Intramolecular Pauson–Khand Reactions of Methylenecyclopropane and Bicyclopropylidene Derivatives as an Approach to Spiro(cyclopropanebicyclo[*n*.3.0]alkenones)**

Armin de Meijere,*[a] Heike Becker,[a] Andreas Stolle,[a] Sergei I. Kozhushkov,[a] M. Teresa Bes,[b, c] Jacques Salaün,[d] and Mathias Noltemeyer[b]

Abstract: The trimethylsilyl-protected enynes **9a–c** and **14a,b** with alkynyl substituents on the three-membered ring or on the double bond of a methylenecyclopropane or a bicyclopropylidene moiety were prepared in two steps from the alcohols **6a–c** and **12a,b**, respectively, by conversion to the iodides and their coupling with lithium (trimethylsilyl)acetylide (**8**) in 38–73% overall yields. The bicyclopropylidene derivative **9d** was synthesized in 49% yield directly from bicyclopropylidene (**3**) by lithiation followed by coupling with (5-iodopent-1-ynyl)trimethylsilane (**11**). Enynes **9b–d** were protiodesilylated by treatment with K_2CO_3 in methanol to give the corresponding unprotected enynes **10b–d** in 53, 74 and 94% yield, respectively. Enynes **17a–c** with a carbonyl group adjacent to the acetylenic moiety were synthesized from oxo derivatives **15a–c** by Wittig olefination followed by coupling with **8** in 47, 18 and 12% overall yield, respectively. Pauson–Khand reactions of the methylenecyclopropane derivatives with a substituent on the ring (**9a,b** and **10a**) as well as on the double bond (**14a,b** and their in situ prepared protiodesilylated analogues) proceeded smoothly by stirring of the corresponding enyne with $[Co_2(CO)_8]$ in dichloromethane at ambient temperature followed by treatment of the formed complexes with trimethylamine *N*-oxide under an oxygen atmosphere at −78 °C to give tricyclic or spirocyclopropanated bicyclic enones **18a,b**, **19a**, **20a,b**, **21a,b** in good yields. Alkynylbicyclopropylidene derivatives **9c,d** and **10c,d** formed the corresponding cobalt complexes at −78 to −20 °C. Treatment of the latter with *N*-methylmorpholine *N*-oxide under an argon atmosphere at −20 °C gave the spirocyclopropanated tricyclic enones **18c**, **19c** and **18d** in 31–45% yields. The structure of **19c** was proved by X-ray crystal structure analysis. The cyclization of enynones **17a–c** in MeCN at 80 °C gave the spirocyclopropanated bicyclic diketones **22a–c** in 38–65% yields. Intramolecular PKRs of the enynes **25a,d** with a chiral auxiliary adjacent to the triple bond gave the corresponding products **26a,d** in 70 and 79% yield, respectively, as 5:1 and 8:1 mixtures of diastereomers, respectively. Addition of lithium dimethylcuprate or higher order cuprates to the double bond of the former furnished bridgehead-substituted bicyclo[3.3.0]octanones **27a–c** in 57–86% yields. Protiodesilylation of **27a** followed by acetal cleavage gave the enantiomerically pure spirocyclopropanated bicyclo[3.3.0]octanedione (1*R*,5*R*)-**29a** with $[\alpha]_D^{20} = -148$ ($c = 1.0$ in $CHCl_3$) in 55% overall yield.

Keywords: alkynes · bicyclopropylidene · cobalt · cyclization · cyclopropanes · spiro compounds

[a] Prof. Dr. A. de Meijere, Dr. H. Becker, Dr. A. Stolle, Dr. S. I. Kozhushkov
Institut für Organische und Biomolekulare Chemie
der Georg-August-Universität Göttingen
Tammannstrasse 2, 37077 Göttingen (Germany)
Fax: (+49) 551-399-475
E-mail: armin.demeijere@chemie.uni-goettingen.de

[b] Dr. M. T. Bes, Dr. M. Noltemeyer
Institut für Anorganische Chemie
der Georg-August-Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)

[c] Dr. M. T. Bes
Current address:
Departamento de Bioquímica y Biología, Molecular y Celular
Facultad de Ciencias, Universidad de Zaragoza
Pedro Cerbuna 12, 50009 Zaragoza (Spain)

[d] Prof. Dr. J. Salaün
Laboratoire des Carbocycles (Associé au CNRS)
Institut de Chimie Moléculaire d'Orsay, Bât. 420
Université de Paris-Sud, 91405 Orsay (France)

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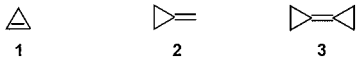
Introduction

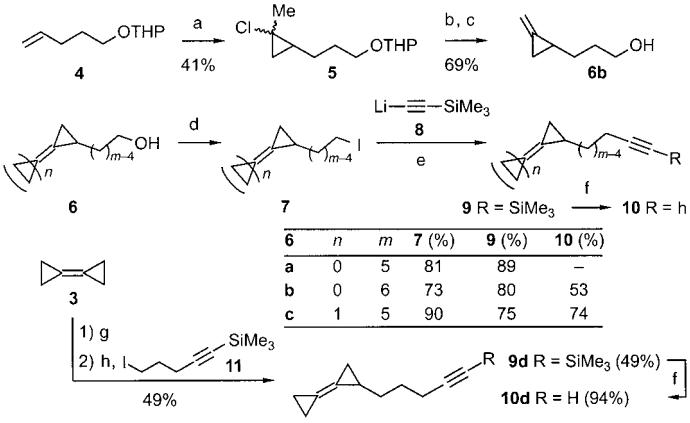
Among the known methods for the construction of five-membered carbocycles, the Pauson–Khand reaction (PKR), that is the cobalt-mediated cocyclization of an alkyne and an alkene with carbonyl insertion yielding a cyclopentenone, has attracted particular interest of synthetically[2] as well as theoretically[3] oriented organic chemists. Among numerous reported PKRs, those of substrates containing a three-membered ring are of special interest, as multifunctional cyclopropane derivatives have established their potential as useful building blocks in organic synthesis.[4–6] The release of strain involved in the formation of the intermediate bi- or spirocyclic metallacycle has proved to make such reactive alkenes as cyclopropene (**1**),[7] methylenecyclopropane (**2**) and bicyclopropylidene (**3**)[8] particularly useful in PKRs.



From the preparative point of view, PKRs of such alkenes offer a convenient synthetic approach to cyclopentenones containing fused (PKR of **1**),[7] spiro-linked (PKR of **2**)[1] and simultaneously fused and spiro-attached (PKR of **3**) cyclopropane moieties. Surprisingly, after the first examples of intermolecular[9] and intramolecular[1] PKRs of **2**, only a few more cases for reactions of **2**[7b,10] and none for **3** and their derivatives have been published during the last decade. This contribution summarizes our results in this area, most of which were obtained after our preliminary communications.[1] As our results on enantioselective intramolecular PKRs of methylenecyclopropane derivatives[1b] have recently been reproduced and further improved by Krafft et al. and published as a full paper,[10e] this article focuses mainly on the new intramolecular PKRs of methylenecyclopropane and bicyclopropylidene derivatives tethered with alkynyl groups on the ring and on the double bond in the light of our preliminary reports.

Results and Discussion

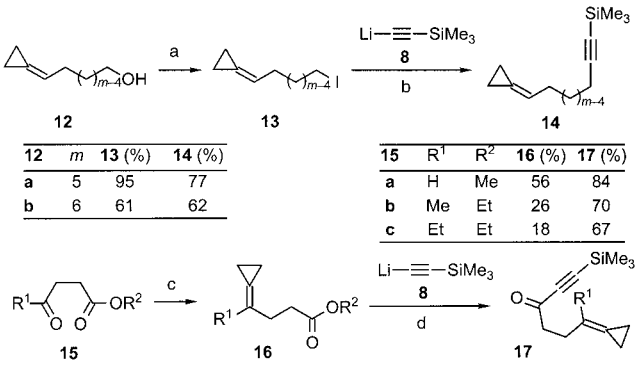
Preparation of the starting materials: The trimethylsilyl-protected enynes **9a–c** were prepared in two steps from the known 2-(2-methylenecyclopropyl)ethanol (**6a**),[11a] 3-(2-methylenecyclopropyl)propan-1-ol (**6b**)[12] and 2-(bicyclopropyliden-2-yl)ethanol (**6c**),[11b] in 72, 58 and 68% overall yield, respectively, by conversion to the iodides applying a protocol of Corey et al.[13] followed by coupling with lithium (trimethylsilyl)acetylide (**8**) in the presence of DMPU[14] (Scheme 1). The starting material **6b**, however, was synthesized from 5-(tetrahydropyran-2-yloxy)pent-1-ene (**4**)[15] adopting a protocol of Binger et al.[16] On the other hand, the bicyclopropylidene derivative **9d** was prepared directly from bicyclopropylidene (**3**)[17] by lithiation with *n*-butyllithium in THF[18] followed by coupling with (5-iodopent-1-ynyl)trimethylsilane (**11**)[19] (Scheme 1). Protiodesilylation of enynes **9b–d** by treatment with potassium carbonate in MeOH gave the corresponding unprotected enynes **10b–d** in 53, 74 and 94% yield, respectively.



6	n	m	7 (%)	9 (%)	10 (%)
a	0	5	81	89	–
b	0	6	73	80	53
c	1	5	90	75	74

Scheme 1. Preparation of alkynyl-substituted methylenecyclopropane and bicyclopropylidene derivatives **9**, **10** with the tether on the cyclopropane ring. a) 1,1-dichloroethane, *n*BuLi, Et_2O, −35 °C, 1 h; b) *t*BuOK, DMSO, 20 °C, 12 h; c) *p*TsOH, MeOH, 20 °C, 16 h; d) Ph_3P, Im-H, I_2, Et_2O/MeCN 3:2, 0 °C, 1 h; e) THF/DMPU, 0 °C, 1 h; f) K_2CO_3, MeOH, 20 °C, 3–6 h; g) *n*BuLi, THF, 0 °C, 1 h; h) THF, −78 to 0 °C, 1 h.

Applying the same sequence of operations as for **9a–c**, the known 4-(cyclopropylidene)butan-1-ol (**12a**)[20] and 5-(cyclopropylidene)pentan-1-ol (**12b**)[21] were converted into trimethylsilyl-protected enynes **14a**,**b** with a tether on the double bond in 73 and 38% overall yield, respectively (Scheme 2). Their analogues **17a**,[1b,22] **17b**[23] and **17c** containing a carbonyl group adjacent to the acetylenic moiety, were synthesized from the known methyl 4-oxobutanoate (**15a**),[24] ethyl 4-oxopentanoate (**15b**) and ethyl 4-oxohexanoate (**15c**)[25] by Wittig olefination according to a protocol of Balme et al.[20] followed by coupling with lithium (trimethylsilyl)acetylide (**8**) under boron trifluoride etherate catalysis in 47, 18 and 12% overall yield, respectively (Scheme 2).

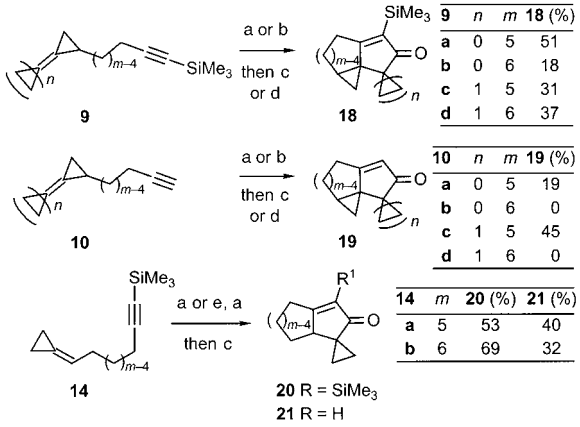


12	m	13 (%)	14 (%)
a	5	95	77
b	6	61	62

15	R^1	R^2	16 (%)	17 (%)
a	H	Me	56	84
b	Me	Et	26	70
c	Et	Et	18	67

Scheme 2. Preparation of alkynyl-substituted methylenecyclopropane derivatives **14**, **17** with the tether on the double bond. a) Ph_3P, Im-H, I_2, Et_2O/MeCN, 0 °C, 1–2 h; b) THF, DMPU, 0 °C, 1 h; c) $Br(CH_2)_3P^+Ph_3Br^-$,[26] NaH, DME, 70 °C, 11–13 h; d) $BF_3{\cdot}Et_2O$, THF, −100 to −78 °C, 1.5 h.

Pauson–Khand cyclizations of enynes 9, 10, 14 and 17: The formation of cobalt complexes from the methylenecyclopropane derivatives with the alkynyl substituent tethered to the ring (**9a**,**b** and **10a**,**b**) as well as to the double bond (**14a**,**b** and their in situ prepared protiodesilylated analogues) proceeded smoothly upon stirring the corresponding enyne with 1.1 equivalents of $[Co_2(CO)_8]$ in dichloromethane at ambient temperature. Treatment of these complexes with trimethylamine *N*-oxide (TMANO)[27] under an oxygen atmosphere at −78 °C gave the tricyclic 4-trimethylsilyl-1,1a,2,3-tetrahydrocyclopropa[*c*]pentalen-5-one (**18a**), 5-trimethylsilyl-1a,2,3,4-tetrahydro-1*H*-cyclopropa[*d*]inden-6-one (**18b**) and 1,1a,2,3-tetrahydrocyclopropa[*c*]pentalen-5-one (**19a**) as well as the bicyclic spirocyclopropanated 3′-trimethylsilyl-4′,5′,6′,6′a-tetrahydro-1′*H*-spiro(cyclopropane-1,1′-pentalen-2′-one) (**20a**), 1′,4′,5′,6′,7′,7′a-hexahydro-3′-trimethylsilylspiro(cyclopropane-1,1′-inden-2′-one) (**20b**), 4′,5′,6′,6′a-tetrahydro-1′*H*-spiro(cyclopropane-1,1′-pentalen-2-one) (**21a**) and 1′,4′,5′,6′,7′,7′a-hexahydrospiro(cyclopropane-1,1′-inden-2-one) (**21b**) in 51, 18, 19, 53, 69, 40 and 32 % yield, respectively (Scheme 3).



9	*n*	*m*	18 (%)
a	0	5	51
b	0	6	18
c	1	5	31
d	1	6	37

10	*n*	*m*	19 (%)
a	0	5	19
b	0	6	0
c	1	5	45
d	1	6	0

14	*m*	20 (%)	21 (%)
a	5	53	40
b	6	69	32

Scheme 3. PKRs of the enynes **9**, **10** and **14**. a) $[Co_2(CO)_8]$, CH_2Cl_2, 20 °C, 1–2 h; b) $[Co_2(CO)_8]$, CH_2Cl_2, −78 to −20 °C, 2 h; c) TMANO, O_2, −78 to 20 °C, 16 h; d) NMO, −20 to 20 °C, 16 h; e) K_2CO_3, MeOH, 20 °C, 12 h.

