Gold(I)-Catalyzed Cyclodehydration Enabled by the Triisopropylsilyl Group: A Synthetically Versatile Methodology

by **Dmitry L. Usanov**[a])[1]), **Marina Naodovic**[a])[2]), **Malte Brasholz**[a])[3]), and **Hisashi Yamamoto***[a])[b])

[a]) Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, IL, 60637, USA (e-mail: yamamoto@uchicago.edu)
[b]) Adjunct affiliation: Chemistry Department, King Abdulaziz University, Jeddah, 21589, Saudi Arabia

Dedicated to Prof. *Dieter Seebach* on the occasion of his 75th birthday

Introduction of a triisopropylsilyl group into allyl and allenyl carbinols greatly enhances the efficiency of gold(I)-catalyzed cyclodehydration, which can provide rapid access to a library of various compounds including 1*H*-indenes (*Table 2* and *Scheme 5*), benzofulvenes (*Table 3*), indan-2-ones (*Scheme 2*), fulvenes (*Table 4*), cyclopentadienes (*Table 4*), 5*H*-dibenzo[*a,c*][7]annulenes (*Scheme 6*) and dibenzosuberones (*Scheme 6*). The developed method enables unprecedented product generality for several classes of cyclodehydration reactions, which is particularly notable for the preparation of 1*H*-indenes. The first synthesis of non-benzo-fused fulvenes *via* cyclodehydration of allenyl vinyl carbinols could be accomplished. The protocol is remarkable for mild conditions, operational convenience, and easy access to starting materials.

Introduction. – In the recent years, gold salts and complexes have been extensively utilized as powerful and versatile catalysts for a large number of organic transformations, being usually notable for high reactivity, chemoselectivity, and mild reaction conditions [1]. Our recent communication [2] provided another contribution to the field of gold catalysis describing the beneficial effect of the triisopropylsilyl (TIPS) group on the efficiency of Au^I-mediated cyclodehydration. In this report, we would like to consider this methodology in a broader context and emphasize its convenience and significant synthetic potential[4]).

1*H*-Indene Synthesis. – Cyclodehydration of easily accessible allyl alcohols is one of the most straightforward approaches to the 1*H*-indene scaffold. However, before the disclosure of our results [2], the majority of existing methods involved the use of strong *Lewis* or *Brønsted* acids and required the presence of multiple aryl/alkyl stabilizing groups in the substrates [3]. Thus, the synthesis of minimally functionalized 1*H*-indenes

---

[1])   Current Address: Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA 02138, USA.
[2])   Current Address: Department of Chemistry, University of Rochester, RC Box 270216, Rochester, NY, 14627, USA.
[3])   Current Address: Institute of Organic Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg.
[4])   Data of compounds not given in the *Exper. Part* are available in the Supporting Information to [2].

was beyond the scope of dehydrative cyclization. On the contrary, we discovered that introduction of a triisopropylsilyl auxiliary group alleviates the necessity of polysubstitution and enables excellent yields in the 1*H*-indene synthesis catalyzed by a milder system consisting of chloro(triphenylphosphine)gold(I) ([AgCl(PPh$_3$)]) and silver hexafluoroantimonate(V) (AgSbF$_6$). The efficiency of the catalysis appeared to be strongly dependent on steric factors: bulkier silyl moieties provided better yields (*Table 1*). The nature of the catalyst and the silyl auxiliary demonstrated synergistic effects on the reaction outcome: classical *Lewis* acids, *e.g.*, boron trifluoride, could also be employed with silylated substrates albeit with significantly lower yields; an identical trend with respect to the size of the silyl moiety was observed (*Table 1*).

Table 1. *Influence of the Catalyst and the Silyl Group on the 1*H-*Indene Synthesis*
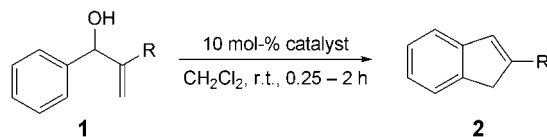
R ^{a})	Yield [%]	
	BF$_3 \cdot$ Et$_2$O	[AuCl(PPh$_3$)]
H	< 1	< 1
TMS	6	5
TES	51	56
TIPS	67	92

^{a}) Abbreviations: TMS = trimethylsilyl, TES = triethylsilyl, TIPS = triisopropylsilyl.

On the contrary to the [AuCl(PPh$_3$)]/AgSbF$_6$ system, other gold catalysts appeared to be of low preparative importance, with the notable exception of gold(III) chloride which demonstrated efficient catalysis albeit with somewhat lower yields. The use of the [AuCl(PPh$_3$)]/AgBF$_4$ combination furnished a similar outcome; however, the catalytic system involving AgSbF$_6$ appeared to be more stable. The use of gold(I) choride resulted in virtually no turnover due to the rapid decomposition of the catalyst. AuBr$_3$ provided far inferior results compared to the corresponding chloride. A gold(I) system with a more electron-rich phosphine ligand ([1,1′-biphenyl]-2-yl)di(*tert*-butyl)phosphine) was shown to be catalytically inactive even with the most reactive substrates. NHC-Derived systems (NHC = N-heterocyclic carbene ligand) did not render the reaction sufficiently clean.

As can be seen from *Table 2*, various types of products **2** can be obtained in excellent yields from allyl alcohols **1** with the [AuCl(PPh$_3$)]/AgSbF$_6$ system. This involves the simple benzaldehyde-derived 1*H*-indenes **2a – 2g** as well as the products obtained from naphthalenecarboxaldehydes (see **2h** and **2i**) and ketones (see **2j – 2n**). Substitution at position 1 of the 1*H*-indene product was possible by the use of terminally alkylated substrate **1f**. The naphthalene-2-carboxaldehyde-derived substrate **1i** demonstrated exclusive formation of angular product **2i**. It is particularly noteworthy that the isomeric couples **2h/2i** and **2f/2j** could be isolated without any complications associated with the C=C bond scrambling, which would take place under

Table 2. *Substrate Screening for Au^I-Catalyzed Cyclodehydration*^{a}). TIPS = ^{i}Pr$_3$Si.
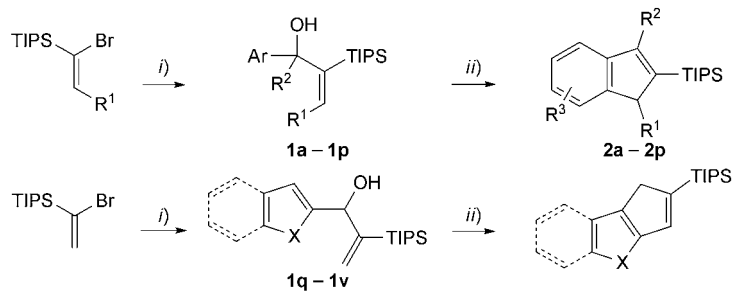
		Yield [%]^b)			Yield [%]^b)
1a		90	**2a**		92
1b		92	**2b**		97
1c		96	**2c**	5-Me/7-Me 1.7:1	92
1d		72	**2d**	5-Br/7-Br 3.3:1	70
1e		92	**2e**		91
1f		73	**2f**		99
1g		96	**2g**		80
1h		93	**2h**		99

