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Chiral Auxiliary-Induced Stereocontrol in Intramolecular Pauson-Khand Reactions Leading to Angular Triquinanes.

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Abstract: The thermally induced Pauson-Khand intramolecular cyclization of 1-(3-alkoxy-2-propynyloxy)methylcyclopentenes (**2**) and 1-(5-alkoxy-4-pentynyl)cyclopentenes (**3**), derived from chiral secondary alcohols, leads to the tricyclic enones (**9**) and (**10**), respectively, in moderate yields and with variable diastereoselectivities. Among the chiral alcohols that we have examined, enynes derived from Oppolzer's 3-(neopentyloxy)isoborneol **4c** afford chromatographically-separable diastereomers, and those derived from 10-(methylthio)isoborneol **4d** are cyclized with outstanding stereocontrol (up to 12:1 d.r., one of the highest values recorded to date for chiral auxiliary-stereocontrolled intramolecular Pauson-Khand reactions). These results open for the first time a way to the enantioselective synthesis of angular triquinanes in which the tricyclic skeleton is stereoselectively constructed in a single step from a monocyclic enyne without internal stereogenic centers.

Introduction

Although the Pauson-Khand cyclopentenone synthesis[1] has been used in several instances for the direct construction of the three possible types of fused triquinanes –i.e., linear (A),[2] angular (B),[3] and perhydrotriquinacenic (C)[4] (Figure 1)–, none of these approaches has addressed the problem of the absolute configuration of the stereogenic centers of these important, naturally-occurring polycyclic systems.[5,6]

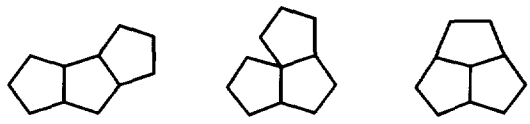
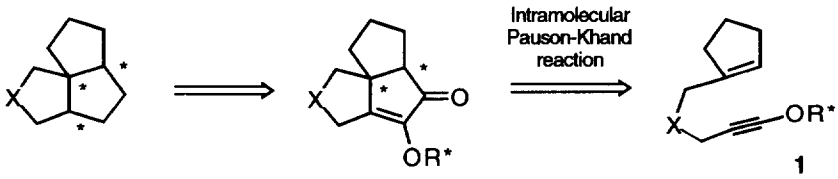


Figure 1

In the course of our studies on the chiral auxiliary-stereodirected Pauson-Khand reactions,[7,8] we have developed practical, enantioselective routes both to bicyclo[3.3.0]octan-3-ones[7b,c] and to bicyclo[4.3.0]nonan-8-ones,[7d] based on the intramolecular cycloaddition of alkoxyenynes derived from chiral alcohols. We wish to

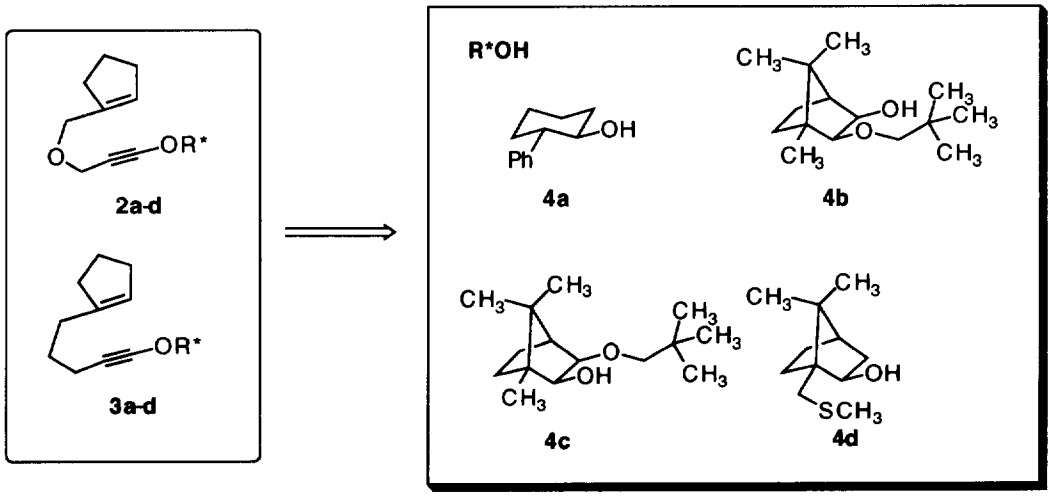
disclose in this paper an extension of this strategy that allows for the first time the enantiocontrolled access to the angular triquinane skeleton (B) starting from 1-alkoxy-5-(1-cyclopentenyl)-1-pentynes of general structure **1** (Scheme 1).



Scheme 1

Results and Discussion

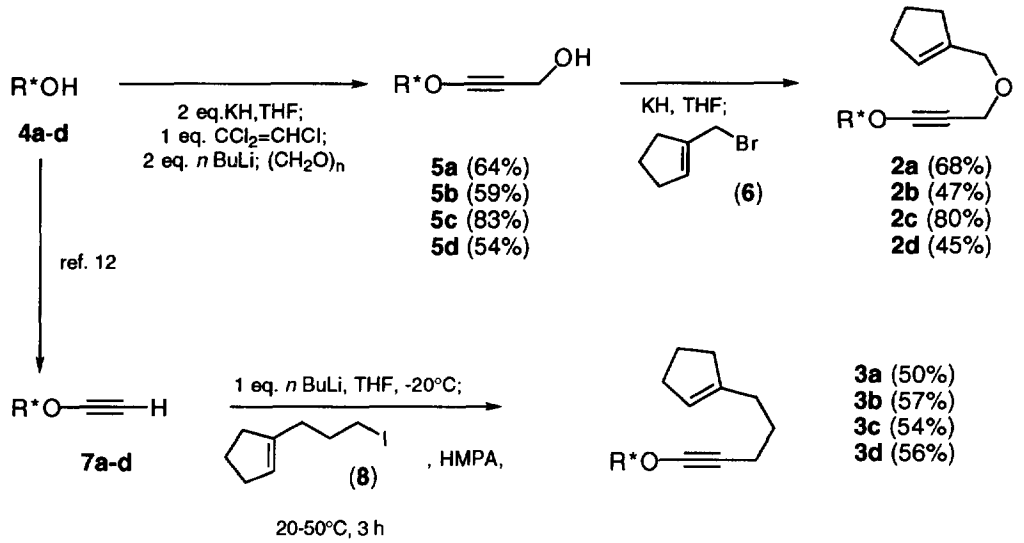
In order to test the concept outlined in Scheme 1, we prepared two different sets of cyclopentenyl-derived alkoxyalkynes, **2** and **3**, according to the nature of the three-membered chain joining the olefinic and acetylenic moieties. The chiral alkoxy group to be incorporated into each of these basic structures was selected at the light of our work[7a,7c,8b,8c] on the diastereoselective Pauson-Khand reactions leading to bicyclic systems (Scheme 2). It is worth noting that all of the requisite chiral alcohols (**4a-d**) are either commercially available in enantiopure form or can be easily obtained according to known procedures (**4a**,[9] **4b**,[10] **4c**[10], **4d**[11]).



Scheme 2

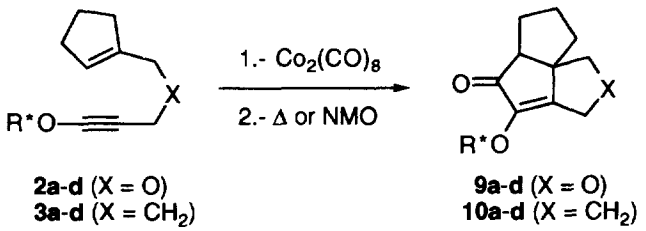
The preparation of the enyne substrates **2a-d** and **3a-d** from the corresponding alcohols **4a-d** is shown in Scheme 3. These alcohols were first converted to their propargyl derivatives **5a-d** by means of the high-yield, one-pot procedure previously applied by us for the preparation of alkoxypropargyl allyl ethers,[7b,7c] as an extension of the direct synthesis of alkoxyacetylenes from trichloroethylene and the corresponding alcohols.[12] Subsequent treatment of the potassium alkoxydes derived from **5a-d** with (1-cyclopentenyl)methyl bromide **6**[13] gave access to the oxygen-tethered enynes **2a-d**. On the other hand, the all-carbon alkoxyenynes **3a-d** were

conveniently prepared through the alkylation of alkoxyacetylenes **7a-d** with 3-(1-cyclopentenyl)propyl iodide **8**,[14] *via* the corresponding lithium acetylides.



Scheme 3

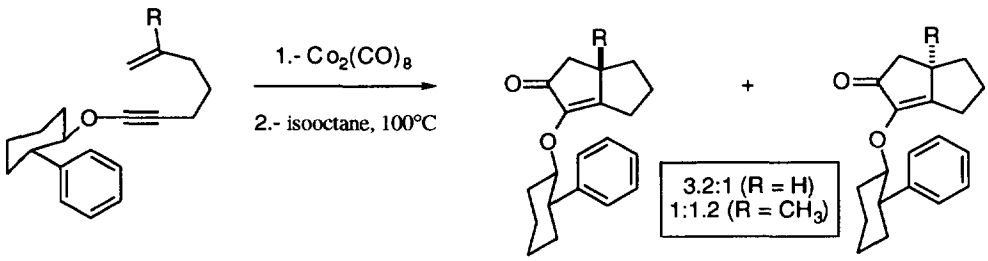
With the required cyclopentenyl-derived alkoxyalkynes in hand, we undertook the study of their intramolecular Pauson-Khand reactions (Equation 1) with the aim of selecting the chiral auxiliary giving the best levels of diastereoselectivity in the construction of the angular triquinane skeleton. The cyclizations were run under standard thermal conditions,[1] by heating a preformed isooctane solution of the hexacarbonyl dicobalt complex until its complete consumption; the alternative *N*-oxide-mediated protocol,[15] which was also systematically examined, proved generally unsuccessful (see below). The yields and diastereoselectivities obtained in the reaction of **2a-d** and **3a-d** are shown in Table 1.



Equation 1

Among the chiral auxiliaries that we have examined, *trans*-2-phenylcyclohexanol **4a**, which exhibits very good levels of diastereoselectivity (up to 11:1) in the intramolecular Pauson-Khand reaction of 1-alkoxy-1-hepten-6-ynes[7b] and 1-alkoxy-1-octen-7-ynes,[7d] gave access to the tricyclic enones **9a** and **10a** (entries 1 and 6 in Table 1) with low diastereomeric excesses. These results were not totally unexpected, since we had previously observed that the presence of a methyl substituent at C-2 on the enyne skeleton had a deleterous

effect on the diastereoselectivity of the cyclization of 1-(*trans*-2-phenylcyclohexyloxy)-6-hepten-1-ynes (Scheme 4),[7a] a fact that can be related to the appearance of destabilizing steric interactions in the cobaltacycle intermediate leading to the major diastereomer.[7e]



Scheme 4

Table 1: Yields[a] and Diastereomeric ratios[b] in the Intramolecular Pauson-Khand Reactions of Alkoxyalkynes **2a-d** and **3a-d**.

