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Combination of RCM and the Pauson–Khand Reaction: One-Step Synthesis of Tricyclic Structures

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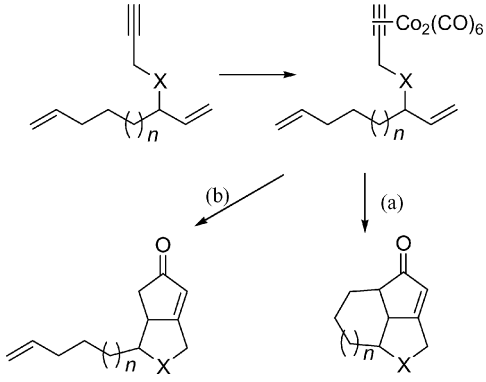
The combination of ring-closing metathesis (RCM) followed by an intramolecular Pauson–Khand reaction gives direct entry to tricyclic compounds. The RCM was carried out on a hexacarbonylcobalt-complexed alkyne, this complex acting as a protecting group against enyne metathesis. The procedure was studied for dienynes containing heteroatoms and allows the building of [6,5,5] and [7,5,5] tricyclic systems. The feasibility of the process depends strongly on the nature of the substrate.

Introduction

Metathesis reactions catalyzed by ruthenium carbenes have become a mature tool in synthetic chemistry. The use of ring-closing metathesis (RCM) in natural product syntheses is common and current challenges include the combination of these reactions with other processes to enhance their synthetic power.[1] Among the transition-metal-catalyzed or -mediated reactions capable of producing polycyclic scaffolds that can be further functionalized, Pauson–Khand reactions (PKRs) are outstanding.[2] The construction of tricyclic structures by PKRs for the total synthesis of natural products such as dendrobine,[3] asteriscanolide,[4] and epoxydictimene[5] has been reported by several groups. Five- to eight-membered cycles as well as macrocycles have readily been obtained by the RCM reaction. These cycloalkenes could take part in PKRs. If an alkynyl moiety is suitably situated, RCM followed by an intramolecular PKR would give a tricyclic cyclopentenone. As reported by many groups, competition between RCM and enyne metathesis generally favors the latter reaction, so the combination of RCM and a PKR would require the protection of the triple bond. The formation of a hexacarbonyldicobalt complex prior to the RCM reaction would solve the problem, giving the cobalt a dual role in the transformation (Scheme 1, path a). Green[6] and Young and co-workers[7] have recently shown the feasibility of carrying out RCM in structures containing hexacarbonyldicobalt–alkyne complexes. As the PKR usually needs promoters or severe reaction conditions, this reaction (Scheme 1, path b) hopefully would not take place before completion of the RCM. We have shown in a preliminary communication of this work our first results of the RCM/PKR of acyclic dienes bearing a complexed triple bond.[8] We present herein our complete study of the combination of these two powerful reactions.



Scheme 1. General scheme of the RCM/PKR process.

Results and Discussion

Our first aim was the synthesis of substrates containing a propargyl ether moiety, which normally gives good results in PKRs. Thus, starting from the corresponding alkenols or from 7-bromohept-1-ene, we synthesized compounds **3** following the strategy depicted in Scheme 2. Compounds **3a**,**b** were obtained in 51 and 95%, respectively, overall yields after three steps, whereas compound **3c** required four steps and was obtained in 19% overall yield.

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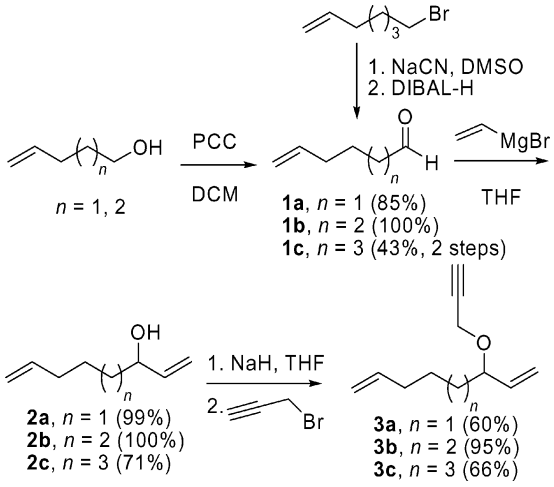
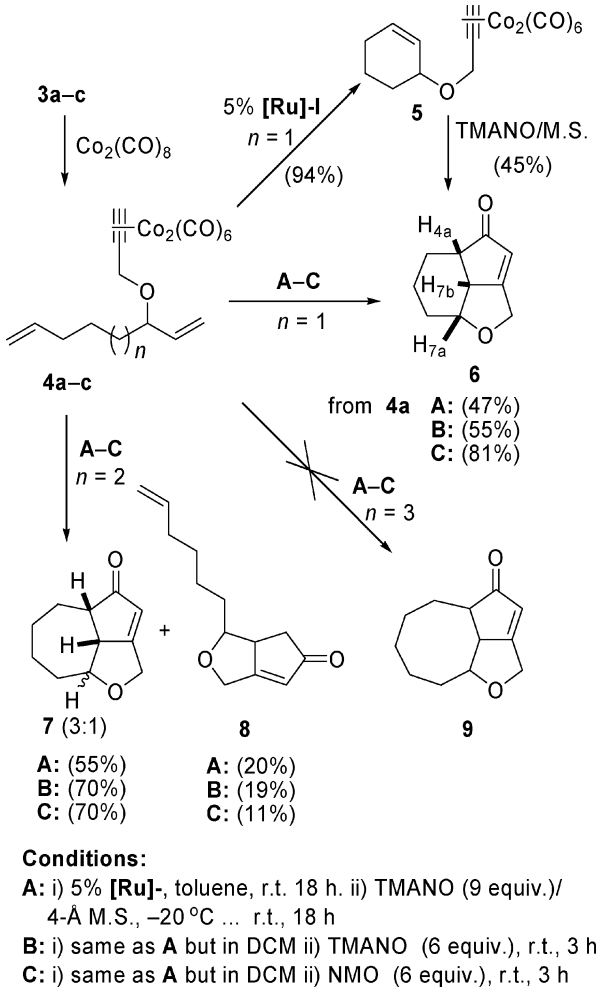


Scheme 2. Synthesis of oxygen-containing dienynes.

Compound **3a** was treated with 5% Grubbs' catalyst, $[(Cy_3P)_2Cl_2Ru{=}CHPh]$ (**[Ru]-I**), to explore the competition among the possible metathesis processes. We obtained a complex mixture that could not be separated and that contained at least three metathesis products. Thus we complexed compound **3a** to octacarbonyldicobalt and submitted the resulting hexacarbonyldicobalt–alkyne complex **4a** to the same conditions. The reaction did not take place unless the cobalt complex had previously been purified in which case clean conversion to **5** was observed; the product was then obtained in 94% yield after purification (Scheme 3). We then submitted compound **5** to PK reaction conditions using our procedure based on the use of molecular sieves and trimethylamine *N*-oxide (TMANO) as co-promoters of the reaction.[9] We obtained the desired compound **6** as a single diastereomer in 45% yield.

We then carried out the reaction of complex **4a** with Grubbs' catalyst **[Ru]-I** and when TLC showed complete disappearance of the starting material we added a promoter for the PKR. Several promoters were examined: A combination of molecular sieves and TMANO in toluene (conditions A),[9] TMANO in DCM (conditions B), and NMO in DCM (conditions C). The best conditions (conditions C) gave the desired compound **6** as a single diastereomer in 81% yield. The relative stereochemistry of **6** was assigned on the basis of NOE experiments; the *cis* configuration was determined, as depicted in Scheme 3.[10] Compound **3b** was treated with $[Co_2(CO)_8]$ and the resulting pure complex **4b** (83%) was treated as above. In this case the RCM was not complete after 18 hours. NMR analysis of an aliquot of the reaction mixture showed 75% conversion. Addition of more ruthenium catalyst did not improve the conversion. We attempted the reaction with the second-generation catalyst $[(Cy_3P)(NHC)Cl_2Ru{=}CHPh]$ (**[Ru]-II**), but this complex did not give any conversion after 20 hours, even when heating the reaction at 40 °C. Thus, we proceeded with the PKR and obtained a mixture of diastereomers **7** that could not be separated, along with compound **8**. In this case the formation of a seven-membered ring does not allow complete

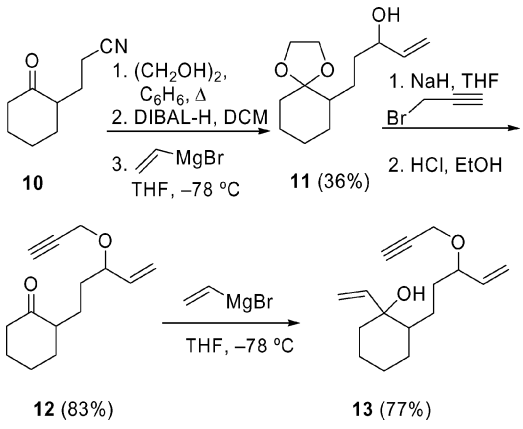


Scheme 3. One-pot RCM/PKR with dienynes **3**.

diastereoselectivity in the Pauson–Khand process. Comparison of the three reaction conditions used for the PKR showed that NMO (conditions C) gave the best yields of **7** and minimized the formation of **8**. Finally, none of the reaction conditions tested gave any conversion with cobalt complex **4c**. The one-pot process was sluggish and gave mixtures in which no RCM products could be detected (Scheme 3).

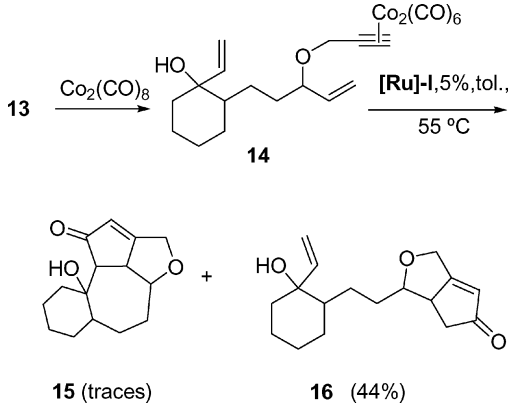
The latter result is caused by the problematic formation of an eight-membered ring by RCM. This metathesis would need harsh conditions that would allow the PKR to occur before the formation of the RCM product. Next we designed a substrate with less conformational mobility to see if this would favor the formation of medium-sized rings under mild conditions. Thus, we synthesized dienyne **13** starting from 3-(2-oxocyclohexyl)propanenitrile (**10**), which was first protected as the ethylene acetal and subsequently reduced with DIBAL-H to give the corresponding aldehyde (Scheme 4). This intermediate was treated with vinylmagnesium bromide to give **11** in 36% yield after the three steps. The sodium alkoxide derived from **11** was treated with propargyl bromide to give, after hydrolysis of the acetal, **12**. At this point, **12** was transformed into **13** by reaction with

vinylmagnesium bromide. The final dienyne was obtained in good overall yields as a mixture of two diastereomers, which were inseparable by traditional chromatography. As our aim was the study of the feasibility of the one-pot RCM/PKR process, we did not develop a selective synthesis of **13** and used the mixture in the following steps.



