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

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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 $PtCl_2$ or $PtCl_4$, 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, $PtCl_2$ and $PtCl_4$ 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.

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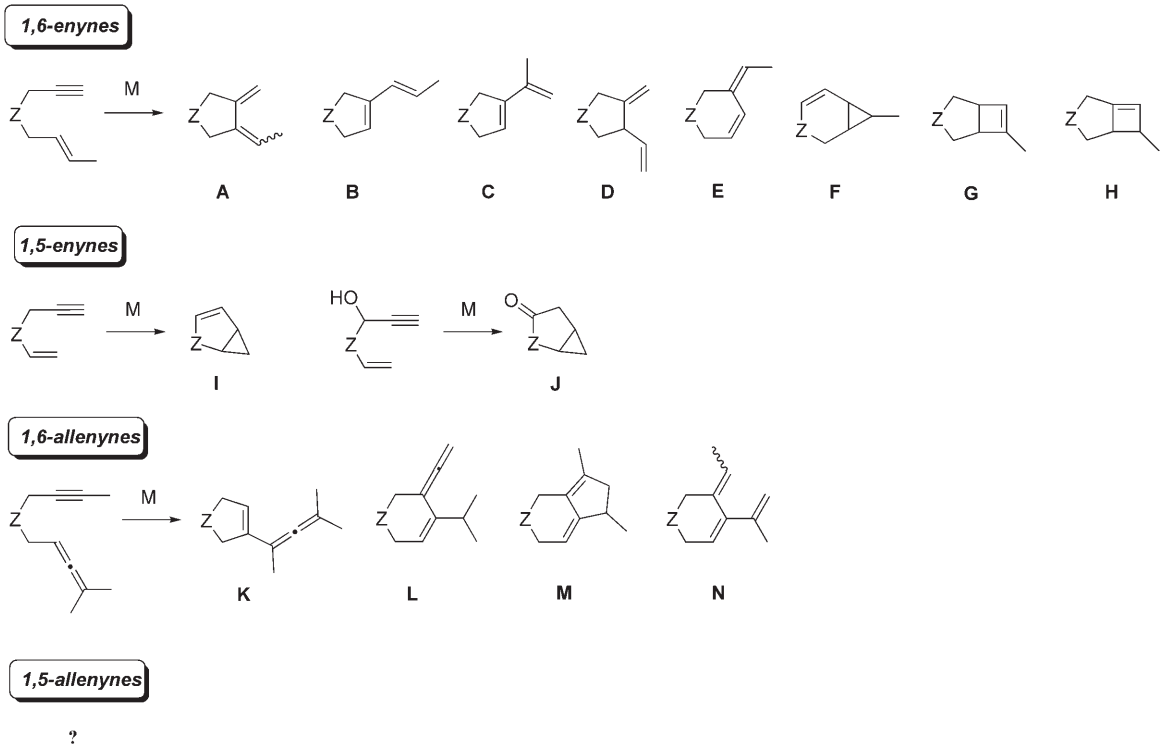
Results and Discussion

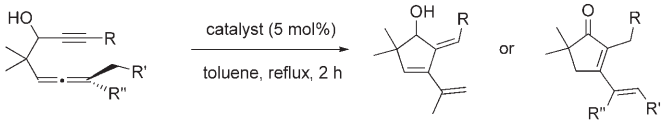
Starting compounds **1a**–**n** (see Tables 1 and 2) were prepared by addition of lithium acetylide to β-allenyl aldehydes. These precursors were obtained via Claisen–Cope rearrangement of propargyl vinyl ethers derived from *p*-toluenesulfonic acid-catalyzed condensation of aldehydes to propargyl alcohols, 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** ($R=SiMe_3$, Table 1, entry 1), **1d** ($R=Si\mathit{t}BuMe_2$, Table 1, entry 7), **1e** ($R=SiPhMe_2$, Table 1, entry 9), **1f** ($R=SiPh_3$, Table 1, entry 11), and **1g** ($R=Si\mathit{i}Pr_3$, Table 1, entry 13) were converted in high



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

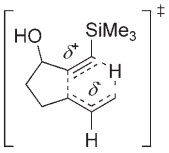
Table 1. Thermal or platinum-catalyzed cycloisomerization of hydroxylated 1,5-allenynes to cyclopentenols or cyclopentenones (yields of isolated products).