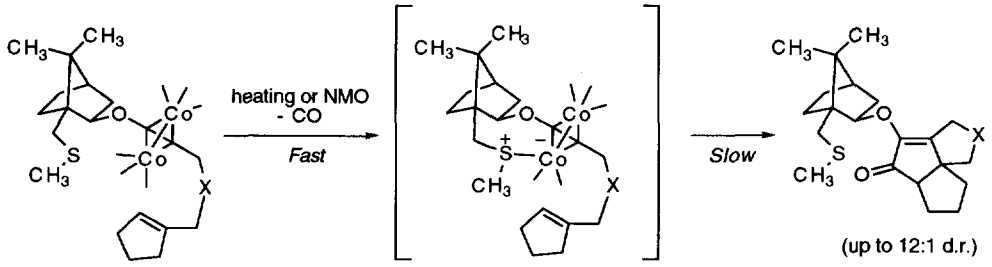
Entry	Enyne	Conditions[c]	Time (h)	Product	Yield (%)	Diast. Ratio
1	**2a**	Iso, 80°C	12	**9a**	43	1.6:1
2	**2b**	Iso, 80°C	12	**9b**	46	2.6:1
3	**2c**	Iso, 80°C	12	**9c**	52	3.3:1[d]
4	**2d**	Iso, 80°C	3	**9d**	32	9.5:1
5	**2d**	NMO	20	**9d**	20	8:1
6	**3a**	Iso, 100°C	7	**10a**	42	1.4:1
7	**3b**	Iso, 100°C	8	**10b**	32	1.5:1
8	**3c**	Iso, 100°C	8	**10c**	29	2.8:1[d]
9	**3d**	Iso, 80°C	10	**10d**	34	12:1

[a]Isolated yield after chromatographic purification. [b]By ^1H and ^{13}C NMR. [c]Conditions: Iso, XX°C=heating of the preformed complex in isooctane solution at the specified temperature; NMO: chemical activation of the complex by *N*-methylmorpholine-*N*-oxide in dichloromethane solution. [d]In this case, the two diastereomers were separable by column chromatography.

Better results were obtained with the camphor-derived auxiliary **4c** developed by Oppolzer, which we had previously used with excellent results in the Pauson-Khand bicyclization of alkoxypropargyl allyl ethers.[7c]

Although the increases in diastereoselectivity were only modest (see entries 3 and 8 in Table 1), the diastereomers of **9c** and **10c** could be readily separated by simple column chromatography, and this observation is of high significance with regard to the ultimate goal of obtaining enantiomerically pure angular triquinane systems.

A substantial improvement in the stereocontrol of the process could be finally reached in the cyclization of the 10-methylthioisoborneol derived enynes **2d** and **3d** (entries 4, 5 and 9 in Table 1). As observed in the *intermolecular* Pauson-Khand reaction of (10-methylthioisobornyloxy)ethyne with strained olefins,[8c] this high selectivity could be associated with the intermediacy of a sulfur-chelated dicobalt pentacarbonyl complex, whose formation can be easily detected by TLC (Scheme 5) and which smoothly reacts to the bicyclic products. It should be noticed here that when we performed the Pauson-Khand cyclization of all the studied enynes under *N*-oxide-mediated[15] conditions, only in the case of enyne **2d** were we able to isolate the expected cyclopentenone (see entry 5 in Table 1), but with lower yield and diastereoselectivity.[8d] In all other instances, the oxidative treatment led to the complete destruction of the starting material and to the formation of complex reaction mixtures from which no cyclopentenone could be isolated.

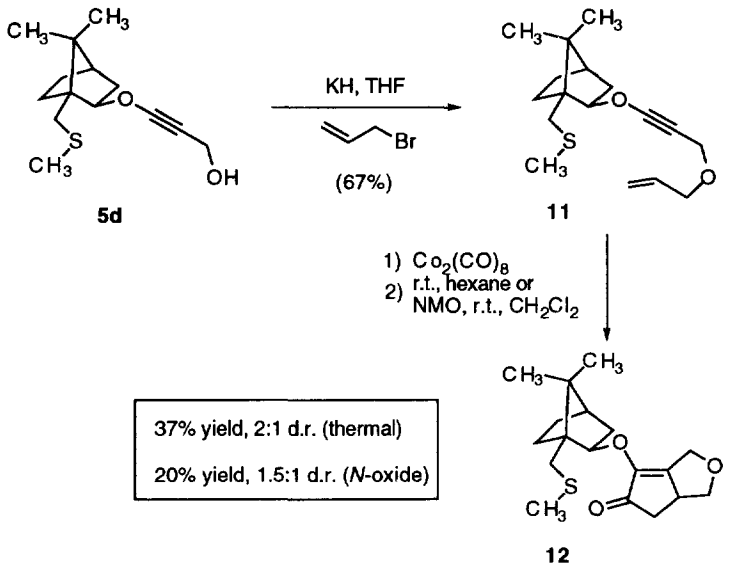


Scheme 5

It is important to realize that these cyclizations represent the first examples of successful stereocontrol of an *intramolecular* Pauson-Khand reaction mediated by a chelating chiral auxiliary. In the previously studied *intermolecular* cases, success in the utilization of **4d** has relied on the possibility of separating the formation of the pentacarbonyl complex (in which the methylthio group is acting as a semi-labile ligand on cobalt) from the subsequent Pauson-Khand reaction. This was achieved by simply adding the olefin to the reaction mixture once the formation of the intermediate complex had been completed.

Encouraged by the results obtained in the cyclizations of **2d** and **3d**, the extension of the use of **4d** to the stereoselective formation of diquinanes was also attempted. To this end, alkoxypropargyl allyl ether **11** was readily assembled in 67% yield from **5d** and allyl bromide. Quite dissapointingly, however, when the Pauson-Khand bicyclization of **11** was studied, either under thermal or NMO promoted conditions, the corresponding adduct **12** was obtained with low diastereoselectivity (Scheme 6). It is worth noting here that the formation of the intermediate pentacarbonyl complex was never observed during the Pauson-Khand reactions of **11**. These results strongly suggest that achievement of stereocontrol in intramolecular Pauson-Khand reactions of alkoxyenynes derived from the chelating chiral alcohol **4d** depends on the relative rates of formation of the intermediate pentacarbonyl complex and its subsequent conversion into the Pauson-Khand adduct: Only when

heavily substituted, rather unreactive olefins are involved in the process, like in **2d** or **3d**, high levels of diastereoselectivity have to be expected. Under these circumstances the reactions mainly proceed through the chelated intermediate, which efficiently controls the stereochemical outcome of the process by directing the coordination of the olefin and subsequent cobaltacycle formation to one of the diastereotopic cobalt atoms, probably the one to which the methylthiomethyl ligand was coordinated.



Scheme 6

Finally, and although we have not determined the absolute configuration of the Pauson-Khand cycloadducts, it should be mentioned that by comparison of the circular dichroism spectra of the major diastereomers of **2c** and **3c** with that of a closely related triquinane system of known absolute configuration,[16] we have been able to assign their absolute configuration as (*1R,5R*) (Figure 2). These results can be rationalized by assuming a dicobalt pentacarbonyl complex in which the more accessible *pro-S* cobalt atom coordinates to the cyclopentenyl moiety from the $C_{2'}$-*re* face, leading to the observed (*1R,5R*) configuration *via* a *cis*-cobaltatricyclic intermediate.[17] Interestingly, the sense of the asymmetric induction in the formation of **2c** and **3c** is the same as in the formation of the related compound **13**[7c] from the corresponding enyne containing the same chiral auxiliary, so that the absolute configuration of these Pauson-Khand cycloadducts (**2c**, **3c** and **13**) appears to be independent of the substitution pattern of the olefin.

With respect to the adducts containing the chelating alcohol **4d**, the absolute configuration of the major stereoisomer of **12** has been established as shown in Scheme 7. Treatment of a 2:1 diastereomeric mixture of **12** with methanol in the presence of a catalytic amount of anhydrous HCl, a method that we have previously employed for the recovery of chiral alcohols from similar diquinanes,[7c] leads to the formation of a dextrorotatory scalemic mixture **14** in quantitative yield and to the recovery of **4d** in 83% yield.

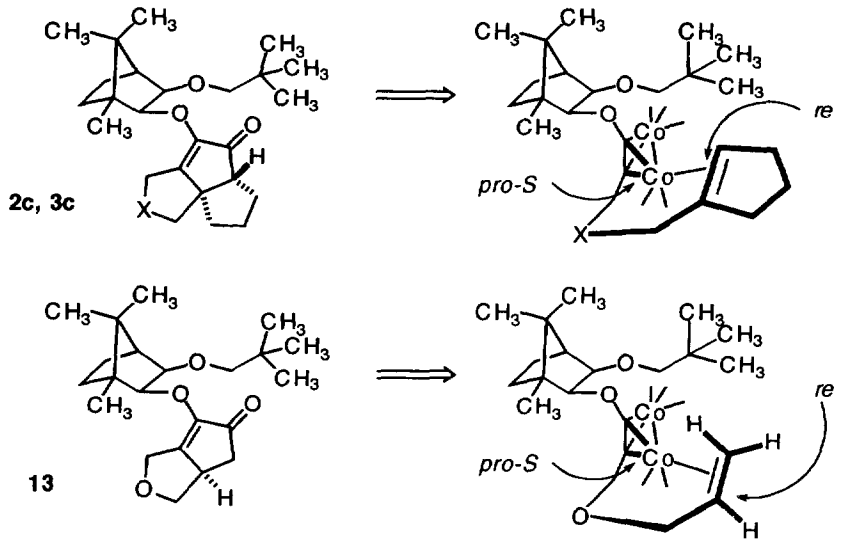
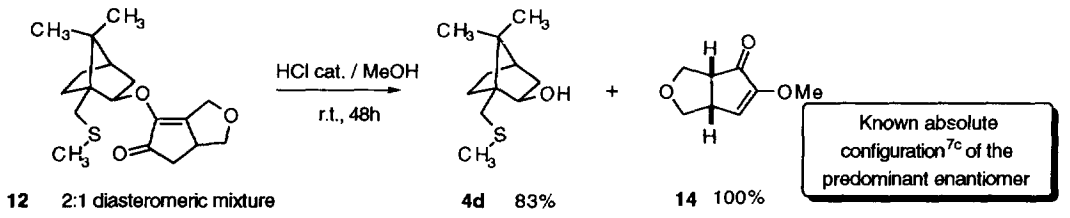


Figure 2



12 2:1 diastereomeric mixture **4d** 83% **14** 100%

Scheme 7

Since the absolute configuration of the dextrorotatory enantiomer of **14** is known[7c] to be (1*R*,5*S*), that of the major diastereomer of **12**, has to be 5*S*. Given the regularities observed up to now in the configurations of the major stereoisomers of the Pauson-Khand adducts arising from families of alkoxyenynes containing the same chiral auxiliary, the establishment of the absolute configuration in the case of **14** allows a tentative assignment of those of the major stereoisomers of **2d** and **3d** (Figure 3). Theoretical calculations[18] on the effect of the methylthiomethyl group on the diastereoselectivity of this reaction are currently underway. Preliminary results show that the most stable sulfur-chelated pentacarbonyl complex (see Scheme 5) has the methylthio ligand attached to the *pro-R* cobalt. Subsequent coordination of the C_2-*si* face of the olefin to this cobalt would then lead to the major (5*S*) adduct.

