

Alkyne versus Allene Activation in Platinum- and Gold-Catalyzed Cycloisomerization of Hydroxylated 1,5-Allenynes

Riadh Zriba, Vincent Gandon, Corinne Aubert, Louis Fensterbank,* and Max Malacria*[a]

Abstract: Chemo- and stereoselective transformations of 3-hydroxy-1,5-allenynes **1** into a variety of new and potentially useful cyclic compounds have been achieved. Substrates bearing a silyl group at the alkyne moiety undergo purely thermal or Lewis acid catalyzed Alder-ene type transformations into 2-methylene-3-vinylcyclopent-3-enol derivatives **2**. When heated in the presence of a catalytic amount of PtCl₂ or PtCl₄, these incipient cyclopentenols could be further transformed into 3-vinylcyclopent-2-enones **3**. On the other hand, alkyl-substituted 3-hydroxy-1,5-

allenynes proved to be stable under refluxing conditions. Nevertheless, PtCl₂ and PtCl₄ could selectively activate the alkyne moiety of these substrates toward intramolecular nucleophilic attack of the internal allene double bond to yield unprecedented 6-methylenebicyclo[3.1.0]hexan-3-one derivatives **4**. With gold-based catalysts, provided that the reaction is carried

out in dichloromethane, both Au^I and Au^{III} complexes selectively activate the allene fragment of the substrates toward intramolecular nucleophilic attack of the hydroxyl group to yield 2-ethynyl-3,6-dihydro-2*H*-pyrans **5**. Compounds of type **4** can also be formed with Au^I and Au^{III} complexes if the reaction is carried out in toluene. The reactivity of these new compounds has been partially investigated, and polycyclic ketones were obtained after oxidation under mild conditions or gold-catalyzed cycloisomerization.

Keywords: cyclization • gold • homogeneous catalysis • platinum • synthetic methods

Introduction

It is now well established that gold and platinum salts can activate alkynes, alkenes, and allenes toward nucleophilic attack.^[1] In the case of 1,6-enynes, electrophilic activation of the alkyne triggers nucleophilic attack by the alkene to give a metallacyclopropyl carbene intermediate that can evolve along different pathways to give various types of dienes (Scheme 1, **A–E**) or bicyclic derivatives (**F–H**).^[1e,g] 1,5-Enynes, on the other hand, were selectively transformed into bicyclo[3.1.0]hex-2-enes (**I**) or bicyclo[3.1.0]hexan-3-ones (**J**) when starting from 3-hydroxylated substrates.^[2] 1,6-Allenynes were also successfully converted into valuable cyclic compounds including vinylallenes (**K**, **L**), dienes (**M**),

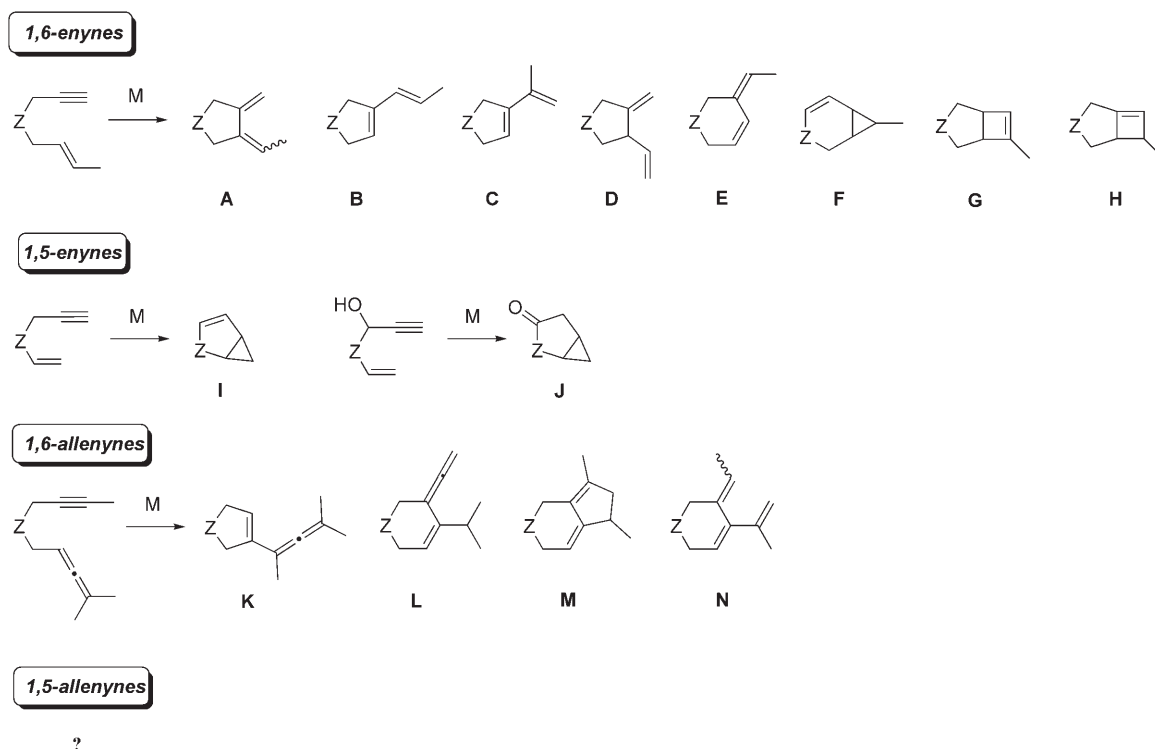
and trienes (**N**).^[3] In contrast, cycloisomerization of 1,5-allenynes has remained underexplored in the fields of gold and platinum catalysis.^[3a,4,5] Here we describe in detail our findings concerning the cycloisomerization of 3-hydroxy-1,5-allenynes in the presence of Pt^{II}, Pt^{IV}, Au^I, and Au^{III} salts.

Results and Discussion

Starting compounds **1a–n** (see Tables 1 and 2) were prepared by addition of lithium acetylide to β-allenyl aldehydes. These precursors were obtained via Claisen–Cope rearrangement of propargyl vinyl ethers derived from *p*-toluenesulfonic acid-catalyzed condensation of aldehydes to propargyl alcohols, as described in the literature.^[6]

Cycloisomerization to 2-methylene-3-vinylcyclopent-3-enol or 3-vinylcyclopent-2-enone derivatives: We found that some of the allenynes could be cycloisomerized without catalyst (Table 1). Silylated allenynes **1a** (R = SiMe₃, Table 1, entry 1), **1d** (R = Si^{*i*}BuMe₂, Table 1, entry 7), **1e** (R = SiPhMe₂, Table 1, entry 9), **1f** (R = SiPh₃, Table 1, entry 11), and **1g** (R = Si^{*i*}Pr₃, Table 1, entry 13) were converted in high

[a] Dr. R. Zriba, Dr. V. Gandon, Dr. C. Aubert, Prof. Dr. L. Fensterbank, Prof. Dr. M. Malacria
Laboratoire de Chimie Organique UMR 7611
Institut de Chimie Moléculaire FR2769
Université Pierre et Marie Curie
Tour 44-54, 4 place Jussieu 75252 Paris (France)
Fax: (+33) 144-277-3-60
E-mail: louis.fensterbank@upmc.fr
max.malacria@upmc.fr



Scheme 1. Typical cycloisomerizations of 1,6-enynes, 1,5-enynes, and 1,6-allenynes under gold and platinum catalysis.

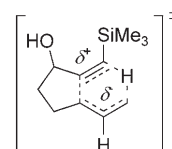
Table 1. Thermal or platinum-catalyzed cycloisomerization of hydroxylated 1,5-allenynes to cyclopentenols or cyclopentenones (yields of isolated products).

Entry	Substrate	R	R'	R''	Catalyst	Yield [%] (2/3)
1	1a	SiMe ₃	H	Me	none	98/0
2	1a	SiMe ₃	H	Me	PtCl ₄	0/98
3	1a	SiMe ₃	H	Me	PtCl ₂	0/79
4	1b	SiMe ₃	H	H	PtCl ₄	0/48
5	1b	SiMe ₃	H	H	PtCl ₂	0/79
6	1c	SiMe ₃		(CH ₂) ₂	PtCl ₄	0/79
7	1d	Si(<i>t</i> Bu)Me ₂	H	Me	none	89/0
8	1d	Si(<i>t</i> Bu)Me ₂	H	Me	PtCl ₄	0/65
9	1e	SiPhMe ₂	H	Me	none	86/0
10	1e	SiPhMe ₂	H	Me	PtCl ₄	0/79
11	1f	SiPh ₃	H	Me	none	67/0
12	1f	SiPh ₃	H	Me	PtCl ₄	67/0
13	1g	Si <i>i</i> Pr ₃	H	Me	none	95/0
14	1g	Si <i>i</i> Pr ₃	H	Me	PtCl ₄	95/0
15	1h	CH ₂ Ph	H	Me	none	0/0
16	1i	CH ₂ <i>i</i> Pr	H	Me	none	0/0
17	1j	CH ₂ OMe	H	H	none	0/0
18	1k	CH ₂ OMe	H	Me	none	0/0
19	1l	<i>n</i> C ₆ H ₁₃	H	Me	none	0/0

yields to 2-methylene-3-vinylcyclopent-3-enol derivatives **2a** and **2d–g** within 2 h in refluxing toluene. The stereochemistry was proposed on the basis of the NOE effect between

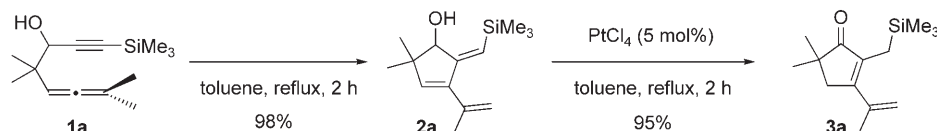
be stabilized by silyl groups (Scheme 2).

the exocyclic vinylic proton and the methylene fragment. These unprecedented products presumably result from thermal Alder-ene cycloisomerizations, which are quite unusual at such a low temperature. With alkyl groups at the alkyne moiety (**1h–l**, Table 1, entries 15–19), thermal transformation no longer took place. The ease with which silylated compounds transform could be explained by the well-known silicon β effect:^[7] if the pericyclic reaction proceeds in an asynchronous manner (i.e., the C1–H bond is formed early in the transition state), a positive charge developing at C2 would



Scheme 2. Postulated asynchronous Alder-ene transition state.

With the exception of the sterically crowded allenynes **1f** and **1g** (Table 1, entries 12 and 13), the thermally labile silylated substrates **1a**, **1d**, and **1e** could be transformed into another type of compound: when refluxed in the presence of 5 mol % of PtCl₂ or PtCl₄, 3-vinylcyclopent-2-enone derivatives **3a**, **3d**, and **3e** (Table 1, entries 2–6, 8, 10) were obtained in good yields. These reactions are also possible with standard Lewis acids such as ZnCl₂ or AlCl₃, but the reaction rates are much lower. As shown by the stepwise transformation of compound **1a** into first **2a** and then **3a** (Scheme 3), cyclopentenols seem indeed to be likely precursors to the cyclopentenones.

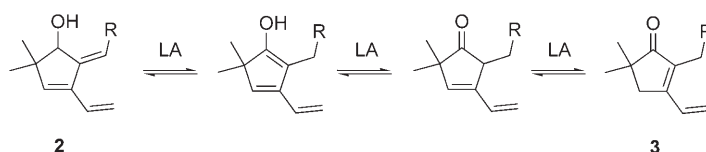


Scheme 3. Stepwise transformation of allenyne **1a** into cyclopentenone **3a**.

Thus, Lewis acids promote rearrangement of the unsaturated framework to yield conjugated compounds. The first step could be an exocyclic/endocyclic migration of the silylated double bond to give a cyclopentadienol intermediate (Scheme 4). Keto/enol tautomerism would then lead to a β,γ -unsaturated cyclopentenone. Finally, a proton-shift would produce a $\alpha,\beta,\gamma,\delta$ -unsaturated cyclopentenone as thermodynamic product.

