

Divergent Gold-Catalyzed Rearrangement of 1-Alkenyl-2-alkynylcyclopropanes: Enyne Transformation Controlled by a Silicon Moiety

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Abstract. Here we report a gold(I)-catalyzed rearrangement for a special type of alkenylcyclopropanes, such as (6-ethynylbicyclo[3.1.0]hex-2-en-6-yl)silanes. These enynes evolved through an isomerization reaction towards the formation of isomeric alkenylcyclopropanes instead of the expected alkenylcyclohexadienes. A computational study on the reaction mechanism revealed the participation of a polycyclic gold(I) carbene complex as intermediate instead of a σ -allylic gold cation which is in agreement with the expected influence in the energy of those intermediates due to the presence of the silyl group. Finally, this gold(I) carbene intermediate could be experimentally intercepted through intramolecular cyclopropanations.

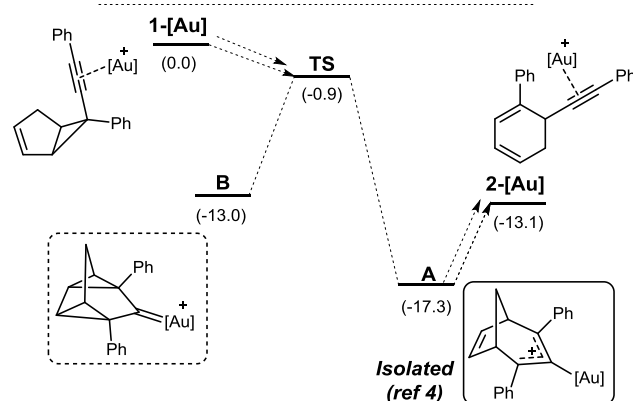
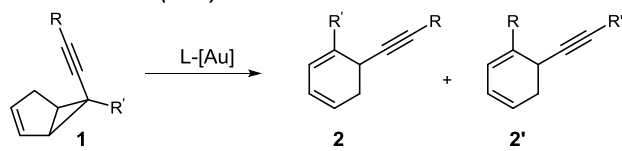
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Alkyne activation through homogeneous gold catalysis has experienced during the last two decades a strong development as a valuable methodology for a plethora of organic synthetic transformations.^[1] Among these procedures, 1,*n*-enyne cycloisomerizations have received a preferential attention.^[2] In this field, our group reported a gold-catalyzed cycloisomerization of 1-alkenyl-2-alkynylcyclopropanes, a particular class of 1,5-enynes, which could be readily transformed into alkenylcyclohexadienes^[3] (Figure 1; *top*). For this transformation, we recently described a careful computational and experimental study revealing the participation of a σ -gold^[4] allylic intermediate that could be, for the first time, isolated and characterized (Figure 1; *middle*).^[4a] This computational mechanistic study revealed the existence of a bifurcation leading to a σ -gold allylic intermediate **A** and also to a polycyclic gold(I) carbene complex **B**.^[5] However, carbene intermediate **B** could not be experimentally detected, directly or indirectly.

Focusing our target on carbene intermediate **B** we decided to modify the structure of 1-alkenyl-2-

alkynylcyclopropanes **1** through the incorporation of a silicon moiety. Due to the electronic properties of the silicon atom,^[6] we expected that this modification could trigger an inversion in the relative energetic stability between both species (**A** and **B**),^[7] driving the reaction course through carbene intermediate (Figure 1; *middle*).

