane (9 mL), previously degassed by three freeze-pump-thaw cycles, and the reaction mixture was stirred at reflux overnight. The solution was then purified by flash chromatography on deactivated alumina (4% H_2O) or on silica gel.

Complexes 26a, Method A: R_f = 0.27 (PE/EE = 9:1). − Yield 0.086 g (78%.). − IR (C_6D_6): $\tilde{\nu}$ = 3100, 2940, 2860, 1690, 1445, 1435, 1370, 1350, 1320, 1300, 1250, 1230, 1185, 1170, 1145, 1130, 1110, 1080, 1060, 1010, 995, 845, 835, 800, 770 cm^{-1}. − ***endo*-26a** (characteristic data): ^1H NMR (400 MHz, C_6D_6): δ = −0.13 (dd, *J* = 12.7, 7.6 Hz, 1 H), 1.35 (d, *J* = 7.6 Hz, 1 H), 2.16 (t, *J* = 4.6 Hz, 1 H), 2.53 (d, *J* = 12.7 Hz, 1 H), 2.65 (dt, *J* = 17.6, 6.1 Hz, 1 H), 3.60 (s, 3 H), 3.57−3.68 (m, 1 H), 3.88 (ddd, *J* = 16.8, 8.1, 5.1 Hz), 4.48 (s, 5 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 50.5, 51.9, 52.7, 78.0, 82.8 (5 C), 90.2, 92.9, 183.5. − ***exo*-26a** (characteristic data): ^1H NMR (400 MHz, C_6D_6): δ = 0.64 (m, 1 H), 1.39 (d, *J* = 8.1 Hz, 1 H), 2.20 (t, *J* = 4.6 Hz, 1 H), 2.51 (d, *J* = 12.7 Hz, 1 H), 2.58 (dt, *J* = 18.8, 5.1 Hz, 1 H), 3.57−3.68 (m, 1 H), 3.60 (s, 3 H), 4.48 (s, 5 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 40.7, 50.1, 50.4, 78.0, 83.0 (5 C), 90.4, 92.9, 176.6. − **(*endo* + *exo*)-26a** (not attributed): ^1H NMR (400 MHz, C_6D_6): δ = 0.66−0.73 (m, 1 H), 1.46−2.13 (m, 17 H), 2.27−2.46 (m, 3 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 23.0 (2 C), 23.4, 23.6, 24.0 (2 C), 24.4, 25.0, 27.4, 27.9, 28.1, 28.5, 29.7, 31.1, 32.7, 33.2.

Complexes 26b, Method A: R_f = 0.36 (PE/EE = 9:1). − Yield 0.108 g (94%.). − IR (C_6D_6): $\tilde{\nu}$ = 3080, 2920, 2840, 1720, 1680, 1425, 1365, 1340, 1305, 1230, 1200, 1180, 1160, 1100, 1075, 1060, 1040, 1000, 990, 790, 770 cm^{-1}. − ***exo*-26b** (characteristic data): ^1H NMR (400 MHz, C_6D_6): δ = 0.60 (m, 1 H), 0.86 (m, 1 H), 1.51 (m, 1 H), 3.54 (s, 3 H), 4.57 (s, 5 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 32.3, 39.6, 49.7, 50.5, 72.5, 82.5 (5 C), 92.0, 94.6, 176.2. − ***endo*-26b** (characteristic data): ^1H NMR (400 MHz, C_6D_6): δ = 0.09 (m, 1 H), 2.11 (m, 1 H), 2.52 (m, 1 H), 3.56 (s, 3 H), 4.45 (s, 5 H), − ^{13}C NMR (100 MHz, C_6D_6): δ = 31.8, 47.5, 48.2, 50.5, 72.8, 82.9 (5 C), 92.3, 94.3, 176.3. − **(*endo* + *exo*)-26b** (not attributed): ^1H NMR (400 MHz, C_6D_6): δ = 0.90−0.97 (m), 3.64−3.77 (m), 2.55−2.87 (m), 1.15−2.25 (m). − ^{13}C NMR (100 MHz, C_6D_6): δ = 23.5 (2 C), 24.0, 24.2, 26.4, 26.6, 26.7, 26.8, 27.2, 27.4, 27.9 (2 C), 33.9 (2 C), 36.8 (2 C).