The next step of our investigation was to evaluate the reactivity of the thermally stable alkyl-substituted hydroxylated allenynes **1h–m** in the presence of gold and platinum complexes (vide infra).

Cycloisomerization to 6-methylenebicyclo[3.1.0]hexan-3-one or 2-ethynyl-3,6-dihydro-2H-pyran derivatives: Efficient cycloisomerization of allenynes **1h–m** was achieved by using a catalytic amount of PtCl₂ or PtCl₄ (Table 2, entries 1–10). Instead of cyclopentenols of type **2** or cyclopentenones of type **3**, unprecedented 6-methylenebicyclo[3.1.0]hexan-3-one derivatives **4h–m** were isolated in good yields after 24–36 h in refluxing toluene.^[8] For instance, allenynes **1i** (Table 2,



Scheme 4. Lewis acid (LA) catalyzed rearrangement of cyclopentenols **2** to cyclopentenones **3**.

entry 3) and **1k** (Table 2, entry 6) were transformed into **4i** and **4k** in 87 and 80% yield of isolated product, respectively.^[9] Remarkably, this reaction tolerates the presence of an-

other C–C triple bond (**1m**, Table 2, entry 9).

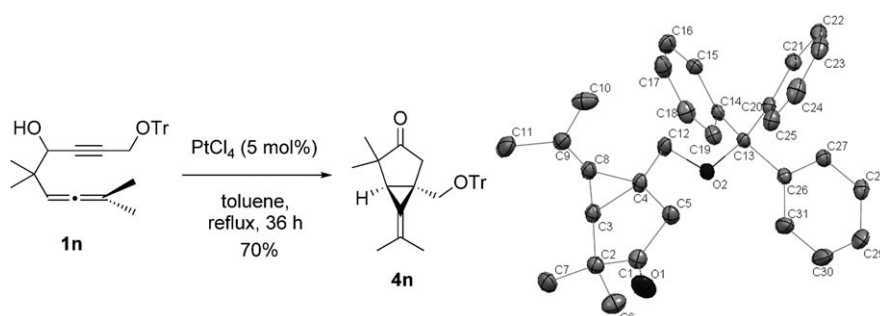
As expected, these compounds were obtained as single diastereomers of *cis* configuration at the ring junction, as confirmed by NOE experiments. Although most of these products were obtained as oils, we

were able to obtain single crystals of the trityl derivative **4n** and carry out an X-ray diffraction study, which confirmed the proposed structure (Scheme 5).^[10]

Table 2. Platinum- and gold-catalyzed cycloisomerization of hydroxylated 1,5-allenynes to bicyclic ketones or dihydropyrans (yields of isolated products).

Entry	Substrate	R	R'	R''	Conditions	Yield [%] (4/5)
1	1h	CH ₂ Ph	Me	Me	PtCl ₄ (5 mol %), toluene, reflux, 36 h	75/0
2	1h	CH ₂ Ph	Me	Me	PtCl ₂ (5 mol %), toluene, reflux, 36 h	55/0
3	1i	CH ₂ iPr	Me	Me	PtCl ₄ (5 mol %), toluene, reflux, 36 h	87/0
4	1i	CH ₂ iPr	Me	Me	PtCl ₂ (5 mol %), toluene, reflux, 36 h	87/0
5	1j	CH ₂ OMe	Me	H	PtCl ₄ (5 mol %), toluene, reflux, 36 h	85/0 ^[a]
6	1k	CH ₂ OMe	Me	Me	PtCl ₄ (5 mol %), toluene, reflux, 36 h	80/0
7	1k	CH ₂ OMe	Me	Me	PtCl ₂ (5 mol %), toluene, reflux, 36 h	70/0
8	1l	<i>n</i> C ₆ H ₁₃	Me	Me	PtCl ₄ (5 mol %), toluene, reflux, 24 h	66/0
9	1m	(CH ₂) ₃ CCSiMe ₃	Me	Me	PtCl ₄ (5 mol %), toluene, reflux, 36 h	68/0
10	1m	(CH ₂) ₃ CCSiMe ₃	Me	Me	PtCl ₂ (5 mol %), toluene, reflux, 36 h	70/0
11	1a	SiMe ₃	Me	Me	[AuCl(PPh ₃)] (2 mol %), AgSbF ₆ (2 mol %), CH ₂ Cl ₂ , reflux, 1 h	0/96
12	1b	SiMe ₃	Me	H	[AuCl(PPh ₃)] (2 mol %), AgSbF ₆ (2 mol %), CH ₂ Cl ₂ , reflux, 1 h	0/48 ^[b]
13	1c	SiMe ₃	(CH ₂) ₅		[AuCl(PPh ₃)] (2 mol %), AgSbF ₆ (2 mol %), CH ₂ Cl ₂ , reflux, 1 h	0/45
14	1i	CH ₂ iPr	Me	Me	[AuCl(PPh ₃)] (2 mol %), AgSbF ₆ (2 mol %), CH ₂ Cl ₂ , reflux, 1 h	0/72
15	1k	CH ₂ OMe	Me	Me	[AuCl(PPh ₃)] (2 mol %), AgSbF ₆ (2 mol %), CH ₂ Cl ₂ , reflux, 1 h	0/73
16	1k	CH ₂ OMe	Me	Me	[AuCl(PPh ₃)] (2 mol %), AgSbF ₆ (2 mol %), toluene, RT, 1 h	0/55
17	1k	CH ₂ OMe	Me	Me	AuCl (2 mol %), CH ₂ Cl ₂ , RT, 6 h	0/41
18	1k	CH ₂ OMe	Me	Me	AuCl ₃ (2 mol %), CH ₂ Cl ₂ , RT, 6 h	0/55
19	1k	CH ₂ OMe	Me	Me	AuCl (2 mol %), toluene, reflux, 6 h	45/0
20	1k	CH ₂ OMe	Me	Me	AuCl ₃ (2 mol %), toluene, reflux, 6 h	58/0

[a] Separated mixture of *E/Z* isomers (1.7/1). [b] Inseparable mixture of isomers (1/1).

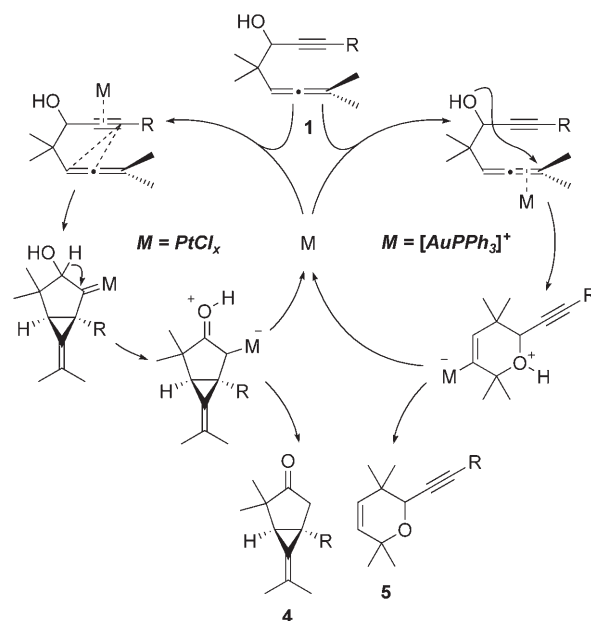
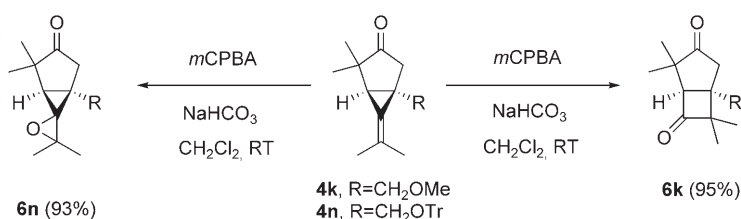
Scheme 5. Synthesis of **4n** and structure obtained from X-ray diffraction analysis.

It seems clear that these bicyclic compounds arise from the activation of the triple bond by the platinum catalyst followed by intramolecular nucleophilic attack of the internal allene double bond, as in the case of hydroxylated 1,5-enynes.^[2e] Although similar reactivity was expected with gold catalysts, a different outcome ensued: on using a catalytic amount of $[\text{Au}(\text{PPh}_3)]^+$, generated in situ from $[\text{AuCl}(\text{PPh}_3)]$ and AgSbF_6 , allenynes **1i** and **1k** were transformed into 2-ethynyl-3,6-dihydro-2*H*-pyran derivatives **5i** (Table 2, entry 14) and **5k** (Table 2, entry 15) in 72 and 73 % yield, respectively.^[11] The corresponding transformations were reported in the β -hydroxyallene series.^[12]

These reactions came to completion within 1 h in CH_2Cl_2 at room temperature. The yield of **5k** was significantly lowered in toluene instead of CH_2Cl_2 (Table 2, entry 16, 55 %). AuCl and AuCl_3 proved to be less efficient catalysts: **5k** was obtained in 41 and 55 % yield, respectively, after 6 h at room temperature in CH_2Cl_2 (Table 2, entries 17 and 18). Interestingly, when the reaction was carried out in toluene instead of CH_2Cl_2 , AuCl and AuCl_3 led to **4k** in 45 and 58 % yield, respectively (Table 2, entries 19 and 20). Clearly, whereas $[\text{Au}(\text{PPh}_3)]^+$ remains a well-defined species in both toluene and CH_2Cl_2 due to the presence of a stabilizing phosphane ligand, the “low-tech”^[13] gold salts AuCl and AuCl_3 may give rise to different active species depending on the solvent and the temperature of the reaction mixture.

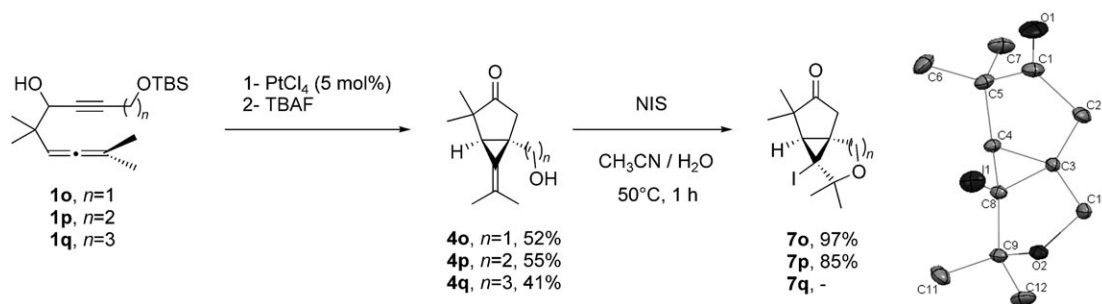
Thus, hydroxylated 1,5-allenynes behave like hydroxylated 1,5-enynes or β -hydroxyallenes depending on the reaction conditions.^[14] However, in spite of potential competition between the two nucleophilic sites (i.e., the OH group and the internal allene double bond), we encountered only chemospecific transformations in which $[\text{Au}(\text{PPh}_3)]^+$ selectively activated the allene moiety, whereas PtCl_x ($x=2,4$) activates only the triple bond (Scheme 6).^[15]

Synthetic applications of compounds 4: Although many new compounds were formed from hydroxylated 1,5-allenynes, as far as synthetic applications are concerned, the peculiar framework of compounds **4** appeared the most fascinating. We thus started to evaluate these intriguing compounds as potential precursors to more complex molecules. First, we found that the alkene fragment is highly reactive toward *m*-chloroperbenzoic acid (*m*CPBA; Scheme 7). Ketone **4n** underwent selective epoxidation to give tricyclic spiro com-

Scheme 6. Mechanistic interpretation ($x=2, 4$).Scheme 7. Reaction of compounds of type **4** with *m*CPBA.

netic stabilization, subsequent rearrangement into a cyclobutanone takes place.^[16]

We next envisaged treating compounds **4** with halogenating agents. Hydroxyalkyl derivatives **4o–q** were prepared by PtCl_4 -catalyzed cycloisomerization of allenynes **1o–q** followed by fluorodesilylation (Scheme 8). Treatment of **4o** with *N*-iodosuccinimide (NIS) produced tricyclic **7o** in 97 % yield as a single regio- and diastereomer arising from 5-*endo* cyclization. The stereochemical assignment of this product was ascertained by X-ray diffraction.^[17] With longer methyl-

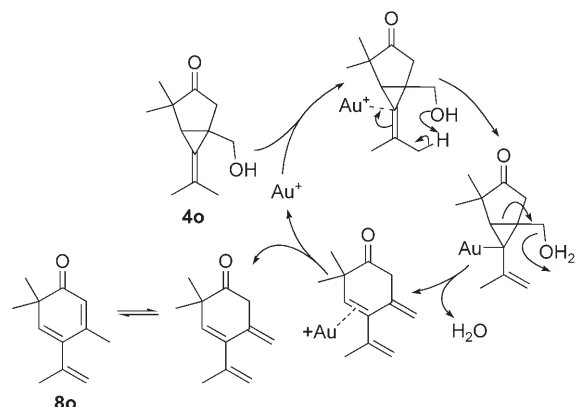


Scheme 8. Iodoalkoxylation of the 6-methylene bond.

ene spacers, the same reaction conditions led to **7p** in 85 % yield, but only to degradation in the case of **4q**.