Previous work (ref 3)



This work

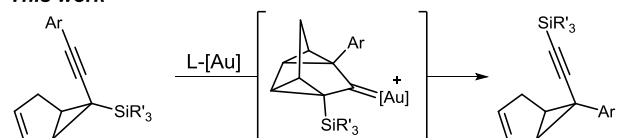
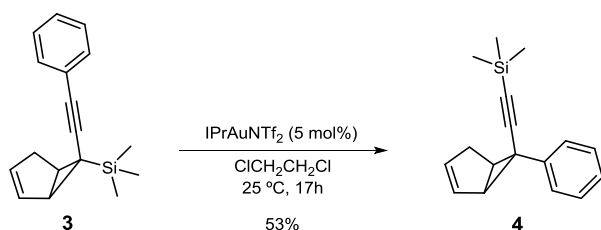


Figure 1. Previous results and working hypothesis. Free energies for computational data are in kcal mol⁻¹ relative to gold-activated 1-alkenyl-2-alkynylcyclopropane **1**-[Au].

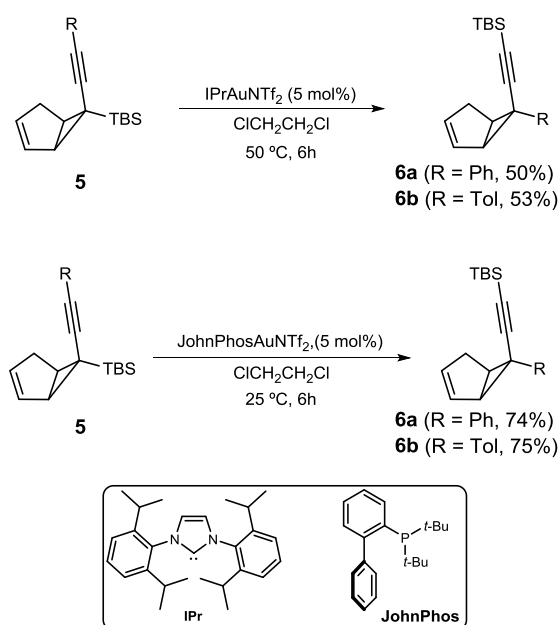
Here we report, a gold(I)-catalyzed rearrangement of (6-ethynylbicyclo[3.1.0]hex-2-en-6-yl)silanes - specific 1,5-enynes- involving the participation of a polycyclic gold(I) carbene complex. The rearrangement resulted in a formal exchange between silicon and alkynyl moieties (Figure 1; *bottom*). In addition, a polycyclic gold(I) carbene complex intermediate could be intramolecularly intercepted through cyclopropanation reactions.

Continuing with our efforts to discover new mechanistic insights from gold-catalyzed 1,5-enyne rearrangements, we stirred a solution of 2-alkenyl-1-alkynyl-1-silylcyclopropane **3**,^[8] which bears a silicon moiety attached to the bicyclic skeleton, in the presence of a gold(I) catalyst. Thus, treatment of compound **3** with a 5 mol% of IPrAuNTf₂ (IPr=1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-imidazol-2-ylidene), in 1,2-dichloroethane at 25 °C, resulted in its isomerization to alkynylcyclopropane **4**, without formation of the expected alkynylcyclohexadiene **2** (Scheme 1).



Scheme 1. Gold(I)-catalyzed isomerization of enyne **3**.

Next, in order to explore the participation of any sort of fragmentation of the carbon-silicon bond in this rearrangement, we decided to incorporate a more robust silicon group (*tert*-butyldimethylsilyl (TBS)) instead of a trimethylsilyl. **Moreover**, a higher stability for compounds **6** was expected (Scheme 2). Following this methodology, isomerization of **5** provided similar results, independently of the nature of the silicon group. These results pointed to a lack of participation of the carbon-silicon bond. Additionally, the use of JohnPhos as a ligand for the gold catalyst slightly increased the reaction yield, probably due to **less** decomposition of reaction products **6**, as the reaction occurs under milder conditions.



Scheme 2. Gold-catalyzed isomerization of 2-alkenyl-1-alkynyl-1-silylcyclopropanes **5**. TBS = *Tert*-butyldimethylsilyl.

From all these isomerization reactions it can be inferred that the reaction course is dramatically influenced by the presence of the silicon moiety. Thus, gold(I)-catalyzed rearrangement from the same family of 1,5-enynes could be divergently directed to the formation of either alkynylcyclohexadienes **2** or alkynylcyclopropanes **4,6**.

