GOLD CARBENES FROM CYCLOHEPTATRIENES: GENERATION AND FATE.

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Gold Carbenes from Cycloheptatrienes: Generation and Fate

DOCTORAL THESIS

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HAGO CONSTAR que este trabajo de investigación titulado "Gold Carbenes from Cycloheptatrienes: Generation and Fate", que presenta Yahui Wang para la obtención del título de doctor, ha sido realizado bajo mi dirección en el Institut Català d'Investigació Química vinculado a la Universidad Rovira I Virgili.

Tarragona, 14 de maig de 2014

El director de la Tesis Doctoral

Prof. Antonio M. Echavarren

To my wife.

In gold we trust.

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"Intermolecular Reactions of Gold(I)-Carbenes with Furans by Related Mechanisms"

David Lebœuf, Morgane Gaydou, Yahui Wang, and Antonio M. Echavarren, *Org. Chem. Front.* **2014**, *1*, DOI: 10.1039/c4qo00130c.

"Formal (4+1) Cycloaddition of Methylencyclopropanes with 7-Aryl-1,3,5-cycloheptatrienes by Triple Gold(I) Catalysis"

Yahui Wang, Michael E. Muratore, Zhouting Rong, and Antonio M. Echavarren, *Angew. Chem. Int. Ed.* **2014**, *53*, DOI: 10.1002/anie.201404029.

"Gold(I) Carbenes by Retro-Buchner Reaction: Generation and Fate"

Yahui Wang, Paul R. McGonigal, Bart Herlé, Maria Besora, and Antonio M. Echavarren, *J. Am. Chem. Soc.* **2014***, 136*, 801–809.

"Gold for the Generation and Control of Fluxional Barbaralyl Cations"

Paul R. McGonigal, Claudia de León, Yahui Wang, Anna Homs, César R. Solorio-Alvarado, and Antonio M. Echavarren, *Angew. Chem. Int. Ed.* **2012**, *51*, 13093–13096.

"Cyclopropanation with Gold(I) Carbenes by Retro-Buchner Reaction from Cycloheptatrienes"

César R. Solorio-Alvarado, Yahui Wang, and Antonio M. Echavarren, *J. Am. Chem. Soc.* **2011**, *133*, 11952–11955.

Table of Contents

Prólogo

This thesis has been divided into one introduction and three research chapters.

◆ The introduction provides some basic concepts and methods for the generation of free carbenes and gold(I) carbenes.

◆ Chapter 1 presents all of the reactions (except reactions discussed in Chapter 2 and 3) we have found based on the gold-catalyzed retro-Buchner reaction. Part of this work on the cyclopropanation of gold-carbenes is included in the following publication: César R. Solorio-Alvarado, Yahui Wang, and Antonio M. Echavarren, *J. Am. Chem. Soc.* **2011**, *133*, 11952–11955. To avoid overlap with the thesis of Dr. César R. Solorio-Alvarado, his work in this publication is not included in this thesis.

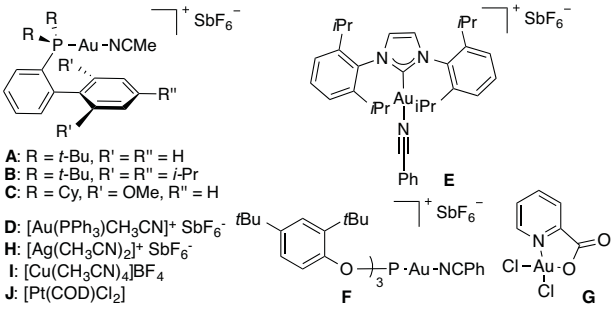
We present some reactions of cycloheptatrienes that do not undergo retro-Buchner reactions. Some results presented in this chapter support the mechanism of "Gold for the Generation and Control of Fluxional Barbaralyl Cations", as published in: Paul R. McGonigal, Claudia de León, Yahui Wang, Anna Homs, César R. Solorio-Alvarado, and Antonio M. Echavarren, *Angew. Chem. Int. Ed.* **2012**, *51*, 13093–13096.

◆ Chapter 2 gives the detailed study on a new formal (4+1) cycloaddition strategy by using methylenecyclopropanes or cyclobutenes as synthetic equivalent of 1,3-dienes. The entirety of this work was published in: Yahui Wang, Michael E. Muratore, Zhouting Rong, and Antonio M. Echavarren, *Angew. Chem. Int. Ed.* **2014**, *53*, DOI: 10.1002/anie.201404029.

◆ Chapter 3 discusses a formal C-H insertion of gold carbenes generated by retro-Buchner reaction. The entirety of this work was published in: Yahui Wang, Paul R. McGonigal, Bart Herlé, Maria Besora, and Antonio M. Echavarren, *J. Am. Chem. Soc.* **2014***, 136*, 801–809.

List of Catalysts, Abbreviations and Acronyms

All of the gold(I) complexes used in this thesis have been listed bellow. They were prepared according to our previous publications.[1]



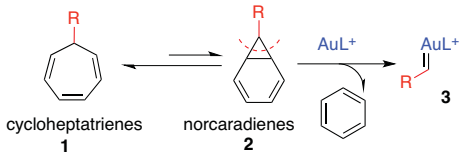
In this manuscript, the abbreviations and acronyms used follow the recommendations found in the on-line "Guidelines for authors" of *the Journal of Organic Chemistry*.

[1] (a) Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Cárdenas, D. J.; Buñuel, E.; Nevado, C.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 6146–6148. (b) López, S.; Herrero-Gómez, E.; Pérez-Galán, P.; Nieto-Oberhuber, C.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2006**, *45*, 6029–6032. (c) Amijs, C. H. M.; López-Carrillo, V.; Raducan, M.; Pérez-Galán, P.; Ferrer, C.; Echavarren, A. M. *J. Org. Chem.* **2008**, *73*, 7721–7730. (d) M. Raducan, PhD thesis, ICIQ, 2010.

Resumen

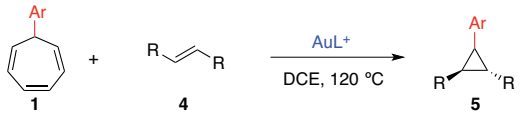
Los carbenos metálicos son uno de los intermedios más fundamentales en síntesis orgánica y se han sido utilizados ampliamente para preparar moléculas muy complejas.[2] Se han utilizado varios metales de transición para la descomposición de diazocompuestos como un método muy potente de generación de carbenos.[3]

Considerando el interés de nuestro grupo en el desarrollo de nuevas transformaciones catalizadas por oro,[4,5] descubrimos un nuevo método para generar carbenos de oro(I) **3** a través de una reacción retro-Buchner del tautómero norcaradieno **2** basado en su equilibrio con el cicloheptatireno **1**. Los carbenos de oro(I) **3** son especies muy reactivas respeto a varios tipos de nucleófilos para formar diferentes tipos de productos que no son fáciles de preparar con otros métodos. Además, esta estrategia constituye una alternativa más segura en la síntesis de carbenos metálicos evitando el uso de diazocompuestos que son altamente explosivos (Esquema 1).



Esquema 1. Carbenos de oro(I) a partir de cicloheptatrienos.

Los carbenos de oro(I) con un arilo como sustituyente generados a través de la reacción retro-Buchner pueden atraparse con alquenos para formar ciclopropanos 1,2,3-trisustituidos con rendimientos excelentes (Esquema 2).[6]



Esquema 2. Reacción de ciclopropanación.

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[2] Libros y reviews seleccionados: (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919–939. (b) Moss, R. A.; Platz, M. S.; Jones, M. Jr., *Reactive Intermediate Chemistry*; Wiley: New York, 2004. (c) Jones, M. Jr.; Moss, R. A., *Carbenes*; John Wiley & Sons, New York, 1973.

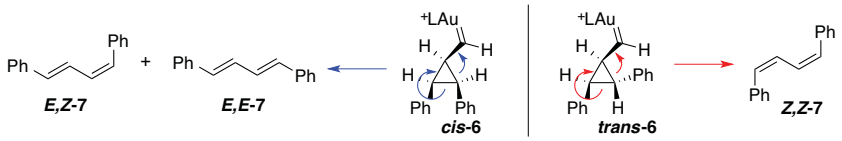
[3] Reviews seleccionados sobre el uso de diazocompuestos como precursores de carbenos: (a) Díaz-Requejo, M. M.; Pérez, P. J. *Chem. Rev.* **2008**, *108*, 3379–3394. (b) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417–424. (c) Zhang, Z.; Wang, J. *Tetrahedron* **2008**, *64*, 6577–6605. (d) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977–1050.

[4] (a) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326–3350. (b) Obradors, C.; Echavarren, A. M. *Chem. Commun.* **2014**, *50*, 16–28. (c) Obradors, C.; Echavarren, A. M. *Acc. Chem. Res.* **2014**, *47*, 902–912.

[5] Solorio-Alvarado, C. R.; Echavarren, A. M. *J. Am. Chem. Soc.* **2010**, *132*, 11881–11883.

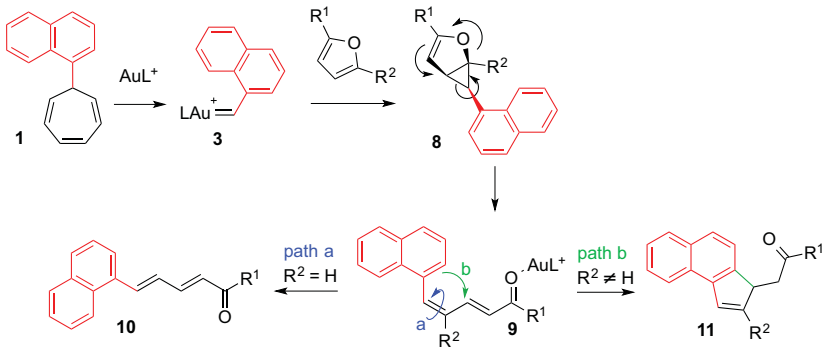
[6] Solorio-Alvarado, C. R.; Wang, Y.; Echavarren, A. M. *J. Am. Chem. Soc.* **2011**, *133*, 11952–11955.

Los carbenos de oro(I) sustituidos con un ciclopropilo ***cis*-6** y ***trans*-6** fueron generados con el método de la reacción retro-Buchner pero mostraron una reactividad diferente. La configuración relativa de los dos grupos fenilos juega un papel clave en la estereoquímica del producto final obtenida durante el proceso (Esquema 3).



Esquema 3. Carbenos de oro(I) con un ciclopropilo.

Los carbenos de oro(I) **3** generados desde los cicloheptatrienos pueden atraparse intermolecularmente con furanos para formar el intermedio **8**, el cual no es muy estable y reacciona a través de un reordenamiento sigmatrópico para obtener **9**. La reactividad de los intermedios **9** depende completamente de los sustituyentes del furano. Tal y como se muestra en el Esquema 4, cuando $R^2 = H$, se produce una isomerización muy rápida (ruta a) obteniendo dienos lineales tipo **10**. En cambio, cuando $R^2 \neq H$, domina una adición tipo Mukaiyama-Michael (ruta b) promovida por oro(I) para formar los productos cíclicos **11**.[7]



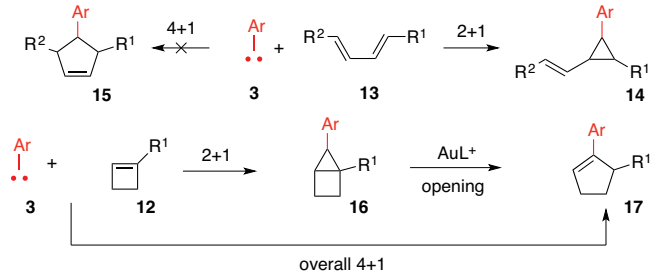
Esquema 4. Reacción entre cicloheptatrienos y furanos.

Además, descubrimos que los metilenciclopropanos (MCPs)[8] y los ciclobutenos también pueden usarse para atrapar los carbenos de oro(I) generados desde los cicloheptatrienos dando lugar a cicloadiciones (4+1) con muy buenos rendimientos (Esquema 5). Esta reacción representa una nueva y complicada estrategia para usar

[7] Lebœuf, D.; Gaydou, M.; Wang, Y.; Echavarren, A. M. *Org. Chem. Front.* **2014**, *1*, DOI: 10.1039/c4qo00130c.

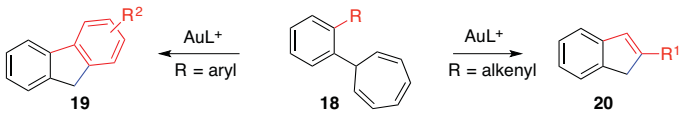
[8] Los metilociclopropanos pueden transformarse en ciclobutenos usando catálisis de platino o paladio: (a) $PtCl_2$: Fürstner, A.; Aissa, C. *J. Am. Chem. Soc.* **2006**, *128*, 6306–6307. (b) Paladio: Shi, M.; Liu, L.-P.; Tang, J. *J. Am. Chem. Soc.* **2006**, *128*, 7430–7431.

metilenciclopropanos o ciclobutenos como equivalentes sintéticos de 1,3-dienos en una cicloadición (4+1) con carbenos. A parte de los carbenos de oro(I) generados en la reacción retro-Buchner desde 7-arilo-1,3,5-cicloheptatrienos, otros precursores, por ejemplo derivados de diazocompuestos[3] o acetatos propargílicos,[9] también se pueden usar en esta nueva estrategia de adición (4+1).[10]



Esquema 5. Cicloadición (4+1).

Los carbenos de oro(I) generados a través de la reacción retro-Buchner desde los 1,3,5-cicloheptatrienos **18** pueden atraparse intramolecularmente con arenos o alquenos para formar fluorenos **19** o indenos **20**. Esta metodología representa una estrategia completamente nueva para la síntesis de estos compuestos y puede aplicarse en la síntesis de indenofluorenos usados en materiales orgánicos electrónicos (Esquema 6). Estas reacciones se llevan a cabo a través de una reacción Friedel−Crafts intramolecular atacando el carbeno de oro(I), que es altamente electrofílico, con un alqueno o un areno. La reactividad de los intermedios catiónicos generados con la reacción retro-Buchner es más similar a los carbenos de rodio o cobre, o incluso a los carbenos libres, que a la de los carbocationes.[11]



Esquema 6. Síntesis directa de fluorenos y indenos.

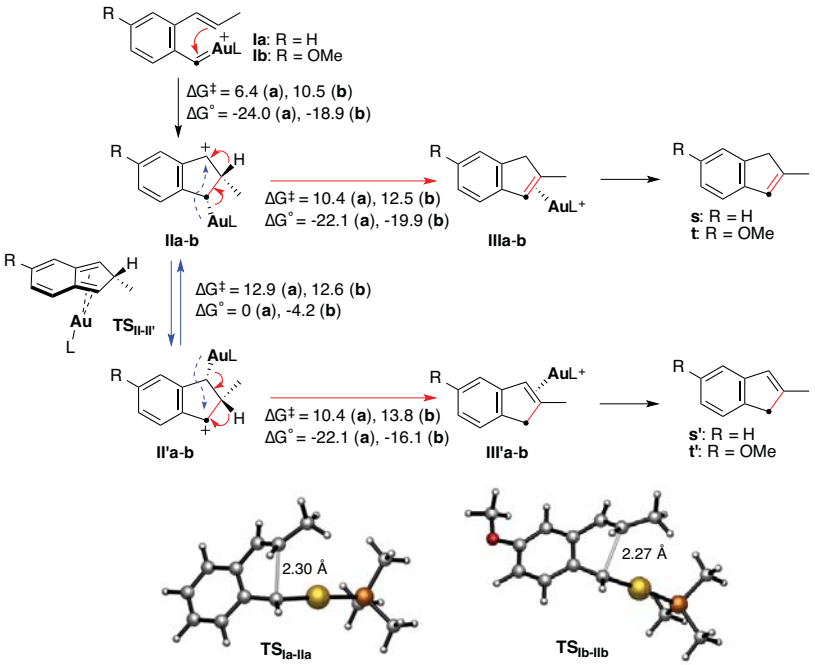
Los correspondientes cálculos DFT del mecanismo de estas reacciones revelaron detalles muy intrigantes de las diferentes rutas (Esquema 7). Así, en la síntesis de

[9] Reviews de reordenamientos de carboxilatos propargílicos catalizados por oro: (a) de Haro, T.; Gómez-Bengoa, E.; Cribiú, R.; Huang, X.; Nevado, C. *Chem. Eur. J.* **2012**, *18*, 6811–6824. (b) Wang, S.; Zhang, G.; Zhang, L. *Synlett* **2010**, 692–706. (c) Shiroodi, R. K.; Gevorgyan, V. *Chem. Soc. Rev.* **2013**, *42*, 4991–5001. (d) Correa, A.; Marion, N.; Fensterbank, L.; Malacria, M.; Nolan, S. P.; Cavallo, L. *Angew. Chem. Int. Ed.* **2008**, *47*, 718–721. (e) Marco-Contelles, J.; Soriano, E. *Chem. Eur. J.* **2007**, *13*, 1350–1357. (f) Amijs, C. H. M.; López-Carrillo, V.; Echavarren, A. M. *Org. Lett.* **2007**, *9*, 4021–4024.

[10] Wang, Y.; Muratore, M. E.; Rong, Z.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2014**, *53*, DOI: 10.1002/anie.201404029.

[11] Wang, Y.; McGonigal, P. R.; Herlé, B.; Besora, M.; Echavarren, A. M. *J. Am. Chem. Soc.* **2014**, *136*, 801–809.

indenos, descubrimos que una migración 1,4- del metal compite con la ruta principal de formación del complejo de oro(I) coordinado al producto con una 1,2-H migración/eliminación concertada del oro(I). La formación de los fluorenos incluye un proceso tipo diatrópico para la formación del complejo (η^1-fluoren)-oro(I).



Esquema 7. Proposición mecanística.

General Introduction

Singlet and triplet carbenes

Carbenes, carbanions, carbocations and radicals are four types of fundamental reactive intermediates in organic synthesis. Among them, carbenes have been widely used as one-carbon synthon source for the construction of complex molecules.[12] Depending on the electronic spins they possess, in general, free carbenes can be classified into two types: singlet and triplet carbenes (Figure 1). The singlet state, with its two paired electrons and unfilled *p* orbital, exhibits electrophilic reactivity and the cyclopropanation with alkene in a concerted pattern should be stereospecific. In contrast, the triplet carbene reacts like a diradical and the additions would not be stereospecific.

Figure 1

Fischer and Schrock carbenes

Two types of metal-coordinated carbenes, $L_nM{=}CR_2$, can be distinguished: the singlet-derived Fischer carbenes and triplet-derived Schrock carbenes.

The first Fischer carbene complex was prepared in the laboratory of E. O. Fischer in 1964 by the attack of methyllithium on the tungsten hexacarbonyl complex followed by methylation (Scheme 1).[13] Soon after the discovery of Fischer type complexes their chemistry was systematically explored and they have been since well established as valuable species in organic synthesis as well as in catalytic processes.[14]

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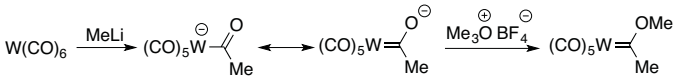
[12] Selected reviews and books: (a) Baird, M. S. *Chem. Rev*. **2003**, *103*, 1271–1294. (b) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. *Chem. Rev.* **2010**, *110*, 704–724. (c) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271–288. (d) Moss, R. A. *Acc. Chem. Res*. **2006**, *39*, 267–272. (e) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919–939. (f) Barluenga, J.; Santamaría, J.; Tomás, M. *Chem. Rev*. **2004**, *104*, 2259–2284. (g) Cheng, Y.; Meth-Cohn, O. *Chem. Rev.* **2004**, *104*, 2507–2530. (h) Brookhart, M.; Studabaker, W. B. *Chem. Rev*. **1987**, *87*, 411–432. (i) Moss, R. A.; Platz, M. S.; Jones, M. Jr., *Reactive Intermediate Chemistry*; Wiley: New York, 2004. (j) Jones, M. Jr.; Moss, R. A., *Carbenes*; John Wiley & Sons, New York, 1973.

[13] Fischer, E. O.; Maasböl, A. *Angew. Chem. Int. Ed.* **1964**, *3*, 580–581.

[14] Selected recent publications of Fischer carbenes: (a) Barluenga, J.; Santamaría, J.; Tomás, M. *Chem. Rev*. **2004**, *104*, 2259–2284. (b) Barluenga, J.; Vicente R.; Barrio, P.; López, L. A.; Tomás, M.; Borge, J.



Scheme 1

Fischer carbenes normally contain a π-donating group, such as −OMe or $-NMe_2$, on the carbene carbon to stabilize the empty *p* orbital on the carbene carbon by π-donation from one of the lone pairs of the heteroatom. This stability effect makes the metal to carbene π-back-donation very weak and the direct carbene to metal σ-donation predominates. Therefore, the carbon tends to be positively charged, and the carbene behaves as an electrophile (Figure 2).

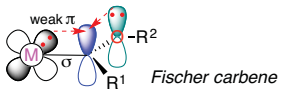


Figure 2

In the Schrock case, two covalent bonds between metal and triplet carbene are formed, and each metal-carbon bond is polarized toward the carbon because of its higher electronegativity. As a result, the carbon tends to be more negatively charged, and the carbene exhibits nucleophilic character. Binding of a Schrock carbene is considered to increase the oxidation state of the metal by two units. Alternatively, the Schrock carbene can also be considered as a Fischer carbene with a very strong back-donation (Figure 3).

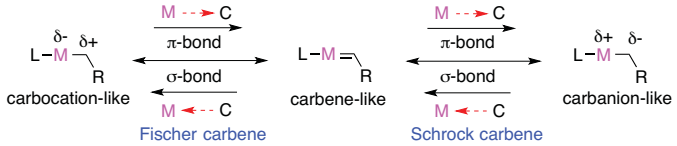


Figure 3 Fischer carbene and Schrock carbene.

Due to their more electronegative properties and more stable M (d_π) orbitals, generally, most of the late transition metal carbenes can be classified into Fischer carbenes and act as electrophiles.

J. Am. Chem. Soc. **2004**, *126*, 14354–14355. (c) Barluenga, J.; Vicente R.; Barrio, P.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2004**, *126*, 5974–5975. (d) Barluenga, J.; Vicente R.; López, L. A.; Rubio, E.; Tomás, M.; Álvarez-Rúa, C. *J. Am. Chem. Soc.* **2004**, *126*, 470–471. (e) Barluenga, J.; Vicente R.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2006**, *128*, 7050–7056.

Gold carbenes

Gold(I) carbenes have very often been proposed as the key intermediates in many gold-catalyzed reactions, and are structurally related to singlet carbenes and posses similar reactivity.[4] However, the structure of gold carbenes has been questioned, because in some cases both the gold carbene and the gold-stabilized carbocation intermediates can be invoked to rationalize the outcome of a given reaction.[15]

In 2009, chemists began to make substantial progress towards resolving this controversy.[16]

The ligand and carbene can both donate their paired electrons to gold, forming a three-center-four-electron σ-hyperbond. The gold center can also form two π-bonds by back-donation of its electrons from two filled *d*-orbitals into empty π-acceptors on the ligand and carbene (Figure 4).

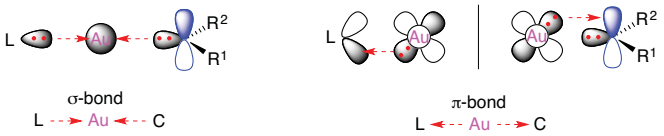


Figure 4 Bonding of gold carbenes.

The more carbene-like structure occurs with an increase in gold-carbon π-bonding and a decrease in the σ-bonding. Considering the competition between ligand and carbene for the electron density from gold,[17] strongly σ-donating and weakly π-acidic ligands are expected to increase carbene-like reactivity. In contrast, π-acidic ligands increase carbocation-like reactivity of the intermediate by decreasing gold-to-carbene π-donation (Figure 5).

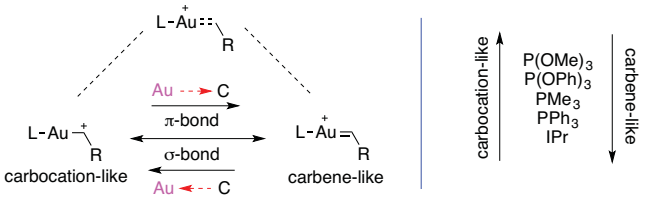


Figure 5 Carbocation-like or carbene-like.

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[15] (a) Fürstner, A.; Morency, L. *Angew. Chem. Int. Ed.* **2008**, *47*, 5030–5033. (b) Seidel, G.; Mynott, R.; Fürstner, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 2510–2513.

[16] (a) Benitez, D.; Shapiro, N. D.; Tkatchouk, E.; Wang, Y.; Goddard III, W. A.; Toste, F. D. *Nat. Chem.* **2009**, *1*, 482–486. (b) Echavarren, A. M. *Nat. Chem.* **2009**, *1*, 431–433.

[17] For a review on ligand effects in homogeneous gold catalysis: Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351–3378.

N-Heterocyclic carbenes (NHCs) are strong σ-donors and weak π-acceptors. These ligands are strong σ-donors because the carbon of these carbenes is softer and less electronegative than most heteroatom Lewis bases. The NHC ligands acts as a strong π-donor to the unoccupied *p*-orbital of the NHC carbon center. This participation of the *p*-orbital at carbon on NHC minimizes the π-donation from gold to the NHC. Therefore, the π-back-donation from gold to carbon center is increased, and the intermediate should be more carbene-like (Figure 6).

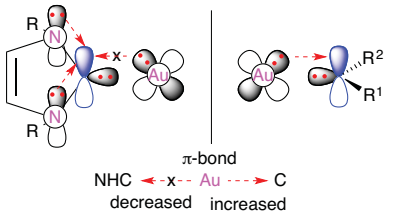
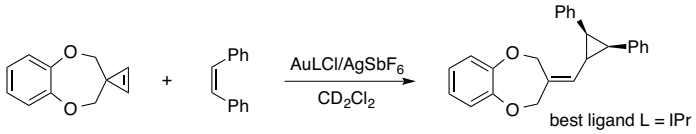


Figure 6 NHC ligands increase π-back-donation from gold to carbene center.

For example, gold complexe with IPr[18] has been shown to be the best catalyst for the cyclopropanation of *cis*-stilbene. In this transformation, the intermediate shows a carbene-like reactivity (Scheme 2).[16a]



Scheme 2

Recently, a diaryl gold carbene complex (**a** in Figure 7) was isolated and characterized by X-ray diffraction by Alois Fürstner and his coworker.[19] The Au–C carbene bond length (2.039(5) Å) is not significantly different from the bond length normally associated with gold-carbon single bond (for comparison, the Au–C bond length in [Ph_3PAu–Ph] is 2.045(6) Å).[20] However, the bond between the carbene center and the aryl group is shortened appreciably. The more contracted C–C bond connects to an aryl ring that is nearly co-planar with the carbene center to enable efficient orbital overlap, which stabilizes the electron-deficient carbene center. These observations are quite comparable to the structural features of diarylcarbenium ions, such as **c**.

For complex **a**, electron back donation from the filled *d*-orbitals of gold to the empty *p*-orbital of the carbene alone is not sufficient and is actually very weak, and the

[18] IPr: 1,3-bis(2,6-diisopropylphenyl)imidazolidene.
[19] Seidel, G.; Fürstner, A. *Angew. Chem. Int. Ed.* **2014**, *53*, 4807–4811.
[20] Fernández, E. J.; Laguna, A.; Olmos, M. E. *Adv. Organomet. Chem.* **2004**, *52*, 77–141.

substituted arene rings play a dominant role in stabilizing the gold carbene (see **b***). Therefore, Alois Fürstner concluded: *Since carbon species that carry a formal positive charge (or a good leaving group) and a carbon–metal bond at the same site are commonly called "carbenoids",*[21] *gold carbenes should be scientifically called gold carbenoids and the structure like* ***a*** *is not recommended to use.*

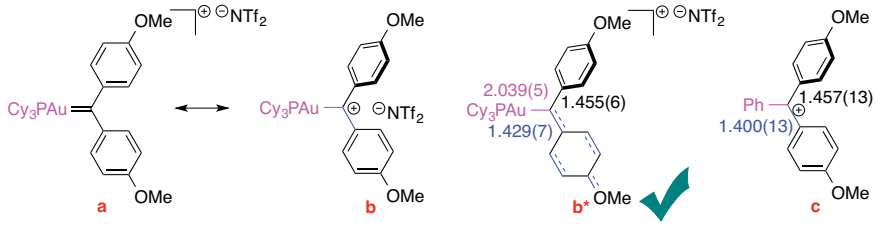


Figure 7

However, the structure chosen in Figure 7 is a very special example, since the 4-methoxyl phenyl substituent is a very strong electron-donating group and its powerful ability to stabilize the carbene center gives gold no chance to back-donate electrons to the empty *p* obital of carbene. Predictably, in cases in which the carbene center cannot obtain enough stabilization from substituents, the back-donation from gold is still a source of stabilization, and the gold carbene bonding model is still a pertinent representation.

As noted above, actually for Fischer carbenes, the π-back-donation from metal to carbene is always weak. Therefore, we cannot exclude gold carbenes from the Fischer carbene family, based solely on the bonding arrangement shown in Figure 7, which shows the π-back-donation is negligible in this extreme case.[22]

In our opinion, so far, the best description of gold carbene originates from Toste and Goddard: *"The reactivity in gold(I)-coordinated carbenes is best accounted for by a continuum ranging from a metal-stabilized singlet carbene to a metal-coordinated carbocation. The position of a given gold species on this continuum is largely determined by the carbene substituents and the ancillary ligand".*[16a]

In this thesis manuscript, we have chosen to employ *Occam's razor* and represent gold–carbon bonds in the manner which best describes their observed reactivity. The reactions discussed in the following chapters are best described by invoking gold-coordinated carbenes as intermediate species; however, we advise the reader to

[21] IUPAC´s definition of carbenoid: "Complexed carbene-like entities that display the reactivity characteristics of carbenes, either directly or by acting as sources of carbenes".
[22] For a recent discussion about the structure of gold carbenes: Hussong, M. W.; Rominger, F.; Krämer, P.; Straub, B. F. *Angew. Chem. Int. Ed.* **2014**, *53*, DOI: 10.1002/anie.201404032.

bear in mind the discussion concerning the continuum that exists between gold-stabilized singlet carbene and gold-coordinated carbocation.

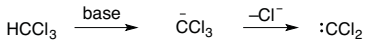
Methods for generating free carbenes

Because of their electron-deficient nature (six valence electrons), most carbenes are highly reactive and are normally generated *in situ*.

Some of the classical, transition metal-free, ways of forming carbene intermediates are summarized below.

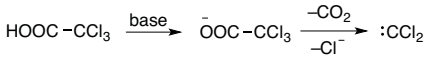
1. α-Elimination

Carbenes can be generated by the α-elimination of a hydrogen halide from a suitable alkylhalide. The most common example is the formation of dichlorocarbene upon treating chloroform with a strong base.[23] A 50% aqueous NaOH solution and benzyltriethylammonium chloride, as phase transfer catalyst, are frequently employed to promote α-elimination efficiently (Scheme 3).



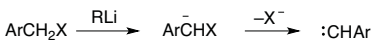
Scheme 3

There is an alternative route for the generation of dichlorocarbene by the treatment of trichloroacetic acid with a base through decarboxylation and loss of chloride (Scheme 4).[24]



Scheme 4

Similar α-elimination methodology can also be applied to dichloromethane and benzyl chlorides with alkyl lithium reagents. The aromatic group provides the carbanion extra stabilization, which makes the lithiation feasible (Scheme 5).[25]



Scheme 5

These α-elimination methods shown above are restricted to halohydrocarbon without β-hydrogens, because β-elimination occurs preferentially.

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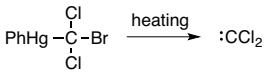
[23] (a) Hine, J. *J. Am. Chem. Soc.* **1950**, *72*, 2438–2445. (b) Hine, J.; Dowell Jr., A. M. *J. Am. Chem. Soc.* **1954**, *76*, 2688–2692.
[24] Wagner, W. M.; Kloosterziel, H.; Bickel, A. F. *Recl. Trav. Chim. Pays–Bas.* **1962**, *81*, 933–946.
[25] Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1960**, *82*, 5723–5728.

The α-elimination method can also be applied in organomercury compounds for carbene generation. The carbon-mercury bond is more covalent than the C-Li bond, therefore, the organomercury reagents are generally stable at room temperature and isolable (Scheme 6).[26]

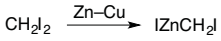


Scheme 6

Because of the high toxicity of organomercury compounds, they have seldom been used for synthetic purposes.

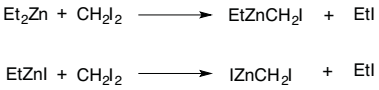
2. From halomethylzinc reagents

Methylene iodide with a zinc-copper couple, referred as Simmons-Smith reagent, is very useful for the transfer of a methylene unit to alkenes.[27] Although it looks like a carbene mechanism [28], the reactive intermediate has been identified as iodomethylzinc iodide (Scheme 7).[29]



Scheme 7

The results of classical Simmons-Smith conditions have been found to be sensitive to the method of zinc activation and are sometimes difficult to reproduce. The combination of diethylzinc and diiodomethane, the Furukawa modification, has been developed as a convenient and reliable method for Simmons-Smith reaction.[30] Both the $EtZnCH_2I$ and ICH_2ZnI generated in the reaction are reactive reagents toward cyclopropanation with alkenes (Scheme 8).



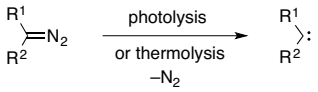
Scheme 8

[26] Seyferth, D.; Burlitch, J. M.; Minasz, R. J.; Mui, J. Y.; Simmons, H. D.; Treiber, A. J. H.; Dowd, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 4259–4270.
[27] Simmnos, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 5323–5324.
[28] According to IUPAC´s definition of carbenoid, Simmons–Smith reagents should be called carbenoids.
[29] (a) Charette, A. B.; Marcoux, J.-F. *J. Am. Chem. Soc.* **1996**, *118*, 4539–4549. (b) Nakamura, M.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 2341–2350.
[30] Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron* **1968**, *24*, 53–58.

The main limitation of Simmons-Smith reaction is that only the methylene unit can be transferred successfully, although some other modifications have been developed.[31]

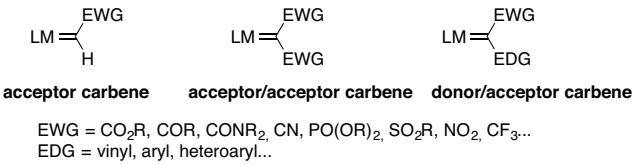
3. Decomposition of diazo compounds

Decomposition of diazo compounds is one of the most general ways of generating carbenes. The driving force for decomposition of diazo compounds to carbenes is the formation of the very stable nitrogen molecule (Scheme 9).



Scheme 9

Although carbenes can be formed by photolysis or thermolysis, metal-catalyzed decomposition of diazo derivatives[32] is particularly powerful and allows the diazo compounds to undergo various transformations delivering many functionalized products under very mild conditions. The reactivity depends on their electronic properties as well as the nature of the metal-based catalysts (Scheme 10).



Scheme 10

The main drawback of this method is the limited stability of the diazo compounds. In order to counter their relatively facile dimerization, the diazo compound is usually added slowly into the reaction mixture using a syringe pump.

4. From diazirines

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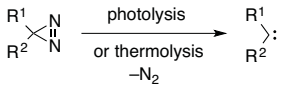
[31] (a) Vicente, R.; González, J.; Riesgo, L.; González, J.; López, L. A. *Angew. Chem. Int. Ed.* **2012**, *51*, 8063–8067. (b) Lévesque, É.; Goudreau, S. R.; Charette, A. B. *Org. Lett.* **2014**, *16*, 1490–1493 and references cited therein.

[32] Selected reviews on the use of diazo compounds as carbene precursors: (a) Díaz-Requejo, M. M.; Pérez, P. J. *Chem. Rev.* **2008**, *108*, 3379–3394. (b) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417–424. (c) Davies, H. M. L.; Denton, J. R. *Chem. Soc. Rev.* **2009**, *38*, 3061–3071. (d) Zhang, Z.; Wang, J. *Tetrahedron* **2008**, *64*, 6577–6605. (e) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091–1160. (f) Forbes, D. C.; Doyle, M. P. *Chem. Rev.* **1998**, *98*, 911–935. (g) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977–1050.

The diazirines are the cyclic isomers of diazo compounds and are highly reactive carbene precursors resulting from their highly strained structure and also the potential for loss of nitrogen (Scheme 11).[33]

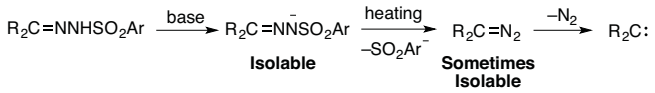


Scheme 11

Because of their difficult preparation, diazirines are normally only applicable to mechanistic studies.

5. From sulfonylhydrazones

Sulfonylhydrazones can be used as precursors for diazo compounds. In the presence of base under photochemical irradiation or by heating, they can decompose to form diazo intermediates, which usually generate carbenes under the same conditions.[34] Sometimes, this method can be used to prepare several relatively stable diazo derivatives (Scheme 12).[35]



Scheme 12

Recently, transition metals have also been exploited to generate carbene intermediates from sulfonylhydrazones under very mild conditions, and many potentially useful reactions have been developed.[36]

6. From oxadiazolines

Thermolysis of oxadiazolines can generate $(CH_3O)_2C$: and related dioxacarbenes.[37] Similarly, dithiacarbenes can also be formed by this method (Scheme 13).[38]

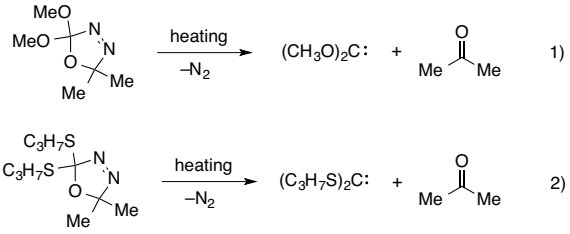
---

[33] (a) Liu, M. T. H. *Chemistry of Diazirines*, 2 vols., CRC Press, Boca Raton, FL, 1987. For reviews: (b) Liu, M. T. H. *Chem. Soc. Rev.* **1982**, *11*, 127–140. (c) Moss, R. A. *Acc. Chem. Res.* **2006**, *39*, 267–272. For synthesis, see: (d) Martinu, T.; Dailey, W. P. *J. Org. Chem.* **2004**, *69*, 7359–7362 and references cited therein.

[34] (a) Kaufman, G. M.; Smith, J. A.; Vander Stouw, G. G.; Shechter, H. *J. Am. Chem. Soc*. **1965**, *87*, 935–937. For recent examples: (b) Barluenga, J.; Tomás-Gamasa, M.; Aznar, F.; Valdés, C. *Nat. Chem.* **2009**, *1*, 494–499. (c) Li, H.; Wang, L.; Zhang, Y.; Wang, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 2943–2946.

[35] For example, phenyl diazomethane was prepared by this method: (a) Zhou, Y.; Trewyn, B. G.; Angelici, R. J.; Woo, L. K. *J. Am. Chem. Soc*. **2009**, *131*, 11734–11743. (b) Creary, X. *Org. Synth.* **1986**, *64*, 207.

[36] Selective publications: (a) Zhang, Y.; Wang, J. *Topics in Current Chemistry*, Stereoselective Alkene Synthesis, Edited by Jianbo Wang, Springer, 2012, *327*, 239–270. (b) Xia, Y.; Liu, Z.; Xiao, Q.; Qu, P.; Ge, R.; Zhang, Y.; Wang, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 5714–5717. (c) Ye, F.; Ma, X.; Xiao, Q.; Li, H.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2012**, *134*, 5742–5745. (d) Zhou, L.; Ye, F.; Ma, J.; Zhang, Y.; Wang, J. *Angew. Chem. Int. Ed.* **2011**, *50*, 3510–3514.

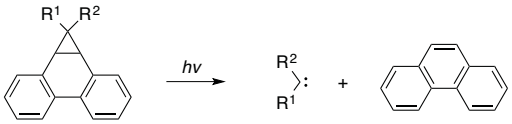


Scheme 13

Interestingly, these carbenes are quite different from the carbenes discussed above and they exhibit some nucleophilic properties through donation of electron density from the heteroatoms into the vacant *p*-orbital of the carbene center.[39]

7. From phenanthrene precursors

Free carbenes can be generated from phenanthrene precursors under photochemical conditions.[40] The driving force for this reaction is the release of stable phenanthrene. Interestingly, this can be regarded as a special retro-Buchner process (Scheme 14).



Scheme 14

However, due to the difficulty of preparing phenanthrene derivatives, this route of forming carbenes is not suitable for application in organic synthesis.

8. Atomic carbon mediated carbene formation

Atomic carbon is a highly reactive species.[41] Since most of the reactions involving C atoms are very fast and extremely exothermic, it suggests that there is no energy barrier for these reactions. Carbenes are often the intermediates in C atom reactions,

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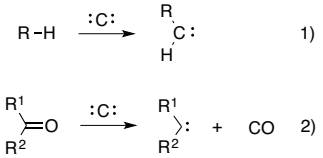
[37] Warkentin, J. *Acc. Chem. Res.* **2009**, *42*, 205–212.
[38] (a) Rigby, J. H.; Danca, M. D. *Tetrahedron Lett.* **1999**, *40*, 6891–6894. (b) Rigby, J. H.; Laurent, S. *J. Org. Chem*. **1999**, *64*, 1766–1767.
[39] (a) Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15–21. (b) Venneri, P. C.; Warkentin, J. *Can. J. Chem.* **2000**, *78*, 1194–1203. (c) Pole, D. L.; Sharma, P. K.; Warkentin, J. *Can. J. Chem.* **1996**, *74*, 1335–1340. (d) Couture, P.; Warkentin, J. *Can. J. Chem.* **1997**, *75*, 1281–1294.
[40] (a) Graves, K. S.; Thamattoor, D. M.; Rablen, P. R. *J. Org. Chem.* **2011**, *76*, 1584–1591. (b) Moore, K. A.; Vidaurri-Martinez, J. S.; Thamattoor, D. M. *J. Am. Chem. Soc.* **2012**, *134*, 20037−20040. (c) Nigam, M.; Platz, M. S.; Showalter, B. M.; Toscano, J. P.; Johnson, R.; Abbot, S. C.; Kirchhoff, M. M. *J. Am. Chem. Soc.* **1998**, *120*, 8055–8059. (d) Glick, H. C.; Likhotvorik, I. R.; Jones, M. *Tetrahedron Lett.* **1995**, *36*, 5715–5718. (e) Richardson, D. B.; Durrett, L. R.; Martin, J. M.; Putnam, W. E.; Slaymaker, S. C.; Dvoretzky, I. *J. Am. Chem. Soc.* **1965**, *87*, 2763–2765.
[41] Moss, Robert A; Jones, Maitland (2004). "Atomic carbon". *Reactive intermediate chemistry.* pp. 463–500.

and in general there are two ways in which carbenes can be produced: C–H insertion of alkanes[42] and deoxygenation of carbonyl compounds (Scheme 15).[43]



Scheme 15

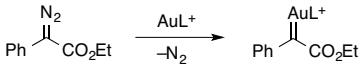
However, because of the lack of general and convenient method for atomic carbon generation, the chemistry of carbenes from C atom is still a relatively young field.[44]

Generation of gold carbenes

Additionally, several ways of generating gold(I) carbene intermediates are illustrated below.

1. Diazo compounds

Gold(I) complexes have also been found limited application with diazo precursors (Scheme 16).[45] However, rhodium and copper complexes are more popular catalysts for the decomposition of diazo compounds.



Scheme 16

2. Cyclopropenes

It has been demonstrated that ring cleavage of cyclopropenes gives vinyl gold(I) carbene intermediates (Scheme 17).[46]

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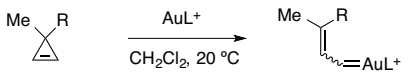
[42] Skell, P. S.; Engel, R. R. *J. Am. Chem. Soc.* **1966**, *88*, 4883–4890.

[43] Selected references: (a) Dewar, M. J. S.; Nelson, D. J.; Shevlin, P. B.; Biesiada, K. A. *J. Am. Chem. Soc.* **1981**, *103*, 2802–2807. (b) Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 3685–3689.

[44] *"Future researchers should be encouraged by the fact that is difficult to imagine a molecule that will not react with atomic carbon."---by Philip B. Shevlin in* (2004). "Atomic carbon". *Reactive intermediate chemistry.* (eds. Moss, Robert A; Jones, Maitland) pp. 495.

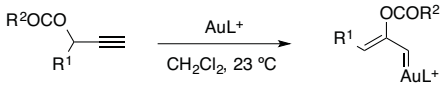
[45] (a) Fructos, M. R.; Belderrain, T. R.; de Frémont, P.; Scott, N. M.; Nolan, S. P.; Díaz-Requejo, M. M.; Pérez, P. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 5284–5288. (b) Prieto, A.; Fructos, M. R.; Díaz-Requejo, M. M.; Pérez, P. J.; Pérez-Galán, P.; Delpont, N.; Echavarren, A. M. *Tetrahedron* **2009**, *65*, 1790–1793. (c) Rivilla, I.; Gõmez-Emeterio, B. P.; Fructos, M. R.; Díaz-Requejo, M. M.; Pérez, P. J. *Organometallics* **2011**, *30*, 2855–2860. (d) Pérez, P. J.; Díaz-Requejo, M. M.; Rivilla, I. *Beilstein J. Org. Chem.* **2011**, *7*, 653–657. (e) Yu, Z.; Ma, B.; Chen, M.; Wu, H.-H.; Liu, L.; Zhang, J. *J. Am. Chem. Soc.* **2014**, *136*, 6904–6907.



Scheme 17

3. Propargylic carboxylates

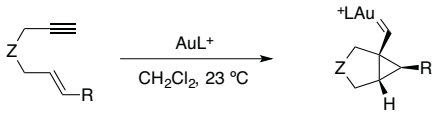
In the presence of a gold(I) catalyst, propargylic carboxylates undergo 1,2-acyloxy migration to generate vinyl gold carbene intermediates, which can be trapped by 1,3-diones, alkenes, or electron-rich aromatics intra- or intermolecularly.[47] Because propargylic carboxylates are readily available, they are very effective and common carbene precursors in gold catalysis (Scheme 18).



Scheme 18

4. 1,6-Enynes

We have revealed that cyclopropanyl gold carbenes are the intermediates of 1,6-enyne cycloisomerizations. These reactive intermediates exhibit various reactivities toward many functional groups intra- or intermolecularly (Scheme 19).[48]



Scheme 19

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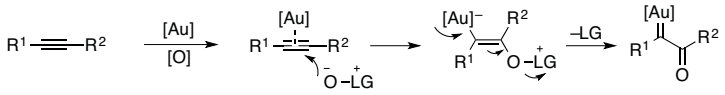
[46] (a) Hadfield, M. S.; Bauer, J. T.; Glen, P. E.; Lee, A.-L. *Org. Biomol. Chem.* **2010**, *8*, 4090–4095. (b) For review on gold(I) catalyzed transformations of cyclopropenes: Miege, F.; Meyer, C.; Cossy. J. *Beilstein. J. Org. Chem.* **2011**, *7*, 717–734.

[47] For reviews and lead references on gold-catalyzed propargylic carboxylate rearrangement: (a) de Haro, T.; Gómez-Bengoa, E.; Cribiú, R.; Huang, X.; Nevado, C. *Chem. Eur. J.* **2012**, *18*, 6811–6824. (b) Wang, S.; Zhang, G.; Zhang, L. *Synlett* **2010**, 692–706. (c) Shiroodi, R. K.; Gevorgyan, V. *Chem. Soc. Rev.* **2013**, *42*, 4991–5001. (d) Correa, A.; Marion, N.; Fensterbank, L.; Malacria, M.; Nolan, S. P.; Cavallo, L. *Angew. Chem. Int. Ed.* **2008**, *47*, 718–721. (e) Marco-Contelles, J.; Soriano, E. *Chem. Eur. J.* **2007**, *13*, 1350–1357. (f) Amijs, C. H. M.; López-Carrillo, V.; Echavarren, A. M. *Org. Lett.* **2007**, *9*, 4021–4024. (g) Li, G.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2008**, *130*, 3740–3741. (h) Shapiro, N. D.; Shi, Y.; Toste, F. D. *J. Am. Chem. Soc.* **2009**, *131*, 11654–11655. (i) Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* **2008**, *130*, 9244–9245. (j) Gorin, D. J.; Dubé, P.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 14480–14481. For Cu(I) and Pt(II) catalyzed this rearrangement: (k) Barluenga, J.; Riesgo, L.; Vicente, R.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2007**, *129*, 7772–7773.

[48] (a) Escribano-Cuesta, A.; López-Carrillo, V.; Janssen, D.; Echavarren, A. M. *Chem. Eur. J.* **2009**, *15*, 5646–5650. (b) López, S.; Herrero-Gómez, E.; Pérez-Galán, P.; Nieto-Oberhuber, C.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2006**, *45*, 6029–6032. For reviews, see: (c) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326–3350. (d) Obradors, C.; Echavarren, A. M. *Chem. Commun.* **2014**, *50*, 16–28. (e) Obradors, C.; Echavarren, A. M. *Acc. Chem. Res.* **2014**, *47*, 902–912. (f) Taduri, B. P.; Sohel, S. M. A.; Cheng, H.-M.; Lin, G.-Y.; Liu, R.-S. *Chem. Commun.* **2007**, 2530–2532.

5. Gold-catalyzed alkyne oxidation

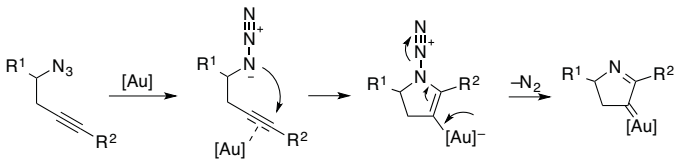
The groups of Zhang and Toste demonstrated that alkynes effectively serve as precursors to versatile *α*-oxo gold carbenes in the presence of a suitable oxidant. In general, sulfoxides are the best oxidants for intramolecular alkyne oxidation and pyridine or quinoline N-oxides are suitable for intermolecular reactions (Scheme 20).[49]



Scheme 20

6. Acetylenic Schmidt reaction

Similar to alkyne oxidation, azides can serve as leaving-group-bearing nucleophiles. After loss of dinitrogen, gold(I) iminocarbene intermediates are generated. Subsequent rearrangements produce 1*H*-pyrroles as the final products (Scheme 21).[50]



Scheme 21

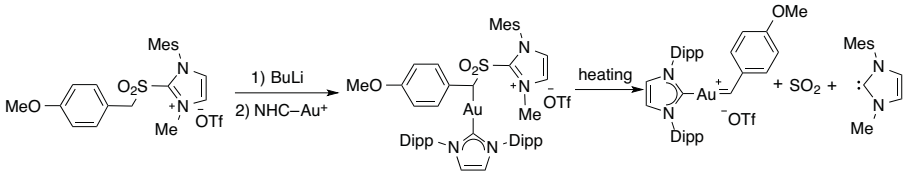
7. Loss of SO_2 and imidazolylidene

The SO_2-imidazolium moiety in the gold complex can act as a leaving group. By heating, the gold carbene is formed with the dissociation of SO_2 and imidazolylidene (Scheme 22). [51]

[49] (a) Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 4160–4161. (b) Ye, L.; Cui, L.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 3258–3259. (c) He. W.; Li, C.; Zhang, L. *J. Am. Chem. Soc.* **2011**, *133*, 8482–8485. (d) Noey, E. L.; Luo, Y.; Zhang, L.; Houk, K. N. *J. Am. Chem. Soc.* **2012**, *134*, 1078–1084. (e) Luo, Y.; Ji, K.; Li, Y.; Zhang, L. *J. Am. Chem. Soc.* **2012**, *134*, 17412–17415. (f) Ji, K.; Zhao, Y.; Zhang, L. *Angew. Chem. Int. Ed.* **2013**, *52*, 6508–6512. (g) Lu, B.; Li, Y.; Wang, Y.; Aue, D. H.; Luo, Y.; Zhang, L. *J. Am. Chem. Soc.* **2013**, *135*, 8512–8524. (h) Ji, K.; Zhang, L. *Org. Chem. Front.* **2014**, *1*, 34–38. For a review, see: (i) Zhang, L. *Acc. Chem. Res.* **2014**, *47*, 877–888.

[50] (a) Gorin, D. J.; Davis, N. R.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 11260–11261. (b) Lu, B.; Luo, Y.; Liu, L.; Ye, L.; Wang, Y.; Zhang, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 8358–8362. (c) Yan, Z.; Xiao, Y.; Zhang, L. *Angew. Chem. Int. Ed.* **2012**, *51*, 8624–8627.

[51] Ringger, D. H.; Chen, P. *Angew. Chem. Int. Ed.* **2013**, *52*, 4686–4689.

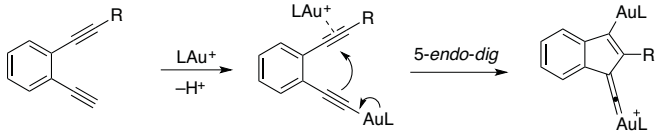


Scheme 22

Similarly, cationic N-heterocyclic carbene (NHC) gold(I) benzylidene complex can also be generated from a phosphonium ylide.[52]

8. Gold vinylidenes from (2-ethynylphenyl)alkynes

Gold vinylidenes are proposed as the most likely intermediates in the gold catalyzed cycloisomerization of (2-ethynylphenyl)alkynes (Scheme 23). The gold vinylidene intermediates are highly reactive and can undergo intramolecular/intermolecular C-H insertions, cyclopropanations/ring-expansions with alkenes.[53] Recently, a new aryne generation method from related substrates by hexadehydro-Diels–Alder (HDDA) reaction has attracted much attention.[54] Interestingly, in some cases, simple silver salts, such as AgOTf, $AgSbF_6$ and $AgNO_3$, are effective for promoting the HDDA aryne formation under milder conditions.[55]

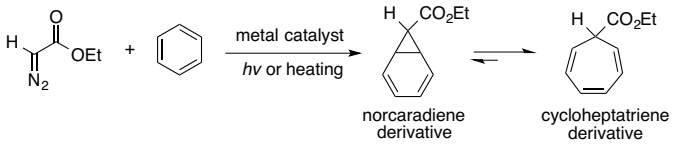


Scheme 23

[52] Fedorov, A.; Moret, M.-E.; Chen, P. *J. Am. Chem. Soc.* **2008**, *130*, 8880–8881.
[53] (a) Ye, L.; Wang, Y.; Aue, D. H.; Zhang, L. *J. Am. Chem. Soc.* **2012**, *134*, 31–34. (b) Hashmi, A. S. K.; Braun, I.; Nösel, P.; Schädlich, J.; Wieteck, M.; Rudolph, M.; Rominger, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 4456–4460. (c) Hashmi, A. S. K.; Wieteck, M.; Braun, I.; Rudolph, M.; Rominger, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 10633–10637. (d) Hansmann, M. M.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem. Int. Ed.* **2013**, *52*, 2593–2598.
[54] (a) Hoye, T. R.; Baire, B.; Niu, D.; Willoughby, P. H.; Woods, B. P. *Nature* **2012**, *490*, 208–212. (b) Niu, D.; Willoughby, P. H.; Woods, B. P.; Baire, B.; Hoye, T. R. *Nature* **2013**, *501*, 531–534. (c) Niu, D.; Hoye, T. R. *Nat. Chem.* **2013**, *6*, 34–40. (d) Holden, C.; Greaney, M. F. *Angew. Chem. Int. Ed.* **2014**, *53*, 5746–5749.
[55] Yun, S. Y.; Wang, K.-P.; Lee, N.-K.; Mamidipalli, P.; Lee, D. *J. Am. Chem. Soc.* **2013**, *135*, 4468–4471.

Buchner ring expansion

The Buchner ring expansion is a carbene addition to benzene or its homologs to form cycloheptatrienes.[56] This reaction was first reported by E. Buchner and T. Curtius in 1885.[57] One typical example is shown below. The first step involves formation of a carbene from ethyl diazoacetate, which cyclopropanates benzene to form a norcaradiene derivative. Ring expansion occurs in the second step, with an electrocyclic opening of the cyclopropane to form a 7-membered ring. Although photochemical or thermal conditions can be used to initiate the carbene formation, transition metal catalysts (mainly rhodium- and copper-based) are often used to perform this reaction under very mild conditions (Scheme 24).[58]

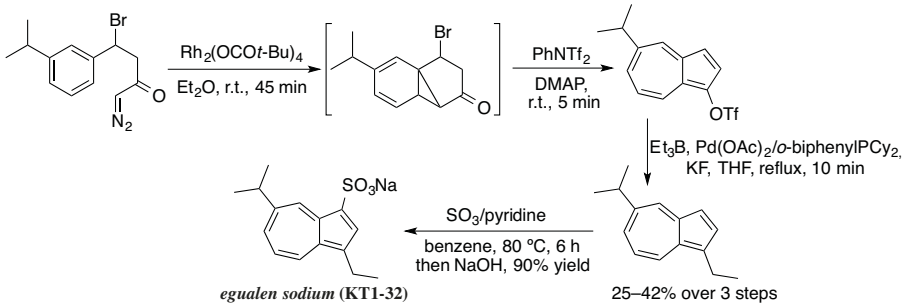


Scheme 24

Because the regioselectivity is not easy to control, Buchner reactions are normally only applied in synthesis in cases where the insertion occurs in an intramolecular fashion. Two recent total syntheses featuring Buchner reactions as key steps are listed below.

