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Gold Catalysis of Non-Conjugated Haloacetylenes

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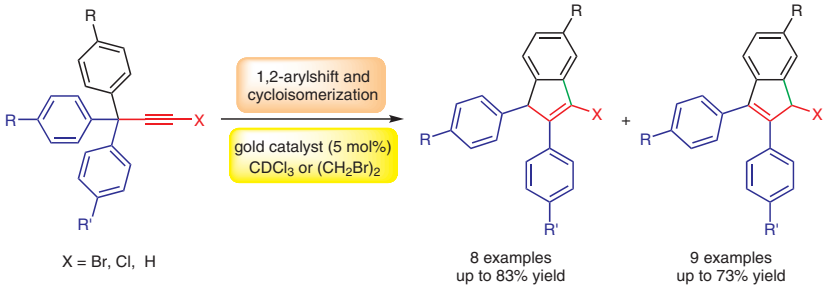

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Abstract Gold-catalyzed reactions of conjugated haloacetylenes are well known and usually result in the formation of addition or dimerization products. Herein, we report a gold-catalyzed reaction of non-conjugated haloacetylenes, which leads exclusively to the halogenated cyclization products. Remarkable is the gold-catalyzed reaction of tritylhaloacetylenes to haloindene derivatives, as mechanistic studies reveal that an 1,2-aryl shift occurs in the initially formed gold complex. The potential functionalization at the halogen atom and the wide scope of these cyclization reactions make them an attractive method for the construction of cyclic systems.

Key words gold catalysis, haloacetylenes, indene, chromene, chromane, 1,2-aryl shift, cyclization

Halogenated compounds are among the most used reagents for carbon–carbon bond forming reactions in organic chemistry. In contrast to alkyl, vinyl, and aryl halides, haloacetylenes[1] are rarely employed for the linking of carbon–carbon bonds. This is astonishing as they are readily available from the corresponding terminal acetylenes and decompose, with the exception of fluoroacetylenes,[2] only at higher temperatures.[3] There are a few examples of conversions of haloacetylenes, whereby the halogen moiety is retained during the reaction, allowing a further transformation of the reactive halogen-substituted center.[4–12]

In the field of homogenous gold catalysis,[13] alkynes are probably the most frequently used substrates due to their high reactivity. At the beginning, only the formation of new carbon–heteroatom bonds was reported.[14] Nowadays, there are many examples of gold-catalyzed carbon–carbon bond forming reactions of alkynes,[15] and yet haloacetylenes have been rarely employed in gold catalysis. One of the first reactions was carried out by Hashmi et al.[11,12] They were able to show via dual gold catalysis[16,17] that head-to-tail dimers **4**–**6** can be obtained from haloacetylenes **1**–**3** (Scheme 1a).[11] Recently, we were able to show that the mono gold(I)-catalyzed dimerization of chloro- and bromoarylacetylenes **2** and **3** delivers the head-to-head products **7** and **8** (Scheme 1b).[8] In the presence of arylacetylenes a haloalkynylation reaction of the acetylene can be achieved instead of dimerization.[5] Both quantum chemical calculations and investigations by means of ^{13}C-labeled compounds have shown that the formation of the addition products takes place via at least one rearrangement.[6] Haloacetylenes can also be added to alkenes via gold catalysis.[4,7,9,10] Depending on the substrate and the catalyst, the corresponding [2+2] cycloaddition[10] or 1,2-haloalkynylation products[9] are formed.

Until now, mainly aryl-substituted haloacetylenes have been used in gold catalysis.[4–12] Here, we investigated the behavior of the readily available[1] non-conjugated haloacetylenes in the presence of different gold catalysts. In all three non-conjugated systems including (homo)propargylic ethers and tritylhaloacetylenes neither the formation of the addition products nor the reaction to dimerization products was observed. Interestingly, in all cases an intramolecular cyclization took place. The gold-catalyzed conversion of the tritylhaloacetylenes is of special interest, as investigations by means of NMR spectroscopy, X-ray structure analysis and quantum chemical calculations show that an aryl shift occurred in the initially formed gold complex. Furthermore, we describe mechanistic studies and the wide scope of these new gold-catalyzed cyclization reactions (Scheme 1c).

For the investigation of the gold(I)-catalyzed reaction of non-conjugated haloacetylenes, we chose compounds **9** and **10** as model systems (Scheme 2). These systems can be prepared in only two steps: The propargylic ether is synthesized starting from the corresponding phenol and aniline

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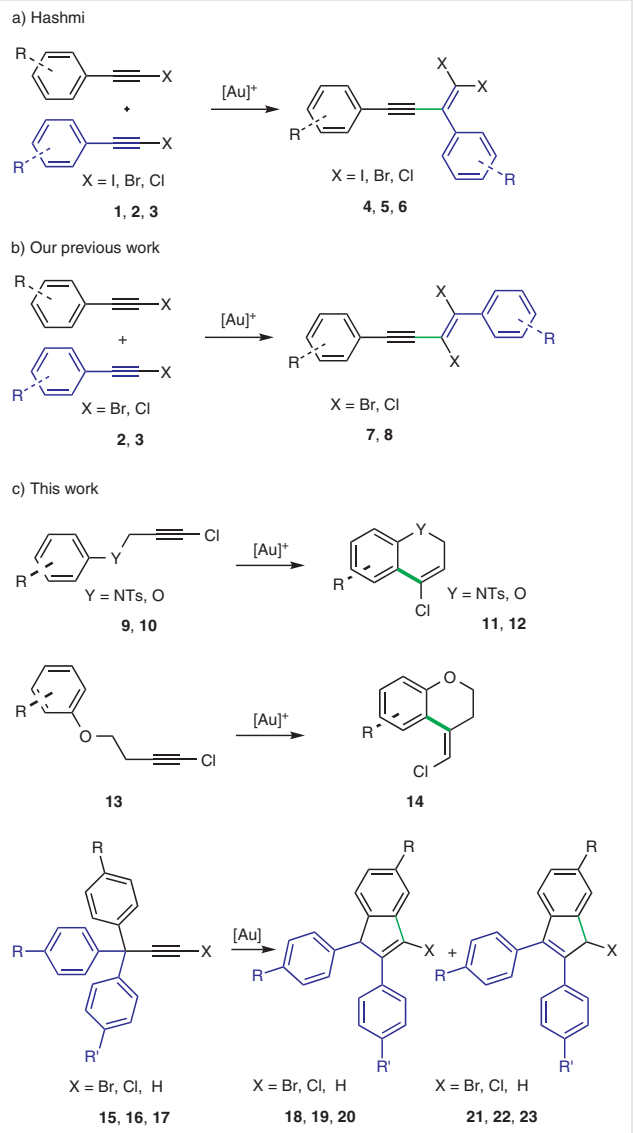
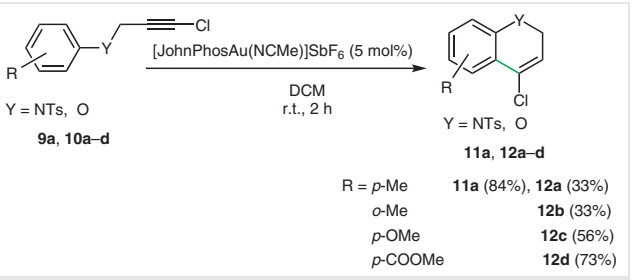


Scheme 1 Gold(I)-catalyzed dimerization of haloarylacetylenes **1–3** leads to head-to-tail products **4–6** (a) and to head-to-head dimers **7**, **8** (b). The gold(I)-catalyzed reaction of propargylic and homopropargylic chloroacetylenes **9**, **10**, **13** leads to cyclization products **11**, **12**, **14**, whereas the gold-catalyzed conversion of trityl compounds **15–17** results in the formation of indenes **18–23** (c).

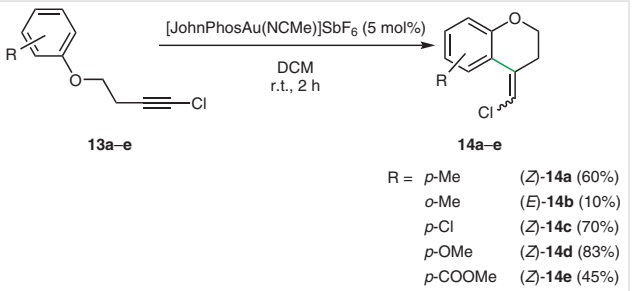
derivatives and propargyl bromide.[18] The resulting compounds were then converted into the chloroacetylenes **9** and **10** with *N*-chlorosuccinimide.[19] First, we investigated the conversion of **10a** with the gold(I) catalyst [JohnPhosAu(NCMe)]SbF_6 (**S1**) in deuterated chloroform, which was monitored by ^{1}H NMR spectroscopy. Fortunately, we could observe a complete conversion into one main product with a yield of 90%. By analyzing the 1D and 2D NMR spectra, we could confirm the formation of 2*H*-chromene **12a** via a 6-*endo-dig* cyclization (Scheme 2). An analogous gold(I)-catalyzed cyclization has already been observed for terminal propargylic ethers.[20–23]



Scheme 2 Gold(I)-catalyzed cyclization of chloroacetylenes **9**, **10** to 1,2-dihydroquinoline **11a** and 2*H*-chromenes **12**

The experiment was repeated on a preparative scale with different propargylic chloroacetylenes to evaluate the scope of the reaction (Scheme 2). The highest yield was obtained for the conversion of chloroacetylene **9a** to dihydroquinoline **11a** (84%). Using a propargylic ether led to the formation of 2*H*-chromene in a significantly lower yield (**12a**, 33%). Changing the substitution position from *para* (**12a**, 33%) to *ortho* (**12b**, 33%) had no effect on the yield. However, a methoxy group in the *para* position increased the yield to 56% (**12c**). The conversion of **10d** leads to an even higher yield (**12d**, 73%).

As second model, the non-conjugated acetylenes **13** were chosen (Scheme 3). The synthesis of these homopropargylic ethers was accomplished via a Mitsunobu reaction[24] and followed by chlorination[19] with *N*-chlorosuccinimide. Fortunately, the reaction of **13a** with [JohnPhosAu(NCMe)]SbF_6 in deuterated chloroform also showed a complete conversion into one main product with an NMR yield of 93%. Based on the aromatic signals in the ^{1}H NMR spectrum, a ring formation was assumed. Further 1D and 2D NMR spectroscopic studies confirmed a 6-*exo-dig* cyclization. The evaluation of the NOESY spectrum shows that the main product represents the *Z* isomer of **14a** (Scheme 3 and Figure S8).



Scheme 3 Gold(I)-catalyzed cyclization of chloroacetylenes **13** to chromanes **14**

In the next step, the reaction was carried out on a preparative scale (Scheme 3). Changing the methyl group from *para* to *ortho* position leads to a significant decrease in the reaction yield from 60% (**14a**) to 10% (**14b**). Here, the reaction of the *ortho*-substituted homopropargylic ether **13b** surprisingly results in the formation of the *E* isomer. With a chlorine atom in *para* position, the corresponding cyclization product **14c** could be isolated in 70% yield. The highest yield delivers the chloroacetylene with a methoxy group in the *para* position (83%, **14d**). Using a methyl ester as substituent (**13e**) results in the formation of the chromane **14e** in lower yield (45%). The molecular structure of **14e** obtained via X-ray diffraction shows that the *Z* isomer was formed, which agrees with our findings from the NMR spectroscopic investigations (Figure 1).