At this point, in order to give light to the reaction mechanism, we decided to perform a computational study (B3PW91-D3/CC-Pvdz-pp//b3pw91/CC-Pvdz-pp level) using (6-phenylethynylbicyclo[3.1.0]hex-2-en-6-yl)silane **7** as a model compound (Figure 2). **The use of SiH₃ and Au-PH₃ for modelling SiR₃ and Au-PR₃, respectively, is a common practice in theoretical calculations, which leads to accurate results.**^{[9],[10]}

This study reveals a higher stability of the isomerized 1,5-enyne **8** relative to the starting material **7** in about 2.6 kcal mol⁻¹.

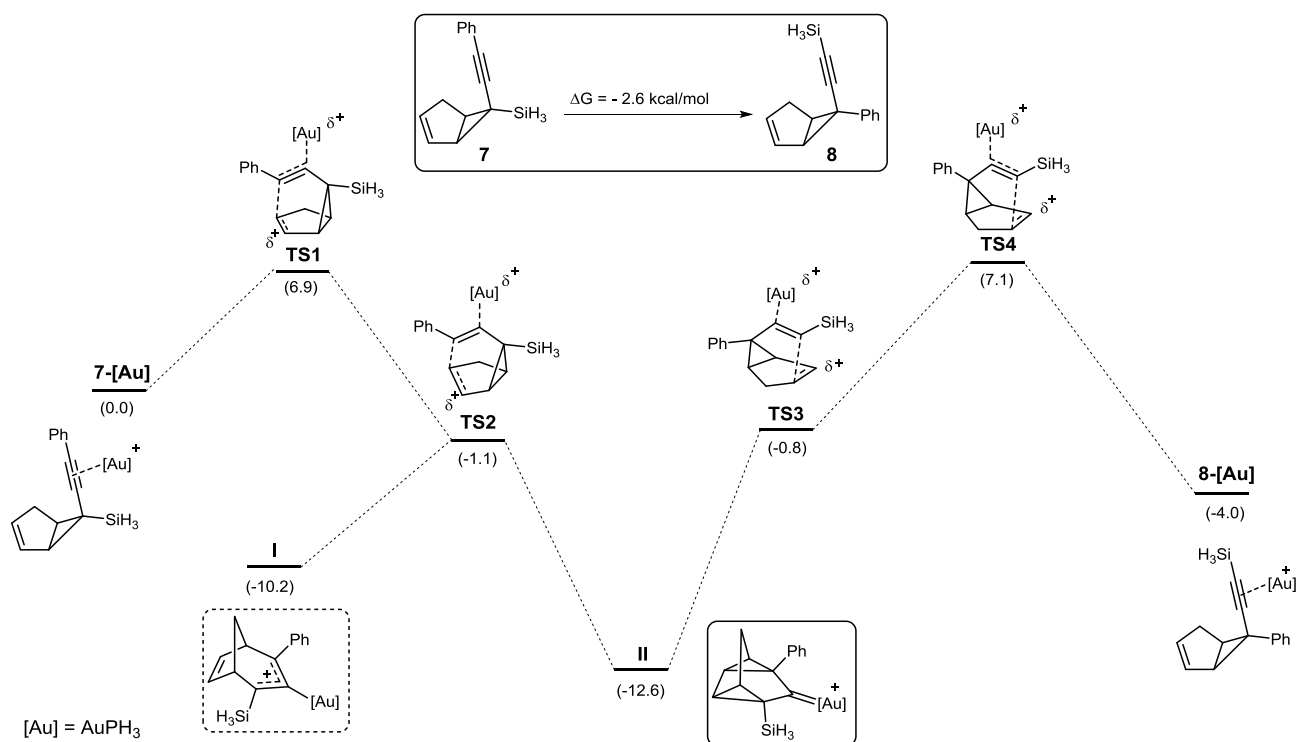


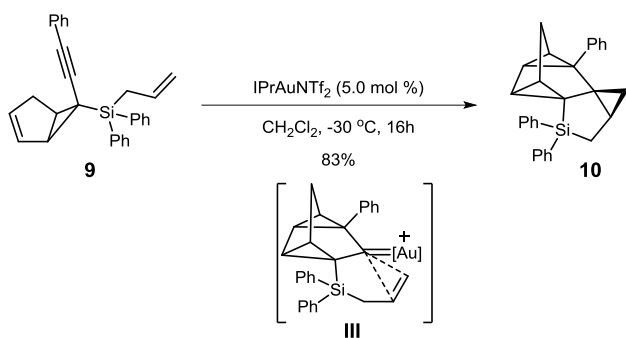
Figure 2. Computed energies for isomerization of compound **7**. Free energies in kcal mol⁻¹ relative to **7-[Au]**.

The calculated mechanism indicates a similar behavior in the initial steps compared to the reaction path previously described for the isomerization of **1-[Au]** to **2-[Au]** (See above; Figure 1).^[4] Thus, starting from species **7-[Au]**, the intrinsic reaction coordinate (IRC) indicates a 6-endo-dig π_{C-C} attack to gold-activated alkyne leading to transition state **TS1** (+6.9 kcal mol⁻¹). From **TS1** the IRC brings to transition state **TS2** (-1.1 kcal mol⁻¹), which showed an elongation on the initial double bond (from 1.341 to 1.454 Å) and the imminent formation of a new C-C bond (1.585 Å). Since the IRC calculation connects two transition states, along the IRC there must lie a valley-ridge inflection (VRI) also known as a bifurcation.^[11] Finally, **TS2** can evolve towards allylic gold cation **I** (-10.2 kcal mol⁻¹) or gold carbene complex **II** (-12.6 kcal mol⁻¹). According to our computational studies, polycyclic carbene complex **II** emerged as the key intermediate in the divergent rearrangement for silyl substituted alkynylcyclopropanes **7**. This intermediate **II** is observed to be 2.4 kcal/mol more stable than σ -gold(I) allylic cation intermediate **I** and therefore seems to control the reaction pathway. This observation sharply contrasts with the 4.3 kcal mol⁻¹ of higher energy obtained for the aryl substituted carbene analogue **B**, compared to the corresponding allylic cation **A** (See above; Figure 1).