1a–k 2a–k 3a–k

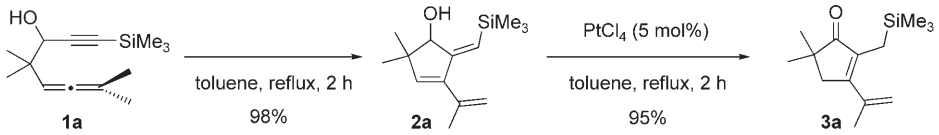
Entry	Substrate	R	R′	R″	Catalyst	Yield [%] (**2**/**3**)
1	**1a**	$SiMe_3$	H	Me	none	98/0
2	**1a**	$SiMe_3$	H	Me	$PtCl_4$	0/98
3	**1a**	$SiMe_3$	H	Me	$PtCl_2$	0/79
4	**1b**	$SiMe_3$	H	H	$PtCl_4$	0/48
5	**1b**	$SiMe_3$	H	H	$PtCl_2$	0/79
6	**1c**	$SiMe_3$	$(CH_2)_2$		$PtCl_4$	0/79
7	**1d**	$Si(t\mathrm{Bu})Me_2$	H	Me	none	89/0
8	**1d**	$Si(t\mathrm{Bu})Me_2$	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**	$Si\mathit{i}Pr_3$	H	Me	none	95/0
14	**1g**	$Si\mathit{i}Pr_3$	H	Me	$PtCl_4$	95/0
15	**1h**	CH_2Ph	H	Me	none	0/0
16	**1i**	$CH_2\mathit{i}Pr$	H	Me	none	0/0
17	**1j**	CH_2OMe	H	H	none	0/0
18	**1k**	CH_2OMe	H	Me	none	0/0
19	**1l**	$n\mathrm{C_6H_{13}}$	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 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 be stabilized by silyl groups (Scheme 2).



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 $PtCl_2$ or $PtCl_4$, 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 $ZnCl_2$ or $AlCl_3$, 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.

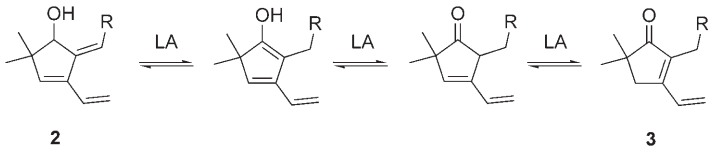


Scheme 3. Stepwise transformation of allenyne **1a** into cyclopentenone **3a**.

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 α,β,γ,δ-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).

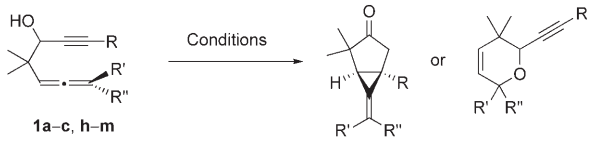
Cycloisomerization to 6-methylenebicyclo[3.1.0]hexan-3-one or 2-ethynyl-3,6-dihydro-2*H*-pyran derivatives: Efficient cycloisomerization of allenynes **1h–m** was achieved by using a catalytic amount of $PtCl_2$ or $PtCl_4$ (Table 2, entries 1–10). Instead of cyclopentenols of type **2** or cyclopentenones 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, 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 another C–C triple bond (**1m**, Table 2, entry 9).