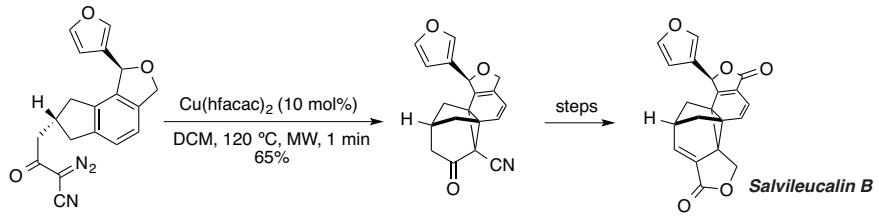
In 2001, the group of Danheiser reported a new ring expansion-annulation strategy for the synthesis of substituted azulenes (Scheme 25). This method was successfully used as a key step to construct the skeleton of antiulcer drug *egualen sodium* (KT1-32).[59]

[56] For reviews, see: (a) Dave, V.; Warnhoff, E. W. *Org. React.* **1970**, *18*, 217–401. (b) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091–1160. (c) Reisman, S. E.; Nani, R. R.; Levin, S. *Synlett* **2011**, 2437–2442.
[57] Buchner, E.; Curtius, T. *Chem. Ber.* **1885**, *18*, 2371–2377.
[58] Anciaux, A. J.; Demonceau, A.; Noels, A. F.; Hubert, A. J.; Warin, R.; Teyssie, P. *J. Org. Chem.* **1981**, *46*, 873–876.
[59] Kane, J. L.; Shea, K. M.; Crombie, A. L.; Danheiser, R. L. *Org. Lett.* **2001**, *3*, 1081–1084.



Scheme 25

In 2011, Reisman reported the enantioselective total synthesis of (+)-salvileucalin B. The synthetic route features a copper-catalyzed arene cyclopropanation reaction to provide the unusual norcaradiene core (Scheme 26).[60]

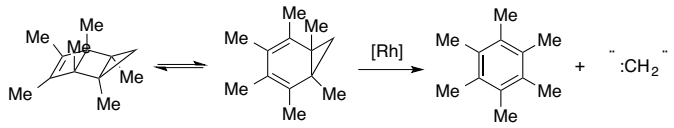


Scheme 26

Retro-Buchner reactions

There have only been few reported examples of retro-Buchner processes, all of which are lacking generality and simplicity to make them synthetically useful.

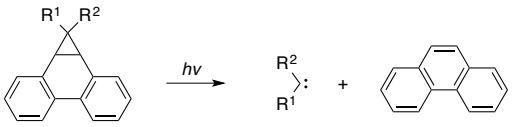
1,2,3,4,5,6-Hexamethyltricyclo[4.1.0.0$^{2.5}$]hept-3-ene reacts in the presence of $[Rh(CO)_2Cl]_2$ to give quantitatively hexamethylbenzene. The carbene ($:CH_2$) generated alongside could be trapped with cyclohexene (Scheme 27).[61] However, its lower methylated analogues proved to be inactive.



Scheme 27

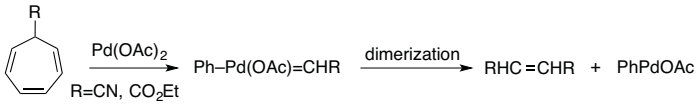
[60] Levin, S.; Nani, R. R.; Reisman, S. E. *J. Am. Chem. Soc.* **2011**, *133*, 774–776.
[61] Volger, H. C.; Hogeveen, H.; Roobeek, C. F. *Recueil* **1973**, *92*, 1223–1231.

It has been shown previously in this chapter that free carbenes can be generated from phenanthrene precursors under photochemical conditions (Scheme 28).[40]



Scheme 28

The reaction of 7-ethoxycarbonyl-1,3,5-cycloheptatriene with an equimolecular amount of $Pd(OAc)_2$ at 80 °C in MeCN has been reported to give ethyl 2-and 4-formylbenzoate (8% each) by cleavage of one cyclopropane C-C bond of the corresponding norcaradienes. In addition, diethyl maleate (14% yield) was formed, presumably by a dimerization of a Pd(II) carbene formed by a retro-Buchner process (Scheme 29).[62]



Scheme 29

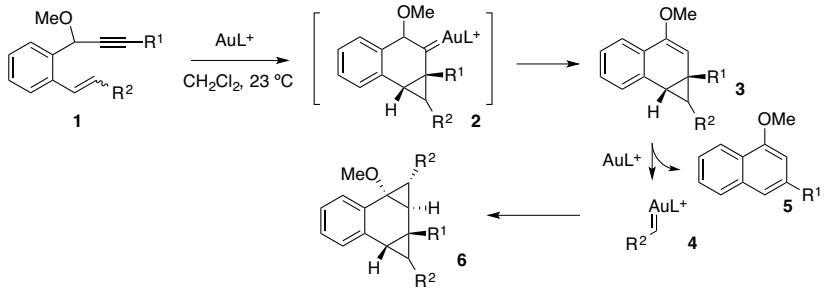
[62] Saito, K.; Kozaki, M.; Takahashi, K. *Chem. Pharm. Bull.* **1993**, *41*, 2187−2189.

Chapter 1. The generation and fate of gold carbenes by retro-Buchner reactions

Background

Several representative methods for generating gold(I) carbenes intermediates are listed in the general introduction.

A new example of gold(I) carbene formation through retro-cyclopropanation was reported by our laboratory in 2010 (Scheme 1-1).[5] This gold(I) carbene **4** was generated from intermediate **3** by cycloisomerization of 1,6-enynes with the general structure **1** through a mechanism that involves loss of one molecule of 1-methoxynaphthalene **5**. The gold(I) carbene **4** can be trapped by intermediate **3** to form di-cyclopropanated naphthalene derivatives **6**. This was the first time that of gold(I) catalyzed retro-cyclopropanation was achieved in the context of bench chemistry with easy to handle reagents.[63]



Scheme 1- 1 Gold(I) carbenes through retro-cyclopropanations.

A similar process was also proposed in the gas phase cleavage of 1-ethoxy-2-methoxycyclopropane with $[AuIMes]^+$ on the basis of collision-induced dissociation (CID) experiments and theoretical calculations.[64]

[63] Cleavage of cyclopropanes to form metal carbenes had only been reported previously with low efficiency using highly electrophilic $PhWCl_3/RAlCl_2$ (R = Et, Cl): (a) Gassman, P. G.; Johnson, T. H. *J. Am. Chem. Soc.* **1976**, *98*, 6057–6058. (b) Gassman, P. G.; Johnson, T. H. *J. Am. Chem. Soc.* **1976**, *98*, 6058–6059.

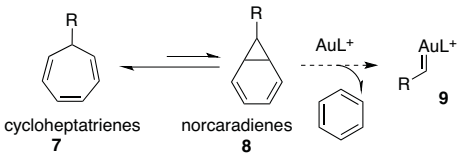
[64] (a) Batiste, L.; Fedorov, A.; Chen, P. *Chem. Commun.* **2010**, *46*, 3899–3901. (b) Fedorov, A.; Chen, P. *Organometallics* **2010**, *29*, 2994–3000. (c) Fedorov, A.; Batiste, L.; Bach, A.; Birney D. M.; Chen, P. *J. Am. Chem. Soc.* **2011**, *133*, 12162–12171. (d) Batiste, L.; Chen, P. *J. Am. Chem. Soc.* **2014**, *136*, DOI: 10.1021/ja4084495.

Objectives

Although gold(I) carbenes can be generated by this annulation/fragmentation process shown in Scheme 1-1, the tedious preparation of the required substrates detracts significantly from its synthetic utility.

It is known that cycloheptatrienes **7** are in equilibrium with norcaradienes **8**. In general, the equilibrium lies on the side of the cycloheptatriene tautomer, as a result of the strained cyclopropane ring present in the norcaradiene (Scheme 1-2).[65]

We postulated that gold(I) carbenes could be generated by a similar retro-cyclopropanation from the norcaradiene tautomer, as shown in Scheme 1-2.



Scheme 1- 2 Gold(I) carbenes from cycloheptatrienes.

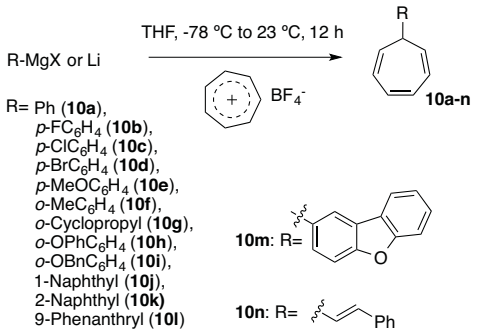
[65] (a) Ciganek, E. *J. Am. Chem. Soc.* **1965**, *87*, 1149–1150. For recent review on this equilibrium: (b) McNamara, O. A.; Maguire. A. R. *Tetrahedron* **2011**, *67*, 9–40.

Synthesis of 7-aryl cycloheptatrienes

7-Aryl cycloheptatrienes **10** were easily prepared in good yields by reactions of organolithium or Grignard reagents with tropylium tetrafluoroborate or tropylium bromide (Scheme 1-3).[66]

It is worthy to note that organolithium reagents, generated *in situ* by lithium-bromine exchange, normally give better results than Grignard reagents for this reaction. This is due to the ease of homo-coupling of Grignard reagents and the quite similar polarity of biaryl byproduct to the desired 7-arylcycloheptatrienes **10**, which makes the separation very difficult. We also found the commercially available organolithium reagents, such as phenyl lithium, give poorer results compared with reagents generated *in situ* by lithium-bromine exchange.

In Chapter 3 of this Thesis we also present a series of *o*-styryl substituted cycloheptatrienes obtained through this procedure.



Scheme 1- 3 Synthesis of 7-aryl cycloheptatrienes from organolithium or Grignard reagents.

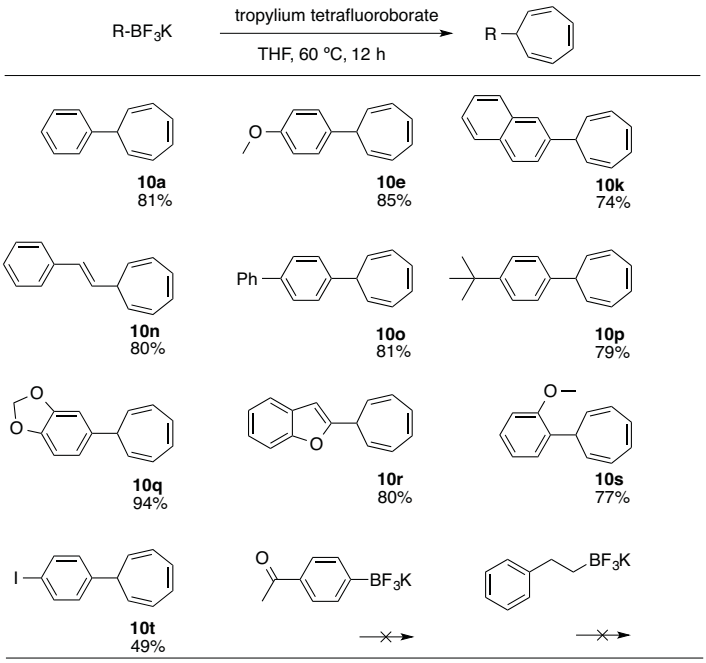
Alternatively, we also prepared 7-substituted cycloheptatrienes **10** under mild conditions employing commercially available or easily accessible potassium trifluoroborate salts[67] instead of organolithium or Grignard reagents (Table 1-1). By using this method, no biaryl byproduct was observed. Acetal (**10q**), iodide (**10t**) and benzofuran (**10r**) containing cycloheptatrienes were successfully obtained in good yields. Unfortunately, electron-deficient and alkyl nucleophiles were unreactive under these conditions.

---

[66] Tropylium tetrafluoroborate was purchased from Alfa Aesar (€ 657/100 g) or can be easily prepared according to: (a) Conrow, K. *Org. Synth.* **1963**, *43*, 101–103. Tropylium bromide was prepared according to the reported procedure: (b) Doering, W. E.; Knox, L. H. *J. Am. Chem. Soc*. **1957**, *79*, 352–356.

[67] Trifluoroborate salts were prepared from boronic acids $RB(OH)_2$ and potassium bifluoride $K[HF_2]$. For reviews on their application in synthesis, see: (a) Darses, S.; Genet, J. P. *Chem. Rev.* **2008**, *108*, 288–325. (b) Molander, G. A.; Ellis, N. *Acc. Chem. Res.* **2007**, *40*, 275–286.

Table 1- 1 Cycloheptatrienes from potassium trifluoroborate salts.[a]



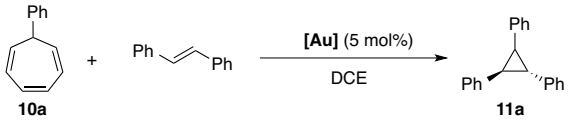
[a] Reaction at 60 °C, 0.12 M in THF, 2 equiv of potassium trifluoroborate salts, 12 h. Yields are for isolated products.

Results and discussions

Cyclopropanation

With the cycloheptatrienes in hand, the first reaction between **10a** and *trans*-stilbene was tested. After screening different gold(I) catalysts, solvents, and temperatures, we found the best conditions for this transformation: by heating in 1,2-dichloroethane (DCE) at 120 ºC for 2 h in the presence of 5 mol% cationic gold(I) complex **B**, namely [*t*-BuXPhosAu(CH_3CN)]SbF_6. Under these standard conditions, tri-substituted cyclopropane **11a** was obtained in 84% yield (Table 1-2).[68] The overall transformation can be regarded as a retro-Buchner reaction. Interestingly, the reverse process, formation of cycloheptatrienes, occurs as a side reaction in the gold(I)-catalyzed reaction between ethyl diazoacetate and arenes.[45a, c]

Table 1- 2 Cyclopropanation of trans-stilbene with cycloheptatriene 1-1a.[a]



Entry	Catalyst	Temp, Time	Yield(%)[b]	Entry	Catalyst	Temp, Time	Yield(%)[b]
1	**A**	80 ºC, 8 h	26	6	**C**	80 ºC, 10 h	-[c]
2	**A**	100 ºC, 5 h	31	7	**D**	80 ºC, 8 h	-[c]
3	**B**	80 ºC, 8 h	49	8	**E**	80 ºC, 8 h	43
4	**B**	100 ºC, 5 h	73	9	**E**	100 ºC, 5 h	64
5	**B**	120 ºC, 2 h	84	10	**E**	120 ºC, 2 h	70

[a] Reaction at 0.2 M in DCE, 2 equiv of **10a**, catalyst (5 mol%). [b] Isolated yields were reported. [c] Not detected.

There are several points worthy of comment:

1) It is necessary to heat the reaction to 120 ºC for it to occur effectively (so far,[69] the lowest temperature that successfully led to product formation is 80 ºC). Thus, thermally labile gold complexes (e.g. **C**, **D**, **F**, **G**) are not suitable catalysts.

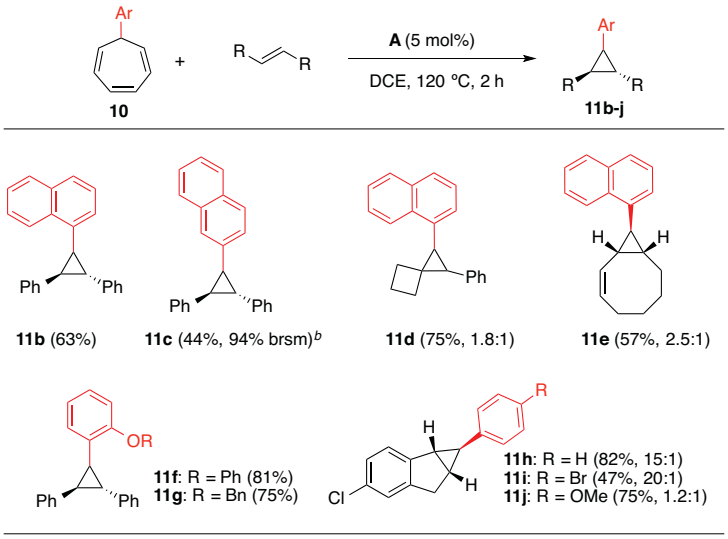
2) Toluene can also be used as solvent, but this requires longer reaction time.

[68] The optimization of this reaction was done by Dr. César Rogelio Solorio-Alvarado. For the detailed information, see his PhD thesis and reference 6.
[69] 27/06/2014

3) [JohnPhosAu(CH_3CN)]SbF_6 (**A**) and [IPrAu(PhCN)]SbF_6 (**E**) are the other two alternative catalysts for this transformation, although in this case the yields are lower than using [*t*-BuXPhosAu(CH_3CN)]SbF_6 (**B**). It should be mentioned that for some substrates, catalyst **A** and **E** perform better than **B**.

Some examples [70] are illustrated in Table 1-3. Interestingly, 1-naphthyl-cycloheptatriene (**10j**) and 2-naphthyl-cycloheptatriene (**10k**) exhibited different reactivities with *trans*-stilbene (**11b**, **11c**). The reaction with methylenecyclobutane derivative led to spiro-compound (**11d**) in good yield. Mono-cyclopropanated product (**11e**) was obtained from cycloocta-1,3-diene, albeit with low diasteroselectivity. Interestingly, the intermolecular cyclopropanation of gold(I) carbene (**11f**, **11g**) is favored over the possible intramolecular C_{sp2}-H insertion with ether as tethering group. Finally, 6-chloro-1*H*-indene also took part in the cyclopropanation reaction with gold carbenes leading to **11h**, **11i**, **11j**.

Table 1- 3 Cyclopropanation of different subtrates.[a]

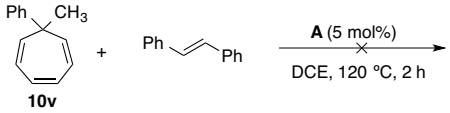


[a] Reaction at 120 °C, 0.2 M in DCE, 2 equiv of olefins, 2 h. Yields are for isolated adducts. The ratio of isomers was determined by ^{1}H NMR. [b] Catalyst **B** was used. brsm: based on unrecovered starting materials.

When 7,7-disubstituted cycloheptatriene **10v** was submitted to the standard conditions, however, no desired product was observed (Scheme 1-4). Since the cycloheptatriene/norcaradiene equilibrium exists with disubstituted **10v** according to the literature,[65b] we hypothesized that its sluggish reactivity may result from the

[70] More examples of the reaction scope, see PhD thesis of Dr. César Rogelio Solorio-Alvarado and reference 6.

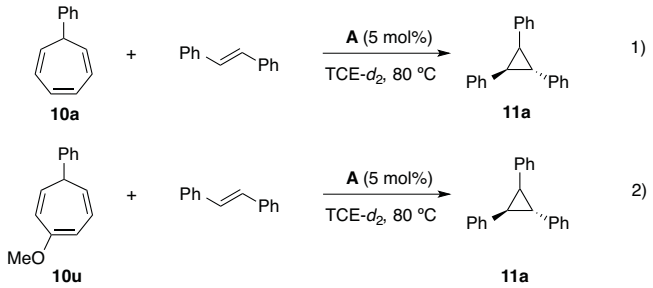
steric hindrance presented by the geminal disubstitution, which inhibits the approach of the gold complex.



Scheme 1- 4 7,7-Disubstituted cycloheptatriene.

Kinetic study of cyclopropanation

A kinetic study of **10a** and its electron-rich analog **10u** is shown below (Scheme 1-5).



Scheme 1- 5

The electronic effect has a significant influence on the rate at which the gold(I) carbene is generated (Figure 1-1). Due to the high reactivity of 3-methoxy-7-phenylcyclohepta-1,3,5-triene (**10u**), it was found to be fully consumed within 1 h. We also performed this experiment at 60 ºC. In this case, the reaction involving 7-phenylcyclohepta-1,3,5-triene (**10a**) did not proceed, but that of **10u** gave the desired product **11a**. This observation suggested the gold(I) catalyzed retro-Buchner reaction is a electrophilic ring-opening process, which is in accord with the DFT calculations shown below.

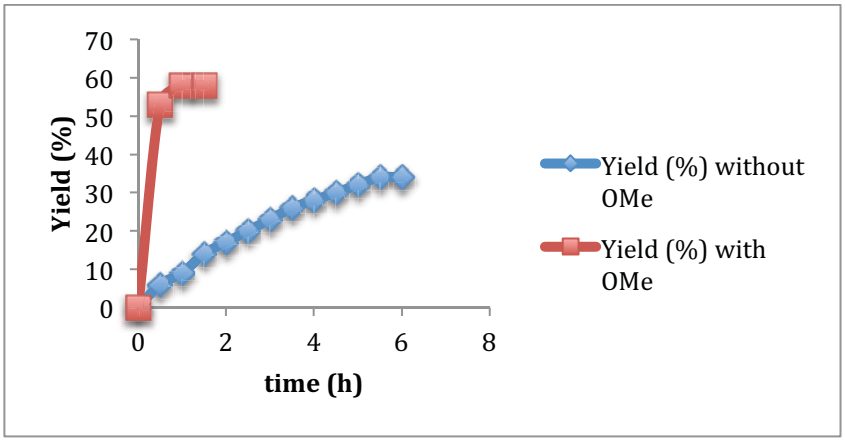


Figure 1- 1 Kinetic study of cyclopropanation.[a]

[a] Reaction conditions: 18 mg (0.1 mmol) of (*E*)-1,2-diphenylethene, 3.7 mg (5 mol%) gold complex **A** and 7-phenylcyclohepta-1,3,5-triene (**10a**, 25 mg, 0.15 mmol) or 3-methoxy-7-phenylcyclohepta-1,3,5-triene[71] (**10u**, 30 mg, 0.15 mmol) were dissolved in 0.5 mL 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2, 99.5 atom%D)[72] in a NMR tube. The mixture was heated to 80 ºC and monitored by ^{1}H NMR. The signal of $CDCl_2CHCl_2$ was used as internal standard to calculate the yield of product.

DFT calculations of the retro-Buchner reaction

Our DFT computational study of the gold-catalyzed retro-Buchner reaction (M06 level, 1,2-dichloroethane) was complicated by the likely existence of several η^2-coordinated gold(I) species in solution. Thus, in addition to η^2-coordinated cycloheptatriene (**Ia**) and norcaradiene (**Ib**), the (η^1-arene)gold(I) complex **Ic** was also found as a local minimum (Figure 1-2). An intermediate norcaradiene in which gold(I) is η^2-coordinated to the cyclopropane C−C bond (**Id**) was also found at a free energy 12.7 kcal·mol^{-1} higher than that of **Ib**.

Previously, on the basis of related DFT calculations, we proposed the formation of related edge- or corner-metalated cyclopropanes as products in intra- and intermolecular gold(I)-catalyzed cyclopropanations of alkenes with 1,6-enynes[73] and intramolecular cyclopropanation of 1,5-enynes.[74]

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[71] Prepared according to the literature: Tatsuya, S.; Hirofuni, N.; Tetsuo, N.; Shigenori, K. *Tetrahedron Lett.* **1990**, *31,* 895–898.
[72] The abundance was rechecked by NMR using 1,4-Diacetylbenzene as internal standard.
[73] (a) Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Jiménez-Núñez, E.; Buñuel, E.; Cárdenas, D. J.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 1694–1702. (b) Pérez-Galán, P.; Herrero-Gómez, E.; Hog, D. T.; Martin, N. J. A.; Maseras, F.; Echavarren, A. M. *Chem. Sci.* **2011**, *2*, 141–149.
[74] López-Carrillo, V.; Huguet, N.; Mosquera, Á; Echavarren, A. M. *Chem. Eur. J.* **2011**, *17*, 10972–10978.

A transition state ($\mathbf{TS_{Id–II}}$) was found for the electrophilic cleavage of intermediate **Id** (Figure 1-2), which lies 23.3 kcal·mol^{-1} higher than the most stable initial complex **Ib**. This value for the activation energy of the retro-Buchner reaction is consistent with the range of temperatures required for these reactions (100−120 °C). Transition state $\mathbf{TS_{Id–II}}$ leads to Wheland-type intermediate **II**, which is in a shallow minimum that smoothly evolves through $\mathbf{TS_{II–III}}$ to form phenyl gold(I) carbene **III** and benzene. Although the overall process of the retro-Buchner reaction is moderately endothermic, further reactions of gold(I) carbene **III** with alkenes are highly exothermic processes.

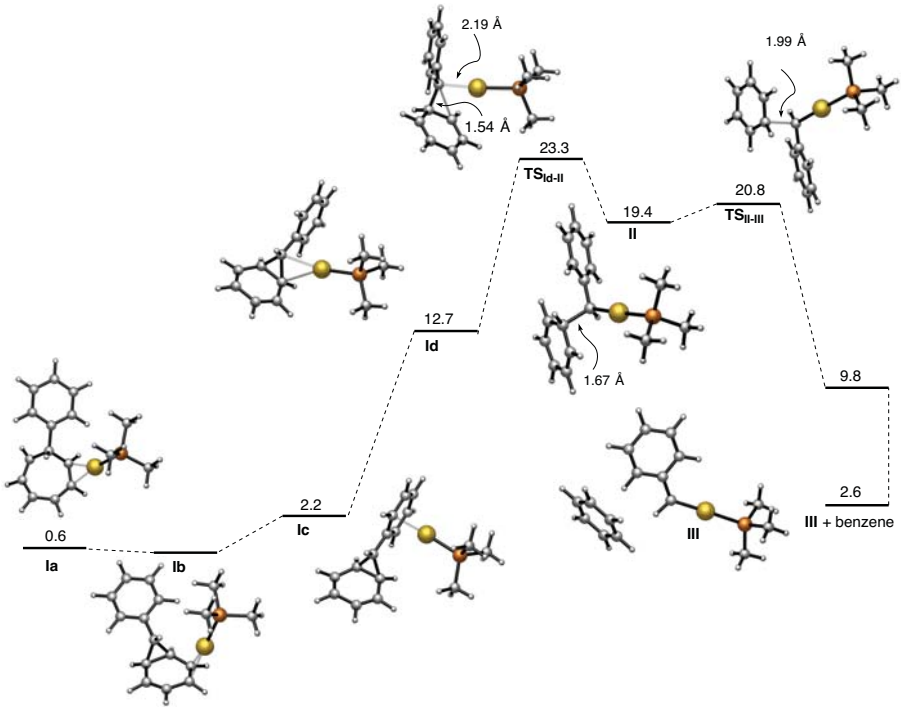
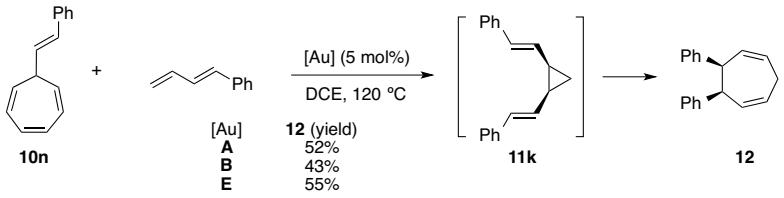


Figure 1- 2 DFT calculations of retro-Buchner reaction. Free energies in kcal·mol^{-1}.

Cyclopropanation/Cope-rearrangement

1-Phenyl-1,3-butadiene reacted with cycloheptatriene **10n** in the presence of gold(I) catalysts to give **11k** as a result of the cyclopropanation at the least-substituted double bond. Interestingly, it is not stable at high temperature and undergoes Cope

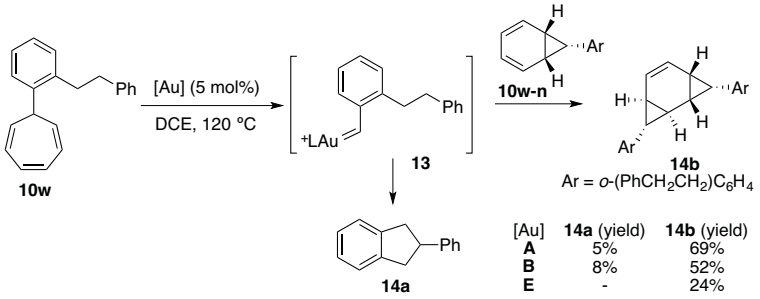
rearrangement to form *cis*-6,7-diphenylcyclohepta-1,4-diene (**12**) in 43–55% yield as the only isolated product (Scheme 1-6).[75]



Scheme 1- 6 Cyclopropanation/Cope-rearrangement cascade.

C-H insertions

We envisioned that a gold(I) carbene formed by retro-Buchner reaction could undergo facile intramolecular C-H insertion.[76] For this purpose, we chose cycloheptatriene **10w** as a substrate that could form 2-phenylindane **14a** via gold(I) carbene **13**. Interestingly, although **14a** was indeed obtained in this reaction, the major product was the unsymmetrical biscyclopropane **14b**, which was formed by trapping of gold(I) carbene **13** with *endo*-norcaradiene **10w-n** (Scheme 1-7). This result highlights the high propensity of gold(I) carbenes to react with alkenes in cyclopropanation reactions.



Scheme 1- 7 Dimerization of 10w.

1,3-Diones (**10a** and **10h**) did react with the gold(I) carbenes generated from cycloheptatrienes and formal C-H insertion products **15a** and **15b** were exclusively obtained in good yields (Scheme 1-8). To our surprise, di-alkylation was not observed in this reaction even with excess of cycloheptatriene starting material.

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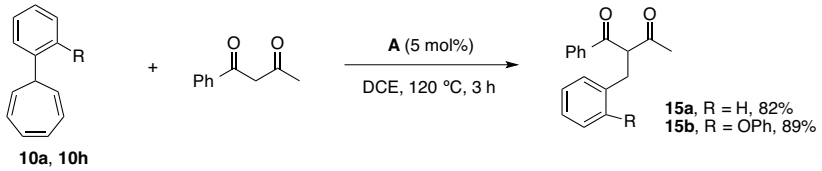
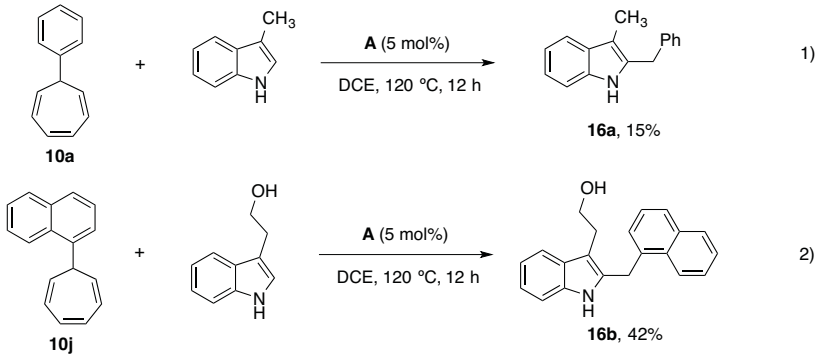
[75] For lead references on cyclopropanation/Cope–rearrangement: (a) Parr, B. T.; Davies, H. M. L. *Angew. Chem. Int. Ed.* **2013**, *52*, 10044–10047. (b) lian, Y.; Miller, L. C.; Born, S., Sarpong, R.; Davies, H. M. L. *J. Am. Chem. Soc.* **2010**, *132*, 12422–12425 and the references cited therein.

[76] Horino, Y.; Yamamoto, T.; Ueda, K.; Kuroda, S.; Toste, F. D. *J. Am. Chem. Soc.* **2009**, *131*, 2809–2811.



Scheme 1- 8 Carbene C-H insertion of 1,3-dione.

3-Substituted indoles exhibited low reactivity toward gold(I) carbenes, and the desired product of formal C-H insertion, **16a** and **16b**, were obtained with low yields. Even when 1.5 equiv of cycloheptatriene starting material were employed, indole substrates were still not fully consumed (Scheme 1-9). In addition, 2-substituted indoles failed at trapping gold carbenes generated by this method.[77]



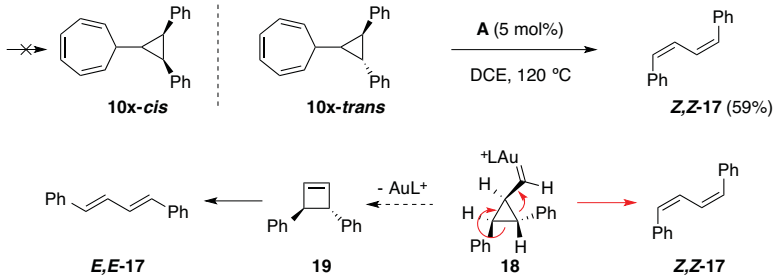
Scheme 1- 9 Reactions with indoles.

Formation of cyclopropyl gold(I) carbenes

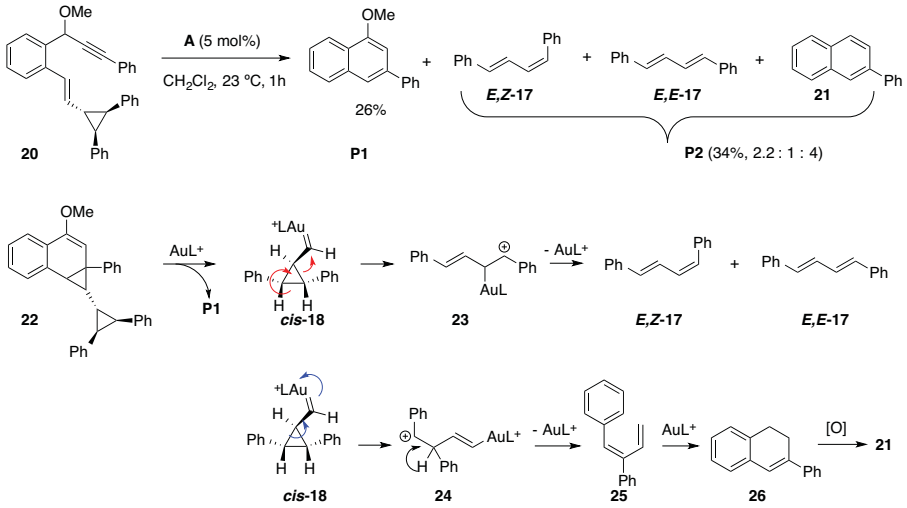
We conjectured that a expected retro-Buchner reaction of (*trans*-2,3-diphenylcyclopropyl)cyclohepta-1,3,5-triene **10x-*trans*** would generate cyclopropyl gold(I) carbene **18**, which could evolve to cyclobutene **19**[78] and subsequently (*E,E*)-**17** by thermal conrotatory opening (Scheme 1-10).[79] However, reaction of **10x-*trans*** with catalyst **A** led exclusively to (*Z,Z*)-**17**. This surprising result suggests that intermediate **18** evolves by a mechanism analogous to the skeletal rearrangement of 1,6-enynes,[80] bypassing the formation of cyclobutene **19**. We decided to prepare a

[77] It is reported that a 2-substituted indole react with vinyl Rh-carbene to generate chiral 3-substituted indoles: Lian, Y.; Davies, H. M. L. *Org. Lett.* **2012**, *14*, 1934–1937.
[78] López-Carrillo, V.; Echavarren, A. M. *J. Am. Chem. Soc.* **2010**, *132*, 9292–9294.
[79] Wilcox, C. F.; Carpenter, B. K. *J. Am. Chem. Soc.* **1979**, *101*, 3897–3905.
[80] Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Cárdenas, D. J.; Buñuel, E.; Nevado, C.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 6146–6148.

similar substrate with two *cis*-phenyls **10x-*cis*** to study its effect on the stereochemical outcome of this process.



Scheme 1- 10 Cycloproply gold carbene reactivity.



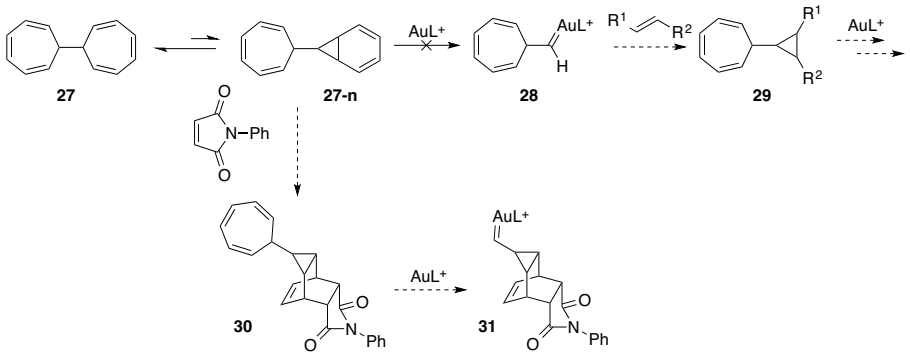
Scheme 1- 11 Cycloproply gold carbene reactivity.

However, due to the difficulty in synthesizing **10x-*cis***, we prepared **20** instead, in which the enyne system has the potential to form similar cyclopropyl gold carbene.[5] Indeed, enyne **20** reacted with gold complex **A** at room temperature and two fractions **P1** and **P2** were obtained from this reaction mixture (Scheme 1-11). The first product with higher polarity was identified as naphthalene derivative **P1**, which confirms that the fragmentation occurs. The other fraction **P2** was a mixture of three compounds. All of the three compounds are known and well characterized. By comparing the NMR and MS, the structures of these three compounds were determined: (*E,Z*)-**17**, (*E,E*)-**17**, and **21**.

Regarding the mechanism, enyne **20**, in the presence of gold catalyst **A**, cyclized to give intermediate **22**, which can be isolated[81] when performing this reaction at room temperature for a period of 10 min. According to our previous work,[5] release of a naphthalene derivative (**P1**) is much more favorable than that of a benzene, which permits formation of related intermediate ***cis*-18** at lower temperature. After similar ring opening of cyclopropyl gold carbene ***cis*-18**, a gold-containing cationic species **23** was proposed and the final two isomeric dienes ((*E,Z*)-**17**, (*E,E*)-**17**) were obtained with regeneration of the gold catalyst. The other competing pathway of ***cis*-18** is also possible, and it is through this pathway that intermediate **24**, an isomer of **23**, was also formed. After protodeauration and probable gold-catalyzed ring closure followed by spontaneous oxidative aromatization, naphthalene derivative **21** was formed as one component of the mixture **P2**. Detailed study of related stereochemical effects is still ongoing in our laboratory.

Biscycloheptatriene

We envisaged that gold complex could react with **27-n**, the norcaradiene-form of biscycloheptatriene **27**, to generate an interesting cycloheptatrienyl gold carbene **28**. The carbene intermediate **28** could then be trapped by an olefin intermolecularly to give **29**. This cyclopropanyl structure has been demonstrated to be reactive towards further carbene formation in the presence of gold (Scheme 1-12).



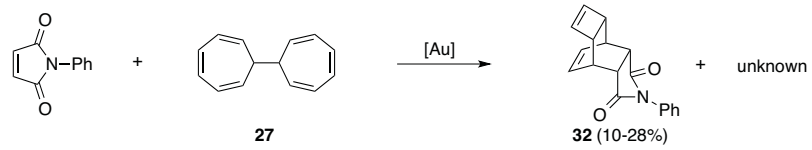
Scheme 1- 12 Biscycloheptatriene.

Unfortunately, when we tested this idea under the standard conditions with *trans*-stilbene as trapping reagent, no product was observed. The sluggish reactivity of **27** may result from the very low concentration of norcaradiene-form **27-n** in the equilibrium.

[81] Unpublished results by Masha Kirillova.

Based on the fact that cycloheptatrienes can undergo thermal induced Diels–Alder reaction with some dienophiles,[82] we expected that a similar cyclopropanyl gold-carbene intermediate **31** should be formed more easily from the initial Diels–Alder adduct **30**.

Indeed, when the reaction depicted in Scheme 1-13 was performed, the desired polycyclic compound **32**[83] was isolated, albeit in low yield. For this reaction, we screened many conditions, including: the three best gold catalysts (**A**, **B**, **E**) for retro-Buchner reaction, a range of solvents, lower temperature, and other dienophiles. In all cases, the yields were in the range of 10–28%. The formation of a large amount of a highly insoluble compound was observed, which was also obtained in the absence of gold catalyst. We tentatively suggest this insoluble byproduct may be the double Diels-Alder adduct of **27**.

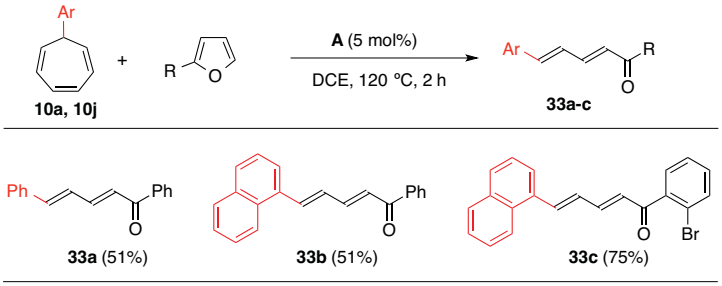


Scheme 1- 13

Reaction with furans

Monoarylsubstituted furans reacted with 7-arylcycloheptatrienes **10a**, **10j** under the standard conditions to form α, β, γ, δ-unsaturated ketones **33a-c** with exclusive *E,E*-configuration (Table 1-4).

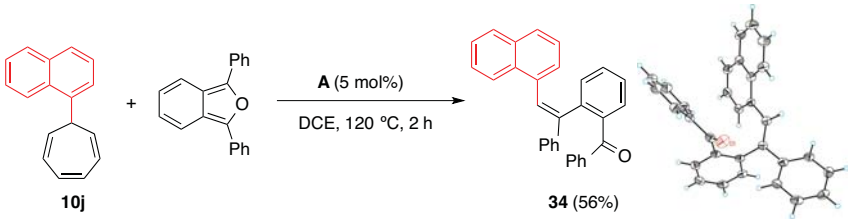
Table 1- 4 With monoarylsubstituted furans.



[82] (a) Mori, A.; Mametsuka, H.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2072–2077. (b) Ohnishi, Y.; Akasaki, Y.; Ohno, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3307–3308.

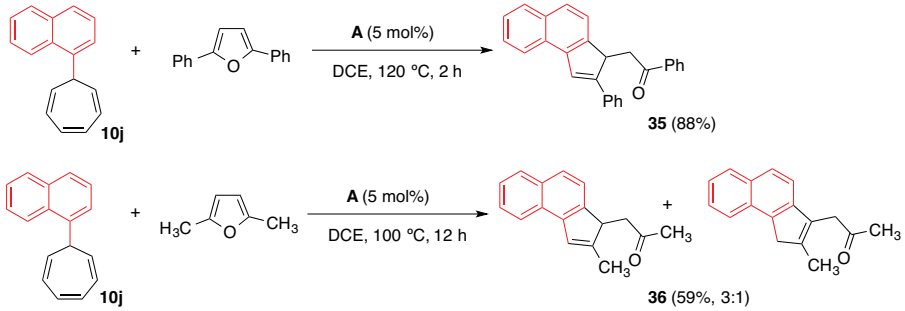
[83] This is a known compound and was prepared from Diels-Alder reaction of cyclooctatetraene (COT) with *N*-phenylmaleimide. It has been used as a monomer for the ring-opening metathesis polymerization: Charvet, R.; Novak, B. M. *Macromolecules* **2001**, *34*, 7680–7685.

Mixing 1,3-diphenylisobenzofuran with **10j** produced benzene-tethered ketone **34** via the similar pathway. The configuration of the double bond of **34** was confirmed by X-ray diffraction (Scheme 1-14).



Scheme 1- 14

However, this reaction is not general and is very sensitive to the substituent nature of the furans. For example, 2,5-diphenylfuran reacted with **10j** to give indene derivative **35** in good yield (Scheme 1-15). Probably, the initially formed α, β, γ, δ-unsaturated ketone was not stable at high temperature and cyclized again to give the observed product. Heating 2,5-dimethylfuran with **10j** in the presence of gold complex **A** at 100 ºC overnight (considering the volatility of dimethylfuran) afforded **36**, as a 3:1 mixture of two isomers.

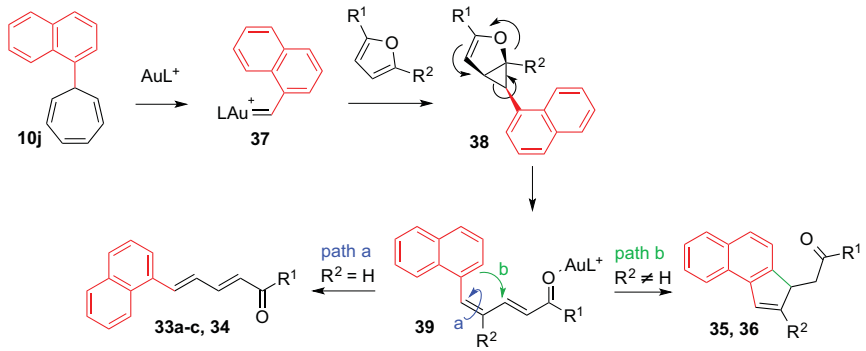


Scheme 1- 15

We proposed a mechanism for the reaction with furans that proceeds as follows (Scheme 1-16).[84] Gold carbenes **37** generated from cycloheptariene **10j** are trapped intermolecularly by the furan to form intermediates **38**, which is followed by a sigmatropic rearrangement leading to **39**. The reactivity of intermediate **39** is quite dependent on the substituents of furans. As shown in Scheme 1-16, when R^2 = H, fast isomerization (path a) occurs to give linear dienes **33a-c** and **34**. Whereas, when

[84] It is reported that gold-carbenes, generated by rearrangement of cyclopropenes, reacted with furans to give trienes through a similar pathway: Hadfield, M. S.; Lee, A.-L. *Chem. Commun.* **2011**, *47*, 1333–1335.

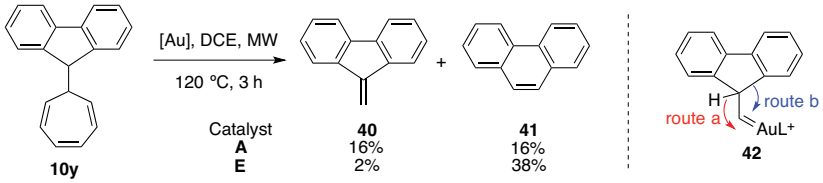
$R^2 \neq H$, a Mukaiyama-Michael-type addition (path b) promoted by gold(I) dominates to form cyclized products **35**, **36**.



Scheme 1- 16 Proposed mechanism for reactions with furans.

7-Alkylcycloheptatriene

Scheme 1-17 shows the only example of a 7-alkylcycloheptatriene that we have found so far which can undergo this retro-Buchner reaction. When catalyst **A** was used, a 1:1 mixture of **40** and **41** was obtained due to the two competing pathways in intermediate **42** shown in Scheme 1-17. The selectivity was enhanced to 19:1 when **E** was used as catalyst, but the yield was still low.



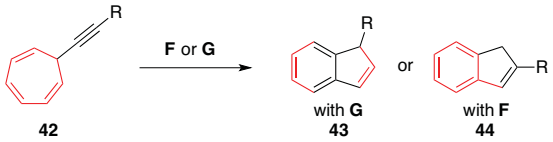
Scheme 1- 17 9-(Cyclohepta-2,4,6-trien-1-yl)-9*H*-fluorene.

7-Alkynyl cycloheptatrienes

7-Alkynyl cycloheptatrienes reacted with cationic gold(I) complex in a different fashion. Instead of resulting in aryl gold-carbenes, gold-stabilized fluxional barbaralyl cations were generated which followed several complicated rearrangement pathways and, in the absence of nucleophile, ultimately gave rise to indenes.[85]

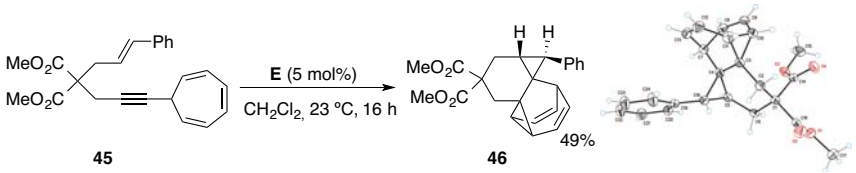
[85] For details of this reaction, see: McGonigal, P. R.; de_Leoń, C.; Wang, Y.; Homs, A.; Solorio-Alvarado, C. R.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 13093–13096.

Interestingly, the nature of the gold catalyst affects the fluxionality and evolution of the cationic intermediates. ^{13}C labeling experiments revealed that the ring of cycloheptatriene was split in the presence of gold(III) complex **G**, whereas, the ring contraction of cycloheptatriene was observed when highly electrophilic phosphite–gold(I) complex **F** was employed as catalyst (Scheme 1-18).



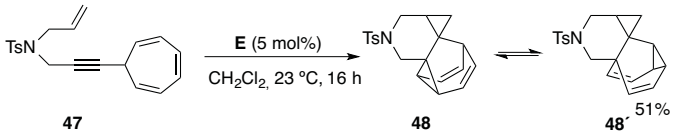
Scheme 1- 18

In order to gain some insight into the mechanism of this unusual reaction, we prepared several alkene-tethered substrates in order to trap the intermediate generated in the process of this reaction. A polycyclic barbaralane derivative **46** was obtained with excellent diasteroselectivity when **45** was treated with 5 mol% gold catalyst **E**, and the structure was confirmed by X-ray diffraction (Scheme 1-19).

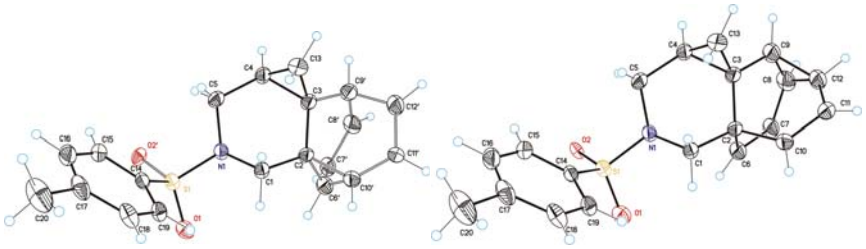


Scheme 1- 19

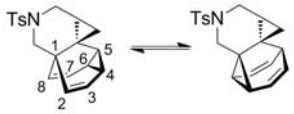
The tautomeric barbaralanes **48** and **48´**, obtained similarly, interconvert rapidly on the NMR timescale at room temperature in $CDCl_3$ through a strain-assisted Cope rearrangement and were even detected as a 1:1 mixture in the crystal state (Scheme 1-20).[86]



[86] For similar observations: (a) Bosse, D.; de Meijere, A. *Tetrahedron Lett.* **1978**, *19*, 965–968. (b) Siegwarth, J.; Bornhöft, J.; Näther, C.; Herges, R. *Org. Lett.* **2009**, *11*, 3450–3452.



Scheme 1- 20



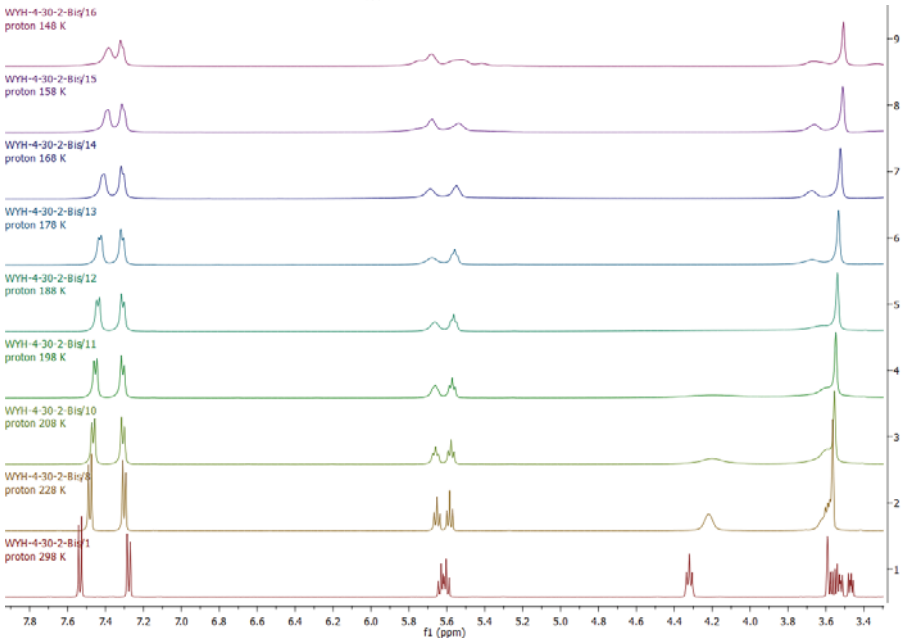


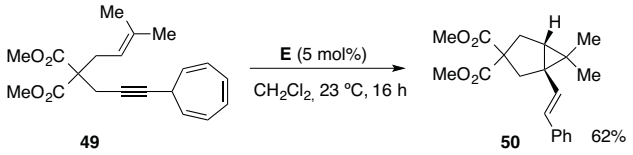
Figure 1- 3 Variable temperature experiment (500 MHz, THF-*d*8/CS_2 = 1:5) spectra of 48/48'

Variable temperature NMR spectra of **48**/**48´** recorded under ambient conditions show sharp signals due to rapid exchange on the NMR timescale, averaging the resonances due to protons 2 and 4, or 6 and 8. As the temperature was lowered, the peaks broadened and merged with the baseline before reappearing at 148 K at which point exchange is slow on the NMR timescale and one isomer exists in solution as the major species. At room temperature, protons 3 and 7 resonate at 5.6 ppm but protons 2, 4, 6 and 8 do not appear in the olefin region. At 148 K, four protons

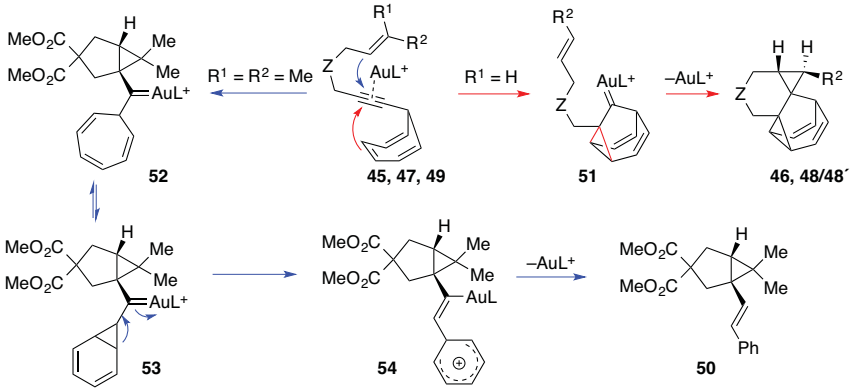
appear in the olefin region (5.9–5.3 ppm), protons 3 and 7, as well as two more protons–either 2 and 8 or 4 and 6.

The overall transformation of these two reactions is quite relevant to the gold(I)-catalyzed intramolecular cyclopropanation of dienynes.[87] Therefore, we proposed that the first step of generating barbaralyl cations from alkynyl cycloheptatrienes is forming cyclopropyl, cycloheptatrienyl gold-carbene intermediates.

Interestingly, a similar substrate with two geminal methyls gave different product under the same conditions (Scheme 1-21). Probably, in this case, the more electron-rich alkene, instead of cycloheptatriene, reacted preferentially with gold(I) activated alkyne to generate another intermediate. Subsequently, the cyclopropane ring in the norcaradiene-form was opened, due to the high electrophilicity of the adjacent gold(I) carbene. After protodeauration, the final product was obtained. The proposed mechanism for the formations of **46**, **48**/**48´** and **50** is shown in Scheme 1-22.



Scheme 1- 21

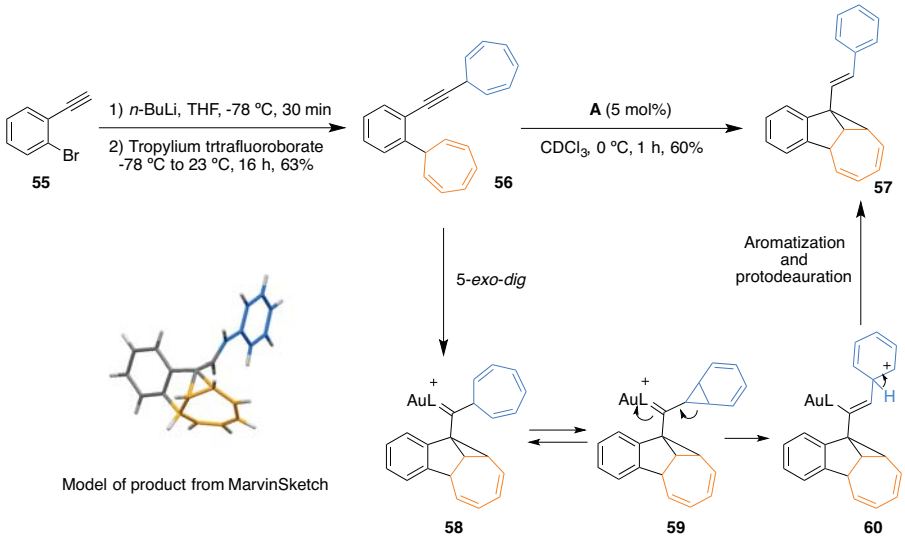


Scheme 1- 22

In the alkene-tethering 7-alkynyl cycloheptatriene reactions (Scheme 1-22), we assumed the alkene could also be from a cycloheptatriene ring. For this purpose, substrate **56** (Scheme 1-23) was prepared. As expected, cycloheptatrienyl gold(I) carbene **58** was generated through this special enyne cyclization. Similarly, the ring-

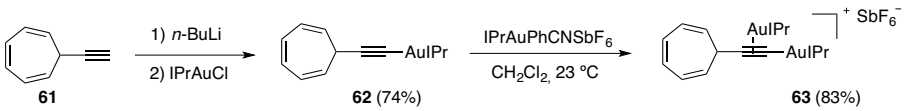
[87] Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Jiménez-Núñez, E.; Buñuel, E.; Cárdenas, D. J.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 1694–1702.

contraction occurred in the same manner, and followed by protodeauration to afford the final product **57**.[88]



Scheme 1- 23

In order to test a gold(I)-catalyzed gold-containing alkynyl cycloheptatriene reaction, we prepared **62** from 7-ethynylcyclohepta-1,3,5-triene **61**. In the presence of one equivalent of $IPrAuPhCNSbF_6$ (**E**) at room temperature, a digold complex **63**[89] was isolated in good yield (Scheme 1-24). The structure was confirmed by X-ray diffraction (Figure 1-4). Interestingly, it is very stable, and even by heating at 100 ºC for 1 hour, no decomposition of this digold complex was observed.