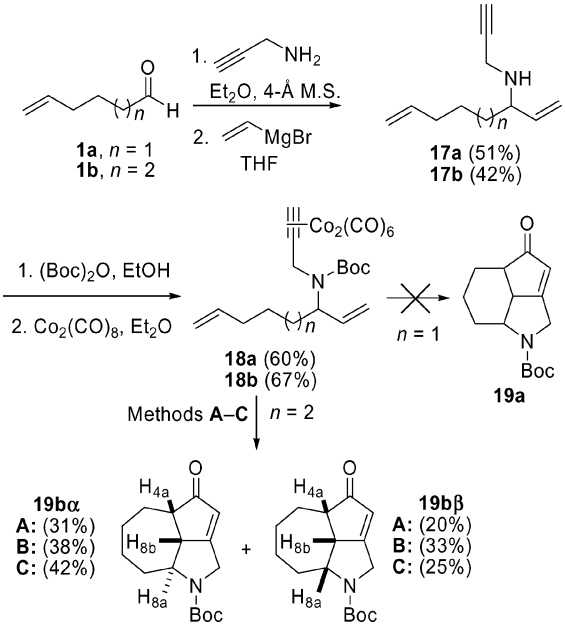
Scheme 4. Synthesis of substrate **13**.

Compound **13** was transformed into the corresponding cobalt complex **14**, which was submitted to different RCM reaction conditions. Unfortunately no conversion took place at room temp. using either **[Ru]-I** or **[Ru]-II** catalysts and DCM or toluene as solvents. Complex **14** was stirred in toluene, gradually elevating the temperature in the presence of 5% **[Ru]-I;** no reaction was observed until 55 °C. After disappearance of the starting material, we isolated compound **16** in 44% yield as the only reaction product. Traces of the desired polycycle **15** were detected in the crude mixture but could not be isolated. Compound **16** is the result of PKR of the complex **14** (Scheme 5).



Scheme 5. Behavior of substrate **13a** under RCM/PKR conditions.

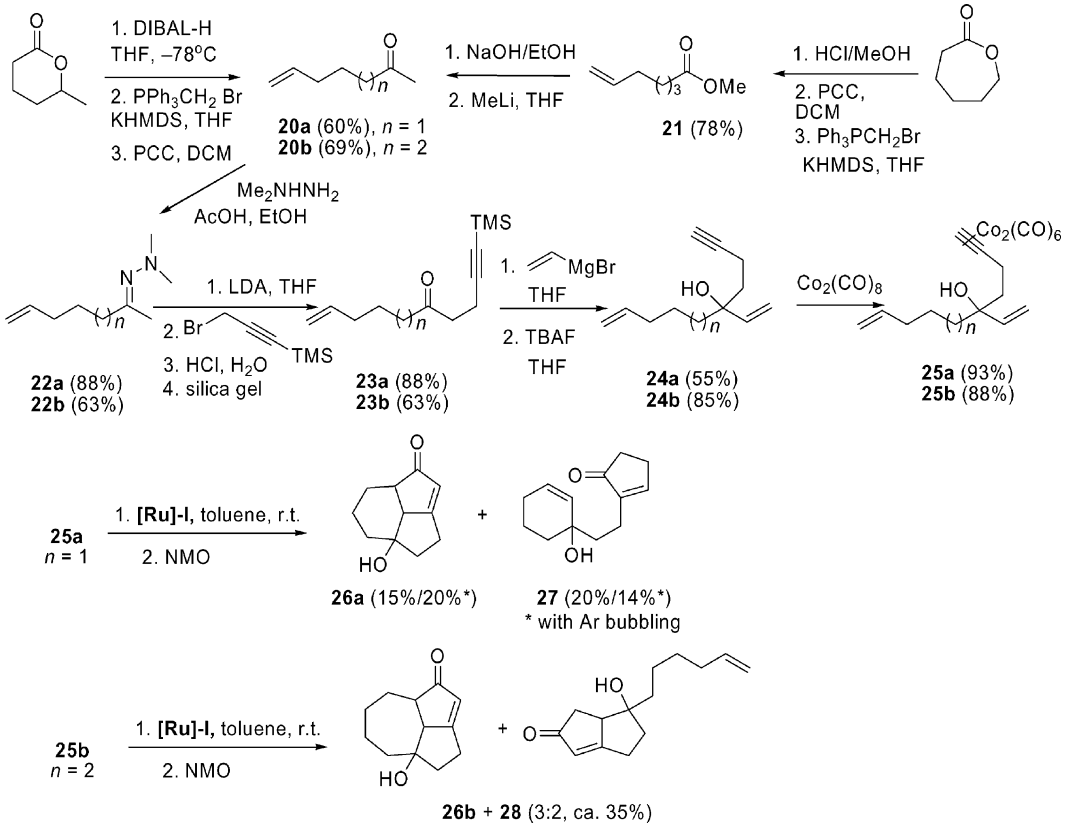
The next step consisted of the synthesis of a nitrogen-containing substrate. Thus, from hex-5-enal and hept-6-enal we carried out the synthesis of propargylamines **17a**,**b** by reaction of the corresponding propargylimine with a vinyl Grignard reagent. Compounds **17a**,**b**, obtained in moderate yields, were protected as Boc derivatives and complexed with cobalt to give **18a**,**b**. The one-pot reaction of substrate **18b** led to the desired tricyclic products **19bα** and **19bβ** as a (3:2) mixture of diastereomers,[11] which were separated and assigned by NOE experiments (Scheme 6).[12] The major isomer was in this case the *cis*,*trans* compound **19bα**. Again, the formation of the seven-membered ring led to a mixture of diastereomers. The three methods used gave similar results in terms of yield and diastereoselectivity. On the other hand, compound **18a** was unreactive under all the conditions tested, leading to partial recovery of the starting material. One possible reason for this lack of reactivity in the RCM step is the steric hindrance of the bulky Boc group in the starting product.



Scheme 6. Synthesis and one-pot RCM/PKR of dienynes **18**.

Finally we planned the synthesis of skeletons with no heteroatoms. The starting dienynes were obtained from pentan-5-olide and hexan-6-olide. The first starting material was reduced to the corresponding lactol which, upon Wittig reaction and oxidation, gave the ketone **20a**. On the other hand, hydrolysis, oxidation, and Wittig reaction of hexan-6-olide gave ester **21** in 78% overall yield. Saponification of **21** followed by reaction with MeLi yielded the parent ketone **20b**. These ketones were converted into the dimethylhydrazones **22a**,**b** following the procedure of Kitching and co-workers,[13] and the corresponding enolates were treated with trimethylsilylpropargyl bromide to give, after hydrolysis, **23a**,**b** in good yields. Finally, the reaction with vinylmagnesium bromide and subsequent desilylation gave **24a**,**b**. The overall yields for the synthesis of these dienynes were 25 and 23%, respectively (Scheme 7).

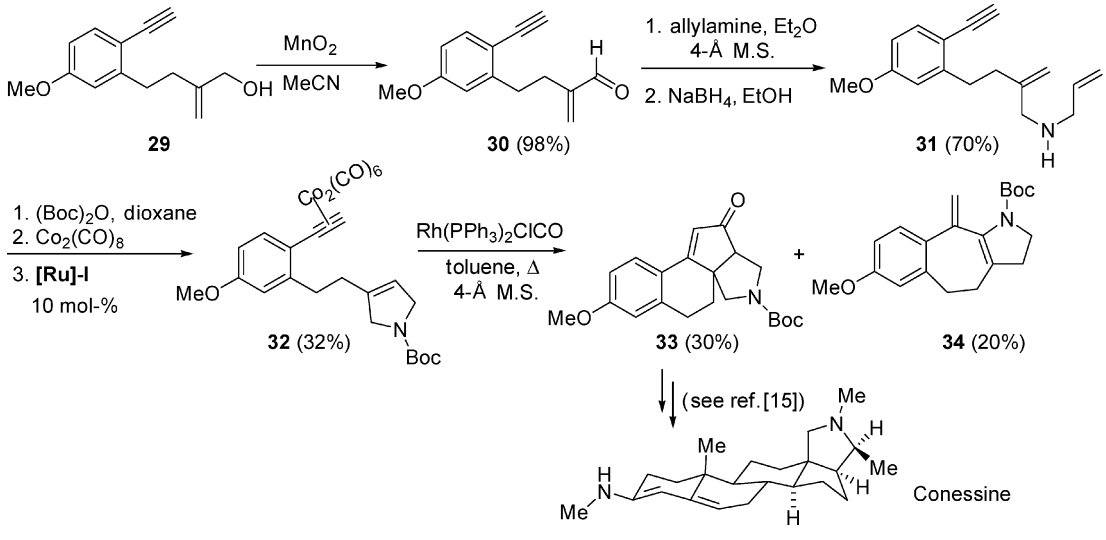
When we carried out the one-pot RCM/PKR process with complex **25a** under the same set of experimental conditions as described above we obtained only 15% yield of the desired product **26a** as a single diastereomer with 20% of another compound whose structure, in accord with its NMR spectroscopic data, was assigned to **27**. This latter product implies that the Pauson–Khand reaction occurred with the ethylene formed in the metathesis process. To avoid



Scheme 7. Synthesis and one-pot RCM/PKR of dienynes **24**.

the formation of **27** we carried out another experiment in which argon was bubbled through the reaction mixture after completion of the metathesis. In this case **27** was isolated in 14% yield and **26a** in 20% yield. The formation of a six-membered ring in the RCM allows total diastereoselectivity in the Pauson–Khand process, as in the synthesis of **6**. On the other hand, the reaction of complex **25b** required a temperature of 40 °C. In this case, an inseparable (3:2) mixture of products **26b** and **28** was obtained, the latter coming from the PKR of **25b**. This mixture was obtained in around 35% yield.