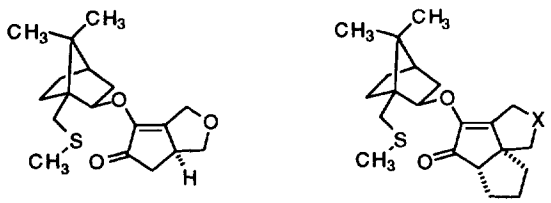


Figure 3

In summary, the angularly fused triquinane skeleton can be constructed in a stereocontrolled way by means of intramolecular Pauson-Khand reactions of cyclopentenyl-derived enynes possessing a camphor-derived chiral alkoxy group attached to the triple bond. Although 10-methylthioisoborneol **4d** has led to the largest diastereomeric excesses, 3-(neopentyloxy)isoborneol **4c** offers the advantage of the easiest separation of the diastereomers. The application of this strategy to the enantioselective synthesis of naturally occurring angular triquinanes is currently being studied in our laboratories and will be reported in forthcoming publications.[16]

Experimental

General. Melting points were determined in open ended capillary tubes on a Büchi-Tottoli apparatus or on a Reichert-Thermovar Köfler apparatus and are uncorrected. Infrared spectra were measured with a Perkin-Elmer 681 or with a Nicolet FT-IR 510 spectrometer using film NaCl or KBr pellet techniques. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, on a Varian Gemini-200 or on a Varian Unity-300 spectrometer with tetramethylsilane or chloroform as an internal standard. Chemical shifts are expressed in δ (ppm) units downfield by TMS. The multiplicity in ^{13}C NMR spectra was determined by means of DEPT techniques. Mass spectra were recorded at 70 eV ionizing voltage on a Hewlett-Packard 5890 apparatus. Ammonia was used generally for chemical ionization (CI) or FAB. MS spectra are presented as *m/z* (% rel. int.). Optical rotations were measured with a Perkin-Elmer 241 MC automatic polarimeter. DSC measurements were performed on a Mettler DSC30 instrument at the "Servei de Calorimetria de Reacció i Anàlisi Tèrmica. Divisió III. Universitat de Barcelona". THF and diethyl ether used in the reactions were dried by distillation over metallic sodium and benzophenone, dichloromethane, chloroform, DMF and DMSO were distilled over calcium hydride and benzene over metallic sodium. All reactions were carried out in oven-dried glassware under an atmosphere of pre-purified nitrogen. The course of all of the reactions described could be conveniently monitored by TLC (Merck DC-Alufolien KIESELGEL 60 F_{254}). Silicagel (J. T. Baker, 70-230 mesh) was used for column chromatography.

General Procedure for the Preparation of 3-(alkyloxy) propargyl alcohols.

To a stirred suspension of potassium hydride (11.3 mmol, 35 % in oil) in THF (11 mL), a solution of the chiral alcohol **4** (5.7 mmol) in THF (11 mL) was added, and stirring was continued at room temperature for 30 minutes. After cooling to - 40 °C, a solution of trichloroethylene (5.7 mmol) in THF (10 ml) was added. The resulting mixture was allowed to warm to room temperature and stirred for 1 additional hour. The reaction flask was cooled to - 78 °C and 2 equivalents of *n*-BuLi in hexanes were added. The reaction mixture was allowed to warm slowly to 0 °C, stirred for 1 additional hour at 0 °C and cooled again to -40 °C. At this point, 3 equivalents of paraformaldehyde were added in one portion. The resulting suspension was allowed to warm to room temperature, treated with 2 mL of methanol and poured into saturated aqueous NH_4Cl. The aqueous layer was extracted with 3x50 mL of diethyl ether, and the combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo* to afford a crude product, which was purified by column chromatography on triethylamine-pretreated (2.5% v/v) silica gel, eluting with 1 to 5% hexane/diethyl ether mixtures.

(±)-3-(*Trans*-2-phenylcyclohexyloxy)-2-propyn-1-ol, 5a: Prepared by the general procedure from **4a** in 64 % yield (0.84 g). Colorless oil. IR (film NaCl): 3360, 3080, 3060, 3020, 2930, 2850, 2250, 1600, 1590, 1490, 1445, 1350, 1320, 1250, 1215, 1120, 1065, 995, 925, 890, 865, 845, 820, 775, 750, 695 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 7.31 - 7.20 (m, 5H); 4.13 (s, 2H); 4.09 (td, J= 10 Hz, J= 4 Hz, 1H); 2.73 (td, J= 10Hz, J= 4 Hz, 1H); 2.5 - 2.3 (m, 1H); 2.0 - 1.2 (m, 8H); ^{13}C-NMR (50 MHz, $CDCl_3$): 143.0 (C), 128.9 (CH), 128.2 (CH), 127.2 (CH), 93.6 (C), 90.5 (CH), 51.4 (CH_2), 49.8 (CH), 38.9 (C), 34.3 (CH_2), 31.6 (CH_2), 26.0 (CH_2), 25.2 (CH_2).

3-[(1*S*, 2*R*, 3*S*, 4*R*)-3-(2, 2-Dimethylpropoxy)-4, 7, 7-trimethylbicyclo [2.2.1] hept-2-yloxy]-2-propyn-1-ol, 5b: Prepared by the general procedure from **4b** in 59 % yield (0.72 g). Colorless oil. IR (film NaCl): 3340, 2940, 2860, 2250, 1475, 1455, 1410, 1390, 1360, 1315, 1285, 1255, 1220, 1190, 1140, 1115, 1085, 1060, 1010, 990, 905, 835 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 4.30 (d, J= 5.5 Hz, 2H); 4.17, 3.27 (AB, J= 7.8 Hz, 2H); 3.37, 2.95 (AB, J= 7.8 Hz, 2H); 2.13 (d, J= 5 Hz, 1H); 1.8 - 1.2 (m, 5H); 1.10 (s, 3H); 0.91 (s, 9H); 0.89 (s, 3H); 0.80 (s, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$): 95.6 (C), 93.4 (CH), 87.9 (CH), 83.5 (CH_2), 51.5 (CH_2), 50.4 (C), 49.3 (CH), 47.1 (C), 46.4 (C), 33.8 (CH_2), 33.0 (C), 27.2 (CH_3), 23.7 (CH_2), 21.3 (CH_3), 20.6 (CH_3), 11.8 (CH_3); $[\alpha]^{25}_D$ = - 63.0 ($CHCl_3$, c = 2.6).

3-[(1*R*, 2*S*, 3*R*, 4*S*)-3-(2, 2-Dimethylpropoxy)-1, 7, 7-trimethylbicyclo [2.2.1] hept-2-yloxy]-2-propyn-1-ol, 5c: Prepared by the general procedure from **4c** in 83 % yield (1.03 g). Colorless oil. IR (film NaCl): 3360, 2970, 2880, 2280, 1490, 1400, 1370, 1325, 1270, 1230, 1195, 1150, 1115, 1090, 1070, 1020, 965, 925, 850, 750 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 4.27 (d, J = 5 Hz, 2H); 3.98, 3.52 (AB, J= 6.5 Hz, 2H); 3.16 (s, 2H); 1.83 (d, J= 4.5 Hz, 1H); 1.75 - 0.82 (m, 5H); 1.08 (s, 3H); 0.98 (s, 3H); 0.92 (s, 9H); 0.79 (s, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$): 96.8 (CH), 96.7 (C), 84.4 (CH), 81.5 (CH_2), 51.0 (CH_2), 49.3 (C), 48.5 (CH), 46.9 (C), 45.9 (C), 32.9 (CH_2), 32.1 (C), 26.7 (CH_3), 23.8 (CH_2), 21.0 (CH_3), 20.3 (CH_3), 11.1 (CH_3); $[\alpha]^{25}_D$ = - 59.0 (CCl_4, c = 1.6).

3-[(1*S*, 2*R*, 4*R*)-7, 7-Dimethyl-1-methylsulfenylmethylbicyclo[2.2.1]hept-2-yloxy]-2-propyn-1-ol, 5d: Prepared by general procedure from **4d** in 54 % yield (0.82 g). Colorless oil. IR (film NaCl): 3380, 2960, 2880, 2270, 1450, 1390, 1320, 1260, 1200, 1160, 1080, 1010, 975, 930, 860, 825, 790

cm^{-1}: ^{1}H-NMR (200 MHz, $CDCl_3$): 4.32 (dd, J= 11.5 Hz, J= 3.5 Hz, 1H); 4.27 (s, 2H); 2.71, 2.46 (AB, J= 12 Hz, 2H); 2.16 (s, 3H); 1.92 - 1.00 (m, 8H); 0.96 (s, 3H); 0.86 (s, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$): 93.6 (C), 93.0 (CH), 53.6 (C), 50.9 (CH_2), 47.8 (C), 45.2 (CH), 37.7 (C), 37.2 (CH_2), 33.0 (CH_2), 30.3 (CH_2), 26.7 (CH_2), 20.3 (CH_3), 19.8 (CH_3), 17.6 (CH_3); MS (CI, NH_3): 272 ($[M+18]^+$, 5 %); 255 ($[M+1]^+$, 65 %); 183 ($[M-C_5H_{11}]^+$, 100 %); $[\alpha]^{25}_D$ = - 52.0 (CH_2Cl_2, c = 1.3).

General Procedure for the Preparation of 1-[(3-(alkyloxy)-2-propynyloxy)methyl] cyclopentenes.

To a stirred suspension of potassium hydride (0.56 mmol, 35 % in oil) in THF (5 mL), a solution of the propargyl alcohol **5** (0.51 mmol) in THF (2 mL) was added. The resulting mixture was stirred at room temperature for 30 minutes. After cooling to 0 °C, a solution of bromide **6** (0.51 mmol) in THF (2 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours. Saturated aqueous NH_4Cl (5 mL) was added and the mixture extracted with 2x20 mL of CH_2Cl_2. The extracts were washed with 25 mL of saturated aqueous NaCl and dried (Na_2SO_4). The solvent was removed *in vacuo* and the crude product was purified by column chromatography on triethylamine-pretreated (2.5% v/v) silica gel, eluting with 1 to 5% hexane/diethyl ether mixtures.

(±)-1-[(3-(*Trans*-2-phenylcyclohexyloxy)-2-propynyloxy)methyl] cyclopentene, 2a: Prepared by the general procedure from **5a** in 68 % yield (0.107 g). Colorless oil. IR (film NaCl): 3080, 3030, 2930, 2850, 2280, 1650, 1600, 1490, 1445, 1400, 1350, 1315, 1290, 1250, 1220, 1190, 1120, 1070, 1015, 990, 930, 895, 865, 820, 785, 755, 695 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 7.38 - 7.11 (m, 5H); 5.62 (quin, J= 2 Hz, 1H); 4.10 (td, J= 10 Hz, J= 4 Hz, 1H); 4.08 (s, 2H); 3.99 (s, 2H); 2.75 (td, J=10 Hz, J= 4 Hz, 1H); 2.5 - 2.21 (m, 5H); 2.0 - 1.22 (m, 9H); ^{13}C-NMR (50 MHz, C_6D_6): 143.3 (C), 142.2 (C), 129.1 (CH), 128.3 (CH), 127.6 (CH), 127.4 (CH), 93.8 (C), 89.8 (CH), 68.4 (CH_2), 58.1 (CH_2), 49.7 (CH), 37.3 (C), 34.4 (CH_2), 33.7 (CH_2), 33.1 (CH_2), 31.7 (CH_2), 26.0 (CH_2), 25.2 (CH_2), 24.1 (CH_2); MS (CI, NH_3): 328 ($[M+18]^+$, 55 %); 311 ($[M+1]^+$, 17 %); 248 ($[M+18-C_6H_8]^+$, 100 %).