Scheme 1- 24

[88] In collaboration with Dr. Paul R. McGonigal.
[89] Digold complexes have been observed during previous research in the group: (a) Obradors, C.; Echavarren, A. M. *Chem. Eur. J.* **2013**, *19*, 3547–3551. (b) Homs, A.; Obradors, C.; Leboeuf, D.; Echavarren, A. M. *Adv. Synth. Catal.* **2014**, *356*, 221–228.

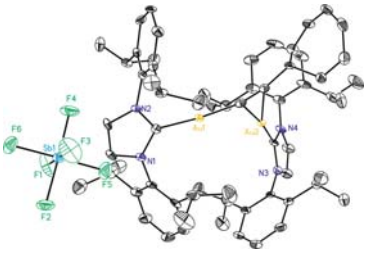
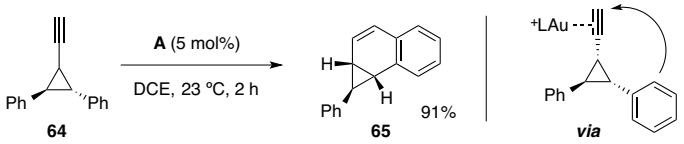


Figure 1- 4

Another feasible route of *in situ* generation of the substrates for gold-catalyzed retro-Buchner reaction is shown below (Scheme 1-25). Tricyclic structure **65** was obtained in excellent yield by a gold(I) catalyzed hydroarylation of cyclopropyl-tethered alkyne **64**. Surprisingly, product **65** is stable enough at room temperature to withstand purification by chromatography. Future work may focus on a gold-catalyzed cascade reaction, combining this new method of substrate synthesis and retro-Buchner reaction.



Scheme 1- 25

Conclusions

We have found that cationic gold(I) complexes promote the retro-Buchner reaction of 1,3,5-cycloheptatrienes to form substituted gold(I) carbenes that can be trapped intermolecularly by alkenes as a new cyclopropanation reaction. 1,2,3-Trisubstituted cyclopropanes, which are not easily prepared by other methods, can be synthesized from 1,2-substituted alkenes and readily available 7-substituted 1,3,5-cycloheptatrienes as a safe alternative to the use of explosive diazo compounds.

Using this methodology, we generated substituted cyclopropyl gold(I) carbenes and revealed some mechanistic insight into 1,6-enynes cyclization.

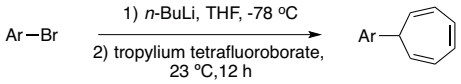
Some very interesting structures can be constructed by trapping these very reactive gold(I) carbenes with furans.

We also described a new type of gold(I)-catalyzed intramolecular cyclopropanation of dienynes with cycloheptatriene-containing substrates. These results gave some mechanistic support for a very complicated rearrangement of fluxional barbaralyl cations generated by gold(I)-catalyzed reaction of alkynyl cycloheptatrienes. An interesting cycloheptatriene-containing digold complex was also synthesized.

In addition, we also developed two alternative ways of generating substrates for retro-Buchner reaction: coupling of potassium trifluoroborate salts with tropylium tetrafluoroborate and gold-catalyzed hydro-aromatization.

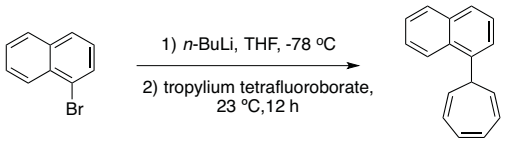
Experimental part

General procedure from organolithium



n-BuLi (1.3 equiv) was added dropwise to the solution of corresponding aryl bromide (1.2 equiv) in dry THF (6 mL/mmol) at -78 ºC under argon. The mixture was stirred for 30 min at -78 ºC, and then tropylium tetrafluoroborate (1 equiv) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature (23 ºC) for 12 h. The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with cyclohexane as eluent unless otherwise stated.

1-(Cyclohepta-2,4,6-trien-1-yl)naphthalene (10j)



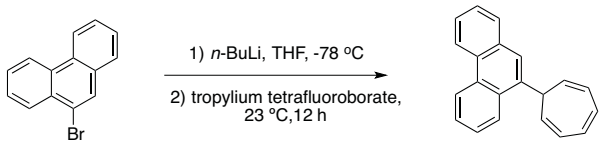
This compound (yellow oil, 1.47 g, yield: 67%) was prepared according to the general procedure from 1-bromonaphthalene (2.07 g, 10 mmol), *n*-BuLi (1.6 M, 6.9 mL, 11 mmol) and tropylium tetrafluoroborate (1.78 g, 10 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.56 - 7.46 (m, 3H), 6.84 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.38 - 6.33 (m, 2H), 5.64 (dd, *J* = 8.7, 5.4 Hz, 2H), 3.51 - 3.47 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 134.3, 131.5, 131.0, 128.9, 127.4, 126.8, 125.7, 125.5, 125.5, 124.5, 124.5, 124.4, 42.4.

HRMS-ESI: calculated for $C_{17}H_{15}$ $[M+H]^+$: 219.1174; found: 219.1179.

9-(Cyclohepta-2,4,6-trien-1-yl)phenanthrene (10l)



This compound (yellow solid, 1.47 g, yield: 70%) was prepared according to the general procedure from 9-bromophenanthrene (2 g, 7.78 mmol) and tropylium tetrafluoroborate (1.38 g, 7.78 mmol). The product was purified by trituration with hot ethanol (50 mL, then left to cool to r.t.).

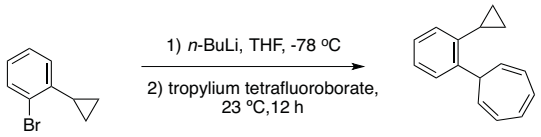
M.p.: 133-135 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.2 Hz, 1H), 8.72 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.96 - 7.90 (m, 2H), 7.72 - 7.58 (m, 4H), 6.86 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.39 (dddd, *J* = 8.9, 3.9, 2.6, 1.4 Hz, 2H), 5.73 (dd, *J* = 8.7, 5.6 Hz, 2H), 3.51 (t, *J* = 5.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 131.7, 131.1, 131.0, 130.8, 129.9, 128.5, 126.8, 126.4, 126.4, 126.3, 126.2, 125.2, 125.0, 124.6, 123.4, 122.5, 42.5.

HRMS-APCI: calculated for $C_{21}H_{17}$ $[M+H]^+$: 269.1325; found: 269.1331.

7-(2-Cyclopropylphenyl)cycloheptа-1,3,5-triene (10g)



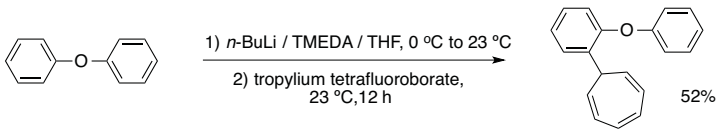
This compound (colorless oil, 250 mg, yield: 64%) was prepared according to the general procedure from 1-bromo-2-cyclopropylbenzene[90] (370 mg, 1.88 mmol) and tropylium tetrafluoroborate (335 mg, 1.88 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.28 (td, *J* = 7.6, 1.5 Hz, 1H), 7.23 (td, *J* = 7.5, 1.5 Hz, 1H), 7.08 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.77 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.29 (dddd, *J* = 8.9, 3.9, 2.6, 1.6 Hz, 2H), 5.45 (dd, *J* = 8.6, 5.5 Hz, 2H), 3.37 (t, *J* = 5.4 Hz, 1H), 1.90 - 1.83 (m, 1H), 0.87 - 0.80 (m, 2H), 0.69 - 0.59 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 141.1, 130.8, 127.0, 126.9, 126.5, 126.3, 126.3, 124.4, 41.7, 13.1, 7.3.

HRMS-APCI: calculated for $C_{16}H_{17}$ $[M+H]^+$: 209.1325; found: 209.1318.

7-(2-Phenoxyphenyl)cycloheptа-1,3,5-triene (10h)



[90] Prepared according to literature: He, Z.; Yudin, A. K. *Org. Lett.* **2006**, *8*, 5829–5832.

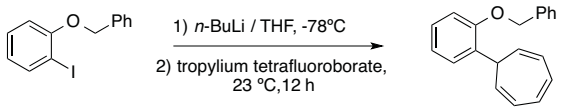
n-BuLi (1.6 M in hexanes, 15 mL, 24 mmol) was added dropwise to the solution of diphenyl ether (3.4 g, 20 mmol) and tetramethylethylenediamine (2.79 g, 3.58 mL, 24 mmol) in 50 mL THF at 0 ºC. After stirring at room temperature (23 ºC) for 5 h, tropylium tetrafluoroborate (3.56 g, 20 mmol) was added, and stirred at room temperature overnight. The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with cyclohexane as eluent to give 2.7 g colorless oil in 52% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.34 - 7.24 (m, 3H), 7.19 (td, *J* = 7.5, 1.3 Hz, 1H), 7.10 - 7.05 (m, 1H), 6.97 - 6.93 (m, 3H), 6.68 (dd, *J* = 3.6, 2.7 Hz, 2H), 6.22 - 6.25 (m, 2H), 5.46 (dd, *J* = 8.8, 5.6 Hz, 2H), 3.18 (tt, *J* = 5.6, 1.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 154.7, 134.8, 130.8, 129.6, 129.3, 127.9, 126.3, 124.4, 123.9, 122.8, 119.5, 118.3, 40.2.

HRMS-MALDI: calculated for $C_{19}H_{15}O$ $[M-H]^+$: 259.1117; found: 259.1111.

7-(2-(Benzyloxy)phenyl)cyclohepta-1,3,5-triene (10i)



n-BuLi (2.0 M in hexanes, 5.5 mL, 11 mmol) was added dropwise to the solution of 1-(benzyloxy)-2-iodobenzene[91] (3.1 g, 10 mmol) in 40 mL THF at -78 ºC. After stirring for 0.5 h, tropylium tetrafluoroborate (2.0 g, 11 mmol) was added, and stirred at room temperature overnight (12 h). The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel to give 1.7 g colorless oil in 62% yield.

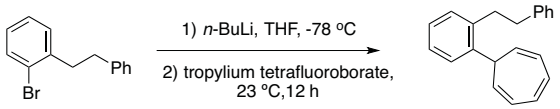
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.25 (m, 7H), 7.06 - 6.99 (m, 2H), 6.75 (dd, *J* = 3.7, 2.6 Hz, 2H), 6.27 (dddd, *J* = 8.9, 3.9, 2.6, 1.4 Hz, 2H), 5.52 (dd, *J* = 8.7, 5.6 Hz, 2H), 5.14 (s, 2H), 3.31 - 3.21 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 137.3, 132.2, 130.8, 128.9, 128.4, 127.8, 127.6, 127.0, 126.7, 124.2, 121.1, 112.6, 70.0, 40.6.

[91] 1-(Benzyloxy)-2-iodobenzene was prepared according to the reported procedure: Cakir, S. P.; Stokes, S.; Sygula, A.; Mead, K. T. *J. Org. Chem.* **2009**, *74*, 7529–7532.

HRMS-APCI: calculated for $C_{20}H_{19}O$ $[M+H]^+$: 275.1430; found: 275.1428.

7-(2-Phenethylphenyl)cyclohepta-1,3,5-triene (10w)



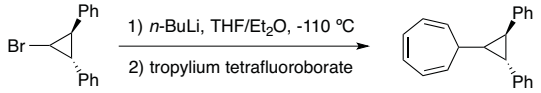
This compound (colorless oil, 1.18 g, yield: 45%) was prepared according to the general procedure from 1-bromo-2-cyclopropylbenzene[92] (2.52 g, 9.6 mmol), *n*-BuLi (2.0 M, 5.3 mL, 10.6 mmol) and tropylium tetrafluoroborate (1.7 g, 9.6 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.7, 1.0 Hz, 1H), 7.32 (td, J = 7.3, 1.8 Hz, 1H), 7.27-7.14 (m, 5H), 7.12-7.05 (m, 2H), 6.78 (dd, J = 3.5, 2.8 Hz, 2H), 6.29-6.26 (m, 2H), 5.37 (dd, J = 8.7, 5.4 Hz, 2H), 3.01 (t, J = 5.4 Hz, 1H), 2.83-2.77 (m, 2H), 2.75- 2.65 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 142.0, 140.0, 131.1, 129.9, 128.5, 128.5, 127.6, 127.1, 127.1, 126.7, 126.1, 124.7, 41.3, 38.2, 36.0.

HRMS-APCI: calculated for $C_{21}H_{21}$ $[M+H]^+$: 273.1643; found: 273.1634.

7-((2*R,3*R**)-2,3-diphenylcyclopropyl)cyclohepta-1,3,5-triene (10x-*trans*)**



n-BuLi (2.0 M, 3.7 mL, 7.4 mmol) was added dropwise to the solution of ((1*R**,2*R**)-3-bromocyclopropane-1,2-diyl)dibenzene [93] (2 g, 7.3 mmol) in dry THF/Et_2O (10 mL/10 mL) at -110 ºC under argon. The mixture was stirred for 30 min at -110 ºC, and then tropylium tetrafluoroborate (1.43 g, 8.1 mmol) was added in one portion. The cooling bath was removed and the reaction was warmed to room temperature (23 ºC) slowly. The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on basic aluminum with cyclohexane as eluent to give 600 mg (yield 64%) white solid.

M.p.: 72-73 ºC.

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[92] Prepared according to literature: Parham, W. E.; Jones, L. D.; Sayed, Y. A. *J. Org. Chem.* **1976**, *41*, 1184–1186.

[93] Fox, M. A.; Chen, C. C.; Campbell, K. A. *J. Org. Chem.* **1983**, *48*, 321–326.

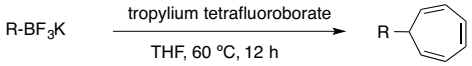
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.12 (m, 10H), 6.58-6.39 (m, 2H), 6.15 (dd, J = 9.4, 4.8 Hz, 1H), 6.03 (dd, J = 9.3, 4.8 Hz, 1H), 5.41 (dd, J = 9.3, 5.4 Hz, 1H), 5.29 (dd, J = 9.3, 5.3 Hz, 1H), 2.64 (dd, J = 9.1, 5.6 Hz, 1H), 2.29 (t, J = 5.4 Hz, 1H), 2.03-1.81 (m, 1H), 1.31-1.17 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 137.9, 130.9, 130.4, 129.1, 128.4, 127.9, 126.3, 126.2, 126.1, 126.0, 125.7, 124.9, 124.4, 38.7, 33.2, 31.8, 27.5.

HRMS-APCI: calculated for $C_{19}H_{18}$ $[M+H]^+$: 285.1643; found 285.1636.

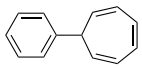
For the synthesis of other cycloheptatrienes, see reference 68.

General procedure from potassium trifluoroborate salts



The 4 mL THF solution of 1 mmol Potassium trifluoroborate salts and 0.5 mmol tropylium tetrafluoroborate was heated at 60 ºC under argon overnight (12 h). The solution was cooled down to room temperature (23 ºC), and passed through a short column of silicon gel. After removing solvent, the crude was purified by chromatography to yield the arylcycloheptatrienes.

7-Phenylcyclohepta-1,3,5-triene (10a)

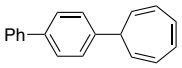


This compound was prepared according to the general procedure from 0.5 mmol (92 mg) potassium phenyltrifluoroborate and 0.25 mmol (45 mg) tropylium tetrafluoroborate, colorless oil 34 mg, yield 81%.

The spectroscopic data match with those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.30 (m, 5H), 6.78 (dd, J = 3.7, 2.7 Hz, 2H), 6.32 - 6.28 (m, 2H), 5.46 (dd, J = 8.7, 5.5 Hz, 2H), 2.76 (t, J = 5.5 Hz, 1H).

4-(Cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (10o)



This compound was prepared according to the general procedure from 1 mmol (260 mg) potassium 4-phenyl-phenyltrifluoroborate and 0.5 mmol (89 mg) tropylium tetrafluoroborate, white solid 99 mg, yield 81%.

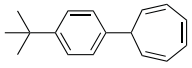
M.p.: 71-73 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 4H), 7.50 - 7.45 (m, 4H), 7.40 - 7.34 (m, 1H), 6.80 (t, *J* = 3.1 Hz, 2H), 6.32 (d, *J* = 8.9 Hz, 2H), 5.50 (dd, *J* = 9.2, 5.6 Hz, 2H), 2.81 (t, *J* = 5.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 140.9, 139.6, 130.9, 128.7, 128.0, 127.4, 127.1, 127.0, 126.1, 124.5, 44.9.

HRMS-APCI: calculated for $C_{19}H_{17}$ $[M+H]^+$: 245.1330; found: 245.1331.

7-(4-(*tert*-Butyl)phenyl)cyclohepta-1,3,5-triene (10p)



This compound was prepared according to the general procedure from 1 mmol (240 mg) potassium 4-(*tert*-butyl)phenyltrifluoroborate and 0.5 mmol (89 mg) tropylium tetrafluoroborate, white crystal 88 mg, yield 79%.

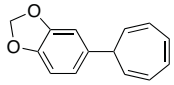
M.p.: 43-46 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.78 (dd, *J* = 3.6, 2.7 Hz, 2H), 6.31 - 6.27 (m, 2H), 5.46 (dd, *J* = 8.8, 5.6 Hz, 2H), 2.72 (t, *J* = 5.6 Hz, 1H), 1.38 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 140.8, 130.9, 127.2, 126.4, 125.5, 124.2, 44.8, 34.4, 31.4.

HRMS-APCI: calculated for $C_{17}H_{21}$ $[M+H]^+$: 225.1643; found: 225.1647.

5-(Cyclohepta-2,4,6-trien-1-yl)benzo[*d*][1,3]dioxole (10q)



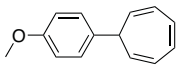
This compound was prepared according to the general procedure from 1 mmol (228 mg) potassium 3,4-(methylenedioxy)phenyltrifluoroborate and 0.5 mmol (89 mg) tropylium tetrafluoroborate, yellow oil 100 mg, yield 94%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 - 6.81 (m, 3H), 6.76 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.29 - 6.25 (m, 2H), 5.99 (s, 2H), 5.41 (dd, *J* = 8.7, 5.6 Hz, 2H), 2.68 (tt, *J* = 5.6, 1.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.1, 137.9, 130.9, 126.4, 124.3, 120.4, 108.3, 108.0, 100.9, 45.0.

HRMS-APCI: calculated for $C_{14}H_{12}O_2$ $[M]^+$: 212.0837; found: 212.0827.

7-(4-Methoxyphenyl)cyclohepta-1,3,5-triene (10e)

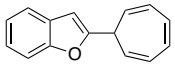


This compound was prepared according to the general procedure from 1 mmol (214 mg) potassium 4-methoxylphenyltrifluoroborate and 0.5 mmol (89 mg) tropylium tetrafluoroborate, colorless oil 84 mg, yield 85%.

The spectroscopic data match with those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.77 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.29-6-26 (m, 2H), 5.43 (dd, *J* = 8.7, 5.6 Hz, 2H), 3.85 (s, 3H), 2.70 (t, *J* = 5.6 Hz, 1H).

2-(Cyclohepta-2,4,6-trien-1-yl)benzofuran (10r)



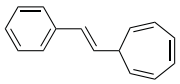
This compound was prepared according to the general procedure from 1 mmol (224 mg) potassium 2-benzofuranyltrifluoroborate and 0.5 mmol (89 mg) tropylium tetrafluoroborate, colorless oil 83 mg, yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.32 - 7.22 (m, 2H), 6.79 (dd, *J* = 3.6, 2.7 Hz, 2H), 6.66 (s, 1H), 6.38 - 6.34 (m, 2H), 5.62 (dd, *J* = 9.2, 5.6 Hz, 2H), 3.12 - 3.09 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 154.8, 131.2, 128.6, 125.3, 123.6, 122.6, 122.2, 120.6, 111.0, 102.0, 39.4.

HRMS-APCI: calculated for $C_{15}H_{13}O$ $[M+H]^+$: 209.0966; found: 209.0962.

(*E*)-7-styrylcyclohepta-1,3,5-triene (10n)

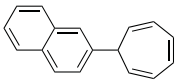


This compound was prepared according to the general procedure from 0.5 mmol (105 mg) potassium *trans*-styryltrifluoroborate and 0.25 mmol (45 mg) tropylium tetrafluoroborate, yellow oil 39 mg, yield 80%.

The spectroscopic data match with those reported in the literature.[6]

1H NMR (400 MHz, $CDCl_3$) *δ* 7.40 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.70 (dd, *J* = 3.5, 2.8 Hz, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.28-6.22 (m, 2H), 5.34 (dd, *J* = 8.8, 5.7 Hz, 2H), 2.48-2.40 (m, 1H).

2-(Cyclohepta-2,4,6-trien-1-yl)naphthalene (10k)

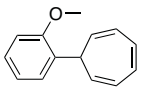


This compound was prepared according to the general procedure from 0.5 mmol (117 mg) potassium 2-naphthalenetrifluoroborate and 0.25 mmol (45 mg) tropylium tetrafluoroborate, white solid 40 mg, yield 74%.

The spectroscopic data match with those reported in the literature.[6]

1H NMR (400 MHz, $CDCl_3$) δ 8.14-7.68 (m, 4H), 7.60-7.40 (m, 3H), 6.93-6.69 (m, 2H), 6.47-6.14 (m, 2H), 5.54 (dd, J = 8.8, 5.7 Hz, 2H), 2.92 (t, J = 5.3 Hz, 1H).

7-(2-Methoxyphenyl)cyclohepta-1,3,5-triene (10s)



This compound was prepared according to the general procedure from 0.5 mmol (107mg) potassium 2-methoxyphenyltrifluoroborate and 0.25 mmol (45 mg) tropylium tetrafluoroborate, colorless crystal 38 mg, yield 77%.

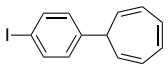
M.p.: 72-75 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.23 (m, 2H), 7.05 - 6.90 (m, 2H), 6.76 – 6.71 (m, 2H), 6.25 (d, J = 9.3Hz, 2H), 5.44 (dd, J = 9.3, 5.6 Hz, 2H), 3.83 (s, 3H), 3.15 (td, J = 5.5, 1.8 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 131.7, 130.7, 128.9, 127.7, 127.1, 124.1, 120.7, 110.9, 55.3, 40.4.

HRMS-APCI: calculated for $C_{14}H_{15}O$ $[M+H]^+$: 199.1123; found: 199.1123.

7-(4-Iodophenyl)cyclohepta-1,3,5-triene (10t)



This compound was prepared according to the general procedure from 0.45 mmol (139 mg) potassium 4-iodophenyltrifluoroborate and 0.225 mmol (40 mg) tropylium tetrafluoroborate, colorless oil 32 mg, yield 49%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 6.76 (dd, J = 3.7, 2.7 Hz, 2H), 6.32 – 6.28 (m, 2H), 5.39 (dd, J = 8.7, 5.6 Hz, 2H), 2.73 (dd, J = 6.4, 4.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.7, 131.0, 129.6, 125.4, 124.8, 91.7, 44.7.

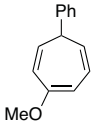
HRMS-MALDI: calculated for $C_{17}H_{21}$ $[M-H]^+$: 292.9827; found: 292.9794.

7-Methyl-7-phenylcyclohepta-1,3,5-triene (10v)

7-Methyl-7-phenylcyclohepta-1,3,5-triene was prepared according to the reported method.[94]

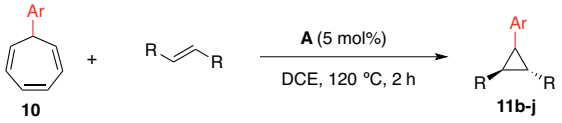
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.21 (m, 2H), 7.18 - 7.07 (m, 3H), 6.39 - 6.37 (m, 2H), 6.35 - 6.28 (m, 2H), 5.50 (d, *J* = 8.8 Hz, 2H), 1.58 (s, 3H).

3-Methoxy-7-phenylcyclohepta-1,3,5-triene (10u)



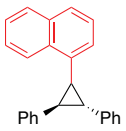
3-Methoxy-7-phenylcyclohepta-1,3,5-triene was prepared according to the reported method.[95]

General procedure for gold catalyzed cyclopropanations



A solution of the arylcycloheptatriene substrate (0.15 mmol), olefin (0.3 mmol) and gold complex **A** (5.5 mg, 5 mol%) in 1,2-dichloroethane (DCE, 0.75 mL) was heated at 120 ºC in a sealed tube until the starting material had been fully consumed (2-3 h). After the reaction mixture had been allowed to cool to room temperature, the solvent was removed *in vacuo* and the crude residue was purified by preparative TLC. The reaction was performed under an air atmosphere with no special precautions taken to exclude water.

1-((2*R,3*R**)-2,3-diphenylcyclopropyl)naphthalene (11b)**



[94] Adam, W.; Adamsky, F.; Klarner, F.-G.; Peters, E.-M.; Peters, K.; Rebollo, H.; Rungeler, W.; Schnering, H. G. *Chem. Ber.* **1983**, *116*, 1848–1859.
[95] Tatsuya, S.; Hirofuni, N.; Tetsuo, N.; Shigenori, K. *Tetrahedron Lett.* **1990**, *31*, 895–898.

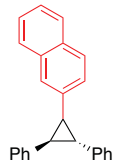
The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (52 mg, 0.24 mmol), (*E*)-stilbene (36 mg, 0.2 mmol) and gold complex **A** (3.7 mg, 2.5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. After the reaction mixture had been allowed to cool to room temperature, the solvent was removed *in vacuo* and the crude residue was purified by preparative TLC to obtain 40 mg yellow oil (yield: 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 - 8.24 (m, 1H), 7.84 - 7.79 (m, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.50 - 7.30 (m, 9H), 7.05 - 6.93 (m, 5H), 3.31 (dd, *J* = 9.3, 6.4 Hz, 1H), 3.13 (t, *J* = 6.0 Hz, 1H), 3.01 (dd, *J* = 9.4, 5.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 138.2, 133.5, 133.4, 133.3, 128.6, 128.3, 127.5, 127.1, 126.9, 126.5, 126.2, 125.7, 125.6, 125.5, 125.0, 124.6, 34.6, 33.0, 30.3.

HRMS-APCI: calculated for $C_{25}H_{21}$ $[M+H]^+$: 321.1643; found: 321.1649.

2-((2*R,3*R**)-2,3-diphenylcyclopropyl)naphthalene (11c)**



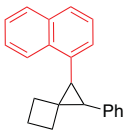
This compound was prepared as single stereoisomer, using gold catalyst **B** according to the general procedure, starting form *trans*-stilbene (1 equiv) and 2-(cyclohepta-2,4,6-trien-1-yl)naphthalene (3 equiv). Colorless oil (44%, 93% brsm).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.76 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 7.3 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.59 (s, 1H), 7.46-7.37 (m, 6H), 7.33-7.29 (m, 1H), 7.20-7.04 (m, 6H), 3.02 (d, *J* = 7.7 Hz, 2H), 2.94 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 142.1, 137.8, 135.6, 133.4, 132.2, 129.1, 128.7, 128.1, 127.7, 127.6, 127.5, 126.6, 126.3, 126.2, 125.9, 125.4, 34.9, 34.8, 31.1.

HRMS-APCI: calculated for $C_{25}H_{21}$ $[M+H]^+$: 321.1643; found: 321.1638.

1-(2-Phenylspiro[2.3]hexan-1-yl)naphthalene (11d)



This compound was prepared as a mixture of diastereoisomers using gold catalyst **A** (5.5 mg, 5 mol%) according to the general procedure, starting form

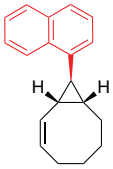
(cyclobutylidenemethyl)benzene[96] (43 mg, 0.3 mmol) and 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (33 mg, 0.15 mmol). Colorless oil (32 mg, yield: 75%, 1.8:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 8.4, 1.1 Hz, *minor*1H), 8.35 - 8.30 (m, *major*1H), 7.95 (dd, J = 8.5, 1.2 Hz, *minor*1H), 7.89 - 7.85 (m, *major*1H), 7.80 (dd, J = 8.3, 1.2 Hz, *minor*1H), 7.75 (dd, J = 8.3, 1.2 Hz, *major*1H), 7.67 (ddd, J = 8.4, 6.8, 1.4 Hz, *minor*1H), 7.59 (ddd, J = 8.1, 6.8, 1.3 Hz, *minor*1H), 7.52 - 6.70 (m, *major*9H + *minor*7H), 2.82 - 2.74 (m, *major*1H + *minor*1H), 2.65 - 1.95 (m, *major*7H + *minor*6H), 1.75 - 1.68 (m, *minor*1H).

^{13}C NMR (101 MHz, $CDCl_3$, *mixed signals*) δ 140.4, 138.8, 136.0, 134.0, 133.9, 133.8, 133.7, 132.5, 128.9, 128.8, 128.6, 128.4, 128.3, 127.3, 127.2, 126.8, 126.8, 126.0, 125.7, 125.6, 125.5, 125.5, 125.4, 125.0, 125.0, 125.0, 124.8, 124.4, 35.3, 34.0, 33.9, 33.7, 32.9, 32.7, 31.9, 27.3, 27.1, 24.4, 17.0, 16.7.

HRMS-APCI: calculated for $C_{22}H_{21}$ $[M+H]^+$: 285.1638; found: 285.1631.

1-(Bicyclo[6.1.0]non-2-en-9-yl)naphthalene (11e)



This compound was prepared as a mixture of diastereoisomers using gold catalyst **A** (3.7 mg, 5 mol%) according to the general procedure, starting form 1,3-cyclooctadiene (32 mg, 0.3 mmol) and 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol). Colorless oil (14 mg, yield: 57%, 2.5:1 dr).

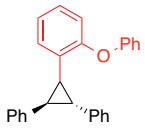
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.3 Hz, *major*1H), 8.27 (d, J = 8.3 Hz, *minor*1H), 7.89 - 7.85 (m, *major*1H + *minor*1H), 7.76 - 7.70 (m, *major*1H + *minor*1H), 7.58 - 7.30 (m, *major*4H + *minor*4H), 5.90 - 5.77 (m, *minor*2H), 5.59 - 5.51 (m, *major*1H), 5.19 (dd, J = 11.2, 1.8 Hz, *major*1H), 2.52 - 1.33 (m, *major*7H + *minor*8H), 1.19 (dtd, J = 13.7, 12.0, 3.4 Hz, *major*1H).

^{13}C NMR (101 MHz, $CDCl_3$, *mixed signals*) δ 139.3, 135.7, 135.1, 134.5, 134.3, 133.6, 133.4, 128.5, 128.4, 127.3, 126.6, 126.3, 125.8, 125.7, 125.6, 125.5, 125.5, 125.4, 125.2, 125.2, 124.6, 123.4, 123.3, 31.5, 31.0, 29.9, 29.7, 28.8, 27.9, 26.6, 25.8, 25.1, 24.8, 24.0, 23.3, 20.9, 19.5.

HRMS-APCI: calculated for $C_{19}H_{21}$ $[M+H]^+$: 249.1638; found: 249.1634.

((1*R*,2*R*)-3-(2-phenoxyphenyl)cyclopropane-1,2-diyl)dibenzene (11f)

[96] Mubarak, M. S.; Jennermann, T. B.; Ischay, M. A.; Peters, D. G. *Eur. J. Org. Chem.* **2007**, 5346–5352.



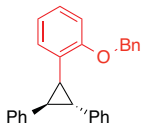
A solution of 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene (26 mg, 0.1 mmol), (*E*)-1,2-diphenylethene (36 mg, 0.2 mmol) and gold complex **A** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. After cooling to room temperature, the solvent was removed *in vacuo* and the residue was purified by preparative TLC (eluent: cyclohexane) to give 29.2 mg the title compound in 81% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 6.96 (m, 13H), 7.05 - 6.96 (m, 3H), 6.76 - 6.66 (m, 3H), 3.02 - 2.95 (m, 2H), 2.81 (dd, *J* = 8.6, 6.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 156.4, 141.8, 138.2, 130.3, 129.5, 128.5, 128.4, 128.1, 127.7, 127.5, 126.6, 126.1, 125.7, 122.8, 122.8, 118.5, 118.2, 34.3, 30.3, 29.6.

HRMS-APCI: calculated for $C_{27}H_{23}O$ $[M+H]^+$: 363.1743; found: 363.1740.

((1*R,2*R**)-3-(2-(benzyloxy)phenyl)cyclopropane-1,2-diyl)dibenzene (11g)**



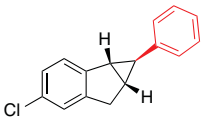
A solution of 7-(2-(benzyloxy)phenyl)cyclohepta-1,3,5-triene (27 mg, 0.1 mmol), (*E*)-1,2-diphenylethene (36 mg, 0.2 mmol) and gold complex **A** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. After cooling to room temperature, the solvent was removed *in vacuo* and the residue was purified by preparative TLC (eluent: cyclohexane) to give 28.4 mg the title compound in 75% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 - 7.26 (m, 10H), 7.20 - 7.10 (m, 5H), 7.00 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.88 (td, *J* = 7.5, 1.1 Hz, 1H), 6.81 - 6.77 (m, 1H), 5.06 (d, *J* = 12.2 Hz, 1H), 4.88 (d, *J* = 12.2 Hz, 1H), 3.06 (dd, *J* = 9.6, 6.4 Hz, 1H), 2.95 (t, *J* = 6.0 Hz, 1H), 2.83 (dd, *J* = 9.6, 5.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 142.2, 138.7, 137.5, 129.9, 128.5, 128.4, 128.0, 127.6, 127.6, 127.5, 127.0, 126.7, 126.1, 126.0, 125.6, 120.3, 111.6, 69.8, 34.2, 30.6, 29.7.

HRMS-APCI: calculated for $C_{28}H_{25}O$ $[M+H]^+$: 377.1900; found: 377.1890.

(1*R,1a*R**,6a*R**)-4-chloro-1-phenyl-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene (11h).**



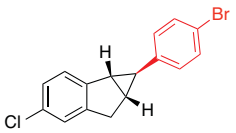
This compound was prepared using gold catalyst **A** (3.7 mg, 5 mol%) according to the general procedure, starting from 6-chloro-1*H*-indene (30 mg, 0.2 mmol)[97] and 7-phenylcyclohepta-1,3,5-triene (17 mg, 0.1 mmol). Colorless oil (20 mg, yield: 82%, 15.5:1 dr). Signals for the *exo* stereoisomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.06 -7.02 (m, 1H), 6.80 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.76 (s, 1H), 3.09 (dd, *J* = 17.6, 7.0 Hz, 1H), 2.87 (ddd, *J* = 8.1, 6.2, 1.5 Hz, 1H), 2.62 (d, *J* = 17.6 Hz, 1H), 2.37 (t, *J* = 8.2 Hz, 1H), 2.31-2.23 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 141.4, 134.4, 132.8, 131.4, 131.1, 126.4, 125.5, 124.8, 120.0, 31.9, 29.5, 26.7, 22.8.

HRMS-APCI: calcd for $C_{16}H_{13}Cl$ $[M+H]^+$: 240.0705; found 240.0706.

(1*R,1a*R**,6a*R**)-1-(4-bromophenyl)-4-chloro-1,1a,6,6a-tetrahydrocyclopropa[*a*]in- dene (11i).**



This compound was prepared using gold catalyst **A** (3.7 mg, 5 mol%) according to the general procedure, starting from 6-chloro-1*H*-indene (30 mg, 0.2 mmol) and 7-(4-bromophenyl)cyclohepta-1,3,5-triene (25 mg, 0.1 mmol). White solid (15 mg, yield: 47%, 20:1 dr). Signals for *exo* stereoisomer.

M.p.: 139-141 ºC

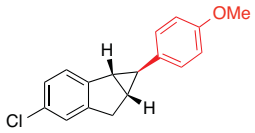
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.06 -7.02 (m, 1H), 6.80 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.76 (s, 1H), 3.09 (dd, *J* = 17.6, 7.0 Hz, 1H), 2.87 (ddd, *J* = 8.1, 6.2, 1.5 Hz, 1H), 2.62 (d, *J* = 17.6 Hz, 1H), 2.37 (t, *J* = 8.2 Hz, 1H), 2.31-2.23 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 141.4, 134.4, 132.8, 131.4, 131.1, 126.4, 125.5, 124.8, 120.0, 31.9, 29.5, 26.7, 22.8.

[97] Lindsay, D. G.; McGreevy, B. J.; Reese, C. B. *Chem. Comm.* **1965**, *16*, 379–380.

HRMS-APCI: calcd for $C_{16}H_{12}ClBr$ $[M+H]^+$: 317.9811; found 317.9812.

(1*R,1a*R**,6a*R**)-4-chloro-1-(4-methoxyphenyl)-1,1a,6,6a-tetrahydrocyclopropa[*a*]- indene (11j).**



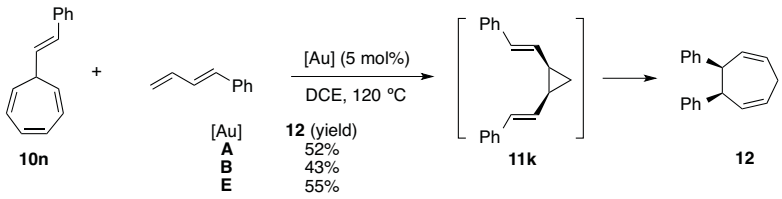
This compound was prepared as mixture of stereoisomers using gold catalyst **A** (3.7 mg, 5 mol%) according to the general procedure, starting from 6-chloro-1*H*-indene (30 mg, 0.2 mmol) and 7-(4-methoxyphenyl)cyclohepta-1,3,5-triene (20 mg, 0.1 mmol). Colorless oil (21 mg, yield: 75%, 1.2:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 1H, *exo*), 7.20 (d, *J* = 8.0 Hz, 1H, *syn*), 7.15 (s, 1H, *syn*), 7.09 (dd, *J* = 8.0, 2.0 Hz, 1H, *syn*), 7.02 (dd, *J* = 8.0, 1.8 Hz, 1H, *exo*), 6.96 (d, *J* = 8.7 Hz, 2H, *exo*), 6.89-6.80 (m, 4H, *syn*), 6.73 (s, 1H, *exo*), 6.60 (d, *J* = 8.7 Hz, 2H, *exo*), 3.78 (s, 3H, *syn*), 3.68 (s, 3H, *exo*), 3.30 (dd, *J* = 17.5, 6.7 Hz, 1H, *syn*), 3.14-2.99 (m, 1H *cis* + 1H *exo*), 2.85-2.80 (m, 1H, *exo*), 2.65 (d, *J* = 17.5 Hz, 1H, *exo*), 2.59-2.51 (m, 1H, *cis*), 2.37 (t, *J* = 8.3 Hz, 1H, *exo*), 2.24-2.20 (m, 1H, *exo*), 2.17- 2.02 (m, 1H, *syn*), 1.45 (t, *J* = 3.2 Hz, 1H, *syn*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 157.7, 145.5, 144.7, 144.5, 141.9, 134.0, 132.0, 131.4, 131.0, 127.2, 126.5, 126.4, 126.1, 125.7, 125.4, 124.6, 124.5, 114.1, 113.4, 55.5, 55.2, 36.3, 35.3, 33.9, 31.9, 29.6, 27.5, 26.5, 22.8.

HRMS-APCI: calcd for $C_{17}H_{16}OCl$ $[M+H]^+$: 271.0890; found 271.0887.

(6*R,7*S**)-6,7-diphenylcyclohepta-1,4-diene (12)**



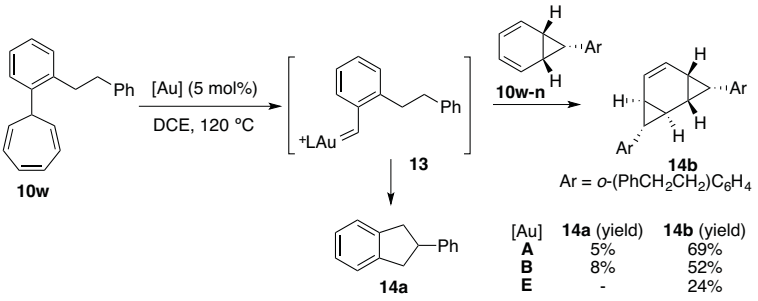
This compound (27 mg, yield: 55%) was synthesized following the general procedure, starting from (*E*)-buta-1,3-dien-1-ylbenzene (52 mg, 0.4 mmol) and **10n** (40 mg, 0.2 mmol) (colorless oil, yield: [Au]=**A**, 52%; [Au]=**B**, 43%; [Au]=**E**, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.08 (m, 6H), 6.93-6.74 (m, 4H), 5.91 (t, *J* = 9.7 Hz, 2H), 5.76 (ddd, *J* = 10.1, 6.6, 3.0 Hz, 2H), 4.07 (br, 2H), 3.43-3.28 (m, 1H), 2.79 (dt, *J* = 19.8, 7.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 133.1, 129.6, 128.0, 127.3, 126.3, 50.1, 27.9.

HRMS-APCI: calcd for $C_{19}H_{18}$ $[M+H]^+$: 246.1409; found 246.1416.

(1*R,2*R**,3*S**,4*R**,7*R**)-3,8-bis(2-phenethylphenyl)tricyclo[5.1.0.02,4]oct-5-ene (14b)**



This compound (16 mg, yield: 69%) was synthesized as a colorless oil following the general procedure starting from **10w** (27 mg, 0.1 mmol) and gold catalyst **A** (3.7 mg, 5 mol%). Reaction with catalyst **B** gave **14b** in 52% yield. Reaction with catalyst **E** gave exclusively **14b** in 24% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.33-7.06 (m, 16H), 6.89-6.82 (m, 1H), 5.66 (dd, *J* = 9.8, 4.6 Hz, 1H), 5.55 (dd, *J* = 9.8, 4.7 Hz, 1H), 3.11 - 3.02 (m, 4H), 2.98-2.86 (m, 4H), 2.27 (t, *J* = 8.6 Hz, 1H), 2.14 (t, *J* = 4.5 Hz, 1H), 2.10 (d, *J* = 8.7 Hz, 1H), 1.80 (dd, *J* = 8.7, 4.9 Hz, 1H), 1.62 (td, *J* = 8.7, 4.7 Hz, 1H), 1.01 (dt, *J* = 8.9, 4.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 142.4, 142.3, 140.7, 139.8, 135.4, 131.8, 129.2, 128.6, 128.6, 128.6, 128.6, 127.1, 126.5, 126.4, 126.1, 126.0, 125.2, 125.0, 121.1, 37.4, 37.1, 35.8, 35.3, 33.9, 30.1, 23.2, 23.1, 20.3, 16.0.

HRMS-APCI: calcd for $C_{36}H_{35}$ $[M+H]^+$: 467.2739; found 467.2757.

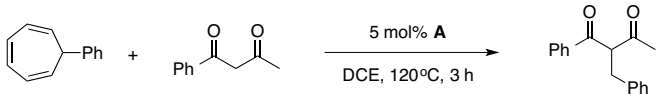
The spectroscopic data of 2-phenyl-2,3-dihydro-1*H*-indene (**14a**) match with those reported in the literature.[98]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 4H), 7.25-7.16 (m, 5H), 3.72 (quint, *J* = 8.5 Hz, 1H), 3.35 (dd, *J* = 15.4, 8.4 Hz, 2H), 3.09 (dd, *J* = 15.4, 8.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 143.1, 128.6, 127.2, 126.6, 126.4, 124.5, 45.7, 41.1.

2-Benzyl-1-phenylbutane-1,3-dione (15a)

[98] Kirmse, W.; Konrad, W.; Özkir, I. S. *Tetrahedron* **1997**, *53*, 9935–9964.



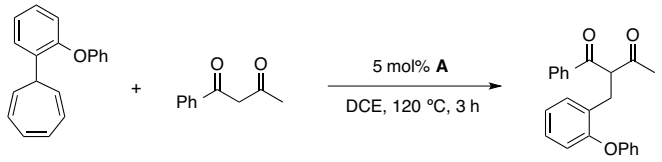
The solution of phenylcycloheptatriene (0.2 mmol, 34 mg), 1-phenylbutane-1,3-dione (0.1 mmol, 16 mg) and gold complex (3.7 mg, 5 mol%) in DCE (0.4 mL) was heated at 120 ºC in a sealed tube for 3 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC directly to give 21 mg yellow oil in 82% yield.

The spectroscopic data match with those reported in the literature.[99]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (dd, *J* = 8.4, 7.3 Hz, 2H), 7.29 - 7.25 (m, 2H), 7.23 - 7.16 (m, 3H), 4.82 (t, *J* = 7.2 Hz, 1H), 3.37 (dd, *J* = 14.1, 7.2 Hz, 1H), 3.32 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.2, 195.7, 138.3, 136.4, 133.7, 128.8, 128.8, 128.7, 128.6, 126.6, 64.8, 34.7, 28.6.

2-(2-Phenoxybenzyl)-1-phenylbutane-1,3-dione (15b)



The solution of 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene (0.3 mmol, 78 mg), 1-phenylbutane-1,3-dione (0.15 mmol, 24 mg) and gold complex **A** (5.5 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 3 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC directly to give 46 mg yellow oil in 89% yield.

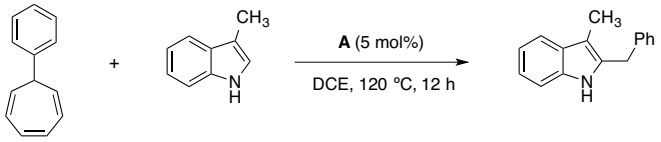
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 - 7.30 (m, 5H), 7.21 - 7.09 (m, 2H), 7.07 - 6.96 (m, 3H), 6.86 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.99 (t, *J* = 7.1 Hz, 1H), 3.45 - 3.27 (m, 2H), 2.14 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 203.2, 196.1, 157.2, 154.8, 136.3, 133.6, 132.0, 129.9, 129.5, 128.8, 128.7, 128.3, 123.8, 123.2, 118.9, 118.1, 62.5, 30.1, 28.9.

HRMS-ESI: calculated for $C_{23}H_{20}NaO_3$ $[M+Na]^+$: 367.1305; found: 367.1314.

2-Benzyl-3-methyl-1*H*-indole (16a)

[99] Rueping, M.; Nachtsheim, B. J. and Kuenkel, A. *Org. Lett.*, **2007**, *9*, 825–828.



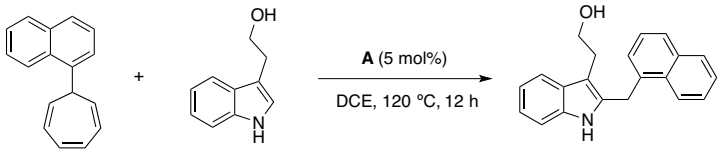
The solution of phenylcycloheptatriene (0.3 mmol, 50 mg), 3-methyl-1*H*-indole (0.2 mmol, 26 mg) and gold complex **A** (7.5 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 12 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC directly to give 7 mg yellow oil in 15% yield.

The spectroscopic data match with those reported in the literature.[100]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 - 7.53 (m, 2H), 7.33 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.28 - 7.22 (m, 4H), 7.15 - 7.12 (m, 2H), 4.14 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 135.5, 133.0, 129.3, 128.7, 128.7, 126.6, 121.3, 119.1, 118.3, 110.3, 108.0, 32.3, 8.6.

2-(2-(Naphthalen-1-ylmethyl)-1*H*-indol-3-yl)ethan-1-ol (16b)



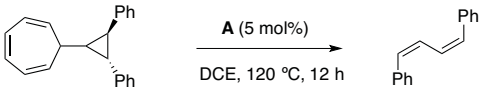
The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (0.3 mmol, 65 mg), 2-(1*H*-indol-3-yl)ethan-1-ol (0.2 mmol, 32 mg) and gold complex **A** (7.5 mg, 5 mol%) in DCE (1 mL) was heated at 120 ºC in a sealed tube for 12 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC directly to give 25 mg colorless oil in 42% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 - 8.03 (m, 1H), 7.95 - 7.91 (m, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.66 - 7.61 (m, 2H), 7.57 - 7.49 (m, 2H), 7.45 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.33 - 7.30 (m, 1H), 7.21 - 7.11 (m, 3H), 4.60 (s, 2H), 3.97 (t, *J* = 6.5 Hz, 2H), 3.18 (t, *J* = 6.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 134.4, 134.2, 134.0, 132.0, 128.8, 128.6, 127.9, 126.9, 126.6, 126.0, 125.7, 123.6, 121.5, 119.5, 118.3, 110.7, 108.1, 62.9, 29.9, 28.0.

(1*Z*,3*Z*)-1,4-diphenylbuta-1,3-diene (*Z*,*Z*-17)

[100] Baccolini, G.; Bartoli, G.; Marotta, E.; Todesco, P. E. *J. Chem. Soc. Perkin Trans. I* **1983**, 2695–2697.



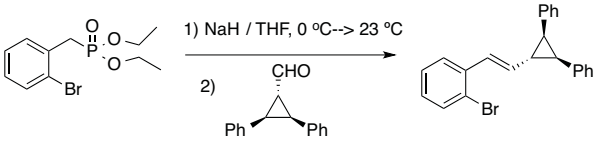
The solution of 7-((2*R**,3*R**)-2,3-diphenylcyclopropyl)cyclohepta-1,3,5-triene (0.2 mmol, 56 mg) and gold complex **A** (7.4 mg, 5 mol%) in DCE (2 mL) was heated at 120 ºC in a sealed tube for 12 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC carefully to give 25 mg white solid in 59% yield.

The spectroscopic data match with those reported in the literature.[101]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.33 (m, 8H), 7.28 (t, J = 7.2 Hz, 2H), 6.77-6.68 (m, 2H), 6.63-6.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 132.2, 129.3, 128.4, 127.4, 126.7.

(((*E*)-2-bromostyryl)cyclopropane-1,2-diyl)dibenzene



To a suspension of NaH (60% in oil, 99 mg, 2.47 mmol) in THF (4 mL) at 0 ºC was slowly added diethyl 2-bromobenzylphosphonate (759 mg, 2.47 mmol). The resulting suspension was stirred for 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC again, and then a 1 mL THF solution of trans-2,trans-3-diphenylcyclopropanecarboxaldehyde[102] (500 mg, 2.25 mmol) was added dropwise and slowly warmed to room temperature. After stirring for 12 h, the reaction was quenched with ice water and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine and dried over $MgSO_4$. After concentration *in vacuo*, the residue was purified by silica gel flash column chromatography with cyclohexane as eluent to give 710 mg colorless solid in 84% yield.

M.p.: 114-116 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.1, 1.3 Hz, 1H), 7.56 (dd, J = 7.9, 1.7 Hz, 1H), 7.29 (dd, J = 7.7 Hz, 1H), 7.20 - 7.08 (m, 7H), 7.05 - 6.99 (m, 5H), 6.15 (dd, J = 15.6, 8.3 Hz, 1H), 2.72 (d, J = 5.6 Hz, 2H), 2.61 - 2.56 (m, 1H).

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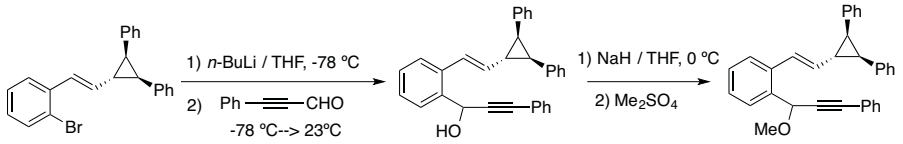
[101] Yang, L. Y.; Liu, R. S. H.; Boarman, K. L.; Wendt, N. L.; Liu, J. *J Am. Chem. Soc*. **2005**, *127*, 2404–2405.
[102] Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7512–7519.

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 137.1, 135.3, 132.9, 128.9, 128.2, 127.8, 127.5, 127.4, 126.5, 126.0, 123.1, 33.4, 30.0.

HRMS-APCI: calculated for $C_{23}H_{20}Br$ $[M+H]^+$: 375.0743; found: 375.0740.

((1*R,2*S**,3*S**)-3-((*E*)-2-(1-methoxy-3-phenylprop-2-yn-1-yl)styryl)cyclopropane-1,2-diyl)dibenzene (20)**



n-BuLi (2.5 M in hexanes, 0.23 mL, 0.59 mmol) was added dropwise to the solution of (((*E*)-2-bromostyryl)cyclopropane-1,2-diyl)dibenzene (200 mg, 0.53 mmol) in 2 mL dry THF at -78 ºC under argon. The mixture was stirred for 10 min at -78 ºC, and then 3-phenylpropiolaldehyde (83 mg, 0.64 mmol) was added slowly. After 20 min, the reaction was warmed to room temperature (23 ºC) and quenched with water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The residue was passed through a short pad of silicon gel to give the crude alcohol.

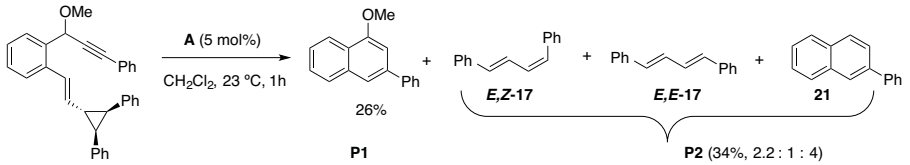
The alcohol obtained from last step was dissolved in 2 mL THF and added to the solution of NaH (23 mg, 0.59 mmol) in 2 mL THF/1 mL DMF at 0 ºC. After keeping at 0 ºC for 10 min, 0.1 mL Me_2SO_4 was added. The mixture was stirred at 23 ºC for 1 h and quenched with water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by preparative TLC to give the final product (104 mg, colorless oil, yield: 44%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.49 - 7.47 (m, 2H), 7.37 - 7.24 (m, 5H), 7.19 - 7.11 (m, 7H), 7.01 - 6.97 (m, 4H), 6.12 (dd, *J* = 15.6, 8.2 Hz, 1H), 5.53 (s, 1H), 3.55 (s, 3H), 2.73 - 2.68 (m, 2H), 2.65 - 2.55 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.3, 136.6, 135.0, 134.7, 131.7, 128.9, 128.6, 128.4, 128.2, 128.1, 127.8, 127.0, 126.3, 125.9, 125.8, 122.6, 88.0, 86.7, 71.7, 56.1, 33.4, 30.1.

HRMS-APCI calculated for $C_{33}H_{29}O$ $[M+H]^+$: 441.2213; found: 441.2207.

***E*, *Z*-17 and *E*, *E*-17**



The solution of **20** (0.1 mmol, 44 mg) and gold complex (3.7 mg, 5 mol%) in CH_2Cl_2 (1 mL) was stirred at 23 ºC in for 1 h. The reaction mixture was purified by preparative TLC carefully to give 6 mg **P1** white solid in 26% yield and 7 mg **P2** as a mixture (2.2 : 1 : 4) in 34% yield.

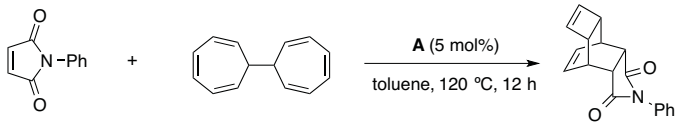
The spectroscopic data of **P1** match with those reported in the literature.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.77 - 7.73 (m, 2H), 7.66 (s, 1H), 7.56 - 7.50 (m, 4H), 7.44 - 7.39 (m, 1H), 7.10 (d, *J* = 1.5 Hz, 1H), 4.11 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 141.6, 138.9, 134.6, 128.8, 127.7, 127.4, 127.3, 126.8, 125.2, 124.8, 121.9, 118.4, 103.8, 55.6.