Comparison of these results for enynes **9a**,**b** and **10a**,**b** with the alkynyl group tethered to the ring demonstrate that PKRs are more suitable for the preparation of tricyclo[4.3.0.0^{1,3}]non-6-en-8-ones **18a**, **19a** than for their homologous tricyclo[5.3.0.0^{1,3}]dec-7-en-9-ones **18b** and **19b**, and that the bicyclizations of the trimethylsilyl-protected alkynyl derivatives proceed more efficiently than those with terminal triple bonds. Contrary to this, methylenecyclopropane derivatives **14a**,**b** with the alkynyl group tethered to the double bond do not differ as drastically in their bicyclization efficiency with respect to a protected and unprotected terminal triple bond, so that all of the spirocyclopropanated bicyclo[3.3.0]oct- (**20a**, **21a**) and bicyclo[4.3.0]nonenones (**20b**, **21b**) were obtained in comparable and relatively good yields.

An attempted preparation of the cobalt complexes of the bicyclopropylidene derivatives **9c**,**d** and **10c**,**d** under the same conditions as mentioned above led to the formation of side products, and this caused low yields in the PKRs (at best 18 % for **9c**). However, stirring of the respective enyne with 1.1 equiv of $[Co_2(CO)_8]$ in dichloromethane at −78 to −20 °C followed by treatment with *N*-methylmorpholine *N*-oxide[28] (NMO, 8 equiv) under an argon atmosphere at −20 °C gave 7′-trimethylsilylspiro(cyclopropane-1,9′-tricyclo[4.3.0.0^{1,3}]non-6′-en-8′-one) (**18c**), its desilylated analogue **19c** and 8′-trimethylsilylspiro(cyclopropane-1,10′-tricyclo[5.3.0.0^{1,3}]dec-7′-en-9′-one) (**18d**) in 31, 45 and 37 % yield, respectively. The attempted bicyclization of **10d** was unsuccessful. These cobalt-mediated bicyclizations of bicyclopropylidene derivatives **9c**,**d** and **10c** leading to the interesting spirocyclopropanated tricyclic products **18c**,**d** and **19c** are the most striking examples for intramolecular Pauson–Khand reactions involving a tetrasubstituted double bond. These successful bicyclizations once again demonstrate the unique reactivity of the strained double bond in bicyclopropylidene and its derivatives (Scheme 3). The structure of compound **19c** was rigorously proved by X-ray crystal structure analysis (Figure 1).

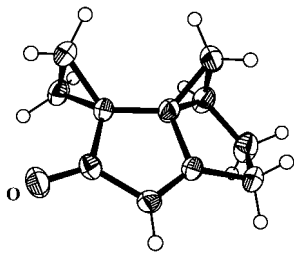
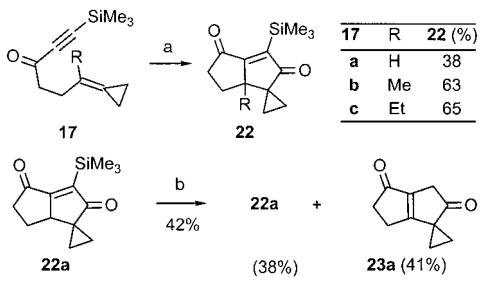


Figure 1. Molecular structure of spiro(cyclopropane-1,9′-tricyclo[4.3.0.0^{1,3}]-non-6′-en-8′-one) [1′,1′a,2′,3′-tetrahydrospiro(cyclopropane-1,6′-cyclopropa-[*c*]pentalen-5′-one)] (**19c**) in the crystal.[29]

At last, the bicyclizations of enynones **17a–c** were performed adopting a protocol of Hoye et al.[30] (Scheme 4).

While the yield of the spirocyclopropanated bicyclic parent diketone **22a** was only moderate (38 %) and not very well reproducible, as compound **22a** is prone to undergo protiodesilylation accompanied with double-bond migration upon column chromatography on deactivated silica gel, the methyl- and ethyl-substituted spirocyclopropanated bicyclic



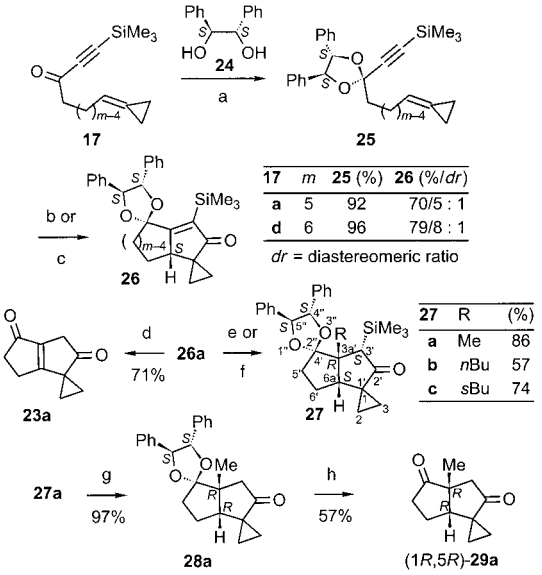
17	R	22 (%)
a	H	38
b	Me	63
c	Et	65

Scheme 4. PKRs of the enynes **17**. a) $[Co_2(CO)_8]$, MeCN, 80 °C, 16 h, then (for **17b**,**c**) TMANO, CH_2Cl_2, 20 °C, 1 h; b) silica gel deactivated with Et_3N.

diketones **22b** and **22c** were obtained in 63 and 65% yield, respectively. However, desilylations of **22b** and **22c** surprisingly could not be brought about.

In order to demonstrate the full potential of this approach to spiro(cyclopropane-1,4′-bicyclo[3.3.0]oct-1′-en-3′,8′-diones), the possibility of asymmetrically inducing the cyclization with a chiral auxiliary adjacent to the triple bond in the 1,6- and 1,7-enyne was also tested. As Magnus et al. have demonstrated,[31] high diastereoselectivities can be obtained in intramolecular PKRs. On the basis of their mechanistic rationalization it was conceived that a cyclopropylidenalkyne of type **25** with a C_2-symmetric acetal moiety next to the triple bond might lead to an asymmetric induction in the cyclization step. The enynes **25a** and **25d** were obtained by transacetalization of enynes **17a** and **17d**[32] with commercially available (*S*,*S*)-(−)-hydrobenzoin (**24**) and trimethyl orthoformate in 92 and 96% yield, respectively (Scheme 5). Although heavily substituted, the trimethylsilyl protected alkynes **25a** and **25d** underwent trialkylamine *N*-oxide-promoted PKR quite well (70 and 79% yield, respectively, Scheme 5).[33] The diastereoselection in the cyclization of **25a** was 5:1, according to gas chromatographic and ^{1}H NMR-spectroscopic analysis, and increased to 8:1 for the homologue **25d**.[34]

The diastereomers of **26a**,**d** could be separated by column chromatography or (in the case of **26d**) simply by recrystallization from hexane. According to the predictions of Magnus et al., the main diastereomer should possess (6′a*S*) configuration, and this was proven by X-ray crystal structure analysis in the case of **26d**, the absolute configuration of which was assigned as (7′a*S*) on the basis of the known (*S*,*S*)-configuration of the hydrobenzoin **24**, used in the synthesis of the precursor **25d** (Figure 2).



Scheme 5. Preparation and PKRs of the enynes **25a**,**d** as well as subsequent transformations of (6′a*S*,4″*S*,5″*S*)-4′,5′,6′,6′a-tetrahydro-3′-trimethylsilyldispiro(cyclopropane-1,1′-pentalene-2′-one-4′,2″-1,3-dioxolane) **26a**. a) HC(OMe)$_3$, *p*TsOH, benzene, 50°C, 16–17 h; b) [Co$_2$(CO)$_8$], CH$_2$Cl$_2$, 20°C, 1 h; then NMO (5 equiv), 20°C, 20 h; c) [Co$_2$(CO)$_8$], CH$_2$Cl$_2$, 20°C, 3 h; then TMANO, O$_2$, −78 to 20°C, 16 h; d) *p*TsOH, acetone, 56°C, 16 h; e) Me$_2$CuLi, Et$_2$O, 0°C, 2 h; f) R$_2$Cu(CN)Li$_2$, Et$_2$O, BF$_3$·Et$_2$O, −78°C, 0.5 h; g) *p*TsOH, acetone, 20°C, 2 h; h) *p*TsOH, acetone, 56°C, 27 h.

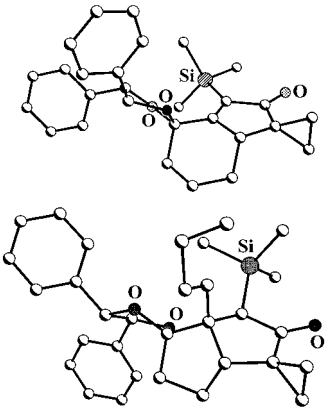


Figure 2. Molecular structures of (7′a*S*,4″*S*,5″*S*)-1′,4′,5′,6′,7′,7′a-hexahydro-3′-trimethylsilyldispiro(cyclopropane-1,1′-inden-2′-one-4′,2″-1,3-dioxolane) (**26d**, top) and (3′*S*,3′a*R*,6′a*S*,4″*S*,5″*S*)-hexahydro-3a-*n*-butyl-3-trimethylsilyldispiro(cyclopropane-1,1′-pentalene-2′-one-4′,2″-1,3-dioxolane) (**27b**, bottom) in the crystal.[29]

Further transformations were performed with the major diastereomer of **26a**, which was also assumed to have (6′a*S*) configuration. First, it was attempted to cleave off the chiral auxiliarity in the acetal moiety. Upon treatment of **26a** with *p*-toluenesulfonic acid, however, not only acetal cleavage, but also protiodesilylation and double bond migration occurred to yield, as in the previous case (cf. Scheme 4), the achiral bicyclo[3.3.0]octendione **23a**, albeit in better yield (71%, Scheme 5). Therefore, lithium dimethylcuprate was first added to the enone moiety in **26a** to give **27a** as a mixture of (3′*S*,3′a*R*,6′a*S*)- and (3′*R*,3′a*R*,6′a*S*)-diastereomers in a ratio of 7:1 (Scheme 5; only the major diastereomer is shown). Surprisingly, lithium di-*n*-butylcuprate did not add to **26a** under the same conditions, but the higher order cuprates,[35] derived from *n*-butyl- and *sec*-butyllithium and cuprous cyanide according to an established procedure (see Experimental Section), did add under activation with boron trifluoride etherate to furnish the corresponding adducts **27b** and **27c** in 57 and 74% yield, respectively, as a single diastereomer in the former and a 1.25:1 mixture of diastereomers in the latter case. X-ray crystal structure analysis of **27b** disclosed its absolute configuration to be (3′*S*,3′a*R*,6′a*S*), as assigned on the basis of the known (*S*,*S*)-configuration of the acetal moiety in **27b** (Figure 2).

Surprisingly, acetal cleavage in **27a** was quite slow, within 2 h at ambient temperature only protiodesolylation occurred to give **28a** in virtually quantitative yield. Only upon prolonged heating under reflux the latter eventually gave the dione (3′a*R*,6′a*R*)-**29a** with $[\alpha]_D^{20} = -148$ ($c = 1.0$ in CHCl$_3$).[35] The CD curve with a negative peak at 287 nm (ellipticity of 550°) is consistent with the absolute configuration being (3′a*R*,6′a*R*) (cf.[36]).

Conclusion

Methylenecyclopropane and even bicyclopropylidene moieties, the latter with a tetrasubstituted double bond, in 1,6- and 1,7-enynes do favor intramolecular Pauson–Khand reactions to furnish spirocyclopropanated or/and cyclopropane-annelated bicyclo[3.3.0]octanone or bicyclo[4.3.0]nonanone derivatives in good yields. The angularly cyclopropane-annelated skeletons can be regarded as mimics of the corresponding bridgehead-methylated compounds. With a chiral acetal moiety adjacent to the triple bond in the starting material, spirocyclopropanated bicyclo[3.3.0]octanediones can be obtained in enantiomerically pure form.

Experimental Section

General aspects: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 250 instrument (250 MHz for ^{1}H and 62.9 MHz for ^{13}C NMR) in $CDCl_3$, if not otherwise specified, multiplicities were determined by DEPT (distortionless enhancement by polarization transfer) measurements. Chemical shifts are referred to $\delta_{TMS}=0.00$ according to the chemical shifts of residual $CHCl_3$ signals. IR spectra were recorded with a Bruker IFS 66 (FT-IR) spectrophotometer as KBr pellets or oils between KBr plates. Mass spectra (EI, 70 eV) were measured with Finnigan MAT 95 spectrometer. High resolution spectra were obtained with a VG-70–250S instrument, pre-selected ion peak matching at $R \geqslant 10000$ to be within ± 2 ppm of the exact masses. Melting points were determined on a Büchi 510 capillary melting point apparatus, values are uncorrected. TLC analyses were performed on precoated aluminum sheets (Macherey–Nagel, 0.25 mm Sil G/UV$_{254}$). Column chromatography was performed using Merck silica gel, grade 60, 230–400 mesh. Starting materials: bicyclopropylidene (**3**),[17] 5-(tetrahydropyran-2-yloxy)pent-1-ene (**4**),[15] 2-(2-methylenecyclopropyl)ethanol (**6a**),[11a] 2-(2-iodoethyl)bicyclopropylidene (**7c**),[11b] (5-iodopent-1-ynyl)trimethylsilane (**11**),[19] 4-(cyclopropylidene)-butan-1-ol (**12a**),[20] 5-(cyclopropylidene)pentan-1-ol (**12b**),[21] methyl 4-oxobutyroate (**15a**),[24] ethyl 4-oxohexanoate (**15c**),[25] 6-cyclopropylidene-1-(trimethylsilyl)hex-1-yn-3-one (**17a**),[22] 3-bromopropyltriphenylphosphonium bromide,[26] and 7-cyclopropylidene-1-trimethylsilylhept-1-yn-3-one (**17d**)[32] were prepared according to previously published procedures. All operations in anhydrous solvents were performed under an argon atmosphere, if not otherwise specified, and in flame-dried glassware. Dimethoxyethane, diethyl ether and THF were dried by distillation from sodium/benzophenone, pyridine, DMSO, DMPU and triethylamine from calcium hydride, MeCN, CH_2Cl_2 and petroleum ether from P_2O_5. All other chemicals were used as commercially available. Organic extracts were dried over $MgSO_4$, if not otherwise specified.

