Cobalt(I)-Mediated Intramolecular [2+2+2] Cocyclizations of (Methylenecyclopropyl)diynes as an Easy Access to Cyclopropanated Oligocycles[‡]

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Enediynes with methylenecyclopropane moieties attached either through the three-membered ring or the double bond smoothly underwent cobalt-mediated [2+2+2] cocyclizations to give cyclopropane-fused and spirocyclopropanated cobalt-complexed tricyclo[7.3.0.0^{2,6}]dodeca-1,6-dienes (1,2,3,3a,4,6,7,8-octahydro-*as*-indacenes) under relatively mild conditions in yields ranging from 31 to 94 % (6 examples). Electron-withdrawing substituents at the acetylenic terminus of the precursor are essential for a successful oligocyclization. While diphenyloxyphosphinyl-substituted enediynes provided tricyclo[7.3.0.0^{2,6}]dodeca-1,6-diene complexes as mixtures of two diastereomers in high yields, the analogous methoxycarbonyl-substituted precursors gave only one diastereomer.

Introduction

Cyclopropane derivatives are found throughout nature and their importance in chemistry is growing constantly.[1] Among these substances are a number of highly cytotoxic spirocyclopropanated oligohydroindenes with representative examples like Illudin S (**1**)[2] and Ptaquiloside (**2**)[3] (Figure 1).

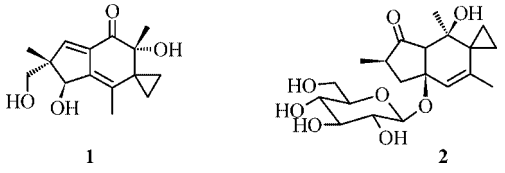

Figure 1. Naturally occurring cytotoxic spirocyclopropanated oligohydroindene derivatives.[2,3]

Both compounds are highly potent alkylating agents towards the nucleobases of DNA. The mechanism of their action is reasonably well understood, and these compounds have served as lead structures for the development of new chemotherapeutics.[4] Although a number of approaches to such compounds have been developed, principally new ways of assembling the basic skeleton of this class of compounds and analogues thereof are still of interest.

As part of our ongoing program on metal-catalyzed and -mediated cocyclizations aimed at the construction of stripped-down analogues of natural products,[5,6] we envisioned to prepare spirocyclopropanated oligocyclic compounds through cobalt(I)-mediated intramolecular [2+2+2] cocyclizations of readily accessible acyclic enediynes[7] incorporating methylenecyclopropane (MCP) and bicyclopropylidene (BCP)[8] moieties. Whereas methylenecyclopropane and bicyclopropylidene derivatives have been successfully employed in cobalt-mediated [2+2+1] cocyclizations known as the Pauson–Khand reaction,[9] to the best of our knowledge no examples of cobalt(I)-mediated [2+2+2] cocyclizations involving such partners have been recorded in the literature. Herein, we describe the first examples of cobalt(I)-mediated cocyclizations of various enediynes containing methylenecyclopropane or bicyclopropylidene units, providing an easy access to oligocycles containing either fused and spiroannelated cyclopropane rings or even both.

Results and Discussion

Several acyclic (methylenecyclopropyl)diynes were synthesized according to established protocols (Scheme 1). Treatment of an excess of 1,6-heptadiyne (**3**) in tetrahydrofuran (THF) with *n*-butyllithium led, after an equilibration period for the disappearance of the initially formed

[‡] For one of us (A. de M.), this is to be counted as Part 113 in the series "Cyclopropyl Building Blocks for Organic Synthesis". Part 112: F. Brackmann, D. S. Yufit, A. de Meijere, *Synthesis* **2005**, in press; Part 111: F. Brackmann, M. Es-Sayed, A. de Meijere, *Eur. J. Org. Chem.* **2005**, in press.

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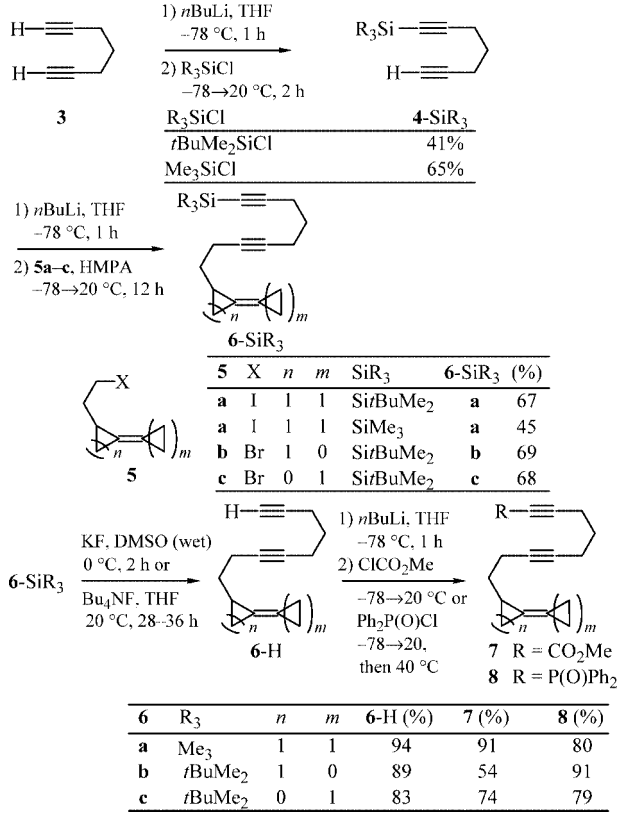
dianion, to a clean formation of the monoanion, which was subsequently trapped with a trialkylsilyl chloride (tBuMe$_2$SiCl or Me$_3$SiCl) in moderate to good yield.[10] The monosilylated diynes **4**-SiR$_3$ were once again deprotonated with n-butyllithium, and the resulting lithium acetylides alkylated with (methylenecyclopropyl)ethyl and (bicyclopropylidenyl)-ethyl halides **5a**,[11a] **5b** and **5c**,[11b] which were prepared according to literature procedures. Addition of a stoichiometric amount of hexamethylphosphoric triamide (HMPA) proved to be essential for a successful alkylation with both the iodide **5a** and the bromides **5b**,**c**.



5	X	n	m	SiR$_3$	6-SiR$_3$	(%)
a	I	1	1	SitBuMe$_2$	**a**	67
a	I	1	1	SiMe$_3$	**a**	45
b	Br	1	0	SitBuMe$_2$	**b**	69
c	Br	0	1	SitBuMe$_2$	**c**	68

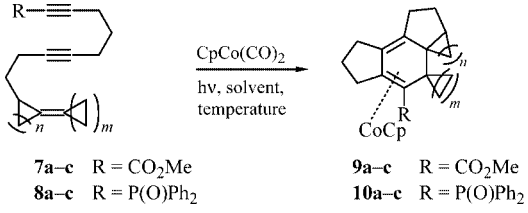
6	R$_3$	n	m	6-H (%)	7 (%)	8 (%)
a	Me$_3$	1	1	94	91	80
b	tBuMe$_2$	1	0	89	54	91
c	tBuMe$_2$	0	1	83	74	79

Scheme 1. Synthesis of enediynes with methylenecyclopropane moieties.

Further functionalization of the thus obtained enediynes was accomplished by fluoride-induced protiodesilylation (with KF in wet DMSO for removal of the Me$_3$Si, Bu$_4$NF in THF for removal of the tBuMe$_2$Si group), subsequent deprotonation of the resulting terminal alkyne and electrophilic substitution with methyl chloroformate or diphenylphosphinic chloride, respectively. Whereas methyl chloroformate reacted readily at –78 °C, inverse addition at –20 °C of the lithium acetylide to an excess of the diphenylphosphinic chloride was found to be most effective.

The initial cocyclization was carried out with the enediyne **6a**-SiMe$_3$, featuring a bicyclopropylidene unit and a trimethylsilyl group. Upon exposure to a stoichiometric amount of [CpCo(CO)$_2$] in refluxing xylene under irradiation, TLC monitoring disclosed consumption of the starting material, but the reaction eventually only led to intractable materials. The desilylated enediyne **6a**-H, when subjected to the same cyclization conditions, afforded only traces of a red-brown oil. Due to unavoidable line broadening, the ^{1}H-NMR spectrum remained unassignable, but the ^{13}C-NMR spectrum showed the characteristic signals of an η^4-dienecobalt complex. Interestingly, six distinct cyclopropane signals were observed showing clearly the presence of two intact cyclopropane moieties.