Since the hydroxylated ketones **4o–q** display both a methylenecyclopropane fragment and a nucleophilic site, we figured that these substrates could also be good candidates for gold-catalyzed transformations. Pertinent to this idea was the recently described gold(I)-catalyzed hydroamination of methylenecyclopropanes.^[18] We found that the outcome of the reaction of compounds of type **4** with gold(I) was critically dependent on the length of the methylene spacer (Table 3). For instance with $n=1$ (Table 3, entry 1), **4o** was selectively transformed into cyclohexadienone **8o** in 77 % yield in the presence of 2 mol % of $[\text{Au}(\text{PPh}_3)]^+$. On the other hand, with $n=2$ (Table 3, entry 2), products arising from attack of the alcohol at the double bond (**9p**, 42 %) or at the cyclopropane moiety (**10p**, 30 %) were obtained. Spiro compound **10q** was formed as sole product for $n=3$ (Table 3, entry 3). A different product distribution was obtained on using AuCl with $n=1$ and $n=2$ (Table 3, entries 4 and 5), but **10q** was still obtained selectively with $n=3$ (Table 3, entry 6). It is note worthy that compounds of type **9** and **10** were formed as single diastereomers.^[19,20]

The formation of **8o** can be summarized as follows (Scheme 9): electron depletion of the methylenecyclopropane moiety induced by gold coordination promotes elimination of an allylic proton and hence formation of a hydronium cation. Elimination of water and opening at the ring junction leads to a gold-complexed 5-methylenecyclohex-3-



Scheme 9. Mechanistic rationale for Au^{I} -catalyzed transformations of **4o** into **8o**.

enone intermediate. After regeneration of the catalyst, this compound rearranges into the more stable $\alpha,\beta,\gamma,\delta$ -unsaturated ketone **8o**.

With a longer tether ($n=2$ or 3; Scheme 10), nucleophilic attack of the double bond, or of the cyclopropyl ring, by the alkoxyl group becomes faster than proton elimination. In the latter case, this transformation leads to a vinylgold species that includes a spiranic moiety. Elimination of H^+ followed by acidic cleavage of the C–Au bond regenerates the catalyst and delivers **10p,q**.

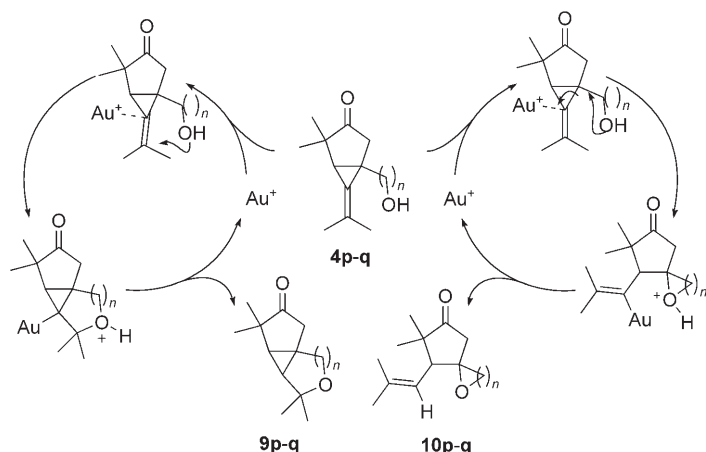
Conclusion

We have shown that hydroxylated 1,5-allenynes can be cycloisomerized in the presence of platinum- and gold-based catalysts to yield distinct products. Among them, 6-methylenebicyclo[3.1.0]hexan-3-ones were formed on using PtCl_2 or PtCl_4 , whereas 2-ethynyl-3,6-dihydro-2H-pyrans were obtained with $[\text{Au}(\text{PPh}_3)]^+$. Thus, platinum salts show an extensive degree of alkynophi-

Table 3. Gold-catalyzed transformations of compounds **4o–q** (yields of isolated products).

Entry	Substrate	n	Conditions	Yield [%] (8/9/10)
1	4o	1	$[\text{AuCl}(\text{PPh}_3)]$ (2 mol %), AgSbF_6 (2 mol %), CH_2Cl_2 , reflux, 1 h	77/0/0
2	4p	2	$[\text{AuCl}(\text{PPh}_3)]$ (2 mol %), AgSbF_6 (2 mol %), CH_2Cl_2 , reflux, 1 h	0/42/30 ^[a]
3	4q	3	$[\text{AuCl}(\text{PPh}_3)]$ (2 mol %), AgSbF_6 (2 mol %), CH_2Cl_2 , reflux, 1 h	0/0/74
4	4o	1	AuCl (5 mol %), CH_2Cl_2 , reflux, 2 h	54/38/0 ^[a]
5	4p	2	AuCl (5 mol %), CH_2Cl_2 , reflux, 2 h	0/44/0
6	4q	3	AuCl (5 mol %), CH_2Cl_2 , reflux, 2 h	0/0/80

[a] Separated.



Scheme 10. Mechanistic rationale for Au^{I} -catalyzed transformations of **4p,q** into **9p,q** and **10p,q**.

licity, as opposed to $[\text{Au}(\text{PPh}_3)]^+$, which proved to be substantially allenophilic. 6-Methylenebicyclo[3.1.0]hexan-3-ones were oxidized by *m*CPBA or NIS to give polycyclic compounds regio- and diastereoselectively. On the other hand, $[\text{Au}(\text{PPh}_3)]^+$ allowed the formation of tricyclic or spiro derivatives from hydroxyalkyl-substituted substrates depending on the tether length. Overall, these compounds were obtained in three steps from hydroxylated allenynes by a unique sequence of platinum- and then gold-catalyzed transformations.

Experimental Section

General methods: Reactions were carried out under argon in oven-dried glassware. THF was distilled over sodium benzophenone ketyl. Toluene was distilled from CaH_2 . Thin-layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel. Merck Gerudan SI 60 Å silica gel (35–70 μm) was used for column chromatography. NMR spectra (^1H , ^{13}C , DEPT, ^1H , ^1H and ^1H , ^{13}C COSY) were recorded at room temperature on a 400 MHz Bruker ARX400 spectrometer. Chemical shifts are given in parts per million, referenced to the residual proton resonance of the solvents ($\delta = 7.26$ ppm for CDCl_3) or to the residual carbon resonance of the solvent ($\delta = 77.16$ ppm for CDCl_3). When possible, ^1H and ^{13}C signals were assigned mostly on the basis of DEPT and 2D NMR (COSY, HMBC) experiments. In the description of the ^{13}C NMR spectra, a number at the beginning of the information in parentheses refers to accidentally isochronous carbon atoms. Elemental analyses were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie-Paris 6. High-resolution mass spectra (HRMS) were measured by the Service de Spectrométrie de Masse de l'Université Pierre et Marie Curie-Paris 6. Infrared (IR) spectra were recorded on a Bruker Tensor 27 spectrometer. Melting points were obtained on a Büchi capillary apparatus and were not corrected.

Synthesis of the precursors allenynes: general procedure for preparation of 1a–q: *n*BuLi (5.6 mL, 2.3 M in hexanes, 13 mmol) was added to a solution of the alkyne (10 mmol) in dry THF (14 mL) at -78°C . After 20 min, a solution of the allene aldehyde (9.9 mmol, 1 equiv) in dry THF (14 mL) was added. The mixture was then allowed to warm to room temperature. The mixture was quenched with saturated NH_4Cl solution and extracted with diethyl ether. The combined organic layers were washed with brine, dried over MgSO_4 , and evaporated to give a crude oil, which

was purified by flash chromatography on silica gel (petroleum ether/AcOEt 9/1).

1a (prepared from trimethylsilylacetylene and 2,2,5-trimethyl-3,4-hexadienal, 96 %): Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.19$ (s, 9H), 1.09 (s, 3H), 1.10 (s, 3H), 1.72 (d, $J = 3.0$ Hz, 6H), 4.07 (s, 1H), 5.01 ppm (sept, $J = 3.0$ Hz, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta = 0.03$ (CH_3), 20.8 (2C, CH_3), 24.1 (2C, CH_3), 27.0 (C), 70.8 (CH), 90.2 (C), 95.3 (C), 97.1 (C), 105.4 (CH), 201.2 ppm (C); IR (neat): $\tilde{\nu} = 1725$, 2171, 3396 cm^{-1} .

1b (prepared from trimethylsilylacetylene and 2,2-dimethyl-3,4-hexadienal, 67 %): Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.15$ (s, 9H), 1.06 (s, 3H), 1.08 (s, 3H), 1.65 (dd, $J = 6.8$, 3.3 Hz, 3H), 2.18 (brs, OH), 4.04 (s, 1H), 5.08–5.21 ppm (m, 2H); ^{13}C NMR (CDCl_3): $\delta = -0.11$ (CH_3), 14.6 (CH_3), 23.6 (CH_3), 23.9 (CH_3), 40.2 (C), 70.7 (CH), 87.7 (CH), 90.4 (C), 96.5 (CH), 104.9 (C) 204.0 ppm (C); IR (neat): $\tilde{\nu} = 1960$, 2171, 3378 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{13}\text{H}_{22}\text{OSiNa}$: 245.1338; found: 245.1332.

1c (prepared from trimethylsilylacetylene and 4-cyclohexylidene-2,2-dimethyl-3-butenal, 34 %): Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.19$ (s, 9H), 1.10 (s, 3H), 1.12 (s, 3H), 1.41–1.62 (m, 6H), 2.09–2.22 (m, 4H), 4.08 (d, $J = 6.8$ Hz, 1H), 5.02 ppm (sept, $J = 2.3$ Hz, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta = 0.03$ (CH_3), 23.8 (CH_3), 24.4 (CH_3), 26.2 (2C, CH_2), 27.0 (C), 27.6 (2C, CH_2), 31.9 (CH_2), 40.7 (C), 70.9 (CH), 90.5 (C), 94.9 (CH), 104.9 (C), 197.9 ppm (C); IR (neat): $\tilde{\nu} = 1958$, 2171, 3402 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{17}\text{H}_{28}\text{OSiNa}$: 299.1807; found: 299.1798.