Table 2 (cont.)
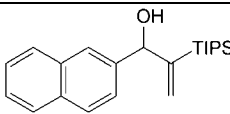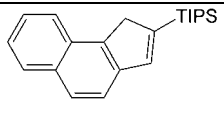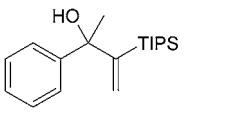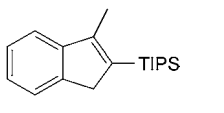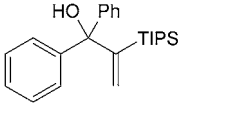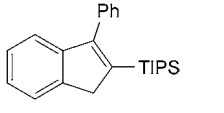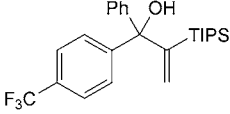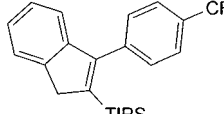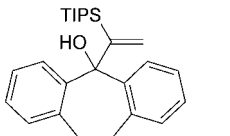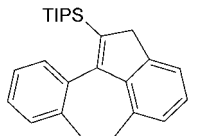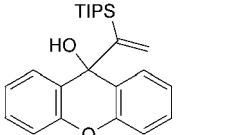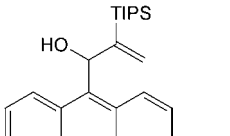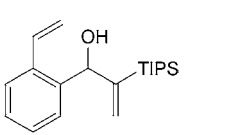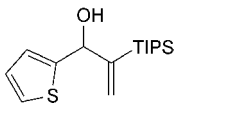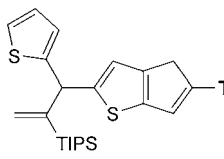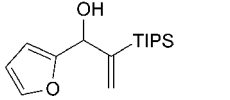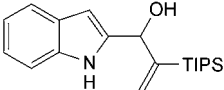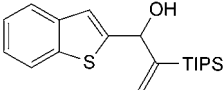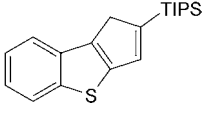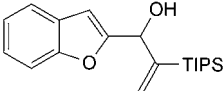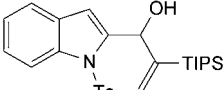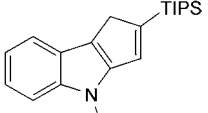
		Yield [%][b]			Yield [%][b]
1i		99	**2i**		87
1j		75 [c]	**2j**		82 [d]
1k		97	**2k**		99
1l		77	**2l**		94
1m		99	**2m**		90 [d]
1n		99	**2n**	no reaction	–
1o		99	**2o**	–[e]	–
1p		61	**2p**	–[e]	–
1q		72 [f]	**2q**		35 [g]
1r		76 [f]	**2r**	–[e]	–

Table 2 (cont.)

		Yield [%][b])				Yield [%][b])
1s		99 [h])	**2s**	–[e])		–
1t		95	**2t**			84
1u		94	**2u**	–[e])		–
1v		69	**2v**			91

[a])Reaction conditions: *i*) 1. BuLi, THF, $-78°$, 1 h; 2. 0.8 equiv of aldehyde or ketone, THF, $-78°$, 1 h. *ii*) 10 mol-% [AuCl(PPh₃)], 10 mol-% AgSbF₆, CH₂Cl₂, r.t., 10 min to 2 h. [b]) Yield of isolated **1** or **2** after CC. [c]) Prepared *via* transmetallation of the organolithium compound with 2 LiCl·CeCl₃ for 1 h at $-78°$, followed by the addition at $-78°$ for 16 h. [d]) Carried out at $0°$. [e]) A complex mixture of products was obtained. [f]) A bromide/aldehyde ratio of 1:1 was used. [g]) Reaction conditions: 10 mol-% [AuCl(P(*o*-tol)₃)], 10 mol-% AgSbF₆, CH₂Cl₂, $-20°$, 9 h. [h]) A bromide/aldehyde ratio of 2.5:1 was used.

Brønsted acid catalysis. *meta*-Substituted benzaldehyde derivatives expectedly furnished mixtures of isomers; *meta*-bromo substrate **1d** demonstrated greater regioselectivity (3.3:1) compared to its *meta*-methyl counterpart **1c** (1.7:1), which apparently is due to the combination of steric and electronic factors. Interestingly, di-*ortho*-alkylated substrate **1g** could also undergo annulation resulting in rearranged product **2g**; this can easily be explained by a 1,2-methyl shift in the intermediate cationic species (*Scheme 1*) [4].

Scheme 1. *Rationale for the Rearrangement on the Way to* **2g** *and the Loss of the TIPS Group Concomitant with the Formation of* **2j** [4]
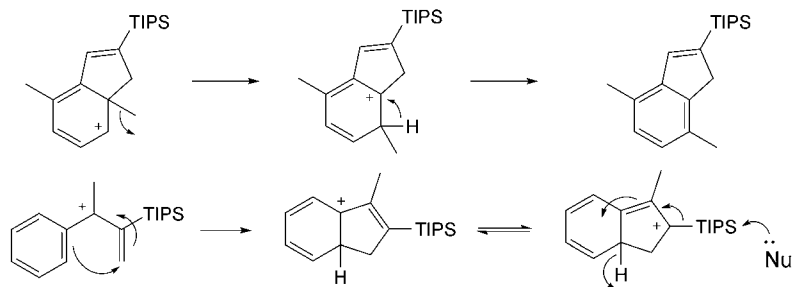
Alcohols derived from both alkyl aryl (see **1j**) and aryl aryl ketones (see **1k** – **1m**) could be employed with equal success. Indeed, a complete regioselectivity of annulation was observed for the benzophenone-derived substrate **1l** with a deactivated aryl moiety. Besides 1*H*-indenes, a tetracyclic system **2m** could be constructed from dibenzosuberone ($=5H$-dibenzo[*a,d*]cyclohepten-5-one). An analogous transformation could not be accomplished with **1n**, which is a precursor to an antiaromatic cation; the starting material was isolated back unaltered. Notably, for substrates **1j** and **1m**, partial loss of the silyl moiety was detected when the reactions were run at room temperature; this might be associated with longer lifetimes of the more stable intermediates, which increases the chances of the silyl moiety to be attacked by some nucleophilic species (*Scheme 1*). Fortunately, this issue could be easily overcome by carrying out the catalysis at 0°. The attempts to prepare 6- and 7-membered rings were not successful: complex mixtures of products were obtained on exposure of substrates **1o** and **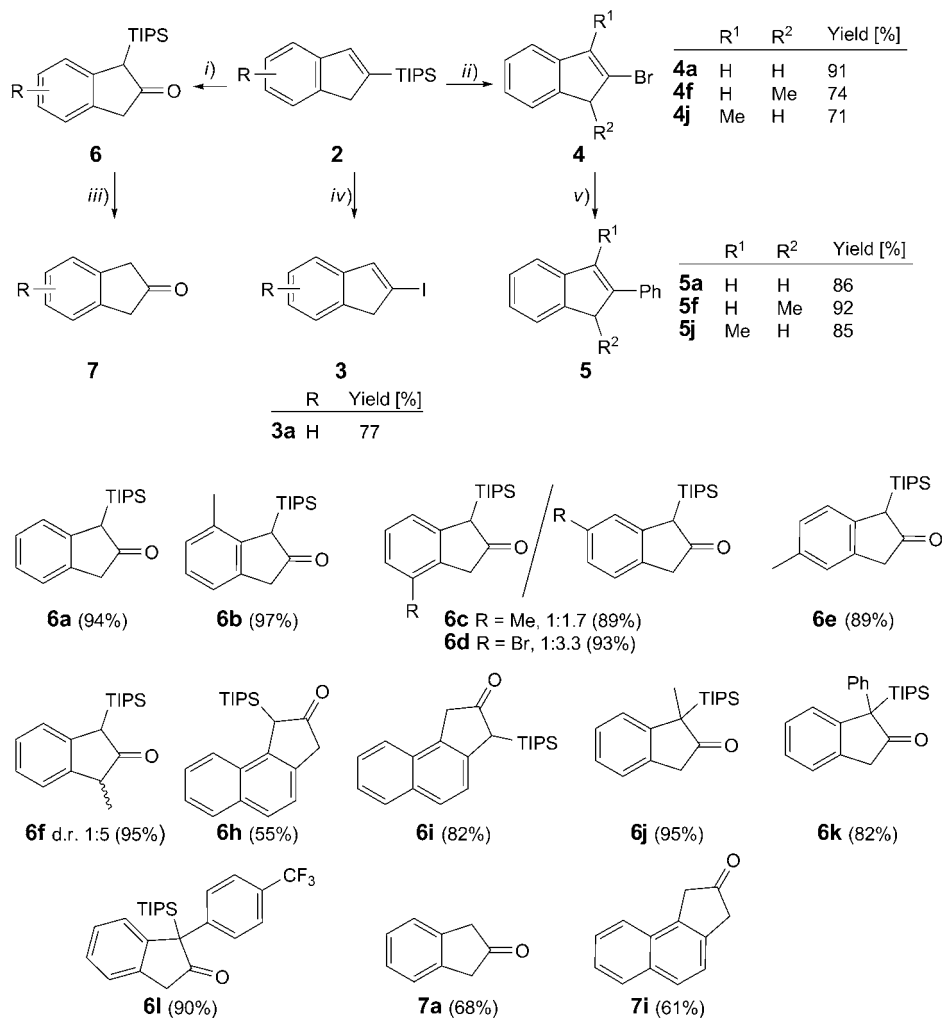1p** to the gold(I) catalytic system. However, the construction of 7-membered rings *via* the developed methodology was achieved on a different type of substrates – *vide infra*.