Our final aim was the synthesis of a polycyclic structure described as an intermediate in the synthesis of the steroidic alkaloid Conessine. This natural product, which has significant biological activity against dysentery,[14] has been synthesized by Meyers[15] and other groups.[16] In particular, Meyers and co-workers described a nonracemic synthesis of Conessine in which polycyclic enone **33** was obtained as



Scheme 8. Intramolecular PKR of allenynes.

an intermediate, although with benzyl as a protecting group. We envisioned that this tetracyclic framework could be created by RCM/PKR starting from dienyne **31**. Thus, compound **29**[17] was oxidized to the corresponding aldehyde **30**, which was transformed into amine **31** by reductive amination. Then the amine group was protected and the triple bond was complexed to cobalt. The subsequent RCM gave the desired dihydropyrrole **32** in moderate yield. The reaction conditions for the PKR used with previous substrates were unsuccessful with **32**. The problem with this substrate is the substitution at the double bond. This implies the formation of a quaternary carbon in the PKR, which is normally problematic. In previous studies we have succeeded in making these kinds of substrates reactive by adding an additional rhodium catalyst to the reaction.[17] Thus, when **32** was refluxed in toluene in the presence of molecular sieves and with 5% [$Rh(PPh_3)ClCO$], we obtained the desired product **33** in 30% yield along with another product which could not be completely purified. These products appeared in the crude mixture as a 3:2 mixture. We have assigned provisionally the latter product to structure **34** on the basis of its ^{1}H NMR spectroscopic data. This product is a result of the isomerization of the double bond formed in the RCM and insertion of the complexed triple bond into a C–H bond of the olefinic fragment, a well-known side-reaction in PK chemistry (Scheme 8).

Conclusions

In summary we have developed a new access to tricyclic structures by means of a combined RCM/Pauson–Khand process. The methodology is currently being extended to new precursors of systems with different ring sizes.

Experimental Section

General Procedure for the Oxidation of Alcohols: A solution of the corresponding alcohol (10.0 mmol) in DCM (4 mL) was added to a suspension of PCC (15.0 mmol) in DCM (15 mL) at 0 °C. The crude was stirred at room temperature until completion of the reaction (TLC). The reaction was diluted by addition of Et_2O (50 mL) and filtered through a small pad of silica gel (with ether rinsing). The solvent was removed under vacuum at room temperature. The product was used without further purification.

Hex-5-enal (1a): Following the general procedure for the oxidation of alcohols, from hex-5-en-1-ol (5.00 g, 58.1 mmol), 4.14 g (85%) of **1a** were obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.72–1.77 (m, 2 H), 2.09–2.12 (m, 2 H), 2.46 (t, J = 7.7 Hz, 2 H), 4.98–5.07 (m, 2 H), 5.71–5.81 (m, 1 H), 9.79 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 32.8, 43.0, 115.4, 137.4, 202.5 ppm. IR (film): $\tilde{\nu}$ = 3080, 1760, 1640 cm^{-1}.

Hept-6-enal (1b): Following the general procedure for the oxidation of alcohols, from hept-6-en-1-ol (0.94 g, 9.4 mmol), 0.92 g (100%) of **1b** were obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39–1.49 (m, 2 H), 1.60–1.68 (m, 2 H), 2.05–2.12 (m, 2 H), 2.45 (td, J_1 = 7.4, J_2 = 1.6 Hz, 2 H), 4.95–5.05 (m, 2 H), 5.73–5.86 (m, 1 H), 9.77 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 28.4, 33.7, 43.5, 114.8, 138.5, 200.5 ppm. IR (film): $\tilde{\nu}$ = 3080, 2940, 1730, 1640 cm^{-1}.

Oct-7-enal (1c): A dried two-necked flask equipped with a condenser and a magnetic stirrer under vacuum was charged with NaCN (0.67 g, 13.8 mmol). This flask was heated at 110 °C for 20 min. Upon cooling to 90 °C, DMSO (4 mL) and 7-bromohept-1-ene (2.00 g, 11.3 mmol) were added. The mixture was stirred at 90 °C overnight (around 15 h). Then, water (3 mL) was added and the crude was extracted with diethyl ether (3 × 5 mL) and dried with sodium sulfate. Oct-7-enenitrile was isolated (1.31 g, 94%) as a colorless oil. DIBAL-H (6.76 mL (6.7 mmol) was added dropwise to a solution of oct-7-enenitrile (0.67 g, 5.4 mmol) in anhydrous ether (25 mL) at –78 °C. The resulting mixture was stirred at –78 °C for 2 h. The reaction was quenched with saturated NH_4Cl (10 mL) and stirred for 15 min, after which 5% H_2SO_4 (5 mL) was added and the mixture was stirred for 10 min more. The reaction was extracted with diethyl ether (3 × 20 mL), dried, filtered, and concentrated. Product **1c** was isolated (0.44 g, 43%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29–1.46 (m, 4 H), 1.59–1.68 (m, 2 H), 2.01–2.08 (m, 2 H), 2.43 (td, J_1 = 7.1, J_2 = 1.6 Hz, 2 H), 4.91–5.03 (m, 2 H), 5.74–5.83 (m, 1 H), 9.76 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 28.5, 28.5, 33.4, 43.7, 114.4, 138.6, 202.8 ppm. IR (film): $\tilde{\nu}$ = 2940, 2240, 1720, 1640 cm^{-1}.

General Procedure for the Reaction of Grignard Reagents with Carbonyl Compounds: The corresponding aldehyde (15.0 mmol) in anhydrous THF (5 mL) was added dropwise to a solution of the Grignard reagent at 0 °C. The crude was stirred at room temperature until completion of the reaction (TLC). Then the reaction was poured into an ice/water bath and extracted with EtOAc (3 × 20 mL). The organic layer was washed with brine (20 mL), dried with $MgSO_4$, filtered, and concentrated. Purification was accomplished by column chromatography.

Octa-1,7-dien-3-ol (2a): Following the general procedure for the reaction of Grignard reagents with carbonyl compounds, from hex-5-enal (1.50 g, 15.3 mmol), 1.91 g (99%) of **2a** (hexane/AcOEt 10%) were obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44–1.56 (m, 4 H), 2.08–2.11 (m, 2 H), 4.12 (br. s, 1 H), 4.95–5.26 (m, 4 H), 5.80–5.88 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.5, 33.5, 36.3, 72.8, 114.3, 114.5, 138.5, 141.2 ppm. IR (film): $\tilde{\nu}$ = 3380, 3080, 2940, 1640 cm^{-1}. $C_8H_{14}O$ (126.20): calcd. C 76.14, H 11.18; found C 76.95, H 11.42.

Nona-1,8-dien-3-ol (2b): Following the general procedure for the reaction of Grignard reagents with carbonyl compounds, from hept-6-enal (2.00 g, 17.8 mmol), 2.50 g (100%) of **2b** (hexane/AcOEt 10%) were obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.60 (m, 6 H), 2.03–2.08 (m, 2 H), 4.09–4.12 (m, 1 H), 4.93–5.26 (m, 4 H), 5.77–5.93 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7, 28.7, 33.6, 36.7, 73.1, 114.3, 114.5, 138.8, 141.2 ppm. IR (film): $\tilde{\nu}$ = 3360, 3080, 2920, 1640 cm^{-1}. $C_9H_{16}O$ (140.12): calcd. C 77.09, H 11.50; found C 76.91, H 11.62.

Deca-1,9-dien-3-ol (2c): Following the general procedure for the reaction of Grignard reagents with carbonyl compounds, from **1c** (0.44 g, 3.2 mmol), 0.38 g (71%) of **2c** (hexane/AcOEt 10%) were obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32–1.46 (m, 6 H), 1.49–1.58 (m, 2 H), 2.01–2.08 (m, 2 H), 4.09–4.11 (m, 1 H), 4.91–5.25 (m, 4 H), 5.74–5.92 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.1, 28.7, 28.9, 33.6, 36.9, 73.1, 114.2, 114.4, 139.0, 141.3 ppm. IR (film): $\tilde{\nu}$ = 3300, 3060, 2920, 2840, 1640 cm^{-1}. $C_{10}H_{18}O$ (154.14): calcd. C 77.87, H 11.76; found C 78.02, H 11.89.

General Procedure for the Propargylation Reaction: A solution of the corresponding alcohol (1 mmol) in anhydrous THF (3 mL) was

added to a suspension of NaH (60% dispersion in mineral oil, 3 mmol, washed with hexane) in anhydrous THF (1 mL) at 0 °C. The resulting mixture was stirred at room temperature for 30 min. Then propargyl bromide was added dropwise and the reaction was left to reach room temp. overnight. The mixture was cooled down to 0 °C and was quenched with water dropwise, after which it was extracted with AcOEt (3 × 20 mL), dried, filtered, and concentrated. The residue was purified by column chromatography.

3-(Prop-2-ynyloxy)octa-1,7-diene (3a): Following the general procedure for the propargylation reaction, from **2a** (1.00 g, 7.9 mmol), 0.78 g (60%) of **3a** (hexane) were obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40–1.69 (m, 6 H), 2.40 (t, J = 2.2 Hz, 1 H), 3.84–3.91 (m, 1 H), 4.02 (dd, J_1 = 15.7, J_2 = 2.5 Hz, 1 H), 4.19 (dd, J_1 = 15.7, J_2 = 2.5 Hz, 1 H), 4.93–5.04 (m, 2 H), 5.22–5.27 (m, 2 H), 5.58–5.70 (m, 1 H), 5.74–5.87 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.5, 33.5, 34.5, 55.0, 73.7, 79.9, 80.1, 114.5, 118.1, 137.8, 138.6 ppm. IR (film): $\tilde{\nu}$ = 3300, 3180, 2940, 2120, 1640 cm^{-1}. $C_{11}H_{16}O$ (164.24): calcd. C 80.44, H 9.82; found C 80.69, H 10.03.

3-(Prop-2-ynyloxy)nona-1,8-diene (3b): Following the general procedure for the propargylation reaction, from **2b** (1.00 g, 7.1 mmol), 1.23 g (95%) of **3b** (hexane/AcOEt 5%) were obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36–1.43 (m, 6 H), 2.03–2.07 (m, 2 H), 2.39 (t, J = 2.5 Hz, 1 H), 3.83–3.91 (m, 1 H), 4.02 (dd, J_1 = 15.7, J_2 = 2.5 Hz, 1 H), 4.19 (dd, J_1 = 15.7, J_2 = 2.5 Hz, 1 H), 4.92–5.03 (m, 2 H), 5.21–5.26 (m, 2 H), 5.57–5.69 (m, 1 H), 5.74–5.88 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7, 28.7, 33.6, 35.0, 55.1, 73.7, 80.1, 80.2, 114.3, 118.1, 137.9, 138.9 ppm. IR (film): $\tilde{\nu}$ = 2120, 1740, 1640 cm^{-1}. $C_{12}H_{18}O$ (178.14): calcd. C 80.85, H 10.18; found C 80.99, H 10.34.