1d (prepared from *tert*-butyldimethylsilylacetylene and 2,2,5-trimethyl-3,4-hexadienal, 68 %): Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.09$ (s, 6H), 0.92 (s, 9H), 1.06 (s, 3H), 1.08 (s, 3H), 1.68 (d, $J = 3.0$ Hz, 6H), 4.06 (d, $J = 6.5$ Hz, 1H), 5.04 ppm (sept, $J = 3.0$ Hz, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta = -4.50$ (CH_3), 16.6 (C), 20.7 (CH_3), 20.8 (CH_3), 23.7 (CH_3), 24.3 (CH_3), 26.2 (CH_3), 40.8 (C) 70.9 (CH), 88.7 (C), 95.3 (CH), 97.5 (C) 105.8 (C), 201.3 ppm (C); IR (neat): $\tilde{\nu} = 1968$, 2170, 3400 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{17}\text{H}_{30}\text{OSiNa}$: 301.1958; found: 301.1964.

1e (prepared from dimethylphenylsilylacetylene and 2,2,5-trimethyl-3,4-hexadienal, 63 %): Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.43$ (s, 3H), 0.44 (s, 3H), 1.11 (s, 3H), 1.13 (s, 3H), 1.71 (d, $J = 3.0$ Hz, 6H), 4.14 (d, $J = 1.3$ Hz, 1H), 5.04 (sept, $J = 3.0$ Hz, 1H), 7.36–7.41 (m, 3H), 7.61–7.68 ppm (m, 2H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta = -0.71$ (CH_3), 20.7 (CH_3), 20.8 (CH_3), 23.8 (CH_3), 24.3 (CH_3), 40.8 (C), 71.0 (CH), 88.5 (C), 95.2 (CH), 97.5 (C), 107.0 (C), 127.9, 129.5, 133.7 (CH_{arom}), 136.9 (C), 201.3 ppm (C); IR (neat): $\tilde{\nu} = 1967$, 2170, 3438 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{19}\text{H}_{26}\text{OSiNa}$: 321.1654; found: 321.1651.

1f (prepared from triphenylsilylacetylene and 2,2,5-trimethyl-3,4-hexadienal, 49 %): Pale yellow oil; ^1H NMR (CDCl_3): $\delta = 1.16$ (s, 3H), 1.19 (s, 3H), 1.68 (d, $J = 3.0$ Hz, 6H), 4.24 (d, $J = 6.0$ Hz, 1H), 5.09 (sept, $J = 3.0$ Hz, 1H), 7.59–7.74 ppm (m, 15H), OH unobserved; IR (neat): $\tilde{\nu} = 1967$, 2170, 3400 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{29}\text{H}_{30}\text{OSiNa}$: 445.1964; found: 445.1958.

1g (prepared from triisopropylsilylacetylene and 2,2,5-trimethyl-3,4-hexadienal, 60 %): Colorless oil; ^1H NMR (CDCl_3): $\delta = 1.07$ (s, 3H), 1.08 (d, $J = 5.5$ Hz, 18H), 1.09 (s, 3H), 1.10–1.20 (m, 3H), 1.70 (d, $J = 2.2$ Hz, 6H), 4.08 (d, $J = 6.5$ Hz, 1H), 5.03 ppm (sept, $J = 3.0$ Hz, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta = 18.5$ (CH_3), 18.7 (CH), 20.8 (CH_3), 20.9 (CH_3), 23.6 (CH_3), 24.5 (CH_3), 40.9 (C), 71.0 (CH), 86.6 (C), 94.8 (C), 95.4 (CH), 97.5 (C), 201.3 ppm (C); IR (neat): $\tilde{\nu} = 2172$, 3387 cm^{-1} .

1h (prepared from 3-phenyl-1-propyne and 2,2,5-trimethyl-3,4-hexadienal, 58 %): Colorless oil; ^1H NMR (CDCl_3): $\delta = 1.12$ (s, 3H), 1.14 (s, 3H), 1.72 (d, $J = 2.9$ Hz, 6H), 3.62 (s, 2H), 4.15 (s, 1H), 5.05 (sept, $J = 3.0$ Hz, 1H), 7.36–7.49 ppm (m, 5H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta = 20.6$ (CH_3), 20.7 (CH_3), 23.8 (CH_3), 24.2 (CH_3), 25.2 (CH_2), 40.8 (C), 70.8 (CH), 81.7 (C), 83.7 (C), 95.4 (CH), 97.3 (C), 126.6 (CH), 127.9 (CH), 128.5 (CH), 136.7 (C), 201.2 ppm (C); IR (neat): $\tilde{\nu} = 1967$, 2220, 3406 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{18}\text{H}_{22}\text{ONa}$: 277.1568; found: 277.1565.

1i (prepared from 4-methyl-1-pentyne and 2,2,5-trimethyl-3,4-hexadienal, 69 %): Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.94$ (s, 3H), 0.96 (s, 3H), 1.04 (s, 3H), 1.05 (s, 3H), 1.67 (d, $J = 2.9$ Hz, 6H), 1.70–1.85 (m, 1H),

2.10 (dd, $J=6.3$, 2.0 Hz, 2H), 4.04 (s, 1H), 4.99 ppm (sept, $J=3.0$ Hz, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=20.7$ (CH_3), 20.8 (CH_3), 22.1 (CH_3), 23.7 (CH_3), 24.3 (CH_3), 28.0 (CH), 28.1 (CH_2), 40.8 (C), 70.7 (CH), 80.2 (C), 85.3 (C), 95.4 (CH), 97.2 (C), 201.2 ppm (C); IR (neat): $\tilde{\nu}=1968$, 2222, 3390 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{15}\text{H}_{24}\text{ONa}$: 243.1725; found: 243.1719.

1j (prepared from methyl propargyl ether and 2,2-dimethyl-3,4-hexadienal, 47%): Colorless oil; ^1H NMR (CDCl_3): $\delta=1.08$ (s, 3H), 1.10 (s, 3H), 1.75 (d, $J=2.8$ Hz, 6H), 3.38 (s, 3H), 4.10 (d, $J=2.8$ Hz, 1H), 4.15 (d, $J=1.5$ Hz, 2H), 5.00 ppm (sept, $J=2.8$ Hz, 1H); ^{13}C NMR (CDCl_3): $\delta=20.7$ (CH_3), 23.8 (CH_3), 24.1 (CH_3), 40.7 (C), 57.5 (CH_3), 59.9 (CH_2), 70.5 (CH), 81.5 (C), 86.0 (C), 95.3 (CH), 97.4 (C), 201.2 ppm (C); IR (neat): $\tilde{\nu}=1720$, 1968, 3405 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{Na}$: 217.1204; found: 217.1199.

1k (prepared from methyl propargyl ether and 2,2,5-trimethyl-3,4-hexadienal, 89%): Colorless oil; ^1H NMR (CDCl_3): $\delta=1.07$ (s, 3H), 1.08 (s, 3H), 1.64 (d, $J=3.5$ Hz, 6H), 3.35 (s, 3H), 4.10 (brs, 1H), 4.14 (s, 2H), 5.07–5.21 ppm (m, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=14.6$ (CH_3), 23.6 (CH_3), 23.7 (CH_3), 24.0 (CH_3), 40.3 (C), 57.6 (CH_3), 59.9 (CH_2), 70.5 (CH), 81.6 (C), 85.8 (C), 87.9 (CH), 96.6 (CH), 204.1 ppm (C); IR (neat): $\tilde{\nu}=1725$, 1961, 3418 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Na}$: 231.1361; found: 231.1357.

1l (prepared from 1-octyne and 2,2,5-trimethyl-3,4-hexadienal, 61%): Colorless oil; ^1H NMR (CDCl_3): $\delta=0.88$ (t, $J=7.0$ Hz, 3H), 1.05 (s, 3H), 1.07 (s, 3H), 1.21–1.49 (m, 6H), 1.45–1.56 (m, 2H), 1.69 (d, $J=2.8$ Hz, 6H), 2.21 (td, $J=7.0$, 2.0 Hz, 2H), 4.04 (td, $J=3.8$, 2.0 Hz, 1H), 4.99 ppm (sept, $J=2.8$ Hz, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=14.1$ (CH_3), 18.8 (CH_2), 20.82 (CH_3), 20.83 (CH_3), 22.6 (CH_2), 23.6 (CH_3), 24.3 (CH_3), 28.6 (CH_2), 28.7 (CH_2), 31.4 (CH_2), 40.8 (C), 70.7 (CH), 79.2 (C), 86.5 (C), 95.4 (CH), 97.3 (C), 201.2 ppm (C); IR (neat): $\tilde{\nu}=1714$, 2224, 3397 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{17}\text{H}_{28}\text{ONa}$: 271.2038; found: 271.2032.

1m (prepared from hepta-1,6-diynyltrimethylsilane and 2,2,5-trimethyl-3,4-hexadienal, 58%): Colorless oil; ^1H NMR (CDCl_3): $\delta=0.14$ (s, 9H), 1.06 (s, 3H), 1.07 (s, 3H), 1.65–1.79 (m, 8H), 2.26–2.39 (m, 4H), 4.03 (d, $J=6.5$ Hz, 1H), 4.98 ppm (sept, $J=2.7$ Hz, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=0.11$ (CH_3), 17.8 (CH_2), 19.0 (CH_2), 20.6 (2C, CH_3), 23.7 (2C, CH_3), 27.7 (CH_2), 40.7 (C), 60.3 (C), 70.6 (CH), 80.1 (C), 85.1 (C), 95.5 (CH), 97.0 (C), 106.1 (C), 201.1 ppm (C); IR (neat): $\tilde{\nu}=1717$, 2173, 3410 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{19}\text{H}_{30}\text{OSiNa}$: 325.1964; found: 325.1958.

1n (prepared from 3-*O*-(triphenylmethyl)prop-1-yn-3-ol and 2,2,5-trimethyl-3,4-hexadienal, 65%): Colorless oil; ^1H NMR (CDCl_3): $\delta=1.13$ (s, 3H), 1.15 (s, 3H), 1.75 (d, $J=2.8$ Hz, 6H), 3.38 (d, $J=1.5$ Hz, 2H), 4.13 (brs, 1H), 5.06 (sept, $J=2.8$ Hz, 1H), 7.33–7.39 (m, 10H), 7.47–7.58 ppm (m, 5H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=20.75$ (CH_3), 20.78 (CH_3), 23.8 (CH_3), 24.1 (CH_3), 40.7 (C), 53.2 (CH_2), 70.5 (CH), 82.4 (C), 84.7 (C), 87.4 (C), 95.2 (CH), 97.3 (C), 127.1 (CH_{arom}), 127.9 (CH_{arom}), 128.6 (CH_{arom}), 143.5 (C), 201.2 ppm (C); IR (neat): $\tilde{\nu}=1737$, 1967 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{31}\text{H}_{32}\text{O}_2\text{Na}$: 459.2297; found: 459.2294.

1o (prepared from *tert*-butyl(dimethyl)(2-propyloxy)silane and 2,2,5-trimethyl-3,4-hexadienal, 87%): Colorless oil; ^1H NMR (CDCl_3): $\delta=0.11$ (s, 6H), 0.90 (s, 9H), 1.06 (s, 3H), 1.08 (s, 3H), 1.70 (d, $J=3.5$ Hz, 6H), 4.09 (brs, 1H), 4.35 (d, $J=1.8$ Hz, 2H), 4.99 ppm (sept, $J=3.5$ Hz, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=-5.0$ (CH_3), 18.3 (C), 20.8 (2C, CH_3), 23.7 (2C, CH_3), 24.2 (CH_3), 25.9 (CH_3), 40.8 (C), 68.0 (CH), 81.9 (C), 84.5 (C), 95.2 (CH), 97.4 (C), 201.3 ppm (C); IR (neat): $\tilde{\nu}=3422$ cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{18}\text{H}_{32}\text{O}_2\text{SiNa}$: 331.2069; found: 331.2063.