Since the presence of a phosphane oxide or an ester group at the alkyne terminus previously had been shown to dramatically enhance the yields of cobalt-mediated cocyclizations of ene- and allenediynes, as well as the stability of the product complexes,[7c,7e,7f] reactions were conducted with the advanced precursors **7a** and **8a**. The transformation of **8a** proceeded smoothly under irradiation in boiling THF within 1.5 h to give an inseparable mixture of two diastereomers **10a** in excellent yield (94%). The yield of the cyclization product **9a** from **7a** was significantly lower (42%), but surprisingly only one diastereomer was isolated (Scheme 2, Table 1).



7a–c R = CO$_2$Me
8a–c R = P(O)Ph$_2$

9a–c R = CO$_2$Me
10a–c R = P(O)Ph$_2$

Scheme 2. Cobalt(I)-mediated intramolecular cocyclization reactions of enediynes with methylenecyclopropane moieties. For details see Table 1.

Under the same conditions, the enediynes **7b**, **8b**, as well as **7c**, **8c** with methylenecyclopropane units attached through the cyclopropane ring or the double bond, respec-

Table 1. Cobalt(I)-mediated intramolecular cocyclization reactions of enediynes with methylenecyclopropane moieties (see Scheme 2).

Precursor	R	n	m	Solvent	Temp. [°C]	Product	Yield (%)	dr[a]
6a-SiMe$_3$	Me$_3$Si	1	1	xylene	139	**9a**	–	–
6a-H	H	1	1	toluene	110	**9a**	trace	–
7a	CO$_2$Me	1	1	THF	66	**9a**	42	1:0
8a	P(O)Ph$_2$	1	1	THF	66	**10a**	94	1.5:1
7b	CO$_2$Me	1	0	THF	66	**9b**	31	1:0
8b	P(O)Ph$_2$	1	0	THF	66	**10b**	85	2.1:1
7c	CO$_2$Me	0	1	THF	66	**9c**	47	1:0
8c	P(O)Ph$_2$	0	1	THF	66	**10c**	91	1.8:1

[a] Diastereomeric ratio according to ^{1}H NMR spectrum.

tively, behaved analogously. Consistently, the phosphane oxide-terminated precursors **8b** and **8c** gave the oligocyclization products **10b** and **10c** in very high yields (85 and 91%, respectively), and as inseparable mixtures of diastereomers, whereas the methoxycarbonyl-substituted precursors **7b** and **7c** gave the oligocyclic diene complexes **9b** and **9c** in moderate yields (31 and 47%, respectively), yet as single diastereomers. When the oligocyclization of **7c** was performed in benzene or xylene, respectively, the yield of **9c** was slightly lower, and the diastereomeric ratio was the same. The underlying reason for the diastereoselectivity in the formation of **9a**, **9b** and **9c** is not clear at present. The initial formation of the second diastereomer – taking the reduced yield into account – appears to be possible, but selective decomposition under either the reaction conditions or during chromatographic purification may be a possibility.

Although all of the complexes were conveniently handled and initially stable towards oxygen and silica gel, they did show distinct signs of degradation upon prolonged efforts to grow good quality crystals.

It is noteworthy that the oligocyclizations of the enediynes **7b**, **8b** and **7c**, **8c** with ring-attached methylenecyclopropane units, require longer reaction times than those of the precursors **7a**, **8a** with bicyclopropylidene units thus reflecting probably the decreased amount of strain release in the reactions of the former molecules.

In accordance with previous findings,[7e,7f] the configurations of the obtained single diastereomer complexes **9a**, **9b**, **9c** were assumed to be *exo*. This was supported by an NOE study of complex **9b**, which did not exhibit any interaction between the hydrogen atoms of the cyclopropyl methylene group and the protons of the Cp ligand on cobalt. In addition, a suitable crystal of **9a** (Figure 2) was subjected to an X-ray crystal structure analysis, which unambiguously proved the *exo* configuration.[12]

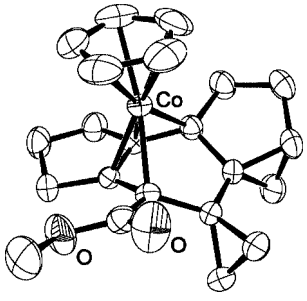


Figure 2. Structure of compound **9a** in the crystal.[12]

It is also noteworthy that no products arising from an opening of a cyclopropane unit, by way of a cyclopropylmethyl to homoallyl rearrangement at an intermediate stage, were observed. The cobalt-mediated transformations of all the enediyne precursors with methylenecyclopropane moieties are consistent with previous observations according to which oligocyclizations of acyclic enediynes bearing a phosphane oxide or ester group at the alkyne terminus predominantly led to *exo*-configured cyclohexadiene complexes.[7e,7f] These new results are also in agreement with earlier assumptions concerning the mechanism of these transformations. The observation that in the current cases the methoxycarbonyl-substituted enediynes provided the *exo*-configured complexes exclusively, may be attributed to an instability of the *endo* complexes either under the reaction conditions or during the purification.

In conclusion, methylenecyclopropyldiynes with an electron-withdrawing substituent at the acetylenic terminus are suitable substrates for cobalt-mediated intramolecular [2+2+2] cocyclizations to provide both cyclopropane-fused and spirocyclopropanated tricyclic skeletons in moderate to excellent yields.

Experimental Section

General Methods: Reactions were carried out under argon in flame-dried glassware, with magnetic stirring and degassed anhydrous solvents. All commercially available reagents were used without further purification unless otherwise noted. All solvents were reagent grade and distilled under positive pressure of dry nitrogen before use. THF was distilled from sodium/benzophenone. Xylenes and benzene were distilled from CaH_2. Solid reagents were dried in vacuo (0.5 to 0.1 Torr). Starting materials: Hepta-1,6-diyne (**3**),[13] 2-(2-iodoethyl)bicyclopropylidene (**5a**),[11a] and 1-bromo-4-cyclopropylidenebutane (**5c**)[11b] were prepared according to previously published procedures. Thin layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel or Macherey–Nagel TLC plates Alugram® Sil G/UV254. Detection under UV-light at 254 nm, development with MOPA reagent (10%, solution in ethanol). Merck Geduran SI 60 Å silica gel (35–70 μm) and Merck Silica 60 (0.063–0.200 mm, 70–230 mesh ASTM) was used for column chromatography. The dimensions of the columns are given as "diameter × height of the silica column". ^{1}H NMR and ^{13}C NMR spectra were recorded with 200 MHz Bruker AC 200, 250 MHz Bruker AM 250, 400 MHz Bruker ARX 400, 500 MHz Varian Inova 500 and 600 MHz Varian Inova 600 spectrometers. Chemical shifts are given in ppm, referenced to the residual proton resonances of the solvents (δ = 7.26 ppm for $CHCl_3$; δ = 7.16 ppm for C_6D_5H). Coupling constants (J) are given in Hertz (Hz). The terms m, s, d, t, q, quint refer to multiplet, singlet, doublet, triplet, quartet, quintet; br. means that the signal is broad. Elemental analyses were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie or by the Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen. Infrared spectra (IR) were recorded with a Bruker Tensor 27 spectrometer or Bruker IFS 66, respectively. Absorbance frequencies are given at the peak maximum. Mass spectra were acquired with a Finnigan MAT 95 spectrometer. High resolution mass data (HRMS) were obtained by preselected-ion peak matching at $R \approx 10000$ to be within ± 2 ppm of the exact mass. Melting points were obtained on a Büchi capillary apparatus and were not corrected.