3-(Prop-2-ynyloxy)deca-1,9-diene (3c): Following the general procedure for the propargylation reaction, from **2c** (1.60 g, 10.4 mmol), 0.76 g (66%) of **3c** (hexane/AcOEt 5%) were obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27–1.41 (m, 8 H), 2.01–2.06 (m, 2 H), 2.40 (t, J = 2.5 Hz, 1 H), 3.83–3.89 (m, 1 H), 4.02 (dd, J_1 = 15.7, J_2 = 2.5 Hz, 1 H), 4.19 (dd, J_1 = 15.7, J_2 = 2.5 Hz, 1 H), 4.92–5.04 (m, 2 H), 5.21–5.27 (m, 2 H), 5.58–5.69 (m, 1 H), 5.75–5.88 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.1, 28.8, 28.9, 33.7, 35.1, 55.1, 73.7, 80.2, 80.2, 114.2, 118.1, 137.9, 139.1 ppm. IR (film): $\tilde{\nu}$ = 2120, 1740, 1640 cm^{-1}. $C_{13}H_{20}O$ (192.15): calcd. C 81.20, H 10.48; found C 81.01, H 10.73.

General Procedure for the Complexation of Enynes with [$Co_2(CO)_8$]: [$Co_2(CO)_8$] (1.1 mmol) was added to a solution of the corresponding alkyne (1.0 mmol) in anhydrous ether (7 mL). The resulting mixture was stirred until total complexation of the alkyne (TLC). The crude was filtered through diatomaceous earth and the solvent evaporated under vacuum. The residue was purified by column chromatography.

Complex 4a: Hexacarbonyldicobalt–3-(Prop-2-ynyloxy)octa-1,7-diene: Following the general procedure, from **3**[a] (0.50 g, 3.05 mmol), 1.13 g (82%) of **4a** (hexane/AcOEt 5%) were obtained as a dark-red oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46–1.53 (m, 2 H), 1.58–1.69 (m, 2 H), 2.03–2.10 (m, 2 H), 3.83–3.90 (m, 1 H), 4.47 (dd, J_1 = 13.2, J_2 = 1.1 Hz, 1 H), 4.67 (dd, J_1 = 13.2, J_2 = 1.1 Hz, 1 H), 4.93–5.03 (m, 2 H), 5.20–5.25 (m, 2 H), 5.66–5.84 (m, 2 H), 6.02 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.4, 33.6, 34.7, 68.0, 71.4, 81.2, 92.3, 114.5, 117.4, 138.7, 138.7, 199.8 ppm. IR (film): $\tilde{\nu}$ = 2100, 2060, 2020 cm^{-1}.

Complex 4b: Hexacarbonyldicobalt–3-(Prop-2-ynyloxy)nona-1,8-diene: Following the general procedure, from **3b** (0.50 g, 2.8 mmol), 1.08 g (83%) of **4b** (hexane/AcOEt 1%) were obtained as a dark-red oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22–1.64 (m, 6 H), 2.03 (br. s, 2 H), 3.84–3.86 (m, 1 H), 4.47 (d, J = 13.7 Hz, 1 H), 4.67 (d, J = 13.2 Hz, 1 H), 4.92–5.02 (m, 2 H), 5.20–5.25 (m, 2 H), 5.68–5.77 (m, 2 H), 6.02 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.6, 28.8, 33.7, 35.1, 68.0, 71.4, 81.3, 92.3, 114.2, 117.4, 138.8, 138.9, 199.8 ppm. IR (film): $\tilde{\nu}$ = 2100, 2060, 2020 cm^{-1}.

Complex 4c: Hexacarbonyldicobalt–3-(Prop-2-ynyloxy)deca-1,9-diene: Following the general procedure, from **3c** (0.18 g, 0.9 mmol), 0.34 g (83%) of **4c** (hexane/AcOEt 1%) were obtained as a dark-red oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27–1.42 (m, 6 H), 1.52–1.60 (m, 2 H), 2.03–2.05 (m, 2 H), 3.81–3.88 (m, 1 H), 4.47 (d, J = 13.2 Hz, 1 H), 4.66 (d, J = 13.7 Hz, 1 H), 4.92–5.02 (m, 2 H), 5.19–5.25 (m, 2 H), 5.65–5.82 (m, 2 H), 6.02 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9, 28.8, 29.0, 33.7, 35.2, 68.0, 71.4, 81.3, 92.3, 114.2, 117.4, 138.8, 139.1, 199.9 ppm. IR (film): $\tilde{\nu}$ = 2100, 2060, 2020 cm^{-1}.

Complex 5: Hexacarbonyldicobalt–3-(Prop-2-yn-1-yloxy)cyclohexene: [Ru]-I (0.82 g, 0.1 mmol) was added to a solution of **4a** (0.48 g, 1.1 mmol) in anhydrous toluene (100 mL) under argon. The resulting mixture was stirred at room temperature until completion of the reaction (TLC) The crude mixture was filtered through diatomaceous earth and the solvent evaporated under vacuum. The residue was purified by column chromatography (hexane/AcOEt 2%) to obtain 0.42 g (94%) of **5** as a dark-red oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.69–1.89 (m, 4 H), 1.98–2.05 (m, 2 H), 4.09 (br. s, 1 H), 4.66–4.75 (m, 2 H), 5.79–5.91 (m, 2 H), 6.06 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.0, 25.2, 28.3, 68.0, 71.8, 72.7, 92.4, 127.2, 131.3, 199.6 ppm. IR (film): $\tilde{\nu}$ = 2100, 2060, 2020 cm^{-1}.

Procedure for the RCM/Pauson–Khand Reaction: [Ru]-I (0.05 mmol) was added to a solution of the hexacarbonyldicobalt–alkyne complex (1 mmol) in anhydrous DCM (or toluene in method A) (50 mL) under argon, was added. The reaction was stirred at room temp. and when TLC showed the disappearance of the starting material, the promoters for the Pauson–Khand reaction were added.

Method A: After cooling the reaction to –20 °C, eight times the mass of the enyne of powdered molecular sieves and a suspension of TMANO (9 mmol) in anhydrous toluene (2 mL) were added.

Method B: A suspension of TMANO (6 mmol) in anhydrous DCM (2 mL) was added to the reaction at room temp.

Method C: A suspension of NMO (6 mmol) in anhydrous DCM (2 mL) was added to the reaction at room temp.

(4a*S,7a*R**,7b*R**)-4a,5,6,7,7a,7b-Hexahydroindeno[7,7a,1-*bc*]furan-4(2*H*)one (6):** Treatment of **4a** (0.54 g, 1.2 mmol) as described in method C for the RCM/Pauson–Khand reaction afforded 0.16 g (81%) of **6** as a colorless oil (hexane/AcOEt 35%) as a single diastereomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99–1.26 (m, 3 H), 1.57–1.61 (m, 1 H), 1.83–1.91 (m, 1 H), 1.96–2.05 (m, 1 H), 2.83–2.91 (m, 1 H), 3.35 (t, J = 7.2 Hz, 1 H), 4.34–4.42 (m, 1 H), 4.57–4.70 (m, 2 H), 5.97 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 25.3, 28.6, 46.7, 47.5, 64.6, 75.2, 121.8, 182.0, 213.2 ppm. IR (film): $\tilde{\nu}$ = 1710, 1650 cm^{-1}. NOE (7a-H → 7b-H 5%, 7b-H → 7a-H 5%, 7b-H → 4a-H 5%, 4a-H → 7b-H 5%). $C_{10}H_{12}O_2$ (164.08): calcd. C 73.15, H 7.37; found C 73.01, H 7.25.

(4a*S,8a*R**,8b*R**)- and (4a*S**,8a*S**,8b*R**)-5,6,7,8,8a,8b-Hexahydro-2*H*-azuleno[8,8a,1-*bc*]furan-4(4a*H*)-one (7) and 3-(Hex-5-enyl)-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (8):** Treatment of **4b** (0.46 g, 1.0 mmol) as described in method B for the RCM/Pauson–Khand reaction afforded (hexane/AcOEt 10%) 0.14 g (70%) of **7**

as a mixture of diastereomers that were not separable by traditional chromatography (as colorless oil) and 0.05 g (19%) of pure **8** as a colorless oil.

7: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00–1.40 (m, 6 H), 1.56–1.77 (m, 4 H), 1.92–2.23 (m, 6 H), 2.55–2.64 (m, 1 H), 2.72 (q, J = 6.0 Hz, 1 H), 3.06 (br. t, J = 8.8 Hz, 1 H), 3.37 (td, J_1 = 11.2, J_2 = 1.6 Hz, 1 H), 3.59 (br. t, J = 6.6 Hz, 1 H), 4.30–4.37 (m, 1 H), 4.51–4.64 (m, 3 H), 4.73 (d, J = 15.4 Hz, 1 H), 6.02 (s, 1 H), 6.17 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.1, 26.4, 27.0, 27.1, 32.9, 37.5, 46.2, 48.4, 53.0, 56.2, 63.5, 63.8, 66.2, 77.7, 79.9, 81.2, 124.6, 124.9, 183.0, 183.4, 210.4, 211.5 ppm. IR (film): $\tilde{\nu}$ = 1710, 1640 cm^{-1}.

8: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.49 (m, 4 H), 1.66–1.83 (m, 2 H), 2.06–2.16 (m, 3 H), 2.61 (dd, J_1 = 17.6, J_2 = 6.0 Hz, 1 H), 2.86–2.88 (m, 1 H), 3.39–3.47 (m, 1 H), 4.55 (d, J = 15.9 Hz, 1 H), 4.73 (d, J = 15.9 Hz, 1 H), 4.93–5.04 (m, 2 H), 5.73–5.87 (m, 1 H), 6.03 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9, 28.6, 33.4, 34.0, 39.0, 50.6, 65.7, 83.1, 114.4, 124.0, 138.4, 185.0, 208.7 ppm. IR (film): $\tilde{\nu}$ = 1710, 1640 cm^{-1}. $C_{13}H_{18}O_2$ (206.13): calcd. C 75.69, H 8.80; found C 75.84, H 8.89.