1p (prepared from *tert*-butyl(dimethyl)(3-butyloxy)silane and 2,2,5-trimethyl-3,4-hexadienal, 66%): Colorless oil; ^1H NMR (CDCl_3): $\delta=0.06$ (s, 6H), 0.88 (s, 9H), 1.05 (s, 3H), 1.06 (s, 3H), 1.70 (d, $J=3.0$ Hz, 6H), 2.44 (td, $J=7.0$, 1.8 Hz, 2H), 3.71 (t, $J=7.3$ Hz, 2H), 4.03 (d, $J=7.0$ Hz, 1H), 4.95–5.03 ppm (m, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=-5.1$ (CH_3), 18.4 (C), 20.8 (CH_3), 23.2 (CH_2), 23.7 (CH_3), 24.2 (CH_3), 25.9 (CH_3), 40.8 (C), 62.0 (CH_2), 70.7 (CH), 80.4 (C), 83.2 (C), 95.3 (CH), 97.3 (C), 135.5 (C), 201.3 ppm (C); IR (neat): $\tilde{\nu}=1968$, 2226,

3433 cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{19}\text{H}_{34}\text{O}_2\text{SiNa}$: 345.2226; found: 345.2221.

1q (prepared from *tert*-butyl(dimethyl)(4-pentyloxy)silane and 2,2,5-trimethyl-3,4-hexadienal, 69%): Colorless oil; ^1H NMR (CDCl_3): $\delta=0.04$ (s, 6H), 0.88 (s, 9H), 1.05 (s, 3H), 1.07 (s, 3H), 1.70 (d, $J=3.1$ Hz, 6H), 1.61–1.73 (m, 2H), 2.25–2.35 (m, 2H), 3.68 (t, $J=6.0$ Hz, 2H), 4.09 (br d, 1H), 4.98 ppm (sept, $J=3.1$ Hz, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=-5.3$ (CH_3), 15.2 (CH_2), 18.4 (C), 20.8 (2C, CH_3), 23.7 (CH_3), 24.3 (CH_3), 25.9 (CH_3), 31.8 (CH_2), 40.8 (C), 61.7 (CH_2), 70.7 (CH), 81.9 (C), 86.0 (C), 95.3 (CH), 97.3 (C), 201.3 ppm (C); IR (neat): $\tilde{\nu}=1967$, 2225, 3449 cm^{-1} .

General procedure for thermal Alder-ene cycloisomerization reactions: A stirred solution of allenyne in dry toluene ($c=0.05\text{M}$) was heated under reflux for 1 h. After cooling to room temperature, the mixture was filtered through a short pad of silica gel and concentrated in vacuo.

General procedure for PtCl_2 - and PtCl_4 -catalyzed cycloisomerization: The platinum catalyst was added to a stirred solution of allenyne in dry toluene ($c=0.05\text{M}$) under argon, and the solution was heated under reflux for 2–36 h. After cooling to room temperature, the mixture was filtered through a short pad of silica gel and concentrated in vacuo.

Compounds **4o–q** were obtained after a cycloisomerization step as described previously, followed by treatment with 1.5 equiv of a 1 M solution of tetra-*n*-butylammonium fluoride (TBAF) in THF and purification by flash chromatography on silica gel (petroleum ether/AcOEt 1/1).

General procedure for AuCl - and AuCl_3 -catalyzed cycloisomerization reactions: The gold catalyst was added to a stirred solution of allenyne in dry CH_2Cl_2 ($c=0.05\text{M}$) under argon, and the solution was heated under reflux for 2 h. After cooling to room temperature, the mixture was filtered through a short pad of silica gel and concentrated in vacuo.

General procedure for $[\text{Au}(\text{PPh}_3)]\text{SbF}_6$ -catalyzed cycloisomerization reactions: Allenyne (0.45 mmol) in CH_2Cl_2 (9 mL) was added to a solution formed by adding 2 mol % of ClAuPPh_3 and 2 mol % of AgSbF_6 to CH_2Cl_2 . The mixture was stirred under reflux for 2 h. After cooling to room temperature, the mixture was filtered through a short pad of silica gel and concentrated in vacuo.

2a: Colorless oil; ^1H NMR (CDCl_3): $\delta=0.18$ (s, 9H), 1.07 (s, 6H), 1.89 (s, 3H), 4.24 (d, $J=6.0$ Hz, 1H), 5.09 (s, 1H), 5.10 (s, 1H), 5.75 (s, 1H), 5.80 ppm (s, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=0.52$ (CH_3), 21.3 (CH_3), 22.9 (CH_3), 27.1 (CH_3), 45.8 (C), 81.8 (CH), 115.0 (CH_2), 123.1 (CH), 132.2 (C), 138.3 (C), 142.8 (CH), 161.2 ppm (C); IR (neat): $\tilde{\nu}=3420$ cm^{-1} .

2f: Colorless oil; ^1H NMR (CDCl_3): $\delta=0.95$ (s, 3H), 0.98 (s, 3H), 1.95 (s, 3H), 4.02 (d, $J=5.0$ Hz, 1H), 5.17 (s, 1H), 5.26 (s, 1H), 5.91 (s, 1H), 6.29 (s, 1H), 7.21–7.46 (m, 10H), 7.55–7.69 ppm (m, 5H); ^{13}C NMR (CDCl_3): $\delta=15.3$ (CH_3), 21.5 (CH_3), 26.5 (CH_3), 45.7 (C), 82.2 (CH), 114.6 (CH), 115.5 (CH_2), 128.0 (CH_{arom}), 129.5 (CH_{arom}), 130.1 (CH_{arom}), 135.1 (C), 138.2 (C), 142.9 (C), 143.9 (CH), 165.2 ppm (C).

2g: Colorless oil; ^1H NMR (CDCl_3): $\delta=1.08$ (d, $J=7.3$ Hz, 18H), 1.21 (s, 3H), 1.23 (s, 3H), 1.28–1.38 (m, 3H), 1.91 (s, 3H), 4.14 (d, $J=7.6$ Hz, 1H), 5.10 (s, 1H), 5.12 (s, 1H), 5.69 (s, 1H), 5.79 ppm (s, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta=12.4$ (CH), 18.7 (CH_3), 21.1 (CH_3), 22.8 (CH_3), 27.1 (CH_3), 46.2 (C), 82.3 (CH), 115.1 (CH_2), 118.7 (CH), 138.6 (C), 141.9 (CH), 143.7 (C), 161.8 ppm (C); IR (neat): $\tilde{\nu}=3420$ cm^{-1} .

3a: Colorless oil; ^1H NMR (CDCl_3): $\delta=-0.04$ (s, 9H), 1.07 (s, 6H), 1.87 (s, 2H), 2.00 (s, 3H), 2.47 (s, 2H), 5.17 (s, 1H), 5.20 ppm (s, 1H); ^{13}C NMR (CDCl_3): $\delta=-0.76$ (C), 14.7 (CH_2), 22.3 (CH_3), 25.6 (CH_3), 41.8 (C), 49.5 (CH_2), 117.5 (CH_2), 136.1 (C), 141.6 (C), 160.0, 214.1 ppm (C); IR (neat): $\tilde{\nu}=1695$ cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{14}\text{H}_{24}\text{OSiNa}$: 259.1494; found: 259.1485.

3b: Colorless oil; ^1H NMR (CDCl_3): $\delta=-0.05$ (s, 9H), 1.09 (s, 6H), 1.73 (s, 2H), 2.48 (s, 2H), 5.38 (dd, $J=10.6$, 1.3 Hz, 1H), 5.58 (dd, $J=17.4$, 1.3 Hz, 1H), 6.80 ppm (dd, $J=17.4$, 10.7 Hz, 1H); ^{13}C NMR (CDCl_3): $\delta=-1.0$ (CH_3), 13.8 (CH_2), 25.6 (CH_3), 42.1 (C), 42.3 (CH_2), 119.3 (CH_2), 131.9 (CH), 137.7 (C), 156.2 (C), 213.8 ppm (C); IR (neat): $\tilde{\nu}=1692$ cm^{-1} ; HRMS (ES+) calcd for $\text{C}_{13}\text{H}_{22}\text{OSiNa}$: 245.1338; found: 245.1326.

3c: Colorless oil; ^1H NMR (CDCl_3): $\delta = -0.03$ (s, 9H), 1.07 (s, 6H), 1.56–1.75 (m, 4H), 1.86 (s, 2H), 2.15–2.29 (m, 4H), 2.46 (s, 2H), 6.04 ppm (m, 1H); ^{13}C NMR (CDCl_3): $\delta = -0.7$ (CH_3), 14.6 (CH_2), 21.9 (CH_2), 22.7 (CH_2), 25.6 (CH_3), 25.9 (CH_2), 27.8 (CH_2), 41.7 (C), 45.6 (CH_2), 129.8 (CH), 134.2 (C), 135.6 (C), 161.5 (C), 214.2 ppm (C); IR (neat): $\tilde{\nu} = 1691\text{ cm}^{-1}$; HRMS (ES^+ , M^+): calcd for $\text{C}_{17}\text{H}_{29}\text{OSi}$: 277.1988; found: 277.1982.

3d: Colorless oil; ^1H NMR (CDCl_3): $\delta = -0.13$ (s, 6H), 0.84 (s, 3H), 0.89 (s, 9H), 1.09 (s, 6H), 1.89 (s, 2H), 2.01 (s, 3H), 2.48 (s, 2H), 5.15–5.24 ppm (m, 2H); ^{13}C NMR (CDCl_3): $\delta = -5.4$ (CH_3), 10.3 (CH_2), 17.0 (C), 25.6 (2C, CH_3), 26.4 (CH_3), 41.9 (C), 46.1 (CH_2), 117.3 (CH_2), 136.2 (C), 141.8 (C), 160.0 (C), 214.1 ppm (C); IR (neat): $\tilde{\nu} = 1697\text{ cm}^{-1}$.

3e: Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.29$ (s, 6H), 1.07 (s, 6H), 1.87 (s, 3H), 2.12 (s, 2H), 2.45 (s, 2H), 5.08–5.15 (m, 2H), 7.31–7.42 ppm (m, 5H); ^{13}C NMR (CDCl_3): $\delta = -2.2$ (CH_3), 14.1 (CH_2), 22.0 (CH_3), 25.5 (CH_3), 41.9 (C), 46.1 (CH_2), 117.3 (CH_2), 127.7 (CH_{arom}), 129.0 (CH_{arom}), 133.8 (CH_{arom}), 135.5 (C), 138.6 (C), 141.6 (C), 163.2 (C), 214.0 ppm (C); IR (neat): $\tilde{\nu} = 1698\text{ cm}^{-1}$.

4h: Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.97$ (s, 3H), 1.04 (s, 3H), 1.75 (s, 3H), 1.79 (s, 4H), 2.26 (d, A of AB, $J = 17.9\text{ Hz}$, 1H), 2.67 (d, B of AB, $J = 17.9\text{ Hz}$, 1H), 2.80 (d, A of AB, $J = 13.6\text{ Hz}$, 1H), 3.02 (d, B of AB, $J = 13.6\text{ Hz}$, 1H), 7.13–7.39 ppm (m, 5H); ^{13}C NMR (CDCl_3): $\delta = 21.9$ (CH_3), 22.3 (CH_3), 22.7 (CH_3), 26.1 (CH_3), 26.5 (C), 34.7 (CH), 39.9 (CH_2), 42.5 (CH_2), 50.3 (C), 126.1 (C), 126.8 (CH), 128.6 (C), 128.7 (CH), 129.8 (CH), 139.5 (C), 220.1 ppm (C); IR (neat): $\tilde{\nu} = 1740\text{ cm}^{-1}$; HRMS (ES^+) calcd for $\text{C}_{18}\text{H}_{22}\text{ONa}$: 277.1568; found: 277.1566.