2-[3-(2-Chloro-2-methylcyclopropyl)propyloxy]tetrahydropyran (5): To a vigorously stirred solution of 5-(tetrahydropyran-2-yloxy)pent-1-ene (**4**)[15] (36.0 g, 211 mmol) and 1,1-dichloroethane (41.0 g, 414 mmol) in anhydrous diethyl ether (100 mL) was added *n*BuLi (389 mmol, 165 mL of a 2.36 M solution in hexane) at −35 °C over a period of 1 h. After stirring for an additional 1 h, the reaction mixture was poured into ice-cold water (100 mL), and the inorganic phase was extracted with Et_2O (3×50 mL). The combined organic extracts were washed with water (3×50 mL), dried, concentrated under reduced pressure and distilled in vacuo to give **5** (20.2 g, 41 %) as a colorless oil. B.p. 45 °C (0.1 Torr), mixture of four diastereomers. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta=4.61$–4.52 (m, 1H), 3.90–3.74 (m, 2H), 3.62–3.38 (m, 2H), 2.0–0.3 (m, 16H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta=98.70$, 98.67, 98.61, 98.57 (CH), 67.0, 66.9, 66.79, 66.76 (CH_2), 62.19, 62.17, 62.11, 62.07 (CH_2), 45.44, 45.41, 42.73, 42.69 (C), 30.6 (CH_2), 29.3, 29.2 (CH_2), 27.3, 27.24, 27.1 (CH_2), 28.7, 27.07 (CH_3), 26.1, 25.4, 25.3 (CH_2), 25.23, 25.2, 22.5 (CH), 22.98, 22.01, 21.8 (CH_2), 19.5, 19.47 (CH_2); IR (film): $\tilde{\nu}=2942$, 2896, 1442, 1121, 1077, 1034 cm^{-1}; MS (70 eV): *m*/*z* (%): 232 (1) [M^+], 197 (1) [M^+-Cl], 148 (1), 85 (100) [$C_5H_9O^+$].

3-(2-Methylenecyclopropyl)propan-1-ol (6b): To a solution of the chloride **5** (20.0 g, 86.0 mmol) in anhydrous DMSO (20 mL) was added dropwise under vigorous stirring a solution of *t*BuOK (19.0 g, 169 mmol) in DMSO (80 mL) at 20 °C, the resulting mixture was stirred at ambient temperature for an additional 12 h and poured into ice-cold water (100 mL). The inorganic phase was extracted with Et_2O (3×100 mL), the combined organic extracts were washed with water (3×50 mL), brine (50 mL), dried, concentrated under reduced pressure and distilled in vacuo to give 2-[3-(2-methylenecyclopropyl)propyloxy]tetrahydropyran (14.4 g, 85 %) as a colorless oil. B.p. 85 °C (1 Torr); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta=5.38$ (m, 1H; =CH_2), 5.33–5.31 (m, 1H; =CH_2), 4.57 (t, $J=3.4$ Hz, 1H), 3.88–3.71 (m, 2H), 3.53–3.36 (m, 2H), 1.84–1.16 (m, 12H), 0.70 (m, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta=136.6$ (C), 102.4 (CH_2), 98.6 (CH), 67.0 (CH_2), 62.1 (CH_2), 30.6 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 25.4 (CH_2), 19.5 (CH_2), 15.2 (CH), 9.2 (CH_2); IR (film): $\tilde{\nu}=$ 2932, 2869, 1122, 1077, 1034 cm^{-1}; MS (70 eV): *m*/*z* (%): 195 (1) [M^+ +H], 125 (1), 85 (100) [$C_5H_9O^+$], 79 (15); elemental analysis calcd (%) for $C_{12}H_{20}O_2$ (196.3): C 73.42, H 10.27; found C 73.36, H 10.33.

This material (14.1 g, 71.8 mmol) was taken up with MeOH (200 mL), *p*-TsOH·H_2O (1.0 g, 7.2 mmol) was added, and the resulting solution was stirred at ambient temperature for 16 h. The solvent was evaporated at ambient pressure through a 20 cm Vigreux column, the residue was taken up with Et_2O (200 mL), washed with water and brine (50 mL each), dried and concentrated at ambient pressure. The residue was distilled at ambient pressure to give **6b** (6.55 g, 81 %) as a colorless liquid, the ^{1}H and ^{13}C NMR data of which were identical to the reported ones.[12]

Preparation of iodides 7a,b and 13a,b

General procedure GP 1: To a vigorously stirred solution of the respective alcohol (26.7 mmol), Ph_3P (12.3 g, 46.9 mmol) and imidazol (3.40 g, 49.9 mmol) in a mixture of anhydrous Et_2O (90 mL) and anhydrous MeCN (60 mL) was added iodine (13.2 g, 52.0 mmol) in small portions at 0 °C. After stirring at this temperature for an additional 1 h, the mixture was diluted with Et_2O (100 mL), filtered, washed with aq. 20 % $Na_2S_2O_3$ solution (80 mL) and brine (3×50 mL), dried and concentrated under reduced pressure. The residue was pre-absorbed on silica gel (1 g) and purified by column chromatography.

2-(2-Iodoethyl)methylenecyclopropane (7a): Column chromatography (35 g of silica gel, column 20×2.5 cm, pentane) of the reaction mixture obtained from the alcohol **6a** (3.93 g, 40.05 mmol), Im-H (5.10 g, 74.85 mmol), Ph_3P (18.45 g, 70.35 mmol), and I_2 (19.8 g, 78.0 mmol) according to GP 1 gave the iodide **7a** (6.83 g, 81 %) as a colorless oil. $R_f=$ 0.76 (pentane), the ^{1}H and ^{13}C NMR data of which were identical to the reported ones.[11b]

2-(3-Iodopropyl)methylenecyclopropane (7b): Column chromatography (30 g of silica gel, column 20×2 cm, pentane) of the reaction mixture obtained from the alcohol **6b** (3.00 g, 26.7 mmol), Im-H (3.40 g, 49.9 mmol), Ph_3P (12.3 g, 46.9 mmol), and I_2 (13.2 g, 52.0 mmol) according to GP 1 gave the iodide **7b** (4.31 g, 73 %) as a colorless oil. $R_f=0.78$ (pentane); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta=5.40$–5.39 (m, 1H; =CH_2), 5.36–5.35 (m, 1H; =CH_2), 3.23 (t, $J=7.0$ Hz, 2H; CH_2I), 1.97 (quin, $J=7.0$ Hz, 2H; CH_2), 1.54–1.36 (m, 3H), 1.27–1.19 (m, 1H; CH_2 Cpr), 0.80–0.73 (m, 1H; CH_2 Cpr); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta=136.0$ (C), 103.0 (CH_2), 33.6 (CH_2), 33.3 (CH_2), 14.4 (CH), 9.3 (CH_2), 6.5 (CH_2); IR (film): $\tilde{\nu}=3066$, 2972, 2929, 2849, 1446, 1223, 1173, 888 cm^{-1}; MS (70 eV): *m*/*z* (%): 222 (1) [M^+], 194 (24), 155 (15) [$M^+-C_5H_7$], 127 (4) [I^+], 95 (92) [M^+-I], 79 (16), 67 (100) [$C_5H_7^+$], 55 (43); elemental analysis calcd (%) for $C_7H_{11}I$ (222.1): C 37.86, H 4.99; found C 37.70, H 4.79.

4-Cyclopropylidenebutyl iodide (13a): Column chromatography (15 g of silica gel, column 10×2 cm, pentane) of the reaction mixture obtained from the alcohol **12a** (593 mg, 5.29 mmol), Im-H (667 mg, 9.79 mmol), Ph_3P (2.43 g, 9.26 mmol), and I_2 (2.63 g, 10.4 mmol) according to GP 1 gave the iodide **13a** (1.11 g, 95 %) as a colorless oil. $R_f=0.88$ (pentane); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta=5.74$–5.68 (m, 1H; =CH), 3.20 (t, $J=7.0$ Hz, 2H; CH_2I), 2.32–2.24 (m, 2H; CH_2), 1.98 (quin, $J=7.0$ Hz, 2H; CH_2), 1.05–1.03 (m, 4H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta=122.8$ (C), 115.9 (CH), 33.0 (CH_2), 32.4 (CH_2), 6.67 (CH_2), 2.3

(CH_2), 2.1 (CH_2); IR (film): $\tilde{\nu}$ = 3049, 2977, 2931, 1429, 1220, 1166 cm^{-1}; MS (70 eV): *m/z* (%): 222 (1) [M^+], 193 (35), 155 (19) [$M^+-C_5H_7$], 127 (11) [I^+], 95 (100) [M^+-I], 79 (13), 67 (49) [$C_5H_7^+$]; elemental analysis calcd (%) for $C_7H_{11}I$ (222.1): C 37.86, H 4.99; found C 37.63, H 5.14.

5-Cyclopropylidenepentyl iodide (13b): Column chromatography (20 g of silica gel, column 15×2 cm, pentane) of the reaction mixture obtained from the alcohol **12b** (600 mg, 4.75 mmol), Im-H (600 mg, 8.81 mmol), Ph_3P (2.18 g, 8.31 mmol), and I_2 (2.36 g, 9.30 mmol) according to GP 1 gave the iodide **13b** (680 mg, 61%) as a colorless oil. R_f = 0.71 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 5.76–5.70 (m, 1H; =CH), 3.20 (t, *J* = 7.0 Hz, 2H; CH_2I), 2.25–2.12 (m, 2H; CH_2), 1.90–1.70 (m, 2H; CH_2), 1.59–1.49 (m, 2H; CH_2), 1.03–1.01 (m, 4H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 121.8 (C), 117.4 (CH), 33.1 (CH_2), 30.6 (CH_2), 30.1 (CH_2), 7.1 (CH_2), 2.2 (CH_2), 1.9 (CH_2); IR (film): $\tilde{\nu}$ = 3048, 2977, 2931, 2852, 1209, 1167, 962, 932 cm^{-1}; MS (70 eV): *m/z* (%): 236 (1) [M^+], 207 (3), 155 (7), 109 (60) [M^+-I], 81 (51), 67 (100) [$C_5H_7^+$]; elemental analysis calcd (%) for $C_8H_{13}I$ (236.1): C 40.69, H 5.55; found C 40.78, H 5.37.

Coupling of iodides 7a–c and 13a,b with lithium (trimethylsilyl)acetylide (8)

General procedure GP 2: To a vigorously stirred solution of trimethylsilylacetylene (496 mg, 0.7 mL, 5.05 mmol) in anhydrous THF (5 mL) was added dropwise at 0 °C *n*BuLi (3.78 mmol, 1.6 mL of a 2.36 M solution in hexane). After stirring at this temperature for an additional 0.5 h, a solution of the respective iodide (3.36 mmol) in anhydrous DMPU (7 mL) was added dropwise, the resulting mixture was stirred at 0 °C for an additional 1 h with TLC monitoring and then poured into ice-cold water (20 mL). The aqueous phase was extracted with pentane (3×10 mL), the combined organic extracts were washed with brine (2×20 mL), dried and concentrated under reduced pressure. The residue was purified by column chromatography.

Trimethyl[4-(2-methylenecyclopropyl)but-1-ynyl]silane (9a): Column chromatography (5 g of silica gel, column 15×1 cm, pentane) of the reaction mixture obtained from trimethylsilylacetylene (496 mg, 0.7 mL, 5.05 mmol), *n*BuLi (3.78 mmol, 1.6 mL of a 2.36 M solution in hexane) and iodide **7a** (700 mg, 3.36 mmol) according to GP 2 gave the enyne **9a** (535 mg, 89%) as a colorless oil. R_f = 0.41 (pentane), which was contaminated with some of the protiodesilylated product. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 5.43 (br s, 1H; =CH_2), 5.36 (br s, 1H; =CH_2), 2.34 (t, *J* = 7.0 Hz, 2H; CH_2), 1.61–1.51 (m, 2H; CH_2), 1.29–1.18 (m, 2H; Cpr-H), 0.88–0.77 (m, 1H; Cpr-H), 0.15 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 135.9 (C), 107.0 (C), 103.0 (CH_2), 84.5 (C), 32.3 (CH_2), 19.9 (CH_2), 15.0 (CH), 9.4 (CH_2), −0.1 ($3CH_3$).

Trimethyl[5-(2-methylenecyclopropyl)pent-1-ynyl]silane (9b): Column chromatography (5 g of silica gel, column 15×1 cm, pentane) of the reaction mixture obtained from trimethylsilylacetylene (2.55 g, 3.6 mL, 26.0 mmol) in THF (25 mL), *n*BuLi (19.4 mmol, 8.2 mL of a 2.36 M solution in hexane) and iodide **7b** (3.84 g, 17.3 mmol) in DMPU (30 mL) according to GP 2 gave the enyne **9b** (2.67 g, 80%) as a colorless oil. R_f = 0.41 (pentane) which was contaminated with some protiodesilylated product **10b**. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 5.42–5.39 (m, 1H; =CH_2), 5.34–5.33 (m, 1H; =CH_2), 2.30–2.23 (m, 2H; CH_2), 1.71–1.34 (m, 5H; $2CH_2$ + Cpr-H), 1.26–1.18 (m, 1H; Cpr-H), 0.78–0.70 (m, 1H; Cpr-H), 0.14 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 136.5 (C), 107.3 (C), 102.6 (CH_2), 84.4 (C), 32.1 (CH_2), 28.5 (CH_2), 19.5 (CH_2), 15.1 (CH), 9.3 (CH_2), 0.1 ($3CH_3$); IR (film): $\tilde{\nu}$ = 2939, 2858, 2175, 1250, 843 cm^{-1}; MS (70 eV): *m/z* (%): 177 (5) [M^+−Me], 159 (7), 118 (14), 91 (8), 73 (100) [Me_3Si^+], 59 (18).

[4-(Bicyclopropyliden-2-yl)but-1-ynyl]trimethylsilane (9c): Column chromatography (5 g of silica gel, column 15×1 cm, pentane) of the reaction mixture obtained from trimethylsilylacetylene (1.28 g, 1.8 mL, 13.0 mmol) in THF (24 mL), *n*BuLi (10.4 mmol, 4.4 mL of a 2.36 M solution in hexane) and iodide **7c** (2.50 g, 10.7 mmol) in DMPU (20 mL) according to GP 2 gave the enyne **9c** (1.64 g, 75%) as a colorless oil. R_f = 0.63 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 2.36 (t, *J* = 7.0 Hz, 2H; CH_2), 1.67–1.59 (m, 3H; CH_2 + Cpr-H), 1.42–1.35 (m, 1H; Cpr-H), 1.17 (br s, 4H; Cpr-H), 0.94–0.88 (m, 1H; Cpr-H), 0.14 (s, 9H, $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 115.2 (C), 110.2 (C), 107.2 (C), 84.4 (C), 32.6 (CH_2), 20.0 (CH_2), 15.4 (CH), 9.8 (CH_2), 2.9 (CH_2), 2.8 (CH_2), 0.1 ($3CH_3$); IR (film): $\tilde{\nu}$ = 3050, 2961, 2855, 2175, 1249, 759 cm^{-1}; MS (70 eV): *m/z* (%): 203 (1) [M^+−H], 189 (4) [M^+−Me], 173 (2), 161 (11), 145 (5), 129 (7), 97 (4) [$Me_3SiC{\equiv}C^+$], 91 (12), 83 (10), 73 (100) [Me_3Si^+], 59 (18); elemental analysis calcd (%) for $C_{13}H_{20}Si$ (204.4): C 76.40, H 9.86; found C 76.60, H 9.94.