1-[(3-[(1*S*, 2*R*, 3*S*, 4*R*)-3-(2, 2-Dimethylpropoxy)-4, 7, 7-trimethylbicyclo [2.2.1] hept-2-yloxy]prop-2-inyloxy)methyl] cyclopentene, 2b: Prepared by the general procedure from **5b** in 47 % yield (0.119 g). Colorless oil. IR (film NaCl): 2940, 2870, 2250, 1635, 1470, 1455, 1405, 1390, 1355, 1310, 1285, 1255, 1215, 1185, 1140, 1110, 1080, 1040, 1015, 990, 960, 925, 905, 825, 805 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6): 5.76 (t, J= 2 Hz, 1H); 4.33 (s, 2H); 4.21 (s, 2H); 4.09, 3.06 (AB, J= 6.6 Hz, 2H); 3.58, 2.91 (AB, J= 8.9 Hz, 2H); 2.48 - 2.27 (m, 4H); 2.24 (d, J= 5.3 Hz, 1H); 1.85 (quin, J= 8 Hz, 2H); 1.65 - 1.15 (m, 4H); 1.43 (s, 3H); 1.11 (s, 9H); 0.98 (s, 3H); 0.75 (s, 3H); ^{13}C-NMR (50 MHz, C_6D_6): 140.7 (C), 127.2 (CH), 95.6 (C), 93.0 (CH), 87.5 (CH), 83.2 (CH_2), 68.0 (CH_2), 57.6 (CH_2), 50.2 (C), 49.3 (CH), 47.0 (C), 35.6 (C), 33.4 (CH_2), 33.2 (CH_2), 32.6 (CH_2), 26.9 (CH_3), 23.6 (CH_2), 23.5 (CH_2), 20.8 (CH_3), 20.7 (CH_3), 11.5 (CH_3); MS (CI, NH_3): 392 ($[M+18]^+$, 3 %); 375 ($[M+1]^+$, 1 %); 223 ($[M-C_9H_{11}O_2]^+$, 100 %); $[\alpha]^{25}_D$ = - 47 (CH_2Cl_2, c = 1).

1-[(3-[(1*R*, 2*S*, 3*R*, 4*S*)-3-(2, 2-Dimethylpropoxy)-1, 7, 7-trimethylbicyclo [2.2.1] hept-2-yloxy]-2-propynyloxy)methyl] cyclopentene, 2c: Prepared by the general procedure from **5c** in 80 % yield (0.200 g). Colorless oil. IR (film NaCl): 3050, 2960, 2850, 2270, 1660, 1485, 1465, 1415, 1400, 1370, 1325, 1270, 1230, 1190, 1145, 1115, 1115, 1080, 1030, 965, 935, 850 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6): 5.78 (t, J= 2 Hz, 1H); 4.33 (s, 2H); 4.23 (s, 2H); 3.95, 3.33 (AB, J= 6.5 Hz, 2H); 3.34, 3.11 (AB, J= 8.5 Hz, 2H); 2.51 - 2.27 (m, 4H); 1.87 (quin, J= 7.5 Hz, 2H); 1.76 (d, J= 4.5 Hz, 1H); 1.58 - 0.61 (m, 4H); 1.36 (s, 3H); 1.15 (s, 9H); 1.08 (s, 3H); 0.74 (s, 3H); ^{13}C-NMR (50 MHz, C_6D_6): 142.3 (C), 127.1 (CH), 97.3 (CH), 97.1 (C), 84.6 (CH), 81.9 (CH_2), 68.0 (CH_2), 57.6 (CH_2), 49.5 (C), 49.2 (CH), 47.0 (C), 33.8 (C), 33.3 (CH_2), 32.9 (CH_2), 32.6 (CH_2), 32.3 (C), 27.0 (CH_3), 24.0 (CH_2), 23.6 (CH_2), 21.0 (CH_3), 20.8 (CH_3), 11.2 (CH_3); MS (CI, NH_3): 392 ($[M+18]^+$, 3 %); 375 ($[M+1]^+$, 5 %); 223 ($[M-C_9H_{11}O_2]^+$, 100 %); $[\alpha]^{25}_D$ = - 53.0 (CH_2Cl_2, c = 4).

1-[(3-[(1*S*, 2*R*, 4*R*)-7, 7-Dimethyl-1-methylsulfenylmethylbicyclo[2.2.1]hept-2-yloxy]-2-propynyloxy)methyl]cyclopentene, 2d: Prepared by the general procedure from **5d** in 45 % yield (0.101 g). Colorless oil. IR (film NaCl): 3030, 2940, 2840, 2250, 1640, 1450, 1390, 1370, 1310, 1255, 1205, 1150, 1075, 1020, 980, 965, 930, 860, 825, 790 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6): 5.77 (t, J= 2 Hz, 1H); 4.40 (dd, J= 11.5 Hz, J= 3.5 Hz, 1H); 4.35 (s, 2H); 4.23 (s, 2H); 2.83, 2.41 (AB, J= 12.8 Hz, 2H); 2.45 - 1.85 (m, 4H); 2.05 (s, 3H); 1.87 (quin, J= 7.5 Hz, 2H); 1.68 - 0.72 (m, 7H); 1.02 (s, 3H); 0.70 (s, 3H); ^{13}C-NMR (50 MHz, C_6D_6): 141.7 (C), 127.1 (CH), 94.0 (C), 93.1 (CH), 67.9 (CH_2), 57.1 (CH_2), 53.8 (C), 47.7 (C), 45.5 (CH), 37.5 (C), 37.3 (CH_2), 33.3 (CH_2), 33.2 (CH_2), 32.6 (CH_2), 30.5 (CH_2), 26.7 (CH_2), 23.6 (CH_2), 20.2 (CH_3), 19.9 (CH_3), 17.4 (CH_3); MS (CI, NH_3): 352 ($[M+18]^+$, 3 %); 335 ($[M+1]^+$, 38 %); 183 ($M-C_9H_{11}O_2]^+$, 100 %); $[\alpha]^{25}_D$ = - 48 (CH_2Cl_2, c = 1.6).

General Procedures for the Intramolecular Pauson-Khand Reaction of 1-[(3-(Alkoxy)-2-propynyloxy)methyl]cyclopentenes.

Thermal Reaction: To a stirred solution of a 1-[(3-alkoxy)-2-propynyloxy)methyl] cyclopentene (0.1 mmol) in anhydrous isooctane (8 mL), dicobaltoctacarbonyl (0.11 mmol) was added in one portion, and the resulting dark-coloured solution was stirred at room temperature for 1 hour, after which time the formation of the hexacarbonyldicobalt complex was complete (TLC). The reaction mixture was heated at 80 °C during 3-12 hours (until complete disappearence of the complex; see Table 1), filtered through Celite and directly submitted to column chromatography on silicagel, eluting with 1 to 3% hexane/diethyl ether mixtures.

Tertiary Amine *N*-Oxide Mediated Reaction: To a stirred solution of a 1-[(3-alkoxy)-2-propynyloxy)methyl]cyclopentene (0.097 mmol) in anhydrous dichloromethane (7 mL), dicobaltoctacarbonyl (0.1 mmol) was added in one portion, and the resulting dark-coloured solution was stirred at room temperature for 1 hour, after which time the formation of the hexacarbonyldicobalt complex was complete (TLC). The reaction mixture was externally cooled with ice, solid anhydrous *N*-methylmorpholino-*N*-oxide (0.58 mmol, 6 equiv.) was added in one portion, the reaction mixture was allowed to attain the room temperature by removal of the cooling bath and the extent of the reaction was monitored by TLC. This treatment was repeated until complete disappearence of the complex (6 to 12 equivalents of *N*-oxide). After 2 hours of additional stirring at room

temperature, the resulting suspension was filtered through Celite, the solvent was evaporated *in vacuo* and the residue was purified by column chromatography on silicagel, eluting with 1 to 3% hexane/diethyl ether mixtures.

(±)-(*1R*,5R)-7-(*Trans*-2-phenylcyclohexyloxy)-10-oxa-tricyclo[6.3.0.0^{1,5}]undec-7-en-6-one, 9a:** Prepared by thermal reaction from **2a** in 43 % yield (0.015 g), as a 1.6:1 diastereomeric mixture. Colorless oil. IR (film NaCl): 3060, 3030, 2935, 2860, 1715, 1665, 1600, 1490, 1450, 1340, 1290, 1235, 1115, 1090, 1020, 950, 905, 885, 755, 700 cm^{-1}; ^{1}H-NMR (300 MHz, C_6D_6), major diastereomer: 7.26 - 7.01 (m, 5H); 5.00 (td, J= 10 Hz, J= 4.5 Hz, 1H); 4.27, 4.21 (AB, J= 15 Hz, 2H); 3.55, 2.92 (AB, J= 7.5 Hz, 2H); 2.72 - 2.52 (m, 1H); 2.50 - 2.40 (m, 1H); 2.15 - 2.05 (m, 1H); 1.90 (d, J= 7.5 Hz, 1H); 1.82 - 1.02 (m, 12H), minor diastereomer: 4.62 (td, J= 10 Hz, J= 4.5 Hz, 1H); 4.39, 4.12 (AB, J= 15 Hz, 2H); 3.56, 3.06 (AB, J= 7.5 Hz, 2H); 2.00 (d, J= 7.5 Hz, 1H); ^{13}C-NMR (75 MHz, C_6D_6), major diastereomer: 205.9 (C), 154.4 (C), 149.2 (C), 144.7 (C), 129.1 (CH), 128.4 (CH), 127.4 (CH), 81.8 (CH), 77.6 (CH_2), 64.4 (CH_2), 55.8 (C), 53.7 (CH), 52.9 (CH), 36.8 (CH_2), 34.8 (CH_2), 34.7 (CH_2), 29.4 (CH_2), 26.6 (CH_2), 25.8 (CH_2), 25.5 (CH_2), minor diastereomer: 205.8 (C), 157.3 (C), 149.0 (C), 144.8 (C), 129.2 (CH), 127.3 (CH), 83.1 (CH), 77.7 (CH_2), 55.9 (C), 53.6 (CH), 53.6 (CH), 52.1 (CH), 36.7 (CH_2), 34.4 (CH_2), 34.3 (CH_2), 29.7 (CH_2), 26.7 (CH_2), 25.7 (CH_2); MS (CI, NH_3): 356 ([M+18]$^+$, 72 %); 339 ([M+1]$^+$, 9 %); 194 ([M+18-$C_{10}H_{10}O_2$]$^+$, 34%).