5-(1,4-Dioxaspiro[4.5]decan-6-yl)pent-1-en-3-ol (11): A flask equipped with a Dean–Stark apparatus was charged with **10** (2.00 g, 19.9 mmol), ethane-1,2-diol (0.90 g, 21.85 mmol), and *p*-toluenesulfonic acid (0.30 g, 1.58 mmol) in benzene (225 mL). The solution was refluxed for 18 h. The crude was concentrated under vacuum, poured into water (100 mL) and extracted with Et_2O (3 × 50 mL). The organic layer was washed with a solution of 5% $NaHCO_3$ (100mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (hexane/AcOEt, 4:1) obtaining 3.00 g (77%) of 3-(1,4-dioxaspiro[4.5]decan-6-yl)propanenitrile. DIBAL-H (65.7 mL, 65.66 mmol) was added dropwise to a solution of this product (6.50 g, 32.83 mmol) in anhydrous DCM (20 mL) at –78 °C. The mixture was stirred for 2 h at this temperature. The reaction was quenched at –78 °C with AcOEt (8.3 mL) and a saturated solution of sodium potassium tartrate (150 mL). The resulting mixture was stirred overnight. The crude was extracted with AcOEt (3 × 75 mL). The residue was purified by column chromatography (hexane/AcOEt, 9:1) to obtain 4.24 g (66%) of 3-(1,4-dioxaspiro[4.5]decan-6-yl)propanal. The aldehyde (1.10 g, 5.61 mmol) obtained before in anhydrous THF (35 mL) was added dropwise to a flask charged with a solution of vinylmagnesium bromide (7.3 mL, 7.30 mmol) at –78 °C. The solution was stirred for 15 min at the same temperature and then warmed to 0 °C and stirred for 4 h. The reaction was quenched with saturated NH_4Cl (10 mL), and extracted with AcOEt (3 × 5 mL). The residue was purified by column chromatography (hexane/AcOEt 10%) to obtain 0.89 g (71%) of **11** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03–1.83 (m, 13 H), 3.91–3.99 (m, 4 H), 4.09 (br. s, 1 H), 5.10 (d, J = 10.4 Hz, 1 H), 5.23 (dd, J_1 = 17.6, J_2 = 1.6 Hz, 1 H), 5.82–5.94 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8, 23.9, 24.0, 24.4, 29.2, 29.3, 34.5, 34.6, 35.1, 35.1, 44.3, 44.5, 64.1, 64.7, 64.7, 73.2, 73.8, 110.8, 114.4, 114.6, 141.2, 141.3 ppm. IR (film): $\tilde{\nu}$ = 3430, 1640 cm^{-1}.

2-[3-(Prop-2-ynyloxy)pent-4-enyl]cyclohexanone (12): Following the general procedure for the propargylation reaction, from alcohol **11** (2.00 g, 8.85 mmol), 2.06 g (88%) of 5-(1,4-dioxaspiro[4.5]decan-6-yl)pent-1-en-3-ol were obtained as a yellow oil. Concentrated HCl (3.0 mL) was added to a solution of this enyne (0.68 g, 2.49 mmol) in EtOH (6 mL). The resulting mixture was stirred for 15 min at room temp. and quenched with water (10 mL) dropwise. The crude was then extracted with AcOEt (3 × 5 mL). The organic layer was washed with saturated $NaHCO_3$ (15 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo to yield 0.52 g (95%) of **12** as a yellow oil (hexane/AcOEt 5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13–1.85 (m, 9 H), 1.96–2.08 (m, 2 H), 2.18–2.31 (m, 2 H), 2.35 (t, J = 2.2 Hz, 1 H), 3.76–3.84 (m, 1 H), 3.92 (dd, J_1 = 14.3, J_2 = 1.7 Hz, 1 H), 4.11 (dd, J_1 = 15.4, J_2 = 2.2 Hz, 1 H), 5.15–5.21 (m, 2 H), 5.50–5.63 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7, 24.8, 24.8, 25.2, 25.5, 27.8, 27.9, 32.3, 32.7, 33.7, 33.9, 41.8, 41.9, 50.2, 50.5, 54.9, 55.0, 73.7, 73.7, 79.9, 80.1, 118.0, 118.1, 137.4, 137.5, 193.6, 193.7 ppm. IR (film): $\tilde{\nu}$ = 2100, 1700, 1640 cm^{-1}.

2-[3-(Prop-2-ynyloxy)pent-4-enyl]-1-vinylcyclohexanol (13): Following the general procedure for the reaction of Grignard reagents with carbonyl compounds, from **12** (0.50 g, 2.27 mmol), 0.43 g (77%) of **13** were obtained as a yellow oil (hexane/AcOEt 5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96–1.78 (m, 13 H), 2.39 (t, J = 2.2 Hz, 1 H), 3.76–7.84 (m, 1 H), 4.01 (dd, J_1 = 16.0, J_2 = 1.8 Hz, 1 H), 4.17 (dd, J_1 = 16.0, J_2 = 2.8 Hz, 1 H), 5.08 (dd, J_1 = 12.1, J_2 = 1.1 Hz, 1 H), 5.20–5.27 (m, 3 H), 5.53–5.67 (m, 1 H), 5.78–5.89 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 25.2, 25.3, 25.7, 25.8, 26.5, 26.6, 33.1, 33.2, 38.9, 38.9, 43.9, 44.0, 55.0, 73.7, 74.6, 80.0, 80.1, 80.2, 80.5, 111.5, 111.6, 137.6, 137.8, 146.1, 146.2 ppm. IR (film): $\tilde{\nu}$ = 3490, 2110, 1680 cm^{-1}.

Complex 14: Hexacarbonyldicobalt–2-[3-(Prop-2-ynyloxy)pent-4-enyl]-1-vinylcyclohexanol: Following the general procedure, from **13** (0.05 g, 0.20 mmol), 0.10 g (95%) of **14** (hexane/AcOEt 2%) were obtained as a dark-red oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94–1.02 (m, 1 H), 1.15–1.35 (m, 3 H), 1.38–1.74 (m, 9 H), 3.79 (br. s, 1 H), 4.45 (d, J = 13.2 Hz, 1 H), 4.64 (d, J = 13.2 Hz, 1 H), 5.07 (d, J = 11.0 Hz, 1 H), 5.18–5.27 (m, 3 H), 5.62–5.74 (m, 1 H), 5.82 (dd, J_1 = 17.6, J_2 = 11.0 Hz, 1 H), 6.01 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 25.2, 25.8, 26.6, 33.7, 38.9, 44.3, 68.0, 71.4, 74.7, 81.5, 111.6, 117.4, 138.7, 146.2, 296.6 ppm. IR (film): $\tilde{\nu}$ = 2930, 2860, 2250, 2090, 2050, 2020 cm^{-1}.

3-[2-(2-Hydroxy-2-vinylcyclohexyl)ethyl]-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (16): [Ru]-I (0.04 g, 0.058 mmol) was added to a solution of **14** (0.30 g, 0.58 mmol) in anhydrous toluene (80 mL). The resulting mixture was stirred at room temperature After 72 h TLC showed the presence of starting material. The reaction was warmed to 55 °C overnight. The crude was filtered through diatomaceous earth and the solvent evaporated under vacuum. The residue was purified by column chromatography (hexane/AcOEt 2%) obtaining 0.07 g (44%) of **16** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05–1.95 (m, 13 H), 2.11 (dt, J_1 = 17.6, J_2 = 2.76 Hz, 1 H), 2.54–2.64 (m, 1 H), 2.84 (br. s, 1 H), 3.33–3.41 (m, 1 H), 4.52 (d, J = 16.0 Hz, 1 H), 4.71 (d, J = 16.5 Hz, 1 H), 5.08 (dt, J_1 = 11.0, J_2 = 1.6 Hz, 1 H), 5.24 (dd, J_1 = 15.9, J_2 = 1.6 Hz, 1 H), 5.82 (dd, J_1 = 17.0, J_2 = 6.6 Hz, 1 H), 6.02 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 21.3, 25.6, 25.6, 25.7, 26.5, 26.6, 32.3, 32.5, 39.0, 39.3, 39.3, 43.9, 44.1, 50.8, 50.9, 65.9, 74.5, 83.6, 83.6, 111.8, 111.9, 124.2, 124.2, 145.9, 146.0, 185.1, 209.1 ppm. IR (film): $\tilde{\nu}$ = 3490, 1710, 1680, 1640 cm^{-1}.

***N*-(Prop-2-ynyl)octa-1,7-dien-3-amine (17a):** Propargylamine (45.0 mmol) was added to a solution of **1a** (4.00 g, 40.8 mmol) in anhydrous ether (150 mL) and powdered molecular sieves (four times the mass of the aldehyde, 16.00 g). The reaction was then stirred at room temp. overnight (around 12 h). The resulting mixture at 0 °C was added dropwise to a 1.0 M solution of vinylmagnesium bromide (80.0 mmol). The crude was stirred at room temp. until completion of the reaction (TLC) and then quenched with saturated NH_4Cl (200 mL) and extracted with diethyl ether (3 × 200 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by column

chromatography, obtaining 3.39 g (51%) of **17a** (hexane/AcOEt 10%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37–1.49 (m, 4 H), 2.03–2.10 (m, 2 H), 2.20 (t, J = 2.5 Hz, 1 H), 3.19–3.23 (m, 1 H), 3.31 (dd, J_1 = 17.0, J_2 = 2.2 Hz, 1 H), 3.46 (dd, J_1 = 17.0, J_2 = 2.7 Hz, 1 H), 3.66 (t, J = 6.6 Hz, 1 H), 4.93–5.04 (m, 2 H), 5.13–5.20 (m, 2 H), 5.46–5.58 (m, 1 H), 5.73–5.87 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0, 33.6, 34.7, 35.4, 60.1, 71.0, 82.3, 114.6, 117.1, 138.5, 139.9 ppm. IR (film): $\tilde{\nu}$ = 3300, 3180, 2940, 1640 cm^{-1}. $C_{11}H_{17}N$ (163.14): calcd. C 80.93, H 10.50, N 8.58; found C 80.70, H 10.35, N 8.71.

***N*-(Prop-2-ynyl)nona-1,8-dien-3-amine (17b):** Following the same procedure as for the synthesis of **17a**, from **1b** (0.92 g, 8.2 mmol), 0.61 g (42%) of **17b** (hexane/AcOEt 20%) were obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31–1.48 (m, 6 H), 2.01–2.07 (m, 2 H), 2.20 (t, J = 2.5 Hz, 1 H), 3.21 (q, J = 7.7 Hz, 1 H), 3.31 (dd, J_1 = 17.0, J_2 = 2.7 Hz, 1 H), 3.46 (dd, J_1 = 17.0, J_2 = 2.8 Hz, 1 H), 3.65 (t, J = 6.6 Hz, 1 H), 4.93–5.03 (m, 2 H), 5.14–5.20 (m, 2 H), 5.47–5.58 (m, 1 H), 5.74–5.88 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.1, 28.7, 33.5, 35.1, 35.3, 60.1, 71.0, 82.1, 114.2, 117.0, 138.6, 139.9 ppm. IR (film): $\tilde{\nu}$ = 3300, 3080, 2940, 1640 cm^{-1}. $C_{12}H_{19}N$ (177.15): calcd. C 81.30, H 10.80, N 7.90; found C 81.41, H 11.00, N 8.03.

General Procedure for the Protection of Amines as *tert*-Butoxycarbonyl Derivatives: $(Boc)_2O$ (10.0 mmol) was added to a solution of the corresponding amine (5.0 mmol) in methanol (15 mL) was and the reaction was stirred at room temp. overnight. The product was purified by distillation.