[6-(Cyclopropylidene)hex-1-ynyl]trimethylsilane (14a): Column chromatography (5 g of silica gel, column 15×1 cm, pentane) of the reaction mixture obtained from trimethylsilylacetylene (709 mg, 1.0 mL, 7.22 mmol) in THF (7 mL), *n*BuLi (5.4 mmol, 2.3 mL of a 2.36 M solution in hexane) and iodide **13a** (1.10 g, 4.95 mmol) as a solution in a mixture of DMPU (5 mL) and THF (5 mL) according to GP 2 gave the enyne **14a** (733 mg, 77%) as a colorless oil. R_f = 0.78 (pentane), which was contaminated with some of the protiodesilylated product. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 5.77–5.70 (m, 1H; =CH), 2.32–2.16 (m, 4H; $2CH_2$), 1.67 (quin, *J* = 7.0 Hz, 2H; CH_2), 1.03–1.01 (m, 4H; Cpr-H), 0.14 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 122.1 (C), 117.1 (C), 107.4 (C), 84.4 (C), 30.8 (CH_2), 28.2 (CH_2), 19.3 (CH_2), 2.8 (CH_2), 1.8 (CH_2), 0.1 ($3CH_3$); IR (film): $\tilde{\nu}$ = 3051, 2959, 2860, 2175, 1249, 842, 759 cm^{-1}; MS (70 eV): *m/z* (%): 191 (1) [M^+−H], 177 (4) [M^+−Me], 149 (9), 117 (15), 109 (6), 83 (7), 73 (100) [Me_3Si^+], 59 (19).

[7-(Cyclopropylidene)hept-1-ynyl]trimethylsilane (14b): Column chromatography (5 g of silica gel, column 15×1 cm, pentane) of the reaction mixture obtained from trimethylsilylacetylene (425 mg, 0.6 mL, 4.33 mmol) in THF (5 mL), *n*BuLi (2.8 mmol, 1.2 mL of a 2.36 M solution in hexane) and iodide **13b** (600 mg, 2.54 mmol) as a solution in a mixture of DMPU (2 mL) and THF (4 mL) according to GP 2 gave the enyne **14b** (325 mg, 62%) as a colorless oil. R_f = 0.50 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 5.78–5.71 (m, 1H; =CH), 2.26–2.17 (m, 4H; $2CH_2$), 1.56–1.50 (m, 4H; $2CH_2$), 1.02–1.01 (m, 4H; Cpr-H), 0.14 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 121.3 (C), 117.9 (C), 107.6 (C), 84.3 (C), 31.2 (CH_2), 28.4 (CH_2), 28.2 (CH_2), 19.7 (CH_2), 2.2 (CH_2), 1.9 (CH_2), 0.2 ($3CH_3$); IR (film): $\tilde{\nu}$ = 3051, 2937, 2858, 2175, 1249, 843 cm^{-1}; MS (70 eV): *m/z* (%): 191 (3) [M^+−Me], 163 (4) [M^+−Me−C_2H_4], 131 (7), 117 (9), 91 (22), 73 (100) [Me_3Si^+], 59 (15); elemental analysis calcd (%) for $C_{13}H_{22}Si$ (206.4): C 75.65, H 10.74; found C 76.49, H 10.48.

[5-(Bicyclopropyliden-2-yl)pent-1-ynyl]trimethylsilane (9d): To a vigorously stirred solution of *n*BuLi (4.36 mmol, 1.85 mL of a 2.36 M solution in hexane) in anhydrous THF (5 mL) was added dropwise at −10 °C a solution of bicyclopropylidene (**3**) (380 mg, 4.74 mmol) in THF (3 mL). After stirring at 0 °C for an additional 1 h, the reaction mixture was cooled to −78 °C, and a solution of (5-iodopent-1-ynyl)trimethylsilane (**11**)[19] (1.00 g, 3.76 mmol) in THF (4 mL) was added dropwise at this temperature. The resulting mixture was allowed to warm up to 0 °C over a period of 1 h and then poured into ice-cold water (10 mL). The aqueous phase was extracted with Et_2O (3×10 mL), the combined organic extracts were washed with water and brine (10 mL each), dried and concentrated under reduced pressure. The residue was purified by column chromatography (15 g of silica gel, column 10×2 cm, pentane) to give **9d** (402 mg, 49%) as a colorless oil. R_f = 0.52 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 2.33–2.26 (m, 2H; CH_2), 1.71–1.30 (m, 6H; $2CH_2$ + 2Cpr-H), 1.17 (br s, 4H; Cpr-H), 0.88–0.83 (m, 1H; Cpr-H), 0.14 (s, 9H, $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 115.7 (C), 109.8 (C), 107.6 (C), 84.3 (C), 32.3 (CH_2), 28.6 (CH_2), 19.5 (CH_2), 15.5 (CH), 9.6 (CH_2), 2.9 (CH_2), 2.7 (CH_2), 0.2 ($3CH_3$); IR (film): $\tilde{\nu}$ = 3051, 2960, 2859, 2175, 1249, 841 cm^{-1}; MS (70 eV): *m/z* (%): 203 (18) [M^+−Me], 175 (22), 128 (38), 73 (100) [Me_3Si^+], 59 (46); elemental analysis calcd (%) for $C_{14}H_{22}Si$ (218.4): C 76.99, H 10.15; found C 76.94, H 10.28.

Protiodesilylation of compounds 9b–d

General procedure GP 3: A solution of the respective trimethylsilyl-protected enyne **9b–d** (1 mmol) in methanol (8 mL) was vigorously stirred at ambient temperature with potassium carbonate (691 mg, 5 mmol) for the indicated time, and the mixture then was poured into ice-cold water (10 mL). The aqueous phase was extracted with pentane (3×10 mL), the combined organic extracts were washed with brine (2×15 mL), dried and concentrated under reduced pressure. The residue was purified by column chromatography (15 g of silica gel, column 10×2 cm, pentane).

1-Methylene-2-(pent-4-ynyl)cyclopropane (10b): Column chromatography of the residue obtained from **9b** (410 mg, 2.13 mmol) according to GP 3 after 6 h of stirring gave the enyne **10b** (137 mg, 53%) as a colorless liquid. R_f=0.27 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ= 5.41–5.39 (m, 1H; =CH_2), 5.32–5.31 (m, 1H; =CH_2), 2.27 (dt, J=2.4, 6.9 Hz, 2H; CH_2), 1.95 (t, J=2.4 Hz, 1H; ≡CH), 1.52–1.12 (m, 6H; 2CH_2 + 2Cpr-H), 0.80–0.71 (m, 1H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ=136.5 (C), 102.7 (CH_2), 84.4 (CH), 68.3 (C), 32.0 (CH_2), 28.3 (CH_2), 18.1 (CH_2), 15.1 (CH), 9.4 (CH_2); IR (film): $\tilde{\nu}$=3306, 3068, 2974, 2939, 2860, 2118, 1441, 887, 633 cm^{-1}.

2-(But-3-ynyl)bicyclopropylidene (10c): Column chromatography of the residue obtained from **9c** (215 mg, 1.05 mmol) according to GP 3 after 4 h of stirring gave the enyne **10c** (103 mg, 74%) as a colorless liquid. R_f=0.67 (pentane); ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ=2.36 (dt, J= 2.6, 7.0 Hz, 2H; CH_2), 1.97 (t, J=2.6 Hz, 1H; ≡CH), 1.73–1.51 (m, 3H; CH_2 + Cpr-H), 1.42–1.34 (m, 1H; Cpr-H), 1.18 (brs, 4H; Cpr-H), 0.94–0.83 (m, 1H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ=115.1 (C), 110.3 (C), 84.4 (CH), 68.3 (C), 32.4 (CH_2), 18.6 (CH_2), 15.3 (CH), 9.7 (CH_2), 3.0 (CH_2), 2.8 (CH_2); IR (film): $\tilde{\nu}$=3309, 3051, 2982, 2930, 2855, 2118, 631 cm^{-1}; MS (70 eV): m/z (%): 131 (17) [M^+−H], 117 (24) [M^+ −Me], 115 (36), 103 (17), 91 (100), 79 (19) [$C_6H_7^+$], 77 (47), 65 (24), 51 (20).

2-(Pent-4-ynyl)bicyclopropylidene (10d): Column chromatography of the residue obtained from **9d** (200 mg, 0.92 mmol) according to GP 3 after 3 h of stirring gave the enyne **10d** (126 mg, 94%) as a colorless oil. R_f= 0.48; ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ=2.28–2.21 (m, 2H; CH_2), 1.92 (t, J=2.6 Hz, 1H; ≡CH), 1.72–1.20 (m, 6H; 2CH_2 + 2Cpr-H), 1.16 (brs, 4H; Cpr-H), 0.88–0.79 (m, 1H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ=115.6 (C), 109.9 (C), 84.5 (CH), 68.2 (C), 32.1 (CH_2), 28.4 (CH_2), 18.0 (CH_2), 15.4 (CH), 9.6 (CH_2), 2.9 (CH_2), 2.6 (CH_2); IR (film): $\tilde{\nu}$=3304, 3051, 2978, 2938, 2859, 2118, 1440, 960, 633 cm^{-1}; MS (70 eV): m/z (%): 146 (2) [M^+], 131 (20), 129 (11), 105 (28), 91 (100), 79 (48) [$C_6H_7^+$], 65 (27), 51 (25); elemental analysis calcd (%) for $C_{11}H_{14}$ (146.2): C 90.34, H 9.66; found C 90.28, H 9.83.

Preparation of the esters 16a–c with a methylenecyclopropane moiety

General procedure GP 4: Sodium hydride (4.70 g, 196 mmol) and thoroughly powdered 3-bromopropyltriphenylphosphonium bromide[26] (45.41 g, 97.8 mmol) were suspended in anhydrous dimethoxyethane (DME), ethanol (2–3 drops) was added, and the resulting mixture was vigorously stirred at 70°C for 7 h. After this, a solution of the respective aldo/keto ester **15a–c** (38.5 mmol) in DME (40 mL) was added dropwise, and the resulting mixture was stirred for the indicated time at the same temperature After cooling, the mixture was poured into ice-cold aq. sat. NH_4Cl solution (120 mL), the aqueous phase was extracted with pentane (3×100 mL), the combined organic extracts were dried and concentrated under reduced pressure. The residue was vigorously stirred with pentane (100 mL) at ambient temperature for 1 h and filtered. The filtrate was concentrated under reduced pressure again, and the product was purified by column chromatography.

Methyl 4-(cyclopropylidene)butanoate (16a): Column chromatography (180 g of silica gel, column 20×5 cm, petroleum ether/Et_2O 50:1) of the residue obtained from the aldoester **15a**[24] (4.47 g, 38.5 mmol), NaH (4.70 g, 196 mmol) and $Br(CH_2)_3P^+Ph_3Br^-$ (45.41 g, 97.8 mmol) according to GP 4 after 11 h of stirring gave the ester **16a** (3.02 g, 56%) as a colorless liquid. R_f=0.30 (petroleum ether/Et_2O 50:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ=5.70–5.65 (m, 1H, =CH), 3.56 (s, 3H; CH_3), 2.38 (brs, 4H; 2CH_2), 0.92 (s, 4H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ=173.5 (C), 122.1 (C), 115.9 (CH), 51.1 (CH_3), 33.3 (CH_2), 26.9 (CH_2), 1.7 (2CH_2); IR (film): $\tilde{\nu}$=2982, 2953, 2846, 1744, 1255, 959, 936 cm^{-1}; MS (70 eV): m/z (%): 140 (1) [M^+], 98 (23), 81 (100) [M^+−CO_2Me], 59 (31) [MeO_2C^+], 53 (26) [$C_4H_5^+$].

Ethyl 4-(cyclopropylidene)pentanoate (16b):[23] Column chromatography (180 g of silica gel, column 20×5 cm, petroleum ether/Et_2O 60:1) of the residue obtained from the ketoester **15b** (2.41 g, 16.7 mmol), NaH (2.0 g, 83.3 mmol) and $Br(CH_2)_3P^+Ph_3Br^-$ (19.3 g, 41.6 mmol) according to GP 4 after 13 h of stirring gave the ester **16b** (733 mg, 26%) as a colorless oil. R_f=0.24 (petroleum ether/Et_2O 60:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ=4.12 (q, J=7.1 Hz, 2H; OCH_2), 2.56–2.47 (m, 4H; 2CH_2), 1.82 (t, J=1.4 Hz, 3H; CH_3), 1.25 (t, J=7.1 Hz, 3H; CH_3), 1.07–1.03 (m, 2H; Cpr-H), 0.94–0.90 (m, 2H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ=173.6 (C), 122.5 (C), 115.7 (C), 60.1 (CH_2), 32.4 (CH_2), 31.6 (CH_2), 20.8 (CH_3), 14.1 (CH_3), 3.1 (CH_2), 0.9 (CH_2); IR (film): $\tilde{\nu}$= 2978, 2912, 1737, 1446, 1372, 1275, 1177 cm^{-1}; MS (70 eV): m/z (%): 168 (3) [M^+], 153 (5) [M^+−Me], 139 (5) [M^+−Et], 123 (30) [M^+−OEt], 105 (8), 95 (100) [M^+−CO_2Et], 79 (28); HRMS: m/z (%): calcd for $C_{10}H_{16}O_2$: 168.1150; found 168.1150.

Ethyl 4-(cyclopropylidene)hexanoate (16c): Column chromatography (180 g of silica gel, column 20×5 cm, petroleum ether/Et_2O 60:1) of the residue obtained from the ketoester **15c** (2.65 g, 16.8 mmol), NaH (2.0 g, 83.3 mmol) and $Br(CH_2)_3P^+Ph_3Br^-$ (19.3 g, 41.6 mmol) according to GP 4 after 13 h of stirring gave the ester **16c** (550 mg, 18%) as a colorless oil. R_f=0.26 (petroleum ether/Et_2O 60:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ=4.12 (q, J=7.1 Hz, 2H; OCH_2), 2.58–2.44 (m, 4H; 2CH_2), 2.18 (q, J=7.5 Hz, 2H, CH_2), 1.25 (t, J=7.1 Hz, 3H, CH_3), 1.07 (t, J=7.5 Hz, 3H, CH_3), 0.99 (brs, 4H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ=173.8 (C), 127.8 (C), 114.5 (C), 60.1 (CH_2), 32.6 (CH_2), 29.9 (CH_2), 28.5 (CH_2), 14.2 (CH_3), 12.4 (CH_3), 1.7 (CH_2), 1.3 (CH_2); IR (film): $\tilde{\nu}$=2976, 2936, 1737, 1372, 1254, 1177, 734 cm^{-1}; MS (70 eV): m/z (%): 182 (46) [M^+], 167 (16) [M^+−Me], 153 (33) [M^+−Et], 137 (95) [M^+−OEt], 109 (80) [M^+−CO_2Et], 93 (100), 79 (64), 67 (29); elemental analysis calcd (%) for $C_{11}H_{18}O_2$ (182.3): C 72.49, H 9.95; found C 72.55, H 9.90.

Coupling of esters 16b,c with trimethylsilyl-protected lithioacetylene (8)

General procedure 5 (GP 5): To a vigorously stirred solution of trimethylsilylacetylene (1.42 g, 2.00 mL, 14.4 mmol) in anhydrous THF (27 mL) was added dropwise nBuLi (12.0 mmol, 5.1 mL of a 2.35 M solution in hexane) at −78°C. After stirring at this temperature for an additional 10 min, the solution was cooled to −100°C, and a solution precooled to −78°C of the respective ester **16b,c** (3.03 mmol) in THF (8 mL) was added dropwise followed by BF_3·Et_2O (2.8 mL). The reaction mixture was allowed to warm up to −78°C, stirred at this temperature for an additional 1.5 h and poured, while still cold, into ice-cold aq. sat. NH_4Cl solution (20 mL). The aqueous phase was extracted with diethyl ether (3×20 mL), the combined organic extracts were washed with aq. sat. $NaHCO_3$ solution (2×20 mL), dried and concentrated under reduced pressure. The residue was purified by column chromatography.