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

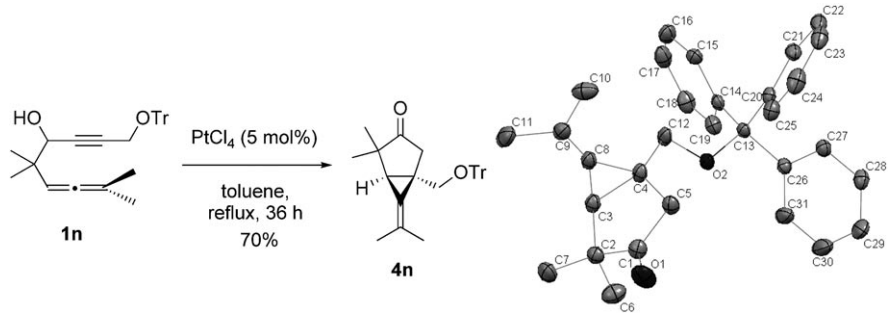
As expected, these compounds were obtained as single diastereomers of *cis* configuration at the ring junction, as confirmed by NOE experiments. Although most of these products were obtained as oils, we were able to obtain single crystals of the trityl derivative **4n** and carry out an X-ray diffraction 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_2Ph	Me	Me	$PtCl_4$ (5 mol%), toluene, reflux, 36 h	75/0
2	**1h**	CH_2Ph	Me	Me	$PtCl_2$ (5 mol%), toluene, reflux, 36 h	55/0
3	**1i**	CH_2iPr	Me	Me	$PtCl_4$ (5 mol%), toluene, reflux, 36 h	87/0
4	**1i**	CH_2iPr	Me	Me	$PtCl_2$ (5 mol%), toluene, reflux, 36 h	87/0
5	**1j**	CH_2OMe	Me	H	$PtCl_4$ (5 mol%), toluene, reflux, 36 h	85/0[a]
6	**1k**	CH_2OMe	Me	Me	$PtCl_4$ (5 mol%), toluene, reflux, 36 h	80/0
7	**1k**	CH_2OMe	Me	Me	$PtCl_2$ (5 mol%), toluene, reflux, 36 h	70/0
8	**1l**	nC_6H_{13}	Me	Me	$PtCl_4$ (5 mol%), toluene, reflux, 24 h	66/0
9	**1m**	$(CH_2)_3CCSiMe_3$	Me	Me	$PtCl_4$ (5 mol%), toluene, reflux, 36 h	68/0
10	**1m**	$(CH_2)_3CCSiMe_3$	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_2Cl_2, reflux, 1 h	0/96
12	**1b**	$SiMe_3$	Me	H	[AuCl(PPh$_3$)] (2 mol%), $AgSbF_6$ (2 mol%), CH_2Cl_2, reflux, 1 h	0/48[b]
13	**1c**	$SiMe_3$	$(CH_2)_5$		[AuCl(PPh$_3$)] (2 mol%), $AgSbF_6$ (2 mol%), CH_2Cl_2, reflux, 1 h	0/45
14	**1i**	CH_2iPr	Me	Me	[AuCl(PPh$_3$)] (2 mol%), $AgSbF_6$ (2 mol%), CH_2Cl_2, reflux, 1 h	0/72
15	**1k**	CH_2OMe	Me	Me	[AuCl(PPh$_3$)] (2 mol%), $AgSbF_6$ (2 mol%), CH_2Cl_2, reflux, 1 h	0/73
16	**1k**	CH_2OMe	Me	Me	[AuCl(PPh$_3$)] (2 mol%), $AgSbF_6$ (2 mol%), toluene, RT, 1 h	0/55
17	**1k**	CH_2OMe	Me	Me	AuCl (2 mol%), CH_2Cl_2, RT, 6 h	0/41
18	**1k**	CH_2OMe	Me	Me	$AuCl_3$ (2 mol%), CH_2Cl_2, RT, 6 h	0/55
19	**1k**	CH_2OMe	Me	Me	AuCl (2 mol%), toluene, reflux, 6 h	45/0
20	**1k**	CH_2OMe	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).

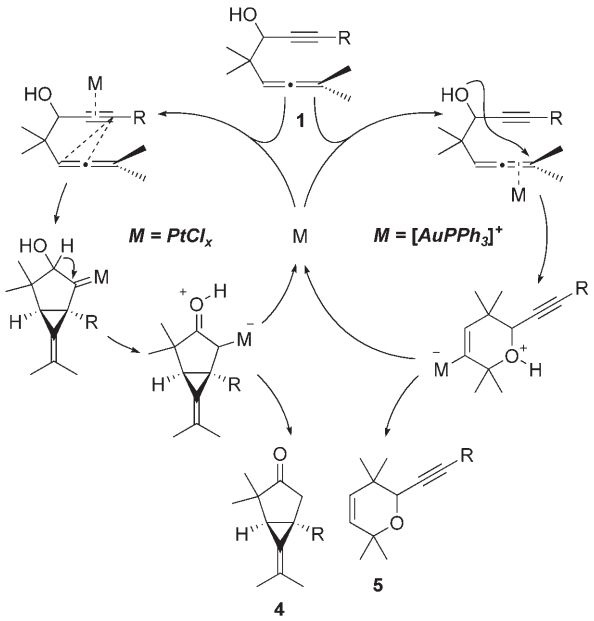


Scheme 5. Synthesis of **4n** and structure obtained from X-ray diffraction analysis.