Complex 18a: Hexacarbonyldicobalt–[*N*-(*tert*-Butoxycarbonyl)-*N*-(prop-2-ynyl)octa-1,7-dien-3-amine]: Following the general procedure for the protection of amines as *tert*-butoxycarbonyl derivatives, from **17a** (0.60 g, 3.7 mmol), 0.66 g (68%) of *tert*-butyl octa-1,7-dien-3-yl(prop-2-yn-1-yl)carbamate were obtained as a white oil. Treatment of this carbamate (0.40 g, 1.5 mmol) as described in the general procedure for the synthesis of hexacarbonyldicobalt–alkyne complexes afforded pure **18a** (0.92 g, 88%) as a dark-red oil after flash chromatography (hexane/AcOEt 10%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41–1.54 (m, 11 H), 1.69–1.73 (m, 2 H), 2.08–2.15 (m, 2 H), 4.27–4.31 (m, 1 H), 4.45–4.56 (m, 2 H), 4.97–5.22 (m, 4 H), 5.77–5.94 (m, 2 H), 6.00 (s, 1 H) ppm.

Complex 18b: Hexacarbonyldicobalt–[*N*-(*tert*-Butoxycarbonyl)-*N*-(prop-2-ynyl)nona-1,8-dien-3-amine]: Following the general procedure for the protection of amines as *tert*-butoxycarbonyl derivatives, from **17b** (0.30 g, 1.7 mmol), 0.41 g (88%) of *tert*-butyl nona-1,8-dien-3-yl(prop-2-ynyl)carbamate were obtained as a white oil. Treatment of this carbamate (0.34 g, 1.2 mmol) as described in the general procedure for the synthesis of hexacarbonyldicobalt–alkyne complexes afforded pure **18b** (0.52 g, 76%) as a dark-red oil after flash chromatography (hexane/AcOEt 5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29–1.38 (m, 4 H), 1.48 (s, 9 H), 1.69–1.72 (m, 2 H), 2.06–2.09 (m, 2 H), 4.29 (br. s, 1 H), 4.44–4.56 (m, 2 H), 4.95–5.22 (m, 4 H), 5.77–5.88 (m, 2 H), 6.00 (s, 1 H) ppm.

***tert*-Butyl (4a*S**,8a*S**,8b*R**)-4-Oxo-1,2,4,4a,5,6,7,8,8a,8b-decahydroazuleno[8,8a,1-*bc*]pyrrole-1-carboxylate (19bα) and *tert*-Butyl (4a*S**,8a*R**,8b*R**)-4-Oxo-1,2,4,4a,5,6,7,8,8a,8b-decahydroazulene-[8,8a,1-*bc*]pyrrole-1-carboxylate (19bβ):** Treatment of **18b** (0.35 g, 0.6 mmol) as described in method B for the RCM/Pauson–Khand reaction afforded **19bα** (0.07 g, 38%) and pure **19bβ** (0.06 g, 33%) both as brown oils (hexane/AcOEt 20%).

19bα: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10–1.40 (m, 4 H), 1.40 (s, 9 H), 1.68–2.00 (m, 3 H), 2.50–2.60 (m, 1 H), 2.90–2.95 (m, 1 H), 3.03–3.10 (m, 1 H), 3.17–3.22 (m, 1 H), 4.22–4.34 (m, 2 H), 5.94 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.2, 27.5, 27.9, 28.4, 33.4, 47.2, 49.5, 56.6, 62.2, 80.2, 124.7, 156.0, 176.3, 210.2 ppm. IR (film): $\tilde{\nu}$ = 1700, 1650 cm^{-1}. NOE (8b-H→8a-H 8%, 8b-H→4a-H 12%, 4a-H→8b-H 12%). $C_{16}H_{23}NO_3$ (277.17): calcd. C 69.29, H 8.36, N 5.05; found C 69.37, H 8.67, N 4.99.

19bβ: Obtained as a mixture of two rotamers. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97–1.47 (m, 4 H), 1.47 (s, 9 H), 1.60–1.75 (m, 2 H), 1.76–1.93 (m, 1 H), 2.10–2.30 (m, 1 H), 2.65–2.75 (m, 1 H), 3.49 (q, J = 8.2 Hz, 1 H), 4.09–4.33 (m, 3 H), 6.14, 6.18 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.8, 26.3, 27.9, 28.0, 28.4, 28.4, 45.2, 45.7, 47.1, 51.9, 52.5, 59.7, 60.4, 80.0, 126.1, 126.3, 153.3, 153.7, 179.6, 180.1, 211.3, 211.2 ppm. IR (film): $\tilde{\nu}$ = 1700, 1650 cm^{-1}. NOE (8b-H→4a-H 12%, 4a-H→8b-H 6%). $C_{16}H_{23}NO_3$ (277.17): calcd. C 69.29, H 8.36, N 5.05; found C 69.53, H 8.49, N 4.97.

General Procedure for the Wittig Reaction: KHMDS (1.3 mmol, 0.5 M) was added dropwise to a solution of the corresponding phosphonium salt (1.5 mmol) in anhydrous THF (8 mL). The resulting solution was stirred at room temperature for 30 min and subsequently added to a THF solution (4 mL) of the aldehyde (1.0 mmol). The reaction was stirred at room temp. until completion (TLC). The resulting suspension was poured into a (1:1) Et_2O/H_2O mixture, the aqueous phase was extracted with AcOEt (3×20 mL), and the combined organic layers were dried with Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography with hexane/AcOEt mixtures as eluent.

Hept-6-en-2-one (20a): A solution of DIBAL-H (53 mL, 52.6 mmol) in anhydrous THF (60 mL) was added to a solution of 5-hexanolide (5.00 g, 43.8 mmol) in anhydrous THF (150 mL) at –78 °C. The resulting mixture was stirred at the same temperature for 4 h. Then the reaction was quenched with saturated sodium tartrate (50 mL) and slowly warmed to room temperature. The mixture was transferred to a separating funnel and extracted with AcOEt (50 mL). The organic layer was washed with water (2×20 mL) and dried with $MgSO_4$. Removal of the solvent in vacuo gave 5.00 g (100%) of 6-methyltetrahydro-2*H*-pyran-2-ol (mixture of isomers) as a colorless oil. Treatment of this product (4.00 g, 34.5 mmol) as described in the general procedure for the Wittig reaction afforded 2.38 g (60%) of pure hept-6-en-2-ol as a colorless oil after flash chromatography (hexane/AcOEt 10%). Finally, this oil (3.41 g, 29.9 mmol) was treated as described in the general procedure for the oxidation of alcohols, obtaining 2.65 g (100%) of **20a** (hexane/AcOEt 10%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63–1.72 (m, 2 H), 2.03–2.10 (m, 2 H), 2.14 (s, 3 H), 2.44 (t, J = 7.4 Hz, 2 H), 4.96–5.05 (m, 2 H), 5.70–5.84 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.7, 29.9, 33.0, 42.8, 115.1, 137.9, 208.8 ppm. IR (film): $\tilde{\nu}$ = 1720, 1640 cm^{-1}. $C_7H_{12}O$ (112.09): calcd. C 74.95, H 10.78; found C 75.07, H 10.85.

2-(Hept-6-en-2-ylidene)-1,1-dimethylhydrazine (22a): Compound **20a** (2.64 g, 23.6 mmol) and a catalytic amount of AcOH were added to a solution of *N*,*N*-dimethylhydrazine (70.7 mmol) in absolute EtOH (150 mL). The mixture was refluxed for 4 h. The solvent was eliminated, and the crude was extracted with AcOEt (2×20 mL). The organic layer was washed with saturated $NaHCO_3$ (2×20 mL), and dried with $MgSO_4$. Removal of the solvent in vacuo gave 3.18 g (88%) of **22a** as a colorless oil after vacuum distillation. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56–1.68 (m, 4 H), 1.92 (s, 3 H, minor), 1.94 (s, 3 H, major), 2.04–2.14 (m, 4 H), 2.18–2.23 (m, 4 H), 2.40 (s, 3 H, minor), 2.43 (s, 3 H, major), 4.95–5.07 (m, 4 H), 5.74–5.88 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.5, 22.6, 25.7, 26.3, 31.0, 33.3, 33.8, 38.5, 47.0, 47.5, 114.9, 115.2, 138.0, 138.2, 167.6, 169.3 ppm. IR (film): $\tilde{\nu}$ = 1720,

1640 cm^{-1}. $C_9H_{18}N_2$ (154.15): calcd. C 70.08, H 11.76, N 18.16; found C 70.21, H 11.88, N 18.26.

1-(Trimethylsilyl)dec-9-en-1-yn-5-one (23a): *n*BuLi (19.4 mmol) was added dropwise to a solution of *i*Pr_2NH (2.0 g, 19.4 mmol) in anhydrous THF (50 mL) at –40 °C and the reaction was stirred at –40 °C for 3 h. The solution was cooled down to –78 °C and **22a** (1.50 g, 9.7 mmol) in anhydrous THF (10 mL) was added. The reaction was stirred for another 3 h at the same temperature. Finally, (3-bromoprop-1-ynyl)trimethylsilane (2.2 g, 11.6 mmol) in anhydrous THF (6 mL) was added to the reaction and the resulting mixture was allowed to stir at room temp. overnight. Then it was poured into a (1:1) water/ether mixture and transferred to a separating funnel. Upon extraction, the organic layer was washed with water (2 × 40 mL) and brine (2 × 40 mL). The organic layer was concentrated under vacuum to half of the initial volume. MeOH (20 mL), silica gel (2.0 g), and HCl (0.6 mL) were added to the resulting solution, which was stirred for 4 h, extracted with diethyl ether (2 × 40 mL) and the combined organic layers were washed with brine (40 mL) and dried with $MgSO_4$. The solvent was evaporated under vacuum and the crude purified by flash chromatography (hexane/AcOEt 5%) obtaining 1.90 g (88%) of **23a** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 9 H), 1.65–1.75 (m, 2 H), 2.03–2.10 (m, 2 H), 2.42–2.51 (m, 4 H), 2.63–2.67 (m, 2 H), 4.97–5.05 (m, 2 H), 5.70–5.84 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.0, 14.4, 22.6, 33.0, 41.5, 41.9, 84.9, 105.7, 115.2, 137.8, 208.6 ppm. IR (film): $\tilde{\nu}$ = 2180, 1720, 1640 cm^{-1}. $C_{13}H_{22}OSi$ (222.14): calcd. C 70.21, H 9.97; found C 70.38, H 9.81.