We then turned our attention to the more sensitive heterocyclic substrates **1q** – **1s**. The standard reaction conditions resulted in rapid decomposition of the thiophene derivative **1q**; however, conducting the catalysis at $-20°$ enabled isolation of dimeric compound **2q** as a result of aromatic substitution in the highly reactive bicyclic dehydration product. No preparative outcome could be achieved for the furan counterpart **1r**. We decided to tune the reactivity of heterocyclic substrates by the introduction of benzo fusion, which enabled the isolation of tricyclic product **2t** from **1t** but was not helpful for the furan analogue **1u**. The reactivity of the highly activated 1*H*-indole derivative **1s** could also be successfully tuned; the introduction of an *N*-tosyl moiety resulted in clean cyclodehydration of **1v** leading to compound **2v**. Despite the inapplicability of the developed methodology to a number of reactive heterocyclic systems, the possibility to isolate the sensitive products **2t** and **2v** in high yields is quite remarkable, as these compounds would not be compatible with conventional *Lewis* or *Brønsted* acids previously utilized for cyclodehydration.

Catalyst loadings lower than 10 mol-% could also be used for efficient cyclodehydration as exemplified for substrate **1h**: the use of 5 mol-% of [AuCl(PPh$_3$)]/AgSbF$_6$ still furnished the 1*H*-indene product **2h** in excellent yield (99%). Further decrease of the gold content was possible (1 mol-%); however, a lower yield was achieved (82%), presumably due to catalyst decomposition. The use of 10 mol-% was chosen for the substrate-screening experiments (*Table 2*) due to the generally higher yields compared to lower catalyst loadings.

It is important to emphasize the sharp contrast between our methodology and the previous approaches involving polysubstituted compounds. As the presence of a sole silyl auxiliary group is sufficient for clean cyclodehydration, silyl 1*H*-indenes with unsubstituted positions 1 and 3 could be easily prepared. Moreover, unlike alkyl or aryl stabilizing groups, the triisopropylsilyl moiety is labile and could be replaced by other groups. As shown in *Scheme 2*, the synthetic versatility of the TIPS group in 1*H*-indenes **2** can provide access to a number of different types of compounds. Halodesilylation [5] enabled preparation of synthetically valuable 2-iodo- and 2-bromo-1*H*-indenes **3** and **4**, which in turn could be converted to the arylated 1*H*-indenes **5** *via Suzuki* coupling. The

Scheme 2. *Synthetic Utility of Silyl 1H-Indenes* **2**

	R¹	R²	Yield [%]
4a	H	H	91
4f	H	Me	74
4j	Me	H	71

	R¹	R²	Yield [%]
5a	H	H	86
5f	H	Me	92
5j	Me	H	85

	R	Yield [%]
3a	H	77

6a (94%)   **6b** (97%)   **6c** R = Me, 1:1.7 (89%)   **6e** (89%)
6d R = Br, 1:3.3 (93%)

6f d.r. 1:5 (95%)   **6h** (55%)   **6i** (82%)   **6j** (95%)   **6k** (82%)

6l (90%)   **7a** (68%)   **7i** (61%)

i) Epoxidation/*Meinwald* rearrangement: 1. *m*-chloroperbenzoic acid, CH₂Cl₂; 2. 0.1 mol-% (CF₃SO₂)₂NH. *ii*) *N*-Bromosuccinimide, (CF₃)₂CHOH, CH₂Cl₂. *iii*) Bu₄NF, THF. *iv*) *N*-Iodosuccinimide, (CF₃)₂CHOH, CH₂Cl₂. *v*) *Suzuki* coupling: PhB (OH)₂, [Pd(OAc)₂], P(*o*-tol)₃, Ba(OH)₂.

epoxidation/*Meinwald* rearrangement sequence is noteworthy as a convenient route to α-silyl-substituted indan-2-ones **6**. Whereas the overwhelming majority of studies on the *Meinwald* rearrangement involves the use of *Lewis* acids [6], we could carry out this transformation without introduction of any metal species; it is particularly notable that as low as 0.1 mol-% of triflimide ((CF₃SO₂)₂NH) was sufficient for a rapid one-pot isomerization. The possibility to run this process under so mild conditions apparently stems from the electronic influence of the silyl moiety, as the developing positive charge

can be stabilized by hyperconjugation (β-Si effect) [7]. The silyl indanones **6** could also be easily desilylated to furnish unsubstituted indan-2-ones **7**. Thus, the presence of the silyl auxiliary not only enabled the 1*H*-indene synthesis but also significantly increased the synthetic value of the resulting 1*H*-indene products.

The general nature of the developed methodology is additionally emphasized by the convenient accessibility of the starting materials. The common precursor of compounds **1** could be easily synthesized in three steps in 82% overall yield (*Scheme 3*, R = H) [8]. This approach employed inexpensive chemicals and was operationally straightforward; the intermediate reactions proceeded cleanly so that only one purification step was required for the whole sequence. Substituted analogues could also be prepared likewise by using various *Grignard* reagents in the second step [8b] (*Scheme 3*), which provided ample functionalization opportunities at position 1 of the silyl 1*H*-indene products (exemplified herein by the methylated compound **2f**).

Scheme 3. *Preparation of the Precursors for Silylated Allyl Alcohols* **1**. TIPS = $^{i}Pr_3Si$; LDA = lithium diisopropylamide.
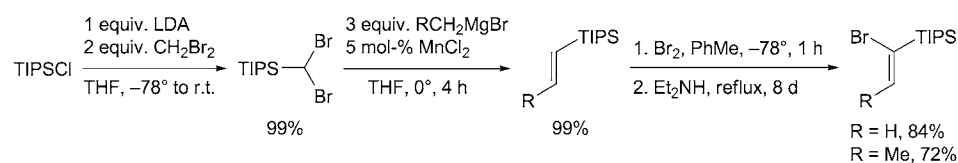
Silylated allyl alcohols **1** were prepared *via* standard organolithium chemistry at $-78°$; it is noteworthy that undesired elimination leading to (triisopropylsilyl)acetylene proceeded under these conditions, which could result in the formation of *ca.* 10% of the corresponding propargylic alcohols. Fortunately, this problem was solved by using an aldehyde/bromovinylsilane ratio of 1:1.25 as the undesired alkynyllithium species were far less reactive at $-78°$ compared to the vinyl counterparts. Substrate **1j** derived from highly enolizable acetophenone was prepared *via* transmetallation of the organolithium species with the 2 LiCl · CeCl$_3$ complex [9].

Preparation of Benzofulvenes. – Along with the cyclodehydration of allyl alcohols (*vide supra*) we considered an analogous transformation with allenyl carbinols leading to benzofulvenes. Only few protocols involving direct construction of the benzofulvene scaffold from acyclic/monocyclic compounds have been reported; similar to the 1*H*-indene synthesis, all the reported methods required the presence of multiple stabilizing aryl groups in the substrates [10]. To our delight, the alcohols **8** substituted by a sole silyl group could be smoothly converted to the corresponding benzofulvenes **9** (*Scheme 4*), this finding represents the first example of the cyclodehydrative approach to minimally functionalized benzofulvenes, which dramatically expands the scope of accessible products compared to the existing methodologies. Interestingly, in contrast to the 1*H*-indene case, benzofulvene synthesis was successfully accomplished even for trimethylsilyl-substituted allenyl carbinols; however, lower yields were obtained. The effect of the triisopropylsilyl group was also superior to other bulky silyl substituents (*Scheme 4*).