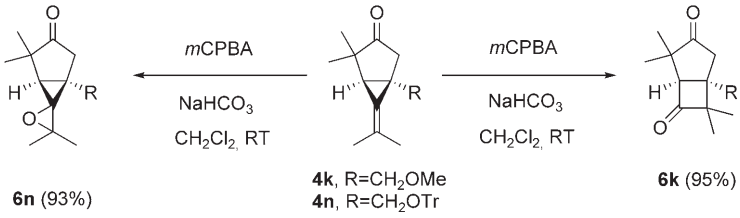
It seems clear that these bicyclic compounds arise from the activation of the triple bond by the platinum catalyst followed by intramolecular nucleophilic attack of the internal allene double bond, as in the case of hydroxylated 1,5-enynes.[2e] Although similar reactivity was expected with gold catalysts, a different outcome ensued: on using a catalytic amount of $[Au(PPh_3)]^+$, generated in situ from [AuCl-(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 $[Au(PPh_3)]^+$ 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 $[Au(PPh_3)]^+$ selectively activated the allene moiety, whereas $PtCl_x$ ($x=2,4$) activates only the triple bond (Scheme 6).[15]



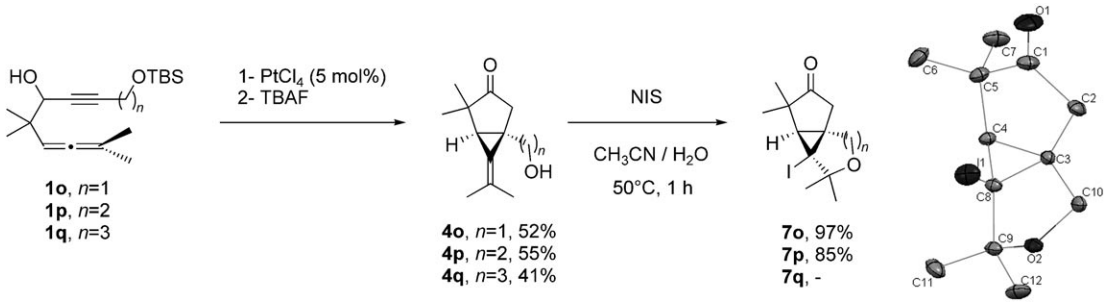
Scheme 6. Mechanistic interpretation ($x=2, 4$).



Scheme 7. Reaction of compounds of type **4** with *m*CPBA.

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 compound **6n** in 93% yield. On the other hand, diketone **6k** was regioselectively obtained in 95% yield from the less sterically crowded substrate **4k**. The ring junction proton resonates at $\delta=$ 3.27 ppm, which supports the proposed regiochemistry. It seems likely that, in this case, the spiranic framework is also formed but, due to a lack of kinetic 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-

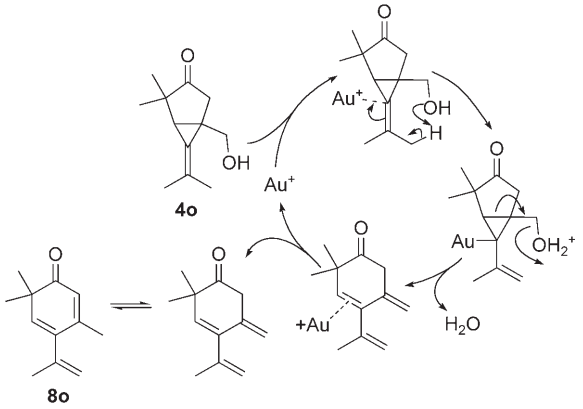


Scheme 8. Iodoalkoxylation of the 6-methylene bond.

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 $[Au(PPh_3)]^+$. 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-enone intermediate. After regeneration of the catalyst, this compound rearranges into the more stable α,β,γ,δ-unsaturated ketone **8o**.



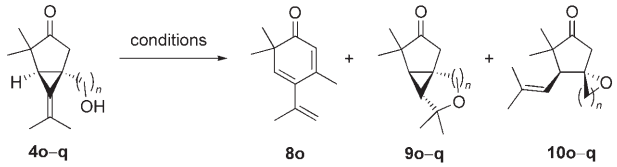
Scheme 9. Mechanistic rationale for Au^I-catalyzed transformations of **4o** into **8o**.