***tert*-Butyl(hepta-1,6-diynyl)dimethylsilane (4-Si*t*BuMe$_2$):** To a solution of diyne **3** (13.821 g, 17.18 mL, 150 mmol) in anhydrous THF (350 mL) was added *n*BuLi (165 mmol, 100 mL of a 1.65 M solution in hexane) at –78 °C over a period of 40 min. After an additional stirring for 20 min, TBDMSCl (154 mmol, 42.23 g of a 55% solution in toluene) was added at this temp. in 10 min, and the reaction mixture was warmed to ambient temp. over a period of 2 h. The reaction mixture was poured into ice-cold water (200 mL), and the aqueous layer was extracted with diethyl ether (2 × 100 mL). The

combined organic extracts were washed with brine (100 mL), dried, concentrated under reduced pressure and distilled in vacuo to give **4**-Si*t*BuMe$_2$ (12.736 g, 41%) as a colorless oil, b. p. 48–52 °C (0.5 mbar). ^{1}H NMR: δ = 0.07 (s, 6 H, 2 CH$_3$), 0.91 (s, 9 H, 3 CH$_3$), 1.72 (quint, J = 7.0 Hz, 2 H, CH$_2$), 1.95 (t, J = 2.6 Hz, 1 H, ≡CH), 2.30 (td, J = 2.6, 7.0 Hz, 2 H, CH$_2$), 2.35 (t, J = 7.0 Hz, 2 H, CH$_2$) ppm. ^{13}C NMR: δ = –4.5 (2 CH$_3$), 16.5 (C), 17.4 (CH$_2$), 18.9 (CH$_2$), 26.0 (3 CH$_3$), 27.6 (CH$_2$), 68.8 (C), 83.3 (C), 83.5 (C), 106.5 (C) ppm.

2-(2′-Bromoethyl)methylenecyclopropane (5b): To a solution of triphenylphosphane (6.61 g, 25.2 mmol) in anhydrous dichloromethane (60 mL) was added bromine (1.28 mL, 24.9 mmol) at –10 °C over a period of 10 min. After an additional stirring for 30 min, a mixture of pyridine (1.91 g, 24.1 mmol) and 2-(methylenecyclopropyl)ethan-1-ol (2.37 g, 24.1 mmol) was added dropwise. The reaction mixture was allowed to reach room temp. overnight and water (50 mL) was added. The aqueous phase was extracted with dichloromethane (2 × 50 mL), the combined organic extracts were washed with brine (100 mL) and dried with MgSO$_4$. The solvent was distilled off using a 20 cm Vigreux column, the precipitate was filtered off and the resulting oil subjected to column chromatography (30 × 3 cm, pentane/diethyl ether, 20:1, R_f = 0.9) to give **5a** (2.58 g, 66%) as a colorless oil containing residual pentane. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.76–0.90 (m, 1 H, 2-H), 1.15–1.27 (m, 1 H, 3-H), 1.43–1.64 (m, 1 H, 3-H), 1.78–2.01 (m, 2 H, 1′-H), 3.43 (t, ^3J = 7.0 Hz, 2 H, 2′-H), 5.37 (br. s, 1 H, C=C*H*H), 5.42 (br. s, 1 H, C=CH*H*) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$, DEPT): δ = 9.33 (–, *c*Pr-C), 14.09 (+, *c*Pr-C), 32.76 (–, C-1′*), 36.31 (–, C-2′*), 103.58 (–, C=*C*H$_2$), 134.87 (C$_{quat}$, *c*Pr-C) ppm.

General Procedure for the Alkylation of Terminal Alkynes with Alkyl Bromides (GP1): A solution of 5.00 mmol of the terminal alkyne in 10 mL of anhydrous THF is added to a stirred solution of 5.25 mL of butyllithium (2.5 M in hexane) at –78 °C, and the mixture is stirred for 1 h. After dropwise addition of 896 mg (5.00 mmol) of hexamethylphosphoric triamide, the mixture was stirred for an additional 30 min and then 5.00 mmol of the respective alkyl halide was added slowly. The reaction mixture was warmed to room temperature overnight, the reaction quenched with water (10 mL), and the aqueous phase was extracted with diethyl ether (3 × 15 mL). The combined organic layers were washed with brine, dried with MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography eluting with pentane/ether.

General Procedure for the Protiodesilylation of *t*BuMe$_2$Si-Protected Alkynes (GP2): To a solution of 1.00 mmol of the silyl-protected alkyne in 5 mL of THF was added dropwise 2.00 mmol (2.00 mL, 1 M in THF cont. 3% H$_2$O, Aldrich) of tetrabutylammonium fluoride solution at 0 °C. The resulting solution was stirred until the starting material could not be detected any more (TLC monitoring), the reaction quenched with 5 mL of water, and the aqueous layer was extracted with pentane (5 × 10 mL). The combined organic extracts were washed with brine, dried with MgSO$_4$ and the solvents were removed by careful distillation through a Vigreux column. The resulting residue was purified by column chromatography eluting with pentane.

General Procedure for the Preparation of Methyl Alkynylcarboxylates (GP3): To a solution of 1.50 mmol of the respective terminal alkyne in 5 mL of anhydrous THF was added dropwise a solution of 1.50 mmol of butyllithium (2.5 M in hexane) at –78 °C, and the mixture stirred at this temperature for 30 min. Subsequently, 284 mg (3.00 mmol) of methyl chloroformate was added, and the mixture was stirred for an additional 30 min before letting it warm up to room temperature. The mixture was poured into ice water, and the aqueous phase was extracted with diethyl ether (3 × 10 mL). After washing the combined organic extracts with brine, they were dried with MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography eluting with pentane/ether.

General Procedure for the Preparation of Alkynyldiphenylphosphane Oxides (GP4): To a solution of 1.00 mmol of the respective terminal alkyne in 3 mL of anhydrous THF was added dropwise a solution of 1.00 mmol of butyllithium (2.5 M in hexane) at –78 °C, and the mixture was stirred for 30 min at this temperature. The resulting solution was transferred dropwise through cannula to a solution of 284 mg (1.20 mmol) of diphenylphosphinic chloride in 5 mL of anhydrous THF kept at –20 °C. Then the mixture was placed in a water bath kept at 40 °C, and stirred for an additional 15 min. The mixture was poured into ice water and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). After washing the combined organic extracts with brine, they were dried with MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography eluting with pentane/ethyl acetate.

General Procedure for the Cobalt-Mediated Intramolecular Oligocyclization of Enediynes (GP5): A solution of 250 μmol of the respective enediyne in 5 mL of anhydrous solvent in a round-bottomed flask, equipped with a reflux condenser, which had been passivated with hexamethyldisilazane was carefully deoxygenated by three freeze-pump-thaw cycles and heated under reflux. Then, 30 μL (250 μmol) of cyclopentadienyl(dicarbonyl)cobalt was added, and the mixture irradiated by means of a projector lamp (General Electric GE ELH 120 V/300 W, 80% of its power) until the starting material had been consumed (TLC monitoring). Subsequently, the mixture was cooled to room temperature and the solvent removed by vacuum transfer. The residue was purified by column chromatography.

[(9-Bicyclopropyliden-2-yl)nona-1,6-diynyl]-*tert*-butyldimethylsilane (6a-Si*t*BuMe$_2$): According to GP1, diyne **4**-Si*t*BuMe$_2$ (9.52 g, 46.1 mmol), *n*BuLi (29.4 mL, 48.5 mmol, 1.65 M in hexanes) and HMPT (9.3 mL) were reacted with iodide **5a** (10.83 g, 46.3 mmol) in THF. Column chromatography (20 × 6 cm, hexane/benzene, 10:1, R_f = 0.38) of the reaction mixture gave enediyne **6a**-Si*t*BuMe$_2$ (9.66 g, 67%) as a colorless oil. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.07 (s, 6 H, 2 CH$_3$), 0.92 (s, 9 H, 3 CH$_3$), 1.16 (q, J = 2.0 Hz, 4 H, *c*Pr-H), 1.36 (tt, J = 2.1, 8.0 Hz, 1 H, *c*Pr-H), 1.50–1.76 (m, 6 H), 2.23–2.38 (m, 6 H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = –4.5 (2 CH$_3$), 2.8 (CH$_2$), 2.9 (CH$_2$), 9.7 (CH$_2$), 15.4 (CH), 16.5 (C$_{quat}$), 17.9 (CH$_2$), 18.9 (CH$_2$), 19.0 (CH$_2$), 26.0 (3 CH$_3$), 28.2 (CH$_2$), 33.0 (CH$_2$), 79.1 (C$_{quat}$), 80.6 (C$_{quat}$), 82.9 (C$_{quat}$), 107.0 (C$_{quat}$), 110.0 (C$_{quat}$), 115.3 (C$_{quat}$) ppm.