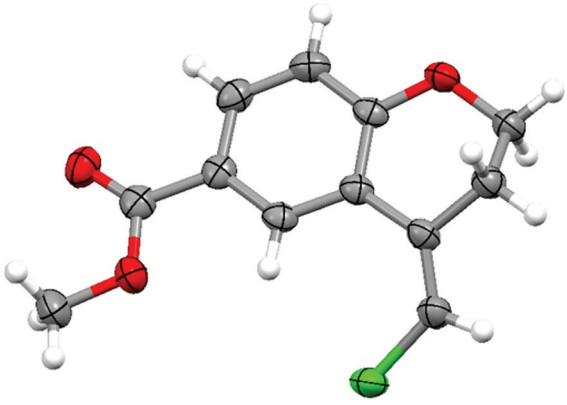
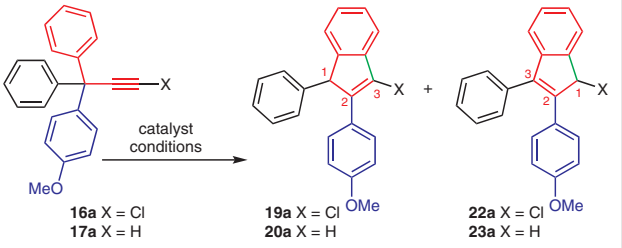


Figure 1 Molecular structure of the chromane **14e** in the solid state. Displacement ellipsoids are drawn at the 70% probability level, and hydrogen atoms as spheres of arbitrary radii.

Furthermore, we synthesized different tritylchloro- and -bromoacetylenes and treated them with arylalkynes in the presence of gold catalysts. The tritylacetylenes **15** and **16** (see the Supporting Information) were synthesized from the corresponding tritylacetylenes **17** by reaction with *N*-chlorosuccinimide (NCS) and *N*-bromosuccinimide (NBS), respectively, according to known procedures.[19,25] Besides the phenyl group, we used *p*-tolyl and *p*-methoxyphenyl as aryl groups. For the first investigation, we chose **16a** as a model system (Scheme 4). The characteristic ^{1}H NMR signal of the methyl group, which is separated from other signals at a chemical shift of about δ = 3.8, can be used as reference signal to determine the conversion of **16a** and the yield of possible haloalkynylation products.

The initial gold(I)-catalyzed reaction of **16a** with 1-phenylprop-1-yne showed only a conversion of the chloride **16a**. Since no reaction of the arylalkyne was observed, the arylalkyne was omitted for further investigations. To optimize yields, the experiment was carried out at room temperature and at 65 °C using different solvents, ligands, and counterions. The catalyst selection ranged from gold(III) to



Scheme 4 Gold-catalyzed reaction of alkynes **16a** and **17a** under different conditions

carbene gold and to phosphine gold complexes. As solvents chloroform, acetonitrile, and benzene were tested. In order to monitor the reaction process, the experiments were carried out in NMR tubes. The conversion of the reactant and the yield of the products were determined using hexamethylbenzene as internal standard. The thus obtained results are summarized in Table 1.

A glance at the NMR investigations shows that two products were formed (Scheme 4). Both exhibit an ^{1}H NMR signal in the range of δ = 5–6, which is typical for an olefinic or benzylic proton. The conversion and the ratio of the products **19a** and **22a** strongly depend on the catalyst and the reaction conditions. In general, phosphine ligands delivered conversions up to 93% and product **22a** is preferentially formed (entries 1–6, 8, 9, and 13). The yield of **22a** was as high as 59% (entry 8). When using carbene ligands, the formation of **19a** prevails in one case (entry 12), however, the yield of 43% is moderate. The best yields were obtained with the gold(III) complex dichloro(2-picolinato)gold(III) in chloroform at 65 °C (**22a**, 72%; entry 14).

For structural analysis 2D NMR spectra of **19a** and **22a** were recorded. According to NOESY and HMBC spectra, **19a** and **22a** are indene derivatives showing a methoxyphenyl group in the C2 position. Both indenes **19a** and **22a** differ only in the position of the halogen atom and the phenyl group. In **19a**, the phenyl group is attached to the C1 atom and thus **19a** represents a vinylic chloride. In the case of **22a**, the phenyl group and the chlorine atom are changed compared to **19a**. Thus, **22a** is a benzylic chloride. This assignment is clearly plausible based on the coupling of the benzylic protons in the NOESY spectra. In the NOESY spectrum of **22a** a coupling between the benzylic proton (δ = 5.80) and both the protons of the *para*-substituted ring (δ = 7.25) and the protons of the six-membered ring of the indene (δ = 7.71) is found (see Figure S10). The NOESY spectrum of **19a** exhibits in addition to the above described couplings an interaction of the benzylic proton (δ = 5.03) with the unsubstituted phenyl group (δ = 7.16) (see Figure S9). Please note, that the treatment of a mixture of **19a** and **22a** with different bases (sodium ethoxide and triethylamine) does not lead to selective interconversion of the two isomers.

Table 1 Optimization of the Reaction Conditions for the Gold-Catalyzed Reaction of Alkyne **16a** Using ^{1}H NMR Experiments[a]

Entry	Catalyst	Conditions	Yield (%)		Conversion (%)
			19a	**22a**	
1	[JohnPhosAu(NCMe)]SbF_6[26]	r.t., 7 d, $CDCl_3$	19	42	86
2[b]	[JohnPhosAu(NCMe)]SbF_6	r.t., 24 h, $CDCl_3$	30	30	93
3[c]	[JohnPhosAu(NCMe)]SbF_6	r.t., 24 h, $CDCl_3$	11	28	55
4	[JohnPhosAu(NCMe)]SbF_6	r.t., 24 h, CD_3CN	–	–	14
5	[JohnPhosAu(NCMe)]SbF_6	r.t., 24 h, C_6D_6	8	10	32
6	JohnPhosAuNTf_2[27]	r.t., 7 d, $CDCl_3$	29	43	91
7	*t*BuXPhosAuNTf_2[27]	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	37	–	92
8[d]	CyJohnPhosAuCl/AgNTf_2[28]	r.t., 7 d, $CDCl_3$	7	59	88
9[d]	CyJohnPhosAuCl/AgSbF_6	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	9	56	92
10[d]	IPrAuCl/AgNTf_2[29]	r.t., 7 d, $CDCl_3$	16	21	70
11[d]	IPrAuCl/AgSbF_6	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	9	16	36
12[d]	IPrAuCl/Na$BArF_{24}$	r.t., 24 h, $CDCl_3$	43	7	91
13[d]	Ph_3PAuCl/AgNTf_2[30]	r.t., 24 h, $CDCl_3$	–	30	58
14	dichloro(2-picolinato)gold(III)[31]	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	5	72	84

[a] If not stated otherwise, the concentration of the alkyne **16a** was 0.1 M and 5 mol% of the catalyst was used.
[b] The concentration of the alkyne **16a** was 0.5 M.
[c] 2.5 mol% of the catalyst was used.
[d] 10 mol% of the silver or sodium salt, respectively, was used.

Furthermore, we were able to grow single crystals of **19a** and **22a**, which were analyzed via X-ray diffraction. The molecular structures of **19a** and **22a** confirmed the indene structures (see Figure 2). In both cases, the methoxyphenyl unit and the indene moiety are almost parallel to each other, which suggests a good conjugation of the two aromatic rings. However, the phenyl group is twisted out of this plane in both cases. A glance at the products and the starting materials reveals that an 1,2-aryl shift has taken place. A comparable gold-catalyzed aryl rearrangement has already been observed in trityl systems,[32] whereby two alkyne units, one terminal and one internal trityl-substituted alkyne unit, were converted into benzofluorenone derivatives.

In contrast to the previously observed gold-catalyzed conversions of chloroacetylenes[5,8] no chlorine shift takes place, which raises the question whether the halogen atom has any importance for the mechanism. To examine this issue, we studied the reaction of the terminal tritylacetylene **17a** with different gold catalysts (see Table 2). Analogous to

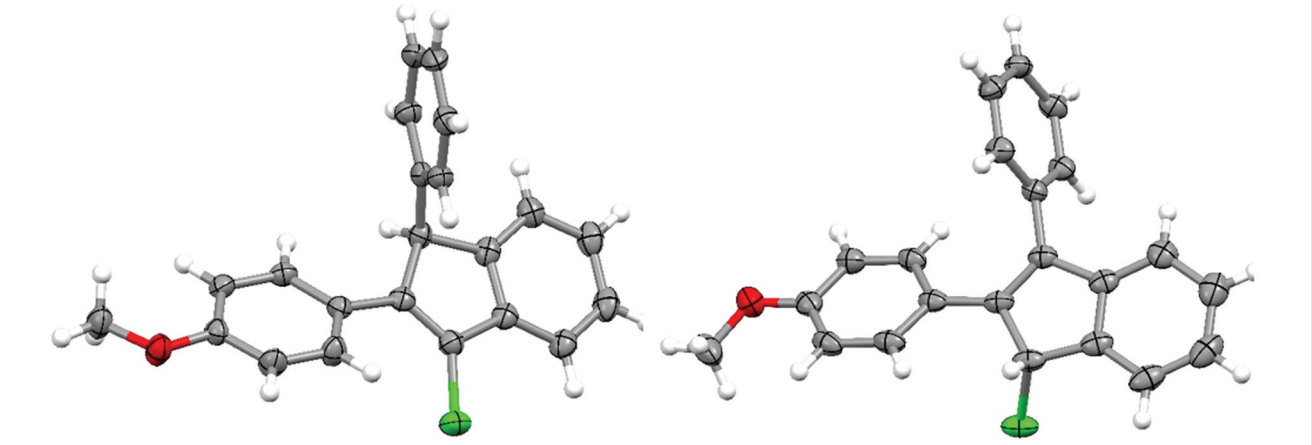


Figure 2 Molecular structures of the indenes **19a** (left) and **22a** (right) in the solid state. In the case of indene **19a**, two independent molecules are found in the asymmetric unit; only one of them is displayed. Displacement ellipsoids are drawn at the 70% probability level, and hydrogen atoms as spheres of arbitrary radii.

Table 2 Optimization of the Reaction Conditions for the Gold-Catalyzed Reaction of Alkyne **17a** Using ^{1}H NMR Experiments[a]

Entry	Catalyst	Conditions	Yield (%)		Conversion (%)
			20a	**23a**	
1	[JohnPhosAu(NCMe)]SbF_6	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	88	9	98
2	JohnPhosAuNTf_2	r.t., 7 d, $CDCl_3$	16	–	26
3	JohnPhosAuNTf_2	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	5	54	75
4	*t*BuXPhosAuNTf_2	r.t., 7 d, $CDCl_3$	57	10	76
5	*t*BuXPhosAuNTf_2	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	–	73	90
6[b]	CyJohnPhosAuCl/AgNTf_2	r.t., 7 d, $CDCl_3$	24	–	38
7[b]	CyJohnPhosAuCl/AgNTf_2	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	4	89	97
8[b]	CyJohnPhosAuCl/$AgSbF_6$	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	–	–	0
9[b]	IPrAuCl/AgNTf_2	r.t., 7 d, $CDCl_3$	26	10	42
10[b]	IPrAuCl/AgNTf_2	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	4	71	88
11[b]	IPrAuCl/$AgSbF_6$	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	–	–	0
12[b]	IPrAuCl/$NaBArF_{24}$	r.t., 24 h, $CDCl_3$	75	–	93
13[b]	Ph_3PAuCl/AgNTf_2	r.t., 7 d, $CDCl_3$	14	8	22
14[b]	Ph_3PAuCl/AgNTf_2	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	4	72	76
15	dichloro(2-picolinato)gold(III)	r.t., 7 d, $CDCl_3$ then 65 °C, 24 h, $CDCl_3$	–	–	0

[a] If not stated otherwise, the concentration of the alkyne **17a** was 0.1 M and 5 mol% of the catalyst was used.
[b] 10 mol% of the silver or sodium salt, respectively, was used.