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

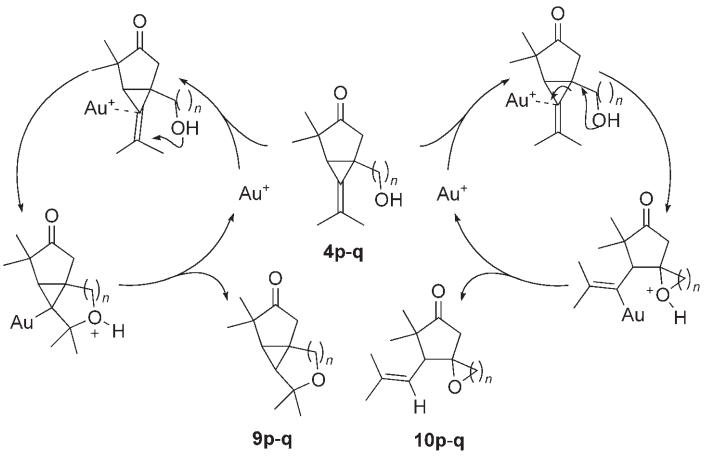
We have shown that hydroxylated 1,5-allenynes can be cycloisomerized in the presence of platinum- and gold-based catalysts to yield distinct products. Among them, 6-methylenebicyclo[3.1.0]hexan-3-ones were formed on using $PtCl_2$ or $PtCl_4$, whereas 2-ethynyl-3,6-dihydro-2*H*-pyrans were obtained with $[Au(PPh_3)]^+$. 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	$[AuCl(PPh_3)]$ (2 mol%), $AgSbF_6$ (2 mol%), CH_2Cl_2, reflux, 1 h	77/0/0
2	**4p**	2	$[AuCl(PPh_3)]$ (2 mol%), $AgSbF_6$ (2 mol%), CH_2Cl_2, reflux, 1 h	0/42/30[a]
3	**4q**	3	$[AuCl(PPh_3)]$ (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 $[Au(PPh_3)]^+$, 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, $[Au(PPh_3)]^+$ 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 (br s, 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 $C_{13}H_{22}OSiNa$: 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 $C_{17}H_{28}OSiNa$: 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 $C_{17}H_{30}OSiNa$: 301.1958; found: 301.1964.

1e (prepared from dimethylphenysilylacetylene 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 $C_{19}H_{26}OSiNa$: 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 $C_{29}H_{30}OSiNa$: 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 $C_{18}H_{22}ONa$: 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 $C_{15}H_{24}ONa$: 243.1725; found: 243.1719.

1j (prepared from methyl propargyl ether and 2,2-dimethyl-3,4-hexadienal, 47%): Colorless oil; ^{1}H 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 $C_{12}H_{18}O_2Na$: 217.1204; found: 217.1199.

1k (prepared from methyl propargyl ether and 2,2,5-trimethyl-3,4-hexadienal, 89%): Colorless oil; ^{1}H 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 $C_{13}H_{20}O_2Na$: 231.1361; found: 231.1357.

1l (prepared from 1-octyne and 2,2,5-trimethyl-3,4-hexadienal, 61%): Colorless oil; ^{1}H 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 $C_{17}H_{28}ONa$: 271.2038; found: 271.2032.

1m (prepared from hepta-1,6-diynyltrimethylsilane and 2,2,5-trimethyl-3,4-hexadienal, 58%): Colorless oil; ^{1}H 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 $C_{19}H_{30}OSiNa$: 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; ^{1}H 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 $C_{31}H_{32}O_2Na$: 459.2297; found: 459.2294.

1o (prepared from *tert*-butyl(dimethyl)(2-propynoxy)silane and 2,2,5-trimethyl-3,4-hexadienal, 87%): Colorless oil; ^{1}H 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 $C_{18}H_{32}O_2SiNa$: 331.2069; found: 331.2063.

1p (prepared from *tert*-butyl(dimethyl)(3-butynoxy)silane and 2,2,5-trimethyl-3,4-hexadienal, 66%): Colorless oil; ^{1}H 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 $C_{19}H_{34}O_2SiNa$: 345.2226; found: 345.2221.

1q (prepared from *tert*-butyl(dimethyl)(4-pentynoxy)silane and 2,2,5-trimethyl-3,4-hexadienal, 69%): Colorless oil; ^{1}H 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 ($c=0.05$ 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 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 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 $[Au(PPh_3)]SbF_6$-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; ^{1}H 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; ^{1}H 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; ^{1}H 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; ^{1}H 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 $C_{14}H_{24}OsiNa$: 259.1494; found: 259.1485.

3b: Colorless oil; ^{1}H 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 $C_{13}H_{22}OSiNa$: 245.1338; found: 245.1326.

3c: Colorless oil; ^{1}H 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 cm^{-1}; HRMS (ES+, M+H): calcd for $C_{17}H_{29}OSi$: 277.1988; found: 277.1982.

3d: Colorless oil; ^{1}H 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 cm^{-1}.