[(9-Bicyclopropyliden-2-yl)nona-1,6-diynyl]trimethylsilane (6a-SiMe$_3$): According to GP1, diyne **4**-SiMe$_3$ (4.08 g, 24.8 mmol), *n*BuLi (10.8 mL, 25.2 mmol, 2.33 M in hexanes) and HMPT (5 mL) were reacted with iodide **5a** (6.32 g, 27 mmol) in THF. Column chromatography (20 × 6 cm, hexane/benzene, 10:1.5, R_f = 0.39) of the reaction mixture gave enediyne **6a**-SiMe$_3$ (3.05 g, 45%) as a colorless oil. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.13 (s, 9 H, 3 CH$_3$), 0.85–0.93 (m, 1 H, *c*Pr-H), 1.19 (q, J = 1.9 Hz, 4 H, *c*Pr-H), 1.39 (tt, J = 2.0, 7.9 Hz, 1 H, *c*Pr-H), 1.49–1.79 (m, 5 H), 2.19–2.40 (m, 6 H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 0.1 (3 CH$_3$), 2.8 (CH$_2$), 2.9 (CH$_2$), 9.7 (CH$_2$), 15.4 (CH), 17.9 (CH$_2$), 18.9 (CH$_2$), 19.0 (CH$_2$), 28.1 (CH$_2$), 33.0 (CH$_2$), 79.1 (C$_{quat}$), 80.6 (C$_{quat}$), 84.8 (C$_{quat}$), 106.6 (C$_{quat}$), 110.0 (C$_{quat}$), 115.3 (C$_{quat}$) ppm.

2-(Nona-3,8-diynyl)bicyclopropylidene (6a-H): A solution of **6a**-SiMe$_3$ (0.5 g, 1.85 mmol) in DMSO (20 mL) was stirred for 2 h in

the presence of potassium fluoride (0.09 g, 1.5 mmol). After being diluted with diethyl ether, the reaction mixture was washed with water. The organic layer was dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash chromatography (light petroleum/diethyl ether, 99:1) to afford **6a**-H (0.345 g, 94%). IR (film): $\tilde{\nu}$ = 3302 cm^{-1}, 3050, 2978, 2933, 2854, 2119, 1433, 960, 639. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88–0.92 (m, 1 H, *c*Pr-H), 1.15–1.19 (m, 4 H, *c*Pr-H), 1.35–1.40 (m, 1 H, *c*Pr-H), 1.55–1.64 (m, 3 H, *c*Pr-H, CH_2–*c*Pr), 1.71 (quint, J = 7.0 Hz, 2 H, CH_2), 1.96 (t, J = 2.5 Hz, 1 H, HC≡), 2.27–2.33 (m, 6 H, 3 × CH_2–C≡C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 2.8 (*c*Pr-C, CH_2), 2.9 (*c*Pr-C, CH_2), 9.7 (*c*Pr-C, CH_2), 15.4 (*c*Pr-C, CH), 17.5 (≡C–*C*H_2), 17.8 (≡C–*C*H_2), 18.9 (≡C–*C*H_2), 27.9 (CH_2), 33.0 (CH_2), 68.6 (≡CH), 78.9 (–C≡), 80.8 (–C≡), 83.8 (–C≡), 110.0 (*C*=C), 115.3 (C=*C*) ppm. $C_{15}H_{18}$ (198.3): calcd. C 90.85, H 9.15; found C 90.68, H 9.16.

Methyl 10-(Bicyclopropyliden-2-yl)deca-2,7-diynoate (7a): According to GP3, **6a**-H (198 mg, 1.0 mmol) and *n*BuLi (0.4 mL, 1.0 mmol, 2.5 M in hexane) in 5 mL of THF were treated with methyl chloroformate (0.189 g, 155 μL, 2.0 mmol) to afford, after work-up and purification by flash chromatography (light petroleum/ether, 95:5), **7a** (0.234 g, 91%). IR (film): $\tilde{\nu}$ = 3040 cm^{-1}, 2978, 2935, 2236, 1716, 1434, 1255, 1076, 959, 752. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.86–0.92 (m, 1 H, *c*Pr-H), 1.17–1.20 (m, 4 H, *c*Pr-H), 1.35–1.40 (m, 1 H, *c*Pr-H), 1.50–1.67 (m, 3 H, *c*Pr-H, CH_2–*c*Pr), 1.76 (quint, J = 7.1 Hz, 2 H, CH_2), 2.25–2.33 (m, 4 H, CH_2–C≡C–CH_2), 2.47 (t, J = 7.1 Hz, 2 H, CH_2≡C–CO_2Me), 3.76 (s, 3 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 2.8 (*c*Pr-C, CH_2), 3.0 (*c*Pr-C, CH_2), 9.8 (*c*Pr-C, CH_2), 15.4 (*c*Pr-C, CH), 17.7 (≡C–*C*H_2), 18.0 (≡C–*C*H_2), 18.9 (≡C–*C*H_2), 26.9 (CH_2), 32.9 (CH_2), 52.6 (OCH_3), 73.1 (–C≡), 78.3 (–C≡), 81.3 (–C≡), 89.0 (–C≡), 110.1 (*C*=C), 115.3 (C=*C*), 154.2 (C=O) ppm. $C_{17}H_{20}O_2$ (256.3): calcd. C 79.65, H 7.86; found C 79.57, H 8.02.

2-[9-(Diphenylphosphinoyl)nona-3,8-diynyl]bicyclopropylidene (8a): According to GP4, **6a**-H (0.345 g, 1.74 mmol) and *n*BuLi (0.7 mL, 1.74 mmol, 2.5 M in hexane) in 5 mL of THF were treated with diphenylphosphinic chloride (0.3 mL, 1.74 mmol, 1 equiv.). Work-up and purification by flash chromatography (light petroleum/AcOEt, 20:80) gave **8a** (0.553 g, 80%). IR (ATR): $\tilde{\nu}$ = 3054 cm^{-1}, 2975, 2929, 2852, 2359, 2193, 1438, 1206, 1120, 1106, 752, 723, 703, 695. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89–0.92 (m, 1 H, *c*Pr-H), 1.15–1.20 (m, 4 H, *c*Pr-H), 1.35–1.39 (m, 1 H, *c*Pr-H), 1.53–1.65 (m, 3 H, *c*Pr-H, CH_2–cPr), 1.81 (quint, J = 7.0 Hz, 2 H, CH_2), 2.26–2.34 (m, 4 H, CH_2–C≡C–CH_2), 2.60 [td, J = 7.3, 3.6 Hz, 2 H, CH_2≡C–P(O)Ph_2], 7.45–7.56 (m, 6 H, Ar-H), 7.80–7.86 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 2.8 (*c*Pr-C, CH_2), 2.9 (*c*Pr-C, CH_2), 9.8 (*c*Pr-C, CH_2), 15.4 (*c*Pr-C, CH), 18.7 (≡C–*C*H_2), 18.9 (≡C–*C*H_2), 19.0 (≡C–*C*H_2), 27.1 (CH_2), 33.1(CH_2), 73.9 (–C≡), 78.3 (–C≡), 81.3 (–C≡), 108.9 (C_{quat}), 110.1 (*C*=C), 115.4 (C=*C*), 128.6 (d, J_{CP} = 13 Hz, 4 C), 131.0 (d, J_{CP} = 11 Hz, 4 C), 132.1 (2 C), 133.4 (d, J_{CP} = 121 Hz, 2 C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.82 ppm.

(η^5-Cyclopentadienyl){methyl 3′,4′,8′,9′-η^4-spiro[cyclopropane-1,2′-tetracyclo[7.4.0.0^{1,12}.0^{4,8}]trideca-3′,8′-diene-3′-carboxylate]}cobalt (9a): According to the procedure GP5, enediyne **7a** (0.234 g, 0.91 mmol) in toluene (20 mL) was refluxed in the presence of [$CpCo(CO)_2$] (120 μL, 0.91 mmol). After removal of the solvent in vacuo, flash chromatography (pentane, then pentane/ether, 1:1) on deactivated alumina (4% H_2O) furnished **9a** (0.146 g, 42%). ^1H NMR (400 MHz, $CDCl_3$): δ = –0.33 to –0.26 (m, 1 H), –0.01 to 0.01 (m, 2 H), 0.15–0.31 (m, 1 H), 0.40–0.54 (m, 1 H), 1.16–3.44 (m, 12 H), 3.72 (s, 3 H), 4.59 (s, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.0 (*c*Pr-C, CH_2), 12.7 (*c*Pr-C, CH_2), 14.6 (*c*Pr-C, CH_2), 23.1 (C_{quat}), 24.6 (CH_2), 25.2 (*c*Pr-C, CH), 28.9 (CH_2), 29.1 (CH_2), 30.6 (CH_2), 33.5 (CH_2), 41.6 (C_{quat}), 50.7 (CH_3), 53.0 (C_{quat}), 74.9 (C_{quat}), 82.5 (5 C, Cp), 97.0 (C_{quat}), 98.1 (C_{quat}), 175.8 (C=O) ppm.