5-Vinyldec-9-en-1-yn-5-ol (24a): Following the general procedure for the reaction of Grignard reagents with carbonyl compounds, from **23a** (1.80 g, 8.1 mmol), 1.45 g (72%) of 1-trimethylsilyl-5-vinyldec-9-en-1-yn-5-ol were obtained as a colorless oil. This product (1.45 g, 5.8 mmol) was dissolved in anhydrous THF (30 mL) at 0 °C followed by dropwise addition of TBAF (12.9 mL, 11.8 mmol, 1.1 M). The reaction mixture was stirred for 2 h at this temperature. The residue was taken up in a mixture of ether/hexane (1:1, 60 mL). The organic layer was washed with water (40 mL), dried with $MgSO_4$, and concentrated. The crude was purified by flash chromatography (hexane/AcOEt 15%) obtaining 0.78 g (76%) of **24a** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37–1.58 (m, 4 H), 1.68–1.90 (m, 2 H), 1.98 (t, J = 2.7 Hz, 1 H), 2.02–2.08 (m, 2 H), 2.21–2.28 (m, 2 H), 4.94–5.04 (m, 2 H), 5.17 (dd, J_1 = 10.7, J_2 = 1.4 Hz, 1 H), 5.25 (dd, J_1 = 17.3, J_2 = 1.4 Hz, 1 H), 5.72–5.86 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.9, 22.5, 33.8, 38.8, 40.5, 68.6, 75.1, 84.7, 113.3, 114.6, 138.4, 142.5 ppm. IR (film): $\tilde{\nu}$ = 2120, 1640 cm^{-1}. $C_{12}H_{18}O$ (178.19): calcd. C 80.85, H 10.18; found C 80.73, H 10.25.

Complex 25a: Hexacarbonyldicobalt–5-Vinyldec-9-en-1-yn-5-ol: Treatment of **24a** (0.50 g, 2.8 mmol) as described in the general procedure to obtain enyne complexes with $[Co_2(CO)_8]$ afforded 1.22 g (93%) of pure **25a** as a dark-red oil after flash chromatography (hexane/AcOEt 10%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43–1.46 (m, 2 H), 1.58–1.61 (m, 2 H), 1.79–1.89 (m, 2 H), 2.06–2.09 (m, 2 H), 2.84–2.89 (m, 2 H), 4.95–5.05 (m, 2 H), 5.18–5.29 (m, 2 H), 5.81–5.86 (m, 2 H), 6.01 (s, 1 H) ppm.

4a-Hydroxy-3,4,4a,5,6,7,7a,7b-octahydro-1*H*-cyclopenta[*cd*]inden-1-one (26a) and 2-[2-(1-Hydroxycyclohex-2-enyl)ethyl]cyclopent-2-enone (27): Treatment of **25a** (1.22 g, 2.6 mmol) as described in method C (but in toluene) for the RCM/Pauson–Khand reaction afforded pure **26a** (0.09 g, 20%) and 0.08 g (14%) of **27**, both as colorless oils after flash chromatography (hexane/AcOEt 10%).

26a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06–1.19 (m, 1 H), 1.26–1.36 (m, 1 H), 1.43–1.71 (m, 3 H), 1.79 (s, 1 H), 2.02–2.10 (m, 2 H), 2.21–2.32 (m, 1 H), 2.52–2.65 (m, 1 H), 2.71–2.80 (m, 1 H), 2.84–2.95 (m, 1 H), 3.05–3.06 (m, 1 H), 5.77 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3, 25.5, 25.8, 35.2, 41.3, 44.9, 55.5, 76.0, 123.3, 185.8, 210.8 ppm. IR (film): $\tilde{\nu}$ = 3450, 1690, 1630 cm^{-1}. $C_{11}H_{14}O_2$ (178.10): calcd. C 74.13, H 7.92; found C 74.01, H 7.78.

27: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67–1.75 (m, 6 H), 1.94–2.09 (m, 2 H), 2.25–2.30 (m, 2 H), 2.39–2.42 (m, 2 H), 2.56–2.58 (m, 2 H), 5.64 (d, J = 9.9 Hz, 1 H), 5.80–5.86 (m, 1 H), 7.33 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 19.1, 25.1, 26.4, 34.6, 35.2, 39.9, 69.4, 130.2, 132.1, 146.4, 157.4, 210.2 ppm. IR (film): $\tilde{\nu}$ = 3440, 3020, 1690, 1630 cm^{-1}. $C_{13}H_{18}O_2$ (206.13): calcd. C 75.69, H 8.80; found C 75.80, H 8.89.

Methyl Hept-6-enoate (21): A solution of 6-hexanolide (3.00 g, 26.3 mmol) in dry MeOH (20 mL) was bubbled with dry HCl gas for 15 min. The reaction was refluxed overnight and upon cooling to room temp. the solvent was evaporated under vacuum half and a saturated $NaHCO_3$ solution was added until basic pH. The mixture was extracted with EtOAc (3 × 20 mL). The organic layers were washed with brine (20mL), dried with $MgSO_4$, filtered, and concentrated in vacuo to yield 3.86 g (100%) of methyl 6-hydroxyhexanoate. Following the general procedure for the oxidation of alcohols, from methyl 6-hydroxyhexanoate (15.00 g, 102.7 mmol), 13.6 g (92%) of methyl 6-oxohexanoate were obtained as a colorless oil. Treatment of the aldehyde (4.37 g, 29.9 mmol) as described in the general procedure for the Wittig reaction afforded **21** (3.6 g, 85%) as a colorless oil (hexane/AcOEt 10%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40–1.48 (m, 2 H), 1.61–1.70 (m, 2 H), 2.07 (q, J = 7.1 Hz, 2 H), 2.32 (t, J = 7.7 Hz, 2 H), 3.68 (s, 3 H), 4.94–5.05 (m, 2 H), 5.76–5.85 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.3, 28.2, 33.3, 33.8, 51.3, 114.6, 138.3, 174.0 ppm. IR (film): $\tilde{\nu}$ = 1740, 1640 cm^{-1}. $C_8H_{14}O_2$ (142.10): calcd. C 67.57, H 9.92; found C 67.49, H 10.07.

Oct-7-en-2-one (20b): A solution of 1 N NaOH (144.2 mL, 144.2 mmol) was added to a solution of **21** (2.05 g, 14.4 mmol) in EtOH (70 mL). The reaction was refluxed for 4 h, cooled to room temp., concentrated under vacuum, and concentrated HCl added to acid pH. The resulting crude was extracted with DCM (3 × 20 mL) and the organic layers were washed with brine (20mL), dried with $MgSO_4$, filtered, and concentrated in vacuo to yield 1.73 g (94%) of hept-6-enoic acid as a colorless oil. CH_3Li (17 mL, 27 mmol) in anhydrous THF (25 mL) was added dropwise to a solution of this acid (1.57 g, 12.2 mmol) in anhydrous THF (25 mL) at –78 °C. The final mixture was stirred for 10 min at the same temperature and then allowed to stir for 3 h at room temp. The crude was poured into 1 N HCl (90 mL) at 0 °C and then extracted with diethyl ether (3 × 20 mL). The organic layer was washed with saturated $NaHCO_3$ (2 × 20 mL) and brine (20 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo to yield 1.45 g (94%) of **20b** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34–1.44 (m, 2 H), 1.55–1.62 (m, 2 H), 2.07 (q, J = 7.1 Hz, 2 H), 2.15 (s, 3 H), 2.44 (t, J = 7.4 Hz, 2 H), 4.94–5.09 (m, 2 H), 5.73–5.89 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.2, 28.3, 29.8, 33.5, 43.5, 114.6, 138.4, 209.1 ppm. IR (film): $\tilde{\nu}$ = 1720, 1640 cm^{-1}.

1,1-Dimethyl-2-(oct-7-en-2-ylidene)hydrazine (22b): Compound **20b** (2.00 g, 17.9 mmol) was treated as for the synthesis of **22a**, yielding 1.70 g (63%) of **22b** (mixture of isomers) as a colorless oil after vacuum distillation. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36–1.57 (m, 8 H), 1.91 (s, 3 H, minor), 1.94 (s, 3 H, major), 2.03–2.10 (m, 4 H), 2.17–2.22 (m, 4 H), 2.40 (s, 3 H, minor), 2.43 (s, 3 H, major), 4.93–5.03 (m, 4 H), 5.73–5.86 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.3, 22.5, 25.7, 26.3, 28.3, 28.7, 31.1, 33.3, 33.4, 38.7,

46.9, 47.4, 114.4, 114.5, 138.4, 138.5, 167.7, 169.4 ppm. IR (film): $\tilde{\nu}$ = 1760, 1640 cm^{-1}. $C_{10}H_{20}N_2$ (168.16): calcd. C 71.37, H 11.98, N 16.65; found C 71.50, H 12.13, N 16.83.

1-(Trimethylsilyl)undec-10-en-1-yn-5-one (23b): Treatment of **22b** (0.95 g, 5.6 mmol) as described for the synthesis of **23a** afforded pure **23b** (0.84 g, 63%) as a colorless oil after flash chromatography (hexane/AcOEt 5%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 9 H), 1.34–1.44 (m, 2 H), 1.56–1.66 (m, 2 H), 2.03–2.10 (m, 2 H), 2.42–2.51 (m, 4 H), 2.63–2.68 (m, 2 H), 4.94–5.04 (m, 2 H), 5.73–5.86 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.1, 14.3, 23.0, 28.2, 33.3, 41.3, 42.5, 84.8, 105.6, 114.6, 138.2, 208.5 ppm. IR (film): $\tilde{\nu}$ = 2180, 1720, 1640 cm^{-1}. $C_{14}H_{24}OSi$ (236.16): calcd. C 71.12, H 10.23; found C 71.33, H 10.40.

5-Vinylundec-10-en-1-yn-5-ol (24b): Following the general procedure for the reaction of a Grignard reagent with carbonyl compounds, from **23b** (0.84 g, 3.6 mmol), 0.92 g (100%) of 1-(trimethylsilyl)-5-vinylundec-10-en-1-yn-5-ol were obtained as a colorless oil. This product (1.00 g, 3.8 mmol) was dissolved in anhydrous THF (20 mL) at 0 °C followed by dropwise addition of TBAF (8.9 mL, 8.1 mmol, 1.1 M). The reaction mixture was stirred for 2 h at this temperature. The residue was then taken up in a mixture of ether/hexane (1:1, 50 mL). The organic layer was washed with water, dried with $MgSO_4$, and concentrated. The crude was purified by flash chromatography (hexane/AcOEt 10%) to obtain 0.62 g (85%) of **24b** as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.44 (m, 4 H), 1.49–1.61 (m, 2 H), 1.68–1.90 (m, 2 H), 1.98 (t, J = 2.8 Hz, 1 H), 2.02–2.09 (m, 2 H), 2.21–2.29 (m, 2 H), 4.93–5.03 (m, 2 H), 5.17 (d, J = 10.4 Hz, 1 H), 5.25 (d, J = 17.6 Hz, 1 H), 5.73–5.87 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7, 22.6, 29.0, 33.4, 38.7, 40.8, 68.4, 75.0, 84.6, 113.1, 114.2, 138.5, 142.4 ppm. IR (film): $\tilde{\nu}$ = 3460, 3300, 2940, 2120, 1640 cm^{-1}. $C_{13}H_{20}O$ (192.15): calcd. C 81.20, H 10.48; found C 81.04, H 10.56.