3e: Colorless oil; ^{1}H 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 cm^{-1}.

4h: Colorless oil; ^{1}H 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 Hz, 1H), 2.67 (d, B of AB, J = 17.9 Hz, 1H), 2.80 (d, A of AB, J = 13.6 Hz, 1H), 3.02 (d, B of AB, J = 13.6 Hz, 1H), 7.13–7.39 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ = 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 cm^{-1}; HRMS (ES+) calcd for $C_{18}H_{22}ONa$: 277.1568; found: 277.1566.

4i: Colorless oil; ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (d, J = 6.5 Hz, 3H), 0.97 (d, J = 6.5 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 Hz, 1H), 2.73 ppm (d, B of AB, J = 17.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 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 cm^{-1}; HRMS (ES+) calcd for $C_{15}H_{24}ONa$: 273.1467; found: 273.1463.

4j (*E* isomer): Colorless oil; ^{1}H NMR ($CDCl_3$): $\delta = 1.07$ (s, 3H), 1.19 (s, 3H), 1.79 (d, J = 6.5 Hz, 3H), 1.80 (s, 1H), 2.28 (d, A of AB, J = 17.9 Hz, 1H), 2.94 (d, B of AB, J = 17.9 Hz, 1H), 3.37 (s, 3H), 3.38 (d, A of AB, J = 10.3 Hz, 1H), 3.51 (d, B of AB, J = 10.3 Hz, 1H), 5.94 ppm (qd, J = 6.5, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 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 cm^{-1}; HRMS (ES+) calcd for $C_{12}H_{18}O_2Na$: 217.1204; found: 217.1199.

4j (*Z* isomer): Colorless oil; ^{1}H 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 Hz, 1H), 2.32 (d, A of AB, J = 18.1 Hz, 1H), 2.97 (d, B of AB, J = 18.1 Hz, 1H), 3.35 (d, A of AB, J = 10.4 Hz, 1H), 3.38 (s, 3H), 3.67 (d, B of AB, J = 10.4 Hz, 1H), 5.89 ppm (qd, J = 6.5, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 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 cm^{-1}; HRMS (ES+) calcd for $C_{12}H_{18}O_2Na$: 217.1204; found: 217.1199.

4k: Colorless oil; ^{1}H 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 Hz, 1H), 2.96 (d, B of AB, J = 17.9 Hz, 1H), 3.30 (d, A of AB, J = 10.3 Hz, 1H), 3.39 (s, 3H), 3.66 ppm (d, B of AB, J = 10.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 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 cm^{-1}; HRMS (ES+) calcd for $C_{13}H_{20}O_2Na$: 231.1361; found: 231.1355.

4l: Colorless oil; ^{1}H 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 Hz, 1H), 1.74 (d, J = 1.2 Hz, 3H), 1.75 (s, 3H), 2.25 (d, A of AB, J = 17.9 Hz, 1H), 2.78 ppm (d, B of AB, J = 17.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 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 cm^{-1}; HRMS (ES+) calcd for $C_{17}H_{28}ONa$: 271.2038; found: 271.2035.

4m: Colorless oil; ^{1}H 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 Hz, 1H), 2.69 ppm (d, B of AB, J = 17.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 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 $C_{19}H_{30}OSiNa$: 325.1964; found: 325.1958.

4n: White solid; m.p. 118–120 °C; ^{1}H 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 Hz, 1H), 3.12 (d, B of AB, J = 18.2 Hz, 1H), 3.14 (d, A of AB, J = 9.6 Hz, 1H), 3.42 (d, B of AB, J = 9.6 Hz, 1H), 7.25–7.38 (m, 8H), 7.42–7.53 ppm (m, 7H); ^{13}C NMR ($CDCl_3$): δ = 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 cm^{-1}; HRMS (ES+) calcd for $C_{31}H_{32}O_2Na$: 459.2297; found: 459.2295; elemental analysis calcd (%) for $C_{31}H_{32}O_2$: C 85.27, H 7.39; found: C 85.31, H 7.25.

4o: Colorless oil; ^{1}H 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 Hz, 1H), 2.96 (d, B of AB, J = 18.2 Hz, 1H), 3.57 (d, A of AB, J = 11.4 Hz, 1H), 3.88 ppm (d, B of AB, J = 11.4 Hz, 1H), OH unobserved; ^{13}C NMR ($CDCl_3$): δ = 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 $C_{12}H_{18}O_2Na$: 217.1204; found: 217.1199.