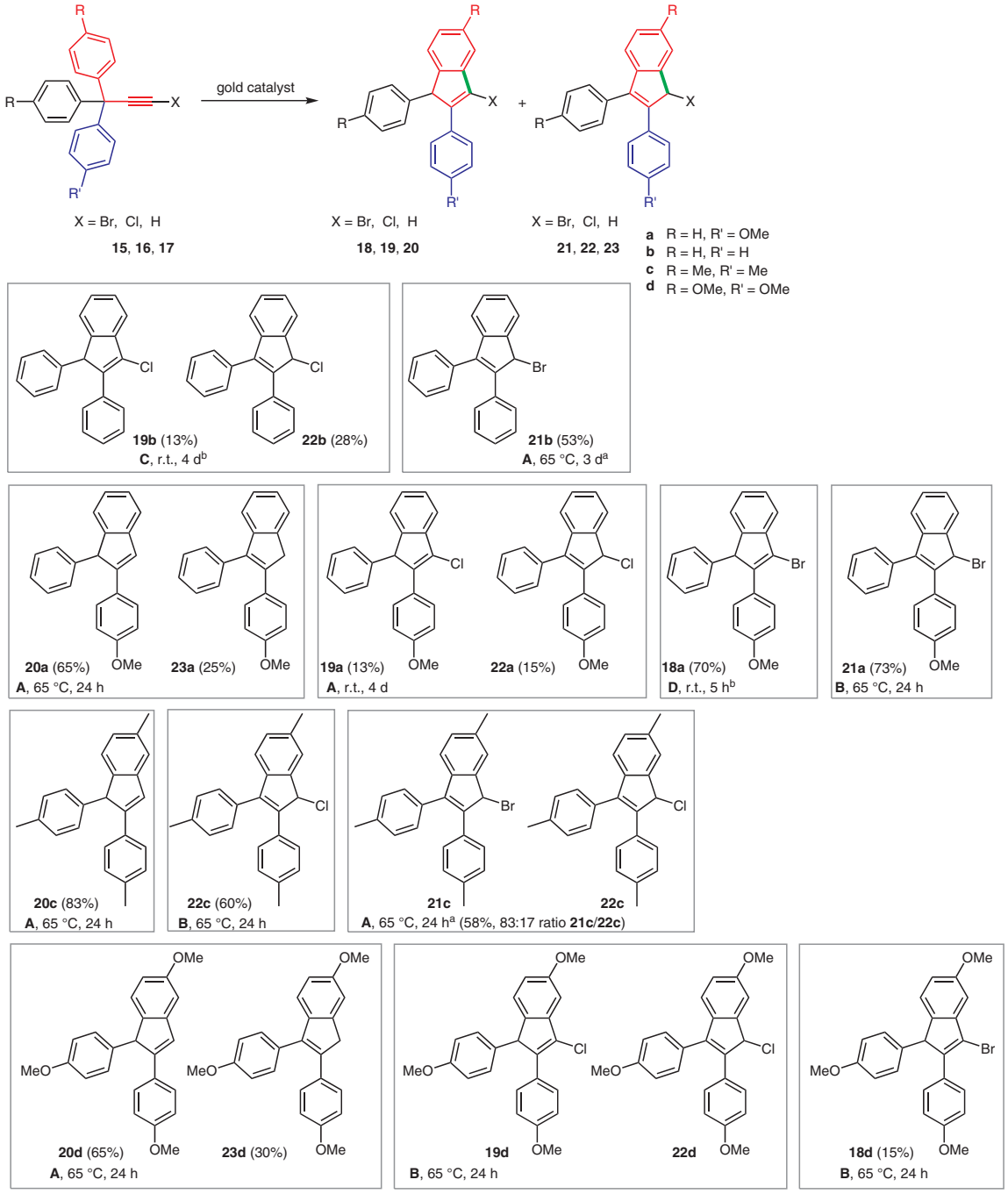
the reaction of chloroalkyne **16a**, the corresponding indenes **20a** and **23a** were formed. Interestingly, the reaction with the gold(III) complex dichloro(2-picolinato)gold(III) did not lead to any conversion (entry 15). The highest yield of **20a** was obtained with [JohnPhosAu(NCMe)]SbF_6 at 65 °C (88%; entry 1), whereas the best reaction conditions for the preparation of **23a** are CyJohnPhosAuNTf_2 as catalyst at a temperature of 65 °C (89%; entry 7). Comparing the ratio of both products, it becomes obvious that the tendencies are strongly dependent on the temperature. In addition, a change of the ratio can be observed during the reaction. For example, if *t*BuXPhosAuNTf_2 is used as catalyst, the ratio of **20a** to **23a** amounts to 57:10 after one week at room temperature (entry 4). Subsequent heating of this sample to 65 °C for 24 hours causes a reverse of the ratio to 0:73 (entry 5); i.e. a conversion of **20a** into **23a** must have occurred.

After the NMR experiments, we performed the reaction on a preparative scale. To evaluate the scope of the gold-catalyzed cyclization of tritylacetylenes, different trityl systems were converted into the corresponding indenes **18**–**23** (Scheme 5). Besides the methoxy-substituted compounds **15a**–**17a**, the unsubstituted systems **15b**–**17b** and the trimethyl- and trimethoxy-substituted compounds **15c**–**17c** and **15d**–**17d** were tested. The conversion of the terminal alkynes **17** were conducted using [JohnPhosAu(NCMe)]SbF_6 as catalyst. For the reaction of the tritylhaloalkynes **15** and **16** different catalysts were used (see Scheme 5).

In the case of the terminal alkynes **17**, the indene formation can only be observed when the trityl system contains electron-rich aromatic rings. Thus, alkyne **17b** shows no reaction. The conversion of the other terminal alkynes always shows the preferred formation of **20** over **23**. For example, the reaction of the methyl-substituted system only delivers indene **20c**. The indenes **20** and **23** could be isolated in total yields (**20** and **23** together) up to 83–95%.

The chloroacetylenes **16** are more reactive than the corresponding terminal alkynes **17**; the gold-catalyzed reaction therefore leads to the corresponding indenes in all cases. The total yields (**19** and **22** together) are in the range of 28–60%, whereby indene **22** is always preferentially formed. The higher reactivity could also be a reason for the lower total yields compared to the terminal alkynes. In the case of the trimethyl-substituted system **16c**, the formation of **22c** is strongly preferred. Therefore, the amount of compound **19c** was too small to be isolated. Due to their high reactivity the indenes **22d** and **19d** could only be identified in NMR experiments. Any attempt to isolate and characterize them failed.

Interestingly, the substitution of chlorine by bromine, leads to the formation of only one indene product using dichloro(2-picolinato)gold(III) as catalyst. In three cases, the benzylic bromide (**21a**–**21c**) and in one case the vinylic bromide (**18d**) were isolated. Unfortunately, compounds **21b** and **21c** could not be separated from byproducts. The latter could be identified as the chloroindenes **22b** and **22c**,



Scheme 5 Gold-catalyzed reaction of alkynes **15–17** leads to the indenes **18–23**. If not stated otherwise, $CDCl_3$ was used as solvent and 5 mol% of the catalyst was employed. Compounds listed in one box were formed as isomers in the same reaction. The following catalysts were used: [JohnPhosAu(NCMe)]SbF_6 (**A**), dichloro(2-picolinato)gold(III) (**B**), IPrAuCl/$AgSbF_6$ (**C**), IPrAuCl/$NaBArF_{24}$ (**D**). [a] 1,2-Dibromoethane was employed as solvent. [b] 10 mol% of the silver or sodium salt, respectively, was used.

respectively. They were formed during the reaction with dichloro(2-picolinato)gold(III) in chloroform via a bromine–chlorine exchange. Repeating the reactions with [JohnPhosAu(NCMe)]SbF_6 in dibromoethane only led in the case of alkyne **15b** to the selective formation of the bromo-substituted indene **21b**. Using the bromoacetylene **15a**, it could be shown that the conversion with IPrAuCl/$NaBArF_{24}$ leads to the selective formation of the vinylic bromide **18a**.

This is in contrast to the results obtained by dichloro(2-picolinato)gold(III), where selectively the benzylic bromide **21a** was formed.

In addition to the bromo- and chloroacetylenes **15a** and **16a** the corresponding iodoacetylene was treated with a gold(III) and gold(I) catalyst, respectively. However, the conversion of the starting material proceeded very slowly and after workup only an indenone derivative instead of the corresponding iodoindene could be isolated (see Supporting Information).

In the next step, we wanted to gain insight into the reaction mechanism. As model systems we have chosen the methoxy-substituted tritylchloroacetylene **16a** and the unsubstituted tritylchloroacetylene **16b**. Compound **16a** was used for the NMR experiments and **16b** is the simplest representative of the tritylchloroacetylenes. For the quantum chemical calculations, we only considered a mono gold(I)-catalyzed mechanism, in which the activation of the alkyne takes place by only one gold center. This approach is insofar justified, as a dual gold catalysis can be ruled out for the reaction of chloroacetylenes with phosphine gold(I) complexes.[8] As ligands for the gold(I) complex, the neutral phosphine ligands PMe_3 and JohnPhos were chosen. The geometrical parameters of all stationary points were optimized using the density functional B3LYP[33–35] with additional dispersion correction with Becke–Johnson damping (D3BJ).[36] As basis sets 6-31G(d) was used for the light elements C, H, Cl, and P, whereas def2-TZVP[37,38] basis was employed for Au. Furthermore, the energies of the stationary points were calculated using the density functional B3LYP, the additional dispersion correction D3BJ and the basis set 6-311++G(d,p) for C, H, Cl, and P. For Au the def2-TZVP basis set was employed. To determine the solvent effect, single point calculations were performed using chloroform as solvent. The thus obtained data are summarized in Figure 3 and in the Supporting Information (Figures S1–S4 and Tables S1 and S2).