(*1R*,5R)-7-[(1*S*, 2*R*, 3*S*, 4*R*)-3-(2, 2-Dimethylpropoxy)-4, 7, 7-trimethylbicyclo [2.2.1]hept-2-yloxy]-10-oxatricyclo[6.3.0.0^{1,5}]undec-7-en-6-one, 9b:** Prepared by thermal reaction from **2b** in 46 % yield (0.031 g), as a 2.6:1 diastereomeric mixture. Colorless oil. IR (film NaCl): 2950, 2870, 1715, 1655, 1455, 1390, 1360, 1340, 1320, 1300, 1235, 1150, 1135, 1120, 1100, 1065, 1045, 1020, 940, 920, 885 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6), major diastereomer: 4.72, 4.50 (AB, J= 14 Hz, 2H); 4.46, 3.27 (AB, J= 6.6 Hz, 2H); 3.69, 3.32 (AB, J= 8 Hz, 2H); 3.59, 2.96 (AB, J= 7.5 Hz, 2H); 2.24 - 2.12 (m, 2H); 1.81 (d, J= 6 Hz, 1H); 1.75 - 0.85 (m, 9H); 1.50 (s, 3H); 1.15 (s, 9H); 1.08 (s, 3H); 0.81 (s, 3H), minor diastereomer: 4.40, 3.17 (AB, J= 6.6 Hz, 2H); 3.72, 3.41 (AB, J= 8 Hz, 2H); 3.43, 3.04 (AB, J= 7.5 Hz, 2H); 1.90 (d, J= 6 Hz, 1H); 1.52 (s, 3H); 1.07 (s, 3H); ^{13}C-NMR (50 MHz, C_6D_6), major diastereomer: 204.6 (C), 151.3 (C), 127.6 (C), 88.4 (CH), 84.7 (CH), 83.4 (CH_2), 77.3 (CH_2), 64.6 (CH_2), 56.2 (C), 53.3 (CH), 51.6 (CH), 50.3 (C), 47.5 (C), 37.0 (CH_2), 34.1 (CH_2), 33.1 (C), 29.7 (CH_2), 27.6 (CH_3), 27.5 (CH_3), 25.4 (CH_2), 24.2 (CH_2), 21.6 (CH_3), 12.3 (CH_3), minor diastereomer: 127.5 (C), 89.5 (CH), 84.6 (CH), 77.7 (CH_2), 64.7 (CH_2), 56.4 (C), 53.1 (CH), 50.7 (CH), 50.5 (C), 37.1 (CH_2), 34.0 (CH_2), 29.6 (CH_2), 25.5 (CH_2), 24.5 (CH_2); MS (CI, NH_3): 420 ([M+18]$^+$, 100 %); 403 ([M+1]$^+$, 23 %).

(*1R,5R*)- and (*1S,5S*)-7-[(1*R*,2*S*,3*R*,4*S*)-3-(2,2-Dimethylpropoxy)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yloxy]-10-oxa-tricyclo[6.3.0.0^{1,5}]undec-7-en-6-one, 9c: Prepared by thermal reaction from **2c**. After filtration and evaporation, 0.170 g of material was obtained. The crude product was purified by column chromatography on silicagel eluting with 1 % hexane/diethyl ether, to afford 0.038 g (33 % yield) of major diastereomer (*1R,5R*), 0.006 g (5 % yield) of minor diastereomer (*1S,5S*) and 0.016 g (14 % yield) of a mixture (1:1) of diastereomers. Colorless oils. Major diastereomer: IR (film NaCl): 2955, 2870, 1710, 1665, 1480, 1460, 1410, 1395, 1360, 1315, 1290, 1235, 1185, 1140, 1100, 1080, 1025, 1000, 960, 940, 885, 790, cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6): 4.99, 3.59 (AB, J= 6.5 Hz, 2H); 4.81, 4.51 (AB, J= 14.5 Hz, 2H); 3.78, 3.57 (AB, J= 7.5 Hz, 2H); 3.11, 2.99 (AB, J= 8.5 Hz, 2H); 2.43 - 2.15 (m, 3H);

1.84 (d, J= 4.5 Hz, 1H); 1.78 - 0.83 (m, 8H); 1.48 (s, 3H); 1.11 (s, 3H); 0.99 (s, 9H); 0.85 (s, 3H); ^{13}C-NMR (50 MHz, C_6D_6): 204.7 (C), 151.8 (C), 128.7 (C), 85.9 (CH), 85.6 (CH), 80.8 (CH_2), 77.3 (CH_2), 64.2 (CH_2), 55.2 (C), 53.5 (CH), 49.3 (C), 47.8 (CH), 47.3 (C), 36.4 (CH_2), 33.6 (CH_2), 21.0 (C), 29.2 (CH_2), 27.1 (CH_3), 24.9 (CH_2), 24.1 (CH_2), 21.4 (CH_3), 21.1 (CH_3), 11.6 (CH_3); MS (CI, NH_3): 420 ([M+18]$^+$, 100 %); 403 ([M+1]$^+$, 59 %); $[\alpha]^{25}_D$ = - 38 (CH_2Cl_2, c = 1.8). Minor diastereomer: IR (film NaCl): 2955, 2870, 1715, 1655, 1475, 1360, 1300, 1235, 1140, 1105, 1075, 1040, 1015, 1000, 965, 890, 735 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6): 4.71, 4.53 (AB, J= 14 Hz, 2H); 3.98, 3.29 (AB, J= 7 Hz, 2H); 3.77, 3.51 (AB, J= 8.5 Hz, 2H); 3.12, 2.89 (AB, J= 8.5 Hz, 2H); 2.45 - 2.15 (m, 3H); 1.81 (d, J= 4.5 Hz, 1H); 1.78 - 0.83 (m, 8H); 1.53 (s, 3H); 1.14 (s, 3H); 0.98 (s, 9H); 0.84 (s, 3H); MS (CI, NH_3): 420 ([M+18]$^+$, 100 %); 403 ([M+1]$^+$, 38 %).

(*1R,5R*)-7-[(1*S*,2*R*,4*R*)-7, 7-Dimethyl-1-methylsulfenylmethylbicyclo[2.2.1]hept-2-yloxy]-10-oxatricyclo[6.3.0.0^{1,5}]undec-7-en-6-one, 9d: Prepared from **2d** by thermal reaction in 32 % yield (0.02 g) as a 9.5:1 diastereomeric mixture and by *N*-oxide mediated reaction in 20 % yield (0.007 g) as a 8:1 diastereomeric mixture. Colorless oil. IR (film NaCl): 2950, 1715, 1660, 1450, 1360, 1340, 1300, 1120, 1100, 1045, 1020, 940, 890, 740 cm^{-1}; ^{1}H-NMR (300 MHz, C_6D_6), major diastereomer: 4.63, 4.49 (AB, J=14.5 Hz, 2H); 4.29 (dd, J= 8.2 Hz, J= 3 Hz, 1H); 3.71, 3.33 (AB, J= 7.7 Hz, 2H); 3.12, 2.41 (AB, J= 12 Hz, 2H); 2.25 - 2.12 (m, 2H); 1.99 (s, 3H); 1.80 (d, J= 11 Hz, 1H); 1.70 - 0.85 (m, 11H); 1.23 (s, 3H); 0.77 (s, 3H), minor diastereomer: 4.82, 4.50 (AB, J= 14.5 Hz, 2H); 3.68, 3.25 (AB, J= 7.7 Hz, 2H); 1.96 (s, 3H); 0.79 (s, 3H); ^{13}C-NMR (75 MHz, C_6D_6), major diastereomer: 204.2 (C), 149.6 (C), 85.9 (CH), 76.9 (CH_2), 64.1 (CH_2), 56.0 (C), 54.1 (C), 52.3 (CH), 47.8 (C), 45.8 (CH), 40.5 (CH_2), 36.6 (CH_2), 33.8 (CH_2), 31.0 (CH_2), 29.2 (CH_2), 27.1 (CH_2), 25.1 (CH_2), 20.5 (CH_3), 20.4 (CH_3), 17.3 (CH_3), minor diastereomer: 84.8 (CH), 77.2 (CH_2), 64.5 (CH_2), 38.8 (CH_2), 20.6 (CH_3); MS (CI, NH_3): 380 ([M+18]$^+$, 15 %); 363 ([M+1]$^+$, 100 %); 183 ([M-$C_{10}H_{11}O_3$]$^+$, 24 %).

1-(3-Iodopropyl) cyclopentene, 8:

a) *tert*-Butyl 3-(1-cyclopentenyl)propanoate: To a solution of LDA in THF (30 mL), prepared at - 20 °C from 2.29 mL (0.016 mol) of diisopropylamine and 9.51 mL of BuLi (1.7 M in hexanes), was added at - 78 °C a solution of *tert*-butyl acetate (1.875 g, 0.016 mol) in THF (5 mL). After stirring at - 78 °C for 45 minutes, the resulting mixture was added at - 78 °C to a solution of 0.87 g (5.4 mmol) of bromide **6** in THF-DMPU (60 mL, 2:1). The reaction was stirred for 3 hours at - 78 °C, and treated with 1 mL of acetic acid. The resulting mixture was poured into H_2O. The aqueous layer was extracted with 2x50 mL of diethyl ether, and the combined organic layers were washed whith saturated aqueous NaCl. Drying ($MgSO_4$), filtration and evaporation gave 3.07 g of crude product, which was purified by column chromatography on silica gel, eluting with 1 to 3% hexane/diethyl ether mixtures, to afford 0.71 g (70 %) of pure *tert*-butyl 3-(1-cyclopentenyl)propanoate. Colorless oil. IR (film NaCl): 3060, 2970, 2940, 2860, 1740, 1655, 1450, 1400, 1375, 1345, 1305, 1260, 1155, 1045, 990, 960, 855, 825, 760 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 5.34 (s, 1H); 2.36 - 2.17 (m, 8H); 1.84 (quin, J= 7 Hz, 2H); 1.44 (s, 9H); ^{13}C-NMR (50 MHz, $CDCl_3$): 172.8 (C), 143.1 (C), 123.7 (CH), 80.0 (C), 35.0 (CH_2), 34.0 (CH_2), 32.4 (CH_2), 28.0 (CH_3), 26.6 (CH_2), 23.3 (CH_2); MS (CI, NH_3): 231 ([M+35]$^+$, 25 %); 214 ([M+18]$^+$, 100 %); 195 ([M+1]$^+$, 66 %).