^[4] Next, from the most stable intermediate **II**, a symmetrical pathway involving the carbon that bears the silicon moiety, through consecutive transition states **TS3** (-0.8 kcal mol⁻¹) and **TS4** (+7.1 kcal mol⁻¹), leads to the final structure **8-[Au]**, which shows a higher stability

(-4.0 kcal mol⁻¹) than starting **7-[Au]** (See Supporting Information for computational details).

This modification on the reaction mechanism could be explained in order to the double influence exerted by the silyl group on the reaction intermediates. On the one hand, a destabilization of the σ -allyl cationic intermediate **I** due to the unfavourable α -silyl substitution,^[12] that is increased by the lack of the stabilization by the aromatic ring. On the other, the stabilizing effect (β -silyl effect)^[12,13] on the carbene intermediate **II** due to the hyperconjugative interaction between the C-Si σ -bond and the empty p-orbital of the adjacent carbon to the gold.^[14]

With those results in hand and in order to confirm the new reaction pathway, we decided to attempt an intermolecular capture of carbene complex **II** from the reaction course. In this sense, several oxidation^[15] and alkene cyclopropanation^[16] reactions were performed without any success. However, when alkenylalkynylcyclopropane **9**, with an allyl group attached to the silicon atom, was subjected, in dichloromethane at low temperature, to the presence of a gold catalyst it rearranged to compound **10** that was isolated in a 83% yield. Polycyclic compound **10**, which contains up to five new stereogenic centers, was obtained as a single diastereoisomer^[17] (Scheme 3).