The spectroscopic data of **P2** match with those reported in the literature.[103]

(3a*R*,4*R*,4a*R*,6a*S*,7*S*,7a*S*)-2-phenyl-3a,4,4a,6a,7,7a-hexahydro-1*H*-4,7-ethenocyclobuta[*f*]isoindole-1,3(2*H*)-dione (32)



The solution of N-phenylmaleimide (26 mg, 0.15 mmol), [1,1'-bi(cycloheptane)]-2,2',4,4',6,6'-hexaene[66b] (55 mg, 0.3 mmol) and gold complex **A** (5.5 mg, 5 mol%) in toluene (0.5 mL) was heated at 120 ºC in a sealed tube for 12 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC to give 10 mg white solid in 24% yield.

The spectroscopic data match with those reported in the literature.[104]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.41 - 7.36 (m, 1H), 7.24 - 7.19 (m, 2H), 6.06 - 6.02 (m, 2H), 5.94 (s, 2H), 3.30 (br, 2H), 2.98 (t, *J* = 1.6 Hz, 2H), 2.92 - 2.87 (br, 2H).

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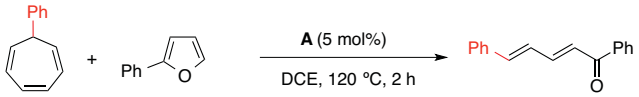
[103] (a) Alacid, E.; Nájera, C. *J. Org. Chem.* **2008**, *73*, 2315–2322. (b) Alacid, E.; Nájera, C. *Adv. Synth. Catal.* **2006**, *348*, 2085–2091. (c) Shen, H. C.; Pal, S.; Lian, J. J.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 15762–15763.

[104] Charvet, R.; Novak, B. M. *Macromolecules* **2001**, *34*, 7680–7685.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 138.0, 132.0, 129.1, 128.6, 128.4, 126.5, 44.1, 43.4, 37.1.

(2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-one (33a)



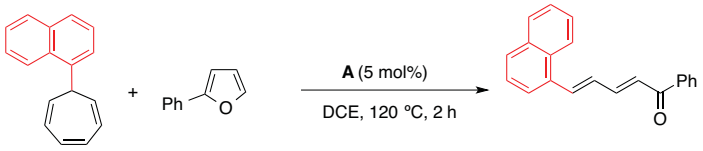
The solution of 7-phenylcyclohepta-1,3,5-triene (0.15 mmol, 25 mg), 2-phenylfuran[105] (0.3 mmol, 43 mg) and gold complex **A** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC to give 18 mg yellow oil in 51% yield.

The spectroscopic data match with those reported in the literature.[106]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.69 - 7.58 (m, 2H), 7.55 - 7.48 (m, 4H), 7.43 - 7.34 (m, 3H), 7.12 (d, *J* = 15.0 Hz, 1H), 7.08 - 6.92 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 144.9, 141.9, 138.2, 136.1, 132.7, 129.2, 128.9, 128.6, 128.4, 127.3, 127.0, 125.5.

(2*E*,4*E*)-5-(naphthalen-1-yl)-1-phenylpenta-2,4-dien-1-one (33b)



The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (0.1 mmol, 22 mg), 2-phenylfuran (0.2 mmol, 29 mg) and gold complex **A** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC to give 20 mg yellow oil in 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.07 - 8.02 (m, 2H), 7.92 - 7.74 (m, 5H), 7.64 - 7.50 (m, 6H), 7.21 - 7.09 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 145.0, 138.6, 138.2, 133.8, 133.3, 132.7, 131.2, 129.6, 129.5, 128.8, 128.6, 128.4, 126.7, 126.1, 125.7, 125.5, 124.2, 123.3.

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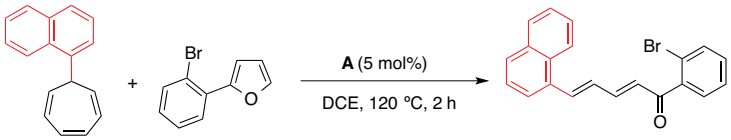
[105] The 2-phenylfuran was prepared according to the reference: Kuhl, N.; Hopkinson, M. N.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 8230–8234

[106] Pinto, D. C. G. A.; Silva, A. M. S.; Lévai, A.; Cavaleiro, J. A. S.; Patonay, T. and Elguero, J. *Eur. J. Org. Chem.,* **2000**, 2593–2599.

HRMS-APCI: calculated for $C_{21}H_{17}O$ $[M+H]^+$: 285.1274; found: 285.1272.

(2*E*,4*E*)-1-(2-bromophenyl)-5-(naphthalen-1-yl)penta-2,4-dien-1-one (33c)



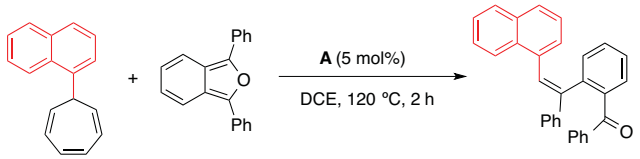
The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (0.1 mmol, 22 mg), 2-(2-bromophenyl)furan[107] (0.2 mmol, 45 mg) and gold complex **A** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC to give 27 mg yellow oil in 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.92 - 7.86 (m, 2H), 7.83 - 7.74 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.60 - 7.48 (m, 3H), 7.47 - 7.44 (m, 2H), 7.40 - 7.32 (m, 2H), 7.10 (ddd, *J* = 15.2, 11.1, 0.7 Hz, 1H), 6.71 (d, *J* = 15.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 146.9, 141.2, 139.1, 133.8, 133.4, 133.0, 131.3, 131.1, 129.9, 129.7, 129.2, 129.1, 128.8, 127.4, 126.7, 126.2, 125.6, 124.4, 123.2, 119.5.

HRMS-APCI: calculated for $C_{21}H_{16}OBr$ $[M+H]^+$: 363.0379; found: 363.0373.

(*Z*)-(2-(2-(naphthalen-1-yl)-1-phenylvinyl)phenyl)(phenyl)methanone (34)



The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (0.3 mmol, 65 mg), 1,3-diphenylisobenzofuran (0.1 mmol, 27 mg) and gold complex **A** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC to give 23 mg yellow solid in 56% yield. (The structure was confirmed by X-ray diffraction.)

M.p.: 141-144 ºC.

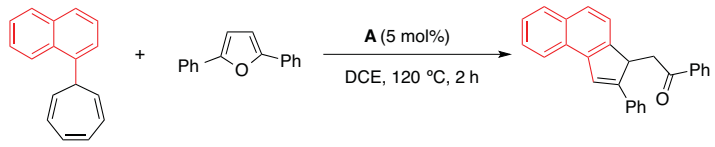
[107] 2-(2-Bromophenyl)furan was prepared according to: Becht, J. A.; Ngouela, S.; Wagner, A.; Mioskowski, C. *Tetrahedron* **2004**, *60*, 6853–6857.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 - 7.89 (m, 1H), 7.67 - 7.62 (m, 1H), 7.59 – 7.56 (m, 1H), 7.47 – 7.44 (m, 3H), 7.39 - 7.15 (m, 14H), 7.04 (dd, *J* = 8.2, 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 143.4, 142.9, 141.1, 139.5, 136.1, 134.9, 133.3, 132.5, 132.4, 132.1, 130.1, 129.7, 129.1, 128.1, 128.1, 128.1, 127.8, 127.5, 127.4, 127.3, 126.8, 126.2, 125.8, 125.5, 125.1, 124.4.

HRMS-APCI: calculated for $C_{31}H_{23}O$ $[M+H]^+$: 411.1743; found: 411.1741.

1-phenyl-2-(2-phenyl-3*H*-cyclopenta[*a*]naphthalen-3-yl)ethan-1-one (35)



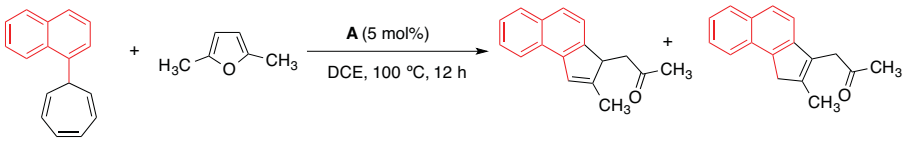
The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (0.1 mmol, 22 mg), 2,5-diphenylfuran (0.2 mmol, 44 mg) and gold complex **A** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 120 ºC in a sealed tube for 2 h. The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC to give 31 mg yellow oil in 88% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.90 (dd, *J* = 8.3 Hz, 1H), 7.80 (s, 1H), 7.69 - 7.64 (m, 3H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.58 - 7.55 (m, 2H), 7.51 - 7.42 (m, 5H), 7.34 (t, *J* = 7.4 Hz, 1H), 5.09 - 4.95 (m, 1H), 3.50 (dd, *J* = 18.1, 2.5 Hz, 1H), 3.10 (dd, *J* = 18.1, 10.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 151.1, 145.9, 139.8, 136.9, 134.9, 133.3, 133.0, 129.0, 128.6, 128.5, 128.2, 127.7, 127.6, 126.9, 125.8, 125.4, 125.3, 124.4, 123.8, 122.4, 45.2, 40.9.

HRMS-ESI: calculated for $C_{27}H_{20}NaO$ $[M+Na]^+$: 383.1406; found: 383.1412.

1-(2-methyl-3*H*-cyclopenta[*a*]naphthalen-3-yl)propan-2-one (36)



The solution of 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (0.1 mmol, 22 mg), 2,5-dimethylfuran (0.5 mmol, 48 mg) and gold complex **A** (3.7 mg, 5 mol%) in DCE (0.5 mL) was heated at 100 ºC in a sealed tube overnight (12 h). The reaction mixture was cooled down to room temperature, after removing the solvent *in vacuo*, purified by preparative TLC to give 13 mg yellow oil in 59% yield. (The two isomers can be separated partially by careful preparative TLC)

^{1}H NMR (400 MHz, $CDCl_3$, major) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.56 - 7.42 (m, 3H), 7.08 (d, *J* = 0.7 Hz, 1H), 4.05 - 3.93 (m, 1H), 2.95 (dd, *J* = 17.2, 5.4 Hz, 1H), 2.68 (dd, *J* = 17.2, 7.9 Hz, 1H), 2.19 (s, 3H), 2.17 (d, *J* = 1.5 Hz, 3H).

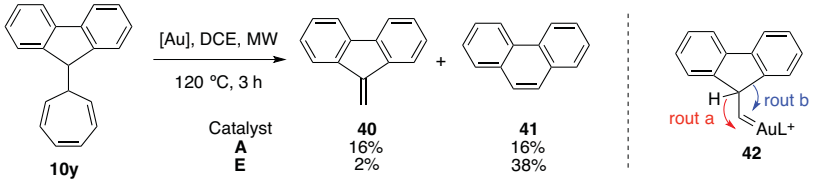
^{13}C NMR (101 MHz, $CDCl_3$, major) δ 207.5, 149.1, 144.1, 140.5, 132.9, 128.3, 127.1, 125.4, 125.0, 124.6, 124.1, 123.9, 121.6, 48.5, 44.2, 30.7, 15.5.

^{1}H NMR (400 MHz, $CDCl_3$, minor) δ 7.91 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.49 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.39 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 3.71 (s, 2H), 3.70 (s, 2H), 2.24 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, minor) δ 206.4, 143.1, 141.4, 138.3, 131.3, 130.8, 129.8, 128.9, 127.2, 126.2, 124.3, 123.3, 118.1, 41.7, 41.6, 29.0, 14.3.

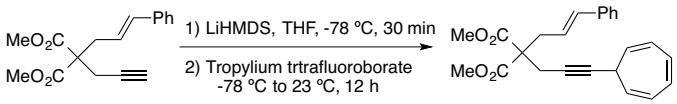
HRMS-ESI: calculated for $C_{17}H_{16}NaO$ $[M+Na]^+$: 259.1093; found: 259.1096.

9-Methylene-9*H*-fluorene (40) and phenanthrene (41)



The solution of 9-(cyclohepta-2,4,6-trien-1-yl)-9*H*-fluorene[108] (26 mg, 0.1 mmol) and gold complex **A** (3.7 mg, 5 mol%) in 1 mL DCE was heated to 120 ºC with microwave for 3 h. After removing the solvent *in vacuo*, purified by preparative TLC directly to give white solid 5.7 mg (32%, 1:1). When catalyst **E** was used, the product is mainly phenanthrene 10.1 mg (38%). **40** (CAS: 4425-82-5) and **41** (CAS: 85-01-8) are known compounds.

Dimethyl 2-cinnamyl-2-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)malonate (45)



[108] Prepared according reported procedure: Minabe, M.; Tomiyama, T.; Nozawa, T.; Noguchi, M.; Nakao, A.; Oba, T.; Kimura, T. *Bull. Chem. Soc. Jpn.*, **2001**, *74*, 1093–1100.

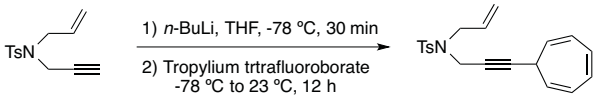
LiHMDS (1.0 M, 5.0 mL, 5.0 mmol) was added dropwise to the solution of dimethyl 2-cinnamyl-2-(prop-2-yn-1-yl)malonate[109] (1.2 g, 4.2 mmol) in 10 mL dry THF at -78 ºC. The mixture was stirred for 30 min at -78 ºC then tropylium tetrafluoroborate (822 mg, 4.62 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at 23 ºC overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with diethyl ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by chromatography using cyclohexane/EtOAc as eluent (30:1) to give the product (555 mg, 35%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 6.67 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.54 (d, *J* = 15.7 Hz, 1H), 6.21 – 6.16 (m, 2H), 6.06 (dt, *J* = 15.5, 7.6 Hz, 1H), 5.31 (dd, *J* = 9.0, 5.4 Hz, 2H), 3.78 (s, 6H), 3.01 (dd, *J* = 7.6, 1.3 Hz, 2H), 2.91 (d, *J* = 2.3 Hz, 2H), 2.52 - 2.49 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 137.0, 134.4, 130.9, 128.4, 127.4, 126.2, 124.6, 123.6, 123.4, 85.1, 74.8, 57.6, 52.7, 36.0, 31.6, 23.2.

HRMS-APCI: calculated for $C_{24}H_{24}NaO_4$ $[M+Na]^+$: 399.1572; found: 399.1567.

N-allyl-N-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (47)



n-BuLi (1.6 M, 1.5 mL, 2.4 mmol) was added dropwise to the solution of *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (500 mg, 2 mmol) in dry THF (20 mL, 0.1 M) at -78 ºC. The mixture was stirred for 30 min at -78 ºC, and then tropylium tetrafluoroborate (356 mg, 2 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at 23 ºC overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with diethyl ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by chromatography using cyclohexane/EtOAc as eluent (20:1) to give the product (378 mg, 56%) as yellow solid.

M.p.: 72.4-73.6 ºC.

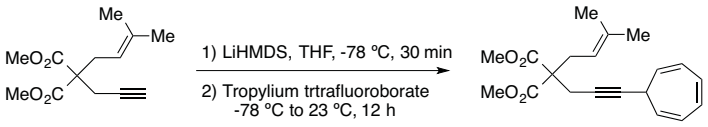
[109] Synthesized according to the procedure reported in: Jiménez-Núñez, E.; Claverie, C. K.; Bour, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem. Int. Ed*. **2008**, *47*, 7892–7895.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.64 (t, *J* = 3.1 Hz, 2H), 6.18 – 6.06 (m, 2H), 5.80 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H), 5.33 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.0, 1.4 Hz, 1H), 4.97 (dd, *J* = 9.0, 5.4 Hz, 2H), 4.15 (d, *J* = 2.1 Hz, 2H), 3.88 (d, *J* = 6.4 Hz, 2H), 2.39 (s, 3H), 2.20 – 2.17 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 136.0, 132.1, 130.9, 129.5, 127.8, 124.6, 122.9, 119.8, 87.3, 72.5, 49.1, 36.2, 31.3, 21.5.

HRMS-APCI: calculated for $C_{20}H_{21}NO_2SNa$ $[M+Na]^+$: 362.1198; found: 362.1191.

Dimethyl 2-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-2-(3-methylbut-2-en-1-yl)malonate (49)



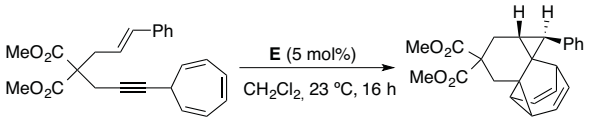
LiHMDS (1.0 M, 5.0 mL, 5.0 mmol) was added dropwise to the solution of dimethyl 2-(3-methylbut-2-en-1-yl)-2-(prop-2-yn-1-yl) malonate (1 g, 4.2 mmol) in dry THF (10 mL) at -78 ºC. The mixture was stirred for 30 min at -78 ºC, and then tropylium tetrafluoroborate (822 mg, 4.62 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at 23 ºC overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with diethyl ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by chromatography using cyclohexane/EtOAc as eluent (30:1) to give the product (539 mg, 39%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 - 6.62 (m, 2H), 6.20 - 6.17 (m, 2H), 5.29 (ddd, *J* = 9.5, 5.5, 0.8 Hz, 2H), 4.95 (dddd, *J* = 7.8, 6.3, 2.9, 1.5 Hz, 1H), 3.76 (s, 6H), 2.86 - 2.79 (m, 4H), 2.45 (ddt, *J* = 6.9, 3.2, 1.6 Hz, 1H), 1.73 (d, *J* = 1.4 Hz, 3H), 1.69 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 136.7, 130.9, 124.6, 123.8, 117.2, 84.6, 75.3, 57.5, 52.6, 31.7, 30.8, 26.1, 22.8, 18.0.

HRMS-APCI: calculated for $C_{20}H_{24}O_4Na$ $[M+Na]^+$: 351.1572; found: 351.1572.

(±)(1*R*,1a*S*,4a*S*,5*S*,5a*R*,6*R*)-dimethyl 5-phenyl-1,4,4a,5,6,8a-hexahydro-1,6-ethenodicyclopropa[d,i]naphthalene-3,3(2H)-dicarboxylate (46)



A solution of gold complex **E** (4 mg, 5 mol%) and dimethyl 2-cinnamyl-2-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)malonate (38 mg, 0.1 mmol) in CH_2Cl_2 (1 mL, 0.1 M) was stirred for 16 h at 23 ºC. The crude reaction mixture was purified by preparative TLC using cyclohexane/EtOAc (10:1) to give the title compound as a colorless solid (19 mg, yield: 49%).

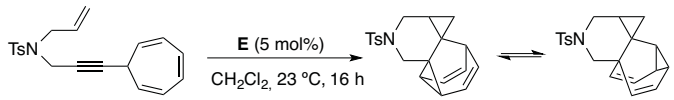
M.p.: 171.6-173.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.12 (m, 5H), 5.77 (ddd, *J* = 9.1, 6.7, 1.3 Hz, 1H), 5.69 (ddd, *J* = 9.1, 6.4, 0.8 Hz, 1H), 5.62 (dd, *J* = 9.0, 6.4 Hz, 1H), 5.33 (ddd, *J* = 9.1, 6.6, 1.3 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 2.99 (ddd, *J* = 14.5, 8.4, 1.9 Hz, 1H), 2.55 (d, *J* = 14.2 Hz, 1H), 2.35 (ddd, *J* = 7.9, 6.5, 1.4 Hz, 1H), 2.11 (ddd, *J* = 7.6, 6.4, 1.3 Hz, 1H), 2.00 (dd, *J* = 14.2, 1.8 Hz, 1H), 1.89 (d, *J* = 5.2 Hz, 1H), 1.80 – 1.67 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 171.4, 139.2, 129.0, 127.6, 125.7, 124.8, 122.5, 122.2, 121.0, 52.7, 52.6, 52.3, 35.6, 35.1, 34.7, 32.4, 31.3, 30.4, 28.2, 25.8, 17.8.

HRMS-APCI: calculated for $C_{24}H_{24}O_4Na$ $[M+Na]^+$: 399.1572; found: 399.1585.

(±)(3a*S*,5a*R*,6a*S*,6b*S*)-2-tosyl-1,2,3,5a,6,6a,7,7a-octahydro-3a,6-ethenodicyclopropa[d,f]isoquinoline (48/48´)



A solution of gold complex **E** (4 mg, 5 mol%) and *N*-allyl-*N*-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (34 mg, 0.1 mmol) in CH_2Cl_2 (1 mL, 0.1 M) was stirred for 16 h at 23 ºC. The crude reaction mixture was purified by preparative TLC using cyclohexane/EtOAc (10:1) to give the title compound as a colorless solid (18 mg, yield: 51%).

M.p.: 101.7-103.2 ºC.

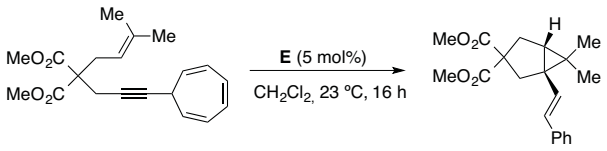
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.71 (td, *J* = 7.7, 3.4 Hz, 2H), 4.51 – 4.42 (m, 2H), 3.69 (dd, *J* = 12.0, 5.3 Hz, 1H), 3.59 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H), 3.51 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 3.29 (d, *J* = 12.0 Hz, 1H), 3.25 (dd, *J* = 12.0, 1.8 Hz, 1H), 2.83 (d, *J* = 11.8 Hz, 1H), 2.45 (s,

3H), 1.66 (t, *J* = 6.8 Hz, 1H), 1.08 – 1.03 (m, 1H), 0.36 (dd, *J* = 8.5, 5.5 Hz, 1H), 0.30 (t, *J* = 5.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 134.6, 129.6, 127.2, 122.0, 121.5, 85.8, 85.2, 71.4, 67.6, 49.0, 43.3, 35.6, 31.6, 21.5, 15.5, 13.9, 11.2.

HRMS-APCI: calculated for $C_{20}H_{21}NO_2SNa$ $[M+Na]^+$: 362.1191; found: 362.1196.

Dimethyl (1*S,5*R**)-6,6-dimethyl-1-((*E*)-styryl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (50)**



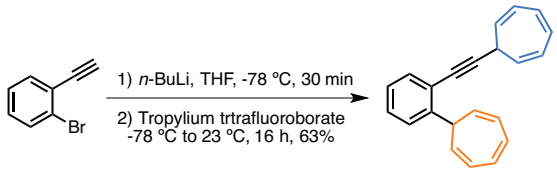
A solution of gold complex **E** (4 mg, 5 mol%) and dimethyl 2-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-2-(3-methylbut-2-en-1-yl)malonate (33 mg, 0.1 mmol) in CH_2Cl_2 (1 mL, 0.1 M) was stirred for 16 h at 23 ºC. The crude reaction mixture was purified by preparative TLC using cyclohexane/EtOAc (10:1) to give the title compound as a colorless oil (21 mg, yield: 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.28 (m, 4H), 7.22 - 7.17 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 2.84 - 2.72 (m, 2H), 2.44 (d, *J* = 14.7 Hz, 1H), 2.03 (dd, *J* = 14.5, 2.7 Hz, 1H), 1.59 - 1.54 (m, 1H), 1.14 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 171.4, 137.9, 132.4, 128.8, 128.5, 126.7, 125.8, 67.8, 52.8, 52.6, 41.3, 38.6, 37.4, 33.8, 31.4, 23.8, 16.7.

HRMS-APCI: calculated for $C_{20}H_{24}O_4Na$ $[M+Na]^+$: 351.1572; found: 351.1557.

7-((2-(cyclohepta-2,4,6-trien-1-yl)phenyl)ethynyl)cyclohepta-1,3,5-triene (56)



To a solution of 1-bromo-2-ethynyl-benzene (289 mg, 1.59 mmol) in THF (6.4 ml) at -78 °C was added *n*-BuLi (2.04 mL, 1.6 M, 3.27 mmol). The mixture was stirred for 30 min, solid tropylium tetrafluoroborate was added (710 mg, 3.99 mmol), and then the mixture was stirred for 16 h during which time it was allowed to gradually warm to room temperature. The crude mixture was diluted with EtOAc (40 mL) then washed with aqueous saturated ammonium chloride solution (40 mL) followed

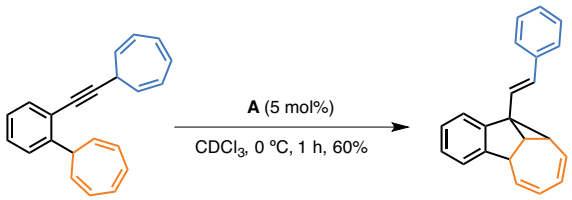
by water (40 mL) then brine (40 mL). The organic layer was dried ($MgSO_4$), concentrated under reduced pressure and the resulting residue purified by column chromatography to give the title compound (283 mg, 63%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.36 (td, *J* = 7.6, 1.3 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.77 – 6.71 (m, 2H), 6.68 – 6.63 (m, 2H), 6.31 – 6.23 (m, 2H), 6.21 – 6.13 (m, 2H), 5.47 (dd, *J* = 9.2, 5.6 Hz, 2H), 5.32 (dd, *J* = 9.1, 5.5 Hz, 2H), 3.36 (t, *J* = 5.7 Hz, 1H), 2.66 (t, *J* = 5.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 132.8, 131.1, 131.0, 128.6, 127.3, 126.6, 124.8, 124.6, 124.6, 123.2, 123.1, 95.9, 79.3, 44.0, 32.5.

HRMS-APCI: calculated for $C_{22}H_{19}$ $[M+H]^+$: 283.1481; found: 283.1479.

(*E*)-4b-styryl-4a,4a^1,4b,8b-tetrahydrobenzo[*a*]cyclopropa[*cd*]azulene (57)



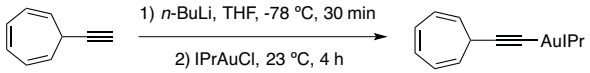
To a solution of 7-((2-(cyclohepta-2,4,6-trien-1-yl)phenyl)ethynyl)cyclohepta-1,3,5-triene (40.0 mg, 142 µmol) chloroform-*d* (0.5 mL) at 0 °C was added gold complex **A** (5.5 mg, 5 mol%) and the resulting solution stirred for 1 h. Solvent was evaporated under reduced pressure and the resulting residue was purified by preparative TLC (eluent: pentane R_f = 0.05) to give the title compound (24 mg, yield: 60%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.35 – 7.28 (m, 3H), 7.24 – 7.19 (m, 2H), 7.16 (td, *J* = 7.4, 1.2 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 16.1 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 6.32 (dd, *J* = 10.7, 8.7 Hz, 1H), 5.85 (dd, *J* = 11.4, 3.8 Hz, 1H), 5.80 (dd, *J* = 10.9, 5.8 Hz, 1H), 5.58 (ddd, *J* = 11.4, 5.8, 0.9 Hz, 1H), 4.26 – 4.21 (m, 1H), 2.46 (t, *J* = 7.1 Hz, 1H), 2.22 (dd, *J* = 7.3, 3.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 143.7, 137.7, 133.2, 133.0, 131.0, 129.4, 128.7, 128.5, 128.0, 127.1, 126.9, 126.4, 125.9, 124.7, 123.6, 44.3, 35.2, 34.9, 34.2.

HRMS-APCI: calculated for $C_{22}H_{19}$ $[M+H]^+$: 283.1481; found: 283.1482.

Digold complex 63

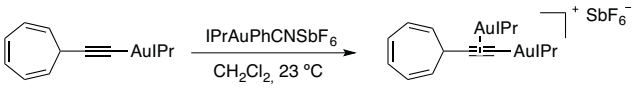


n-BuLi (1.6 M, 0.3 mL, 0.48 mmol) was added dropwise to the solution of 7-ethynylcyclohepta-1,3,5-triene[110] (56 mg, 0.48 mmol) in 5 mL THF at -78 ºC. The mixture was stirred for 10 min at -78 ºC, and then IPrAuCl (200 mg, 0.32 mmol) in 5 mL THF was added. The cooling bath was removed and the reaction was stirred at 23 ºC for 4 h. The solvent was evaporated under reduced pressure. The crude reaction mixture was purified by chromatography on aluminum using cyclohexane/EtOAc as eluent (10:1) to give the product **62** (white crystal, 168 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 - 7.48 (m, 2H), 7.33 - 7.27 (m, 6H), 6.54 - 6.51 (m, 2H), 6.05 - 6.00 (m, 2H), 5.30 (dd, *J* = 8.6, 5.5 Hz, 2H), 2.63 (p, *J* = 6.9 Hz, 4H), 2.43 (tt, *J* = 5.5, 1.5 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 134.4, 130.4, 130.4, 126.5, 124.2, 123.1, 115.9, 105.4, 33.10, 28.80, 24.57, 24.04.

HRMS-ESI: calculated for $C_{36}H_{43}AuN_2Na$ $[M+Na]^+$: 723.2984; found: 723.3015.



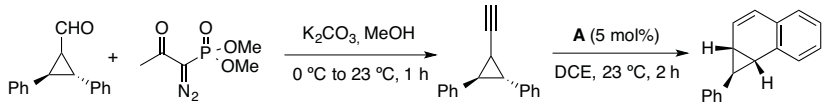
$IPrAuPhCNSbF_6$ (gold complex **E**, 26.4 mg, 28.6 μmol) was added in one portion to 3 mL CH_2Cl_2 solution of (cyclohepta-2,4,6-trien-1-ylethynyl) goldIPr complex (20 mg, 28.6 μmol) at 23 ºC. After stirred for 5 min, the solvent was removed and the solid crude was washed with *c*-hexane and is pure enough for nmr (**63**, 36 mg, yield: 83%). The crystal was obtained by growing in CH_2Cl_2:*c*-hexane=1:2.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 - 7.50 (m, 4H), 7.31 - 7.24 (m, 12H), 6.51 - 6.46 (m, 2H), 5.93 - 5.90 (m, 2H), 4.56 (dd, *J* = 9.0, 5.6 Hz, 2H), 2.46 (hept, *J* = 6.9 Hz, 8H), 2.31 - 2.26 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 24H), 1.10 (d, *J* = 6.9 Hz, 24H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 182.9, 145.5, 133.6, 132.8, 132.2, 130.8, 130.8, 129.1, 124.8, 124.2, 124.1, 122.2, 119.6, 115.0, 33.6, 28.7, 24.6, 23.9.

HRMS-ESI: calculated for $C_{63}H_{79}Au_2N_4^+$ $[M]^+$: 1285,5630; found: 1285,5639.

(1*S,1a*S**,7b*S**)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (65)**



[110] Prepared according to: Hoskinson, R. M. *Aust. J. Chem.* **1970**, *23*, 399–402.

Dimethyl (1-diazo-2-oxopropyl)phosphonate[111] (114 mg, 0.59 mmol) was added to a 2 mL dry MeOH solution of (2*R**,3*R**)-2,3-diphenylcyclopropane-1-carbaldehyde (120 mg, 0.54 mmol) at 0 ºC, then K_2CO_3 (149 mg, 1.08 mmol) was added in one portion. The mixture was stirred at 23 ºC for 1 h, then quenched by water and extracted with ether. After column chromatography on SiO_2, the product **64** was obtained as a white solid (83 mg, yield: 70%).

M.p.: 92-94 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.21 (m, 10H), 2.73 - 2.62 (m, 2H), 2.16 (ddd, *J* = 8.8, 5.5, 2.2 Hz, 1H), 1.97 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 137.0, 128.6, 128.4, 128.0, 126.7, 126.6, 126.3, 82.2, 69.5, 32.8, 32.6, 19.1.

HRMS-APCI: calculated for $C_{17}H_{15}$ $[M+H]^+$: 219.1168; found: 219.1166.

To a solution of ((1*S**,2*S**)-3-ethynylcyclopropane-1,2-diyl)dibenzene (22 mg, 0.1 mmol) in DCE (1 mL) at 23 °C was added gold complex **A** (3.7 mg, 5 mol%) and the resulting solution stirred for 2 h. Solvent was evaporated under reduced pressure and the resulting residue was purified by preparative TLC to give the title compound **65** (20 mg, yield: 91%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.32 (m, 3H), 7.26 - 7.16 (m, 4H), 7.08 (dd, *J* = 8.3, 1.4 Hz, 2H), 6.47 - 6.35 (m, 2H), 2.82 (dd, *J* = 7.9, 4.5 Hz, 1H), 2.41 (dtd, *J* = 8.0, 4.4, 1.0 Hz, 1H), 1.30 (t, *J* = 4.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 134.4, 130.6, 128.5, 128.2, 127.8, 127.8, 127.4, 126.2, 125.6, 125.3, 124.3, 32.4, 29.2, 26.9.

HRMS-APCI: calculated for $C_{17}H_{15}$ $[M+H]^+$: 219.1168; found: 219.1174.

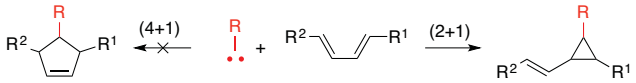
[111] Known: Rauhut, C. B.; Cervino C.; Krasovskiy, A.; Knochel, P. *Synlett.* **2009**, 67–70.

Chapter 2. (4+1) Cycloaddition of methylenecyclopropanes or cyclobutenes with gold(I) carbenes

Background

From both synthetic applications and mechanistic understanding points of view, much attention has been focused on the addition reaction between carbenes and alkenes to form cyclopropanes.[12]

On the other hand, there are very few reported analogous (4+1)[112] cycloadditions due to the high propensity of carbenes to cyclopropanate 1,3-dienes (Scheme 2-1).[113] Of the few (4+1) cycloadditions that have been successfully achieved, most involve the reactions of chromium aminocarbenes[114] and dialkoxycarbenes.[115] Several representative reactions are discussed in the following paragraph.



Scheme 2- 1

Fischer alkoxy(alkenyl)carbene complexes reacted with electronically neutral 1,3-dienes to give a mixture of (3+2) and (4+1) cycloadducts (Scheme 2-2).[114c,d] Interestingly, the solvent has a strong influence on the selectivity of this reaction. When toluene was used, (3+2) products were obtained exclusively with excellent yields. Whereas heating the reaction in THF at 120 ºC in a sealed flask afforded

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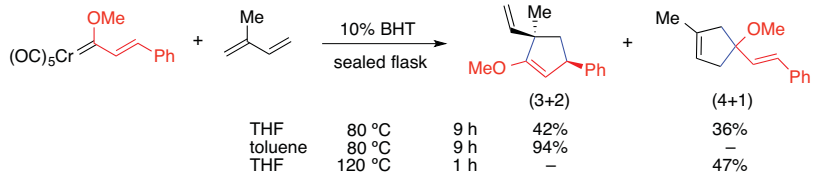
[112] According to the IUPAC, two different notations can be used to describe cycloaddition reactions. Round and square brackets describe the number of atoms or electrons, respectively, involved in the cycloaddition. Therefore, a reaction between a carbene and a conjugated diene should be described as a (4+1) cycloaddition or as a [4+2] cycloaddition. See: Muller, P. *Pure Appl. Chem.* **1994**, *66*, 1077–1184. To avoid any confusion with the Diels–Alder cycloaddition, we shall use the former throughout.

[113] For theoretical investigations on the concerted (4+1) cycloaddition and its competitive cyclopropanation reaction, see: (a) Fujimoto, H.; Hoffmann, R. *J. Phys. Chem.* **1974**, *78*, 1167–1173. (b) Schoeller, W. W.; Yurtsever, E. *J. Am. Chem. Soc.* **1978**, *100*, 7548–7550. (c) Bauld, N. L.; Wirth, D. *J. Comput. Chem.* **1981**, *2*, 1–6. (d) Schoeller, W. W.; Aktekin, N. *J. Chem. Soc., Chem. Commun.* **1982**, 20–22. (e) Evanseck, J. D.; Mareda, J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 73–80 and references cited therein.

[114] (a) Kurahashi, T.; Wu, Y.-T.; Meindl, K.; Ruhl, S.; de Meijere, A. *Synlett* **2005**, 805–808. (b) Kamikawa, K.; Shimizu, Y.; Takemoto, S.; Matsuzaka, H. *Org. Lett.* **2006**, *8*, 4011–4014. (c) Barluenga, J.; López, S.; Flórez, J. *Angew. Chem. Int. Ed.* **2003**, *42*, 231–233. (d) Zaragoza Dorwald, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 1332–1334. (e) Déry, M.; Lefebvre, L.-P. D.; Aissa, K.; Spino, C. *Org. Lett.* **2013**, *15*, 5456–5459. (f) Sierra, M. A.; Soderberg, B.; Lander, P. A.; Hegedus, L. S. *Organometallics* **1993**, *12*, 3769–3771.

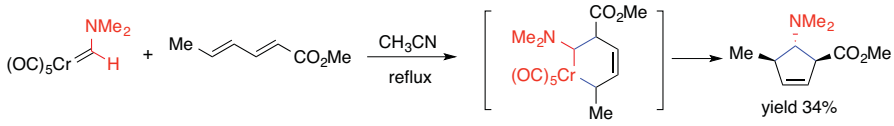
[115] (a) Spino, C.; Rezaei, H.; Dupont-Gaudet, K.; Bélanger, F. *J. Am. Chem. Soc.* **2004**, *126*, 9926–9927. (b) Boisvert, L.; Beaumier, F.; Spino, C. *Org. Lett.* **2007**, *9*, 5361–5363. (c) For a detailed discussion regarding (4+1) cycloadditions: Beaumier, F.; Dupuis, M.; Spino, C.; Legault, C. Y. *J. Am. Chem. Soc.* **2012**, *134*, 5938–5953.

only the (4+1) cycloadduct in moderate yield. However, only three examples were given in this publication, which shows the apparent limitations of this reaction.



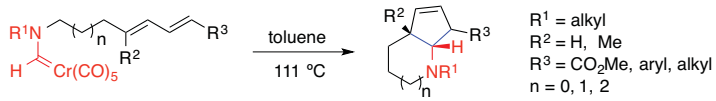
Scheme 2- 2

Chromium aminocarbenes have been found to be less reactive toward alkenes and can react with electron deficient dienes to give exclusively (4+1) cycloadduct albeit in low yields (Scheme 2-3).[114f]



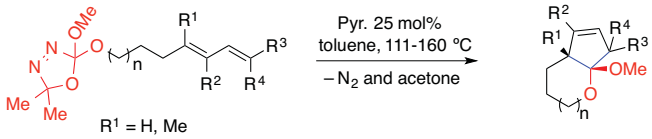
Scheme 2- 3

Interestingly, intramolecular (4+1) cycloadditions proceed more satisfactorily with comparatively broader scopes (Scheme 2-4).[114e]



Scheme 2- 4

Dialkoxycarbenes, generated by the pyrolysis of 2,2-dialkoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazolines, exhibit outstanding reactivity towards (4+1) cycloaddition with 1,3-dienes (Scheme 2-5).[115] Although they can react intermolecularly with dienes activated by electron-withdrawing groups with modest yields, the intramolecular version exhibits much broader scope, higher yields, regio- and diastereoselectivity.



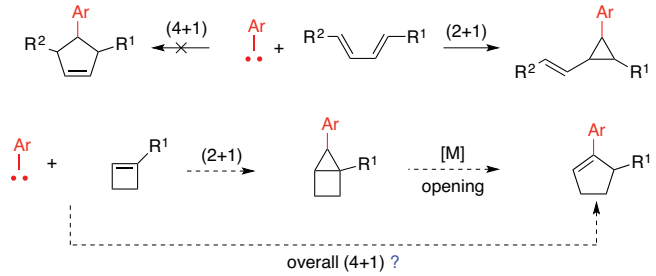
R^1 = H, Me
R^2 = H, CO_2Me
R^3 = alkyl, CO_2Me, SO_2Ph, CN, CHO, COR, NO_2, $CONEt_2$, CF_3, boronic ester
R^4 = H, Me
n = 0, 1, 2, 3

Scheme 2- 5

Objectives

To the best of our knowledge, there is no report on the (4+1) cycloaddition of simple aryl carbenes with 1,3-dienes, which is still a challenging topic in carbene chemistry.

We postulated that cyclobutenes could be used as synthetic equivalents of 1,3-dienes for the development of a (4+1) cycloaddition with metal carbenes. As shown in Scheme 2-6, after (2+1) addition of cyclobutenes with carbenes, the expected intermediate contains a highly strained bicyclo[2.1.0]pentane structure. This high strain makes the intermediate rather unstable and prone to collapse. In the presence of a metal complex, it may afford the thermodynamically more favored cyclopentene derivatives. The overall transformation would be a formal (4+1) cycloaddition and could be applied as a new strategy for effective synthesis of cyclopentene derivatives.

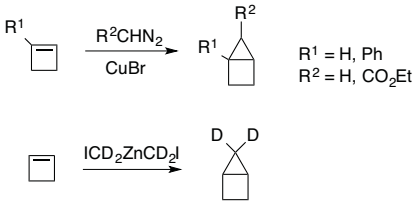


Scheme 2- 6 New strategy for (4+1) addition.

This newly proposed strategy is based on two fundamental steps: cyclopropanation of cyclobutenes and ring-opening of the bicyclo[2.1.0]pentanes. A survey of the literature indicated that there is precedent for both.

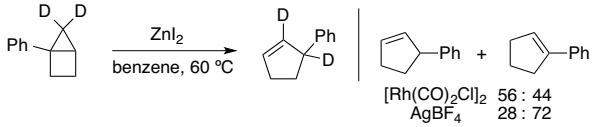
Cyclobutenes can be cyclopropanated with diazo compounds or Simmons-Smith reagents to form bicyclo[2.1.0]pentanes (Scheme 2-7).[116]

[116] (a) Gassman, P. G.; Mansfield, K. T. *J. Org. Chem.* **1967**, *32*, 915–920. (b) Wiberg, K. B.; Ashe III, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 63–74. (c) Gassman, P. G.; Atkins, T. J.; Lumb, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 7757–7761. (d) Wiberg, K. B.; Bishop III, K. C. *Tetrahedron Lett.* **1973**, *14*, 2727–2730. (e) McKinney, Michael A.; Chou, S. K. *Tetrahedron Lett.* **1974**, *15*, 1145–1148. (f) Wiberg, K. B.; Williams Jr., V. Z.; Friedrich, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 564–567. (g) Wittig, G.; Wingler, F. *Chem. Ber.* **1964**, *97*, 2146–2164.



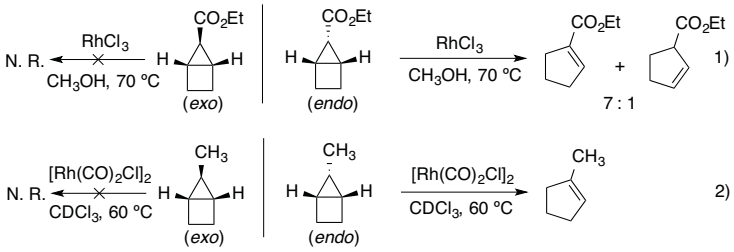
Scheme 2- 7

The cleavage of bicyclo[2.1.0]pentanes catalyzed by different metals to form cyclopentenes is also reported.[117] ZnI_2 was found to be the best reagent to promote this transformation, whereas Rh(I) and Ag(I) in this case gave a mixture of two regio-isomers (Scheme 2-8).[117f]



Scheme 2- 8

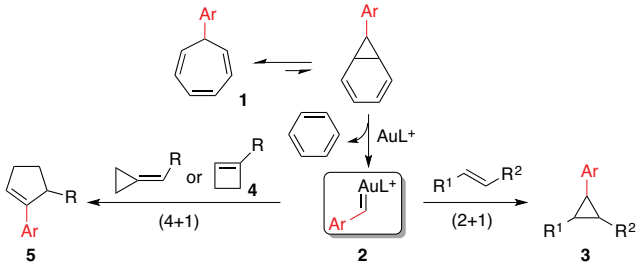
Interestingly, the stereochemistry has a strong influence on the reactivity of the substrates towards this cleavage. The *endo*-isomers can give the desired products in the presence of appropriate rhodium catalysts, whereas the *exo*-isomers show no reactivity under the standard conditions (Scheme 2-9).[117c]



Scheme 2- 9

[117] Cleavage of bicyclo[2.1.0]pentanes to form cyclopentenes with Rh(I): (a) Gassman, P. G.; Atkins, T. J.; Lumb, J. T. *Tetrahedron Lett.* **1971**, *12*, 1643–1646. (b) Gassman, P. G.; Atkins, T. J.; Lumb, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 7757–7761. (c) Wiberg, K. B.; Bishop III, K. C. *Tetrahedron Lett.* **1973**, *14*, 2727–2730. (d) Yamaguchi, R.; Kawanisi, M. *J. Org. Chem.* **1984**, *49*, 4460–4462. (e) Sohn, M.; Blum, J.; Halpern, J. *J. Am. Chem. Soc.* **1979**, *101*, 2694–2698. (f) Cleavage with Zn(II): McKinney, Michael A.; Chou, S. K. *Tetrahedron Lett.* **1974**, *15*, 1145–1148. (g) Cleavage via radical cations with tris(aryl)aminium hexachloroantimonates: Adam. W.; Sahin, C. *Tetrahedron Lett.* **1994**, *35*, 9027–9030.

It is known that methylenecyclopropanes (MCPs) can undergo rearrangement to give cyclobutenes under platinum or palladium catalysis.[8,118] Based on our novel and practically safe method to generate aryl gold-carbenes from 7-substituted 1,3,5-cycloheptatrienes through a retro-Buchner pathway, we decided to test the feasibility of the proposed new (4+1) strategy with this carbene precursor and readily available methylenecyclopropanes[119] (Scheme 2-10).



Scheme 2- 10

[118] For one recent intramolecular reaction of α-imino rhodium(II) carbenes generated from *N*-Sulfonyl 1,2,3-Triazoles with methylenecyclopropanes: Chen, K.; Zhu, Z.-Z.; Zhang, Y.-S.; Tang, X.-Y.; Shi, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 6645–6649.

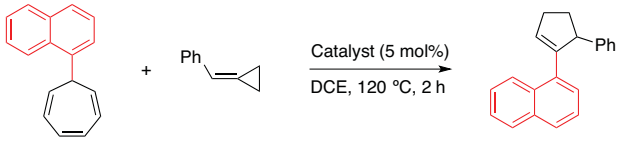
[119] Methylenecyclopropanes (MCPs) can be readily prepared in one step by Wittig olefination of carbonyl compounds with commercially available 3-bromo-triphenylphosphonium bromide. For recent reviews on the chemistry of MCPs: (a) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev.* **2014**, *114*, DOI: 10.1021/cr400686j. (b) Zhang, D.-H.; Tang, X.-Y.; Shi, M. *Acc. Chem. Res.* **2014**, *47*, 913–924. (c) Shi, M.; Lu, J.-M.; Wei, Y.; Shao, L.-X. *Acc. Chem. Res.* **2012**, *45*, 641–652. (d) Yu, L.; Guo, R. *Org. Prep. Proc. Int.* **2011**, *43*, 209–259. (e) Pellissier, H. *Tetrahedron* **2010**, *66*, 8341–8375. (f) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev*. **2003**, *103*, 1213–1269.

Results and discussions

Reaction with methylenecyclopropanes (MCPs)

We first examined the reaction of 7-naphthyl-cyclohepta-1,3,5-triene (**1a**) with phenylmethylenecyclopropane (**3a**) in the presence of gold(I) complexes (Table 2-1). To our delight, using cationic [JohnphosAu(MeCN)]SbF_6 complex **A** in 1,2-dichloroethane at 120 ºC, the desired disubstituted cyclopentene **5a** was obtained in 76% isolated yield (Table 2-1, entry 1). Carbene complex **E** gave a lower yield and catalysts **B**, **C** and **D** also led to poor results (Table 2-1, entries 2-5). Catalysts **F** and **G** were unable to promote this transformation, due to their instability at the high temperature required to initiate the retro-Buchner process. In contrast, other typical metal cations used in carbene chemistry, such as silver(I), copper(I) and platinum(II) complexes (**H**, **I**, and **J**) failed at catalyzing this transformation.

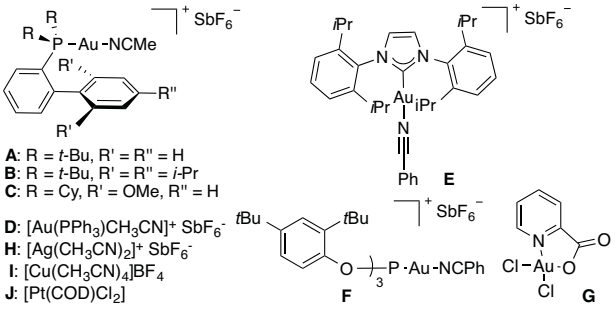
Table 2- 1 Screening of conditions for the (4+1) cycloaddition.[a]



1a **3a** **5a**

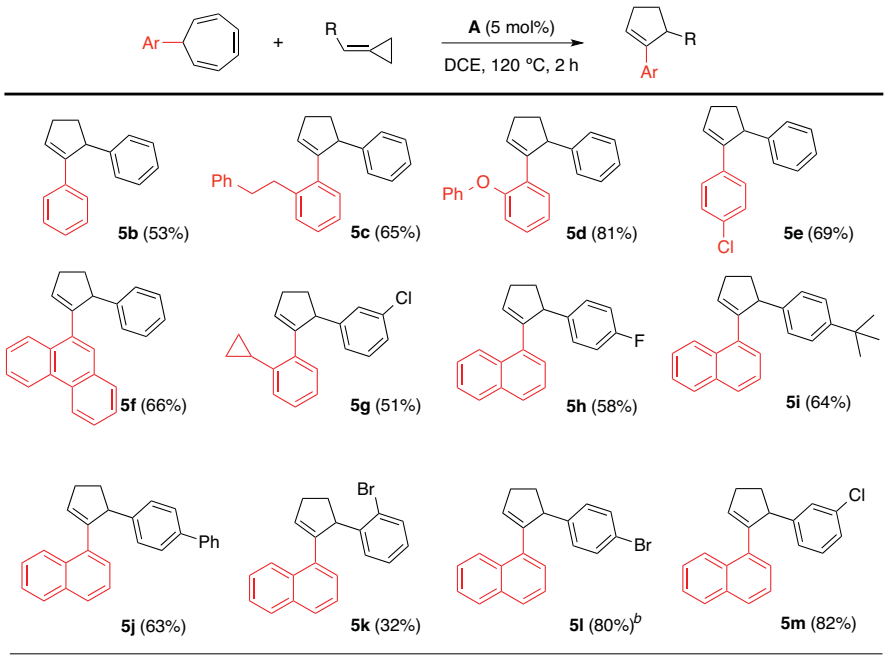
Entry	Catalyst	Yield (%)[b]	Entry	Catalyst	Yield (%)
1	**A**	81 (76)[c]	6	**F**	-[d]
2	**B**	25	7	**G**	-[d]
3	**C**	28	8	**H**	-[d]
4	**D**	<5	9	**I**	-[d]
5	**E**	47	10	**J**	-[d]

[a] Reaction at 120 °C (0.2 M in 1,2-dichloroethane), 2 equiv of **3a**, catalyst (5 mol%), 2 h. [b] Yields determined by ^{1}H NMR using 1,4-diacetylbenzene as internal standard. [c] Isolated yield. [d] Not detected.



With the best conditions in hand, the substrate scope was investigated (Table 2-2).[120] 7-Aryl-cyclohepta-1,3,5-trienes containing substituents with different electronic and steric effects at the *ortho*, *meta*, or *para* positions partook in the reaction to yield (4+1) cycloadducts in good yields (**5b**-**5g**). The scope with regard to the MCP component was also studied. The (4+1) cycloaddition can tolerate various MCPs bearing substituted arenes including fluoro-, chloro- and bromo-substituents. However, it is a slightly sensitive to *ortho* substituent, affording cycloadduct **5k** in lower yield. The structure of **5k** was confirmed by X-ray diffraction (Figure 2-1). To demonstrate the synthetic utility of this method, cyclopentene **5l** was prepared on 500 mg scale using only 1 mol% gold catalyst **A** in 51% yield after purification by column chromatography.

Table 2- 2 Substrate scope of (4+1) cycloaddition from MCPs.[a]



[a] Reaction at 120 °C, 0.2 M in 1,2-dichloroethane, 2 equiv of **3a**-**k**, catalyst **A** (5 mol%), 2 h. Yields are for isolated adducts. [b] Reaction time = 3 h.

[120] In collaboration with Dr. Michael E. Muratore.

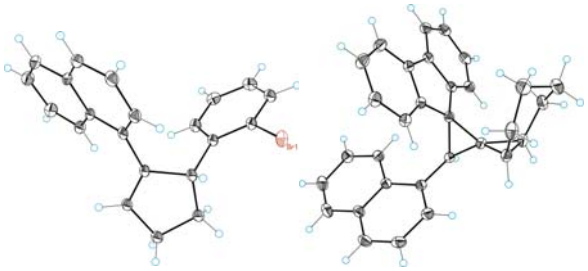
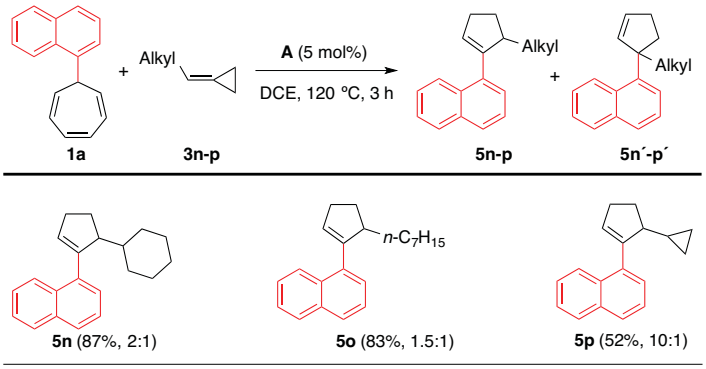


Figure 2- 1 X-ray crystal structures of 5k and 6.

MCPs substituted with alkyl groups gave (4+1) cycloaddition products as a mixture of isomers **5n/n´-5p/p´** (the major products are list in Table 2-3). Interestingly, the selectivity of the reaction was much higher with a cyclopropyl substituent (**5p**, **5p´**). Other stable gold(I) catalysts were screened, but all led to poor selectivities. The formation of minor products is rationalized in the mechanistic discussion later in this chapter.

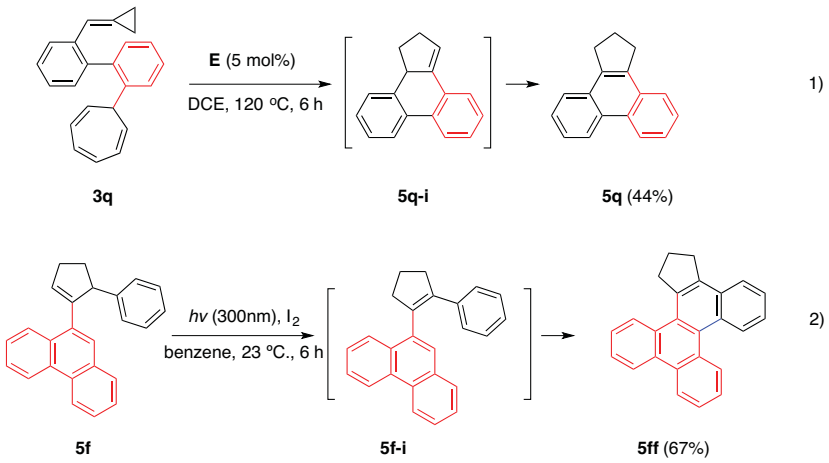
Table 2- 3 Scope with alkyl-substituted MCPs.



Substrate **3q**, which is predisposed to undergo an intramolecular cycloaddition, was prepared by using biphenyl as linking group. In the presence of gold complex **E**, initially formed **5q-i** was not stable at high temperature and isomerized to symmetrical compound 9,10-cyclopentanyl-fused phenanthrene **5q**, presenting an extended conjugated system, in moderate isolated yield (Scheme 2-11, eq. 1).

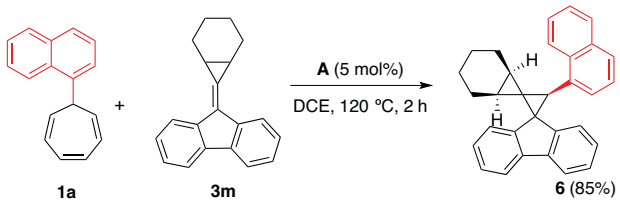
Compound **5f**, prepared with our method (see: Table 2-2), can undergo a one pot photo-induced isomerization/oxidative Mallory cyclization[121] to give cyclopentanyl fused benzo[*g*]chrysene **5ff** in good yield (Scheme 2-11, eq. 2). This procedure may be applicable to the synthesis of polycyclic aromatic hydrocarbons (PAHs).

[121] Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1–456.



Scheme 2- 11 Intramolecular cyclization and photo-induced isomerization/oxidative Mallory cyclization.

Tetrasubstituted MCP **3m** reacted with 7-naphthyl-cyclohepta-1,3,5-triene **1a** to give cyclopropanated product **6** in good yield without detection of any other isomers (Scheme 2-12). The structure of **6** was confirmed by X-ray diffraction (Figure 2-1). Given that **3m** cannot undergo ring-expansion to cyclobutene, the isolation of spiro biscyclopropyl derivative **6** instead of the corresponding cyclopentene strongly suggests that the cyclopropanation of MCP is not the initial step in the formal (4+1) cycloaddition and that cyclobutenes are likely intermediates in this transformation.



Scheme 2- 12 Cyclopropanation of tetrasubstituted MCP 3m.