b) 3-(1-Cyclopentenyl)-1-propanol: To a stirred solution of the propanoate described above (0.053 g, 0.27 mmol) in diethyl ether (4 mL) at - 20 °C was added 0.67 mL of DIBAH (1 M in hexanes). The reaction was stirred for 30 minutes at - 20 °C, 72 hours at room temperature, treated with 1 mL of methanol and poured into a saturated aqueous NaCl solution. The aqueous layer was extracted wit 2x25 mL of diethyl ether, and the combined organic layers were dried ($MgSO_4$), filtered and stripped of solvents to give 0.037 of crude product, which was purified by column chromatography on silica gel, eluting with 1 to 10 % hexane/diethyl ether mixtures, to afford 0.025 g (74 %) of pure 3-(1-cyclopentenyl)-1-propanol. Colorless oil. IR (film NaCl): 3330, 3040, 2940, 2850, 1650, 1445, 1295, 1060, 950, 920, 800, 670 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 5.36 (quin, J= 2 Hz, 1H); 3.65 (t, J= 12.5 Hz, 2H); 2.3 - 2.0 (m, 6H); 1.86 (quin, J= 6 Hz, 2H); 1.77 - 1.41 (m, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$): 144.2 (C), 123.8 (CH), 62.9 (CH_2), 35.0 (CH_2), 32.4 (CH_2), 30.8 (CH_2), 27.5 (CH_2), 23.5 (CH_2); MS (EI): 126 ($[M]^+$, 18 %); 108 ($[M-H_2O]^+$, 8 %).

c) 1-(3-Iodopropyl) cyclopentene: To a stirred solution of methyltriphenoxyphosphonium iodide (1.86 g, 4.12 mmol) in DMF (15 mL) at room temperature was added a solution of 3-(1-cyclopentenyl)-1-propanol (0.26 g, 2.06 mmol) in 10 mL of DMF. The reaction was stirred at room temperature for 2 hours, and subsequently poured onto saturated aqueous Na_2SO_3. The aqueous layer was extracted with 3x25 mL of hexane, and the combined organic layers were washed with saturated aqueous NaCl, dried ($MgSO_4$), filtered and evaporated to afford 1.064 g of crude product. Purification by column chromatography on silica gel, eluting with hexane, afforded 0.445 g (92 %) of pure iodide **8**. Colorless oil. IR (film NaCl): 3050, 2930, 2900, 2850, 1640, 1440, 1295, 1255, 1210, 1165, 1035, 940, 820, 790 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): 5.38 (t, J= 2 Hz, 1H); 3.18 (t, J= 7 Hz, 2H); 2.4 - 2.1 (m, 6H); 2.05 - 1.75 (m, 4H); ^{13}C-NMR (50 MHz, $CDCl_3$): 142.5 (C), 124.6 (CH), 34.9 (CH_2), 32.4 (CH_2), 31.8 (CH_2), 31.5 (CH_2), 23.4 (CH_2), 6.8 (CH_2); MS (EI): 236 ($[M]^+$, 38 %); 109 ($[M-I]^+$, 30 %); 81 ($[M-C_2H_4I]^+$, 100 %).

General Procedure for the Preparation of 1-[5-(Alkoxy)-4-pentynyl] cyclopentenes.

To a stirred solution of an alkoxyacetylene **7** (0.45 mmol) in THF (0.5 mL) at -10 °C was added 0.27 mL of BuLi (1.7 M in hexanes). The mixture was stirred at - 10 °C for 30 minutes. A solution of iodide **8** (0.89 mmol) in HMPA (1 mL) was added and the resulting mixture was heated at 50 °C during 3 hours. This mixture was poured onto saturated aqueous NH_4Cl, and the aqueous layer was extracted whith 3x25 mL of hexane. The combined organic layers were dried (Na_2SO_4), filtered and evaporated *in vacuo*. The residue was purified by column chromatography on triethylamine-pretreated (2.5% v/v) silicagel, eluting with hexane.

(±)-1-[5-(*trans*-2-Phenylcyclohexyloxy)4-pentynyl]cyclopentene, 3a: Prepared by general procedure from **7a** in 50 % yield (0.085 g). Colorless oil. IR (film NaCl): 3060, 3040, 2270, 2200, 1650, 1605, 1490, 1450, 1355, 1340, 1295, 1235, 1205, 1170, 1120, 995, 935, 895, 865, 815, 750, 695 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6): 7.35 - 7.13 (m, 5H); 5.48 - 5.38 (m, 1H); 3.98 (td, J=10.5 Hz, J= 4.5 Hz, 1H); 2.74 (td, J= 10 Hz, J= 4.5 Hz, 1H); 2.5 - 2.0 (m, 7H); 1.96 - 0.98 (m, 13H); ^{13}C-NMR (50 MHz, C_6D_6): 144.2 (C), 143.1 (C), 128.6 (CH), 127.9 (CH), 126.8 (CH), 123.7 (CH), 88.3 (CH), 49.2 (CH), 38.7 (C), 35.2 (CH_2), 33.9 (CH_2), 32.7 (CH_2), 31.3 (CH_2), 30.6 (CH_2), 28.4 (CH_2), 25.6 (CH_2), 24.7 (CH_2), 23.8 (CH_2), 17.6 (CH_2); MS (FAB, glycerol): 309 ($[M+1]^+$, 2 %); 158 ($[M-C_{10}H_{14}O]^+$, 100 %).

1-[5-[(1*S*,2*R*,3*S*,4*R*)-3-(2,2-Dimethylpropoxy)-4,7,7-trimethylbicyclo[2.2.1]hept-2-yloxy]-4-pentynyl]cyclopentene, 3b: Prepared by the general procedure from **7b** in 57 % yield (0.136 g). Colorless oil. IR (film NaCl): 3040, 2950, 2880, 2840, 2270, 1475, 1460, 1390, 1360, 1290, 1235, 1140, 1115, 1085, 1060, 1030, 1020, 1000, 910, 820 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6): 5.38 (m, 1H); 4.03, 3.00 (AB, J= 6.5 Hz, 2H); 3.53, 2.84 (AB, J= 8 Hz, 2H); 2.4 - 1.95 (m, 6H); 1.9 - 1.55 (m, 4H); 1.49 - 0.65 (m, 7H); 1.37 (s, 3H); 1.02 (s, 9H); 0.90 (s, 3H); 0.68 (s, 3H); ^{13}C-NMR (50 MHz, C_6D_6): 144.0 (C), 123.8 (CH), 92.5 (CH), 90.8 (C), 87.8 (CH), 83.2 (CH_2), 49.9 (C), 49.2 (CH), 46.6 (C), 35.6 (CH_2), 33.5 (CH_2), 32.7 (CH_2), 32.6 (C), 30.6 (CH_2), 30.1 (C), 28.4 (CH_2), 26.9 (CH_3), 23.8 (CH_2), 23.6 (CH_2), 20.9 (CH_3), 20.8 (CH_3), 17.6 (CH_2), 11.5 (CH_3); MS (FAB, glycerol): 373 ([M+1]$^+$, 3 %); 152 ([M-$C_{15}H_{24}O$]$^+$, 100 %); $[\alpha]^{25}_D$ = - 45 (CH_2Cl_2, c = 1.1).

1-[5-[(1*R*,2*S*,3*R*,4*S*)-3-(2,2-Dimethylpropoxy)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yloxy]-4-pentynyl]cyclopentene, 3c: Prepared by the general procedure from **7c** in 54 % yield (0.074 g). Colorless oil. IR (film NaCl): 3040, 2950, 2270, 1480, 1455, 1390, 1360, 1240, 1140, 1110, 1060, 1030, 960, 815 cm^{-1}; ^{1}H-NMR (300 MHz, C_6D_6): 5.32 (quin, J= 2 Hz, 1H); 3.83, 3.24 (AB, J= 6.5 Hz, 2H); 3.27, 2.99 (AB, J= 8 Hz, 2H); 2.42 - 1.98 (m, 6H); 1.75 (quin, J= 7 Hz, 2H); 1.62 (quin, J= 5.5 Hz, 2H); 1.45 - 0.51 (m, 7H); 1.24 (s, 3H); 1.02 (s, 9H); 0.98 (s, 3H); 0.61 (s, 3H); ^{13}C-NMR (75 MHz, C_6D_6): 144.3 (C), 123.8 (CH), 97.0 (CH), 92.7 (C), 84.9 (CH), 82.0 (CH_2), 49.6 (C), 49.5 (CH), 47.1 (C), 35.6 (C), 35.4 (CH_2), 33.2 (CH_2), 32.8 (CH_2), 32.4 (C), 30.7 (CH_2), 28.5 (CH_2), 27.1 (CH_3), 24.2 (CH_2), 23.8 (CH_2), 21.1 (CH_3), 20.9 (CH_3), 17.7 (CH_2), 11.4 (CH_3); MS (FAB, glycerol): 373 ([M+1]$^+$, 5 %); 223 ([M-$C_{10}H_{13}O$]$^+$, 33 %); 153 ([M-$C_{15}H_{24}O$+1]$^+$, 76 %); $[\alpha]^{25}_D$ = - 47 (CH_2Cl_2, c = 0.9).

1-[5-[(1*S*,2*R*,4*R*)-7,7-Dimethyl-1-methylsulfenylmethylbicyclo[2.2.1]hept-2-yloxy] -4-pentynyl]cyclopentene, 3d: Prepared by the general procedure from **7d** in 56 % yield (0.075 g). Colorless oil. IR (film NaCl): 3040, 2940, 2840, 2270, 1650, 1455, 1440, 1390, 1375, 1315, 1300, 1235, 1210, 1120, 1045, 1025, 995, 985, 970, 940, 865, 820 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6): 5.36 (quin, J= 2 Hz, 1H); 4.30 (dd, J= 8 Hz, J= 3.5 Hz, 1H); 2.78, 2.31 (AB, J= 12.5 Hz, 2H); 2.33 - 1.29 (m, 19 H); 1.95 (s, 3H); 0.95 (s, 3H); 0.61 (s, 3H); ^{13}C-NMR (50 MHz, C_6D_6): 144.3 (C), 123.8 (CH), 92.1 (CH), 89.1 (C), 53.8 (C), 47.7 (C), 45.6 (CH), 38.1 (C), 37.5 (CH_2), 35.3 (CH_2), 33.2 (CH_2), 32.8 (CH_2), 30.6 (CH_2 x 2), 28.4 (CH_2), 26.9 (CH_2), 23.8 (CH_2), 20.3 (CH_3), 20.0 (CH_3), 17.7 (CH_2), 17.5 (CH_3); MS (FAB, glycerol): 333 ([M+1]$^+$, 2 %); 183 ([M-$C_{10}H_{13}O$]$^+$, 73 %); $[\alpha]^{25}_D$ = - 45 (CH_2Cl_2, c = 0.8).

General Procedure for the Intramolecular Pauson-Khand Reaction of 1-[5-(Alkoxy)-4-pentynyl]cyclopentenes.

Thermal Reaction: To a stirred solution of a 1-[5-(alkoxy)-4-pentynyl]cyclopentene **3** (0.15 mmol) in anhydrous isooctane (10 mL), dicobaltoctacarbonyl (0.16 mmol) was added in one portion, and the resulting dark-coloured solution was stirred at room temperature for 1 hour, after which time the formation of the hexacarbonyldicobalt complex was complete (TLC). The reaction mixture was heated (80 °C/reflux, see Table 1) during 7-10 hours (until complete disappearence of the complex; see Table 1), filtered through Celite and directly submitted to column chromatography on silicagel, eluting with 1 to 3% hexane/diethyl ether mixtures.