Scheme 3. Intramolecular capture of carbene intermediate **III**.

In addition, an X-ray crystal structure analysis performed with a single crystal^[18] -obtained from a methylene chloride-pentane mixture- allowed to unambiguously confirm the structure of polycyclic compound **10** (Figure 3).

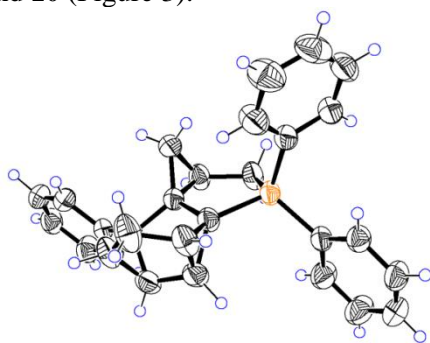


Figure 3. ORTEP view of polycycle **10**. Thermal ellipsoids at the 50% level.

Relevantly, formation of polycycle **10** confirms the participation of carbene complex **III** as a reaction intermediate, as it was predicted by the computational analysis. Thus, using allyl(6-phenylethynylbicyclo[3.1.0]hex-2-en-6-yl)silane **11**, as a model compound, carbene complex **IV** could be located on the potential energy surface (Figure 4). This intermediate shows a similar structure and comparable relative energy to that calculated for intermediate **III** (See above; Figure 2).

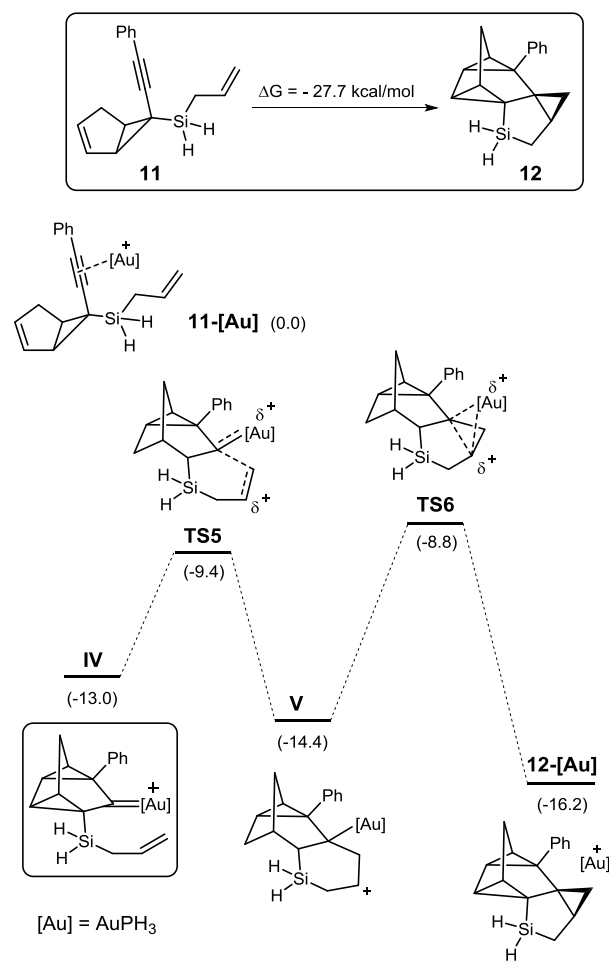
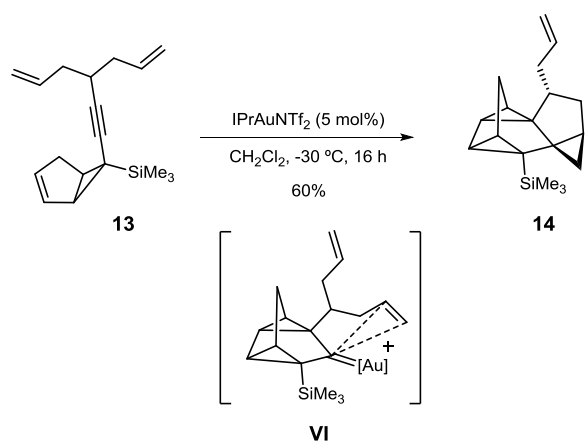


Figure 4. Computed energies for evolution of carbene intermediate **IV**.