(η^5-Cyclopentadienyl){3′,4′,8′,9′-η^4-Spiro[cyclopropane-1,2′-diphenyl{tetracyclo[7.4.0.0^{1,12}.0^{4,8}]trideca-3′,8′-dien-3′-yl}phosphane oxide]}cobalt (10a): According to the procedure GP5, enediyne **8a** (0.250 g, 0.63 mmol) in THF (15 mL) was refluxed in the presence of [$CpCo(CO)_2$] (78 μL, 0.63 mmol). After removal of the solvent in vacuo, flash chromatography on deactivated alumina (4% H_2O) gave **10a** (0.307 g, 94%) as an inseparable mixture of diastereomers (*dr* = 1.5:1, ^1H NMR). Different attempts of separation allowed the isolation and the characterization of almost pure major compound **10a**: ^1H NMR (400 MHz, $CDCl_3$): δ = –0.83 to –0.72 (m, 1 H, *c*Pr-H), –0.63 to –0.58 (m, 1 H), –0.47 (dt, J = 15.2, 6.1 Hz, 1 H), (–0.25)–(0.35) (m, 1 H), 0.70 (tt, J = 8.2, 4.0 Hz, 1 H), 0.82 (dd, J = 8.1, 4.0 Hz, 1 H), 1.08 (dd, J = 8.1, 3.0 Hz, 1 H), 1.63 (tt, J = 9.8, 4.0 Hz, 1 H), 1.71 (dd, J = 13.7, 7.6 Hz, 1 H), 1.76 (tt, J = 9.8, 7.6 Hz, 1 H), 1.97 (dd, J = 13.7, 7.8 Hz, 1 H), 2.31–2.55 (m, 2 H), 2.35–2.72 (m, 2 H), 2.90 (dt, J = 14.7, 8.1 Hz, 1 H), 3.95–4.12 (m, 1 H), 4.49 (s, 5 H), 7.29–7.42 (m, 8 H), 8.20–8.35 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.2, 12.0, 16.6, 19.4, 19.6 (d, J_{CP} = 32 Hz), 23.7, 24.4, 27.4, 27.9, 29.7, 32.6, 46.4 (d, J_{CP} = 107 Hz), 74.1, 82.5 (5 C), 98.2 (d, J_{CP} = 12 Hz), 102.3, 127.6 (d, J_{CP} = 11 Hz, 2 C), 127.9 (d, J_{CP} = 10 Hz, 2 C), 130.5, 131.2, 131.3 (d, J_{CP} = 10 Hz, 2 C), 132.8 (d, J_{CP} = 188 Hz, 1 C), 132.9 (d, J_{CP} = 186 Hz, 1 C), 133.3 (d, J_{CP} = 8 Hz, 2 C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 33.7 ppm.

***tert*-Butyl(dimethyl)-9-(2′-methylenecyclopropyl)nona-1,6-diynylsilane (6b-Si*t*BuMe$_2$):** According to GP1, *tert*-butyl(1,6-heptadiynyl)-dimethylsilane (**4**-Si*t*BuMe$_2$, 1.24 g, 6.01 mmol), *n*BuLi (2.74 mL, 6.30 mmol, 2.3 M in hexanes) and HMPA (1.08 g, 6.03 mmol) were reacted with 1-(2′-bromoethyl)-2-methylenecyclopropane (**5b**, 966 mg, 6.00 mmol) in 15 mL anhydrous THF. Column chromatography on silica gel (4 × 20 cm, pentane, R_f = 0.15) gave **6b**-Si*t*BuMe$_2$ (1.19 g, 69%) as a colorless oil. IR (film): $\tilde{\nu}$ = 2950 cm^{-1}, 2930, 2857, 2173, 1470, 1458, 1363, 1251, 1009, 886, 775, 682. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.07 [s, 6 H, $Si(CH_3)_2$], 0.73–0.82 (m, 1 H, 1′-H), 0.92 [s, 9 H, $C(CH_3)_3$], 1.20–1.30 (m, 1 H, 3′-H), 1.49–1.58 (m, 3 H, 3′-H, 9-H), 1.71 (tt, ^3J = 7.1, 7.1 Hz, 2 H, 4-H), 2.23–2.39 (m, 6 H, 3-H, 5-H, 8-H), 5.35 (br. s, 1 H, C=C*H*H), 5.41 (br. s, 1 H, C=CH*H*). ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = –4.49 [+, 2 C, $Si(CH_3)$], 9.37 (–, *c*Pr-C), 15.10 (+, *c*Pr-C), 16.49 [C_{quat}, *C*$(CH_3)_3$], 17.88 (–, C-5*), 18.80 (–, C-3*), 18.99 (–, C-8*), 26.05 [+, 3 C, C(*C*$H_3)_3$], 28.19 (–, C-4), 32.71 (–, C-9), 79.31 (C_{quat}, C-7), 80.42 (C_{quat}, C-6), 82.95 (C_{quat}, C-1), 102.86 (–, C=*C*H_2), 107.04 (C_{quat}, C-2), 136.27 (C_{quat}, *c*Pr-C) ppm. MS (200 eV, DCI, NH_3): *m*/*z* (%) = 304 (100) [M + NH_4^+], 287 (3) [M + H^+].

1-Methylene-2-(nona-3′,8′-diynyl)cyclopropane (6b-H): According to GP2, a solution of *tert*-butyl(dimethyl)-9-(2′-methylenecyclopropyl)nona-1,6-diynylsilane (**6b**-Si*t*BuMe$_2$, 1.38 g, 4.82 mmol) in 25 mL of THF was treated with TBAF (9.60 mL, 9.60 mmol, 1 M in THF containing 3% H_2O) and stirred for 36 h. Column chromatography on silica gel (3 × 30 cm, pentane, R_f = 0.20) gave **6b**-H (736 mg, ~89%) as a colorless liquid, containing residual pentane, which was used directly. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.72–0.81 (m, 1 H, 2-H), 1.17–1.28 (m, 1 H, 3-H), 1.44–1.58 (m, 3 H, 3-H, 1′-H), 1.71 (tt, ^3J = 7.0, 7.0 Hz, 2 H, 6′-H), 1.95 (t, ^4J = 2.6 Hz, 1 H, 9′-H), 2.20–2.35 (m, 6 H, 2′-H, 5′-H, 7′-H), 5.34 (br. s, 1 H, C=C*H*H), 5.41 (br. s, 1 H, C=CH*H*) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 9.36 (–, *c*Pr-C), 15.08 (+, *c*Pr-C),

17.47 (–, C-2′*), 17.81 (–, C-7′*), 18.78 (–, C-5′*), 27.89 (–, C-6′), 32.70 (–, C-1′), 68.62 (+, C-9′), 79.09 (C_{quat}, C-3′), 80.55 (C_{quat}, C-4′), 83.72 (C_{quat}, C-8′), 102.85 (–, C=*C*H_2), 136.23 (C_{quat}, *c*Pr-C) ppm.