Let us consider the values obtained by means of B3LYP-D3BJ/6-311++G(d,p),def2-TZVP(SMD) with JohnPhos as ligand of the gold catalyst. The first step is the formation of the alkyne gold complexes **24a**,**b** from the alkynes **16a**,**b** and the cationic gold catalysts. These complexes undergo rearrangement via an 1,2-aryl shift to form the cations **26a**,**b** (Figure 3). The activation barrier for this rearrangement is strongly dependent on the migrating aryl group. If a shift of the electron-rich methoxyphenyl moiety takes place, the free energy for transition state **25a** amounts to 9.0 kcal/mol. By contrast, the shift of the unsubstituted phenyl group exhibits a significant higher activation barrier (**25b**: 12.6 kcal/mol). For this reason, the gold-catalyzed reaction of **16a** results selectively in a shift of the electron-rich methoxyphenyl group. A comparison of the activation barriers for the 1,2-aryl shift (9.0 kcal/mol for **25a** and 12.6 kcal/mol for **25b**) and the gold-catalyzed dimerization of **16a**,**b** (29.6 kcal/mol for **29a** and 30.7 kcal/mol for **29b** calculated on the same level of theory; see left side of Figure 3)

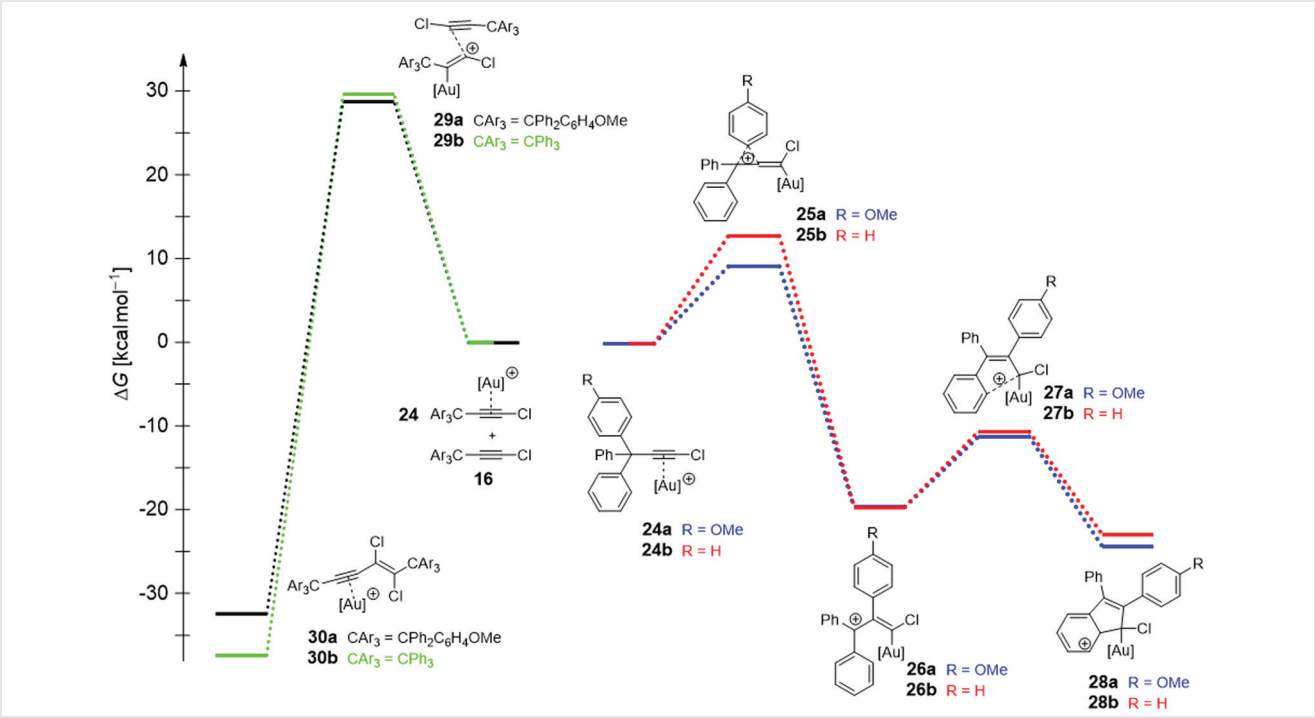


Figure 3 Free energy (Δ*G*) profile of the gold(I)-catalyzed reaction of alkynes **16a** (R = OMe) and **16b** (R = H) calculated by means of B3LYP-D3BJ/6-311++G(d,p),def2-TZVP(SMD). $[Au]^+$ = JohnPhosAu$^+$.

reveals that the 1,2-aryl shift exhibits considerably smaller values. Thus, no dimerization reaction is observed. The second step is a cyclization to cations **28a**,**b**, which are only slightly more stable than cations **26a**,**b**. The activation barriers for both systems are similar and amount to 11.0 kcal/mol and 10.4 kcal/mol, respectively. After rearomatization via deprotonation, the last step is a protodesauration. Depending on the regioselective attack of the proton, either indenes **19a**,**b** or indenes **22a**,**b** are formed. Whether the ratio of **19** to **22** is only determined by the attack of the proton, can not be answered, since subsequent isomerization of **19** and **22** is also conceivable (see Table 2).

In conclusion, we have developed a gold-catalyzed reaction method to synthesize chromene, dihydroquinoline, chromane, indene, and haloindene derivatives with yields up to 83% starting from terminal and halogen-substituted non-conjugated acetylenes. Advantages of this reaction are the readily available starting materials and the retainment of the halogen atom in the product allowing a further functionalization of the cyclization products. According to quantum chemical calculations, the reaction of tritylhaloacetylenes catalyzed by gold complexes proceeds via a different mechanism compared to the gold-catalyzed reaction of other haloacetylenes. Instead of rearrangement via a chloronium ion, a 1,2-aryl shift takes place. In the next step, a Friedel–Crafts type-cyclization and the following protodesauration leads to the formation of the indenes. This reaction represents a new possibility to achieve halogen-substituted cycles starting from simple systems.

All chemicals were reagent grade and were used as purchased from ABCR, Alfa Aesar, Acros Organics, Carbolution, TCI, or Sigma-Aldrich. Reactions were monitored by TLC analysis with silica gel 60 F254 thin-layer plates. Flash chromatography was carried out on silica 60 (40–63 µm, 230–400 mesh). ^{1}H and ^{13}C NMR spectra were measured with Bruker Avance DRX 500, Avance NEO 400, DMX 300 and Avance HD 600 spectrometers. The spectra were referenced to the peak for the protium impurity in the deuterated solvents indicated in brackets in the analytical data (CD_2Cl_2, ^{1}H: δ = 5.32, ^{13}C: δ = 53.84; CD_3CN, ^{1}H: δ = 1.94, ^{13}C: δ = 1.32; $CDCl_3$, ^{1}H: δ = 7.26, ^{13}C: δ = 77.16). ^{13}C NMR spectra were measured with ^{1}H decoupling. ^{13}C assignment was achieved via HSQC, HMBC and COSY spectra. The ^{13}C signals were referred to p (primary), s (secondary), t (tertiary), q (quaternary) carbon atoms. HRMS spectra were recorded with a Bruker BioTOF III mass spectrometer with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) as ionization source. UV/Vis absorption spectra were obtained with a Jasco V-550 spectrophotometer. IR absorption spectra were recorded with a Varian 3100 FT-IR spectrophotometer. Melting points were measured with a Büchi melting point apparatus Model B-540 with an open capillary and are uncorrected. [JohnPhosAu(NCMe)]SbF_6 (**S1**)[26] was synthesized according to the literature procedure. Haloacetylenes were prepared from the corresponding terminal acetylenes, see the Supporting Information for details.

Gold(I)-Catalyzed Cyclization of Chloroacetylenes 9, 10, and 13; General Procedure

In a 2-mL screw-capped vial, chloroacetylene (0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). The gold catalyst (0.02 mmol, 0.05 equiv) was added. The mixture was stirred at r.t. until full conversion (TLC monitoring). The solvent was removed under reduced pressure and the residue purified by flash chromatography to yield the desired heterocycles.

4-Chloro-6-methyl-1-tosyl-1,2-dihydroquinoline (11a)

According to the general procedure, acetylene **9a** (133.5 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, cyclohexane/EtOAc 95:5) to yield **11a** (112 mg, 0.34 mmol, 84%) as a colorless solid; R_f (cyclohexane/EtOAc 95:5) = 0.24.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.60–7.57 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, $C_{ar}H$), 7.29–7.27 (s, 2 H, $C_{ar}H$), 7.24–7.22 (s, 1 H, $C_{ar}H$), 7.20–7.17 (d, 1 H, $C_{ar}H$), 7.12–7.10 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, $C_{ar}H$), 5.62–5.59 (t, $^3J_{H,H}$ = 4.6 Hz, 1 H, CH=CCl), 4.44–4.41 (d, $^3J_{H,H}$ = 4.6 Hz, 2 H, CH_2), 2.37 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 143.9 (q, C_{ar}), 137.2 (q, C_{ar}), 135.7 (q, C_{ar}), 133.2 (q, C_{ar}), 130.2 (t, C_{ar}), 129.4 (t, C_{ar}), 129.1 (q, CCl), 128.0 (q, C_{ar}), 127.4 (t, C_{ar}), 127.2 (t, C_{ar}), 125.1 (t, C_{ar}), 121.1 (t, CH=CCl), 46.1 (s, CH_2), 21.7 (p, CH_3), 21.4 (p, CH_3).

The NMR data agree with those in the literature.[39]

4-Chloro-6-methyl-2*H*-chromene (12a)

According to the general procedure, acetylene **10a** (72.3 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, *n*-hexane) to yield **12a** (23 mg, 0.13 mmol, 33%) as a colorless oil; R_f (*n*-hexane) = 0.20.

IR (ATR): 2920, 2834, 2729, 1746, 1694, 1632, 1578, 1489, 1414, 1371, 1321, 1283, 1273, 1234, 1211, 1152, 1130, 1088, 1059, 974, 936, 882, 864, 818, 789, 762, 735, 698, 683, 638, 604 cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.25–7.22 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, $C_{ar}H$), 7.00–6.97 (dd, $^3J_{H,H}$ = 2.0 Hz, 1 H, $C_{ar}H$), 6.73–6.70 (d, 1 H, $C_{ar}H$), 5.90–5.88 (t, $^3J_{H,H}$ = 4.0 Hz, 1 H, ClC=CH), 4.82–4.78 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, OCH_2), 2.30 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 152.5 (q, C_{ar}), 131.1 (q, C_{ar}), 131.0 (t, C_{ar}), 128.4 (q, C_{ar}), 125.1 (t, C_{ar}), 121.1 (q, C_{ar}), 119.0 (t, ClC=CH), 115.7 (t, C_{ar}), 66.1 (s, OCH_2), 20.8 (p, CH_3).

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{10}{}^{35}ClO^+$: 181.0415; found: 181.0413.

UV/Vis (CH_3CN): λ_{max} (log ε) = 219 (4.28), 264 (3.57), 319 nm (3.38).

4-Chloro-8-methyl-2*H*-chromene (12b)

According to the general procedure, acetylene **10b** (72.3 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, *n*-hexane) to yield **12b** (23 mg, 0.13 mmol, 33%) as a colorless oil; R_f (*n*-hexane) = 0.30.

IR (ATR): 2839, 1634, 1601, 1516, 1495, 1466, 1433, 1379, 1329, 1300, 1263, 1242, 1225, 1198, 1163, 1098, 1080, 1053, 1007, 978, 943, 901, 827, 787, 775, 739, 710 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 7.30–7.28 (dd, $^3J_{H,H}$ = 7.7 Hz, 1 H, $C_{ar}H$), 7.07–7.05 (dd, $^3J_{H,H}$ = 7.7 Hz, 1 H, $C_{ar}H$), 6.87–6.84 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, $C_{ar}H$), 5.90–5.88 (t, $^3J_{H,H}$ = 4.0 Hz, 1 H, ClC=CH), 4.87–4.83 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, CH_2), 2.18 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 152.7 (q, C_{ar}), 132.3 (t, C_{ar}), 128.7 (q, CCl), 125.3 (q, C_{ar}), 122.5 (t, C_{ar}), 121.0 (q, C_{ar}), 120.9 (t, C_{ar}), 118.6 (t, ClC=CH), 66.1 (s, CH_2), 15.7 (p, CH_3).

HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{10}H_{10}{}^{35}ClO^+$: 181.0415; found: 181.0409.