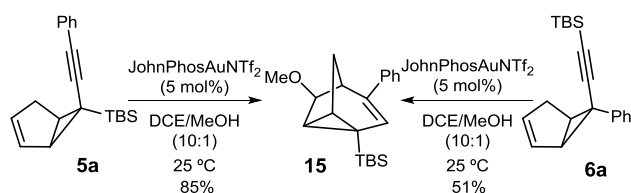
In fact, **IV** should be 13.0 kcal mol⁻¹ more stable than initial **11-[Au]**. From **IV**, the cyclization through **TS5** has a low energy barrier, 3.6 kcal mol⁻¹, and leads to silinane structure **V**, which shows a higher stability (-1.4 kcal mol⁻¹) than **IV**. Finally, the transition state **TS6** that evolves from intermediate **V** to the most stable cyclopropanated **12-[Au]** also has a low barrier energy, in this case 5.6 kcal mol⁻¹.

Similarly, the key intermediate gold(I) carbene complex could also be intercepted starting from alkynylcyclopropane **13** bearing two allyl groups in its structure. Thus, treatment of alkynylcyclopropane **13** under the standard reaction conditions led to the formation of polycyclic compound **14** in good yield,^[19] as the result of an intramolecular alkene cyclopropanation from the corresponding gold(I) carbene intermediate **VI** (Scheme 4)^[20].



Scheme 4. Rearrangement of compound **13**

Finally, we performed some control experiments in order to study a possible reversibility of the reaction. First, when isomerization of bicyclic compound **5a** was performed in the presence in a (10:1) mixture of dichloroethane (DCE) and methanol, carbene intermediate could react with formation of tricyclic compound **15** (Scheme 5). Similarly, starting from isomerized compound **6a**, led also to the formation compound **15**. These experiments allowed us to confirm the reversibility of the isomerization reaction.



Scheme 5. Nucleophilic attack to isomerization intermediate

In conclusion, in this study a divergent mechanistic pathway for gold(I)-catalyzed rearrangement of 1-alkenyl-2-alkynylcyclopropanes is presented. The incorporation of a silyl group to the cyclopropane skeleton triggers an important modification of the reaction mechanism, leading to the formation of a new isomeric enyne. A computational study performed reveals that the electronic influence of the silicon moiety implies a destabilization of the expected σ -allyl gold(I) cationic intermediate. This destabilization involves a deviation of the reaction course to the more stable gold(I) carbene intermediate. Finally, the new reaction pathway could be experimentally supported by two complementary gold(I)-catalyzed intramolecular captures of the polycyclic gold carbene intermediate through cyclopropanation reactions and formation of complex polycyclic skeletons.

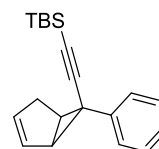
Experimental Section

All operations were carried out under argon atmosphere using conventional Schlenk techniques. All common reagents were obtained from commercial suppliers. 1,2-dichloroethane and methylene chloride were distilled from calcium hydride prior to its use. Hexane and ethyl acetate were used from commercial suppliers. TLC was performed on aluminium-backed plates coated with silica gel 60, with F254 indicator and flash chromatographic columns were carried out on silica gel (50-200 micron) High-resolution mass spectra were determined on an Impact II Bruker mass spectrometer. NMR spectra were run on Bruker AV-300 and DPX-300 spectrometers using CDCl_3 as solvent. Melting points were measured on a Büchi-Tottoli apparatus and were not corrected.

Experimental procedure for isomerization of alkylnylcyclopropanes **3** and **5**.