Scheme 4. *Screening of the Silyl Auxiliary in Au^I-Mediated Benzofulvene Synthesis*

'Si'	Yield
Me$_3$Si	71%
Me$_3$SiSiMe$_2$	60%
PhMe$_2$Si	65%
^{i}Pr$_3$Si	92%
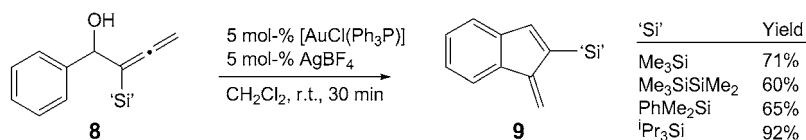
A range of benzofulvenes were obtained with excellent yields regardless of the electronic properties of the substituents at the aromatic ring (*Table 3*). Preparation of the starting materials could be accomplished in a very straightforward manner from aldehydes and methyl(triisopropylsilyl)acetylene *via* organotitanium species. An Au^I-based catalytic system appeared to be even more specific for allenyl carbinols: various *Brønsted* and soft *Lewis* acids (including AuCl$_3$) did not catalyze the reaction.

Table 3. *Substrate Screening for Au^I-Mediated Benzofulvene Synthesis^a)*. TIPS = ^{i}Pr$_3$Si.

	R	Yield [%]^b)		Yield [%]^b)
8a	H	82	**9a**	94
8b	Me	77	**9b**	95
8c	Br	84	**9c**	90
8d	MeO	78	**9d**	90
8e	NO$_2$	81	**9e**	89

^{a}) Reaction conditions: *i*) 1. ^{t}BuLi, THF, $-78°$, 1 h; 2. Ti(O^{i}Pr)$_4$, 0°, 30 min; 3. aldehyde, $-78°$, 2–12 h. *ii*) 5 mol-% [AuCl(PPh$_3$)], 5 mol-% AgBF$_4$, CH$_2$Cl$_2$, r.t., 30 min. ^{b}) Yield of isolated **8** or **9** after CC.

We were very interested in the synthetic potential of benzofulvene products **9**, which could potentially be used for the construction of a variety of diverse silylated 1*H*-indenes **10** through the sequential interactions with appropriate nucleophile/electrophile combinations (*Scheme 5*) [11]. Various organolithium reagents could add to the conjugated system of **9** furnishing carbanions which were then trapped by benzaldehyde, resulting in a rapid construction of product complexity. Thus, the highly functionalized 1*H*-indenes **10** could be prepared *via* a highly regioselective one-pot procedure in good yield, which further expanded the product scope available through the cyclodehydration of allyl alcohols.

Thus, the combination of the gold(I)-based protocols reported herein enabled the preparation of 1*H*-indenes with unprecedented structural freedom hitherto never accessible *via* the cyclodehydration pathway. Positions 1, 2, and 3 of the five-membered fragment as well as the aromatic part could be variously functionalized, yet largely unsubstituted products were easily obtained from silylated allyl alcohols. The use of allenyl carbinols allowed the convenient preparation of a diverse library of otherwise

Scheme 5. *A Three-Step Synthetic Approach to Diverse Libraries of Compounds from Aldehydes.*
TIPS = ^{i}Pr$_3$Si; LDA = lithium diisopropylamide
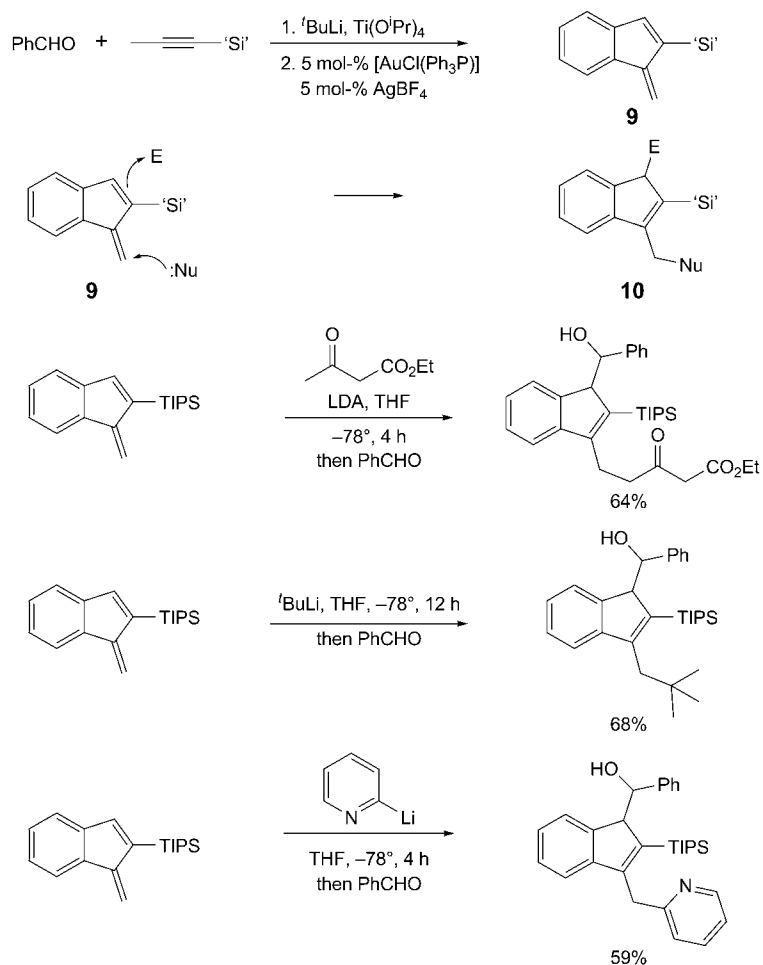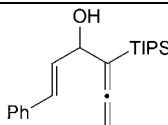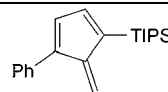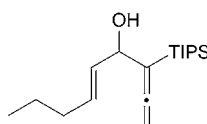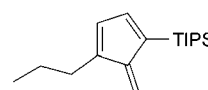
poorly accessible 1- and 1,3-substituted 2-silyl 1*H*-indenes through benzofulvene intermediates. In combination with operational simplicity, robustness and accessibility of the starting materials, the generality of the developed methodology makes it superior to any of the previously designed cyclodehydration methods used for the 1*H*-indene synthesis.

Preparation of Cyclopentadienes and Fulvenes. – To our delight, the stabilizing effect of the silyl auxiliary appeared to be sufficient for the construction of non-benzo-fused five-membered rings by the [AuCl(PPh$_3$)]/AgSbF$_6$-promoted cyclodehydration; thus, sensitive cyclopentadiene and fulvene products could also be successfully isolated (*Table 4*). The importance of the α-substituent R^1 in the aldehyde precursors to the

Table 4. *Au^I-Mediated Cyclopentadiene and Fulvene Synthesis*^{a}). TIPS = ^{i}Pr$_3$Si.

		Yield [%]^b)			Yield [%]^b)
11a		98	**12a**	–	–
11b		89	**12b**		73^c)
11c		94	**12c**		91^c)
11d		90	**12d**		89^d)
11e		54	**12e**		21^c)
11f		89	**12f**		96^d)
11g		84	**12g**		69^d)
11h		90^e)	**12h**	–^{f})	–
11i		95	**12i**	–^{f})	–

Table 4 (cont.)

		Yield [%][b])			Yield [%][b])
11j	OH / TIPS / Ph (structure)	71	**12j**	TIPS / Ph (structure)	87
11k	OH / TIPS (structure)	70	**12k**	TIPS (structure)	83