(±)-(*1R*,5R)-7-(*trans*-2-Phenylcyclohexyloxy)tricyclo[6.3.0.0^{1,5}]undec-7-en-6-one, 10a:** Prepared by thermal reaction from **3a** in 42 % yield (0.021 g), as a 1.4:1 diastereomeric mixture. Colorless oil. IR (film NaCl): 3060, 3040, 2940, 2860, 1705, 1650, 1450, 1340, 1120, 1080, 1030, 760, 700 cm^{-1}; ^{1}H-NMR (300 MHz, C_6D_6), major diastereomer: 7.26 - 6.88 (m, 5H); 5.14 (td, J= 9 Hz, J= 4.5 Hz, 1H); 2.58 - 2.33 (m, 2H); 2.22 - 0.62 (m, 20H), minor diastereomer: 4.73 (td, J= 9 Hz, J= 4.5 Hz, 1H); 2.61 (td, J= 10 Hz, J= 4.5 Hz, 1H); ^{13}C-NMR (75 MHz, C_6D_6), major diastereomer: 205.8 (C), 161.9 (C), 148.5 (C), 144.4 (C), 128.0 (CH), 127.8 (CH), 126.1 (CH), 79.5 (CH), 55.4 (CH), 54.8 (C), 52.4 (CH), 36.5 (CH_2), 35.7 (CH_2), 34.7 (CH_2), 34.0 (CH_2), 28.6 (CH_2), 25.8 (CH_2), 24.9 (CH_2), 24.7 (CH_2), 24.4 (CH_2), 22.6 (CH_2), minor diastereomer: 205.7 (C), 163.9 (C), 148.3 (C), 128.1 (CH), 127.9 (CH), 126.0 (CH), 80.8 (CH), 55.2 (CH), 55.0 (C), 51.4 (CH), 36.8 (CH_2), 35.6 (CH_2), 34.1 (CH_2), 33.5 (CH_2), 28.9 (CH_2), 25.9 (CH_2), 24.8 (CH_2), 24.6 (CH_2), 24.5 (CH_2), 23.0 (CH_2); MS (FAB, glycerol): 337 ([M+1]$^+$, 5 %); 178 ([M-$C_{12}H_{14}$]$^+$, 100 %); 158 ([M-$C_{11}H_{14}O_2$]$^+$, 75 %).

(*1R*,5R)-7-[(1*S*,2*R*,3*S*,4*R*)-3-(2,2-Dimethylpropoxy)-4,7,7-trimethylbicyclo [2.2.1]hept-2-yloxy]tricyclo[6.3.0.0^{1,5}]undec-7-en-6-one, 10b:** Prepared by thermal reaction from **3b** in 32 % yield (0.028 g), as a 1.5:1 diastereomeric mixture. Colorless oil. IR (film NaCl): 2950, 2870, 1710, 1645, 1475, 1390, 1340, 1315, 1275, 1135, 1120, 910 cm^{-1}; ^{1}H-NMR (300 MHz, C_6D_6), major diastereomer: 4.95, 3.28 (AB, J= 6.5 Hz, 2H); 3.65, 2.95 (AB, J= 8 Hz, 2H); 3.03 - 2.91 (m, 1H); 2.59 - 2.45 (m, 1H); 2.27 - 2.11 (m, 3H); 1.91 - 1.81 (m, 1H); 1.72 - 0.72 (m, 12H); 1.49 (s, 3H); 1.06 (s, 9H); 0.78 (s, 3H); 0.77 (s, 3H), minor diastereomer: 4.91, 3.24 (AB, J= 6.5 Hz, 2H); 3.57, 2.99 (AB, J= 8 Hz, 2H); 1.51 (s, 3H); 1.02 (s, 9H); 0.90 (s, 3H); 0.73 (s, 3H); ^{13}C-NMR (75 MHz, C_6D_6), major diastereomer: 205.2 (C), 161.8 (C), 148.0 (C), 88.4 (CH), 83.1 (CH), 82.6 (CH_2), 55.5 (CH), 55.3 (C), 50.6 (CH), 49.7 (C), 46.5 (C), 36.7 (CH_2), 36.1 (CH_2), 33.6 (CH_2), 32.4 (C), 29.2 (CH_2), 26.9 (CH_3), 24.9 (CH_2), 24.8 (CH_2), 23.7 (CH_2), 23.5 (CH_2), 21.2 (CH_3), 21.1 (CH_3), 11.7 (CH_3), minor diastereomer: 159.9 (C), 147.9 (C), 88.5 (CH), 82.9 (CH), 55.4 (CH), 51.9 (C), 50.3 (CH), 37.2 (CH_2), 36.2 (CH_2), 28.9 (CH_2), 26.5 (CH_3), 24.7 (CH_2), 23.8 (CH_2), 23.6 (CH_2); MS (FAB, glycerol): 401 ([M+1]$^+$, 3 %); 178 ([M-$C_{15}H_{26}O$]$^+$, 50 %); 152 ([M-$C_{16}H_{24}O_2$]$^+$, 90 %).

(*1R,5R*)- and (*1S,5S*)-7-[(1*R*,2*S*,3*R*,4*S*)-3-(2,2-Dimethylpropoxy)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yloxy]tricyclo[6.3.0.0^{1,5}]undec-7-en-6-one, 10c: Prepared by thermal reaction from **3c**. After filtration and evaporation, 0.138 g of material was obtained. The crude product was purified by column chromatography on silica gel eluting with 1 % hexane/diethyl ether, to afford 0.014 g (20 % yield) of major diastereomer (*1R,5R*), 0.004 g (6 % yield) of minor diastereomer (*1S,5S*) and 0.002 g (3 % yield) of a mixture (2:1) of both diastereomers. Colorless oils. Major diastereomer: IR (film NaCl): 2960, 2880, 1710, 1655, 1475, 1395, 1355, 1150, 1110, 1020, 960, 875 cm^{-1}; ^{1}H-NMR (300 MHz, C_6D_6): 5.20, 3.59 (AB, J= 6.5 Hz, 2H); 3.04, 3.02 (AB, J= 8.5 Hz, 2H); 3.18 - 2.98 (m, 1H); 2.66 - 2.52 (m, 1H); 2.28 - 2.18 (m, 4H); 1.82 - 0.72 (m, 12H); 1.47 (s, 3H); 1.06 (s, 3H); 0.90 (s, 9H); 0.83 (s, 3H); ^{13}C-NMR (75 MHz, C_6D_6): 205.0 (C), 159.4 (C), 148.7 (C), 86.4 (CH), 84.8 (CH), 80.9 (CH_2), 56.3 (CH), 55.0 (C), 49.2 (C), 48.2 (CH), 47.4 (C), 37.3 (CH_2), 36.4 (CH_2), 33.7 (CH_2), 32.1 (C), 29.4 (CH_2), 27.1 (CH_3), 25.3 (CH_2), 24.8 (CH_2), 24.3 (CH_2), 23.6 (CH_2), 21.6 (CH_3), 21.3 (CH_3), 11.7 (CH_3); MS (ICI, NH_3): 418 ([M+18]$^+$, 19 %); 401 ([M+1]$^+$, 100 %); $[\alpha]^{25}_D$ = - 26 (CH_2Cl_2, c = 0.8). Minor diastereomer: IR (film NaCl): 2970, 2880, 1715, 1660, 1480, 1400, 1350, 1210, 1150, 1110, 1020, 960 cm^{-1}; ^{1}H-NMR (300 MHz, C_6D_6): 4.50,

3.42 (AB, J= 6.5 Hz, 2H); 3.09, 2.97 (AB, J= 8 Hz, 2H); 2.58 - 2.44 (m, 1H); 2.34 - 2.16 (m, 4H); 1.81 - 0.65 (m, 13H); 1.49 (s, 3H); 1.07 (s, 3H); 0.92 (s, 9H); 0.78 (s, 3H); MS (CI, NH_3): 418 ($[M+18]^+$, 40 %); 401 ($[M+1]^+$, 100 %).

(*1R*,5R)-7-[(1*S*,2*R*,4*R*)-7,7-Dimethyl-1-methylsulfenylmethylbicyclo[2.2.1]hept-2-yloxy]tricyclo[6.3.0.0^{1,5}]undec-7-en-6-one, 10d:** Prepared from **3d** by thermal reaction in 34 % yield (0.015 g), as a 12:1 diastereomeric mixture. Colorless oil. IR (film NaCl): 2950, 2870, 1710, 1650, 1450, 1390, 1345, 1315, 1290, 1275, 1200, 1160, 1115, 1100, 1075, 1045, 1020, 1000, 950, 875 cm^{-1}; ^{1}H-NMR (300 MHz, C_6D_6), major diastereomer: 4.52 (dd, J= 8 Hz, J= 3.5 Hz, 1H); 3.19, 2.38 (AB, J= 12 Hz, 2H); 2.48 - 2.32 (m, 1H); 2.28 - 1.98 (m, 4H); 1.95 (s, 3H); 1.79 - 0.82 (m, 15H); 1.22 (s, 3H); 0.73 (s, 3H), minor diastereomer: 4.85 (dd, J= 8 Hz, J= 3.5 Hz, 1H); 3.14, 2.35 (AB, J= 12 Hz, 2H); 1.93 (s, 3H); 0.74 (s, 3H); ^{13}C-NMR (75 MHz, C_6D_6), major diastereomer: 205.5 (C), 158.3 (C), 149.9 (C), 85.4 (CH), 56.3 (C), 55.3 (CH), 54.2 (C), 48.2 (C), 46.0 (CH), 40.7 (CH_2), 37.2 (CH_2), 36.7 (CH_2), 34.1 (CH_2), 31.2 (CH_2), 29.6 (CH_2), 27.5 (CH_2), 25.6 (CH_2), 25.2 (CH_2), 24.0 (CH_2), 20.9 (CH_3), 20.7 (CH_3), 17.6 (CH_3), minor diastereomer: 84.2 (CH), 39.4 (CH_2), 37.3 (CH_2), 31.4 (CH_2), 25.4 (CH_2), 24.2 (CH_2), 21.0 (CH_3); MS (CI, NH_3): 378 ($[M+18]^+$, 11 %); 361 ($[M+1]^+$, 100 %).

(1*S*,2*R*,4*R*)-2-(3-Allyloxy-1-propynyloxy)-7,7-dimethyl-1-methylsulfenylmethyl bicyclo[2.2.1]heptane, 11: To a stirred suspension of potassium hydride (5.9 mmol, 35 % in oil) in THF (15 mL), a solution of the propargyl alcohol **5d** (3.9 mmol) in THF (5 mL) was added. The resulting mixture was stirred at room temperature for 30 minutes. After cooling to 0 °C, allyl bromide (0.65 mL, 7.8 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours. Saturated aqueous NH_4Cl (15 mL) was added and the mixture extracted with 2x60 mL of CH_2Cl_2. The extracts were washed with 75 mL of saturated aqueous NaCl and dried (Na_2SO_4). The solvent was eliminated *in vacuo* and the crude product was purified by column chromatography on triethylamine-pretreated (2.5% v/v) silica gel, eluting with 5% hexane/diethyl ether, to give the alkoxyenyne **11** (0.77 g, 67% yield) as a colorless oil. IR (film NaCl): 3070, 2950, 2850, 2270, 1390, 1370, 1260, 1080, 980, 860 cm^{-1}.^{1}H-RMN (200 MHz, $CDCl_3$): 0.86 (s, 3H); 0.96 (s, 3H); 1.00-1.86 (m, 7H); 2.16 (s, 3H); 2.47, 2.78 (AB system, J=12Hz, 2H); 4.03 (d, J=5Hz, 2H); 4.18 (s, 2H); 4.33 (m, 1H); 5.13-5.38 (m, 2H); 5.81 6.03 (m, 1H). ^{13}C-RMN (50 MHz, $CDCl_3$): 17.6 (CH_3), 19.8 (CH_3), 20.3 (CH_3), 26.7 (CH_2), 30.3 (CH_2), 33.0 (CH_2), 34.9 (q), 37.2 (CH_2), 45.3 (CH), 47.7 (q), 53.6 (q), 57.4 (CH_2), 69.8 (CH_2), 93.0 (CH), 93.8 (q), 117.1 (CH_2), 134.4 (CH).