UV/Vis (CH_3CN): λ_{max} (log ε) = 192 (4.27), 217 (4.18), 267 (3.61), 314 nm (3.25).

4-Chloro-6-methoxy-2*H*-chromene (12c)

According to the general procedure, acetylene **10c** (78.6 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, cyclohexane/EtOAc 95:5) to yield **12c** (44 mg, 0.22 mmol, 56%) as a yellow oil; R_f (cyclohexane/EtOAc 95:5) = 0.19.

IR (ATR): 2834, 1732, 1688, 1653, 1626, 1607, 1578, 1483, 1402, 1383, 1348, 1310, 1294, 1265, 1204, 1153, 1086, 1032, 1017, 972, 936, 912, 868, 849, 822, 793, 766, 743, 725, 700, 691, 669, 638, 623 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 7.00–6.99 (dd, 1 H, $C_{ar}H$), 6.76–6.74 (m, 2 H, $C_{ar}H$), 5.95–5.93 (t, $^3J_{H,H}$ = 4.1 Hz, 1 H, CH=CCl), 4.79–4.77 (d, $^3J_{H,H}$ = 4.1 Hz, 2 H, CH_2), 3.79 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 154.4 (q, C_{ar}), 148.5 (q, C_{ar}), 128.3 (q, C_{ar}), 122.2 (q, C_{ar}), 119.8 (t, CH=CCl), 116.6 (t, C_{ar}), 116.0 (t, C_{ar}), 109.9 (t, C_{ar}), 66.1 (s, CH_2), 56.0 (p, OCH_3).

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{10}H_{10}{}^{35}ClO_2{}^+$: 197.0364; found: 197.0361.

UV/Vis (CH_3CN): λ_{max} (log ε) = 221 (4.34), 330 nm (3.54).

Methyl 4-Chloro-2*H*-chromene-6-carboxylate (12d)

According to the general procedure, acetylene **10d** (89.9 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, cyclohexane/EtOAc 95:5) to yield **12d** (66 mg, 0.29 mmol, 73%) as a colorless solid; mp 107 °C; R_f (cyclohexane/EtOAc 95:5) = 0.25.

IR (ATR): 2955, 2866, 1715, 1647, 1605, 1578, 1489, 1458, 1435, 1424, 1389, 1331, 1316, 1261, 1248, 1240, 1192, 1173, 1128, 1105, 1059, 1013, 988, 972, 920, 907, 866, 839, 797, 781, 758, 731, 706, 646, 613 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 8.10–8.09 (d, $^3J_{H,H}$ = 2.1 Hz, 1 H, $C_{ar}H$), 7.90–7.87 (dd, $^3J_{H,H}$ = 2.1 Hz, 8.5 Hz, 1 H, $C_{ar}H$), 6.83–6.80 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, $C_{ar}H$), 5.93–5.92 (t, $^3J_{H,H}$ = 3.9 Hz, 1 H, CH=CCl), 4.96–4.94 (d, $^3J_{H,H}$ = 3.9 Hz, 2 H, CH_2), 3.90 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 166.5 (q, COOMe), 158.4 (q, C_{ar}), 132.6 (t, C_{ar}), 127.6 (q, CCl), 126.5 (t, C_{ar}), 123.6 (q, C_{ar}), 120.7 (q, C_{ar}), 119.3 (t, CH=CCl), 116.0 (t, C_{ar}), 66.8 (s, CH_2), 52.2 (p, OCH_3).

HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{11}H_{10}{}^{35}ClO_3{}^+$: 225.0313; found: 225.0311.

UV/Vis (CH_3CN): λ_{max} (log ε) = 195 (4.23), 241 (4.58), 281 nm (3.68).

(*Z*)-4-(Chloromethylene)-6-methylchromane (14a)

According to the general procedure, acetylene **13a** (77.9 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, cyclohexane/EtOAc 95:5) to yield **14a** (47 mg, 0.24 mmol, 60%) as a colorless oil; R_f (cyclohexane/EtOAc 95:5) = 0.63.

IR (ATR): = 2971, 2928, 2878, 1487, 1464, 1418, 1377, 1327, 1296, 1277, 1254, 1229, 1217, 1169, 1128, 1076, 1042, 1001, 945, 905, 883, 806, 781, 745, 735, 696, 648 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 8.10–8.07 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, $C_{ar}H$), 7.06–7.01 (dd, $^3J_{H,H}$ = 2.0 Hz, 8.4 Hz, 1 H, $C_{ar}H$), 6.78–6.75 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, $C_{ar}H$), 6.02–5.99 (t, $^4J_{H,H}$ = 1.3 Hz, 1 H, C=CHCl), 4.28–4.25 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, OCH_2), 2.62–2.58 (td, $^3J_{H,H}$ = 5.6 Hz, $^4J_{H,H}$ = 1.3 Hz, 2 H, CH_2), 2.30 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 152.6 (q, C_{ar}), 131.1 (t, C_{ar}), 130.0 (q, C=CHCl), 129.2 (q, C_{ar}), 128.5 (t, C_{ar}), 118.7 (q, C_{ar}), 116.9 (t, C_{ar}), 110.8 (t, C=CHCl), 66.7 (s, OCH_2), 31.9 (s, CH_2), 20.9 (p, CH_3).

HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{11}H_{12}{}^{35}ClO^+$: 195.0571; found: 195.0568.

UV/Vis (CH_3CN): λ_{max} (log ε) = 216 (4.37), 256 (4.16), 312 nm (3.77).

(*E*)-4-(Chloromethylene)-8-methylchromane (14b)

According to the general procedure, acetylene **13b** (77.9 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, cyclohexane/EtOAc 95:5) to yield **14b** (8 mg, 0.04 mmol, 10%) as a colorless oil; R_f (cyclohexane/EtOAc 95:5) = 0.28.

IR (ATR): 2974, 2916, 2872, 1734, 1659, 1616, 1541, 1470, 1456, 1425, 1377, 1341, 1308, 1275, 1254, 1206, 1171, 1119, 1086, 1069, 1042, 1003, 945, 912, 893, 874, 810, 766, 733, 677, 646 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 7.29–7.26 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, $C_{ar}H$), 7.07–7.04 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, $C_{ar}H$), 6.82–6.77 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, $C_{ar}H$), 6.60 – 6.59 (t, $^4J_{H,H}$ = 1.8 Hz, 1 H, C=CHCl), 4.26 – 4.22 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, OCH_2), 2.84–2.81 (td, $^3J_{H,H}$ = 5.9 Hz, $^4J_{H,H}$ = 1.8 Hz, 2 H, CH_2), 2.20 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 152.5 (q, C_{ar}), 132.0 (q, C=CCl), 130.8 (t, C_{ar}), 127.2 (q, C_{ar}), 121.2 (t, C_{ar}), 120.5 (t, C_{ar}), 119.8 (q, C_{ar}), 111.8 (t, C=CHCl), 65.7 (s, OCH_2), 26.4 (s, CH_2), 16.2 (p, CH_3).

HRMS (APCI): *m/z* $[M + H]^+$ calcd for $C_{11}H_{12}{}^{35}ClO^+$: 195.0571; found: 195.0569.

UV/Vis (CH_3CN): λ_{max} (log ε) = 192 (4.33), 219 (4.48), 262 (4.27), 308 nm (3.90).

(*Z*)-4-(Chloromethylene)-6-chlorochromane (14c)

According to the general procedure, acetylene **13c** (86.0 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, cyclohexane/EtOAc 95:5) to yield **14c** (61 mg, 0.28 mmol, 70%) as a yellow oil; R_f (cyclohexane/EtOAc 95:5) = 0.39.

IR (ATR): = 2882, 1626, 1560, 1458, 1429, 1216, 1377, 1323, 1289, 1267, 1248, 1221, 1192, 1169, 1125, 1098, 1074, 1040, 945, 903, 882, 862, 816, 733, 718, 673, 625 cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.27–8.26 (d, $^3J_{H,H}$ = 2.6 Hz, 1 H, $C_{ar}H$), 7.18–7.15 (dd, $^3J_{H,H}$ = 2.6 Hz, 8.8 Hz, 1 H, $C_{ar}H$), 6.81–6.78 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, $C_{ar}H$), 6.08 (t, $^4J_{H,H}$ = 1.2 Hz, 1 H, C=CHCl), 4.30–4.25 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, OCH_2), 2.62–2.58 (td, $^3J_{H,H}$ = 5.6 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 H, CH_2).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 153.3 (q, C_{ar}), 130.2 (t, C_{ar}), 128.9 (q, C=CCl), 127.9 (t, C_{ar}), 125.0 (q, C_{ar}), 120.2 (q, C_{ar}), 118.5 (t, C_{ar}), 112.4 (t, C=CHCl), 66.8 (s, OCH_2), 31.4 (s, CH_2).

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_9{}^{35}Cl_2O^+$: 213. 9947; found: 213.9940.

UV/Vis (CH_3CN): λ_{max} (log ε) = 192 (4.27), 219 (4.30), 254 (4.07), 193 nm (3.70).

(*Z*)-4-(Chloromethylene)-6-methoxychromane (14d)

According to the general procedure, acetylene **13d** (84.3 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, cyclohexane/EtOAc 95:5) to yield **14d** (70 mg, 0.33 mmol, 83%) as a yellow oil; R_f (cyclohexane/EtOAc 95:5) = 0.32.

IR (ATR): = 2934, 2874, 2832, 1719, 1622, 1572, 1481, 1462, 1424, 1379, 1339, 1308, 1296, 1271, 1256, 1206, 1167, 1130, 1119, 1072, 1047, 1032, 953, 907, 897, 875, 855, 805, 752, 737, 696, 654, 619, 610 cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.89–7.88 (d, $^4J_{H,H}$ = 2.9 Hz, 1 H, $C_{ar}H$), 6.85–6.82 (dd, $^3J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 2.9 Hz, 1 H, $C_{ar}H$), 6.81–6.78 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, $C_{ar}H$), 6.04–6.03 (t, $^4J_{H,H}$ = 1.2 Hz, 1 H, CHCl), 4.25–4.23 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, OCH_2), 3.79 (s, 3 H, OCH_3), 2.61–2.59 (td, $^3J_{H,H}$ = 5.6 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 H, CH_2).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 152.9 (q, C_{ar}), 149.0 (q, C_{ar}), 129.9 (q, C=CHCl), 119.1 (q, C_{ar}), 117.8 (t, C_{ar}), 117.5 (t, C_{ar}), 112.2 (t, C_{ar}), 111.6 (t, CHCl), 66.7 (s, OCH_2), 55.9 (p, OCH_3), 31.9 (s, CH_2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{12}{}^{35}ClO_2{}^+$: 211.0520; found: 211.0511.

UV/Vis (CH_3CN): λ_{max} (log ε) = 214 (4.27), 250 (4.07), 328 nm (3.74).

Methyl (*Z*)-4-(Chloromethylene)chromane-6-carboxylate (14e)

According to the general procedure, acetylene **13e** (95.5 mg, 0.4 mmol, 1.0 equiv) was dissolved in dry DCM (0.4 mL, 1 M). [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 20 µmol, 5 mol%) was added. The mixture was stirred at r.t. for 2 h and then the solvent was removed in vacuo to give a residue which was purified by flash chromatography (silica gel, cyclohexane/EtOAc 95:5) to yield **14e** (44 mg, 0.18 mmol, 45%) as a colorless solid; mp 64 °C; R_f (cyclohexane/EtOAc 95:5) = 0.21.