6-Cyclopropylidene-1-(trimethylsilyl)hept-1-yn-3-one (17b): Column chromatography (20 g of silica gel, column 15×2 cm, petroleum ether/Et_2O 40:1) of the residue obtained from trimethylsilylacetylene (1.42 g, 2.00 mL, 14.4 mmol), nBuLi (12.0 mmol, 5.1 mL of a 2.35 M solution in hexane), ester **16b** (509 mg, 3.03 mmol) and BF_3·Et_2O (2.8 mL) according to GP 5 gave the ketoenyne **17b** (468 mg, 70%) as a colorless oil. R_f= 0.40; ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ=2.79 (t, J=7.6 Hz, 2H; CH_2), 2.51 (t, J=7.6 Hz, 2H; CH_2), 1.82 (t, J=1.6 Hz, 3H; CH_3), 1.08–1.05 (m, 2H; Cpr-H), 0.95–0.91 (m, 2H; Cpr-H), 0.24 (s, 9H; 3CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ=187.6 (C), 122.0 (C), 116.1 (C), 101.9 (C), 97.5 (C), 43.2 (CH_2), 30.7 (CH_2), 20.9 (CH_3), 3.2 (CH_2), 1.0 (CH_2), −0.8 (3CH_3); IR (film): $\tilde{\nu}$=2973, 2909, 1677, 1252, 1105, 847, 762 cm^{-1}; MS (70 eV): m/z (%): 220 (12) [M^+], 205 (17) [M^+−Me], 177 (7), 163 (9), 125 (50) [M^+−C_7H_{11}], 97 (38), [$Me_3SiC{\equiv}C^+$], 73 (100) [Me_3Si^+]; elemental analysis calcd (%) for $C_{13}H_{20}OSi$ (220.4): C 70.85, H 9.15; found C 70.96, H 9.19.

6-Cyclopropylidene-1-(trimethylsilyl)oct-1-yn-3-one (17c): Column chromatography (20 g of silica gel, column 15×2 cm, petroleum ether/Et_2O 120:1) of the residue obtained from trimethylsilylacetylene (1.33 g, 1.87 mL, 13.5 mmol), nBuLi (10.6 mmol, 4.6 mL of a 2.30 M solution in hexane), ester **16c** (519 mg, 2.85 mmol) and BF_3·Et_2O (2.6 mL) according to GP 5 gave the ketoenyne **17c** (450 mg, 67%) as a colorless oil. R_f= 0.31 (petroleum ether/Et_2O 120:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25°C): δ=2.79 (t, J=7.4 Hz, 2H; CH_2), 2.52 (t, J=7.4 Hz, 2H; CH_2), 2.18 (q, J=7.5 Hz, 2H; CH_2), 1.07 (t, J=7.5 Hz, 3H; CH_3), 1.00 (brs, 4H; Cpr-H), 0.24 (s, 9H; 3CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25°C): δ=187.9 (C), 127.4 (C), 114.9 (C), 102.0 (C), 97.6 (C), 43.4 (CH_2), 29.0 (CH_2), 28.5 (CH_2), 12.4 (CH_3), 1.9 (CH_2), 1.5 (CH_2), 0.8 (3CH_3); IR (film): $\tilde{\nu}$=2965, 1678, 1253, 1105, 847, 762 cm^{-1}; MS (70 eV): m/z (%): 234 (12) [M^+], 219 (12) [M^+−Me], 105 (18) [M^+−Et], 187 (12), 125 (21) [M^+−C_8H_{13}],

97 (31), [$Me_3SiC{\equiv}C^+$], 73 (100) [Me_3Si^+]; HRMS: *m*/*z* (%): calcd for $C_{14}H_{22}OSi$: 234.1439; found 234.1439.

Transacetalization of enynes 17a and 17d

General procedure GP 6: A solution of the respective ketoenyne **17a** or **17d** (1 mmol), (*S*,*S*)-(−)-hydrobenzoin (**24**) (2–2.2 equiv), trimethyl orthoformate (2 equiv) and *p*-toluenesulfonic acid (10 mg) in anhydrous benzene (10 mL) was stirred at 50 °C for the indicated time (16–17 h) with TLC monitoring, then cooled and poured into sat. aq. $NaHCO_3$ solution (20 mL). The aqueous phase was extracted with diethyl ether (3× 15 mL), the combined organic extracts were dried over a Na_2SO_4/K_2CO_3 mixture (2:1) and concentrated under reduced pressure. The residue was purified by column chromatography.

(4*S*,5*S*)-2-(3′-Cyclopropylidenepropyl)-4,5-diphenyl-2-(2″-trimethylsilylethynyl)-1,3-dioxolane (25a): Column chromatography (100 g of silica gel, column 20×4 cm, petroleum ether/Et_2O 60:1) of the residue obtained from ketoenyne **17a** (2.09 g, 10.1 mmol), **24** (4.30 g, 20.1 mmol), $HC(OMe)_3$ (2.11 g, 19.9 mmol) and *p*TsOH (0.1 g) according to GP 6 (16 h of stirring) gave the acetal **25a** (3.74 g, 92%) as a colorless solid. R_f=0.70 (petroleum ether/Et_2O 60:1); m.p. 50 °C; $[\alpha]_D^{20}=-30.0$ (*c*=1.0 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=7.29–7.12 (m, 10H; Ar-H), 5.81–5.75 (m, 1H; 3′-H), 4.99 (d, *J*=8.5 Hz, 1H; 5*-H), 4.58 (d, *J*=8.5 Hz, 1H; 4*-H), 2.54–2.45 (m, 2H; 1′-H), 2.21–2.15 (m, 2H; 2′-H), 0.96–0.95 (m, 4H; Cpr-H), 0.15 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=137.6 (C), 135.7 (C), 128.5 (2 CH), 128.3 (2 CH), 128.2 (CH), 128.1 (CH), 127.1 (2 CH), 126.7 (2 CH), 121.6 (C), 117.1 (CH), 104.2 (C), 103.6 (C), 89.6 (C), 86.5 (CH), 86.2 (CH), 39.4 (CH_2), 26.1 (CH_2), 2.0 ($2CH_2$), −0.2 ($3CH_3$); IR (KBr): $\tilde{\nu}$=3052, 2960, 2903, 1253, 1216, 1194, 1122, 1095, 1060, 1041, 1026, 976, 951, 843, 768, 533 cm^{-1}; MS (70 eV): *m*/*z* (%): 321 (9) [$M^+-C_6H_9$], 309 (2), 197 (39), 175 (47), 156 (35), 125 (58), 97 (83) [$Me_3SiC{\equiv}C^+$], 81 (20); elemental analysis calcd (%) for $C_{26}H_{30}O_2Si$ (402.6): C 77.57, H 7.51; found C 77.57, H 7.59.

(4*S*,5*S*)-2-(4′-Cyclopropylidene-*n*-butyl)-4,5-diphenyl-2-(2″-trimethylsilylethynyl)-1,3-dioxolane (25d): Column chromatography (25 g of silica gel, column 20×2 cm, petroleum ether/Et_2O 80:1) of the residue obtained from ketoenyne **17d** (380 mg, 1.72 mmol), **24** (810 mg, 3.78 mmol), $HC(OMe)_3$ (365 mg, 3.44 mmol) and *p*TsOH (15 mg) according to GP 6 (17 h stirring) gave the acetal **25d** (688 mg, 96%) as a colorless oil. R_f= 0.70 (petroleum ether/Et_2O 80:1); $[\alpha]_D^{20}=-28.1$ (*c*=1.0 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=7.40–7.23 (m, 10H; Ar-H), 5.86–5.79 (m, 1H; 4′-H), 5.09 (d, *J*=8.5 Hz, 1H; 5*-H), 4.68 (d, *J*=8.5 Hz, 1H; 4*-H), 2.36–2.28 (m, 2H; 3′-H), 2.17–2.10 (m, 2H; 1′-H), 1.94–1.81 (m, 2H; 2′-H), 1.06–1.04 (m, 4H; Cpr-H), 0.25 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=137.6 (C), 135.7 (C), 128.4 (2 CH), 128.3 (2 CH), 128.2 (CH), 128.1 (CH), 127.1 (2CH), 126.7 (2CH), 121.6 (C), 117.8 (CH), 104.4 (C), 103.8 (C), 89.4 (C), 86.5 (CH), 86.2 (CH), 39.5 (CH_2), 31.6 (CH_2), 23.2 (CH_2), 2.2 (CH_2), 2.0 (CH_2), −0.2 ($3CH_3$); IR (film): $\tilde{\nu}$=3034, 2958, 1251, 1024, 844, 762, 699 cm^{-1}; MS (CI): *m*/*z* (%): 850 (4) [$2M^+$+NH_4] 434 (82) [M^++NH_4], 417 (100) [M^++H]; elemental analysis calcd (%) for $C_{27}H_{32}O_2Si$ (416.6): C 77.84, H 7.74; found C 77.64, H 7.64.

TMANO-induced PKRs of enynes 9a,b, 10a,b, 14a,b and 25d

General procedure GP 7: To a vigorously stirred solution of the respective enyne (0.25 mmol) in anhydrous dichloromethane (10 mL) was added in the dark at ambient temperature $[Co_2(CO)_8]$ (94 mg, 0.27 mmol). The reaction mixture was stirred at the same temperature for an additional 1–3 h with TLC monitoring, cooled to −78 °C, trimethylamine *N*-oxide (TMANO) (113 mg, 1.5 mmol, 6 equiv) was added, the reaction flask was connected to an oxygen cylinder, and the reaction mixture was allowed to warm up with continued stirring within 16 h. The reaction mixture was filtered through a 1 cm pad of silica gel, the solid residue was washed with Et_2O (15 mL), and the combined filtrates were concentrated under reduced pressure. The residue was purified by column chromatography.

4-Trimethylsilyl-1,1a,2,3-tetrahydrocyclopropa[*c*]pentalen-5-one (18a): Column chromatography (5 g of silica gel, column 15×1 cm, petroleum ether/Et_2O 10:1) of the residue obtained from enyne **9a** (91 mg, 0.51 mmol), $[Co_2(CO)_8]$ (230 mg, 0.67 mmol) and TMANO (270 mg, 3.59 mmol) according to GP 7 gave the enone **18a** (54 mg, 51%) as a colorless oil. R_f=0.18 (petroleum ether/Et_2O 10:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=2.65–2.60 (m, 1H), 2.59 (d, *J*=18.4 Hz, 1H; CH_2), 2.48 (d, *J*=18.4 Hz, 1H; CH_2), 2.21–2.04 (m, 3H), 1.87 (m, 1H; Cpr-H), 1.13 (dd, *J*=4.3, 7.7 Hz; 1H, Cpr-H), 0.96 (dd, *J*=4.3, 4.3 Hz, 1H; Cpr-H), 0.19 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=213.4 (C), 197.6 (C), 134.7 (C), 42.1 (CH_2), 39.3 (C), 29.2 (CH_2), 24.7 (CH), 23.5 (CH_2), 17.1 (CH_2), −1.0 ($3CH_3$); IR (film): $\tilde{\nu}$=2959, 1688, 1592, 1407, 1246, 1049, 840 cm^{-1}; MS (70 eV): *m*/*z* (%): 206 (13) [M^+], 191 (100) [M^+−Me], 147 (2), 135 (3), 115 (5), 91 (4), 73 (16) [Me_3Si^+]; HRMS: *m*/*z* (%): calcd for $C_{12}H_{18}OSi$: 206.1126; found 206.1126.

5-Trimethylsilyl-1a,2,3,4-tetrahydro-1*H*-cyclopropa[*d*]inden-6-one (18b): Column chromatography (5 g of silica gel, column 15×1 cm, petroleum ether/Et_2O 10:1) of the residue obtained from enyne **9b** (200 mg, 1.04 mmol), $[Co_2(CO)_8]$ (423 mg, 1.24 mmol) and TMANO (470 mg, 6.26 mmol) according to GP 7 gave the enone **18b** (41 mg, 18%) as a colorless oil. R_f=0.27 (petroleum ether/Et_2O 10:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=2.67 (ddd, *J*=7.1, 7.1, 17.2 Hz, 1H), 2.48 (d, *J*=18.8 Hz, 1H; CH_2), 2.32 (d, *J*=18.6 Hz, 1H; CH_2), 2.41–2.29 (m, 1H), 1.95–1.50 (m, 5H), 1.27 (dd, *J*=5.0, 5.0 Hz, 1H; Cpr-H), 1.12 (dd, *J*=5.0, 8.4 Hz, 1H, Cpr-H), 0.20 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=212.1 (C), 190.7 (C), 137.1 (C), 46.5 (CH_2), 30.8 (C), 26.7 (CH_2), 23.9 (CH), 22.4 (CH_2), 21.4 (CH_2), 20.1 (CH_2), −0.4 ($3CH_3$); IR (film): $\tilde{\nu}$=2949, 2859, 1683, 1559, 1246, 841 cm^{-1}; MS (70 eV): *m*/*z* (%): 220 (29) [M^+], 205 (76) [M^+−Me], 177 (4), 131 (12), 73 (20) [Me_3Si^+], 59 (8); HRMS: *m*/*z* (%): calcd for $C_{13}H_{20}OSi$: 220.1283; found 220.1283.

1,1a,2,3-Tetrahydrocyclopropa[*c*]pentalen-5-one (19a): The trimethylsilyl-protected enyne **9a** (280 mg, 1.57 mmol) was treated with potassium carbonate according to GP 3. The crude enyne **10a** was taken up with anhydrous CH_2Cl_2 (15 mL), and the solution treated with $[Co_2(CO)_8]$ (575 mg, 1.68 mmol) and then with TMANO (644 mg, 8.57 mmol) according to GP 7. Column chromatography (5 g of silica gel, column 15×1 cm, petroleum ether/Et_2O 3:1) of the residue gave the enone **19a** (40 mg, 19%) as a colorless oil. R_f=0.13 (petroleum ether/Et_2O 3:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=5.95 (s, 1H; =CH), 2.67–2.50 (m, 3H), 2.22–2.07 (m, 3H), 1.88 (m, 1H; Cpr-H), 1.16 (dd, *J*=4.6, 7.7 Hz, 1H; Cpr-H), 1.01 (dd, *J*=4.2, 4.6 Hz, 1H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=209.9 (C), 190.8 (C), 124.1 (CH), 41.3 (CH_2), 29.2 (CH_2), 28.0 (C), 24.8 (CH), 22.8 (CH_2), 16.4 (CH_2); IR (film): $\tilde{\nu}$=2936, 2869, 1698, 1614, 1501, 1407, 1237, 824, 731 cm^{-1}; MS (70 eV): *m*/*z* (%): 134 (78) [M^+], 119 (15), 106 (31), [M^+−CO], 91 (100), 78 (33), 65 (12); elemental analysis calcd (%) for $C_9H_{10}O$ (134.2): C 80.56, H 7.51; found C 80.55, H 7.57.