4i: Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.91$ (d, $J = 6.5\text{ Hz}$, 3H), 0.97 (d, $J = 6.5\text{ Hz}$, 3H), 1.02 (s, 3H), 1.15 (s, 3H), 1.30–1.49 (m, 1H), 1.65–1.67 (m, 1H), 1.69–1.89 (m, 2H), 1.76 (s, 3H), 1.77 (s, 3H), 2.30 (d, A of AB, $J = 17.9\text{ Hz}$, 1H), 2.73 ppm (d, B of AB, $J = 17.9\text{ Hz}$, 1H); ^{13}C NMR (CDCl_3): $\delta = 22.0$ (CH_3), 22.1 (CH_3), 22.7 (CH_3), 22.8 (CH_3), 24.3 (CH_3), 24.4 (C), 26.2 (CH_3), 27.2 (CH), 35.4 (CH), 43.7 (CH_2), 43.9 (CH_2), 49.9 (C), 125.1 (C), 127.4 (C), 220.8 ppm (C); IR (neat): $\tilde{\nu} = 1741\text{ cm}^{-1}$; HRMS (ES^+) calcd for $\text{C}_{15}\text{H}_{24}\text{ONa}$: 273.1467; found: 273.1463.

4j (*E* isomer): Colorless oil; ^1H NMR (CDCl_3): $\delta = 1.07$ (s, 3H), 1.19 (s, 3H), 1.79 (d, $J = 6.5\text{ Hz}$, 3H), 1.80 (s, 1H), 2.28 (d, A of AB, $J = 17.9\text{ Hz}$, 1H), 2.94 (d, B of AB, $J = 17.9\text{ Hz}$, 1H), 3.37 (s, 3H), 3.38 (d, A of AB, $J = 10.3\text{ Hz}$, 1H), 3.51 (d, B of AB, $J = 10.3\text{ Hz}$, 1H), 5.94 ppm (qd, $J = 6.5$, 1.5 Hz, 1H); ^{13}C NMR (CDCl_3): $\delta = 17.3$ (CH_3), 22.0 (CH_3), 25.1 (C), 26.4 (CH_3), 33.4 (CH), 41.9 (CH_2), 50.3 (C), 58.8 (CH_3), 75.3 (CH_2), 117.6 (CH), 131.3 (C), 219.7 ppm (C); IR (neat): $\tilde{\nu} = 1741\text{ cm}^{-1}$; HRMS (ES^+) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{Na}$: 217.1204; found: 217.1199.

4j (*Z* isomer): Colorless oil; ^1H NMR (CDCl_3): $\delta = 1.04$ (s, 3H), 1.16 (s, 3H), 1.74 (dd, $J = 6.5$, 1.8 Hz, 3H), 1.79 (d, $J = 2.2\text{ Hz}$, 1H), 2.32 (d, A of AB, $J = 18.1\text{ Hz}$, 1H), 2.97 (d, B of AB, $J = 18.1\text{ Hz}$, 1H), 3.35 (d, A of AB, $J = 10.4\text{ Hz}$, 1H), 3.38 (s, 3H), 3.67 (d, B of AB, $J = 10.4\text{ Hz}$, 1H), 5.89 ppm (qd, $J = 6.5$, 1.0 Hz, 1H); ^{13}C NMR (CDCl_3): $\delta = 17.1$ (CH_3), 21.3 (CH_3), 24.9 (C), 26.2 (CH_3), 34.1 (CH), 41.4 (CH_2), 49.6 (C), 59.1 (CH_3), 74.8 (CH_2), 118.1 (CH), 131.2 (C), 219.7 ppm (C); IR (neat): $\tilde{\nu} = 1741\text{ cm}^{-1}$; HRMS (ES^+) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{Na}$: 217.1204; found: 217.1199.

4k: Colorless oil; ^1H NMR (CDCl_3): $\delta = 1.7$ (s, 3H), 1.18 (s, 3H), 1.78 (s, 3H), 1.81 (s, 4H), 2.30 (d, A of AB, $J = 17.9\text{ Hz}$, 1H), 2.96 (d, B of AB, $J = 17.9\text{ Hz}$, 1H), 3.30 (d, A of AB, $J = 10.3\text{ Hz}$, 1H), 3.39 (s, 3H), 3.66 ppm (d, B of AB, $J = 10.3\text{ Hz}$, 1H); ^{13}C NMR (CDCl_3): $\delta = 21.9$ (CH_3), 22.3 (CH_3), 22.6 (CH_3), 25.7 (C), 26.3 (CH_3), 34.4 (CH), 41.1 (CH_2), 50.1 (C), 59.0 (CH_3), 75.1 (CH_3), 124.8 (C), 126.8 (C), 220.2 ppm (C); IR (neat): $\tilde{\nu} = 1741\text{ cm}^{-1}$; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Na}$: 231.1361; found: 231.1355.

4l: Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.82$ – 0.99 (m, 3H), 1.01 (s, 3H), 1.11 (s, 3H), 1.20–1.39 (m, 8H), 1.45–1.65 (m, 2H), 1.55 (d, $J = 1.1\text{ Hz}$, 1H), 1.74 (d, $J = 1.2\text{ Hz}$, 3H), 1.75 (s, 3H), 2.25 (d, A of AB, $J = 17.9\text{ Hz}$, 1H), 2.78 ppm (d, B of AB, $J = 17.9\text{ Hz}$, 1H); ^{13}C NMR (CDCl_3): $\delta = 14.1$ (CH_3), 22.0 (CH_3), 22.2 (CH_3), 22.6 (CH_2), 22.7 (CH_3), 25.2 (C), 26.5 (CH_3), 27.5 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 31.8 (CH_2), 34.1 (CH_2), 34.2 (CH), 43.1 (CH_2), 50.1 (C), 124.9 (C), 127.6 (C), 220.8 ppm (C); IR

(neat): $\tilde{\nu} = 1742\text{ cm}^{-1}$; HRMS (ES^+) calcd for $\text{C}_{17}\text{H}_{28}\text{ONa}$: 271.2038; found: 271.2035.

4m: Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.14$ (s, 9H), 1.03 (s, 3H), 1.14 (s, 3H), 1.51–1.68 (m, 4H), 1.74 (s, 1H), 1.75 (s, 3H), 1.77 (s, 3H), 2.19–2.29 (m, 2H), 2.28 (d, A of AB, $J = 17.9\text{ Hz}$, 1H), 2.69 ppm (d, B of AB, $J = 17.9\text{ Hz}$, 1H); ^{13}C NMR (CDCl_3): $\delta = 0.29$ (CH_3), 20.2 (CH_2), 22.0 (CH_3), 22.3 (CH_3), 22.7 (CH_3), 24.9 (C), 26.5 (CH_2), 26.6 (CH_3), 33.3 (CH_2), 34.3 (CH), 43.2 (CH_2), 50.2 (C), 85.0 (C), 107.1 (C), 125.5 (C), 127.2 (C), 220.4 ppm (C); IR (neat): $\tilde{\nu} = 1741$, 2173 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{19}\text{H}_{30}\text{OSiNa}$: 325.1964; found: 325.1958.

4n: White solid; m.p. 118–120 °C; ^1H NMR (CDCl_3): $\delta = 1.13$ (s, 3H), 1.30 (s, 3H), 1.78 (s, 4H), 1.81 (s, 3H), 2.37 (d, A of AB, $J = 18.2\text{ Hz}$, 1H), 3.12 (d, B of AB, $J = 18.2\text{ Hz}$, 1H), 3.14 (d, A of AB, $J = 9.6\text{ Hz}$, 1H), 3.42 (d, B of AB, $J = 9.6\text{ Hz}$, 1H), 7.25–7.38 (m, 8H), 7.42–7.53 ppm (m, 7H); ^{13}C NMR (CDCl_3): $\delta = 21.9$ (CH_3), 22.4 (CH_3), 22.5 (CH_3), 25.3 (C), 26.4 (CH_3), 34.3 (CH), 41.4 (CH_2), 50.1 (C), 65.6 (CH_2), 86.2 (C), 125.0 (C), 126.7 (C), 127.0 (CH_{arom}), 128.3 (CH_{arom}), 130.1 (CH_{arom}), 144.2 (C), 220.4 ppm (C); IR (neat): $\tilde{\nu} = 1741\text{ cm}^{-1}$; HRMS (ES^+) calcd for $\text{C}_{31}\text{H}_{32}\text{O}_2\text{Na}$: 459.2297; found: 459.2295; elemental analysis calcd (%) for $\text{C}_{31}\text{H}_{32}\text{O}_2$: C 85.27, H 7.39; found: C 85.31, H 7.25.

4o: Colorless oil; ^1H NMR (CDCl_3): $\delta = 1.05$ (s, 3H), 1.15 (s, 3H), 1.76 (s, 3H), 1.79 (s, 4H), 2.31 (d, A of AB, $J = 18.2\text{ Hz}$, 1H), 2.96 (d, B of AB, $J = 18.2\text{ Hz}$, 1H), 3.57 (d, A of AB, $J = 11.4\text{ Hz}$, 1H), 3.88 ppm (d, B of AB, $J = 11.4\text{ Hz}$, 1H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta = 21.9$ (CH_3), 22.5 (CH_3), 22.6 (CH_3), 26.4 (CH_3), 27.4 (C), 33.7 (CH), 40.6 (CH_2), 50.1 (C), 65.2 (CH_2), 124.6 (C), 127.1 (C), 220.1 ppm (C); IR (neat): $\tilde{\nu} = 1730$, 3401 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{Na}$: 217.1204; found: 217.1199.

4p: Colorless oil; ^1H NMR (CDCl_3): $\delta = 1.04$ (s, 3H), 1.15 (s, 3H), 1.72 (s, 1H), 1.78 (s, 6H), 1.93 (t, $J = 7.0\text{ Hz}$, 2H), 2.33 (d, A of AB, $J = 18.2\text{ Hz}$, 1H), 2.78 (d, B of AB, $J = 18.2\text{ Hz}$, 1H), 3.74 ppm (t, $J = 7.0\text{ Hz}$, 2H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta = 21.7$ (CH_3), 22.0 (CH_3), 22.5 (2C, CH_3 and C), 22.6 (CH_3), 34.3 (CH), 36.7 (CH_2), 43.4 (CH_2), 50.0 (C), 61.2 (CH_2), 125.6 (C), 126.7 (C), 220.6 ppm (C); IR (neat): $\tilde{\nu} = 1734$, 3384 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Na}$: 231.1361; found: 231.1356.

4q: Colorless oil; ^1H NMR (CDCl_3): $\delta = 1.01$ (s, 3H), 1.11 (s, 3H), 1.52–1.69 (m, 4H), 1.60 (s, 1H), 1.73 (s, 3H), 1.74 (s, 3H), 2.26 (d, A of AB, $J = 18.2\text{ Hz}$, 1H), 2.68 (d, B of AB, $J = 18.2\text{ Hz}$, 1H), 3.56–3.71 ppm (m, 2H), OH unobserved; ^{13}C NMR (CDCl_3): $\delta = 21.9$ (CH_3), 22.3 (CH_3), 22.7 (CH_3), 25.8 (C), 26.5 (CH_3), 30.2 (CH_2), 30.6 (CH_2), 34.1 (CH), 43.1 (CH_2), 50.2 (C), 62.9 (CH_2), 125.4 (C), 127.1 (C), 220.7 ppm (C); IR (neat): $\tilde{\nu} = 1737$, 3394 cm^{-1} ; HRMS (ES^+) calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{Na}$: 245.1517; found: 245.1512.