^a) Reaction conditions: *i*) 1. BuLi, THF, − 78°, 1 h; 2. 0.8 equiv of aldehyde, THF, − 78°, 1 h. *ii*) 10 mol-% [AuCl(PPh₃)], 10 mol-% AgSbF₆, CH₂Cl₂, r.t., 30 min. *iii*) 1. *'*BuLi, THF, − 78° 1 h; 2. Ti(O*ⁱ*Pr)₄, 0°, 30 min; 3. aldehyde, − 78°, 2 – 12 h. *iv*) 5 mol-% [AuCl(PPh₃)], 5 mol-% AgBF₄, CH₂Cl₂, r.t., 30 min. ^b) Yield of isolated **11** or **12** after CC. ^c) > 90% of the shown isomer. ^d) A mixture of C=C bond isomers was obtained. ^e) The substrate with a diastereoisomer ratio of 1 : 0.3 was used. ^f) A complex mixture of products was detected.
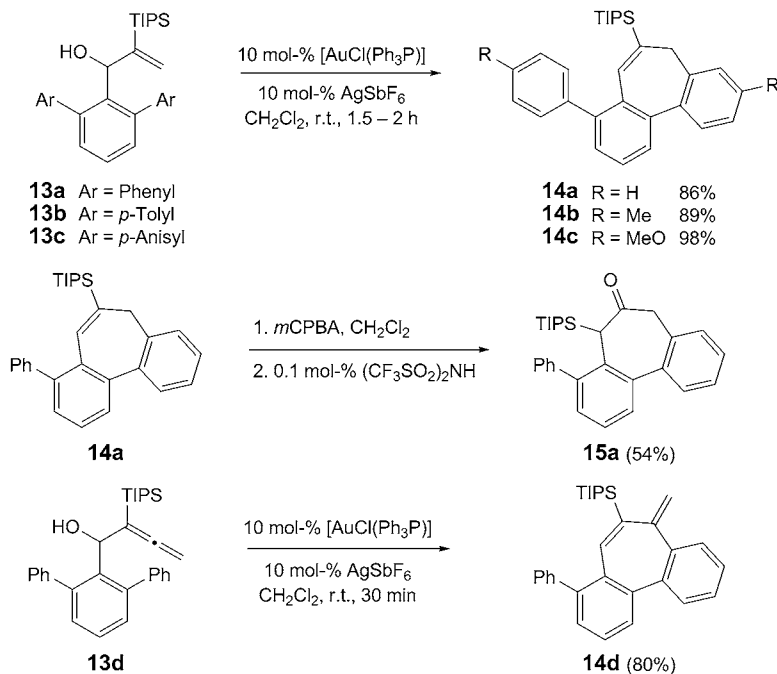
divinyl carbinols was realized: under various conditions of gold(I) catalysis, a (*E*)-cinnamaldehyde derivative **11a** furnished a complex mixture of products. However, an α-methyl group in substrate **11b** was already sufficient to render the reaction clean; a bulkier alkyl group provided further increase of the yield (→ product **12c**). An aryl substituent was necessary for efficient catalysis in either α- or β-position; inferior performance was observed with dialkyl analogues **11g** – **11i**. Interestingly, whereas the derivatives of α-alkyl-β-aryl-substituted aldehydes, *i.e.*, **11b**, **11c**, and **11e**, furnished virtually single isomers of cyclopentadiene **12**, the use of α-aryl-β-alkyl-substituted counterparts, *i.e.*, **11d** and **11f**, resulted in all possible arrangements of the C=C bonds; excellent overall yields of **12** were still obtained. The use of methylated substrate **11e** resulted in a sluggish reaction; the corresponding tetrasubstituted cyclopentadiene **12e** was isolated in poor yield. It is notable that the few existing reports on cyclopentadiene synthesis from divinyl carbinols did involve the use of multiple aryl/alkyl stabilizing groups [12]; preparation of trisubstituted cyclopentadienes was thus beyond the product scope of cyclodehydration before the disclosure of our results.

Disubstituted fulvenes **12j** and **12k** were also prepared in good yields (*Table 4*); on the contrary to cyclopentadienes, neither α-substitution nor the presence of an aryl group in the parent aldehydes was crucial for the efficient reaction outcome. To the best of our knowledge, this is the first example of a fulvene synthesis *via* cyclodehydration of allenyl vinyl carbinols.

**Construction of Seven-Membered Rings.** – Our studies showed that the developed methodology was not limited to the construction of five-membered rings. Terphenyl-carboxaldehyde-derived allyl alcohols **13a** – **13c** with the *ortho*-positions blocked by aryl groups underwent a different type of transformation: the intermediate cationic species appeared to attack one of the *ortho*-substituents to furnish 5*H*-dibenzo[*a,c*]-

[7]annulene derivatives **14a–14c** with excellent yields (*Scheme 6*)[5]). The resulting 6,7,6-tricyclic system is particularly interesting in light of its presence in allocolchici-noids, the class of compounds of great importance in cancer chemotherapy[6]). Interestingly, an identical transformation could also be carried out with **13d**, leading

Scheme 6. *Construction of Seven-Membered Rings* via *Au^I-Catalyzed Cyclodehydration.* TIPS = ^{i}Pr$_3$Si; *m*CPBA = 3-ClC$_6$H$_4$CO$_3$H.

13a Ar = Phenyl
13b Ar = *p*-Tolyl
13c Ar = *p*-Anisyl

14a R = H   86%
14b R = Me   89%
14c R = MeO 98%

14a

1. *m*CPBA, CH$_2$Cl$_2$
2. 0.1 mol-% (CF$_3$SO$_2$)$_2$NH

15a (54%)

13d

10 mol-% [AuCl(Ph$_3$P)]
10 mol-% AgSbF$_6$
CH$_2$Cl$_2$, r.t., 30 min

14d (80%)

---

5) The ^{13}C-NMR spectrum of **14c** exhibited three peaks in the area of δ(C) 110–120, which indicates the broken symmetry of one of the aryl groups leading to three structural types of C-atoms adjacent to the atoms bearing MeO groups. In the IR spectrum of **15a**, the C=O band was observed at 1681 cm^{-1} which is in agreement with a 7-membered cyclic ketone structure (C=O frequencies of indanones **6** are located at 1720–1740 cm^{-1}). Along with NOESY studies (see formula below), these features provide ample evidence that in the course of the reaction, an *ortho*-aryl group is attacked leading to the formation of the 5*H*-dibenzo[*a,c*][7]annulene scaffold. The axial chirality of compounds **14a–14c** results in the presence of an *AB* system of benzylic H-atoms in the ^{1}H-NMR spectra, as two *d* separated by 0.28–0.29 ppm with *J* = 12.6–12.8 Hz.

14c
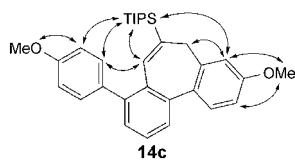
6) The members of this family, *e.g.*, allocolchicine, *N*-acetylcolchicinol methyl ether, *N*-acetylcolchi-cinol, and its dihydrogen phosphate (ZD 6126) have received much attention in the context of antitumor activity. For the most recent synthetic works and further details, see [13].

to product **14d** with an exocyclic methylene group. Preparation of a dibenzosuberone (= 5*H*-dibenzo[*a,d*]cyclohepten-6-one) scaffold, exemplified by derivative **15a**, was also achieved by means of the epoxidation/*Meinwald* rearrangement sequence previously implemented in the indan-2-one synthesis (see above, *Scheme 2*).

Conclusions. – We discovered the beneficial effect of a triisopropylsilyl auxiliary group on the efficiency of a gold(I)-catalyzed cyclodehydration of allyl and allenic alcohols, which provides rapid access to a library of various compounds including 1*H*-indenes, benzofulvenes, indan-2-ones, fulvenes, cyclopentadienes, 5*H*-dibenzo[*a,-c*][7]annulenes, and dibenzosuberones. The protocol is mild, robust, and operationally convenient; the starting materials can be easily prepared from inexpensive chemicals. This approach provides unprecedented product generality for several product classes of the cyclodehydration reaction, which is particularly notable for the 1*H*-indene synthesis. The first example of the synthesis of non-benzo-fused fulvenes *via* cyclodehydration is demonstrated. In light of the numerous advantages of the developed methodology, we hope that extensive synthetic applications thereof can be expected in future.

Experimental Part

General. IR Spectra: *Nicolet 20-SXB* FTIR spectrometer; thin films on NaCl plates; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker Avance-500* spectrometer; at 500 and 125 MHz, resp.; in CDCl$_3$, at 298 K; δ in ppm rel. to Me$_4$Si as internal standard, *J* in Hz. For additional experimental details, see [2].

Au^I-Catalyzed Cyclodehydration: General Procedure. A dry test tube (*Fisherbrand* 16×100 mm) sealed with a 14 mm sleeve stopper was charged with silver hexafluoroantimonate(V) (21 mg, 0.06 mmol) in the glovebox; it was taken out, quickly charged with [AuCl(PPh$_3$)] (30 mg, 0.06 mmol), evacuated, and filled with Ar. CH$_2$Cl$_2$ (4 ml) was added. The substrate (0.6 mmol) was added quickly in CH$_2$Cl$_2$ (2 ml overall), and the mixture was left stirring for the indicated time (10 min to 2 h; TLC AcOEt/hexanes 1:5) monitoring. The soln. was then passed through a short silica gel (SiO$_2$) plug which was thoroughly washed with CH$_2$Cl$_2$ (an alternative workup protocol involved quenching with sat. aq. NaHCO$_3$ soln. followed by extraction with hexanes). The soln. was concentrated and the residue purified by column chromatography (CC) (SiO$_2$, hexanes).