IR (ATR): = 3071, 2947, 2903, 1703, 1634, 1613, 1570, 1487, 1389, 1329, 1285, 1265, 1248, 1231, 1194, 1125, 1107, 1080, 1036, 982, 9499, 916, 899, 885, 835, 816, 806, 785, 760, 739, 719, 679, 638, 613 cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.99–8.96 (d, $^3J_{H,H}$ = 2.2 Hz, 1 H, $C_{ar}H$), 7.91–7.88 (dd, $^3J_{H,H}$ = 2.2 Hz, 8.7 Hz, 1 H, $C_{ar}H$), 6.90–6.87 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, $C_{ar}H$), 6.12–6.11 (t, $^4J_{H,H}$ = 1.3 Hz, 1 H, C=CHCl), 4.37–4.33 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, OCH_2), 3.90 (s, 3 H, OCH_3), 2.65–2.61 (td, $^3J_{H,H}$ = 5.6 Hz, $^4J_{H,H}$ = 1.3 Hz, 2 H, CH_2).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 166.9 (q, C_{ar}), 158.3 (q, C_{ar}), 131.6 (t, C_{ar}), 130.7 (t, C_{ar}), 129.0 (q, C=CCl), 122.1 (q, C_{ar}), 118.8 (q, C_{ar}), 117.3 (t, C_{ar}), 112.5 (t, C=CHCl), 67.3 (s, OCH_2), 52.2 (p, OCH_3), 31.3 (s, CH_2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{12}{}^{35}ClO_3{}^+$: 239.0469; found: 239.0463.

UV/Vis (CH_3CN): λ_{max} (log ε) = 191 (4.19), 246 (4.51), 304 nm (3.53).

Gold-Catalyzed Synthesis of Indenes; General Procedure

The acetylene (1.0 equiv) was dissolved in $CDCl_3$ or 1,2-dibromoethane and the gold catalyst (0.05 equiv) was added. The mixture was stirred until ^{1}H NMR spectra or TLC showed complete conversion. The solvent was removed in vacuo to give a residue which was purified by flash chromatography.

2-(4-Methoxyphenyl)-1-phenyl-1*H*-indene (20a) and 2-(4-Methoxyphenyl)-3-phenyl-1*H*-indene (23a)

According to the general procedure acetylene **17a** (119.4 mg, 0.4 mmol, 1 equiv) was dissolved in $CDCl_3$ (0.8 mL); [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 0.02 mmol, 0.05 equiv) was added and the mixture was stirred overnight at 65 °C. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/DCM 4:1) to yield **20a** (78 mg, 0.26 mmol, 65%) as a white solid and **23a** (31 mg, 0.10 mmol, 25%) as an orange solid.

2-(4-Methoxyphenyl)-1-phenyl-1*H*-indene (20a)

R_f (*n*-hexane/DCM 1:1) = 0.49.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.45–7.43 (m, 2 H, $C_{ar}H$), 7.39–7.37 (m, 1 H, $C_{ar}H$), 7.24–7.21 (m, 4 H, $C_{ar}H$ + $C_{ali}H$), 7.17–7.14 (m, 4 H, $C_{ar}H$), 7.09–7.06 (m, 1 H, $C_{ar}H$), 6.80–6.79 (m, 2 H, $C_{ar}H$), 4.93 (s, 1 H, C*H*Ph), 3.76 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 159.1 (q, $C_{ar}OCH_3$), 149.7 (q, C=C), 149.0 (q, C_{ar}), 143.7 (q, C_{ar}), 140.4 (q, C_{ar}), 129.0 (t, C_{ar}), 128.0 (t, C_{ar}), 128.0 (t, C_{ar}), 127.1 (t, C_{ar}), 126.8 (t, C_{ar}), 126.3 (t, C=C), 125.2 (t, C_{ar}), 123.9 (t, C_{ar}), 120.8 (t, C_{ar}), 114.1 (t, C_{ar}), 56.4 (t, *C*HPh), 55.3 (p, OCH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}O^+$: 299.1430; found: 299.1426.

The NMR data agree with those in the literature.[40]

2-(4-Methoxyphenyl)-3-phenyl-1*H*-indene (23a)

R_f (*n*-hexane/DCM 1:1) = 0.54.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35–7.51 (m, 1 H, $C_{ar}H$), 7.46–7.35 (m, 5 H, $C_{ar}H$), 7.28–7.18 (m, 5 H, $C_{ar}H$), 6.78–6.74 (m, 2 H, $C_{ar}H$), 3.90 (s, 2 H, CH_2), 3.78 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.7 (q, $C_{ar}OCH_3$), 147.3 (q, C_{ar}), 142.3 (q, C=C), 140.9 (q, C=C), 138.5 (q, C=C), 136.5 (q, C_{ar}), 129.6 (t, C_{ar}), 129.3 (q, C_{ar}), 129.0 (t, C_{ar}), 127.4 (t, C_{ar}), 126.6 (t, C_{ar}), 124.9 (t, C_{ar}), 123.6 (t, C_{ar}), 120.2 (t, C_{ar}), 113.8 (t, C_{ar}), 55.3 (p, OCH_3), 41.3 (s, CH_2).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}O^+$: 299.1430; found: 299.1425.

The NMR data agree with those in the literature.[40]

1-Bromo-2-(4-methoxyphenyl)-3-phenyl-1*H*-indene (21a)

According to the general procedure acetylene **15a** (150.9 mg, 0.4 mmol, 1 equiv) was dissolved in $CDCl_3$ (0.8 mL); dichloro(2-picolinato)gold(III) (7.8 mg, 0.02 mmol, 0.05 equiv) was added and the mixture was stirred overnight at 65 °C. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/DCM 2:1) to yield **21a** (111 mg, 0.29 mmol, 73%) as a yellow solid; mp 157–159 °C; R_f (*n*-hexane/DCM 2:1) = 0.26.

IR (ATR): 3026, 2999, 2839, 1599, 1512, 1487, 1460, 1441, 1418, 1298, 1250, 1179, 1152, 1115, 1072, 1047, 1026, 883, 868, 831, 814, 783, 770, 750, 737, 706, 696, 648, 637, 611 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.65–7.63 (m, 1 H, $C_{ar}H$), 7.44–7.35 (m, 5 H, $C_{ar}H$), 7.32–7.27 (m, 2 H, $C_{ar}H$), 7.20–7.15 (m, 3 H, $C_{ar}H$), 6.82–6.78 (m, 2 H, $C_{ar}H$), 5.96 (s, 1 H, C*H*Br), 3.79 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 159.2 (q, $C_{ar}OCH_3$), 143.9 (q, C_{ar}), 143.7 (q, C_{ar}), 142.0 (q, C=C), 139.3 (q, C=C), 134.7 (q, C_{ar}), 130.6 (t, C_{ar}), 129.3 (t, C_{ar}), 128.9 (t, C_{ar}), 128.1 (t, C_{ar}), 126.6 (t, C_{ar}), 126.3 (q, C_{ar}), 125.1 (t, C_{ar}), 121.0 (t, C_{ar}), 113.8 (t, C_{ar}), 55.3 (p, OCH_3), 49.9 (t, *C*HBr).

HRMS (ESI): *m*/*z* [M – ^{79}Br]$^+$ calcd for $C_{22}H_{17}O^+$: 297.1274; found: 297.1276.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 255 (4.39), 304 (3.94), 347 nm (3.81).

3-Bromo-2-(4-methoxyphenyl)-1-phenyl-1*H*-indene (18a)

According to the general procedure acetylene **15a** (150.9 mg, 0.4 mmol, 1 equiv) was dissolved in $CDCl_3$ (4 mL); IPrAuCl (12.4 mg, 0.02 mmol, 0.05 equiv) and $NaBArF_{24}$ (35.4 mg, 0.04 mmol, 0.1 equiv) were added and the mixture was stirred for 5 h at r.t. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/DCM 2:1) to yield **18a** (106 mg, 0.28 mmol, 70%) as a colorless oil; R_f (*n*-hexane/DCM 2:1) = 0.47.

IR (ATR): 3059, 3025, 2957, 2930, 2905, 2835, 1601, 1505, 1493, 1441, 1246, 1177, 1042, 1026, 941, 835, 779, 752, 729, 696, 683, 617, 604 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.59–7.56 (m, 2 H, $C_{ar}H$), 7.51–7.49 (m, 1 H, $C_{ar}H$), 7.39–7.35 (m, 1 H, $C_{ar}H$), 7.21–7.11 (m, 5 H, $C_{ar}H$), 7.07–7.05 (m, 2 H, $C_{ar}H$), 6.86–6.82 (m, 2 H, $C_{ar}H$), 4.99 (s, 1 H, C*H*Ph), 3.77 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 159.2 (q, $C_{ar}OCH_3$), 146.1 (q, C=C), 145.8 (q, C=C), 143.3 (q, C=C), 139.1 (q, C=C), 130.3 (t, C_{ar}), 128.9 (t, C_{ar}), 128.2 (t, C_{ar}), 127.6 (t, C_{ar}), 127.1 (t, C_{ar}), 126.8 (q, C=C), 126.6 (t, C_{ar}), 123.7 (t, C_{ar}), 120.6 (t, C_{ar}), 117.3 (q, C=C), 113.8 (t, C_{ar}), 58.1 (t, *C*HPh), 55.3 (p, OCH_3).

HRMS (ESI): *m*/*z* [M – ^{79}Br]$^+$ calcd for $C_{22}H_{17}O^+$: 297.1274; found: 297.1274.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 227 (4.25), 310 nm (4.35).

1-Chloro-2-(4-methoxyphenyl)-3-phenyl-1*H*-indene (22a) and 3-Chloro-2-(4-methoxyphenyl)-1-phenyl-1*H*-indene (19a)

According to the general procedure acetylene **16a** (133.1 mg, 0.4 mmol, 1 equiv) was dissolved in $CDCl_3$ (0.8 mL); [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 0.02 mmol, 0.05 equiv) was added and the mixture was stirred for 4 d at r.t. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/DCM 4:1 to 3:1) to yield **19a** (17.6 mg, 0.05 mmol, 13%) as a light brown solid and **22a** (19.4 mg, 0.06 mmol, 15%) as a yellow solid.

3-Chloro-2-(4-methoxyphenyl)-1-phenyl-1*H*-indene (19a)

Mp 117 °C; R_f (*n*-hexane/DCM 1:1) = 0.47.

IR (ATR): 2926, 2835, 1603, 1576, 1562, 1506, 1495, 1439, 1418, 1343, 1300, 1267, 1248, 1177, 1074, 1047, 1026, 970, 914, 874, 839, 829, 808, 779, 762, 752, 735, 696, 644, 619, 610 cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.64–7.61 (m, 2 H, $C_{ar}H$), 7.52–7.51 (m, 1 H, $C_{ar}H$), 7.38–7.35 (m, 1 H, $C_{ar}H$), 7.21–7.17 (m, 4 H, $C_{ar}H$), 7.16–7.13 (m, 1 H, $C_{ar}H$), 7.10–7.09 (m, 2 H, $C_{ar}H$), 6.86–6.83 (m, 2 H, $C_{ar}H$), 5.03 (s, 1 H, C*H*Ph), 3.77 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 159.1 (q, $C_{ar}OCH_3$), 145.8 (q, *C*Cl), 142.1 (q, C_{ar}), 141.9 (q, *C*PhOCH$_3$), 139.3 (q, C_{ar}), 130.2 (t, C_{ar}), 128.9 (t, C_{ar}), 128.1 (t, C_{ar}), 127.5 (t, C_{ar}), 127.3 (q, C_{ar}), 127.1 (t, C_{ar}), 126.6 (t, C_{ar}), 126.2 (q, C_{ar}), 123.7 (t, C_{ar}), 119.3 (t, C_{ar}), 113.8 (t, C_{ar}), 56.8 (t, *C*HPh), 55.3 (p, OCH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{18}{}^{35}ClO^+$: 333.1041; found: 333.1037; *m*/*z* [M – Cl]$^+$ calcd for $C_{22}H_{17}O^+$: 297.1274; found: 297.1276.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 226 (3.93), 312 nm (4.10).