3′-Trimethylsilyl-4′,5′,6′,6′a-tetrahydro-1′*H*-spiro(cyclopropane-1,1′-pentalen-2′-one) (20a): Column chromatography (20 g of silica gel, column 15×2 cm, petroleum ether/Et_2O 10:1) of the residue obtained from enyne **14a** (179 mg, 0.93 mmol), $[Co_2(CO)_8]$ (440 mg, 1.29 mmol) and TMANO (480 mg, 6.39 mmol) according to GP 7, gave the enone **20a** (109 mg, 53%) as a colorless oil. R_f=0.47 (petroleum ether/Et_2O 10:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=2.88 (dd, *J*=7.3, 12.6 Hz, 1H), 2.69–2.51 (m, 2H), 2.13–1.90 (m, 2H), 1.85–1.75 (m, 1H), 1.29–1.22 (m, 1H; Cpr-H), 1.20–1.06 (m, 1H), 0.97–0.79 (m, 3H; Cpr-H), 0.17 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=213.1 (C), 196.9 (C), 135.0 (C), 54.7 (CH), 33.2 (C), 28.4 (CH_2), 27.8 (CH_2), 25.7 (CH_2), 14.1 (CH_2), 12.8 (CH_2), −1.2 ($3CH_3$); IR (film): $\tilde{\nu}$=2957, 1679, 1603, 1247, 1109, 841 cm^{-1}; MS (70 eV): *m*/*z* (%): 220 (25) [M^+], 205 (100) [M^+ −Me], 177 (7), 131 (14), 91 (7), 73 (12) [Me_3Si^+]; elemental analysis calcd (%) for $C_{13}H_{20}OSi$ (220.4): C 70.85, H 9.15; found C 71.02, H 9.23.

1′,4′,5′,6′,7′,7′a-Hexahydro-3′-trimethylsilylspiro(cyclopropane-1,1′-inden-2′-one) (20b): Column chromatography (20 g of silica gel, column 15× 2 cm, petroleum ether/Et_2O 10:1) of the residue obtained from enyne **14b** (127 mg, 0.62 mmol), $[Co_2(CO)_8]$ (275 mg, 0.80 mmol) and TMANO (280 mg, 3.73 mmol) according to GP 7 gave the enone **20b** (100 mg, 69%) as a colorless oil. R_f=0.44 (petroleum ether/Et_2O 10:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=3.10–3.03 (m, 1H), 2.47 (dd, *J*=5.4, 12.6 Hz, 1H), 2.24 (ddd, *J*=5.4, 12.9, 12.9 Hz, 1H), 2.07–1.97 (m, 1H), 1.90–1.81 (m, 2H), 1.54–0.80 (m, 7H), 0.23 (s, 9H; $3CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=212.2 (C), 189.9 (C), 135.7 (C), 49.4 (CH), 33.0 (C), 32.9 (CH_2), 32.0 (CH_2), 27.7 (CH_2), 25.0 (CH_2), 15.4 (CH_2), 12.6

(CH_2), −0.2 ($3\,CH_3$); IR (film): $\tilde{\nu}$ = 2932, 2856, 1685, 1588, 1247, 843 cm^{-1}; MS (70 eV): *m/z* (%): 234 (28) [M^+], 219 (100) [M^+−Me], 95 (2), 73 (11) [Me_3Si^+]; elemental analysis calcd (%) for $C_{14}H_{22}OSi$ (234.4): C 71.73, H 9.46; found C 71.86, H 9.50.

4′,5′,6′,6′a-Tetrahydro-1′*H*-spiro(cyclopropane-1,1′-pentalen-2-one) (21a): The trimethylsilyl-protected enyne **14a** (323 mg, 1.68 mmol) was treated with potassium carbonate according to GP 3. The crude product was taken up with anhydrous CH_2Cl_2 (20 mL), and the mixture treated with [$Co_2(CO)_8$] (672 mg, 1.97 mmol) and then with TMANO (760 mg, 10.1 mmol) according to GP 7. Column chromatography (5 g of silica gel, column 15 × 1 cm, petroleum ether/Et_2O 5:1) of the residue gave the enone **21a** (100 mg, 40%) as a colorless oil. R_f = 0.22 (petroleum ether/Et_2O 5:1); ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 5.95 (d, J = 1.6 Hz, 1H; =CH), 2.89 (dd, J = 7.1, 12.1 Hz, 1H), 2.73–2.46 (m, 2H), 2.12–1.91 (m, 2H), 1.88–1.77 (m, 1H), 1.31–1.24 (m, 1H; Cpr-H), 1.17–1.03 (m, 1H), 0.99–0.82 (m, 3H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 210.0 (C), 189.5 (C), 124.6 (CH), 52.8 (CH), 33.2 (C), 28.6 (CH_2), 26.6 (CH_2), 25.5 (CH_2), 14.3 (CH_2), 13.3 (CH_2); IR (film): $\tilde{\nu}$ = 2997, 2963, 2940, 1679, 1621, 1270, 1120, 866, 841 cm^{-1}; MS (70 eV): *m/z* (%): 148 (80) [M^+], 133 (14), 120 (58) [M^+−CO], 105 (68), 91 (100), 79 (29), 62 (15), 51 (14); elemental analysis calcd (%) for $C_{10}H_{12}O$ (148.2): C 81.04, H 8.16; found C 80.87, H 8.03.

1′,4′,5′,6′,7′,7′a-Hexahydrospiro(cyclopropane-1,1′-inden-2-one) (21b): The trimethylsilyl-protected enyne **14b** (140 mg, 0.68 mmol) was treated with potassium carbonate according to GP 3. The crude product was taken up with anhydrous CH_2Cl_2 (15 mL), and the mixture treated with [$Co_2(CO)_8$] (282 mg, 0.82 mmol) and then with TMANO (310 mg, 4.13 mmol) according to GP 7. Column chromatography (5 g of silica gel, column 15 × 1 cm, petroleum ether/Et_2O 5:1) of the residue gave the enone **20b** (35 mg, 32%) as a colorless oil. R_f = 0.17 (petroleum ether/Et_2O 5:1); ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 5.95 (t, J = 1.6 Hz, 1H; =CH), 2.89–2.82 (m, 1H), 2.50 (dd, J = 5.3, 12.4 Hz, 1H), 2.35–2.21 (m, 1H), 2.07–1.95 (m, 1H), 1.92–1.75 (m, 2H), 1.51–0.81 (m, 7H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 208.6 (C), 182.5 (C), 126.2 (CH), 47.5 (CH), 33.3 (C), 32.3 (CH_2), 31.3 (CH_2), 27.2 (CH_2), 24.9 (CH_2), 15.4 (CH_2), 12.7 (CH_2); IR (film): $\tilde{\nu}$ = 2932, 2857, 1697, 1618, 1348, 1126, 850 cm^{-1}; MS (70 eV): *m/z* (%): 162 (67) [M^+], 147 (17) [M^+−Me], 134 (38) [M^+−CO], 119 (39), 105 (38), 91 (100), 77 (27); HRMS: *m/z* (%): calcd for $C_{11}H_{14}O$: 162.1044; found 162.1044.

(7′a*S*,4″*S*,5″*S*)-1′,4′,5′,6′,7′,7′a-Hexahydro-3′-trimethylsilyldispiro(cyclopropane-1,1′-inden-2′-one-4′,2″-1,3-dioxolane) (26d): Column chromatography (20 g of silica gel, column 15 × 2 cm, petroleum ether/Et_2O 15:1) of the residue obtained from enyne **25d** (200 mg, 0.48 mmol), [$Co_2(CO)_8$] (196 mg, 0.56 mmol) and TMANO (216 mg, 2.88 mmol) according to GP 7 gave the enone **26d** (168 mg, 79%) as a colorless solid. M.p. 145–155 °C; R_f = 0.38 (petroleum ether/Et_2O 15:1), which essentially was a 8:1 mixture of two diastereomers. Recrystallization from hexane gave pure (7′a*S*,4″*S*,5″*S*)-**26d**; m.p. 162 °C; $[\alpha]_D^{20}$ = −91 (c = 1.0 in $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 7.39–7.19 (m, 10H; Ar-H), 4.90 (d, J = 8.4 Hz, 1H; 5″*-H), 4.75 (d, J = 8.4 Hz, 1H; 4″*-H), 3.05 (dd, J = 5.2, 12.2 Hz, 1H; 7′a-H), 2.42–2.38 (m, 1H; 5′-H), 1.94–1.82 (m, 4H; 7′-H, 6′-H, 5′-H), 1.29–0.91 (m, 5H; Cpr-H + 7′-H), 0.23 (s, 9H; 3 CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 212.1 (C), 184.8 (C), 136.7 (C), 135.9 (C), 134.6 (C), 128.6 (2CH), 128.5 (2 CH), 128.4 (CH), 128.3 (CH), 127.1 (2CH), 126.1 (2CH), 109.8 (C), 86.5 (CH), 84.3 (CH), 48.6 (CH), 38.6 (CH_2), 33.7 (CH_2), 33.5 (C), 22.3 (CH_2), 16.5 (CH_2), 13.4 (CH_2), 1.0 ($3\,CH_3$); IR (KBr): $\tilde{\nu}$ = 2941, 1687, 1277, 1105, 1022, 845, 766 cm^{-1}; MS (CI): *m/z* (%): 906 (8) [$2M^+$+NH_4] 462 (1) [M^++NH_4], 445 (100) [M^++H]; elemental analysis calcd (%) for $C_{28}H_{32}O_3Si$ (444.6): C 75.63, H 7.25; found C 75.85, H 7.38. The structure of this compound was also verified by X-ray crystal structure analysis.

NMO-induced PKRs of enynes 9c,d, 10c,d and 25a

General procedure GP 8: To a vigorously stirred solution of the respective enyne (0.56 mmol) in anhydrous dichloromethane (25 mL) was added at −78 °C [$Co_2(CO)_8$] (220 mg, 0.64 mmol), the reaction mixture was allowed to warm up to −20 °C and stirred at this temperature for an additional 2 h. *N*-Methylmorpholine *N*-oxide (NMO, 527 mg, 4.50 mmol) was added, the reaction mixture was allowed to warm up to ambient temperature over a period of 16 h and then worked up according to GP 7.

7′-Trimethylsilylspiro(cyclopropane-1,9′-tricyclo[4.3.0.0^{1,3}]non-6′-ene-8′-one) (18c): Column chromatography (20 g of silica gel, column 15 × 2 cm, petroleum ether/Et_2O 10:1) of the residue obtained from enyne **9c** (115 mg, 0.56 mmol), [$Co_2(CO)_8$] (220 mg, 0.64 mmol) and NMO (527 mg, 4.50 mmol)) according to GP 8, gave the enone **18c** (40 mg, 31%) as a colorless solid. R_f = 0.29 (petroleum ether/Et_2O 10:1); m.p. 36–37 °C; ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 2.72–2.63 (m, 1H), 2.34–2.07 (m, 3H), 1.66 (m, 1H; Cpr-H), 1.25 (ddd, J = 3.1, 6.3, 10.1 Hz, 1H; Cpr-H), 1.05 (ddd, J = 3.1, 6.3, 10.1 Hz, 1H; Cpr-H), 0.95 (dd, J = 4.6, 4.6 Hz, 1H; Cpr-H), 0.79 (dd, J = 4.6, 7.9 Hz, 1H; Cpr-H), 0.70–0.54 (m, 2H; Cpr-H), 0.21 (s, 9H, $3\,CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 212.5 (C), 195.3 (C), 134.1 (C), 45.5 (C), 31.8 (C), 29.7 (CH_2), 24.1 (CH_2), 23.7 (CH), 14.8 (CH_2), 14.4 (CH_2), 13.6 (CH_2), −0.8 ($3\,CH_3$); IR (KBr): $\tilde{\nu}$ = 3057, 2990, 2917, 2895, 1679, 1588, 1247, 1163, 1080, 836 cm^{-1}; MS (70 eV): *m/z* (%): 232 (28) [M^+], 217 (100) [M^+−Me], 201 (9), 73 (23) [Me_3Si^+]; HRMS: *m/z* (%): calcd for $C_{14}H_{20}OSi$: 232.1283; found 232.1283.

1′,1′a,2′,3′-Tetrahydrospiro(cyclopropane-1,6′-cyclopropa[*c*]pentalen-5′-one) (19c): Column chromatography (20 g of silica gel, column 15 × 2 cm, petroleum ether/Et_2O 5:1) of the residue obtained from enyne **10c** (130 mg, 0.98 mmol), [$Co_2(CO)_8$] (372 mg, 1.09 mmol) and NMO (918 mg, 7.84 mmol) according to GP 8, gave the enone **19c** (71 mg, 45%) as a colorless solid. R_f = 0.20 (petroleum ether/Et_2O 5:1); m.p. 61 °C; ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 6.08 (s, 1H; =CH), 2.66–2.55 (m, 1H), 2.35–2.03 (m, 3H), 1.66 (m, 1H; Cpr-H), 1.32–1.25 (m, 1H; Cpr-H), 1.15–1.04 (m, 1H; Cpr-H), 0.98 (dd, J = 4.9, 4.9 Hz, 1H; Cpr-H), 0.82 (dd, J = 4.9, 8.0 Hz, 1H; Cpr-H), 0.74–0.61 (m, 2H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 209.3 (C), 188.2 (C), 123.3 (CH), 44.1 (C), 31.7 (C), 29.6 (CH_2), 23.8 (CH), 23.4 (CH_2), 14.2 (CH_2), 14.0 (CH_2), 13.8 (CH_2); IR (KBr): $\tilde{\nu}$ = 3038, 2992, 2934, 2867, 1670, 1608, 1124, 829 cm^{-1}; MS (70 eV): *m/z* (%): 160 (100) [M^+], 145 (17), 132 (52) [M^+−CO], 117 (83), 104 (26), 91 (66), 77 (19), 65 (19), 51 (21); HRMS: *m/z* (%): calcd for $C_{11}H_{12}O$: 160.0888; found 160.0888; elemental analysis calcd (%) for $C_{11}H_{12}O$ (160.2): C 82.46, H 7.55; found C 82.53, H 7.55.