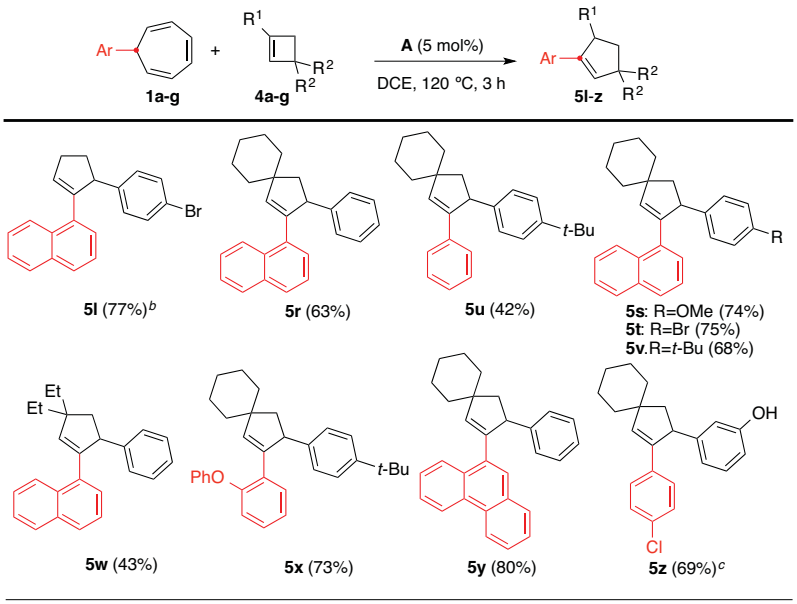
Reaction with cyclobutenes

To confirm the hypothesis that cyclobutenes are intermediates in the (4+1) reaction of MCPs, we performed the reaction of cycloheptatriene **1a** with cyclobutene **4a**, which was isolated from the reaction mixture for preparing **5l** from corresponding methylenecyclopropane **3g**. Under identical conditions, cycloadduct **5l** was isolated in 77% yield (Table 2-4), similar to the 82% yield obtained by reaction of the corresponding MCP **3g** (Table 2-2).

Trisubstituted cyclobutenes, which were prepared by the intermolecular gold(I)-catalyzed [2+2] cycloaddition of alkynes with alkenes, reported by our laboratory,[78] also took part in the (4+1) cycloaddition reaction to afford desired cyclopentenes **5r-z** (Table 2-4). However, the attempt to develop a one pot [2+2]/(4+1) cycloadditions was unsuccessful. Control experiments show that either the excess of alkene or alkyne deactivates the gold catalyst for the sensitive (4+1) addition.

It is worthy of note that when using cyclobutenes instead of a MCP slightly longer reaction times (in general 3 h) were required, perhaps due to steric hindrance presented by the bulky tethering group (cyclohexyl or diethyl). Cyclopentenes **5s** and **5z** with strong electron donating group were successfully obtained, which was found to be problematic in the past due to the ease of the dimerization of these cyclobutenes.[8a]

Table 2- 4 Substrate scope of (4+1) cycloaddition from cyclobutenes.[a]

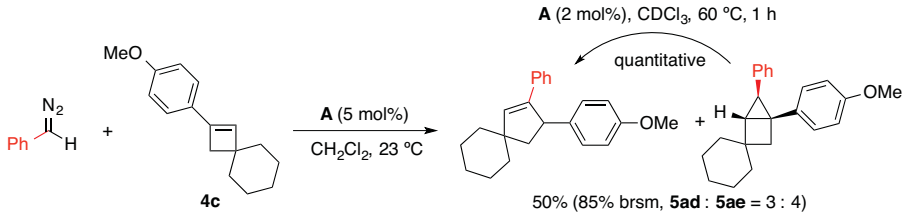


[a] Reaction at 120 °C, 0.2 M in 1,2-dichloroethane, 2 equiv of **4a-g**, catalyst **A** (5 mol%), 3 h. Yields are for isolated adducts. [b] Cyclobutene **4a** was isolated from the reaction mixture for preparing **5l**. [c] 2 equiv of 7-(4-chlorophenyl)cyclohepta-1,3,5-triene was used, 4 h.

Mechanistic studies

To test the generality of new this strategy for (4+1) cycloadditions, other carbene precursors were also studied. Cyclobutenes also react with intermediate gold(I) carbenes generated by 1,2-acyloxy migration of propargylic acetates[47] to give

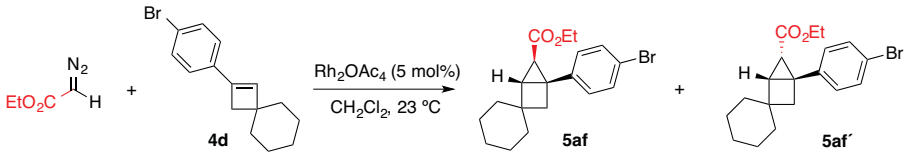
desired products as a mixture of two regioisomers with excellent yields.[122] Mixing phenyl diazomethane with cyclobutene **4c** in the presence of gold catalyst **A** at room temperature led to an inseparable mixture of **5ad** and **5ae** (with *exo* configuration). Interestingly, heating the isolated mixture (**5ad** and **5ae**) at 60 ºC in the presence of gold gave **5ad** quantitatively (Scheme 2-13). This strongly suggested that cyclopropanation of cyclobutenes[116] is the initial step for this overall (4+1) cycloaddition. However, it also gave the same mixture (**5ad** and **5ae**) when this reaction was performed at 60 ºC with gold complex **A**. It seems as though gold catalyst is poisoned by some byproduct, probably, benzalazine (Ph=N–N=Ph), generated during the course of the reaction.[123]



Scheme 2- 13 (4+1) cycloadditions of cyclobutenes with phenyl diazomethane.

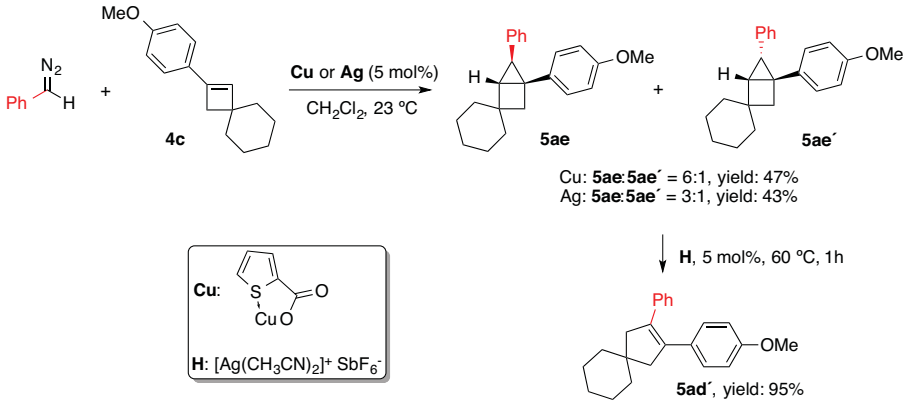
We also screened some representative disubstituted diazomethanes, like methyl 2-diazo-2-phenylacetate, but only homo-coupling product of diazo compound was observed. Because of the presence of 1,2-hydrogen shift in our proposed mechanism, we presumed that only monosubstituted diazomethanes would be suitable substrates for this transformation. Commercially available ethyl diazoacetate (EDA) was also tested with cyclobutenes in the presence of $Rh_2(OAc)_4$. Along with the dimerized byproduct, a similar cyclopropanated intermediate was also obtained as a mixture of *endo* and *exo*-isomers, **5af**, **5af´** without detection of the desired (4+1) adduct (Scheme 2-14). However, when this isolated mixture was heated at 60 ºC in the presence of gold complex **A** for 1 h, only the major isomer was consumed. Due to difficulties in its purification, we were unable to assign the structure of the resulting product.

[122] This study was carried out by Zhouting Rong. For the details, see: reference 10.
[123] For detection of the benzalazine formation by diazo decomposition, see: (a) Bailey, R. J.; Card, P. J.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6096–6103. (b) Nakajima, M.; Anselme, J.-P. *J. Chem. Soc.* **1980**, 796–797. (c) Onaka, M.; Kita, H.; Izumi, Y. *Chem. Lett.* **1985**, *14*, 1895–1898. Synthesis of $Au(C_6F_5)(Ph_2C{=}N{-}N{=}CPh_2)$ from $Au(C_6F_5)(SC_4H_8)$ and Ph_2CN_2: (d) Bordoni, S.; Busetto, L.; Cassani, M. C. *Inorganica Chimica Acta* **1994**, *222*, 267–273.



Scheme 2- 14 using ethyl diazoacetate

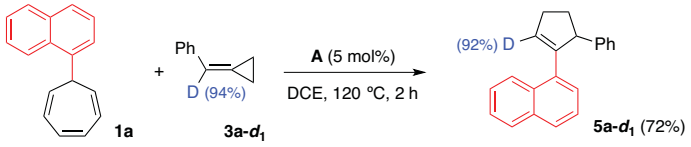
Because it is known that the *exo*-isomer of bicyclo[2.1.0]pentane intermediate reacts sluggishly for the next ring-opening step compared with its *endo*-isomer,[117c] we presumed that the *endo*-isomer was also generated in our reaction, but was converted to the final product even at room temperature. For this purpose, milder coinage metals were chosen for catalyzing the decomposition of phenyl diazomethane. As expected, two isomers (*exo*-**5ae** and *endo*-**5ae´**) were isolated as an inseparable mixture in moderate yield with silver(I) or copper(I) complexes (Scheme 2-15). However, heating of this mixture with the same silver complex **H** at 60 ºC for 1 h led exclusively to unexpected **5ad´** in excellent yield,[124] whereas with copper complex, no reaction was observed. These observations suggest that copper(I), silver(I) and gold(I) complexes have very different reactivities towards the ring-opening of bicyclo[2.1.0]pentane intermediate.



Scheme 2- 15 Comparing silver and copper with gold catalysts.

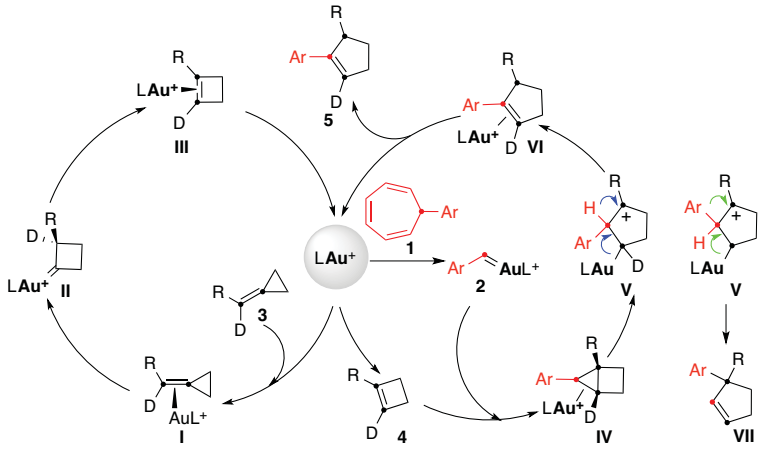
To shed additional light on the mechanism of this unusual (4+1) cycloaddition, we carried out the reaction of cycloheptatriene **1a** with MCP **3a-*d*$_1$** in the presence of catalyst **A** (Scheme 2-16). In this experiment, **5a-*d*$_1$** was obtained with the deuterium label transferred completely to C-3.

[124] A silver mirror was formed after 1 h at 60 ºC.



Scheme 2- 16 Cycloaddition of deuterated MCP 3a-d_1.

We propose a mechanism that fits all of the experimental results for this (4+1) cycloaddition from cycloheptatrienes **1** and MCPs in which gold(I) plays a triple role (Scheme 2-17). In the first catalytic cycle, MCP-gold(I) complexes **I** undergoes ring expansion to form intermediate **II**. Subsequent 1,2-H shift of this intermediate gives cyclobutene-gold(I) complexes **III**. Associative ligand exchange with the 7-aryl-1,3,5-cycloheptatriene, then followed by retro-Buchner reaction leads to highly reactive gold(I) carbenes, which are trapped by cyclobutenes **4** to form unstable bicyclo[2.1.0]pentane-gold(I) complexes **IV**. Electrophilic cyclopropane opening[125] forms tertiary carbocation **V**, followed by a final 1,2-H shift leads to complexes **VI**. Formation of regioisomeric 3-alkyl-3-arylcyclopent-1-enes together with **5n-p** in the reaction of alkyl-substituted MCPs can be explained by the competitive migration of the aryl group in intermediates **V**.



Scheme 2- 17 Proposed mechanism for (4+1) cycloaddition.

[125] The cyclopropanation of **4** by **2**, followed by electrophilic cleavage probably follows a pathway similar to that occurring in the gas phase cyclopropanation/retrocyclopropanation of enol ethers with gold(I) carbenes: Fedorov, A.; Batiste, L.; Bach, A.; Birney D. M.; Chen, P. *J. Am. Chem. Soc.* **2011**, *133*, 12162–12171.

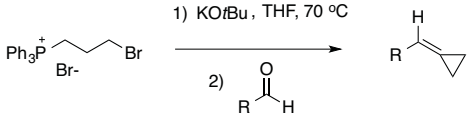
Conclusion

We found that methylenecyclopropanes (MCPs) and cyclobutenes can be used as synthetic equivalents of 1,3-dienes for very challenging (4+1) cycloadditions with carbenes. In addition to using gold(I) carbenes generated by retro-Buchner reaction from 7-aryl-1,3,5-cycloheptatrienes, other methods of carbene formation can also be applied in this new (4+1) cycloaddition strategy.

Experimental part

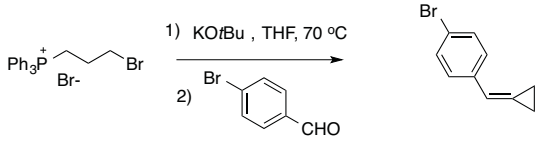
1. Cycloheptatrienes have been described in Chapter 1

2. The procedure for the preparation of methylenecyclopropanes was adapted from literature[126]



To a suspension of (3-bromopropyl)triphenylphosphonium bromide (1.1 equiv) in anhydrous THF (3 mL/mmol) was added KO*t*-Bu (2.2 equiv) in THF (1 mL/mmol) at room temperature (23 ºC). The mixture was then heated at 70 ºC for 10 min, and the aldehyde (1 equiv) was added dropwise, then heating at 70 ºC was continued for 2-4 h. The reaction mixture was then cooled to room temperature. Cyclohexane (20 mL) was added and filtered. The solvent was removed *in vacuo*, and the resulting crude material was subjected to flash column chromatography to afford the desired methylenecyclopropane.

1-Bromo-4-(cyclopropylidenemethyl)benzene (3g)



3-Bromopropylphosphonium bromide (2.79 g, 6 mmol, 1.2 equiv) was dissolved in dry THF (10 mL) and *t*-BuOK (1.35 g, 12 mmol, 2.4 equiv) was added as a solution in dry THF (10 mL). The resulting suspension was heated at reflux for 10 minutes and 4-bromobenzaldehyde (925 mg, 5 mmol, 1 equiv) was added as a solution in dry THF (5 mL). The mixture was heated at reflux for 2 h. After cooling down to room temperature, the mixture was layered with cyclohexane (20 mL) and the cloudy suspension filtered over Celite washing thoroughly with cyclohexane. The filtrate was concentrated and the residue purified by chromatography on silica gel eluting with cyclohexane to afford 780 mg of colorless solid (yield: 75%).

NMR data in agreement with the literature.[127]

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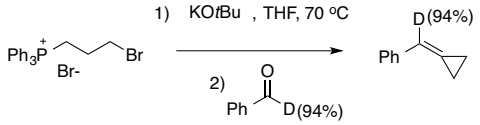
[126] (a) Hui, W.-Q.; Chiba, S. *Org. Lett.* **2009**, *11*, 729–732. (b) Shi, M.; Liu, L.-P.; Tang, J. *J. Am. Chem. Soc*. **2006**, *128*, 7430–7431.
[127] Katritzky, A.R.; Du, W.; Levell, J. R.; Li, J. *J. Org. Chem.* **1998**, *63*, 6710–6711.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 - 7.44 (m, 2H), 7.43 - 7.38 (m, 2H), 6.71 (s, 1H), 1.42 (ddd, *J* = 10.0, 5.8, 2.3 Hz, 2H), 1.19 (ddd, *J* = 9.9, 5.8, 1.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 131.5, 128.1, 125.3, 120.3, 117.2, 4.2, 0.6.

(Cyclopropylidenemethyl-*d*)benzene (3a-d_1)



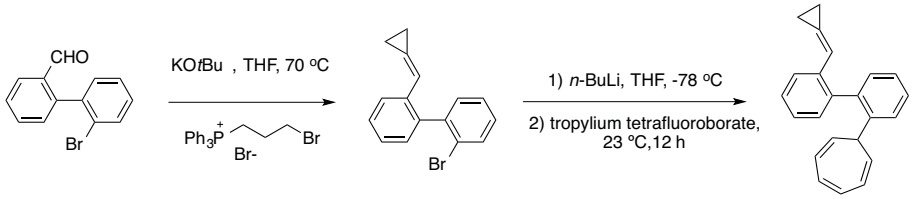
The title compound (colorless liquid, 1.64 g, yield: 93%) was prepared according to the general procedure from d_1-benzaldehyde[128] (1.45 g, 13.5 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 6.77 - 6.80 (m, residual signal, 6%), 1.49 - 1.43 (m, 2H), 1.25 - 1.18 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 128.4, 126.7, 126.6, 124.2, 117.9 (t, *J* = 24.1 Hz), 4.1, 0.5.

HRMS-APCI: calculated for $C_{10}H_{10}D$ $[M+H]^+$: 132.0924; found: 132.0928.

2-(Cyclohepta-2,4,6-trien-1-yl)-2'-(cyclopropylidenemethyl)-1,1'-biphenyl (3q)



2-Bromo-2'-(cyclopropylidenemethyl)-1,1'-biphenyl (colorless oil, 1.52 g, yield: 68%) was synthesized according to the general procedure from known 2'-bromo-[1,1'-biphenyl]-2-carbaldehyde[129] (2.04 g, 7.8 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.47 - 7.18 (m, 6H), 6.48 (s, 1H), 1.51 - 1.36 (m, 2H), 1.18 - 1.05 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 139.6, 136.0, 132.6, 131.7, 129.9, 128.8, 127.9, 127.1, 126.3, 125.5, 125.3, 124.1, 115.8, 4.3, 0.7.

HRMS-APCI: calculated for $C_{16}H_{14}Br$ $[M+H]^+$: 285.0273; found: 285.0270.

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[128] Prepared according to: Gajewski, J. J.; Bocian, W.; Harris, N. J.; Olson, L. P.; Gajewski, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 326–334.
[129] Wang, H.; Zhao, W.; Zhou, Y.; Duan, Z.; Mathey, F. *Eur. J. Inorg. Chem*. **2011**, 4585–4589.

n-BuLi (2.5 M in hexanes, 0.67 mL, 1.68 mmol) was added dropwise to a solution of 2-bromo-2'-(cyclopropylidenemethyl)-1,1'-biphenyl (400 mg, 1.4 mmol) in 10 mL of dry THF at −78 ºC under argon. The mixture was stirred for 1 h at −78 ºC and tropylium tetrafluoroborate (299 mg, 1.68 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature (23 ºC) for 12 h. The reaction was quenched by addition of water. The aqueous phase was extracted with diethyl ether, the combined organic extracts were dried over $MgSO_4$ and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with cyclohexane as eluent to obtain 232 mg (yield: 56%) of white solid.

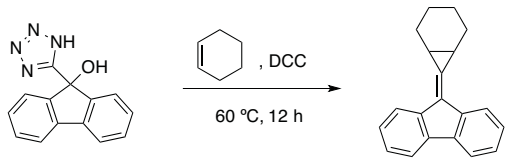
M.p.: 84-86 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.48 (td, *J* = 7.6, 1.5 Hz, 1H), 7.35 - 7.08 (m, 5H), 6.54 - 6.47 (m, 2H), 6.42 (s, 1H), 6.09 (dddd, *J* = 10.9, 6.1, 3.0, 1.6 Hz, 2H), 5.36 (dd, *J* = 9.4, 5.4 Hz, 1H), 5.25 (dd, *J* = 9.3, 5.4 Hz, 1H), 2.71 - 2.63 (m, 1H), 1.42 - 1.21 (m, 2H), 1.10 - 1.02 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 140.6, 139.1, 136.4, 130.4, 130.3, 130.1, 128.0, 127.4, 127.2, 127.1, 127.1, 126.1, 126.0, 125.5, 124.7, 124.0, 124.0, 116.6, 42.0, 3.9, 0.7.

HRMS-APCI: calculated for $C_{23}H_{21}$ $[M+H]^+$: 297.1638; found: 297.1638.

9-(Bicyclo[4.1.0]heptan-7-ylidene)-9*H*-fluorene (3m)



The solution of 9-(1*H*-tetrazol-5-yl)-9*H*-fluoren-9-ol[130] (400 mg, 1.6 mmol) and DCC (660 mg, 3.2 mmol) in 5 mL of cyclohexene was heated at 60 ºC overnight. After cooling to room temperature, the mixture was directly loaded on silica gel and purified by column chromatography to obtain 198 mg of white solid (yield: 48%).

M.p.: 122-124 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.42 - 7.33 (m, 4H), 2.23 - 2.18 (m, 2H), 2.13 - 2.05 (m, 4H), 1.40 - 1.28 (m, 2H), 1.26 - 1.16 (m, 2H).

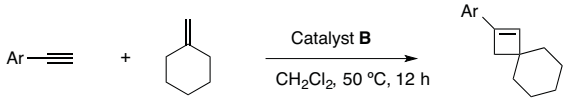
[130] Prepared according to: Wardrop, D. J.; Komenda, J. P. *Org. Lett.* **2012**, *14*, 1548–1551.

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5, 138.4, 136.7, 127.2, 126.8, 126.7, 122.2, 119.7, 22.0, 21.4, 12.6.

HRMS-APCI: calculated for $C_{20}H_{19}$ $[M+H]^+$: 259.1481; found: 259.1482.

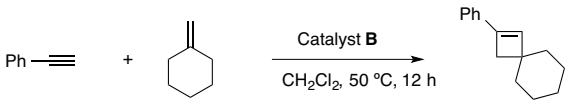
3. Procedure for the preparation of cyclobutenes

Cyclobutenes were prepared using a modified literature procedure.[78]



A solution of arylacetylene (1 equiv), alkene (5 equiv) and gold complex **B** (3 mol%) in dichloromethane (0.5 mL/mmol) was heated at 50 ºC overnight (12 h). The solvent and excess alkene were removed under vacuum. The crude was purified by flash column chromatography to obtain the desired cyclobutene.

2-Phenylspiro[3.5]non-1-ene (4b)



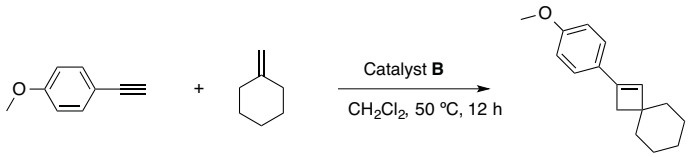
The title compound (colorless oil, 499 mg, yield: 92%) was synthesized according to the general procedure from phenylacetylene (279 mg, 2.73 mmol) and methylenecyclohexane (788 mg, 8.19 mmol).

NMR data in agreement with the literature.[78]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.31 (m, 4H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.57 (s, 1H), 2.46 (s, 2H), 1.64 - 1.39 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 135.6, 135.3, 128.2, 127.4, 124.3, 44.3, 40.2, 36.5, 26.0, 24.5.

2-(4-Methoxyphenyl)spiro[3.5]non-1-ene (4c)



The title compound (white solid, 870 mg, yield: 42%) was synthesized according to the general procedure from 1-ethynyl-4-methoxybenzene (1.19 g, 9 mmol) and methylenecyclohexane (1.73 g, 18 mmol).

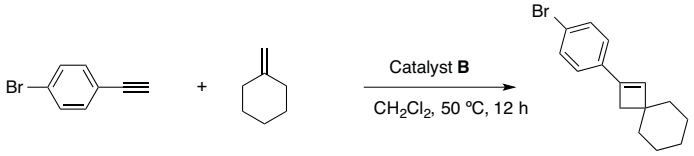
M.p.: 76-79 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.42 (s, 1H), 3.83 (s, 3H), 2.42 (s, 2H), 1.62 - 1.47 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 142.9, 133.0, 128.5, 125.7, 113.7, 55.3, 44.1, 40.3, 36.6, 26.0, 24.6.

HRMS-APCI: calculated for $C_{16}H_{21}O$ $[M+H]^+$: 229.1587; found: 229.1587.

2-(4-Bromophenyl)spiro[3.5]non-1-ene (4d)



The title compound (white solid, 420 mg, yield: 55%) was synthesized according to the general procedure from 1-bromo-4-ethynylbenzene (500 mg, 2.76 mmol) and methylenecyclohexane (797 mg, 8.29 mmol).

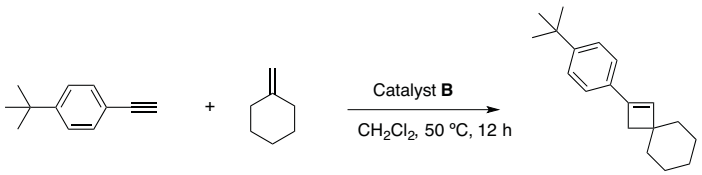
M.p.: 85-87 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.58 (s, 1H), 2.43 (s, 2H), 1.64 - 1.40 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 136.5, 134.2, 131.4, 126.0, 121.1, 44.5, 40.1, 36.3, 25.9, 24.5.

HRMS-APCI: calculated for $C_{15}H_{18}Br$ $[M+H]^+$: 277.0586; found: 277.0575.

2-(4-(*tert*-Butyl)phenyl)spiro[3.5]non-1-ene (4e)



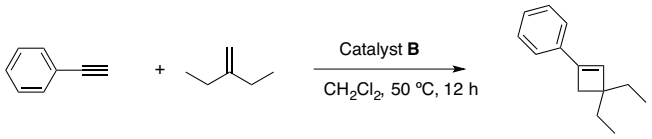
The title compound (colorless oil, 610 mg, yield: 95%) was synthesized according to the general procedure from 1-(*tert*-butyl)-4-ethynylbenzene (400 mg, 2.53 mmol) and methylenecyclohexane (1.22 g, 12.64 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.51 (s, 1H), 2.44 (s, 2H), 1.64 - 1.47 (m, 10H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 143.2, 134.7, 132.7, 125.2, 124.0, 44.3, 40.2, 36.5, 34.6, 31.3, 26.0, 24.6.

HRMS-APCI: calculated for $C_{19}H_{27}$ $[M+H]^+$: 255.2107; found: 255.2098.

(3,3-Diethylcyclobut-1-en-1-yl)benzene (4f)



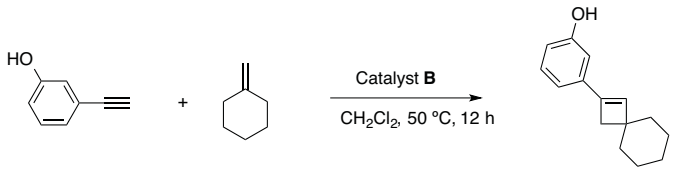
The title compound (colorless oil, 490 mg, yield: 54%) was synthesized according to the general procedure from phenylacetylene (500 mg, 4.9 mmol) and 3-methylenepentane (2.06 g, 24.5 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.31 (m, 4H), 7.25 (t, *J* = 7.1 Hz, 1H), 6.49 (s, 1H), 2.44 (s, 2H), 1.65 - 1.55 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 135.2, 134.5, 128.2, 127.3, 124.3, 46.9, 38.1, 28.9, 9.5.

HRMS-EI: calculated for $C_{14}H_{18}$ $[M]^+$: 186.1409; found: 186.1408.

3-(Spiro[3.5]non-1-en-2-yl)phenol (4g)



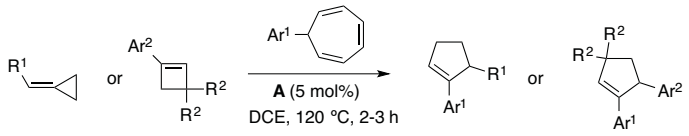
The title compound (colorless oil, 270 mg, yield: 93%) was synthesized according to the general procedure from phenylacetylene (160 mg, 1.35 mmol) and 3-methylenepentane (391 mg, 4.06 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.83 (dd, *J* = 2.6, 1.4 Hz, 1H), 6.73 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H), 6.55 (s, 1H), 4.71 (s, 1H), 2.42 (s, 2H), 1.68 - 1.41 (m, 10H).

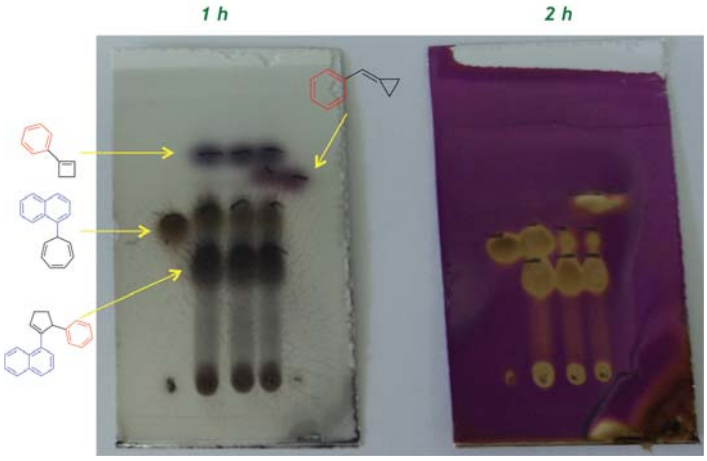
^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 143.0, 137.1, 136.3, 129.5, 117.1, 114.4, 111.1, 44.4, 40.2, 36.4, 26.0, 24.5.

HRMS-APCI: calculated for $C_{15}H_{19}O$ $[M+H]^+$: 215.1430; found: 215.1436.

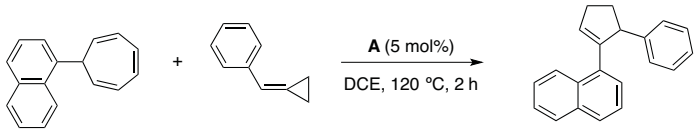
4. Procedure for gold catalyzed (4+1) reactions



A solution of the arylcycloheptatriene substrate (0.15 mmol), methylenecyclopropane or cyclobutene (0.3 mmol) and gold complex **A** (5.5 mg, 5 mol%) in 1,2-dichloroethane (DCE, 0.75 mL) was heated at 120 ºC in a sealed tube until the starting material had been fully consumed (2-3 h). After the reaction mixture had been allowed to cool to room temperature, the solvent was removed *in vacuo* and the crude residue was purified by preparative TLC. The reaction was performed under an air atmosphere with no special precautions taken to exclude water.



1-(5-Phenylcyclopent-1-en-1-yl)naphthalene (5a)



The title compound (white solid, 20.5 mg, yield: 76%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and (cyclopropylidenemethyl)benzene (26 mg, 0.2 mmol).

M.p.: 72-74 ºC.

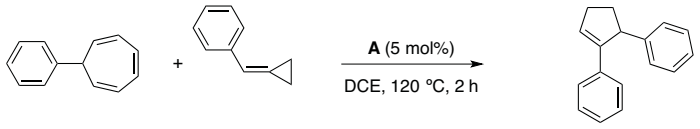
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.84 - 7.80 (m, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.55 - 7.45 (m, 2H), 7.28 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.21 -

7.13 (m, 5H), 7.06 - 7.12 (m, 1H), 6.18 (q, *J* = 2.1 Hz, 1H), 4.52 - 4.45 (m, 1H), 2.93 - 2.82 (m, 1H), 2.82 - 2.66 (m, 2H), 2.18 - 2.07 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 144.8, 135.7, 133.8, 132.7, 131.8, 128.3, 128.2, 127.6, 126.9, 125.9, 125.6, 125.4, 125.3, 125.1, 125.1, 55.4, 34.9, 32.7.

HRMS-APCI: calculated for $C_{21}H_{19}$ $[M+H]^+$: 271.1481; found: 271.1487.

Cyclopent-2-ene-1,2-diyldibenzene (5b)



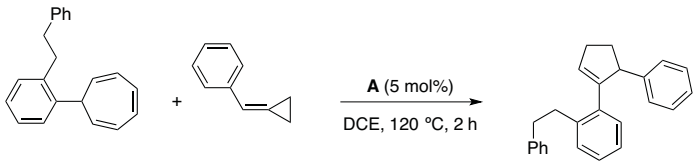
The title compound (colorless oil, 11.6 mg, yield: 53%) was synthesized according to the general procedure from 7-phenylcyclohepta-1,3,5-triene (17 mg, 0.1 mmol) and (cyclopropylidenemethyl)benzene (26 mg, 0.2 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.10 (m, 10H), 6.48 - 6.45 (m, 1H), 4.37 - 4.28 (m, 1H), 2.69 - 2.48 (m, 3H), 1.97 - 1.89 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 144.6, 136.0, 128.8, 128.5, 128.1, 127.3, 126.7, 126.3, 126.0, 51.7, 35.4, 31.6.

HRMS-APCI: calculated for $C_{17}H_{17}$ $[M+H]^+$: 221.1325; found: 221.1318.

1-Phenethyl-2-(5-phenylcyclopent-1-en-1-yl)benzene (5c)



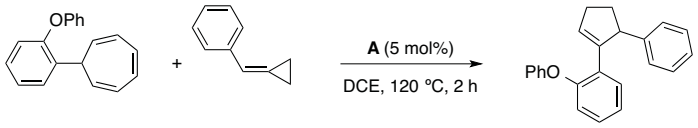
The title compound (colorless oil, 21.0 mg, yield: 65%) was synthesized according to the general procedure from 7-(2-phenethylphenyl)cyclohepta-1,3,5-triene (27 mg, 0.1 mmol) and (cyclopropylidenemethyl)benzene (26 mg, 0.2 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.33 (m, 2H), 7.29 - 7.19 (m, 5H), 7.19 - 7.09 (m, 5H), 7.04 (td, *J* = 7.6, 1.6 Hz, 1H), 7.00 (td, *J* = 8.0, 1.6 Hz, 1H), 5.90 (q, *J* = 2.1 Hz, 1H), 4.23 (d qui, *J* = 8.8, 2.3 Hz, 1H), 3.94 - 2.70 (m, 5H), 2.69 - 2.57 (m, 2H), 2.12 - 2.03 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 145.0, 142.2, 139.3, 137.2, 130.9, 129.1, 129.0, 128.4, 128.4, 128.3, 128.2, 128.2, 127.6, 126.7, 125.9, 125.9, 125.4, 55.4, 37.9, 35.4, 34.6, 32.4.

HRMS-APCI: calculated for $C_{25}H_{25}$ $[M+H]^+$: 325.1951; found: 325.1958.

1-(Phenoxymethyl)-2-(5-phenylcyclopent-1-en-1-yl)benzene (5d)



The title compound (colorless oil, 25.2 mg, yield: 81%) was synthesized according to the general procedure from 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene (26 mg, 0.1 mmol) and (cyclopropylidenemethyl)benzene (26 mg, 0.2 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.28 (m, 3H), 7.25 - 7.19 (m, 2H), 7.17 - 7.13 (m, 3H), 7.13 - 7.07 (m, 2H), 6.99 (td, *J* = 7.6, 1.3 Hz, 1H), 6.90 - 6.85 (m, 2H), 6.83 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.53 - 6.50 (m, 1H), 4.50 - 4.43 (m, 1H), 2.67 - 2.46 (m, 3H), 1.90 - 1.81 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 154.1, 145.6, 141.7, 133.2, 130.1, 129.5, 128.9, 128.2, 127.7, 127.6, 125.7, 123.4, 122.5, 119.8, 118.1, 53.2, 35.0, 32.2.

HRMS-APCI: calculated for $C_{23}H_{21}O$ $[M+H]^+$: 313.1587; found: 313.1583.

1-Chloro-4-(5-phenylcyclopent-1-en-1-yl)benzene (5e)

The title compound (colorless oil, 26.2 mg, yield: 69%) was synthesized according to the general procedure from 7-(4-chlorophenyl)cyclohepta-1,3,5-triene (30.4 mg, 0.15 mmol) and (cyclopropylidenemethyl)benzene (39 mg, 0.3 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.26 (m, 4H), 7.25 - 7.18 (m, 5H), 6.47 - 6.45 (m, 1H), 4.34 - 4.27 (m, 1H), 2.67 - 2.46 (m, 3H), 1.90 - 1.81 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 143.6, 134.5, 132.3, 129.4, 128.6, 128.3, 127.5, 127.3, 126.1, 51.7, 35.3, 31.7.

HRMS-APCI: calculated for $C_{17}H_{14}Cl$ $[M-H]^+$: 253.0779; found: 253.0784.

9-(5-Phenylcyclopent-1-en-1-yl)phenanthrene (5f)

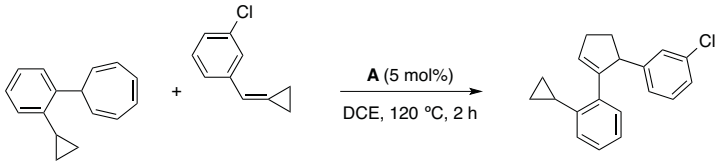
The title compound (colorless oil, 31.5 mg, yield: 66%) was synthesized according to the general procedure from 9-(cyclohepta-2,4,6-trien-1-yl)phenanthrene (40 mg, 0.15 mmol) and (cyclopropylidenemethyl)benzene (39 mg, 0.3 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 - 8.68 (m, 1H), 8.61 (d, *J* = 8.2 Hz, 1H), 8.36 - 8.32 (m, 1H), 7.72 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.68 - 7.62 (m, 2H), 7.58 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 7.41 (s, 1H), 7.24 - 7.20 (m, 2H), 7.19 - 7.14 (m, 2H), 7.09 - 7.04 (m, 1H), 6.22 (q, *J* = 2.1 Hz, 1H), 4.58 - 4.52 (m, 1H), 2.93 - 2.86 (m, 1H), 2.82 - 2.70 (m, 2H), 2.22 - 2.15 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 145.1, 134.1, 132.8, 131.4, 131.1, 130.5, 129.6, 128.4, 128.2, 127.5, 126.4, 126.4, 126.3, 126.1, 126.1, 125.9, 125.9, 122.8, 122.3, 55.4, 34.7, 32.6.

HRMS-APCI: calculated for $C_{25}H_{21}$ $[M+H]^+$: 321.1638; found: 321.1641.

1-(5-(3-Chlorophenyl)cyclopent-1-en-1-yl)-2-cyclopropylbenzene (5g)



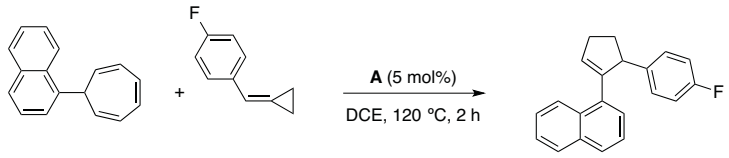
The title compound (colorless oil, 15 mg, yield: 51%) was synthesized according to the general procedure from 7-(2-cyclopropylphenyl)cyclohepta-1,3,5-triene (21 mg, 0.1 mmol) and 1-chloro-3-(cyclopropylidenemethyl)benzene (33 mg, 0.2 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 1.8 Hz, 1H), 7.14 - 6.97 (m, 6H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.11 (q, *J* = 2.1 Hz, 1H), 4.41 - 4.34 (m, 1H), 2.77 - 2.67 (m, 1H), 2.66 - 2.54 (m, 2H), 2.10 (tt, *J* = 8.5, 5.4 Hz, 1H), 2.02 - 1.93 (m, 1H), 1.03 - 0.87 (m, 2H), 0.73 (dtd, *J* = 9.7, 5.5, 4.2 Hz, 1H), 0.63 (dtd, *J* = 9.1, 5.6, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 145.5, 140.6, 137.5, 133.9, 131.8, 129.4, 128.4, 127.7, 126.8, 126.0, 125.9, 125.0, 124.2, 54.6, 34.6, 32.3, 13.9, 9.9, 8.0.

HRMS-APCI: calculated for $C_{20}H_{20}Cl$ $[M+H]^+$: 295.1248; found: 295.1255.

1-(5-(4-Fluorophenyl)cyclopent-1-en-1-yl)naphthalene (5h)



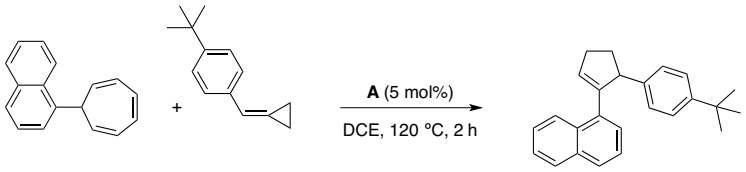
The title compound (colorless oil, 16.7 mg, yield: 58%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and 1-(cyclopropylidenemethyl)-4-fluorobenzene (30 mg, 0.2 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.83 - 7.78 (m, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.53 - 7.43 (m, 2H), 7.28 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.13 - 7.07 (m, 3H), 6.86 - 6.79 (m, 2H), 6.15 (q, *J* = 2.1 Hz, 1H), 4.49 - 4.42 (m, 1H), 2.88 - 2.79 (m, 1H), 2.77 - 2.65 (m, 2H), 2.11 - 2.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 160.0, 144.7, 140.8, 140.8, 135.4, 133.7, 132.7, 131.7, 128.9, 128.8, 128.4, 127.0, 125.7, 125.6, 125.6, 125.5, 125.4, 125.1, 125.0, 115.1, 114.8, 54.7, 34.8, 32.5.

HRMS-APCI: calculated for $C_{21}H_{18}F$ $[M+H]^+$: 289.1387; found: 289.1388.

1-(5-(4-(*tert*-Butyl)phenyl)cyclopent-1-en-1-yl)naphthalene (5i)



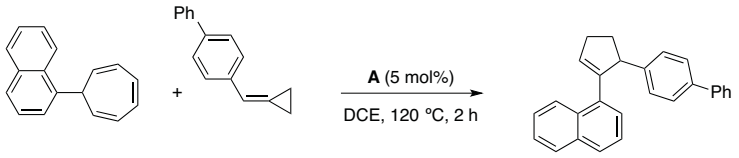
The title compound (colorless oil, 21 mg, yield: 64%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and 1-(*tert*-butyl)-4-(cyclopropylidenemethyl)benzene (37 mg, 0.2 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.82 - 7.78 (m, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.48 (app. qui d, *J* = 6.9, 1.6 Hz, 2H), 7.28 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.19 - 7.14 (m, 3H), 7.11 - 7.06 (m, 2H), 6.15 (q, *J* = 2.1 Hz, 1H), 4.48 - 4.41 (m, 1H), 2.88 - 2.78 (m, 1H), 2.74 - 2.62 (m, 2H), 2.14 - 2.05 (m, 1H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 144.7, 142.0, 135.8, 133.7, 132.7, 131.8, 128.2, 127.0, 126.7, 125.8, 125.5, 125.3, 125.1, 54.7, 34.9, 34.2, 32.5, 31.3.

HRMS-APCI: calculated for $C_{25}H_{27}$ $[M+H]^+$: 327.2107; found: 327.2103.

1-(5-([1,1'-Biphenyl]-4-yl)cyclopent-1-en-1-yl)naphthalene (5j)



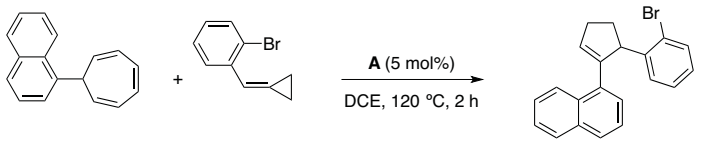
The title compound (colorless oil, 22 mg, yield: 63%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and 4-(cyclopropylidenemethyl)-1,1'-biphenyl (41 mg, 0.2 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.79 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.52 - 7.42 (m, 4H), 7.40 - 7.33 (m, 4H), 7.30 - 7.24 (m, 2H), 7.24 - 7.19 (m, 2H), 7.17 (dd, *J* = 7.1, 1.3 Hz, 1H), 6.18 (q, *J* = 2.2 Hz, 1H), 4.53 - 4.46 (m, 1H), 2.89 - 2.81 (m, 1H), 2.77 - 2.66 (m, 2H), 2.17 - 2.08 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 144.3, 141.0, 138.7, 135.6, 133.8, 132.9, 131.8, 128.6, 128.3, 127.9, 127.0, 127.0, 126.9, 126.9, 126.8, 125.7, 125.6, 125.4, 125.1, 125.0, 55.0, 34.9, 32.6.

HRMS-APCI: calculated for $C_{27}H_{23}$ $[M+H]^+$: 347.1794; found: 347.1787.

1-(5-(2-Bromophenyl)cyclopent-1-en-1-yl)naphthalene (5k)



The title compound (white solid, 22.1 mg, yield: 32%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and 1-bromo-2-(cyclopropylidenemethyl)benzene (84 mg, 0.4 mmol).

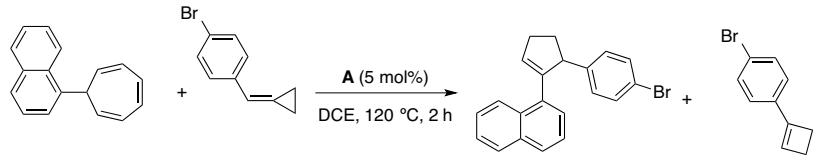
M.p.: 151-153 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.53 (ddd, *J* = 8.5, 6.8, 1.6 Hz, 1H), 7.48 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.31 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.23 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.19 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.04 (td, *J* = 7.6, 1.3 Hz, 1H), 6.90 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 6.32 (q, *J* = 2.3 Hz, 1H), 5.08 (dddd, *J* = 8.9, 6.3, 4.6, 2.4 Hz, 1H), 2.86 - 2.66 (m, 3H), 1.96 - 1.86 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.3, 134.9, 134.2, 133.9, 132.4, 131.7, 128.5, 128.4, 127.5, 127.4, 127.0, 125.7, 125.6, 125.6, 125.4, 125.1, 124.8, 124.6, 53.6, 33.9, 32.4.

HRMS-APCI: calculated for $C_{21}H_{16}Br$ $[M-H]^+$: 347.0430; found: 347.0425.

1-(5-(4-Bromophenyl)cyclopent-1-en-1-yl)naphthalene (5l)



The title compound (white solid, 42 mg, yield: 80%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (33 mg, 0.15 mmol) and 1-bromo-4-(cyclopropylidenemethyl)benzene (63 mg, 0.3 mmol).

Procedure for reaction scale-up:

1-(Cyclohepta-2,4,6-trien-1-yl)naphthalene (262 mg, 1.2 mmol, 1 equiv) and 1-bromo-4-(cyclopropylidenemethyl)benzene (502 mg, 2.4 mmol, 2 equiv) were placed in a microwave vial and [JohnPhosAu(NCMe)]SbF_6 (9.3 mg, 1 mol%) was added as a solution in 1,2-dichloroethane (4 mL). The vial was sealed and the mixture heated at 120 °C for 8 h.

TLC showed full conversion of the limiting cycloheptatriene reagent.

The solvent was removed under a stream of nitrogen and the residue triturated with cyclohexane and loaded on silica gel. Purification by column chromatography (long path column) eluting with pentane/cyclohexane 2:1 to 1:1 then cyclohexane gave 215 mg of pale yellow oil (51%, contains *ca.* 5% of impurity).

80 mg of pure 1-Bromo-4-(cyclobut-1-en-1-yl)benzene (**4a**) were also isolated (16%, based on amount of methylenecyclopropane substrate engaged).

The product may be crystallized from hot hexane (then cooled to r.t., 4 ºC and finally −30 ºC). 150 mg of oil crystallized to give 127 mg of colorless solid (85%).

M.p.: 90-92 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.81 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.50 (ddd, *J* = 8.7, 6.9, 1.9 Hz, 1H), 7.47 (ddd, *J* = 8.1, 6.8, 1.6 Hz, 1H), 7.30 - 7.24 (m, 3H), 7.11 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.05 - 7.01 (m, 2H), 6.17 (q, *J* = 2.1 Hz, 1H), 4.43 (app. tdt, *J* = 6.0, 4.7, 2.2 Hz, 1H), 2.88 - 2.77 (m, 1H), 2.75 - 2.66 (m, 2H), 2.08 - 2.01 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 144.2, 135.3, 133.8, 133.0, 131.7, 131.3, 129.3, 128.4, 127.1, 125.7, 125.5, 125.5, 125.1, 125.0, 119.6, 54.8, 34.7, 32.6.

HRMS-APCI: calculated for $C_{21}H_{18}Br$ $[M+H]^+$: 349.0586 & 351.0566; found: 349.0586 & 351.0567.

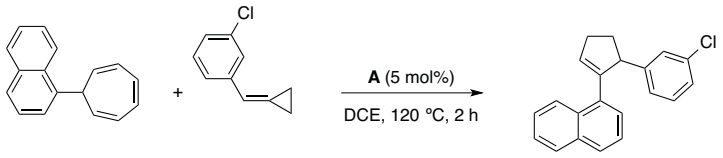
1-Bromo-4-(cyclobut-1-en-1-yl)benzene (4a)

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.33 (s, 1H), 2.81 - 2.78 (m, 2H), 2.52 (t, *J* = 2.5 Hz, 2H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.7, 134.4, 131.7, 128.6, 126.2, 121.4, 29.0, 26.6.

HRMS-APCI: calculated for $C_{10}H_{10}Br$ $[M+H]^+$: 208.9960 & 210.9940; found: 208.9957 & 210.9936.

1-(5-(3-Chlorophenyl)cyclopent-1-en-1-yl)naphthalene (5m)



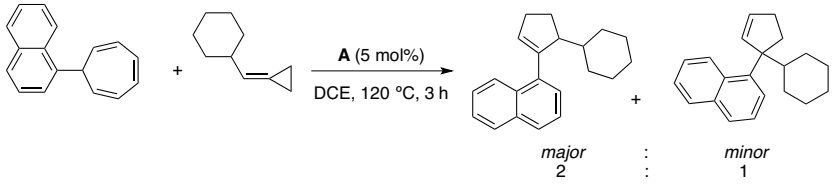
The title compound (colorless oil, 25.1 mg, yield: 82%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and 1-chloro-3-(cyclopropylidenemethyl)benzene (33 mg, 0.2 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.84 - 7.79 (m, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.54 - 7.44 (m, 2H), 7.30 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.20 - 7.18 (m, 1H), 7.14 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.07 - 6.99 (m, 3H), 6.19 (q, *J* = 2.1 Hz, 1H), 4.47 - 4.40 (m, 1H), 2.89 - 2.81 (m, 1H), 2.77 - 2.66 (m, 2H), 2.13 - 2.04 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 144.2, 135.2, 133.9, 133.8, 133.1, 131.7, 129.5, 128.4, 127.7, 127.1, 126.1, 125.7, 125.7, 125.5, 125.5, 125.1, 125.0, 55.1, 34.6, 32.6.

HRMS-APCI: calculated for $C_{21}H_{18}Cl$ $[M+H]^+$: 305.1092; found: 305.1088.

1-(5-Cyclohexylcyclopent-1-en-1-yl)naphthalene (5n, 5n´)



The title compound (colorless oil, 24 mg, overall yield: 87%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and (cyclopropylidenemethyl)cyclohexane (27 mg, 0.2 mmol) as

a 2:1 mixture of isomers. These two isomers can be partially separated by careful preparative TLC.

^{1}H NMR (400 MHz, $CDCl_3$, *major*) δ 8.20 - 8.16 (m, 1H), 7.90 - 7.85 (m, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.52 - 7.43 (m, 3H), 7.33 (dd, *J* = 7.1, 1.3 Hz, 1H), 5.92 (q, *J* = 2.2 Hz, 1H), 3.32 - 3.24 (m, 1H), 2.64 - 2.49 (m, 2H), 2.14 (dtd, *J* = 13.1, 9.0, 7.0 Hz, 1H), 1.95 (ddt, *J* = 13.2, 8.1, 5.2 Hz, 1H), 1.68 - 0.84 (m, 11H).

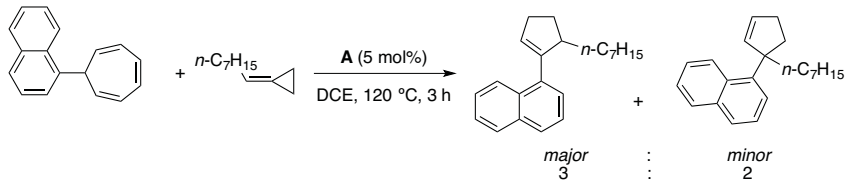
^{13}C NMR (101 MHz, $CDCl_3$, *major*) δ 144.6, 136.8, 133.9, 131.8, 131.5, 128.3, 126.8, 126.0, 125.5, 125.5, 125.2, 125.1, 54.4, 39.9, 32.8, 32.2, 27.0, 26.7, 26.6, 26.4, 25.2.

^{1}H NMR (400 MHz, $CDCl_3$, *minor*) δ 8.35 - 8.31 (m, 1H), 7.91 - 7.86 (m, 1H), 7.71 (dd, *J* = 6.9, 2.3 Hz, 1H), 7.52 - 7.44 (m, 2H), 7.39 - 7.34 (m, 2H), 6.23 (dt, *J* = 6.0, 2.1 Hz, 1H), 5.96 (dt, *J* = 5.9, 2.1 Hz, 1H), 2.82 - 2.71 (m, 1H), 2.48 - 2.38 (m, 3H), 2.34 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.99 - 1.91 (m, 1H), 1.86 - 1.78 (m, 1H), 1.65 - 0.84 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$, *minor*) δ 146.4, 135.1, 134.2, 131.0, 130.3, 129.4, 126.8, 126.7, 124.8, 124.7, 124.7, 124.5, 62.0, 46.8, 35.9, 33.4, 29.5, 28.3, 27.0, 27.0, 26.6.

HRMS-APCI: calculated for $C_{21}H_{25}$ $[M+H]^+$: 277.1951; found: 277.1950.

1-(5-Heptylcyclopent-1-en-1-yl)naphthalene (5o, 5o´)



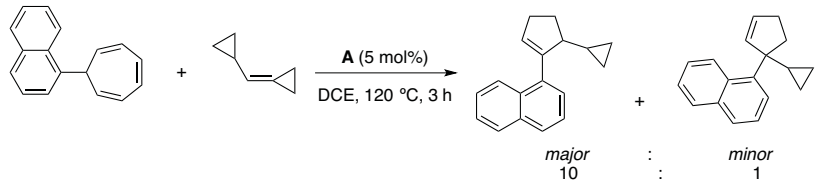
The title compound (colorless oil, 24.2 mg, overall yield: 83%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and octylidenecyclopropane (30 mg, 0.2 mmol) as a 3:2 mixture of isomers.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 - 8.31 (m, 1H *minor*), 8.15 - 8.09 (m, 1H *major*), 7.91 - 7.84 (m, 1H *major* + 1H *minor*), 7.77 (d, *J* = 8.3 Hz, 1H *major*), 7.73 (dt, *J* = 7.8, 1.1 Hz, 1H *minor*), 7.54 - 7.34 (m, 3H *major* + 4H *minor*), 7.31 (dd, *J* = 7.1, 1.3 Hz, 1H *major*), 6.29 (dt, *J* = 5.9, 1.7 Hz, 1H *minor*), 5.95 (dt, *J* = 5.6, 1.8 Hz, 1H *minor*), 5.85 (q, *J* = 2.2 Hz, 1H *major*), 3.28 - 3.15 (m, 1H *major*), 2.71 - 2.29 (m, 3H *major* + 2H *minor*), 2.18 (ddd, *J* = 13.5, 11.8, 4.5 Hz, 1H *minor*), 2.00 (ddd, *J* = 13.5, 12.0, 4.4 Hz, 1H *minor*), 1.77 (ddt, *J* = 12.7, 8.8, 6.4 Hz, 1H *major*), 1.48 - 0.75 (m, 15H *major* + 15H *minor*).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 145.4, 137.7, 136.8, 135.0, 133.7, 132.0, 131.2, 130.2, 129.5, 129.3, 128.2, 127.0, 126.8, 126.5, 126.0, 125.5, 125.2, 125.2, 125.2, 124.9, 124.8, 124.6, 124.1, 57.7, 49.2, 42.1, 37.5, 34.0, 32.7, 32.1, 31.8, 31.8, 30.2, 30.1, 29.7, 29.2, 29.1, 27.7, 25.6, 22.6, 14.1.

HRMS-APCI: calculated for $C_{22}H_{29}$ $[M+H]^+$: 293.2264; found: 293.2259.