Complexes 30a, Method B: R_f = 0.33 (PE/EE = 9:1). − Yield 0.071 g (62%.). − IR (C_6D_6): $\tilde{\nu}$ = 3100, 2930, 2870, 2830, 1730, 1700, 1460, 1445, 1370, 1345, 1290, 1260, 1165, 1130, 1110, 1035, 1010, 860, 800 cm^{-1}. − ***endo*-30a** (fully described): ^1H NMR (400 MHz, C_6D_6): δ = 1.07 (t, *J* = 7.1 Hz, 3 H), 1.45−2.29 (m, 14 H), 1.33 (m, 1 H), 2.70 (t, *J* = 9.6 Hz, 1 H), 2.82 (d, *J* = 3.6 Hz, 1 H), 4.03 (q, *J* = 7.1 Hz, 2 H), 4.44 (s, 5 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 14.4, 23.4, 23.5, 23.8, 26.9, 29.5, 31.9, 35.5, 44.6, 47.2, 52.5, 59.8, 72.5, 81.7 (5 C), 89.7, 90.0, 173.1. − ***exo*-30a** (characteristic data): ^1H NMR (400 MHz, C_6D_6): δ = 1.09 (t, *J* = 7.1 Hz, 3 H), 4.10 (q, *J* = 6.0 Hz, 2 H), 4.61 (s, 5 H), − ^{13}C NMR (100 MHz, C_6D_6): δ = 14.3, 45.4, 47.1, 60.0, 80.9 (5 C), 174.9.

Complexes 30b, Method B: R_f = 0.36 (PE/EE = 9:1). − Yield 0.085 g (71%.) − IR (C_6D_6): $\tilde{\nu}$ = 3080, 3020, 2990, 2970, 2920, 2840, 1710, 1440, 1360, 1270, 1110, 1100, 1025, 1000, 800 cm^{-1}. − ***endo*-30b** (fully described): ^1H NMR (400 MHz, C_6D_6): δ = 0.62 (qd, *J* = 12.4, 2.6 Hz), 1.14 (t, *J* = 7.0 Hz, 3 H), 1.41 (dd, *J* = 6.0, 1.4 Hz, 1 H), 1.01−2.53 (m, 15 H), 2.65 (m, 1 H), 3.00 (d, *J* = 1.4 Hz, 1 H), 4.18 (m, 2 H), 4.56 (s, 5 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 14.5, 23.5, 24.2, 26.1, 27.5 (2 C), 30.0, 35.8, 36.3, 46.1, 48.8, 50.6, 60.1, 69.2, 81.6 (5 C), 90.3, 91.4, 174.7. − ***exo*-30b** (characteristic data): ^1H NMR (400 MHz, C_6D_6): δ = 4.52 (s, 5 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 81.0 (5 C).

Complex *endo*-32, Method A: R_f = 0.43 (PE/EE = 8:2). − Yield 0.085 g (65%.). − ^1H NMR (400 MHz, C_6D_6): δ = 0.63 (q, *J* = 10.6 Hz, 1 H), 0.73 (q, *J* = 12.0 Hz, 1 H), 1.20−1.98 (m, 12 H), 1.95 (q, *J* = 13.8 Hz, 1 H), 2.07 (q, *J* = 10.2 Hz, 1 H), 2.87 (d, *J* = 10.6 Hz, 1 H), 3.58 (t, *J* = 12.2 Hz, 1 H), 3.67 (s, 3 H), 4.54 (s, 5 H), 5.58 (s, 1 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 27.7, 28.1, 29.8, 30.8, 33.0, 33.1, 39.1, 41.0, 46.7, 49.3, 51.1, 72.8, 75.3, 77.1, 79.0, 82.0 (5 C), 173.5.

Complexes 35, Method B: R_f = 0.43 (PE/EE = 9:1). − Yield 0.124 g (81%.). − IR (C_6D_6): $\tilde{\nu}$ = 3100, 3010, 2940, 2860, 1710, 1450, 1390, 1370, 1330, 1300, 1280, 1260, 1230, 1180, 1160, 1120, 1110, 990, 800 cm^{-1}. − ***endo*-35** (fully described): ^1H NMR (400 MHz, C_6D_6): δ = 0.86 (t, *J* = 5.9 Hz, 3 H), 0.99 (m, 6 H), 1.00−2.40 (m, 20 H), 2.40−2.80 (m, 7 H), 3.12 (s, 1 H), 4.62 (s, 5 H), 5.12 (m, 1 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 16.5, 20.9, 22.0, 23.4, 24.1, 25.9, 26.4, 26.7, 27.4, 29.9, 30.0, 31.4, 34.4, 35.7, 36.2, 41.4, 46.0, 47.5, 49.0, 50.6, 69.2, 73.2,.81.5 (5 C), 90.2, 91.3, 174.9. − ***exo*-35** (characteristic data): ^1H NMR (400 MHz, C_6D_6): δ = 4.52 (s, 5 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 16.4, 48.9, 50.2, 69.0, 73.5, 80.9 (5 C), 173.9.