8′-Trimethylsilylspiro(cyclopropane-1,10′-tricyclo[5.3.0.0^{1,3}]dec-7′-ene-9′-one) (18d): Column chromatography (5 g of silica gel, column 15 × 1 cm, petroleum ether/Et_2O 10:1) of the residue obtained from enyne **9d** (86 mg, 0.39 mmol), [$Co_2(CO)_8$] (150 mg, 0.44 mmol) and NMO (310 mg, 2.65 mmol), according to GP 8 gave the enone **18d** (36 mg, 37%) as a colorless oil. R_f = 0.18 (petroleum ether/Et_2O 10:1); ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 2.83–2.71 (m, 1H), 2.51–2.39 (m, 1H), 1.88–1.52 (m, 4H), 1.49–1.33 (m, 1H), 1.20 (dd, J = 5.4, 5.4 Hz, 1H; Cpr-H), 1.13 (ddd, J = 3.2, 6.6, 9.9 Hz, 1H; Cpr-H), 1.00 (ddd, J = 3.1, 6.6, 9.9 Hz, 1H; Cpr-H), 0.79 (dd, J = 5.4, 8.7 Hz, 1H; Cpr-H), 0.61 (ddd, J = 3.1, 6.6, 9.6 Hz, 1H; Cpr-H), 0.50 (ddd, J = 3.2, 6.6, 9.6 Hz, 1H; Cpr-H), 0.23 (s, 9H; $3\,CH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 211.5 (C), 188.9 (C), 135.8 (C), 35.7 (C), 33.9 (C), 26.9 (CH_2), 22.2 (CH_2), 21.7 (CH_2), 21.5 (CH), 17.0 (CH_2), 14.0 (CH_2), 13.3 (CH_2), −0.3 ($3\,CH_3$); IR (film): $\tilde{\nu}$ = 3079, 2998, 2951, 2858, 1673, 1562, 1406, 1325, 1247, 1032 cm^{-1}; MS (70 eV): *m/z* (%): 246 (58) [M^+], 231 (100) [M^+−Me], 215 (13), 203 (9), 141 (7), 73 (35) [Me_3Si^+]; HRMS: *m/z* (%): calcd for $C_{15}H_{22}OSi$: 246.1439; found 246.1439.

(6′a*S*,4″*S*,5″*S*)-4′,5′,6′,6′a-Tetrahydro-3′-trimethylsilyldispiro(cyclopropane-1,1′-pentalene-2′-one-4′,2″-1,3-dioxolane) (26a): To a vigorously stirred solution of the enyne **25a** (67 mg, 0.17 mmol) in anhydrous dichloromethane (5 mL) was added [$Co_2(CO)_8$] (70 mg, 0.20 mmol), and the reaction mixture was stirred at ambient temperature for an additional 1 h. NMO (100 mg, 0.85 mmol) was added, the reaction mixture stirred at ambient temperature for an additional 20 h then worked up according to GP 7. Column chromatography (8 g of silica gel, column 20 × 1 cm, petroleum ether/Et_2O 10:1) of the residue gave the enone **26a** (50 mg, 70%) as a colorless oil, which essentially was a 5:1 mixture of two diastereomers. Repeated column chromatography gave pure (6′a*S*,4″*S*,5″*S*)-**26a** as a colorless solid. R_f = 0.32 (petroleum ether/Et_2O 10:1); m.p. 93 °C; $[\alpha]_D^{20}$ = −218.1 (c = 1.0 in $CHCl_3$); ^1H NMR (250 MHz, C_6D_6, 25 °C): δ = 7.27–7.10 (m, 10H; Ar-H), 5.21 (d, J = 8.5 Hz, 1H; 5″*-H), 4.92 (d, J =

8.5 Hz, 1H; 4″*-H), 3.08 (dd, J=8.9, 10.6 Hz, 1H; 6′-H), 2.42–2.32 (m, 1H; 5′-H), 2.22–2.10 (m, 1H; 7′-H), 1.54–1.41 (m, 2H; 6′-H), 1.24–1.10 (m, 2H; Cpr-H), 0.79–0.71 (m, 1H; Cpr-H), 0.66–0.55 (m, 1H; Cpr-H), 0.60 (s, 9H; 3CH_3); ^{13}C NMR (62.9 MHz, C_6D_6, 25 °C): δ=211.5 (C), 187.2 (C), 138.2 (C), 137.8 (C), 136.4 (C), 128.9 (2 CH), 128.5 (2CH), 128.4 (CH), 127.5 (CH), 127.3 (2CH), 126.7 (2CH), 113.3 (C), 86.3 (CH), 84.9 (CH), 50.1 (CH), 39.9 (CH_2), 34.1 (C), 24.7 (CH_2), 15.1 (CH_2), 14.4 (CH_2), 0.5 (3CH_3); IR (KBr): $\tilde{\nu}$=2937, 1695, 1121, 845, 699, 668 cm^{-1}; MS (70 eV): m/z (%): 430 (10) [M^+], 324 (48), 296 (30), 268 (16), 219 (54), 206 (47), 180 (100), 165 (22), 105 (20), 91 (14), 73 (45); elemental analysis calcd (%) for $C_{27}H_{30}O_3Si$ (430.6): C 75.31, H 7.02; found C 75.40, H 7.06.

Minor diastereomer [(6′a*R*,4″*S*,5″*S*)-**26a**]: colorless solid; R_f=0.27 (petroleum ether/Et_2O 10:1); m.p. 122–125 °C; $[\alpha]_D^{20}$=+118.5 (c=1.0 in $CHCl_3$); ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ=7.45–7.11 (m, 10H; Ar-H), 5.27 (d, J=8.8 Hz, 1H; 5″*-H), 5.06 (d, J=8.8 Hz, 1H; 4″*-H), 2.87 (dd, J=7.3, 12.2 Hz, 1H; 5′-H), 2.27–2.21 (m, 2H; 7′-H), 1.55–1.45 (m, 1H; Cpr-H), 1.45–1.36 (m, 1H; 6′-H), 1.14–1.12 (m, 1H; Cpr-H), 1.08–1.01 (m, 1H; 6′-H), 0.77–0.64 (m, 2H; Cpr-H), 0.63 (s, 9H, 3 CH_3); ^{13}C NMR (62.9 MHz, C_6D_6, 25 °C): δ=212.6 (C), 187.8 (C), 140.0 (C), 137.8 (C), 134.7 (C), 128.6 (2 CH), 128.4 (2 CH), 128.3 (CH), 127.0 (CH), 126.7 (2 CH), 126.1 (2 CH), 111.3 (C), 84.7 (CH), 83.3 (CH), 52.6 (CH), 41.2 (CH_2), 33.4 (C), 25.5 (CH_2), 15.1 (CH_2), 14.4 (CH_2), −0.1 (3CH_3); elemental analysis calcd (%) for $C_{27}H_{30}O_3Si$ (430.6): C 75.31, H 7.02; found C 75.44, H 6.93.

Thermally induced PKRs of enynones 16a–c

General procedure GP 9: A thick-walled Pyrex bottle equipped with an argon inlet was charged with a solution of the respective enynone (0.45 mmol) in anhydrous MeCN (6 mL), then [$Co_2(CO)_8$] (170 mg, 0.50 mmol) was added at ambient temperature, the bottle was hermetically closed with a screw cap, and the reaction mixture was stirred at 80 °C for 16 h. After cooling, the reaction mixture was worked up according to GP 7.

2′,3′,3′a,4′-Tetrahydro-6′-trimethylsilylspiro(cyclopropane-1,4′-pentalene-1′,5′-dione) (22a): a) Column chromatography (5 g of silica gel deactivated with Et_3N, column 15×1 cm, petroleum ether/Et_2O 2:1) of the residue obtained from enynone **17a** (92 mg, 0.45 mmol) and [$Co_2(CO)_8$] (170 mg, 0.50 mmol) according to GP 9 gave the enedione **22a** (40 mg, 38%) and 2′,3′,4′,6′-tetrahydrospiro(cyclopropane-1,4′-pentalene-1′,5′-dione) (**23a**) (30 mg, 41%). **22a**: a yellow oil; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ= 4.63 (dd, J=7.3, 11.1 Hz, 1H), 2.61–2.54 (m, 2H), 2.21–2.10 (m, 1H), 1.59–1.42 (m, 2H; 3′-H + Cpr-H), 1.14–1.00 (m, 3H; Cpr-H), 0.26 (s, 9H; 3CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=212.1 (C), 203.3 (C), 180.1 (C), 146.1 (C), 51.4 (CH), 40.2 (CH_2), 35.3 (CH_2), 25.3 (C), 16.2 (CH_2), 15.0 (CH_2), −1.2 (3CH_3); R_f=0.46; IR (film): $\tilde{\nu}$=2961, 1729, 1685, 1248, 1105, 855 cm^{-1}; MS (70 eV): m/z (%): 234 (3) [M^+], 219 (100) [M^+−Me], 191 (5) [M^+−Me−CO], 177 (36), 73 (10) [Me_3Si^+]; **23a**: a colorless solid; R_f=0.07 (petroleum ether/Et_2O 2:1); m.p. 151–154 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=3.14 (t, J=3.0 Hz, 2H), 2.69–2.66 (m, 2H), 2.51–2.48 (m, 2H), 1.66–1.47 (m, 4H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=214.3 (C), 201.7 (C), 183.7 (C), 141.3 (C), 37.8 (CH_2), 37.5 (C), 37.2 (CH_2), 23.2 (CH_2), 18.9 (2CH_2); IR (KBr): $\tilde{\nu}$=2926, 1735, 1682, 1602, 1415, 1211, 1095, 1018, 890 cm^{-1}; MS (70 eV): m/z (%): 162 (100) [M^+], 133 (15), 120 (23) [M^+−$COCH_2$], 105 (21), 91 (74), 78 (26); elemental analysis calcd (%) for $C_{10}H_{10}O_2$ (162.2): C 74.06, H 6.22; found C 73.88, H 6.10. Repeated column chromatography of **22a** gave an additional 12 mg (16%) of **23a** (total yield 57%).

b) A solution of the enone **26a** (50 mg, 0.12 mmol) and *p*-toluenesulfonic acid (100 mg) in anhydrous acetone (10 mL) was stirred under reflux for 16 h and then worked up according to GP 6. Column chromatography (4 g of silica gel, column 10×1 cm, petroleum ether/Et_2O 5:1) of the residue gave 14 mg (71%) of **23a**.

3′a-Methyl-2′,3′,3′a,4′-tetrahydro-6′-trimethylsilylspiro(cyclopropane-1,4′-pentalene-1′,5′-dione) (22b): The residue obtained from enynone **17b** (165 mg, 0.75 mmol) and [$Co_2(CO)_8$] (310 mg, 0.91 mmol) according to GP 9 was taken up with CH_2Cl_2 (5 mL), the mixture stirred with TMANO (200 mg, 2.66 mmol) for an additional 1 h, filtered again and concentrated under reduced pressure. Column chromatography (5 g of silica gel, column 15×1 cm, petroleum ether/Et_2O 5:1) of the residue gave **22b** (117 mg, 63%) as a yellow solid. R_f=0.46 (petroleum ether/Et_2O 5:1); m.p. 37–38 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=2.72–2.40 (m, 2H), 1.82–1.70 (m, 2H), 1.40–1.33 (m, 1H; Cpr-H), 1.10 (s, 3H; CH_3), 1.10–0.83 (m, 3H; Cpr-H), 0.20 (s, 9H; 3CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=212.1 (C), 203.9 (C), 185.4 (C), 143.7 (C), 50.9 (C), 41.9 (C), 37.6 (CH_2), 31.0 (CH_2), 24.0 (CH_3), 17.1 (CH_2), 13.7 (CH_2), −1.3 (3CH_3); IR (KBr): $\tilde{\nu}$=2959, 1722, 1692, 1249, 1081, 849 cm^{-1}; MS (70 eV): m/z (%): 248 (3) [M^+], 233 (100) [M^+−Me], 215 (2), 205 (7), 191 (11), 177 (83), 75 (13), 73 (6) [Me_3Si^+]; elemental analysis calcd (%) for $C_{14}H_{20}O_2Si$ (248.4): C 67.70, H 8.12; found C 67.83, H 8.12.

3′a-Ethyl-2′,3′,3′a,4′-tetrahydro-6′-trimethylsilylspiro(cyclopropane-1,4′-pentalene-1′,5′-dione) (22c): The residue obtained from enynone **17c** (200 mg, 0.85 mmol) and [$Co_2(CO)_8$] (365 mg, 1.07 mmol) according to GP 9 was taken up with CH_2Cl_2 (5 mL), the mixture stirred with TMANO (200 mg, 2.66 mmol) for an additional 1 h, filtered again and concentrated under reduced pressure. Column chromatography (5 g of silica gel, column 15×1 cm, petroleum ether/Et_2O 5:1) of the residue gave **22c** (146 mg, 65%) as a yellow solid. R_f=0.46 (petroleum ether/Et_2O 5:1); m.p. 71–72 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=2.74–2.44 (m, 2H), 1.85–1.78 (m, 2H), 1.67 (dq, J=7.2, 14.4 Hz, 1H; CH_2), 1.52 (ddd, J=3.7, 7.1, 10.0 Hz, 1H; Cpr-H), 1.39 (dq, J=7.2, 14.4 Hz, 1H; CH_2), 1.08 (ddd, J=3.3, 7.1, 9.6 Hz, 1H; Cpr-H), 0.97 (ddd, J=3.3, 7.1, 10.0 Hz, 1H; Cpr-H), 0.85 (ddd, J=3.7, 7.1, 9.6 Hz, 1H; Cpr-H), 0.64 (t, J=7.2 Hz, 3H; CH_3), 0.26 (s, 9H; 3CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=212.2 (C), 204.1 (C), 183.1 (C), 145.8 (C), 54.9 (C), 39.5 (C), 37.8 (CH_2), 30.7 (CH_2), 27.8 (CH_2), 17.9 (CH_2), 13.7 (CH_2), 8.3 (CH_3), −1.2 (3CH_3); IR (KBr): $\tilde{\nu}$=2960, 1724, 1682, 1258, 1086, 850 cm^{-1}; MS (70 eV): m/z (%): 262 (6) [M^+], 247 (100) [M^+−Me], 233 (5) [M^+−Et], 219 (6), 205 (21), 145 (2), 115 (3), 75 (11), 73 (8) [Me_3Si^+]; elemental analysis calcd (%) for $C_{15}H_{22}O_2Si$ (262.4): C 68.65, H 8.45; found C 68.70, H 8.53.

(3′*S*,3′a*R*,6′a*S*,4″*S*,5″*S*)-Hexahydro-3a-methyl-3-trimethylsilyldispiro(cyclopropane-1,1′-pentalene-2′-one-4′,2″-1,3-dioxolane) (27a): To a stirred suspension of cuprous iodide (200 mg, 1.05 mmol) in anhydrous Et_2O (5 mL) was added methyl lithium (1.9 mmol, 1.2 mL of a 1.6 M solution in Et_2O) at 0 °C. After stirring at this temperature for an additional 5 min, a solution of **26a** (145 mg, 0.34 mmol) in Et_2O (4 mL) was added dropwise, the reaction mixture was stirred at this temperature for an additional 2 h and then poured into ice-cold sat. aq. NH_4Cl solution (25 mL). The aqueous phase was extracted with diethyl ether (3×20 mL), the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography (4 g of silica gel, column 10×1 cm, petroleum ether/Et_2O 15:1, R_f=0.39) of the residue gave **27a** (130 mg, 86%) as a colorless foam, which essentially was a 7:1 mixture of presumably (3′a*R*,3′*S*,6′a*S*,4″*S*,5″*S*)-**27a** and (3′a*R*,3′*R*, 6′a*S*,4″*S*,5″*S*)-**27a**.