5a: Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.17$ (s, 9H), 0.98 (s, 3H), 1.09 (s, 3H), 1.24 (s, 3H), 1.28 (s, 3H), 4.19 (s, 1H), 5.42 (d, $J = 10.1\text{ Hz}$, 1H), 5.48 ppm (d, $J = 10.1\text{ Hz}$, 1H); ^{13}C NMR (CDCl_3): $\delta = 0.19$ (CH_3), 22.6 (CH_3), 25.5 (2C, CH_3), 29.7 (CH_3), 35.2 (C), 70.4 (CH), 73.9 (C), 90.3 (C), 103.5 (C), 132.3 (CH), 133.7 ppm (CH).

5b (major isomer): Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.17$ (s, 9H), 0.98 (s, 3H), 1.12 (s, 3H), 1.24 (d, $J = 6.6\text{ Hz}$, 3H), 4.08 (s, 1H), 4.18–4.26 (m, 1H), 5.45 (dd, $J = 10.2$, 1.3 Hz, 1H), 5.57 ppm (dd, $J = 10.2$, 2.0 Hz, 1H); ^{13}C NMR (CDCl_3): $\delta = 0.01$ (CH_3), 21.4 (CH_3), 23.2 (CH_3), 25.2 (CH_3), 35.2 (C), 71.8 (CH), 74.8 (CH), 91.0 (C), 102.2 (C), 128.3 (CH), 135.1 ppm (CH); IR (neat): $\tilde{\nu} = 2181\text{ cm}^{-1}$; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{22}\text{OSiNa}$: 245.1338; found: 245.1335.

5b (minor isomer): Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.17$ (s, 9H), 1.06 (s, 3H), 1.07 (s, 3H), 1.24 (d, $J = 6.8\text{ Hz}$, 3H), 4.22 (s, 1H), 4.39–4.46 (m, 1H), 5.45 (dd, $J = 10.2$, 1.3 Hz, 1H), 5.57 ppm (dd, $J = 10.2$, 2.0 Hz, 1H); ^{13}C NMR (CDCl_3): $\delta = 0.17$ (CH_3), 20.2 (CH_3), 23.7 (CH_3), 27.1 (CH_3), 35.0 (C), 67.6 (CH), 71.3 (CH), 98.0 (C), 102.3 (C), 128.2 (CH), 133.5 ppm (CH); IR (neat): $\tilde{\nu} = 2181\text{ cm}^{-1}$; HRMS (ES^+) calcd for $\text{C}_{13}\text{H}_{22}\text{OSiNa}$: 245.1338; found: 245.1335.

5c: Colorless oil; ^1H NMR (CDCl_3): $\delta = 0.20$ (s, 9H), 1.00 (s, 3H), 1.12 (s, 3H), 1.31–1.80 (m, 10H), 4.23 (s, 1H), 5.52 (d, $J = 10.1\text{ Hz}$, 1H), 5.58 ppm (d, $J = 10.1\text{ Hz}$, 1H); ^{13}C NMR (CDCl_3): $\delta = 0.11$ (CH_3), 22.0 (CH_2), 22.1 (CH_2), 22.8 (CH_3), 25.4 (CH_3), 25.7 (CH_2), 33.7 (C), 38.1 (2C,

CH₂), 69.6 (CH), 74.5 (C), 89.9 (C), 103.8 (C), 131.2 (CH), 134.2 ppm (CH); IR (neat): $\tilde{\nu}$ = 2180 cm⁻¹.

5i: Colorless oil; ¹H NMR (CDCl₃): δ = 0.97 (d, J = 6.0 Hz, 6H), 0.98 (s, 3H), 1.09 (s, 3H), 1.24 (s, 3H), 1.27 (s, 3H), 1.83 (non, J = 6.6 Hz, 1H), 2.10–2.19 (m, 2H), 4.18 (t, J = 2.0 Hz, 1H), 5.41 (d, J = 10.1 Hz, 1H), 5.48 ppm (d, J = 10.1 Hz, 1H); ¹³C NMR (CDCl₃): δ = 22.1 (2C, CH₃), 22.6 (CH₃), 25.44 (CH₃), 25.45 (CH₃), 28.1 (CH), 28.2 (CH₂), 29.7 (CH₃), 35.20 (C), 70.1 (CH), 73.6 (C), 78.5 (C), 85.1 (C), 132.2 (CH), 133.8 ppm (CH); IR (neat): $\tilde{\nu}$ = 2235 cm⁻¹.

5k: Colorless oil; ¹H NMR (CDCl₃): δ = 0.97 (s, 3H), 1.08 (s, 3H), 1.22 (s, 3H), 1.25 (s, 3H), 3.35 (s, 3H), 4.13 (s, 2H), 4.21 (s, 1H), 5.40 (d, J = 10.4 Hz, 1H), 5.45 ppm (d, J = 10.4 Hz, 1H); ¹³C NMR (CDCl₃): δ = 22.5 (CH₃), 25.2 (CH₃), 25.3 (CH₃), 29.5 (CH₃), 35.0 (C), 57.6 (CH₃), 60.09 (CH₂), 69.9 (CH), 73.7 (C), 81.4 (C), 84.0 (C), 132.0 (CH), 133.5 ppm (CH); HRMS (ES+) calcd for C₁₃H₂₀O₂Na: 231.1361; found: 231.1355.

General procedure for oxidation with mCPBA: A solution of **4k-n** (1.2 mmol) in dry CH₂Cl₂ (10 mL) was treated with NaHCO₃ (192 mg, 2.2 mmol) and mCPBA (70%, 430 mg, 1.74 mmol). The mixture was stirred at room temperature for 2 h, diluted with a saturated aqueous NaHCO₃ solution, vigorously stirred for 15 min, and extracted with CH₂Cl₂. The combined organic layers were washed successively with water and then brine, dried over MgSO₄, filtered, and evaporated under reduced pressure. **6k-n** were purified by flash chromatography on silica gel (petroleum ether/AcOEt 9/1).

6k: Colorless oil; ¹H NMR (CDCl₃): δ = 1.00 (s, 3H), 1.07 (s, 3H), 1.12 (s, 3H), 1.22 (s, 3H), 2.54 (d, J = 19.2 Hz, 1H), 2.90 (d, J = 19.2 Hz, 1H); 3.27 (s, 1H), 3.38 (s, 3H), 3.58 (d, J = 9.6 Hz, 1H), 3.65 ppm (d, J = 9.6 Hz, 1H); ¹³C NMR (CDCl₃): δ = 19.2 (CH₃), 19.3 (CH₃), 20.1 (CH₃), 27.6 (CH₃), 41.2 (CH₂), 41.4 (C), 48.9 (C), 59.3 (CH₃), 61.4 (C), 71.1 (CH), 75.8 (CH₂), 214.7 (C), 220.7 ppm (C); IR (neat): $\tilde{\nu}$ = 1736, 1770 cm⁻¹; HRMS (ES+) calcd for C₁₃H₂₀O₃Na: 247.1311; found: 247.1304.

6n: Colorless oil; ¹H NMR (CDCl₃): δ = 1.12 (s, 3H), 1.27 (s, 3H), 1.28 (s, 3H), 1.40 (s, 3H), 1.70 (s, 1H), 2.41 (d, J = 18.4 Hz, 1H), 2.98 (d, J = 18.4 Hz, 1H); 3.22 (d, J = 9.6 Hz, 1H), 3.36 (d, J = 9.6 Hz, 1H), 7.15–7.41 (m, 8H), 7.45–7.55 ppm (m, 7H); ¹³C NMR (CDCl₃): δ = 20.1 (CH₃), 22.4 (CH₃), 22.5 (CH₃), 24.0 (C), 27.1 (CH₃), 30.0 (CH), 38.5 (CH₂), 47.9 (C), 63.1 (CH₂), 71.7 (C), 86.4 (C), 127.0 (C), 127.1 (CH), 127.8 (CH), 128.5 (CH), 143.8 (C), 218.3 ppm (C); IR (neat): $\tilde{\nu}$ = 1743 cm⁻¹; HRMS (ES+) calcd for C₃₁H₃₂O₃Na: 475.2249; found: 475.2243.

General procedure for iodocyclization with NIS: A solution of **4o.p** (0.25 mmol) and NIS (68 mg, 0.3 mmol) in CH₃CN (1 mL) and H₂O (0.5 mL) was stirred for 1 h at 50°C. The reaction was quenched with a saturated aqueous solution of Na₂S₂O₃, extracted with diethyl ether, dried over MgSO₄, and concentrated under reduced pressure. **7o.p** were purified by flash chromatography on silica gel (petroleum ether/AcOEt 9/1).

7o: White solid; m.p. 115–116°C; ¹H NMR (CDCl₃): δ = 1.11 (s, 3H), 1.27 (s, 3H), 1.28 (s, 3H), 1.40 (s, 3H), 1.44 (s, 1H), 2.32 (d, A of AB, J = 18.7 Hz, 1H), 3.00 (d, B of AB, J = 18.7 Hz, 1H), 3.86 (d, A of AB, J = 8.9 Hz, 1H), 3.90 ppm (d, B of AB, J = 8.9 Hz, 1H); ¹³C NMR (CDCl₃): δ = 18.1 (CH₃), 22.3 (CH₃), 28.6 (CH₃), 29.0 (CH₃), 33.4 (C), 35.0 (C), 36.3 (CH), 39.4 (CH₂), 50.9 (C), 66.4 (CH₂), 85.3 (C), 216.4 ppm (C); HRMS (ES+) calcd for C₁₂H₁₇O₂INa: 343.0171; found: 343.0165.

7p: Colorless oil; ¹H NMR (CDCl₃): δ = 1.11 (s, 3H), 1.25 (s, 3H), 1.36 (s, 3H), 1.59 (s, 1H), 1.60 (s, 3H), 1.99–2.08 (m, 1H), 2.19–2.26 (m, 1H), 2.41 (d, A of AB, J = 18.9 Hz, 1H), 2.78 (d, B of AB, J = 18.9 Hz, 1H), 3.62–3.86 ppm (m, 2H); ¹³C NMR (CDCl₃): δ = 19.2 (CH₃), 24.2 (CH₂), 26.1 (C), 26.6 (CH₃), 27.9 (CH₃), 28.5 (CH₃), 37.8 (CH), 41.4 (C), 50.4 (CH₂), 51.7 (C), 57.4 (CH₂), 74.5 (C), 217.9 ppm (C); IR (neat): $\tilde{\nu}$ = 1739 cm⁻¹; HRMS (ES+) calcd for C₁₃H₁₉O₂INa: 357.0327; found: 357.0324.

8o: Colorless oil; ¹H NMR (CDCl₃): δ = 1.16 (s, 6H), 1.89 (t, J = 1.3 Hz, 3H), 2.03 (d, J = 1.3 Hz, 3H), 4.80–4.83 (A of ABm, 1H), 5.03–5.06 (B of ABm, 1H), 5.89 (s, 1H), 5.98 ppm (s, 1H); ¹³C NMR (CDCl₃): δ = 21.3 (CH₃), 24.3 (CH₃), 25.6 (CH₃), 46.1 (C), 115.6 (CH₂), 124.1 (CH), 137.1 (C), 143.8 (C), 144.0 (CH), 153.9 (C), 205.4 ppm (C); IR (neat): $\tilde{\nu}$ =

1660 cm⁻¹; HRMS (ES+) calcd for C₁₂H₁₆O₂Na: 199.1099; found: 199.1093.