Methyl 10-(2′-Methylenecyclopropyl)deca-2,7-diynoate (7b): According to GP3, 1-methylene-2-(nona-3′,8′-diynyl)cyclopropane (**6b**-H, 345 mg, 2.00 mmol) and *n*BuLi (800 μL, 2.00 mmol, 2.5 M in hexane) were treated with methyl chloroformate (380 mg, 4.02 mmol) in 7 mL of anhydrous THF. Column chromatography on silica gel (2 × 30 cm, pentane/diethyl ether, 10:1, R_f = 0.55) yielded **7b** (248 mg, 54%) as a colorless oil. IR (film): $\tilde{\nu}$ = 2990 cm^{-1}, 2935, 2866, 2839, 2361, 2237, 1717, 1434, 1254, 1077, 889, 752, 670. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.71–0.80 (m, 1 H, 1′-H), 1.17–1.29 (m, 1 H, 3′-H), 1.42–1.56 (m, 3 H, 10-H, 3′-H), 1.73 (tt, ^3J = 7.0, 7.0 Hz, 2 H, 5-H), 2.17–2.32 (m, 4 H, 6-H, 9-H), 2.44 (t, ^3J = 7.0 Hz, 2 H, 4-H), 3.73 (s, 3 H, OCH_3), 5.33 (br. s, 1 H, C=C*H*H), 5.40 (br. s, 1 H, C=CH*H*) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 9.32 (–, *c*Pr-C), 15.02 (+, *c*Pr-C), 17.62 (–, C-9*), 17.92 (–, C-4*), 18.71 (–, C-6*), 26.90 (–, C-5), 32.60 (–, C-10), 52.51 (+, OCH_3), 73.08 (C_{quat}, C-2), 78.45 (C_{quat}, C-8), 81.07 (C_{quat}, C-7), 88.85 (C_{quat}, C-3), 102.86 (–, C=*C*H_2), 136.12 (C_{quat}, *c*Pr-C), 154.07 (C_{quat}, C=O) ppm. MS (200 eV, DCI, NH_3): *m*/*z* (%) = 478 (1) [2 M + NH_4^+], 365 (3) [M + NH_4^+ + NH_3], 248 (100) [M + NH_4^+].

[9-(2′-Methylenecyclopropyl)nona-1,6-diynyl](diphenyl)phosphane Oxide (8b): According to GP4, 1-methylene-2-(nona-3′,8′-diynyl) cyclopropane (**6b**-H, 326 mg, 1.89 mmol) was reacted with *n*BuLi (760 μL, 1.90 mmol, 2.5 M in hexane) in 7 mL of THF and the reaction mixture added onto diphenylphosphinoyl chloride (537 mg, 2.27 mmol) in 10 mL of THF. Column chromatography on silica gel [3 × 30 cm, EtOAc/pentane, 7:3, R_f = 0.60 (EtOAc)] gave **8b** (640 mg, 91%) as a pale yellow oil. IR (film): $\tilde{\nu}$ = 3057 cm^{-1}, 2989, 2935, 2194, 1719, 1590, 1483, 1437, 1308, 1208, 1123, 1103, 1067, 1027, 997, 955, 888, 754, 725, 697, 639, 606, 539. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.69–0.80 (m, 1 H, 1′-H), 1.16–1.28 (m, 1 H, 3′-H), 1.41–1.57 (m, 3 H, 9-H, 3′-H), 1.77 (tt, ^3J = 7.0, 7.0 Hz, 2 H, 4-H), 2.16–2.33 (m, 4 H, 5-H, 8-H), 2.56 (td, ^3J = 7.0, $^4J_{PH}$ = 3.4 Hz, 2 H, 3-H), 5.32 (br. s, 1 H, C=C*H*H), 5.39 (br. s, 1 H, C=CH*H*), 7.38–7.58 (m, 6 H, Ar-H), 7.78–7.90 (m, 4 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 9.39 (–, *c*Pr-C), 15.05 (+, *c*Pr-C), 18.01 (–, C-8*), 18.76 (–, 2 C, C-5*, C-3*), 26.94 (–, C-4), 32.63 (–, C-9), 73.91 (C_{quat}, C-2), 78.40 (C_{quat}, C-7), 81.26 (C_{quat}, C-6), 102.94 (–, C=*C*H_2), 108.75 (C_{quat}, d, $^1J_{PC}$ = 30.5 Hz, C-1), 128.53 (+, d, $^3J_{PC}$ = 13.7 Hz, 4 C, Ar-C), 130.80 (+, d, $^2J_{PC}$ = 11.9 Hz, 4 C, Ar-C), 132.05 (+, d, $^4J_{PC}$ = 2.9 Hz, 2 C, Ar-C), 133.22 (C_{quat}, d, $^1J_{PC}$ = 123.9 Hz, 2 C, Ar-C), 136.14 (C_{quat}, *c*Pr-C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 372 (11) [M^+], 371 (33) [M^+ – H], 343 (6) [M^+ – C_2H_5], 305 (7), 253 (25), 240 (16), 201 (100) [$P(O)(C_6H_5)_2^+$], 183 (19), 170 (26), 155 (29), 115 (30), 77 (28). $C_{25}H_{25}OP$ (372.4): calcd. C 80.62, H 6.77; found C 80.50, H 6.52.

(η^5-Cyclopentadienyl)(methyl 3,4,8,9-η^4-tetracyclo[7.4.0.0^{1,12}.0^{4,8}]-trideca-3,8-diene-3-carboxylate)cobalt (9b): According to GP5, **7b** (127 mg, 551 μmol) were treated with $CpCo(CO)_2$ (66 μL, 551 μmol) in 10 mL of deoxygenated THF and irradiated for 6 h at 66 °C. Column chromatography on aluminum oxide (4% H_2O, 2 × 30 cm, pentane/diethyl ether, 10:1, R_f = 0.55) gave **9b** (60.5 mg, 31%) as a dark-red oil. IR (film): $\tilde{\nu}$ = 2985 cm^{-1}, 2930, 2854, 1688, 1432, 1249, 1223, 1161, 805. ^{1}H NMR (250 MHz, C_6H_6): δ = 0.32–0.44 (m, 2 H, *c*Pr-H), 0.49–0.56 (m, 1 H, *c*Pr-H), 1.02–1.43 (m, 4 H, 6-H, 11-H), 1.76–1.89 (m, 1 H, 2-H), 2.05–2.64 (m, 6 H, 5-H, 7-H, 10-H), 3.52 (s, 3 H, OCH_3), 3.61–3.79 (m, 1 H, 2-H), 4.49 (s, 5 H, Cp-H). ^{13}C NMR (62.9 MHz, C_6H_6, DEPT): 14.56(–, *c*Pr-C), 24.32 (–), 26.69 (+, *c*Pr-C), 27.55 (–), 28.53 (–), 30.00 (–), 31.72 (–), 33.35 (C_{quat}, C-1), 35.20 (–), 46.84 (C_{quat}, C-3*), 50.22 (+, OCH_3), 74.65 (C_{quat}, C-4*), 81.72 (+, 5 C, Cp-C), 95.83 (C_{quat}, C-9*), 99.27 (C_{quat}, C-8*), 176.00 (C_{quat}, C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 354 (100) [M^+], 337 (5), 282 (12), 252 (6), 225 (8), 199 (99) [M^+ – C_5H_5 – Co – OCH_3], 171 (15) [M^+ – C_5H_5 – Co – CO_2CH_3], 165 (9), 141 (13), 128 (15), 124 (12), 115 (10), 91 (5), 59 (9), 41 (3). $C_{20}H_{23}CoO_2$ (354.3): calcd.: 354.1030; found 354.1030 (correct HRMS).