1-(5-Cyclopropylcyclopent-1-en-1-yl)naphthalene (5p, 5p´)



The title compound (colorless oil, 24.5 mg, yield: 52% in total) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (44 mg, 0.2 mmol) and (cyclopropylidenemethyl)cyclopropane[131] (38 mg, 0.4 mmol) as a 10:1 mixture of isomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.04 (m, 1H *major*), 8.04 - 7.99 (m, 1H *minor*), 7.88 - 7.83 (m, 1H *major* + 1H *minor*), 7.76 (d, *J* = 8.2 Hz, 1H *major*), 7.59 (dt, *J* = 7.1, 1.2 Hz, 1H *minor*), 7.52 - 7.41 (m, 3H *major* + 4H *minor*), 7.35 (dd, *J* = 7.1, 1.3 Hz, 1H *major*), 6.84 (d, *J* = 11.8 Hz, 1H *minor*), 5.99 (d, *J* = 11.7 Hz, 1H *minor*), 5.83 (q, *J* = 2.3 Hz, 1H *major*), 2.70 - 2.48 (m, 3H *major* + 2H minor), 2.38 - 2.27 (m, 1H *major*), 1.88 (ddt, *J* = 12.8, 8.9, 5.8 Hz, 1H *major*), 1.02 (tt, *J* = 8.3, 5.2 Hz, 1H *minor*), 0.93 - 0.83 (m, 1H *minor*), 0.74 - 0.63 (m, 1H *major*), 0.34 - 0.16 (m, 1H *major* + 3H *minor*), 0.07 - −0.03 (m, 2H *major* + 2H *minor*), −0.25 - −0.33 (m, 1H *major*).

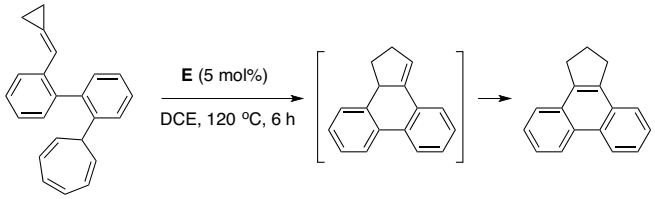
^{13}C NMR (101 MHz, $CDCl_3$, *major*) δ 146.5, 137.3, 133.6, 132.1, 130.3, 128.1, 126.7, 126.0, 125.5, 125.4, 125.4, 125.1, 54.0, 31.9, 30.2, 15.4, 4.1, 2.1.

Detected signals for minor isomer: δ 137.8, 128.2, 127.0, 126.5, 125.6, 125.5, 16.1, 12.7, 2.7.

HRMS-APCI: calculated for $C_{18}H_{19}$ $[M+H]^+$: 235.1481; found: 235.1480.

2,3-Dihydro-1*H*-cyclopenta[*l*]phenanthrene (5q)

[131] Prepared according to: Kopp, R.; Hanack, M. *Angew. Chem.* **1975**, *87*, 874–875



A solution of 2-(cyclohepta-2,4,6-trien-1-yl)-2'-(cyclopropylidenemethyl)-1,1'-biphenyl (60 mg, 0.2 mmol) and gold complex **E** (7.4 mg, 5 mol%) in 1,2-dichloroethane (DCE, 2 mL) was heated at 120 ºC in a sealed tube for 6 h. After the reaction mixture had been allowed to cool to room temperature, the solvent was removed *in vacuo* and the crude residue was purified by preparative TLC to obtain 19.8 mg of white solid (yield: 44%).

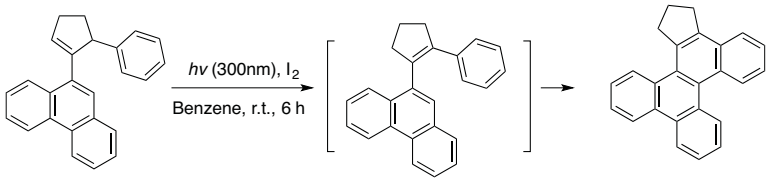
M.p.: 135-138 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 - 8.71 (m, 2H), 7.93 - 7.87 (m, 2H), 7.69 - 7.61 (m, 4H), 3.40 (t, *J* = 7.5 Hz, 4H), 2.39 (qui, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 130.1, 130.1, 126.6, 125.5, 124.9, 123.1, 32.3, 23.4.

HRMS-APCI: calculated for $C_{17}H_{15}$ $[M+H]^+$: 219.1168; found: 219.1159.

2,3-Dihydro-1*H*-benzo[*g*]cyclopenta[*p*]chrysene (5ff)



A solution of 9-(5-phenylcyclopent-1-en-1-yl)phenanthrene (48 mg, 0.15 mmol) and iodine (76 mg, 0.3 mmol) in 100 mL benzene was stirred in a Rayonet photochemical reactor under 300 nm light irradiation for 6 h. The solvent was removed *in vacuo* and the product (32 mg, white solid, yield: 67%) was obtained by preparative TLC.

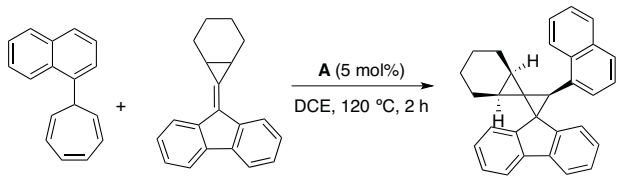
M.p.: 175-182 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8.0 Hz, 1H), 8.80 - 8.68 (m, 4H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.74 - 7.55 (m, 6H), 3.84 (t, *J* = 7.1 Hz, 2H), 3.44 (t, *J* = 7.2 Hz, 2H), 2.36 (qui, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 136.8, 130.9, 130.4, 130.1, 129.9, 129.6, 129.2, 127.7, 126.8, 126.6, 126.6, 126.2, 125.9, 124.8, 124.1, 123.4, 123.2, 38.5, 31.4, 26.1.

HRMS-APCI: calculated for $C_{25}H_{19}$ $[M+H]^+$: 319.1481; found: 319.1468.

(1*R,3'*R**,6*S**)-3'-(Naphthalen-1-yl)dispiro[bicyclo[4.1.0]heptane-7,1'-cyclopropane-2',9''-fluorene] (6)**



The title compound (white solid, 34 mg, yield: 85%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and 9-(bicyclo[4.1.0]heptan-7-ylidene)-9*H*-fluorene (52 mg, 0.2 mmol).

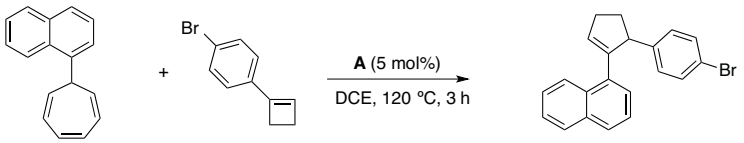
M.p.: 158-161 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 - 7.90 (m, 1H), 7.79 - 7.72 (m, 3H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.51 - 7.42 (m, 3H), 7.31 - 7.26 (m, 1H), 7.16 - 7.11 (m, 2H), 7.06 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 1H), 6.74 (td, *J* = 7.6, 1.1 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 3.80 (s, 1H), 2.35 (ddd, *J* = 9.1, 7.1, 2.1 Hz, 1H), 1.91 (ddd, *J* = 9.0, 7.2, 2.2 Hz, 1H), 1.81 - 1.56 (m, 4H), 1.02 - 0.89 (m, 2H), 0.60 - 0.50 (m, 1H), 0.49 - 0.38 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 142.5, 140.3, 140.3, 134.2, 133.7, 133.5, 128.1, 127.4, 126.5, 126.3, 126.1, 125.7, 125.7, 125.4, 125.1, 124.7, 124.2, 123.2, 121.2, 120.0, 119.5, 41.7, 35.9, 32.6, 21.1, 21.0, 20.8, 20.8, 14.0, 13.8.

HRMS-MALDI: calculated for $C_{31}H_{26}^{+\square}$ ($M^{+\square}$): 398.2029; found: 398.2010.

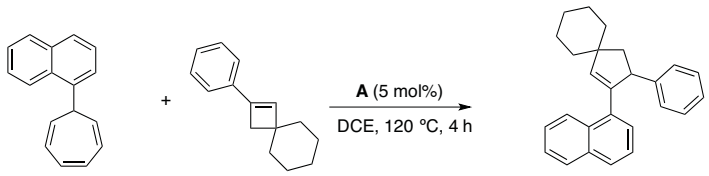
1-(5-(4-Bromophenyl)cyclopent-1-en-1-yl)naphthalene (5l)



1-(5-(4-Bromophenyl)cyclopent-1-en-1-yl)naphthalene (white solid, 27 mg, yield: 77%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and 1-bromo-4-(cyclobut-1-en-1-yl)benzene (42 mg, 0.2 mmol). The collected NMR data were identical to that

obtained previously from 1-(5-(4-bromophenyl)cyclopent-1-en-1-yl)naphthalene and 1-bromo-4-(cyclopropylidenemethyl)benzene.

2-(Naphthalen-1-yl)-3-phenylspiro[4.5]dec-1-ene (5r)



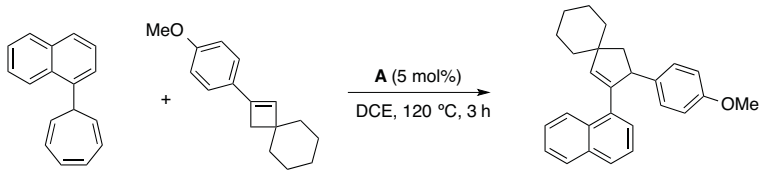
The title compound (colorless oil, 21.2 mg, yield: 63%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and 2-phenylspiro[3.5]non-1-ene (40 mg, 0.2 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.55 - 7.40 (m, 2H), 7.30 - 6.97 (m, 7H), 6.12 (s, 1H), 4.62 (t, *J* = 8.2 Hz, 1H), 2.61 (dd, *J* = 13.1, 8.4 Hz, 1H), 1.92 - 1.40 (m, 11H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 142.7, 141.2, 135.5, 133.8, 131.8, 128.4, 128.1, 127.9, 126.8, 125.8, 125.6, 125.6, 125.4, 125.1, 125.0, 53.8, 49.4, 47.4, 39.4, 36.9, 26.1, 23.7, 23.5.

HRMS-APCI: calculated for $C_{26}H_{27}$ $[M+H]^+$: 339.2107; found: 339.2105.

3-(4-Methoxyphenyl)-2-(naphthalen-1-yl)spiro[4.5]dec-1-ene (5s)



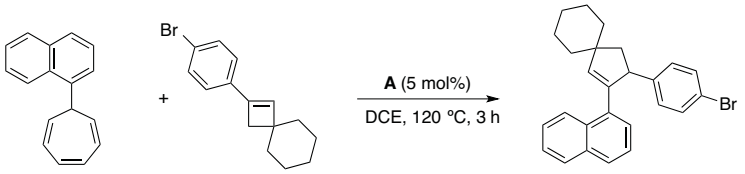
The title compound (colorless oil, 41 mg, yield: 74%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (33 mg, 0.15 mmol) and 2-(4-methoxyphenyl)spiro[3.5]non-1-ene (69 mg, 0.3 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.56 - 7.44 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 8.2 Hz, 2H), 6.12 (s, 1H), 4.62 (td, *J* = 8.3, 2.1 Hz, 1H), 3.68 (s, 3H), 2.62 (dd, *J* = 13.1, 8.4 Hz, 1H), 1.87 - 1.45 (m, 11H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 142.5, 141.6, 137.5, 135.6, 133.8, 131.8, 128.7, 128.4, 126.7, 125.6, 125.4, 125.2, 125.1, 113.6, 55.1, 53.0, 49.3, 47.5, 39.4, 37.0, 26.1, 23.7, 23.5.

HRMS-ESI: calculated for $C_{27}H_{29}O$ $[M+H]^+$: 369.2213; found: 369.2229.

3-(4-Bromophenyl)-2-(naphthalen-1-yl)spiro[4.5]dec-1-ene (5t)



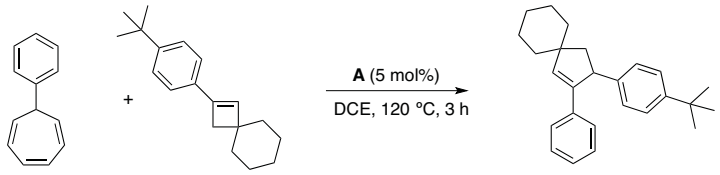
The title compound (colorless oil, 47.2 mg, yield: 75%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (33 mg, 0.15 mmol) and 2-(4-bromophenyl)spiro[3.5]non-1-ene (83 mg, 0.3 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.83 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.57 - 7.48 (m, 2H), 7.32 - 7.28 (m, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.18 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.17 (s, 1H), 4.63 (td, *J* = 8.4, 2.1 Hz, 1H), 2.63 (dd, *J* = 13.2, 8.5 Hz, 1H), 1.87 - 1.41 (m, 11H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 143.0, 140.8, 135.1, 133.9, 131.7, 131.3, 129.6, 128.5, 127.0, 125.8, 125.5, 125.4, 125.2, 125.0, 119.5, 53.3, 49.5, 47.3, 39.4, 36.9, 26.1, 23.7, 23.5.

HRMS-APCI: calculated for $C_{26}H_{26}Br$ $[M+H]^+$: 417.1212; found: 417.1202.

3-(4-(*tert*-Butyl)phenyl)-2-phenylspiro[4.5]dec-1-ene (5u)



The title compound (white solid, 14.5 mg, yield: 42%) was synthesized according to the general procedure from 7-phenylcyclohepta-1,3,5-triene (17 mg, 0.1 mmol) and 2-(4-(*tert*-butyl)phenyl)spiro[3.5]non-1-ene (51 mg, 0.2 mmol).

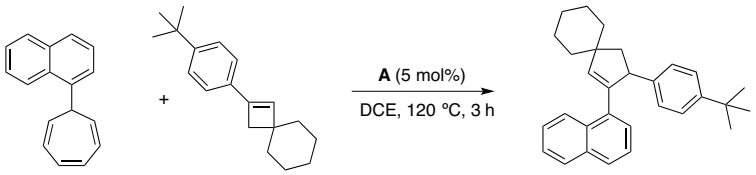
M.p.: 146-149 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.26 - 7.09 (m, 7H), 6.34 (d, *J* = 1.8 Hz, 1H), 4.45 - 4.38 (m, 1H), 2.48 (dd, *J* = 13.1, 9.2 Hz, 1H), 1.71 (dd, *J* = 13.1, 6.2 Hz, 1H), 1.63 - 1.34 (m, 10H), 1.29 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 143.2, 141.5, 138.5, 136.4, 128.0, 127.2, 126.5, 126.5, 125.2, 50.2, 48.6, 47.7, 38.7, 37.7, 34.3, 31.4, 26.0, 23.6, 23.4.

HRMS-APCI: calculated for $C_{26}H_{33}$ $[M+H]^+$: 345.2577; found: 345.2563.

3-(4-(*tert*-Butyl)phenyl)-2-(naphthalen-1-yl)spiro[4.5]dec-1-ene (5v)



The title compound (white solid, 40.5 mg, yield: 68%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (33 mg, 0.15 mmol) and 2-(4-(*tert*-butyl)phenyl)spiro[3.5]non-1-ene (76 mg, 0.3 mmol).

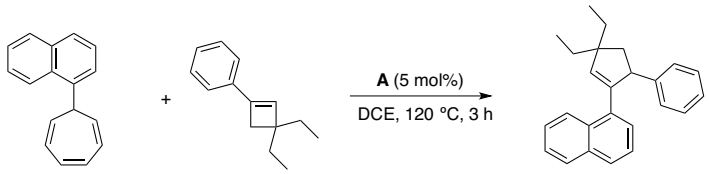
M.p.: 106-108 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.58 - 7.45 (m, 2H), 7.34 - 7.06 (m, 6H), 6.15 (s, 1H), 4.66 (t, *J* = 8.2 Hz, 1H), 2.63 (dd, *J* = 13.1, 8.4 Hz, 1H), 1.94 - 1.41 (m, 11H), 1.24 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 142.8, 142.3, 141.3, 135.7, 133.9, 131.9, 128.3, 127.4, 126.6, 125.8, 125.6, 125.4, 125.1, 125.1, 53.2, 49.3, 47.5, 39.4, 37.0, 34.3, 31.4, 26.1, 23.7, 23.5.

HRMS-APCI: calculated for $C_{30}H_{35}$ $[M+H]^+$: 395.2733; found: 395.2728.

1-(3,3-Diethyl-5-phenylcyclopent-1-en-1-yl)naphthalene (5w)



The title compound (white solid, 21 mg, yield: 43%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (33 mg, 0.15 mmol) and (3,3-diethylcyclobut-1-en-1-yl)benzene (56 mg, 0.3 mmol).

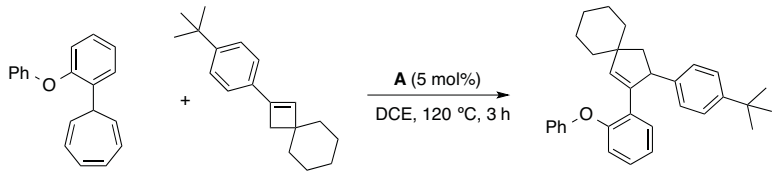
M.p.: 74-76 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.57 - 7.43 (m, 2H), 7.31 - 6.98 (m, 7H), 5.99 (d, *J* = 2.2 Hz, 1H), 4.67 (td, *J* = 8.4, 2.2 Hz, 1H), 2.46 (dd, *J* = 13.2, 8.5 Hz, 1H), 1.92 (dd, *J* = 13.2, 8.3 Hz, 1H), 1.80 - 1.55 (m, 4H), 1.10 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 142.4, 141.5, 135.6, 133.9, 131.8, 128.4, 128.2, 127.8, 126.7, 125.8, 125.7, 125.6, 125.4, 125.0, 54.5, 52.7, 45.2, 32.1, 31.5, 9.6, 9.3.

HRMS-APCI: calculated for $C_{25}H_{27}$ $[M+H]^+$: 327.2107; found: 327.2105.

3-(4-(*tert*-Butyl)phenyl)-2-(2-phenoxyphenyl)spiro[4.5]dec-1-ene (5x)



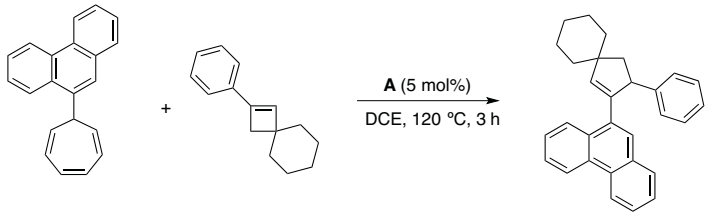
The title compound (colorless oil, 48 mg, yield: 73%) was synthesized according to the general procedure from 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene (39 mg, 0.15 mmol) and 2-(4-(*tert*-butyl)phenyl)spiro[3.5]non-1-ene (76 mg, 0.3 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.32 - 7.24 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.13 - 6.97 (m, 5H), 6.82 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.76 (dd, *J* = 8.7, 1.0 Hz, 2H), 6.31 (s, 1H), 4.61 - 4.47 (m, 1H), 2.40 (dd, *J* = 12.9, 8.7 Hz, 1H), 1.64 - 1.35 (m, 11H), 1.31 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 153.7, 148.1, 142.9, 142.5, 139.6, 130.3, 129.7, 129.4, 127.7, 127.5, 125.0, 123.6, 122.3, 120.1, 117.9, 51.5, 48.7, 47.9, 38.8, 36.8, 34.3, 31.5, 26.1, 23.7, 23.4.

HRMS-APCI: calculated for $C_{32}H_{37}O$ $[M+H]^+$: 437.2839; found: 437.2825.

9-(3-Phenylspiro[4.5]dec-1-en-2-yl)phenanthrene (5y)



The title compound (colorless oil, 31 mg, yield: 80%) was synthesized according to the general procedure from 9-(cyclohepta-2,4,6-trien-1-yl)phenanthrene (27 mg, 0.1 mmol) and 2-phenylspiro[3.5]non-1-ene (40 mg, 0.2 mmol).

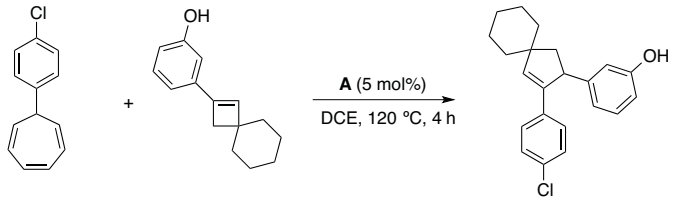
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 - 8.68 (m, 1H), 8.63 - 8.60 (m, 1H), 8.47 - 8.43 (m, 1H), 7.75 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.70 - 7.65 (m, 2H), 7.61 - 7.51 (m, 2H), 7.48 (s, 1H), 7.24 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.14 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.07 -

7.00 (m, 1H), 6.20 (d, *J* = 2.1 Hz, 1H), 4.79 - 4.71 (m, 1H), 2.69 (dd, *J* = 13.2, 8.6 Hz, 1H), 1.93 (dd, *J* = 13.2, 7.8 Hz, 1H), 1.88 - 1.48 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 142.9, 141.6, 134.0, 131.5, 131.1, 130.6, 129.5, 128.4, 128.2, 127.9, 126.5, 126.3, 126.3, 126.1, 126.1, 125.9, 125.9, 122.9, 122.3, 54.0, 49.4, 47.4, 39.3, 37.1, 26.1, 23.8, 23.5.

HRMS-APCI: calculated for $C_{30}H_{29}$ $[M+H]^+$: 389.2264; found: 389.2278.

3-(3-(4-Chlorophenyl)spiro[4.5]dec-3-en-2-yl)phenol (5z)



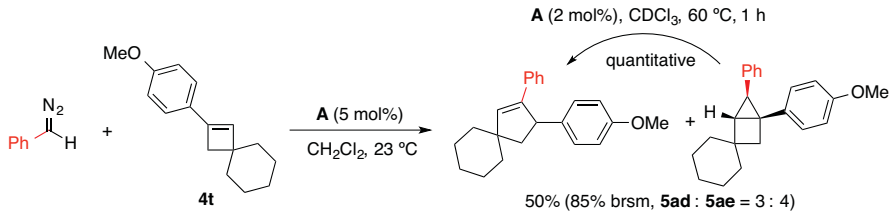
The title compound (colorless oil, 35 mg, yield: 69%) was synthesized according to the general procedure from 7-(4-chlorophenyl)cyclohepta-1,3,5-triene (61 mg, 0.3 mmol) and 3-(spiro[3.5]non-1-en-2-yl)phenol (32 mg, 0.15 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.65 - 6.61 (m, 2H), 6.33 (s, 1H), 4.75 (s, 1H), 4.34 (ddd, *J* = 9.2, 6.2, 1.8 Hz, 1H), 2.49 (dd, *J* = 13.2, 9.2 Hz, 1H), 1.72 (dd, *J* = 13.2, 6.2 Hz, 1H), 1.63 - 1.38 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 148.2, 140.1, 139.3, 134.6, 132.3, 129.7, 128.2, 127.7, 120.4, 114.4, 112.9, 50.6, 48.8, 47.3, 38.6, 37.6, 26.0, 23.5, 23.3.

HRMS-APCI: calculated for $C_{22}H_{24}ClO$ $[M+H]^+$: 339.1510; found: 339.1507.

3-(4-Methoxyphenyl)-2-phenylspiro[4.5]dec-1-ene (5ad)



To the 1 mL CH_2Cl_2 solution of 2-(4-methoxyphenyl)spiro[3.5]non-1-ene (34 mg, 0.15 mmol) and gold complex **A** (5.5 mg, 5 mol%) was added phenyl diazomethane[132] (0.21 M in toluene, 1.43 mL, 0.3 mmol) by syringe pump, over 1 h,

[132] Prepared and titrated according to reference: Zhou, Y.; Trewyn, B. G.; Angelici, R. J.; Woo, L. K. *J. Am. Chem. Soc*. **2009**, *131*, 11734–11743.

at room temperature. After addition, stirring was continued for 0.5 h. After removing the solvent, the starting material 2-(4-methoxyphenyl)spiro[3.5]non-1-ene (14 mg) and the product (24 mg, colorless oil, 3 : 4 mixture, overall yield: 50%, 85% brsm) were obtained by preparative TLC.

To this mixture (20 mg, 0.063 mmol) in 1 mL $CDCl_3$ was added gold complex **A** (1 mg, 2 mol%) and the solution was heated at 60 ºC for 1 h. After filtering through a short silica gel column, the product 3-(4-methoxyphenyl)-2-phenylspiro[4.5]dec-1-ene (**5ad**) was collected (colorless oil, 20 mg, yield: quantitative).

3-(4-Methoxyphenyl)-2-phenylspiro[4.5]dec-1-ene (5ad)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.29 (m, 2H), 7.22 - 7.17 (m, 2H), 7.14 - 7.10 (m, 3H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.32 (d, *J* = 1.9 Hz, 1H), 4.39 (ddd, *J* = 9.2, 6.1, 1.8 Hz, 1H), 3.76 (s, 3H), 2.47 (dd, *J* = 13.1, 9.2 Hz, 1H), 1.68 (dd, *J* = 13.1, 6.1 Hz, 1H), 1.63 - 1.40 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 141.6, 138.5, 138.4, 136.3, 128.6, 128.1, 126.6, 126.5, 113.8, 55.1, 49.9, 48.6, 47.7, 38.7, 37.8, 26.0, 23.6, 23.4.

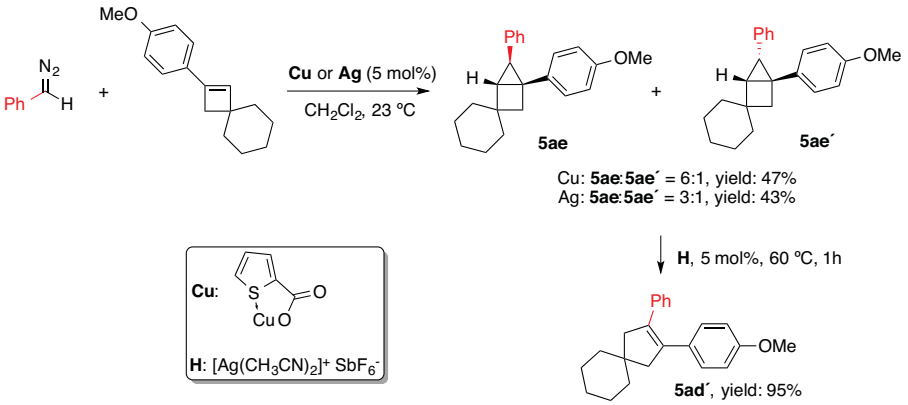
HRMS-APCI: calculated for $C_{23}H_{27}O$ $[M+H]^+$: 319.2056; found: 319.2058.

Signals detected in the mixture for:

(1*R,4*R**,5*R**)-4-(4-methoxyphenyl)-5-phenylspiro[bicyclo[2.1.0]pentane-2,1'-cyclohexane] (5ae)**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 - 7.09 (m, 3H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.91 - 6.87 (m, 2H), 6.70 (d, *J* = 8.6 Hz, 2H), 3.74 (s, 3H), 2.72 (s, 1H), 2.27 (s, 1H), 1.67 - 1.25 (m, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 139.3, 131.8, 130.0, 128.0, 127.6, 125.2, 113.2, 55.1, 44.1, 39.4, 37.4, 37.4, 36.3, 33.7, 32.6, 26.3, 23.2, 22.7.



To the 0.8 mL CH_2Cl_2 solution of 2-(4-methoxyphenyl)spiro[3.5]non-1-ene (28 mg, 0.12 mmol) and copper(I) thiophene-2-carboxylate (1.1 mg, 5 mol%) was added phenyl diazomethane (0.21 M in toluene, 1.1 mL, 0.24 mmol) by syringe pump, over 1 h, at room temperature. After addition, stirring was continued for 0.5 h. After removing the solvent, the product (18 mg, colorless oil, **5ae**:**5ae´**=6:1 mixture, overall yield: 47%) was obtained by preparative TLC.

To the 0.8 mL CH_2Cl_2 solution of 2-(4-methoxyphenyl)spiro[3.5]non-1-ene (28 mg, 0.12 mmol) and silver complex **H** (2.6 mg, 5 mol%) was added phenyl diazomethane (0.21 M in toluene, 1.1 mL, 0.24 mmol) by syringe pump, over 1 h, at room temperature. After addition, stirring was continued for 0.5 h. After removing the solvent, the product (16 mg, colorless oil, **5ae**:**5ae´**=3:1 mixture, overall yield: 43%) was obtained by preparative TLC.

Signals detected in the mixture for **5ae´**:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 - 6.80(m, 5H), 3.83 (s, 3H), 2.79 (d, *J* = 6.5 Hz, 1H), 2.18 (d, *J* = 6.5 Hz, 1H), 1.67 - 1.25 (m, 12H).

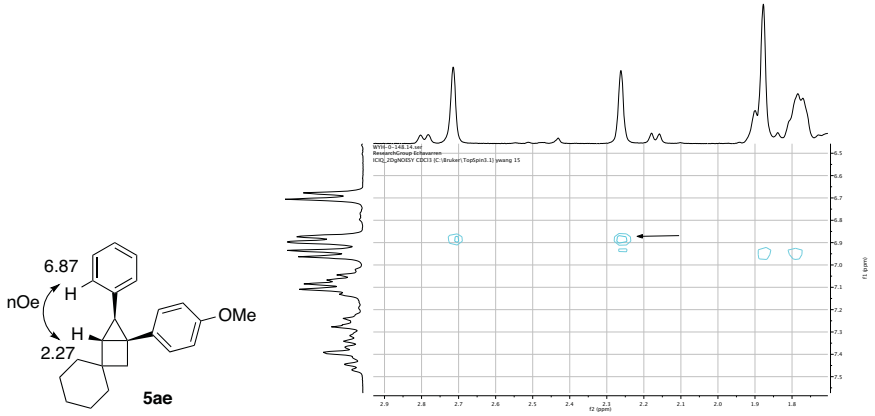
^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 131.8, 130.6, 128.6, 128.0, 127.5, 125.5, 113.7, 62.9, 55.3, 40.6, 37.7, 37.1, 36.6, 32.2, 28.4, 26.2, 23.1, 22.9.

To this mixture (16 mg, 0.05 mmol) in 1 mL $CDCl_3$ was added gold complex **H** (1 mg, 5 mol%) and the solution was heated at 60 ºC for 1 h. After filtering through a short silica gel column, the product **5ad´** was collected (colorless oil, 15 mg, yield: 95%).

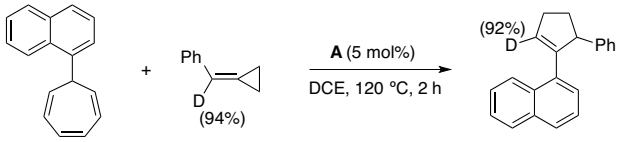
NMR for **5ad´**:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 - 7.16 (m, 5H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.71 (s, 4H), 1.66 - 1.41 (m, 10H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 139.0, 135.0, 134.4, 131.0, 129.2, 128.1, 128.0, 126.3, 113.4, 55.2, 51.5, 39.9, 38.6, 26.2, 23.5.



***d*-1-(5-Phenylcyclopent-1-en-1-yl)naphthalene (5a-d_1)**



The title compound (white solid, 25.1 mg, yield: 72%) was synthesized according to the general procedure from 1-(cyclohepta-2,4,6-trien-1-yl)naphthalene (22 mg, 0.1 mmol) and (cyclopropylidenemethyl-*d*)benzene (26 mg, 0.2 mmol).

M.p.: 73-75 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.83 - 7.80 (m, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.55 - 7.46 (m, 2H), 7.32 - 7.28 (m, 1H), 7.23 - 7.14 (m, 5H), 7.12 - 7.06 (m, 1H), 6.19 (q, residual signal 8%), 4.49 (ddt, *J* = 8.3, 4.9, 2.7 Hz, 1H), 2.92 - 2.82 (m, 1H), 2.79 - 2.67 (m, 2H), 2.18 - 2.06 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 144.6, 135.7, 133.8, 132.5 (t, *J* = 25.0 Hz), 131.8, 128.3, 128.2, 127.6, 126.9, 125.9, 125.7, 125.6, 125.4, 125.1, 125.1, 55.4, 34.9, 32.5.

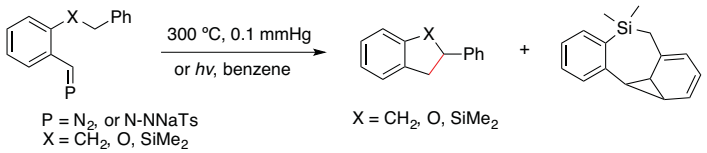
HRMS-APCI: calculated for $C_{21}H_{18}D$ $[M+H]^+$: 272.1544; found: 272.1544.

Chapter 3. Formal C-H insertions of gold carbenes

Background

Various selective C-H bond functionalization methods[133] developed in recent years have rapidly become powerful tools for direct C-C bond constructions. Among them, methods for the intramolecular insertion of metal-carbene complexes into C-H bonds[134] have attracted much attention due to their specificity in terms of both regio- and stereo-chemical control.

There have been many publications in this area that focus on the use of diazo derivatives or analogues as carbene precursors (shown below). Competitive reactions with side-chain C-H bonds and phenyl groups are anticipated for reactions involving such reactants. It has been known that neighboring heteroatoms influence the reactivity of the C-H bonds as well as that of the carbene.[135] Pyrolysis of tosylhydrazone sodium salts or photolysis of diazo derivatives (with X = CH_2, O) gave C-H insertions (Scheme 3-1). Surprisingly, substrates with a silicon tethering group afforded a mixture under the same conditions. Along with the expected 1,1-dimethylsilacyclopentane, a norcaradiene derivative, instead of its cycloheptatriene-form, was identified as the other major component, which was generated by a cyclopropanation of the terminal phenyl group.



Scheme 3- 1

When silicon was used as linking group, six-membered ring formation through C-H insertion of the carbene is possible, albeit with low selectivity (Scheme 3-2).[135]

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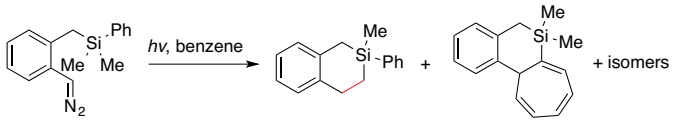
[133] (a) Shilov, A. E.; Shul´pin, G. B. *Chem. Rev*. **1997**, *97*, 2879–2932. (b) Dick, A. R.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 2439–2463. (c) Godula, K.; Sames, D. *Science* **2006**, *312*, 67–72. (d) Bergman, R. G. *Nature* **2007**, *446*, 391–393. (e) Dyker, G. (ed.) Handbook of C–H Transformations Vols 1 & 2, Wiley–VCH, Weinheim, **2005**.

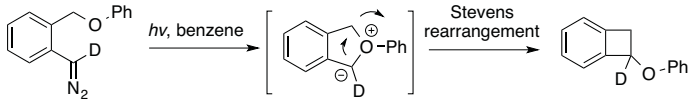
[134] For reviews: (a) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417–424. (b) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861–2903. (c) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911–936.

[135] Kirmse, W.; Konrad, W.; Özkir, I. S. *Tetrahedron* **1997**, *53*, 9935–9964.



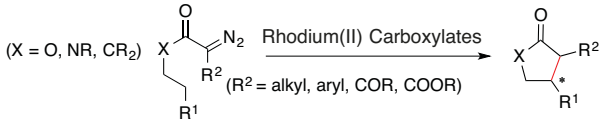
Scheme 3- 2

An ylide can also be generated from the substrates with a judiciously positioned heteroatom. In the case shown in Scheme 3-3, subsequent Stevens rearrangement gives rise to 7-phenoxybicyclo[4.2.0]octa-1,3,5-triene. A direct C-H insertion pathway was excluded by the deuterium labeling experiment (Scheme 3-3).[135]



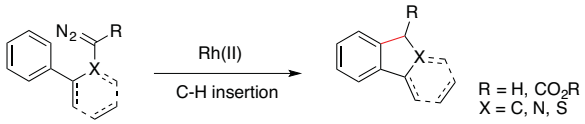
Scheme 3- 3

When chiral metal complexes (mainly rhodium-based) were involved, enantioselective sp^3 C-H insertion products were obtained in good yields under mild conditions.[134b] In general, formation of five-membered rings dominates.



Scheme 3- 4

Metal carbenes (mainly rhodium derivatives) can also undergo sp^2 C-H insertion to form fluorene-type of products in good yields. Reactions of this type generally tolerate a wide range of functional groups.[136]

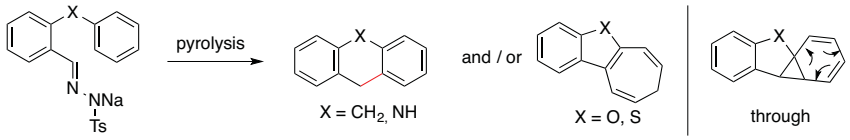


Scheme 3- 5

Interestingly, the formation of six-membered rings in such intramolecular C-H insertion reactions is more difficult and often leads to a mixture of several compounds. The constitution of the products depends largely on the nature of the

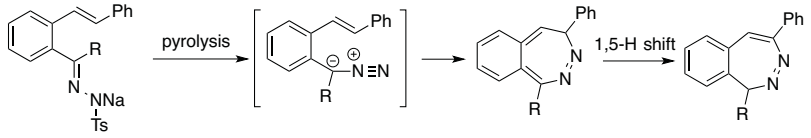
[136] (a) Hrytsak, M.; Etkin, N.; Durst, T. *Tetrahedron Lett.* **1986**, *27*, 5679–5682; (b) Doyle, M. P.; Shanklin, M. S.; Pho, H. Q.; Mahapatro, S. N. *J. Org. Chem.* **1988**, *53*, 1017–1022; (c) Kim, J.; Ohk, Y.; Park, S. H.; Jung, S.; Chang, S. *Chem. Asian J.* **2011**, *6*, 2040–2047 and references cited therein.

tethering group.[137] When tosylhydrazone sodium salts, with CH_2 or NH as linking group, were pyrolyzed, the desired C-H insertions occurred preferentially. Conversely, for substrates tethered by O or S, benzo[*b*]cyclohepta[*d*]furans or benzo[*b*]cyclohepta[*d*]thiophenes and their tautomers were obtained. It seems likely that such products arise from Buchner insertion into the aromatic ring, followed by electrocyclic ring-opening and 1,5-hydrogen migration (Scheme 3-6).



Scheme 3- 6

Based on the precedent for C-H insertions discussed above, one might expect that similar reactivity could occur between metal carbenes and the C-H bonds of olefins. To our surprise, however, no example of alkenyl C-H insertion has ever been reported starting from diazo derivatives. In one case, 1,7-electrocyclization followed by 1,5-hydrogen shift was observed instead, to give 1*H*-2,3-benzodiazepines (Scheme 3-7).[138] This study demonstrates that diazo derivatives serve as a 1,3-dipoles, rather than carbene precursors, towards reactions with alkenes that are predisposed to undergo intramolecular cyclization.



Scheme 3- 7

An interesting intramolecular reductive coupling of CF_3 group and C-H bond was reported (Scheme 3-8).[139] The substrates undergo a low-valent niobium-mediated formal dehydrofluorination from benzylic C-F bond and aromatic ortho C-H bond to form 9,9-difluorofluorene intermediates. The final fluorenes were obtained by *in situ* reduction, and a formal "carbene-like" C-H insertion transformation was achieved through this reductive coupling procedure.

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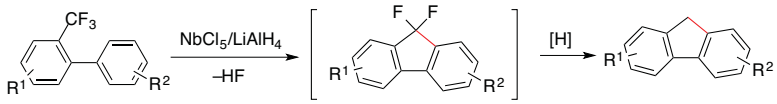
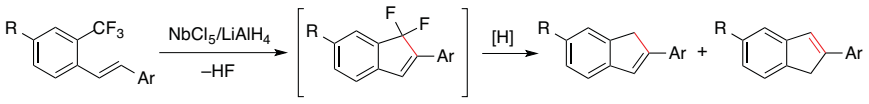
[137] Crow, W. D.; McNab, H. *Aust. J. Chem.* **1981**, *34*, 1037–1350.
[138] (a) Munro, D. P.; Sharp, J. T. *J. Chem. Soc. Perkin Trans. 1.* **1984**, 849–858. (b) Munro, D. P.; Sharp, J. T. *Tetrahedron Lett.* **1980**, *21*, 4109–4110. (c) Padwa, A.; Ku, H. *J. Org. Chem.* **1980**, *45*, 3756–3766. (d) Reid, A. A.; Sharp, J. T.; Sood, H. R.; Thorogood, P. B. *J. Chem. Soc. Perkin Trans. 1.* **1973**, 2543–2551. (e) Blake, A. J.; Harding, M.; Sharp, J. T. *J. Chem. Soc. Perkin Trans. 1.* **1994**, 3149–3161.
[139] Fuchibe, K.; Akiyama, T. *J. Am. Chem. Soc.* **2006**, *128*, 1434–1435.



Scheme 3- 8

Similarly, indenes can also be obtained by this reaction (Scheme 3-9).[140] However, when a labeling group was anchored to desymmetrize the product, a mixture of two isomers was obtained. The exact mechanism for this formal isomerization is still unknown.

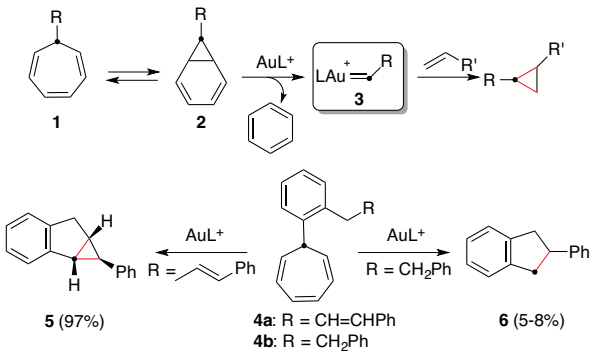


Scheme 3- 9

[140] Fuchibe, K.; Mitomi, K.; Akiyama, T. *Chem. Lett.* **2007**, *36*, 24–25.

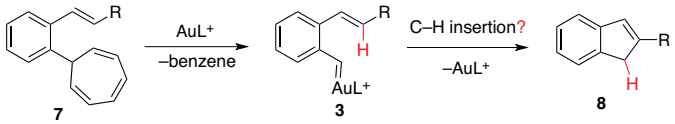
Objectives

We recently found that 7-substituted 1,3,5-cycloheptatrienes **1** react with cationic gold(I) complexes under catalytic conditions through their norcaradiene tautomers **2** to generate gold(I) carbenes **3**. These gold(I) carbenes can be trapped by alkenes inter- or intramolecularly. However intramolecular sp^3 C-H insertion of gold(I) carbenes were found not to be effective, and the desired product **6** was obtained only as a minor product (Scheme 3-10).[141]



Scheme 3- 10

Based on our own research, we postulated that gold(I) carbenes generated by retro-Buchner reaction may undergo this sp^2 C-H insertion to give indenes more easily. (Scheme 3-11) and that fluorenes could be also obtained by a similar procedure.



Scheme 3- 11 C-H insertion.

Although much has been done to advance our understanding of the C-H insertion of carbenes, as shown in the introduction of this chapter, previous attempts to perform intramolecular C-H insertion of carbenes to form indenes from diazo derivatives failed. This appears to be a consequence of the tendency of diazo compounds to serve as 1,3-dipoles instead of carbene precusors.

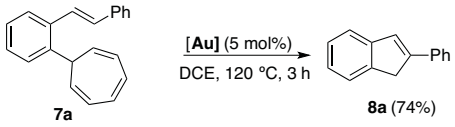
[141] See chapter 1 of this thesis for details.

Results and discussions

Formation of indenes

We subjected 7-arylcycloheptatriene substrate **7a**, which features an olefin in the *ortho* position, to our standard gold(I)-catalyzed retro-Buchner reaction conditions (see Chapter 1). To our delight, the desired product, 2-phenyl-1*H*-indene (**8a**), was obtained with nearly the same yields using cationic gold(I) complexes **A**, **B**, and **E**. We chose [JohnPhosAu(MeCN)]SbF_6 (**A**) as the catalyst for further scope investigation since it is commercially available and generally robust (Table 3-1).

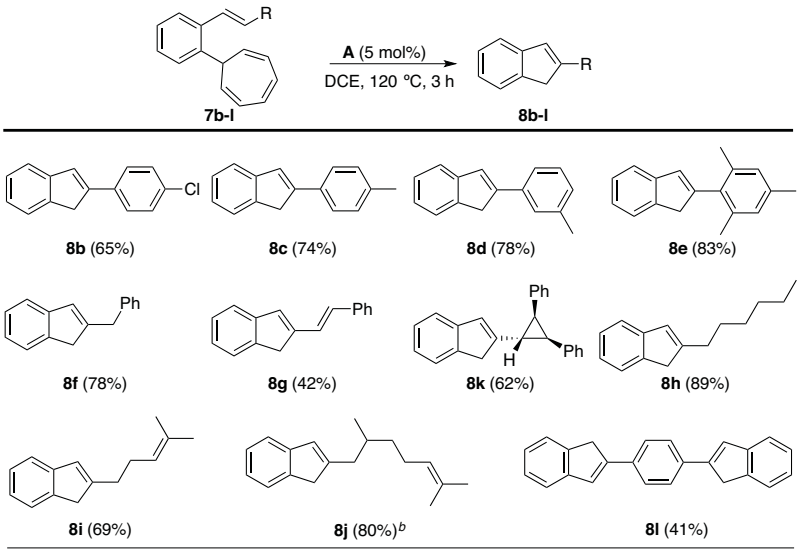
Table 3- 1 indene 8a formation.



[Au]	**8a** (yield) [a]
A	86%
B	86%
C	67%
D	8%
E	85%

[a] Determined by ^{1}H NMR using 1,4-diacetylbenzene as internal standard.

Table 3- 2 Reaction scope. [a]

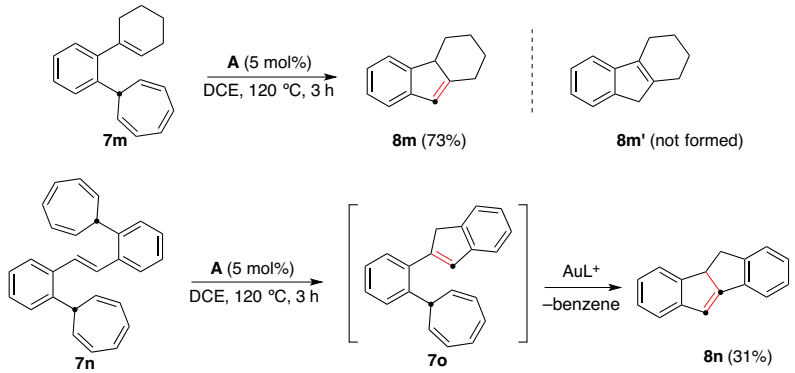


[a] Reaction at 120 °C (0.1 M in DCE), **A** (5 mol%), 3 h, isolated yields are reported. [b] Reaction with catalyst **E** (5 mol%), 12 h.

With the best conditions in hand, the reaction scope was studied in detail. As illustrated in Table 3-1, this reaction proceeds in a rather general manner. Many

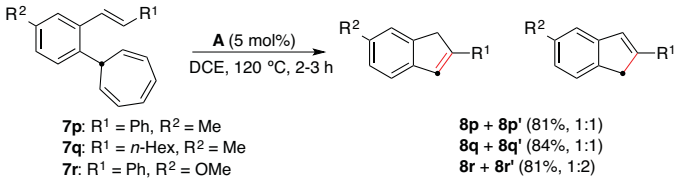
substituents, such as aryl (**8b-e**), alkyl (**8f**, **8h**), alkenyl (**8g**), or even cyclopropyl (**8k**) groups are tolerated. In the cases of **8i** and **8j**, only the closest double bond reacts with the carbene intermediate. The highly insoluble 1,4-di(1*H*-inden-2-yl)benzene **8l** could also be isolated in moderate yield in a double annulation reaction.

At first glance, indenes **8a-l** appear to have been formed by a Csp^2-H insertion of a gold(I) carbene intermediate. However, the annulation of **7m** gave exclusively 2,3,4,4*a*-tetrahydro-1*H*-fluorene (**8m**). The more stable isomer **8m′**,[142] which was the expected product of direct C-H insertion, was not observed (Scheme 3-12). Similarly, symmetrical derivative **7n** underwent two sequential retro-Buchner reactions (via intermediate **7o**) to give 4*b*,5-dihydroindeno[2,1-*a*]indene (**8n**). These results excluded the direct C-H insertion of a gold(I) carbene as the mechanism for this reaction.



Scheme 3- 12 Direct C-H insertion mechanism was excluded.

To gain further mechanistic insight, we performed the following experiments (Scheme 3-13).



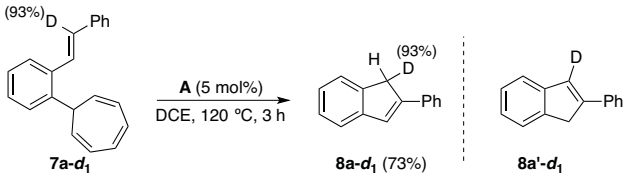
Scheme 3- 13 Unsymmetrical indenes formation.

Substrates (**7p**, **7q**) led to 1:1 mixtures of indenes **8p**/**8p′** and **8q**/**8q′**. By performing the reaction at lower temperature (100 °C for 3 h, with 57% conversion), a 1:1

[142] Based on DFT calculations (B3LYP, 6–31G(d)), isomer **8m'** is 5.6 kcal·mol^{-1} more stable than **8m**.

regioisomeric ratio was also obtained. Interestingly, **7r**, with strong electron-donating group, gave a higher selectivity (**8r´** as the major isomer). This result suggests that an electrophilic addition of a gold(I) carbene to the alkene may operate in these systems.

The regioisomeric indenes **8p´**, **8q´**, and **8r´** could have arisen from isomerization of **8p**, **8q**, and **8r** by two consecutive [1,5]-H sigmatropic migrations[143] (or the other way around). However, reaction of **7a-*d*$_1$** with catalyst **A** led exclusively to **8a-*d*$_1$** with the deuterium label at the methylene, which is not consistent with an isomerization via [1,5]-H sigmatropic migrations that would have also formed **8a´-*d*$_1$** (Scheme 3-14). Additionally, no deuterium incorporation was observed when performing the reaction of **7a** in 1,2-dichloroethane saturated with D_2O. Finally, no kinetic isotope effect[144] was observed in the reaction of a 1:1 mixture of **7a** and **7a-*d*$_1$** with gold(I) complex **A** at 100 °C.[145]



Scheme 3- 14 Deuterated experiment.

DFT calculations

Based on all of those experimental results, we studied computationally the formation of model indenes **8s** and **8t** from the corresponding gold(I) carbenes by the DFT methods at the M06 level including solvent effects for 1,2-dichloroethane (Scheme 3-15). After the retro-Buchner reaction, highly electrophilic gold(I) carbenes **Ia-b** (L = PMe_3) react intramolecularly with the alkene through **TS$_{Ia-IIa}$** and **TS$_{Ib-IIb}$** in highly exothermic processes to form benzylic carbocations **IIa-b**. Despite being formally a 5-*endo-trig* cyclization from the perspective of the alkene,[146] the high electrophilicity of the gold(I) carbenes renders this process kinetically and thermodynamically favorable.

---

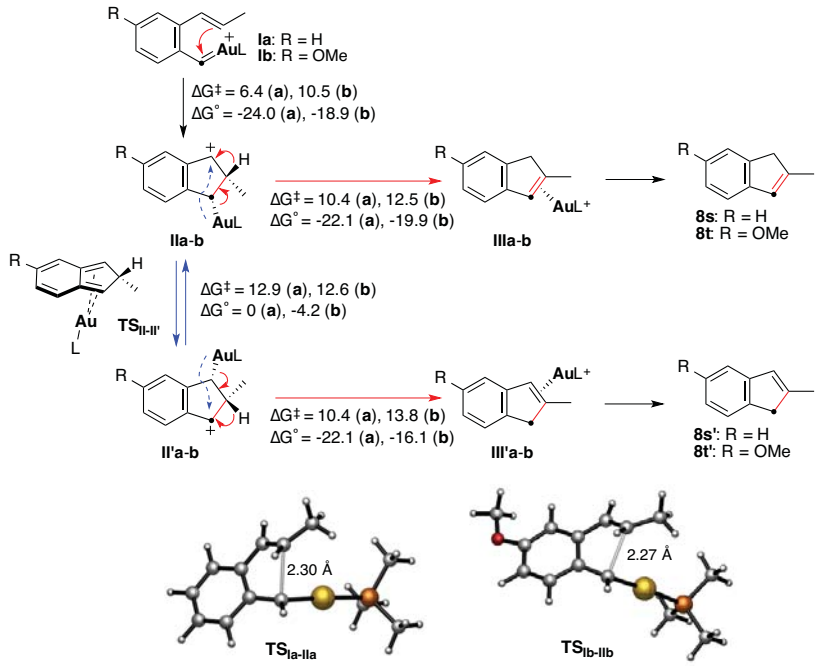
[143] (a) Roth, W. R. *Tetrahedron Lett.* **1964**, 1009–1013. (b) Miller, L. L.; Greisinger, R.; Boyer, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 1578–1580. (c) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187–217.

[144] Recent essay on the interpretation of deuterium kinetic isotope effects (KIE) in C–H Bond functionalizations by transition-metal complexes: Simmons, E. M.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2012**, *51*, 3066–3072.

[145] A high barrier (free energy of activation = 38.7 kcal·mol^{-1}) was calculated for the first [1,5]-H migration to form the intermediate isoindene, which is higher than that required for the generation of the gold(I) carbene by retro-Buchner reaction.

[146] 5-*Endo-trig* cyclizations for the formation of indenes are very rare processes: Ichikawa, J.; Sakoda, K.; Mihara, J.; Ito, N. *J. Fluor. Chem.* **2006**, *127*, 489–504.

DFT calculations show that intermediates **II** can evolve into **II´** by a formal metal migration from C-1 to C-3, which actually corresponds to a suprafacial 1,4-metalotropic migration.[147] Whereas for intermediate **IIa** this migration is degenerate, in the case of the *p*-OMe substituted substrate, **II´b** is 4.2 kcal·mol^{-1} more stable than **IIb** as a result of the stabilization of the benzylic carbocation by the *p*-MeO group. Transitions states $\mathbf{TS_{II\text{-}II'}}$ for the 1,4-metalotropic migration show a η^4-(2*H*-indene)Au(I) structure, with shorter distances from the metal center to the internal carbons C4a-C7a (2.51-2.54 Å) than to C1 and C3 (2.86-2.88 Å). The experimental results support the DFT calculations. Thus, in Scheme 3-3, for R=Me (**8p**/**8p´**, **8q**/**8q´**) the regioisomeric ratios are 1:1. Whereas for R=OMe (**8r**/**8r´**), because intermediate **II´b** is more stable, the ratio is 1:2 favoring the formation of **8r´**.

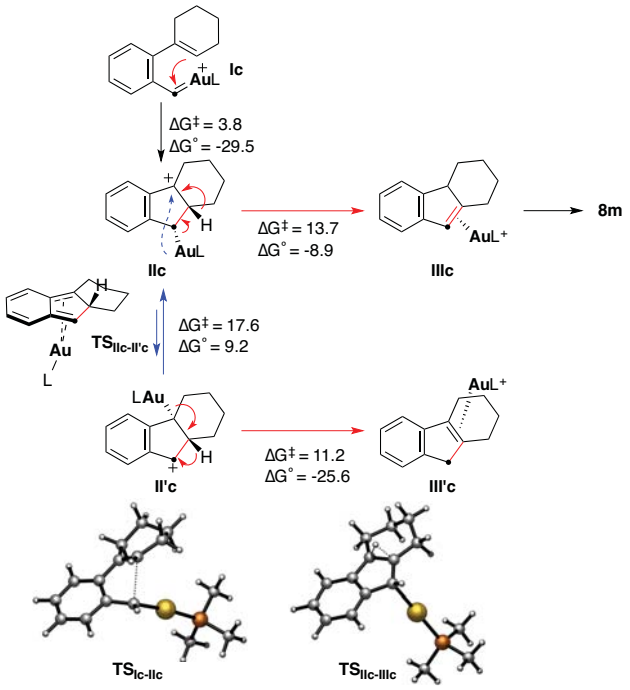


Scheme 3- 15 DFT calculations.

To study in detail why **8m** and **8n** were exclusively formed in Scheme 3-12, DFT calculations were carried out (Scheme 3-16). According to DFT calculations, the formation of 2,3,4,4*a*-tetrahydro-1*H*-fluorene (**8m**) followed a similar pathway by the intramolecular electrophilic attack of the gold(I) carbene on the alkene in **Ic** to form intermediate **IIc**, which undergoes 1,2-H shift to give η^2-alkene Au(I) complex

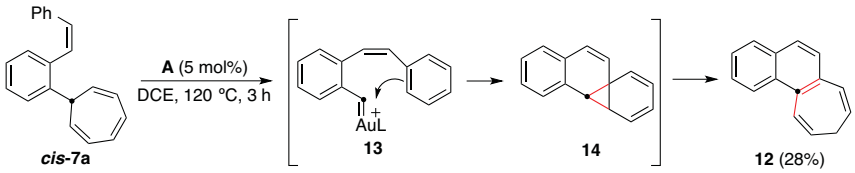
[147] For other 1,n-metal migrations, which are mechanistically unrelated, see the following lead references: (a) Zhang, J.; Liu, J.-F.; Ugrinov, A.; Pillai, A. F. X.; Sun, Z. M.; Zhao, P. *J. Am. Chem. Soc.* **2013**, *135*, 17270–17273. (b) Ikeda, Y.; Takano, K.; Kodama, S.; Ishii, Y. *Chem. Comm.* **2013**, *49*, 11104–11106.