9o: Colorless oil; ¹H NMR (CDCl₃): δ = 0.90 (d, J = 3.0 Hz, 1H), 1.01 (s, 3H), 1.14 (s, 3H), 1.20 (s, 3H), 1.22 (s, 3H), 1.40 (d, J = 3.0 Hz, 1H), 2.37 (d, A of AB, J = 18.2 Hz, 1H), 2.85 (d, B of AB, J = 18.2 Hz, 1H), 3.90 (d, J = 8.5 Hz, 1H), 3.93 ppm (d, J = 8.5 Hz, 1H); ¹³C NMR (CDCl₃): δ = 20.3 (CH₃), 24.5 (CH₃), 25.9 (CH₃), 27.0 (CH₃), 29.6 (C), 32.7 (CH), 37.1 (CH), 38.0 (C), 47.6 (C), 67.7 (CH₂), 81.2 (C), 218.8 ppm (C); IR (neat): $\tilde{\nu}$ = 1739 cm⁻¹; HRMS (ES+) calcd for C₁₂H₁₈O₂Na: 217.1204; found: 217.1200.

9p: Colorless oil; ¹H NMR (CDCl₃): δ = 0.27 (d, J = 4.0 Hz, 1H), 0.99 (s, 3H), 1.13 (s, 3H), 1.19 (s, 3H), 1.23 (d, J = 4.0 Hz, 1H), 1.34 (s, 3H), 1.81–1.89 (A of ABm, 1H), 1.91–2.05 (B of ABm, 1H), 2.30 (d, A of AB, J = 18.4 Hz, 1H), 2.69 (d, B of AB, J = 18.4 Hz, 1H), 3.44–3.53 (A of ABm, 1H), 3.58–3.66 ppm (B of ABm, 1H); ¹³C NMR (CDCl₃): δ = 19.9 (C), 20.54 (CH₃), 25.2 (CH₂), 26.6 (CH₃), 27.4 (CH), 28.2 (CH), 32.5 (CH₃), 24.7 (CH₃), 45.8 (CH₂), 48.5 (C), 57.7 (CH₂), 69.5 (C), 220.7 ppm (C); IR (neat): $\tilde{\nu}$ = 1738 cm⁻¹.

10p: Colorless oil; ¹H NMR (CDCl₃): δ = 0.94 (s, 3H), 1.06 (s, 3H), 1.75 (s, 3H), 1.85 (d, J = 1.0 Hz, 3H), 2.10–2.21 (m, 2H), 2.50–2.65 (m, 3H), 3.78–3.92 (m, 2H), 4.97 ppm (s, 1H); ¹³C NMR (CDCl₃): δ = 17.1 (CH₃), 18.1 (CH₃), 20.0 (CH₃), 27.8 (CH₃), 31.2 (CH₂), 40.8 (CH₂), 42.2 (CH), 55.8 (C), 66.0 (CH₂), 94.8 (C), 121.2 (CH), 138.2 (C), 221.1 ppm (C); IR (neat): $\tilde{\nu}$ = 1735 cm⁻¹; HRMS (ES+) calcd for C₁₃H₂₀O₂Na: 231.1361; found: 231.1355.

10q: White solid; m.p. 146–147°C; ¹H NMR (CDCl₃): δ = 0.89 (s, 3H), 1.10 (s, 3H), 1.58–1.65 (m, 1H), 1.68 (d, J = 1.3 Hz, 3H), 1.76 (d, J = 1.5 Hz, 3H), 1.85–1.96 (m, 2H), 2.01–2.10 (m, 1H), 2.42 (d, A of AB, J = 18.8 Hz, 1H), 2.53 (d, B of AB, J = 18.8 Hz, 1H), 2.99 (d, J = 11.0 Hz, 1H), 3.64–3.83 (m, 2H), 4.99–5.08 ppm (m, 1H); ¹³C NMR (CDCl₃): δ = 18.3 (CH₃), 20.7 (CH₃), 25.6 (CH₃), 26.1 (CH₃), 26.5 (CH₃), 33.0 (CH₂), 50.4 (C), 50.6 (CH₂), 54.4 (CH), 67.0 (CH₂), 87.2 (C), 120.0 (CH), 136.1 (C), 221.2 ppm (C); IR (neat): $\tilde{\nu}$ = 1737 cm⁻¹; HRMS (ES+) calcd for C₁₄H₂₂O₂Na: 245.1517; found: 245.1512.

Acknowledgement

This work was supported by CNRS, MRES, IUF, and ANR BLAN 06-2_159258. R.Z. is thankful to CNRS for a grant. V.G. thanks Prof. Philippe Bertus for fruitful discussions.

- [1] For recent reviews, see: a) S. A. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; b) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403; c) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; d) C. H. M. Amijs, C. Ferrer, A. M. Echavarren, *Chem. Commun.* **2007**, 698–700; e) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Commun.* **2007**, 333–346; f) A. R. Chianese, S. J. Lee, M. R. Gagné, *Angew. Chem.* **2007**, *119*, 4118–4136; *Angew. Chem. Int. Ed.* **2007**, *46*, 4042–4059; g) L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271–2296; h) M. Malacria, J.-P. Goddard, L. Fensterbank in *Comprehensive Organometallic Chemistry*, Vol. 10, 3rd ed. (Eds.: R. Crabtree, M. Mingos), Elsevier, Amsterdam, Chap. 10.07, pp. 299–368, **2006**.
- [2] For examples, see: a) C. Blaszykowski, Y. Harrak, C. Brancour, K. Nakama, A.-L. Dhimane, L. Fensterbank, M. Malacria, *Synthesis* **2007**, 2037–2049; b) C. Nieto-Oberhuber, M. Paz Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1677–1693; c) L. Zhang, S. A. Kozmin, *J. Am. Chem. Soc.* **2005**, *127*, 6962–6963; d) C. Nieto-Oberhuber, M. Paz Muñoz, E. Buñuel, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 2456–2460; *Angew. Chem. Int. Ed.* **2004**, *43*, 2402–2406; e) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 8654–8655; f) M. R. Luzung, J. P. Markham, F. D. Toste, *J. Am. Chem. Soc.* **2004**, *126*, 10858–10859; g) A. Fürstner, F. Stelzer, H. Szillat, *J. Am.*

- Chem. Soc.* **2001**, 123, 11863–11869; h) A. Fürstner, P. Hennen, *Chem. Eur. J.* **2006**, 12, 3006–3019; i) C. Fehr, J. Galindo, *Angew. Chem.* **2006**, 118, 2967–2970; *Angew. Chem. Int. Ed.* **2006**, 45, 2901–2904.
- [3] For gold-, platinum-, and gallium-catalyzed cycloisomerization of 1,6-allenynes, see: a) G.-Y. Lin, C.-Y. Yang, R.-S. Liu, *J. Org. Chem.* **2007**, 72, 7466–7468; b) T. Matsuda, S. Kadowaki, T. Goya, M. Murakami, *Synlett* **2006**, 575–578; c) T. Matsuda, S. Kadowaki, M. Murakami, *Helv. Chim. Acta* **2006**, 89, 1672–1680; d) S. I. Lee, S. H. Sim, S. M. Kim, K. Kim, Y. K. Chung, *J. Org. Chem.* **2006**, 71, 7120–7123; e) N. Cadran, K. Cariou, G. Hervé, C. Aubert, L. Fensterbank, M. Malacria, J. Marco-Contelles, *J. Am. Chem. Soc.* **2004**, 126, 3408–3409; f) G. Lemière, V. Gandon, N. Agenet, J.-P. Goddard, A. de Kozak, C. Aubert, L. Fensterbank, M. Malacria, *Angew. Chem.* **2006**, 118, 7758–7761; *Angew. Chem. Int. Ed.* **2006**, 45, 7596–7599; for rhodium-catalyzed cycloisomerizations of 1,6-allenynes, see: g) K. M. Brummond, T. O. Painter, D. A. Probst, B. Mitasev, *Org. Lett.* **2007**, 9, 347–349; h) K. M. Brummond, H. Chen, P. Sill, L. You, *J. Am. Chem. Soc.* **2002**, 124, 15186–15187; for thermal, microwave-assisted, and metal-catalyzed [2+2] cycloadditions of 1,6-allenynes, see inter alia: i) H. Ohno, T. Mizutani, Y. Kadoh, K. Miyamura, T. Tanaka, *Angew. Chem.* **2005**, 117, 5243–5245; *Angew. Chem. Int. Ed.* **2005**, 44, 5113–5115; j) K. M. Brummond, D. Chen, *Org. Lett.* **2005**, 7, 3473–3475; k) C. H. Oh, A. K. Gupta, D. I. Park, N. Kim, *Chem. Commun.* **2005**, 5670–5672, and references therein.
- [4] We thank Prof. F. D. Toste, UC-Berkeley, for sharing with us some findings on that topic.
- [5] These compounds undergo thermal and molybdenum- or palladium-catalyzed [2+2] cycloadditions to give bicyclo[3.2.0]hepta-1,5-dienes; for examples, see: a) C. H. Oh, D. I. Park, S. H. Jung, V. R. Reddy, A. K. Gupta, Y. M. Kim, *Synlett* **2005**, 2092–2094. They also give rise to Alder-ene-type cycloisomerizations to 5-methylene-1-vinylcyclopent-1-enes mediated by titanium(II): b) T. Yamazaki, H. Urabe, F. Sato, *Tetrahedron Lett.* **1998**, 39, 7333–7336.
- [6] a) R. S. Bly, S. U. Kooek, *J. Am. Chem. Soc.* **1969**, 91, 3292–3298; b) M. Depature, J. Diewok, J. Grimaldi, J. Hatem, *Eur. J. Org. Chem.* **2000**, 275–280.
- [7] M. A. Brook in *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, **2000**.
- [8] The unfunctionalized 6-methylenebicyclo[3.1.0]hexane framework is known; see inter alia: J. J. Gajewski, S. K. Chou, *J. Am. Chem. Soc.* **1977**, 99, 5696–5707.
- [9] It is noteworthy that, although *gem*-dimethyl substitution in the tether improves the yield, it is not a necessary feature for such cycloisomerizations. Indeed, the reaction of an allenyne similar to **1k** without substituents at C4 led to the corresponding cyclopentenone in 50 % yield of isolated product under the same experimental conditions.
- [10] CCDC-662257 contains 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.
- [11] Examples of distinctly different behavior of platinum and gold catalysts are rare; see, for instance: G. Zhang, V. J. Catalano, L. Zhang, *J. Am. Chem. Soc.* **2007**, 129, 11358–11359.
- [12] a) B. Gockel, N. Krause, *Org. Lett.* **2006**, 8, 4485–4488; for related gold-catalyzed cycloisomerization of α -aminoallenes to 3-pyrrolines, see: b) N. Morita, N. Krause, *Eur. J. Org. Chem.* **2006**, 4634–4641; c) N. Morita, N. Krause, *Org. Lett.* **2004**, 6, 4121–4123; d) for related gold-catalyzed cyclization of allene-substituted malonate esters, see: J. Piera, P. Krumlinde, D. Strübing, J.-E. Bäckvall, *Org. Lett.* **2007**, 9, 2335–2337.
- [13] A. Fürstner, H. Szillat, B. Gabor, R. Mynott, *J. Am. Chem. Soc.* **1998**, 120, 8305–8314.
- [14] Protecting the hydroxyl group as an acetate led only to Alder-ene cycloisomerization products with or without catalyst. Interestingly, no acetate migration was observed (see ref. [1]).
- [15] The reason for this chemoselectivity is not well understood at this time.
- [16] J. K. Crandall, W. W. Conover, *J. Org. Chem.* **1978**, 43, 3533–3535.
- [17] CCDC-662258 contains 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.
- [18] M. Shi, L.-P. Liu, J. Tang, *Org. Lett.* **2006**, 8, 4043–4046.
- [19] We found that reaction of compounds **4** with SmI_2 gave a mixture of iodine-containing compounds **7** and reduction products **9**. The NMR data of these products are identical to those obtained with NIS for **7** and by gold-catalyzed cycloisomerization for **9**. Therefore, we believe that compounds of type **9** display the same stereochemical arrangement as compounds **7**.
- [20] Although the proposed stereochemistry of compounds **10** seems likely, it was not established by NOE experiments.

Received: September 25, 2007
Published online: November 22, 2007