4p: Colorless oil; ^{1}H 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 Hz, 2H), 2.33 (d, A of AB, J = 18.2 Hz, 1H), 2.78 (d, B of AB, J = 18.2 Hz, 1H), 3.74 ppm (t, J = 7.0 Hz, 2H), OH unobserved; ^{13}C NMR ($CDCl_3$): δ = 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 $C_{13}H_{20}O_2Na$: 231.1361; found: 231.1356.

4q: Colorless oil; ^{1}H 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 Hz, 1H), 2.68 (d, B of AB, J = 18.2 Hz, 1H), 3.56–3.71 ppm (m, 2H), OH unobserved; ^{13}C NMR ($CDCl_3$): δ = 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 $C_{14}H_{22}O_2Na$: 245.1517; found: 245.1512.

5a: Colorless oil; ^{1}H 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 Hz, 1H), 5.48 ppm (d, J = 10.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 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; ^{1}H NMR ($CDCl_3$): $\delta = 0.17$ (s, 9H), 0.98 (s, 3H), 1.12 (s, 3H), 1.24 (d, J = 6.6 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 ($CDCl_3$): δ = 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 cm^{-1}; HRMS (ES+) calcd for $C_{13}H_{22}OSiNa$: 245.1338; found: 245.1335.

5b (minor isomer): Colorless oil; ^{1}H NMR ($CDCl_3$): $\delta = 0.17$ (s, 9H), 1.06 (s, 3H), 1.07 (s, 3H), 1.24 (d, J = 6.8 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 ($CDCl_3$): δ = 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 cm^{-1}; HRMS (ES+) calcd for $C_{13}H_{22}OSiNa$: 245.1338; found: 245.1335.

5c: Colorless oil; ^{1}H 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 Hz, 1H), 5.58 ppm (d, J = 10.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 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,

CH_2), 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 ($CDCl_3$): $\delta=0.97$ (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); ^{13}C NMR ($CDCl_3$): $\delta=22.1$ (2C, CH_3), 22.6 (CH_3), 25.44 (CH_3), 25.45 (CH_3), 28.1 (CH), 28.2 (CH_2), 29.7 (CH_3), 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 ($CDCl_3$): $\delta=0.97$ (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); ^{13}C NMR ($CDCl_3$): $\delta=22.5$ (CH_3), 25.2 (CH_3), 25.3 (CH_3), 29.5 (CH_3), 35.0 (C), 57.6 (CH_3), 60.09 (CH_2), 69.9 (CH), 73.7 (C), 81.4 (C), 84.0 (C), 132.0 (CH), 133.5 ppm (CH); HRMS (ES+) calcd for $C_{13}H_{20}O_2Na$: 231.1361; found: 231.1355.

General procedure for oxidation with *m*CPBA: A solution of **4k–n** (1.2 mmol) in dry CH_2Cl_2 (10 mL) was treated with $NaHCO_3$ (192 mg, 2.2 mmol) and *m*CPBA (70%, 430 mg, 1.74 mmol). The mixture was stirred at room temperature for 2 h, diluted with a saturated aqueous $NaHCO_3$ solution, vigorously stirred for 15 min, and extracted with CH_2Cl_2. The combined organic layers were washed successively with water and then brine, dried over $MgSO_4$, 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 ($CDCl_3$): $\delta=1.00$ (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); ^{13}C NMR ($CDCl_3$): $\delta=19.2$ (CH_3), 19.3 (CH_3), 20.1 (CH_3), 27.6 (CH_3), 41.2 (CH_2), 41.4 (C), 48.9 (C), 59.3 (CH_3), 61.4 (C), 71.1 (CH), 75.8 (CH_2), 214.7 (C), 220.7 ppm (C); IR (neat): $\tilde{\nu}=1736$, $1770\ cm^{-1}$; HRMS (ES+) calcd for $C_{13}H_{20}O_3Na$: 247.1311; found: 247.1304.