IIIc. In this case, however, the energy required for the suprafacial 1,4-metalotropic migration (**IIc** to **II´c**) was found to be 3.9 kcal·mol^{-1} higher than that of the 1,2-H shift and moreover **II´c** is destabilized with respect to **IIc**, which explains the selective formation of **8m** over more stable **8m´** from **7m**.



Scheme 3- 16 DFT calculations.

Surprisingly, ***cis*-7a** did not behave in the same manner as its *trans* isomer in the presence of catalyst **A** (Scheme 3-17).

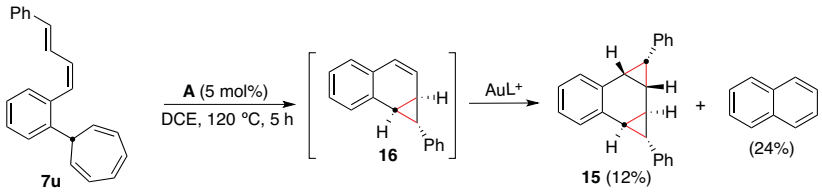


Scheme 3- 17 *Cis*-substrate reacts differently.

Presumably, as a result of the proximity of the phenyl ring to the gold carbene in intermediate **13**, an intramolecular Buchner reaction takes place preferentially to

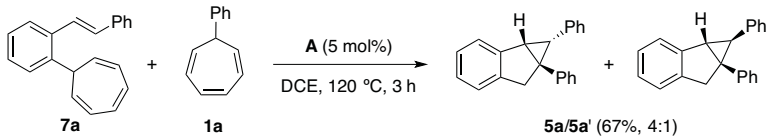
form **14**, which then undergoes disrotatory norcaradiene to cycloheptatriene opening, followed by a 1,5-H shift, to give **12**.[148]

The gold carbene generated from *cis*-substrate **7u** is cyclopropanated by alkene intramolecularly to give intermediate **16**. Subsequently, naphthalene is released and the concomitantly formed reactive gold carbene ($PhCH{=}AuL^+$) trapped by **16** to give **15** (Scheme 3-18).[149]



Scheme 3- 18

In our previous study[6] we found that indenes are suitable substrates for intermolecular cyclopropanation by gold-carbenes generated in a retro-Buchner reaction. An efficient tandem transformation was achieved by combining indene formation and intermolecular cyclopropanation with $[LAu{=}CHPh]^+$ by reacting **7a** with **1a** to give **5a** and **5a´** in a 4:1 ratio (67% yield) (Scheme 3-19).



Scheme 3- 19 Tandem reaction.

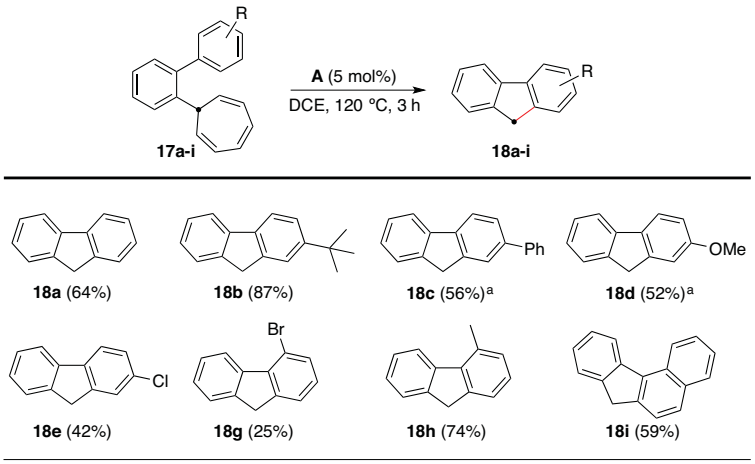
Formation of fluorenes

o-Biphenyl gold(I) carbenes generated by retro-Buchner reactions behave like free carbenes leading to fluorenes. Thus, reaction of 2-cycloheptatrienyl biphenyls **17a-i** with catalysts **A** or **B** gave fluorenes **18a-i** in moderate to good yields by a Friedel-Craft-type methylenation reaction (Table 3-3).[150] The annulation proceeded satisfactorily with substituents at different positions, although fluorene **18g**[151] was obtained in low yield.

---

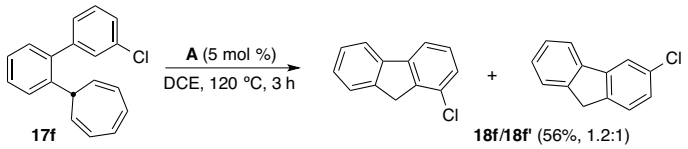
[148] For similar process, see: (a) Munro, D. P.; Sharp, J. T. *J. Chem. Soc. Perkin Trans. 1.* **1984**, 849–858. (b) Munro, D. P.; Sharp, J. T. *Tetrahedron Lett.* **1980**, *21*, 4109–4110. (c) Maguire, A. R.; Buckley, N. R.; O´Leary, P.; Ferguson, G. *Chem. Commun.* **1996**, 2595–2596.
[149] From **16** to **15** is a known process: reference 5.
[150] In collaboration with Dr. Paul R. McGonigal.
[151] In collaboration with Bart Herlé.

Table 3- 3 Reaction scope of fluorene synthesis [a]



[a] Reaction at 120 °C (0.1 M in DCE), **A** (5 mol%), 3 h, isolated yields are reported. [b] Reaction with catalyst **E** (5 mol%)

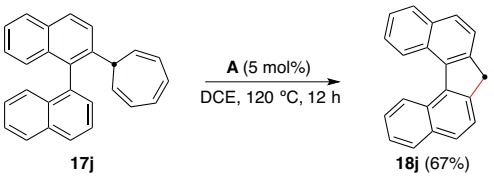
As expected, in the case of *m*-ClC_6H_4 derivative **17f**, a mixture of two regioisomers **18f** and **18f´** was obtained (Scheme 3-20).



Scheme 3- 20

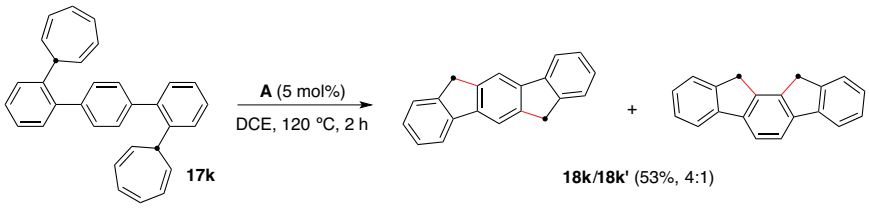
Using this method, 2-binaphthyl cycloheptatriene **17j**, prepared in one step from 2-bromo-1,1´-binaphthalene, was converted into non-planar 7*H*-dibenzo[*c,g*]fluorene (**18j**) (Scheme 3-21).[152,153] This is the shortest synthesis of **18j**, whose anion, dibenzo[*c,g*]fluorenide, has attracted recent interest for its particular aromatic character[154] and as a 6-π electron donor ligand in organometallic chemistry.[155]

[152] (a) Martin, R. H. *J. Chem. Soc.* **1941**, 679–685. (b) Harvey, R. G.; Pataki, J.; Cortez, C.; Di Raddo, P.; Yang, C. *J. Org. Chem.* **1991**, *56*, 1210–1217. (c) Régimbald-Krnel, M.; Wentrup, C. *J. Org. Chem.* **1998**, *63*, 8417–8423.
[153] In collaboration with Bart Herlé.
[154] Pammer, F.; Sun, Y.; Weismann, D.; Sitzmann, H.; Thiel, W. R. *Chem. Eur. J.* **2010**, *16*, 1265–1270.
[155] (a) Pammer, F.; Sun, Y.; Sieger, M.; Fiedler, J.; Sarkar, B.; Thiel, W. R. *Organometallics* **2010**, *29*, 6165–6168. (b) Pammer, F.; Sun, Y.; May, C.; Wolmershäuser, G.; Kelm, H.; Krüger, H.-J.; Thiel, W. R. *Angew. Chem. Int. Ed.* **2007**, *46*, 1270–1273.



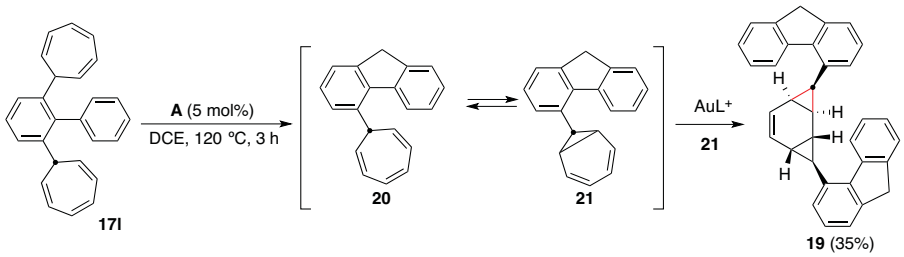
Scheme 3- 21

Indenofluorenes (IFs) have found various applications in organic electronics on account of the conjugation along their aromatic framework and their high rigidity, which stems from the methylene bridged unit of their biphenyl core.[156] By extending our new method to a double annulation, we prepared (1,2-*b*)-indenofluorene (**18k**) as a mixture with (2,1-*a*)-indenofluorene (**18k´**) in 53% isolated yield from **17k** (Scheme 3-22).



Scheme 3- 22 Indenofluorene formation.

During our attempts to form 4,8-dihydrocyclopenta[*def*]fluorene by generating two gold(I) carbenes on the same aromatic ring, we found that the rigidity of the fluorene backbone makes the second annulation unfavorable. Instead, an intermolecular dimerization occurred to give **19**, without indication of other diastereoisomers (Scheme 3-23).

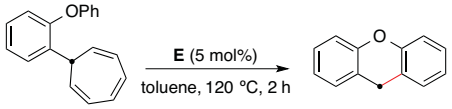


Scheme 3- 23 Attempt to generate two gold(I) carbenes on the same aromatic ring.

[156] (a) Thirion, D.; Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Jeannin, O. *Chem. Eur. J.*, **2010**, *16*, 13646–13658. (b) Poriel, C.; Liang, J.-J.; Rault-Berthelot, J.; Barrière, F.; Cocherel, N.; Slawin, A. M. Z.; Horhant, D.; Virboul, M.; Alcaraz, G.; Audebrand, N.; Vignau, L.; Huby, N.; Wantz, G.; Hirsch, L. *Chem. Eur. J.*, **2007**, *13*, 10055–10069, and references cited therein.

The reaction proceeds by retro-Buchner reaction from **17l** to form **20**, followed by a second retro-Buchner reaction of its tautomer **21** to form fluorenyl gold(I) carbene intermediate that cyclopropanates one of the double bonds of **21**.

Arylcarbenes generated by pyrolysis of the aryl diazomethanes undergo formal insertion into the adjacent *ortho*-position of the XC_6H_5 ring to form dihydroanthracenes (X = CH_2) and dihydroacridines (X = NH), whereas substrates with X = O or S lead to products of Bucher reaction.[157] In our case, reaction of cycloheptatrienyl derivative **22a** gave 9*H*-xanthene (**23a**), the product of a formal insertion into the *ortho*-position of the phenyl, albeit in low yield (Scheme 3-24).



22a **23a** (30%)

Scheme 3- 24

[157] Crow, W. D.; McNab, H. *Aust. J. Chem.* **1981**, *34*, 1037–1350.

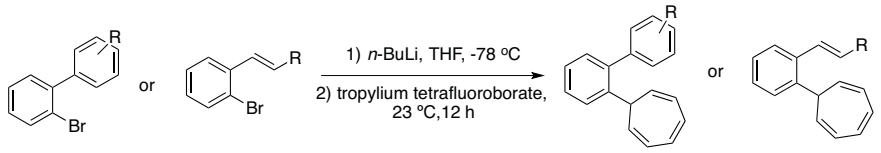
Conclusions

Gold(I) carbenes generated by the retro-Buchner reaction of 1,3,5-cycloheptatrienes catalyzed by cationic gold(I) complexes can be trapped intramolecularly by alkenes or arenes to form indenes or fluorenes. This methodology provides a new synthetic approach to indenes and fluorenes and may be applied to the synthesis of indenofluorenes used in organic electronics. These reactions proceed via intramolecular Friedel−Crafts-type attack of the highly electrophilic gold(I) carbenes to the alkenes and arenes. The reactivity displayed by the cationic intermediates generated by the retro-Buchner reaction is more similar to that of metal carbenes of rhodium or copper or even free carbenes than that of carbocations.

Closer scrutiny of the mechanisms of these reactions has revealed some intriguing details. Thus, in the indene synthesis, we have found that a novel 1,4-metallotropic migration competes with the primary pathway for the formation of the (η^2-indene) gold(I) complexes by a concerted 1,2-H migration/gold(I) elimination. The formation of fluorenes involves a diatropic-type process in the formation of an (η^1-fluorene)-gold(I) complex.

Experimental part

1. General procedure for the synthesis of arylcycloheptatrienes



Procedure A

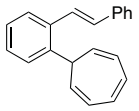
n-BuLi (1.6 M in hexanes, 0.33 mL, 0.53 mmol) was added dropwise to the solution of corresponding aryl bromide[158] (0.5 mmol) in dry THF (2 mL, 0.2 M) at -78 ºC under argon. The mixture was stirred for 30 min at -78 ºC, and then tropylium tetrafluoroborate (0.33 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature (23 ºC) for 12 h. The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with cyclohexane as eluent unless otherwise stated.

Procedure A-2

n-BuLi (1.6 M in hexanes, 0.63 mL, 1 mmol) was added dropwise to the solution of corresponding aryl bromide (0.5 mmol) in dry THF (5 mL, 0.1 M) at -78 ºC under argon. The mixture was stirred for 30 min at -78 ºC, and then tropylium tetrafluoroborate or tropylium bromide (1 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature (23 ºC) for 12 h. The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The crude reaction mixture was purified by column chromatography on silica gel with cyclohexane as eluent unless otherwise stated.

(*E*)-7-(2-Styrylphenyl)cyclohepta-1,3,5-triene (7a)

[158] The aryl bromides were prepared according to the literature procedures: (a) Li, C.-W.; Wang, C.-I.; Liao, H.-Y.; Chaudhuri, R.; Liu, R.-S. *J. Org. Chem.* 2007, *72*, 9203–9207. (b) Rossi, R.; Carpita, A.; Ribecai, A.; Mannina, L. *Tetrahedron*. **2001**, *57*, 2847–2856. (c) Qi, W.-Y.; Zhu, T.-S.; Xu, M.-H. *Org. Lett.* **2011**, *13*, 3410–3413. (d) de Meijere, A.; Song, Z.-Z.; Lanskya, A.; Hyudaa, S.; Raucha, K.; Noltemeyera, M.; Konig, B.; Knieriem, B. *Eur. J. Org. Chem.* **1998**, 2289–2299.



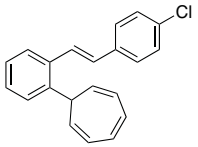
This compound was prepared as a yellow oil in 74% yield according to the general procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.52 - 7.42 (m, 3H), 7.39 - 7.26 (m, 6H), 6.96 (d, *J* = 16.1 Hz, 1H), 6.78 (t, *J* = 3.2 Hz, 2H), 6.35 - 6.29 (m, 2H), 5.48 (dd, *J* = 9.0, 5.4 Hz, 2H), 3.12 (tt, *J* = 5.6, 1.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 137.5, 136.4, 130.9, 130.6, 128.6, 127.9, 127.6, 127.6, 126.9, 126.6, 126.6, 126.5, 124.5, 42.5.

HRMS-APCI: calculated for $C_{21}H_{19}$ $[M+H]^+$: 271.1487; found: 271.1497.

(*E*)-7-(2-(4-Chlorostyryl)phenyl)cyclohepta-1,3,5-triene (7b)



This compound was prepared as a colorless solid in 63% yield according to the general procedure A.

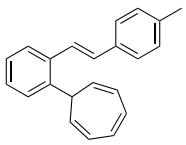
M.p.: 65-67 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.52 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.40 - 7.30 (m, 6H), 7.26 (d, *J* = 16.0 Hz, 1H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.79 (t, *J* = 3.2 Hz, 2H), 6.35 - 6.30 (m, 2H), 5.47 (dd, *J* = 9.1, 5.4 Hz, 2H), 3.09 (t, *J* = 5.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 136.0, 136.0, 133.1, 130.9, 129.2, 128.8, 128.1, 127.7, 127.6, 127.2, 126.9, 126.5, 126.4, 124.5, 42.5.

HRMS-APCI: calculated for $C_{21}H_{18}Cl$ $[M+H]^+$: 305.1097; found: 305.1092.

(*E*)-7-(2-(4-Methylstyryl)phenyl)cyclohepta-1,3,5-triene (7c)



This compound was prepared as a colorless solid in 76% yield according to the general procedure A.

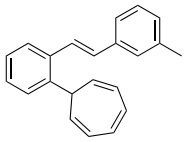
M.p.: 70-72 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.0, 2.3 Hz, 1H), 7.51 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.39 - 7.33 (m, 4H), 7.25 (d, *J* = 15.9 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 16.1 Hz, 1H), 6.78 (t, *J* = 3.2 Hz, 2H), 6.33 - 6.29 (m, 2H), 5.49 (dd, *J* = 9.1, 5.4 Hz, 2H), 3.12 (t, *J* = 5.4 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 137.5, 136.6, 134.8, 130.9, 130.5, 129.3, 127.7, 127.6, 126.8, 126.6, 126.5, 126.4, 125.6, 124.5, 42.5, 21.2.

HRMS-APCI calculated for $C_{22}H_{21}$ $[M+H]^+$: 285.1643; found: 285.1641.

(*E*)-7-(2-(3-Methylstyryl)phenyl)cyclohepta-1,3,5-triene (7d)



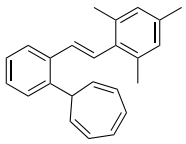
This compound was prepared as a yellow oil in 83% yield according to the general procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.51 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.39 - 7.32 (m, 2H), 7.31 - 7.24 (m, 4H), 7.09 (d, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 16.1 Hz, 1H), 6.79 (t, *J* = 3.2 Hz, 2H), 6.36 - 6.29 (m, 2H), 5.49 (dd, *J* = 9.0, 5.4 Hz, 2H), 3.12(t, *J* = 5.3 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 138.2, 137.5, 136.5, 130.9, 130.8, 128.5, 128.4, 127.8, 127.6, 127.4, 126.9, 126.6, 126.5, 126.4, 124.5, 123.5, 42.5, 21.4.

HRMS-APCI calculated for $C_{22}H_{21}$ $[M+H]^+$: 285.1643; found: 285.1634.

(*E*)-7-(2-(2,4,6-Trimethylstyryl)phenyl)cycloheptа-1,3,5-triene (7e)



This compound was prepared as a white solid in 60% yield according to the general procedure A.

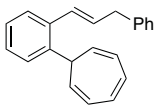
M.p.: 89-91 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.53 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.40 – 7.36 (m, 2H), 6.98 - 6.88 (m, 3H), 6.80 - 6.70 (m, 3H), 6.27 – 6.25 (m, 2H), 5.46 (dd, *J* = 9.0, 5.4 Hz, 2H), 3.07 (dd, *J* = 6.2, 4.6 Hz, 1H), 2.30 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 137.1, 136.3, 136.1, 134.2, 131.6, 130.9, 129.1, 128.6, 127.8, 127.3, 126.8, 126.6, 126.5, 124.5, 42.2, 21.1, 20.9.

HRMS-APCI calculated for $C_{24}H_{25}$ $[M+H]^+$: 313.1956; found: 313.1960.

(*E*)-7-(2-(3-Phenylprop-1-en-1-yl)phenyl)cyclohepta-1,3,5-triene (7f)



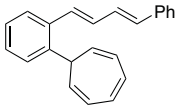
This compound was prepared as a yellow oil in 49% yield according to the general procedure A.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.33 - 7.30 (m, 3H), 7.28 - 7.19 (m, 4H), 6.76 (t, *J* = 3.2 Hz, 2H), 6.59 (d, *J* = 15.5 Hz, 1H), 6.29 - 6.27 (m, 2H), 6.19 (dt, *J* = 15.5, 6.9 Hz, 1H), 5.43 (dd, *J* = 9.1, 5.4 Hz, 2H), 3.52 (dd, *J* = 7.0, 1.5 Hz, 2H), 3.04 (t, *J* = 5.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 140.1, 136.8, 131.4, 130.8, 129.0, 128.6, 128.4, 127.4, 127.3, 126.8, 126.7, 126.6, 126.0, 124.4, 42.2, 39.5.

HRMS-APCI calculated for $C_{22}H_{21}$ $[M+H]^+$: 285.1643; found: 285.1649.

7-(2-((1*E*,3*E*)-4-Phenylbuta-1,3-dien-1-yl)phenyl)cyclohepta-1,3,5-triene (7g)



This compound was prepared as a colorless solid in 82% yield according to the general procedure A from 1-bromo-2-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)benzene (see **7u** synthesis).

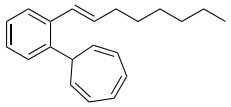
M.p.: 124-125 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 - 7.64 (m, 1H), 7.49 - 7.44 (m, 3H), 7.37 - 7.30 (m, 4H), 7.25 (t, *J* = 7.3 Hz, 1H), 6.94 (ddd, *J* = 15.5, 5.9, 4.1 Hz, 1H), 6.90 - 6.84 (m, 2H), 6.79 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.68 (d, *J* = 15.3 Hz, 1H), 6.36 - 6.29 (m, 2H), 5.45 (dd, *J* = 9.0, 5.3 Hz, 2H), 3.10 (t, *J* = 5.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 137.3, 136.1, 132.8, 131.0, 130.9, 130.3, 129.5, 128.6, 127.9, 127.5, 126.8, 126.8, 126.4, 126.2, 124.5, 42.4.

HRMS-APCI calculated for $C_{23}H_{21}$ $[M+H]^+$: 297.1643; found: 297.1650.

(*E*)-7-(2-(Oct-1-en-1-yl)phenyl)cyclohepta-1,3,5-triene (7h)



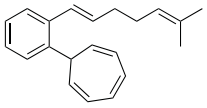
This compound was prepared as a yellow oil in 69% yield according to the general procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.45 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.32 - 7.24 (m, 2H), 6.76 (t, *J* = 3.2 Hz, 2H), 6.50 (d, *J* = 15.5 Hz, 1H), 6.32 - 6.26 (m, 2H), 6.03 (dt, *J* = 15.5, 6.9 Hz, 1H), 5.43 (dd, *J* = 9.1, 5.5 Hz, 2H), 3.05 (t, *J* = 5.2 Hz, 1H), 2.17 (qd, *J* = 7.1, 1.5 Hz, 2H), 1.45 - 1.25 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 137.2, 133.5, 130.8, 127.5, 127.4, 127.1, 126.9, 126.7, 126.6, 124.3, 42.3, 33.2, 31.7, 29.2, 28.8, 22.6, 14.1.

HRMS-APCI calculated for $C_{21}H_{27}$ $[M+H]^+$: 279.2113; found: 279.2108.

(*E*)-7-(2-(6-Methylhepta-1,5-dien-1-yl)phenyl)cyclohepta-1,3,5-triene (7i)



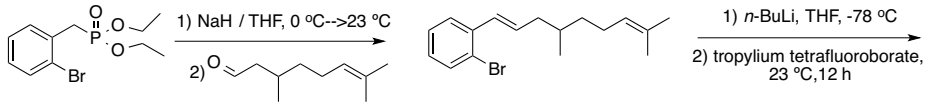
This compound was prepared as a colorless oil in 78% yield according to the general procedure A.

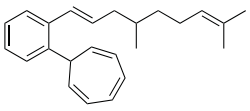
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.44 (m, 2H), 7.34 - 7.22 (m, 2H), 6.76 (t, *J* = 3.2 Hz, 2H), 6.52 (d, *J* = 15.6 Hz, 1H), 6.30 - 6.26 (m, 2H), 6.05 (dt, *J* = 15.6, 6.7 Hz, 1H), 5.43 (dd, *J* = 9.1, 5.5 Hz, 2H), 5.17 - 5.13 (m, 1H), 3.04 (t, *J* = 5.6 Hz, 1H), 2.24 - 2.17 (m, 2H), 2.13 (q, *J* = 6.9 Hz, 2H), 1.71 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 137.1, 132.9, 131.9, 130.8, 127.8, 127.4, 127.2, 126.9, 126.7, 126.6, 124.3, 123.7, 42.3, 33.4, 27.8, 25.7, 17.7.

HRMS-APCI calculated for $C_{21}H_{25}$ $[M+H]^+$: 277.1956; found: 277.1969.

(*E*)-7-(2-(4,8-Dimethylnona-1,7-dien-1-yl)phenyl)cyclohepta-1,3,5-triene (7j)





To a suspension of NaH (60% in oil, 290 mg, 7.3 mmol) in THF (20 mL) at 0 ºC was slowly added diethyl 2-bromobenzylphosphonate[159] (2 g, 6.6 mmol). The resulting suspension was stirred for 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then (±)-citronellal (1.02 g, 6.6 mmol) was added dropwise and slowly warmed to room temperature. After stirring overnight (12 h), the reaction was quenched with ice water and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine and dried over $MgSO_4$. After concentration in vacuo, the residue was purified by silica gel flash column chromatography to give 1.65g (*E*)-1-bromo-2-(4,8-dimethylnona-1,7-dien-1-yl)benzene as colorless oil in 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.30 - 7.22 (m, 1H), 7.08 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 6.72 (d, *J* = 15.7 Hz, 1H), 6.17 (dt, *J* = 15.7, 7.3 Hz, 1H), 5.19 - 5.05 (m, 1H), 2.35 - 2.27 (m, 1H), 2.19 - 1.98 (m, 3H), 1.77 - 1.61 (m, 7H), 1.50 - 1.42 (m, 1H), 1.28 - 1.20 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 132.8, 132.8, 131.3, 129.8, 128.1, 127.4, 126.9, 124.7, 123.1, 40.5, 36.7, 32.8, 25.7, 25.6, 19.5, 17.7.

HRMS-APCI calculated for $C_{17}H_{24}Br$ $[M+H]^+$: 307.1056; found: 307.1050.

The title compound was prepared according to general procedure A from (*E*)-1-bromo-2-(4,8-dimethylnona-1,7-dien-1-yl)benzene as colorless oil in 71% yield.

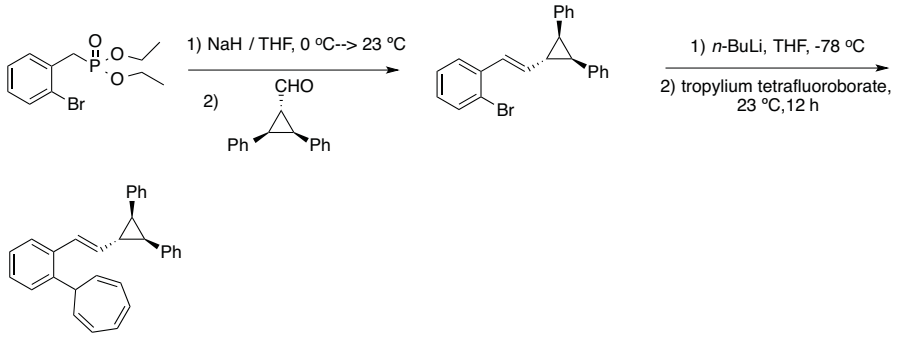
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.31 - 7.25 (m, 2H), 6.75 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.30 - 6.24 (m, 2H), 6.01(dt, *J* = 15.5, 7.3 Hz, 1H), 5.45 - 5.39 (m, 2H), 5.12 (ddt, *J* = 8.6, 5.7, 1.4 Hz, 1H), 3.13 - 3.00 (m, 1H), 2.24 - 2.16 (m, 1H), 2.07 - 1.95 (m, 3H), 1.71 (s, 3H), 1.64 - 1.56 (m, 4H), 1.43 - 1.34 (m, 1H), 1.20 – 1.15 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 137.3, 132.0, 131.1, 130.8, 128.9, 127.4, 127.2, 126.9, 126.9, 126.7, 124.8, 124.3, 42.4, 40.6, 36.6, 32.8, 25.7, 25.6, 19.5, 17.7.

HRMS-APCI calculated for $C_{24}H_{31}$ $[M+H]^+$: 319.2420; found: 319.2429.

7-(2-((*E*)-2-((1*R,2*S**,3*R**)-2,3-diphenylcyclopropyl)vinyl)phenyl)cyclohepta-1,3,5-triene (7k)**

[159] Alexander, J. B.; Mervyn, H.; John, T. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3149–3161.

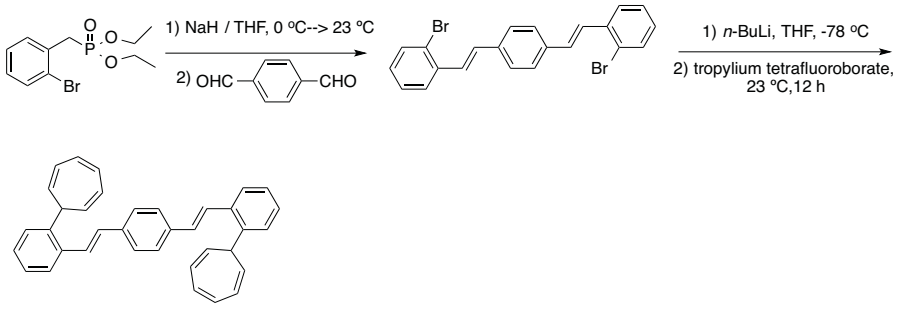


The title compound was prepared according to general procedure A from (((*E*)-2-bromostyryl)cyclopropane-1,2-diyl)dibenzene[160] as colorless oil in 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.49 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.35 - 7.29 (m, 2H), 7.18 - 7.09 (m, 6H), 6.99 - 6.95 (m, 4H), 6.82 - 6.76 (m, 3H), 6.34 - 6.30 (m, 2H), 5.99 (dd, *J* = 15.5, 8.3 Hz, 1H), 5.47 (dd, *J* = 9.1, 5.4 Hz, 2H), 3.13 - 3.09 (m, 1H), 2.63 (d, *J* = 5.5 Hz, 2H), 2.46 (dt, *J* = 8.3, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 137.4, 136.5, 134.5, 130.9, 128.9, 127.8, 127.6, 127.4, 126.9, 126.8, 126.5, 126.5, 125.9, 124.5, 42.3, 33.3, 30.1.

HRMS-APCI calculated for $C_{30}H_{27}$ $[M+H]^+$: 387.2107; found: 387.2105.

1,4-Bis((*E*)-2-(cyclohepta-2,4,6-trien-1-yl)styryl)benzene (7l)



To a suspension of NaH (60% in oil, 217 mg, 5.42 mmol) in THF (4 mL) at 0 ºC was slowly added diethyl 2-bromobenzylphosphonate (1.51 g, 4.92 mmol). The resulting suspension was stirred for 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then a solution of terephthalaldehyde (300 mg, 2.24 mmol) in THF (2 mL) was added dropwise and slowly warmed to room temperature. After stirring for 2 days at room temperature (during which time a precipitate formed), the reaction was quenched with ice water and the precipitate

[160] Which has been described in Chapter 1.

was collected by filtering, and washed with Et_2O and water, dried with vacuum. 1,4-bis((*E*)-2-bromostyryl)benzene was obtained as a light yellow solid. (620 mg, 63%).

M.p.: 170-172 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.62 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.59 (s, 4H), 7.53 (d, *J* = 16.2 Hz, 2H), 7.35 (td, *J* = 7.6, 1.2 Hz, 2H), 7.15 (td, *J* = 7.7, 1.7 Hz, 2H), 7.08 (d, *J* = 16.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 136.8, 133.1, 130.9, 128.8, 127.5, 127.2, 126.6, 124.2.

HRMS-LDI+ calculated for $C_{22}H_{16}Br_2$ $[M]^+$: 437.9619; found: 437.9621

The title compound was prepared according to general procedure **A-2** from the 1,4-bis((*E*)-2-bromostyryl)benzene as yellow solid in 41% yield.

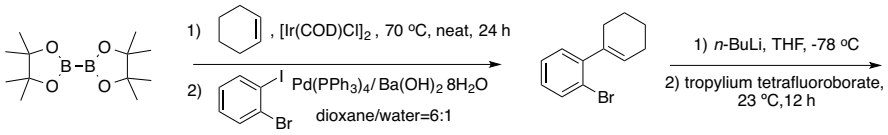
M.p.: 161-163 ºC.

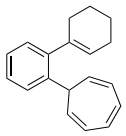
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 - 7.66 (m, 2H), 7.54 - 7.26 (m, 12H), 6.97 (d, *J* = 16.0 Hz, 2H), 6.80 (t, *J* = 3.1 Hz, 4H), 6.32 - 6.30 (m, 4H), 5.50 (dd, *J* = 9.0, 5.3 Hz, 4H), 3.15 - 3.08 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 136.9, 136.3, 130.9, 130.1, 127.9, 127.7, 126.9, 126.8, 126.6, 126.5, 126.5, 124.5, 42.6.

HRMS-LDI+ calculated for $C_{36}H_{29}$ $[M-H]^+$: 461.2269; found: 461.2264.

2'-(Cyclohepta-2,4,6-trien-1-yl)-2,3,4,5-tetrahydro-1,1'-biphenyl (7m)





2'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl was prepared according to a reported procedure.[161]

$[Ir(COD)Cl]_2$ (2 mol%, 20 mg) and bis(pinacolato)diboron (1.5 mmol, 381 mg) were dissolved in 1 mL neat cyclohexene. The reaction mixture was stirred at 70 °C for 24 h under argon. After cooling to room temperature the reaction mixture was

[161] Olsson, V. J.; Szabó, K. J. *Angew. Chem. Int. Ed.* **2007**, *46*, 6891–6893.

diluted with a dioxane/water (6:1) mixture (4 ml), then 2-bromoiodobenzene (1.5 mmol), $Pd(PPh_3)_4$ (5 mol %, 80 mg) and $Ba(OH)_2 \cdot 8H_2O$ (3.0 mmol, 946 mg) were added. Then stirring was continued for 24 h at 70 ºC. The crude reaction mixture was evaporated and the residue was purified by silica gel column chromatography to give 240 mg aryl bromide as colorless oil in 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.25 (td, *J* = 7.4, 1.2 Hz, 1H), 7.17 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.10 (td, *J* = 7.9, 1.8 Hz, 1H), 5.65 (tt, *J* = 3.8, 1.8 Hz, 1H), 2.32 – 2.28 (m, 2H), 2.22 - 2.16 (m, 2H), 1.83 - 1.76 (m, 2H), 1.75 - 1.66 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 139.1, 132.6, 130.0, 127.9, 127.1, 127.0, 122.5, 29.3, 25.3, 22.8, 21.9.

HRMS-EI calculated for $C_{12}H_{13}Br\,[M]^+$: 236.0201; found: 236.0204.

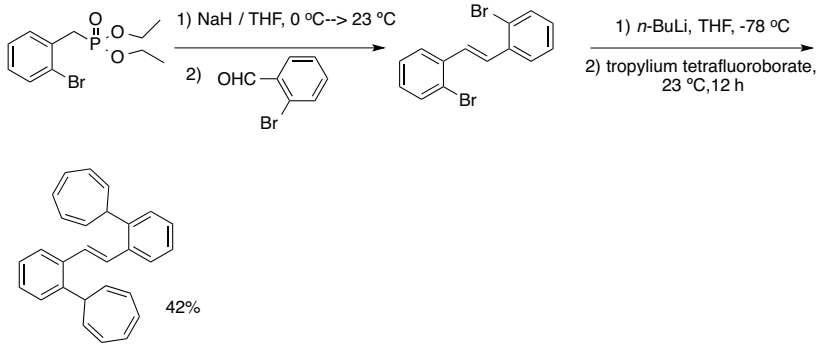
This title compound was prepared as a colorless oil in 55% yield according to the general procedure A from 2'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.35 (td, *J* = 7.5, 1.5 Hz, 1H), 7.25 (td, *J* = 7.4, 1.4 Hz, 1H), 7.14 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.73 (t, *J* = 3.2 Hz, 2H), 6.26 - 6.22 (m, 2H), 5.49 - 5.47 (m, 1H), 5.37 (dd, *J* = 9.0, 5.4 Hz, 2H), 2.95 (t, *J* = 5.6 Hz, 1H), 2.10 - 2.03 (m, 4H), 1.64 - 1.51 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 141.5, 138.0, 130.6, 128.4, 127.8, 127.1, 126.1, 126.1, 124.0, 42.0, 30.9, 25.2, 22.9, 22.0.

HRMS-EI calculated for $C_{19}H_{20}\,[M]^+$: 248.1565; found: 248.1562.

(*E*)-1,2-Bis(2-(cyclohepta-2,4,6-trien-1-yl)phenyl)ethane (7n)



To a suspension of NaH (60% in oil, 145 mg, 3.63 mmol) in THF (4 mL) at 0 ºC was slowly added diethyl 2-bromobenzylphosphonate (1 g, 3.3 mmol). The resulting suspension was stirred for 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then a solution of 2-bromobenzaldehyde (611 mg, 3.3

mmol) in THF (2 mL) was added dropwise and slowly warmed to room temperature. After stirring overnight, the reaction was quenched with ice water and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by silica gel flash column chromatography to give 730 mg (*E*)-1,2-bis(2-bromophenyl)ethene as a colorless solid in 65% yield. The spectroscopic data match with those reported in the literature.[162]

The title compound was prepared according to general procedure **A-2** from (*E*)-1,2-bis(2-bromophenyl)ethene as white solid in 42% yield.

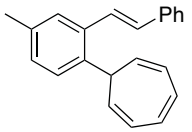
M.p.: 135-137ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.48 (m, 4H), 7.38-7.27 (m, 4H), 7.10 (s, 2H), 6.76 (t, *J* = 3.1 Hz, 4H), 6.29 (d, *J* = 9.0 Hz, 4H), 5.45 (dd, *J* = 9.1, 5.5 Hz, 4H), 3.10 (t, *J* = 5.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 136.6, 130.9, 128.5, 127.9, 127.6, 126.9, 126.7, 126.5, 124.5, 42.4.

HRMS-MALDI: calculated for $C_{28}H_{24}$ $[M]^+$: 360.1878; found: 360.1935.

(*E*)-7-(4-Methyl-2-styrylphenyl)cyclohepta-1,3,5-triene (7p)



This compound was prepared as a white solid in 59% yield according to the general procedure A from (*E*)-1-bromo-4-methyl-2-styrylbenzene.[163]

M.p.: 75-76 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.31 - 7.24 (m, 2H), 7.18 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.78 (t, *J* = 3.2 Hz, 2H), 6.34 - 6.28 (m, 2H), 5.47 (dd, *J* = 9.1, 5.5 Hz, 2H), 3.09 (t, *J* = 5.6 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 137.6, 136.3, 136.1, 130.9, 130.3, 128.7, 128.6, 127.6, 127.5, 127.1, 126.9, 126.6, 126.5, 124.4, 42.2, 21.1.

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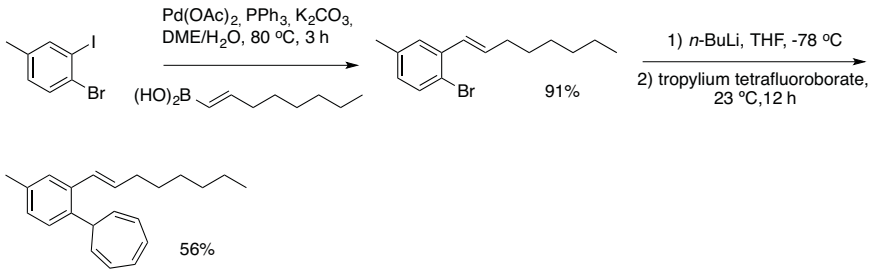
[162] Wyatt, P.; Hudson, A.; Charmant, J.; Orpen, A. G.; Phetmung, H. *Org. Biomol. Chem.* **2006**, *4*, 2218–2232.

[163] (*E*)-1-Bromo-4-methyl-2-styrylbenzene is a known compound: Watanabe, S.; Yamamoto, K.; Itagaki, Y.; Iwamura, T.; Iwama, T.; Kataoka, T. *Tetrahedron* **2000**, *56*, 855–863. It can be also prepared by the Heck reaction of 1-bromo-2-iodo-4-methylbenzene with styrene.

HRMS-APCI calculated for $C_{22}H_{21}$ $[M+H]^+$: 285.1643; found: 285.1613.

(*E*)-7-(4-Methyl-2-(oct-1-en-1-yl)phenyl)cyclohepta-1,3,5-triene (7q)



(*E*)-1-Bromo-4-methyl-2-(oct-1-en-1-yl)benzene

To a DME/H_2O (5 ml/2 ml) solution of 15 mg $Pd(OAc)_2$, 50 mg PPh_3, 424 mg K_2CO_3 and 243 mg (1.56 mmol) (*E*)-oct-1-en-1-ylboronic acid was added 1-bromo-2-iodo-4-methylbenzene (420 mg, 1.41 mmol) at room temperature. The mixture was then heated at 80 °C for 3 h. After cooling to room temperature, the mixture was quenched by adding saturated $NH_4Cl_{(aq)}$. The mixture was extracted with ethyl acetate, and the combined organic extracts were dried over $MgSO_4$. The solvent was removed in vacuo, and the crude residue was purified by silica gel flash column chromatography (SiO_2, c-hexane) to give (*E*)-1-bromo-4-methyl-2-(oct-1-en-1-yl)benzene (360 mg) colorless oil in 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 1H), 7.32 (s, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 15.7 Hz, 1H), 6.18 (dt, *J* = 15.7, 7.0 Hz, 1H), 2.32 (s, 3H), 2.30 - 2.22 (m, 2H), 1.54 - 1.46 (m, 2H), 1.41 - 1.30 (m, 6H), 0.92 (t, *J* = 6.9 Hz, 3H).

HRMS-APCI calculated for $C_{15}H_{22}Br$ $[M+H]^+$: 281.0899; found: 281.0901.

(*E*)-7-(4-Methyl-2-(oct-1-en-1-yl)phenyl)cyclohepta-1,3,5-triene

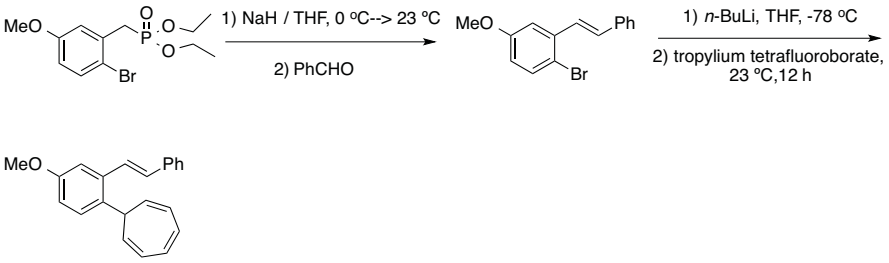
The title compound was prepared as a colorless oil in 56% yield according to general procedure A from (*E*)-1-bromo-4-methyl-2-(oct-1-en-1-yl)benzene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 1H), 7.30 (s, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.75 (dd, *J* = 3.6, 2.6 Hz, 2H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.31 - 6.24 (m, 2H), 6.03 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.50 - 5.36 (m, 2H), 3.03 - 2.97 (m, 1H), 2.38 (s, 3H), 2.16 (qd, *J* = 7.1, 1.5 Hz, 2H), 1.47 - 1.40 (m, 2H), 1.35 – 1.27 (m, 6H), 0.92 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 137.0, 136.1, 133.2, 130.8, 127.9, 127.6, 127.4, 127.4, 127.2, 124.2, 42.0, 33.2, 31.7, 29.3, 28.8, 22.6, 21.1, 14.1.

HRMS-APCI calculated for $C_{22}H_{29}$ $[M+H]^+$: 293.2264; found: 293.2263.

(*E*)-7-(4-Methoxy-2-styrylphenyl)cyclohepta-1,3,5-triene (7r)



To a suspension of NaH (60% in oil, 131 mg, 3.28 mmol) in THF (4 mL) at 0 ºC was slowly added diethyl 2-bromo-5-methoxylbenzylphosphonate (1 g, 3 mmol). The resulting suspension was stirred for an additional 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then a solution of benzaldehyde (290 mg, 2.73 mmol) in THF (1 mL) was added dropwise and slowly warmed to room temperature. After stirring overnight (12 h), the reaction was quenched with ice water and extracted with Et_2O, dried with $MgSO_4$. (*E*)-1-bromo-4-methoxy-2-styrylbenzene was obtained as a colorless solid by silica gel column chromatography. (612 mg, yield: 78%).

M.p.: 65-67 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 16.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 3.0 Hz, 1H), 7.05 (d, *J* = 16.2 Hz, 1H), 6.75 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 137.8, 136.9, 133.6, 131.5, 128.7, 128.1, 127.5, 126.9, 115.1, 114.9, 111.8, 55.6.

HRMS-APCI calculated for $C_{15}H_{14}BrO$ $[M+H]^+$: 289.0223; found: 289.0218.

(*E*)-7-(4-Methoxy-2-styrylphenyl)cyclohepta-1,3,5-triene

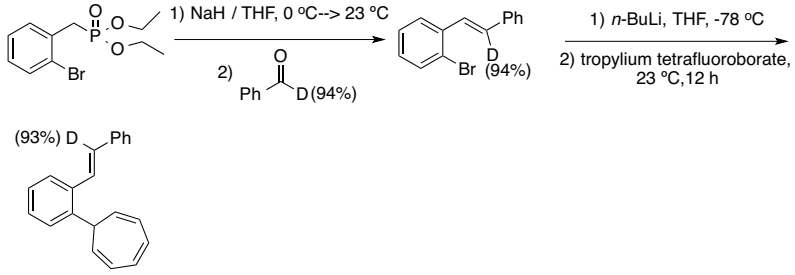
The title compound was prepared according to general procedure A as colorless oil in 86% yield from (*E*)-1-bromo-4-methoxy-2-styrylbenzene.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 - 6.92 (m, 10H), 6.77 (t, *J* = 3.2 Hz, 2H), 6.31 - 6.26 (m, 2H), 5.51 - 5.38 (m, 2H), 3.90 (s, 3H), 3.04 (t, *J* = 5.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 137.5, 137.4, 133.6, 130.9, 130.7, 128.8, 128.7, 127.7, 127.0, 126.6, 126.5, 124.4, 113.6, 111.6, 55.4, 41.9.

HRMS-APCI calculated for $C_{22}H_{21}O$ $[M+H]^+$: 301.1587; found: 301.1587.

(*E*)-7-(2-styrylphenyl)cyclohepta-1,3,5-triene-d_1 (7a-d_1)



The isotopically labeled (*E*)-1-bromo-2-styrylbenzene-d_1 [164] was synthesized as follows:

To a suspension of NaH (60% in oil, 145 mg, 3.63 mmol) in THF (4 mL) at 0 ºC was slowly added diethyl 2-bromobenzylphosphonate (1 g, 3.3mmol). The resulting suspension was stirred for an additional 1 h at room temperature (23 ºC). The reaction mixture was cooled to 0 ºC, and then a solution of benzaldehyde-α-d_1 [165] (353 mg, 3.3 mmol) in THF (2 mL) was added dropwise and slowly warmed to room temperature. After stirring overnight (12 h), the reaction was quenched with ice water and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by silica gel flash column chromatography to give 650 mg isotopically labeled (*E*)-1-bromo-2-styrylbenzene-d_1 as colorless oil in 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.63 - 7.57 (m, 3H), 7.50 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.38 - 7.30 (m, 2H), 7.15 (td, *J* = 7.8, 1.7 Hz, 1H), 7.08 (d, *J* = 16.1 Hz, 6% residual signal).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 136.9, 133.0, 131.1 (t, J_{CD} = 23.5 Hz), 128.7, 128.7, 128.0, 127.5, 127.3, 126.8, 126.7, 124.1.

HRMS-APCI calculated for $C_{14}H_{11}DBr$ $[M+H]^+$: 260.0185; found: 260.0189.

The title compound was prepared according to general procedure A from isotopically labeled (*E*)-1-bromo-2-styrylbenzene-d_1 as yellow oil in 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.52 - 7.42 (m, 3H), 7.39 - 7.26 (m, 6H), 6.96 (residual signal, 7%), 6.78 (t, *J* = 3.2 Hz, 2H), 6.35 - 6.30 (m, 2H), 5.47 (dd, *J* = 9.0, 5.4 Hz, 2H), 3.12 (tt, *J* = 5.6, 1.6 Hz, 1H).

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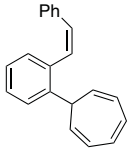
[164] Xue, F.; Li, X.; Wan, B. *J. Org. Chem*. **2011**, *76*, 7256–7262.
[165] Gajewski, J. J.; Bocian, W.; Harris, N. J.; Olson, L.P.; Gajewski, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 326–334.

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 137.4, 136.4, 130.9, 130.2 (t, *J* = 23.1 Hz), 128.6, 127.9, 127.6, 127.6, 126.9, 126.6, 126.5, 126.4, 124.5, 42.5.

HRMS-APCI calculated for $C_{21}H_{18}D$ $[M+H]^+$: 272.1550; found: 272.1538.

(*Z*)-7-(2-Styrylphenyl)cyclohepta-1,3,5-triene (*cis*-7a)

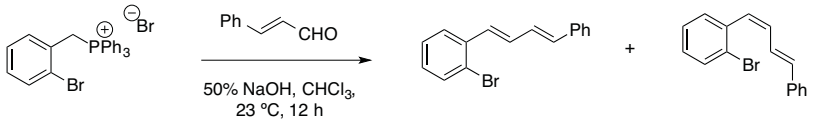


This compound was prepared as a colorless oil from (*Z*)-1-bromo-2-styrylbenzene[166] in 78% yield according to the general procedure A.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.35 (td, *J* = 7.5, 1.8 Hz, 1H), 7.22 - 7.13 (m, 5H), 7.12 - 7.03 (m, 2H), 6.71 (t, *J* = 3.2 Hz, 2H), 6.61 (d, *J* = 12.1 Hz, 1H), 6.55 (d, *J* = 12.0 Hz, 1H), 6.25 - 6.19 (m, 2H), 5.38 (dd, *J* = 9.1, 5.5 Hz, 2H), 3.09 - 3.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 136.9, 136.6, 131.0, 130.7, 129.7, 129.1, 129.0, 128.0, 127.8, 127.3, 127.0, 126.5, 126.3, 124.5, 42.4.

HRMS-EI calculated for $C_{21}H_{18}$ $[M]^+$: 270.1409; found: 270.1400.



To a solution of 2-bromobenzyltriphenylphosphonium bromide (2 g, 3.9 mmol) and (*E*)-cinnamaldehyde (516 mg, 3.9 mmol) in 30 mL chloroform was slowly added 50% $NaOH_{(aq)}$ (780 mg NaOH, 19.5 mmol). The resulting mixture was stirred overnight (12 h) at room temperature (23 ºC). The layers were separated, and the aqueous phase extracted twice with DCM. The combined organic extracts were washed with water then dried over $MgSO_4$. After concentration *in vacuo*, 5 mL *c*-hexane was added and the resulting triphenylphosphine oxide precipitate was removed by filtration. The *c*-hexane solution was passed through a short pad of silica gel then concentrated in vacuo to give 860 mg colorless oil (77%, *Z*:*E* = 1:1). The pure samples of *Z* (320mg, colorless oil) and *E* (280mg, light yellow solid) products were obtained by very careful silica gel chromatography using *c*-hexane as eluent.

[166] de Meijere, A.; Zhong, S. Z.; Lansky, A.; Hyuda, S.; Rauch, K.; Noltemeyer, M.; König, B.; Knieriem, B. *Eur. J. Org. Chem.* **1998**, 2289–2299.

Note: The (1*E,*3*E*) sample can be also prepared from diethyl 2-bromobenzylphosphonate and (*E*)-cinnamaldehyde using the same procedure described for deuterated (*E*)-1-bromo-2-styrylbenzene synthesis shown in this SI as well. By using this HWE olefination, only the desired (1*E,*3*E*) isomer was obtained, and the purification is easier.

1-Bromo-2-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)benzene

M.p.: 104-105 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.33 - 7.26 (m, 2H), 7.12 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 7.08 - 7.03 (m, 2H), 6.97 - 6.90 (m, 1H), 6.75 (d, *J* = 16.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 136.9, 134.0, 133.1, 131.8, 131.0, 129.0, 128.7, 128.6, 127.8, 127.4, 126.5, 126.3, 123.9.

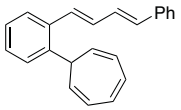
1-Bromo-2-((1*Z*,3*E*)-4-phenylbuta-1,3-dien-1-yl)benzene

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.41 - 7.22 (m, 6H), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H), 7.12 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.77 (d, *J* = 15.6 Hz, 1H), 6.63 - 6.50 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 137.1, 135.4, 132.7, 131.2, 131.2, 129.7, 128.6, 128.6, 127.8, 127.0, 126.6, 124.7, 124.0.

HRMS-MALDI: calculated for $C_{16}H_{13}Br$ $[M]^+$: 284.0195; found: 284.0166.

7-(2-((1*E*,3*E*)-4-Phenylbuta-1,3-dien-1-yl)phenyl)cyclohepta-1,3,5-triene (7g)



This compound was prepared as a white solid in 82% yield according to the general procedure A from 1-bromo-2-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)benzene.

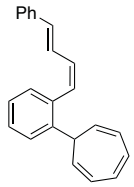
M.p.: 124-125 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 - 7.64 (m, 1H), 7.49 - 7.44 (m, 3H), 7.37 - 7.30 (m, 4H), 7.25 (t, *J* = 7.3 Hz, 1H), 6.94 (ddd, *J* = 15.5, 5.9, 4.1 Hz, 1H), 6.90 - 6.84 (m, 2H), 6.79 (dd, *J* = 3.7, 2.7 Hz, 2H), 6.68 (d, *J* = 15.3 Hz, 1H), 6.36 - 6.29 (m, 2H), 5.45 (dd, *J* = 9.0, 5.3 Hz, 2H), 3.10 (t, *J* = 5.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 137.3, 136.1, 132.8, 131.0, 130.9, 130.3, 129.5, 128.6, 127.9, 127.5, 126.8, 126.8, 126.4, 126.2, 124.5, 42.4.

HRMS-APCI calculated for $C_{23}H_{21}$ $[M+H]^+$: 297.1643; found: 297.1650.

7-(2-((1*Z*,3*E*)-4-Phenylbuta-1,3-dien-1-yl)phenyl)cyclohepta-1,3,5-triene (7u)



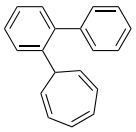
This compound was prepared as a colorless oil in 49% yield according to the general procedure A from1-bromo-2-((1*Z*,3*E*)-4-phenylbuta-1,3-dien-1-yl)benzene.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.43 - 7.21 (m, 8H), 7.07 (ddd, *J* = 15.6, 10.9, 0.9 Hz, 1H), 6.73 (dd, *J* = 3.6, 2.8 Hz, 2H), 6.67 (d, *J* = 15.6 Hz, 1H), 6.51 (d, *J* = 11.3 Hz, 1H), 6.42 (td, *J* = 11.1, 0.8 Hz, 1H), 6.31 - 6.24 (m, 2H), 5.42 (dd, *J* = 8.8, 5.4 Hz, 2H), 3.02 (ddd, *J* = 5.4, 3.9, 1.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 137.3, 136.3, 134.3, 131.0, 130.8, 130.5, 129.3, 128.5, 127.9, 127.6, 127.3, 126.5, 126.4, 126.3, 125.4, 124.6, 42.46.

HRMS-MALDI: calculated for $C_{23}H_{19}$ $[M-H]^+$: 295.1481; found: 295.1496.

2-(Cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17a)



2-Biphenylmagnesium bromide solution (0.5 M, 5.6 mL, 2.8 mmol) was added dropwise to a solution of tropylium tetrafluoroborate (500 mg, 2.8 mmol) in 10 mL dry THF at 0 ºC under argon. The reaction was then stirred at room temperature (23 ºC) overnight (12 h). The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The crude reaction mixture was purified by chromatography to give the title compound (460 mg) as a colorless solid in 67% yield.

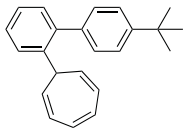
M.p.: 48-50 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.45 (td, *J* = 7.5, 1.7 Hz, 1H), 7.37 - 7.18 (m, 7H), 6.57 (t, *J* = 3.2 Hz, 2H), 6.22 - 6.13 (m, 2H), 5.37 (dd, *J* = 9.0, 5.3 Hz, 2H), 2.88 (t, *J* = 5.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 141.0, 130.5, 130.1, 129.2, 128.0, 127.8, 127.7, 127.6, 126.8, 126.3, 124.1, 41.9.

HRMS-APCI calculated for $C_{19}H_{17}$ $[M+H]^+$: 245.1330; found: 245.1334.

4'-(*tert*-Butyl)-2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17b)



This compound was prepared as a colorless solid in 76% yield according to the general procedure A.