*Allenic Alcohols **8**, **11j**, and **11k**: General Procedure.* To a soln. of triisopropyl(prop)-1-yn-1-yl)silane (196 mg, 1.0 mmol) in THF, 1.7M *tert*-butyllithium in pentane (590 µl, 1.0 mmol) was added dropwise at 0° and stirred for 60 min. After 1 h, titanium(IV) tetrakis(isopropoxide) (296 µl, 284 mg, 1.0 mmol) was added and the resulting mixture was stirred at 0° for 30 min. It was then cooled to $-78°$, and the aldehyde (1.0 mmol) was added dropwise. The mixture was stirred at $-78°$ for 2–12 h. Upon completion of the reaction (TLC monitoring), the crude mixture was quenched with H$_2$O and extracted with Et$_2$O, the extract dried (Na$_2$SO$_4$) and concentrated, and the crude product purified by CC (SiO$_2$, 0.35% AcOEt/hexanes).

Au^I-Mediated Fulvene/Benzofulvene Synthesis: General Procedure. A flame-dried test tube (16×100 mm) was charged with [AuCl(PPh$_3$)] (12 mg, 0.025 mmol) and AgBF$_4$ (5 mg, 0.025 mmol) in the glovebox, and the resulting mixture was dissolved in CH$_2$Cl$_2$ (5 ml) and stirred under Ar. To that soln., the allenylsilane derivative was added dropwise, and the mixture was stirred at r.t. for 30 min, After 30 min, the crude mixture was filtered through a short alumina plug (basic alumina, *Brockmann* activity I), the soln. concentrated, and the residue purified by CC (SiO$_2$, hexanes/AcOEt).

α-{1-[Tris(1-methylethyl)silyl]propa-1,2-dien-1-yl}benzenemethanol (**8a**): IR: 3445, 2944, 2888, 2866, 1925, 1463, 1041, 699, 676. ^{1}H-NMR: 7.40 (*d, J* = 7, 2 H); 7.31 – 7.34 (*t, J* = 7, 7.5, 2 H); 7.26 (*s*, 1 H); 5.16 (*d, J* = 6, 1 H); 4.65 (*m*, 2 H); 1.19 (*m*, 3 H); 1.08 (*d, J* = 7.3, 18 H). ^{13}C-NMR: 129.4; 128.2; 128.1; 127.7; 127.1; 127.0; 73.1; 73.0; 72.5; 72.4; 18.4.

4-Methyl-α-{1-[tris(1-methylethyl)silyl]propa-1,2-dien-1-yl}benzenemethanol (**8b**): IR: 3282, 3088, 2025, 1963, 1280, 1041, 867, 790. ^{1}H-NMR: 7.28 (*d, J* = 11, 2 H), 6.94 (*d, J* = 11, 2 H); 5.12 (*m*, 1 H); 4.66 (*m*, 2 H); 2.87 (*s*, 3 H); 1.15 (*m*, 3 H); 1.09 (*d, J* = 7, 9 H); 0.94 (*d, J* = 7, 9 H). ^{13}C-NMR: 132.7; 128.4; 113.5; 73.2; 71.8; 71.7; 55.1; 18.4; 11.6.

4-Bromo-α-{1-[tris(1-methylethyl)silyl]propa-1,2-dien-1-yl}benzenemethanol (**8c**): IR: 3372, 3040, 2866, 1958, 1684 1580, 1041, 814. ^{1}H-NMR: 7.51 (*d, J* = 10, 2 H); 7.26 (*d, J* = 10, 2 H); 5.14 (*m*, 1 H); 4.62 (*m*, 2 H); 1.19 (*m*, 3 H); 1.09 (*d, J* = 7.3, 9 H); 0.97 (*d, J* = 7.3, 9 H). ^{13}C-NMR: 131.2; 128.7; 73.3; 73.2; 71.8; 71.7; 18.5; 11.6.

4-Methoxy-α-{1-[tris(1-methylethyl)silyl]propa-1,2-dien-1-yl}benzenemethanol (**8d**): IR: 3582, 2786, 2431, 2277, 2094, 1968, 1276, 1021, 870. ^{1}H-NMR: 7.29 (*d, J* = 11.5, 2 H); 6.86 (*d, J* = 11.5, 2 H); 5.10 (*m*, 1 H); 4.66 (*m*, 2 H); 3.80 (*s*, 3 H); 1.14 (*m*, 3 H); 1.06 (*d, J* = 7, 9 H), 0.94 (*d, J* = 7, 9 H). ^{13}C-NMR: 128.4; 113.5; 73.2; 71.8; 71.7; 55.1; 18.4; 11.6.

4-Nitro-α-{1-[tris(1-methylethyl)silyl]propa-1,2-dien-1-yl}benzenemethanol (**8e**): IR: 3679, 2515, 2054, 1880, 1527, 1351, 853. ^{1}H-NMR: 7.59 (*d, J* = 10, 2 H); 7.50 (*d, J* = 10, 2 H); 5.24 (*m*, 1 H); 4.59 (*m*, 2 H); 1.19 (*m*, 3 H); 1.09 (*d, J* = 5.0, 9 H); 0.97 (*d, J* = 5.0, 9 H). ^{13}C-NMR: 138.6; 124.2; 73.5; 73.2; 72.1; 71.7; 18.5; 11.6.

1-Methylene-2-[tris(1-methylethyl)silyl]-1H-indene (**9a**): IR: 3090, 3049, 1905, 1684. 1133. ^{1}H-NMR: 7.61 (*s*, 1 H); 7.29 – 7.25 (*m*, 3 H); 7.21 – 7.19 (*m*, 1 H); 6.19 (*s*, 1 H); 5.82 (*s*, 1 H); 1.42 – 1.35 (*m*, 3 H); 1.15 – 1.09 (*s*, 18 H). ^{13}C-NMR: 151.8; 127.8; 125.3; 120.2; 119.2; 115.2; 18.8; 11.8.

6-Methyl-1-methylene-2-[tris(1-methylethyl)silyl]-1H-indene (**9b**): IR: 3082, 1598, 1280, 1083. ^{1}H-NMR: 7.44 (*s*, 1 H); 7.18 – 7.15 (*m*, 2 H); 6.15 (*s*, 1 H); 5.77 (*s*, 1 H); 2.40 (*s*, 3 H); 1.38 – 1.33 (*m*, 3 H); 1.11 – 1.09 (*s*, 18 H). ^{13}C-NMR: 142.0; 138.3; 137.9; 136.8; 120.6; 124.7; 110.9; 50.2; 18.8; 11.9.

6-Bromo-1-methylene-2-[tris(1-methylethyl)silyl]-1H-indene (**9c**): IR: 3046, 1889, 1693, 1083. ^{1}H-NMR: 7.40 (*s*, 1 H); 7.27 (*m*, 2 H); 6.19 (*s*, 1 H); 6.01 (*s*, 1 H); 1.37 – 1.33 (*m*, 3 H); 1.11 – 1.09 (*s*, 18 H). ^{13}C-NMR: 151.8; 140.2; 139.8; 138.0; 136.7; 136.3; 129.5; 127.7; 17.8; 12.2.

6-Methoxy-1-methylene-2-[tris(1-methylethyl)silyl]-1H-indene (**9d**): IR: 3083, 3038, 1636, 1285, 1056. ^{1}H-NMR: 7.25 – 7.12 (*m*, 3 H); 7.12 (*s*, 1 H); 6.80 (*d*, 1 H); 3.85 (*s*, 3 H); 1.38 – 1.32 (*m*, 3 H); 1.14 – 1.10 (*d, J* = 7.4, 18 H). ^{13}C-NMR: 157.8; 139.4; 137.9; 134.6; 129.6; 114.7; 113.1; 55.6; 18.8; 11.9.