6n: Colorless oil; ^1H NMR ($CDCl_3$): $\delta=1.12$ (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); ^{13}C NMR ($CDCl_3$): $\delta=20.1$ (CH_3), 22.4 (CH_3), 22.5 (CH_3), 24.0 (C), 27.1 (CH_3), 30.0 (CH), 38.5 (CH_2), 47.9 (C), 63.1 (CH_2), 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 $C_{31}H_{32}O_3Na$: 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 CH_3CN (1 mL) and H_2O (0.5 mL) was stirred for 1 h at 50°C. The reaction was quenched with a saturated aqueous solution of $Na_2S_2O_3$, extracted with diethyl ether, dried over $MgSO_4$, 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 ($CDCl_3$): $\delta=1.11$ (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); ^{13}C NMR ($CDCl_3$): $\delta=18.1$ (CH_3), 22.3 (CH_3), 28.6 (CH_3), 29.0 (CH_3), 33.4 (C), 35.0 (C), 36.3 (CH), 39.4 (CH_2), 50.9 (C), 66.4 (CH_2), 85.3 (C), 216.4 ppm (C); HRMS (ES+) calcd for $C_{12}H_{17}O_2INa$: 343.0171; found: 343.0165.

7p: Colorless oil; ^1H NMR ($CDCl_3$): $\delta=1.11$ (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); ^{13}C NMR ($CDCl_3$): $\delta=19.2$ (CH_3), 24.2 (CH_2), 26.1 (C), 26.6 (CH_3), 27.9 (CH_3), 28.5 (CH_3), 37.8 (CH), 41.4 (C), 50.4 (CH_2), 51.7 (C), 57.4 (CH_2), 74.5 (C), 217.9 ppm (C); IR (neat): $\tilde{\nu}=$ $1739\ cm^{-1}$; HRMS (ES+) calcd for $C_{13}H_{19}O_2INa$: 357.0327; found: 357.0324.

8o: Colorless oil; ^1H NMR ($CDCl_3$): $\delta=1.16$ (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); ^{13}C NMR ($CDCl_3$): $\delta=21.3$ (CH_3), 24.3 (CH_3), 25.6 (CH_3), 46.1 (C), 115.6 (CH_2), 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 $C_{12}H_{16}ONa$: 199.1099; found: 199.1093.

9o: Colorless oil; ^1H NMR ($CDCl_3$): $\delta=0.90$ (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); ^{13}C NMR ($CDCl_3$): $\delta=$ 20.3 (CH_3), 24.5 (CH_3), 25.9 (CH_3), 27.0 (CH_3), 29.6 (C), 32.7 (CH), 37.1 (CH), 38.0 (C), 47.6 (C), 67.7 (CH_2), 81.2 (C), 218.8 ppm (C); IR (neat): $\tilde{\nu}=1739\ cm^{-1}$; HRMS (ES+) calcd for $C_{12}H_{18}O_2Na$: 217.1204; found: 217.1200.

9p: Colorless oil; ^1H NMR ($CDCl_3$): $\delta=0.27$ (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); ^{13}C NMR ($CDCl_3$): $\delta=19.9$ (C), 20.54 (CH_3), 25.2 (CH_2), 26.6 (CH_3), 27.4 (CH), 28.2 (CH), 32.5 (CH_3), 24.7 (CH_3), 45.8 (CH_2), 48.5 (C), 57.7 (CH_2), 69.5 (C), 220.7 ppm (C); IR (neat): $\tilde{\nu}=1738\ cm^{-1}$.

10p: Colorless oil; ^1H NMR ($CDCl_3$): $\delta=0.94$ (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); ^{13}C NMR ($CDCl_3$): $\delta=17.1$ (CH_3), 18.1 (CH_3), 20.0 (CH_3), 27.8 (CH_3), 31.2 (CH_2), 40.8 (CH_2), 42.2 (CH), 55.8 (C), 66.0 (CH_2), 94.8 (C), 121.2 (CH), 138.2 (C), 221.1 ppm (C); IR (neat): $\tilde{\nu}=1735\ cm^{-1}$; HRMS (ES+) calcd for $C_{13}H_{20}O_2Na$: 231.1361; found: 231.1355.

10q: White solid; m.p. 146–147°C; ^1H NMR ($CDCl_3$): $\delta=0.89$ (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); ^{13}C NMR ($CDCl_3$): $\delta=$ 18.3 (CH_3), 20.7 (CH_3), 25.6 (CH_3), 26.1 (CH_2), 26.5 (CH_3), 33.0 (CH_2), 50.4 (C), 50.6 (CH_2), 54.4 (CH), 67.0 (CH_2), 87.2 (C), 120.0 (CH), 136.1 (C), 221.2 ppm (C); IR (neat): $\tilde{\nu}=1737\ cm^{-1}$; HRMS (ES+) calcd for $C_{14}H_{22}O_2Na$: 245.1517; found: 245.1512.

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[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.

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[20] Although the proposed stereochemistry of compounds **10** seems likely, it was not established by NOE experiments.

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