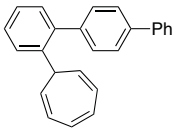
M.p.: 87-89 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.38 - 7.31 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.61 (t, *J* = 3.2 Hz, 2H), 6.25 - 6.16 (m, 2H), 5.40 (dd, *J* = 9.1, 5.2 Hz, 2H), 3.00 (t, *J* = 5.2 Hz, 1H), 1.35 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 142.0, 141.7, 137.9, 130.5, 130.3, 128.9, 127.8, 127.8, 127.7, 126.2, 124.7, 124.1, 41.9, 34.4, 31.3.

HRMS-APCI calculated for $C_{23}H_{25}$ $[M+H]^+$: 301.1956; found: 301.1957.

2-(Cyclohepta-2,4,6-trien-1-yl)-1,1':4',1''-terphenyl (17c)



This compound was prepared as a white solid in 59% yield according to the general procedure A.

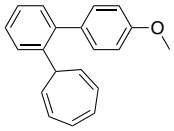
M.p.: 86-89 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.52 - 7.44 (m, 3H), 7.39 - 7.32 (m, 5H), 6.60 (t, *J* = 3.2 Hz, 2H), 6.24 – 6.21 (m, 2H), 5.43 (dd, *J* = 9.0, 5.3 Hz, 2H), 3.00 (t, *J* = 5.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 141.4, 140.7, 140.0, 139.5, 130.6, 130.1, 129.7, 128.7, 128.0, 127.9, 127.6, 127.2, 127.0, 126.5, 126.3, 124.2, 41.9.

HRMS-APCI calculated for $C_{25}H_{21}$ $[M+H]^+$: 321.1643; found: 321.1647.

2-(Cyclohepta-2,4,6-trien-1-yl)-4'-methoxy-1,1'-biphenyl (17d)



This compound was prepared as a white solid in 76% yield according to the general procedure A.

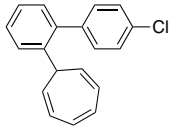
M.p.: 74-75 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.46 (td, *J* = 7.5, 1.8 Hz, 1H), 7.38 - 7.29 (m, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.62 (dd, *J* = 3.6, 2.6 Hz, 2H), 6.20-6.22 (m, 2H), 5.40 (dd, *J* = 9.0, 5.3 Hz, 2H), 3.83 (s, 3H), 2.91 (t, *J* = 5.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 142.0, 141.5, 133.4, 130.6, 130.3, 130.2, 127.8, 127.7, 127.7, 126.2, 124.1, 113.3, 55.2, 41.9.

HRMS-APCI calculated for $C_{20}H_{19}O$ $[M+H]^+$: 275.1436; found: 275.1442.

4'-Chloro-2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17e)



This compound was prepared as a white solid in 74% yield according to the general procedure A.

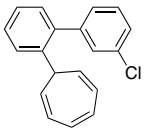
M.p.: 114-115 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.49 (td, *J* = 7.6, 1.5 Hz, 1H), 7.36 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31 - 7.25 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.63 (t, *J* = 3.2 Hz, 2H), 6.24 - 6.18 (m, 2H), 5.38 (dd, *J* = 9.0, 5.3 Hz, 2H), 2.83 (tt, *J* = 5.3, 1.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 140.6, 139.4, 132.9, 130.6, 130.5, 130.0, 128.3, 128.0, 127.8, 127.2, 126.4, 124.2, 41.9.

HRMS-APCI calculated for $C_{19}H_{16}Cl$ $[M+H]^+$: 279.0941; found: 279.0942.

3'-Chloro-2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17f)



This compound was prepared as a white solid in 71% yield according to the general procedure A.

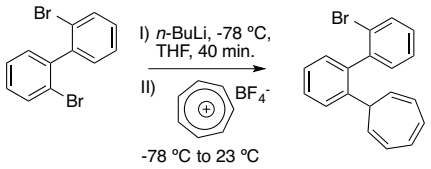
M.p.: 89-90 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.50 (td, *J* = 7.5, 1.6 Hz, 1H), 7.36 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31 - 7.24 (m, 4H), 7.12 (dt, *J* = 6.8, 1.7 Hz, 1H), 6.63 (t, *J* = 3.2 Hz, 2H), 6.24 - 6.20 (m, 2H), 5.39 (dd, *J* = 9.1, 5.3 Hz, 2H), 2.81 (tt, *J* = 5.4, 1.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 141.8, 140.5, 133.7, 130.6, 129.9, 129.3, 129.0, 128.4, 127.8, 127.4, 127.1, 126.9, 126.4, 124.2, 41.9.

HRMS-APCI calculated for $C_{19}H_{16}Cl$ $[M+H]^+$: 279.0941; found: 279.094.

2-Bromo-2'-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17g)



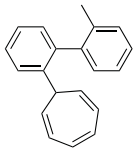
A solution of 2,2'-dibromobiphenyl (1.258 g, 4 mmol) in THF (16 mL) in a dried 50 mL round-bottom flask was cooled to -78 ºC and a *n*-BuLi solution (2.5 M in hexanes, 1.68 mL, 4.2 mmol) was added. After stirring for 40 minutes, tropylium tetrafluoroborate (1.424 g, 8 mmol) was added and the cooling bath was removed. When the reaction reached ambient temperature (23 ºC), cyclohexane (30 mL) was added and the mixture was loaded directly onto a column of SiO_2 and purified by flash chromatography (cyclohexane as eluent), yielding the desired cycloheptatriene (958 mg, 2.9 mmol, 74%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.61 - 7.54 (m, 1H), 7.50 (td, *J* = 7.6, 1.5 Hz, 1H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.30 - 7.10 (m, 4H), 6.61 - 6.45 (m, 2H), 6.22 - 6.05 (m, 2H), 5.45 (dd, *J* = 9.4, 5.4 Hz, 1H), 5.23 (dd, *J* = 9.3, 5.4 Hz, 1H), 2.56 (tt, *J* = 5.5, 1.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 183.3, 132.5, 131.3, 130.9, 130.3, 130.0, 128.9, 128.8, 127.4, 127.1, 126.9, 126.4, 126.2, 124.5, 124.3, 42.2.

HRMS-APCI calcd for $C_{19}H_{16}Br$ $[M+H]^+$: 323.0430; found: 323.0427.

2-(Cyclohepta-2,4,6-trien-1-yl)-2'-methyl-1,1'-biphenyl (17h)



This compound was prepared as a colorless solid in 79% yield according to the general procedure A.

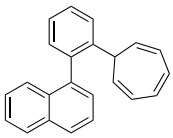
M.p.: 58-60 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.48 (td, *J* = 7.6, 1.5 Hz, 1H), 7.34 (td, *J* = 7.5, 1.4 Hz, 1H), 7.24 - 7.11 (m, 4H), 7.05 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.55 - 6.52 (m, 2H), 6.19 - 6.09 (m, 2H), 5.39 (dd, *J* = 9.4, 5.4 Hz, 1H), 5.26 (dd, *J* = 9.3, 5.3 Hz, 1H), 2.58 (tt, *J* = 5.4, 1.6 Hz, 1H), 2.03 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 141.2, 140.5, 135.9, 130.5, 130.3, 129.6, 129.5, 129.5, 127.9, 127.3, 127.1, 127.0, 126.9, 126.1, 125.2, 124.5, 124.1, 41.9, 20.2.

HRMS-APCI calculated for $C_{20}H_{19}$ $[M+H]^+$: 259.1487; found: 259.1488.

1-(2-(Cyclohepta-2,4,6-trien-1-yl)phenyl)naphthalene (17i)



n-BuLi (1.6 M in hexanes, 0.23 mL, 0.37 mmol) was added dropwise to the solution of 1-(2-bromophenyl)naphthalene (100 mg, 0.23 mmol) in dry THF (1.4 mL, 0.25 M) at -78 ºC under argon. The mixture was stirred for 30 min at -78 ºC, and then tropylium tetrafluoroborate (75 mg, 0.42 mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature (23 ºC) overnight (12 h). The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The crude reaction mixture was purified by preparative TLC (eluent: pentane) to yield the title compound as a colorless oil that solidified upon standing (67 mg, 64%).

M.p.: 80-81 ºC.

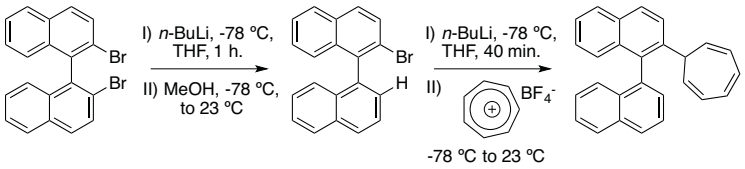
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.54 (td, *J* = 7.6, 1.5 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.32 (m, 4H), 7.27 (ddd, *J* = 9.6, 7.3, 1.1 Hz, 2H), 6.39 (dd, *J* = 11.0, 5.6 Hz, 1H), 6.31 (dd, *J* = 11.0, 5.7 Hz, 1H), 6.08 (dd, *J* = 9.3, 5.7 Hz, 1H), 5.97 (dd, *J*

= 9.3, 5.7 Hz, 1H), 5.37 (dd, *J* = 9.3, 5.4 Hz, 1H), 5.28 (dd, *J* = 9.3, 5.4 Hz, 1H), 2.54 (t, *J* = 5.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 140.0, 138.7, 133.5, 132.4, 131.0, 130.6, 130.3, 128.4, 128.1, 127.7, 127.6, 127.2, 127.2, 127.0, 126.5, 126.2, 125.8, 125.7, 125.1, 124.5, 124.1, 42.3.

HRMS-MALDI: calculated for $C_{23}H_{17}$ $[M-H]^+$: 293.1330; found: 293.1361.

2-(Cyclohepta-2,4,6-trien-1-yl)-1,1'-binaphthalene (17j).



Following a literature procedure, a solution of 2,2'-dibromo-1,1'-binaphtyl (412 mg, 1 mmol) in THF (10 mL) in a dried 25 mL round-bottom flask was cooled to -78 ºC and a *n*-BuLi solution (2.5 M in hexanes, 0.4 mL, 1 mmol) was added. After stirring for 1 hour, methanol (5 mL) was added and 10 minutes later the reaction was allowed to warm to room temperature (23 ºC). The solution was concentrated on a rotary evaporator and then purified by flash chromatography (cyclohexane) to yield 2-bromo-1,1'-binaphtyl (312 mg, 0.94 mmol, 94%) as a colorless solid. The spectroscopic data matched with those reported in the literature.[167]

A 10 mL round-bottom flask with a solution of 2-bromo-1,1'-binaphtyl (288 mg, 0.87 mmol) in THF (3.5 mL) was cooled to -78 ºC and *n*-BuLi solution (2.5 M in hexanes, 0.381 mL, 1.1 equiv.) was added. After stirring for 40 minutes, tropylium tetrafluoroborate (308 mg, 1.73 mmol, 2 equiv.) was added and the solution was allowed to warm to room temperature. The reaction was quenched with water, extracted with diethyl ether and washed with two portions of water and brine. After drying and concentrating, the mixture was purified by flash chromatography (cyclohexane) to yield the target compound (186 mg, 0.54 mmol, 62%) as a viscous pale-yellow oil.

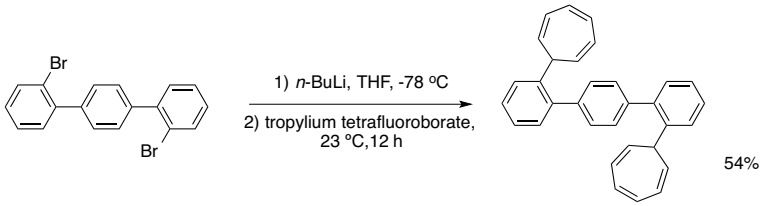
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 7.9 Hz, 3H), 7.53 - 7.38 (m, 3H), 7.31 (d, *J* = 6.9 Hz, 1H), 7.26 - 7.19 (m, 3H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.40 (d, *J* = 16.3 Hz, 1H), 6.30 (d, *J* = 16.3 Hz, 1H), 6.10 (dd, *J* = 9.3, 5.5 Hz, 1H), 5.96 (dd, *J* = 9.2, 5.5 Hz, 1H), 5.38 (d, *J* = 28.5 Hz, 2H), 2.58 (t, *J* = 5.1 Hz, 1H).

[167] Nagaki, A.; Takabayashi, N.; Tomida, Y.; Yoshida, J. *Org. Lett.* **2008**, *10*, 3937–3940.

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 136.3, 133.5, 133.3, 133.0, 132.3, 130.7, 130.3, 128.9, 128.1, 128.1, 127.9, 127.9, 127.2, 127.0, 126.5, 126.3, 126.0, 125.9, 125.5, 125.5, 125.4, 124.6, 124.3, 42.9.

HRMS-APCI calcd for $C_{27}H_{21}Br$ $[M+H]^+$: 345.1638; found: 345.1646.

2,2''-Di(cyclohepta-2,4,6-trien-1-yl)-1,1':4',1''-terphenyl (17k)



The title compound was prepared according to general procedure **A-2** from the known compound 2,2''-dibromo-1,1':4',1''-terphenyl[168] as a colorless solid in 54% yield.

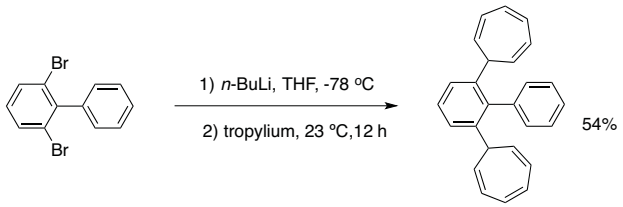
M.p.: 182-184 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.47 (ddd, *J* = 7.8, 7.0, 1.8 Hz, 2H), 7.39 - 7.31 (m, 4H), 7.19 (s, 4H), 6.61 (dd, *J* = 3.8, 2.7 Hz, 4H), 6.23 - 6.18 (m, 4H), 5.39 (ddd, *J* = 9.5, 5.3, 0.8 Hz, 4H), 2.94 (ddd, *J* = 5.4, 3.8, 1.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 141.5, 139.4, 130.6, 130.2, 128.8, 127.9, 127.8, 127.5, 126.3, 124.1, 41.8.

HRMS-APCI calculated for $C_{32}H_{27}$ $[M+H]^+$: 411.2113; found: 411.2113.

2,6-Di(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl (17l)



n-BuLi (1.6 M in hexanes, 2.2 mL, 3.53 mmol) was added dropwise to the solution of 550 mg (1.76 mmol) 2,6-dibromo-1,1'-biphenyl[169] in 20 mL THF at -78 ºC under argon. After addition, the mixture was warmed to room temperature (23 ºC) slowly and allowed to stir for 1 h. After cooling down to -78 ºC again, tropylium

[168] Velian, A.; Lin, S.; Miller, A. J. M.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2010**, *132*, 6296–6297.
[169] Machuy, M. M.; Würtele, C.; Schreiner, P. R. *Synthesis* **2012**, *44*, 1405–1409.

tetrafluoroborate (628mg, 3.53mmol) was added in one portion. The cooling bath was removed and the reaction was stirred at room temperature overnight (12 h). The reaction was quenched by addition of water. The aqueous phase was extracted with ether, the combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated. The crude reaction mixture was purified by chromatography to yield 320 mg of the title compound as a colorless crystalline solid (yield: 54%).

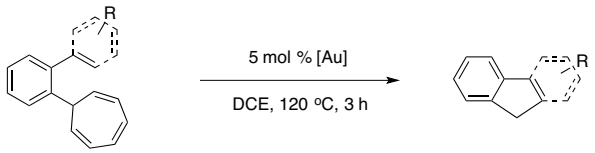
M.p.: 137-138 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 - 7.55 (m, 3H), 7.18 – 7.16 (m, 3H), 7.02 - 6.97 (m, 2H), 6.49 (dd, *J* = 3.8, 2.7 Hz, 4H), 6.14 - 6.11 (m, 4H), 5.35 (dd, *J* = 8.7, 5.4 Hz, 4H), 2.52 (tt, *J* = 5.4, 1.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 141.5, 138.4, 130.3, 129.4, 128.4, 127.5, 127.3, 126.6, 125.3, 123.9, 42.6.

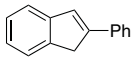
HRMS-MALDI: calculated for $C_{26}H_{22}$ $[M]^+$: 334.1722; found: 334.1711.

2. General procedure B for the gold-catalyzed formation of indenes and fluorenes



A solution of the *o*-arylcycloheptatriene substrate (0.1 mmol) and gold complex (5 mol %) in 1,2-dichloroethane (DCE, 1 mL) was heated at 120 ºC in a sealed tube until the starting material had been fully consumed (2-3 h). The reaction was performed under an air atmosphere with no special precautions taken to exclude water. After the reaction mixture had been allowed to cool to room temperature, the solvent was removed in vacuo, and the crude residue was purified by preparative TLC.

2-Phenyl-1*H*-indene (8a)



This compound was prepared as a colorless solid in 74% yield from **7a** according to the general procedure B.

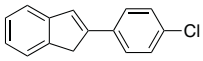
The spectroscopic data match with those reported in the literature.[170]

[170] Deng, R.; Sun, L.; Li, Z. *Org. Lett.* **2007**, *9*, 5207–5210.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.1 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.46 - 7.40 (m, 3H), 7.34 - 7.26 (m, 3H), 7.23 (td, *J* = 7.4, 1.2 Hz, 1H), 3.83 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 145.3, 143.1, 136.0, 128.7, 127.5, 126.6, 126.5, 125.6, 124.7, 123.6, 121.0, 39.0.

2-(4-Chlorophenyl)-1*H*-indene (8b)



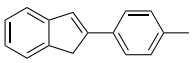
This compound was prepared as a colorless solid in 65% yield from **7b** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[171]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.31 (td, *J* = 7.5, 1.1 Hz, 1H), 7.26 - 7.18 (m, 2H), 3.79 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 145.0, 143.0, 134.5, 133.1, 128.8, 127.1, 126.8, 126.7, 125.0, 123.7, 121.1, 38.9.

2-(*p*-Tolyl)-1*H*-indene (8c)



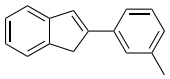
This compound was prepared as a colorless solid in 74% yield from **7c** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[172]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.25 - 7.18 (m, 4H), 3.81 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 145.5, 143.0, 137.4, 133.2, 129.3, 126.5, 125.6, 125.5, 124.5, 123.6, 120.8, 39.0, 21.2.

2-(*m*-Tolyl)-1*H*-indene (8d)



[171] Greifenstein, L. G.; Lambert, J. B.; Nienhuis, R. J.; Fried, H. E.; Pagani, G. A. *J. Org. Chem.* **1981**, *46*, 5125–5132.
[172] Jayamani, M.; Pant, N.; Ananthan, S.; Narayanan, K.; Pillai, C. N. *Tetrahedron* **1986**, *42*, 4325–4332.

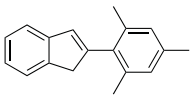
This compound was prepared as a colorless solid in 78% yield from **7d** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[171]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 - 7.47 (m, 3H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (s, 1H), 7.22 (td, *J* = 7.4, 1.2 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 3.83 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 145.4, 143.1, 138.2, 135.9, 128.6, 128.3, 126.6, 126.4, 124.6, 123.6, 122.8, 120.9, 39.0, 21.5.

2-Mesityl-1*H*-indene (8e)



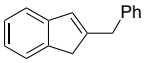
This compound was prepared as a colorless solid in 83% yield from **7e** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[173]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.35 (td, *J* = 7.4, 1.0 Hz, 1H), 7.25 (td, *J* = 7.5, 1.2 Hz, 1H), 6.98 (s, 2H), 6.69 (s, 1H), 3.60 (s, 2H), 2.37 (s, 3H), 2.22 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.4, 143.5, 136.7, 136.2, 134.7, 130.2, 128.0, 126.4, 124.2, 123.5, 120.7, 42.1, 21.0, 20.5.

2-Benzyl-1*H*-indene (8f)



This compound was prepared as a colorless solid in 78% yield from **7f** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[174]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.22 (m, 8H), 7.13 (td, *J* = 7.4, 1.3 Hz, 1H), 6.55 (s, 1H), 3.85 (s, 2H), 3.32 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 145.3, 143.4, 140.0, 128.8, 128.4, 127.8, 126.2, 126.2, 123.8, 123.4, 120.2, 40.8, 37.9.

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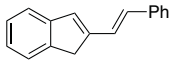
[173] Lebedev, A. Y.; Izmer, V. V.; Asachenko, A. F.; Tzarev, A. A.; Uborsky, D. V.; Homutova, Y. A.; Shperber, E. R.; Canich, J. A. M.; Voskoboynikov, A. Z. *Organometallics* **2009**, *28*, 1800–1816.
[174] Martinez, A.; Fernandez, M.; Estevez, J. C.; Estevez, R. J.; Castedo, L. *Tetrahedron* **2005**, *61*, 485–492.

(*E*)-2-Styryl-1*H*-indene (8g)



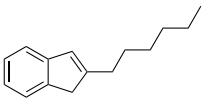
This compound was prepared as a colorless solid in 42% yield from **7g** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[175]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.40 - 7.35 (m, 3H), 7.31 - 7.19 (m, 4H), 6.88 (s, 1H), 6.81 (d, *J* = 16.2 Hz, 1H), 3.70 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 145.1, 142.8, 137.3, 131.3, 129.4, 128.7, 127.5, 126.6, 126.3, 125.0, 124.9, 123.6, 120.9, 37.4.

2-Hexyl-1*H*-indene (8h)



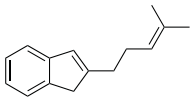
This compound was prepared as a colorless solid in 89% yield from **7h** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[176]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 1H), 7.31 - 7.22 (m, 2H), 7.13 (td, *J* = 7.3, 1.3 Hz, 1H), 6.53 (s, 1H), 3.34 (s, 2H), 2.51 (t, *J* = 7.6 Hz, 2H), 1.71 - 1.59 (m, 2H), 1.43 - 1.29 (m, 6H), 0.92 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 145.7, 143.1, 126.2, 126.0, 123.4, 123.3, 119.8, 41.0, 31.7, 31.2, 29.1, 29.0, 22.6, 14.1.

2-(4-Methylpent-3-en-1-yl)-1*H*-indene (8i)



This compound was prepared as a colorless oil in 69% yield from **7i** according to the general procedure B.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.13 (td, *J* = 7.3, 1.3 Hz, 1H), 6.55 (s, 1H), 5.21 (t, *J* = 7.0

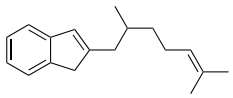
[175] Deng, R.; Sun, L.; Li, Z. *Org. Lett.* **2007**, *9*, 5207–5210.
[176] Lee, D.-H.; Kwon, K.-H.; Yi, C. S. *Science* **2011**, *333*, 1613–1616.

Hz, 1H), 3.34 (d, *J* = 1.3 Hz, 2H), 2.58 - 2.51 (m, 2H), 2.33 (q, *J* = 7.4 Hz, 2H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 145.7, 143.1, 132.0, 126.2, 126.2, 123.9, 123.5, 123.3, 119.8, 41.1, 31.4, 27.6, 25.7, 17.7.

HRMS-EI calculated for $C_{15}H_{18}$ $[M]^+$: 198.1409; found: 198.1405.

2-(2,6-Dimethylhept-5-en-1-yl)-1*H*-indene (8j)



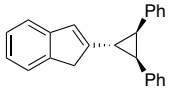
A 1 mL DCE solution of substrate **7j** (32 mg, 0.1 mmol) and gold catalyst **E** (4 mg, 5 mol%) was heated at 120 °C overnight. After cooling to room temperature, the solvent was removed in vacuo. The residue was purified with preparative TLC to give **8j** as a colorless oil (19.2 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.1 Hz, 1H), 7.13 (td, *J* = 7.3, 1.3 Hz, 1H), 6.54 (d, *J* = 1.1 Hz, 1H), 5.19 - 5.09 (m, 1H), 3.34 (d, *J* = 22.9 Hz, 1H), 3.32 (d, *J* = 22.7 Hz, 1H), 2.52 (ddd, *J* = 14.2, 6.1, 1.4 Hz, 1H), 2.33 (ddd, *J* = 14.0, 8.0, 1.2 Hz, 1H), 2.15 - 1.98 (m, 2H), 1.82 – 1.76 (m, 1H), 1.73 (s, 3H), 1.65 (s, 3H), 1.48 – 1.43 (m, 1H), 1.28 – 1.19 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 145.7, 143.3, 131.3, 127.5, 126.2, 124.7, 123.5, 123.4, 119.8, 41.2, 39.1, 37.0, 32.7, 25.7, 25.6, 19.8, 17.7.

HRMS-APCI: calculated for $C_{18}H_{25}$ $[M+H]^+$: 241.1951; found: 241.1953.

2-((1*R,2*S**,3*R**)-2,3-diphenylcyclopropyl)-1*H*-indene (8k)**



This compound was prepared according to the general procedure B. The 1 mL DCE solution of substrate **7k** (39 mg, 0.1 mmol) and gold catalyst A (3.7 mg, 5 mol%) was heated at 120 °C for 2 h. After cooling to room temperature, the solvent was removed in vacuo. The residue was purified with preparative TLC to give **8k** as a colorless solid (19.2 mg, 62%).

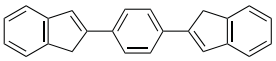
M.p.: 129-131 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 7.1 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.21 - 7.11 (m, 7H), 7.05 - 7.01 (m, 4H), 6.75 (s, 1H), 3.48 (s, 2H), 2.85 - 2.75 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 145.4, 142.4, 137.5, 128.9, 127.9, 126.5, 126.0, 125.6, 123.8, 123.5, 120.0, 39.8, 34.3, 27.8.

HRMS-APCI calculated for $C_{24}H_{21}$ $[M+H]^+$: 309.1638; found: 309.1637.

1,4-Di(1*H*-inden-2-yl)benzene (8l)



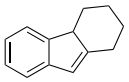
This compound was prepared from **7l** according to the general procedure B. A highly insoluble yellow solid was collected by filtration after cooling down to r.t. (in 41% yield). No further purification was necessary.

^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2; 398 K) δ 7.60 (s, 4H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.19 (s, 2H), 7.15 (t, *J* = 7.3 Hz, 2H), 3.78 (s, 4H).

^{13}C NMR (126 MHz, 1,1,2,2-tetrachloroethane-d_2; 398 K) δ ^{13}C NMR (126 MHz, 1,1,2,2-tetrachloroethane-d_2) δ 145.7, 144.8, 142.6, 134.9, 126.2, 126.1, 125.4, 124.3, 123.0, 120.4, 38.6.

HRMS-MALDI: calculated for $C_{24}H_{18}$ $[M]^+$: 306.1403; found 306.1402.

2,3,4,4a-Tetrahydro-1*H*-fluorene (8m)



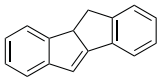
This compound was prepared as a colorless oil in 73% yield from **7m** according to the general procedure B.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.24 (td, *J* = 7.5, 1.1 Hz, 1H), 7.13 (td, *J* = 7.5, 1.3 Hz, 1H), 6.40 (s, 1H), 3.08 (dd, *J* = 12.5, 6.1 Hz, 1H), 2.82 - 2.76 (m, 1H), 2.59 - 2.54 (m, 1H), 2.42 - 2.34 (m, 1H), 2.07 - 2.00 (m, 1H), 1.92 - 1.88 (m, 1H), 1.65 - 1.58 (m, 1H), 1.29 - 1.21 (m, 1H), 0.94 (qd, *J* = 12.8, 3.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 147.7, 144.8, 126.3, 123.4, 122.3, 121.7, 120.0, 50.0, 32.4, 29.2, 28.0, 25.4.

HRMS-APCI: calculated for $C_{13}H_{15}$ $[M+H]^+$: 171.1174; found: 171.1169.

4b,5-Dihydroindeno[2,1-*a*]indene (8n)



This compound was prepared from **7n** according to the general procedure B as a colorless solid in 31% yield.

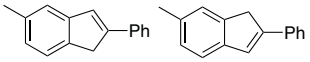
M.p.: 103-105 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.31 - 7.26 (m, 2H), 7.23 – 7.16 (m, 2H), 6.75 (d, *J* = 2.5 Hz, 1H), 4.45 (td, *J* = 8.5, 2.6 Hz, 1H), 3.45 (dd, *J* = 14.8, 8.6 Hz, 1H), 2.70 (dd, *J* = 14.7, 8.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 151.1, 149.2, 145.2, 136.9, 127.3, 127.0, 126.9, 125.7, 124.1, 123.5, 121.8, 121.7, 119.1, 58.5, 33.1.

HRMS-MALDI: calculated for $C_{16}H_{12}$ $[M]^+$: 204.0939; found: 204.0957.

5-Methyl-2-phenyl-1*H*-indene (8p′) and 6-methyl-2-phenyl-1*H*-indene (8p)



1:1

This mixture of compounds was prepared as a colorless solid in 81% yield (1:1 mixture) from **7p** according to the general procedure B.

M.p.: 180-181 ºC.

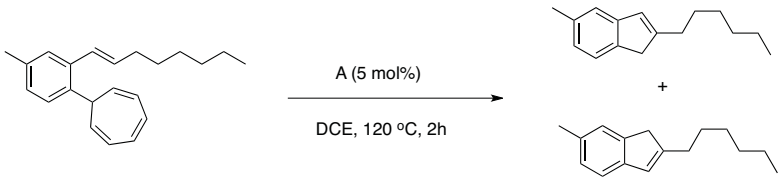
Some proton signals arising of the two isomers could be differentiated (labeled as *isomer a* and *isomer b*); however, these could not be assigned definitively to **8p** or **8p**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 - 7.66 (m, 2H), 7.45 - 7.23 (m, 6H), 7.16 - 7.13 (d, *J* = 7.9 Hz, 1H, *isomer a*), 7.06 (dd, *J* = 7.7, 1.5 Hz, 1H, *isomer b*), 3.80 (s, 2H), 2.46 (s, 3H, *isomer a*), 2.45 (s, 3H, *isomer b*).

^{13}C NMR (126 MHz, $CDCl_3$, mixture of signals) δ 146.6, 145.6, 145.3, 143.5, 142.7, 140.2, 136.2, 136.1, 134.5, 128.6, 127.4, 127.3, 127.3, 126.5, 126.4, 125.6, 125.5, 124.6, 123.3, 121.7, 120.6, 38.8, 38.6, 21.5, 21.5.

HRMS-APCI calculated for $C_{16}H_{15}$ $[M+H]^+$: 207.1174; found: 207.1173.

2-Hexyl-5-methyl-1*H*-indene (8q′) and 2-hexyl-6-methyl-1*H*-indene (8q)



84%, 1:1

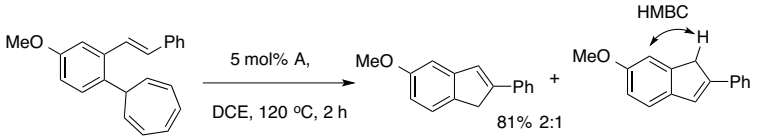
This mixture of compounds was prepared as a colorless oil in 84% yield (1:1 mixture) from **7q** according to the general procedure B.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.7 Hz, 1H), 7.23 (s, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.48 (m, 2H), 3.29 (s, 4H), 2.53 - 2.47 (m, 4H), 2.40 (s, 6H), 1.68 - 1.58 (m, 4H), 1.39 - 1.29 (m, 12H), 0.94 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 149.9, 146.0, 143.5, 143.1, 140.2, 135.7, 133.0, 126.8, 126.0, 125.8, 124.4, 124.2, 123.0, 120.6, 119.4, 40.8, 40.6, 31.8, 31.3, 31.2, 29.1, 29.0, 22.6, 21.5, 21.4, 14.1.

HRMS-APCI calculated for $C_{16}H_{23}$ $[M+H]^+$: 215.1794; found: 215.1801.

5-Methoxyl-2-phenyl-1*H*-indene (8r′) and 6-methoxyl-2-phenyl-1*H*-indene (8r)



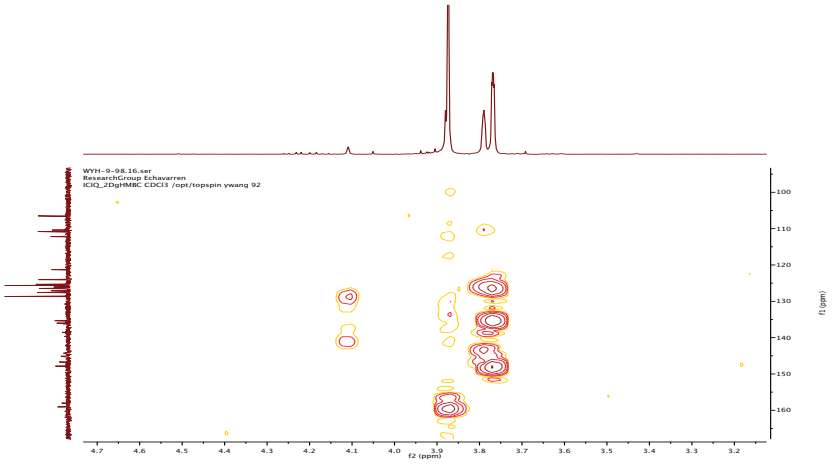
This mixture of compounds was prepared as a colorless solid in 81% yield (2:1 mixture, **8r′** as the major product) from **7r** according to the general procedure B. The ratio of products was determined by integration of peaks in the ^{1}H NMR spectrum. HMBC was used to elucidate which were the major and minor products.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 - 7.61 (m, *major* 2H + *minor*2H), 7.44 - 7.31 (m, *major* 4H + *minor* 4H), 7.20 (s, *major* 1H + *minor* 1H), 7.10 (d, *J* = 0.7 Hz, *minor* 1H), 6.99 (d, *J* = 2.4 Hz, *major* 1H), 6.87 (dd, *J* = 8.2, 2.4 Hz, *minor* 1H), 6.78 (dd, *J* = 8.1, 2.4 Hz, *major* 1H), 3.87 (s, *major* 3H + *minor* 3H), 3.79 (s, *minor* 2H), 3.77 (s, *major* 2H).

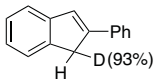
^{13}C NMR (101 MHz, $CDCl_3$, mixed signals) δ 159.1, 158.0, 147.8, 146.7, 145.1, 144.2, 138.5, 136.2, 136.0, 135.3, 128.7, 128.6, 127.6, 127.1, 126.5, 126.1, 125.6, 125.3, 124.1, 121.3, 112.2, 110.8, 110.4, 106.5, 55.6, 55.5, 39.1, 38.3.

HRMS-APCI calculated for $C_{16}H_{15}O$ $[M+H]^+$: 223.1117; found: 223.1116.

HMBC cross peak of **8r** (δ (H) 3.79, δ (C) 110.25)



2-Phenyl-1*H*-indene-d_1 (8a-d_1)



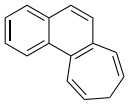
This compound was prepared as a colorless solid in 73% yield from **7a-d_1** according to the general procedure B.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.46 - 7.40 (m, 3H), 7.33 - 7.29 (m, 2H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.22 (td, *J* = 7.4, 1.1 Hz, 1H), 3.81 (s, 1H and 7% residual signal).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 145.4, 143.1, 136.0, 128.6, 127.5, 126.6, 126.5, 125.6, 124.7, 123.6, 120.9, 38.7 (t, J_{CD} = 19.7 Hz).

HRMS-APCI calculated for $C_{15}H_{12}D$ $[M+H]^+$: 194.1080; found: 194.108.

9*H*-Cyclohepta[*a*]naphthalene (12)



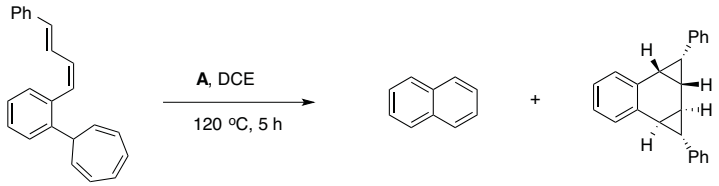
This compound was prepared as a colorless oil in 28% yield from ***cis*-7a** according to the general procedure B.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.6 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.61 - 7.51 (m, 2H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.24 (d, *J* = 10.0 Hz, 1H), 6.82 (d, *J* = 10.0 Hz, 1H), 6.05 (ddt, *J* = 9.9, 8.6, 6.9 Hz, 2H), 2.41 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.8, 133.6, 132.2, 131.7, 130.3, 128.8, 128.3, 128.2, 126.9, 126.5, 126.2, 125.7, 125.2, 124.8, 26.5.

HRMS-EI calculated for $C_{15}H_{12}$ $[M]^+$: 192.0939; found: 192.0939.

(1*R,1a*S**,1b*S**,2*S**,2a*S**,6b*S**)-1,2-diphenyl-1,1a,1b,2,2a,6b-hexahydrodicyclopropa[*a*,*c*]naphthalene (15)**



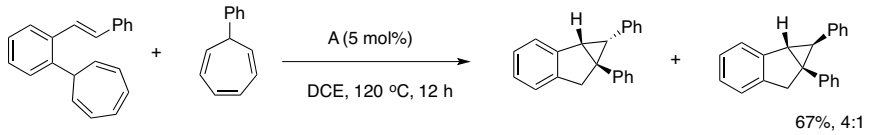
The 1 mL DCE solution of **7u** (45 mg, 0.15 mmol) and gold catalyst **A** (5.5 mg, 5 mol %) was heated at 120 °C for 5 h. After cooling to room temperature, the solvent was removed *in vacuo*. The residue was passed through a short column of silica, and naphthalene (colorless solid, 4.6 mg, 24%) was separated from the crude residue. The remaining mixture was purified carefully with preparative TLC to give **15** as a colorless solid (5.9 mg, 12%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 - 7.10 (m, 12H), 7.00 (td, *J* = 7.5, 1.4 Hz, 1H), 6.90 (dd, *J* = 7.6, 1.4 Hz, 1H), 2.59 (dd, *J* = 9.4, 8.2 Hz, 1H), 2.38 - 2.32 (m, 2H), 2.11 (t, *J* = 4.6 Hz, 1H), 2.06 (dd, *J* = 8.5, 4.7 Hz, 1H), 1.66 (dd, *J* = 8.6, 4.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 136.6, 135.8, 131.3, 130.9, 130.1, 128.5, 128.3, 127.6, 125.7, 125.6, 125.5, 125.4, 125.3, 35.7, 29.7, 29.0, 25.4, 20.8, 20.2.

HRMS-APCI calculated for $C_{24}H_{21}$ $[M+H]^+$: 309.1643; found: 309.1649.

(1*R,1a*S**,6a*R**)-1,6a-diphenyl-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene (5a) and (5a′)**



The DCE solution of (*E*)-7-(2-styrylphenyl)cyclohepta-1,3,5-triene **7a** (27 mg, 0.1 mmol) and gold complex (3.7mg, 5 mol %) was heated at 120 ºC for 2h. After cooling to room temperature, 7-phenylcyclohepta-1,3,5-triene **1a** (34 mg, 0.2 mmol) was added, and the mixture was heated to 120 °C overnight (12 h). The reaction mixture was cooled to room temperature, the solvent was removed *in vacuo*, and the

resulting residue was purified by preparative TLC to give 19 mg of the title mixture (67%, 4:1) as a colorless solid.

M.p.: 85-88 ºC.

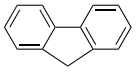
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 6.83 (m, aromatic 14H *major* + 14H *minor*), 3.68 (d, *J* = 16.9 Hz, 1H *minor*), 3.49 (d, *J* = 17.0 Hz, 1H *minor*), 3.42 (d, *J* = 17.3 Hz, 1H *major*), 3.34 (dd, *J* = 8.4, 1.6 Hz, 1H *major*), 3.26 (dd, *J* = 3.6, 1.5 Hz, 1H *minor*), 3.16 (d, *J* = 17.3 Hz, 1H *major*), 2.88 (d, *J* = 8.3 Hz, 1H *major*), 2.11 (d, *J* = 3.5 Hz, 1H *minor*).

^{13}C NMR (101 MHz, $CDCl_3$, *major* + *minor*) δ 146.3, 145.1, 142.6, 141.8, 139.8, 138.7, 135.4, 130.7, 129.8, 128.6, 128.1, 127.6, 127.2, 126.3, 126.1, 126.1, 125.8, 125.6, 125.3, 125.2, 124.2, 124.1, 123.3, 45.3, 41.7, 41.5, 38.5, 38.4, 37.7, 37.2, 35.9.

The relative configuration was confirmed by NOE.

HRMS-APCI: calculated for $C_{22}H_{19}$ $[M+H]^+$: 283.1481; found: 283.1498.

9*H*-Fluorene (18a)



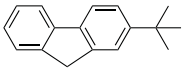
This compound was prepared as a colorless solid in 64% yield from **17a** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[177]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.4 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.41 (td, *J* = 7.5, 1.1 Hz, 2H), 7.33 (td, *J* = 7.4, 1.2 Hz, 2H), 3.94 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.7, 126.7, 126.6, 125.0, 119.8, 36.9.

2-(*tert*-Butyl)-9*H*-fluorene (18b)



This compound was prepared as a colorless solid in 87% yield from **17b** according to the general procedure B.

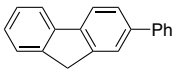
The spectroscopic data match with those reported in the literature.[178]

[177] Clive, D. L. J.; Sunasee, R. *Org. Lett.* **2007**, *9*, 2677–2680.
[178] Fuchibe, K. *J. Am. Chem. Soc.* **2006**, *128*, 1434–1435.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.53 (s, 1H), 7.47 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 3.83 (s, 2H), 1.33 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 143.2, 143.0, 141.6, 139.0, 126.5, 126.1, 124.8, 123.8, 121.8, 119.5, 119.2, 36.9, 34.7, 31.5.

2-Phenyl-9*H*-fluorene (18c)



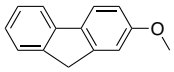
This compound was prepared as a colorless solid in 56% yield from **17c** according to the general procedure B using catalyst **E**.

The spectroscopic data match with those reported in the literature.[179]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.80 (m, 3H), 7.73 - 7.64 (m, 3H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.45 - 7.32 (m, 3H), 4.00 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 143.4, 141.5, 141.4, 140.9, 139.8, 128.7, 127.1, 127.1, 126.8, 126.7, 126.0, 125.0, 123.8, 120.1, 119.9, 37.0.

2-Methoxy-9*H*-fluorene (18d)



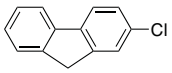
This compound was prepared as a colorless solid in 52% yield from **17d** according to the general procedure B using catalyst **E**.

The spectroscopic data match with those reported in the literature.[180]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.26 (td, *J* = 7.4, 1.1 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.96 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.90 (s, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 145.0, 142.6, 141.6, 134.7, 126.7, 125.5, 124.8, 120.5, 119.0, 112.9, 110.5, 55.5, 37.0.

2-Chloro-9*H*-fluorene (18e)



[179] Mu, B.; Li, T.; Li, J.; Wu, Y. *J. Organomet. Chem.* **2008**, *693*, 1243–1251.
[180] Hwang, S.-J.; Kim, H.-J.; Chang, S. *Org. Lett.*, **2009**, *11*, 4588–4591.

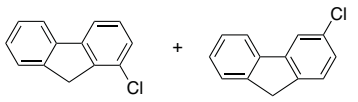
This compound was prepared as a colorless solid in 42% yield from **17e** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[180]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.59 - 7.53 (m, 2H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.38 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.34 (td, *J* = 7.4, 1.2 Hz, 1H), 3.92 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 142.9, 140.6, 140.2, 132.3, 127.0, 126.9, 126.9, 125.3, 125.0, 120.7, 119.9, 36.8.

1-Chloro-9*H*-fluorene (18f) and 3-Chloro-9*H*-fluorene (18f')



1.2 : 1

These compounds were prepared as a colorless solid in 56% yield from **17f** according to the general procedure B.

Their spectroscopic data match with those reported in the literature. [180]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.76 (m, *major* 1H, *minor* 2H), 7.70 (dd, *J* = 7.3, 1.1 Hz, *major*1H), 7.63 – 7.54 (m, *major* 1H, *minor* 1H), 7.48 – 7.27 (m, *major* 4H, *minor* 4H), 3.95 (s, *major* 2H), 3.88 (s, *minor* 2H).

^{13}C NMR (101 MHz, $CDCl_3$, *major*+*minor*) δ 143.7, 143.5, 143.5, 142.6, 141.3, 141.1, 140.6, 128.4, 127.3, 126.9, 126.6, 126.6, 125.9, 125.1, 120.3, 120.1, 118.2, 36.6, 36.5.

4-Bromo-9*H*-fluorene (18g)

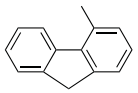
Gold catalyst **B** (13.5 mg, 0.015 mmol) and 2-bromo-2'-(cyclohepta-2,4,6-trien-1-yl)-1,1'-biphenyl **17g** (97 mg, 0.3 mmol) were mixed in a Biotage 2–5 mL microwave vial. The solids were dissolved in 1,2-dichloroethane (1.2 mL) before the vial was sealed and heated to 120 ºC in a Biotage initiator microwave for 8 h. Afterwards, the solution was filtered through Celite, concentrated and purified by flash chromatography (cyclohexane) to yield the desired fluorene (18.1 mg, 0.074 mmol, 25%) as a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, *J* = 9.0 Hz, 1H), 7.60 - 7.32 (m, 5H), 7.14 (t, *J* = 7.7 Hz, 1H), 3.95 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 143.7, 141.2, 140.0, 131.9, 127.6, 127.4, 126.6, 124.9, 123.9, 123.7, 117.0, 37.4.

HRMS-APCI calculated for $C_{13}H_9Br$ $[M]^+$: 243.9882; found: 243.9880.

4-Methyl-9*H*-fluorene (18h)



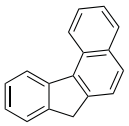
This compound was prepared as a colorless solid in 74% yield from **17h** according to the general procedure B.

The spectroscopic data match with those reported in the literature.[180]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.44 (td, *J* = 7.6, 1.1 Hz, 2H), 7.35 (td, *J* = 7.4, 1.2 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 3.96 (s, 2H), 2.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 143.6, 142.7, 139.8, 133.0, 128.9, 126.6, 126.4, 126.0, 124.8, 123.1, 122.4, 37.1, 21.1.

7*H*-benzo[*c*]fluorene (18i)



A solution of 1-(2-(cyclohepta-2,4,6-trien-1-yl)phenyl)naphthalene **17i** (20.2 mg, 69 μmol) and gold complex **A** (2.6 mg, 3.4 μmol) in DCE (0.68 mL) was heated at 120 ºC in a sealed tube until the starting material had been fully consumed (3 h). The reaction mixture was cooled to room temperature, the solvent was removed in vacuo, and the crude residue was purified by chromatography (Combiflash 4 g column, cyclohexane eluent) to give the title compound in 59% yield as a colorless solid (8.7 mg).

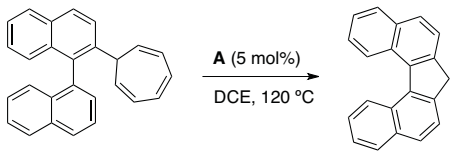
The spectroscopic data match with those reported in the literature.[181]

[181] Laali, K. K; Okazaki, T.; Sultana, F.; Bunge, S. D.; Banik, B. K.; Swartz, C. *Eur. J. Org. Chem.* **2008**, 1740–1752.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.56 – 7.48 (m, 2H), 7.36 (td, *J* = 7.4, 1.0 Hz, 1H), 4.03 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 142.9, 142.4, 136.2, 133.5, 129.7, 129.3, 127.8, 127.0, 126.6, 125.8, 125.1, 125.0, 123.8, 123.4, 123.0, 37.9.

7*H*-Dibenzo[*c*,*g*]fluorene (18j)

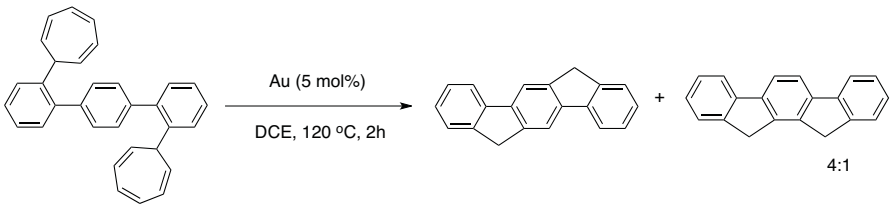


This compound was synthesized in 67% yield as a colorless solid following the general procedure B, starting from 2-(cyclohepta-2,4,6-trien-1-yl)-1,1'-binaphthalene **17j** and gold catalyst **A**. After cooling to room temperature, the solution was filtered through Celite, concentrated and purified by flash chromatography (cyclohexane) to yield the title compound. The spectroscopic data matched with those reported in the literature.[182]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (dq, *J* = 7.9, 0.9 Hz, 2H), 8.00 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.63 - 7.50 (m, 4H), 4.14 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 138.5, 134.0, 129.0, 128.9, 127.7, 126.8, 125.0, 124.9, 123.0, 39.0.

6,12-Dihydroindeno[1,2-*b*]fluorene (18k/18k′)



The 1 mL DCE solution of substrate **17k** (41 mg, 0.1 mmol) and gold catalyst **A** (3.7 mg, 5 mol%) was heated at 120 °C for 2 h. After cooling to room temperature, the solvent was removed *in vacuo*. 1 mL acetone was added to dissolve some of the

[182] (a) Laali, K. K.; Okazaki, T.; Sultana, F.; Bunge, S. D.; Banik, B. K.; Swartz, C. *Eur. J. Org. Chem.* **2008**, 1740–1752. (b) Harvey, R. D.; Pataki, J.; Cortez, C.; Raddo, P. D.; Yang, C.-X. *J. Org. Chem.* **1991**, *56*, 1210–1217.

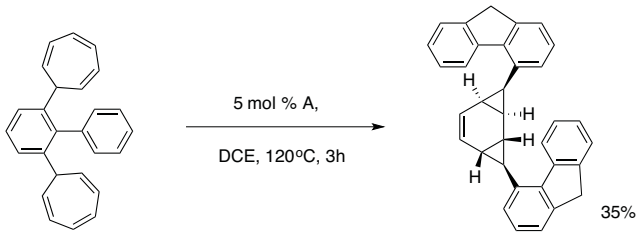
residue. The liquid was decanted, leaving behind a colorless solid which was dried in vacuo to give a 4:1 mixture of **18k**/**18k′** (13.5 mg, 53%).

The spectroscopic data match with those reported in the literature.[183]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H, *major*), 7.85 - 7.81 (m, 2H *major* + 4H *minor*), 7.60 - 7.56 (m, 2H *major* + 2H *minor*), 7.42 (td, *J* = 7.5, 1.2 Hz, 2H *major* + 2H *minor*), 7.32 (td, *J* = 7.4, 1.3 Hz, 2H *major* + 2H *minor*), 4.00 (s, 4H *major*), 3.98 (s, 4H *minor*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 142.3, 141.8, 140.8, 126.8 (*minor*), 126.7, 126.5 (*minor*), 126.4, 125.1 (*minor*), 125.0, 119.9 (*minor*), 119.5, 118.7 (*minor*), 116.4, 36.7, 35.5 (*minor*).

(1*R,2*R**,3*R**,4*R**,7*R**,8*S**)-3,8-di(9*H*-fluoren-4-yl)tricyclo[5.1.0.0^{2,4}]oct-5-ene (19)**



This compound (**19**) was prepared as a yellow oil in 35% yield from **17l** according to the general procedure B.

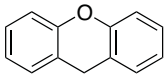
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.8 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.61 - 7.56 (m, 2H), 7.50 - 7.31 (m, 7H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 5.76 (dd, *J* = 9.8, 4.5 Hz, 1H), 5.68 (dd, *J* = 9.8, 4.6 Hz, 1H), 3.95 (s, 2H), 3.90 (s, 2H), 2.83 (t, *J* = 8.5 Hz, 1H), 2.67 (t, *J* = 4.7 Hz, 1H), 2.54 (t, *J* = 8.5 Hz, 1H), 2.09 - 1.94 (m, 2H), 0.97 (dt, *J* = 8.6, 4.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 143.6, 143.5, 142.6, 142.2, 141.9, 140.6, 136.1, 132.0, 130.6, 127.1, 126.6, 126.5, 126.3, 126.0, 125.9, 125.5, 124.9, 124.7, 124.7, 123.5, 123.2, 122.8, 122.6, 121.4, 37.1, 36.9, 35.3, 30.7, 21.9, 21.5, 20.5, 17.4.

HRMS-MALDI: calculated for $C_{34}H_{26}$ $[M]^+$: 434.2035; found: 434.2098.

9*H*-xanthene (23a)

[183] Major isomer: (a) Poriel, C.; Liang, J.-J.; Rault-Berthelot, J.; Barrière, F.; Cocherel, N.; Slawin, A. M. Z.; Horhant, D.; Virboul, M.; Alcaraz, G.; Audebrand, N.; Vignau, L.; Huby, N.; Wantz, G.; Hirsch, L. *Chem. Eur. J.* **2007**, *13*, 10055–10069. Minor isomer: (b) Thirion, D., Poriel, C., Rault-Berthelot, J.; Barrière, F.; Jeannin, O. *Chem. Eur. J.* **2010**, *16*, 13646–13658.



A solution of 7-(2-phenoxyphenyl)cyclohepta-1,3,5-triene **22a** (26 mg, 0.1 mmol) and gold complex **E** (4 mg, 5 mol%) in toluene (1 mL) was heated at 120 ºC in a sealed tube for 2 h. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified by preparative TLC (eluent: cyclohexane) to give 5.5 mg the title compound in 30% yield as a colorless solid.

The spectroscopic data match with those reported in the literature.[184]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 - 7.18 (m, 4H), 7.09 - 7.03 (m, 4H), 4.08 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 128.9, 127.6, 122.9, 120.6, 116.4, 27.9.

[184] Okuma, K.; Nojima, A.; Matsunaga, N.; Shioji, K. *Org. Lett.* **2009**, *11*, 169–171.

General conclusions

Based on the known equilibrium of cycloheptatrienes **1** and norcaradienes **2**, we found a new method by which to generate gold(I) carbenes **3** through the retro-Buchner reaction of the norcaradiene tautomer.

Figure 1 summarizes the progress we have made recently on the intermolecular cycloaddition of gold(I) carbenes generated by retro-Buchner reaction.

- The gold(I) carbenes **3** can be trapped intermolecularly by alkenes to form synthetically useful cyclopropanes **4**.
- Alternatively, gold(I) carbenes **3** can also react with furans **6** to form cyclopentene derivatives **7**.
- Methylenecyclopropanes or cyclobutenes **5** were successfully used as synthetic equivalent of 1,3-dienes for very challenging (4+1) cycloadditions.

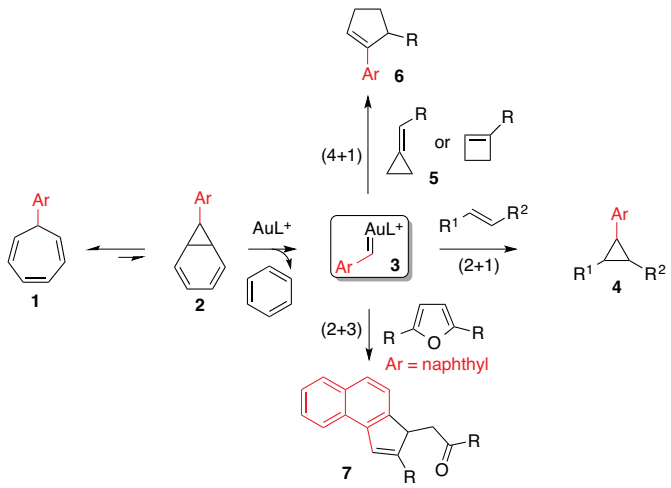
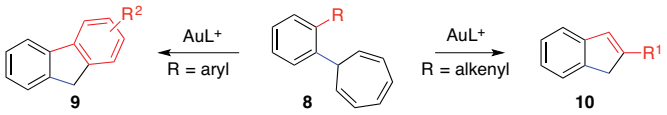


Figure 1. Intermolecular cycloadditions.

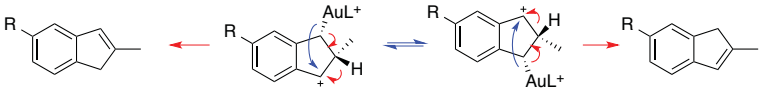
Gold(I) carbenes generated by the retro-Buchner reaction of 1,3,5-cycloheptatrienes catalyzed by cationic gold(I) complexes can be trapped intramolecularly by arenes or alkenes to form fluorenes **9** or indenes **10**. This methodology provides a new synthetic approach to fluorenes and indenes and may be applied to the synthesis of indenofluorenes used in organic electronics (Scheme 1). These reactions proceed via intramolecular Friedel−Crafts-type attack of the highly electrophilic gold(I) carbenes to the alkenes and arenes. The reactivity displayed by the cationic

intermediates generated by the retro-Buchner reaction is more similar to that of metal carbenes of rhodium or copper or even free carbenes than that of carbocations.



Scheme 1

Closer scrutiny of the mechanisms of these reactions has revealed some intriguing details (Scheme 2). Thus, in the indene synthesis, we have found that a novel 1,4-metallotropic migration competes with the primary pathway for the formation of the (η^2-indene) gold(I) complexes by a concerted 1,2-H migration/gold(I) elimination. The formation of fluorenes involves a diatropic-type process in the formation of an (η^1-fluorene)-gold(I) complex.



Scheme 2