(5*S*) and (5*R*)-[(1*S*,2*R*,4*R*)-7,7-Dimethyl-1-methylsulfenylmethylbicyclo[2.2.1]hept-2-yloxy]-7-oxabicyclo[3.3.0]oct-1(2)-en-3-one, 12: To a stirred solution of the enyne **11** (100 mg, 0.34 mmol) in anhydrous hexane (30 mL), $Co_2(CO)_8$ (116 mg, 0.34 mmol) was added in one portion. After stirring for 3 hours at room temperature under a gentle stream of nitrogen, TLC analysis showed that neither the starting enyne nor the corresponding hexacarbonyldicobalt complex were present in the reaction mixture, which was filtered through Celite and directly submitted to column chromatography on triethylamine-pretreated silicagel (2.5% v/v), eluting with hexane/ethyl acetate mixtures of increasing polarity, to afford 41mg (37% yield) of the

bicyclic enone **12** as a 2:1 diastereomeric mixture. IR (NaCl film): 2940, 2870, 1725, 1660, 1450, 1410, 1350, 1300, 1110, 1025, 885 cm^{-1}. ^{1}H-RMN (200 MHz, $CDCl_3$): 0.88 (s, 3H); 1.08 (s, 3H); 1.53-2.22 (m, 6H); 2.06 [major diast.], 2.10 [minor diast.] (s, 3H); 2.46 [major diast.], 2.94 [major diast.], 2.46 [minor diast.], 2.96 [minor diast.] (AB, J=12Hz, 2H); 2.53-2.70 (m, 1H); 3.02-3.28 (m, 2H); 4.05-4.15 (dd, J=3Hz, J'=7Hz, 1H); 4.22-4.36 (m, 2H); 4.55-4.75 (m, 3H); ^{13}C-RMN (50 MHz, $CDCl_3$): 17.5 (CH_3), 20.1 (CH_3), 20.4 (CH_3), 27.0 (CH_2), 30.6 [major diast.], 30.8 [minor diast.] (CH_2), 33.5 (CH_2), 33.7 (CH_2), 40.2 (CH), 40.6 (CH_2), 45.5 (CH), 47.1 (q), 53.7 (q), 64.9 [major diast.], 65.4 [minor diast.] (CH_2), 71.8 [major diast.], 72.3 [minor diast.] (CH_2); 84.3 [minor diast.], 85.1 [major diast.] (CH); MS (CI, NH_3): 323 ($[M+1]^+$, 14%), 339 ($[M+17]^+$, 97%).

The absolute configuration of both diastereomers was established as follows: A solution of **12** (40 mg) in dry methanol (5 mL) was treated with a few drops of a saturated methanol solution of hydrogen chloride, and stirred at room temperature during 2 days. Elimination of the solvent *in vacuo* followed by column chromatography on triethylamine-pretreated silicagel (2.5% v/v), eluting with hexane/ethyl acetate mixtures of increasing polarity gave 20 mg (83% yield) of the alcohol **4d** and 20 mg (100% yield) of optically active **14**. Since this product exhibited a positive specific rotation in chloroform solution at 22°C, the absolute configuration of the major diastereomer of **12** has to be (5*S*).[7c]

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References and Notes:

1.- For reviews on the Pauson-Khand reaction, see: (a) Pauson, P. L.; Khand, I. U. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 2-14. (b) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855-5860. (c) Pauson, P. L. in *Organometallics in Organic Synthesis. Aspects of a Modern Interdisciplinary Field;* de Meijere, A.; tom Dieck, H. Eds.; Springer: Berlin, 1988, pp. 233-246. (d) Harrington, P. J. *Transition Metals in Total Synthesis*; Wiley: New York, 1990, pp. 259-301. (e) Schore, N. E. *Organic Reactions* **1991**,*40*, 1-90. (f) Schore, N. E. in *Comprehensive Organic Synthesis*; Trost, B. M. Ed.; Pergamon Press: Oxford, 1991; vol. 5, pp. 1037-1064.

2.- (a) Gybin, A. S.; Smit, W. A.; Caple, R.; Veretenov, A. L.; Shashkov, A. S.; Vorontsova, L. G.; Kurella, M. G.; Chertkov, V. S.; Carapetyan, A. A.; Kusnikov, A. Y.; Alexanyan, M. S.; Lindemar, S. V.; Panov, V. N.; Maleev, A. V.; Strychkov, Y. T.; Sharpe, S. M. *J. Am. Chem. Soc.* **1992**, *114*, 5555-5566. (d) Veretenov, A. L.; Koltun, D. O.; Smit, W. A.; Strelenko, Y. A. *Tetrahedron Lett.* **1995**, *36*, 4651-4654.

3.- (a) Schore, N. E.; Knudsen, M. J. *J. Org. Chem.* **1984**, *49*, 5025-5026. (b) Schore, N. E.; Knudsen, M. J. *J. Org. Chem.* **1987**, *52*, 569-580. (c) Schore, N. E.; Rowley, E. G. *J. Am. Chem. Soc.* **1988**,

110, 5224-5225. (d) Rowley, E. G.; Schore, N. E. *J. Org. Chem.* **1992**, *57*, 6853-6861. (e) Rowley, E. G.; Schore, N. E. *J. Organomet. Chem.* **1991**, *413*, C5-C9. (f) Clive, D. L. J.; Cole, D. C.; Tao, Y. *J. Org. Chem.* **1994**, *59*, 1396-1406. For the synthesis of angularly fused triquinanes by an "anomalous" intermolecular Pauson-Khand annelation, see: (g) Montaña, A.-M.; Moyano, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron* **1985**, *41*, 5995-6003. (h) Billington, D. C.; Kerr, W. J.; Pauson, P. L.; Farnocchi, C. F. *J. Organomet. Chem.* **1988**, *356*, 213-219.

4.- (a) Carceller, E.; Centellas, V.; Moyano, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron Lett.* **1985**, *26*, 2475-2476. (b) Carceller, E.; García, M. Ll.; Moyano, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron* **1986**, *42*, 1831-1839. (c) Paquette, L. A.; Borrelly, S. *J. Org. Chem.* **1995**, *60*, 6912-6921.

5.- Except for the case of using a chiral nonracemic enyne substrate for the Pauson-Khand cycloaddition. See: Almansa, C.; Moyano, A.; Serratosa, F. *Tetrahedron* **1988**, *44*, 2657-2662.

6.- For related zirconocene-mediated cyclocarbonylation of enynes or dienes leading to linear and/or angular triquinanes, see: (a) Davis, J. M.; Whitby, R. J.; Jaxa-Chamiec, A. *Synlett* **1994**, 110-112. (b) Saitoh, F.; Mori, M.; Okamura, K.; Date, T. *Tetrahedron* **1995**, *51*, 4439-4446. (c) Meyer, C.; Marek, I.; Normant, J.-F. *Tetrahedron Lett.* **1996**, *37*, 857-860.

7.- Intramolecular version: (a) Poch, M.; Valentí, E.; Moyano, A.; Pericàs, M. A.; Castro, J.; De Nicola, A.; Greene, A. E. *Tetrahedron Lett.* **1990**, *31*, 7505-7508. (b) Castro, J.; Sörensen, H.; Riera, A.; Morin, C.; Moyano, A.; Pericàs, M. A.; Greene, A. E. *J. Am. Chem. Soc.* **1990**, *112*, 9388-9389. (c) Verdaguer, X.; Moyano, A.; Pericàs, M. A.; Riera, A.; Greene, A. E.; Piniella, J.; Alvarez-Larena, A. *J. Organomet. Chem.* **1992**, *433*, 305-310. (d) Castro, J.; Moyano, A.; Pericàs, M. A.; Riera, A.; Greene, A. E. *Tetrahedron: Asymmetry* **1994**, *5*, 307-310. (e) Castro, J.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron* **1995**, *51*, 6541-6556.

8.- Intermolecular version: (a) Bernardes, V.; Verdaguer, X.; Moyano, A.; Pericàs, M. A.; Riera, A.; Greene, A. E. *J. Organomet. Chem.* **1994**, *470*, C12-C14. (b) Bernardes, V.; Verdaguer, X.; Kardos, N.; Riera, A.; Moyano, A.; Pericàs, M. A.; Greene, A. E. *Tetrahedron Lett.* **1994**, *35*, 575-578. (c) Verdaguer, X.; Moyano, A.; Pericàs, M. A.; Riera, A.; Bernardes, V.; Greene, A. E.; Alvarez-Larena, A.; Piniella, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 2153-2154. (d) Fonquerna, S.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron* **1995**, *51*, 4239-4254. (e) Bernardes, V.; Kann, N.; Riera, A.; Moyano, A.; Pericàs, M. A.; Greene, A. E. *J. Org. Chem.* **1995**, *60*, 6670-6671.

9.- Schwartz, A.; Madan, P.; Whitesell, J. K.; Lawrence, R. M. *Org. Synth.* **1990**, *69*, 1-9.

10.- Oppolzer, W.; Chapuis, C.; Dupuis, D.; Guo, H. *Helv. Chim. Acta* **1985**, 68, 2100-2114.

11.- Furukawa, W.; Sugihara, Y.; Fujihara, H. *J. Org. Chem.* **1989**, *54*, 4222-4224.

12.- Moyano, A.; Charbonnier, F.; Greene, A. E. *J. Org. Chem.* **1987**, *52*, 2919-2922.

13.- (a) Pal, P. R.; Skinner, C. G.; Dennis, R. L.; Shive, W. *J. Am. Chem. Soc.* **1956**, *78*, 5116-5118. (b) Ohira, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1902-1907.

14.- This compound was prepared through a three-step sequence involving: a) alkylation of the lithium enolate of *tert*-butyl acetate with bromide **6**, b) reduction of the resulting ester with DIBAL, and c) reaction with methyltriphenoxyphosphonium iodide (see experimental section).

15.- (a) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289-5292. (b) Jeong, N.; Chung, Y. K.; Lee, B. Y.; Lee, S. H.; Yoo, S.-E. *Synlett* **1991**, 204-206.

16.- Tormo, J.; Moyano, A.; Pericàs, M. A.; Riera, A., submitted for publication.

17.- (a) Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861-5869. (b) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851-4854.

18.- Calculations performed with the PM3 (tm) semiempirical MO program, as implemented in Spartan 4.1.1 (Wavefunction, Inc.).

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