1-Methylene-6-nitro-2-[tris(1-methylethyl)silyl]-1H-indene (**9e**): IR: 3445, 2944, 2888, 2866, 1925, 1463, 1041, 699, 676. ^{1}H-NMR: 7.38 (*s*, 1 H); 7.35 – 7.37 (*m*, 2 H); 6.20 (*s*, 1 H); 5.83 (*s*, 1 H); 1.37 – 1.34 (*m*, 3 H); 1.12 (*s*, 18 H). ^{13}C-NMR: 153.0; 137.5; 137.4; 134.8; 117.6; 111.9; 111.1; 19.4, 10.7.

(1E)-1-Phenyl-4-[tris(1-methylethyl)silyl]hexa-1,4,4-trien-3-ol (**11j**): IR: 3287, 3094, 2866, 1985, 1663, 1052, 895. ^{1}H-NMR: 7.39 – 7.24 (*m*, 5 H); 6.58 (*d, J* = 16, 1 H); 6.29 (*dd, J* = 8, 16, 1 H); 4.71 – 4.64 (*m*, 3 H); 1.24 (*m*, 3 H); 1.09 – 1.05 (*m*, 18 H). ^{13}C-NMR: 136.7; 131.7; 130.2; 128.5; 127.6; 126.5; 72.9; 70.7; 70.6; 18.6; 11.6.

(5E)-3-[Tris(1-methylethyl)silyl]nona-1,2,5-trien-4-ol (**11k**): IR: 3445, 2944, 2888, 2866, 1925, 1463, 1041, 699, 676. ^{1}H-NMR: 5.69 – 5.64 (*m*, 1 H); 5.57 – 5.55 (*m*, 1 H); 4.64 – 4.57 (*dd, J* = 13, 24, 2 H); 4.48 (*m*, 1 H); 2.03 (*dd, J* = 7, 21, 2 H); 1.41 (*dd, J* = 8, 22, 2 H); 1.22 (*m*, 3 H); 1.09 – 1.06 (*m*, 18 H); 0.9 (*m*, 3 H). ^{13}C-NMR: 132.2; 132.0; 72.6; 70.8; 70.7; 34.1; 22.1; 18.5; 13.7; 11.5.

5-Methylene-1-phenyl-4-[tris(1-methylethyl)silyl]cyclopenta-1,3-diene (**12j**): IR: 3083, 3019, 1754, 1671, 1177. ^{1}H-NMR: 7.42 – 7.38 (*m*, 5 H); 6.34 (*d, J* = 10.7, 1 H); 6.28 (*s*, 1 H); 5.94 (*d, J* = 11, 1 H); 5.84 (*s*, 1 H); 1.40 – 1.36 (*m*, 3 H); 1.14 (*s*, 18 H). ^{13}C-NMR: 144.8; 137.6; 137.2; 136.7; 135.4; 128.0; 127.7; 117.3; 21.4; 13.5.

5-Methylene-1-propyl-4-[tris(1-methylethyl)silyl]cyclopenta-1,3-diene (**12k**): IR: 3445, 2944, 2888, 2866, 1925, 1463, 1041, 699, 676. ^{1}H-NMR: 6.27 (*s*, 1 H); 6.21 (*d, J* = 12, 1 H); 5.87 (*s*, 1 H); 5.81 (*d, J* = 12.4, 1 H); 2.17 (*d, J* = 8.2, 22, 2 H); 1.47 (*d, J* = 8, 22, 2 H); 1.38 – 1.32 (*m*, 3 H); 1. 28 (*m*, 3 H); 1.11 (*s*, 18 H). ^{13}C-NMR: 133.6; 132.9; 132.6; 132.5; 131.4; 131.3; 32.7; 24.9; 20.9; 15.3; 13.8.

α-{1-[Tris(1-methylethyl)silyl]propa-1,2-dien-1-yl}[1,1':3',1''-terphenyl]-2'-methanol (**13d**): IR: 3576, 3551, 3440, 3078, 3056, 3026, 2942, 2864, 1926, 1812, 1599. ^{1}H-NMR: 7.43 – 7.30 (*m*, 10 H); 7.28 (*t, J* = 7.5,

1 H); 7.15 (*d*, *J* = 7.5, 2 H); 5.38 – 5.33 (*m*, 1 H); 4.26 (*dd*, *J* = 11.5, 3.7, 1 H); 4.18 (*dd*, *J* = 11.5, 4.0, 1 H); 1.96 (*d*, *J* = 11.4, 1 H); 1.02 (*sept.*, *J* = 7.5, 3 H); 0.78 (*d*, *J* = 7.5, 9 H); 0.75 (*d*, *J* = 7.5, 9 H). ^{13}C-NMR: 210.3; 142.1; 141.4; 137.9; 132 – 129 (br.); 129.5; 128.1; 127.1; 125.9; 98.8; 72.4; 70.6; 18.3; 18.2; 11.5. TOF-ES-MS (pos.): 477.2585 ([$M + $Na]$^+$, $C_{31}H_{38}NaOSi^+$; calc. 477.2590).

*5-Methylene-8-phenyl-6-[tris(1-methylethyl)silyl]-5*H-*dibenzo[a,c]cycloheptene* (**14d**): IR: 3059, 3026, 2864, 2756, 2724, 1946, 1877, 1806, 1622. ^{1}H-NMR: 7.67 – 7.61 (*m*, 2 H); 7.41 – 7.25 (*m*, 10 H); 6.58 (*s*, 1 H); 5.04 (*s*, 1 H); 4.97 (*d*, *J* = 1.3, 1 H); 1.13 (*sept.*, *J* = 7.4, 3 H); 0.96 (*d*, *J* = 7.4, 9 H); 0.90 (*d*, *J* = 7.4, 9 H). ^{13}C-NMR: 149.2; 146.5; 145.4; 141.8; 141.7; 139.6; 137.6; 136.9; 134.7; 129.8; 129.6; 129.0; 128.6; 128.0; 127.3; 127.1; 127.0; 126.9; 126.4; 112.4; 18.7; 18.7; 11.6. EI-MS (pos.): 436.25779 (*M*$^+$, $C_{31}H_{36}Si^+$; calc. 436.25863).