Major diastereomer: ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=7.39–7.12 (m, 10H; Ar-H), 4.77–4.66 (m, 2H; 4″-H, 5″-H), 2.54 (s, 1H; 3′-H), 2.37–1.97 (m, 4H; 6′a-H, 6′-H, 5′-H), 1.67–1.52 (m, 1H; 6′-H), 1.56 (s, 3H; CH_3), 1.27–0.78 (m, 4H; Cpr-H), 0.22 (s, 9H; 3CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=218.6 (C), 137.4 (C), 136.2 (C), 128.7 (2 CH), 128.5 (2CH), 128.3 (CH), 128.0 (CH), 126.7 (2CH), 126.3 (2 CH), 120.3 (C), 85.7 (CH), 85.0 (CH), 53.6 (C), 52.2 (CH), 50.1 (CH), 35.9 (C), 34.9 (CH_2), 25.3 (CH_2), 21.3 (CH_3), 20.7 (CH_2), 11.7 (CH_2), 0.2 (3CH_3); IR (KBr): $\tilde{\nu}$=3033, 2967, 1705, 1456, 1309, 1290, 1249, 1211, 1182, 1159, 1132, 1107, 1046, 840, 762, 698 cm^{-1}; MS (70 eV): m/z (%): 446 (3) [M^+], 373 (1) [M^+−$SiMe_3$], 312 (13), 251 (14), 235 (27), 193 (14), 179 (100), 165 (24), 91 (27), 73 (57); elemental analysis calcd (%) for $C_{28}H_{34}O_3Si$ (446.7): C 75.29, H 7.67; found C 75.44, H 7.68.

Addition of higher order cuprates to 26a

General procedure GP 10: A solution of the respective alkyllithium (2.23 mmol) was added dropwise to a stirred suspension of cuprous cyanide (100 mg, 1.12 mmol) in anhydrous diethyl ether (4 mL) at −78 °C. The reaction mixture was allowed to warm to −40 °C and stirred at this temperature for ca. 20 min until a clear solution had formed. After this, the reaction mixture was recooled to −78 °C, and a solution of the enone **26a** (0.25 mmol) in Et_2O (3 mL), followed by boron trifluoride etherate

(0.2 mL), was added dropwise. After stirring at this temperature for an additional 30 min with TLC monitoring, the reaction was quenched by adding a 1:1 mixture of sat. aq. NH_4Cl solution and 25% aq. ammonia (5 mL), and the reaction mixture was allowed to warm up to ambient temperature The aqueous phase was extracted with diethyl ether (2× 5 mL), the combined organic extracts were dried and concentrated under reduced pressure. The product was purified by column chromatography.

(3′*S*,3′a*R*,6′a*S*,4″*S*,5″*S*)-Hexahydro-3a-*n*-butyl-3-trimethylsilyldispiro(cyclopropane-1,1′-pentalene-2′-one-4′,2″-1,3-dioxolane) (27b): Column chromatography (20 g of silica gel, column 15×2 cm, petroleum ether/Et_2O 20:1) of the residue obtained from enone **26a** (160 mg, 0.37 mmol), CuCN (100 mg, 1.12 mmol), *n*BuLi (2.24 mmol, 0.95 mL of a 2.36 M solution in hexane) and $BF_3{\cdot}Et_2O$ (0.2 mL) according to GP 10 furnished a single diastereomer of **27b** (104 mg, 57%) as a colorless solid. R_f=0.48 (petroleum ether/Et_2O 20:1); m.p. 131 °C; $[\alpha]_D^{20}=-163.2$ (c=1.0 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=7.40–7.17 (m, 10H; Ar-H), 4.77 (d, J=8.6 Hz, 1H; 5″*-H), 4.72 (d, J=8.6 Hz, 1H; 4″*-H), 2.72 (s, 1H; 3′-H), 2.44–2.18 (m, 3H; 5′-H, 6′a-H), 2.07–1.84 (m, 2H; 6′-H), 1.82–1.11 (m, 8H; 2Cpr-H + 3CH_2), 0.99 (t, J=7.0 Hz, 3H; CH_3), 0.94–0.86 (m, 2H; Cpr-H), 0.22 (s, 9H; 3 CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=219.9 (C), 137.7 (C), 136.1 (C), 128.5 (2CH), 128.3 (2CH), 128.2 (CH), 128.0 (CH), 127.0 (2CH), 126.3 (2CH), 120.6 (C), 85.2 (CH), 85.0 (CH), 57.6 (C), 50.4 (CH), 48.9 (CH), 36.4 (C), 36.1 (CH_2), 34.1 (CH_2), 28.7 (CH_2), 26.7 (CH_2), 24.0 (CH_2), 21.4 (CH_2), 14.1 (CH_3), 13.8 (CH_2), 0.8 (3CH_3); IR (KBr): $\tilde{\nu}$=2953, 2928, 1702, 1245, 1147, 1023, 840, 759, 698 cm^{-1}; MS (70 eV): m/z (%): 488 (1) [M^+], 415 (1) [M^+-SiMe_3], 382 (12), 251 (9), 180 (100), 91 (6), 73 (16). The structure of this compound was verified by X-ray crystal structure analysis.

(3′*S*,3′a*R*,6′a*S*,4″*S*,5″*S*)-Hexahydro-3a-*sec*-butyl-3-trimethylsilyldispiro(cyclopropane-1,1′-pentalene-2′-one-4′,2″-1,3-dioxolane) (27c): Column chromatography (20 g of silica gel, column 15×2 cm, petroleum ether/Et_2O 20:1) of the residue obtained from enone **26a** (120 mg, 0.28 mmol), CuCN (100 mg, 1.12 mmol), *s*BuLi (2.24 mmol, 1.6 mL of a 1.4 M solution in hexane) and $BF_3{\cdot}Et_2O$ (0.1 mL) according to GP 10 furnished a 1.25:1 mixture of diastereomers of **27c** (101 mg, 74%) as a colorless solid. R_f= 0.44 (petroleum ether/Et_2O 20:1); m.p. 136–142 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=7.38–7.24 (m, 10H; Ar-H), 4.93, 4.92 (d, J=8.7 Hz, 1H; 5″*-H), 4.70, 4.69 (d, J=8.7 Hz, 1H; 4″*-H), 3.38, 3.28 (s, 1H; 3′-H), 2.45–2.34, 2.12–2.05, 1.90–1.82, 1.70–1.24, (several m; 8H), 1.21–1.14 (m, 3H; CH_3), 1.01–0.83 (m, 7H; 4Cpr-H + CH_3), 0.23, 0.22 (s, 9H; 3 CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=220.0 (C), 138.1, 138.0 (C), 136.3, 136.1 (C), 128.5 (2CH), 128.2 (2 CH), 128.1 (CH), 126.6 (CH), 126.5 (2 CH), 126.4 (2CH), 118.8 (C), 85.3 (CH), 83.3, 83.2 (CH), 62.8, 62.5 (C), 47.8, 47.7 (CH), 47.1 (CH), 39.7, 39.1 (CH_2), 38.9 (CH), 34.7, 34.5 (C), 27.3, 27.1 (CH_2), 26.3 (CH_2), 20.8, 20.7 (CH_2), 16.9, 16.1 (CH_3), 15.7 (CH_2), 13.0, 12.6 (CH_3), 1.3, 1.1 (3CH_3); IR (KBr): $\tilde{\nu}$=2969, 2877, 1701, 1245, 1149, 1019, 837, 760 cm^{-1}; MS (70 eV): m/z (%): 488 (1) [M^+], 473 (1) [M^+-CH_3], 421 (1), 415 (1) [M^+-SiMe_3], 382 (8), 326 (3), 291 (2), 180 (100), 91 (5), 73 (13); elemental analysis calcd (%) for $C_{31}H_{40}O_3Si$ (488.7): C 76.18, H 8.25; found C 76.14, H 8.09.

(3′a*R*,6′a*R*,4″*S*,5″*S*)-Hexahydro-3a-methyldispiro(cyclopropane-1,1′-pentalene-2′-one-4′,2″-1,3-dioxolane) (28a): A solution of the compound **27a** (93 mg, 0.21 mmol) and *p*-toluenesulfonic acid (10 mg) in anhydrous acetone (10 mL) was stirred at ambient temperature for 2 h and then worked up according to GP 6. Column chromatography (5 g of silica gel, column 15×1 cm, petroleum ether/Et_2O 10:1) of the residue gave **28a** (76 mg, 97%) as a colorless oil. R_f=0.16 (petroleum ether/Et_2O 10:1); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ=7.36–7.15 (m, 10H; Ar-H), 4.77–4.70 (m, 2H; 4″*-H, 5″*-H), 2.82 (d, J=19.0 Hz, 1H; 3′-H), 2.33 (d, J= 19.0 Hz, 1H; 3′-H), 2.24–1.98 (m, 4H; 5′-H, 6′-H, 6′a-H), 1.71–1.56 (m, 1H; 6′-H), 1.48 (s, 3H; CH_3), 1.30–1.23 (m, 2H; Cpr-H), 1.02–0.86 (m, 2H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=218.6 (C), 137.1 (C), 135.9 (C), 128.5 (2CH), 128.4 (2CH), 128.2 (CH), 128.0 (CH), 126.9 (2CH), 126.3 (2CH), 119.7 (C), 86.1 (CH), 85.2 (CH), 51.2 (CH), 49.9 (C), 48.4 (CH_2), 35.7 (C), 34.9 (CH_2), 25.9 (CH_2), 22.1 (CH_3), 21.7 (CH_2), 13.3 (CH_2); IR (film): $\tilde{\nu}$=2955, 1726, 1456, 1183, 1104, 1027, 763 cm^{-1}; MS (70 eV): m/z (%): 374 (2) [M^+], 268 (39), 251 (25), 180 (100), 165 (22), 105 (31), 91 (62), 77 (36); elemental analysis calcd (%) for $C_{25}H_{26}O_3$ (374.5): C 80.18, H 6.99; found C 80.05, H 6.98.

(3′a*R*,6′a*R*)-Hexahydro-3a-methylspiro(cyclopropane-1,1′-pentalene-2′,4′-dione) (29a): This compound was prepared under conditions of the previous experiment from **28a** (70 mg, 0.19 mmol) and *p*-toluenesulfonic acid (20 mg) in anhydrous acetone (80 mL), but the reaction mixture was stirred under reflux for 27 h. Column chromatography (5 g of silica gel, column 15×1 cm, petroleum ether/Et_2O 2:1) gave **29a** (19 mg, 57%) as a colorless solid. R_f=0.13 (petroleum ether/Et_2O 2:1); m.p. 62–63 °C; $[\alpha]_D^{20}=-148$ (c=1.0 in $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ= 2.40 (d, J=18.6 Hz, 1H; 3′-H), 1.90 (d, J=18.6 Hz, 1H; 3′-H), 1.95–1.71 (m, 2H; 5′-H), 1.57 (t, J=6.6 Hz, 1H; 6′a-H), 1.38–1.22 (m, 1H; 6′-H), 1.19–1.10 (m, 1H; 6′-H), 1.02–0.75 (m, 2H; Cpr-H), 0.88 (s, 3H; CH_3), 0.39–0.28 (m, 2H; Cpr-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ=218.5 (C), 213.7 (C), 51.0 (C), 50.2 (CH), 46.1 (CH_2), 36.0 (C), 32.8 (CH_2), 22.9 (CH_2), 22.5 (CH_3), 18.2 (CH_2), 14.0 (CH_2); IR (KBr): $\tilde{\nu}$=2963, 1728, 1410, 1372, 1323, 1126, 1097, 1043 cm^{-1}; MS (70 eV): m/z (%): 178 (100) [M^+], 150 (22) [M^+-CO], 135 (28) [$M^+-CO-CH_3$], 122 (41) [M^+-2CO], 108 (13), 93 (27), 79 (50); HRMS: m/z (%): calcd for $C_{11}H_{14}O_2$: 178.0993; found 178.0993.

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Crystal data for **19c**: $C_{11}H_{12}O$ (160.21), crystal size $0.90\times0.80\times0.50\,mm^3$, $T=153(2)$ K, monoclinic, $Z=4$, space group $P2_1/n$, $F(000)=344$, $a=8.3120(10)$, $b=11.764(2)$, $c=8.7500(10)$ Å, $\alpha=\gamma=90$, $\beta=96.090(10)°$, $V=850.8(2)$ Å^3, $\rho=1.251\,g\,cm^{-3}$, $\mu=0.078\,mm^{-1}$, intensities measured: 1602 ($2\theta_{max}=45.82°$), independent: 1469 ($R_{int}=0.0547$), 109 parameters refined, $R_1=0.0623$, w$R_2=0.1531$ for 1468 reflections with $I > 2\sigma(I_o)$, R_1 (all data) $=0.0833$, wR_2 (all data) $=0.1774$, GOF $=1.062$, maximum and minimum residual electron density 0.616 and $-0.278\,e\,Å^{-3}$.
Crystal data for **26d**: $C_{28}H_{32}O_3Si$ (444.63), crystal size $0.60\times0.50\times0.50\,mm^3$, $T=193(2)$ K, orthorhombic, $Z=4$, space group $P2_12_12_1$, $F(000)=952$, $a=9.881(5)$, $b=10.558(4)$, $c=24.100(14)$ Å, $\alpha=\gamma=\beta=90°$, $V=2514(2)$ Å^3, $\rho=1.175\,g\,cm^{-3}$, $\mu=0.119\,mm^{-1}$, intensities measured: 3793 ($2\theta_{max}=44.98°$), independent: 3281 ($R_{int}=0.0387$), 292 parameters refined, $R_1=0.0400$, w$R_2=0.1027$ for 3279 reflections with $I > 2\sigma(I_o)$, R_1 (all data) $=0.0413$, wR_2 (all data) $=0.1045$, GOF $=1.041$, maximum and minimum residual electron density 0.143 and $-0.219\,e\,Å^{-3}$.
Crystal data for **27b**: $C_{31}H_{40}O_3Si$ (488.72), crystal size $0.50\times0.20\times0.20\,mm^3$, $T=193(2)$ K, monoclinic, $Z=2$, space group $P2_1$, $F(000)=528$, $a=9.630(2)$, $b=8.680(2)$, $c=16.530(3)$ Å, $\alpha=\gamma=90$, $\beta=93.30(3)°$, $V=1379.4(5)$ Å^3, $\rho=1.177\,g\,cm^{-3}$, $\mu=0.144\,mm^{-1}$, intensities measured: 2315 ($2\theta_{max}=46.02°$), independent: 2258 ($R_{int}=0.1940$), 320 parameters refined, $R_1=0.0717$, w$R_2=0.1609$ for 2258 reflections with $I > 2\sigma(I_o)$, R_1 (all data) $=0.1051$, wR_2 (all data) $=0.1609$, GOF $=1.132$, maximum and minimum residual electron density 0.638 and $-0.260\,e\,Å^{-3}$. The X-ray crystal structure analysis of the latter compound does establish its stereochemistry, but the unsatisfactory high R values do permit neither to discuss any structural peculiarities in **27b** nor to save the results of this measurements in the Cambridge Crystallographic Data Centre.
CCDC-252041 (**19c**) and -252040 (**26d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
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