1-Chloro-2-(4-methoxyphenyl)-3-phenyl-1*H*-indene (22a)

Mp 169 °C; R_f (*n*-hexane/DCM 1:1) = 0.41.

IR (ATR): 3077, 3042, 2999, 2940, 2843, 1599, 1514, 1454, 1441, 1416, 1337, 1298, 1285, 1252, 1206, 1182, 1167, 1113, 1072, 1049, 1026, 936, 914, 887, 868, 833, 814, 783, 768, 750, 737, 719, 694, 654, 637, 627, 615, 602 cm^{-1}.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.66–7.63 (m, 1 H, $C_{ar}H$), 7.44–7.41 (m, 2 H, $C_{ar}H$), 7.40–7.36 (m, 3 H, $C_{ar}H$), 7.34–7.29 (m, 2 H, $C_{ar}H$), 7.22–7.20 (m, 2 H, $C_{ar}H$), 7.19–7.16 (m, 1 H, $C_{ar}H$), 6.82–6.79 (m, 2 H, $C_{ar}H$), 5.80 (s, 1 H, C*H*Cl), 3.79 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 159.1 (q, $C_{ar}OCH_3$), 144.1 (q, C_{ar}), 143.2 (q, C_{ar}), 141.6 (q, *C*PhOCH$_3$), 139.7 (q, *C*Ph), 134.6 (q, C_{ar}), 130.7 (t, C_{ar}), 129.3 (t, C_{ar}), 129.1 (t, C_{ar}), 129.0 (t, C_{ar}), 128.1 (t, C_{ar}), 126.5 (t, C_{ar}), 126.0 (q, C_{ar}), 124.6 (t, C_{ar}), 120.9 (t, C_{ar}), 113.8 (t, C_{ar}), 60.4 (t, *C*HCl), 55.3 (p, OCH_3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{17}{}^{35}ClONa^+$: 355.0860; found: 355.0859; *m*/*z* [M – ^{35}Cl]$^+$ calcd for $C_{22}H_{17}O^+$: 297.1274; found: 297.1274.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 251 (4.03), 307 (3.62), 339 nm (3.61).

1-Bromo-2,3-diphenyl-1*H*-indene (21b)

Acetylene **15b** (138.9 mg, 0.4 mmol, 1 equiv) was dissolved in 1,2-dibromoethane (0.8 mL); [JohnPhosAu(NCMe)]SbF_6 (14.5 mg, 0.02 mmol, 0.05 equiv) was added and the mixture was stirred for 3 d at 65 °C. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/Et_2O 20:1) to yield **21b** (72 mg, 0.21 mmol, 53%) as a yellow solid; mp 157–159 °C; R_f (*n*-hexane/Et_2O 20:1) = 0.49.

IR (ATR): 3057, 3023, 2920, 1603, 1485, 1458, 1441, 1356, 1167, 1121, 1028, 939, 916, 883, 868, 785, 766, 752, 710, 691, 664, 635, 613, 606 cm^{-1}.

^{1}H NMR (CD_3CN, 600 MHz): δ = 7.68–7.65 (m, 1 H, $C_{ar}H$), 7.45–7.40 (m, 3 H, $C_{ar}H$), 7.37–7.32 (m, 4 H, $C_{ar}H$), 7.31–7.22 (m, 5 H, $C_{ar}H$), 7.19–7.16 (m, 1 H, $C_{ar}H$), 6.22 (s, 1 H, C*H*Br).

^{13}C NMR (CD_3CN, 151 MHz): δ = 145.0 (q, C=C), 144.2 (q, C=C), 144.0 (q, C=C), 141.3 (q, C=C), 135.2 (q, C=C), 135.0 (q, C=C), 130.3 (t, C_{ar}), 130.0 (t, C_{ar}), 130.0 (t, C_{ar}), 129.8 (t, C_{ar}), 129.2 (t, C_{ar}), 129.1 (t, C_{ar}), 128.7 (t, C_{ar}), 127.9 (t, C_{ar}), 126.1 (q, C_{ar}), 122.0 (t, C_{ar}), 51.2 (t, *C*HBr).

HRMS (ESI): *m*/*z* [M – ^{79}Br]$^+$ calcd for $C_{21}H_{15}{}^+$: 267.1168; found: 267.1169.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 249 (4.40), 301 (3.86), 331 nm (3.75).

1-Chloro-2,3-diphenyl-1*H*-indene (22b) and 3-Chloro-1,2-diphenyl-1*H*-indene (19b)

According to the general procedure acetylene **16b** (121.1 mg, 0.4 mmol, 1 equiv) was dissolved in $CDCl_3$ (0.8 mL); IPrAuCl (12.4 mg, 0.02 mmol, 0.05 equiv) and $AgSbF_6$ (15.5 mg, 0.04 mmol, 0.1 equiv) were added and the mixture was stirred for 4 d at r.t. The solvent was removed in vacuo and the residue was purified by flash chromatogra-

phy (silica gel, *n*-hexane/DCM 4:1) to yield **19b** (13.7 mg, 0.05 mmol, 13%) as a yellow oil and **22b** (32.4 mg, 0.11 mmol, 28%) as a white solid.

3-Chloro-1,2-diphenyl-1*H*-indene (19b)

R_f (*n*-hexane/DCM 1:1) = 0.58.

IR (ATR): 3059, 3025, 2928, 1601, 1578, 1590, 1491, 1458, 1443, 1343, 1296, 1263, 1177, 1152, 1099, 1072, 1026, 1003, 968, 939, 912, 870, 831, 824, 795, 733, 691, 671, 621, 611 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 7.66–7.64 (m, 2 H, $C_{ar}H$), 7.56–7.55 (m, 1 H, $C_{ar}H$), 7.40–7.37 (m, 1 H, $C_{ar}H$), 7.33–7.30 (m, 2 H, $C_{ar}H$), 7.24–7.18 (m, 5 H, $C_{ar}H$), 7.16–7.13 (m, 1 H, $C_{ar}H$), 7.10–7.08 (m, 2 H, $C_{ar}H$), 5.08 (s, 1 H, *CH*Ph).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 146.0 (q, C=C), 142.4 (q, C=C), 141.9 (q, C=C), 139.0 (q, C=C), 133.6 (q, C=C), 128.9 (t, C_{ar}), 128.9 (t, C_{ar}), 128.8 (q, C=C), 128.4 (t, C_{ar}), 128.2 (t, C_{ar}), 127.8 (t, C_{ar}), 127.5 (t, C_{ar}), 127.1 (t, C_{ar}), 127.0 (t, C_{ar}), 123.8 (t, C_{ar}), 119.6 (t, C_{ar}), 56.9 (t, *C*HPh).

HRMS (ESI): *m*/*z* [M – $^{35}Cl]^+$ calcd for $C_{21}H_{15}^+$: 267.1168; found: 267.1168.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 231 (4.03), 303 nm (4.15).

1-Chloro-2,3-diphenyl-1*H*-indene (22b)

Mp 163 °C; R_f (*n*-hexane/DCM 1:1) = 0.52.

IR (ATR): 3059, 3025, 2928, 1605, 1497, 1485, 1458, 1441, 1356, 1341, 1292, 1202, 1177, 1152, 1082, 1072, 1047, 1028, 1003, 984, 941, 918, 887, 870, 845, 795, 764, 754, 725, 714, 691, 669, 644, 621 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 7.68–7.65 (m, 1 H, $C_{ar}H$), 7.43–7.31 (m, 7 H, $C_{ar}H$), 7.27–7.21 (m, 6 H, $C_{ar}H$), 5.83 (s, 1 H, *CH*Cl).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 143.9 (q, C=C), 143.5 (q, C=C), 142.0 (q, C=C), 141.2 (q, C=C), 134.3 (q, C=C), 133.6 (q, C=C), 129.5 (t, C_{ar}), 129.3 (t, C_{ar}), 129.1 (t, C_{ar}), 129.0 (t, C_{ar}), 128.3 (t, C_{ar}), 128.2 (t, C_{ar}), 127.7 (t, C_{ar}), 126.9 (t, C_{ar}), 124.6 (t, C_{ar}), 121.2 (t, C_{ar}), 60.3 (t, *C*HCl).

HRMS (ESI): *m*/*z* [M – $^{35}Cl]^+$ calcd for $C_{21}H_{15}^+$: 267.1168; found: 267.1168.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 247 (4.38), 309 (3.86), 326 nm (3.84).

5-Methyl-1,2-di(4-tolyl)-1*H*-indene (20c)

According to the general procedure acetylene **17c** (112.4 mg, 0.36 mmol, 1 equiv) was dissolved in $CDCl_3$ (0.72 mL); [JohnPhosAu(NCMe)]SbF_6 (13.2 mg, 0.018 mmol, 0.05 equiv) was added and the mixture was stirred overnight at 65 °C. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/EtOAc 98:2) to yield **20c** (93 mg, 0.30 mmol, 83%) as an orange solid; mp 172–174 °C; R_f (*n*-hexane/EtOAc 98:2) = 0.21.

IR (ATR): 3026, 2916, 2868, 1607, 1510, 1470, 1449, 1377, 1188, 1109, 1036, 1020, 895, 856, 843, 812, 799, 783, 729, 716, 650 cm^{-1}.

^1H NMR ($CDCl_3$, 600 MHz): δ = 7.40–7.39 (m, 2 H, $C_{ar}H$), 7.25–7.20 (m, 2 H, $C_{ar}H$ + $C_{ali}H$), 7.06–7.04 (m, 3 H, $C_{ar}H$), 7.03–7.00 (m, 4 H, $C_{ar}H$), 6.91–6.89 (m, 1 H, $C_{ar}H$), 4.89 (s, 1 H, *CH*Ar), 2.36 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$, 151 MHz): δ = 150.4 (q, C=C), 146.7 (q, C=C), 143.7 (q, C=C), 137.5 (q, C_{ar}), 137.2 (q, C_{ar}), 136.6 (q, C_{ar}), 136.1 (q, C_{ar}), 132.6 (q, C_{ar}), 129.7 (t, C_{ar}), 129.3 (t, C_{ar}), 127.8 (t, C_{ar}), 127.1 (t, C_{ali}), 126.7 (t, C_{ar}), 126.2 (t, C_{ar}), 123.5 (t, C_{ar}), 121.7 (t, C_{ar}), 55.6 (t, *C*HAr), 21.6 (p, CH_3), 21.3 (p, CH_3), 21.2 (p, CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{23}^+$: 311.1794; found: 311.1793.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 227 (4.08), 321 nm (4.13).