REFERENCES

[1] A. Arcadi, S. D. Giuseppe, *Curr. Org. Chem.* **2004**, *8*, 795; L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271; E. Jiménez-Núñez, A. M. Echavarren, *Chem. Commun.* **2007**, 333; A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; H. C. Shen, *Tetrahedron* **2008**, *64*, 3885; H. C. Shen, *Tetrahedron* **2008**, *64*, 7847; N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776; D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351; A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266; J. Muzart, *Tetrahedron* **2008**, *64*, 5815; R. Skouta, C.-J. Li, *Tetrahedron* **2008**, *64*, 4917; Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239; R. A. Widenhoefer, *Chem. – Eur. J.* **2008**, *14*, 5382; A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766; A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208; A. S. K. Hashmi, *Pure Appl. Chem.* **2010**, *82*, 657; N. D. Shapiro, F. D. Toste, *Synlett* **2010**, 675; S. P. Nolan, *Acc. Chem. Res.* **2011**, *44*, 91.
[2] D. L. Usanov, H. Yamamoto, *Org. Lett.* **2012**, *14*, 414.
[3] S. Goldschmidt, B. Acksteiner, *Chem. Ber.* **1958**, *91*, 502; N. C. Deno, C. U. Pittman, J. O. Turner, *J. Am. Chem. Soc.* **1965**, *87*, 2153; W. E. Parham, D. C. Egberg, *J. Org. Chem.* **1972**, *37*, 1545; W. G. Miller, C. U. Pittman, *J. Org. Chem.* **1974**, *39*, 1955; G. Singh, H. Ila, H. Junjappa, *Synthesis* **1986**, 744; C. U. Pittman, W. G. Miller, *J. Am. Chem. Soc.* **1973**, *95*, 2947; P. G. Gassman, J. A. Ray, P. G. Wenthold, J. W. Mickelson, *J. Org. Chem.* **1991**, *56*, 5143; I. H. Jeong, Y. S. Park, M. S. Kim, S. T. Oh, *Bull. Korean Chem. Soc.* **2001**, *22*, 1173; D. Basavaiah, M. Bakthadoss, G. J. Reddy, *Synthesis* **2001**, 919; ; Z. Xi, R. Guo, S. Mito, H. Yan, K. Kanno, K. Nakajima, T. Takahashi, *J. Org. Chem.* **2003**, *68*, 1252; S. Radix-Large, S. Kucharski, B. R. Langlois, *Synthesis* **2004**, 456; X. Zhou, H. Zhang, X. Xie, Y. Li, *J. Org. Chem.* **2008**, *73*, 3958; S. Guo, Y. Liu, *Org. Biomol. Chem.* **2008**, *6*, 2064; J. Wang, L. Zhang, Y. Jing, W. Huang, X. Zhou, *Tetrahedron Lett.* **2009**, *50*, 4978; C. D. Smith, G. Rosocha, L. Mui, R. A. Batey, *J. Org. Chem.* **2010**, *75*, 4716.
[4] D. J. Gorin, F. D. Toste, *Nature (London, U.K.)* **2007**, *446*, 395; A. Fürstner, L. Morency, *Angew. Chem.*, *Int. Ed.* **2008**, *47*, 5030; A. S. K. Hashmi, *Angew. Chem.*, *Int. Ed.* **2008**, *47*, 6754; G. Seidel, R. Mynott, A. Fürstner, *Angew. Chem.*, *Int. Ed.* **2009**, *48*, 2510; D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482; A. S. K. Hashmi, *Angew. Chem.*, *Int. Ed.* **2010**, *49*, 5232.
[5] E. A. Ilardi, C. E. Stivala, A. Zakarian, *Org. Lett.* **2008**, *10*, 1727.
[6] B. Rickborn, in 'Comprehensive Organic Synthesis', Eds. B. M. Trost, I. Fleming, Pergamon, Oxford, 1991, Vol. 3, pp. 733 – 775 and ref. cit. therein; K. Maruoka, T. Ooi, H. Yamamoto, *Tetrahedron* **1992**, *48*, 3303; K. Maruoka, N. Murase, R. Bureau, T. Ooi, H. Yamamoto, *Tetrahedron* **1994**, *50*, 3663; K. Ishihara, N. Hanaki, H. Yamamoto, *Synlett* **1995**, 721; S. Kulasegaram, R. J. Kulawiec, *J. Org. Chem.* **1997**, *62*, 6547; B. C. Ranu, U. Jana, *J. Org. Chem.* **1998**, *63*, 8212; K. Suda, K. Baba, S. Nakajima, T. Takanami, *Tetrahedron Lett.* **1999**, *40*, 7243; A. M. Anderson, J. M. Blazek, P. Garg, B. J. Payne, R. S. Mohan, *Tetrahedron Lett.* **2000**, *41*, 1527; F. Martínez, C. del Campo, E. F. Llama, *J. Chem. Soc.*, *Perkin Trans. 1* **2000**, 1749; K. A. Bhatia, K. J. Eash, N. M. Leonard, M. C. Oswald, R. S. Mohan, *Tetrahedron Lett.* **2001**, *42*, 8129; Y. Kita, J. Futamura, Y. Ohba, Y. Sawama, J. K. Ganesh, H. Fujioka, *J. Org. Chem.* **2003**, *68*, 5917; I. Karamé, M. L. Tommasino, M. Lemaire, *Tetrahedron Lett.* **2003**, *44*, 7687; K. Suda, T. Kikkawa, S. Nakajima, T. Takanami, *J. Am. Chem. Soc.* **2004**, *126*, 9554;

A. Procopio, R. Dalpozzo, A. De Nino, M. Nardi, G. Sindona, A. Tagarelli, *Synlett* **2004**, 2633; S.-H. Lee, J.-C. Lee, M.-X. Li, N.-S. Kim, *Bull. Korean Chem. Soc.* **2005**, *26*, 221; X.-M. Deng, X.-L. Sun, Y. Tang, *J. Org. Chem.* **2005**, *70*, 6537; M. W. C. Robinson, K. S. Pillinger, A. E. Graham, *Tetrahedron Lett.* **2006**, *47*, 5919; N.-H. Ko, H.-S. Kim, S.-O. Kang, M.-S. Cheong, *Bull. Korean Chem. Soc.* **2008**, *29*, 682; J. R. Donald, R. J. K. Taylor, *Synlett* **2009**, 59; K. Suda, S. Nakajima, Y. Satoh, T. Takanami, *Chem. Commun.* **2009**, 1255; E. Ertür, M. Göllü, A. S. Demir, *Tetrahedron* **2010**, *66*, 2373; M. W. C. Robinson, K. S. Pillinger, I. Mabbett, D. A. Timms, A. E. Graham, *Tetrahedron* **2010**, *66*, 8377.

 [7] J. B. Lambert, *Tetrahedron* **1990**, *46*, 2677; J. M. White, *Aust. J. Chem.* **1995**, *48*, 1227.

 [8] a) K. Yoon, D. Y. Son, *J. Organomet. Chem.* **1997**, *545 – 546*, 185; b) H. Kakiya, H. Shinokubo, K. Oshima, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2139; c) R. K. Boeckman Jr., D. M. Blum, B. Ganem, N. Halvey, *Org. Synth.* **1978**, *58*, 152.

 [9] P. Jiao, M. Kawasaki, H. Yamamoto, *Angew. Chem.*, *Int. Ed.* **2009**, *48*, 3333.

[10] F. Toda, N. Ooi, K. Akagi, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1050; P. Langer, *Chem. Commun.* **1999**, 1217; P. Langer, M. Döring, D. Seyferth, H. Görls, *Chem. – Eur. J.* **2001**, *7*, 573. J.-M. Lu, M. Shi, *Chem. – Eur. J.* **2009**, *15*, 6065; P. Cordier, C. Aubert, M. Malacria, E. Lacôte, V. Gandon, *Angew. Chem.*, *Int. Ed.* **2009**, *48*, 8757.

[11] T. Kauffmann, K. Berghus, A. Rensing, *Chem. Ber.* **1985**, *118*, 4507; S. Wang, Q. Yang, T. C. W. Mak, Z. Xie, *Organometallics* **2000**, *19*, 334; P. E. Gaede, *J. Organomet. Chem.* **2000**, *616*, 29; H. Ma, J. Huang, Y. Qian, *J. Organomet. Chem.* **2002**, *650*, 114; S. V. Kovalenko, S. Peabody, M. Manoharan, R. J. Clark, I. V. Alabugin, *Org. Lett.* **2004**, *6*, 2457; S. W. Peabody, B. Breiner, S. V. Kovalenko, S. Patil, I. V. Alabugin, *Org. Biomol. Chem.* **2005**, *3*, 218; A. C. Möller, R. Blom, R. H. Heyn, O. Swang, C.-H. Görbitz, T. Seraidaris, *Eur. J. Inorg. Chem.* **2005**, 1759.

[12] C. M. Garner, M. E. Prince, *Tetrahedron Lett.* **1994**, *35*, 2463; R. S. Threlkel, J. E. Bercaw, P. F. Seidler, J. M. Stryker, R. G. Bergman, *Org. Synth.* **1987**, *65*, 42; P. Jutzi, J. Dahlhaus, *Synthesis* **1993**, 684; P. G. Gassman, J. W. Mickelson, J. R. Sowa Jr., *J. Am. Chem. Soc.* **1992**, *114*, 6942; H. Fang, Q. Song, Z. Wang, Z. Xi, *Tetrahedron Lett.* **2004**, *45*, 5159; S. D. R. Christie, K. W. Man, R. J. Whitby, A. M. Z. Slawin, *Organometallics* **1999**, *18*, 348; Z. Wang, H. Fang, Z. Xi, *Tetrahedron* **2006**, *62*, 6967.

[13] F.-D. Boyer, X. Le Goff, I. Hanna, *J. Org. Chem.* **2008**, *73*, 5163; F.-D. Boyer, I. Hanna, *Eur. J. Org. Chem.* **2008**, *2008*, 4938; N. Nicolaus, J. Zapke, P. Riesterer, J.-M. Neudörfl, A. Prokop, H. Oschkinat, H.-G. Schmalz, *ChemMedChem* **2010**, *5*, 661; F.-D. Boyer, J. Dubois, S. Thoret, M.-E. Tran Huu Dau, I. Hanna, *Bioorg. Chem.* **2010**, *38*, 149; S. Djurdjevic, F. Yang, J. R. Green, *J. Org. Chem.* **2010**, *75*, 8241; N. Nicolaus, J. Reball, N. Sitnikov, J. Velder, A. Termath, A. Y. Fedorov, H.-G. Schmalz, *Heterocycles* **2011**, *82*, 1585.