To a 1,2-dichloroethane (5 mL) solution of the corresponding alkylnylcyclopropanes **3** or **5** (0.5 mmol), prepared at 25 °C under argon atmosphere, 0.025 mmol (5 mol%) of the corresponding gold catalyst were added. Next, the mixture was stirred at 25 °C (for **3** or **5** using JohnPhos as gold ligand) or 50 °C (for **5** using IPr as gold ligand) for 27 h (for **3**) or 6h for **5**. After that period, the solvent was removed under reduced pressure and the residue purified by chromatographic column on silica gel and using hexane as eluent.

(1*S**,5*R**,6*R**)-6-Phenyl-6-(*tert*-butyldimethylsilylethynyl)bicyclo[3.1.0]hex-2-ene (**6a**)

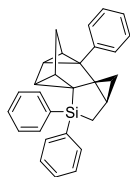


Yield 74% (JohnPhos); 50% (IPr); Yellowish solid; m.p.: 65-67 °C; Rf = 0.16 (Hexanes). ^1H NMR (300 MHz, CDCl_3): δ 7.44-7.15 (m, 5H), 5.96-5.73 (m, 2H), 2.89-2.73 (m, 1H), 2.70-2.52 (m, 2H), 2.30-2.21 (m, 1H), 0.97 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 141.8 (C), 133.8 (CH), 129.0 (CH), 128.2 (2 x CH), 125.8 (CH), 125.2 (2 x CH), 103.8 (C), 86.3 (C), 44.7 (CH), 35.5 (CH_2), 35.3 (CH), 28.5 (C), 26.2 (3 x CH_3), 16.5 (C), -4.2 (2 x CH_3). HRMS (EI) for $\text{C}_{20}\text{H}_{27}\text{Si}$ [M+H]: Calc.: 295.0157; found: 295.0159.

Experimental procedure for the synthesis of polycycles **10** and **12**.

To a solution, cooled to -30 °C, of the corresponding alkylnylcyclopropane **9** or **11** (0.2 mmol) in 1,2-dichloromethane (2 mL), 8.7 mg (0.01 mmol; 5 mol%) of IPrAuNTf₂ was added. After stirring the mixture for 16 hours, the solvent was evaporated under vacuum and the residue purified by chromatographic column through silica gel. Following this methodology, respective polycyclic compounds **10** and **12** were obtained as pure compounds.

Compound 10



Yield 83%; White solid; m.p.: 47-49 °C; Rf = 0.40 (Hexanes). ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ 7.71-7.59 (m, 2H), 7.52-7.35 (m, 7H), 7.32-7.15 (m, 5H), 2.28 (d, *J* = 12.2 Hz, 1H), 2.16 (dd, *J* = 6.4 and 3.8 Hz, 1H), 2.13-2.01 (m, 2H), 1.92 (ddd, *J* = 6.6, 5.0 and 1.8 Hz, 1H), 1.88 (dd, *J* = 5.3 and 3.8 Hz, 1H), 1.73 (ddd, *J* = 15.2, 6.4 and 0.7 Hz, 1H), 1.41 (d, *J* = 15.3 Hz, 1H), 0.96-0.81 (m, 2H), 0.70-0.40 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 140.3 (C), 136.3 (C), 135.2 (C), 135.2 (2 x CH), 135.1 (2 x CH), 130.8 (2 x CH), 129.4 (CH), 129.3 (CH), 127.9 (2 x CH), 127.9 (2 x CH), 127.8 (2 x CH), 126.5 (CH), 46.5 (C), 39.8 (C), 31.7 (CH), 30.8 (CH), 30.2 (C), 30.0 (CH), 29.1 (CH), 26.4 (CH₂), 16.2 (CH), 15.5 (CH₂), 10.5 (CH₂). HRMS (EI) for C₂₉H₂₇Si [M+H]⁺: Calc: 403.1876; found: 403.1879.

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