1-Bromo-6-methyl-2,3-di(4-tolyl)-1*H*-indene (21c) and 1-Chloro-6-methyl-2,3-di(4-tolyl)-1*H*-indene (22c)

Acetylene **15c** (155.7 mg, 0.4 mmol, 1 equiv) was dissolved in 1,2-dibromoethane (0.8 mL); [JohnPhosAu(NCMe)]SbF_6 (14.5 mg, 0.02 mmol, 0.05 equiv) was added and the mixture was stirred overnight at 65 °C. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/Et_2O 30:1) to yield **21c** (74 mg, 0.19 mmol, 48%) and **22c** (14 mg, 0.04 mmol, 10%) as an inseparable mixture (yellow solid).

Mixture 21c and 22c

Mp 141–142 °C; R_f (silica gel, *n*-hexane/Et_2O 30:1) = 0.41.

IR (ATR): 3021, 2916, 2731, 1701, 1607, 1516, 1503, 1478, 1182, 1121, 1036, 1018, 856, 816, 766, 754, 735, 721, 706, 677, 664, 638 cm^{-1}.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 256 (4.49), 305 (4.02), 341 nm (3.86).

1-Bromo-6-methyl-2,3-di(4-tolyl)-1*H*-indene (21c)

^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.47 (br s, 1 H, $C_{ar}H$), 7.22 (br s, 4 H, $C_{ar}H$), 7.16–7.05 (m, 6 H, $C_{ar}H$), 5.97 (s, 1 H, *CH*Br), 2.43 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3).

^{13}C NMR (CD_2Cl_2, 101 MHz): δ = 144.4 (q, C=C), 141.4 (q, C=C), 141.4 (q, C=C), 140.3 (q, C=C), 138.3 (q, C_{ar}), 137.8 (q, C_{ar}), 137.1 (q, C_{ar}), 131.9 (q, C=C), 131.6 (q, C=C), 129.8 (t, C_{ar}), 129.7 (t, C_{ar}), 129.5 (t, C_{ar}), 129.3 (t, C_{ar}), 129.2 (t, C_{ar}), 126.2 (t, C_{ar}), 121.1 (t, C_{ar}), 50.7 (t, *C*HBr), 21.6 (p, CH_3), 21.5 (p, CH_3), 21.3 (p, CH_3).

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}Br^+$: 389.0899; found: 389.0905.

1-Chloro-6-methyl-2,3-di(4-tolyl)-1*H*-indene (22c)

According to the general procedure acetylene **16c** (138.0 mg, 0.4 mmol, 1 equiv) was dissolved in $CDCl_3$ (0.8 mL); the catalyst dichloro(2-picolinato)gold(III) (7.8 mg, 0.02 mmol, 0.05 equiv) was added and the mixture was stirred overnight at 65 °C. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/DCM 4:1) to yield **22c** (84 mg, 0.24 mmol, 60%) as a yellow solid; mp 145–148 °C; R_f (*n*-hexane/DCM 4:1) = 0.32.

IR (ATR): 3021, 2916, 2859, 2733, 1516, 1503, 1478, 1445, 1348, 1175, 1130, 1018, 932, 856, 835, 820, 797, 777, 764, 741, 723, 712, 675, 631 cm^{-1}.

^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.47–7.46 (m, 1 H, $C_{ar}H$), 7.23 (m, 4 H, $C_{ar}H$), 7.16–7.13 (m, 3 H, $C_{ar}H$), 7.09–7.06 (m, 3 H, $C_{ar}H$), 5.80 (s, 1 H, *CH*Cl), 2.43 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3).

^{13}C NMR (CD_2Cl_2, 101 MHz): δ = 143.9 (q, C=C), 141.7 (q, C=C), 141.1 (q, C=C), 140.7 (q, C=C), 138.3 (q, C_{ar}), 137.8 (q, C_{ar}), 137.1 (q, C_{ar}), 131.8 (q, C=C), 131.3 (q, C=C), 129.9 (t, C_{ar}), 129.8 (t, C_{ar}), 129.5 (t, C_{ar}), 129.3 (t, C_{ar}), 129.2 (t, C_{ar}), 125.7 (t, C_{ar}), 120.9 (t, C_{ar}), 60.9 (t, *C*HCl), 21.6 (p, CH_3), 21.5 (p, CH_3), 21.3 (p, CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}{}^{35}Cl^+$: 345.1405; found: 345.1397; *m*/*z* [M – Cl]$^+$ calcd for $C_{24}H_{21}^+$: 309.1638; found: 309.1645.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 252 (4.55), 306 (4.10), 337 nm (4.01).

6-Methoxy-2,3-bis(4-methoxyphenyl)-1*H*-indene (23d) and 5-Methoxy-1,2-bis(4-methoxyphenyl)-1*H*-indene (20d)

According to the general procedure acetylene **17d** (143.4 mg, 0.4 mmol, 1 equiv) was dissolved in $CDCl_3$ (0.8 mL); [JohnPhosAu(NCMe)]SbF_6 (15.4 mg, 0.02 mmol, 0.05 equiv) was added and the mixture was

stirred overnight at 65 °C. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/DCM 1:1) to yield **20d** (93 mg, 0.26 mmol, 65%) as a white solid and **23d** (42 mg, 0.12 mmol, 30%) as a white solid.

5-Methoxy-1,2-bis(4-methoxyphenyl)-1*H*-indene (20d)

R_f (*n*-hexane/DCM 1:1) = 0.17.

^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.46–7.42 (m, 2 H, $C_{ar}H$), 7.16–7.16 (m, 1 H, $C_{ali}H$), 7.04–7.00 (m, 3 H, $C_{ar}H$), 6.94–6.93 (m, 1 H, $C_{ar}H$), 6.82–6.78 (m, 2 H, $C_{ar}H$), 6.78–6.74 (m, 2 H, $C_{ar}H$), 6.63–6.61 (m, 1 H, $C_{ar}H$), 4.87 (s, 1 H, *CH*PhOCH$_3$), 3.80 (s, 3 H, OCH$_3$), 3.75 (s, 3 H, OCH$_3$), 3.72 (s, 3 H, OCH$_3$).

^{13}C NMR (CD_2Cl_2, 101 MHz): δ = 159.7 (q, C_{ar}OCH$_3$), 159.6 (q, C_{ar}OCH$_3$), 158.8 (q, C_{ar}OCH$_3$), 151.6 (q, C_{ali}), 145.3 (q, C_{ar}), 142.0 (q, C_{ar}), 132.9 (q, C_{ar}), 129.0 (t, C_{ar}), 128.3 (t, C_{ar}), 128.2 (q, C_{ar}), 126.1 (t, C_{ali}), 124.3 (t, C_{ar}), 114.5 (t, C_{ar}), 114.2 (t, C_{ar}), 110.9 (t, C_{ar}), 106.7 (t, C_{ar}), 55.8 (p, OCH$_3$), 55.6 (p, OCH$_3$), 55.5 (p, OCH$_3$), 55.0 (t, *C*HPhOCH$_3$).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{23}O_3^+$: 359.1642; found: 359.1639.

The NMR data agree with those in the literature.[40]

6-Methoxy-2,3-bis(4-methoxyphenyl)-1*H*-indene (23d)

R_f (*n*-hexane/DCM 1:1) = 0.23.

^{1}H NMR (CD_3CN, 400 MHz): δ = 7.25–7.22 (m, 2 H, $C_{ar}H$), 7.22–7.18 (m, 2 H, $C_{ar}H$), 7.13–7.12 (m, 1 H, $C_{ar}H$), 7.02–6.97 (m, 3 H, $C_{ar}H$), 6.83–6.82 (m, 1 H, $C_{ar}H$), 6.78–6.74 (m, 2 H, $C_{ar}H$), 3.83 (s, 3 H, OCH$_3$), 3.82 (s, 2 H, CH_2), 3.80 (s, 3 H, OCH$_3$), 3.74 (s, 3 H, OCH$_3$).

^{13}C NMR (CD_3CN, 101 MHz): δ = 156.0 (q, C_{ar}OCH$_3$), 159.5 (q, C_{ar}OCH$_3$), 159.1 (q, C_{ar}OCH$_3$), 145.2 (q, C_{ar}), 141.2 (q, C_{ar}), 139.5 (q, C=C), 138.2 (q, C=C), 131.4 (t, C_{ar}), 130.4 (q, C=C), 130.2 (t, C_{ar}), 129.5 (q, C=C), 121.0 (t, C_{ar}), 115.2 (t, C_{ar}), 114.5 (t, C_{ar}), 112.9 (t, C_{ar}), 111.1 (t, C_{ar}), 56.1 (p, OCH$_3$), 55.9 (p, OCH$_3$), 55.8 (p, OCH$_3$), 41.7 (s, *C*H$_2$).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{23}O_3^+$: 359.1642; found: 359.1633.

The NMR data agree with those in the literature.[40]

3-Bromo-5-methoxy-1,2-bis(4-methoxyphenyl)-1*H*-indene (18d)

According to the general procedure acetylene **15d** (175 mg, 0.4 mmol, 1 equiv) was dissolved in $CDCl_3$ (0.8 mL); dichloro(2-picolinato)gold(III) (7.8 mg, 0.02 mmol, 0.05 equiv) was added and the mixture was stirred overnight at 65 °C. The solvent was removed in vacuo and the residue was purified by flash chromatography (silica gel, *n*-hexane/DCM 1:2) to yield **18d** (28 mg, 0.06 mmol, 15%) as an orange solid; mp 130–132 °C; R_f (*n*-hexane/DCM 1:2) = 0.33.

IR (ATR): 2992, 2926, 2832, 1601, 1506, 1474, 1460, 1433, 1418, 1339, 1300, 1281, 1244, 1202, 1163, 1109, 1030, 957, 864, 839, 812, 802, 777, 762, 741, 718, 675, 642 cm^{-1}.

^{1}H NMR (CD_3CN, 400 MHz): δ = 7.62–7.58 (m, 2 H, $C_{ar}H$), 7.04–7.02 (m, 2 H, $C_{ar}H$), 6.98–6.94 (m, 2 H, $C_{ar}H$), 6.91–6.87 (m, 2 H, $C_{ar}H$), 6.78–6.76 (m, 1 H, $C_{ar}H$), 6.74–6.70 (m, 2 H, $C_{ar}H$), 5.07 (s, 1 H, *CH*Ar), 3.84 (s, 3 H, OCH$_3$), 3.76 (s, 3 H, OCH$_3$), 3.67 (s, 3 H, OCH$_3$).

^{13}C NMR (CD_3CN, 101 MHz): δ = 160.8 (q, C_{ar}OCH$_3$), 160.4 (q, C_{ar}OCH$_3$), 159.6 (q, C_{ar}OCH$_3$), 149.0 (q, C=C), 145.2 (q, C=C), 139.8 (q, C=C), 132.2 (q, C=C), 131.4 (t, C_{ar}), 129.9 (t, C_{ar}), 127.6 (q, C=C), 125.2 (t, C_{ar}), 116.8 (q, C=C), 115.0 (t, C_{ar}), 114.6 (t, C_{ar}), 113.5 (t, C_{ar}), 106.4 (t, C_{ar}), 56.9 (t, *C*HAr), 56.2 (p, OCH$_3$), 55.9 (p, OCH$_3$), 55.8 (p, OCH$_3$).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}{}^{79}BrO_3^+$: 437.0747; found: 437.0746; *m*/*z* [M – ^{79}Br]$^+$ calcd for $C_{24}H_{21}O_3^+$: 357.1485; found: 357.1489.

UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 227 (4.08), 321 nm (4.13).

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Supporting Information

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