(η^5-Cyclopentadienyl)(3,4,8,9-η^4-diphenyl{tetracyclo[7.4.0.0^{1,12}.0^{4,8}]-trideca-3,8-dien-3-yl}phosphane oxide)cobalt (10b): According to GP5, **8b** (93 mg, 250 μmol) was treated with $[CpCo(CO)_2]$ (30 μL, 250 μmol) in 5 mL of deoxygenated THF and irradiated for 6 h at 66 °C. Column chromatography on aluminum oxide [10% H_2O, 2 × 30 cm, EtOAc/pentane, 7:3, R_f = 0.60 (EtOAc)] gave **10b** (105 mg, 85%) as a dark-red oil consisting of two diastereomers (*dr* = 2.1:1, ^{1}H NMR). IR (film): $\tilde{\nu}$ = 3075 cm^{-1}, 3053, 2927, 2847, 1435, 1170, 1112, 1099, 812, 697. ^{1}H NMR (250 MHz, C_6H_6, only characteristic data): δ = –0.12 to 0.06 (m, 1 H, *c*Pr-H_{minor}), 0.27–0.45 (m, 2 H *c*Pr-H_{minor}) 0.45–0.54 (m, 1 H *c*Pr-H_{major}), 0.58–0.70 (m, 1 H *c*Pr-H_{major}), 4.72 (s, 5 H, Cp-H_{minor}), 4.76 (s, 5 H, Cp-H_{major}), 6.98–7.19 (m, 2 × 6 H, Ar-H), 7.69–7.90 (m, 6 H, Ar-H), 8.14–8.36 (m, 2 H, Ar-H_{minor}) ppm. ^{13}C NMR (150.8 MHz, C_6H_6, APT, only characteristic data): δ = 9.53 (–, *c*Pr-C_{major}), 18.14 (–, *c*Pr-C_{minor}), 24.50 (+, *c*Pr-C_{major}), 26.95 (+, *c*Pr-C_{minor}), 73.81 (–, C=C_{minor}), 75.05 (–, C=C_{major}), 78.91 (–, C=C_{major}), 81.70 (–, C=C_{minor}), 82.24 (+, 5 C, Cp-C_{major}), 82.43 (+, 5 C, Cp-C_{minor}), 98.18 (–, C=C_{major}), 99.04 (–, C=C_{minor}), 103.21 (–, 2 C, C=C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 496 (100) [M^+], 430 (51) [M^+ – C_5H_6], 371 (48) [M^+ – C_5H_5 – Co], 201 (20). $C_{30}H_{30}CoOP$ (496.5): calcd.: 496.1366; found: 496.1366 (correct HRMS).

***tert*-Butyl(11-cyclopropylideneundeca-1,6-diynyl)dimethylsilane (6c-Si*t*BuMe$_2$):** According to GP5, *tert*-butyl(hepta-1,6-diynyl)dimethylsilane (**4**-Si*t*BuMe$_2$, 894 mg, 4.33 mmol), *n*BuLi (1.98 mL, 4.55 mmol, 2.3 M in hexanes) and HMPA (774 mg, 4.32 mmol) were reacted with 1-(4′-bromobutylidene)cyclopropane (**5c**, 760 mg, 4.34 mmol) in 10 mL of anhydrous THF. Column chromatography on silica gel (4 × 20 cm, pentane, R_f = 0.15) yielded **6c**-Si*t*BuMe$_2$ (883 mg, 68%) as a colorless oil. IR (film): $\tilde{\nu}$ = 3051 cm^{-1}, 2954, 2930, 2902, 2857, 2174, 1468, 1431, 1409, 1388, 1251, 1045, 1006, 962, 936, 840, 829, 808, 775, 680, 637, 595. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 6 H, $Si(CH_3)_2$], 0.92 [s, 9 H, $C(CH_3)_3$], 1.00–1.05 (m, 4 H, *c*Pr–H), 1.56–1.78 (m, 4 H, 4-H, 9-H), 2.11–2.40 (m, 8 H, 3-H, 5-H, 8-H, 10-H), 5.69–5.79 (m, 1 H, 11-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = –4.49 [+, 2 C, $Si(CH_3)$], 1.87 (–, *c*Pr-C), 2.17 (–, *c*Pr-C), 16.49 [C_{quat}, *C*$(CH_3)_3$], 17.90 (–, C-8*), 18.24 (–, C-5*), 18.99 (–, C-3*), 26.04 [+, 3 C, C(*C*$H_3)_3$], 28.27 (–, C-4**), 28.69 (–, C-10**), 30.90 (–, C-9**), 79.13 (C_{quat}, C-7), 80.71 (C_{quat}, C-6), 82.90 (C_{quat}, C-1), 107.10 (C_{quat}, C-2), 117.29 (+, C-11), 121.84 (C_{quat}, *c*Pr-C) ppm. MS (200 eV, DCI, NH_3): *m*/*z* (%) = 318 (100) [M + NH_4^+], 185 (5), 147 (9). $C_{20}H_{32}Si$ (300.6): calcd. C 79.92, H 10.73; found C 79.63, H 10.46.

1-(Undeca-5′,10′-diynylidene)cyclopropane (6c-H): According to GP2, a solution of *tert*-butyl(11-cyclopropylideneundeca-1,6-diynyl)dimethylsilane (**6c**-Si*t*BuMe$_2$, 968 mg, 3.22 mmol) in 15 mL of THF was treated with TBAF (6.45 mL, 6.45 mmol, 1 M in THF cont. 3% H_2O) and stirred for 28 h. Column chromatography on silica gel (3 × 30 cm, pentane, R_f = 0.20) gave **6c**-H (498 mg, 83%) as a colorless liquid. IR (film): $\tilde{\nu}$ = 3307 cm^{-1}, 3050, 2979, 2934, 2906, 2860, 2840, 2173, 2118, 1432, 1409, 1347, 1329, 1250, 1067, 1045, 1003, 962, 933, 839, 808, 775, 740, 679, 634. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.04 (m, 4 H, *c*Pr–H), 1.57–1.79 (m,

4 H, 3′-H, 8′-H), 1.95 (t, ^4J = 2.5 Hz, 1 H, 11′-H), 2.10–2.37 (m, 8 H, 2′-H, 4′-H, 7′-H, 9′-H), 5.66–5.78 (m, 1 H, 1′-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.86 (–, *c*Pr-C), 2.17 (–, *c*Pr-C), 17.47 (–, C-4′*), 17.83 (–, C-7′*), 18.23 (–, C-9′*), 28.27 (–, C-8′**), 28.69 (–, C-2′**), 30.90 (–, C-3′**), 68.58 (+, C-11′), 78.92 (C_{quat}, C-5′), 80.86 (C_{quat}, C-6′), 83.77 (C_{quat}, C-10′), 117.27 (+, C-1′), 121.85 (C_{quat}, *c*Pr-C) ppm. MS (200 eV, DCI, NH_3): *m*/*z* (%) = 204 (100) [M + NH_4^+], 187 (22) [M + H^+], 145 (9), 119 (21).

Methyl 12-Cyclopropylidenedodeca-2,7-diynoate (7c): According to GP3, 1-(undeca-5′,10′-diynylidene)cyclopropane (**6c**-H, 266 mg, 1.43 mmol) and *n*BuLi (580 μL, 1.45 mmol, 2.5 M in hexanes) were reacted with methyl chloroformate (283 mg, 2.99 mmol) in 5 mL of anhydrous THF. Column chromatography on silica gel (2 × 30 cm, pentane/diethyl ether, 10:1, R_f = 0.55) yielded **7c** (259 mg, 74%) as a pale yellow oil. IR (film): $\tilde{\nu}$ = 2981 cm^{-1}, 2952, 2931, 2859, 2236, 2172, 1717, 1435, 1253, 1077, 962, 933, 839, 809, 776, 748, 738. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.04 (m, 4 H, *c*Pr–H), 1.61 (tt, ^3J = 7.0, 7.0 Hz, 2 H, 5-H*), 1.74 (tt, ^3J = 7.0, 7.0 Hz, 2 H, 10-H*), 2.09–2.32 (m, 6 H, 6-H, 9-H, 11-H), 2.46 (t, ^3J = 7.0 Hz, 2 H, 4-H), 3.75 (s, 3 H, OCH_3), 5.68–5.77 (m, 1 H, 12-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.79 (–, *c*Pr-C), 2.10 (–, *c*Pr-C), 17.57 (–, C-4*), 17.89 (–, C-9*), 18.12 (–, C-6*), 26.94 (–, C-5**), 28.56 (–, C-11**), 30.86 (–, C-10**), 52.09 (+, OCH_3), 73.03 (C_{quat}, C-2), 78.51 (C_{quat}, C-7), 81.34 (C_{quat}, C-8), 88.87 (C_{quat}, C-3), 117.14 (+, C-12), 121.80 (C_{quat}, *c*Pr-C), 154.05 (C_{quat}, C=O) ppm. MS (200 eV, DCI, NH_3): *m*/*z* (%) = 506 (2) [2 M + NH_4^+], 262 (100) [M + NH_4^+].