Complexes 36, Method B: R_f = 0.43 (PE/EE = 9:1). − Yield 0.113 g (74%.). − IR (C_6D_6): $\tilde{\nu}$ = 3100, 3020, 2940, 2870, 1710, 1450, 1390, 1375, 1330, 1300, 1280, 1265, 1235, 1180, 1160, 1120, 1110, 990, 805 cm^{-1}. − ***endo*-36** (fully described): ^1H NMR (400 MHz, C_6D_6): δ = 0.82 (s, 3 H), 0.86 (s, 3 H), 1.01 (s, 3 H), 0.99−2.19 (m, 17 H), 1.43 (m, 1 H), 2.39−2.79 (m, 7 H), 3.09 (br. s, 1 H), 4.61 (s, 5 H), 5.35 (m, 1 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 13.9, 18.9, 19.8, 23.5, 24.2, 26.1, 27.4, 27.5, 27.7, 28.5, 30.0, 36.3, 37.4, 37.6, 45.3, 45.8, 47.9, 49.0, 49.1, 51.1, 69.0, 79.2, 81.6 (5 C), 90.4, 91.4, 174.9. − ***exo*-36** (characteristic data): ^1H NMR (400 MHz, C_6D_6): δ = 4.43 (s, 5 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 174.8, 81.0 (5 C).

Compound 38: $CuCl_2·2H_2O$ (42 mg, 0.24 mmol, 1.1 equiv.) was added at room temperature to a solution of cobalt complexes **35−37** (0.22 mmol, 1 equiv.) in CH_3CN (10 mL). After 10 min, the reaction mixture was concentrated, diluted with Et_2O (5 mL), and added to a suspension of $LiAlH_4$ (0.33 mmol, 1.5 equiv.) in Et_2O (5 mL). After 10 min, the resulting solution was diluted in CH_2Cl_2, hydrolyzed with a saturated solution of Na_2SO_4, filtered through Celite, concentrated, and purified by flash chromatography. R_f = 0.32 (PE/EE = 6:4). − Yield 0.043 g (90%.). − IR (neat): $\tilde{\nu}$ = 3600, 3420, 3020, 3000, 2920, 2850, 1440, 1380, 1230, 1040, 1000, 890, 820 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.99−1.84 (m, 10 H), 1.89−2.39 (m, 6 H), 2.64−2.79 (m, 2 H), 3.51 (dd, *J* = 5.5, 1.7 Hz, 2 H), 5.37 (br. s, 1 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.6, 24.2, 25.2, 26.9, 28.8, 30.0, 31.4, 36.2, 40.2, 43.8, 65.8, 119.0, 125.3, 134.8, 135.1.

Complexes 39, Method B: R_f = 0.29 (PE/AcOEt = 3:7). − Yield 0.145 g (68%.). − IR (C_6D_6): $\tilde{\nu}$ = 3050, 2970, 2920, 2840, 2820, 1725, 1585, 1450, 1435, 1260, 1230, 1125, 1110, 1020, 990, 905, 790, 750, 725, 690 cm^{-1}. − ***endo*-39** (2 *endo* complexes, fully described): ^1H NMR (400 MHz, C_6D_6): δ = 1.19−2.59 (m, 32 H), 1.30 (d, *J* = 6.1 Hz, 2 H), 2.64−2.74 (m, 2 H), 3.08 (s, 2 H), 3.28−3.42 (m, 12 H), 3.60−3.79 (m, 6 H), 3.89−4.00 (m, 2 H), 4.29−4.85 (m, 4 H), 4.63 (s, 5 H), 4.64 (s, 5 H), 7.19 (m, 12 H), 8.10 (m, 8 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 23.5 (2 C), 24.2 (2 C), 26.0 (2 C), 27.4 (2 C), 28.8 (2 C), 29.9 (2 C), 35.8 (2 C), 36.2 (2 C), 45.7 (2 C), 48.7 (2 C), 50.7 (2 C), 56.4 (2 C), 58.7 (2 C), 63.4 (2 C), 69.1 (2 C), 71.2 (2 C), 79.1 (2 C), 81.7 (10C), 84.9 (2 C), 90.3 (2 C), 91.3 (2 C), 128.6 (8 C, *J* = 7.1 Hz), 128.7 (8 C, *J* = 7.1 Hz), 132.1 (4 C), 141.6 (4 C, *J* = 74.6 Hz), 174.6 (2 C). − ^{31}P NMR (162 MHz, C_6D_6): δ = 31.6. − ***exo*-39** (2 *exo* complexes, characteristic data): ^1H NMR (400 MHz, C_6D_6): δ = 4.59 (s, 5 H), 4.60 (s, 5 H). − ^{13}C NMR (100 MHz, C_6D_6): δ = 81.0 (10C). − ^{31}P NMR (162 MHz, C_6D_6): δ = 31.5.

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