Complex 25b: Hexacarbonyldicobalt–5-Vinylundec-10-en-1-yn-5-ol: Treatment of **24b** (0.46 g, 2.2 mmol) as described in the general procedure for the synthesis of hexacarbonyldicobalt–alkyne complexes afforded pure **25b** (1.02 g, 88%) as a dark-red oil after flash chromatography (hexane/AcOEt 10%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27–1.43 (m, 4 H), 1.49–1.59 (m, 2 H), 1.71–1.89 (m, 2 H), 2.02–2.10 (m, 2 H), 2.84–2.92 (m, 2 H), 4.95–5.05 (m, 2 H), 5.17–5.30 (m, 2 H), 5.75–5.89 (m, 2 H), 6.02 (s, 1 H) ppm.

4a-Hydroxy-4,4a,5,6,7,8,8a,8b-octahydrocyclopenta[*cd*]azulen-1(3*H*)-one (26b) and 6-(Hex-5-en-1-yl)-6-hydroxy-4,5,6,6a-tetrahydropentalen-2(1*H*)-one (28): [Ru]-I (0.17 g, 0.1 mmol) was added to a solution of **25b** (1.02 g, 2.1 mmol) in anhydrous toluene (150 mL) under argon. The reaction was stirred at room temp. After 48 h the TLC showed the presence of the starting material. The reaction was warmed to 40 °C, and a suspension of NMO (12 mmol) in anhydrous toluene (4 mL) was added to the reaction mixture, which was then stirred overnight. The crude was filtered through diatomaceous earth and the solvent evaporated under vacuum. The residue was purified by column chromatography (hexane/AcOEt 35%), obtaining 0.18 g of a mixture of **26b** and **28** (3:2) which were inseparable by chromatography. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.24–1.31 (m, 2 H), 1.41–1.46 (m, 2 H), 1.53–1.75 (m, 6 H), 1.86–1.94 (m, 1 H), 2.02–2.25 (m, 8 H), 2.36–2.38 (m, 2 H), 2.50–2.58 (m, 1 H), 2.70–2.74 (m, 4 H), 2.88–2.90 (m, 2 H), 2.96 (d, J = 7.4 Hz, 1 H, major), 4.95–5.04 (m, 2 H, minor), 5.74–5.87 (m, 1 H, minor), 5.94 (br. s, 1 H, major), 5.99 (br. s, 1 H, minor) ppm.

4-(2-Ethynyl-5-methoxyphenyl)-2-methylenebutanal (30): MnO_2 (1.39 g, 16.0 mmol) was added to a solution of **29** (0.35 g, 1.6 mmol) in MeCN (15 mL). The crude was stirred at room temperature overnight and then was filtered through diatomaceous earth and the solvent evaporated under vacuum to obtain 0.34 g (98%) of **30** as a yellow oil. The product was used without further purification. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.53–2.57 (m, 2 H), 2.84–2.90 (m, 2 H), 3.15 (s, 1 H), 3.74 (s, 3 H), 5.95 (s, 1 H), 6.15 (s, 1 H), 6.63–6.66 (m, 2 H), 7.35 (dd, J_1 = 9.3, J_2 = 2.2 Hz, 1 H), 9.50 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3, 32.4, 54.9, 79.5, 82.0, 111.4, 113.5, 114.2, 133.9, 134.6, 145.2, 148.7, 159.6, 194.3 ppm. IR (film): $\tilde{\nu}$ = 2100, 1690, 1610 cm^{-1}.

***N*-Allyl-4-(2-ethynyl-5-methoxyphenyl)-2-methylenebutan-1-amine (31):** Molecular sieves (1.4 g) and allylamine (0.13 mL, 1.8 mmol) were added to a solution of **30** (0.34 g, 1.6 mmol) in anhydrous ether (20 mL) under argon. The resulting mixture was stirred at room temp. overnight. The reaction was filtered and concentrated in vacuo. The residue was redissolved in absolute EtOH (10 mL) and $NaBH_4$ (0.12 g, 3.20 mmol) was added. The mixture was stirred for 4 h at room temp. The crude was concentrated under vacuum, Et_2O (15 mL) was added, and the mixture was washed with brine (20mL), dried with $MgSO_4$, filtered, and concentrated. The reaction afforded 0.28 g (70%) of **31** as a yellow oil without further purification. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.33–2.38 (m, 2 H), 2.86–2.92 (m, 2 H), 3.15 (s, 1 H), 3.21–3.23 (m, 4 H), 3.78 (s, 3 H), 4.89 (s, 1 H), 4.94 (s, 1 H), 5.07 (d, J = 10.4 Hz, 1 H), 5.15 (dd, J_1 = 17.0, J_2 = 1.6 Hz, 1 H), 5.83–5.96 (m, 1 H), 6.65–6.73 (m, 2 H), 7.38 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.4, 33.1, 34.8, 51.4, 53.3, 54.9, 79.2, 82.1, 110.2, 111.1, 113.4, 114.1, 115.6, 134.0, 136.6, 146.2, 146.8, 159.6 ppm. IR (film): $\tilde{\nu}$ = 3290, 2100, 1610 cm^{-1}.

Complex 32: Hexacarbonyldicobalt–1-(*tert*-Butoxycarbonyl)-3-[2-(2-ethynyl-5-methoxyphenyl)ethyl]-2,5-dihydro-1*H*-pyrrole: $(Boc)_2O$ (0.49 g, 2.2 mmol) was added to a solution of **31** (0.28 g, 1.1 mmol) in dioxane (6 mL) and the reaction was allowed to stir at room temp. for 4 h. The residue was concentrated and taken up in a mixture of diethyl ether/water (1:1, 20 mL). The organic layer was washed with brine, dried with $MgSO_4$, and concentrated. The crude was purified by flash chromatography (hexane/AcOEt, 20:1), obtaining 0.25 g (64%) of *tert*-butyl allyl[4-(2-ethynyl-5-methoxyphenyl)-2-methylenebutyl]carbamate as a yellow oil. Treatment of this product (0.15 g, 0.43 mmol) as described in the general procedure for the synthesis of hexacarbonyldicobalt–alkyne complexes afforded the corresponding pure hexacarbonyldicobalt complex as a dark-red oil. **[Ru]-I** (0.03 g, 0.04 mmol) was added to a solution of this complex (0.43 mmol) in anhydrous benzene (30 mL) under argon. The reaction mixture was stirred for 17 h at room temp., filtered through diatomaceous earth, and the solvent evaporated under vacuum. The residue was purified by column chromatography (hexane/AcOEt 10%) to obtain 0.13 g (50%) of **32** as a dark-red oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 9 H), 2.32–2.39 (m, 2 H), 2.85–2.92 (m, 2 H), 3.80 (s, 3 H), 4.04–4.14 (m, 4 H), 5.48 (d, J = 17.0 Hz, 1 H), 6.31 (s, 1 H), 6.66 (d, J = 2.2 Hz, 1 H), 6.81 (d, J = 8.8 Hz, 1 H), 7.57 (dd, J_1 = 8.8, J_2 = 2.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.5, 29.8, 32.2, 53.2, 54.7, 55.1, 75.0, 79.3, 87.0, 112.7, 114.2, 119.1, 126.9, 136.1, 138.9, 141.0, 154.2, 159.5, 199.6 ppm. IR (film): $\tilde{\nu}$ = 2090, 2040, 2020, 1700, 1660, 1600 cm^{-1}.

***tert*-Butyl 2-Methoxy-6-oxo-6a,7,8,9,10,11-hexahydro-6*H*-benzo[4,5]indeno[1,7a-*c*]pyrrole-8-carboxylate (33) and *tert*-Butyl 7-Methoxy-10-methylene-1,2,3,4,5,10-hexahydrobenzo[5,6]cyclohepta[1,2-*b*]pyrrole-1-carboxylate (34):** Molecular sieves (0.11 g) and $[Rh(PPh_3)_2ClCO]$ (3.2 mg, 0.005 mmol) were added to a solution of **32** (0.06 g, 0.09 mmol) in anhydrous toluene (1.8 mL). The reaction was refluxed at room temperature under argon for 24 h. The

crude was filtered through diatomaceous earth and the solvent evaporated under vacuum. The residue was purified by column chromatography (hexane/AcOEt 5%), obtaining 0.02 g (30%) of **33** as a colorless oil and 0.01 g (20%) of **34** as a yellow oil.

33: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (s, 9 H), 1.99–2.09 (m, 1 H), 2.23 (dd, J_1 = 12.6, J_2 = 3.3 Hz, 1 H), 2.62 (d, J = 6.6 Hz, 1 H), 2.92–3.13 (m, 2 H), 3.31 (d, J = 11.5 Hz, 1 H), 3.41–3.47 (m, 1 H), 3.47–3.86 (m, 1 H), 3.86 (s, 3 H), 4.03 (d, J = 11.5 Hz, 1 H), 6.24 (s, 1 H), 6.74 (s, 1 H), 6.84 (d, J = 8.8 Hz, 1 H), 7.58 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.9, 28.3, 32.2, 47.3, 53.1, 53.2, 55.4, 57.2, 79.9, 113.6, 113.7, 120.8, 121.9, 129.8, 140.5, 154.5, 162.1, 170.0, 208.4 ppm. IR (film): $\tilde{\nu}$ = 1690, 1630 cm^{-1}. $C_{21}H_{25}NO_4$ (355.43): calcd. C 70.96, H 7.09, N 3.94; found C 70.82, H 7.31, N 4.05.

34: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (s, 9 H), 1.60–1.69 (m, 2 H), 1.79–1.82 (m, 2 H), 2.73–2.94 (m, 2 H), 3.38–3.64 (m, 2 H), 3.73 (s, 3 H), 4.93 (s, 1 H), 5.41 (br. s, 1 H), 6.64 (s, 1 H), 6.75 (d, J = 8.8 Hz, 1 H), 7.57 (d, J = 8.8 Hz, 1 H) ppm.

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[10] When irradiating 7b-H a NOE increment of 5% was observed both in the signal of 7a-H and 4a-H.

[11] Calculated by integration of the signals corresponding to the olefinic proton in the ^{1}H NMR spectrum of the crude mixture.

[12] Compound **19bα**: No NOE increments in 8a-H were observed when irradiating 8b-H or 4a-H. Compound **19bβ**: when irradiating 8b-H a NOE increment of 8% was observed in the signal of 8a-H and a 12% increment was observed in the signal of 4a-H. The signals were assigned on the basis of a COSYGR experiment.

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