(11-Cyclopropylideneundeca-1,6-diynyl)(diphenyl)phosphane Oxide (8c): According to GP4, 1-(undeca-5′,10′-diynylidene)cyclopropane (**6c**-H, 203 mg, 1.09 mmol) was reacted with *n*BuLi (440 μL, 1.10 mmol, 2.5 M in hexanes) in 3 mL of THF and the resulting mixture was added onto diphenylphosphinic chloride (310 mg, 1.31 mmol) in 5 mL of THF. Column chromatography on silica gel [2 × 30 cm, EtOAc/pentane, 7:3 R_f = 0.58 (EtOAc)] gave **8c** (333 mg, 79%) as a yellow oil. IR (film): $\tilde{\nu}$ = 3054 cm^{-1}, 2978, 2935, 2862, 2839, 2194, 1590, 1483, 1437, 1339, 1309, 1208, 1124, 1104, 1067, 1027, 997, 958, 929, 844, 754, 725, 695, 639, 606, 563, 539. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97–1.02 (m, 4 H, *c*Pr–H), 1.61 (tt, ^3J = 7.1, 7.1 Hz, 2 H, 4-H*), 1.78 (tt, ^3J = 7.1, 7.1 Hz, 2 H, 9-H*), 2.08–2.33 (m, 6 H, 5-H, 8-H, 10-H), 2.57 (td, ^3J = 7.1, $^4J_{PH}$ = 3.4 Hz, 2 H, 3-H), 5.67–5.75 (m, 1 H, 11-H), 7.34–7.55 (m, 6 H, Ar-H), 7.74–7.84 (m, 4 H, Ar-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.89 (–, *c*Pr-C), 2.19 (–, *c*Pr-C), 18.01 (–, C-8*), 18.20 (–, C-5*), 18.74 (–, C-3*), 26.97 (–, C-4**), 28.63 (–, C-10**), 30.91 (–, C-9**), 78.21 (C_{quat}, C-7), 81.56 (C_{quat}, C-2), 108.74 (C_{quat}, d, $^1J_{PC}$ = 30.0 Hz, C-1), 117.20 (+, C-11), 121.91 (C_{quat}, *c*Pr-C), 128.52 (+, d, $^3J_{PC}$ = 13.3 Hz, 4 C, Ar-C), 130.82 (+, d, $^2J_{PC}$ = 11.3 Hz, 4 C, Ar-C), 132.02 (+, d, $^4J_{PC}$ = 3.0 Hz, 2 C, Ar-C), 133.24 (C_{quat}, d, $^1J_{PC}$ = 122.1 Hz, 2 C, Ar-C). Signal of C-6 not detected. MS (EI, 70 eV): *m*/*z* (%) = 386 (6) [M^+], 385 (23) [M^+ – H], 357 (17) [M^+ – C_2H_5], 253 (41), 240 (36), 201 (100) [$P(O)(C_6H_5)_2^+$], 169 (37), 155 (35), 77 (55).

(η^5-Cyclopentadienyl){methyl 1′,2′,6′,7′-η^4-spiro[cyclopropane-1,8′-tricyclo[7.3.0.0^{2,6}]dodeca-1′,6′-diene-7′-carboxylate]}cobalt (9c): According to GP5, **7c** (65 mg, 266 μmol) was treated with [$CpCo(CO)_2$] (32 μL, 266 μmol) in 5 mL of deoxygenated THF and irradiated for 4 h at 66 °C. Column chromatography on aluminuma oxide (4% H_2O, 2 × 30 cm, pentane/diethyl ether, 10:1, R_f = 0.55) gave 9c (46 mg, 47%) as a dark-red oil. IR (film): $\tilde{\nu}$ = 2949 cm^{-1}, 2841, 1717, 1691, 1434, 1225, 1103, 807. ^{1}H NMR (250 MHz, C_6H_6): δ = 0.03–0.17 (m, 1 H, *c*Pr-H), 0.28–0.54 (m, 2 H, *c*Pr-H), 0.99–1.13 (m, 1 H, *c*Pr-H), 1.57–1.90 (m, 4 H, 4′-H, 11′-H), 1.96–2.20 (m, 4 H, 10′-H, 12′-H), 2.26–2.40 (m, 2 H, 3′-H*), 2.68–2.85 (m, 2 H, 5′-H*), 3.43 (s, 3 H, OCH_3), 3.48–3.66 (m, 1 H, 9′-H), 4.39 (s, 5 H, Cp-H) ppm. ^{13}C NMR (62.9 MHz, C_6H_6, DEPT): δ = 11.10 (–, *c*Pr-C), 11.24 (–, *c*Pr-C), 19.06 (C_{quat}, *c*Pr-C), 22.36 (–, C-3′*), 23.74 (–, C-5′*), 29.15 (–, C-12′**), 29.42 (–, C-10′**), 30.94 (–, C-11′**), 32.75 (–, C-4′**), 49.27 (+, C-9′), 58.83 (+, OCH_3), 70.97 (C_{quat}, C-7′***), 81.72 (+, 5 C, Cp-C), 86.83 (C_{quat}, C-6′***), 97.67 (C_{quat}, C-1′***), 98.95 (C_{quat}, C-2′***), 173.88 (C_{quat}, C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 368 (55) [M^+], 340 (8), 243 (5), 213 (100) [M^+ – C_5H_5 – Co – OCH_3], 185 (19), 157 (9), 129 (10), 124 (10), 91 (5), 59 (6), 41 (4). $C_{21}H_{25}CoO_2$ (368.4): calcd.: 368.1186; found: 368.1186 (correct HRMS).

(η^5-Cyclopentadienyl){1′,2′,6′,7′-η^4-spiro[cyclopropane-1,8′-tricyclo-[7.3.0.0^{2,6}]dodeca-1′,6′-diene-7′-yl(diphenyl)phosphane oxide]}cobalt (10c): According to GP5, **8c** (156 mg, 404 μmol) was treated with [$CpCo(CO)_2$] (50 μL, 417 μmol) in 10 mL of deoxygenated THF and irradiated for 4 h at 66 °C. Column chromatography on aluminum oxide [10% H_2O, 2 × 30 cm, EtOAc/pentane, 7:3, R_f = 0.60 (EtOAc)] gave 10c (187 mg, 91%) as a dark-red oil consisting of two diastereomers (*dr* = 1.8:1, ^{1}H NMR). IR (film): $\tilde{\nu}$ = 3055 cm^{-1}, 2950, 2837, 1435, 1278, 1171, 1111, 812, 748, 697. ^{1}H NMR (500 MHz, C_6H_6, only characteristic data): δ = –0.66 to –0.56 (m, 1 H, *c*Pr-H_{major}), –0.53 to –0.41 (m, 1 H, *c*Pr-H_{major}), –0.33 to –0.11 (m, 2 H, *c*Pr-H_{minor}), –0.01 to 0.11 (m, 1 H, *c*Pr-H), 0.14–0.30 (m, 1 H, *c*Pr-H), 0.39–0.58 (m, 2 H, *c*Pr-H), 0.80–0.93 (m, 2 H), 4.52 (s, 5 H, Cp-H_{major}), 4.56 (s, 5 H, Cp-H_{minor}), 6.99–7.10 (m, 2 × 3 H, Ar-H), 7.20–7.35 (m, 2 × 3 H, Ar-H), 7.80–7.91 (m, 2 × 2 H, Ar-H), 8.38–8.46 (m, 2 H, Ar-H_{major}), 8.46–8.52 (m, 2 H, Ar-H_{minor}) ppm. ^{13}C NMR (150.8 MHz, C_6H_6, APT, only characteristic data): δ = 8.73 (–, *c*Pr-C_{minor}), 11.41 (–, *c*Pr-C_{major}), 12.16 (–, *c*Pr-C_{major}), 13.30 (–, *c*Pr-C_{minor}), 60.02 (–, 2 C, C=C), 70.56 (–, C=C_{major}), 73.76 (–, C=C_{minor}), 83.39 (+, 5 C, Cp-C_{major}), 84.04 (+, 5 C, Cp-C_{minor}), 96.13 (–, C=C_{minor}), 98.32 (–, C=C_{major}), 103.05 (–, C=C_{major}), 103.45 (–, C=C_{minor}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 510 (100) [M^+], 482 (25), 442 (10), 414 (30), 385 (18), 357 (14), 309 (20) [M^+ – C_5H_5 – Co – C_6H_5], 243 (10), 201 (33), 155 (9), 124 (20), 91 (4), 77 (6), 59 (11), 47 (3). $C_{31}H_{32}CoOP$ (510.5): calcd.: 510.1523; found: 510.1523 (correct HRMS).

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